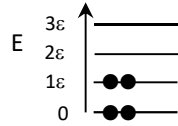


## Chapter 12 Problems: The Statistical Definition of Entropy

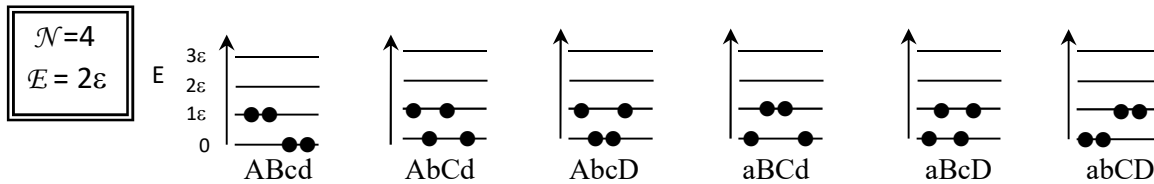
1. Calculate the number of ways of arranging the energy states and find all the microstates consistent with the distribution numbers (2,2,0,0). Find the average energy for the distribution. (Assume distinguishable systems.)



*Answer:* There are four total systems,  $\mathcal{N} = 4$ , and two packets of energy,  $\mathcal{E} = 2\varepsilon$ . Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(2,2,0,0) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{4!}{2! 2! 0! 0!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{(2 \cdot 1)(2 \cdot 1)} = 6$$

So we should find six microstates:



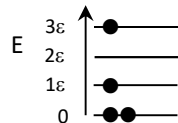
The average energy using Eq. 12.2.4 is:

$$\langle E \rangle = \frac{1}{\mathcal{N}} \sum_i n_i E_i = \frac{2(0) + 2(1) + 0(2) + 0(3)}{4} = \frac{1}{2} \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$\langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{2\varepsilon}{4} = \frac{1}{2} \varepsilon$$

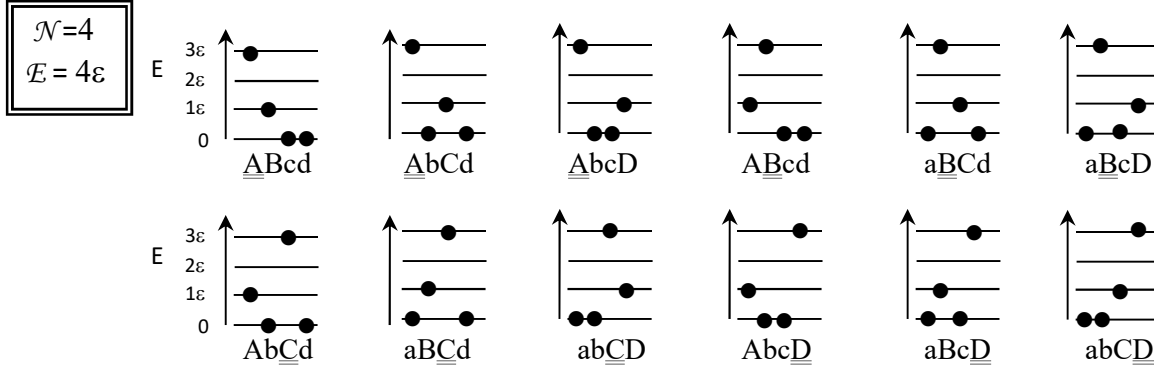
2. Calculate the number of ways of arranging the energy states and find all the microstates consistent with the distribution numbers (2,1,0,1). Find the average energy for the distribution. (Assume distinguishable systems.)



*Answer:* There are four total systems,  $\mathcal{N} = 4$ , and four packets of energy,  $\mathcal{E} = 4\varepsilon$ . Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(2,1,0,1) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{4!}{2! 1! 0! 1!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{(2 \cdot 1)(1)(1)(1)} = 12$$

So we should find 12 microstates:



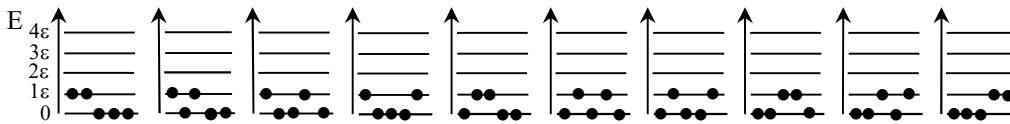
The average energy using Eq. 12.2.4 is:

$$\langle E \rangle = \frac{1}{\mathcal{N}} \sum_i n_i E_i = \frac{2(0) + 1(1) + 0(2) + 1(3)}{4} = \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$\langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{4\varepsilon}{4} = \varepsilon$$

3. Given the following microstates:



- Find the set of distribution numbers.
- Specify the macrostate.
- Find the number of ways of arranging the energy states for the system for the set of distribution numbers. Is the given set of microstates complete?
- Find the statistical weight for the macrostate.
- Find the degeneracy for the macrostate.
- Find  $\langle E \rangle$  and  $U - U(0)$ .
- Find the probability of occurrence of the first microstate, within the given macrostate.
- Find another macrostate with the same number of systems and the same energy. Which is more probable, the given macrostate or the new macrostate?
- What is the most probable distribution and  $\mathcal{W}_{\max}$  subject to  $\mathcal{N} = 5$  and  $\mathcal{E} = 2\varepsilon$ ?
- What is the equilibrium distribution?

Answers: (a). The distribution numbers are (3,2,0,0). (b) The macrostate is specified by the set of distribution numbers, (3,2,0,0). (c). Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(3,2,0,0) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{5!}{3! 2! 0! 0!} = \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(3 \cdot 2 \cdot 1)(2 \cdot 1)} = 10$$

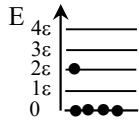
The given ten microstates are complete, since  $\mathcal{W} = 10$ . (d). The statistical weight is  $\mathcal{W}$ . (e). The degeneracy is also  $\mathcal{W}$ . (f). The average energy and internal energy using Eq. 12.2.4 are:

$$U - U(0) = \langle E \rangle = \frac{1}{\mathcal{N}} \sum_i n_i E_i = \frac{3(0) + 2(1) + 0(2) + 0(3)}{5} = 2/5 \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$U - U(0) = \langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{2\varepsilon}{5} = 2/5 \varepsilon$$

(g). Each microstate has an equal *a priori* probability. The probability of each individual microstate within the given macrostate is  $1/10$ . Each microstate appears one-tenth of the time. (h). The only other macrostate with the same number of systems and energy is (4,0,1,0):



The new statistical weight is:

$$\mathcal{W}(4,0,1,0) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{5!}{4! 0! 1! 0!} = \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(4 \cdot 3 \cdot 2 \cdot 1)(1)(1)(1)} = 5$$

which is less probable than the original macrostate. (i). The most probable distribution is (3,2,0,0) with  $\mathcal{W}_{\max} = 10$ , subject to the constraints. (h). The equilibrium distribution is the most probable distribution, (3,2,0,0), subject to the given constraints.

4. Assume a system has equally spaced energy states with spacing  $\varepsilon$ . (a). Find  $\mathcal{N}$ ,  $\mathcal{E}$ ,  $\langle E \rangle$ , and  $U - U(0)$  for the distributions (26,14,9,5,3,2,1) and (25,16,8,5,3,2,1). (b). Which distribution is the more probable macrostate? (c). Find the difference between the two macrostates in the number of ways of arranging the energy states for the system. (d). One of the two is the most probable distribution. Which macrostate corresponds to the equilibrium state?

Answer: (a). Both sets of distribution numbers correspond to  $\mathcal{N} = 60$  and  $\mathcal{E} = 75$  for

$$U - U(0) = \langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{75 \varepsilon}{60} = 1.25 \varepsilon$$

(b). Using Eq. 12.2.8, the number of ways of arranging the energy states is given using a calculator or Excel as:

$$\mathcal{W}(26,14,9,5,3,2,1) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{60!}{26! 14! 9! 5! 3! 2! 1!} = 4.5292 \times 10^{35}$$

and  $\mathcal{W}(25,16,8,5,3,2,1) = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} = \frac{60!}{25! 16! 8! 5! 3! 2! 1!} = 4.4160 \times 10^{35}$

The first distribution is the more probable.

(c). The difference is  $1.13 \times 10^{34}$ . The first distribution is more probable by a very large number of microstates. (d). The first macrostate, (26,14,9,5,3,2,1), is the most probable state and correspondingly is the equilibrium state.

5. Calculate the residual entropy for a crystalline solid like N=N=O assuming the energy difference for the two crystalline alignments is  $0.300 \text{ kJ mol}^{-1}$ . Assume that the distribution of alignments is “frozen in” at the melting point. Assume the melting point is  $-90.8^\circ\text{C}$ . Compare the result to Eq. 12.4.10. Why is there a difference?

*Answer:* The plan is to use  $S = -R \sum p_i \ln p_i$ , Eq. 12.4.14, with a Boltzmann distribution over two states at energies  $\varepsilon_0 = 0$  and  $\varepsilon_1 = 0.300 \text{ kJ mol}^{-1}$ . At the melting point:

$$RT = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (273.2 - 90.8 \text{ K}) = 1516. \text{ J K}^{-1} \text{ mol}^{-1}$$

The lower energy state has a Boltzmann weighting factor of  $e^{-\varepsilon_0/RT} = e^0 = 1$ . The higher energy alignment has a Boltzmann weighting factor of:

$$e^{-\varepsilon_1/RT} = e^{-300. \text{ J mol}^{-1}/1516. \text{ J K}^{-1} \text{ mol}^{-1}} = 0.8205$$

The partition function, which is the probability normalization factor, is the sum of the weighting factors:

$$q = e^{-\varepsilon_0/RT} + e^{-\varepsilon_1/RT} = 1 + 0.8205 = 1.8205$$

The corresponding probabilities are:

$$p_1 = e^{-\varepsilon_1/RT}/q = 0.8205/1.8205 = 0.4507$$

$$p_0 = e^{-\varepsilon_0/RT}/q = 1/1.8205 = 0.5493$$

Finally the entropy, based on Eq. 12.4.14, is:

$$\begin{aligned} S &= -R \sum p_i \ln p_i = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (0.5493 \ln 0.5493 + 0.4507 \ln 0.4507) \\ &= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (-0.6882) = 5.722 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The result using Eq. 12.4.10 is  $S = -R \ln 2 = 5.763 \text{ J K}^{-1} \text{ mol}^{-1}$ , with  $w = 2$ . The difference is that Eq. 12.4.10 with  $w = 2$  assumes that the two orientations are equally probable, which is true if the difference in alignment energies is less than  $RT$ ,  $\varepsilon_1 - \varepsilon_0 = \Delta\varepsilon \ll RT$ . In this problem,  $\Delta\varepsilon/RT = 0.2$ , which is small enough to give the equal populations result, to within expected experimental error.

6. The goal of this problem is to help you become more comfortable with partition functions. Consider the residual entropy of N=N=O. Define the lowest energy alignment as having energy

$\epsilon_0$  and the higher energy alignment at  $\epsilon_1$ . A reasonable way to assess the degree of alignment is to calculate the fraction of molecules in the low energy state,  $f_0$ , and the fraction of the molecules in the high energy state,  $f_1$ :

$$f_0 = \frac{n_0}{n_0 + n_1} \quad f_1 = \frac{n_1}{n_0 + n_1}$$

where  $n_0$  is the number of molecules in the low energy alignment and  $n_1$  is the number of molecules in the high energy alignment.<sup>1</sup> Of course,  $f_0 + f_1 = 1$ . (a). The number of molecules in a specific energy state is proportional to the Boltzmann weighting factor,  $n_i \propto e^{-\epsilon_i/kT}$ . Use this proportionality to find the fractions  $f_0$  and  $f_1$ . (b). Alternatively, the probability of finding a molecule in a specific energy state,  $\epsilon_i$ , is given by Eqs. 12.4.13 (Eq. 8.9.5). Show that your answers to part (a) are consistent with Eqs. 12.4.13.

*Answer:* (a). Given the proportionality  $n_i \propto e^{-\epsilon_i/kT}$ , the fractions are:

$$f_0 = \frac{n_0}{n_0 + n_1} = \frac{e^{-\epsilon_0/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}} \quad f_1 = \frac{n_1}{n_0 + n_1} = \frac{e^{-\epsilon_1/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}}$$

(b). The partition function for the two-state system is:

$$q = \sum_i e^{-\epsilon_i/kT} = e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}$$

Notice that the partition function is the same as the denominators for the fractions in part (a). The Boltzmann probabilities using Eqs. 12.4.13 (Eq. 8.9.5) are then:

$$p_0 = f_0 = \frac{e^{-\epsilon_0/kT}}{q} = \frac{e^{-\epsilon_0/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}}$$

$$p_1 = f_1 = \frac{e^{-\epsilon_1/kT}}{q} = \frac{e^{-\epsilon_1/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}}$$

as we derived in part (a). The partition function,  $q$ , and the denominator of the fractions,  $n_0 + n_1$ , play the same role; they normalize the probability to give either  $\sum p_i = 1$  or  $\sum f_i = 1$ .

7. Calculate the number of ways of arranging 10 distinguishable balls in three boxes with 3 in the first box, 5 in the second box, and 2 in the third box.

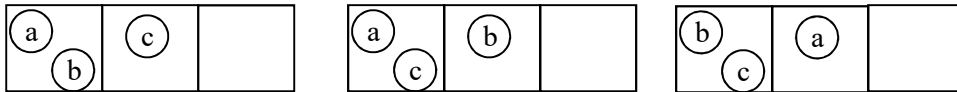
*Answer:* The statistical weight is given by Eq. 12.2.8 with the distribution numbers (3,5,2):

$$\mathcal{W} = \frac{\mathcal{M}!}{n_0! n_1! n_2! \dots} = \frac{10!}{3! 5! 2!} = 2520$$

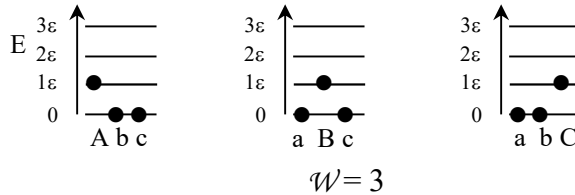
8. (a). Calculate the number of ways of arranging 3 distinguishable balls among 3 boxes with 2 balls in the first box, 1 ball in the second box, and 0 balls in the third box. (b). Calculate the number of ways of arranging the energy states of the system with 3 molecules given that 2 molecules are in the first energy level, 1 molecule is in the second energy level, and 0 molecules are in the third energy level. Draw the arrangements.

*Answer:* (a) The number of ways of arranging 3 distinguishable balls among 3 boxes with 2 balls in the first box, 1 ball in the second box, and 0 balls in the third box is given by Eq. 12.2.8 with the distribution numbers (2,1,0):

$$\mathcal{W} = \frac{\mathcal{M}!}{n_0! n_1! n_2! \dots} = \frac{3!}{2! 1! 0!} = 3$$



(b). The statistical weight is the same as in part (a):



9. Find the set of distribution numbers that maximizes the number of arrangements for 3 balls in 3 boxes.

*Answer:* The statistical weight is given by Eq. 12.2.8 with  $n_1$  balls in box 1,  $n_2$  balls in box 2, and  $n_3$  balls in box 3:

$$\mathcal{W} = \frac{3!}{n_1! n_2! n_3!}$$

Notice that permuting the same set of distribution numbers among the boxes gives the same statistical weight. That is  $\mathcal{W}(3,0,0) = \mathcal{W}(0,3,0) = \mathcal{W}(0,0,3)$ , so we only need to look for unique sets of  $(n_1, n_2, n_3)$ . The possibilities are:

$$\mathcal{W}(3,0,0) = \frac{3!}{3! 0! 0!} = 1 \quad \mathcal{W}(2,1,0) = \frac{3!}{2! 1! 0!} = 3 \quad \mathcal{W}(1,1,1) = \frac{3!}{1! 1! 1!} = 6$$

$\mathcal{W}_{\max}$  results for (1,1,1). The distribution with equal occupancies is called the uniform distribution. The distribution with the maximum number of ways of arrangement is always the uniform distribution in the absence of any constraints. The Boltzmann distribution arises because of the constraint on the total energy of the ensemble.

10. (a). Starting with  $N! \approx (N/e)^N$  show that  $\ln N! \approx N \ln N - N$ . (b). Starting with  $N! \approx \sqrt{2\pi N} (N/e)^N$  show that  $\ln N! = N \ln N - N + \frac{1}{2} \ln 2\pi N$ . (c) Compare the exact value of  $\ln N!$  and the two approximations for the largest number your calculator can use.

*Answer:* (a). Taking the log of  $N! \approx (N/e)^N$ :

$$\ln N! \approx \ln((N/e)^N) = N \ln(N/e) = N \ln N + N \ln(1/e) = N \ln N - N \ln e$$

since  $\ln(1/x) = -\ln(x)$ . For the last term,  $\ln(x)$  and  $e^x$  are inverse functions and  $\ln(e^1) = 1$ .

$$\ln N! \approx N \ln N - N \tag{Eq. 12.4.2}$$

(b). Taking the log of  $N! = \sqrt{2\pi N} (N/e)^N$ :

$$\ln N! \approx \ln((N/e)^N) + \ln\sqrt{2\pi N}$$

Using the result for  $\ln((N/e)^N)$  from part (a) simplifies the first term and noting that  $\sqrt{x} = x^{1/2}$ :

$$\begin{aligned} \ln N! &\approx N \ln N - N + \ln(2\pi N)^{1/2} \\ \ln N! &\approx N \ln N - N + \frac{1}{2} \ln 2\pi N \end{aligned} \tag{Eq. 12.9.12}$$

(c). The following values were calculated for  $N = 69$ :

$$69! = 1.71122 \times 10^{98} \quad \text{with the exact } \ln N! = 226.1905$$

The approximations give:

$$\begin{aligned} \ln N! &\approx N \ln N - N + \frac{1}{2} \ln 2\pi N = 226.1893 \quad \text{for a negligible error} \\ \text{and } \ln N! &\approx N \ln N - N = 223.1533 \quad \text{for a 1.34\% error from the exact value.} \end{aligned}$$

11. Show that the percent error using Sterling's approximation for  $\ln(N!)$  decreases with increasing  $N$ . (Excel has a larger range for valid  $N$  than most calculators.)

*Answer:* Excel maintains 15 significant figures for  $N!$  up to  $N = 170$ . The following spreadsheet was set-up using Eqs. 12.4.2 and 12.9.12 as approximations for  $\ln N!$ . The percent error is the error using  $\ln N! \approx N \ln N - N$  compared to the exact value to 15 significant figures.

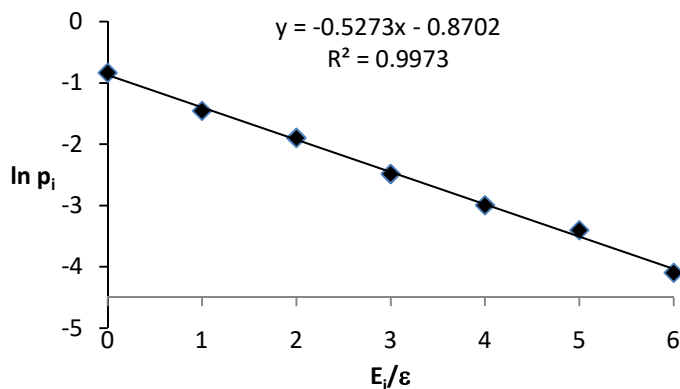
N	N!	ln N! exact	$N \ln N - N + (\ln 2\pi N)/2$	$N \ln N - N$	% error
30	2.65253E+32	74.6582	74.6555	72.0359	3.51
69	1.71122E+98	226.1905	226.1893	223.1533	1.34
80	7.15695E+118	273.6731	273.6721	270.5621	1.14
90	1.48572E+138	318.1526	318.1517	314.9829	1.00
100	9.33262E+157	363.7394	363.7385	360.5170	0.89
150	5.71338E+262	605.0201	605.0196	601.5953	0.57
170	7.25742E+306	706.5731	706.5726	703.0857	0.49

The thermodynamic limit is for very large numbers of systems, where  $N \approx 10^{23}$ . Sterling's approximation introduces negligible error for such large numbers.

12. In Problem 4 the most probable distribution was determined, choosing from (26,14,9,5,3,2,1) and (25,16,8,5,3,2,1). Verify that the most probable distribution is a Boltzmann distribution.

*Answer:* The first distribution is the most probable distribution, (26,14,9,5,3,2,1). You can verify that the first macrostate corresponds to a Boltzmann distribution, as closely as possible given the small number of systems, by plotting  $\ln p_i$  versus  $E_i$  as in Example 12.4.2:

$E_i/\epsilon$	$n_i$	$p_i$	$\ln p_i$
0	26	0.4333	-0.8363
1	14	0.2333	-1.4553
2	9	0.15	-1.8971
3	5	0.0833	-2.4849
4	3	0.05	-2.9957
5	2	0.0333	-3.401
6	1	0.0167	-4.0943



13. The fundamental vibration frequency for  $I_2$  is  $214.50 \text{ cm}^{-1}$ . Assume the vibrational states are equally spaced with spacing  $214.50 \text{ cm}^{-1}$ . Iodine vapor is held in an oven at elevated temperature. The relative occupations of the vibrational states were found to be 1.000 : 0.467 : 0.222 : 0.100. Calculate the temperature.

*Answer:* Following Example 12.4.2, the spacing between the energy states is given by:

$$\begin{aligned} \epsilon &= \Delta E = \frac{hc}{\lambda} = h c \tilde{\nu}_0 N_A & 1 \\ &= 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^8 \text{ m s}^{-1}) (214.5 \text{ cm}^{-1}) (100 \text{ cm/1 m}) (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= 2.566 \text{ kJ mol}^{-1} \end{aligned}$$

The relative populations of the states,  $r_i$ , is determined by dividing the probability by the population of the  $i = 0$  state; so the probability of the  $i^{\text{th}}$  state is determined by:

$$r_i = \frac{p_i}{p_0} \quad \text{giving } p_i = r_i p_0 \quad 2$$

The sum of the  $p_i$  is given by normalization:  $\sum p_i = 1$ . The sum of the  $r_i$  values is:

$$\sum r_i = \frac{\sum p_i}{p_0} = \frac{1}{p_0} \quad \text{giving } p_0 = \frac{1}{\sum r_i} \quad 3$$



Substitution of this last value for  $p_0$  into Eq. 2 gives:

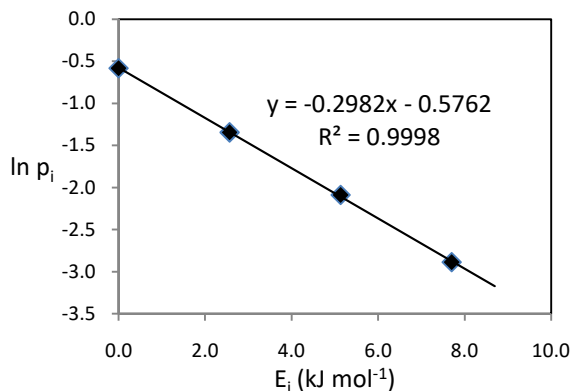
$$p_i = \frac{r_i}{\sum r_i}$$

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Using Eq. 4 the probabilities are calculated and the data are plotted as in Example 12.4.2:

i	$E_i$ (kJ mol <sup>-1</sup> )	Rel. pop.	$p_i$	$\ln p_i$
0	0.000	1	0.559	-0.582
1	2.566	0.467	0.261	-1.343
2	5.132	0.222	0.124	-2.087
3	7.698	0.1	0.056	-2.884

slope	-0.2982	-0.5762	intercept
±	0.0030	0.0143	±
r <sup>2</sup>	0.9998	0.0171	s(y)
F	10059.0807	2.0000	df
SS <sub>regression</sub>	2.9272	0.0006	SS <sub>residual</sub>



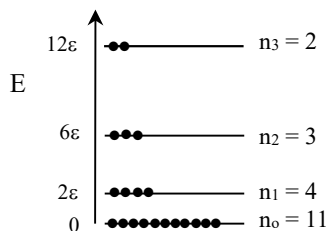
$$\text{slope} = -1/RT = -0.2982 \text{ kJ}^{-1} \text{ mol}$$

$$RT = 3.353 \text{ kJ mol}^{-1}$$

$$T = \frac{3.353 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} = 403. \text{ K} \pm 4. \text{ K}$$

The relative populations for vibrational states can be easily determined by the intensity of vibrational transitions that start from states higher than  $v = 0$ . These bands are called **hot bands**.

14. Is the following system at thermal equilibrium? Give the approximate temperature, assuming the unit of energy,  $\epsilon$ , is  $10.0 \text{ cm}^{-1}$ .



*Answer:* The plan is to make a plot using Eq. 12.4.29 to check for linearity, similar to Example 12.4.2. There are 20 systems for this problem. The value for  $\epsilon$  in  $\text{kJ mol}^{-1}$  is given by:

$$\epsilon = \Delta E = \frac{hc}{\lambda} = h c \tilde{\nu}_0 N_A$$

$$= 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^8 \text{ m s}^{-1})(10.0 \text{ cm}^{-1})(100 \text{ cm/1 m})(6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 0.1196 \text{ kJ mol}^{-1}$$

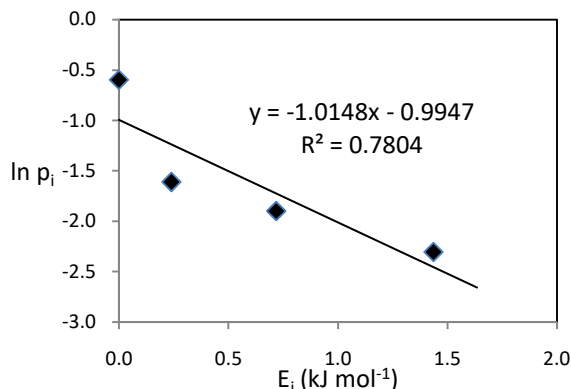
The plot using Eq. 12.4.29 with units in  $\text{kJ mol}^{-1}$  is:

state i	$E_i$ (kJ mol <sup>-1</sup> )	$n_i$	$p_i$	$\ln p_i$
0	0.000	11	0.550	-0.598
1	0.239	4	0.200	-1.609
2	0.718	3	0.150	-1.897
3	1.436	2	0.100	-2.303

$$\text{slope} = -1/RT = -1.015 \text{ kJ}^{-1} \text{ mol}$$

$$RT \approx 0.985 \text{ kJ mol}^{-1}$$

$$T \approx \frac{0.985 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} \approx 120 \text{ K}$$



The plot is not linear so the system is not at equilibrium. Since the system is not at equilibrium, an effective temperature cannot be determined. However, using the slope of the fit curve, a rough measure of the temperature for the equivalent Boltzmann distribution is 120 K with a large error.

The energy states in this problem are further apart as the energy increases. The energy states are said to “diverge” instead of being equally spaced. Translational and rotational energy states diverge. However, rotational energy states have a degeneracy of  $(2J+1)$ , where  $J$  is the index for the energy state. The energy states in this problem then energetically equivalent to rotational levels but are non-degenerate.

15. The conformational entropy for butane was determined in Example 12.4.3 using the *gauche-anti*-energy difference from molecular mechanics. Use a molecular orbital calculation to estimate the energy difference and determine the corresponding conformational entropy. How sensitive is the conformational entropy to the value of the energy difference? Your instructor will assign a molecular orbital method from the following list depending on the resources available: AM1, PM3, HF 3-21G(\*), HF 6-31G\*, B3LYP/6-31G\*, MP2/6-311G\*//HF 6-31G\* (single point energy at MP2/6-311G\* for the geometry calculation at 6-31G\*).

*Answer:* The energies are given below in the energy units normally associated with the calculation method:

State	units	$E_{\text{gauche}}$	$E_{\text{anti}}$	$\Delta E$
MMFF	kcal mol <sup>-1</sup>	-4.2554	-5.0348	0.7794
AM1	kcal mol <sup>-1</sup>	-30.4195	-31.1262	0.7067
PM3	kcal mol <sup>-1</sup>	-28.5375	-29.0632	0.5257
HF 3-21G(*)	Hartrees	-156.431	-156.432	0.001223
HF 6-31G*	Hartrees	-157.297	-157.298	0.001514
B3LYP 6-31G*	Hartrees	-158.457	-158.458	0.001388
MP2 6-311G*	Hartrees	-157.885	-157.886	0.000999

The difference in energy was converted to kJ mol<sup>-1</sup> and the entropy calculated following Example 12.4.3:

State	$\Delta E$ (kJ mol <sup>-1</sup> )	gauche e <sup>-E/RT</sup>	q	p <sub>gauche</sub>	p <sub>anti</sub>	S (J K <sup>-1</sup> mol <sup>-1</sup> )
MMFF	3.26101	0.26839	1.53677	0.174643	0.65072	7.39
AM1	2.956833	0.30342	1.60684	0.18883	0.6223	7.69
PM3	2.199529	0.41182	1.82363	0.225822	0.54836	8.33
HF 3-21G(*)	3.210987	0.27386	1.54771	0.176943	0.64612	7.44
HF 6-31G*	3.974744	0.20125	1.40250	0.143493	0.71301	6.64
B3LYP 6-31G*	3.643406	0.23003	1.46005	0.157546	0.68491	7.00
MP2 6-311G*	2.622087	0.34728	1.69456	0.204939	0.59012	7.99

The MP2/6-311G\* calculation was a single point energy based on the HF 6-31G\* optimized geometry. It is interesting to note that, at least for this simple compound, molecular mechanics represents the torsional interaction as well as lower level quantum mechanical calculations. The torsional entropy is moderately sensitive to the level of the calculation. The experimental value is 0.67 kcal mol<sup>-1</sup> or 2.8 kJ mol<sup>-1</sup>.<sup>2</sup>

16. Determine the conformational entropy for 1,2-dichlorobutane. Your instructor will assign a molecular mechanics or molecular orbital method from the following list depending on the resources available: MMFF, PM3, HF 3-21G(\*), HF 6-31G\*, B3LYP/6-31G\*, MP2/6-311G\*//HF 6-31G\* (single point energy at MP2/6-311G\* for the geometry calculation at 6-31G\*)

*Answer:* The energies are given below in the energy units normally associated with the calculation method:

State	units	E <sub>gauche</sub>	E <sub>anti</sub>	$\Delta E$
MMFF	kcal mol <sup>-1</sup>	6.2564	5.0273	1.2291
PM3	kcal mol <sup>-1</sup>	-24.0718	-24.6829	0.6111
HF 3-21G(*)	Hartrees	-992.435	-992.438	0.002923
HF 6-31G*	Hartrees	-997.028	-997.031	0.003047
B3LYP 6-31G*	Hartrees	-999.016	-999.019	0.002713
MP2 6-311G*	Hartrees	-997.646	-997.648	0.002430

The difference in energy was converted to kJ mol<sup>-1</sup> and the entropy calculated following Example 12.4.3 and Eq. 12.4.11:

State	$\Delta E$ (kJ mol <sup>-1</sup> )	gauche e <sup>-E/RT</sup>	q	p <sub>gauche</sub>	p <sub>anti</sub>	S (J K <sup>-1</sup> mol <sup>-1</sup> )
MMFF	5.142554	0.12565	1.25130	0.10042	0.79917	5.33
PM3	2.556842	0.35654	1.71308	0.20813	0.58374	8.04
HF 3-21G(*)	7.674337	0.04526	1.09051	0.04150	0.91700	2.86
HF 6-31G*	7.999899	0.03969	1.07937	0.03677	0.92646	2.61
B3LYP 6-31G*	7.121931	0.05655	1.11310	0.05080	0.89839	3.32
MP2 6-311G*	6.379177	0.07630	1.15261	0.06620	0.86760	4.01

The results are surprisingly dependent on the method. The experimental  $\Delta E$  is 1.08 kcal mol<sup>-1</sup> or 4.52 kJ mol<sup>-1</sup>.<sup>2%</sup>WJH

17. The process of folding a protein to produce the active conformation restricts torsions along the polypeptide backbone and side chain torsions for amino acids that are buried in the interior of the protein. Calculate the conformational entropy of the side chain of the amino acid valine at 298.2 K. Use molecular mechanics with the MMFF force field in the gas phase for the zwitter-ionic form to determine the low energy side chain conformations and the corresponding energies.

*Answer:* The calculation of the entropy parallels Example 12.4.3. The low energy conformations for zwitter-ionic valine in the gas phase using the MMFF94x force field are -3.0881, -5.3433, -4.4024 kcal mol<sup>-1</sup> at -51.8°, 57.6°, -168.7° respectively. The dihedral angle was measured from the carbonyl carbon to the side chain methine-hydrogen, O=C-C<sub>α</sub>-C-H. Using the lowest energy conformer as the reference, the energies in kJ mol<sup>-1</sup> in increasing order are then: 0, 3.937, 9.436 kJ mol<sup>-1</sup>.

The Boltzmann weighting factor for the lowest energy conformer is 1, since e<sup>0</sup> = 1. The Boltzmann weighting factors for the higher energy conformers are:

$$e^{-\varepsilon_2/RT} = e^{-9.436 \times 10^3 \text{ J} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.2 \text{ K})} = 0.0222$$

$$e^{-\varepsilon_1/RT} = e^{-3.937 \times 10^3 \text{ J} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.2 \text{ K})} = 0.2043$$

The partition function, Eq. 12.4.13 (Eq. 8.9.7), is the normalization for the probability distribution:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + 0.2043 + 0.0222 = 1.2265$$

The probabilities for each state are then:

$$p_2 = e^{-\varepsilon_2/RT} / q = 0.0222 / 1.2265 = 0.0181$$

$$p_1 = e^{-\varepsilon_1/RT} / q = 0.2043 / 1.2265 = 0.1666$$

$$p_0 = e^{-\varepsilon_0/RT} / q = 1/q = 1/1.2265 = 0.8153$$

The molar conformational entropy as given by Eq. 12.4.14:

$$S = -R \sum_i p_i \ln p_i \quad \text{(molecular probabilities)}$$

$$S = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [0.8153 \ln(0.8153) + 0.1666 \ln(0.1666) + 0.0181 \ln(0.0181)]$$

$$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [-0.1665 + (-0.2986) + (-0.0726)]$$

$$= 4.47 \text{ J K}^{-1} \text{ mol}^{-1}$$

When the side chain is bound in a restricted environment, most of this entropy is lost. Notice that the highest energy conformer plays a minor role in the overall entropy, because the state is not easily accessible at 298.2 K. In other words, at room temperature RT = 2.48 kJ mol<sup>-1</sup> and the highest energy conformer is at 9.44 kJ mol<sup>-1</sup>. If the energy differences were very small the conformational entropy would have been S = R ln 3 = 9.13 J K<sup>-1</sup> mol<sup>-1</sup>. Torsional conformational isomers are often called rotameric states. The side chain of valine has three rotameric states.

18. Assume that the *gauche*-energy states for a 1,2-disubstituted ethane, X-CH<sub>2</sub>-CH<sub>2</sub>-Y, are at energy  $\varepsilon$  above the *anti*-state. The *anti*-state is set at the reference state. Show that the conformational entropy for the C-C bond in disubstituted ethane compounds is given by:

$$S = -\frac{R}{(1 + 2 e^{-\varepsilon/RT})} \left[ \ln\left(\frac{1}{1 + 2 e^{-\varepsilon/RT}}\right) + 2 e^{-\varepsilon/RT} \ln\left(\frac{e^{-\varepsilon/RT}}{1 + 2 e^{-\varepsilon/RT}}\right) \right]$$

*Answer:* The Boltzmann weighting factor for the *anti*-conformer is 1, since we chose a reference energy of zero for the *anti*-conformer and  $e^0 = 1$ . The Boltzmann weighting factor for the *gauche*-conformer with the given energy of  $\varepsilon$  is:

$$e^{-E_{gauche}/RT} = e^{-\varepsilon/RT}$$

The partition function is the normalization for the probability distribution:

$$q = \sum_i e^{-E_i/kT} = 1 + 2 e^{-\varepsilon/RT}$$

The probabilities for each *gauche* and *anti*-energy state are then:

$$p(\text{gauche}) = \frac{e^{-E_{gauche}/RT}}{q} = e^{-\varepsilon/RT}/(1 + 2 e^{-\varepsilon/RT})$$

$$p(\text{anti}) = \frac{e^{-E_{anti}/RT}}{q} = 1/q = 1/(1 + 2 e^{-\varepsilon/RT})$$

The conformational entropy as given by Eq. 12.4.9 is for a sum over all the energies for a system. The entropy is given using Eq. 12.4.11:

$$S = -R \sum_i p_i \ln p_i = -R [p_{anti} \ln p_{anti} + p_{gauche} \ln p_{gauche} + p_{gauche} \ln p_{gauche}]$$

$$S = -\frac{R}{(1 + 2 e^{-\varepsilon/RT})} \left[ \ln\left(\frac{1}{1 + 2 e^{-\varepsilon/RT}}\right) + 2 e^{-\varepsilon/RT} \ln\left(\frac{e^{-\varepsilon/RT}}{1 + 2 e^{-\varepsilon/RT}}\right) \right]$$

19. Show that the maximum conformational entropy for freely rotating sp<sub>3</sub> hybridized bonds is given by  $S = R \ln 3$ . In other words, assume that the energy differences between the three conformational states is much less than RT. You also need to assume that the three conformations are distinguishable, as in the central butane dihedral or the side chain of valine but not -CH<sub>3</sub> torsions.

*Answer:* Assign the lowest energy conformer as the reference state with  $\varepsilon_0 = 0$ . Then the remaining conformers have energies  $\varepsilon_1$  and  $\varepsilon_2$ . Assume that  $\varepsilon_1 \ll RT$  and  $\varepsilon_2 \ll RT$ . The Boltzmann weighting factor for each level is then essentially equivalent,  $e^{-\varepsilon_i/RT} \approx 1$ . The partition function is then  $\sum e^{-\varepsilon_i/RT} = 3$ . Then the probability for finding each conformational state is equal,

$p_0 = p_1 = p_2 = 1/3$ . There is no conformational biasing, because the energy differences are small compared to the available thermal kinetic energy. The conformational entropy, using Eq. 12.4.14, is:

$$S = -R \sum_i p_i \ln p_i = -R [1/3 \ln 1/3 + 1/3 \ln 1/3 + 1/3 \ln 1/3] = -R \ln 1/3 = R \ln 3$$

In general, the maximum conformational entropy is given by  $S = R \ln w$ , where  $w$  is the number of distinguishable conformational states. (See the previous problem for more information about distinguishability.)

20. Calculate the conformational entropy for the  $C(sp_3)-C(sp_2)$  bond torsion leading to the phenyl ring in the side chain of the amino acid phenylalanine. Use molecular mechanics with the MMFF force field for gas phase energies. To obtain values that are appropriate for protein folding studies, build a protein in the alpha-helical form with 11 residues: five alanines followed by phenylalanine followed by five alanines. Acetylate the N-terminus and amidate the C-terminus to help stabilize the alpha-helix. Once the lowest energy structure is found, fix (or freeze) all of the atoms except those in the phenyl side chain. Then determine the low energy conformers as you rotate around the  $C_\alpha-C_\beta(sp_3)-C_{ring}(sp_2)-C_{ring}$  dihedral. You will find four low energy conformers. However, the conformers are in two equivalent pairs. The conformers in each pair differ by rotation of the phenyl ring by  $180^\circ$ . The phenyl ring is symmetrical with respect to rotation by  $180^\circ$ , so the conformational states that differ by  $180^\circ$  are indistinguishable. The counting of states for calculation of the entropy is over distinguishable states. To correct for symmetry, then, calculate the entropy by summing over only the two unique, distinguishable states. The structure and the required dihedral is illustrated below, Figure P12.1.

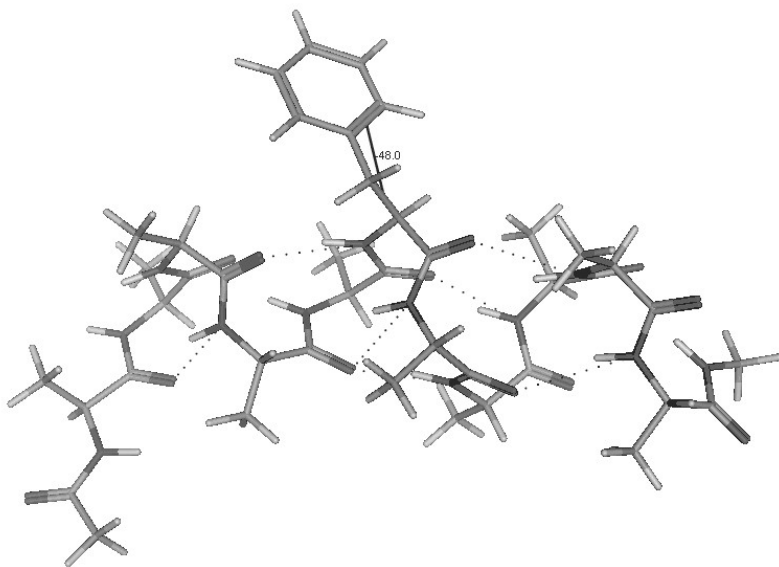


Figure P12.1: An alpha-helical 11-mer with phenylalanine in the center. The required dihedral is depicted with the angle of  $-48.0^\circ$ , giving the lowest energy conformer. The dotted lines show the hydrogen-bonding pattern. The distortions in the hydrogen-bonding pattern are caused by the shortness of the peptide. Your model may differ in the conformations of the terminal residues.

*Answer:* The calculation of the entropy parallels Example 12.4.3. The low energy conformations in the gas phase using the MMFF94x force field are 3.3441 and 6.2248 kcal mol<sup>-1</sup> at -48.0° and 7.2° respectively. The dihedral angle was measured from the *alpha*-carbon to the side chain *beta*-carbon to the ring sp<sup>2</sup>-C, and finishing with another ring-carbon: C<sub>α</sub>-C<sub>β</sub>(sp<sup>3</sup>)-C<sub>ring</sub>(sp<sup>2</sup>)-C<sub>ring</sub>. The dihedral for the methylene, β-carbon and the alpha-carbon for this structure was 163°. Using the lowest energy conformer as the reference, the relative energy of the higher energy conformer is 12.05 kJ mol<sup>-1</sup>.

The Boltzmann weighting factor for the lowest energy conformer is 1, since e<sup>0</sup> = 1. The Boltzmann weighting factor for the higher energy conformer is:

$$e^{-\varepsilon_1/RT} = e^{-12.05 \times 10^3 \text{ J} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.2 \text{ K})} = 0.00774$$

The partition function, Eq. 12.4.13 (Eq. 8.9.7), is the normalization for the probability distribution:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + 0.00774 = 1.0077$$

The probabilities for each state are then:

$$p_1 = e^{-\varepsilon_1/RT} / q = 0.00774 / 1.0077 = 7.68 \times 10^{-3}$$

$$p_0 = e^{-\varepsilon_0/RT} / q = 1 / q = 1 / 1.0077 = 0.9924$$

The molar conformational entropy as given by Eq. 12.4.14:

$$S = -R \sum_i p_i \ln p_i \quad (\text{molecular probabilities})$$

$$S = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [0.9924 \ln(0.9924) + 7.68 \times 10^{-3} \ln(7.68 \times 10^{-3})]$$

$$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [(-7.57 \times 10^{-3}) + (-0.037)]$$

$$= 0.37 \text{ J K}^{-1} \text{ mol}^{-1}$$

The conformational entropy is quite small. Burying phenylalanine side chains in the interior of proteins has favorable energetic and solvation entropic effects with little conformational entropy penalty. Notice that the higher energy conformer plays a minor role in the overall entropy, because the state is not easily accessible at 298.2 K. In other words, at room temperature RT = 2.48 kJ mol<sup>-1</sup> and the higher energy conformer is at 12.05 kJ mol<sup>-1</sup>. If the energy differences were very small the conformational entropy would have been S = R ln 2 = 5.76 J K<sup>-1</sup> mol<sup>-1</sup>. Torsional conformational isomers are often called rotameric states. The side chain of phenylalanine has four rotameric states, but only two distinguishable states.

Your results may have been rather different for this problem. Reliable estimates of the conformational entropy of amino acid side chains is a difficult computational problem and very sensitive to the details of the computation and the computational method.

21. The Boltzmann distribution is often derived directly by maximizing  $\mathcal{W}$  instead of maximizing the entropy using Eq. 12.4.9. In this problem, we derive the Boltzmann distribution

in several steps directly from the statistical weights. (a) Starting with Eq. 12.4.1, show that without constraints:

$$d(\ln \mathcal{W}) = \sum \left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) dn_i$$

(b). Add in the constraints to give:

$$0 = \sum \left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) dn_i + \alpha \sum dn_i - \beta \sum E_i dn_i$$

(c). Show that the constrained maximization results in

$$\left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) + \alpha - \beta E_i = 0$$

(d). Note that the summation variable in Eq. 12.4.5 is an arbitrary index. We can also write:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_j n_j \ln n_j$$

Show that the derivative of  $\ln \mathcal{W}$  with respect to  $n_i$  while holding all the other distribution numbers constant gives just one term, which is:

$$\left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) = -(\ln n_i + 1) \approx -\ln n_i$$

(e). Substitute this last result into the result from part (c) and solve for  $n_i$  to find:

$$n_i = e^{\alpha - \beta E_i} = e^{\alpha} e^{-\beta E_i}$$

(f). Use normalization to find the Boltzmann distribution:

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Q}$$

*Answer:* (a). Maximizing the entropy is equivalent to maximizing  $\ln \mathcal{W}$ . The statistical weights are:

$$\mathcal{W} = \frac{\mathcal{N}!}{n_0! n_1! n_2! \dots} \quad 1$$

The total number of systems in the ensemble and the total ensemble energy is:

$$\mathcal{N} = \sum_i n_i \quad \mathcal{E} = \sum_i n_i E_i \quad 2$$

where the sum is over all energy states,  $i$ . The logarithm of the statistical weights is, Eq. 12.4.1:

$$\ln \mathcal{W} = \ln \mathcal{N}! - \sum \ln n_i! \quad 3$$

The number of systems in each state is changed by  $dn_i$  to find the maximum in  $\ln \mathcal{W}$ . The total differential of  $\ln \mathcal{W}$  is:



$$d(\ln \mathcal{W}) = \sum \left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) dn_i \quad 4$$

(b). However, since the ensemble is isolated, we can't change the number of systems in the ensemble nor the total energy. The constraints are:

$$\text{Constraints: } d\mathcal{N} = dn_0 + dn_1 + dn_2 + dn_3 + \dots = \sum dn_i = 0 \quad 5$$

$$d\mathcal{E} = E_0 dn_0 + E_1 dn_1 + E_2 dn_2 + E_3 dn_3 + \dots = \sum E_i dn_i = 0 \quad 6$$

Any constant multiple of these constraints will also give zero:

$$\alpha \sum dn_i = 0 \quad \text{and} \quad \beta \sum E_i dn_i = 0 \quad 7$$

where  $\alpha$  and  $\beta$  are undetermined multipliers. Adding in the constraints and setting the result equal to zero to find the maximum gives:

$$0 = \sum \left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) dn_i + \alpha \sum dn_i - \beta \sum E_i dn_i \quad 8$$

(c). Now the  $n_i$ 's can be treated as independent! Combining sums and distributing out the factor of  $dn_i$  gives:

$$0 = \sum \left( \left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) + \alpha - \beta E_i \right) dn_i \quad 9$$

The only way for this sum to always give zero for any changes in the  $dn_i$  is for each term in the sum to give zero:

$$\left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) + \alpha - \beta E_i = 0 \quad 10$$

(d). We can now substitute in Eq. 3 into this last equation. Using Sterling's formula,  $\ln x! = x \ln x - x$ , for the factorials gives:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_j (n_j \ln n_j - n_j) \quad 11$$

Notice that the last term in the sum gives the total number of systems in the ensemble,  $\sum n_j = \mathcal{N}$  giving Eq. 12.4.5:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_j n_j \ln n_j \quad 12$$

The derivative of this last equation with respect to  $n_i$  while holding all the other occupation numbers constant only results in the single term:

$$\left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) = - \left( n_i \frac{\partial \ln n_i}{\partial n_i} + \ln n_i \right) \quad 13$$

since all the other derivatives are zero. Taking the derivative of  $\ln n_i$  gives:

$$\left( \frac{\partial \ln \mathcal{W}}{\partial n_i} \right) = - \left( n_i \frac{1}{n_i} + \ln n_i \right) \quad 14$$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = -(\ln n_i + 1) \approx -\ln n_i \quad 15$$

The final approximation is valid since we work in the thermodynamic limit where all the occupation numbers are very large.

(e). The derivation from this point parallels Eqs. 12.4.7-12.4.14. Substituting this last equation for the derivative into Eq. 10 gives:

$$-\ln n_i + \alpha - \beta E_i = 0 \quad 16$$

Solving for the  $\ln n_i$ :

$$\ln n_i = \alpha - \beta E_i \quad 17$$

and exponentiating both sides of the last equation results in the occupation number for the  $i^{\text{th}}$  state for the most probable distribution:

$$n_i = e^{\alpha - \beta E_i} = e^{\alpha} e^{-\beta E_i} \quad 18$$

(f). We can solve for the normalization by substituting Eq. 18 into Eq. 2 to give:

$$\mathcal{N} = \sum_i n_i = \sum_i e^{\alpha} e^{-\beta E_i} = e^{\alpha} \sum_i e^{-\beta E_i} \quad 19$$

Solving for the normalization constant gives:

$$e^{\alpha} = \frac{\mathcal{N}}{\sum_i e^{-\beta E_i}} \quad 20$$

The sum in the denominator is defined as the partition function,  $Q$ :

$$Q = \sum_i e^{-\beta E_i} \quad 21$$

which upon substitution into Eq. 20 gives the final result for the occupation numbers in the most probable distribution:

$$n_i = \frac{\mathcal{N}}{Q} e^{-\beta E_i} \quad 22$$

where  $n_i$  is the number of systems in energy state  $E_i$ . The probability of occurrence of a system in energy state  $E_i$  is then obtained by dividing by the number of systems in the ensemble, to give the ensemble average:

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Q} \quad 23$$

which is probability of finding a system in energy state  $E_i$ .

22. Consider the bowl shaped function,  $f(x,y) = 1 - x^2 - y^2$ . Maximize the function subject to the constraint  $y = 0.5$  using the Lagrange method of undetermined multipliers.

Answer: The function and the constraint are shown in Figure P.1:

$$f(x,y) = 1 - x^2 - y^2 \tag{1}$$

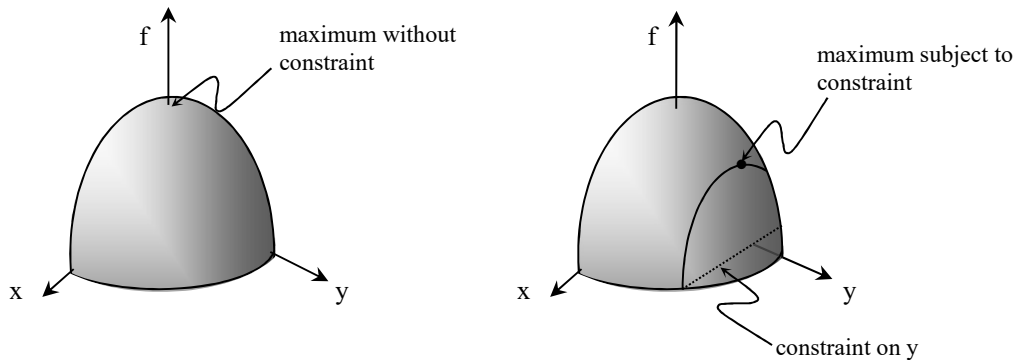


Figure P.1: Constrained maximization of  $f(x,y) = 1 - x^2 - y^2$ .

The total differential is:

$$df = -2x dx - 2y dy = 0 \tag{maximum} \tag{2}$$

The unconstrained maximum for this function is calculated by setting  $df$  equal to 0, giving  $x = 0$  and  $y = 0$  for the maximum,  $f_{\max} = 1$ . The constraint is given as:

$$y = 0.5 \quad \text{or} \quad c = y - 0.5 = 0 \tag{constraint} \tag{3}$$

as shown in Figure P.1. As  $x$  and  $y$  are changed to find the maximum, the differential of the constraint gives:

$$dc = dy = 0 \tag{constraint} \tag{4}$$

This equation can be multiplied by a constant,  $\lambda$ , and still give zero; the constant is the Lagrange multiplier:

$$\lambda(dy) = 0 \tag{constraint} \tag{5}$$

Adding Eqs. 1 and 4 still gives zero:

$$-2x dx - 2y dy + \lambda(dy) = 0 \tag{constrained} \tag{6}$$

or collecting terms in  $dx$  and  $dy$ :

$$-2x dx + (-2y + \lambda) dy = 0 \tag{constrained} \tag{7}$$

We can now treat  $dx$  and  $dy$  as independent of each other. The only way for Eq. 6 to always equal zero is if the coefficients of  $dx$  and  $dy$  are both always equal to zero:

$$\begin{aligned} (-2x) &= 0 \\ (-2y + \lambda) &= 0 \end{aligned} \quad \text{(constrained) } 8$$

The first equation gives  $x = 0$ . The constraint requires  $y = 0.5$ . The maximum in our function occurs when  $x = 0$  and  $y = 0.5$ . The value of  $f$  at the constrained maximum is then obtained from Eq. 1:

$$f(0, 1/2) = 1 - (0)^2 - (0.5)^2 = 0.75 \quad \text{(constrained) } 9$$

as shown in the figure. This problem is really just a one dimensional problem since  $y$  is constrained to a constant value. We didn't need to use Lagrange multipliers. However, the problem gives us a simple opportunity to explore the meaning of the Lagrange multiplier. The Lagrange multiplier,  $\lambda$ , is used for the constraint on the value of  $y$ . Solving Eq. 8 gives  $\lambda = 2y$ , which is just  $-(\partial f / \partial y)_x$ . Looking back to the derivation of the Boltzmann distribution,  $\beta$  is the Lagrange multiplier used to constrain the total energy of the ensemble, which also constrains the average energy of a system in the ensemble. Similarly to this problem,  $\beta = (1/k)(\partial S / \partial U)_V = (1/k)(\partial S / \partial \langle E \rangle)_V$ , using Eq. 12.5.20. The Lagrange multiplier is proportional to the slope of the function that is being maximized with respect to changes in the corresponding constraint.

23. A scientific instrument company produces two different widgets. Let the number of widgets produced by the factory per day of the two different widgets be  $n_1$  and  $n_2$ , respectively. The profit obtained by selling type-one widgets,  $P_1$ , and type-two widgets,  $P_2$ , is given as:

$$P_1 = 40 n_1 - n_1^2 \quad P_2 = 20 n_2 - 0.5 n_2^2$$

The negative terms in the profit equations result because as the production increases, the cost of labor increases (extra people need to be hired) and the marketing costs increase. The factory can make at most 25 widgets per day. Find the optimal level of production for the two widgets to maximize the overall profit. Compare the constrained result to the unconstrained result assuming the factory can produce any number of widgets per day.

*Answer:* This problem follows the Lagrange Multipliers example in Addendum 12.7. The total profit is given by  $P = P_1 + P_2$ . The total differential of the profit, as the production rates are varied, is:

$$\begin{aligned} dP &= \left( \frac{\partial P}{\partial n_1} \right)_{n_2} dn_1 + \left( \frac{\partial P}{\partial n_2} \right)_{n_1} dn_2 \\ dP &= (40 - 2 n_1) dn_1 + (20 - n_2) dn_2 \end{aligned} \quad 1$$

Setting  $dP = 0$  gives the optimum result with no production constraint. If  $dn_1$  and  $dn_2$  can vary freely, then the only way we can guarantee that  $dP = 0$  is if both coefficients are equal to zero:

$$(40 - 2 n_1) = 0 \quad \text{and} \quad (20 - n_2) = 0 \quad \text{(unconstrained) } 2$$

Solving for the production gives  $n_1 = 20$  and  $n_2 = 20$ , which exceeds the maximum production possible by the factory. The production constraint is given by  $n_1 + n_2 = 25$ , or subtracting the constant from both sides of the equation to give the constraint equation equal to zero:

$$c = n_1 + n_2 - 25 = 0 \quad (\text{constraint}) \quad 3$$

The total differential of the constraint as  $n_1$  and  $n_2$  are varied is:

$$dc = dn_1 + dn_2 = 0 \quad (\text{constraint}) \quad 4$$

In other words, the total number of widgets produced is constant. So if more type-one widgets are produced, then an equal number fewer type-two widgets can be produced. Eq. 4 can be multiplied by a constant and still satisfy the constraints:

$$\lambda (dn_1 + dn_2) = 0 \quad (\text{constraint}) \quad 5$$

Adding Eqs. 1 and 5 still gives zero for the maximum profit:

$$(40 - 2n_1) dn_1 + (20 - n_2) dn_2 + \lambda (dn_1 + dn_2) = 0 \quad (\text{constrained}) \quad 6$$

Collecting terms in  $dn_1$  and  $dn_2$ :

$$(40 - 2n_1 + \lambda) dn_1 + (20 - n_2 + \lambda) dn_2 = 0 \quad (\text{constrained}) \quad 7$$

Since  $dn_1$  and  $dn_2$  can now be treated as independent variables, the only way we can guarantee  $dP = 0$  is if both coefficients are separately equal to zero:

$$\begin{aligned} 40 - 2n_1 + \lambda &= 0 \\ 20 - n_2 + \lambda &= 0 \end{aligned}$$

Subtracting the second equation from the first gives:

$$20 - 2n_1 + n_2 = 0 \quad \text{and then} \quad n_2 = 2n_1 - 20 \quad (\text{constrained max.}) \quad 8$$

Since  $n_1 + n_2 = 25$  from the constraint, we can solve for  $n_1$  and substitute  $n_1 = 25 - n_2$  into the last equation to give:

$$n_2 = 50 - 2n_2 - 20 \quad \text{giving} \quad n_2 = 10 \quad (\text{constrained max.}) \quad 9$$

and then from the original constraint,  $n_1 = 25 - n_2 = 15$ . The maximum profit is then:

$$P = P_1 + P_2 = (40n_1 - n_1^2) + (20n_2 - 0.5n_2^2) = 525 + 150 = 675$$

24. Thermodynamic state functions can be written directly in terms of the partition function,  $Q$ , which adds to the importance of this central concept. Using Eqs. 12.4.9, 12.4.12, 12.2.6, and 12.1.2, show that the entropy can be written as:

$$S = k \ln Q + \frac{U - U(0)}{T}$$

*Answer:* Starting from Eq. 12.4.9, we need to find the  $\ln p_i$ . Taking the logarithm of  $p_i$  from Eq. 12.4.12 gives Eq. 12.5.29:

$$\ln p_i = \frac{-E_i}{kT} - \ln Q$$

Substituting this last equation into Eq. 12.4.9 gives:

$$S = -k \sum_i p_i \left( \frac{-E_i}{kT} - \ln Q \right)$$

$$= \frac{k}{kT} \sum_i p_i E_i + k \sum_i p_i \ln Q$$

The first summation is just the average energy from Eq. 12.2.6. In the second summation,  $\ln Q$  is a constant, which factors out in front of the summation:

$$S = \frac{\langle E \rangle}{T} + k \ln Q \sum_i p_i$$

The ensemble average energy is  $U - U(0)$ , Eq. 12.1.2. The sum of the  $p_i$  is equal to one, because the probabilities are normalized,  $\sum p_i = 1$ , giving:

$$S = k \ln Q + \frac{U - U(0)}{T}$$

The partition function gives the number of accessible states; therefore the more accessible states the greater the energy dispersal. In addition energy transfer into the system, as given by  $U - U(0)$ , increases the number of accessible states, because more energy is available to the system. The entropy given as a function of  $Q$  will play an important role in Chapt. 32.

25. What is the probability of selecting an Ace in 10 total cards? To avoid statistical complications, assume that after each selection the card is returned to the deck, so that each selection is made from a full deck of 52 cards.

*Answer:* The probability of being dealt an Ace on a single selection is  $4/52$ . The probability of being dealt an Ace in 10 selections is  $10(4/52) = 40/52$ . It doesn't matter which selection of the 10 results in an Ace, so being dealt a single Ace is an "OR" series of events.

26. The next five problems concern the relationship between statistical weights and the probability of occurrence of a particular set of events. The number of ways of selecting  $n$  objects from  $N$ , which we called  $C[N \text{ choose } n]$ , is also called the binomial coefficient and given the symbol  $\binom{N}{n}$ . Using Eq. 12.9.1 show that the binomial coefficient can be expressed as:

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N!}{n!(N-n)!}$$

*Answer:* Starting with Eq. 12.9.1, multiply the numerator and denominator by  $(N-n)!$ :

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N(N-1)\dots(N-n+1)(N-n)!}{n!(N-n)!}$$

However, the numerator is just the complete series of products from N down to 1, which is equivalent to N!:

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N!}{n!(N-n)!}$$

27. In the last problem we showed that the binomial coefficient  $\binom{N}{n}$  can be defined as:

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N!}{n!(N-n)!}$$

The binomial coefficient  $\binom{N}{n}$  is the numerical coefficient for the  $n^{\text{th}}$  term in the  $N^{\text{th}}$ -order polynomial  $(1 + x)^N$ . For example:

$$\begin{aligned} (1 + x)^3 &= (1 + 2x + x^2)(1 + x) \\ &= 1 + 3x + 3x^2 + x^3 \\ &= \binom{3}{0} 1 + \binom{3}{1} x + \binom{3}{2} x^2 + \binom{3}{3} x^3 \end{aligned}$$

Verify the corresponding result for  $(1 + x)^4$ .

*Answer:* Start with the explicit polynomial:

$$(1 + x)^4 = (1 + 3x + 3x^2 + x^3)(1+x) = 1 + 4x + 6x^2 + 4x^3 + x^4$$

In terms of the binomial coefficients, following the pattern from the cubic polynomial, we should find:

$$(1 + x)^4 = \binom{4}{0} 1 + \binom{4}{1} x + \binom{4}{2} x^2 + \binom{4}{3} x^3 + \binom{4}{4} x^4$$

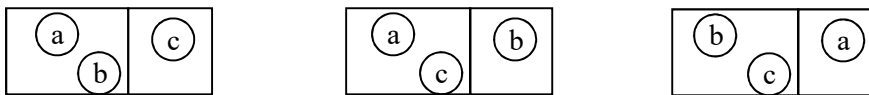
Do the evaluations of the binomial coefficients match up with the expected coefficients: 1 : 4 : 6 : 4 : 1?

$$\binom{4}{0} = \binom{4}{4} = \frac{4!}{0!(4-0)!} = 1 \quad \binom{4}{1} = \binom{4}{3} = \frac{4!}{1!(4-1)!} = 4 \quad \binom{4}{2} = \frac{4!}{2!(4-2)!} = 6$$

28. Assume that 3 distinguishable balls are selected at random for placement into two boxes. The volume of box 1 is  $V_1$  and the volume of box 2 is  $V_2$ . The probability of a single ball landing in box 1 is proportional to its volume,  $p_1 = V_1/(V_1 + V_2)$ . The probability of a single ball landing in box 2 is proportional to its volume,  $p_2 = V_2/(V_1 + V_2)$ . What is the probability that all 3 balls land in the first box? There is only one way for all 3 balls to land in box 1 giving the probability as  $p(3,0) = p_1^3$ . There is only one way for all 3 balls to land in box 2 giving  $p(0,3) = p_2^3$ . Find the probability of 2 balls landing in box 1 and the remaining ball landing in box 2. Relate the results to the statistical weight  $W(2,1)$ .

*Answer:* The probability of a single ball landing in box 1 is  $p_1$ . The probability of two specific balls landing in box 1 is  $p_1^2$  and then the probability of the remaining ball landing in box 2 is  $p_2$ .

The overall probability for a set of specific balls is given as  $(p_1^2 p_2)$ . However, there is more than one way of achieving this distribution:



$$W(2,1) = \frac{3!}{2! 1!} = 3$$

The final probability is then  $p(2,1) = W(2,1) (p_1^2 p_2) = 3 (p_1^2 p_2)$ . This example shows the relationship between  $W$  and the probability of occurrence of a particular set of distribution numbers. Notice that this result can also be expressed using the binomial coefficient, which is the subject of the next problem.

29. Show that for a two-category problem with  $N$  distinguishable objects the binomial coefficient and statistical weight are related by:

$$W(n_1, n_2) = \binom{N}{n_1}$$

An example is the previous two-box problem. The result also holds for any molecular system that has only two energy levels. Use the result of the last problem as a specific example.

*Answer:* In general for a two category selection problem, because there are only two categories the distribution numbers are related by  $n_2 = N - n_1$  and:

$$W(n_1, n_2) = \frac{N!}{n_1! n_2!} = \frac{N!}{n_1! (N-n_1)!} = \binom{N}{n_1}$$

Using the last problem as an example, for 3 balls, the probability for finding two balls in the first box and one ball in the second box depends on the statistical weight for the distribution (2,1):

$$W(2,1) = \frac{3!}{2! 1!} = \frac{3!}{2! (3-2)!} = \binom{3}{2}$$

giving the final probability:

$$p(2,1) = W(2,1) (p_1^2 p_2) = \binom{3}{2} (p_1^2 p_2)$$

The binomial coefficients are the statistical weight for two-category problems. The next problem puts this result in a broader context.

30. Assume that 3 distinguishable balls are selected at random for placement into two boxes. The volume of box 1 is  $V_1$  and the volume of box 2 is  $V_2$ . The probability of a single ball landing in box 1 is proportional to its volume,  $p_1 = V_1/(V_1 + V_2)$ . The probability of a single ball landing in box 2 is proportional to its volume,  $p_2 = V_2/(V_1 + V_2)$ . There is only one way for all 3 balls to



land in box 1 giving the probability as  $p(3,0) = p_1^3$ . There is only one way for all 3 balls to land in box 2 giving  $p(0,3) = p_2^3$ . The probability of 2 balls landing in box 1 and the remaining ball landing in box 2 is  $p(2,1) = 3(p_1^2 p_2)$ , because there are 3 ways of arranging the set of distribution numbers. Likewise  $p(1,2) = 3(p_1 p_2^2)$ . Show the relationship of the probabilities  $p(3,0)$ ,  $p(2,1)$ ,  $p(1,2)$ , and  $p(0,3)$  to the terms in the expansion of the polynomial  $(p_1 + p_2)^3$ .

*Answer:* Expanding the polynomial gives:

$$\begin{array}{ccccccc}
 (p_1 + p_2)^3 = & p_1^3 & + & 3 p_1^2 p_2 & + & 3 p_1 p_2^2 & + & p_2^3 \\
 & \downarrow & & \downarrow & & \downarrow & & \downarrow \\
 & p(3,0) & & p(2,1) & & p(1,2) & & p(0,3)
 \end{array}$$

The first term is the probability of all three balls occurring in the first box. The second term is the probability of finding two balls in the first box and 1 ball in the second box, and so on. The probabilities are related through the statistical weights given by the binomial coefficients. The polynomial can be more generally written using the binomial coefficients as:

$$(p_1 + p_2)^3 = \binom{3}{0} p_1^3 + \binom{3}{1} p_1^2 p_2 + \binom{3}{2} p_1 p_2^2 + \binom{3}{3} p_2^3$$

The probability of occurrence of the different sets of distribution numbers is proportional to the statistical weights. This result is the theoretical foundation for the title of Sec. 12.4.

### Literature Cited:

1. E. I. Kozliak, "Consistent Application of the Boltzmann Distribution to Residual Entropy in Crystals," *J. Chem. Educ.*, **2007**, *84*, 493-498.
2. W. J. Hehre, *A Guide to Molecular Mechanics and Quantum Chemical Calculations*, Wavefunction, Inc., Irvine, CA, 2003. p. 276.