Chapter 5
Entropy & the Boltzmann Law

1. Calculating the entropy of dipoles in a field.

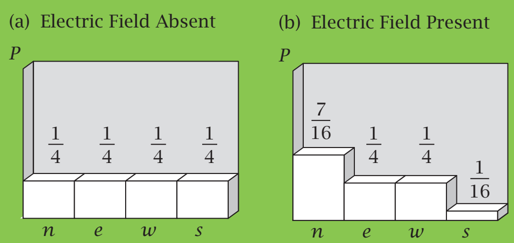
You have a solution of dipolar molecules with a positive charge at the head and a negative charge at the tail. When there is no electric field applied to the solution, the dipoles point north (n), east (e), west (w), or south (s) with equal probabilities. The probability distribution is shown in part (a) of the figure below. However when you apply a field to the solution, you now observe a different distribution, with more heads pointing north, as shown in part (b) of the figure below.

(a) What is the polarity of the applied field? (In which direction does the field have its most positive pole?)

(b) Calculate the entropy of the system in the absence of the field.

(c) Calculate the entropy of the system in the applied field.

(d) Does the system become more ordered or disordered when the field is applied?



(a) Since the field causes more positively charged heads to point north and fewer south, the field is negative at the north pole and positive at the south pole.

(b) The entropy is

$$\begin{aligned} S/k &= -\sum_{i=1}^{4} p(i)\ln p(i) \\ &= -p_N \ln p_N - p_S - \ln p_S - p_E - p_W \ln p_W \\ &= -4\left(\frac{1}{4}\ln\frac{1}{4}\right) = \ln 4 = 1.386, \end{aligned}$$

so

$$S = 1.386k$$

(c) In the presence of the applied field,

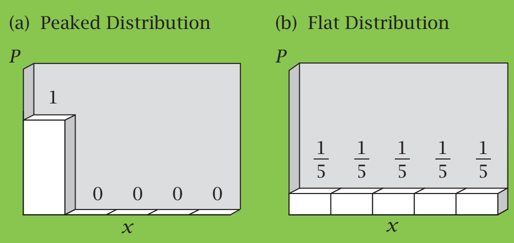
$$\begin{aligned} \frac{S}{k} &= -\left[\left(\frac{7}{16}\right)\ln\left(\frac{7}{16}\right) + \frac{1}{4}\ln\left(\frac{1}{4}\right) + \frac{1}{4}\ln\left(\frac{1}{4}\right) + \frac{1}{16}\ln\left(\frac{1}{16}\right)\right] \\ &= 1.228, \end{aligned}$$

so $S = 1.228k$.

(d) The entropy is reduced by the applied field, so the system is more ordered.

2. Comparing the entropy of peaked and flat distributions.

Compute the entropies for the spatial concentration shown in (a) and (b) below.



(a) $S/k = -\sum p(i)\ln p(i) = -1\ln 1 = 0.$

(b) $S/k = -\sum p(i)\ln p(i) = -5(0.2\ln 0.2) = \ln 5 = 1.609.$

6. The maximum entropy distribution is Gaussian when the second moment is given.

Prove that the probability distribution p_i that maximizes the entropy for die rolls, subject to a constant value of the second moment $\langle i^2 \rangle$, is a Gaussian function. Use $\varepsilon_i = i$.

Maximize the entropy subject to two constraints,

$$\sum_{i=1}^{t} p_i = 1,$$
$$\sum_{i=1}^{t} i^2 p_i = \langle i^2 \rangle = \alpha.$$

Now Equation (5.15) of the text becomes

$$-1 - \ln p_i^* - \lambda - \beta i^2 = 0 \implies p_i^* = e^{-1-\lambda\beta i^2}. \tag{1}$$

Dividing both sides of Equation (1) by

$$\sum_{i=1}^{t} e^{-1-\lambda-\beta i^2}$$

gives

$$p_i^* = \frac{e^{-\beta i^2}}{\sum_{i=1}^{t} e^{-\beta i^2}},$$

which is a Gaussian function of i.

7. Maximum entropy for a three-sided die.

You have a three-sided die, with numbers **1**, **2** and **3** on the sides. For a series of N rolls, you observe an average score or constraint value, of α per roll.

(a) Using the maximum entropy principle, write expressions that show how to compute the relative probabilities of occurrence of the three sides, n_1^*/N, n_2^*/N, and n_3^*/N, if α is given.

(b) Compute n_1^*/N, n_2^*/N, and n_3^*/N if $\alpha = 2$.

(c) Compute n_1^*/N, n_2^*/N, and n_3^*/N, if $\alpha = 1.5$.

(d) Compute n_1^*/N, n_2^*/N, and n_3^*/N if $\alpha = 2.5$.

(a) $$\frac{n_i^*}{N} = \frac{x^i}{q}, \quad q = x + x^2 + x^3, \quad \alpha = \frac{x + 2x^2 + 3x^3}{x + x^2 + x^3} = \frac{1 + 2x + 3x^2}{1 + x + x^2}$$

$\implies (3 - \alpha)x^2 + (2 - \alpha)x + (1 - \alpha) = 0.$

Use the quadratic equation

$$x = \frac{(\alpha - 2) \pm \left[(2 - \alpha)^2 - 4(1 - \alpha)(3 - \alpha)\right]^{1/2}}{2(3 - \alpha)}.$$

(b) $$\alpha = 2 \implies \frac{n_1^*}{N} = \frac{n_2^*}{N} = \frac{n_3^*}{N} = \frac{1}{3}.$$

(c) $$\alpha = 1.5 \implies \frac{n_1^*}{N} = 0.62, \quad \frac{n_2^*}{N} = 0.27, \quad \frac{n_3^*}{N} = 0.11.$$

(d) $$\alpha = 2.5 \implies \frac{n_1^*}{N} = 0.11, \quad \frac{n_2^*}{N} = 0.27, \quad \frac{n_3^*}{N} = 0.62.$$

8. Maximum entropy in Las Vegas.

You play a slot machine in Las Vegas. For every \$1 coin you insert, there are three outcomes: (1) you lose \$1; (2) you win \$1, so your profit is \$0; (3) you win \$5, so your profit is \$4. Suppose you find that your average expected profit over many trials is \$0 (what an optimist!). Find the maximum entropy distribution for the probabilities p_1, p_2, and p_3 of observing outcomes (1), (2), and (3), respectively.

We have three possible payoffs: $f_1 = -1$ (we don't win anything and so have lost \$1), $f_2 = 0$ (we win \$1 for a net profit of zero), and $f_3 = 4$ (we win \$5 for a net profit of \$4). If each of these possible outcomes has associated with it a probability p_i, then the expected net profit