

11. THE BOLTZMANN DISTRIBUTION

The Boltzmann distribution is a law of statistical mechanics, and is related to random distributions of a large number of molecules. In its simplest form it says that

$$(1) \quad P(E) = A \exp(-E/(kT))$$

where $P(E)$ is the probability that a particle has energy E , A is a constant, T is temperature and k is the Boltzmann constant. We think of the function P as the energy distribution.

The law applies to biological systems as well as to classical physics. When we look at proteins, for example, we are really looking a large ensemble of almost identical ones. Since they must fit the Boltzmann distribution, this should be taken into account in any computation of the energy.

We also saw in a previous section how (1) can be used in Monte Carlo computing methods to find the configuration of minimum energy.

Equation (1) is related to the following general principle applies in statistical mechanics:

The most likely thing to happen is what happens.

This general tendency towards the most likely configuration is called *entropy*. The principle can be expressed mathematically and shown to lead to (1). Even though this is usually done using calculus and Lagrange multipliers, we will show how the derivation can be done without using calculus.

11.1. A simple combinatorial problem. We can think about the situation in terms of simple combinatorial problems.

Combinatorial problem I: Given N balls placed randomly in M boxes, what is the most probable distribution?

By distribution we mean the number of balls in each box.

How do we think about it? Suppose we have 7 balls and 3 boxes. One possible distribution is

Box 1: balls 1, 3, 5

Box 2: balls 2, 7

Box 3: balls 4, 6

If we list the number of balls n_j in box j then this distribution is given by $n_1 = 3$, $n_2 = 2$, $n_3 = 2$, or simply 3,2,2. Another possibility giving the same distribution 3,2,2 is

Box 1: balls 1, 3, 6

Box 2: balls 4, 5

Box 3: balls 2, 7

We can think of this as a probability distribution. The probability that a given ball

is in box 1 is $3/7$. For the other boxes the probability is $2/7$.

How many possibilities altogether are there for the distribution 3,2,2? We can get any such distributions by taking a permutation of the numbers 1 to 7 and assigning the first three to box 1, the second two to box 2, and the last two to box 3. Since we don't distinguish the order of balls in a box, divide by the number of permutations of balls in each box. Thus there are

$$\frac{7!}{3!2!2!} = 210$$

possibilities.

If we take another distribution, say 1,1,5, then there are only

$$\frac{7!}{1!1!5!} = 42$$

possibilities, so it seems that 2,2,3 is a more probable configuration than 1,1,5. In the more probable case, 3,3,2, the balls are more equally distributed between the boxes.

We can show that equal distribution, about the same number of balls in each box, has

the greatest probability. In the general situation, suppose that

$n_j =$ the number of balls in box

where $j = 1, \dots, M$. Since there are a total of N balls,

$$(2) \quad n_1 + n_2 + \dots + n_M = N,$$

the probability of a ball in box j is

$$P(j) = \frac{n_j}{N}.$$

The number of possible ways to have the distribution n_1, n_2, \dots, n_M is

$$\frac{N!}{n_1!n_2!\dots n_M!}$$

We can prove that

$$(3) \quad \frac{1}{n_1!n_2!\dots n_M!}$$

is maximum when the balls are equally distributed. We show that

If the distribution n_1, n_2, \dots, n_M maximizes (3) under the constraint (2) then for all i and j , we have the inequality

$$n_i - n_j \leq 1.$$

So any two boxes have almost the same number of balls.

Proof Replace n_i and n_j in the maximal distribution by $n_i - 1$ and $n_j + 1$ respectively. In other words, move one ball from box i to box j . Since the original distribution was maximal, (3) becomes smaller and after cancelation we get

$$\frac{1}{(n_j + 1)!(n_i - 1)!} \leq \frac{1}{n_j! n_i!}$$

and the conclusion follows.

There is almost the same number in each box since n_i and n_j differ by at most 1 for all i and j . The probability distribution $P(j)$ is nearly constant.

Maple Demo

11.2. Probabilities. If we want to think of the likelihood of a distribution, a number between 0 and 1 is needed to describe the probability of each distribution discussed in the previous section. This may be a little confusing at first. Each distribution is in itself a probability function. So now we are asking what is the probability of a given probability function.

What is the total number of distributions of all kinds possible? If we have N balls and M boxes then we can toss the ball each ball randomly into one of the boxes. So there are N random tosses with M possible outcomes and M^N possibilities.

In the previous section there were 3 boxes and 7 balls, so the total number of possible distributions was $3^7 = 2187$. So

$$\text{Probability of } 3,2,2 = \frac{210}{2187} = .1$$

$$\text{Probability of } 1,1,5 = \frac{42}{2187} = .02$$

11.3. What happens if energy is included? To understand the Boltzmann distribution we use an argument similar to the ones above but we also consider the total energy. Suppose that the number of a box indicates the energy of each ball in the box, and suppose that the total amount of energy is fixed at E_{tot} . What is the most probable distribution in this situation?

For simplicity, we restrict the energy levels to integers 1 to M . This would be typical of quantum mechanics where energy levels are discrete.

In addition to the constraint that the total number of balls is N ,

$$(4) \quad n_1 + n_2 + \cdots + n_M = N,$$

we now have the constraint that the total energy is E_{tot} ,

$$(5) \quad n_1 + 2n_2 + \cdots + jn_j + \cdots + Mn_M = E_{\text{tot}}.$$

We will show in this situation the distribution is given as an exponential function of the type (1). This is the main idea of Boltzmann; the role of temperature follows

easily from other physical principles which we won't discuss here.

We note that from (1) we have

$$P(E_2)/P(E_1) = \exp(-(E_2 - E_1)/(kT))$$

so that the ratio of probabilities depends only on the energy difference. This is equivalent to $P(E)$ being an exponential function.

Using the same type of reasoning as above, we can show that if the energy differences $j - i$ and $l - k$ are equal then the quotients n_j/n_i and n_l/n_k are almost equal:

If the distribution n_1, n_2, \dots, n_M maximizes (3) under the constraints (4) and (5) then for all $i, j, k,$ and l with

$$j - i = l - k$$

we have the inequality

$$(6) \quad \frac{n_j}{n_i + 1} \leq \frac{n_l + 1}{n_k}.$$

Proof Change the maximal distribution by putting one ball from box j into box i and one ball from box k into box l . In terms

of energy, think of one particle changing energy

$$\Delta E = j - i$$

and another changing

$$-\Delta E = k - l.$$

This does not change the total energy so since (3) decreases, we have

$$\frac{1}{(n_i + 1)!} \frac{1}{(n_j - 1)!} \frac{1}{(n_k - 1)!} \frac{1}{(n_l + 1)!} \leq \frac{1}{n_i!} \frac{1}{n_j!} \frac{1}{n_k!} \frac{1}{n_l!}$$

and the conclusion follows.

Looking at (6) and thinking of n_i , n_j , n_k and n_l as very large numbers, the inequality says

$$\frac{n_j}{n_i} \leq \frac{n_l}{n_k}.$$

Since we can switch i and j and switch k and l we get

$$\frac{n_j}{n_i} = \frac{n_l}{n_k}$$

or

$$\frac{P(j)}{P(i)} = \frac{P(l)}{P(k)}$$

for

$$j - i = l - k.$$

It can be shown from this that P is an exponential function of the form (1).

11.4. **A proof using Calculus.** If the number of balls is large, think of

$$P(j) = n_j/N = p_j$$

as N variables with

$$(7) \quad \sum_{j=1}^N p_j = 1.$$

We can use the *Stirling approximation*

$$\ln n! = n \ln n - n$$

for large n . Now the problem of maximizing the number of configurations becomes the problem of maximizing

$$S = - \sum p_j \log p_j$$

under the constraints (7) and

$$(8) \quad \sum_{j=1}^N j p_j = E_{\text{tot}}.$$

This problem can be solved using *Lagrange multipliers*. Let

$$g = \sum_{j=1}^N p_j \quad h = \sum_{j=1}^N j p_j$$

be the functions giving the constraints. Solve

$$\frac{\partial S}{\partial p_j} - \alpha \frac{\partial g}{\partial p_j} - \beta \frac{\partial h}{\partial p_j} = 0 \quad j = 1, \dots, N$$

for constants α and β . Computing the partial derivatives, we get

$$-1 - \ln p_j - \alpha - \beta j = 0$$

and so it follows that

$$p_j = e^{-1-\alpha} e^{-\beta j}$$

and again we have shown that the distribution is exponential.

References.

- (1) *General Chemistry*, Linus Pauling
- (2) *Molecular Driving Forces*, Dill and Bromberg