Boltzmann factor

In this article, we will calculate the probability that a system will have a certain particular state. To this end, we will consider a thermal contact between a reservoir and a system at at that particular state. Reservoir is a term that refers to a very large system with certain temperature. Now, let's say that the reservoir and our system is in thermal equilibrium after some thermal contact. Our system has now energy E_S. If the initial energy of the reservoir was E, the reservoir has now energy $E - E_S$. Then the number of possible states for the reservoir is given by $W(E - E_s)$. Also, the number of possible states for our system is 1, since we are considering *a* certain particular state. Therefore, the total number of possible states is given as follows:

$$W(E - E_s) \times 1 = W(E - E_s) \tag{1}$$

Now, the ratio of the probability that our system has energy E_1 to the probability that our system has energy E_2 is given as follows:

$$\frac{P(E_1)}{P(E_2)} = \frac{W(E - E_1)}{W(E - E_2)} \tag{2}$$

since the probability is proportional to the number of states. Using $S = k \ln W$, we have:

$$\frac{P(E_1)}{P(E_2)} = \frac{\exp[S(E - E_1)/k]}{\exp[S(E - E_2)/k]} \tag{3}$$

Given this, we can use Taylor expansion:

$$S(E - E_1) = S(E) - E_1 \frac{\partial S}{\partial E} + \frac{1}{2} E_1^2 \frac{\partial}{\partial E} \left(\frac{\partial S}{\partial E} \right) + \cdots \tag{4}$$

Applying the definition of temperature, we have:

$$S(E - E_1) = S(E) - \frac{E_1}{T} + \frac{1}{2} E_1^2 \frac{\partial}{\partial E} (\frac{1}{T}) + \cdots \tag{5}$$

However, the second term is zero, since the temperature of the reservoir hardly changes even when it loses energy, as the reservoir is very large. The higher terms also vanish for similar reasons. Therefore, we have:

$$S(E - E_1) = S(E) - \frac{E_1}{T} \tag{6}$$

and similarly for $S(E - E_2)$. Plugging these relations to (3), we obtain:

$$\frac{P(E_1)}{P(E_2)} = \frac{\exp[-E_1/(kT)]}{\exp[-E_2/(kT)]} \tag{7}$$

The expression $\exp[-E/(kT)]$ is called Boltzmann factor. Roughly speaking, it implies that the higher energy the less probability. For example, as you go higher and higher in altitude, the air is more scarce.

Given that we have obtained the relative probability (i.e. that probability is proportional to $\exp -E/kT$), could we obtain the absolute probability as well? We can use the fact that the total probability is always 1. If we re-write (7) as:

$$P(E_i) = \frac{\exp(-E_i/kT)}{Z} \tag{8}$$

for Z to be determined, the following condition

$$\sum_i P(E_i) = 1 \tag{9}$$

implies

$$Z = \sum_i \exp(-E_i/kT) \tag{10}$$

Z is called "partition function." We will use the Boltzmann factor to derive the expression for Planck's law of black-body radiation.

Summary

- The expression $\exp[-E/(kT)]$ is called Boltzmann factor. Roughly speaking, it implies that the higher energy the less probability.
- $Z = \sum_i \exp(-E_i/kT)$ is called "partition function."