Thermal Physics Guest Lecture

Boltzmann Statistics

Santanu Bosu Antu

The Boltzmann Factor
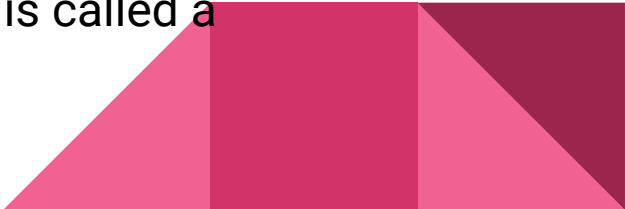
<u>Isolated System</u>

By isolated system, we mean the total energy is fixed, say between E and $E + \Delta E$

From the fundamental postulate of Stat Mech: All the microstates with energy in that range are equally probable to occur.

If a microstate has energy E_r :

$$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

This ensemble of systems where the total energy is fixed is called a **Microcanonical Ensemble.**

System in a thermal equilibrium with Heat Reservoir

In this case, the system can exchange energy with a reservoir, and the probability distribution is not uniform.

The temperature is constant and we call the ensemble of systems a **Canonical Ensemble.**

We <u>specify two microstates</u> s_1 and s_2 with energies E_1 and E_2 .

$\Omega_R(s_1)$ and $\Omega_R(s_2)$ are the multiplicities of the reservoir for the two states respectively. What are the relative probabilities of the system occupying the states?

$$P(s) \propto \Omega_R(s)$$

By Definition, $S = k\ln(\Omega) \rightarrow \ln(\Omega) = \frac{S}{k} \rightarrow \Omega = e^{S/k}$

So, $\dfrac{P(s_2)}{P(s_1)} = \dfrac{\Omega_R(s_2)}{\Omega_R(s_1)} = \dfrac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{\Delta S_R/k}$ (1)

From the thermodynamic identity:

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R) \tag{2}$$

We are considering thermal interaction and when an atom goes to an excited state PdV<<dU. Also dN is 0 as we are not considering exchange of particles. So,

$$\Delta S_R = \frac{1}{T}[U_R(s_2) - U_R(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)] = -\frac{1}{T}\Delta E \tag{3}$$

Plugging this into equation (1):

$$\frac{P(s_2)}{P(s_1)} = e^{-\Delta E/kT} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}} \tag{4}$$

$$\text{Boltzmann factor} = e^{-E(s)/kT} \tag{5}$$

Rearranging the ratios of equation (4):

$$\frac{P(s_2)}{e^{-E(s_2)/kT}} = \frac{P(s_1)}{e^{-E(s_1)/kT}} \qquad (6)$$

The left hand side depends only on s_2 while the right hand side depends on s_1

So, both sides should be equal to a constant:

$$\frac{P(s)}{e^{-E(s)/kT}} = \frac{1}{Z} \qquad (7)$$

In case of non-degenerate states, we could write this distribution as a function of Energy:

$$P(E) = \frac{1}{Z} e^{-E/kT} \qquad (8)$$

The Partition Function

The 'constant' Z that we introduced in the previous slide is called the **partition function.**

But how do we compute it?

Sum up all the probabilities in equation (7) and that should be equal to 1:

$$\sum_s P(s) = \sum_s \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} \sum_s e^{-E(s)/kT} = 1$$

$$\text{So, } Z = \sum_s e^{-E(s)/kT} = \text{sum of all Boltzmann factors} \qquad (9)$$

Z is a constant in the sense that it doesn't depend on any particular state. But it is a function of Temperature.
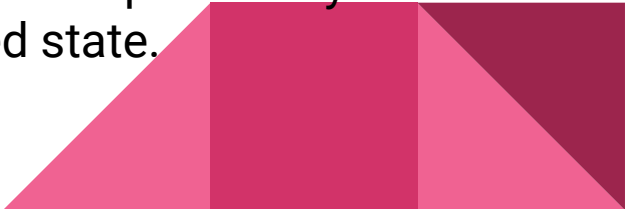
A Quick Application

The sun is a contains a huge amount of Hydrogen (~75% of its mass). We can use Boltzmann distribution to find approximately what portion of the hydrogen is in the excited state.

The surface temperature of the sun is about 5800 K ($kT=0.5$ eV). The energy of the ground state of Hydrogen atom is -13.6 eV and that of the first excited state is -3.4 eV. So,

$$\frac{P(s_2)}{P(s_1)} = e^{-\Delta E/kT} = e^{-10.2eV/0.5eV} \approx 1.5 \times 10^{-9}$$

But there are 4 degenerate states for E=-13.6 eV. So, the actual probability is about 6E-9. Only 6 in a billion atoms are in the first excited state.

Average Values

The probability of a microstate in thermal equilibrium is:
$$P(s) = \frac{1}{Z} e^{-\beta E(s)} \qquad\qquad (10)$$

where we defined $\beta = \frac{1}{kT}$

Now, suppose we want to know the average Energy of the system. How do we calculate average?

If there are n_i states with energy E_i. Then, the average is:
$$\bar{E} = \frac{n_1 E_1 + n_2 E_2 + n_3 E_3 + \ldots}{N}$$
$$= E_1 \left(\frac{n_1}{N}\right) + E_2 \left(\frac{n_2}{N}\right) + E_3 \left(\frac{n_3}{N}\right) + \ldots$$
$$= E_1 P_1 + E_2 P_2 + E_3 P_3 + \ldots$$
$$= \sum_i E_i P_i$$

In our case, the probabilities are given by the Boltzmann distribution. So,

$$\bar{E} = \frac{1}{Z} \sum_s E(s) e^{-\beta T}$$

In general, if any variable X has a value $X(s)$ at microstate s, then

$$\bar{X} = \frac{1}{Z} \sum_s X(s) e^{-\beta T} \tag{11}$$

This only applies to the Canonical ensembles. But in general if we know P_i, we can easily find the average by summing $X_i P_i$.

Thank You!