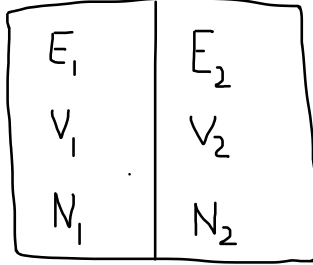# Microcanonical ensemble – II

We will now argue that $\Omega(E)$ is related to the entropy of the system. Consider two subsystems separated by a wall

$E_T = E_1 + E_2$ Energy is conserved as the total system is isolated.

Let $g_1(E_1)$ is density of states of system 1 with energy E_1
$g_2(E_2)$ is density of states of system 2 with energy E_2

Now suppose the wall is thermally conducting so that the energy can be transferred between the two systems. However, the total energy $E_T = E_1 + E_2$ remains constant. What will be the value of E_1 when the system comes to equilibrium?

The density of states of the combined system will be

$$g_T(E_T) = \int_0^{E_T} dE'\, g_1(E_1')\, g_2(E_T - E_1')$$

Now if

$$\Omega_T(E_T) = g_T(E_T)\, \Delta$$
$$\Omega_1(E_1) = g_1(E_1)\, \Delta$$
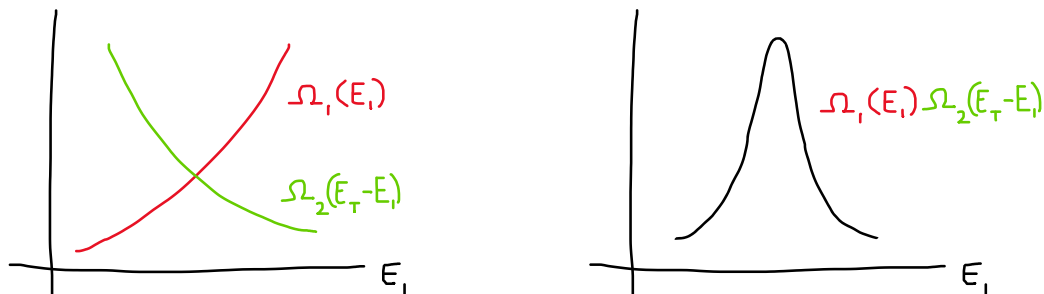$$\Omega_2(E_2) = g_2(E_2)\, \Delta$$

Then the above can be written as

$$\Omega_T(E_T) = \int_0^{E_T} \frac{dE'}{\Delta}\, \Omega_1(E_1')\, \Omega_2(E_T - E_1')$$

The integrant is the number of states with total energy E_T that also have system 1 with energy E_1
Note that $\Omega_1(E_1)$ and $\Omega_2(E_2)$ are the rapidly increasing functions of E_1 and E_2, respectively.
However, $\Omega_2(E_T - E_1)$ is a rapidly decreasing function of E_1.

As the product $\Omega_1(E_1)\, \Omega_2(E_T - E_1)$ shows a sharp maximum with respect the energy E_1,

$$\frac{\partial[\Omega_1(E_1)\,\Omega_2(E_T-E_1)]}{\partial E_1} = 0$$

Implies,

$$\frac{\partial[\Omega_1(E_1)\,]}{\partial E_1}\Omega_2(E_T-E_1) + \Omega_1(E_1)\frac{\partial[\,\Omega_2(E_T-E_1)]}{\partial E_1} = 0$$

As $E_T = E_1 + E_2$ and $0 = dE_1 + dE_2$ as E_T is a constant, we get

$$\frac{\partial[\Omega_1(E_1)\,]}{\partial E_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{\partial[\,\Omega_2(E_2)]}{\partial E_2} = 0$$

$$\frac{1}{\Omega_1}\frac{\partial[\Omega_1(E_1)\,]}{\partial E_1} = \frac{1}{\Omega_2}\frac{\partial[\,\Omega_2(E_2)]}{\partial E_2}$$

$$\frac{\partial[\ln\Omega_1\,]}{\partial E_1} = \frac{\partial[\ln\Omega_2]}{\partial E_2}$$

But from thermodynamics we know that the equilibrium value of E_1 will be determined by the condition,

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T_2}$$

Therefore, following Boltzmann, we identify that $S(E) \propto \ln\Omega(E)$ is the entropy.

Since the relation between thermodynamics and mechanics should be fundamental, Boltzmann proposed that the proportionality constant should be a universal number, and should not depend on a particular system. This constant is Boltzmann constant k_B

$$S(E) = k_B \ln\Omega(E)$$

Where $S(E)$ is entropy and $\Omega(E)$ is number of microstates with energy E. Note that $S(E)$ is a monotonic increasing function of E as it should be.

Ideal gas

We have computed the number of microstates for the ideal gas system, which is

$$\Omega(E,V,N) = \frac{V^N}{h^{3N}}\frac{(2\pi\,mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}\frac{\Delta}{E}$$

Using this, we compute the entropy. Note that for large N, we can use the Stirling formula, i.e., $\ln N! = N\ln N - N$.

$$S(E, V, N) = k_B \ln \Omega(E, V, N)$$

$$S = k_B \left\{ N \ln \left[\frac{V}{h^3} (2\pi \, mE)^{\frac{3}{2}} \right] - \left(\frac{3N}{2} - 1 \right) \ln \left(\frac{3N}{2} - 1 \right) + \left(\frac{3N}{2} - 1 \right) + \ln \frac{\Delta}{E} \right\}$$

As, N is very large we can assume that $\left(\frac{3N}{2} - 1 \right) \cong \frac{3N}{2}$. Also, as $\frac{E}{N} < \Delta \ll E$ we can safely neglect $\ln \frac{\Delta}{E}$ term. We get,

$$S \cong k_B \left\{ N \ln \left[\frac{V}{h^3} (2\pi \, mE)^{\frac{3}{2}} \right] - \left(\frac{3N}{2} \right) \ln \left(\frac{3N}{2} \right) + \left(\frac{3N}{2} \right) \right\}$$

$$S \cong k_B \left\{ N \ln \left[\frac{V}{h^3} (2\pi \, mE)^{\frac{3}{2}} \right] - N \ln \left(\frac{3N}{2} \right)^{3/2} + \left(\frac{3N}{2} \right) \right\}$$

$$S \cong k_B \left\{ N \ln \left[\frac{V}{h^3} \frac{(2\pi \, mE)^{\frac{3}{2}}}{\left(\frac{3N}{2} \right)^{\frac{3}{2}}} \right] + \frac{3N}{2} \right\}$$

$$S \cong N \left\{ \frac{3k_B}{2} + k_B \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi \, m \, \frac{E}{N} \right)^{\frac{3}{2}} \right] \right\}$$

Note that the final result does not depend on Δ as we desired. With the above result, we can calculate the average energy as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{\partial}{\partial E} \left\{ N \frac{3k_B}{2} + N k_B \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi \, m \, \frac{E}{N} \right)^{\frac{3}{2}} \right] \right\}$$

$$\frac{1}{T} = \frac{\partial}{\partial E} \left\{ N k_B \frac{3}{2} \ln E \right\} = \frac{3}{2} N k_B \frac{1}{E}$$

$$E = \frac{3}{2} N k_B T$$

Similarly, using the relation, $\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}$ we get

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{\partial}{\partial V} \left\{ N k_B \ln V \right\} = N k_B \frac{1}{V}$$

$$PV = N k_B T$$

Using the total number of microstates $\Omega(E)$, we have computed the average energy and recovered the ideal gas equation. But there is a problem, In the above equations, S is **not** extensive. If we take $E \rightarrow 2E, \ V \rightarrow 2V, N \rightarrow 2N,$ we do **not** get 2S.

$$S \cong N \left\{ \frac{3k_B}{2} + k_B \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi \, m \, \frac{E}{N} \right)^{\frac{3}{2}} \right] \right\}$$

In the above equation, the $\ln V$ term spoils the desired extensivity property.

Entropy of mixing – Gibb's paradox

Consider two different gases (red and blue) at the same temperature and pressure, separated by a partition.

$$\left. \begin{array}{l} V_1 + V_2 = V \\ E_1 + E_2 = E \\ N_1 + N_2 = N \end{array} \right\} \text{ Constant}$$

E_1	E_2
V_1	V_2
N_1	N_2

Both the gases at same temperature. This implies,

$$E_1 = \frac{3}{2} N_1 k_B T \quad ; \quad V_1 = \frac{N_1 k_B T}{P}$$

$$E_2 = \frac{3}{2} N_2 k_B T \quad ; \quad V_2 = \frac{N_2 k_B T}{P}$$

With the partition in place, the total entropy is, initially,

$$S_i = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2).$$

Now, if we remove the partition and let the gases mix, the temperature and N_1 and N_2 should not change. It means E_1 and E_2 remain constant. The only changes are $V_1 \to V$ and $V_2 \to V$. With the partition removed, the final entropy is

$$S_f(E, V, N_1, N_2) = k_B \ln[\Omega_1(E_1, V, N_1) \, \Omega_2(E_2, V, N_2)]$$

$$S_f = S_1(E_1, V, N_1) + S_2(E_2, V, N_2)$$

The entropy of mixing is $\Delta S = S_f - S_i$

$$S \cong N \left\{ \frac{3k_B}{2} + k_B \ln\left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{\frac{3}{2}} \right] \right\}$$

$$S_i = \frac{3k_B}{2} N_1 + k_B N_1 \ln\left[\frac{V_1}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{\frac{3}{2}} \right] + \frac{3k_B}{2} N_2 + k_B N_2 \ln\left[\frac{V_2}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{\frac{3}{2}} \right]$$

$$S_f = \frac{3k_B}{2} N_1 + k_B N_1 \ln\left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{\frac{3}{2}} \right] + \frac{3k_B}{2} N_2 + k_B N_2 \ln\left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{\frac{3}{2}} \right]$$

$$\Delta S = k_B N_1 \ln\left[\frac{V}{V_1} \right] + k_B N_2 \ln\left[\frac{V}{V_2} \right]$$

Or since, $V_1 = \frac{N_1 k_B T}{P}$, $V_2 = \frac{N_2 k_B T}{P}$, and $V = \frac{(N_1 + N_2) k_B T}{P}$

$$\Delta S = k_B N_1 \ln\left[\frac{N_1 + N_2}{N_1} \right] + k_B N_2 \ln\left[\frac{N_1 + N_2}{N_2} \right] > 0$$

We expect $\Delta S > 0$ since entropy increases when a constant is removed.

When the red gas mixes with the blue gas we get purple gas. The process is **irreversible** – there is no thermodynamic way to separate back into separate volumes of blue and red gas. In irreversible process, the entropy increases (this is just the thermodynamic definition of an irreversible process).

Now, consider what happens if the two gases on either side of the partition were the same type (both red). With the partition removed, the system is a single gas of $N = N_1 + N_2$ particles, with total energy $E = E_1 + E_2$, confined to a volume V. The final state is

$$S_f = S(E, V, N)$$

$$S_f = \frac{3k_B}{2} N + k_B N \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{\frac{3}{2}} \right]$$

$$S_f = \frac{3k_B}{2} (N_1 + N_2) + k_B (N_1 + N_2) \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{3}{2} k_B T \right)^{\frac{3}{2}} \right]$$

$$S_f = \frac{3k_B}{2} N_1 + k_B N_1 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{\frac{3}{2}} \right] + \frac{3k_B}{2} N_2 + k_B N_2 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{\frac{3}{2}} \right]$$

Where we used, $\frac{E}{N} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$

$$S_f = S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2)$$

In general, $S(E, V, N)$, instead of obeying the extensivity relation, obeys $\lambda S(E, V, N) = S(\lambda E, V, \lambda N)$, which is consistent with the above.

So, S_f has exactly the same form when both gases are the same, as when they are different! Hence, we find the same $\Delta S > 0$, as when the gases were different! But this cannot be - when the gases are the same, removing the partition is a reversible process. We can always reinsert the partition and return to a situation of indistinguishable from the initial state. In such a reversible process, we should have $\Delta S = 0$!

The problem lies in whether the particles are distinguishable or indistinguishable. When we considered red and blue gases, which are distinguishable, there was no problem. However, when we consider the gas of same color in both the containers, which is indistinguishable. It was **Gibbs** who realized that to resolve the paradox of mixing entropy, as well as to make the entropy extensive, it was necessary to regard the particles of a gas as indistinguishable from one another.

Indistinguishable particles

In counting the number of microstates $\Omega(E, V, N)$ we have therefore over counted. The correct counting should be

$$\Omega(E, V, N) = \frac{1}{N!} \int_{E-\Delta/2}^{E+\Delta/2} dE' \, g(E')$$

$N!$ since there are N ways to choose which particle is at coordinates (q_1, p_1), $(N-1)$ ways to choose which of the remaining particles at coordinates (q_2, p_2), etc. So, our new result for the entropy is

$$S^{new} = S^{old} - k_B \ln[N!] = S^{old} - k_B \, N \ln[N] + N k_B$$

Where we used Stirling's formula $\ln[N!] = N \ln[N] - N$ for large N. The new result for the entropy of an ideal gas is thus,

$$S(E, V, N) = \frac{5 \, k_B}{2} N + k_B \, N \ln\left[\frac{V}{h^3 \, N} \left(\frac{4}{3} \pi \, m \, \frac{E}{N} \right)^{\frac{3}{2}} \right]$$

It is called Sackur-Tetrode equation. This result clearly shows that now the entropy is **extensive**.