

Microcanonical ensemble

In microcanonical ensemble, at energy E , assigned equal weight to all the states of the system on the surface in the phase space of constant energy $H[q_i, p_i] = E$

To count the number of such states on the energy surface we define the density of states

$$g(E) = \int \frac{dq_i dp_i}{h^{3N}} \delta(H[q_i, p_i] - E)$$

Where h is a constant with units q_i, p_i , h^{3N} represents the volume of the phase space occupied by one "state". Classically, h is totally arbitrary so our thermodynamic results should not depend on it. Quantum mechanically, we will see that h turns out to be the Planck's constant.

At this stage, the factor $1/h^{3N}$ is introduced so that $g(E)$ has the units of 1/energy. We can now define the number of states in a shell of thickness Δ about the energy surface E .

$$\Omega(E) = \int_{E-\Delta/2}^{E+\Delta/2} dE' g(E')$$

Ω is a pure number. Again, Δ is arbitrary, but assumed to be $\frac{E}{N} < \Delta \ll E$. It can be thought of as representing the finite accuracy with which one knows E . Our thermodynamic results should not depend on Δ .

Let's compute Ω for the ideal gas of non-interacting particles, confined to a volume V .

$$H = \sum_i \frac{p_i^2}{2m}$$

$$g(E) = \int \frac{dq_i}{h^{3N}} \int dp_i \delta\left(\sum_i \frac{p_i^2}{2m} - E\right)$$

$$g(E) = \frac{V^N}{h^{3N}} \int dp_i \delta\left(\sum_i \frac{p_i^2}{2m} - E\right)$$

The surface of constant energy is just the surface of a sphere in $3N$ dimensional momentum space given by the coordinates $p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}$. The radius of the sphere is $\sqrt{2mE}$. Let $\wp = \sqrt{\sum_i p_i^2}$ be the length of the momentum vector in the $3N$ dimensional momentum space. Then,

$$\prod_{i=1}^N d^3 p_i = d\wp \wp^{3N-1} d\Omega_{3N}$$

Where $d\Omega_{3N}$ is the differential solid angle in $3N$ dimensional space.

$$g(E) = \frac{V^N}{h^{3N}} \int d\Omega_{3N} \int_0^\infty d\wp \wp^{3N-1} \delta\left(\frac{\wp^2}{2m} - E\right)$$

By considering that $y = \frac{\wp^2}{2m}$ in the above equation, we get

$$g(E) = \frac{V^N}{h^{3N}} S_{3N} \int_0^\infty dy (2my)^{\frac{3N-1}{2}} \frac{\delta(y - E)}{\sqrt{2m y/m}}$$

Here, S_{3N} is the area of unit sphere in $3N$ dimensional space.

$$g(E) = \frac{V^N}{h^{3N}} S_{3N} \int_0^\infty dy m (2my)^{\frac{3N-2}{2}} \delta(y - E)$$

Using the property of the delta function we get

$$g(E) = \frac{V^N}{h^{3N}} S_{3N} m (2mE)^{\frac{3N-2}{2}}$$

The solid angle of an unit sphere in 3N dimensional space (see e.g., Appendix C of the book by Pathria for the details) is given by

$$S_{3N} = \frac{2 \pi^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!}$$

Thus,

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

Finally,

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

Now, the total number of microstates,

$$\Omega(E) = \int_{E-\Delta/2}^{E+\Delta/2} dE' g(E') = g(E)\Delta$$

Proof:

$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!} \int_{E-\Delta/2}^{E+\Delta/2} dE' (E')^{\frac{3N}{2}-1}$$

$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!} \frac{2}{3N} \left[(E + \Delta/2)^{\frac{3N}{2}} - (E - \Delta/2)^{\frac{3N}{2}} \right]$$

$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!} \frac{2}{3N} E^{\frac{3N}{2}} \left[\left(1 + \frac{\Delta}{2E}\right)^{\frac{3N}{2}} - \left(1 - \frac{\Delta}{2E}\right)^{\frac{3N}{2}} \right]$$

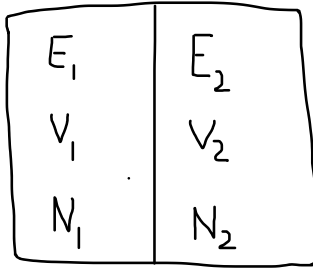
$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!} \frac{2}{3N} E^{\frac{3N}{2}} \left[\left(1 + \frac{3N}{2} \frac{\Delta}{2E}\right) - \left(1 - \frac{3N}{2} \frac{\Delta}{2E}\right) \right]$$

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

Notice that for large N, $\Omega(E)$ is a very rapidly increasing function of E

We will now argue that $\Omega(E)$ is related to the entropy of the system.

Consider two subsystems separated by a wall



$$E_T = E_1 + E_2 \quad \text{Energy is conserved as the total system is isolated.}$$

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

$$\Omega_T(E_T) = g_T(E_T) \Delta$$

$$\Omega_1(E_1) = g_1(E_1) \Delta$$

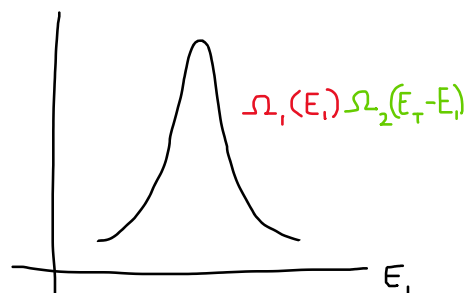
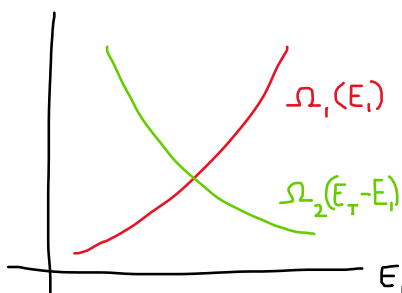
$$\Omega_2(E_2) = g_2(E_2) \Delta$$

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 integrand 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

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

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

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.