Unit 2-4: The Microcanonical Ensemble and Entropy

Density of States $g(E)$ and Number of States $\Omega(E)$

We saw that the microcanonical ensemble, at constant total energy E, assigned equal weight to all systems on the surface of constant energy in phase space, defined by $\mathcal{H}[q_i, p_i] = E$.

To count the number of such states on the constant energy surface, we define the *density of states* $g(E)$, which is the number of states of total energy E per unit energy,

$$g(E) \equiv \int \frac{dq_i dp_i}{h^{3N}}\, \delta(\mathcal{H}[q_i, p_i] - E) \tag{2.4.1}$$

Here $dq_i dp_i$ stands for $\prod_{i=1}^{3N} dq_i dp_i$, i.e. we integrate over all $6N$ of the phase space coordinates. The delta function means we count only coordinates that lie on the surface of constant energy E.

The constant h has units of $q_i p_i$ and is introduced so that $g(E)$ will have the units of $1/energy$. You can think of h as the grid width in discretizing the continuous phase space into a grid of discrete cells, each with phase space volume h^{3N}. Such a discretization is useful since it will allow us to count states, something that is conceptually more difficult when states are specified by continuous coordinates. Classically, h should be small but is otherwise totally arbitrary, and so we expect our thermodynamic results should not depend on its value (though later we will see that this is not always so!). Quantum mechanically we will see that h turns out to be Planck's constant (recall, Planck's constant has the units of $energy \cdot time$ which is the same as the units of $q_i p_i$).

We can now define the *number of states* Ω in a shell of thickness ΔE about the surface of constant energy E,

$$\Omega(E, V, N) = \int_{E-\Delta E/2}^{E+\Delta E/2} dE'\, g(E') \qquad \text{since } g(E) \text{ has units } 1/energy,\ \Omega \text{ is a dimensionless pure number} \tag{2.4.2}$$

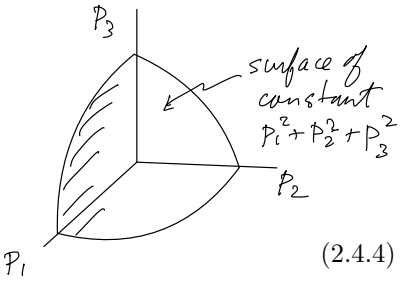
As with h, the energy width ΔE is arbitrary, and so our thermodynamic results should not depend on the value of ΔE. We will assume it to be in the range $E/N < \Delta E \ll E$, so it is larger than the energy per particle but much smaller than the total energy. One can think of ΔE as representing the finite accuracy with which one knows the total energy E. Both h and ΔE are introduced so that Ω is a dimensionless pure number that we can think of as being the number of microscopic states that are occupied in the microcanonical ensemble at total energy E.

Number of States for the Ideal Gas

We will now compute $\Omega(E, N, V)$ for the ideal gas of non-interacting point particles. For this system the energy is entirely the kinetic energy of the particles, and so the Hamiltonian is,

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{2.4.3}$$

We see from $\mathcal{H}$ that the surface of constant energy E is just the surface on which the momenta $\{p_i\}$ satisfy the constraint $\sum_{i=1}^{3N} p_i^2 = 2mE$. This constraint defines the surface of a $3N$ dimensional sphere centered at the origin in momentum space. The radius of that sphere is $\sqrt{\sum_{i=1}^{3N} p_i^2} = \sqrt{2mE}$. We therefore have for the density of states,



$$g(E) = \frac{1}{h^{3N}} \prod_{i=1}^{3N} \int_0^L dq_i \int_{-\infty}^{\infty} dp_i\, \delta\left(\sum_{j=1}^{3N} \frac{p_j^2}{2m} - E\right) \tag{2.4.4}$$

where we assume the system is confined to a box of length L. Since the box volume is $V = L^3$, doing the integration

over the spatial coordinates $\{q_i\}$ gives,

$$g(E) = \frac{V^N}{h^{3N}} \prod_{i=1}^{3N} \int_{-\infty}^{\infty} dp_i \, \delta\left(\sum_{j=1}^{3N} \frac{p_j^2}{2m} - E \right) \tag{2.4.5}$$

Let us now convert the integral over the $\{p_i\}$ to spherical coordinates. This gives,

$$\prod_{i=1}^{3N} \int_{-\infty}^{\infty} dp_i = \int_{\Omega_{3N}} d\Omega_{3N} \int_0^{\infty} dP P^{3N-1} \tag{2.4.6}$$

where $P = \sqrt{\sum_{i=1}^{3N} p_i^2}$ is the magnitude of the $3N$ dimensional vector $\mathbf{P} = (p_1, p_2, \ldots, p_{3N})$, and Ω_{3N} is the $3N$ dimensional solid angle giving the orientation of the vector $\mathbf{P}$ (don't confuse Ω_{3N} with the number of states $\Omega(E, V, N)$!). We then get,

$$g(E) = \frac{V^N}{h^{3N}} \int_{\Omega_{3N}} d\Omega_{3N} \int_0^{\infty} dP \, P^{3N-1} \, \delta\left(\frac{P^2}{2m} - E \right) \tag{2.4.7}$$

$$= \frac{V^N}{h^{3N}} \, S_{3N} \int_0^{\infty} dP \, P^{3N-1} \; \frac{\delta\left(P - \sqrt{2mE} \right)}{(P/m)} \tag{2.4.8}$$

$$= \frac{V^N}{h^{3N}} \, S_{3N} \, m (2mE)^{\frac{3N-2}{2}} \tag{2.4.9}$$

Here S_{3N} is the area of the surface of a sphere with unit radius in $3N$-dimensional space, and we converted the delta function in the integrand using the result that for a monotonic increasing function $f(x)$,

$$\delta(f(x)) = \frac{\delta(x - x_0)}{f'(x_0)} \qquad \text{where } f(x_0) = 0 \text{ and } f'(x) = df/dx. \tag{2.4.10}$$

[Note: for the more general case where $f(x)$ is any continuous function: $\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}$, where the x_i are the zeros of $f(x)$, i.e. $f(x_i) = 0$.]

From appendix C of Pathria and Beale we have $S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$, where $\Gamma(x)$ is the gamma function that obeys $\Gamma(n) = (n-1)!$ for integer n. So, $S_{3N} = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!}$, and we have,

$$g(E) = \frac{V^N}{h^{3N}} \, \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \, m \, \frac{(2mE)^{3N/2}}{2mE} \tag{2.4.11}$$

and so

$$\boxed{g(E) = \frac{V^N}{h^{3N}} \, \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \, \frac{1}{E}} \tag{2.4.12}$$

Integrating $g(E)$ over a shell of energy thickness ΔE then gives for the number of states,

$$\Omega(E) = \int_{E - \Delta E/2}^{E + \Delta E/2} dE' \, g(E') \approx g(E) \Delta E \tag{2.4.13}$$

$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{(\frac{3N}{2}-1)!} \frac{\Delta E}{E} \tag{2.4.14}$$

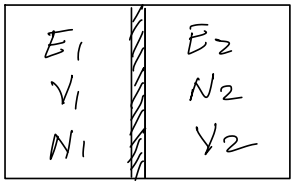
Note, for convenience we write the number of states as $\Omega(E)$ rather than the more complete $\Omega(E, V, N)$.

For large $N \sim 10^{23}$, $\Omega(E) \sim E^{(3N/2)-1}$ is a *very* rapidly increasing function of the total energy E!

Number of States $\Omega(E)$ and the Entropy $S(E)$

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

Consider two subsystems separated by a wall.



The total energy $E_T = E_1 + E_2$ is conserved.

Let $\Omega_1(E_1) = g_1(E_1)\Delta E$ be the number of states at energy E_1 for system 1 and $\Omega_2(E_2) = g_2(E_2)\Delta E$ be the number of states at energy E_2 of system 2.

When the wall is thermally insulating, and E_1 and E_2 are fixed, then the number of states available to the total system is just the product,

$$\Omega_T = \Omega_1(E_1)\Omega_2(E_2) \tag{2.4.15}$$

since system 1 can be in any one of $\Omega_1(E_1)$ states, and system 2 can be in any one of $\Omega_2(E_2)$ states.

Now suppose the wall is thermally conducting so that energy can be transferred between the two systems. Then E_1 can vary but $E_T = E_1 + E_2$ stays fixed. What will be the value of E_1 when the system comes into equlibrium?

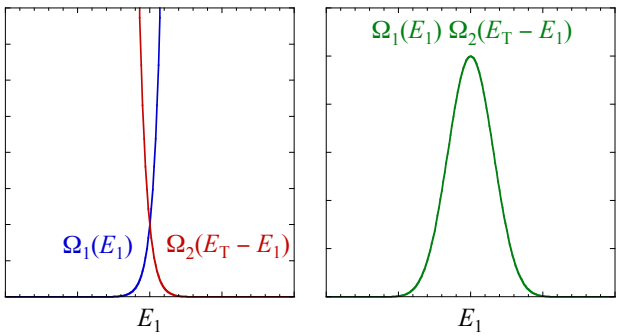
In this case the number of states available to the total system is obtained just by adding up the terms as in Eq. (2.4.15), but now considering all possible divisions of the energy between the two systems,

$$\Omega_T(E_T) = \int_0^{E_T} \frac{dE_1}{\Delta E}\, \Omega_1(E_1)\, \Omega_2(E_T - E_1) \tag{2.4.16}$$

Consider the behavior of the integrand:

For large N_1, $\Omega_1(E_1)$ is a rapidly increasing function of E_1.
For large N_2, $\Omega_2(E_2)$ is a rapidly increasing function of E_2.
So $\Omega_2(E_T - E_1)$ is a rapidly *decreasing* function of E_1.

The product $\Omega_1(E_1)\Omega_2(E_T - E_1)$ therefore has a sharp maximum at some particular value of E_1, as illustrated in the sketches below where I took $N_1 = N_2 = 20$. As N_1 and N_2 increase, Ω_1 and Ω_2 become ever more sharply varying, and the product $\Omega_1\Omega_2$ becomes ever more sharply peaked.



In the microcanonical ensemble all states with total energy E_T are equally likely. So the probability that the total system has its energy divided with E_1 in system 1 and $E_T - E_1$ in system 2 is just proportional to the number of states that have this particular division of energy, i.e. $\Omega_1(E_1)\Omega_2(E_T - E_1)$. The most likely value for the energy E_1 is therefore the value $\bar{E}_1$ that maximizes $\Omega_1(E_1)\Omega_2(E_T - E_1)$. Since this quantity, as argued above, has a very sharp maximum at $\bar{E}_1$ as N gets large, then one is almost certain to find $E_1 = \bar{E}_1$ and the probability to find any other value of E_1 will vanish as the size of the system N gets infinitely large.

What condition determines this maximizing value of E_1? As usual, it is given by the value where the derivative of $\Omega_1(E_1)\Omega_2(E_T - E_1)$ vanishes,

$$\frac{\partial}{\partial E_1}\left[\Omega_1(E_1)\Omega_2(E_T - E_1)\right] = 0 \tag{2.4.17}$$

$$\Rightarrow \quad \left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)\Omega_2(E_T - E_1) + \Omega_1(E_1)\left(\frac{\partial \Omega_2(E_T - E_1)}{\partial E_1}\right) = 0 \tag{2.4.18}$$

$$\Rightarrow \quad \left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)\Omega_2(E_T - E_1) - \Omega_1(E_1)\left(\frac{\partial \Omega_2(E_T - E_1)}{\partial E_2}\right) = 0 \tag{2.4.19}$$

$$\Rightarrow \quad \frac{1}{\Omega_1}\frac{\partial \Omega_1(E_1)}{\partial E_1} = \frac{1}{\Omega_2}\frac{\partial \Omega_2(E_T - E_1)}{\partial E_2} \quad \Rightarrow \quad \frac{\partial}{\partial E_1}\left(\ln \Omega_1\right) = \frac{\partial}{\partial E_2}\left(\ln \Omega_2\right) \tag{2.4.20}$$

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

$$\frac{1}{T_1} = \left(\frac{\partial S_1}{\partial E_1}\right) = \left(\frac{\partial S_2}{\partial E_2}\right) = \frac{1}{T_2} \tag{2.4.21}$$

Comparing Eq. (2.4.20) with Eq. (2.4.21), and following Boltzmann, we therefore identify

$$S(E) \propto \ln \Omega(E) \tag{2.4.22}$$

as the entropy.

Since the relation between thermodynamics and mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above equation should be a universal constant of nature, and not depend on the particular system being considered. That constant is Boltzmann's constant k_B. So finally we have for the entropy,

$$\boxed{S(E) = k_B \ln \Omega(E)} \tag{2.4.23}$$

Looking at Eq. (2.4.14) giving $\Omega(E)$ for the ideal gas, we see as expected that $S(E)$ is a monotonic increasing function of E.