Microcanonical Ensemble at Energy

We saw that the microcanonical ensemble, at energy $E$, assigned equal weight to all systems on the surface in phase space of constant energy $H[\mathbf{q}, \mathbf{p}] = E$.

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

$$g(E) = \int \frac{d\mathbf{q} \, d\mathbf{p}}{h^{3N}} \delta(H[\mathbf{q}, \mathbf{p}] - E)$$

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

At this stage, the factor $\frac{1}{\Delta E}$ is introduced so that $g(E)$ has the units of $1/\text{energy}$.

We can now define the number of states in a shell of thickness $\Delta$ about the energy surface $E$.

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

$\Delta$ is a pure number. Again, $\Delta$ is arbitrary, but
\[ E = \sum_{i} \frac{p_i^2}{2m} \]

\[ g(E) = \int \frac{d^3 r_1}{h^{3N}} \int \frac{d^3 p_i}{h^{3N}} \delta \left( \sum_{i} \frac{p_i^2}{2m} - E \right) \]

\[ = \frac{V^N}{h^{3N}} \int \frac{d^3 p_i}{h^{3N}} \delta \left( \sum_{i} \frac{p_i^2}{2m} - E \right) \]

The surface of constant energy is just the surface of a sphere in 3N dimensional momentum space, given by the coordinates \( p_1, p_2, p_3, \ldots, p_{3N} \). The radius of the sphere is \( \sqrt{2mE} \).

Let \( \mathbf{p} = \sqrt{\sum \frac{p_i^2}{2m}} \) be the length of the momentum vector in the 3N dimensional momentum space.
Then \( \prod_{i=1}^{N} d^{3}p_{i} = dp \ p^{3N-1} d\Omega_{3N} \)

\[
g(E) = \frac{V^{N}}{\frac{a^{3N}}{h^{3N}}} \int d\Omega_{3N} \int_{0}^{\infty} dp \ p^{3N-1} \frac{\delta\left(p - \sqrt{2mE}\right)}{\left(p/m\right)^{1/2}}
\]

\[
= \frac{V^{N}}{\frac{a^{3N}}{h^{3N}}} S_{3N} \int_{0}^{\infty} dp \ p^{3N-1} \frac{\delta\left(p - \sqrt{2mE}\right)}{\left(p/m\right)^{1/2}}
\]

Area of unit sphere in \( 3N \)-dim space

\[
= \frac{V^{N}}{\frac{a^{3N}}{h^{3N}}} S_{3N} \ m \left(2mE\right)^{-\frac{3N-2}{2}}
\]

From Appendix C of Pathria, one has the area of unit sphere in \( d \)-dim space

\[
S_{d} = \frac{2\pi^{d/2}}{\Gamma(d/2)}
\]

where \( \Gamma(n) = (n-1)! \) for integer \( n \), the Gamma function.

So \( S_{3N} = \frac{2\pi^{3N/2}}{(3N-1)!} \)

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

\[
= \frac{V^{N}}{\frac{a^{3N}}{h^{3N}}} \ \frac{2\pi^{3N/2}}{(3N/2-1)!} \ m \left(2mE\right)^{\frac{3N}{2}} \]

\[
\Omega(E) = \frac{g(N) (2\pi m E)^{3N/2}}{\hbar^{3N} (\frac{3N}{2} - 1)} \frac{1}{E} \int_{E - \frac{\Delta}{2}}^{E + \frac{\Delta}{2}} dE' \ g(E') \approx \frac{g(E)}{E} \Delta
\]

For large \(N\), \(\Omega(E)\) is a very rapidly increasing function of \(E\), \(\sim E^{3N-1}\). We will now argue that \(\Omega(E)\) is related to the entropy of the system.

Consider two subsystems separated by a wall

\[E = E_1 + E_2\] energy conserved

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 conductive so that energy can be transferred between the two systems, \(E_1\) can vary but \(E = E_1 + E_2\) is fixed. What will be the value of \(E_1\) when the system comes to equilibrium?
The density of states of the combined system will be

\[ g_T(E_T) = \int_0^\infty dE_i \, g_1(E_i) \, g_2(E_T - E_i) \]

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

\[ \Omega_T(E_T) = \int \frac{dE_1}{\Delta} \Omega_1(E_1) \Omega_2(E_T - E_1) \]

The integrand is the number of states with total energy \( E_T \) that also have system 1 with energy \( E_1 \).

**Remark** Consider the behavior of the integrand
\[ \Omega_1(E_1) \] is a rapidly increasing function of \( E_1 \)
\[ \Omega_2(E_2) \] is a rapidly decreasing function of \( E_2 \)
\[ \Rightarrow \Omega_2(E_T - E_1) \] is a rapidly decreasing function of \( E_1 \)

\( \Rightarrow \) the product \( \Omega_1(E_1) \Omega_2(E_T - E_1) \) has a sharp maximum at some particular value of \( E_1 \).
In the microcanonical ensemble, all states with total energy $E_T$ are equally likely. But the value of $E_1$ that one is most likely to find as the energy of system 1 is the particular value that maximizes $\sqrt{2_1(E_1) \sqrt{2_2(E_T - E_1)}}$. That is, there are more states with the particular value of $E_1$ than with any other value of $E_1$, and since all microscopic states are equally likely, this value of $E_1$ is the most likely. Moreover, since $\sqrt{2_1(E_1)}$ is rapidly increasing in $E_1$, and $\sqrt{2_2(E_T - E_1)}$ is rapidly decreasing in $E_1$, the maximum is extremely sharp. So one is almost certain to find the maximum value of $E_1$ (the probability to find any other value of $E_1$ will vanish as the size of the systems get infinitely large).

What condition determines the maximum value of $E_1$?

$$\frac{\partial}{\partial E_1} \left[ \sqrt{2_1(E_1) \sqrt{2_2(E_T - E_1)}} \right] = 0$$

$$\Rightarrow \left( \frac{\partial \sqrt{2_1(E_1)}}{\partial E_1} \right) \sqrt{2_2(E_T - E_1)} + \sqrt{2_1(E_1)} \left( \frac{\partial \sqrt{2_2(E_T - E_1)}}{\partial E_1} \right) = 0$$

$$\Rightarrow \left( \frac{\partial \sqrt{2_1(E_1)}}{\partial E_1} \right) \sqrt{2_2(E_T - E_1)} - \sqrt{2_1(E_1)} \left( \frac{\partial \sqrt{2_2(E_T - E_1)}}{\partial E_2} \right) = 0$$

$$\Rightarrow \frac{1}{\sqrt{2_1}} \frac{\partial \sqrt{2_1(E_1)}}{\partial E_1} = \frac{1}{\sqrt{2_2}} \frac{\partial \sqrt{2_2(E_T - E_1)}}{\partial E_2}$$
\[ \frac{\partial}{\partial E_1} (\ln \Omega_1) = \frac{\partial}{\partial E_2} (\ln \Omega_2) \]

But from thermodynamics we know that 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

\[ S(E) \propto \ln \Omega(E) \]

as the entropy.

Since the relation between thermodynamics and mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above should be a universal number, and not depend on the particular system. This constant is Boltzmann's constant \( k_B \).

\[ S(E) = k_B \ln \Omega(E) \]

\[ \text{entropy} \quad \quad \text{# states with energy } E \]

\[ S(E) \text{ is a monotonic increasing function of } E \]

as it should be.
Ideal Gas

We had \( \Omega(E,V,N) = \frac{V^N (2\pi m E)^{3N/2}}{\hbar^{3N}(3N/2)^N}, \)

for large \( N \), use Stirling formula \( \ln N! = N \ln N - N \)

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

\[
= k_B \left\{ N \ln \left[ \frac{V}{\hbar^3} \left( \frac{(2\pi m E)^{3/2}}{(3N/2)^{3/2}} \right) \right] - \frac{(3N/2 - 1)}{2} \ln \left( \frac{3N}{2} - 1 \right) + \ln \left( \frac{4}{E} \right) \right\}
\]

\[
\leq k_B \left\{ N \ln \left[ \frac{V}{\hbar^3} \left( \frac{(2\pi m E)^{3/2}}{(3N)^{3/2}} \right) \right] + \ln \left( \frac{3N}{2} \right) + \frac{3N}{2} - 1
\]

\[
+ \ln \left( \frac{4}{E} \right) \right\}
\]

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

Where the remaining terms \( \ln \left( \frac{3N}{2} \right), -1 + \ln \left( \frac{4}{E} \right) \)

are all negligible compared to the above as \( N \to \infty \)

(recall we took \( \frac{E}{N} < \Delta < 2E \), so \( -\ln N \leq \ln \frac{E}{N} \leq 0 \)

is small compared to the term \( \propto N \)

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

Note, our result does not depend on \( \Delta \)

as we desired.
with the above, we recover the expected
\[
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{2}{2E} \left( N k_B \frac{3}{2} \ln E \right) = \frac{3}{2} N k_B \frac{1}{E}
\]

\[\Rightarrow E = \frac{3}{2} N k_B T\]

\[
\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{2}{2V} \left( N k_B \ln V \right) = N k_B \frac{1}{V}
\]

\[\Rightarrow pV = N k_B T\]

so far so good!

But there is a problem – \( S \) above is not extensive. If we take \( E \to 2E, \ V \to 2V, \ N \to 2N \), we do not get \( S \to 2S \).

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

the \( \ln V \) term in above spoils the desired extensivity.

Compare the above to our earlier result for the ideal gas, obtained from combining \( pV = N k_B T \) and \( E = \frac{3}{2} N k_B T \) with the Gibbs-Duhem relation.

(2) \[ S(E,V,N) = \frac{N}{N_0} S_0 + k_B N \ln \left[ (\frac{V}{V_0})^{3/2} (\frac{E}{E_0})^{3/2} (\frac{N}{N_0})^{-5/2} \right] \]

this version is extensive – it scales proportionate to \( N \), here \( V_0, E_0, N_0 \) constants. We have an extra factor \( N^{-1} \) in the log.
Note: The Gibbs-Duhem relation was derived assuming $S$ was extensive. Hence it should not be surprising that our expression (2) for $S$ is extensive.

What is the physical reason why the expression (1) fails to be extensive?