

Microcanonical Ensemble and Entropy

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

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

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

where h is a constant with units of $q_i p_i$.

h^{3N} represents the volume of 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 Planck's constant.

At this stage, the factor $\frac{1}{h^{3N}}$ 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 Δ about the energy surface E .

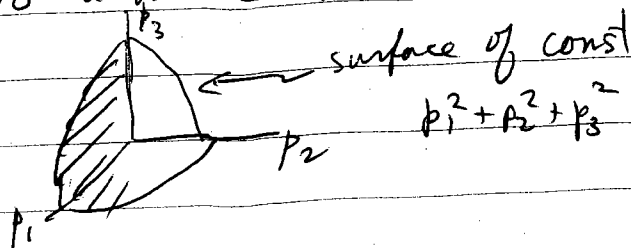
$$\Omega(E, V, N) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' g(E')$$

Ω is a pure number. Again, Δ is arbitrary, but

$\frac{E \Delta K E}{N}$
 assumed to be ~~small~~. It can be thought of as representing the finite accuracy with which one knows E . Our thermodynamic results should not depend on Δ . [both h and Δ are introduced so that ~~the~~ ~~dimension~~ of Ω is a dimensionless pure number that we can think of as being the ~~total~~ number of microscopic states occupied in the microcanonical ensemble at E]

Example: Compute Ω for the ideal gas of non-interacting particles, confined to a volume V

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



$$\begin{aligned}
 g(E) &= \int \frac{d^3 r_i}{h^{3N}} \int d^3 p_i \delta\left(\sum_i \frac{p_i^2}{2m} - E\right) \\
 &= \frac{V^N}{h^{3N}} \int d^3 p_i \delta\left(\sum_i \frac{p_i^2}{2m} - E\right)
 \end{aligned}$$

The surface of constant energy is just the surface of a sphere in $3N$ dimensional momentum space given by the coords $p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}$. The radius of the sphere is $\sqrt{2mE}$.

Let $P \equiv \sqrt{\sum_i p_i^2}$ be the length of the momentum vector in the $3N$ dimensional momentum space.

Then $\prod_{i=1}^N d^3 p_i = dP P^{3N-1} d\Omega_{3N}$

↑ differential solid angle
in $3N$ dimensional space

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

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

↑ area of unit
sphere in $3N$ -dim space

← from
converting the
 δ -function

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

From Appendix C of Pathria (equ C.76) or elsewhere,
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

Γ is the Gamma function

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

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

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

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

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

For large N , $\Omega(E)$ is a very rapidly increasing function of E ! $\sim E^{\frac{3N}{2}-1}$

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

Consider two subsystems separated by a wall

| | |
|-------|-------|
| E_1 | E_2 |
| V_1 | V_2 |
| N_1 | N_2 |

$$E_T = E_1 + E_2 \quad \text{energy conserved}$$

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 conducting so that energy can be transferred between the two systems, $\Rightarrow E_1$ can vary but $E_T = E_1 + E_2$ 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

$$g_T(E_T) = \int_0^{E_T} dE_1 g_1(E_1) g_2(E_T - E_1)$$

$$\text{Now if } \Omega_T(E_T) = g_T(E_T) \Delta$$

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

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

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 .

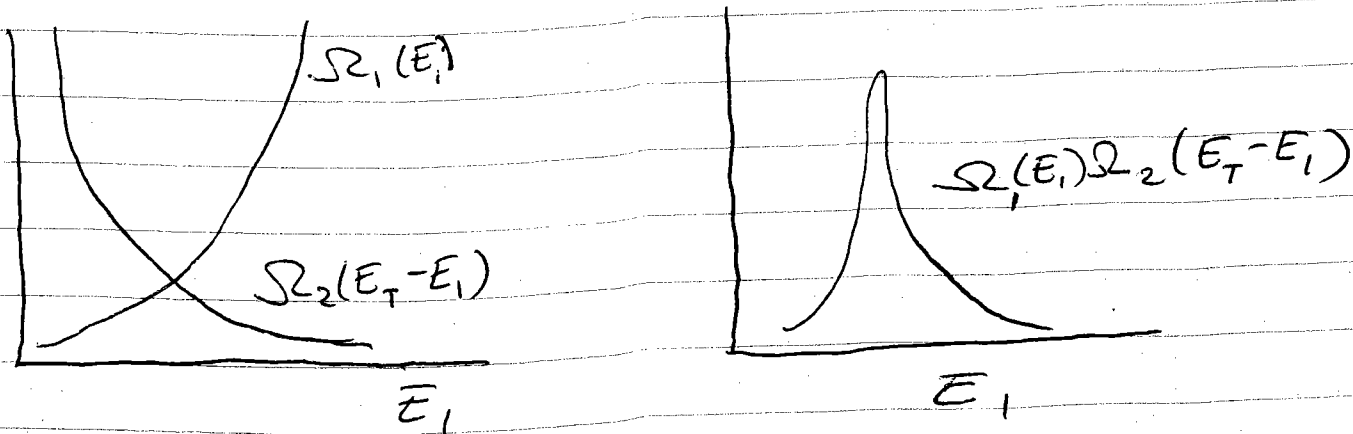
~~Now~~ Consider the behavior of the integrand

$\Omega_1(E_1)$ is a rapidly increasing function of E_1

$\Omega_2(E_2)$ is a rapidly increasing 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 $\Omega_1(E_1)\Omega_2(E_T - E_1)$. That is, there are more states with this 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 $\Omega_1(E_1)$ is rapidly increasing in E_1 and $\Omega_2(E_T - E_1)$ is rapidly decreasing in E_1 , the maximum is extremely sharp. So one is almost certain to find the maximizing 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 this maximizing value of E_1 ?

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

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

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

$$\Rightarrow \frac{1}{\Omega_1} \frac{\partial \Omega_1(E_1)}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2(E_T - E_1)}{\partial E_2}$$

$$\Rightarrow \frac{\partial}{\partial E_1} (\ln \Omega_1) = \frac{\partial}{\partial E_2} (\ln \Omega_2)$$

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

$$S(E) \propto \ln \Omega(E)$$

as the entropy.

Since the relation between thermodynamics & 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 .

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

\uparrow entropy \uparrow # states with energy E

$S(E)$ is a monotonic increasing function of E as it should be.

Ideal gas

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

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

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

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

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

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

where the remaining terms $\ln\left(\frac{3N}{2}\right) - 1 + \ln(\Delta/E)$ are all negligible compared to the above as $N \rightarrow \infty$ (recall we took $\frac{E}{N} < \Delta \ll E$, so $-\ln N \leq \ln \frac{\Delta}{E} \leq 0$ is small compared to the terms $\propto N$)

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

note, our result does not depend on Δ as we desired.

with the above, we recover the expected

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{\partial}{\partial E} \left(N k_B \frac{3}{2} \ln E \right) = \frac{3}{2} N k_B \frac{1}{E}$$

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

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

$$\Rightarrow pV = N k_B T$$

so far so good!

But there is a problem - S above is not extensive.
If we take $E \rightarrow 2E$, $V \rightarrow 2V$, $N \rightarrow 2N$, we do not get $S \rightarrow 2S$.

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

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

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

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?