Micro Canonical Ensemble and Entropy

We saw that the micro canonical 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"

$$\underbrace{g(E)}_{\text{(number of states per unit energy)}} \equiv \int \frac{dq_i \, dp_i}{h^{3N}} \; \delta(H[q_i, p_i] - E)$$

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/energy.

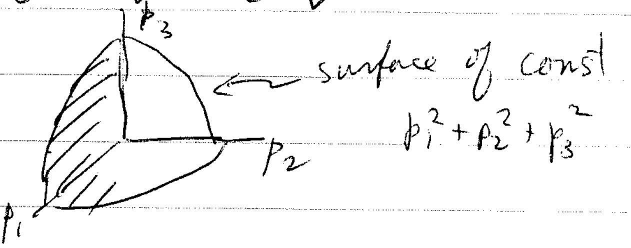
We can now define the number of states in a shell of thickness Δ about the energy surface E.

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

Ω is a pure number. Again, Δ is arbitrary, but 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. [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 ~~[illegible]~~ 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

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m}$$



$$g(E) = \prod_{i=1}^{N} \int \frac{d^3 r_i}{h^{3N}} \int d^3 p_i \;\; \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E \right)$$

$$= \frac{V^N}{h^{3N}} \prod_{i=1}^{N} \int d^3 p_i \;\; \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E \right)$$

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

Let $\mathbb{P} \equiv \sqrt{\sum_{i=1}^{N} |\vec{p}_i|^2}$ be the length of the momentum vector in the 3N dimensional momentum space

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

differential solid angle in 3N dimensional space

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

$$= \frac{V^N}{h^{3N}} \underbrace{S_{3N}}_{\text{area of unit sphere in 3N-dim space}} \int_0^\infty d\mathbb{P}\, \mathbb{P}^{3N-1}\, \frac{\delta\left(\mathbb{P} - \sqrt{2mE}\right)}{(\mathbb{P}/m)}$$

from converting the δ-function

$$\delta(f(x)) = \frac{\delta(x)}{f'(x)}$$

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

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

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

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

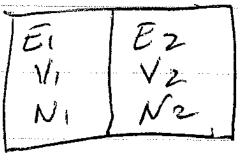
$$\Omega(E) = \int_{E-\frac{\Delta}{2}}^{E+\Delta/2} dE'\, g(E') \approx g(E)\Delta$$

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

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

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

Consider two subsystems separated by a wall



$E_T = E_1 + E_2$ 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 conducting so that energy can be transfered 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

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

Now if $\Omega_T(E_T) \approx g_T(E_T)\Delta$

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

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

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

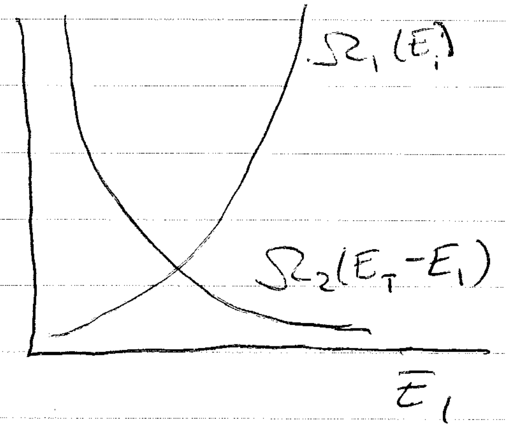
Consider the behavior of the integrand

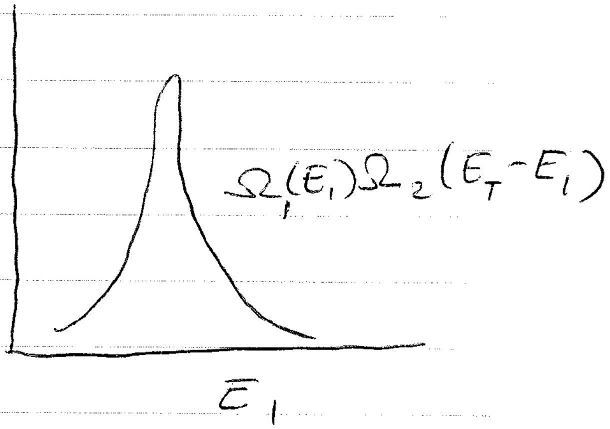
$\Omega_1(E_1)$ is a rapidly increasing function of E_1

$\Omega_2(E_2)$ is a rapidly increasing function of E_2

$\Rightarrow \Omega_2(E_T - E_1)$ is a rapidly <u>decreasing</u> 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?

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

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

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

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

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

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, ad not depend on the particular system. This constant is Boltzmann's constant k_B.

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

entropy

\# states with energy E

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

Ideal gas

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

for large N we use Stirling's formula $\ln N! \simeq N \ln N - N$

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

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

use
$$\begin{aligned}
\ln\left(\frac{3N}{2}-1\right) &\simeq \ln \frac{3N}{2}\left(1-\frac{2}{3N}\right) \\
&= \ln\frac{3N}{2} + \ln\left(1-\frac{2}{3N}\right) \\
&\simeq \ln\frac{3N}{2} - \frac{2}{3N} \qquad \text{expanding the log}
\end{aligned}$$

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

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

as $N \to \infty$ leading terms are

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

(since the terms $\ln\frac{3N}{2} + \ln \Delta/E$ are negligible)

Note: since we took Δ so that

$$\frac{E}{N} < \Delta \ll E$$

then $$-\ln N < \ln\frac{\Delta}{E} \ll 0$$

or $\left|\ln\frac{\Delta}{E}\right| < \ln N$ is of order $\ln N$ ad so can be ignored compared to terms of order N

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

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

with the above, we recover the expected

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

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

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

$$\Rightarrow \quad pV = N k_B T$$

so far so good!

But there is a problem – S above is <u>not</u> extensive. If we take $E \to 2E$, $V \to 2V$, $N \to 2N$, we do <u>not</u> get $S \to 2S$.

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

the $\ln V$ term in above spoils the desired extensivity. Compare the above to our earlier result for the ideal gas, obtained from combining $pV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$ with the Gibbs-Duhem relation

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

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?