

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

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

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

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 .

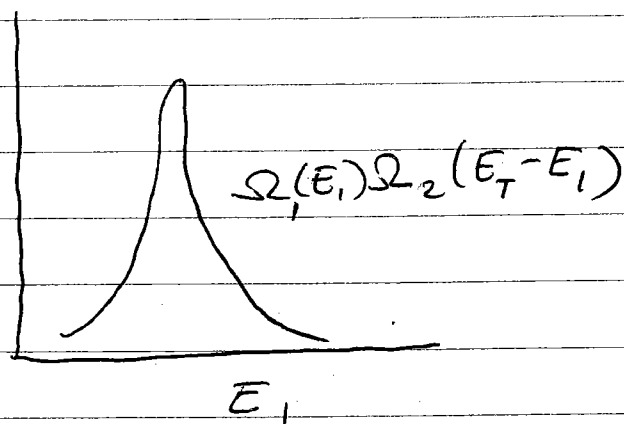
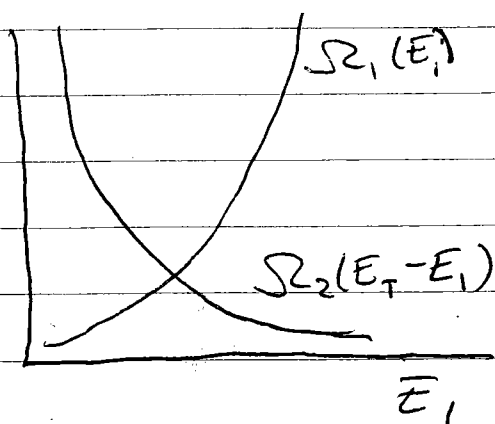
~~Remember~~ Consider the behavior of the integrand

$\Omega_1(E_1)$ 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

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

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

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

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

$$\text{use } \ln \left(\frac{3N}{2} - 1 \right) \approx \ln \frac{3N}{2} \left(1 - \frac{2}{3N} \right)$$

$$= \ln \frac{3N}{2} + \ln \left(1 - \frac{2}{3N} \right)$$

$$\approx \ln \frac{3N}{2} - \frac{2}{3N} \quad \text{expanding the log}$$

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

$$\left. + \ln \frac{3N}{2} - \frac{2}{3N} + \frac{3N}{2} - 1 + \ln \frac{\Delta}{E} \right\}$$

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

$$\left. + \ln \frac{\Delta}{E} \right\}$$

as $N \rightarrow \infty$ leading terms are

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

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

Note: since we took Δ so that

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

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

$$\text{or } |\ln \frac{\Delta}{E}| < \ln N$$

is of order $\ln N$
and so can be ignored
compared to terms of order N

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

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

with the above, we recover the expected

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

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

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

$$\Rightarrow pV = N k_B T$$

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, E, N_0 constants \rightarrow 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?

Entropy of Mixing - Gibbs paradox

Consider two different gases (red and blue) at the same temperature and pressure, separated by a partition

E_1, V_1, N_1	E_2, V_2, N_2
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$$\left. \begin{array}{l} V_1 + V_2 = V \\ N_1 + N_2 = N \\ E_1 + E_2 = E \end{array} \right\} \text{constant}$$

both gases at same T and $p \Rightarrow \begin{cases} E_1 = \frac{3}{2} N_1 k_B T, & V_1 = N_1 k_B T / p \\ E_2 = \frac{3}{2} N_2 k_B T, & V_2 = N_2 k_B T / p \end{cases}$

With the partition in place, the total entropy is initially

$$S_i = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

Now remove the partition and let the gases mix. The temperature ^{and N_1 and N_2} ~~temperature~~ should not change. $\Rightarrow E_1$ and E_2 remain constant. ~~Also N_1 and N_2 remain constant.~~ The only changes are $V_1 \rightarrow V$ and $V_2 \rightarrow V$.

With the partition removed, the final entropy is

$$S_f(E, V, N_1, N_2) = k_B \ln \left[\Omega_1(E_1, V, N_1) \Omega_2(E_2, V, N_2) \right]$$

$$= S_1(E_1, V, N_1) + S_2(E_2, V, N_2)$$

The entropy of mixing is $\Delta S = S_f - S_i$

If we use our result for the ideal gas, we get

$$S_i = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V_1}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{3/2} \right]$$
$$+ \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V_2}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{3/2} \right]$$

and

$$S_f = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_1 \frac{E_1}{N_1} \right)^{3/2} \right]$$
$$+ \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m_2 \frac{E_2}{N_2} \right)^{3/2} \right]$$

$$\Rightarrow \Delta S = k_B N_1 \ln \left(\frac{V}{V_1} \right) + k_B N_2 \ln \left(\frac{V}{V_2} \right)$$

or since $V_1 = N_1 k_B T / p$ and $V_2 = N_2 k_B T / p$ $V = V_1 + V_2$

$$\Delta S = k_B N_1 \ln \left(\frac{N_1 + N_2}{N_1} \right) + k_B N_2 \ln \left(\frac{N_1 + N_2}{N_2} \right) > 0$$

We expect $\Delta S > 0$ since entropy increases when a constraint is removed.

When the red gas mixes with the blue gas we get purple gas! The process is irreversible - there is no thermodynamic way to separate back into separate volumes of blue and red gas. In irreversible processes, the entropy increases (this is just the thermodynamic definition of an irreversible process)

Now consider what happens if the two gases on either side of the partition were the same type (both red).

With the partition removed, the system is a single gas of $N = N_1 + N_2$ particles, with total energy $E = E_1 + E_2$, confined to a volume V . The final state entropy is

$$S_f = S(E, V, N)$$

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

$$= \frac{3}{2} k_B (N_1 + N_2) + k_B (N_1 + N_2) \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi \frac{3}{2} k_B T \right)^{3/2} \right]$$

$$\Rightarrow S_f = \frac{3}{2} k_B N_1 + k_B N_1 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E_1}{N_1} \right)^{3/2} \right]$$

$$+ \frac{3}{2} k_B N_2 + k_B N_2 \ln \left[\frac{V}{h^3} \left(\frac{4}{3} \pi m \frac{E_2}{N_2} \right)^{3/2} \right]$$

where we used $\frac{E}{N} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$.

$$\Rightarrow S_f = S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2)$$

[In general $S(E, V, N)$, instead of obeying the extensivity relation, obeys $\lambda S(E, V, N) = S(\lambda E, V, \lambda N)$, which is consistent with the above]

So S_f has exactly the same form when both gases are the same, as when they are different!

Hence we find the same $\Delta S > 0$, as when the gases were different! But this cannot be - when the gases are the same, removing the partition is a reversible process. We can always reinsert the partition and return to ~~the~~ a situation indistinguishable from the initial state. In such a reversible process, we should have $\Delta S = 0$!

The source of the problem lies in whether or not one should regard the particles of the gas as distinguishable. If we can distinguish each and every particle of the gas from one another, then when we mix two gases of the same type, we do not really have a reversible process. After the partition is reinserted, we have not returned to the initial state because we now have different particles on each side as compared to what was initially. Think of each particle as being a different color, and the point is clear. And if each particle is a different color (ie is distinguishable) it is no longer clear that the entropy should be extensive. If we double the volume, energy, and number of particles, we have not just made a second copy of the original system, since all the new particles must come in new colors!

It was Gibbs who realized that to resolve this paradox of the mixing entropy, as well as to make the entropy extensive, it was necessary to regard the particles of a gas as indistinguishable from one another. This assumption is verified by quantum mechanics.