

The density of states of the combined system will be

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

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

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

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

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 .

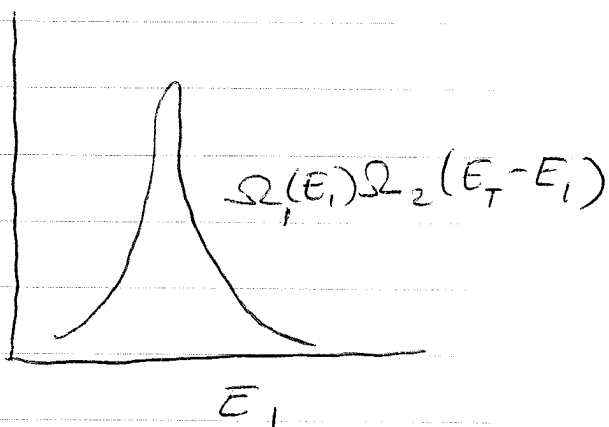
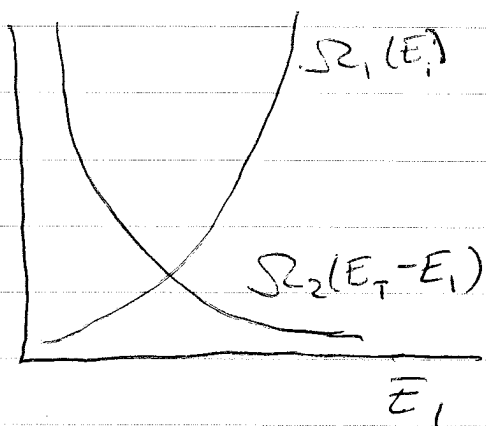
~~When~~ Consider the behavior of the integrand

$\Omega_1(E_1)$ 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 .

$$S(E) = k_B \ln \Omega(E)$$

↑
entropy

↑
states
with energy E

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

Ideal gas

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

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

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

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

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

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

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

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

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

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

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

$\approx |\ln \frac{\Delta}{E}| < \ln N$ 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 $S \rightarrow 2S$.

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

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

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

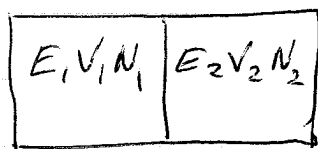
This version is extensive - it scales proportionate to N . here V_0, E_0, N_0 constants. \nearrow we have an extra factor N^{-1} in the log

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



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

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} ~~expressions~~ 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

$$\begin{aligned} S_f(E, V, N_1, N_2) &= k_B \ln [\Omega_1(E_1, V, N_1) \Omega_2(E_2, V, N_2)] \\ &= S_1(E_1, V, N_1) + S_2(E_2, V, N_2) \end{aligned}$$

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)