Recap Lecture, Fri 21/2/2020

canonical ensemble:

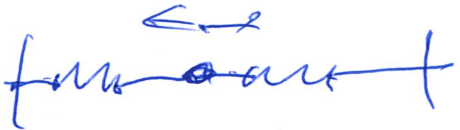
$$p_i = \frac{1}{Z} e^{-\boxed{E_i/T}} \checkmark$$

$$\sum_i p_i = 1$$

$$Z = \sum_{i=1}^{M} e^{-E_i/T} \checkmark$$

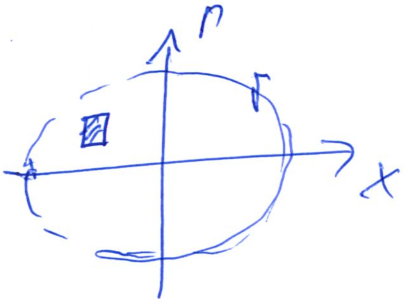
1-particle: $E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$ → no "x" dependence

motion: x, p - diagr.



$x = \cos t$

$p = \sin t \sim \dot{x}$



Qu: ▨ 1-state per volume $\frac{dx\,dp}{2\pi\hbar}$

$$Z_1^{1\text{-dim}}: \quad \sum_i e^{-p^2/2m} \to \underbrace{\int \frac{\overset{L}{\boxed{dx}}\,dp}{2\pi\hbar}}_{\sum_i} e^{-p^2/2m}$$

$$Z_1^{1\text{-dim}} = \frac{L}{2\pi\hbar}\int dp\, e^{-p^2/2m} \checkmark = \frac{L}{2\pi\hbar}\boxed{\sqrt{2\pi m}}$$

5.4 The Gibbs paradox and the mixing entropy

Mathematics is based upon axioms, and theorems, which are proven starting from the axioms. Over the years, the knowledge of Mathematics grows. Assume that one day, a mathematician arrives at an inconsistencies during proof (i.e., by using only what has been rigorously established), e.g. "2=3". The only[8] conclusion left is that the axioms do not hold up and have to be changed. Luckily, this has not happened since more than 5000 years.

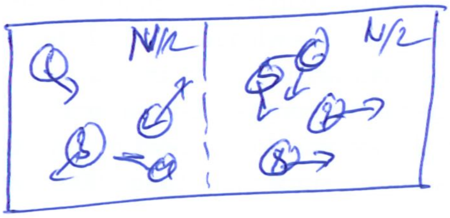
Something similar (and perhaps more likely to occur) can happen in Physics: assume that we have developed a theory (such as thermodynamics) that should describe one aspect of nature. This theory can be an approximation valid only for a certain parameter range. An example is classical mechanics, which is an excellent theory for phenomenons at everyday life scales. This theory is superseded by Quantum Mechanics, which is also valid at particle length scales. Now and then it can happen that such a theory develops a contradiction within in its own framework. This is called a *paradox*. If a mistake in the derivation of the paradox cannot be found, it would lead to the demise of the theory. Such a paradox was indeed found by Gibbs[9] in the context of thermodynamics.

Consider a box of N *distinguishable* particles in a box. Other than being distinguishable, the particles have the same physical properties. Think od f identical billard balls, each with a diffrent number on it. The box is in thermodynamical equilibrium and has two compartments separated by a wall:

---

[8] This might be an assumption: mathematician also study what can be described by mathematics asking whether there can be something outside Mathematics and necessarily remains there.

[9] Josiah Willard Gibbs (February 11, 1839 – April 28, 1903) - E an American scientist



State (A): Let us call this state A. What is it entropy? We did such a calculation in subsection 5.2: since the particles are now distinguishable, the factor $1/N!$ is missing from the partition function Z (46):

$$Z = \left(\frac{L}{\hbar 2\pi}\right)^{3N} \left(2\pi T m\right)^{3N/2} \cdot \cancel{\frac{1}{N!}}$$

disting.

The Helmholtz Free Energy and the entropy is therefore given by

$$\begin{aligned} F(T) &= -NT \ln\left(V \left(\frac{2\pi T m}{\hbar^2 4\pi^2}\right)^{3/2}\right) . \\ S(T) &= -\frac{dF}{dT} = N \ln\left(\frac{V}{\lambda^3}\right) + \frac{3}{2} N , \end{aligned} \qquad (55)$$

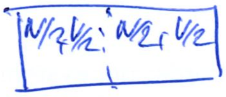
any box, N,V:

with λ in (50). We now can write down the entropy S_A of state (A). It is the sum of entropies for each compartment with volume $V/2$ and particle number $N/2$:

left box   right box

$$S_A = \frac{N}{2}\ln\left(\frac{V}{2}\frac{1}{\lambda^3}\right) + \frac{3}{2}\frac{N}{2} + \frac{N}{2}\ln\left(\frac{V}{2}\frac{1}{\lambda^3}\right) + \frac{3}{2}\frac{N}{2}$$

$$= N\cdot\ln\left(\frac{V}{2}\frac{1}{\lambda^3}\right) + \frac{3}{2}N$$



$$S_A = N\ln\left(\frac{V}{2}\frac{1}{\lambda^3}\right) + \frac{3}{2}N\,. \tag{56}$$

State (B): We arrive at state (B) by removing the separating wall.

$$S_B = N\ln\left(\frac{V}{\lambda^3}\right) + \frac{3}{2}N$$

Now, all N particles are distributed in volume V, and the entropy S_B of state (B) is given by the expression (55):

$$S_B = N\ln\left(V\frac{1}{\lambda^3}\right) + \frac{3}{2}N\,.$$

The entropy has increased as expected:

$$\Delta S = S_B - S_A = N\ln 2\,.$$

State (C): We arrive at state (C) by reinserting the separating wall. During the process, we take care that $N/2$ particles are in each compartment when the process finished. Since both compartments as well as the whole volume in state (B) was at the same temperature T throughout, nothing has changed and we are back at state (A). Hence:

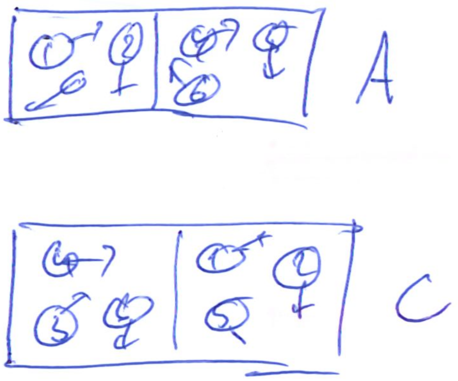
$$S_C = S_A.$$

This, however, is a serious problem for our framework:

$$B \longrightarrow C: \qquad S_B > \overset{S_A =}{S_C}\,.$$

In words: our system evolved from state (B) to state (C), but apparently the entropy has decreased. This violates the second law of thermodynamics (see subsection 3.2), namely that the entropy always increases or stays constant. This seems to be a inconsistency of our approach and is called Gibbs paradox, put forward by Gibbs in 1874-75.

Luckily, something is wrong in the line of arguments in section "State (C)" above. After state (B), wo do *NOT* arrive back at state (A). Remember that the particles are *distinguishable*: starting at state (A), we can number them. A natural choice (but any other would do as well) is to number the particles from 1 to $N/2$ in the left compartment and from $N/2$ to N in the right one. Once we are in state (C), we indeed have $N/2$ particles in each compartment at the same temperature, but the numbering is (most likely) all mixed up. State (C) is not State (A).



State "C" ≠ state "A"

In fact, by redistributing numbers to $N/2$ particle on the left and right hand side produces many possible outcomes form state (C), and hence explains the increase in entropy.

Stirling: 1/N! = ...

However, we could still be in trouble: what happens if the particles are *indistinguishable*? In this case, we would indeed have that state (C) is the same as state (A). Let us check the entropies. We can use formula (51) for the case of an ideal gas with indistinguishable particles:

$$\begin{aligned} S_A &= \frac{N}{2} \ln \left[\mathrm{e} \frac{V/2}{N/2} \frac{1}{\lambda^3} \right] + \frac{3}{2}\frac{N}{2} \\ &+ \frac{N}{2} \ln \left[\mathrm{e} \frac{V/2}{N/2} \frac{1}{\lambda^3} \right] + \frac{3}{2}\frac{N}{2} = N \ln \left[\mathrm{e} \frac{V}{N} \frac{1}{\lambda^3} \right] + \frac{3}{2} N \, . \end{aligned}$$

needed?

For state (B), we have N particles in the volume V, and thus:

$$S_B = N \ln \left[\mathrm{e} \frac{V}{N} \frac{1}{\lambda^3} \right] + \frac{3}{2} N \, .$$

We already said that for indistinguishable particles state (C) and state (A) are identical implying $S_C = S_A$. The crucial observation is that all these entropies are the same:

$$S_A = S_B = S_C \, .$$

This is what Gibbs had in mind: the wall is fictitious. Removing or reinserting it does not change anything.

Also note again that pure information can have a measurable physical effect. Mixing distinguishable particles, which otherwise have identical physical properties, lead to an increase in entropy. This increase is called *mixing entropy*.

5.5 Thermodynamical cycles and engines

5.5.1 Pressure and force

We already used the everyday life intuition and increased the pressure in a container by exerting a force on its movable piston (see subsection 5.3.1). We here formalise this connection.

Law in Physics: An object, described by its position $\vec{x}$ in space, is displaced by a vector $d\vec{x}$ at the presence of a force $\vec{F}(\vec{x})$. Then, the change in energy of the object is given by: $dE = \vec{F} \cdot d\vec{x}$.

ILLUSTRATION: