LECTURE

PERFECT GAS, part I

Goal: We will apply the equilibrium statistical physics machinery described in the last table to different physical systems. The first to analyse is the PERFECT GAS.

A gas consists of molecules moving about fairly freely in space. The perfect gas represents an idealization in which the potential energy of interaction between the molecules is negligible compared to their kinetic energy of motion.

We are interested first to describe the states of the system of N molecules.

(1) Since the interaction between molecules is negligible, the energy of the system of N molecules is

$$E_{system} = \epsilon_{molecule\,1} + \epsilon_{molecule\,2} + \dots + \epsilon_{molecule\,N}.$$

(2) The energy of each molecule, $\epsilon_{molecule}$, is considered to be a member of a list of possible one-particle energies. That is

$\epsilon_{molecule}$ belongs to the set

$$\underbrace{\epsilon_1 \le \epsilon_2 \le \dots \le \epsilon_r \le \dots}_{\text{one-particle energy spectrum}}$$

The label ϵ_r denotes the STATE OF A SINGLE MOLECULE and $\boxed{\text{NOT}}$ the STATE OF the system of N molecules. We need to construct the N-particle state out of the single particle states. This will be our primary aim at this point. To make the passage from 1-molecule states (or, equivalently, single molecule states) to N-molecule states, we will consider a simple example, as easy as possible.

Example

Consider a system of $N=2$ particles. The 1-particle energy spectrum is

$$\epsilon_A = \epsilon_B < \epsilon_C < \epsilon_D$$

and the 1-particle states are

$$A, B, C \text{ and } D$$

We see that the energy $\epsilon_A = \epsilon_B$ is doubly degenerated.

We will generate the states of the 2-particle system.

The set of 2-particle states for <u>DISTINGUISHABLE</u> particles is

Table 1

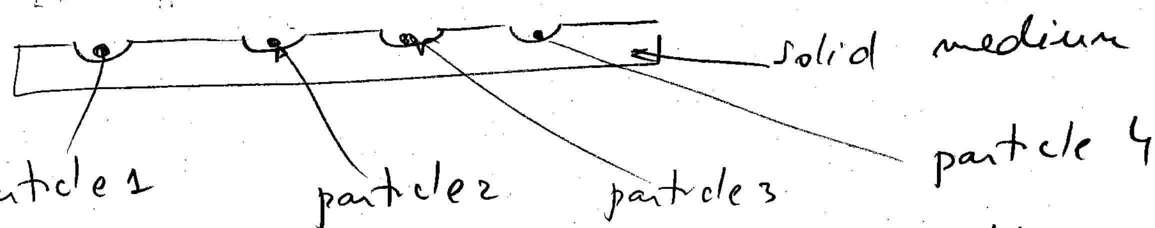
(A, A)
(A, B)
(A, C)
(A, D)
(B, A)
(B, B)
(B, C)
(B, D)
(C, A)
(C, B)
(C, C)
(C, D)
(D, A)
(D, B)
(D, C)
(D, D)

For example the state (B, C) means that particle 1 is in the <u>single particle state B</u> and particle 2 is in the <u>single particle state C</u>.

Now I need to quote a result of quantum mechanics without any explanation (because some of you are not familiar with quantum mechanics)

PAULI EXCLUSION PRINCIPLE

This principle says that we need to exclude state from Table 1. there are too many states in table 1 IF WE CONSIDER A GAS OF IDENTICAL PARTICLES. The idea is that the particle being identical we cannot distinguish them if they are in the gas form. If identical particles are not in a gas form, but, lets say, trapped in a solid medium



then they can be distinguish by the location they achieve in the solid. Each particle can be given an "address" in the solid's lattice, so we know which particle is which. In the gas form though, such an "address" does not exist. Identical particles are indistinguishable. To find the states of a system of many identical and indistinguishable particle we need to classify first the particles in our system.

There are only 2 mutually exclusive classes

Fermions	Bosons
$\boxed{\text{No}}$ two identical fermions can occupy the same single particle state	$\boxed{\text{Any}}$ number of identical bosons can occupy the same single particle state
Example of fermions: electron, proton, neutrons, and others. Fermions have HALF-INTEGER SPIN $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\right)$	Examples of bosons: photon, W and Z bosons, and others. Bosons have INTEGER SPIN $(1, 2, 3, \ldots)$

Going back to our example we have the following 2-particle states (see the explanation on the next page)

For Fermions	For Bosons
(A,B)	(A,A)
(A,C)	(A,B)
(A,D)	(A,C)
(B,C)	(A,D)
(B,D)	(B,B)
(C,D)	(B,C)
	(B,D)
	(C,C)
	(C,D)
	(D,D)

Analyzing the states for indistinguishable fermions and bosons, we see that a N-particle STATE can be described by the OCCUPATION NUMBER OF EACH SINGLE PARTICLE STATE. For example, the state (A, C) is represented as

$\to$ # of particles in state A

$\to$ # of particles in state B

$$(1, 0, 1, 0)$$

$\to$ # of particles in state C

$\to$ # of particles in state D

General case

Let the 1-particle states be

$$A, B, C, D, E, F, G, H, \ldots$$

and suppose we have M such 1-particle states. (M can be infinite)

An N-particle state can be represented in two ways. (I) As a vector of dimension N (the number of particles), like

$$(A\,A\,A\,B\,C\,C\,D\,D\,D\,D\,H \cdots).$$

This reads: 3 particles are in state A, 1 particle in state B, 2 in state C, and so on.

(II) The second way is as a vector of dimension M (the number of 1-particle states) that shows the OCCUPATION NUMBER OF THE 1-particle states.

$$(3, 1, 2, 4, 1, \dots)$$

For state A

For state B

For state C

Conclusion

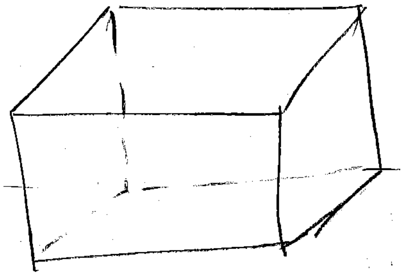
For identical, indistinguishable, noninteracting fermions or bosons, the N-particle state is

$$j = (n_1, n_2, n_3, \dots)$$

\# of particles in state 1

\# of particles in state 2

Now that we now the states we can start to analyze a gas in a box of volume V.



V

Lets start with the canonical distribution. So the total number of particles is fixed to N.

Then

$$j = (n_1, n_2, n_3, \ldots)$$

occupation number

single particle states

$$N = n_1 + n_2 + n_3 + \cdots$$

fixed

$$E_j = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \cdots$$

single particle energy spectrum

$$Z = \sum_j e^{-\beta E_j} = \sum_{\substack{n_1, n_2, \ldots \\ n_1 + n_2 + \cdots = N}}' e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \cdots)}$$

Restriction to summation

Because of the restriction to summation we cannot find the canonical partition function easy

Because N is considered a very large number, $N \sim 10^{26}$, we can compute the thermodynamic properties starting with microcanonical or with the grand canonical distribution, or, of course, with the canonical one. Because the grand canonical distribution do not impose any restriction on the occupation numbers (that is $n_1 + n_2 + \dots$ is not fixed) we may be able to compute the grand canonical distribution

$$\Lambda = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\substack{n_1, n_2, \dots \\ n_1+n_2+\dots = N}} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

$$\Lambda = \sum_{N=0}^{\infty} \sum_{\substack{n_1, n_2, \dots \\ n_1+n_2+\dots = N}} e^{\beta\mu(n_1+n_2+\dots)} \, e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

this sum equals a sum with <u>no</u> restrictions for the occupation numbers

$$\sum_{N=0}^{\infty} \sum_{\substack{n_1, n_2, \dots \\ n_1+n_2+\dots = N}} = \sum_{n_1} \sum_{n_2} \dots$$

So

$$\Lambda = \sum_{n_1} \sum_{n_2} \cdots \left[\left(e^{\beta\mu - \beta\epsilon_1}\right)^{n_1} \left(e^{\beta\mu - \beta\epsilon_2}\right)^{n_2} \cdots \right]$$

$$\Lambda = \left[\sum_{n_1} e^{(\beta\mu - \beta\epsilon_1) n_1} \right] \left[\sum_{n_2} e^{(\beta\mu - \beta\epsilon_2) n_2} \right] \cdots$$

In words, the grand canonical partition function is the product OVER THE 1-PARTICLE STATES of factors of the form

$$\sum_{n}{}' \, e^{(\beta\mu - \beta\epsilon) n}$$

So

$$\Lambda = \prod_{\text{1-particle sates}} \left[\sum_{n}{}' \, e^{(\beta\mu - \beta\epsilon_{\text{1-particle states}}) n} \right]$$

Now we need to specify the range of summation over n in $\sum_n{}'$. The range will depend on the type of particles:

For Fermions $\quad n = 0$ or 1 only

For Bosons $\quad n = 0, 1, 2, 3, \ldots$

Fermions

$$\sum_{n=0}^{1} e^{(\beta\mu - \beta\,\epsilon_{1\text{-particle states}})n} =$$

$$= \underbrace{e^{(\beta\mu - \beta\,\epsilon_{1\text{-particle states}})\cdot 0}} + e^{(\beta\mu - \beta\,\epsilon_{1\text{-particle states}})\cdot 1} =$$

$$= 1 + e^{\beta\mu - \beta\,\epsilon_{1\text{-particle states}}}$$

$$\boxed{\Lambda_{\text{FERMIONS}} = \prod_{1\text{-particle states}} \left[1 + e^{\beta\mu - \beta\,\epsilon_{1\text{-particle states}}}\right]}$$

Compare !

Bosons

$$\sum_{n=0}^{\infty} e^{(\beta\mu - \beta\,\epsilon_{1\text{-particle states}})n} =$$

$$= 1 + q + q^2 + \cdots = \frac{1}{1-q}$$

with $q = e^{\beta\mu - \beta\,\epsilon_{1\text{-particle states}}}$

if $q < 1$

So

$$\Lambda_{\text{BOSONS}} = \prod_{\text{1-particle states}} \left[1 - e^{\beta\mu - \beta\epsilon_{\text{1-particle states}}} \right]^{-1}$$

if $\quad e^{\beta\mu - \beta\epsilon_{\text{1-particle states}}} < 1$

This condition says that

$$\mu < \text{all } \epsilon_{\text{1-particle states}}$$

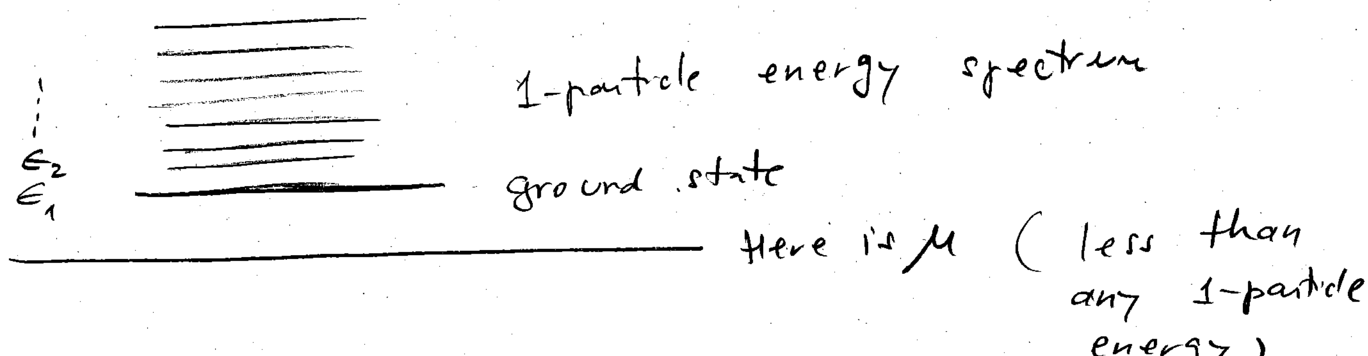


Figure 1. The chemical potential for the Bose gas is less than any 1-particle energy

Conclusion

$$\boxed{\Lambda = \prod_{\text{1-particle states}} \left[1 \mp e^{\beta\mu - \beta\epsilon_{\text{1-particle states}}} \right]^{\mp 1}}$$

upper sign for BOSONS (−)

lower sign for FERMIONS (+)

Now we can find the average number of particles

$$\langle N \rangle = kT \left(\frac{\partial \ln \Lambda}{\partial \mu} \right)_{T,V}$$

and the internal energy of the gas

$$U = -\left(\frac{\partial \ln \Lambda}{\partial \beta} \right)_{\beta\mu, V} = -\left(\frac{\partial \ln \Lambda}{\partial \beta} \right)_{\mu, V} + \mu \langle N \rangle$$

Here $\beta\mu$ should be kept constant

Here μ should be kept constant

The average number of particles is

$$\langle N\rangle = kT\frac{\partial}{\partial\mu}\underbrace{\sum_{\substack{\text{1-particle}\\ \text{states}}} \ln\left(1 \mp e^{\beta\mu-\beta\epsilon_{\text{1-particle states}}}\right)}_{\text{This is } \ln\Lambda}$$

$$\langle N\rangle = kT\left(\mp\sum_{\substack{\text{1-particle}\\ \text{states}}}\frac{\mp\beta e^{\beta\mu-\beta\epsilon_{\text{1-particle states}}}}{1\mp e^{\beta\mu-\beta\epsilon_{\text{1-particle states}}}}\right)$$

$$\langle N\rangle = \sum_{\substack{\text{1-particle}\\ \text{states}}}\frac{1}{e^{-\beta\mu+\beta\epsilon_{\text{1-particle states}}}\mp 1}$$

at this step notice that $kT=\frac{1}{\beta}$ simplifies with β and the divide the numerator and the denumerator with $e^{\beta\mu-\beta\epsilon_{\text{1-particle states}}}$

So

$$\langle N \rangle = \sum_{\substack{\text{1-particle} \\ \text{states}}}' \langle N_{\text{1-particle states}} \rangle$$

where

$$\boxed{\langle N_{\text{1-particle states}} \rangle = \frac{1}{e^{-\beta\mu + \beta\epsilon_{\text{1-particle states}}} \mp 1}}$$

is the average number of particles in the 1-particle state. ($-$ for BOSONS and $+$ for FERMIONS)

Thermodynamic Equation of state

We can continue to find the internal energy U, the Helmholtz potential F and so on. Of a particular importance is the thermodynamic relation that connects the pressure, volume and temperature. We get this thermodynamic equation of state from

$$pV = kT \ln \Lambda$$

So

$$\frac{pV}{kT} = \mp \sum_{\text{1-particle states}} \ln\left(1 \mp e^{\beta\mu - \beta\epsilon_{\text{1-particle states}}}\right)$$

or, if we sum over the energy levels

$$\frac{pV}{kT} = \mp \sum_{\substack{\text{1-particle} \\ \text{energy} \\ \text{levels } \epsilon}}' \Omega(\epsilon) \ln\left(1 \mp e^{\beta\mu - \beta\epsilon}\right)$$

the degenaracy of the energy level ϵ

To go further we need to specify the one-particle energy levels