



9. Quantum Statistics, 2

lecture 32, November 13, 2017

housekeeping

Honors project

Instructions for 3 people are up

that was easy

This week, remember:

homework workshop will be Wednesday

homework will be due Friday

lectures will happen M,T,F



today

statistical physics - ~~classically~~ speaking

quantum mechanically

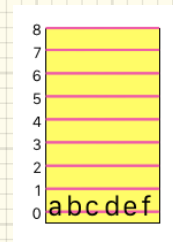
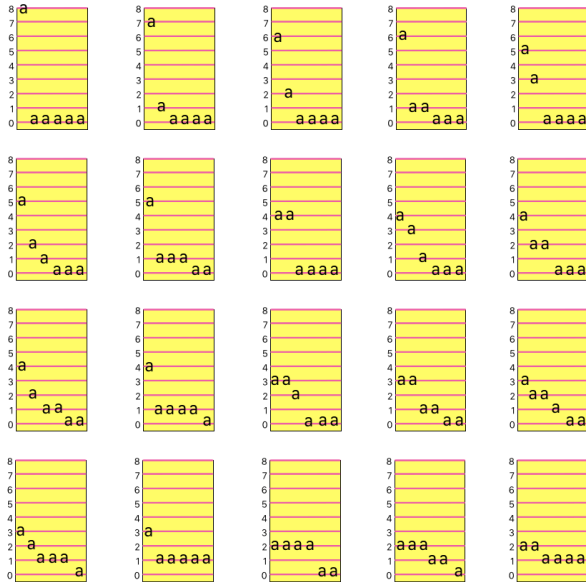


Last Friday: game of 6 molecules, 9 energy states: goal to count # ways to make

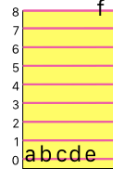
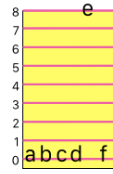
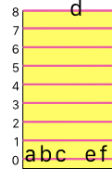
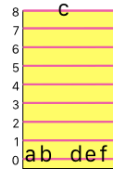
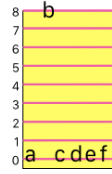
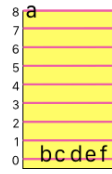
$$E_{\text{TOTAL}} = 8$$

← 0 20

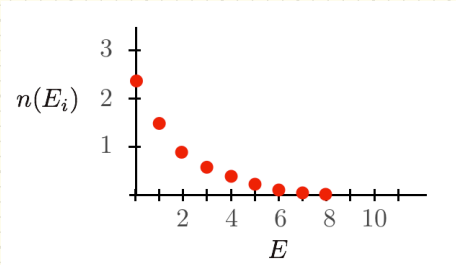
But now let the 6 molecules be distinguishable:



Distinguishability took to ↘



energy slot value										
Mac(i)	0	1	2	3	4	5	6	7	8	# micro
1	5	0	0	0	0	0	0	0	1	6
2	4	1	0	0	0	0	0	1	0	30
3	4	0	1	0	0	0	1	0	0	30
4	4	0	0	1	0	1	0	0	0	30
5	4	0	0	0	2	0	0	0	0	15
6	3	2	0	0	0	0	1	0	0	60
7	3	0	2	0	1	0	0	0	0	60
8	3	0	1	2	0	0	0	0	0	60
9	3	1	1	0	0	1	0	0	0	120
10	3	1	0	1	1	0	0	0	0	120
11	2	0	4	0	0	0	0	0	0	15
12	2	2	0	2	0	0	0	0	0	90
13	2	1	2	1	0	0	0	0	0	180
14	2	2	1	0	1	0	0	0	0	60
15	2	3	0	0	0	1	0	0	0	30
16	1	4	0	0	1	0	0	0	0	120
17	1	3	1	1	0	0	0	0	0	60
18	1	2	3	0	0	0	0	0	0	60
19	0	4	2	0	0	0	0	0	0	15
20	0	5	0	1	0	0	0	0	0	6
$n(E)$	2.31	1.54	0.98	0.59	0.33	0.16	0.07	0.02	0.005	1287



Then, using distinguishability as key ... from an ideal gas:

Maxwell velocity distribution \rightarrow Maxwell Speed distribution

$$f(v_i) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv_i^2}{2kT}}$$
$$n(v) dv = n \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}} dv$$

Then ... changed to energy:

$$n(E) dE = n \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} E^{1/2} e^{-E/kT} dE \quad \text{ideal gas}$$

$$n(E) dE = A e^{-E/kT} dE \quad \text{general}$$

$$n(E) = g(E) F_{MB}(E) \quad \text{Density of States}$$

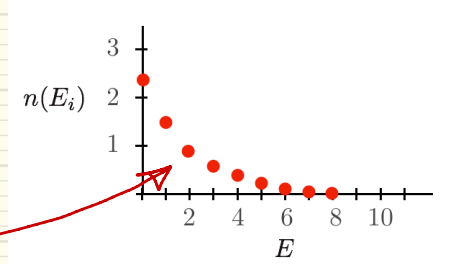
number of ways a system can achieve an energy E

$$\left\{ \begin{array}{l} F_{MB} = A e^{-E/kT} \\ \text{Maxwell-Boltzmann} \\ \text{Distribution Function} \end{array} \right.$$

ω_i discretely...

$$n(E_i) = g_i(E_i) F_{MB}(E)$$

$$F_{MB} = A e^{-E/kT}$$



The MB distribution is relevant for "classical" situations



indistinguishability not relevant

can still be quantum mechanical
in the sense of quantized
energy states...

In a stellar atmosphere of $T = 3000 \text{ K}$... what is the relative population of the ground state and first excited state for atomic hydrogen?

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

$$g_n = n^2$$

$$E_1 = -13.6 \text{ eV}$$

$$E_2 = -3.4 \text{ eV}$$

$$n_1 = g_1 A e^{-E_1/kT}$$

$$n_2 = g_2 A e^{-E_2/kT}$$

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = \frac{4}{1} e^{-(13.6 - 3.4)/kT} = 4 e^{-10.2 / (8.617 \times 10^{-5}) (3000)}$$

$$\frac{n_2}{n_1} = 4 e^{-39} \approx 3 \times 10^{-17} \Rightarrow \text{overwhelmingly in ground state}$$

When classical $\hat{=}$ when quantum mechanical?



MB applies



Something else applies

Take our gas again

$$\frac{3}{2} kT = \frac{1}{2} \frac{p^2}{2m}$$

$$\xrightarrow{QM} p = \frac{h}{\lambda}$$

if $\lambda \ll$ average distance between molecules \Rightarrow classical should be good.

$$p = \sqrt{3mkT}$$

$$\text{so } \lambda = \frac{h}{\sqrt{3mkT}}$$

$$\ll \sqrt[3]{\frac{V}{N}} \quad \dots \text{ish}$$

$$\text{So when: } \left(\frac{N}{V}\right) \frac{h^3}{(3mkT)^{3/2}} \ll 1$$

we would expect MB to be okay.

high T and/or small m

Can MB statistics be used for hydrogen gas @ STP?

$$\text{STP} \Rightarrow N_{\text{mol}} = N_A = 6.02 \times 10^{23} \text{ molecules}$$

$$\# \text{ in } V = 22.4 \text{ l} = 22.4 \times 10^{-3} \text{ m}^3 \quad \frac{5}{2} T = 300 \text{ K}$$

$$m_{\text{H}_2} = 3.34 \times 10^{-27} \text{ kg.}$$

$$\left(\frac{N}{V}\right) \frac{h^3}{(2\pi m h^2)^{3/2}} = \frac{(6.02 \times 10^{23}) (6.626 \times 10^{-34})^3}{(22.4 \times 10^{-3}) (3)(3.34 \times 10^{-27})(1.4 \times 10^{-23})(300)}$$
$$= 3.37 \times 10^{-5} \ll 1$$

So MB statistics can be used.

Go back to the Energy-box game. \rightarrow consider quantum mechanics.

distinguishability \rightarrow indistinguishability

For that $E=8$ state which had 6 distinguishable microstates... now we have just 1:

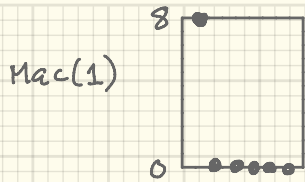
Mac(1)



is indistinguishable from the other 5

\Rightarrow 20 distinguishable states, all equally likely

\rightarrow no restriction on number in any state \Rightarrow **BOSONS**

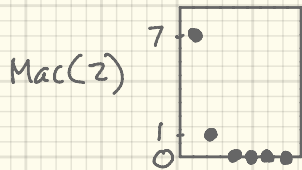


The average number of particles with $E=0$
for $\text{Mac}(1) = 5$

$$\langle n_0(i) \rangle = n_0(i) P_i$$

\uparrow \uparrow \leftarrow likelihood of $\text{Mac}(1)$
 average # $E=0$ in $\text{Mac}(1)$
 # with $E=0$
 for $\text{Mac}(1)$

$$\langle n_0(i) \rangle = 5 \left(\frac{1}{20} \right) = 0.25$$



$$\langle n_0(2) \rangle = 4 \left(\frac{1}{20} \right) = 0.20$$

$$\langle n_0 \rangle = \sum_{i=1}^{20} \langle n_0(i) \rangle = \sum_{i=1}^{20} n_0(i) P_i = 2.45$$

"Bose-Einstein"



E	n_{MB}	n_{BE}
0	2.31	2.45
1	1.54	1.55
2	0.98	0.90
3	0.59	0.45
4	0.33	0.30
5	0.16	0.15
6	0.07	0.10
7	0.02	0.05
8	0.005	0.05

More quantum mechanics:

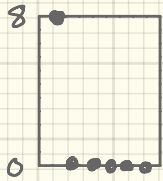
indistinguishable — Bosons

+

Pauli exclusion principle — Fermions:

no state can have more than $2s + 1$ particles

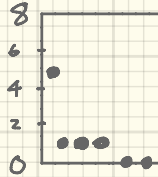
Mac(1)



is illegal

more than 1

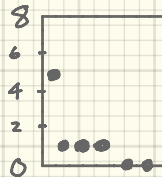
Mac(7)



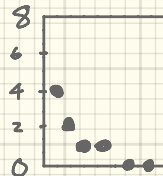
diffs

BUT:

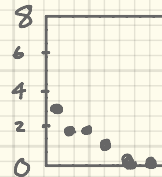
Mac(7)



Mac(14)



Mac(15)



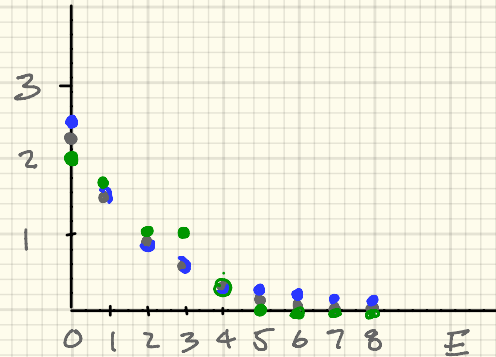
A-OK...
the only ones

$$\text{So } \langle n_o \rangle_{\text{FD}} = \sum_{i=1}^3 \langle n_o(i) \rangle = \sum_{i=1}^3 n_o(i) P_i$$
$$= 2 \left(\frac{1}{3} \right) + 2 \left(\frac{1}{3} \right) + 2 \left(\frac{1}{3} \right) = 2.0$$

Fermi-Dirac

Complete the table:

E	n_{MB}	n_{BE}	n_{FD}
0	2.31	2.45	2
1	1.54	1.55	1.67
2	0.98	0.90	1
3	0.59	0.45	1
4	0.33	0.30	0.33
5	0.16	0.15	0
6	0.07	0.10	0
7	0.02	0.05	0
8	0.005	0.05	0



Differences will be noticeable
with more particles

Remember ψ_A and ψ_S

↑
appropriate
for FD
quanta

↑ appropriate for BE quanta

2 identical Bosons:

$$\psi_S = \sqrt{\frac{1}{2}} \left[\psi_\alpha(1) \psi_\beta(2) + \psi_\beta(1) \psi_\alpha(2) \right]$$

↑
normalization
b/c $\psi_\alpha \neq \psi_\beta$
are normalized.

$\alpha \neq \beta$: all identifiers for "a state"

Put both in same state $\Rightarrow \alpha = \beta$

$$\psi_s = \sqrt{\frac{1}{2}} \left[\psi_\beta(1) \psi_\beta(2) + \psi_\beta(2) \psi_\beta(1) \right]$$

$$\psi_s = \sqrt{2} \psi_\beta(1) \psi_\beta(2)$$

$$\text{so } \psi_s^* \psi_s = 2 \psi_\beta^*(1) \psi_\beta^*(2) \psi_\beta(1) \psi_\beta(2)$$

Suppose indistinguishability not required

Then

$$\psi_D = \psi_\alpha(1) \psi_\beta(2)$$

$$\text{same state: } \psi_D^* \psi_D = \psi_\beta^*(1) \psi_\beta^*(2) \psi_\beta(1) \psi_\beta(2)$$

Notice:

$$P(\psi_s) = 2 P(\psi_D)$$

How about 3 such particles?

$$\begin{aligned}\psi_S = \sqrt{1/6} & \left[\psi_\alpha(1) \psi_\beta(2) \psi_\gamma(3) + \psi_\beta(1) \psi_\gamma(2) \psi_\alpha(3) \right. \\ & + \psi_\gamma(1) \psi_\alpha(2) \psi_\beta(3) + \psi_\gamma(1) \psi_\beta(2) \psi_\alpha(3) \quad 6 \text{ terms} \dots \\ & \left. + \psi_\beta(1) \psi_\alpha(2) \psi_\gamma(3) + \psi_\alpha(1) \psi_\gamma(2) \psi_\beta(3) \right] \quad \text{OBTW} = 3!\end{aligned}$$

same state $\Rightarrow \alpha = \beta = \gamma$

$$\psi_S = \sqrt{1/6} \cdot 6 \psi_\beta(1) \psi_\beta(2) \psi_\beta(3)$$

$$\begin{aligned}\psi_S^* \psi_S &= \underbrace{\frac{1}{6} \cdot 6^2}_{\frac{1}{3!} \cdot (3!)}} \underbrace{\psi_\beta^*(1) \psi_\beta^*(2) \psi_\beta^*(3) \psi_\beta(1) \psi_\beta(2) \psi_\beta(3)}_{\psi_D^* \psi_D}\end{aligned}$$

$$\psi_S^* \psi_S = 3! \psi_D^* \psi_D$$

indistinguishability of

an enhancement effect for Bosons: $n!$

Think of it this way:

Imagine an empty state... add a boson $\Rightarrow P_1 =$ probability that it will land in state 1

Add more... each would have same probability for distinguishable quanta

$$P_n^D = \underbrace{P_1^D \cdot P_1^D \cdot P_1^D \dots P_1^D}_{n \text{ times}} \\ = (P_1^D)^n$$

But:

For distinguishable - Boson - quanta

$$P_n^B = n! P_n^D = n! (P_1^D)^n$$

stay with me...

The probability that there would be $n+1$

$$P_{n+1}^B = (n+1)! P_{n+1}$$

note $(n+1)! = (n+1)n!$

$$(n+1) \underbrace{(n+1-1)(n+1-2)\dots}_{n!}$$

$$P_{n+1}^B = (n+1)n! P_{n+1}$$

and $P_{n+1} = (P_i)^{n+1} = (P_i)^n P_i = P_n^D P_i$

so $P_{n+1}^B = (n+1)n! \underbrace{P_n^D}_{P_n^B} P_i$

$$\downarrow$$
$$P_n^B$$

$$P_{n+1}^B = (n+1) P_n^B P_i = (n+1) P_i P_n^B$$

prob that there are n in state

prob of adding 1 D'ably.

\Rightarrow if there are already n bosons in state

probability that 1 more can add is $(n+1) \times P_i^D$

EQUILIBRIUM

Imagine a collection of distinguishable particles in thermal equilibrium
They each have energy... can't influence the others except in
elastic collisions

→ consider 2 different energy states ϵ_1 and ϵ_2

Average number with ϵ_1 : n_1

Average number with ϵ_2 : n_2

1 $\xrightarrow{\text{can}}$ 2 ... average rate R_{12} per particle

2 \rightarrow 1 ... average rate R_{21} per particle

Total rate at which particles go 1 \rightarrow 2: $n_1 R_{12}$

" 2 \rightarrow 1: $n_2 R_{21}$

If that's all that can happen:

$$n_1 R_{12} = n_2 R_{21}$$

So then

$$\frac{n_1}{n_2} = \frac{R_{2-1}}{R_{1-2}}$$

average # n_i of particles to be in ϵ_i is gotten from F_{MB}

$$n_i = n(\epsilon_i) = A e^{-\epsilon_i/kT}$$

ditto

$$n_2 = n(\epsilon_2) = A e^{-\epsilon_2/kT}$$

So

$$\frac{n_1}{n_2} = \frac{e^{-\epsilon_1/kT}}{e^{-\epsilon_2/kT}} = \frac{R_{21}}{R_{12}}$$

Remember the Boson enhancement.

Equilibrium:

$$n_1 R_{1 \rightarrow 2}^B = n_2 R_{2 \rightarrow 1}^B$$

relate to distinguishable form, D ,

$$R_{1 \rightarrow 2}^B = (1 + n_2) R_{1 \rightarrow 2}^D$$

$$R_{2 \rightarrow 1}^B = (1 + n_1) R_{2 \rightarrow 1}^D$$

So!

$$n_1 (1 + n_2) R_{1 \rightarrow 2}^D = n_2 (1 + n_1) R_{2 \rightarrow 1}^D$$

$$\frac{n_1 (1 + n_2)}{n_2 (1 + n_1)} = \frac{R_{2 \rightarrow 1}^D}{R_{1 \rightarrow 2}^D} = \frac{e^{-\epsilon_1 / kT}}{e^{-\epsilon_2 / kT}}$$

$$\frac{n_1(1+n_2)}{n_2(1+n_1)} = \frac{R_{2 \rightarrow 1}^D}{R_{1 \rightarrow 2}^D} = \frac{e^{-\epsilon_1/hT}}{e^{-\epsilon_2/hT}}$$

$$\frac{n_1}{1+n_1} e^{+\epsilon_1/hT} = \frac{n_2}{1+n_2} e^{+\epsilon_2/hT} \equiv h(T)$$

$$\text{def } h(T) = e^{-\alpha(T)}$$

$$\frac{n_1}{1+n_1} e^{+\epsilon_1/hT} = h$$

$$\frac{n_1}{1+n_1} = h \cdot e^{-\epsilon_1/hT} = e^{-\alpha} e^{-\epsilon_1/hT}$$

$$n_1 = n_1 e^{-(\alpha + \epsilon_1/hT)} + e^{-(\alpha + \epsilon_1/hT)}$$

$$n_1 \left[1 - e^{-(\alpha + \epsilon_1/hT)} \right] = e^{-(\alpha + \epsilon_1/hT)}$$

$$n_1 = \frac{e^{-(\alpha + \epsilon_1/hT)}}{1 - e^{-(\alpha + \epsilon_1/hT)}} = \frac{1}{e^{\alpha} e^{\epsilon_1/hT} - 1}$$

ditto n_2

$$n_B(E) = \frac{1}{e^\alpha e^{E/kT} - 1}$$

The Bose Einstein Distribution

book calls $e^\alpha = B_{BE}$

Fermions ...

same argumentation \rightarrow an inhibition factor

$$R_{1 \rightarrow 2}^F = (1 - n_2) R_{1 \rightarrow 2}^D$$

$$R_{2 \rightarrow 1}^F = (1 - n_1) R_{2 \rightarrow 1}^D$$

• same
•
•

$$n_F(E) = \frac{1}{e^\alpha e^{E/kT} + 1}$$

book calls $e^\alpha = B_{FD}$
see problem 9-21

Three Probability Distributions

$$F_{MB} = \frac{1}{A e^{E/kT}}$$

$$\frac{E/kT \gg 1}{\text{tiny}}$$

$$F_{BE} = \frac{1}{B e^{E/kT} - 1}$$

$$\rightarrow F_{MB}$$

$$F_{FD} = \frac{1}{C e^{E/kT} + 1}$$

$$\rightarrow F_{MB}$$

