Lecture 13

So far we've dealt with regime $n \ll n_Q$
Although we've incorporated some elements of quantum mechanics, we've also left out some important ones:

Quantum mechanics included so far

Maxwell-Boltzmann

- quantized energies / discrete states
  (exception: classical regime + equipartition, where $k_B T \gg \Delta E$ and we treat states as continuum)
- indistinguishability
  $$\therefore \quad Z_N = \frac{Z_1^N}{N!}$$
  For ideal gas $Z_1 = n_Q V$

What we've done so far is known as Maxwell-Boltzmann (MB) statistics, ignores issues that arise from:

- occupancy of states.
  2 cases:

Fermi-Dirac

Fermions – particles with ½-integer spin
(ex: e^-, p, n, ^3He ...)
Obey <u>Pauli exclusion principle</u> – no two fermions can occupy the same state

Ex: e^- in atomic orbitals

⋮

2s ↑↓ 2p ↑↓ ↑↓ ↑↓

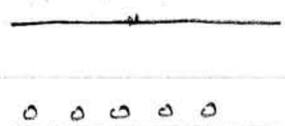
1s ↑↓

Pauli exclusion means that e^- fill up higher orbitals leads to different <u>elements</u>

Single particle state = "orbital"

Bose-Einstein

Bosons — particles with integer spin
(ex: photons, ^4He ...)
Arbitrary # of bosons can occupy one state



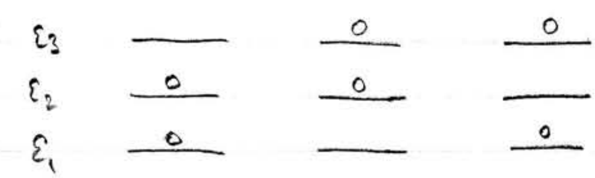
leads to different kinds of phenomena — Bose-Einstein condensation

Because of different properties, obey different statistics
Fermi-Dirac (FD) vs. Bose-Einstein (BE)

Maxwell-Boltzmann statistics counts states incorrectly because it does not account for these differences in state occupancy

Ex: Take simple example of 2 particles with 3 possible orbitals $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$. Find partition function:

For Fermions:



$e^{-\beta(\varepsilon_1+\varepsilon_2)}$ $\quad e^{-\beta(\varepsilon_2+\varepsilon_3)}$ $\quad e^{-\beta(\varepsilon_1+\varepsilon_3)}$

$$\therefore \quad Z_{FD} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_2+\varepsilon_3)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} \qquad (\underline{\text{correct}})$$

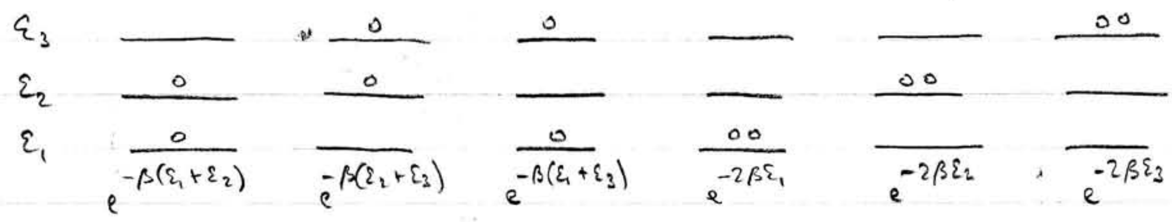
Compared to MB statistics:

$$Z_{MB} = \frac{1}{2!} Z_1^2 = \frac{1}{2}\left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3}\right)^2$$

$$= e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_2+\varepsilon_3)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + \frac{1}{2}\left(e^{-2\beta\varepsilon_1} + e^{-2\beta\varepsilon_2} + e^{-2\beta\varepsilon_3}\right) \qquad (\underline{\text{incorrect}})$$

MB overcounts multiple occupancy states, which are not allowed

For Bosons:



$$\therefore \quad Z_{BE} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_2+\varepsilon_2)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + e^{-2\beta\varepsilon_1} + e^{-2\beta\varepsilon_2} + e^{-2\beta\varepsilon_3}$$

(correct)

MB undercounts multiple occupancy states for Bosons

Notice that MB gets the correct terms for single occupancy states, but fails with multiple occupancy. MB works fine so long as probability for multiple occupancy is negligible

When does this happen? Let's find the average occupancy of a state i

$$p_i = \text{prob. to be in state } i = \frac{e^{-\beta\varepsilon_i}}{Z_1}$$

independent of state i

For N particles, the average occupancy is:

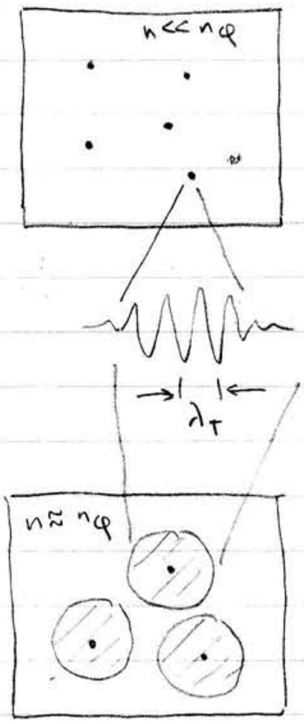
$$\langle n_i \rangle_{MB} = N p_i = \frac{N}{Z_1} e^{-\beta\varepsilon_i}$$

For ideal gas $Z_1 = n_Q V$

$$= \frac{N}{n_Q V} e^{-\beta\varepsilon_i} = \frac{n}{n_Q} e^{-\beta\varepsilon_i}$$

$\therefore$ For $n \ll n_Q$ $\quad \langle n_i \rangle_{MB} \ll 1$ so multiple occupancy is not an issue

So MB statistics work only when $n \ll n_Q$



Recall that $n_Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \frac{1}{\lambda_T^{\,3}}$

λ_T: Thermal deBroglie wavelength

Each particle is surrounded by volume λ_T^3. When particles are packed closer than this, wavefunctions begin to overlap and quantum effects are important. Must take into account occupancy

How do we treat FD and BE statistics generally? Think of a system of orbitals with energy ε_i

Total energy $E_{tot} = n_1 \varepsilon_1 + n_2 \varepsilon_2 + n_3 \varepsilon_3 + \cdots$

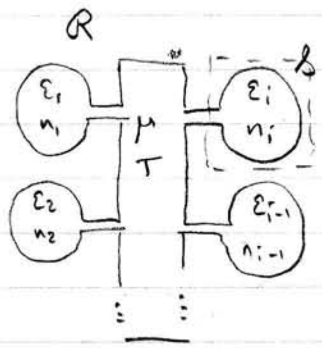
with n_i = occupancy of ith orbital
$= 0, 1$ for Fermion
$= 0, 1, 2 \cdots$ for Boson

$N = \sum_i n_i$ = total # of particles

Since the occupancy of each orbital can vary, a natural way to think about it is to use the grand canonical ensemble where the system $\mathcal{S}$ is the ith orbital

What is the reservoir $\mathcal{R}$?

$\mathcal{R}$ is simply all the other orbitals! They provide the reservoir of N particles that can occupy or not occupy the system $\mathcal{S}$



$\mathcal{S}$ is in thermal + diffusive equilibrium with $\mathcal{R}$, sets: μ, T.

The rest is easy:

For Fermions, write Gibbs sum for ith orbital:

$$\mathcal{Z}_i = e^{\beta(\mu\cdot 0 - \varepsilon_i\cdot 0)} + e^{\beta(\mu\cdot 1 - \varepsilon_i\cdot 1)}$$
$$= 1 + e^{\beta(\mu - \varepsilon_i)}$$

The average occupancy is:

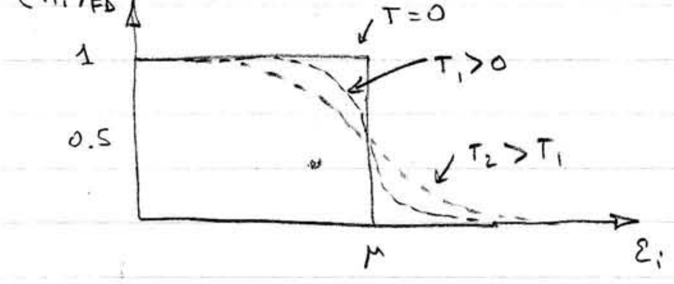
$$\langle n_i\rangle_{FD} = \frac{0\cdot 1 + 1\cdot e^{\beta(\mu-\varepsilon_i)}}{\mathcal{Z}_i}$$
$$= \frac{e^{\beta(\mu-\varepsilon_i)}}{1 + e^{\beta(\mu-\varepsilon_i)}}$$
$$= \frac{1}{e^{\beta(\varepsilon_i-\mu)} + 1}$$

(Could also use $\langle n_i\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z}_i$)

Chemical potential μ must satisfy constraint that

$$N = \langle N\rangle = \sum_i \langle n_i\rangle_{FD} = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1}$$

Assuming μ is fixed

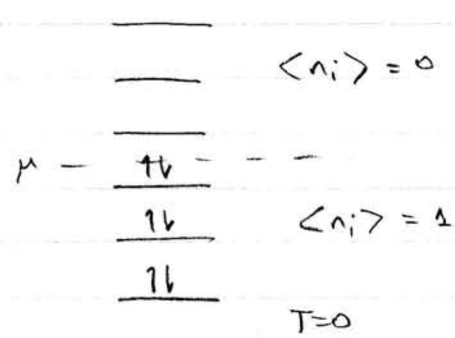


$0 \le \langle n_i \rangle_{FD} \le 1$ as expected

At $T=0$, $\langle n_i \rangle_{FD}$ is a step function $= 1 \quad \varepsilon_i < \mu$

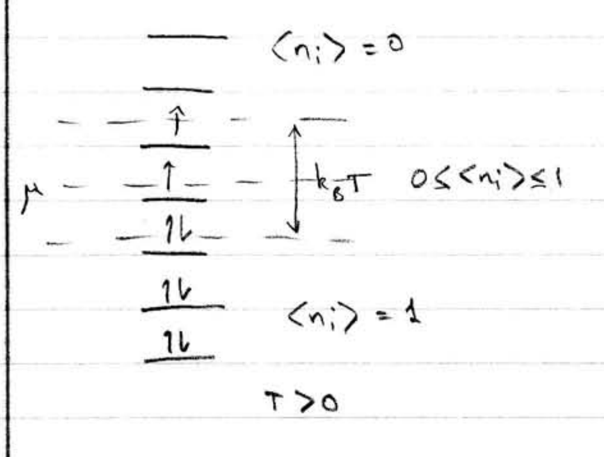
$= 0 \quad \varepsilon_i > \mu$

This makes sense. At $T=0$, fermions fill up orbitals like e^- in atom



once N particles are used up higher ε orbitals remain empty

$\therefore \mu(T=0) =$ energy of highest filled orbital for fermions



At $T > 0$, orbitals near μ (about $\sim k_B T$ of energy) can vary in occupancy some are occupied, some not.

Now look at Bosons

$$\mathcal{Z}_i = e^{\beta(\mu-\varepsilon_i)\cdot 0} + e^{\beta(\mu-\varepsilon_i)\cdot 1} + e^{\beta(\mu-\varepsilon_i)\cdot 2} + \cdots$$

$$= \sum_{n_i=0}^{\infty} e^{\beta(\mu-\varepsilon_i)n_i} = \frac{1}{1-e^{\beta(\mu-\varepsilon_i)}}$$

Note that this sum converges only if $\mu < \varepsilon_i$, true for all orbitals
$\therefore$ $\mu <$ smallest ε_i (ground state) for bosons

Now average occupancy

$$\langle n_i \rangle_{BE} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln \mathcal{Z}_i = \frac{e^{\beta(\mu-\varepsilon_i)}}{1-e^{\beta(\mu-\varepsilon_i)}}$$

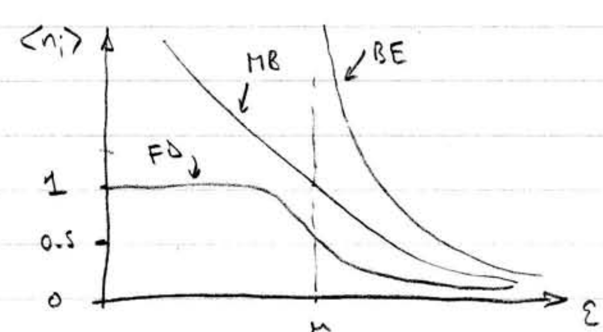
$$= \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$ can be arbitrarily large

Before plotting this, consider limit as $\varepsilon_i \gg \mu$

$$\langle n_i \rangle_{BE} \cong e^{-\beta(\varepsilon_i-\mu)} \cong \langle n_i \rangle_{FD}$$

Recall $\langle n_i \rangle_{MB} = \frac{n}{n_Q} e^{-\beta\varepsilon_i} = e^{-\beta(\varepsilon_i-\mu)}$ since $\mu = -k_B T \ln \frac{n}{n_Q}$

$\therefore$ $\langle n_i \rangle_{BE} = \langle n_i \rangle_{FD} = \langle n_i \rangle_{MB}$ for $\varepsilon_i \gg \mu$



All three statistics converge in that limit. Corresponds to high T or small $n \ll n_Q$ when $\mu \ll \varepsilon_i$

Summary

$$\mathcal{Z}_{i\,\substack{FD\\BE}} = \left(1 \pm e^{\beta(\mu-\varepsilon_i)}\right)^{\pm 1}$$

$$\langle n_i \rangle_{\substack{FD\\BE}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1}$$

$$N = \sum_i \langle n_i \rangle_{\substack{FD\\BE}} = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} \qquad \text{determines } \mu$$