Lecture 15 – Quantum Statistics

PREVIOUSLY: The ideal gas partition function (Lect. 5) introduces the quantum density

$$n_Q(T) = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \frac{1}{\lambda_T^{\,3}}$$

The thermal deBroglie wavelength λ_T is roughly the deBroglie wavelength of a particle with energy k_BT. n_Q corresponds to one particle in volume $\lambda_T^{\,3}$.

So far we've dealt with regime $n \ll n_Q$. When particles are packed close, $n \sim n_Q$, wavefunctions begin to overlap and quantum effects become important.

TODAY: Quantum statistics
Although we've included elements of QM, we've also left out some important ones

Quantum mechanics included so far:

Maxwell-Boltzmann

- Quantized energies / discrete states
  (although in classical regime, where $k_BT >> \Delta\varepsilon$, and we treat energy levels as a continuum)
- Indistinguishability

  Ex: $Z_N = \dfrac{Z_1^N}{N!}$, with $Z_1 = n_QV$ for an ideal gas

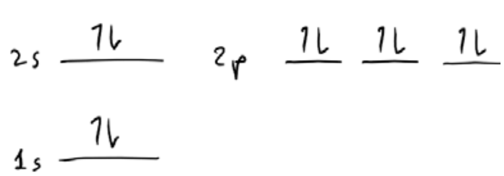
  What we've done so far is known as Maxwell-Boltzmann (MB) statistics – ignores issues that arise from multiple occupancy of states

Quantum mechanics not included – two types of particles:

Fermi-Dirac

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

  Ex: e^- in atomic orbitals:

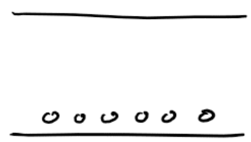


Pauli exclusion principle means that e^- fill up higher orbitals – leads to different elements

"orbital" = single-particle state or level

- Bosons – particles with integer spin (ex: photon, ^{4}He …)
  Arbitrary number of bosons can occupy one state

Bose-Einstein

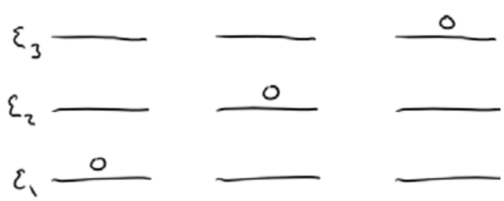


Leads to different kinds of phenomena – Bose-Einstein condensation

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

Maxwell-Boltzmann statistics count states incorrectly because they do not account for these differences in state occupancy

Ex: take simple example of system with 3 possible orbitals or energy levels $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$.
Consider 1 particle in this system:



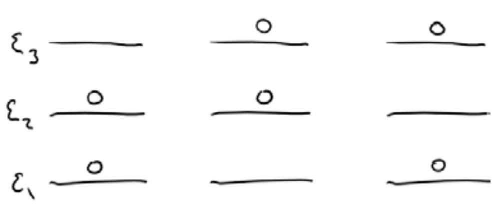
$e^{-\beta\varepsilon_1}$ $\quad$ $e^{-\beta\varepsilon_2}$ $\quad$ $e^{-\beta\varepsilon_3}$

$Z = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_1}$
and the answer is the same for fermions or bosons

Now consider 2 particles in this 3-orbital system:

Question 1: Write down the partition function for this system with 2 fermionic particles (assume both are spin up for simplicity, so we don't worry about spin degeneracy.)

Hint: use a diagram of energy levels



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

So, $Z_{FD} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_2+\varepsilon_3)} + e^{-\beta(\varepsilon_1+\varepsilon_3)}$ (correct)

Compare this result to what we would have written using MB statistics
The particles are independent so:

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

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

MB statistics overcount multiple occupancy states, which are not allowed for fermions

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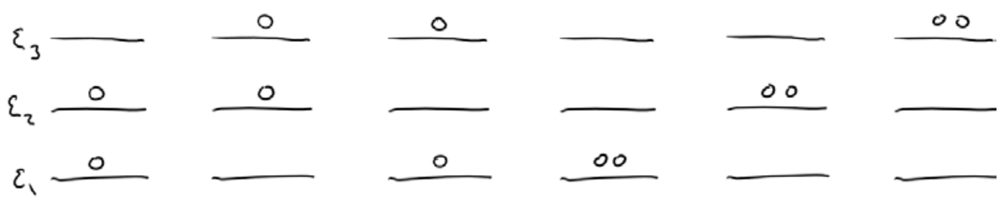
Question 2: Write down the partition function for this system with 2 bosonic particles.

Again use diagram:



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

So, $Z_{BE} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_2+\varepsilon_3)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + e^{-2\beta\varepsilon_1} + e^{-2\beta\varepsilon_2} + e^{-2\beta\varepsilon_3}$ (correct)

MB statistics undercount 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 the probability for multiple occupancy is negligible.

When does this happen? Let's find the average occupancy of a state *i* for an ideal gas:

$$\text{prob. for 1 particle to be in state } i = p_i = \frac{e^{-\beta\varepsilon_i}}{Z_1}$$

independent of the state *i*

For *N* particles, the average occupancy (i.e. the average # of particles in state *i*) is:

$$\langle N_i \rangle_{MB} = Np_i = \frac{N}{Z_1} e^{-\beta\varepsilon_i} = \frac{N}{n_Q V} e^{-\beta\varepsilon_i} = \frac{n}{n_Q} e^{-\beta\varepsilon_i}$$

For $n \ll n_Q$, $\langle N_i \rangle_{MB} \ll 1$, so multiple occupancy is not an issue.

KEY CONCEPT: Fermi-Dirac and Bose-Einstein distributions
How do we treat FD and BE statistics generally?
Think of a system of orbitals with energy ε_i

$$\text{Total energy } E_{tot} = N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 + \cdots = \sum_i N_i\varepsilon_i$$

$$\text{Total \# of particles } N = N_1 + N_2 + N_3 + \cdots = \sum_i N_i$$

with N_i = occupancy of ith orbital
= 0, 1 for fermion
= 0, 1, 2, 3 … N for boson

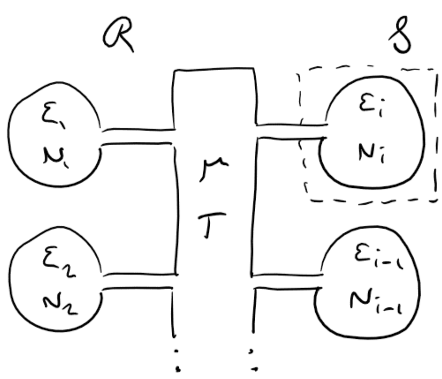
If it weren't for the constraint $N = \sum_i N_i$, the partition function could be easily evaluated the same way as before. For example if N_i = 0, 1, 2 … and does not have to sum up to a fixed number N, we get photon/phonon statistics:

$$Z = \sum_{N_1, N_2, N_3 \cdots} e^{-\beta(N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 \cdots)} = \left(\sum_{N_1=0}^{\infty} e^{-\beta N_1\varepsilon_1}\right)\left(\sum_{N_2=0}^{\infty} e^{-\beta N_2\varepsilon_2}\right)\left(\sum_{N_3=0}^{\infty} e^{-\beta N_3\varepsilon_3}\right)\cdots$$

$$= \left(\frac{1}{1-e^{-\beta\varepsilon_1}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_2}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_3}}\right)\cdots = \prod_i \frac{1}{1-e^{-\beta\varepsilon_i}}$$

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

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



$\mathfrak{S}$ is in thermal & diffusive equilibrium with $\mathfrak{R}$, sets μ and T

The rest is easy:

Question 3: Write down a) the Gibbs sum and b) the average occupancy for the *i*th orbital of a fermion system

a) Each orbital can be in one of two states, occupied or not occupied.
The Gibbs sum is exactly the same as for the Mb + O_2 system we studied in Lect. 12:

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

b) The average occupancy is:

$$\langle N_i \rangle_{FD} = \frac{e^{\beta(\mu-\varepsilon_i)}}{\mathcal{Z}_i} = \frac{e^{\beta(\mu-\varepsilon_i)}}{1+e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} \equiv f_{FD}(\varepsilon_i, T)$$

which is called the <u>Fermi-Dirac distribution</u>. (We could also have used $\langle N_i \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \mathcal{Z}_i$).

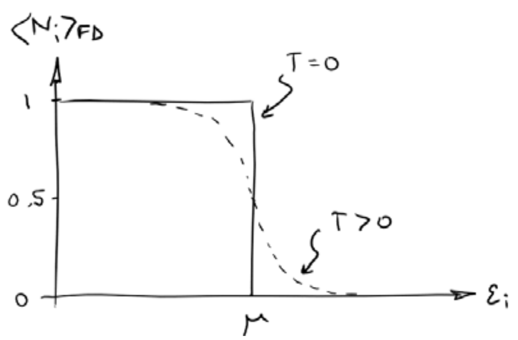
The chemical potential μ must satisfy the constraint that

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

The average energy is given by

$$U = \sum_i \langle N_i \rangle_{FD} \varepsilon_i = \sum_i \varepsilon_i f_{FD}(\varepsilon_i, T) = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i-\mu)}+1}$$

What does the Fermi-Dirac distribution look like?
Assuming μ is constant vs. temperature (Note: it's not)



As expected $0 \le f_{FD}(\varepsilon_i, T) \le 1$

At T = 0, $f_{FD}(\varepsilon_i, T)$ is a step function:

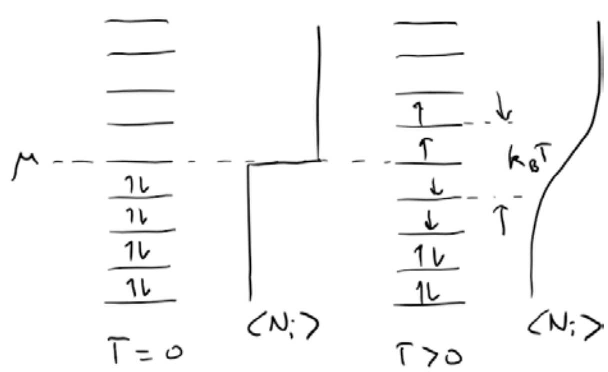
$$f_{FD}(\varepsilon_i, T=0) = \begin{cases} 0 & \text{for } \varepsilon_i > \mu \\ 1 & \text{for } \varepsilon_i < \mu \end{cases}$$

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

Once N particles are used up, higher ε orbitals remain empty

$\mu(T = 0)$ = energy of highest filled orbital for fermions – the <u>Fermi energy</u>

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



Now look at bosons:
The Gibbs sum for the ith orbital is

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

when N >> 1 (i.e. ~10^{20}), we can take the sum to ∞ to a very good approximation

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

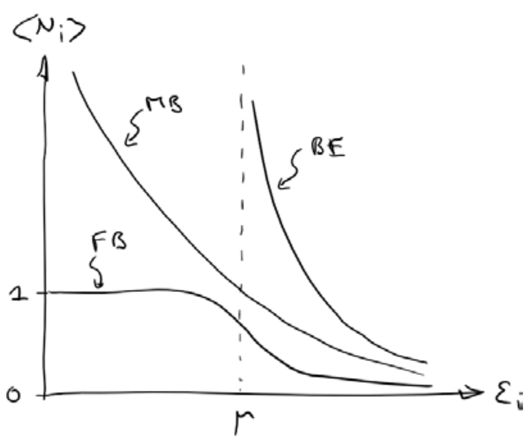
and the average occupancy is:

$$\langle N_i \rangle_{BE} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z}_i = \frac{e^{\beta(\mu-\varepsilon_i)}}{1-e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1} \equiv f_{BE}(\varepsilon_i, T)$$

which is called the Bose-Einstein distribution

> Note: compare this to what we derived for photons & phonons – the same expression, but with μ = 0. Photons & phonons are bosons and obey Bose-Einstein statistics. However, their number is not conserved, so μ = 0.

$\langle N_i \rangle_{BE}$ can be arbitrarily large but finite, so long as $\mu < \varepsilon_i$ for all orbitals, i.e. $\mu <$ smallest orbital energy ε_0 (ground state).



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

$$f_{BE}(\varepsilon_i, T) \approx e^{-\beta(\varepsilon_i-\mu)} \approx f_{FD}(\varepsilon_i, T)$$

Recall that under Maxwell-Boltzmann statistics

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

So, all three statistics converge in the limit $\varepsilon_i \gg \mu$

Corresponds to high-T or small $n << n_Q$ limit when $\varepsilon_i \gg \mu$

In summary:

$$\mathcal{Z}_{i\,FD/BE} = \left(1 \pm e^{\beta(\mu-\varepsilon_i)}\right)^{\mp 1} \qquad f_{FD/BE}(\varepsilon_i, T) = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} \quad N = \langle N \rangle = \sum_i f_{FD/BE}(\varepsilon_i, T) = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1}$$