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- Poll class: when to have recitations next week?
- Large Hadron Collider talk

Key points from last lecture

$$P_s[E_s, N_s] = \frac{e^{-\beta[E_s - \mu N_s]}}{\Xi} \quad \Xi = \sum_s e^{-\beta[E_s - \mu N_s]}$$

$$\langle N \rangle = \frac{kT \partial \ln \Xi}{\partial \mu}, \quad \langle E \rangle = \mu kT \frac{\partial \ln \Xi}{\partial \mu} - \frac{\partial \ln \Xi}{\partial \beta}$$

$$\Phi = \text{grand potential} = F - \mu N = U - TS - \mu N$$

$$= -kT \ln \Xi$$

$$d\Phi = -SdT - PdV - Nd\mu \Rightarrow S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V, \mu}, \quad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu}$$

↑↑ in both extensive

Examps: hemoglobin

o/faction

surface adsorption, Langmuir isotherm

↳ stories about Irving Langmuir

Section 7.2: apply Gibbs factor to study dense quantum ideal gases consisting of identical weakly interacting particles (electrons, photons, etc)

For classical ideal gas, could apply approximation

$$Z_N \approx \frac{1}{N!} Z_1^N$$

This holds when there are many energy levels and few particles so unlikely for two particles to have same energy. But  $Z_1$  has physical meaning of the total number of states whose energies are within distance  $kT$  of the ground state. If system has  $N$  particles then inequality

$$Z_1 \lesssim N$$

implies we can't use Chapter 6 result that  ~~$Z_N \approx \frac{1}{N!} Z_1^N$~~   $Z_N \approx \frac{1}{N!} Z_1^N$ .

Since for ideal gas

$$Z_1 = \frac{V}{V_Q} Z_{int} \lesssim N$$

$$V_Q = \left( \frac{h}{\sqrt{2\pi m k T}} \right)^3$$

we conclude that new approach is needed when

- low temperature  $T$ , then  $V_Q$  is big,  $Z_1$  small
- low mass like electrons, neutrinos,  $V_Q$  large,  $Z_1$  small
- large densities, so  $\frac{N}{V} \gg \frac{Z_{int}}{V_Q}$
- some combination of above

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Strategy for dealing with dense or cold quantum ideal gases is to observe that "weakly interacting" for quantum system means each particle has its own quantum state and energy, independent of ~~presence~~<sup>presence</sup> of other particles. So total energy of system will be sum of individual energies

$$E = n_1 E_1 + n_2 E_2 + \dots + n_k E_k = \sum_k n_k E_k$$

where  $E_1, E_2, \dots$  are energy levels of single particle.

For point particle in 1d box with impenetrable sidewalls

$$E_n = \frac{\hbar^2 n^2}{8mL^2}, \quad n \gg 1$$

conjugated molecules  
approximate  
1d box well



where  $m$  = mass of particle,  $L$  = length of box

At finite temperature, collisions, vibrations, interactions cause given particle to transition from one energy level to another, the numbers  $n_1, n_2, \dots$  are changing over time. We conclude that

$$\langle E \rangle = \sum_k \langle n_k \rangle E_k$$

average  $\langle n_k \rangle$  number of particles with energy  $E_k$  is called the "occupation number" of energy  $E_k$ , varies with temperature and external parameters like  $B, \vec{g}, m$ .

Strategy: use Gibbs factor to calculate the  $\langle n_k \rangle$

$$\text{use } C = \frac{d\langle E \rangle}{dT}, \quad S = \int_0^T \frac{C(T)}{T} dT, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S, N}$$

to compute thermodynamic properties of system

Calculation of occupation number  $\langle n_k \rangle$  depends on whether quantum particle is boson or fermion

boson: named after Satyendra Bose (1894-1974) are particles such that arbitrarily many identical particles can be in same state of energy (gregarious)

examples: photons, pions, phonons (quantized sound waves),  $He^4$  nucleus,  $He^4$  atom, gluons, Higgs particle

fermion: named after Enrico Fermi, particles such that at most one can be in any energy state (loners)

examples: electrons, protons, neutrons, neutrinos,  $He^3$  nucleus, quarks

large classical particles do not satisfy either constraint, can't treat as single non-interacting particle

exception: for particles in 2D systems, like 2D gas of electrons trapped between two semiconductor layers, can get other properties, get behavior called "anyons"

and of course there are macroscopic particles called "monons" but these are dangerous to work with.

# How to identify type of particle, boson or fermion?

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All quantum particles, even composite ones, have intrinsic angular momentum called spin. (Doesn't make sense classically, how can point electron have finite angular momentum, nothing inside to rotate and  $\vec{L} = m\vec{v} \times \vec{r}$ .) Comes in multiples of  $\frac{\hbar}{2}$

$$\hbar \approx 1.05 \cdot 10^{-34} \frac{\text{m}^2 \text{kg}}{\text{s}}$$

tiny!

Powerful spin-statistics theorem of quantum field theory, which combines special relativity with quantum mechanics, deduces that:

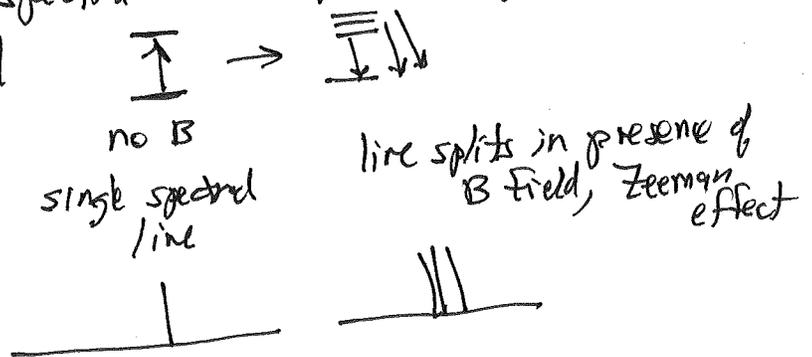
fermions have <sup>spin with</sup> odd multiple of  $\frac{\hbar}{2}$ :  $\frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$

bosons have spin with even multiple of  $\frac{\hbar}{2}$ :  $0, \frac{\hbar}{2}, 2\frac{\hbar}{2}, 3\frac{\hbar}{2}, \dots$

Experiments confirm the spin-statistics theorem.

Can measure spin itself in two ways:

- by spectroscopy, look at spectral lines in presence of external electric or magnetic field

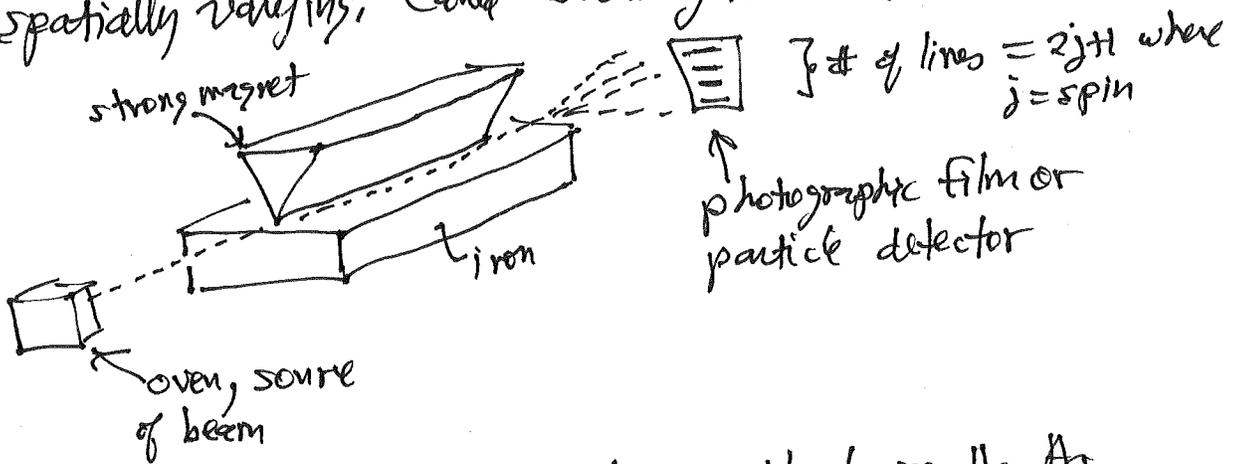


can use this trick in reverse, can measure strength of remote magnetic field, say on surface of star or in galaxy

# Identifying bosons, fermions cont'd

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Second way to identify spin is by creating beam of particles and sending beam through inhomogeneous magnetic field, spatially varying. Called Stern-Gerlach expt



Story of how Stern but not Gerlach was able to see the Ag lines the first time, ...

Inhomogeneous B field is found to split beam physically into distinct spots, proof of quantum energies since classically get continuous smear. Number of spots =  $2j+1$  where  $j = \text{spin}$   
 E.g. Ag atom is spin  $\frac{1}{2}$  particle so found  $2(\frac{1}{2})+1 = 2$  spots

Composite particles  
 rules of adding angular momentum lead to

$\text{boson} + \text{boson} = \text{boson}$        $\text{He}^4 - \text{He}^4$   
 $\text{boson} + \text{fermion} = \text{fermion}$   
 $\text{fermion} + \text{fermion} = \text{fermion or boson}$

proton = uud      neutron = udd

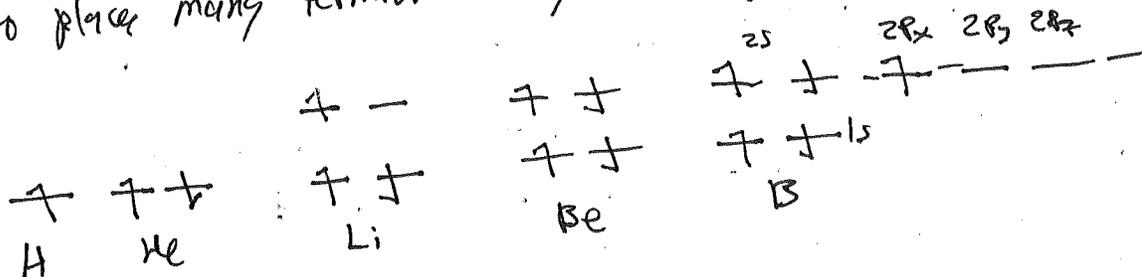
odd # of fermions requires p, n to be fermions

$e + e \rightarrow$  Cooper pair, boson in cold metal  $\Rightarrow$  superconductivity

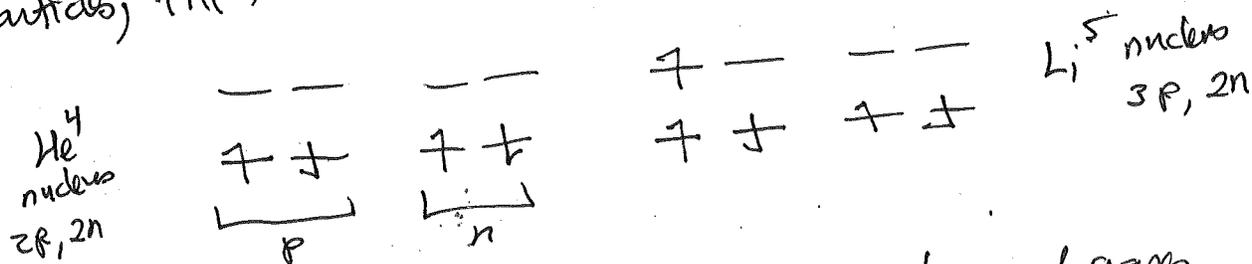
# Aufbau principle for fermions

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Because at most 1 fermion can occupy given energy state  
have to place many fermions in higher and higher energy states



Holds for nuclei also except protons and neutrons, as distinguishable particles, fill their own energy levels separately (shell model of nucleus)



closed shell nuclei particularly stable, analogous to noble gases  
He, Ne, Xe, etc.

Example of how fermions and bosons occupy multiple energy states, Problem 7.8, p. 265 of Schroeder

Consider artificial example of quantum system with single energy level  $E=0$  that is 10-fold degenerate



} 10 distinct states, same energy, like 3s, 3p, 3d energy level of H

(1) What is partition  $f^N Z_1$  if only one particle?  
 $Z_1 = d_1 e^{-\beta E_1} = d_1 = \Omega = \binom{10}{1} = 10$

(2) What is  $Z_1$  for 2 distinguishable particles?  
 $Z_1 =$  "ten ways to choose 1st level"  $\times$  "ten ways to choose 2nd level"  
 $= 10 \times 10 = 100$

(3)  $Z_1$  for two identical bosons?  
 $Z_1 = \binom{10}{2} + \binom{10}{1} = \frac{10 \cdot 9}{1 \cdot 2} + 10 = 55$

# of ways I can put two identical particles in distinct levels = # ways to choose two distinct states

# of ways I can put 2 particles in same level, i.e., A level

(4)  $Z_1$  for two identical fermions?  
 $Z_1 = \binom{10}{2} = 45$

two fermions can't be in same state so have to go into distinct states

Problem 7.8 continued: 10-fold degenerate level

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(5) What is  $\frac{1}{N!} Z_1^N$  for  $N=2$  distinguishable particles?

$$Z_2 = \frac{1}{2!} Z_1^2 = \frac{1}{2} \cdot 100 = 50$$

$\neq 45$

$\neq 55$

notice how  
answer is  
midway between  
fermions, bosons

(6) What is probability to find both particles in same state?

Fermions: 0

bosons:  $\frac{\binom{10}{1}}{55} = 18\%$

distinguishable particles:  $\frac{10}{100} = 10\%$

bosons "crowd together", more likely to be found in same state.

# Occupation number $\langle n_k \rangle$ for fermions

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Since at finite temperature, number of particles in quantum gas  $n_k$  that have given energy  $\epsilon_k$  fluctuates, could make rather crazy guess that, maybe, we could treat single energy state as an actual physical system, like hemoglobin, that can pick up or lose particles as if in equilibrium with reservoir at constant temp. T. This remarkably leads to ~~correct~~ <sup>correct</sup> answer, detailed justification is too hard for this course.

So for single energy level  $\epsilon$ , we can form little table to prepare for applying Gibbs factor:

$\frac{n_s}{0}$	$\frac{\epsilon_s}{0}$	$\frac{d_s}{1}$	} energy level has only <del>two</del> two possible states like paramagnet
$1$	$\epsilon$	$1$	

$$Z = e^{-\beta[0-\mu \cdot 0]} + e^{-\beta[\epsilon-\mu \cdot 1]} = 1 + e^{-\beta(\epsilon-\mu)}$$

$$\bar{n}(\epsilon) = \langle n(\epsilon) \rangle = 0 \cdot P_0 + 1 \cdot P_1 = 1 \cdot \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}}$$

or 
$$\bar{n}_{FD}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

or apply  $\langle n \rangle = kT \frac{\partial \ln Z}{\partial \mu}$

FD = "Fermi-Dirac statistics", named after two scientists who proposed this independently

# Fermion occupation number, continued

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There is a normalization condition for the occupation numbers:  
if system has total of  $N$  particles and particles are indestructible  
(not true for relativistic particles), then all particles have to  
be present at all times, i.e.

$$\sum_{\epsilon} \bar{n}(\epsilon) = \sum_{\epsilon} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = N$$

For given temperature  $T$ , given # of particles  $N$ , can solve (at  
least in principle) for chemical potential  $\mu = \mu(T, N)$ .

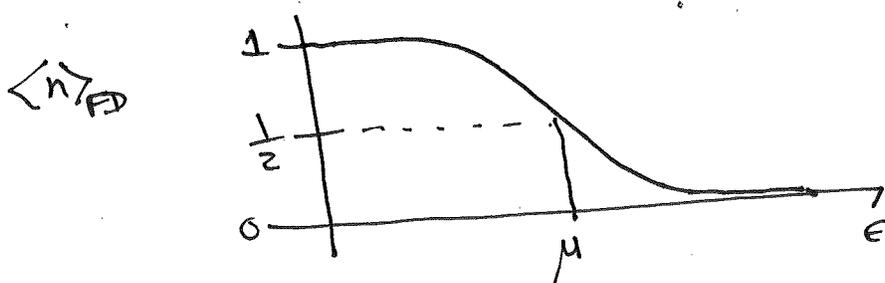
## Properties of $\bar{n}_{FD}(\epsilon)$ :

for fixed  $T$ ,  $\epsilon \gg \mu \Rightarrow \bar{n}_{FD}(\epsilon) \approx e^{-\beta(\epsilon-\mu)}$  exponential decay as  $\epsilon$  of  $\epsilon$

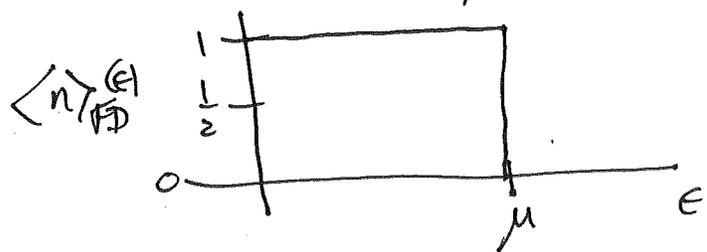
$$\epsilon = \mu \Rightarrow \bar{n}_{FD}(\epsilon) = \frac{1}{2}$$

$$\epsilon \ll \mu \Rightarrow \bar{n}_{FD}(\epsilon) \approx 1$$

$$e^{-\beta(\epsilon-\mu)} = \frac{1}{e^{\beta(\mu-\epsilon)}} \approx 0$$



curve for finite temperature  
few levels occupied for  $\epsilon > \mu$



$T=0$ , all ~~particle~~ levels  
occupied up to  $\epsilon = \mu$

Reason:  $T \rightarrow 0, \beta \rightarrow \infty$  so  
 $e^{\beta(\epsilon-\mu)} = \infty \quad \epsilon > \mu$   
 $= 0 \quad \epsilon < \mu$

# Occupation number $\bar{n}_{BE}(\epsilon)$ for bosons

Let's repeat argument: treat single energy level  $\epsilon$  as physical system in equil. with reservoir with temp  $T$ , chem. pot  $\mu$ . Possible states are now:

$n_s$	$\epsilon_s$	$d_s$
0	0	1
1	$\epsilon$	1
2	$2\epsilon$	1
$\vdots$	$\vdots$	$\vdots$

} infinitely many states possible,  $\sim N^{10^{23}}$  for macroscopic system

$$Z = e^{-\beta(0-\mu \cdot 0)} + e^{-\beta(\epsilon-\mu \cdot 1)} + e^{-\beta(2\epsilon-\mu \cdot 2)} + \dots$$

$$= 1 + x + x^2 + \dots$$

$$x = e^{-\beta(\epsilon-\mu)}$$

$$|x| < 1 \Leftrightarrow \epsilon > \mu \text{ for all } \epsilon$$

$$Z = \frac{1}{1-x} = \frac{1}{1-e^{-\beta(\epsilon-\mu)}}$$

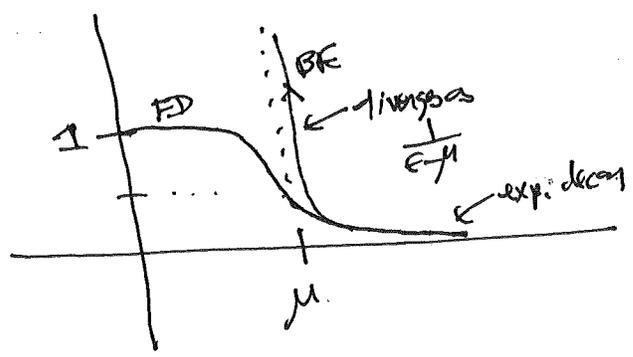
$$\bar{n}_{BE}(\epsilon) = \frac{hT}{2\pi} \frac{2\ln Z}{2\mu} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

same form as Fermi-Dirac case but minus sign in denominator makes huge difference in physics

for fixed  $T$ , fixed  $\beta$ , if  $\epsilon \gg \mu$ ,  $\bar{n}_{BE}(\epsilon) \approx e^{-\beta(\epsilon-\mu)}$  exp. decay just like FD case  
 $\epsilon \rightarrow \mu^+$ ,  $\bar{n}_{BE}(\epsilon) \rightarrow \infty$

$$e^{\beta(\epsilon-\mu)} \approx 1 + \beta(\epsilon-\mu) \quad \epsilon \approx \mu^+$$

$$\frac{1}{e^{\beta(\epsilon-\mu)} - 1} \approx \frac{1}{\beta(\epsilon-\mu)}$$



Again have normalization condition for  $\bar{n}_{BE}(\epsilon)$

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finite-mass indistinguishable particles:  $N = \sum_s \frac{1}{e^{\beta(E_s - \mu)} - 1}$   
particle number variable,  $\mu = 0$  determines  $\mu$

Boltzmann occupation number,  $\bar{n}_{Bolt}(\epsilon)$ , for classical particles:

$$\text{prob}(E = E_j) = \frac{e^{-\beta E_j}}{Z_1}$$

$$\bar{n}(\epsilon) = N \cdot \text{prob}(E = E_j) = \frac{N}{Z_1} e^{-\beta E_j}$$

But  $F = -kT \ln Z_N$ ,  $Z_N = \frac{1}{N!} Z_1^N$   
 $= -kT (N \ln Z_1 - N \ln N + N)$

$$\mu = \frac{\partial F}{\partial N} = -kT \ln \left( \frac{Z_1}{N} \right) \Rightarrow \frac{N}{Z_1} = e^{\mu/\beta}$$

$\bar{n}_{Bolt}(\epsilon) = e^{-\beta(E - \mu)}$ , same ~~as~~ <sup>as</sup> BE, ~~as~~ <sup>as</sup> FD

