

Thermal Physics

PHYS/BMME 441

Gökçe Başar

Lectures 21 - 24

When & Where: Mon. / Wed. 8:45- 10:00 AM, Phillips 247

Textbook: *An Introduction to Thermal Physics*, Daniel V. Schroeder

Website: sakai.unc.edu

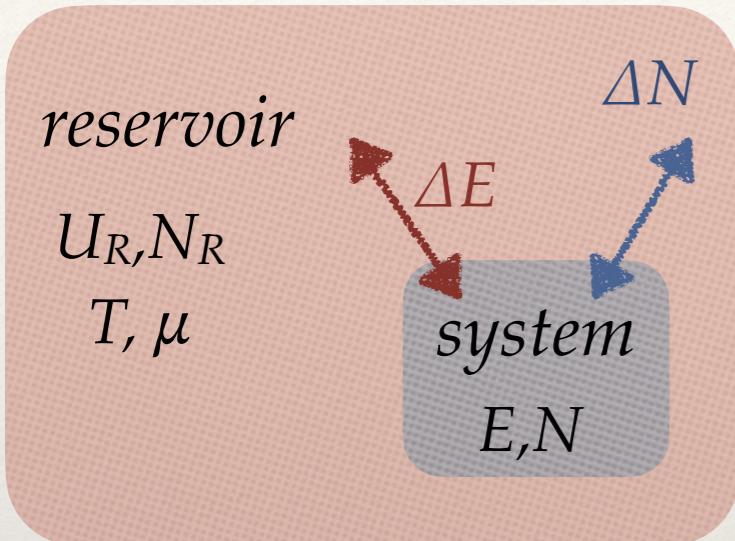
Outlook for the next few weeks

Chapter 7: Quantum Statistics (chapters 7.1 to 7.6)

read chapters:

- 7.1 Gibbs Factor
- 7.2 Bosons and Fermions
- 7.3 Degenerate Fermi Gas
- 7.4 Blackbody Radiation
- 7.5 Debye Theory of Solids
- 7.6 Bose-Einstein Condensation

The Gibbs Factor



So far we have kept the number of particles fixed.

Now we let the system exchange *energy and particles* with the reservoir.

Probability of the system
being in state state s_2 (s_1)

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

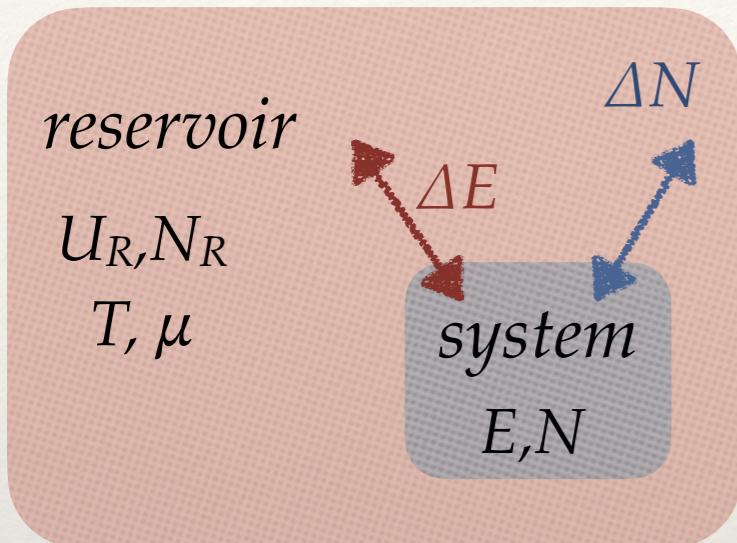
Multiplicity of the microstates of the
reservoir such that the *system* is in
state s_2 (s_1)

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = e^{[S_R(s_2) - S_R(s_1)]/k} = \frac{e^{-\beta(E_2 - \mu N_2)}}{e^{-\beta(E_1 - \mu N_1)}}$$

$$dS_R = \frac{1}{T} (dU_R + pdV_R - \mu dN_R) = \frac{1}{T} \left(-(E_2 - E_1) - \mu(-(N_2 - N_1)) \right)$$

negligible

The Gibbs Factor



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``Grand
Canonical Ensemble''

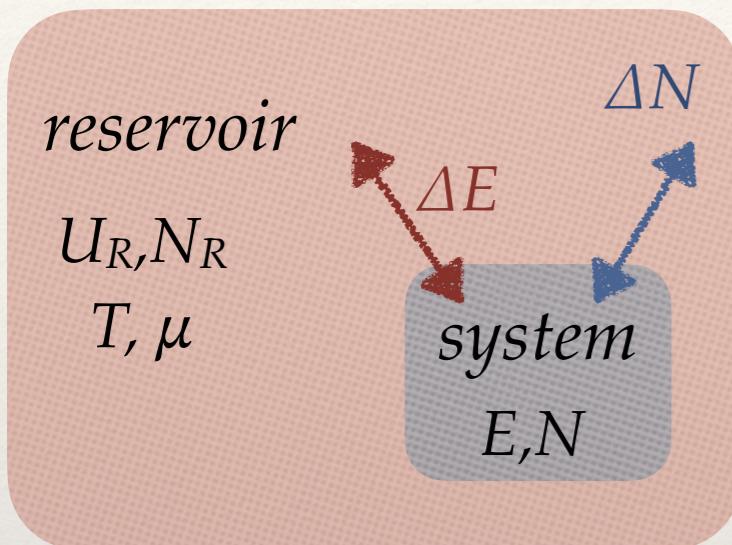
$$P(E, N) = \frac{1}{\mathcal{Z}} e^{-\beta(E - \mu N)} \quad \text{“Gibbs factor”}$$

“Grand partition function”

$$\mathcal{Z}(T, \mu) = \sum_{s: \text{states of the system}} e^{-\beta(E_s - \mu N_s)} \quad \beta = \frac{1}{kT}$$

recall: Boltzmann factor = $\frac{1}{Z} e^{-\beta E}$

The Gibbs Factor



``Grand
Canonical Ensemble''

So far we have kept the number of particles fixed.

Now we let the system exchange *energy and particles* with the reservoir.

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = e^{[S_R(s_2) - S_R(s_1)]/k} = \frac{e^{-\beta(E_2 - \mu N_2)}}{e^{-\beta(E_1 - \mu N_1)}}$$

$$P(E, N) = \frac{1}{\mathcal{Z}} e^{-\beta(E - \mu N)} \quad \text{"Gibbs factor"}$$

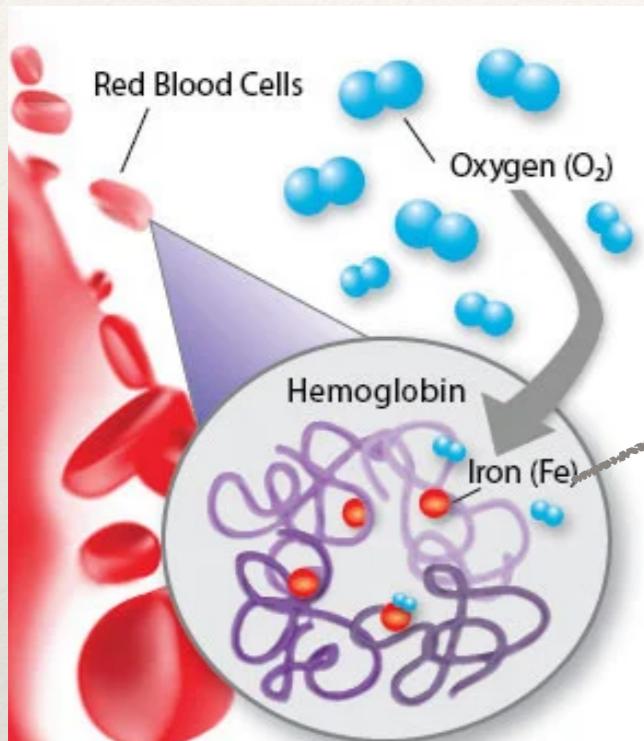
$$\mathcal{Z}(T, \mu) = \sum_{s: \text{states}} e^{-\beta(E_s - \mu N_s)} \quad \text{"Grand partition function"}$$

$$\beta = \frac{1}{kT}$$

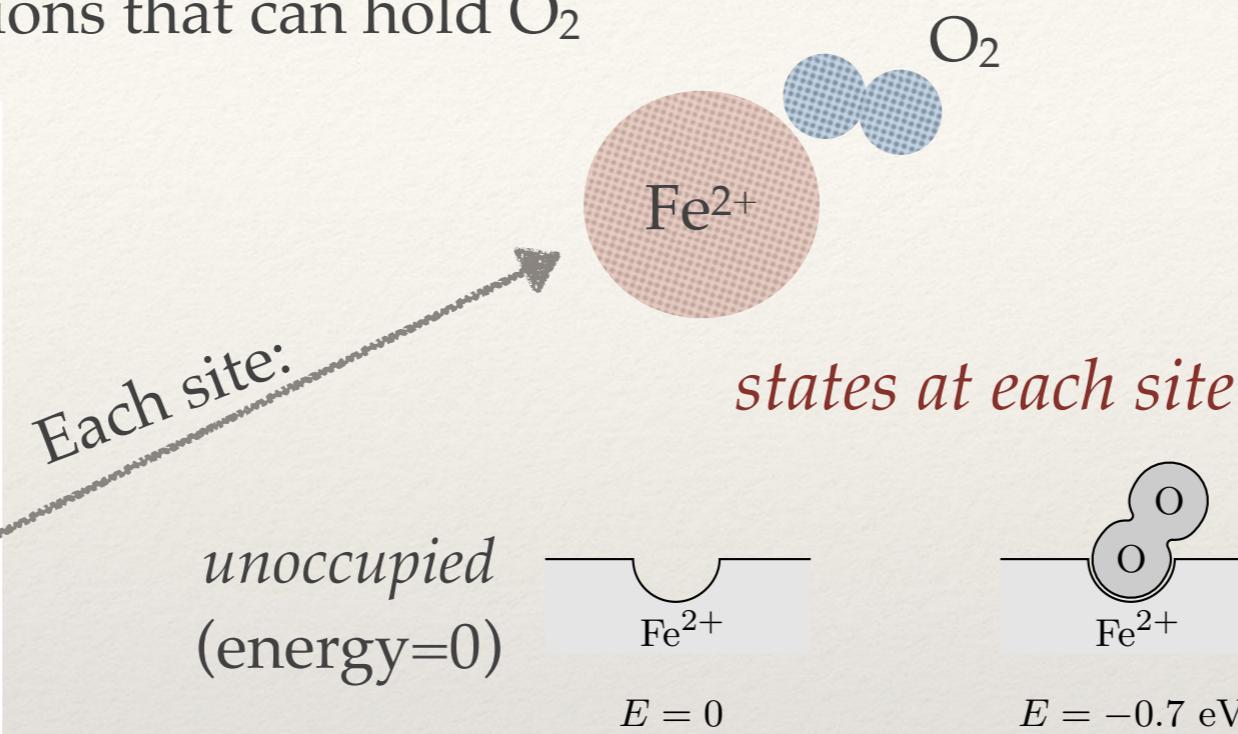
$$\text{recall: Boltzmann factor} = \frac{1}{Z} e^{-\beta E}$$

Classroom Exercise: CO poisoning

4 sites that has Fe^{2+} ions that can hold O_2



[source: MedicineNet]



$$\mu = -kT \log \left(\frac{NZ_{\text{int}}}{Vv_Q} \right)$$

(near the lungs where blood and air are in diffusive equilibrium)

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT}$$

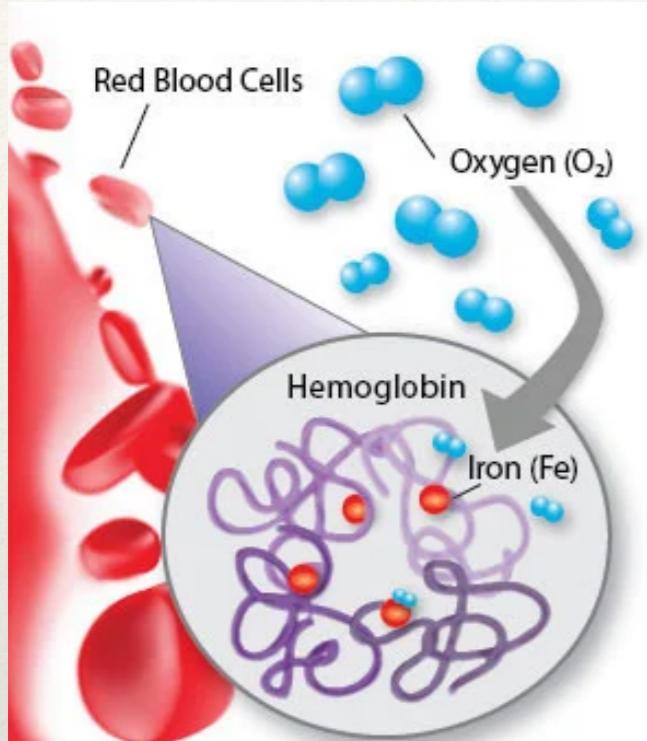
$$\mu_{\text{O}_2} \approx -0.6\text{ eV}$$

$$T_{\text{body}} = 310K, \quad p_{\text{O}_2} = 0.2\text{atm}$$

$$\text{Gibbs factor} = 1 + e^{-(\epsilon - \mu)/kT} \approx 40$$

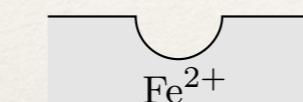
$$P(\text{occupied by } \text{O}_2) = \frac{40}{1 + 40} \approx 98\%$$

Classroom Exercise: CO poisoning



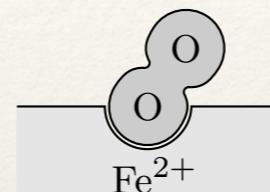
[source: MedicineNet]

when there is CO present



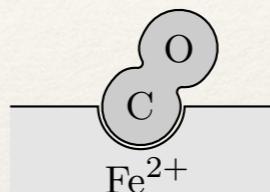
$$E = 0$$

$$\mu_{O_2} \approx -0.6 \text{ eV}$$



$$E = -0.7 \text{ eV}$$

Assume CO is x100
less abundant than O_2



$$E = -0.85 \text{ eV}$$

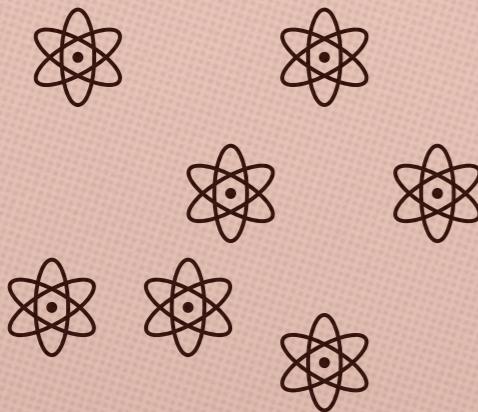


$$kT \log 100 = 0.12 \text{ eV}$$

$$\mu_{CO} \approx -0.72 \text{ eV}$$

What is the probability of the site occupied by O_2 ?

Bosons and Fermions



Recall: N identical, non-interacting particles

$$Z = \frac{1}{N!} Z_1^N$$

Z_1 : single particle
partition function

$N!$: number of ways interchanging particles among different states.

However this is correct only every particle is in a *different* state
(i.e. no state is occupied by more than one particle)

This assumption is fairly accurate at high temperatures $e^{-E_i/kT} \lesssim 1$

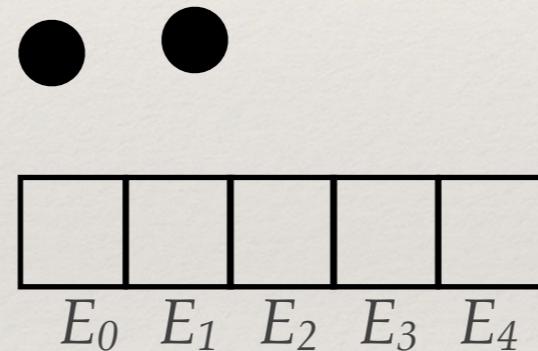
but not as much at low temperatures $e^{-E_0/kT} \ll e^{-E_1/kT} \ll e^{-E_2/kT} \dots$

where most of the particles tend to occupy lowest lying states

Classroom Exercise

$N!$: number of ways interchanging particles among different states
only when all the particles occupy different states

e.g. two particles, five different states



$$E_0 = E_1 = E_2 = E_3 = E_4 = 0$$

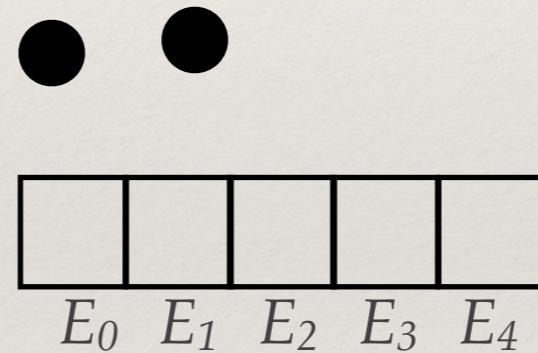
What is the number of arrangements if the particles are distinguishable?

What is the number of arrangements if the particles are indistinguishable?

Classroom Exercise

$N!$: number of ways interchanging particles among different states
only when all the particles occupy different states

e.g. two particles, five different states



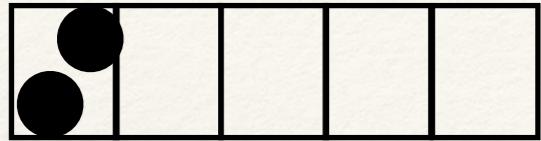
$$E_0=E_1=E_2=E_3=E_4=0$$
$$Z_1=1+1+1+1+1=5$$

What is the number of arrangements if the particles are distinguishable? $Z = 5 \times 5 = 25$

What is the number of arrangements if the particles are indistinguishable?

$$Z = \frac{1}{2!} 5 \times 5 = 12.5???$$

Bosons and Fermions



Can two identical particles occupy the same state?

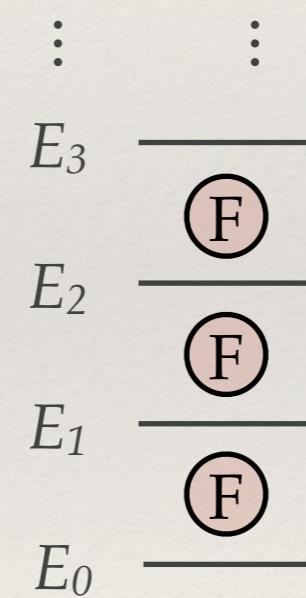
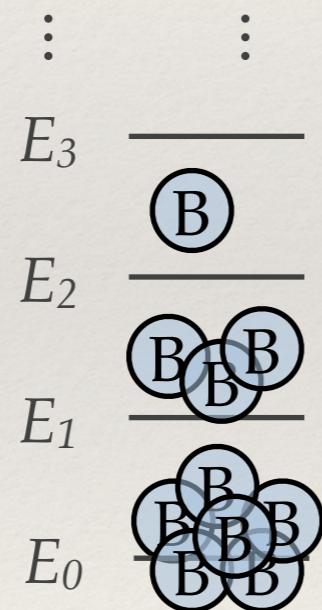
There are two types of particles...

Those who can occupy the same state: ``*bosons*''

(e.g. photons, W bosons, Higgs, pions, ${}^4\text{He}$,...)

and those who cannot: ``*fermions*''

(e.g. protons, neutrons, electrons, ${}^3\text{He}$,...)

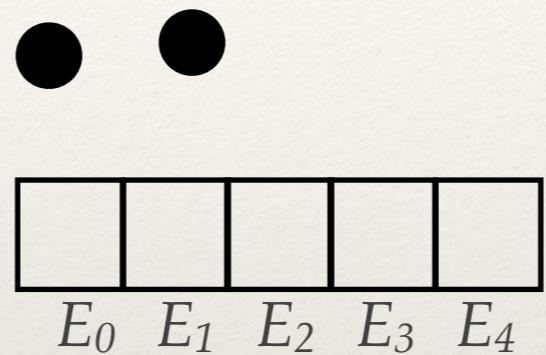


Any number of identical bosons
can occupy the same state

No two identical fermions
can occupy the same state
Pauli exclusion principle

Classroom Exercise

e.g. two particles, five different states



$$E_0 = E_1 = E_2 = E_3 = E_4 = 0$$

What is the partition function for if the two particles are bosons?

What is the partition function for if the two particles are fermions?

Quantum Gases

The assumption that each state is occupied by at most one particle is accurate when
Number of available states >> number of particles (i.e. $Z_1 \gg N$)

$$Z_1 = \frac{VZ_{\text{int}}}{v_Q} \gg N \Rightarrow \frac{V}{N} \gg v_Q = \lambda_{dB}^3 = \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2}$$

density = $\frac{N}{V}$

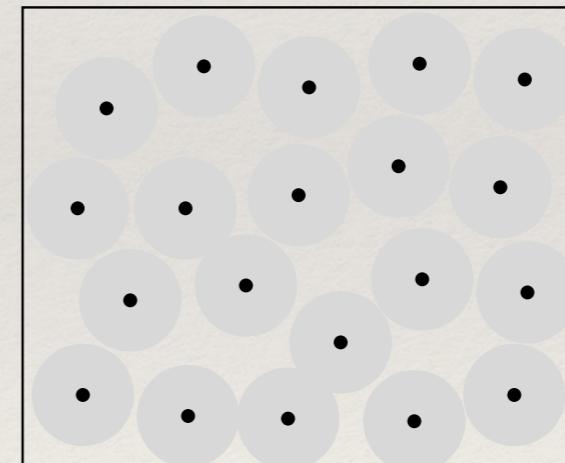
volume per particle >> typical size of the wave-function

low density
high temperature



Normal gas, $V/N \gg v_Q$

Wave-functions do not overlap



Quantum gas, $V/N \approx v_Q$

Wave-functions overlap

high density
low temperature

Distribution Functions

Let's focus on a given single-particle state with energy ε : ``system''

configuration:



energy of the system:

$$0 \quad \varepsilon$$

Gibbs factor:

$$1 \quad e^{-\beta(\varepsilon-\mu)}$$

configuration:



energy of the system:

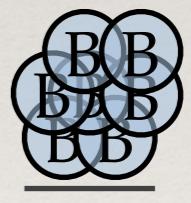
$$0 \quad \varepsilon$$

Gibbs factor:

$$1 \quad e^{-\beta(2\varepsilon-2\mu)}$$



...



...

$$2\varepsilon$$

$$3\varepsilon$$

...

$$n\varepsilon$$

...

$$e^{-\beta(3\varepsilon-3\mu)}$$

$$e^{-\beta(n\varepsilon-n\mu)}$$

Distribution Functions

Let's focus on a given single-particle state with energy ε : ``system''

configuration:

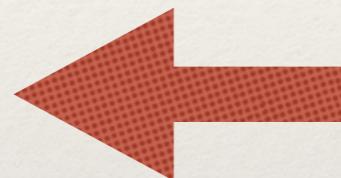
$$\underline{\hspace{1cm}} \quad \textcircled{F}$$

energy of the system:

$$0 \quad \varepsilon$$

Gibbs factor:

$$1 \quad e^{-\beta(\varepsilon-\mu)}$$



Let's start with fermions

configuration:

$$\underline{\hspace{1cm}} \quad \textcircled{B}$$

energy of the system:

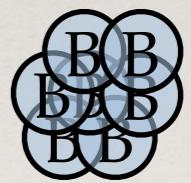
$$0 \quad \varepsilon$$

Gibbs factor:

$$1 \quad e^{-\beta(\varepsilon-\mu)}$$



...



...

$$2\varepsilon$$

$$3\varepsilon$$

...

$$n\varepsilon$$

...

$$e^{-\beta(2\varepsilon-2\mu)}$$

$$e^{-\beta(3\varepsilon-3\mu)}$$

$$e^{-\beta(n\varepsilon-n\mu)}$$

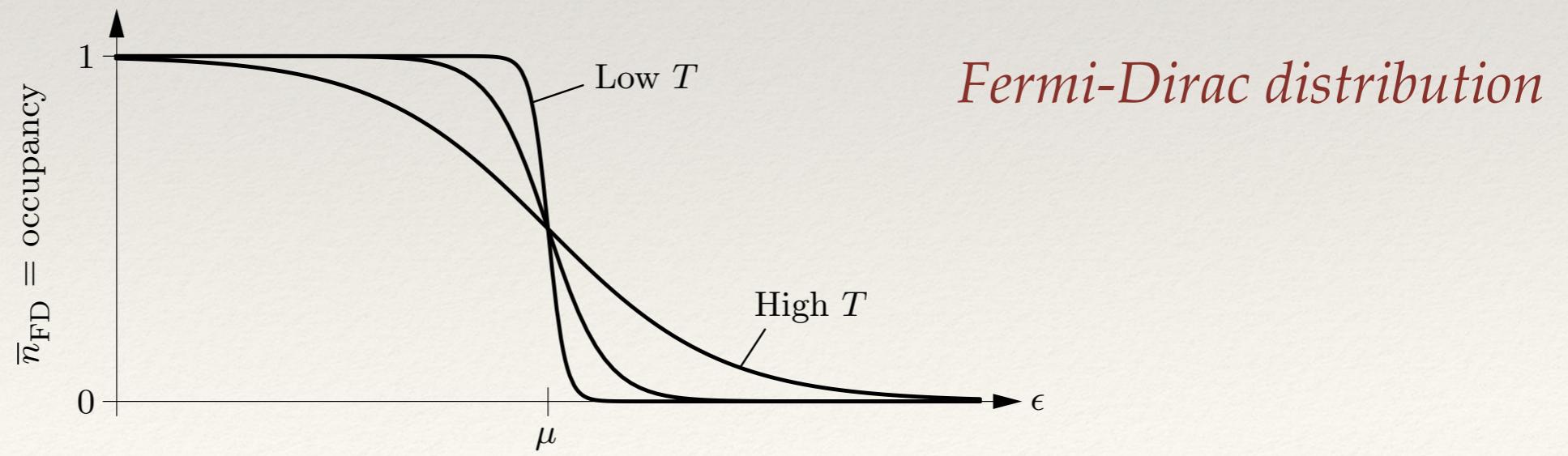
Distribution Functions: Fermions

configuration:	—	\textcircled{F}	Partition function:
energy of the system:	0	ϵ	$\mathcal{Z}_F = 1 + e^{-\beta(\epsilon - \mu)}$
Gibbs factor:	1	$e^{-\beta(\epsilon - \mu)}$	

What is the average number of particles that occupy our state?

$$\bar{n}_{FD} = \sum_{n \in \text{configs.}} n \text{Prob}(n) = 0 \times \text{Prob}(0) + 1 \times \text{Prob}(1) = 1 \times \frac{e^{-\beta(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}} = \frac{1}{1 + e^{\beta(\epsilon - \mu)}}$$

$$0 \leq \bar{n}_F \leq 1 \quad \checkmark$$



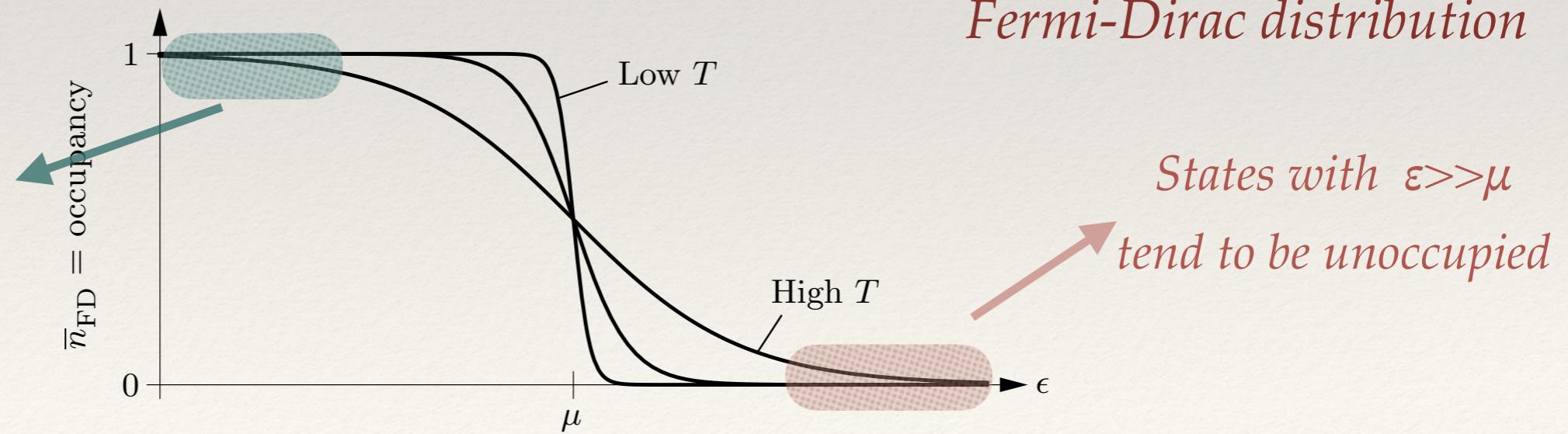
Distribution Functions

<i>configuration:</i>	—	\textcircled{F}	<i>Partition function:</i>
<i>energy of the system:</i>	0	ϵ	$\mathcal{Z}_F = 1 + e^{-\beta(\epsilon-\mu)}$
<i>Gibbs factor:</i>	1	$e^{-\beta(\epsilon-\mu)}$	

What is the average number of particles that occupy our state?

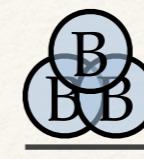
$$\bar{n}_{\text{FD}} = \sum_{n \in \text{configs.}} n \text{Prob}(n) = 0 \times \text{Prob}(0) + 1 \times \text{Prob}(1) = 1 \times \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} = \frac{1}{1 + e^{\beta(\epsilon-\mu)}}$$

States with $\epsilon \ll \mu$
tend to be occupied

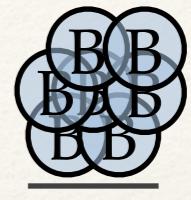


Distribution Functions: Bosons

configuration:



...



...

energy of the system:

0

ϵ

2ϵ

3ϵ

...

$n\epsilon$

...

Gibbs factor:

1

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

$e^{-\beta(2\epsilon-2\mu)}$

$e^{-\beta(3\epsilon-3\mu)}$

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

Partition function:

$$\mathcal{Z} = 1 + e^{-\beta(\epsilon-\mu)} + e^{-2\beta(\epsilon-\mu)} + e^{-3\beta(\epsilon-\mu)} + \dots = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}$$

Classroom Exercise: Discuss the conditions for this summation

Distribution Functions: Bosons

configuration:

	<u>—</u>	<u>(B)</u>	<u>BB</u>	<u>B B B</u>	...	<u>BB B B B</u>	...
energy of the system:	0	ϵ	2ϵ	3ϵ	...	$n\epsilon$...
Gibbs factor:	1	$e^{-\beta(\epsilon-\mu)}$	$e^{-\beta(2\epsilon-2\mu)}$	$e^{-\beta(3\epsilon-3\mu)}$		$e^{-\beta(n\epsilon-n\mu)}$	

Partition function:

$$\mathcal{Z} = 1 + e^{-\beta(\epsilon-\mu)} + e^{-2\beta(\epsilon-\mu)} + e^{-3\beta(\epsilon-\mu)} + \dots = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}$$

$$1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \quad \text{for } x < 1 \quad x = e^{-\beta(\epsilon-\mu)} < 1 \Rightarrow \mu < \epsilon$$

Also notice that the same condition ensures $Z>0$

Distribution Functions: Bosons

configuration:

	<u>—</u>	<u>(B)</u>	<u>BB</u>	<u>BBB</u>	...	<u>BBB</u>	...
energy of the system:	0	ϵ	2ϵ	3ϵ	...	$n\epsilon$...

Gibbs factor:

$$1 \quad e^{-\beta(\epsilon-\mu)} \quad e^{-\beta(2\epsilon-2\mu)} \quad e^{-\beta(3\epsilon-3\mu)} \quad e^{-\beta(n\epsilon-n\mu)}$$

Partition function:

$$\mathcal{Z} = 1 + e^{-\beta(\epsilon-\mu)} + e^{-2\beta(\epsilon-\mu)} + e^{-3\beta(\epsilon-\mu)} + \dots = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}$$

Average number of particles:

$$\bar{n}_{BE} = \sum_{n=0}^{\infty} n \text{Prob}(n) = \sum_{n=0}^{\infty} n \frac{e^{-n\beta(\epsilon-\mu)}}{\mathcal{Z}} \quad x \equiv \beta(\epsilon - \mu)$$

$$\bar{n}_{BE} = \sum_{n=0}^{\infty} n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \sum_{n=0}^{\infty} \frac{\partial}{\partial x} e^{-nx} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

Bose-Einstein distribution

Distribution Functions

Recall: Boltzmann statistics (Chapter 6)

Probability of a single particle occupying a state with energy ϵ $\text{Prob}(\epsilon) = \frac{1}{Z_1} e^{-\beta\epsilon}$

With N independent particles total, the average number of particles that occupy our state:

$$\bar{n}_{Boltzmann} = N \text{Prob}(\epsilon) = \frac{N}{Z_1} e^{-\beta\epsilon}$$

Recall:

$$dF = -SdT + pdV + \mu dN$$

$$F = -kT \log Z = -kT \log \left(\frac{Z_1^N}{N!} \right) = -NkT \left[\log \left(\frac{Z_1}{N} \right) + 1 \right]$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT \log \left(\frac{Z_1}{N} \right)$$

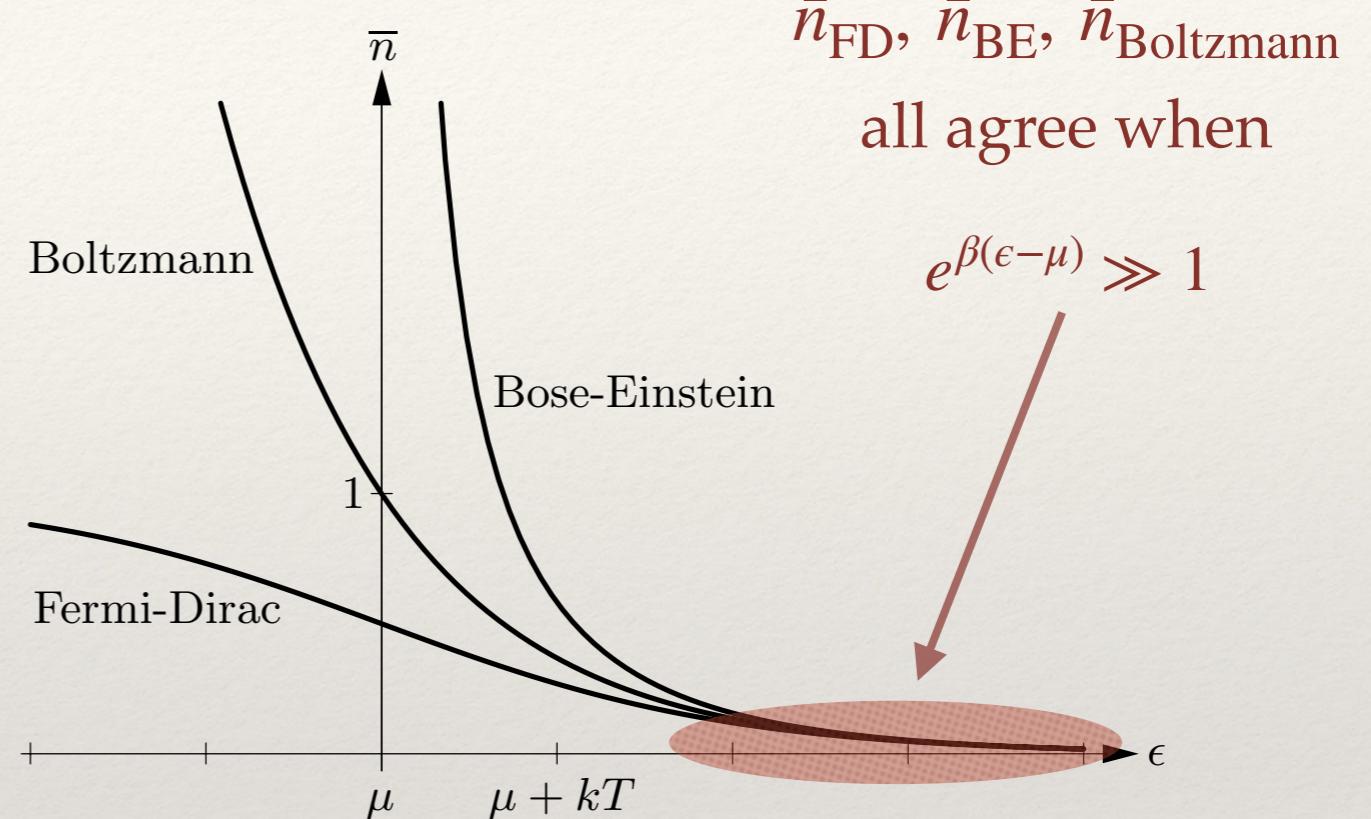
$$\bar{n}_{Boltzmann} = e^{-\beta(\epsilon-\mu)}$$

Distribution Functions

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

$$\bar{n}_{\text{BE}} = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

$$\bar{n}_{\text{Boltzmann}} = e^{-\beta(\epsilon - \mu)}$$



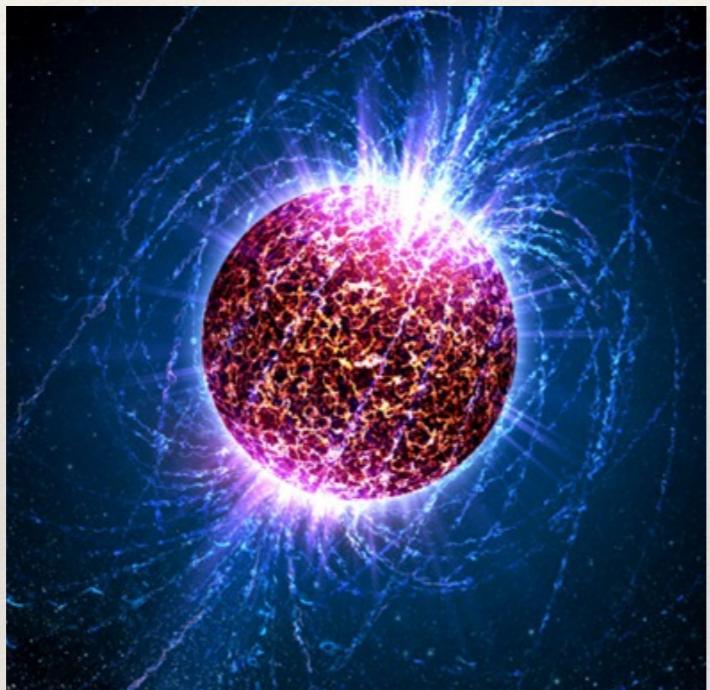
assume the ground state energy $\epsilon=0$. the condition $e^{\beta(\epsilon - \mu)} \gg 1$ is true for all the states

when $\mu \ll -kT$

$$\mu = -kT \log \left(\frac{Z_1}{N} \right) \Rightarrow Z_1 \gg N \quad \checkmark$$

Fermi Gas

Consider a gas of fermions at very low temperature / high density



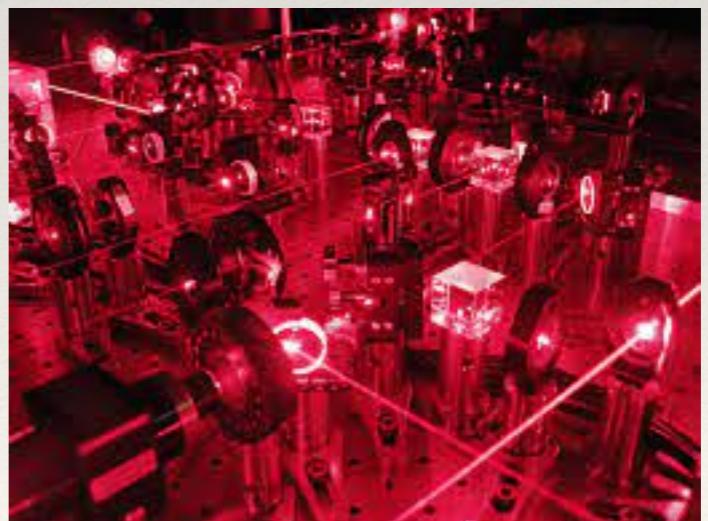
Casey Reed (Penn State University)/Wikimedia Commons

Neutron stars ($\rho \sim 10^{17} \text{ kg/m}^3$)

Electrons in a metal



*Ultracold atoms
(e.g. ${}^3\text{Li}$, ${}^3\text{He}$)*



[image: <http://www.lkb.upmc.fr/en/gaz-quantiques/>]

Fermi Gas

Consider a gas of fermions at very low temperature / high density

What is low temperature? room temperature?, -40 °F?, 3K, 10mK?

T where the condition for Boltzmann statistics is badly violated

$$\frac{V}{N} \ll v_Q = \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2}$$

e.g. air at $T=300\text{K}$, $p=1\text{ atm}$

$$v_Q = \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} = \left(\frac{2\pi\hbar^2 N_A}{m_{\text{mole}} k T} \right)^{3/2} = \left(\frac{2\pi (1.05 \times 10^{-34}\text{Js})^2 (6.02 \times 10^{23})}{(0.028\text{kg})(1.38 \times 10^{-23}\text{J/K})(300\text{K})} \right)^{3/2} \approx (0.02\text{nm})^3$$

$$\frac{V}{N} = \frac{kT}{p} = \frac{(1.38 \times 10^{-23}\text{J/K})(300\text{K})}{105^5\text{Pa}} \approx (3\text{ nm})^3$$

$$\frac{V}{N} \gg v_Q \Rightarrow \text{Boltzmann} \quad \checkmark$$

Classroom Exercise

$$\frac{V}{N} ??? v_Q = \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2}$$

In a typical metal there is roughly one conduction electron per atom.

Does the Boltzmann condition hold for metals at room T (300K)?

mass of the electron

$$m_{e^-} = 9.1 \times 10^{-31} \text{kg}$$

typical size of an atom

$$r_{\text{atom}} \approx 0.1 \text{nm} \Rightarrow V_{\text{atom}} \approx \frac{4\pi}{3} r_{\text{atom}}^3 \approx (0.2 \text{nm})^3$$

Fermi Gas at Zero Temperature

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

$$T \rightarrow 0 \Leftrightarrow \beta \rightarrow \infty \quad e^{\beta(\epsilon - \mu)} \rightarrow \begin{cases} 0, & \text{for } \epsilon - \mu < 0 \\ \infty, & \text{for } \epsilon - \mu > 0 \end{cases}$$

$$\epsilon_F = \mu(T=0) \quad \text{``Fermi energy''}$$

all states with $\epsilon < \epsilon_F$

are occupied

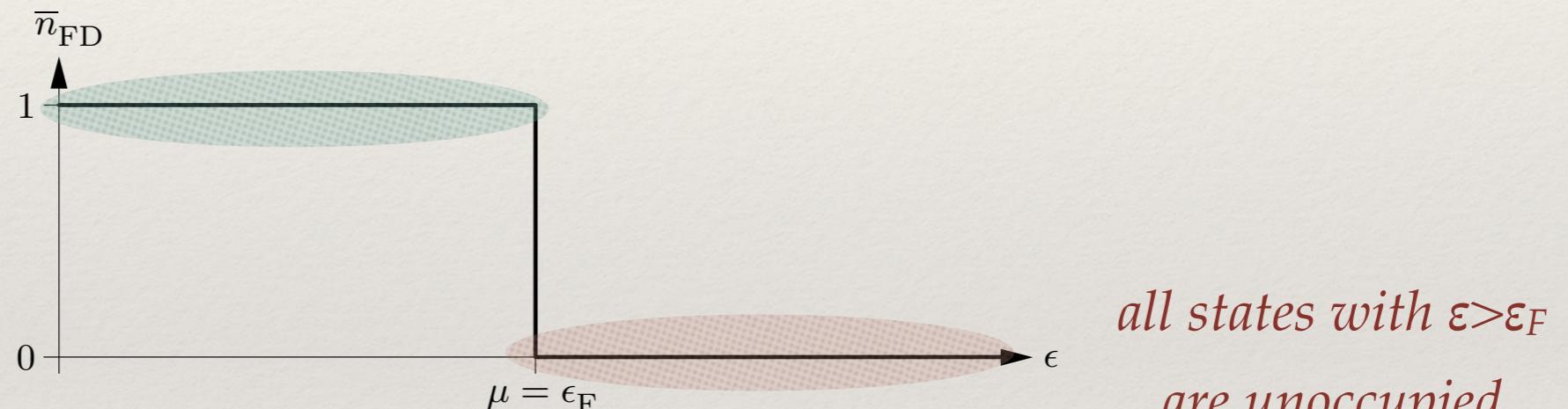
\vdots

ϵ_F —————

ϵ_2  —————

ϵ_1  —————

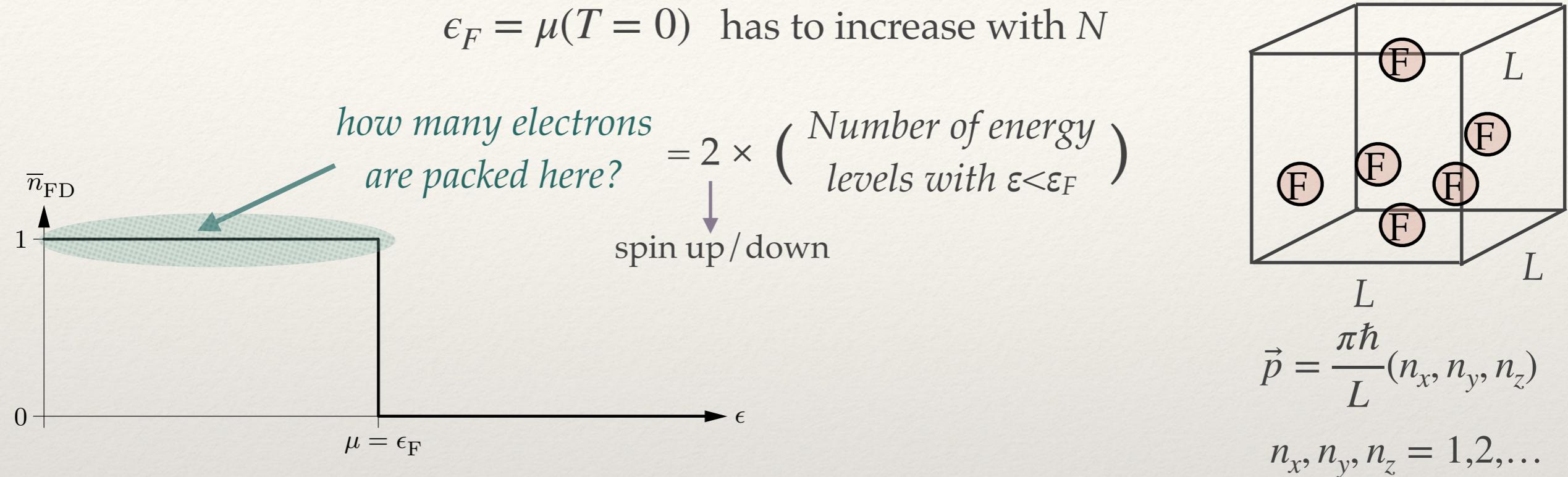
ϵ_0  —————



“Degenerate Fermi Gas”

The word degenerate here has nothing to do with the same word that describes multiple states that have the same energy

Degenerate Fermi Gas



Single particle energy levels:

$$\epsilon_{n_x, n_y, n_z} = \frac{p_{n_x}^2 + p_{n_y}^2 + p_{n_z}^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

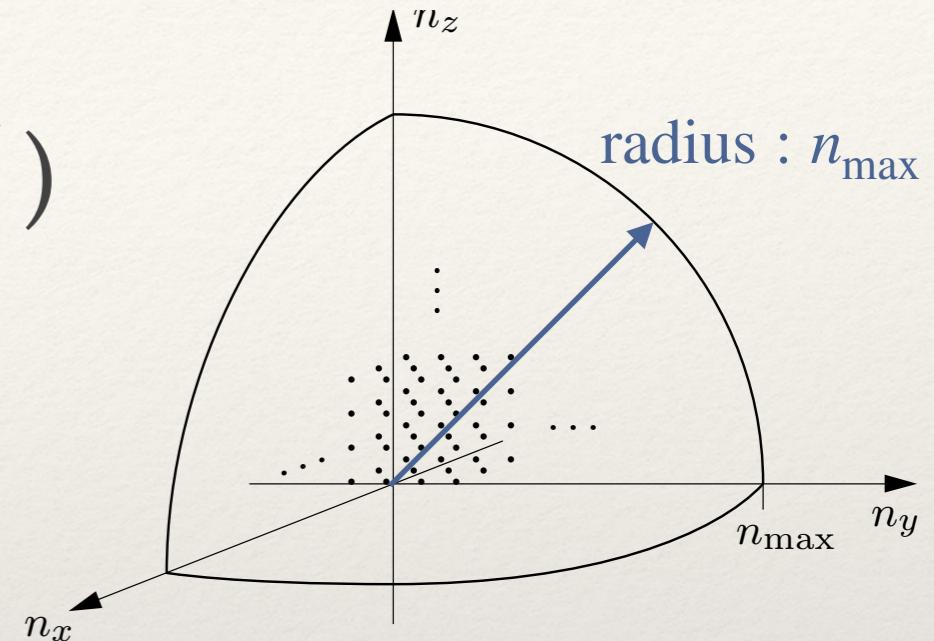
Fermi energy: energy of the highest level occupied

$$\epsilon_F = \frac{\pi^2 \hbar^2 n_{\max}^2}{2mL^2}$$

Degenerate Fermi Gas

$$\epsilon_F = \frac{\pi^2 \hbar^2 n_{\max}^2}{2mL^2} \quad \xleftrightarrow{relate} \quad N = 2 \times \left(\begin{array}{c} \text{Number of energy} \\ \text{levels with } \varepsilon < \varepsilon_F \end{array} \right)$$

$$\epsilon_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) : 1/8^{\text{th}} \text{ of the sphere}$$



$$N = 2 \times \left(\begin{array}{c} \text{Number of energy} \\ \text{levels with } \varepsilon < \varepsilon_F \end{array} \right) = 2 \times \left(\begin{array}{c} \text{Volume of } 1/8^{\text{th}} \text{ of} \\ \text{the sphere} \end{array} \right) = 2 \times \frac{1}{8} \frac{4\pi}{3} n_{\max}^3 = \frac{\pi}{3} \left(\frac{\sqrt{\epsilon_F 2mL}}{\pi \hbar} \right)^3$$

$$\epsilon_F = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3n}{\pi} \right)^{2/3}$$

Degenerate Fermi Gas

$$\epsilon_F = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3n}{\pi} \right)^{2/3}$$

Remarks:

- ϵ_F : intensive (depends on density $n=N/V$)
- The expression is valid for any shape (not just a box)
- What is low temperature for quantum effects to be relevant?

$$\frac{V}{N} \ll v_Q \Leftrightarrow kT \ll \epsilon_F \quad T_F \equiv \frac{\epsilon_F}{k} \quad T \ll T_F : \text{cold}$$

room temperature: (300K), $kT \sim 1/40$ eV

e.g.

typical ϵ_F in metals $\sim 2\text{-}10$ eV

$T_{\text{room}} \ll T_F$

Density of States

We now turn to usual thermodynamic properties such as energy, pressure, etc...
 In order to properly count the number of states we have to introduce the notion of
 “density of states”

$$\epsilon_{\vec{n}} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\pi^2 \hbar^2 n^2}{2mL^2} \Rightarrow n = \frac{\sqrt{2m\epsilon} L}{\pi \hbar}$$

density of states: $g(\epsilon)\Delta\epsilon = \text{number of states that has energy between } \epsilon \text{ and } \epsilon + \Delta\epsilon$

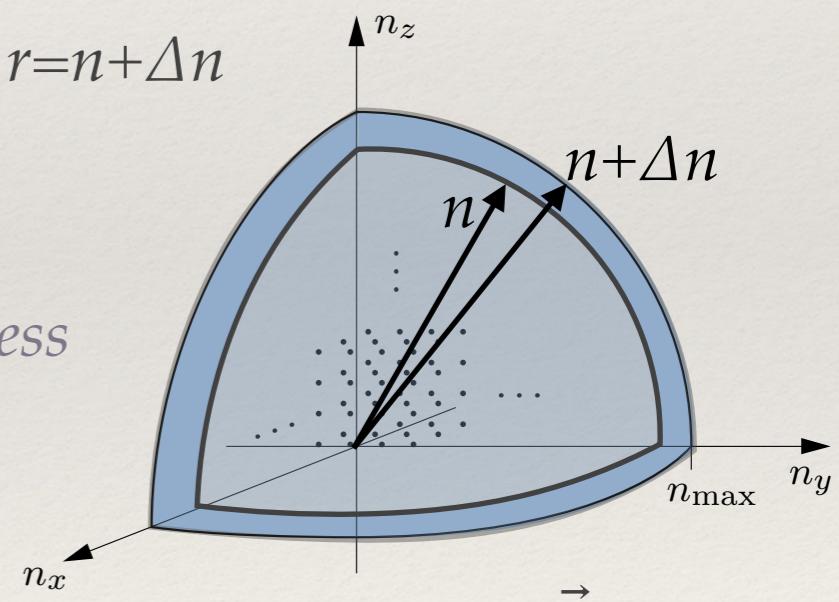
$g(\epsilon)\Delta\epsilon = 2 \times \text{volume of the thin shell between radii } r=n \text{ and } r=n+\Delta n$

$$dn = \frac{dn}{d\epsilon} d\epsilon \\ = \frac{dn}{\sqrt{2m\epsilon}} \frac{d\epsilon}{2\sqrt{\epsilon}}$$

$$g(\epsilon)d\epsilon = 2 \times \frac{1}{8} \times 4\pi n^2 \times dn$$

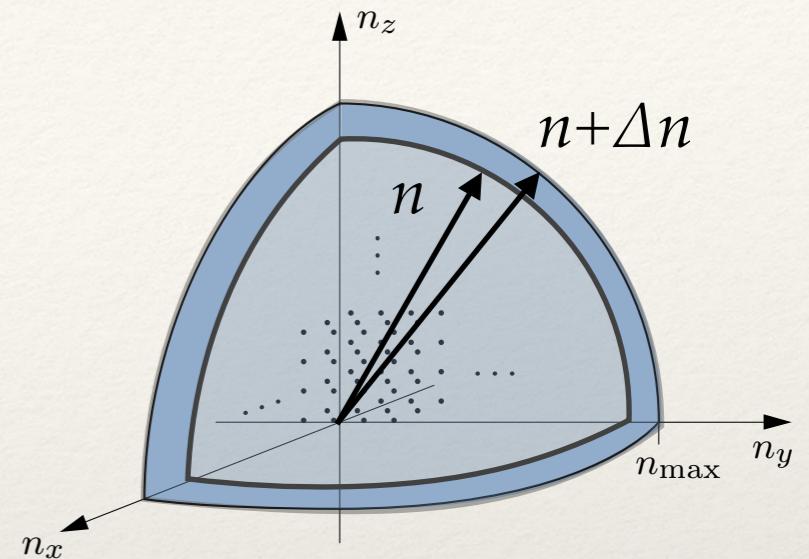
↑
spin factor ↑
 surface area ← thickness

$$g(\epsilon)d\epsilon = \frac{(2m)^{3/2} L^3}{2\pi^2 \hbar^3} \sqrt{\epsilon} d\epsilon = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon} d\epsilon$$



Degenerate Fermi Gas, Energy

$$g(\epsilon)d\epsilon = \frac{(2m)^{3/2}L^3}{2\pi^2\hbar^3}\sqrt{\epsilon}d\epsilon = \frac{3N}{2\epsilon_F^{3/2}}\sqrt{\epsilon}d\epsilon$$



$$U = \sum_{\vec{n}} \epsilon(\vec{n}) \times \mathcal{N}(\vec{n}) = \int_0^{n_{\max}} \epsilon(\vec{n}) \mathcal{N}(\vec{n}) dn = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon$$

↓

Number of states that has energy ϵ

↓

$\mathcal{N}(\vec{n})dn = g(\epsilon)d\epsilon$

$$U = \int_0^{\epsilon_F} \frac{3N}{2\epsilon_F^{3/2}} \epsilon^{3/2} d\epsilon = \frac{3N}{2\epsilon_F^{3/2}} \frac{2}{5} \epsilon_F^{5/2} = \frac{3N}{5} \epsilon_F$$

Average energy per electron: $\frac{U}{N} = \frac{3}{5} \epsilon_F$

Classroom Exercise: Degenerate Fermi Gas, Pressure

recall $dU = Tds - pdV + \mu dN$

$$p = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

$$U = \frac{3N}{5}\epsilon_F, \quad \epsilon_F = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

What is the pressure of degenerate Fermi Gas?

Classroom Exercise: Degenerate Fermi Gas, Pressure

recall $dU = Tds - pdV + \mu dN$

$$p = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \quad U = \frac{3N}{5} \epsilon_F, \quad \epsilon_F = \frac{\pi^2 \hbar^2}{2m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

$$p = - \left(\frac{\partial U}{\partial V} \right)_{T,N} = - \frac{\partial}{\partial V} \left(\frac{3N}{5} \frac{\pi^2 \hbar^2}{2m} \left(\frac{3N}{\pi V} \right)^{2/3} \right) = \frac{2N\epsilon_F}{5V} = \frac{2U}{3V}$$

Degeneracy Pressure

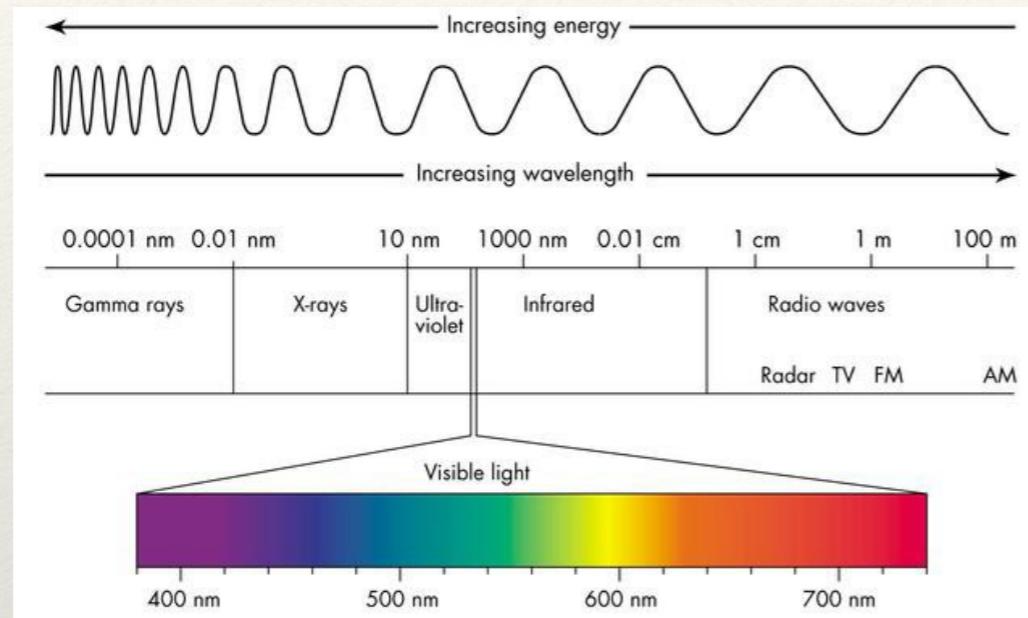
This is pressure due to the exclusion principle. When you try to compress an electron gas the wavelengths of the wave functions have to decrease and this takes energy.

Degeneracy pressure is what keeps matter collapsing due to attractive electrostatic force between protons and electrons.

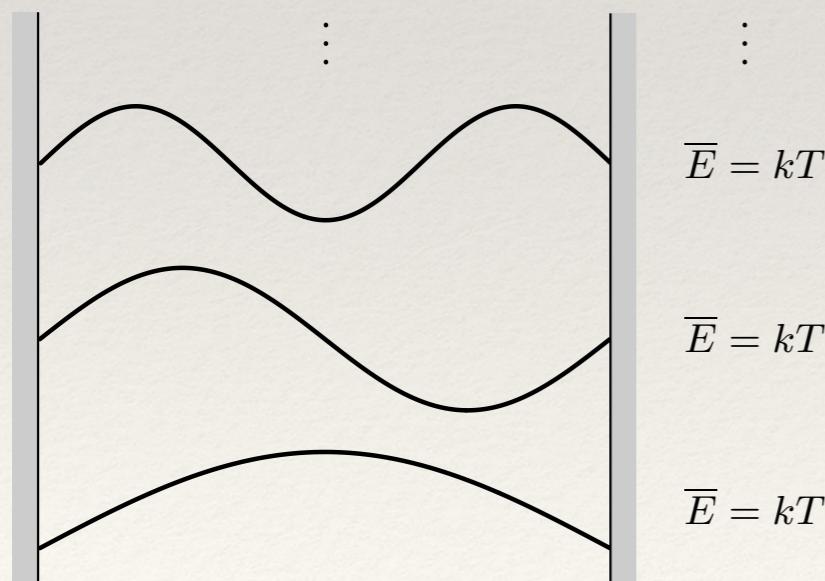
Blackbody Radiation

Electromagnetic radiation inside some box (e.g. an oven)

smaller λ
(UV)



larger λ
(IR)



Each wavelength has 2 degrees of freedom
(two transverse planes of oscillation i.e. polarization)

Average energy for each λ : $\bar{E} = 2 \times \frac{1}{2}kT = kT$

There are infinitely many wavelengths

$$\bar{E}_{total} = kT \times \infty \quad ???$$

Ultraviolet Catastrophe

Planck Distribution

The solution to the ultraviolet catastrophe comes from *quantum mechanics*

More precisely it led to the *birth* of quantum mechanics

Each EM wave is like a harmonic oscillator. In quantum mechanics the energy levels of a harmonic oscillator take discrete values (i.e. “quantized”)

$$E_n = 0, \hbar\omega, 2\hbar\omega, 3\hbar\omega, \dots$$

$$Z = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

Average energy: $\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \equiv \hbar\omega \times \bar{n}_{\text{Pl}} \longrightarrow$

one unit of energy 

average number of units of energy

$$\bar{n}_{\text{Pl}} \equiv \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$\bar{n}_{\text{Pl}} \rightarrow e^{-\beta\hbar\omega} \rightarrow 0 \quad \text{for} \quad \hbar\omega \gg kT \quad (\beta\hbar\omega \gg 1)$$

The high energy UV modes are exponentially suppressed!

A gas of photons

The quantized units of electromagnetic energy
describes particles: *photons* (γ)

mass=0, spin=1 (2 degrees of freedom: 2
transverse polarizations): *bosons*

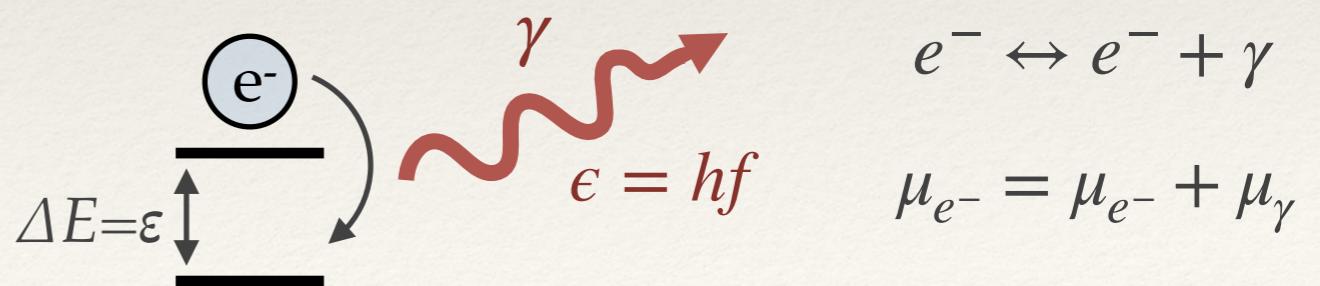
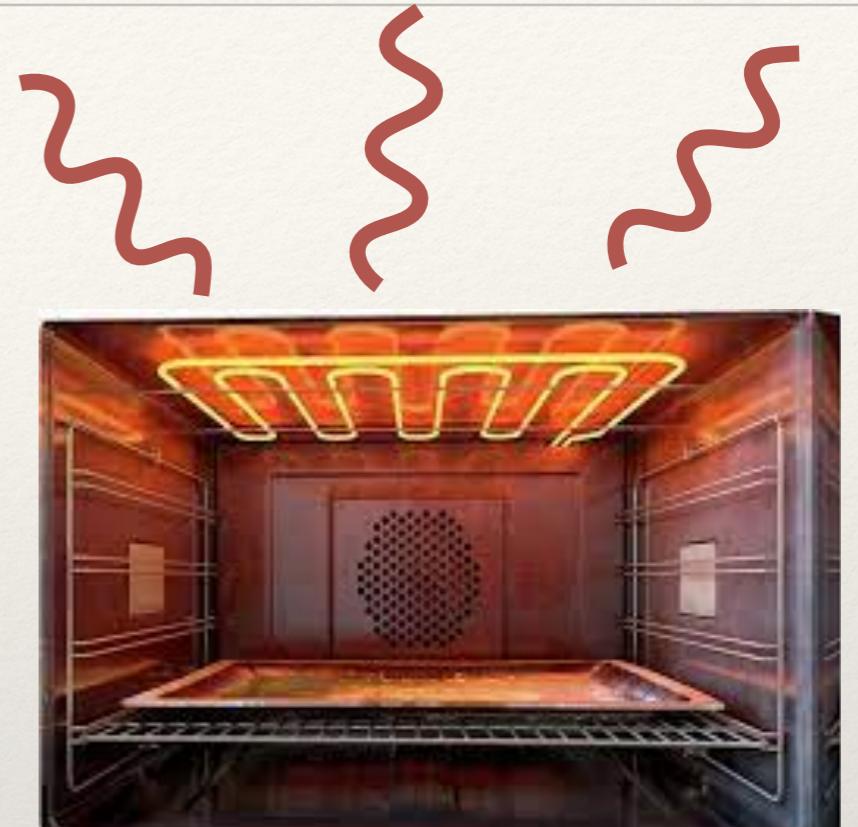
EM radiation in a box = boson gas

Planck distribution \Leftrightarrow *Bose-Einstein distribution*

$$\bar{n}_{\text{Pl}} \equiv \frac{1}{e^{\beta \hbar \omega} - 1} \quad \Leftrightarrow \quad \bar{n}_{BE} = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \quad \longrightarrow \quad \epsilon = \hbar \omega \quad \mu = 0$$

$\mu=0$: photon number is *not* conserved

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 \quad F: \text{minimum at equilibrium}$$



Total Energy of a Photon Gas

Photons have zero mass. Every particle with zero mass travels with the speed of light (c)

Energy spectrum: $\epsilon(\vec{n}) = c \cdot \vec{p} = \frac{\pi \hbar c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\pi \hbar c n}{L}$

Density of states: $g(\epsilon) d\epsilon = 2 \times \frac{1}{8} \times 4\pi n^2 \times dn = \frac{V}{\pi^2 \hbar^3 c^3} \epsilon^2 d\epsilon$

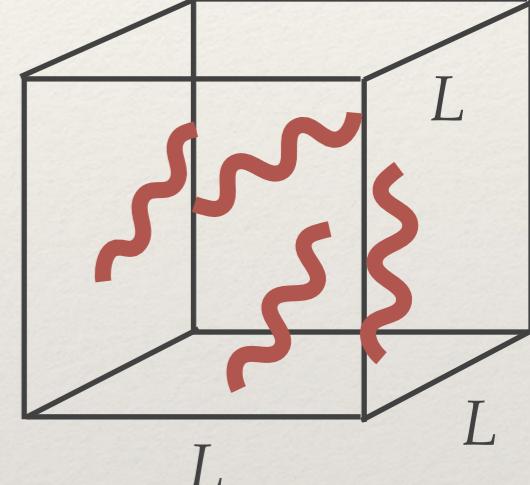
\nearrow
polarizations

Total energy per volume: $\frac{U}{V} = \frac{1}{V} \int_0^\infty \epsilon g(\epsilon) \bar{n}_{\text{BE}}(\epsilon) d\epsilon = \frac{1}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$

$$x \equiv \beta\epsilon = \frac{\epsilon}{kT}$$

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$\frac{U}{V} = \frac{(kT)^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^2 (kT)^4}{15 \hbar^3 c^3} = \frac{\pi^2}{15} \times \frac{(kT)^4}{\hbar^3 c^3}$$



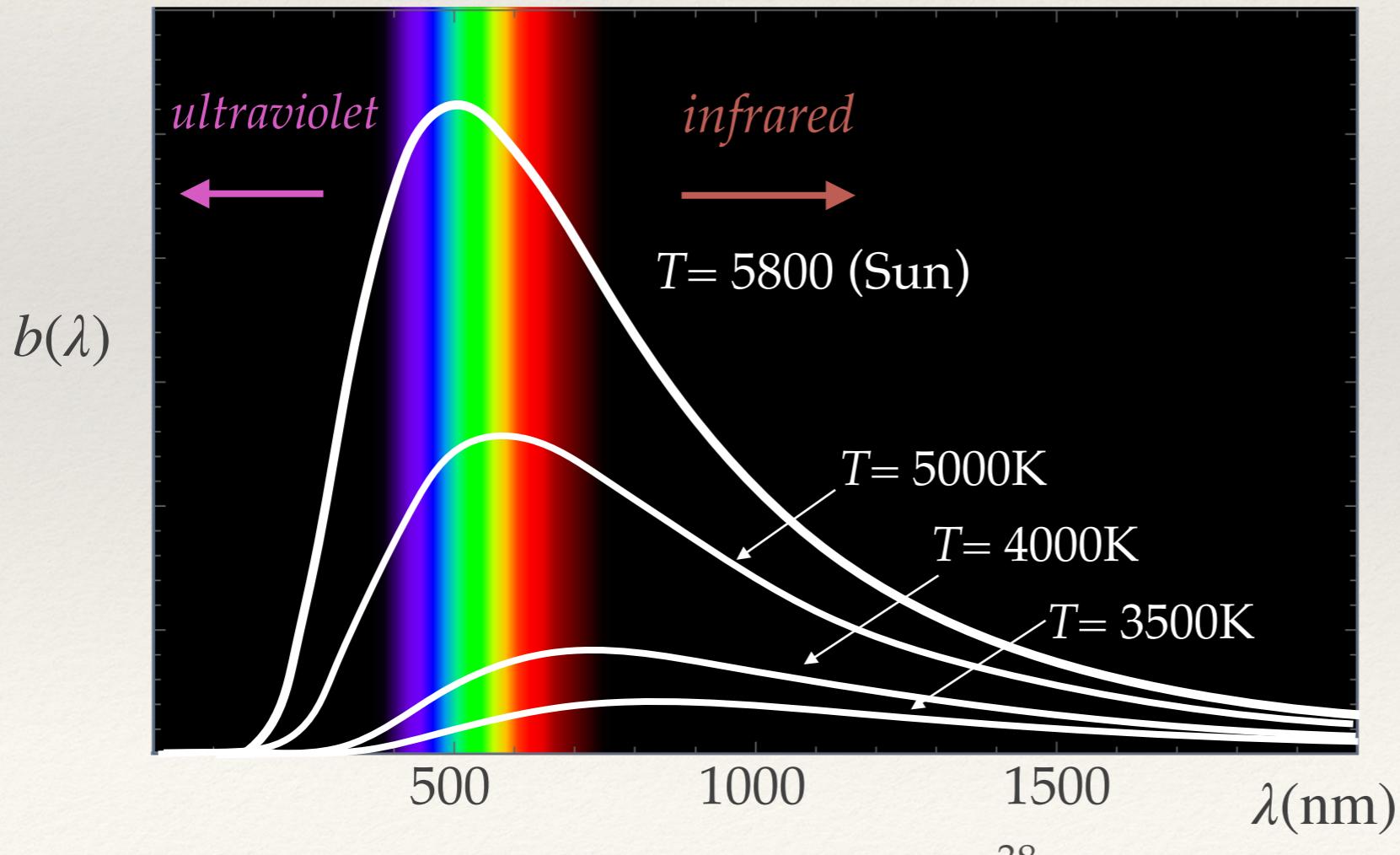
Expect from dimensional grounds

Planck Spectrum

$$\frac{U}{V} = \int_0^\infty \frac{\epsilon^3 / (\pi^2 \hbar^3 c^3)}{e^{\beta\epsilon} - 1} d\epsilon = \int_0^\infty \frac{8\pi hc / \lambda^5}{e^{\beta 2\pi \hbar c / \lambda} - 1} d\lambda$$

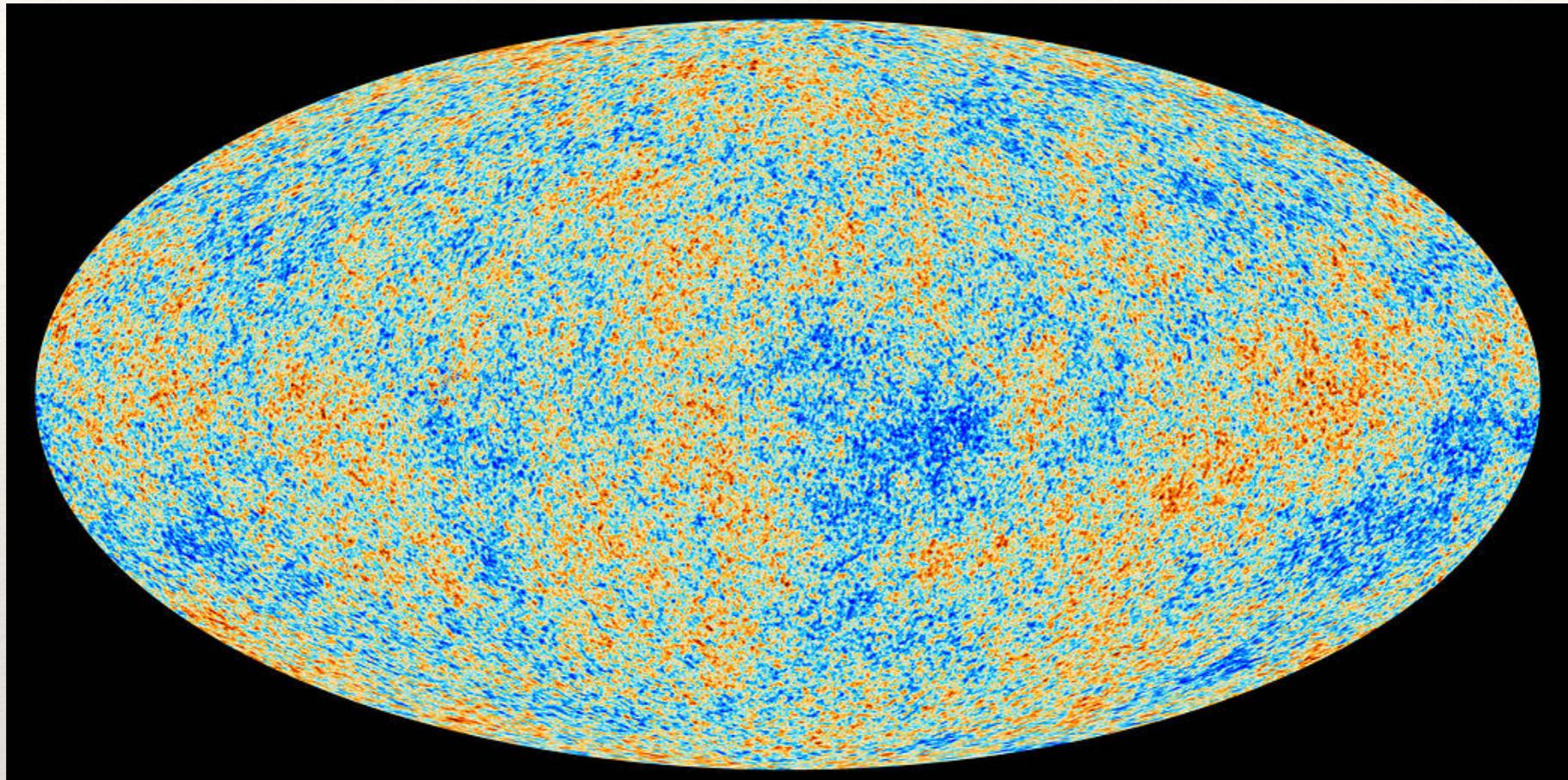
$b(\lambda) \equiv \frac{16\pi^2 \hbar c / \lambda^5}{e^{\beta 2\pi \hbar c / \lambda} - 1}$: energy density per wavelength

$$energy \quad \longleftrightarrow \quad \epsilon = \frac{2\pi \hbar c}{\lambda} \quad wavelength$$



[image:NASA]

Cosmic Microwave Background



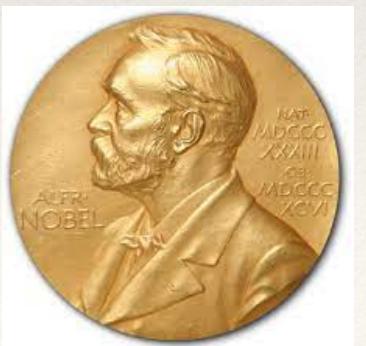
[image: Planck satellite, NASA]

Leftover radiation from early universe (when it was \sim 379,000 years old)

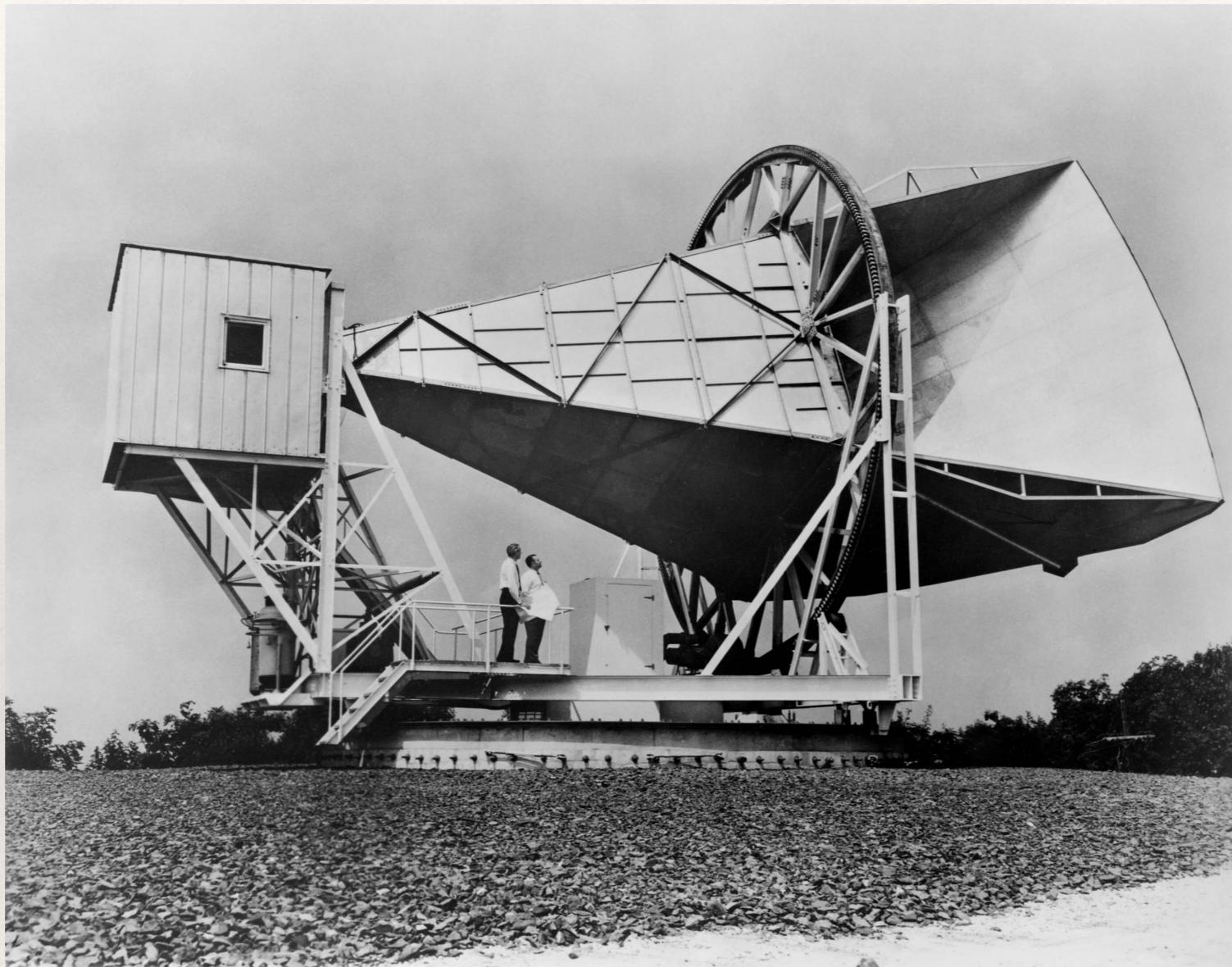
light from billions of years ago...

Mostly in the mm wavelength range, discovered accidentally.

[Penzias, Wilson; 1978]



Cosmic Microwave Background



Holmdel, NJ, 1964

[Penzias, Wilson; 1978]

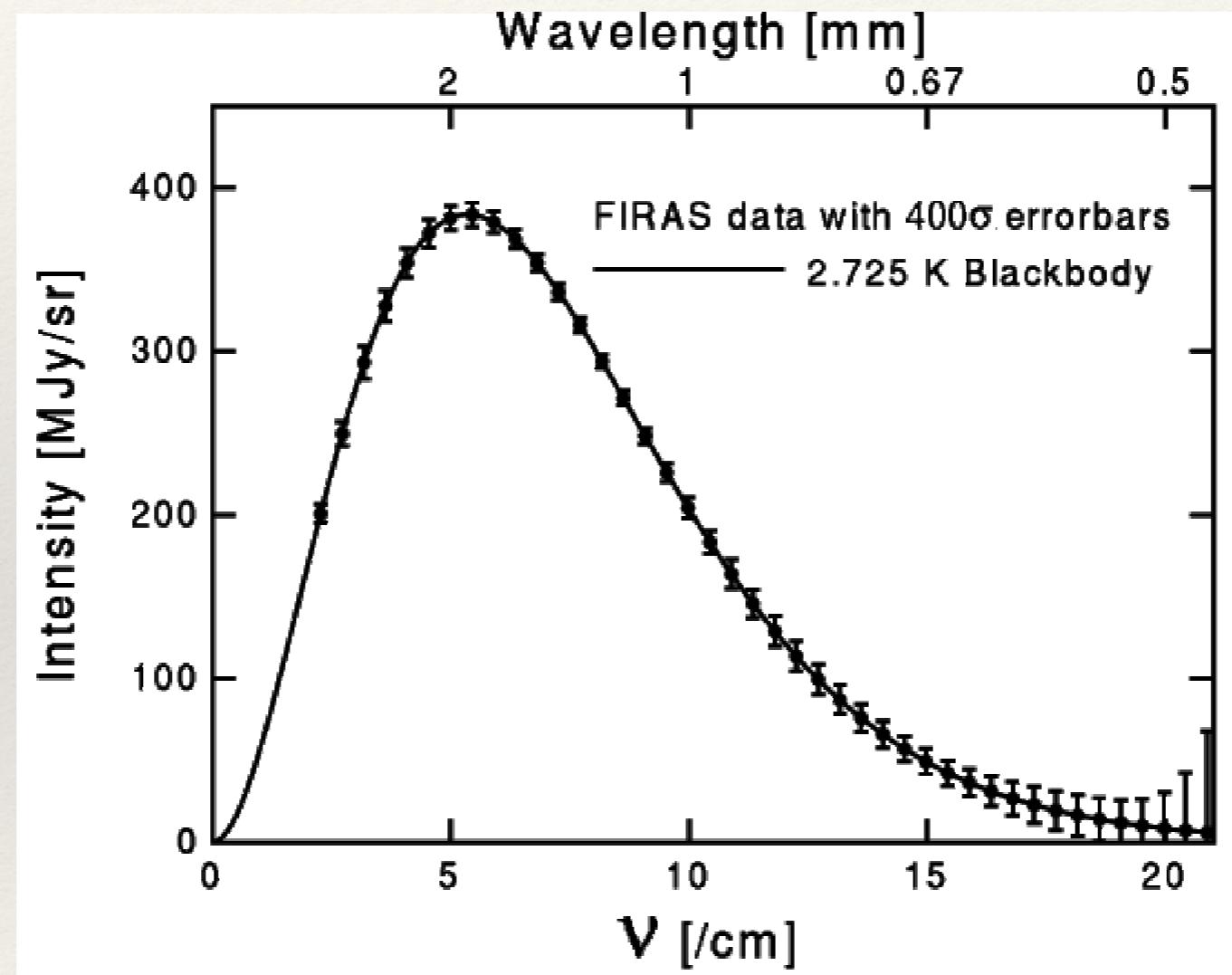


Cosmic Microwave Background

The observed spectrum from FIRAS (far infrared absolute spectrophotometer) in the COBE (Cosmic Background Explorer) satellite, early 1990s



[image: NASA]



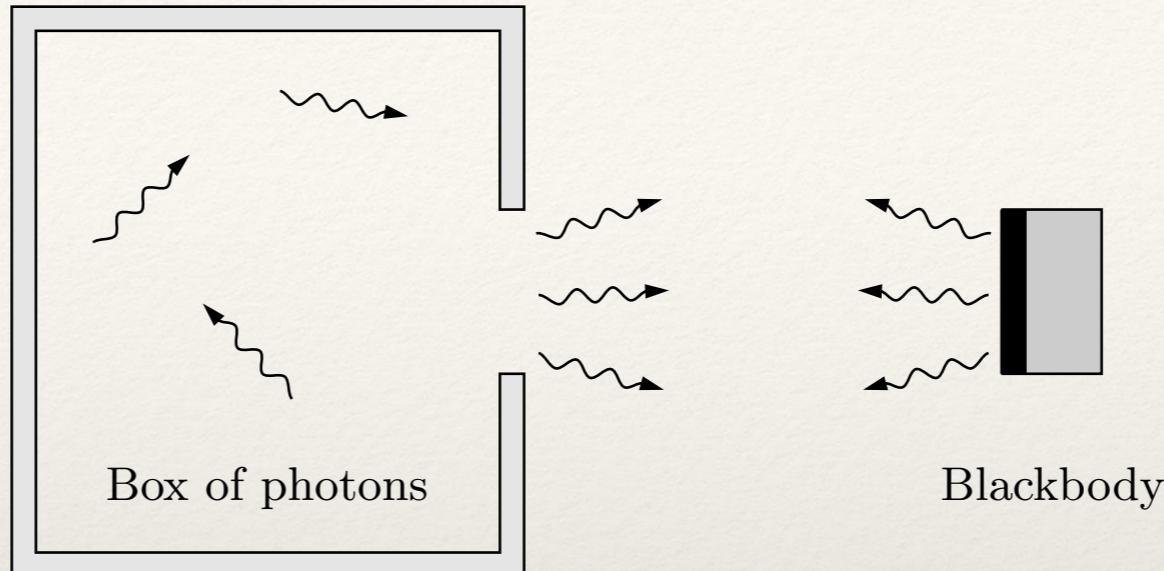
[Mather, Smoot; 2006]

Amazing agreement with the Planck Spectrum with $T=2.725$ K !!!

Blackbody Radiation

$$\frac{\text{power}}{\text{area}} = \frac{\text{energy}}{\text{time} \times \text{area}}$$

$$= (\text{energy density}) \times \frac{\text{length}}{\text{time}}$$



Power radiated by
a box of photons per unit area

$$= \frac{P}{A} = \frac{c}{4} \frac{U}{V}$$

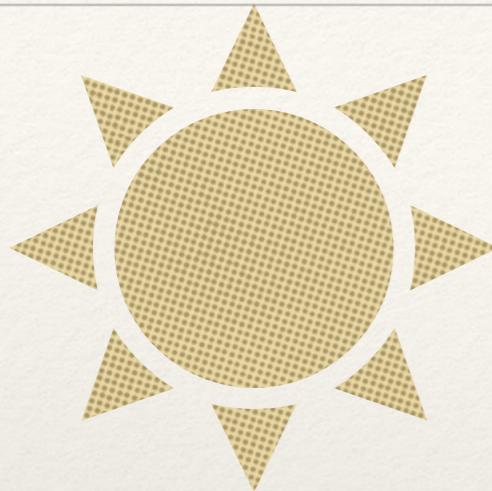
Power/area radiated by
a nonreflecting surface

$$\frac{P}{A} = \frac{\pi^2 k^4 T^4}{60 \hbar^3 c^2} \equiv \sigma T^4$$

$$\sigma = \frac{\pi^2 k^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$$

Stefan-Boltzmann constant

Solar Radiation



$$R_{Sun} = 7 \times 10^9 m$$

$$T_{Sun} = 5800 K$$

Sun's power output
“luminosity”

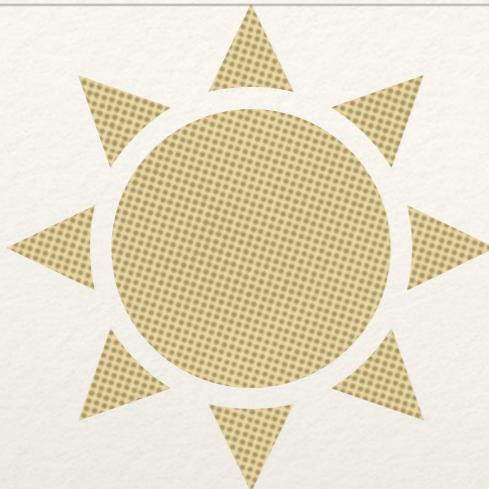
$$P_{Sun} = A_{Sun} \sigma T_{Sun}^4 = 3.9 \times 10^{26} W$$



Classroom Exercise:

What is the power per m^2 at the surface of the Earth?
(radius of Earth's orbit ~150 million km)

Solar Radiation



$$R_{\text{Sun}} = 7 \times 10^8 \text{ m}$$

$$T_{\text{Sun}} = 5800 \text{ K}$$

Sun's power output
“luminosity”

$$P_{\text{Sun}} = A_{\text{Sun}} \sigma T_{\text{Sun}}^4 = 3.9 \times 10^{26} \text{ W}$$



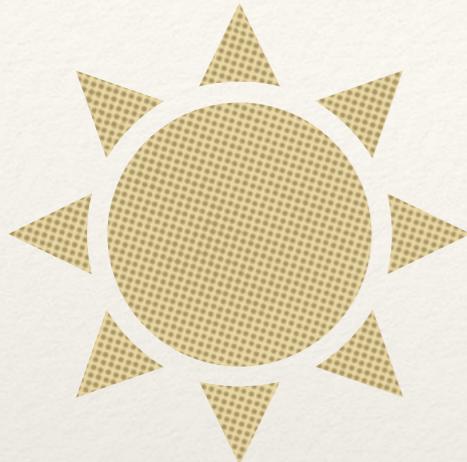
Classroom Exercise:

What is the power per m^2 at the surface of the Earth?
(radius of Earth's orbit ~ 150 million km)

$$\frac{P}{A} = \frac{A_{\text{Sun}}}{4\pi R_{\text{orbit}}^2} \sigma T_{\text{Sun}}^4 = \left(\frac{R_{\text{Sun}}}{R_{\text{orbit}}} \right)^2 \sigma T_{\text{Sun}}^4 \approx 1.4 \text{ kW/m}^2$$

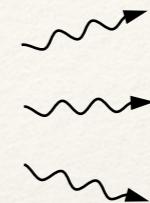
``Solar constant''
more precisely 1.360 kW/m²

Solar Radiation



Thermodynamic equilibrium:

Earth emits same amount of energy it absorbs



30% of sunlight is reflected from the atmosphere

70% of sunlight is absorbed by the Earth

$$P_{\text{absorbed}} = (\pi R_{\text{Earth}}^2) \times 0.7 \times (\text{solar constant}) = (4\pi R_{\text{Earth}}^2) \times \sigma T_{\text{Earth}}^4 = P_{\text{emitted}}$$

$$T_{\text{Earth}} = \left(\frac{0.7 \times (\text{solar constant})}{4\sigma} \right)^{1/4} = \left(\frac{0.7 \times R_{\text{Sun}}^2}{4R_{\text{orbit}}^2} \right)^{1/4} T_{\text{Sun}} \approx 255\text{K} = -18^\circ\text{C}$$



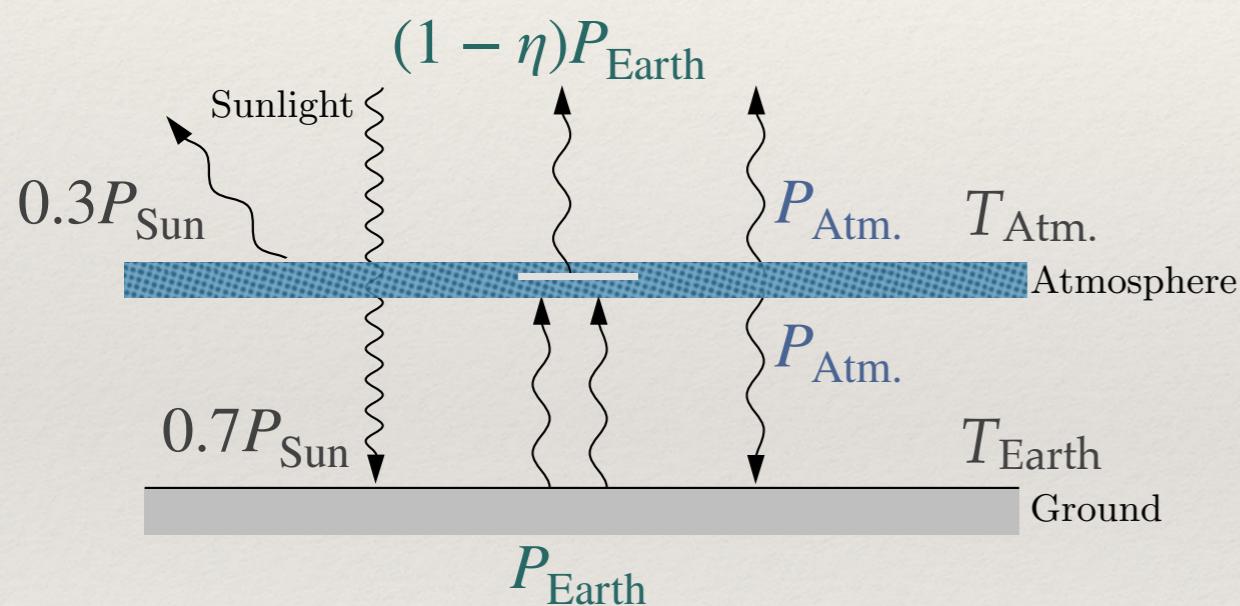
?????

Solar Radiation, Greenhouse Effect

-18 °C is the temperature if there was no atmosphere

Water vapor and CO₂ in the atmosphere absorb IR radiation (wavelengths \geq microns) emitted from the surface of the Earth

Assume the atmosphere absorbs ηP_{Earth} of the radiation from the surface ($\eta \approx 0.8$)



Thermodynamic equilibrium:

Atmosphere emits radiation (power=2P_{Atm.})

- half of it (P_{Atm.}) escapes into space,
- half of it is absorbed back by the Earth

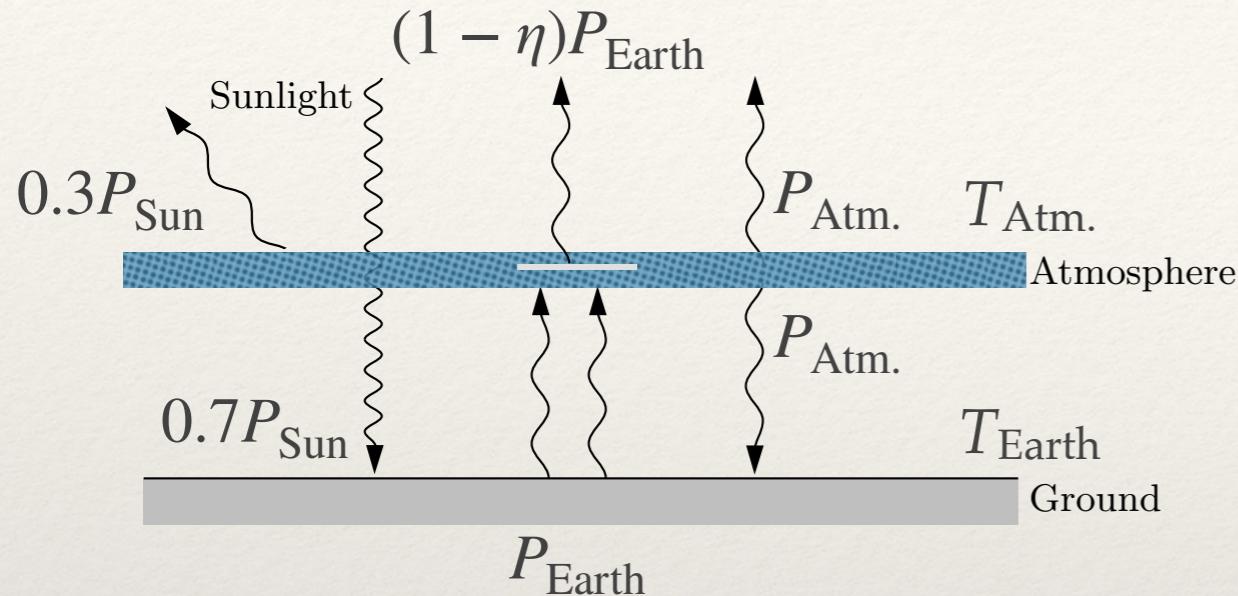
$$\text{Atmosphere: } P_{\text{Sun}} = (1 - \eta)P_{\text{Earth}} + P_{\text{Atm.}} + 0.3P_{\text{Sun}}$$

$$\text{Surface: } 0.7P_{\text{Sun}} + P_{\text{Atm.}} = P_{\text{Earth}}$$

$$T_{\text{Earth}} = \left(\frac{0.7 \times (\text{solar constant})}{4(1 - \eta/2)\sigma} \right)^{1/4} \approx 291\text{K} = 18^{\circ}\text{C}$$

Much closer to the actual value!!
(15 °C)

Classroom Exercise



Thermodynamic equilibrium:

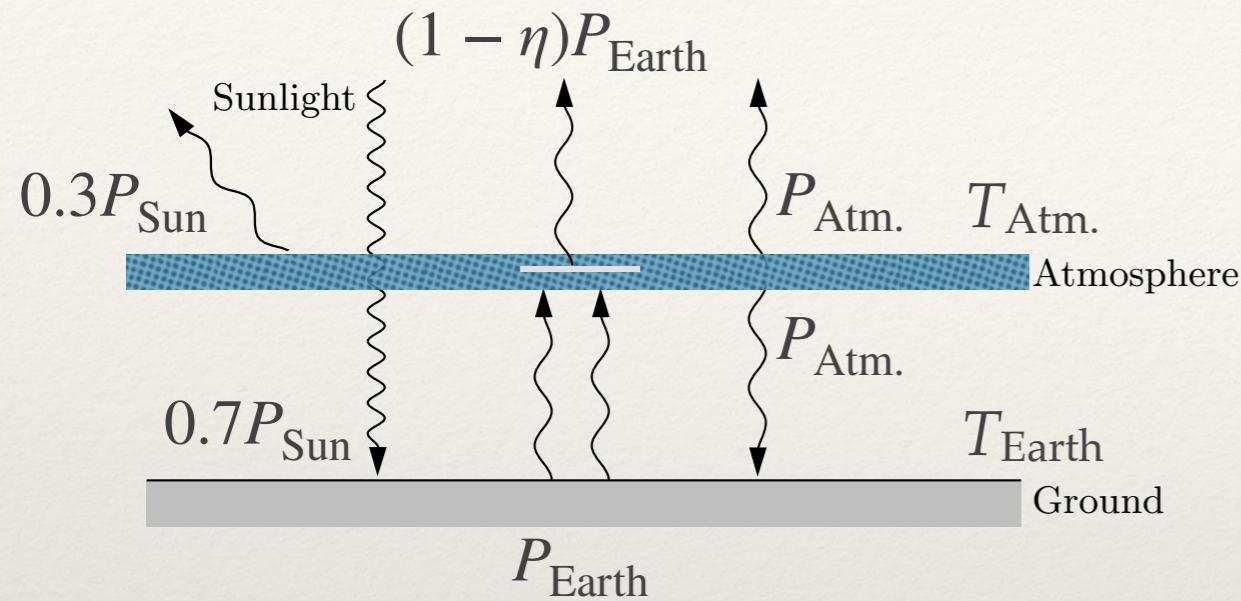
$$\text{Atmosphere: } P_{\text{Sun}} = (1 - \eta)P_{\text{Earth}} + P_{\text{Atm.}} + 0.3P_{\text{Sun}}$$

$$\text{Surface: } 0.7P_{\text{Sun}} + P_{\text{Atm.}} = P_{\text{Earth}}$$

$$T_{\text{Earth}} \approx 291\text{K} = 18^\circ\text{C}$$

Estimate the temperature of the atmosphere. Interpret your result.

Classroom Exercise



Thermodynamic equilibrium:
Atmosphere emits radiation (*power*=P_{Atm.})
Half of P_{Atm.} escapes into space
half of it is absorbed back by the Earth: “blanket”

Atmosphere:

$$P_{\text{Sun}} = (1 - \eta)P_{\text{Earth}} + (1 - \eta)P_{\text{Atm.}} + 0.3P_{\text{Sun}}$$

Surface: $0.7P_{\text{Sun}} + P_{\text{Atm.}} = P_{\text{Earth}}$

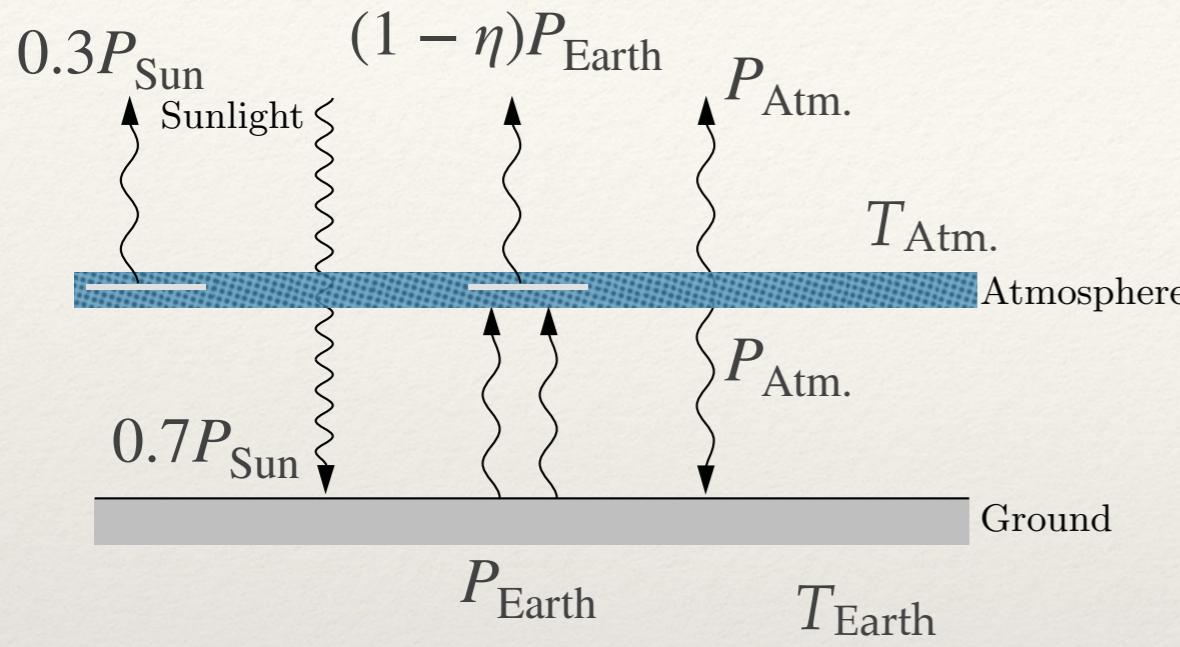
$$T_{\text{Earth}} \approx 291\text{K} = 18^{\circ}\text{C}$$

Estimate the temperature of the atmosphere. Interpret your result.

$$P_{\text{Atm.}} = \frac{\eta}{2}P_{\text{Earth}} \quad \Rightarrow \quad T_{\text{Atm.}} = \left(\frac{\eta}{4}\right)^{1/4} T_{\text{Earth}} \approx 232\text{K} = -42^{\circ}\text{C}$$

Here we assumed that the atmosphere is a single layer which is a simplification. Nevertheless this value is fairly close to the temperature at the top of the *troposphere* (~10 km above the surface) below which most of the absorbent part of the atmosphere is.

Classroom Exercise



Thermodynamic equilibrium:
Atmosphere emits radiation (*power*= $P_{\text{Atm.}}$)
Half of $P_{\text{Atm.}}$ escapes into space
half of it is absorbed back by the Earth: “blanket”

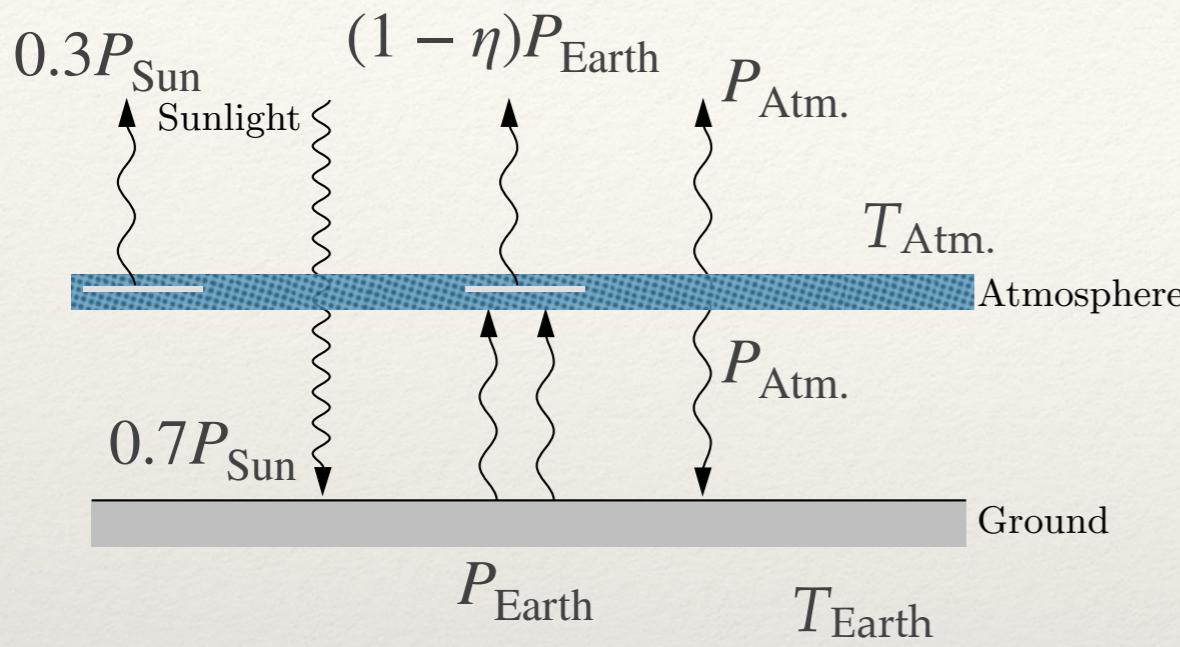
Atmosphere:

$$P_{\text{Sun}} = (1 - \eta)P_{\text{Earth}} + (1 - \eta)P_{\text{Atm.}} + 0.3P_{\text{Sun}}$$

Surface: $0.7P_{\text{Sun}} + P_{\text{Atm.}} = P_{\text{Earth}}$

Estimate what would Earth's surface temperature be if the atmosphere absorbed *all* of the radiation from Earth's surface.

Classroom Exercise



Thermodynamic equilibrium:
 Atmosphere emits radiation (power= $P_{\text{Atm.}}$)
 Half of $P_{\text{Atm.}}$ escapes into space
 half of it is absorbed back by the Earth: “blanket”

Atmosphere:

$$P_{\text{Sun}} = (1 - \eta)P_{\text{Earth}} + (1 - \eta)P_{\text{Atm.}} + 0.3P_{\text{Sun}}$$

Surface: $0.7P_{\text{Sun}} + P_{\text{Atm.}} = P_{\text{Earth}}$

Estimate what would Earth's surface temperature be if the atmosphere absorbed *all* of the radiation from Earth's surface.

In this case we would have $\eta \approx 1$

$$T_{\text{Earth}} = \left(\frac{0.7 \times (\text{solar constant})}{4(1 - 1/2)\sigma} \right)^{1/4} \approx 30^{\circ}\text{C}$$

Bose-Einstein Condensate

A gas of bosons at low temperatures has some fascinating properties!

Consider a *fixed number* (N) of spin-0 atoms (e.g. ${}^4\text{He}$) in a box

Single particle energy spectrum:

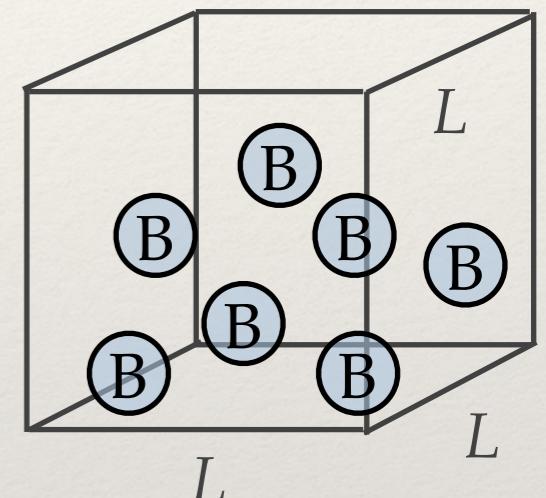
$$\epsilon_{\vec{n}} = \frac{\vec{p}^2}{2m} = \frac{\pi^2 \hbar^2 n^2}{2m L^2}$$

Density of states: $g(\epsilon) d\epsilon = 1 \times \frac{1}{8} \times 4\pi n^2 \times dn = \frac{(2m)^{3/2} L^3}{4\pi^2 \hbar^3} \sqrt{\epsilon} d\epsilon$

$$N = \int_0^\infty g(\epsilon) \bar{n}_{\text{BE}}(\epsilon) d\epsilon = \frac{(2m)^{3/2} L^3}{4\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon - \mu)} - 1} d\epsilon$$

$$N = V \times \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \times \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^{-\beta\mu} e^x - 1} dx$$

$$\vec{p} = \frac{\pi\hbar}{L}(n_x, n_y, n_z)$$



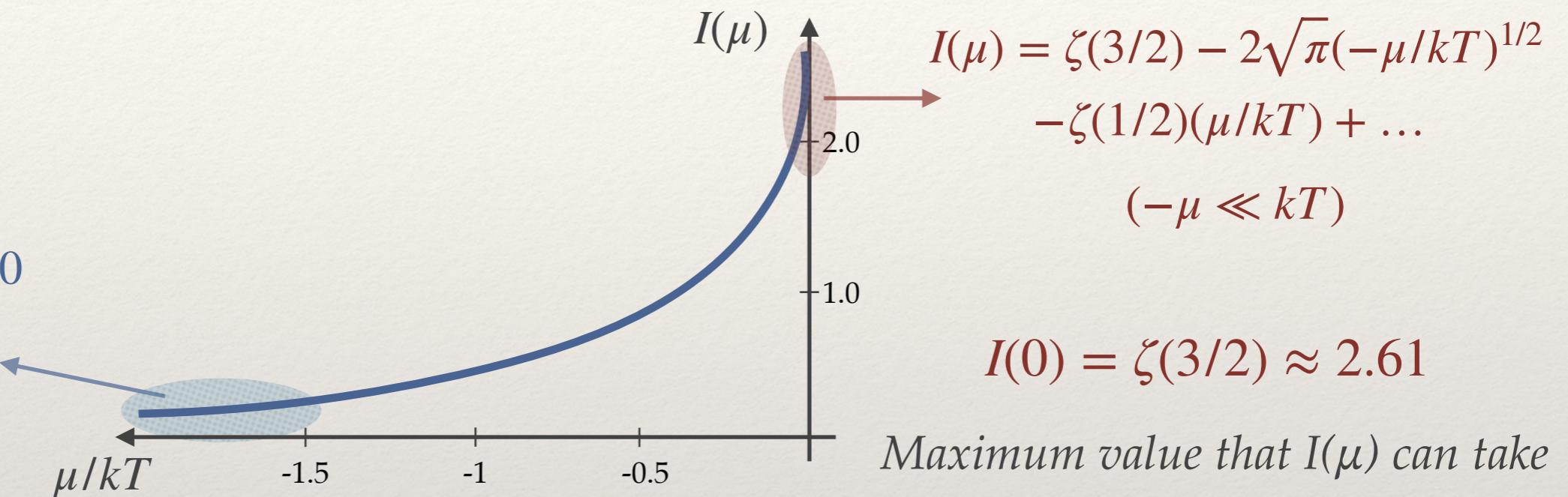
$$x \equiv \beta\epsilon = \frac{\epsilon}{kT}$$

$$\left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} = \lambda_{\text{dB}}^3 = v_Q \text{ ``quantum volume''}$$

Bose-Einstein Condensate

$N = \frac{V}{v_Q} I(\mu)$: Implicitly determines value of the chemical potential for a given N

$$I(\mu) \sim \frac{e^{-2\mu/kT}}{2\sqrt{2}} \rightarrow 0 \quad (-\mu \gg kT)$$



Suppose we cool the system at fixed volume

$v_Q \propto 1/T^{3/2}$ increases: $I(\mu)$ has to increase with the same rate in order to keep N unchanged.

But $I(\mu)$ cannot increase past $I(0)=\zeta(3/2)$!

The value of T where $I(\mu)$ reaches its maximum ($\mu=0$)

$$T_C = \left(\frac{2\pi\hbar^2}{mk} \right) \left(\frac{1}{\zeta(3/2)} \frac{N}{V} \right)^{2/3}$$

Critical temperature

Bose-Einstein Condensate

What happens when $T < T_C$?

$$N = \frac{V}{v_Q(T_C)} \zeta(3/2) \quad T < T_C \Rightarrow v_Q(T) > V \times \zeta(3/2)$$

N decreases??

Also around T_C : $v_Q \sim V$: quantum volume comparable to physical volume??

Bose-Einstein Condensate

What happens when $T < T_C$?

$$N = \frac{V}{v_Q(T_C)} \zeta(3/2) \quad T < T_C \Rightarrow v_Q(T) > V \times \zeta(3/2)$$

N decreases??

nope... we cannot simply make particles disappear by cooling them

Where are the missing particles?

Bose-Einstein Condensate

Where are the missing particles?

When counting the number of states we approximated the discrete sum over the quantized momenta with an integral

$$\sum_{\vec{p}} (\dots) \approx \frac{(2m)^{3/2} L^3}{4\pi^2 \hbar^3} \int (\dots) \sqrt{\epsilon} d\epsilon$$

$\sqrt{\epsilon} \rightarrow$ particles that occupy the ground state ($\epsilon = 0$) are missing in our calculation

Number of particles in ground state: $n_0 = \frac{1}{e^{-\mu/kT} - 1}$

n_0 is typically a small number and it is OK to ignore it...
except when $\mu \ll kT$ such that n_0 is comparable to N

Bose-Einstein Condensate

Correct expression:

$$N = \frac{V}{v_Q} I(\mu) + \frac{1}{e^{-\beta\mu} - 1}$$

excited states ground state

$$n_0 = \frac{1}{e^{-\mu/kT} - 1} \rightarrow \infty \quad \mu \ll kT$$

Plenty of room for N!

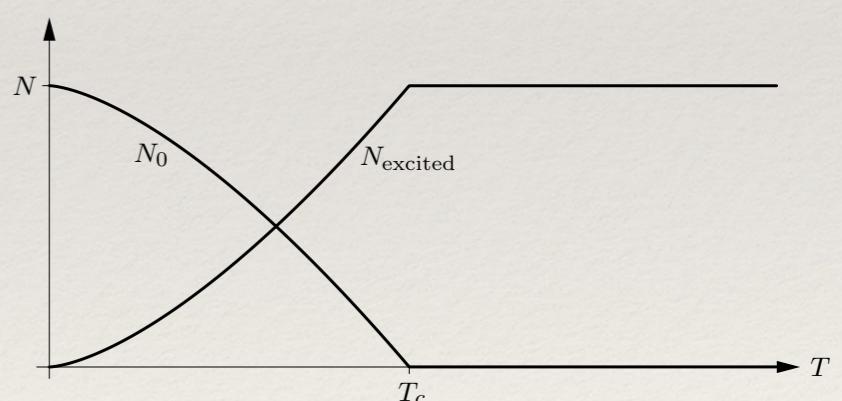
What happens when $T < T_C$?

As T decreases, v_Q increases, μ decreases. As a result more particles start to occupy the ground state. (since they are bosons this is possible) “Bose Einstein condensation”

*Fraction of particles
in ground state*

$$\frac{n_0}{N} = 1 - \frac{V}{Nv_q} \zeta(3/2) = 1 - \left(\frac{T}{T_C} \right)^{3/2}$$

Macroscopically large quantum system!



Remark: μ never reaches 0 for any finite value of T but becomes very small: $\mu \sim -kT/N$

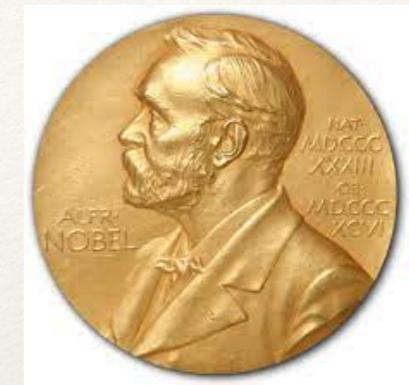
Bose-Einstein Condensate in the Lab

First BECs were formed experimentally in 1995
by using Rb, Li, Na atoms with $N \sim 10^4 - 10^7$

JILA/NIST Experiment; '95, Boulder

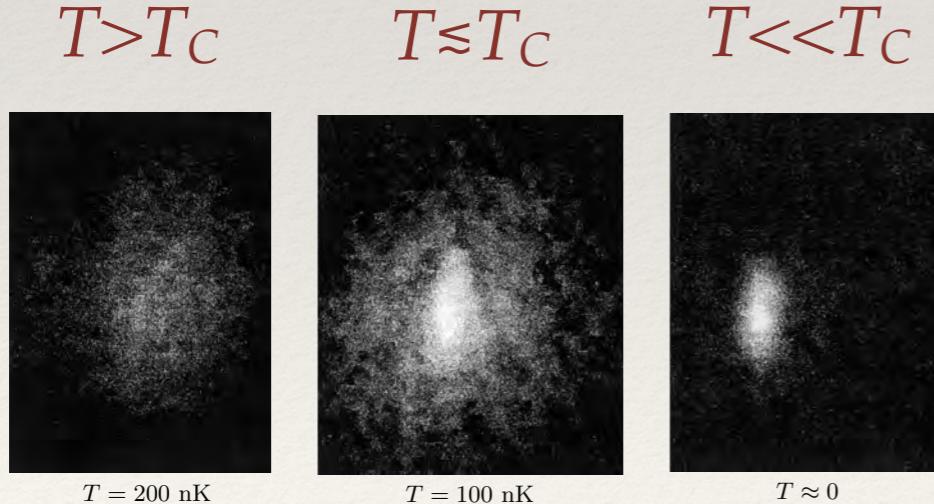
$V \sim (0.2\text{mm})^3$, $N \sim 10^4$ ^{87}Rb atoms

$T_c \sim 100 \text{ nK}$ (compare with $T_{\text{outer space}} = 2.7 \text{ K}$)



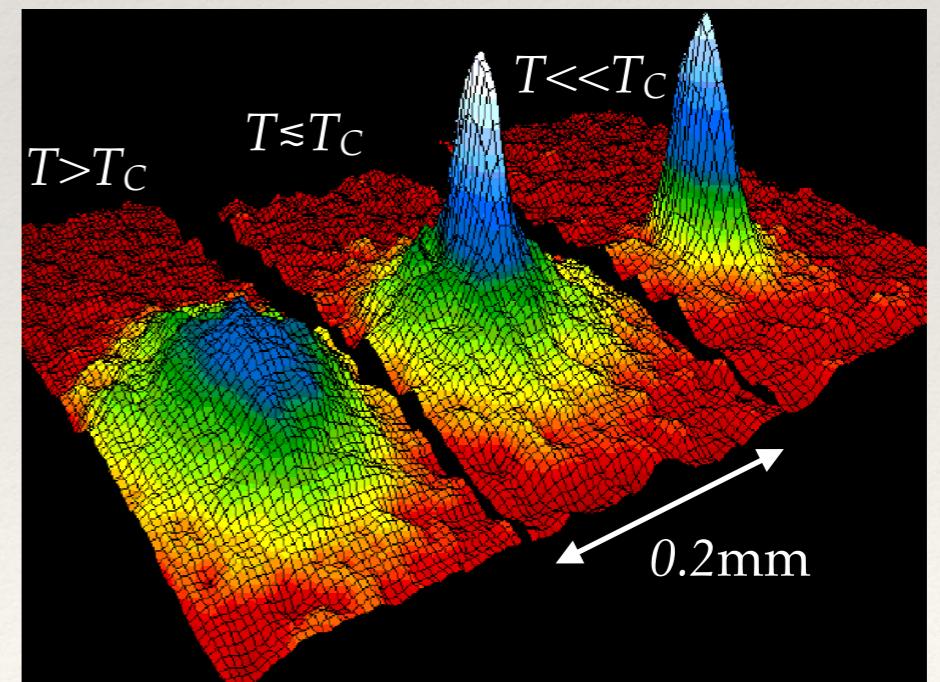
[Cornell, Ketterle, Wiemann, 2001]

Photo of BEC



[image: Wiemann, AJP 64,854 '96]

Velocity distribution



[image: JILA]

Debye Theory of Solids

Atoms in a solid are arranged in crystalline patterns (e.g. figure)

They are stuck in their positions but they can vibrate.

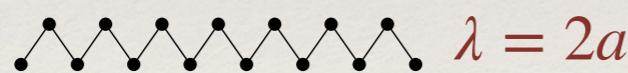
Einstein model: each atom vibrates independently

- Good starting point but not very accurate
- Atoms vibrate *collectively*: one atom wiggles, its neighbors start to wiggle too. *sound waves*

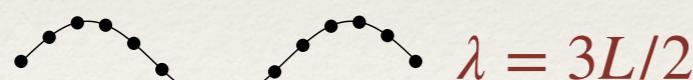


Sound waves are very similar to EM waves with some differences:

1. They travel with the speed of sound ($c_s \sim$ few thousand m/s in solids)
2. They have 3 polarizations (2 transverse “shear waves”, 1 longitudinal “pressure wave”)
3. The wavelength can’t be shorter than twice the distance between atoms (a)



:



Debye Theory of Solids

Quantum mechanically sound waves have a discrete energy spectrum:

$$\epsilon = \hbar\omega = c_s \hbar |\vec{k}| = c_s \frac{2\pi\hbar}{\lambda} = \frac{\pi\hbar c_s n}{L}$$

Quantized sound waves: *phonons* (similar to quantized EM waves, *photons*)

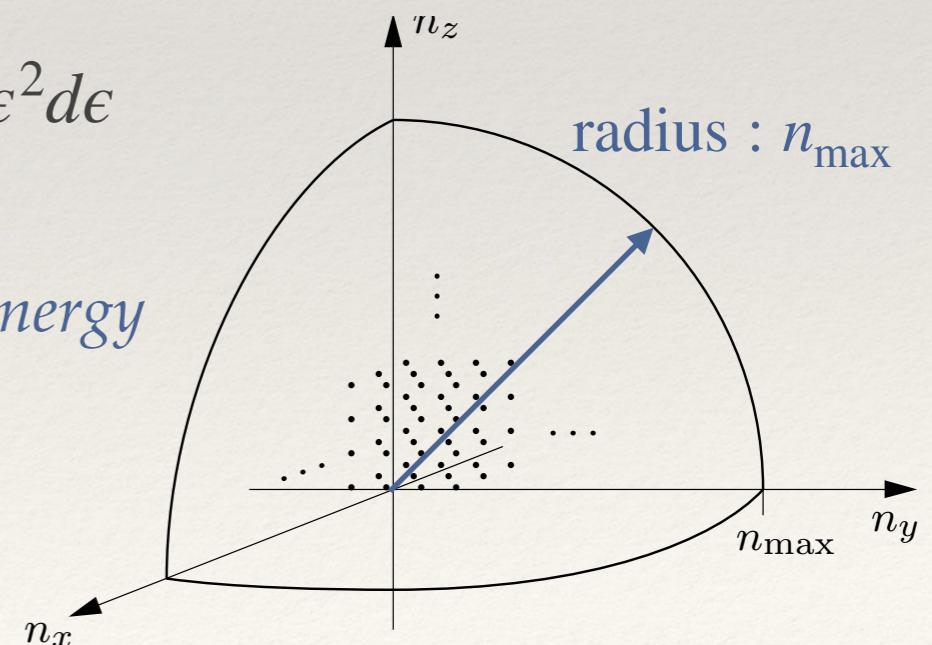
They are spin-1 bosons: 3 spin d.o.f = 3 polarizations

Debye theory of solids: a gas of phonons

Density of states: $g(\epsilon)d\epsilon = 3 \times \frac{1}{8} \times 4\pi n^2 \times dn = \frac{3V}{2\pi^2\hbar^3c_s^3}\epsilon^2d\epsilon$

Minimum wavelength \leftrightarrow Maximum $n \leftrightarrow$ Maximum energy

$$n_{\max} \sim \frac{1}{\lambda_{\min}} \sim \frac{1}{\text{lattice spacing}} \sim \left(\frac{V}{N}\right)^{1/3}$$



Debye Theory of Solids

Debye's smart idea: number of single phonon states = $\int_0^{\epsilon_{\max}} g(\epsilon) d\epsilon = N_{dof} = 3N$ 3=number of space dimensions

Each single phonon state represents a degree of freedom!

$$\int_0^{\epsilon_{\max}} g(\epsilon) d\epsilon = \frac{3V}{2\pi^2 \hbar^3 c_s^3} \int_0^{\epsilon_{\max}} \epsilon^2 d\epsilon = \frac{V \epsilon_{\max}^3}{2\pi^2 \hbar^3 c_s^3} = 3N \Rightarrow \epsilon_{\max} = \frac{\hbar c_s}{L} (6N\pi^2)^{1/3}$$

$$n_{\max} = \left(\frac{6N}{\pi} \right)^{1/3}$$

$$T_D = \frac{\epsilon_{\max}}{k} = \frac{\hbar c_s}{k} \left(\frac{6N\pi^2}{V} \right)^{1/3}$$

Temperature where the highest frequency phonon starts to get excited

Ranges from 100K (soft materials) to 2000K (diamond)

For most solids $T_D \sim$ room temp. $\pm 100K$

Debye Theory of Solids

Total phonon energy:

$$U = \int_0^{\epsilon_{\max}} g(\epsilon) \bar{n}_{\text{BE}}(\epsilon) \epsilon d\epsilon = \frac{3V}{2\pi^2 \hbar^3 c_s^3} \int_0^{\epsilon_{\max}} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

- *High T: $T \gg T_D$* $\Rightarrow x_{\max} = T_D/T \ll 1 \Rightarrow \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \approx \int_0^{T_D/T} \frac{x^3}{x} dx = \frac{1}{3} \left(\frac{T_D}{T} \right)^3$

$$U \approx 3NkT \quad (\text{equipartition theorem}) \quad C_V = \frac{\partial U}{\partial T} = 3Nk \quad (T \gg T_D)$$

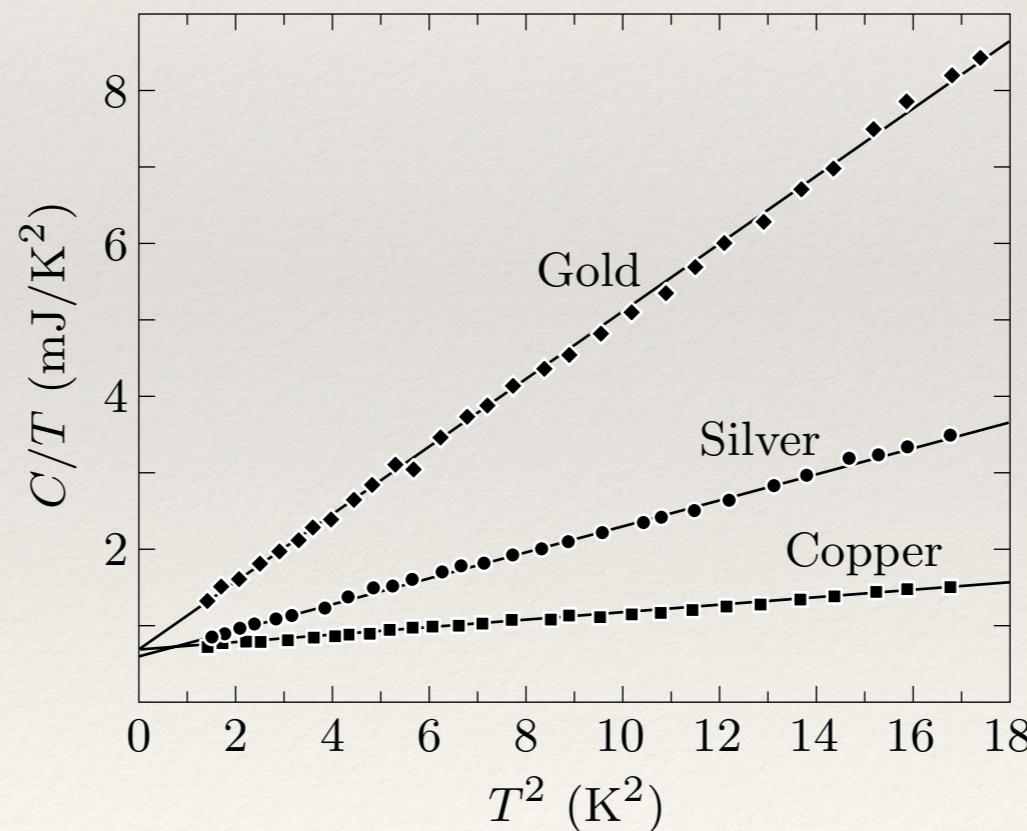
- *Low T: $T \ll T_D$* $\Rightarrow x_{\max} = T_D/T \gg 1 \Rightarrow \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \approx \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$

$$U \approx \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3} \quad C_V = \frac{\partial U}{\partial T} = \frac{12\pi^4}{5} \frac{NkT^3}{T_D^3} \quad (T \ll T_D)$$

Debye Theory of Solids

In *metals* in addition to phonons, *conduction electrons* also contribute to the heat capacity. Their contribution is *linear* in T

$$C_V = \frac{\pi^2 N k^2}{2\epsilon_F} T + \frac{12\pi^4}{5} \frac{N k T^3}{T_D^3} \quad (T \ll T_D)$$



Thank you!