9. Quantum Statistics, 3

lecture 33, November 14, 2017

housekeeping

Honors project

- Instructions for 3 people are up
  - *that was easy*

This week, remember:

- homework workshop will be tomorrow
- homework will be due Friday
- lectures will happen M,T,F

today

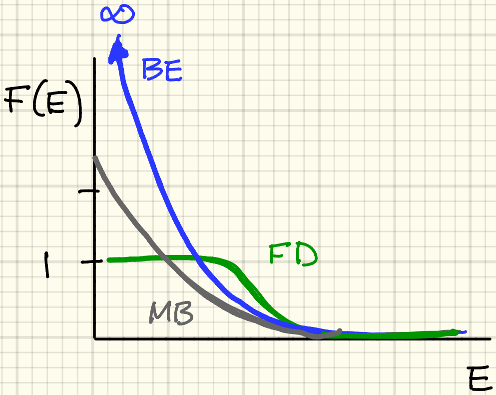
statistical physics - quantum mechanically

Three Probability Distributions

$$F_{MB} = \frac{1}{A\,e^{E/kT}} \qquad \frac{E/kT >> 1}{\text{tiny}}$$

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

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



Remember what these are:

$$n(E)\,dE = g(E)\,F_x(E)\,dE$$

$$\uparrow$$

F_{MB}, F_{BE}, or F_{FD}

can determine A, B, C (e^{α}'s) by

$$\left(\frac{N}{V}\right)_{BE} = \int_0^{\infty} g(E)\,F_{BE}(E)\,dE$$

$$\left(\frac{N}{V}\right)_{FD} = \int_0^{\infty} g(E)\,F_{FD}(E)\,dE$$

Fermi Dirac Distribution

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

typically write $e^{\alpha} = e^{-\varepsilon_F/kT}$

$\varepsilon_F \equiv$ "Fermi Energy"

$$F_{FD}(E) = \frac{1}{e^{(E-\varepsilon_F)/kT} + 1}$$

notice when

- $E = \varepsilon_F$

$$F_{FD}(E) = \frac{1}{1+1} = 0.5$$

$\Rightarrow$ half of the states have $E > \varepsilon_F$

- $E << \varepsilon_F$

$$F_{FD}(E) = \frac{1}{e^{-\varepsilon_F/kT} + 1} \sim 1$$

- $T \to 0$

$F_{FD}(E) \to 0 \quad E > \varepsilon_F$

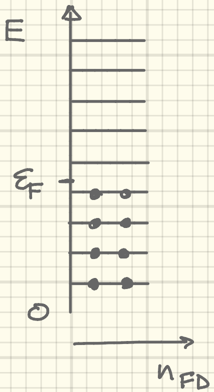
$\to 1 \quad E < \varepsilon_F$

1 per state, as expected.

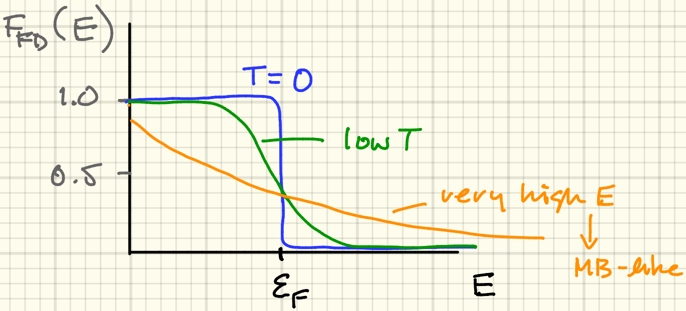
$$F_{FD}(E) = \frac{1}{e^{(E-\varepsilon_F)/kT}+1}$$

at $T=0$

energy levels!



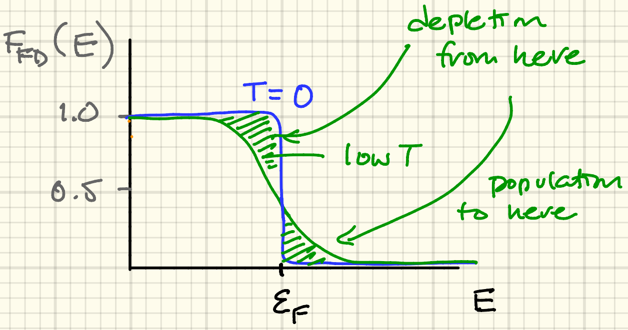
$g(E) = 2$

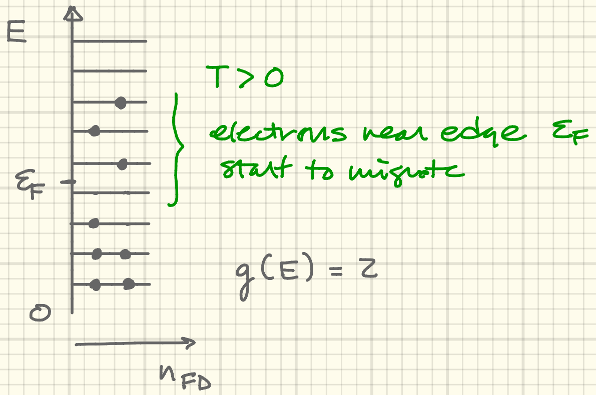


$$n_{FD}(E)\,dE = g(E)\,F_{FD}(E)\,dE$$

↑ # per unit volume

As temperature increase above T=0:





$g(E) = 2$

A metal.

what's the density of states?

General calculation of density of states – variation on book

remember the wave number $\quad k = \frac{2\pi}{\lambda} = \frac{2\pi f}{c}$

$\lambda f = \frac{\omega}{k}$

$\omega = \lambda f k$

$\lambda = \frac{c}{f}, \ \omega = ck$

ME's for harmonic, say, $\vec{E}$

$\vec{E} = \vec{E}(x_1 x_2 x_3) e^{i\omega t}$ lead to the wave equation

$$\nabla^2 \vec{E} = \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}$$

for just one direction, E_1

$$\nabla^2 E_1 = -\mu_0 \epsilon_0 \omega^2 E_1$$

$$\nabla^2 E_1 = -\mu_0 \epsilon_0 c^2 k_1^2 E_1$$

$$\nabla^2 E_1 + k_1^2 E_1 = 0 \longrightarrow k^2 = k_1^2 + k_2^2 + k_3^2$$

w/ harmonic oscillator-like solutions: $E_1 = A \sin(k_1 x_1) \sin(k_2 x_2) \sin(k_3 x_3)$

Put waves inside a cavity of sides L

w/ boundary conditions at sides of cavity: $E=0$ at $x_i=0$ & $x_i=L$

$$\Rightarrow k_i L = n_i \pi$$

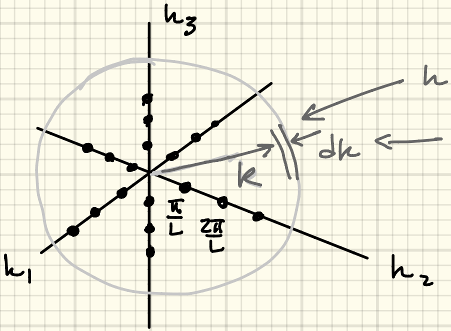
$$n_i = 1,2,3\ldots$$

So: $$k^2 = \frac{\pi^2}{L^2}\left(n_1^2+n_2^2+n_3^2\right)$$

Want density of states..

now for "really classical" electric field standing waves

$$k_i = \frac{n_i \pi}{L}$$



k is a "length" in "k-space"

dk ← another spherical shell

2 polarization states

$$N_{s.w.}(k)\,dk = \frac{4\pi k^2 dk}{(\pi/L)^3} \times \frac{1}{8} \times 2$$

only octant counts

$$N(k)dk = \frac{V k^2 dk}{\pi^2}$$

$$g(k)dk = \frac{k^2 dk}{\pi^2}$$

Now, electrons...

after all, a metal is a container full of electron wave-functions which similarly vanish at edges.

→ your book uses a 3-d infinite well to calculate $g(E)$

We can use the $\vec{E}$ mode calculation

$\times 2$ for polarization → $\times 2$ electron spin ✓

But, k is different... need energy:

$$E = \frac{p^2}{2m_e} = \frac{\hbar^2 k^2}{2m_e} \Rightarrow k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

$$dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2} E^{-1/2} dE$$

Substituting:

$$g(E)\,dE = \frac{8\sqrt{2}\,\pi m^{3/2}}{h^3} dE$$

$$g(E)\,dE = \frac{8\sqrt{2}\,\pi m^{3/2}}{h^3} E^{1/2}\,dE$$

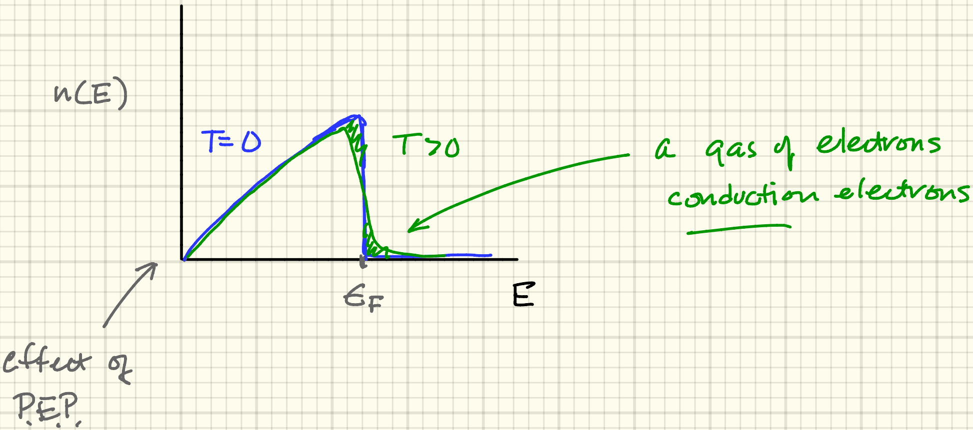
finally

$$n(E)\,dE = g(E)\,F_{FD}(E)\,dE$$

$$n(E)\,dE = \frac{8\sqrt{2}\,\pi m^{3/2}}{h^3} \frac{E^{1/2}}{e^{(E-\epsilon_F)/kT}+1}$$

@ $T=0$, easy

for $T>0$, numerical solution

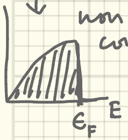


Example – what is the Fermi Energy for gold? How fast are conduction electrons moving at ϵ_F?

$$n(E)\,dE = \frac{8\sqrt{2}\,\pi\, m^{3/2}}{h^3}\,\frac{E^{1/2}}{e^{(E-\epsilon_F)/kT}+1}\,dE$$

can determine ϵ_F at $T=0$
then $F_{FD}(T=0) = 1$

$$\frac{N}{V} = \int n(E)\,dE = \frac{8\sqrt{2}\,\pi\, m_e^{3/2}}{h^3}\int_0^{\epsilon_F} E^{1/2}\,dE = \frac{2}{3}\,\frac{8\sqrt{2}\,\pi\, m^{3/2}}{h^3}\,\epsilon_F^{3/2}$$



so $$\epsilon_F = \frac{h^2}{2m_e}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

Need N/V:

$\rho(\text{gold}) = 19.32\ \text{g/cm}^3$
molar mass $= 197\ \text{g/mol}$

$$\frac{N}{V} = \left(19.32\ \frac{\text{g}}{\text{cm}^3}\right)\left(\frac{1}{197\ \text{g/mol}}\right) N_A\,(\text{mol}^{-1})$$

$$\frac{N}{V} = 5.9\times 10^{28}\ \text{electrons}/\text{m}^3$$

so $\epsilon_F(0) = 8.85\times 10^{-19}\ \text{J} = 5.53\ \text{eV}$

speed: $\epsilon_F = \frac{1}{2} m v^2 \Rightarrow v = \left(\frac{2\epsilon_F}{m}\right)^{1/2} = 1.39\times 10^{6}\ \text{m/s}$ } **FAST**

If a gas of electrons were heated... $kT_F = \epsilon_F$, $T_F = 64\ \text{kK}$!

"fermi temp"

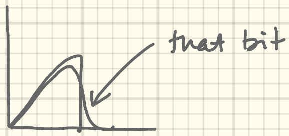
People were confused...

If electrons were classical, heat capacities would be large

$$U = N\left(\frac{3}{2}kT\right) = \frac{3}{2}RT$$

$$C_{el} = \frac{\partial U}{\partial T} = 3/2\,R$$ too large compared to expt.

BUT: only a few percent of electrons contribute



BOSONS

Consider a "gas" of photons $\qquad n(E)dE = g(E)F_{BE}(E)dE$

need (E) ... we did that! $\quad$ We found $\quad g(k)dk = \frac{k^2 dk}{\pi^2}$

since $\quad k = \frac{2\pi f}{c} \qquad g(f)df = \frac{8\pi f^2 df}{c^3}$

since $\quad f = E/h \qquad g(E)dE = \frac{8\pi E^2}{(hc)^3} dE$

$\downarrow$

number with E between E & $E+dE$

Now:

energy density: $\quad u(E)dE = E\,n(E)dE = E\,g(E)F_{BE}(E)dE$

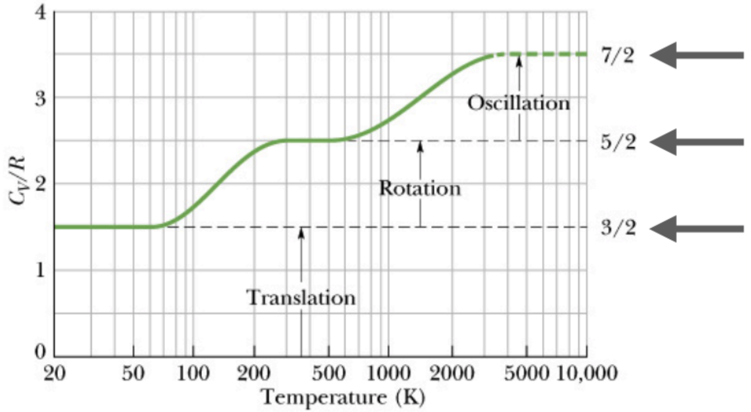
$$u(E)dE = \frac{8\pi}{(hc)^3}\frac{E^3 dE}{e^{E/kT}-1}$$

or

$$u(f)df = \frac{8\pi}{c^3}\frac{f^3}{e^{hf/kT}-1}df$$

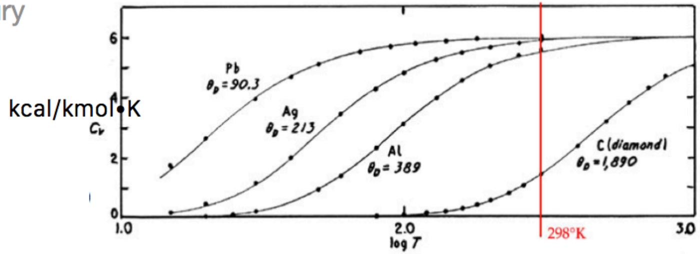
PLANCK'S FORMULA

Einstein's argument, almost.



Specific heats of solids had been confused

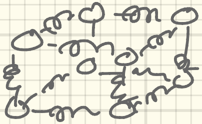
for nearly a century



Lewis & Randall, *Thermodynamics*, Revised by Pitzer & Brewer, 2nd Edition, McGraw-Hill, 1961, p. 56.

MORE BOSONS

Einstein guessed that a crystal lattice must vibrate



→ these vibrations would be quantized according to S.H.O.

Like actual quanta that exist inside lattice

→ "Quasi-particles"

For 1d oscillator ∃ 2 dof: KE & PE, each contributing $\frac{1}{2}kT$

For 3d oscillator: $3 \cdot 2 \cdot \frac{1}{2} kT = 3kT$

energy per mole: $E = 3N_A kT = 3RT$

Remember $C = \frac{\partial E}{\partial T} = 3R$ constant... but experiment saw something different

Probability of having quasi-particles of oscillation is F_{BE}

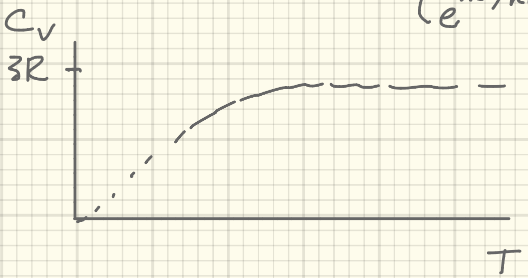
So energy per mole is from $E = 3N_A kT \Rightarrow 3N_A \hbar\omega \times$ prob of having oscillations.

$$E = 3N_A \hbar\omega \frac{1}{e^{E/kT}-1} = 3N_A\hbar\omega \frac{1}{e^{\hbar\omega/kT}-1}$$

Now

$$C_V = \frac{\partial E}{\partial T} = 3N_A\hbar\omega \frac{(e^{\hbar\omega/kT})(\hbar\omega/kT^2)}{(e^{\hbar\omega/kT}-1)^2}$$

$$= [3R]\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}$$



quasi particles are phonons

still MORE BOSONS   Helium

Consider now a gas of bosons → not spin 1, so 1 d.o.f.

$$g(E)\,dE = \frac{8\sqrt{2}\,\pi m^{3/2}}{h^3} E^{1/2}\,dE$$ ... but take back that factor of 2

$$\downarrow$$

$$g_B(E)\,dE = \frac{4\sqrt{2}}{h^3}\pi\, m_B^{3/2} E^{1/2}\,dE$$

$$n_B(E)\,dE = g_B(E)\,F_{BE}(E)\,dE \qquad F_{BE}(E) = \frac{1}{B e^{E/kT} - 1}$$

$$B \leftarrow e^{-\mu/kT}$$

$$N = \int_0^\infty n(E)\,dE = V \cdot \frac{4\sqrt{2}\,\pi\, m_B^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2}\,dE}{e^{(E-\mu)/kT} - 1}$$

$$N = \int_0^\infty n(E)\,dE = V \cdot \frac{4\sqrt{2}}{h^3} \pi m_B^{3/2} \int_0^\infty \frac{E^{1/2}\,dE}{e^{(E-\mu)/kT} - 1}$$

N can't be negative!

$e^{(E-\mu)/kT}$ must be > 0 -- E is > 0 ... so $\mu(T) < 0$ $\exists$ T

change variables $x = E/kT$ & let T $\downarrow$

$$N = V \cdot \frac{4\sqrt{2}}{h^3} \pi m^{3/2} k^{3/2} T^{3/2} \int_0^\infty \frac{x^{1/2}}{e^{x-\mu/kT} - 1}\,dx$$

constant as T $\downarrow$

goes $\downarrow$ as T $\downarrow$

must $\uparrow$ as T $\downarrow$ $\Rightarrow$ $|\mu(T)| \downarrow$

$\Rightarrow$ $\mu(T) \to 0$ as T $\downarrow$

But: problem. At some point $\mu(T) = 0$ $\longrightarrow$ at T_c $\leftarrow$ "critical"

$$N = V \cdot \frac{4\sqrt{2}\,\pi m^{3/2} k^{3/2} T^{3/2}}{h^3} \int_0^\infty \frac{x^{1/2}}{e^{x-\mu/kT} - 1}\, dx$$

max: $$\int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1} = 2.315 \quad \ldots \quad \text{ie, when} \quad \mu(T_c) = 0$$

$$N = V \cdot \frac{4\sqrt{2}\,\pi m^{3/2} k^{3/2} T^{3/2}}{h^3} (2.315)$$

can't compensate to keep N constant

Problem:

can't continue $T \downarrow$

Below T_c ? Trouble. Einstein to the rescue in 1924

Einstein's way out: separate out the ground state, $E=0$

$$N = \int_0^\infty n(E)\,dE = \frac{V \cdot 4\sqrt{2}\,\pi\, m_B^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2}\,dE}{e^{(E-\mu)/kT} - 1}$$

only applies for particles not in g.s.: $E > 0$, not $E = 0$

Below T_c ...

$$N = N_0 + N_n$$

normal LHe: He_I

ground state of He_{II}

as $T \downarrow$ ... N_n is depleted and N_0 increases.

$$T < T_c < T < T_V = 4.2\,K$$

He_{II}

He_I a liquid satisfying $N(T)$

something different

phase transition