VIII. Free Electron Model of Metals[†]

- An electron in a metal encounters the influence of an array (possibly undergoing lattice vibrations) of ions AND the other electrons

  ⇒ A very difficult many-body problem!

- But in metals, electrons move around rather freely!
- Let's assume that
  - interactions with ions are not important!
  - electron-electron interaction is not important!

  ⇒ Free electrons!

- But include the quantum effect that electrons are fermions

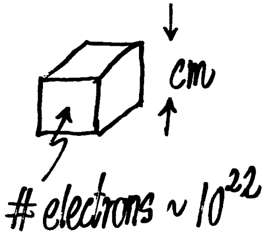
> Q: How far can we go by treating a piece of metal as PARTICLES IN A BIG BOX?

[†] This chapter is a review on materials covered in Quantum Physics and Statistical Mechanics Courses.

A. Free electron Model of Metals

- Conduction electrons are free to move within the solid

$$\therefore \underbrace{\text{Particles}}\ \text{in}\ \underbrace{\text{a big box}}$$



(i) typically $\sim 10^{22\text{-}23}$ conduction electrons in cm^3

(ii) Need Pauli Exclusion Principle

Closely spaced allowed energies ⇒ quasi-continuous

[No new principles!]

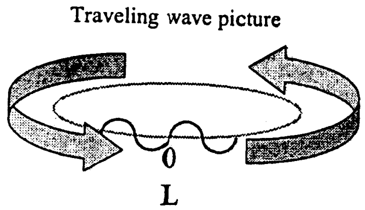
B. 1D Box: Periodic B.C.

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

- In doing solid state physics, it is more convenient to consider travelling waves [instead of standing waves as before]

How? Use a mathematical trick –

Periodic Boundary Condition



like a ring of circumfence L
(mimic an infinite system)

Require:

$$\boxed{\psi(x) = \psi(x+L)}$$

emphasize that surface effect is not important in large piece of metal

$$V=0 \Rightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx} = E\psi$$

$\psi(x) \sim e^{ikx}$ is a travelling wave solution
[k can be negative or positive]

B.C.: $e^{ikx} = e^{ik(x+L)}$

$$\Rightarrow e^{ikL} = 1$$

$$\Rightarrow \boxed{k = \frac{2\pi n_x}{L}\ , \quad n_x = 0, \pm 1, \pm 2, \cdots}$$

Again, we have quantization of wave vector
$\Rightarrow$ quantization of allowed energies

Allowed energies:

$$E_{n_x} = \frac{\hbar^2 k^2}{2m} = \frac{n_x^2 h^2}{2mL^2}$$

$$n_x = 0, \pm 1, \pm 2, \cdots$$

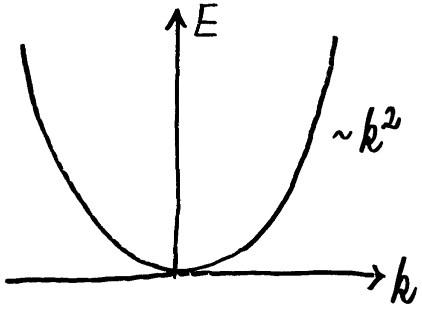
- These are travelling waves solution
- As in standing waves case, k and E are quantized
- Solids: $L \sim$ cm $\Rightarrow$ Big

$\therefore E_{n_x}$ are $\underbrace{\text{closely spaced}}_{(\text{e.g. } \sim 10^{-7}\,\text{eV})}$

"Classical" Physics: (No quantization)

$$E = \frac{\hbar^2 k^2}{2m}$$

$\uparrow$
free particle



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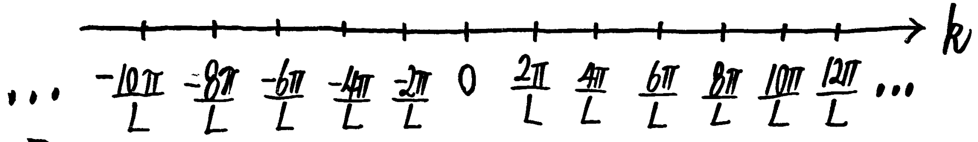
† Note: By convention, "k" is used in describing electronic states and "q" is used in lattice vibrations. They take on similar allowed values.

- Let's indicate the allowed k-values on a k-axis

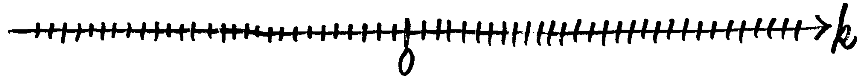
$$k_{n_x} = \frac{2\pi n_x}{L} \;, \quad n_x = 0, \pm 1, \pm 2, \dots$$



"Zoom in"

Note: L large ⇒ allowed k-values are closely spaced

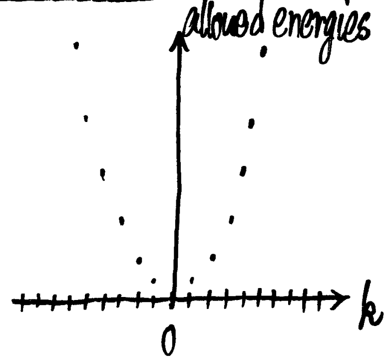
"Zoom Out"



- densely spaced allowed k-values
- $\frac{2\pi}{L}$ between neighboring allowed values

- This k-axis forms a "k-space" (1D)
- Each allowed k-value occupies $\frac{2\pi}{L}$ of k-space

same result as in previous discussion on "q", using periodic B.C.



k-values: evenly spaced
allowed Energies: Not evenly spaced

Concept:

Density of states in k-space†

- How many allowed k-values are there in one unit of k-space? [question is useful as allowed k-values are densely spaced]

$$D(k) = \frac{L}{2\pi} \qquad (1D)$$

- Consider N free electrons in the system
  - ⇒ Pauli Exclusion Principle applies
  - ⇒ fill up allowed states from lowest energy up to an energy called Fermi energy

new concept: important as it sets the energy scale or temperature scale of the problem

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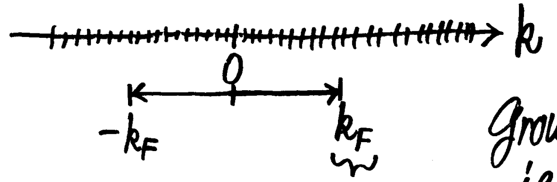
† This is exactly the same result for allowed q-values or allowed $\vec{q}$'s in the phonon problem, since the result stems from the periodic B.C.

- Using <u>Pauli Exclusion Principle</u>:
  - Each allowed k-values $\Rightarrow \underbrace{2}_{\text{"spin-up"/"spin-down"}}$ states $(m_s = \pm 1/2)$
  - fill to $\pm k_F$ in k-space



Ground state i.e. $T = 0$ K

Fermi wave vector

Number of k-values filled

$$= (2k_F) \cdot \underbrace{\left(\frac{L}{2\pi}\right)}_{D(k)}$$

Total electronic states filled

$$= \underbrace{2}_{\substack{\text{spin}\\ \text{up/down}}} \cdot\ 2k_F \cdot \frac{L}{2\pi} = \underbrace{N}_{\substack{\text{must have accommodated}\\ \text{all } N \text{ electrons}}}$$

$$\therefore\ k_F = \frac{N\pi}{2L} \quad (1D)$$

$$\boxed{E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{h^2}{32m}\left(\frac{N}{L}\right)^2}$$

This is $T = 0$K result. But electrons have to fill up to E_F.

- $E_F \sim$ maximum kinetic energy of conduction electrons at 0K (Fermi energy)
- $\dfrac{N}{L} = \dfrac{\text{number of conduction electrons}}{\text{system size (1D)}}$

  = conduction electron "density" (No. per unit length)

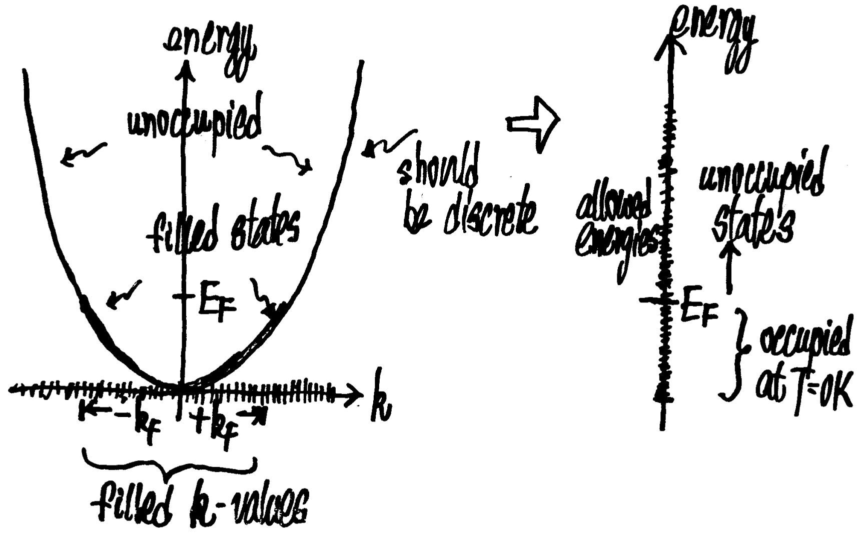
  $\therefore\ E_F \propto (\text{electron number density})^2 \quad (1D)$

<u>Summary (1D)</u>[†]: but concepts applicable in higher dimensions

- periodic BC's: travelling waves
- allowed k's and allowed E
- solid $\Rightarrow$ big system $\Rightarrow$ quasi-continuous k
- Counting $\Rightarrow$ density of states in k-space $\left(\frac{L}{2\pi}\right)$
- Pauli Exclusion Principle $\Rightarrow k_F, E_F$
- E_F is usually quite large as it depends on $\left(\frac{N}{L}\right)^2$
- Although $T = 0$K, electrons fill up to E_F
- Fermi "surface": 2 points $\pm k_F$

[†] This is 1D Ideal Fermi Gas at $T = 0$.

1D box

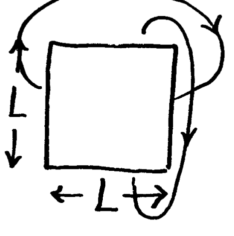


"Fermi Surface": The boundary in k-space that separates occupied and unoccupied states at $T=0$

1D: Fermi surface: 2 points $\pm k_F$

C. 2D Box

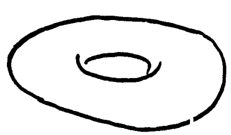
- Consider $L \times L$ 2D Box
- To consider travelling waves solutions, use periodic boundary conditions



$\Downarrow$

- connect ψ of top side to bottom
- connect ψ of left side to right

effectively, we have



"torus"

$$\therefore \quad \psi(x,y) = \psi(x+L,y)$$
$$\psi(x,y) = \psi(x,y+L)$$

recall technique of separation of variables?

Travelling waves: $\psi(x,y) = A e^{ik_x x} e^{ik_y y}$

If we introduce a 2D vector,
$\vec{k} = (k_x, k_y)$
and position vector $\vec{r} = (x,y)$, then
$$\psi(x,y) = A e^{i\vec{k}\cdot\vec{r}}$$

Apply periodic boundary conditions:

$$e^{ik_xL}=1 \text{ and } e^{ik_yL}=1$$

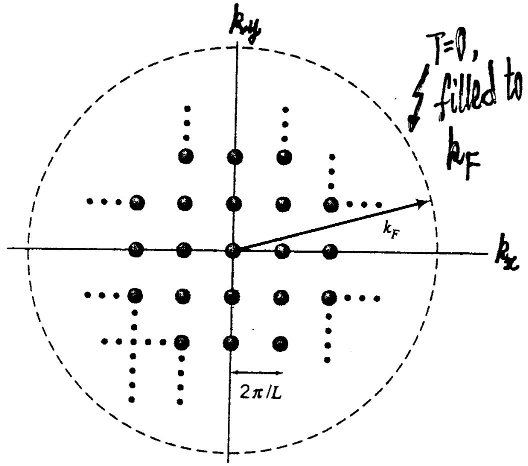
$$\Rightarrow \boxed{\begin{array}{l} k_x=\frac{2\pi n_x}{L} \text{ and } k_y=\frac{2\pi n_y}{L} \\ \text{with } n_x=0,\pm1,\pm2,\dots \\ \qquad n_y=0,\pm1,\pm2,\dots \end{array}}$$

Quantized (k_x,k_y)

Allowed energies: "free-particle states"

$$\boxed{\begin{aligned} E(n_x,n_y) &= \frac{\hbar^2}{2m}(k_x^2+k_y^2) \\ &= \frac{h^2}{2mL^2}(n_x^2+n_y^2) \end{aligned}}$$

Let's indicate the allowed $\vec{k}$-values, i.e. (k_x,k_y) on the 2D $\vec{k}$-space formed by (k_x,k_y)



Allowed electron states in two-dimensional free-electron metal represented by points in a square lattice in two-dimensional k-space.

- Each allowed $\vec{k}$-value occupies $\left(\frac{2\pi}{L}\right)^2$ of k-space
- Density of states in k-space (2D)

$$D(k)=\left(\frac{L}{2\pi}\right)^2 \quad (2D)$$

\# $\vec{k}$-values in one unit "area" of $\vec{k}$-space

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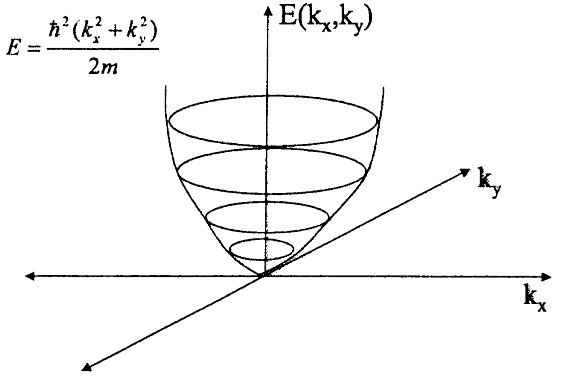


- T=0, fill $\vec{k}$-values up to some $|\vec{k}|=k_F$ (see figure on previous page)
- \# of $\vec{k}$-values in (πk_F^2) area of $\vec{k}$-space $=\left(\frac{L}{2\pi}\right)^2\cdot(\pi k_F^2)$

2D: <u>Fermi surface</u> is a circle of radius k_F (free electron model)

- There are 2 electronic states for each allowed (k_x, k_y) due to spin up/down

$$\therefore \quad N = 2\cdot\left(\frac{L}{2\pi}\right)^2 \pi k_F^2$$

$$\text{OR} \quad k_F^2 = 2\pi\underbrace{\left(\frac{N}{L^2}\right)}_{\substack{\text{areal conduction}\\ \text{electron number density}}} \quad \underline{\text{OR}} \quad \overset{\substack{\text{Fermi wavevector}\\ \downarrow}}{k_F} = \left(\frac{2\pi N}{L^2}\right)^{1/2}$$

$$\text{Fermi energy} = E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$\Rightarrow \boxed{E_F = \frac{h^2}{4\pi m}\left(\frac{N}{L^2}\right) = \frac{\pi\hbar^2}{m}\left(\frac{N}{L^2}\right)} \quad (2D)$$

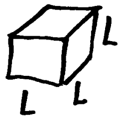
$$\sim \underset{\substack{\uparrow\\ \text{areal number}\\ \text{density}}}{n^1}$$

$$\text{c.f. } \underline{1D}: \quad E_F \propto \underset{\substack{\uparrow\\ \sim(\text{linear number density})^2}}{\left(\frac{N}{L}\right)^2} \quad (1D)$$

This is 2D Ideal Fermi Gas at $T=0$.

D. 3D Box [bulk metal]

- Again apply periodic conditions



(L^3)

$$\psi(x,y,z) = A e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

$$= A e^{i\vec{k}\cdot\vec{r}}$$

Now, $\vec{k} = (k_x, k_y, k_z)$; $\vec{r} = (x,y,z)$

- $$\boxed{\begin{array}{l}\text{B.C.'s} \Rightarrow \text{Allowed } \vec{k}\text{'s are quantized}\\ k_x = \dfrac{2\pi n_x}{L}, \quad k_y = \dfrac{2\pi n_y}{L}, \quad k_z = \dfrac{2\pi n_z}{L}\\ n_x, n_y, n_z = 0, \pm1, \pm2, \pm3, \ldots\end{array}}$$

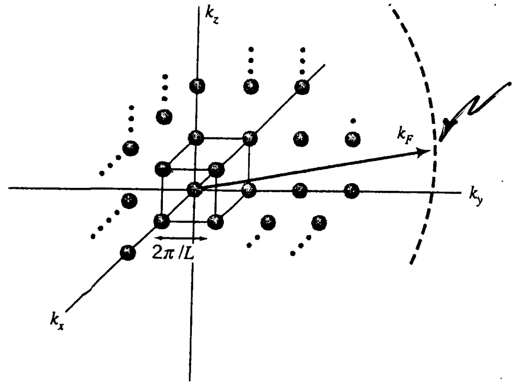
- Allowed energies

$$E(n_x, n_y, n_z) = E(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$= \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\text{Again, Quantized but } \underbrace{\underline{\text{closely spaced}}}_{L\sim \text{cm or mm}}!$$

- Let's indicate the allowed $\vec{k}$-values (k_x, k_y, k_z) on a 3D $\vec{k}$-space



Allowed electron states in three-dimensional free-electron metal represented by points in a cubic lattice in three-dimensional k-space.

T=0
fill up to k_F

3D: Fermi surface is a spherical surface of radius k_F

- Each $\vec{k}$-value "occupies" a "volume" of $\left(\frac{2\pi}{L}\right)^3$
- Density of states in $\vec{k}$-space

$$D(\vec{k}) = \left(\frac{L}{2\pi}\right)^3$$

\# allowed $\vec{k}$-values per unit "volume" of $\vec{k}$-space

- T=0, fill allowed $\vec{k}$-values to a radius of $\underbrace{k_F}_{\text{Fermi wave vector}}$

Filled $\vec{k}$-values form a sphere

$$E_F = \text{Fermi Energy} = \frac{\hbar^2 k_F^2}{2m}$$

$$N = \underbrace{2}_{\text{spin}} \cdot \underbrace{\left(\frac{4\pi}{3} k_F^3\right)}_{\substack{\text{volume of}\\ \text{filled states}\\ \text{in } k\text{-space}}} \cdot \left(\frac{L}{2\pi}\right)^3$$

$$\therefore \quad k_F^3 = 3\pi^2 \underbrace{\left(\frac{N}{L^3}\right)}_{n}$$

n = conduction electron number density $\sim 10^{22}/\text{cm}^3$

the "N_e" in Drude model

$$\text{or } k_F = (3\pi^2 n)^{1/3}$$

$$\boxed{E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{L^3}\right)^{2/3} \qquad (3D)} \sim n^{2/3}$$

- Note different dependence of E_F on "number density" in 1D, 2D, 3D
- A number worths remembering:

$$\boxed{\frac{\hbar^2}{\underset{\substack{\uparrow\\ \text{use mass of electron}}}{m}} = 7.62 \text{ eV} \cdot \text{Å}^2}$$

Useful for doing estimations

- Alkali metals, $\frac{N}{L^3} \sim 10^{22}\text{-}10^{23}/\text{cm}^3$ or $10^{28}\text{-}10^{29}/\text{m}^3$

$$\boxed{E_F \sim \text{few eV (e.g. } 4-5\text{ eV)}}$$

$$k_F^3 = 3\pi^2\left(\frac{N}{L^3}\right) \Rightarrow \boxed{k_F \sim 10^{10}\text{ m}^{-1}}$$

$\hbar k_F \sim$ momentum

$$\boxed{\frac{\hbar k_F}{m} \equiv \text{Fermi velocity} \sim 10^6\text{ ms}^{-1}} = \text{maximum electron velocity } (T=0)$$

($\lesssim 1\%$ of speed of light)

These are typical numbers for metals

Note: This is $\underline{T=0}$ situation.

- But Pauli Exclusion Principle requires that electrons fill up to $E_F \sim$ few eV
- In terms of temperature, (still $T=0$ physics)

$$\boxed{T_F \equiv \frac{E_F}{k_B} \sim 10^4\text{ K} \quad \text{(Fermi Temperature)}}$$

k_B ↗ Boltzmann constant

$\therefore$ the system has a characteristic temp. scale of 10^4K

room temp. or lower ↘ $T < T_F \Rightarrow$ "low temp", $\therefore$ usually dealing with low temperatures!

		Fermi Energy ↓	Fermi Temperature ↓	Fermi wavevector ↓	Fermi velocity ↓
ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm^{-1}	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

[a] The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 9.11 \times 10^{-28}$ grams.

[from Ashcroft and Mermin, Solid State Physics]

- Appreciate how a little piece of quantum physics, namely Pauli Exclusion Principle, leads to a drastic change in the understanding of metals!
- Important to note order of magnitude.

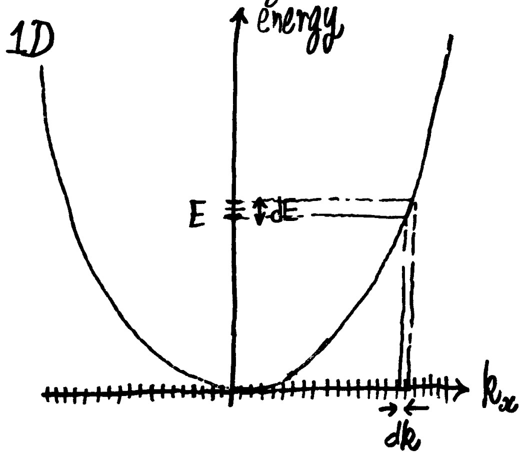
Remark:

- Why k-space?
  - Note that it is a reciprocal space, as the units of k_x, k_y, k_z are $1/m$ or $1/cm$
  - Convenient since allowed k-values (states) are uniformly distributed in k-space.

E. Density of states in Energy[+]

- This is the most important quantity in describing a solid

What is the question?



How many allowed electronic states are there at energy E in an interval dE?

Ans: $\underbrace{g(E)}_{\text{DOS in energy or DOS}}dE$

[+] See the discussion on $D(\omega)$.

- The answer depends on:
  - 1D or 2D or 3D
  - $E(k_x)$, $E(k_x, k_y)$, $E(k_x, k_y, k_z)$ i.e. $\underbrace{E(\vec{k})}_{\text{"Band structure"}}$

1D: (See figure on previous page)

- Project from E on to k-space

Do you see that for the same dE, there are more states (higher g(E)) for small E and fewer states (lower g(E)) for high E?

$$g(E)\,dE = \boxed{2}\cdot D(k)\,dk \cdot 2$$

spin

projected onto +k and -k

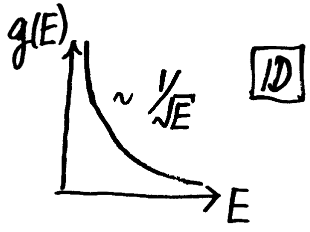
when up and down spins follow the same E(k)

$$\Rightarrow g(E) = 4\cdot\left(\frac{L}{2\pi}\right)\cdot\frac{1}{\left(\frac{dE}{dk}\right)}$$

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow \frac{dE}{dk} = \frac{\hbar^2 k}{m} = \hbar\sqrt{\frac{2E}{m}}$$

$$\therefore\quad g(E) = \frac{L\sqrt{2m}}{\pi\hbar}\,\frac{1}{\sqrt{E}} \sim E^{-1/2} \quad (1D)^{\dagger}$$

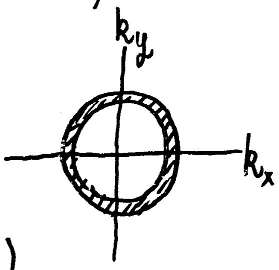
[useful in quasi 1D systems, e.g. quantum wire]



2D: Project from E on to k-space (a ribbon or ring on k-space)

$$g(E)\,dE = \overset{\text{spin}}{\boxed{2}} \cdot \overbrace{D(k)}^{\left(\frac{L}{2\pi}\right)^2} \cdot (2\pi k\,dk)$$

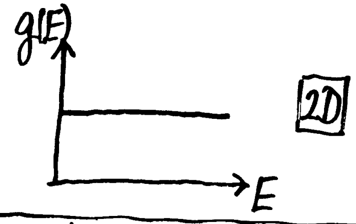
$$g(E) = 2\left(\frac{L}{2\pi}\right)^2 2\pi k \frac{1}{\frac{dE}{dk}}$$



Using $E = \frac{\hbar^2 k^2}{2m}$, (isotropic)

$$g(E) = \frac{mL^2}{\pi\hbar^2} \propto E^0 \quad (2D)^{\dagger}$$

(independent of E)



(useful in quantum well, 2D electron gas)

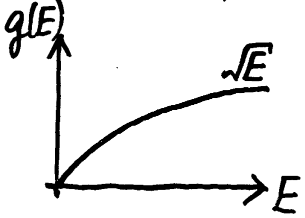
[†] In some books, g(E) is defined to be the DOS <u>per unit volume</u> of sample. In that case, the factor L and $L^2 = A$ in the results are cancelled off.

3D:

$$g(E)\,dE = 2 \cdot \left(\frac{L}{2\pi}\right)^3 \cdot \underbrace{4\pi k^2\,dk}_{\text{project from E to k-space is a shell}}$$

Using $E = \frac{\hbar^2 k^2}{2m}$,

$$g(E) = \frac{L^3}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \sqrt{E} \quad \propto E^{1/2} \quad (3D)$$



$L^3 = V$ = volume of sample

Key result:

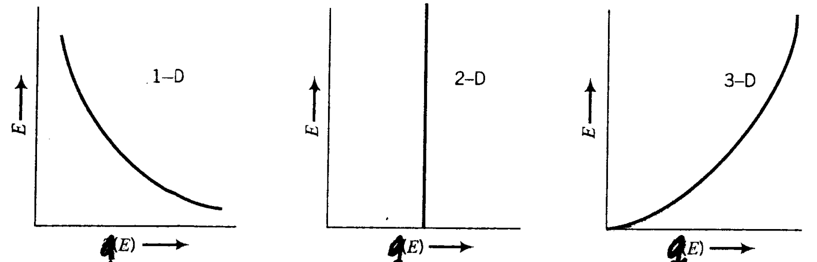
For 3D "parabolic band", i.e. $E = \frac{\hbar^2 k^2}{2m}$,

the DOS $g(E) \sim \sqrt{E}$

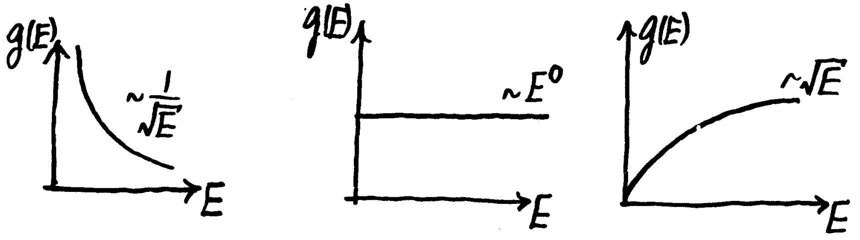
[useful in considering semiconductors]

- Even identical $E = \frac{\hbar^2 k^2}{2m}$, different dimensions give very different DOE!

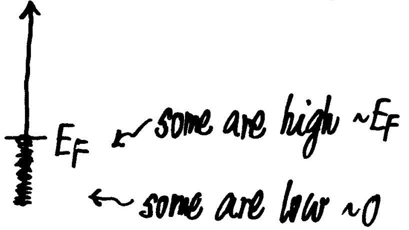
DOE



Shapes of density-of-states function $Z(E)$ in 1-D, 2-D, and 3-D free-electron metals.



Average energy of electron at $T=0$?



average = ?

- states are occupied to E_F

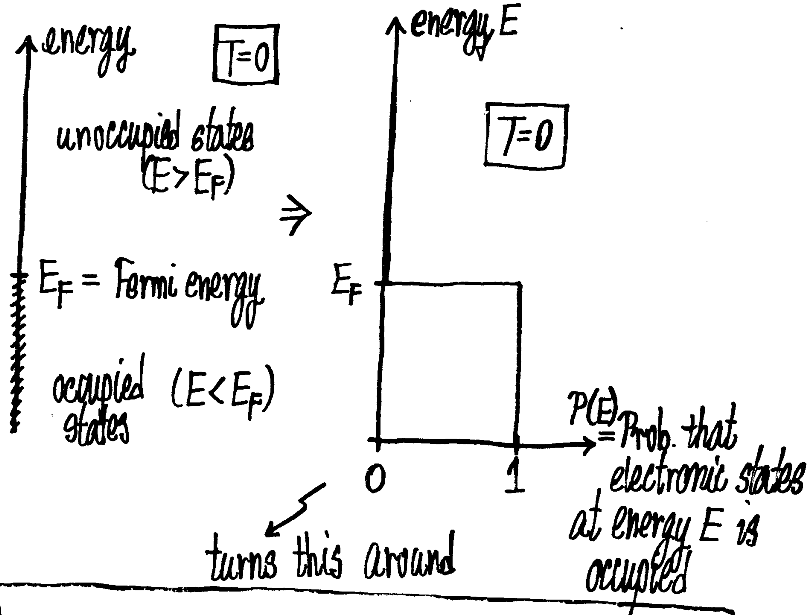
$$\therefore\ N = \underbrace{\int_0^{E_F} g(E)\,dE}_{\text{add up all states with } E < E_F}$$

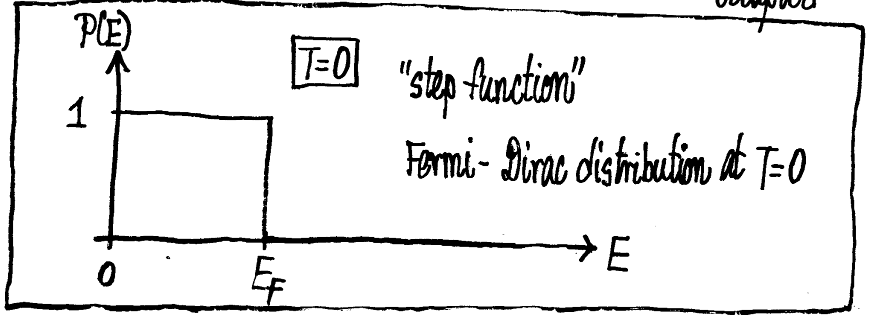
$$\int_0^{E_F} E\cdot g(E)\,dE = \text{total energy of all occupied states}$$

Average electron energy (3D)

$$= \frac{\int_0^{E_F} E\cdot\sqrt{E}\,dE}{\int_0^{E_F}\sqrt{E}\,dE} = \underbrace{\frac{3}{5}E_F}_{\text{quite high!}}$$

F. Temperature effects





"step function"

Fermi-Dirac distribution at $T=0$

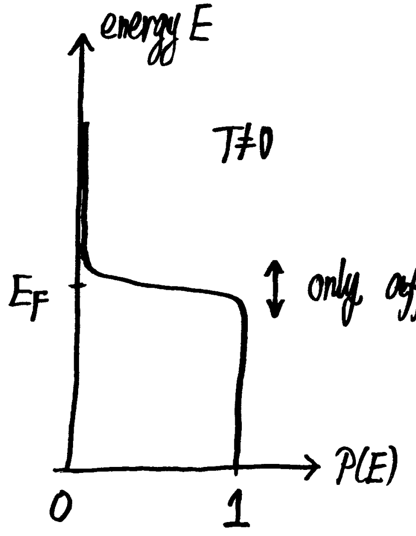
$T \neq 0 \Rightarrow$ Some thermal energy available for the electrons

- Recall : $T_F \sim 10^4$ K

  Room temperature : $\underbrace{T \ll T_F}$

  $\therefore$ Due to Pauli Exclusion Principle, k_BT <u>can't do much</u>!

  - Can only affect those electrons near E_F



$\updownarrow$ only affects a small range of $\sim k_BT$ near E_F

Mathematically,

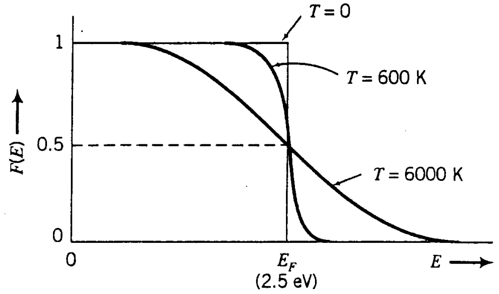
$$\boxed{\text{Fermi-Dirac distribution function: } F_{FD}(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}}$$

μ = chemical potential

$\mu(T=0) = E_F$

$\mu = \mu(T)$

This applies to systems of many electrons



Shape of Fermi function $F(E)$ at different temperatures (for $E_F = 2.5$ eV).

$$F_{FD}(E=\mu) = \frac{1}{2} \quad \text{for } T \neq 0$$

- States far above E_F, i.e. $(E-E_F) \gg k_BT$, are <u>hardly occupied</u> as[+]

$$F_{FD}(E) \approx e^{-(E-E_F)/k_BT} \quad \text{(tiny chance)}$$

- States far below E_F, i.e. $E_F - E \gg k_BT$, are <u>hardly unoccupied</u> as

$$F_{FD}(E) \approx 1 - e^{-(E_F-E)/k_BT} \approx 1$$

[+] For temperatures of interest and E_F for good conductors, $\mu(T)$ shifts only slightly with T.

- Comparing what is being changed at $T \neq 0$ and $T = 0$, only a tiny fraction of electrons at $E \cong E_F$ are changed

  ⇒ "Fermi Surface effects"

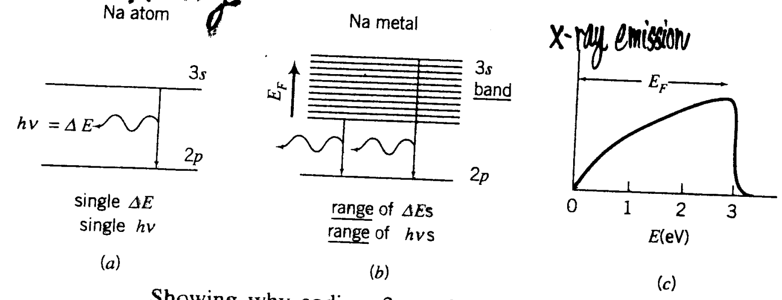
  (Don't need to worry about low-lying states!)

G. Measuring Fermi Energy with X-ray spectroscopy

Q: Do conduction electrons in metals really behave as if they are free electrons?

- Use high-energy electrons to knock out inner shell electrons

  ⇒ X-ray



Showing why sodium $3s \rightarrow 2p$ electron transition gives (a) a single x-ray energy in an isolated atom, but (b) a range of energies (equal to the Fermi energy) in solid sodium. (c) X-ray emission data from $3s \rightarrow 2p$ transition in solid sodium, setting $E = 0$ for transition from bottom of $3s$ band. (Adapted from F. Seitz, *Modern Theory of Solids*, McGraw-Hill, New York, 1940.) The width of the x-ray emission band yields an experimental value for the Fermi energy.

- From range of X-ray emission ⇒ E_F

Experimental and Calculated Values of Fermi Energy (in eV)

Element	Li	Na	K	Cu	Au	Be	Mg	Zn	Al
E_F(calculated)	4.7	3.2	2.6	7.1	5.5	14.3	7.2	9.5	12.8
E_F(experimental)	3.9	2.8	1.9	6.5	5.4	13.8	7.6	11.5	11.8

- Measured values are in reasonable agreement with free-electron model

∴ Conduction electrons in metals are not very different from free electron waves in a big box!