

# Solid State Physics

PHY2002

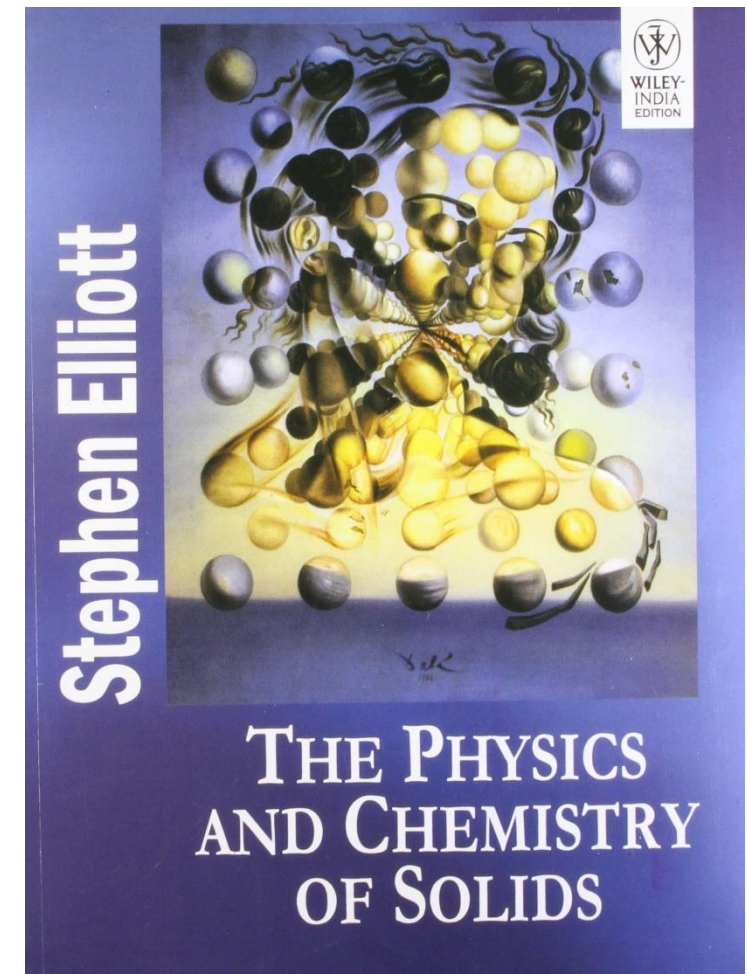
# Electrical Properties of Solids

(8 lectures + 1 assignment class)

- Dr Raymond McQuaid (IRCEP office 01.021)
- Contact by email ([r.mcquaid@qub.ac.uk](mailto:r.mcquaid@qub.ac.uk)) or Teams
- Canvas: Lecture notes, recordings and 2nd assignment

# Textbooks

- Many books on solid state cover material in this course (we will not follow a particular text):
- “Solid state physics” J. S. Blakemore (QC176 BLAK)  
Nice balance of description and rigour
- “Introduction to Solid State Physics”, Kittel (QC176 KITT)  
Classic text in its eighth edition; authoritative but not overly descriptive
- “The physics and chemistry of solids” Elliott (QC176 ELLI)  
Nice balance between description and rigour
- Online accessible:  
"Solid state physics" Hook & Hall, (ebook link on Canvas)



# 4th Quarter lectures

## Lectures 1-2

Classical theory, quantum free-electron gas

## Lectures 3-6

Periodic lattice potential, semiconductors, holes, effective mass,

## Lectures 7,8

Doping and devices,

## Lecture 9

Assignment class

# Some key takeaways from this part of the course

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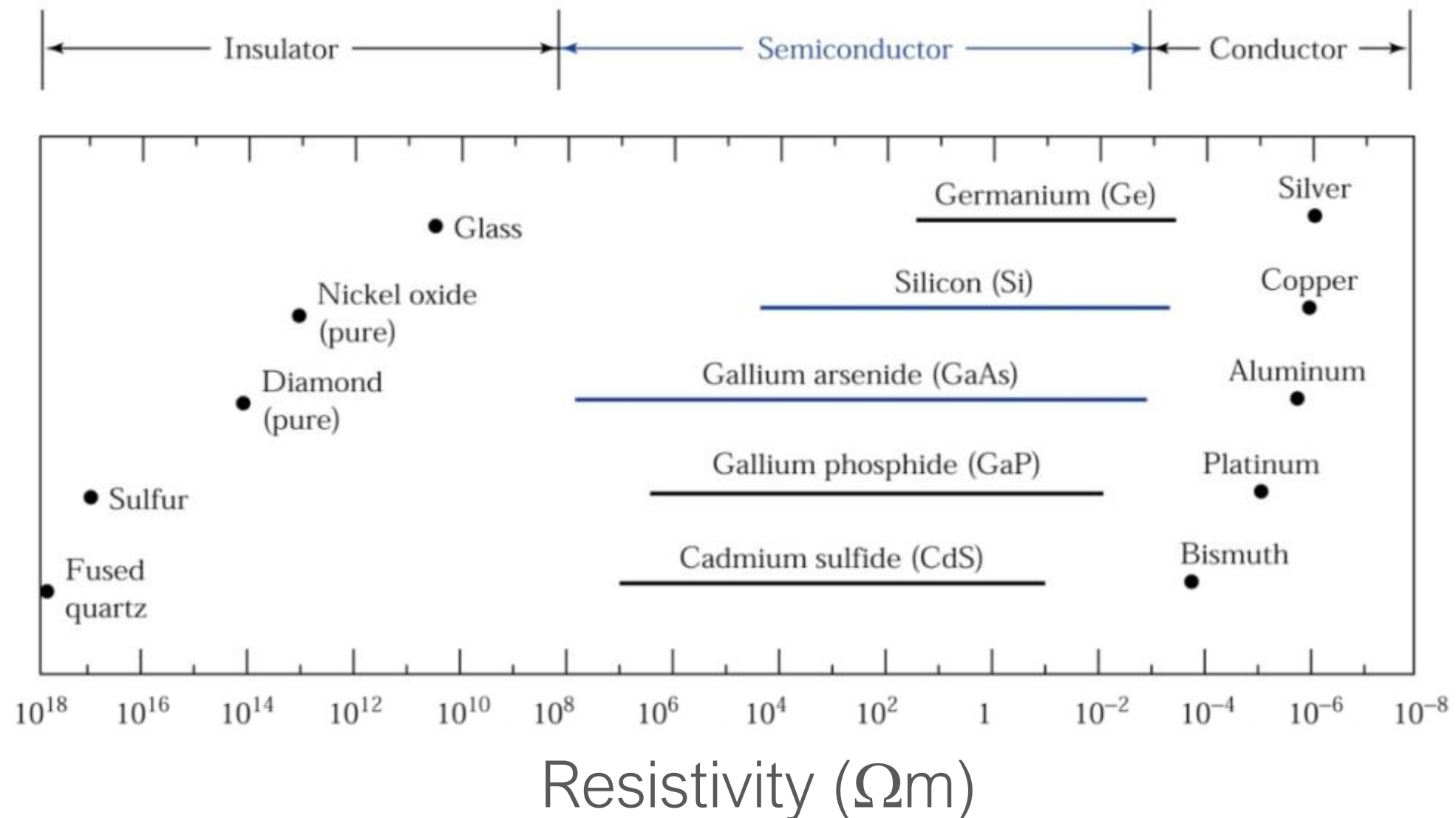
- The classical theory of metals has a number of serious shortcomings and outright failures
- These can only be resolved through a quantum picture of the “free electron gas” where electrons are treated as waves and occupy states according to Fermi-Dirac statistics. The idea of the “Fermi level” becomes all-important in determining thermal and electrical transport properties .
- The effect of the periodic ion lattice on the electron waves leads to “energy bands” and the possibility of insulating and semiconducting behaviour as a result
- The behaviour of intrinsic semiconductors can be described through energy bands and classical statistics and the classical picture of transport becomes useful in this case
- The effect of doping, and its consequences for devices, can be accounted for by considering the behaviour of the Fermi level

# Aims & Objectives (first part)

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- Revisit classical picture of metallic behaviour and identify its successes/shortcomings
- Introduce electron wave approach and see how this can begin to reconcile issues with classical approach (Matthiessen's rule)
- Identify assumptions and formalism of the free electron gas description of electrons in a metal
- Obtain the free electron  $E$ - $k$  dispersion and the related Density of States  $D(E)$  function
- Appreciate implications for electron state occupation given by Fermi-Dirac statistics  $f(E)$  and derive the Fermi Energy  $E_F$
- Explain how electron  $k$ -state occupation is consistent with no current in ambient conditions and how applied electric fields lead to prediction of a current

# Current flow in solids is almost all due to movement of electrons



- Conduction of electricity in solids varies widely
- Resistivity spanning  $\sim 10^{24}$  orders of magnitude perhaps the widest range occupied by any physical property measurable in the lab

# Recap of classical theory of electrical transport in metals

## Physical picture:

- A metal is pictured as formed of stationary charged ions where outer electrons have become fully detached and freely roam the crystal, colliding with ions (but not other electrons) under random thermal motion
- Electric field ( $\varepsilon$ ) accelerates electrons between ion collisions leading to average 'drift velocity' along field axis and net current flow

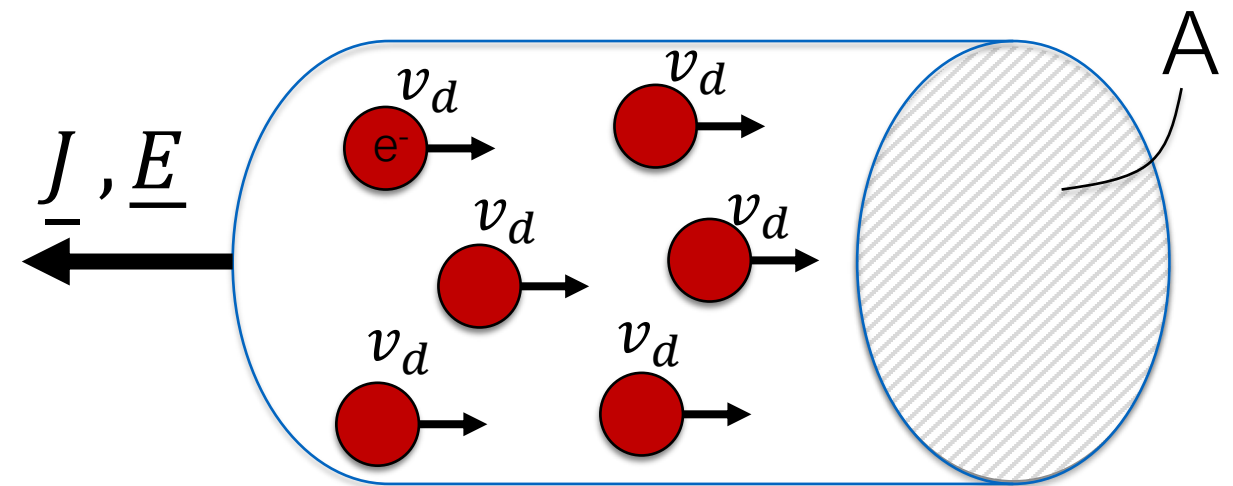
$$J = \frac{I}{A} = nq v_d$$

$$v_d = \langle \Delta v \rangle = -\frac{e\varepsilon\tau}{m_e}$$

$\tau$  is average time between electron-ion scattering events

$$J = -ne \left[ -\frac{e\varepsilon\tau}{m_e} \right] = \frac{ne^2\tau}{m_e} \varepsilon$$

$$J = \sigma \varepsilon \quad \text{where} \quad \sigma = \frac{ne^2\tau}{m_e}$$





# Success and failures of classical (Drude) theory

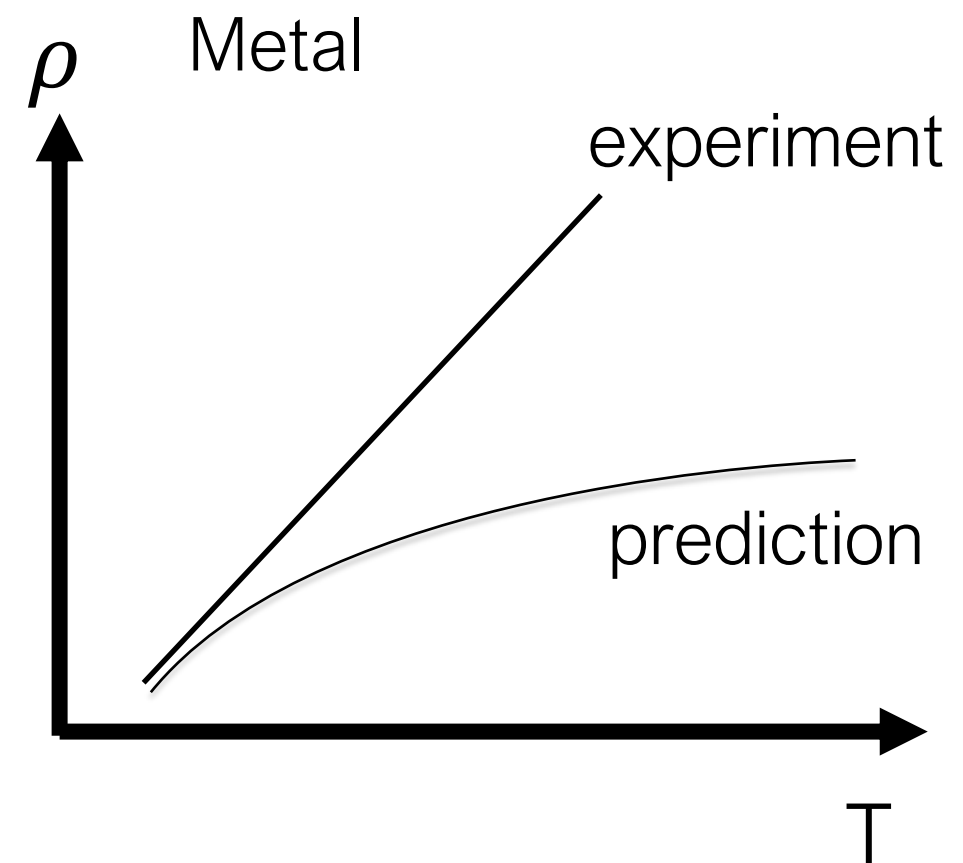
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## Successes:

1. Explanation for microscopic origin of resistance (electron scattering)
2. Can predict Ohm's Law
3. Good order of magnitude value of conductivity

## Failures :

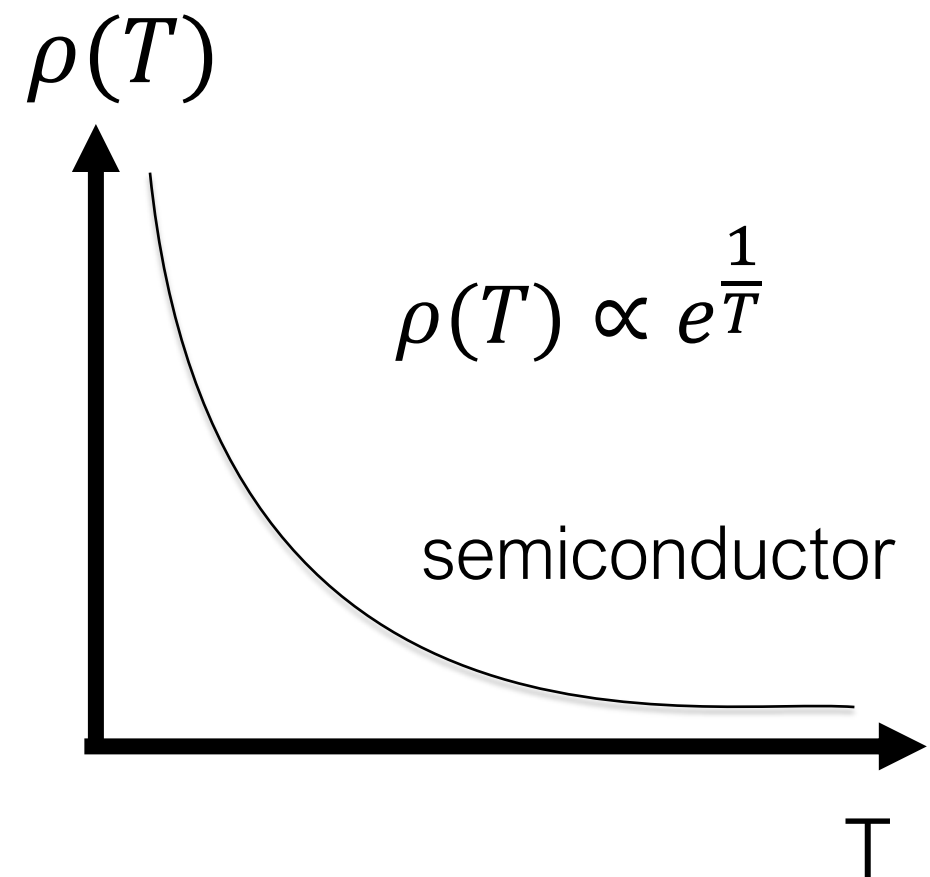
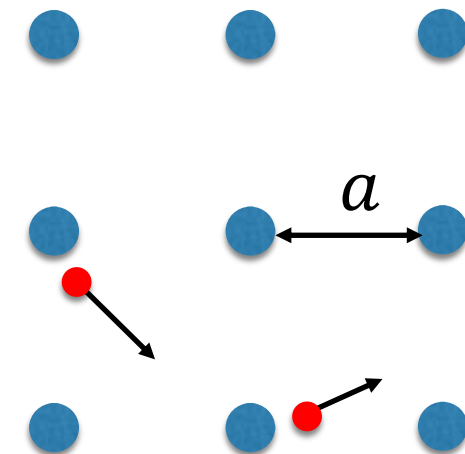
1. Conductivity  $\sigma$  expected to increase proportionally with the number density of valence electrons  $n$  for a wide range of common metals that have similar sized ions and packing densities. Not the case experimentally (e.g.  $\sigma_{Cu} > \sigma_{Pb}$ , even though Pb has 4 free electrons per atom and Cu only has 1)
2. Resistivity predicted to scale with temperature as  $T^{0.5}$  but experimentally  $\rho(T) \propto T$



# Success and failures of Drude's theory

## Failures :

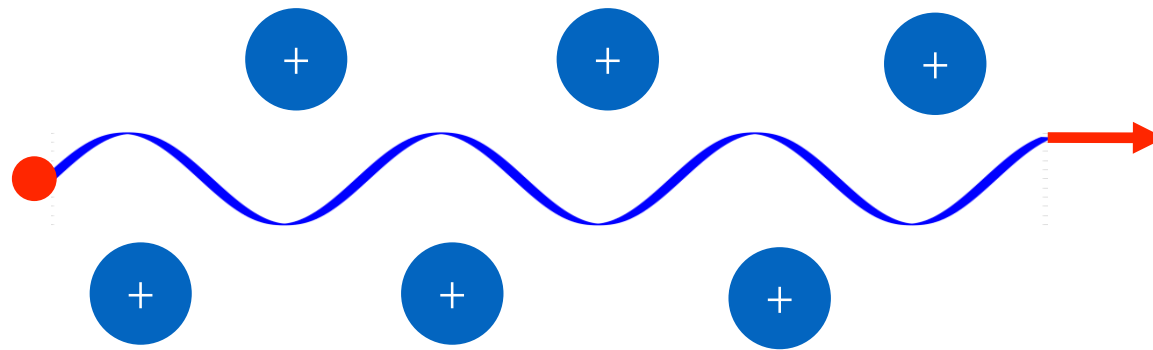
3. Mean free path of electrons: For random scattering from hard-sphere ions, expect mean free path  $\lambda$  on order of the inter-ionic separation  $a$ , i.e.  $\sim 1-10 \text{ \AA}$ . Experimentally,  $\lambda \sim 1000 \text{ \AA}$  as temperature is cooled. For some very pure metals at low temperature,  $\lambda \sim 1 \text{ cm}$  i.e. electron travels  $\sim 10^8$  interatomic spacings before a single collision!
4. Prediction of semiconducting behaviour (decreasing resistivity as temperature increased)
5. Unable to rationalise positive Hall coefficients (existence of electron holes)
6. Grossly overestimates contribution of electrons to heat capacity



# Electron wave picture (towards a quantum description)

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- Here we consider electron wavefunctions travelling through the solid
- As in the classical case, the microscopic origin of resistance is due to electron **scattering** but treated in a wave picture

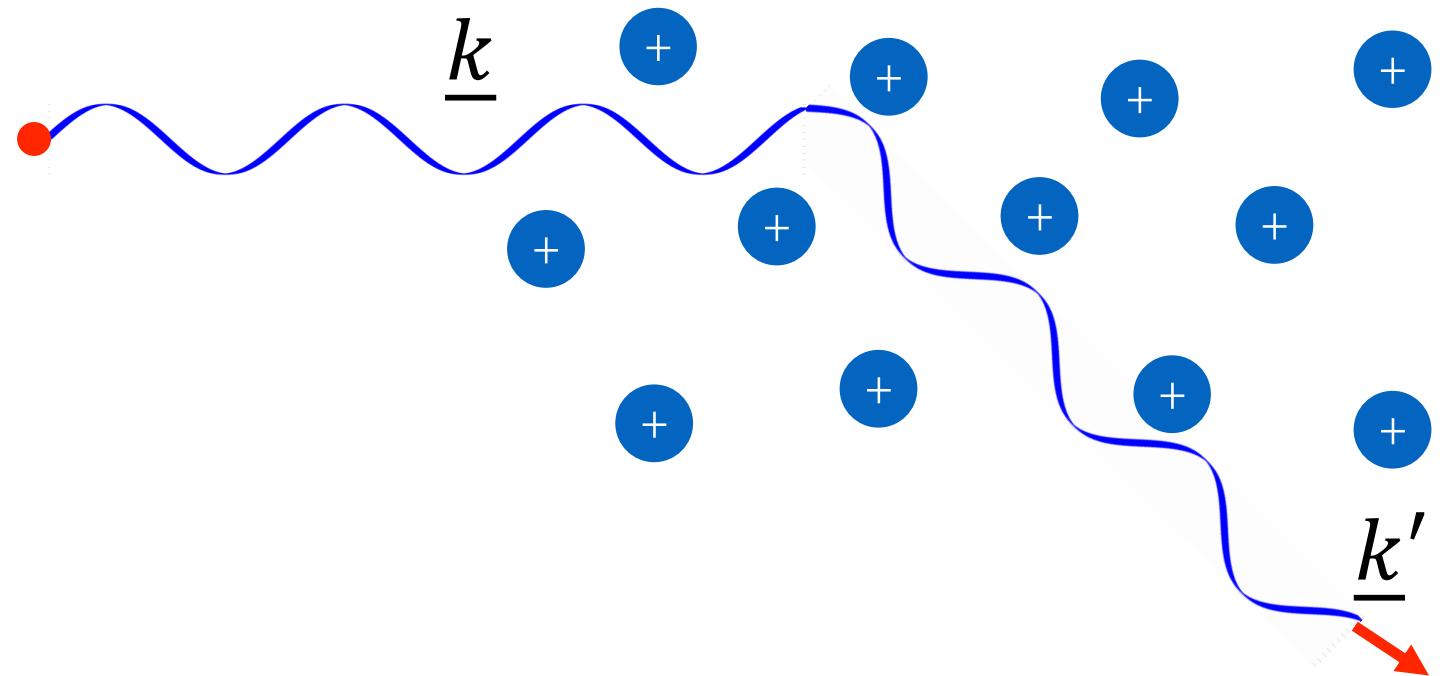


**Key idea:** A perfect periodic lattice does not scatter electron waves and resistance is due to any deviations from perfect lattice periodicity. Therefore, electron scattering is due to:

1. Finite temperature: vibrations of the ions (phonons) about their equilibrium positions due to thermal excitation
2. Impurity scattering from ions with different radii or valency
3. Other crystal imperfections such as vacancies, dislocations or grain boundaries

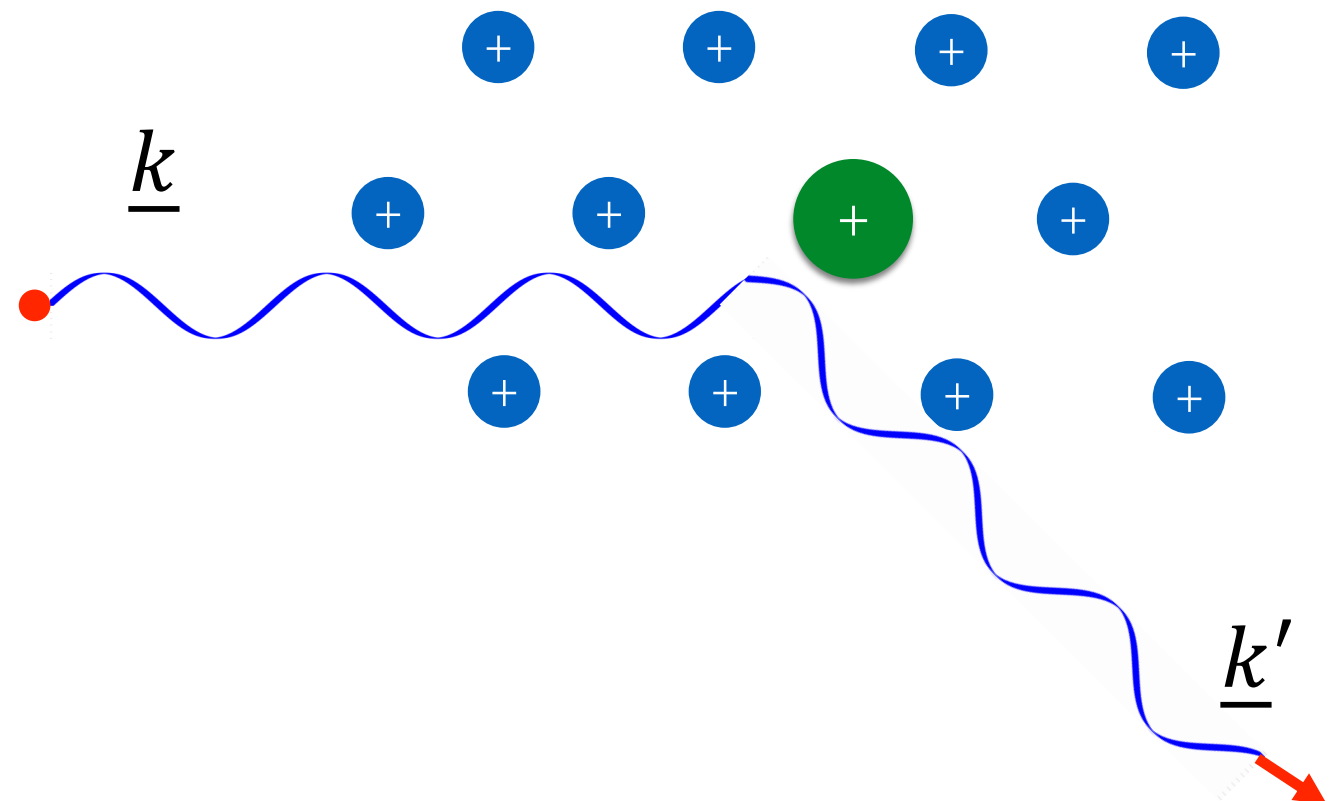
Temperature scattering:  
(electron-phonon scattering)

Occurs only for  $T > 0\text{K}$



Impurity scattering (e.g. Zn in Cu):

Occurs even for  $T = 0\text{K}$

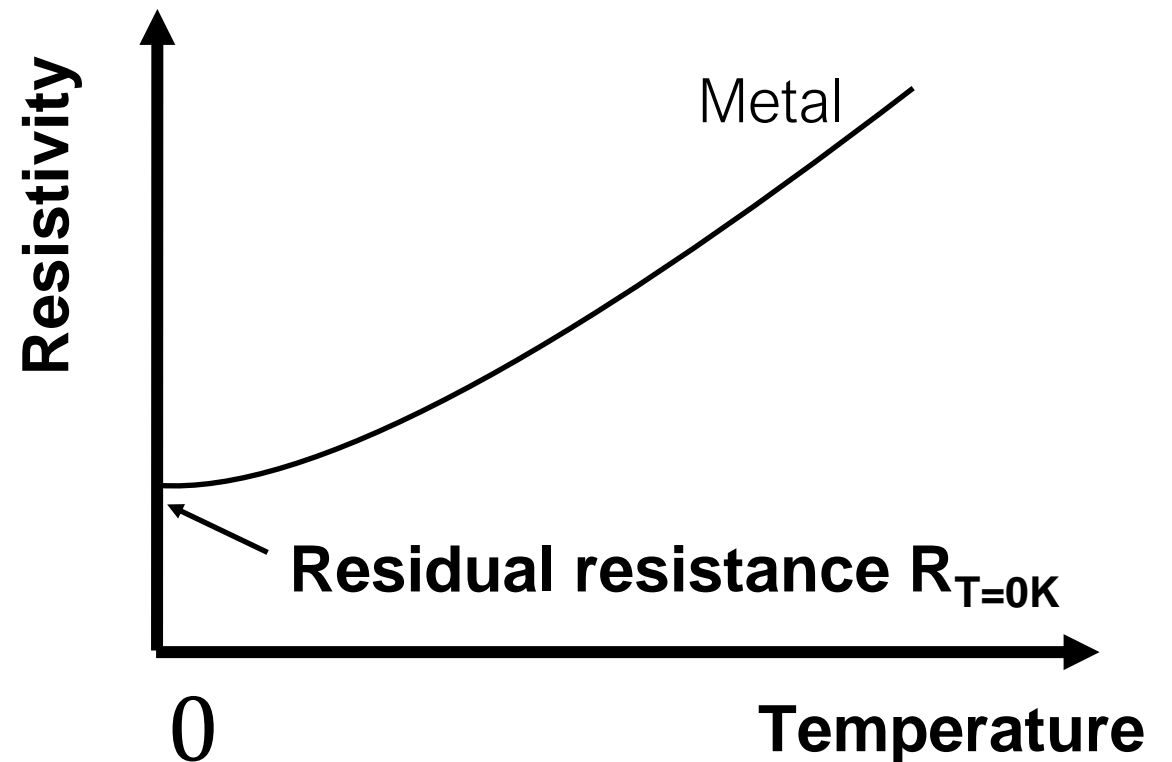


# Temperature dependence of resistivity (metal)

$$\frac{\Delta\rho}{\rho_0} = \alpha\Delta T$$

- $\alpha$  is the linear temperature coefficient of resistance
- $\rho_0$  is a known resistivity at temperature  $T_0$  (empirical)

$$\rho = \rho_0[1 + \alpha(T - T_0)]$$



- Resistivity tends to increase linearly above about 15K for metals due to electron scattering by thermal vibrations.
- At lower temperatures the resistance is dominated by impurities and the value is a good indicator of sample purity.

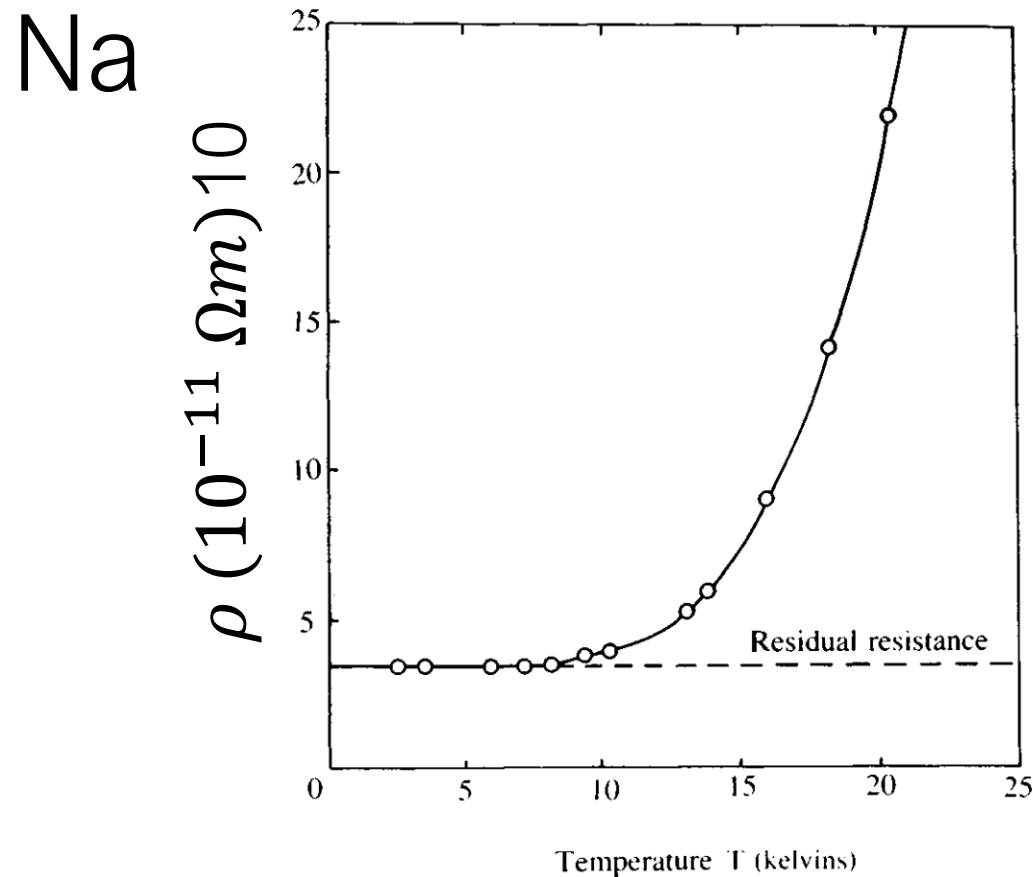
## Matthiessen's Rule

- Contributions to the resistivity can be added in series

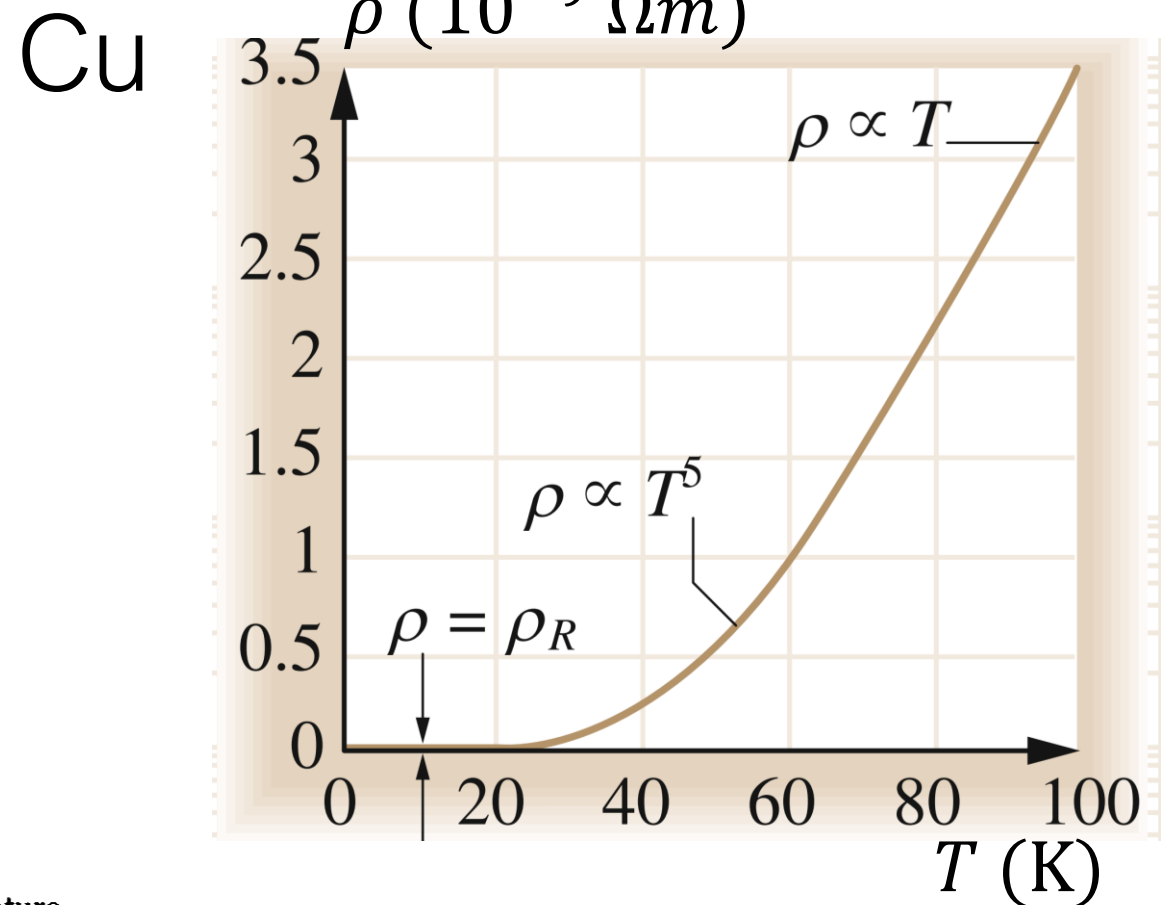
$$\rho = \rho_I + \rho_{ph}(T)$$

*impurity scattering*

*Temperature scattering  
(electron-phonon collisions)*



**Figure 3-15** The electrical resistivity of a metal, showing the low temperature limit set by imperfection scattering (the residual resistance), and the superimposed resistance caused by phonon scattering. According to Matthiessen's Rule, the two resistivities add simply. The data here are for sodium, after D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. A202, 103 (1950).

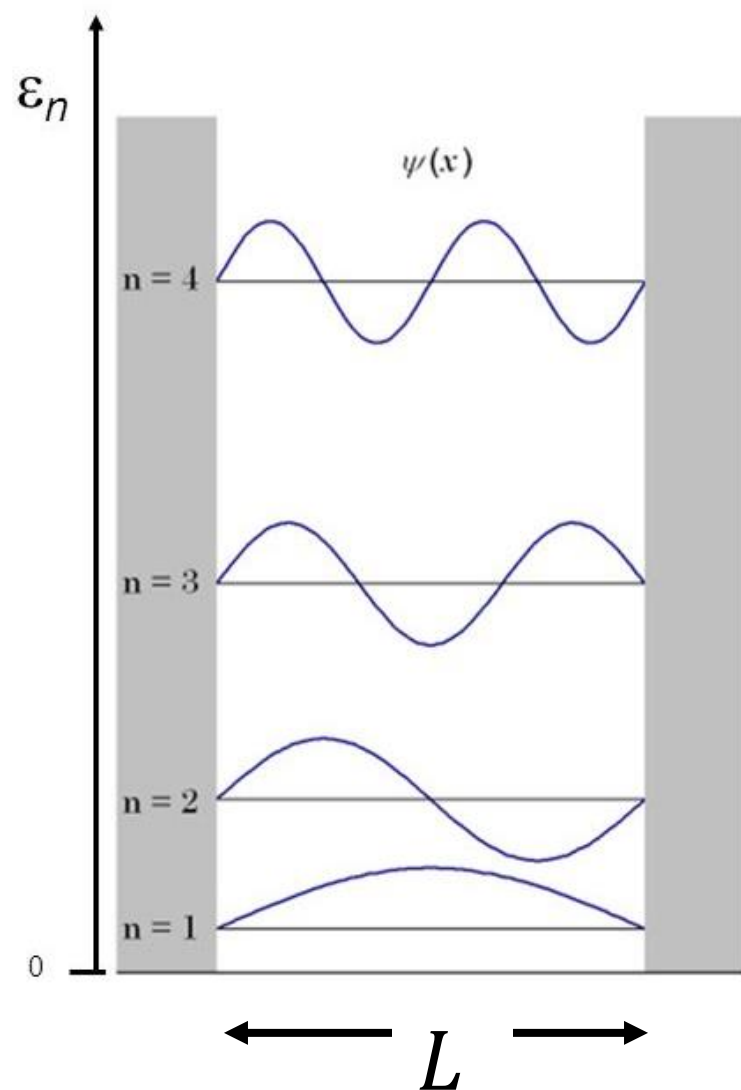


After S.O. Kasap: Principles of Electronic Materials and Devices, 4th edn.

- As temperature is reduced  $T \rightarrow 0$  we expect the number of active phonon modes to be vanishing (phonons aggregate in the ground state)
- Therefore the electron-phonon scattering contribution to resistivity  $\rho_{ph}(T) \rightarrow 0$  and  $\rho \approx \rho_i$  ( $\rho_i$  is a temperature independent term)
- This can account for the fact that very long mean free paths between scattering events (up to cm) are observed in ultra-pure metallic crystals (where  $\rho_i$  is small and hence total  $\rho$  is small)
- Reminder: we don't consider scattering from stationary lattice ions as a source of resistance in the wave picture (c.f. classical picture)

# Quantum approach: The free electron gas in 3D

- We need to quantify how many degenerate quantum states exist over an interval of energy i.e. a density of states function  $D(E)$ . We use the **free electron gas model** to describe the electrons in the metal, where it is assumed that:
  - The potential inside the crystal due to the ions is constant
  - Each atom donates a number of outer electrons to the 'gas' which are free to move
  - No interactions between electrons ("independent electron approximation")
  - The electrons are contained in the crystal by an infinite potential at the edges



Recall analysis for 1d potential well:

$$\text{TISE: } -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi.$$

$$\psi_n = A \sin(k_n x)$$

$$\text{where } k_n = \frac{2\pi}{\lambda_n}$$

Boundary conditions:

$$\psi(0) = \psi(L) = 0$$

$$\text{hence } \lambda_n = \frac{2L}{n} \text{ and } k_n = \frac{n\pi}{L}$$

Sub  $\psi_n$  into TISE to get  
parabolic dispersion  
relationship in 1D:

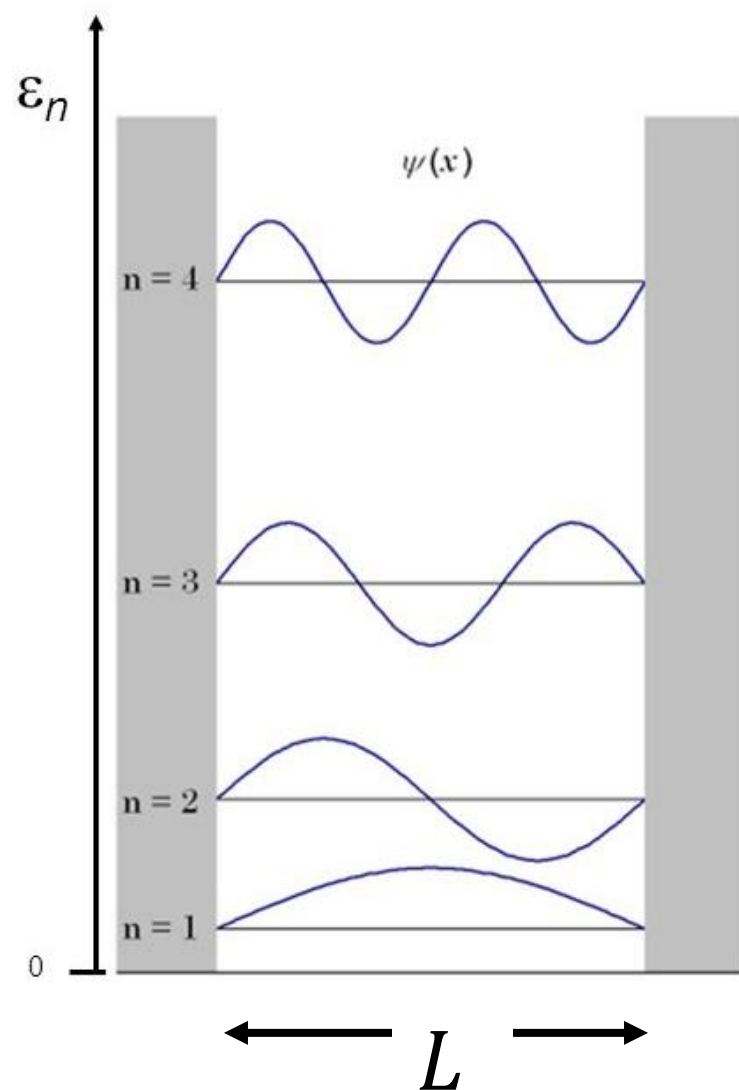
$$E_k = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$

# Quantum approach: The free electron gas in 3D

- We need to quantify how many degenerate quantum states exist over an interval of energy i.e. a density of states function  $D(E)$ .
- The simplest QM model used to describe metals is the **free electron gas model**

It is assumed that:

- the potential  $V(x)$  inside the crystal due to the ions is zero (i.e.  $V(x) = 0$ )
- No interactions between electrons (“independent electron approximation”)
- the electrons are contained in the crystal by an infinite potential at the edges



Recall analysis for 1d potential well:

$$\text{TISE: } -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi.$$

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Sub  $\psi_n$  into TISE to get  
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$$E_k = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$



- A more suitable approach is to carry out the same analysis in 3d where the solid body is pictured as a three dimensional volume of side  $L$  enclosed by high potential barriers at the sides
- The free-particle Schrodinger equation in 3d:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\underline{r}) = E\psi(\underline{r}).$$

- The standing wave solution takes the form:

$$\psi_n(\underline{r}) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

- If we relax the boundary conditions to being periodic with  $\psi_n(x + L, y, z) = \psi_n(x, y, z)$  (and similarly for y,z), travelling plane waves are allowed:

$$\psi_k(\underline{r}) = A e^{i\mathbf{k} \cdot \underline{r}} = A e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

and the allowed wavevector components are quantised according to:

$$(k_x, k_y, k_z) = \left( \pm \frac{2\pi n_x}{L}, \pm \frac{2\pi n_y}{L}, \pm \frac{2\pi n_z}{L} \right) \quad n_x; n_y; n_z = 0, 1, 2, 3 \dots$$

- The 3-components of the wavevector almost completely characterise each individual free electron in the metal (also need to consider spin  $+\frac{1}{2}$  and  $-\frac{1}{2}$  for filling of states).

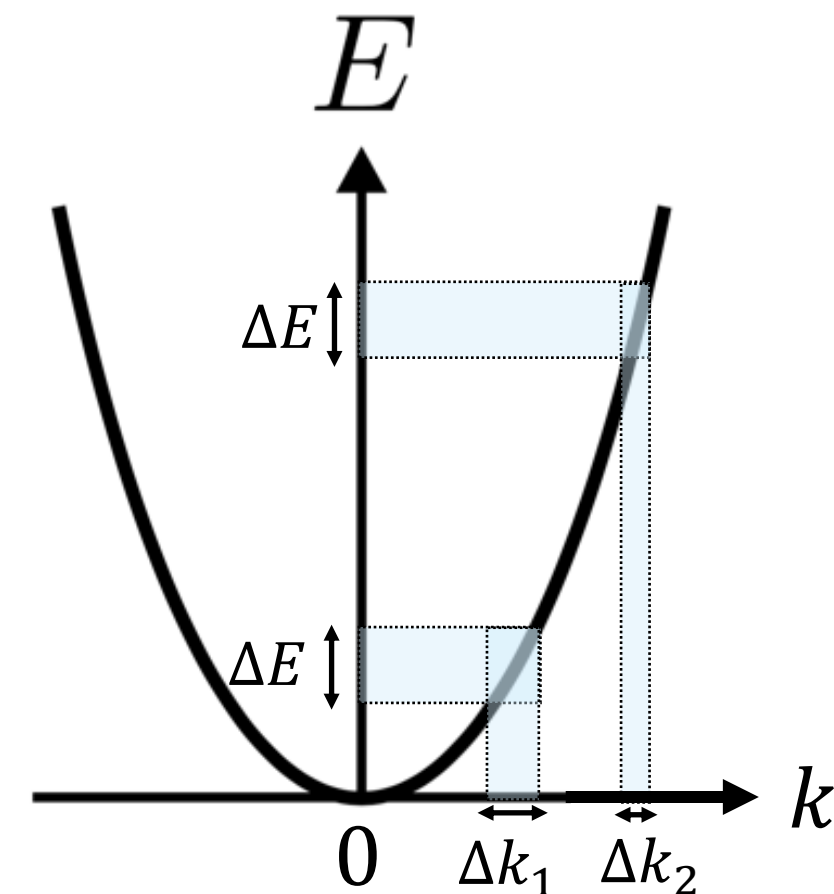
- Substitute the trial solution  $\psi_n(r)$  into the TISE to determine an expression for the energy  $E_n$  of a given level as a function of wavevector  $k_n$  :

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

$E(k)$  dispersion  
relationship for free  
electron gas

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

- We get a quadratic relationship between the electron wave energy  $E$  and the wavevector  $k$  (i.e.  $2\pi$  times reciprocal wavelength  $\lambda_n^{-1}$ )
  - Allowed electron states are quantised (as expected) with higher energy states characterised by having shorter wavelengths
  - The function is often drawn as a continuous  $E(k)$  function because the spacing between electron energy levels is much less than the energy-width of the band but it is actually made up of discrete  $(E, k)$  points
- To determine Density of States (DoS), need to recognise:
- (1) width of  $dk$  for a fixed energy interval  $dE$  is not constant but depends on  $k$
  - (2) Any given magnitude of  $k$  may be made up of several combinations of  $k_x$ ,  $k_y$ ,  $k_z$ , each of which is a distinct electron state – need to consider this also



For fixed width of  $\Delta E$ , width of  $\Delta k$  decreases as  $E$  increases

# What is the free electron gas density of states $D(E)$ in 3d?

- How to go about counting up all the states that are filled at  $T = 0 \text{ K}$ ?
- In general, the total number of occupied electron states  $N$  over some energy interval  $E_1 \leq E \leq E_2$  is given by  $\int_{E_1}^{E_2} f(E) D(E) dE$

$$D(E) = \frac{dN(E)}{dE}$$

Density of states at a given energy  $E$  is given by the number of distinct quantum states  $dN$  that exist within a small energy interval  $dE$

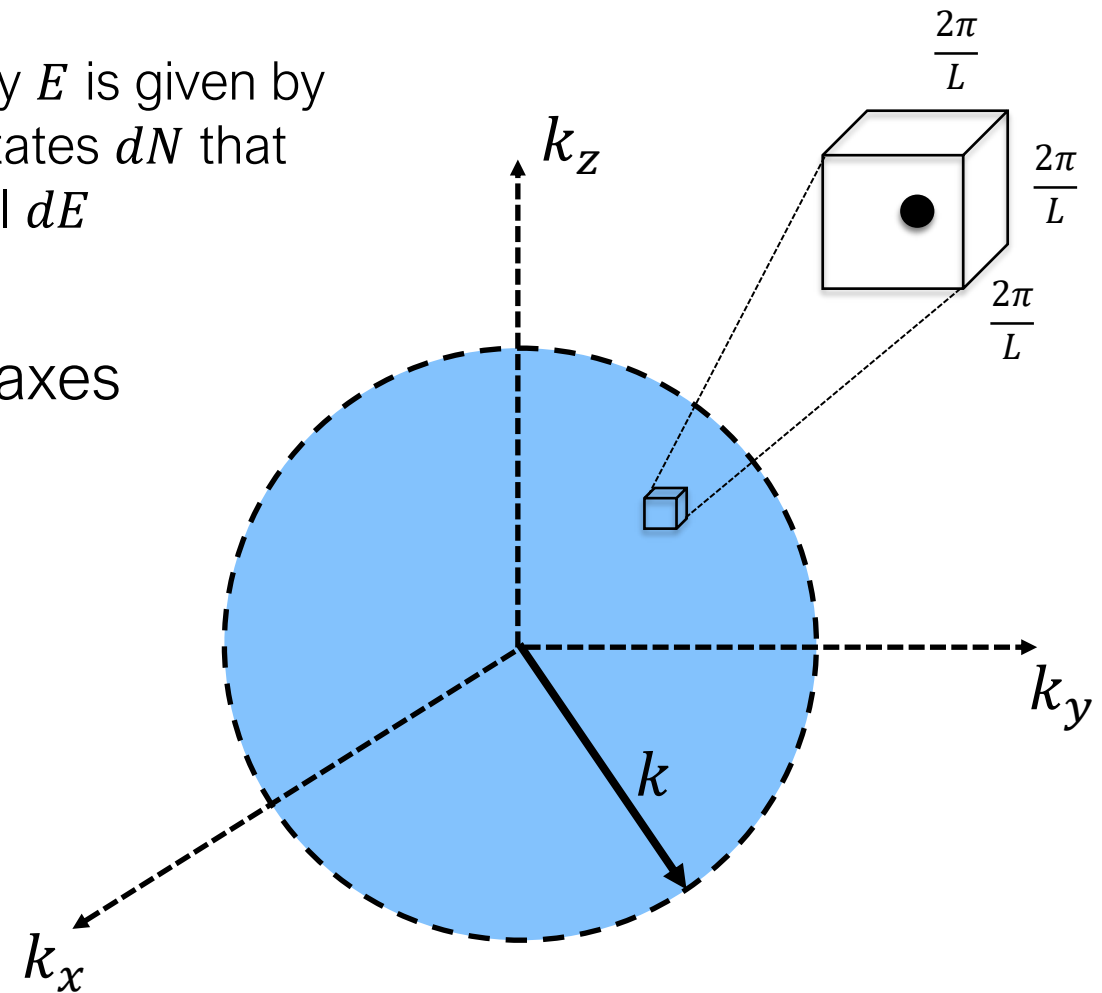
- k-states are separated by  $\frac{2\pi}{L}$  along the  $k_x, k_y$ , and  $k_z$  axes so in k-space each state occupies a 'volume'  $\left(\frac{2\pi}{L}\right)^3$

Total no. of states  $N$  contained within a sphere of radius  $k$

$$N = \underset{\substack{\nearrow \\ \text{spin } \uparrow\downarrow}}{2} \times \frac{(\text{volume of sphere})}{(\text{vol. per state})}$$

$$N(k) = 2 \cdot \left(\frac{4}{3}\pi k^3\right) \cdot \left(\frac{L}{2\pi}\right)^3 = \frac{Vk^3}{3\pi^2}$$

where  $V = L^3$  is volume of solid

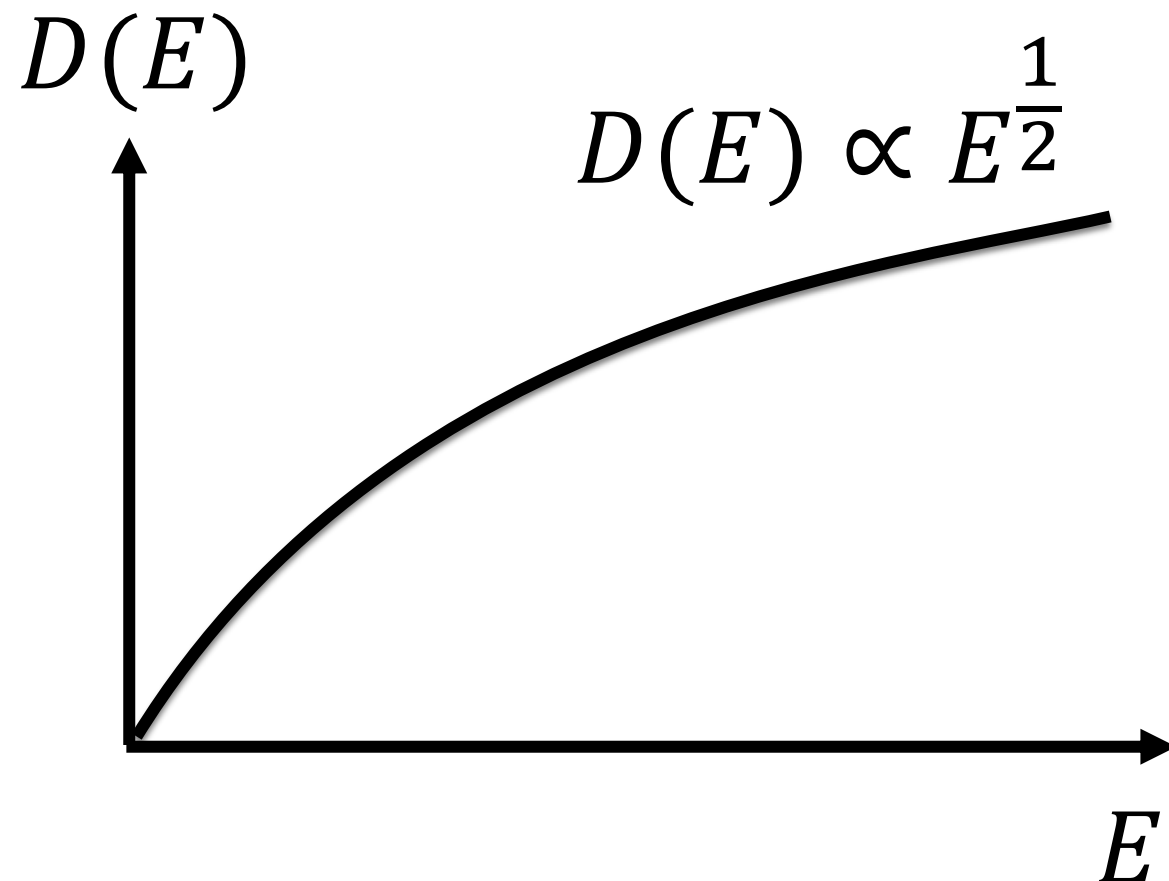


E-k dispersion relation:  $E = \frac{\hbar^2 k^2}{2m} \quad \therefore k^2 = \frac{2mE}{\hbar^2}$

$$N(k) = \frac{V k^3}{3\pi^2} \quad \text{hence } N(E) = \frac{V}{3\pi^2} \left[ \frac{2mE}{\hbar^2} \right]^{\frac{3}{2}}$$

$$D(E) = \frac{dN(E)}{dE} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}$$

Density of States for the free electron gas in 3-dimensions



By taking into account both the  $E$ - $k$  dispersion relationship for electrons, and the fact that there are more degenerate  $k$ -states with increasing magnitude of  $k$ , we see that DoS increases with energy according to  $E^{\frac{1}{2}}$

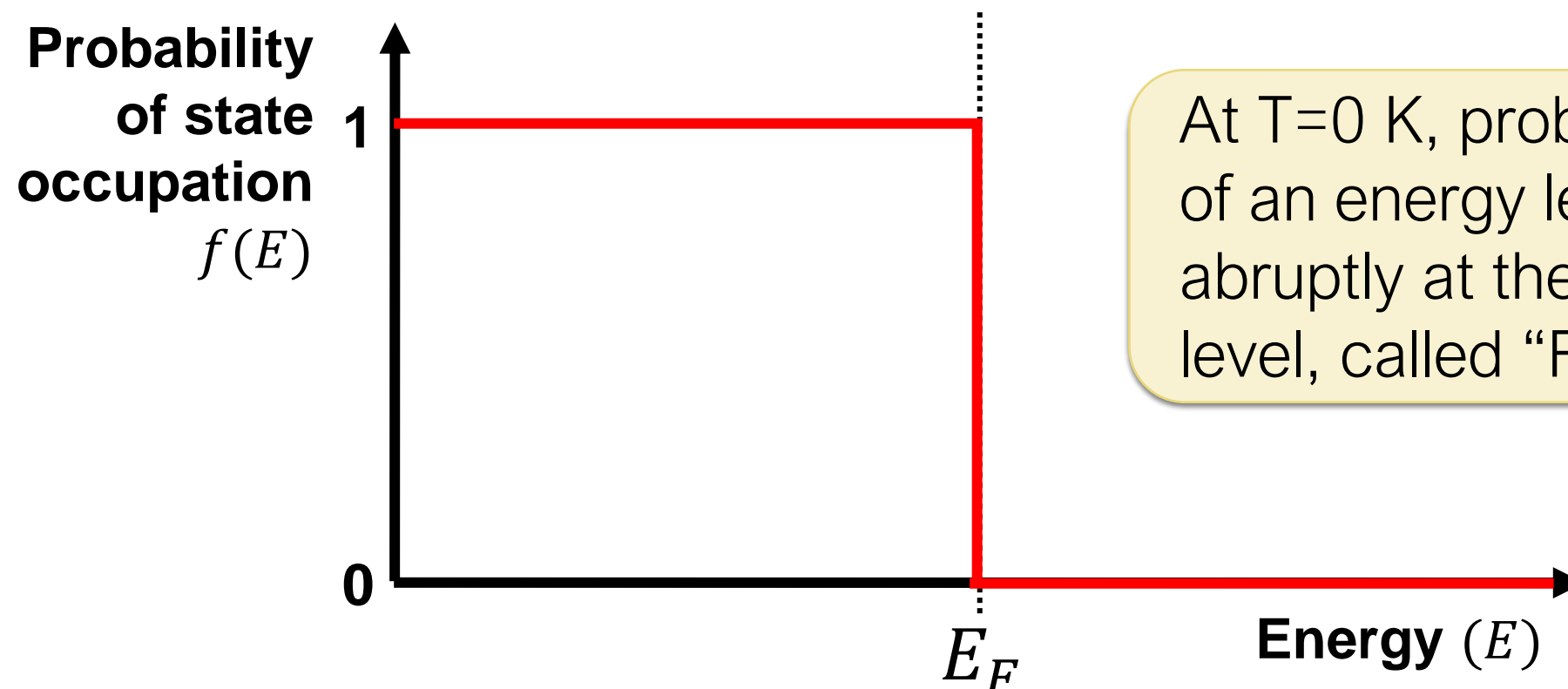
# The Fermi-Dirac distribution (at $T=0\text{K}$ )

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How will  $N$  electrons be distributed in energy levels at  $T=0\text{ K}$ ? Consider:

1. **Pauli exclusion:** Electrons are fermions  $\therefore$  No two electrons can occupy the same quantum state in the same region of space
2. **Thermodynamics:** Tendency for electrons to generally occupy lowest available energy states

**Result:** Lowest energy  $N/2$  states all occupied with 100% probability with the highest filled energy level  $E_F$  called the “Fermi Energy”



At  $T=0\text{ K}$ , probability of occupation of an energy level  $E$  goes from 1 to 0 abruptly at the highest energy filled level, called “Fermi Energy”  $E_F$

- So,  $N = \int f(E)D(E)dE$  gives  $N = \int_0^{E_F} 1 \cdot D(E)dE$ , with  $N$  here being the total no. of electrons in the metal, giving:

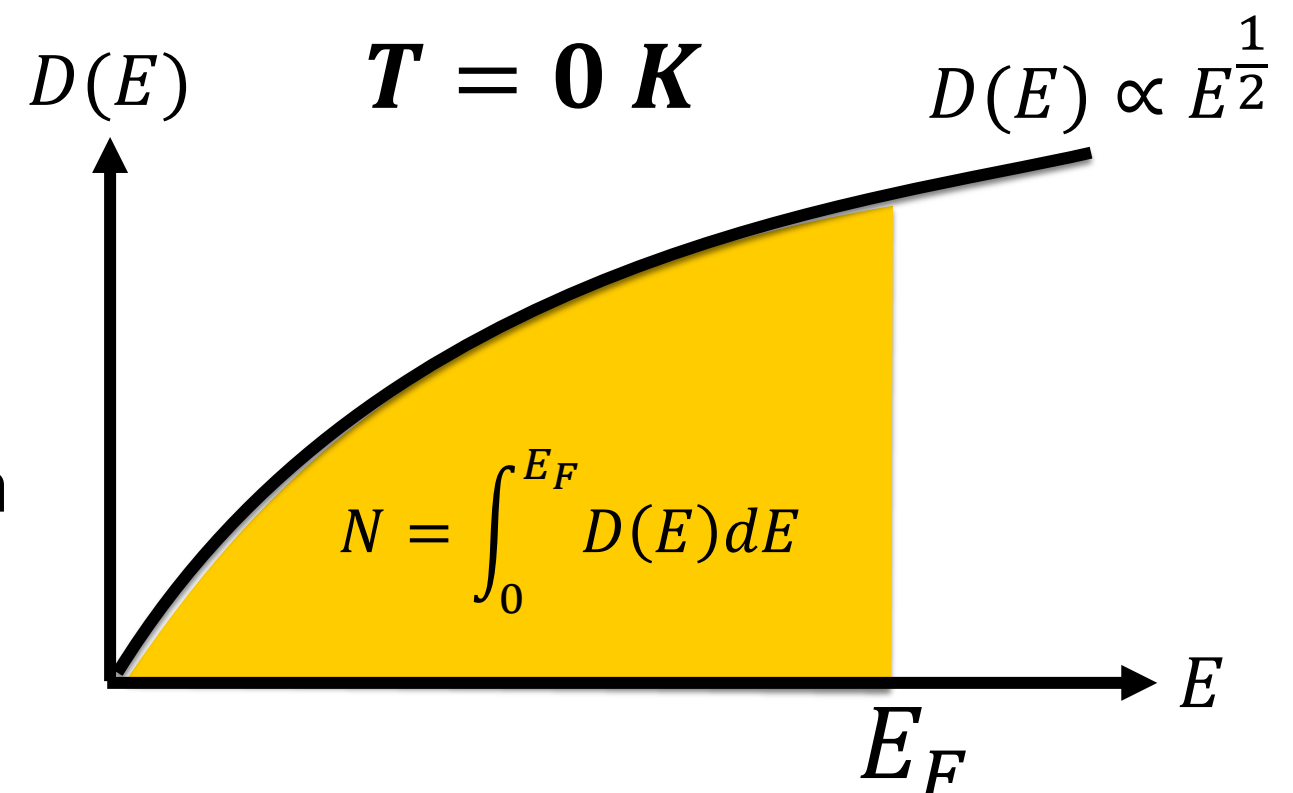
$$N = \frac{V}{3\pi^2} \left( \frac{2mE_F}{\hbar^2} \right)^{\frac{3}{2}}$$

- Noting that, in a metal, the energy of the highest occupied level at  $T = 0 \text{ K}$  is called the “Fermi energy”  $E_F$ :

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

The maximum filled energy state at  $T = 0 \text{ K}$  depends on the electron concentration  $n = N/V$

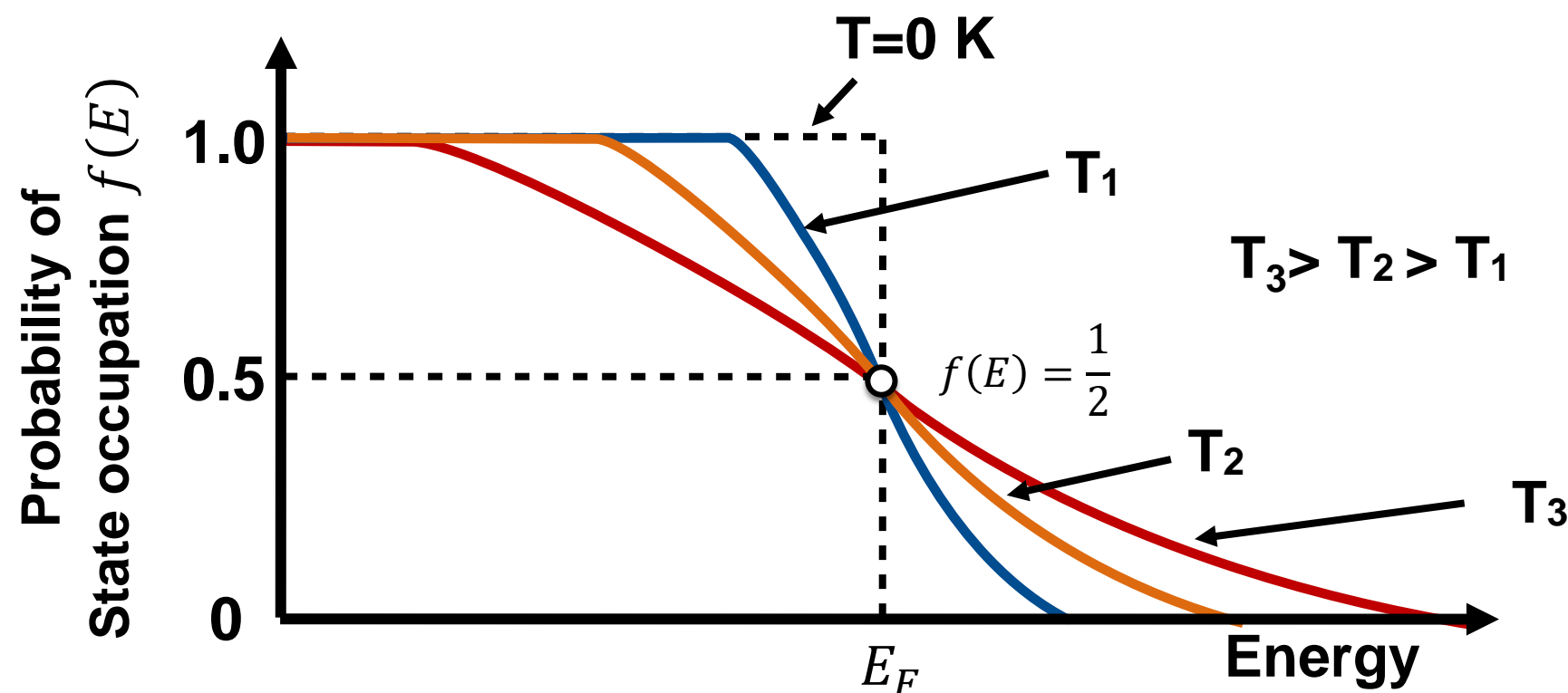
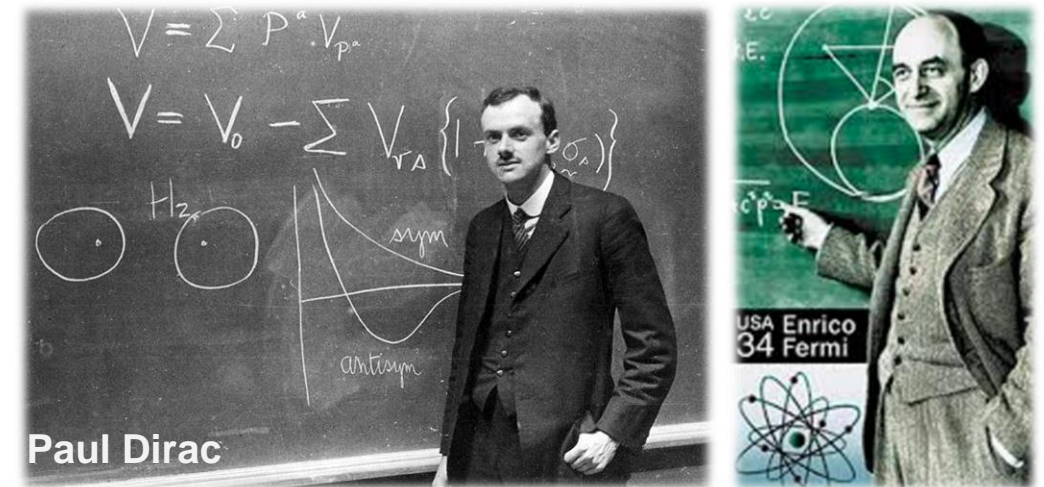
- $E_F \sim n^{\frac{2}{3}}$  is not a classical result – arises from parabolic form of  $E(k)$  assumed for free electron gas and because electrons fill states according to Fermi-Dirac distribution (i.e. obey Pauli exclusion)



- Our analysis so far of the distribution of electrons among their energy states has been restricted to  $T = 0K$ , with electrons adopting the lowest available energy states only. As temperature increases, this distribution will change according to Fermi-Dirac statistics

## Fermi Dirac distribution:

$$f(E) = \frac{1}{e^{\left(\frac{E-\mu}{k_B T}\right)} + 1}$$



$f(E)$  is the probability that a level of energy  $E$  is occupied at temperature  $T$ .

- “Fermi energy”  $E_F$  is defined as the energy where  $f(E) = 0.5$  at  $T = 0K$
- The “Fermi level” or “chemical potential”  $\mu(T)$  is the energy value where  $f(E) = 0.5$  and is a function of temperature
- Energies close to  $\mu$  are mainly of interest in a metal as only the occupancy of these states is influenced by temperature



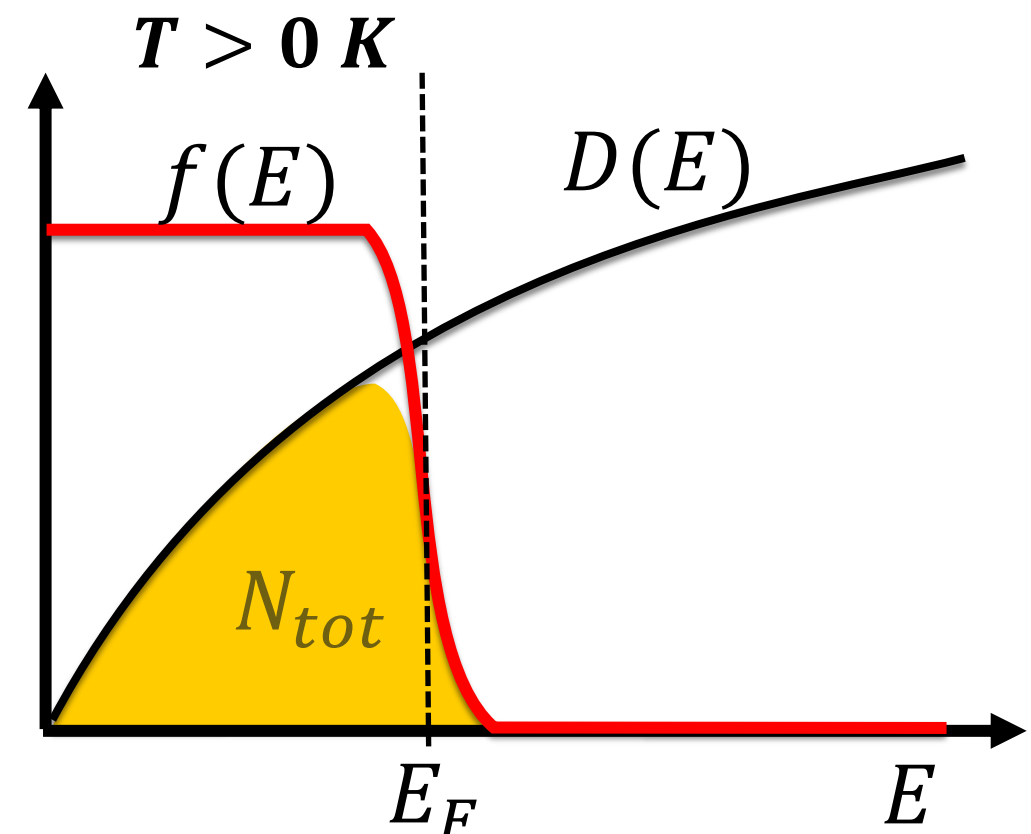
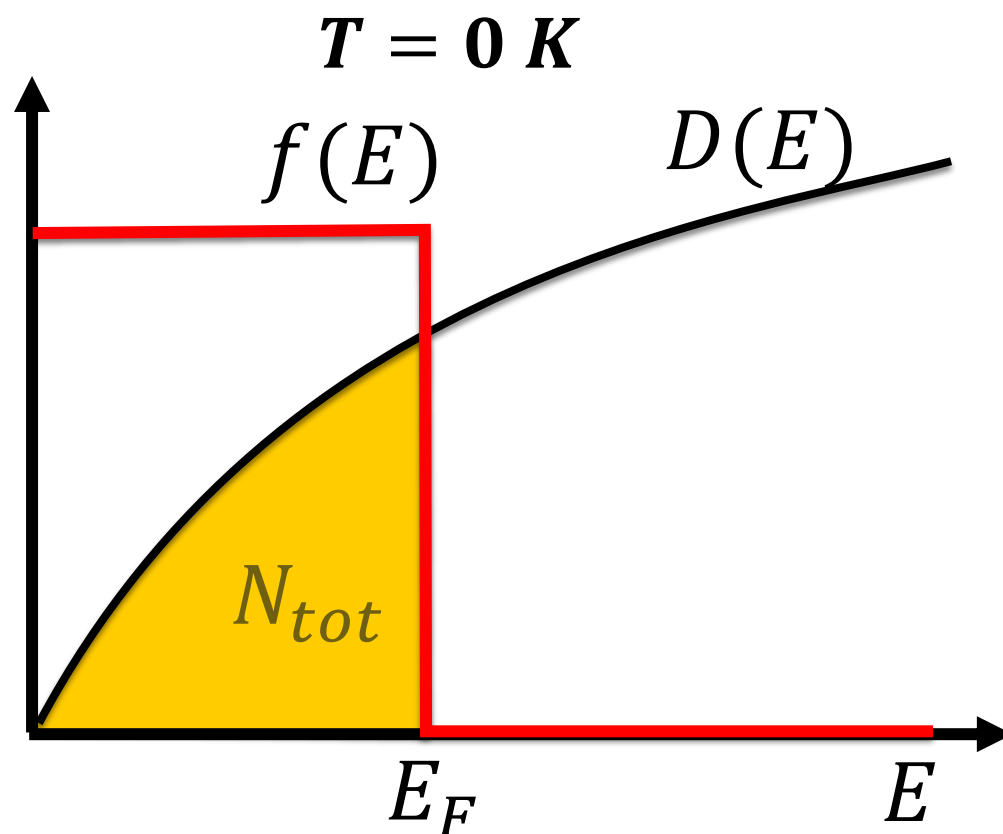
# Electron population distribution

- To determine the actual number of electrons in some interval  $dE$  about an energy  $E$  at finite temperature ( $T > 0$ ) we need to weight the density of states distribution by the FD statistical distribution

$$N(E) = D(E)f(E)dE \quad \text{Total no. of electrons in an energy interval } dE \text{ about an energy } E$$

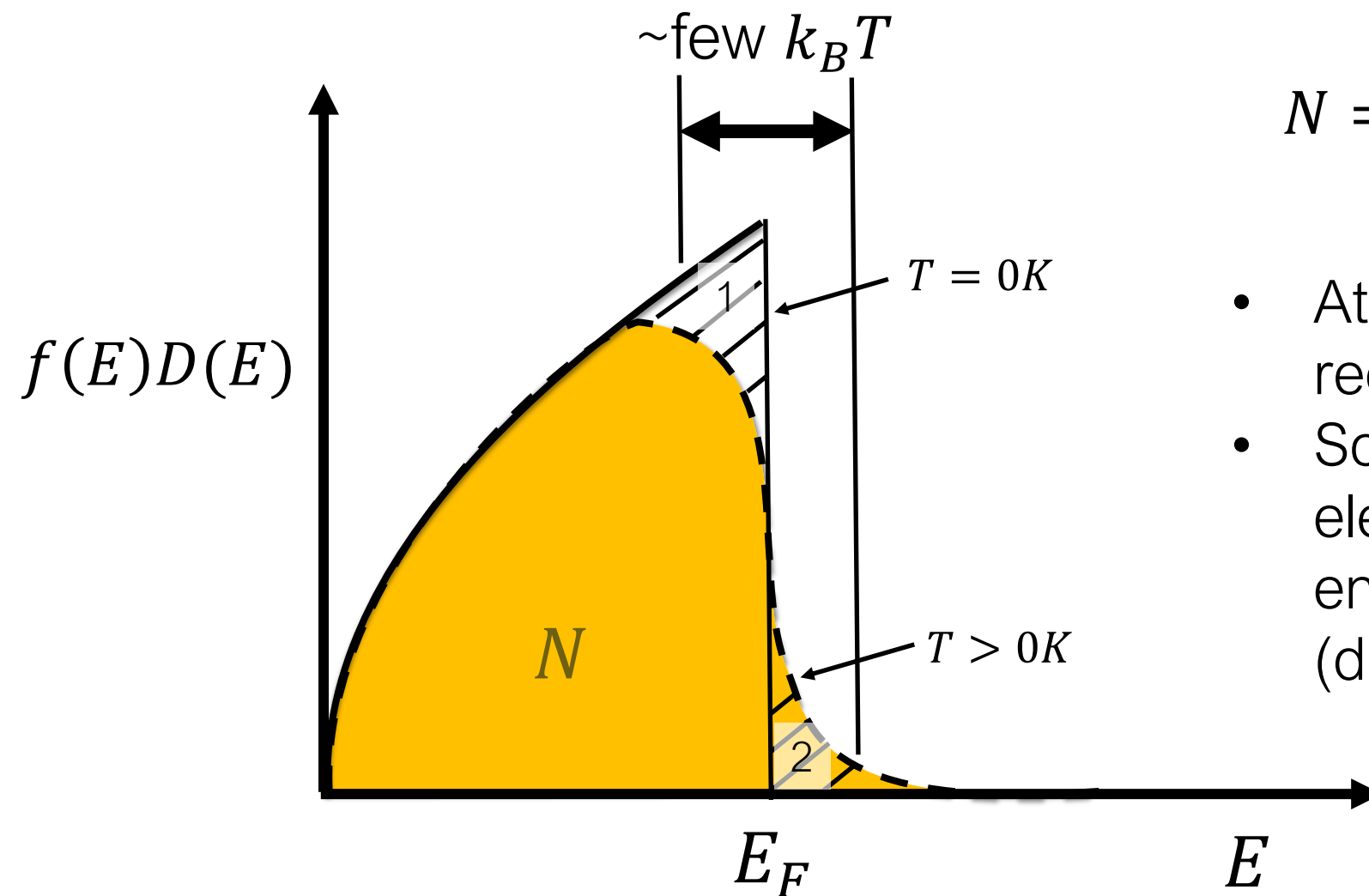
$$N_{tot} = \int_0^{E_F} D(E)f(E)dE = \int_0^{E_F} D(E)dE \quad \text{At } T = 0 \text{ K only states up to the Fermi energy are occupied and with a probability of unity}$$

$$N_{tot} = \int_0^{E_{max}} D(E)f(E)dE \quad \text{To evaluate distribution of electrons in the energy band at finite temperatures we need to know the behaviour of } f(E)$$





# Electron population distribution

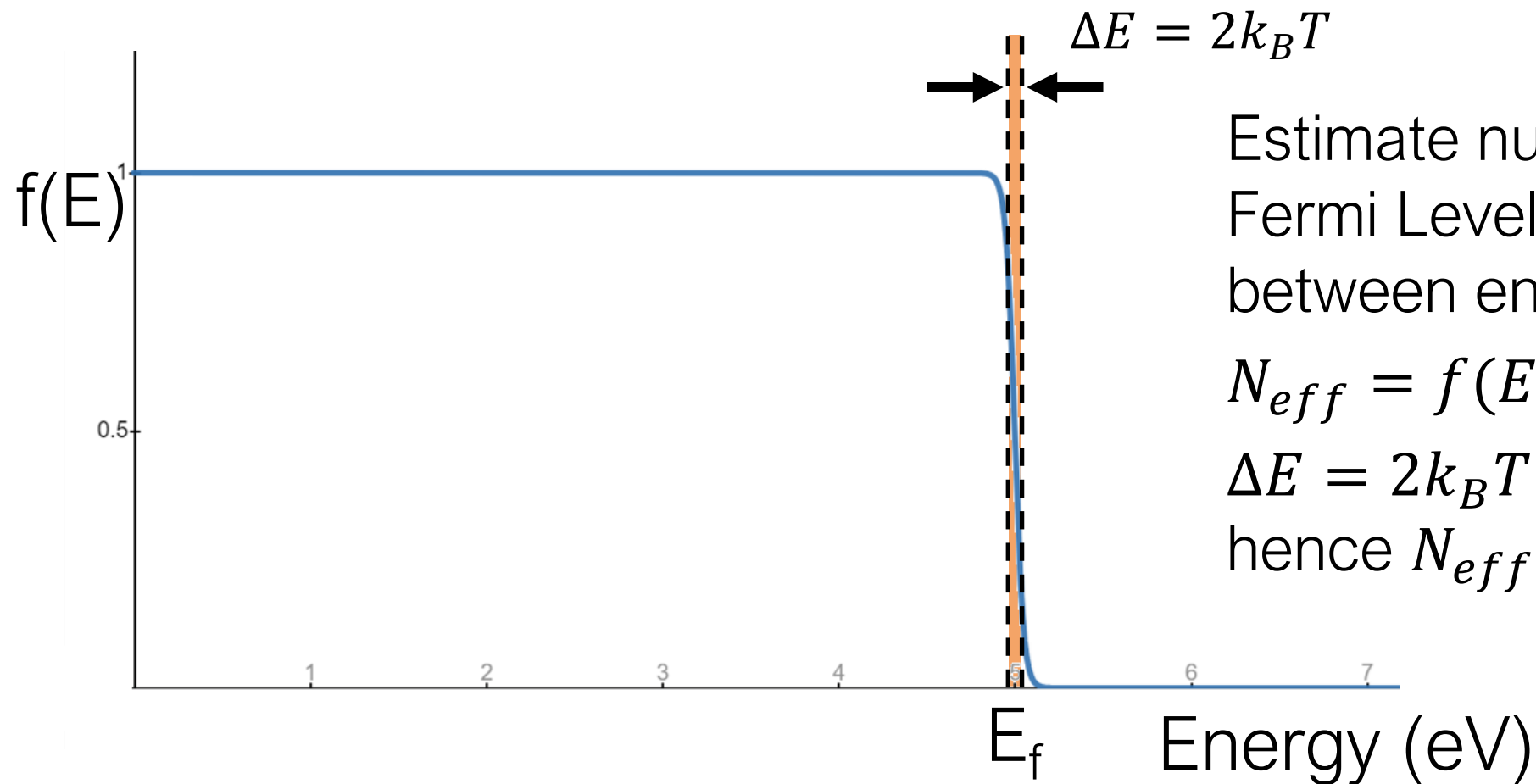


$$N = \int_0^{E_{max}} D(E)f(E)dE$$

- At  $T > 0 K$  electrons are excited from region 1 to region 2
- Solid line is the number of filled electron states  $D(E)f(E)$  per unit energy as a function of  $E$  at  $T = 0 K$ , (dashed line is  $T > 0 K$  case).

- Note that  $k_B T \sim \frac{1}{40}$  eV at RT and  $E_F \sim$  several eV, hence only small proportion of electrons near  $E_F$  expected to be able to change energy state (verified by heat capacity measurements in metals).
- Reason: For  $E \ll E_F$  all energy levels are filled so there are no vacant energy states for electrons to transition into

# Consequences for electronic heat capacity (thermal transport)



Estimate number of electrons near Fermi Level that are able to transition between energy states as:

$$N_{eff} = f(E)D(E)\Delta E \text{ with } f(E) = \frac{1}{2},$$

$$\Delta E = 2k_B T, D(E) = D(E_F),$$

$$\text{hence } N_{eff} \approx D(E_F)k_B T$$

Fraction of electrons in free electron gas able to absorb thermal energy and contribute to heat capacity is  $N_{eff}/N$ :

$$N_{eff}/N = D(E_f)k_B T/N$$

Use previous results that  $N = \frac{V}{3\pi^2} \left[ \frac{2mE_F}{\hbar^2} \right]^{\frac{3}{2}}$  and  $D(E_F) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E_F^{\frac{1}{2}}$

See that  $\frac{N_{eff}}{N} \approx \frac{k_B T}{E_F} \approx 0.5\%$  for  $E_F = 5\text{eV}$  at room temp

Only a small proportion of electrons in the free electron gas contribute to heat capacity, explaining why it is much smaller than classically expected

# Values of the Fermi energy and velocity at $E_F$ for sample metals

- Use our result from the free electron Fermi gas model to estimate the Fermi Energy  $E_F$  based on the electron concentration  $n = N/V$

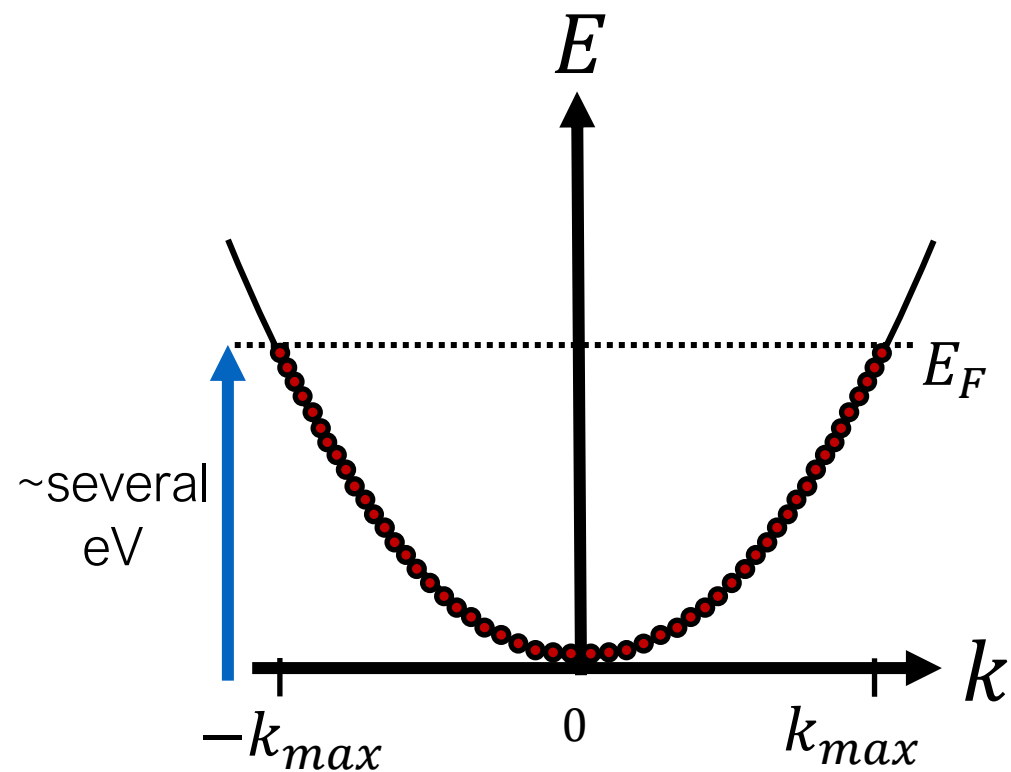
$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}$$

- In free electron gas, all energy is kinetic so  $E_F = \frac{1}{2} m v_F^2$
- The velocity  $v_F$  at  $E_F$  at  $T = 0K$  is an order of magnitude greater than the room temperature classical theory prediction (also, classical theory predicts  $v \rightarrow 0$  as  $T \rightarrow 0 K$ )

	No. outer electrons per atom	$n$ ( $\times 10^{28} \text{ m}^{-3}$ )	$E_F$ (eV)	$v$ at $E_F$ ( $\times 10^6 \text{ ms}^{-1}$ )
Sodium	1	2.7	3.2	1.1
Copper	1	8.5	7.0	1.6
Gold	1	5.9	5.5	1.4
Aluminium	3	18.1	11.6	2.0
Lead	4	13.2	9.4	1.8

- Despite these high electron velocities, we know no net current flows in absence of an external applied E-field so we also have to also rationalise that the net velocity of all electrons is zero (i.e. zero drift velocity)

# Electron distribution with no applied electric field



No applied electric field

The net electron current is proportional to the sum of the individual velocity vectors for each of the occupied states

$$J_{tot} = \frac{-e}{V} \sum_{k(\text{filled})} v_k$$

Note that the velocity of a k-state,  $v_k$ , is found from the local gradient of the dispersion plot

$$v_k = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

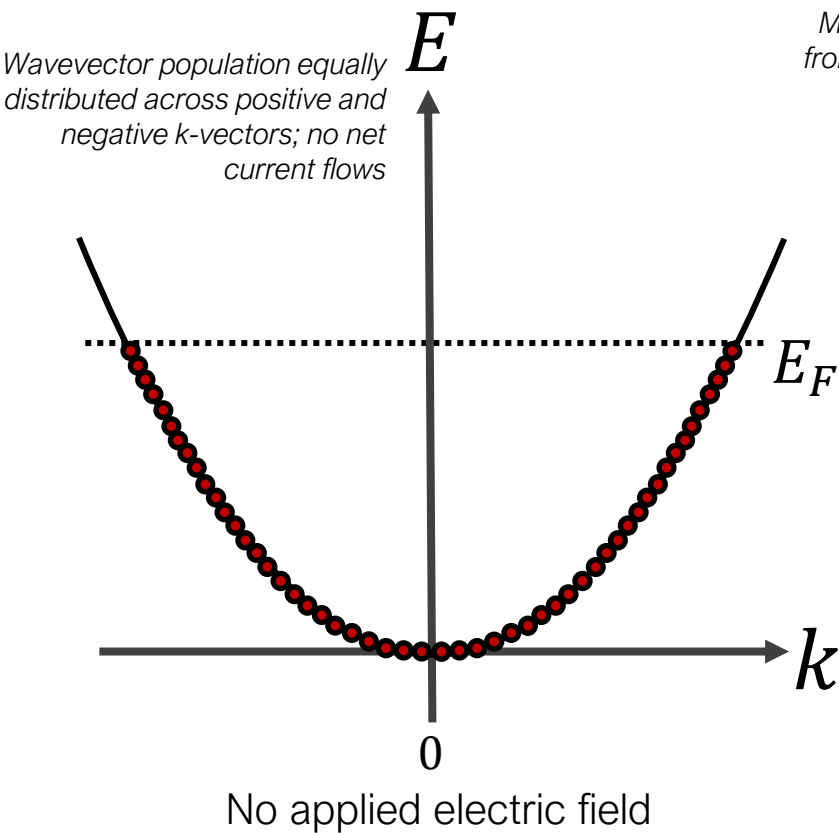
See that the symmetry of parabolic band gives  $v_k = -v_{-k}$  (i.e.  $\partial E / \partial k$  is an odd function)

$$\text{So: } J_{tot} = \frac{-e}{V} \sum_{-k_{max}}^{k_{max}} v_k = \frac{-e}{V} \left[ \sum_{k=0}^{k_{max}} v_k + \sum_{k=0}^{k_{max}} v_{-k} \right] = \frac{-e}{V} \left[ \sum_{k=0}^{k_{max}} v_k - \sum_{k=0}^{k_{max}} v_k \right] = 0$$

- Result: In the absence of applied electric field electrons are **equally distributed across positive and negative k-states** so no net current flows

# Prediction of current flow from changes in electron energy-wavevector distribution due to an applied electric field

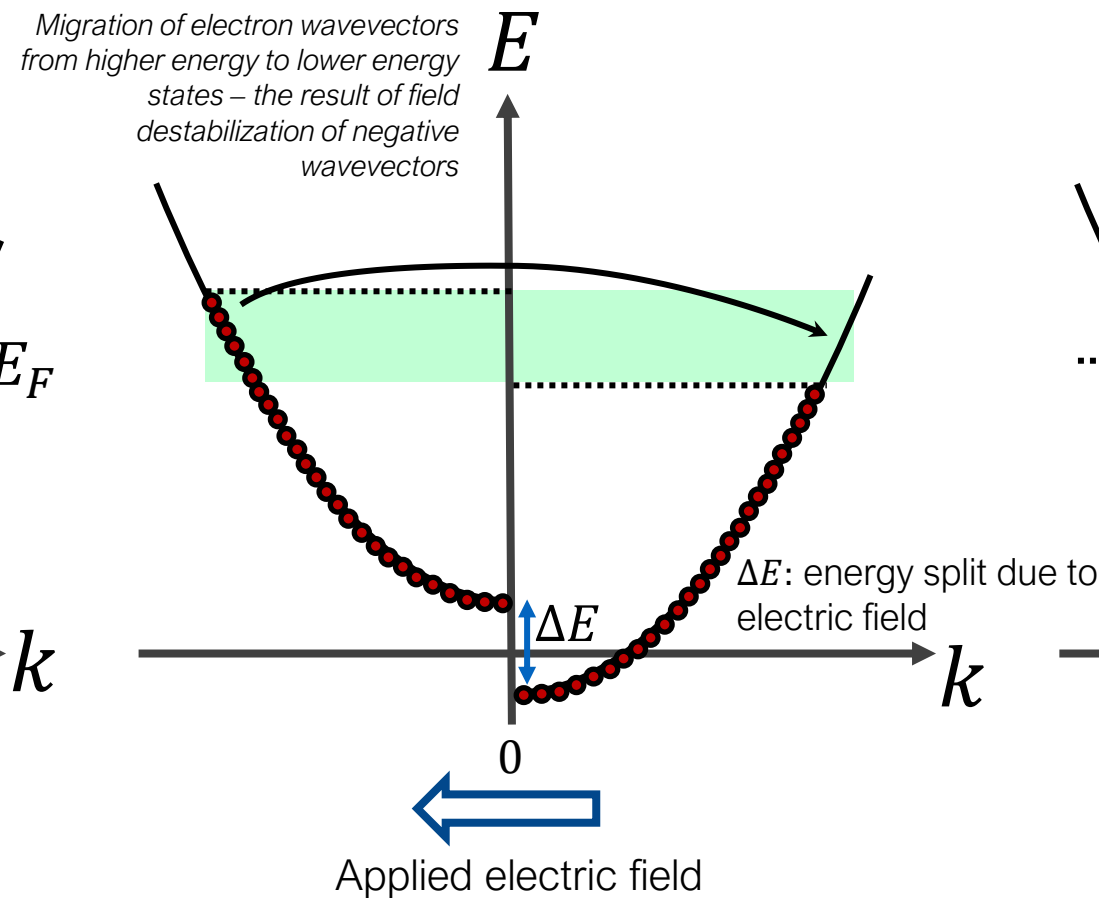
(a)



$$J_{tot} = \frac{-e}{V} \sum_{k(\text{filled})} v_k = 0$$

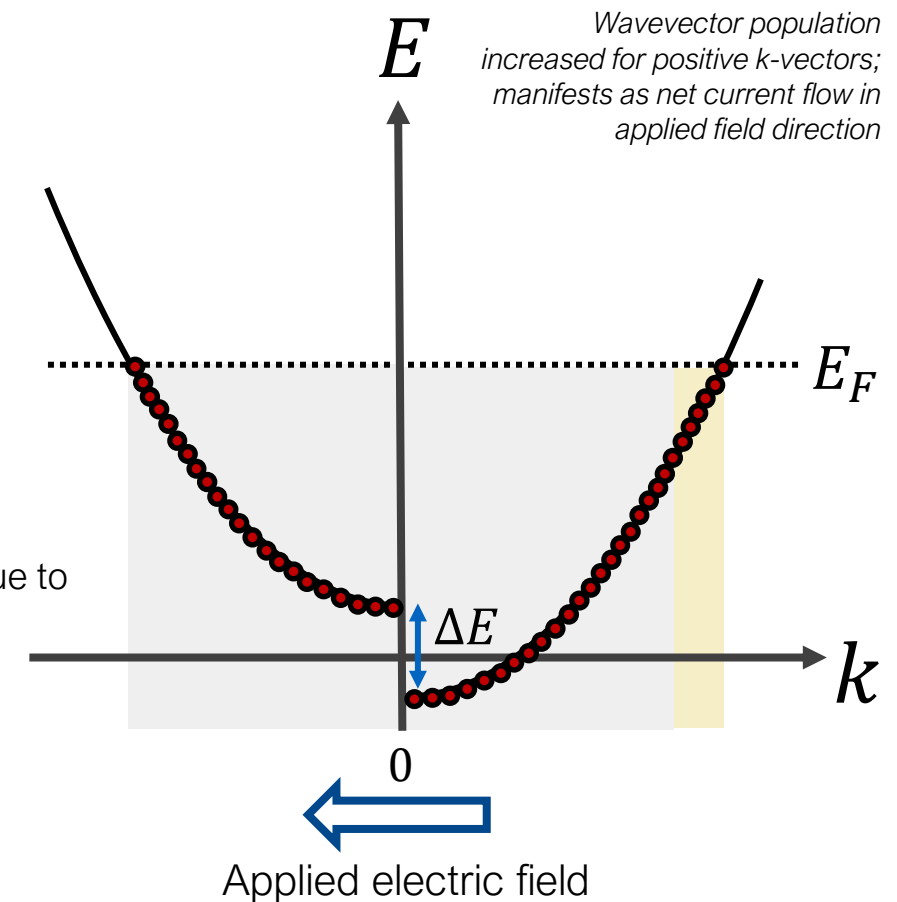
In no applied field, all individual electron currents cancel pairwise i.e for each  $+k$  electron state there is an occupied  $-k$  state which travels in the opposite direction with the same velocity  $v$

(b)



Applied field lowers energy for electron states with  $k$  vector directed opposite to the field compared to those with  $k$ -vectors aligned with the field. There is now the possibility for some electrons to lower their energy by transitioning into lower energy vacant states

(c)



$$J_{tot} = \frac{-e}{V} \sum_{k(\text{filled})} v_k \neq 0$$

There is now a net electron current in the applied field direction associated with the excess uncompensated electrons (yellow shaded region) that have changed into the  $+ve$   $k$ -states