

# FoP 3B Part II

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Room 151

## Lecture 1: Band gaps in Semiconductors

# Course outline

## Semiconductors

**Lectures 1-6**

**Example Class 1,2**

**Weekly Problem Set 1, 2, 3**

## Superconductors

**Lectures 7-9**

**Example Class 3,4**

**Weekly Problem 4**

## Dielectrics

**Lectures 10-12**

**Example Class 5**

**Supplementary Weekly Problems**

**+ 1 Revision Lecture (May)**

## Suggested Reading

- (1) C Kittel, *Introduction to Solid State Physics* (course broadly based on this textbook)
- (2) DA Neamen, *An introduction to Semiconductor devices* (Chapters 3,5; easy reading)
- (3) JF Annett, *Superconductivity, Superfluids and Condensates* (Chapter 3, 4)
- (4) NW Ashcroft and ND Mermin, *Solid State Physics* (slightly more advanced)

Lecture summaries available on Blackboard Ultra

## Aim of today's lecture

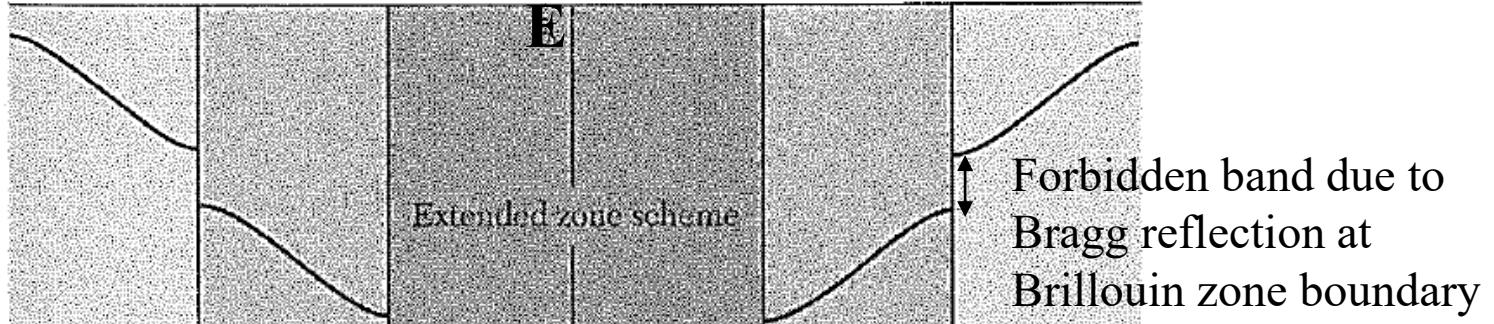
Q: How is a semiconductor different from a metal?

A: Band gaps

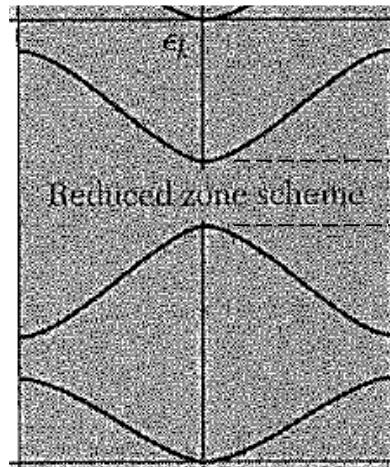
*Key concepts:*

- Origin of band gaps (review of previous material)
- Example crystal structures of semiconductors
- Direct vs indirect band gaps and Vegard's law
- Effective mass of electrons

# Origin of band gaps (revision)

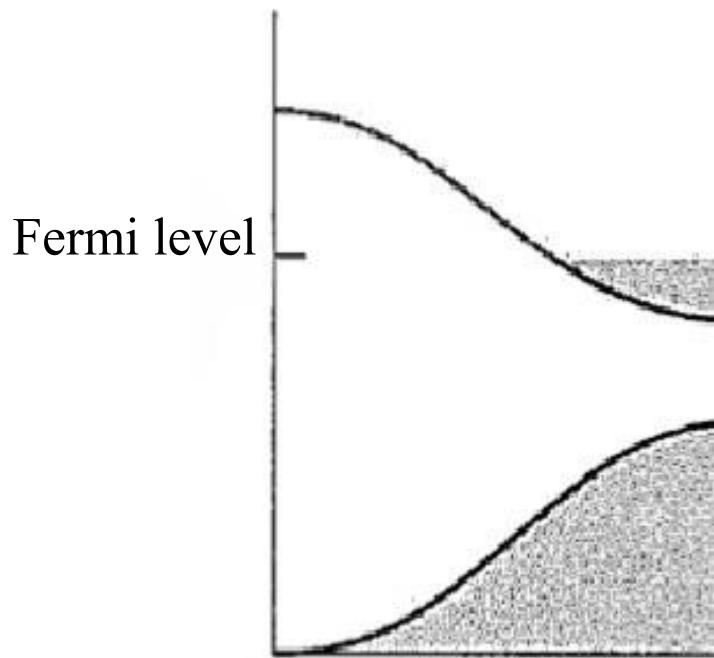


Extended zone scheme

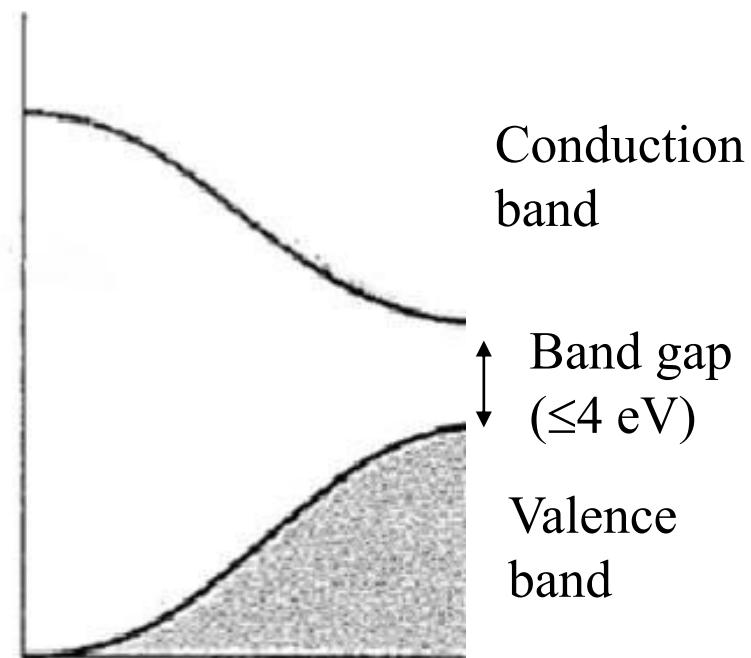


Reduced zone scheme

# Metals vs semiconductors



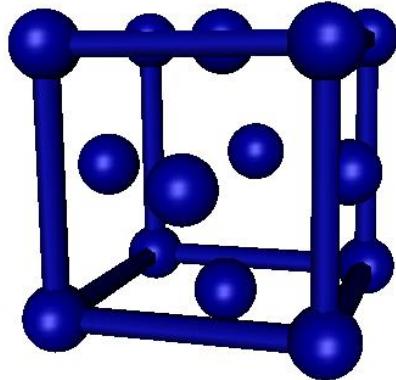
Metal: incompletely filled conduction band



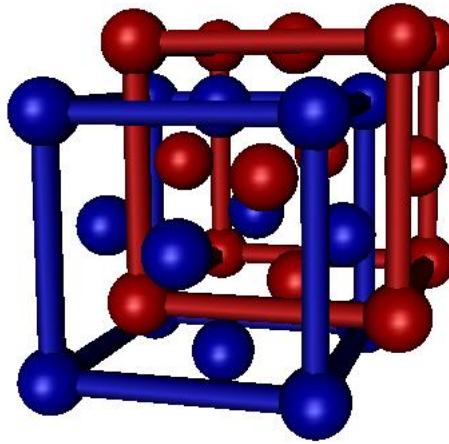
Semiconductor: valence (conduction) band completely full (empty) at 0 K\*

# Examples of semiconductors (diamond lattice)

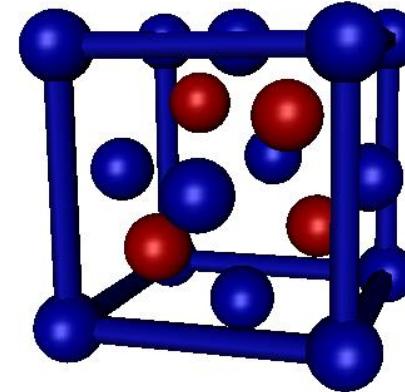
Elemental semiconductors, such as Si =  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ .



An fcc lattice



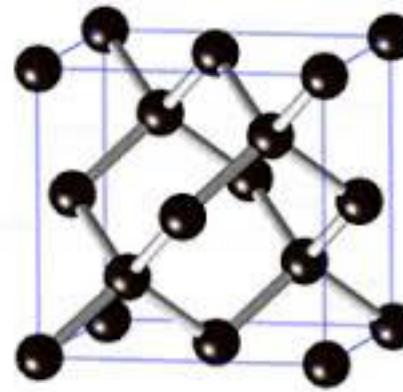
Two fcc lattices shifted  
by  $(1/4, 1/4, 1/4)$ .



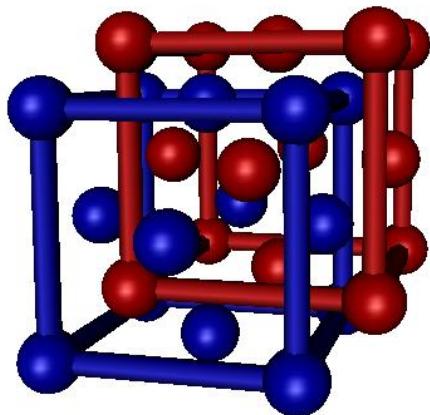
Keeping only atoms  
inside the cubic unit cell

If all atoms are the same:

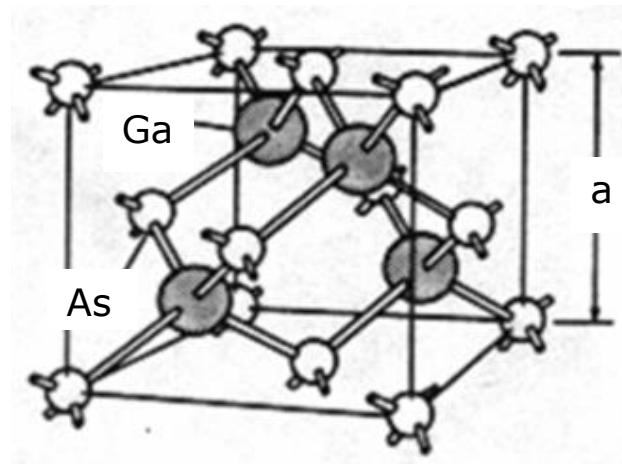
Each atom has four bonds (Group IV; octet rule).



# Compound semiconductors (zinc blende structure)

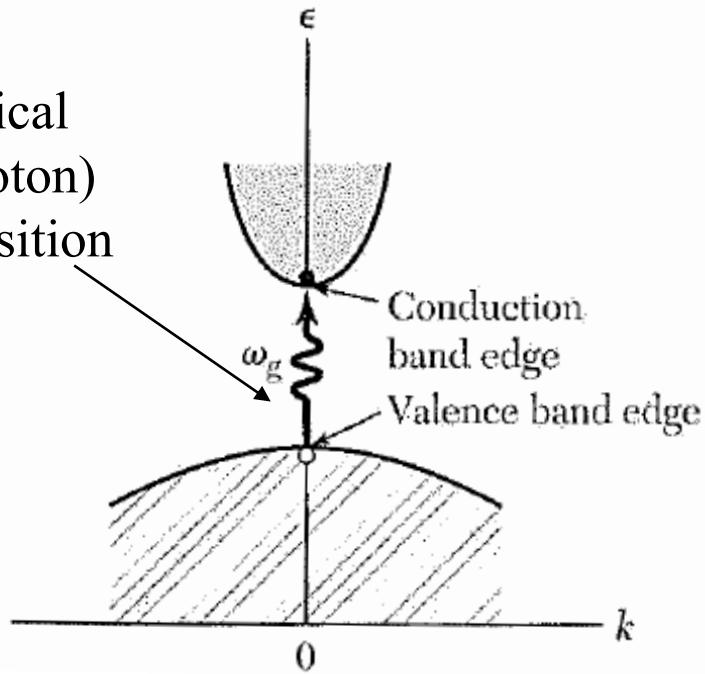


If there are two atom types  
e.g. ZnS, **GaAs**, CdTe

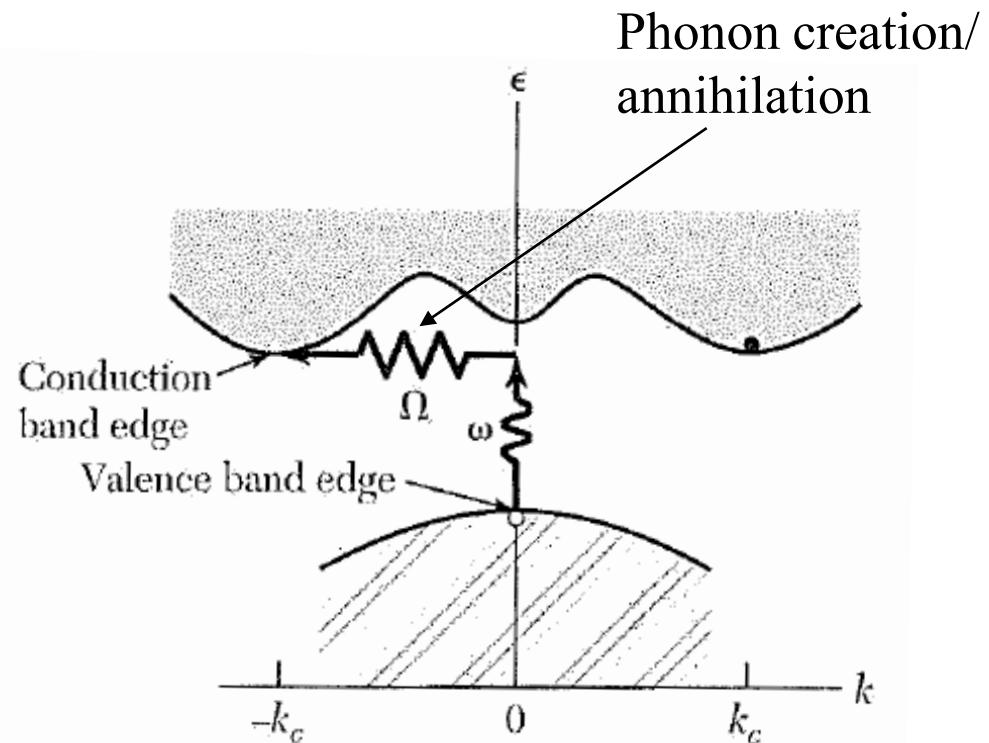


# Direct vs indirect band gaps (photon absorption)

Optical  
(photon)  
transition



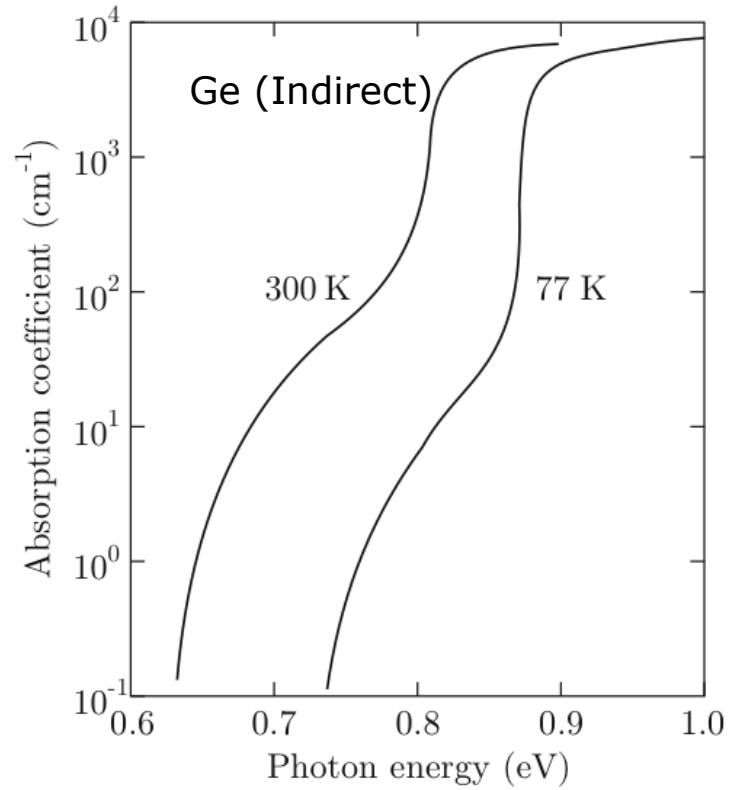
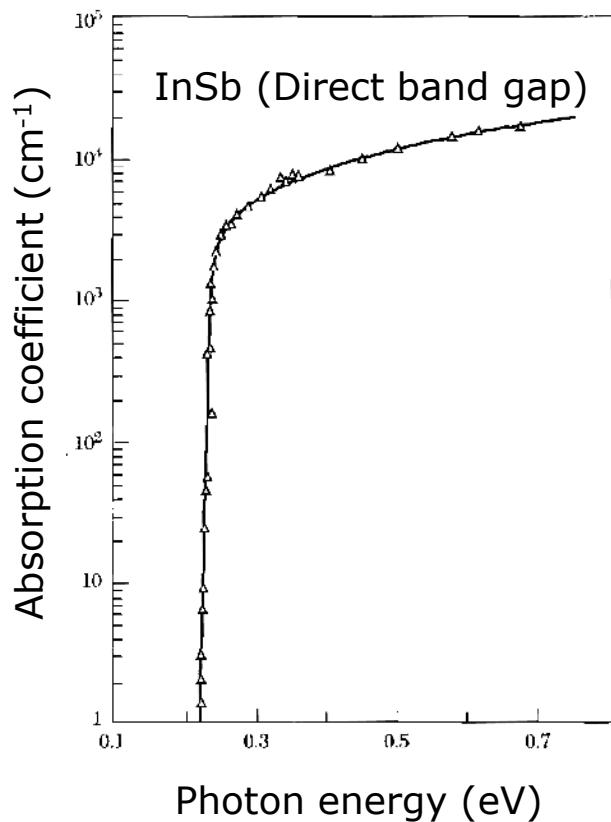
Direct band gap



Indirect band gap

Band gap is the minimum photon energy required to promote an electron into an unoccupied level. Both energy and momentum must be conserved during the transition.

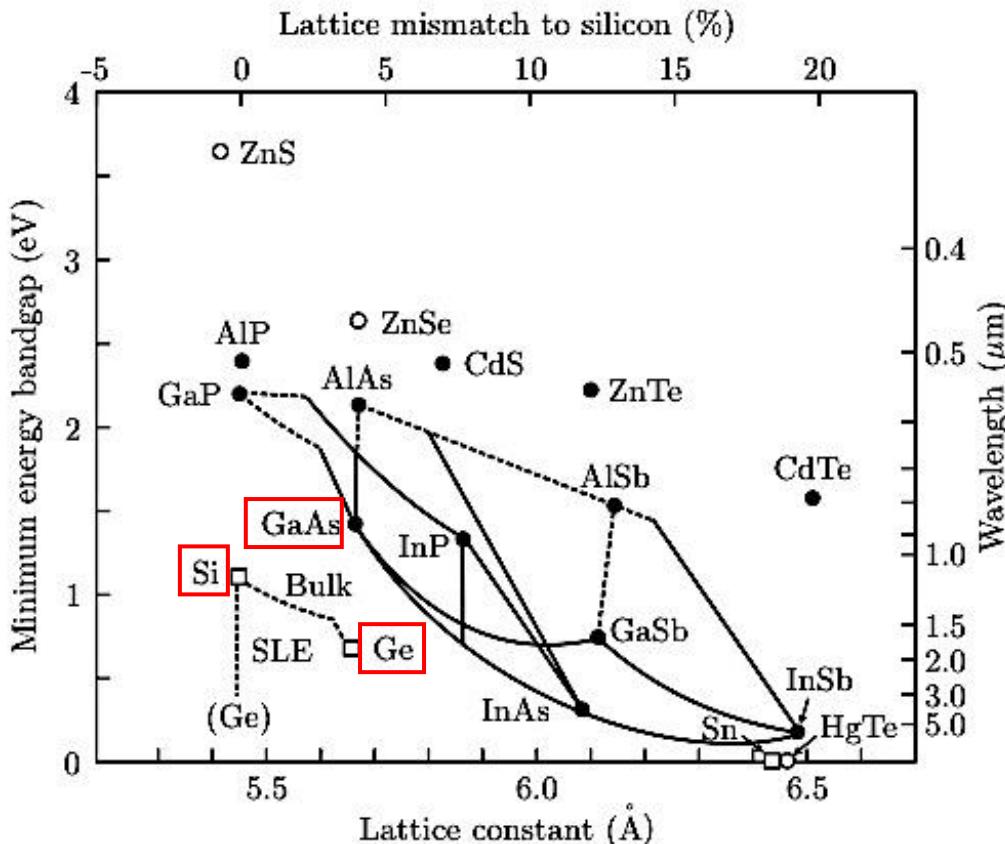
# Band gap measurement (photoabsorption)



NB: Weak absorption onset and strong temperature dependence for indirect band gap (due to phonon mediation)

# Band gap variations in alloy semiconductors

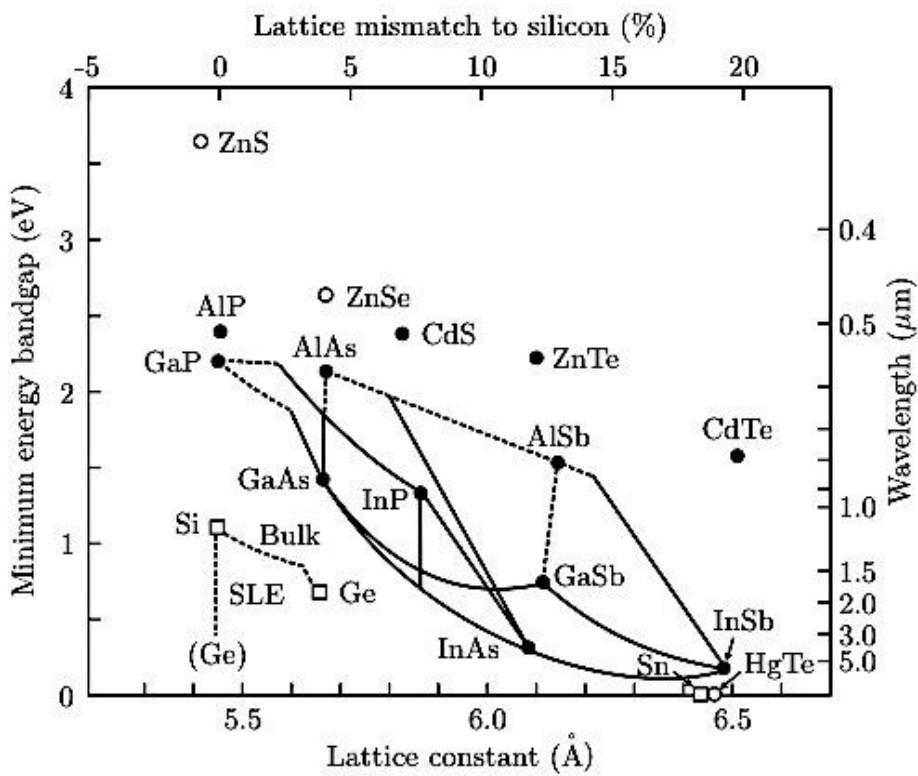
For many applications, it is **desirable** to **tune** the value of the band gap.



Solid curves - direct gaps.

Dashed curves - indirect gaps.

# Vegard's law



For a semiconductor alloy\*  $A_xB_{1-x}$

## Band gap energy

$$E_{g,AB} = xE_{g,A} + (1 - x)E_{g,B} - bx(1 - x)$$

b is called the **Bowing parameter**

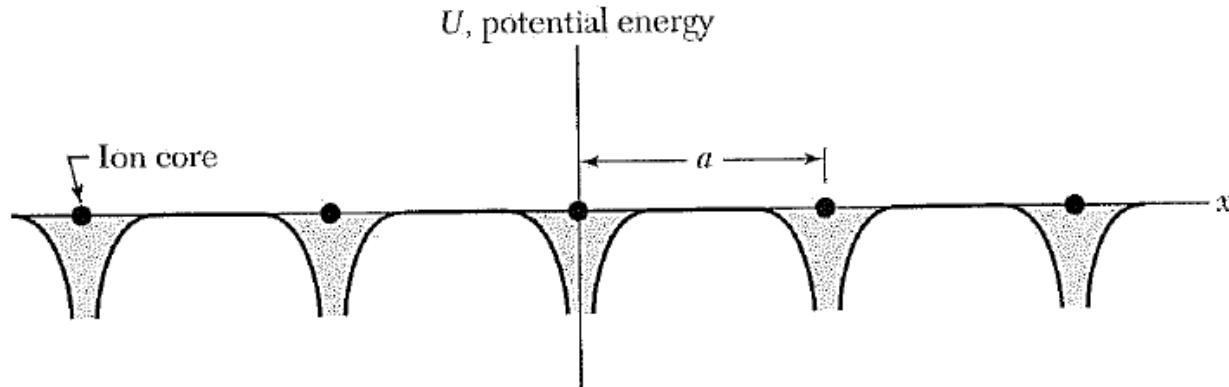
## Lattice Parameter:

$$a_{AB} = xa_A + (1 - x)a_B$$

\* A, B can represent elements or compounds (e.g. Si/Ge or GaAs/InAs)

In device applications the semiconductor is typically deposited on a substrate. The lattice parameter of the semiconductor and substrate must be similar to minimise strain.

## 'Effective' mass of electrons in a crystal



- Electrons in a crystal are subjected to a periodic potential from the ion-cores.
- The response to an external force  $F$  (e.g. electric/magnetic field) is therefore different to an electron in free space.
- Define an effective mass  $m^*$ , such that  $F = m^*a$  is obeyed.

# Expression for effective mass\*

*Key Results:*

$$v = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \quad (\text{group velocity of Bloch wave})$$

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt}$$

Substituting in  $F = m^*a = m^*(dv/dt)$  gives:

$$m^* = \hbar^2 / \frac{d^2 E}{dk^2}$$

For anisotropic crystals (effective mass tensor):

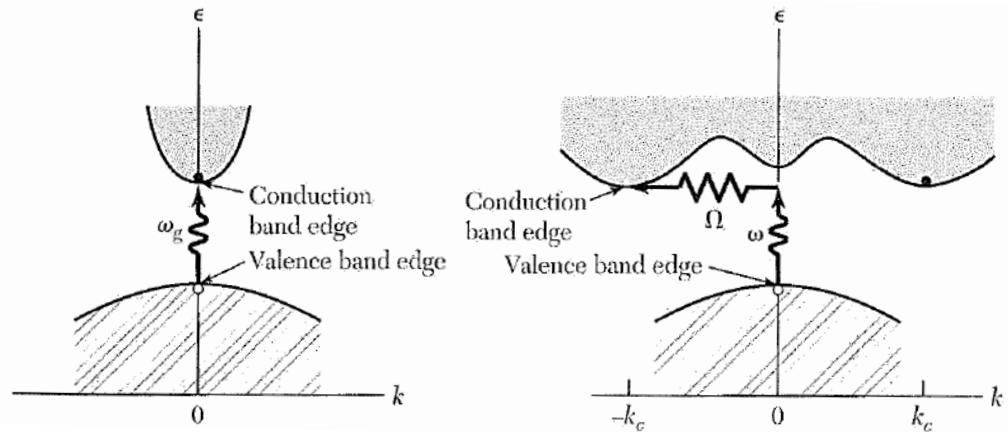
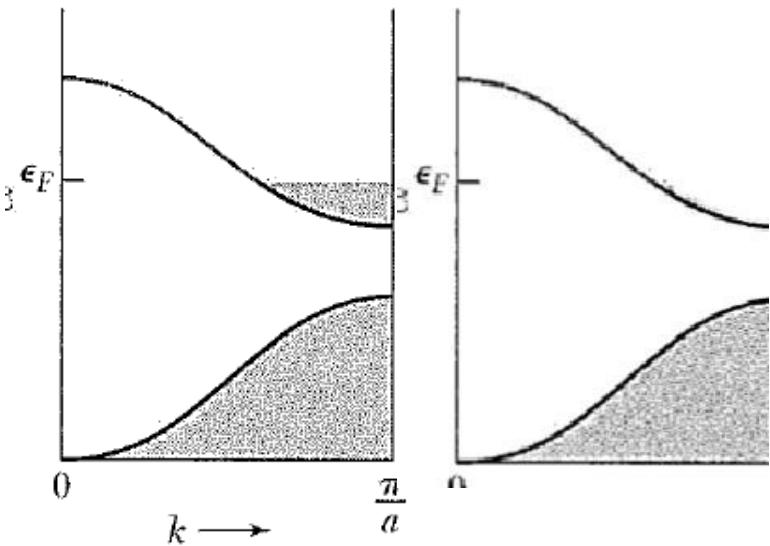
$$m_{ij}^* = \hbar^2 / \frac{d^2 E}{dk_i dk_j}$$

# FoP 3B Part II

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Room 151

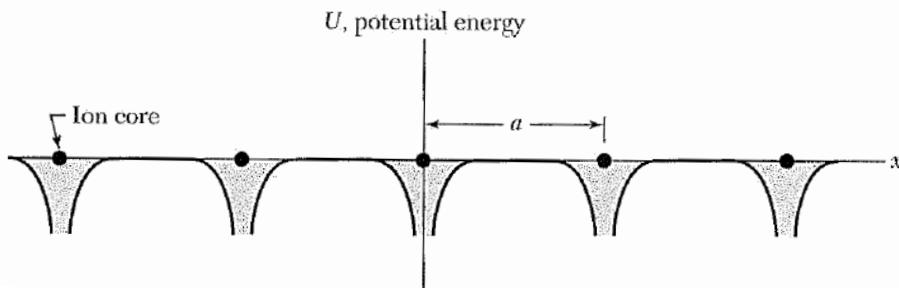
## Lecture 2: Electrons and holes

# Summary of Lecture 1



Direct vs indirect band gaps

Metals vs semiconductors



Effective mass

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt}$$

$$V = \frac{1}{\hbar} \frac{dE}{dk}$$

$$m^* = \hbar^2 / \frac{d^2 E}{dk^2}$$

## Aim of today's lecture

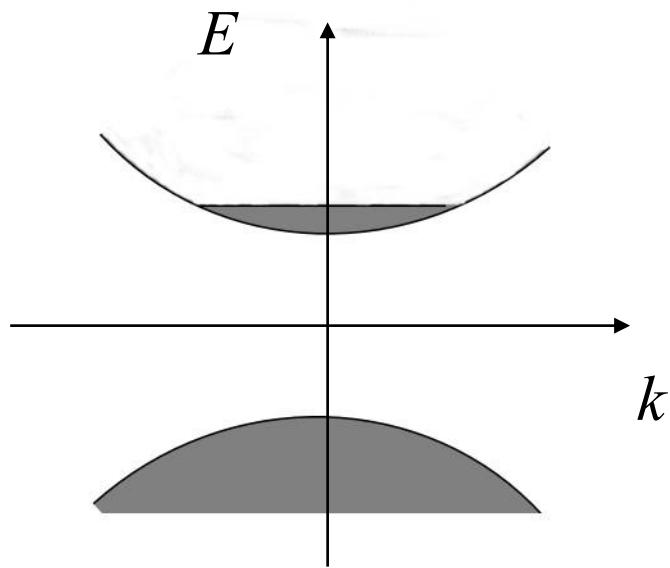
Q: How does a material conduct electricity?

A: Electrons (nearly empty band) and holes (nearly full band)

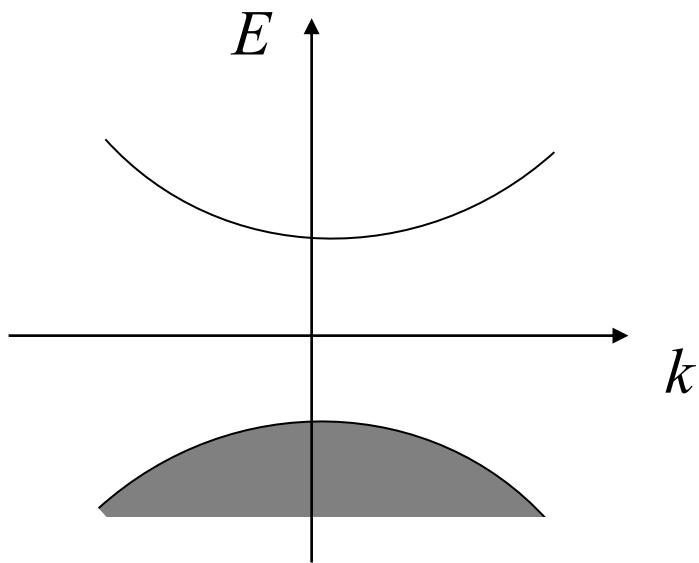
*Key concepts:*

- Conduction in a completely full band
- Conduction in a nearly empty band (electrons)
- Conduction in a nearly full band: concept of holes

# Bands at zero electric field



Metal (partially full band)

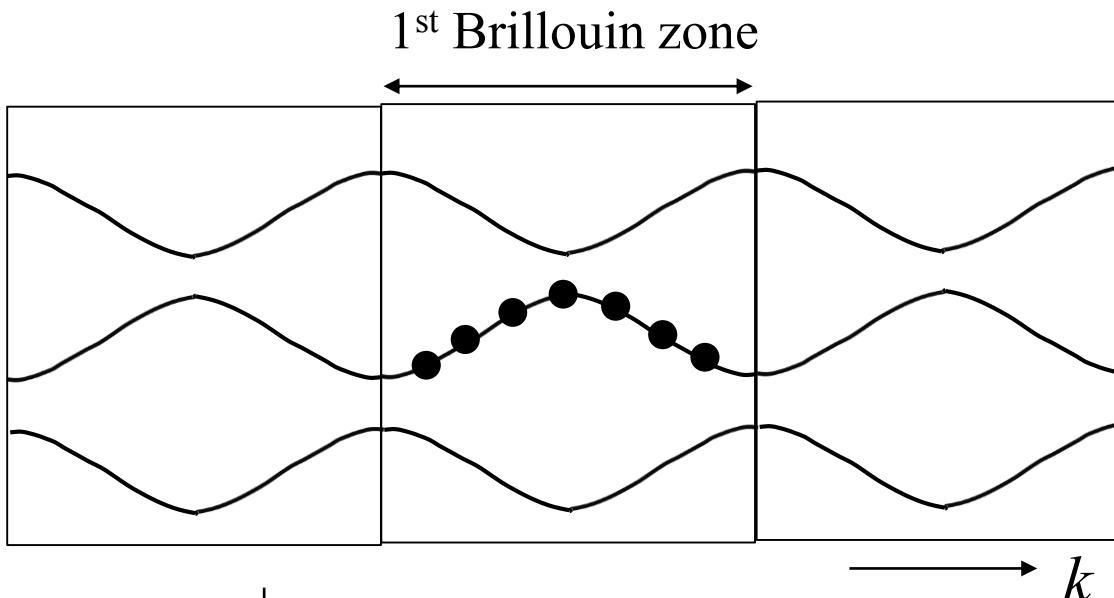


Semiconductor (full band)

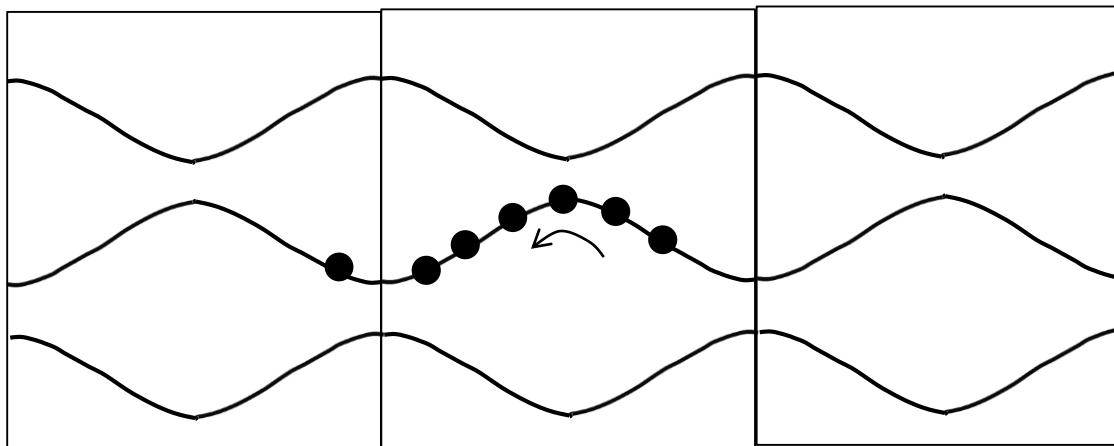
From symmetry:

- (i)  $\sum \mathbf{k} = 0$  (no net crystal momentum)
- (ii)  $\sum \mathbf{v} = 0$  (no net current)

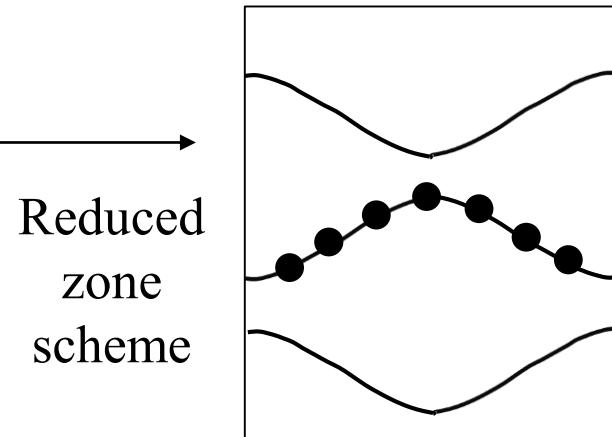
# Conduction in a full band



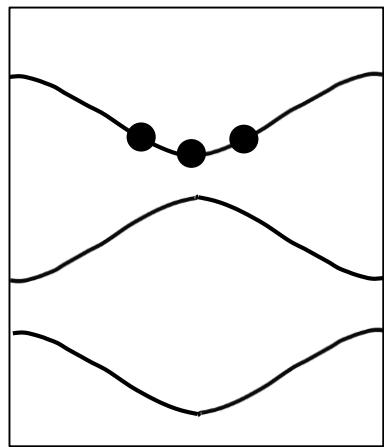
Electric field applied in  $+k$  direction  
and using  $\mathbf{F} = \hbar d\mathbf{k}/dt$



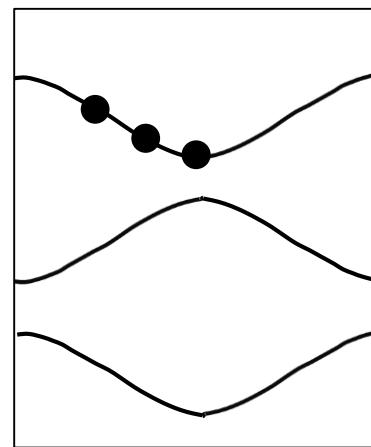
- Filled bands do not conduct electricity.
- Reason why semiconductors are insulating at 0K.



# Conduction in a nearly empty band (electrons)

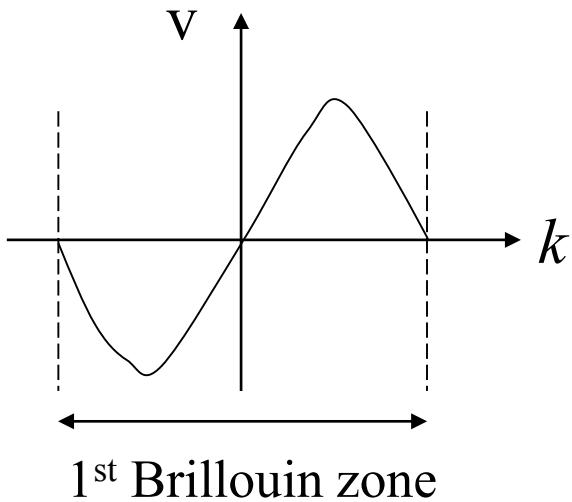


Apply electric field  
in  $+k$  direction



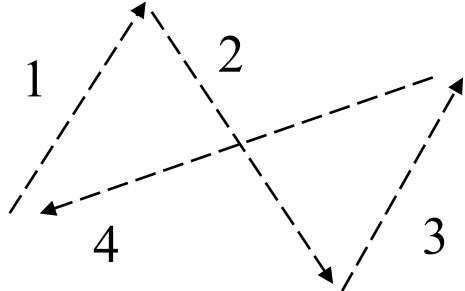
- $\sum \mathbf{k}$ ,  $\sum \mathbf{v} \neq 0$

-instantaneous  
current in field  
direction

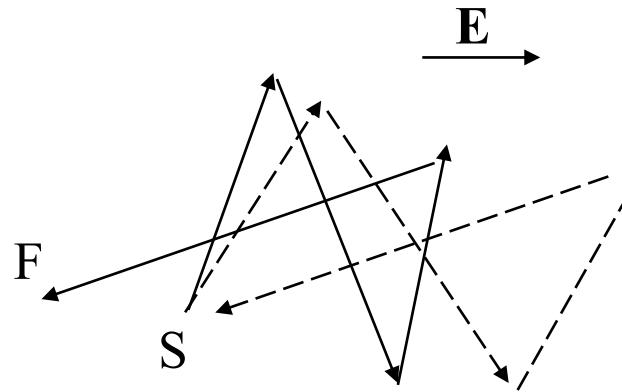


- The *time averaged* velocity of an electron is however zero.
- This implies that a *perfect* crystal with nearly empty band does not carry a current for any appreciable time!

# Scattering in real materials (I)



Electron trajectory (no electric field)



Electron trajectory with electric field  
(dashed lines- zero electric field)

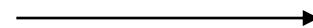
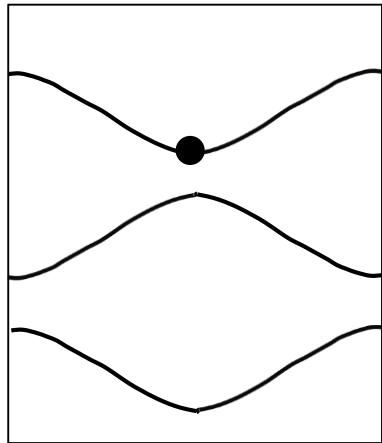
Electron acquires a net *drift* velocity  $\mathbf{v}_d$  given by:

$$\mathbf{v}_d = -\mu \mathbf{E}$$

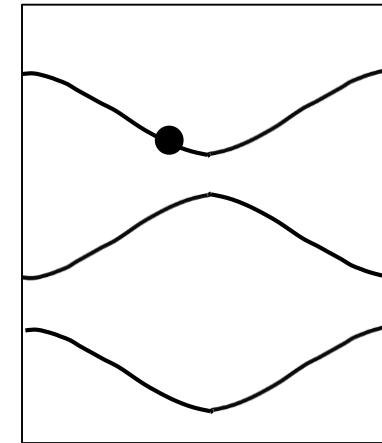
where  $\mu$  is the *mobility*\*.

\* See supplementary notes for a derivation and Hall measurement technique (non-examinable).

## Scattering in real materials (II)

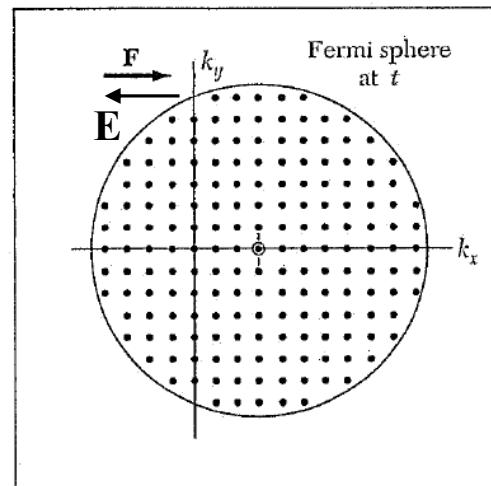
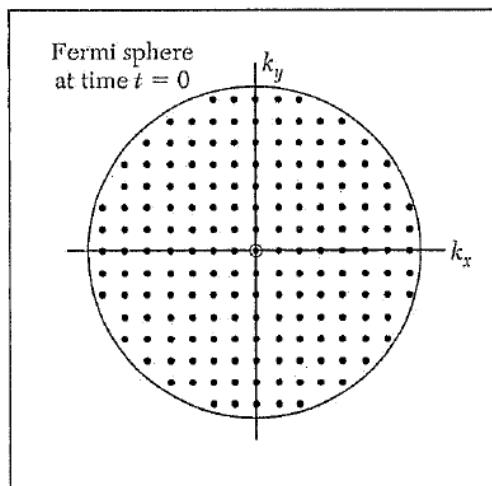


Apply electric field  
in  $+k$  direction

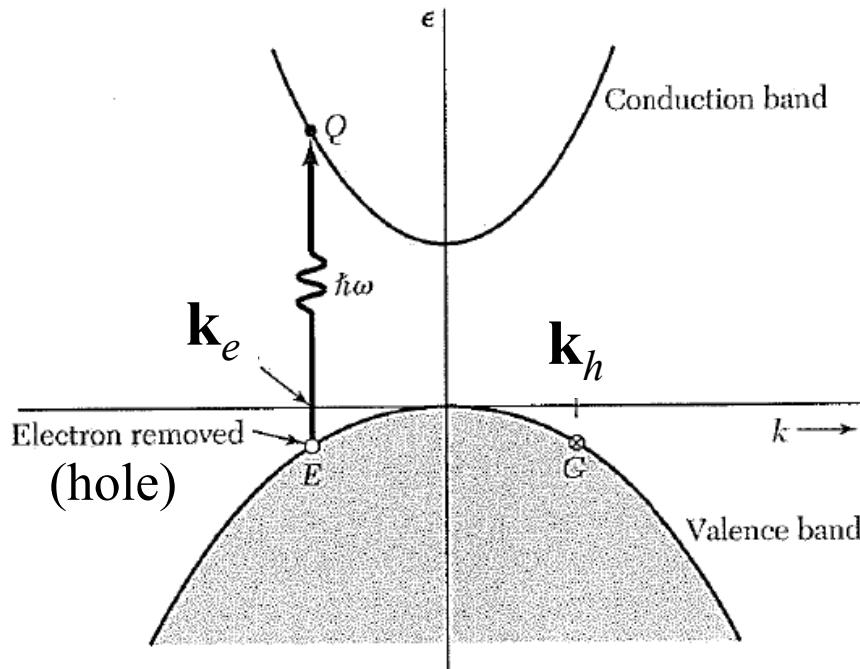


Electron at bottom of conduction band before applying electric field

*Time averaged* state of electron in an electric field (scattering included)



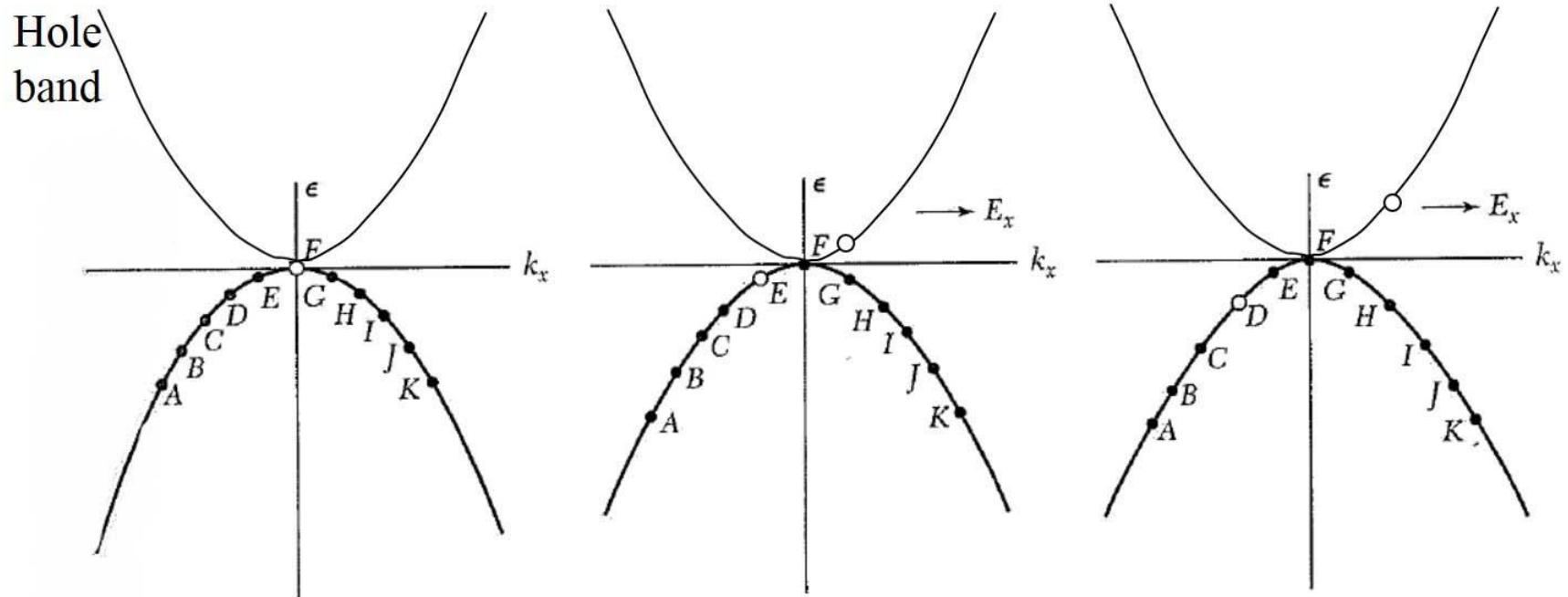
# Conduction in a nearly full band (holes)- I



Semiconductors: photon/thermal excitation of valence electron into conduction band

- For a full band:  $\sum \mathbf{k} = 0$
- After photon/thermal excitation:  $\sum \mathbf{k} = -\mathbf{k}_e = \mathbf{k}_h$   
( $\mathbf{k}$  of hole opposite to that of excited electron)

# Conduction in a nearly full band (holes)- II



- Conduction of valence electrons equivalent to positively charged hole in hole band
- From the symmetry of valence and hole bands:

$$\mathbf{k}_h = -\mathbf{k}_e \text{ (k vector)}$$

$$\epsilon_h = -\epsilon_e \text{ (energy)}$$

$$\mathbf{v}_h = \mathbf{v}_e \text{ (velocity)}$$

$$m_h^* = -m_e^* \text{ (effective mass)}$$

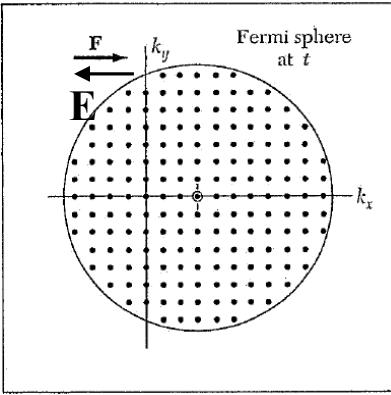
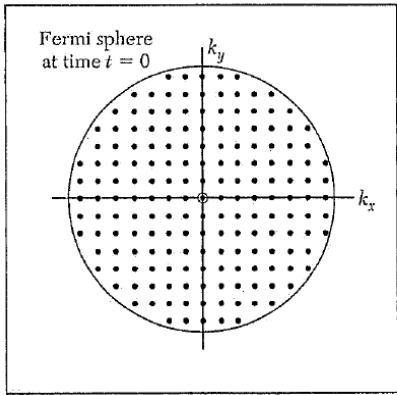
# FoP 3B Part II

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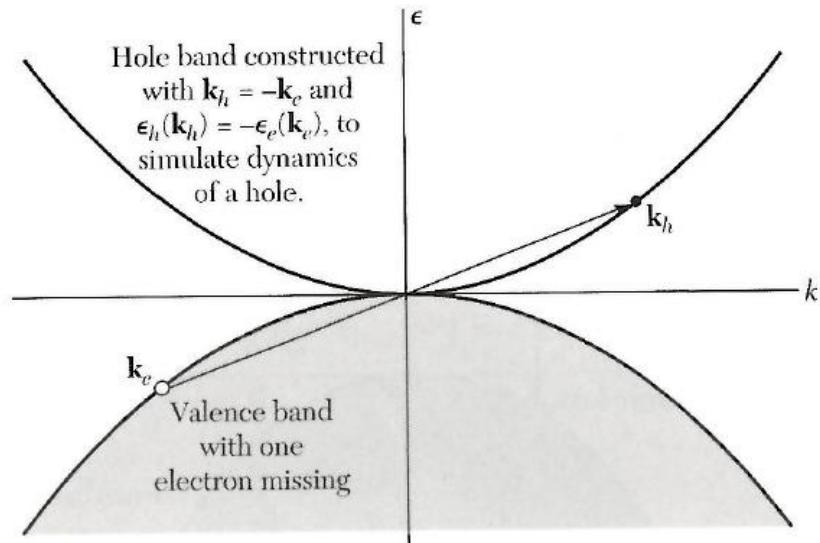
Room 151

Lecture 3: Statistical Physics of semiconductors

# Summary of Lecture 2

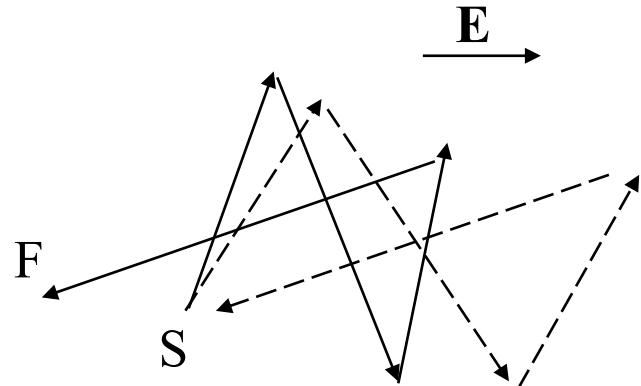
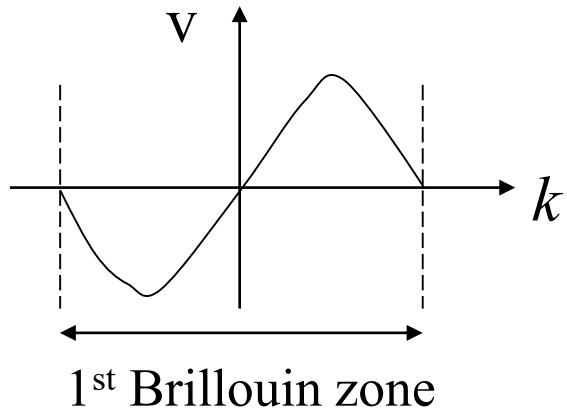


Conduction: nearly empty band (electrons)



Conduction: nearly full band (holes)

Role of scattering in electron/hole conduction:



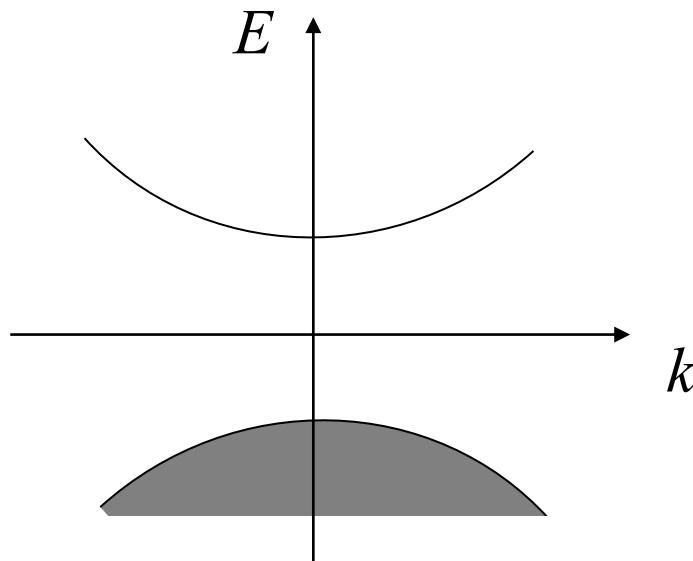
## Aim of today's lecture

Q: How to calculate electron and hole populations in a semiconductor at a given temperature?

*Key concepts:*

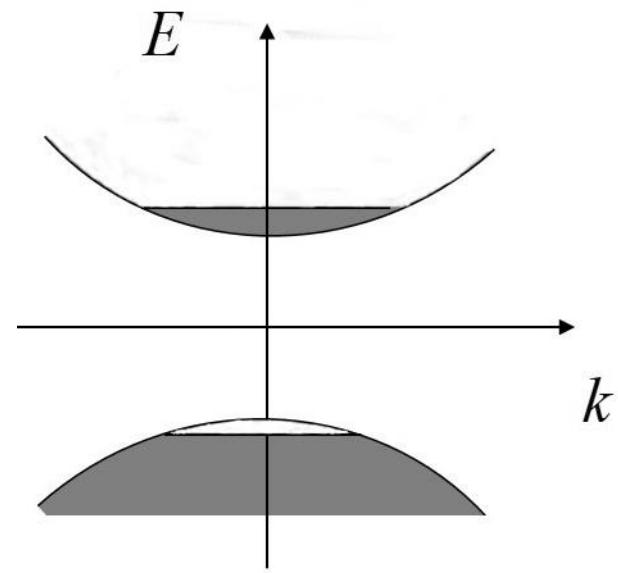
- Statistical physics of electrons and holes
- Fermi level/chemical potential in an intrinsic semiconductor
- Law of mass action
- Effect of temperature on conductivity

# Semiconductor in equilibrium: effect of temperature



Absolute zero ( $T = 0 \text{ K}$ )

Increase Temp



Finite temp

- Electrons and holes thermally generated.
- For thermal generation number of electrons in the conduction band ( $n$ ) = number of holes in the valence band ( $p$ ).
- $n$  and  $p$  at room temp are small since  $kT \ll \text{band gap}$ .

## Calculating *equilibrium* electron, hole concentrations at a given temperature

- (1) Since the semiconductor is in equilibrium Fermi-Dirac statistics apply.
- (2) The number of electrons between energy levels  $E$  and  $E+dE$  is:

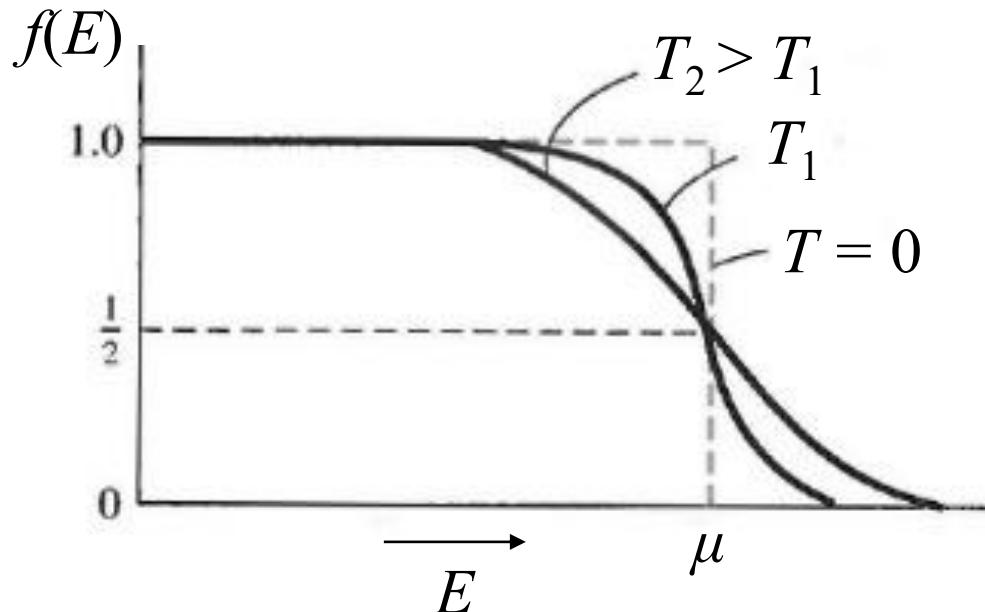
$$f(E)g(E)dE$$

- (3) Number of electrons missing between energy levels  $E$  and  $E+dE$ :

$$[1 - f(E)]g(E)dE$$

This is equal to the number of holes.

## Pre-requisites: Fermi-Dirac distribution function



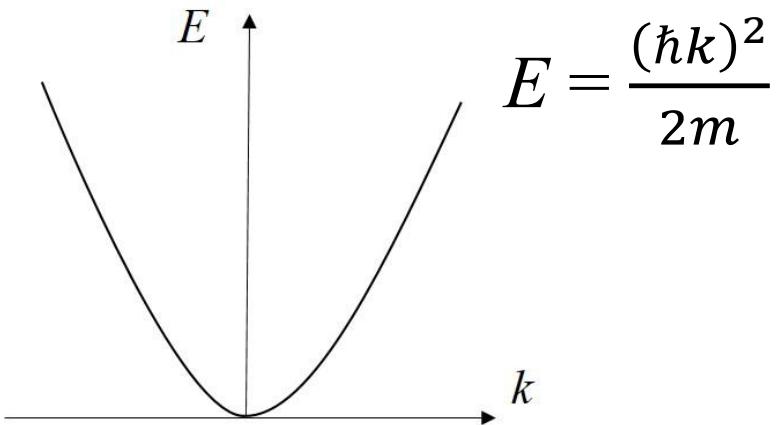
$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{kT}\right)}$$

- $\mu$ : chemical potential
- $0 \leq f(E) \leq 1$  (Pauli exclusion principle)

# Pre-requisites: Density of states

Assume a free electron solid.

Then:

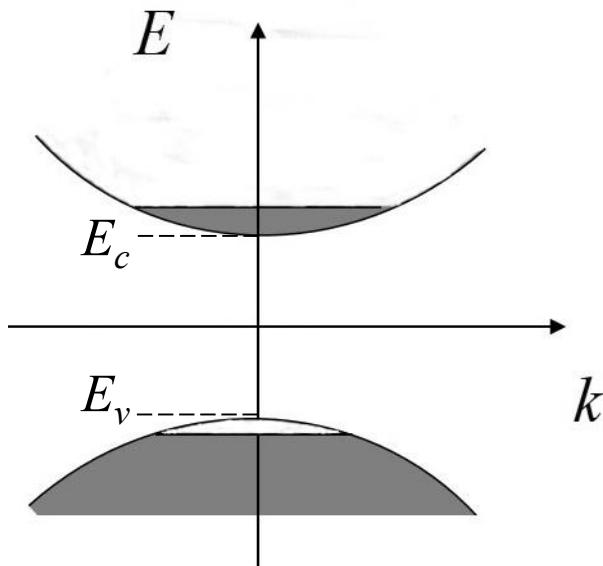


Density of states:

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

See Kittel, Chapter 6

$$g_e(E) = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$

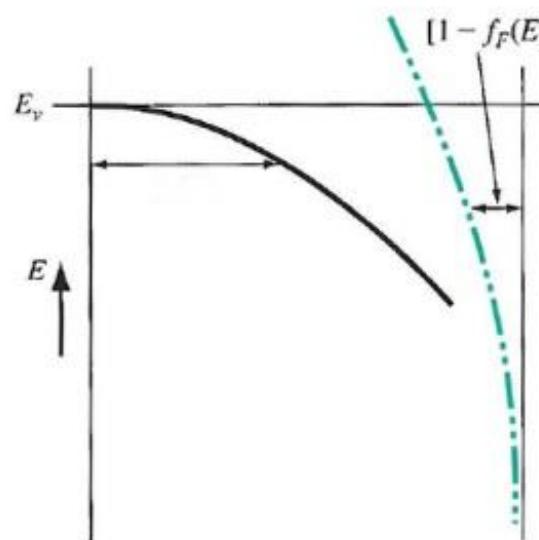
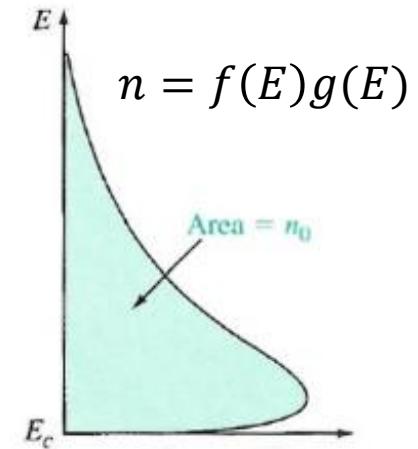
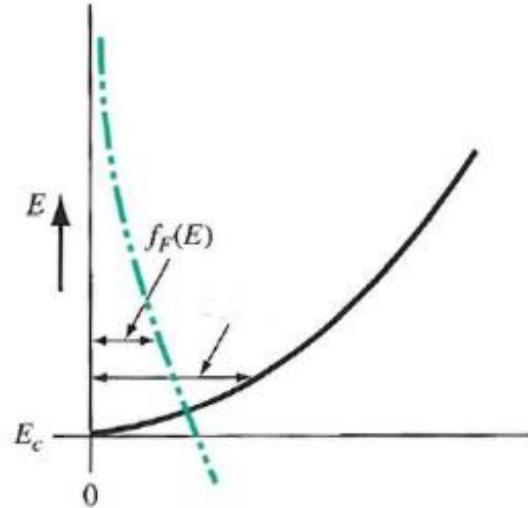
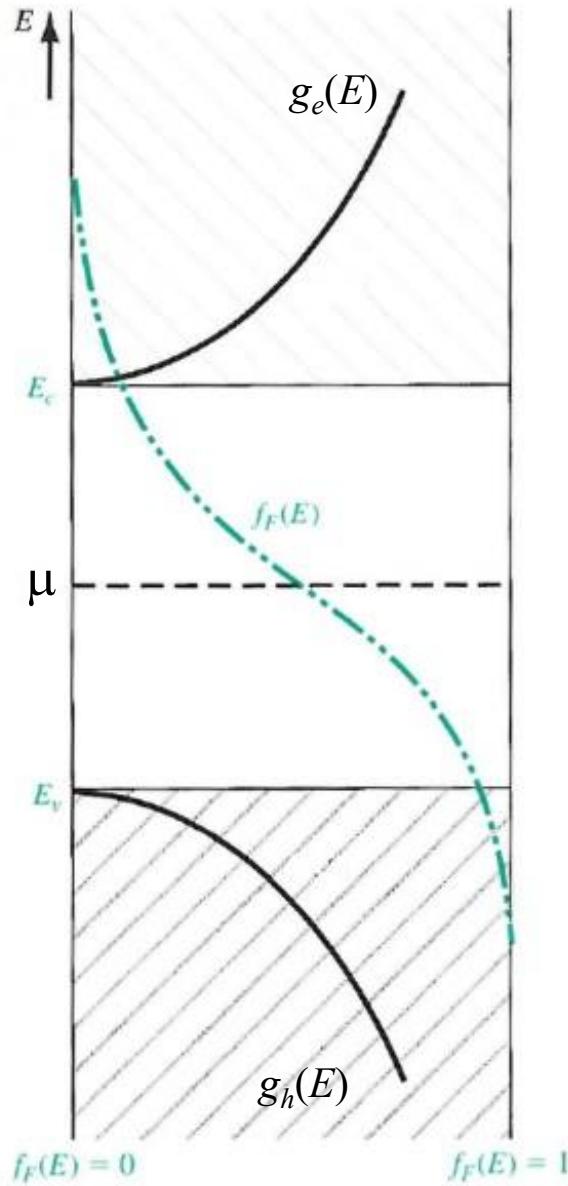


$$g_h(E) = \frac{1}{2\pi^2} \left( \frac{2m_h^*}{\hbar^2} \right)^{3/2} \sqrt{E_v - E}$$

$g_e(E)$ : density of states for conduction band

$g_h(E)$ : density of states for valence band

# Equilibrium electron, hole concentrations (I)



$$p = [1 - f(E)]g(E)$$

## Equilibrium electron, hole concentrations (II)

Substituting expressions for  $f(E)$ ,  $g(E)$  gives\*:

$$n = N_c \exp \left[ -\frac{(E_c - \mu)}{kT} \right] \quad \text{where} \quad N_c = 2 \left( \frac{m_e^* kT}{2\pi\hbar^2} \right)^{3/2}$$

$$p = N_v \exp \left[ -\frac{(\mu - E_v)}{kT} \right] \quad \text{where} \quad N_v = 2 \left( \frac{m_h^* kT}{2\pi\hbar^2} \right)^{3/2}$$

$N_c$ ,  $N_v$  are the effective density of states for the conduction and valence band respectively.

\* Derivation given in lecture and DUO notes.

## Fermi level position in an intrinsic semiconductor

- For an *intrinsic* semiconductor (i.e. no impurities) the number of electrons and holes are equal, since both are produced by thermal excitation.
- Equating  $n = p$  gives:

$$\mu = E_{mid-gap} + \frac{3}{4} kT \ln \left( \frac{m_h^*}{m_e^*} \right)$$

Fermi level approximately in the middle of the band gap for  $m_h \sim m_e$ . Note that  $E_{mid-gap} = (E_c + E_v)/2$ .

## Law of mass action

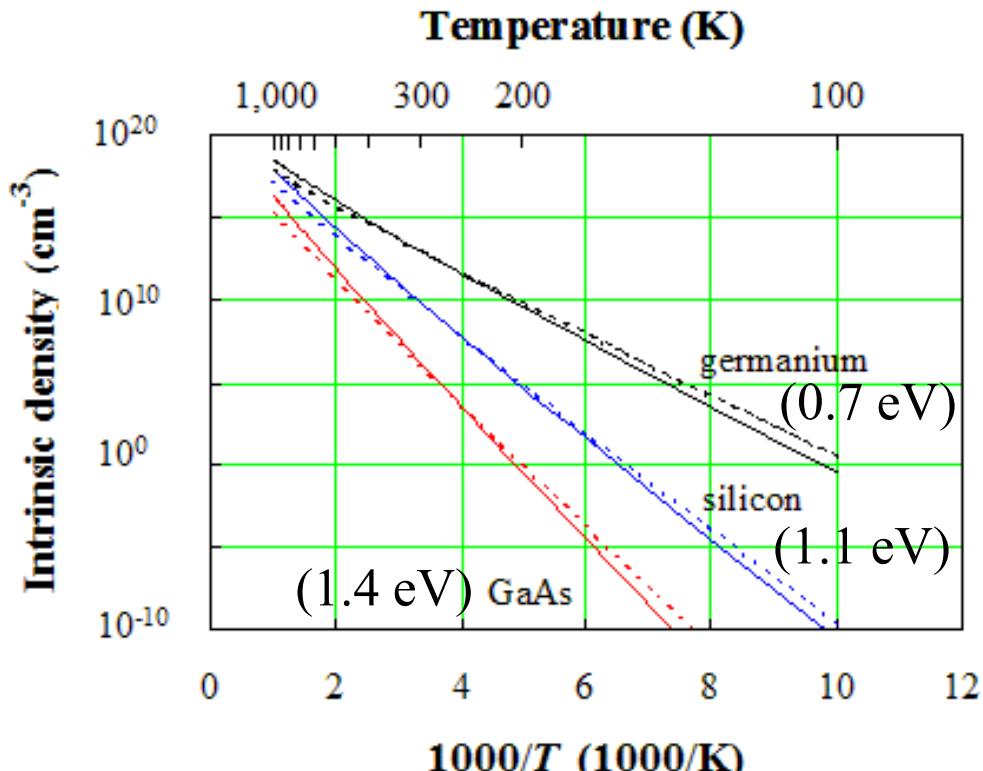
-The product  $np$  is given by:

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right) \propto T^3 \exp\left(-\frac{E_g}{kT}\right)$$

-In an intrinsic semiconductor ( $n = p = n_i$ ) both electron and hole concentrations increase with temperature.

-Carrier concentrations are larger for small band gap semiconductors.

# Effect on conductivity of semiconductor



From  $\mathbf{J} = qn\mathbf{v}$ :

$$\mathbf{J} = -en\mathbf{v}_e + ep\mathbf{v}_h$$

Electron current

Hole current

For electrons  $\mathbf{v}_e = -\mu_e \mathbf{E}$   
holes  $\mathbf{v}_h = \mu_h \mathbf{E}$

$$\begin{aligned}\therefore \mathbf{J} &= (en\mu_e + ep\mu_h)\mathbf{E} \\ &= \sigma\mathbf{E}\end{aligned}$$

For an intrinsic semiconductor  $n$  and  $p$  increase exponentially with temp. This means conductivity ( $\sigma$ ) increases with temp; cf. metals\*.

\* See supplementary reading for more info.

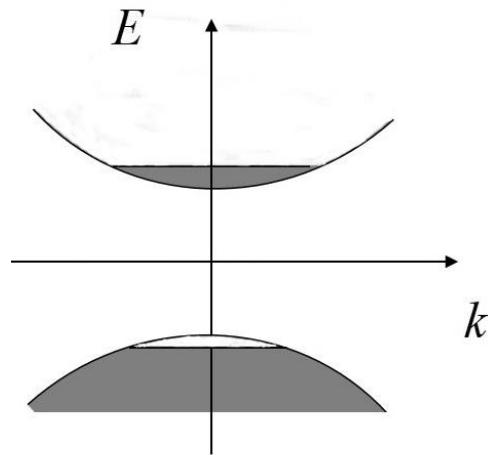
# FoP 3B Part II

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Room 151

## Lecture 4: Extrinsic semiconductors

## Summary of Lecture 3

Electron/hole concentrations:



$$n = \int f(E) g_e(E) dE$$

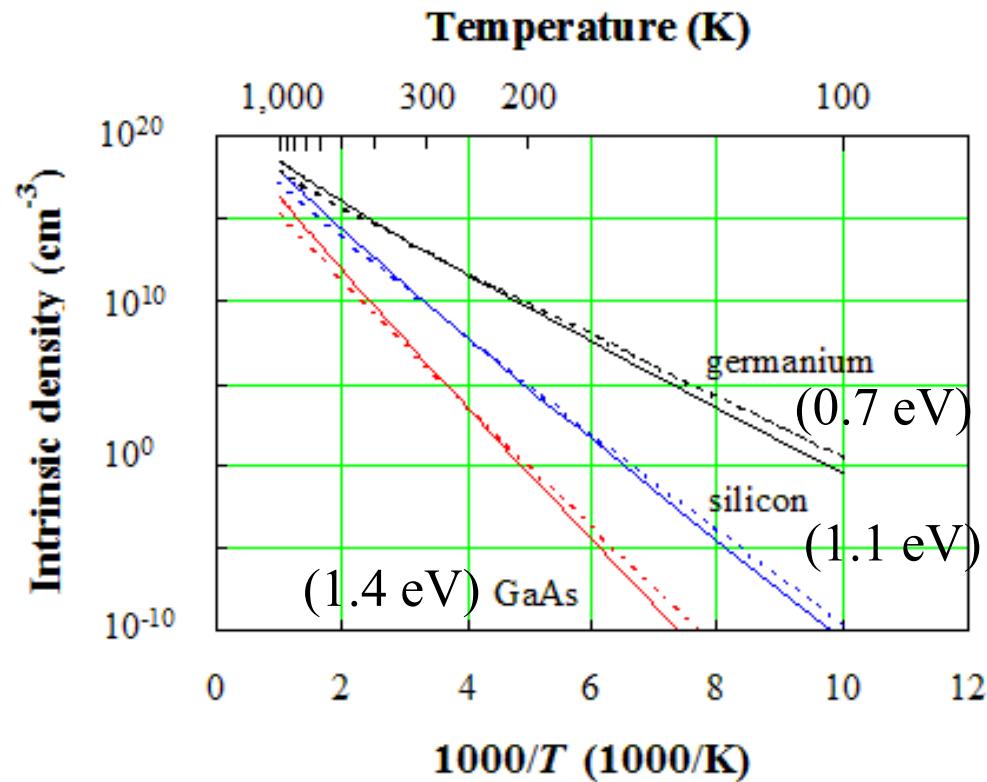
$$p = \int [1 - f(E)] g_h(E) dE$$

Law of mass action:

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

Conductivity vs temp:

$$\mathbf{J} = (en\mu_e + ep\mu_h)\mathbf{E} = \sigma\mathbf{E}$$



## Aim of today's lecture

Q: How can we manipulate conductivity at room temperature?

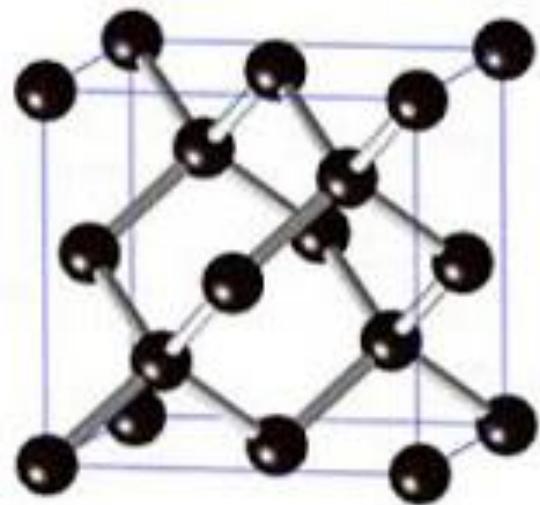
A: 'doping' with foreign atoms

*Key concepts:*

- Donor and acceptor doping
- Role of temperature on doping
- Carrier concentrations and..
- Chemical potential in extrinsic semiconductors

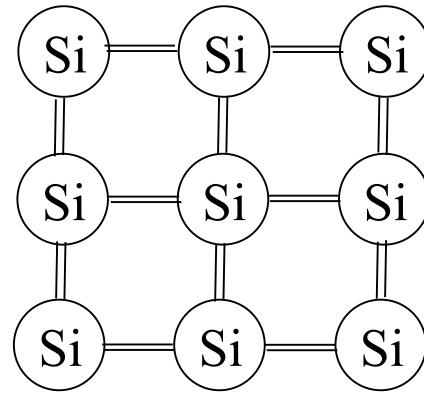
\* See supplementary information for purification and doping methods (non-examinable).

# Donor impurities

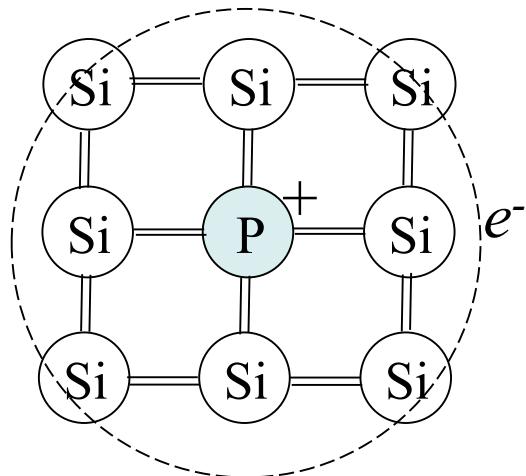


Diamond cubic crystal structure

	5 <b>B</b> boron 10.81 [10.806, 10.821]	6 <b>C</b> carbon 12.011 [12.009, 12.012]	7 <b>N</b> nitrogen 14.007 [14.006, 14.008]
12	13 <b>Al</b> aluminium 26.982	14 <b>Si</b> silicon 28.085 [28.084, 28.086]	15 <b>P</b> phosphorus 30.974
30	<b>Zn</b> zinc 65.38(2)	31 <b>Ga</b> gallium 69.723	32 <b>Ge</b> germanium 72.630(8)
48	<b>Cd</b> cadmium 112.41	49 <b>In</b> indium 114.82	50 <b>Sn</b> tin 118.71
			51 <b>Sb</b> antimony 121.76



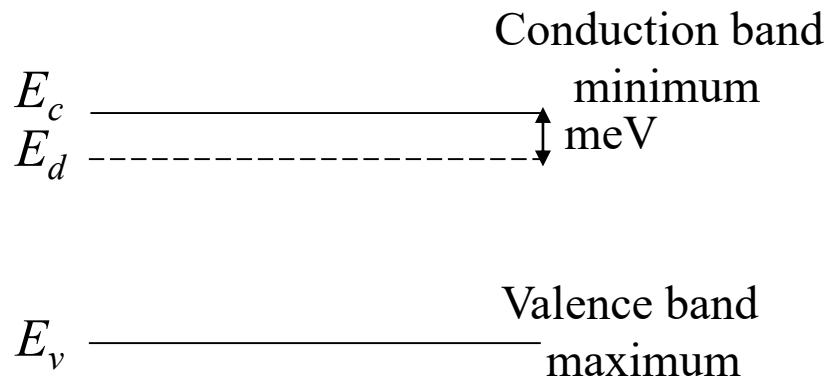
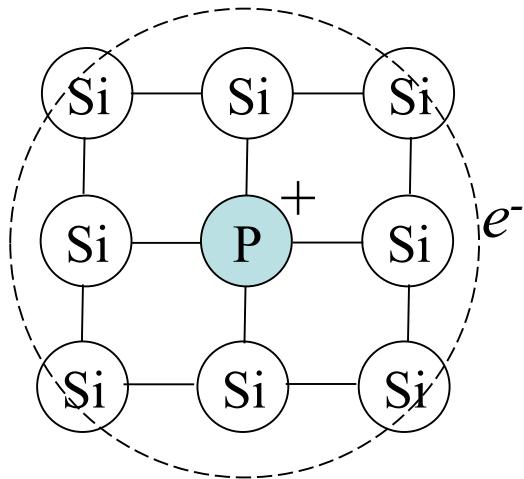
Perfect crystal



Group V substitutional atom (e.g. N, P)

# Donor electron energy level

Adapt Bohr's atomic model:



Energy level diagram  
 $E_d$ : donor level

Energy level:

$$E_D = \frac{e^4 m_e^*}{2(4\pi\epsilon_r \epsilon_0 \hbar)^2} = \frac{m_e^*}{m \epsilon_r^2} \left[ \frac{e^4 m}{2(4\pi\epsilon_0 \hbar)^2} \right] \underbrace{\frac{e^4 m}{2(4\pi\epsilon_0 \hbar)^2}}_{13.6 \text{ eV}}$$

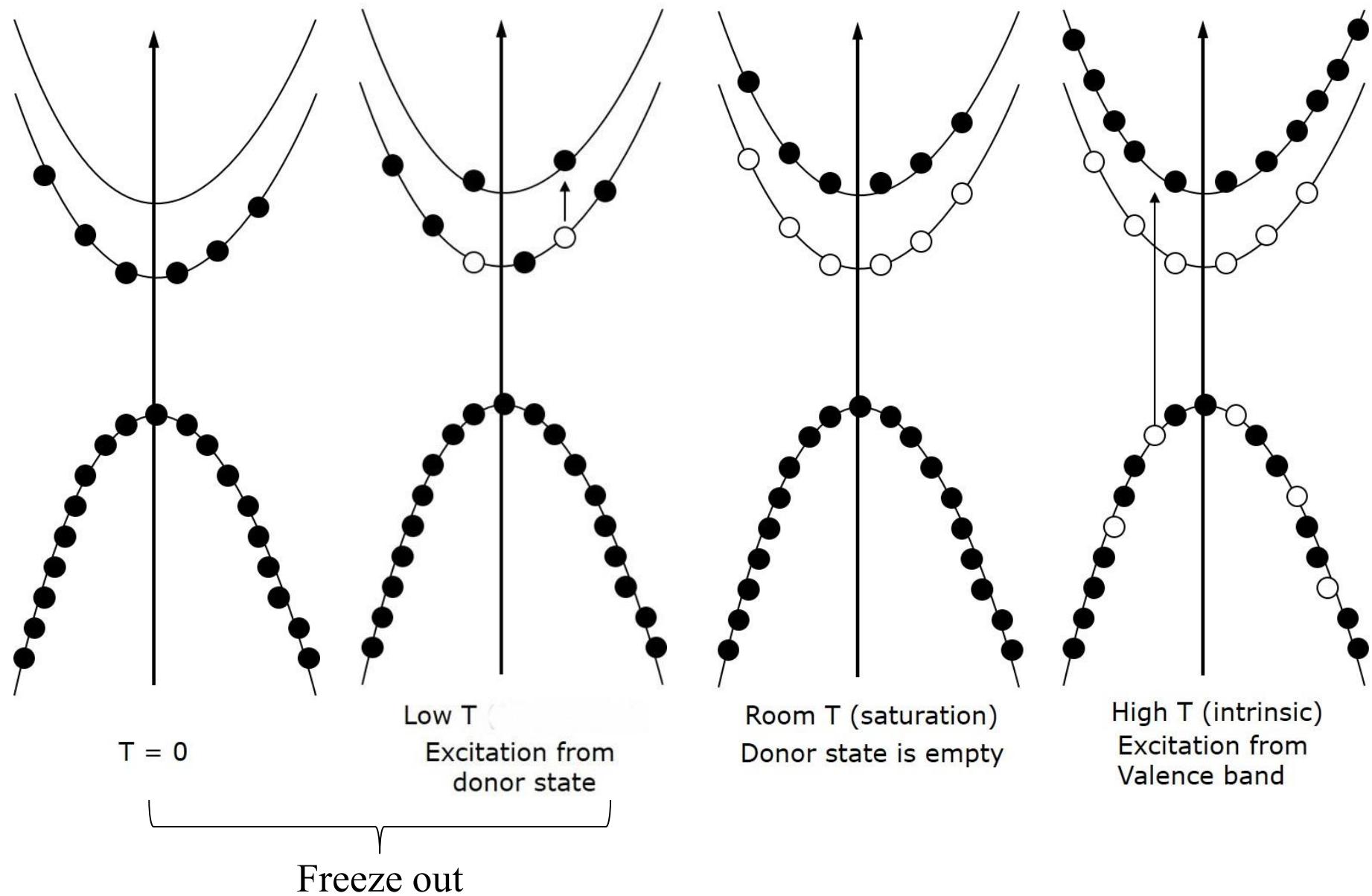
⇒ Typical energies meV

Orbit radius:

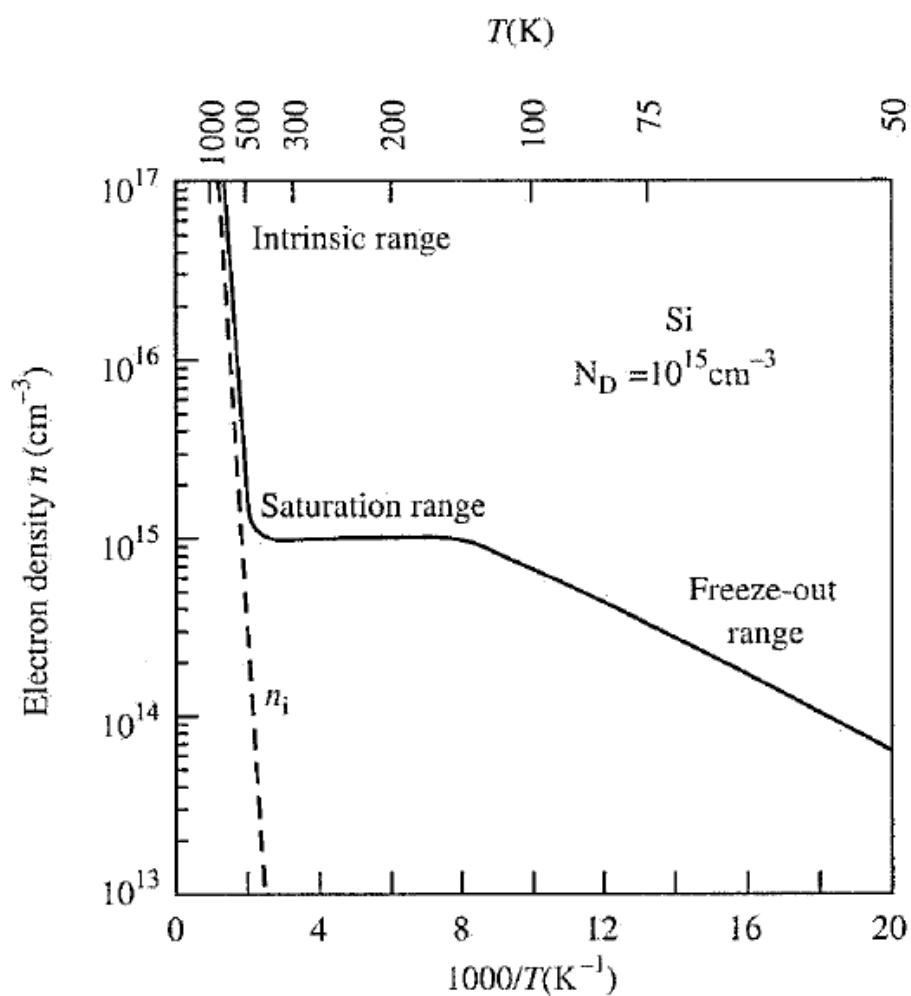
$$r = \frac{4\pi\epsilon_r \epsilon_0 \hbar^2}{m_e^* e^2} = \frac{\epsilon_r m}{m_e^*} \left( \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \right) \underbrace{\frac{4\pi\epsilon_0 \hbar^2}{m e^2}}_{0.5 \text{ \AA}}$$

⇒ Typical radius nm

# Temperature effects on donor ionisation



# Electron, hole concentrations in saturation regime



Law of mass action:

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$
$$np = n_i(T)^2 \quad \dots (1)$$

$n_i(T)$  = electron/hole concentration for intrinsic semiconductor at temp  $T$

Charge conservation:

$$n = p + N_D \quad \dots (2)$$

$N_D$  = donor concentration

Combining (1) and (2):

$$n = \frac{N_D}{2} + \sqrt{\left(\frac{N_D}{2}\right)^2 + n_i^2}$$

## Electron, hole concentrations in saturation regime

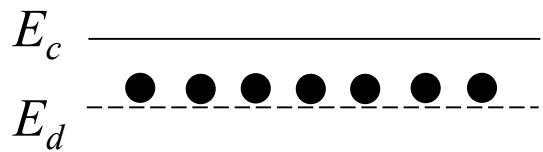
$$n = \frac{N_D}{2} + \sqrt{\left(\frac{N_D}{2}\right)^2 + n_i^2}$$

Assuming  $N_D \gg n_i(T)$  then:

$$\begin{aligned} n &\sim N_D \\ p &\sim n_i^2/N_D \text{ (law of mass action)} \end{aligned}$$

In other words  $n > n_i$  and  $p = n_i(n_i/N_D) < n_i$ . Electrons are therefore the *majority* carriers and holes the *minority* carriers. The semiconductor is said to be doped *n*-type.

# Chemical potential in *n*-type extrinsic semiconductor



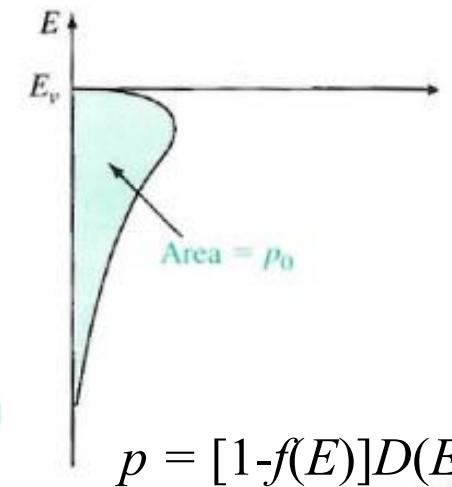
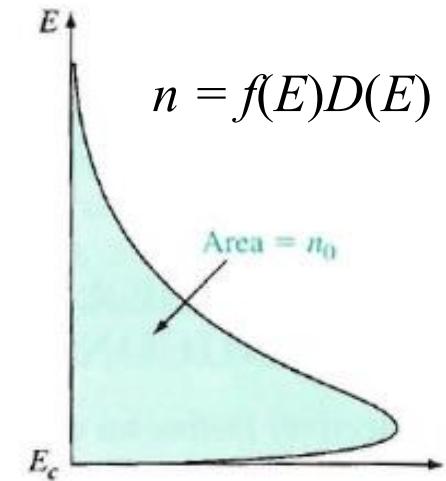
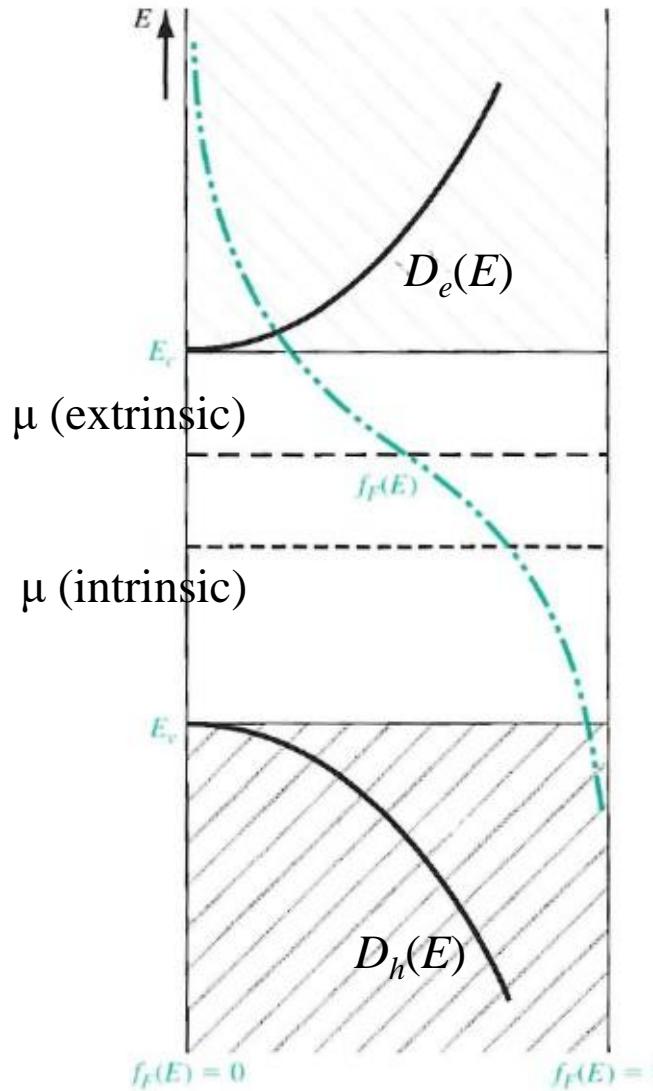
*n*-type semiconductor at 0K  
(Fermi level above  $E_d$ )

From

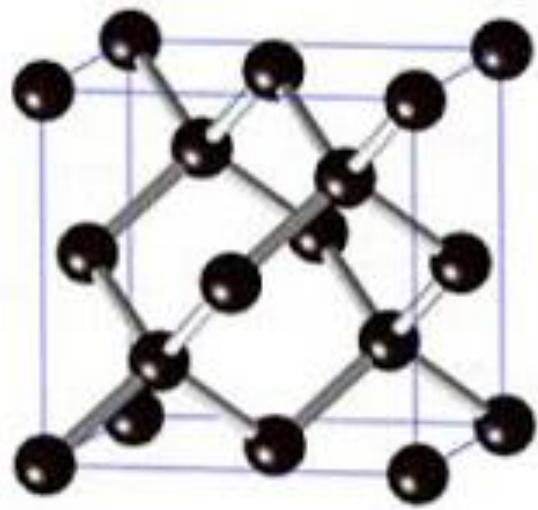
$$n = N_c \exp \left[ -\frac{(E_c - \mu)}{kT} \right]$$

and substituting  $n \sim N_D$

$$\mu = E_c - kT \ln \left( \frac{N_c}{N_D} \right)$$

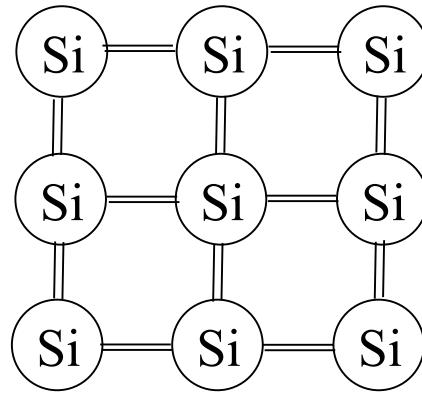


# Acceptor impurities

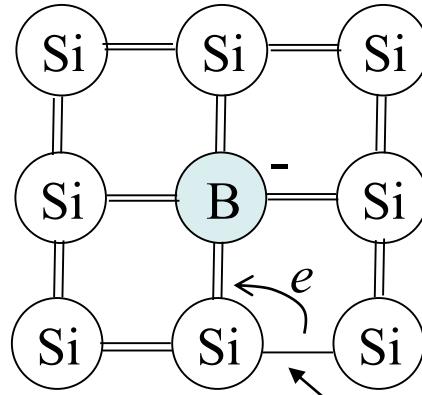


Diamond cubic crystal structure

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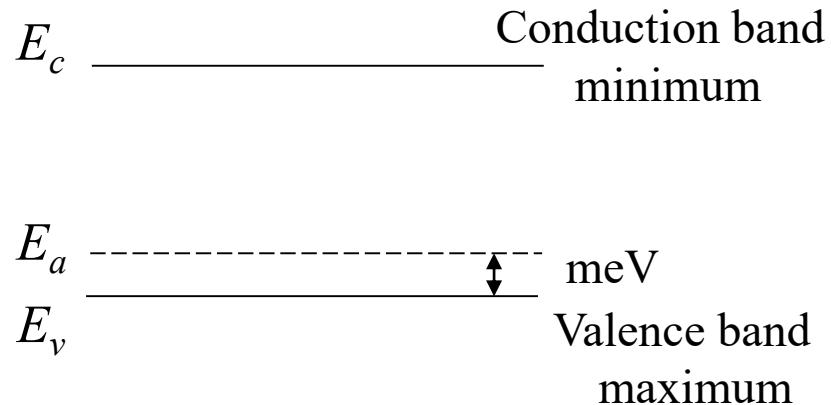
Perfect crystal



vacant site

Group III substitutional  
atom (e.g. B, Al)

# Acceptor energy level



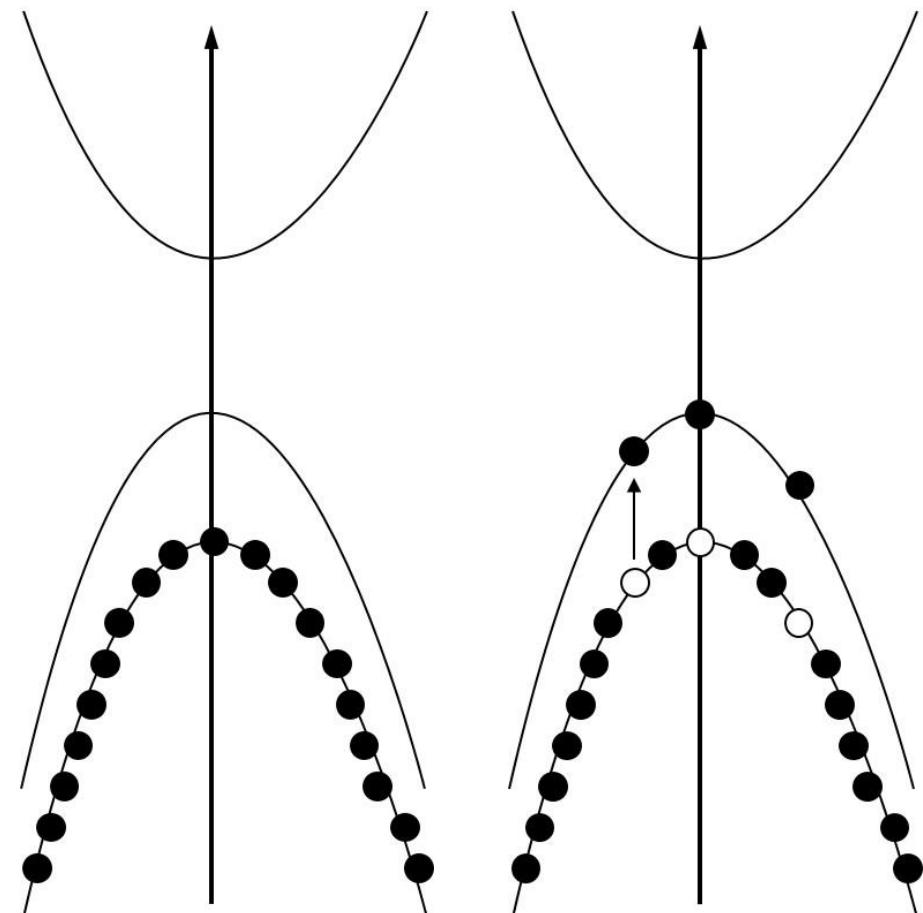
Energy level diagram  
 $E_a$ : acceptor level

Saturation regime:

$$p \sim N_A \text{ (acceptor concentration)}$$

$$n \sim n_i^2 / N_A$$

Holes are *majority* carriers,  
electrons are *minority* carriers.  
Semiconductor is *p*-type.



$T = 0$

Low T  
(freeze-out)

# Chemical potential in *p*-type extrinsic semiconductor

$E_c$  —————

$E_a$  -----

$E_v$  ● ● ● ● ● ● ●

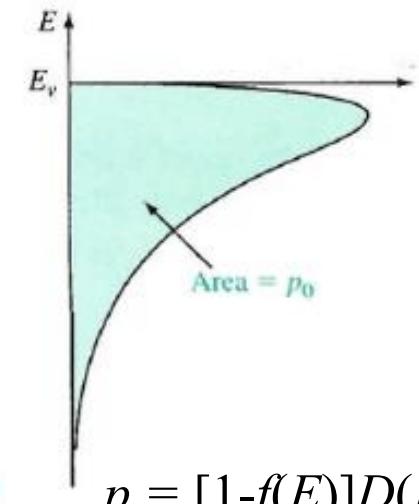
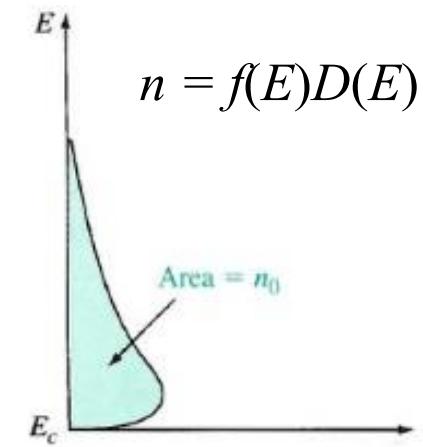
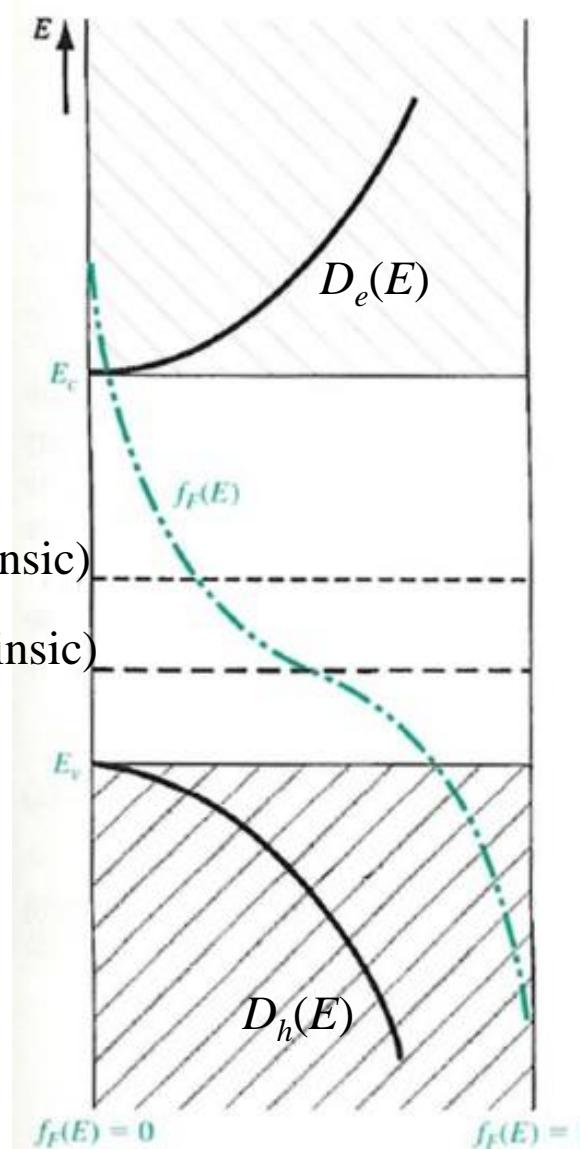
*p*-type semiconductor at 0K  
(Fermi level below  $E_a$ )

From

$$p = N_v \exp \left[ -\frac{(\mu - E_v)}{kT} \right]$$

and substituting  $p \sim N_A$

$$\mu = E_v + kT \ln \left( \frac{N_v}{N_A} \right)$$

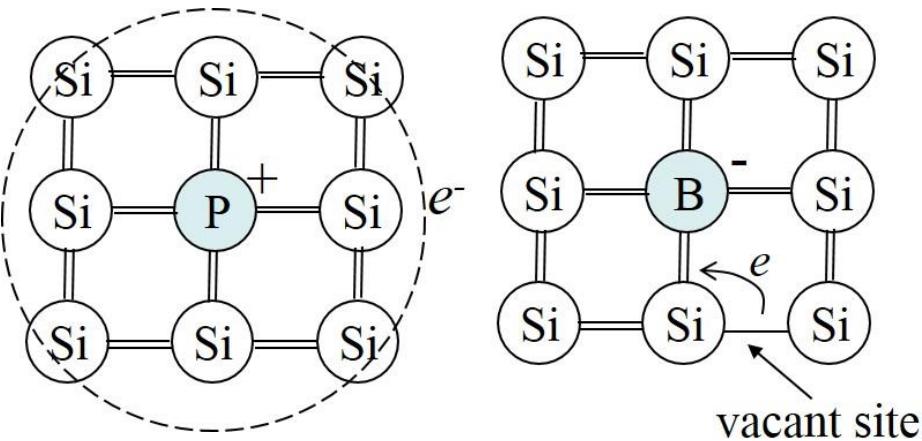


# FoP 3B Part II

Dr Budhika Mendis ([b.g.mendis@durham.ac.uk](mailto:b.g.mendis@durham.ac.uk))  
Room 151

Lecture 5: pn junction (part I)

# Summary of Lecture 4



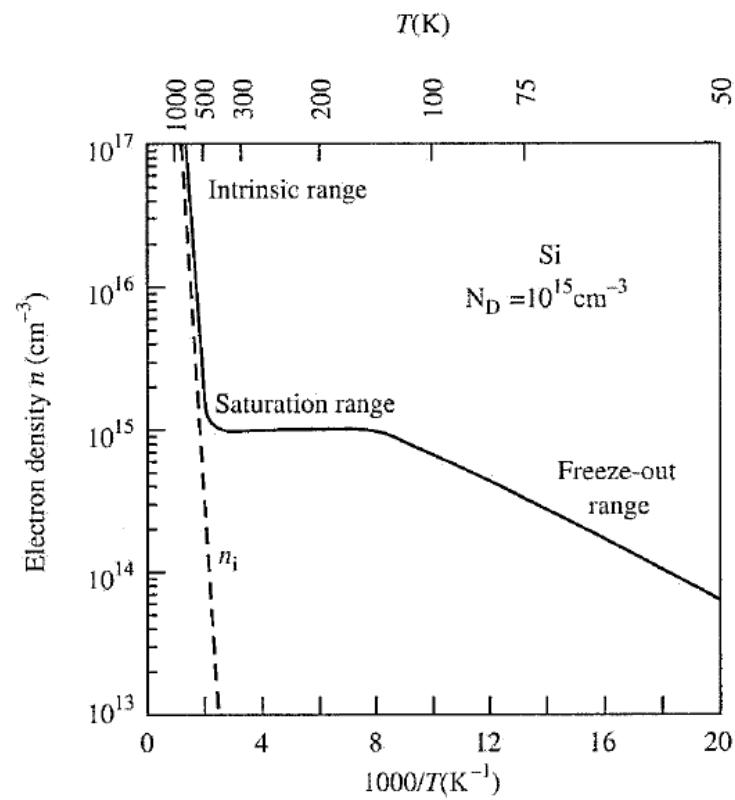
Donor and acceptor ‘impurities’

Carrier concentrations and Fermi level  
(e.g.  $n$ -type semiconductor):

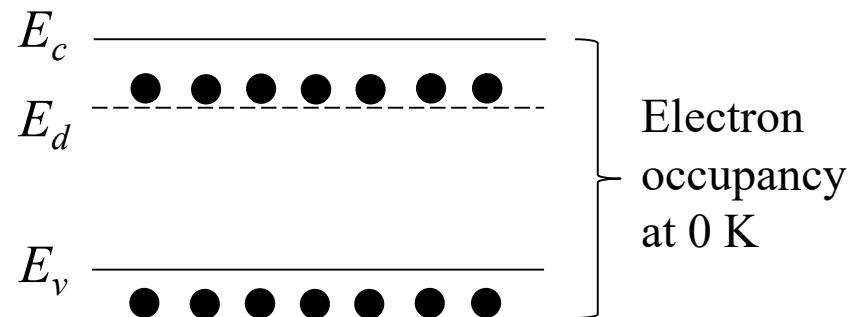
$$n \sim N_D$$

$$p \sim n_i^2/N_D$$

$$\mu = E_c - kT \ln \left( \frac{N_c}{N_D} \right)$$



Temp dependence  
of doping



## Aim of today's lecture

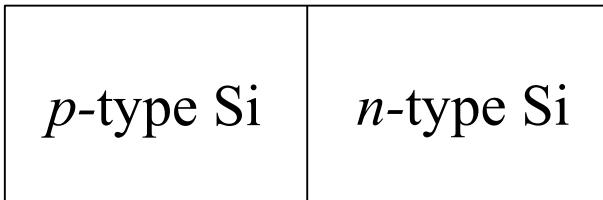
- To describe the equilibrium\* properties of a pn-junction

*Key concepts:*

- Depletion approximation
- derive electric field and potential for pn-junction

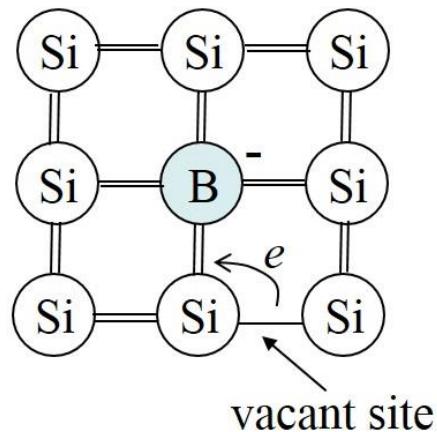
\* Assumes no light or electrical biasing.

# What happens when we bring p- and n-doped regions together?

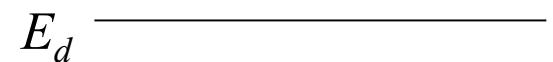
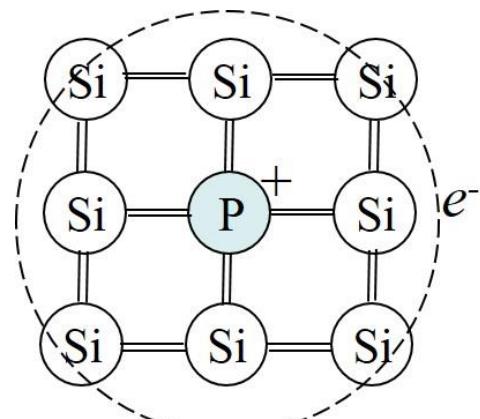


- Concentration gradient for electrons and holes.
- Electrons diffuse to the p-region and holes diffuse to the n-region.

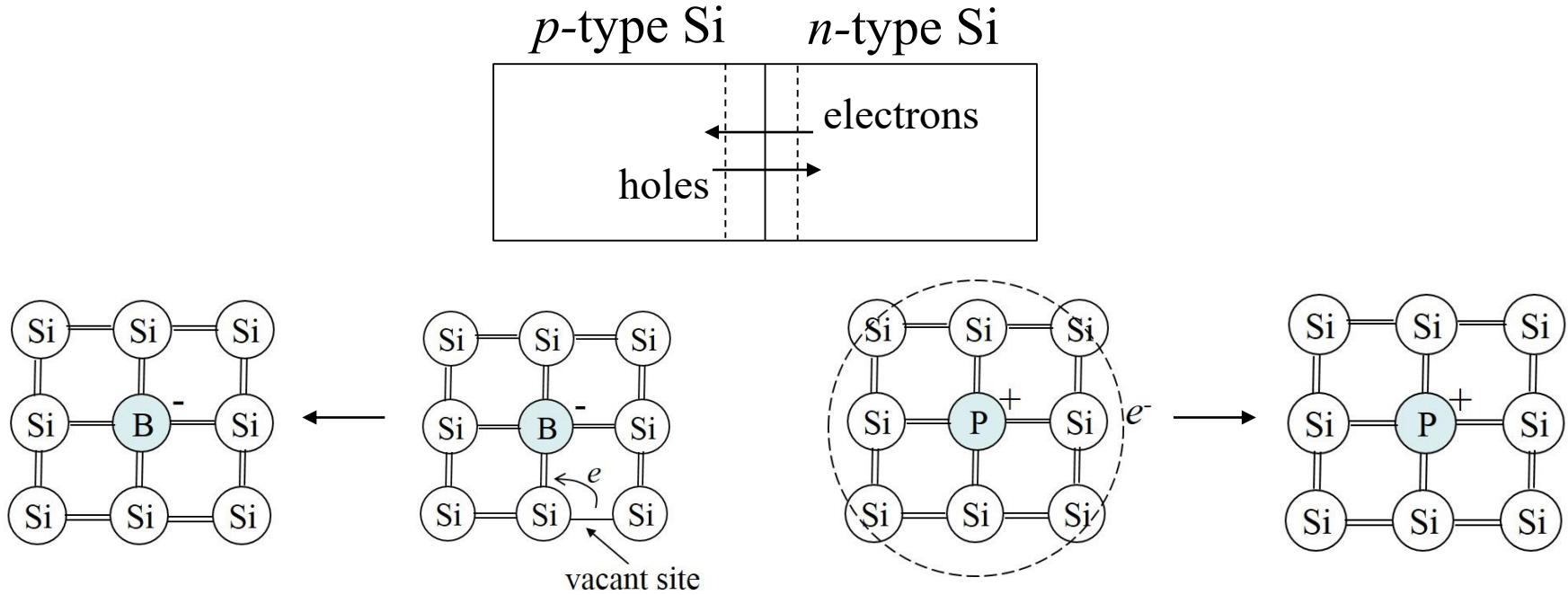
p-region



n-region

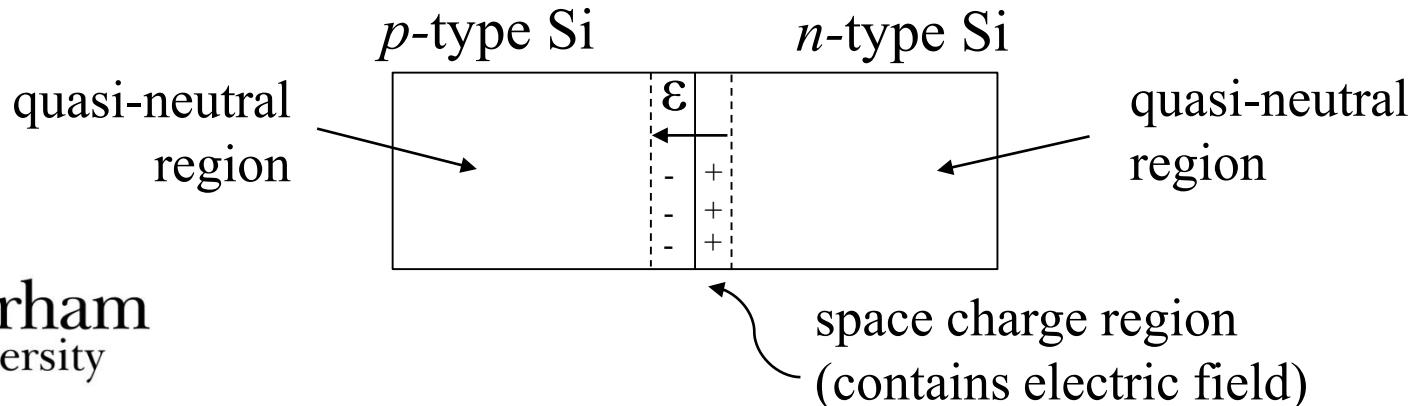


# Carrier diffusion and built-in electric field



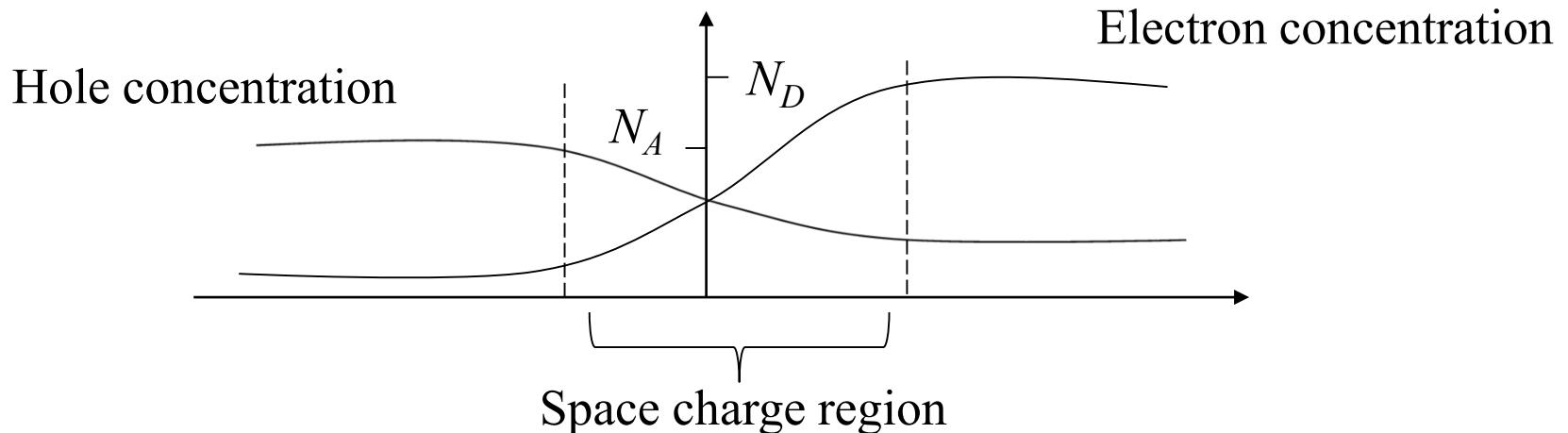
## Net negative charge from *ionised* acceptors

## Net positive charge from *ionised* donors

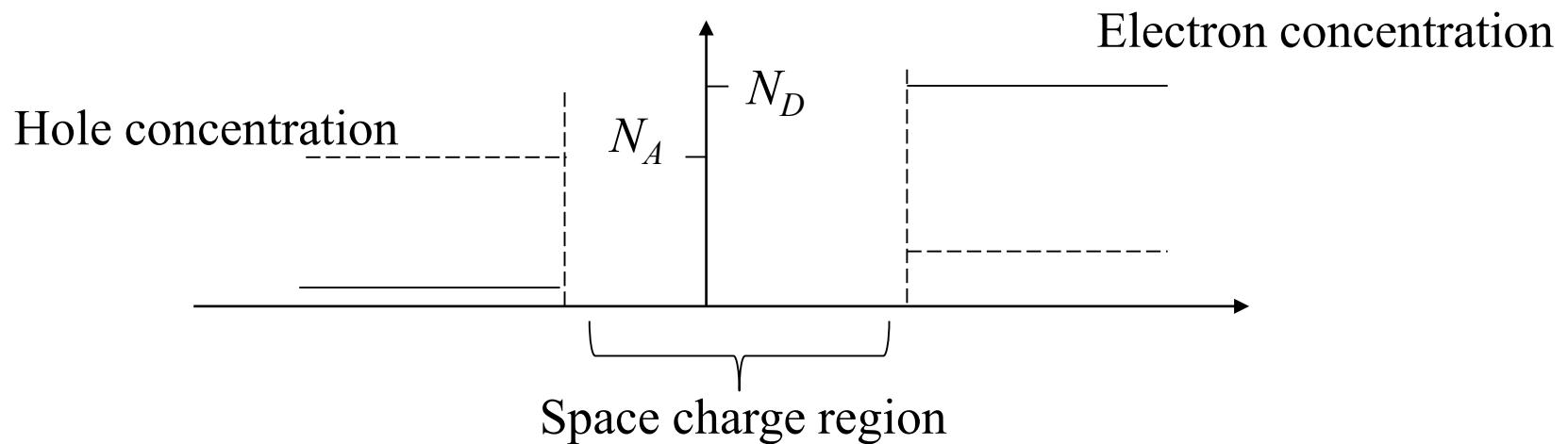


# The depletion approximation

Expected carrier diffusion profile:

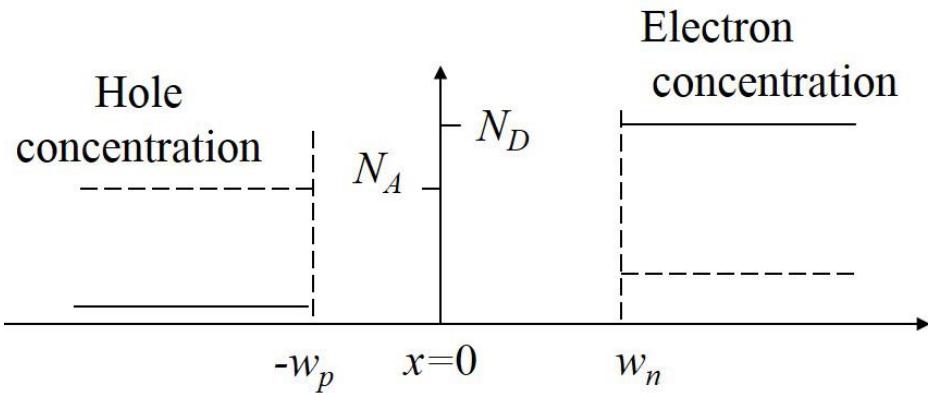


Depletion approximation (no carriers within space charge region):



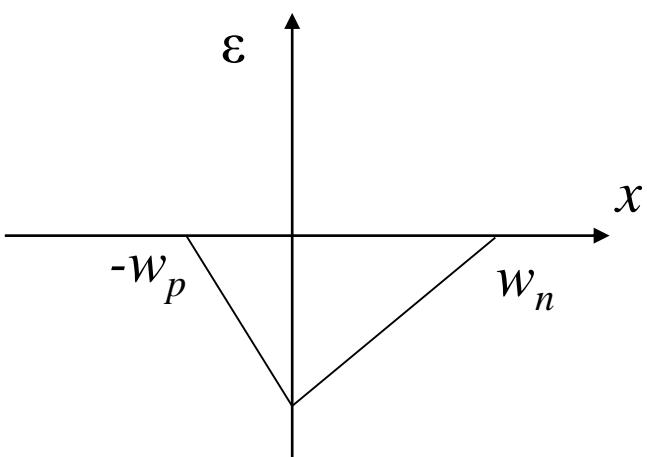
# Built-in electric field

Gauss' law:



$$\vec{\nabla} \cdot \vec{\mathcal{E}} = \frac{d\mathcal{E}}{dx} = \frac{\rho(x)}{\epsilon_r \epsilon_0}$$

$$\rho(x) = \begin{cases} -eN_A & -w_p < x < 0 \\ eN_D & 0 < x < w_n \\ 0 & \text{elsewhere} \end{cases}$$



$$\rightarrow \mathcal{E}(x) = \begin{cases} -\frac{eN_A}{\epsilon_r \epsilon_0}(x + w_p) & -w_p < x < 0 \\ \frac{eN_D}{\epsilon_r \epsilon_0}(x - w_n) & 0 < x < w_n \end{cases}$$

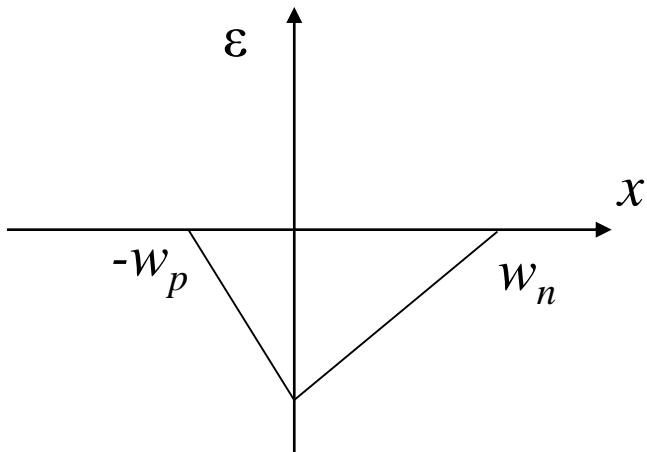
Continuity of electric field at the boundary  $x = 0$  gives:

$$N_A w_p = N_D w_n$$

(charge neutrality condition)

# Electric potential

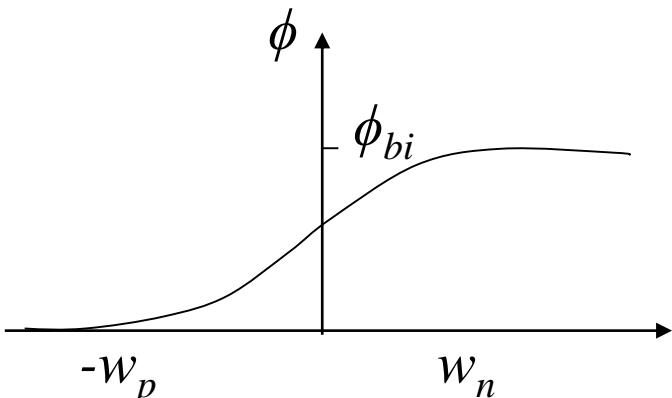
From  $\vec{\mathcal{E}} = -\vec{\nabla}\phi$  ( $\phi$  = electrostatic potential)



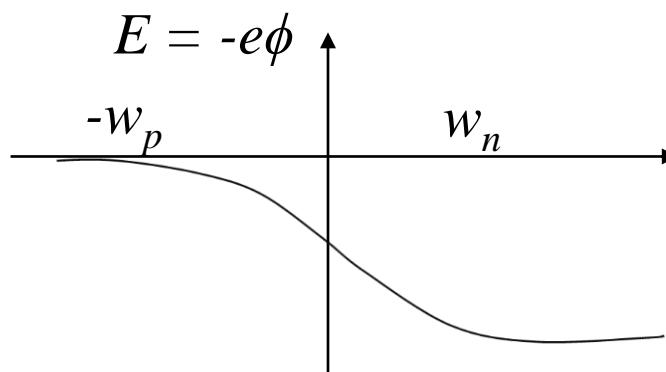
$$\epsilon(x) = \begin{cases} -eN_A(x + w_p)/\epsilon_r\epsilon_0 & -w_p < x < 0 \\ eN_D(x - w_n)/\epsilon_r\epsilon_0 & 0 < x < w_n \\ 0 & \text{elsewhere} \end{cases}$$

$$\phi(x) = \begin{cases} \frac{eN_A}{2\epsilon_r\epsilon_0}(x + w_p)^2 & -w_p < x < 0 \\ \phi_{bi} - \frac{eN_D}{2\epsilon_r\epsilon_0}(x - w_n)^2 & 0 < x < w_n \end{cases}$$

( $\phi_{bi}$  = built-in potential)

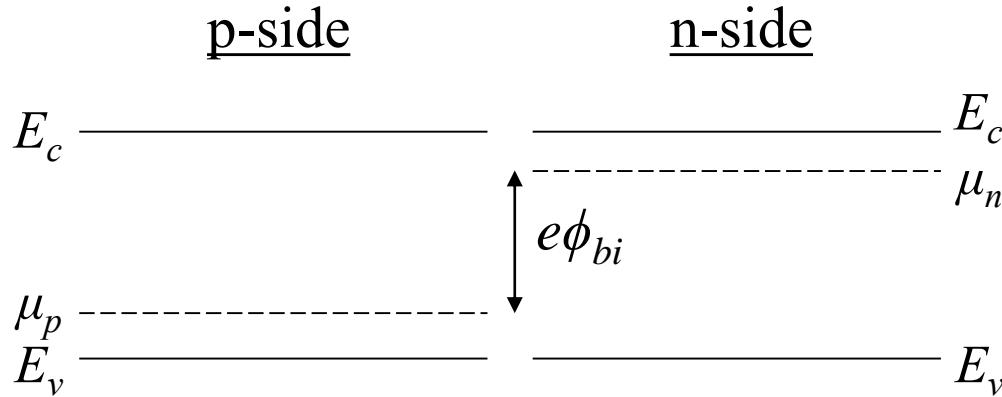


Potential

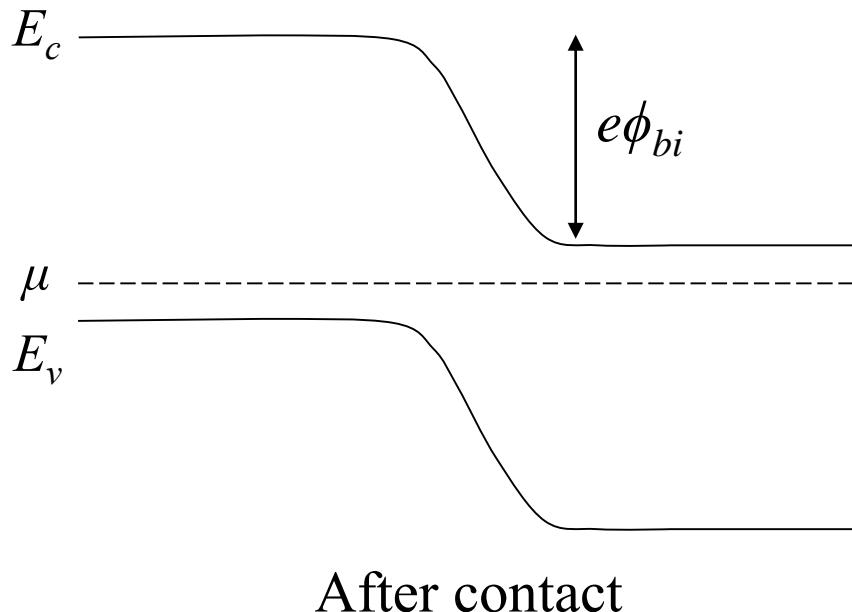


Electron energy

# Energy level diagram for pn-junction



Before contact (unequal chemical potential  $\mu = \frac{\partial G}{\partial n}$ )



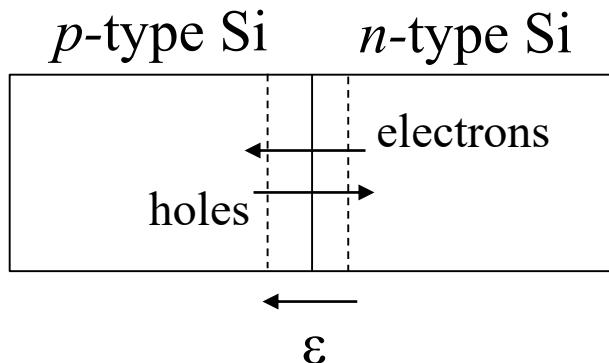
Note constant chemical potential after contact.

# FoP 3B Part II

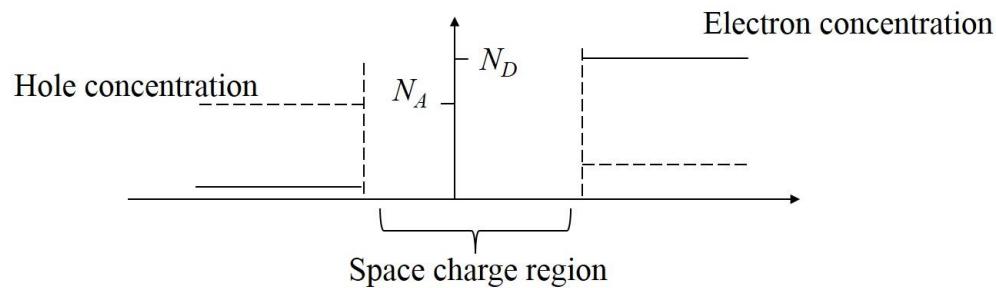
Dr Budhika Mendis ([b.g.mendis@durham.ac.uk](mailto:b.g.mendis@durham.ac.uk))  
Room 151

Lecture 6: pn junction (II)

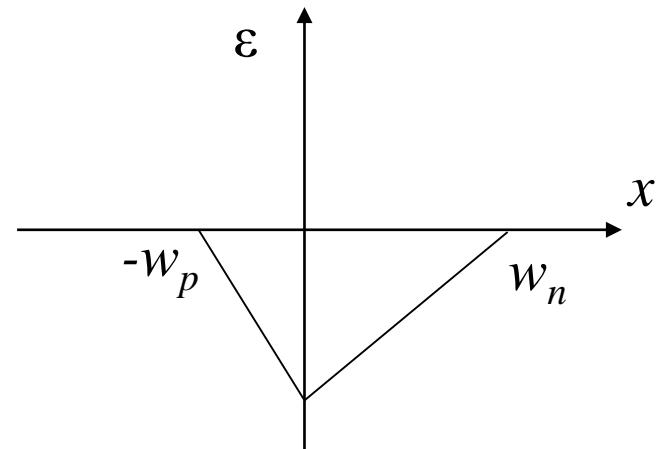
# Summary of Lecture 5



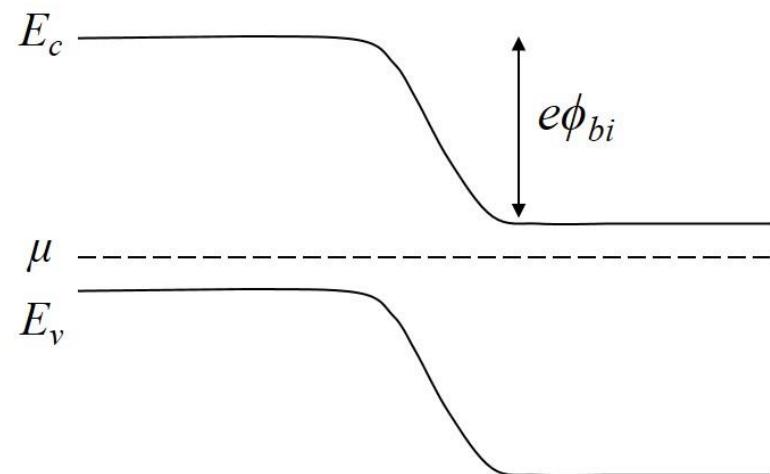
Depletion approximation:



Electric field:



Band bending:



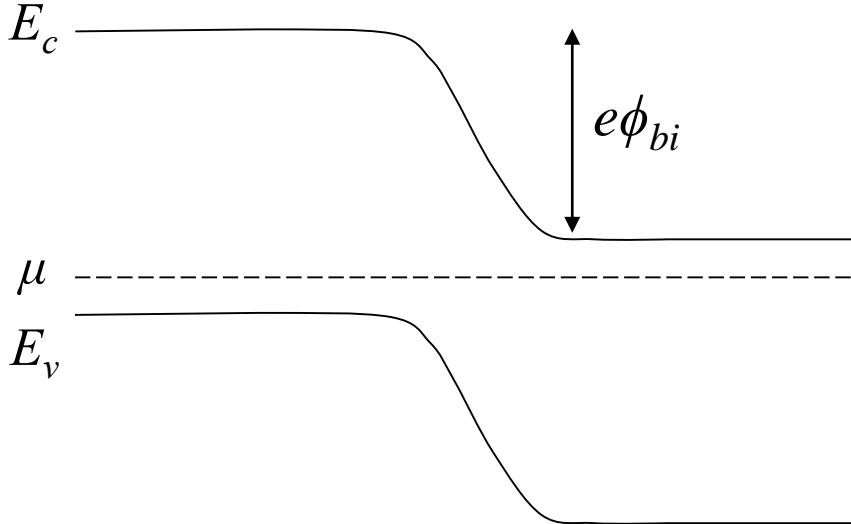
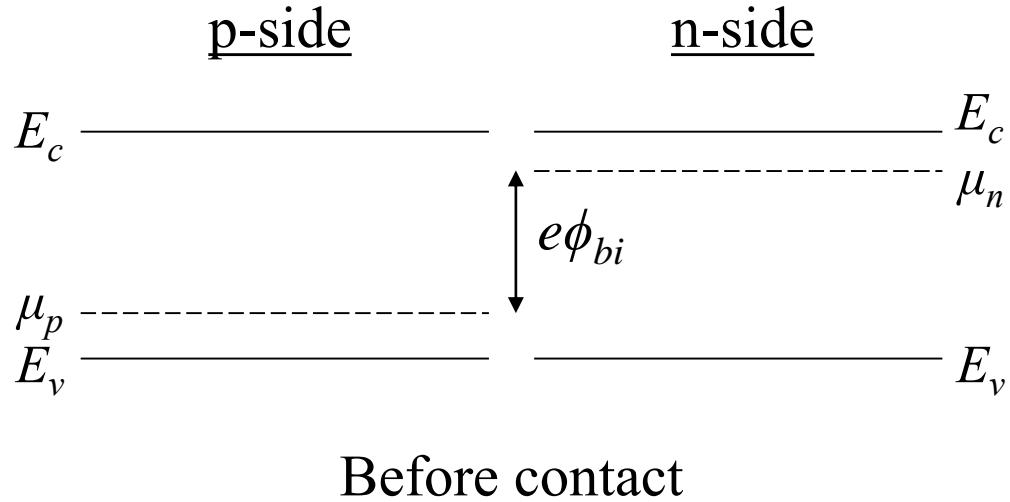
## Aim of today's lecture

- Complete analysis of the pn-junction under equilibrium and describe behaviour under electrical biasing

*Key concepts:*

- Calculate built-in potential and space charge region widths
- Forward and reverse bias: rectification
- Solar cell and light emitting diode devices

# Energy level diagram for pn-junction



$$\phi_{bi} = (\mu_n - \mu_p)/e$$

From lectures 3 and 4:

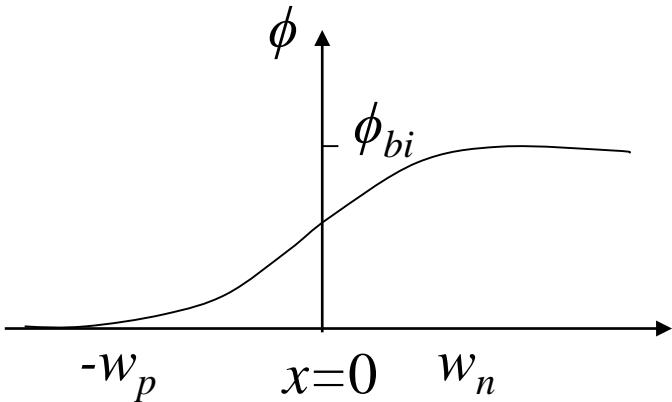
$$\mu_n = E_c - kT \ln \left( \frac{N_c}{N_D} \right)$$

$$\mu_p = E_v + kT \ln \left( \frac{N_v}{N_A} \right)$$

$$np = n_i^2 = N_c N_v \exp \left( - \frac{E_g}{kT} \right)$$

$$\therefore \phi_{bi} = \frac{kT}{e} \ln \left( \frac{N_A N_D}{n_i^2} \right)$$

# Space charge region widths



$$\phi(x) = \begin{cases} \frac{eN_A}{2\epsilon_r\epsilon_0}(x + w_p)^2 & -w_p < x < 0 \\ \phi_{bi} - \frac{eN_D}{2\epsilon_r\epsilon_0}(x - w_n)^2 & 0 < x < w_n \end{cases}$$

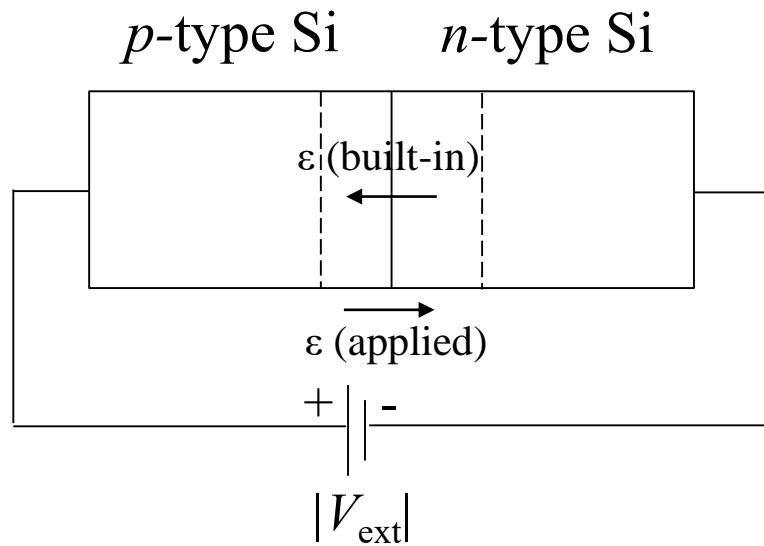
Since the potential is continuous at  $x = 0$  and using the fact that  $N_A w_p = N_D w_n$  (charge conservation) gives:

$$w_n = \left[ \frac{2\epsilon_r\epsilon_0\phi_{bi}}{e} \left( \frac{N_A}{N_D} \right) \left( \frac{1}{N_A + N_D} \right) \right]^{1/2}$$

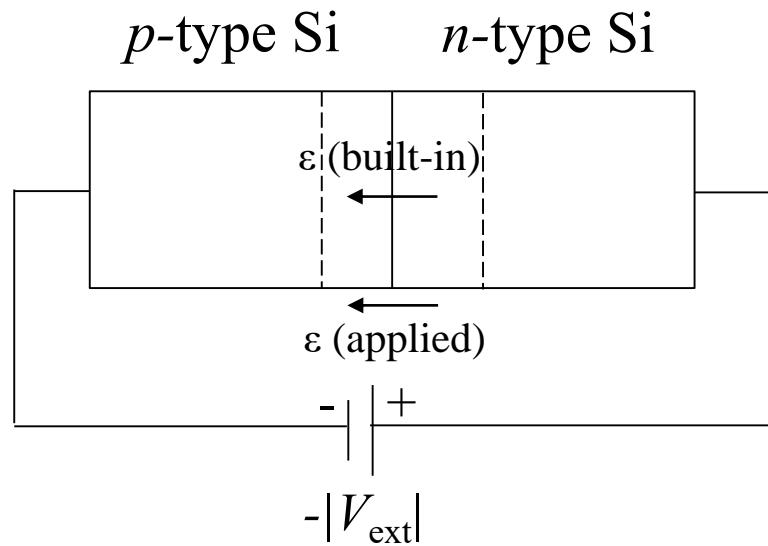
$$w_p = \left[ \frac{2\epsilon_r\epsilon_0\phi_{bi}}{e} \left( \frac{N_D}{N_A} \right) \left( \frac{1}{N_A + N_D} \right) \right]^{1/2}$$

# What happens when we electrically bias the pn-junction?

Forward bias



Reverse bias



- Applied electric field concentrated in space charge region.
- Net electric field smaller under forward bias and vice-versa for reverse bias.

## Space charge widths under biasing

In equilibrium  $\phi_{bi}$  is given by:

$$\phi_{bi} = \frac{kT}{e} \ln \left( \frac{N_A N_D}{n_i^2} \right)$$

Under bias replace  $\phi_{bi}$  with  $(\phi_{bi} - V_{ext})$ . Note that for forward bias  $V_{ext}$  is positive and negative for reverse bias.

Therefore:

$$w_n = \left[ \frac{2\epsilon_r \epsilon_0 (\phi_{bi} - V_{ext})}{e} \left( \frac{N_A}{N_D} \right) \left( \frac{1}{N_A + N_D} \right) \right]^{1/2}$$

$$w_p = \left[ \frac{2\epsilon_r \epsilon_0 (\phi_{bi} - V_{ext})}{e} \left( \frac{N_D}{N_A} \right) \left( \frac{1}{N_A + N_D} \right) \right]^{1/2}$$

Space charge region is narrower under forward bias and wider for reverse bias.

# Electric field and potential under biasing

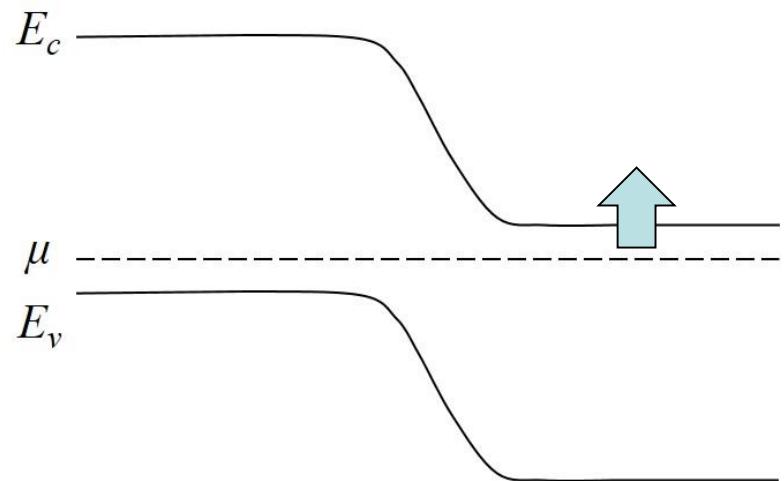
$$\varepsilon(x) = \begin{cases} -N_A e(x + w_p)/\epsilon_r \epsilon_0 & -w_p < x < 0 \\ N_D e(x - w_n)/\epsilon_r \epsilon_0 & 0 < x < w_n \\ 0 & \text{elsewhere} \end{cases}$$

Similar equations as equilibrium, but use new values for  $w_p$  and  $w_n$

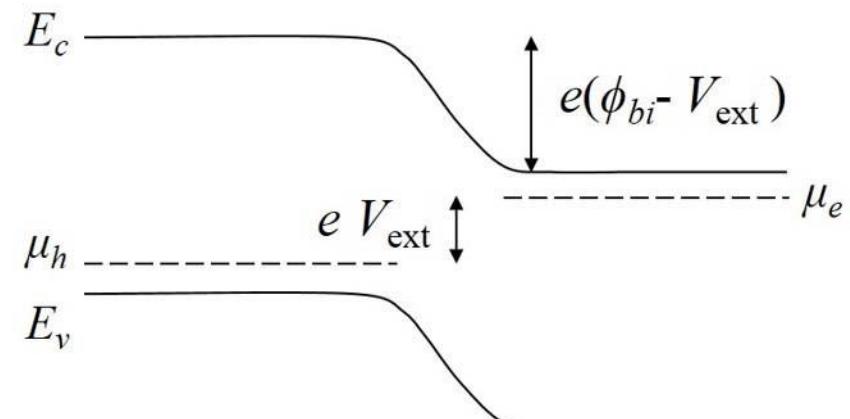
$$\phi(x) = \begin{cases} \frac{eN_A}{2\epsilon_r \epsilon_0} (x + w_p)^2 & -w_p < x < 0 \\ (\phi_{bi} - V_{ext}) - \frac{eN_D}{2\epsilon_r \epsilon_0} (x - w_n)^2 & 0 < x < w_n \end{cases}$$

Similar equations as equilibrium, but use new values for  $w_p$ ,  $w_n$  and replace  $\phi_{bi}$  with  $(\phi_{bi} - V_{ext})$

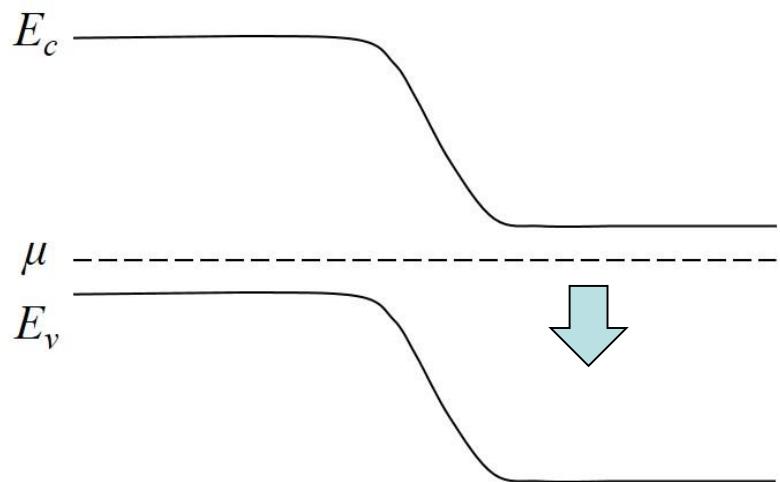
# Energy level diagram under biasing



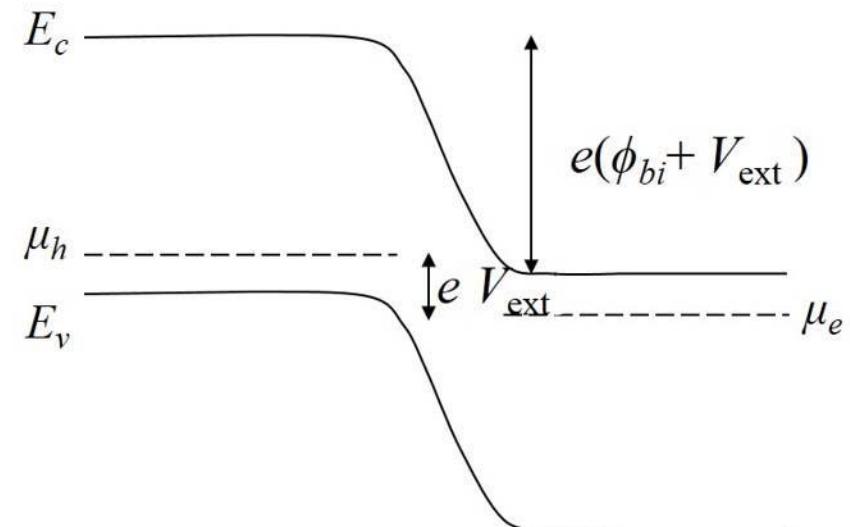
Equilibrium



Forward bias



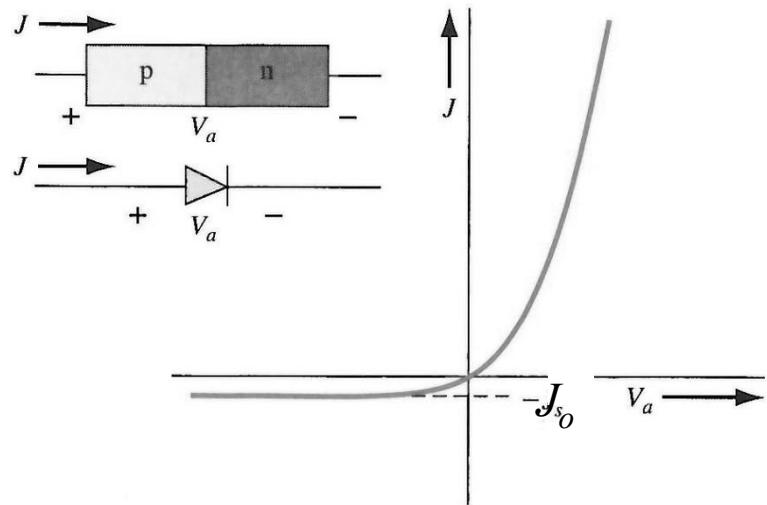
Equilibrium



Reverse bias

# $J(V)$ behaviour- rectification

Current density ( $J$ ):



$$J = J_o \left[ \exp\left(\frac{eV_{ext}}{kT}\right) - 1 \right]$$

$J_o$  = reverse saturation current density

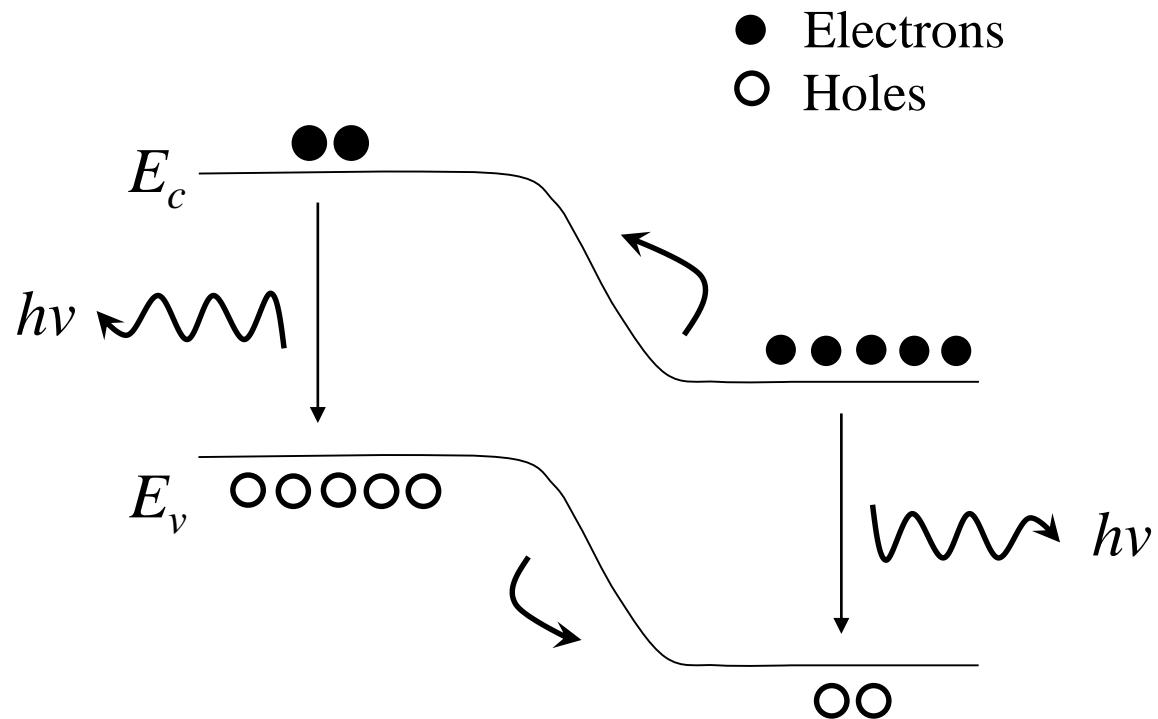
→ Current conduction only in forward bias direction

# pn junction devices- light emitting diodes

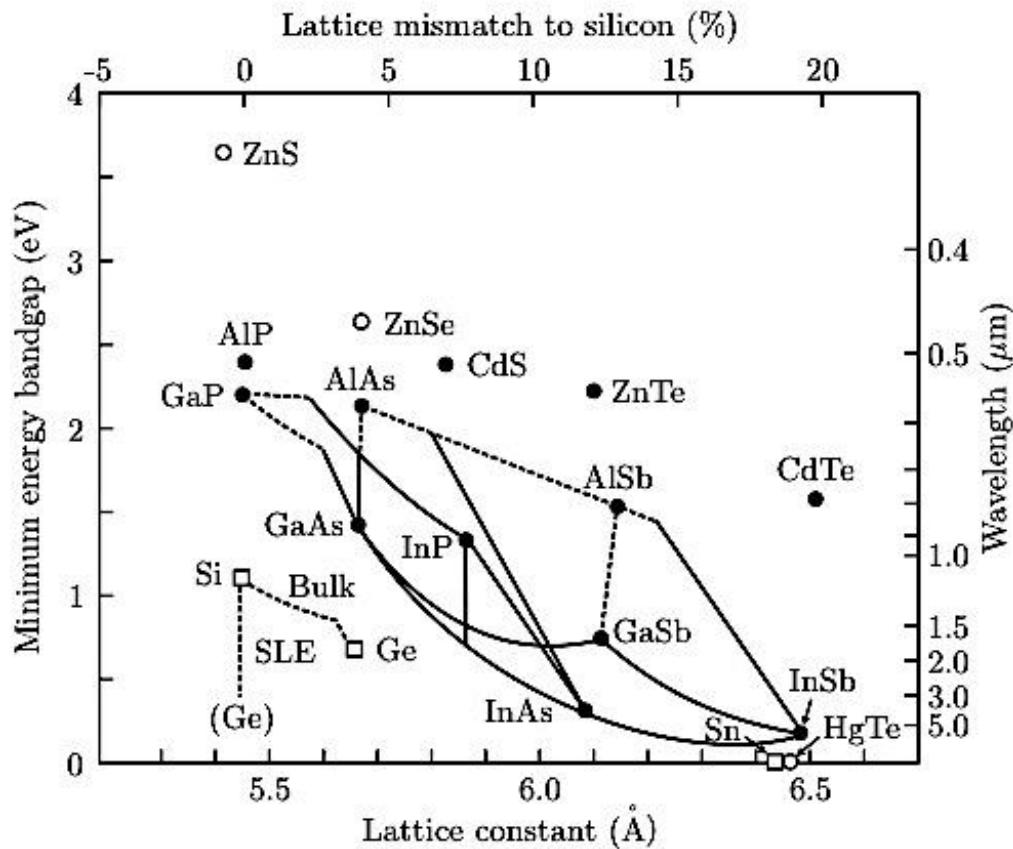
-In forward bias electrons/holes injected across space charge region.

-This creates excess *minority carriers* in the quasi-neutral regions.

-Recombination of excess minority carriers with majority carriers emits light.



# pn junction devices- light emitting diodes



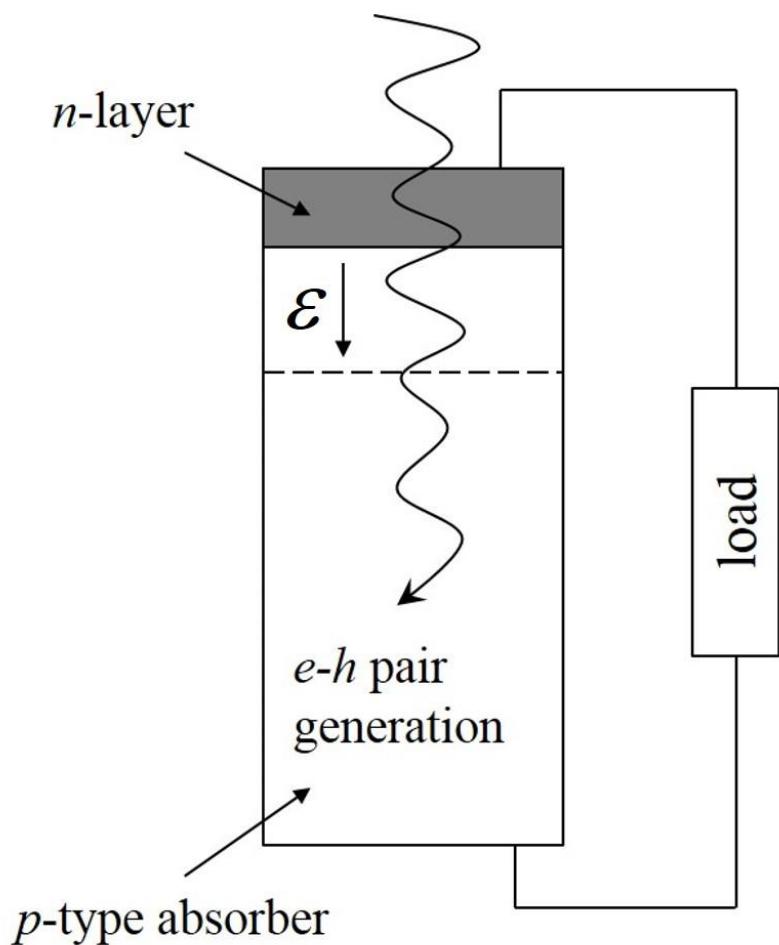
Example LED materials:

AlGaInP alloy: red emission  
InGaN: green-blue emission

Organic LEDs also widely used (e.g. OLED TVs)

- Band gap of semiconductor LED must be matched with the photon energy.
- Direct band gap semiconductor required for high efficiency

# pn junction devices- solar cells



- Light absorption in *p*-layer generates electron-hole pairs due to promotion of valence band electron into conduction band.
- Excess electrons and holes diffuse randomly and do not produce a net electric current
- However, *minority carriers* diffusing into the space charge region can be extracted by the built-in electric field to produce an electric current.

# FoP 3B Part II

Dr Budhika Mendis ([b.g.mendis@durham.ac.uk](mailto:b.g.mendis@durham.ac.uk))

Room 151

## Lecture 7: Introduction to Superconductors

## Aim of today's lecture

- What are the characteristic features of superconductivity?

*Key concepts:*

- Critical temperature (superconductivity as a phase transition)
- Meissner effect (leading to diamagnetism)
- Critical magnetic fields- Type I vs Type II superconductors

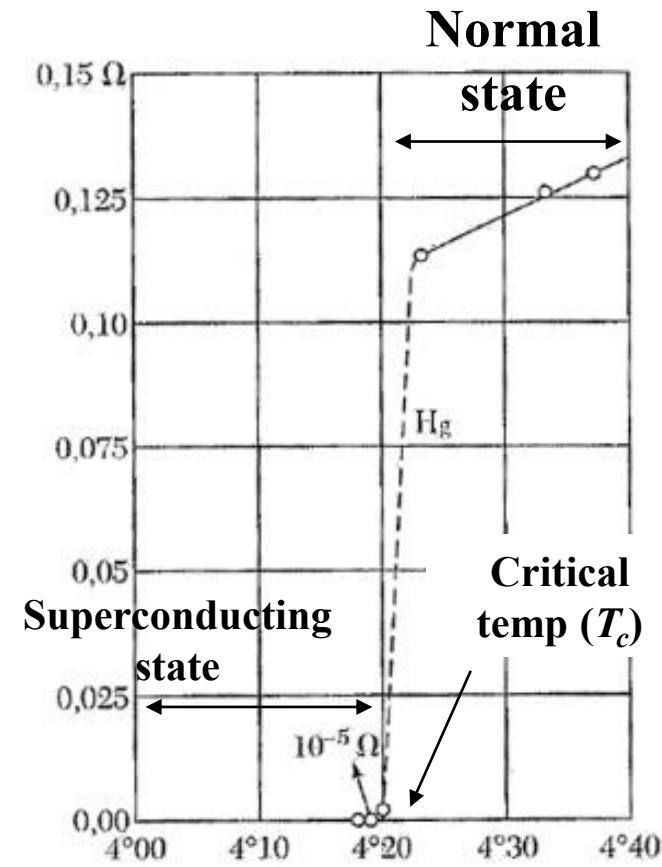
# Resistivity vs temperature for a metal

$$\rho(T) = \rho_o + aT^2 + bT^5$$

↑                   ↑                   ↑  
Impurity effects   electron-electron scattering   electron-phonon scattering

- Below critical temp ( $T_c$ ) resistivity suddenly drops to zero.
- Abrupt change implies a phase transition, i.e. superconductivity is a new form of matter.

Kammerling Onnes  
measurement on Hg (1911)  $\Rightarrow$



# Examples of superconducting materials

	Substance	$T_c$ (K)	
Elemental superconductors	Al	1.2	
	Hg	4.1	First superconductor, discovered 1911
	Nb	9.3	Highest $T_c$ of an element at normal pressure
	Pb	7.2	
	Sn	3.7	
	Ti	0.39	
	Tl	2.4	
	V	5.3	
	W	0.01	
	Zn	0.88	
Superconductivity under high pressure	Zr	0.65	
	Fe	2	High pressure
	H	300	Predicted, under high pressure
	O	30	High pressure, maximum $T_c$ of any element
Used in superconducting magnets	S	10	High pressure
	Nb <sub>3</sub> Ge	23	A15 structure, highest known $T_c$ before 1986
'High' $T_c$ cuprates	Ba <sub>1-x</sub> Pb <sub>x</sub> BiO <sub>3</sub>	12	First perovskite oxide structure
	La <sub>2-x</sub> Ba <sub>x</sub> CuO <sub>4</sub>	35	First high $T_c$ superconductor
	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-δ</sub>	92	First superconductor above 77 K
	HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+δ</sub>	135–165	Highest $T_c$ ever recorded
	K <sub>3</sub> C <sub>60</sub>	30	Fullerene molecules
	YNi <sub>2</sub> B <sub>2</sub> C	17	Borocarbide superconductor
	MgB <sub>2</sub>	38	Discovery announced in January 2001
	Sr <sub>2</sub> RuO <sub>4</sub>	1.5	Possible <i>p</i> -wave superconductor
	UPt <sub>3</sub>	0.5	"Heavy fermion" exotic superconductor
	(TMTSF) <sub>2</sub> ClO <sub>4</sub>	1.2	Organic molecular superconductor
	ET-BEDT	12	Organic molecular superconductor

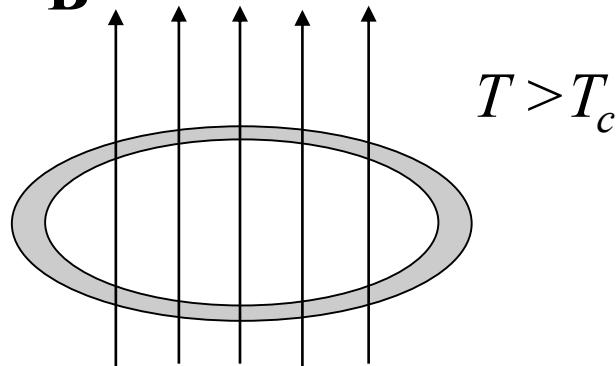
# Persistent currents (I)- is the resistivity really zero?

From  $\mathbf{J} = \sigma \mathcal{E}$  electric field within a superconductor must be zero for constant current.

Applying Faraday's law of induction:

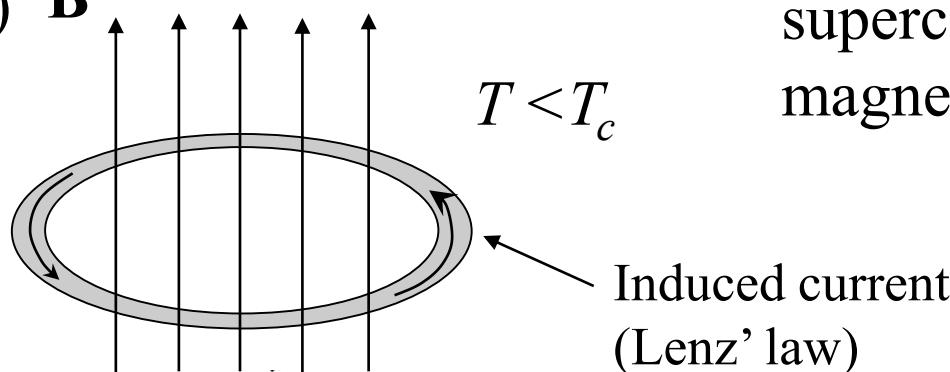
$$\vec{\nabla} \times \vec{\mathcal{E}} = -\frac{\partial \mathbf{B}}{\partial t} = 0$$

(i)



- Immerse metal ring in magnetic field at  $T > T_c$ .
- Cool to below  $T_c$  and switch magnetic field off.
- Persistent current induced in superconductor (to maintain constant magnetic flux through the ring).

(ii)



## Persistent currents (II)- is the resistivity really zero?

Decay of current density given by:

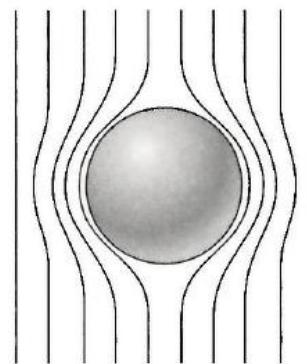
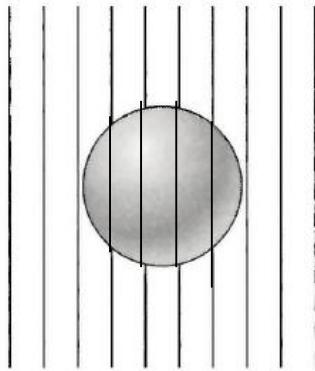
$$J(t) = J_o \exp(-t/\tau)$$

$\tau$  = average time between scattering events.

For a metal  $\tau \sim 10^{-13}$  s, i.e. current decays to 1% its starting value within 1 picosecond.

For superconductors no noticeable decay in current even after several years  $\Rightarrow$  resistivity less than  $10^{-25}$   $\Omega\text{m}$  (resistivity of Cu  $\sim 10^{-8}$   $\Omega\text{m}$ )

# Meissner effect (perfect diamagnetism)



$$T > T_c$$

(Normal state; paramagnet)

$$T < T_c$$

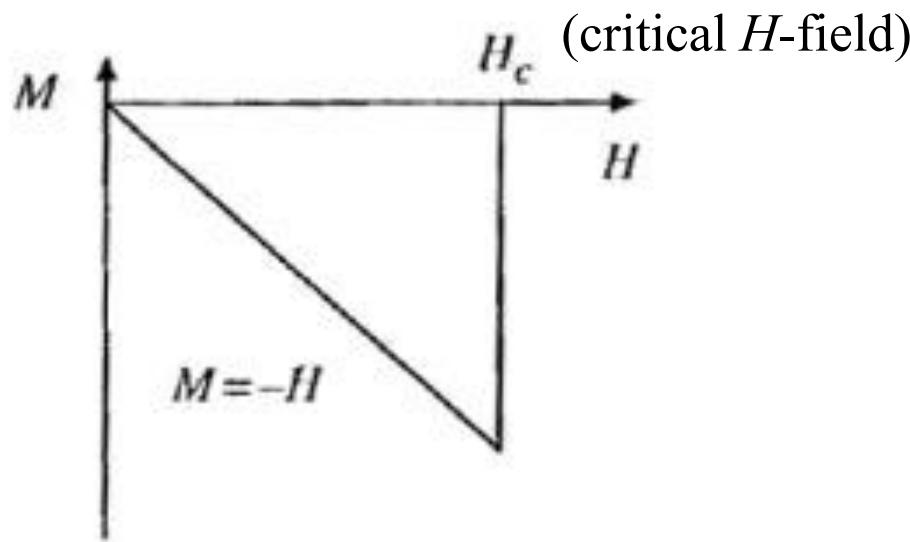
(Superconductor; diamagnet)

$\mathbf{B} = 0$  in superconducting state. From  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ :

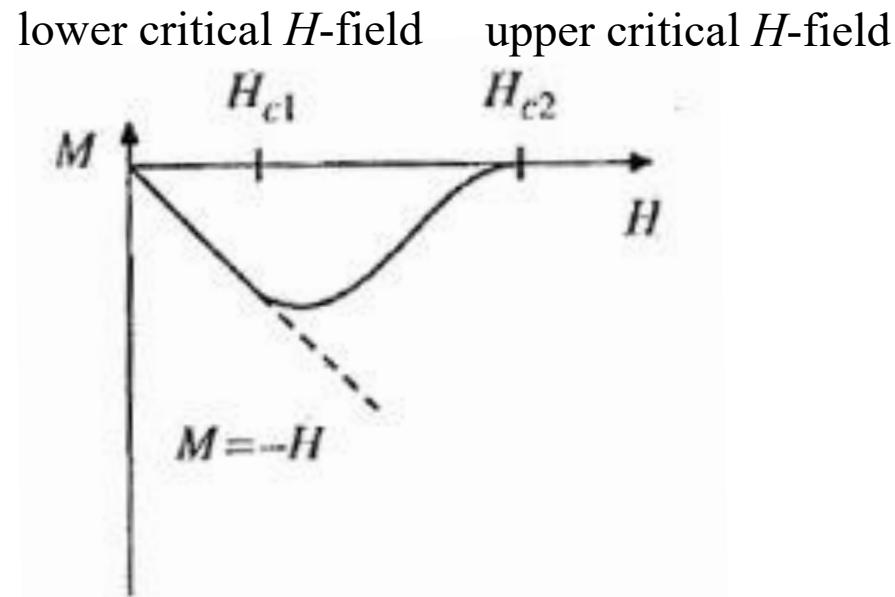
$$\chi = \frac{M}{H} = -1$$

↗  
Magnetic susceptibility

# Type I vs Type II superconductors



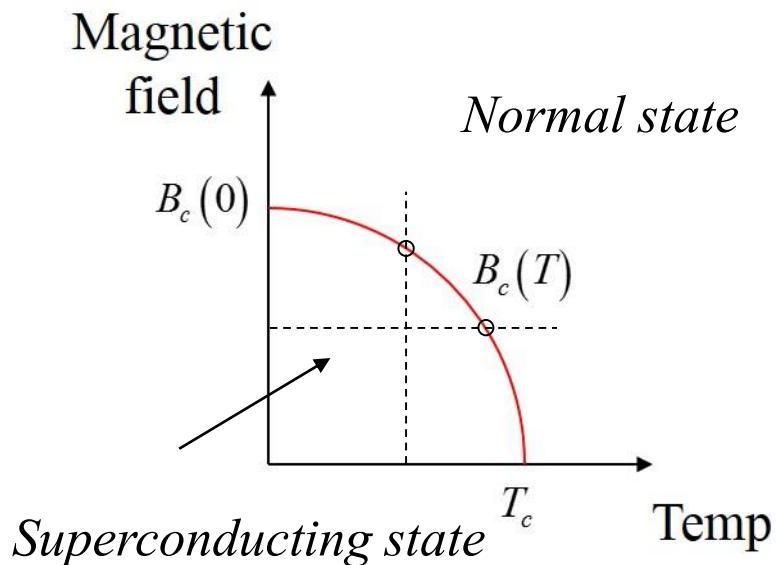
Type I behaviour



Type II behaviour

- Strong magnetic fields destroy superconductivity.
- For Type I the transition from superconducting to normal state is at a single critical field. In Type II a ‘mixed’ (or ‘vortex’) state exists between a lower and upper critical field.

# Type I superconductors



Critical field at a given temp:

$$B_c(T) = B_c(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

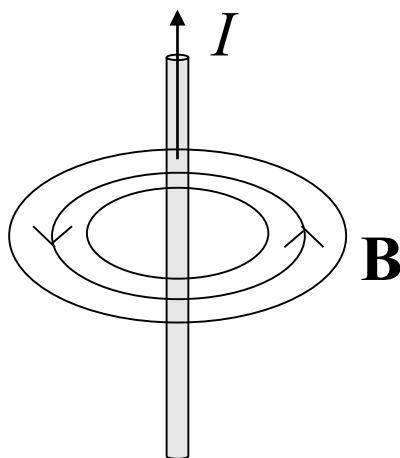
Implications for a current carrying wire

Magnetic field for wire of radius  $R$  :

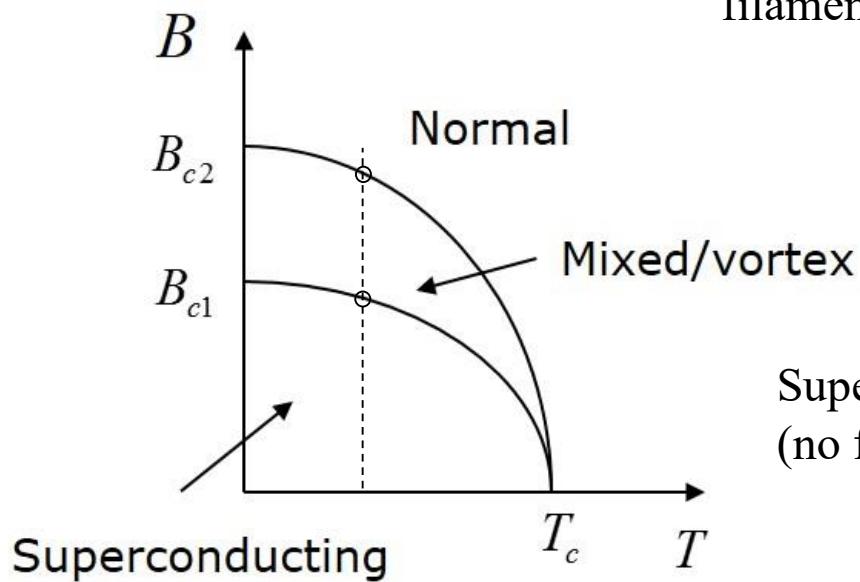
$$B = \frac{\mu_o I}{2\pi R} \quad (\text{Ampere's law})$$

∴ Max allowed current:

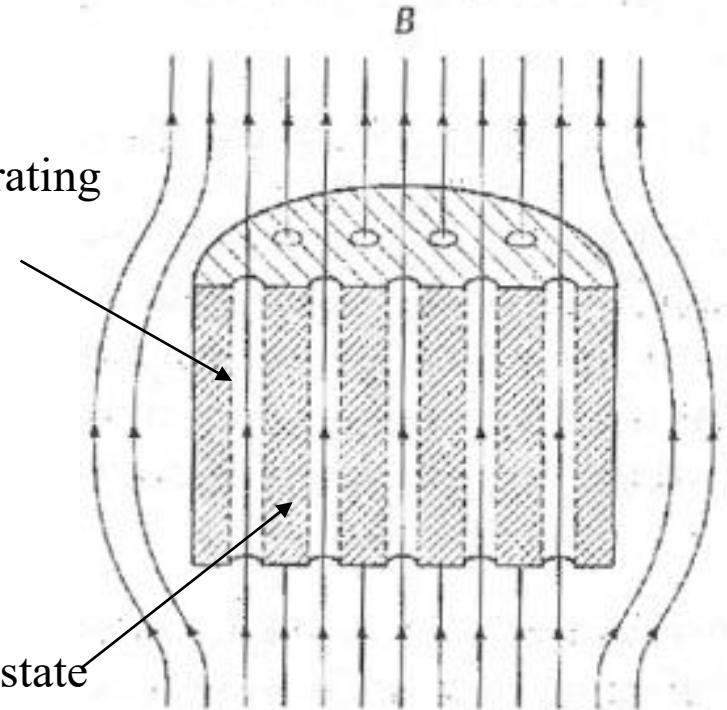
$$I_{max} = \frac{2\pi R B_c(T)}{\mu_o}$$



# Type II superconductors

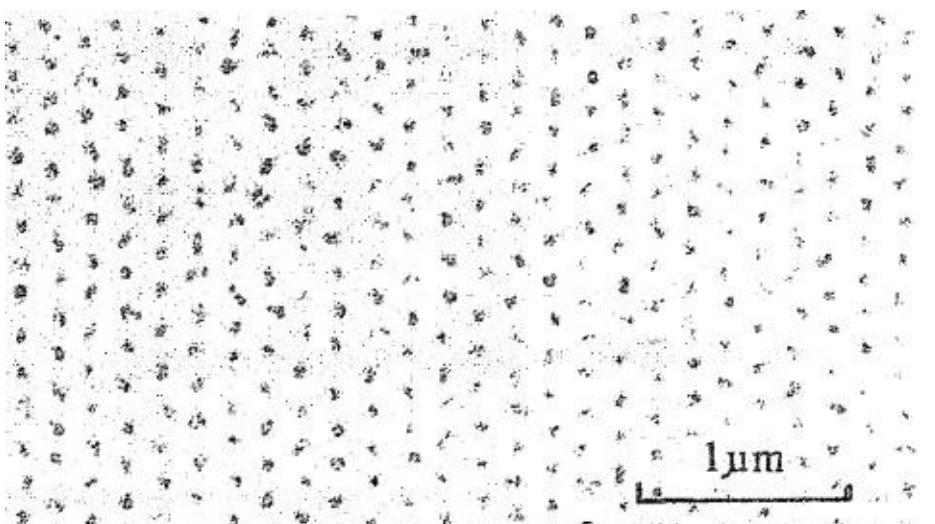
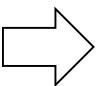


Magnetic field penetrating  
through Normal state  
'filaments'



Superconducting state  
(no field penetration)

Experimental micrograph of  
mixed state  
(ferromagnetic powder  
exposes filaments)



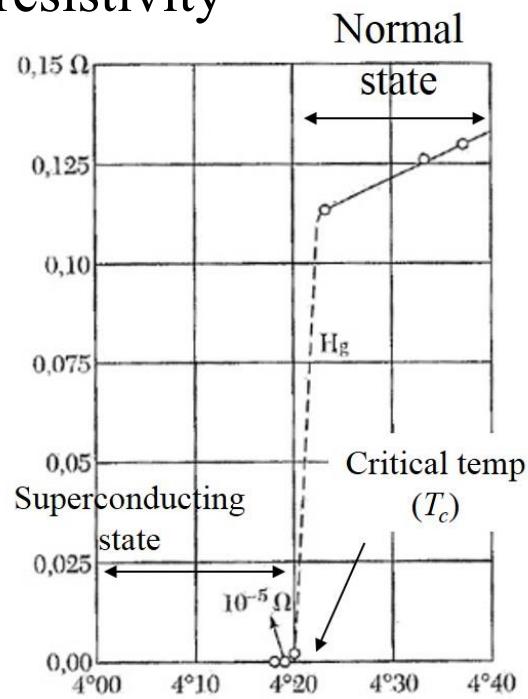
# FoP 3B Part II

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Room 151

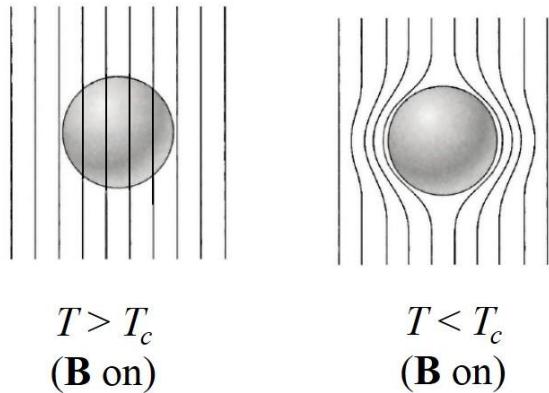
Lecture 8: London equation and thermodynamics  
of the superconducting phase transition

# Summary of Lecture 7

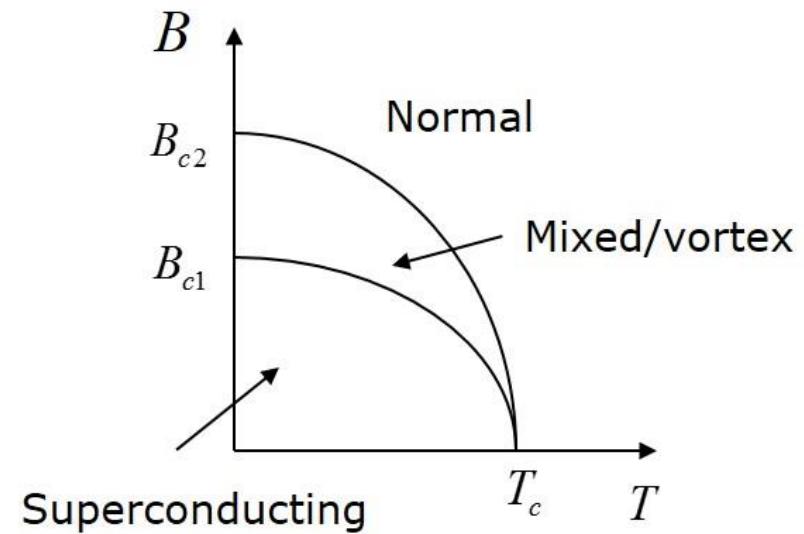
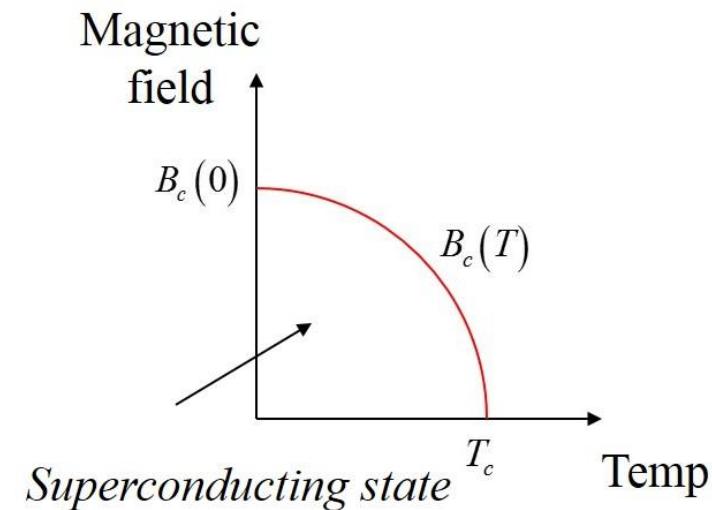
Zero resistivity



Meissner effect (diamagnetism)



Type I vs Type II behaviour:



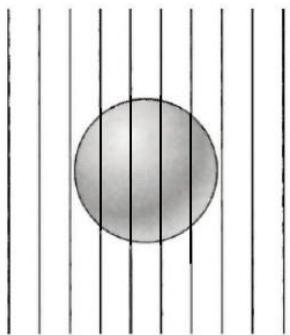
## Aim of today's lecture

- Explain the origin of the Meissner effect and describe the thermodynamics of the superconducting phase transition

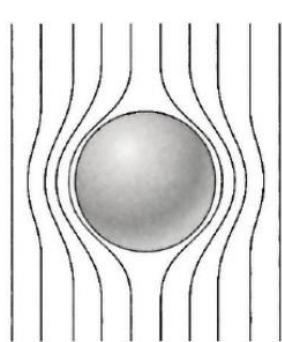
*Key concepts:*

- London equation: London penetration depth and supercurrents
- Thermodynamics of the superconducting phase transition: condensation energy and second order transition.

# Meissner effect and supercurrent



$T > T_c$   
( $\mathbf{B}$  on)



$T < T_c$   
( $\mathbf{B}$  on)

- Magnetic field within a superconductor is always zero (perfect diamagnetism).
- Implies supercurrent  $\mathbf{j}$  that depends on applied field (supercurrent cancels magnetic field within the superconductor).

Hence:

$$\mathbf{j} = -\frac{1}{\mu_0 \lambda_L^2} \mathbf{A}$$

( $\lambda_L$  = London penetration depth)

where  $\mathbf{A}$  is the magnetic vector potential (i.e.  $\mathbf{B} = \nabla \times \mathbf{A}$ ). Here the London gauge  $\nabla \cdot \mathbf{A} = 0$  is used so that charge is conserved, i.e.:

# London equation

We have:

$$\vec{\nabla} \times \mathbf{j} = -\frac{1}{\mu_0 \lambda_L^2} \mathbf{B} \quad (\text{London equation})$$

$$\vec{\nabla} \times \mathbf{B} = \mu_0 \mathbf{j} \quad (\text{Maxwell's equation; steady state})$$

Therefore:

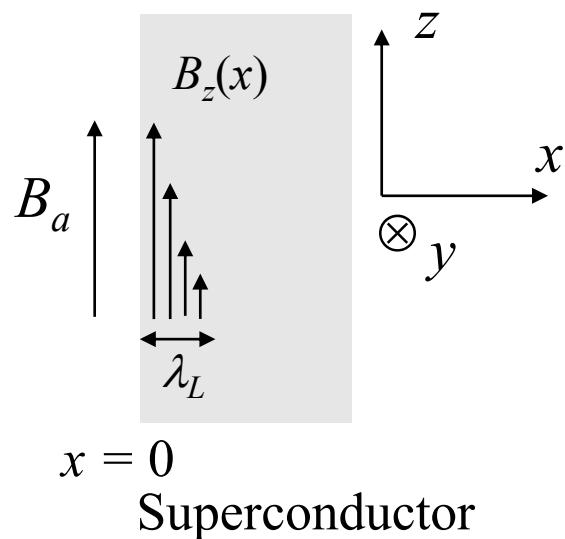
$$\vec{\nabla} \times \vec{\nabla} \times \mathbf{B} = -\frac{1}{\lambda_L^2} \mathbf{B}$$



$$\boxed{\nabla^2 \mathbf{B} = \frac{1}{\lambda_L^2} \mathbf{B}} \quad *$$

\* NB:  $\nabla \times \nabla \times \mathbf{B} = \nabla (\cancel{\nabla \cdot \mathbf{B}}) - \nabla^2 \mathbf{B}$

# Application of the London equation (semi-infinite superconducting slab)



$$\frac{d^2 B_z}{dx^2} = \frac{B_z}{\lambda_L^2}$$

Solutions are of the form:

$$B_z(x) = A \exp\left(\frac{x}{\lambda_L}\right) + B \exp\left(-\frac{x}{\lambda_L}\right)$$

From the boundary condition  $B_z(0) = B_a$ , we have:

$$B_z(x) = B_a \exp\left(-\frac{x}{\lambda_L}\right)$$

The supercurrent is derived from  $\nabla \times \mathbf{B} = \mu_0 \mathbf{j}$ :

$$j_y(x) = \frac{B_a}{\mu_0 \lambda_L} \exp\left(-\frac{x}{\lambda_L}\right)$$

Magnetic field and supercurrents decay over  $\lambda_L$  distance from surface

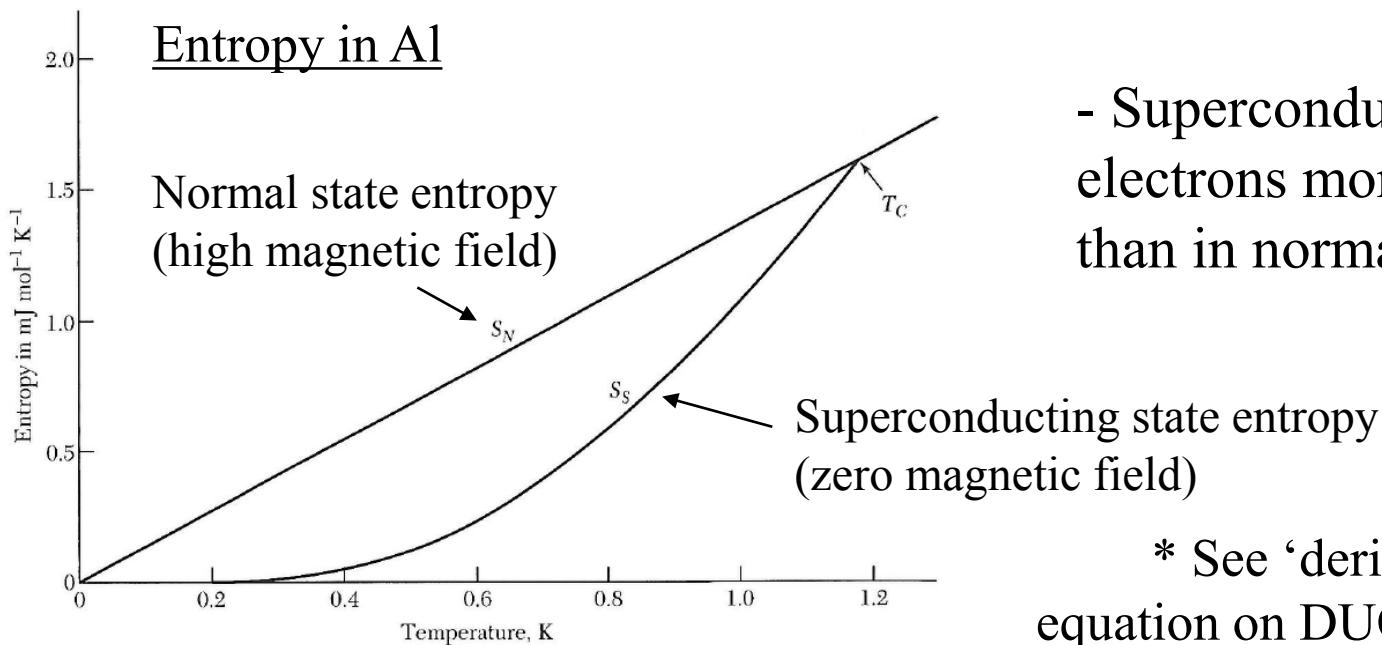
# The London penetration depth

It can be shown that\*:

$$\lambda_L = \sqrt{\frac{m}{\mu_0 n_s e^2}}$$

electron mass  
electron charge

$n_s$  = number density of *superconducting* electrons (increases with cooling below  $T_c$ ; see below)

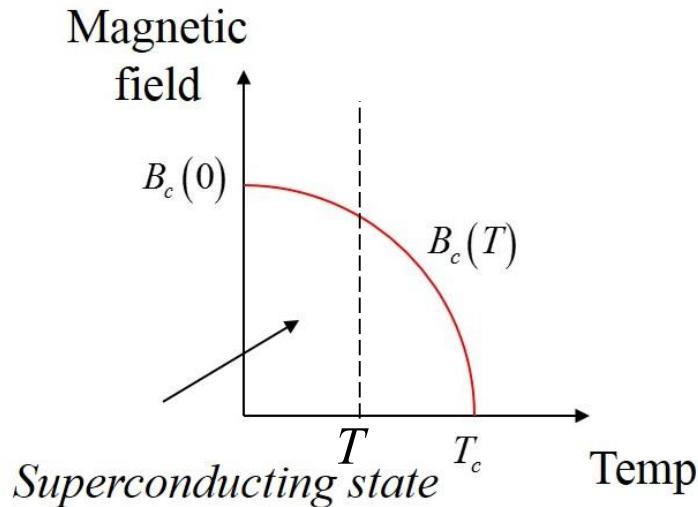


- Superconducting electrons more ordered than in normal state

\* See ‘derivations’ of London equation on DUO; non-examinable

# Thermodynamics of superconducting phase transition

Consider a Type I superconductor:



What is the free energy difference between superconducting and normal state?

-At  $T < T_c$  start from zero magnetic field and gradually increase field up to  $B_c(T)$

-Potential energy of a magnetic dipole moment  $\mu$  in a  $\mathbf{B}$ -field is  $-\mu \cdot \mathbf{B}$ . Therefore the work done per unit volume on a given material by changing the magnetic field is :

$$dW = -\mathbf{M} \cdot d\mathbf{B}$$

$$\begin{aligned}\Rightarrow G_s[B_c(T)] - G_s[0] &= - \int_0^{B_c(T)} \mathbf{M} \cdot d\mathbf{B} \\ &= \int_0^{B_c(T)} \frac{B}{\mu_0} dB = \frac{B_c(T)^2}{2\mu_0}\end{aligned}$$

(Assuming perfect diamagnetism, i.e.  
 $M = -H$ , for superconducting state)

# Condensation energy

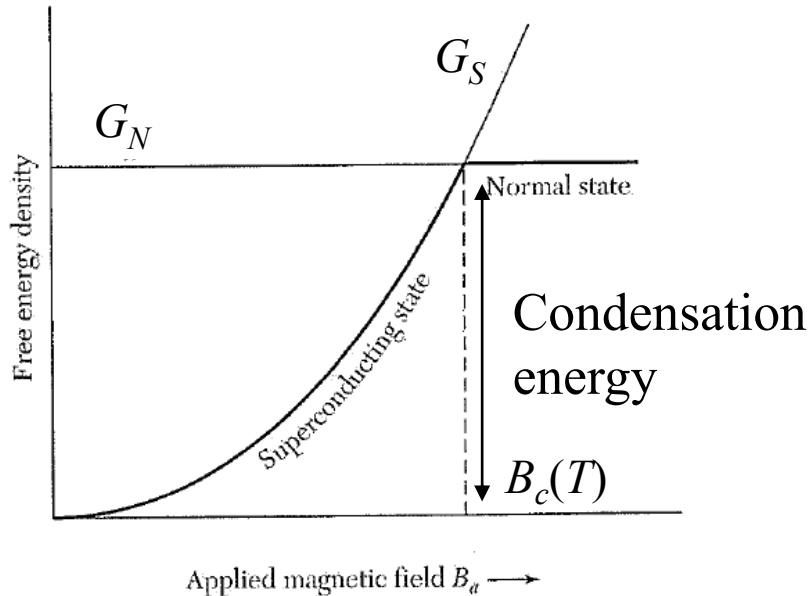
For the normal state assuming negligible magnetisation  $\mathbf{M}$ :

$$G_N[B_c(T)] - G_N[0] = - \int_0^{B_c(T)} \mathbf{M} \cdot d\mathbf{B} = 0$$

At critical field  $G_s[B_c(T)] = G_N[B_c(T)] = G_N[0]$ , so that

$$G_N[0] - G_s[0] = \frac{B_c(T)^2}{2\mu_0}$$

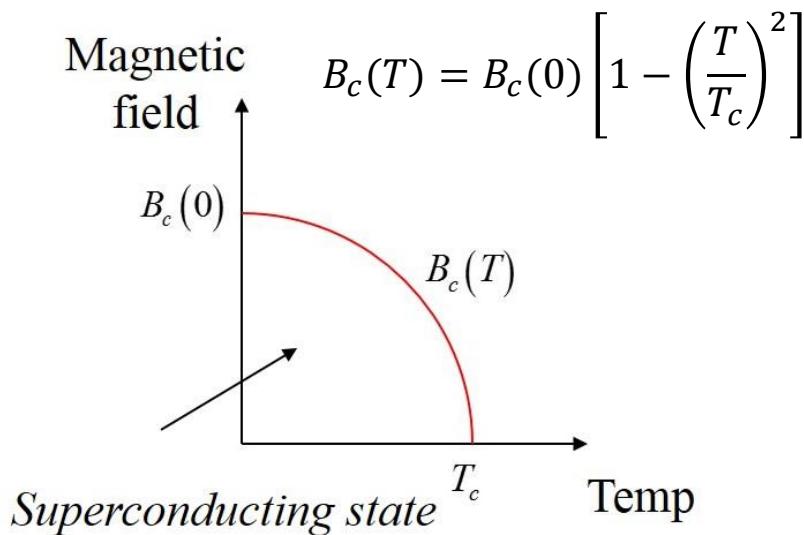
Condensation energy



Note:

- (i)  $G_s$  quadratic dependence on B-field
- (ii)  $G_N$  independent of B-field
- (iii) Superconductor has lower free energy below  $B_c(T)$
- (iv) Condensation energy extremely small ( $\mu\text{eV}/\text{atom}$ )

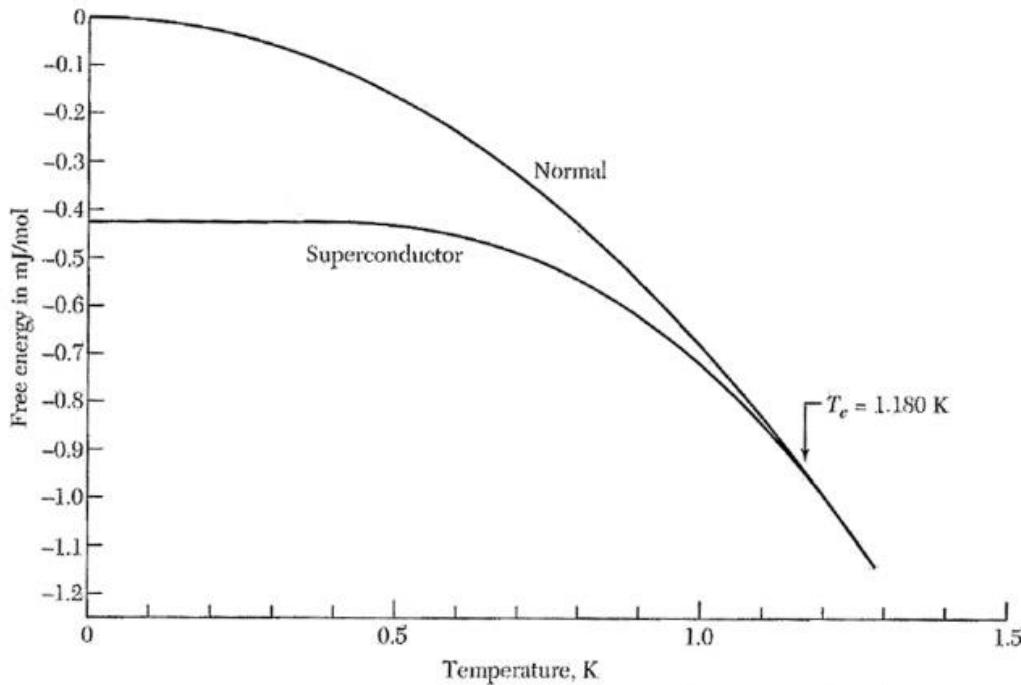
# Order of phase transformation



$$G_N[0] - G_S[0] = \frac{B_c(T)^2}{2\mu_0}$$

-Free energy of superconducting and normal states equal at  $T_c$ , i.e. no latent heat/entropy change.

-Hence second order phase transition. Link to temp dependence of superconducting electrons  $n_s$



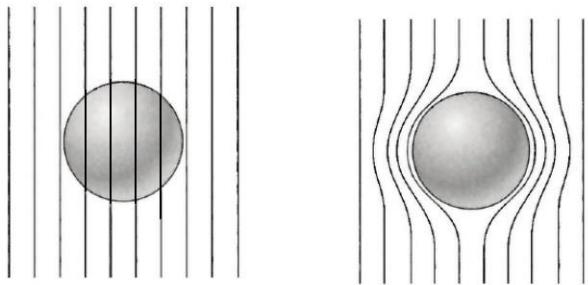
# FoP 3B Part II

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Room 151

## Lecture 9: Ginzburg-Landau theory

# Summary of Lecture 8

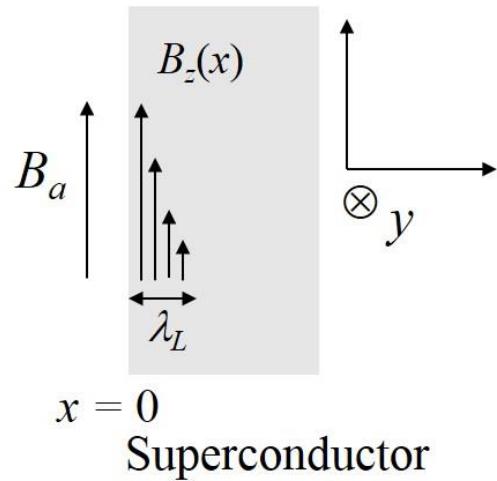
London equation



$T > T_c$   
( $\mathbf{B}$  on)

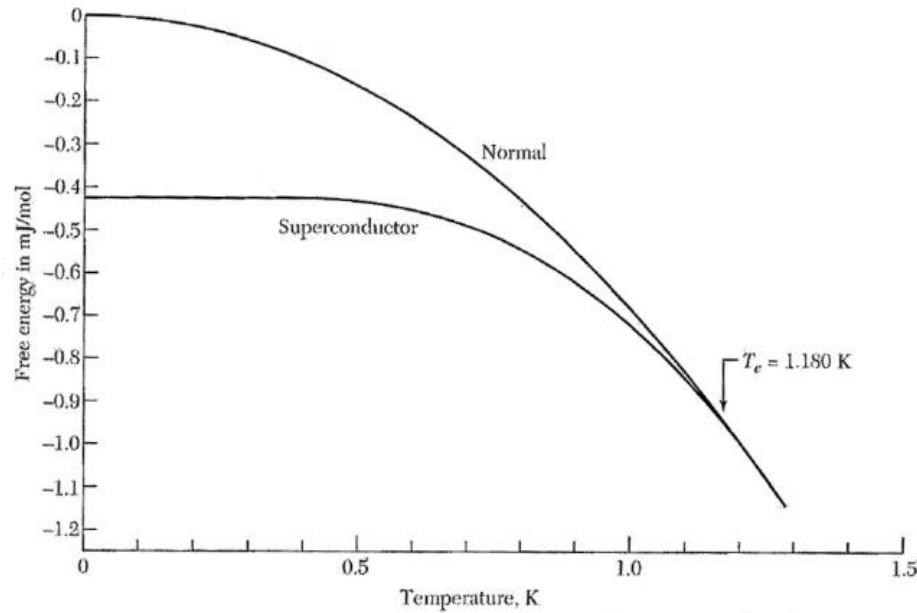
$T < T_c$   
( $\mathbf{B}$  on)

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda_L^2} \mathbf{B}$$



Condensate energy

$$G_N[0] - G_s[0] = \frac{B_c(T)^2}{2\mu_0}$$



- No latent heat
- Second order phase transition

## Aim of today's lecture

- What causes superconductivity and how do we model it?

*Two approaches\*:*

- (i) Bardeen, Cooper and Schrieffer (BCS theory)  
-microscopic theory of superconductivity (1957)  
*-Key concepts:* Cooper pairs, band gap
- (ii) Ginzburg-Landau (GL) theory  
-phenomenological theory of superconductivity (1950)  
*-Key concepts:* coherence length, Type I vs Type II

behaviour

(Note that Ginzburg-Landau theory can be derived from BCS, so the two are formally equivalent)

## GL theory and modelling of second order transitions

- Assume phase transition characterised by an order parameter (e.g. magnetisation for a ferromagnetic-paramagnetic transition)
- For superconductivity GL postulated order parameter is  $|\psi|^2$ , where  $\psi$  is a complex number. In the normal state  $|\psi|^2 = 0$ , while  $|\psi|^2 \neq 0$  for the superconducting state.
- Assume zero magnetic field and spatially uniform material\*. Around the transition temperature  $T_c$ :

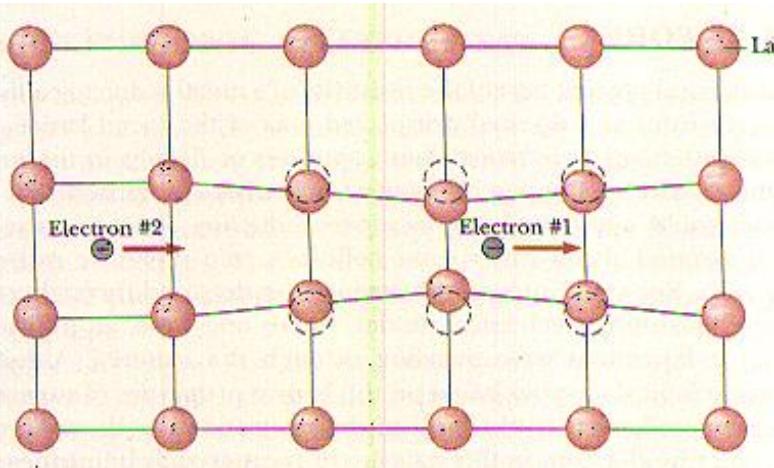
$$G_s(T) = G_N(T) + a(T)|\psi|^2 + \frac{b(T)}{2}|\psi|^4$$

$a(T)$  and  $b(T)$  are constants that vary with temperature.  $G_{s,N}$  is the free energy of superconducting and normal phases respectively.

\*GL theory can be extended to include magnetic fields and spatially non-uniform materials

# Cooper pairs

What does  $|\psi|^2$  represent? Answer: Cooper pairs

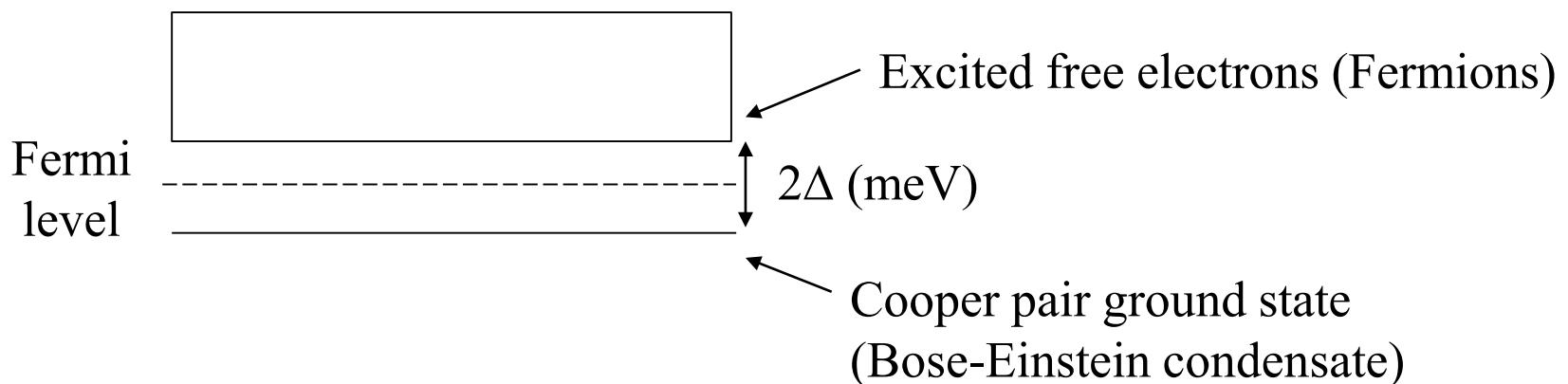


Electrons can *attract* via electron-phonon interactions.

$$|\psi|^2 = n_s/2$$

( $n_s$  = density of superconducting electrons)

Superconducting band gap ( $2\Delta$ ) predicted:

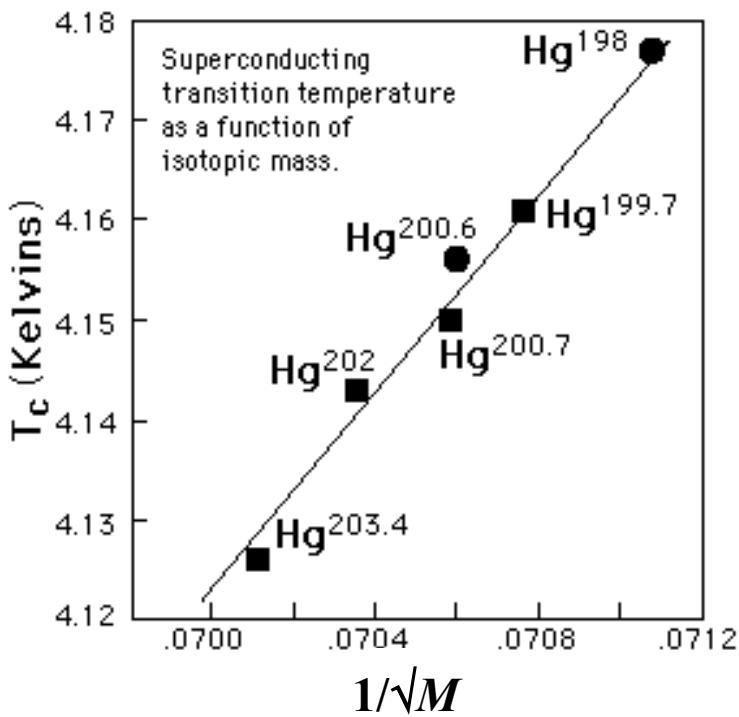


# Evidence for Cooper pairs and band gaps

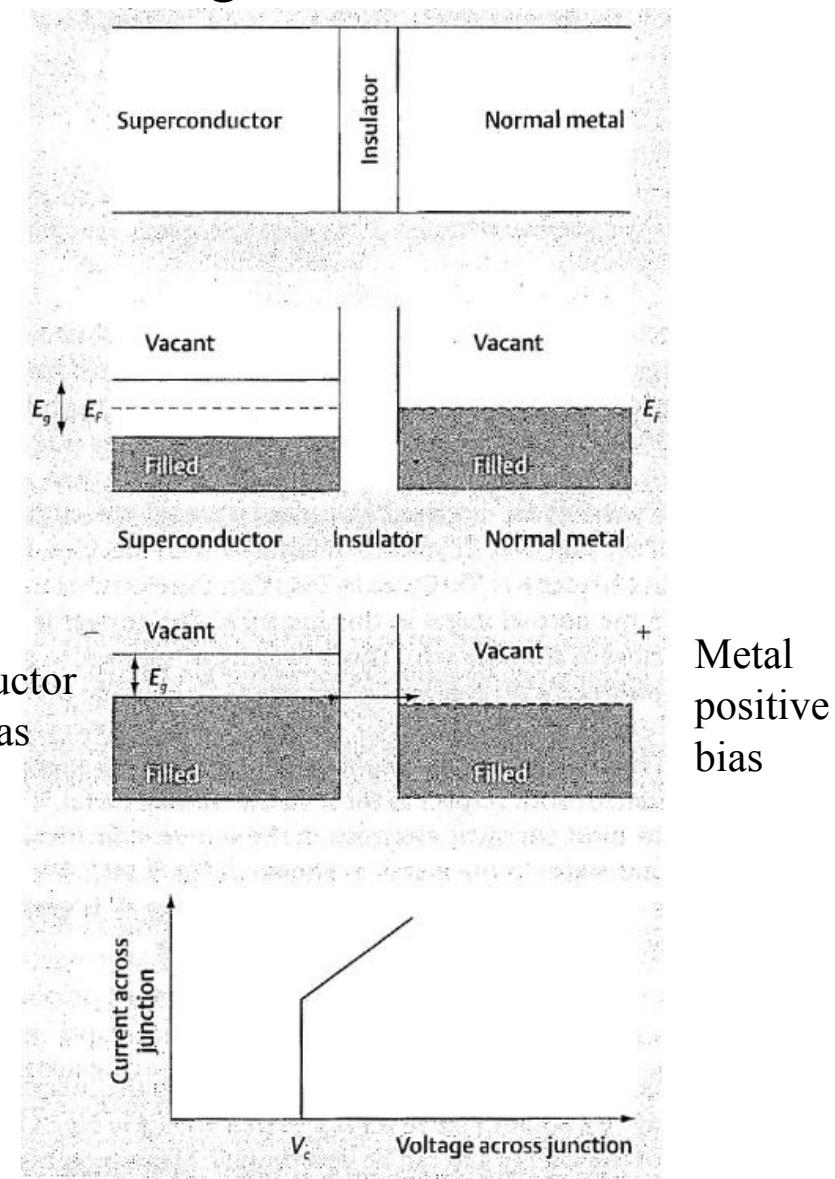
## (1) Isotope effect

$$T_c \propto \frac{1}{\sqrt{M}}$$

( $M$  = atomic mass)



## (2) Tunneling current



# GL energy

$$G_s(T) = G_N(T) + a(T)|\psi|^2 + \frac{b(T)}{2}|\psi|^4$$

(i) For energy minimum require  $b(T) > 0$ .

(ii) When  $a(T) > 0$  only minimum is at  $|\psi| = 0$ ; (normal state)

When  $a(T) < 0$  minima at  $|\psi|^2 = -a(T)/b(T)$ ; (superconducting state)

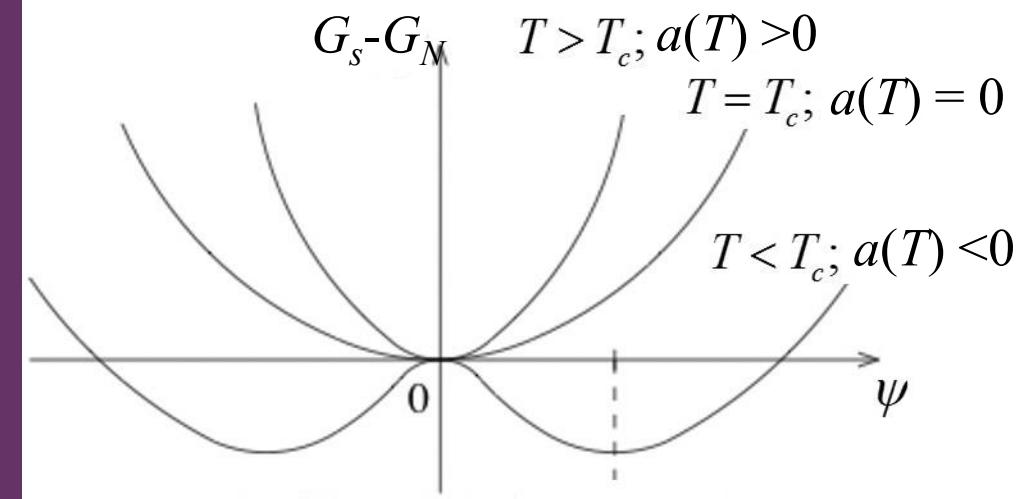
Therefore:

$$a(T) \approx \dot{a}(T - T_c) + \dots \quad (\dot{a} > 0)$$

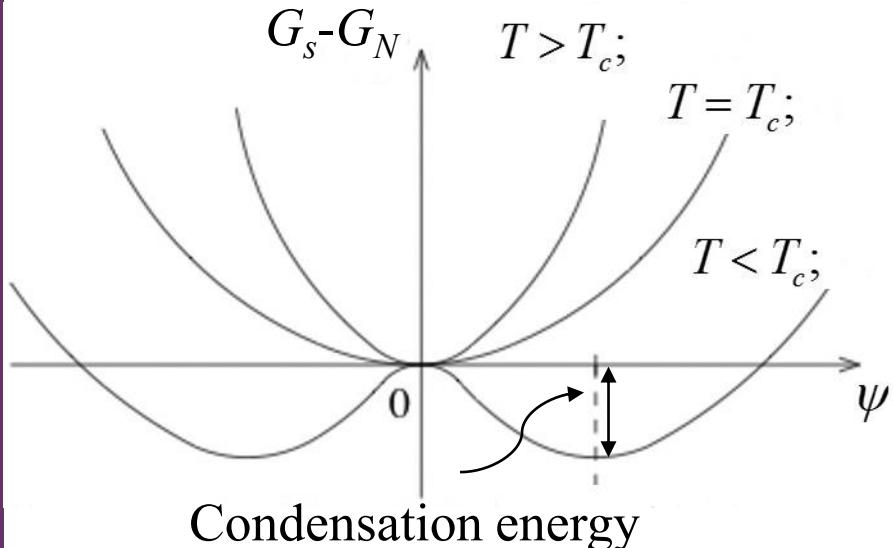
$$b(T) \approx b + \dots \quad (b > 0)$$

And:

$$|\psi|^2 = \begin{cases} \left[ \frac{\dot{a}(T_c - T)}{b} \right] & T < T_c \\ 0 & T > T_c \end{cases}$$



# Predicting superconducting properties using GL theory



Equating condensation energies:

$$\frac{[\dot{a}(T - T_c)]^2}{2b} \quad (\text{GL})$$

$$\frac{B_c(T)^2}{2\mu_0} \quad (\text{Thermodynamics})$$

$$\frac{[\dot{a}(T - T_c)]^2}{2b} = \frac{B_c(T)^2}{2\mu_0}$$

⇒ Gives value for  $\dot{a}^2/b$

From  $S = -(dG/dT)$  the entropy change:

$$S_s(T) - S_N(T) = -\frac{\dot{a}^2}{b}(T_c - T)$$

⇒ No latent heat/entropy change at  $T_c$  (second order transition)

# GL theory in inhomogenous systems\*

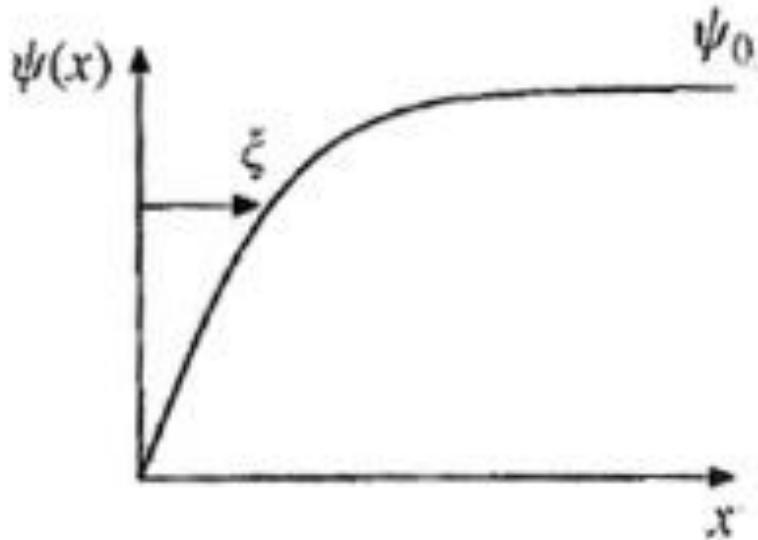
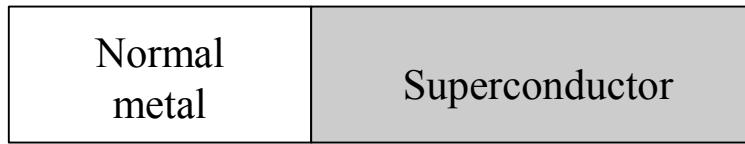
$$G_s(T, \mathbf{r}) = G_N(T, \mathbf{r}) + \frac{\hbar^2}{2m} |\nabla \psi(\mathbf{r})|^2 + a(T) |\psi(\mathbf{r})|^2 + \frac{b(T)}{2} |\psi(\mathbf{r})|^4$$

Minimise:

$$G_s(T) = G_N(T) + \int \left( \frac{\hbar^2}{2m} |\nabla \psi(\mathbf{r})|^2 + a(T) |\psi(\mathbf{r})|^2 + \frac{b(T)}{2} |\psi(\mathbf{r})|^4 \right) d\mathbf{r}$$

$$\Rightarrow \frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + \left[ a(T) + \frac{b(T)}{2} |\psi(\mathbf{r})|^2 \right] \psi(\mathbf{r}) = 0$$

# Application of GL theory to normal metal-superconductor interface\*



$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + a(T)\psi(x) + \frac{b(T)}{2}\psi(x)^2 = 0$$

$$\psi(x) = \psi_0 \tanh\left(\frac{x}{\sqrt{2}\xi(T)}\right)$$

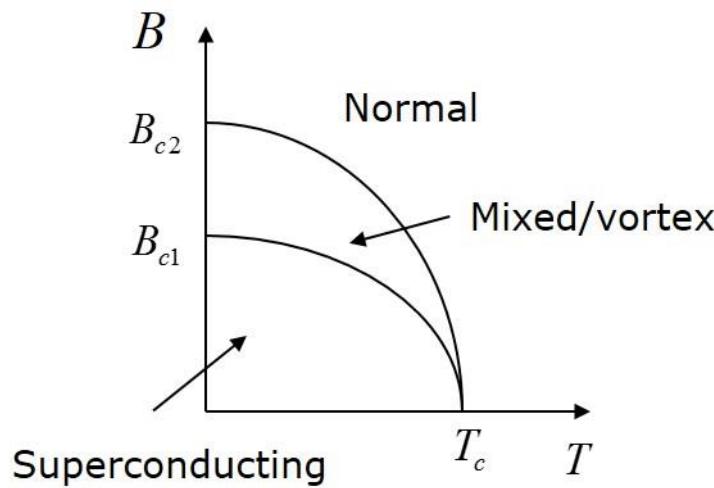
$$\xi(T) = \left( \frac{\hbar^2}{2m|a(T)|} \right)^{1/2}$$

- $\xi(T)$  is the coherence length, i.e. distance of separation of Cooper pair electrons

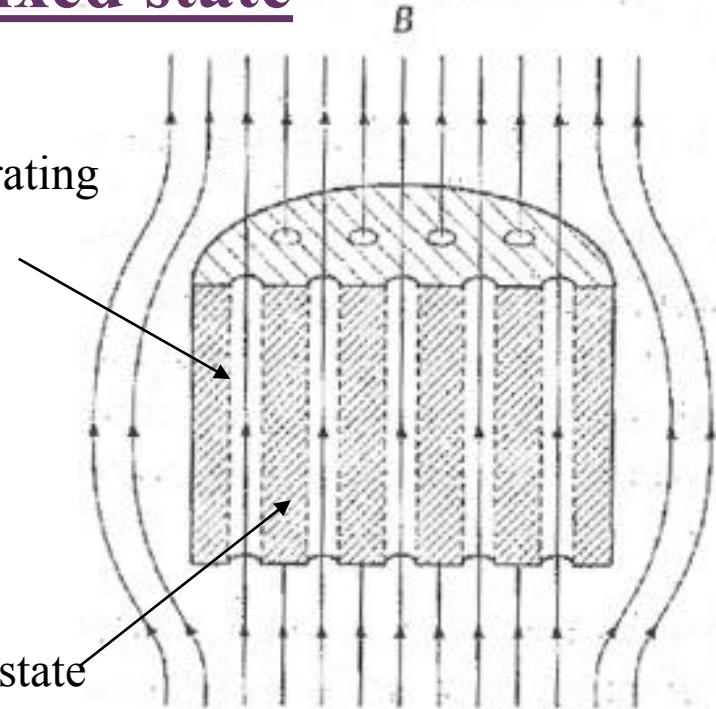
-  $\xi(T)$  decreases with  $T$  due to  $|a(T)|$  term  
(at  $T_c$  coherence length is divergent)

\* Equations non-examinable

# Type II superconductors in the mixed state

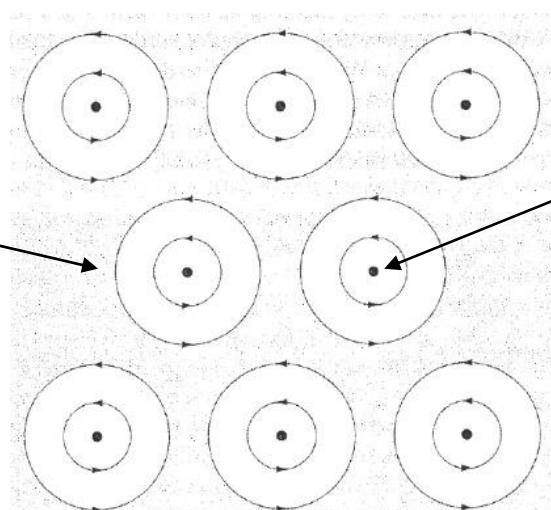


Magnetic field penetrating  
through Normal state  
'filaments'



Superconducting state  
(no field penetration)

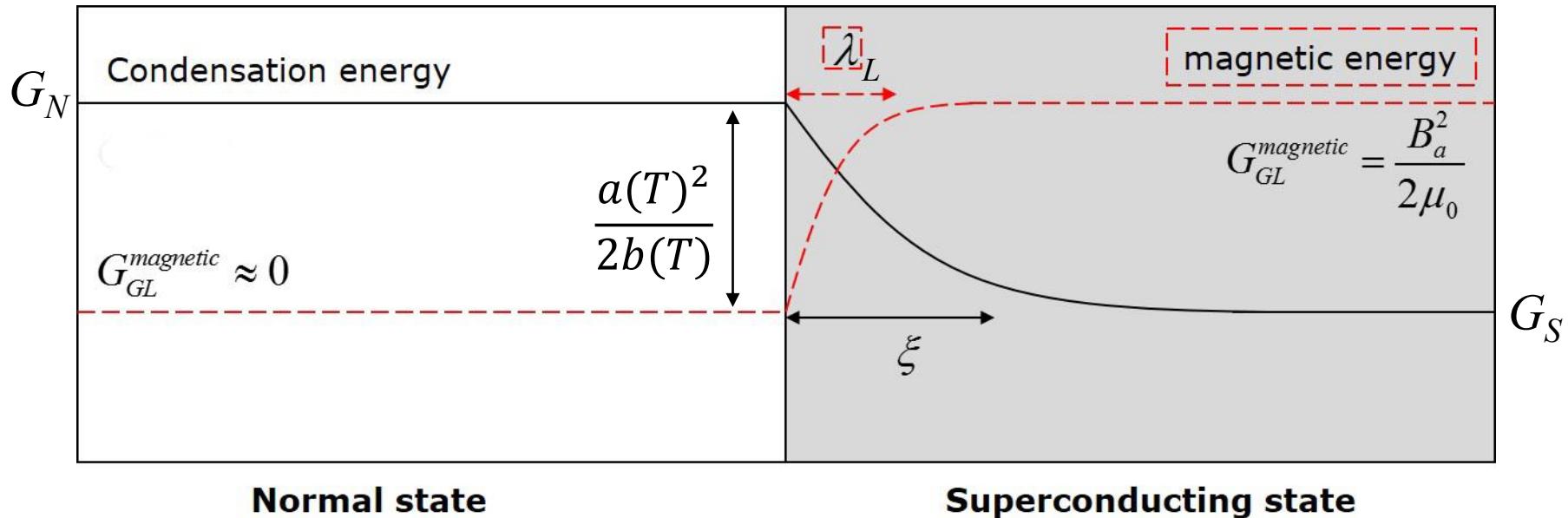
Supercurrents  
(see London equation)



Normal core  
region

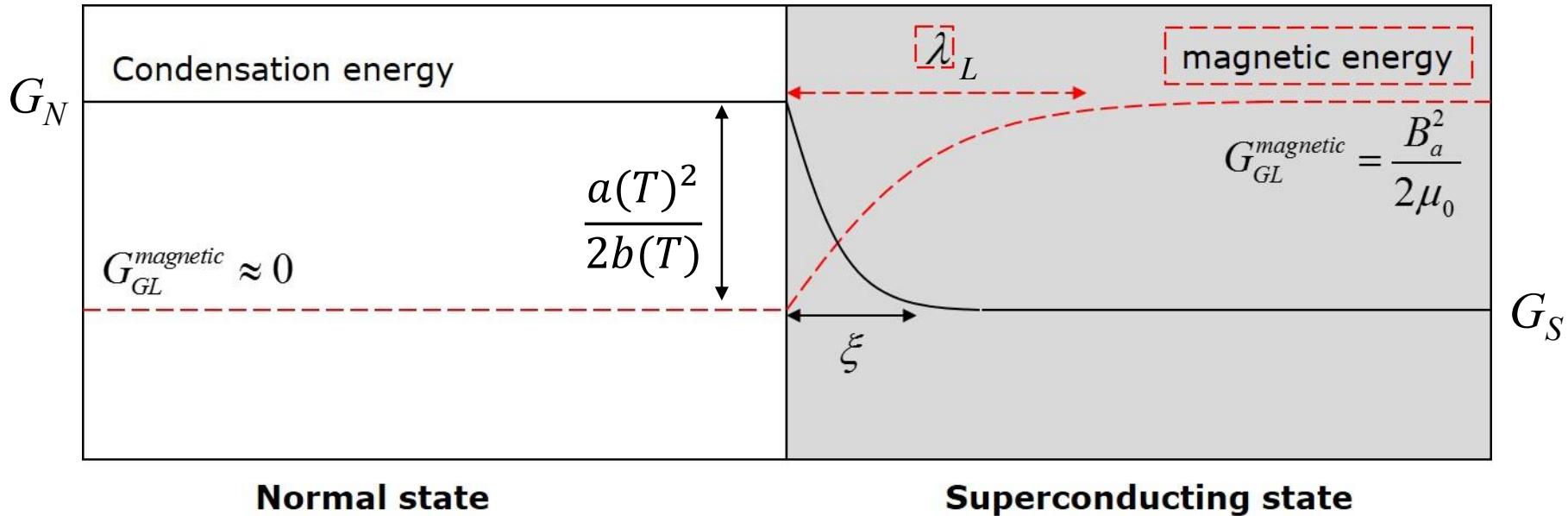
-Magnetic field from supercurrent  
 cancels external field passing through  
 normal metal core

# Type I superconductors: $\xi > \lambda_L$



- Magnetic energy due to field penetration increases at a *faster* rate than energy decrease due to Cooper pair condensation
- Leads to *high* interfacial energy
  - i.e. co-existence of normal and superconducting regions *not allowed* in Type I
- Coherence length  $\xi$  typically larger for elements: reason for Type I behaviour in elements and Type II behaviour in compounds

## Type II superconductors: $\xi < \lambda_L$



- Magnetic energy due to field penetration increases at a *slower* rate than energy decrease due to Cooper pair condensation
- Leads to *low* interfacial energy
  - i.e. co-existence of normal and superconducting regions *allowed* in Type II

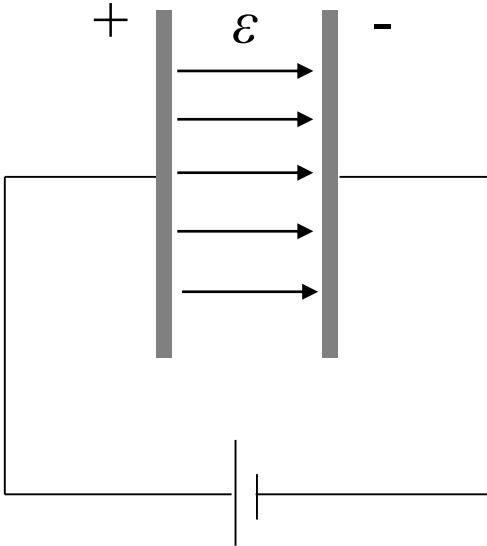
# FoP 3B Part II

Dr Budhika Mendis ([b.g.mendis@durham.ac.uk](mailto:b.g.mendis@durham.ac.uk))  
Room 151

## Lecture 10: Polarisation in Dielectrics

# Dielectrics in capacitors

Capacitance is defined by:



$$C = \frac{Q}{V} = \epsilon_0 \epsilon_r \frac{A}{d}$$

dielectric constant

capacitor plate area  
 plate separation

Material	Dielectric Constant	Material	Dielectric Constant
Vacuum	1	Benzene	2.28
Helium	1.000065	Diamond	5.7
Neon	1.00013	Salt	5.9
Hydrogen	1.00025	Silicon	11.8
Argon	1.00052	Methanol	33.0
Air (dry)	1.00054	Water	80.1
Nitrogen	1.00055	Ice (-30° C)	99
Water vapor (100° C)	1.00587	KTaNbO <sub>3</sub> (0° C)	34,000

$\text{BaTiO}_3$  ] Ferroelectric  
 $\text{PbTiO}_3$  ] ‘perovskites’

- Experimentally it is found that inserting a dielectric in a capacitor causes a smaller potential drop across the plates (charge is however conserved).
- This is due to *polarisation* of the dielectric.

## Aim of today's lecture

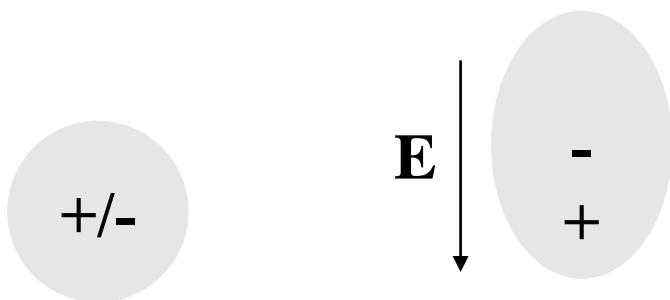
*Definition:* Dielectrics are insulator materials that can be polarised by an applied electric field.

- Develop the electrostatic framework used for describing dielectric media

*Key concepts:*

- Polarisation in dielectrics
- Microscopic vs macroscopic electric fields

# Definition of polarisation



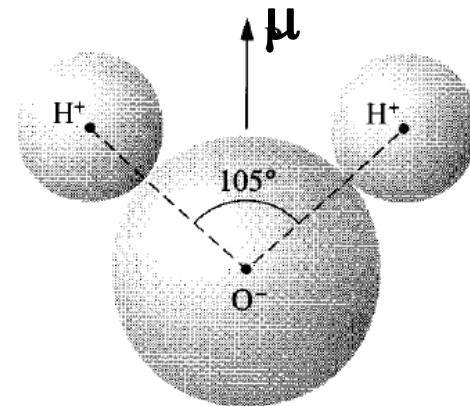
Unpolarised atom  
Electric field OFF

Polarised atom  
Electric field ON

More ‘complex’ polarisations:

Electric dipole moment defined by:  
$$|\boldsymbol{\mu}| = qd$$

The direction of  $\boldsymbol{\mu}$  is from negative to positive charge.

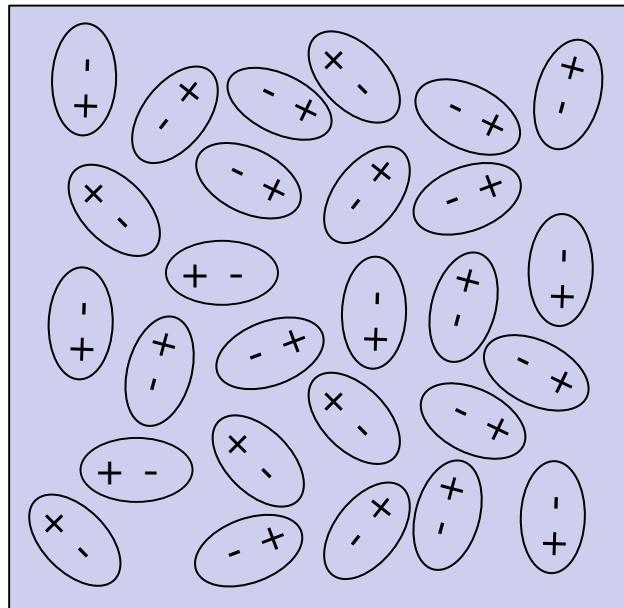


Water molecule: *permanent* electric dipole

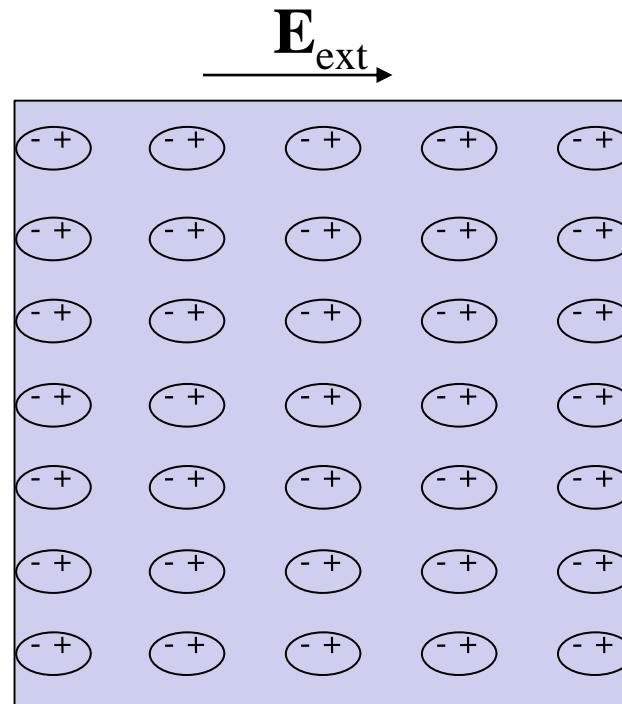
Torque due to electric field:  $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{E}$

Potential energy due to electric field:  $U = -\boldsymbol{\mu} \cdot \mathbf{E}$

# Dielectric media in an electric field (e.g. capacitor)



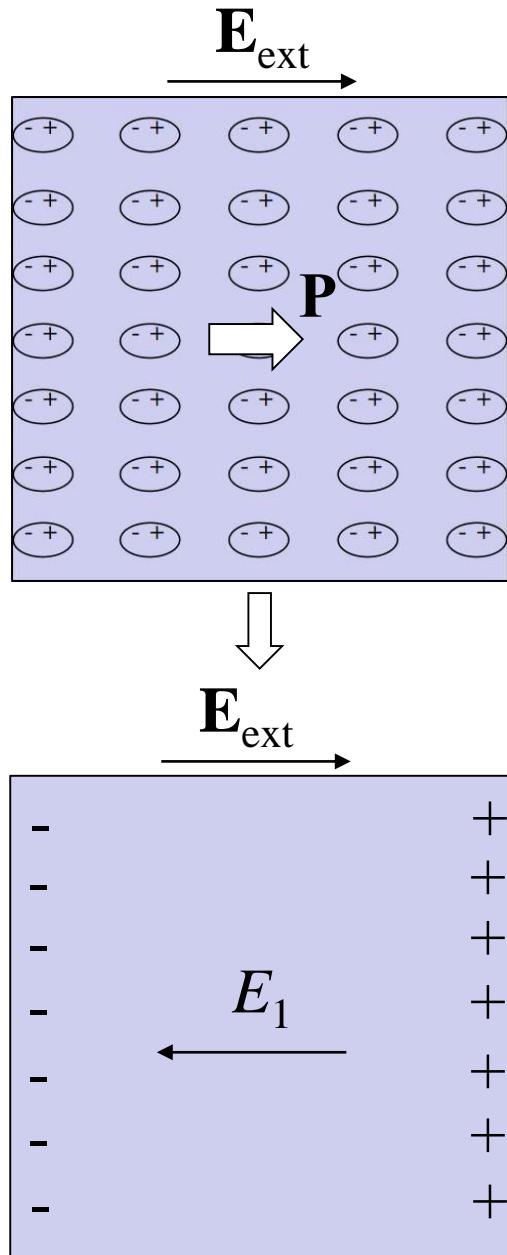
Electric field OFF



Electric field ON

- Torque on permanent dipoles rotate them to the minimum energy configuration.
- Define polarisation  $\mathbf{P}$  as dipole moment per unit volume, i.e.  $\mathbf{P} = N\mu$ , where  $N$  is the number density of dipoles.

# Macroscopic electric field



Electric field due to a single dipole is given by\*:

$$\mathbf{E}(\mathbf{r}) = \frac{3(\mu \cdot \mathbf{r})\mathbf{r} - r^2\mu}{4\pi\epsilon_0 r^5}$$

For *uniform* polarisation  $\mathbf{P}$  the collective effect of all dipoles can be modelled by a surface charge density ( $\sigma$ ) \*:

$$\sigma = \mathbf{P} \cdot \hat{\mathbf{n}} \quad \begin{matrix} \leftarrow \\ \text{Unit surface} \\ \text{normal vector} \end{matrix}$$

A depolarisation field is therefore present:

$$E_1 = -\frac{\sigma}{\epsilon_0} \quad (\text{Gauss' law})$$

Internal field is  $(E_{\text{ext}} - |E_1|)$ .

\* See for example Griffiths, *Introduction to Electrodynamics*, Chapters 3, 4 (non-examinable)

# Macroscopic vs microscopic fields

$E_1$  is a *macroscopic* electric field ‘smoothed’ over many dipoles. The local *microscopic* field at an individual dipole can however defer significantly from  $E_1$ .

The polarisability ( $\alpha$ ) of a single dipole is defined as:

$$\mu = \alpha E_{\text{local}}$$

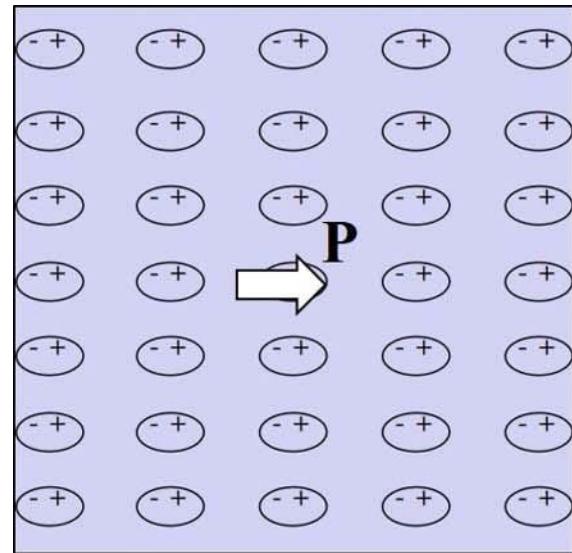
↗                      ↙  
Electric dipole moment      Local microscopic electric field

Q: What is the local electric field at a dipole?

Q: How do you calculate polarisability?

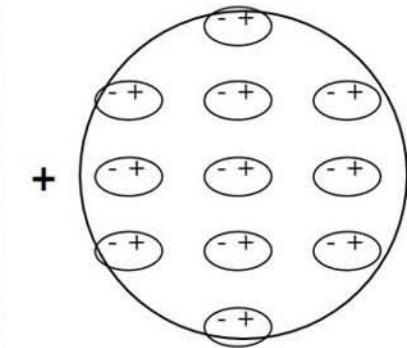
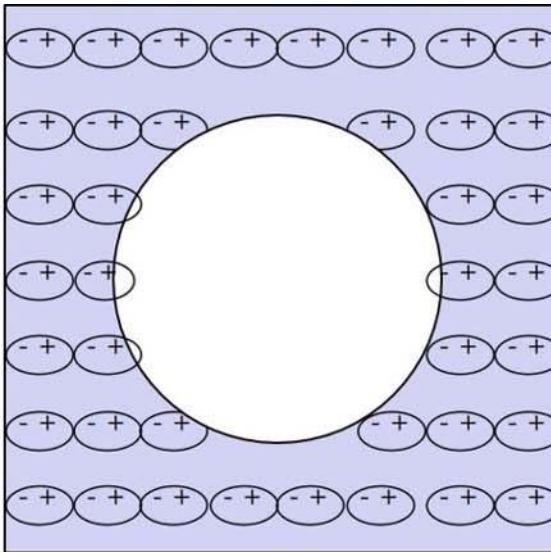
(Clausius-Mossotti relation- next lecture)

# Local electric field

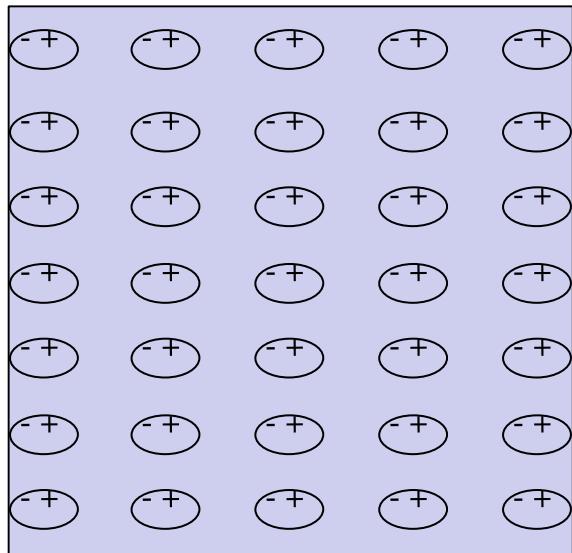


$\mathbf{E}_{\text{ext}}$

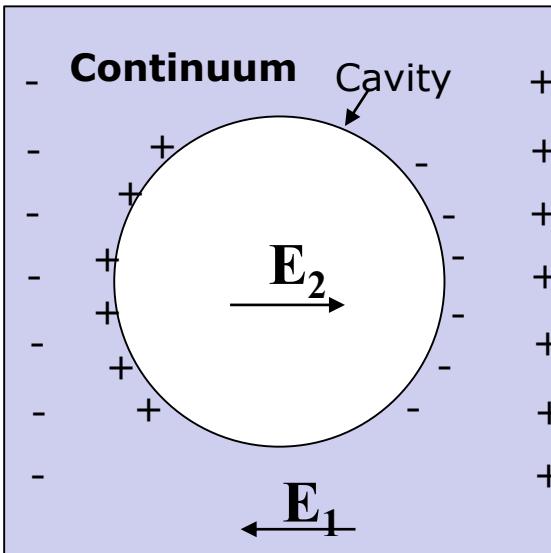
split



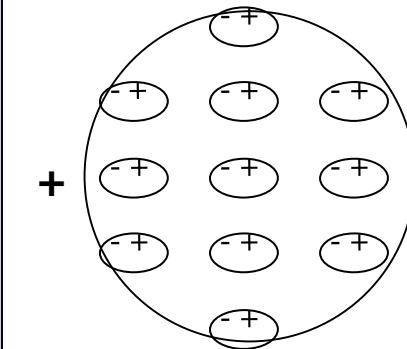
+



split



**Atomistic**

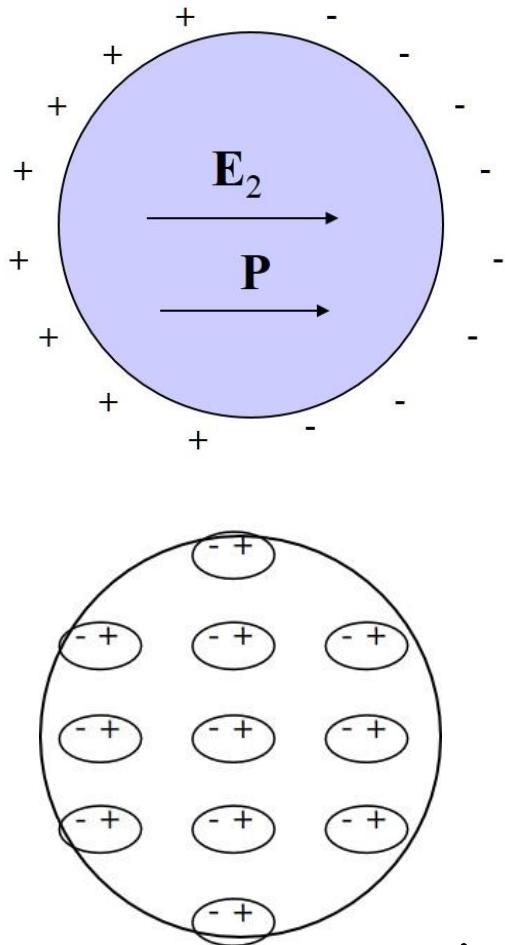


+

$\mathbf{E}_3$

$$\text{Local electric field } \mathbf{E}_{\text{local}} = (\mathbf{E}_{\text{ext}} + \mathbf{E}_1) + \mathbf{E}_2 + \mathbf{E}_3$$

# Lorentz ( $E_2$ ) and atomistic ( $E_3$ ) fields



Lorentz field is given by\*:

$$E_2 = \frac{\mathbf{P}}{3\epsilon_0}$$

Atomistic field is given by:

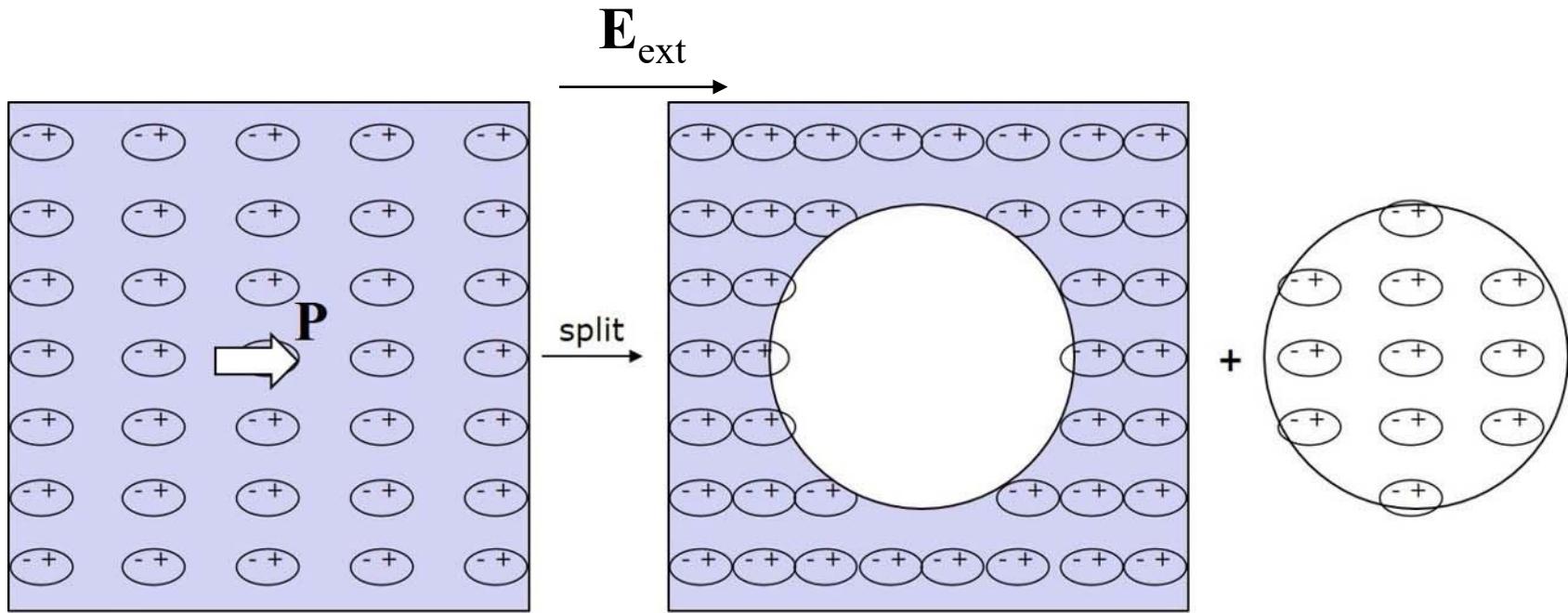
$$\begin{aligned} E_3 &= \sum_{\text{dipoles } i} \frac{3(\mathbf{\mu}_i \cdot \mathbf{r}_i)\mathbf{r}_i - r_i^2 \mathbf{\mu}_i}{4\pi\epsilon_0 r_i^5} \\ &= \mu \sum_i \frac{3x_i^2 - r_i^2}{4\pi\epsilon_0 r_i^5} = 0 \end{aligned}$$

For polarisation along  $x$  and *cubic* crystal.

$\therefore$  only the Lorentz field alters the microscopic field from the macroscopic field.

\* See for example Griffiths, *Introduction to Electrodynamics*, Chapter 4 (non-examinable)

# Local electric field



$$\text{Local electric field } \mathbf{E}_{\text{local}} = (\mathbf{E}_{\text{ext}} + \mathbf{E}_1) + \mathbf{E}_2 + \mathbf{E}_3$$

$E_1 = -\sigma/\epsilon_0$ ,  $E_2 = P/3\epsilon_0$ ,  $E_3 = 0$  gives:

$$\mathbf{E}_{\text{local}} = \mathbf{E}_{\text{ext}} - \frac{\sigma}{\epsilon_o} + \frac{P}{3\epsilon_o}$$

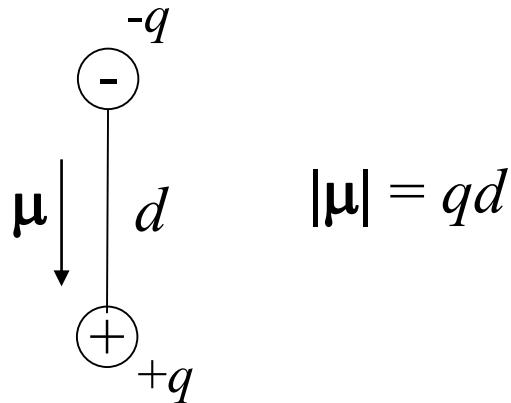
# FoP 3B Part II

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Room 151

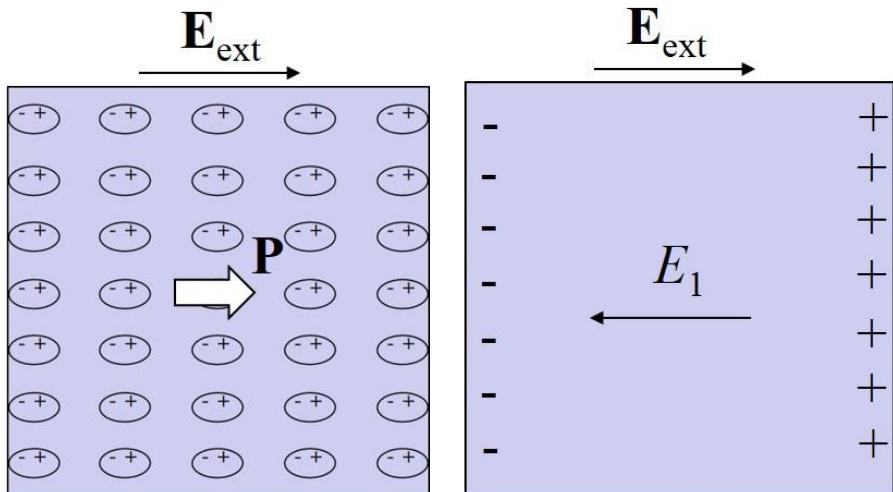
## Lecture 11: Ferroelectric crystals

## Summary of lecture 10

## Electric dipole moment:



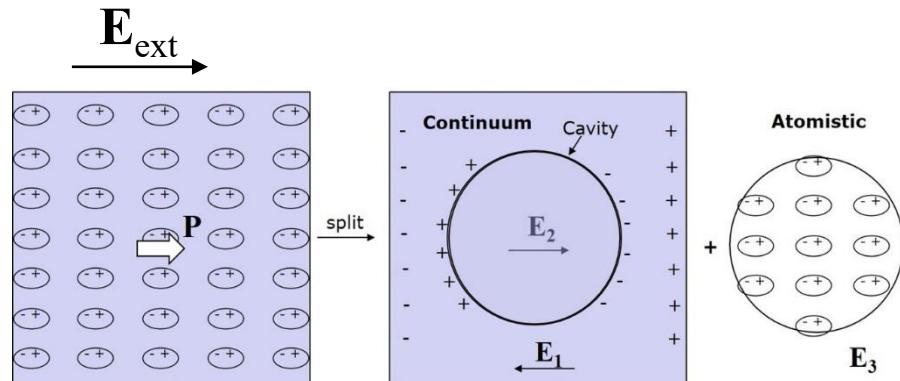
## Polarisation and depolarising fields:



## Local vs macroscopic fields:

$$\mu = \alpha \mathbf{E}_{\text{local}}$$

↑  
polarisability



$$E_{\text{local}} = \left( E_{\text{ext}} - \frac{\sigma}{\epsilon_0} \right) + \frac{P}{3\epsilon_0}$$


  
 $E_{\text{macro}}$

## Aim of today's lecture

- Discuss polarisability, polarisation mechanisms and ferroelectric crystals

*Key concepts:*

- Clausius-Mossoti relationship and polarisability
- Electronic polarisation: frequency dependence of dielectric function
- Ferroelectric crystals

# Clausius-Mossotti relation

The polarisation magnitude  $P$  is given by:

$$P = N\mu = N\alpha E_{\text{local}}$$

Dipole density      Dipole moment      Polarisability

Local electric field

Using  $E_{\text{local}} = E_{\text{macro}} + (P/3\epsilon_0)$  gives\*:

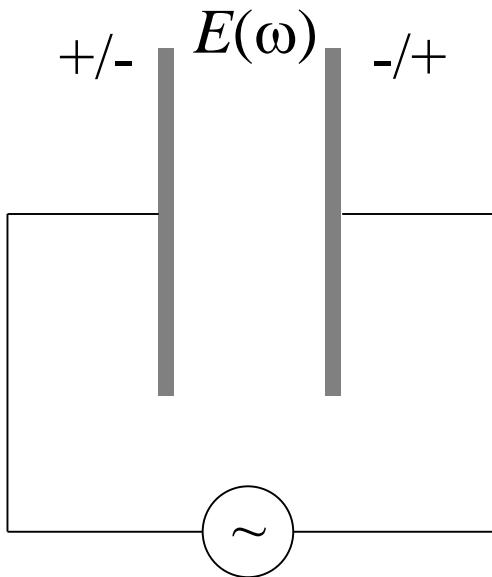
$$N\alpha = \frac{(P/E_{\text{macro}})}{1 + \frac{1}{3\epsilon_0}(P/E_{\text{macro}})}$$

From the definition of electric displacement  $D = \epsilon_0 E_{\text{macro}} + P = \epsilon_0 \epsilon_r E_{\text{macro}}$ :

$$\boxed{\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}}$$

\*  $E_{\text{macro}}$  here is the *internal macroscopic* field, i.e. sum of external and depolarising ( $E_1$ ) fields

# Polarisation mechanisms

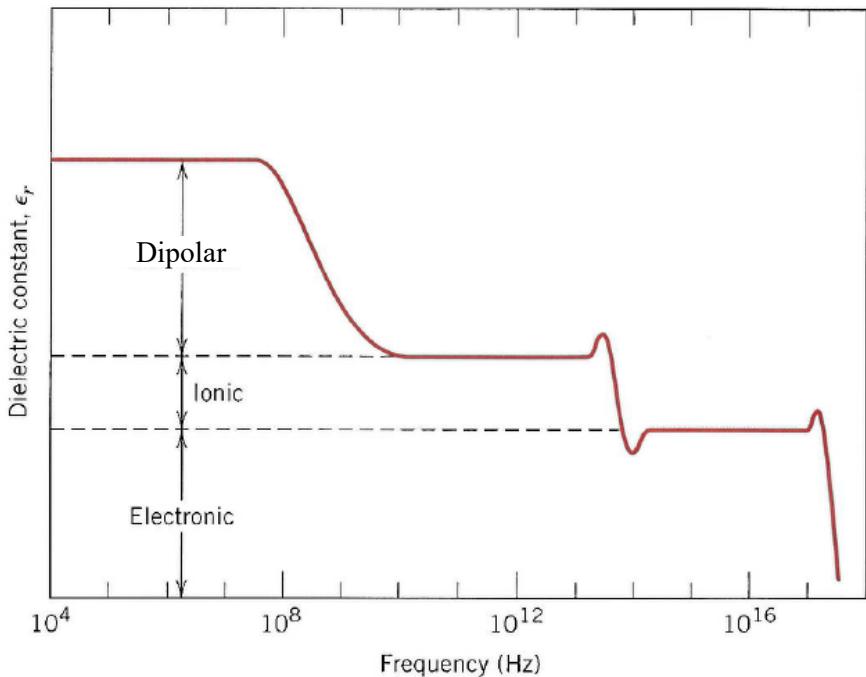


-If the capacitor is connected to an AC circuit polarisation of medium will oscillate with electric field  $E$  (frequency  $\omega$ ).

-Hence:

$$C = \epsilon_0 \epsilon_r(\omega) \frac{A}{d}$$

dielectric constant for frequency  $\omega$

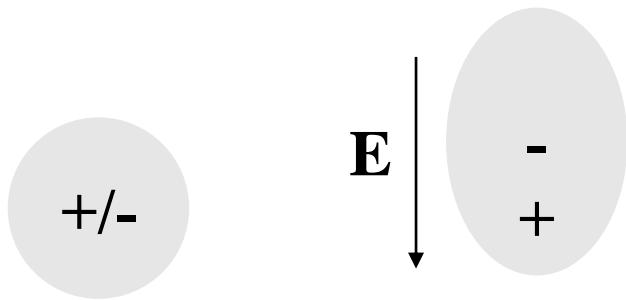


Electronic: polarisation of electron cloud w.r.t nucleus

Ionic: polarisation of oppositely charged ions

Dipolar: polarisation and re-orienting of molecules (e.g. H<sub>2</sub>O) with permanent electric dipoles

# Electronic polarisation



Unpolarised atom  
Electric field OFF

Polarised atom  
Electric field ON

-Electron-nuclear bond treated as an oscillating spring (spring constant  $K = m\omega_o^2$ ).

-Assume an oscillating *local* electric field  $\mathbf{E}_{\text{local}}(\omega) = \mathbf{E}_o \exp(i\omega t)$ .

-Electron position is  $\mathbf{r}(\omega) = \mathbf{r}_o \exp(i\omega t)$ .  
 $\therefore \mu(\omega) = -e \mathbf{r}(\omega)$

-Equation of motion for electron:

$$m\ddot{\mathbf{r}} = -K\mathbf{r} - e\mathbf{E}_{\text{local}}$$

↗                      ↗  
SHM restoring force      Force due to electric field

- Substituting for  $\mathbf{r}$  and using  $\mu(\omega) = \alpha(\omega)\mathbf{E}_{\text{local}}(\omega)$  gives:

$$\alpha(\omega) = \frac{e^2}{m(\omega_o^2 - \omega^2)} \quad (\omega_o = \sqrt{K/m})$$

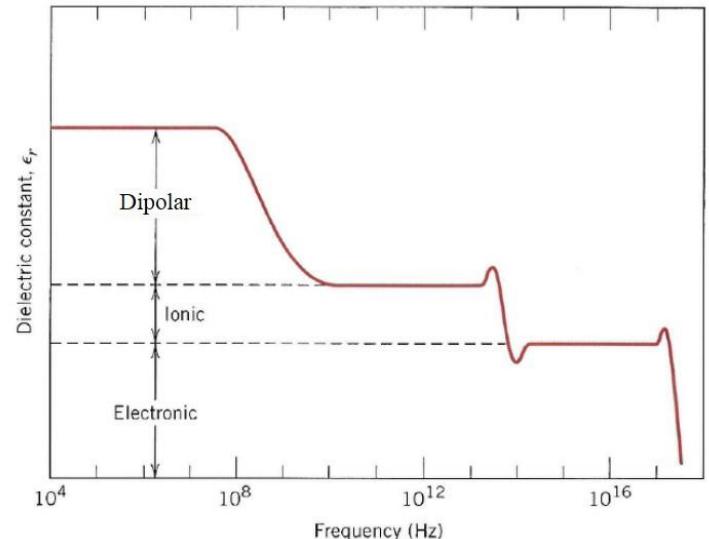
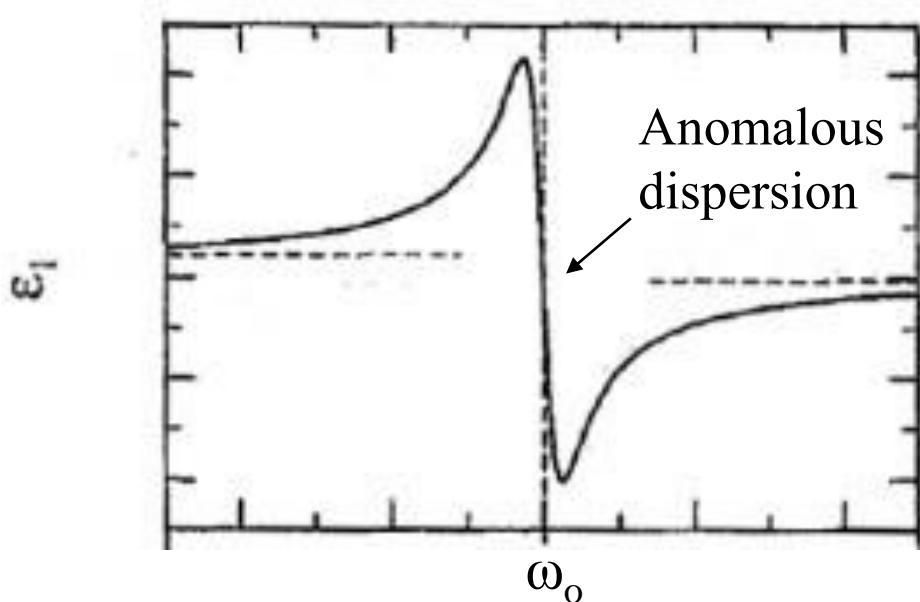
# Dielectric function due to electronic polarisation

From the Clausius-Mossotti relation:

$$\epsilon_r(\omega) = 1 + \frac{N\alpha(\omega)}{\epsilon_o - [N\alpha(\omega)/3]}$$

Substituting for  $\alpha(\omega)$ :

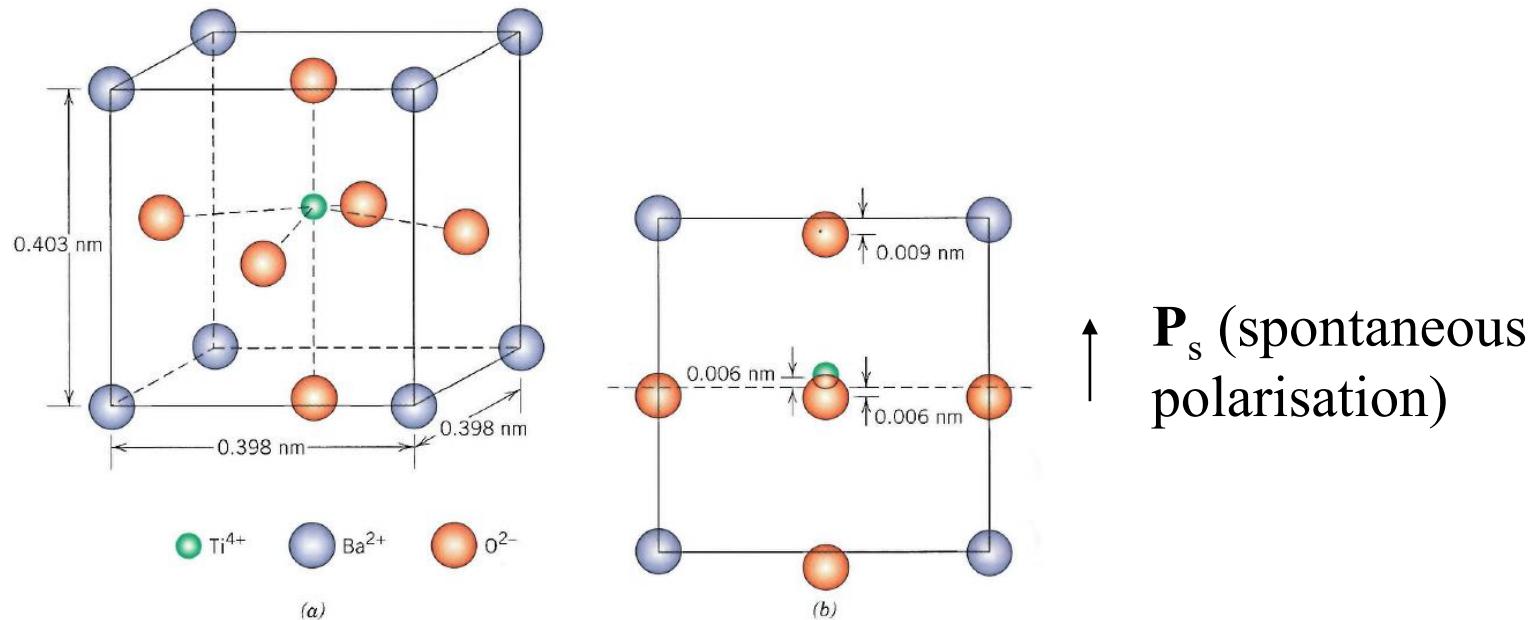
$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{m\epsilon_o(\omega_o^2 - \omega^2) - (Ne^2/3)}$$



# Ferroelectric crystals

Material	Dielectric Constant	Material	Dielectric Constant
Vacuum	1	Benzene	2.28
Helium	1.000065	Diamond	5.7
Neon	1.00013	Salt	5.9
Hydrogen	1.00025	Silicon	11.8
Argon	1.00052	Methanol	33.0
Air (dry)	1.00054	Water	80.1
Nitrogen	1.00055	Ice (-30° C)	99
Water vapor (100° C)	1.00587	<b>KTaNbO<sub>3</sub> (0° C)</b>	<b>34,000</b>

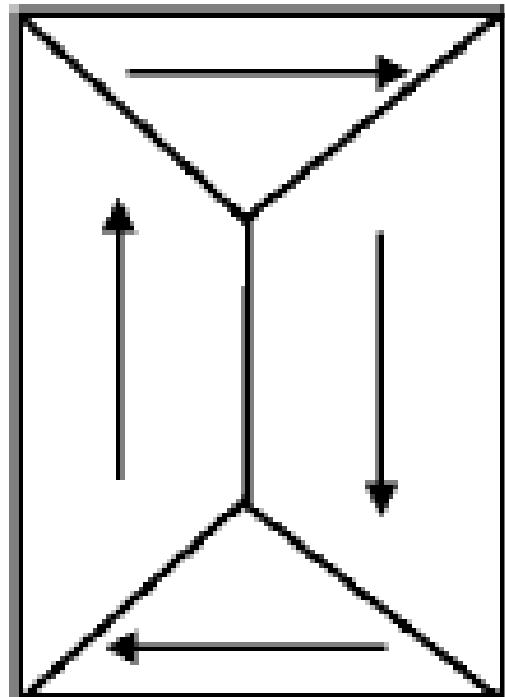
$\text{BaTiO}_3$  } Ferroelectric  
 $\text{PbTiO}_3$  } ‘perovskites’



Crystal structure of  $\text{BaTiO}_3$

# Domain formation

For a dielectric with no free carriers:



$$\vec{\nabla} \cdot \mathbf{D} = 0$$

↑  
electric displacement field

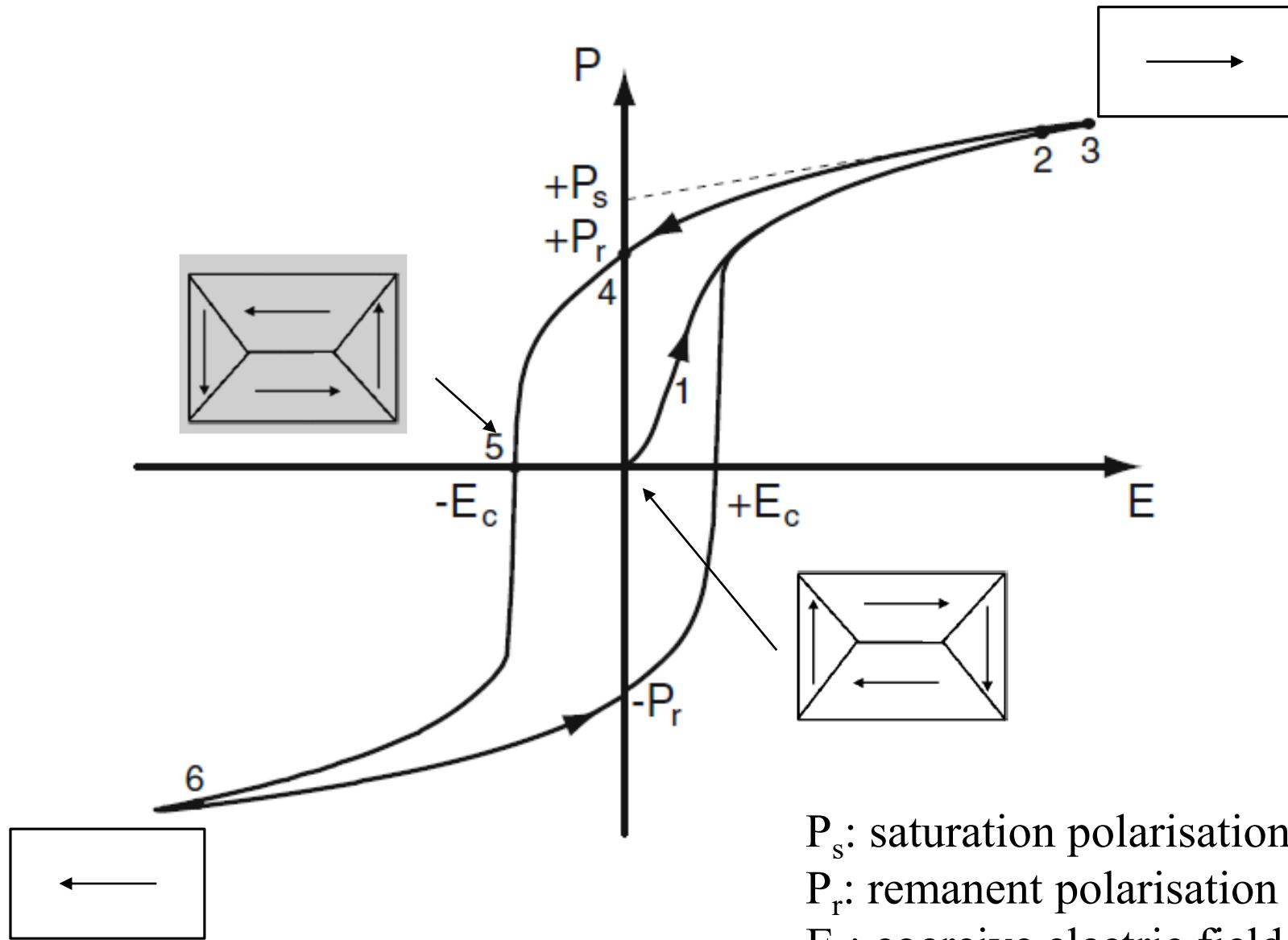
Therefore:

$$\epsilon_0 \vec{\nabla} \cdot \mathbf{E} = -\vec{\nabla} \cdot \mathbf{P}$$

At sample surface  $\nabla \cdot \mathbf{P} \neq 0$ , so that electric field induced within sample.

Domains form to minimise energy due to internal electric field (cf. ferromagnetic domains).

# Hysteresis curve



$P_s$ : saturation polarisation  
 $P_r$ : remanent polarisation  
 $E_c$ : coercive electric field

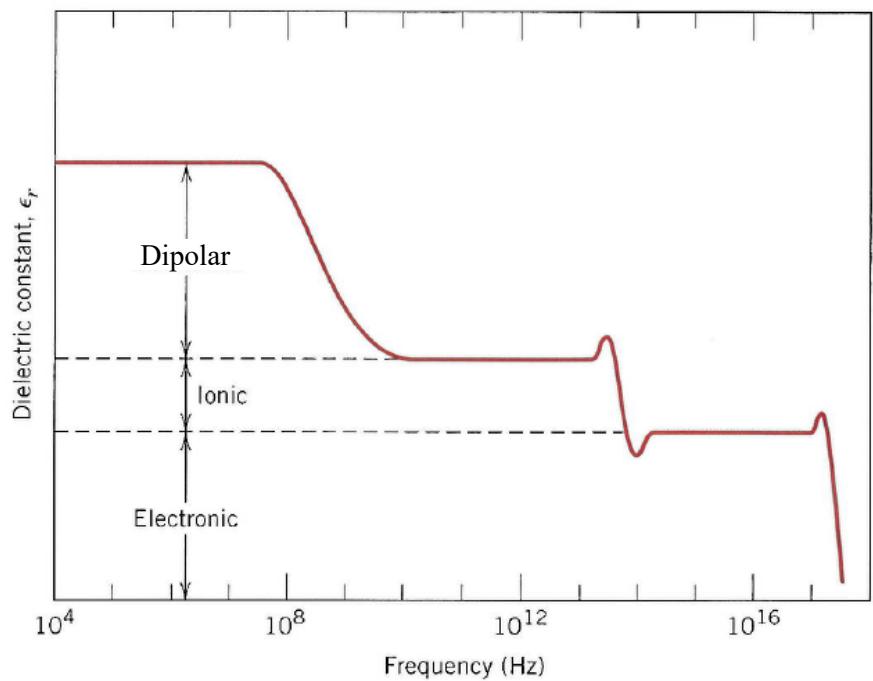
# FoP 3B Part II

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Room 151

Lecture 12: Ginzburg-Landau theory of  
ferroelectrics

# Summary of lecture 13

Polarisation mechanisms:

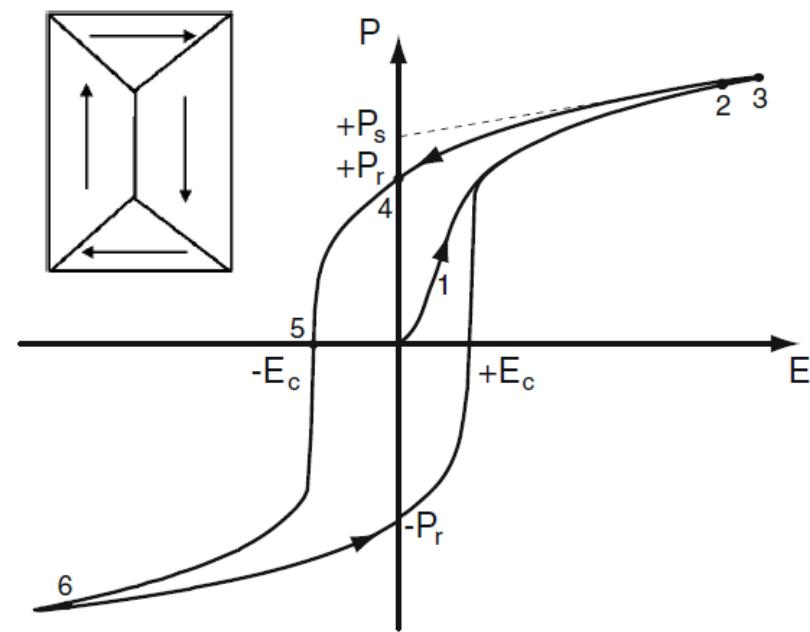
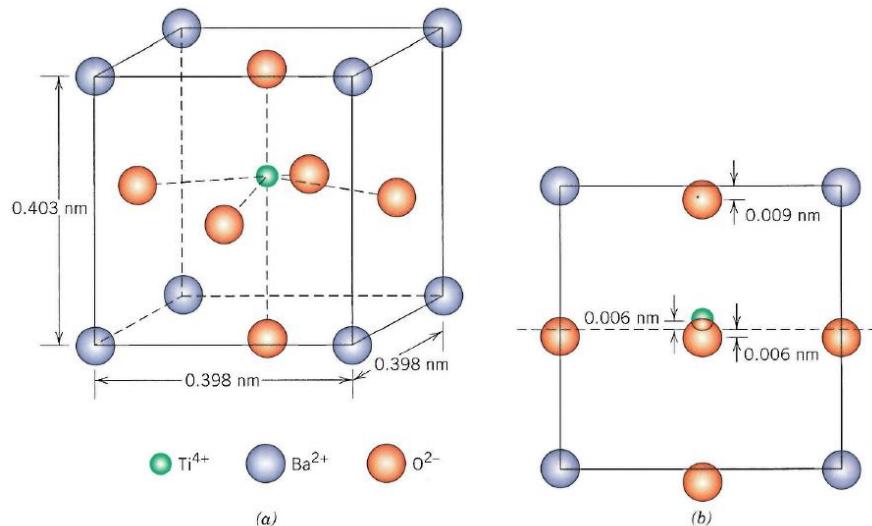


Electronic polarisation:

$$\alpha(\omega) = \frac{e^2}{m(\omega_0^2 - \omega^2)}$$

Electrons in atoms treated as harmonic oscillators

Ferroelectric crystals:



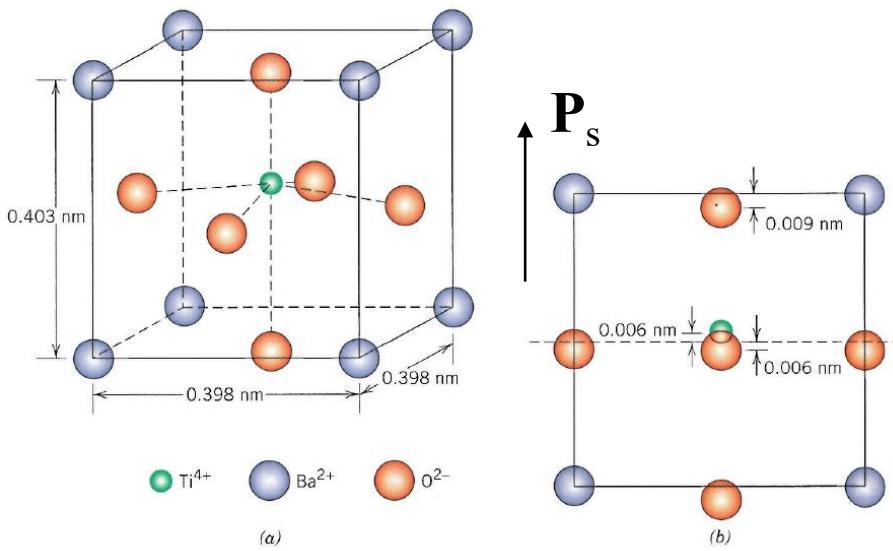
## Aim of today's lecture

- Develop Ginzburg-Landau theory of ferroelectric crystals

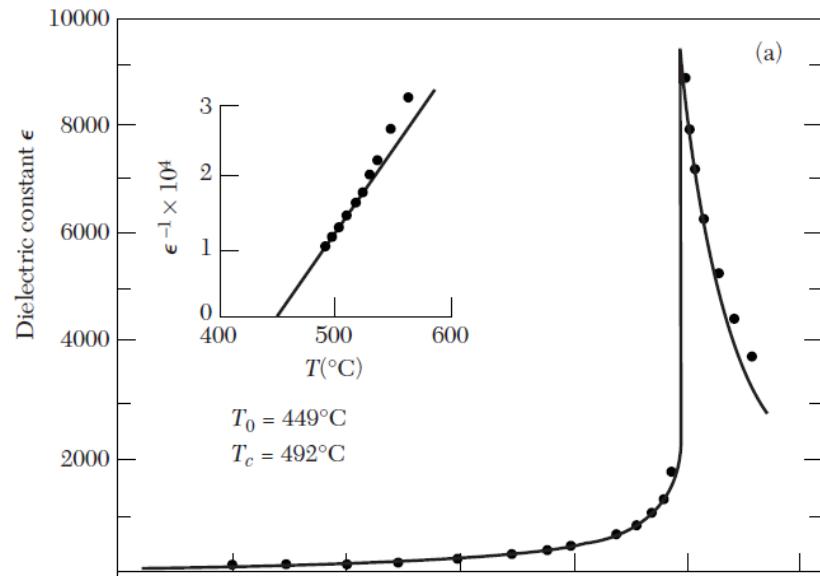
*Key concepts:*

- Ferroelectric to paraelectric transition
- Dielectric function close to transition temperature
- First order and second order transitions

# Ferroelectric to paraelectric transition

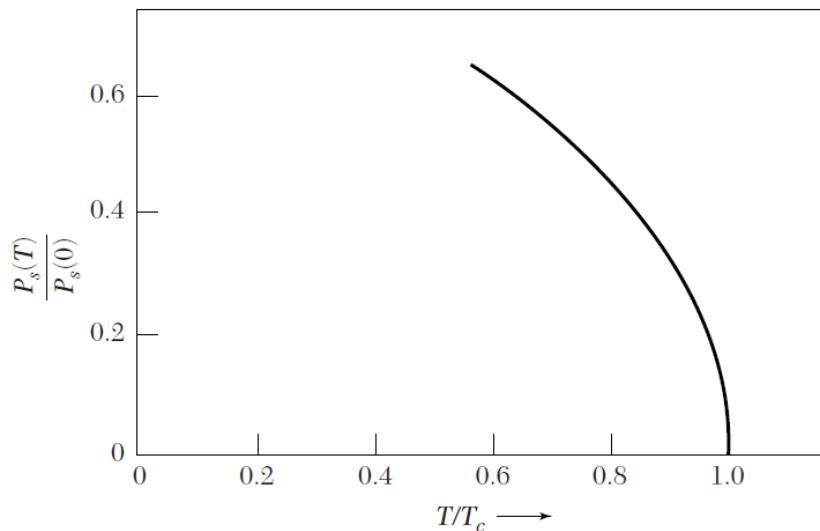


- Relative shift of positive and negative ions destroyed at high temperatures.
- Material converts to *paraelectric* state at the *Curie temperature*, with almost zero polarisation.
- Large increase in dielectric constant at transition temperature.

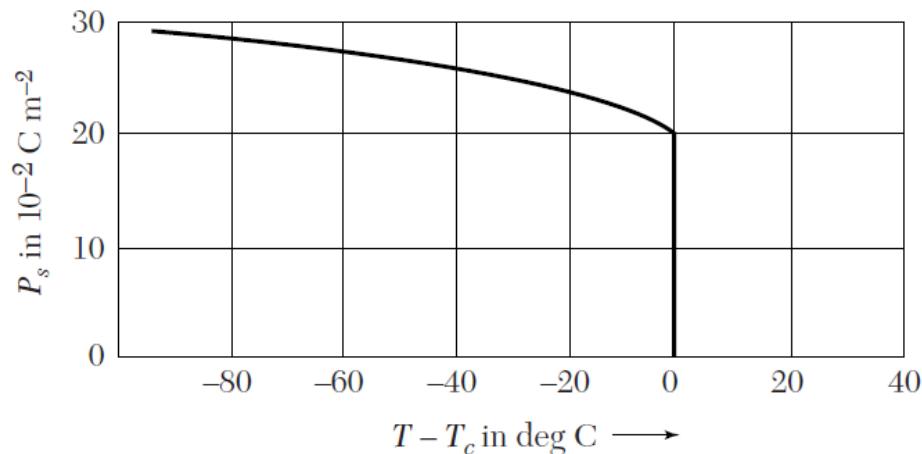


Above: Dielectric constant for  $\text{PbTiO}_3$

# Polarisation change at transition temperature



Second order transition (e.g. LiTaO<sub>3</sub>)



First order transition (e.g. BaTiO<sub>3</sub>)

-Spontaneous polarisation ( $\mathbf{P}_s$ ) is an order parameter in ferroelectrics (cf. Cooper pairs in superconductors or spontaneous magnetisation  $\mathbf{M}_s$  in ferromagnets).

-Continuous decrease of  $\mathbf{P}_s$  to zero (paraelectric state) for second order transformation. Discontinuous change in  $\mathbf{P}_s$  for first order transformation.

## Ginzburg-Landau theory (second order transitions)

For zero electric field conditions:

$$G_{FE}(T) = G_{PE}(T) + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4$$

Free energy  
ferroelectric state      Free energy  
paraelectric state

- Free energy dependent only on even powers of polarisation  $P$ , since must be invariant on reversal of polarisation direction.
  - For energy minimum require  $g_4 > 0$ .
  - $g_2 = \gamma(T - T_o)$ , where  $\gamma > 0$  and  $T_o$  is a positive constant (NB:  $T_o$  is equal to the Curie temperature only for second order transitions)

# Spontaneous polarisation (second order transitions)

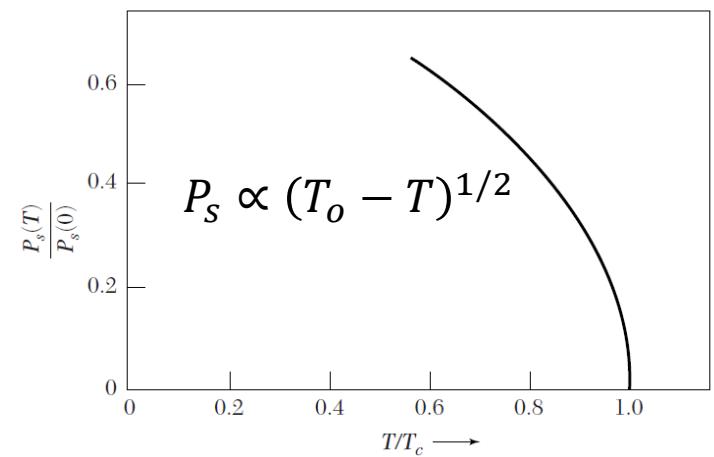
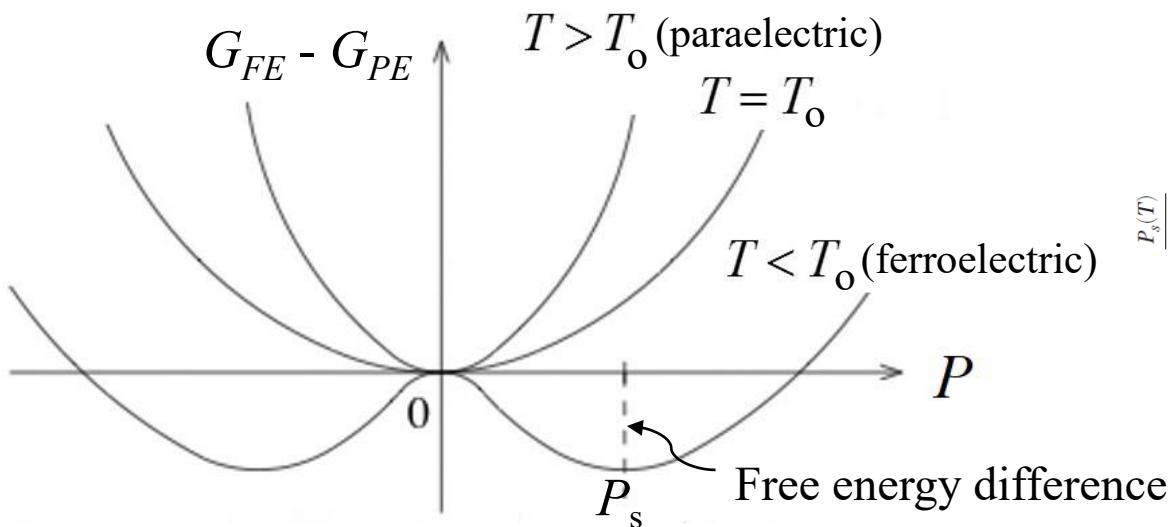
To determine spontaneous polarisation minimise  $G_{FE}$  w.r.t  $P$ :

$$P(g_2 + g_4 P^2) = 0$$

Two possible solutions:

$$(i) \quad P_s = 0 \quad (ii) \quad P_s = \left( -\frac{g_2}{g_4} \right)^{1/2} = \left( \frac{\gamma}{g_4} \right)^{1/2} (T_o - T)^{1/2}$$

Solution (ii) only valid for  $T < T_o$ . Above  $T_o$  only solution (i) exists (i.e. paraelectric state).  $T_o$  is therefore the Curie temperature.



## Effect of applied field (second order transitions)

In the presence of an applied electric field ( $E$ ):

$$G_{FE}(T) = G_{PE}(T) - EP + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4$$

↗  
Dipole potential energy

Minimising free energy:

$$E = g_2P + g_4P^3$$

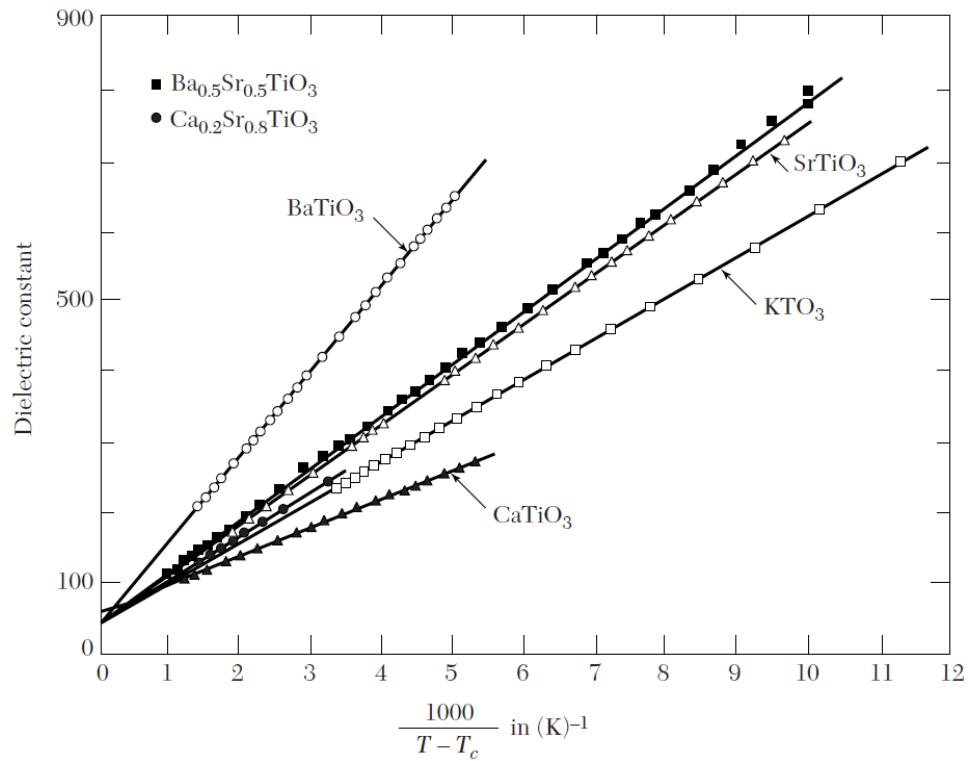
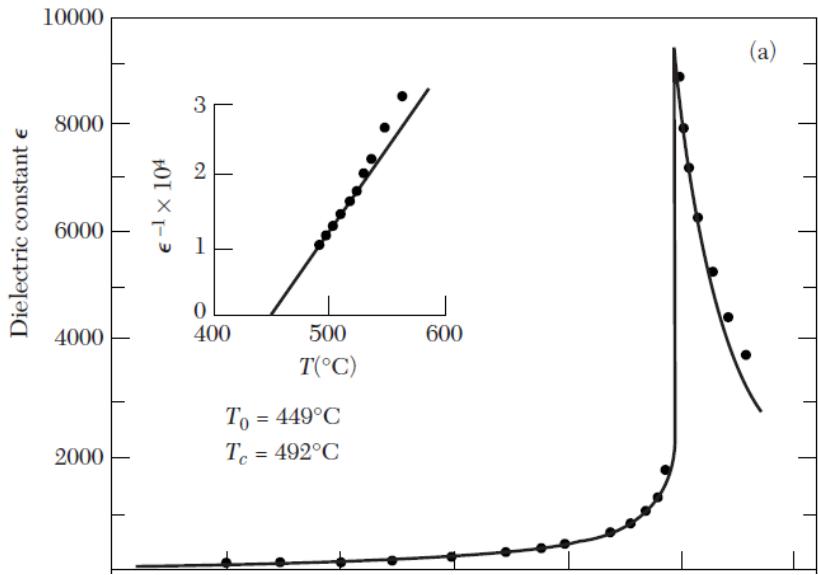
Above the Curie temperature  $P \approx 0$ . Therefore:

$$\frac{P}{E} = \frac{1}{g_2} = \frac{1}{\gamma(T - T_o)}$$

From  $D = \epsilon_0 E + P = \epsilon_0 \epsilon_r E$ , we have:

$$\epsilon_r = 1 + \frac{1}{\epsilon_0} \left( \frac{P}{E} \right) = 1 + \frac{1}{\gamma \epsilon_0 (T - T_o)}$$

# Dielectric constant



$$\epsilon_r = 1 + \frac{1}{\gamma \epsilon_o (T - T_o)}$$

## Ginzburg-Landau theory (first order transitions)

For zero electric field conditions:

$$G_{FE}(T) = G_{PE}(T) + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 + \frac{1}{6}g_6P^6$$

← Additional higher order term

- For energy minimum require  $g_6 > 0$ .
- $g_4$  is now negative.  $g_4 = -|g_4|$
- $g_2 = \gamma(T - T_o)$ , where  $\gamma > 0$  and  $T_o$  is a constant (NB:  $T_o$  is smaller than the Curie temperature for first order transitions)

# Spontaneous polarisation in first order transitions

Minimising  $G_{FE}$  w.r.t  $P$ :

$$\frac{\partial G_{FE}}{\partial P} = P \underbrace{(g_2 + g_4 P^2 + g_6 P^4)}_{\text{quadratic in } P^2} = 0$$

Two possible solutions for spontaneous polarisation:

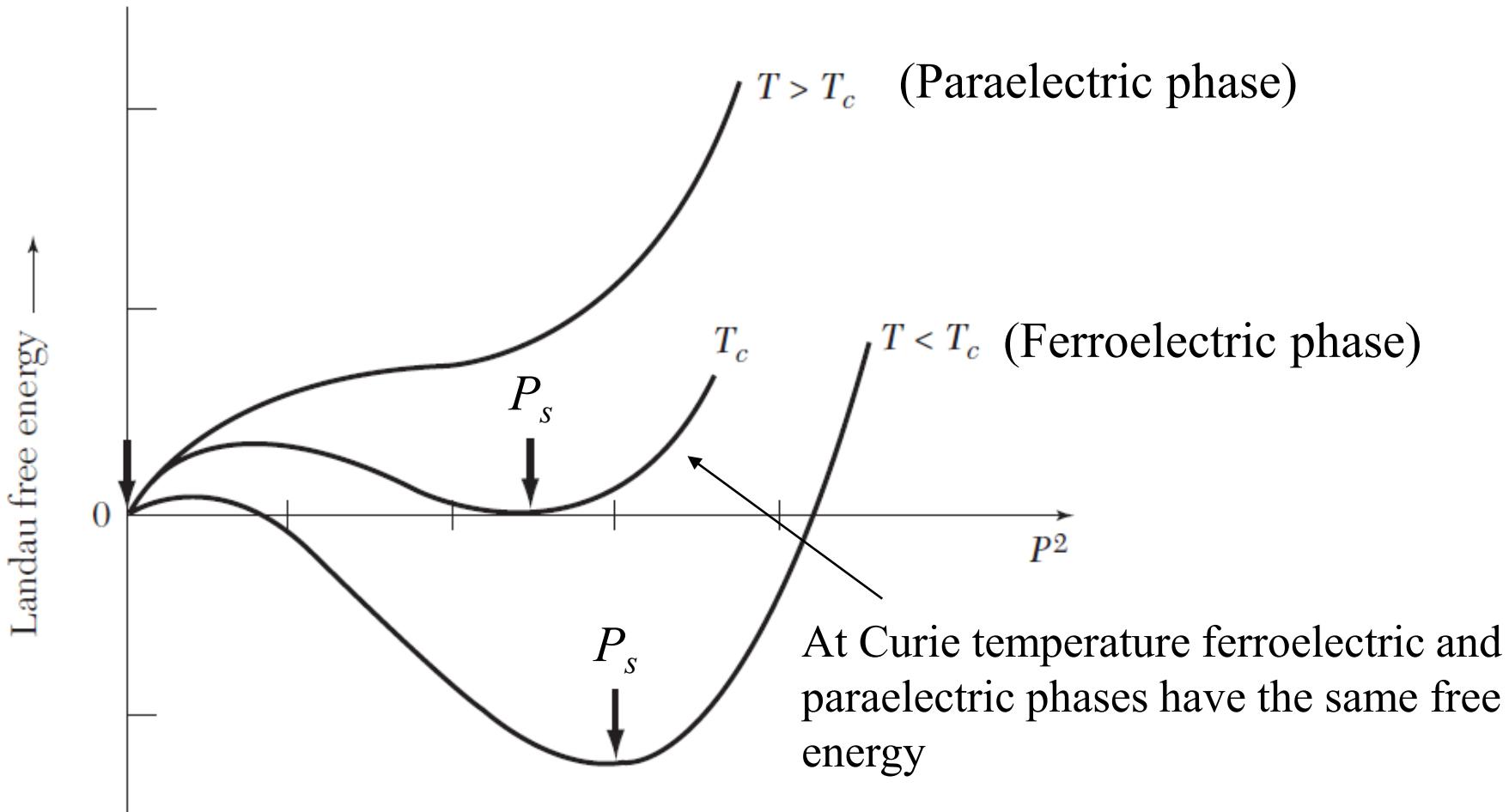
(i)  $P_s = 0$  (paraelectric state)

(ii)  $P_s^2 = \frac{-g_4 \pm \sqrt{g_4^2 - 4g_6g_2}}{2g_6}$  (ferroelectric state; select solution

with a free energy minimum)

# Ginzburg-Landau theory (first order transitions)

Plot free energy as a function of polarisation:



Note discontinuous change in spontaneous polarisation at  $T_c$  (cf. second order transitions)

*End of Part 2!*