

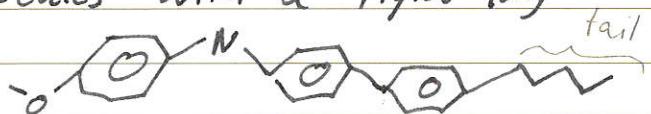
B. Materials for Devices

No. VI

Date 10. 12. 18

Liquid Crystals & Optical Polarisation

- Crystalline materials are anisotropic: their long range order means that their properties may differ depending on the direction of measurement.
- By contrast, liquids are isotropic - invariant w.r.t direction
- Liquid crystals are anisotropic liquids:
 - typically rod-shaped molecules with a rigid long axis but flexible tail
 - the molecules can flow past each other \Rightarrow no long-range positional order
 - but their shape leads to some orientational order as the molecules tend to align on the long axes.
 - this leads to the Nematic LC structure, wherein orientational order is defined by a Director \vec{D} .



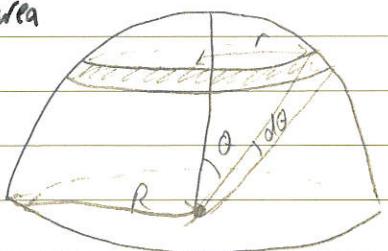
- The degree of orientational order is temp-dependent.
 - at sufficiently high temp, random thermal agitation overcomes alignment interactions so the LC \rightarrow isotropic liquid
 - at very low temp LC \rightarrow normal crystal
 - so there is a given band of temperatures for a particular LC material to have LC properties.
- We can describe the degree of orientational order with the order parameter Q , where

$$Q = \frac{3 \langle \cos^2 \theta \rangle - 1}{2}$$

\vec{D} ↑
molecule

- for perfect alignment, $\langle \cos^2 \theta \rangle = 1 \Rightarrow Q = 1$.
- for isotropic liquids, $\langle \cos^2 \theta \rangle = 1/3 \Rightarrow Q = 0$.
- this can be derived by considering the area of a small band: $dA = 2\pi r \cdot R d\theta$

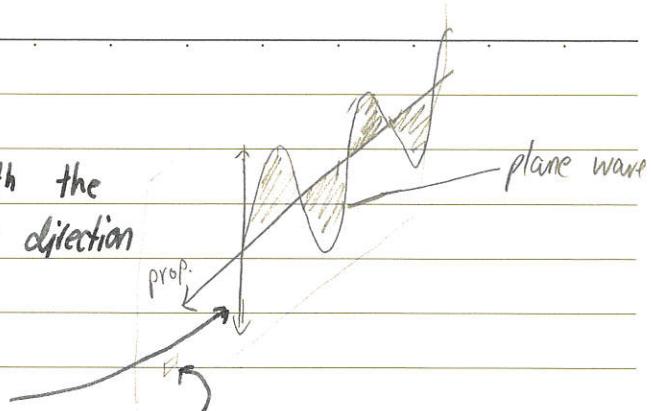
$$\text{then } \langle \cos^2 \theta \rangle = \frac{\int_0^{\pi/2} \cos^2 \theta \cdot 2\pi R^2 \sin \theta d\theta}{2\pi R^2} = \frac{1}{3}$$



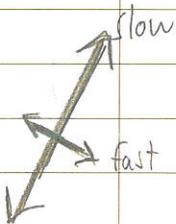
Surface area of hemisphere.

Polarised light

- Light is a transverse EM wave with the E field oscillating orthogonal to the direction of propagation
 - the direction of polarisation is the vibration axis of the E field
 - the plane of polarisation contains the directions of prop. and polarisation



EM waves incident on a single polymer molecule will couple strongly in one direction (not necessarily the long axis) and weakly through the perp. direction.



- in an isotropic polymer sample (e.g. high temp), there will be no effect on polarisation.
- but in a nematic LC there will be a direction with strong coupling (slow axis) and a direction with weak coupling (fast axis)
- these permitted vibration directions (PVDs) are the only axes on which the transverse E field can oscillate.
- Because the speed of light is different for each PVD, the refractive index is different. The birefringence is the difference between the refractive indices : $\Delta n = n_1 - n_2$

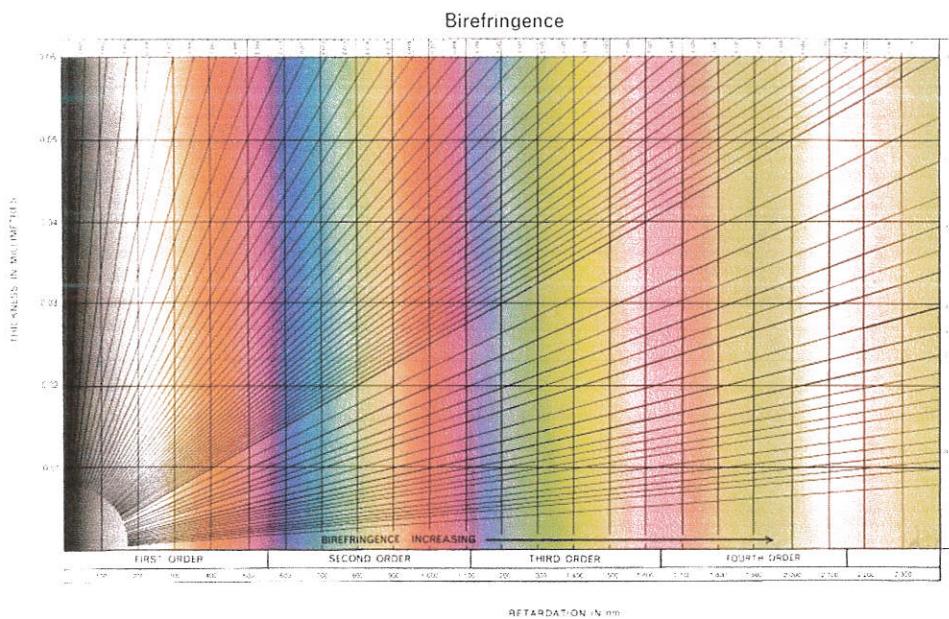
• Polarised materials (polaroids) are made from polymers with such strong coupling along the director that only light vibrating perpendicular can be transmitted.

- When polarised light is incident on a birefringent material, it is split into a component for each PVD.
 - because of birefringence, there is an optical path difference when they come out the other side
 - if the thickness is t: $O.P.D = \Delta n \cdot t$

- The phase difference δ is then given by

$$\frac{\delta}{2\pi} = \frac{\Delta n \cdot t}{\lambda} - \text{wavelength in free space.}$$

- Birefringent materials can rotate the plane of polarisation because of this phase difference
 - if $o.p.d = \lambda/2$ (i.e. $\delta = \pi$), the resulting plane of pol. will be perpendicular to the original
 - ↳ light will be transmitted even through crossed polars.
 - if $\delta = 2\pi$, the plane of pol. will be rotated 360° back to the original so no light through crossed polars.
- If a birefringent sample is illuminated with polychromatic light, one wavelength will be lost (λ for which $\delta = 2\pi$).
 - ↳ we will observe the complementary colour.



- The Michel-Levy chart shows the complementary spectrum for increasing birefringence. retardation (o.p.d) which is affected by birefringence and thickness
- On the far left, there is little retardation so light is not transmitted.
- Moving across, there are higher order colours as $o.p.d = \lambda, 2\lambda, 3\lambda \dots$
- For high retardations, several wavelengths are lost as $o.p.d = 2\lambda, 3\lambda \dots$ so the colours become more washed out.

- If a quartz wedge is placed between crossed polars, it will display the M-L chart because it is a material with constant Δn but increasing thickness.

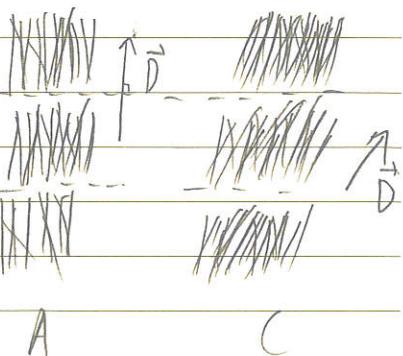
Extinction positions

- If incident light has its plane of pol. parallel to a PVD, there will be no component in the direction of the other PVD.
 ↳ no phase diff \Rightarrow no rotation \Rightarrow extinction between X polars.
- Thus the PVDs can be determined by rotating a sample between X polars: max intensity when PVDs at 45° .
- Which PVD is fast/slow (i.e. the sign of the birefringence) can be determined by adding a compensator, an anisotropic sample e.g. Quartz with known Δn , on top of the sample both at 45° .
 - ↳ ADDITION: higher colour \Leftrightarrow o.p.d increase \Leftrightarrow fast directions parallel
 - ↳ SUBTRACTION: lower colour \Leftrightarrow o.p.d decrease \Leftrightarrow fast directions antiparallel
- In an LC, PVDs will be aligned with the director.
- But a nematic LC sample may not have a uniform director: domains with different orientations.
- There will be disclinations where domains meet, forming a schlieren texture between X polars.
- Dark whenever the director aligns with the polariser or analyser.
- Also dark if director is parallel to light path, because an LC is isotropic along the optic axis

$\begin{matrix} \circ & \circ & \circ & \circ \\ \circ & \circ & \circ & \circ \end{matrix}$ Looking along
the Director.

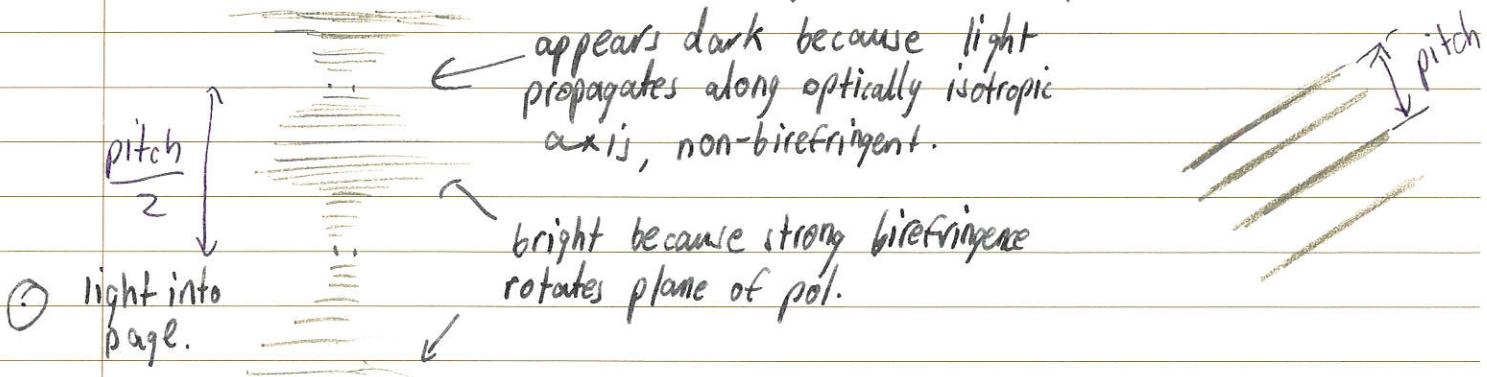
Smectic LCs

- Smectic LCs have some overall positional order, with molecules organising into layers.
- No pos. order within layers
- Smectic A: director parallel to layer normal
- Smectic C: director nonparallel to layer normal



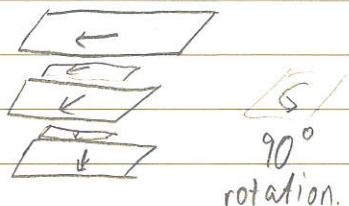
Chiral Nematic LCs

- Molecules in a chiral nematic (cholesteric) LC have their director in a plane, which rotates along the axis perpendicular to the plane to trace out a helix.
- Polarised light propagating along this axis will have its plane of pol. rotate with the director.
- The pitch is the distance required for \vec{D} to rotate 360° .
- Generally, higher temperatures lead to more twisting so pitch is reduced.
- The twisted structure occurs because the molecules are chiral (e.g asymmetric α -helix), leading to a twisting alignment.
↳ shorter molecules tend to be more strongly asymmetric, thus have more twist and lower pitch.
- Observing a chiral nematic LC between crossed polars (with light perp. to the axis of the helix) gives a stripy pattern

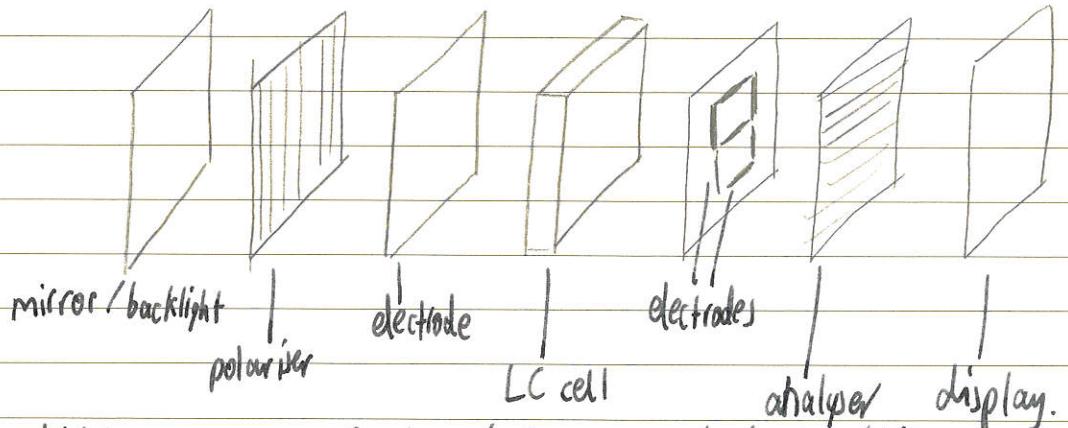


LCDs

- The director of an LC can be encouraged to lie along a direction using a grooved surface.
- Sandwiching an LC between 2 plates with 1 groove leads to a precise twisted nematic structure. Normally requires addition of a chiral nematic dopant.



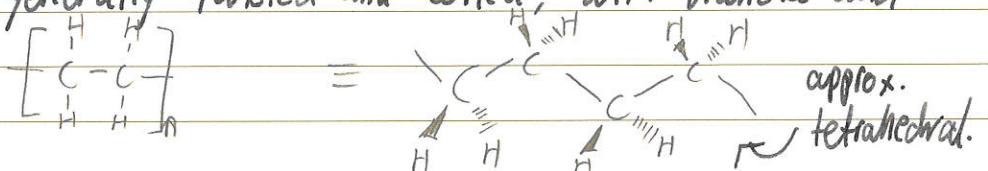
- When viewed between crossed polars (along the axis of rotation), sample will be bright because the twisted nematic structure rotates the plane of pol. by 90° .
 ↳ this is the ON state for an LC cell.
- Applying an \vec{E} field causes the molecules to align normal to the grooved plates, in the Freedericksz transition
 - ↳ molecules near grooves stay aligned, but the rest become parallel to the \vec{E} field
 - ↳ optically isotropic \Rightarrow no rotation \Rightarrow dark cell
 - ↳ this is the OFF state.



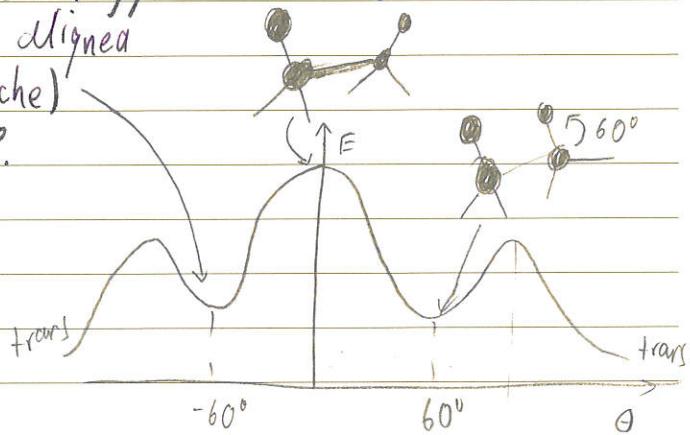
- Light enters from front and is reflected by ~~backlight~~ mirror.
- By default, plane of pol. twisted by LC so everything bright.
- When a p.d. is applied across the electrode plate and a shaped electrode (all transparent), light is blocked and an image appears.
- Colour LCD can be made with backlighting and colour filters to make RGB sub-pixels.

Polymers

- Polymers are macromolecules made from long chains of monomers.
- The chains are generally twisted and coiled, with branches and cross-linking.

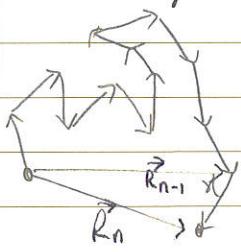


- Rotation about the C-C bond leads to changes in conformation
 - lowest energy when C-C bonds staggered (*trans*)
 - highest energy when C-C bonds aligned
 - intermediate conformations (*gauche*) with bonds misaligned by 60° .
- In reality, a molecule will have many different conformations.
- Increasing temp allows for more conformational change (can climb the energy barrier)
 - ↳ polymers become more flexible when heated.



Size of polymer molecules

- A polymer molecule can be modeled as a random walk of n segments of length l (i.e. assume free rotation)
- the length is then the root mean square of the end-end vector \vec{R}_n .



$$\vec{R}_n = \sum_{i=1}^n \vec{r}_i \quad \text{and} \quad \vec{R}_n = \vec{R}_{n-1} + \vec{r}_n$$

$$|\vec{R}_n|^2 = (\vec{R}_{n-1} + \vec{r}_n) \cdot (\vec{R}_{n-1} + \vec{r}_n) = \vec{R}_{n-1}^2 + 2\vec{R}_{n-1} \cdot \vec{r}_n + \vec{r}_n^2$$

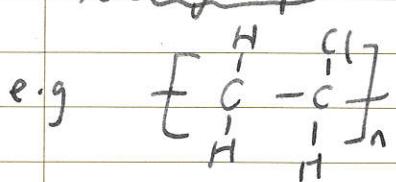
$$\therefore \langle R_n^2 \rangle = \langle R_{n-1}^2 \rangle + l^2 \quad \text{since } \langle \vec{r}_n \cdot \vec{R}_{n-1} \rangle = 0$$

By induction, $\langle R_n^2 \rangle = n l^2$

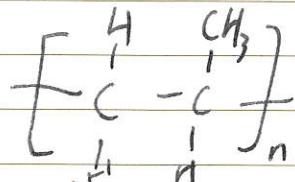
$$\therefore \text{RMS : } \langle R^2 \rangle^{1/2} = l \sqrt{n}$$

- Because of steric hindrance, real polymer chains have some stiffness. We can improve the model by redefining l as the length scale below which the chain is straight and rigid (rather than the monomer length). Must reduce n accordingly.
- This is the Kuhn length, and is sometimes written as $K \times c$ -c length. Higher K means stiffer.

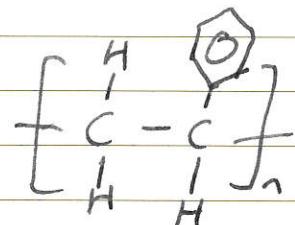
Side groups



PVC

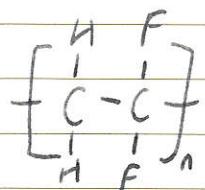


polypropylene



polystyrene

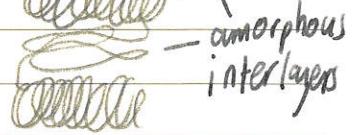
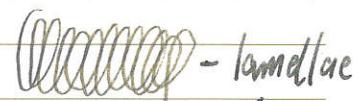
- The molecule's configuration/tacticity refers to the arrangement of the side groups along the chain.
 - Isotactic - side group always on the same side
 - Syndiotactic - side group on alternate sides
 - Atactic - side groups distributed randomly.
- These affect charge distribution. In an extreme case like polyvinylidene fluoride (PVDF), the charge imbalance leads to important properties.



Polymer microstructure

- At higher temperatures, chains can flex, coil, slide. As temp lowers, there is less conformational change and less space for movement, so viscosity increases until the glass temperature is reached.
- A rubber is a cross-linked polymer: chain segments can undergo conformational change but cannot slide past each other to give permanent shape changes.
- Plasticisers are small molecule additives which space out the chains and increase mobility.

- Polymers can exist in a partially crystalline form when chains fold and pack into a regular structure.
- Alternates between crystalline layers called lamellae and amorphous regions.
- The relative thickness of the layers defines the percentage crystallinity of such a polymer.
- Crystallisation is easier for polymers with very regular chains (e.g. isotactic/syndiotactic); bulky side groups or atacticity hinder packing.
- Highly crystalline polymers are stiffer or more brittle, and generally more opaque because of light scattering between layers.

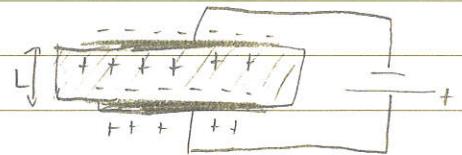


Electrical Polarisation

- A dielectric is an insulator that is electrically polarisable.
- Polarisation occurs by the creation of electric dipoles (i.e charge sep.):
 - electronic pol.: distortion of electron cloud when \vec{E} field applied
 - ionic: elastic distortion of ionic bonds
 - orientational/molecular: rotation of pre-existing permanent dipole moments, especially common in polar liquids
- For equal but opposite charges separated by \vec{r} , the dipole moment is defined by: $\vec{\mu} = q \vec{r}$ 
- The polarisation is the dipole moment per unit volume $\vec{P} = n \vec{\mu}$ ($C m^{-2}$), where n = no. of dipoles per unit volume.
- Alternatively, it is the charge per unit surface area: $\rho = Q/A$.
- When an \vec{E} field is applied to a dielectric, a charge density \vec{D} will develop, with a magnitude depending on the material's permittivity ϵ .
$$\vec{D} = \epsilon \vec{E} = K \epsilon_0 \vec{E} \quad K = \frac{\epsilon}{\epsilon_0}$$
 is the Dielectric Constant of the material
- We can consider \vec{D} (a.k.a displacement field) to be made from 2 components: free space and the polarisation of the material i.e $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$
- Equating this to the previous result gives \vec{P} in terms of \vec{E} and K
$$\vec{P} = \vec{D} - \epsilon_0 \vec{E} = \{\epsilon_0 \vec{E} (K-1)\}$$
- A capacitor stores charge. The capacitance is defined as $C = \frac{Q}{V}$.
- For an empty parallel-plate cap.
 - ↪ charge density between plates is $\epsilon_0 E$, so $Q = \epsilon_0 E A$ — area of plate
 - ↪ if plates separated by distance L , $V = EL$
- $\therefore C = \frac{Q}{V} = \frac{\epsilon_0 EA}{EL} \Rightarrow C = \frac{\epsilon_0 A}{L}$

- With a dielectric, there is a higher charge density so more charge on the plates

$$D = \epsilon_0 E + P \rightarrow Q' = (\epsilon_0 E + P) A = \epsilon_0 K A$$



$$C' = \epsilon_0 K \frac{A}{L}$$

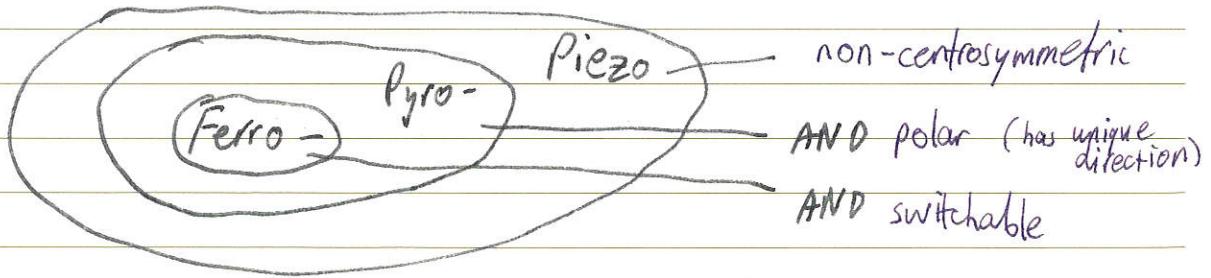
- Thus a dielectric increases capacitance:

- when battery connected, V constant but $Q \uparrow$, so $C \uparrow$
- when disconnected, Q constant but $E \downarrow$ and $V \downarrow$, so $C \uparrow$.

- Though we model dielectrics as the constant of proportionality in a linear relationship between \vec{P} and \vec{E} , for very high fields the dielectric may allow current to flow: dielectric breakdown. The maximum field that can be sustained is the dielectric strength.

Dipole formation & symmetry

- If a crystal is centrosymmetric (has a centre of symmetry), then any line through the centre will connect equivalent faces/atoms.
- A unique direction is a lattice vector which is not repeated by the present symmetry.
- centrosymmetric crystals have no unique direction, so there cannot be a net electric dipole without an external E field.
- Non-centrosymmetric crystals do not necessarily have a unique direction, e.g sphalerite (ZnS).
- A polar material, which can demonstrate dielectric polarisation, must have a unique direction.
- Electrical properties depend on this asymmetry



Piezoelectrics

- Piezoelectricity is the change in polarisation on application of stress

$$\{ P = d\sigma \}$$

$d \equiv$ piezoelectric coefficient $C N^{-1}$

$\sigma \equiv$ stress (tension or compression) $N m^{-2}$

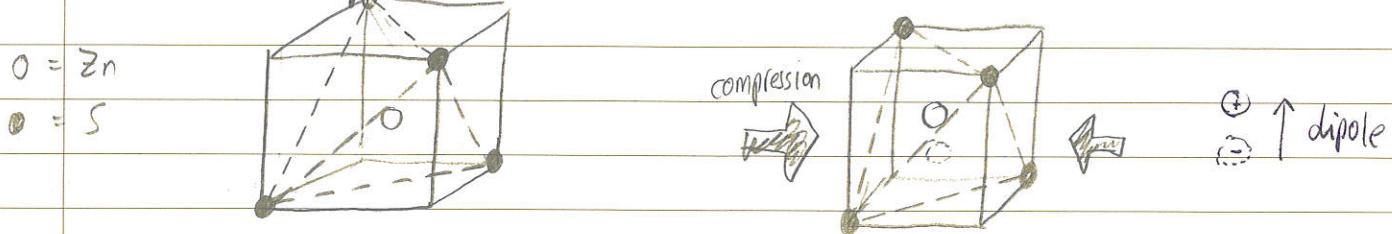
$$P = \frac{Q}{A} = \frac{CV}{A} = \frac{\epsilon_0 K V}{L} \quad \therefore$$

$$\{ V = \frac{d\sigma L}{K\epsilon_0} \}$$

RESULTANT
VOLTAGE

(not applied).

- sphalerite
- Quartz and crystals containing tetrahedral groups, e.g. ZnS are piezoelectric because stress distorts the tetrahedron



- the centre of mass (and charge centre) of the S^{2-} ions doesn't move during compression
- but the Zn^{2+} ion moves to maintain equal bond lengths
- generator effect: stress changes P and leads to voltage
- e.g. igniters: pressure induces $\sim kV$ which causes dielectric breakdown across an air gap ($\sim 1\text{mm}$).
- The motor effect is when applying an E field leads to a structural change in a piezoelectric, e.g. watches.

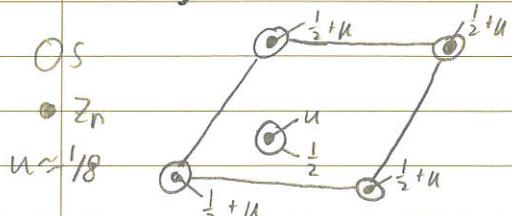
Pyroelectrics

- Pyroelectricity is the change in polarisation due to a change in temp.
- Adsorption of polar impurities masks the true surface polarisation, so we measure ΔP :

$$\Delta P = p \Delta T \Rightarrow \Delta V = \frac{p \Delta T L}{K\epsilon_0}$$

where $p \equiv$ pyroelectric coefficient $C m^{-2} K^{-1}$

- e.g. in Hex P ZnS (wurtzite):

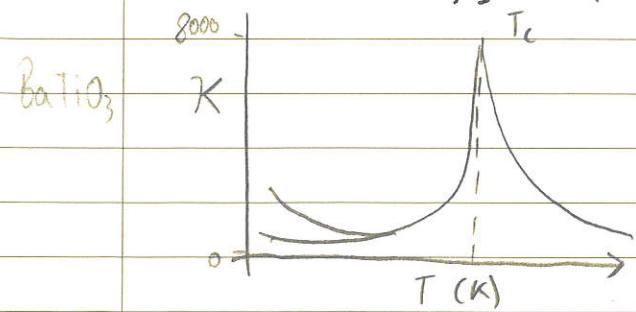


- non ideal σ/α
 - only upward-pointing tetrahedra are filled
 - [001] is a unique direction

- Can be applied in burglar alarms (or IR detectors)

- one sample behind IR filter/reflector, another exposed.
 - voltage difference between both must be due to IR
 - used to isolate the ~60W of IR from a burglar.

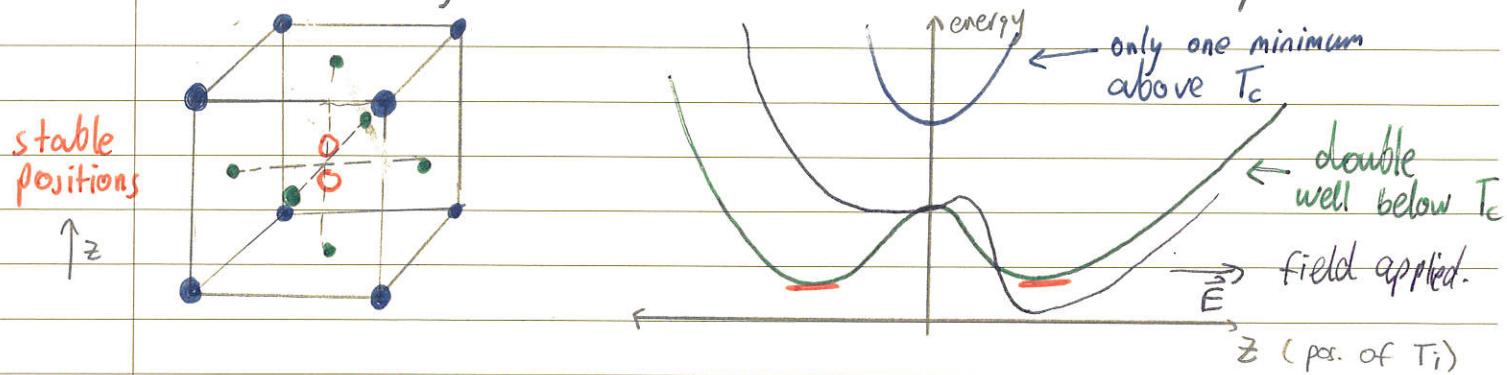
Ferroelectrics



- at the peak, the central ion can easily move, hence easy to induce dipole.
 - = two K values because tetragonal phase is electrically anisotropic.

- Impurities or dopants can lead to significant variations in dielectric properties.

- Ferroelectricity occurs when ions sit in double-well potentials



- (below T_c)
- in the absence of an E field, both **stable minima** are equally likely.
 - when E applied, one minimum will be much more favourable
 - ion will remain in that position once the field is removed.

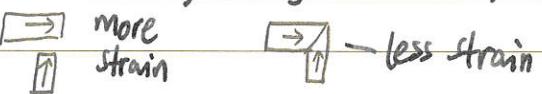
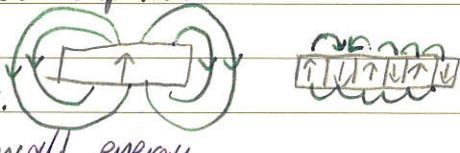
- A domain is a local region with aligned dipoles.

- Stray fields have an energy cost, which encourages differently-oriented domains.

- But this must compromise with domain wall energy.

↳ depends on orientation: can be polarised along any $\langle 100 \rangle$.

↳ tend to form at oblique angles



- The polarisation of a FE can be switched with an E field.

↳ cycling E field leads to hysteresis loop

- Unpolarised, randomly oriented. Behaves like a linear dielectric for very small E .

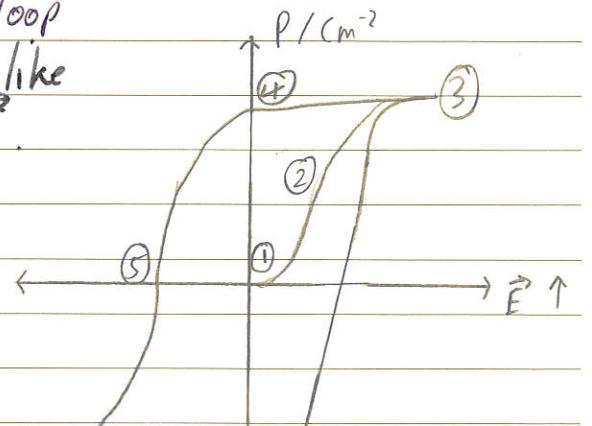
- Favourably aligned domains grow

- Saturation polarisation (P_{sat}): one aligned domain in sample.

- Even with zero field, there is a remnant polarisation P_r

- As field is reversed, opposite domains nucleate and grow. The field required to return to $P=0$ is the coercive field E_c

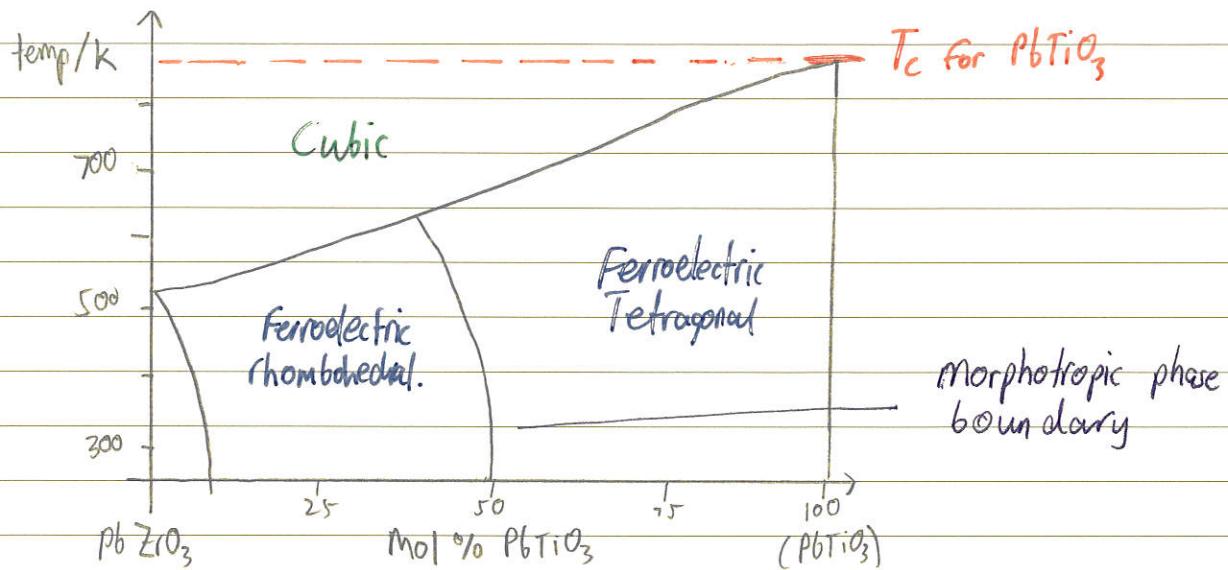
- Saturation in opposite direction.



$\text{Energy} \propto \text{area}$
 crystal defects may result in domain walls being pinned \Rightarrow higher E_c

Applying ferroelectrics

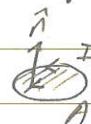
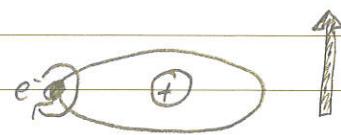
- Often, FE properties ignored and they are just used as dielectrics, e.g. BaTiO_3 has high K values and is used for camera flash capacitors.
- Switchable states can be used in FE-RAM - non-volatile, low voltage, radiation hard.
↳ needs high P_{sat} and P_r , high K and low E_c , high T_c .
- The materials are fabricated as thin films to minimize switching voltage: film e.g. 10-300nm, switch takes ~ 50 ns.
- During the switch, heat is given off.
- One of the most widely used for piezoelectrics is PZT - $\text{Pb}(\text{Zr}_{x_c}\text{Ti}_{1-x_c})\text{O}_3$.
 - Zr/Ti ions occupy the perovskite B site.
 - properties changed by varying x_c .



Along the morphotropic phase boundary, polarisation states can form along the 6 possible $\langle 100 \rangle$ tetragonal distortions OR the 8 possible $\langle 111 \rangle$ rhombohedral distortions.
 ↳ 14 possible orientations \Rightarrow easy to pole and switch.

Magnetic materials

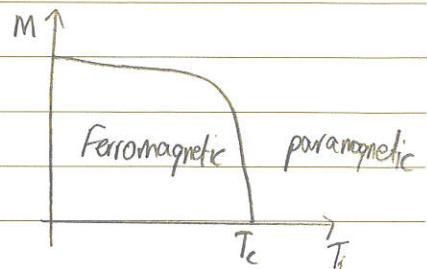
- Magnetic moments are produced by spinning electrons orbiting the nucleus.
 - The net magnetisation of a material depends on the strength and alignment of individual moments
 - depends on valence electrons because e^- pairs in complete shells have opposite spin.
 - The magnetic moment on a current loop: $\vec{M} = IA\hat{n}$
 - The magnetisation M is the magnetic moment per unit volume, $A\text{m}^2 \text{ per m}^3$ i.e Am^{-1} .
- $$M = \chi H \quad \chi \equiv \text{susceptibility (dimensionless).}$$
- $$H \equiv \text{magnetic field } (\text{A m}^{-1})$$



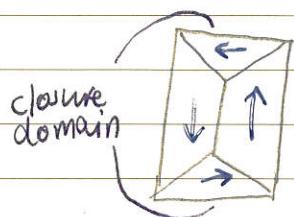
- Diamagnetism: shells filled, so no unpaired e^- and no net moment in the absence of a field. When an external mag. field is applied, electron orbits move to oppose flux, developing an opposite moment i.e χ is negative e.g $\sim -10^{-5}$ (noble gases, graphite).
- Paramagnetism: some unpaired e^- so dipoles exist, but are non-interacting and randomly oriented. No overall moment when $H=0$.
 - when $H > 0$, there is partial alignment of moments
 - χ is positive but small e.g $\sim 10^5$ (most metals).
- Ferromagnetism: many unpaired e^- . Because of QM effects (the exchange interaction), moments tend to align and there is long range magnetic order.
 - χ large, e.g 5×10^3 for Fe
 - moments remain aligned even with no external field.
- Antiferromagnetism: many moments, but they interact such that an anti parallel arrangement is most favourable. No net dipole. e.g Cr
- Ferrimagnetism: a material with two ferromagnetic sublattices oppositely oriented \Rightarrow net magnetisation
 - behaves like ferromagnet with low susceptibility ($\chi \approx 0.1$)
 - e.g magnetite (Fe_3O_4).

Ferromagnetic materials

- Above the Curie temp, thermal agitation overcomes the exchange interaction because of the phase transition.
- χ becomes large when $T \rightarrow T_c$, as the magnetic moment can easily be changed.

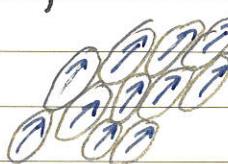


- The preferred direction of the magnetic moment depends on the crystal. Magnetocrystalline anisotropy means that there will be easy and hard crystallographic axes (but hard to know a priori).
- Because stray fields have an energy cost, magnetic domains form
- One consequence of this is shape anisotropy: lower energy for magnetisation to lie along the length of a long thin sample.



LOWER ENERGY →

HIGHER ENERGY

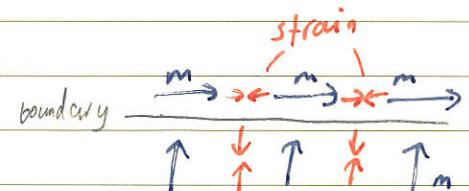


e.g. the elongated grains in a polycrystalline sample may result in strong directional magnetisation.

- On magnetisation, a crystal experiences strain and will change dimensions.
↳ the magnetostriction coefficient λ is the fractional change in length (in a particular direction) as magnetisation goes from zero to saturation.

may

- Because neighbouring domains have different dimensional changes, there is high strain at the boundary; elastic strain energy stored.

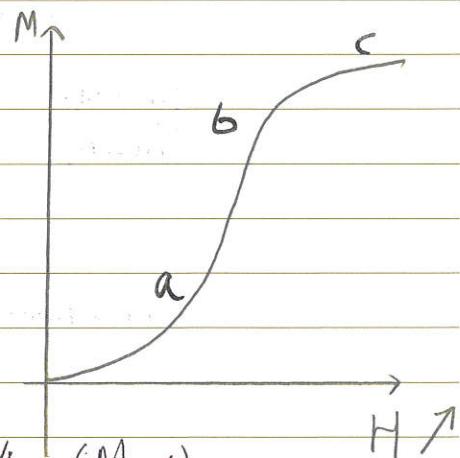


- The width of a domain wall / Bloch wall is a compromise between:
 - exchange interaction energy → wants wide walls with gradual twist of moments
 - magnetocrystalline/anisotropy energy → wants abrupt walls so moments align with easy axis.
- The exact value depends on material properties. Typically 5-100 nm.

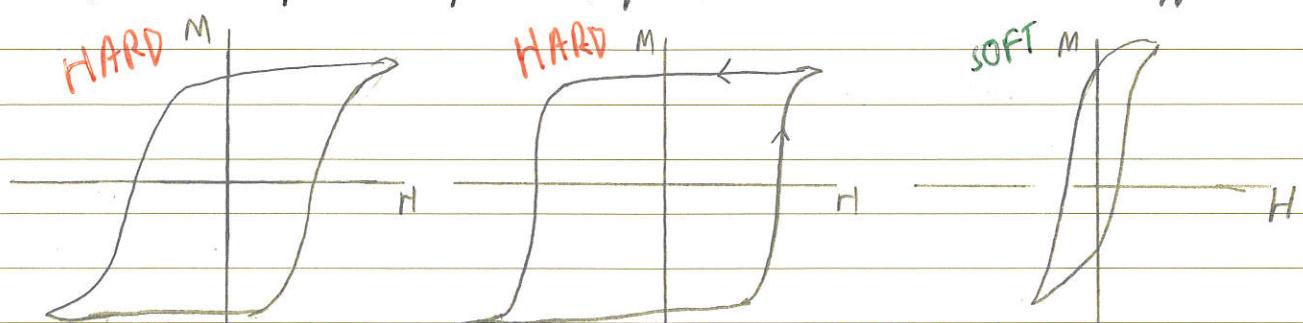
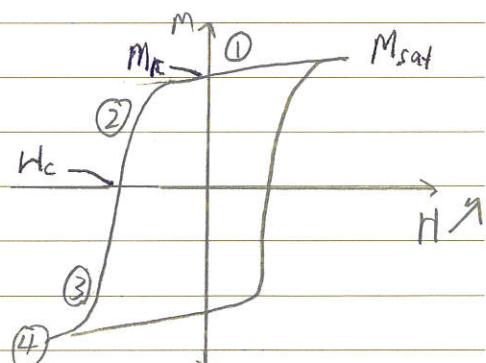
- A domain structure won't form in a small particle/grain if the wall energy > stray field. For a small enough grain, it will have one domain.
 \hookrightarrow stray fields $\propto r^3$, domain wall energy $\propto r^2$

Ferromagnetic hysteresis

- When a field is applied:
 - favouredly oriented domains (which lie on easy axes) grow by wall motion. This is irreversible, because of pinning imperfections.
 - The whole sample is aligned along the easy axis closest to H's direction.
 - Moment aligns with H : saturation magnetisation (M_{sat})



- Cycling the field produces hysteresis:
 - Moment relaxes to easy crystallographic axis but remains stable as $H \downarrow$: remanent magnetisation. H_c
 - As $H \downarrow$, the roughly parallel domains grow.
 - Single domain along easy axis
 - Moment rotates to align with H.
 - area within loop \propto energy dissipated (i.e. 2x switch energy).
 - Impurities pin domain walls \Rightarrow increased coercive field.
 - Different shapes of hysteresis loop are desirable for different applications



Permanent magnets:

- Need high, stable mag.
- Large M_r and H_c

Memory devices

- Need well-defined switch
- i.e. very steep around H_c

Transformer cores:

- Easy switching
- High M_{sat} , low H_c .

- To make **SOFT** magnetic materials, we need to remove imperfections that would pin domain walls
 - ↪ use annealing to form 'perfect' crystals, or use very homogeneous materials ($H_c \sim 3 \text{ Am}^{-1}$)
- To make **HARD** magnetic materials, incorporate imperfections by:
 - quenching, which doesn't allow grains to reorganise during cooling.
 - sintering → compressing fine powders to have many particles ($H_c \sim 10^6$)

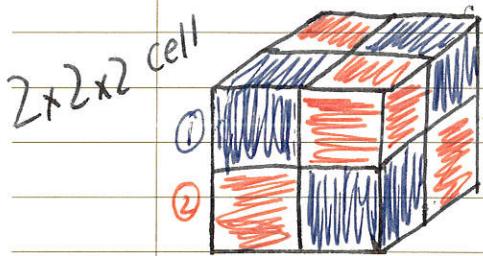
In practice, we don't measure M , we measure the magnetic flux density B (a.k.a. inductance). It has units of Tesla.

$$B = \mu H = \mu_0(H+M) = \mu_0 H(1+\chi)$$

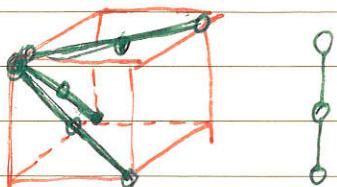
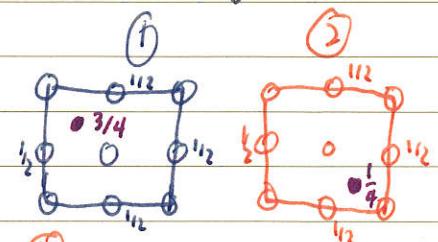
$\mu \equiv$ permeability
 $\mu_0 \equiv$ permeability of free space (H m^{-1})

Ferrimagnetism

- The Spinel structure consists of (almost) CCP oxygen ions with two cation sites, $A\text{B}_2\text{O}_4$ with A^{2+} and B^{3+}



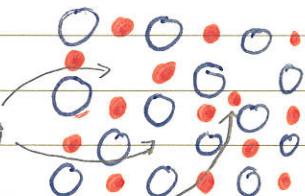
- $\frac{1}{8}$ tetrahedral interstices occupied by ①
- $\frac{2}{4}$ octahedral interstices occupied by ②, only in ②.
- tetrahedra unconnected, pointing opposite directions



- In the Inverse Spinel Structure, we have $A(\text{AB})\text{O}_4$.
- e.g. in Fe_3O_4 (magnetite), $A \equiv \text{Fe}^{3+}$, $B \equiv \text{Fe}^{2+}$.
 - spin moments of Fe^{3+} on A sites cancel with B sites
 - the remaining Fe^{2+} moments align, resulting in a net moment.
 - thus, Fe_3O_4 is ferrimagnetic.

Solid Ionic Conductors

- Ceramics are compounds of metallic cations with non-metallic anions, e.g. metal oxides. They generally have high melting points and low electrical conductivity.
- Ionic lattices tend to have imperfections
 - Shottky defect: one pair of cation/anion missing
 - Frenkel defect: cation moves into interstice
- These defects mean that ions can move through the lattice, leading to ionic conduction. This can happen because of:
 - a concentration gradient of ions or vacancies, i.e. a diffusion current
 - an external electric field, causing a drift current.
- Mobility depends on the number of vacant sites as well as the energy barrier between lattice sites.



Ionic currents

- The atomic/ionic flux J is the no. of atoms crossing a unit area per second.
- For steady state diffusion in a uniform 1D conc. gradient:

$$J = -D \frac{\partial n}{\partial x} \quad D \equiv \text{diffusivity } (\text{m}^2 \text{s}^{-1})$$

$\frac{\partial n}{\partial x} \equiv \text{conc. gradient } (\text{m}^{-4})$

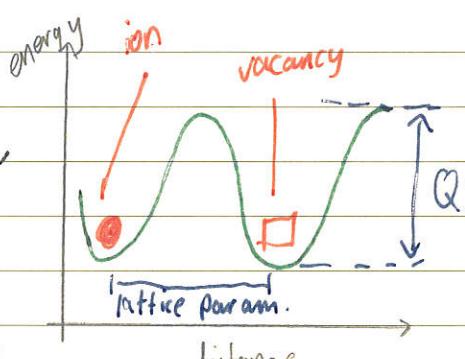
- We can then find the diffusion current density j .

$$j = -q D \frac{\partial n}{\partial x} \quad (\text{A m}^{-2})$$

- The diffusivity depends on the probability that an atom/ion can overcome the activation energy Q , given by the Arrhenius equation

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad \text{or} \quad D = D_0 \exp\left(-\frac{Q}{kT}\right)$$

if Q is given in J mol^{-1} if Q is J atom^{-1}



- This can be found empirically by linearising and plotting:

$$\ln D = \ln D_0 - \frac{Q}{RT}$$

- When an E field is applied, the activation energy is reduced in one direction.

- The drift current density depends on the field and the conductivity σ ($\Omega^{-1} m^{-1}$)

$$j = -\sigma \frac{\partial V}{\partial x} = \sigma \vec{E} \quad (\text{movement of +ve charge}).$$

- The number of diffusing ions in an electric potential follows a Boltzmann statistic: $n = n_0 \exp(-qV/kT)$.

$$\frac{\partial n}{\partial x} = \frac{\partial n}{\partial V} \frac{\partial V}{\partial x} = -\frac{nq}{kT} \frac{\partial V}{\partial x} = \frac{nq \vec{E}}{kT} \rightarrow \vec{E} \text{ field} \Rightarrow \text{conc gradient}$$

- But in a steady state equilibrium, no ions escape so the diffusion current must balance the drift current: $j_{\text{diff}} + j_{\text{drift}} = 0$.

$$\therefore qD \frac{\partial n}{\partial x} = \sigma \vec{E} \rightarrow qD \left(\frac{nq \vec{E}}{kT} \right) = \sigma E$$

Leads to the Nernst-Einstein equation

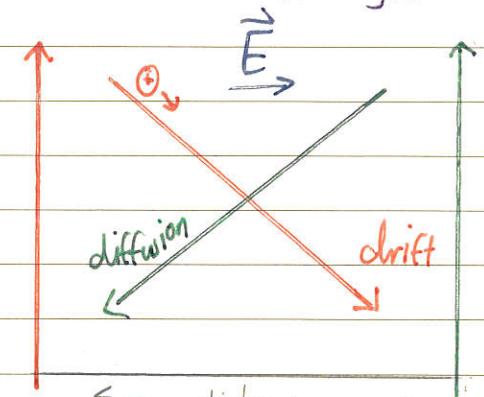
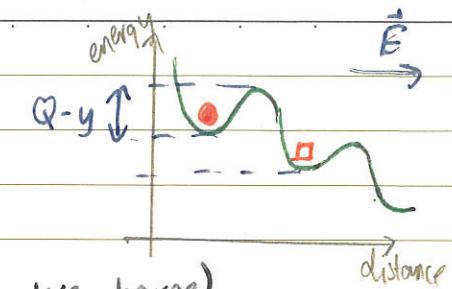
both Temp.
dependent. $\approx \frac{\sigma}{D} = \frac{nq^2}{kT}$

- We can use this to find a relationship between σ and temperature:

$$\sigma = \frac{Dnq^2}{kT} = \frac{q^2}{kT} \left[D_0 \exp\left(-\frac{q}{kT}\right) \right] \left[n_0 \exp\left(-\frac{qV}{kT}\right) \right].$$

oversimplification

$$\therefore \ln \sigma = \ln \sigma_0 - \left(\frac{q}{k} \right) \frac{1}{T}, \text{ assuming } \underbrace{\sigma_0 = \frac{D_0 n_0 q^2}{kT}}_{\approx \text{constant}} \simeq \text{constant}$$

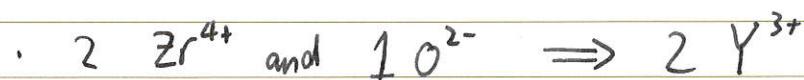
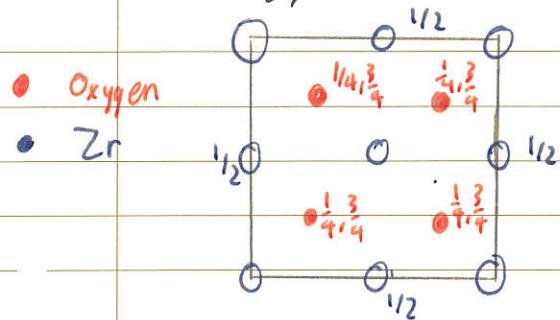


\leftarrow distance \rightarrow

\approx no when \vec{E} small and $qV \ll kT$.

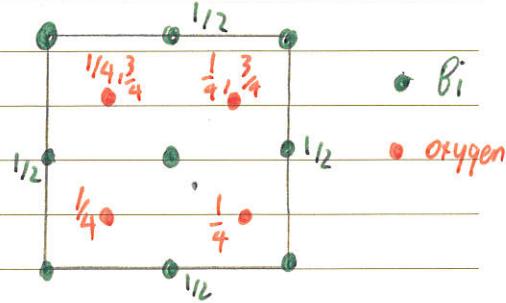
Applications of solid ionic conductors

- The ideal ionic conductor will have many vacancies & defects
- Yttrium-Stabilised Zirconia (YSZ) is made by doping ZrO_2 with Y_2O_3 , which creates oxygen vacancies.



The doping also leads to a stable cubic fluorite structure, i.e. fcc Zr with O^{2-} ions in most tetrahedral interstices.

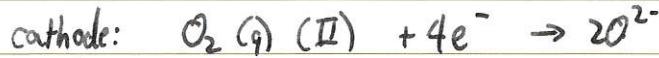
- $S-Bi_2O_3$ is another common choice. It has the fluorite structure with two formula units per unit cell



- Thus there are 2 O^{2-} vacancies, which creates a fast-ion channel
- In general, these ionic conductors can replace electrolytes whenever the transferred ion is O^{2-} .

e.g. Oxygen concentration cell

- Monitors O_2 conc: if reference $pO_2 < \text{test } pO_2$, there will be diffusion and redox



- Electrodes are made of porous platinum (catalyst)



- We can use the electrochemical formula to find the potential:

moles of e^- produced

$$E = -\frac{RT}{nF} \ln \frac{\prod_i (\text{activity of product } i)^{x_i}}{\prod_i (\text{activity of reactant } i)^{y_i}}$$

molar ratios

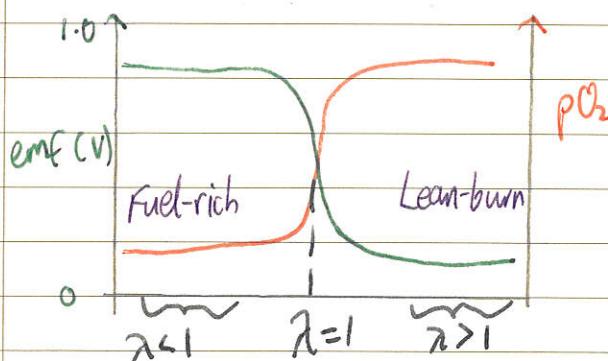
in this case, $E = -\frac{RT}{4F} \ln \frac{pO_2(I)}{pO_2(II)}$

- This is used in a Lambda sensor in car exhausts, measuring the O₂ conc in exhaust gas.

- a heating implement maintains constant conductivity for the YSZ

- the potential feeds into the fuel-injection system.

- The ideal air-to-fuel ratio (by weight) for complete combustion is 14.6. Defining $\lambda = \text{measured ratio}/14.6$, we can plot:



- When pO₂ high, $\lambda > 1$, so fuel should be added

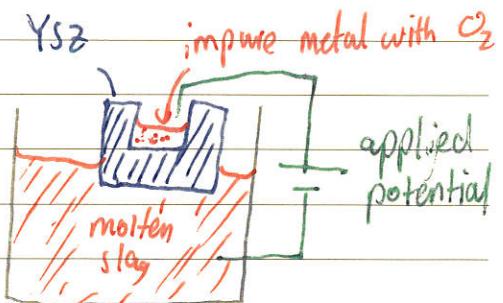
- When pO₂ low, $\lambda < 1$ so air should be added.

- Aiming for $\lambda = 1$.

e.g. Oxygen pump

- To purify some metal, we can place it in a YSZ container in molten slag and apply a p.d.

- This drives O²⁻ ions from the metal to the slag, purifying it.



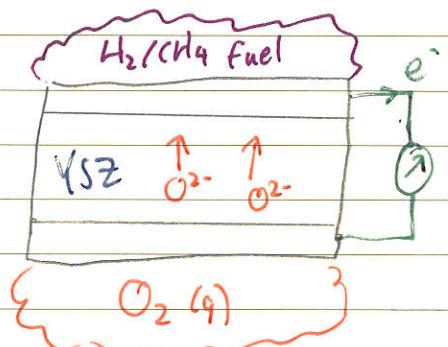
e.g. Fuel cell

- Fuel cells convert chemical energy directly into electrical energy.

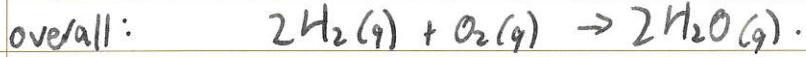
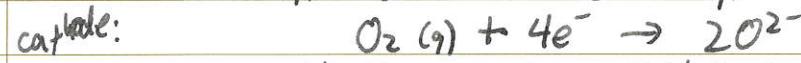
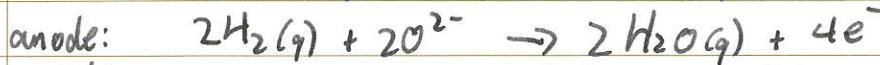
- The fuel is H₂ or CH₄, which is oxidised to produce a flow of electrons.

- The advantages of a fuel cell are:

- high efficiency compared to internal combustion engine
- noiseless
- 'clean', i.e. no NO_x or CO.

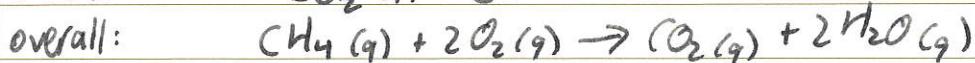


- Using H₂ fuel:



$$E = -\frac{RT}{4F} \ln \frac{(p_{H_2O})^2}{(p_{H_2})^2 p_{O_2}}$$

- Using CH₄ fuel:



$$E = -\frac{RT}{8F} \ln \frac{p_{CO_2}(p_{H_2O})^2}{(p_{CH_4})(p_{O_2})^2}$$

- The YSZ electrolyte needs high temperatures to be effective (1000K).

↳ this is a challenge because the anode operates in an ~~oxidise~~ a highly reducing env, and the cathode in a highly oxidising env.

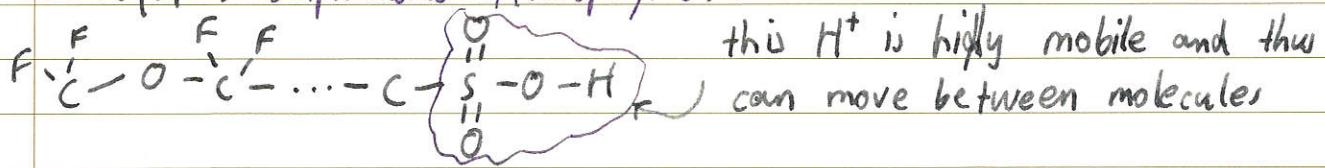
- The anode is often a conducting ceramic (porous).

- The cathode is often doped porous manganite (doesn't oxidise).

e.g. Polymer Electrolyte Membrane fuel cells

- Because a YSZ fuel cell presents many challenges, PEM fuel cells have been developed, which conduct protons instead of O²⁻.

- Requires sulphonated fluoropolymers:



- These have much lower running temps (80°C) but require expensive Pt-based catalysts.

