Lecture 4 - Dielectrics

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Lecture Summary

- Origin of ionic polarisation
- Capacitor operation and definitions
- Impedance spectroscopy
    - definitions
    - ideal responses
- piezoelectricity
- ferroelectricity

Introduction

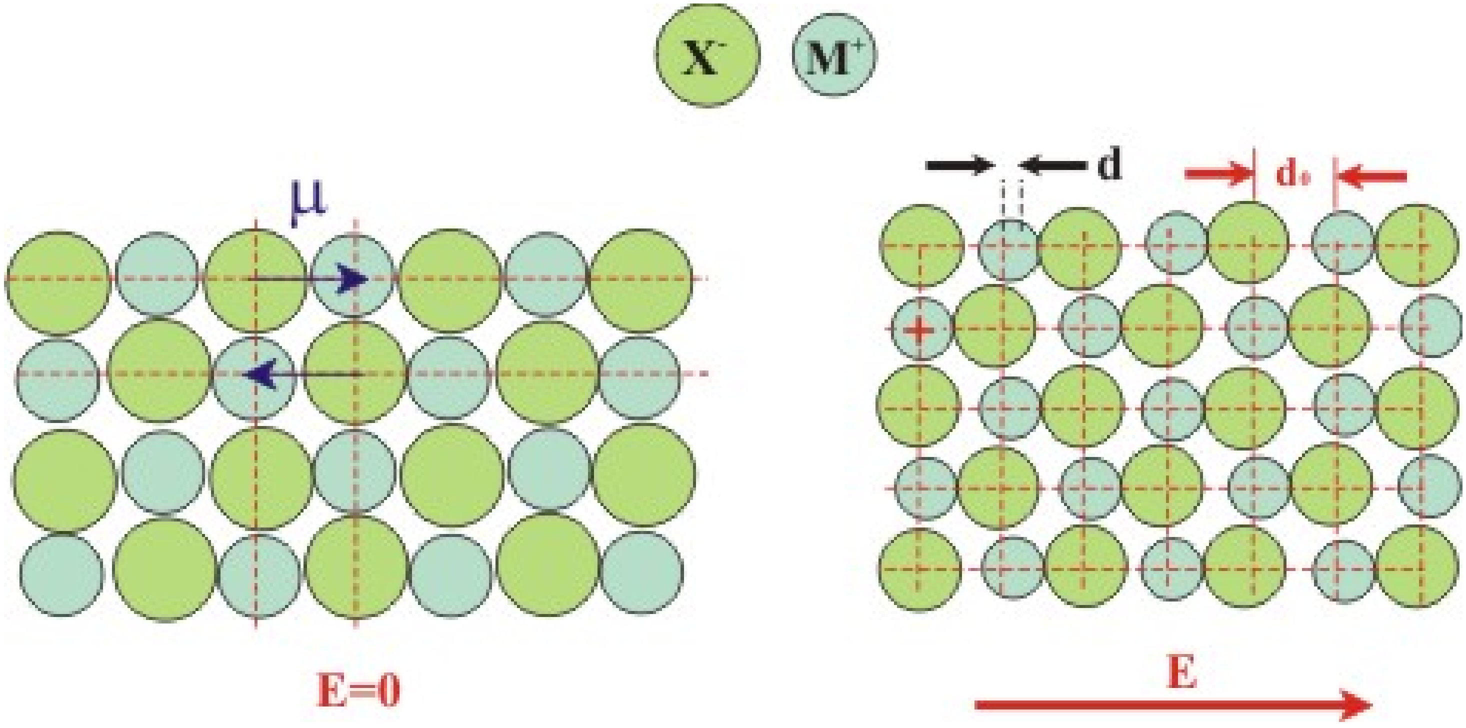
- Ionic conduction is a long-range effect
  - Important in batteries, fuel cells etc.
- In some situations, a highly insulating material is preferred
- Remember, ions are not static with time (e.g. phonons)
  - Short-range atomic motion is important for electrical properties

Polarisation

Ionic solids are made up of cations and anions

- locally, this creates dipoles (μ)
- across a whole crystal at equilibrium, these dipoles normally cancel

Under an applied electric field, ions displace from equilibrium



Is this useful?

If the dipoles do not cancel under an applied field, the crystal will develop an overall dipole moment

- can occur if e.g. number of cations $\neq$ number of anions

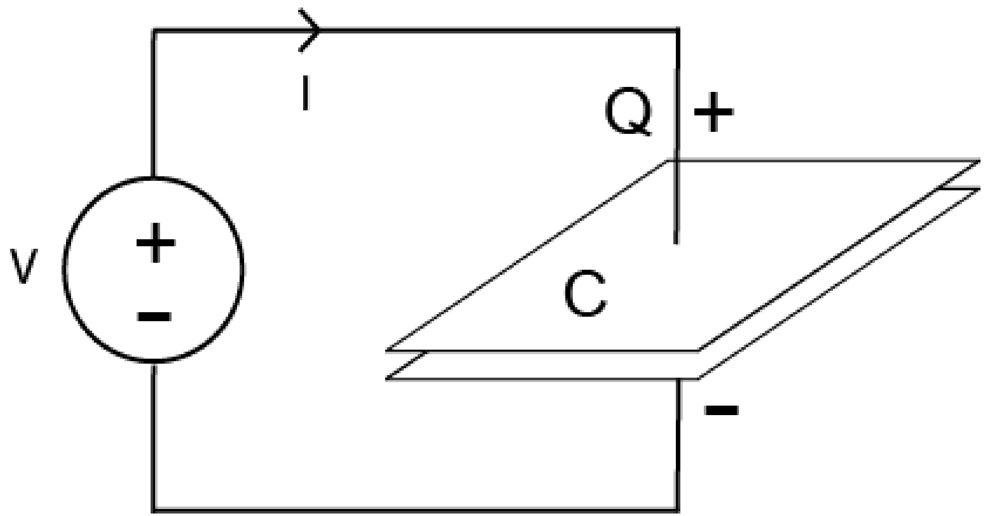
Can use this to screen electric fields

- Useful in e.g. wireless communication filters, sensor devices, transformers, and **capacitors**

Capacitors

- Vital component of most electronic devices
  - Used to store charge, smooth signals, filter, etc...
  - $20bn per year industry

Essentially, a capacitor is an arrangement of two electrodes of area *A*, separated by a distance *d*.



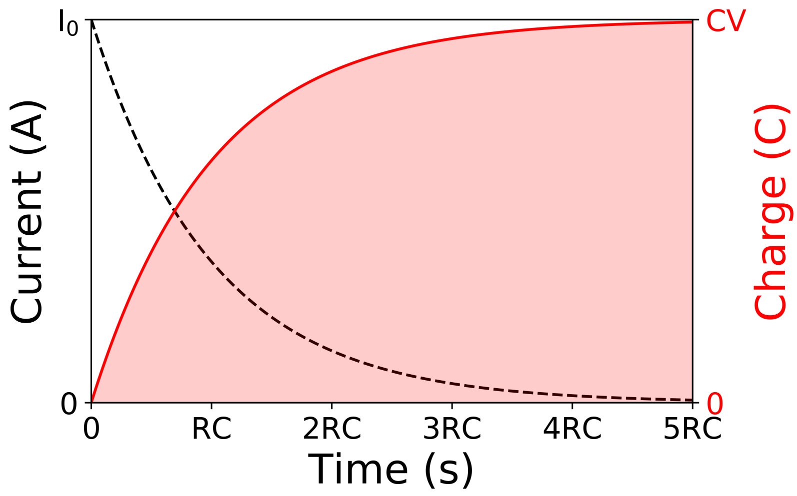
The maximum charge stored, $Q = CV$ where C is the capacitance (in Farads).

Charge stored

With constant voltage V, current (I) decays with time, while charge stored (Q) increases:

$$I_t = I_0 e^{\left(\frac{-t}{RC}\right)} \qquad\qquad Q_t = CV\left[1 - e^{\left(\frac{-t}{RC}\right)}\right]$$

where C is the capacitance and R is the resistance between voltage source and capacitor (e.g. in the wires)



- As charge increases on the plates, it becomes harder to increase further.
- At infinite time, $Q = CV$.

Capacitance

Two electrodes separated by vacuum have a capacitance C;

$$C = \frac{\epsilon_0 A}{d}$$

where ϵ_0 is the permittivity of free space = 8.854×10^{-12} C^2 J^{-1} m^{-1}

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To increase C (and therefore Q):

- decrease d or increase A, **but**
- electrons will tunnel from one plate to the other if d gets too small.

Improving charge stored

Alternatively, we can use a **dielectric**

- opposing electric field stabilises charge on capacitor plates

$$C_{\text{dielec}} = \frac{\epsilon_r \epsilon_0 A}{d}$$

where ε_r is the relative permittivity of the dielectric ($\varepsilon_r = \varepsilon / \varepsilon_0$) and $\varepsilon_r > \varepsilon_0$

Example permittivities

Material	Relative Permittivity, ε_r
Vacuum	1
Paper	2.0 - 6.0
Polymers	2.0 - 6.0
Silicon oil	2.7 - 2.8
Quartz	3.8 - 4.4
Glass	4 - 15
Al_2O_3	10
Ta_2O_5	26
TiO_2	100
$CaTiO_3$	130
$SrTiO_3$	285
$BaTiO_3$	1000 - 10000

Characterising dielectrics

- Because dielectrics are insulating, conductivity measurements are not very useful
- Alternatively, oscillate between +ve and -ve potentials to change polarisation direction

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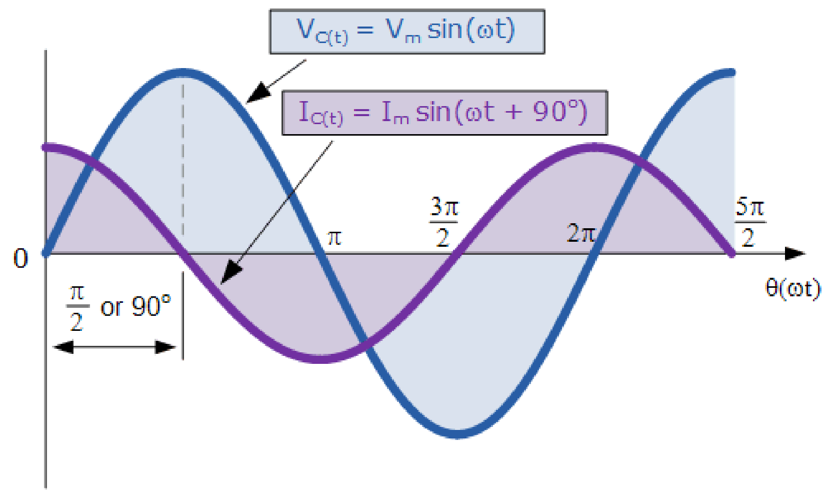
Impedance spectroscopy applies an alternating (sinusoidal) field at different frequencies f, and measures the resulting current

- Applied field, $E_t = E_0 \sin(\omega t)$, where $\omega = 2\pi f$
- Response current, $I_t = I_0 \sin(\omega t + \phi)$



Impedance

Similar to Ohm's law $(R = \frac{V}{I})$ for constant voltages, we can define *impedance* as the 'resistance' to an alternating voltage

$$Z(\omega) = \frac{E_t}{I_t}$$

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The total impedance can be represented as a complex number:

$$Z(\omega) = Z_0 e^{i\phi} = Z_0(\cos\phi + i \sin\phi)$$

- ϕ is the 'phase-shift' between voltage and current.

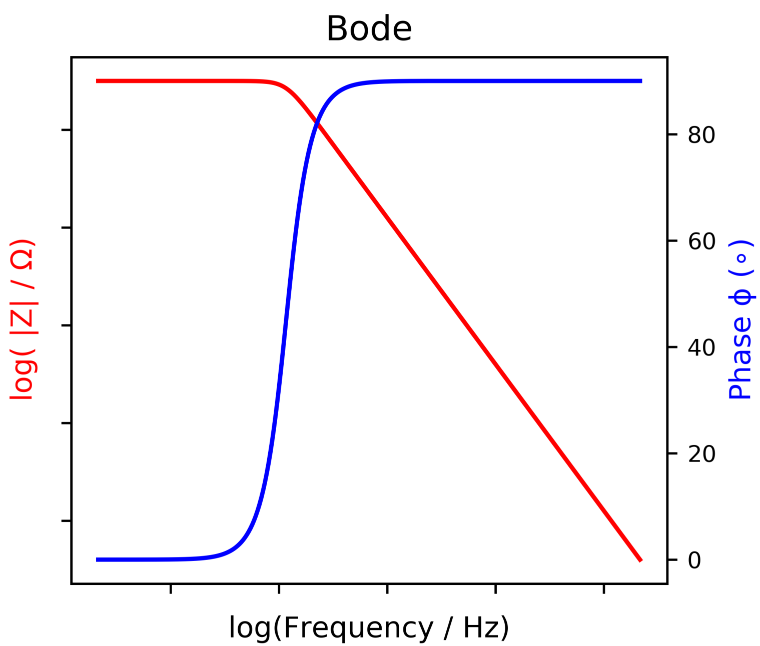
Useful introduction to impedance here

Impedance analysis

ϕ, Z and ω (or f) are all important features of impedance.
Two 'standard' ways to display data:

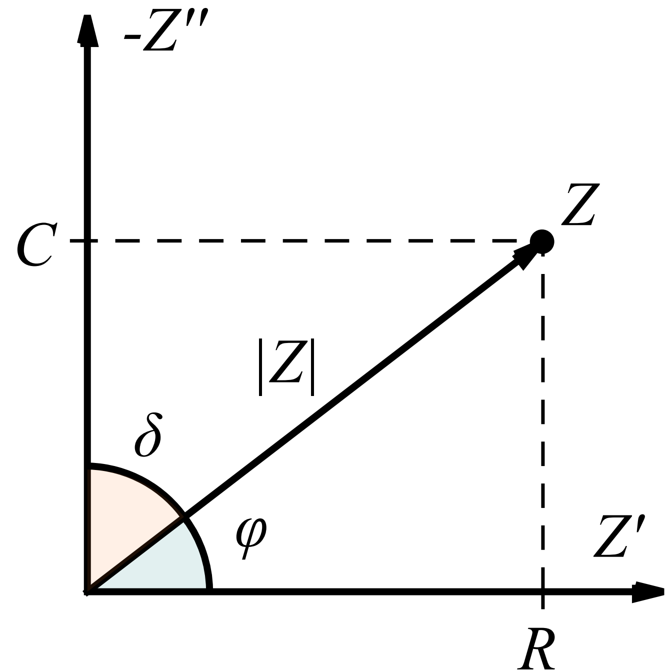
Bode plot: $|Z|$ and ϕ plotted vs frequency

- often log axes



Nyquist plot: Z plotted in a 2D plane (like an Argand diagram)

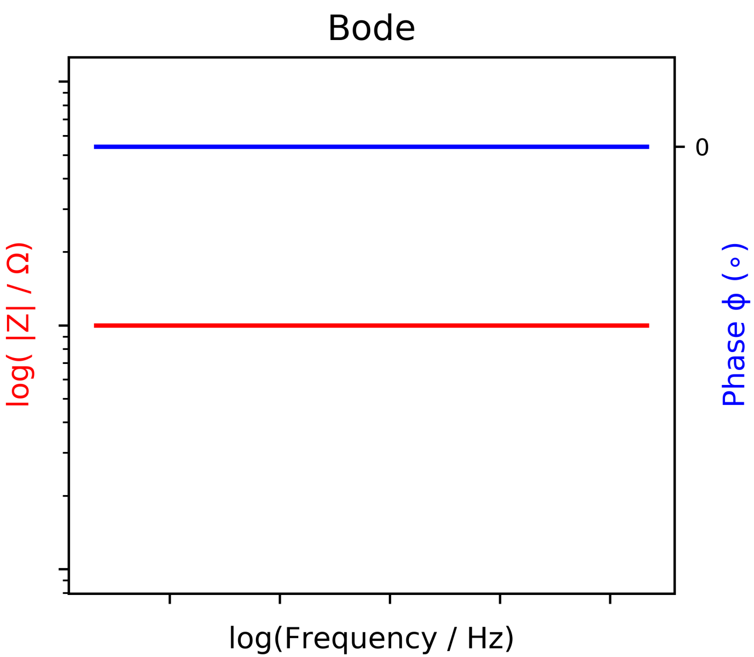
- N.B. usually inverted y-axis

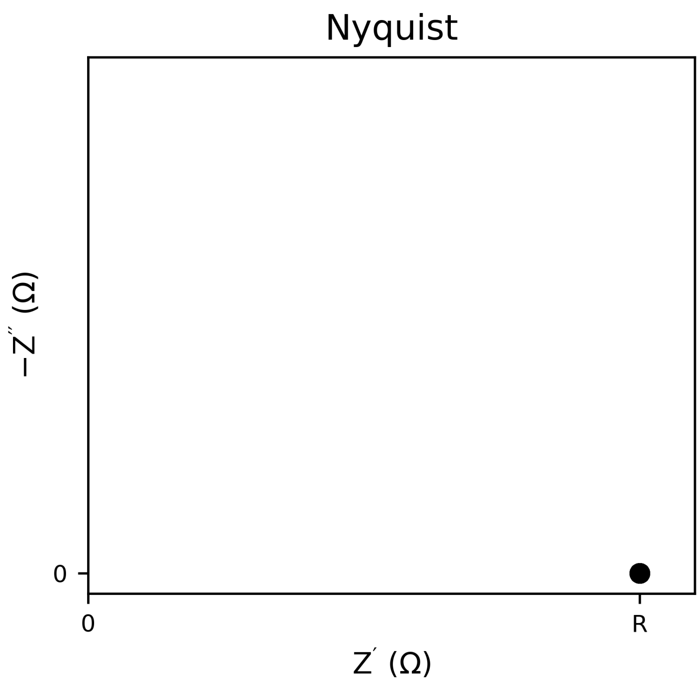


Ideal resistor response

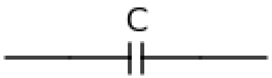
In an ideal resistor electrons should flow instantly under an applied potential

- E and I should match (i.e. $\phi = 0$)
- $\phi = 0$ so $Z(\omega) = Z_0(\cos 0 + i \sin 0) = Z_0$
- Ideally, Z is also independent of ω
  - Electrons can change direction 'infinitely' fast

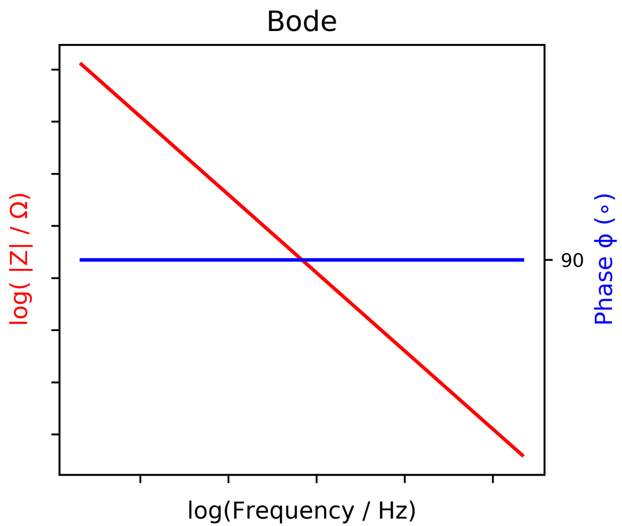


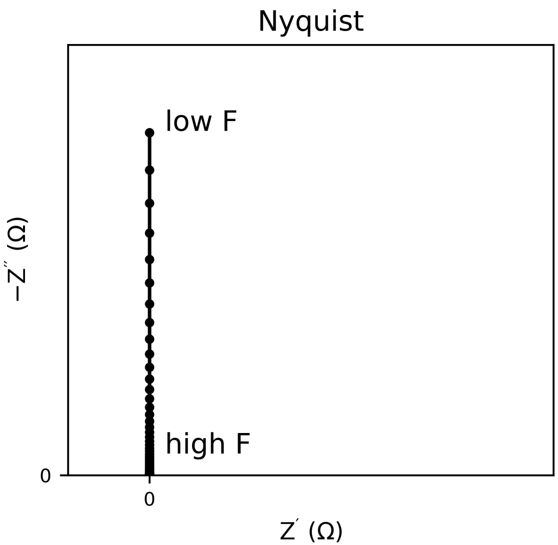


'Ideal' capacitor response



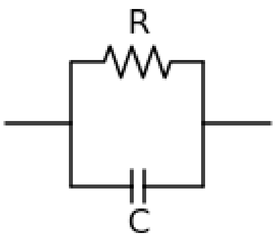
- No electrons can flow between the plates
  - For small ω, very large impedance
- Current is largest when potential is first applied (near 0), decreasing as potential gets larger
  - Overall, $\phi = 90$
- At high ω, I is always near maximum
  - $|Z| \to 0$ as ω increases

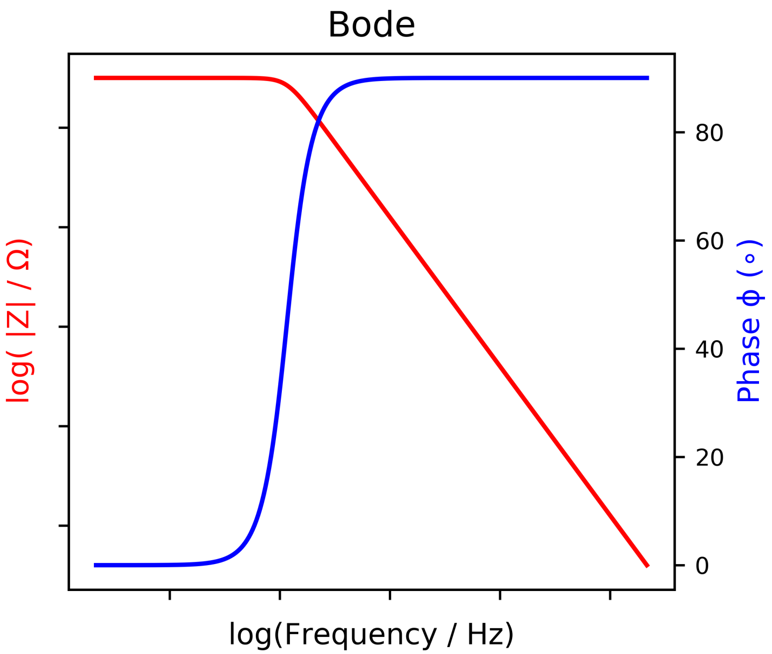


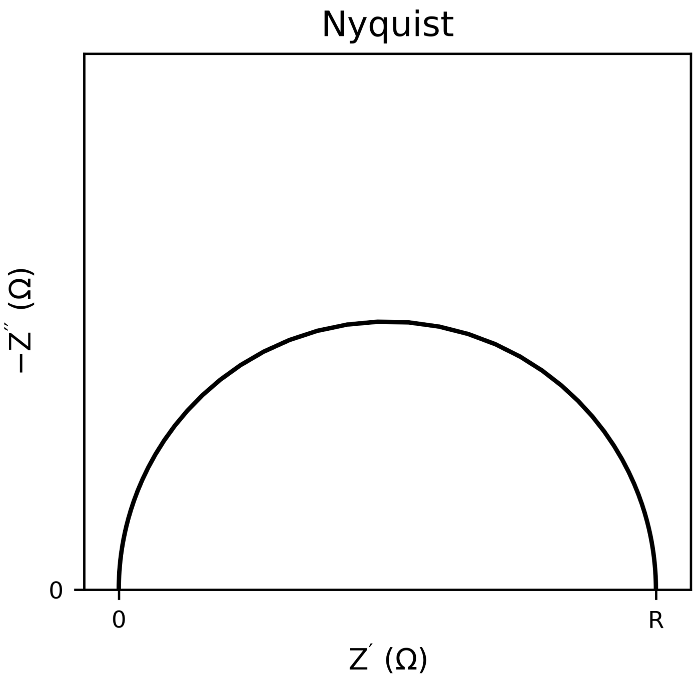


'Real' Impedance

- Many materials behave like a parallel RC circuit:
  - Ions flowing in solution, forming a layer on the electrode
  - Ionic conduction in a ceramic forming a charge gradient

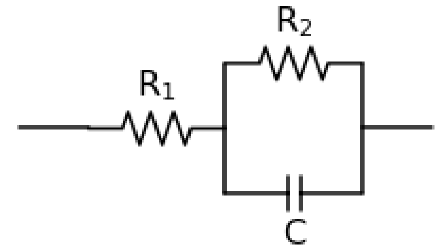






More complex behaviour is often observed, and can be modelled using *equivalent circuits*

Real dielectric response



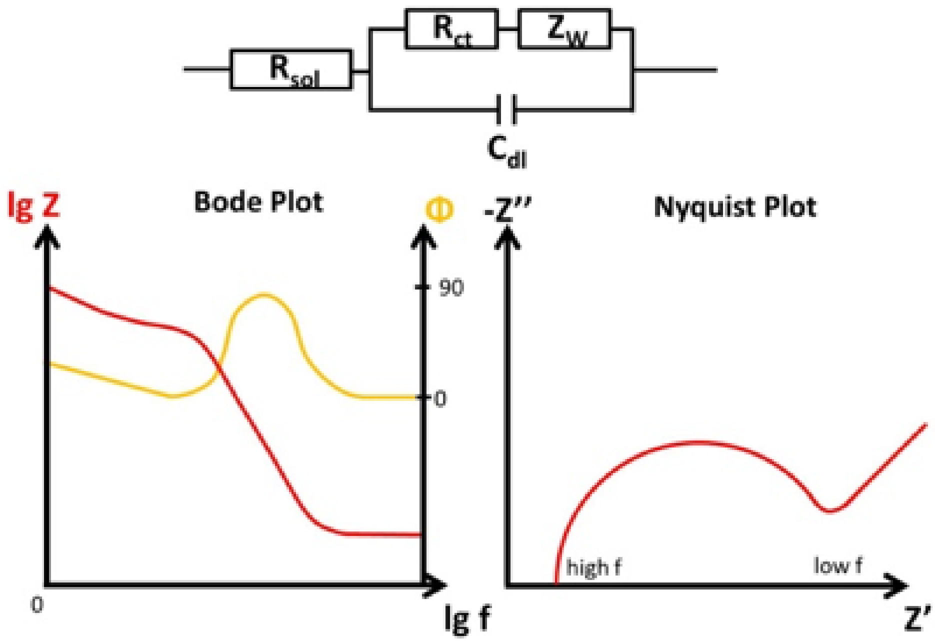
Dielectrics are not ideal-they leak!

- Ions have mass, so cannot move instantly
- At high ω, some resistance remains
    - energy lost as heat
- peak in ϕ vs ω, corresponding to the maximum energy loss.
    - often reported as $\tan\delta$ (where $\delta = 90^\circ - \phi$)

Other materials

In ionically conducting materials, an additional signal is often observed at low ω

- Interactions between mobile ion and electrode(s)



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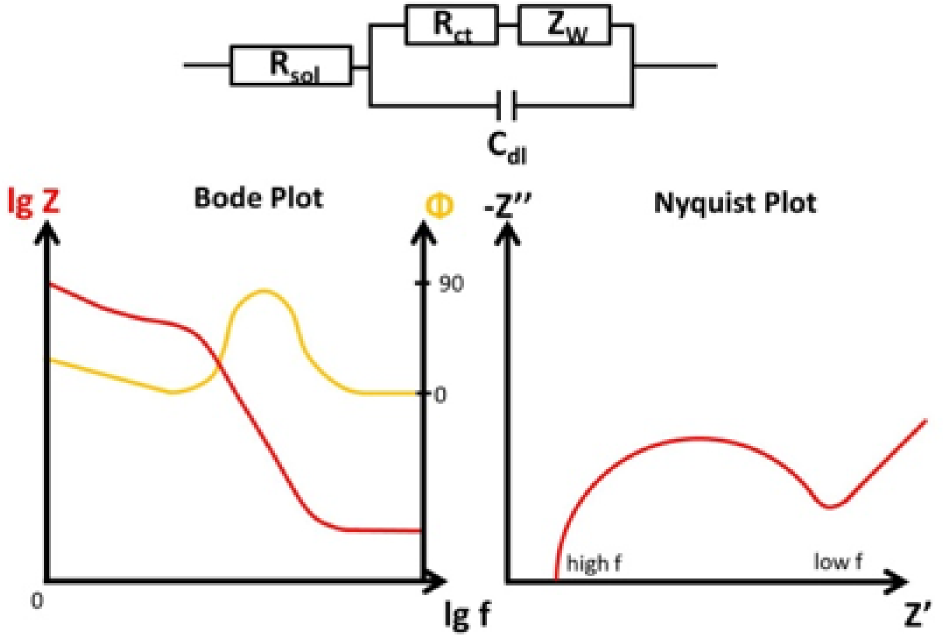


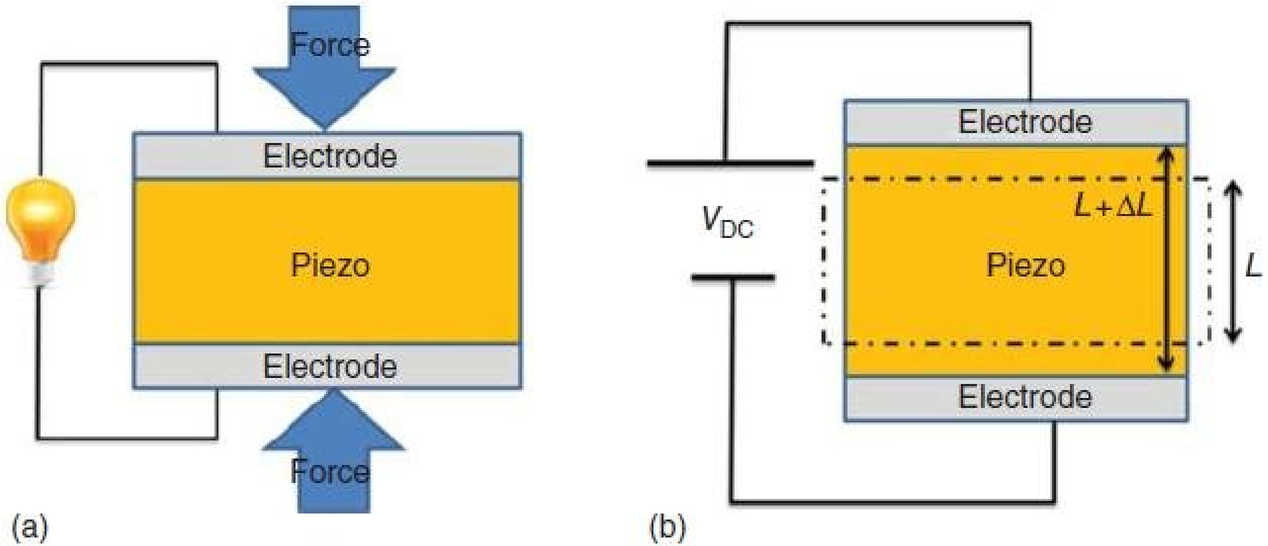
Real materials usually consist of closely-packed ceramic grains.

- different R/C effects for grain boundaries *vs.* bulk
- gives rise to two (often overlapping) semicircles.

Piezoelectricity

In some dielectric materials, applying E can result in a mechanical stress (or *vice versa*)

- Stress = change in lattice parameters



Direct effect
Applications:

- pressure sensors
- ultrasonic imaging

Converse effect
Applications:

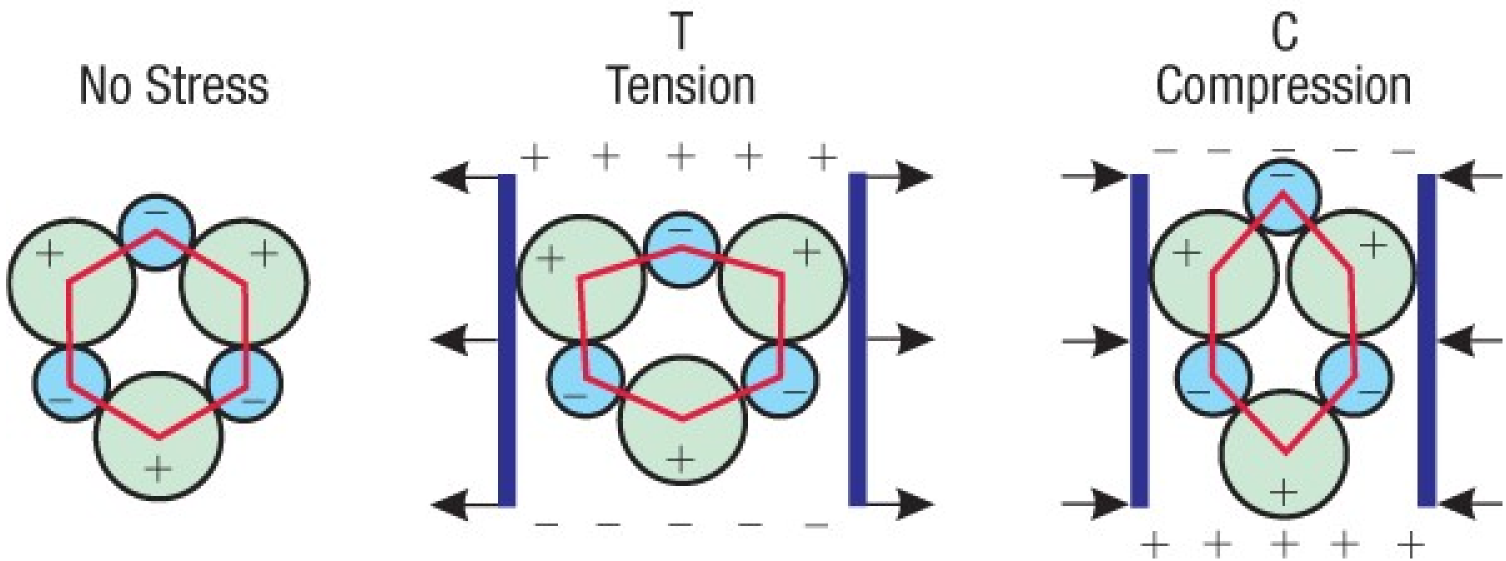
- Actuators/motors
- crystal oscillator (watches)

Structural Aspects

Stresses arise due to unbalanced dipoles

- Can only occur if the structure is **non-centrosymmetric**

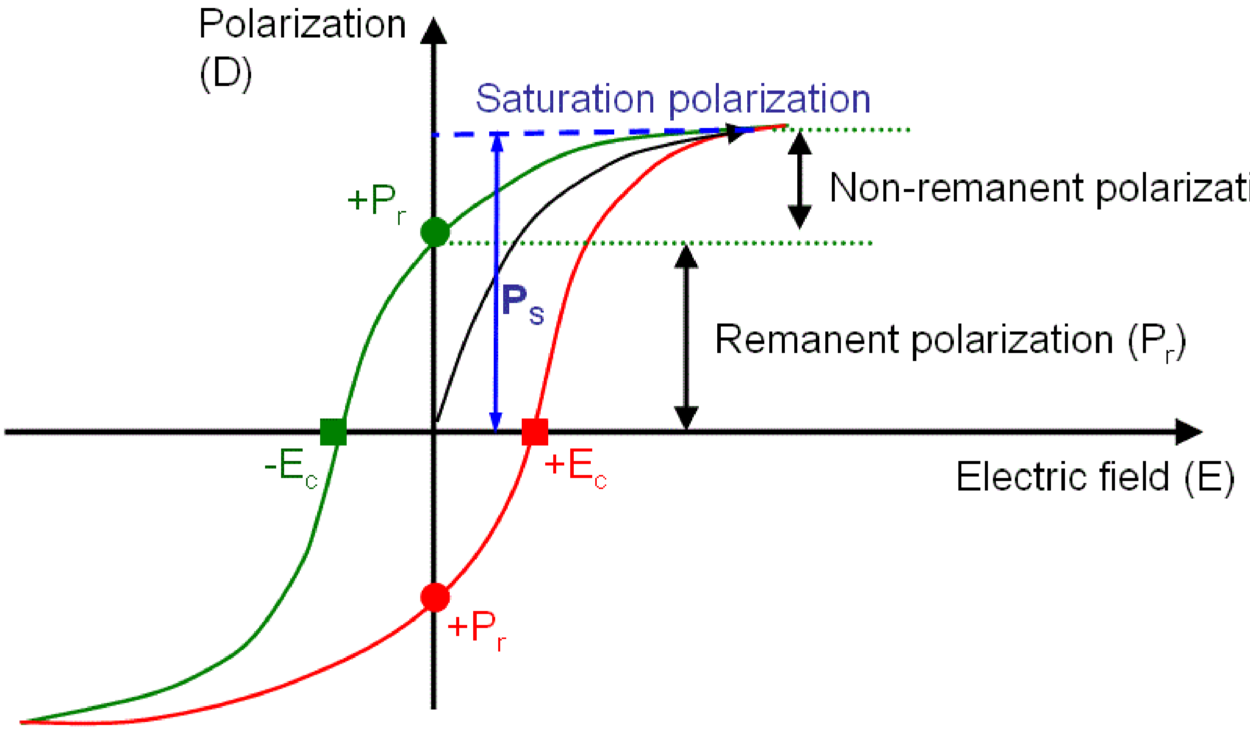
Example: Quartz (SiO_2)



Spontaneous polarisation

Some materials exhibit a net dipole *without* an applied electric field (**pyroelectric**)

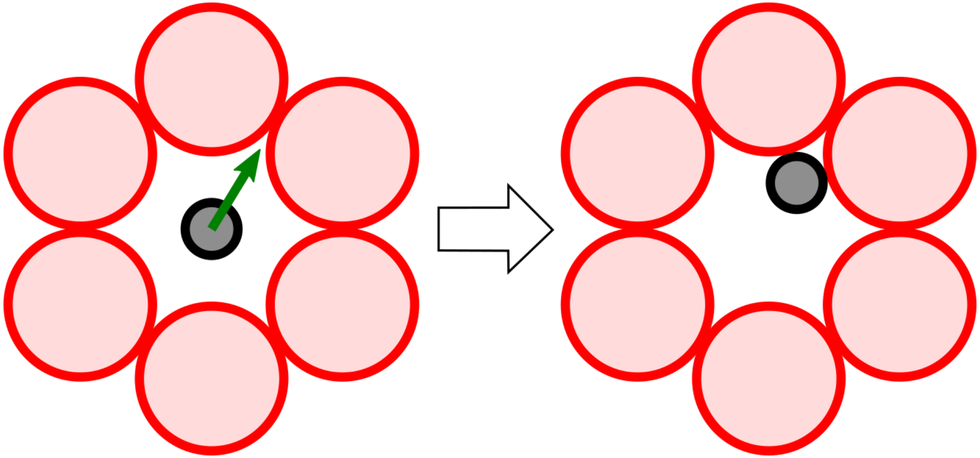
If the polarisation can be switched with an electric field - **Ferroelectric**

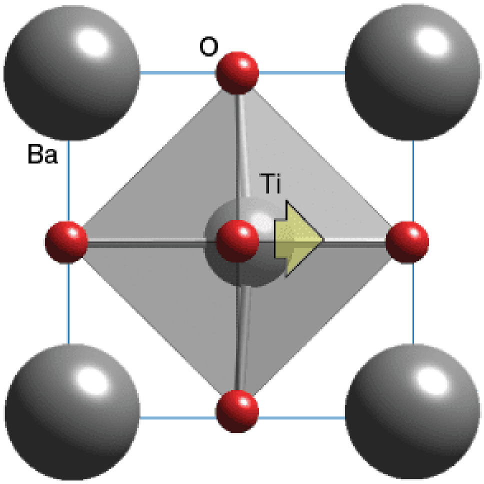


Structural origin

Precise origin of ferroelectricity is unknown!
Often, displacement of small ion in a large 'cavity' is partly reponsible

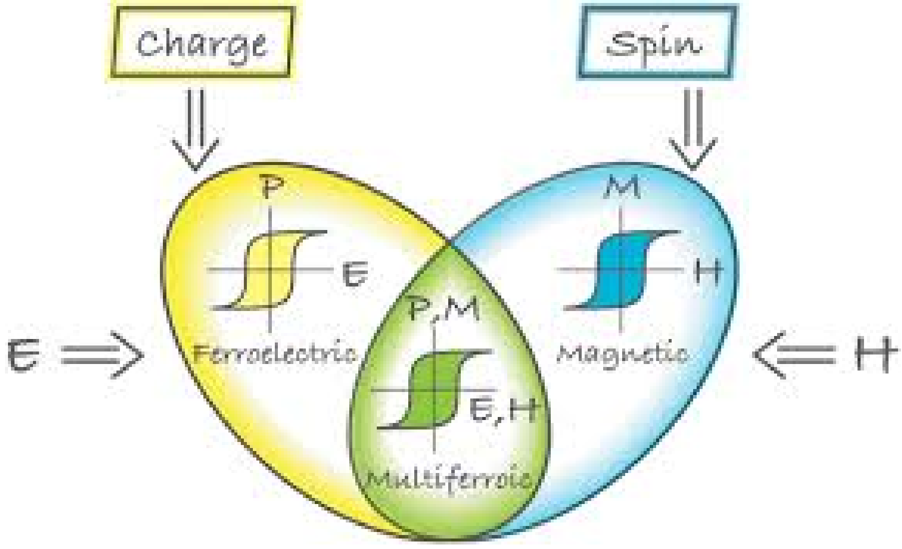
- Driven by anharmonicity or pseudo-Jahn-Teller effects
- *sometimes* this results in long-range order of dipoles...
- Many perovskites are ferroelectric (e.g. $\mathrm{BaTiO_3}$)





Applications

- Ferroelectrics often have the largest ϵ_r
  - important for high-C capacitors
- Could be coupled with e.g. ferromagnetism
  - **Multiferroics** are currently popular for electrical control of magnetic fields (e.g. in hard drives)



Nice summary of ferroelectric mechanisms and multiferroics

Hierarchy of dielectrics

Dielectric
Insulators that may change polarisation under an applied electric field
Polar or non-polar

Piezoelectric
Change in polarisation is proportional to mechanical stress
Non-centrosymmetric, polar or non-polar

Pyroelectric
Show spontaneous polarisation
Polar material

Ferroelectric
Exhibit polarisation
switchable by electric field

Lecture recap

- Polarisation arises from cation-anion dipoles
    - Can be modified by external electric field
- Important in capacitors
    - charge stored increased by high ϵ_r dielectric
- Impedance spectroscopy can characterise ionic motion
    - Oscillating potential generates oscillating current
    - Impedance $Z(\omega)$ has both phase (ϕ) and magnitude ($|Z|$)
    - Many materials behave like parallel RC circuits
- Piezoelectricity is the linear relationship between polarisation and mechanical stress
    - requires non-centrosymmetric structures
- Pyro- and ferro-electrics exhibit spontaneous polarisation without applied electric fields
    - used where high permittivity is needed (e.g. capacitors)
    - current interest in multiferroics