

FoP3B Part II Lecture 11: Ferroelectric crystals

Previously we discussed **macroscopic** and **microscopic** electric fields. The latter cannot be measured, but is important since the **electric dipole moment** μ of an atom or molecule is linked to the *local* microscopic field E_{local} via $\mu = \alpha E_{\text{local}}$, where α is the **polarisability**. E_{local} can be calculated from the polarisation \mathbf{P} . A similar approach is adopted for α , this time using the **dielectric constant** or **relative permittivity** ϵ_r as the macroscopic variable. This gives rise to the **Clausius-Mossotti** relationship.

Dielectrics were introduced as **polarisable** media under static DC electric fields. Here the discussion will be broadened to *oscillating AC electric fields*. ϵ_r is then a function of the AC oscillation frequency ω ; we will explore the different contributing factors to $\epsilon_r(\omega)$ and derive its form for the special case of **electronic polarisation**. $\epsilon_r(\omega)$ is the *most general description of the dielectric properties of the material*, and the static DC scenario is a special case where $\omega \rightarrow 0$. Although not covered in this module $\epsilon_r(\omega)$ provides useful information on how a material interacts with light and other electromagnetic waves (recall that EM waves have oscillating electric fields). For example, using $\epsilon_r(\omega)$ it is possible to derive the **refractive index** and **absorption coefficient** of the material.

Finally, **ferroelectric** crystals, such as BaTiO_3 , will also be introduced. These are similar to **ferromagnets**, except that instead of a spontaneous *magnetisation* \mathbf{M} we have a spontaneous *polarisation* \mathbf{P} . Ferroelectrics share many features in common with ferromagnets, such as **hysteresis loops** and **domains**.

Clausius-Mossotti relationship

Since polarisation (\mathbf{P}) is the net dipole moment per unit volume and $\mu = \alpha E_{\text{local}}$ we can write:

$$\mathbf{P} = N\mu = N\alpha E_{\text{local}} \quad \dots (1)$$

where N is the number density of dipole moments¹. From the previous lecture $E_{\text{local}} = E_{\text{macro}} + (P/3\epsilon_0)$, where E_{macro} is the *internal* macroscopic field due to an external applied field E_{ext} , i.e. $E_{\text{macro}} = E_{\text{ext}} - \sigma/\epsilon_0$, with σ being the surface charge density. Substituting the expression for E_{local} in (1) and re-arranging for $N\alpha$:

$$N\alpha = \frac{(P/E_{\text{macro}})}{1 + \frac{1}{3\epsilon_0} (P/E_{\text{macro}})} \quad \dots (2)$$

The term (P/E_{macro}) is equal to $\epsilon_0\chi_e$, where χ_e is the **electric susceptibility** (it is similar to the *magnetic susceptibility* M/H). We now derive an alternative expression for (P/E_{macro}) using the definition for the **electric displacement field** \mathbf{D} :

¹ It is assumed that all dipoles are identical with dipole moment μ . This is however a simplification. Although not discussed the Clausius-Mossotti relationship can be generalised without this simplification.

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \epsilon_r \mathbf{E} \quad \dots (3)$$

Substituting E_{macro} for \mathbf{E} in Equation (3) we get $(P/E_{\text{macro}}) = \epsilon_0(\epsilon_r - 1)$. Therefore, Equation (2) simplifies to:

$$\frac{N\alpha}{3\epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad \dots (4)$$

This is the Clausius-Mossotti relationship that links polarisability α to ϵ_r .

Dielectric properties under an oscillating electric field

Consider connecting a capacitor with a dielectric to an AC current source (Figure 1a). The equation for capacitance (C) can be generalised from the static DC case to $C = \epsilon_0 \epsilon_r(\omega) A/d$, where ϵ_r is now a function of frequency ω of the AC circuit (A is the capacitor plate area and d is the plate spacing). The graph of $\epsilon_r(\omega)$ as a function of ω is shown in Figure 1b. Three different regimes can be identified, which are labelled as *electronic*, *ionic* and *dipolar*. **Electronic polarisation is the polarising or displacement of the electron cloud centre of mass w.r.t the nucleus of an atom by an electric field.** Since the electron mass is relatively small the displacement can happen at high frequencies (Figure 1b). **Ionic polarisation is due to displacement of individual positive and negative ions by the electric field.** Since the ions are relatively heavy this mechanism only occurs at intermediate frequencies. **Dipolar polarisation is the rotation of an entire molecule (e.g. water H_2O) with permanent dipole moment by the electric field.** This mechanism is only active at low frequencies, due to the fact that entire molecules must be rotated.

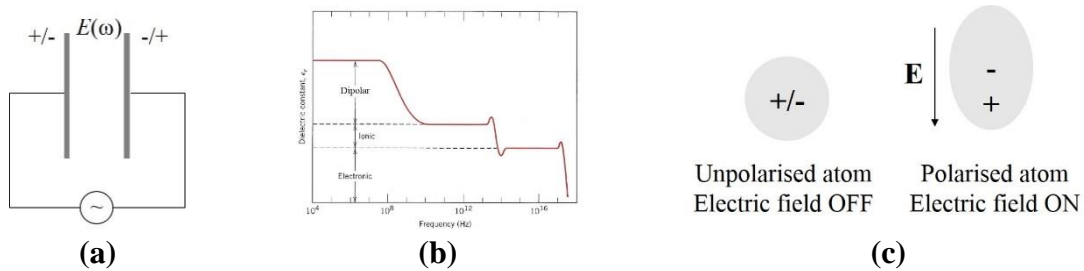


Fig 1: (a) capacitor connected to AC current of frequency ω , (b) $\epsilon_r(\omega)$ plot as a function of ω and (c) displacement of the centre of mass of an electron cloud in an atom due to an electric field \mathbf{E} .

An expression for $\epsilon_r(\omega)$ due to electronic polarisability will now be derived. With no electric field the centre of mass of the negatively charged electron cloud overlaps with the positively charged nucleus and the atom has no dipole moment (Figure 1c). Once an electric field \mathbf{E} is applied however the electron cloud is easily displaced w.r.t the nucleus to give rise to a dipole moment μ , which can be expressed as:

$$\mu(\omega) = -e r(\omega) \quad \dots (5)$$

Here e is the magnitude of electron charge and \mathbf{r} is the position vector of the centre of mass of the electron cloud (the nucleus is at the origin). $\boldsymbol{\mu}$ and \mathbf{r} are functions of ω , since we are interested in an oscillating electric field. Furthermore, in equation (5) a negative sign is included since the direction of \mathbf{r} is from the positively charged nucleus to the electron cloud centre of mass (i.e. opposite to the direction of $\boldsymbol{\mu}$). The displacement $\mathbf{r}(\omega)$ can be modelled by treating the electron-nucleus bond as a spring of spring constant K . From **simple harmonic motion** the **restoring force** of the spring is $-K\mathbf{r}(\omega)$; NB: the direction of the restoring force is opposite to \mathbf{r} . The other force acting on the electron cloud is the force generated by the oscillating electric field $-e\mathbf{E}_{\text{local}}(\omega)$ (NB: for an individual dipole we must use the microscopic, rather than macroscopic, electric field). The equation of motion is therefore:

$$m \frac{d^2 \mathbf{r}(\omega)}{dt^2} = -K\mathbf{r}(\omega) - e\mathbf{E}_{\text{local}}(\omega) \quad \dots (6)$$

Now an oscillating local electric field can be expressed as $\mathbf{E}_{\text{local}}(\omega) = \mathbf{E}_o \exp(i\omega t)$, where t is time and \mathbf{E}_o is the local electric field at $t = 0$. Since the electron cloud can react almost instantaneously to the electric field we have $\mathbf{r}(\omega) = \mathbf{r}_o \exp(i\omega t)$. Substituting expressions for $\mathbf{E}_{\text{local}}(\omega)$ and $\mathbf{r}(\omega)$ in (6) and simplifying:

$$\mathbf{r}(\omega) = \frac{e\mathbf{E}_{\text{local}}(\omega)}{m(\omega^2 - \omega_o^2)} \quad \dots (7)$$

where $\omega_o = (K/m)^{1/2}$ is the **resonant frequency** of the simple harmonic oscillator. Substituting in (5) gives:

$$\boldsymbol{\mu}(\omega) = \frac{e^2 \mathbf{E}_{\text{local}}(\omega)}{m(\omega_o^2 - \omega^2)} \quad \dots (8)$$

From the definition of polarisability α we have $\boldsymbol{\mu}(\omega) = \alpha(\omega)\mathbf{E}_{\text{local}}(\omega)$. By comparing with Equation (8) we obtain an expression for $\alpha(\omega)$:

$$\alpha(\omega) = \frac{e^2}{m(\omega_o^2 - \omega^2)} \quad \dots (9)$$

Substituting in the Clausius-Mossotti relationship (Equation 4) then gives:

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{m\epsilon_o(\omega_o^2 - \omega^2) - (\frac{Ne^2}{3})} \quad \dots (10)$$

The shape of $\epsilon_r(\omega)$, as predicted by Equation (10), is plotted schematically in Figure 2. *There is an abrupt change in shape of $\epsilon_r(\omega)$ close to the resonance frequency ω_0 .* This is known as the **anomalous dispersion** region, since ϵ_r decreases w.r.t. ω , whereas typically it increases.

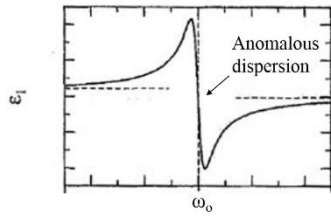


Fig 2: $\epsilon_r(\omega)$ as a function of ω due to electronic polarisability. The anomalous dispersion region occurs close to the resonance frequency ω_0 .

Ferroelectric crystals

Ferroelectric crystals are characterised by a large **spontaneous polarisation** (\mathbf{P}_s) that is present even in the absence of an electric field. In the case of BaTiO_3 \mathbf{P}_s is due to a small ($<1 \text{ \AA}$) displacement of negatively charged oxygen ions w.r.t. positively charged Ba or Ti ions (Figure 3a). Ferroelectric crystals have many similarities with ferromagnets. For example, *the material is organised into polarisation domains* (Figure 3b). This is because for a dielectric with no free charge by Maxwell's equation $\vec{\nabla} \cdot \mathbf{D} = \vec{\nabla} \cdot (\epsilon_0 \mathbf{E} + \mathbf{P}) = 0$ or $\epsilon_0 \vec{\nabla} \cdot \mathbf{E} = -\vec{\nabla} \cdot \mathbf{P}$. If there were no domains $\vec{\nabla} \cdot \mathbf{P} \neq 0$ at a free surface, so that a **depolarising electric field** must be present in order to satisfy Maxwell's equation. This increases the energy of the system (recall that the potential energy of a dipole moment $\boldsymbol{\mu}$ in electric field \mathbf{E} is $-\boldsymbol{\mu} \cdot \mathbf{E}$; hence energy increases when the depolarising field is anti-parallel to \mathbf{P}_s). By forming domains the discontinuity in polarisation \mathbf{P} at the free surface is avoided. The presence of domains gives rise to **hysteresis** behaviour in \mathbf{P} vs. \mathbf{E} curves (Figure 3c). The shape of the hysteresis loop is explained by the energy of individual domains in the presence of an applied electric field, i.e. domains where the internal polarisation \mathbf{P} is parallel to \mathbf{E} have the lowest energy.

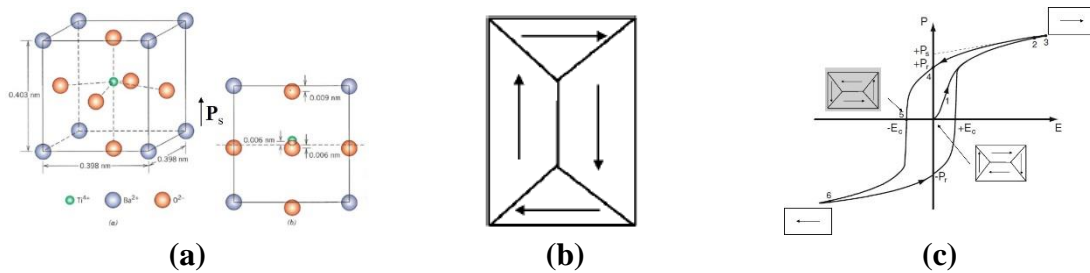


Fig 3: (a) Origin of spontaneous polarisation in BaTiO_3 , (b) stable domain configuration in a ferroelectric crystal and (c) P vs E hysteresis loops.