<u>**FoP3B Part II Lecture 10: Polarisation in Dielectrics**</u>

Dielectrics *are insulating materials that can be* **polarised** *by an applied electric field*. To illustrate this consider a capacitor attached to a battery. The **capacitance** (C) is the charge (Q) stored per unit voltage (V) or:

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

… (1)

where ϵ_o is the permittivity of free space, A is the capacitor plate area and d is the plate spacing. ϵ_r is the **dielectric constant** or **relative permittivity** (a dimensionless value). In some materials, such as $BaTiO_3$ (a widely used dielectric), ϵ_r is extremely large. Consider inserting $BaTiO_3$ in between the capacitor plates. From Equation (1) the capacitance increases significantly; this could be due to either Q increasing or V decreasing or both. Since the $BaTiO_3$ is charge neutral (i.e. no additional charge added to the capacitor) and there is no loss of charge due to $BaTiO_3$ being insulating Q must be constant. Hence *increased capacitance must be due to a decrease in voltage across the capacitor*. *This implies that the dielectric generates an opposing electric field to the battery*. The dielectric is electrically <u>polarised</u> under the applied electric field. In this lecture we explore the microscopic origins of polarisation and discuss the concept of **microscopic** and **macroscopic** electric fields in a dielectric.

Polarisation and macroscopic electric field

The microscopic origin of polarisation is the **electric dipole moment**, which is due to the spatial separation of positive and negative charge (Figure 1a). The dipole moment vector **μ** extends from the negative to positive charge. The magnitude of **μ** is qd, where q is the magnitude of either the positive or negative charge (both are equal) and d is their separation (NB: do not confuse d with the capacitor plate spacing in Equation 1). *There are many ways by which an electric dipole moment can be formed in a dielectric*. One method is the polarisation of the electron cloud in an otherwise neutral atom under an applied electric field (Figure 1b). This is known as **electronic polarisation**. On the other hand in molecules such as water (H_2O) the oxygen is highly *electronegative*, which means it attracts some of the electrons in the bond towards it. The oxygen becomes negatively charged and the hydrogen positively charged, resulting in a <u>permanent</u> electric dipole, which is present independent of an electric field (Figure 1c).
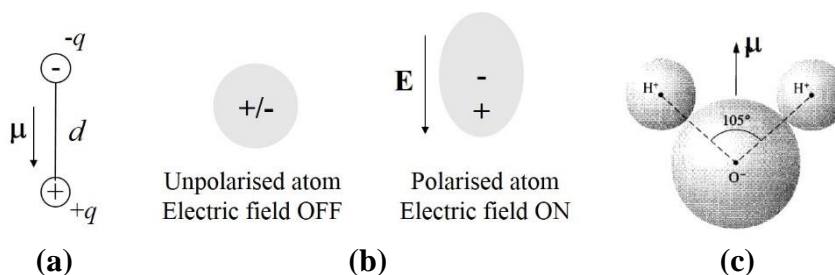

Fig. 1: (a) An electric dipole moment **μ**, (b) electronic polarisation of the electron cloud of a neutral atom under an electric field **E** and (c) the permanent dipole in a H_2O molecule

Consider first a solid with permanent electric dipoles. We define the <u>polarisation</u> **P** as the *dipole moment per unit volume*. With no electric field present the permanent electric dipole moments

are all randomly oriented (Figure 2a), so that **P** is negligible. *When an external electric field* **E**ₑₓₜ *is applied there is a torque* (**μ** x **E**ₑₓₜ) *acting on the electric dipole, which rotates it until the potential energy -***μ·E**ₑₓₜ *is minimised*. <u>The minimum energy is when the dipole moment **μ** is parallel to the electric field (Figure 2b)</u>. In this particular example we considered a solid with permanent dipoles, but it should be clear that an electric field will generate a non-zero polarisation **P** even in the absence of permanent dipoles, due to electronic polarisation.
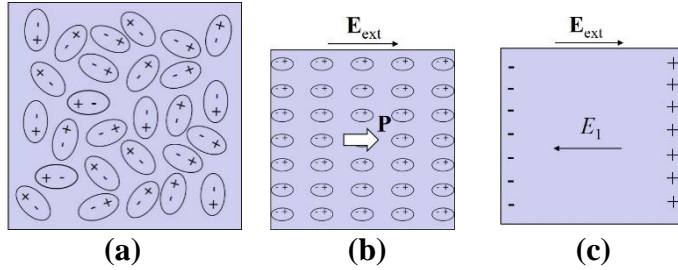

Fig 2: dipole moments (a) before and (b) after applying an external electric field **E**ₑₓₜ and (c) the continuum equivalent of (b) with surface charge and internal electric field E_1.

Now each dipole moment **μ** will generate its own electric field according to:

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

$$\ldots (2)$$

where **r** is the position vector (in the above equation the dipole is at the origin). The random dipole orientations in Figure 2a will generate a zero net dipole electric field, but not so for the non-zero polarisation **P** configuration in Figure 2b. *From a theorem in electrostatics the collective effect of dipoles in a material of uniform polarisation* **P** *can be modelled as a surface charge density* σ = **P·n**, *where* **n** *is the surface unit normal of the solid*. The oriented dipoles in Figure 2b is then equivalent to the continuum slab of material in Figure 2c with surface charge as indicated. The surface charge gives rise to an internal electric field E_1 which is opposite to the external applied field. By **Gauss' law** $E_1 = -\sigma/\epsilon_o$. The **macroscopic field** within the material is therefore ($E_{ext} - \sigma/\epsilon_o$), i.e. the electric field is reduced due to the polarisation and the capacitance increases.

Microscopic electric fields

The macroscopic field is the electric field accessible to experimental measurement. It is a smooth, continuous field. Real materials however consist of discrete dipoles and are therefore not smooth and continuous at the atomic length scale. The *local* **microscopic** electric field **E**ₗₒcₐₗ at an electric dipole is therefore different from the macroscopic field. Although not directly accessible by measurement the microscopic field is nevertheless important since it determines the dipole moment **μ** via the **polarisability** α, i.e.:

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

$$\ldots (3)$$

In this section the procedure for calculating **E**ₗₒcₐₗ from the macroscopic field will be presented. Consider calculating the local electric field at the centre of the material shown in Figure 2b.

The material is divided into two regions (Figure 3): the first is a sphere about the origin. Since this is close to the centre the electric fields due to individual dipole moments within this region are discretely summed, i.e. the material is analysed at the atomistic level. The region outside the sphere is considered to be sufficiently far away from the centre that macroscopic fields can be applied. i.e. this region is treated as a continuum. Since the polarisation within this outer region is uniform we can model it via surface charges given by $\sigma = \mathbf{P} \cdot \mathbf{n}$. This results in surface charges at the outer edges of the solid, as well as within the cavity walls (Figure 3). *The outer region is therefore a superposition of two electric fields*: (i) the field $\mathbf{E}_1 = -\sigma/\epsilon_o$ due to a slab with no cavity (see previous section) and (ii) a field $\mathbf{E}_2$ due a cavity with surface charges. Note that the surface charges within the cavity walls are such that $\mathbf{E}_2$ is opposite to $\mathbf{E}_1$. $\mathbf{E}_2$ is known as the **Lorentz field** and its value can be calculated using standard electrostatic methods:

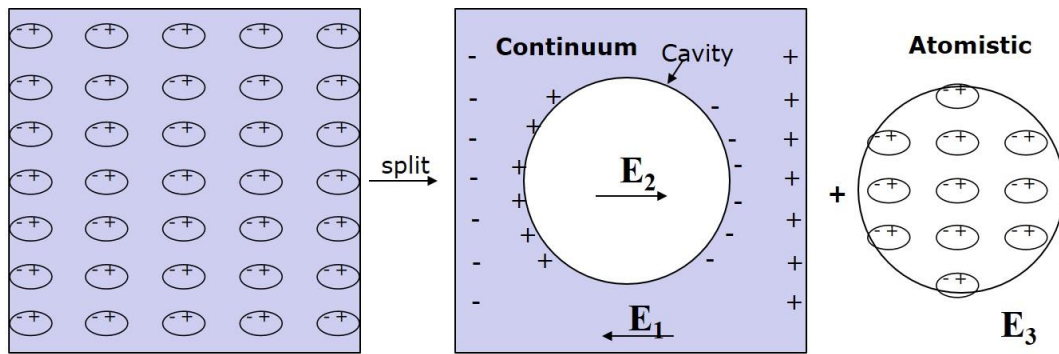$$\mathbf{E}_2 = \frac{\mathbf{P}}{3\epsilon_o}$$

$$\dots (4)$$

Fig 3: Breakdown of solid into continuum and atomistic region for calculating the local electric field at the centre

Next consider the atomistic electric field $\mathbf{E}_3$ at the origin within the sphere. We need to sum the dipole electric field in Equation (2) for all dipoles within the sphere. In Figure 3 the dipole moments are along the *x*-axis and therefore $\boldsymbol{\mu} = (\mu, 0, 0)$. Consider $\mathbf{E}_{3,x}$ which is the *x*-component of the electric field $\mathbf{E}_3$. From Equation (2) we have:

$$\mathbf{E}_{3,x}(0) = \sum_i \frac{3\mu x_i^2 - r_i^2 \mu}{4\pi\epsilon_o r^5} = \mu \sum_i \frac{3x_i^2 - r_i^2}{4\pi\epsilon_o r^5}$$

$$\dots (5)$$

where the summation is over all dipoles *i* located within the sphere and at position vector $\mathbf{r}_i = (x_i, y_i, z_i)$. Now assume that the solid has a *cubic* arrangement of dipoles so that the *x,y* and *z*-axes are equivalent. Therefore:

$$\sum_i x_i^2 = \sum_i y_i^2 = \sum_i z_i^2$$

$$\dots (6)$$

Because $r_i^2 = x_i^2 + y_i^2 + z_i^2$ from Equation (6) we then have $\mathbf{E}_{3,x}(0) = 0$. Consider the y-component $\mathbf{E}_{3,y}$. From Equation (2):

$$\mathbf{E}_{3,y}(0) = \sum_i \frac{3\mu x_i y_i}{4\pi\epsilon_o r^5}$$

$$\dots (7)$$

The above expression is an odd function w.r.t x_i and y_i. Hence summing over all y_i for fixed x_i would give zero (equivalently we could sum over all x_i keeping y_i fixed). Therefore $\mathbf{E}_{3,y}(0) = 0$ and similarly it can be shown that $\mathbf{E}_{3,z}(0) = 0$. Therefore, $\mathbf{E}_3 = 0$.

The local electric field is given by:

$$\mathbf{E}_{\text{local}} = \mathbf{E}_{\text{ext}} + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$$

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

$$\dots (8)$$