

PHY481 - Lecture 26: Dielectric materials

Griffiths: Chapter 4

Polarization at the atomic/molecular scale

To understand the broad aspects of dielectric materials and polarization, we first look at two simple models of atomic level polarization. These models apply to dilute gases where the effect of the neighboring atoms/molecules is ignored. The first model applies to both polar atoms/molecules that have a permanent dipole moment and to non-polar atoms/molecules that do not have a permanent dipole moment. The second model is an additional polarization arising in materials with a permanent dipole moment.

Induced polarization/dipole moment due to an electric field

Atoms and symmetric and/or covalently bonded molecules do not have a permanent dipole moment. Nevertheless these molecules do respond to an electric field. In the simplest case the polarization (= oriented dipole) induced by an electric field is linear in the magnitude of the electric field, so that,

$$\vec{p} = \alpha \vec{E} \quad (1)$$

where α called the polarizability. In the case of a metal sphere, we found that $p = 4\pi\epsilon_0 R^3 E$, so that $\alpha = 4\pi\epsilon_0 R^3$. It is not too surprising that the polarizability of inert atoms is about the same as this value, and that bigger atoms have larger polarizability. Of course this can also be calculated quantum mechanically. Taking the radius of Helium to be about 1 Angstrom, we find $\alpha/(4\pi\epsilon_0) \approx 10^{-30} m^3$, while a full quantum calculation gives, $2/3 \times 10^{-30} m^3$. The polarizabilities of atoms and molecules are tabulated in many places and are one of their fundamental properties. The induced dipole-dipole interaction is dependent on the polarizability and is the origin of the attractive term in dispersion forces, also known as the van der Waal's attraction or the attractive part of the Lennard-Jones interaction. Classically the dipole moment is $\vec{p} = \int \rho(\vec{r}) \vec{r} d^3r$. Quantum mechanically the dipole moment is $\langle \psi | -e\vec{r} | \psi \rangle$, where ψ is the wave function in the presence of an electric field. For the Hydrogen atom, the result is,

$$\vec{p} = \frac{9}{2k} (a_B^3 E_0) \quad \text{while a conducting sphere of radius } a_B \text{ has} \quad (2)$$

where $k = 1/(4\pi\epsilon_0)$. A conducting sphere of radius a_B has an induced dipole moment given by,

$$\vec{p} = \frac{1}{k} (a_B^3 E_0) \quad (3)$$

The reason that the conducting sphere of radius a_B has a lower polarization as compared to the H atom is that the application of the electric field leads to mixing with higher orbitals of the H atom and their orbitals have significantly larger radii than a_B . E.g. if we use $2a_B$ instead of a_B , we get a factor of 8 in the conducting sphere case. The choice of the radius used for the sphere is thus critical. Nevertheless the trend is captured correctly.

Polarization of permanent dipoles due to temperature and electric field

Molecules that have ionic bonding have permanent dipole moments, for example H_2O . The dipole moment is larger for more ionic bonding and for larger molecules. The unit of molecular dipole moments is $1D$, where D stands for Debye. $1D = 3.34 \times 10^{-30} Cm$ ($= (1/c) \times 10^{-21} Cm^2/s$). The permanent dipole moment of a water molecule is $1.84D$. If we consider that in H_2O , the H atoms donate their electron completely to O , then we would find $p = 2ed$ (actually the charge transfer is smaller than this), where the bond length is about 1 Angstrom and the bond angle is about 104.5° . If we take the effective distance between the positive and negative charges to be 0.5 Angstrom , we get $p = 10^{-29} Cm \approx 3D$. This is in the right ballpark, but is too large primarily because we assumed perfect charge transfer in the ionic bond.

When an electric field is applied to a polar molecule, two things can happen, there is an induced polarization as occurs for non-polar molecules and there is tendency toward alignment of the permanent dipoles in the molecules with the applied field due to the energy gain $U = -\vec{p} \cdot \vec{E}$. In small polar molecules, the permanent dipole term dominates and the polarization effect of an applied electric field is due to the alignment of the permanent dipoles with the electric field rather than the induced polarization. In this case we need to use statistical physics to calculate the polarization effect. This calculation proceeds by assuming that initially we have a set of dipoles of magnitude p_0 , but that are randomly oriented due to thermal disorder, and there is no macroscopic polarization. When an electric field is applied, the dipoles can reduce their energy by aligning with the electric field. We calculate the average polarization by using statistical physics to average over all orientations of the molecules, so that for an electric field in the z direction,

$$\langle p_z \rangle = \frac{\int_0^{2\pi} \int_0^\pi e^{-U/k_B T} p_0 \cos\theta d\phi p_0^2 \sin\theta d\theta}{\int_0^{2\pi} \int_0^\pi e^{-U/k_B T} d\phi p_0^2 \sin\theta d\theta} \quad (4)$$

or

$$\langle p_z \rangle = \frac{\int_0^{2\pi} \int_0^\pi e^{p_0 E \cos \theta / k_B T} p_0 \cos \theta d\phi \sin \theta d\theta}{\int_0^{2\pi} \int_0^\pi e^{p_0 E \cos \theta / k_B T} d\phi \sin \theta d\theta} \quad (5)$$

Doing the ϕ integral and using $u = \cos \theta$, this reduces to,

$$\langle p_z \rangle = p_0 \frac{\int_{-1}^1 du e^{p_0 E u / k_B T} u du}{\int_{-1}^1 du e^{p_0 E u / k_B T}} = \frac{p_0}{a} \frac{e^{au}(-1 + au)|_{-1}^1}{e^{au}|_{-1}^1} = p_0 \left[-\frac{1}{a} + \coth(a) \right] \quad (6)$$

where we used $\int e^{au} u du = e^{-au}(-1 + au)/a^2$, and $a = p_0 E / k_B T$. This is called the Langevin formula and is a non-linear relation between the applied electric field and the polarization. In the high temperature limit, it becomes linear and we have $\langle p_z \rangle = p_0^2 E / 3k_B T$. In the high temperature limit the linear polarizability can then be written as,

$$\alpha = \alpha_0 + p_0^2 / 3k_B T, \quad (7)$$

where α_0 is the polarizability of the molecular orbitals and $p_0^2 / 3k_B T$ is the average alignment of the permanent dipoles. Most of our discussion will involve linear dielectrics where the response at the atomic level is of the form

$$\vec{p} = \alpha \vec{E} \quad (8)$$

At the macroscopic level the linear response is written as,

$$\vec{P} = \epsilon_0 \chi_e \vec{E} \quad (9)$$

where χ_e is the dielectric susceptibility and is the quantity that is frequently measured. It is important to find connections between the atomic level polarizabilities, α , and the macroscopic behavior characterized by the dielectric susceptibility χ_e . We shall discuss a simple model for this relation below. But first, we need to develop some of the macroscopic concepts further, particularly the connection between \vec{P} and the concept of bound charge.

Polarization and bound charge

Polarization and bound charge are the two most fundamental quantities in extending Maxwell's equations to insulating (dielectric) materials. The macroscopic polarization used in Maxwell's equation is related to the dipole moments at the atomic level. We call this variable \vec{P} , which can be thought of as an average over the atomic level dipole moments in a very small region of the material - we can think of the material being made up of a vast number of small electric dipoles, so that,

$$\vec{P}(\vec{r}) = \frac{1}{\delta V} \int_{\delta V} \vec{p}(\vec{r} - \vec{r}') d\tau' \quad (10)$$

We want to generalize Maxwell's equations to take account of the effect of these dipoles, in addition to the "free" charges that we treated before when we studied metals. Note that the term "free charge" is a misnomer, the free charge is really excess charge or net charge that appears for example in Gauss's law. In contrast, the charge in the atomic level dipoles is always balanced, i.e. there are as many negative charges as positive charges. For this reason the charges in the dipoles are called the bound charges. Therefore we introduce two charge densities the free charge ρ_f and the bound charge ρ_b . Many of the methods we developed before can be extended to find the electric field and electrostatic potential generated by the free charge ρ_f . The new aspect we have to understand is the bound charge ρ_b .

To understand the origin of bound charge consider a sheet of dielectric material where the polarization is aligned in the direction normal to the sheet surface. We also assume that there is *no applied electric field*, so this material is an electret or ferroelectric which can have finite polarization in the absence of an applied field. If the polarization is uniform, the interior of the material is charge neutral but the surfaces are charged. The excess charge density at the two surfaces (which must be equal and opposite) is called the bound charge. From this discussion it is clear that bound charge occurs due to the fact that the dielectric is made up of little dipoles. Moreover it is evident that the bound charge density is proportional to the polarization. The relation between the density of the polarization \vec{P} and the bound charge is,

$$\sigma_b = \hat{n} \cdot \vec{P}; \quad (11)$$

Due to the bound charge at the surfaces of the material, there is an electric field inside the material $\vec{E} = \sigma_b/\epsilon_0$.

Another important relation is that the density of bound charge is related to the polarization through,

$$\rho_b = -\vec{\nabla} \cdot \vec{P} \quad (12)$$

If there is no gradient in the dipole density, there is no gradient in the bound charge (remember that \vec{P} is averaged over regions much larger than the dipole size d). Proof of these relations is easiest by starting with the expression for the electrostatic potential due to the polarization $\vec{P}(\vec{r})$ which is a density of dipoles so we integrate over a dipole potential,

$$V(\vec{r}) = \int \frac{\vec{P}(\vec{r}') \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} d\tau' = \int \vec{P}(\vec{r}') \cdot \vec{\nabla}' \left(\frac{1}{|\vec{r} - \vec{r}'|} \right) d\tau' \quad (13)$$

Now we can use the product rule number 5,

$$\vec{\nabla}' \cdot \left[\frac{\vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] = \vec{P}(\vec{r}') \cdot \vec{\nabla}' \left[\frac{1}{|\vec{r} - \vec{r}'|} \right] + \frac{1}{|\vec{r} - \vec{r}'|} [\vec{\nabla}' \cdot \vec{P}(\vec{r}')] \quad (14)$$

so that

$$V(\vec{r}) = \int \vec{P}(\vec{r}') \cdot \vec{\nabla}' \left[\frac{1}{|\vec{r} - \vec{r}'|} \right] d\tau' = \int d\tau' \vec{\nabla}' \cdot \left[\frac{\vec{P}(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] - \int d\tau' \frac{1}{|\vec{r} - \vec{r}'|} [\vec{\nabla}' \cdot \vec{P}(\vec{r}')] \quad (15)$$

Now we use the Divergence theorem to write,

$$V(\vec{r}) = \int_S \frac{\vec{P}(\vec{r}') \cdot d\vec{a}'}{|\vec{r} - \vec{r}'|} - \int_\tau d\tau' \frac{1}{|\vec{r} - \vec{r}'|} [\vec{\nabla}' \cdot \vec{P}(\vec{r}')] = \int_S da' \frac{\sigma_b(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int_\tau d\tau' \frac{\rho_b(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (16)$$

where we defined $\sigma_b(\vec{r}) = \hat{n} \cdot \vec{P}(\vec{r})$, $\rho_b(\vec{r}) = -\vec{\nabla} \cdot \vec{P}$, as in Eqs. (11) and (12).

The practical consequence of this is that now we can use superposition to find the electrostatic potential and electric field using the bound charge configuration. For example for a slab if the polarization is $\vec{P} = P\hat{z}$, then the electric field is $\vec{E} = -\frac{\sigma_b}{\epsilon_0}\hat{z}$.

Example of a boundary value problem - Uniformly polarized sphere

If we have a sphere where there is a uniform density of polarization, $\vec{P} = P_0\hat{z}$, then at the surface of a sphere, the bound charge is

$$\sigma_b = \hat{r} \cdot P_0\hat{z} = P_0 \cos\theta. \quad (17)$$

We can construct an electrostatic potential corresponding to this charge distribution, by trying the $l = 1$ spherical solution, in which case,

$$V_{int}(r, \theta) = C_1 r \cos\theta; \quad V_{ext}(r, \theta) = \frac{C_2}{r^2} \cos\theta \quad (18)$$

The potential must be continuous across at $r = a$, which implies that $C_1 = C_2/a^3$. Using $E_r = -\partial V/\partial r$, the radial component of the electric field obeys,

$$E_r^{ext}(a, \theta) - E_r^{int}(a, \theta) = \frac{\sigma_b}{\epsilon_0} = \frac{2C_2}{a^3} \cos\theta + C_1 \cos\theta = \frac{2C_2}{a^3} \cos\theta + \frac{C_2}{a^3} \cos\theta = \frac{P_0 \cos\theta}{\epsilon_0} \quad (19)$$

From this we find, $C_2 = P_0 a^3/3\epsilon_0$, $C_1 = P_0/3\epsilon_0$ so that,

$$V_{int} = \frac{P_0 r}{3\epsilon_0} \cos\theta = \frac{P_0 z}{3\epsilon_0}; \quad V_{ext} = \frac{P_0 a^3}{3\epsilon_0 r^2} \cos\theta \quad (20)$$

The electric field inside the sphere is given by,

$$\vec{E}_{int} = -\frac{\partial V_{int}}{\partial z} \hat{z} = \frac{-P_0 \hat{z}}{3\epsilon_0} \quad (21)$$

The electric field is thus uniform and is in the opposite direction to the polarization. The potential outside the sphere is like that of a dipole, and the dipole moment is found by equating the general expression for a dipole with the potential V_{ext} ,

$$\frac{1}{4\pi\epsilon_0} \frac{\vec{p} \cdot \hat{r}}{r^2} = \frac{P_0 a^3}{3\epsilon_0 r^2} \cos\theta \quad (22)$$

which shows that the magnitude of the dipole moment of the uniformly polarized sphere is given by, $p = \frac{4\pi}{3} a^3 P_0$. As expected, the magnitude of the dipole moment of the sphere is the volume of the sphere times the uniform polarization of the sphere.