Dielectrics resumé

DIELECTRIC RESPONSE

Review of simple polarisation concepts – dipole moment $\underline{p} = q\underline{s}$ ($p_o = qs$), polarisation $\underline{P} = N\underline{p}$ (N is the number of dipoles per unit volume), surface charge density $\sigma_b = \underline{P}.\underline{n}$, volume charge density $\rho_b = -\nabla.\underline{P}$, polarisation current density $\underline{J}_b = \partial\underline{P}/\partial t$, polarisation $\underline{P} = \varepsilon_o\chi\underline{E}$ for a linear, isotropic homogeneous medium where χ is the susceptibility.

Equivalent circuit model of a dielectric. $C^* = \varepsilon^*C_o = (\varepsilon' - j\varepsilon'')C_o$ with ε' and ε'' ($= 1/(\omega RC_o)$), the real and imaginary components of the relative permittivity as a function of frequency, ω. The loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$. ε'' and more importantly, $\tan\delta$ is important for energy losses within the dielectric.

Resonance (damped simple harmonic motion) model for the electronic component (the only component present at optical frequencies) of the contribution to the polarisation / susceptibility as a function of frequency gives

$$\chi(\omega) = \chi_r - j\chi_i = \frac{Nq^2}{m\varepsilon_o} \cdot \frac{1}{[(\omega_o^2 - \omega^2) + j\omega\gamma]}$$

where γ is an appropriate energy dissipation term. ω_o lies in the UV region of the spectrum. $\varepsilon' = 1 + \chi_r$ has typical resonance structure near ω_o and $\varepsilon'' = \chi_I$ peaks a little below ω_o. In relation to optical measurements $\varepsilon' = n_r^2 - n_i^2$, $\varepsilon'' = 2n_r n_I$ where $n^* = n_r - jn_I$ is the complex refractive index. $n_r = c/v_{ph}$, $n_I = c\alpha/(2\omega)$ where α is the absorption constant.

A similar resonance model for the ionic contribution to χ has structure in the IR region of the spectrum due to the slower response of the ions compared to that of the electrons.

The dipolar contribution to the polarisation and static ($\omega = 0$) susceptibility, due to the reorientation of permanent dipoles in the presence of an electric field, is

$$P_{sat} = \frac{Np_o^2 E}{3k_B T} \quad , \quad \chi_D = \frac{Np_o^2}{3k_B T\varepsilon_o}$$

where P_{sat} is the (maximum) saturation polarisation at a given temperature T (provided that $p_oE \ll k_BT$, otherwise a full Langevin function integration must be performed). When considering the frequency dependence, the contribution to the susceptibility is

$$\chi(\omega) = \frac{Np_o^2}{3k_B T\varepsilon_o} \cdot \frac{1}{(1 + j\omega\tau)}$$

where τ is the relaxation time. The form of this result is typical of that for a whole range of relaxation processes. A single such process gives a response in the electrical frequency regime which may be well represented by the Debye equations:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1 + j\omega\tau)} \quad , \quad \varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1 + \omega^2\tau^2)} \quad , \quad \varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{(1 + \omega^2\tau^2)}$$

where ε_s and ε_∞ are the static and high (cf electrical) frequency permittivities respectively. For all such relaxation processes ε'' peaks at the frequency $\omega = 1/\tau$ and the peak in $\tan\delta$ occurs when $\omega = (\varepsilon_s/\varepsilon_\infty)^{1/2}/\tau$. In the electrical frequency regime the electronic and ionic contributions to the real part of the permittivity may be considered constant and the imaginary contributions are zero.

A very useful connection between the real and imaginary components of the dielectric reponse is given by the Kramers-Kronig relations which state, in the electrical frequency regime, that:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi}\int_0^\infty \frac{\omega'\varepsilon''(\omega')}{(\omega'^2-\omega^2)}\cdot d\omega' \quad , \quad \varepsilon''(\omega) = -\frac{2}{\pi}\int_0^\infty \frac{\omega[\varepsilon'(\omega')-\varepsilon_\infty]}{(\omega'^2-\omega^2)}\cdot d\omega'$$

In practice, the integral is only carried out over the electrical frequency range in which the relaxation process contributions to the permittivity are significant. If ε_∞ is replaced by 1 then the results apply to the <u>whole</u> frequency range to above UV where even the electronic contributions to the polarisation vanish.

LOCAL FIELD EFFECTS

In order to make better connection between the *macroscopic* measurements of permittivity and the *microscopic* scale induced dipole moment of a particular dipole it is convenient to express the local electric field experienced by a particular dipole as $E_{local} = E_A + E_{LOR} + E_{SPH}$.

E_{local} is the actual electric field seen by a dipole and E_A, E_{LOR} and E_{SPH} are respectively the average macroscopic electric field, the field at the centre of an imaginary spherical cavity within the dielectric centred on the dipole in question and the field due to the detailed, microscopic calculation of the field at the centre of the material "removed" from the cavity (excluding the central dipole). For a "large" sphere it is found by using a macroscopic continuum integration that $E_{LOR} = P/3\varepsilon_o$. For a cubic system it can be shown that $E_{SPH} = 0$ so we have that $E_{local} = E_A + P/3\varepsilon_o$. Given that $P = \varepsilon_o\chi E_A$ we then have that $E_{local} = (1 + \chi/3)E_A = (\varepsilon + 2)E_A/3$. Defining a polarisability, α, via $p = \alpha E_{local}$ we then have the <u>Clausius-Mossotti</u> result that

$$\alpha = \frac{3\varepsilon_o(\varepsilon-1)}{N(\varepsilon+2)} \quad , \quad or \quad \sum_i N_i\alpha_i = \frac{3\varepsilon_o(\varepsilon-1)}{(\varepsilon+2)}$$

the latter applying if more than one type of contribution is present. In the case of a monatomic low pressure gas α and χ are related via $\alpha = \varepsilon_o\chi/N$.

PIEZO-, FERRO- AND PYROELECTRIC MATERIALS

When a <u>piezoelectric</u> (PZ) material is subjected to mechanical strain this results in the appearance of a surface polarisation and hence induced electric field. Alternatively, if such a material is subjected to an electric field this results in the appearance of polarisation and there is an induced mechanical strain. To exhibit this effect there must be no centre of inversion - the material must be non-centrosymmetric. 20 out of 32 crystal classes show this effect. (Ionic structures which do have inversion symmetry can, however, exhibit the 2nd order <u>electrostriction</u> effect - an applied E field leads to a change in length $\propto$ E^2.) For PZ materials we define a <u>piezoelectric coefficient</u>, g, via E = -gT where T is the stress in pascals and a good value is g ~ 2×10^{-2} m²C⁻¹. In terms of the <u>piezoelectric charge constant</u>, d, we also have S = d.E where S is the strain and a good value of d is ~ 3×10^{-10} mV⁻¹. Given that S = sT where s is the <u>compliance</u> (the reciprocal of Young's modulus) g and d are then not independent. In practice, the PZ response is very much direction dependent. Examples of PZ materials are: Rochelle salt, PZT (lead zirconium titanate), ADP (ammonium dihydrogen phosphate), KDP (potassium dihydrogen phosphate) and quartz. Applications include: transducers, ultrasonic generators, resonators, displacement control, high voltage generation, sensors and motors. The <u>bilaminar flexure unit</u> (bimorph) is used in strain gauges, accelerometers and PZ motors.

<u>Ferroelectric</u> materials, which have a domain structure, are able to exhibit a permanent polarisation (P without E) which can be altered using an E field. In this case P depends on the history of the sample $\Rightarrow$ hysteresis. The <u>"spontaneous"</u> polarisation, P_s, vanishes at the ferroelectric Curie point. Also of importance are the <u>remanent polarisation</u>, P_r, and the <u>coercive field</u>, E_c. It is not straightforward to define ε or χ for such a system but at the Curie point values in excess of 10^4 can be obtained. TGS (triglycine sulphate), KDP, barium and strontium titanate and Rochelle salt are examples of

ferroelectric materials. A number of electro-optic applications are possible for these materials. FRAM's and FLCD's have been produced.

Ferroelectrics are a subset of <u>pyroelectric</u> materials (10 crystal classes) which are, in turn a subset of the PZ materials. The pyroelectrics exhibit the property that a change in polarisation occurs in response to a change in temperature. The <u>pyroelectric coefficient</u>, p_c, is defined via $\Delta P = p_c \Delta T$ where ΔP is the change in polarisation and ΔT the change in temperature. TGS is an example of a material with a good response - at 35° C $p_c = 5.5 \times 10^{-4}$ Cm^{-2} K^{-1}. Pyroelectrics are mainly used as detectors of IR radiation.