3.2 Mechanisms of Polarization

3.2.1 General Remarks

We have a material and we want to know its dielectric constant ϵ_r or dielectric susceptibility χ. We would want to have those quantities as functions of various variables for the same basic materials, e.g.

- $\chi = \chi(\omega)$,
  i.e. χ as a function of the ***angular frequency*** ω of the electrical field.
- $\chi = \chi(T)$;
  i.e. the dependence on the temperature ***T***.
- $\chi = \chi$**(structure)**,
  i.e. the dependence of χ on the structure of a material including the kind and density of defects in the material. As an example we may ask how χ differs from *amorphous* to *crystalline* quartz (SiO_2).

The answers to all of these questions must be contained in the *mechanisms* with which atoms and molecules respond to an electrical field, i.e. in the mechanisms leading to the formation and/or orientation of dipoles. These mechanisms are called **polarization mechanisms**.

- We want a general *theory of polarization*. This is a complex task as well it must be, given the ***plethora*** of dielectric phenomena. However, the *basic principles* are rather simple, and we are only going to look at these.

There are essentially *four basic kinds of polarization mechanisms*:

- **Interface polarization**.
  Surfaces, grain boundaries, interphase boundaries (including the surface of precipitates) may be *charged*, i.e. they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material.
- ***Electronic polarization,***
  also called atom or **atomic polarization**. An electrical field will always displace the center of charge of the electrons with respect to the nucleus and thus induce a dipole moment as discussed before. The ***paradigmatic*** materials for the simple case of *atoms with a spherical symmetry* are the noble gases in all aggregate forms.
- **Ionic polarization**.
  In this case a (solid) material must have some ionic character. It then automatically has internal dipoles, but these built-in dipoles exactly cancel each other and are unable to rotate. The external field then *induces net dipoles* by slightly displacing the ions from their rest position. The paradigmatic materials are all simple ionic crystals like **NaCl**.
- **Orientation polarization**.
  Here the (usually liquid or gaseous) material must have *natural dipoles* which can rotate freely. In thermal equilibrium, the dipoles will be randomly oriented and thus carry no net polarization. The external field aligns these dipoles to some extent and thus induces a polarization of the material. The paradigmatic material is water, i.e. H_2O in its liquid form.

Some or all of these mechanisms may act simultaneously. Atomic polarization, e.g., is always present in any material and thus becomes superimposed on whatever other mechanism there might be.

- Real materials thus can be very complicated in their dielectric behavior. In particular, *non-spherical atoms* (as, e.g., **Si** in a crystal with its four sp^3 orbitals) may show complex electronic polarization, and mixtures of ionic and covalent bonding (e.g. in SiO_2, which has about equal ionic and covalent bonding contributions) makes calculations even more difficult. But the basic mechanisms are still the ones described above.

The last three mechanisms are ***amenable*** to basic considerations and calculations; ***interface polarization***, however, defies basic treatment. There is simply no *general* way to calculate the charges on ***interfaces*** nor their contribution to the total polarization of a material.

- Interface polarization is therefore often omitted from the discussion of dielectric properties. Here, too, we will not pursue this matter much further.
- It would be totally wrong, however, to conclude that *interface polarization is technically not important* because, on the one hand, many dielectrics in real capacitors rely on interface polarization while, on the other hand, interface polarization, if present, may "kill" many electronic devices, e.g. the **MOS** transistor!
- Let's look at this in an exercise:

Exercise 3.2-2
Maximum polarization of water

Questionaire

Multiple Choice questions to 3.2.1