

3.2.6 Local Field and Clausius - Mosotti Equation

- ▶ "Particles", i.e. atoms or molecules in a liquid or solid are basking in electrical fields - the external field that we apply from the outside is not necessarily all they "see" in terms of fields.
 - First, of course, there is a tremendous electrical field *inside* any atom. We have after all, positive charges and negative charges separated by a distance roughly given by the diameter of the atom.
 - Second, we have fields *between* atoms, quite evident for ionic crystals, but also possible for other cases of bonding.
- ▶ However, if you look at the materials at a scale somewhat larger than the atomic scale, all these fields must *average to zero*. Only then do we have a field-free interior as we always assume in **electrical engineering** ("no electrical field can penetrate a metal").
- ▶ Here, however, we are looking at the effect an external field has on *atoms* and *molecules*, and it would be **preposterous** to assume that what an atom "sees" as *local* electrical field is identical to what we apply from the outside.
 - Since all our equations obtained so far always concerned the *local* electrical field - even if we did not point that out in detail before - we now must find a relation between the external field and the local field, if we want to use the insights we gained for understanding the behavior of dielectrics on a macroscopic scale.
- ▶ We define the **local field** E_{loc} to be the field felt by *one* particle (mostly an atom) of the material at its position (x, y, z) .
 - Since the superposition principal for fields always holds, we may express E_{loc} as a superposition of the external field E_{ex} and some field E_{mat} introduced by the surrounding material. We thus have

$$E_{loc} = E_{ex} + E_{mat}$$

- ▶ All electrical fields can, in principle, be calculated from looking at the charge distribution $\rho(x, y, z)$ in the material, and then solving the [Poisson equation](#) (which you should know). The Poisson equation couples the charge distribution and the potential $V(x, y, z)$ as follows:

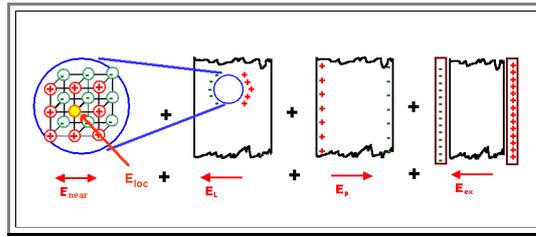
$$\Delta V = - \frac{\rho(x, y, z)}{\epsilon \cdot \epsilon_0}$$

$$\Delta = \text{Delta operator} = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2}$$

- The electrical field then is just the (negative) gradient of the potential; $E = -\nabla V$.
- ▶ Doing this is pretty tricky, however. We can obtain usable results in a good approximation in a much simpler way, by using the time-honored **Lorentz** approach or the **Lorentz model**.
 - In this approach we decompose the total field into *four* components.
 - For doing this, we *imagine* that we remove a small sphere containing a few **10** atoms from the material. We want to know the local field in the center of this sphere while it is still in the material; this is the local field E_{mat} we are after. We define that field by the force it exerts on a charge at the center of the sphere that acts as a "probe".
- ▶ The essential trick is to calculate the field produced from the atoms inside the sphere and the field inside the now empty sphere in the material. The total local field then is simple the sum of both.
 - Like always, we do not consider the charge of the "probe" in computing the field that it probes. *The cut-out sphere thus must not contain the charge we use as the field probe!*
 - The cut-out material, in general, could produce an electrical field at its center since it is composed of charges. This is the **1st** component of the field, E_{near} which takes into account the contributions of the atoms or ions inside the sphere. We will consider that field in an approximation where we average over the volume of the small sphere. To make things clear, we look at an ionic crystal where we definitely have charges in our sphere.
- ▶ E_{near} , however, is not the *only* field that acts on our probe. We must include the field that all the other atoms of the crystal produce *in* the hollow sphere left after we cut out some material. This field now fills the "empty" void left by taking out our sphere.
 - This field is called E_L (the "L" stands for Lorentz); it compensates for the cut-out part - and that provides our **2nd** component.
- ▶ Now we only have to add the "macroscopic" fields from **1.** the polarization of the material and **2.** the external field that causes everything:
 - The field E_{pol} is induced by the macroscopic polarization (i.e. by area charges equal to the polarization); it is the **3rd** component.

The external field $E_{ex} = U/d$ from the applied voltage at our capacitor which supplies the 4th component.

In a visualization, this looks like this:



The blue "sphere" cuts through the lattice (this is hard to draw). The yellow "point" is where we consider the local field; we have to omit the contribution of the charged atom there. We now have

$$E_{loc} = E_{ex} + E_{pol} + E_L + E_{near}$$

How large are those fields? We know the external field and also the field from the polarization (always assuming that the material completely fills the space inside the capacitor).

$$E_{ex} = \frac{U}{d} \quad E_{pol} = - \frac{P}{\epsilon_0}$$

We do not know the other two fields, and it is not all that easy to find out how large they are. The results one obtains, however, are quite simple:

Lorentz showed that $E_{near} = 0$ for *isotropic materials*, which is easy to imagine. Thus for cubic crystals (or polycrystals, or amorphous materials), we only have to calculate E_L .

E_L needs some thought. It is, however, a standard problem from electrostatics in a slightly different form.

In the standard problem one calculates the field in a materials with a DK given by ϵ_r that does *not* fill a rectangular capacitor totally, but is in the shape of an ellipsoid including the extreme cases of a *pure sphere*, a *thin plate* or a *thin needle*. The result is always

$$E_{ellipse} = N_p \cdot \frac{P}{\epsilon_r \cdot \epsilon_0}$$

In words: The field inside a dielectric in the shape of an ellipsoid (of any shape whatsoever) that is put between the parallel plates of a typical capacitor arrangement, is whatever it would be if the dielectric fills the space between the plates completely times a *number* N_p , the value of which depends on the geometry.

N_p is the so-called **depolarization factor**, a *pure number*, that only depends on the shape of the ellipsoid. For the extreme cases of the ellipsoid we have fixed and well-known **depolarization factors**:

- **Thin plate:** $N = 1$
- **Needle:** $N = 0$
- **Sphere:** $N = 1/3$

Our case consists of having a sphere with $\epsilon_r = 1$. We thus obtain

$$E_L = \frac{P}{3\epsilon_0}$$

We have now all components and obtain

$$E_{\text{loc}} = \frac{U}{d} - \frac{P}{\epsilon_0} + \frac{P}{3\epsilon_0}$$

- $U/d - P/\epsilon_0$ is just the field we would use in the Maxwell equations, we call it E_0 . It is the *homogeneous field* averaged over the whole volume of the homogeneous material
- The *local field* finally becomes

$$E_{\text{loc}} = E_0 + \frac{P}{3\epsilon_0}$$

This seems a bit odd? How can the *local* field be different from the *average* field?

- This is one of the tougher questions one can ask. The answer, not extremely satisfying, comes from the basic fact that *all* dipoles contribute to E_0 , whereas for the *local field* you discount the effect of *one* charge - the charge you use for probing the field (the field of which must not be added to the rest!).
- If you feel somewhat uneasy about this, you are perfectly right. What we are excluding here is the action of a charge on itself. While we may do that because that was *one* way of defining electrical fields (the other one is Maxwells equation defining a field as directly resulting from charges), we can not so easily do away with the *energy* contained in the field of a single charge. And if we look at this, the whole theory of electromagnetism blows up! If the charge is a point charge, we get infinite energy, and if it is not a point charge, we get other major contradictions.
- Not that it matters in everyday aspects - it is more like a philosophical aspect. If you want to know more about this, read chapter 28 in the "[Feynman lectures, Vol. 2](#)"

But do not get confused now! The relation given above is perfectly valid for everyday circumstances and ordinary matter. Don't worry - be happy that a relatively complex issue has such a simple final formula!

We now can relate the *macroscopic* and *microscopic* parameters. With the [old relations](#) and the new equation we have a grand total of:

$$\begin{aligned} \mu &= \alpha \cdot E_{\text{loc}} \\ P &= N \cdot \alpha \cdot E_{\text{loc}} \\ E_{\text{loc}} &= E_0 + \frac{P}{3\epsilon_0} \end{aligned}$$

From this we obtain quite easily

$$\begin{aligned} P &= N \cdot \alpha \cdot \left(E_0 + \frac{P}{3\epsilon_0} \right) \\ P &= \frac{N \cdot \alpha \cdot E_0}{1 - N \cdot \alpha / 3\epsilon_0} \end{aligned}$$

With N = density of dipoles

Using the [definition](#) of P

$$P = \epsilon_0 \cdot \chi \cdot E = \epsilon_0 \cdot (\epsilon_r - 1) \cdot E$$

- and inserting it into the equations above gives as *final result* the connection between the polarizability α (the microscopic quantity) and the relative dielectric constant ϵ_r (the macroscopic quantity):

$$\frac{N \cdot \alpha}{3 \epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2}$$
$$= \frac{\chi}{\chi + 3}$$

- ▶ This is the **Clausius - Mosotti equation**, it relates the *microscopic* quantity α on the left hand side to the *macroscopic* quantity ϵ_r (or, if you like that better, $\chi = \epsilon_r - 1$) on the right hand side of the equation. This has two far reaching consequences
 - We now can *calculate* (at least in principle) the dielectric constants of all materials, because we know how to calculate α .
 - We have an *instrument* to measure *microscopic* properties like the polarizability α , by measuring *macroscopic* properties like the dielectric constant and converting the numbers with the Clausius-Mosotti equation.
- ▶ You must also see this in an historical context: With the Clausius-Mosotti equation the dielectric properties of materials were essentially reduced to known electrical properties. There was nothing mysterious anymore about the relative dielectric constant. The next logical step now would be to apply quantum theory to dielectric properties.