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- 1. Lorentz's field.***
  - 2. Clausius-Massotti formula***

# *Non-polar dielectrics. Lorentz's field. Clausius-Massotti formula.*

For a *non-polar system* the fundamental equation for the dielectric permittivity (2.49) is simplified to:

$$\frac{\varepsilon - 1}{4\pi} \mathbf{E} = \sum_k N_k \alpha_k (\mathbf{E}_i)_k \quad (2.50)$$

In this case, only the relation between the internal field and the Maxwell field has to be determined.

Let us use the *Lorentz approach* in this case. He calculated the internal field in homogeneously polarized matter *as the field in a virtual spherical cavity*.

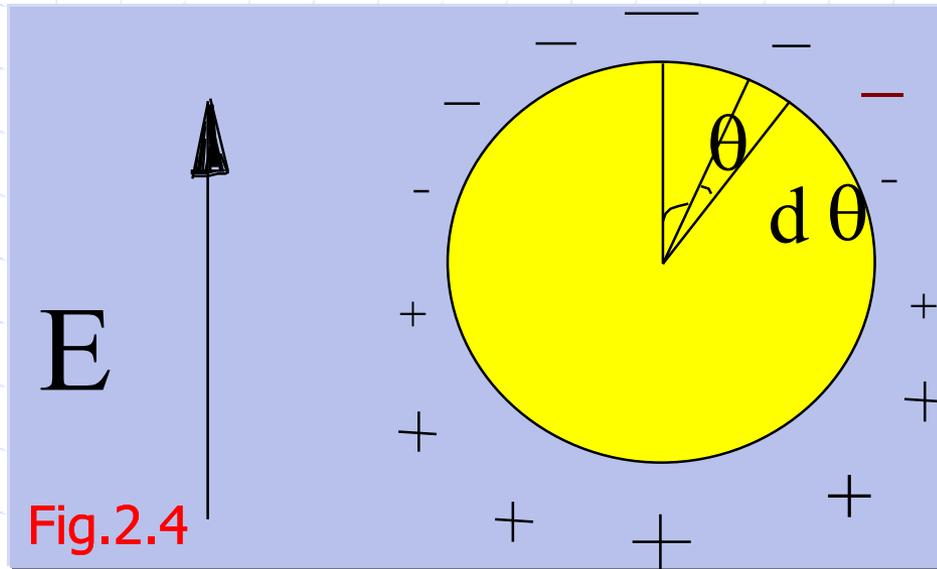
The field in such a cavity differs from the field in a real cavity, given by (2.14), because in the latter case the polarization adjusts itself to the presence of the cavity.

Therefore the **polarization in the environment of a real cavity is not homogeneous**, whereas the polarization in the environment of a virtual cavity remains homogeneous.

$$\mathbf{E}_C = \frac{3\varepsilon}{2\varepsilon + 1} \mathbf{E}_0 \quad (2.14)$$

The field in a virtual spherical cavity, which we call the **Lorentz field  $E_L$** , is the sum of:

1. the Maxwell field  **$E$**  caused by the external charges and by the apparent charges on the outer surface of the dielectric, and
2. the field  **$E_{sph}$**  induced by the apparent charges on the boundary of the cavity (see fig.2.4).



The field  **$E_{sph}$**  is calculated by subdividing the boundary in infinitesimally small rings perpendicular to the field direction. The apparent surface charge density on the rings is  **$-P \cos \theta$** , their surface is  **$2\pi r^2 \sin \theta d\theta$**  so that the total charge on each ring amounts to:

$$de = -2\pi r^2 \sin \theta d\theta P \cos \theta \quad (2.51)$$

According to **Coulomb's law**, a charge element  **$de$**  to the field component in the direction of the external field, given by:

$$dE = \frac{de}{r^2} \cos\theta \quad (2.52)$$

Combining (2.51) and (2.52), we find for the component of  $\mathbf{E}_{sph}$  in the direction of the external field :

$$\mathbf{E}_{sph} = \mathbf{P} \int_0^\pi 2\pi \sin\theta \cos^2\theta d\theta = \frac{4\pi}{3} \mathbf{P} \quad (2.53)$$

For the reasons of symmetry, the other components of  $\mathbf{E}_{sph}$  are zero, and we have with  $\mathbf{E}_L = \mathbf{E} + \mathbf{E}_{sph}$ :

$$\mathbf{E}_L = \frac{\varepsilon + 2}{3} \mathbf{E} \quad (2.54)$$

***This is Lorentz's equation for the internal field.***

Substituting (2.54) into (2.50), we find:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_k N_k \alpha_k \quad (2.55)$$

This relation is generally called the ***Clausius-Massotti equation.***

For a pure compound it is reduced to:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha \quad (2.56)$$

From the *Clausius-Mossotti equation* for a pure compound, it follows that it is useful to define a **molar polarization**  $[P]$ :

$$[P] = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} \quad (2.57)$$

where  $d$  is the density and  $M$  the molecular weight. When the *Clausius-Mossotti equation* is valid  $[P]$  is a constant for a given substance:

$$[P] = \frac{4\pi}{3} N_A \alpha \quad (2.58)$$

The *Clausius-Mossotti equation* can also be used for polar systems in high-frequency alternating fields:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi}{3} \sum_k N_k \alpha_k \quad (2.59)$$

in which  $\epsilon_\infty$  is the dielectric constant at a frequency at which the permanent dipoles (i.e. the orientation polarization) can no longer follow the changes of the field but where the atomic and electronic polarization are still the same as in static fields.

Often this equation is used for still higher frequencies, where the atomic polarization too cannot follow the changes of the field. If according to Maxwell relation for the dielectric constant and the refractive index  $\epsilon_\infty = n^2$ , it is possible to write:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum_k N_k \alpha_k^e \quad (2.60)$$