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Dipole moments and electrostatic problems

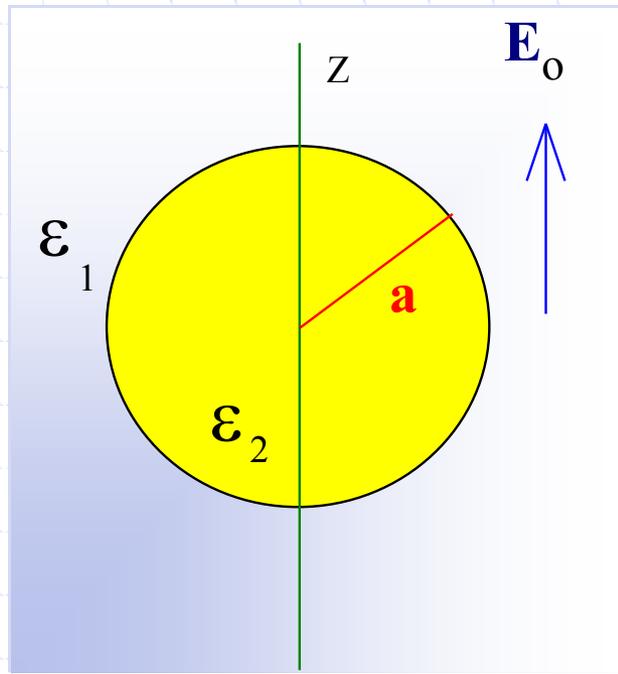


Figure 1

Let us put a dielectric sphere of radius a and dielectric constant ϵ_2 , in a dielectric extending to infinity (**continuum**), with dielectric constant ϵ_1 , to which an external electric field is applied. Outside the sphere the potential satisfies *Laplace's equation* $\Delta\phi=0$, since no charges are present except the charges at a great distance required to maintain the external field. On the surface of the sphere *Laplace's equation* is **not valid**, since there is an apparent surface charge.

Inside the sphere, however, *Laplace's equation* can be used again. Therefore, for the description of ϕ , we use two different functions, ϕ_1 and ϕ_2 , outside and inside the sphere, respectively.

Let us consider the center of the sphere as the origin of the coordinate system, we **choose z-axis** in the direction of the uniform field. Following relation in the terms of *Legendre polynomial* represents the general solution of *Laplace's equation*:

$$\phi_1 = \sum_{n=0}^{\infty} \left(A_n r^n + \frac{B_n}{r^{n+1}} \right) P_n(\cos \theta)$$

$$\phi_2 = \sum_{n=0}^{\infty} \left(C_n r^n + \frac{D_n}{r^{n+1}} \right) P_n(\cos \theta)$$

The boundary conditions are:

$$1. \quad (\phi_1)_{r \rightarrow \infty} = -E_0 z = -E_0 r \cos \theta \quad (2.1)$$

$$2. \quad (\phi_1)_{r=a} = (\phi_2)_{r=a} \quad \text{Since } \phi \text{ is continuous across a boundary} \quad (2.2)$$

$$3. \quad \epsilon_1 \left(\frac{d\phi_1}{dr} \right)_{r=a} = \epsilon_2 \left(\frac{d\phi_2}{dr} \right)_{r=a} \quad \text{since the normal component of } \mathbf{D} \text{ must be continuous at the surface of the sphere} \quad (2.3)$$

4. At the center of the sphere ($r=0$) ϕ_2 must not have a singularity.

On account of the *first boundary condition* and the fact that the *Legendre functions* are linearly independent, all coefficients A_n are zero except A_1 , which has the value $A_1 = -E_0$. On account of the fourth boundary condition, all coefficients D_n are zero. Thus, one can write:

$$\phi_1 = \sum_{n=0}^{\infty} \frac{B_n}{r^{n+1}} P_n(\cos \theta) - E_0 r \cos \theta \quad (2.4)$$

$$\phi_2 = \sum_{n=0}^{\infty} C_n r^n P_n(\cos \theta) \quad (2.5)$$

Applying the second and third boundary condition to (2.4) and (2.5), we have for any of n except $n=1$:

$$\frac{B_n}{a^{n+1}} = C_n a^n \quad (2.6)$$

and

$$-\varepsilon_1 (n+1) \frac{B_n}{a^{n+2}} = \varepsilon_2 n C_n a^{n-1} \quad (2.7)$$

From these equations it follows that $B_n=0$ and $C_n=0$ for all values of n except $n=1$. When $n=1$, it can be written:

$$\frac{B_1}{a^2} - E_0 a = C_1 a,$$

$$\varepsilon_1 \left(\frac{2B_1}{a^3} + E_0 \right) = -\varepsilon_2 C_1$$

Hence:

$$B_1 = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} a^3 E_0$$

$$C_1 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} E_0$$

Substitution of these values in (2.4) and (2.5) gives:

$$\phi_1 = \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \frac{a^3}{r^3} - 1 \right) E_0 z \quad (2.8)$$

$$\phi_2 = -\frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2} E_0 z \quad (2.9)$$

Since the potential due to the external charges is given by $\phi = -E_0 z$, it follows from (2.8) and (2.9) that the contributions ϕ'_1 and ϕ'_2 due to the apparent surface charges are given by:

$$\phi'_1 = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \frac{a^3}{r^3} E_0 z \quad (2.10)$$

$$\phi'_2 = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} E_0 z \quad (2.11)$$

The expression (2.10) is identical to that for the potential due to an *ideal dipole at the center of the sphere*, surrounded by a dielectric continuum, the dipole vector being directed along the z-axis and given by:

$$\mathbf{m} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} a^3 \mathbf{E}_0 \quad (2.12)$$

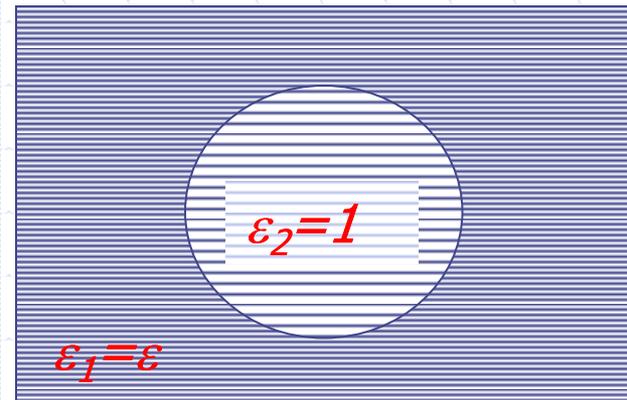
The total field E_2 inside the sphere is according to (2.9), given by:

$$E_2 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} E_0 \quad (2.13)$$

A spherical cavity in dielectric

In the special case of a spherical cavity in dielectric ($\varepsilon_1 = \varepsilon$; $\varepsilon_2 = 1$), equation (2.13) is reduced to:

$$E_C = \frac{3\varepsilon}{2\varepsilon + 1} E_0$$



$$(2.14)$$

This field is called the "***cavity field***". The lines of dielectric displacement given by $D_c = 3D_0 / (2\varepsilon + 1)$ are more dense in the surrounding dielectric, since D is larger in the dielectric than in the cavity

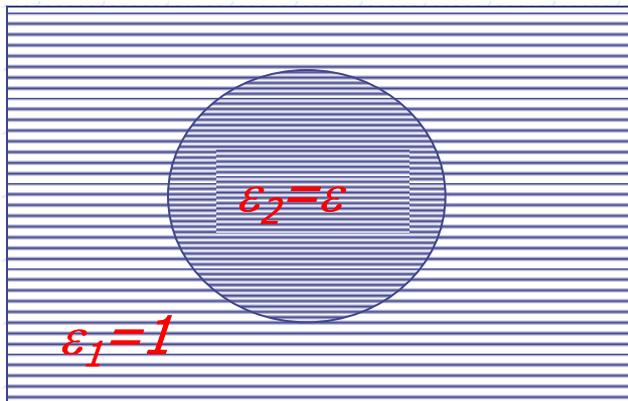
A dielectric sphere in vacuum

For a dielectric sphere in a vacuum ($\epsilon_1=1$; $\epsilon_2=\epsilon$), the equation (2.13) is reduced to:

$$\mathbf{E} = \frac{3}{2\epsilon + 1} \mathbf{E}_0 \quad (2.15)$$

where \mathbf{E} is the field inside the sphere.

The density of the lines of dielectric displacement \mathbf{D}_s is higher in the sphere than in the surrounding vacuum, since inside the sphere $\mathbf{D}_s = 3\epsilon\mathbf{E}_0 / (\epsilon + 2)$. Consequently, it is larger than \mathbf{E}_0 .



According to (2.12), the field outside the sphere due to the apparent surface charges is the same as the field that would be caused by a dipole \mathbf{m} at the center of the sphere, surrounded by a vacuum, and given by:

$$\mathbf{m} = \frac{\epsilon - 1}{\epsilon + 2} a^3 \mathbf{E}_0 \quad (2.16)$$

This is the ***electric moment of the dielectric sphere***. Therefore (2.16) can be checked in another way. The uniform field \mathbf{E}_s in the dielectric sphere, given by (2.15), causes a **homogeneous polarization** of the sphere. The induced dipole moment per cm^3 is according to the definition of \mathbf{P} , given by:

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi} \mathbf{E}_s = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{3}{4\pi} \mathbf{E}_0 \quad (2.17)$$

Hence the total moment of the sphere is:

$$\mathbf{m} = \frac{4}{3} \pi a^3 \mathbf{P} = \frac{\varepsilon - 1}{\varepsilon + 2} a^3 \mathbf{E}_0 \quad (2.18)$$

which is in accordance with (2.16).

Polarizability α

When a body is placed in a uniform electric field E_0 *in vacuum*, caused by a fixed charge distribution, its dipole moment will in general change.

The difference between the dipole moments before and after the application of the field E_0 is called the induced dipole moment m . If a body shows an induced dipole moment differing from zero upon application of a uniform field E_0 , it is said to be *polarizable*.

In most cases polarizable bodies are polarized linearly, that is, the induced moment m is proportional to E_0 . In this case one has:

$$m = \alpha E_0 \quad (2.19)$$

where α is called the *(scalar) polarizability of the body*.

From the dimensions of the dipole moment, $[e][l]$, and the field intensity, $[e][l]^{-2}$, it follows that the polarizability has the dimension of a volume. Using the above definition of the polarizability, we conclude from equation (2.12) that a dielectric sphere of dielectric constant ϵ and with radius a has a polarizability:

$$m \quad \alpha = \frac{\epsilon - 1}{\epsilon + 2} a^3 E_0 \quad (2.20)$$

For a **conducting sphere** in the case $\epsilon \rightarrow \infty$ from the relation (2.20) one can obtain that a conducting sphere with radius a has a polarizability:

$$\alpha = a^3 \quad (2.21)$$

There is the **fundamental difference** between the two types of polarization. In the case of **dielectric sphere every volume element is polarized**, whereas in the case of a **conducting sphere the induced dipole moment arises from true surface charges**.

In some simple cases of spherical molecules, it is possible with α to describe the **induced polarization**. In general, it is not true and we have to use a **polarizability tensor α** provided the effects remain linear. It leads to:

$$\mathbf{m} = \alpha \mathbf{E}_0 \quad (2.22)$$

*In such a case the **induced dipole moment** need to have **the same direction** as the **applied field**. In general this direction will depend on the position of the body relative to the polarizing field.*

Polarization and Energy

Very often it is useful to collect some of the elementary charges into a group forming an atom, a molecule, a unit cell of a crystal, or some larger unit. Let the j th unit of this type contain the s elementary charges $e_{j1}, e_{j2}, \dots, e_{jk}, \dots, e_{js}$ and let

$$x_j = (\mathbf{r}_{j1}, \mathbf{r}_{j2}, \dots, \mathbf{r}_{jk}, \dots, \mathbf{r}_{js}) \quad (2.23)$$

be an abbreviation for the set of all their displacements $\mathbf{r}_{j1}, \dots, \mathbf{r}_{js}$.

Then

$$\mathbf{m}(x_j) = \sum_{k=1}^s e_{jk} \mathbf{r}_{jk} \quad (2.24)$$

is the **electric moment** of this j th group of charges, and

$$\mathbf{M}(X) = \sum_j \mathbf{m}(x_j) \quad (2.25)$$

where the sum extends over all the groups.

The **vector sum** of their individual moments $m(x_j)$ thus forms the **total moment** $M(X)$. The main aim of this part is to find the average displacements, and hence the **average electric moment** under the influence of an external electric field.

In order to obtain a preliminary idea about the average contributions of certain displacements to the electric moment we shall consider two cases, each of which has its characteristic type of displacement:

- 1) The displaced charge is bound elasticity to an equilibrium position; *(induced dipole moment)*
- 2) A charge has several equilibrium positions, each of which it occupies with a probability which depends on the strength of an external field. *(Permanent dipole moment)*

In the first case the displacement of the charge e , carried out by a particle of mass m on a distance r , restoring force proportional to $-r$ acts on the particle in a direction opposite to the displacement (hence the - sign). Thus if the constant external field E is applied:

$$\frac{d^2 \mathbf{r}}{dt^2} = -\omega_0^2 \mathbf{r} + \frac{e}{m} \mathbf{E} \quad (2.26)$$

where $\omega_0/2\pi$ denotes the frequency of oscillation, and $-m\omega_0^2 \mathbf{r}$ is the restoring force. Equation (2.26) can be written

$$\frac{d^2}{dt^2} (\mathbf{r} - \mathbf{r}') = -\omega_0^2 (\mathbf{r} - \mathbf{r}') \quad (2.27)$$

where

$$\mathbf{r}' = \frac{e}{m\omega_0^2} \mathbf{E} \quad (2.28)$$

i.e. $d\mathbf{r}'/dt=0$. The charge e , therefore, carries out harmonic oscillations about the position \mathbf{r}' which thus represents the time average of its displacement, i.e. if C and δ are constant

$$\mathbf{r} = \mathbf{r}' + C \cos(\omega_0 t + \delta)$$

The **average electric moment (induced)** is, therefore,

$$\mu_{\alpha} = er' = \frac{e}{m\omega_0^2} E \quad (2.29)$$

For an example of the second mechanism of polarization let us consider a particle with the **charge e** that can be in two different equilibrium position **A** and **B** , separated by a distance **b** . In the absence of an electric field the particle has the same energy in each position.

Thus, it may be assumed to move in a potential field of the type shown in Fig.2.2. In equilibrium with its surroundings it will **oscillate** with an **energy of order kT** about either of the equilibrium positions, say about **A** .

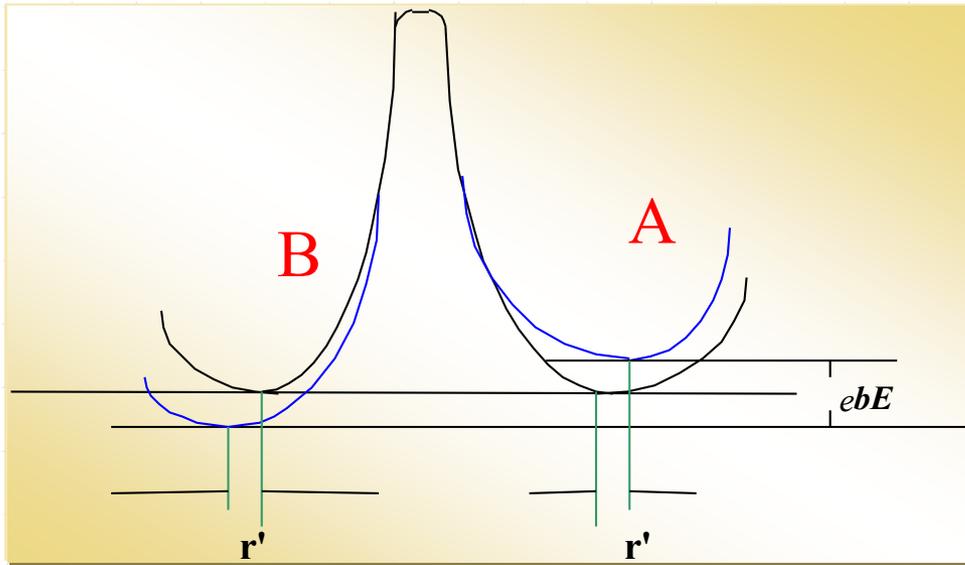


Fig.2.2

Occasionally, however, through a fluctuation, it will be acquire sufficient energy to jump over the potential wall separating it from **B**. On the time of average, therefore, it will stay in **A** as long as in **B**, i.e. the **probability** of finding it in either **A** or **B** is **0.5**.

The presence of a field **E** will affect this in two ways. **Firstly**, as in case (1), the equilibrium position will be shifted by amount **r'** which for simplicity will be assumed to be the same in **A** and **B**. **Secondly**, the potential energies V_A , V_B of the particle in the two equilibrium positions will be altered because its interaction energy with the external field differs by $e(bE)$, i.e.

$$V_A - V_B = e(bE) \quad (2.30)$$

Therefore, in average, the particle should spend more time near B than near A . Actually, since according to statistical mechanics, the probability of finding a particle with energy V is proportional to $e^{-V/kT}$,

$$p_A = \frac{e^{-V_A/kT}}{e^{-V_A/kT} + e^{-V_B/kT}}, \quad p_B = \frac{e^{-V_B/kT}}{e^{-V_A/kT} + e^{-V_B/kT}} \quad (2.31)$$

are the probabilities for positions A and B respectively. They have been normalized in such a way as to make

$$p_A + p_B = 1 \quad (2.32)$$

in agreement with the physical condition that the particle must be in one of the two positions. Thus from (2.31) and (2.30)

$$p_B - p_A = \frac{e^{e(\mathbf{bE})/kT} - 1}{e^{e(\mathbf{bE})/kT} + 1} > 0. \quad (2.33)$$

It follows from the definition of the probabilities p_A and p_B that if the condition of the system over a long time t_1 is considered, the particle will spend a time (use 2.32)

$$p_A t_1 = \left[\frac{1}{2} - \frac{1}{2} (p_B - p_A) \right] t_1$$

in position **A**, and

$$p_B t_1 = \left[\frac{1}{2} - \frac{1}{2} (p_B - p_A) \right] t_1$$

in position **B**. It has thus been displaced by the distance **b** from **A** to **B** during the fraction $1/2(p_B - p_A)$ of the time t_1 . The **average moment induced** by the field is thus

$$\frac{1}{2} e \mathbf{b} (p_B - p_A) \quad (2.34)$$

Hence, if θ is the angle between **b** and **E**, the projection of the induced moment into the field direction is, using (2.34) and (2.33) given by

$$\frac{1}{2} e b \cos \theta \frac{e^{ebE \cos \theta / kT} - 1}{e^{ebE \cos \theta / kT} + 1} > 0. \quad (2.35)$$

In most cases it is permissible to assume

$$e b E \ll k T \quad (2.36)$$

for putting $e=4.8 \cdot 10^{-10}$ e.s.u., $E=300$ v/cm.=1 e.s.u., $b=10^{-8}$ cm. \approx distance between neighboring atoms in a molecule, and $T=300^\circ\text{C}$ (room temperature) one finds

$$\frac{ebE}{kT} \cong \frac{4.8 \times 10^{-10} \times 10^{-8} \times 1}{1.38 \times 10^{-16} \times 300} \cong 10^{-4}$$

Developing (2.35) in terms of ebE/kT , the average induced moment in the field direction is found to be

$$\frac{\left(\frac{1}{2}eb\right)^2 \cos^2 \theta}{kT} E + er' \quad (2.37)$$

where er' is a term similar to those considered in case (1) which has been added to account for the elastic displacement. Often two charges $+e$ and $-e$ are strongly bound, forming an electric dipole $\mu=ea$, where a is the distance between them. The above case (2) then leads to the same as that of a dipole μ having two equilibrium positions with opposite dipole direction, but with equal energy in the absence of a field.

In a field \mathbf{E} the energy of interaction between field and dipole is given by

$$- (\boldsymbol{\mu} \mathbf{E}) \quad (2.38)$$

so that $2\mu E \cos\theta$ is the energy between the two positions if $\angle\theta$ is the angle $\boldsymbol{\mu}$ and \mathbf{E} . This equivalent to equation (2.30) if

$$\boldsymbol{\mu} = \frac{1}{2} e \mathbf{b} \quad (2.39)$$

Actually putting an immobile charge $-e$ halfway between A and B turns case (2) into the present case. Clearly the induced moment must be the same for both cases because the charge $-e$ is immobile, and its distance from A and B is $1/2 \mathbf{b}$, leading to a dipole $\boldsymbol{\mu}$. Introducing (2.39) into (2.37) yields for the induced moment in the field direction

$$\frac{\mu^2 \cos^2 \theta}{kT} E + e r' \quad (2.40)$$

In contrast to case (1) the electric moment (orientation polarization) now depends on temperature. A matter consisting of a great number of such dipoles will have a temperature-dependent dielectric permittivity in contrast to a substance in which all charges are bound elastically.

This means that in the ***dipolar case the entropy of the substance is decreased by the field.***

The difference between the action of the field in the two cases (1) and (2) is essential for the whole theory of dielectric permittivity.

In the **case (1)**, the field **exerts a force** on elastically bound charge, thus shifting its equilibrium position. In **case (2)** this force of the field on the charge again leads to contribution of type (1) denoted by **ϵ'** in equations (2.37) and (2.40). It would be **wrong**, however, to assume that the field by this force turns a dipole from one equilibrium position into another. This is affected in a more indirect way because the field slightly alters the **probabilities** of a jump of a dipole from one equilibrium position to another.

Internal field; Langeven function

In dielectric *two essentially different types of interaction forces should be distinguished*. Forces due to chemical bonds, van der Waals attraction, repulsion forces, and others have all *such short ranges that usually interaction between nearest neighbors only need be considered*. Compared with these forces *dipolar interaction forces have a very long range*.

As it was shown above *a polarized dielectric can be considered as composed of small regions each having a certain dipole moment, and the total dipole moment of the body is the vector sum of the moments of these regions*. It is also known from macroscopic theory that the *energy per unit volume of a macroscopic specimen depends on its shape*. This implies that interaction between dipoles must be taken into account even at macroscopic distances.

Due to the long range of the dipolar forces an accurate calculation of the interaction of a particular dipole with all other dipoles of a specimen would be very complicated.

A very good approximation can be made by considering that the dipoles beyond a certain distance, say a_m can be replaced by a **continuous medium**, having the macroscopic dielectric properties of the specimen.

Thus the dipole whose interaction with the rest of the specimen we are calculating may be considered as surrounded by a sphere of radius a_m containing a discrete number of particles, beyond which there is a continuous medium To make this a good approximation **the dielectric properties of the whole region within the sphere should be equal to those of a macroscopic specimen**, i.e. it should contain a sufficient number of molecules to make fluctuations very small.

Lorentz's method for the treatment of dipolar interaction: *from a macroscopic specimen select a microscopic spherical region, which is sufficiently large to have the same dielectric properties as a macroscopic specimen. The interaction between the dipoles inside the spherical region will then be calculated in an exact way, but for the calculation of their interaction with the rest of the specimen the latter is considered as a continuous medium.*

We shall now investigate the dependence of the polarization on the electric fields working on a single molecule. For the **induced polarization** P_α we write:

$$P_\alpha = \sum_k N_k \alpha_k (E_i)_k \quad (2.41)$$

where N is the number of particles per cm^3 , α the **scalar polarizability** of a particle and E_i the **average field strength** acting upon that particle. The index k refers to the k -th kind of particle.

The field E_i is called the internal field. It is defined as the total electric field at the position of the particle minus the field due to the particle itself. The calculation of E_i is one of the important problems associated with the theory of dielectrics. This calculation can be executed both in the **continuum approach** for the environment of the molecule and with the help of **statistical mechanics**.

The **orientation polarization** can be written as:

$$P_\mu = \sum_k N_k \bar{\mu}_k \quad (2.42)$$

where μ_k is the value of the **permanent dipole vector averaged** over all orientations.

The value μ_k can be computed from the energy of the permanent dipole in the electric field. This energy is dependent on the part of the electric field tending to direct the permanent dipoles. This part of the field is called the **directing field E_d** .

The dependence of μ_k on E_d is computed from the energy of dipole in electric field as we did above:

$$W = -\boldsymbol{\mu} \cdot \mathbf{E}_d = -\mu E_d \cos \theta \quad (2.43)$$

where θ is the angle between the directions of E_d and μ . *Since W is the only part of the energy, which depends on the orientation of the dipole, the relative probabilities of the various orientations of the dipole depend on this energy W according to Boltzmann's distribution law.*

Let us consider the average value of $\langle \cos \theta \rangle$. For a random distribution of the dipoles in matter we have $\langle \cos \theta \rangle = 0$, whereas $\langle \cos \theta \rangle = 1$ if all the dipoles have the same direction as E_d .

From Boltzmann's law

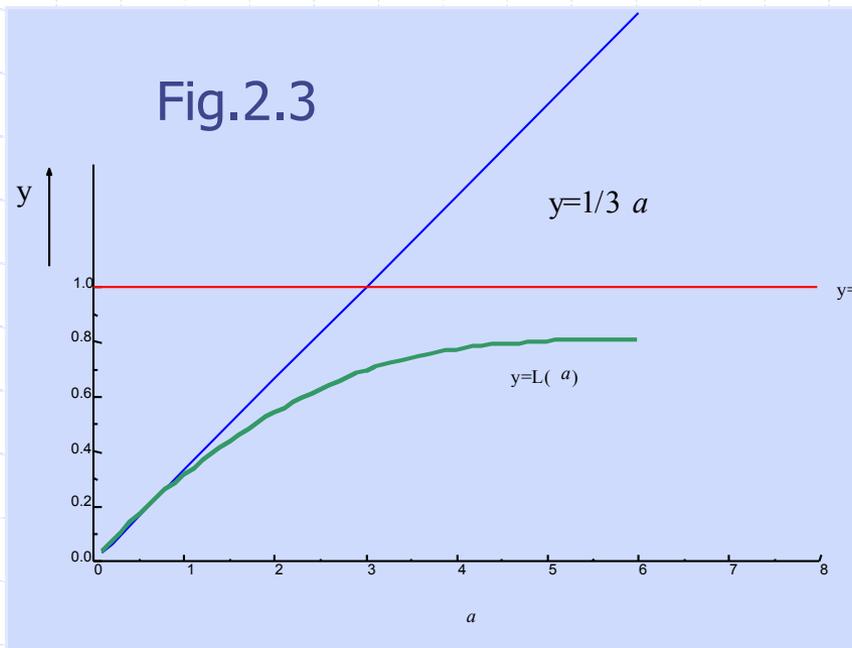
$$\begin{aligned} \overline{\cos \theta} &= \frac{\int_0^\pi \cos \theta e^{\frac{\mu E_d \cos \theta}{kT}} \frac{1}{2} \sin \theta d\theta}{\int_0^\pi e^{\frac{\mu E_d \cos \theta}{kT}} \frac{1}{2} \sin \theta d\theta} = \frac{1}{a} \frac{\int_{-a}^a e^x x dx}{\int_{-a}^a e^x dx} = \\ &= \frac{1}{a} \frac{[xe^x - e^x]_{-a}^{+a}}{[e^x]_{-a}^{+a}} = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} = \cot \operatorname{an}ha - \frac{1}{a} = L(a), \end{aligned} \quad (2.44)$$

where $\frac{\mu E_d \cos \theta}{kT} = x$ and $\frac{\mu E_d}{kT} = a$

$L(a)$ is called **Langeven function**

In Fig.2.3 the Langeven function $L(a)$ is plotted against a . $L(a)$ has a limiting value **1**, which was to be expected since this is the maximum of $\cos \theta$. For small values of a , $\langle \cos \theta \rangle$ is linear in E_d :

$$\overline{\cos \theta} = \frac{1}{3} a = \frac{\mu E_d}{3kT} \quad \text{if } 0 \leq a \ll 1 \quad (2.45)$$



The approximation of equation (2.45) may be used as long as

$$a = \frac{\mu E_d}{kT} < 0.1 \text{ or } E_d < \frac{0.1kT}{\mu}.$$

At room temperature ($T=300^\circ \text{ K}$) this gives for a dipole of $4D$:

$$E_d < \frac{0.1kT}{\mu} = 3 \cdot 10^5 \text{ v/cm}$$

For a value of μ smaller than the large value of $4D$, the value calculated for E_d is even larger. In usual dielectric measurements, E_d is much smaller than 10^5 v/cm and the use of (2.45) is allowed.

From equation (2.45) it follows that:

$$\boldsymbol{\mu} = \mu \langle \cos \theta \rangle = \frac{\mu^2}{3kT} \mathbf{E}_d \quad (2.46)$$

Substituting this into (2.42) we get:

$$\mathbf{P}_\mu = \sum_k N_k \frac{\mu^2}{3kT} (\mathbf{E}_d)_k \quad (2.47)$$

From the first lecture we had

$$\frac{\varepsilon - 1}{4\pi} \mathbf{E} = \mathbf{P}_\alpha + \mathbf{P}_\mu \quad (2.48)$$

We now substitute (2.41) and (2.47) into (2.48) and find:

$$\frac{\varepsilon - 1}{4\pi} \mathbf{E} = \sum_k N_k \left[\alpha_k (\mathbf{E}_i)_k + \frac{\mu_k^2}{3kT} (\mathbf{E}_d)_k \right] \quad (2.49)$$

This is the **fundamental equation** is the starting point for expressing \mathbf{E}_i and \mathbf{E}_d as functions of the **Maxwell field \mathbf{E}** and the dielectric constant ε .

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:

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

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*.

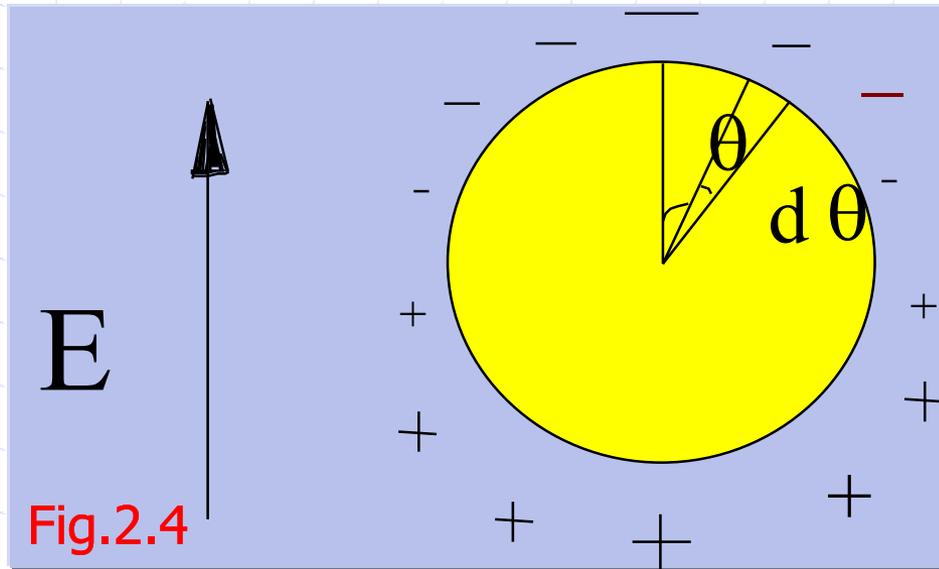
The field in such a cavity differs from the field in a real cavity, given by (2.14), because in the latter case the polarization adjusts itself to the presence of the cavity.

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.

$$\mathbf{E}_c = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E}_0$$

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 ϵ_{∞} 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:

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