The Problems of Electric Polarization

Dielectrics in Static Field

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Tutorial lecture

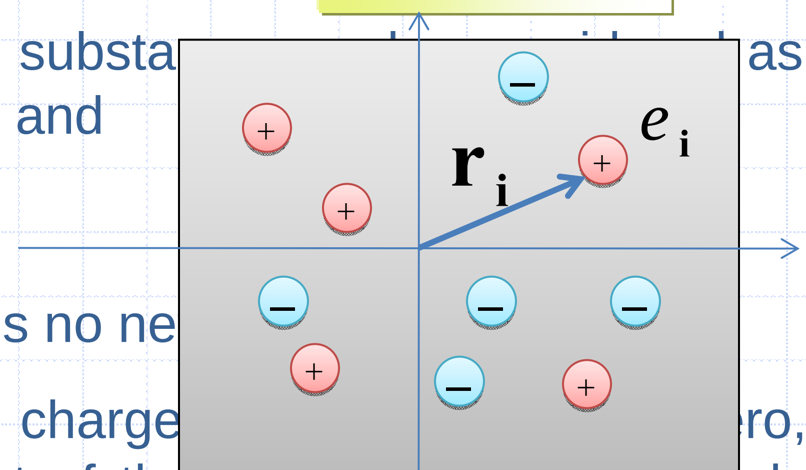
Electric dipole - definition

The electric moment of a point charge relative to a fixed point is defined as $e\boldsymbol{r}$, where $\boldsymbol{r}$ is the radius vector from the fixed point to e.

Consequently, the total dipole moment of a whole system of charges e_i relative to a fixed origin is defined as:

$$\boldsymbol{m} = \sum_i e_i \boldsymbol{r}_i$$

A dielectric substa… as consisting of elementary charges e_i, and



if it contains no ne…

If the net charge … ero, the electric moment is independent of the choice of the origin: when the origin is displaced over a distance $\boldsymbol{r}_o$, the change in $\boldsymbol{m}$ is given by:

$$\Delta \boldsymbol{m} = -\sum_i e_i \mathbf{r}_o = -\mathbf{r}_o \sum_i e_i$$

Thus $\Delta \boldsymbol{m}$ equals zero when the net charge is zero.

Then $\boldsymbol{m}$ is independent of the choice of the origin. In this case equation (1.1) can be written in another way by the introduction of the electric centers of gravity of the positive and the negative charges.

These centers are defined by the equations:

$$\sum_{positive} e_i \mathbf{r}_i = \mathbf{r}_\mathrm{p} \sum_{positive} e_i = \mathbf{r}_\mathrm{p} Q$$

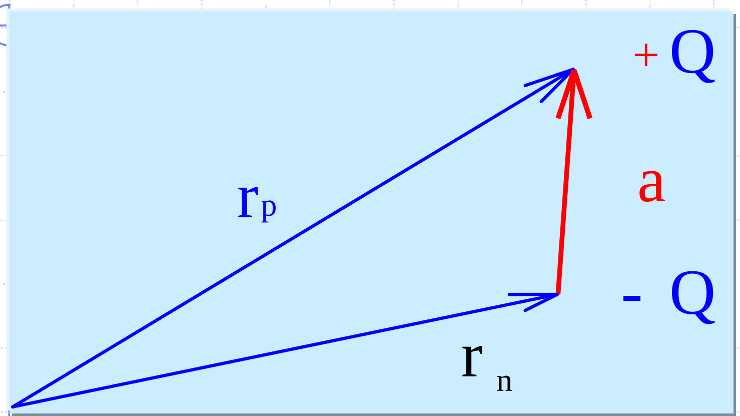
and

$$\sum_{negative} e_i \mathbf{r}_i = \mathbf{r}_\mathrm{n} \sum_{negative} e_i = \mathbf{r}_\mathrm{n} Q$$

in which the radius vectors from the origin to the centers are represented by $\boldsymbol{r}_p$ and $\boldsymbol{r}_n$ respectively and the total positive charge is called $\boldsymbol{Q}$.

$$\boldsymbol{m} = (\boldsymbol{r}_\mathrm{p} - \boldsymbol{r}_\mathrm{n})\mathrm{Q}$$

The difference $\boldsymbol{r}_p$-$\boldsymbol{r}_n$ is equal to the vector distance between the centers of gravity, represented by a vector ***a***, pointing from the negative to the positive center (Fig.1).



Thus we have:

$$\boldsymbol{m} = \boldsymbol{a}Q$$

Therefore the *electric moment of a system of charges with zero net charge is generally called the* ***electric dipole moment*** *of the system.*

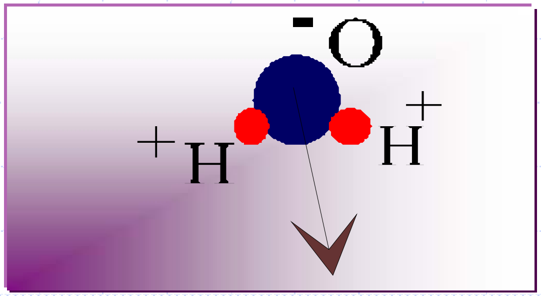
A simple case is a system consisting of only two point charges ***+*** *e and - e at a distance* ***a.***

Such a system is called a ***(physical) electric dipole,*** *its moment is equal to e****a,*** *the vector* ***a*** *pointing from the negative to the positive charge.*

Under the influence of the external electrical field, the *positive* and *negative charges* in the particle are moved apart: *the particle is polarized*. In general, these *induced dipoles* can be treated as *ideal*; *permanent dipoles*, however, may generally not be treated as ideal when the field at molecular distances is to be calculated.

The values of *molecular dipole moments* are usually expressed in *Debye units*. The Debye unit, abbreviated as *D*, equals 10^{-18} *electrostatic units* (e.s.u.).

The permanent dipole moments of non-symmetrical molecules generally lie between *0.5 and 5D*. It is come from the value of the elementary charge e_o that is $4.4 \cdot 10^{-10}$ *e.s.u.* and the distance *s* of the charge centers in the molecules amount to about 10^{-9}-10^{-8} *cm*.

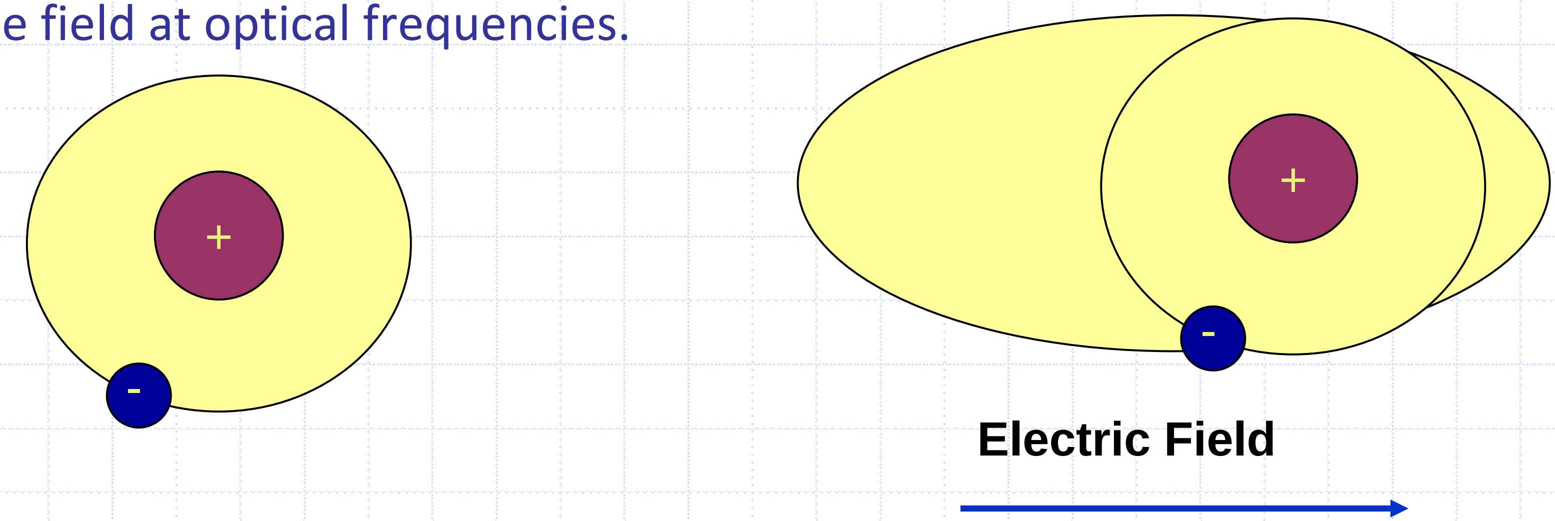


In the case of polymers and biopolymers one can meet much higher values of dipole moments ~ hundreds or even thousands of Debye units. To transfer these units to *SI system* one have to take into account that $1D=3.3 \cdot 10^{-30}$ *coulombs·m*.

Types of polarization

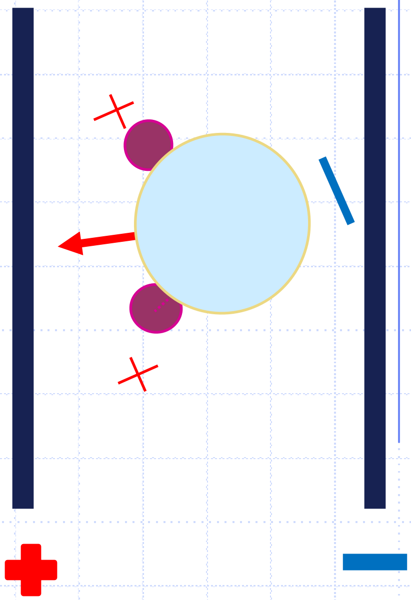
Deformation polarization

a. **Electron polarization** - the displacement of nuclear and electrons in the atom under the influence of external electric field. As electrons are very light they have a rapid response to the field changes; they may even follow the field at optical frequencies.

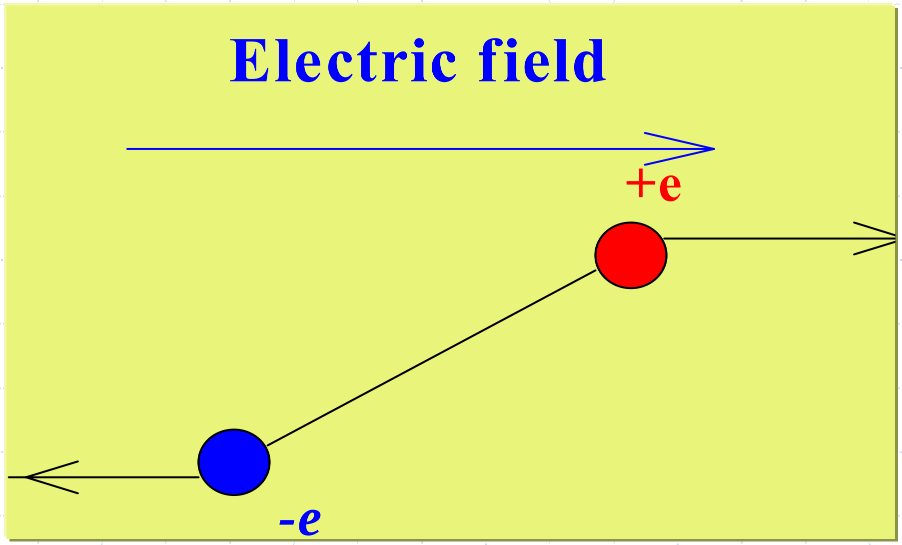


b. **Atomic polarization** - the displacement of atoms or atom groups in the molecule under the influence of external electric field.

Orientation polarization:

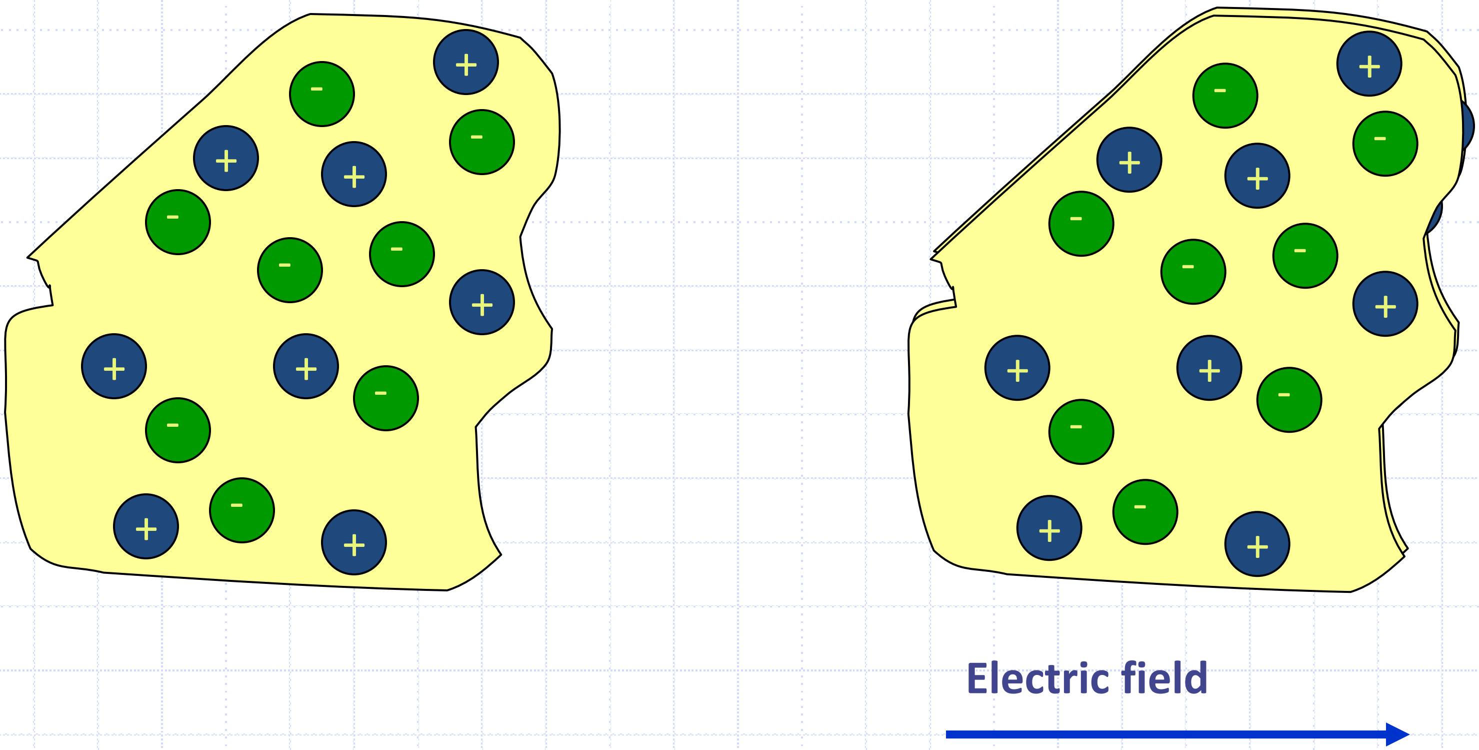


The electric field tends to direct the permanent dipoles.



Ionic Polarization

In an ionic lattice, the positive ions are displaced in the direction of the applied electric field whilst the negative ions are displaced in the opposite direction, giving a resultant dipole moment to the whole body.



The vector fields *E* and *D*.

For measurement inside matter, the definition of ***E*** ***in vacuum***, cannot be used.

There are two diff [...] of the problem how to measure ***E*** inside [...]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1. The matter can [...]n in which, by a sort of thought exper[...]ade. (*Kelvin, Maxwell*). Inside these ca[...] can be used.

2. The molecular [...] as a collection of point charges in vacuu[...]pes. The application here of the vacuum d[...]lled ***microscopic field*** *(Lorentz, Rosen*[...]his microscopic field is averaged, one obtains the ***macroscopic or Maxwell field E*** .

The ***main problem of physics of dielectrics*** is passing from a phenomenological macroscopic ***linear dielectric response*** to the microscopic structure in terms of electrons, nuclei, atoms, molecules and ions. In general case the problem is still unresolved completely.

For the solution of this problem of how to determine the electric field inside matter, it is also possible first to introduce a new vector field ***D*** in such a way that for this field the *source equation will be valid*.

$$div\mathbf{D} = 4\pi\rho$$

According to *Maxwell*, matter is regarded as a continuum. To use the definition of the field vector ***E***, a *cavity* has to be made around the point where the field is to be determined.

However, the force acting upon a test point charge in this cavity will generally depend on the *shape of the cavity*, since this force is at least partly determined by effects due to the walls of the cavity. This is the reason that two vector fields defined in physics of dielectrics:

The *electric field strength* ***E*** *satisfying curl**E**=0, and the dielectric displacement* ***D***, *satisfying div **D**=4$\pi\rho$.*

The *Maxwell continuum* can be treated as a *dipole density of matter*. *Difference* between the values of the field vectors arises from differences in their sources. Both the *external charges and the dipole density* of the piece of matter act as *sources of these vectors*.

The external charges contribute to ***D*** and to ***E*** in the same manner. Because of the different cavities in which the field vectors are measured, *the contribution of dipole density to* ***D*** and ***E*** *are not the same*. It can be shown that

$$\boldsymbol{D} - \boldsymbol{E} = 4\pi \boldsymbol{P}$$

where ***P*** *called the* ***POLARIZATION****.*

Generally, the polarization ***P*** depends on the electric strength ***E***. ***The electric field polarizes the dielectric.***

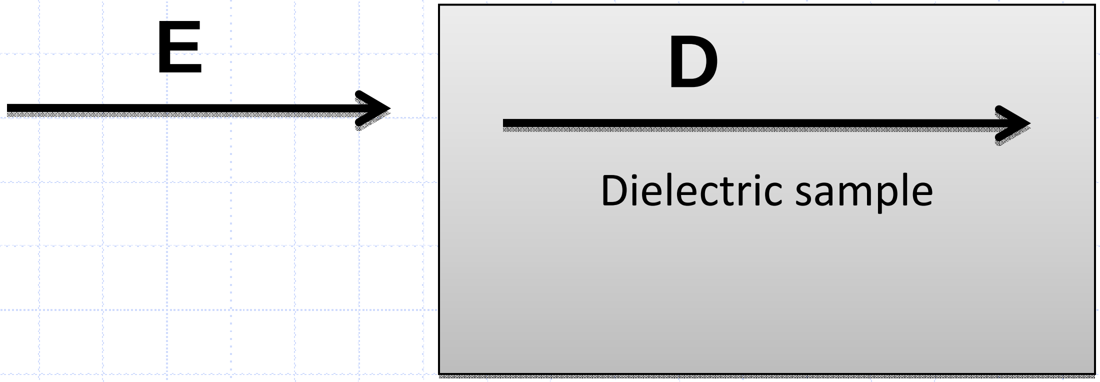
The dependence of P on E can take several forms:

$$\boldsymbol{P} = \chi \boldsymbol{E}$$

The polarization proportional to the field strength. The proportional factor χ *is called the* ***dielectric susceptibility*****.**

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P} = (1 + 4\pi\chi)\boldsymbol{E} = \varepsilon\boldsymbol{E}$$

in which ε is called the ***dielectric permittivity***. It is also called the *dielectric constant*, because it is independent of the field strength. It is, however, dependent on the *frequency of applied field*, the *temperature*, the *density* (or the *pressure*) and the *chemical composition of the system*.



$$\mathbf{D} = \varepsilon\,\mathbf{E}$$

Polar and Non-polar Dielectrics

- To investigate the dependence of the polarization on molecular composition, it is convenient to assume the total polarization ***P*** to be divided into two parts: the induced polarization $\boldsymbol{P}_{\alpha}$ caused by the translation effects, and the dipole polarization $\boldsymbol{P}_{\mu}$ caused by the orientation of the permanent dipoles.

$$\frac{\varepsilon - 1}{4\pi}\boldsymbol{E} = \boldsymbol{P}_{\alpha} + \boldsymbol{P}_{\mu}$$

A ***non-polar dielectric*** *is one whose molecules possess no permanent dipole moment.*

A ***polar dielectric*** *is one in which the individual molecules possess a dipole moment even in the absence of any applied field (i.e. the center of positive charge is displaced from the center of negative charge).*

Induced and orientation polarizations

Orientation polarization

$$\mathbf{P}_\mu = \sum_k N_k \langle \boldsymbol{\mu}_k \rangle$$

$$\alpha = \frac{\varepsilon - 1}{\varepsilon + 2} a^3$$

N_k is the number of particles per volume unit;

α is the **scalar polarizability** of a particle ;

E_i is the Internal Field, the average field strength acting upon that particle. It is defined as the total electric field at the position of the particle minus the field due to the particle itself.

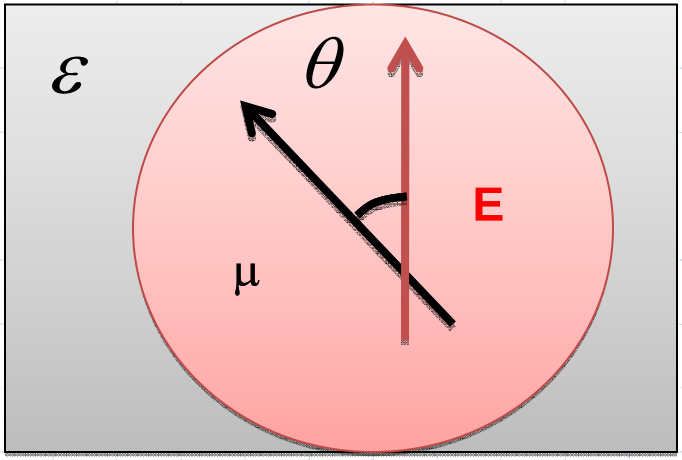
$\langle \boldsymbol{\mu}_k \rangle$ is the value of the **permanent dipole vector averaged** over all orientations.

k is the index referred to the k-th kind of particle.

Orientation polarization, Average dipole moment

The energy of the random oriented permanent dipole μ in the electric field 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***.

$$W_k = -\boldsymbol{\mu_k} \cdot \mathbf{E_d} = -\mu E_d \cos\theta_k \xrightarrow{\textit{Averaging}} \langle W \rangle = -\mu E_d \langle \cos\theta \rangle$$



The relative probabilities of the various orientations of dipole depend on this energy according to Boltzmann's distribution law:

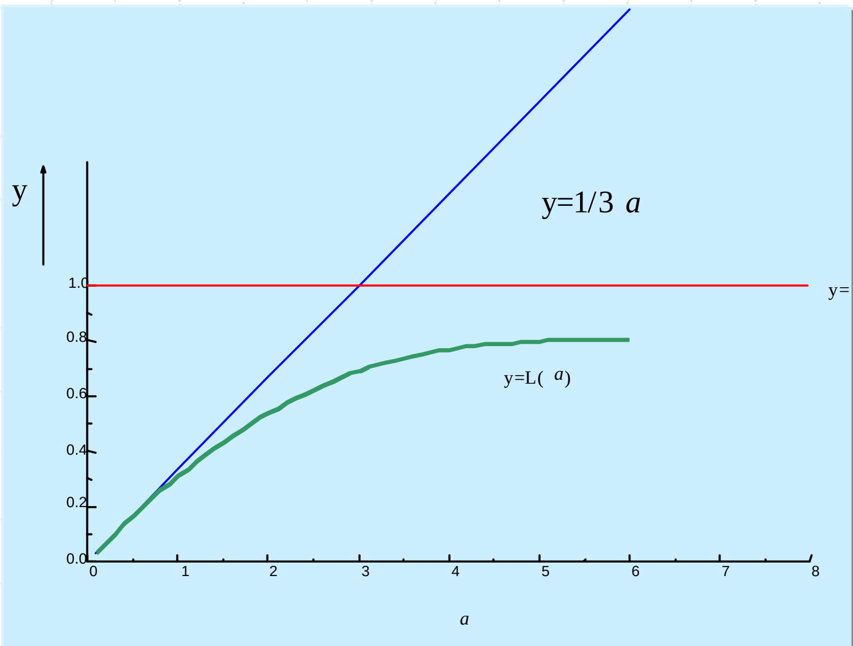
$$p(\theta)d\theta \sim \exp\left(\frac{\mu E_d \cos\theta}{kT}\right)\frac{1}{2}\sin\theta d\theta$$

$$\overline{\cos\theta} = \frac{\int_0^{\pi} \cos\theta e^{\frac{\mu E_d \cos\theta}{kT}} \frac{1}{2}\sin\theta d\theta}{\int_0^{\pi} e^{\frac{\mu E_d \cos\theta}{kT}} \frac{1}{2}\sin\theta d\theta} = \frac{1}{a}\frac{\int_{-a}^{a} e^x x dx}{\int_{-a}^{a} e^x dx} =$$

$$= \frac{1}{a}\frac{[xe^x - e^x]_{-a}^{+a}}{[e^x]_{-a}^{+a}} = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} = \mathbf{cot}anh(a) - \frac{1}{a} = L(a),$$

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

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



In Fig. 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:

$$\overline{\cos\theta} = \frac{1}{3}a = \frac{\mu E_d}{3kT} \quad \text{if} \quad 0 \le a << 1$$

The approximation of $\overline{cos}$ 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=300º K) this gives for a dipole of *4D*:

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

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 $\overline{cos}$ is allowed.

From the linear response approximation it follows that:

$$\boldsymbol{\mu} = \mu\langle cos\,\theta\rangle = \frac{\mu^2}{3kT}\boldsymbol{E}_d$$

Substituting this into the main relationship for the orientation polarization, we get:

$$\boldsymbol{P}_\mu = \sum_k N_k \frac{\mu^2}{3\kappa T}(\mathbf{E}_d)_k$$

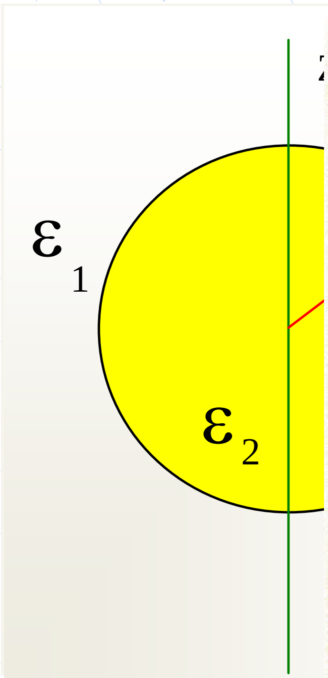
Fundamental equation

$$\frac{\varepsilon - 1}{4\pi}\boldsymbol{E} = \boldsymbol{P}_\alpha + \boldsymbol{P}_\mu$$

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

This is the **fundamental equation** is the starting point for expressing $\boldsymbol{E_i}$ and $\boldsymbol{E_d}$ as functions of the Maxwell field **E** and the dielectric constant ε.

Dipole moments and electrostatic problems



Let us put a dielectric sphere of radius ***a*** and
...ant ε_2, in a dielectric extending
...*inuum*), with dielectric constant
...external electric field is applied.

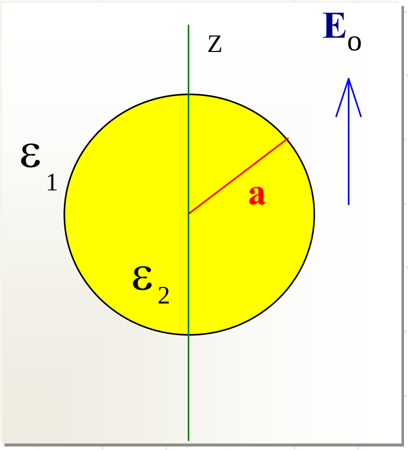
...here the potential satisfies
...*tion* ***Δφ=0***, since no charges are
...the charges at a great distance
...intain the external field. On the
...sphere *Laplace's equation* is *not*
...re is an apparent surface

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. $\left(\phi_1\right)_{r\to\infty} = -E_0 z = -E_0 r\cos\theta$
2. $\left(\phi_1\right)_{r=a} = \left(\phi_2\right)_{r=a}$ Since ϕ is continuous across a boundary
3. $\varepsilon_1\left(\frac{d\phi_1}{dr}\right)_{r=a} = \varepsilon_2\left(\frac{d\phi_2}{dr}\right)_{r=a}$ since the normal component of ***D*** must be continuous at the surface of the sphere
4. At the center of the sphere ***(****r=0****)*** ϕ_2 must not have a singularity.

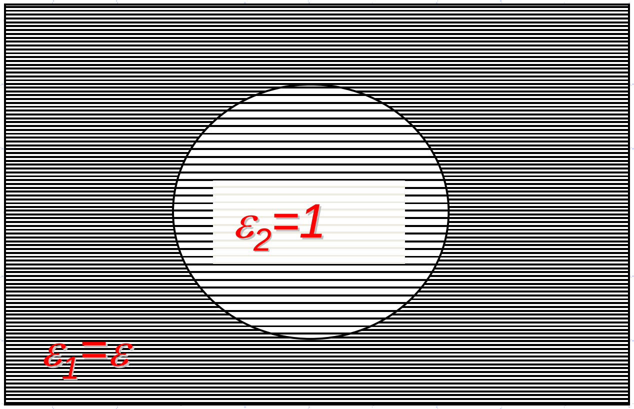
The total field $\boldsymbol{E}_2$ inside the sphere is accordingly is given by:

$$\boldsymbol{E}_2 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \boldsymbol{E}_0$$

A spherical cavity in dielectric

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

$$\boldsymbol{E}_C = \frac{3\varepsilon}{2\varepsilon + 1} \boldsymbol{E}_0$$



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

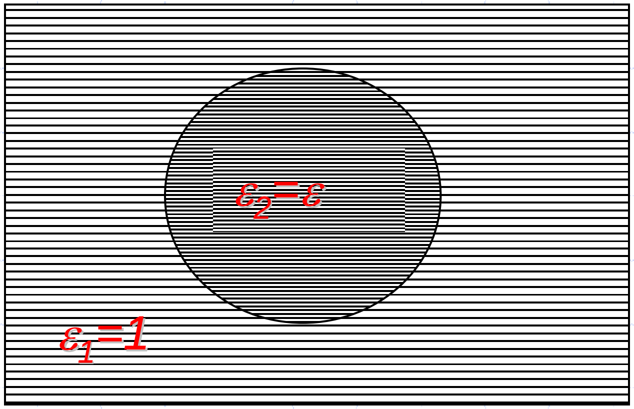
A dielectric sphere in vacuum

For a dielectric sphere in a vacuum ($\varepsilon_1=1$; $\varepsilon_2=\varepsilon$), the equation is reduced to:

$$\boldsymbol{E} = \frac{3}{2\varepsilon+1}\boldsymbol{E}_0$$

where ***E*** is the field inside the sphere.

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



The field outside the sphere due to the apparent surface charges is the same as the field that would be caused by a dipole ***m*** at the center of the sphere, surrounded by a vacuum, and given by:

$$\boldsymbol{m} = \frac{\varepsilon-1}{\varepsilon+2}a^3\boldsymbol{E}_0$$

Type of interactions

Two types of interaction forces:

-Short range forces- interaction between nearest neighbors:

- ***Chemical bonds,***
- ***Van der Waals attraction,***
- ***Repulsion forces,***

etc.

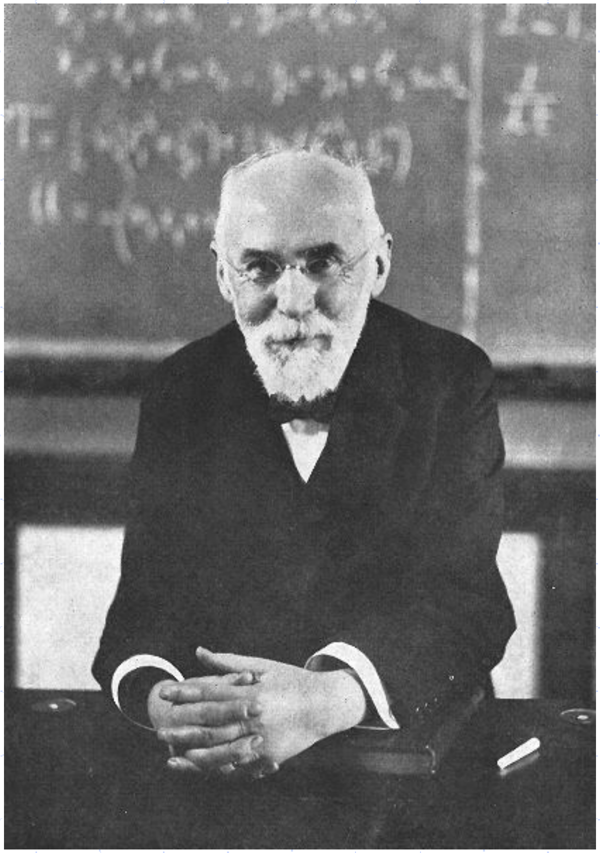
Long rang dipolar interaction forces

Dipole-dipole interaction
Dipole -charge interaction

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.

The different approaches where developed for solving this problem.

Lorentz's method

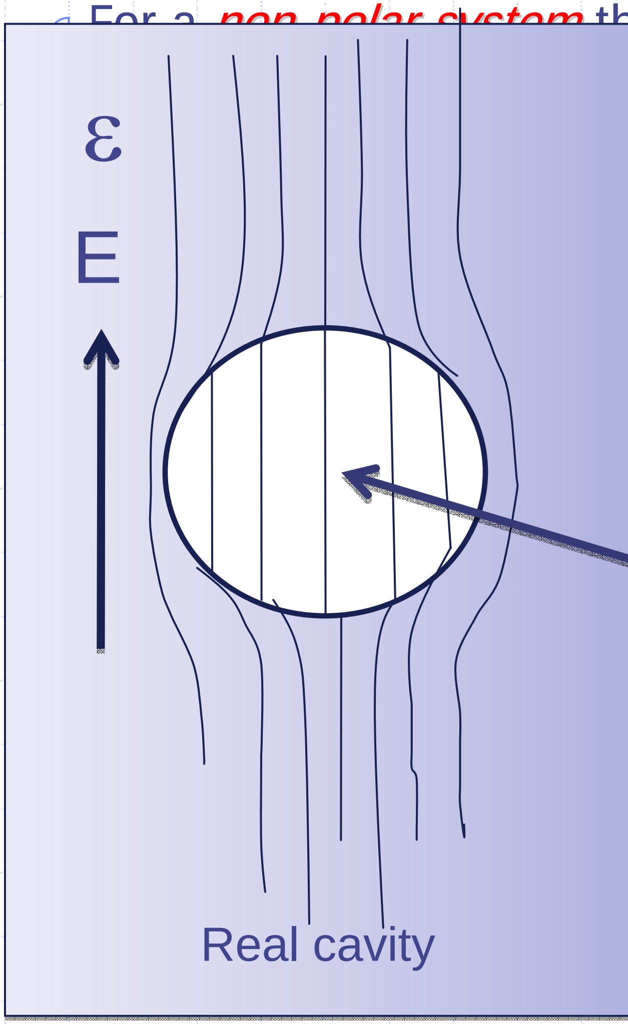


Non-polar dielectrics. Lorentz's field.
Clausius-Massotti formula.

For a *non-polar system* the fundamental equation fo

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

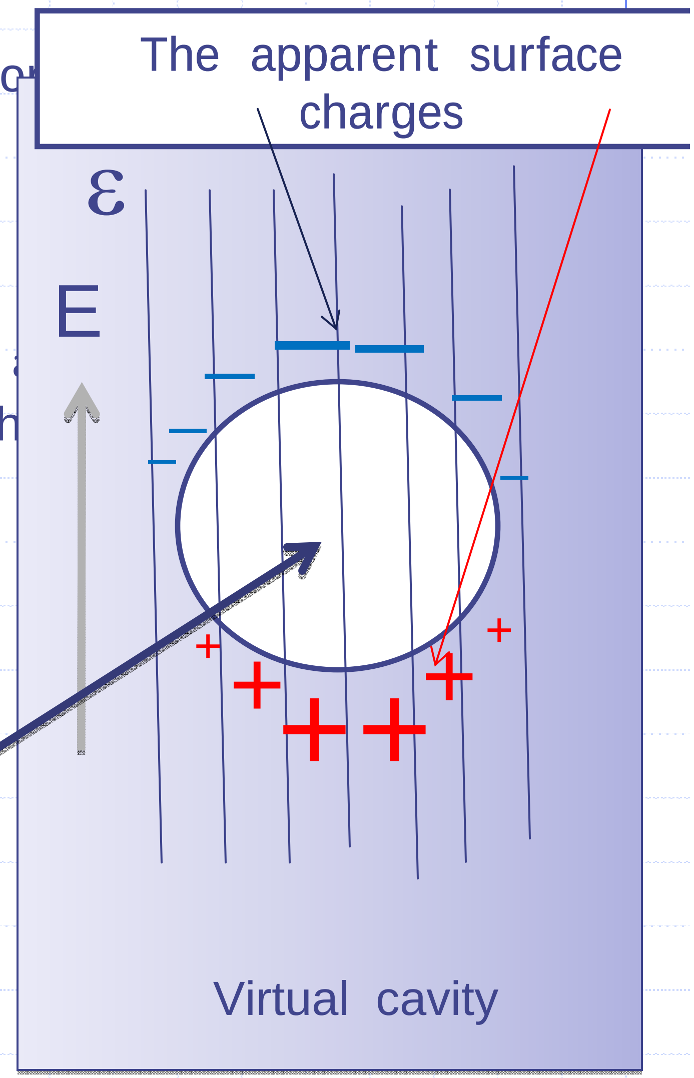
n between the internal field a
the *Lorentz approach* in th
neously polarized matter



$$\boldsymbol{E}_C = \frac{3\varepsilon}{2\varepsilon + 1}\boldsymbol{E}$$

Lorentz's field

$$\boldsymbol{E}_L = \frac{\varepsilon + 2}{3}\boldsymbol{E}$$



Lines of dielectric displacement

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

For a pure compound (k=1)

$$\boldsymbol{E}_i = \boldsymbol{E}_L = \frac{\varepsilon + 2}{3}\boldsymbol{E}$$

Clausius-Massotti formula

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

Debye theory; Gases and polar molecules in non-polar solvent

$$\frac{\varepsilon-1}{4\pi}\mathbf{E}=\sum_k \ldots)_k$$

$$k=1; \quad \ldots \mathbf{E}$$

This is generally called ... the first relationship that made the connection ... parameter of the substance being tested and the *p... ic)* parameter that can be experimentally measured.

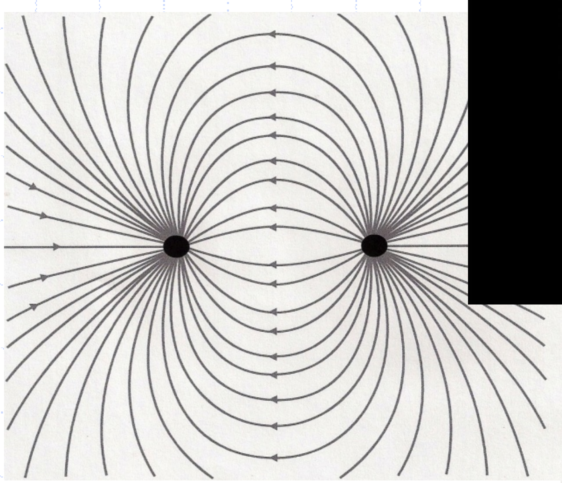
But in many cases, howe... considerable *disagreement* with the ex... for *gases at normal pressures*. In this case on... be written as:

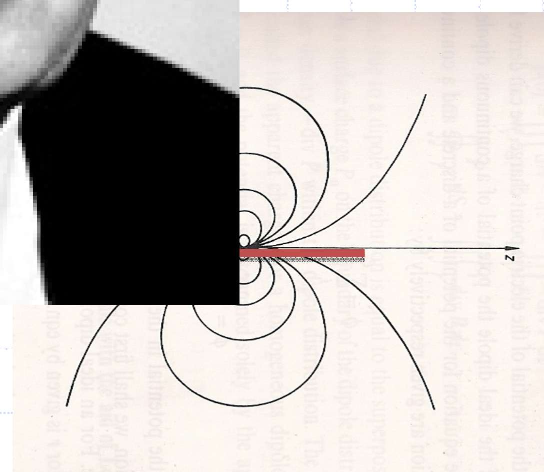
$$\varepsilon-1=4\pi N\left(\alpha+\frac{\mu^2}{3kT}\right)$$

The reaction field and Onsager's approach

When a molecule witl ... μ is surrounded by other particles, the inhomo ... anent dipole polarizes its environment. In the ... nents proportional to the polarizability are indu ... have a permanent dipole moment their orienta ... ate this effect one can use a simple model: *an ide ... ierical cavity.*

The inhomogenec ... dipole





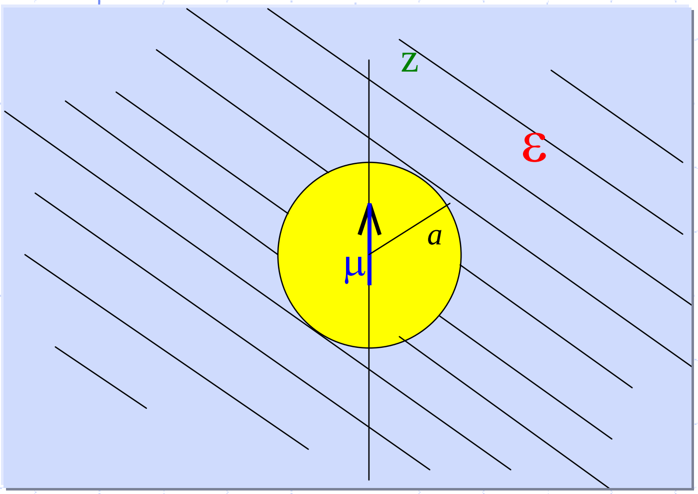
Electric dipole field lines

Line of force in the dipole field

The reaction field of a non-polarizable point dipole

Let us assume that only one kind of molecule is presented and ***a*** *is value approximately equal to what is generally considered to be the "molecular radius"*

Solving the Laplace equation with slightly different boundary conditions :



1. $$\left(\phi_1\right)_{r\to\infty} = 0$$

2. $$\left(\phi_1\right)_{r=a} = \left(\phi_2\right)_{r=a}$$

3. $$\varepsilon\left(\frac{d\phi_1}{dr}\right)_{r=a} = \left(\frac{d\phi_2}{dr}\right)_{r=a}$$

We can calculate:

The field in the cavity is a superposition of the dipole field in vacuum and a uniform field ***R***, given by:

$$\boldsymbol{R} = \frac{1}{a^3}\frac{2(\varepsilon-1)}{2\varepsilon+1}\mu$$

and the factor of the reaction field is equal to

$$f = \frac{1}{a^3}\frac{2(\varepsilon-1)}{2\varepsilon+1}$$

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Formally, the field of dielectric can be described as the field of a virtual dipole μ_c at the center of the cavity, given by:

$$\mu_c = \frac{3\varepsilon}{2\varepsilon+1}\mu$$

The presented model involves a number of simplifications, since the ***dipole*** is assumed to be ***ideal*** and ***located at the center of the molecule,*** which is supposed to be ***spherical and surrounded by a continuous dielectric.***

The reaction field of a polarized point dipole

In this case the permanent dipole has an average polarizability α, and therefore the reaction field ***R*** induces a dipole α***R*** and satisfies the equation:

$$\boldsymbol{R} = f(\boldsymbol{\mu} + \alpha\boldsymbol{R})$$

Under the influence of the reaction field *the dipole moment is increased considerably,* the increased moment is:

$$\boldsymbol{\mu}^* = \boldsymbol{\mu} + \alpha\boldsymbol{R}$$

Considering

$$\frac{\alpha}{a^3} = \frac{n^2-1}{n^2+2} \qquad \varepsilon_\infty = n^2$$

We can obtain that

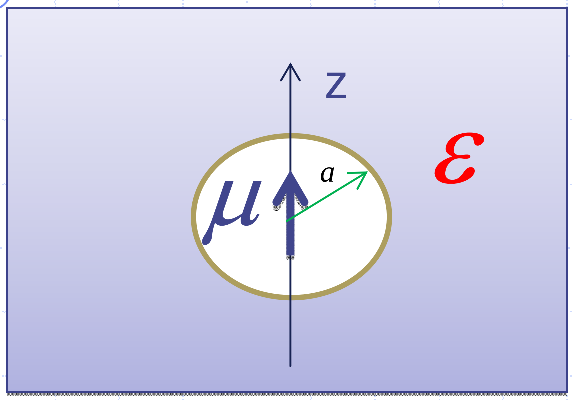
$$\boxed{\frac{\mu^*}{\mu} = \frac{2\varepsilon+1}{2\varepsilon+n^2}\frac{n^2+2}{3}}$$

In the case of polar dielectrics, the molecules have a permanent dipole moment μ, and both parts of the fundamental must be taken into account.

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

In the case of *non-polar liquids* the internal field can be considered as the sum of two parts; one being the cavity field and another the reaction field of the dipole induced in the molecule $\boldsymbol{E_i = E_c + R}$.

For *polar molecules* the internal field can also built up from the cavity field and the reaction field, taking into account now the reaction field of the *total dipole moment of the molecule*.

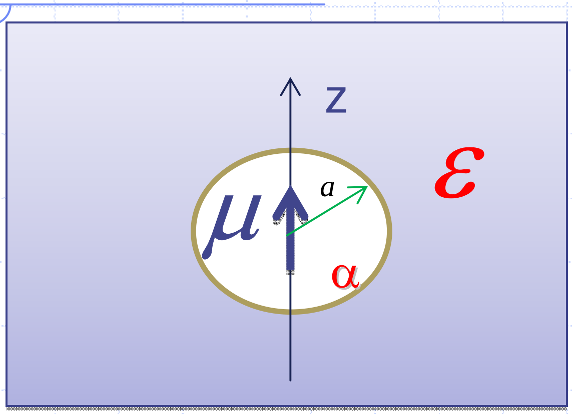


The *angle* between the *reaction field* of the permanent part of the dipole moment and the *permanent dipole moment itself* will be constant during the movements of the molecule.

It means that *in a spherical cavity the permanent dipole moment and the reaction field caused by it will have the same direction.* Therefore, this reaction field $\boldsymbol{R}$ does not influence the direction of the dipole moment of the molecule under consideration, and does not contribute to the directing field $\boldsymbol{E}_d$.

On the other hand, the reaction field does contribute to the internal field $\boldsymbol{E}_i$, because it polarizes the molecule. As a result, we find a difference between the internal field $\boldsymbol{E}_i$ and the directing field $\boldsymbol{E}_d$.

Since the reaction field $\boldsymbol{R}$ belongs to one particular orientation of the dipole moment, the difference between $\boldsymbol{E}_i$ and $\boldsymbol{E}_d$ will give by the value of the reaction field averaged over all orientations of the polar molecule:



$$\boldsymbol{E}_i - \boldsymbol{E}_d = \langle \boldsymbol{R} \rangle$$

The direction field $\boldsymbol{E}_d$ can be obtained by the following procedure:

α) *remove the permanent dipole* of a molecule without changing its polarizability;

β) let the surrounding dielectric adapt itself to the new situation;

γ) then fix the charge distribution of the surroundings and *remove* the central molecule.

The average field in the cavity so obtained is equal to the value of $\boldsymbol{E}_d$ that is to be calculated, since we have eliminated the contribution of $\boldsymbol{R}$ to $\boldsymbol{E}_i$ by removing the permanent dipole of the molecule.

TABLE

Compound	ref.	μ_{ons}	μ_{gas}
Chloromethane	a, b, c	1.74	1.87
Bromomethane	a, b, c	1.55	1.81
Iodomethane	b, c	1.27	1.62
Chloroform	a	1.18	1.01
Bromoform	d	0.92	0.99
Nitromethane	a	3.44	3.46
Cyanomethane	a, c	3.39	3.92
2,2-Dichloropropane	a	2.45	2.27
Propanone	a	3.03	2.88
Trimethylamine	b	0.66	0.61
2-Chloro-2-methylpropane	b	2.39	2.13
Ethoxyethane	a, b	1.40	1.15
Ethylthioethane	a	1.64	1.54
Chlorobenzene	b, d	1.40	1.67
Bromobenzene	e	1.33	1.70
Iodobenzene	e	1.05	1.70
Nitrobenzene	b, d	4.06	4.22
Triethylamine	a	0.66	0.66
Cyanobenzene	b	3.48	4.18
Hydrogen cyanide	b	5.66	2.98

[a] Estimate of Buckley and Maryott.[20]

[b] Estimate of Weaver and Parry.[19]

[c] Estimate of Abbott and Bolton.[21]

Relationships between the different kinds of electric fields

In order to describe the polarization of matter the different kinds of electric fields where introduced : Maxwell's field $\mathbf{E}$, internal field $\mathbf{E_i}$; Lorentz field $\mathbf{E_L}$; direction field $\mathbf{E_d}$, reaction field $\mathbf{R}$ and the cavity field $\mathbf{E_C}$

Let us consider the relationships between these fields in the different systems.

Gases and polar molecules in non-polar solvent

$$\mathbf{E_d} = \mathbf{E}_I = \mathbf{E}_L = \mathbf{E}_C = \frac{\varepsilon + 2}{3}\mathbf{E}$$

The non-polar liquids

In this case of the internal field can be considered as the sum of two parts; one being the cavity field and the other the reaction field of the dipole induced in the molecule:

$$\mathbf{E}_I = \mathbf{E}_L = \mathbf{E}_C + \mathbf{R} = \frac{\varepsilon + 2}{3}\mathbf{E}$$

Polar molecules

For *polar molecules* the internal field can also built up from the cavity field and the reaction field, taking into account now the reaction field of the *total dipole moment of the molecule*:

Since the reaction field R belongs to one particular orientation of the dipole moment, the difference between E_i and E_d will give by the value of the reaction field averaged over all orientations of the polar molecule:

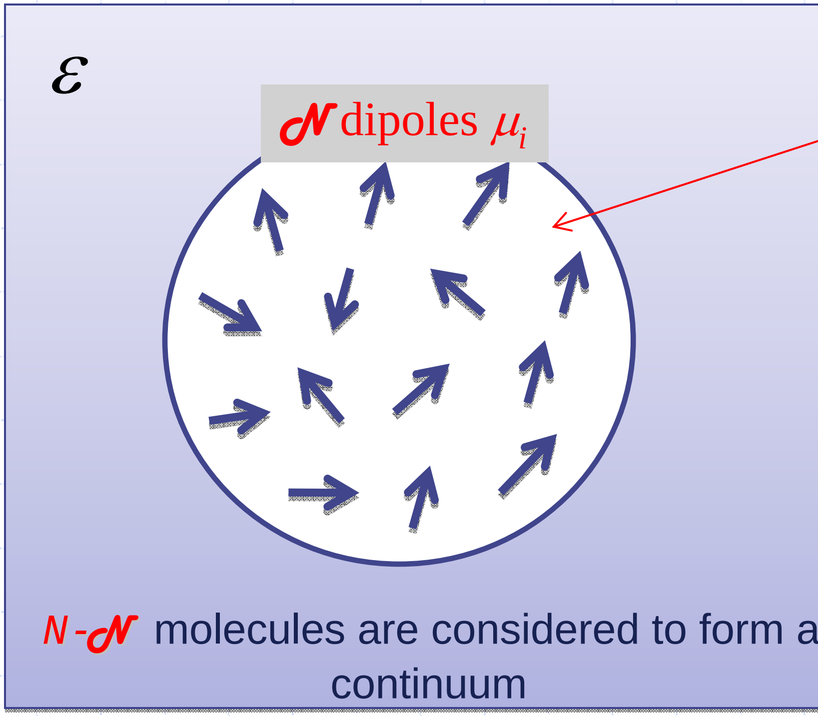
$$E_i - E_d = \langle R \rangle$$

The Kirkwood –Froehlich approach

In the above app... considered non-polar systems, p... ms and polar systems withou... eractions. In all these cases ***the... eractions between molecules wher... account.***

A more general ... oped by Kirkwood and subsequent... ehlich. This approach takes ... dipole-dipole interactions, which appears in a more dense state ***under the influence of the short range interactions***

In this case the external field working in the sphere is the cavity field



$$\boldsymbol{E_0} = \boldsymbol{E}_C = \frac{3\varepsilon}{2\varepsilon+1}\boldsymbol{E}$$

E is the Maxwell field in the material outside the sphere

$$(\varepsilon-1) = 4\pi n\left(\frac{\partial E_0}{\partial E}\right)_{E=0}\left[\frac{1}{n} < \mathbf{e}\cdot\mathbf{A}\cdot\mathbf{e} >_0 + \frac{1}{3kTn} < M^2 >_0\right]$$

Here $n=\mathcal{N}/V$ is the number density, and the **tensor** $\boldsymbol{A}$ plays the role of a polarizability;

$$< M^2 >_0 = \sum_{i=1}^{\mathcal{N}}\sum_{j=1}^{\mathcal{N}}\langle \mu_i \mu_j \rangle_0 \qquad \boldsymbol{M} = \sum_{i=1}^{\mathcal{N}} \mu_i$$

For non polarizable molecules $< \mathbf{e}\cdot\mathbf{A}\cdot\mathbf{e} >_0 = 0$

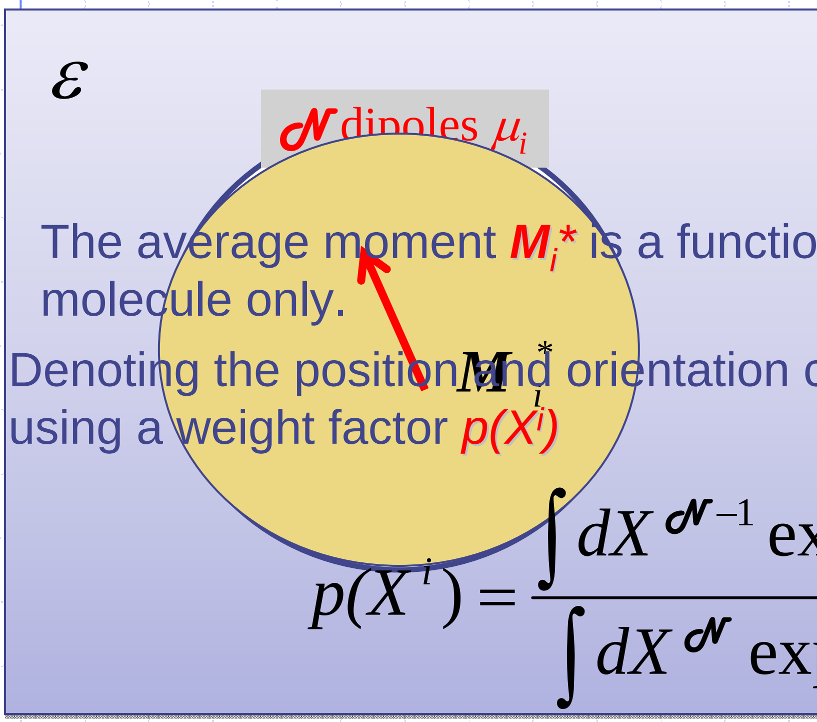
$$(\varepsilon-1) = \frac{4\pi}{V}\frac{3\varepsilon}{2\varepsilon+1}\frac{< M^2 >_0}{3kT}$$

$$\langle M^2 \rangle_0 = \sum_{i=1}^{\mathcal{N}} \frac{\int dX^{\mathcal{N}} \mu_i \cdot \boldsymbol{M} \exp(-U/kT)}{\int dX^{\mathcal{N}} \exp(-U/kT)}$$

In this equation the superscript $\mathcal{N}$ to dX to emphasize that the integration is performed over the positions and orientations of $\mathcal{N}$ molecules (here $dX=r^2\sin\theta\, dr\, d\theta\, d\varphi$, *is the expression for a volume element in spherical coordinates*).

Since μ_i is a function of the orientation of the *i-th* molecule only, the integration over the positions and orientations of all other molecules, denoted as $\mathcal{N}-i$, can be carried out first. In this way we obtain (apart from a normalizing factor) the average moment of the sphere in the field of the *i-th* dipole with fixed orientation. The averaged moment, denoted by $\boldsymbol{M}_i^*$, can be written as:

$$\boldsymbol{M}_i^* = \frac{\int dX^{\mathcal{N}-i}\, \boldsymbol{M} \exp(-U/kT)}{\int dX^{\mathcal{N}-i} \exp(-U/kT)}$$



The average moment $\boldsymbol{M}_i^*$ is a function of the position and orientation of the *i*-th molecule only.

Denoting the position and orientation coordinates of the *i*-th molecule by X_i and using a weight factor $p(X^i)$

$$p(X^i) = \frac{\int dX^{\mathcal{N}-1} \exp(-U/kT)}{\int dX^{\mathcal{N}} \exp(-U/kT)}$$

$$\langle M^2 \rangle_0 = \sum_{i=1}^{\mathcal{N}} \int p(X^i)\mu_i \cdot \boldsymbol{M}_i^* dX^i = \mathcal{N} \int p(X^i)\mu_i \cdot \boldsymbol{M}_i^* dX^i$$

$$\mu_i \cdot \boldsymbol{M}_i^* = \mu^2 \sum_{j=1}^{\mathcal{N}} \frac{\int dX^{\mathcal{N}-i} \cos\theta_{ij} \exp(-U/kT)}{\int dX^{\mathcal{N}-i} \exp(-U/kT)}$$

$$\langle M^2 \rangle_0 = \mathcal{N}\mu^2 \sum_{j=1}^{\mathcal{N}} \int p(X^i) \frac{\int dX^{\mathcal{N}\text{-}i} \cos\theta_{ij} \exp(-U/kT)}{\int dX^{\mathcal{N}\text{-}i} \exp(-U/kT)} dX^i$$

$$< \cos\theta_{ij} >= \int p(X^i) \frac{\int dX^{\mathcal{N}\text{-}i} \cos\theta_{ij} \exp(-U/kT)}{\int dX^{\mathcal{N}\text{-}i} \exp(-U/kT)} dX^i$$

$$< M^2 >_0 = \mathcal{N}\mu^2 \sum_{j=1}^{\mathcal{N}} < \cos\theta_{ij} >$$

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{12\pi\varepsilon}=\frac{N}{3kT}\int p(X^i)\mu_i\cdot\boldsymbol{M}_i^*dX^i=\frac{N}{3kT}\mu^2\sum_{j=1}^{\mathcal{N}}<\cos\theta_{ij}>$$

The left part of the Onsager equation for the non polarized molecules

The deviations of M_i from the value μ_i are the result of molecular interactions between the i-th molecule and its neighbors.*

It is well known that liquids are characterized by short-range order and long-range disorder. The correlations between the orientations (and also between positions) due to the short-range ordering will lead to values of ***M_i**** differing from μ_i. This is the reason that *Kirkwood* introduced a correlation factor ***g*** which accounted for the deviations of

$$\int p(X^i)\mu_i\cdot\boldsymbol{M}_i^*dX^i=\mu^2\sum_{j=1}^{\mathcal{N}}<\cos\theta_{ij}>$$ from the value μ^2:

$$g=\frac{1}{\mu^2}\int p(X^i)\mu_i\cdot\boldsymbol{M}_i^*dX^i=\sum_{j=1}^{\mathcal{N}}<\cos\theta_{ij}>$$

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{12\pi\varepsilon}=\frac{N}{3kT}g\mu^2$$

- When there is no more correlation between the molecular orientations than can be accounted for with the help of the continuum method, one has *g=1*⇒ we are going to *Onsager* relation for the non-polarizable case, for rigid dipoles with $\varepsilon_\infty=1$.
- An approximate expression for the *Kirkwood correlation factor* can be derived by taking only nearest-neighbors interactions into account. In that case the sphere is shrunk to contain only the *i-th* molecule and its *z* nearest neighbors. We then have:

$$M_i^*=\frac{\int dX^{\mathcal{N}-1}\left(\mu_i+\sum_{j=1}^{z}\mu_j\right)\exp(-U/kT)}{\int dX^{\mathcal{N}-1}\exp(-U/kT)}$$

with $\mathcal{N}=z+1$.

Since after averaging the result of the integration will be not depend on the value of *j*, all terms in the summation are equal and we may write:

$$g=1+\sum_{j=1}^{z}\int p(X^i)dX \ldots \frac{\ldots U/kT)}{\int dX^{\mathcal{N}-i}\exp(-U/kT)}$$

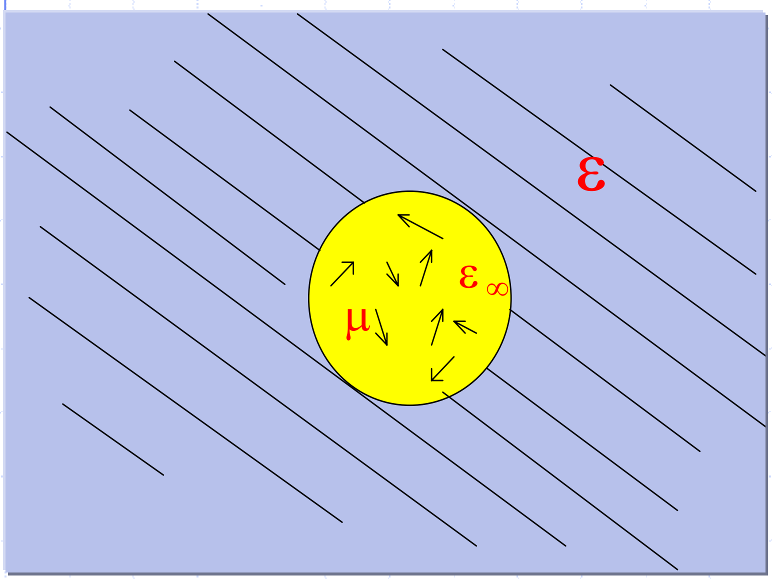
$$\boldsymbol{g=1+z<\cos\theta_{ij}>}$$

g will be different from 1 when $\langle\cos\theta_{ij}\rangle \neq 0$, i.e. when there is correlation between the orientations of neighboring molecules.

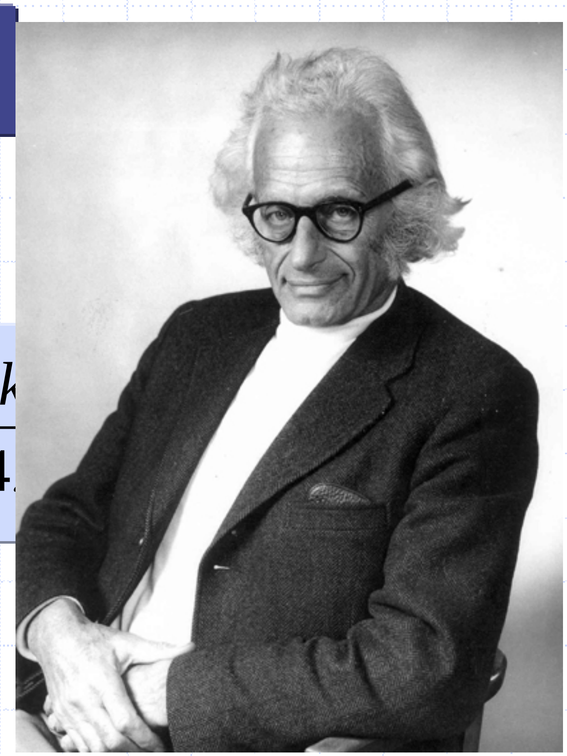
When the molecules tend to direct themselves with parallel dipole moments, $\langle\cos\theta_{ij}\rangle$ will be positive and g >1.

When the molecules prefer an ordering with anti-parallel dipoles, g <1.

Approximation of Fröhlich



$$g\mu^2 = \frac{9k\cdots}{4\cdots}$$



Main relationships in static dielectric theory

Non-polar systems

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

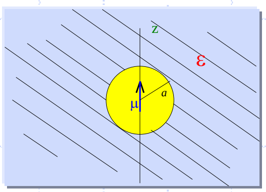
Clausius-Mossotti equation

Polar diluted systems

$$\varepsilon-1=4\pi N\left(\alpha+\frac{\mu^2}{3kT}\right)$$

Debye equation

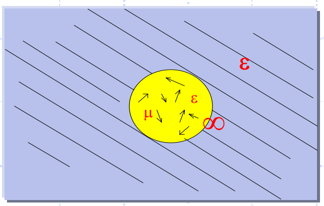
Polar systems



$$\mu^2=\frac{9kT}{4\pi N}\frac{(\varepsilon-\varepsilon_\infty)(2\varepsilon+\varepsilon_\infty)}{\varepsilon(\varepsilon_\infty+2)^2}$$

Onsager Equation

Polar systems, short range interactions



$$g\mu^2=\frac{9kT}{4\pi}\frac{(\varepsilon-\varepsilon_\infty)(2\varepsilon+\varepsilon_\infty)}{\varepsilon(\varepsilon_\infty+2)^2}$$

Kirkwood-Fröhlich equation