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 α of the atoms or molecules constituting the dielectric.

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A general review on the derivation of Clausius-Mossotti relation

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ABSTRACT

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1. Introduction

The Clausius–Mossotti relation is named after the Italian physicist Ottaviano-Fabrizio Mossotti, whose 1850 book http://en.wikipedia.org/wiki/Clausius%E2%80%93Mossotti_relationcite_note-0 [1] analyzed the relationship between the dielectric constants of two different media, and the German physicist Rudolf Clausius, who gave the formula explicitly in his 1879 book http://en.wikipedia.org/wiki/Clausius%E2%80%93Mossotti_relationcite_note-1 [2] in the background not of dielectric constants but of indices of refraction [3]. The same formula also arises in the background of conductivity, in which it is known as Maxwell's formula. It arises yet again in the background of refractivity, in which it is known as the Lorentz–Lorenz equation [4–8]. It is used when there is no contribution from permanent electric dipole moments to the polarization, either because the molecules are nonpolar or because the frequency of the applied field is high.

2. Derivations of Clausius–Mossotti relation and dependent relations

For explain of Clausius–Mossotti relation we should survey the polarization density. The polarization density is determined by three factors: (1) The electronic polarization α_e produced by oppo-

* Corresponding author. *E-mail address:* m.talebian@urmia.ac.ir (M. Talebian). site displacements of negative electrons and positive nuclei inside the same atoms. (2) The ionic polarizability α_i produced by opposite displacements of positive and negative ions in the material [9]. (3) Contributions from the permanent dipole moments of complex ions or molecules at any time when such permanent dipoles are present in the material. It is possible to express this in below form

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This manuscript offers a general review on the derivation of Clausius-Mossotti relation.

Clausius-Mossotti relation seems to hold best for gases and gives reasonably good results for many liquids

and solids. In physics, this relation connects the relative permittivity of a dielectric to the polarizability

$$P = N\left(\alpha_{\rm e} + \alpha_{\rm i} + \frac{\mu^2}{3kT}\right) \tag{1}$$

The number of atoms or molecules per unit volume is N.

For best realizing of Eq. (1) should explain some about derivative of this relation for this purpose we plot the element of solid angle $d\omega$ on a unit sphere.

From Fig. 1, we can see for $d\omega$ in below expression:

$$d\omega = 2\pi \sin \theta \, d\theta \tag{2}$$

This relation is the number of dipoles/cu. meter having dipole moment between the value θ and $(\theta + d\theta)$ is given by:

$$dN = A \varepsilon^{(\mu E \cos \theta / kT)} \sin \theta \, d\theta \tag{3}$$

where *A* is a constant of proportionality. The constant *A* may be computed making use of the fact that *N*, namely the total number of molecules per unit volume equals the integration of right hand side of Eq. (3) over the limit 0 to π . Then we have:

$$A = \frac{N}{\int_0^{\pi} \varepsilon^{(\mu E \cos \theta / kT)} \sin \theta \, d\theta} \tag{4}$$



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Fig. 1. Element of solid state angle $d\omega$ on a sphere of unit radius.

The contribution to the total dipole moment in the *z* direction by dipoles which having dipole moments between θ and $(\theta + d\theta)$ are given by [12–14]:

$$dP = dN \ \mu \ \cos\theta \tag{5}$$

The total dipole moment in the z direction is in form which expressed by:

$$P = \int_{\theta}^{\pi} dN \ \mu \ \cos\theta = A\mu \int_{\theta}^{\pi} \varepsilon^{(\mu E \cos\theta/kT)} \sin\theta \ \cos\theta \ d\theta \tag{6}$$

By using of Eq. (4) into Eq. (6), we get:

$$P = N\mu \frac{\int_{\theta}^{\pi} \varepsilon^{(\mu E \cos\theta/kT)} \sin\theta \cos\theta \, d\theta}{\int_{\theta}^{\pi} \varepsilon^{(\mu E \cos\theta/kT)} \sin\theta \, d\theta}$$
(7)

By replacing of $b = \mu E/kT$, $x = \cos\theta$, we find for dx, $dx = -\sin\theta d\theta$. So Eq. (7) simplifying to below form:

$$P = N\mu \frac{\int_{-1}^{1} \varepsilon^{bx} x \, dx}{\int_{-1}^{1} \varepsilon^{bx} dx} \tag{8}$$

To evaluate the integral in the numerator, we integrate by part. Then we will have [15–17]:

$$P = N\mu \left(\coth \ b - \frac{1}{b} \right) = N\mu L(b)$$
(9)

where $L(b) = \coth b - 1/b$, the function L(b) was introduced by Langevin in 1905 and is called the Langevin function. At room temperature, for typical electric fields in laboratories, $\mu E \ll kT$, so we have:

$$L(b) \approx \frac{b}{3} = \frac{\mu E}{3kT} \tag{10}$$

Via Eq. (9) we get below relation for the average dipole moment:

$$P = \frac{N\mu^2 E}{3kT} \tag{11}$$

The orientational polarizability per molecule is given by:

$$\alpha_0 = \frac{P/N}{E} = \frac{\mu^2}{3kT} \tag{12}$$

 μ has values of the order of 10^{-30} coulomb-meter. At room temperature we find that α_0 has value of order 10^{-40} cubic-meter. This value of α_0 is of the same order as electronic polarizability α_e . In a polyatomic gas, total polarization may result from electronic, ionic and orientational polarizabilities. Then, the total polarization per unit volume is given by Eq. (1). Eq. (1) is based on the assumption that the total polarization is proportional to *E*.



Fig. 2. Parallel plate capacitor.

The electric susceptibility is then obtained via substituting Eq. (1) in $\chi = k - 1$ as we know, also $P = \varepsilon_0 \chi E$:

$$\chi = k - 1 = N\left(\alpha_{\rm e} + \alpha_{\rm i} + \frac{\mu^2}{3kT}\right) \tag{13}$$

The contribution to *P* from the permanent dipoles present in the matter is temperature-dependent. It is thus possible to measure these dipole moments by observing the temperature dependence of the electric susceptibility. No restrictions have been placed on the nature of the dielectric material, that is, whether it is a gas, a liquid, or a crystalline substance. If attention is limited to crystals, then it is necessary to take into account the influence on an atom of the internal field produced by the dipoles surrounding the atoms as well as the influence of the externally applied field. The procedure of finding E_{total} is described in Figs. 2 and 3.

Point P which the reference molecule is situated is the center of a sphere of sufficiently large radius and then the dielectric is outside it may be treated as a continuum. If we imagine the molecules inside the sphere removed the polarization outside considered frozen, so the field acting on the molecule at P maybe thought of as comes from the following sources.

$$E_{\text{total}} = E_1 + E_2 + E_3 \tag{14}$$

(1) The free charges at the electrodes of the capacitor. The field due to these charges is equal to the applied field $E_{1.}(2)$ The charges on the spherical cavity surface. The field due to these charges is denoted by $E_{2.}(3)$ The charge due to all the other molecules inside the cavity and shown by $E_{3.}$

To find the field E_2 , we express that the charge distribution on a dielectric sphere removed from a uniformly polarized dielectric slab is exactly the same, but of opposite sign to that on the spherical cavity (Figs. 2 and 3). Hence, the fields due to these charge distribution have the same magnitude and opposite directions. As we know that from $E_P = -\nabla \varphi = -P/3\varepsilon_0$ due to a uniformly polarized dielectric sphere:

$$E_2 = -E_P = \frac{P}{3\varepsilon_0} \tag{15}$$



Fig. 3. Spherical cavity.

The molecules inside the spherical cavity are polarized in the presence of an electric field and thus either act as induced dipoles or if they have a permanent dipole moment, arrange in a line themselves to a certain extent towards the direction of the field. The field E_1 due to the dipoles within the cavity would depend on the structure of the dielectric material. It has been shown that $E_1 = 0$ for materials whose atoms have a simple cubic lattice structure. For most isotropic materials $E_1 \simeq 0$. Then with Eqs. (15) and (16) we will have:

$$E_{\text{total}} = E_1 + \frac{P}{3\varepsilon_0} \tag{16}$$

Eq. (16) is known as the Lorentz relation. P_{total} is the dipole moment of a molecule in a polarized isotropic dielectric; we defined the polarizability α of a molecule of the dielectric:

$$p_{\text{total}} = \varepsilon_0 \alpha E_{\text{total}} \tag{17}$$

The polarization *P* is defined by:

$$P = Np_{\text{total}} = \varepsilon_0 N \alpha E_{\text{total}} = \varepsilon_0 N \alpha \left(E + \frac{P}{3\varepsilon_0} \right)$$
(18)

where *N* is the molecules per unit volume. By sum displacements for *P* parameter we have:

$$P = \frac{N\alpha}{1 - N\alpha/3}\varepsilon_0 E\tag{19}$$

Comparing Eq. (19) with $\chi = k - 1$ we can observe that:

$$P = \varepsilon_0 \chi_e E = \varepsilon_0 (k - 1)E \tag{20}$$

With solving of above relation for χ , we observe that:

$$\chi_{\rm e} = k - 1 = \frac{N\alpha}{1 - N\alpha/3} \tag{21}$$

This relation relates the macroscopic susceptibility χ_e or dielectric constant *k* to the microscopic polarizability α of the molecules of the dielectric. Eq. (21) simply changes to below relation for α [18–21]:

$$\alpha = \frac{3}{N} \left(\frac{k-1}{k+2} \right) \tag{22}$$

Eq. (22) is known as the Clausius–Mossotti relation. It used to determine of the electrical polarizabilities of the atoms if the dielectric constant is known. Conversely, the dielectric constants of new materials can be predicted from knowledge of the individual polarizabilities of the atoms according to Eq. (22), the polarizabilities are additive. This relation is also valid for electronic polarizabilities α_e and dipolar polarizabilities α_d . Eq. (22) can be written in form of:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} \sum_{i} n_i \alpha_i \tag{23}$$

where $k = n^2$ and $N\alpha = \sum_i n_i \alpha_i$. Eq. (23) is called the Lorenz–Lorentz relation. When *n* is very nearly equal to unity, then $n^2 + 2 \simeq 3$, Eq. (23) becomes:

$$n^2 = k = 1 + \sum_i n_i \alpha_i \tag{24}$$

Eq. (24) can be compared with $k = 1 + \chi_e$. With multiplying of M/D to both sides of Eq. (23) we will have:

$$\frac{M}{D}\frac{n^2-1}{n^2+2} = \frac{1}{3}N_0\alpha$$
(25)

where *M* is the molecular weight and *D* is the density, N_0 is Avogadro's number and α is the polarizability of a molecule, then Eq. (25) can be used to calculate the molar polarizability or the molar refractivity. Above relation allows one to relate the index of refraction of a crystal to its structure.

3. Remarks and conclusions

- 1) If we generalized Eq. (12) in general form for the molecular polarizability which in present of induced electronic and orientational polarization, then, Eq. (12) indicates a temperature dependence of the form A+B/T which seems to be well confirmed by experiment [22].
- **2)** The subject of this paper is put in appropriate historical context and addressed from different physical aspects. With the Clausius–Mossotti relation the dielectric properties of materials were essentially reduced to known electrical properties. This relation is between the dielectric constant of a material to the polarizability of its atoms [23,24]. If the Clausius–Mossotti is taken seriously, we should able to calculate α from the refractive index in gas phase and then predict *k* or n^2 in the liquid phase at much higher density.

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