A GENERALIZATION OF BOTTDHER'S THEORY
OF THE DIELECTRIC CONSTANT
OF LIQUIDS
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A Generalization of Bottcher's Theory of the Dielectric Constant of Liquids

Abstract

A theory of the dielectric constant of polar liquids has been developed by Bottcher on the basis of a simple molecular model. A molecule is represented by a sphere bearing a polarizable mathematical (point) dipole at its centre, the surroundings being treated as a homogeneous substance with the macroscopic dielectric constant. Notwithstanding its simplicity, this model gives a remarkably satisfactory description of the experimental data. In the thesis it is shown that Bottcher's final formula still holds when the molecules are represented by a sphere with a finite dipole of arbitrary position and direction, thus contributing to the understanding as to why Bottcher's theory is as satisfactory as it is.

Finally, the energy of a molecule containing a finite arbitrarily located dipole is calculated and it is found that, even for small eccentricities, the energy is considerably different from that calculated by Onsager for a point dipole at the centre of a sphere. It is indicated that this generalization helps to explain the difference between the observed and predicted results on certain polar molecules.

Introduction

1. Concept of a Dielectric Substance

The aim of any theory of dielectrics is to find a relation between the observables $\varepsilon$ and $\mu$ and the molecular quantities $\mu$ and $\kappa$.

Consider first of all a dielectric substance consisting of
elementary charges $e_i$ then:

$$\sum e_i = 0$$  \hspace{1cm} (1:a)$$

if the substance has no net charge. The total electric moment of the charges $e_i$ relative to a fixed point $O$, a vector distance $\vec{d}$ away, is given by:

$$\vec{M} = \sum e_i \vec{r}_i$$  \hspace{1cm} (2:a)$$

This quantity is independent of the origin, for from (fig. 1), let $O'$ be a new origin a distance $\vec{d}'$ from $O$. Then:

$$\vec{r}_i' + \vec{d}' = \vec{r}_i$$

so that:

$$\vec{M} = \sum e_i (\vec{r}' + \vec{r}_i') = \sum e_i \vec{r}_i' + \vec{d} \sum e_i$$

$$\Rightarrow \vec{M} = \sum e_i \vec{r}_i' = \sum e_i \vec{r}_i$$  \hspace{1cm} (3:a)$$

Now in the ground state of the substance the position vector will be denoted by $\vec{r}_{io}$ and it will be assumed that in this state the total moment of the substance vanishes, i.e.

$$\vec{M}_o = \sum e_i \vec{r}_{io} = 0$$  \hspace{1cm} (4:a)$$

In a higher state, where the charges are displaced from their equilibrium positions $\vec{r}_{io}$ by an amount $\vec{r}_i$, we will have a new position vector:

$$\vec{r}_i = \vec{r}_{io} + \vec{r}_i$$
So that the moment of the substance becomes:
\[
\vec{M} = \sum_i e_i \vec{r}_i = \sum_i e_i \vec{r}_i^0 + \sum_i e_i \vec{r}_i
\]
\[\therefore \quad \vec{M} = \sum_i e_i \vec{r}_i \quad (5:a)\]

Our task now is to obtain some idea of the displacement of
the elementary charges under the influence of some local external field
\(\vec{f}\) applied to the dielectric substance. There are two characteristic

(i) The displaced charges are bound elastically by Hooke’s Law
to an equilibrium position.

(ii) A charge has several equilibrium positions each of which it
occupies with a probability depending on the strength of
the external field.

Let us consider first of all case (i).

Consider a charge "\(q\)" of mass "\(m\)" bound elastically to an
equilibrium position and suffering a small displacement \(\vec{r}\), so that when
a periodic local field \(\vec{f} = \vec{f} e^{i\omega t}\) is applied to the particle we
have the differential equation of the motion given by:
\[
m \frac{d^2 \vec{r}}{dt^2} + k \vec{r} = e \vec{f} e^{i\omega t}
\]
where \(k\) is the force constant. Thus we must solve:
\[
\vec{r}'' + \frac{k}{m} \vec{r} = \frac{e}{m} \vec{f} e^{i\omega t} \quad (6:a)
\]
The particular integral of this equation will be of the form:
\[
\vec{r} = A e^{i\omega t} \quad (7:a)
\]
so that:
\[
(-\omega^2 + \frac{k}{m}) A = \frac{e \vec{f}}{m}
\]
giving:
\[
A = \frac{e \vec{f}}{m \left(\omega^2 - \frac{k}{m}\right)}
\]
Now \(\omega_0 = \sqrt{\frac{k}{m}}\) is the natural (angular) frequency of the vibration in
the absence of the impressed periodic field. Hence, we may write
the particular integral as:

$$\overline{\mathbf{r}} = \frac{e^{\frac{1}{2}e^{i\omega t}}}{m(\omega_0^2 - \omega^2)}$$

The average electric moment of the particle is thus:

$$\overline{m} = \frac{e^2}{m(\omega_0^2 - \omega^2)} \overline{f}$$

where: $$\overline{f} = \overline{f}' e^{i\omega t}$$

For our purposes we will, of course, be interested in stationary fields hence $$\overline{f} = \overline{f}'$$ and for the static case the average moment is given by:

$$\overline{m} = \frac{e^2}{m \omega_0^2} \overline{f}$$

(9:a)

There will of course be a complimentary solution to (6:a) given by:

$$\overline{\mathbf{r}} = \overline{\mathbf{B}} e^{i\omega t}$$

The total displacement is thus:

$$\overline{\mathbf{r}} = \overline{\mathbf{r}} + \overline{\mathbf{B}} e^{i\omega t}$$

(10:a)

so that in essence the impressed local field has merely shifted the equilibrium position of the charge $\mathbf{r}$.

As an example of case (ii) consider a particle with charge $\mathbf{c}$ and mass $\mathbf{m}$ possessing two equilibrium positions $\mathbf{A}'$ and $\mathbf{B}'$ separated by a directed distance $\mathbf{b}$. (see fig. 2).

![Fig 1](image)

The presence of $\overline{f}$ will affect the potential energy curve in two ways. Firstly, it will displace the equilibrium positions $\mathbf{A}'$ and $\mathbf{B}'$ by an
amount \( \mathcal{L} \) and, secondly, the potential energies \( V_A \) and \( V_B \) of the particle in the two equilibrium positions will be altered so that:

\[
V_A - V_B = e \mathbf{B} \cdot \mathbf{P}
\]

The probability of finding the particle at \( A \) is:

\[
P_A = \frac{e^{-V_A/\mathcal{L}}} {e^{-V_A/\mathcal{L}} + e^{-V_B/\mathcal{L}}}
\]

while that of finding it at \( B \) is:

\[
P_B = \frac{e^{-V_B/\mathcal{L}}} {e^{-V_A/\mathcal{L}} + e^{-V_B/\mathcal{L}}}
\]

so that:

\[
P_B > P_A \quad \text{and} \quad P_B + P_A = 1
\]

and:

\[
P_B - P_A = \frac{e^{-V_B/\mathcal{L}} - e^{-V_A/\mathcal{L}}} {e^{-V_A/\mathcal{L}} + e^{-V_B/\mathcal{L}}} = \frac{e^{-V_B/V_A} - 1} {e^{-V_B/V_A} + 1}
\]

\[
P_B - P_A = \frac{e^{-V_B/\mathcal{L}} - 1} {e^{-V_B/\mathcal{L}} + 1} > 0
\]

Over a long period of time "\( \xi \)" the particle will spend a time at \( A \) given by \( T_A \) where:

\[
T_A = P_A t = \frac{P_B - P_B + P_A} {2} \xi
\]

\[
T_A = P_A t = \frac{1 - (P_B - P_A)} {2} \xi
\]

While the time spent at \( B \) will be \( T_B \) given by:

\[
T_B = P_B t = \frac{P_B - P_A} {2} \xi
\]

\[
T_B = \frac{1 + (P_B - P_A)} {2} \xi
\]

It has thus been displaced from \( A \) to \( B \) a fraction given by \( \frac{1}{2} (P_B - P_A) \) of the time "\( \xi \)." The average contribution to the moment induced by the field from this phenomenon is thus:

\[
\mathbf{\overrightarrow{m}} = \frac{1}{2} e \mathbf{B} \cdot (P_B - P_A)
\]
Letting \( \phi \) be the angle between \( \mathbf{r} \) and \( \mathbf{F} \) the moment in the direction of the field is:

\[
\mathbf{r}_p = \frac{1}{2} e \mathbf{b} \cos \phi \left( \frac{e \mathbf{b} \cos \phi}{e \mathbf{b} \cos \phi + 1} \right)
\]

Now in general:

\[
e \mathbf{b} < < \mathbf{e} \mathbf{F}
\]

Hence:

\[
\mathbf{r}_p = \frac{1}{2} e \mathbf{b} \cos \phi \left( \frac{1 + \frac{e \mathbf{b} \cos \phi}{e \mathbf{b} \cos \phi + 1}}{1 + \frac{e \mathbf{b} \cos \phi}{e \mathbf{b} \cos \phi + 1}} \right) - 1
\]

\[
= \frac{1}{4} e^2 \mathbf{b} \cos \phi \cos^2 \phi
\]

\[
\mathbf{r}_p = \left( \frac{e \mathbf{b} \cos \phi}{2} \right)^2 \frac{e \mathbf{F}}{e \mathbf{F} + 1}
\]

The second contribution will arise from the displacement \( \pi \) of the particle in the potential minima and hence the total moment induced in the direction of the field is:

\[
\mathbf{r} = \frac{1}{2} e \mathbf{b} \cos \phi \frac{e \mathbf{F}}{e \mathbf{F} + 1} + e \pi \cos \phi
\]  \hspace{1cm} (11:a)

It is easy to see that the effect of the field in this case is to cause the charge in the two equilibrium positions to act like a dipole \( \mu_p \) of strength:

\[
\mu_p = \frac{1}{2} e \mathbf{b}
\]  \hspace{1cm} (12:a)

The most significant difference between the two cases is that in case (i) the dipole moment should be independent of temperature to the same extent that the force constant \( \mathbf{F} \) and hence the electronic polarizability \( \alpha = \frac{E}{m \omega^2} \) is temperature independent. In the second case, however, the moment is clearly temperature dependent although only
for very high temperatures or low electronic resonance frequencies is the
$at \cos \phi$ term comparable to the $(\frac{1}{2} e a \cos \phi)^2 \frac{f}{\epsilon T}$ term.
For example, with $\epsilon T$ at room temperatures and $\phi = 0$ we have:
$$\frac{m \omega}{e \epsilon} \approx 1500$$
where: $m$ electron mass and $\omega_0$ corresponds to frequency of sodium
"D" line.

2. Dipolar Interaction

In a dielectric two essentially different types of forces
should be distinguished. Forces due to chemical bonds, van der Waals
attraction, Born repulsion, etc. are short range forces affecting only
nearest neighbours. On the other hand, dipolar interaction forces
have a very long range. We are thus led to Lorentz's\footnote{Lorentz, H.A.\break Theory of Electrons (Teubner 1909).} method for the
treatment of dipolar interaction, which will be briefly revived. First
of all, we select from the macroscopic dielectric a spherical specimen
which is sufficiently large to have the same dielectric properties as
the macroscopic dielectric. Next, we consider the medium outside the
spherical region to be a continuum characterized by the macroscopic
dielectric constant. When an external electric field $\vec{E}$ is set up in
the substance all the electrons in the atoms will be displaced by the
same amount (case (1)) thereby forming dipoles of strength:
$$\vec{m} = \alpha \vec{f}$$  \hspace{1cm} (13:a)
where $\vec{f}$ is the local field acting on each electron and is, of course,
assumed to be the same for each dipole formed.
To find $\mathbf{F}$ we will separate the sources of $\mathbf{F}$ into those outside the spherical specimen $\mathbf{F}_e$ and those inside given by $\mathbf{F}_i$.

Without going into the details of Lorentz's work, let it be sufficient to say that for the induced dipole in the centre of the spherical specimen the local field $\mathbf{F}_i^0$ if the dielectric substance is isotropic.

The field $\mathbf{F}_e$ is the field inside the spherical region due to all sources except the polarization in this region. If we remove the homogeneously polarized spherical specimen from the dielectric substance without disturbing the state of the polarization, we find that the field inside the sphere (called the "self field" - see (35:a)) is given by:

$$\mathbf{E}_s = -\frac{4\pi}{3} \mathbf{P}$$

where $\mathbf{P}$ is the moment per unit volume (polarization) of the sphere.

Hence the self field is directed opposite to the polarization.

By definition, it follows that:

$$\mathbf{F}_e = \mathbf{E} - \mathbf{E}_s$$

$$\mathbf{F}_i = \mathbf{E} + \frac{4\pi}{3} \mathbf{P}$$

(14:a)

From Maxwell's equations we have:

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \varepsilon \mathbf{E}$$

for an isotropic medium and hence:

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi} \mathbf{E}$$

We get, therefore, that:

$$\mathbf{F}_e = \mathbf{F} = \frac{\varepsilon + 2}{3} \mathbf{E}$$

(15:a)

a result independent of the radius of the spherical specimen.
The induced dipole moment in the dielectric specimen is thus:

\[ \vec{m} = \alpha \vec{F} = \frac{\varepsilon+2}{3} \alpha \vec{E} \]

Let there be \( N_0 \) dipoles per unit volume, then:

\[ \vec{P} = N_0 \vec{m} = \frac{\varepsilon-1}{4\pi} \vec{E} \]

hence:

\[ \frac{\varepsilon+2}{3} N_0 \alpha = \frac{\varepsilon-1}{4\pi} \]

or:

\[ \frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3} N_0 \alpha \] (16:a)

This is just the Clausius-Mossotti formula. It holds fairly well for simple non-polar substances.

It will be noted that the result (14:a) is independent of the radius of the spherical specimen. Onsager has shown that (16:a) applies to a single isotropic spherical molecule if short range forces between the molecules are neglected and the effective volume occupied by a single molecule is defined as:

\[ \frac{4\pi}{3} a^3 = \frac{1}{N_0} \]

Thus we obtain for a single molecule:

\[ \frac{\varepsilon-1}{\varepsilon+2} = \frac{\alpha}{a^3} \] (17:a)

where \( \alpha \) refers to both atomic and electronic polarization. Onsager's result will be given later under the general theory of polar liquids.

Let us consider in some detail the formula (16:a) applied to a sphere of polarizable material.

3. Clausius-Mossotti relation for a Sphere

Care must be exercised in distinguishing between the macroscopic Clausius-Mossotti formula for a large sphere composed of

---

of many molecules and the corresponding Onsager result (17:a).

To derive the macroscopic formula, let us consider a large sphere of continuous isotropic dielectric $\varepsilon$ brought into a homogenous field $\mathbf{E}$. The local field existing in this sphere (see (26:a)) will be:

$$F = \frac{3}{2 + \varepsilon} \mathbf{E}$$

Now let $\alpha_m$ be the macroscopic polarizability of this sphere then the total moment is:

$$\mathbf{M} = \alpha_m \mathbf{E}$$

on the other hand we may calculate this moment as:

$$\mathbf{M} = \left(\frac{\varepsilon - 1}{4\pi}\right) F \left(\frac{4\pi}{3}\alpha_m^3\right)$$

where $\alpha_m$ is the radius of the sphere. Thus:

$$\alpha_m = \frac{\varepsilon - 1}{3} \alpha_m^3 \cdot \frac{3}{2 + \varepsilon}$$

$$\therefore \quad \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\alpha_m}{\alpha_m^3}$$

is the Clausius-Mosotti formula for a macroscopic sphere. From the molecular point of view (18:a) has, of course, no significance. Van Vleck* has found that $\alpha_m$ is independent of temperature provided the density is kept constant.

To obtain the molecular Clausius-Mossotti formula we will assume that the macroscopic polarizability $\alpha_m$ can be expressed in terms of the molecular polarizability $\alpha$ (a constant independent of both temperature and density) by:

$$\alpha_m = N \alpha$$

where \( N \) is the number of molecules in the macroscopic sphere of radius \( a_m \), i.e.:

\[
N = \frac{\frac{4}{3} \pi a_m^3}{\frac{4}{3} \pi a^3} = \frac{a_m^3}{a^3}
\]

Thus (18:a) becomes for a single molecule:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\alpha}{a^3} \tag{19:a}
\]

Now the quantity \( \frac{4}{3} \pi a^3 = \frac{1}{N_0} \), the average volume occupied by a single molecule, is also given by \( \frac{1}{N_0} = \frac{W}{\rho A} \) where \( W \) is the molecular weight, \( \rho \) the density, and \( A \) is Avogadro's number. Hence from (19:a) we get:

\[
\frac{\alpha}{a^3} = \left( \frac{3\alpha}{4\pi} \cdot \frac{A}{W} \right) \rho \tag{20:a}
\]

and hence \( \frac{\alpha}{a^3} \) should be proportional to the density of the substance.

No such conclusion can be drawn, however, from (18:a) where \( \frac{a_m^3}{a_m^3} \) may depend on density in an unspecified way.

At this point it is desirable to deviate from the general discussion and consider a simple electrostatic problem in order to better understand the concepts of self field, cavity field, reaction field, etc., which are so important to the understanding of formulae (14:a) and (20:a) as well as Bottcher's ideas on pure polar liquids, which will follow shortly.


Let us consider, therefore, a sphere of dielectric constant \( \varepsilon_i \) and radius \( a \) which is homogeneously polarized \( \mu^i \) (in the \( \hat{z} \) direction) with polarization \( P \). Also in this sphere let there be a (point) dipole \( \vec{\mu} \) (in the \( \hat{z} \) direction) at the centre. Let the medium outside the sphere have a macroscopic dielectric constant \( \varepsilon_0 \) and let there be a homogeneous external field \( \vec{E} \) applied to the whole system (see fig. 3).
Using spherical coordinates $\rho, \theta, \phi$ we have that the potentials both inside and outside are $\phi$ independent. Thus the respective potentials inside and outside are given by:

$$V_i = \frac{\mu \cos \theta}{\epsilon} + \sum_{n=0}^{\infty} A_n \rho^n P_n(\cos \theta)$$

$$V_o = \sum_{n=0}^{\infty} \left( C_n \rho^n + \frac{B_n}{\rho^{n+1}} \right) P_n(\cos \theta)$$

For $\rho \to \infty$ we have the condition that the field becomes equal to $E$.

Thus:

$$\lim_{\rho \to \infty} (V_o) = -E \rho \cos \theta = C_0 + C_1 \rho \cos \theta = C_0 + \sum_{n=2}^{\infty} C_n \rho^n P_n(\cos \theta)$$

Hence:

$$C_0 = C_2 = C_3 = \ldots = 0$$

$$C_1 = -E$$

Thus:

$$V_o = -E \rho \cos \theta + \sum_{n=2}^{\infty} \frac{B_n}{\rho^{n+1}} P_n(\cos \theta)$$

is the outside potential. In order to simplify the work, at this point the statement will be made that the coefficients $A_n$ and $B_n$ are all zero if $m \neq 1$. This fact arises because of the nature of the boundary conditions. It is, of course, not necessary to make this assumption and the reader may, if he desires, carry the coefficients $A_n$ and $B_n$ for $m \neq 1$ through the whole process of solution and in the end show for himself that $A_n = B_n = 0$ if $m \neq 1$. 
The potentials inside and outside become therefore:

\[ \nabla_i = \left( \frac{\mu}{e_i \lambda^2} + A_i \lambda \right) \cos \theta \]  
\[ \nabla_0 = \left( -E \lambda + \frac{B_1}{\lambda^2} \right) \cos \theta \]

The boundary conditions on the sphere \( \lambda = \alpha \) are:

(i) that \( \nabla_i = \nabla_0 \)

(ii) and that: \( \epsilon_i \frac{A_i}{\alpha} - 4\pi P_3 = \epsilon_0 \frac{2V_i}{\alpha} \)

Condition (i) gives:

\[ \frac{\mu}{\epsilon_i \alpha^3} + A_i = -E + \frac{B_1}{\alpha^3} \]  
(23:a)

While (ii) yields:

\[ -\frac{3\mu}{\alpha^3} + \epsilon_i A_i - 4\pi P_3 = -\epsilon_0 E - \frac{2\epsilon_0 B_1}{\alpha^3} \]  
(24:a)

Solving these two equations for \( A_i \) and \( B_1 \), one finds that:

\[ A_i = \frac{-3\epsilon_0}{2\epsilon_0 + \epsilon_i} E + \frac{2(e_i - \epsilon_0)}{\epsilon_i (e_i + 2\epsilon_0)} \frac{A_i}{\alpha^3} + \frac{4\pi P_3}{\epsilon_i + 2\epsilon_0} \]  
(25:a)

\[ B_1 = -\frac{(\epsilon_0 - \epsilon_i) \alpha^3}{\epsilon_i + 2\epsilon_0} E + \frac{3\mu}{\epsilon_i + 2\epsilon_0} + \frac{4\pi P_3 \alpha^3}{\epsilon_i + 2\epsilon_0} \]  
(26:a)

Case (a) "The Cavity Field."

Consider now \( \mu = 0 \) and \( P_3 = 0 \) so that we have a dielectric sphere imbedded in a dielectric. In this case:

\[ A_i = \frac{-3\epsilon_0}{2\epsilon_0 + \epsilon_i} E \]

\[ B_1 = -\frac{(\epsilon_0 - \epsilon_i) \alpha^3}{2\epsilon_0 + \epsilon_i} E \]

so that the field inside the sphere is homogeneous and in the \( \beta \)-direction and is given by:

\[ G = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_i} E \]  
(27:a)

If in particular \( \epsilon_i = 1 \), we have what is often referred to as the "cavity field":

\[ \frac{E_C}{E} = \frac{3\epsilon_0}{2\epsilon_0 + 1} \]  
(28:a)
On the other hand, if the sphere is in a vacuum the field inside becomes:
\[
\frac{\mathbf{E}^0}{\varepsilon_0} = \frac{3}{2 + \varepsilon_i} \mathbf{E}^0
\]  
(29:a)

Case (b) "The Directing Field"

Let us consider once again the case where \( \mu = 0 \) and \( P = 0 \) then the total moment of the sphere is:
\[
\overline{M}^0 = \frac{4\pi}{3} a^3 \mathbf{P} \\
= \frac{4\pi}{3} a^3 \left( \varepsilon_i - 1 \right) \mathbf{E}^0 \\
= \frac{a^3}{3} \left( \varepsilon_i - 1 \right) \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_i} \mathbf{E}^0 \\
\therefore \overline{M}^0 = \frac{a^3\varepsilon_0 \left( \varepsilon_i - 1 \right)}{2\varepsilon_0 + \varepsilon_i} \mathbf{E}^0
\]  
(30:a)

Now let us fix the polarized charges in the sphere (so that the total moment is also fixed) and put this sphere in a vacuum. What uniform field must we apply externally to the sphere in order for it to have a moment given by (27:a)? The answer is what we define as the "directing field" \( \mathbf{E}_d \). From the Clausius-Mossotti formula *(18:a) for a sphere of refractive index \( \mu^2 \) we have that the polarizability of the sphere is:
\[
\alpha_m = \frac{\mu_i^2 - 1}{\mu_i^2 + 2} a^3
\]

* The concept of the directing field will be applied to molecules, hence we are actually using the corresponding Onsager result (17:a).
So that by definition:
\[ \alpha_m \mathbf{E}_d = \mathbf{M} = \alpha^3 \frac{\varepsilon_0 (n^2 - 1)}{2\varepsilon_0 + n^2} \mathbf{E} \]
and hence:
\[ \mathbf{E}_d = \frac{n^2 + 2}{n^2 - 1} \frac{\varepsilon_0 (n^2 - 1)}{2\varepsilon_0 + n^2} \mathbf{E} \]
\[ \therefore \mathbf{E}_d = \frac{\varepsilon_0 (n^2 + 2)}{n^2 + 2\varepsilon_0} \mathbf{E} \] (31a)

Case (c) "The Reaction Field"

Consider now \( \mathbf{E} = 0 \) and \( \mathbf{P} = 0 \) so that we have a point dipole at the centre of a spherical cavity. For this case the field inside the sphere is given by:
\[ \frac{\mathbf{R}'}{\varepsilon_i (2\varepsilon_0 + \varepsilon_i)} = \frac{\mathbf{\mu}}{\alpha^3} \] (32a)

For \( \varepsilon_i = 1 \) we have what is called the "reaction field":
\[ \mathbf{R}^r = \frac{2(\varepsilon_0 - 1)}{2\varepsilon_0 + 1} \frac{\mathbf{\mu}}{\alpha^3} \] (33a)

It is to be noted that this field has the direction of \( \mathbf{\mu} \) and is the field existing in the spherical cavity after the dipole \( \mathbf{\mu} \) and the medium \( \varepsilon_i \) have been removed, the polarized state of the outside medium being fixed, of course. Note also that for a point dipole in the centre of the cavity that the reaction field is homogeneous.

Case (d) "The dipole Moment in the Gas Phase"

Consider once more the case where \( \mathbf{E} = 0 \) and \( \mathbf{P} = 0 \). The potential outside is given by:
\[ \mathbf{V}_o = \left( \frac{3\mathbf{\mu}}{2\varepsilon_i + 2\varepsilon_0} \right) \cos \theta \frac{\mathbf{\mu}}{\alpha^2} \]
If now we put \( \varepsilon_0 = 1 \) so that we have a sphere containing a dipole placed in a vacuum, we get:
\[ (\mathbf{V}_o)_{\text{vac}} = \left( \frac{3\mathbf{\mu}}{2 + \varepsilon_i} \right) \cos \theta \frac{\mathbf{\mu}}{\alpha^2} \]
But this is just a dipolar field due to a single molecular dipole (in the gas phase) given by:

\[ \mu_g = \frac{3\mu}{2+\varepsilon_i} \]  

(34a)

Thus we see that the dipole moment of a molecule in the gaseous state is lower than the actual dipole moment.

**Case (e) "The Self-Field"**

For this case consider \( E=0 \), \( \mu=0 \) and \( \varepsilon_i = \varepsilon_0 = 1 \) so that we have an unpolarizable sphere in vacuum. The field existing inside this sphere we define as the "Self-field" and it is given by:

\[ E_s^0 = -\frac{4\pi}{3} \bar{P}_s^0 \]  

(35a)

Now let us surround this sphere by a medium of dielectric constant \( \varepsilon_0 \) then the increase in the field inside the sphere is given by:

\[ \bar{X} = -\frac{4\pi}{1+2\varepsilon_0} \bar{P} + \frac{4\pi}{3} \bar{P}_s^0 \]

\[ = \frac{2(\varepsilon_0-1)}{2\varepsilon_0+1} \times \frac{4\pi}{3} \bar{P}_s^0 \]

\[ = \frac{2(\varepsilon_0-1)}{2\varepsilon_0+1} \cdot \frac{\bar{M}_s^0}{\alpha^3} \]  

(36a)

But this is just the reaction field, \( \bar{X} = R \). Hence we obtain the general result that the reaction field of a point dipole \( \mu \) at the centre of the sphere is the same as that of an extended dipole \( \bar{M}_s \) (of the same strength as \( \mu \), of course) arising from a homogeneous polarization of the sphere.

It is now possible to state the general result that the reaction field of a point dipole \( \mu \) in the centre of a homogeneously polarized sphere of total moment \( \bar{M}_s \) (not necessarily having the same
direction as \( \vec{\mu} \) is given by:

\[
\overline{R}'' = \frac{2}{a^3} \left( \frac{\varepsilon_0 - 1}{2 \varepsilon_0 + 1} \right) \left( \overline{M}_S + \overline{\mu} \right)
\]

\[
\overline{R}'' = f \left( \overline{M} + \overline{\mu} \right)
\]

where:

\[
f = \frac{2(\varepsilon_0 - 1)}{a^3 (2 \varepsilon_0 + 1)}
\]

This reaction field, therefore, has the direction of the resultant of the vectors \( \overline{\mu} \) and \( \overline{M}_S \), and is homogeneous.

From the results of this simple electrostatic problem, we see immediately from the expression for the Self-field, (35:a), that the contribution from sources external to the large spherical region in the Lorentz model is given by (14:a).

Another method of obtaining (15:a) at once presents itself from the result (36:a). Consider once more a homogenous external field \( \overline{E} \) acting on a dielectric \( \varepsilon \), and let us concentrate on a large spherical region of radius \( a \) used by Lorentz. This region will take on a polarization:

\[
\overline{P} = \frac{\varepsilon - 1}{\varepsilon + 1} \overline{E}
\]

and hence the total moment induced in it is:

\[
\overline{M} = \nabla \overline{P}
\]

where \( \nabla \) is the volume. Now let us fix the polarized states of the charges outside \( \nabla \) and remove the sphere from the dielectric. What is the field inside the cavity? We can write down immediately that this field is:

\[
\overline{X} = (\text{Cavity Field}) + (\text{Reaction Field of a homogeneously polarized sphere})
\]
Hence we have an alternative method of obtaining the local field producing the dipoles under the Lorentz consideration.

5. Dielectric Constant of a Pure Polar Gas.

Consider a simple gas composed of polar molecules at a reasonably low density. Then $N_0$ is small in (16:a) and hence $\varepsilon - 1$ is also small. Let $\varepsilon - 1 = S$, where $S$ is small, then the local field acting on a molecule is given by:

\[ \vec{f} = \left( \frac{\varepsilon + 2}{3} \right) \vec{E} \]
\[ = \left( 1 + \frac{S}{3} \right) \vec{E} \]
\[ \therefore \vec{f} = \frac{\varepsilon + 2}{3} \vec{E} \]

(40:a)

a result which one would expect if the density is low enough. Now, the moment of any molecule will be:

\[ \vec{m} = \alpha \vec{f} + \vec{\mu}_g \]

(41:a)

where $\vec{\mu}_g$ is the intrinsic moment of the molecule in the gas phase.

(From (34:a) we have $\vec{S} = \vec{m}$. Thus, for this purpose $\vec{\mu}_g = \frac{3\vec{\mu}}{2 + \vec{m}}$).

From (40:a) we have for this case that:

\[ \vec{m} = \alpha \vec{E} + \vec{\mu}_g \]

Now before the field $\vec{E}$ is applied, the directions of $\vec{\mu}_g$ will be randomly distributed so that without a field the average value of the moment will
be zero. With a field, however, the average value of the moment in the 
\( \vec{E} \) direction will be:
\[
\overline{m} = \alpha \vec{E} + \overline{\vec{M}} = \alpha \vec{E} + \mu g \cos \phi
\]
where \( \phi \) is the angle between the dipole and the field. The potential
energy of this dipole is:
\[
W = -\mu g \cdot \vec{E} = -\mu g E \cos \phi
\]
These energies will, of course, have a Boltzmann distribution, hence the
average value is:
\[
\mu g \cos \phi = \frac{\int_0^\pi \mu g \cos \phi \cdot \frac{\mu E \cos \phi}{\epsilon \tilde{T}} \cdot d(\cos \phi)}{\int_0^\pi \frac{\mu E \cos \phi}{\epsilon \tilde{T}} \cdot d(\cos \phi)}
\]
and assuming \( \mu g E \ll k \tilde{T} \) we get:
\[
\mu g \cos \phi = -\frac{\mu g E}{2 k \tilde{T}} \left[ \frac{\cos^3 \phi}{3} \right]_0^\pi
\]
\[
\therefore \mu g \cos \phi = \frac{\mu g^2 E}{3 k \tilde{T}} \quad \text{(4.2a)}
\]
Now let there be \( N_0 \) molecules per unit volume, then we have, since
the gas is "pure", that the polarization is:
\[
P = N_0 \overline{m}
\]
\[
\Rightarrow (\frac{E}{4\pi}) \vec{E} = N_0 \left( \alpha \vec{E} + \frac{\mu g E}{3 k \tilde{T}} \right)
\]
hence:
\[
\varepsilon - 1 = \frac{4\pi N_0}{(\alpha + \frac{\mu g^2}{3 k \tilde{T}})} \quad \text{(4.3a)}
\]
Thus we have arrived at a formula for the dielectric constant of a polar
gas. If the gas is non-polar, we may write:
\[
\varepsilon - 1 = \frac{4\pi N_0}{\alpha} \quad \text{(4.4a)}
\]
which is also seen immediately from equation (16.a). Now for high
enough frequencies, the dipoles \( \mu g \) will not be able to follow the
oscillations of the field, and hence there will be no contributions from
\( \mathbf{\mu}_0 \) at these frequencies. The dielectric constant is thus written as
\( \varepsilon_0 \)
where:
\[
\varepsilon_0 - 1 = 4\pi N_0 \alpha
\]

Hence, for high enough frequencies the polar gas behaves like a non-polar
one. In view of (45a) we may write (43a) as:
\[
\varepsilon = \varepsilon_0 + 4\pi N_0 \frac{\mu_0^2}{3 \varepsilon_0}
\]

6. Pure Polar Liquids

(a) Debye Formula

From consideration of a pure polar gas, the most obvious thing
to do in the case of a polar liquid is to consider the local field acting
on each molecule as:
\[
f = \frac{\mathbf{\varepsilon} + 2}{3} \mathbf{E}
\]
Where, for this case, \( \varepsilon - 1 \) is not small because \( N_0 \) is not small.

Hence, the moment of a molecule becomes:
\[
\mathbf{m} = \alpha \left( \frac{\mathbf{\varepsilon} + 2}{3} \right) \mathbf{E} + \mathbf{\mu}_0
\]

As before, let the angle between the dipole \( \mathbf{\mu}_0 \) and the local field \( f \)
be \( \phi \) then the potential energy of the dipole is
\[
\mathbf{W} = -\mathbf{\mu}_0 f \cos \phi
\]
so that the average moment in the \( \mathbf{E} \) direction is:
\[
\mathbf{m} = \alpha f + \frac{\mathbf{\mu}_0^2}{3} f
\]
\[
\mathbf{m} = \left( \alpha + \frac{\mathbf{\mu}_0^2}{3 N_0} \right) \frac{\mathbf{\varepsilon} + 2}{3} \mathbf{E}
\]
The moment per unit volume thus becomes:
\[
\mathbf{P} = \frac{\mathbf{\varepsilon} - 1}{4\pi} \mathbf{E} = N_0 \left( \alpha + \frac{\mathbf{\mu}_0^2}{3 N_0} \right) \frac{\mathbf{\varepsilon} + 2}{3} \mathbf{E}
\]
leading to:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N_0 \left(\alpha + \frac{\mu^2}{3kT}\right)
\]  \hspace{1cm} (48:a)

This is the Debye formula* (obtained in 1912). At sufficiently high frequencies, the dipoles give no contribution. Hence, we have:

\[
\frac{\varepsilon_{oo} - 1}{\varepsilon_{oo} + 2} = \frac{4\pi}{3} N_0 \alpha
\]  \hspace{1cm} (49:a)

so that the polar liquid acts like a pure non-polar liquid.

Substituting (49:a) into (48:a) leads to:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\varepsilon_{oo} - 1}{\varepsilon_{oo} + 2} = \frac{4\pi N_0}{9kT} \mu^2
\]

For a polar gas Debye measured \( \varepsilon \) at various temperatures and plotted \( \frac{(\varepsilon - 1)}{(\varepsilon + 2)} vs. \frac{1}{T} \) (see (fig.4)). The slope of this curve is, of course, a measure of \( \mu^2 \) and the intercept on the vertical axis is a measure of \( \varepsilon_{oo} \).

* Debye, P. *Polar Molecules* (New York 1929)
Next, Debye made dilute solutions of polar liquid in a non-polar liquid. If \( N_p \) refers to the number of polar molecules per unit volume and \( N_n \) the number of non-polar molecules per unit volume, the Debye equation becomes:

\[
\frac{E-1}{E+2} = \frac{4\pi}{3} (N_p M_p + N_n M_n) + \frac{4\pi N_p}{9kT} (\mu^2)
\]

or:

\[
\frac{E-1}{E+2} - \frac{E_0-1}{E_0+2} = \frac{4\pi N_p}{9kT} (\mu^2)
\]

Proceeding as with a gas, Debye now found \( \mu^2 \) for various concentrations of the polar liquid. His results showed that:

(i) \( (\mu^2)_{\text{liquid}} \) became less for increasing concentrations of the polar in the non-polar liquid.

(ii) For over 2,000 polar substances studied, the moment in the liquid state is always less than the corresponding moment measured in the gas-phase.

Debye attempted to explain these results by assuming that the polar molecules tend to "associate" with each other in the liquid in such a way that their dipoles were aligned anti-parallel, thereby reducing the average moment. However, by extrapolating the \( (\mu^2)_{\text{liquid}} \) concentration curve down to small concentrations, Debye found that even for infinite dilutions \( (\mu^2)_{\text{liquid}} < (\mu^2)_{\text{gas}} \).

Debye's results are of fundamental importance to the theory of polar liquids for it is from them that Onsager was led to reconsider the whole problem and formulate the concept of the reaction field (33a).
Before proceeding to Onsager's work, however, let us clarify the concepts of $E_\infty$ and $\mu^2$, introduced above. To do this, we will consider the dispersion curve of a gas over the complete spectrum. The application to liquids will become obvious from discussion.

(b) The Complete Dispersion Curve of a Polar Substance

For convenience in this section, we may use the Debye Formula which in any case works fairly well for a polar gas*. We have:

$$\frac{E-1}{E+2} = \frac{4\pi}{3} N_0 \left( \alpha + \frac{\mu^2}{3kT} \right)$$

where $N_0$ for a gas may be written as $N_0 = \frac{Z}{\omega} A$, $\rho$ being the density, $\omega$ Avogadro's number and $\omega$ the molecular weight. We may thus write the molecular polarization $\mathcal{P}$ as:

$$\mathcal{P} = \frac{\omega Z}{\rho} \left( \frac{E-1}{E+2} \right) = \frac{4\pi}{3} A \left( \alpha + \frac{\mu^2}{3kT} \right)$$ (50:a)

For a non-polar gas the only term contributing to $\mathcal{P}$ is $\frac{4\pi}{3} \alpha$ and hence for this case $\mathcal{P}$ should be independent of temperature and density. For a polar substance, of course, only the dipole term is temperature dependent.

The molecular polarization $\mathcal{P}$ is due to contributions from the:

(i) Electronic polarization $\mathcal{P}_e$, of the molecules due to a displacement of the electron clouds with respect to the nuclei of the atoms.

(ii) Atomic polarization, $\mathcal{P}_a$, caused by a displacement of the atoms with respect to each other in diatomic molecules,

* For polar liquids the formula of Onsager and Bottcher may be used.
or a "bending" of groups of atoms with respect to each other in molecules more complex than diatomic ones.

(iii) Orientation polarization, $P_o$, due to the directing influence of the electric field on the permanent dipoles \( \mu \) of the molecules.

Thus from (50a) we may write:

$$P = P_e + P_a + P_o$$  \hspace{5cm} (51a)

where:

$$P_e = \frac{4\pi}{3} A \alpha_e$$

and:

$$P_a = \frac{4\pi}{3} A \alpha_a$$

and:

$$P_o = \frac{4\pi}{9\beta^2} \mu^2.$$

The electronic polarization has been studied closely by Maxwell and more recently by the methods of Quantum Mechanics. Original workers in this field being Cauchy and Sellmeyer. The result (8a) when extended to all the electrons in a molecule gives:

$$P_e = \sum_i \frac{C_i}{\nu_i^2 - \nu^2}$$  \hspace{5cm} (52a)

where \( i \) refers to the \( i^{th} \) electron and \( \nu_i \) is the resonant frequency of the \( i^{th} \) electron and \( C_i \) is a constant belonging to \( \nu_i \).

Equation (52a) checks also with Quantum mechanics except at the absorption frequencies \( \nu_i \) where \( P_e = \pm \infty \) is predicted. This result is due to the fact that no allowance was made for the internal "friction". The resonant frequencies of the electrons are in the visible or ultra-violet region (\( \nu = 10^4 \sim 10^{15} \) c.p.s.).

The Orientation Polarization, $P_o$, is approximately constant up to about \( \nu = 10^9 \) c.p.s. when the dipoles can no longer follow the oscillations of the field. Thus, in the graph of $P_o v$ we find,
as \( \nu \) increases, a constant value of \( \rho \) up to about \( \nu = 10^9 \text{ c.p.s.} \). At this point there is a sudden drop in \( \rho \) due to the cut-off of the dipole contribution. The polarization at this and higher frequencies is then due to \( \rho_a + \rho_e \) alone. The total, or "static" polarization may, therefore, be measured up to frequencies of about \( 10^6 \text{ c.p.s.} \).

The Atomic polarization is by far the most difficult of the three quantities to predict theoretically. Van Vleck* found that for \( \text{HCl} \) the atomic polarization was given by:

\[
\rho_a = \frac{4\pi}{3} A \left( \frac{q^2}{\varkappa} \right)
\]

where "\( q \)" is the effective nuclear charge and "\( \varkappa \)" is the force constant of the atomic vibration. \( q^2 \) is found by spectral intensity measurements, while \( \varkappa \) is found by the resonant frequency of the vibration spectra of \( \text{HCl} \). The value that he found, however, was one hundred times smaller than that measured for gaseous \( \text{HCl} \) by Zahn**

Mecke*** has considered more complicated molecules such as the linear triatomic type molecule like \( \text{CO}_2 \) and the triangular type such as \( \text{H}_2\text{O} \) and Dekker**** has shown that a formula similar to that used by van Vleck gives results somewhat lower than those observed. The atomic resonance frequencies are, of course, in the infra-red, \( \nu = 10^3 \sim 10^5 \text{ c.p.s.} \). Above this frequency, the nuclei can no longer follow the electromagnetic vibrations.

* van Vleck, J.H.  Phys. Rev.  30, 31, 1937
** Zahn, C.T.  Phys. Rev.  27, 455, 1926
*** Mecke, R.  Leipziger Vorträge  1931, 22
**** Dekker, A.J.  Recueil des Travaux Chimiques des Pays-Bas.
The plot of the molecular polarization of a substance as a function of frequency is shown in fig. 5. The different curves shown for the orientation polarization are for different temperatures \( T \).

In the limit as \( T \to \infty \) we have what corresponds to a pure non-polar substance (Curve \( AB \)). The frequencies \( \nu_0, \nu_a \) and \( \nu_e \) refer to the dipole, cut-off frequency and the atomic and electronic resonance frequencies, respectively. The curve is shown with two electronic absorption frequencies \( \nu_{e1} \) and \( \nu_{e2} \) and for frequencies higher than these the polarization becomes zero.

The \( \mathcal{E} \) corresponding to the dipole cut-off frequency \( \nu_0 \) is often called \( \mathcal{E}_0 \) while for frequencies between \( \nu_0 \) and \( \nu_a \) the dielectric constant is represented by \( \kappa^2 \). Even for frequencies above \( \nu_a \) the dielectric constant is called \( \kappa^2 \) but this should more
properly be given the symbol $m_e^2$.

(c) Onsager's Formula*

Onsager has assumed in his derivation for a polar liquid that:

(i) A molecule occupies a sphere of radius $\alpha$ and is polarizable.

(ii) The short range interaction energy between molecules is negligible.

On the assumptions made above, the formula for any polar fluid can be found for either the liquid in its pure state or as a mixture. In both cases, it is assumed that the local field $\vec{F}$ acting on a molecule consists of the cavity field (which is the same for all molecules) and a reaction field (which is different for different molecules).

Let us consider first of all, a pure polar liquid composed of molecules of radius $\alpha$ and polarizability $\alpha$ containing an intrinsic dipole $\mu_0$. Then the total moment of the polarizable molecule is:

$$\vec{m} = \vec{\mu}_0 + \alpha \vec{F}$$

where:

$$\vec{F} = \vec{E}_c + \vec{R}$$

Now the reaction field is given by:

$$\vec{R}^o = \frac{2(\epsilon - 1)}{\alpha^3(\epsilon + 1)} \vec{m} = F \vec{m}$$

$$\therefore \vec{R} = F \vec{\mu}_0 + \alpha F \vec{F}$$

Thus the local field may be written as:

\[ \mathbf{f} = \mathbf{E} + f \mathbf{\mu} + \alpha f \mathbf{F} \]

or:

\[ \mathbf{f} = \frac{\mathbf{E} + f \mathbf{\mu}}{1 - \alpha f} \]

Hence the total moment becomes:

\[ \mathbf{m} = \mathbf{\mu} + \alpha f \mathbf{E} + \frac{\alpha f \mathbf{\mu}}{1 - \alpha f} \]

\[ \therefore \quad \mathbf{m} = \frac{\mathbf{\mu}}{1 - \alpha f} + \frac{\alpha f \mathbf{E}}{1 - \alpha f} \]

The average moment in the \( \mathbf{E} \)-direction is, of course:

\[ \overline{\mathbf{m}} = \frac{\alpha f \mathbf{E}}{1 - \alpha f} \]

Now the potential energy of the dipole is

\[ W = -\mathbf{\mu} \cdot \mathbf{F} = -\mathbf{E} \cdot \mathbf{\mu} \cos \phi \]

where \( \phi \) is the angle between the dipole and the \( \mathbf{E} \)-direction thus:

\[ W = -\mathbf{\mu} \cdot \mathbf{F} = -\frac{\mathbf{E} \cdot \mathbf{\mu} \cos \phi}{1 - \alpha f} \]

Assuming a Boltzmann distribution of these energies, we have that the average value of \( \cos \phi \) is:

\[ \mu_g \cos \phi = \frac{\int_0^\pi \mu_g \cos \phi e^{-\frac{E}{kT}} d(\cos \phi)}{\int_0^\pi e^{-\frac{E}{kT}} d(\cos \phi)} \]

As before, let us assume that \( \mathbf{\mu} \cdot \mathbf{F} \ll kT \) as well as \( f \frac{\mu^2}{1 - \alpha f} \ll kT \) then:

\[ \mu_g \cos \phi = \frac{\mu_g^2 \mathbf{E}}{3 kT} \cdot \frac{E}{1 - \alpha f} \]

(56:a)
Hence the average moment is given by:

\[
\overline{m} = \frac{\alpha E_c}{1-\alpha f} + \frac{\mu_g^2}{32 \pi \rho (1-\alpha f)^2}
\]

\[
\therefore \overline{m} = \left[ \alpha + \frac{\mu_g^2}{32 \pi (1-\alpha f)} \right] \frac{E_c}{(1-\alpha f)}
\]

Letting \( N_0 \) be the number of molecules per unit volume we obtain, therefore:

\[
\overline{\rho} = \frac{\varepsilon-1}{4\pi} \frac{E^0}{E} = N_0 \left[ \alpha + \frac{\mu_g^2}{32 \pi (1-\alpha f)} \right] \frac{3 \varepsilon}{(2 \varepsilon + 1)(1-\alpha f)}
\]

\[
\therefore \frac{(\varepsilon-1)(2 \varepsilon+1)}{12 \pi \varepsilon} = N_0 \left[ \frac{\alpha}{1-\alpha f} + \frac{\mu_g^2}{32 \pi (1-\alpha f)^2} \right]
\]

(1) Consider first of all a pure non-polar liquid

Then \( \mu_g = 0 \) and we have:

\[
\frac{(\varepsilon-1)(2 \varepsilon+1)}{12 \pi \varepsilon} = \frac{\alpha N_0}{1-\alpha f}
\]

The average volume occupied by a molecule is:

\[
\frac{4\pi}{3} a^3 = \frac{1}{N_0}
\]

Hence we have that:

\[
\frac{(\varepsilon-1)(2 \varepsilon+1)}{12 \pi \varepsilon} = \frac{\alpha}{1-\alpha f} \frac{3}{4\pi a^3}
\]

or:

\[
\frac{(\varepsilon-1)(2 \varepsilon+1)}{9 \pi \varepsilon} = \frac{\alpha}{1-\alpha f} a^3
\]

from (38:a) and solving (58:a) for \( \alpha \) we get:

\[
\frac{\alpha}{a^3} = \frac{\varepsilon-1}{\varepsilon+2}
\]
which corresponds to the result (19:a). Since \( \kappa \) depends only upon \( \alpha_a \) and \( \alpha_e \) (see Sec.6(b)), we write the above as:

\[
\frac{\alpha}{a^3} = \frac{m^2-1}{m^2+2}
\]

Thus we may write:

\[
1-\alpha_f = 1 - a^3 \left( \frac{m^2-1}{m^2+2} \right) \frac{2(\varepsilon-1)}{a^3(2\varepsilon+1)}
\]

\[
\therefore (1-\alpha_f) = \frac{3(2\varepsilon+n^2)}{(2\varepsilon+1)(m^2+2)}
\]

also, we have:

\[
\frac{\alpha N_0}{1-\alpha_f} = a^3 \left( \frac{m^2-1}{m^2+2} \right) \frac{1}{3} \cdot \frac{a^3}{4\pi \varepsilon} \cdot \frac{(2\varepsilon+1)(m^2+2)}{3(2\varepsilon+n^2)}
\]

\[
\therefore \frac{\alpha N_0}{1-\alpha_f} = \frac{(2\varepsilon+1)(m^2-1)}{4\pi \varepsilon (2\varepsilon+n^2)}
\]

(ii) Thus for a pure polar liquid we get that:

\[
\frac{(\varepsilon-1)(2\varepsilon+1)}{12\pi \varepsilon} = \frac{\alpha N_0}{1-\alpha_f} + \frac{\mu_0^2 N_0}{3\pi \varepsilon} (1-\alpha_f)
\]

by means of (60:a) and (61:a) this becomes:

\[
\frac{\varepsilon-1}{12\pi \varepsilon} = \frac{m^2-1}{4\pi (2\varepsilon+n^2)} + \frac{\mu_0^2 N_0 (2\varepsilon+1)(m^2+2)^2}{9 (2\varepsilon+n^2)}
\]

which reduces to:

\[
\frac{(\varepsilon-m^2)(2\varepsilon+n^2)}{12\pi \varepsilon} = \frac{\mu_0^2 N_0}{3kT} \left( \frac{m^2+2}{3} \right)^2
\]

or:

\[
\frac{\alpha^3 (\varepsilon-m^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2} = \frac{\mu_0^2}{3kT}
\]
Measuring $\varepsilon$ at various temperatures, $T$, and inserting both $\mu$ and $T$ in this equation leads to consistent values of $\mu^2$ over a large range of temperatures. Furthermore, when (62:a) is applied to the substance in the gas-phase, the results show the same values for $\mu^2$ as in the liquid phase. For the substance in the gas-phase we have: $m^2 \geq 1$ also $\varepsilon \leq 1$.

Thus for a polar gas we have, approximately, from (63:a) that:

$$\frac{\varepsilon - m^2}{4\pi} = \frac{\mu^2 N_0}{3\varepsilon k T}$$

$$\therefore \varepsilon - m^2 = 4\pi N_0 \left( \frac{\mu^2}{3\varepsilon k T} \right)$$

(64:a)

which agrees with (46:a) if $m^2 = \varepsilon_0$.

(iii) Consider now a mixture of polar liquids, and let us concentrate on the molecule type " $\gamma$ ".

Let the number of molecules of this type be $N_\gamma$ per unit volume then the moment per unit volume of the liquid is:

$$\bar{p} = (\frac{\varepsilon - m}{4\pi}) \varepsilon$$

$$= \sum \frac{N_\gamma}{\theta} \left[ \frac{\mu^2}{3\varepsilon k T (1 - \alpha_\theta f_\theta)} \right] \frac{3\varepsilon \bar{p}}{2\varepsilon + \varepsilon \alpha_\theta f_\theta}$$

Hence:

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{12\pi \varepsilon} = \sum \left[ \frac{N_\delta \alpha_\delta}{1 - \alpha_\theta f_\delta} + \frac{N_\gamma}{1 - \alpha_\theta f_\theta} \right] \frac{\mu^2}{3\varepsilon k T}$$

(65:a)

Letting:

$$\frac{N_\delta \alpha_\delta}{1 - \alpha_\theta f_\delta} = \frac{(2\varepsilon + 1)(m_\sigma^2 - 1)}{4\pi \varepsilon (2\varepsilon + m_\sigma^2)}$$
and:

$$\frac{N_0}{(1-\omega f_0)^2} = \frac{3}{4\pi a_0^2} \left[ \frac{(2E+1)(m_0^2+2)}{3(2E+m_0^2)} \right]^2$$

in accordance with (61:a) and (60:a) we get:

$$\frac{E-1}{3E} = \sum \frac{m_0^2-1}{2E+m_0^2} + \left\{ \frac{2E+1}{(2E+m_0^2)a_0^2} \left( \frac{m_0^2+2}{3} \right)^2 \right\}$$

(d) **Kirkwood's Formula**

It is to be recalled that Onsager's formula was derived neglecting short range interaction forces. Kirkwood, by a more elaborate treatment of polar liquids in which short range forces between nearest neighbours are considered, has arrived at the formula:

$$\frac{(E^2-1)(2E+m_0^2)}{12\pi \mathcal{E}} = \frac{\mu_0^2 N_0}{3 \lambda T} \left( \frac{m_0^2+2}{3} \right)^2 \left( 1 + \frac{1}{2} \overline{\cos \phi} \right)$$

where \( \overline{\cos \phi} \) is the average number of nearest neighbours and \( \overline{\cos \phi} \) is the time average of the cosine between neighbouring dipoles. At high temperatures, we would have, therefore, that Kirkwood's formula is the same as Onsager's formula. Experimentally, however, it is found that Onsager's formula holds very well over large ranges of temperature and hence we must conclude that \( \overline{\cos \phi} \) is always small and that Kirkwood's refinement leads to no important predictions in this particular instance.

(e) Bottcher's Consideration of Polar Liquids

Using Onsager's concept of the reaction field, Bottcher* successfully showed that the well-known Van Arkel and Snoek** semi-empirical formula for the dielectric constant of a polar liquid could be predicted theoretically. This formula is:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_{\sigma} n_\sigma \left( \alpha_\sigma + \frac{\mu_\sigma^2}{3kT + \sigma N_0 \frac{4\pi}{3} R_\sigma} \right) \tag{68; a}$$

where $C_\sigma$ is a constant for the molecule being considered.

Experimentally, it was found that $C_\sigma$ was little influenced by concentration and was nearly the same for a great number of substances.

Using Onsager's concept of the reaction field, Bottcher showed that:

$$C_\sigma N_0 \frac{\mu_\sigma^2}{2} = \mu_\sigma \overline{R_\sigma} \tag{69; a}$$

where $R_\sigma$ is the reaction field for the molecule type "\( \sigma \)". After some algebra, Bottcher showed that (68; a) reduces to Onsager's formula (62; a).

Bottcher's method of obtaining the formula for a mixture of polar liquids is somewhat more direct than that used by Onsager, and serves better to introduce the model for a polar molecule discussed by the author in Part "B". Following Bottcher, therefore, we may write down at once the moment per unit volume of a polar liquid as:

$$\overline{P} = \frac{\varepsilon - 1}{\varepsilon + 2} \overline{E} = \sum_{\sigma} N_\sigma \left( \alpha_\sigma \overline{E}_{\sigma}^\sigma + \frac{\mu_\sigma^2}{3kT} \overline{E}_{\sigma}^\sigma \right) \tag{70; a}$$

---


** Van Arkel and Snoek *Phys.Z* 33, 662 (1932); 187 (1934).
\[ \text{Where: } N_{\gamma} \text{ is the number of molecules of type } \sigma \text{ per unit volume} \]

having a polarizability \( \alpha_{\gamma} \) and a dipole moment in the gas-phase of \( \mu_{\gamma} \).

The field \( E_{i\gamma} \) is the internal field acting on the molecule of type \( \sigma \) while the field \( E_{d\gamma} \) is the directing field trying to orientate the dipole in the \( \overrightarrow{E} \) direction.

To get Debye's result (48:a), we assume that the internal field and the directing field are the same for all molecules and equal to that local field introduced by Lorentz; (15:a), i.e:

\[ \overrightarrow{E}_{d\gamma} = \overrightarrow{E}_{i\gamma} = \frac{\varepsilon + 2}{3} \varepsilon \]

leading to:

\[ \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4 \pi}{3} \sum_{\sigma} N_{\sigma} \left( \alpha_{\sigma} + \frac{\mu_{\sigma}^2}{3 k_{B} T} \right) \]  

(71:a)

Now as we know, from the concept of the reaction field, not all of the internal field is trying to orientate the dipole, hence

\( E_{d\sigma} < E_{i\gamma} \), and since the reaction field is in the same direction as \( \mu_{\gamma} \) we may write:

\[ E_{d\gamma} = E_{i\gamma} - R_{\gamma} \cos \phi_{\gamma} \]  

(72:a)

where \( \phi_{\gamma} \) is the angle between the directing field and the dipole and \( \cos \phi_{\gamma} \) is its time average.

The reaction field \( R_{\gamma} \) acting on the molecule type \( \sigma \) is given by:

\[ R_{\gamma} = \frac{2(\varepsilon - 1)}{\alpha_{\gamma}^2 (2\varepsilon + 1)} \mu_{\gamma} = f_{\sigma} \mu_{\gamma} \]  

(73:a)

for a non-polarizable dipole.
Clearly, for a polarizable dipole we must have:
\[
\overrightarrow{R_0} = f_0 \overrightarrow{\mu_0} + \alpha_0 f_0 \overrightarrow{R_0}
\]
\[
\therefore \quad \overrightarrow{R_0} = \frac{f_0}{1 - \alpha_0 f_0} \overrightarrow{\mu_0}
\] (74:a)

Now by the methods of statistical mechanics:
\[
\cos \phi_0 = \frac{\mu_0^2}{3kT} \overrightarrow{E_0}
\] (75:a)

Thus (72:a) together with (73:a) gives:
\[
\overrightarrow{E_0} = \overrightarrow{E_i} - \frac{f_0}{1 - \alpha_0 f_0} \cdot \frac{\mu_0^2}{3kT} \overrightarrow{E_0}
\]
or:
\[
\overrightarrow{E_i} = \left[ 1 + \frac{f_0}{1 - \alpha_0 f_0} \cdot \frac{\mu_0^2}{3kT} \right] \overrightarrow{E_0}
\] (76:a)

Now the problem is to find the directing field \( \overrightarrow{E_d} \). Clearly, this directing field must be proportional with \( \overrightarrow{E} \) and independent of the reaction field, for it will exist in the molecule in the \( \overrightarrow{E} \)-direction even if \( \mu_0 = 0 \).

To find \( \overrightarrow{E_d} \), consider a spherical cavity of radius \( r \) in a homogeneous field \( \overrightarrow{E} \). The field inside the cavity, i.e. ("Cavity Field") is given by:
\[
\overrightarrow{E_c} = \frac{3\varepsilon}{2\varepsilon + 1} \overrightarrow{E}
\]
(for all "\( r \)"

Let us now "fill up" the cavity with a medium of polarizability "\( \alpha \)", then the polarized state of the surroundings will change. Fixing the outside state and taking out "\( \alpha \)" again we will get a new field inside the cavity. This new field is the directing field \( \overrightarrow{E_d} \). We have,
therefore:
\[
E_{d\sigma} = E_c + \alpha_{\sigma} f_\sigma E_{d\sigma}
\]
or:
\[
E_{d\sigma} = \frac{E_c}{1 - \alpha_{\sigma} f_\sigma}
\]  
(77:a)

Using \(f_\sigma\) as defined by (73:a) together with \(E_c = \frac{3\varepsilon}{2\varepsilon + 1}E\) and using \(\alpha_{\sigma} = \alpha^2 \left(\frac{\mu^2 - 1}{\mu^2 + 2}\right)\), we obtain for the directing field*:
\[
E_{d\sigma} = \frac{(n_{\sigma}^2 + 2)\varepsilon}{n_{\sigma}^2 + 2\varepsilon} E
\]  
(78:a)

Substituting (78:a) and (76:a) into (70:a) leads to the Onsager-Bottcher formula** for the dielectric constant of a mixture of polar liquids.

We note once more that \(E_{d\sigma}\) is independent of \(R^p\) and is proportional with \(E\). Hence, \(E_{d\sigma}\) is independent of both the position and the type of dipole which is in the molecule. The expression (78:a) for \(E_{d\sigma}\) assumes only that the molecules are spherical. On the other hand, however, the internal field (76:a) assumes that the dipole is a "point" dipole with a central position. In short, therefore, \(E_{d\sigma}\) is the only term which depends on the model used for the dipole in the molecule.

* In Section 4 (b), Pg. 14, we have found the directing field by an alternate method. It is obvious that this method and the one above must lead to the same result, (78:a) or (31:a).

** It is to be stressed that Bottcher's considerations do not lead to a formula different from Onsager's, (62:a).
Clearly, therefore, models for which the expression:

\[
\frac{f_0}{1 - \alpha f_0}
\]

are the same, will all lead to the same Onsager-Bottcher result for polar liquids.

Dekker \* has shown, for an eccentric, centrally directed, point dipole in a sphere, that (79:a) is the same. In Part "B" of this thesis, it is shown that a molecule bearing a finite dipole of arbitrary position and direction leaves (79:a) unchanged. Hence, the Onsager-Bottcher formula remains unchanged even for this more realistic model.

\* Dekker, A.J. Physica XII No.4, July 1946.
The Electrostatic Problem

Consider a dipole formed by two charges $q$ and $-q$, a distance $d$ apart, with an arbitrary position inside a sphere of radius $R$. The coordinate system is chosen such that the line joining the centre of the sphere and the midpoint of $d$ is taken as the $z$-axis and the dipole lies in the $xy$-plane (fig. 6). We assume the dielectric constant of the homogeneous substance inside the sphere to be $\varepsilon_i = n^2$ whereas the outside is defined by $\varepsilon_0$.

A general solution of Laplace's equation in spherical coordinates $r$, $\theta$, and $\phi$ is:

$$V = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \left( \frac{B_{mn}}{R^{n+1}} - \frac{A_{mn}}{R^n} \right) P_n^m(\cos \theta) \cos m\phi$$

where: $P_n^m(\cos \theta) = \frac{\sin \theta}{\sin \frac{\theta}{2}} \frac{d^n}{d(\cos \theta)^n} \left[ P_n(\cos \theta) \right]$.

Because the solution must be regular at infinity, the potential $V_0$ outside the sphere is given by:

$$V_0 = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{B_{mn}}{R^{n+1}} P_n^m(\cos \theta) \cos m\phi$$

The potential $V_i$ inside the sphere is equal to:

$$V_i = V_0 + \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{A_{mn}}{R^n} P_n^m(\cos \theta) \cos m\phi$$

For convenience in the notation we let:

$$A_{mn} = \frac{\alpha_{mn}}{R^n} ; \quad B_{mn} = \frac{\beta_{mn}}{R^{n+1}}$$
The first problem is to express $\mathbf{V}_{ji}$ in a form suitable for the application of boundary conditions on the sphere.

so that:

$$V_0 = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \beta_{nm}(R) P_m(\cos \theta) \cos m \phi$$  \hspace{1cm} (1:b)

$$V_i = V_{pole} + \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} a_{mn} \left( \frac{1}{R} \right)^m P_m(\cos \theta) \cos m \phi$$  \hspace{1cm} (2:b)

The potential of the dipole is, of course, given by:

$$V_{pole} = \frac{q}{\varepsilon_i} \left( \frac{1}{R^2} - \frac{1}{R_1^2} \right)$$

Fig. VI

The first problem is to express $V_{dipole}$ in a form suitable for the application of boundary conditions on the sphere.
To this end we write:

\[
\begin{align*}
\frac{1}{\rho_1} &= (a_1^2 + \alpha^2 - 2a_1 \alpha \cos \phi) \frac{1}{\xi} = \sum_{m=0}^{\infty} \frac{a_m}{\lambda^{m+1}} P_m(\cos \phi) \\
\frac{1}{\rho_2} &= (a_2^2 + \alpha^2 - 2a_2 \alpha \cos \phi) \frac{1}{\xi} = \sum_{m=0}^{\infty} \frac{a_m}{\lambda^{m+1}} P_m(\cos \phi)
\end{align*}
\]

(4:1b)

Now by the addition formula for Legendre polynomials we have for two lines passing through the origin with polar and azimuthal angles, \( \Theta, \phi, \) and \( \Theta_2, \phi_2 \) respectively that:

\[
P_m(\cos \phi) = \sum_{m=0}^{\infty} \frac{(2-\delta_{m0})(m-m)!}{(m+m)!} P_m(\cos \Theta) P_m(\cos \Theta_2) \cos m(\phi - \phi_2)
\]

where \( \delta \) is the angle between the lines and \( \delta_{m0} = 1 \) for \( m = 0 \) and zero for \( m \neq 0 \). If we apply this result to \( a_1 \) and \( a_2 \) and \( a_2 \) and \( a_2 \) (fig. ) we get:

\[
P_m(\cos \phi) = \sum_{m=0}^{\infty} \frac{(2-\delta_{m0})(m-m)!}{(m+m)!} P_m(\cos \Theta) P_m(\cos \Theta_2) \cos m(\phi - \phi_2)
\]

Substituting these results into (4:1b) leads to:

\[
\begin{align*}
\frac{1}{\rho_1} &= \sum_{m=0}^{\infty} \sum_{n=0}^{m} \frac{a_n}{\lambda^{n+1}} \frac{(2-\delta_{m0})(m-m)!}{(m+m)!} P_n(\cos \Theta) P_n(\cos \Theta_2) (-1)^n \cos m\phi \\
\frac{1}{\rho_2} &= \sum_{m=0}^{\infty} \sum_{n=0}^{m} \frac{a_n}{\lambda^{n+1}} \frac{(2-\delta_{m0})(m-m)!}{(m+m)!} P_n(\cos \Theta) P_n(\cos \Theta_2) \cos m\phi
\end{align*}
\]

So that (3:1b) becomes:

\[
\nabla D_{\text{Dipole}} = \frac{q}{\xi} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{C_{m,n}}{\lambda^{n+1}} P_n(\cos \Theta) \cos m\phi
\]

where:

\[
C_{m,n} = (2-\delta_{m0})\frac{(m-m)!}{(m+m)!}[a_2^n P_n(\cos \Theta) - (-1)^n a_1^n P_n(\cos \Theta_2)]
\]
The angles $\theta_1$ and $\theta_2$, determined by the geometry of the system, are given by:

\[
\cos \theta_1 = \frac{a_1}{d_1} (a - \frac{1}{2} d \cos \beta)
\]

\[
\cos \theta_2 = \frac{a_2}{d_2} (a + \frac{1}{2} d \cos \beta)
\]

where:

\[
a_1 = \left[ a^2 + \left( \frac{d}{2} \right)^2 - 2a \left( \frac{d}{2} \right) \cos \beta \right]^{\frac{1}{2}}
\]

\[
a_2 = \left[ a^2 + \left( \frac{d}{2} \right)^2 + 2a \left( \frac{d}{2} \right) \cos \beta \right]^{\frac{1}{2}}
\]

Thus we have:

\[
V_0 = \sum_{n=0}^{\infty} \sum_{m=0}^{n} b_{m,n} \left( \frac{R}{a} \right)^{n+1} P_n^m (\cos \theta) \cos m \phi
\]

\[
V_i = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \left[ \frac{V_i e_i + a_{m,n} \left( \frac{a}{b} \right)^n}{\lambda_{n+1}} \right] P_n^m (\cos \theta) \cos m \phi
\]

The boundary conditions on the sphere are:

\[
V_0 = V_i \text{ at } \lambda = R \text{ for all } \theta \text{ and } \phi
\]

\[
e_0 \frac{\partial V_i}{\partial \lambda} = e_i \frac{\partial V_i}{\partial \lambda} \text{ at } \lambda = R
\]

Substituting (8:b) and (9:b) into (10:b) and (11:b) and recalling the orthogonality properties of the associated Legendre polynomials and of the sine and cosine functions we easily obtain that:

\[
a_{m,n} = \frac{C_{m,n}}{R^{n+1}} \cdot \frac{q(n+1)(1 - e_i)}{n e_i + (n+1) e_0}
\]

\[
b_{m,n} = \frac{C_{m,n}}{R^{n+1}} \cdot \frac{q(2n+1)}{n e_i + (n+1) e_0}
\]
The Reaction Potential and Reaction Field

The concept of the reaction field arises as follows:

In the electrostatic problem just solved the polarized state of the substance outside the sphere is due to the presence of the dipole $\vec{\mu}$ and the medium $\varepsilon_i$ and is completely determined by the coefficients $b_{mnm}$ in (8:b). Suppose now that the charge distribution outside is fixed; i.e., $b_{mnm}$ is kept constant, and that the dipole and the medium is removed from the sphere, then the reaction field is defined as the new field existing in the sphere.

From equations (12:b) and (13:b) one may write:

$$A_{m,n} = (1 - \frac{\varepsilon_0}{\varepsilon_i}) \cdot \frac{m + 1}{2m + 1} b_{mnm} \quad (14:b)$$

The reaction potential in the cavity is thus given by:

$$V_\lambda = -(\varepsilon_0 - 1) \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(m+1)}{2m+1} b_{mnm} (\frac{1}{R^m}) P_m(\cos \theta) \cos m\phi$$

We repeat that, although $\varepsilon_i$ is put equal to one in the first factor of (14:b), $b_{mnm}$ is kept constant and hence still contains the parameter $\varepsilon_i$.

For convenience let us write:

$$A_{m,n}' = (\varepsilon_0 - 1) \cdot \frac{m + 1}{2m + 1} \cdot \frac{b_{mnm}}{R_m}$$

$$\therefore A_{m,n}' = \frac{(\varepsilon_0 - 1)}{R^m} \cdot \frac{(m+1)}{\mu \varepsilon_i + (m+1)\varepsilon_0} \cdot \frac{b_{mnm}}{R_m} \quad (15:b)$$

So that the reaction potential becomes:

$$V_\lambda = -\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A_{m,n}' \cdot \lambda^m P_m(\cos \theta) \cos m\phi \quad (16:b)$$
The reaction field is given by:

\[ E_n = - \nabla \psi_n \]

Let us calculate the average value of the reaction field defined by:

\[ \overline{E}_n = \frac{\iiint E_n \, d\tau}{\iiint d\tau} \quad \text{with} \quad d\tau = r^2 \sin \theta \, dr \, d\theta \, d\phi \]

where the integrations extend over the volume of the sphere. In the case under consideration the reaction field has three components defined by:

\[ (E_n)_\hat{x} = -\frac{\partial \psi_n}{\partial x} ; \quad (E_n)_\hat{y} = \frac{\partial \psi_n}{\partial y} ; \quad (E_n)_\hat{z} = \frac{\partial \psi_n}{\partial z} \]

Thus we obtain:

\[ (E_n)_\hat{x} = \sum_{m=0}^{\infty} \sum_{n=0}^{m} A_n^m (\cos \theta) \sin m \phi \]

\[ (E_n)_\hat{y} = \sum_{m=0}^{\infty} \sum_{n=0}^{m} A_n^m \frac{d \psi_n}{d (\cos \theta)} \sin \theta \cos m \phi \]

\[ (E_n)_\hat{z} = \sum_{m=0}^{\infty} \sum_{n=0}^{m} A_n^m (\cos \theta) \sin \theta \sin m \phi \]

We are interested in the volume averages of the field components in the \(x\), \(y\) and \(z\) directions respectively and, because the dipole is in the \(z\)-plane we have a symmetry such that the average component in the \(y\)-direction will vanish. This statement will be proved formally, however. We have:

\[ \overline{(E_n)_i} = \frac{\iiint (E_n)_i \, d\tau}{\iiint d\tau} \quad \text{where} \quad i = \hat{x}, \hat{y}, \hat{z} \]

where:

\[ (E_n)_x = \left[ (E_n)_\hat{x} \sin \theta + (E_n)_\hat{y} \cos \theta \right] - (E_n)_\hat{z} \sin \phi \]
\[ (E_n)_y = \left[ (E_n)_\hat{x} \sin \theta + (E_n)_\hat{y} \cos \theta \right] + (E_n)_\hat{z} \cos \phi \]
\[ (E_n)_z = (E_n)_\hat{x} \cos \theta - (E_n)_\hat{y} \sin \theta \]
It follows easily, from (18:b) and (20:b) that:

\[
(E_{x}) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{n} \sum_{m}^{n-1} \left\{ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) - \omega P_{m+1}^{(n)}(\omega) \right\} \cos m \phi \cos n \phi \\
+ \frac{P_{m}(\omega)}{\sqrt{1-w^{2}}} \sin m \phi \sin n \phi
\]

\[
(E_{y}) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{n} \sum_{m}^{n-1} \left\{ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) - \omega P_{m+1}^{(n)}(\omega) \right\} \cos m \phi \sin n \phi \\
- \frac{P_{m}(\omega)}{\sqrt{1-w^{2}}} \sin m \phi \cos n \phi
\]

\[
(E_{z}) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{n} \sum_{m}^{n-1} [m + (m-n)w^{2}] P_{m}(\omega) + \sqrt{1-w^{2}} P_{m+1}^{(n)}(\omega) \right\} \cos m \phi
\]

where \( \omega = \cos \theta \).

Let us find first of all \( \bar{(E_{x})} \)

\[
\bar{(E_{x})} \, dx = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{n} \sum_{m}^{n-1} \int_{0}^{2\pi} \int_{0}^{2\pi} \cos m \phi \cos n \phi \\
\times \int_{0}^{2\pi} \left[ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) - \omega P_{m+1}^{(n)}(\omega) \right] \cos m \phi \cos n \phi \\
\times \sum_{w=1}^{2\pi} \left[ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) + \sqrt{1-w^{2}} P_{m+1}^{(n)}(\omega) \right] \cos m \phi \cos n \phi \\
\times \sum_{w=1}^{2\pi} \left[ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) + \sqrt{1-w^{2}} P_{m+1}^{(n)}(\omega) \right] \cos m \phi \cos n \phi
\]

Now \( \int_{0}^{2\pi} \cos m \phi \cos n \phi = \begin{cases} 0 & \text{if } m \neq n \\
2\pi \delta_{m,n} & \text{if } m = n \end{cases} \)

Hence only the \( m = 0 \) terms give a contribution to \( \bar{(E_{x})} \). Thus:

\[
\bar{(E_{x})} \, dx = 2\pi \sum_{n=0}^{\infty} A_{n} \int_{0}^{2\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} \left[ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) + \sqrt{1-w^{2}} P_{m+1}^{(n)}(\omega) \right] \cos m \phi \cos n \phi \\
\times \sum_{w=1}^{2\pi} \left[ \frac{m + (m-n)w^{2}}{\sqrt{1-w^{2}}} P_{m}(\omega) + \sqrt{1-w^{2}} P_{m+1}^{(n)}(\omega) \right] \cos m \phi \cos n \phi
\]

where

\[
P_{m}(\omega) = (1-\omega^{2})^{1/2} \frac{dP_{m}(\omega)}{d\omega}
\]
Now from a well-known recurrence formula for Legendre polynomials, we have:

$$m w P_m(w) + (1-w^2) P'_m(w) = m P_{m-1}(w)$$

Thus the integral above becomes:

$$\int \frac{1}{m} P_{m-1}(w) \, dw = m (2 \delta_{m,1})$$

which is another well-known result. Hence only the $m=1$ term gives a contribution. We obtain, therefore:

$$\begin{align*}
\int \mathcal{E}_n(a) \, d\tau &= \frac{4 \pi}{3} R^3 A_{0,1} \\
\therefore \mathcal{E}_n(a) &= A_{0,1} 
\end{align*}$$

(24.1b)

Now let us find $\mathcal{E}_n(x)$. We have:

$$\begin{align*}
\int \mathcal{E}_n(x) \, d\tau &= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A_{m,n} \frac{R^{m+2}}{R^{m+2}} \left\{ \int \left[ \frac{m(\omega^2 - 1)}{1-\omega^2} P_m^x(\omega) - \omega P_{m+1}^x(\omega) \right] \, d\omega \right. \\
&\quad \left. \times \int \cos \theta \cos \phi \, d\phi + \int \frac{P_m^x(\omega) \, d\omega}{\sqrt{1-\omega^2}} \int_{\phi=0}^{\phi=0} \sin \theta \sin \phi \, d\phi \right\}
\end{align*}$$

Now:

$$\int_0^{2\pi} \cos \theta \cos \phi \, d\phi = \int_0^{2\pi} \sin \theta \sin \phi \, d\phi = \pi \delta_{m,1}$$

Hence only the $m=1$ terms give a contribution. Thus:

$$\begin{align*}
\int \mathcal{E}_n(x) \, d\tau &= \pi \sum_{m=0}^{\infty} A_{m,1} \frac{R^{m+2}}{m+2} \\
&\quad \times \left\{ \int \left[ \frac{m(\omega^2 - 1) + 1 + \omega^2}{\sqrt{1-\omega^2}} P_m^x(\omega) - \omega P_{m+1}^x(\omega) \right] \, d\omega \right\}
\end{align*}$$

Now:

$$P_m^x(\omega) = \sqrt{1-\omega^2} P_m(\omega)$$

$$P_m^{xx}(\omega) = (1-\omega^2) P_m''(\omega)$$
So that the part in square brackets becomes:

\[ \begin{align*}
\left\{ \frac{n+1}{2} \right\}^2 & = \left\{ n(1-\omega^2) + (n+1)\omega \right\} P_n'(\omega) - \omega(1-\omega^2) P_n(\omega) \\
& = \left\{ n(1-\omega^2) + (n+1)\omega \right\} P_n'(\omega) - \omega(1-\omega^2) P_n(\omega)
\end{align*} \]

But from Legendre's equation we have:

\[ (1-\omega^2) P_n''(\omega) = 2\omega P_n'(\omega) - n(1+1) P_n(\omega) \]

so that:

\[ \begin{align*}
\left\{ \frac{n+1}{2} \right\}^2 & = \left\{ n(1-\omega^2) + (n+1)\omega \right\} P_n'(\omega) - 2\omega P_n'(\omega) \\
& + n(1+1)\omega P_n(\omega)
\end{align*} \]

\[ = (1-\omega^2)(n+1) P_n'(\omega) + n(1+1)\omega P_n(\omega) \]

\[ = (n+1) \left\{ (1-\omega^2) P_n'(\omega) + n\omega P_n(\omega) \right\} \]

\[ = n(1+1) P_{n-1}(\omega) \]

Hence we have:

\[ \mathcal{S} \mathcal{S} \mathcal{S} (E_n)_x d\tau = \frac{\pi}{\alpha} \sum_{n=0}^{\infty} \alpha_n \frac{R^{n+2}}{n+2} \int_1^{R} P_n(\omega) d\omega \]

As before the integral is given by \( 2 \alpha_n \),

so that:

\[ \mathcal{S} \mathcal{S} \mathcal{S} (E_n)_x d\tau = \frac{4\pi}{3} R^3 A_{1,1} \]

\[ \therefore (E_n)_x = A_{1,1} \]

(25:b)

In a similar way we may set up an expression for the average \( y \)-component of the reaction field. We will arrive at the integrals:

\[ \int_0^{\pi} \cos m \phi \sin \phi d\phi = \int_0^{\pi} \sin m \phi \cos \phi d\phi = 0 \]

Hence:

\[ (E_n)_y = 0 \]

(26:b)
It is convenient at this point to calculate the coefficients $C_{mn}$ from equations (5b), (6b) and (7b):

\[
C_{0,0} = P_0(\cos \theta) - P_0(\cos \theta_1) = 0
\]
\[
C_{0,1} = a_2 P_1(\cos \theta) - a_1 P_1(\cos \theta_1) = a_2 \cos \theta - a_1 \cos \theta_1
\]
\[
C_{0,2} = d \cos \theta
\]
\[
C_{1,1} = \frac{1}{2} \left[ a_2 P_1(\cos \theta) + a_1 P_1(\cos \theta_1) \right] = a_2 \sin \theta + a_1 \sin \theta_1
\]

Now from (fig. 6) we see that:

\[
\frac{\sin \theta_2}{d_2} = \frac{\sin (\theta - \theta_2)}{d_2} = \frac{\sin \beta}{d_2}
\]

and

\[
\frac{\sin \theta_1}{d_1} = \frac{\sin \beta}{d_1} \quad \text{hence:} \quad a_2 \sin \theta_2 = \frac{d_2}{2} \sin \beta = a_1 \sin \theta_1
\]

Therefore:

\[
C_{1,1} = d \sin \beta
\]

Similarly:

\[
C_{2,2} = 2a_2 \cos \beta
\]
\[
C_{2,2} = a_1 \sin \beta
\]
\[
C_{2,2} = 0 \quad \text{etc.}
\]

We have from (15b) that:

\[
A_{0,1} = \frac{E_0 - 1}{R^3} \cdot \frac{2q}{E_2 + 2E_0} \quad \text{and} \quad C_{0,1} = \frac{E_0 - 1}{R^3} \cdot \frac{3 \mu \cos \theta}{E_1 + 2E_0}
\]

and

\[
A_{1,1} = \frac{E_0 - 1}{R^3} \cdot \frac{2q}{E_2 + 2E_0} \quad \text{and} \quad C_{1,1} = \frac{E_0 - 1}{R^3} \cdot \frac{3 \mu \sin \beta}{E_1 + 2E_0}
\]
Thus we obtain the result that the average value of the reaction field is given by:

\[
\begin{align*}
(\overline{E_n})_x &= \frac{2(\varepsilon_0 - 1)}{R^3(\varepsilon + 2 \varepsilon_0)} \mu \sin \beta \\
(\overline{E_n})_y &= 0 \\
(\overline{E_n})_z &= \frac{2(\varepsilon_0 - 1)}{R^3(\varepsilon + 2 \varepsilon_0)} \mu \cos \beta
\end{align*}
\]  

(27:b) (28:b) (29:b)

The average total field will be:

\[
(\overline{E_n})_{\text{tot.}} = \left\{ (\overline{E_n})_x^2 + (\overline{E_n})_y^2 + (\overline{E_n})_z^2 \right\}^{\frac{1}{2}}
\]

\[
(\overline{E_n})_{\text{tot.}} = \frac{2(\varepsilon_0 - 1) \mu}{R^3(\varepsilon + 2 \varepsilon_0)}
\]

(30:b)

Thus we see that the average total reaction field in the cavity is independent of:

(i) The eccentricity of the dipole.

(ii) The angle of twist "$\beta$" of the dipole from the axis.

The reaction field depends only on the strength of the dipole and hence a "point" dipole or a "real" dipole of the same strength give the same reaction field.

Now Bottcher has shown, for a polarizable mathematical dipole in the centre of a spherical cavity of radius $R$, that the reaction field is given by:

\[
R' = \frac{\varepsilon}{1 - \varepsilon} \frac{\varepsilon}{\mu} \gamma
\]

(31:b)
where:
\[ f = \frac{2(\varepsilon_0 - 1)}{R^3(2\varepsilon_0 + 1)} \quad (32:b) \]
and \( \mu_g \) = the dipole moment of the molecule in the gas-phase.

Hence in order to compare Bottcher's result with our result we must know the moment in the gas-phase. This result is easily obtained by considering a single spherical molecule in vacuum.

We have from (8:b) that the potential in the outside medium is:
\[ V_0 = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \mathbf{b}_{mn}(R)_{n+1} \mathbf{P}_n(\cos \phi) \cos m\phi \]
where:
\[ \mathbf{b}_{mn} = \frac{c_{mn}}{R^n+1} \left( \frac{2m+1}{i} \right) \varepsilon_0 \]
Putting \( \varepsilon_0 = 1 \), we have the potential of a "free" molecule; viz:
\[ \left( \frac{V_0}{V_{vac}} \right) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \frac{c_{mn}}{2n+1} \mathbf{P}_n(\cos \phi) \cos m\phi \]
\[ = \frac{C_{0,0}}{2} + \frac{3g}{(2+6\varepsilon_0)\sqrt{2}} \left[ C_{0,2} \cos \phi + C_{1,0} \sin \phi \cos \phi \right] \]
\[ + \frac{5g}{(3+2\varepsilon_0)\sqrt{6}} \left[ C_{0,2} \frac{3}{2} \cos^2 \phi - \frac{1}{2} + C_{2,0} \mathbf{P}_2(\cos \phi) \cos \phi \right] \]
\[ + C_{2,2} \mathbf{P}_2(\cos \phi) \cos 2\phi \]

And by utilizing the expressions given for the coefficients \( c_{mn} \), this
becomes:

\[
(V_0)_{\text{vac.}} = \frac{3 \mu}{(2+i)^2} \pi^2 \left[ \cos \beta \cos \theta + \sin \beta \sin \theta \cos \phi \right] \\
+ \frac{5 \mu}{(3+2\epsilon i)^3} \left[ \cos \beta (3 \cos^2 \theta - 1) \right. \\
\left. + \sin \beta \sin \theta \cos \theta \cos \phi \right]
\] 

\[
(V_0)_{\text{vac.}} = \frac{3 \mu}{(2+i)^2} \pi^2 \left[ \cos \beta \cos \theta + \sin \beta \sin \theta \cos \phi \right]
\] 

(33b)

\[
+ \frac{5 \mu}{(3+2\epsilon i)^3} \left[ \cos \beta (3 \cos^2 \theta - 1) \right. \\
\left. + \sin \beta \sin \theta \cos \theta \cos \phi \right]
\]

For Bottcher's model, of course, the distance \(a = 0\). Thus let us consider a "point" dipole \(\mu g\) at the centre in the \(x^3\)-plane.

**Fig. VII**

We have from (fig. 7) that the potential at \(P\) is:

\[
V_P = \frac{\mu g \cos \phi}{\pi^2}
\]
Now the direction cosines of the radius vector and the dipole are, respectively:

| Radius Vector | \( \sin \theta \cos \phi : \sin \theta \sin \phi : \cos \theta \) |
| Dipole        | \( \sin \beta : 0 : \cos \beta \) |

Thus the angle \( \phi \) between the dipole and the radius vector is given by:

\[
\cos \phi = \cos \beta \cos \theta + \sin \beta \sin \theta \cos \phi
\]

Thus the potential at \( P \) due to \( \mu_g \) is:

\[
V_P = \frac{\mu_g}{\kappa} (\cos \beta \cos \theta + \sin \theta \sin \phi \cos \phi)
\]

Comparing coefficients in (33:b) and (34:b) we have:

\[
\mu_g = \frac{3 \mu}{2 + \epsilon_i}
\]

Thus the moment in the gaseous state of a molecule is smaller than the actual dipole moment \( \mu \). This reduction is, of course, caused by the polarization of the medium comprising the molecule. In an actual molecule \( \epsilon_i \mu = \mu^* \) where \( \mu \) is the index of refraction. If the molecule is unpolarizable then \( \mu_g = \mu \).

Bottcher's formula (31:b) becomes:

\[
R' = \frac{3 \mu}{2 + \epsilon_i}
\]

Now for a single molecule of radius \( R \) the Clausius-Mossetti formula gives:

\[
\alpha = R^3 \left( \frac{\epsilon_i - 1}{\epsilon_i + 2} \right)
\]
and from (32:b) we get:

$$1 - \alpha f = 1 - \frac{2(\varepsilon_0 - 1)}{2\varepsilon_0 + 1} \frac{\varepsilon_i - 1}{\varepsilon_i + 2}$$

$$= \frac{2(2\varepsilon_0 + \varepsilon_i)}{(2\varepsilon_0 + 1)(\varepsilon_i + 2)}$$

$$\therefore \frac{1}{\alpha f} = \frac{2(\varepsilon_i + 2)(\varepsilon_0 - 1)}{3 R^3 (2\varepsilon_0 + \varepsilon_i)}$$

Hence Bottcher's formula (31:b) becomes:

$$R' = \frac{2(\varepsilon_0 - 1)}{R^3 (2\varepsilon_0 + \varepsilon_i)} \mu$$

(36:b)

Comparing (36:b) with (30:b) we see that:

Bottcher's special model of a mathematical dipole at the centre of a sphere gives the same result as our more real model of a finite dipole located in the sphere with arbitrary position and direction, provided that in the latter case we consider the reaction field to be the average value of the total reaction field in the sphere.

The generalization given here applies, of course, to molecules bearing more than one finite dipole. As long as one adheres to a spherical model, Bottcher's formula will hold.

The Energy Required to Take a Molecule from the "Inside" to the "Outside" of the Liquid.

Referring to (fig. 6) we have that the above energy will be:

$$\mathcal{W} = \frac{1}{2} q \left[ V_2(a_2, \theta_2, \phi_2) - V_2(a_1, \theta_1, \phi_1) \right]$$
\[-\frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_{nm}' \left\{ a_2^m P_n^m (\cos \theta) - (-1)^m a_1^m P_n^m (\cos \theta) \right\} \]

Now:
\[a_2^m P_n^m (\cos \theta) - (-1)^m a_1^m P_n^m (\cos \theta) = \frac{C_{mn}}{2 - \delta_{m,0}} \frac{(ut+m)!}{(2m)!}!\]

and:
\[A_{nm}' = \frac{E_{0-1}}{R^{2m+1}} \frac{(ut+1)q}{Mei + (ut+1)E_0} C_{mn} \]

Thus:
\[W = -\frac{1}{2} q \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{E_{0-1}}{R^{2m+1}} \frac{(ut+1)}{Mei + (ut+1)E_0} \frac{C_{mn}^2}{2 - \delta_{m,0}} \frac{(ut+m)!}{(2m)!}!\]

Upon simplification with the aid of the coefficients \(C_{mn}\), this becomes:
\[W = -\frac{1}{2} \left\{ \mu^2 \left[ \frac{2(E_{0-1})}{R^3 (E_0 + 2E_0)} + \frac{3(E_{0-1})a^2}{R^5 (2E_0 + 3E_0)} (3 + \cos^2 \theta) \right] \right. \]
\[+ \left. \text{terms of the order } \left( \frac{a^3}{R^3} \right), \left( \frac{\mu^3}{R^3} \right), \left( \frac{A^2}{R^3} \right) \right\} \]

(37b)

(1) For a point dipole at the centre we have \(a = d = 0\) and (37b) becomes:
\[\bar{W}_0 = \bar{W}_{\text{Onsager}} = -\frac{1}{2} \left\{ \frac{(E_0)_{\text{tot}}}{(E_0)} \right\} \mu \]

which agrees with Onsager's formula*. It must be recalled that

(37:b) and (38:b) were derived assuming no short range forces to be acting. However, for very strong dipoles the above two formulae will give a significant contribution to the energy required to evaporate one molecule of liquid. Corrections to these formulae could no doubt be made using Kirkwood's theorems* on short range interaction energies.

(ii) For an eccentrically located dipole, it is to be noted that (38:b) will be a good approximation only if:

\[
\frac{2}{\varepsilon_i + 2\varepsilon_0} \gg \frac{3\alpha^2(3 + \cos^2 \beta)}{R^2 (2\varepsilon_i + 3\varepsilon_0)}
\]  

(39:b)

to a first approximation. The higher order terms will contain "A" but from (37:b) even very large values of this separation will give practically no contribution. Formula (39:b) is, therefore, a criterion for Onsager's formula (38:b).

Suppose, for example, that: \( \alpha \approx \frac{1}{2} R \) and \( \beta \approx 0; \) \( \varepsilon_i \approx 1.33 \) \( \varepsilon_0 \approx 8 \)

then:

\[
\frac{2(\varepsilon_i - 1)}{\varepsilon_i + 2\varepsilon_0} \approx 1 \approx \frac{3(\varepsilon_i - 1)}{2\varepsilon_i + 3\varepsilon_0}
\]

Thus from (37:b) we have:

\[
W = -\frac{1}{2} \left( \frac{\mu^2}{R^3} + \frac{4\mu^2a^2}{R^5} \right)
\]

\[
= -\frac{1}{2} \left( \frac{\mu^2}{R^3} + \frac{\mu^2}{R^3} \right)
\]

\[
= -\frac{\mu^2}{R^3}
\]

While (38:b) predicts: \[ W_0 = -\frac{1}{2} \frac{\mu^2}{R^3} \]. Hence, for water, we see that an eccentricity of \( a = \frac{\sqrt{2}}{2} \) will about double the polar contribution to the latent heat predicted by Onsager.

Considering the small radius of the hydrogen atom compared with that of oxygen, the assumption of a spherical molecule is not too bad in the case of water; in addition, \( \beta \approx 0 \) for the water molecule. It is to be expected, therefore, that formula (37:b) will be of use in the consideration of the latent heats of strongly polar liquids.
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* See also: Transactions of the Faraday Society - 42a., (1946).