Dielectric properties of dipolar substances†

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From an investigation of structure it is shown that there exists a large group of dipolar organic solids whose dipoles have two equilibrium positions with opposite dipole direction. To calculate the dielectric properties Onsager's theory has been extended and developed into a systematic approximation which converges above a critical temperature. To derive the local field acting on a dipole we have replaced the surroundings by a continuum whose dynamic dielectric properties we have taken into account. As a result we find larger dielectric constants and smaller dielectric losses than in Onsager's theory. We have also shown that liquids with high viscosity behave similarly to solids, while for liquids with low viscosity there are no such deviations from Onsager's theory.

I. Introduction

1. The purpose of this paper is twofold. First, from an analysis of their structure we shall show that there exists a large group of dipolar solids whose dipoles do not rotate but have two stable positions with opposite dipolar direction. Secondly, we shall develop into a systematic theory a method which has been widely used in order to account for dipolar interaction. It is the method whereby the local field acting upon a dipole is obtained by replacing by a continuous medium the surroundings of this dipole outside a cavity. Debye (1929), who first applied this method to dipolar substances, assumed that the local field is given by the usual Lorentz theory. His local field is thus deduced on the assumption that the dielectric polarization inside the cavity is identical with the average macroscopic polarization. Onsager (1936) pointed out that this was incorrect when a permanent dipole is being placed inside the cavity. He showed that the local field is composed of two components: (i) the cavity field which is the field produced inside the cavity by the external field on the assumption that the dipole has been removed; (ii) the reaction field which is the field at the position of the dipole which is produced through the action of the dipole on its surroundings. Onsager then assumed that this reaction field has always the same direction as the dipole. Thus it does not exert any force upon the dipole and can be omitted. This procedure is open to objections (see also Sauer & Temperley 1940). It is true the equilibrium value of the reaction field has the direction of the dipole. This equilibrium value will, however, never be established in view of the frequent changes of the direction of the dipole. It will thus be necessary to take the reaction field into account, and to calculate it from the dynamic dielectric properties of the surrounding medium. Nevertheless, we shall find that Onsager's theory constitutes a correct zero approximation although for reasons different from

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those given by him. We shall see that, for the substances which we treat here, the method of replacing the surroundings of a dipole by a continuous medium is restricted to temperatures above a critical temperature $T_0$, where the energy $kT_0$ is of the order of magnitude of the dipolar interaction. Thus in zero order this interaction, and hence the reaction field, can be neglected. Clearly the deviations of the more exact theory from Onsager's theory increase with decreasing temperature. While they may be appreciable for solids and for liquids with high viscosity we shall find that for liquids with low viscosity Onsager's theory is always a very good approximation.

In the following we shall start with a discussion of the structure of substances consisting of long-chain molecules. We shall then develop the general mathematical method and finally use it to calculate the dielectric constant and the dielectric loss.

II. Model and structure

2. Solids. The structure of many of the substances with which we are concerned in this paper can be derived from the structure of paraffins which has been investigated by Müller (1928). Paraffins are long-chain molecules forming a plane zigzag with a CH$_2$ group at each corner and a CH$_3$ group at the ends. Polar molecules can be obtained from paraffins by introducing polar groups. Thus a ketone is obtained by replacing a CH$_2$ group by a C=O group (figure 1). In the paraffin structure the chains are arranged in layers whose thickness is approximately equal to the chain length. Within such a layer the molecules form rectangular cells with side lengths $a$, $b$, $c$ where $a \approx 5$ Å, $b \approx 7.5$ Å and $c$ slightly larger than the chain length. Figure 2 shows how the chains, whose cross-sections are indicated, intersect the $a$-$b$ plane. The next layer on top of the one considered just now is slightly shifted in the $b$-direction. From this structure other long-chain structures can be obtained by choosing as unit cell a parallelepiped with arbitrary angles.

All these lattice structures strongly suggest that each chain has a second position of equilibrium obtained by turning the chain plane by 180°, thus reversing the direction of the dipole (see figure 2). The existence of two positions for each molecule should lead to order-disorder transitions connected with an anomaly in the specific heat as has actually been observed for paraffins (see Müller 1932; Ubbelohde 1938). The transition from one state of a molecule into the other has been investigated previously (Fröhlich 1942) for the case of dipolar chain molecules dissolved in paraffin wax.

Let us now restrict ourselves to molecules which contain only a single dipolar group which usually lies in the chain plane. In this case the position of a molecule can be described in a unique way by the position and direction of a single dipole. We may thus speak of dipolar interaction when we think of that part of the interaction between molecules which depends on the direction of the chain planes.

† This would probably entail some displacement of the molecules.
The conception of two stable dipolar directions has already been used by Debye (1929), but it has not been brought into connexion with any actual structure. Usually the conception of rotating dipoles (cf. Pauling 1930) is being used. While we do not doubt that such molecules as HCl have to be considered as rotating dipoles, even in the solid state there is certainly a large group of solids, the dipoles of which do not rotate. For these substances we shall adopt the following model:

(i) The substance consists of a continuous medium containing dipoles which form some crystalline lattice. The continuous medium has the real dielectric constant $\varepsilon_\infty$ independent of the frequency of an external field, i.e. the corresponding polarization is loss-free and relatively inertia-free.

(ii) All dipoles have the dipolar momentum $\mu$. Apart from their mutual interaction they are subject to non-dipolar forces which tend to orient them into either of two opposite directions. We shall call them stable positions or equilibrium positions of the dipoles. The potential energy of the dipoles is supposed to be the same for the two positions if the mutual interaction between dipoles is being neglected.

(iii) Occasionally a dipole will have sufficient kinetic energy to jump over the potential hill separating the two equilibrium positions. Let $p$ be the probability per second for such a transition, neglecting dipolar interaction. We then define a time of relaxation $\tau$ of the dipole by

$$2\tau = 1/p.$$  \hspace{1cm} (2.1)
In an external electric field $E$ a dielectric polarization $M$ is induced per unit volume defining the dielectric constant $\varepsilon$ by

$$M = \frac{\varepsilon - 1}{4\pi} E.$$  \hspace{1cm} (2.2)

If $P$ denotes the contribution of the dipoles to $M$ then

$$M = P + \frac{\varepsilon_\infty - 1}{4\pi} E.$$  \hspace{1cm} (2.3)

In alternating fields it is useful to introduce complex quantities. Let $\omega$ be the angular frequency of the field, then we shall write

$$E = E_0 e^{i\omega t}$$  \hspace{1cm} (2.4)

and

$$\varepsilon = \varepsilon' - i\varepsilon''.$$  \hspace{1cm} (2.5)

where $\varepsilon'$ and $\varepsilon''$ as well as $\varepsilon_\infty$ are real. This way of writing means that the field strength is the real part of (2.4) while the electric displacement is the real part of $\varepsilon E$. Hence the dielectric loss per second and per unit volume is given by

$$\frac{1}{2}\varepsilon' \omega E_0^2 \tan \theta$$

where the loss angle $\theta$ is given by $\tan \theta = \frac{\varepsilon''}{\varepsilon'}$.  \hspace{1cm} (2.6)

Our way to introduce the non-dipolar contributions to the polarization (i.e. $(\varepsilon_\infty - 1) E/4\pi$) differs from the usual way where a molecular polarization is first introduced and connected with $\varepsilon_\infty$ with the help of the Clausius-Mosotti formula (see Debye 1929). The use of this formula is, however, objectionable (see, for instance, Kurtz & Ward 1937).

3. liquids. From X-ray investigations it is known that in a liquid the neighbours of a given molecule are mostly arranged according to a certain crystalline structure except for some small deviations. Accordingly we shall assume that, even in a liquid, a molecule, and hence a dipole, has two stable positions relative to its neighbours. Thus if we approximate the surroundings of a molecule by a macroscopic liquid this must be assumed to adhere to the surface of our molecule. Thus, if we neglect the transitions of the dipole between its two equilibrium positions, we are led to Debye’s model where the motion of a dipolar molecule in a liquid is treated in the same way as the motion of a macroscopic body (Debye 1929). Let $\tau_D$ be the time of relaxation according to Debye which is proportional to the viscosity of the liquid. Then whenever $\tau_D \ll 1/p$ (see equation (2.1)), as is probably the case for liquids with small viscosities, Debye’s model is applicable. For substances with very high viscosity, however, probably $\tau_D \gg 1/p$. In this case, therefore, our solid model is more appropriate. For not too high temperatures, this should apply in particular to amorphous organic substances which have no sharp melting-point.
III. The mathematical method

4. It is the purpose of this section to calculate the dipolar contribution to the dielectric polarization induced by the external field $E$. For solids we shall always assume that we are dealing with polycrystalline material and, therefore, average over the angle $\theta$ between field and dipolar direction. If we neglect the interaction between dipoles, the energy of one dipole becomes $\mu E \cos \theta$. For weak static fields ($\mu E \ll kT$) the Boltzmann theorem yields at once for the polarization per unit volume

$$P = \frac{\mu^2 n E}{3kT},$$

(3.1)

where $n$ is the number of dipoles per unit volume. To neglect the dipolar interaction is, however, permissible only in the relatively uninteresting case $\varepsilon - \varepsilon_\infty \ll 1$. The main difficulty to account for this interaction is its long range $\sim 1/r^3$ which makes it impossible to take into consideration the interaction between nearest neighbours only.

In order to simplify this problem we shall follow a method in which the action upon a selected dipole of the external field and of all dipoles is being described by a local field $F$ which has been calculated in a simplified manner. It is then assumed that on an average all dipoles behave in the same way as the selected one. The polarization is thus obtained from (3.1) if $E$ is replaced by $F$. To determine $F$ we surround the selected dipole by a cavity of volume $1/n$ and treat the outside as a continuous medium whose dielectric properties are the same as the macroscopic dielectric properties which we want to calculate. Following Onsager (1936) we split $F$ into two parts: (i) the cavity field $G$ which is obtained on the assumption that the dipole has been removed from the cavity; (ii) the reaction field $R$ which is the change of the field at the position of the dipole through its action upon the surrounding dipoles,

$$F = G + R.$$  

(3.2)

Our definition of $G$ is slightly different from Onsager’s who removes not only the dipole from the cavity in order to determine $G$ but the whole molecule. Thus the dielectric constant of the empty cavity is $\varepsilon_\infty$ in our case, but unity in his. The actual value of $G$ depends on the shape of the cavity. For a sphere of radius $a$, given by

$$\frac{4\pi}{3} a^3 = \frac{1}{n},$$

(3.3)

we obtain, following Onsager’s calculation,

$$G = \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} E,$$

(3.4)

independent of $a$. It should be noticed that this expression remains correct for alternating fields if $\varepsilon$ represents the complex dielectric constant at the frequency in question.
Our treatment of the reaction field $R$ is essentially different from Onsager’s who assumes that $R$ is equivalent to $R_1$, the value which $R$ tends to reach if the dipole remains in a given direction for a time which is long compared to the relaxation time $\tau$. This, however, is not the case, and, therefore, we shall describe $R$ by its dynamic properties, i.e. by its time-dependent differential equation. From the definition of the time of relaxation it follows that

$$\tau \frac{dR}{dt} = -R + R_1 \frac{\mu}{\mu},$$

(3-5)

an equation which we shall justify below (see text between equations (3-17) and (3-18)). $\mu/\mu$ is the unit vector in the direction of the dipole (which depends on time) and obviously

$$|R| < R_1,$$

(3-6)

unless the dipole remains infinitely long in the same direction. For a spherical cavity $R_1$ can be calculated similarly to Onsager’s calculation of his $R$. Given a sphere of radius $a$ with the static dielectric constants $\epsilon_\infty$ and $\epsilon_s$ inside and outside the sphere ($\epsilon_s$ is the static value of $\epsilon$). Let $\psi$ be the electric potential so that

$$\nabla^2 \psi = \mu \cos \theta / \epsilon_\infty r^2$$

would be a solution if $\epsilon_\infty = \epsilon_s$, i.e. if there were no dipoles present. ($r =$ distance from the centre of the sphere, $\theta =$ angle between $r$ and $\mu$.) If, however, $\epsilon_s \neq \epsilon_\infty$ we find from $\nabla^2 \psi = 0$,

$$\psi = \left( \frac{\mu}{\epsilon_\infty r^2} - R_1 r \right) \cos \theta, \quad \text{if } r < a,$$

$$\psi = \frac{\mu^*}{\epsilon_s r^2 \cos \theta}, \quad \text{if } r > a.$$

The constants $R_1$ and $\mu^*$ have to be determined from the boundary conditions at the surface of the sphere (continuity of the tangential component of the electric field strength and of the normal component of the electric displacement). This leads to

$$R_1 = \frac{2(\epsilon_s - \epsilon_\infty)}{\epsilon_\infty(2\epsilon_s + \epsilon_\infty) a^3} \frac{\mu}{\epsilon_s r^2}.$$

(3-7)

Onsager treats $R$ not as a dynamic but as a static quantity, i.e. he uses $R = R_1 \mu/\mu$. The energy $-(\mu, R)$ of the dipole in the field $R$ is in his case $-\mu R_1$. It is thus independent of the dipole direction and can be omitted. This would be correct only if $1/\tau$ were large compared to $d(\mu/\mu)/dt$. This is the case only for the non-dipolar part of Onsager’s reaction field. In our treatment of the reaction field we have defined $R$ as being due to dipoles only, while the non-dipolar contributions, described by $\epsilon_\infty$, have been assumed to be free of inertia.

5. Range of validity. Before starting with the actual calculation we want to investigate the range of validity of our method. One of the main points of the method is to calculate the reaction field with the help of the macroscopic dielectric constant.
of the substance making use of the fact that in the absence of an external field the polarization vanishes everywhere if we imagine the dipole to be removed from the cavity. In the presence of the dipole an electric field is set up whose order of magnitude is $R$ in the neighbourhood of the cavity. Now consider a small region of the continuum in the neighbourhood of the cavity co-ordinated to a selected dipole. This region is being polarized through the action of this dipole. We might, however, have selected any other dipole which would induce a different polarization in this region. Our method will work only if these various polarizations do not influence each other, i.e. if they superpose linearly. This is the case if we do not approach saturation. Since saturation is approached if the local field is larger than $kT/\mu$, our condition is $\mu R < kT$ or with (3·6), and introducing a temperature $T_0 = \mu R_0/k$,

$$\mu R_1 = kT_0 < kT.$$  \hfill (3·8)

A similar condition is obtained from a consideration of the cavity field $G$. From (3·4) we see that $G$ vanishes in the absence of an external field. Thus the field at the position of a dipole should be due to the reaction field only, i.e. it should vanish if we imagine this dipole to be removed. In the average this should be the case for liquids and for the disordered state of the dipoles in solids, but in general not for the ordered state. Thus if the order-disorder transition $\dagger$ occurs at the temperature $T_1$, we require $T \sim T_1$. $kT_1$ is of the order of magnitude of the energy required to turn at $T = 0$ a dipole from one equilibrium position into the other. If we assume that this energy is due to the electric interaction between the dipoles then $T_1 \sim T_0$.

Equation (3·8) has been derived as a necessary condition for the application of our method. It should be realized that we have no means of estimating the deviation of our approximation from the exact solutions. In connexion with this it is of importance that Van Vleck (1937 a, b) has shown that the exact partition function of an assembly of dipoles can be developed into a convergent power series in $1/T$ if $kT$ is large enough. For a model which corresponds to our low viscosity liquid model he found that his results are identical with Onsager’s up to the third order in $1/T$. In § 7 we shall also find that Onsager’s approximation is very good for such liquids but we shall find stronger deviations for solids. Van Vleck’s method naturally is much more difficult than Onsager’s, and it would probably be very complicated if applied to alternating electric fields. His method is of importance, however, as it provides a justification for the applicability of methods in which the surroundings of a dipole are replaced by a continuous medium (as used by Debye, Onsager and in the present paper).

6. The fundamental equations. Solids. We shall now derive the fundamental differential equations of our theory for the model of a solid dielectric, described in § 2, in which each dipole has two stable positions with opposite dipole direction. These we shall call the 1- and the 2-directions. Our aim is to calculate the polarization

$\dagger$ A study of order-disorder transitions in solid dielectrics of a type which we do not consider here was given by R. H. Fowler (1935).
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P induced by the field \( E \). If \( n_1 \) and \( n_2 \) are the numbers of dipoles per unit volume in the 1- and 2-directions respectively, clearly

\[
P = \mu (n_1 - n_2) \cos \theta,
\]

where \( \theta \) is the angle between the field and the 1-direction over which we shall average (polycrystalline material). Throughout we shall assume weak external fields, i.e.

\[
\frac{\mu E}{kT} \ll 1, \quad \text{and hence} \quad \frac{\mu G}{kT} \ll 1.
\]

We also remember that according to (3.8) we can introduce a parameter \( \gamma < 1 \) by

\[
\gamma = \frac{\mu R_1}{kT} < 1.
\]

This enables us to build up a systematic approximation by developing all expressions into power series in \( \gamma \). For the present we do not require the actual value of \( \gamma \) but only the fact that \( \gamma < 1 \), and we shall calculate the polarization \( P \) up to the first order in \( \gamma \). In our zero order, \( \gamma \), and hence the reaction field, is neglected entirely as in Onsager’s theory. This theory is, therefore, a correct zero order approximation. The reason for this is, however, not the fact that the reaction field immediately follows the dipole and thus does not exert any force (Onsager), but it is due to \( \mu R_1 < kT \) whenever our method is applicable.

Let us follow Debye (1929) in giving a brief derivation of the zero-order equations. If \( w_{12} \) and \( w_{21} \) are the probabilities per second for the dipolar transitions 1 \( \rightarrow \) 2 and 2 \( \rightarrow \) 1 respectively, clearly

\[
\frac{dn_1}{dt} = - \frac{dn_2}{dt} = - w_{12} n_1 + w_{21} n_2,
\]

and

\[
n_1 + n_2 = n.
\]

Now since we neglect \( R \) in zero order, the local field \( F \) is given by \( G \), and the energy of a dipole is \( \mp G \cos \theta \) for the 1- and 2-directions respectively. In the equilibrium state and for static fields, \( dn_1/dt = 0 \) and thus \( n_1/n_2 = w_{21}/w_{12} \). From Boltzmann’s theorem we find

\[
\frac{n_1}{n_2} = \frac{w_{21}}{w_{12}} = e^{2\mu G \cos \theta/kT},
\]

or, using (3.10), and the fact that \( w_{21}(G) \) must be equal to \( w_{12}(-G) \),

\[
w_{21} = c e^{\mu G \cos \theta/kT} \sim c \left(1 + \frac{\mu G \cos \theta}{kT}\right), \quad w_{12} = c e^{-\mu G \cos \theta/kT} \sim c \left(1 - \frac{\mu G \cos \theta}{kT}\right),
\]

where \( c \) may depend on \( T \). Assume now (3.14) to hold also for time-dependent fields \( G \) which is correct if the frequency of the field is small compared to the proper
frequencies of the dipole. Then inserting (3·14) into (3·12) we find, using (3·13) and (3·9), and neglecting quadratic terms in $G$,

$$\frac{dP}{dt} = -\frac{P}{\tau} + \frac{P_0}{\tau},$$  \hspace{1cm} (3·15)$$

where

$$\frac{1}{\tau} = 2c,$$  \hspace{1cm} (3·16)$$

and, averaging over $\theta$,

$$P_0 = \frac{\mu^2 nG \cos^2 \theta}{kT} = \frac{\mu^2 nG}{3kT}.$$  \hspace{1cm} (3·17)$$

Let us now turn to the first-order approximation taking into account the reaction field $R$. Since $R$ itself is small of the first order it will be sufficient to calculate $R$ from the zero-order equation. This we have already done in equation (3·5) which is identical with (3·15). Since in solids the dipole can have only two directions, (3·5) and (3·6) become

$$\tau \frac{dR}{dt} = -R + R_1, \quad \text{dipole in 1-direction}$$

and

$$\tau \frac{dR}{dt} = -R - R_1, \quad \text{dipole in 2-direction}$$

and

$$-R_1 < R < R_1.$$  \hspace{1cm} (3·19)$$

In contrast to the zero-order approximation the energy of a dipole is now

$$\mp \mu(G \cos \theta + R),$$

where the $-$ stands for the 1-direction and the $+$ for the 2-direction. Consequently instead of (3·14) we have now, using (3·16),

$$w_{21} = \frac{1}{2\tau} e^{\mu(G \cos \theta + R)/kT}, \quad w_{12} = \frac{1}{2\tau} e^{-\mu(G \cos \theta + R)/kT},$$

from which we obtain approximately

$$w^+ = \tau(w_{21} + w_{12}) \sim 1 + \gamma \beta x,$$  \hspace{1cm} (3·20)$$

$$w^- = \tau(w_{21} - w_{12}) \sim \beta + \gamma x,$$

where $\uparrow x = R/R_1$, and

$$\beta = \frac{\mu G \cos \theta}{kT}.$$  \hspace{1cm} (3·21)$$

In equation (3·12), which is an exact equation, the transition probabilities $w_{12}$, $w_{21}$ now contain $R$ given by the differential relations (3·18) which implicitly depend on $n_1$ and $n_2$. Thus in first order (3·12) cannot be solved so easily as in zero order. To find a solution we introduce a probability function $p_1(R) dR$ denoting the probability that at the time $t$ a dipole is in the 1-direction while the reaction field has

$\uparrow$ Our final result (i.e. the expression for $P$) will be proportional to $\beta$. We have thus to keep terms $\sim \beta^2$ but neglect terms $\sim \beta^2$ and $\sim \gamma^2$ in order to find $P$ correct in the first order in $\gamma$. 


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a value between $R$ and $R + dR$. Similarly, we introduce $p_2(R)$ for the 2-direction. Thus

$$n_i = n \int_{-R_i}^{R_i} p_i(R) dR \quad (i = 1, 2). \quad (3.22)$$

$p_i$, and hence $n_i$, may depend on the time $t$. We shall now develop the kinetic equations for $p_i(R)$. The differential coefficient of $p_i$ with respect to the time is composed of two terms

$$\frac{\partial p_i}{\partial t} = \left( \frac{\partial p_i}{\partial t} \right)_{\text{dipole}} + \left( \frac{\partial p_i}{\partial t} \right)_R. \quad (3.23)$$

The first term refers to a change in dipole direction keeping $R$ constant, whereas in the second term $R$ varies but the dipole direction is kept constant. Clearly in analogy to (3.12)

$$\left( \frac{\partial p_1(R)}{\partial t} \right)_{\text{dipole}} = - \left( \frac{\partial p_2(R)}{\partial t} \right)_{\text{dipole}} = - w_{12} p_1(R) + w_{21} p_2(R). \quad (3.24)$$

To find the second term we notice that in the time interval $dt$, $R$ increases by $\dot{R}dt$ ($\dot{R} = dR/dt$). Thus $p(R)dR$ at the time $t$ is equal to $p(R - \dot{R} dt) d(R - \dot{R} dt)$ at the time $t - dt$, i.e. developing $p(R)$,

$$p(R)dR \bigg|_t = p(R - \dot{R} dt) d(R - \dot{R} dt) \bigg|_{t - dt} = \left[ p(R) - \frac{\partial p(R)}{\partial R} \dot{R} dt \right] [dR - d\dot{R} dt] \bigg|_{t - dt}. \quad (3.25)$$

Now, neglecting $dt^2$ we obtain

$$\left( \frac{\partial p_i}{\partial t} \right)_R = \left[ p_i(R) dR \bigg|_{t - p_i(R) dR \bigg|_{t - dt}} \right] \frac{1}{dR dt} \frac{dR}{dt} = - \frac{\partial p_i}{\partial R} \dot{R} - p_i \frac{d\dot{R}}{dR}. \quad (3.26)$$

We now make use of equations (3.18) for $\dot{R}$ and find

$$\left( \frac{\partial p_1}{\partial t} \right)_R = \frac{\partial p_1}{\partial R} \frac{R - R_1}{\tau} + \frac{p_1}{\tau}, \quad \left( \frac{\partial p_2}{\partial t} \right)_R = \frac{\partial p_2}{\partial R} \frac{R + R_1}{\tau} + \frac{p_2}{\tau}. \quad (3.27)$$

Inserting (3.24) and (3.25) into (3.23) we obtain

$$\tau \frac{\partial p_1}{\partial t} = (R - R_1) \frac{\partial p_1}{\partial R} + p_1 + \tau w_{21} p_2 - \tau w_{12} p_1, \quad (3.26)$$

$$\tau \frac{\partial p_2}{\partial t} = (R + R_1) \frac{\partial p_2}{\partial R} + p_2 + \tau w_{21} p_2 + \tau w_{12} p_1.$$ 

To bring these equations into a mathematically more useful form we use the dimensionless variable $x$ defined by

$$x = \frac{R}{R_1}, \quad (-1 < x < 1), \quad (3.27)$$

and instead of $p_1$ and $p_2$ we introduce the functions

$$f(x) = (p_1 + p_2) R_1, \quad (3.28)$$

and

$$g(x) = (p_1 - p_2) R_1. \quad (3.29)$$
We then obtain from (3.26), using (3.20),
\[ \tau \frac{\partial f}{\partial t} = \frac{\partial}{\partial x} (xf - g), \] (3.30)
\[ \tau \frac{\partial g}{\partial t} = \frac{\partial}{\partial x} ((xg - f) - w^+ g + w^- f). \] (3.31)

These two differential equations have to be solved under the following conditions. First, since the total number of dipoles per unit volume, \( n = n_1 + n_2 \), is a constant, we find from (3.28), (3.22) and (3.27)
\[ \int_{-1}^{1} f(x) \, dx = 1. \] (3.32)

Furthermore, in the expressions \( \left( \frac{\partial p_i}{\partial t} \right)_R \) the dipolar direction is kept constant.

Therefore
\[ \int_{-R_1}^{R_1} \left( \frac{\partial p_i}{\partial t} \right)_R \, dR = 0 \quad (i = 1, 2). \]

Using equations (3.27), (3.28), (3.29), (3.25) as well as (3.32) this condition becomes
\[ \int_{-1}^{1} \frac{\partial}{\partial x} ((xg - f) \, dx = 0. \] (3.33)

From the four equations (3.30)–(3.33) we have to determine the polarization \( P \). Thus according to (3.9) we require \( n_1 - n_2 \) which, using (3.22), (3.27) and (3.29), is given by
\[ n_1 - n_2 = n \int_{-1}^{1} g(x) \, dx = nJ. \] (3.34)

To find the integral \( J \) we integrate equation (3.31) from \( x = -1 \) to \( x = 1 \). Inserting \( w^\pm \) from (3.20) we obtain, making use of the conditions (3.32) and (3.33),
\[ \tau \frac{dJ}{dt} = -J - \gamma \beta \int_{-1}^{1} xg \, dx + \beta + \gamma \int_{-1}^{1} xf \, dx. \]

Here the integral \( \int xg \) has a factor \( \gamma \beta \). The function \( g(x) \) is, therefore, required in zero order in \( \gamma \) and \( \beta \) only, i.e. neglecting the effect of an external field as well as of the reaction field. In this approximation both \( \partial f/\partial t \) and \( \partial g/\partial t \) vanish if we assume equilibrium, and \( w^+ = 1, w^- = 0 \). Equations (3.30) and (3.31) thus become
\[ 0 = \frac{\partial}{\partial x} (xf - g) \quad \text{and} \quad 0 = \frac{\partial}{\partial x} ((xg - f) - g), \quad \text{if} \quad \gamma = 0, \beta = 0. \]

Multiplying the second of these equations by \( x \) and integrating yields
\[ \int_{-1}^{1} xg \, dx = \int_{-1}^{1} x \frac{\partial}{\partial x} ((xg - f) \, dx = x^2g - xf \bigg|_{-1}^{1} - \int_{-1}^{1} xg \, dx + \int_{-1}^{1} f \, dx, \]
while an integration over the first equation leads to

\[ 0 = \int_{-1}^{1} \frac{\partial}{\partial x} (xf-g) \, dx = \left| xf-g \right|_{-1}^{1} = \left| xf - x^2 g \right|_{-1}^{1}. \]

Thus with (3.32) we obtain

\[ \int_{-1}^{1} xg \, dx = \frac{1}{2}, \quad \text{if} \quad \gamma = 0, \quad \beta = 0, \]

and hence

\[ \tau \frac{dJ}{dt} = -J - \frac{\gamma \beta}{2} + \beta + \gamma \int_{-1}^{1} xf \, dx. \] (3.35)

To eliminate \( \int xf \) we notice that, according to (3.30) with (3.34),

\[ \tau \int_{-1}^{1} x \frac{df}{dt} \, dx = \int_{-1}^{1} x \frac{\partial}{\partial x} (xf-g) \, dx = - \int_{-1}^{1} xf \, dx + J \]

if we make use of the fact that according to (3.33) \( \left. x^2 f - xg \right|_{-1}^{1} = 0 \). Let us now differentiate (3.35) with respect to \( t \) and introduce

\[ \frac{d}{dt} \int_{-1}^{1} xf \, dx = \int_{-1}^{1} x \frac{df}{dt} \, dx \]

from the above equation. Using once more (3.35) we can eliminate \( \int_{-1}^{1} xf \) and obtain

\[ \tau^2 \frac{d^2 J}{dt^2} + 2\tau \frac{dJ}{dt} + (1-\gamma) J = \left(1 - \frac{\gamma}{2}\right) \left(\beta + \frac{d\beta}{dt}\right). \]

Finally, in order to obtain \( P \) (see (3.9) and (3.34)) we multiply this equation by \( \mu_n \cos \theta \) and replace \( \cos^2 \theta \) by \( 1/3 \) (polycrystalline material). Introducing \( \beta \) from (3.21) we obtain

\[ \tau^2 \frac{d^2 P}{dt^2} + 2\tau \frac{dP}{dt} + (1-\gamma) P = \frac{\mu^2 n}{3kT} \left(1 - \frac{\gamma}{2}\right) \left(G + \frac{dG}{dt}\right). \] (3.36)

Thus for static fields, \( G = G_0 \), the equilibrium value \( P_0 \) of \( P \) becomes, if we neglect \( \gamma^2 \) and higher powers in \( \gamma \),

\[ P_0 = \frac{\mu^2 n G_0}{3kT} \left(1 + \frac{\gamma}{2}\right). \] (3.37)

For time-dependent fields suppose

\[ G = G_0 \phi(t), \]

where \( G_0 \) is time independent and \( \phi(t) \) is a function of time. Introducing this and (3.37) into (3.36) we find

\[ \tau^2 \frac{d^2 P}{dt^2} + 2\tau \frac{dP}{dt} + (1-\gamma) P = (1-\gamma) P_0 \left(\phi + \frac{d\phi}{dt}\right). \] (3.39)

Equations (3.37) and (3.39) clearly demonstrate the deviations of the first-order values of the polarization from the zero order (i.e. Onsager's theory), equations
We see that the effect of the reaction field is twofold. First, the static polarization is larger by a factor $1 + \gamma/2 < 3/2$ and thus lies between the values according to Onsager and according to Debye. Secondly, the time dependence is different from both Onsager's and Debye's theories. The dipoles are no longer independent of each other and thus reach an equilibrium value no longer $\sim e^{-\omega t}$ but in a more complicated way. Let us calculate the time dependence of $P$ in a periodic field

$$\phi(t) = e^{i\omega t}. \quad (3.40)$$

Inserting this into (3.39) we find in first order in $\gamma$

$$P = \frac{P_0 e^{i\omega t}}{1 + i\omega \tau} \left[ 1 - \gamma + \frac{\gamma}{(1 + i\omega \tau)^2} \right], \quad (3.41)$$

which for $\gamma = 0$, of course, is identical with the well-known Debye formula.

7. Liquids with low viscosity. We have seen that in solids a dipole has two equilibrium positions with opposite dipole direction. An external field alters the transition probabilities between the two positions in such a way that a dipole will prefer one of the two directions thus giving rise to a polarization. In liquids, on the other hand, a dipole may have any direction. An external field tends to turn a dipole into a direction parallel to its own, against frictional forces and thermal motion. In spite of this difference from the solid case, the polarization in liquids is in our zero order determined by equations of the same type as in solids ((3.15), (3.17)) as can be seen from the work of Debye (1929). The whole difference lies in the different expressions for the time of relaxation which in solids is connected with the transition probabilities between the two equilibrium positions (see equation (2.1)) while in liquids with low viscosity it can be derived from the viscosity (see § 3).

Taking into account the reaction field, however, low-viscosity liquids behave differently from solids and high-viscosity liquids. We do not want to give details of the calculations because they only show that in low-viscosity liquids the influence of the reaction field is negligible. For the static polarization, for instance, the first-order value of the polarization is found to be $(1 + \gamma/24)$ of its zero order value in contrast to a factor $(1 + \gamma/2)$ in solids (3.37). Thus it follows that for low-viscosity liquids, Onsager's theory (i.e. our zero approximation) is a very good approximation, as is also suggested by the work of Van Vleck (1937b). This difference between such liquids and solids is due to the fact that in these liquids a dipole changes its direction more gradually than in solids, thus giving the reaction field a greater chance to adapt itself to the dipolar direction.

IV. Results and discussion

From the calculations of the previous sections we can now derive our final results for the dielectric constant and the dielectric losses. We shall restrict ourselves to a discussion of solids and liquids with high viscosity because, as we saw in § 7, Onsager's theory is a sufficiently good approximation for liquids with low viscosity.
8. The static dielectric constant. From expression (3.37) for the static polarization we obtain the static dielectric constant \( \varepsilon_s \), using equations (2.2), (2.3) and (3.3),

\[
\varepsilon_s = \varepsilon_\infty + \frac{\mu^2}{\alpha^2 k T} \left( 1 + \frac{\gamma}{2} \frac{G_0}{E_0} \right),
\]

where \( E_0 \) is the static electric field. \( G_0 \) as well as \( \gamma \) depend on the shape of the cavity. For the simplified case of a spherical cavity we can insert \( G_0 \) from (3.4) and find

\[
\varepsilon_s = \varepsilon_\infty + \frac{3\varepsilon_\infty}{2\varepsilon_s + \varepsilon_\infty} \frac{\mu^2}{\alpha^2 k T} \left( 1 + \frac{\gamma}{2} \right),
\]

where, according to (3.11) and (3.7),

\[
\gamma = \frac{\mu R_1}{k T} = \frac{\mu^2}{\alpha^2 k T} \frac{2(\varepsilon_s - \varepsilon_\infty)}{\varepsilon_\infty(2\varepsilon_s + \varepsilon_\infty)} < 1.
\]

Here we can calculate \( \mu^2/\alpha^2 k T \) from equation (4.2) and insert it into (4.3). As usual we have to neglect \( \gamma^2 \) terms, and obtain

\[
\gamma = 3 \left( \frac{(\varepsilon_s - \varepsilon_\infty)^2}{\varepsilon_s \varepsilon_\infty} \right) < 1.
\]

Thus finally

\[
\varepsilon_s = \varepsilon_\infty + \frac{3\varepsilon_\infty}{2\varepsilon_s + \varepsilon_\infty} \frac{\mu^2}{\alpha^2 k T} \left( 1 + \frac{1}{3} \frac{(\varepsilon_s - \varepsilon_\infty)^2}{\varepsilon_s \varepsilon_\infty} \right).
\]

It should be remembered that this formula holds for temperatures \( T \) larger than a critical temperature \( T_0 \), which has to be determined from the condition \( \gamma < 1 \), which, using (4.4), is equivalent to

\[
\varepsilon_s < \frac{7 + \sqrt{33}}{4} \varepsilon_\infty \sim 3\varepsilon_\infty.
\]

This condition thus means that coming from high temperatures where \( \varepsilon_s \) approaches \( \varepsilon_\infty \) equation (4.5) is valid until we reach a temperature \( T_0 \), where \( \varepsilon_s \sim 3\varepsilon_\infty \). Nothing can be said from the present theory about the behaviour of \( \varepsilon_s \) for \( T < T_0 \). Our expression (4.5) for \( \varepsilon_s \) contains two parameters, the high-frequency dielectric constant \( \varepsilon_\infty \) and \( \mu^2/\alpha^2 k \) which has the dimension of a temperature. To compare (4.5) with experimental results we require measurements over a fairly large temperature range which we found in a paper by Garton (1939). He has measured the dielectric constant of a chemically pure synthetic resin (glycol phthalate) between room temperature and about 200°C. Such resins are amorphous substances which gradually soften as the temperature increases but have no well-defined melting-point. According to §3 we may expect such substances to behave according to our solid model as is actually suggested by the agreement of our theory with the experiments as shown in figure 3. The experiments are carried out at frequencies of 50 kyce./sec., 50 cyc./sec. and for static fields. They can be used to deduce the static dielectric constant \( \varepsilon_s(T) \) since the function \( \varepsilon_s(T) \) forms the envelope to the set of temperature curves \( \varepsilon_\nu(T) \) where the suffix \( \nu \) denotes the frequency of the field.
The experiments suggest $\varepsilon_\infty \sim 3$. The remaining unknown constant $\mu^2/\alpha^3 k$ was determined as 1140° abs. by equating theoretical and experimental values for $T = 200^\circ$ C. Figure 3 shows good agreement between theory and experiment. To show the influence of the $\gamma$-terms we notice that the factor $1 + \gamma/2$ (see equation (4.2)) is 1.25 at 200° C, and 1.45 at 80° C. In order to come to a final decision about the validity of equation (4.5), more experiments would be required.

![Figure 3. Full line: Theoretical curve according to equation (4.5) with $\varepsilon_\infty = 3$ as suggested by experiment. The unknown parameter $\mu^2/\alpha^3 k$ was determined as 1140° K by equating (4.5) with the experimental value at 200° C. Dotted lines: Experimental curves (from Garton 1939), 1, static; 2, 50 cyc./sec.; 3, 50 keyc./sec. Curve 3 is practically identical with the theoretical curve for $T > 120^\circ$ C. The theory becomes invalid when $\varepsilon$ reaches $\varepsilon = 9$.](http://rspa.royalsocietypublishing.org/)

9. Dielectric loss. In alternating fields we find from (2.2), (2.3), (2.5), (3.41), (3.40), (3.37) and (3.38)

$$
\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\mu^2}{\alpha^3 k T} \frac{1}{1 + i\omega \tau} \left[ 1 - \frac{\gamma}{2} + \frac{\gamma}{(1 + i\omega \tau)^2} \right] \frac{G}{E^2},
$$

or for spherical cavities, using (3.4),

$$
\varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \frac{\mu^2}{\alpha^3 k T} \frac{1}{1 + i\omega \tau} \left[ 1 - \frac{\gamma}{2} + \frac{\gamma}{(1 + i\omega \tau)^2} \right],
$$

where $\gamma < 1$ is now given by (4.4). Separating real and imaginary parts this permits us to calculate $\varepsilon''/\varepsilon'$ and hence $\tan \theta$ (see (2.6)). The result would lead to a very complicated formula. Great simplifications can be made, however, if we assume

$$
(\varepsilon - \varepsilon_\infty) \frac{2\varepsilon + \varepsilon_\infty}{2\varepsilon} = \left( \varepsilon - \frac{\varepsilon_\infty}{2} \right) \left[ 1 - \frac{\varepsilon_\infty^2}{2\varepsilon(\varepsilon - \varepsilon_\infty/2)} \right] \sim \varepsilon - \frac{\varepsilon_\infty}{2},
$$

which is correct unless $\varepsilon$ approaches $\varepsilon_\infty$. An elementary calculation shows that with this approximation

$$
\tan \theta = \frac{1}{\varepsilon'} \left[ (\varepsilon_s - \varepsilon') \left( \varepsilon' - \frac{\varepsilon_\infty}{2} \right) \right] \left( 1 - \frac{\gamma}{2} \right),
$$
This can be compared with the well-known Debye formula

\[ \tan \theta = \frac{1}{\varepsilon'} \left[ (\varepsilon_s - \varepsilon^0) (\varepsilon' - \varepsilon_\infty) \right]^{1/2}. \] (4.11)

The first difference we notice is that for \( \gamma = 0, \varepsilon_\infty \) in (4.11) has been replaced by \( \varepsilon_\infty/2 \). This, however, is of minor importance in view of approximation (4.9). In fact we would obtain in (4.10) \( \varepsilon' - \varepsilon_\infty \) instead of \( \varepsilon' - \varepsilon_\infty/2 \) if we had assumed \( \varepsilon - \varepsilon_\infty \) to be small. The main difference of our formula (4.10) is thus a reduction of the Debye formula (4.11) by a factor \( 1 - \gamma/2 \) which can take values between 1/2 and 1. In fact, most experimental values of \( \tan \theta \) are smaller than required by equation (4.11) (see, for instance, Garton (1939)). Our formula (4.10), therefore, will give better agreement than (4.11). Even so, the theoretical values of \( \tan \theta \) are still larger by nearly a factor 2 than those observed by Garton. This probably means that the time of relaxation has at a given temperature a whole range of values as suggested by Garton and others.† This in fact follows at once from our model if we remember that resins are amorphous substances. Different molecules are, therefore, in slightly different positions relative to their neighbours which should give rise to different transition probabilities between the two stable positions of the dipoles. We thus require experiments on crystalline solids of this type considered here but unfortunately could not find any publications. We have, therefore, no possibility at present to compare our results on dielectric losses with experiments.

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References


† A theoretical analysis of this question has been given by Fuoss & Kirkwood (1941).