Dielectric properties of dipolar solids

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A quantitative theory of the dielectric properties of crystalline solids consisting of dipolar long-chain molecules is developed (one dipole per molecule). In these solids the dipoles are concentrated in dipolar planes. In the ground state the dipolar planes have a permanent polarization, but usually the polarizations of successive planes have opposite directions. The static dielectric constant rises with increasing temperature up to a critical temperature $T_0$ and then decreases. At $T_0$ the substance has a phase transition of the second kind. Comparison with experiments by Muller on a solid ketone lead to good agreement.

For chains with an even number of C-atoms metastable states with a permanent polarization are predicted, and a method to reach these states is discussed.

The interaction between dipoles plays a predominant role at temperatures below $T_0$. It is shown that Lorentz’s or Onsager’s methods are invalid in this temperature range.

1. Introduction

Dipolar solids consisting of long-chain molecules find a wide application as dielectrics. The most important of them, e.g. plastics, have a fairly complicated structure. One can hardly hope to reach a full understanding of their dielectric properties unless the dielectric behaviour of long-chain solids with a simple structure (e.g. solid ketones) is understood first. We shall, therefore, in the present paper develop a quantitative theory of the dielectric properties of simple crystalline solids consisting of long-chain molecules.

Substances of this type have already been investigated in a previous paper (Fröhlich & Sack 1944, quoted as I), where it was shown that the methods usually used to account for the interaction between dipoles become invalid below a temperature $T_0$ where $kT_0$ is of the order of the dipolar interaction energy. Since $T_0$ may be fairly high (for ketones it approximately coincides with the melting-point), a new method must be found to treat dipolar interaction. As was shown in I the dipoles undergo an order-disorder transition near the temperature $T_0$. Approximate methods have been developed to deal with these transitions, and it will be seen that they can be used in the case of the substances discussed here.

As a main result it will be found that the static dielectric constant increases with temperature up to $T_0$ and then decreases (§ 3). Experiments by A. Muller (1938) on solid ketones lead to good agreement with the present results, as will be shown in § 4. Moreover, from a discussion of structure (§ 2), a number of interesting conclusions concerning the possible existence of a permanent polarization can be drawn. Experiments to check these conclusions will be suggested in § 4.

It will be of interest to notice that as in I the internal field acting on a dipole is not proportional to the macroscopic polarization. Thus an application of the method of the Lorentz field would lead to wrong results for the substances discussed in this paper.

* Based on report L/147 of the British Electrical and Allied Industries Research Association (E.R.A.).
2. Structure and properties of the ground state

Throughout this paper discussion will be restricted to crystalline solids consisting of long-chain molecules each of which contains one dipole. In solids such molecules form plane zigzags, and it will be assumed that the dipole lies in the chain plane and is perpendicular to the chain axis, as is probably the case for ketones. In the simplest case these solids have a paraffin structure, i.e. according to Muller (1928) the molecular 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 length $a$, $b$, $c$, where $a \sim 5\AA$, $b \sim 7.5\AA$ and $c$ slightly larger than the chain length. As discussed in 1, each molecule has two equilibrium positions with opposite dipole direction. In the ground state the paraffin structure requires that they are oriented in such a way that they are nearly parallel as shown in figure 1. It will be shown below that this also corresponds to the lowest interaction energy between the dipoles of one layer.

![Diagram of dipolar structure of the ground state.](image)

In such a structure all the dipoles of one layer lie in one plane (perpendicular to the chain axis) which will be called the dipolar plane. The unit cell of the dipoles of a dipolar plane is shown in figure 1. In the ground state these dipolar planes are thus polarized in the $b$-direction, and it is of great importance for the behaviour of the whole crystal to know the relative direction of the polarization of successive dipolar planes. First, then, consider the position of successive layers in paraffins. According to Muller (1929) distinction must be made between two cases, according to whether the number of C-atoms of a chain is even or odd. Figure 2 shows the positions of two successive layers for the two cases. Now attach a dipole to each molecule at distances $c_1$ and $c_2$ from the two ends, i.e. $c_1 + c_2 = \text{chain length}$. For both even and odd chains there exist now two possibilities. Except for the gap between the chains the distance between successive planes is $(a) c_1 + c_2$, or $(b)$ it is alternately $2c_1$ and $2c_2$. Figure 3 shows that for odd chains both cases lead to opposite directions of the polarizations of successive dipolar planes. For even chains, however, this is only so in case $(b)$, whereas in case $(a)$ successive layers have the same direction of polarization. This latter case will thus lead to a strong polarization of the crystal with all dipoles nearly parallel, while in the other cases the polarizations of successive layers cancel.
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For paraffins both cases (a) and (b) are identical. Their energies, therefore, differ only in the contributions of the dipoles. To calculate the dipolar interaction energy notice that the distance between neighbouring dipoles within a dipolar plane is less than 5 Å, and is thus much smaller than the distance between neighbouring planes (unless the chain length is very small). First, then, one may calculate the interaction energy of a dipole with all the dipoles of the same dipolar plane, and then consider its interaction with the other dipolar planes. As in I, we assume the dipoles to be dispersed in a continuous medium with dielectric constant \( \varepsilon_\infty \). The interaction energy between two dipoles whose distance is \( r \) is then given by

\[
\frac{1}{\varepsilon_\infty r^3} \left[ \mu_1 \cdot \mu_2 - \frac{3}{r^2} \mu_1 \cdot \mu_2 \right],
\]

(1)

\[
\begin{array}{c}
\text{odd} \\
\text{even}
\end{array}
\]

\[
\begin{array}{c}
\text{odd} \\
\text{even}
\end{array}
\]

\textbf{Figure 2.} Position of paraffin chains in the ground state.

\textbf{Figure 3.} The two possible positions of dipoles in the ground state.

where \( \mu_1 \) and \( \mu_2 \) are the dipole moments of the two dipoles respectively. According to figure 1 the dipoles form an angle of about \( \pm 30^\circ \) with the \( b \) axis. Thus their components \( \mu_a \) and \( \mu_b \) in the \( a-b \) frame are given by

\[
\mu_a = \mu \sin (\pm 30^\circ) = \pm \frac{\mu}{2}, \quad \mu_b = \mu \cos (\pm 30^\circ) = \frac{\sqrt{3}}{2} \mu.
\]

(2)

The interaction of the central dipole of figure 1 with its four nearest neighbours is thus given by (considering that \( b/a = 1.5 \))

\[
\frac{4\mu^2}{\varepsilon_\infty r^3} \left[ \left( \frac{1}{2} + \frac{3}{4} \right) - \frac{3}{2 \times 25} \left( \frac{1}{2} + \frac{\sqrt{3}}{2} \times 1.5 \right) \left( \frac{1}{2} + \frac{\sqrt{3}}{2} \times 1.5 \right) \right] \simeq -\frac{3.3\mu^2}{\varepsilon_\infty r^3}.
\]

To this interaction the contributions of the further distant dipoles of the same dipolar plane have to be added. This, however, is very small. Taking a total of twenty neighbours the interaction energy becomes

\[
W \simeq -\frac{3.5\mu^2}{\varepsilon_\infty r^3}, \quad r^2 = \frac{a^2 + b^2}{4}.
\]

(3)
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It is thus seen that the main contribution is due to the interaction between nearest neighbours. This is of great importance for the calculation of the interaction in the excited states (§ 3). It is due to the strongly anisotropic structure of long-chain substances. In other crystals the nearest neighbours frequently contribute only a small fraction to the total dipolar interaction energy.

Since according to (1) each dipole has two equilibrium positions with opposite dipole direction, other structures can be considered in which some of the arrows in the unit cell in figure 1 have the opposite direction, and which would lead to a vanishing polarization of a dipolar plane. It is found that they all lead to a higher interaction energy between dipoles than the arrangement of figure 1.

To obtain the total interaction of a dipole with all other dipoles, its interaction with the other dipolar planes must be added. In view of their large distance it seems reasonable to consider a dipolar plane as a two-dimensional continuum with a constant polarization in the b-direction (dipole moment \( \sqrt{3} \mu / 2 \) per surface \( ab / 2 \)). This would lead to a reduction of the interaction between a dipole and a dipolar plane to an interaction of the dipole with the charge at the circumference of the dipolar plane. This latter interaction energy vanishes if the dipolar plane becomes infinitely large. In order to check this result, Mr R. Sack kindly calculated that the interaction energy between a dipole and an infinite dipolar plane at a distance \( z \) is of the order of magnitude

\[
18\pi^2 \frac{\mu^2}{b^3} e^{-3\pi z/b},
\]

which is thus about \( e^{3\pi z/b} / 100 \) times smaller than the interaction between neighbouring dipoles. For a distance of \( z \sim 20 \text{ Å} \) (30 Å) this leads to a factor \( 10^{10} (10^{14}) \). It thus seems to be a very good approximation to treat the dipolar planes as a continuum. Hence the interaction of a dipole with all the dipolar planes except its own can be reduced to its interaction with the surface charges which they produce at the surface of the crystal in view of the fact that each dipolar plane is polarized. To these surface charges may be added the surface charge due to the dipole's own dipolar plane, because the interaction of the dipole with the surface charge of a single dipolar plane is negligible if the crystal size is large compared with the distance between neighbouring dipoles. The surface charges produce an electrical field \( E \) inside the crystal which in general depends on its macroscopic shape. It gives rise to the interaction energy \( -(\mu E) \).

The total interaction energy \( U \) of a dipole with the other dipoles is thus given by (making use of (3))

\[
U = W - (\mu E) = -\frac{3 \cdot 5 \mu^2}{\varepsilon_\infty r^3} - (\mu E). \tag{4}
\]

The field \( E \) has to be calculated from the charges at the surface of the crystal which will be considered as of macroscopic dimensions. For all practical purposes it thus vanishes if the macroscopic polarization of the crystal vanishes. In the absence of an external field this is always the case for odd chains where successive dipolar
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planes have opposite polarization, so that the contributions of their surface charges to the field $E$ inside the crystal cancel. For even chains, however, it was seen that the direction of the polarizations of successive dipolar planes may either be equal or opposite. Such a crystal may, therefore, have a certain permanent polarization $P$. Suppose, as an extreme case, that all dipolar planes have the same polarization and that the crystal has the shape of a thin plane parallel plate with the polarization perpendicular to the surface. Then the polarization is given by

$$P = \frac{\sqrt{3} \mu}{abc},$$

since each dipole occupies the volume $\frac{1}{2}(abc)$ and contributes $\sqrt{3} \mu/2$ to the polarization in the $b$-direction. In the absence of a field due to external charges, the electric displacement $D$ vanishes, i.e. since $(\varepsilon_\infty - 1)E/4\pi$ in the polarization of the continuum

$$D = \varepsilon_\infty E + 4\pi P = 0,$$

or

$$E = -\frac{4\pi P}{\varepsilon_\infty} = -\frac{4\pi \sqrt{3} \mu}{abc \varepsilon_\infty}.$$ 

In this case, therefore, the energy $U$ becomes (considering that $(\mu E) = \frac{\sqrt{3}}{2} \mu E$)

$$U = \frac{3 \cdot 5 \mu^2}{\varepsilon_\infty \varepsilon^3} + \frac{6\pi \mu^2}{abc \varepsilon_\infty}.$$  

(5)

Since the total dipolar energy of a crystal of $N$ dipoles is $NU/2$ it is seen that crystals with a permanent polarization have a higher energy than unpolarized crystals. As mentioned before the magnitude of the $(\mu E)$ term depends on the macroscopic shape of the crystal. Actually it may be smaller than $6\pi \mu^2/abc \varepsilon_\infty$, but in the case of a permanent polarization its contribution to $U$ is always positive.*

The physical implications of this result will be discussed in § 4.

3. Excited states

According to I each chain has two equilibrium positions with opposite dipole direction. Thus from the ground state discussed in § 2 excited states can be obtained by turning a chain (including its dipole) by $180^\circ$ around the chain axis. In equilibrium, chains will always be considered as plane. Thus, if from now on one speaks of a certain direction of a dipole, this implies the direction of the whole chain, i.e. turning a dipole by $180^\circ$ from the one to the other equilibrium position implies a turning of the whole chain over the potential hill separating the two equilibrium

* For isotropic crystals Sauer (1940) has carried out similar calculations. In his final remarks he says that electric dipole coupling leads to results which are different from magnetic dipole coupling. Surely this cannot be correct, since in both cases he assumes exactly the same form for the interaction between individual dipoles so that the sum over a number of dipoles must also give the same result considering that no external fields are contemplated in both cases. His mistake seems to be that he thinks that 'nothing in the electrical case corresponds to the demagnetization factor in the magnetic' which in the case of permanent electric polarization can hardly be correct.
positions. A detailed description of this process was given in a previous paper (Fröhlich 1942). The first object in this section is to calculate the energy of an excited state. As in § 2 first consideration will be given to the interaction between chains of the same layer, i.e. dipoles of the same dipolar plane, and then the interaction with the chains outside it and with fields due to external charges will be added. Consider first the interaction between nearest neighbours and suppose that they are directed as in figure 1, i.e. the b-components of the dipoles are parallel. Now turn one of the dipoles (i.e. the whole chain) by 180° into its second equilibrium position and denote by $2V$ the increase of the interaction energy with one of its four nearest neighbours. Then $8V$ will be the increase in the interaction energy of the central dipole with its four neighbours if it is turned by 180°. If, on the other hand, $n$ of its four neighbours have the opposite direction from that indicated in figure 1, then the corresponding energy increase is only

$$ (4 - 2n) 2V. $$

The energy $V$ can be written as

$$ V = \frac{W}{4} + V', $$

where $W$ is the dipolar interaction energy given by eqn. (3), while $V'$ is due to non-dipolar interaction between molecules. This latter energy decreases quickly with distance so that interaction between nearest neighbours only has to be considered. The same holds of the dipolar interaction energy of a dipole with the dipoles of the same dipolar plane, because the number of dipoles within a distance $r$ from a central one increases proportional to $r^2$ whereas their interaction decreases proportional to $1/r^3$. In fact it was seen in § 2 that in the ground state the nearest neighbours account for more than 90% of the total interaction. To obtain the contribution due to the interaction with chains of a different layer it seems reasonable to neglect the non-dipolar part, i.e. to assume that this part of the interaction is independent of the dipole direction. The dipolar interaction can be treated as in § 2. Thus a dipolar plane outside the plane of the dipole in question can be treated as a continuum. Its total interaction with all the outside planes thus reduces to its interaction with the surface charges which are produced by the polarization of the dipolar planes. These charges, together with possible external charges, produce the macroscopic electric field $E$ inside the crystal whose interaction with the dipole is

$$ - (\mu E) = - \mu_a E_a - \mu_b E_b, $$

where $E_a$ and $E_b$ are the components of $E$ in the $a$- and $b$-directions respectively.

In the structure indicated in figure 1 there are two types of dipoles, those forming an angle of about 30° (or 210° in their second equilibrium position) with the $b$-axis, and those for which this angle is $-30^\circ$ ($150^\circ$). Unless the field $E$ vanishes, these two types of dipoles behave in a different way. In order to simplify the following calculations the $a$-components of the dipoles will be neglected, thus not dealing with the structure indicated in figure 1 but treating that of figure 4 instead, in which all dipoles are in the $b$-direction and have the moment $\mu_b$. This does not affect the short-range interaction which will be used in the general form (6) which does not contain
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explicitly the dipole direction. Moreover, the \( \mu_a \) terms contribute less than 3% to the total dipolar interaction \( W \) as can be seen from eqns. (1) and (2). No appreciable influence of this simplification may therefore be anticipated. The two possible dipole directions will be denoted by + and −. Then, using (6) and (8), the energy required to turn a dipole from the + into the − direction is

\[
(4 - 2n) 2V + 2\mu_b E \cos \theta, \tag{9}
\]

if \( n \) of its nearest neighbours are in the − direction, i.e. \( 4 - n \) are in the + direction. \( \theta \) is the angle between \( E \) and \( \mu_b \). With an appropriate normalization of the energy it can thus be said that a dipole in the + (−) direction has the energy \(-(+)B\), where

\[
B = (4 - 2n) V + \mu_b E \cos \theta. \tag{10}
\]

\[\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{dipole_structure.png}
\caption{Simplified dipolar structure. The dotted arrow indicates the second equilibrium position for each dipole.}
\end{figure}\]

Next calculate the probability that a dipole has the + direction. To do this a method by Bethe (1935) will be used. Bethe’s original method would apply to \( E = 0 \). Weak fields will be assumed throughout, i.e.

\[
\mu_b E \ll kT, \tag{11}
\]

where \( T \) is the absolute temperature.

Let \( w_n^+ (w_n^-) \) be the probability that a dipole is in the + (−) direction while \( n \) of its four neighbours are in the − direction. Then according to the Boltzmann theorem, making use of (10)

\[
\frac{w_n^+}{w_n^-} = e^{2B/kT} = e^{2V(4-2n)/kT + 2\mu_b E \cos \theta/kT}.
\]

Developing this expression with respect to \( E \) (making use of (11)) one obtains

\[
\frac{w_n^+}{w_n^-} = \frac{x^n}{x^{4-n}} \frac{1 + F}{1 - F}, \tag{12}
\]

where

\[
x = e^{-2B/kT} \tag{13}
\]

and

\[
F = \frac{\mu_b E \cos \theta}{kT} \ll 1. \tag{14}
\]
First consider the zero-order problem $F = 0$. This reduces exactly to Bethe’s case. Therefore, only the results will be given. Bethe’s $z$ is equal to $4$ in the present case, while his $\varepsilon$ will be denoted by $\lambda$. Then according to Bethe

\[
 w_n^+ = C \binom{4}{n} x^n \lambda^n, \tag{15}
\]

\[
 w_n^- = C \binom{4}{n} x^{4-n} \lambda^n. \tag{16}
\]

The total probability of finding the dipole in the $+$ direction is thus

\[
 w = \sum_{n=0}^{n=4} w_n^+ = C (1 + \lambda x)^4, \tag{17}
\]

whereas for the opposite direction it is

\[
 1 - w = \sum w_n^- = C (\lambda + x)^4. \tag{18}
\]

Hence

\[
 C = \frac{1}{(1 + \lambda x)^4 + (\lambda + x)^4}. \tag{19}
\]

![Figure 5. $\lambda$ as a function of $x = (\frac{1}{2})^{1/r}$.](http://rspa.royalsocietypublishing.org/)

The parameter $\lambda$ is obtained from the condition that all dipoles are equivalent. This leads to

\[
 1 - w = \sum \frac{n}{4} (w_n^+ + w_n^-). \tag{20}
\]

Inserting (15) and (16) into (20), and equating it with (18), leads with the use of (19) to

\[
 \lambda = \left( \frac{\lambda + x}{1 + \lambda x} \right)^{3/4}. \tag{21}
\]

A solution of this equation is shown in figure 5. In particular

\[
 \lambda \approx x^3, \quad \text{if } x \ll 1, \quad \text{i.e. } kT \ll V, \tag{22}
\]

and

\[
 \lambda = 1, \quad \text{if } x \geq \frac{1}{2}. \tag{23}
\]
Hence $w = 1$ if $T = 0$, i.e. all dipoles are parallel in the $+$ direction. With $\lambda$, also $1/\lambda$ is a solution leading to $w = 0$ for $T = 0$, i.e. to the case in which all dipoles are in the $-$ direction. $\lambda = 1$, according to eqns. (17)–(19), leads to $w = 1 - w = \frac{1}{2}$, i.e. to disorder. The order-disorder transition thus occurs at $x = \frac{1}{2}$; i.e. using (13), at the temperature $T_0$ given by

$$kT_0 = 2V/\log 2.$$  \hfill (24)

Let us now introduce the $F$-terms. Then from (12) it follows that (15) and (16) have now to be replaced by

$$w_n^+ = C\left(\frac{4}{n}\right)x^n\lambda^n(1 + F), \quad w_n^- = C\left(\frac{4}{n}\right)x^n\lambda^n(1 - F),$$

where $C'$ and $\lambda'$ depend on $F$. Since for zero order in $F$ they must be identical with $C$ and $\lambda$ respectively, then, neglecting higher order terms,

$$C' = C(1 + \gamma F), \quad \lambda' = \lambda\left(1 + \eta\frac{F}{4}\right), \quad \lambda'^n = \lambda^n\left(1 + \frac{n}{4}\eta F\right).$$

Thus

$$w_n^+ = C\left(\frac{4}{n}\right)x^n\lambda^n\left[1 + F\left(\gamma + \frac{n}{4}\eta + 1\right)\right], \hfill (25)$$

$$w_n^- = C\left(\frac{4}{n}\right)x^n\lambda^n\left[1 + F\left(\gamma + \frac{n}{4}\eta - 1\right)\right]. \hfill (26)$$

Let us denote by $w_F$ the probability that in the presence of the field the dipole has the positive direction, while $w$ as before refers to $F = 0$. Using (15) and (16)

$$w_F = \Sigma w_n^+ = w\left[1 + F\left(\gamma + \eta\frac{\lambda x}{1 + \lambda x} + 1\right)\right], \hfill (27)$$

$$1 - w_F = \Sigma w_n^- = (1 - w)\left[1 + F\left(\gamma + \eta\frac{\lambda}{\lambda + x} - 1\right)\right]. \hfill (28)$$

Adding these two equations leads to

$$0 = \gamma + \eta\left[w\frac{\lambda x}{1 + \lambda x} + (1 - w)\frac{\lambda}{\lambda + x}\right] + 2w - 1.$$  

Using (17), (18) and (21) the second term is found to be $\eta(1 - w)$. Thus

$$\gamma = 1 - 2w - \eta(1 - w). \hfill (29)$$

In order to obtain $\eta$, eqn. (20) is extended to the first order, i.e.

$$1 - w_F = \Sigma\frac{n}{4}(w_n^+ + w_n^-).$$

Inserting (25) and (26) and making use of (27), (28), (17), (18) and (21) a short calculation leads to

$$\eta = \frac{2(1 + \lambda x)(\lambda + x)}{\lambda(1 - x^2) - \frac{1}{2}(2\lambda + x + \lambda^2 x)}. \hfill (30)$$
From (27) the increase in the probability of positive dipole direction caused by the field is found to be

$$w_F - w = w F \left( \gamma + \eta \frac{\lambda x}{1 + \lambda x} + 1 \right),$$

or inserting $\gamma$ from (29)

$$w_F - w = w (1 - w) F \left[ 2 + \eta \left( \frac{\lambda x}{1 + \lambda x} \cdot \frac{1}{1 - w} - 1 \right) \right].$$

Since according to (18), (19) and (21)

$$\frac{1}{1 - w} = 1 + \frac{1 + \lambda x}{\lambda x},$$

then, using (30),

$$w_F - w = \frac{2w (1 - w) F}{1 - 4\lambda (1 - x^2)/(2\lambda + x + \lambda^2 x)},$$

(31)

Thus of $N$ dipoles, $N(w_F - w)$ will be turned by the field. Each turned dipole produces a dipolar moment $2\mu_0 \cos \theta$ in the field direction. Considering polycrystalline material, i.e. averaging over all angles $\theta$ (thus replacing $\cos^2 \theta$ by 1/3), the moment $M$ induced by the field $E$ is given by (cf. (31) and (14))

$$M = \frac{\mu_0^2 N}{3kT} E G(T/T_0),$$

(32)

where

$$G(T/T_0) = \frac{4w (1 - w)}{1 - 4\lambda (1 - x^2)/(2\lambda + x + \lambda^2 x)}.$$  

(33)

Since, according to (13) and (24),

$$x = (\frac{1}{2})^{T/T_0},$$

(34)

and since $\lambda$ is a function of $x$, $G$ is a function of $T/T_0$. For $G = 1$ expression (32) becomes identical with the induced moment if the interaction between dipoles is neglected. Thus $G$ is the factor which accounts for the interaction. Let us calculate it in some limiting cases. If $T > T_0$, $\lambda = 1$ and $w = \frac{1}{2}$. Thus in the case of disorder

$$G = \frac{1}{1 - 2(1 - x)}.$$

(35)

Thus $G \to 1$ as $T \to \infty$. At the transition point $T = T_0$, $x = \frac{1}{2}$ and hence $G \to \infty$. On the other hand, for $T \ll T_0$, using (22), (34), and (17)–(19)

$$G \sim 4x^4 = 4(\frac{1}{2})^4 T \sqrt{T} \quad (T \ll T_0).$$

(36)

Thus $M \to 0$ as $T \to 0$.

4. Results and Discussion

We are now prepared to discuss the dielectric properties of crystalline solids with a paraffin structure consisting of long-chain molecules each of which contains one electric dipole such as ketones. According to § 2 chains with an even number of carbon atoms (even chains) may be expected to behave differently from those
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containing an odd number (odd chains) because for the former there exists the possibility of a permanent polarization. The simpler case of odd chains will be considered first.

Odd chains. According to §§ 2 and 3 the dipoles of these substances are concentrated in dipolar planes. Below the temperature $T_0$ given by eqn. (24) these dipolar planes have a permanent polarization. The polarizations of successive dipolar planes have opposite direction, so that in the absence of an external field the total polarization vanishes. At $T_0$ the substances undergo a phase transition of the second kind ($\lambda$-point). A lower limit for $T_0$ can be given if the non-dipolar energy terms $V'$ in $V$ be neglected, eqn. (7). From eqns. (24), (7) and (3), making use of (2), it is found that

$$kT_0 = -\frac{1}{3} W \log 2 = \frac{1.7 \mu_0^2}{\epsilon_\infty r^2 \log 2} = \frac{3.2 \mu_0^2}{\epsilon_\infty r^2}, \quad r^2 = \frac{a^2 + b^2}{4}. \quad (37)$$

As mentioned before, this result will be obtained for the actual structure (figure 1) as well as for the simplified one used for the present calculations (figure 4), since they lead to a dipolar interaction which differs by less than 3%. With $a = 5 \text{ A}$, $b = 7.5 \text{ A}$, $\epsilon_\infty = 2.5$ and $\mu = 2 \times 10^{-18} \text{ e.s.u.}$, then $T_0 = 300^\circ \text{ abs.}, \text{i.e. room temperature.}$

To obtain the static dielectric constant $\epsilon_s$ the non-dipolar contributions are required in addition to the dipolar moment (32). As in I the substance will be considered as consisting of a continuous medium with a dielectric constant $\epsilon_\infty$ in which dipoles are dispersed according to the structure. Thus if $M'$ is the dipolar moment per unit volume

$$\epsilon_s = \epsilon_\infty + 4\pi \frac{M'}{E'},$$

or with (32)

$$\epsilon_s = \epsilon_\infty + \frac{4\pi \mu_0^3 N}{3 kT} G(T/T_0), \quad (38)$$

where $N$ is now the number of dipoles per unit volume. The function $T_0/T \cdot G(T/T_0)$ has been plotted in figure 6. It should be noted that $\epsilon_s$ refers to constant volume (independent of $T$). The most characteristic feature of our result is that for $T < T_0$, the dielectric constant $\epsilon_s$ increases with increasing $T$ in contrast to its behaviour above $T_0$. Previous theories always lead to a decrease of $\epsilon_s$ with $T$, but then, as was shown in I, they are valid only for $T > T_0$. Eqn. (38) contains two unknown parameters, $T_0$ and $\mu_0$, while $N$ can be easily determined from the structure. On the assumption that the interaction $V$ is entirely of dipolar nature, $\mu_0$ can be eliminated with the help of eqn. (37). Thus

$$\epsilon_s = \epsilon_\infty + 1.3 \epsilon_\infty N r^2 \frac{T_0}{T} G(T/T_0), \quad (39)$$

where $r$, the distance between nearest neighbours, can also be easily obtained from the structure.

† If $T \gg T_0$, expression (35) for $G$ can be developed (cf. (34)) into a power series in $T_0/T$. Eqn. (38) then becomes

$$\epsilon_s = \epsilon_\infty + \frac{4\pi \mu_0^3 N}{3 kT} \left( 1 + \frac{2T_0}{T} \log 2 + \ldots \right).$$
It is fortunate that experiments of exactly the type required to check the theory have been carried out by Muller (1938). He investigated the dielectric constant at constant volume of an odd ketone \([\text{CH}_3(\text{CH}_3)_2\text{CO}(\text{CH}_2)_2\text{CH}_3]\) at a frequency of \(10^7\) cyle./sec., in a temperature range up to the melting-point which is near \(340^\circ\) abs.

\[\text{Figure 6. Full line: the function } T_0/T \cdot G(T/T_0) \text{ which is proportional to the dipolar contribution to the dielectric constant. Dotted line: experimental value of } 10(\epsilon-2.5)/3.5 \text{ for the ketone measured by Muller (1938). The experimental value of } T_0 \text{ has been determined by equating theoretical and experimental curves at the point marked with *}.\]

It seems likely that his results represent the static dielectric constant because a theoretical estimate of the time of relaxation \(\tau\) from eqn. (12) of Fröhlich (1942), i.e.

\[2\pi\tau = \exp \left( -50.4 + \frac{\pi^2}{4} \frac{5600}{T} \tanh \frac{\nu}{26} \right)\]

\((\nu = \text{number of C-atoms, i.e. } \nu = 17)\) yields \(\tau \sim 10^{-12}\) at \(T \sim 300^\circ\) abs. Thus \(\tau\) is much smaller than the period of \(10^{-7}\) sec. Muller gives all his results in terms of \((\epsilon-1)/(\epsilon+2)\), from which \(\epsilon\) can be calculated and thus a number of curves for various volumes are obtained, giving an increasing \(\epsilon\) with rising \(T\) right up to the melting-point. It is remarkable that at the melting-point the dielectric constant is the same for all volumes. Since the change of \(N_\gamma^3\) with volume is very small this suggests that melting occurs at a constant value of the reduced temperature \(T/T_0\).

The experimental curves for \(\epsilon\) are in good agreement with eqn. (39) if the reduced temperature of the melting-point is chosen to be 0.965, independent of the volume.
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In fact, since the chain length is about $23 \times 10^{-8}$ cm., or using $a = 5$ Å, $b = 7.5$ Å, $N = 1.2 \times 10^{21}$ per c.c., i.e. $r^3 = (a^2 + b^3)^{3/2}/8 = 0.9 \times 10^{-22}$ c.c. With $\varepsilon_{\infty} = 2.5$ which is suggested by the low-temperature part of the experimental curves, eqn. (39) becomes

$$\frac{10}{3.5} (\varepsilon_\infty - 2.5) = \frac{T_0}{T} G(T/T_0).$$

In figure 6 the dotted line represents the average of the experimental values of $10(\varepsilon - 2.5)/3.5$. The only appreciable deviations from the theoretical curve occur for small values of $\varepsilon - \varepsilon_{\infty}$. This should be anticipated because the value chosen for $\varepsilon_{\infty}$ is probably not very accurate. This close agreement suggests that the interaction $V$ is actually mainly of dipolar nature because otherwise agreement with eqn. (38) only should be anticipated.† Thus eqn. (37) may be used to estimate $\mu_0$, and hence, using eqn. (2), the dipole moment of a ketone found. With the experimental values $T_0 = 340^\circ$ abs. and $\varepsilon_{\infty} = 2.5$, then

$$\mu = \left(\frac{4}{3} \frac{\varepsilon_{\infty} r^3}{3.2 kT_0}\right)^{\frac{1}{4}} = 2.1 \times 10^{-18} \text{ e.s.u.}$$

Although this is a reasonable value more experiments should be carried out in order to establish whether the interaction $V$ is actually mainly dipolar nature. This could be done by varying the chain length as well as the volume over a fairly large range. Then, for a given distance $r$ between nearest neighbours, $T_0$ should not vary with chain length if $V$ is of dipolar nature. An experimental determination of the time of relaxation $\tau$ should also be carried out so as to make sure that the estimate that $\tau < 10^{-7}$ sec. is correct. This is of importance because in alternating fields at sufficiently low temperatures the dielectric constant increases with temperature even if the static dielectric constant decreases. This increase depends, however, strongly on frequency. It would, therefore, be sufficient to show that Muller's experimental curve does not change appreciably if the frequency of the field is altered.

**Even chains.** In contrast to odd chains the polarizations of two successive dipolar planes may be either parallel or antiparallel for even chains. This may lead to a permanent polarization of a crystal although it has been shown in §2 that in the absence of an external field a state with a permanent polarization has a higher energy than an unpolarized one. Suppose for a moment that it would be possible to reach equilibrium in these crystals. Then, owing to an external field, a number of dipolar planes would change the direction of their polarizations. Let $d$ be the number of dipoles in a dipolar plane, and let $ad\mu$ be its dipole moment. Then, if one neglects the small change of the polarization of a dipolar plane due to a weak external field, $\pm \alpha = 1 - 2w$, where $w$ has been calculated in §3, i.e. $w = 1$ at $T = 0$, and $w = \frac{1}{4}$ for

† Unless it is an accidental agreement which then should hold for the chain length $\nu = 17$ only.
$T \geq T_0$. It now follows from eqn. (9) that the energy required to reverse the polarization of a dipolar plane in an external field is $2d\mu z E \cos \theta$ (where $E$ and the polarization). This leads to a dielectric constant

$$
\varepsilon_s = \varepsilon_\infty + 4\pi \cos^2 \theta \frac{z^2 \mu^2}{kT} Nd,
$$

i.e. $\varepsilon_s - \varepsilon_\infty$ is $d$ times larger than for $N$ independent dipoles of strength $\mu$. Even for small single crystals $d$ is at least $10^3$. This clearly would lead to enormous values for the static dielectric constant.

In order to reach this equilibrium value the chains of some dipolar planes would be required to reverse the direction of their chain axis because they have to make the transition from the position shown in figure 3b (even) into 3a (odd). It is difficult to imagine that in the solid state such a transition is possible. It would, therefore, be expected that if a field is applied to a solid ketone of even chain length the equilibrium requiring a turning of dipolar planes cannot be reached and that such a ketone behaves like an odd ketone. If, on the other hand, it should be possible to bring a ketone into a state of polarization of the type discussed above, then one would expect this polarization to persist for a long time after removal of the external field. A possible way to reach this state might be to cool an even ketone in the presence of an electric field from a high temperature (liquid state) to a temperature below $T_0$.

**Phase transition of the second kind.** According to the discussion in §3 the substances will undergo phase transitions of the second kind at the temperature $T_0$ where the dipoles of a dipolar plane undergo an order-disorder transition. Such phase transitions are also to be expected in paraffins (Fröhlich 1944), and it would be of interest to compare the transition points of paraffins and ketones of the same chain length and with the same specific volume because this would allow conclusions to be drawn upon the influence of purely dipolar interaction. For the particular ketone whose dielectric behaviour was discussed above, $T_0$ is higher than the melting-point and thus cannot be observed directly. This may, however, be different for ketones of a different chain length.

From a discussion of the entropy change connected with the phase transition it was concluded that in paraffins the chains may be twisted at temperatures near and above $T_0$. This might also be so in the present case, and some modification of the theory might be required at temperatures near and above $T_0$. This modification should, however, be small if (i) the interaction $V$ (cf. eqn. (7)) does not depend on the state of twisting, e.g. if it is of dipolar nature only, and (ii) if the energy differences between the twisted states and the untwisted one do not depend on the direction of the dipole. From a comparison of our results with Muller's experiments it had already been concluded that condition (i) was fulfilled, and it may now be concluded that this also holds for condition (ii). It thus seems likely that the theory would require only minor modifications to account for the twisting of chains. It should be emphasized, however, that for molecules with more than one dipole—which are not considered in the present paper—the effect of twisting should be of major
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importance because it may affect the value of the total dipolar moment of such a molecule.

Comparison with the previous theory. The present theory holds for an isotropic crystalline material only. It can, therefore, not be considered as an extension of the theory developed previously (Fröhlich & Sack 1944), which can claim validity for isotropic crystals and for amorphous substances but only at temperatures $T > T_0$, that is, in the temperature region in which the dielectric constant decreases with $T$. There is, therefore, no theory, at present, which covers amorphous substances (e.g. plastics) at temperatures below $T_0$. It seems likely, however, that qualitatively the present results should apply to plastics as well. This means that the existence of a transition temperature $T_0$ may be expected below which the static dielectric constant increases, and above which it decreases with increasing temperature.

The local field. In the development of the theory of dipolar interaction, one of the main problems is to find the local field $f$ acting on an individual dipole. Energetically $f$ may be defined by equating $2f$ with the energy required to reverse the direction of a dipole. Lorentz suggested the expression

$$f = E + \frac{4\pi}{3} P,$$

where $P$ is the macroscopic polarization due to the macroscopic field $E$. This expression was widely used until Onsager (1936) showed that a part of the local field $f$ is due to the reaction field $R$ produced by the interaction of the dipole with its surroundings. Lorentz's expression is obtained if the local moment due to the dipole is replaced by the average macroscopic polarization which obviously is incorrect. Instead, Onsager suggests that the reaction field has always the same direction as the dipole. By reversing the direction of the dipole the reaction field would also reverse its direction and does thus not contribute to the energy required for this reversal. He thus finds (to simplify the following discussion it will be assumed that there are only dipolar contributions to the polarization)

$$f = \frac{3\varepsilon}{2\varepsilon + 1} E = E + \frac{4\pi P}{2\varepsilon + 1}.$$

It was shown in I that this would mean that the reaction field is free of inertia which is not the case. From I, § 6, it follows that for a given dipole direction the average value of the reaction field is $R_1/2$, where $R_1$ is the value which it would have if the dipole would never change its direction. Thus

$$f = E + \frac{4\pi P}{2\varepsilon + 1} + \frac{R_1}{2}.$$

There is a fundamental difference between this expression and both Onsager's and Lorentz's. They both vanish if the external field $E$ vanishes (since $4\pi P = (\varepsilon - 1) E$), while that given here becomes $R_1/2$. The present local field (cf. (9)) is of the same type, but the way to calculate $R_1$ and its influence upon the dipole differs. While in I it
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was treated as a perturbation it is of predominant influence in the present paper.*
Thus, in conclusion, it may be said that at low temperatures below the transition point \( T_0 \) the local field is nearly independent of an external field in contrast to temperatures above \( T_0 \). Sufficiently well above \( T_0 \) the \( R_1 \) terms become negligible and Onsager's field becomes correct. The Lorentz field, however, is in dipolar substances only correct when the temperature is so high that \( \epsilon - 1 \ll 1 \).

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*Addendum added 14 December 1945*

Dr V. Daniel (Electrical Research Association) kindly drew my attention to a numerical mistake in comparing the results of the theory with experiments by Muller. The number \( N \) of dipoles per c.c. is \( 2 \times 10^{21} \), and not \( 1 \times 10^{21} \) as stated. This means that Muller's experiments are not in agreement with (39). Agreement with (38) will be obtained, however, if

\[
\frac{4\pi \mu_0^2 N}{3 \ kT_0} = 3.5 \times 10^5
\]

because this leads to figure 6. Hence, using (2), \( T_0 = 340^\circ \), and the above value for \( N \), one finds \( \mu = 1.6 \times 10^{-18} \) e.s.u. instead of \( 2.1 \times 10^{-18} \) as stated before.

The disagreement of the experiments with eqn. (39) means that the interaction \( V \) should no longer be considered as of dipolar nature only, for this (cf. (37)) would lead to \( T_0 = 230^\circ \) instead of \( 340^\circ \). This is rather more satisfactory than the results obtained previously (\( V \) purely dipolar) since paraffins, although being non-polar, show a transition of the type discussed here.

Finally it should be emphasised that \( \mu \) is the average dipole moment in an equilibrium direction which in view of thermal oscillations and of chain twisting should be lower than the absolute dipole moment. Actually the value for the latter is usually given as \( 2.8 \times 10^{-18} \) e.s.u. This indicates appreciable chain twisting in agreement with the conclusions reached for paraffins (cf. Fröhlich 1944).

**References**


* The corresponding problem for liquids has been treated in an interesting paper by Kirkwood (1939).