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The Problem of Calculating the Internal Field in Polycrystalline Dipole Dielectrics in the Case of Relaxation Polarization

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A method is proposed for calculating the internal field for the case of relaxation polarization in dipolar polycrystalline dielectrics. The parameters characterizing the relaxation polarization are computed for the particular case of organic dipolar polycrystals.

IT is known that only in relatively rare cases (non-polar liquids, diatomic cubic crystals) can the acting (local) field in liquid and solid dielectrics be determined, in first approximation, by the well-known Lorentz equation

$$E = E_{\text{av}} + \frac{4\pi}{3} I, \tag{1}$$

where I is the electric moment per unit volume.

If the structure of the crystal is known, it is possible to find the internal field using the method of structural coefficients[1].

This article represents an effort to determine the internal-field coefficients for dielectrics of complex and unknown structure from experimental data on the relaxation polarization. Such a determination is of interest for two reasons. First, it permits greater precision in the evaluation of those parameters characteristic of relaxation polarization, which are of substantial significance in themselves (potential barrier that limits the motion of the relaxing dipole or ion group, or the natural frequencies of these groups). Second, it gives an idea of the behavior of the field acting in a polycrystalline dipolar dielectric, how it differs from the Lorentz field, and how it is related to the values of the dielectric constants at zero and infinite frequencies.

According to the Lorentz method, the acting field can be represented in the form of a sum:

$$E = E_{\text{av}} + \frac{4\pi}{3} I + E_{\text{add}} \tag{2}$$

where E_{add} is the additional field due to the particles within the Lorentz sphere. Using the method of structural coefficients[1] it is possible to represent the field acting on the ith particle as follows:

$$E_i = E_{\text{av}} + \frac{4\pi}{3} I + \sum_{k=1}^{m} \alpha_k C_{ik} E_k + \sum_{k=1}^{m'} \alpha'_k C'_{ik} E_k. \tag{3}$$

Here α_k is the relaxation polarizability of the kth dipole group (or of the group of weakly-coupled ions); α'_k is the elastic polarizability of the kth group of particles; C_{ik} are the structural coefficients, accounting for the dipole distribution in the lattice; C'_{ik} are the structural coefficients accounting for the elastically-bound particles in the lattice; m is the number of dipole groups differently distributed in the crystal cell; m' is the number of particle groups differently distributed in the crystal cell and having "elastic" polarization; E_k is the field acting on the kth particle located in the vicinity of the ith particle under consideration (i varies from 1 to m'; $m \geq m'$).

Assuming that all particles in the dielectric are under the influence of the same averaged local field, Eq. (3) can be written:

$$E = \frac{1}{m'} \sum_{i=1}^{m'} E_i = E_{\text{av}} + \frac{4\pi}{3} I + \frac{1}{m'} \sum_{i=1}^{m'} \sum_{k=1}^{m} \alpha_k C_{ik} E_k + \frac{1}{m'} \sum_{i=1}^{m'} \sum_{k=1}^{m'} \alpha'_k C'_{ik} E_k. \tag{4}$$

Since we do not know the structural coefficients (not knowing the lattice structure) let us

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[1] G. I. Skanavi, J. Exper. Theoret. Phys. 17, 399 (1947)

introduce the generalized coefficients β_1 and β_2 of the internal field:

$$E = E_{\text{av}} + \beta_1 I_{\text{rel}} + \beta_2 I_0, \tag{5}$$

where I_{rel} and I_0 are the electric moments per unit volume, due to the relaxation and to the displacement polarization respectively.

According to Eq. (4), the generalized coefficients can be expressed in terms of the structural coefficients

$$\beta_1 = \frac{4\pi}{3} + \frac{1}{m' I_{\text{rel}}} \sum_{i=1}^{m'} \sum_{k=1}^{m} \frac{C_{ik} I_{\text{rel}k}}{n_k}, \tag{6}$$

$$\beta_2 = \frac{4\pi}{3} + \frac{1}{m' I_0} \sum_{i=1}^{m'} \sum_{k=1}^{m'} \frac{C'_{ik} I_{0k}}{n_{0k}}. \tag{7}$$

Here $I_{\text{rel}k}$ and $I_{\text{o}k}$ are electric moments per unit volume, due respectively to the relaxation and displacement polarizations of the kth-group particles.

For the case of linear polarization considered in this article, the electric moment per unit volume is proportional to the acting field strength, and the coefficients β_1 and β_2 are therefore independent of the field.

According to Fröhlich[2], who generalized Kirkwood's equation for polar fluids to include the case of dipolar solids, the basic quantity characterizing the relaxation polarization in crystalline dipolar substances is not the individual dipole or group of dipoles, as in the case of dipolar liquids, but the individual crystalline cell, which has a certain effective dipole $\mathbf{m}_j$, depending on the orientations of the dipoles contained in the cell. This difference between crystalline dipolar substances and dipolar liquids is due to the difference in the construction of the crystal and the liquid.

In evaluating the interaction between dipoles, we shall assume, in agreement with Kirkwood and Fröhlich, that a sphere surrounding a given cell with a fixed dipole moment $\mathbf{m}_j$ has a dipole moment $\mathbf{m}_j^*$. In the first approximation, we shall characterize the relaxation polarization of the dipolar crystalline cells by a single potential barrier, and consequently, by a single relaxation time. This is permissible if the density with which which the values of relaxation time are grouped about the probable value is sufficiently high.

Assuming that each crystalline dipolar unit cell has only two equilibrium positions, corresponding to opposite directions of the electric moments, the equation for relaxation polarization[3] can be used in the following simple form:

$$\frac{d(\Delta N_j)}{dt}\frac{e^{U/kT}}{\nu} = -\Delta N_j\left(e^{\Delta U_j/kT} + e^{-\Delta U_j/kT}\right) + \frac{N_0}{6}\left(e^{\Delta U_j/kT} - e^{-\Delta U_j/kT}\right), \tag{8}$$

where ΔN_j is the increase per cm^3 in the number of crystalline cells (due to the superposition of the external field) having a dipole moment $\mathbf{m}_j$ directed along the field; N_0 is the total number of crystalline cells per cm^3 in the dielectric ν is the natural frequency of the effective dipole of the crystalline cell; U is the potential barrier restricting the orientation of the unit cell; and ΔU_j is the change in the potential barrier due to the external field.

For a given dipole direction in the unit cell, the dipole moment per unit volume produced by the relaxation polarization equals

$$I_{\text{relj}} = 2\Delta N_j \mathbf{m}_j. \tag{9}$$

Multiplying both halves of Eq. (8) by $2\mathbf{m}_j$ we obtain

$$\frac{e^{U/kT}}{\nu}\frac{dI_{\text{relj}}}{dt} = -I_{\text{relj}}\left(e^{\Delta U_j/kT} + e^{-\Delta U_j/kT}\right) + \frac{N_0 \mathbf{m}_j}{3}\left(e^{\Delta U_j/kT} - e^{-\Delta U_j/kT}\right).$$

If $\Delta U_j \ll kT$, we have

$$\tau\frac{d\, I_{\text{relj}}}{dt} = -\mathbf{I}_{\text{рел}\,j} + \frac{N_0}{3}\mathbf{m}_j\frac{\Delta U_j}{kT},$$

where

$$\tau = (1/2\,\nu)\, e^{U/kT}$$

Considering that the energy of a dipole unit cell is an external electric field is determined (because of the interaction between dipole cells) not by the dipole moment $\mathbf{m}_j$ of the cell itself, but by the dipole moment $\mathbf{m}_j^*$ of the sphere surrounding the given cell, and assuming the dipole moment of the cell itself to be fixed, we have

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[2] H. Fröhlich, Theory of Dielectrics: Dielectric Constant and Dielectric Loss, Oxford, 1949.

[3] G. I. Skanavi, Fisika Dielektrikov (Physics of Dielectrics), GITTL, 1949.

$$\Delta U_j = \mathbf{m}_j^* \cdot E$$

hence

$$\tau = \frac{dI_{\mathrm{relj}}}{dt} = -I_{\mathrm{relj}} + \frac{N_0}{3}\frac{\mathbf{m}_j \cdot \mathbf{m}^*_j}{kT}\,\mathrm{E}.$$

Averaging over all possible dipole orientations, taking into account the probability of finding the dipoles in a given configuration, and considering that the internal field has the same direction as $\mathbf{I}_{\mathrm{rel}}$ and $\mathbf{I}_0$ [see Eq.(5)], we obtain finally

$$\tau\frac{dI_{\mathrm{rel}}}{dt} = -I_{\mathrm{rel}} + BE, \tag{10}$$

where

$$\mathrm{B} = N_0\frac{\overline{(\mathbf{mm}^*)}}{3kT}.$$

Replacing E of Eq. (10) by its value in (5):

$$\tau(dI_{\mathrm{rel}}/dt) = -I_{\mathrm{rel}} + BE_{\mathrm{av}} + \beta_1 BI_{\text{рел}} + \beta_2 BI_0. \tag{11}$$

To solve (11) it is essential to express I_0 in terms of E_{av} and I_{rel}.
For the general case,

$$I_0 = \sum_{k=1}^{m'} I_{0k} = n_2\alpha_1 E_1 + n_2\alpha_2 E_2 + \dots + n_{m'}\alpha_{m'}E_{m'}.$$

Here $\alpha_1, \alpha_2 \dots \alpha_{m'}$ are the elastic polarizabilities. Introducing, as before, an averaged acting field

$$E = \frac{1}{m'}\sum_{i=1}^{m'} E_i,$$

we obtain

$$I_0 = \cdot E\left[n_1\alpha_1 m' E_1\left(\sum_{i=1}^{m'} E_i\right)^{-1} + n_2\alpha_2 m' E_2\left(\sum_{i=1}^{m'} E_i\right)^{-1} \dots + n_{m'}\alpha_{m'} m' E_{m'}\left(\sum_{i=1}^{m'} E_i\right)^{-1}\right] \tag{12}$$

The sum in the brackets can be replaced by the product of the equivalent quantities $n_{\mathrm{eq}}\alpha_{\mathrm{eq}}$,

$$I_0 = n_{\mathrm{eq}}\alpha_{\mathrm{eq}}E. \tag{13}$$

Using (5), (11), and (13), and making some simple transformations, we obtain a fundamental equation

$$\tau(dI_{\mathrm{rel}}/dt) = -I_{\mathrm{rel}}[1 - \beta_1 B(1+A)] + E_{\mathrm{av}}B(1+A). \tag{14}$$

Here

$$A = \beta_2 n_{\mathrm{eq}}\alpha_{\mathrm{eq}}/(1 - \beta_2 n_{\mathrm{eq}}\alpha_{\mathrm{eq}} \tag{15}$$

Solving Eq. (14) for the case of a static field, we obtain

$$I_{\mathrm{rel}} = \frac{B(1+A)}{\gamma}(1 - e^{-t\gamma/\tau})E_{\mathrm{av}}$$

where

$$\gamma = 1 - \beta_1 B(1+A), \tag{16}$$

and the quantity $\theta = \tau/\gamma$ is the time constant of the relaxation polarization.

If the external field is periodic and in its steady-state we obtain:

$$E_{\mathrm{av}} = E_m e^{i\omega t}, \quad I_{\mathrm{rel}} = I_m e^{i(\omega t - \delta)}.$$

For the case of linear polarization we have

$$\tau(dI_{\mathrm{rel}}/dt) = i\omega\tau I_{\mathrm{rel}} \tag{17}$$

Equating (17) and (14) and separating real and imaginary parts, we get

$$I^*_{\mathrm{rel}} = \frac{\gamma B(1+A)E_{\mathrm{av}}}{\gamma^2 + \omega^2\tau^2} - i\frac{B(1+A)\omega\tau E_{\mathrm{av}}}{\gamma^2 + \omega^2\tau^2}. \tag{18}$$

Using the relationships

$$\varepsilon^* = 1 + 4\pi I^*_{\mathrm{rel}}/E_{\mathrm{av}} \quad \text{and} \quad \varepsilon^* = \varepsilon' - i\varepsilon'',$$

where ϵ^* and I^* are the complex expressions for the dielectric constant and the total electric moment per unit volume respectively, and making use of Eq. (18), we obtain, after separating the real and imaginary parts of the expressions for ϵ' and ϵ'':

$$\varepsilon' = 1 + \frac{4\pi A}{\beta_2} + \frac{4\pi B(1+A)(1+(\beta_1/\beta_2)A)\gamma}{\gamma^2+\omega^2\tau^2}; \qquad (19)$$

$$\varepsilon'' = \frac{4\pi\omega\tau B(1+A)(1+(\beta_1/\beta_2)A)}{\gamma^2+\omega^2\tau^2} \qquad (20)$$

For $\omega \to \infty$ we have

$$\varepsilon_\infty = 1 + 4\pi A/\beta_2. \qquad (21)$$

For $\omega = 0$ we have

$$\varepsilon_0 = 1 + \frac{4\pi A}{\beta_2} + \frac{4\pi B(1+A)(1+(\beta_1/\beta_2)A)}{\gamma}. \qquad (22)$$

Using Eq. (21) and (22), as well as (19) and (20), we can express ϵ' and ϵ'' in terms of ϵ_0 and ϵ_∞ (the dielectric constants at zero and infinite frequency) *

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0-\varepsilon_\infty)\gamma^2}{\gamma^2+\omega^2\tau^2}, \qquad (23)$$

$$\varepsilon'' = \frac{(\varepsilon_0-\varepsilon_\infty)\omega\tau\gamma}{\gamma^2+\omega^2\tau^2}. \qquad (24)$$

It follows from Eqs. (23) and (24) that

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\omega\tau(\varepsilon_0-\varepsilon_\infty)\gamma}{\varepsilon_0\gamma^2+\varepsilon_\infty\omega^2\tau^2}$$

whenever the conductivity is low.

The frequency-temperature value at which tan δ is maximum can be obtained by differentiating tan δ with respect to $\omega\tau$ and setting the result equal to zero. This value is:

$$(\omega\tau)_m = \sqrt{\varepsilon_0/\varepsilon_\infty}\,\gamma.$$

Comparison of equations (19) and (20) with (23) and (24) yields

$$\varepsilon_0 - \varepsilon_\infty)\gamma = 4\pi B(1+A)[1+(\beta_1/\beta_2)A]. \qquad (25)$$

The relationship between the quantities β_1, β_2, γ, and B can be found by using Eqs. (16), (21), and (25). This relationship is of the form:

$$\beta_1 = \frac{4\pi(\varepsilon_0-\varepsilon_\infty)}{B(\varepsilon_0-1)[4\pi+(\varepsilon_\infty-1)\beta_2]} - \frac{4\pi}{\varepsilon_0-1}; \qquad (26)$$

$$\gamma = \frac{\beta_1(\varepsilon_\infty-1)+4\pi}{\beta_1(\varepsilon_0-1)+4\pi}. \qquad (27)$$

The unknowns in (26) and (27) are β_1, β_2, γ, and $B = N_0\,\overline{m\cdot m^*}/3kT$. . The value of B can be determined from Fröhlich's basic equation for the polarization of dipolar substances

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{9\varepsilon_0} = \frac{4\pi}{3}N_0\frac{\overline{m\cdot m^*}}{3kT}. \qquad (28)$$

Substituting the value of B obtained from (28), we get for (26):

$$\beta_1 = \frac{48\pi^2\varepsilon_0}{(\varepsilon_0-1)(2\varepsilon_0+\varepsilon_\infty)[4\pi+(\varepsilon_\infty-1)\beta_2]} - \frac{4\pi}{(\varepsilon_0-1)}. \qquad (29)$$

If the dielectric consists of a mixture of a polar polycrystalline compound and a non-polar filler, this will affect, to first approximation, only the value of B In this case B can be determined from Kirkwood's equation, obtained for the case of a mixture of a polar polymer with a non-polar one[4]. This equation has been generalized by us, in analogy with Fröhlich's equation, to read:

$$\frac{(\varepsilon_0-1)(2\varepsilon_0+1)}{9\varepsilon_0} - \frac{(\varepsilon_\infty-1)(2\varepsilon_\infty+1)}{9\varepsilon_\infty} = \frac{4\pi}{3}N_0\frac{\overline{m\cdot m^*}}{3kT}. \qquad (30)$$

In this case we obtain, instead of Eq. (29), the following expression:

$$\beta_1 = \frac{48\pi^2\varepsilon_0\varepsilon_\infty}{(2\varepsilon_0\varepsilon_\infty+1)(\varepsilon_0-1)[4\pi+\beta_2(\varepsilon_\infty-1)]} - \frac{4\pi}{(\varepsilon_0-1)}. \qquad (31)$$

If one of the three quantities β_1,β_2, or γ is known, Eqs. (27), (29), and(31) become the basic equations from which the other two quantities can be determined.

In the general case, the coefficient β_2 can be determined from Eqs. (15) and (21):

$$\beta_2 = \frac{1}{n_{eq}\,\alpha_{eq}} - \frac{4\pi}{\varepsilon_\infty-1}$$

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* If $\gamma = (\epsilon_\infty+2)/(\epsilon_0+2)$, Eqs. (23) and (24) reduce to the corresponding Debye equations. Substituting the value of B obtained from (28), we get for (26):

[4] J. Kirkwood and R. Fuoss, Journ. Chem. Phys. 9, 329 (1941)

If the fields E_i differ little from the averaged field E, Eq. (12) yields

$$n_{eq}\alpha_{eq} \approx \sum_{i=1}^{i=m'} n_i\alpha_i,$$

hence

$$\beta_2 = \left(\sum_{i=1}^{m'} n_i\alpha_i\right)^{-1} - 4\pi(\varepsilon_\infty - 1)^{-1}.$$

Consequently, if the concentration and polarizabilities of the elastically-polarized particles are known, the coefficient β_2 can be determined; then the coefficient β_1 and the parameter γ can be expressed in terms of ϵ_0 and ϵ_∞, i.e., the stated problem can be solved. On the other hand, if the composition of the dielectric is complicated and unknown, the coefficient β_2 cannot be calculated with sufficient accuracy, and an expression for the internal-field coefficients in terms of ϵ_0 and ϵ_∞ can be derived only for special cases.

For the special case of dielectrics that contain no ions (for example, organic substances), i.e., dielectrics having only electron-displacement polarization at $\omega \to \infty$, it is possible to assume

$$\beta_2 = 4\pi/3.$$

In fact it follows from Eq. (4) that

$$E = E_{av} + \frac{4\pi}{3} I_{rel} + \frac{4\pi}{3} I_0 + E'_{add} + E''_{add}$$

where

$$E'_{add} = \frac{1}{m'} \sum_{i=1}^{m'} \sum_{k=1}^{m} \alpha_k C_{ik} E_i,$$

$$E''_{add} = \frac{1}{m'} \sum_{i=1}^{m'} \sum_{k=1}^{m'} \alpha'_k C'_{ik} E_i.$$

If $\omega \to \infty$

$$E = E_{av} + \frac{4\pi}{3} I_0 + E''_{add}$$

It can be shown[3] that a dielectric having polarization of the electron-displacement type, and having a low refractive index, obeys the Clausius-Mossotti equation. It is therefore possible to assume for this case

$$E''_{add} \approx 0,$$

i.e., the electron polarization does not contribute to E_{add}, and consequently it follows from (7) that $\beta_2 = 4\pi/3$. In addition, if ϵ_∞ has the usual range (2-4), then

$$\sum_{i=1}^{m'} n_i\alpha_i = \frac{3(\varepsilon_\infty - 1)}{4\pi(\varepsilon_\infty + 2)} \sim 0.1,$$

corresponding to $n \sim 10^{22}$ cm^{-3} and $\alpha \sim 10^{-23}$ cm^3, which are of the correct order of magnitude (the electron polarizability of a molecule of solid dielectric equals approximately the cube of the molecular radius[3]). Using this approximation ($\beta_2 = 4\pi/3$), we obtain the following expressions instead of (29) and (23):

$$\beta_1 = \frac{4\pi[9\varepsilon_0 - (\varepsilon_\infty + 2)(2\varepsilon_0 + \varepsilon_\infty)]}{(2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_\infty + 2)(\varepsilon_0 - 1)}, \tag{32}$$

$$\beta_1 = \frac{4\pi[9\varepsilon_0\varepsilon_\infty - (2\varepsilon_0\varepsilon_\infty + 1)(\varepsilon_\infty + 2)]}{(2\varepsilon_0\varepsilon_\infty + 1)(\varepsilon_\infty + 2)(\varepsilon_0 - 1)}, \tag{33}$$

These permit determining β_1 and γ [from Eq. (27)], provided ϵ_0 and ϵ_∞ are known. Obviously $\beta_1 \neq 4\pi/3$ and $\gamma \neq (\epsilon_\infty + 2)/(\epsilon_0 + 2)$, and the resultant equations differ considerably from the known Debye equations.

Equations (32) and (33) make it possible to study the variation of β_1 with ϵ_0 and ϵ_∞. It follows from (32) that $\beta_1 = 0$ whenever

$$\varepsilon_0 = \varepsilon_\infty(\varepsilon_\infty + 2)/(5 - 2\varepsilon_\infty). \tag{34}$$

This condition can be satisfied if ϵ_∞ varies between 1 and 2.5 (ϵ_0 varies accordingly between 1 and ∞). As ϵ_0 varies within this range, the sign of β_1 depends on the value of ϵ_0: if $\epsilon_0 > \epsilon_\infty > (\epsilon_\infty + 2)/(5-2\epsilon_\infty)$, then $\beta_1 > 0$; otherwise $\beta_1 < 0$. On the other hand, if $\epsilon_\infty \geqslant 2.5$, then $\beta_1 \leqslant 0$ always (Fig. 1). Equation (32) can be represented graphically by a family of curves $\beta_1 = \phi(\epsilon_0)$ for various values of the parameter ϵ_∞. Fig. 2 shows such curves for ϵ_∞ = 2,3, and 4. It can be seen from Fig. 2 that if $\epsilon_\infty \geqslant 2.5$ the absolute magnitude of β_1 diminishes as ϵ_0 increases, and that it passes through its maximum when $\epsilon_\infty < 2.5$.

If a polycrystalline dipolar dielectric having only electron and dipolar polarizations satisfies Eq. (34), the average field acting on it can be shown to equal

$$E = E_{av} + \frac{4\pi}{3} I_0, \tag{35}$$

the presence of relaxation polarization notwithstanding. Such dielectrics obey the following simple relationship between ϵ_0 and ϵ_∞:

$$\frac{\varepsilon_0 - 1}{\varepsilon_\infty + 2} = \frac{4\pi}{3}\left[\sum_{i=1}^{m'} n_i \alpha_i + N_0 \alpha_{\mathrm{rel}}\right],$$

where $\alpha_{\mathrm{rel}} = \overline{\mathrm{m}\cdot\mathrm{m}^*}/3kT$ is the relaxation polarizability of a single crystal cell. In these cases the parameter γ becomes unity [see Eq. (27)] and the calculation of the characteristics of the relaxation polarization is considerably simplified 5 .

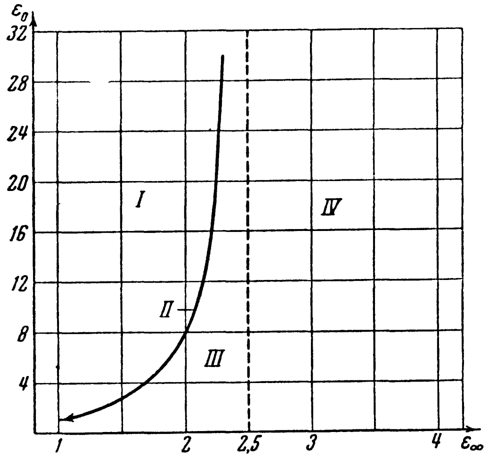

Fig. 1. Graphic representation of Eq. (34): I–domain values of ϵ_0 and ϵ_∞ for which $\beta_1 > 0$; III and IV–$\beta_1 < 0$; curve II corresponds to the condition $\beta_1 = 0$.

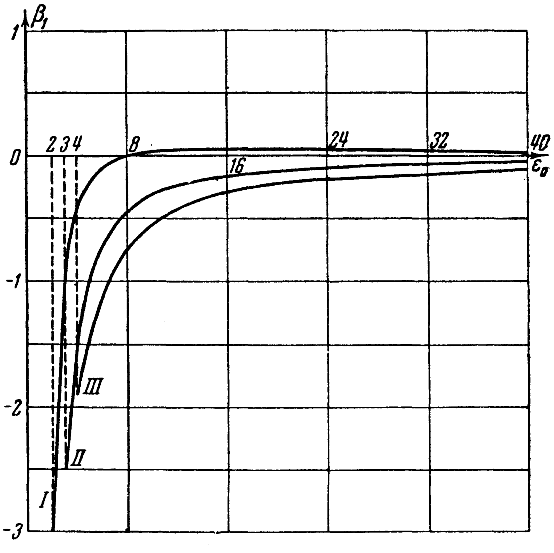

Fig. 2. Variation of β_1 with ϵ_0 for various constant values of ϵ_∞ [Eq. (32)] ; I–ϵ_∞=2; II–ϵ_∞=3; III–ϵ_∞=4.

Equation (33) permits analogous calculation of the coefficient β_1 for a mixture of polar and non-polar substances. Computations show that the coefficient β_1 can vanish also in this case; β_1 is always negative when $\epsilon_\infty \gg 2.5$, and decreases in absolute magnitude with increasing ϵ_0 for a given value of $\epsilon_\infty \gg 2.5$.

If ϵ_0 is sufficiently large, β_1 may become a very small quantity; this holds for both pure dipolar polycrystals [Eq. (32)] and a mixture of polar and non-polar substances [Eq. (33)] . Thus,for example, if $\epsilon_\infty = 3$ and $\epsilon_0 = 100$, a value $\beta_1 = -0.01$ is obtained from both equations (32) and (33). The negative sign of the coefficient β_1 indicates that the relaxation polarization reduces the acting field.

Knowing the coefficients β_1 and β_2 of the internal field, it is possible to determine from Eq. (5) the extent to which the acting field deviates from the acting macroscopic one. In fact, assuming as before $\beta_2 = 4\pi/3$, and using

$$I_0 = \frac{\varepsilon_\infty - 1}{4\pi} E_{\mathrm{av}} \quad \text{and} \quad I_{\mathrm{rel}} = \frac{\varepsilon' - \varepsilon_\infty}{4\pi} E_{\mathrm{av}},$$

where ϵ' is the dielectric constant for a given frequency ω, it is easy to obtain an expression for the acting field in terms of its average macroscopic value:

$$E = \left[\frac{(\varepsilon_\infty + 2)}{3} + \beta_1 \frac{(\varepsilon' - \varepsilon_\infty)}{4\pi}\right] E_{\mathrm{av}}. \tag{36}$$

Evidently this expression differs from the corresponding expression for the case when the internal field equals the Lorentz field:

$$E = \frac{\varepsilon' + 2}{3} E_{\mathrm{av}}. \tag{37}$$

If $\epsilon_\infty = 3$, $\epsilon' = 15$, and $\beta_1 = -0.1$, Eq. (35) yields $E = 1.6E_{\mathrm{av}}$, while Eq. (37) yields $E = 6E_{\mathrm{av}}$ for the same case. On the other hand, if $\beta_1 = 0$ [see condition (34)], we obtain $E = [\,(\epsilon_\infty + 2)/3\,]\,E_{\mathrm{av}}$, which corresponds to the acting field (35).

Thus,in the case of a clearly pronounced relaxation polarization, the acting field differs much less from the average macroscopic field than from the acting Lorentz field.

Table 1 lists the values of coefficient β_1 and parameter γ computed in the manner given above for oleo-waxes of various degrees of plasticity, using data from our previous work [5].

In the case of oleo-wax compound 1, which contained the minimum amount of the amorphous phase, the coefficient β_1 was computed from Eq. (32). Equation (33) was used for compounds 2,3

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[5] G. I. Skanavi and A. N. Gubkin, J. Exper. Theoret. Phys. USSR **27**, 742 (1954)

Table 1

Hydrogenized castor oils (oleo-waxes)	Experimental data[5]			19°C			45°C		
				β_1,	γ		β_1,	γ	
	ϵ_∞	ϵ_o at 19°C	ϵ_o at 45°C	Eq. (32) for Comp.#1 Eq. (33) for Comp. #2,3,4.	$\frac{\epsilon_\infty+2}{\epsilon_o+2}$	Eq. (27)	Eq. (32) for Comp.#1 Eq. (33) for Comp. #2,3,4.	$\frac{\epsilon_\infty+2}{\epsilon_o+2}$	Eq. (27)
Compound 1	3.4	21.8	25.2	-0.14	0.23	1.27	-0.12	0.20	1.26
" 2	3.2	13.3	14.1	-0.15	0.34	1.14	-0.13	0.32	1.13
" 3	3.2	11.9	13.0	-0.17	0.37	1.13	-0.15	0.35	1.14
" 4	3.8	5.5	5.5	-0.68	0.77	1.12	-0.68	0.77	1.12

Table 2

Hydrogenized castor oils (oleo-waxes)	Frequency corresponding to maximum tan δ		Relaxation time $10^6.\tau$ sec.		Activation energy, U. eV	Natural frequency sec^{-1}
	19°C	45°C	19°C	45°C		
Compound 1	25 100	91 200	2.0	0.6	0.38	0.8×10^{11}
" 2	19 950	50 120	1.9	0.8	0.28	1.7×10^9
" 3	19 950	50 120	1.7	0.7	0.26	1.0×10^9
" 4	12 590	22 390	1.7	1.0	0.18	3.4×10^7

and 4, which contained some amount of amorphous non-polar filling. For the sake of comparison, the table contains the values of the coefficient $\gamma = (\epsilon_\infty + 2)/(\epsilon_o + 2)$.

It is evident from table 1 that the coefficients β_1 and γ, obtained with the above method from experimental values of ϵ_∞ and ϵ_o, differ sharply from the values $\beta_1 = 4\pi/3$ and $\gamma = (\epsilon_\infty + 2)/(\epsilon_o + 2)$, used in the theory of relaxation polarization and based on the use of a Lorentz acting field.

Once the coefficient β_1 is determined, the general equations for computing the characteristics of relaxation polarization[5] can be used to find the activation energy, the relaxation time, and the natural frequency of the dipolar unit cell. Such computations were made for the four oleo-wax compounds at two temperatures (Table 2).

It can be seen from Table 2 that the relaxation time is of the order of 10^{-5} seconds for oleo-waxes of various degrees of plasticity, and hardly changes with the composition of the substance. On the other hand, calculations in which the internal field was assumed not to differ from the Lorentz field[5] show a gradual increase of τ with the plasticity of the compound. The activation energy decreases as the plasticity of the compound increases. In all but compound 4 the activation energy obtained is somewhat lower than the value obtained by previous computations[5]. As the plasticity of the compound increases, the natural frequency of the dipolar unit cell drops from a value on the order of 10^{11} to values on the order of 10^7 sec^{-1}. Compared with the natural frequency computed in reference[5], the results obtained by the method given here are lower by approximately a factor of ten.

The method given in refernce[5] for computing the increase in the relaxation time does not involve the internal field. The method is thus applicable also to the present case. On the other hand, application of the theory of absolute reaction rates (see[5]) gives results that differ somewhat from those obtained when the Lorentz field is used, inasmuch as the use of a different internal field causes that theory to be premised on different

Table 3

Hydrogenized castor oils (oleo-waxes)	T, °K	Relaxation time, $\tau.10^5$ seconds	ΔF, kgm-calories	ΔS cal/deg	ΔH, kgm-calories
Compound 1	292	2.0	10.8	-9.9	7.9
	318	0.6	11.0	-9.8	
Compound 2	292	1.9	10.8	-17.8	5.6
	318	0.8	11.2	-17.6	
Compound 3	292	1.7	10.7	-17.1	5.7
	318	0.7	11.1	-17.0	
Compound 4	292	1.7	10.7	-25.7	3.2
	318	1.0	11.4	-25.8	

values of relaxation time τ.

Table 3 lists the values of the difference in heat content, difference in entropy, and difference in free energy for an internal field differing from the Lorentz field. It can be seen from Table 3 that the absolute magnitudes of the activation entropy are higher than those obtained in reference[5]. This can most probably be explained by the fact that the present work accounts more fully for the interaction between the dipole groups.

The method presented above for determining the internal-field coefficients can also be used for liquid dipolar dielectrics. It would then be necessary to consider the polar liquid molecule instead of the dipolar cell of the crystal.

$$\mathbf{m} = \vec{\mu}, \quad \mathbf{m}^* = \vec{\mu}^*,$$

where $\vec{\mu}$ is the dipole moment of the molecule, and $\vec{\mu}^*$ is the dipole moment of the sphere surrounding a given molecule, provided its dipole moment has a fixed direction; since all dipole directions are equivalent in a liquid, we have $\overline{\mathrm{m}\cdot\mathrm{m}}=\vec{\mu}\vec{\mu}^*$.

In this case, Fröhlich's general equation (28) reduces to Kirkwood's equation for polar liquids (see[2])

$$\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{9\varepsilon_0} = \frac{4\pi}{3} N_0 \frac{\vec{\mu}\cdot\vec{\mu}^*}{3kT},$$

where N_0 is the number of dipoles per cm^3, and the quantity B entering into the relaxation equations equals

$$B = N_0 \frac{\vec{\mu}\cdot\vec{\mu}^*}{3kT}.$$

Taking the above into account, it is possible to derive analogously Eqs. (29) and (31), which will then be valid also for liquid dielectrics.

Translated by J. G. Adashko
11