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### MODERN THEORIES OF DIPOLE POLARIZATION OF CONDENSED MOLECULAR SYSTEMS

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#### 1. INTRODUCTION

INVESTIGATION of dielectric properties of molecular systems enables one to study the structure and the physical properties of these systems, since modern theories of polarization of dielectrics relate the fundamental parameters of the dielectric to quantities which characterize the intermolecular interaction.

In addition to the theories of polarization due to Onsager and Kirkwood new theoretical papers have appeared in recent years in the field of polarization of dielectrics. The principal ones among them are the theories of Fröhlich, Harris, Alder, and Buckingham which have attracted the attention of both theoreticians and experimentalists working in this field. An examination of these theories shows that they lead to different expressions relating the macroscopic and the microscopic parameters of a dielectric. It is therefore of interest to analyze the reasons for such differences and to determine which of the theories can be applied to provide the most rigorous approach to the interpretation of experimental results.

#### 2. ONSAGER'S MODEL THEORY

As is well known, the first equation for the polarization in the case of a polar system, which was proposed by Debye on the basis of the formula for the internal Lorentz field, has the following form

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4}{3} \pi N_0 \left( \alpha + \frac{\mu_0^2}{3kT} \right), \quad (1)$$

where  $\epsilon$  is the dielectric permittivity,  $\mu_0$  is the constant dipole moment of a free molecule,  $\alpha$  is the deformation polarizability, and  $N_0$  is the number of molecules per unit volume. This expression for the internal field is obtained if we assume that the centers of the molecules surrounding the given molecule are distributed completely at random, and that their orien-

tations are not correlated with the orientation of the molecule under consideration. In this case the short-range order is taken into account neither in the positions nor in the orientations of the molecules; only the polarization of the medium outside the macroscopic sphere at the center of which the given molecule is situated is taken into account. As has been demonstrated by Böttcher<sup>1</sup> and by Fröhlich<sup>2</sup> the Lorentz field represents the value of the internal field averaged over the total volume. Therefore, the use of the internal Lorentz field and consequently also of formula (1) for the study of polar dielectrics is possible only in the one case when the polarization of a polar gas is considered at low pressures and the intermolecular interaction is neglected.

Debye attempted to introduce a correction to the theory of polarization of polar gases in extending this theory to the case of polarization of polar liquids. The new Debye theory is based on the assumption that at each point inside the liquid there exists a field which tends to orient the molecule and which is due to the interaction between the molecules. However, Debye did not obtain a satisfactory expression for the magnitude of the internal field. A criticism of the new Debye theory is given in detail in the papers of Ansel'm.<sup>3,4</sup>

The most successful solution of the problem of the internal field in a liquid polar dielectric and of the interaction of a polar molecule with its surroundings has been given by Onsager.<sup>5</sup> Onsager's theory is a model theory since it is based on a particular model of a molecule. Onsager starts with the assumption that a molecule in a polar liquid is represented by a hollow sphere of radius  $a$  at the center of which there exists a point dipole. The dipole moment of such a molecule is given by

$$\mathbf{m} = \mu_0 + \alpha \mathbf{E}_{in}, \quad (2)$$

where  $E_{in}$  is the internal field acting on the molecule.

The molecule is situated in a continuous medium of dielectric permittivity  $\epsilon$ . In accordance with this model the field acting on the given molecule is composed of two parts:

$$E_{in} = G + R, \quad (3)$$

where  $G$  is the cavity field,  $R$  is the reactive field. The dependence of  $R$  and  $G$  on  $m$ ,  $a$  and  $\epsilon$  is calculated by means of the Laplace equation for the potential due to a dipole:

$$R = \frac{2(\epsilon-1)}{2\epsilon+1} \frac{m}{a^3} = f m, \quad f = \frac{2(\epsilon-1)}{2\epsilon+1} \frac{1}{a^3}, \quad (4)$$

$$G = \frac{3\epsilon}{2\epsilon+1} E_{med}. \quad (5)$$

From this it follows that the intensity of the internal field is given according to Onsager by

$$E_{in} = G + R = \frac{3\epsilon}{2\epsilon+1} E_{med} + \frac{m}{a^3} \frac{2(\epsilon-1)}{2\epsilon+1}. \quad (6)$$

By utilizing Onsager's internal field we can determine the effect of the medium surrounding a given molecule on the magnitude of its dipole moment.

The dipole moment of a molecule in the condensed state differs from the dipole moment of a free molecule because an additional dipole moment is induced, since the molecule is acted upon by a field produced by the neighboring molecules surrounding it. In the general case the magnitude of the dipole moment in the medium is given by the following formula

$$\mu = \mu_0 + \frac{N \int \alpha_2 E(r, \omega) e^{-\frac{W}{kT}} dr d\omega}{\int e^{-\frac{W}{kT}} dr d\omega}, \quad (7)$$

where  $E(r, \omega)$  is the field acting on the given particle due to the other molecules in a given configuration;  $W$  specifies the energy of the intermolecular interaction.

It is clear that if we do not know the structure of the material it is impossible to determine the quantities  $E(r, \omega)$  and  $W$  in order to evaluate exactly the value of  $\mu$ . Therefore, the only alternative is an approximate calculation making use of models.

On the basis of Onsager's model we can obtain the following expression for the dipole moment

$$m = \frac{n^2+2}{3} \frac{2\epsilon+1}{2\epsilon+n^2} \mu_0 + \frac{\epsilon(n^2-1)}{2\epsilon+n^2} a^3 E_{med} = \mu + \frac{\epsilon(n^2-1)}{2\epsilon+n^2} a^3 E_{med}. \quad (8)$$

In this case

$$\mu = \frac{n^2+2}{3} \frac{2\epsilon+1}{2\epsilon+n^2} \mu_0 \quad (9)$$

according to Onsager gives the dipole moment of the molecule in the medium. It will be shown later that in modern statistical theories of polarization it is necessary to evaluate the quantity  $\mu$ , the dipole moment in the condensed phase.

The general equation obtained by Onsager has the following form

$$\frac{(e-n^2)(2\epsilon+n^2)}{\epsilon(n^2+2)^2} = 4\pi N_0 \frac{\mu_0^2}{9kT}, \quad (10)$$

where  $n$  is the optical index of refraction.

Onsager's theory is the first approximation to the solution of the problem of the polarization of polar dielectrics. The simple relationship, which has been derived by Onsager, between the microscopic parameters of the dielectric and the macroscopic quantities allows a direct comparison of experimental and calculated quantities. Therefore, in spite of the simplified model adopted by Onsager the theory proposed by him has been widely used. Model concepts have been greatly developed in the papers of Böttcher,<sup>6,7</sup> in which a detailed analysis may be found of such concepts as internal, orienting and reactive fields. Böttcher<sup>8</sup> finds it useful to apply the internal field obtained from model considerations to nonpolar dielectrics in order to introduce a correction to the Clausius-Mossotti equation. One finds in recent literature a number of papers which develop individual points of Onsager's theory. Thus, Wilson<sup>9</sup> has taken into account the anisotropy of the polarizability of the molecule. Calculations for the internal field of a particle in the shape of a spheroid and an ellipsoid have been carried out by Schelte,<sup>10</sup> Abbot and Bolton,<sup>11</sup> and Buckingham.<sup>12</sup> Frood and Dekker<sup>13</sup> have derived Onsager's formula for the case when instead of a point dipole a dipole of moment  $\mu_0$  is used consisting of two charges  $+q$  and  $-q$  separated by a distance  $d$ .

The main deficiencies of Onsager's theory are that his model cannot yield an exact estimate of the reactive field and take into account the intermolecular interaction.

The reactive field is a result of the polarization of molecules surrounding the central dipole. Therefore, the value of the reactive field evaluated on the basis of a continuous medium will differ from that in the case of a discrete medium. It is very difficult to evaluate the magnitude, and in many substances even the sign, of the error which is introduced in the evaluation of the reactive field with the aid of Onsager's model of the molecule. By treating the medium surrounding the given molecule as continuous and having a macroscopic dielectric permittivity  $\epsilon$ , Onsager does not take into account the interaction between the molecule and its nearest neighbors. Onsager does not take into consideration even the electrostatic interaction between the nearest dipoles and, moreover, does not take into account the nondipolar molecular interaction which can be quite significant in a number of liquids. Therefore, the greatest discrepancies between the experimental data and the calculations in accordance with Onsager's formula are observed for those substances in which there exists a strong intermolecular interaction.

Thus, further development of the theory of polarization depends upon a more rigorous method of taking

into account the intermolecular interaction, and this is possible only by utilizing statistical methods.

### 3. STATISTICAL THEORIES OF POLARIZATION

#### a. Kirkwood's Theory

The first statistical theory of polarization which took into account the interaction between nearest dipoles was Kirkwood's theory.<sup>14</sup> Kirkwood gave a general method of solving the problem which had an influence on all the subsequent theories. Therefore, in spite of the fact that Kirkwood evaluated the deformation polarization, incorrectly, we must examine it in greater detail.

Kirkwood considers a spherical region of the dielectric B of radius  $r_0$ , which is sufficiently large in comparison with molecular dimensions. The sphere B is a part of the spherical sample A which is situated in a vacuum. The radius of this sphere A is  $R \gg r_0$ , and, therefore, the dielectric medium outside the sphere B can be regarded as continuous with a dielectric permittivity  $\epsilon$ .

Kirkwood considers the average component of the dipole moment of the molecule in the field  $E_{in}$

$$\bar{m}_E = \bar{\mu}_E + \alpha E_{in}, \quad (11)$$

where  $E_{in}$  is the field acting on a molecule of the dielectric substance,  $\bar{\mu}_E$  is the average component of the dipole moment of the molecule in the direction of the field. In Kirkwood's theory the quantity  $\bar{\mu}_E$  differs from the component  $\mu_{0E}$  of the characteristic dipole moment along the direction of the field E since the particles surrounding the given polar molecule hinder its rotation. Thus, the determination of  $\bar{\mu}_E$  is associated with taking the intermolecular interaction into account. In order to calculate the average component of the dipole moment it is necessary to know the total energy of the sphere in the electric field. This total comprises the potential energy  $ME_0$  of this sphere placed in the electric field, and the energy of the intermolecular forces  $U_N$ , which takes into account all forms of interaction between the molecules (dipolar, multipolar interactions, van der Waals forces, etc.) Therefore, the average component of the dipole moment of the molecule  $\bar{\mu}_E$  along the direction of the field is given by Gibb's formula

$$\bar{\mu}_E = \frac{\int \dots \int \mu_{iE} e^{-\frac{U_N - (ME_0)}{kT}} d\tau_1 \dots d\tau_n}{\int \dots \int e^{-\frac{U_N - (ME_0)}{kT}} d\tau_1 \dots d\tau_n}, \quad (12)$$

where  $d\tau$  is the element of configuration space which characterizes the position and the orientation of the molecule. By expanding the integrand in powers of  $E_0$  and by restricting ourselves to the first order terms we can obtain:

$$\bar{\mu}_{iE} = \frac{E_0}{3kT} \mu_i \bar{M}_i = \frac{\epsilon + 2}{9kT} \mu_i \bar{M}_i E_{med}, \quad (13)$$

where  $E_{med}$  is the intensity of the average macroscopic field with the spherical dielectric,  $\mu_i$  is the dipole moment of the molecule. The quantity  $\bar{M}_i$  is determined by the formula

$$\bar{M}_i = \frac{\int \dots \int M_i e^{-\frac{U_N}{kT}} d\tau_1 \dots d\tau_n}{\int \dots \int e^{-\frac{U_N}{kT}} d\tau_1 \dots d\tau_n} \quad (14)$$

and represents the average value of the electric moment of the whole dielectric if the position of one of its molecules is fixed. Since all the molecules are identical, the suffix i may be omitted from now on. The main problem is the determination of the quantity  $\bar{M}$ , which can be related to the moment of the spherical dielectric B of radius  $r_0$  picked out within the region A. The moment  $\bar{M}$  is defined by the equation

$$\bar{M} = M_B(R, r_0) + \int P dV, \quad (15)$$

where  $M_B(R, r_0)$  is the magnitude of the electric moment of the sphere B, and the second term represents the polarization of the medium situated outside the sphere B.

For  $R \rightarrow \infty$  we have:

$$\bar{M} = \frac{3}{\epsilon + 2} \frac{3\epsilon}{2\epsilon + 1} M_B. \quad (16)$$

Thus, we obtain

$$\bar{\mu}_E = \frac{\mu M_B \epsilon}{(2\epsilon + 1) kT} E_{med}. \quad (17)$$

Since

$$m_E = \frac{\mu M_B \epsilon E_{med}}{(2\epsilon + 1) kT} + \alpha E_{in} \quad (18)$$

and

$$P = mN_0, \quad E_{med} = \frac{4\pi P}{\epsilon - 1},$$

then we have

$$\epsilon - 1 = \frac{4\pi\epsilon}{2\epsilon + 1} \frac{\mu M_B}{kT} + 4\pi\alpha N \frac{E_{in}}{E_{med}}. \quad (19)$$

Equation (19) is exact since it was derived without making any simplifying assumptions. However, in this form it cannot be utilized for the study of the polarization of a polar dielectric, since we have not defined such quantities as  $M_B$  and the internal field within the dielectric  $E_{in}$ .

Let us investigate what is represented by the quantity  $M_B$  in Kirkwood's theory. By definition  $M_B$  is the moment of the spherical region B if the position of one of its molecules is fixed, i.e., this quantity is equal to the sum of the moments of the fixed molecule and of the surrounding molecules

$$M_B = \mu + \mu N \int \cos \gamma p(r, \omega) dr d\omega, \quad (20)$$

$\gamma$  is the angle between the direction of the dipole moment of a representative molecule and the direction of

the dipole moment of the given fixed molecule, and  $p(r, \omega)$  is the probability of having this position and orientation.

If there is no interaction between the molecules, the second term in this formula is equal to zero, for owing to the random nature of the thermal motion the moments of neighboring molecules will cancel out in the absence of some sort of preferential orientation of the molecules. In this case  $M_B = \mu$ . If a strong intermolecular interaction exists between the given molecule and the surrounding particles, then the orientation of the molecule under consideration is related to the orientation of the other molecules and  $M_B \neq \mu$ . By taking into account the interaction between nearest neighbors only, Eq. (19) can be simplified as follows:

$$M_B = \mu(1 + z \overline{\cos \gamma}), \quad (21)$$

where  $z$  is the average number of nearest neighbors of the given molecule, and  $\overline{\cos \gamma}$  is the average value of the cosine of the angle between the directions of the axes of the given molecule and of one of its  $z$  neighbors.

From this it follows that

$$\mu M_B = \mu^2(1 + z \overline{\cos \gamma}) = \mu^2 g, \quad (22)$$

where  $g$  is a quantity which is constant for a given liquid and which characterizes the intermolecular interaction and the short range structure.

The second term in Kirkwood's equation is associated with the evaluation of the internal field  $E_{in}$ . The solution of this problem is the weakest point of Kirkwood's theory. Kirkwood identifies the field  $E_{in}$  with Onsager's cavity field, i.e., he assumes that

$$E_{in} = G = \frac{3\epsilon}{2\epsilon+1} E_{med}. \quad (23)$$

In this connection Frenkel' and Gubanov<sup>15</sup> have pointed out that such an assumption is without sufficient foundation. The identification of  $E_{in}$  with Onsager's cavity field means essentially that the reactive field is not taken into account. In its final form the equation obtained by Kirkwood has the following form

$$\epsilon - 1 = \frac{9\epsilon}{2\epsilon+1} \frac{4\pi N_0}{3} \left( \alpha + \frac{\mu^2 g}{3kT} \right). \quad (24)$$

Kirkwood's theory shows that the utilization of statistical mechanics enables us to abandon the simplified models and to determine the effect of the intermolecular interaction on the dielectric properties of a polar liquid. However, the approximations which were introduced in the evaluation of the internal field make Kirkwood's theory insufficiently accurate. Therefore, in the most recent theories of polarization due to Fröhlich and to Harris and Alder an attempt was made to make this point more precise. The most general of these theories is Fröhlich's theory.

## b. Fröhlich's theory

Fröhlich<sup>16,17</sup> considers an infinite homogeneous region within a dielectric. Within this region he picks out a macroscopic volume  $V$  sufficiently large to have the same macroscopic properties as the whole dielectric under consideration. We evaluate the component of the average electric moment of the sphere within the dielectric parallel to the direction of the macroscopic field. Outside the sphere the dielectric may be regarded as a continuous medium of dielectric permittivity  $\epsilon$ . It is also assumed that the electric field is sufficiently small to avoid saturation.

The spherical region consists of a number of elementary charges  $e_i$ , which are displaced by specified distances from their equilibrium positions. The displacement is characterized by the vector  $r_i$ . The displacement of all the charges is characterized by the quantity

$$X(r_1 r_2 \dots r_i).$$

Owing to fluctuations, there exists the probability

$$\frac{e^{-\frac{U(X, E)}{kT}} dX}{\int e^{-\frac{U(X, E)}{kT}} dX}$$

that the whole system will have a displacement lying in the interval between  $X(r_1, r_2 \dots r_i)$  and  $X+dX(r_1 + dr_1 \dots r_i + dr_i)$ . Here  $U(X, E)$  is the potential energy of the system and characterizes the configuration when the electric field  $E$  is applied. The existence of the displacement  $X$  leads to the appearance of the electric moment  $M(X) = \sum e_i r_i$ . The average component of the electric moment  $M(X)$  parallel to the direction of the field is defined in the following manner:

$$M_E = \frac{\int M(X) \cos \theta e^{-\frac{U(X, E)}{kT}} dX}{\int e^{-\frac{U(X, E)}{kT}} dX}, \quad (25)$$

where  $\theta$  is the angle between  $M(X)$  and the direction of the field  $E$ .

When the dielectric is placed in the electric field the probability of the given configuration  $X$  is altered. Moreover, this leads to the appearance of a homogeneous field  $G$  (the cavity field) within the spherical cavity. The potential energy of the dielectric in the field  $G$  is given by

$$-M(X)G = -\frac{3\epsilon}{2\epsilon+1} EM(X) \cos \theta,$$

i.e., the total energy is

$$U(X, E) = U(X) - \frac{3\epsilon}{2\epsilon+1} EM(X) \cos \theta. \quad (26)$$

This value of the energy can be utilized for the evaluation of  $M_E$ . Since we are considering regions far from saturation then in the expansion in powers of  $E$

$$e^{-\frac{U(X,E)}{kT}} = e^{-\frac{U(X)}{kT}} \left( 1 + \frac{3}{2\epsilon+1} \frac{M(X)E}{kT} \cos\theta + \dots \right) \quad (27)$$

we can neglect the higher-order terms

$$\int M(X) \cos\theta e^{-\frac{U(X)}{kT}} dX = 0, \quad (28)$$

since this integral is proportional to the average moment parallel to  $E$  in the absence of the field. In final form we obtain:

$$M_E = \frac{3\epsilon}{2\epsilon+1} \frac{EI}{kT} \int M^2(X) \cos^2\theta e^{-\frac{U(X)}{kT}} dX, \quad (29)$$

$$\frac{1}{I} = \int e^{-\frac{U(X)}{kT}} dX.$$

By utilizing the expressions relating the dielectric permittivity to the moment of the sample we obtain:

$$\epsilon - 1 = \frac{4\pi M_E}{VE} = \frac{4\pi}{3V} \frac{3\epsilon}{2\epsilon+1} \frac{\overline{M^2}}{kT}, \quad (30)$$

where

$$\overline{M^2} = I \int M^2(X) e^{-\frac{U(X)}{kT}} dX. \quad (31)$$

This equation gives in a general form the main result of Fröhlich's theory. The dielectric permittivity is determined by the mean square of the spontaneous polarization of the sphere immersed into an infinite medium of the same dielectric properties. It is evident that for the solution of this equation we must first determine the quantity  $\overline{M^2}$ .

The fundamental equation is too general and is not applicable to calculations involving actual systems. Fröhlich specializes it further by utilizing the method proposed by Kirkwood.

The spherical region is divided into  $N$  cells each of which contains  $k$  elementary particles. In a liquid the cell contains one molecule, in a crystal it contains a crystal cell, etc. If  $m(x_j)$  is the dipole moment of the cell, then  $M(X)$  can be written as the vector sum of  $m(x_j)$

$$M(X) = \sum_{j=1}^N m(x_j) \text{ and } M^2(X) = M(X) \cdot M(X) = \sum_{j=1}^N m(x_j) \cdot M(x). \quad (32)$$

In this case the expression for  $\overline{M^2}$  can be written in the form

$$\overline{M^2} = \sum_{j=1}^N I \int m(x_j) M(X) e^{-\frac{U(X)}{kT}} dX, \quad dX = dX_j dx_j, \quad (33)$$

where

$$dX_j = dx_1 dx_2 \dots dx_{j-1} dx_{j+1} \dots dx_N, \quad (34)$$

i.e., the integration can be carried out first of all over the whole spherical region excluding the  $j$ -th cell, and then over all the cells. The quantity  $m(x_j)$  depends only on the displacement  $x_j$  and is constant with respect to integration over  $dX_j$ . From this it follows that

$$I \int m(x_j) M(X) e^{-\frac{U}{kT}} dX = I \int m(x_j) \left( \int M(X) e^{-\frac{U}{kT}} dX_j \right) dx_j = \int m(x_j) m^*(x_j) p(x_j) dx_j, \quad (35)$$

where

$$m^*(x_j) = \frac{\int M(X) e^{-\frac{U}{kT}} dX_j}{\int e^{-\frac{U}{kT}} dX_j}, \quad p(x_j) = \frac{\int e^{-\frac{U}{kT}} dX_j}{\int e^{-\frac{U}{kT}} dX}$$

$m^*(x_j)$  is the average moment of the whole sphere for a given displacement  $x_j$  having the moment  $m(x_j)$ , i.e., the moment of the large spherical region polarized by one of the cells whose moment is equal to  $m$ ; therefore, as in the case of the evaluation of the quantity  $M_B$  in Kirkwood's theory, the quantity  $m^*$  is determined by the intermolecular interaction.

Thus, we have

$$\overline{M^2} = \sum_{j=1}^N \int m(x_j) m^*(x_j) p(x_j) dx_j = N \left[ \int m(x_j) m^*(x_j) p(x_j) dx_j \right] = N \overline{mm^*}. \quad (36)$$

Fröhlich's general equation has the following form

$$\epsilon - 1 = \frac{3\epsilon}{2\epsilon+1} \frac{4\pi N}{V} \frac{\overline{mm^*}}{kT}. \quad (37)$$

Fröhlich's theory was extended to anisotropic molecules by Powles.<sup>18</sup> In this case the dielectric permittivity is anisotropic. The volume of dielectric under consideration in this case is chosen in the form of an ellipsoid whose principal axes are proportional to  $\epsilon_i^{1/2}$ , where  $\epsilon_i$  is the dielectric permittivity in the direction  $i$ . Fröhlich's equation in the anisotropic case is given by:

$$\epsilon_i - 1 = \frac{3\epsilon_i}{2\epsilon_i+1} \frac{4\pi N}{V} \frac{3\overline{mm^*}}{kT}, \quad i = 1, 2, 3. \quad (38)$$

Fröhlich's general theory treats the case of low intensity fields when the dielectric permittivity does not depend on the field. In one of the most recent papers<sup>19</sup> Fröhlich's theory was extended to the case of strong fields. On writing the dielectric permittivity in the form

$$\epsilon = \epsilon_s + f(E), \quad (39)$$

where  $\epsilon_s$  is the static dielectric permittivity, which is independent of the field, Fröhlich's equation for that case can be obtained in the form

$$\epsilon = \epsilon_s + \frac{4\pi}{V} \frac{1}{9} \left( \frac{3\epsilon_s}{2\epsilon_s+1} \right)^3 \frac{E^2}{k^3 T^3} \{3\overline{M^4} - 5(\overline{M^2})^2\}. \quad (40)$$

All the expressions given above which follow from Fröhlich's theory are general and have been derived without making any simplifications. They can be applied both to liquid and to crystalline dielectrics. In each case it is necessary to choose a structural element of dipole moment  $m$ . However, in studying the

dielectric properties of an actual system difficulties arise first of all in the determination of the quantity  $\mu\mu^*$ .

We consider the application of Fröhlich's theory to a polar liquid. For an individual cell we take in this case a polar molecule. Therefore  $m = \mu$ . In accordance with this  $m^* = \mu^*$  and represents the moment of the spherical dielectric if one of its molecules occupies some definite fixed position. In this case the moment of the sphere is made up of the dipole moment of the fixed molecule and the sum of the moments of all the particles surrounding the given molecule

$$\mu^* = \mu + \mu N \int \cos \gamma p(\omega, r) d\omega dr, \quad (41)$$

where  $N$  is the number of molecules,  $\gamma$  is the angle between the direction of the dipole of the fixed molecule and the direction of the dipole of a neighboring molecule,  $p(\omega, r)$  is the probability of occurrence of this position and orientation with respect to the fixed molecule. If the fixed molecules are oriented independently of each other, then it is clear that the second term of the sum vanishes and  $\mu^* = \mu$ . This means that in the absence of an electric field the moments of all the other molecules in the sample when the given molecule is held fixed will cancel each other, owing to the random nature of thermal motion. In the case  $\mu^* \neq \mu$  this is associated with the existence of short range forces between the molecules which produce a preferred orientation of molecules with respect to the given molecule even if no external field is applied to the sample.

Since in a liquid all the directions of the dipoles are equivalent, we have  $\overline{\mu\mu^*} = \mu\mu^*$  and Fröhlich's equation for a polar liquid assumes the form

$$\varepsilon - 1 = \frac{3\varepsilon}{2\varepsilon + 1} \frac{4\pi N}{V} \frac{\mu\mu^*}{3kT}. \quad (42)$$

In order to apply this equation to a real polar liquid it is necessary to determine the quantities  $\mu$  and  $\mu^*$ . In studying the dielectric properties of a polar liquid, Fröhlich finds it useful to introduce certain simplifications and to treat the polarization due to electronic displacement macroscopically by utilizing the value of the index of refraction. In this case the molecular dipole is considered to be rigid or nonpolarizable, and because of this it is no longer necessary to carry out a complicated calculation of the reactive field. On taking this into account, it is necessary to introduce certain changes into the derivation of the general equation.

If  $M_d$  is the moment due to the electronic displacement, then we have

$$n^2 - 1 = \frac{4\pi}{VE} M_d. \quad (43)$$

The spherical region is now regarded as the totality of the electric charges  $e_i$ , which obey the laws of statistical mechanics and which are placed into an infinite

medium of dielectric permittivity equal to  $n^2$ . If  $M_0$  is the moment due to all kinds of displacement other than electronic, then  $M_0 + M_d$  represents the total moment of the dielectric. Therefore we obtain the equation

$$\varepsilon - 1 = \frac{4\pi(M_0 + M_d)}{VE},$$

or

$$\varepsilon - n^2 = \frac{4\pi M_0}{VE}. \quad (44)$$

The general results obtained previously must now be somewhat modified. It is necessary to note that in this case  $M_0(x)$ ,  $\mu$  and  $\mu^*$  do not take electronic displacement into account. Moreover, the following changes must be introduced:

1. The cavity field  $G$  must be replaced by the cavity field  $G'$  within the spherical region of dielectric permittivity  $n^2$ , i.e.,

$$G' = \frac{3\varepsilon}{2\varepsilon + n^2} E. \quad (45)$$

2. In the derivation of the equation the equality

$$\varepsilon - 1 = \frac{4\pi M_E}{VE}$$

is replaced by

$$\varepsilon - n^2 = \frac{4\pi M_{0E}}{VE}. \quad (46)$$

As a result of this we obtain Fröhlich's equation

$$\varepsilon - n^2 = \frac{3\varepsilon}{2\varepsilon + n^2} \frac{4\pi N_0}{3} \frac{\mu\mu^*}{kT}. \quad (47)$$

It should be noted that in the discussion of the energy  $U(X)$  needed for the evaluation of  $\mu$  and  $\mu^*$ , the electronic polarization must be taken into account on a macroscopic basis.

By considering the spherical region as the totality of electric charges  $e_i$  placed inside an infinite sphere of dielectric permittivity  $n^2$ , we can find the relation between the dipole moment in the medium and the dipole moment of the free molecule.

It is known from electrostatics that

$$\mu = \frac{n^2 + 2}{3} \mu_0, \quad (48)$$

where  $\mu_0$  is the dipole moment of the free molecule,  $n$  is the index of refraction, and  $\mu$  is the dipole moment of the molecule in the condensed phase.

The quantity  $\mu^*$  is determined by the intermolecular interaction. If we take into account only the interaction between the  $z$  neighboring molecules, then the general formula for the evaluation of  $\mu^*$  reduces to the simpler one:

$$\mu\mu^* = \mu^2 (1 + z \overline{\cos \gamma}), \quad (49)$$

where  $\overline{\cos \gamma}$  is the average value of the cosine of the angle between neighboring dipoles,

$$\overline{\cos \gamma} = \frac{\int \cos \gamma e^{-\frac{U}{kT}} d\omega dr}{\int e^{-\frac{U}{kT}} d\omega dr}, \quad (50)$$

$U$  is the interaction energy between neighboring molecules of the liquid, which is determined not only by electrostatic forces but also takes into account all forms of interaction between the molecules of the liquid.

Thus, by taking into account all the simplifications introduced into Fröhlich's general theory for a polar liquid we obtain:

$$\left. \begin{aligned} \epsilon - n^2 &= \frac{3\epsilon}{2\epsilon + n^2} \frac{4\pi N}{V} \frac{\mu^2}{3kT} (1 + z \overline{\cos \gamma}), \\ \epsilon - n^2 &= \frac{3\epsilon}{2\epsilon + n^2} \left(\frac{n^2 + 2}{3}\right)^2 \frac{4\pi N}{V} \frac{\mu_0^2}{3kT} g, \end{aligned} \right\} \quad (51)$$

where the quantity  $g = 1 + z \overline{\cos \gamma}$  is the correlation parameter which takes into account the nearest neighbor intermolecular interaction.

The principal difficulties in Fröhlich's theory are associated with the evaluation of the energy of interaction of the spherical sample with the surrounding infinite medium. In order to avoid the evaluation of the reactive field required for determining this interaction, Fröhlich introduces an approximation by treating the polarization of the electronic displacement macroscopically.

In contrast to Fröhlich, Harris and Alder<sup>20</sup> consider a macroscopic sphere immersed not into an infinite macroscopic medium, but into vacuum, and this in the opinion of these authors simplifies the evaluation of the energy of interaction between the sample and the field.

### c. The Theory of Harris and Alder

Let us consider the fundamental assumptions of the theory of Harris and Alder. Like Kirkwood, Harris and Alder consider a macroscopic sample of the dielectric containing  $N$  molecules within the volume  $V$  and placed in vacuum. The potential energy  $U_N$  depends on the position of the centers of gravity of the molecules  $r = f(r_1, r_2, \dots, r_N)$ , on their orientation  $\Omega = \varphi(\omega_1, \dots, \omega_N)$ , and on the polarization of the molecules which is characterized by the coordinates of the charges  $X(x_1, x_2, \dots, x_N)$ . The configuration of the system is defined by the quantities  $r$  and  $\Omega$ , the polarization is described by means of  $X$ . The average component of the moment of the sample parallel to the direction of the field is given by the formula

$$\overline{M}_{E_0} = \frac{\int [M(r, \Omega, X) e^{-\frac{U_N(r, \Omega, X) + ME_0}{kT}}] dr d\Omega dX}{\int e^{-\frac{U_N + ME_0}{kT}} dr d\Omega dX}. \quad (52)$$

The quantity  $M$  can be written as a sum of two terms

$$M(r, \Omega, X) = M_0(r, \Omega) + M_d(r, \Omega, X), \quad (53)$$

where  $M_0(r, \Omega)$  represents that part of the electric

moment which is determined by the given configuration including also the inductive part which occurs in the case when the electric field is absent. The average value of  $M_d(r, \Omega, X)$  is related to the polarization (both electronic, and atomic polarization), which arises in the presence of an external electric field. Thus, we obtain for the component of the average electric moment of the sphere parallel to the direction of the field:

$$\overline{M}_{E_0} = \frac{\int [M_0(r, \Omega) + M_d(r, \Omega, X)] e^{-\frac{U_N + M_0 E_0 + M_d E_0}{kT}} dr d\Omega dX}{\int e^{-\frac{U_N + (M_0 + M_d) E_0}{kT}} dr d\Omega dX} \quad (54)$$

By expanding the integrand in powers of  $E_0$  and by neglecting the higher order terms Harris and Alder have obtained the following expression for the moment  $\overline{M}_{E_0}$ :

$$\overline{M}_{E_0} = \frac{E_0}{kT} \overline{M}_0^2 + \overline{M}_d(X_E). \quad (55)$$

Let us discuss the evaluation of the quantity  $M_d(X)$ . It is difficult to evaluate rigorously the dependence of the quantity  $M_d$  on  $\alpha$ . However, we can discuss the dependence of this quantity on the high frequency dielectric permittivity  $\epsilon$ . The use in this case of the quantity  $n^2$  would eliminate the polarization due to the atomic displacement. If we apply to the dielectric a field of such high frequency that no molecular orientation occurs, then the polarization is characterized by the quantity  $\epsilon_\infty$ :

$$\frac{\epsilon_\infty - 1}{4\pi} E = \frac{\overline{M}_d}{V}. \quad (56)$$

For a spherical sample we have

$$E = \frac{3}{\epsilon_\infty + 2} E_0, \quad (57)$$

and therefore

$$M_d = \frac{3V}{4\pi} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} E_0.$$

The first term in the expression for  $\overline{M}_{E_0}$ ,  $\overline{M}_0^2$  represents the value of the mean square of the moment of the spherical sample situated in vacuum when the external electric field is equal to zero. We must remember that in taking the average we have included the coordinates associated only with the molecular orientation of the molecules. Harris and Alder have attempted in the evaluation of  $\overline{M}_0^2$  to express this quantity in terms of the mean square of the moment of the sample situated inside a sphere placed in vacuum under the condition that the radius of this sphere tends to infinity. In order to do this they have utilized the relations (20), (21)

$$(\overline{M}_0^2)_{\text{vac}} = \frac{3}{\epsilon + 2} \frac{3\epsilon}{2\epsilon + 1} (\overline{M}_0^2)_{\text{sph}}. \quad (58)$$

On substituting the value of  $\overline{M}_E$  into the general expression for the polarization Harris and Alder have

obtained the equation

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{9VkT} \frac{3}{\epsilon+2} \frac{3\epsilon}{2\epsilon+1} (\overline{M^2}) + \frac{\epsilon_\infty-1}{\epsilon_\infty+2}. \quad (59)$$

In accordance with Kirkwood's method the quantity  $\overline{M^2}$  can be written in the form

$$\overline{M^2} = \frac{N}{3} (\mu\mu^*), \quad (60)$$

where  $\mu^*$  is the moment of the sphere when the position of one of the molecules of moment  $\mu$  within it is fixed. Therefore the expression for  $\mu\mu^* = \mu^2g$  is determined, just as in Kirkwood's theory, by means of formula (20). The quantity  $\mu$  characterizes the dipole moment of the molecule in the condensed phase which cannot be determined exactly, as has been shown previously in the discussion of Onsager's theory. Harris and Alder consider that it is possible in the evaluation of  $\mu$  to use for the first approximation Onsager's relation in order to take into account to some extent the effect of the surrounding medium on the value of the dipole moment

$$\mu = \mu_0 \frac{n^2+2}{3} \frac{2\epsilon+1}{2\epsilon+n^2}. \quad (61)$$

The final result of Harris and Alder reduces to the following expression:

$$\epsilon - \epsilon_\infty = \frac{4\pi N}{V} \frac{3\epsilon}{2\epsilon+1} \frac{\epsilon_\infty+2}{3} \frac{\mu\mu^*}{3kT}, \quad (62)$$

or

$$\epsilon - \epsilon_\infty = \frac{4\pi N}{V} \frac{3\epsilon}{(2\epsilon+\epsilon_\infty)^2} \frac{(\epsilon_\infty+2)(2\epsilon+1)}{3} \left(\frac{\epsilon_\infty+2}{3}\right)^2 \frac{\mu_0^2 g}{3kT}.$$

In analyzing the above statistical theories of polarization it should be noted that they present in principle the possibility of determining the intermolecular interaction, i.e., an investigation of the polarization of polar liquids gives a method for the study of the statistical behavior of molecules in the liquid phase. It is necessary to analyze these theories in greater detail, to compare them and to determine which one of them will provide us with the most rigorous approach to the evaluation of the polarization of polar systems.

#### d. Comparison of the Theories of Fröhlich and of Harris and Alder

Kirkwood's theory has been examined in detail in a number of papers. Frenkel' and Gubanov,<sup>15</sup> and also Fröhlich,<sup>22</sup> Harris and Alder,<sup>23</sup> and Buckingham<sup>24</sup> have noted its principal defect associated with an incorrect evaluation of the internal field and of the polarization due to deformation. This theory can be applied only in the case when we neglect the quantity  $\epsilon_\infty$  in comparison with  $\epsilon$ , i.e.,  $\epsilon \gg \epsilon_\infty$ , and if we assume the molecules to be nonpolarizable. It is clear that this approximation is too inexact and, therefore, at present Kirkwood's theory is utilized only rarely.

We consider the fundamental equations obtained in the theories of Fröhlich and of Harris and Alder. If

we assume that  $n^2 \sim \epsilon_\infty$ , then the equations have the following form:

Fröhlich's equation

$$\epsilon - \epsilon_\infty = \frac{3\epsilon}{2\epsilon+\epsilon_\infty} \left(\frac{\epsilon_\infty+2}{3}\right)^2 \frac{4\pi N \mu_0^2 g}{V 3kT}, \quad (63)$$

Harris-Alder equation

$$\epsilon - \epsilon_\infty = \frac{3\epsilon}{(2\epsilon+\epsilon_\infty)^2} \left(\frac{\epsilon_\infty+2}{3}\right)^2 \frac{(2\epsilon+1)(\epsilon_\infty+2)}{3} \frac{4\pi N \mu_0^2 g}{V 3kT}. \quad (64)$$

In the absence of intermolecular short-range interaction,  $g = 1$  and Fröhlich's equation reduces to Onsager's equation (10). On setting  $g = 1$  in the Harris-Alder equation we find that this equation differs from Onsager's equation even in the absence of short range interaction. The comparison of the two formulas (63) and (64) shows that they differ from one another by the factor  $f = (\epsilon_\infty + 2)(2\epsilon + 1)/3(2\epsilon + \epsilon_\infty)$ , which contains only the macroscopic constants  $\epsilon$  and  $\epsilon_\infty$ . Therefore, it is necessary to examine the reason for the discrepancy between two theories both utilizing the macroscopic point of view without attempting to examine and to improve the microscopic model of the dielectric.

As has been shown previously, the general formula obtained by Fröhlich for the macroscopic sphere immersed into the same medium has the form

$$\epsilon - 1 = \frac{4\pi}{3V} \frac{3\epsilon}{2\epsilon+1} \frac{(\overline{M^2})_\epsilon}{kT}, \quad (65)$$

where  $(\overline{M^2})_\epsilon$  is the mean square of the moment of the macroscopic sphere placed into a medium of dielectric permittivity  $\epsilon$ . The statistical average in this case includes all possible fluctuations, and, in particular, the fluctuations both of the dipoles being oriented, and of the charges undergoing displacement.

Since Harris and Alder considered the fluctuations of the moment of this sphere placed in vacuum it is useful to examine the relation between the values of the average moment of the sphere placed in vacuum and in a medium of dielectric permittivity  $\epsilon$ .

Fröhlich has shown that the following relation exists between the fluctuation moment of a sphere placed in a medium of dielectric permittivity  $\epsilon$  and the fluctuation moment of this sphere placed in vacuum

$$(\overline{M^2})_{\text{vac}} = \frac{3}{\epsilon+2} \frac{3\epsilon}{2\epsilon+1} (\overline{M^2})_\epsilon. \quad (65a)$$

It should be emphasized that the statistical averages occurring in this equation take into account all possible fluctuations, and, in particular, the fluctuations of the dipoles being oriented and of the charges undergoing displacement.

On returning to the Harris-Alder theory we note that in considering a sphere of dielectric material situated in vacuum the authors of the theory decomposed the moment into two parts, one of which depends on the coordinates of all the molecules, i.e., it includes the moment determined by the configuration of the dipoles and takes into account the moment induced by this configuration. The second part of the



moment depends on the applied field (since this moment is due to the displacement of the elastically bound charges). This part of the moment is treated on a macroscopic basis and is expressed in terms of the high frequency dielectric permittivity. Therefore, in general form Harris and Alder have obtained the equation

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{9VkT} (\overline{M^2})_{\text{vac}} + \frac{\epsilon_\infty-1}{\epsilon_\infty+2}. \quad (66)$$

This equation is less general than Fröhlich's equation given earlier, since it does not include the coordinates of the elastically bound charges. This can also be seen from the fact that the equation obtained by them is applicable to the dielectric sphere not containing any dipoles ( $\epsilon = \epsilon_\infty$ ) only for  $(\overline{M^2})_{\text{vac}} = 0$ . However, Harris in going over from the sphere in vacuum to the sphere in a dielectric of radius  $R$  utilizes for  $R \rightarrow \infty$  the relation between  $(\overline{M^2})_{\text{vac}}$  and  $(\overline{M^2})_\epsilon$  [cf. (58)], and obtains his equation in the form

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{9kTV} \frac{3}{\epsilon+2} \frac{3\epsilon}{2\epsilon+1} (\overline{M^2})_\epsilon + \frac{\epsilon_\infty-1}{\epsilon_\infty+2}. \quad (67)$$

Equation (67) is incorrect, since the statistical averaging in (65a), on the basis of which (67) has been obtained, has a somewhat different meaning than that in the equation given above. However, as Fröhlich has shown, it is possible to derive a completely general relation between the fluctuation moments  $(\overline{M^2})_\epsilon$  and  $(\overline{M^2})_{\text{vac}}$ , where the statistical averaging includes the fluctuations of the dipoles changing their orientation, but does not take into account the fluctuations of the elastically bound charges. This enables us to correctly transform the initial macroscopic formula of Harris and Alder.

A spherical macroscopic sample of dielectric permittivity  $\epsilon$  is placed into a continuous macroscopic medium of dielectric permittivity  $\epsilon_1$ . This includes the special cases when the sample is situated in vacuum ( $\epsilon_1 = 1$ ) and when it is placed into a medium of dielectric permittivity  $\epsilon_1 = \epsilon$ . The energy of the sample of moment  $M$  consists of two terms:

$$F(M) = F_1 + F_2, \quad (68)$$

where  $F_1$  is the free energy of the sphere in vacuum,  $F_2$  is the electrostatic energy of interaction with the surrounding medium. It can be shown<sup>17</sup> that

$$F_1 = \frac{1}{2} \frac{4\pi}{3V} \frac{\epsilon+2}{\epsilon-1} M^2, \quad F_2 = -\frac{1}{2} MR, \quad R = gM, \quad (69)$$

where

$$g = \frac{4\pi}{3V} \frac{2(\epsilon_1-1)}{2\epsilon_1+1}. \quad (70)$$

Therefore, in the given general case we have

$$F(M) = \frac{1}{2} \frac{4\pi}{V} \frac{2\epsilon_1+\epsilon}{(\epsilon-1)(2\epsilon_1+1)} M^2. \quad (71)$$

The moment  $M$  can be separated into a number of independent parts which can be experimentally distin-

guished by measuring the dielectric permittivity at different frequencies.

Thus, in a manner similar to Harris and Alder it is possible to write the moment as the sum of two terms:

$$M = M_d(\epsilon_1) + M_0(\epsilon_1), \quad (72)$$

where  $M_d/V$  is the polarization due to electronic displacement, which can be determined in terms of the dielectric permittivity at high frequencies  $\epsilon_\infty$ , when the dipoles are not oriented. In this case  $M_0$  is the part of the total moment  $M$  associated with dipole orientation, including the moment induced by the displacement when there is no electric field. In this case the energy depends on both parts  $M_d$  and  $M_0$  and can be written in the form of the sum

$$F(M_d, M_0) = \frac{1}{2} \frac{M_d^2(\epsilon_1)}{\beta(\epsilon_1)} + \frac{1}{2} \frac{M_0^2(\epsilon_1)}{\gamma(\epsilon_1)}, \quad (73)$$

where  $\beta$  and  $\gamma$  are parameters which must be determined. As Fröhlich has shown, if the sample is placed in vacuum the quantities  $\beta(1)$  and  $\gamma(1)$  have the form

$$\beta(1) = \frac{3V}{4\pi} \frac{\epsilon_\infty-1}{\epsilon_\infty+2}, \quad (74)$$

$$\gamma(1) = \frac{3V}{4\pi} \left( \frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2} \right).$$

In the case  $\epsilon_1 \neq 1$  the energy is increased by  $F_2(M)$ .

Therefore, we have

$$F(M_d, M_0) = \frac{1}{2} \frac{M_d^2(1)}{\beta(1)} + \frac{1}{2} \frac{M_0^2(1)}{\gamma(1)} - \frac{1}{2} g [M_d(1) + M_0(1)]^2. \quad (75)$$

If the sphere is surrounded by a medium of dielectric permittivity  $\epsilon_1$ , then the new values of  $M_d(\epsilon_1)$  and  $M_0(\epsilon_1)$  have the following form

$$M_d(\epsilon_1) = M_d(\epsilon_1) - \frac{\alpha g}{1-\alpha g} M_0(1), \quad M_0(\epsilon_1) = \frac{M_0(1)}{1-\alpha g}. \quad (76)$$

It should be noted that  $M_d(1)$  differs from  $M_d(\epsilon_1)$  by the term  $\alpha g M_0(\epsilon_1)$  since  $g M_0(\epsilon_1)$  is the reactive field and  $\alpha g M_0(\epsilon_1)$  is the moment due to the displacement induced by this field. In this case the quantities  $\beta(\epsilon_1)$  and  $\gamma(\epsilon_1)$  have the form

$$\beta(\epsilon_1) = \frac{V}{4\pi} (\epsilon_\infty-1) \frac{2\epsilon_1+1}{2\epsilon_1+\epsilon_\infty},$$

$$\gamma(\epsilon_1) = \frac{V}{4\pi} (\epsilon-\epsilon_\infty) \frac{(2\epsilon_1+1)^2}{(2\epsilon_1+\epsilon_\infty)(2\epsilon_1+\epsilon)}. \quad (77)$$

The fundamental equation for the determination of the fluctuation moment can be written in the following form:

$$\overline{M^2} = \frac{\int_0^\infty M^2 e^{-\frac{F(M)}{kT}} M^2 dM}{\int_0^\infty e^{-\frac{F(M)}{kT}} M^2 dM}. \quad (78)$$

In the case under consideration we have

$$\overline{M^2} = \overline{M_d^2}(\epsilon) + \overline{M_0^2}(\epsilon). \quad (79)$$

Therefore

$$\overline{M}_d^2(\epsilon_1) = 3kT\beta(\epsilon_1), \quad \overline{M}_v^2(\epsilon_1) = 3kT\gamma(\epsilon_1).$$

On the basis of this we can obtain a relation between the fluctuation moments due to orientation of the dipoles in the cases of a sphere situated in vacuum, and a sphere immersed into the same medium, and this relation is the one that should be utilized in the derivation of the Harris-Alder formula

$$(\overline{M}_0^2)_{\text{vac}} = \frac{3\epsilon}{2\epsilon+1} \frac{2\epsilon+\epsilon_\infty}{2\epsilon+1} \frac{3}{\epsilon+2} \frac{3}{\epsilon_\infty+2} (\overline{M}_0^2)_{\epsilon_1}. \quad (80)$$

It should be emphasized that this equation by its nature is macroscopic and does not depend on the details of the structure of the medium.

On the basis of all these transformations we can obtain an improved Harris-Alder formula. In order to do this we must substitute into the Harris-Alder equation

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{9VkT} (\overline{M}_0^2)_{\text{vac}} + \frac{\epsilon_\infty-1}{\epsilon_\infty+2} \quad (81)$$

the correct value of  $(\overline{M}_0^2)_{\text{vac}}$  (80), in place of Eq. (58) which they used,

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi N}{9VkT} \frac{3\epsilon}{2\epsilon+1} \frac{2\epsilon+\epsilon_\infty}{2\epsilon+1} \frac{3}{\epsilon+2} \frac{3}{\epsilon_\infty+2} (\mu\mu^*) + \frac{\epsilon_\infty-1}{\epsilon_\infty+2}. \quad (82)$$

In the case when it is possible to neglect the short range forces of molecular interaction we have  $\mu = \mu^*$  as has been shown earlier. By utilizing Onsager's formula for the evaluation of  $\mu$  [cf. Eq. (61)] we obtain finally:

$$\epsilon - \epsilon_\infty = \frac{4\pi N}{3V} \frac{3\epsilon}{2\epsilon+\epsilon_\infty} \left( \frac{\epsilon_\infty+2}{3} \right)^2 \frac{\mu_0^2}{kT}, \quad (83)$$

which agrees with Eq. (10) derived by Onsager. This shows that in the case when the fluctuation moment is calculated correctly a formula can be obtained utilizing the Harris-Alder method which (like Fröhlich's formula) reduces to Onsager's equation in the absence of short range interaction. Just as before, the short range interaction is taken into account by means of the correlation parameter  $g$ . In this case the Harris-Alder equation has the form

$$\epsilon - \epsilon_\infty = \frac{4\pi N}{3V} \frac{3\epsilon}{2\epsilon+\epsilon_\infty} \frac{(\epsilon_\infty+2)^2}{9} \frac{\mu_0^2 g}{kT}, \quad (84)$$

which agrees with Eq. (63) derived by Fröhlich. The identity of the equations obtained by Fröhlich and by Harris and Alder, provided the averaging is carried out properly, can also be proved by a somewhat less general method, as was done in reference 26.

Thus, the analysis of the theories of Harris and Alder and of Fröhlich shows that if the averaging is carried out correctly these theories are identical and may be equally well utilized for the investigation of dielectric polarization.

As has been shown previously, in going over to real systems (for example, to a polar liquid) it is inevitably necessary to use a number of simplifica-

tions due to present lack of an exact theory of the structure of liquids. Thus, in the Harris-Alder theory the dipole moment of a molecule in the condensed phase is calculated on the basis of Onsager's relation. In fact, the dipole moment of the molecule in the medium  $\mu$  is a function of the coordinates of all the molecules of the sample, i.e.,  $\mu_i$  (1, 2, 3, ..., N), and can be written in the form

$$\mu_j = \mu_0 + \alpha \sum_i T_{ij} \mu_i, \quad (85)$$

where  $T_{ij} = -\nabla_j R_{ij} / R_{ij}^3$  gives the dipole field acting on the  $j$ -th molecule due to the  $i$ -th molecule situated at a distance  $R_{ij}$ .

The evaluation of the magnitude of the dipole moment in the condensed phase in accordance with Onsager's formula means that

$$\mu_j = \mu_0 + \alpha \left( \sum_i T_{ij} \mu_i \right) \quad (86)$$

[i.e., the second term in (85) is evaluated on the assumption that the given molecule is surrounded by a continuous macroscopic medium]. The averaging shows that in this case the fluctuations of the dipole moment are neglected. In this connection we should refer in conclusion to Buckingham's last paper,<sup>24</sup> in which he poses the problem of the change introduced into the fundamental equations of the statistical theories of polarization when the discrete nature of the particles surrounding the given particle is taken into account.

#### e. Buckingham's Theory

We consider a macroscopic sphere of volume  $\nu$  of dielectric permittivity  $\epsilon$ , so that

$$(\epsilon-1)E = \frac{4\pi}{V} \overline{M}_E, \quad (87)$$

where  $V$  is the volume of the small sphere taken at the center of the large volume  $\nu$ ,  $\overline{M}_E$  is the average moment in the direction of the field. Since the intensity of the field in the spherical sample is equal to  $E = 3E_0/(\epsilon+2)$ , we have

$$\frac{\epsilon-1}{\epsilon+2} E_0 = \frac{4\pi}{3V} \overline{M}_E. \quad (88)$$

If we consider an ensemble of particles whose position and orientation can be described by the variables  $\tau$ , then  $\overline{M}$  is a function of  $\tau$  and  $E_0$ . In this case we have

$$\overline{M}_E = \frac{\int M(\tau, E_0) e^{-\frac{U(\tau, E_0)}{kT}} d\tau}{\int e^{-\frac{U(\tau, E_0)}{kT}} d\tau}, \quad (89)$$

where  $U(\tau, E_0)$  is the total potential energy of the system with the configuration  $\tau$  and placed in the external field  $E_0$ .

For weak fields when the electric saturation is neglected, i.e., when  $\epsilon$  does not depend on the field, we have

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3V} \left( \frac{\partial \bar{M}}{\partial E_0} \right)_{E_0=0}. \quad (90)$$

On carrying out the differentiation we obtain:

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{V} \left[ \frac{\partial M(\tau, E_0)}{\partial E_0} + \frac{1}{kT} \overline{M(\tau, 0) \mathcal{M}(\tau, 0)} \right]. \quad (91)$$

In Eq. (21)  $\mathcal{M}(\tau, 0)$  is the moment of the large sphere with the configuration  $\tau$  and  $E = 0$ . It can be obtained from the fundamental relation

$$\frac{\partial}{\partial E_0} U(\tau, E_0) = -\mathcal{M}(\tau, E_0). \quad (92)$$

For  $E_0 = 0$  all the directions of  $\mathcal{M}$  and  $M$  are equally probable, and therefore

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3V} \left[ \frac{\partial \overline{M(\tau, E_0)}}{\partial E_0} + \frac{1}{3kT} \overline{M \mathcal{M}} \right]. \quad (93)$$

The first term in (93) is proportional to the average polarizability of the inner sphere and can be expressed in terms of the high-frequency dielectric permittivity:

$$\frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2} = \frac{4\pi}{9kTV} \overline{M \mathcal{M}}. \quad (94)$$

If we consider a sphere of volume  $V$  in vacuum, and not surrounded by the larger sphere, then we have

$$\frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2} = \frac{4\pi}{9kTV} (\overline{M^2})_{\text{vac}}. \quad (95)$$

As has been shown earlier, this result was obtained in the Harris-Alder theory (83).

We now carry out an evaluation of the quantity  $(\overline{M^2})_{\text{vac}}$

$$M = \sum \mu_i \quad (96)$$

(where  $\mu_i$  is the moment of the  $i$ -th molecule in the sphere), and the summation is taken over  $N$  identical molecules in the sample.  $\mu_i$  is a function of the configuration  $\tau$  and may be written in the form of a sum of a constant moment  $\mu_{0i}$  and of the induced moment  $m_i$ ;  $m_i$  is therefore proportional to the polarizability of the  $i$ -th molecule:

$$\mu_i = \mu_{0i} + m_i.$$

Thus we have

$$(\overline{M^2})_{\text{vac}} = \sum_i (\mu_{0i} + m_i) \overline{M} = \sum_i \overline{\mu_{0i} M} + \sum_{i,j} \overline{\mu_{0i} m_j} + \sum_{i,j} \overline{m_i m_j}, \quad (97)$$

or for  $N$  identical molecules in the sample

$$\overline{M^2} = N \overline{\mu_{01} M} + N \overline{\mu_{01} M'} + O(\alpha^2), \quad (98)$$

where  $M' = \sum_i m_i$  is the total induced moment of all the molecules.

For the evaluation of the quantity  $\overline{M^2}$  the dielectric is divided into two regions: one region is small in size and is characterized by the moment  $\bar{m}_1$ , if we fix within this region a molecule of moment  $\mu_{01}$ ; the other region is the remainder of the sample.

The first term in this equation is determined by means of the relation derived by Kirkwood [cf. Eq.

(16)], i.e., the moment of the whole dielectric  $M$  is expressed in terms of the moment of the small sphere  $\bar{m}_1$

$$M = \frac{9\epsilon}{(2\epsilon+1)(\epsilon+2)} \bar{m}_1. \quad (99)$$

Therefore we have

$$\overline{\mu_{01} M} = \frac{9\epsilon}{(2\epsilon+1)(\epsilon+2)} \mu_{01} \bar{m}_1. \quad (100)$$

In the evaluation of the second term of (98) it is necessary to estimate the magnitude of  $M'$  which is the total induced moment of all the molecules in the sample, if the position and the orientation of one of its molecules situated within the sphere  $\bar{m}_1$  is fixed. The evaluation of this term is broken up into two stages since the induced moment of all the molecules situated outside the sphere  $\bar{m}_1$  can be evaluated macroscopically; at the same time the induced moment of the molecules within the small sphere must take into account the short-range interaction.

The determination of the macroscopic part of the quantity  $M'$  is carried out as follows. The moment of that part of the dielectric which is situated outside the sphere  $\bar{m}_1$ , is given by

$$\frac{9\epsilon}{(2\epsilon+1)(\epsilon+2)} \bar{m}_1 - \bar{m}_1 = -\frac{2(\epsilon-1)^2}{(2\epsilon+1)(\epsilon+2)} \bar{m}_1, \quad (101)$$

since the moment of the whole dielectric  $M$  is determined by the quantity  $\bar{m}_1$  in accordance with formula (99).

Owing to the existence of this moment, the effective field is equal to the average moment divided by the polarizability  $3V(\epsilon-1)/4\pi(\epsilon+2)$ . Therefore, the average induced moment of that part of the dielectric which is situated outside the small sphere is equal to

$$-\frac{2(\epsilon-1)(\epsilon_\infty-1)}{(2\epsilon+1)(\epsilon_\infty+2)}. \quad (102)$$

The other part of  $M'$  is determined by the short-range interaction; this term can be written in the form

$$\bar{m}_1 - \bar{\mu}_{01}, \quad (103)$$

where  $\bar{\mu}_{01}$  is that part of the moment of the small macroscopic sphere which is due to the constant moment  $\mu_{01}$ ; at the same time we have

$$\bar{\mu}_{01} \bar{\mu}_{01} = \frac{\sum_i \int (\mu_{01} \mu_{0i}) e^{-\frac{U(\tau, 0)}{kT}} d\tau_1}{\int e^{-\frac{U(\tau, 0)}{kT}} d\tau_1}, \quad \mu_{01} \bar{m}_1 = \frac{\sum_i \int (\mu_{01} m_i) e^{-\frac{U(\tau, 0)}{kT}} d\tau_1}{\int e^{-\frac{U(\tau, 0)}{kT}} d\tau_1}, \quad (104)$$

where  $\Sigma_i$  denotes summation over all the molecules within the inner region, and  $\int d\tau_1$  indicates that the integration is carried out over all the configurations with the exception of 1.

By utilizing the value for  $M'$ , we obtain:

$$\begin{aligned} \overline{\mu_{01} M'} &= \left[ \frac{-2(\epsilon-1)(\epsilon_\infty-1)}{(2\epsilon+1)(\epsilon_\infty+2)} \bar{m}_1 + \bar{m}_1 - \bar{\mu}_{01} \right] \mu_{01} \\ &= \frac{3(2\epsilon+\epsilon_\infty)}{(2\epsilon+1)(\epsilon_\infty+2)} \mu_{01} \bar{m}_1 - \mu_{01} \bar{\mu}_{01}. \end{aligned} \quad (105)$$

By neglecting terms of order  $\alpha^2$  we obtain the general expression for the dielectric permittivity:

$$\frac{3(\epsilon - \epsilon_\infty)}{(\epsilon + 2)(\epsilon_\infty + 2)} = \frac{4\pi N}{9kTV} \left[ \frac{6(\epsilon^2 + 5\epsilon + 2\epsilon\epsilon_\infty + \epsilon_\infty)}{(2\epsilon + 1)(\epsilon + 2)(\epsilon_\infty + 2)} \mu_0 \bar{m} - \mu_0 \bar{\mu}_0 \right],$$

or, since  $(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = 4\pi N\alpha/3V$ ,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{9kTV} \left[ \left( 1 + \frac{9\epsilon}{(2\epsilon + 1)(\epsilon + 2)} \right) \mu_0 \bar{m} - \mu_0 \bar{\mu}_0 \right] + \frac{4\pi N\alpha}{3V} \left[ 1 - \frac{2(\epsilon - 1)^2}{9\epsilon} \right]. \quad (106)$$

The results obtained above show that in an exact treatment of the problem of the dielectric polarization of a polar liquid two moments are introduced:  $\bar{m}$  and  $\bar{\mu}_0$ .

The product  $\mu_0 \bar{\mu}_0$  can be expressed in terms of the correlation parameter  $g$  introduced by Kirkwood which is determined by the short range molecular interaction:

$$g\mu_0^2 = \mu_0 \bar{\mu}_0, \quad g = \frac{\mu_i \bar{\mu}_0}{\mu_0^2} \sum_i \overline{\cos \gamma_i}, \quad (107)$$

where  $\gamma_i$  is the angle between the directions of the constant dipoles of the fixed molecule and its  $i$ -th neighbor.

The quantity  $\bar{m}$ , as has been mentioned previously, is equal to the moment of the small sphere surrounding the fixed molecule and must be evaluated taking into account the discrete nature of the particles surrounding the given molecule. Therefore, in the present state of the theory of the structure of liquids it is necessary to use some definite model for the evaluation of  $\bar{\mu}_0$  and  $\bar{m}$ .

Coming back to the model proposed by Onsager in which there are no short range interactions we consider the equation proposed by Buckingham:

$$\bar{\mu}_0 = \mu_0^2. \quad (108)$$

In this case the moment  $\bar{m}$  represents the moment of the molecule in the condensed phase if its immediate surroundings are treated as a continuous medium of dielectric permittivity  $\epsilon$ , i.e.,

$$m = \frac{(2\epsilon + 1)(\epsilon_\infty + 2)}{3(2\epsilon + \epsilon_\infty)} \mu_0. \quad (109)$$

Therefore

$$\mu_0 \bar{m} = \frac{(2\epsilon + 1)(\epsilon_\infty + 2)}{3(2\epsilon + \epsilon_\infty)} \mu_0^2 \quad (110)$$

and  $\overline{\mu_{0i} M'} = 0$ .

The fundamental equation reduces to Onsager's equation

$$\frac{4\pi N\mu_0^2}{9kTV} = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2}. \quad (111)$$

If we take the short range molecular forces into account and in the evaluation of the quantity  $\bar{m}$  utilize Onsager's model, then Eq. (111) assumes the form

$$\frac{4\pi N\mu_0^2 g}{9kTV} = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2}, \quad (112)$$

which agrees with Fröhlich's equation (63) and with

the corrected (on the basis of proper averaging) Harris-Alder equation (84).

As Buckingham<sup>24</sup> points out, Onsager's relation between  $m$  and  $\mu_0$  is a sufficiently good approximation for many polar liquids. The investigation of the effect of fluctuations on the value of the dipole moment in the condensed phase carried out by Harris,<sup>21</sup> also indicates the possibility of using this approximation in evaluating the dielectric polarization of polar systems.

Thus, the analysis of the theoretical papers carried out above enables us to make the following conclusions:

1. The theories of dielectric polarization based on statistical mechanics provide a possibility in principle of determining the intermolecular interaction.

2. Of all the theories examined, Kirkwood's is the least accurate, for in it the polarization due to deformation has been incorrectly calculated. Therefore, at present Kirkwood's equation is rarely used in calculations of dielectric polarization. The papers of Fröhlich, Harris and Alder, and Buckingham represent in this respect a considerable step forward in the development of the statistical theory of polarization.

3. The present state of the theory of the structure of liquids requires the use of some models for the calculation of the polarization due to deformation and of the dipole moment in the condensed phase (model of the molecule due to Onsager, Fröhlich), and this leads to less general and rigorous equations for the evaluation of the polarization of real systems.

4. The discrepancies between the equations obtained by Fröhlich and by Harris and Alder were due to the incorrect statistical averaging carried out in the theory of Harris and Alder.

5. In evaluating the polarization of polar dielectrics one should use Fröhlich's equation (68) which agrees with the Harris-Alder equation (108) obtained on the basis of correct averaging, and with Eq. (112) proposed by Buckingham. If we consider the case when short range molecular interaction is absent then all the proposed relationships reduce to Onsager's equation.

#### 4. APPLICATION OF THE THEORIES OF POLARIZATION TO THE INVESTIGATION OF MOLECULAR INTERACTION IN CONDENSED SYSTEMS

As has been shown earlier, application of statistical theories of polarization enables us to determine the effective dipole moment and the correlation parameter characterizing the molecular interaction. In some cases it is possible from the value of the correlation parameter  $g$  to draw conclusions with respect to the mutual orientation of the dipoles of neighboring molecules. Polar liquids for which the magnitude of  $g$  differs from unity are often referred to as "associated" liquids. From this point of view the correlation parameter is no less important than the dipole moment. In the case when such a distribution of the mole-

centration of the correlation parameter calculated from the experimental data by means of Kirkwood's theory. This work is of interest from the point of view that in it an attempt has been made to analyze by the method of dielectric polarization the manner in which the molecular interaction varies in polar solutions.

In addition to the investigation of polar liquids the study of molecular interaction in polymers is also of great interest.

In the theoretical papers by O. B. Ptitsyn and T. M. Birshtein,<sup>35</sup> and also by O. B. Ptitsyn and Yu. A. Sharonov<sup>36</sup> it was shown that the value of the effective dipole moment in polymers depends on the internal rotation in polymer chains, which is greatly hindered due to the presence of strong molecular interaction. Therefore, an investigation of the dielectric polarization of polymers enables us to obtain new data on the molecular interaction in these compounds.

We consider in greater detail the use of modern theories of dielectric polarization in the investigation of molecular interaction in polymers. By applying formula (84) or

$$\epsilon - n^2 = \frac{4\pi N}{V} \frac{\epsilon}{(2\epsilon + 1)^2} \frac{2\epsilon + n^2}{kT} \mu^2 g, \quad (116)$$

it is possible on the basis of experimental data to determine the value of the effective dipole moment in the system being studied  $\mu_{\text{eff}}^2 = \mu^2 g$ . As noted previously,  $\mu$  in these formulas characterizes the dipole moment of the molecule in the medium which differs from the dipole moment of the isolated molecule, since an additional dipole moment is induced in the surrounding medium. The dipole moment in the medium can be found from Onsager's theory

$$\mu = \frac{n^2 + 2}{3} \frac{2\epsilon + 1}{2\epsilon + n^2} \mu_0.$$

The quantity  $\mu\sqrt{g} = \mu_{\text{eff}}$  in polymers characterizes the average value of the effective dipole moment evaluated per single monomer unit in the macromolecule. Therefore, the ratio  $(\mu_{\text{eff}}/\mu)^2 = g$  or  $\sqrt{g}$  will characterize the degree of hindrance in the rotation of monomer chains in the polymer due to their interaction. The quantity  $\mu$  is evaluated from the experimental data in terms of  $\mu_0$  — the dipole moment (characterizing the stereochemical structure of the molecular unit in the macromolecule) which can be determined by Debye's method of dilute solutions by studying a low molecular weight compound of similar structure. Hydrated monomers can be utilized for such compounds.

Of particular interest is the investigation of the dielectric polarization and of the effective dipole moments of polymers in solutions at infinite dilution, when there is no interaction between neighboring molecules of the polymer. Under conditions of infinite dilution of a low molecular weight polar system there is no interaction between polar molecules, since a polar molecule is surrounded by nonpolar molecules

of the solvent. As regards the polymer, even at infinite dilution it is not possible to eliminate the interaction between polar groups belonging to the same chain. This must show up in the variation of the effective dipole moment per monomer link in the polymer and of the correlation parameter compared to the same quantities for corresponding low molecular weight compounds (hydrated monomers).

The initial formulas of the statistical theories of polarization can be transformed in the case of infinite dilution of a polar substance in a nonpolar solvent:

$$\begin{aligned} \frac{kT}{4\pi N_A} \left\{ \frac{(\epsilon_1 - 1)(2\epsilon_1 + 1)}{\epsilon_1} \left[ M_1 \left( \frac{dv_1}{dx_2} \right)_{x_2=0} - M_1 V_1 + M_2 V_1 \right] \right. \\ \left. + M_1 V_1 \frac{2\epsilon_1^2 + 1}{\epsilon_1^2} \left( \frac{d\epsilon}{dx_2} \right)_{x_2=0} - \frac{6V_1(n_1^2 - 1)^2}{(2\epsilon_1 + n_1^2)^2} \left( \frac{d\epsilon}{dx_2} \right)_{x_2=0} \right. \\ \left. + \frac{3(2\epsilon_1 + 1)(n_1^2 - 1)}{2\epsilon_1 + n_1^2} V_1 \right. \\ \left. - \frac{3(2\epsilon_1 + 1)(n_2^2 - 1)}{2\epsilon_1 + n_2^2} V_2 \right\} = \lim (\mu^2 g)_{x_2 \rightarrow 0} = \lim (\mu^2)_{\text{eff}}, \quad (117) \end{aligned}$$

where  $\epsilon_1$  and  $v_1$  are the dielectric permittivity and the specific volume of the solution at infinite dilution,  $M_1$ ,  $V_1$ , and  $n$  are respectively the molecular weight, the molar volume, and the index of refraction. The subscripts 1 and 2 refer to the nonpolar solvent and the polar substance respectively. All these quantities can be determined experimentally.

Let us examine the results of the investigation of the dielectric polarization of polymers and the application to them of statistical theories in the case of several ethers of metacrylic acid, polymethylacrylate, and poly-p-chlorostyrol. In reference 37 the following representatives of the series have been studied: polymethylmetacrylate, polyethylmetacrylate, polypropylmetacrylate, and polybutylmetacrylate. Hydrated monomers — the appropriate ethers of isobutyric acid — were used for the determination of  $\mu$ . In calculating  $\mu_{\text{eff}}$  for polymethylacrylate we have used for  $\mu_0$  the value of  $\mu_0$  for the methyl ether of propionic acid, in the case of poly-p-chlorostyrol we have taken the corresponding value of  $\mu_0$  for p-chlorotoluol. All the measurements were made in benzene and the results were extrapolated to infinite dilution. The results of the investigations of all the studied compounds, and the quantities characterizing the molecular interaction calculated in accordance with formula (117), are listed in Table III.\* The table lists also the calculated correlation parameter for the hydrated monomers at infinite dilution in the absence of interaction between polar groups, and when the correlation parameter must be equal to unity.

On comparing the results obtained we can see that for all the polymers at infinite dilution in a nonpolar solvent the correlation parameter is smaller than for

\*In reference 37 all the analogous calculations were carried out on the basis of the Harris-Alder formula (62) reduced to infinite dilution.<sup>35</sup>

cules in the liquid is possible that their dipole moments are antiparallel the value of the correlation parameter is less than unity, while in the case of parallel orientation  $g$  is greater than unity. It should be noted that the greatest deviation of the value of the correlation parameter from unity is observed in the case of compounds with hydrogen bonds. This was shown both theoretically and experimentally in references 27 and 28, in which the dielectric polarization of a number of alcohols was studied. However, for a number of substances which have no hydrogen bonds the value of the correlation parameter also differs from unity. These results support the hypothesis that in the case of polar liquids it is necessary to take short range forces into account in calculating the polarization.

The calculation of the theoretical value of  $g$  has turned out to be possible for a number of aliphatic alcohols, since x-ray spectroscopic data are available on the structure of these compounds. The x-ray spectrograms of the alcohols have led to the conclusion that for them the average coordination number is equal to two. Therefore, we can assume that alcohol molecules form chains, owing to the presence of hydrogen bonds in them. This assumption was used as the basis of the theoretical calculation of the correlation parameter  $g$  carried out by Oster and Kirkwood.<sup>27</sup> These authors assume that each molecule of alcohol is a link in an infinite chain and that the correlation in the orientation exists only along the chain. It was assumed that the rotation about the hydrogen bond is free.

On the basis of this model

$$g = 1 + 2 \sum_{n=1}^{\infty} \overline{\cos \gamma_n}, \quad (113)$$

where  $\gamma$  is the angle between the dipole moment of the given molecule and the dipole moment at a distance of  $n$  bonds. At the same time

$$\overline{\cos \gamma_n} = f \left( \cos^2 \frac{\theta}{2} \right)^n, \quad f = \frac{(\mu_H + \mu_R)(\mu_H + \mu_R \cos \theta)}{(\mu_H^2 + \mu_R^2 + 2\mu_H \mu_R \cos \theta)}, \quad (114)$$

where  $\mu_H$  and  $\mu_R$  are the dipole moments of the OR, OH bonds and  $\theta$  is the angle between these bonds assumed to be equal to  $105^\circ$ . On carrying out the summation for an infinite chain we obtain

$$g = 1 + 2f \operatorname{ctg}^2 \frac{\theta}{2}. \quad (115)^*$$

For all the aliphatic alcohols the value  $g = 2.57$  was found.

The values of the correlation parameter obtained in the study of the dielectric polarization in a number of alcohols are given in Table I. The discrepancy between the values of  $g$  calculated on the basis of a definite structural model and those obtained from the investigation of the dielectric polarization must be attributed to the approximations used in the course of the calculation. The inclusion of correlation in the orientation of neighboring chains, and also of hindered

\*ctg = cot.

rotation about the bonds, should alter the calculated value of  $g$ .

At the same time we should note the large value of the parameter  $g$  (with  $g > 1$ ). This indicates the high degree of correlation between the alcohol molecules due to the existence of hydrogen bonds which leads to the parallel orientation of dipole moments.

In contrast to compounds with hydrogen bonds, in a number of polar liquids the quantity  $g$  can be less than unity. As has been shown in reference 30, the replacement in butyl alcohol of the OH radical by a halogen leads to a sharp change in the magnitude of the correlation parameter.

Table\* II gives values of  $g$  for butyl bromide and butyl chloride. The value for butyl alcohol is given for comparison. The results quoted ( $g < 1$ ) indicate that in these compounds there is a correlation in orientation such that the dipole moments are antiparallel and mutually cancel one another.

Table I

Substance, $t = 20^\circ\text{C}$	$g$
Methyl alcohol	3.0
Ethyl alcohol	3.1
Propyl alcohol	3.1
Butyl alcohol	3.3

Table II

Substance	$t, ^\circ\text{C}$	$g$
Butyl alcohol	20	3.3
Butyl bromide	14	0.76
Butyl chloride	13.6	0.85

At the present time there exists a number of articles devoted to the experimental study of the correlation parameter on the basis of the statistical theories of polarization.

The study of the value of  $g$  as a function of temperature and pressure in polar liquids and as a function of concentration in polar solutions is of interest.

In the paper of Harris, Hoycock and Alder<sup>30</sup> a study is made of the variation of intermolecular interaction at different pressures. The effect of temperature on the magnitude of  $g$  was investigated for a number of alcohols in the papers by R. Cole and his co-workers.<sup>28</sup> An investigation of the correlation parameter enables us to draw conclusions with respect to structural changes in the liquid.

One should also note the paper by Heyden, Nicuradze and Ulbreich,<sup>32</sup> in which it was shown that the changes in the correlation parameter of a number of organic mixtures occur in the same direction as the changes of other characteristics determining the intermolecular interaction. A study of the correlation parameter in solutions of polar substances in nonpolar solvents has been carried out in the papers by Oster<sup>33,34</sup> where an investigation is made of the dependence on the con-

\*The calculation of the correlation parameter was carried out on the basis of the data of reference 30 in accordance with formula (84). In the case of n-butyl alcohol  $\mu_0$  is equal to<sup>31</sup> 1.68 D, in the case of n-butyl chloride  $\mu_0$  is equal to 2.11 D, and in the case of n-butyl bromide  $\mu_0$  is equal to 2.15 D.

Table III

Name of compound	$\mu_0 D$	$\sqrt{g}$
Methylmetacrylate	1.78	hydrated monomer { 1.04
		polymer { 0.81
Ethylmetacrylate	1.85	hydrated monomer { 1.00
		polymer { 0.77
Propylmetacrylate	1.89	hydrated monomer { 1.02
		polymer { 0.80
Butylmetacrylate	1.88	hydrated monomer { 1.00
		polymer { 0.81
Methylacrylate	1.75	hydrated monomer { 1.00
		polymer { 0.81
Poly-p-chlorostyrol p-chlorotoluol	1.96	hydrated monomer { 1.00
		polymer { 0.68

the low molecular weight compounds under the same conditions. In this case the decrease in the correlation parameter is associated with the existence of interaction between polar links of the polymer molecule. This interaction leads to some orientation of polar links, as a result of which the effective moment referred to a monomer link is reduced. If there is no interaction between polar links then the magnitude of the correlation parameter approaches the value obtained in the hydrated monomers at infinite dilution in a nonpolar solvent.

The study of the dielectric polarization of polymers in bulk and the comparison of the effective dipole moments obtained in this manner with dipole moments of the same systems in solution can tell us whether the method of dielectric polarization provides information on the interaction between polar groups of neighboring chains of macromolecules. The method of determining the effective dipole moments of polymers in the highly elastic state is described in reference 36. Table IV

Table IV

Name of polymer	$\sqrt{g}$	
	in solution	in highly elastic state
Polymethylmetacrylate	0.81	0.85
Polypropylmetacrylate	0.80	0.86
Polybutylmetacrylate	0.81	0.85
Polymethylacrylate	0.81	0.84
Poly-p-chlorostyrol	0.68	0.67

gives the calculated correlation parameters for a number of polymers in the highly elastic state and of comparing them with the same quantities in the case of solutions.

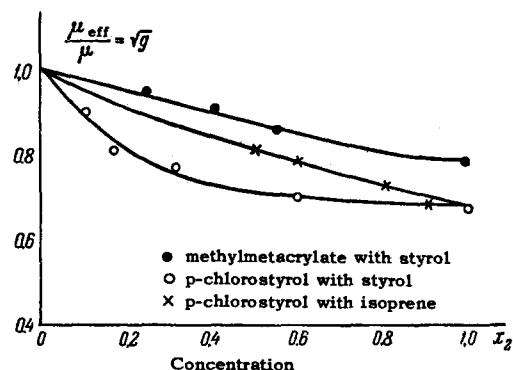
From the data quoted it can be seen that quantities characterizing the molecular interaction differ but little from one another. This shows that there is no correlation between the polar groups of different

macromolecules in a polymer in a highly elastic state. The data obtained provide evidence on the dominant effect of the intramolecular interaction in macromolecules on the highly elastic properties of the polymer.

In investigating the effect of the interaction between polar groups belonging to the same chain on the dielectric polarization the copolymers of a polar monomer and a nonpolar one are of great interest.

As is well known, the relative positions of the different monomer links in a copolymer are determined by statistical probability, and must therefore be just as uniform as in the case of solutions. A study of copolymers in which the concentration of the polar component varies within wide limits enables us to study polymer chains in which we can alter the interaction between polar groups. At high concentrations of the polar component it is not possible to eliminate the interaction of the polar groups along the chain. At the same time, at relatively low concentrations the polar groups of the same polymer chain are separated by nonpolar links, i.e., in this case we can take into account conditions which exist in low molecular weight compounds at infinite dilution in a nonpolar solvent.

It was shown<sup>36</sup> in the study of the system methylmetacrylate-styrol that by varying the percentage composition of the polar component in a copolymer the value of the effective dipole moment is altered. The diagram shows the dependence on the concentration



Dependence of the correlation parameter on concentration.

of the correlation parameters for the copolymers that have been studied. The correlation parameter varied from the value characterizing the polymer to the correlation parameter for the monomer at infinite dilution in a nonpolar solvent. This supports the point of view stated above, i.e., at low concentrations of the polar component the polar groups are separated from each other and, therefore, there is practically no interaction between them, just as in solutions of low molecular weight compounds at low concentrations of the polar component. As the concentration of the polar monomer in a copolymer is increased, the interaction between the polar groups in the chain increases, and the dependence of the correlation parameter on the concentration characterizes the change in the molecular interaction as a function of the structure of the chain of the copolymer. The results obtained show

that this method is sufficiently sensitive for the analysis of the distribution of polar groups in the chain of a copolymer and enables us to trace the alternation of the polar and the nonpolar components in a copolymer.

On the other hand, a comparison of the results obtained for different copolymers enables us to analyze the interaction in a polymer chain. From this point of view we have investigated the dielectric polarization of copolymers of two types: p-chlorostyrol with styrol, and p-chlorostyrol with isoprene.

The investigation of these systems is of great interest since the polar component in both copolymers is the same, i.e., the dipole moment  $\mu_0$  characterizing the stereochemical structure of the monomer link of the polar polymer is the same. At the same time, the chains have a completely different structure, due to the difference in the nonpolar components, and, therefore, we can expect differences in the values of the effective dipole moment characterizing the molecular interaction.

The diagram shows the experimentally obtained dependence of the correlation parameter on the concentration. Just as in the case of methylmetacrylate and styrol, graphs are obtained for both types of copolymers characterizing the gradual transition from systems in which there is no interaction between polar groups (this occurs in the investigation of a low molecular weight compound at infinite dilution in a nonpolar solvent where the polar groups are practically uncorrelated) to the polymer in which it is impossible to eliminate the interaction of polar groups belonging to the same chain. At the same time, by analyzing the curves obtained we can see that the difference in the structure of the copolymers has affected the value of the correlation parameter characterizing the molecular interaction in the polymer. At the same molar concentration (for example,  $x_2 = 0.5$ , when we can assume that on the average each polar group alternates with a nonpolar one) the correlation parameter is larger for the copolymer of p-chlorostyrol with isoprene, than in the case of p-chlorostyrol with styrol. From the general assumptions of the theory of polarization we can see that an increase in the correlation parameter indicates a decrease in the molecular interaction in the polymer. On the basis of the structure of the copolymers investigated, the decrease in the molecular interaction between the polar groups in the copolymer of p-chlorostyrol with isoprene can be explained by an increase in the distance between the polar groups due to the larger number of carbon atoms in an isoprene molecule.

Thus, the analysis of the data quoted shows that an investigation of the dielectric polarization of polymers opens up great possibilities for the investigation of intramolecular interaction in polymers.

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