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THE INTRAMOLECULAR FIELD AND THE DIELECTRIC CONSTANT

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ABSTRACT

A statistical calculation of the average internal field in a dielectric is carried out. The following relation is obtained between the dielectric constant, ϵ, and the molecular polarizability, p_0:

$$\frac{\epsilon-1}{\epsilon+2}V=\frac{4\pi Np_0}{3}\,\frac{1}{1-\lambda_0\rho}$$

where V is the molal volume, ρ is the density and

$$\lambda_0=\frac{32\pi^2N^2p_0^2}{45B}\left(1+\frac{1}{3}\,\frac{A}{BRT}\right).$$

Here A and B are the constants of a van der Waal type equation of state. This expression becomes identical with the familiar Clausius-Mosotti relation in the limit of zero density. The formula is applied to dielectric constant measurements on several gases.

INTRODUCTION

THE concept of the dielectric constant rests upon a simple empirical basis. Faraday's experiments suggested that the intensity of the field arising from a given distribution of charge was less in a material substance than in free space. There was, moreover, evidence that the field intensity in a non-conducting substance was proportional to the original field intensity in free space. These facts were formulated in the following equation:

$$D=\epsilon E \tag{1}$$

where D, the dielectric displacement, is most simply interpreted as the field intensity existing in free space for the given charge distribution and E is the field intensity arising from the same distribution in a substance of dielectric constant ϵ. In view of the molecular character of the dielectric, it is clear that the measured field E is an average value, for macroscopic measuring systems are incapable of detecting the fluctuations in E occurring in the intervals of space and time associated with the thermal motion of the molecules. The fluctuations in the molecular configuration must, nevertheless, play an important part in determining the average polarization of the moving molecules constituting the dielectric.

Before it is possible to correlate the dielectric constant with the polarizability of the molecules, it is necessary to calculate the average value of the

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field effective in polarizing a molecule. Moreover, it is evident that the average internal field, referred to the moving molecule will not be identical with the field E referred to a point fixed relative to the external measuring system.

The Clausius-Mosotti relation is usually accepted as giving the relation between the dielectric constant of a substance and the polarizability of its constituent molecules. The computation of the internal field which leads to this formula purports to be based upon molecular considerations, but in the analysis, use is made of the device of a spherical cavity excised about the molecule. This seems justifiable only when the dielectric material is considered to be a continuum. The empirical success of the resulting formula in no way answers the logical objections to this analysis. For this reason, the use of the Clausius-Mosotti relation except in the case of gases at low density, where it has received adequate empirical confirmation, has been attended by great uncertainty.

There is here presented a statistical calculation of the average internal field leading to a formula which becomes identical with the Clausius-Mosotti relation in the limit of zero density, but which deviates somewhat from it at higher densities.

LIMITATIONS OF THE CASE CONSIDERED AND DERIVATION OF DIELECTRIC CONSTANT FORMULA

The considerations to follow will be restricted to the relatively simple case of a gas of sufficiently low density so that the probability of molecular encounters involving more than two molecules is insignificantly small; and to temperatures sufficiently high so that an inappreciable fraction of the molecules are in quantized collision states such as may occur in molecular aggregation. Under these conditions the molecules may be regarded as continuously distributed in configuration, and moreover, the potential energy may be expressed as a sum of terms involving the relative coördinates of only two molecules.

It is desired to investigate the effect on the molecules constituting the fluid of an homogeneous external electric field. Take for consideration the region between the parallel plates of a condenser assumed to be filled with a fluid in equilibrium consisting of $n+1$ molecules of identical polarizability. Select for observation a molecule j not in the immediate neighborhood of the boundaries. The instantaneous and total field F_j acting on j may be written,

$$F_j = D + F_j' \tag{2}$$

where, as before, D, the dielectric displacement, is the field arising from the external charge distribution on the condenser plates and F_j' is the field arising from the other molecules of the dielectric. If, however, F_{jk}' is the field arising from an arbitrary molecule k we may write,

$$F_j' = \sum_{k=1}^{n} F_{jk}'. \tag{3}$$

The average value of any F_{jk}' term may be written:

$$\bar{\bar{F}}_{jk}' = \frac{\int \cdots \int F_{jk}' e^{-u^*/kT} d\tau_1 \cdots d\tau_n}{\int \cdots \int e^{-u^*/kT} d\tau_1 \cdots d\tau_n} \tag{4}$$

where u^* is the total potential energy of the system and $d\tau_1$ is an element of the complete configuration space of a single molecule. The integration is to be extended over all of configuration space available to the molecules.

It will occasionally be convenient to consider F_{jk}' as averaged only over the orientations of the molecules, designated by $\overline{F_{jk}'}$, while the final average of $\overline{F}_{jk}'$ over all configurations of the centers of gravity of the molecule will be denoted by $\bar{\bar{F}}_{jk}'$.

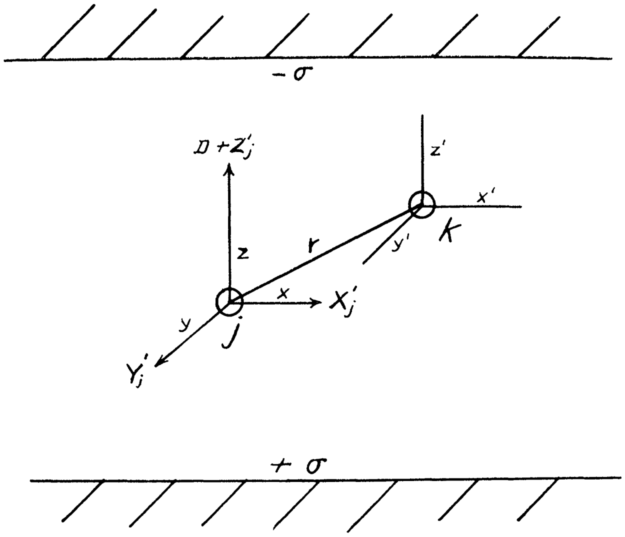

Fig. 1.

We proceed to calculate F_{jk}', the molecular field acting on the molecule j originating in an arbitrary molecule k. Choose a system of rectangular coördinates (x, y, z) whose origin is at the center of gravity of j and z axis parallel to the vector D. Similarly choose a second system (x', y', z'), with origin at the center of gravity of k with axes parallel to (x, y, z) see Fig. 1.

Suppose molecule k to consist of an assembly of charges $e_1 \cdots e_i$ whose average positions in the isolated molecule are given by the coordinates x_{1o}', y_{1o}', $z_{1o}' \cdots x_{io}'$, y_{io}', z_{io}'. When a field is present it will be assumed that the perturbed positions, x_i', y_i', z_i' are given by

$$\begin{aligned} x_i' &= x_{i0}' + f_i X_k \\ y_i' &= y_{i0}' + f_i Y_k \\ z_i' &= z_{i0}' + f_i Z_k \end{aligned} \tag{5}$$

where the f_i's are constants and X_k, Y_k, Z_k are the components of the field acting on k. By expanding the potential at the center of j due to all the charges constituting k in a series of powers of x_i', y_i', z_i' there results for the potential ϕ_{jk}'.

$$\begin{aligned}\phi_{jk}' = {} & \sum\frac{e_i}{r} - \frac{1}{r^2}\left[\frac{x}{r}\sum e_i x_i' + \frac{y}{r}\sum e_i y_i' + \frac{z}{r}\sum e_i z_i'\right] \\ & + \frac{1}{2r^3}\left[\left(\frac{3x^2}{r^2}-1\right)\sum e_i x_i'^2 + \left(\frac{3y^2}{r^2}-1\right)\sum e_i y_i'^2\right. \\ & + \left(\frac{3z^2}{r^2}-1\right)\sum e_i z_i'^2 + 6\frac{xy}{r^2}\sum e_i x_i' y_i' + 6\frac{xz}{r^2}\sum e_i x_i' z_i' \\ & \left. + 6\frac{yz}{r^2}\sum e_i y_i' z_i'\right] + \cdots \end{aligned} \tag{6}$$

of which the first term is zero for a neutral molecule. Here x, y, and z represent the coordinates of the center of gravity of k relative to j and r is the separation of the centers. We assume that the field, F_{jk}', defined by this potential may be regarded as homogeneous over the small region occupied by a molecule. For its z component we may write

$$\begin{aligned}Z_{jk}' = {} & -\frac{\partial\phi_{jk}'}{\partial(-z)} = \frac{1}{r^3}\left[\left(\frac{3z^2}{r^2}-1\right)\sum e_i z_i' + \frac{3xz}{r^2}\sum e_i x_i' + \frac{3yz}{r^2}\sum e_i y_i'\right] \\ & - \frac{1}{2r^4}\left[\left(15\frac{z^3}{r^3} - 9\frac{z}{r}\right)\sum e_i z_i'^2 + \left(15\frac{x^2 z}{r^3} - 3\frac{z}{r}\right)\sum e_i x_i'^2\right. \\ & + \left(15\frac{y^2 z}{r^3} - 3\frac{z}{r}\right)\sum e_i y_i'^2 + \left(30\frac{xz^2}{r^3} - 6\frac{x}{r}\right)\sum e_i x_i' z_i' \\ & \left. + \left(30\frac{yz^2}{r^3} - 6\frac{y}{r}\right)\sum e_i y_i' z_i' - 30\frac{xyz}{r^3}\sum e_i x_i' y_i'\right] + \cdots . \end{aligned} \tag{7}$$

Using this expression for Z_{jk}' in Eq. (4) and integrating over all possible molecular orientations[1] we obtain

$$\bar{\bar{Z}}_{jk}' = \frac{\int \cdots \int \overline{Z_{jk}'} e^{-u/kT} dx_1 dy_1 dz_1 \cdots dx_n dy_n dz_n}{\int \cdots \int e^{-u/kT} dx_1 dy_1 dz_1 \cdots dx_n dy_n dz_n} \tag{8}$$

where u is that part of the potential energy dependent upon the configuration of the centers of gravity of the molecules, $x_1 \cdots z_n$. With the aid of Eq. (4) we may express $\bar{Z}_{jk}'$, the value of Z_{jk}' averaged over all orientations of the molecules with respect to their centers of gravity as

[1] P. Debye, Polar Molecules, 27 (1929).

$$\overline{Z}_{jk}' = \frac{\beta_1}{r^3} + \frac{\beta_2}{r^4} + \cdots = \sum_{m=1}^{\infty} \frac{\beta_m}{r^{m+2}} \tag{9}$$

where

$$\begin{aligned}
\beta_1 &= p_0[(3z^2/r^2 - 1)\overline{Z}_k + 3xz\,\overline{X}_k/r^2 + 3yz\overline{Y}_k/r^2] \\
\beta_2 &= \tfrac{1}{2}k_0[(15z^3/r^3 - 9z/r)\overline{Z_k}^2 + (15x^2z/r^3 - 3z/r)\overline{X_k}^2 \\
&\quad + (15y^2z/r^3 - 3z/r)\overline{Y_k}^2 + (30xz^2/r^3 - 6x/r)\overline{X_kZ_k} \\
&\quad + (30yz^2/r^3 - 6y/r)\overline{Y_kZ_k} - 30xyz\overline{X_kY_k}/r^3]
\end{aligned}$$

and $p_0 = \alpha + \mu^2/3kT$

$$k_0 = \sum e_i f_i^2 + \frac{2\mu}{3kT}\sum e_i r_{i0} f_i + \frac{\mu^2}{15k^2T^2}\sum e_i r_{i0}^2.$$

Here α is the sum of the electronic and atomic polarizabilities, $\sum e_i f_i$, μ is the permanent electric moment of the molecule, r_{i0} the distance of the charge e_i from the center of gravity of the molecule k, k is Boltzmann's constant and T the absolute temperature. $\overline{X}_k$, $\overline{Y}_k$, $\overline{Z}_k$, etc., are the components of the field acting on k, averaged over all molecular orientations.

We shall write Eq. (9) in a slightly different manner:

$$\overline{Z}_{jk}' = \left\{\frac{\beta_1'}{r^3} + \frac{\beta_2'}{r^4} + \cdots\right\} + \left\{\frac{\beta_1''}{r^3} + \frac{\beta_2''}{r^4} + \cdots\right\} \tag{10}$$

where β_1', β_2' $\cdots$ are formed by replacing $\overline{Z}_k$, $\overline{X}_k$, $\overline{Y}_k$ etc. in β_1, β_2, by their average values $\overline{\overline{Z}}_k$, $\overline{\overline{X}}_k$, $\overline{\overline{Y}}_k$. Likewise, β_1'', β_2'', are formed by replacing these quantities in β_1, β_2 $\cdots$ by the fluctuations from their average values, $\overline{Z}_k - \overline{\overline{Z}}_k$, $\overline{X}_k - \overline{\overline{X}}_k$, $\overline{Y}_k - \overline{\overline{Y}}_k$, etc. It is apparent that the first series on the right hand side of Eq. (10) gives the magnitude which $\overline{Z}_{jk}'$ would have if the molecule k remained rigidly polarized by the average field $\overline{\overline{F}}_k$ throughout all configurations of the centers of gravity of the molecules. The second series gives the contribution to $\overline{Z}_{jk}'$ resulting from the fluctuation of $\overline{F}_k$ from its average value $\overline{\overline{F}}_k$.

From Eqs. (2) and (3) we have

$$Z_j' = \sum_{k=i}^{n} Z_{jk}'$$

and

$$\overline{\overline{Z}}_j' = \sum_{k=1}^{n} \overline{\overline{Z}}_{jk}'. \tag{11}$$

Moreover, it is evident that all of the $\overline{\overline{Z}}_{jk}'$ must be identical, since the molecule k was selected at random from the n molecules surrounding j. Therefore

$$\overline{\overline{Z}}_j' = n\overline{\overline{Z}}_{jk}. \tag{11a}$$

From Eqs. (8), (10) and (11) we obtain

$$\bar{\bar{Z}}_j = I_1 + I_2$$

where

$$I_1 = n\frac{\int \cdots \int \left(\sum_{m=1}^{\infty} \beta_m'/r^{m+2} \right) e^{-u/kT} dx_1 dy_1 dz_1 \cdots dx_n dy_n dz_n}{\int \cdots \int e^{-u/kT} dx_1 dy_1 dz_1 \cdots dx_n dy_n dz_n}$$

$$I_2 = n\frac{\int \cdots \int \left[\sum_{m=1}^{\infty} \beta_m''/r^{m+2} \right] e^{-u/kT} dx_1 \cdots dz_n}{\int \cdots \int e^{-u^0/kT} dx_1 \cdots dz_n}.$$

The potential energy of the system may be written

$$u = \tfrac{1}{2} \sum_{j=1}^{n} \sum_{k=1}^{n} (u_{jk}^0 + u_{jk}')$$

where u_{jk}^0 is the normal potential energy of two molecules j and k which has been assumed to depend only upon the relative coordinates of the two, and u'_{jk} is the additional energy when there is an external field present.

It is easily shown that for weak fields, u_{jk}' is always so small relative to kT, that it may be neglected in the evaluation of the integrals of Eq. (10). It will therefore suffice to consider u as given by the normal potential energy u_{jk}^0.[I]

Note I. If $\bar{m}_j$ and $\bar{m}_k$ designate the electric moments of j and k along the z axis, averaged over all molecular orientations, then there may be written approximately, neglecting a term which is constant throughout the region considered.

$$u_{jk}' = -\frac{\bar{m}_j \bar{m}_k}{r^s} \left\{ \frac{2z^2}{r^3} + \frac{\alpha}{r^3} \left(\frac{3z^2}{r^2} + 1 \right) \right\} \tag{a}$$

where

$$\bar{m}_j = p_0(D + \bar{\bar{F}}_j') \qquad \bar{m}_k = p_0(D + \bar{F}_k').$$

We may anticipate the result of the calculation of $\bar{\bar{F}}_j'$ by assigning to it the approximation $-(8\pi/3)\rho N p_0 D$, where ρ is the density. Also approximately

$$[\overline{(\bar{F}_j' - \bar{\bar{F}}_j')^2}]^{1/2} = \frac{8\pi}{3} N p_0 D \left(\frac{3\rho}{4\pi N \sigma^s} \right)^{1/2}$$

where σ is the distance of nearest approach of two molecules. It may therefore be safely assumed that m_j and m_k are in general of the order of magnitude of $p_0 D$. Thus from Eq. (a), the maximum value assignable to $|u_{jk}'|$ is the order of magnitude of

$$|u_{jk}| = (2p_0^2 D^2/\sigma^3)(2 + \alpha/\sigma^3).$$

For hydrogen at 300°K we have

$$kT = 4.11 \times 10^{-14} \text{ ergs}$$
$$p_0 = \alpha = 8 \times 10^{-25} \text{ cc}$$
$$\sigma = 2.3 \times 10^{-8} \text{ cm}.$$

For a value of D of 900 volts/cm, there results:

$$|u_{jk}'|/kT \backsim 4 \times 10^{-10}.$$

. . . .

Since the series

$$\beta_1'/r^3 + \beta_2'/r^4 + \cdots$$

depends only upon the relative coördinates of j and k, the first integral I_1 becomes

$$I_1 = n\frac{\int\int\int\left(\sum_{m=1}^{\infty}\beta_m'/r^{m+2}\right)e^{-u^0{}_{jk}/kT}dx_kdy_kdz_k}{\int\int\int e^{-u^0{}_{jk}/kT}dx_kdy_kdz_k}.$$

In evaluating the latter integral it will be sufficient to employ the van der Waal's or rigid-sphere molecular model. It is assumed then, that the molecules have spherical symmetry relative to the coordinate system fixed in space by the vector D. Lack of spherical symmetry resulting from the orientation of a permanent dipole in the molecule, as well as from the induced deformation of the average configuration of the charges constituting the molecule, will be negligible unless the external field is very large. It will be further assumed that a distance of nearest approach, σ, exists such that

$$u_{jk}{}^0 = \infty \text{ for } r_{jk} \leqq \sigma$$

When $r_{jk} > \sigma$, $e^{-u_{jk}{}^0/kT}$ is to be expanded as

$$1 + \sum_{s=1}^{\infty}\frac{1}{S!}\left(-\frac{u_{jk}{}^0}{KT}\right)^s.$$

The evaluation of I_1 leads to the result

$$I_1 = -\frac{8\pi}{3}n\frac{p_0}{V}\bar{\bar{Z}}_k.$$

If $I_2 = \lambda\bar{\bar{Z}}_k$ there results,

$$\bar{\bar{Z}}_j' = -\bar{\bar{Z}}_k\left(\frac{8\pi}{3}\frac{n}{V}p_0 - \lambda\right).$$

There is no physical distinction between molecules j and k and accordingly $\bar{\bar{Z}}_j$ and $\bar{\bar{Z}}_k$ must be equal.[II]

Note II. First make the approximation

$$\int\int\int e^{-u_{jk}^0/kT}dx\,dy\,dz$$

where V is the total volume between the plates of the condenser. It will differ from the above integral only by a quantity of the order of magnitude of the volume of a single molecule. After transforming to polar coordinates we obtain:

$$I_1 = \frac{np_0}{V}\int_0^{2\pi}\left[\int_0^{\pi/2}\int_\sigma^{z_1\sec\theta} + \int_{\pi/2}^{\pi}\int_\sigma^{z_2\sec\theta}\right]\left\{\frac{\beta_1'}{r}+\frac{\beta_2'}{r^2}+\cdots\right\}$$
$$\left\{1+\sum_{s=1}^{\infty}\frac{1}{s!}\left(-\frac{u_{jk}^0}{kT}\right)^s\right\}dr\sin\theta d\theta d\phi$$

where z_1 and z_2 are the distances of the molecule j from the two plates of the condenser.

It is possible to expand u_{jk}^0 in powers of $1/r$ of which the dominant term is a/r^6.[2]
It is therefore obvious that when the multiplication indicated in the integrand is carried out, all terms except β_1'/r will contain $1/r$ to the second or higher powers. The contribution of these terms to the integral will decrease so rapidly with r that we may safely take the upper limit in the integration over r as ∞. We then may write

$$I_1 = \frac{np_0}{V}\int_0^{2\pi}\left[\int_0^{\pi/2}\int_\sigma^{z_1\sec\theta} + \int_{\pi/2}^{\pi}\int_\sigma^{z_2\sec\theta}\right]\frac{\beta_1'}{r}\sin\theta d\theta dr d\phi + \frac{np_0}{V}\int_\sigma^{\infty}\int_0^{2\pi}\int_0^{\pi}\frac{\beta_1'}{r}\sum_{s=1}^{\infty}\frac{1}{s!}\left(-\frac{u_{jk}^0}{kT}\right)^s$$
$$+\left\{\frac{\beta_2'}{r^2}+\cdots\right\}\left\{1+\sum_{s=1}^{\infty}\frac{1}{s!}\left(-\frac{u_{jk}^0}{kT}\right)^s\right\}\sin\theta d\theta d\phi dr.$$

It is to be remembered that u_{jk}^0 is independent of θ and ϕ, since it has spherical symmetry around j because of the averaging over all mutual orientations of j and k. Moreover, each of the coefficients β_1', β_2', $\cdots$ satisfies the relation

$$\int_0^{2\pi}\int_0^{\pi}\beta_m'\sin\theta d\theta d\phi = 0.$$

It follows that through integration over the angles the second integral vanishes term by term and there remains when we insert the value of β_1'

$$\frac{np_0}{V}\int_0^{2\pi}\left[\int_0^{\pi/2}\int_\sigma^{z_1\sec\theta} + \int_{\pi/2}^{\pi}\int_\sigma^{z_2\sec\theta}\right]\left\{\bar{\bar{Z}}_k(3\cos^2\theta-1)+3\bar{\bar{X}}_k\sin\theta\cos\phi\right.$$
$$\left.+3\bar{\bar{Y}}_k\sin\theta\sin\phi\right\}\sin\theta d\theta\frac{dr}{r}d\phi$$

Integration over r and ϕ yields

$$\frac{2\pi n}{V}p_0\bar{\bar{Z}}_k\left\{-\int_0^{\pi}(3\cos^2\theta-1)\log\cos\theta\sin\theta d\theta+\int_0^{\pi/2}(3\cos^2\theta-1)\log\frac{\sigma}{z_1}\sin\theta d\theta\right.$$
$$\left.+\int_{\pi/2}^{\pi}(3\cos^2\theta-1)\log\frac{\sigma}{z_2}\sin\theta d\theta\right\} = -\frac{8\pi}{3}\frac{np_0}{V}\bar{\bar{Z}}_k.$$

It is to be noted that this quantity is independent both of z_1 and z_2 as well as of σ.

The subscripts may therefore be neglected and the average value of the Z-component of the internal field becomes, if it is remembered that $Z=Z'+D$ (Eq. 4).

$$\bar{\bar{Z}} = \frac{D}{1+\frac{8\pi}{3}\frac{n}{V}p_0-\lambda}\cdot \tag{13}$$

A similar calculation shows that $\bar{\bar{Y}}_j$ and $\bar{\bar{X}}_j$ vanish, and the average value of the resultant internal field F is merely,

$$\bar{\bar{F}} = \frac{D}{1+\frac{8\pi}{3}\frac{n}{V}p_0-\lambda} \tag{14}$$

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[2] Eisenschitz and London, Zeits. f. Physik, **60**, 491 (1930).

This equation when combined with the usual classical relations,

$$D = \epsilon E$$

$$D = E + 4\pi P$$

$$P = \frac{n}{V} p_0 \bar{\bar{F}}$$

gives;

$$\frac{\epsilon - 1}{\epsilon + 2} V = \frac{4\pi}{3} N p_0 \frac{1}{1 - \lambda} \tag{15}$$

where v is the molal volume and ϵ is the dielectric constant. Equation (15) reduces to the familiar Clausius-Mosotti relation

$$\frac{\epsilon - 1}{\epsilon + 2} v = \frac{4\pi}{3} N p_0 \tag{16}$$

only if λ is identically zero for all temperatures and pressures. This is not in general true. The quantity λ is a measure of the contribution of the fluctuations in $\bar{F}$. It will be shown that λ is proportional to the density as long as only binary molecular encounters need be considered. For very dense gases, on the other hand, the effect of the fluctuations is less important and λ will be smaller than the formula indicates.

In evaluating the quantity λ it will be sufficient to retain only the dipole term in the $\bar{Z}_{jk}'$ series. It will be conveneint to make use of the identity

$$\bar{Z}_k - \bar{\bar{Z}}_k = \sum_{l=1}^{n-1} (\bar{Z}_{kl}' - \bar{\bar{Z}}_{kl}') + \bar{Z}_{kj}' - \bar{\bar{Z}}_{kj}'$$

λ may then be written

$$\frac{n}{\bar{\bar{Z}}} \frac{\int \cdots \int \psi e^{-u/kT} dx_1 \cdots dz_n}{\int \cdots \int e^{-u/kT} dx_1 \cdots dz_n}$$

where

$$\psi = \frac{p_0}{r^3} \left\{ \left(\frac{3z^2}{r^2} - 1 \right) \left[\sum_{l=1}^{n-1} (\bar{Z}_{kl}' - \bar{\bar{Z}}_{kl}') + (\bar{Z}_{kj}' - \bar{\bar{Z}}_{kj}') \right. \right.$$
$$+ \frac{3xz}{r^2} \left[\sum_{l=1}^{n-1} (\bar{X}_{kl}' - \bar{\bar{X}}_{kl}') + (\bar{X}_{kj}' - \bar{\bar{X}}_{kj}') \right]$$
$$\left. + \frac{3yz}{r^2} \left[\sum_{l=1}^{n-1} (\bar{Y}_{kl}' - \bar{\bar{Y}}_{kl}') + (\bar{Y}_{kj}' - \bar{\bar{Y}}_{kj}') \right] \right\}.$$

If the integration over the coordinates of all the l molecules is carried out under the assumption that each of the $\bar{Z}_{kl}$ terms is independent of the relative positions of j and k, there results (consistent with the original postulate of binary encounters)

$$\lambda = \frac{n}{\bar{\bar{Z}}V}\int\int\int\frac{p_0}{r^3}\left[\left(\frac{3z^2}{r^2}-1\right)(\bar{Z}_{kj}'-\bar{\bar{Z}}_{kj}') + \frac{3xz}{r^2}\quad\bar{X}'_{kj}\ \frac{3yz}{r^2}\bar{Y}'_{kj}\right]e^{-u_{jk}/kT}dxdydz$$

where $\bar{X}_{kj}'$, $\bar{Y}_{kj}'$, $\bar{Z}_{kj}'$ now denote the values of these quantities when the *average field* from the other molecules is acting on both j and k. It is obvious that

$$\bar{Z}_{kj}' = \bar{Z}_{jk}'.$$

Transformation to polar coordinates and integration over the azimuthal angle ϕ yields, since $\bar{X}_{kj}'$ and $\bar{Y}_{kj}'$ are obviously independent of ϕ.

$$\lambda = \frac{2\pi n}{\bar{\bar{Z}}V}\int\int\kappa[\bar{Z}_{kj}'-\bar{\bar{Z}}_{kj}']e^{-u_{jk}^0/kT}r^2\sin\theta dr d\theta$$

and

$$\kappa = \frac{p_0}{r^3}(3\cos^2\theta-1).$$

It will be seen immediately that the contribution arising from $\bar{\bar{Z}}_{kj}'$ may be ignored since it amounts to

$$-\frac{8\pi n p_0}{V}\frac{\bar{\bar{Z}}_{kj}}{\bar{\bar{Z}}}$$

a quantity of the order of magnitude of $1/n$ since $\bar{\bar{Z}}'=n\bar{\bar{Z}}'_{kj}$. Moreover, it is obvious that after the integration over ϕ

$$\bar{Z}_{kj}' = \kappa\bar{Z}_i = \kappa\left(\sum_{l=1}^{n-1}\bar{\bar{Z}}_{jl}+\bar{Z}_{jk}'\right)$$

$\sum_{l-1}^{n-1}\bar{\bar{Z}}_{jk}$ differs from $\bar{\bar{Z}}$ by a quantity of the order of magnitude of $1/n$. Since $\bar{Z}_{jk}'=\bar{Z}_{kj}'$ the expression for λ becomes, after solving for $\bar{Z}_{kj}$;

$$\lambda = \frac{2\pi n}{V}\int_0^{\pi}\int_0^{\infty}\frac{\kappa^2}{1-\kappa}e^{-u_{jk}^0/kT}r^2\sin\theta dr.$$

When $2p_0/\sigma^3$ is small relative to unity and only the first two terms are retained in the expansion of $e^{-u^0{}_{jk}/kT}$, the above expression is closely approximated by[III]

$$\frac{32\pi^2N^2p_0^2}{45BV}\left(1+\frac{1}{3}\frac{A}{BRT}\right)$$

where A and B are the constants of the van der Waal type of equation of state and v is the molal volume. The condition that $2p_0/\sigma^3$ be small relative to unity is in general fulfilled by non-polar substances. (hydrogen; $2p_0/\sigma^3 = 0.12$). For polar substances where $2p_0/\sigma^3$ often exceeds unity (ammonia; $2p_0/\sigma^3 = 1.6$), it is probable that the above expression is still a fair representation of λ.

Note III. If $\kappa^2/1-\kappa$ is expanded and only the first term of the resulting series retained, the expression for λ becomes

$$\frac{2\pi n}{V}\int_0^\pi \int_\sigma^\infty \frac{p_0^2}{r^4}(3\cos^2\theta - 1)e^{-\overset{0}{u}_{jk}/kT}\sin\theta d\theta dr.$$

If $e^{\overset{0}{u}_{jk}/kT}$ is expanded and only the first two terms

$$1 - \frac{u_{jk}{}^0}{kT}$$

are retained, and further if it is assumed that

$$u_{jk}{}^0 = -\frac{a}{r^6} + \cdots$$

one obtains

$$\lambda = \frac{16\pi p_0^2}{15\sigma^3}\,\frac{n}{V}\left(1 + \frac{Na}{3RT\sigma^3}\right).$$

Since the van der Waal's cohesive pressure constant, A, is given by

$$\frac{\pi N^2}{3}\int_\sigma^\infty e^{-\overset{0}{u}_{jk}/kT}\frac{\partial \overset{0}{u}_{jk}}{\partial r}r^3 dr = \frac{2\pi N^2 a}{3\sigma^3} + \cdots$$

and the volume constant is

$$B = \frac{2\pi}{3}N\sigma^3.$$

It is found approximately that

$$\lambda = \frac{1}{v}\,\frac{32\pi^2 N^2 p_0^2}{45B}\left(1 + \frac{1}{3}\,\frac{A}{BRT}\right).$$

If the aggregation effect is ignored and one sets $e^{u_{jk}{}^0/kT}$ equal to unity, one has

$$\lambda' = \frac{2\pi n}{V}\int_0^\pi \int_\sigma^\infty \frac{p_0^2(3\cos^2\theta - 1)}{r^3 - p_0(3\cos^2\theta - 1)}\sin\theta d\theta\frac{dr}{r}\,.$$

This integral may be exactly evaluated as

$$\frac{2\pi p_0}{3}\,\frac{n}{V}\left[4x^2 - \frac{8}{3} + (2x - 2x^3)\,ln\frac{x+1}{x-1}\right]$$

where

$$x = \left(\frac{1 + p_0/\sigma^3}{3p_0/\sigma^3}\right)^{1/2}.$$

The quantity remains finite as long as $2p_0/\sigma^3 < 1$. When the logarithm is expanded the first term is

$$\frac{16\pi p_0^2}{15\sigma^3}\,\frac{n}{V}$$

which agrees with the previous result. Moreover when p_0/σ^3 is in the neighborhood of 0.1, the error introduced by neglecting the remaining terms is found to be less than 3 percent representation of λ. Even in this case $2p_0/r^3$ remains small until very small values of r are reached. Thus for ammonia $2p_0/r^3<0.2$ when $r>2\sigma$. For smaller values of r, the formulation of the integral ceases to be exact. Here the intensity of the mutual field of j and k becomes so great that an electrical saturation sets in and the electric moments of the two molecules are no longer proportional to the field intensity. If in a very rough manner one replaces p_0 by

$$p_0 + \left\{ \frac{1}{\bar{Z}_k} L\left(\frac{\mu \bar{Z}_k}{kT}\right) - \frac{\mu^2}{3kT} \right\}$$

where $L(x)$ is the Langevin function, it is seen that while $1-\kappa$ may differ appreciably from unity, it never becomes extremely small. Moreover, the effect will produce a corresponding diminution in κ^2 so that it should not strongly affect the magnitude of the factor $\kappa^2/(1-\kappa)$ in the integrand.

If one sets $\lambda = \lambda_0 \rho$ where ρ is the density in moles per cc and designates $4\pi Np_0/3$ by P_0, Eq. (15) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} v = \frac{4\pi N p_0}{3} \frac{1}{1 - \lambda_0 \rho} \tag{18}$$

where

$$\lambda_0 = \frac{2P_0{}^2}{5B}\left(1 + \frac{1}{3}\frac{A}{BRT}\right).$$

Equation (18) becomes identical with the Clausius-Mosotti formula only in the limit of zero density. When ρ is small, they may, however, approximate each other very closely over a considerable range of density. A calculation of λ_0 for air, nitrogen and hydrogen indicates that the factor $1/1-\lambda_0\rho$ gives rise to a deviation of less than .05 percent from the Equation (16) at 100 atm. and 20°C. This is in accord with the experimental results of Tangl[3] who found no measureable deviation from the Clausius-Mosotti law for these substances. Measurements of the dielectric constant of carbon dioxide[4] at high densities indicate that the Clausius-Mosotti function, $(\epsilon-1/\epsilon+2)v$, increases with increasing density as Eq. (18) demands. However, the rate of increase is about twenty times that to be expected from the value of λ_0 calculated from the equation of state constants. It is probable that this gas may not be treated as an assembly of molecules of identical polarizability at the temperatures of the dielectric constant measurements.[IV]

Note IV. [Suppose a mixture of several molecular types corresponding to various vibrational states of the molecule. It is easy to see that if these various states differed in polarizability, a shift in the distribution among them due to a change in density, might well increase the mean molecular polarizability in such a manner as to give rise to the observed effect.]

Measurements of the dielectric constant of ammonia[5] yield values of $(\epsilon-1)v/(\epsilon+2)$ which to 30 to 40 atm. follow Eq. (14), with a value of λ_0 calculated from the equation of state constants. In the higher pressure region the slope of the experimental curve decreases rapidly and a negative deviation from

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[3] K. Tangl, Ann. d. Physik **29**, 59 (1908).

[4] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36**, 754 (1930).

[5] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36** (1930).

Eq. (14) occurs. This is not surprising since the assumptions underlying the whole of the present analysis are highly simplified.

In the present discussion it has been assumed that the boundaries of the dielectric material consist of two planes perpendicular to the direction of an homogeneous external field. It seems probable that if the boundary surface of the dielectric is of an irregular character, inhomogenity in the average internal field will arise and Eq. (18) will no longer be strictly valid. Such considerations would of course not be of importance at low densities where $\bar{\bar{F}}$ is small compared to D. Under the latter conditions the simple relation

$$\frac{\epsilon - 1}{3} v = \frac{4\pi}{3} N p_0$$

is valid regardless of the character of the boundary surface.

It is a matter of great interest that the observed deviations from the Clausius-Mosotti relation at high densities are much lower than Eq. (18) predicts. This is not difficult to understand when it is observed that collisions involving more than two molecules will decrease the value of λ, the measure of the contributions of the fluctuations to the average molecular field. In fact, barring effects due to quantized vibrations or rotations, the Clausius-Mosotti function would be expected, on the basis of the present theory, to approach absolute constancy when the molecules were at all instants continuously under one another's mutual influence. The dielectric constant data for liquid carbon dioxide under various pressures proves the supposition tentatively, for the computed Clausius-Mosotti function shows no variation.

Symbols

E	Mean field intensity.
D	Dielectric displacement.
n	Number of molecules.
ϵ	Dielectric constant.
F_j	Total field (sum of molecular and external fields) acting on a molecule j in a dielectric.
F_j'	Molecular field acting on j.
F_{jk}'	The component of F_j' arising from a single molecule k.
$\bar{F}_j'$	Average value of F_j' over all molecular orientations.
$\bar{\bar{F}}_j'$	Average value of F_j' over all configurations of the centers of gravity of the molecules.
$d\tau$	Element of configuration space of a single molecule k.
$[x, y, z]$	Rectangular coordinate system with origin at center of gravity of the molecule j and with z axis parallel to D.
$[x', y', z']$	Rectangular coördinate system with origin at center of molecule k.
$e_1 \cdots e_i$	The charges constituting the molecule k.
$x_{i0}'\ y_{i0}'\ z_{i0}'$	Average coordinates of the charge e_i when there is a perturbing field.
f_i	Elastic constant for linear displacements of e_i from its average position in the molecule.
ϕ_{jk}'	Potential in the interior of the molecule j due to the molecule k.
r	Separation of the centers of gravity of j and k.
$X_j,\ Y_j,\ Z_j$	Components of F_j along the axes of the coördinate system $[x, y, z]$.
$X_j',\ Y_j',\ Z_j'$	Components of F_j' along the axes of the coördinate system $[x, y, z]$.

U^*	Total potential energy of the ensemble of molecules.
U_{jk}^*	Mutual potential energy of the two molecules j and k.
U_{jk}	That part of U_{jk} dependent only upon the configuration of the centers of gravity of j and k.
U^0_{jk}	The value of U_{jk} when there is no external field.
p_0	Polarizability of a molecule.
α	Sum of electronic and atomic polarizabilities.
μ	Fixed dipole moment of a molecule.
σ	Distance of closest approach of two molecules.
V	Volume of the system.
v	Molal volume.
ρ	Molal density.