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Dielectric Constants of Non-Polar Fluids. I. Theory

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The dielectric constant of a classical fluid, composed of spherically symmetric molecules with dipole-dipole interactions, is calculated by a method that leads to formulas previously derived by Yvon but is more direct and yields additional results. The relations of the formulas of Lorentz, Yvon, Kirkwood, and Böttcher to one another are clarified. An accurate calculation of the deviation from the Clausius-Mosotti formula requires knowledge of molecular distribution functions of various orders, but an approximate calculation is possible on the basis of the radial distribution function alone. It is shown that the success of Böttcher's approximation is partly the result of an approximate cancellation of errors, and that a practically equivalent formula can be obtained by another method that lends itself more readily to improvement. The distinctive feature of the present calculation is the introduction of quantities $\mathbf{p}_i^{(h)}$, the mean moment of molecule i when the positions of it and of $h-1$ other molecules are specified; Lorentz's formula corresponds to the approximation $\mathbf{p}_i^{(2)} = \mathbf{p}_i^{(1)}$, and other formulas to various approximate evaluations of the difference $\mathbf{p}_i^{(2)} - \mathbf{p}_i^{(1)}$.

1. INTRODUCTION

NON-POLAR fluids under high pressure show significant deviations from the Clausius-Mosotti formula for the variation of the static dielectric constant ϵ with density d .¹ According to this formula, $(\epsilon-1)/[(\epsilon+2)d]$ should, for a given substance, be independent of density. The usual derivation is based on Lorentz's formula for the mean electric field intensity acting on a molecule;² this is only an approximation, and its failure in the case of polar fluids is well known.³ For non-polar fluids, formulas intended to supersede Lorentz's have been derived by Yvon,⁴ by Kirkwood,⁵ and by Böttcher.⁶ Yvon's and Kirkwood's calculations are based on rigorous molecular theory and lead to series formulas, of which Yvon's have a wider range of validity because fewer special assumptions are introduced. Böttcher's calculation is based on the Onsager model, in which one molecule is treated explicitly and the rest are replaced by a continuum; it leads to a formula in closed form, but the errors inherent in the model are difficult to estimate.

The problem will be treated here by a method that is based on the same physical assumptions as that of Yvon and of Kirkwood, but differs in procedure and leads to more complete results. The distinctive feature of the method is the introduction of a set of quantities $\mathbf{p}_i^{(1)}$,

$\mathbf{p}_{ij}^{(2)}$, etc., representing respectively the mean electric moment of molecule i without further specification, the mean moment of molecule i when the position of a second molecule j with respect to it is specified, etc. By this device it proves possible to obtain directly formulas that otherwise would require inversion of a series, to see more clearly the relations of previous formulas to each other, and to analyze Böttcher's theory critically.

2. DEFINITIONS AND NOTATION

A homogeneous fluid containing N identical molecules is assumed to occupy a volume V . The molecules are assumed to interact mechanically according to a law of intermolecular force consistent with spherical symmetry but otherwise arbitrary, and to interact electrostatically as point dipoles with constant, isotropic polarizability α .

The field intensity at point O due to a dipole of moment \mathbf{p} at point P is, in Gaussian units, $[-\mathbf{p} + 3\mathbf{l}\mathbf{l} \cdot \mathbf{p}]/r^3$, where \mathbf{r} is the vector from O to P , of magnitude r and in the direction of the unit vector \mathbf{l} . This field intensity may be written $\mathbf{\Lambda} \cdot \mathbf{p}$, where $\mathbf{\Lambda}$ represents the linear operator (dyadic)

$$\mathbf{\Lambda} \equiv [-1 + 3\mathbf{l}\mathbf{l}]/r^3; \quad (2-1)$$

here \mathbf{l} represents a unit vector along \mathbf{r} , whereas 1 represents the operator that leaves the operand unchanged (idem factor).

The macroscopic field intensity \mathbf{E} is calculated by adding to the applied field intensity \mathbf{E}_0 (due to external sources) a term due to the polarized fluid. This latter term is the Coulomb (inverse-square-law) field intensity of a fictitious distribution of charges of volume density $-\text{div}\mathbf{P}$ and surface density $\mathbf{n} \cdot \mathbf{P}$, where \mathbf{P} is the macroscopic polarization (electric moment per unit volume) and \mathbf{n} is the outward normal to the surface of the dielectric. At points outside the fluid and distant from it by a distance large on the molecular scale, \mathbf{E} as so defined is equal to $\mathbf{E}_0 + \int \mathbf{\Lambda} \cdot \mathbf{P} d\tau$ (where $d\tau$ is a volume element) and may be interpreted as the actual force per unit charge accessible to macroscopic observation; but

¹ S. S. Kurtz, Jr., and A. L. Ward, *J. Franklin Inst.* **222**, 563-592 (1936); **224**, 583-601 and 697-728 (1937).

² H. A. Lorentz, *Theory of Electrons* (B. G. Teubner, Leipzig, 1909), pp. 137ff.

³ See Ann. N. Y. Acad. Sci. **40**, 289-482 (1940); Trans. Faraday Soc. **42A**, 1-256 (1946); H. Fröhlich, *Theory of Dielectrics: Dielectric Constant and Dielectric Loss* (Oxford University Press, London, 1949).

⁴ J. Yvon, *Recherches sur la Théorie Cinétique des Liquides: I, Fluctuations en Densité; II, La Propagation et la Diffusion de la Lumière. Actualités Scientifiques et Industrielles, Nos. 542 and 543* (Hermann et Cie., Paris, 1937). Yvon's thesis (Paris, 1937) contains the same material. For a brief summary of the dielectric constant calculation, see Jacques Yvon, *Comptes Rendus* **202**, 35-37 (1936).

⁵ John G. Kirkwood, *J. Chem. Physics* **4**, 592-601 (1936).

⁶ C. J. F. Böttcher, *Physica* **9**, 937-944 and 945-953 (1942); *The Theory of the Dielectric Constant* (announced by Elsevier Publishing Company, New York, as in press, 1949).

at internal points, \mathbf{E} is best regarded as having only mathematical significance. To simplify the calculations, the body of fluid will be assumed ellipsoidal in shape, with principal axes along the coordinate axes and with depolarizing (demagnetizing) factors L_1, L_2, L_3 .⁷ Then if \mathbf{P} is uniform, its contribution to \mathbf{E} will be uniform within the fluid. Such a uniform state will be assumed; whether it can actually be maintained is a question to be answered by the subsequent analysis, and therefore \mathbf{E}_0 will not be assumed in advance to be a uniform field or even a physically producible one. Under the assumed conditions $\text{div} \mathbf{P} = 0$, and $E_x = E_{0x} - L_1 P_x$ etc.; or

$$\mathbf{E} = \mathbf{E}_0 - \boldsymbol{\lambda} \cdot \mathbf{P}, \quad (2-2)$$

where the dyadic $\boldsymbol{\lambda}$ has a diagonal matrix with elements L_1, L_2, L_3 .

For the evaluation of averages over a statistical ensemble, it is convenient to introduce molecular distribution functions, or simultaneous densities,⁸⁻¹¹ for which a slight modification of Yvon's notation will be used. The probability of finding h specified, infinitesimal volume elements $d\tau_1, d\tau_2, \dots, d\tau_h$ simultaneously occupied by the centers of h distinct, but unspecified, molecules will be written $\nu_{12}^{(h)} \dots d\tau_1 d\tau_2 \dots d\tau_h$; the subscripts will sometimes be omitted, in which case $\nu^{(h)}$ is to be understood as meaning $\nu_{123}^{(3)}$ rather than, for instance, $\nu_{124}^{(3)}$.¹² In general $\nu^{(h)}$ is a function of the h position vectors $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_h$ of the specified volume elements; but for a fluid under homogeneous equilibrium conditions, $\nu^{(1)}$ (the number density of molecules) is independent of position, except very near the surface of the fluid, and $\nu_{12}^{(2)}$ is a function only of $r_{12} \equiv |\mathbf{r}_2 - \mathbf{r}_1|$. The probability of finding the centers of h specified molecules, numbers $1, 2, \dots, h$, in $d\tau_1, d\tau_2, \dots, d\tau_h$ respectively is $[(N-h)!/N!] \nu^{(h)} d\tau_1 d\tau_2 \dots d\tau_h$. The conditional probability of finding molecule $h+1$ in $d\tau_{h+1}$, given that molecules $1, 2, \dots, h$ are in $d\tau_1, d\tau_2, \dots, d\tau_h$, respectively, is therefore $\nu^{(h+1)} d\tau_{h+1} / (N-h) \nu^{(h)}$, and

$$\int_V \nu^{(h+1)} d\tau_{h+1} = (N-h) \nu^{(h)}. \quad (2-3)$$

The mean number density of molecules other than 1, at distance r_{12} from the center of 1, is $\nu_{12}^{(2)}/\nu^{(1)}$. When

r_{12} is large on a molecular scale, this density has a constant value that differs from $\nu^{(1)}$ by terms of order $1/N$. The ratio of the value at distance r to the limiting value at large r will be represented by $\rho(r)$; by definition, therefore, $\rho(\infty) = 1$ exactly. The term "radial distribution function," as used here, will refer to this function $\rho(r)$, which differs from $\nu^{(2)}/[\nu^{(1)}]^2$ by terms of order $1/N$, and which satisfies the relation¹³

$$4\pi \int_0^\infty [\rho(r) - 1] r^2 dr = kT\kappa - 1/\nu^{(1)}, \quad (2-4)$$

where k and T have their usual meaning and κ is the compressibility. Terms of order $1/N$ are important in Eq. (2-4) but may be neglected in certain integrals that will occur later.

A useful approximation, introduced by Kirkwood,⁸ expresses $\nu^{(3)}$ in terms of $\nu^{(1)}$ and $\nu^{(2)}$:

$$\nu_{123}^{(3)} = \nu_{12}^{(2)} \nu_{23}^{(2)} \nu_{31}^{(2)} / [\nu^{(1)}]^3. \quad (2-5)$$

Here terms of order $1/N$ have been disregarded.

The mean electric moment of molecule 1, when the positions of it and of $h-1$ other molecules $2, 3, \dots, h$ are specified, will be written $\mathbf{p}_{1,2,3,\dots,h}^{(h)}$; again subscripts will at times be omitted, and then $\mathbf{p}_1^{(3)}, \mathbf{p}_2^{(3)}, \mathbf{p}_3^{(3)}$ will mean $\mathbf{p}_{1,2,3}^{(3)}, \mathbf{p}_{2,3,1}^{(3)}, \mathbf{p}_{3,1,2}^{(3)}$ respectively. Successive $\mathbf{p}^{(h)}$'s satisfy the relation

$$\int_V \nu^{(h+1)} \mathbf{p}_1^{(h+1)} d\tau_{h+1} = (N-h) \nu^{(h)} \mathbf{p}_1^{(h)}. \quad (2-6)$$

For a homogeneous fluid, the mean moment $\mathbf{p}^{(1)}$ of a molecule with only its own position specified is independent of that position, except at positions very close to the surface; and the macroscopic polarization is

$$\mathbf{P} = \nu^{(1)} \mathbf{p}^{(1)}. \quad (2-7)$$

3. FORMULATION OF THE PROBLEM

When all the positions are specified, the moments $\mathbf{p}^{(N)}$ are determined by the N vector equations

$$\mathbf{p}_i^{(N)} = \alpha \left\{ \mathbf{E}_0 + \sum_{\substack{j=1 \\ j \neq i}}^N \boldsymbol{\Lambda}_{ij} \cdot \mathbf{p}_j^{(N)} \right\}; \quad i = 1, 2, \dots, N. \quad (3-1)$$

$\boldsymbol{\Lambda}_{ij}$ is given by (2-1) with $\mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. The method of Yvon and of Kirkwood is to solve these equations by successive approximations, on the assumption that $\mathbf{p}_i^{(N)}$ can be expressed as a power series in α , and then to average the result over all configurations, with proper statistical weights. Instead, let us average Eq. (3-1) as it stands over all configurations of molecules $h+1, h+2, \dots, N$, the positions of molecules

⁷ J. C. Maxwell, *Treatise on Electricity and Magnetism*, 3d edition (Oxford University Press, London, 1904), Vol. 2, pp. 66-72.

⁸ John G. Kirkwood, *J. Chem. Physics* **5**, 300-313 (1935); John G. Kirkwood and Elizabeth Monroe Boggs, *J. Chem. Physics* **10**, 394-402 (1942).

⁹ J. Yvon, *La Théorie Statistique des Fluides et l'Équation d'État. Actualités Scientifiques et Industrielles, No. 203* (Hermann et Cie., Paris, 1935). See also reference 4.

¹⁰ Joseph E. Mayer and Elliott Montroll, *J. Chem. Phys.* **9**, 2-16 (1941).

¹¹ M. Born and H. S. Green, *Proc. Roy. Soc. A* **188**, 10-18 (1946).

¹² $\nu_{123}^{(3)} = \nu_{123}$ (Yvon) $= n_3^{(123)}$ (Born and Green) $= N(N-1) \times (N-2) V^{-3} F_3\{3\}$ (Montroll and Mayer) $= N(N-1)(N-2) V^{-3} \times \exp\{-[W_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - W_0]/kT\}$ or $N(N-1)(N-2) V^{-3} \cdot \rho_2(\mathbf{R}_1, \mathbf{R}_2) \cdot \rho_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ (Kirkwood and Boggs).

¹³ L. Ornstein and F. Zernike, *Physik. Zeits.* **27**, 761 (1926); J. Yvon, reference 4.

1, 2, ..., h being specified. This gives

$$\mathbf{p}_i^{(h)} = \alpha \left\{ \mathbf{E}_0 + \sum_{\substack{j=1 \\ j \neq i}}^h \mathbf{A}_{ij} \cdot \mathbf{p}_j^{(h)} + \frac{1}{\nu^{(h)}} \int_V \nu^{(h+1)} \mathbf{A}_{i, h+1} \cdot \mathbf{p}_{h+1}^{(h+1)} d\tau_{h+1} \right\} \quad (3-2)$$

($i=1, 2, \dots, h$; $h=1, 2, \dots, N-1$).

Here the integral, which is the sum of $N-h$ identical contributions by molecules $h+1, h+2, \dots, N$, has been expressed as $(N-h)$ times the contribution of molecule $(h+1)$.

For $h > 1$ the applied field may be eliminated by subtracting from Eq. (3-2) the corresponding equation with $h=1$, after renumbering the variable of integration in the latter equation $h+1$. This gives

$$\mathbf{p}_i^{(h)} - \mathbf{p}^{(1)} = \alpha \sum_{\substack{j=1 \\ j \neq i}}^h \mathbf{A}_{ij} \cdot \mathbf{p}_j^{(h)} + \alpha \int \mathbf{A}_{i, h+1} \cdot \left\{ \frac{\nu^{(h+1)}}{\nu^{(h)}} \mathbf{p}_{h+1}^{(h+1)} - \frac{\nu_{i, h+1}^{(2)}}{\nu^{(1)}} \mathbf{p}_{h+1, i}^{(2)} \right\} d\tau_{h+1} \quad (3-3)$$

($i=1, 2, \dots, h$; $h=2, 3, \dots, N-1$).

For large $|\mathbf{r}_{h+1}|$ the interactions of molecule $h+1$ with molecules 1, 2, ..., h become negligible; the two \mathbf{p} 's in the integrand become equal, and their coefficients in the braces become $\nu^{(1)}$ to within terms of order $1/N$. The quantity in braces therefore vanishes, to within terms of order $1/N$, as $r_{i, h+1} \rightarrow \infty$, and the integrand vanishes faster than $1/r_{i, h+1}^3$. For $h \approx 1$ the terms of order $1/N$ may be disregarded. (They contribute a shape-dependent integral of order $\alpha \mathbf{p}^{(1)}/V$; its ratio to either term on the left is of order $\alpha/V \approx a^3/V$, where a is the radius of the molecular sphere of exclusion.) The integral in Eq. (3-3) may then be extended over all space.

Equation (3-2) for $h=1$ requires a different treatment. This equation is

$$\mathbf{p}^{(1)} = \alpha \left\{ \mathbf{E}_0 + \int_V \frac{\nu_{12}^{(2)}}{\nu^{(1)}} \mathbf{A}_{12} \cdot \mathbf{p}_{2,1}^{(2)} d\tau_2 \right\}. \quad (3-4)$$

In the integral, write $\mathbf{p}_{2,1}^{(2)} = \mathbf{p}^{(1)} + [\mathbf{p}_{2,1}^{(2)} - \mathbf{p}^{(1)}]$. The integral containing $\mathbf{p}_{2,1}^{(2)} - \mathbf{p}^{(1)}$ may be extended over all space as before. The integral containing $\mathbf{p}^{(1)}$ depends on the shape of the fluid body; it is the electrostatic field intensity of a continuous distribution of dipole sources of polarization $\nu_{12}^{(2)} \mathbf{p}^{(1)}/\nu^{(1)}$. Everywhere except in the vicinity of the point 1, this polarization is constant and equal, to within an error of order $1/N$, to $\nu^{(1)} \mathbf{p}^{(1)} = \mathbf{P}$; at point 1, it vanishes strongly because of the factor $\nu_{12}^{(2)}$. This factor insures convergence of the integral and permits its calculation from the equivalent charge densities, which reduce in this case to a surface

density $\mathbf{n} \cdot \mathbf{P}$ on the ellipsoidal surface of the fluid and a volume density $-\text{div}[\nu_{12}^{(2)} \mathbf{p}^{(1)}/\nu^{(1)}]$ in the neighborhood of point 1. The corresponding field intensities are $-\lambda \cdot \mathbf{P}$ and $4\pi \mathbf{P}/3$. The value of the latter is dependent on the fact that $\nu_{12}^{(2)}$ is a function only of r_{12} , vanishes at $r_{12}=0$, and attains the constant value $\nu^{(1)2}$ (to within error of order $1/N$) at some value of r_{12} well inside the fluid surface; it is independent of the other properties of this function.

Since $\mathbf{E}_0 - \lambda \cdot \mathbf{P}$ is the macroscopic field intensity \mathbf{E} , Eq. (3-4) becomes

$$\mathbf{p}^{(1)} = \alpha \left\{ \mathbf{E} + \frac{4}{3} \mathbf{P} + \nu^{(1)} \int \rho(r_{12}) \mathbf{A}_{12} \cdot [\mathbf{p}_{2,1}^{(2)} - \mathbf{p}^{(1)}] d\tau_2 \right\}; \quad (3-5)$$

the integration may be extended over all space, and the approximation $\nu_{12}^{(2)} \approx \nu^{(1)2} \rho(r_{12})$ introduces negligible error.

If the approximation $\mathbf{p}_{2,1}^{(2)} = \mathbf{p}^{(1)}$ is made, the integral in Eq. (3-5) drops out and the expression in braces reduces to Lorentz's expression for the "local field." The Lorentz formula, then, assumes that the mean moment of a molecule known to be at a specified position with respect to another molecule is the same as the mean moment of a molecule without such specification. In the usual derivation of Lorentz's formula, this assumption enters at the point where it is argued that the field intensity due to molecules within a "physically small" sphere about a given molecule must vanish. It is seldom stated explicitly and is sometimes adroitly concealed—as in the "proof" of Lorentz's lemma given by Fowler.¹⁴

Equation (3-5) can be reduced to scalar form. By linearity and symmetry,

$$\mathbf{p}_{1,2}^{(2)} = \mathbf{p}_{2,1}^{(2)} = \{1 + \mathbf{\Pi}_{12}\} \cdot \mathbf{p}^{(1)}, \quad (3-6)$$

where $\mathbf{\Pi}_{12} = \mathbf{\Pi}(\mathbf{r}_{12})$ is a dyadic of the form

$$\mathbf{\Pi}(\mathbf{r}) = g(r) + [f(r) - g(r)] \mathbf{11}. \quad (3-7)$$

This may be seen by resolving $\mathbf{p}^{(1)}$ into components along and transverse to \mathbf{r}_{12} and considering each separately. (Eq. (2-6) for $h=1$ is not exactly satisfied by this form of $\mathbf{p}^{(2)}$; but on the basis of the behavior of $\mathbf{\Pi}(\mathbf{r})$ at large r deduced later, the fractional error is of order α/V .) The product $\mathbf{A}_{12} \cdot \mathbf{\Pi}_{12}$ contains a term in $\mathbf{1}$ and a term in $\mathbf{11}$; the average of the latter over angles is $\frac{1}{3}$, and therefore the integral in Eq. (3-5) ultimately reduces to a scalar times $\nu^{(1)} \mathbf{p}^{(1)}$ or \mathbf{P} . This form of the equation shows that the vectors \mathbf{E} and \mathbf{P} (or $\mathbf{p}^{(1)}$) have the same direction and justifies the definition of a scalar dielectric constant ϵ . Solution for \mathbf{E} and hence for

¹⁴ R. H. Fowler, *Statistical Mechanics*, 2d edition (The Macmillan Company, New York, 1936), p. 440.

the ratio $E/P = 4\pi/(\epsilon - 1)$ gives

$$\frac{1}{\epsilon - 1} = \frac{1}{4\pi\nu^{(1)}\alpha} - \frac{1}{3}(1 + 2C), \quad (3-8)$$

where

$$C = \int_0^\infty \rho(r)[f(r) - g(r)]r^{-1}dr. \quad (3-9)$$

Since the relation of \mathbf{E} to \mathbf{P} is independent of position, uniform \mathbf{P} implies uniform \mathbf{E} within the fluid and can, by (2-2), be maintained by a uniform \mathbf{E}_0 .

Equation (3-8) may be written

$$\frac{\epsilon + 2}{\epsilon - 1} = \frac{3}{4\pi\nu^{(1)}\alpha} - 2C, \quad (3-10)$$

which reduces to the Clausius-Mosotti formula for $C=0$. The correction to the Clausius-Mosotti formula is determined by the integral (3-9). Evaluation of this integral requires knowledge of the radial distribution function $\rho(r)$ and of the functions $f(r)$ and $g(r)$ that appear in the dyadic $\Pi(r)$, i.e., in the expression for $\mathbf{p}^{(2)}$ as a linear vector function of $\mathbf{p}^{(1)}$. Determination of this function requires solution of the system of Eqs. (3-3).

4. SERIES SOLUTION

Since all the $\mathbf{p}^{(h)}$'s become equal to $\mathbf{p}^{(1)}$ when the r_{ij} 's are large in comparison with $\alpha^{\frac{1}{2}}$, i.e., when the quantities α/r_{ij}^3 are small, it is reasonable to assume series expansions

$$\mathbf{p}_i^{(h)} = \mathbf{p}^{(1)} + \sum_{s=1}^{\infty} \mathbf{p}_i^{(h)(s)} \alpha^s \quad (4-1)$$

in which the leading term is $\mathbf{p}^{(1)}$. In contrast, Yvon's and Kirkwood's calculations are based on expansions in which the leading term is $\alpha\mathbf{E}_0$. Choice of the form (4-1) implies choice of $\mathbf{p}^{(1)}$ or \mathbf{P} , rather than of \mathbf{E}_0 or \mathbf{E} , as independent variable; this choice is consistent with the form already chosen for Eq. (3-8) or (3-10).

If the series (4-1) is substituted in Eqs. (3-3) and coefficients of α^s are equated, the result is

$$\mathbf{p}_i^{(h)(1)} = \sum_{j=1}^h \mathbf{A}_{ij} \cdot \mathbf{p}^{(1)} + \int \left[\frac{\nu^{(h+1)}}{\nu^{(h)}} - \frac{\nu_{i, h+1}^{(2)}}{\nu^{(1)}} \right] \mathbf{A}_{i, h+1} \cdot \mathbf{p}^{(1)} d\tau_{h+1}; \quad (4-2)$$

$$\mathbf{p}_i^{(h)(s)} = \sum_{j=1}^h \mathbf{A}_{ij} \cdot \mathbf{p}_j^{(h)(s-1)} + \int \mathbf{A}_{i, h+1} \cdot \left[\frac{\nu^{(h+1)}}{\nu^{(h)}} \mathbf{p}_{h+1}^{(h+1)(s-1)} - \frac{\nu_{i, h+1}^{(2)}}{\nu^{(1)}} \mathbf{p}_{h+1, i}^{(2)(s-1)} \right] d\tau_{h+1}, \quad s > 1. \quad (4-3)$$

Given the distribution functions $\nu^{(h)}$, any desired accuracy in Π can in principle be attained by an iterative procedure based on these formulas. Evaluation of Π or $\mathbf{p}^{(2)}$ (and hence of C) to the first order in α requires only the zero-order approximation, $\mathbf{p}^{(1)}$, to $\mathbf{p}^{(3)}$; evaluation of Π to the second order requires the first-order approximation to $\mathbf{p}^{(3)}$, which in turn requires only the zero-order approximation to $\mathbf{p}^{(4)}$; and so on. However, present knowledge of the higher order distribution functions is too scanty to permit calculation, by this method, of approximations beyond the first. Equation (4-2) for $h=2$ gives the first-order approximation

$$\Pi_{12} = \alpha \left\{ \Lambda_{12} + \int \left[\frac{\nu_{123}^{(3)}}{\nu_{12}^{(2)}} - \frac{\nu_{13}^{(2)}}{\nu^{(1)}} \right] \Lambda_{13} d\tau_3 \right\}, \quad (4-4)$$

and this can be used directly if $\nu^{(3)}$ is approximated by means of Kirkwood's formula (2-5).

Let $\mathbf{r} = \mathbf{r}_{12}$, $\mathbf{t} = \mathbf{r}_{13}$, $\mathbf{s} = \mathbf{r}_{23}$, $\mathbf{l}_r = \mathbf{r}/r$ etc., $\theta = \cos^{-1}(\mathbf{l}_t \cdot \mathbf{l}_r)$; then in polar coordinates (r, θ, ϕ) , the average of $[-1 + 3\mathbf{l}_t \mathbf{l}_r]$ over ϕ is $[-1 + 3\mathbf{l}_r \mathbf{l}_r]P_2(\cos\theta)$. Therefore (4-4) may be written

$$\Pi(\mathbf{r}) = \alpha[-1 + 3\mathbf{l}_r \mathbf{l}_r][r^{-3} + \nu^{(1)}\Phi(r)], \quad (4-5)$$

where

$$\Phi(r) = \int \frac{\nu_{13}^{(2)}}{\nu^{(1)2}} \left[\frac{\nu^{(1)}\nu_{123}^{(3)}}{\nu_{12}^{(2)}\nu_{13}^{(2)}} - 1 \right] P_2(\cos\theta) \frac{1}{t^3} d\tau_3. \quad (4-6)$$

Equation (4-5) implies

$$\frac{1}{2}f(r) = -g(r) = \alpha[r^{-3} + \nu^{(1)}\Phi(r)], \quad (4-7)$$

and therefore

$$C = 3\alpha \int_0^\infty \rho(r)[r^{-3} + \nu^{(1)}\Phi(r)]dr/r. \quad (4-8)$$

Insertion of (4-6) in (4-8) and of the result in (3-8) or (3-10) gives the correction to the Clausius-Mosotti formula in a form already given by Yvon.⁴

Use of Kirkwood's approximation (2-5) with neglect of terms of order $1/N$ gives

$$C = 3\alpha A + 6\pi\nu^{(1)}\alpha B \quad (4-9)$$

with

$$A = \int_0^\infty \rho(r)dr/r^4, \quad (4-10)$$

$$B = \int_0^\infty \int_0^\infty \int_{|t-r|}^{t+r} \rho(r)\rho(t)[\rho(s) - 1] \times P_2(\cos\theta) s ds dt dr / t^2 r^2, \quad (4-11)$$

since $d\tau_3 = 2\pi t^2 \sin\theta d\theta dt = 2\pi s ds dt / r$ with $0 \leq \theta \leq \pi$ or $|t-r| \leq s \leq t+r$. B can also be evaluated by use of Fourier transforms. The results to be given in Section 5 were calculated by both methods.

5. WORKING FORMULAS BASED ON THE FIRST-ORDER APPROXIMATION

The triple integration of Eq. (4-11) can be reduced to a single integration, for approximate calculations, by the following method. As a first approximation, $\rho(r)$ may be replaced by the step function

$$\rho_0(r) = \begin{cases} 0, & r < a; \\ 1, & r > a. \end{cases} \quad (5-1)$$

Then for a better approximation

$$\rho(r) = \rho_0(r) + \rho_1(r), \quad (5-2)$$

where the correction $\rho_1(r)$ is appreciable only in the neighborhood of $r=a$. The constant a is an effective molecular diameter, whose value is to some extent arbitrary. An approximate value of the integral in (4-11) may now be obtained by neglecting terms of order higher than the first in $\rho_1(r)$. When all the integrations have been carried out that do not require knowledge of the function $\rho_1(r)$, the result is

$$\frac{\epsilon+2}{\epsilon-1} = -\frac{1}{z} - c_0 + c_1 z, \quad (5-3)$$

where

$$z \equiv 4\pi\nu^{(1)}\alpha/3, \quad (5-4)$$

and

$$c_0 = 2\alpha/a^3 + 6\alpha \int_0^\infty \rho_1(r) dr/r^4 \quad (5-5)$$

(exact),

$$c_1 = 15/16 + (1/a) \int_0^\infty \rho_1(r) g(r/a) dr \quad (5-6)$$

(to the first order in $\rho_1(r)$), with

$$g(x) = \begin{cases} (3/8)(6 - 17x^2 + 12x^3 - x^5), & x < 2; \\ 12/x^4, & x > 2. \end{cases} \quad (5-7)$$

For gases at not too high densities it may be permissible to use Kirkwood's⁵ distribution function for rigid spheres of radius a subject to van der Waals attractive forces. For $r > a$ the intermolecular potential energy is $-C'/r^6$; if $C'/kTa^6 \ll 1$ and if ternary encounters are neglected,

$$\rho_1(r) = \begin{cases} 0, & r < a; \\ \mu/r^6, & r > a, \end{cases} \quad (5-8)$$

with

$$\mu = C'/kT. \quad (5-9)$$

Equations (5-5) and (5-6) give

$$c_0 = (2\alpha/a^3)(1 + \mu/3a^6), \quad (5-10)$$

$$c_1 = (15/16)[1 + (2/5)(\mu/a^6)(32/45 - \ln 2)] \\ = (15/16)[1 + 0.007186\mu/a^6]. \quad (5-11)$$

To get a formula directly comparable with Kirkwood's, the reciprocal of the right member of Eq. (5-3) (or of the equivalent formula for $1/(\epsilon-1)$) must be expanded as a series in α through the term in α^3 . The resulting

formula for $(\epsilon-1)/(\epsilon+2)$ (or for $\epsilon-1$) is identical with Kirkwood's except that he neglected the effect of $\rho_1(r)$ on c_1 —an effect that is in fact, according to Eq. (5-11), negligibly small.

For liquids an approximate formula can be derived by a method due to Yvon.⁴ This consists in replacing $\rho_1(r)$ by a constant times $\delta(r-a)$ (where $\delta(x)=0$ for $x \neq 0$, but $\int_{-\epsilon'}^{\epsilon'} \delta(x)dx = 1$ for $\epsilon' > 0$) and evaluating the constant by means of Eq. (2-4), with the term in κ neglected. This gives

$$c_0 = 4\alpha/a^3 - 3\alpha/2\pi\nu^{(1)}a^6, \quad (5-12)$$

$$c_1 = 15/16. \quad (5-13)$$

In observations of the variation of ϵ with density, the second term in c_0 will combine with the term $1/z$ in (5-3) to give a variation according to the law

$$\frac{\epsilon+2}{\epsilon-1} = \frac{1}{z'} - c_0' + c_1' z' \quad (5-14)$$

with

$$z' = (4\pi\nu^{(1)}\alpha/3)/(1 + 2\alpha^2/a^6), \quad (5-15)$$

$$c_0' = 4\alpha/a^3, \quad (5-16)$$

$$c_1' = (15/16)(1 + 2\alpha^2/a^6). \quad (5-17)$$

In general, the integrals in (5-5) and (5-6) will be density- and temperature-dependent. If, therefore, the data at constant temperature are fitted to a formula of the form (5-14) with

$$z' \equiv d/d_0, \quad (5-18)$$

and with d_0 , c_0' , and c_1' constants, the precise interpretation of these constants requires evaluation of the integrals by use of detailed information about the function $\rho_1(r)$. In order of magnitude, however, $c_0' \cong c_0 \cong 2\alpha/a^3$ and $c_1' \cong c_1 \cong 1$. If a is taken just small enough so that $\rho(r)$ practically vanishes for $r < a$, then as r increases from a the function $\rho_1(r)$ has a positive maximum followed by a less pronounced minimum;¹⁵ for liquids the minimum is negative.⁸ The function $g(x)$ is negative and small for $1 < x < 1.35$, positive and considerably larger for $1.35 < x < 2$. The net effect of $\rho_1(r)$ on c_0 and c_1 is therefore likely to be positive; and since Eq. (5-17) suggests $c_1' > c_1$, probably $c_1' > 15/16$. For a molecule pictured as a conducting sphere of diameter a , $\alpha = a^3/8$, so that $c_0' \cong \frac{1}{4}$ is to be expected.

The empirical formula of Eykman,¹⁶ as applied to dielectric constant data by Kurtz and Ward,¹ assumes the following form when its constant is evaluated by use of the relation $(\epsilon-1)/4\pi\nu^{(1)}\alpha \rightarrow 1$ as $\nu^{(1)} \rightarrow 0$:

$$(\epsilon-1)/(\epsilon^{\frac{1}{2}}+0.4) = (3/1.4)z. \quad (5-19)$$

Expansion of this formula in the form (5-3) gives $c_0 = 1/14$, $c_1 = 45/56$. The signs and orders of magnitude

¹⁵ Elliott W. Montroll and Joseph E. Mayer, J. Chem. Phys. 9, 626-637 (1941), Fig. 3.

¹⁶ J. F. Eykman, Rec Trav Chim. 14, 185 (1895).

agree with those deduced from molecular theory; no more theoretical standing than this can be claimed for the formula.

6. INTEGRAL EQUATION METHOD

Since the functions $\nu^{(4)}$, $\nu^{(6)}$, etc., are not well known, an approximate method of calculating $\Pi(\mathbf{r})$ will now be developed which requires no knowledge of them. The basis of this method is the introduction of an approximate formula for $\mathbf{p}_1^{(3)}$ in terms of $\mathbf{p}^{(1)}$ and $\mathbf{p}_1^{(2)}$, analogous to Kirkwood's formula for $\nu^{(3)}$. Such a formula can be obtained by assuming that the change in the mean moment of molecule 1 that results from specification of the positions of molecules 2 and 3 (with respect to it) can be found, with sufficient accuracy, by superposing the changes due to specification of 2 and 3 separately. This assumption can be justified by arguments similar to those used to justify Kirkwood's approximation (2-5). It leads to the formula

$$\mathbf{p}_{1,2,3}^{(3)} = \{1 + \Pi_{12} + \Pi_{13}\} \cdot \mathbf{p}^{(1)}, \quad (6-1)$$

and insertion of this and of (2-5) in Eq. (3-3) for $h=2$ gives the following integral equation for Π :

$$\begin{aligned} \Pi_{12} &= \alpha \Lambda_{12} \cdot [1 + \Pi_{12}] \\ &+ \nu^{(1)} \alpha \int \rho_{13}(\rho_{23} - 1) \Lambda_{13} \cdot [1 + \Pi_{31}] d\tau_3 \\ &+ \nu^{(1)} \alpha \int \rho_{13} \rho_{23} \Lambda_{13} \cdot \Pi_{32} d\tau_3. \end{aligned} \quad (6-2)$$

If a solution is assumed in the form

$$\Pi_{ij} = \sum_{s=1}^{\infty} \Pi_{ij}^{(s)} \alpha^s, \quad (6-3)$$

then by equating coefficients of α^s it is found that

$$\Pi_{12}^{(1)} = \Lambda_{12} + \nu^{(1)} \int \rho_{13}(\rho_{23} - 1) \Lambda_{13} d\tau_3, \quad (6-4)$$

$$\begin{aligned} \Pi_{12}^{(s)} &= \Lambda_{12} \cdot \Pi_{12}^{(s-1)} \\ &+ \nu^{(1)} \int \rho_{13}(\rho_{23} - 1) \Lambda_{13} \cdot \Pi_{31}^{(s-1)} d\tau_3 \\ &+ \nu^{(1)} \int \rho_{13} \rho_{23} \Lambda_{13} \cdot \Pi_{32}^{(s-1)} d\tau_3, \quad (s > 1). \end{aligned} \quad (6-5)$$

The first-order solution (6-4) is the same as that obtained by the method of Section 4. The higher order terms have been considerably simplified.

This approximation may be regarded as the second in a series of successively better approximations, of which Lorentz's is the first. For quantities $\Delta \mathbf{p}^{(h)}$ may be defined by the equations

$$\mathbf{p}_{1,2}^{(2)} = \mathbf{p}^{(1)} + \Delta \mathbf{p}_{1,2}^{(2)}, \quad (6-6)$$

$$\mathbf{p}_{1,2,3}^{(3)} = \mathbf{p}^{(1)} + \Delta \mathbf{p}_{1,2}^{(2)} + \Delta \mathbf{p}_{1,3}^{(2)} + \Delta \mathbf{p}_{1,2,3}^{(3)}, \quad (6-7)$$

where the last term in each case takes account of effects that are appreciable only when all the molecules considered in the equation are close together. The Lorentz approximation is $\Delta \mathbf{p}^{(2)} = 0$ and the present approximation $\Delta \mathbf{p}^{(3)} = 0$; a still better approximation could be obtained by retaining $\Delta \mathbf{p}^{(3)}$ but neglecting a similarly defined term $\Delta \mathbf{p}^{(4)}$.

For the simplified distribution function $\rho_0(r)$, the integrations give

$$\frac{\epsilon + 2}{\epsilon - 1} = \frac{1}{z} - c_0 + c_1 z - c_2 z^2 + \cdots, \quad (6-8)$$

where

$$c_0 = (2/3) \ln[(1+x)/(1-2x)], \quad (6-9)$$

$$\begin{aligned} c_1 &= \frac{15}{16} \left[1 + \left(\frac{29}{15} - \frac{2}{5} \ln 2 \right) x + \cdots \right] \\ &= 0.9375 + 1.55257x + \cdots, \end{aligned} \quad (6-10)$$

$$c_2 = \frac{80,071}{107,520} + \cdots = 0.744708 + \cdots, \quad (6-11)$$

with

$$x = \alpha/a^3, \quad (6-12)$$

$$z = 4\pi \nu^{(1)} \alpha/3 \equiv d/d_0. \quad (6-13)$$

The results (6-10) and (6-11) are presented with less assurance than the other results of this article; they have been checked, but not by a method completely independent of the original calculation method. The calculation, with checks, filled about 100 pages, each 17 in. \times 22 in.; that size of paper (with the long dimension horizontal) permits writing each step in a single line and is recommended to anyone who undertakes to verify the integrations—which, while tedious, are elementary.

The precision of present data on ϵ vs. d and on $\rho(r)$ does not justify carrying these calculations further.

7. CRITICAL ANALYSIS OF BÖTTCHER'S THEORY

Böttcher calculates the moment of molecule 1 by supposing that it is at the center of a spherical cavity of radius a , outside of which is a continuum whose dielectric constant ϵ is that of the actual dielectric. Now the moment is given rigorously by Eq. (3-4), in which the integral may be regarded as the field intensity of a continuous polarization

$$\begin{aligned} \mathbf{P}' &= \nu_{12}^{(2)} \mathbf{p}_{2,1}^{(2)} / \nu^{(1)} = \rho(r_{12}) \nu^{(1)} \mathbf{p}_{2,1}^{(2)} [1 + 0(1/N)] \\ &= \rho(r_{12}) [1 + \Pi_{12}] \cdot \mathbf{P}, \end{aligned} \quad (7-1)$$

with neglect of terms in $1/N$. In Böttcher's calculation, therefore, \mathbf{P}' is replaced by 0 for $r < a$ and is evaluated for $r > a$ as if molecule 1 were a dipole at the center of a macroscopic cavity.

It is clear that if this method has any strict justifica-

tion, that justification can apply only to the special distribution function $\rho(r) = \rho_0(r)$ of Eq. (5-1), with a the radius of the molecular sphere of exclusion. Comparison of Eq. (7-1) with the continuum polarization calculated by Böttcher's method then shows that Böttcher's theory is equivalent to the assumption

$$\Pi_{12} = C'' \Lambda_{12} \quad (7-2)$$

with

$$C'' = \frac{\epsilon - 1}{2\epsilon + 1} \left[\frac{3}{4\pi\nu^{(1)}} - a^3 \right]; \quad (7-3)$$

and in fact if this formula is used in Eqs. (3-9) and (3-10), it leads to Böttcher's final formula, which may be written

$$z = \frac{4\pi\nu^{(1)}\alpha}{3} = \frac{\epsilon - 1}{9\epsilon} \left\{ (2\epsilon + 1) - 2(\epsilon - 1) \frac{\alpha}{a^3} \right\}. \quad (7-4)$$

If this formula is solved for $(\epsilon + 2)/(\epsilon - 1)$ and the result is expanded in the form (5-3), it gives $c_0 = 2\alpha/a^3$, $c_1 = 2$. For $\rho(r) = \rho_0(r)$ the correct values are $2\alpha/a^3$ and 15/16 respectively. Böttcher's approximation therefore gives an error in the term of order 1 in the polarizability. In this respect it is inferior to the approximation of Section 6, which is exact to the first order in α and which furthermore permits the introduction of an arbitrary radial distribution function $\rho(r)$.

The success of Böttcher's formula in fitting experimental data may be attributed to the approximate cancellation of two errors. The use of the simplified distribution function $\rho_0(r)$ would, by itself, result in too low a value (15/16) of c_1 by omitting the integral in Eq. (5-6); but in the calculation of the local field a further error is made, which raises the too low value 15/16 to a value 2 that may be approximately correct.

The use of macroscopic concepts in calculating the electrostatic effect of molecule 1 on the surrounding fluid is legitimate in a region where \mathbf{E} and \mathbf{P} are varying slowly, but not in the region $r \cong a$, where they are varying fast. The form (7-2) is therefore valid for $r \gg a$ but not for $r \cong a$; and because it gives incorrect values of \mathbf{P}' in the region $r \cong a$, its use in this region probably results in an erroneous estimate of the "shielding effect" of near molecules on the field at large r , and therefore of the value of C'' in the region where the general form (7-2) is valid. This latter error, however, is probably small; the chief error is in the estimation of \mathbf{P}' at $r \cong a$ and therefore of the contribution of this region to the local field acting on molecule 1.

A partial verification of these ideas can be obtained as follows. The method of Section 6 has been seen to involve no error in the term of first order in α . Let us now, in this method, commit an error similar to Böttcher's and observe the result. An asymptotic solution of the integral equation (6-2), valid at large r , can be found for $\rho(r) = \rho_0(r)$ by assuming the form (7-2), evaluating the integrals, and neglecting terms that vanish at infinity

faster than $1/r^3$. This gives

$$C'' = \alpha \frac{1 - 4\pi\nu^{(1)}a^3/3}{1 + 4\pi\nu^{(1)}\alpha/3}. \quad (7-5)$$

The two values of C'' , (7-3) and (7-5), are not exactly equal (if they are equated, the result is the Clausius-Mosotti formula); and since each is based on approximations, it cannot be easily decided which value is better. If the form (7-2), with the value (7-5) of C'' , is now used in the formula (3-9) as if it were valid over the entire region $r > a$, the following formula is obtained:

$$\frac{\epsilon + 2}{\epsilon - 1} = \frac{3}{4\pi\nu^{(1)}\alpha} - \frac{2\alpha}{a^3} \frac{1 - 4\pi\nu^{(1)}a^3/3}{1 + 4\pi\nu^{(1)}\alpha/3}; \quad (7-6)$$

and to the first order in α , this is identical with the result obtained by expanding Böttcher's formula. It therefore appears that the chief error is not the incorrect evaluation of the constant in the long-range effect of molecule 1, but the incorrect evaluation of the mean moments in its immediate neighborhood.

8. GENERAL REMARKS

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To the experimentalist who is primarily interested in finding a formula on which he can rely, it is confusing to find in the literature a number of apparently incompatible formulas, derived independently by different authors. I hope that the discussion given here will help to clarify the relations of the formulas of Lorentz, Yvon, Kirkwood, and Böttcher to each other. I wish particularly to call attention to Yvon's work, which has seldom been cited in English-language publications. His discussion of dielectric properties⁴ includes, besides the material already mentioned, a detailed analysis of the dynamical behavior at optical frequencies; and his treatment of distribution functions⁹ contains a number of results that have since been rederived by other authors.

A complete theory would have to take account of several factors disregarded here: anisotropy of the molecules,^{5,17} variation of the polarizability of a molecule with distance from its neighbors,¹⁸ and quantum-mechanical aspects of the problem.¹⁹ It seems to me, however, that these matters can be treated more satis-

¹⁷ C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. **A117**, 589-599 (1928); see also P. O. John, Phil. Mag. **22**, 274-281 (1936).

¹⁸ Michels, de Boer, and Bijl, Physica **4**, 981-994 (1937); S. R. de Groot and C. A. ten Seldam, Physica **13**, 47-48 (1947).

¹⁹ J. H. Van Vleck, J. Chem. Phys. **5**, 556-558 and 991 (1937).

