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MS. received 19th February 1970

Abstract. Expressions for the dielectric constant of a pure liquid are obtained from quantum electrodynamics, and compared with those obtained from electrostatic arguments. The Lorentz cavity field is shown to be associated with off-resonance intermolecular exchange of excitation. An application of perturbation theory up to a level including such excitation exchange leads to the Debye equation for pure non-polar liquids, and an analogue of the Onsager equation for polar liquids.

1. Introduction

The refractive index and dielectric constant of condensed phase systems are often described in terms of the polarizabilities of the constituent molecules. Each molecule is considered to contribute to the bulk property as if it alone were present, the effect of the surrounding molecules upon its contribution being neglected. Any allowance for the bulk effect of the medium upon a particular molecule is made by an electrostatic modification of the bulk property that is to be calculated. Thus the electric field at a molecule is given in terms of the applied field by the Lorentz cavity field. The molecular property is then calculated as though the effective local field were the applied field.

In an earlier paper (Dissado 1970 a) the operator (1), formally similar to (4) given by Power and Zienau (1957), was derived for interaction between solute molecules and the medium radiation field, valid in the dipole approximation

$$H_{\text{int}} = -q_m{}^s(r) \cdot \epsilon^{\perp}(r) \tag{1}$$

with effective solute transition dipole moment $q_m{}^s(r)$ given by

$$q_m{}^s(r) = q^s(r)/n_m. \tag{2}$$

In finding (1) the polarization field produced by an electromagnetic wave is written as a sum of the expectation value of the transition dipole moment operator over all the states of a molecule and over all the molecular sites. This polarization is then separated into two parts, one for the medium, the other the solute polarization. The solute polarization may here be due either to a transition of a molecule of the same species as those of the medium (system contains only one molecular species), or to those of a molecule of a different species (the solute) embedded in small concentration in a dielectric of different species (the solvent). The solute transition must be one which is dipole allowed and with an absorption band that has no appreciable overlap with that of the medium. If the medium is considered to be a uniform isotropic dielectric of unit magnetic permeability all interactions between the electromagnetic field and the medium can be absorbed into the operator (1) connecting an effective solute transition dipole moment (2) and an effective medium field. In (1) and (2)

n_m is the medium refractive index at the frequency of solute absorption. The effective field is

$$\boldsymbol{\epsilon}^{\perp}(\boldsymbol{r}) = \sum_{\lambda \kappa} \mathrm{i} \left(\frac{2\pi\hbar c\kappa}{n_m V}\right)^{1/2} \{a_\kappa \exp(\mathrm{i}\boldsymbol{\kappa}\,.\,\boldsymbol{r}) - a_\kappa{}^+ \exp(-\mathrm{i}\boldsymbol{\kappa}\,.\,\boldsymbol{r})\} e_\lambda \tag{3}$$

in the usual notation. The operator (1) goes over into the usual field-dipole operator (4) (Power and Zienau 1957) for unit refractive index:

$$H_{\mathrm{int}} = -\sum_t q^t(\boldsymbol{r})\,.\,\boldsymbol{E}^{\perp}(\boldsymbol{r}) \tag{4}$$

which gives the interaction as a sum over all possible transitions; (1) replaces the sum by an interaction between the effective field and effective transition dipole of a state coupled strongly to the electromagnetic field (close to the absorption peak). The transition dipole moment operator has been replaced by the expectation value for the isolated molecule in (1) and (4). In this form operator (1) is correct to the first-order of perturbation theory in medium-field interactions. It may be applied to the calculation of the intermolecular resonance interaction energy (5) between two molecules embedded in a dielectric (Dissado 1970 a):

$$\Delta E = \frac{q_i{}^s q_j{}^s}{n^2} \left[\beta_{ij}\left\{\frac{\cos(R/\lambda_m{}^s)}{R^3} + \frac{\sin(R/\lambda_m{}^s)}{\lambda_m{}^s R^2}\right\} - \alpha_{ij}\frac{\cos(R/\lambda_m{}^s)}{(\lambda_m{}^s)^2 R}\right] \tag{5}$$

with $\alpha_{ij} = \delta_{ij} - \hat{R}_i\hat{R}_j$ and $\beta_{ij} = \delta_{ij} - 3\hat{R}_i\hat{R}_j$, i and j being components in a suitable coordinate frame. R is the intermolecular separation and $\lambda_m = \lambda/2\pi n_m$ the reduced transition wavelength in the medium.

2. Derivation of the dielectric constant and refractive index

2.1. *Pure liquid of isotropic molecules*

The operator (1) will be used to determine the equations relating refractive indices and dielectric constants of a condensed medium with the spectroscopic properties of the individual molecules. In deriving these relationships, the Heitler-Ma (Heitler 1954) theory of radiation damping will be applied to a system consisting of a pure liquid and an electromagnetic wave. The initial state has all molecules in their ground state, no photons of the incident electromagnetic wave having been absorbed. An arbitrary state y describes a situation in which one photon has been absorbed by a molecule which is now in the excited state y.

In the general theory the amplitudes of the initial state 0, and state y, as a function of time are then given by b_0 and b_y respectively.

$$b_0(t) = \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}E \exp\{\mathrm{i}(E_0 - E)t/\hbar\}}{E - E_0 + \mathrm{i}\hbar\Gamma(E)/2} \tag{6}$$

$$b_y(t) = \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}E\, U_{y0}(E)\zeta(E - E_y) \exp\{\mathrm{i}(E_y - E_0)t/\hbar\}}{E - E_0 + \mathrm{i}\hbar\Gamma(E)/2}. \tag{7}$$

$\Gamma(E)$ and $U_{y0}(E)$ are found by solving the coupled equations (8):

$$\hbar\Gamma(E)/2 = \mathrm{i}H_{00} + \mathrm{i}\sum_{m \neq 0} H_{0m}\zeta(E - E_m)U_{m0}(E)$$

$$U_{y0}(E) = H_{y0} + \sum_{m \neq 0} H_{ym}\zeta(E - E_m)U_{m0}(E) \tag{8}$$

and

$$\zeta(E - E_m) = \lim_{\eta \to 0} (E + i\eta - E_m)^{-1}.$$

The H_{ym} are matrix elements of the interaction operator (1) for states y and m diagonal in the unperturbed Hamiltonian for the radiation field H_{RAD}, and free molecules H_{mol}.

In the liquid the state y is no longer that of a free molecule, but of the molecules collectively. The yth transition of the collection (energy E_y) is excited by an electromagnetic wave (initial state 0) containing both positive and negative frequency components. The coupling of the light to the remaining liquid states is to be absorbed into the interaction operator as that of a medium whose dielectric is $(n')^2$. Here $(n')^2 - 1$ is the value of the contribution of the other medium states to the dielectric constant measured at the frequency of the transition to the yth state.

The problem of choosing a wave function to represent the state y now arises. As in a solid the liquid is a set of N molecules, having N-fold degeneracy for the Hamiltonian H_{mol}, but the crystalline solid possesses permanent translational symmetry in the lattice which allows the use of the Bloch functions (9a) as wave functions (Craig and Walmsley 1968).

$$\psi_y(\mathbf{K}) = \frac{\sum\limits_{p} \exp(i\mathbf{K} \cdot \mathbf{p})\phi_p{}^y}{(N)^{1/2}} \tag{9a}$$

where the site function $\phi_p{}^y$ is a product wave function of all the single molecule wave functions, with only the molecule whose centre is at the vector position $\mathbf{p}$ excited to the state y, all other molecules being in the ground state. $\mathbf{K}$ is a wave vector having the magnitude of reciprocal length. The wave functions (9a) describe a set of states (exciton band), one for each (mechanical) wave vector $\mathbf{K}$, stationary with respect to a Hamiltonian including only Coulumb interactions. Excitation of the crystal by an electromagnetic wave of the same frequency as the transition restricts the states excited to one having the same wave vector as the incident wave. This value is obtained from a self-consistent solution of the expression relating the wave vector of the electromagnetic field and its circular frequency. It is, however, often assumed to be the value for the field in vacuo, which for optical transitions is taken to be zero. For thin crystals (dimension along the wave path less than one wavelength) the equality condition breaks down and all exciton states couple to the field of which the wave vector is determined by the dispersion expression.

In the case of a liquid there is no permanent order and functions (9a) do not describe stationary states. However, the presence of an electromagnetic field (of plane wave form) external to the liquid will produce in the liquid a polarization wave having plane-wave characteristics, of arbitrary wave vector $\mathbf{K}'$. It is the properties of this wave that we measure, i.e., the refractive index n and spatial attenuation κ which are determined by the real and imaginary parts of $\mathbf{K}'$ for a given real circular frequency ω. These in turn depend on the energy of an excited molecule in the presence of the polarization produced by the electromagnetic field. The value of $\mathbf{K}'$ must therefore be obtained by self-consistent methods. In order to relate the factors determining n and κ for the polarization wave, we write this wave in terms of its Fourier components, normalized to the liquid (or crystal) boundaries. Each of these components have wave vectors $\mathbf{K}$ determined by the boundary conditions which relate the internal and external values of the electric, magnetic and displacement fields (Kliewer and

Fuchs 1966). If the dimensions of the liquid are large the components of K along each of three perpendicular axes are given by

$$2Ka = 0, m\pi$$

where m is an integer and $2a$ the thickness along the appropriate coordinate. Only in the case of a crystal which possesses translational symmetry can K be written in terms of translations which leave the crystal unchanged (with the assumption of periodic boundary conditions), as required for Bloch functions.

When the Fourier components are summed over all allowable transitions the form of the polarization wave is given by ($9b$):

$$\psi(K') = \frac{\sum_t \sum_K \sum_p \exp(iK \cdot p)\phi_p{}^t}{(N)^{1/2}}. \tag{9b}$$

The polarization wave of arbitrary frequency ω has thus been written as being made up of all the allowable transitions t of the liquid. When ω is equal to the frequency of a particular transition, absorption occurs and the polarization is due to that transition only. For the model considered here the frequency is taken to be close to the transition y, the polarization being written as the effective polarization of that state, the contribution due to all other states being absorbed into the refractive index n'. This leads to an effective dipole moment operator (Dissado 1970 a) for the state y. Using the effective dipole moment operator, the polarization wave can be represented by

$$\psi(K') = \frac{\sum_K \sum_p \exp(iK \cdot p)\phi_p{}^y}{(N)^{1/2}}. \tag{9c}$$

A finite response time will be required for the molecular polarization to be produced by the exciting field (about 10^{-16} s for electronic transitions). Although the liquid possesses no permanent order there will be an instantaneous arrangement during the response time.

An average should be taken over all arrangements; thus the molecular wave function $\phi_p{}^y$ must be taken as referring to a molecule possessing an average orientation. It is of course essential to the argument that the molecules be isotropic, so that the transition dipoles are always in the direction of the electric intensity, and normal to the propagation direction of the field. The polarization wave defining the energy of an excited molecule and described by ($9c$) with an arbitrary value of K' might thus be thought of as a linear combination of instantaneous stationary states similarly to the thin crystal result.

As will be shown, the measurable properties (n and κ) of the electromagnetic field depend upon the modulus of the square of the matrix element coupling the field and the molecular states, which is proportional to the square of the transition dipole moment component along the direction of the electric field vector. For a liquid this must be averaged over all orientations, we therefore take the transition dipole moment of the wave function $\phi_p{}^y$ as the root-mean-square value ($\overline{q^y}$) of the component of the transition dipole moment in the direction of the electric field vector. The direction of the mean transition dipole moment is taken to be along the electric field vector.

The operator (1) only connects states in which the number of photons and excited molecules change by one. Hence the matrix element H_{00} is zero for molecules possessing no permanent dipole moment.

In solving equations (8) for $U_{yK,0}$, intermolecular interactions are allowed for by inclusion of the states m in (10). Since the system is a pure liquid there is only one solute transition (y) to be considered. The interactions are resonance interactions, hence (10) will give an energy shift without a correction to the wave function.

$$U_{yK,0} = H_{yK,0} + \sum_{m \neq 0} H_{yK,m} \zeta(E - E_m) U_m(E).\qquad(10)$$

The only states m for which $H_{yK,m}$ is non-zero, are those containing either one photon or one photon and two excited molecules. The matrix element $U_{m0}(E)$ for these states is taken to the first non-vanishing order only.

The coupled equations can then be solved as for the crystal (Craig and Dissado 1968) to give $U_{yK,0}$:

$$U_{yK,0} = H_{yK,0} - \tfrac{1}{2}i\hbar\gamma(E, K) U_{yK,0}(E) \zeta(E - E_{yK})\qquad(11)$$

where

$$\frac{i\hbar}{2}\gamma(E, K) = \sum_{p \neq l} \exp(i K \cdot p - l) \sum_{\lambda f} \left(\frac{\langle \phi_p{}^y | q_m \cdot \epsilon^\perp | f \rangle \langle f | q_m \cdot \epsilon^\perp | \phi_l{}^y \rangle}{E - \hbar c f/n'} \right.$$

$$\left. + \frac{\langle \phi_p{}^y | q_m \cdot \epsilon^\perp | \phi_p{}^y \phi_l{}^y f \rangle \langle f \phi_p{}^y \phi_l{}^y | q_m \cdot \epsilon^\perp | \phi_l{}^y \rangle}{E - 2E_y - \hbar c f/n'} \right)$$

f, λ, being the wave vector and polarization index respectively of the photon in the intermediate state. An expression of this form for $n' = 1$ has been evaluated by Philpott (1968) giving $\gamma(E, K)$ as

$$\frac{i\hbar}{2}\gamma(E, K) = \sum_{R \neq 0} \left[q_i{}^y q_j{}^y \exp(in'k'R) \left[-\alpha_{ij} \frac{(k')^2}{R} + \beta_{ij} \left\{ \frac{-ik'}{n'R^2} + \frac{1}{(n')^2 R^3} \right\} \right] \right]$$

$$\times \exp(i K \cdot R).\qquad(12)$$

k' is the magnitude of the wave vector appropriate to the energy E, which is that of the coupled radiation plus polarization field system. The real part of $i\gamma(E, K)$ is the sum of the intermolecular interactions (5), the imaginary part being the radiative damping factor for the condensed state (Craig and Dissado 1968).

Substituting (11) into integral (7) we obtain

$$b_{yK}(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{dE \, H_{yK,0} \exp\{i(E_y - E)t/\hbar\}}{\{E - E_0 + \tfrac{1}{2}\hbar\Gamma(E)\}\{E - E_y + i\tfrac{1}{2}\hbar\gamma(E, K)\}}.\qquad(13)$$

We have now to examine the initiation state 0. This is made up of two components of energy $\hbar c Q/n'$ and $-\hbar c Q/n'$ respectively, Q being the wave vector for the coupled field. The ground-state energy being taken as an energy zero. The first component corresponds to the photon that is absorbed, the second component to initial emission of a real photon of energy $\hbar c Q/n'$. The matrix element $H_{yK,0}$ for the second component is thus opposite in sign to that for the first:

$$H_{yK,+Q} = -H_{yK,-Q}.\qquad(14)$$

All other matrix elements involving the initial state 0 are identical for the two

components. The complete expression for $b_{yK}(t)$ is

$$b_{yK}(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega |H_{Ky,Q}| \exp\{i(\omega_y - \omega)t\}}{\{\omega - \omega_y + i\gamma(\omega, K)/2\}}$$

$$\times \left\{ \frac{1}{\omega - cQ/n' + i\Gamma(\omega)/2} - \frac{1}{\omega + cQ/n' + i\Gamma(\omega)/2} \right\} \qquad (15)$$

where ω and ω_y are the circular frequencies of the coupled state (energy E) and unperturbed molecular state (energy E_y) respectively. The energies of the coupled state are given by the poles of this integral, which occur on the second Riemann Sheet (Goldberger and Watson 1964). The poles are obtained by solving equation (16), where $i\Gamma(\omega)$ and $i\gamma(\omega, K)$ are evaluated on the second Riemann Sheet.

$$[i\omega\Gamma(\omega) - \Gamma^2(\omega)/4 + \{\omega^2 - Q^2c^2/(n')^2\}]\{\omega - \omega_y + i\gamma(\omega, K)/2\} = 0. \qquad (16)$$

$\Gamma(\omega)$ is found from (11) and (8):

$$\frac{\Gamma(\omega)}{2} = \sum_K \frac{i|H_{yK,Q}|^2}{\omega - \omega_y + i\gamma(\omega, K)/2} \qquad (17)$$

but the matrix element $H_{yK,Q}$ may be written as

$$H_{yK,Q} = \frac{A \sum_p \exp\{i(Q - K) \cdot p\}}{(N)^{1/2}}$$

where A is a factor independent of the vector position p. The liquid is regarded as being continuous, allowing us to replace the sum over molecular centres with a volume integral. If we choose the direction of $Q - K$ as the z axis of a cartesian coordinate system with a as the coordinates of the boundaries along this axis, we have

$$H_{yK,Q} = (A\sqrt{N})(1/V) \int\int dx \, dy \int_{-a}^{a} \exp\{i(Q - K)z \, dz\}$$

$$= (A\sqrt{N}) \frac{\sin\{(Q - K)a\}}{(Q - K)a}. \qquad (18)$$

In the limit of $|Ka|$ very large the integral is a representation of the Dirac delta function $\delta(K - Q)$ which reduces the sum over K in (17) to a single term, that of K equal to Q. Thus the equality of the wave vector of the exciting electromagnetic field and the polarization wave is explicitly confirmed. It is to be noted that this condition applies in all cases (excepting strong absorption) independently of the use of boundary conditions, periodic or otherwise, to define the allowed values of K. The breakdown of the delta function property for small values of $|Ka|$ is shown here explicitly. In this case the electromagnetic field couples to all of the waves defined by K and (9c) represents the Fourier components of the electromagnetic field in the liquid, the amplitude of each component being given by

$$\frac{\sin\{(Q - K)a\}}{(Q - K)a}$$

and the energy of an excited molecule in such a field may be written either as the sum

over that due to each of the Fourier components or as that due to a polarization field of wave vector Q whose value is determined from a self-consistent solution of the dispersion expression. $\Gamma^2(\omega)$ is very small compared with ω and may be neglected. (16) becomes

$$-2\omega|H_{yK,Q}|^2 + \{\omega^2 - Q^2c^2/(n')^2\}\{\omega - \omega_y + i\gamma(\omega, Q)/2\} = 0 \qquad (19)$$

and on rearrangement, with the use of

$$\frac{c^2Q^2}{\omega^2} = d = n^2 \qquad (20)$$

an expression (21) is obtained for the dielectric constant d.

$$d = n^2 = (n')^2 + \frac{2(n')^2|H_{yK,Q}|^2}{\omega\{\omega - \omega_y + i\gamma(\omega, Q)/2\}}. \qquad (21)$$

Evaluation of $(H_{yK,Q})$ reduces (21) to

$$n^2 = (n')^2 + \frac{4\pi N(\overline{q^y \cdot e_\lambda})^2\omega_y}{V\omega\{\omega_y - i\gamma(\omega, Q)/2 - \omega\}}. \qquad (22)$$

Here $\overline{(q^y \cdot e_\lambda)}^2$ denotes the average of the square of the component of the transition dipole moment for the yth state in the direction of polarization of the light. We note that in a solid of anisotropic molecules the orientation of the transition moment is fixed, and not averaged as here. N/V in (22) may be taken to be $1/V_0$ where V_0 is the molecular volume, if the volume of the liquid is large enough to be the volume of quantization. This should be at least a cube of side λ, the wavelength of the incident wave.

The relationship (22) brings out the physical significance of the interaction operator (1). All the states of the medium that have been removed from explicit consideration in the Hamiltonian contribute n' to the refractive index. This contribution has been returned to the equation by use of the modified interaction operator.

The derivation of (1) replaces the transition dipole moment operator of the molecule by the contribution to the polarization of the expectation value (in the condensed state) for each molecular transition. The wave function from which the expectation values are obtained should be the exact wave function for the molecular system. The operator (4) may then be written in matrix form as

$$-(q) \cdot E^{\perp}(r)$$

where (q) is a diagonal matrix whose elements are $q^t(r)$, the expectation value of the transition dipole moment operator obtained using the exact wave function for the collective state t of the system. The operator (1) is the reduction of this matrix to a single equivalent interaction between an effective dipole moment for the state s, and the medium field.

So far the expectation values used have been those for an isolated molecule. This is the zero-order approximation (in intermolecular coupling) and allows only for intermolecular resonance interactions. Inclusion of non-resonance intermolecular interactions (§ 2.2) requires the corrections of the wave function (9b) from which the transition dipole moment is obtained. The coupling matrix will then connect the field with expectation values of the transition dipole moment corrected for all intermolecular interactions. Subsequent use of the operator (1) is then equivalent to the reduction of this matrix.

2.2. First-order correction to the transition dipoles

In this case the dipoles $\overline{q^y}$ are now replaced by the fully corrected transition dipoles $\overline{q^{yc}}$, and (22) becomes

$$n^2 = (n')^2 + \frac{4\pi N(\overline{q^{yc}} \cdot e_\lambda)^2 \omega_y}{V\omega\{\omega_y - i\gamma^c(\omega, Q)/2 - \omega)\}}. \tag{23}$$

Here $\gamma^c(\omega, Q)$ contains all the intermolecular interactions for the state y. For frequencies far from resonance (23) becomes

$$n^2 = 1 + \sum_y \frac{4\pi N}{V} \frac{(\overline{q^{yc}} \cdot e_\lambda)^2 2\omega_y}{(\omega_y^2 - \omega^2)}. \tag{24}$$

We are now concerned with obtaining $\overline{q^{yc}}$ in terms of $\overline{q^y}$ and n'. This will lead to a new refractive index equation, and give expressions for the medium corrected dipole examined in part II (Dissado 1970 b—to be referred to as II.)

Expressions (22)–(24) depend only on the average component of q^y parallel to the polarization vector e_λ. Thus we continue to work with isotropic molecules and shall use a model in which all the transition dipoles lie along the polarization vector, and possess a magnitude $\bar{q}$. The interaction operator (4) for photons in free space is now appropriate, since non-resonance interaction with all other medium states is to be taken into account separately. The coupling matrix will then be reduced by use of the operator (1) to connect the exciting wave and the state y.

Philpott (1966) has derived an expression for the coupling matrix correct to the third-order of perturbation theory. In this order all intermolecular interactions between states containing only one excited molecule are included. The form of the corrected dipole moment is given by

$$\overline{q_i^{yc}} = \overline{q_i^y} + \sum_{x \neq y} \sum_{R \neq 0} \exp(i\boldsymbol{K} \cdot \boldsymbol{R}) V(R, k_y) \left(\frac{1}{E_y - E_x} - \frac{1}{E_y + E_x} \right) \overline{q_i^{xc}} \tag{25}$$

where $V(R, k_y)$ is the retarded interaction

$$V(R, k_y) = \overline{q_i^{xc}} \overline{q_i^y} \left[\beta_{ii} \left\{ \frac{\cos(k_y R)}{R^3} + \frac{\sin(k_y R) k_y}{R^2} \right\} - \alpha_{ii} \frac{\cos(k_y R)(k_y)^2}{R} \right]. \tag{26}$$

The first sum in (25) is over molecular states and k_y is the wave-vector for the transition to the yth state. The term having the denominator $(E_y + E_x)$, does not appear in the static correction to the wave function to the first order of perturbation theory. The second correction to the energy (fourth order in the molecule field coupling and second order in the static theory) contains a term with denominator $E_y + E_x$. In the static theory it is from interactions between states with one excited molecule and those with three. Since correction of the wave function to the first order should give the energy correct to the third order, the presence of a term for the first-order corrected transition dipole with a denominator $E_y + E_x$ is to be expected. Its absence from the static theory is bound up with the use of ground state functions which only allow for molecules in their ground state and the use of the field-molecule interaction operator to carry interactions between molecules gives the correct consistent expressions for the transition dipole and the energy. The neglect of this term in the static theory must be remembered when identification is made of matrix elements with the refractive index in II.

We shall take the Coulomb limit of the retarded interaction $V(R, k_y)$, since the sum of the retarded interactions gives oscillating surface-dependent terms in addition to the Coulomb contribution. These extra terms are required to satisfy the boundary conditions and do not contribute to the interaction energy. Thus (25) becomes

$$\overline{q_i^{yc}} = \overline{q_i^{y}} + \left[\sum_{x \neq y} \sum_{R \neq 0} \exp(i\boldsymbol{K} . \boldsymbol{R}) \frac{\overline{q_i^{xc}}}{R^3} \overline{q_i^{y}} \beta_{ii} \left\{ \frac{1}{E_y - E_x} - \frac{1}{E_y + E_x} \right\} \right] \overline{q_i^{xc}}. \quad (27)$$

The intermolecular interaction sum can be evaluated for a continuous medium by integration:

$$\sum_{R \neq 0} \exp(i\boldsymbol{K} . \boldsymbol{R}) \frac{\overline{q_i^{xc} q_j^{y}}}{R^3} \beta_{ij} = \frac{1}{V_0} \int \exp(i\boldsymbol{K} . \boldsymbol{R}) \frac{\overline{q_i^{xc} q_j^{y}}}{R^3} \beta_{ij} \, d^3R$$

$$= - \frac{4\pi}{3V} \overline{q_i^{xc} q_j^{y}} (\delta_{ij} - 3\hat{K}_i \hat{K}_j). \quad (28)$$

The medium is considered to be continuous up to the boundary of the molecule, hence the lower limit of the integral in (28) is the molecular radius r. The value given in (28) is obtained in the limit of $r = 0$, for a small non-zero value of r the leading correction term is of the order of $(|K|r)^3$ which can be neglected for magnitudes of $|K|$ less than those corresponding to x-ray frequencies. Since $\overline{q_i^{xc}}$ and $\overline{q_j^{y}}$ are parallel and lie along e_λ perpendicular to K, (equal to Q for the polarization wave) (28) is independent of K, both in magnitude and direction. Thus (28) becomes

$$- \frac{4\pi}{3V} \overline{q_i^{xc} q_i^{y}}. \quad (29)$$

Under the restrictive conditions on the transition moments, an identical result is obtained for the more usual wave functions $\psi_y(K = 0)$. Substituting in (25) and rearranging we obtain $\overline{q^{yc}}$:

$$\overline{q_i^{yc}} = \overline{q_i^{y}} + \sum_{x \neq y} \frac{4\pi}{3V_0} (q_i^{xc})^2 \left(\frac{1}{E_x - E_y} + \frac{1}{E_x + E_y} \right) \overline{q_i^{y}}. \quad (30)$$

From (24) we see that the correction factor is one third the contribution to the refractive index of all states other than y, at the transition frequency of y. It is therefore $(n'^2 - 1)/3$ which gives the corrected transition dipole moment as

$$\overline{q_i^{yc}} = \frac{(n'+2)}{3} \overline{q_i^{y}}. \quad (31)$$

The correction obtained is identical with that found electrostatically by use of the Lorentz cavity field. This can be further demonstrated by substituting in (23) which on arrangement gives the Debÿe equation. Remembering that

$$\frac{3(n^2 - n'^2)}{(n^2 + 2)(n'^2 + 2)} = \frac{n^2 - 1}{n^2 + 2} - \frac{n'^2 - 1}{n'^2 + 2}$$

we obtain

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n'^2 - 1}{n'^2 + 2} + \frac{(4\pi/3V_0)(\overline{q^y})^2 (\omega_y/\omega)\{(n'^2 + 2)/(n^2 + 2)\}}{\omega_y - i\gamma^c(\omega, Q)/2 - \omega} \quad (32)$$

which on taking $n' \simeq n$ for the correction factor gives the refractive index equation

as obtained electrostatically using the Lorentz cavity field. The correction to the effective field due to polarization on the cavity wall, which forms the electrostatic Lorentz field, is now seen to be associated with non-resonance intermolecular inter-action, and would be effective for a classical permanent dipole embedded in an iso-tropic dielectric as well as for the dielectric alone.

2.3. *Contribution of field-oriented permanent dipoles*

If the liquid molecules possess a permanent dipole moment μ, the presence of a low-frequency electromagnetic field will orient the dipoles to give a non-zero contri-bution to the field along the electric field vector. We may distinguish two extreme types of situation:

(i) The dielectric constant d is large

(ii) The dielectric constant $d \simeq n^2$, n being the liquid refractive index at the appropriate frequency.

The mean orientation of the permanent dipoles will depend upon their potential energy in the electric field in relation to their thermal energy (kT). When the system of molecules and incident electromagnetic field has reached a dynamic equilibrium the permanent dipoles will contribute to the field along the external electric field vector. It is the potential energy of a permanent dipole in this total field that must be used to determine the mean orientation which in turn determines the magnitude of the permanent dipole distribution. When determining the expression for the dielectric constant this permanent dipole field contribution must be written as a function of the dielectric constant, leading to a rearrangement of the equation. The magnitude of this extra field will be of the order of $\mu\cos\theta$, θ being the mean orientation angle which in its first approximation depends upon μ/kT, therefore this term is proportional to $(d-n^2)$ which is very small for case (ii), but large for case (i). In neglecting this contribution as we do here, we are in fact restricting the applicability of our derived expression to case (ii). We further restrict the model to those molecules with a permanent dipole and an isotropic polarizability, i.e. molecules which are isotropic with respect to the transition dipole moments of their excited states. This is the usual model involved in the derivation of the Clausius–Mossotti equations whose analogue we wish to derive here. Because of the restriction to case (ii) we do not expect our expression to be correct for liquids of high dielectric constant, any alteration due to molecular anisotropy will also not be reproduced.

In the presence of the low-frequency electromagnetic field, the oriented permanent dipoles (lying along the electric field vector) will lie in the polarization field due to the surrounding molecules. The part of this field due to the excitation of collective liquid states described by the wave function (9*b*) leads to a mixing in of excited states into the ground-state wave function. The part due to the oriented permanent dipoles will give an energy shift to the molecular ground state, redefining the energy zero without changing the coupling to the electromagnetic wave.

Correcting the oriented ground-state wave function Φ_{G0} for interaction with the excited states gives

$$\Phi_{G0}{}^c = \Phi_{G0} + \sum_{K,y\,\neq\,G} \frac{4\pi}{3V_0} \left(\frac{\overline{q^{yc}}}{E_y} \mu \right) \sum_p \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{p})\phi_p{}^{yc} \qquad (33)$$

where (33) is obtained in the same way as (30). The interacting states are again assumed to be corrected for all interactions except that of the ground state. From

(33) the corrected oriented dipole moment μ^c is given by

$$(\phi_G|\boldsymbol{\mu}|\phi_{G0}) = N\mu^c = N\mu\tfrac{1}{3}\{n(0)+2\} \tag{34}$$

where Φ_G is the wave function for the non-oriented state, and $n(0)$ is the static refractive index.

When deriving the expression (32) the matrix element H_{00} is taken to be zero in evaluating $\Gamma(\omega)$. H_{00} is the self energy of the initial state which comprises ground state molecules and field. When the molecules possess no permanent dipole moment it is zero. For molecules with permanent dipole moments however, the self energy is that of orientation of the dipoles in the presence of the field. This is given by the average over all θ of H_{00}

$$H_{00} = \langle \Phi_G| - \boldsymbol{\mu}_m\boldsymbol{\epsilon}_m^{\perp}\cos\theta|\Phi_{G0}\rangle \tag{35}$$

where θ is the angle between the dipole moment μ and the field polarization vector.

The mean value of $\cos\theta$ is found from the Boltzmann distribution of oriented states (Onsager 1936) and is

$$\boldsymbol{\mu}_m{}^c\boldsymbol{\epsilon}^{\perp}/3kT \tag{36}$$

k is the Boltzmann constant. If the matrix element (35) is described in second quantized form, it is seen to be quadratic in photon creation and annihilation operators. The orientation of the dipole corresponds to an initial state of photon and unoriented molecule, and a final state of scattered photon and oriented molecule, that is to simultaneous absorption and emission of a photon by the molecule to be oriented.

Substituting (3) for $\epsilon_m^{\perp}$ the matrix element H_{00} becomes

$$H_{00} = -\frac{2\pi N\omega}{3VkT}\left(\frac{\mu^c}{n'}\right)^2 \tag{37}$$

ω is the frequency of the interacting field, and n' the refractive index of the medium neglecting the dipole orientation, and evaluated at ω. Including this term in (17) for $\Gamma(\omega)$ and substituting in (16) we obtain an expression corresponding to (22):

$$d = n'^2 + \frac{4\pi}{9kTV_0}\frac{\{n(0)^2+2\}^2\mu^2}{3} \tag{38}$$

where the interaction of all the excited states with the field has been included in $(n')^2$, arising from the reduced form of the molecule–field interaction operator given by (1).

Expression (38) may be arranged in a similar way to that previously to give

$$\frac{d-1}{d+2} = \frac{n'^2-1}{n'^2+2} + \frac{4\pi}{9kT}\frac{\mu^2}{V_0}\frac{\{n(0)^2+2\}^2}{(d+2)(n'^2+2)}. \tag{39}$$

This modification of the Clausius–Mossotti equation is to be compared with that of Onsager (1936) who gives

$$\frac{d-1}{d+2} = \frac{n^2-1}{n^2+2} + \frac{4\pi\mu^2}{9kTV_0}\frac{3d(n^2+2)}{(2d+n^2)(d+2)}. \tag{40}$$

The factor multiply multiplying $4\pi\mu^2/9kTV_0$, $f(d, n^2)$ is plotted in figure 1 for the two equations. The Clausius–Mossotti equation is obeyed when this is 1. The two expressions agree with each other and the Clausius–Mossotti equation when d is

equal to n^2. The derived expression shows poor agreement in the region $d < n^2$, the peak given by Onsager's expression is not obtained and the value for $d = 1$ is large and depends upon the value of n^2. For $d > n^2$, $f(d, n^2)$ from (39) shows the
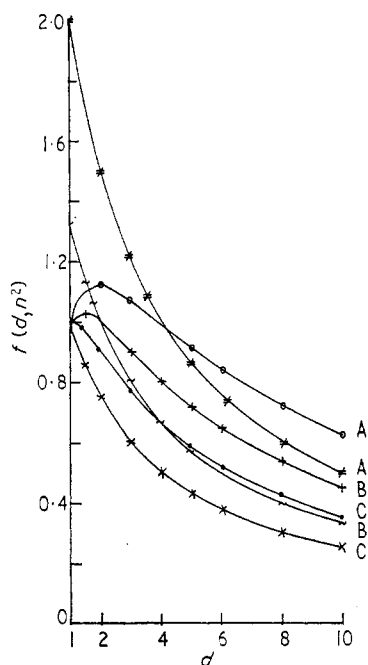

Figure 1. Comparison of $f(d, n^2)$ for expressions (40) and (39). Values are given for $n^2 = 1, 2, 4$, labelled A, B and C respectively.

$$\begin{array}{l} \bullet \\ + \\ \circ \end{array} \left\{ \begin{array}{l} n^2 = 1 \\ n^2 = 2 \\ n^2 = 4 \end{array} \right\} \text{ expression (44)}$$

$$\begin{array}{l} \times \\ \sim \\ \neq \end{array} \left\{ \begin{array}{l} n^2 = 1 \\ n^2 = 2 \\ n^2 = 4 \end{array} \right\} \text{ expression (43).}$$

same shape as Onsager's curve and in the region of $d \gg n^2$ has a limiting value which is one third less than that of (40).

On comparing with the experimentally deduced relationship (Wyman 1936)

$$\frac{4\pi\mu d}{9kTA} \tag{41}$$

for which A is found to be between 6·2 and 11, Onsager (1936) shows that these values of A correspond to a range of refractive indices given by

$$1·25 < n < 1·64.$$

Our expression would give a slightly higher range for n of

$$1·5 < n < 1·94$$

which are still reasonably acceptable values.

Therefore in the regions ($d \simeq n^2$) for which our model applies we find a quantitative agreement between our expression and that of Onsager determined from the electrostatic reaction field. For large values of d the same form for the relationship is obtained without qualitative agreement. It is therefore to be expected that calculations of the spectral solvent effect based on the model advanced should show good agreement with those found from the use of reaction fields, for solvents with low dielectric constants, and at least qualitative agreement for solvents with high dielectric constant.

3. Conclusions

We have shown here that the Debye equation previously obtained by electrostatic arguments can be obtained from a microscopic treatment of a homogeneous liquid system by the inclusion of non-resonance excitation exchange interactions between a representative molecule and all other molecules of the medium. Therefore, when applying quantum mechanics to calculations of such a system, the inclusion of intermolecular interaction must be regarded as the inclusion of the Lorentz cavity field. Formulations which include both as separate effects are incorrect. The application to polar liquids demonstrates a qualitative similarity to Onsager's (Onsager 1936) theory of reaction fields for $d > n^2$, and should therefore give results in qualitative agreement with those derived from the use of reaction fields in this range. In the region $d < n^2$ there is little relationship, however these values of d are not often found in practice. Expressions identical to those of Onsager should be obtained by an application of perturbation theory to higher orders.

Acknowledgments

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