

DIELECTRIC SATURATION IN LIQUIDS
CONSISTING OF ATOMS OR NONDIPOLAR MOLECULES

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A new approach to the theory of dielectric saturation in isotropic bodies is proposed taking into account, in addition to hyperpolarisability, the fluctuation of number density, translational fluctuations as well as fluctuations of the fields of electric molecular quadrupoles and octupoles. The theory is applied to liquid argon and to an explanation of the latest measurements in CCl_4 , CS_2 and C_6H_6 .

Recently, measurements of dielectric saturation in liquid CS_2 , C_6H_6 and CCl_4 have been reported [1, 2]. The occurrence of dielectric saturation in nondipolar gases of the type CS_2 is explained within the framework of the Langevin-Debye theory [3] by orientation of the polarisability ellipsoids of the molecules in the strong external electric field. On the other hand, the presence of dielectric saturation in liquids like CCl_4 is not accessible to an explanation by the Langevin-Debye theory of molecular orientation but stems from two other mechanisms [4, 5]; one, considered by Buckingham [4], resides in the hyperpolarisability of the atoms or isotropic molecules due directly to nonlinear distortion of their electronic shells in the intense electric field. The hyperpolarisability (or Voigt's) effect is essential in atomic gases, especially at high temperatures and rarefaction [5]. Kielich [6] showed that anisotropy is induced in atomic liquids or ones consisting of tetrahedral molecules by yet another, statistical mechanism residing in the translational fluctuations considered by Kirkwood [7] in his linear theory of nonpolar dielectrics. Radial interactions cause the atoms or isotropic molecules to re-group themselves into pairwise, triple (and generally multiple) assemblages, which can undergo orientation by the external electric field [6-10].

We consider a macroscopic spherical specimen of volume V , containing N microsystems. In the case of a weak measuring electric field, the relation between the mean macroscopic field E^m existing in the specimen and the field E_0^m externally applied in its absence is of the well-known form $3E_0^m = (\epsilon + 2)E^m$, where ϵ is the dielectric constant. On the assumption that the weak measuring field E_0^m causes but linear polarisation whereas the strong field E_0 gives rise to nonlinear polarisation of the medium, we have in a semi-macroscopic approach, to within satisfactory approximation [5]:

$$VP_i = M_i + (A_{ij} + B_{ijk}E_{0k} + \frac{1}{2}C_{ijkl}E_{0k}E_{0l} + \dots)E_{0j}^m + \dots, \quad (1)$$

where summation over recurring indices $j, k, l \dots$ is implicate, M_i is the electric dipole moment at $E_0 = 0$, A_{ij} is the tensor of linear polarisability of the medium, and the tensors $B_{ijk}, C_{ijkl} \dots$ define nonlinear variations in polarisability induced by the strong electric field.

Under the influence of the strong field E_0 , the dielectric permittivity ϵ becomes a tensorial quantity, ϵ_{ij} , which undergoes the following quadratic variation resulting by the expansion (1) and classical statistical mechanics:

$$\delta\epsilon_{ij} = S[(\epsilon + 2)/3]^4 (\delta_{ij}E_kE_k + 2E_iE_j), \quad (2)$$

δ_{ij} denoting Kronecker's unit tensor.

The saturation constant S consists of contributions from the various tensors of the expansion (1); for simplicity, we shall deal with them as totally symmetric. The part resulting from nonlinear polarisa-

bility of the medium is

$$S_{\text{NL}} = (2\pi/15V) \langle C_{\alpha\alpha\beta\beta} + 4\kappa B'_{\alpha\alpha\beta} M_{\beta} \rangle, \quad (3)$$

where the brackets $\langle \rangle$ denote statistical averaging, and $\kappa = 1/kT$. Another, hitherto not considered contribution to S stems from statistical fluctuations (denoted by Δ) of the trace of the linear polarisability and the square of the dipole moment of the medium $M^2 = M_{\alpha} M_{\alpha}$:

$$S_{\text{FL}} = (2\pi\kappa/9V) \langle (\Delta A_{\alpha\alpha} + \kappa \Delta M^2)^2 \rangle. \quad (4)$$

Other contributions to S depend on higher powers of the inverse temperature $\kappa = 1/kT$ and are of the general form:

$$S_{\text{A}} = (4\pi\kappa/45V) \langle 3A_{\alpha\beta} A_{\alpha\beta} - A_{\alpha\alpha} A_{\beta\beta} \rangle; \quad (5)$$

$$S_{\text{AM}} = (8\pi\kappa^2/45V) \langle 3A_{\alpha\beta} M_{\alpha} M_{\beta} - A_{\alpha\alpha} M_{\beta} M_{\beta} \rangle; \quad (6)$$

$$S_{\text{M}} = -(4\pi\kappa^3/45V) \langle M^4 \rangle. \quad (7)$$

By measuring $\delta\epsilon_{ij}$ in appropriate experiments parallel and perpendicular to the strong, saturation-inducing electric field E we obtain with regard to the general equation (2):

$$\delta\epsilon_{\parallel} = 3\delta\epsilon_{\perp} = 3S[(\epsilon + 2)/3]^4 E^2. \quad (8)$$

(i) Atomic liquids. Here, two mechanisms are essential in inducing electric anisotropy, namely hyperpolarisability [4] and translational fluctuations [6, 7]. Consequently, the constants (3) and (4) reduce to:

$$S_{\text{NL}} = (2/3)\pi\rho\gamma \{1 + (48/5)\alpha^2 \langle r^{-6} \rangle + \dots\}; \quad (9)$$

$$S_{\text{FL}} = 2\pi\kappa\rho\alpha^2 (\rho k T \beta_T + 8\alpha^2 \langle r^{-6} \rangle + \dots) \quad (10)$$

to within pairwise radial correlations; α is the linear polarisability of the atom, γ - its second-order hyperpolarisability, β_T - the isothermal compressibility coefficient, and $\rho = N/V$ - the number density of atoms, mutually distant by r . The terms $\alpha^2 \langle r^{-6} \rangle$ result by translational fluctuations, whereas $\rho k T \beta_T$ is due to fluctuations in number of atoms. Owing to the translational fluctuations, the anisotropic constant (5) also is non-zero; in a satisfactory approximation, it yields [6]:

$$S_{\text{A}} = (16/5)\pi\kappa\rho\alpha^4 (\langle r^{-6} \rangle + 2\alpha \langle r^{-9} \rangle + \dots). \quad (11)$$

The constants (6) and (7) differ from zero if fluctuations of the dispersional fields of London interactions intervene; however, their contribution is numerically negligible.

(ii) Tetrahedral molecules. In liquids consisting of tetrahedral molecules, a good approximation is achieved by applying the expressions (9) - (11) which, in general, have to be supplemented by contributions from fluctuations of the electric fields of molecular octupoles $\Omega = \Omega_{123}$ [8]. Numerically, these contributions are insignificant; the essential part comes from the constants (5) and (6):

$$S_{\text{A}} = (256/35)\pi\kappa\rho\beta^2 \Omega^2 \langle r^{-10} \rangle + \dots; \quad (12)$$

$$S_{\text{AM}} = (256/35)\pi\kappa^2\rho\alpha^4 \Omega^2 \langle r^{-13} \rangle + \dots, \quad (13)$$

with $\beta = \beta_{123}$ - the first-order hyperpolarisability for tetrahedral symmetry [8].

(iii) Quadrupolar molecules. If the molecules of the liquid are axially symmetric and possess permanent electric quadrupoles Θ [8], then in addition to the expressions (9) - (11) (still applicable in a satisfactory approximation) we have the following contributions in the approximation of pairwise correlations:

$$S_{\text{A}} = (8/45)\pi\kappa\rho(\alpha_{\parallel} - \alpha_{\perp})^2 \{1 + (2\kappa/35)\Theta^2 [(\alpha_{\parallel} - \alpha_{\perp}) \langle r^{-8} \rangle + 2\Theta^2 \langle r^{-10} \rangle + \dots]\} \\ + (32/63)\pi\kappa\rho(\alpha_{\parallel} - \alpha_{\perp})\gamma\Theta^2 \langle r^{-8} \rangle + \dots; \quad (14)$$

$$S_{\text{AM}} = (64/25)\pi\kappa^2\rho\alpha^4 \Theta^2 \langle r^{-11} \rangle + \dots, \quad (15)$$

with $\alpha_{\parallel} - \alpha_{\perp}$ the anisotropy of linear polarisability of the molecule.

Table 1
Comparison of calculated and experimental variations of the electric permittivity in several liquids

Liquid	Electric saturation constants in 10^{-14} esu					$\delta\epsilon_{\parallel}/E^2$ in 10^{-12} esu	
	S_{NL}	S_{FL}	S_A	S_{AM}	S_{total}	Theoretical	Experimental
Argon (85°K)	3.0	4.0	0.7	--	7.7	0.5	--
Carbon tetrachloride	9.8	1620.0	290.0	6.0	1925.8	231.2	166 [1] 426 [2]
Benzene	--	1850.0	612.0	8.5	2470.5	311.2	568 [2]
Carbon disulphide	150.0	3150.0	2210.0	13.0	5523.0	938.6	332 [1] 1098 [2]

The expressions (9) - (15) fail to take account of contributions from triple-, four-molecule and higher correlations; these are of rather involved form not well-adapted to numerical evaluations [9-11]. These can be performed numerically by resorting to Kirkwood's radial distribution function [7] for rigid spheres of diameter d and volume $v = \pi d^3/6$, yielding for $n \geq 4$ [10]:

$$\langle r^{-n} \rangle = [4\pi\rho/(n-3)](\pi/6v)^{(n-3)/3}. \quad (16)$$

More highly accurate computations can be made using radial distribution function with the Lennard-Jones s - t central potential

$$g_{s-t}(r) = \exp\{y_{st}^2[(\sigma/r)^t - (\sigma/r)^s]\}, \quad (17)$$

which leads to a result adapted to numerical tabulation:

$$\langle r_{st}^{-n} \rangle = \frac{4\pi\rho}{s\sigma^{n-3}} y_{st} \frac{2(3-n)/s}{st} \sum_{m=0}^{\infty} \frac{1}{m!} y_{st}^{2m} \frac{2m(s-t)/s}{st} \Gamma\left(\frac{mt+n-3}{s}\right), \quad (18)$$

with $y_{st}^2 = [\epsilon s\kappa/(s-t)](s/t)^t/(s-t)$, where ϵ and σ are well-known central forces parameters having the dimensions of an energy and force, respectively.

Table 1 contains results calculated for several liquids by eqs. (8) - (16) and available data [6, 10]. For liquid argon at 85°K we get a variation $\delta\epsilon_{\parallel} \geq 5 \times 10^{-13} E^2$ well accessible to measurement by recently developed highly sensitive methods [1, 2]. The quadratic variations $\delta\epsilon_{\parallel}$ calculated for CCl_4 , C_6H_6 and CS_2 are seen to be in satisfactory agreement with experiment [1, 2].

Recent measurements at this Institute show that $\delta\epsilon$ is by no means a quadratic function of E and undergoes complete saturation in solutions of macromolecules [2, 12] and partial saturation in solutions of molecules [2]. In sufficiently intense fields saturation should appear even in liquids like CCl_4 , for which in place of the quadratic variation (8) one should write the relation:

$$\delta\epsilon_{\parallel} = 16\pi\rho d^{-3} \alpha^2 [(\epsilon + 2)/3]^2 R_{\alpha}(q), \quad (19)$$

involving the molecular reorientation function:

$$R_{\alpha}(q) = \frac{1}{2}\{3L_2(q) - 1\} + 3q\{L_4(q) - L_2^2(q)\}, \quad (20)$$

where L_2 and L_4 are even Langevin functions [12] and $q = \alpha^2(\epsilon + 2)^2 E^2 / 3d^3 kT$ is a parameter of re-orientation in the field E of an assemblage of two molecules mutually distant by d polarizing each another in accordance with Silberstein's model. Eq. (19) yields results in satisfactory agreement with the latest measurements by Przeniczny [2] in CCl_4 versus the applied field E .

The electric saturation $\delta\epsilon$ in liquids and dilute solutions with anisotropic molecules like C_6H_6 or CS_2 can be calculated with the formulas derived earlier [12] for solutions of macromolecules.

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