Theory of the nonlinear refractive index of liquids

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(Submitted April 24, 1974)
Zh. Eksp. Teor. Fiz. 67, 1859–1869 (November 1974)

The nonlinear refractive index n_2 is calculated for isolated and for interacting atoms and molecules. It is shown that dipole-dipole and dipole-quadrupole interactions of the particles in principle change n_2 as compared with the nonlinear index in a system of noninteracting particles. The theory as a whole agrees well with measurements of the Kerr constant K of a number of liquids, and also of the diameters of hyperfine filaments in liquid argon and in carbon tetrachloride.

1. INTRODUCTION

Knowledge of the nonlinear index of refraction n_2 of a substance is in principle necessary in many problems of nonlinear optics. But usually n_2 is estimated from indirect measurements (for example, by the Kerr effect), and then this estimated value is used in the theory. In this procedure, no consideration at all is given to the role of intermolecular interactions (IMI) in the medium, which in themselves may be a cause of optical nonlinearity.

It was shown earlier by the author[1] that the nonlinearities that occur in an ensemble of interacting molecules can advantageously be classified into intramolecular and intermolecular nonlinearities. The aim of the present work is, by use of this classification, to construct a quantitative theory of the nonlinear index of refraction n_2 of comparatively simple liquids, and to test it by means of experimental data available in the literature for several nonlinear effects. We remark that for simplicity we shall neglect the frequency dispersion of the linear and nonlinear susceptibilities, whose role in the averaged quantity n_2 is slight.

2. THE CONNECTION BETWEEN THE NONLINEAR POLARIZABILITY OF THE MOLECULES AND THE NONLINEAR INDEX OF REFRACTION OF LIQUIDS

The connection between the microscopic characteristics of the molecules and the macroscopic characteristics of the medium can prove to be nontrivial, in consequence of IMI, even in linear optics. For example, the simple Lorentz-Lorenz relation between the linear index of refraction n_0 and the linear polarizability α_0 of the molecules,

$$(n_0^2-1)/(n_0^2+2)={}^4/_3\pi N\alpha_0 \qquad (1)$$

(where N is the number of molecules in a unit volume), is an approximation, since it does not take into account the direct interactions of the molecules. Investigation of these was begun by the papers of Kirkwood[2], in which formula (1) was modified.

A more radical approach in the improvement of the Lorentz model was that of Onsager[3], who introduced the concept of the reaction field in a liquid; it is produced by feedback between the molecule and the surrounding medium. According to Onsager the internal field in a liquid is

$$\mathbf{f}_{\mathrm{Ons}}=G\mathbf{E}+R\boldsymbol{\mu}, \qquad (2)$$

where μ is the total dipole moment of the molecule,

$$G=\frac{3n_0^2}{2n_0^2+1},\quad R=\frac{2(n_0^2-1)}{a^3(2n_0^2+1)} \qquad (3)$$

and a is the Onsager radius of the molecule. From Onsager's theory it follows that the ratio of the internal field f to the mean field E is

$$\frac{f_{\mathrm{Ons}}}{E}\equiv L_{\mathrm{Ons}}=\frac{G}{1-\alpha_0 R}, \qquad (4)$$

whereas in Lorentz's theory

$$f_{\mathrm{Lor}}/E\equiv L_{\mathrm{Lor}}={}^1/_3(n_0^2+2). \qquad (5)$$

We note that (4) with use of (3) becomes (5) under the condition that the Onsager radius of the molecule can be found from the relation

$${}^4/_3\pi Na^3=1. \qquad (6)$$

But as was shown in a paper of the author[4], the relation (6) is not satisfied for real molecules.

A nonlinear analog of the Lorentz-Lorenz formula (1) was obtained in papers of Bloembergen and coworkers[5,6] on the basis of Maxwell's equations in a medium with nonlinear sources of field. If n_2 and α_2 are the coefficients in the expansion in powers of the field of the index of refraction and of the induced dipole moment p of the molecule,

$$n=n_0+n_2E^2,\quad p=\alpha_0 f+\alpha_2 f^3, \qquad (7)$$

then the relation between n_2 and α_2 in the Lorentz model is the following:

$$n_{2\mathrm{Lor}}=4\pi NL_{\mathrm{Lor}}^4\,\alpha_2/2n_0. \qquad (8)$$

In Onsager's theory, the relation between the tensors of nonlinear susceptibility $\epsilon_{\alpha\beta\gamma\delta}$ of the medium and of nonlinear polarizability $\alpha_{\alpha\beta\gamma\delta}$ of the molecules, with allowance for frequency dispersion, was obtained by the author[7]. In the application to the scalar quantities n_2 and α_2 and in the absence of dispersion, it has the form

$$n_{2\,\mathrm{Ons}}=\frac{2\pi N}{n_0 G}L_{\mathrm{Ons}}^4\alpha_2. \qquad (9)$$

In both variants of the theory of the internal field, the factor L enters in the fourth power in the ratio n_2/α_2; this follows directly from the equations of electrodynamics with nonlinear sources. In view of this, the use by Close et al.[8] and by Brewer et al.[9] of a factor L_{Lor}^2 in (8) is entirely incorrect; it was a consequence of an invalid extrapolation of the Lorentz-Lorenz formula (1), which is correct only for relating the linear quantities n_0 and α_0, to the region of nonlinear optics.

We note that the ratio n_2/α_2 is considerably smaller in value in Onsager's theory (9) than in Lorentz's theory (8). Therefore a comparison of the theoretical values of n_2 with experimental data can serve as one of the criteria for the correctness of one or another theory of the internal field in liquids.

3. NONLINEAR POLARIZABILITY OF INTERACTING ATOMS AND MOLECULES

We shall consider the behavior of molecules directly in a mean field $\mathbf{E}$, remembering that when we go over to the index of refraction n_2 it is necessary to take account of the correction to the local field contained in (8) and (9). In an ensemble of noninteracting molecules, there are only electronic (intramolecular) and Kerr (intermolecular) nonlinearities. The first of these, described by the hyperpolarizability tensor of the molecules, was first considered by Buckingham and Pople[10]; the second has been considered by a number of authors[6, 8, 9]. For calculating the mean value of α_2, it is convenient to use the method of statistical averaging of the tensor polarizabilities in the presence of an external field E, proposed in[10]. According to this method, one introduces the differential polarizability tensor of the molecules

$$\Pi_{\alpha\beta}=dp_\alpha/dE_\beta. \tag{10}$$

One averages statistically the scalar quantity

$$\Pi(\tau, E)=\Pi_{\alpha\beta}e_\alpha e_\beta, \tag{11}$$

where e_α are the direction cosines of the field E in a laboratory (L) coordinate system, and where τ designates the position and orientation of the molecules.

Having found the total energy $u(\tau, E)$ of the molecules in the presence of an external field, one can by means of the Gibbs distribution calculate the mean differential polarizability $\overline{\Pi}(E)$ of the molecules in an external field. The nonlinear polarizability α_2, which will be the coefficient of the third power of the field in the expansion of the induced dipole moment p (see (7)), is obviously

$$\alpha_2={}^1/_2(\partial^2\overline{\Pi}/\partial E^2)_{E=0}. \tag{12}$$

In the calculation of the second derivative with respect to E, the mean nonlinear polarizability α_2 will be expressed in the form of a sum of several terms, each of which is the Gibbs average (we shall denote it by the symbol $\{\ldots\}$) of some quantity in zero external field, when the energy of the system is $u^{(0)}(\tau)$.

By the method described, it is easy to obtain the well-known expression[6, 8, 9] for the Kerr nonlinear polarizability of noninteracting molecules,

$$\alpha_{2\mathrm{Kerr}}^{(0)}=2g_0^2/45kT, \tag{13}$$

where g_0 is the anisotropy of the tensor $\alpha_{\alpha\beta}^{(0)}$ of linear polarizability of a molecule in a rarefied gas. Correspondingly one obtains for the mean electronic polarizability the expression

$$\alpha_{2\mathrm{hyp}}^{(0)}=\gamma/2, \tag{14}$$

where γ is the constant to which the components $\gamma_{1111} = \gamma$ and $\gamma_{1122} = \gamma/3$ of the tensor $\gamma_{\alpha\beta\gamma\delta}$ reduce for isotropic particles.

Turning to the calculation of the effect of IMI, we note that they not only renormalize the nonlinear polarizabilities $\alpha_{2\mathrm{Kerr}}^{(0)}$ and $\alpha_{2\mathrm{hyp}}^{(0)}$, but also produce new forms of nonlinearity in an ensemble of interacting particles. Omitting the quite weak effect of renormalization of the electronic nonlinearity, we shall consider the remaining forms of nonlinearity of interacting particles one at a time.

A. Kerr Nonlinearity

The dipole-dipole interaction of atoms and molecules, studied by Jansen and Mazur[11] on the basis of the quantum-mechanical perturbation theory, changes the linear polarizability of an isolated particle, and this naturally leads to renormalization of the Kerr nonlinearity. This can be shown by use of the expression for the quantum-mechanical mean operator of the dipole moment of a molecule,

$$\langle\hat{p}_\alpha^{(i)}\rangle=\langle\hat{p}_\alpha^{(i)}\rangle^{(1)}+\langle\hat{p}_\alpha^{(i)}\rangle^{(2)}=\alpha_{0,\alpha\beta}^{(i)}E_\beta-\alpha_{0,\alpha\beta}^{(i)}\sum_{j\neq i}T_{\beta\gamma}^{(ij)}\alpha_{0,\gamma\delta}^{(j)}E_\delta, \tag{15}$$

obtained by Jansen and Mazur[11] in the second order of perturbation theory on the basis of the interaction Hamiltonian

$$H_{int}=-\sum_{i=1}^{N}\hat{p}_\alpha^{(i)}E_\alpha+\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\hat{p}_\alpha^{(i)}T_{\alpha\beta}^{(ij)}\hat{p}_\beta^{(j)}. \tag{16}$$

Here $\hat{p}^{(i)}$ is the operator of the dipole moment of the i-th molecule, and $T_{\alpha\beta}^{(ij)}$ is the dipole-dipole interaction tensor of the particles, introduced by Kirkwood[2]:

$$T_{\alpha\beta}^{(ij)}=T_{\alpha\beta}^{(ji)}=\left[\nabla_i\nabla_j\left(\frac{1}{r_{ij}}\right)\right]_{\alpha\beta}=\frac{1}{r_{ij}^3}\left(\delta_{\alpha\beta}-\frac{3r_\alpha^{(ij)}r_\beta^{(ij)}}{r_{ij}^2}\right). \tag{17}$$

As was shown in[11], the change of the linear polarizability of the molecules occurs only in the third order H_{int} and is, to within a constant close to unity,

$$\Delta\Pi_{\alpha\beta}^{(i)}=\alpha_{0,\alpha\gamma}^{(i)}\sum_{j\neq i}T_{\gamma\delta}^{(ij)}\alpha_{0,\delta\rho}^{(j)}T_{\rho\varepsilon}^{(ji)}\alpha_{0,\varepsilon\beta}^{(i)}. \tag{18}$$

On carrying out in this expression an independent averaging over orientations of molecules j and over orientations of the vectors $\mathbf{r}_{ij}$, which occur in the definition (17), we get

$$\begin{aligned}\{\Delta\Pi_{\alpha\beta}^{(i)}\}&=\alpha_{0,\alpha\gamma}^{(i)}\alpha_{0,\varepsilon\beta}^{(i)}\sum_{j\neq i}\{T_{\gamma\delta}^{(ij)}T_{\rho\varepsilon}^{(ji)}\}\{\alpha_{0,\delta\rho}^{(j)}\}=\alpha_0\alpha_{0,\alpha\gamma}^{(i)}\alpha_{0,\varepsilon\beta}^{(i)}\sum_{j\neq i}\{T_{\gamma\delta}^{(ij)}T_{\delta\varepsilon}^{(ji)}\}\\&=2\alpha_0\alpha_{0,m}^2\sum_{j\neq i}\langle r_{ij}^{-6}\rangle,\end{aligned} \tag{19}$$

where $\alpha_{0,m}$ (m = 1, 2, 3) are the principal values of the polarizability tensor $\alpha_{0,\alpha\beta}$ of an isolated molecule.

The averaging over distances r_{ij} in (19), in accordance with the definition[12], is accomplished by means of the radial distribution function of the molecules, g(r):

$$\sum_{j\neq i}\langle r_{ij}^{-6}\rangle=\rho_0\int_0^\infty r_{ij}^{-6}g(r_{ij})r_{ij}^2\,dr_{ij}, \tag{20}$$

where ρ_0 is the mean concentration of particles. In the case of gases, this method of averaging is unique. But in liquids, a molecule can interact simultaneously with only a finite number Z (called the coordination number) of nearest neighbors. Therefore

$$\sum_{j\neq i}\langle r_{ij}^{-6}\rangle=Z\langle r_{ij}^{-6}\rangle. \tag{21}$$

But if we neglect fluctuations of the distances between molecules in the first coordination sphere, i.e., if we replace all r_{ij} by a certain mean value $\bar{r}$ (which lies close to the first maximum of the radial function g(r)), then one can express (21) in the form

$$\sum_{j\neq i}\langle r_{ij}^{-6}\rangle\approx Z\frac{1}{\bar{r}^6}. \tag{22}$$

Thus on substituting (22) in (19), we find that the principal values of the polarizability of interacting molecules are

$$\alpha_{\mathrm{int},m}=\alpha_{0,m}+\{\Delta\Pi_m\}=\alpha_{0,m}+2Z\bar{r}^{-6}\alpha_0\alpha_{0,m}^2. \tag{23}$$

On determining by means of (23) the anisotropy of the polarizability tensor of interacting molecules,

$$g_{\mathrm{int}}^2=\frac{3}{2}\sum_{m=1}^{3}\alpha_{\mathrm{B3},m}^2-\frac{1}{2}\Big[\sum_{m=1}^{3}\alpha_{\mathrm{B3},m}\Big]^2, \tag{24}$$

we find by analogy with (13) the nonlinear Kerr polarizability of an interacting molecule:

$$\alpha_{2\,\mathrm{Kerr}}^{(\mathrm{B3})}=2g_{\mathrm{int}}^2/45kT. \tag{25}$$

B. Radial Nonlinearity

Radial interaction of atoms and molecules because of the dipole moments induced in the particles by an external field **E** leads to the occurrence of a peculiar radial nonlinearity in a liquid. This is evident from analysis of the expression (15) obtained by Jansen and Mazur in[11]. In each molecule, besides the moment $\langle\hat{p}\rangle^{(1)}$ induced directly by the external field **E**, there is induced an additional moment $\langle\hat{p}\rangle^{(2)}$ caused by dipole-dipole interaction with neighbors. It is important that even in the case of atoms and isotropic molecules, in which the polarization is a scalar, the direction of the additional dipole moment $\langle\hat{p}\rangle^{(2)}$ does not coincide with the direction of the external field **E**, since the field produced by each primary dipole $\langle\hat{p}^{(j)}\rangle^{(1)}$ is anisotropic. This "anisotropic" term in the dipole moment of a molecule also causes a radial nonlinearity in liquids, which has also been studied by Kielich[13].

The radial differential polarizability of molecules according to (15) is

$$\Pi_{\alpha\beta}^{\mathrm{rad}}=-\alpha_{0,\alpha\gamma}^{(i)}\sum_{j\neq i}T_{\gamma\rho}^{(ij)}\alpha_{0,\rho\beta}^{(j)},\qquad \Pi^{\mathrm{rad}}=\Pi_{\alpha\beta}^{\mathrm{rad}}e_\alpha e_\beta. \tag{26}$$

The energy of the molecule in the external field is

$$u(\tau,E)=u^{(0)}(\tau)-{}^1/_2\Pi_{\alpha\beta}^{\mathrm{rad}}e_\alpha e_\beta E^2. \tag{27}$$

On calculating by means of (27) the statistical mean $\overline{\Pi}^{\mathrm{rad}}(E)$ of the differential polarizability in the presence of a field and expanding the result as a series in powers of the field, we find on the basis of (12) the nonlinear radial polarizability, which according to (26) and (27), when E = 0, contains just two terms:

$$\alpha_{2\,\mathrm{rad}}=\frac{1}{2}\left(\frac{\partial^2\overline{\Pi}^{\mathrm{rad}}}{\partial E^2}\right)_{E=0}=\frac{1}{2kT}\left[\{\Pi^{\mathrm{rad}}\}\left\{\frac{\partial^2 u}{\partial E^2}\right\}-\left\{\Pi^{\mathrm{rad}}\frac{\partial^2 u}{\partial E^2}\right\}\right]. \tag{28}$$

On differentiating the total energy u(τ, E) of the molecule with respect to E, we find finally

$$\alpha_{2\,\mathrm{rad}}=\frac{1}{2kT}[\{(\Pi^{\mathrm{rad}})^2\}-\{\Pi^{\mathrm{rad}}\}^2]. \tag{29}$$

We substitute (26) in (29) and average the resulting expression over directions of the external field and over orientations of all the molecules with respect to the L-system:

$$\alpha_{2\,\mathrm{rad}}=\frac{1}{135kT}\Big(\sum_{m=1}^{3}\alpha_{0,m}^2\Big)^2\Big[\sum_{j\neq i}\{T_{\alpha\beta}^{(ij)}\,T_{\beta\alpha}^{(ij)}\}+\sum_{\substack{j\neq i\\ k\neq i,j}}\{T_{\alpha\beta}^{(ij)}\,T_{\beta\alpha}^{(ik)}\}\Big]. \tag{30}$$

In the derivation of (30), we have used the fact that

$$\sum_{\alpha}T_{\alpha\alpha}^{(ij)}=0, \tag{31}$$

as follows from the definition (17). By use of the same definition, it is easy to see that the second term in (30) vanishes, if we neglect ternary interactions of molecules; their probability is small. On carrying out the averaging in (30), we finally obtain an expression for the radial nonlinear polarizability of anisotropic molecules:

$$\alpha_{2\,\mathrm{rad}}^{\mathrm{anis}}=\frac{2Z}{45kT\bar{r}^6}\Big(\sum_{m=1}^{3}\alpha_{0,m}^2\Big)^2, \tag{32}$$

in the case of atoms and isotropic molecules this becomes

$$\alpha_{2\,\mathrm{rad}}^{\mathrm{is}}=\frac{2Z}{5kT\bar{r}^6}\alpha_0^4. \tag{33}$$

C. Quadrupolar Nonlinearity

Molecules possessing a quadrupole moment Q induce in neighboring molecules a dipole moment whose quantum-mechanical average differs from zero[14, 15]:

$$\langle\hat{p}_\alpha^{(i)}\rangle_Q=-\frac{1}{2}\alpha_{0,\alpha\beta}^{(i)}\sum_{k\neq i}T_{\beta\gamma\delta}^{(ik)}\langle\hat{Q}_{\gamma\delta}^{(k)}\rangle. \tag{34}$$

Here $T_{\alpha\beta\gamma}^{(ik)}$ is the dipole-quadrupole interaction tensor[14]

$$T_{\alpha\beta\gamma}^{(ik)}=-\nabla_\alpha\nabla_\beta\nabla_\gamma\left(\frac{1}{r_{ik}}\right)=3r_{ik}^{-7}[5r_\alpha^{ik}r_\beta^{ik}r_\gamma^{ik}-r_{ik}^2(r_\alpha^{ik}\delta_{\beta\gamma}+r_\beta^{ik}\delta_{\alpha\gamma}+r_\gamma^{ik}\delta_{\alpha\beta})]; \tag{35}$$

$Q_{\alpha\beta}^{(k)}$ is the quadrupole-moment tensor of the k-th molecule,

$$Q_{\alpha\beta}^{(k)}=Ql_\alpha^{(k)}\,l_\beta^{(k)}, \tag{36}$$

where l_α are the direction cosines that describe the direction of the axis of the molecule in space.

Thus nonpolar molecules that possess a quadrupole moment become, in the presence of neighbors, "weakly polar"; that is, they acquire a capacity to be oriented in an external field. The mean projection $\overline{(\langle\hat{p}\rangle_Q e)}$ of the dipole-moment vector of the molecule in the direction of the field thereby becomes different from zero; it can be found by means of the Gibbs distribution with the energy

$$u(\tau,E)=u^{(0)}(\tau)+(\langle\hat{p}\rangle_Q\mathbf{E}). \tag{37}$$

As is well known, the statistical integral over angles in the case of an averaging over orientations of rigid dipoles reduces to the Langevin function, so that

$$\overline{(\langle\hat{p}\rangle_Q\mathbf{e})}=p_QL(b), \tag{38}$$

where p_Q is the modulus of the vector $\langle\hat{p}\rangle_Q$. The Langevin function L(b) has the form

$$L(b)=\int xe^{bx}dx\Big/\int e^{bx}dx, \tag{39}$$

the parameter b is

$$b=p_QE/kT. \tag{40}$$

The function L(b) has two asymptotes. For b ≪ 1, the function L(b) = b/3. This case, as is evident from (40), corresponds to weak fields E and describes a linear optical effect–the quadrupolar contribution to the linear polarizability of the medium. At sufficiently large fields E, the parameter b in (40) can become much larger than unity; then the function changes its asymptote:

$$L(b)=(1-1/b)_{b\gg1}. \tag{41}$$

We shall call

$$b_{\mathrm{cr}}=1 \tag{42}$$

the critical value of the parameter b, so that (41) is already satisfied at $b = 2b_{cr}$. To the condition (42) there corresponds a certain critical value of the field E_{cr}, which can be determined from (40):

$$E_{cr}=kTb_{cr}/p_Q=kT/p_Q. \tag{43}$$

For $E > 2E_{cr}$, according to (40) and (41), equation (38) takes the form

$$\overline{(\langle\hat{\mathbf{p}}^{(i)}\rangle_Q \mathbf{e})} = p_Q^{(i)} - kT/E, \quad E > 2E_{cr}. \tag{44}$$

We expand this expression as a series about the point $E = 2E_{cr}$ and retain only terms of order $(E - 2E_{cr})^3$:

$$\overline{(\langle\hat{\mathbf{p}}^{(i)}\rangle_Q \mathbf{e})} = \frac{1}{2}p_Q^{(i)} + \frac{1}{4}\frac{p_Q^{(i)2}}{kT}(E-2E_{cr}) - \frac{1}{8}\frac{p_Q^{(i)3}}{(kT)^2}(E-2E_{cr})^2 + \frac{1}{16}\frac{p_Q^{(i)4}}{(kT)^3}(E-2E_{cr})^3 \ldots \tag{45}$$

We find the mean differential polarizability of the molecule by differentiating the expression (45) with respect to E, in accordance with the definition (10):

$$\overline{\Pi}^{\mathrm{qu}}(E) = \frac{d}{dE}\overline{(\langle\hat{\mathbf{p}}^{(i)}\rangle_Q \mathbf{e})}. \tag{46}$$

Accordingly, the nonlinear quadrupolar polarizability is, by the definition (12),

$$\alpha_{2\mathrm{qu}} = \frac{1}{2}\left(\frac{\partial^2\overline{\Pi}^{\mathrm{qu}}}{\partial E^2}\right)_{E=2E_{cr}}, \tag{47}$$

where we have taken into account that the expression (44) is valid only for $E > 2E_{cr}$. On carrying out the differentiations indicated in (46) and (47), we get from (45)

$$\alpha_{2\mathrm{qu}} = 3p_Q^{(i)4}/16(kT)^3. \tag{48}$$

It remains to determine $p_Q^{(i)}$. This can be done by calculating the scalar square of the vector $\langle\hat{\mathbf{p}}^{(i)}\rangle_Q$ on the basis of the definition (34) and averaging the quadratic expression over orientations of the molecules and of the radius vectors $\mathbf{r}^{(ik)}$, and also over the distances r_{ik} between molecules. As a result we get

$$p_Q^{(i)} = \left[3Q^2Z\bar{r}^{-8}\sum_{m=1}^{3}\alpha_{0,m}^2\right]^{1/2}. \tag{49}$$

On substituting (49) in (48), we finally find the nonlinear quadrupolar polarizability of the molecules:

$$\alpha_{2\mathrm{qu}} = \frac{27}{16(kT)^3}\left[Q^2Z\bar{r}^{-8}\sum_{m=1}^{3}\alpha_{0,m}^2\right]^2. \tag{50}$$

The nonlinear quadrupole effect has a threshold character with respect to the field E: it is turned on only at $E > 2E_{cr}$, and, as is evident from (44), it saturates at large E. For molecules of the type H_2, CO_2, and CS_2, which possess a comparatively large quadrupole moment Q, this effect may make an appreciable contribution to the nonlinear index of refraction in the range of field values in which saturation of the Kerr and radial nonlinearities has already begun.

4. QUANTITATIVE RESULTS; TEST OF THE THEORY

On combining all the effects considered above, we exhibit the nonlinear index of refraction n_2 of a liquid in the form of a sum:

$$n_2 = n_{2\,\mathrm{hyp}} + n_{2\,\mathrm{rad}} + n_{2\,\mathrm{Kerr}}^{(\mathrm{int})} + n_{2\,\mathrm{qu}} \tag{51}$$

In the case of atoms and isotropic molecules, only the first and second terms in (51) contribute to n_2. The quadrupole term has been calculated only for the linear molecule CS_2, which possesses an appreciable quadrupole moment $Q = 3.07 \times 10^{-26}$ cgs esu[16] (the critical field for this molecule is $E_{cr} = 4 \times 10^7$ V/cm).

Nonlinear index of refraction $n_2 \cdot 10^{13}$ of several liquids (in cgs esu)

Liquid	$\frac{Z}{(\bar{r})^6}\cdot 10^{-45}$, cm^{-6}	$\gamma\cdot 10^{36}$, cgs esu [13, 18]	Onsager Model (9)						$K\cdot 10^{13}$, cgs esu [19-23]	n_2 ex	n_2^{theor} Lor (8)
			n_2 hyp	n_2 rad	$n_2^{(0)}$ Kerr	n_2^{int} Kerr	n_2 qu	$n_2^{(\mathrm{theor})}$ Ons			
Aragon	3.38	0.59	0.54	1.54				2.08			2.34
Carbon tetrachloride	0.219	9.96	3.66	17.50				21.16	4.76	35.80	27.77
Benzene	0.214	6.46	2.53	21.74	30.0	35.24		59.51	35.0	37.0	87.05
Toluene	0.150	27.20	8.83	25.43	38.84	45.58		79.84	45.4	51.54	116.24
Carbon disulfide	0.262	57.35	37.13	31.50	131.30	157.32	27.64	253.59	194.2	254.95	435.26
Chloroform	0.146	4.80	1.44	4.12	3.59	3.90		9.46	10.0	9.76	17.83
Nitrobenzene	0.219	85.0	23.28	40.07	45.43	73.40		136.75	141.5	144.17	323.70

The values of the coordination number Z and of the mean distances $\bar{r}$ between molecules, which are necessary for the calculations, have been determined by x-ray measurements of the radial distribution function g(r) in liquids[17]. The hyperpolarizabilities γ of atoms and molecules were taken from papers[13, 18]. The results of calculations of the value of n_2 and of its components in the Onsager model (9) for seven liquids, for which it was possible to find all the necessary data, are given in the table. Here are also given, for comparison, values of n_2 in the Lorentz model (8).

In the last columns of the table are given experimental values[19-23] of the Kerr constant K of the liquids, and the values of the nonlinear index of refraction $n_{2\mathrm{ex}}$ calculated from them. The connection between K and $n_{2\mathrm{ex}}$ is established as follows. According to[10] the difference $n_0^{\parallel} - n_0^{\perp}$ of the indices of refraction of the liquids along the external field and perpendicular to it is determined by the differente $\overline{\Pi}^{\parallel} - \overline{\Pi}^{\perp}$ of the mean values of the differential polarizability of the molecules in these directions. Therefore

$$n_0^{\parallel} - n_0^{\perp} \approx \frac{1}{2n_0}(n_0^{\parallel 2} - n_0^{\perp 2}) = \frac{2\pi N}{n_0}(\overline{\Pi}^{\parallel} - \overline{\Pi}^{\perp}). \tag{52}$$

As was shown by Buckingham and Pople[10], the difference $\overline{\Pi}^{\parallel} - \overline{\Pi}^{\perp}$ is proportional to the square of the intensity of the field at the position of the molecule:

$$\overline{\Pi}^{\parallel} - \overline{\Pi}^{\perp} = \frac{1}{2}\left[\frac{\partial^2(\overline{\Pi}^{\parallel} - \overline{\Pi}^{\perp})}{\partial E^2}\right]_{E=0} L^2E^2; \tag{53}$$

the factor L^2 appears because of the difference between the mean and local fields.

On defining the Kerr constant K in the usual way,

$$K = (n_0^{\parallel} - n_0^{\perp})/E^2 \tag{54}$$

and using the results of[10] for the second derivative in (53), one can easily show, by a comparison with (9), that the following relations must be satisfied:

$$n_{2\,\mathrm{rad}} + n_{2\,\mathrm{Kerr}}^{\mathrm{int}} = {}^2/_3(K_{\mathrm{rad}} + K_{\mathrm{or}})G^{-1}L_{\mathrm{Ons}}^2, \tag{55}$$

$$n_{2\mathrm{hyp}} = {}^3/_2 K_{\mathrm{el}} G^{-1} L_{\mathrm{Ons}}^2. \tag{56}$$

Here K_{or}, K_{rad}, and K_{el} are the parts of the total Kerr constant that describe, respectively, the orientational, radial, and electronic Kerr effects. In view of the fact that in an experiment one measures only the total constant K, we found the share of the electronic part $n_{2\,\mathrm{hyp}}$ of the theoretical value of the total nonlinear index of refraction n_2 and multiplied the corresponding part of the constant K by 3/2, the remaining part by

2/3. The sum of the quantities obtained, with allowance for the factor $G^{-1}L^2_{Ons}$, also gave the experimental value n_{2ex} in the Onsager model. In the Lorentz model, the right side of the relations (55) and (56) should contain the factor L^2_{Lor}.

We note that in the relations that connect the nonlinear index of refraction n_2 and the Kerr constant K with the differential polarizability of the molecules, the local-field factor L occurs to different powers–the fourth and the second, respectively. This is directly due to the fact that in the Kerr effect one measures the difference of the linear refractions of the medium, $n_0^{\parallel}-n_0^{\perp}$; this difference, however, is proportional to the square of the external field E. The nature of the appearance of the factor E^2 in the nonlinear index of refraction n_{nonl} and in the difference $n_0^{\parallel}-n_0^{\perp}$ of the linear indices is altogether different: in the first case it is due to the manifestation of a nonlinear optical effect, in the second to nonlinearity with respect to E of the energy of a molecule in the external field (with retention of the linear character of the refraction of a light signal passing through the medium in the presence of an external field). This is often forgotten[24, 20, 25], and the connection between n_2 and K is written in the form $n_2 = 2/3\ K$, with omission, on the right side of this relation, of the factor L^2. For this reason, values of $n_{2\,ex}$ must not be considered correct that have been determined from the Kerr constant and are cited in these and a number of other papers.

Assessing the quantitative results of the present theory for n_2 in its Onsager variant, we can see from the table that the theory agrees with experiment very well for carbon disulfide and chloroform, not badly for nitro-benzene, satisfactorily for benzene and toluene, and unsatisfactorily for carbon tetrachloride, if we believe the measured value of the Kerr constant in the last liquid. At the same time, the Lorentz model for the internal field in liquids gives results for n_2 that are clearly too large.

The question of the actual discrepancy of theory with experiment for CCl_4 remains open, because there is some doubt about the value of the constant K cited in the literature. In fact, in this liquid there have been observed[26] hyperfine filaments of self-focusing of the radiation of a neodymium laser ($\lambda = 1.06\ \mu m$) that gave a pulse width of 1 psec. The measured diameters of the filaments (or of the moving foci) were $7.9 \pm 0.2\ \mu m$ for peak field intensity in the filament $E_0 = 1.3 \times 10^7$ V/cm. If we calculate the diameter of a filament by the approximate formula[27] of geometric optics

$$d^2=(0.61\lambda)^2/2n_0\Delta n, \qquad (57)$$

where $\Delta n = 1/2 n_2 E_0^2$, then by use of the theoretical value of n_2 given in the table, we get $d_{theor} = 8.59\ \mu m$ ($n_0 = 1.44$ at the frequency of the laser light). But if we use the value $n_{2\,ex} = 5.8 \times 10^{-13}$ cgs esu, corresponding to the value of the Kerr constant cited in the literature, then the theoretical value of the diameter of a filament should be 17 μm, which clearly contradicts experiment[26].

Hyperfine filaments of self-focusing of the pulses of the same laser were observed also[28] in liquid argon. In a field $E = 3 \times 10^7$ V/sec characteristic of this case (ionization of the liquid by pulses of picosecond duration sets in at fields of order 10^8 V/sec), the diameter of a filament $d_{theor} = 9.05\ \mu m$, which agrees well with the experimental value 5 to 10 μm. Thus the theory is corroborated also for argon.

In regard to other liquids in which filament diameters have been measured[26], it must be remarked that this experimental information cannot serve as a reliable test of the theory for n_2, for two reasons. First, the time of Kerr orientational relaxation is considerably longer than the duration of the pulses used in[26], so that it is not known what portion of $n_{2\,Kerr}$ may contribute to Δn. Second, the greater portion of the energy of the beam in self-focusing, on attainment of a certain energy density in the beam, begins to be transformed to scattered light[29, 30], so that the filaments do not succeed in constricting to the diameters predicted on the basis of a maximum increase of the index of refraction Δn.

The material presented above shows that the proposed theory of the nonlinear index of refraction of liquids is in agreement with experiment for a number of liquids. A more accurate test of the theory requires direct measurements of nonlinear refraction in liquids.

The author is sincerely grateful to B. Ya. Zel'dovich and A. P. Sukhorukov for their interest in the research and for valuable discussions.

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Translated by W. F. Brown, Jr.
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