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INFLUENCE OF STATISTICAL FLUCTUATIONAL PROCESSES ON HIGHER ORDER NONLINEAR REFRACTIVE INDEX OF SIMPLER FLUIDS

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Nonlinear changes in refractive index due to nonlinear polarisability, reorientation, fluctuations in number density of molecules and translational fluctuations are calculated numerically for liquid argon, CCl_4, C_6H_6 and CS_2, yielding qualitative agreement with recent observations of self-trapped filaments of laser beams in simple liquids.

Buckingham [1] showed intense light to cause optical birefringence even in atomic substances owing to nonlinear distortion of electronic shells. Kielich [2] proved that optical and electric birefringence can be induced by anisotropic fluctuations of electric fields (Kirkwood-Yvon translational fluctuations) causing short range asymmetry in the spatial distribution of atoms and isotropically polarisable molecules. Various recent papers [3–5] deal with the influence of molecular reorientation and redistribution on quadratic changes in index. Here, we shall take into consideration moreover fluctuations in number density of molecules which contribute largely to the nonlinear changes in index, and shall adduce numerical calculations of variations Δn quadratic in the electric field amplitude E_0 of a light wave, as well as of variations bi-quadratic in E_0 for several simple fluids:

$$\Delta n = n_2 E_0^2 + n_4 E_0^4 + \dots, \tag{1}$$

with

$$n_2 = \frac{1}{4n_0}\left(\frac{n_0^2+2}{3}\right)^4 R_2, \tag{2}$$

$$n_4 = \frac{1}{4n_0}\left(\frac{n_0^2+2}{3}\right)^6 R_4, \tag{3}$$

n_0 being the intensity-independent refractive index.

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The constants R_2, R_4 depend on the microstructure of the medium and stem from a number of mechanisms, of which we shall consider here the contribution

$$R_2^{NL} = 2\pi\varrho c \left(1 + \frac{48}{5} a^2 \langle r^{-6}\rangle + \frac{66}{5} a^3 \langle r^{-9}\rangle + \ldots\right) \tag{4}$$

resulting by nonlinear third-order polarisability of molecules $c = c_{\alpha\alpha\beta\beta}/5$ and fluctuational changes in the linear polarisability $a = a_{\alpha\alpha}/3$ of molecules at mutual distance r. The statistical mean values $\langle r^{-n}\rangle = 4\pi\varrho \int r^{-n+2} g(r) dr$ are accessible to numerical computation for prescribed radial correlation functions $g(r)$ [5, 6].

Another, hitherto not numerically considered contribution to R_2 results by statistical fluctuations of effective polarisabilities of molecules [5, 6]. To within pairwise correlations, this contribution is of the form:

$$R_2^{FL} = \frac{2\pi}{kT} a^2 \{\langle(\Delta\varrho)^2\rangle V + 8a^2 \varrho(\langle r^{-6}\rangle + a \langle r^{-9}\rangle + \ldots)\}, \tag{5}$$

where the first term (like Rayleigh light scattering) results by fluctuations in number density of molecules $\varrho = N/V$, which can be calculated from Smoluchowski's formula $V\langle(\Delta\varrho)^2\rangle = \varrho^2 kT \beta_T$ once the isothermal compressibility β_T of the fluid is known. The subsequent terms are due to fluctuations of molecular fields causing changes in linear polarisabilities.

A third contribution stems from Langevin molecular reorientation, angular correlations [2], and translational fluctuations [3–5]:

$$R_2^{RT} = \frac{8\pi\varrho}{45kT} \left\{\delta^2(1+J_2) + 2\left(9a^4 + \frac{28}{5} a^2\delta^2 + \frac{2}{3} a\delta^3 + \frac{67}{225} \delta^4\right) \langle r^{-6}\rangle + 36a^5 \langle r^{-9}\rangle\right\}, \tag{6}$$

with $\delta = a_{33} - a_{11}$ the optical anisotropy of axially-symmetric molecules and J_2 a parameter of their pairwise angular correlations [2].

The preceding molecular mechanisms intervene moreover essentially in optical nonlinearities of higher orders [7], yielding the following contributions to the constant R_4:

$$R_4^{NL} = \frac{15\pi}{56} \varrho e \left(1 + \frac{662}{35} a^2 \langle r^{-6}\rangle + \frac{1206}{35} a^3 \langle r^{-9}\rangle + \ldots\right), \tag{7}$$

$$R_4^{FL} = \frac{\pi\varrho a}{360kT} \left\{45\varrho kT\beta_T \left(5c - \frac{2a^2}{kT}\right) + 2a^2 \left(1769c + 792 \frac{a^2}{kT}\right) \langle r^{-6}\rangle\right\}, \tag{8}$$

$$R_4^{RT} = \frac{8\pi\varrho}{35k^2T^2} \left\{\frac{\delta^3}{27} (1 + 3J_2 + J_3) + 2a^6 (\langle r^{-9}\rangle + 6\mathrm{a} \langle r^{-12}\rangle + \ldots)\right\}, \tag{9}$$

where $e = e_{\alpha\alpha\beta\beta\gamma\gamma}/15$ is the nonlinear polarisability of the fifth order and J_3 — a triple angular molecular parameter [7].

In addition to these, we have yet another contribution due to superposition (cross-effects) of nonlinear polarisability and molecular redistribution (as well as reorientation, which we omit):

$$R_4^{CR} = \frac{\pi\varrho}{15kT} a^3 c \left(45 \langle r^{-6}\rangle + \frac{2537}{21} a \langle r^{-9}\rangle + \ldots\right). \tag{10}$$

Table gives the numerical values of these various contributions, calculated from Eqs (4)–(10). The role of the contributions from fluctuations in number density and translational fluctuations is found to be considerable, whereas that of nonlinear distortion is smaller.

TABLE

Calculated constants R_2 and R_4, arising from nonlinear distortional (R_2^{NL}, R_4^{NL}), fluctuational (R_2^{FL}, R_4^{FL}), reorientational and translational (R_2^{RT}, R_4^{RT}) and cross (R_4^{CR}) effects. Values n_2 and n_4 were calculated using these constants R_2 and R_4

Liquid[1]	Quadratic variations of n_2, in 10^{-12} e. s. u.				Bi-quadratic variations of n_4, in 10^{-24} e. s. u. ( )				
	R_2^{NL}	R_2^{FL}	R_2^{RT}	n_2	R_4^{NL} [2]	R_4^{FL}	R_4^{RT}	R_4^{CR}	n_4
Ar	0.10	2.7	0.25	1.16	0.02	19.7	0.15	0.10	10.45
CCl_4	0.09	16.8	2.95	12.20	0.01	853.6	9.40	0.57	1007.01
C_6H_6	−0.15	19.6	5.58	16.99	0.01	1003.3	15.98	−1.00	1395.66
CS_2	4.07	33.0	18.54	50.20	0.01	1565.6	3.94	34.33	3518.91

[1] values of physical quantities required for the numerical computations for liquid argon at 85° K were taken from a paper by S. Kielich, *J. Chem. Phys.*, **46**, 4090 (1967) and for other liquids at 293° K from Refs [2, 7, 10] and from the papers by B. Kasprowicz, S. Kielich, *Acta Phys. Polon.*, **31**, 787 (1967); **33**, 495 (1968).

[2] as the mean value of the tensor $e_{\alpha\alpha\beta\beta\gamma\gamma}$ of fifth-order polarisability was not yet available, we assumed $e = 1 \times 10^{-48}$ e. s. u. for all the liquids.

These results are in agreement with the latest observations of self-trapped filaments in liquid argon [8]. Similar observations in rarefied gases [9] revealed a predominant role of nonlinear polarisability [10] — a reasonable finding in the light of our theory, since correlational processes recede into the background as rarefaction increases.

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