THE MAGNITUDE AND RELAXATION OF THE STRAIN-OPTIC

CONSTANTS IN LIQUIDS APPROPRIATE TO LIGHT SCATTERING EXPERIMENTS

Herbert R. Carleton†

Materials Science Department

State University of New York at Stony Brook

Stony Brook, L. I., New York   11790

State University of New York

College of Engineering Report #171

June, 1969

ABSTRACT

The dependence of the optical properties of liquids on parameters associated with hydrodynamic variables has been evaluated from a molecular theory. The results agree to lowest order with the theory of Lorentz-Lorenz and do not exhibit relaxation. Relaxing terms are found to be associated with molecular correlations and comprise about twenty percent of the total contribution. It is predicted that an anisotropy correction to the Lorentz field is the dominant term in depolarized scattering from hydrodynamic longitudinal and transverse waves in liquids.

THE MAGNITUDE AND RELAXATION OF THE STRAIN-OPTIC

CONSTANTS IN LIQUIDS APPROPRIATE TO LIGHT SCATTERING EXPERIMENTS

Herbert R. Carleton

Materials Science Department

State University of New York at Stony Brook

Stony Brook, L. I., New York 11790

The study of the liquid state by light scattering experiments
has received heavy emphasis recently, particularly in that area
where the scattering originates from hydrodynamic modes. The scat-
tering in this case results in the presence of Brillouin lines in
the spectrum of the scattered radiation from which the hypersonic
wave velocity, absorption, Landau-Placzek ratio, and other thermo-
dynamically related quantities can be determined from spectroscopic
analysis.[1, 2] The theory of the scattering from hydrodynamic modes
in a liquid was derived by Rytov[3] for the case where there is no
dispersion in the viscoelastic properties and has been extended to
the more general case by Mountain.[4]

The interpretation of absolute intensities in scattering experiments is made difficult by the absence of an adequate theory relating the perturbations in the dielectric constant of the medium to variations in density and temperature. This problem is especially apparent in cases in which the strain-optic constants can be expected to be dispersive, as in scattering from viscous media. Hence, although rough theoretical estimates of the adiabatic strain-optic constants can be obtained from the phenomenological theory of Lorentz-Lorenz[5] or can be determined at ultrasonic frequencies by ultrasonic diffraction as in the work of Riley and Klein,[6] any relaxation effects that may be present are difficult to interpret. This has been pointed out by Motulevich and Fabelinskii,[7] who have made comparative measurements on several liquids under isothermal and adiabatic conditions and have noted a discrepancy of approximately ten percent between the values of p measured at 50 Hz and 10^7 Hz.

In addition to these problems related to the dependence of the dielectric constant on density, Stegeman and Stoicheff[8] have shown that it is possible to obtain depolarized Brillouin scattering from shear waves in viscous liquids. Hence, the dependence of the optical dielectric constant on shear strains and velocity gradients in the liquid must be known in addition to its dependence on density.

We have attempted to theoretically determine the dependence of the appropriate optical constants of a liquid on the hydrodynamic state from a fundamental viewpoint. To this end, the exact description of the optical dielectric constant of a liquid as

developed by Kirkwood and Yvon and extended to optical frequencies by Fixman[9] has been adopted as a starting point in the theory. For example, Fixman has shown that the optical dielectric constant of a liquid comprised of molecules with isotropic polarizibility α is given by

$$\varepsilon_0(\varepsilon - \varepsilon_0)^{-1} = \frac{1}{\alpha\rho}\left[1 - \frac{\alpha\rho}{3} - \frac{2}{\alpha\rho}\int_V (g_{12} - 1)T_{12}e^{ik\cdot R_{12}}d^3R_2\right.$$
$$\left. -\alpha^2\rho\int_V g_{12}T_{12}T_{21}d^3R_2 + \ldots\right],$$

(1)

where T_{12} is the propagator relating the field at $\tilde{r}_1$ to the dipole moment at $\tilde{r}_2$ and ρ, g_{12}, etc., are the multiparticle distribution functions.

This description is first generalized to include optically anisotropic molecules, and it is shown that the complete dependence of the optical properties on the hydrodynamic variables can be derived from a knowledge of the molecular distribution functions. In this initial calculation, the optical constants are derived in the adiabatic limit and the relaxation, where present, is estimated phenomenologically.

Since the liquid is initially isotropic, it can be shown that the strain-optic properties can be described with two independent constants, p_{11} and p_{12}.[10] Both the dependence of the dielectric constant on density and the birefringence can be determined by considering the distortion of g_{12} associated with a uniaxial strain in the fluid. Hence, for example, if the fluid is subjected to a suddenly applied force the liquid will behave like a solid in times short compared to a relaxation time. The response will be a

strain S in the direction of the z axis which will tend to relax away in 10^{-10} to 10^{-12} seconds. Hence, since the dielectric constant can be described in terms of molecular distribution functions, $g_{12}(R)$ etc., then the dielectric constant under the distortion is described in terms of $g_{12}(R')$ etc., where $R' = \sqrt{x^2 + y^2 + (1 + S)^2 z^2}$. It is interesting to note that a non-relaxing distortion of the distribution functions will occur if the liquid is subject to a gradient in the local velocity of flow.

If the previous ideas are now included in a computation of the variation of equation (1) subject to changes in the corresponding distribution functions the following results are obtained:

$$\epsilon_o \frac{\partial}{\partial S} (\epsilon - \epsilon_o)^{-1} = \frac{1}{\alpha\rho} \left\{ \left[\mathbb{1} - \frac{2}{15} \mathbb{B} - \Gamma(\omega) \left[\frac{76}{105} \mathbb{1} - \frac{11}{105} \mathbb{B} \right] \right] + \left[\frac{1}{(n^2 - 1)} \frac{\Delta(\omega)}{30} \mathbb{B} \right] \right\} \tag{2}$$

where tensors 1 and B are defined as follows:

$$\mathbb{1} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \mathbb{B} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix}$$

and α is the average molecular polarizibility, ρ is the density,

$$\Gamma(\omega) = \frac{\alpha}{4\pi} \int_o^\infty g_{12}(r) \frac{dr}{r^4},$$

the frequency dependence being implicit in $g_{12}(r)$. The properties of $\Delta(\omega)$ will be discussed in the next paragraph.

In equation (2) the various contributions to the strain-
optic constants have been bracketed separately to facilitate dis-
cussion. The terms in the first bracket are attributable to a
liquid comprised of molecules with both optical and mechanical
isotropy. The first term within the bracket is the usual contri-
bution in the Lorentz-Lorenz approximation and the second term
is due to the distortion of the Lorentz-Lorenz sphere. It is
clear that neither of these terms is subject to relaxation. The
third term in the first bracket is due to the molecular correla-
tion. This fact has been shown by making the factor Γ frequency
dependent. Preliminary studies have shown that Γ lies between
the values of 1 and 2. Since the two particle correlation func-
tion defines the equation of state of a liquid, the value Γ may be
expected to change indirectly as a function of temperature and
density. The relaxation time involved is very short, of the order
of 10^{-13} second. In some situations, however, if a form of struc-
tural relaxation is involved, the relaxation time can be expected
to be longer with a dispersion maximum in the frequency range of
hydrodynamic waves.

The second bracketed term is due to anisotropy of the
optical properties of the molecule. This term has been computed
by assuming that an initial random orientation of molecules is
distorted to the same asymmetry as the molecular distribution func-
tion. This can be justified on the assumption that after a rapidly
applied strain the orientational chaos will be restored at a rate
corresponding to the rotational diffusion constant D_r. It is clear
that if the responding strain is associated with frequencies ω,

then the appropriate dispersion relation for this term will be

$$\Delta(\omega) = \frac{i\omega D_r}{1+i\omega D_r} \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha} \tag{3}$$

in a single relaxation time approximation.

These results can be used to compute the two independent strain-optic constants for an isotropic fluid and lead to the expressions

$$p_{11} = \frac{(n^2-1)^2}{n^4} \left[\frac{1}{\alpha\rho} + \frac{4}{15} - \frac{98}{105} \Gamma(\omega) - \frac{1}{15} \frac{\Delta(\omega)}{n^2-1} \right] \tag{4}$$

$$p_{12} = \frac{(n^2-1)^2}{n^4} \left[\frac{1}{\alpha\rho} - \frac{2}{15} - \frac{65}{105} \Gamma(\omega) + \frac{1}{30} \frac{\Delta(\omega)}{n^2-1} \right] \tag{5}$$

The coefficient p_{44}, appropriate to depolarized scattering, is given by $p_{44} = \frac{p_{11} - p_{12}}{2}$.

We now consider the possible contributions to p_{44}. Equation (2) reflects the two mechanisms by which the optical anisotropy can be influenced by the hydrodynamic strain. These are the elliptical distortions of the molecular environment and the coupling of the optical anisotropy of the molecule to the strain. (Molecular distortion has been considered but appears as a correction to the Lorentz-Lorenz term). On the other hand, it is known that optical anisotropy is associated with velocity gradients in fluids. The birefringence in such a case is given by $\Delta n = M\frac{\partial v_y}{\partial x}$, where M is the Maxwell coefficient.

In the case of steady-state velocity gradients the dominant mechanism in optical anisotropy is the kinematic alignment of mechanically anisotropic molecules. Consideration of periodic

motion associated with a propagating hydrodynamic wave shows that this mechanism does not effectively contribute to p_{44} due to the absence of net flow. Hence, any contributions to the optical anisotropy from periodic velocity gradients is adequately represented in the second and fourth terms of (4) and (5).

A comparison of the contributions to p_{44} from the Lorentz field correction, optical anisotropy and from flow birefringence is illustrated in Table I for several liquids. The Maxwell coefficients for carbon tetrachloride, chloroform, and ethyl cinnamate were obtained from the work of Champion,[11] and those of the remaining fluids from the work of Peterlin.[12] The possible contribution to p_{44} from flow birefringence must be multiplied by the velocity gradient, and hence is given in units of sec/radian. If it is assumed that variation of the rate of strain of a hydrodynamic wave is the appropriate velocity gradient in flow birefringence, then a frequency f_o can be determined at which the flow birefringence is equal to the birefringence due to the Lorentz field correction. Since the Maxwell constant is roughly proportional to the viscosity of the liquid, f_o is seen to be lower for high viscoscity liquids. However, since this interpretation has limited validity for molecules of high anisotropy, it is probable that f_o is a better indication of the viscosity of a liquid and its ability to support propagating shear waves in the $10^9 H_z$ frequency range.

It would thus seem that the primary contribution to depolarized scattering from hydrodynamic waves in all liquids is due to the Lorentz field correction. This term does not relax and hence no dispersion can be associated with it. The lowest relaxing

terms are $\Delta(\omega)$ and $\Gamma(\omega)$, each of which is not greater than ten to twenty percent of the Lorentz field contribution to the optical anisotropy.

Acknowledgements

1. C. J. Montrose, V. A. Solovyev, and T. A. Litovitz, Jour. Acous. Soc. Amer. 43, 117-130 (Jan. 1968).

2. H. Z. Cummins and R. W. Gammon, J. Chem. Phys. 44, 2785-2796, (Apr. 1966).

3. S. M. Rytov, Soviet Physics - J.E.T.P. 6, 401, 513 (1958).

4. R. Mountain, Jour. of Research (NBS) 72A, 95-100 (Feb. 1968).

5. M. Born and E. Wolf, "Principles of Optics," p. 592, Pergamon Press, London (1959).

6. W. A. Riley and W. R. Klein, Jour. Acoust. Soc. Amer. 42, 1258-1261, (Dec. 1967).

7. G. P. Motulevich and I. L. Fabelinski, Soviet Physics - Doklady 1, 81-34, (1956).

8. G. I. A. Stegeman and B. P. Stoicheff, Phys. Rev. Letters 21, 202-206, (July 1968).

9. M. Fixman, Jour. Chem. Phys. 23, 2074-2079, (Nov. 1955).

10. J. F. Nye, "Physical Properties of Crystals," Clarendon Press, Oxford (1957).

11. J. V. Champion, Proc. Phys. Soc. (London) 75, 421 (1960).

12. A. Peterlin in "Rheology" F. Eirich (Ed.) Vol. I, 615, Academic Press, New York (1956).

| | n | p_{44} | | | Maxwell Constant $(\times 10^{12})$ | f_o (GHz) |
		Lorentz Field	Optical Anisotropy	Flow $\frac{\omega}{}$ $(\times 10^{12})$		
Carbon Tetrachloride	1.472	.058	---	2.64	1.21	12.
Chloroform	1.458	.056	-.007	5.68	2.39	5.6
Benzene	1.501	.062	+.014	1.85	.97	17.
Nitrobenzene	1.553	.069	+.01	13.2	8.5	2.4
Ethyl Cinnamate	1.560	.069	?	86.7	57.	.37

Contributions to birefringence coefficient p_{44} from distortion of the Lorentz field, optical anisotropy, and flow birefringence for a fixed shear strain of several fluids. f_o is the frequency at which the contribution from flow would be equal to the dominant Lorentz field contribution if the velocity gradient of a hydrodynamic wave is the appropriate term in the Maxwell relation. See text. ($\Delta n = \frac{n^3}{2} p_{44} S$)