

# LIGHT SCATTERING IN DENSE MEDIA—ITS THEORY AND PRACTICE

GJURO DEŽELIĆ

*Department of Biocolloidal Chemistry, Andrija Štampar School of Public Health, Faculty of Medicine, University of Zagreb, and Institute "Rugjer Bošković", Zagreb, Croatia, Yugoslavia*

## ABSTRACT

Theories of molecular light scattering (elastic, inelastic and non-linear scattering) have been described, also the experimental procedures for light scattering studies. An attempt has been made to compare theoretical and experimental work in this field. It is concluded that the measurements of spectral distribution of scattered light are capable of giving much new and additional information to the theory of liquids. Light scattering will, it is hoped, form an important technique for investigating the structure of dense media as well as that of polymer and colloidal solutions.

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## INTRODUCTION

In the history of light scattering it is evident that in its early days the theory developed much faster than the experimental information could be gathered. This situation was mainly the result of experimental difficulties caused by the lack of suitable instrumentation, such as intense light sources or highly sensitive photodetectors. By the rapid development of experimental devices one would expect that the gap between the theory and experiment would gradually disappear. The situation, however, seems to be just opposite. Superspecialisation among scientists has led to a separation of the theoretical and experimental work, as can be observed especially in the field dealing with dense fluids. In studying these systems, most of which appear in the liquid phase, it is not possible to formulate simple models as in gases or crystals. This difficulty has compelled theoreticians to use more and more refined mathematical methods, most of which are inadequate for direct numerical evaluation. Even for the simplest liquids it is necessary to introduce approximations which may cause such deviations from reality that comparison with experimental data is often impossible. The theoreticians are, therefore, devoting most of their interest to simple systems which are, as a rule, experimentally hardly accessible. The experimentalists are, on the other hand, working predominantly with complicated systems which are not very suitable for testing theories. In doing so, they often work without a sound theoretical basis, and the data collected are predominantly of an empirical nature.

Aware of this situation, Frisch and Salsburg<sup>1</sup> have recently undertaken an important task to collect facts on the statistical mechanics of liquids. Although their book is devoted primarily to simple liquids, it represents an up-to-date compendium of theoretical and experimental data which are useful for discussing other, more complicated systems. One chapter deals with light scattering, and its scantiness, resulting from lack of experimental data, is the best challenge for experimentalists to intensify their work on liquids.

The aim of this lecture goes beyond the scope of the book of Frisch and Salsburg. It is an effort of an experimentalist to apply the existing theories on light scattering in liquids to systems which are much nearer to macro-molecular chemists—to substances which, in normal laboratory conditions, are liquids. In the growing field of light scattering investigations on macromolecules more and more attention is being paid to the problems of intermolecular interactions, as for instance in concentrated solutions or binary and multicomponent mixtures. Satisfactory theories capable of interpreting experimental phenomena encountered in these systems are still lacking. Here, less complicated systems of similar properties, such as pure liquids, may facilitate the theoretical approach and let us know how to handle more complicated systems both theoretically and experimentally. A unified picture of the present state of investigations in the field of molecular light scattering will be given, and an attempt will be made to show to what extent the theoretical results can be applied in experimental work on pure liquids. There is another practical reason which makes the scattering in liquids quite important. Pure liquids serve widely as standards in calibration of light scattering photometers, and exact knowledge of light scattering properties of liquids should be a part of everyday practice in a light scattering laboratory.

## THEORY OF MOLECULAR LIGHT SCATTERING

### Theory of elastic scattering

The reason why optically homogeneous systems like liquids and gases scatter light lies in the fact that molecules exhibit thermal motions. Thus, the dense medium appears to be homogeneous only when observed macroscopically. A microscopic approach shows that this thermal motion produces fluctuations in thermodynamic functions leading to fluctuations in the refractive index. If we are considering a volume element  $V$ , small in comparison to the wavelength, but big enough to obey the laws of statistical thermodynamics, then the Smoluchowski–Einstein<sup>2,3</sup> theory gives as a result

$$R(90) = (\pi^2/2\lambda_0^4)V \langle (\Delta\varepsilon)^2 \rangle \quad (1)$$

where  $R(90)$  is the Rayleigh ratio measured at a scattering angle of 90 degrees and defined as

$$R(90) = J(90)r^2/J_0V \quad (2)$$

where  $J(90)$  is the intensity scattered by the volume  $V$  at 90 degrees,  $J_0$  is the intensity of the incident unpolarized beam, and  $r$  is the distance between the volume and the detector. Formula 2 can be replaced by a more convenient

expression. If  $n$  is the number of scatterers (particles, molecules) in  $V$ , and  $I(90)$  is the intensity scattered by a single scatterer, then  $J(90) = nI(90)$ , and with the number density  $N = n/V$  one obtains

$$R(90) = NI(90)r^2/J_0. \tag{3}$$

This expression is more customary in single particle scattering and in the work with macromolecules. The symbol  $\lambda_0$  in equation 1 stands for the wavelength of light in vacuo, and  $\langle(\Delta\epsilon)^2\rangle$  is the mean-square fluctuation of the dielectric constant  $\epsilon$  (measured at optical frequencies) about its mean value.

The whole problem of solving the scattering problem is now to evaluate the fluctuation term  $\langle(\Delta\epsilon)^2\rangle$  of a given molecular system. In general this system exhibits optical anisotropy and the fluctuation  $\Delta\epsilon$  has to be regarded as a tensor denoted by  $\Delta\epsilon_{ik}$ .

As known<sup>4</sup>, it is possible to separate  $\Delta\epsilon_{ik}$  into two parts:

$$\Delta\epsilon_{ik} = \Delta\epsilon^{is}\delta_{ik} + \Delta\epsilon_{ik}^{anis}, \tag{4}$$

the first term belonging to the so-called isotropic fluctuations and the second term being connected with anisotropic fluctuations. Here  $\delta_{ik}$  is the Kroneker delta, and the components of  $\Delta\epsilon_{ik}^{anis} = 0$  for  $i = k$ . The total intensity of scattered light should therefore be proportional to

$$J \sim \langle(\Delta\epsilon_{ik})^2\rangle = \langle(\Delta\epsilon^{is})^2\rangle + \langle(\Delta\epsilon_{ik}^{anis})^2\rangle \tag{5}$$

assuming that  $\Delta\epsilon^{is}$  and  $\Delta\epsilon_{ik}^{anis}$  are statistically independent.

Kielich<sup>5</sup> was the first to give a convenient expression for the Rayleigh ratio, written in a slightly different form:

$$R(90) = (\pi^2/10\lambda_0^4)(5F_{is} + 13F_{anis}), \tag{6}$$

where  $F_{is}$  and  $F_{anis}$  are the isotropic and anisotropic molecular scattering factors respectively. Factors  $F_{is}$  and  $F_{anis}$  are proportional to mean-square isotropic and anisotropic fluctuations. This formula is valid if the incident beam is unpolarized and the scattered intensity is measured without placing a polarizer before the detector.

A more generalized expression valid for light of arbitrary polarization and various scattering angles has been deduced<sup>5,6</sup> and can be written in the form:

$${}_iR_s(\theta) = (\pi^2/5\lambda_0^4)[5F_{is} \cos^2 {}_i\Omega_s + (3 + \cos^2 {}_i\Omega_s)F_{anis}] \tag{7}$$

Here  ${}_i\Omega_s$  is the angle between the electrical field vectors  $\vec{E}_i$  and  $\vec{E}_s$  of the incident and scattered beams, respectively. The indices  $i$  and  $s$  in  ${}_iR_s$  and  ${}_i\Omega_s$  denote arbitrary orientation of both vectors.

Most of the light scattering experiments are performed by orienting both  $\vec{E}_i$  and  $\vec{E}_s$  perpendicularly and parallelly to the scattering plane defined by the propagation vectors of the incident and scattered beams. By working with linearly polarized incident beams and measuring linearly polarized components of scattered radiation it is possible to measure four combinations of Rayleigh ratios which we could name "partial Rayleigh ratios":  $\sqrt{R_v}, \sqrt{R_h}, {}_hR_v, {}_hR_h$ , where the indices  $v$  and  $h$  denote vertically and horizontally

oriented electric vectors, respectively. Instead of using the notation  ${}_iR_s$ , we may take a simpler and more customary set of symbols introduced by Krishnan<sup>7</sup>:  $V_v$ ,  $H_v$ ,  $V_h$  and  $H_h$ , where the indices denote the polarization status of the incident beam, and the capital letter stand for the orientation of the polarizer before the detector. It is easy to see that subsequent formulae may be derived from equation 7:

$$- V_v(\theta) = (\pi^2/5\lambda_0^4) (5F_{is} + 4F_{anis}) \quad {}_i\Omega_s = 0 \quad (8)$$

$$V_h(\theta) = H_v(\theta) = (\pi^2/5\lambda_0^4) \cdot 3F_{anis} \quad {}_i\Omega_s = 90^\circ \quad (9)$$

$$H_h(\theta) = (\pi^2/5\lambda_0^4) [5F_{is} \cos^2 \theta + (3 + \cos^2 \theta)F_{anis}] \quad {}_i\Omega_s = \theta. \quad (10)$$

If the incident beam is unpolarized (index  $u$ ) or the polarizer is not placed in the scattered beam (capital letter  $R$ ), four other partial Rayleigh ratios can be measured:

$$V_u(\theta) = R_v(\theta) = V_v(\theta) + V_h(\theta) = (\pi^2/5\lambda_0^4) (5F_{is} + 7F_{anis}) \quad (11)$$

$$H_u(\theta) = R_h(\theta) = H_h(\theta) + H_v(\theta) \\ = (\pi^2/5\lambda_0^4) [5F_{is} \cos^2 \theta + (6 + \cos^2 \theta)F_{anis}] \quad (12)$$

Finally, the total Rayleigh ratio  $R_u(\theta)$  can be represented as a sum of four partial Rayleigh ratios:

$$R_u(\theta) = [V_u(\theta) + V_h(\theta) + H_v(\theta) + H_h(\theta)]/2 \\ = (\pi^2/10\lambda_0^4) [5(1 + \cos^2 \theta)F_{is} + (13 + \cos^2 \theta)F_{anis}] \quad (13)$$

From equations 8 to 13 it is obvious that some of the partial Rayleigh ratios are functions of the scattering angle ( $H_h$ ,  $H_u$ ,  $R_h$ ,  $R_u$ ), whereas the others are constants independent of  $\theta$ .

The molecular scattering factors  $F_{is}$  and  $F_{anis}$  are of the greatest importance in describing a molecular system, since they can be simply evaluated from the absolute values of Rayleigh ratios. They can be theoretically evaluated by the methods of statistical thermodynamics.

From equations 1, 5 and 6 one can deduce the relationships:

$$F_{is} = V \langle (\Delta \epsilon^{is})^2 \rangle \quad (14)$$

and

$$F_{anis} = \frac{5}{13} V \langle (\Delta \epsilon_{ik}^{anis})^2 \rangle \quad (15)$$

From the two mean-square fluctuations the isotropic one can be readily calculated. This was first done by Einstein<sup>3</sup>. The dielectric constant is taken as a function of density and temperature, and the final result is<sup>8</sup>:

$$F_{is} = kT\kappa_T(N\partial\epsilon/\partial N)_T^2 + (RT^2/NC_V)(\partial\epsilon/\partial T)_N^2, \quad (16)$$

where  $R$  is the gas constant, and  $C_V$  the molar heat capacity at constant pressure. Coumou *et al.*<sup>9</sup> have shown that equation 16 can be written with a very good approximation as:

$$F_{is} = kT\kappa_T(N\partial\epsilon/\partial N)_T^2 \quad (17)$$

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature,  $\kappa_T$  the isothermal compressibility,  $N$  the number density of molecules, and  $\epsilon = n^2$

with  $n$  being the refractive index of the dense medium. Thus isotropic scattering arises from density fluctuations, the fluctuations in temperature being negligible. The result of this phenomenological theory is very convenient for numerical evaluation since equation 16 consists only of physical constants which are measurable. There have been attempts to calculate  $F_{\text{is}}$  in terms of mean molecular polarizability  $\alpha$ . Kielich<sup>5</sup> arrived at an expression which in our definition of  $F_{\text{is}}$  has the form:

$$F_{\text{is}} = 16\pi^2 N \alpha^2 [(n^2 + 2)/3]^2 \left\{ 1 + 4\pi \int_0^\infty [g(r) - N] r^2 dr \right\} \quad (18)$$

with  $g(r)$  being the radial correlation function. As shown by Ornstein and Zernike<sup>10</sup>, the expression within the brackets is equal to  $kT\kappa_T N$  and can easily be determined experimentally. An important property of  $kT\kappa_T N$  is, as the system approaches the ideal gas state,  $kT\kappa_T N \rightarrow 1$ . Expression (18) is, however, more difficult to handle than (17), since the molecular polarizability in dense media is strongly influenced by internal fields which are not easy to define at present. At low densities these effects may be neglected, but in liquids they have to be taken into account. It has frequently been overlooked that instead of  $\alpha$ , which is valid for separate, noninteracting molecules, one has to use  $\alpha$ , the effective polarizability of a molecule placed in an internal field<sup>11</sup>. A correction for changes in average polarizability  $\alpha$  owing to the increasing density of the system has also to be taken into account<sup>11</sup>.

The derivation of  $F_{\text{anis}}$  in terms of useful physical constants is more complicated. Kielich<sup>5</sup>, and Pecora and Steele<sup>6</sup> calculated  $\langle (\Delta \epsilon_{\text{ik}}^{\text{anis}})^2 \rangle$  and arrived at simpler expressions only in the case of axially symmetric molecules. This part of scattering can be explained as an effect of fluctuations in the orientation of anisotropic molecules. As shown by Benoit and Stockmayer<sup>12</sup>, in the case of dense systems with strong intermolecular interactions  $F_{\text{anis}}$  is proportional to the mean value<sup>5</sup>  $\langle_{pq} \Sigma (3 \cos^2 \theta_{pq} - 1) \rangle$  where  $\theta_{pq}$  is the angle between the axes of symmetry of a pair of molecules. This factor is also connected with an integral function  $J_A$  containing the orientational correlation function<sup>13</sup>. The whole effect of the orientational correlations of the molecules may be condensed in a factor  $G$  which is related to  $J_A$  by:

$$G = 1 + J_A \quad (19)$$

For axially symmetric molecules  $J_A$  can be written in the form<sup>13</sup>:

$$J_A = \frac{N}{V} \iint (3 \cos^2 \theta_{pq} - 1) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (20)$$

where  $g^{(2)}(\tau_p, \tau_q)$  is the two-molecule correlation function, and  $\tau_p, \tau_q$  are the variables determining the position and orientation of molecules  $p$  and  $q$ . The important property of function  $J_A$  is that the value  $J_A = 0$  indicates the absence of angular correlation between molecules, whereas  $J_A < 0$  should show a tendency to perpendicular orientation of the main molecular axes and  $J_A > 0$  a tendency to parallel orientation.

$F_{\text{anis}}$  depends also of what is called the optical anisotropy  $\delta^2$  of isolated molecules and is defined as:

$$\delta^2 = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{2(\alpha_1 + \alpha_2 + \alpha_3)^2} \quad (21)$$

where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  stand for the polarizabilities in the directions of the three principal molecular axes. Expressed in terms of the fluctuation theory and defined as in equation 6  $F_{\text{anis}}$  can be written as<sup>14</sup>:

$$F_{\text{anis}} = (\delta^2 G/N)(N\partial\varepsilon/\partial N)_T^2. \quad (22)$$

In the practice of light scattering it is also customary to measure ratios of scattered light intensities measured with certain combinations of polaroids in the incident and the scattered beams. One can define:

$$D_v(\theta) = H_v(\theta)/V_v(\theta) = 3F_{\text{anis}}/(5F_{\text{is}} + 4F_{\text{anis}}) \quad (23)$$

$$D_h(\theta) = V_h(\theta)/H_h(\theta) = 3F_{\text{anis}}/[5F_{\text{is}} \cos^2 \theta + (3 + \cos^2 \theta)F_{\text{anis}}] \quad (24)$$

$$D_u(\theta) = H_u(\theta)/V_u(\theta) = [5F_{\text{is}} \cos^2 \theta + (6 + \cos^2 \theta)F_{\text{anis}}]/(5F_{\text{is}} + 7F_{\text{anis}}) \quad (25)$$

These quantities are frequently called depolarization ratios, although the term 'polarization ratios' would appear to be more appropriate<sup>15</sup>. From all polarization ratios  $D_v$  is the most suitable for detection of optical anisotropy, since it is not dependent of scattering angle, and  $D_v \rightarrow 0$  if  $\delta^2 \rightarrow 0$ .

It is also useful to define an apparent optical anisotropy:

$$\Delta^2 = F_{\text{anis}}/F_{\text{is}} = \delta^2 G/kT\kappa_T N = 5D_u(90)/[6 - 7D_u(90)] \quad (26)$$

which passes into  $\delta^2$  as the system approaches the ideal gas state, i.e.  $kT\kappa_T N \rightarrow 1$  and  $G \rightarrow 1$ .

From the foregoing formulae it is obvious that the isotropic light scattering cannot be measured directly. By using one of the polarization ratios it is possible, however, to eliminate  $F_{\text{anis}}$  and obtain the isotropic part. Equation 13 may be written as:

$$R_u(\theta) = R_{\text{is}}(\theta) + R_{\text{anis}}(\theta) \quad (27)$$

with

$$R_{\text{is}}(\theta) = (\pi^2/2\lambda_0^4)(1 + \cos^2 \theta)F_{\text{is}} \quad (28)$$

and

$$R_{\text{anis}}(\theta) = (\pi^2/10\lambda_0^4)(13 + \cos^2 \theta)F_{\text{anis}} \quad (29)$$

It is customary to eliminate  $F_{\text{anis}}$  by using  $D_u$ . For  $\theta = 90$  degrees one arrives at the expression:

$$R_{\text{is}}(90) = R_u(90) \frac{6 - 7D_u(90)}{6 + 6D_u(90)} \quad (30)$$

where  $[6 + 6D_u(90)]/[6 - 7D_u(90)]$  is the well-known Cabannes factor.

$R_{is}$  values determined from (30) may serve now for comparison with the theoretical values derived from:

$$R_{is}(90) = (\pi^2/2\lambda_0^4)kT\kappa_T(N\delta\epsilon/\delta N)_T^2 \quad (31)$$

If the liquid is a multicomponent mixture of molecules exhibiting different polarizabilities, then additional fluctuations in the dielectric constant have to be taken into account. It was shown by Einstein<sup>3</sup> that the additional scattering effect is due to the fluctuations in concentration. As a first approximation, it is possible to suppose that the concentration fluctuations are statistically independent of both the density and anisotropic fluctuations. In the case of a binary mixture the isotropic part in equation 27 can be separated into two parts, as shown by Kirkwood and Goldberg<sup>16</sup>:

$$R_{is}(\theta) = R_d(\theta) + R_c(\theta) \quad (32)$$

where  $R_d$  stands for density fluctuations and  $R_c$  for concentration fluctuations. In order to evaluate  $R_c$  one has to determine  $R_d$  and subtract it from  $R_{is}$  calculated by equation 30<sup>17</sup>.  $R_d$  can be calculated by<sup>18</sup>:

$$R_d = R_{d,0} \frac{\kappa_T(N\delta\epsilon/\delta N)_T^2}{\kappa_{T,0}(N\delta\epsilon/\delta N)_{T,0}^2} \quad (33)$$

where the subscript zero denotes the pure solvent and other nonsubscripted values stand for the solution. It has been proposed by Bullough<sup>19</sup> that an extra term has to be included in the isotropic Rayleigh ratio of mixtures leading to an expression of the form

$$R_{is} = R_d \left[ 1 + \frac{4nc(\partial n/\partial c)_{p,T}}{(N\delta\epsilon/\delta N)_{c,T}} \right] + R_c \quad (34)$$

Generally  $R_c$  depends on the interactions between molecules and deviates from linear mixture rules, so we can write:

$$Kc/R_c = (1/M) + 2Bc \quad (35)$$

with

$$K = 2\pi^2 n_0^2 (\partial n/\partial c)_{p,T}^2 / \lambda_0^4 N_A \quad (36)$$

where  $M$  is the molecular weight of the solute,  $c$  is the concentration of the solute in g/ml, and  $N_A$  Avogadro's number.

A satisfactory theory explaining the anisotropic part of scattering in multicomponent systems is not available at present. Although experimental data indicate<sup>20-22</sup> that in binary systems  $F_{anis}$  factors of both components are additive, it is difficult to give an exact solution of the problem since useful theoretical models for internal fields in multicomponent dense systems have not been developed explicitly.

### Theory of inelastic scattering

Soon after the basic principles of Rayleigh scattering in dense systems

were delineated by Einstein, it became apparent that scattering effects in liquids should produce some spectral broadening of incident radiation frequency. Those effects, predicted first by Brillouin<sup>23</sup> and Madelstam<sup>24</sup>, were experimentally confirmed by Gross<sup>25</sup> and others<sup>4</sup>. Brillouin made his prediction by assuming that light in dense media is scattered on inhomogeneities resulting from the propagation of sound waves, and arrived at the result that the scattered light should consist of a doublet with components symmetrically shifted from the incident frequency  $\nu_0$  by<sup>8</sup>:

$$\Delta\nu = \pm 2\nu_0(v/c) \sin(\theta/2) \quad (37)$$

where  $v$  and  $c$  are the velocities of sound and light in the medium, and  $\theta$  is the scattering angle.

Experimental work has revealed, however, that this doublet is only a part of the whole scattering. It has become obvious that some of the scattering occurs also at the incident frequency  $\nu_0$ , and also that there is always some background scattering, symmetric around  $\nu_0$ , whose frequencies normally extend over much of the range Brillouin's doublet, the so-called 'wings of Rayleigh scattering'.

It is not intended to give here a review of the theory of inelastic scattering since this has been done very thoroughly in the book by Fabelinskii<sup>4</sup>, but only to discuss some important points necessary for understanding recent experimental data.

The first successful approach to explain the fine structure of Rayleigh scattering was done by Landau and Placzek<sup>26</sup>. They started with the isotropic fluctuations  $\langle(\Delta\varepsilon^{is})^2\rangle$ , but instead of taking  $\varepsilon$  as a function of density and temperature, they chose entropy and pressure as the independent variables. In this way, they were able to separate isotropic fluctuations into isobaric entropy fluctuations which do not propagate in liquids and are the source of the central, unshifted Rayleigh component of the scattered light, and into isentropic pressure fluctuations (sound waves) which are the source of the Brillouin doublet. The isotropic molecular scattering factor can be written as:

$$F_{is} = \frac{RT^2}{NC_p} (\partial\varepsilon/\partial T)_p^2 + kT\kappa_s(N\partial\varepsilon/\partial N)_s^2 \quad (38)$$

where  $\kappa_s$  is the adiabatic compressibility and  $C_p$  the molar heat capacity at constant pressure. Here the first term describes the unshifted Rayleigh component and the second belongs to Brillouin components.

Attempts have also been made to develop theories from the standpoint of the molecular theories of liquids. Pecora and Steele<sup>6</sup> have developed a theory valid for fluids consisting of nonspherical molecules and have arrived at expressions for the elastic and inelastic scattering expressed in terms of angular moments of the generalized pair distribution function of the fluid. It was shown that simply, if an additional time dependence of the electric vectors is considered, this leads to formulae containing frequency dependent variables. However, the time dependent  $g^{(2)}(\tau_p, \tau_q)$  functions could not be explicitly obtained so far in terms of some measurable quantities. Mountain<sup>27</sup>

showed that essentially the same results as obtained by Landau and Placzek can be derived if density fluctuations are considered to be time dependent. Other theories<sup>28,29</sup> did not elucidate the situation further, so a proper connection between theory and experiment remains a problem for future investigations.

Although the general theory of Pecora and Steele includes orientational scattering, some more approximate theories seem to be useful in explaining experimental results. Among these, one has to mention the first theory of orientational scattering given by Leontovich<sup>30</sup> who calculated the time dependence of  $\langle(\Delta\epsilon_{ik}^{\text{anis}})^2\rangle$  by assuming that small disturbances from equilibrium are linear. The basic result from his theory is the prediction that the shape of Rayleigh wings should be Lorentzian, and that the ratio of intensities of vertical and horizontal components in the wings,  $I_H$  and  $I_V$ , should be:

$$I_H/I_V = \frac{3}{4} \quad (39)$$

Later theories were developed predominantly by the Russian school<sup>4</sup>, and together with the theories of Pecora and Steele<sup>6</sup> and the recent work of Pinnow *et al.*<sup>29</sup> all predict the Lorentzian form of spectra and  $I_H/I_V = \frac{3}{4}$ .

### Theory of nonlinear scattering

Buckingham<sup>31</sup> was among the first to suppose that intense light beams might induce optical birefringence in isotropic media. This idea was further developed by Kielich<sup>5</sup> in his theory of molecular light scattering and subsequent papers, but was experimentally confirmed only a few years ago by several authors<sup>32,33</sup> who used an intense laser beam. The whole topic was recently reviewed by Kielich<sup>34</sup>, so only a few of the more important points will be mentioned here.

If a molecular system is illuminated with an intense light beam, the scattered intensity  $I$  becomes a nonlinear function of the incident intensity  $I_0$ :

$$I = S_1 I_0 + S_2 I_0^2 + S_3 I_0^3 + \dots \quad (40)$$

Here  $S_1$  defines the normal linear Rayleigh scattering, and  $S_2, S_3, \dots$ , are the factors defining higher order nonlinear scattering due to reorientation of molecules and nonlinear polarizability. The basic process in nonlinear scattering<sup>35</sup> consists of irradiating a molecule with two quanta of frequency  $\nu$  and scattering a single quantum of frequency  $2\nu$ . This process could be observed in  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$  and  $\text{CH}_3\text{CN}$  by Terhune *et al.*<sup>33</sup> by means of a giant-pulse focused ruby laser beam.

Kielich<sup>36</sup> has shown that nonlinear scattering can be treated formally in a similar way to linear scattering. He could estimate the molecular scattering factors for nonlinear second harmonic light scattering and showed that it is possible to separate them into isotropic and anisotropic parts. Second order polarization ratios could be deduced for various types of molecules. Thus, for example, for liquid  $\text{CCl}_4$  the theory gives  $D_v^{2\nu} = \frac{2}{3}$  in the case when the action of the molecular field was neglected. The measured value<sup>33</sup> was about  $\frac{1}{3}$ . If the effect of the molecular field was taken into consideration, the theoretical value could be lowered and brought into a better accordance with the experimental value.

It is important to note that in dense media there exist strong molecular fields which can produce not only linear, but also nonlinear polarization of molecules, even if the external fields are weak<sup>37</sup>. Therefore, the nonlinear scattering appears to be very sensitive to molecular interactions and structure.

The investigations of nonlinear scattering are connected with many difficulties, most of them arising from the experimental side. The effects in molecular systems are mostly small (of the order of  $10^{-13}$  of the incident intensity<sup>33</sup>) and one has to work with extremely intense laser beams, which in turn can provoke some complications (e.g. shock waves and dielectric breakdown<sup>34</sup>). However, in colloid and macromolecular systems the effects are much more pronounced and therefore the nonlinear light scattering appears to be a promising field for future studies.

## EXPERIMENTAL PROCEDURES AND RESULTS

The most important part of the efforts in experimental light scattering work with liquids belongs to the determination of absolute Rayleigh ratios. Seven years ago Kratochvil *et al.*<sup>38</sup> gave a critical survey of Rayleigh and polarization ratios found in the literature in connection with the calibration of light scattering photometers. A part of this discussion was dealing with the reliability of the so-called 'high' values of Rayleigh ratios for liquids. The suggested best values for benzene at 20° are  $R_s(90 \leq 46.5 \times 10^{-6}$  and  $(15.5-16.0) \times 10^{-6} \text{ cm}^{-1}$  for 436 and 546  $\mu\text{m}$ , respectively. Kratochvil *et al.* arrived at these values after careful critical examination of calibration procedures applied in every particular case of the reported Rayleigh ratio for benzene. Since then the great majority of reports on Rayleigh ratios of liquids have confirmed the reliability of the above data.

Although the discussion on proper calibration procedures of light scattering photometers can be regarded as practically concluded, papers occasionally still appear which do not satisfy the requirements of a reliable calibration. It is therefore assumed that a short review of these problems might be of value for future work.

There are two methods which are predominantly used for the determination of Rayleigh ratios: (a) the Brice working-standard method<sup>39</sup>, and (b) the standard scatterer method. Although it is frequently recognized that Brice's method leads to reliable absolute intensities<sup>41</sup>, the experience from author's laboratory has shown that this method can lead to systematic errors, if the geometry of the apparatus has to be changed, and this is not made properly. In some cases, it is difficult to track the sources of these deviations, and calibration with a standard scatterer appears to be the best and most straightforward method. One of the most suitable standard scatterers is liquid benzene, which can be easily prepared in a pure, water- and dust-free form. Rayleigh ratios are obtained from

$$R_i(\theta) = C \cdot C'_j \cdot I_i(\theta) \quad (41)$$

where  $C = R_s(90)/I_s(90)$  is the calibration constant. Here  $I$  denotes galvanometer deflections, the subscript  $s$  stands for the standard (in this particular case it is benzene), and  $C'_j$  is a complex relative optical correction factor consisting of corrections for differences in the refractive index, volume and

reflections. It is always necessary to determine  $C'_j$  when the refractive index of the measured liquid differs from that of the standard.

The correction factors have been thoroughly reviewed<sup>41-43</sup>, and it has been noted that both the refractive index correction<sup>44</sup> and the volume correction<sup>42</sup> are important for the determination of Rayleigh ratios by the standard scatterer method. For the special geometry when the detector 'sees' within the edges of the incident beam Hermans and Levinson<sup>45</sup> have shown that the total correction should be equal to the ratio of the squares of the refractive indices. Most authors simply use the  $n^2$ -correction of Hermans and Levinson without further checking. It could be shown<sup>41</sup> that the  $n^2$ -correction really consists of a product of relative refractive index and volume corrections. Data in *Table 1* may be taken as an example. They were derived

*Table 1.* Relative optical correction factors for the Oster-Aminco photometer at 25° using a rectangular cell.  $n_1$  = refractive index of water;  $n_2$  = refractive index of benzene.

$\lambda_0$ (m $\mu$ )	$(n_2/n_1)^2$	$C'_n$	$C'_E$	$C'_n C'_v$
546	1.268	1.171	1.083	1.270
436	1.282	1.181	1.087	1.283

$C'_n = C_{n,2} C_{n,1}$ ; calculated from the formula of Carr and Zimm. *J. Chem. Phys.* **18**, 1616 (1950).

$C'_v = C_{v,2} C_{v,1}$ ;  $C_{v,1}$  calculated from the formula of Kerker *et al.* *J. Polymer Sci.* **A2**, 303, case II (1964).

for the geometry of the Aminco photometer from equations given in previous papers<sup>41, 42</sup>. It has been proved<sup>14</sup> that the geometry of this photometer satisfies the requirements for the  $n^2$ -correction. If the detector 'sees' past the edges of the incident beam, the  $n^2$ -correction appears to be too low. So, for example, in the case of the Brice-Phoenix photometer with standard apertures when working with the standard scatterer method the real correction should be 2 per cent higher than the  $n^2$ -correction for the system benzene-water at 436 m $\mu$ . Since this method of determining Rayleigh ratios is a relative one, the reflection correction<sup>43, 46</sup> is normally cancelled out<sup>41</sup>. It can be concluded that in the case of a proper geometry (i.e. when the detector 'sees' within the edges of the incident beam) equation 41 can be simply written as:

$$R_i(\theta) = (n/n_s)^2 R_s(90)/I_s(90) I_i(\theta) \quad (42)$$

When polarized Rayleigh ratios have to be determined, one can proceed in various ways. With the Brice working-standard method one can use the Brice original formula, but because of definition 13 there should be an additional factor  $\frac{1}{2}$  in the formula<sup>40</sup>. Another method consists in measuring the attenuation factors of the polarizing filters (or prisms) placed in both the incident and the scattered beams<sup>14</sup>. One can measure it directly or from the scattered intensities of any liquid by adding galvanometer readings.

Another correction appears to be important when working with the standard scatterer method. That is the correction for the different sensitivity of the detector to light beams polarized in different planes.  $C_D$  is defined<sup>41</sup>

as the ratio of galvanometer readings for light directly incidenting onto the detector, i.e.  $C_D = I_v(0)/I_h(0)$ . Therefore all readings made with a horizontally oriented polarizer before the detector should be multiplied by  $C_D$ . This correction factor varies for different detector tubes and wavelength, and in our experience it can take values between 0.9 and 1.1. This difference in sensitivity might influence  $R_u$  values, a fact not taken into consideration in the past. It can be deduced that the polarization correction factor for  $R_u$  amounts to  $[1 + D_u(90)]/[1 + D_u(90)/C_D]$ . In the case when  $D_u(90) = 0.4$  and  $C_D = 1.1$  this factor is 1.03 and may play a role in precise determination of  $R_u$ . In most cases, however, the differences in polarization sensitivity are 2 per cent or less, so that correcting  $R_u$  becomes unimportant.

It is interesting to note that several years ago Rozhdestvenskaya and Vuks<sup>47, 48</sup> described a different method for the determination of Rayleigh ratios of pure liquids. They combined lateral scattering measurements with transmission measurements made both on pure liquids and polymer solutions with the same liquid as the solvent. From the ratio of laterally scattered intensities and from the difference of the logarithms of the transmitted intensities Rayleigh ratios were determined. The authors obtained data nearer to the group of 'low' values. On the basis of these results Vuks<sup>49</sup> has recently made some theoretical considerations in trying to prove the

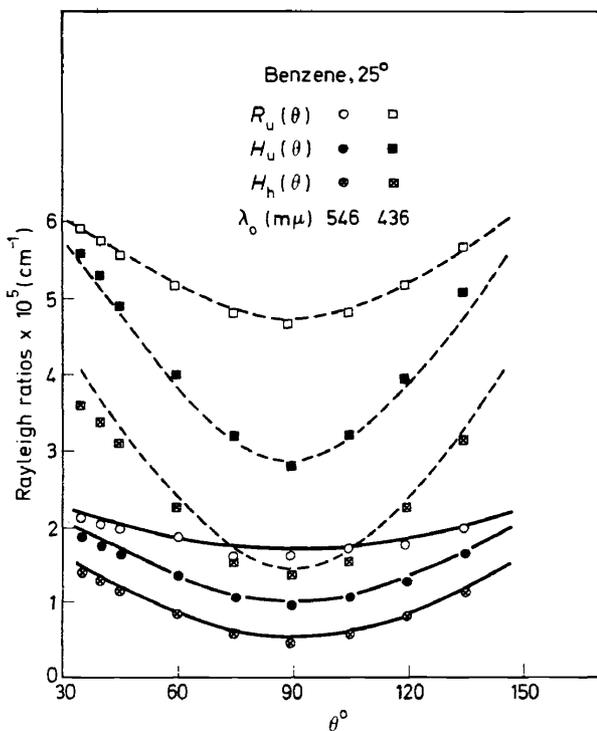


Figure 1. Angular dependence of the Rayleigh ratios  $R_u(\theta)$ ,  $H_u(\theta)$  and  $H_h(\theta)$  of benzene at 25°C and 546 and 436 m $\mu$ . Points are experimental, curves theoretical.

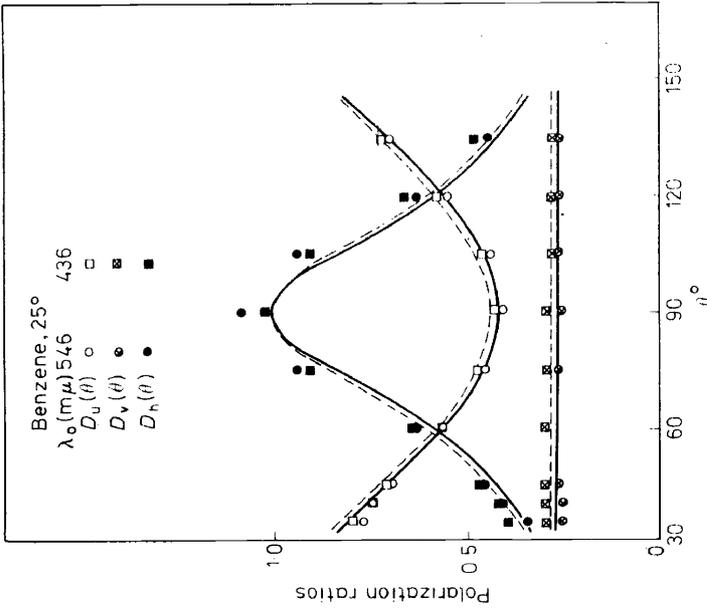


Figure 3. Angular dependence of the polarization ratios  $D_0(\theta)$ ,  $D_v(\theta)$  and  $D_h(\theta)$  of benzene at 25°C and 546 and 436 m $\mu$ . Points are experimental, curves theoretical.

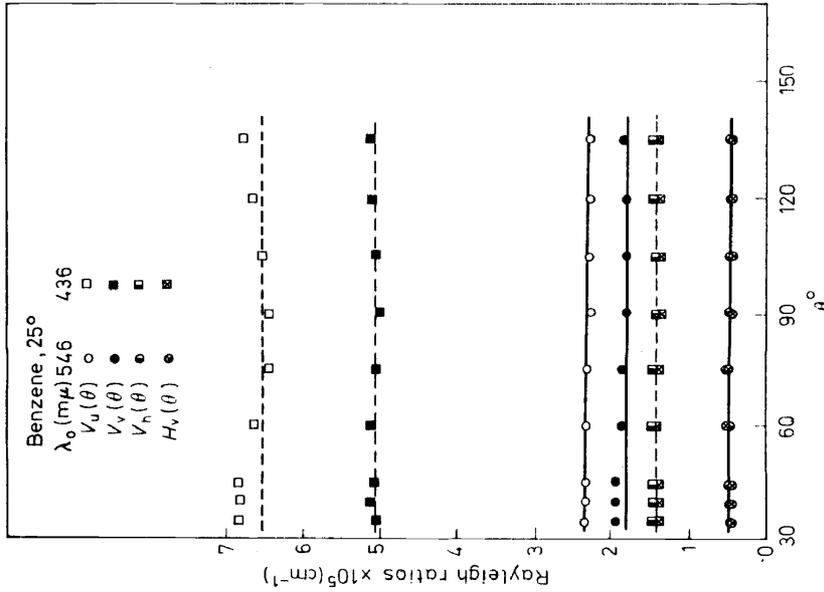


Figure 2. Angular dependence of the Rayleigh ratios  $V_v(\theta)$ ,  $V_h(\theta)$ ,  $V_h(\theta)$  and  $H_v(\theta)$  of benzene at 25°C and 546 and 436 m $\mu$ . Points are experimental, lines theoretical.

exactness of 'low' values. It appears, therefore, to be important to examine the reliability of their experimental procedure. Their method has the advantage of eliminating the  $n^2$ -correction, but one can deduce easily that the precision of the method is mainly influenced by the precision of transmission measurements. In this particular case the main part of the error arises from the transmission measurement of pure benzene. For a cell of 100 cm path length which was actually used one can estimate an error of at least 10 per cent. Since it may be assumed that the other three intensities have an error of several per cent, the total error might be about 20 per cent which by far exceeds the precision of the methods discussed previously and puts some doubt on the reliability of their results.

By studying the angular distribution of the scattered intensities it can be shown that for fluids formulae 8–13 and 23–25 hold without any exception. This behaviour was observed frequently on gases and liquids<sup>18, 50–55</sup>. The only deviation noted<sup>56</sup> could later be attributed to remarkable experimental errors<sup>57</sup>. An illustration of the angular distribution of all measurable light scattering quantities can be seen in *Figures 1 to 3*. The points are the values measured on benzene<sup>14</sup> and the curves are theoretical. The calculation of theoretical values will be discussed later.

By concluding this discussion it should be emphasized that Rayleigh ratios discussed here represent the integrated intensities of the whole spectrum of scattered light. Mostly, experiments are performed with no special precautions for elimination of Raman frequencies, since the amount of those is normally below the experimental error<sup>58</sup>. Therefore, all Rayleigh ratios are a measure for the integral electromagnetic energy scattered with a spectral distribution around the incident frequency  $\nu_0$ .

## COMPARISON OF THEORY AND EXPERIMENT

The crucial point in the evaluation of theoretical light scattering data is the calculation of molecular scattering factors  $F_{is}$  and  $F_{anis}$ .

For comparison with experiments  $F_{is}$  can be derived from equations 28 and 30:

$$F_{is} = (2\lambda_0^4/\pi^2)R_u(90) \frac{6 - 7D_u(90)}{6 + 6D_u(90)} \quad (43)$$

$F_{anis}$  may be derived directly from the measured values of  $V_h(\theta)$  or  $H_v(\theta)$  by equation 9.

In calculating  $F_{is}$  one can start from the approximated equation 17 with the parameter  $(N\partial\epsilon/\partial N)_T$  which can be best determined from the measured  $(\partial n/\partial p)_T$  values, as it follows from thermodynamic relationships. A very convincing proof of this was given by Coumou *et al.*<sup>9</sup> and by others<sup>40, 59</sup>. In the past, however, owing to the lack of experimental  $N\partial\epsilon/\partial N$  data, this quantity was usually determined by one of the relations between the refractive index and density. Einstein<sup>3</sup> used the Lorentz–Lorenz function ;

$$(n^2 - 1)/(n^2 + 2) = cN \quad (44)$$

$c$  being a constant containing the polarizability of molecules, and arrived at the expression:

$$(N\partial\epsilon/\partial N)_T = (n^2 - 1)(n^2 + 2)/3 \quad (45)$$

At that time the experimental values of Rayleigh ratios were systematically too low because the refractive index correction was not applied. As the ratio between these incorrect experimental values and the theoretical ones calculated by equation 31, with  $N\partial\epsilon/\partial N$  calculated from (45), amounted in most cases to roughly the factor  $(n^2 + 2)^2/9$ , Ramanathan<sup>60</sup> and Rocard<sup>61</sup> were led to an artificial assumption that the factor  $(n^2 + 2)^2/9$  arises from the presence of the medium surrounding a molecule and that the properties of this medium do not undergo changes from fluctuations in small volume elements. Therefore, this factor should be regarded as a constant during the differentiation process<sup>62</sup>. So they actually made use of the so-called Newton-Laplace function:

$$n^2 - 1 = cN \quad (46)$$

and obtained

$$(N\partial\epsilon/\partial N)_T = n^2 - 1 \quad (47)$$

It is interesting to note that Vuks<sup>49</sup> has recently tried to derive  $(N\partial\epsilon/\partial N)_T$  using a similar assumption, i.e. by assuming the reacting field fluctuations to be zero, and arrived at the expression:

$$(N\partial\epsilon/\partial N)_T = (n^2 - 1) [3n^2/(2n^2 + 1)] \quad (48)$$

Equation 47 gives too low values of  $N\partial\epsilon/\partial N$  if compared with the experimental values. The values from equation 48 are somewhat higher, but still significantly low. On the other hand, equation 45 tends to give higher values. From other relations between the refractive index and the density the Gladstone-Dale function yields:

$$(N\partial\epsilon/\partial N)_T = 2n(n - 1) \quad (49)$$

and leads to lower values. The best results could be obtained from Eykman's empirical formula<sup>44, 63, 97</sup> which gives after differentiating:

$$(N\partial\epsilon/\partial N)_T = (n^2 - 1) [1 - (n^2 - 1)/2n(n + 0.4)] \quad (50)$$

The values of  $N\partial\epsilon/\partial N$  obtained by different formulae are compared with experimental values in Table 2. It is obvious that none of these derivations leads to fully satisfactory results.

The main shortcoming of all the preceding formulae seems to be in the supposition that the molecular polarizability  $\alpha$  is constant. More refined theories<sup>64, 65</sup> show that in dense media molecules are compressed and the result is a decrease in  $\alpha$  at high pressure. If the density dependence of polarizability is taken into consideration, functions of the form<sup>66</sup>:

$$(n^2 - 1)/(n^2 + 2) = \frac{4\pi}{3} N\alpha [1 + S(N, T)] \quad (51)$$

are obtained, where  $S$  expresses the density and temperature dependence



of  $\alpha$ . The density dependence of the Lorentz-Lorenz function is confirmed by the experiment. One of the first empirical forms of equation 51 was given by Rosen<sup>67</sup>:

$$(n^2 + 2)/(n^2 - 1) = (a/N) + b \quad (52)$$

Here  $a$  and  $b$  are constants for a given temperature and frequency. Theoretical work<sup>68,69</sup> could show that  $b$  is associated with the radial correlation function  $g(r)$  discussed before.

Recently Eisenberg<sup>70,71</sup> has shown that the changes in the refractive index with pressure and temperature can be represented by a function of the form:

$$(n^2 - 1)/(n^2 + 2) = AN^B e^{-CT} \quad (53)$$

where  $A$ ,  $B$  and  $C$  are constants.

By differentiating equation 52 one obtains<sup>11</sup>:

$$(N\partial\epsilon/\partial N)_T = (n^2 - 1)(n^2 + 2)/3(1 + bN/a), \quad (54)$$

and from equation 53 it follows:

$$(N\partial\epsilon/\partial N)_T = B(n^2 - 1)(n^2 + 2)/3 \quad (55)$$

Table 3 gives values of  $(N\partial\epsilon/\partial N)_T$  calculated from both equations. The agreement between the calculated and the measured values is generally better than for the functions without the density correction. In view of the fact that functions (52) and (53) can be associated with the theory of refractive indices in dense media, they seem to be superior to other refractive index functions. Thus it is apparent that the derivation  $(N\partial\epsilon/\partial N)_T$  is less sensitive to internal field changes and models, but mostly to density effects on the polarizability  $\alpha$ . This is indicated by the results of calculations with polarizability functions having differently defined internal fields but no density dependence. Thus, for example, by taking the Lorentz ellipsoidal field<sup>72</sup> the polarizability function can be written in the form:

$$n^2 - 1 = \frac{4\pi}{3} N \sum [1 + (n^2 - 1)A_i] \alpha_i \quad (56)$$

where the summation has to be performed over three axes of the polarizability ellipsoid, and  $A_i$  are the shape factors<sup>73</sup>. One gets the result:

$$(N\partial\epsilon/\partial N)_T = (n^2 - 1) \frac{\sum [1 + (n^2 - 1)A_i] \alpha_i}{\sum \alpha_i} \quad (57)$$

From this formula, by taking the values of the parameters from literature<sup>74</sup>, the value  $(N\partial\epsilon/\partial N)_T = 1.74$  is obtained for benzene, a value near the value calculated for the Lorentz spherical field (Table 3).

An additional proof of the validity of the fluctuation theory of isotropic scattering combined with the idea of density dependent polarizability can be found in temperature dependence of  $R_{90}$ . In Figure 4 data calculated

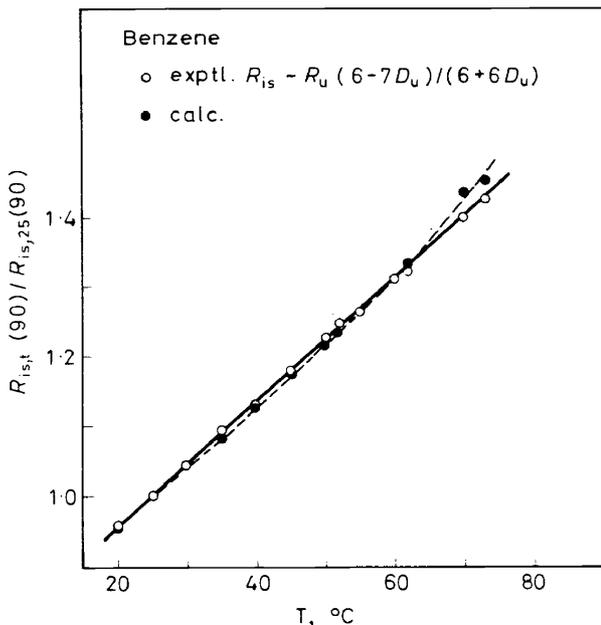


Figure 4. Variation of experimental and calculated isotropic Rayleigh ratios of benzene at 546 m $\mu$  with temperature.

from equation 31 with  $(N\partial\epsilon/\partial N)_T$  derived from equation 54 are compared with the experimental data derived from the paper of Ehl *et al.*<sup>75</sup>. They are in excellent agreement within the experimental error.

For the calculation of  $F_{anis}$  the data for  $\delta^2$  and  $G$  should be known. There are two methods which may be used for the determination of the optical anisotropy  $\delta^2$ . The first method is based on the measurements of polarization ratios on vapours and the evaluation from the formula:

$$\delta^2 = 5D_u(90)/[6 - 7D_u(90)] \quad (58)$$

which follows from (25) and (26). This method was frequently used in the past<sup>58</sup>, but data found in the literature are hardly satisfactory. Most of the data may be regarded as obsolete and new measurements with modern instrumentation are urgently needed. In particular the wavelength dependence of  $D_u$  and  $\delta^2$  should be measured. It was estimated<sup>11</sup> that  $\delta^2$  might differ as much as 10 per cent for wavelengths 546 and 436 m $\mu$  and this may produce remarkable errors in determination of  $F_{anis}$ .

The second method consists of measuring  $H_v$  in diluted solutions with a solvent of low optical anisotropy. This method was developed and extensively used by Bothorel and collaborators<sup>76</sup>. Here the molecules of the solute are assumed to approach the gaseous state when the solution is sufficiently diluted. It is supposed that the molecules of the solute do not interact with the molecules of the solvent.

The orientation correlation factor  $G$  can be derived in principle from any of the physical quantities which depend on optical anisotropy of molecules. This can be done by measuring the depolarization of scattered light, electric, magnetic and streaming birefringence. Generally speaking, all methods consist in comparison of the data measured with the same substance in liquid and vaporous states. In some special cases (benzene, carbon disulphide<sup>11</sup>) it could be shown that agreement with experiment can be obtained. As an illustration, data for benzene are given. In *Table 4* physical constants and scattering factors necessary for the evaluation of all scattering quantities from equations 8–13 and 23–26 are given<sup>14</sup>. The calculated data, compared with the experimental ones in *Table 5* are in remarkable agreement.

*Table 4.* Physical constants and scattering factors for benzene at 25°C

$\lambda_0(\text{m}\mu)$	$n$	$(N\partial\epsilon/\partial N)_T$	$\delta^2 \times 10^2$	$F_{is} \times 10^{24} (\text{cm}^3)$	$F_{anis} \times 10^{24} (\text{cm}^3)$	
		$\kappa_T = 9.65 \times 10^{-11} \text{ dyne}^{-1} \text{ cm}^2, N = 6.74 \times 10^{24} (\text{cm}^3)$				
					$G = 0.53^a$	$G = 0.58^b$
546	1.502	1.624	3.2	10.5	6.7	7.3
436	1.519	1.712	3.4	11.6	7.8	8.5

<sup>a</sup>  $G$  calculated from Kerr constants

<sup>b</sup>  $G$  calculated from polarization ratios.

The same method was applied for calculating curves in *Figures 1–3*. The differences between the theoretical and the experimental values vary from 2–12 per cent. A part of this can be ascribed to rather high experimental errors resulting from the use of polaroid discs which, as known, allow results of only 5–10 per cent accuracy. The other part of the differences comes from different values of  $G$  obtained by different methods. It is probable that improvement of experimental techniques would lead to a far better agreement.

For most other liquids, however, neither  $\delta^2$  nor  $G$  are known with much reliability. Light scattering measurements may provide, however, much information about the apparent optical anisotropy  $\Delta^2$  and the product  $\delta^2 G$ . Especially useful is the quantity  $\delta^2 G$ , since, if we suppose that  $\delta^2$  is a molecular constant, it is possible to get information on changes in  $G$ , and thus gain more insight into the orientation correlation and structure in liquids. A compilation of data from various sources<sup>9, 14, 41, 59</sup> for a series of liquids is presented in *Table 6* together with  $\delta^2 G$  values evaluated from polarization ratios and anisotropic Rayleigh ratios by expressions:

$$\delta^2 G = kT\kappa_T N \frac{5D_u(90)}{6 - 7D_u(90)} \quad (59)$$

and

$$\delta^2 G = \frac{10\lambda_0^4 N R_{anis}(90)}{13\pi^2 (N\partial\epsilon/\partial N)_T^2} \quad (60)$$

where  $R_{anis}$  is calculated either from equations 27 and 31, or directly from:

$$R_{\text{anis}}(90) = R_u(90) \frac{13D_u(90)}{6 + 6D_u(90)} \quad (61)$$

One can see that good agreement is obtained for highly anisotropic liquids with  $D_u > 0.4$  where  $\delta^2 G$  values vary less than 5 per cent. For liquid with low anisotropy the variations are appreciable which is mainly caused by rather low precision of  $D_u$  data.

With known  $\delta^2$  one could determine  $G$ . However, literature data on  $\delta^2$  are rather incomplete, and if found, mostly without known wavelength dependence. So the determination of  $G$  can be performed at present only semi-quantitatively. An attempt is shown in Table 7. Here  $\delta^2$  values are taken from various sources. The data of Stuart<sup>58</sup> are based on measurements with vapours with white sunlight, those of Massoulier<sup>77, 78</sup> were measured with white light of a mercury lamp but corrected to 546 m $\mu$ , and the data of Clément and Bothorel<sup>79</sup> were measured at 546 m $\mu$  in cyclohexane solution.  $G$  was calculated from  $\delta^2 G$  data obtained by equation 59. If we consider Stuart's data to be a little too high for strongly anisotropic liquids because the wavelength correction was not applied and since it seems to be well established now that ancient data are as a rule too high, mostly owing to stray light, we can expect  $G$  values to be in reality somewhat higher. Here

Table 5. Rayleigh ratios<sup>a</sup>, polarization ratios and apparent optical anisotropy of benzene at  $\theta = 90^\circ$  and 25°C

	calculated		experimental		
	$G = 0.53$	$G = 0.58$ $\lambda_0 = 546 \text{ m}\mu$	semioctagonal cell	cylindrical cell s%	
$R_u$	15.5	16.4	16.1	16.2	1.5
$V_u$	22.1	23.0	23.2	22.5	1.4
$H_u$	8.9	9.8	9.7	9.5	2.6
$V_v$	17.6	18.1	18.3	18.4	2.7
$V_h$	4.5	4.8	4.8	5.1	2.2
$H_v$	4.5	4.8	4.5	4.8	4.4
$H_h$	4.5	4.8	4.8	4.7	1.9
$D_u$	0.40	0.42	0.42	0.40	2.0
$D_v$	0.25	0.27	0.25	0.26	3.8
$D_h$	1.00	1.00	1.00	1.08	2.5
$\Delta^2$	0.64	0.70	0.69	0.63	
		$\lambda_0 = 436 \text{ m}\mu$			
$R_u$	43.5	46.1	46.5	46.5	0.3
$V_u$	61.5	64.2	68.6	65.5	2.4
$H_u$	25.6	27.9	30.0	26.0	2.6
$V_v$	48.7	50.1	53.5	50.8	1.1
$V_h$	12.8	14.0	14.0	14.6	1.4
$H_v$	12.8	14.0	14.0	14.0	1.4
$H_h$	12.8	14.0	13.8	13.6	1.3
$D_u$	0.42	0.44	0.44	0.42	1.9
$D_v$	0.26	0.28	0.26	0.29	2.1
$D_h$	1.00	1.00	1.02	1.04	1.6
$\Delta^2$	0.67	0.74	0.75	0.69	

<sup>a</sup> All Rayleigh ratios are in  $\text{cm}^{-1}$  and have to be multiplied by  $10^{-6}$ .  
s — % standard deviation of angular measurements.

Table 6. Comparison of  $\delta^2 G$  evaluated from experimental data on  $D_s(90)$  and  $R_{\text{anis}}(90)$  for  $\lambda_0 = 546 \text{ m}\mu$  at room temperature.

	$R_s(90) \times 10^6 \text{ (cm}^{-1}\text{)}$ <i>experimental</i>	$D_s(90)$	$R_{\text{is}}(90) \times 10^6 \text{ (cm}^{-1}\text{)}$ <i>equation 31</i>	$R_{\text{anis}}(90) \times 10^6 \text{ (cm}^{-1}\text{)}$ <i>equation 27</i>	<i>equation 59</i>	$\delta^2 G \cdot 10^2$ <i>equation 60</i>	<i>equation 61</i>
benzene	16.2	0.40	6.00	10.2	1.68	1.75	1.72
toluene	17.6	0.48	5.21	12.4	1.94	1.95	1.95
nitrobenzene	65.8	0.74	5.10	60.7	5.34	5.40	5.39
carbon disulphide	84.6	0.656	12.2	72.4	9.15	8.92	8.96
carbon tetrachloride	5.53	0.049	5.11	0.42	0.12	0.087	0.12
cyclohexane	4.56	0.049	4.21	0.35	0.11	0.081	0.11
iso-octane	5.15	0.047	4.55	0.60	0.093	0.115	0.096
<i>n</i> -hexane	5.32	0.073	4.47	0.85	0.21	0.23	0.21
<i>n</i> -octane	4.85	0.12	3.94	0.91	0.22	0.17	0.21
<i>n</i> -decane	4.95	0.15	3.79	1.16	0.20	0.16	0.19
<i>n</i> -hexadecane	5.75	0.26	3.42	2.33	0.18	0.15	0.16
methyl-ethyl ketone	4.12	0.147	3.14	0.98	0.44	0.36	0.42
methanol	2.42	0.051	2.07	0.35	0.34	0.50	0.36
water	0.865	0.076	0.796	0.069	0.43	0.21	0.40

Table 7. Values of the orientational correlation factor  $G$  for various liquids

	Stuart <sup>a</sup>	$\delta^2 \times 10^2$		Clément-Bothorel	$\delta^2 G \times 10^2$	Stuart	$G$	
		Massoulier	Clément-Bothorel				Massoulier	Clément-Bothorel
benzene	3.6	3.1	3.7	1.68	0.47	0.54	0.45	
toluene	4.0	—	—	1.94	0.48	—	—	
nitrobenzene	5.1 <sup>b</sup>	—	—	5.34	1.05	—	—	
carbon	—	—	—	—	—	—	—	
disulphide	13.4	12.9	—	9.15	0.68	0.71	—	
carbon	—	—	—	—	—	—	—	
tetrachloride	0	—	—	0.12	—	—	—	
cyclohexane	0.4	—	—	0.11	0.28	—	—	
iso-octane	0.8	—	—	0.093	0.12	—	—	
<i>n</i> -hexane	1.3	0.59	0.27	0.21	0.16	0.36	0.78	
<i>n</i> -octane	1.2	0.84	0.24	0.22	0.18	0.26	0.92	
<i>n</i> -decane	1.1	1.12	0.22	0.20	0.18	0.18	0.91	
<i>n</i> -hexadecane	—	—	0.18	0.18	—	—	1.00	
methyl-ethyl	—	—	—	—	—	—	—	
ketone	2.6	—	—	0.44	0.17	—	—	

<sup>a</sup> The original data given as  $2\delta^2$ .<sup>b</sup> Calculated from the axes of the polarizability ellipsoid.

Massoulier's data for benzene and carbon disulphide seem to be the most reliable at the moment. A puzzling effect can be observed with normal alkanes. Here Clément and Bothorel's data seem to be the best since they are nearest to the  $G$  values ( $G > 1$ ) which could be expected for those chain-like molecules<sup>76</sup>. Massoulier's data indicate augmented  $D_{\parallel}$  values in  $n$ -alkane vapours which cannot be explained without assuming a strong interaction between molecules. It is interesting to note that  $D_{\parallel}$  data preceding Massoulier's data<sup>80,81</sup> are even higher.

An interesting method of determining  $G$  has recently been proposed by Lalanne<sup>82</sup>. He has applied Kielich's method<sup>83</sup> which corrects for differences in the internal field of both the pure liquid and dilute liquid solution and has arrived at some preliminary results which are in accordance with the data for carbon disulphide presented in *Table 7*, but differ much in cases of benzene and  $n$ -decane. It seems that Lalanne's results are afflicted with the same difficulties as the data in *Table 7*, i.e. they are based on imprecise physical constants.

Although the absolute  $G$ -values cannot at present be determined with enough accuracy, much valuable information about molecular interactions and structuring in liquids can be obtained by measuring the temperature dependence of  $\delta^2 G$ . Recently, Schmidt<sup>84</sup> has reported on measurements performed for a series of liquids, and could show, in accordance with previous data<sup>11</sup>, that  $\delta^2 G$ , and consequently  $G$ , rises with temperature in case of benzene and other aromatics. This may indicate a gradual disordering with increasing temperature for liquid aromatics, since it can be supposed with much certainty that for these liquids  $G < 1$ , indicating a prevalence of perpendicular orientations between benzene molecules. For  $n$ -alkanes, however,  $G$  is decreasing with increasing temperature, and that could again be explained with gradual disordering of prevalently parallel intermolecular orientations if we suppose that in the beginning  $G > 1$ .

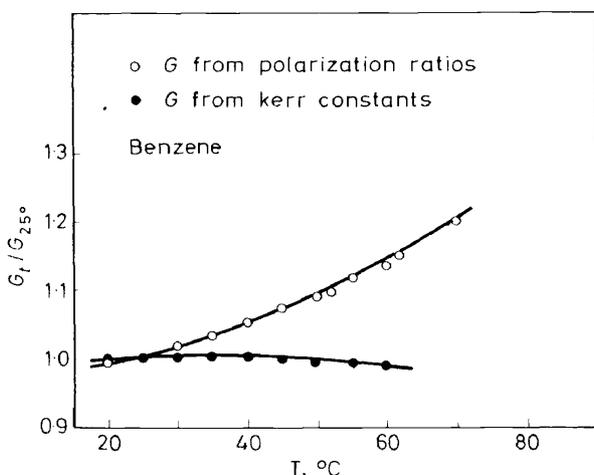


Figure 5. Dependence of  $G$  on temperature for benzene.  $G$  derived from polarization ratios and from Kerr constants.

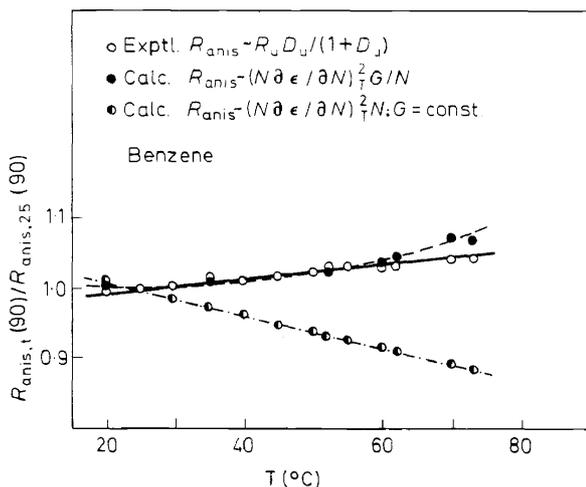


Figure 6. Variation of experimental and calculated anisotropic Rayleigh ratios of benzene at 546 mμ with temperature.

This situation can be observed for benzene in Figures 5 and 6. Here again the experimental values are based on the data of Ehl *et al.*<sup>75</sup>. It is interesting to note the divergence in  $G$  values calculated from polarization ratios, equation 59, and from Kerr constants. The molecular theory of liquids leads to the following expression for the Kerr constant<sup>5</sup> corrected for density dependence of polarizability<sup>11</sup>:

$$K = \frac{(n^2 - 1)(n^2 + 2)(\epsilon - 1)(\epsilon + 2)\delta^2 G}{120\pi n^2 k T N(1 + bN/a)(1 + b_s N/a_s)} \quad (62)$$

where index  $s$  stands for parameters measured in static fields. The curve derived from the Kerr constants measured by LeFèvre and LeFèvre<sup>85</sup> looks unrealistic in view of the above discussion on the temperature dependence of molecular orientations. This may be proved by calculating the temperature dependence of anisotropic scattering. Figure 6 shows that good agreement of theoretical data calculated by equation 60 with experimental values can be obtained only if a temperature variation of  $G$  is assumed.

Finally, a few words on the scattering from multicomponent systems. A series of papers was devoted to this problem (e.g. <sup>17, 18, 22, 63, 86, 87, 97</sup>) and the most important result of these investigations is the possibility of determining activity coefficients and the excess free energy of mixtures. Experimental data based on 'high' values of Rayleigh ratios are in very good agreement with theoretical relations and the data from other experimental techniques (like vapour pressure<sup>17, 22</sup> and electrolyte activity coefficients<sup>87</sup>). The only point which is not fully elucidated is the validity of the Bullough extra term  $C$  in equation 34. While Sicotte<sup>18, 88</sup> considers that this term explains correctly his experimental data, Pethica and Smart<sup>87</sup> claim that it is incorrect to include  $C$  in addition to equation 32. The final word has to be left to future experimental work.

The experimental achievements in the important field of spectral distribution of scattered light will also be only touched here. These light scattering techniques started to expand rapidly after the invention of lasers. After the first report of several groups<sup>89-91</sup> some authors tried to perform more quantitative checking of existing theories.

One of the important points of the theory of nonelastic scattering is the ratio of intensities of the central component,  $I_C$ , to the sum of intensities of Brillouin lines,  $I_B$ , the so-called Landau-Placzek ratio. Landau and Placzek<sup>26</sup> predicted the expression:

$$I_C/2I_B = (\kappa_T - \kappa_S)/\kappa_S \quad (63)$$

which followed from the approximated equation 38. It was found<sup>8,92</sup> that equation (63) should be corrected for dispersion of the quantities  $\kappa_S$  and  $(N\partial\epsilon/\partial N)_S$ , as derived by Fabelinskii<sup>4</sup>. It was also found that both the Rayleigh and Brillouin lines are fully polarized<sup>93</sup> which is proof that they belong to the isotropic part of light scattering.

The measurements of the spectral distribution of scattered light render information on the sound velocity (so-called hypersonic velocity) in liquids and on relaxation times of vibrational degrees of freedom in liquids<sup>94,95</sup>. Laser measurements of the anisotropic part of spectrally displaced scattered light are rather scarce. Shapiro and Broida<sup>96</sup> measured the wings of Rayleigh scattering in carbon disulphide and arrived at results in agreement with theoretical predictions. For  $I_H/I_V$  they found the predicted value  $\frac{3}{4}$ . The measurement of the orientational relaxation in liquids can be interpreted as a diffusion process depending both on the temperature and the structure of molecules<sup>29</sup>.

It may be concluded that the measurements of spectral distribution of scattered light are capable of giving much new and additional information to the theory of liquids. They will certainly be an important technique in future for studying the structure of dense media as well as of polymer and colloidal solutions.

In view of all the facts presented here we can see that very good agreement exists between theory and experiments for the isotropic part of light scattering. However, in treating the anisotropic part some difficulties still remain. It is difficult at present to give much credit to the values of  $G$  calculated from the data available in the literature. One reason is certainly the incompleteness of physical constants which makes it almost impossible to calculate theoretical light scattering quantities, except for a few liquids. Another reason is the inadequacy of present theories of anisotropic scattering. So, for example, it is not possible to give an explicit expression like equation 22 for calculating the anisotropic scattering factor of spherically symmetric molecules (such as carbon tetrachloride) with  $\delta^2 = 0$ . It is not advisable to make far reaching conclusions about the liquid structure and the intermolecular correlations from present  $G$  data since it might be possible that the experimentally determined  $G$  data do not only consist of the functions of the form of equation 19, but might include some terms arising from the nonlinear effects due to remarkable internal fields. It would certainly be possible to improve this situation by collecting more data on more liquids. Complete sets of physical constants measured at the same temperatures and wavelengths, and carried

out with increased precision, would allow additional improvements in the theories of light scattering in dense media.

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