

## Role of Molecular Interaction in Anisotropic Light Scattering by Liquids

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The influence of molecular linear and nonlinear polarizability, anisotropy, shape, radial and angular correlations, and other microscopic factors on anisotropic light scattering is discussed for some models of a liquid within the framework of statistical-molecular theory. An effective optical anisotropy  $\Delta^2$  is introduced and computed numerically for several liquids from the experimental depolarization ratio  $D_u$  and optical birefringence constant  $B_\lambda$ ; for strongly anisotropic substances, this yields  $\Delta^2$  values almost twice smaller than those determined from the anisotropic Rayleigh ratio  $R_{\text{anis}}$ . Theoretical, numerical computations of  $\Delta^2$  basing on the ellipsoidal Lorentz and Onsager-Scholte models result in values close to those from  $D_u$  and  $B_\lambda$ . Finally, the isotropic and anisotropic parts of the refractive index variation due to intense laser light are related, respectively, with the isotropic and anisotropic Rayleigh ratios, by means of which numerical computations are made for various liquids.

### INTRODUCTION

THE fundamentals of the thermodynamical-statistical theory of Rayleigh light scattering due to density fluctuations in optically isotropic regions of linear dimensions small as compared with the light wavelength were established by Smoluchowski<sup>1</sup> and Einstein.<sup>2</sup> Fixman<sup>3</sup> and others<sup>4-7</sup> developed the fluctuational theory in a microscopic approach, assuming however a scattering medium consisting of small, optically isotropic molecules. In a first approximation, this isotropic scattering is linked directly with the two-molecule radial function  $g(r)$ , whereas in higher approximations, with multimolecular radial functions.<sup>8,9</sup> Thus the study of isotropic light scattering can provide information on these radial functions, in the same way as  $g(r)$  is determined from x-ray scattering.<sup>10</sup>

In reality, most substances consist of nonspherical, optically anisotropic molecules, which in the gaseous state<sup>11,12</sup> cause depolarization of light scattered on fluctuations of their polarizability anisotropy. In liquids, such anisotropic scattering is related with angular molecular interactions given by a more general radial-orientational distribution function  $g(r, \omega)$ , and

has been discussed by Anselm<sup>13</sup> and other authors.<sup>14-19</sup>

The angular correlation parameter  $J_A$ , which corrects the "gaseous" anisotropic scattering, occurs also in certain related effects of molecular orientation and thus can be evaluated numerically.<sup>13,16,20</sup> The theoretical calculation of  $J_A$  demands the assumption of a molecular model in the case of liquids, and poses great difficulties. It can be performed for real gases by the virial coefficient method<sup>14,21</sup>—a possible source of valuable information on the nature and size of intermolecular forces as yet insufficiently recurred to for a lack of experimental results. Light scattering, both isotropic and anisotropic, is affected by yet other microscopic factors, e.g., nonlinear polarization of the atoms or molecules,<sup>16,21,22</sup> as well as fluctuations of the molecular field<sup>8,17,23</sup> and of its anisotropy,<sup>17,24</sup> and is related to the  $n$ -particle molecular distribution functions.<sup>8,9,25</sup>

Our aim here is to generalize and develop the previous molecular theory of light scattering by liquids,<sup>17</sup> with particular stress on the role of various microscopic factors (angular molecular correlations,

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<sup>15</sup> J. A. Prins and W. Prins, Physica **22**, 576 (1956); **23**, 253 (1957).

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<sup>19</sup> M. I. Shakhparonov, Dokl. Akad. Nauk **136**, 1162 (1961); Ukr. Fiz. Zh. **7**, 782 (1962).

<sup>20</sup> G. J. Deželić, J. Chem. Phys. **45**, 185 (1966).

<sup>21</sup> S. Kielich, Acta Phys. Polon. **19**, 711 (1960); Poznan. Towarz. Przyjaciół Nauk, Wydział Mat. Przyrod. Prace Komisji Mat. Przyrod. **11**, 51 (1964).

<sup>22</sup> A. D. Buckingham and M. J. Stephen, Trans. Faraday Soc. **53**, 884 (1957).

<sup>23</sup> Y. Rocard, Ann. Phys. (Paris) **10**, 159 (1928); G. Weill, *ibid.* **6**, 1063 (1961).

<sup>24</sup> S. Kielich, Acta Phys. Polon. **19**, 573 (1960); **20**, 83 (1961).

<sup>25</sup> S. Kielich, Bull. Soc. Amis Sci. Lettres Poznan, Ser. B **17**, 43 (1962-1963); Acta Phys. Polon. **23**, 819 (1963); **25**, 85 (1964).

<sup>1</sup> M. Smoluchowski, Ann. Physik **25**, 205 (1908).

<sup>2</sup> A. Einstein, Ann. Physik **33**, 1275 (1910).

<sup>3</sup> M. Fixman, J. Chem. Phys. **23**, 2074 (1955).

<sup>4</sup> J. Yvon, Actualités Sci. et Ind. No. 543 (1937) (quoted from Ref. 3).

<sup>5</sup> B. H. Zimm, J. Chem. Phys. **13**, 144 (1945).

<sup>6</sup> P. Mazur, Advan. Chem. Phys. **1**, 309 (1958).

<sup>7</sup> R. K. Bullough, Phil. Trans. Roy. Soc. (London) **A258**, 387 (1965).

<sup>8</sup> O. Theimer and R. Paul, J. Chem. Phys. **42**, 2508 (1965).

<sup>9</sup> H. L. Frisch and J. McKenna, Phys. Rev. **139**, 168 (1965).

<sup>10</sup> F. Zernike and J. A. Prins, Z. Physik **41**, 184 (1927).

<sup>11</sup> J. Cabannes, *La diffusion moléculaire de la lumière* (Les Presses Universitaires de France, Paris, 1929); M. Born, *Optik* (Julius Springer-Verlag, Berlin, 1933).

<sup>12</sup> M. V. Volkensteyn, *Molekularnaya Optika (Molecular Optics)* (Gostekhizdat, Moskva, 1951); I. L. Fabelinskiy, *Molekularnoye Rassieyeniye Svyeta (Molecular Light Scattering)* (Glavnaya Redaktsiya Fiziko-Matematicheskoy Literatury, Moskva, 1965).

nonlinear polarizability, etc.) in scattering by dense media. We recur to the notion of an "effective optical anisotropy," to be discussed for several molecular models and calculated numerically for several liquids from results on light scattering and optically induced birefringence.

### GENERAL APPROACH TO THE THEORY

We consider an isotropic medium of volume  $V$  with a large number  $N$  of identical, in general optically anisotropic, molecules. The origin of laboratory coordinates  $\{X_\sigma\}$ ,  $\sigma = x, y, z$  is at the center of  $V$ ; the  $p$ th molecule distant therefrom by  $\mathbf{r}_p$  has attached to it a molecular coordinate system  $\{X_\alpha^{(p)}\}$ ,  $\alpha = 1, 2, 3$ ,  $p = 1, 2, \dots, N$ . A light wave with electric vector  $\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$ ,  $\omega = 2\pi c/\lambda$ , is arbitrarily incident on the medium. The linear dimensions of  $V$  are assumed small with respect to  $\lambda$ , permitting to consider only dipole scattering due to oscillation at frequency  $\omega$  of a dipole

of moment  $\mathbf{m}^{(p)}(t)$  induced in the  $p$ th molecule by  $\mathbf{E}(t)$ . In the wave zone, the electric field of the wave scattered by the  $p$ th molecule is now given by<sup>11,17</sup>

$$\mathbf{E}_s^{(p)} = [\exp(ik_s R_0)/\omega^2 R_0] \times (\mathbf{k}_s \times \{\mathbf{k}_s \times (d^2 \mathbf{m}/d\ell^2)^{(p)}(t) \exp[-i(\mathbf{k}_s - \mathbf{k}) \cdot \mathbf{r}_p]\}) \quad (1)$$

$\mathbf{R}_0$  is the radius vector from the center of  $V$  to the observation point;  $\mathbf{k}$  and  $\mathbf{k}_s$  are propagation vectors of the incident and scattered wave, respectively.

The light intensity scattered in unit volume is by definition

$$I_n^s = V^{-1} \langle \sum_{p=1}^N \mathbf{E}_s^{(p)} \cdot \mathbf{n} \rangle^2 \quad (2)$$

( $\mathbf{n}$  being the unit vector perpendicular to  $\mathbf{k}_s$ ) or, with regard to (1)

$$I_n^s = V^{-1} \left( \frac{k_s^2}{\omega^2 R_0} \right)^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \left( \frac{d^2 m_\sigma}{d\ell^2} \right)^{(p)} \left( \frac{d^2 m_\tau}{d\ell^2} \right)^{(q)*} n_\sigma n_\tau \exp[i(\mathbf{k}_s - \mathbf{k}) \cdot \mathbf{r}_{pq}] \right\rangle \quad (3)$$

(the angle brackets  $\langle \rangle$  stand for appropriate statistical averaging; and  $\mathbf{r}_{pq} = \mathbf{r}_q - \mathbf{r}_p$ ). It is convenient to use the tensor of scattered light intensity  $I_{\sigma\tau}^s$  defined thus:

$$I_{\sigma\tau}^s = V^{-1} \left( \frac{k_s}{\omega} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N \left( \frac{d^2 m_\sigma}{d\ell^2} \right)^{(p)} \left( \frac{d^2 m_\tau}{d\ell^2} \right)^{(q)*} \right\rangle, \quad (4)$$

where we have replaced the interference factor  $\exp[i(\mathbf{k}_s - \mathbf{k}) \cdot \mathbf{r}_{pq}]$  by 1, since only intermolecular distances  $r_{pq}$  much smaller than  $\lambda$  are considered.

The dipole moment  $\mathbf{m}^{(p)}$  is a function of the field  $\mathbf{E}$  as given by the expansion

$$m_\sigma^{(p)} = (\partial m_\sigma^{(p)}/\partial E_\tau)_0 E_\tau + \frac{1}{2} (\partial^2 m_\sigma^{(p)}/\partial E_\tau \partial E_\nu)_0 E_\tau E_\nu + \dots \quad (5)$$

The first term yields linear scattering, whereas the second and higher ones, nonlinear light scattering,<sup>25</sup> which is beyond our present scope.

With the linear term, the scattering tensor (4) becomes

$$I_{\sigma\tau}^s = \frac{k_s^4}{V} \left\langle \sum_{p=1}^N \sum_{q=1}^N \frac{\partial m_\sigma^{(p)}}{\partial E_\nu} \frac{\partial m_\tau^{(q)*}}{\partial E_\rho} \right\rangle I_{\nu\rho}, \quad (6)$$

$I_{\sigma\tau} = E_\sigma E_\tau^*$  being the intensity tensor of incident light.

In the case of the isotropic medium, it is useful first to perform averaging in (4) over all possible orientations with regard to the laboratory axes.  $I_{\sigma\tau}^s$  now resolves into an isotropic and anisotropic part:

$$I_{\sigma\tau}^{\text{is}} = k_s^4 F_{\text{is}} I_{\sigma\tau}, \quad (7)$$

$$I_{\sigma\tau}^{\text{anis}} = \frac{1}{5} k_s^4 F_{\text{anis}} (3I\delta_{\sigma\tau} + I_{\sigma\tau}). \quad (8)$$

The factors  $F_{\text{is}}$ ,  $F_{\text{anis}}$  characterize the molecular mechanism of isotropic and anisotropic light scattering, and are given as follows (in a previous paper,<sup>17</sup> they appear without the factor  $\frac{1}{5}V$ ):

$$F_{\text{is}} = (9V)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial m_\beta^{(q)}}{\partial E_\beta} \right\rangle, \quad (9)$$

$$F_{\text{anis}} = (18V)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N \left( 3 \frac{\partial m_\alpha^{(p)}}{\partial E_\beta} \frac{\partial m_\alpha^{(q)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial m_\beta^{(q)}}{\partial E_\beta} \right) \right\rangle, \quad (10)$$

where the differential polarizability tensor  $\partial m_\alpha / \partial E_\beta$  is assumed as symmetrical and real (it is so for optically inactive molecules at frequencies remote from absorption).  $F_{is}$  and  $F_{anis}$  are discussed in detail in the next section.

Let the incident wave propagate in the  $Y$  direction and observation be in the  $XY$  plane at an angle  $\vartheta$  to  $Y$ . Since

$$I_{\sigma\tau}^s = I_{\sigma\tau}^{is} + I_{\sigma\tau}^{anis} \quad (11)$$

is the tensor of total scattered light intensity, we have by (7) and (8) the components<sup>25,26</sup>

$$I_{xx}^{zz} \equiv H_h = k_s^4 I [F_{is} \cos^2 \vartheta + \frac{1}{3} F_{anis} (3 + \cos^2 \vartheta)], \quad (12)$$

$$I_{zz}^{xx} \equiv V_h = I_{xx}^{zz} \equiv H_v = \frac{2}{3} k_s^4 I F_{anis}, \quad (13)$$

$$I_{zz}^{zz} \equiv V_v = k_s^4 I (F_{is} + \frac{4}{3} F_{anis}). \quad (14)$$

One thus sees that the reciprocity principle (13) of Krishnan as well as  $H_v = V_v = H_h \neq V_h$  for  $\vartheta = 90^\circ$ , is fulfilled for an arbitrarily dense medium of small anisotropic molecules.

By (12)–(14), for nonpolarized incident light, the Rayleigh ratio is<sup>17</sup>

$$R(\vartheta) = \frac{1}{10} k_s^4 \left[ \frac{1}{3} (n^2 + 2) \right]^2 \times [5(1 + \cos^2 \vartheta) F_{is} + (13 + \cos^2 \vartheta) F_{anis}], \quad (15)$$

and the depolarization ratio

$$D(\vartheta) = \frac{5F_{is} \cos^2 \vartheta + (6 + \cos^2 \vartheta) F_{anis}}{5F_{is} + 7F_{anis}}. \quad (16)$$

In defining the Rayleigh ratio (15) we have recurred to the relation<sup>17</sup>  $I^M = [3/(n^2 + 2)]^2 I$  between the intensities  $I$  in absence of the medium and  $I^M$  within a sphere of refractive index  $n$  immersed in vacuum.

Similarly, expressions for  $R$  and  $D$  are obtained at

other conditions of observation, as well as relationships between  $R$  and  $D$  and the components (12)–(14).<sup>17,26</sup>

### EFFECTIVE OPTICAL ANISOTROPY

As a first assumption, let the molecules polarize linearly and, when interacting, retain their polarizability. We have thus the linear equation

$$m_\alpha^{(p)} = a_{\alpha\beta}^{(p)} E_\beta, \quad (17)$$

where  $a_{\alpha\beta}^{(p)}$  is the optical (dipolar and linear) polarizability tensor of the  $p$ th molecule in the absence of interactions between the molecules.

By (17), the isotropic scattering factor (9) is

$$F_{is} = V^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p a_q \right\rangle \quad (18)$$

and can reduce to the well-known form

$$F_{is} = \rho a^2 (1 + G_R) = \rho^2 a^2 k T \kappa_T. \quad (19)$$

Above,  $\rho = N/V$  is the number density of molecules,  $a = \frac{1}{3} a_{\alpha\alpha}$  the mean optical polarizability of a molecule,  $\kappa_T$  the isothermal compressibility coefficient,

$$G_R = \frac{\rho}{V} \iint [g^{(2)}(\tau_p, \tau_q) - g^{(1)}(\tau_p) g^{(1)}(\tau_q)] d\tau_p d\tau_q, \quad (20)$$

a radial correlation parameter involving the one- and two-molecule correlation functions  $g^{(1)}(\tau_p)$  and  $g^{(2)}(\tau_p, \tau_q)$ , and  $\tau_p, \tau_q$  variables determining the position and orientation of molecules  $p$  and  $q$ .

In this paper we assume the approximation (19) as sufficient for our aims, but give more detailed consideration to the molecular factor of anisotropic scattering (10), which we write in the form

$$F_{anis} = \rho a^2 \Delta^2. \quad (21)$$

Here, we have introduced the dimensionless quantity

$$\Delta^2 = (18a^2 N)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N \left( 3 \frac{\partial m_\alpha^{(p)}}{\partial E_\beta} \frac{\partial m_\alpha^{(q)}}{\partial E_\beta} - \frac{\partial m_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial m_\beta^{(q)}}{\partial E_\beta} \right) \right\rangle \quad (22)$$

characterizing an effective optical anisotropy. We now discuss it for some special cases.

#### A. Anisotropic, Linearly Polarizable Molecules

In the approximation of Eq. (17) the anisotropy (22) becomes

$$\Delta^2 = (18a^2 N)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N a_{\alpha\beta} a_{\gamma\delta} (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle, \quad (23)$$

$\omega_{\alpha\gamma}^{(pq)}$  denoting the cosine of the angle between the axes  $\alpha$  and  $\gamma$  of the reference systems attached to Molecules  $p$  and  $q$ .

By classical statistical methods, (23) goes over into

$$\Delta^2 = \kappa_a^2 (1 + J_A), \quad (24)$$

with

$$\kappa_a^2 = (3a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta}) / 18a^2, \quad (25)$$

<sup>26</sup> Gj. Deželić and J. Vavra, Croat. Chem. Acta **38**, 35 (1966).

the optical anisotropy of the isolated molecule, and

$$J_A = \frac{a_{\alpha\beta}a_{\gamma\delta}\rho}{18a^2\kappa_a^2V} \iint (3\omega_{\alpha\gamma}^{(pq)}\omega_{\beta\delta}^{(pq)} - \delta_{\alpha\beta}\delta_{\gamma\delta}) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (26)$$

the angular correlations parameter.

For molecules axially symmetric about, e.g., the 3 axis, Eqs. (25) and (26) reduce to

$$\kappa_a^2 = [(a_{33} - a_{11})/3a]^2, \quad (27)$$

$$J_A = \frac{\rho}{2V} \iint (3 \cos^2\theta_{pq} - 1) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (28)$$

where  $\theta_{pq}$  denotes the angle between the symmetry axes of Molecules  $p$  and  $q$ .

The angular correlations parameter in the form (28) has been derived by various authors.<sup>13,14,16-22</sup> In the absence of angular correlations  $J_A = 0$  and, by (24),  $\Delta^2 = \kappa_a^2$  is expressed directly by the optical anisotropy of the isolated molecule in the form (25) or (27). In liquids, where we deal with angular correlations,  $J_A$  corrects the "gaseous" anisotropy in accordance with (24).

Calculations of the parameter (28) for specific liquids are highly involved, but can be performed if the bimolecular correlation function  $g^{(2)}(\tau_p, \tau_q)$  dependent on the  $r_{pq}$ 's and the orientational variables  $\omega_p, \omega_q$  can be represented as

$$g^{(2)}(\tau_p, \tau_q) = \Omega^{-2} g(r_{pq}) \exp(-V_{pq}/kT). \quad (29)$$

Our approximation consists in taking explicitly the part related only with the energy of noncentral bimolecular interaction  $V_{pq} = V(r_{pq}, \omega_p, \omega_q)$  (with  $\Omega = \int d\omega_p = \int d\omega_q$ ). If moreover these (e.g., dipolar, quadrupolar, dispersive, etc.) interactions are not too large to be dealt with as perturbations to the radial (central) interactions, Eq. (29) becomes

$$g^{(2)}(\tau_p, \tau_q) = \Omega^{-2} g(r_{pq}) \left( 1 - \frac{V_{pq}}{kT} + \frac{V_{pq}^2}{2k^2T^2} - \frac{V_{pq}^3}{6k^3T^3} + \frac{V_{pq}^4}{24k^4T^4} - \dots \right) \quad (29')$$

with an accuracy sufficient for various cases. This zeroth approximation (for zero noncentral interactions) obviously leads to vanishing of the parameter (28), which is thus nonzero only if angular interactions exist.

### B. Noncentral Contributions to $J_A$

We proceed to calculate the contributions to  $J_A$  from various noncentral interactions.

(i) Let us begin by non-polar axially symmetric molecules interacting with London's anisotropic dispersive forces yielding the non-central energy<sup>27,28</sup>:

$$V_{pq}^{\text{disp}} = \frac{3}{8} h\nu\alpha^2\kappa_a [2 - 3(1 - \kappa_a)(\cos^2\theta_p + \cos^2\theta_q) - 3\kappa_a(3 \cos\theta_p \cos\theta_q - \cos\theta_{pq})^2] r_{pq}^{-6}. \quad (30)$$

$h\nu$  is the molecule's characteristic energy and  $\kappa_a, \alpha$  its electric anisotropy and mean polarizability.

By (29') and (30), we have from (28) to within the second order of the perturbation

$$J_A^{\text{disp}} = (3\alpha^2\kappa_a^2/100) (h\nu/kT) [R_6 + \frac{3}{4}(h\nu/kT) (1 - \frac{4}{3}\kappa_a + \frac{3}{4}\frac{8}{9}\kappa_a^2) R_{12} + \dots] \quad (31)$$

on introducing the radial parameters

$$R_n = 4\pi\rho \int r_{pq}^{-n+2} g(r_{pq}) dr_{pq}. \quad (32)$$

(ii) For molecules with permanent dipole moments  $\mu$ , in addition to the dispersive energy (30) we take into consideration the energy of dipole-dipole interaction:

$$V_{pq}^{\mu-\mu} = -\mu^2(3 \cos\theta_p \cos\theta_q - \cos\theta_{pq}) r_{pq}^{-3} \quad (33)$$

<sup>27</sup> J. H. De Boer and G. Heller, *Physica* **4**, 1045 (1937); F. London, *J. Chem. Phys.* **46**, 305 (1942); J. De Boer, *Physica* **9**, 363 (1942).

<sup>28</sup> S. Kielich, *Acta Phys. Polon.* **22**, 65 (1962); **28**, 95 (1965).

and that of dipole-induced-dipole interaction<sup>28</sup>

$$V_{pq}^{\mu\text{-ind}\mu} = -\frac{1}{2}\alpha\mu^2[(1-\kappa_\alpha)(3\cos^2\theta_p + 3\cos^2\theta_q + 2) + 6\kappa_\alpha(3\cos\theta_p\cos\theta_q - \cos\theta_{pq})^2]r_{pq}^{-6}. \quad (34)$$

By (28) and (29'), we have the additional contributions

$$J_A^{\mu\text{-}\mu} = \frac{1}{75}(\mu^2/kT)^2[R_6 + \frac{1}{4}\frac{2}{9}(\mu^2/kT)^2R_{12} + \frac{1}{4}\frac{3}{1}(\mu^2/kT)^4R_{18} + \dots], \quad (35)$$

$$J_A^{\mu\text{-ind}\mu} = \frac{2\alpha}{25}\left(\frac{\mu^2}{kT}\right)\left\{\kappa_\alpha R_6 + \frac{4}{7}\left(\frac{\mu^2}{kT}\right)\left[\left(\frac{\mu^2}{kT}\right)(1 + \frac{1}{7}\kappa_\alpha) + \frac{5\alpha\kappa_\alpha}{32}\left(\frac{h\nu}{kT}\right)\left(1 + \frac{97}{70}\kappa_\alpha\right)\right]R_{12} + \dots\right\}. \quad (36)$$

(iii) Finally, for molecules possessing permanent quadrupole moments  $\Theta$ , we have the quadrupole-quadrupole interaction energy:

$$V_{pq}^{\Theta\text{-}\Theta} = \frac{3}{4}\Theta^2[1 - 5(\cos^2\theta_p + 3\cos^2\theta_p\cos^2\theta_q + \cos^2\theta_q) + 2(5\cos\theta_p\cos\theta_q - \cos\theta_{pq})^2]r_{pq}^{-5}, \quad (37)$$

and quadrupole-induced-dipole interaction energy<sup>28</sup>

$$V_{pq}^{\Theta\text{-ind}\mu} = -(9/8)\alpha\Theta^2\{(1-\kappa_\alpha)(2 - 2\cos^2\theta_p - 2\cos^2\theta_q + 5\cos^4\theta_p + 5\cos^4\theta_q) + 3\kappa_\alpha[(5\cos\theta_p\cos^2\theta_q - 2\cos\theta_{pq}\cos\theta_q - \cos\theta_p)^2 + (5\cos^2\theta_p\cos\theta_q - 2\cos\theta_{pq}\cos\theta_p - \cos\theta_q)^2]\}r_{pq}^{-8}, \quad (38)$$

and the respective contributions are

$$J_A^{\Theta\text{-}\Theta} = \frac{4}{35}(\Theta^2/kT)^2[R_{10} - O(\Theta^2)], \quad (39)$$

$$J_A^{\Theta\text{-ind}\mu} = (3\alpha/35)(\Theta^2/kT)[\kappa_\alpha R_8 - \frac{8}{3}\alpha\kappa_\alpha^2(h\nu/kT)R_{11} - 2(\Theta^2/kT)(1 + \frac{2}{7}\kappa_\alpha)R_{13} - \dots]. \quad (40)$$

Consequently, all noncentral contributions to  $J_A$  are related with the radial parameters (32). In order to calculate them, one has to know explicitly the radial correlation function  $g(r_{pq})$ . In the case of not excessively compressed gases, it can be written as

$$g(r_{pq}) = \exp\{-y^2[(\sigma/r_{pq})^s - (\sigma/r_{pq})^t]\}[1 + O(\rho)] \quad (41)$$

and Eq. (32) yields by the Lennard-Jones method<sup>29</sup>

$$R_n = (4\pi\rho/sy^4\sigma^{n-3})H_n^{s-t}(y). \quad (42)$$

The functions

$$H_n^{s-t}(y) = y^{2(2s+3-n)/s} \sum_{m=0}^{\infty} (m!)^{-1} y^{2m(s-t)/s} \Gamma\left(\frac{tm+n-3}{s}\right) \quad (43)$$

are those discussed for  $s=12$ ,  $t=6$  by Pople<sup>30</sup> and for  $s=18$ ,  $t=6$  as well as  $s=20$ ,  $t=7$  by Saxena and Joshi.<sup>31</sup>  $\epsilon$ ,  $\sigma$  are central-forces parameters having the dimensions of an energy and length;  $y^2 = 4\epsilon/kT$ .

Clearly, for the case of real gases, the correlation parameter (20) of isotropic scattering is given directly by the second virial coefficient  $B$  of the equation of state which has been considered in detail for noncentral-

type interactions.<sup>27-36</sup> Since most parameters such as  $\epsilon$ ,  $\sigma$ ,  $\alpha$ ,  $\kappa_\alpha$ ,  $\mu$ , and  $\Theta$  are known for various molecules, one can immediately proceed to numerical evaluations of the contributions (31)–(40), resulting in a rather essential role of noncentral interaction, particularly in the case of dipolar molecules.<sup>21</sup> Regretably, pertinent measurements on light scattering by compressed gases are as yet lacking, though recent years have brought some results on scattering in noble and other gases by laser techniques.<sup>37</sup>

In the case of liquids, it is not possible to give full numerical evaluations of  $J_A$  or to compare them with experiment; however, as shown recently by Deželić<sup>20</sup>

<sup>27</sup> W. H. Stockmayer, *J. Chem. Phys.* **9**, 398 (1941).

<sup>28</sup> J. S. Rowlinson, *Trans. Faraday Soc.* **45**, 974 (1949).

<sup>29</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York 1954).

<sup>30</sup> S. Kielich, *Acta Phys. Polon.* **20**, 433 (1961); *Physica* **28**, 511 (1962).

<sup>31</sup> R. H. Orcutt, *J. Chem. Phys.* **39**, 605 (1963); A. D. King, Jr., *ibid.* **42**, 2610 (1965).

<sup>32</sup> T. V. George, L. Goldstein, L. Slama, and M. Yokoyama, *Phys. Rev.* **137**, A369 (1965); N. J. Bridge and A. D. Buckingham, *J. Chem. Phys.* **40**, 2733 (1964).

<sup>29</sup> S. Kielich, *Physica* **31**, 444 (1965).

<sup>30</sup> J. A. Pople, *Proc. Roy. Soc. (London)* **A221**, 508 (1954); A. D. Buckingham and J. A. Pople, *Trans. Faraday Soc.* **51**, 1173 (1955).

<sup>31</sup> S. C. Saxena and K. M. Joshi, *Phys. Fluids* **5**, 1217 (1962).

for benzene and carbon disulphide, such a confrontation can be made basing on physical constants from various optical effects.<sup>13,16,26</sup>

### C. Atoms with Variable, Linear Polarizability

For isotropically polarizable molecules  $a_{\alpha\beta} = a\delta_{\alpha\beta}$  and the optical anisotropy in the approximation (23) vanishes. Thus atoms and isotropic molecules presenting a constant polarizability do not scatter light anisotropically. It can be shown, however, that if the influence of molecular interactions on the polarizability is taken into account, the anisotropy  $\Delta^2$  is nonzero *even* in the case of atoms, when one has the

relation

$$m_{\alpha}^{(p)} = a_p(E_{\alpha} + F_{\alpha}^{(p)}), \quad (44)$$

$F^{(p)}$  denoting the electric field due to all atoms surrounding Atom  $p$ , when the medium is acted on by the field  $\mathbf{E}$ . In the dipolar approximation<sup>3,17</sup>

$$F_{\alpha}^{(p)} = - \sum_{q=1, q \neq p}^N T_{\alpha\beta}^{(pq)} m_{\beta}^{(q)} \quad (45)$$

with the dipole-dipole interaction tensor

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha}r_{pq\beta} - r_{pq}^2\delta_{\alpha\beta}). \quad (46)$$

From Eqs. (44) and (45), we have to within  $a^2$

$$F_{\alpha}^{(p)} = - \sum_{q=1, q \neq p}^N a_q T_{\alpha\beta}^{(pq)} E_{\beta} + \sum_{q=1, q \neq p}^N \sum_{r=1, r \neq q}^N a_q a_r T_{\alpha\beta}^{(pq)} T_{\beta\gamma}^{(qr)} E_{\gamma} - \dots, \quad (47)$$

whence the anisotropy of (22) becomes

$$\Delta^2 = (18a^2N)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p a_q \left( 3 \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\beta}} \frac{\partial F_{\alpha}^{(q)}}{\partial E_{\beta}} - \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}} \right) \right\rangle \quad (48)$$

or, in a satisfactory approximation,

$$\Delta^2 = \frac{a^2}{6N} \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1, r \neq p}^N \sum_{s=1, s \neq q}^N T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle. \quad (49)$$

This result states that owing to fluctuations of the molecular fields,  $\Delta^2 \neq 0$  and anisotropy of scattering arises *also* in the case of atoms and isotropic molecules whose polarizability varies with interaction.

On restricting further discussions of the anisotropy (49) to pairwise correlations, i.e., neglecting triple and quadruple correlations we obtain simply

$$\Delta^2 = 2a^2 R_6, \quad (50)$$

where the radial correlations parameter  $R_6$  is given by (32) with  $n=6$ .

Thus condensed media, as a result of interaction between induced moments of atoms or isotropic molecules, exhibit anisotropy causing anisotropic scattering. In other words, in a dense medium, there exist pairwise (or higher) assemblages of atoms or molecules, coupled to a greater or lesser degree by radial forces defined by the parameter  $R_6$ . At a given moment, such assemblages will behave as optically anisotropic elements, on which light can undergo scattering anisotropically.

### D. Nonlinearly Polarizable Molecules

Dense media present molecular fields  $\mathbf{F}$  that are strong as compared with the field  $\mathbf{E}$  of a light wave and can induce nonlinear polarization in the atoms or molecules. Since they are present also in the absence of an external field, the following expansion holds for the differential polarizability tensor<sup>22,38</sup>:

$$\partial m_{\alpha}^{(p)} / \partial E_{\chi} = (a_{\alpha\beta}^{(p)} + b_{\alpha\beta\gamma}^{(p)} F_{0\gamma}^{(p)} + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{(p)} F_{0\gamma}^{(p)} F_{0\delta}^{(p)} + \frac{1}{3} q_{\alpha\beta\gamma\delta}^{(p)} F_{0\gamma\delta}^{(p)} + \dots) [\delta_{\beta\chi} + (\partial F_{\beta}^{(p)} / \partial E_{\chi})]_0. \quad (51)$$

$b_{\alpha\beta\gamma}$  and  $c_{\alpha\beta\gamma\delta}$  are tensors of the nonlinear dipolar polarizability induced by the molecular field  $F_{0\gamma}^{(p)}$  and its square  $F_{0\gamma}^{(p)} F_{0\delta}^{(p)}$  at  $\mathbf{E}=0$ , and  $q_{\alpha\beta\gamma\delta}$ , that of quadrupolar polarizability induced by the gradient of  $F_{0\gamma\delta}^{(p)}$  at  $\mathbf{E}=0$ .

In general, the molecular field  $\mathbf{F}^{(p)}$  acting on the  $p$ th molecule in the absence of an external field is<sup>28</sup>

$$F_{0\alpha}^{(p)} = - \sum_{q=1, q \neq p}^N (T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(q)} - \frac{1}{3} T_{\alpha\beta\gamma}^{(pq)} \Theta_{\beta\gamma}^{(q)} + \frac{1}{15} T_{\alpha\beta\gamma\delta}^{(pq)} \Omega_{\beta\gamma\delta}^{(q)} - \dots) - \dots. \quad (52)$$

<sup>38</sup> S. Kielich, Acta Phys. Polon. **22**, 299 (1962).

Here, terms with dipolar, quadrupolar, etc., polarizability have been neglected. The tensors  $\mu_\alpha$ ,  $\Theta_{\alpha\beta}$ ,  $\Omega_{\alpha\beta\gamma}$  of dipole, quadrupole, octupole, etc., moments as well as the interaction tensors  $T_{\alpha\beta\gamma}$ ,  $T_{\alpha\beta\gamma\delta}$  are to be found in explicit form in Refs. 28 and 35.

We now consider tetrahedral molecules (e.g.,  $\text{CCl}_4$ ) whose first nonzero moment is octupolar with components  $\Omega_{123}$ ; similarly, the tensor  $b_{\alpha\beta\gamma}$  has components  $b_{123}$ . Since here the linear polarizability is isotropic,  $a_{\alpha\beta} = a\delta_{\alpha\beta}$ , we have on inserting (51) into (22) and omitting higher-order terms

$$\Delta^2 = (6a^2N)^{-1} \left\langle \sum_{p=1}^N \sum_{q=1}^N b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\delta}^{(q)} F_{0\gamma}^{(p)} F_{0\delta}^{(q)} \right\rangle, \quad (53)$$

whence, simply, with regard to the third term of (52),

$$\Delta^2 = (32/7) (b_{123}/a)^2 \Omega_{123}^2 R_{10}. \quad (54)$$

Similarly, Eqs. (22), (51), and (52) can be applied to dipolar or quadrupolar molecules for calculating the respective nonlinear contributions to the anisotropy  $\Delta^2$ . However, the preceding examples show that this statistical-molecular method fails to yield expressions adapted to immediate evaluation.

### E. Anisotropy for the Lorentz and Onsager Models

Practically, a different method<sup>17,22,24</sup> replacing the molecular field (52) by the corresponding Onsager reaction field  $\mathbf{R}$ , and  $\mathbf{F}$  by the cavity field  $\mathbf{G}$ , is more convenient. On these assumptions and neglecting short-range molecular correlations, (22) becomes

$$\Delta^2 = \kappa_a^2 \frac{(a_1^* - a_2^*)^2 + (a_2^* - a_3^*)^2 + (a_3^* - a_1^*)^2}{(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2}, \quad (55)$$

where

$$\kappa_a^2 = \frac{(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2}{2(a_1 + a_2 + a_3)^2} \quad (56)$$

is the "gaseous" optical anisotropy of polarizability referred to principal axes 1, 2, 3;  $a_1^*$ ,  $a_2^*$ ,  $a_3^*$  are effective principal polarizabilities of the molecule immersed in the medium ( $s, t = 1, 2, 3$ )<sup>39</sup>:

$$a_s^* = \psi_s \{ a_s + [b_{s:t} f_{0t} \mu_t / (1 - f_{0t} \alpha_t)] + \dots \}. \quad (57)$$

In the general case of the Onsager-Scholte model, for an ellipsoidal cavity of semiaxes  $r_1, r_2, r_3$  situated in a medium of refractive index  $n$  and dielectric constant  $\epsilon$ , we have<sup>39,40</sup>

$$\psi_s = \frac{[3n^2/(n^2+2)]}{[n^2 + (1-n^2)A_s](1-f_s a_s)}, \quad (58)$$

<sup>39</sup> S. Kielich, Acta Phys. Polon. 30, 683 (1966); Proc. Phys. Soc. (London) 90, 847 (1967).

<sup>40</sup> D. A. A. S. R. Narayana, Trans. Faraday Soc. 54, 954 (1958).

where

$$f_s = \frac{3A_s(1-A_s)(n^2-1)}{r_1 r_2 r_3 [n^2 + (1-n^2)A_s]}$$

and

$$f_{0t} = \frac{3A_t(1-A_t)(\epsilon-1)}{r_1 r_2 r_3 [\epsilon + (1-\epsilon)A_t]} \quad (59)$$

are reaction-field parameters at  $E \neq 0$  and  $E = 0$ , whereas

$$A_t = \frac{1}{2} r_1 r_2 r_3$$

$$\times \int_0^\infty \frac{dS}{(r_t^2 + S)[(r_1^2 + S)(r_2^2 + S)(r_3^2 + S)]^{1/2}} \quad (60)$$

are shape factors.

Putting  $f_{0t} = 0$  in (57), and replacing  $a_s$  by

$$a_s = \frac{(n^2-1)r_1 r_2 r_3}{3[1 + (n^2-1)A_s]} \quad (61)$$

in (58), we get the ellipsoidal Lorentz model used by Raman and Krishnan<sup>41</sup> for defining the effective polarizability

$$a_s^* = [3/(n^2+2)][1 + (n^2-1)A_s]a_s. \quad (62)$$

For a spherical cavity  $A_s = \frac{1}{3}$ ,  $r_1 = r_2 = r_3 = r_0$ , and the effective polarizabilities (57) and (62) yield for the original Lorentz and Onsager models, respectively,

$$a_s^* = a_s, \quad (62')$$

$$a_s^* = \frac{9n^2 r_0^3 (a_s + b_{s:t} \mu_t^* + \dots)}{(n^2+2)[(2n^2+1)r_0^3 - 2(n^2-1)a_s]}, \quad (57')$$

where we have denoted the "fluctuational" dipole moment

$$\mu_t^* = 2(\epsilon-1)\mu_t / [(2\epsilon+1)r_0^3 - 2(\epsilon-1)\alpha_t]. \quad (63)$$

Thus, in the Lorentz or Onsager model, the effective anisotropy  $\Delta^2$  is expressed by experimentally accessible quantities and hence can be evaluated numerically.

The same method can also be applied for calculating  $\Delta^2$  for quadrupolar molecules, as done previously<sup>24</sup> in the case of Onsager's spherical cavity.

### COMPARISON OF THEORY AND EXPERIMENT

Assuming that isotropic scattering is sufficiently well described by the approximate factor (19) and anisotropic scattering by the exact factor (21), we obtain from (15) and (16) the anisotropic Rayleigh ratio at observation perpendicular to the incident beam in the form

$$R_{\text{anis}} = \frac{1}{10} (2\pi/\lambda)^4 \left[ \frac{1}{3} (n^2+2) \right]^2 \rho a^2 \Delta^2, \quad (64)$$

<sup>41</sup> C. W. Raman and K. S. Krishnan, Phil. Mag. 5, 498 (1928).

and the depolarization ratio in that of

$$D_u = 6\Delta^2 / (5\rho kT\kappa_T + 7\Delta^2). \quad (65)$$

We now discuss these formulas in relation to the effect of optically induced birefringence<sup>39,42</sup> as given by the difference of refractive indices

$$n_{zz} - n_{xx} = \lambda B_\lambda (I_{zz}^M - I_{xx}^M) \quad (66)$$

for incident light of intensity  $I$  propagating in the  $Y$  direction. The optical birefringence constant  $B_\lambda$  is given by<sup>39</sup> (neglecting the part due to the nonlinear optical deformation effect):

$$B_\lambda = (6\pi\rho a^2 / 5n\lambda kT) [\frac{1}{3}(n^2 + 2)]^4 \Delta^2. \quad (67)$$

Thus, by introducing the general definition (22) of optical anisotropy we are able quite generally (independently of the molecular symmetry and state of condensation) to describe the three anisotropic quantities  $R_{\text{anis}}$ ,  $D$ ,  $B_\lambda$  measured in experiments. In Table I are assembled the values of  $\Delta^2$  determined from Eqs. (64), (65), and (67) together with the experimental values of  $R_{\text{anis}}$  and  $D_u$  of Coumou *et al.*<sup>43</sup> and  $B$  measured by Paillette.<sup>44</sup> Significantly, the three experimental constants  $D_u$ ,  $R_{\text{anis}}$ , and  $B_\lambda$  lead to the same effective anisotropy  $\Delta^2 = 0.001$  only in the case of carbon tetrachloride and cyclohexane. In all other cases, smallest values for  $\Delta^2$  are obtained from  $B_\lambda$ , whereas  $R_{\text{anis}}$  yields maximal values on the average twice as large as from  $D_u$ .

The effective anisotropies computed from the ellipsoidal Lorentz and Onsager-Scholte models (Table II) are in general close to those obtained from measurements of  $D_u$  and  $B_\lambda$ . Agreement is better on the Onsager-Scholte model, the considerable discrepancy for nitrobenzene being attributable to omission of nonlinear deformation, an important factor<sup>38</sup> in strongly dipolar molecules [Eq. (57)]. Another source of discrepancy is the omission in this model of short-range angular molecular correlations given by the parameter  $J_A$  [Eqs. (26) or (28)]. Recurring to effective polarizabilities (57') for Onsager's model with spherical cavity one gets  $\Delta^2$ —values that are much too high being close to those obtained for gaseous anisotropy  $\kappa_a^2$ .

Above, Eqs. (64), (65), and (67) have been stated to apply also to atomic fluids whose optical anisotropy  $\Delta^2$  is sufficiently well approximated by Eq. (50). As an example, we consider liquid argon, where x-ray scattering<sup>45</sup> at 84.4°K and 0.8 atm gives a radial correlation parameter<sup>22</sup> of  $R_6 = 4.2 \times 10^{45} \text{ cm}^{-6}$ . Since  $a = 1.63 \times 10^{-24}$

TABLE I. Effective optical anisotropy  $\Delta^2$  for several liquids, as determined from Eqs. (64), (65), (67) and experimental data for  $D_u$ ,  $R_{\text{anis}}$ , and  $B_\lambda$ .<sup>a</sup>

Liquid	$\rho \times 10^{-21}$ ( $\text{cm}^{-3}$ )	$n$ ( $\lambda = 5460 \text{ \AA}$ )	$\kappa_T \times 10^{12}$ ( $\text{cm}^2/\text{dyn}$ )	$a \times 10^{24}$ ( $\text{cm}^3$ )	$\kappa_a^2 \times 10^2$	$D_u \times 10^2$	$R_{\text{anis}} \times 10^6$ ( $\text{cm}^{-1}$ )	$B_\lambda \times 10^9$ (esu) ( $\lambda = 4880 \text{ \AA}$ )	$\Delta^2 \times 10^2$		
									from $D_u$	from $R_{\text{anis}}$	from $B_\lambda$
Carbon tetrachloride	6.22	1.460	106	10.50	0	4.2	0.29	5.1	0.10	0.10	0.11
Carbon disulphide	9.98	1.634	94	8.74	13.4	64.0	71.9	418	8.08	17.10	4.93
Benzene	6.74	1.503	95	10.32	3.58	42.0	9.9	40	1.79	3.30	0.80
Cyclohexane	5.55	1.426	112	10.87	0.55	4.9	0.31	4.1	0.12	0.12	0.10
Iso-octane	3.61	1.391	152	15.44	0.75	4.7	0.58	...	0.10	0.16	...
Toluene	5.65	1.499	92	12.26	4.0	48.0	13.2	93	1.93	3.41	1.44
Nitrobenzene	5.88	1.560	49	12.92	5.00	74.0	60.7	290	5.32	12.10	3.24
Water	33.5	1.334	46	1.59	0.83	10.8	0.31	2.9	0.63	1.06	0.75
Chloroform	7.51	1.446	87	8.23	0.88	20	...	16.5	0.56	...	0.50

<sup>a</sup> The values of  $\rho$ ,  $n$ ,  $\kappa_T$ ,  $D_u$ , and  $R_{\text{anis}}$  have been taken from Ref. 43 for  $t = 23^\circ\text{C}$  with the exception of water [J. P. Kratochvil, M. Kerker, and L. E. Oppenheimer, *J. Chem. Phys.* **43**, 914 (1965); G. Cohen and H. Eisenberg, *ibid.* **43**, 3881 (1965)] and chloroform (Ref. 12). Those of  $B_\lambda$  are from Ref. 44, and of  $a$  and  $\kappa_a^2$  from H. A. Stuart, *Die Struktur des Freien Moleküls* (Springer-Verlag, Berlin, 1952); C. G. Lefevre and R. J. W. Lefevre, *Rev. Pure Appl. Chem.* **5**, 261 (1955).

<sup>42</sup> A. D. Buckingham, *Proc. Phys. Soc. (London)* **B69**, 344 (1956).

<sup>43</sup> D. J. Coumou, E. L. Mackor, and J. Hijmans, *Trans. Faraday Soc.* **60**, 1539, 2244 (1964).

<sup>44</sup> M. Paillette, *Compt. Rend.* **262**, 264 (1966).

<sup>45</sup> H. A. S. Eisenstein and N. S. Gingrich, *Phys. Rev.* **58**, 30 (1940); **62**, 261 (1942).



TABLE II. Effective optical anisotropies calculated theoretically [Eqs. (55), (56), (72)] for the ellipsoidal Lorentz and Onsager-Scholte models.<sup>a</sup>

Liquid	Polarizabilities (10 <sup>24</sup> cm <sup>3</sup> )			Semiaxes (Å)			Shape factors			$\Delta^2 \times 10^3$	
	$a_1$	$a_2$	$a_3$	$r_1$	$r_2$	$r_3$	$A_1$	$A_2$	$A_3$	Lorentz- ellipsoidal	Onsager- Scholte
Carbon disulphide	15.14	5.54	5.54	6.8	3.7	3.7	0.19	0.405	0.405	6.79	8.90
Benzene	12.31	12.31	6.35	7.1	7.1	3.7	0.23	0.23	0.54	1.37	1.88
Toluene	15.64	13.66	7.48	8.5	6.5	4.0	0.19	0.30	0.51	1.38	1.28
Nitrobenzene	17.16	14.19	7.41	8.5	6.5	3.7	0.18	0.25	0.57	1.33	1.70
Chloroform	6.68	9.01	9.01	4.1	7.1	7.1	0.46	0.27	0.27	0.24	0.44

<sup>a</sup> Values of  $a_1$ ,  $a_2$ ,  $a_3$  are from H. A. Stuart, *Die Struktur des Freien Moleküls* (Springer-Verlag, Berlin, 1952); C. G. LeFevre and R. J. W. LeFevre, *Rev. Pure Appl. Chem.* **5**, 261 (1955); those of  $r_1$ ,  $r_2$ ,  $r_3$  from M. Yasumi, H. Okaba-

yashi, and H. Komooka, *Bull. Chem. Soc. Japan* **31**, 673 (1958). The shape factors  $A_1$ ,  $A_2$ ,  $A_3$  have been derived from Ref. 40 and Yasumi, Okabayashi, and Komooka.

cm<sup>3</sup>, Eq. (50) yields  $\Delta^2=0.022$  of the same order as for benzene or toluene (Table I). Considering moreover that  $\rho=21.3 \times 10^{21}$  cm<sup>-3</sup> and  $\kappa_T=204 \times 10^{-12}$  cm<sup>2</sup> dyn<sup>-1</sup>, Eq. (65) yields as much as  $D_u=0.34$  for the scattered light depolarization, an effect already accessible to observation.

Finally, let us revert to the variation of the refractive index as due in liquids to intense light<sup>39,44,46</sup>:

$$\Delta n = \Delta n_p + \Delta n_T + \Delta n_B, \quad (68)$$

where

$$\Delta n_p = (n/4\pi\kappa_T) (\partial n/\partial p) T^2 I \quad (69)$$

is the increment due to the excess pressure  $p$  produced in the liquid by opticostriction<sup>39</sup> ( $\Delta n_T$  is due to the rise in temperature).

With the isotropic Rayleigh ratio in thermodynamical form<sup>43</sup>

$$R_{is} = (2\pi^2 n^2/\lambda^4) (kT/\kappa_T) (\partial n/\partial p) T^2, \quad (70)$$

Eq. (69) takes the form of

$$\Delta n_p = (\lambda^4 R_{is}/8\pi^3 n k T) I \quad (71)$$

permitting to calculate  $\Delta n_p$  from measurements of  $R_{is}$ .

Similarly, Eqs. (64) and (67) lead to

$$B_\lambda = (3\lambda^3 R_{anis}/52\pi^3 n k T) [\frac{1}{3}(n^2+2)]^2. \quad (72)$$

On insertion into (66), this permits to express the increment  $\Delta n_B$  from optical birefringence by means of the anisotropic Rayleigh ratio:

$$\Delta n_B = (3\lambda^4 R_{anis}/52\pi^3 n k T) I. \quad (73)$$

Obviously,  $\Delta n_p$  and  $\Delta n_T$  are of an isotropic nature, whereas  $\Delta n_B$  is, optically, purely anisotropic.

<sup>46</sup> P. D. Maker, R. W. Terhune, and C. M. Savage, *Phys. Rev. Letters* **12**, 507 (1964); G. Mayer and F. Gires, *Compt. Rend.* **258**, 2039 (1964).

Since  $R_{is}$  and  $R_{anis}$  are known for a great number of liquids,<sup>43</sup> it is possible by a simple procedure to compute the variations  $\Delta n_p$  and  $\Delta n_B$ , to which attention has been drawn recently<sup>47</sup> because of their important role in nonlinear optical processes (cf. Table III). For comparison with  $\Delta n_B$ , we moreover find the increment

$$\Delta n_B = \lambda B_\lambda [3/(n^2+2)]^2 I \quad (74)$$

resulting from (66), recurring to experimental values of  $B_\lambda$ .

## CONCLUSIONS

The general theory of anisotropic light scattering proposed above on a statistical-molecular basis is moreover applicable for the calculation of various particular cases, when a well-defined microscopic model can be adopted. The cases considered by us show anisotropic light scattering in dense media to be a highly complex process involving various statistical-molecular factors, such as optical linear and nonlinear polarizabilities, electric dipole, quadrupole, and higher moments, radial and angular correlations, etc. However, molecular-statistical models lead to formulas which, in the case of liquids and at the present stage, cannot be thoroughly evaluated numerically and compared with experiment. Nevertheless, they clearly indicate in each particular case what factors are relevant and the conditions in which anisotropic light scattering can occur. Thus, e.g., atomic fluids are shown to scatter anisotropically owing to their strong radial correlations, which affect the atomic polarizabilities, giving rise to a nonzero effective optical anisotropy. Also, notwithstanding the fact that the permanent dipoles or quadrupoles do not participate directly in interaction with

<sup>47</sup> R. Y. Chiao, E. Garmire, and C. H. Townes, *Phys. Rev. Letters* **13**, 479 (1964); Y. R. Shen, *Phys. Letters* **20**, 378 (1966).

TABLE III. Values of  $\Delta n_p$ ,  $\Delta n_{BR}$ , and  $\Delta n_{B\lambda}$  calculated by Eqs. (71), (73), (74) from experimental values of  $R_{is}$ ,  $R_{anis}$ , and  $B_\lambda$ .

Liquid	$n$ $\lambda = 5460 \text{ \AA}$	$R_{is} \times 10^6$ ( $\text{cm}^{-1}$ )	$R_{anis} \times 10^6$ ( $\text{cm}^{-1}$ )	$B_\lambda \times 10^9$ (esu)	$\Delta n_p \times 10^{13} I^{-1}$	$\Delta n_{BR} \times 10^{13} I^{-1}$	$\Delta n_{B\lambda} \times 10^{13} I^{-1}$
Water	1.334	0.85	0.31	2.9	1.77	0.30	0.89
Nitrobenzene	1.560	5.10	60.7	290	9.13	50.38	64.79
Benzene	1.503	5.90	9.9	40	9.91	8.42	9.69
Toluene	1.499	5.23	13.2	93	9.73	11.35	22.67
Cyclohexane	1.426	4.25	0.31	4.1	8.29	0.28	1.11
Iso-octane	1.391	4.57	0.58		9.19	5.39	
<i>n</i> -Hexane	1.374	4.46	0.86		9.05	0.81	
<i>n</i> -Octane	1.398	3.96	0.89		7.88	0.82	
<i>n</i> -Decane	1.413	3.79	1.16		7.46	1.06	
<i>n</i> -Hexadecane	1.435	3.44	1.71		6.67	1.52	
Carbon tetrachloride	1.460	5.09	0.29	5.1	9.72	0.26	1.31
Carbon disulphide	1.634	12.00	71.9	418	20.52	56.08	84.23
Methyl ethyl ketone	1.379	3.12	1.06		6.30	0.99	

<sup>a</sup>  $R_{is}$  and  $R_{anis}$  for water calculated from the data by Kratochvil, Kerker, and Oppenheim, and Cohen and Eisenberg in Footnote a of Table I for the other liquids taken from Ref. 43.  $B_\lambda$  is from Ref. 44.

the electric field of the light wave, they nevertheless affect light scattering in dense media by way of non-central molecular correlations and molecular fields inducing nonlinear polarizability in the atoms or molecules.

Adoption of the ellipsoidal Lorentz or Onsager-Scholte model leads to formulas for the effective optical anisotropy that permit direct numerical calculations as well as confrontation with experimental data. Such confrontation allows to conclude that, in addition to anisotropy of the molecules' optical properties, an important role in anisotropic light scattering is played by their geometrical shape.

Finally, attention is drawn to the relationship between isotropic light scattering and isotropic variations of the refractive index and similarly between anisotropic scattering and the optical birefringence induced in liquids by intense light. Further, joint investigation of the two (and similar) effects is apt to provide ample interesting data, particularly in the experimental field owing to the laser techniques now utilized in studying linear light scattering in gases<sup>37,48</sup> and in

<sup>48</sup> L. Slama, thesis, C. E. N. Saclay, France, 1963; A. D. May, E. G. Rawson, and H. L. Welsh, *Physics of Quantum Electronics*, P. Kelley, B. Lax, and P. E. Tannenwald, Eds. (McGraw-Hill Book Co., Inc., New York, 1966), p. 260.

liquids<sup>49</sup> as well as nonlinear scattering in gases and liquids.<sup>25,50</sup> In addition to information, on the optical properties of atoms and molecules, this should be a source of data concerning their electrical properties permitting comparison with other methods of determining molecular quadrupoles<sup>35,36,51-54</sup> and octupoles<sup>29,54-56</sup> as well as nonlinear polarizabilities.<sup>39,57</sup>

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