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### EFFECTIVE OPTICAL ANISOTROPY OF POLAR MOLECULES FROM RAYLEIGH LIGHT SCATTERING STUDIES

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**Résumé**. — On calcule l'anisotropie optique effective des molécules polaires dans la deuxième approximation du calcul statistique des perturbations en tenant compte des interactions dispersionnelles, dipôle-dipôle, dipôle-quadrupôle, quadrupôle-quadrupôle, dipôle induit-dipôle, dipôle induit-quadrupôle, ainsi que des répartitions moléculaires. On montre que les interactions radiales à trois molécules abaissent fortement l'effet des interactions radiales à deux molécules. Une analyse est donnée du modèle de la configuration privilégiée à deux molécules, pour des molécules polaires allongées et aplaties. Des calculs numériques sont effectués pour le  $CH_3CN$  et  $CHCl_3$  liquides, dont les molécules présentent respectivement une anisotropie permanente positive et négative de la polarisabilité. La comparaison avec les résultats expérimentaux permet d'établir le pourcentage des molécules formant des paires privilégiées dans le liquide.

Abstract. — The effective optical anisotropy of polar molecules is calculated to within the second approximation of statistical perturbation calculus taking into account dispersional, dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, induced dipole-dipole and induced dipole-quadrupole interactions as well as molecular redistribution. Three-molecule radial interaction is considered, leading to a very large reduction in the effect of two-molecule radial interaction. The model of favoured two-molecule configuration is analyzed for rod- and plate-like polar molecules, and numerical calculations are performed for the liquids  $CH_3CN$  and  $CHCl_3$ , the molecules of which exhibit, respectively, positive and negative intrinsic anisotropy of polarizability. The calculations are compared with the available experimental data, and the percentage of molecules forming privileged pairs in the liquid is determined.

1. Introduction. — The recent intensive studies of matter by optical methods have yielded abundant information on the optical properties of media and their internal structure. In particular, the analysis of linear [1] and especially nonlinear optical phenomena [2] in liquids leads to highly stimulating conclusions as to the intermolecular interactions in this state of condensation. They intervene very markedly, among others, in anisotropic light scattering and the optical Kerr effect in liquids [3-6] and liquid crystals [7]. The measurement of these two effects permits the determination of the effective optical anisotropy  $\Gamma^{2}$  [3, 4], characterizing the optical anisotropy of the linear polarizability of a molecule surrounded by its neighbours in the liquid. The influence of its nearest neighbours on the optical properties of a molecule is weak in strongly rarefied media, such as gases under low pressure, but is considerable in the liquid state. Various intermolecular interactions, primarily of the multipolar kind (e.g. dipole-dipole, dipole-quadrupole, quadrupole-quadrupole) [4], in conjunction with the geometry of the molecule, lead to the emergence of structural order in shortest-range regions in the liquid and the formation of momentary systems of molecules. In the case of molecules endowed with a permanent dipole moment ( $CH_3CN$ ,  $CHCl_3$ ) the dipoledipole interaction is predominant, leading to the formation of privileged two-molecule configurations : an antiparallel, and a parallel configuration, as considered by Piekara [8] for nonlinear molecular reorientation phenomena. Quite generally, molecular liquids can present a diatropic, or paratropic, structure [9].

Here, we perform an analysis of the effective optical anisotropy of dipolar liquids on the assumption that, except for the molecules involved in the above mentioned two-molecule systems, no configuration is favoured as regards the molecules of the liquid, but that nonetheless well-defined radial, dispersional and multipolar interactions exist between them. The effective optical anisotropy is calculated using the molecular-statistical perturbation calculus to the second approximation inclusively, and is shown to depend on angular, radial and angular-radial parameters. A comparison of the theoretical model calculations and effective optical anisotropy values determined experimentally from anisotropic light scattering [10, 11] permits us to assess the percentage of molecules involved in the privileged two-molecule systems.

2. Fundamental formulae. — We consider a liquid, of volume V, with N anisotropic molecules of a single species. In the absence of internal interference and spatial dispersion, the effective optical anisotropy is given as follows [4, 12]:

$$\Gamma^{2} = \frac{3}{2N} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \mathbf{D}_{p} : \mathbf{D}_{q} \right\rangle , \qquad (1)$$

where the symbol  $\langle \rangle$  stands for statistical averaging in the presence of molecular correlations, and  $\mathbf{D}_p$ is the deviator of the symmetric tensor of linear optical polarizability  $\mathbf{A}_p$  of molecule p, acted on by the surrounding medium. The deviator  $\mathbf{D}_p$  has the property of zero trace :  $\mathbf{D} : \mathbf{U} = 0$  (with  $\mathbf{U}$  — the rank 2 unit tensor). Also, if the linear optical polarizability tensor  $\mathbf{A}_p$  is isotropic (as it is for non-interacting, isotropically polarizable atoms and molecules), the deviator  $\mathbf{D}_p = 0$ . However, in the general case,  $\mathbf{A}_p$ depends not only on the optical properties of the molecule considered in isolation (on its linear optical polarizability  $\mathbf{a}_p$ ) but moreover on how the neighbouring molecules perturb its linear optical polarizability  $\mathbf{a}_p$ . In this paper, we shall be dealing with dipolar molecules having the axial symmetry (CH<sub>3</sub>CN, CHCl<sub>3</sub>), for which the tensor elements of  $\mathbf{a}_p$  in the system of principal molecular axes satisfy the relation  $a_1 = a_2 \neq a_3$  (the 3-axis being taken as the symmetry axis). For this class of molecules,  $\mathbf{a}_p$  can be expressed in diagonal form, split into an isotropic and an anisotropic part :

$$\mathbf{a}_{p} = a_{p} \mathbf{U} + \frac{1}{3} \gamma_{p} \mathbf{S}_{p}, \qquad (2)$$

where  $a_p = \mathbf{a}_p : \mathbf{U}/3$  is the mean linear optical polarizability of the isolated *p*-th molecule,  $\gamma_p = a_3^{(p)} - a_1^{(p)}$  its intrinsic anisotropy, and the tensor

$$\mathbf{S}_p = 3 \, \mathbf{k}_p \, \mathbf{k}_p - \mathbf{U}$$

with  $\mathbf{k}_p$ — the unit vector along the symmetry 3-axis of the molecule *p*. Restricting ourselves to translational Yvon [13] and Kirkwood [14] fluctuations and translational-orientational fluctuations [12], we calculate in a dipolar approximation the following, successive approximations of the effective optical anisotropy [5]:

$$\Gamma_0^2 = \frac{1}{6N} \gamma^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \mathbf{S}_p : \mathbf{S}_q \right\rangle , \qquad (3)$$

$$\Gamma_{1}^{2} = \frac{1}{9N} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{r=1}^{N} S(p, q, r) \left\{ 9 a^{2} \gamma \mathbf{S}_{p} : \mathbf{T}_{qr} + 6 a \gamma^{2} \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr}) + \gamma^{3} \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr} \cdot \mathbf{S}_{r}) \right\} \right\rangle,$$
(4)  
$$\Gamma_{2}^{2} = \frac{1}{162N} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{r=1}^{N} \sum_{s=1}^{N} S(p, q, r, s) \left\{ 243 a^{4} \mathbf{T}_{pr} : \mathbf{T}_{qs} + 162 a^{3} \gamma [\mathbf{S}_{p} : (\mathbf{T}_{qr} \cdot \mathbf{T}_{rs}) + 2(\mathbf{S}_{p} \cdot \mathbf{T}_{pr}) : \mathbf{T}_{rs}] + 18 a^{2} \gamma^{2} [6 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr} \cdot \mathbf{T}_{rs}) + 3 \mathbf{S}_{p} : (\mathbf{T}_{qr} \cdot \mathbf{S}_{q} \cdot \mathbf{T}_{qs}) + 3 \mathbf{S}_{p} : (\mathbf{T}_{qr} \cdot \mathbf{S}_{q} \cdot \mathbf{T}_{qs}) + 3 \mathbf{S}_{p} : (\mathbf{T}_{qr} \cdot \mathbf{S}_{q} \cdot \mathbf{T}_{rs}) + 4 (\mathbf{S}_{p} \cdot \mathbf{T}_{pr}) : \mathbf{T}_{rs}] + 18 a^{2} \gamma^{2} [6 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr} \cdot \mathbf{T}_{rs}) + 3 \mathbf{S}_{p} : (\mathbf{T}_{qr} \cdot \mathbf{S}_{q} \cdot \mathbf{T}_{qs}) + 3 \mathbf{S}_{p} : (\mathbf{T}_{pq} \cdot \mathbf{S}_{q} \cdot \mathbf{T}_{rs}) + 6(\mathbf{S}_{p} \cdot \mathbf{T}_{pr}) : (\mathbf{S}_{q} \cdot \mathbf{T}_{qs}) - 2(\mathbf{S}_{p} : \mathbf{T}_{pr}) (\mathbf{S}_{q} : \mathbf{T}_{qs}) ] + 6 a \gamma^{3} [6 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr} \cdot \mathbf{S}_{r} \cdot \mathbf{T}_{rs}) + 3 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qs} \cdot \mathbf{T}_{sr}) + 3 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qs} \cdot \mathbf{S}_{r}) + 6(\mathbf{S}_{p} \cdot \mathbf{T}_{pq} \cdot \mathbf{S}_{q}) : (\mathbf{T}_{rs} \cdot \mathbf{S}_{r}) - 2(\mathbf{S}_{p} \cdot \mathbf{S}_{q}) : \mathbf{T}_{pq} (\mathbf{S}_{r} : \mathbf{T}_{rs}) ] + \gamma^{4} [6 \mathbf{S}_{p} : (\mathbf{S}_{q} \cdot \mathbf{T}_{qr} \cdot \mathbf{S}_{r} \cdot \mathbf{T}_{rs} \cdot \mathbf{S}_{s}) + 3 (\mathbf{S}_{p} \cdot \mathbf{T}_{pr} \cdot \mathbf{S}_{r}) : (\mathbf{S}_{q} \cdot \mathbf{T}_{qs} \cdot \mathbf{S}_{s}) - (\mathbf{S}_{p} \cdot \mathbf{S}_{s}) : \mathbf{T}_{pr} (\mathbf{S}_{q} \cdot \mathbf{S}_{s}) : \mathbf{T}_{qs} \mathbf{S}_{s} : \mathbf{T}_{qs} ] \} \rangle,$$
(5)

where S(p, q, r), S(p, q, r, s) are operators symmetrizing the right-hand quantities in p, q, r and p, q, r, s respectively, whereas  $\mathbf{T}_{pq}$  is the tensor of dipole-dipole interaction between molecules p and q, separated by  $\mathbf{r}_{pq}$ ; in the absence of spatial dispersion,  $\mathbf{T}_{pq}$  is of the form :

$$\mathbf{T}_{pq} = -r_{pq}^{-5} (3 \mathbf{r}_{pq} \mathbf{r}_{pq} - r_{pq}^2 \mathbf{U}) .$$
 (6)

Considering two-molecule interactions only, we obtain [5, 6, 12] :

$$\Gamma_0^2 = \gamma^2 (1 + J_A) , \qquad (7)$$

$$\Gamma_1^2 = 4 \gamma^2 (3 a + \gamma) J_1 + 2 a \gamma (3 a - \gamma) J_2, \qquad (8)$$

$$\Gamma_{2}^{2} = \left(9 a^{4} + \frac{28}{5} a^{2} \gamma^{2} + \frac{2}{3} a \gamma^{3} + \frac{67}{225} \gamma^{4}\right) J_{R} + 7 \gamma^{4} K_{1} + 2 \gamma^{2} \left(9 a^{2} - 14 a \gamma + \frac{11}{3} \gamma^{2}\right) K_{2} + 12 \gamma^{2} \left(a - \frac{1}{3} \gamma\right)^{2} K_{3} + 24 \gamma^{3} \left(a - \frac{1}{3} \gamma\right) K_{4} - 10 \gamma^{3} \left(a - \frac{1}{3} \gamma\right) K_{5} + 2 \gamma^{2} \left(12 a^{2} + \frac{7}{6} \gamma^{2}\right) K_{6} + 3 \gamma \left(a - \frac{1}{3} \gamma\right)^{2} (6 a - \gamma) K_{7} + 2 \gamma^{2} \left(a^{2} - 3 a \gamma + \frac{1}{3} \gamma^{2}\right) K_{8}, \qquad (9)$$

where [15] :

$$J_{\mathbf{A}} = \frac{1}{2} \left\langle \sum_{p \neq q} \left\{ 3 \cos^2 \theta_{pq} - 1 \right\} \right\rangle$$
(10)

is the angular correlation parameter for anisotropically polarizable molecules, with  $\cos \theta_{pq} = \mathbf{k}_p \cdot \mathbf{k}_q$ ;

$$J_{\mathbf{R}} = 2 \left\langle \sum_{p \neq q} r_{pq}^{-6} \right\rangle \tag{11}$$

is the parameter of two-molecule radial interactions [15]; and the parameters  $J_1, J_2, K_1, ..., K_8$  are those of angular-radial correlations [6]:

$$J_{i} = \frac{1}{2} \left\langle \sum_{p \neq q} f_{i}(\cos \theta_{pq}, \cos \theta_{p}, \cos \theta_{q}) r_{pq}^{-3} \right\rangle , \qquad (12)$$

$$K_{i} = \frac{1}{2} \left\langle \sum_{p \neq q} h_{i}(\cos \theta_{pq}, \cos \theta_{p}, \cos \theta_{q}) r_{pq}^{-6} \right\rangle , \qquad (13)$$

where  $\cos \theta_p = \mathbf{k}_p \cdot \mathbf{r}_{pq} / r_{pq}$ , the functions  $f_i$  and  $h_i$  being of the form :

$$f_1 = h_2 = 3\cos\theta_{pq}\cos\theta_p\cos\theta_q - \cos^2\theta_{pq}$$
(14)

$$f_2 = h_7 = 3\cos^2\theta_p + 3\cos^2\theta_q - 2 \tag{15}$$

$$h_1 = 9\cos^2\theta_{pq}\cos^2\theta_p\cos^2\theta_q - 6\cos^3\theta_{pq}\cos\theta_p\cos\theta_q + \cos^4\theta_{pq} - \frac{6}{25}$$
(16)

$$h_3 = 3\cos^4\theta_p + 3\cos^4\theta_q - 3\cos^2\theta_p\cos^2\theta_q - \cos^2\theta_p - \cos^2\theta_q - \frac{1}{5}$$
(17)

$$h_4 = 3\cos\theta_{pq}\cos^3\theta_p\cos\theta_q + 3\cos\theta_{pq}\cos\theta_p\cos^3\theta_q - \frac{2}{5}$$
(18)

$$h_{5} = 3\cos^{2}\theta_{pq}\cos^{2}\theta_{p} + 3\cos^{2}\theta_{pq}\cos^{2}\theta_{q} - \frac{2}{3}$$
(19)

$$h_6 = 9\cos^2\theta_p\cos^2\theta_q - 6\cos\theta_{pq}\cos\theta_p\cos\theta_q + \cos^2\theta_{pq} - \frac{2}{3}$$
(20)

$$h_8 = 3\cos^2\theta_{pq} - 1.$$
 (21)

The functions  $f_i$  and  $h_i$  are defined so as to vanish on isotropic averaging over all orientations with equal probability :

$$\langle f_{i}(\cos\theta_{pq},\cos\theta_{p},\cos\theta_{q})\rangle_{\Omega} = \langle h_{i}(\cos\theta_{pq},\cos\theta_{p},\cos\theta_{q})\rangle_{\Omega} = 0.$$
(22)

One notes that the parameters (10)-(13) are symmetric in the molecules p, q.

If moreover three-molecule interactions are taken into account in the isotropic molecule approximation, the contribution to  $\Gamma_2^2$  from these interactions is of the form (see Appendix A) :

$$\Gamma_2^2 = 144 \ \pi^2 \ \rho^2 \ a^4 \ I \,, \tag{23}$$

where :

$$I = \int_{0}^{\infty} r_{pq} \exp\left[-U(r_{pq})/kT\right] dr_{pq} \int_{0}^{\infty} r_{qr} \exp\left[-U(r_{qr})/kT\right] dr_{qr} \times \\ \times \int_{|r_{pq}-r_{qr}|}^{r_{pq}+r_{qr}} r_{pr} \left\{ \exp\left[-U(r_{pr})/kT\right] - 1 \right\} \frac{3\cos^{2}\theta - 1}{r_{pq}^{3}r_{qr}^{3}} dr_{pr}, \quad (24)$$

with  $\cos \theta = \mathbf{r}_{pq} \cdot \mathbf{r}_{qr} / r_{pq} r_{qr}$ . The integral (24) can be calculated analytically for the rigid sphere case [16].

Nº 12

Liquid	$\rho \times 10^{-21}$ [cm <sup>-3</sup> ] ( <sup>a</sup> )	( <sup>b</sup> ) n	$a_1 \times 10^{24}$ [cm <sup>3</sup> ]	$a_2 \times 10^{24}$ [cm <sup>3</sup> ]	$a_3 \times 10^{24}$ [cm <sup>3</sup> ]	$a \times 10^{24}$ [cm <sup>3</sup> ]	$\gamma \times 10^{24}$ [cm <sup>3</sup> ]	$\begin{array}{c} \mu \times 10^{18} \\ \text{[esu]} \end{array}$	$\Theta \times 10^{26}$ [esu]	$\sigma  imes 10^8$ [cm]	ε/k [K]	$\Gamma_{exp}^{2} \times 10^{48} (h)$ [cm <sup>6</sup> ]
CH <sub>3</sub> CN	11.40	1.340	3.70 (°)	3.70	5.43	4.28	1.73	3.9 (°)	1.8 (°)	4.10 ( <sup>f</sup> )	349 ()	5.33
CHCl <sub>3</sub>	7.47	1.441	9,01 ( <sup>d</sup> )	9.01	6.68	8.23	- 2.33	1.15	_	5.31 ( <sup>g</sup> )	355 ( <sup>g</sup> )	7.64

TABLE I

t = 25 °C,  $\lambda = 6.328 \text{ Å}$ 

(<sup>a</sup>) Determined with  $V_m$  from the paper of TIMMERMANS, J., *Physico-Chemical Constants of Pure Organic Compounds*. Vol. I (Elsevier Publ. Co. New York) 1950.

(<sup>b</sup>) From reference [10].

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(<sup>h</sup>) Determined with the  $R_{an}^{m}$  value of reference [10].

3. Detailed discussion of the effective optical anisotropy of dipolar liquids. — The interaction energy of two dipolar molecules of a liquid in the configurations  $\tau_p$  and  $\tau_q$  can be written in the form :

$$U(\tau_{p}, \tau_{q}) = U(r_{pq}) + V(\tau_{p}, \tau_{q}), \qquad (25)$$

where  $U(r_{pq})$  is the central interaction energy and  $V(\tau_p, \tau_q)$  the noncentral (tensorial) interaction energy of dispersional, electrostatic multipole, and induced multipole origin. Since dipolar molecules can have a quadrupole moment as well (see Table I), the energy  $V(\tau_p, \tau_q)$  takes the form :

$$V = V^{\text{disp}} + V^{\mu-\mu} + V^{\mu-\Theta} + V^{\Theta-\Theta} + V^{\alpha-\mu} + V^{\alpha-\Theta}, \quad (26)$$

with interaction energies :  $V^{\text{disp}}$ -dispersional;  $V^{\mu-\mu}$ dipole-dipole;  $V^{\mu-\theta}$ -dipole-quadrupole;  $V^{\theta-\theta}$ -quadrupole-quadrupole;  $V^{\alpha-\mu}$ -dipole-induced dipole; and  $V^{\alpha-\theta}$ -induced dipole-quadrupole; the interaction energies due to higher order multipoles are omitted here. The energies (26) are dependent on the electric and optical properties of the molecule (their dipole moment  $\mu$ , quadrupole moment  $\Theta$ , optical polarizability *a*, and anisotropy of optical polarizability  $\gamma$ ), their distances, and mutual configurations, and are given in references [2] and [4].

3.1 WEAK INTERACTIONS. — In calculating the correlation parameters J and K we assume the following form of the two-molecule correlation function  $g^{(2)}(\tau_p, \tau_q)$  [3]:

$$g^{(2)}(\tau_p, \tau_q) = \Omega^{-2} g(r_{pq}) \times \\ \times \exp \left\{ - V(r_{pq}, \omega_p, \omega_q)/kT \right\}, \quad (27)$$

where

$$\Omega = \int \mathrm{d}\omega_p = \int \mathrm{d}\omega_q \, .$$

If the intermolecular interactions are not excessively strong, one can proceed by a series expansion of the exponential function. In the zeroth approximation, all J and K except  $J_{\rm R}$  vanish. With the energy  $V(r_{pq}, \omega_p, \omega_q)$  taken into account, the influence of the various interactions (26) on the correlation parameters is found to be given by the following expressions :

$$J_{A} = \left[ \alpha_{A}^{(1)} \frac{hv}{kT} + \alpha_{A}^{(2)} \frac{\mu^{2}}{kT} + \alpha_{A}^{(3)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-6} \rangle + \frac{\Theta^{2}}{kT} \left( \alpha_{A}^{(4)} + \alpha_{A}^{(5)} \frac{\mu^{2}}{kT} \right) \langle r^{-8} \rangle + \alpha_{A}^{(6)} \left( \frac{\Theta^{2}}{kT} \right)^{2} \langle r^{-10} \rangle + \frac{\Theta^{2}}{kT} \left[ \alpha_{A}^{(7)} \frac{hv}{kT} + \alpha_{A}^{(8)} \frac{\mu^{2}}{kT} + \alpha_{A}^{(9)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-11} \rangle + \left[ \alpha_{A}^{(10)} \left( \frac{hv}{kT} \right)^{2} + \alpha_{A}^{(11)} \frac{hv}{kTT} \frac{\mu^{2}}{kT} + \alpha_{A}^{(12)} \left( \frac{\mu^{2}}{kT} \right)^{2} + \alpha_{A}^{(13)} \frac{hv}{kTT} \left( \frac{\mu^{2}}{kT} \right)^{2} + \alpha_{A}^{(14)} \left( \frac{\mu^{2}}{kT} \right)^{3} + \alpha_{A}^{(15)} \left( \frac{\mu^{2}}{kT} \right)^{4} \right] \langle r^{-12} \rangle + \alpha_{A}^{(16)} \left( \frac{\Theta^{2}}{kT} \right)^{2} \langle r^{-13} \rangle + \frac{\Theta^{2}}{kT} \left[ \alpha_{A}^{(17)} \frac{\mu^{2}}{kT} + \alpha_{A}^{(18)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-14} \rangle,$$

$$(28)$$

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$$J_{i} = \left[ \alpha_{i}^{(1)} \frac{hv}{kT} + \alpha_{i}^{(2)} \frac{\mu^{2}}{kT} + \alpha_{i}^{(3)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-9} \rangle + \frac{\Theta^{2}}{kT} \left( \alpha_{i}^{(4)} + \alpha_{i}^{(5)} \frac{\mu^{2}}{kT} \right) \langle r^{-11} \rangle + \alpha_{i}^{(6)} \left( \frac{\Theta^{2}}{kT} \right)^{2} \langle r^{-13} \rangle + \frac{\Theta^{2}}{kT} \left[ \alpha_{i}^{(7)} \frac{hv}{kT} + \alpha_{i}^{(8)} \frac{\mu^{2}}{kT} + \alpha_{i}^{(9)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-14} \rangle + \left[ \alpha_{i}^{(10)} \left( \frac{hv}{kT} \right)^{2} + \alpha_{i}^{(11)} \frac{hv}{kT} \frac{\mu^{2}}{kT} + \alpha_{i}^{(12)} \left( \frac{\mu^{2}}{kT} \right)^{2} + \alpha_{i}^{(13)} \frac{hv}{kT} \left( \frac{\mu^{2}}{kT} \right)^{2} + \alpha_{i}^{(14)} \left( \frac{\mu^{2}}{kT} \right)^{3} + \alpha_{i}^{(15)} \left( \frac{\mu^{2}}{kT} \right)^{4} \right] \langle r^{-15} \rangle + \alpha_{i}^{(16)} \left( \frac{\Theta^{2}}{kT} \right)^{2} \langle r^{-16} \rangle + \frac{\Theta^{2}}{kT} \left[ \alpha_{i}^{(17)} \frac{\mu^{2}}{kT} + \alpha_{i}^{(18)} \left( \frac{\mu^{2}}{kT} \right)^{2} \right] \langle r^{-17} \rangle.$$

$$(29)$$

The  $\alpha_A^{(n)}$  and  $\alpha_i^{(n)}$  are numerical coefficients or ones dependent on the mean linear optical polarizability *a* and its anisotropy  $\gamma$ , and are given in table II. The factors at  $\alpha_A^{(n)}$  and  $\alpha_i^{(n)}$  in eq. (28) and (29) indicate the type of interaction to which the contribution is due (e.g. hv/kT indicates the contribution from dispersional interactions,  $\mu^2/kT$  the dipolar contribution, etc.). The parameters  $K_i$  of the interactions represented by eq. (26) are of the form :

$$K_{i}^{disp} = \beta_{i}^{(1)} \frac{hv}{kT} \langle r^{-12} \rangle + \cdots, \qquad (30)$$

$$K_{i}^{\mu-\mu} = \beta_{i}^{(2)} \left(\frac{\mu^{2}}{kT}\right)^{2} \langle r^{-12} \rangle + \cdots, \qquad (31)$$

$$K_{i}^{\mu-\Theta} = \beta_{i}^{(3)} \left(\frac{\mu\Theta}{kT}\right)^{2} \langle r^{-14} \rangle + \cdots, \qquad (32)$$

$$K_{i}^{\theta-\theta} = \beta_{i}^{(4)} \frac{\Theta^{2}}{kT} \langle r^{-11} \rangle + \cdots, \qquad (33)$$

$$K_{i}^{\alpha-\mu} = \beta_{i}^{(5)} \frac{\mu^{2}}{kT} \langle r^{-12} \rangle + \cdots, \qquad (34)$$

$$K_{i}^{\alpha-\Theta} = \beta_{i}^{(6)} \frac{\Theta^{2}}{kT} \langle r^{-14} \rangle + \cdots .$$
 (35)

The  $\beta_i^{(m)}$ , like the  $\alpha_i^{(m)}$ , are numerical coefficients or ones dependent on such molecular parameters as the mean linear optical polarizability and polarizability anisotropy of the molecule. The coefficients  $\beta_i^{(m)}$  are assembled in table III.

The  $\langle r^{-n} \rangle$  occurring in eq. (28)-(35) are twomolecule radial correlation parameters of the form :

$$\langle r^{-n} \rangle = \frac{\rho}{V} \iint r_{pq}^{-n} g(r_{pq}) \,\mathrm{d}\mathbf{r}_p \,\mathrm{d}\mathbf{r}_q \,.$$
(36)

3.2 STRONG INTERACTION. — By strong interaction we mean the formation of momentary molecular assemblies (e.g. pairs of molecules). Their form depends on the optical, electric and geometrical properties of the isolated molecules.

3.2.1 Molecules with positive anisotropy of linear optical polarizability ( $\gamma > 0$ ). — In a dipolar axially-symmetric molecule, the dipole moment is directed

along the symmetry axis ( $\mu = \mu \mathbf{k}$ ). Molecules with positive anisotropy,  $\gamma > 0$ , tend to form pairs in which the two dipole moments are mutually antiparallel (Fig. 1*a*). With the two molecules thus arrayed, we have the relations :  $\cos \theta_p = \cos \theta_q = 0$ ,  $\cos (\pi - \theta_{pq}) = -\cos \theta_{pq}$ , and the interaction energies of eq. (26) become functions of  $\cos \theta_{pq}$ . We now have [4] :

$$- U/kT = y_0 + y_1 \cos \theta_{pq} - y_2 \cos^2 \theta_{pq} \quad (37)$$
  
where :  
$$y_1 = \frac{\mu^2}{1 \pi r_{pq}^{-3}}, \quad (38)$$

$$y_2 = \frac{1}{8 \, kT} \left[ 12 \, \Theta^2 \, r_{pq}^{-5} - \gamma (hv\gamma + 8 \, \mu^2) \, r_{pq}^{-6} \right]. \tag{39}$$

In order to circumvent integration over  $r_{pq}$  in eq. (10)-(13), we approximate the mutual distance between the two molecules [17]:

$$r_{pq} = \left(\frac{6 u}{\pi \rho}\right)^{1/3} \tag{40}$$

where the parameter u takes values from the interval  $0.6 \le u \le 0.74$ . Our calculations are performed for u = 0.6. For the antiparallel configuration, the parameters J and K can now be written as follows :

$$J_{\rm A} = \frac{1}{2} z \left\{ 3 L_2(y_1, \pm y_2) - 1 \right\}, \tag{41}$$

$$J_{\rm i} = b_{\rm i} \left(\frac{\pi\rho}{6\,u}\right) z , \qquad (42)$$



FIG. 1. — Favoured configurations for rod and plate-like axiallysymmetric dipolar molecules : *a*) antiparallel; *b*) parallel.

### TABLE II

## Coefficients $\alpha_A^{(n)}$ and $\alpha_i^{(n)}$ occurring in eq. (28) and (29)

n	α <sup>(n)</sup>	$\alpha_1^{(n)}$	α <sup>(n)</sup>
1	$\frac{1}{300}\gamma^2$	$\frac{1}{900}\gamma(30\ a-\gamma)$	$\frac{1}{10}a\gamma$
2	$\frac{2}{75}\gamma$	$\frac{2}{225}(15a+4\gamma)$	$\frac{2}{15}a$
3	$\frac{1}{75}$	$\frac{1}{25}$	$\frac{2}{15}$
4	$\frac{2}{35}\gamma$	$\frac{4}{105}(6\ a\ +\ \gamma)$	$\frac{4}{175}(30 a + 7 \gamma)$
5	$\frac{2}{35}$	$\frac{4}{35}$	<u>68</u> 175
6	$\frac{4}{35}$	$\frac{8}{49}$	$\frac{4}{7}$
7	$-\frac{12}{1225}\gamma^2$	$-\frac{3}{1225}\gamma(21a-5\gamma)$	$\frac{1}{175}\gamma(21 a - 8 \gamma)$
8	$-\frac{96}{1225}\gamma$	$-\frac{12}{1225}(21a+17\gamma)$	$-\frac{1}{175}(84 a + 659 \gamma)$
9	$-\frac{48}{1225}$	$-\frac{144}{1225}$	$-\frac{12}{35}$ .
10	$\frac{1}{176\ 400}\gamma^2(441\ a^2\ -\ 84\ a\ \gamma\ +\ 38\ \gamma^2)$	$\frac{1}{176\ 400}\gamma^2(357\ a^2\ +\ 986\ a\gamma\ +\ 38\ \gamma^2)$	$\frac{1}{12\ 600}\gamma^2(45\ a^2\ +\ 63\ a\gamma\ +\ 11\ \gamma^2)$
11	$\frac{1}{22\ 050}\ \gamma(441\ a^2\ +\ 168\ a\gamma\ +\ 62\ \gamma^2)$	$\frac{1}{66\ 150}\gamma(5\ 481\ a^2\ +\ 2\ 037\ a\gamma\ +\ 431\ \gamma^2)$	$\frac{1}{3150}\gamma(720a^2+219a\gamma+65\gamma^2)$
12	$\frac{1}{11\ 025}\ (441\ a^2\ +\ 714\ a\gamma\ +\ 145\ \gamma^2)$	$\frac{1}{33\ 075}\ (9\ 891\ a^2\ +\ 5\ 502\ a\gamma\ +\ 1\ 387\ \gamma^2)$	$\frac{1}{1575}(1350a^2+732a\gamma+1370\gamma^2)$
13	$\frac{1}{44\ 100}\gamma(210\ a\ +\ 97\ \gamma)$	$\frac{1}{14\ 700}\ \gamma(378\ a\ +\ 65\ \gamma)$	$\frac{1}{3150}\gamma(198a+43\gamma)$
14	$\frac{8}{3675}(21 a + 11 \gamma)$	$\frac{32}{3\ 675}(21\ a\ +\ 8\ \gamma)$	$\frac{16}{1575}(51 a + 19 \gamma)$
15	<u>4</u> <u>1 225</u>	<u>8</u> 735	$\frac{16}{525}$
16	$-\frac{4}{245}(21 a + 2\gamma)$	$-\frac{4}{525}(57 a + 47 \gamma)$	$-\frac{144}{1225}(7a+8\gamma)$
17	$\frac{1}{2450}(168a^2+418a\gamma+12\gamma^2)$	$\frac{2}{11025}(5607a^2+2598a\gamma+806\gamma^2)$	$\frac{1}{3\ 675}(10\ 710\ a^2\ +\ 4\ 662\ a\gamma\ +\ 1\ 324\ \gamma^2)$
18	$\frac{1}{3\ 675}(483\ a\ +\ 94\ \gamma)$	$\frac{1}{1\ 225}(399\ a\ +\ 122\ \gamma)$	$\frac{2}{3\ 675}(1\ 617\ a\ +\ 478\ \gamma)$

#### TABLE III

Coefficients  $\beta_i^{(n)}$  occurring in eq. (30)-(35)

i	$\beta_{i}^{(1)}$	$\beta_i^{(2)}$	$\beta_i^{(3)}$	β <sup>(4)</sup>	$\beta_{i}^{(5)}$	$\beta_{i}^{(6)}$
1	$\frac{1}{2940}\gamma(42a+25\gamma)$	$\frac{13}{245}$	$\frac{6}{49}$	$-\frac{228}{1\ 225}$	$\frac{2}{735}(21 a + 32 \gamma)$	$\frac{2}{1225}(84a+47\gamma)$
2	$\frac{1}{900}\gamma(30a-\gamma)$	$\frac{1}{25}$	$-\frac{149}{350}$	0	$\frac{2}{225}\left(15a+4\gamma\right)$	$\frac{4}{105} (6 a + \gamma)$
3	$\frac{1}{1\ 050}\gamma(20\ a\ -\ 7\ \gamma)$	$\frac{2}{1\ 575}$	$\frac{12}{175}$	$\frac{12}{25}$	$\frac{4}{1\ 575}(30\ a\ -\ 11\ \gamma)$	$\frac{1}{525}(120 \ a - 39 \ \gamma)$
4	$\frac{1}{350}\gamma(17 a + 2 \gamma)$	$\frac{46}{525}$	$\frac{288}{1\ 225}$	$-\frac{72}{175}$	$\frac{2}{525}(51 a + 29 \gamma)$	$\frac{32}{3675}$ (42 <i>a</i> + 13 $\gamma$ )
5	$\frac{1}{1\ 050}\gamma(49\ a\ +\ \gamma)$	$\frac{104}{1575}$ .	$\frac{752}{3\ 675}$	0	$\frac{2}{1575}(147 a + 55 \gamma)$	$\frac{8}{1\ 225}\ (49\ a\ +\ 15\ \gamma)$
6	$\frac{1}{900}\gamma(30a+19\gamma)$	$\frac{29}{225}$	$\frac{1}{2}\frac{691}{100}$	$\frac{12}{25}$	$\frac{2}{225}(15 a + 24 \gamma)$	$\frac{2}{525}$ (60 <i>a</i> + 47 $\gamma$ )
7	$\frac{1}{10}a\gamma$	$\frac{2}{15}$	$\frac{68}{175}$	.0	$\frac{2}{15}a$	$\frac{4}{175}(30 a + 7 \gamma)$
8	$\frac{1}{300} \gamma^2$	$\frac{1}{75}$	$. \frac{2}{35}$	0	$\frac{2}{75}\gamma$	$\frac{2}{35}\gamma$

$$K_{\rm i} = c_{\rm i} \left(\frac{\pi\rho}{6\,u}\right)^2 z ,$$
  
$$J_{\rm R} = 2 \left(\frac{\pi\rho}{6\,u}\right)^2 z ,$$

1 2

(43) where z + 1 is the number of molecules forming an assemblage; the L<sub>n</sub>(y<sub>1</sub>, ± y<sub>2</sub>) are Langevin functions
(44) [18]:

$$L_n(y_1, \pm y_2) = \frac{\int_0^{\pi} \cos^n \theta_{pq} \exp\{y_1 \cos \theta_{pq} \pm y_2 \cos^2 \theta_{pq}\} \sin \theta_{pq} d\theta_{pq}}{\int_0^{\pi} \exp\{y_1 \cos \theta_{pq} \pm y_2 \cos^2 \theta_{pq}\} \sin \theta_{pq} d\theta_{pq}}$$
(45)

whereas the coefficients  $b_i$ ,  $c_i$  are given in table V. The higher and higher approximations to the effective optical anisotropy (7)-(9) now become :

$$\Gamma_0^2 = \gamma^2 \left\{ 1 + \frac{1}{2} z [3 L_2(y_1, \pm y_2) - 1] \right\},$$
(46)

$$\Gamma_1^2 = -\left\{ 2 a \gamma (3 a - \gamma) + 2 \gamma^2 (3 a + \gamma) L_2(y_1, \pm y_2) \right\} \frac{\pi \rho}{6 u} z , \qquad (47)$$

$$\Gamma_{2}^{2} = \left\{ 18 a^{4} - 18 a^{3} \gamma + 16 a^{2} \gamma^{2} - \frac{1}{3} a \gamma^{3} - \frac{2}{3} \gamma^{4} + \gamma^{2} \left( 6 a^{2} + 5 a \gamma - \frac{3}{2} \gamma^{2} \right) L_{2}(y_{1}, \pm y_{2}) + \frac{7}{2} \gamma^{4} L_{4}(y_{1}, \pm y_{2}) \right\} \left( \frac{\pi \rho}{6 u} \right)^{2} z .$$
(48)

3.2.2 Molecules with negative anisotropy of linear optical polarizability ( $\gamma < 0$ ). — Molecules with a negative anisotropy ( $\gamma < 0$ ) tend to align with dipoles parallel (Fig. 1b). Their geometrical axes are then parallel to the vector connecting their centres as described by the relation :  $\cos \theta_p = \cos \theta_q = \cos \theta_{pq} = 1$ . The energy (26) does not depend on the angles  $\theta_{pq}$ ,  $\theta_p$ ,  $\theta_q$ , and we have  $J_A = z$ , whereas the parameters  $J_i$ ,  $K_i$  and  $J_R$ 

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are now given by (42), (43) and (44), respectively. The coefficients  $b_i$  and  $c_i$  for this configuration (as well as for the antiparallel one) are given in table V. The effective optical anisotropy (7)-(9) now becomes :

$$\Gamma_0^2 = \gamma^2 (1+z) , (49)$$

$$\Gamma_1^2 = 4 \,\gamma (3 \,a^2 + 2 \,a\gamma + \gamma^2) \frac{\pi \rho}{6 \,\mu} z \,, \tag{50}$$

$$\Gamma_2^2 = 2\left(9 a^4 + 18 a^3 \gamma + 23 a^2 \gamma^2 + \frac{14}{3} a\gamma^3 + 6 \gamma^4\right) \left(\frac{\pi\rho}{6 u}\right)^2 z .$$
 (51)

4. Numerical calculations and conclusions. — We carried out numerical calculations for two selected liquids, namely CH<sub>3</sub>CN and CHCl<sub>3</sub>, with axially-symmetric molecules possessing positive and, respectively, negative anisotropy of their linear optical polarizability. Table I gives the properties characterizing the two liquids as well as their molecules. The effective optical anisotropy  $\Gamma_{exp}^2$ , determined from anisotropic light scattering measurements, differs from the polarizability anisotropy of the isolated molecule  $\gamma^2$ , the difference being due to contributions from various interactions. This difference  $\Gamma_{exp}^2 - \gamma^2$  is positive in both liquids.

With the aim of calculating strictly  $\Gamma_{inter}^2$  — the influence of interactions on the effective optical anisotropy — we took into consideration moreover a higher approximation to effective anisotropy in the isotropic molecule approximation [19] :

$$\Gamma_3^2 = 36 a^5 \langle r^{-9} \rangle. \tag{52}$$

We performed our numerical calculations of the parameters  $\langle r^{-n} \rangle$  with the function  $g(r_{pq})$  in the form :

$$g(r_{pq}) = g_0(r_{pq}) + \rho g_1(r_{pq}) + \rho^2 g_2(r_{pq}) + \cdots, \quad (53)$$

where

$$g_0(r_{pq}) = \exp\{-U(r_{pq})/kT\}$$

the potential  $U(r_{pq})$  being of the Lennard-Jones (18-6) type;  $g_1(r_{pq})$  and  $g_2(r_{pq})$  are successive approximations to the distribution function in the rigid sphere approximation, and are to be found in reference [20]. In table IV we give the contributions to the effective optical anisotropy from various types of interaction calculated in accordance with the considerations of section 3.1. In the case of the liquid CH<sub>3</sub>CN, the

TABLE	V
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Coefficients  $b_i$  and  $c_i$  for antiparallel and parallel configuration

	Antiparallel	Parallel
$b_1$	$-\frac{1}{2}L_2(y_1, \pm y_2)$	1
$b_2$	- 1	2
<i>c</i> <sub>1</sub>	$\frac{1}{2} \left[ L_4(y_1, \pm y_2) - \frac{6}{25} \right]$	$\frac{47}{25}$
<i>c</i> <sub>2</sub>	$-\frac{1}{2}L_2(y_1, \pm y_2)$	1
<i>c</i> <sub>3</sub>	$-\frac{3}{10}$	6 5
<i>c</i> <sub>4</sub>	$-\frac{3}{5}$	$\frac{42}{5}$
<i>c</i> <sub>5</sub>	$-\frac{1}{3}$	$\frac{8}{3}$
<i>c</i> <sub>6</sub>	$\frac{1}{2}\left[L_2(y_1,\pm y_2)-\frac{2}{3}\right]$	$\frac{5}{3}$
<i>c</i> <sub>7</sub>	- 1	2
c <sub>8</sub>	$\frac{1}{2}$ 3 $L_2(y_1, \pm y_2) - 1$	1

decisive contribution, markedly in excess of all the others, is due to dipole-dipole interaction. Twomolecule radial interactions yield a positive contribution, amounting to  $18,13 \times 10^{-48}$  cm<sup>6</sup>, whereas three-molecule radial interactions yield a negative contribution of  $-12,92 \times 10^{-48}$  cm<sup>6</sup>, thus jointly contributing  $5,21 \times 10^{-48}$  cm<sup>6</sup>.

In the case of  $CHCl_3$  the largest contribution to effective optical anisotropy is due to dispersional

#### TABLE IV

Interactions influence on the effective optical anisotropy (in units of  $10^{-48}$  cm<sup>6</sup>), at t = 25 °C

1	2	3	4	5	6	7	8	9	10	11
			_	_						
liquid	$\gamma^2$	disp	$\mu - \mu$	$\mu - \Theta$	$\Theta - \Theta$	$\alpha - \mu$	$\alpha - \Theta$	radial	$\Gamma_{inter}^{2} \\ (3+4+5+6+7+8+9)$	$\frac{\Gamma_{\mathbf{W}}^2}{(2+10)}$
CH₃CN	2.99	1.12	115.64	3.83	- 0.01	1.97	0.11	5.21	127.87	130.86
CHCl <sub>3</sub>	5.43	1.83	- 0.48			- 0.09	_	1.86	3.12	8.55

and radial interactions. It should be noted that the one from two-molecule radial interactions, described by the Lennard-Jones (18-6) potential is considerable amounting to  $77.58 \times 10^{-48}$  cm<sup>6</sup>, but is strongly lowered by the contribution from three-molecular radial interactions, eq. (23), which amounts to  $-75.72 \times 10^{-48}$  cm<sup>6</sup>. The negative sign of the contribution from dipole - dipole interaction  $(-0.48 \times 10^{-48} \text{ cm}^6)$  is due to the negative anisotropy of linear polarizability of the CHCl<sub>3</sub> molecule  $(\gamma < 0)$ .

The effective optical anisotropy thus calculated for CH<sub>3</sub>CN and CHCl<sub>3</sub> amounts to  $130.86 \times 10^{-48}$  cm<sup>6</sup> and  $8.55 \times 10^{-48}$  cm<sup>6</sup> respectively and differs from the experimentally determined values of  $5.33 \times 10^{-48}$  cm<sup>6</sup> and  $7.64 \times 10^{-48}$  cm<sup>6</sup> [10]. The divergence, in the case of CH<sub>3</sub>CN, is very considerable. Consequently, we assume the existence of twomolecule systems as well, as considered in section 3.2, i.e. that the molecules of CH<sub>3</sub>CN tend to array themselves in pairs with antiparallel dipoles and those of CHCl<sub>3</sub> with their dipoles parallel to each other. On this model we obtain by eq. (38), (39) for CH<sub>3</sub>CN  $y_1 = 3.68$  and  $y_2 = -0.02$  and hence by eq. (46)-(48) a value of  $\Gamma_{\parallel}^2 = 2.50 \times 10^{-48}$  cm<sup>6</sup>, where  $\Gamma_{\parallel}^2$ stands for the effective optical anisotropy of the molecule when in a two-molecule pair of antiparallel dipoles. Denoting by x the percentage of molecules forming two-molecular pairs and by  $\Gamma_{\rm W}^2$  the effective optical anisotropy of the molecule at weak interaction with its neighbours (Table IV), one can determine xby comparison with the value of  $\Gamma_{exp}^2$  from anisotropic light scattering measurements. One has :

$$\Gamma_{\exp}^{2} = x\Gamma_{\parallel}^{2} + (1 - x)\Gamma_{W}^{2}, \qquad (54)$$

whence

$$x = \frac{\Gamma_{\mathbf{W}}^2 - \Gamma_{\mathrm{exp}}^2}{\Gamma_{\mathbf{W}}^2 - \Gamma_{\parallel}^2}.$$
 (55)

Insertion into (55) of  $\Gamma_{\rm W}^2 = 130.86 \times 10^{-48} \text{ cm}^6$ ,  $\Gamma_{\rm exp}^2 = 5.33 \times 10^{-48} \text{ cm}^6$ , and  $\Gamma_{\parallel}^2 = 2.50 \times 10^{-48} \text{ cm}^6$  leads to x = 0.977.

Calculations along similar lines for CHCl<sub>3</sub> with  $\Gamma_{\parallel}^2 = 2.71 \times 10^{-48}$  cm<sup>6</sup> from eq. (49)-(51),  $\Gamma_{exp}^2 = 7.64 \times 10^{-48}$  cm<sup>6</sup> from table I, and  $\Gamma_{W}^2 = 8.55 \times 10^{-48}$  cm<sup>6</sup> from table IV lead, by eq. (55), to a value of x = 0.156.

These results show that, in liquid CH<sub>3</sub>CN, the vast majority of molecules form two-molecular systems with antiparallel dipoles of the component molecules. In liquid CHCl<sub>3</sub> the percentage of molecules involved in pairs is very markedly lower, quite obviously because the dipole moment of the CH<sub>3</sub>CN molecule is more than three times larger than the dipole moment of CHCl<sub>3</sub>. By the way, the percentage of molecules involved in pairs in these liquids is probably lower than the percentage calculated above, as in reality molecules in pairs are much closer to each other than the result of eq. (40), which describes the mean distance between molecules in the liquid. Even so, the above model of a liquid, composed of axially-symmetric molecules having a permanent electric dipole moment, provides an adequate interpretation of the effective experimental value of the optical anisotropy.

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### **APPENDIX A**

The contribution to effective optical anisotropy  $\Gamma_2^2$  from triple radial interactions of isotropically polarizable molecules is given by the following expression [2, 15, 19] :

$$\Gamma_{2}^{2} = 18 a^{4} \frac{\rho^{2}}{V} \iiint \{ 3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^{2} - r_{pq}^{2} r_{qr}^{2} \} r_{pq}^{-5} r_{qr}^{-5} g^{(3)}(\mathbf{r}_{p}, \mathbf{r}_{q}, \mathbf{r}_{r}) d\mathbf{r}_{p} d\mathbf{r}_{q} d\mathbf{r}_{r}, \qquad (A.1)$$

where  $\mathbf{r}_p$ ,  $\mathbf{r}_q$ ,  $\mathbf{r}_r$  are position vectors of molecules p, q, r whereas  $g^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)$  is the three-molecule radial correlation function which, in our case, takes the form :

$$g^{(3)}(\mathbf{r}_{p},\mathbf{r}_{q},\mathbf{r}_{r}) = \exp\{-U(r_{pq})/kT\} \exp\{-U(r_{qr})/kT\} \exp\{-U(r_{pr})/kT\}.$$
 (A.2)

On going over to co-ordinates attached to molecule q and on performing integration over  $\mathbf{r}_q$  in eq. (A.1), we get a six-dimensional integral in the variables  $r_{pq}$ ,  $\varphi_{pq}$ ,  $\theta_{pq}$ ,  $r_{qr}$ ,  $\varphi_{qr}$ ,  $\theta_{qr}$ . In order to calculate the integrals, we carry out the transformations indicated in reference [21]. We go over to variables  $\varphi^- = \varphi_{pq} - \varphi_{qr}$ ,  $\varphi^+ = \varphi_{pq} + \varphi_{qr}$ , and integrate over  $\varphi^+$ ; next, we perform a transformation from variables  $\cos \theta_{pq}$ ,  $\cos \theta_{qr}$ ,  $\varphi^-$  to  $\theta$ ,  $\alpha$ ,  $\beta$ , defined in figure 2. The Jacobian of this transformation is  $\sin \theta \cos \theta$ . Finally, on going over from  $\theta$  to  $r_{pr}$ , we have :

$$\Gamma_{2}^{2} = 36 a^{4} \pi \rho^{2} \int_{0}^{\infty} dr_{pq} r_{pq} \exp \left\{ - U(r_{pq})/kT \right\} \int_{0}^{\infty} dr_{qr} r_{qr} \exp \left\{ - U(r_{qr})/kT \right\} \int_{|r_{pq} - r_{qr}|}^{r_{pq} + r_{qr}} dr_{pr} r_{pr} \times \exp \left\{ - U(r_{pr})/kT \right\} \left\{ 3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^{2} - r_{pq}^{2} r_{qr}^{2} \right\} r_{pq}^{-5} r_{qr}^{-5} \int_{0}^{2\pi} d\alpha \int_{-\pi/2}^{+\pi/2} d\beta \cos \beta .$$
 (A.3)



FIG. 2. — Coordinate system for the calculation of the influence of triple molecular radial interactions on the effective optical anisotropy.

Integration in (A.3) over  $\alpha$  and  $\beta$  leads to eq. (23) since, for rigid spheres,

$$\int_{0}^{\infty} dr_{pq} r_{pq}^{-4} \exp\left\{- U(r_{pq})/kT\right\} \int_{0}^{\infty} dr_{qr} r_{qr}^{-4} \exp\left\{-U(r_{qr})/kT\right\} \int_{|r_{pq}-r_{qr}|}^{r_{pq}+r_{qr}} dr_{pr} r_{pr} \left\{3(\mathbf{r}_{pq}\cdot\mathbf{r}_{qr})^{2} - r_{pq}^{2} r_{qr}^{2}\right\} = 0.$$
(A.4)

Likewise, from the general expression (5), one can obtain a term in four-molecule correlations which, in atomic liquids, play an important role leading to a positive contribution [22].

#### **APPENDIX B**

In order to calculate the parameters  $\langle r^{-n} \rangle$  we have recourse to the following forms of the functions  $g_1$  and  $g_2$  from the expansion (53) [20]:

$$g_1(r) = \begin{cases} 2 \pi \sigma^3 \left[ \frac{2}{3} - \frac{1}{2} \frac{r}{\sigma} + \frac{1}{24} \left( \frac{r}{\sigma} \right)^3 \right], & \sigma \le r \le 2 \sigma \\ 0, & \text{otherwise} \end{cases}$$
(B.1)

$$g_2(r) = \varphi(r) + 2 \psi(r)$$
, (B.2)

$$\varphi(r) = \begin{cases} \pi^2 \sigma^6 \left[ -\left(\frac{r}{\sigma}\right)^6 / 1\ 260 + \left(\frac{r}{\sigma}\right)^4 / 20 - \left(\frac{r}{\sigma}\right)^4 / 6 - \left(\frac{r}{\sigma}\right)^2 / 4 + \frac{9}{5} \frac{r}{\sigma} - \frac{9}{4} + \frac{27}{70} \left(\frac{r}{\sigma}\right)^{-1} \right] \sigma \leqslant r \leqslant 3\sigma \\ 0, \quad \text{otherwise,} \end{cases}$$

$$\psi(r) = \begin{cases} \pi^2 \sigma^6 \left(\frac{r}{\sigma}\right)^6 / 1\ 260 - \left(\frac{r}{\sigma}\right)^4 / 20 + \left(\frac{r}{\sigma}\right)^3 / 6 + \left(\frac{r}{\sigma}\right)^2 / 4 - \frac{97}{60}\ \frac{r}{\sigma} + \frac{16}{9} - \frac{9}{35} \left(\frac{r}{\sigma}\right)^{-1} ], \ \sigma \le r \le 2\ \sigma \\ 0, \ \text{otherwise.} \end{cases}$$
(B.4)

Those parts of  $\langle r^{-n} \rangle$  which originate in the functions  $g_1$  and  $g_2$  are of the form :

<

$$\langle r^{-6} \rangle_1 = \frac{\pi^2 \rho^2}{18} (1 + 6 \ln 2),$$
 (B.5)

for  $n \ge 7$  .

$$\langle r^{-n} \rangle_1 = \frac{8 \pi^2 \rho^2}{\sigma^{n-6}} \left[ \frac{2}{3(n-3)} (1-2^{3-n}) - \frac{1}{2(n-4)} (1-2^{4-n}) + \frac{1}{24(n-6)} (1-2^{6-n}) \right], \quad (B.6)$$

and

$$\langle r^{-6} \rangle_2 = 4 \pi^3 \rho^3 \sigma^3 \left( \frac{1}{6} \ln \frac{4}{3} - \frac{37}{864} \right),$$
 (B.7)

$$r^{-9}\rangle_2 = 4 \pi^3 \rho^3 \left[ \frac{1}{1\ 260} \ln \frac{4}{3} + \frac{1\ 523}{217\ 728} \right];$$
 (B.8)

for n = 8 and  $n \ge 10$ 

$$\langle r^{-n} \rangle_{2} = 4 \pi^{3} \rho^{3} \sigma^{9-n} \left[ \frac{1}{1 \ 260(n-9)} \left( 1 - 2^{10-n} + 3^{9-n} \right) - \frac{1}{20(n-7)} \left( 1 - 2^{8-n} + 3^{7-n} \right) + \frac{1}{6(n-6)} \left( 1 - 2^{7-n} + 3^{6-n} \right) + \frac{1}{4(n-5)} \left( 1 - 2^{6-n} + 3^{5-n} \right) - \frac{97}{60(n-4)} \left( \frac{86}{97} - 2^{5-n} + \frac{108}{97} 3^{4-n} \right) + \frac{16}{9(n-3)} \left( \frac{47}{64} - 2^{4-n} + \frac{81}{64} 3^{3-n} \right) - \frac{9}{35(n-2)} \left( \frac{1}{2} - 2^{3-n} + \frac{3}{2} 3^{2-n} \right) \right].$$
(B.9)

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