

## Molecular Interaction in the Classical Theory of Light Scattering

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Presented by A. JABŁOŃSKI on December 23, 1957

The aim of the present paper is to give an account of the effect of interaction between optically anisotropic molecules on the scattering of light in liquids, based on a method previously elaborated [1].

Let us consider a volume  $V$  of the liquid placed at the origin of a system of reference  $(x, y, z)$ , and illuminated by a beam of natural light. We assume the linear dimensions of the volume  $V$  to be small as compared to the incident wavelength, and the volume large enough to contain a great number of molecules.

The component in the direction  $\vec{s}$  of the intensity of the light scattered by the volume  $V$  is given [2] by the equation:

$$(1) \quad I_s = \left(\frac{2\pi}{\lambda}\right)^4 \frac{1}{r^2} \left\langle \left( \Delta \sum_q \vec{p}_q \cdot \vec{s} \right)^2 \right\rangle_{\mathcal{F}},$$

where  $\lambda$  denotes the wave-length *in vacuo* of the incident beam,  $\vec{r}$  — the distance from the origin to the point of observation,  $\vec{p}_q$  — the electric moment of the  $q$ -th molecule induced by the electric vector of the local field  $\vec{E}_0$  of the light wave,  $\vec{s}$  — the unit vector perpendicular to  $\vec{r}$  and determining the position of analyzer, forming the angle  $\Omega$  with the vector  $\vec{E}_0$ .

The magnitude  $\langle (\Delta \sum_q \vec{p}_q \cdot \vec{s})^2 \rangle_{\mathcal{F}}$  represents the statistical mean value of the square of the fluctuation of the  $s$ -component of the electric moment in volume  $V$ . Assuming Gibbs' distribution, the following relation holds for a system in thermodynamical equilibrium:

$$(2) \quad \left\langle \left( \Delta \sum_q \vec{p}_q \cdot \vec{s} \right)^2 \right\rangle_{\mathcal{F}} = C_n \iint \dots \int \left( \Delta \sum_q \vec{p}_q \cdot \vec{s} \right)^2 e^{-\frac{U_{\mathcal{F}} + U_N}{kT}} d\tau_1 d\tau_2 \dots d\tau_N;$$

here,  $C_n$  denotes the normalization factor,  $k$  — Boltzmann's constant,  $T$  — the Kelvin temperature of the system,  $d\tau_q$  — the configurational

element determining the position and the orientation of the  $q$ -th molecule,  $U_{\mathcal{F}}$  — the potential energy of the system in the external field  $\mathcal{F}$  and  $U_N$  — the potential energy of the interaction existing between the molecules of the liquid.

Let  $N$  be the number of molecules within volume  $V$ ; we then have, for the fluctuation of  $N$  and  $\vec{p}_q$ :

$$(3) \quad \Delta N = N - \langle N \rangle_{\mathcal{F}} \quad \text{and} \quad \Delta \vec{p}_q = \vec{p}_q - \langle \vec{p}_q \rangle_{\mathcal{F}},$$

and Eq. (1) may be rewritten as follows:

$$(4) \quad I_s = \left(\frac{2\pi}{\lambda}\right)^4 \frac{1}{r^2} \left( \langle (\Delta N)^2 \rangle_{\mathcal{F}} \langle \vec{p}_q \cdot \vec{s} \rangle_{\mathcal{F}}^2 + \left\langle \left( \sum_{q=1}^{\bar{N}} \Delta \vec{p}_q \cdot \vec{s} \right)^2 \right\rangle_{\mathcal{F}} \right),$$

where the average number of molecules in  $V$  has been denoted by  $\bar{N}$ .  
The magnitude

$$(5) \quad I_s^{(1)} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{1}{r^2} \langle (\Delta N)^2 \rangle_{\mathcal{F}} \langle \vec{p}_q \cdot \vec{s} \rangle_{\mathcal{F}}^2,$$

represents the part of the intensity  $I_s$  scattered as a result of fluctuations of the density of the medium, whereas

$$(6) \quad I_s^{(2)} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{1}{r^2} \left( \left\langle \left( \sum_{q=1}^{\bar{N}} \vec{p}_q \cdot \vec{s} \right)^2 \right\rangle_{\mathcal{F}} - \left\langle \sum_{q=1}^{\bar{N}} \vec{p}_q \cdot \vec{s} \right\rangle_{\mathcal{F}}^2 \right),$$

is the intensity of the light scattered as a result of fluctuations of the moment of the molecule, that is, as a result of fluctuations of its anisotropy and orientation and, consequently, of its interaction with other molecules.

The value of the mean square fluctuation of the number of molecules,  $\langle (\Delta N)^2 \rangle_{\mathcal{F}}$ , within the volume  $V$  of the liquid, was computed by M. Smoluchowski [3] and A. Einstein [4], and is given by the equation

$$(7) \quad \langle (\Delta N)^2 \rangle_{\mathcal{F}} = \gamma \bar{N}; \quad \gamma = \beta N_0 kT,$$

wherein  $N_0 = N/V$  is the number of molecules in unit volume, and  $\beta = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$  — the coefficient of isothermic compressibility of the medium ( $v$  denotes the specific volume,  $p$  — the pressure). For an ideal gas,  $\gamma = 1$ .

In the weak field of a light wave deformational effects may be neglected. Hence, for the  $q$ -th optically anisotropic molecule we may write

$$(8) \quad \vec{p}_q \cdot \vec{s} = \sum_{ij} a_{ij}^0 \alpha_i^{(q)} \beta_j^{(q)} F_0 = \sum_{ijkl} a_{ij}^0 \omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \alpha_k^{(p)} \beta_l^{(p)} F_0,$$

wherein  $a_{ij}^0$  are the components of the tensor of optical polarizability of the molecule,  $\alpha_i^{(q)}$ ,  $\alpha_k^{(p)}$  and  $\beta_j^{(q)}$ ,  $\beta_l^{(p)}$  — the directional cosines determining the orientation of the  $q$ -th and  $p$ -th molecule within the system of reference  $(x, y, z)$  with regard to the vectors  $\vec{F}_0$  and  $\vec{s}$ ,  $\omega_{ik}^{(pq)}$  — is the cosine of the angle formed by the axis  $i$  of the system  $(X_i^{(p)})$  and the axis  $k$  of  $(X_k^{(q)})$  ( $(X_i^{(p)})$ ,  $(X_k^{(q)})$  are systems attached to the  $p$ -th and  $q$ -th molecules respectively), and  $i, j, k, l$  — summation indices taking the values 1, 2, 3.

Assuming the tensor of optical polarizability of the molecule  $a_{ij}^0$  to be referred to the principal axes, on isotropic averaging we may rewrite Eqs. (5) and (6), with regard to (7) and (8), as follows:

$$(9) \quad I_s^{(1)} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\bar{N}}{r^2} \frac{\cos^2 \Omega}{9} \gamma \sum_{ij} a_{ii}^0 a_{jj}^0 F_0^2,$$

$$(10) \quad I_s^{(2)} = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\bar{N}}{r^2} \frac{\cos^2 \Omega}{90} \sum_{ij} a_{ii}^0 a_{jj}^0 \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle F_0^2;$$

the constant index  $p$  refers to the molecule whose position has been fixed.

After substituting (9) and (10) in the fundamental expression (1), a general formula determining the component of the light scattered by the liquid is obtained:

$$(11) \quad I_s = I_0 \left(\frac{2\pi}{\lambda}\right)^4 \frac{\bar{N}}{r^2} \left(\frac{n^2 + 2}{3}\right)^2 \sum_{ij} a_{ii}^0 a_{jj}^0 \times \\ \times \left( \frac{\cos^2 \Omega}{9} \gamma + \frac{\cos^2 \Omega + 3}{90} \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle \right),$$

wherein  $I_0$  denotes the intensity of the incident beam,  $n$  — the optical refractive index and:

$$(12) \quad \langle X(\omega_{ij}) \rangle = C'_n \int \dots \int X(\omega_{ij}) e^{-\frac{U_N}{kT}} d\tau_1 d\tau_2 \dots d\tau_N.$$

It is worth stressing that the expression

$$\left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle$$

appearing in (11) and defining the molecular interaction of the  $N$  molecules present in the volume  $V$  of the liquid also enters the formulae describing the Kerr and Cotton-Mouton constants and those yielding the variation of the permittivity in strong electric and magnetic fields [1], [5]-[7]. Thus, e. g. we have, for the Cotton-Mouton constant,

$$(13) \quad C = \frac{\pi N_0}{15} \left(\frac{n^2 + 2}{3n}\right)^2 \sum_{ij} \left( 3c_{ij,ij}^{om} - c_{ii,jj}^{om} + \frac{a_{ii}^0 a_{jj}^m}{kT} \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle \right) \left(\frac{F_m}{H}\right)^2,$$

and for the Kerr constant

$$(14) \quad K = \frac{\pi N_0}{15} \left( \frac{n^2 + 2}{3n} \right)^2 \sum_{ij} \left( 2c_{ijij}^{0e} + \frac{a_{ii}^0 a_{jj}^e}{kT} \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle + \right. \\ \left. + \frac{4b_{ijij}^{0e} \mu_j}{kT} \left\langle \sum_{q=1}^N \omega_{ij}^{(pq)} \right\rangle + \frac{a_{ii}^0 \mu_j^2}{k^2 T^2} \left\langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pr)} - \omega_{ij}^{(qr)}) \right\rangle \right) \left( \frac{F_e}{E} \right)^2,$$

with  $\mu_i$  denoting the components of the permanent electric moment of the molecule,  $a_{ij}^e$  and  $a_{ij}^m$  — those of the tensor of electric and magnetic polarizability of the molecule, respectively,  $b_{ijij}^{0e}$ ,  $c_{ijij}^{0e}$  and  $c_{ij,ij}^{0m}$  — those of the tensors of electro-optical and magneto-optical deformation of the molecule,  $\vec{E}$  and  $\vec{H}$  the applied electric and magnetic field strength and  $F_e$  and  $F_m$  the local electric and magnetic field.

The degree of depolarization of the light scattered by the liquid (if the primary beam is not polarized) is given by the following general expression obtained from (11):

$$(15) \quad D_n = \frac{6 \sum_{ij} a_{ii}^0 a_{jj}^0 \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle}{\sum_{ij} a_{ii}^0 a_{jj}^0 (10\gamma + 7 \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle)}.$$

Similarly, expression (11) yields a general formula for the light scattering constant of a liquid:

$$(16) \quad R = \frac{1}{2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{9} \right)^2 N_0 \sum_{ij} a_{ii}^0 a_{jj}^0 \left( \gamma + \frac{13}{10} \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle \right).$$

For molecules having axial symmetry,  $a_{11}^0 = a_{22}^0 \neq a_{33}^0$  and expressions (15) and (16) take the form

$$(17) \quad D_n = \frac{6\delta_0^2 R_{CM}}{5\gamma + 7\delta_0^2 R_{CM}},$$

and

$$(18) \quad R = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4 N_0} \left( \gamma + \frac{13}{5} \delta_0^2 R_{CM} \right),$$

where

$$(19) \quad R_{CM} = \frac{1}{2} \left\langle \sum_{q=1}^N (3 \cos^2 \theta_{pq} - 1) \right\rangle = 1 + \frac{3}{2} \left\langle \sum_{q=1}^Z (\cos^2 \theta_{pq} - \frac{1}{3}) \right\rangle,$$

represents the so-called correlation factor accounting for the molecular interaction of the molecules of the liquid;  $\theta_{pq}$  denotes the angle between the axis of symmetry of the  $p$ -th and that of the  $q$ -th molecule and  $Z$  — the number of neighbours of a molecule

$$(20) \quad \delta_0 = \frac{a_{33}^0 - a_{11}^0}{a_{33}^0 + 2a_{11}^0}$$

is termed the optical anisotropy of the molecule.

Similarly, from (13) we obtain, for the Cotton-Mouton constant (for  $c_{ij,kl}^{0m} = 0$ ):

$$(21) \quad C = \frac{\delta_0 \delta_m \chi_m}{10kTN_0} \frac{(n^2-1)(n^2+2)}{n^2} \left(\frac{F_m}{H}\right)^{\frac{1}{2}} R_{CM},$$

and from (14) for Kerr's constant (for  $\mu_i = b_{ijk}^{0e} = c_{ijkl}^{0e} = 0$ ):

$$(22) \quad K = \frac{\delta_0 \delta_e \chi_e}{10kTN_0} \frac{(n^2-1)(n^2+2)}{n^2} \left(\frac{F_e}{E}\right)^{\frac{1}{2}} R_{CM},$$

where

$$(23) \quad \delta_m = \frac{a_{33}^m - a_{11}^m}{a_{33}^m + 2a_{11}^m} \quad \text{and} \quad \delta_e = \frac{a_{33}^e - a_{11}^e}{a_{33}^e + 2a_{11}^e}$$

represent the magnetic and electric anisotropy of the molecule;  $\chi_m$  and  $\chi_e$  are the magnetic and electric susceptibilities and  $R_{CM}$  is defined by Eq. (19).

On neglecting molecular interaction ( $U_N = 0$ ), we have

$$(24) \quad R_{CM} = 1 + \frac{2}{3} Z (\overline{\cos^2 \theta} - \frac{1}{3}) = 1$$

and the formulae (17), (18) and (21), (22) obtained take the form of those already known, applying to gases and liquids [2], [8]-[13].

The correlation factor  $R_{CM}$  given by (19) has been obtained recently in the theory of the effects of molecular orientation [1], [7]. At an earlier date, A. Piekara [9], [10] calculated  $R_{CM}$  in the theory of the Cotton-Mouton effect for dipole pairwise coupling of the molecules in the liquid. Quite recently, A. D. Buckingham [5], in his theory of the second Kerr constant virial coefficient, calculated  $(R_{CM} - 1)$  for various forms of the interaction energy of two molecules.

If the correlation factor  $R_{CM}$  be determined from Eqs. (17), (21) and (22) using experimental values of  $D_n$ ,  $C$  and  $K$ , the magnitude of the effect of molecular interaction on the scattering of light in a liquid is obtained, and thus the consistency of the theory is put to the test.

The following table brings the values of the correlation factor  $R_{CM}$  for a number of polar and non-polar liquids; it will be seen that the values of  $R_{CM}$  as obtained from the various effects are nearly the same.

TABLE

	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>12</sub>	CS <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	CHCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
$\mu \cdot 10^{18}$	0	0	0	0.37	1.05	1.6	4.2
$R_{CM}$ from the degree of depolarization of light	0.52	0.45	0.76	0.83	0.91	1.24	1.56
$R_{CM}$ from the Cotton-Mouton constant	0.62	—	0.94	1.02	1.05	1.35	1.68
$R_{CM}$ from Kerr's constant	0.57	0.47	0.83	—	—	—	—

The constant of scattering of light in benzene was given as  $R = 48 \cdot 10^{-1} \text{ cm.}^{-6}$  by C. Carr and B. Zimm [13], whereas measurements by J. Cabannes, recently corroborated by M. Harrand [8], [13] yielded  $R = 28 \cdot 10^{-6} \text{ cm.}^{-1}$  (for  $T = 298^\circ\text{K}$ ,  $\lambda = 4360 \text{ \AA}$ ).

On calculating the coefficient of scattering  $R$  from Eq. (18) we obtained the following values:  $R = 27 \cdot 10^{-6} \text{ cm.}^{-1}$  for  $R_{CM} = 0.52$  as computed from the degree of depolarization of scattered light (17),  $R = 30 \cdot 10^{-6} \text{ cm.}^{-1}$  for  $R_{CM} = 0.62$  as computed from the Cotton-Mouton constant (21), and  $R = 28.5 \cdot 10^{-6} \text{ cm.}^{-1}$  for  $R_{CM} = 0.57$  as computed from Kerr's constant (22). Thus, the present theory will be seen to be in satisfactory agreement with the measurements of J. Cabannes and M. Harrand.

A detailed account of our work will be published in *Acta Physica Polonica*, where a full list of references will be given.

The author wishes to express his sincere thanks to Professor A. Piekara, Director of the Laboratory of Dielectrics at the Institute of Physics of the Polish Academy of Sciences for his valuable advice and for suggesting the present problem.

#### Summary

A previously elaborated method [1] was applied for determining the general form of the effect of molecular interaction on the scattering of light in a liquid. This effect is determined by the correlation factor  $R_{CM}$  already obtained in the theory of the effects of molecular orientation [1], [7]. The value of  $R_{CM}$  has been computed for a number of liquids from the degree of depolarization of scattered light  $D_n$ , from the Cotton-Mouton constant  $C$  and from Kerr's constant  $K$ .

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#### REFERENCES

- [1] A. Piekara and S. Kielich, *J. Phys. Rad.*, **18** (1957), 490.
- [5] M. Born, *Optik*, Berlin, 1933.
- [3] M. Smoluchowski, *Ann. Physik*, **25** (1908), 205.

- [4] A. Einstein, Ann. Physik, **33** (1910), 1275.
- [5] A. D. Buckingham, Proc. Phys. Soc., A **68** (1955), 910.
- [6] — J. Chem. Phys., **25** (1956), 428.
- [7] S. Kielich, Acta Phys. Polonica, (1957) (in press).
- [8] J. Cabannes, *La diffusion de la lumière*, Paris, 1929.
- [9] A. Piekara, C. R., **208** (1939), 990.
- [10] — Acta Phys. Polonica, **10** (1950), 37, 107.
- [11] R. Servant, J. Phys. Rad., **4** (1943), 105.
- [12] — Ibid. **11** (1950), 153.
- [13] M. Harrand, Ann. de Phys., **8** (1953), 646.