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Abstract

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RAYLEIGH SCATTERING OF LIGHT AND ORIENTATIONAL ORDERING OF MOLECULES

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Let a homogeneous isotropic system consist of $N = \sum_i N_i$ $(i = 1, \dots, M)$ molecules and occupy a volume V. The index i denotes the species of molecule. Then the intensity I_a of monochromatic light scattered by fluctuations of anisotropy at an angle θ to the direction of the incident unpolarized radiation, whose intensity is equal to I_0, can be expressed by the function

$$I_a = \frac{I_0}{2r^2}\left(1+\cos^2\theta\right)\left(\frac{2\pi}{\lambda}\right)^4 \left[\sum_j \left(\Delta\varepsilon_{jlk}^{aH}\right)\frac{v_j}{4\pi}\right]^2, \tag{1}$$

where the summation is carried out over independent volume elements $v_j \ll \lambda^3$, $\sum_j v_j = V$; $\Delta\varepsilon_{jlk}^{aH}$ is the fluctuation of the optical dielectric permittivity in the volume element v_j, caused by fluctuations of orientation; λ is the wavelength of light; r is the distance from the center of the scattering volume to the observation point. Using the Lorentz-Lorenz equation, after a series of known transformations (1) we obtain

$$I_a = Q\left\{\sum_{k=y,z}\sum_{i=1}^{M}\sum_{j=1}^{N_i}\overline{(\Delta a_{zkij})^2} + \sum_{k=y,z}\sum_{i=1}^{M}\sum_{j=1}^{N_i}\sum_{i'=1}^{M}{\sum_{j'=1}^{N_{i'}}}{}'\,\overline{\Delta a_{zkij}\Delta a_{zki'j'}}\right\}, \tag{2}$$

$$Q = \frac{I_0}{2r^2}\left(1+\cos^2\theta\right)\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^4.$$

Here y and z are Cartesian coordinate axes characterizing the direction of the electric vector of the radiation; Δa_{zkij} and $\Delta a_{zki'j'}$ are the components of the fluctuation of the anisotropic polarizability of molecule j of species i, or, respectively, of molecule j' of species i'; n is the refractive index.

The first part of equation (2) expresses the contribution from independent orientations of all molecules; the second part takes into account the connection between the orientations of different molecules ij and $i'j'$.

As we showed earlier (2), the method of differentiating the Lorentz-Lorenz equation proposed by Rocard (3) does not withstand criticism. The correct method is the differentiation method applied earlier by Einstein (4). Therefore, in equation (2) the factor $(n^2+2)/3$ enters to the 4th power, and not to the 2nd.

Let molecule ij have an arbitrary but fixed orientation. Let us place in the molecule a coordinate system such that the axes $\xi_{ij}\eta_{ij}\zeta_{ij}$ coincide with the principal semiaxes of the polarizability ellipsoid of molecule ij. Molecule $i'j'$ does not have a fixed orientation. Introduce coordinate axes $\xi_{i'j'}\eta_{i'j'}\zeta_{i'j'}$, coinciding with the principal semiaxes of the polarizability ellipsoid of molecule $i'j'$ and changing their position in space together with molecule $i'j'$. Applying the calculation method developed by M. Born, R. Gans, and others (see, for example, (1), pp. 238-241), one can obtain the following

general expression for I_a:

$$I_a = \frac{13}{45}QN\left\{\sum_{i=1}^{M} x_i\gamma_i^2 + \frac{1}{2}\sum_{\varkappa}\sum_{\sigma}\sum_{i}\sum_{i'} x_i x_{i'} a_{\varkappa i} a_{\sigma i'}\left[3\overline{(\varkappa\sigma)^2}-1\right]\right\},$$

$$\gamma^2 = \frac{1}{2}\left[(a_{\xi i}-a_{\eta i})^2 + (a_{\xi i}-a_{\zeta i})^2 + (a_{\eta i}-a_{\zeta i})^2\right],$$

$$\varkappa = \xi_{ij}, \eta_{ij}, \zeta_{ij}; \qquad \sigma = \xi_{i'j'}, \eta_{i'j'}, \zeta_{i'j'}. \tag{3}$$

Here $a_{\varkappa i}$ and $a_{\sigma i'}$ are the principal values of the polarizability tensor of molecules i and i'; $\overline{(\varkappa\sigma)^2}$ is the statistical mean of the square of the cosine of the angle between the axes $\varkappa$ and σ. For a chaotic distribution of molecular orientations, all $\overline{(\varkappa\sigma)^2} = 1/3$. Then

$$I_a = \frac{13}{45}QN\sum_{i=1}^{M} x_i\gamma_i^2. \tag{4}$$

For a one-component system, in the general case,

$$I_a = \frac{13}{45}QN\left\{\gamma^2 + \frac{1}{2}\sum_{\varkappa}\sum_{\sigma} a_{\varkappa} a_{\sigma}\left[3\overline{(\varkappa\sigma)^2}-1\right]\right\}. \tag{5}$$

Equation (5) is easily transformed into the expression obtained by Anselm (^{5}).

Table 1

Rayleigh scattering and orientational order of molecules in pure liquids

Liquid	t, ° C	n_D	$\frac{(n_D^2+2)^2}{3}$	$\frac{(n_D^2+2)^4}{3}$	λ, Å	$a_\xi \cdot 10^{23}$	$a_\eta \cdot 10^{23}$	$a_\zeta \cdot 10^{23}$	I	$\Delta \cdot 100$	I_a, exp.	I_a, by eq. (5)	I_a, by ([3], [11])	$\overline{(\sigma,\chi)^2}$
C_6H_6	25	1.501	2.01	4.02	5460	1.114	1.114	0.733	1.00	42.0	0.64	0.58	0.39	1/5
C_6H_5Cl	20	1.525	2.08	4.30	4360	1.470	1.240	0.818	1.47	60.0	1.19	1.16	0.82	1/7
C_6H_5Br	25	1.557	2.20	4.86	5460	1.684	1.213	0.956	1.78	(14) 62.0	1.48	1.72	1.14	1/9
$C_6H_5NO_2$	25	1.554	2.16	4.70	5460	1.600	1.360	0.690	3.14	(13) 71.5	2.90	2.89	1.77	1/3
$C_6H_5CH_3$	25	1.494	2.00	4.00	5460	1.377	1.253	0.904	1.12	48.0	0.79	0.74	0.49	1/3
o-$C_6H_5(CH_3)_2$	25	1.503	2.02	4.07	5460	1.639	1.352	1.075	1.31	55.0	1.00	0.82	0.55	1/3
$(CH_3)_2CO$	20	1.359	1.64	2.70	4360	0.70	(9) 0.684	0.482	0.26	25.0	0.110	0.110	0.098	1/3
CS_2	25	1.625	2.40	5.78	5460	–	–	–	4.12	62.0	3.42	4.15*	2.30	~ 1/3
$CHCl_3$	20	1.446	1.86	3.46	5460	0.90	0.67	0.67	0.40	24.2	0.17	0.18	0.13	1/3
$(C_2H_5)_2O$	25	1.350	1.62	2.63	5460	0.807	1.120	0.673	0.35	(11) 7.0	0.049	0.038	0.031	1/3
CH_3OH	20	1.330	1.60	2.55	4360	0.400	0.256	0.314	0.14	(2) 7.3	0.021	0.085	0.079	~ 1/9

* Calculated from the data of ([9]) on δ^2 and a.

Comparing the values of I_a calculated from equation (4) with the experimental values, and using equations (3) or (5), one can obtain information on the orientational order of molecules. The results of such calculations for a number of individual liquids are given in Table 1. As the unit of measurement of I_a at wavelength λ, the total intensity of Rayleigh scattering of light of the same wavelength in benzene at 25° was chosen. In these units

$$I_a = \frac{R_a}{R_{C_6H_6}}, \qquad R = \frac{I}{I_0}\frac{r^2}{V}.$$

For the scattering coefficient of benzene $R_{C_6H_6}$ we chose the "high" values obtained by Carr and Zimm ([6]) and by a number of other authors, taking into account the correction for the refractive index and the scattering volume. At 25° these values are $48.5 \cdot 10^{-6}$ ($\lambda = 4358$ Å) and $16.3 \cdot 10^{-6}$ ($\lambda = 5460$ Å); at 20°, the values of $R_{C_6H_6}$ are $46.8 \cdot 10^{-6}$ and $15.7 \cdot 10^{-6}$, respectively. Table 1 indicates the wavelength of the radiation for which the calculation was performed. The values $a_\varkappa$ were taken from the works of Lefèvre et al. ([7–9]). The values $a_\varkappa$ given in the works of Stuart and Volkmann (see, for example, ([10])) are apparently incorrect ([5]). Attempts to use these values ([8]) for calculating I_a in a number of cases lead to clearly erroneous results. Table 1 gives the results of calculating I_a using the "low" values ([11]) of $R_{C_6H_6}$ and replacing the factor $[(n^2+2)/3]^4$ by $[(n^2+2)/3]^2$. Since equation (4) contains squares of differences of the values

a_x, possible errors in the values of a_x strongly affect the results of the calculation, which should be kept in mind when comparing experiment with theory. Table 1 shows that for all liquids except methyl alcohol, the values of I_a calculated from equation (4) using $[(n^2+2)/3]^4$ and high values of $R_{C_6H_6}$, within the limits of possible errors, coincide with the values of I_a calculated from experimental data on the total intensity and the degree of depolarization Δ of the scattered light.

It should be noted that, in calculating I_a for methyl alcohol, values known to be inaccurate were used for want of better ones ([10]). However, it may be thought that the discrepancy between equation (4) and experiment in this case is due not only to the inaccuracy of the values of a_x, but also to the orientational ordering of the CH_3OH molecules. Acetone, nitrobenzene, chlorobenzene, bromobenzene, chloroform, and ether approximately follow the theory of polar dielectrics developed by Onsager, which gave grounds to suppose the absence, or else the insignificance, of orientational order in these liquids ([12]). The data of Table 1 constitute new, independent evidence for this assertion.

In summary, we may say that homogeneous, isotropic molecular systems (gases, liquids, etc.) can be divided into two groups: a) systems that do not have orientational ordering of molecules, and b) systems that do have orientational ordering of molecules. The investigation carried out by us makes it possible to establish a physical criterion for such a division and, in a number of cases, to determine the character of the orientational ordering of molecules by calculating $(\varkappa\sigma)^2$ from data on I_a and a_x.

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