Investigation of the intensity of molecular scattering of light in liquids

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Results are presented of an experimental investigation of the absolute light scattering coefficient in such simple liquids as benzene, toluene, acetone, and carbon tetrachloride. The data can be described, within an experimental error of 2–2.5%, by the relaxation theory of light scattering. The data for the scattering coefficient in benzene agree to within ±5% with most of the other experimental data. Some consequences of the relaxation theory of light scattering for glasses and vitrifying liquids are discussed.

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As is well known,[1] the total intensity I of isotropically scattered light in liquids is proportional to the mean square fluctuations of the permittivity of the medium $\langle\delta\varepsilon^2\rangle$ and is directly expressed in terms of the fluctuation of the macroscopic variables describing the state of the liquid. One of the basic difficulties in understanding this phenomenon, which was first encountered and investigated by Fabelinskiĭ, is associated with the presence in most liquids of internal processes of establishing equilibrium (relaxation processes) and the necessity of taking into account the fluctuations of the "hidden" variables, which characterize these processes.[2]

A general relaxation theory of thermal fluctuations has been developed by Rytov,[3] who, in particular, obtained formulas for the calculation of all components of the scattered light intensity in an arbitrarily dispersing medium. In spite of the fact that significant clarity had been achieved in the theoretical sense in the understanding of Rayleigh scattering as a result of Ref. 3, the experimental situation in this problem has turned out to be very vague up to the present time. The divergence of experimental data, obtained by various authors, in the measurement of the total intensity of isotropically scattered light in the same liquid (for example, in benzene) amounted to 30–40%.[2,4,5] In this connection, it is not clear whether the relaxation theory of fluctuations can be applied to the description of light scattering in real liquids or not.

The purpose of the present research is the experimental study of the total intensity of isotropic light scattering in liquids and the comparison of the resultant data with the relaxation theory of Rayleigh scattering.[3] In the first part of the work, we give the basic assumptions and the scheme of calculation of the thermal fluctuations and discuss the ensuing requirements for an experiment to test the obtained theoretical results. The second part of the work is devoted to a description of the experimental setup and to the results of the measurement of the absolution scattering coefficient for four liquids.

BASIC ASSUMPTIONS

a) The scattering liquid, together with the density ρ and the temperature T, is described by a single relaxing parameter ξ. The generalization to the case of several relaxing parameters is obvious. In particular, the presence of tensor relaxing parameters leads to partial depolarization of the scattered light, which will be taken into account below [see (8a)] by the introduction of the Cabannes factor[2] in the scattering coefficient.

b) The connection between the fluctuations of the permittivity and the fluctuations of the macroscopic parameters ρ, T and ξ has a local character:

$$\delta\varepsilon(\mathbf{r},t)=\sum_{i=1}^{3}\frac{\partial\varepsilon}{\partial\varphi_i}\delta\varphi_i(\mathbf{r},t). \tag{1}$$

For brevity, we have introduced the notation

$$\varphi_i=\{\rho,T,\xi\}.$$

We emphasize that the derivatives $(\partial\varepsilon/\partial\varphi_i)$ appearing in (1) have the meaning of ordinary thermodynamic derivatives, for example, $(\partial\varepsilon/\partial\varphi_1)=(\partial\varepsilon/\partial\rho)_{T,\xi}$ and so on.

c) The fluctuations of the macroscopic variables φ_i are described by the equations of hydrodynamics with random forces σ', q' and f, and by the relaxation equation for the quantity ξ:

$$\begin{gathered}\rho_0\frac{\partial\mathbf{V}}{\partial t}=-\nabla P+\eta\Delta\mathbf{V}+\left(\zeta+\frac{1}{3}\eta\right)\nabla\operatorname{div}\mathbf{V}+\operatorname{div}\sigma',\\ \frac{\partial\rho}{\partial t}=-\rho_0\operatorname{div}\mathbf{V}=0,\quad \rho_0T_0\frac{\partial S}{\partial t}=\varkappa\Delta T+\operatorname{div}q',\\ \frac{\partial\xi}{\partial t}=-\alpha\left(\frac{\partial F}{\partial\xi}\right)_{\rho,T}+\alpha f,\end{gathered} \tag{2}$$

α is the kinetic coefficient describing the relaxation ξ, F is the free energy of the liquid. The remaining notation is standard (see, for example, Ref. 6).

THERMAL FLUCTUATIONS AND THE INTENSITY OF THE SCATTERED LIGHT

Starting out from the set of equations (2), with the help of the fluctuation-dissipation theorem,[1] it is not difficult to find the Fourier components of the correlation functions of all the macroscopic quantities and, correspondingly, the correlator of the fluctuations of the permittivity

$$\langle|\delta\varepsilon(\omega,\mathbf{K})|^2\rangle=\sum_{ij}\frac{\partial\varepsilon}{\partial\varphi_i}\frac{\partial\varepsilon}{\partial\varphi_j}\langle\varphi_i\varphi_j\rangle_{\omega,\mathbf{K}}. \tag{3}$$

Without lingering on the details of the calculation of the quantities $\langle\varphi_i\varphi_j\rangle_{\omega,\mathrm{K}}$, we consider the general structure of these expressions and their connection with the inten-

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sity of the light scattering. All the correlators in the $(\omega, \mathbf{K})$ representation have the characteristic polar form and reduce to the expressions

$$\langle \varphi_i \varphi_j \rangle_{\omega,\mathbf{K}} = \frac{\Phi_{ij}(\omega, \mathbf{K})}{\Delta(\omega, \mathbf{K})\,\Delta^*(\omega, \mathbf{K})\,(\omega^2+\tau^{-2})}, \tag{4}$$

where $\Phi_{ij}(\omega, \mathbf{K})$ are polynomials in ω and $\mathbf{K}$, $\tau^{-1} = \alpha \partial^2 F/\partial\xi^2$, while $\Delta(\omega, \mathbf{K})$ is the determinant of the set of hydrodynamic equations (2):

$$\Delta(\omega, \mathbf{K}) = -\rho_0^2 T_0 \left(\frac{\partial S}{\partial T}\right)_{\rho,\xi} \left(-i\omega + \frac{\varkappa K^2}{T_0\rho_0(\partial S/\partial T)_{\rho\xi}}\right)\left\{\omega^2 - K^2\left[\left(\frac{\partial P}{\partial \rho}\right)_{T,\xi} + \frac{1}{\rho_0}\left(\frac{\partial P}{\partial \xi}\right)^2_{T,\rho}\left(\frac{\alpha}{-i\omega+\tau^{-1}}\right)\right] + \frac{i\omega K^2}{\rho_0}\left(\zeta + \frac{4}{3}\eta\right)\right\} - i\omega K^2 T_0^2 \left(\frac{\partial P}{\partial T}\right)^2_{\rho,\xi}. \tag{5}$$

(In this paper we assume that $\partial^2 F/\partial\xi\partial T = 0$. This assumption, being of no principal significance, greatly simplifies all the calculations.)

The light intensity scattered in a given direction, is determined by integration of the expression (3) over all the frequencies. By virtue of (4), these integrals are easily calculated according to the general theorems of the theory of residues. The residue at each of the poles gives the scattering intensity at the corresponding frequencies, which are determined from the equations

$$\Delta(\omega, \mathbf{K}) = 0, \quad \omega + i\tau^{-1} = 0. \tag{6}$$

[In correlation functions that do not include fluctuations of the quantity ξ, $\Phi_{ij}(\omega, \mathbf{K})$ turns out to be proportional to the factor $(\omega^2 + \tau^{-2})$ and the corresponding pole does not contribute to the total intensity.] The first of these equations has four roots: two acoustical, one relaxational, and one thermal, which in the two extreme cases $\omega_{\mathrm{ac}}\tau \gg 1$ and $\omega_{\mathrm{ac}}\tau \ll 1$ are easily found and have the following form:

$$\omega_{\mathrm{ac}}^{(1,2)} = \pm U_\infty K - \frac{i}{2}\left(\frac{U_\infty^2 - U_0^2}{U_\infty^2 \tau} + \gamma\right), \tag{7a}$$

$$\omega_{\mathrm{rel}} = -i\tau^{-1} U_0^2/U_\infty^2, \quad \omega_T = -i\chi K^2$$

at $\omega_{\mathrm{ac}}\tau \gg 1$ and

$$\omega_{\mathrm{ac}}^{(1,2)} = \pm U_0 K - \frac{i}{2}\left[(U_\infty^2 - U_0^2)\tau K^2 + \gamma\right], \quad \omega_{\mathrm{rel}} = -i\tau^{-1}. \quad \omega_T = -i\chi K^2 \tag{7b}$$

at $\omega_{\mathrm{ac}}\tau \ll 1$. Here $U_0 = (\partial P/\partial\rho)^{1/2}_{S,\mathrm{eq}}$ is the low-frequency sound velocity (the subscript "eq" of the thermodynamic derivatives means that the corresponding derivative is taken at a constant value of the field h thermodynamically conjugate to the quantity ξ; just such derivatives determine the behavior of the system at extremely low frequencies), $U_\infty = (\partial P/\partial\rho)_{S,\xi}$ is the high-frequency sound velocity, $\chi = \varkappa/\rho_0 C_P$ is the coefficient of thermal diffusivity, and γ is the sound absorption, due to viscosity and thermal conductivity.[6] We assume that $\gamma\tau \ll 1$.

The roots (7a) and (7b) determine the spectrum of characteristic perturbations in the liquid (the normal modes), which characterize the hydrodynamic stage of the approach of the liquid to equilibrium.

The scattered light thus has a fine structure, the side lobes of which are shifted relative to the frequency of the incident light by an amount $\mathrm{Re}\,\omega_{\mathrm{ac}}^{(1,2)}$. The intensity of the side components I_{MB} is determined by the residues at the acoustic pole $\omega_{\mathrm{ac}}^{(1,2)}$. The intensity of the central maximum I_{cent} is equal to the sum of the three residues at the poles ω_{rel}. ω_T and $\omega'_{\mathrm{rel}} = -i\tau^{-1}$; $I_{\mathrm{cent}} = I_{\mathrm{rel}} + I'_{\mathrm{rel}} + I_T$. Straightforward but rather involved calculations give the following results: at $\omega_{\mathrm{ac}}\tau \gg 1$,

$$I_T = \frac{AT_0}{\rho_0}\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,\mathrm{eq}} \frac{1}{C_P}, \quad 2I_{\mathrm{MB}} = A\rho_0\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{S,\xi} U_\infty^{-2},$$

$$I_{\mathrm{rel}} + I'_{\mathrm{rel}} = A\left\{\rho_0\left[\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{S,\mathrm{eq}} U_0^{-2} - \left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{S,\xi} U_\infty^{-2}\right] + \frac{1}{\rho_0}\left[\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{\rho,\mathrm{eq}} \left(\frac{\partial S}{\partial T}\right)^{-1}_{\rho,\mathrm{eq}} - \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{\rho,\xi}\left(\frac{\partial S}{\partial T}\right)^{-1}_{\rho,\xi}\right] + \left(\frac{\partial\varepsilon}{\partial\xi}\right)^2_{\rho,T} \Big/ \left(\frac{\partial^2 F}{\partial\xi^2}\right)\right\},$$

at $\omega_{\mathrm{ac}}\tau \ll 1$,

$$I_T = \frac{AT_0}{\rho_0}\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,\mathrm{eq}} \frac{1}{C_P}, \quad 2I_{\mathrm{MB}} = A\rho_0\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{S,\xi} U_0^{-2},$$

$$I_{\mathrm{rel}} + I'_{\mathrm{rel}} = A\left\{\frac{1}{\rho_0}\left[\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{\rho,\mathrm{eq}} \left(\frac{\partial S}{\partial T}\right)^{-1}_{\rho,\mathrm{eq}} - \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{\rho,\xi}\left(\frac{\partial S}{\partial T}\right)^{-1}_{\rho,\xi}\right] + \left(\frac{\partial\varepsilon}{\partial\xi}\right)^2_{\rho,T} \Big/ \left(\frac{\partial^2 F}{\partial\xi^2}\right)\right\},$$

where $A = \pi^2 k_B T V I_0/(\lambda^4 L^2)$, k_B is Boltzmann's constant, λ is the wavelength of the exciting light, V is the scattering volume, L is the distance from the scattering volume to the photodetector, I_0 is the intensity of the exciting light.

As was to be expected, the intensity of the Mandel'shtam-Brillouin side components at $\omega_{\mathrm{ac}}\tau \gg 1$ is determined by the high-frequency sound velocity and turns out to be less than in the scattering at small angles (when $\omega_{\mathrm{ac}}\tau \ll 1$). This diminution in the intensity of the side components is completely compensated by the increase in the central component, which is connected with the additional contribution of the relaxation mode to the scattering.

We now state briefly the basic conclusions of the relaxation theory.

1) The scattering coefficient R, which is connected with the total scattered intensity $I = (I_T + 2I_{\mathrm{MB}} + I_{\mathrm{rel}} + I'_{\mathrm{rel}}) \times f(\Delta)$, equals

$$R = \frac{I}{I_0}\frac{L^2}{V} = \frac{\pi^2 k_B T}{\lambda^4}\left\{\frac{\rho(\partial\varepsilon/\partial\rho)^2_{T,\mathrm{eq}}}{(\partial P/\partial\rho)_{T,\mathrm{eq}}} + \frac{(\partial\varepsilon/\partial\xi)^2_{T,\rho}}{\partial^2 F/\partial\xi^2} + \frac{(\partial\varepsilon/\partial T)^2_{\rho\xi}}{(\partial S/\partial T)_{\rho\xi}}\right\} f(\Delta), \tag{8a}$$

where $f(\Delta)$ is the Cabanne factor. In the case of vertically polarized exciting light and a scattering angle of 90°,

$$f(\Delta) = (3 + 3\Delta_V)/(3 - 4\Delta_V);$$

Δ_V is the coefficient of depolarization of the scattered light.[2]

We note that, in spite of the fact that the intensity of the individual components of the spectrum can depend on the quantity $\omega_{\mathrm{ac}}\tau$, the total intensity remains constant. At $(\partial\varepsilon/\partial\xi)_{\rho,T} = (\partial\varepsilon/\partial T)_{\rho,\xi} = 0$ the relation (8a) is identical with the Einstein-Cabannes formula.[2]

2) The relations in the fine structure are

$$2I_{\mathrm{MB}} + I_{\mathrm{rel}} + I'_{\mathrm{rel}} = \mathrm{const}$$

(does not depend on $\omega_{ac}\tau$)

$$\frac{I_T}{2I_{MB}+I_{rel}}=\frac{C_P}{C_V}-1, \tag{8b}$$

$$\frac{I_{cent}}{2I_{MB}}=\begin{cases}(C_P/C_V)-1, & \omega_{ac}\tau\ll 1\\ (C_P U_\infty^2/C_V U_0^2)-1. & \omega_{ac}\tau\gg 1\end{cases}$$

The last two relations are written in the approximation $(\partial\varepsilon/\partial\xi)_{\rho,T}=(\partial\varepsilon/\partial T)_{\xi,\rho}=0$. It is evident that this assumption does not lead to large distortions in the case of simple liquids; in addition, the case $(\partial\varepsilon/\partial T)_{\rho,\mathrm{eq}}\neq 0$ is considered in detail in Ref. 2. The exact relations can be obtained from formulas (7a) and (7b).

3) The central maximum of the scattered light consists of three components.

4) The spectral composition of the scattered light in liquids with high dispersion (glycerine, triacetin, glasses) has an anomalous character: the basic contribution to the scattering in the high-frequency region is made by the relaxation mode.

Other consequences of the relaxation theory can be given; we have discussed only those whose experimental verification is in our opinion most realistic.

EXPERIMENTAL VERIFICATION POSSIBILITIES

The present work is devoted to the measurement of the integrated intensity of the scattered light. Therefore, we consider the relation (8a) in more detail.

The experimental test of the relation (8a) requires independent measurements of the right and left sides of this equation. The specific difficulties of measurement of the scattering coefficient [the left side of (8a)] will be discussed somewhat later. Here we shall treat only the possibility of the direct determination of the right side of (8a). The experimental method that we have proposed allows us to measure directly the first and last terms in (8a). So for the second term, we believe that by choice of suitable liquids it can be made small in comparison with the first. Actually, if we represent the relaxation process as a process of transfer of the energy from the sound wave (the energy of intermolecular interaction) to the internal degrees of freedom of the molecule, and assume that the molecular polarizability changes insignificantly here, then it is not difficult to show that

$$(\partial\varepsilon/\partial\xi)_{\rho,T}/(\rho\partial\varepsilon/\partial\rho)_{T,\mathrm{eq}}\sim\Delta\tilde{\alpha}/\tilde{\alpha}\ll 1$$

($\Delta\tilde{\alpha}$ is the change in the polarizability). Those liquids in which molecules that differ strongly from the original ones are formed in the relaxation process in all probability do not satisfy this condition ($\Delta\tilde{\alpha}/\tilde{\alpha}\ll 1$). These include, in particular, liquid mixtures in which the chemical equilibrium is shifted upon passage of the sound wave. The Einstein-Cabannes formula [formula (8a) without account of the second and third terms in the right hand side] turns out to be inapplicable here, while the complete relation (8a) remains valid. (Experimentally, the presence of the second term in the total intensity of the scattered light can be determined from the presence in the central maximum of a component that is determined by the frequency $\omega'_{rel}=-i\tau^{-1}$.)

EXPERIMENTAL RESULTS

In correspondence with the discussion above, we have selected four liquids for measurement: benzene, toluene, acetone and carbon tetrachloride. For the first two, the contribution of the depolarized scattering to the total is large, ~50–60%; for the other two, it does not exceed 20%. In each pair, one of the liquids (benezene and carbon tetrachloride) possesses large sound-velocity dispersion $[(U_\infty-U_0)/U_0\approx 10\%]$, and in the second a small one $[U_\infty-U_0)/U_0\lesssim 2.5\%]$. Thus, all four possibilities associated with the presence or absence of depolarization and dispersion were considered.

For all four liquids, the condition $\Delta\tilde{\alpha}/\tilde{\alpha}\ll 1$ is satisfied by all appearances, and the second term in the right hand side of (8a) can be neglected. Moreover, the chosen liquids, especially benzene, have been well studied and there is a wealth of experimental data for them which can be used for comparison and calculations.

A. Measurement of the scattering coefficient [left side of (8a)]

In correspondence with the definition, the scattering coefficient is equal to

$$R=W_{sc}/W_0\Omega l,$$

where W_0 is the power of the exciting light, W_{sc} is the light power scattered in the solid angle Ω with path length of the exciting light l; W_{sc} is connected with the total intensity (I), introduced above, by the relation $W_{sc}=I\sigma$, where σ is the area of the photodetector.

As a light source, we used lasers with $\lambda=633.0$ nm and $\lambda=441.6$ nm. The quantities W_{sc}/W_0, Ω and l were determined directly in the experiment.

As is well known, the basic difficulty in the measurement of the quantity R is connected with the fact that the ratio W_{sc}/W_0 is of the order of 10^{-7}–10^{-9}, and in the construction of a scale of such an extent for the simultaneous measurement of W_{sc} and W_0 it is difficult to avoid large systematic errors.

As a basis for the construction of the scale of light flux powers, we used the principle of superposition of electromagnetic fields.[1] With the aid of the superposition of light fluxes of two light-emitting diodes AL307B, the silicon photodiode FD-24K was calibrated, and its linearity turned out to be extraordinarily high. The deviation from linearity of the characteristic with change of the power of the light flux by a factor of 10^4 did not exceed 0.3%, which agrees with the data of Refs. 7 and 8. The neutral light filters NS10 and NS11 were calibrated with the help of a photodiode. These filters had attenuations of 10^2 and 10^4, respectively. Each light filter was calibrated in the operating position. With the use of these light filters, the power of the exciting light W_0 was reduced by a factor of 10^6, after which the powers W_{sc} and W_0 could be measured with the help of a single photodetector. We used the configurations of the setup employed by us previously[9] (see Fig. 1): the photodetector was mounted on the arm of a rotatable fixture; it measured the power of the exciting (position A) and scattered (position B) light. The photodetector was based on a

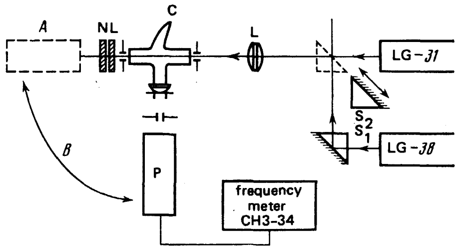

FIG. 1. Diagram of experimental arrangements: P—Photodetector, C—cell, NL—neutral light filters, L—focusing lens, S_1, S_2—exciting-light wavelength switches.

photomultiplier FEU-79 operating in a photon-counting mode and calibrated by means of a photodiode. The total error of measurement of the ratio W_{sc}/W_0 did not exceed 0.8%.

For measurement of the quantities Ω and l, we used a specially prepared cell (Fig. 2) in which these quantities were measured directly without the need for taking into account the refraction of the scattered light at the glass-air interface. This made it possible to avoid the frequently encountered doubt[5] in the validity of the method of allowing for this refraction in the specific geometry of the experiment. The window for the scattered light was a spherical one, as a result of which an image of the object was formed in the plane of a vertical slit. In this case, the solid angle Ω was determined by the area of the diaphragm and was equal in first approximation to $\pi d_1^2/4L^2$ (the notation is shown in Fig. 2). The quantity l was determined by the length of the image of the scattering volume cut off by the slit d_2. For the determination of the quantity l in the scattering volume, a previously calibrated rule (a reticule with divisions) was lowered into the scattering volume and the width of the slit was measured from its image. The total error in measurement of the product Ωl did not exceed 0.8% in the case of a typical value $\Omega l \approx 10^{-3}$.

During the course of the experiment, many other more particular problems arose, connected with the sensitivity of the photodetector to the magnetic field, with the polarization of the light and its distribution over the area of the photocathode, with the effect of temperature, and also with parasitic scattering of light by dust, by the windows and walls of the container, with reflection of light from the window, and so on. All these parasitic effects could either be eliminated or corrections could be made—the value of which, in toto, did not exceed $(5 \pm 0.6)\%$. An almost two-year study of the scattering coefficient of benzene under different experimental conditions aided in the detection of the parasitic effects and their correct account. The stability and reproducibility of the attenuation coefficient of neutral glasses, the effect of parasitic scattering and of the value of Ωl on the result of the measurement were all especially carefully investigated. The product Ωl varied in the range $(0.4-20)\times 10^{-4}$. It was ascertained that *a priori* estimates of the error agreed with the experimental results. The total error of measurement did not exceed 1.5%.

As a control, we measured the scattering coefficients of all four liquids in a cell of more traditional "rectangular" construction, and of benzene also by an indirect method, using an auxiliary strongly scattering medium. A calculation of the values of Ω and l for the "rectangular" cell by the formulas of Carr and Zimm[10] gives an error approaching the value that is typical of the cell with the spherical window. The values of the scattering coefficients obtained for the two types of cell agreed, within the limits of error of the measurement, for all the liquids (the difference did not exceed 3%). In the indirect method, which we attempted to carry out as closely as possible to that described in Ref. 11, we measured the exciting-light attenuation due to scattering in a solution of polystyrene in benzene, the scattering coefficient was calculated, and then the scattering coefficient of benzene was measured by a relative method. In this method, it was not necessary to measure the quantities W_{sc}/W_0, Ω and l directly, and consequently one could hope to obtain more reliable data.[5,10,11] As a result of the measurements, we obtained values that agreed with the data of direct measurements; however, the accuracy of this method turned out to be significantly lower. In the best case, for a container of length 75 cm and $\lambda = 441.6$ nm, the error amounted to 7% and was almost entirely connected with the uncertainty of the positioning of the vessel in the measurements and the refillings. It appears that an error of this order is typical for this method.

As a result of this investigation, we could have confidence in the reliability of the values of the scattering coefficient and the obtained estimates of errors in their measurement. The results $R_{\rm exp}$ of the measurements of the scattering coefficients, obtained by the method just described, are given in the accompanying table.

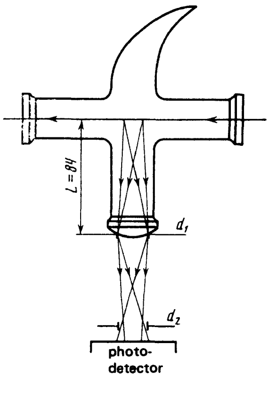

FIG. 2. Diagram of the cell: d_1—circular diaphragm, d_2—slit.

B. Measurement of the right side of (8a)

For the determination of the right side of the relation (8a), we used the thermodynamic relations

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,\mathrm{eq}} = \frac{C_V}{C_P}\left(\frac{\partial P}{\partial \rho}\right)_{S,\mathrm{eq}} = \frac{C_V}{C_P} U^2,$$

$$\left(\frac{\partial \varepsilon}{\partial \rho}\right)_{T,\mathrm{eq}} = 2n\left(\frac{\partial P}{\partial \rho}\right)_{T,\mathrm{eq}} \left(\frac{\partial n}{\partial P}\right)_{T,\mathrm{eq}},$$

where C_P and C_V are the heat capacities at constant

TABLE I.

substances	λ, μ	n	$(\partial n/\partial P)_{T,\text{ eq.}}$, 10^{-10} PA^{-1}	ρ, g/cm^3	U, m/s	C_P, kJ/kg	C_V, kJ/kg	$\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_{T,\text{ eq.}}$	$\left(\frac{1}{\rho}\frac{\partial\rho}{\partial P}\right)_{T,\text{eq.}}$, 10^{-11} Pa^{-1}	Δ_V	R calc, 10^{-6} cm^{-1}	R exp, 10^{-6} cm^{-1}
benzene	441.6 633.0	1.521 1.498	5.18 4.92	0.8790	1324	1.728	1.203	1,690 1,581	93.2	0,274 0.269	57.4 11.5	58.6 11.5
toluene	441.6 633.0	1.512 1,493	4.89 4.62	0,8669	1328	1,685	1.255	1.685 1.575	87.8	0,347 0.335	65.6 13,1	67.3 13.2
acetone	441.6 633.0	1.367 1,35	4.71 4.58	0.7905	1192	2.136	1.529	1,035 0.998	124.4	0,095 0.0935	17.6 3.85	17.7 3.72
CCl_4	441,6 663.0	1.472 1,458	5.24 5,07	1.595	938	0.850	0.586	1.494 1.431	103,3	0.0216 0,0206	25.5 5,53	25.9 5.61

pressure and volume, U is the speed of the ultrasound, n is the index of refraction of the liquid. For the selected liquids, $U=U_0$ with accuracy to within 0.1% for frequencies ≤ 20 MHz. The quantities $(\partial n/\partial P)_{T,\text{eq}}$, $(\partial n/\partial T)_{P,\text{eq}}$, C_P, C_V and Δ_V were measured by us directly. The values of the parameters λ, n, ρ and U were taken from handbooks.[12,13] A Mach-Zehnder interferometer was the basis of the setup to measure the derivatives $(\partial n/\partial P)_T$ and $(\partial n/\partial T)_P$.[14] The cell with the liquid to be measured was placed in one of the arms of the interferometer. The light source was the same as in the setup for measurement of the scattering coefficient. With the help of a feedback circuit, the interferometer was maintained in a state of minimum light transmission, while the pressure and temperature were measured with the help of a calibrating manometer of class 0.16 and a platinum resistance thermometer. The drops in the pressure and temperature were of the order of 1 atm and 0.2 K, respectively. The error in measurement of the derivatives did not exceed 0.5%. The possible effect of dissolution of the helium which transmits the pressure, was estimated not to exceed 0.01%.

The heat capacities C_P and C_V were measured on a standard calometric setup.1) The measurements were carried out by the method described in Ref. 15, with corrections that take into account the small compressibility of the liquids. The experimental error of the heat capacity measurements was 0.2–0.3%.

The values of the coefficients of depolarization were measured at the same time as the measurements of the scattering coefficients, with the help of a polaroid placed in front of the photodetector. The error of measurement did not exceed 0.7%.

The experimental data obtained (see Table I) allowed a direct calculation of the first and last terms of the right side of the relation (8a). For all four liquids, it turned out that the contribution of the temperature fluctuations [the last term in (8a)] to the total intensity of scattering did not exceed 0.03%, which agrees qualitatively with the conclusions of Refs. 2 and 16. In the next-to-the-last column of Table I are given the values of the scattering coefficient calculated from the Einstein-Cabannes formula, with use of the experimental values of the derivatives that enter into it (R_{calc}). The total error of R_{calc} oscillates in the limits of 1.5–2% depending on the contribution of the depolarization scattering. A comparison of the data in the last and the next-to-the-last columns of Table I shows that these quantities are equal within experimental accuracy.

For a comparison of the values obtained for the scattering coefficient of benzene with the results of other researches, we have separated from the integrated scattering intensity the part which does not depend in explicit fashion on the wavelength of the incident light:

$$\tilde R = \frac{R\lambda^4}{(\rho\partial\varepsilon/\partial\rho)^2_{T,\text{eq}}}$$

$\tilde R$ depends on the wavelength only through the Cabannes factor. Moreover, all the data were reduced to the single temperature 20 °C (we have assumed[2] $R^{-1}dR/dT = 0.007\ \text{K}^{-1}$).

Figure 3 gives the values of $\tilde R$, obtained from the data of the summary table of the review,[4] the experimental data of Refs. 11, 18–22, and also our data, as functions of the wavelength. In place of data obtained up to 1961, the averaged "best" value of Refs. 2 and 4 was taken. It is seen that most of the data agree with one another within the limits of typical experimental error of ±5%.

The results of Refs. 4, 11, 18 reveal a significantly large deviation. It is possible that this is connected with the use in our researches of the indirect method of determination of the scattering coefficient. Similar

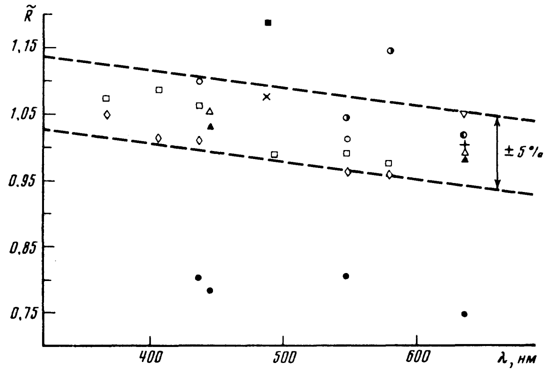

FIG. 3. Experimental values of the scattering coefficient R of benzene as a function of the wavelength of the exciting light (in relative units): ▲—our data —left and right sides of (8a); ○—"best" value[3]; □—data of Classon and Echman,[4] ◇—Cantow[4], ◑—Beridze[4]; ●—Rozhdestvenskaya *et al.*[11], ■—Finnigan and Jacobs[18], +—Pike *et al.*[19] ◐—Leit *et al.*[20], ×—Kato *et al.*[21]; ∇—Kaye and McDaniel[22].

agreement exists also for the other three liquids, although the number of experimental data for them is much less than for benzene. Thus, the relaxation theory adequately explains the molecular scattering of light in liquids in all four cases investigated, and the initial assumption as to the smallness of the parameter $\Delta\tilde{\alpha}/\tilde{\alpha}$ for the given class of liquids is satisfied.

In conclusion, we point out the interesting experimental consequence of this approach, touching on the light scattering in glasses and vitrifying liquids. [Although, strictly speaking, the relaxation theory for vitrifying liquids should be refined (for example, by the introduction of a spectrum of relaxation times[23]), the basic conclusion that the total scattering intensity is independent of $\omega_{\text{ac}}\tau$ should remain unchanged. Also, taking it into account that I_{MB} is inversely proportional to the square of the sound velocity at the corresponding frequency,[2] we obtain the result that the Landau-Placzek relation (the third relation of (8b)) remains valid even in the refined theory.] For such liquids, a large sound velocity dispersion is characteristic. Thus, for glycerin and triacetin $(U_\infty - U_0)/U_0 \sim 50\%$.[2] This means that the intensity of the Mandel'shtam-Brillouin components decreases by a factor of 2–3 and more than half of the entire intensity of the scattering is "pumped over" into the relaxation mode. Failure to account for this fact should lead to a large decrease in the theoretical scattering coefficient in comparison with the experimental. This is well illustrated in Figs. 75 and 76 of Ref. 2.

Starting out from the relaxation theory, we can, by using experimental data on the scattered light intensity, understand the properties of the "equilibrium" state of such strongly dispersive systems.

Actually, the value of the high-frequency sound velocity in glasses, for example, in fused quartz, has a typical "solid-state" value $U_\infty \approx 5000$ m/s. The direct determination of the low-frequency velocity of sound in such systems turns out to be very difficult because of the very long relaxation times. However, under the assumption of the validity of the relaxation theory, the low-frequency sound velocity can be estimated both from the experimental values of the total intensity of the scattered light and from the Landau-Placzek relation.[2,17] Therefore, the entire central component should consist of the contribution from the relaxation mode. Experiment shows that the intensity of this central component is an order of magnitude greater than the intensity of the lateral components.[2,17]

These and other estimates give similar values, having the characteristic "liquid" value of the velocity, approximately equal to 1500–2000 m/s. Thus, the low-frequency properties of glass agree, to all appearances, with the properties of ordinary equilibrium liquids.

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[1] L. D. Landau and E. M. Lifshitz, Elektrodinamikassploshnykh sred (Electrodynamics of Continuous Media) Gostekhizdat, Moscow, 1957. English translation, Pergamon Press, Oxford, 1960.
[2] I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Scattering of Light) Nauka, Moscow, 1965. English translation, Plenum Press, New York, 1968.
[3] S. M. Rytov, Zh. Eksp. Teor. Fiz. **58**, 2154 (1970) [Sov. Phys. JETP **31**, 1163 (1970)].
[4] M. I. Shakhparonov, Ob osnovnykh voprosakh praktiki i teorii releevskogo rasseyaniya sveta v zhidksoti. (On the Basic Problems of Practice and the Theory of Rayleigh Light Scattering in Liquids), in: Sovremennye problemy fizicheskoĭ khimi (Contemporary Problems of Physical Chemistry) vol. 5, MGU Press, 1970.
[5] M. F. Vuks, Rasseyanie sveta v gazakh, zhidkostyakh i rastvorakh (Light Scattering in Gases, Liquids and Solids) LGU Press, 1977. Teoreticheskiĭ raschet intensivnosti rasseyaniya sveta v zhidkostyakh i sravenie s optnymi dannymi (Theoretical Calculation of the Intensity of Light Scattering in Liquids and a Comparison with Experimental Data) in: Sovremennye problemy fizicheskoĭ khimii (Contemporary Problems of Physical Chemistry) vol. 5, MGU Press, 1970.
[6] L. D. Landau and E. M. Lifshitz, Mechanics of Continuous Media) Gostekhizdat, Moscow, 1953 [Pergamon, 1958].
[7] L. P. Zakharchenko, V. E. Krivtsov, V. I. Kuznetsov, L. S. Lovinskiĭ, I. D. Rogovoĭ, and A. S. Markochev, Opt. Mekh. Prom. No. 1, 48 (1979).
[8] P. G. Witherell and M. E. Faulhaber, Appl. Opt. **9**, 73 (1970).
[9] M. A. Anisimov, A. M. Evtyushenkov, Yu. F. Kiyachenko, and I. K. Iudin, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 378 (1974) [JETP Lett. **20**, 170 (1974)].
[10] C. J. Carr and B. H. Zimm, J. Chem. Phys. **18**, 1616 (1950).
[11] N. B. Rozhdestvenskaya, E. N. Gorbacheeva and A. N. Ryabinin, Opt. Spektrosk. **42**, 656 (1977).
[12] Teplofizicheskie svoĭstva beshchestv (Thermophysical Properties of Materials) Handbook edited by N. B. Vargaftik, Gosenergoizdat, Moscow-Leningrad, 1956.
[13] Tablitsy fizicheskikh velichin (Tables of Physical Quantities) Handbook edited by I. K. Kikoin, Atomizdat, Moscow, 1976).
[14] M. Born and E. Wolf, Principles of Optics, 4th ed., Pergamon Press, Oxford, 1970.
[15] V. G. Gorbunova, O. M. Oleĭnik-Dyzadik, V. A. Rabinovich, and N. G. Shmakov, in: Teplofizicheskie svoĭstva veshchestv i materialov (Thermophysical Properties of Substances and Materials) No. 13, Izd. standartov, Moscow, 1979, p. 57.
[16] D. J. Coumou, E. L. Macor and J. Hijmans, Trans. Faraday Soc. **60**, 1539 (1964).
[17] T. H. Wood, Rev. Sci. Instr. **49**, 790 (1976).
[18] J. A. Finnigan and D. J. Jacobs, Chem. Phys. Lett. **6**, 141 (1970).
[19] E. R. Pike, W. R. M. Pomeroy, and J. M. Vaughan, J. Chem. Phys. **62**, 3188 (1975).
[20] R. C. C. Leit, R. S. Moore and S. P. S. Porto, J. Chem. Phys. **40**, 3741 (1975).
[21] Y. Kato and G. A. Zdasiuk, J. Opt. Soc. Amer. **65**, 995 (1975).
[22] W. Kaye and J. B. McDaniel, Appl. Optics, **13**, 1934 (1974).
[23] N. Ostrowski, in: Photon Correlation and Light Beating Spectroscopy, H. Z. Cummins and E. R. Pike, eds., Plenum, 1974.

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