Molecular light scattering of varying multiplicity

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We investigate the angular, temperature, and height dependences of the intensity of light scattered in a nitrobenzene-hexane mixture in the vicinity of the critical stratification point under conditions when the strong critical opalescence causes scatterings of higher multiplicity to make a large contribution to the total light-scattering intensity. A procedure for subdividing the total intensity into that due to single and double scattering and scattering of higher multiplicity is proposed and effected. The relative characteristics of scatterings of varying multiplicity are investigated. As a check on the reliability of the proposed procedure, the values of the critical exponents are determined and are found to agree with the most reliable values within the limit of errors.

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One of the most essential requirements in the study of physical properties of system by light-scattering methods is that the scattering constant be small. The measured intensity consists then almost entirely of singly scattered light, in which the information on the physical properties of the scattering system enters in the simplest manner. This requirement narrows down substantially the class of objects that can be studied by optical methods. Light scattering, however, as at present the only direct method of studying the spectra of thermal fluctuations and optical inhomogeneities, as well as of the correlation properties of scattering systems that have characteristic dimensions of the order of the visible-light wavelength.[1] It becomes therefore necessary to analyze the intensity of the scattered light in those cases when the single-scattering approximation is known to be incorrect.

The first natural step towards the solution of this problem is to make corrections for double scattering of the light. This question has been the subject of many studies in recent years, in connection with the intensive study of phase transitions and critical phenomena.[2-8]

Our present purpose is to study system in which double scattering is commensurate with single scattering, and a noticeable contribution is made by scatterings of higher multiplicity. Among such systems are included, for example, all liquids close to the liquid–vapor critical point. The study of such system, however, is made complicated by another distorting factor, namely the gravitational effect.[9-11] We have therefore chosen to investigate a binary nitrobenzene–hexane mixture, whose pure components have very greatly different refractive indices near the critical stratification point.

The intensities of singly, doubly, triply, etc. reflected light in the vicinity of the critical stratification point can be written in the form

$$I^z_{z(1)} = \frac{I_0}{X^2} R_{\text{scat}}\, e^{-\sigma R^{(1)}} V G(q_1), \tag{1}$$

$$I^z_{z(2)} = \frac{I_0}{X^2} R^2_{\text{scat}} \int\limits_{V_1} d\mathbf{R}_1 \int\limits_{V_2} d\mathbf{R}_2 \frac{e^{-\sigma R^{(2)}}}{R^2_{12}} G(q_1) G(q_2) \left(1 - \frac{R^2_{12,z}}{R^2_{12}}\right)^2, \tag{2}$$

$$I^z_{z(3)} = \frac{I_0}{X^2} R^3_{\text{scat}} \int\limits_{V_1} d\mathbf{R}_1 \int\limits_{V_c} d\mathbf{R}_2 \int\limits_{V_2} d\mathbf{R}_3 \frac{e^{-\sigma R^{(3)}}}{R^2_{12} R^2_{23}} G(q_1) G(q_2) G(q_3) \cdot$$
$$\times \left[1 - \frac{R^2_{12,z}}{R^2_{12}} - \frac{R^2_{23,z}}{R^2_{23}} + \frac{R_{12,z} R_{23,z} (\mathbf{R}_{12}\mathbf{R}_{23})}{R^2_{12} R^2_{23}}\right]^2 \tag{3}$$

etc., where I_0 is the intensity of an incident monochromatic plane light wave propagating along the x axis, the superscripts and subscripts denote the polarizations of the incident and scattered light, respectively, $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$, X is the distance from the scattering volume to the observation point, V_1 is the volume illuminated by the incident light, and V_2 is the volume from which the scattered light goes into the recording unit. In the geometry of our experiment (see Fig. 1 in Ref. 8), V_1 and V_2 can be regarded as cylinders with identical lengths $1L$ and with radii r_1 and r_2; V is the common part of the volumes V_1 and V_2, V_c is the total volume of the cell with the critical mixture; $R^{(\alpha)}$ is the path traversed by the light in the scattering medium, α is the multiplicity of the scattering, σ is the extinction coefficient, $q = 2k \sin(\theta/2)$, $\mathbf{q}$ is the scattering wave vector, k is the wave vector of the incident radiation in the medium, θ is the scattering angle, $\mathbf{q}_i$ is the wave vector in the i-th reradiation,

$$R_{\text{scat}} = \frac{\pi^2}{\lambda^4} \left(\frac{\partial \varepsilon}{\partial c}\right)^2_{P,T} \frac{k_B T}{\rho} \left(\frac{\partial c}{\partial \mu}\right)_{P,T} \tag{4}$$

is the scattering constant, λ is the light wavelength in vacuum, ε is the dielectric constant, μ is the chemical potential of the mixture, ρ is the mass density, k_B is Boltzmann's constant, T is the absolute temperature, P is the pressure,

$$G(q) = \langle |\delta c_{\mathbf{q}}|^2 \rangle / \langle |\delta c_{\mathbf{q}=0}|^2 \rangle,$$

δc_q is the concentration fluctuation. We shall use for $\langle |\delta c_q|^2 \rangle$ the Ornstein-Zernike approximation $\langle |\delta c_q|^2 \rangle = l G(\mathbf{q}) r_c^2$,

$$G(q) = [1 + (q r_c)^2]^{-1}, \tag{5}$$

where r_c is the correlation radius, as well as the corresponding expression for the extinction coefficient[12]

$$\sigma = \frac{\pi}{2} B \left\{ \left[2 + (k r_c)^{-2} + \frac{1}{4} (k r_c)^{-4}\right] \ln[1 + 4(k r_c)^2] - 2 - (k r_c)^{-2} \right\}, \tag{6}$$

$$B = \frac{R_{\text{scat}}}{(k r_c)^2} = \frac{l}{\lambda^2} \left(\frac{\partial n}{\partial c}\right)^2_{P,T}, \tag{7}$$

where n is the refractive index. We recall that according to similarity theory $(\partial c/\partial \mu)_{P,T} \sim r_c^{2-\eta}$ and $r_c = r_0 \tau^{-\nu}$, where $\tau = |T - T_c|/T_c$, $2 - \eta = \gamma/\nu$, T_c is the critical temperature.

In our preceding paper[8] the sextuple integral in (2) could be reduced to a double integral by using the small-

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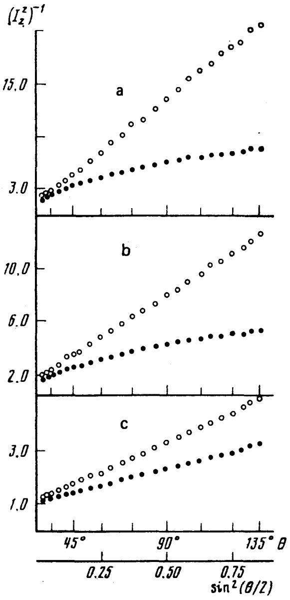

FIG. 1. Reciprocal scattering intensities $(I_z^z)^{-1}$ as functions of $\sin^2(\theta/2)$ at $h = 0$ and at different temperatures: ●) experimental values, ○) values obtained after excluding multiple scattering; a) $\Delta T = 0.014°$ ($kr_c = 2.1$), b) $\Delta T = 0.024°$ ($kr_c = 1.36$); c) $\Delta T = 0.039°$ ($kr_c = 1.0$). The contribution of the multiple scattering at $\Delta T = 0.014°$ was exceedingly large, of the order of 75% at large scattering angles; this point was therefore not used in the determination of the critical exponents. The value $kr_c = 2.1$ was obtained from the experimental indicatrix, and the calculate $kr_c = kr_0\tau^{-\nu} = 1.9$.

ness of the parameters σr_i and r_i/L, with $i = 1$ and 2. It was impossible to simplify the integrals $I^z_{z(3)}$, $I^z_{z(4)}$, etc. to the same degree. From a comparison of (2) and (3) we can draw important general conclusions about the behavior of I^z_z as a function of h. The formulas for $I^z_{z(2)}$, $I^z_{z(3)}$, etc. admit, in the first and last integral, at $h \gg r_2$, a transition to integration along the cylinder axes, and the cylinder cross sections enter only as factors. However, the transition to $h \to 0$ in formula (2) is impossible in this case, since the integral diverges logarithmically at $R_{12} \sim 0$. This leads to a logarithmic growth of $I^z_{z(2)}$ in (2) as $h \to 0$. An exact calculation shows[8] that as $h \to 0$ the intensity $I^z_{x(2)} \sim \ln(L/r_2)$.

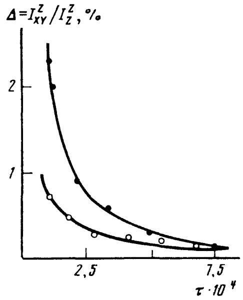

FIG. 2. Degree of depolarization as a function of temperature at $h = 0$ and $\theta = \pi/2$: ●) experimental values, ○) "reduced" experimental values $\tilde{\Delta} = (I^z_{yx}/I^z_z)_e(r_2/r_2')(B/B')$ obtained in Ref. 8 for a $\beta\beta'$-dichlorethyl ether—isooctane mixture, where the primes denote the data of Ref. 8. The degrees of polarization normalized in this manner agree with one another, as expected, at sufficiently large distance from the critical point, where the main contribution to the depolarization is made by double scattering.

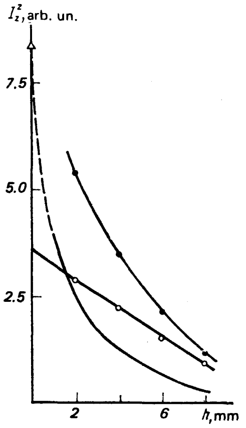

FIG. 3. Scattering intensity $I_z^z(h)$ as a function of the height h at $\Delta T = 0.033°$ ($kr_c = 1.12$) and $\theta = /2$: ●) experimental values solid line—calculated contribution of double scattering; △) calculated limiting value of $I^z_{z(2)}$ at $h = 0$; ○) contribution of scatterings of higher multiplicities $I^z_{z(p)}(h) = I^z_z(h) - I^z_{z(2)}(h)$.

It is easily seen that the presence of additional integrations over the cell volume in $I^z_{z(3)}$, $I^z_{z(4)}$, etc. leads to elimination of the logarithmic growth of these components as $h \to 0$. As a result, the components of scattering with multiplicity higher than second are smooth functions of h at small values of h.

The measurements were performed with the setup described in Ref. 8. The investigated liquid was placed in a cylindrical cell of 30 mm diameter. The temperature was maintained constant within 2×10^{-3} deg. An intensity measurement accuracy ~ 2% was ensured by a circuit that determined the ratio of the intensities of the scattered and transmitted light to the incident-radiation intensity. The angular and height dependences of the scattered-light intensity were measured, as well as the relative change of the intensity of the light passing through the cell, in the range of the relative temperatures τ from 3×10^{-3} to 5×10^{-5}. Although this range corresponds approximately to the range considered by us in Ref. 8, the substantially larger difference between the refractive indices of the mixture components led to the appearance of new distinguishing features in the investigated light-scattering picture.

This pertains first of all to the angular dependence of the component I_z^z of the scattered light. It is seen from Fig. 1 that starting with $\Delta T \leqslant 0.05$ deg the quantity $(I_z^z)^{-1}$ ceases to be a linear function of $\sin^2(\theta/2)$, as should follow from Eq. (1). In addition, the depolarization coefficient increases anomalously (Fig. 2). The

TABLE I. Calculated values of parameters as functions of the number of iterations.

Iteration number	r_0, Å	ν	γ	B, cm^{-1}
1	3.25	0.589	1.225	0.321
2	2.79	0.619	1.210	0.287
3	2.72	0.622	1.213	0.294
Final values	2.7±0.2	0.62±0.02	1.21±0.02	0.29±0.02

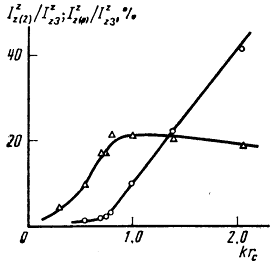

FIG. 4. Relative fraction of double (Δ) and multiple (○) scatterings at $\theta = \pi/2$ and $h = 0$ as a function of kr_c; I^z_{zc} is the experimental value of I^z_z.

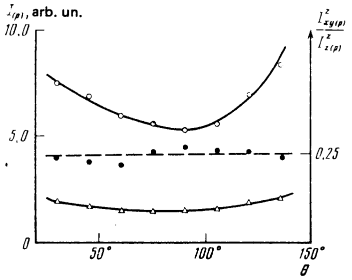

FIG. 6. Angular dependence of the intensity of multiple scattering at $\Delta T = 0.024°$ ($kr_c = 1.36$) for $h = 0$: Δ) experimental values of $I^z_{xy(p)}$, ○) values of the component $I^z_{z(p)}$ extrapolated to $h = 0$; ●) the ratio $I^z_{xy(p)}/I^z_{z(p)}$. At this temperature the fraction of double scattering in the component I^z_{xy} does not exceed several per cent.

first of these facts can be due to a double-scattering contribution that is even larger than in Ref. 8, as well as with scattering of higher multiplicity. As for the degree of depolarization, it follows from the results of Ref. 8 that this growth can not be due to double scattering of light and points to the presence of a noticeable fraction of multiplicity higher than the second, $I_{(p)}$. This calls for development of a new procedure for separating light scatterings of different multiplicity and for determining the parameters ν, γ, r_0, and B of the scattering system.

The procedure proposed by us is based on extrapolating the scatterings of multiplicity higher than second to $h = 0$, starting from the experimental data on the height dependence of the intensity of the scattered light, after subtracting the double scattering calculated theoretically by formulas (5) and (7) of Ref. 8. We have thus used the following iteration procedure. The correlation radii and the values of r_0 and ν were calculated from indicatrices for which the reciprocal intensities revealed no noticeable deviation from a linear dependence on $\sin^2(\theta/2)$ and where the reduced degree of polarization did not differ greatly from that observed in Ref. 8. The data on the temperature dependence of the intensity of the transmitted light were then used to determine the value of B, and the intensity of the scattered light yielded the value of γ. The obtained parameters were used to calculate the intensity of the double scattering of light as a function of h. From the calculated values and the experimental data we obtained at each scattering angle the height dependence $I^z_{z(p)}(h)$, which was then extrapolated to $h = 0$. This procedure is illustrated in Fig. 3. After excluding from the scattering intensity $I^z_z(h = 0)$ the contributions $I_{z(2)}$ and $I^z_{z(p)}$ for all the temperatures, the corrected single-scattering indicatrices were determined and the corrected set of parameters was obtained. The procedure can be continued until the required accuracy is reached. Naturally, the reduction of indicatrices corresponding to smaller values of ΔT calls for a larger number of iteration steps. In practice, the procedure converged rapidly, as is illustrated by Table I. The degree of correction of the indicatrices is shown in Fig. 1.

We note that the obtained critical exponents $\gamma = 0.62 \pm 0.02$ and $\gamma = 1.21 \pm 0.02$ agree with good accuracy with the values obtained for weakly opalescent systems. This confirms that the employed method of reducing the experimental data is reliable enough. Thus, the proposed procedure makes it possible to separate single, double, and higher-multiplicity scattering of light, up to scattering-constant values at which the fraction of the single scattering in the total scattering intensity is ~50%. The relative contribution of double scattering and of scatterings of higher multiplicities is shown in Fig. 4.

Our results permit a comparison of the behavior of scatterings of different multiplicity. As seen from Fig. 5, a relative increase takes place in the intensity of large-angle scattering intensity when the multiplicity is increased. The apparent reason is that whereas with increase of kr_c the single-scattering indicatrix becomes according to (1) more and more elongated forward, independently of the extinction, for multiple scattering the corresponding effect is partially offset by the possi-

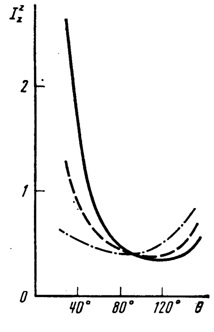

FIG. 5. Angular dependence of single (solid line) double (dashed) and multiple (dash-dot) scatterings at $T = 0.024°$ and $h = 0$.

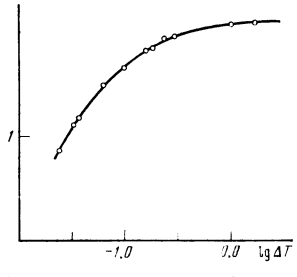

FIG. 7. Dependence of the transmitted light intensity log I on the temperature: points—experimental values, solid line—calculation by formula (6).

bility of backscattering over shorter distances, and hence of smaller attenuation.

The degrees of depolarization of different scattering multiplicities are also substantially different. Single scattering is fully polarized, the degree of depolarization of double scattering is $I^z_{z(2)}/I^z_{z(2)} \sim 2\%$, and scatterings of higher multiplicity have polarization degrees $I^z_{z(p)}/I^z_{z(p)} \sim 20\%$. It follows therefore, in particular, that the influence of multiple scattering $I(p)$ manifests itself much earlier in the depolarized component than in the polarized one when the critical point is approached. A distinguishing feature of multiple scattering is also the close character of the angular dependences of the polarized and depolarized components, as illustrated in Fig. 6.

It is of interest to note that although the considered system opalesces very strongly (the beam attenuation over the cell length reached a factor of 500 under the experimental conditions), the extinction coefficient is nevertheless well described by Eq. (6), as seen from Fig. 7, and the obtained value of B is close to that found for this system in Ref. 7.

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Investigation of the interaction of intense laser radiation with sulfur-hexafluoride molecules by the buffer-gas method

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Measurement results are presented for the coefficient of absorption of intense ($\sim 10^7$W/cm^2) Co_2 laser radiation by SF_6 molecules in the presence of noble gases, in the pressure interval up to 40 bar. The variation of the absorption coefficient with change of pressure and of the sort of buffer gas, as well as with the wavelength and intensity of the incident radiation, makes it possible to trace the evolution of the vibrational-state distribution function of the molecules. The character of this function is decided by the competition between the vibrational relaxation processes and laser-radiation absorption. In the high-pressure limit, $P_{He} \gtrsim 20$–40 bar, a two-level interaction was realized for the first time ever between high-intensity laser radiation and SF_6, wherein molecules excited by the light into the state $v = 1$ relax instantaneously via collisions. Reduction of the experimental data yields an estimate of the dependence of the SF_6 molecule decay rate constant on the number of the vibrational level v in collisions with helium atoms. This dependence is approximated by the formula $k(v) \sim k_{10}v^n$ ($n \approx 4.5$, $k_{10} = 2.5 \times 10^{-12}$cm^2/sec). The aggregate of the experimental data confirms the assumption that the interaction of the laser radiation with the SF_6 molecules is linear.

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The interest in the investigation of the mechanism whereby intense IR laser radiation interacts with polyatomic molecules is due, on the other hand, to the rather complicated character of this interaction, and on the other to its possible practical application in selective photochemistry and for isotope separation by lasers. Despite the large number of experimental[1,2] and theoretical[3-5] studies, many details of this process remain unclear. This is due primarily to the lack of the necessary information on the dependence of the degree of interaction of the vibrationally excited polyatomic molecule with the laser-radiation quantum on the degree of the vibrational excitation. In this paper we deduce some information on the mechanism whereby intense laser radiation of wavelength 10.6 μm interacts with SF_6 molecules. We use the buffer-gas method (BGM), which had given good account of itself in laser-chemistry research.[6-8]