Study of the extinction and scattering of light near the critical point

L. V. Adzhemyan, L.Ts. Adzhemyan, L. Z. Zubkov, and V. P. Romanov

Leningrad State University
(Submitted 2 March 1982)
Zh. Eksp. Teor. Fiz. **83**, 539–544 (August 1982)

The extinction and scattering of light in the vicinity of the critical stratification point are studied in the strongly opalescing BMOAB–isooctane mixture. Owing to the large scattering coefficient, multiple scattering of light plays a major role practically throughout the whole temperature range studied. An iteration procedure is proposed and used for a combined reduction of the experimental data on the basis of the temperature dependence of the transmitted-light intensity and the light-scattering indicatrix. This reduction permits the critical parameters to be determined with good accuracy and diminishes their variance by several times compared to that attained when the results of each of the experiments are analyzed separately.

PACS numbers:78.20.Fm

The determination of the critical material parameters of strongly opalescent substances is made highly complicated by multiple scattering of light. A procedure for exluding multiple scattering from the total intensity was developed in references 1–3 for the case when there exists a temperature interval in which the multiple scattering is not too large, but at the same time the scattering indicatrices exhibits already a noticeable asymmetry. This makes possible at least a rough estimate of the critical parameters, followed by a development of an iteration procedure for excluding the higher-multiplicity scatterings and refining the vaues of the critical parameters.

There exist, however, systems that have no such temperature intervals. In this case it is necessary to find another means of obtaining the zeroth-approximation critical parameters. Such a source can be the change of the attenuation of the transmitted light as a function of the proximity to the critical point. i.e., a study of the temperature dependence of the extinction coefficient. An advantage of such investigations is that the extinction coefficient does not depend on the multiple scatterings that distort strongly the scattering indicatrices of the light. Another advantage is the relative simplicity and considerable accuracy of measurements of this kind. A shortcoming of this approach is the lower sensitivity to the values of the critical parameters, since the extinction coefficient is an integral characteristic of the single scattering. In this connection, the critical parameters are usually determined from such experiments with a much larger variance.[4]

We have investigated the temperature dependence of the scattering intensity of light and of the extinction coefficient in strongly opalescent binary mixture in the vicinity of the critical stratification point. The mixture consists of BMOAB (*p*-*n*-butyl-*p*-metoxy-azoxy-benzene) and isooctance($C_{cr} = 74 \pm 0.3$ molar fractions of isooctane, $T_{cr} = 301.6$ K). These investigations are of interest because the pure BMOAB component is a liquid crystal. The heat capacity of such a mixture was investigated in Ref. 5, where it was shown that despite the presence of an unusual component, the critical exponent α of the mixture has the usual universal value. It is of interest to ascertain whether this universality manifests itself also in the optical properties.

The intensity of the transmitted light was measured with a cooled FÉU-79 photomultiplier (PM-I) operating in the pulse-counting regime. To decrease the influence of the instability of the exciting light, we used circuitry in which the recorded signal was divided by the intensity of the exciting light incident on a second photomultiplier (PM-II). The operating stability of the recording system was checked by placing in front of the two photomultipliers radioactive brightness standards both when the photomultipliers operated in the absolute-intensity counting regime and in the signal-division regime. The signal-measurement accuracy in these tests was better than 1%.

A cell with the investigated mixture was placed in a massive copper jacket, in which the temperature was maintained constant within less than 0.003 K. The intensity of the transmitted light as a function of $\Delta T = |T - T_{cr}|$ was measured in the temperature interval from 3.5 to 0.15 K. It changed in this case by approximately 100 times. In measurements far from the critical point, the intensity of the light incident on the cell was decreased by a neutral filter with an attenuation coefficient $\rho = 12.5 \pm 0.1$ at the wavelength $\lambda = 6328$ Å. The measurement results are shown in Fig. 1.

The angular dependence of the scattered-light intensity was measured in the temperature interval ΔT from 1.5 to

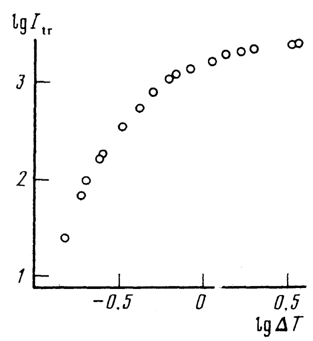

FIG. 1. Temperature dependence of the intensity of the transmitted light.

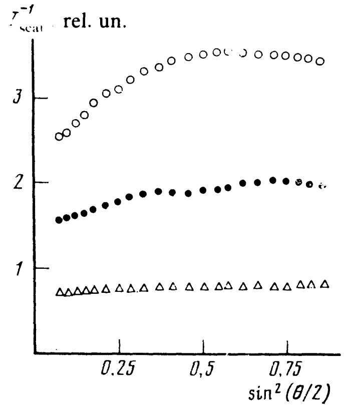

FIG. 2. Angular dependence of the back scattered-light intensity for different temperatures: Δ–$\Delta T = 1.5°$, ●–$\Delta T = 0.405°$, O–$\Delta T = 0.145°$.

0.15 K using the setup described in Ref. 2. Just as in Refs. 2 and 3, at each scattering angle we measured the height dependence of the intensity of the multiple scattering of the light. Typical indicatrices for $h = 0$ are shown in Fig. 2.

The intensity of the singly scattered light in the vicinity of the critical stratification point is given by

$$I_z^z = \frac{I_0}{X^2} R_{\text{scat}}\, e^{-\sigma L} V G(q), \tag{1}$$

where I_0 is the intensity of the incident light propagating along the x axis, the superscript and the subscript denote the polarizations of the incident and scattered light, respectively, V is the scattering volume, X is the distance to the observation point, R_{scat} is the scattering constant, and L is the path traversed by the beam in the critical mixture. In the Ornstein-Zernike approximation we have

$$G(q) = 1/[1+(qr_c)^2], \tag{2}$$

where r_c is the correlation radius, $q = 2k\sin(\theta/2)$, $\mathbf{q}$ is the scattering wave vector $\mathbf{k}$ is the wave vector of the incident radiation in the medium, and θ is the scattering angle. In the same approximation, the extinction coefficient is given by[4]

$$\sigma = \frac{\pi}{2} B \left\{ \left[2+(kr_c)^{-2} + \frac{1}{4}(kr_c)^{-4} \right] \times \ln[1+4(kr_c)^2] - 2 - (kr_c)^{-2} \right\} = Bf(kr_c), \tag{3}$$

where $B = R_{\text{scat}}/(kr_c)^2$.

Equation (1) predicts a linear dependence of the reciprocal intensity of the scattered light on $\sin^2(\theta/2)$. In the investigated mixture the contribution of the multiple scattering was so high that in almost the entire investigated temperature interval we observed a large deviation from linearity (see Fig. 2). This made impossible even a rough determination of the temperature dependence of the correlation radius

$$r_c = r_0 \tau^{-\nu}, \quad \tau \equiv \Delta T / T_{\text{cr}},$$

and consequently, the determination of r_0 and of the critical exponent ν. Therefore, the critical parameters were obtained in the zeroth approximation from data on the attenuation of the transmitted-light intensity. The fraction of the scattered light incident on the photoreceiver was estimated at

$$\delta \sim I^{(1)}_{\text{scat}}(\theta=0) S / I_{\text{tr}} S_0,$$

where S is the receiver surface illuminated by the scattered light and S_0 is the cross section of the transmitted beam. Under the conditions of our experiment, with account taken of the multiple scattering, this fraction does not exceed 0.05%,[1)] and this distorting factor can be neglected, i.e., it can be assumed that the measured intensity is given by

$$I_{\text{tr}} = I_0 \exp(-\sigma L_1), \tag{4}$$

where L_1 is the path of the light in the medium.

To determine the parameters r_0, ν, B, and I_0 we used the least-squares method. We minimized the quantity

$$S_1 = \sum_i [\ln I^{(i)}_{\text{tr}} - \ln I_0 + BLf(kr_0\tau_i^{-\nu})]^2, \tag{5}$$

where $I^{(i)}_{\text{tr}}$ and τ_i are the experimental values of the intensity of the transmitted light and of the reduced temperature. Since the dependence on r_0 and on ν is nonlinear, the least-squares procedure was used for the quantities B and $\ln I_0$ at different values of r_0 and ν, from which we subsequently chose the r_0^* and ν^* corresponding to the absolute minimum of S_1. An estimate of the variance of the parameters was then obtained by linearizing S_1 with respect to $r_0 - r_0^*$ and $\nu - \nu^*$ in the vicinity of r_0^* and ν^*. The obtained values of the parameters and the square roots of their variances are given in the first line of Table I. The relatively large variances are due to the fact that we determined four parameters from the sufficiently smooth dependence of σ on ΔT. We note that the dependence of σ on kr_c at $0.2 \leqslant kr_c \leqslant 2$ is practically linear, so that to decrease the variance of the parameters it is important to use measurement results at $kr_c \leqslant 0.2$, where $\sigma \sim (kr_c)^2$. For the system considered, we were able to measure the attenuation of the light in this region with sufficient accuracy because of the large values of the scattering constant.

The correlation radii were determined from the scattering indicatrices by the method described in Ref. 3. To this end we measured the angular and height dependences of the

TABLE I. Parameters obtained by reducing the experimental data

	ν	r_0	B
Measurement of the intensity of the transmitted light	0.60±0.03	3.4±0.4	1.15±0.30
Measurement of the angular dependence of the scattered-light intensity	0.60±0.04	3.9±1.0	–
Joint reduction of data on the attenuation of scattering of the light.	0.63±0.01	3.2±0.2	0.95±0.04

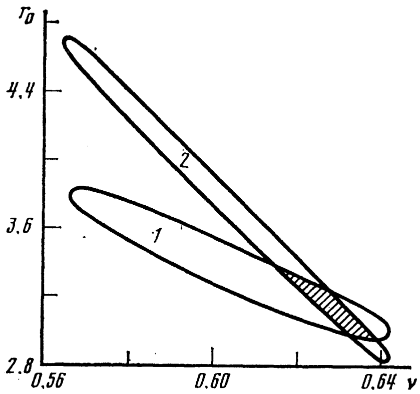

FIG. 3. Confidence regions of the values of the paramters r_0 and ν: 1) for extinction experiment; 2) for light-scattering experiment.

scattered-light intensity $I_z{}^z(\theta,h)$, and then from the values of r_0 and ν obtained by measuring the extinction we calculated the intensity of the doubly scattered light $I_z^{z(2)}(\theta,h)$ as a function of h (Ref. 2). The difference between the measured value of $I(\theta,h)$ and the calculated intensity of the doubly scattered light $I_z^{z(2)}(\theta,h)$ is the sum of the scattering intensities of higher multiplicities $I^{(p)}(\theta,h)$, for which it is known[3] that they should be smooth functions at $h\sim 0$. Thus, exclusion of the multiple scattering from the indicatricies $I_z^z(\theta,h=0)$ is reduced to subtraction of the theoretically calculated intensity of the doubly scattered light, and the higher-multiplicity scatterings obtained by extrapolation to $h=0$.

From the obtained correlation radii we determined the values of r_0 and ν. To this end we minimized the quantity

$$S_2=\sum_i \frac{1}{p_i}(\ln r_{ci}-\ln r_0+\nu\ln\tau_i)^2. \tag{6}$$

For the weighting coefficients p_i we used the quantitites $\langle|\delta r_c|^2\rangle/r_c^2$, where $\langle|\delta r_c|^2\rangle$, is the estimated variance of the correlation radii and is obtained by reducing the corrected indicatrices. The obtained values of r_0 and ν are given in the second line of Table I. It is seen from the table that the use of data on the indicatrices does not lead directly to a decrease of the variances of the determined parameters, so that the iteration procedure cannot be continued. We shall show, however, that the data on the extinction and on the indicatrices actually contain mutually complementary on the values of the parameters so that the accuracy of their determination can be substantially improved.

We consider to this end in greater detail the "regions of permissible values of the parameters," determined by their correlation matrix for each of the experiments. These regions are shown in Fig. 3. Figure 1 was plotted at values of B and $\ln I_0$ corresponding to the minimum of the residual sum S_1. It is seen from the figure that these regions are strongly elongated intersecting gullies. The gully-intersection region corresponds to parameter values that describe in the best fashion both experiments simultaneously. The size of this region is much smaller than the regions of the admissible values corresponding to each experiment separately. It can thus be expected that the joint reduction of the experimental data will lead to a substantial decrease of the variance of the determined critical parameters.

The data reduction was by least squares. We minimized the residual sum

$$S=p^{-1}S_1+S_2. \tag{7}$$

The factor p^{-1} was introduced to take correct account of the relative weight of each of the experiments. It was defined as the reciprocal variance of $\ln I_{tr}$ obtained by reducing the extinction experiment ($p^{1/2}\sim 0.02$). Several iteration steps were made. In each step, the contribution of the multiple scattering to the indicatrix was eliminated with the aid of the parameters obtained in the preceding step. The zeroth approximation consisted of values of the parameters obtained from the extinction data. In each step, the sum S was minimized analytically with respect to the linearly contained parameters $\ln I_0$ and B, and numerically with respect to the parameters r_0 and ν. The variances of the parameters were determined numerically by linearization in the vicinity of the minimum. The iteration procedure converged rapidly, and even in the second step the deviation of the parameter values was much less than their variance. The obtained values of all the parameters are given in the third line of the table. Joint reduction of the experiments actually led to a substantial increase of the accuracy with which the parameters were determined. The critical exponent ν turned out to be the same as in ordinary critical mixtures, the value of r_0 agreed within the limits of errors with the value obtained for the given mixture in Ref. 5 from heat-capacity data.

The joint reduction caused also a substantial change in

TABLE II. Correlation matrix of calculated parameters.

	$\delta\,\widetilde{\ln I_0}$	$\delta\tilde B$	$\delta\tilde r_0$	$\delta\tilde\nu$
$\delta\,\widetilde{\ln I_0}$	1	0.85 0.49	0.96 0.86	−0.92 −0.84
$\delta\tilde B$		1	0.86 0.49	−0.98 −0.70
$\delta\tilde r_0$			1	−0.95 −0.97
$\delta\tilde\nu$				1

Note. Upper numbers—results of reduction of data on the attenuation of the intensity of the transmitted light, lower—data obtained by joint reduction of the experiments on attenuation and scattering of light. Here $\delta\tilde a=\delta a/\langle\delta a^2\rangle^{1/2}$.

the correlations of the determined parameters. The complete correlation matrix is given in Table II. A particularly noticeable decrease was observed in the correlations with the parameter B. This has led, in particular, to a substantial decrease of the error with which the scattering constant $R_{\text{scat}} = B(kr_0\tau^{-\nu})^2$ was determined, from 6% as given by extinction data to 1% obtained by the joint reduction.

Thus, the proposed procedure has made it possible to determine with sufficiently high accuracy the critical parameters in a strongly opalescent system, when sufficiently reliable experimental data can be obtained in a relatively narrow temperature interval. The limitation of the temperature interval from the side of small T is due to the fact that when data on light scattering are reduced it is reasonable to take into account only those indicatrices in which the contribution of multiple scattering does not exceed 50%, for otherwise the error due to exclusion of this scattering increases.

In conclusion, the authors thank I. L. Fabelinskiĭ and M. A. Anisimov for a discussion of the work and I. V. Mel'nik for help with the experiment.

[1)] As will be seen below, the fraction of multiple scattering does not exceed 50% of the total intensity of the scattered light.

[1] L. V. Adzhemyan, L. Ts. Adzhemyan, L. A. Zubkov, and L. A. Romanov, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 11 (1975) [JETP Lett. **22**, 5 (1975).
[2] L. V. Adzhemyan, L. Ts. Adzhemyan, L. A. Zubkov, and V. P. Romanov, Zh. Eksp. Teor. Fiz. **78**, 1051 (1980) [Sov. Phys. JETP **51**, 530 (1980)].
[3] L. V. Adzhemyan, L. Ts. Azhemyan, L. A. Zubkov, and V. P. Romanov, *ibid.* **80**, 551 (1981) [**53**, 278 (1981)].
[4] V. G. Piglielli and N. C. Ford, Jr., Phys. Rev. Lett. **25**, 143 (1970).
[5] M. A. Anisimov, V. M. Zaprudskiĭ, V. M. Mamnitskiĭ, and E. L. Sorkin, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 523 (1979) [JETP Lett. **30**, 491 (1979)].

Translated by J. G. Adashko