Multiple scattering of light in an inhomogeneous medium near the critical point. III. Depolarization of the scattered light

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The depolarization coefficient near the critical point is calculated allowing for the effects of double scattering of light. The results obtained for the range $3\times10^{-3}\leq q^2R_c^2\leq 11$, where q is the transferred wave vector in the case of scattering by an angle $\vartheta=\pi/2$ and R_c is the correlation radius of the density fluctuations, are used to estimate the relative contributions of single and double scattering, as well as to study—near the critical point—the dependences of the scattering properties on the direction of observation for different polarizations and geometrical dimensions of the scattering region. The results of a numerical calculation of the depolarization coefficient are in good agreement with the available experimental data.

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Investigations of the effects of multiple scattering of light near the critical point and the associated depolarization of the scattered light have been attracting considerable attention.[1-13] The most thoroughly investigated process is the depolarization associated with the scattering of light by anisotropic molecules.[14-16] The mechanisms of the depolarization of light scattered by isotropic molecules are now known. For example, it has been shown[17] that the depolarization of singly scattered light may be due to the tensor nature of the permittivity of small regions as a result of perturbations of the distribution function of thermal fluctuations. Another depolarization mechanism is associated with multiple scattering and it is most important in the critical region.

The contribution of double scattering to the depolarization coefficient near the critical point has been studied theoretically[3,6,7,13] and experimentally.[6,9-12] A numerical calculation of the depolarization coefficient Δ was carried out by Oxtoby and Gelbart[3] using their own formulas for the intensity of double scattering in the case of Xe for the range $2\cdot10^{-4}\leqslant q^2R_c^2\leqslant 0.18$, where $q=2^{3/2}\pi/\lambda$ is the transferred wave vector when light is scattered by an angle $\vartheta=\pi/2$ and R_c is the correlation radius of the density fluctuations. In Refs. 3 and 7 the range of validity of the formulas for Δ is limited because of lack of allowance for the doubly scattered light in the polarized component. This aspect becomes important in the range $qR_c\gtrsim 1$, which corresponds to deviation of the temperature from the critical point by $\tau\lesssim 10^{-(4-5)}$ along the critical isochore. It is this range and temperatures closer to the critical point which have been studied in current experiments.

We shall report a self-consistent calculation of the depolarization coeffcient Δ and find numerical values of Δ in the range $3\cdot10^{-3}\leqslant q^2R_c^2\leqslant 11$. We shall use these results to estimate the relative contributions of single and double scattering to the depolarization coefficient. We shall investigate the dependences of the scattering properties in the critical region on the direction of observation for various polarizations, and also on the geometrical dimensions of the scattering region. We shall discuss the possibility of investigating double scattering and the spectral composition of the resultant scattered light. We shall show that the results of a numerical calculation of the depolarization coefficient are in good agreement with the available experimental data.

1. We shall study depolarization of the scattered radiation near the critical point using the double scattering approximation. As before,[2,4,13] we shall assume that our medium is spatially inhomogeneous under the influence of an external field (to be specific, we shall consider a liquid–vapor system in a gravitational field). Naturally, all the results can be applied also to the case of a spatially homogeneous medium and to systems of different physical nature (for example, a magnetic material in an inhomogeneous magnetic field).

The main problem is to find the depolarization coefficient

$$\Delta=I_y^{xz}/I_y^{xx}, \tag{1}$$

and also of the polarization ratio

$$\Delta_1=I_x^{xz}/I_x^{xy}, \tag{2}$$

where the lower index in the scattered-light intensity components indicates the direction of observation and the upper index gives the polarizations of the exciting and scattered light, respectively. The incident light travels along the z axis that coincides with the external field gradient. The intensity components in Eqs. (1) and (2) may be calculated using the general formulas (8) and (9) from Ref. 2 or (5) and (6) from Ref. 4 for fields of light scattered i times with the required polarization; one can also use the expressions which follow from these formulas [see Eq. (10) in Ref. 2] and describe the intensities of singly and doubly scattered light. The explicit expressions for the required components are

$$I_y^{xz}=I_0\frac{4\pi^2VL_z}{L^2}\alpha^2(z,\tau)K_y^{xz}(\sigma_1), \tag{3}$$

$$K_y^{xz}(\sigma_1)=\int\limits_{\sigma_1}\frac{(\mathbf{n}_1\mathbf{n}_0)^2(\mathbf{n}_1\mathbf{m}_0)^2\,d\sigma_1}{[1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1\mathbf{n}_0][1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1[\mathbf{n}_0,\mathbf{m}_0]]}, \tag{3a}$$

$$I_y^{xx}=I_0\frac{2\pi\sigma L_z}{L^2}\frac{\alpha(z,\tau)}{1+\delta(z,\tau)}+I_0\frac{4\pi^2VL_z}{L^2}\alpha^2(z,\tau)K_y^{xx}(\sigma_1), \tag{4}$$

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$$K_y^{xx}(\sigma_1)=\int\limits_{\sigma_1}\frac{(\mathbf{n}_1\mathbf{n}_0)^2\,d\sigma_1}{[1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1\mathbf{n}_0][1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1\mathbf{m}_0]}-2K_y^{xz}(\sigma_1), \tag{4a}$$

$$I_x^{xz}=I_0\frac{4\pi^2VL_z}{L^2}\alpha^2(z,\tau)K_x^{xz}(\sigma_1), \tag{5}$$

$$K_x^{xz}(\sigma_1)=\int\limits_{\sigma_1}\frac{(\mathbf{n}_1\mathbf{n}_0)^2(\mathbf{n}_1\mathbf{m}_0)^2\,d\sigma_1}{[1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1\mathbf{n}_0][1+\delta(z,\tau)-\delta(z,\tau)\mathbf{n}_1\mathbf{m}_0]} \tag{5a}$$

$$I_x^{xy}=I_y^{xz}. \tag{6}$$

We have retained here the notation adopted in Refs. 2 and 4: I_0 is the intensity of the incident light beam of cross section σ; V and L_z are, respectively, the volume and the characteristic linear size of the scattering region; L is the distance from the scattering region to the point of observation;

$$\alpha(z,\tau)=\frac{\pi}{2\lambda^4}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^2 k_BT\beta_T(z,\tau);$$

$$\delta(z,\tau)=8\pi^2\lambda^{-2}f^*(z,\tau)\beta_T(z,\tau);$$

f^* is the parameter representing the nonlocality of the fluctuations; $\beta_T(z,\tau)$ is the local value of the isothermal compressibility; $\mathbf{n}_0$, $\mathbf{m}_0$, and $\mathbf{n}_1$ are unit vectors indicating, respectively, the direction of incidence and the polarizations of the exciting field and the direction of single scattering. The integrals in Eqs. (3a), (4a), and (5a) are summed along all the directions of single scattering in the investigated region (this scattering is responsible for the doubly scattered light entering the detector).

Equations (3)–(6) give averaged (over the height) differential scattering intensities dI/dz which have to be used in the case of a spatially inhomogeneous medium when the experimental information is recorded for layers with local homogeneity.[18] One should draw attention to the fact that the contribution of single scattering occurs only in the polarized (horizontal) component I_y^{xx} [the first term in Eq. (4)]. The "interference" terms of second-order intensities are ignored in Eqs. (3) and (4) because their relative contribution is negligible.[2,4]

Integrating over the solid angle σ_1 in Eqs. (3a), (4a), and (5a), we obtain1)

$$K_y^{xz}=\frac{\pi}{\delta^5}\Big\{(5+15\delta+14\delta^2+4\delta^3)\ln(1+2\delta)-2\delta(1+\delta)^2$$
$$-4(1+\delta)^2(2+4\delta+\delta^2)^{1/2}\ln\frac{(2+4\delta+\delta^2)^{1/2}+\delta}{(2+4\delta+\delta^2)^{1/2}-\delta}\Big\}, \tag{7}$$

$$K_y^{xx}=\frac{4\pi}{\delta^3}\left\{\frac{2(1+\delta)^2}{(2+4\delta+\delta^2)^{1/2}}\ln\frac{(2+4\delta+\delta^2)^{1/2}+\delta}{(2+4\delta+\delta^2)^{1/2}-\delta}-(1+\delta)\ln(1+2\delta)\right\}-2K_y^{xz}, \tag{8}$$

$$K_x^{xz}=\frac{4\pi}{\delta^5}\Big\{\delta(1+\delta)^2+\frac{1+4\delta+6\delta^2+4\delta^4}{(2+4\delta+\delta^2)^{1/2}}\ln\frac{(2+4\delta+\delta^2)^{1/2}+\delta}{(2+4\delta+\delta^2)^{1/2}-\delta}$$
$$-(1+3\delta+3\delta^2+\delta^3)\ln(1+2\delta)\Big\}. \tag{9}$$

The expressions for the depolarization coefficient Δ and the polarization ratio Δ_1 rewritten with the aid of Eqs. (3)–(6) have the form:

$$\Delta=\gamma_1/(1+\gamma_2), \tag{10}$$

$$\gamma_1=I_{2y}^{xz}/I_{1y}^{xx}=s(1+\delta)\delta K_y^{xz}, \tag{11}$$

$$\gamma_2=I_{2y}^{xx}/I_{1y}^{xx}=s(1+\delta)\delta K_y^{xx}, \tag{12}$$

$$\Delta_1=K_x^{xz}/K_y^{xz}, \tag{13}$$

where γ_1 and γ_2 are the coefficients which determine respectively the relative contribution to Δ of the depolarized I_{2y}^{xz} and polarized I_{2y}^{xx} double scattered light (as compared with the contribution of the singly scattered light of intensity I_{1y}^{xx});

$$s=(\rho\,\partial\varepsilon/\partial\rho)_T^2k_BTL_z/8\lambda^2f^* \tag{14}$$

is a parameter which depends weakly on the degree of proximity to the critical point. On the other hand, this parameter depends largely on the thickness L_z of the layer from which the experimental information is obtained.

In the immediate vicinity of the critical point ($\delta\gg1$) the scattered-light intensity components included in the depolarization coefficient Δ are given by

$$I_y^{xx}=I_0\frac{8\pi^3VL_z}{L^2}\frac{\alpha^2}{\delta^2}\left(2\ln2-1+\frac{7\ln2-2}{\delta}-\frac{2\ln\delta}{\delta}\right), \tag{15}$$

$$J_y^{xx}=I_0\frac{2\pi\sigma L_z}{L^2}\frac{\alpha}{\delta}+I_0\frac{16\pi^3VL_z}{L^2}\frac{\alpha^2}{\delta^2}\left(\ln\delta+1-3\ln2+\frac{2\ln\delta}{\delta}-\frac{8\ln2-2}{\delta}\right). \tag{16}$$

In Eqs. (15) and (16) we have retained not only the terms which dominate the contribution at the critical point, but also the slowly decreasing terms proportional to $\delta^{-1}\ln\delta$ and δ^{-1}.

Extrapolation of Eqs. (15) and (16) to the critical point gives the following results:

$$I_y^{xz}=I_0\frac{8\pi^3VL_z}{L^2}(2\ln2-1)\frac{\alpha^2}{\delta^2}, \tag{17}$$

$$I_y^{xx}=I_0\frac{16\pi^3VL_z}{L^2}\frac{\alpha^2}{\delta^2}\ln\delta, \tag{18}$$

$$\Delta=\ln2e^{-1/2}/\ln\delta. \tag{19}$$

The depolarized (vertical) component I_y^{xz} remains finite at the critical point because the ratio is $\alpha/\delta=\text{const}$. The polarized component I_y^{xx} obtained in double scattering has a weak (logarithmic) singularity at the critical point. It follows from Eq. (19) that the depolarization coefficient Δ tends to zero on approach to the critical point. However, it should be mentioned that this applies only to that part of the total depolarization coefficient which is described by the double scattering approximation.

In the opposite limiting case ($\delta\to0$), i.e., far from the critical point where we can ignore the correlation effects (Rayleigh–Einstein approximation), the depolarization coefficient Δ_{RE} should be calculated using the formula

$$\Delta_{RE}=\frac{8\pi^2L_z\alpha}{15+64\pi^2L_z\alpha}\,. \tag{20}$$

Extrapolation of this thermodynamic result to the critical point gives a constant value $\Delta_{RE}=1/8$. This result differs from that given by Eq. (19). The neglect of the correlation effects results in identical singularities of the vertical I_y^{xz} and horizontal I_y^{xx} components ($I_y^{xz}\propto I_y^{xx}\propto\beta_T^2$), which cancel out at the critical point and ensure that the depolarization coefficient Δ_{RE} remains constant.

The dependence of the depolarization coefficient on the linear size L_z of a layer from which the experimental information is obtained changes on approach to the critical point. In the range $s(1+\delta)\delta K_y^{xx}\ll1$, where the contribution of double scattering is small compared with the single scattering, we have $\Delta\propto L_z$. In the region where the opposite inequality $s(1+\delta)\delta K_y^{xx} \gg 1$ applies, i.e., where the contribution of the double scattering to the horizontal component becomes dominant, the depolarization coefficient ceases to depend on the linear size L_z. The intervals of the thermodynamic quantities where these singularities of $\Delta(L_z)$ are observed will be given later.

It is also of some interest to study the scattered radiation of different polarizations near the critical point in the direction of polarization of the incident wave. Since the polarization ratio Δ_1 does not include (as pointed out earlier) a contribution due to the single scattering but is governed solely by the contributions of the double scattering, the geometrical factors VL_z cancel out in Δ_1. This means that the experimentally determined polarization ratio Δ_1 is independent of the thickness of the layer for fixed values of z and τ in the region where the triple or higher orders of scattering can be ignored.

In the immediate vicinity of the critical point ($\delta \gg 1$) the vertical I_x^{xz} and horizontal I_x^{xy} intensity components occurring in the ratio Δ_1 are given by

$$I_x^{xz} = I_0 \frac{16\pi^3 VL_z}{L^2} \frac{\alpha^2}{\delta^2} \left(1 - \ln 2 + \frac{2 - 3\ln 2}{\delta} - \frac{\ln \delta}{\delta}\right), \tag{21}$$

$$I_x^{xy} = I_y^{xz} \, (\delta \gg 1). \tag{22}$$

It follows from Eqs. (21) and (22) that the value of Δ_1 remains finite at the critical point.

2. We shall report a numerical calculation of the values of γ_1 and γ_2 and also of the depolarization coefficient Δ (which is of immediate experimental interest) for the parameters $s = 10^{-1}$, 1, and 10 in the interval $3\cdot 10^{-3} \leqslant q^2R_c^2 \leqslant 1$ in steps of 10^{-3} and in the interval $1 \leqslant q^2R_c^2 \leqslant 11$ in steps of 10^{-2}. The results of this calculation are presented in Fig. 1 on a logarithmic scale. A numerical calculation of Δ, particularly in the range $q^2R_c^2 \ll 1$, requires high precision because the results represent the difference between two numbers close in absolute value. Insufficient accuracy of the calculations may give rise to false extrema in the dependence $\Delta(q^2R_c^2)$ (Ref. 13).

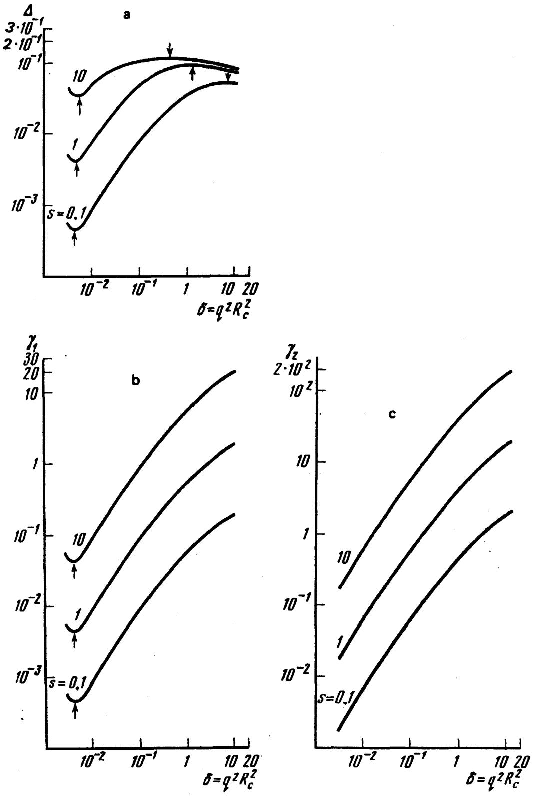

FIG. 1. Dependences of the depolarization coefficient Δ (a) and of the quantities γ_1 (b) and γ_2 (c) on $\delta = q^2R_c^2$ for various values of the parameter s. The arrows identify the extrema.

It is clear from Fig. 1a that the depolarization coefficient Δ goes through a minimum

$$\Delta_{min} = 4.1\cdot 10^{-4} \quad \text{if} \quad \delta_{min} = (q^2R_c^2)_{min} = 4.15\cdot 10^{-3} \text{ and } s = 10^{-1},$$

$$\Delta_{min} = 4.0\cdot 10^{-3} \quad \text{if} \quad \delta_{min} = (q^2R_c^2)_{min} = 4.28\cdot 10^{-3} \text{ and } s = 1,$$

$$\Delta_{min} = 3.1\cdot 10^{-2} \quad \text{if} \quad \delta_{min} = (q^2R_c^2)_{min} = 4.65\cdot 10^{-3} \text{ and } s = 10.$$

Then, the depolarization coefficient begins to rise on approach to the critical point but this rise is not unlimited. Eventually, Δ reaches its maximum:

$$\Delta_{max} = 6.2\cdot 10^{-2} \quad \text{if} \quad \delta_{max} = (q^2R_c^2)_{max} = 7.8 \text{ and } s = 10^{-1},$$

$$\Delta_{max} = 8.5\cdot 10^{-2} \quad \text{if} \quad \delta_{max} = (q^2R_c^2)_{max} = 1.28 \text{ and } s = 1,$$

$$\Delta_{max} = 0.9\cdot 10^{-1} \quad \text{if} \quad \delta_{max} = (q^2R_c^2)_{max} = 4.25\cdot 10^{-1} \text{ and } s = 10,$$

and then Δ begins to fall smoothly on further approach to a critical point. It should be noted that the extrema of the dependences $\Delta(q^2R_c^2)$ and $\gamma_1(q^2R_c^2)$ are not very pronounced.

The nonmonotonic dependence $\Delta(q^2R_c^2)$ can be understood by considering the ratios of the contributions of the doubly scattered depolarized and polarized light relative to the contribution of single scattering, i.e., $\gamma_1(q^2R_c^2)$ and $\gamma_2(q^2R_c^2)$. In the interval $q^2R_c^2 < 5\cdot 10^{-3}$, where γ_1 passes through a minimum (Fig. 1b), we have $\gamma_2 \lesssim 4\times 10^{-3}$ for $s = 10^{-1}$, $\gamma_2 \lesssim 4\times 10^{-2}$ for $s = 1$, and $\gamma_2 \lesssim 0.4$ for $s = 10$ (Fig. 1c). This means that the polarized component is dominated by single scattering and, therefore, the depolarization coefficient is given by $\Delta \approx \gamma_1$. A characteristic minimum in the dependences $\Delta(q^2R_c^2)$ and $\gamma_1(q^2R_c^2)$ is associated with a more rapid rise of the singly scattered component I_{1y}^{xx} in the range $\delta < \delta_{min}$ and its less rapid rise in the range $\delta > \delta_{min}$, compared with the depolarized component I_{2y}^{xz}. The slowing down of this rise and the appearance of a maximum in the dependences $\Delta(q^2R_c^2)$, observed on approach to the critical point, can be explained by a considerable increase and predominance of the contribution of the double scattering to the polarized component I_y^{xx} (Fig. 1c). The subsequent reduction in the depolarization coefficient is associated with the more rapid rise of the component I_{2y}^{xx} compared with the component I_{2y}^{xz} of the doubly scattered light.

An analysis of the results reveals the above-mentioned strong dependence of the values of Δ, γ_1, and γ_2 on the parameter s. We shall now quote an estimate of the parameter s for $L_z \approx 6\times 10^{-2}$ cm, which represents the minimum transverse dimensions of the layers used in the experiments of Ref. 10, on the assumption that $\lambda = 5\times 10^{-5}$ cm and that the quantities in Eq. (14) have the following values typical of high-temperature materials such as benzene:

$$(\rho\,\partial\varepsilon/\partial\rho)_T\approx 4\cdot 10^{-1},\quad T_c\approx 5.6\cdot 10^2\,\mathrm{K},\quad f^*=R_c^2/\beta_T=10^{-(13-14)}\mathrm{H},$$

which gives $s\approx 10^{-(1\,\mathrm{to}\,0)}$.

An analysis of the curves corresponding to the parameter $s=10^{-1}$ shows that, throughout the investigated range of $q^2R_c^2$, the depolarization coefficient and the value of γ_1 remain less than unity, whereas $\gamma_2=1$ for $\delta=4$ and it continues to rise to $\gamma_2\approx 2$ for $\delta=11$.

These results can easily be explained on the basis of the following qualitative considerations. Polarized light incident on a medium consisting of isotropic molecules retains, for scattering of low multiplicity, the predominant direction of the initial polarization. In this case the relative magnitude of the depolarized component γ_1 should be relatively small. However, the contribution of the double scattering to the polarized component rises continuously on approach to the critical point and under certain thermodynamic conditions {for the estimates given above this applies to $\tau=[\lambda^2\delta(\gamma_2=1)/8\pi^2R_0^2]^{-1/2}\leqslant 10^{-4}$ on the critical isochore, where R_0 is the correlation radius far from the critical point and $\nu\approx 2/3$ is the critical index of the temperature dependence of the correlation radius} it begins to predominate over the contribution of the singly scattered light. In the direct vicinity of the critical point ($q^2R_c^2\gg 1$) the light scattered few times simply does not reach the detector and its contribution to the depolarization coefficient vanishes [in the approximation of double scattering this result is illustrated by Eq. (19)]. The scattering thus becomes dominated by the multiple processes. The initial polarization of the incident light ceases to predominate. The contributions of different polarizations to the intensity of the critical scattering become equalized. The asymptotic value of the depolarization coefficient at the critical point then tends to unity.

3. We shall now compare our results on the depolarization of the scattered light near the critical point with the published theoretical and experimental investigations.

A comparison with theoretical calculations[3] shows that for $\lambda=2\pi\times 10^{-5}$ cm and $L_z=0.1$ cm, the parameter s is $\approx 10^{-2}$ for Xe if $f^*=10^{-13}$H and $(\rho\partial\varepsilon/\partial\rho)_T^2=10^{-1}$. In the range $q^2R_c^2<0.18$, where the results of Ref. 3 are reliable, it is meaningful to compare the depolarization coefficient calculated in Ref. 3 with the value of γ_1 because—as mentioned earlier—the contribution of the double scattering to the polarized component is ignored ($\gamma_2=0$) in Ref. 3. It is then found that for the values of λ, L_z, f^*, and $(\rho\partial\varepsilon/\partial\rho)_T^2$ used above, the calculated values of the depolarization coefficient given in Ref. 3 and in the present study are practically identical: for example, the minimum value is $\Delta_{min}\approx 5\cdot 10^{-5}$ and 4.6×10^{-5} in Ref. 3 and, in our case, respectively.

A quantitative agreement is also obtained in the range $q^2R_c^2\lesssim 0.1$ between the values of the depolarization coefficient of CO_2 calculated by us and in Ref. 7 using the following parameters occurring in Eq. (14): $L_z=0.07$ cm, $\lambda=6.3\times 10^{-5}$ cm (Ref. 7), $(\rho\partial\varepsilon/\partial\rho)_T^2\approx 5.10^{-1}$, $f^*=10^{-13}$H.

The formulas for the depolarization coefficient given in Refs. 3 and 7 cease to be reliable in the range $q^2R_c^2\gtrsim 1$ and the difference between the calculated values of Δ increases, reaching tens of percent.

In discussing the experimental investigations[6,9-12] of the depolarization of multiply scattered light in the critical region we shall concentrate especially on the temperature dependence of the depolarization coefficient $\Delta(\tau)$. In most experimental investigations it is found that a sharp minimum of the dependence $\Delta(\tau)$ in the region of $\tau\approx 10^{-3}$ is followed by a considerable rise of the depolarization coefficient on approach to the critical point. The maximum reported values are as follows:

$\Delta\approx 1.2\cdot 10^{-2}$ if $L_z=0.4$ cm, $\tau\approx 1.1\cdot 10^{-4}$ for CO_2 [10],
$\Delta\approx 5\cdot 10^{-1}$ if $L_z\approx 0.5$ cm, $\tau\approx 6\cdot 10^{-5}$ for Xe [10],
$\Delta\approx 10^{-2}$ if $L_z\approx 0.15$ cm, $\tau\approx 3.4\cdot 10^{-4}$ for Xe [11],
$\Delta\approx 4\cdot 10^{-3}$ if $L_z\approx 0.18$ cm, $\tau\approx 1.4\cdot 10^{-3}$ for Xe [12].

In connection with the results of the present study it is interesting to note that Trappeniers *et al.*[10] reported that a maximum of Δ is followed by a slight (up to 10%) fall of the depolarization coefficient of light doubly scattered in CO_2 in the range $\tau\lesssim 10^{-4}$.

The large value of the depolarization coefficient $\Delta\approx 5\times 10^{-1}$ reported in Ref. 10 for Xe indicates, according to the authors, that triple scattering takes place. This explanation is very likely to be true if we bear in mind the nonmonotonic dependence of the depolarization coefficient on the linear dimensions of the layer, reported in Ref. 10, which can be described—after allowance for the triple scattering characterized by $I_3\propto L_z^5$ (Ref. 4)—by the formula

$$\Delta=(\gamma_1+\gamma_3)/(1+\gamma_2+\gamma_4). \tag{23}$$

Here, γ_3 and γ_4 represent the contributions of triple scattering (compared with the single scattering) to the depolarized and polarized components and it is found that $\gamma_3(L_z)\propto\gamma_4(L_z)\propto L_z^2$ and $\gamma_3(\tau)\propto\gamma_4(\tau)\propto\beta_T^2\propto\tau^{-2\gamma}$ on the critical isochore when $q^2R_c^2\ll 1$.

Reliable experimental support is now available for one of the most important theoretical consequences of double scattering,[2,3] which is the dependence of the intensity on the fourth power of the linear dimensions ($I_2\propto L_z^4$) and the directly associated dependence $\Delta\propto L_z$ in the region where $\gamma_2\ll 1$. The first verification of these results was reported in Ref. 6 and this was followed by Refs. 10 and 11.

4. Naturally, on approach to the critical point we can expect an increase in the contribution not only of the double scattering but also the triple etc. scattering. However, there is a range in which the double-scattering corrections to the integrated and spectral intensities of the scattered light predominate in the polarized component I_y^{xx} and this is true also of the contributions of the double scattering to the components I_y^{xz}, I_x^{xz}, and I_x^{xy}. The relative contributions of the scattering of higher multiplicities can be estimated using

$$I_{i+1}/I_i=h_{i+1}/h_i, \tag{24}$$

where $h_k=I_kL^2/I_0V$ is the scattering coefficient which determines the relative contribution of the intensity of the scattering of k-th multiplicity in a given direction.

The relationship (24) must be used in studies of the effects of depolarization of the scattered light, where Eqs. (11)–(13) apply, and in similar cases. In general, estimates of the relative contributions along all directions of successive scattering multiplicities can be obtained conveniently using the extinction coefficients

$$k_i=\int\limits_{\sigma_i} h_i(\sigma_i)\,d\sigma_i. \tag{25}$$

Then, Eq. (24) becomes

$$I_{i+1}/I_i=k_{i+1}/k_i. \tag{26}$$

We shall apply the relationships (24) and (26) to estimate the relative contribution of the double scattering process in the Rayleigh range ($q^2R_c^2 \ll 1$). Since

$$h_{1y}=2\pi\alpha,\quad h_{2y}={}^{48}/_{5}\pi^2\alpha^2L_z,$$
$$k_1={}^{16}/_{3}\pi^2\alpha,\quad k_2=k_1{}^2L_z,$$

it follows that

$$I_{2y}/I_{1y}=h_{2y}/h_{1y}={}^{9}/_{10}k_1L_z,\ I_2/I_1=k_2/k_1=k_1L_z. \tag{27}$$

A calculation, which will be described in detail later, shows that the total intensities obey the relationship

$$I_{i+1}/I_i=k_1L_z \tag{28}$$

valid for any value $i \geqslant 1$ both when $q^2R_c^2<1$ and when $q^2R_c^2>1$.

If $q^2R_c^2>1$, the relative contributions of the successive scattering multiplicities can be obtained from Eq. (28) by taking the extinction coefficient k_1 from the Ornstein–Zernike theory, namely

$$k_1=\frac{2\pi^2\alpha}{\delta}\left[\frac{1+2\delta+2\delta^2}{\delta^2}\ln(1+2\delta)-\frac{2(1+\delta)}{\delta}\right], \tag{29}$$

which—subject to Eqs. (14) and (28)—gives

$$\frac{I_{i+1}}{I_i}=\pi s\left[\frac{1+2\delta+2\delta^2}{\delta^2}\ln(1+2\delta)-\frac{2(1+\delta)}{\delta}\right]. \tag{30}$$

It follows from Eqs. (27) and (28) that in the Rayleigh range on the assumption that $L_z=10^{-1}$ cm, $\lambda=5\times10^{-5}$ cm, and $\beta_T \lesssim 10^{-4}$ Pa, which corresponds to materials such as benzene, and for $\tau \gtrsim 10^{-3}$ on the critical isochore, we have

$$I_2/I_1\approx0.3,\ I_3/I_1\approx0.09,\ I_4/I_1\approx0.027,\ldots, \tag{31}$$

and the contribution of the double scattering to the total scattering intensity is about 30%.

On approach to the critical point in the range $\delta=q^2R_c^2 \gtrsim 1$ a reduction in the linear size L_z ensures predominance of the contribution of the double scattering in the correction to the single scattering. For example, the relationships (31) between the intensities of the scattered light of increasing multiplicities is retained for $\delta=10$, which corresponds to $\tau\approx10^{-5}$ on the critical isochore if we assume that $L_z=10^{-(3-4)}$ cm ($s=10^{-2}$).

Closer to the critical point and for small scattering angles we find from Eqs. (15) and (22) of Ref. 2 that

$$\frac{I_2}{I_1}=\frac{h_{2z}}{h_{1z}}=4\pi s\left(1-\frac{1}{2\delta}\ln 2\delta\right). \tag{32}$$

It is clear from Eq. (32) that the relative contribution of the single and double scattering is also governed by the geometrical factor ($s \propto L_z$) and for actual experimental values $s=10^{-(2-2)}$ in the range $\delta \gg 1$ the ratio $I_2(\vartheta=0)/I_1(\vartheta=0)$ may change considerably.

These estimates allow us to identify the range where the effects of double scattering play the dominant role. Clearly, this should be the range where $I_2/I_1<1$. Then, the relative contributions of the higher multiplicities of scattering to the total intensity of multiple scattering decrease on increase in the multiplicity. Our calculations of Δ, γ_1, and γ_2 carried out for $s=10^{-1}$ indicate that this situation occurs when $\delta<\delta_{\max}=7.8$ ($\tau \gtrsim 10^{-5}$).

It should be noted that on increase in the parameter δ from $\delta_{\max}$ to $\delta=11$, used in our calculations, the contribution of the double scattering to the polarized component I_y^{xx} begins to rise without limit [see Eq. (18)] and the values of the depolarization coefficient Δ decrease significantly (Fig. 1a). It follows that a further increase in the depolarization coefficient becomes meaningless in the double scattering approximation, since in the range $\delta>\delta_{\max}$ the scattering of higher multiplicities becomes important.

5. We shall conclude by considering briefly the possibility of determining the integrated and spectral intensities of the scattering of higher multiplicities in the critical region.

An analysis of the depolarized component free of the contribution of the single scattering is promising in this respect. An investigation of the temperature dependence of this component makes it possible to check one of the nontribial theoretical consequences obtained in Ref. 2, which is the gradual reduction (on approach to the critical point) of the exponent of the temperature dependence of the intensity of the doubly scattered light. The first experimental confirmations of the correctness of these theoretical predictions have already been published.[6, 9, 12] Far from the critical point in the range where $\tau\approx10^{-(2-3)}$ the temperature dependence $I_2(\tau)$ has the exponent 2.52, which is in good agreement with twice the value of the critical index γ. When $\tau \approx 10^{-4}$, there is a gradual transition from the dependence $I_2 \propto \tau^{-2\gamma}$ to the dependence $I_2 \propto \tau^{-\gamma}$, in accordance with Eqs. (21) and (22) of Ref. 2.

A theoretical study of the spectral composition of the doubly scattered light is given in Ref. 4. The main results which have to be checked experimentally are as follows: Double acoustic modes can be expected; the profile of the central component is complex; the half-widths of the quintet found in the spectrum of the doubly scattered light obey the relationship $\Gamma^{(2)}=(\Gamma^{(1)}\Gamma^{(3)})^{1/2}$, which is Eq. (36) of Ref. 4; the temperature dependences of the half-widths should be described by Eqs. (10)–(13) and (19b) of Ref. 4. All these results can be obtained by analyzing the spectrum of the depolarized component I_{2y}^{xz}.

Considerable progress has been made recently in developing high-resolution experimental methods,[20] which brings closer practical applications of the spectra of critical opalescence, subject to allowance for the multiple scattering effects.

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1) In the calculation of the integrals (3a), (4a), and (5a) we used certain integral identities employed in Ref. 19. In the subsequent formulas we have omitted the arguments of the functions $\alpha(z, \tau)$ and $\delta(z, \tau)$, which should cause no confusion in respect of the notation for the critical indices used in the published literature.

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Theory of drift motion of molecules in the field of resonant infrared radiation

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The distinguishing features of the effect of molecule drift in the field of resonant infrared radiation are discussed. The kinetics and hydrodynamics of the drift streams in a multicomponent gas mixture, which take place at a constant summary gas pressure, are formulated with account taken of the collision quenching of the excited molecules and of the rotational relaxation. The stationary distribution of the concentrations of the resonant molecules and of the buffer-gas particles are obtained for a closed cuvette as well as in the case of drift of the gas-mixture components from one vessel to another. Instability of the two-stream flow in a mixture of neutral gases, reminiscent of two-stream instability in a plasma, is predicted.

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Gel'mukhanov and Shalagin[1] have predicted theoretically the existence of a very interesting phenomenon—the onset, under the influence of a traveling resonant wave, of macroscopic atom streams directed along or against the light flux. These streams appear only in the presence of an extraneous buffer gas, which moves in this case opposite to the resonant particles, so that the summary matter flux is zero. A similar phenomenon was apparently observed in the experiment of Ashkin and co-workers,[2] but the cause of the effect remained unexplained. In a recent experiment[3] performed under conditions close to those of Ref. 2, a partial separation of a mixture of sodium vapor and a noble gas (He, Ne) was observed,1) and the direction of the effect was in agreement with the predictions of the theory[1] and with the observations.[2] At the optimal choice of the mixture parameters and of the radiation, the equivalent force acting on the resonant atoms can exceed the force of the spontaneous light pressure by six orders of magnitude. It is therefore of interest to investigate various aspects of this phenomenon in greater detail.

Particularly urgent is the assessment of the possibility of obtaining molecule streams in an infrared (IR) resonant field. First, sources of infrared radiation are available, such as tunable CO_2 lasers,[4] with average