Multiple light-scattering near the critical point

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A review is made of the new theoretical and experimental results on multiple light-scattering near the critical point. Particular attention is paid to the effects of multiple scattering on the integrated intensity, depolarization, and spectrum of the critical opalescence. The features of the temperature, density, and angular dependence of these characteristics are considered for the cases of double and multiple scattering. It is shown the geometry is an important factor in critical opalescence. A study is made of the conditions under which the Born (Rayleigh) concept of scattering order loses meaning. A detailed comparison of theory and experiment is made for the problem of multiple light-scattering in critical opalescence.

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"This science is a dense forest. One can see nothing nearby...

Johann Wolfgang von Goethe

INTRODUCTION

In describing the propagation of electromagnetic waves, one frequently encounters situations in which the single-scattering approximation becomes unsuitable. This may occur both in media of large geometric dimensions in which the scatterers are individual particles or molecules (clouds, fog, artificial aerosols, stellar and planetary atmospheres, etc.) and also in media in which the scatterers are fluctuations of various physical parameters, leading to a marked growth in the extinction coefficient (matter near critical points and second-order phase transitions, a medium with well-developed turbulence, etc.). In cases of this sort it becomes necessary to consider the effects of multiple scattering of the electromagnetic radiation.

Multiple scattering of waves in media with discrete scatterers or well-developed turbulence has been the subject of a number of reviews and monographs (see, e.g., Refs. 1-4). The status of the theoretical and experimental research on multiple light-scattering near the critical point has been covered in less detail. At this same time, the importance of multiple-scattering effects in the critical region is obvious. Light

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scattering is one of the most convenient methods of studying the physical properties of matter in this region, since here the correlation length for fluctuations of the characteristic order parameter of the system is comparable to an optical wavelength.

A deep understanding of the features of the multiplescattering processes is necessary for the following reasons as well: 1) Multiple light-scattering contains certain information on the higher-order space-time correlation functions of the fluctuations of the physical quantities; 2) the effects of multiple scattering must be taken into account in interpreting critical-opalescence studies in the single-scattering approximation, for which there is a reliable theory.

In the last 10–15 years our understanding of the nature of critical phenomena has deepened substantially. The basic cause of the universal behavior of systems of diverse physical natures near the critical point has been discovered—the long-range and long-time correlations of fluctuations of the order parameter. This discovery has come as a result of the development and refinement of the modern theory of phase transitions and critical phenomena—the theories of scaling⁵ (scale invariance) and the renormalization group.⁶

The general progress that has been made in the study of critical phenomena is also reflected in the development of ideas about the role of anomalies of the highermultiple scattering in the phenomenon of critical opalescence. By now there is a large body of accumulated experimental and theoretical material on the integrated and spectral intensities of multiple light-scattering near the critical point. Many results can be regarded as already firmly established. In such a situation the "best and only recourse" is to clarify the present status of research on multiple light-scattering is critical opalescence.

1. DEVELOPMENT OF THE CONCEPTS OF CRITICAL OPALESCENCE

The first observations of the phenomenon of critical opalescence were evidently undertaken in the 1880's and 90's by Gerzi, Altschul, and Wesendonck. The local thermodynamic theory of fluctuations, which was given by Smoluchowski⁷ and Einstein,⁸ explained the omnidirectional growth of the scattered light intensity on approach to the critical point. The spatial nonlocality of the fluctuations, which leads to the fundamental concept of the correlation length $r_{\rm c}$, was first taken into account by Ornstein and Zernike.9 Many papers have been devoted to the justification of the main results of the Ornstein-Zernike theory on both the thermodynamic and molecular levels and also to the experimental verification of this theory; an analysis of these papers is found, for example, in Ref. 10. The Ornstein-Zernike theory, which explains critical opalescence by allowing for long-range correlations, in fact corresponds to the model of noninteracting fluctuations and, of course, does not give an exact description of the analytical properties of fluctuating quantities in the close proximity of the critical point.

The construction of the Ginzburg-Landau theory¹¹ of superconductivity and the establishment of the applicability criterion^{12,13} for the Landau self-consistent field have revealed that the interaction of fluctuations plays an increasing role as the critical point is approached. The modern theories of critical phenomena, due to Patashinskii and Pokrovskii⁵ and to Kadanoff and Wilson,⁶ take this decisive factor into account in a systematic way and have explained a variety of importance new properties of the pair and higher-order correlation functions of the order-parameter fluctuations. In particular, a fundamental consequence of the scale invariance is the appearance of the anomalous-dimensionality exponent η of the pair correlation function, which does not appear in the Ornstein-Zernike theory. The fact that $\eta \neq 0$ should make the reciprocal intensity I_1^{-1} of the singly scattered light have a nonlinear dependence on the square of the change in the wave vector upon scattering at an arbitrary angle.

Together with the growth in the correlation length r_c , there is also an increase in the relaxation time t_c of the long-wavelength fluctuations of the order parameter.

This so-called "critical slowing down" is manifested primarily in a sharp narrowing of the intensely growing central line of the fine structure of the spectrum. The various versions of the dynamical theory of critical phenomena¹⁴⁻¹⁶ provide an extremely firm foundation for studying the spectral characteristics of the critical opalescence in the single-scattering approximation.

The concept of scattering order (multiplicity) in electrodynamics stems, as we know (see, e.g., Refs. 4, 17, and 18), from the iterative solution of the integral equations describing the propagation and scattering of electromagnetic waves in statistically inhomogeneous media; the solution is represented in the form of the Born or Rayleigh series in the polarizability of the molecules (in fluctuations of the dielectric permittivity). The results of an electrodynamic calculation with scale-invariant correlation functions of the orderparameter fluctuations adequately describe the multiple scattering of light near the critical point.¹⁾

The systematic electrodynamic calculation of double light-scattering near the critical point, with the correct correlation function for fluctuations of the order parameter, was performed independently and practically simultaneously in Refs. 21-25. These papers succeeded in explaining theoretically the main features of double scattering (the temperature dependence of the total intensity I_2 and depolarization factor Δ , the nontrivial dependence of I_2 and, hence, of Δ on the characteristic linear dimensions of the scattering volume, the features of the angular dependence of I_2 , etc.). At the same time, however, the papers of Refs. 21-25 did not give due regard to the real geometry of the scattering volume. The corresponding calculations, which are highly necessary for estimating correctly the corrections due to double scattering and multiple scattering in critical opalescence, were carried out in Refs. 26-29. The advent of reliable theoretical calculations of I_2 and Δ (Refs. 21-33) largely motivated the corresponding experimental studies (Refs. 26, 27, and 43-39).

No less interesting is the study of the possible influence of multiple scattering on the spectral characteristics of critical opalescence. This factor must be taken into account in order to verify the assertions of the dynamical theory of critical phenomena (the magnitude of the dynamic exponent \tilde{z} , the exact form of the scaling function for the width Γ_c of the central component, etc.). The first theoretical⁴⁰⁻⁴⁴ and experimental^{42,43,45} studies in this area have already been carried out.

¹⁾Here we will not go into the papers which have used various approximate methods of calculating the double scattering of light near the critical point (see Refs. 19 and 20 for details) and employed well-known methodological procedures for reducing its contribution (decreasing the scattering volume, choosing mixtures whose components have nearly the same refractive indices, etc.). The lack of rigorous theoretical analysis in these papers has, in any case, left open the fundamental question of the magnitude and role of multiple-scattering effects.

2. STUDY OF THE SCATTERING PROCESS IN CRITICAL OPALESCENCE

a) Iterative procedure for solving the electrodynamic problem

There are two basic approaches—macroscopic and microscopic—to the description of the propagation and scattering of electromagnetic waves in a material which is in a near-critical state.

In the macroscopic approach one uses the concept of a fluctuating dielectric permittivity: $\varepsilon(\mathbf{r}, t) = \varepsilon_0(\mathbf{r})$ + $\varepsilon'(\mathbf{r}, t)$, where $\varepsilon_0(\mathbf{r})$ is the average value for the medium and $\varepsilon'(\mathbf{r}, t)$ is the fluctuating part. The dielectric permittivity is assumed to be spatially inhomogeneous on account of the presence of an external field, for example. The concept of scattering order stems from the application of an iterative procedure in solving the wave equation

$$\Delta \mathbf{E} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \, \mathbf{e} \, (\mathbf{r}, t) \, \mathbf{E} - \mathbf{grad} \, \mathrm{div} \, \mathbf{E} = 0, \qquad (2.1)$$

which is written in this form for a nonmagnetic, nonconducting medium. The idea of the iterative procedure is to seek the electric field $\mathbf{E} = \mathbf{E}_0 + \sum_{i=1} \mathbf{E}_i$ in the form of a sum of the field \mathbf{E}_0 of the exciting wave, which satisfies equation (2.1) with $\varepsilon = \varepsilon_0(\mathbf{r})$, and the fields \mathbf{E}_i , which are functionals of the *i*-fold products of $\varepsilon'(\mathbf{r}, t)$. The general recursion formulas for the electric \mathbf{E}_i and magnetic \mathbf{H}_i fields in the (\mathbf{r}, ω) representation are of the form^{41b}

$$\mathbf{E}_{i}(\mathbf{r}, \omega)_{j} = -\pi \int_{\nabla} \int_{-\infty}^{\infty} \varepsilon'(\mathbf{r}_{i}, \omega_{i}) G_{0}^{(-)}(\mathbf{r}, \mathbf{r}_{i}, \omega_{i}) \frac{m_{t} \mathcal{E}_{t-1}(\mathbf{r}_{i}, \omega - \omega_{i})}{\varepsilon_{0}(\mathbf{r}_{i}) |\mathbf{r} - \mathbf{r}_{t}|^{2}} \times \left[1 - i \frac{\omega_{t}}{c} \sqrt{\varepsilon_{0}(\mathbf{r}_{i})} |\mathbf{r} - \mathbf{r}_{t}| - \frac{\omega_{t}^{4}}{c^{4}} \varepsilon_{0}(\mathbf{r}_{i}) |\mathbf{r} - \mathbf{r}_{i}|^{2}}\right] d\mathbf{r}_{t} d\omega_{i},$$

$$(2.2)$$

$$\mathbf{H}_{t}(\mathbf{r},\omega) = \frac{i\pi\omega}{c} \int_{V} \int_{-\infty} \varepsilon' (\mathbf{r}_{t},\omega_{t}) G_{0}^{(-)}(\mathbf{r},\mathbf{r}_{t},\omega_{t}) [\mathbf{n}_{t},\mathbf{m}_{t}]$$

$$\times E_{t-t}(\mathbf{r}_{t},\omega-\omega_{t}) \left[1+i\frac{\omega_{t}}{c}\sqrt{\epsilon_{0}(\mathbf{r}_{t})} |\mathbf{r}-\mathbf{r}_{t}|\right] d\mathbf{r}_{t} d\omega_{t};$$
(2.3)

here $\mathbf{n}_i = (\mathbf{r} - \mathbf{r}_i) / |\mathbf{r} - \mathbf{r}_i|$ is a unit vector in the direction of the observation point, $G_0^{(-)}(\mathbf{r}, \mathbf{r}_i, \omega_i)$ is the causal Green's function of the wave equation, and ω_i is the frequency of the *i*-tuply scattered light. The vector \mathbf{m}_i , which gives the polarization direction of the *i*-tuply scattered wave, satisfies the relation⁴⁶ $\mathbf{m}_i = \mathbf{m}_{i-1} - \mathbf{n}_i(\mathbf{n}_i \cdot \mathbf{m}_{i-1})$.

In the microscopic approach one starts from the relation $^{17}\,$

$$\mathbf{P}(\mathbf{r}_i, t) = \alpha \left[\mathbf{E}_0(\mathbf{r}_i, t) + \sum_{i,j} \hat{T}_{ij} \mathbf{P}(\mathbf{r}_j, t) \right]$$
(2.4)

for the dipole moment $P(\mathbf{r}_i, t)$ induced in a molecule located at point \mathbf{r}_i at time t by the external field $\mathbf{E}_0(\mathbf{r}_i, t)$ and the fields of all the other molecules. In this relation α is the molecular polarizability, which is frequency independent and is taken here to be a scalar, and

$$\hat{T}_{ij} = (\nabla_t \nabla_f + k_0^2 \hat{I}) e^{i k_0 |\mathbf{r}_i - \mathbf{r}_j|} |\mathbf{r}_i - \mathbf{r}_j|^{-1}, \quad k_0 = \frac{2\pi}{\lambda}$$

is the propagator for the electromagnetic field. The field of the scattered wave is determined with the aid of the formulas $\mathbf{E} = \nabla \left(\nabla \cdot \mathbf{\Pi} \right) - \frac{1}{c^2} \frac{\partial^2 \mathbf{\Pi}}{\partial t^2}, \quad \mathbf{\Pi} = \int_{\mathbf{V}} \frac{\mathbf{P}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|/c)}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}'$

in terms of the value of the dipole moment P(r', t), which is found from (2.4) by the formal iterative procedure

$$P(r_{i}, t) = \alpha \mathbf{E}_{0}(r_{i}, t) + \alpha^{2} \sum_{\substack{j \neq i \\ j \neq i}} \hat{T}_{ij} \mathbf{E}_{0}(r_{j}, t) + \alpha^{3} \sum_{\substack{j \neq i \\ l \neq j}} \hat{T}_{ij} \hat{T}_{jl} \mathbf{E}_{0}(r_{l}, t) + \dots$$

$$(2.5)$$

The terms in (2.5) are interpreted as the contributions of the exciting field and of the singly, doubly, etc. scattered fields. The relationship of the two approaches in the theory of multiple scattering is discussed in Ref. 47.

From here the solution of the problem of multiple scattering reduces to the calculations of the Poynting vector

$$\langle \mathbf{S} \rangle = \frac{c}{8\pi} \operatorname{Re} \sum_{i, j} \langle [\mathbf{E}_{i}, \mathbf{H}_{j}^{*}] \rangle.$$
 (2.6)

The terms with i=j give the intensity of the "pure" *i*-fold scattering, while the remaining terms, with $i \neq j$, give the intensity of the so called "interference" effects. The terms with i=1, j=2 and i=2, j=1 are sometimes called the "one-and-one-half-fold" scattering. The angle brackets in (2.6) denote the statistical average over the fluctuations $\varepsilon'(\mathbf{r}, t)$ in the macroscopic approach or to an ensemble average in the microscopic approach.

Thus, to study multiple-scattering processes one must know the space-time correlation functions $G_{i+j} = \langle \Pi_{k=1}^i \varepsilon'(\mathbf{r}_k, t) \Pi_{s=1}^j \varepsilon'(\mathbf{r}_s, t_s) \rangle$ for dielectric-permittivity fluctuations of arbitrary order or the partial statistical distribution functions $F_{i+j}(\mathbf{r}_i t_1; \ldots; \mathbf{r}_i, t_i; \mathbf{r}_1', t_1'; \ldots; \mathbf{r}_j' + t_j')$. In the macro-

scopic approach the space-time correlation function of the dielectric-permittivity fluctuations can, with reasonable accuracy, be replaced by the space-time correlation functions of the density fluctuations (for the sake of definiteness, we shall henceforth treat a liquid-vapor system near the critical point)

$$G_{i+j}^{\mathfrak{s}} = \left(\frac{\partial \mathfrak{s}}{\partial \rho}\right)_{\mathrm{T}}^{i+j} G_{i+j}^{\rho}, \quad G_{l+j}^{\rho} = \left\langle \prod_{k=1}^{i} \Delta \rho \left(\mathbf{r}_{k}, t_{k}\right) \prod_{s=1}^{j} \Delta \rho \left(\mathbf{r}_{s}', t_{s}'\right) \right\rangle. \quad (2.7)$$

For analyzing series expansions in the scattering order for the fields and intensity of the multiply scattered light, diagram techniques analogous to the Feynman technique in quantum field theory find extremely wide use. The summation of these series under certain assumptions reduces to the solution of equations of the Dyson type and Bethe-Salpeter type, respectively, for the field and intensity of the scattered radiation (Refs. 2, 4, 24a, 25a, 30b, 40, and 48).

b) Correlation functions in the critical region

For a long time the only theory of critical fluctuations was the Ornstein-Zernike theory, the main idea of which reduces, as we know, to allowance for the nonlocality of the density fluctuations $\Delta \rho$ near the critical point. For the pair correlation function this gives

$$G_2^{\rho}(\mathbf{r}_1, \mathbf{r}_2) \sim \exp(-|\mathbf{r}_1 - \mathbf{r}_2|/\mathbf{r}_c) |\mathbf{r}_1 - \mathbf{r}_2|^{-1}.$$
 (2.8)

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The correlation length r_{c} , growing without bound as the critical point is approached, provides for the long-range character of the fluctuation correlations.

With the advent of scaling theory it became possible to explain a number of important new properties of the pair and higher-order correlation functions.⁵ Thus it was established that the many-point correlation function $G_n^{A_1,\ldots,A_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ depends on the ratios $|\mathbf{r}_i-\mathbf{r}_j|/\mathbf{r}_c$ and is homogeneous of order $\Delta_{A_1} + \ldots$ $+ \Delta_{A_n}$ as a function of its spatial arguments, where Δ_{A_i} are the scaling dimensionalities characterizing the change in the fluctuating quantities A_i in the scale transformation $A_i(\tilde{\lambda} \mathbf{r}) \rightarrow \tilde{\lambda}^{-\Delta_i} A_i(\mathbf{r})$. For the pair correlation function this result means that

$$G_{2}^{A_{1}, A_{2}}(\mathbf{r}_{1}, \mathbf{r}_{2}) = g\left(\left|\left|\mathbf{r}_{1} - \mathbf{r}_{2}\right|/r_{c}\right)/\left|\mathbf{r}_{1} - \mathbf{r}_{2}\right|^{\Delta A_{1} + \Delta A_{2}}, \quad (2.9)$$

where in the case of order-parameter fluctuations one has $\Delta_{A_1} = \Delta_{A_2} = (d-2+\eta)/2$, where d is the dimensionality of the space, $\eta \le 0.06$ is the anomalous-dimensionality critical exponent of the correlation function, which distinguishes the behavior of the latter from that found in the Ornstein-Zernike approximation, given by (2.8). In (2.9) g(0) = const, and usually $g(x) \sim \exp(-x)$. The correlation length is

$$r_{\rm c} = |\tau|^{-\nu} f(\Delta \rho / \tau^{\beta}), \qquad (2.10)$$

where $\tau = (T - T_c)/T_c$ and $\Delta \rho = (\omega - \rho_c)/\rho_c$ are the dimensionless deviations of the temperature and density from their critical values, and the scaling function f(x) has the asymptotic behavior $f(x \to 0) = a_0 \approx 10^{-(7-8)}$ cm, $f(x \to \infty) \sim x^{-\nu/\beta}$, and $\nu \approx 0.63$ and $\beta \approx 0.34$ are critical exponents.

Using certain consequences of scaling theory,⁵ one can calculate the singularity of the zeroth Fourier components of the higher-order correlation functions near the critical point.

In addition to invariance under change of scale, the correlation functions can also have invariance under a special conformal transformation.^{49,50} In this case the structure of the ternary correlation functions at the critical point is completely determined, and the class of functions describing the quaternary correlation functions is substantially narrowed.

Unfortunately, at this time we do not know explicitly how the higher-order correlation functions depend on the wave vectors along whose directions one must perform the summation of the reradiations in the problem of multiple scattering. However, there is one important circumstance which enables one to calculate the terms in the Poynting vector (2.6). For variables in the region in which the correlation length r_c remains smaller than the wavelength λ of the light, the wavezone condition is satisfied:

$$k_0 \sqrt{e_0(\mathbf{r}_j)} | \mathbf{r}_i - \mathbf{r}_j | \gg 1.$$
(2.11)

Precisely such a situation is realized in many optical experiments. This means that in calculating the scattered fields by recursion formulas (2.2) and (2.3) one is justified in using the asymptotic behavior of the multifrequency correlation functions that was obtained in Refs. 50 and 51, which corresponds to the withdrawal of one group of particles from the other to distances

 $|\mathbf{r}_i - \mathbf{r}_j| \gg \lambda \ge r_{\rm e}$. The features of the space-time correlation functions for the critical fluctuations will be discussed in Section 5.

c) Single-scattering approximation. Distorting factors

The integrated intensity of singly scattered light, I_1 , is proportional to the Fourier transform of the pair correlation function for the density fluctuations. Taking (2.9) into account, we have

 $I_{i} = \frac{c}{8\pi} \operatorname{Re} \left\langle \left[\mathbf{E}_{i}, \mathbf{H}_{1}^{*} \right] \right\rangle \cdot \mathbf{n}_{i} \sim G_{2}(q) \sim 1/\left(r_{0}^{-1} + q^{2} \right)^{1-\eta/2}, \quad (2.12)$ where $q = k_{0} \sqrt{2\varepsilon_{0}} \left(1 - \cos\theta \right)^{1/2}$ is the change in the wave vector upon scattering by angle θ .

It follows from an analysis of formula (2.12) that

1) at the critical point $\gamma_c^{-1} \rightarrow 0$ and $\Gamma_1^{-1} \sim q^{2\eta}$, making it possible in principle to determine the critical exponent η from measurements of the angular dependence of the single scattering;

2) the intensity $I_1(q \rightarrow 0) \sim r_c^{e_{\gamma}} \sim \beta_T$ characterizes the isothermal compressibility:

$$\beta_{\mathbf{T}} = \tau^{-\gamma} f_{i} \left(\frac{\Delta \rho}{\tau^{\beta}} \right), \quad f_{i} \left(x \to 0 \right) = \beta_{\mathbf{T}}^{\alpha} \approx 10^{-(\theta - \theta)} \ \mathrm{Pa}^{-1},$$

$$f_{i} \left(x \to \infty \right) \sim x^{1 - \delta}, \quad \gamma \approx 1.2, \quad \delta \approx 4.5,$$

$$(2.13)$$

enabling one to find the values of the critical exponents γ and δ and the explicit form of the scaling function $f_1(x)$;

3) the angular slope of the plot of $(I_1/\beta_T)^{2/(\eta-2)}$ versus q^2 gives r_c^2 and thereby, upon variation of τ and $\Delta\rho$, yields the critical exponents ν and ν/β and the scaling function f(x) from (2.10).

Similar methods of determining the critical exponents and scaling functions have been used in many experimental studies (see, e.g., Ref. 53).

The consequences of formula (2.12) enumerated above are valid for the asymptotic neighborhood of an isolated critical point. There are a number of factors which distort this idealized critical behavior, and these must be kept in mind when interpreting experimental data on critical opalescence in the single-scattering approximation.

1) External "fields." The anomalous growth in the susceptibility near critical and second-order phasetransition points causes a lowering of the symmetry (breaking of the macroscopic homogeneity) of the medium in the presence of external "fields." For a liquid-vapor system this leads to a narrowing of the true phase-transition region (the gravitational effect).

Suppose that the scattering occurs in a plane-parallel layer $-L_z \le z < L_z$, inhomogeneous with respect to z, at normal incidence of the x-polarized exciting wave on the boundary $z = -L_z$ (Fig. 1). Critical phenomena occur in the layer at the level z = 0 for $\tau \to 0$. The intensity of the singly scattered light, averaged over the layer, is given by the formula

$$I_{1}(2L_{z}) = I_{0} \frac{\pi\sigma}{\lambda^{4}} \left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_{\mathrm{T}}^{2} \frac{1 - (\mathbf{n}_{1} \cdot \mathbf{m}_{0})^{4}}{L^{2}} \int_{-L_{z}}^{L_{z}} \sum_{\mathbf{n}_{z}} \left[G_{2}(q, z) + \frac{|A^{(+)}|^{3}}{|A^{(-)}|^{3}} G_{2}(q^{(+)}, z)\right] \mathrm{d}z.$$

$$(2.14)$$



FIG. 1. Geometry of the scattering problem in Refs. 22, 54, and 55.

Here σ is the cross section of the incident beam, m_0 is a unit vector in the polarization direction of the exciting wave, L is the distance from the scattering volume to the detector, and $G_2(q, z)$ is the Fourier transform of the pair correlation function of the spatially inhomogeneous medium.⁵⁴ The second term is due to the presence of the backward wave.⁵⁵

It follows from (2.14) that: a) $\Delta I_1/\Delta z$, the intensity referred to a unit interval Δz , has a sharp dependence on the vertical coordinate, with a maximum at the z=0level; b) at $z, \tau \rightarrow 0$ and $\theta \rightarrow 0, \pi$ there is an anomalous increase in the magnitude of $\Delta I_1/\Delta z$, but this feature is leveled out in the averaging over the layer, and $I_1(2L_x)$ remains finite even at $\tau \rightarrow 0$ and $\theta \rightarrow 0, \pi$; c) the temperature dependence of $I_1(2L_x)$ on the critical isochore is described by an exponent $\gamma_{eff} < \gamma$; d) the reciprocal quantity $I_1^{-1}(2L_x)$ is characterized by a nonlinear dependence in q^2 even when the Ornstein-Zernike-approximation formula (2.8) is used.

The height dependence of the scattering power near the liquid-vapor critical point was studied in the experiments of Refs. 56-60. At $\tau \approx 10^{-4}$, for example,⁵⁹ a departure of only 1 cm from the z=0 level causes the single-scattering intensity in n-pentane at the angle $\theta = \pi/2$ to decrease by a factor of 80. At fixed heights $z \neq 0$ the extrema of the single-scattering intensity are reached at $\tau \neq 0$.⁶⁰ A decrease of the exponent γ and its approach toward the "classical" value $\gamma = 1$ was observed by Ivanov and Makarov⁶¹ and explained as a gravitational effect by Ivanov and Fedyanin.⁶² The appearance of nonlinearity in the function $I_1^{-1}(q^2)$ in a gravitational field was mentioned in Refs. 54 and 63-65. Leung and Miller⁶⁵ evaluated the exponent η_{grav} describing this nonlinearity and found that it reached a value of unit order in Xe at $2L_z = 10$ cm and $\tau \approx 10^{-5}$.

2) Nonasymptotic and asymmetric neighborhood of the critical point. The use of the simple power-law relations of scaling theory in the interpretation of experimental data generally yields not the limiting values of the critical exponents, but effective values, which change as the critical point is approached. To find the limiting values of the critical exponents one must take into account: a) the nonasymptotic corrections due to the broadening of the neighborhood of the critical and second-order phase transition points in the idealized models of the incompressible magnetic material (lattice-gas) type with spins (atoms) fixed at lattice sites; b) the asymmetric corrections describing the difference between real systems (for example, a liquid-vapor system near the critical point) and the aforementioned idealized models. 5,66,66 The correct processing of experimental data in the critical region with allowance for the nonasymptotic and asymmetric corrections has been carried out in Refs. 69 and 70, for example. Of course, in the broad neighborhood of the critical point one should also take into account not only the singular parts of the physical quantities but also the regular parts, which characterize the values of these quantities far from the critical point ($\tau \approx 1$ and $\Delta \rho \approx 1$).

3) Auxiliary thermodynamic variables. The majority of phase transitions occur on lines or surfaces in the space of thermodynamic variables. For this reason the natural question arises of whether these phase transitions are isomorphic to a phase transition in the only real system with an isolated critical point—a onecomponent fluid characterized by only two independent variables (for example, τ and $\Delta \rho$). A detailed discussion of this question (in particular, the renormalization of the critical exponents when the auxiliary density variables, rather than the field variables, are held fixed) is found in Ref. 53.

4) Crossover. The character of the critical anomalies also changes on approach to higher-order critical points on phase-transition lines or surfaces. For example, near a tricritical point one has, to within logarithmic temperature corrections, $\beta_{\rm T} \sim \tau^{\gamma_1}$ for the compressibility and $r_{\rm c} \sim \tau^{-\gamma_1}$ for the correlation length of the order parameter, where $\gamma_1 = 1$ and $\nu_t = 0.5$. The transition (crossover) from critical to polycritical behavior must be taken into consideration in systems with interacting order parameters.⁷¹

5) Higher-multiple scattering. The discussion of this question is the subject of the remainder of this article.

3. INTEGRATED INTENSITY AND DEPOLARIZATION OF DOUBLY SCATTERED LIGHT IN THE CRITICAL REGION

a) Theory

Experimental efforts to study the features of physical properties of matter (its scattering power, in particular) in the close neighborhood of the critical point $(\tau \le 10^{-3})$ made it necessary to elucidate the basic characteristics of high-multiple scattering in critical opalescence. This stimulated a heightened interest in theoretical calculations of (first of all) double light-scattering, which were done in Refs. 21-33. We note that all the calculations were based on the decoupling of the correlation function G_4 into products of pair correlation functions G_2 ; this decoupling, as we noted earlier [see (2.11)], is valid for $\lambda > r_c$ and corresponds to the actual experimental situation in critical opalescence studies down to $\tau \ge 10^{-5}$.

1) Integrated intensity. The main contribution to the integrated double-scattering intensity is given by the expression^{22,46}

$$I_{2} = I_{0} \left(\frac{\pi}{\lambda^{2}}\right)^{2} \frac{VL_{0}}{L^{2}} \left(\rho \frac{\partial e}{\partial \rho}\right)_{\mathrm{T}}^{4} ,$$

$$\int_{\sigma_{1}} \left[1 - (\mathbf{n}_{1} \cdot \mathbf{m}_{0})^{2}\right] \left[1 - \frac{(\mathbf{n}_{2} \cdot \mathbf{m}_{1})^{2}}{(|\mathbf{m}_{1}|^{2})}\right] G_{2} (q_{1}) G_{2} (q_{2}) d\sigma_{1}, \qquad (3.1)$$

where L_0 is the characteristic linear dimension of the scattering volume V, and q_1 and q_2 are the changes in the wave vector during the successive scattering processes. The integral over the solid angle in (3.1) is the sum over direction of all the single scattering that corresponds to double scattering which can be registered by the detector.

The theoretical consequences of (3.1) are that: 1) I_2 is proportional to the fourth power of the linear dimension $(I_2 \sim VL_0 \sim V^{4/3})$; 2) for $qr_c \ll 1$ (the Rayleigh region) $I_2(\tau) \sim \beta_T^2(\tau) \sim r_c^{2(2-\eta)} \sim \tau^{-2\gamma}$ on the critical isochore, and $I_2(z) \sim \beta_T^2(z) \sim z^{-2(\delta-1)/\delta}$ on the critical isotherm of an inhomogeneous fluid in a gravitational field; 3) for $qr_c \lesssim 1$ and $n_2 \approx n_0$ (small-angle scattering) $I_2 \sim \beta_T + \ln\beta_T$. This result reflects the particulars of the decay of correlations for the four-point correlation function^{5,72,73}; 4) the indicatrix $I_2(\theta)$ is smoother than the indicatrix $I_1(\theta): I_2 \sim 1 + (7/11)\cos^2\theta$, $I_1 \sim 1$ $+ \cos^2\theta$ for $qr_c \ll 1$ and for natural incident light.²⁾

2) Depolarization of scattered radiation. The fundamental mechanisms responsible for depolarization of scattered light include scattering by anisotropy fluctuations,⁷⁴⁻⁷⁶ scattering due to fluctuations of the distribution function of the thermal fluctuations,⁷⁷ and multiple scattering. The object of study is the depolarization factor

$$\Delta = \frac{I_y^{zz}}{I_y^{zx}},\tag{3.2}$$

where the lower index indicates the observation direction and the upper indices give the polarization of the incident and scattered light, respectively (see Fig. 1).

For estimating the relative contributions of the various depolarization mechanisms, it is convenient to use the following relations:

$$\Delta = \frac{I_{\nu,\text{ aniso}}^{xx}}{I_{\nu}^{xx}} + \frac{I_{\nu,\text{ fl}}^{xx}}{I_{\nu}^{yx}} + \frac{I_{\nu,\text{ ms}}^{xx}}{I_{\nu}^{y}},$$

$$I_{\nu}^{xx} \approx I_{\nu 1}^{xx} \sim \lambda^{-4}\beta_{\text{T}}V, \quad I_{\nu,\text{ aniso}}^{xx} \sim \lambda^{-4}V\varphi(\tau),$$

$$I_{\nu,\text{ fl}}^{xx} \sim \lambda^{-4}V\beta_{\text{T}}^{1/2}, \quad I_{\nu,\text{ mn}}^{xx} \approx I_{\nu 2}^{xx} \sim \lambda^{-8}VL_{0}\beta_{\text{T}}^{2},$$

$$(3.3)$$

which are valid for $qr_e \ll 1$.

The character of the anomaly of I_{aniso} in the critical region is an open question at the present time and demands a theoretical solution of its own. The experimental studies (see below) provide grounds for assuming that if I_{aniso} is in fact singular at the critical point, then the singularity is extremely weak, since $\varphi(\tau)\beta_T^{-1}(\tau) \rightarrow 0$ at $\tau \rightarrow 0$. It follows from (3.3) that $I_{y,f1}/I_{y1}^{xz} \sim r_c^{-1}$, i.e., this contribution, like the preceding one, falls off as the critical point is approached. The last depolarization mechanism, multiple scattering, assumes the governing role in the critical region, since $I_{yy}^{xx}/I_{y1}^{xx} \sim \beta_{T}$.

A systematic calculation of the individual components of the double scattering for a spherical sample geometry was carried out by Oxtoby and Gelbart²¹:

$$I_{2}^{xx} \sim V_{1}R_{s}a^{2}\int_{0}^{2\pi} d\phi \int_{0}^{\pi} \frac{d\theta \sin^{3}\theta \cos^{3}\theta \sin^{2}\phi}{(1+a\sin\theta\cos\phi)(1+a\sin\theta\cos\phi)(1+a\sin\theta\cos\phi)}, \quad (3.4a)$$

$$I_{2}^{xx} \sim V_{1}R_{s}a^{2}\int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta \sin^{5}\theta (1+a\sin\theta\cos\phi)^{-1} \times [1+a\sin\theta\cos(\phi+\phi_{s})]^{-1}$$

$$(3.4b)$$

Here V_1 is the illuminated volume, R_s is the radius of the sphere, $a = 2k_0^2/(2k_0^2 + r_e^{-2})$, and φ_s is the scattering angle. It follows from (3.4) that I_2^{xe} , $I_2^{xx} \sim V_1 R_s$, and for $k_0 r_c^4$ [this was already noted in connection with formula (3.1)]. Extrapolation of (3.4a) to the critical point $(k_0 r_e^{-\infty})$ gives a finite value for I_2^{xe} .

In Ref. 23, Oxtoby and Gelbart made a theoretical study of the angular dependence of the polarized component $I^{xx} = I_1^{xx} + I_2^{xx}$. The calculated values of $1/I^{xx}(q^2)$ for Xe at $R_s = 10^{-2}$ cm and $T - T_c = 0.031$ °C revealed deviations of $1/I_1^{xx}(q^2)$ from the linear behavior predicted by the Ornstein-Zernike theory, which were especially noticeable at small scattering angles. Despite the use of the correlation function G_2 from the Ornstein-Zernike theory in the calculation, these deviations are characterized by a nonzero effective value of the anomalous-dimensionality exponent η_{2cr} as a consequence of the allowance for double scattering. As in the case of η_{grav} , ⁶⁵ the value of η_{2cr} is extremely large: $\eta_{2cr} = 0.7$. As the scattering volume decreases, the share of the double scattering in the total intensity decreases, and the value of η_{2cr} decreases accordingly. For $R_s \approx 10^{-3}$ mm one has $\eta_{2cr} \approx 0.1$, which is close to the theoretical value of the anomalous-dimensionality exponent η for the correlation function G_{2} .

Oxtoby and Gelbart²¹ also did a numerical calculation of $\Delta(k_0 r_c)$ for Xe at $R_s = 10^{-3}$ m (Fig. 2). The growth of Δ for $k_0 r_c > 0.04$ ($\tau \le 10^{-2}$ for the critical isochore) is due to the increase in the depolarized component I_{y2}^{xz} . It should be stressed that $I_{y2}^{xz}/I_{y1}^{xx} \sim R_s r_c^2$ for $k_0 r_c \le 0.3$.

The dependence $I_2 \sim VL_0$ was also obtained independently by Kuz'min⁴⁴ and Boots *et al.*^{25a} Those authors used a microscopic approach to the description of multiple scattering in the dipole approximation and a diagram technique similar to that which has been developed for the problem of wave propagation in media with random inhomogeneities.^{2,4}

In Ref. 25b, Boots and co-workers calculated the de-



FIG. 2. Depolarization factor for double scattering in Xe (Ref. 21).

²⁾A number of the results mentioned $(I_2 \sim \beta_1^2 \text{ for } qr_c \leq 1)$, $I_2 I_1 \sim L_0$, and the fact that the angular dependence of $I_2(\theta)$ is smoother than that of $I_1(\theta)$ were obtained earlier¹⁹ in a calculation of the double-scattering intensity near the critical point on the basis of the transport equation for radiation with an indicatrix given by the Ornstein-Zernik theory.

polarization factor Δ in CO₂ for the case in which the exciting radiation is incident perpendicular to the gravitational field gradient. They showed, in particular, that $\Delta = I_{2,dep}/I_{1,pol} \sim L_0$, where L_0 is the vertical dimension of the scattering volume.

The total contribution of the double scattering to the depolarization factor was calculated in Ref. 33. The results obtained in the interval $3 \cdot 10^{-3} \leq q_0^2 r_c^2 \leq 11$ (where $q_0 = \sqrt{2} k_0$ is the change in the wave vector upon scattering by an angle $\theta = \pi/2$) were used to obtain the dependence on $q_0^2 r_c^2$ of the depolarization factor $\Delta = \gamma_1/(1 + \gamma_2)$ and of the quantities

$$\gamma_{t} = \frac{T_{y2}^{xz}}{T_{y1}^{xx}} = s \left(1 + q_{0}^{2} r_{c}^{2}\right) q_{0}^{2} r_{c}^{2} K_{1} \left(q_{0} r_{c}\right), \qquad (3.5a)$$

$$\gamma_2 = \frac{I_{y_1^{\infty}}^{\infty}}{I_{y_1^{\infty}}^{\infty}} = s \left(1 + q_0^2 r_c^2\right) q_0^2 r_c^2 K_2 \left(q_0 r_c\right).$$
(3.5b)

Here K_1 and K_2 are calculated explicitly as functions of $q_0^2 r_c^2$, $s = (\rho (\partial \epsilon / \partial \rho))_T^2 k_B T L_0 / 8\lambda^2 f^*$ is a parameter which depends weakly on τ and $\Delta \rho$, and $f^* = r_c^2 / \beta_T$ is the non-locality factor of the fluctuations.¹⁰

The results of the calculation of Δ shown in Fig. 3 (the arrows indicate the positions of the extrema) support the following qualitative arguments. For lowmultiple scattering, polarized radiation incident on a system of isotropic molecules for the most part retains its initial polarization direction, and for this reason γ_1 should be relatively small. As the critical point is approached, there is an increase in the relative share γ_2 of double scattering in the polarized component. However, in the immediate vicinity of the critical point $(q_0^2 r_c^2 \gg 1)$ low-order multiply scattered light simply does not reach the detector, as can be inferred from the following formula:

$$I_{y}^{xx} = I_{0} \frac{2\pi V L_{0}}{L^{2}} \left(2 \ln 2 - 1\right) \left(\frac{s}{L_{0}}\right)^{2}, \quad I_{y}^{xx} = I_{0} \frac{4\pi V L_{0}}{L^{2}} \left(\frac{s}{L_{0}}\right)^{2} \ln \left(q_{0}^{2} r_{0}^{2}\right)$$
$$\Delta = \frac{\ln 2 - (1/2)}{\ln \left(q_{0}^{2} r_{0}^{2}\right)}.$$

The initial polarization ceases to be preferred, and the contributions to the various polarizations to the critical-scattering intensity tend to become equal. The value of Δ should go asymptotically to unity at the critical point.

The present authors showed in Ref. 33 that as the parameter $q_0^2 r_c^2$ increases to the value $(q_0 r_c)_{max}^2 = 11$, the component I_{y2}^{xx} grows and Δ falls off accordingly. Hence, one sees that it is pointless to continue calculating Δ in the double-scattering approximation, since in the region $(q_0 r_c)^2 \ge (q_0 r_c)_{max}^2$ higher-multiple scattering processes become important.

The results of calculations^{21,25b} of Δ in the double-



FIG. 3. Dependence of the depolarization factor on the parameter $(q_0 r_c)^2$ (Ref. 33).

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scattering approximation are in quantitative agreement with the calculated value³³ of γ_1 in the region $(q_0 r_c)^2 \leq 0.1-0.2$, since the former calculations^{21,25b} did not include the double-scattering contribution to the polarized component I_y^{xx} ($\gamma_2 = 0$). For example, in the region $(q_0 r_c)^2 < 0.18$, where $\gamma_2 \approx 0$, the values used in Ref. 21 $(L_0 = 0.1 \text{ cm}, \lambda = 2\pi \cdot 10^{-5} \text{ cm})$ give $s \approx 10^{-2}$ for Xe $[T_c = 289.757 K, f^* \approx 10^{-6} dn, (\rho \cdot \partial \epsilon / \partial \rho)_T^2 \gtrsim 10^{-1}]$, and the results of the calculations of Δ in Ref. 21 and γ_1 in Ref. 33 practically coincide at $(\rho \cdot \partial \epsilon / \partial \rho)_T^2 \approx 1.74 \cdot 10^{-1}$.

b) Allowance for experimental geometry

A factor of fundamental importance in the calculation of the higher-multiple scattering processes is the particular geometry of the system under study. Allowance for the geometry has given rise to "instrumental" theories²⁶⁻²⁹ which adequately reflect the experimental conditions.

Adzhemyan et al.^{26,29} implemented the original idea that the illuminated volume V_1 and the detected volume V_2 (the upper and lower cylinders in Fig. 4) need not overlap, and one can therefore eliminate the single scattering. These authors did a series of very consistent experimental studies and theoretical calculations of the polarized I_2^{zz} and depolarized $I_2^{z(xy)}$ (the scattered light is studied in the xy plane) components of the double scattering as functions of the distance h between cylinders, the scattering angle θ , and the parameter $k_0 r_c$. Both the calculations and the experiment confirmed that $I_2^{z(xy)}(\theta)$ is a smoother function than $I_1^z(\theta)$, that the fraction of the polarized component I^{**} that is due to double scattering grows with increasing $k_0 r_c$, and the scattering properties depend in a nontrivial way on the linear dimensions of the system. It was also shown that allowance for double scattering leads to an increase in the exponent ν , to a decrease in the exponent γ , and also to a decrease in a_0 (without double scattering the values are $\nu = 0.58$, $\gamma = 1.29$, and $a_0 = 3.20 \cdot 10^{-8}$ cm, and with double scattering they are $\nu = 0.625$, $\gamma = 1.21$, and $a_0 = 2.36 \cdot 10^{-8}$ cm).

Reith and Swinney²⁷ achieved the important result of obtaining the relation

$$\Delta = g\sigma_0 L_0 \qquad (\sigma_0 = \pi^2 / \lambda^4 \left[(n^2 - 1) (n^2 + 2) / 3 \right]^2 k_B T \beta_T) \qquad (3.6)$$

and verifying it experimentally for the case of a scattering volume in the form of a parallelepiped of height L_0 . Using the Monte Carlo method to evaluate the quadruple



FIG. 4. Geometry of experiment²⁹ for studying the depolarization of the scattered light near the critical point.

integral giving the numerical value of g, those authors²⁷ showed that g depends only weakly on L_0 : as L_0 changed from 0.3 to 1.5 mm, the value of g decreased smoothly from $\pi/4$ to 0.76. A numerical calculation²⁸ of Δ for a cylindrical sample of height L_0 and radius r_0 confirmed relation (3.6). Approximate evaluations of the corresponding integrals established that $g = (\pi/4) \ln(1 + \sqrt{2})(2r_0/L_0)$ for $2r_0 \ll L_0$ and $g = (\pi/4) - (1/6)(1 + \pi/2)(2r_0/L_0)^2$ for $2r_0 \gg L_0$. The product gL_0 grows linearly with a slope of $\pi/4$ for $L_0 \ll 2r_0$, then continues to grow but with decreasing slope, and finally reaches the constant value $gL_0 = r_0(\pi/2)\ln(1 + \sqrt{2})$ for $L_0 \gg 2r_0$.

c) Experiment

1) Temperature dependences of Δ and L. Experimental studies of the temperature dependence of the depolarization factor $\Delta(\tau)$ have a rather long history (see the corresponding bibliography in Ref. 78). Beridze⁷⁸ and Kolpakov and Skripov⁷⁹ very correctly asserted that the growth of Δ on approach to the critical point is due to multiple scattering effects. More recent experimental studies^{26,27,34,39} have confirmed the corrections of this conclusion and made it possible to calculate, on the basis of the theoretical results mentioned above, the critical exponents and other characteristics of the double scattering. For example, the experimental data²⁷ on $\Delta(\tau)$ in Xe, which are shown in Fig. 5, can be described by the formula $\Delta = \operatorname{const} \cdot \beta_T^{-1} + g\sigma_0 L_0$, where the first term corresponds to the ratio I_{aniso}/I_1 . Garrabos et al. ^{37a} used the data on $\Delta(\tau)$ in Xe to establish that Δ is a smooth function of T displaying no critical behavior in the region $\Delta T \gtrsim 50^\circ$, while in the interval $5^{\circ} \leq \Delta T \leq 50^{\circ}$, Δ is a decreasing function of τ with exponent $\gamma \approx 1.2$, as can be explained by the growth of I_{y1}^{xx} , the constancy of $I_{an iso}$, and the practical absence of I_{y2}^{xe} . In the region $(1-3)^{\circ} \leq \Delta T \leq 5^{\circ}$ the fall-off of the first term and the growth of the third term in formula (3.3) compensate one another, and the depolarization factor passes through a minimum. Finally, in the region $\Delta T \ge (1-3)^\circ$ one observes a growth of Δ due to the more rapid growth of I_{y2}^{xz} than of I_{y1}^{xx} ; the slope of $\Delta(\tau)$ in this region is again given by the exponent γ .

The maximum attainable experimental values of the depolarization factor are: $\Delta \approx 1.2 \cdot 10^{-2}$ at $\tau \approx 1.1 \cdot 10^{-4}$ in CO₂, ³⁵¹ $\Delta \approx 5 \cdot 10^{-1}$ at $\tau \approx 6 \cdot 10^{-5}$ in Xe, ^{35b} $\Delta \approx 10^{-2}$ at $\tau \approx 3.4 \cdot 10^{-4}$ in Xe, ²⁷ and $\Delta \approx 4 \cdot 10^{-3}$ at $\tau \approx 1.4 \cdot 10^{-3}$ in Xe. ^{37a} It should be noted that Trappeniers *et al.* ^{35a} observed that, after reaching a maximum, Δ decreased slightly (up to 10%) in the region $\tau \leq 10^{-4}$. In spite of the seeming agreement with the calculation³³ of Δ (see



FIG. 5. Temperature dependence of the depolarization factor in Xe for various values of L_0 (Ref. 27).

Fig. 3), the reliability of this result is in doubt, since for $\tau \leq 10^{-4}$ the incipient higher-multiple scattering processes should cause a further increase in Δ . In fact, Trappeniers *et al.*^{35b} expressed the opinion that triple scattering was the casue of the strong growth in $\Delta(\tau)$ and anomalies in $\Delta(L_0)$ which they observed in Xe.

The change in the temperature dependence of the double-scattering intensity I_2 that was predicted in Ref. 21 and 22 was observed experimentally by Beysens *et al.*³⁴ Those authors analyzed the depolarized multiple scattering in a nitrobenzene-*n*-hexane mixture for temperatures $10^{*5} \le \tau \le 10^{-2}$. The angular slope of the multiple (predominantly double) scattering intensity in a log-log plot in the region $\tau \approx 10^{-2}$ came out to be 2.52, which, in accordance with the predictions of Refs. 21 and 22, is in good agreement with the value of 2γ . In the region $\tau \approx 10^{-4}$ the exponent in the function $I_{y2}^{xt}(\tau)$ was observed to decrease from 2γ to γ , as had been noted in Ref. 22. At still smaller values of τ they observed a tendency toward a weaker temperature dependence of I_y^{xt} , which also agrees with the theoretical predictions.^{21,22}

2) Density dependence of Δ . The density dependence of the depolarization factor is not as well-studied as the temperature dependence. Figure 6 shows the measured^{37a} curves of $\Delta(\omega)$ in Xe. For the isotherm closest to critical, $T_0 = 290.74$ K, one observes a decrease in Δ as ρ approaches $\rho_{\rm e}$ in the interval $|\rho - \rho_{\rm e}| > \rho_{\rm o}$. The reason for this is a decrease of the relative contribution I_{aniso}/I_1 . In connection with the possible singularity of I_{aniso} as a function of the order parameter $\Delta \rho$ $[I_{\text{ans io}} \sim \lambda^{-4} V \varphi_1(\Delta \rho)], \text{ it can be stated that } \varphi_1(\Delta \rho) \cdot \Delta \rho^{\delta^{-1}}$ $\rightarrow 0$ as $\Delta \rho \rightarrow 0$. If $\varphi_1(\Delta \rho)$ has no singularity whatsoever at the critical point, then in the interval $|\rho - \rho_c| > \rho_0$ the critical exponent δ is determined from the data on $\Delta(\rho)$ in the region $\tau \ll \Delta \rho^{1/\beta}$, and the scaling function of the isothermal compressibility is given by $\beta_T = \Delta \rho^{1-\delta} g_1(\tau/\tau)$ $\Delta \rho^{1/\beta}$). In the density interval $\rho_e - \rho_0 < \rho < \rho_e + \rho_0$ on the $T = T_0$ isotherm, the growth of the depolarized double scattering becomes dominant. With increasing τ , i.e., upon the transition, for example, to the $T = T_1$ isotherm with $\tau_1 = (T_1 - T_c)/T_c \approx 4\tau_0$, the indicated growth of Δ on account of double scattering should also be observed, but in a narrower density interval $\rho_c - \rho_1 < \rho$ $<\rho_{e}+\rho_{1}$, where, according to estimates, $\rho_{1} \approx 0.1\rho_{0}$. The experiment of Ref. 37a was apparently not de-



FIG. 6. Density dependence of the depolarization factor in Xe in the critical region. 37

signed to monitor $\Delta(\rho)$ at such small deviations from the critical density.

A similar result to that of Ref. 37a was obtained by Alekhin and Burak³⁸ in a study of the height dependence $\Delta(z)$ of the depolarization factor in *n*-pentane with allowance for the gravitational effect. The experimental data obtained for five different wavelengths are presented in Fig. 7. The nonmonotonic change in $\Delta(z)$ was attributed by those authors to the composition between two contributions—the double scattering and I_{t1} (and not I_{aniso} , as in Ref. 37a; see Ref. 77). Then for $q_0 r_c \ll 1$ near an isotherm on which $\tau^{\beta} \ll z^* = \rho_c g_0 (z - z_c)/z$ $p_{\rm c}$ ($g_{\rm o}$ is the acceleration of gravity, $p_{\rm c}$ is the critical pressure, and $z_{\rm c}$ is the level at which $\rho = \rho_{\rm c}$), it follows from (3.3), with (2.10) and (2.13) taken into account, that $\Delta = c_1 z^{*\nu/\beta\delta} + c_2 z^{*(1-\delta)/\delta}$, where $\nu/\beta\delta \approx 0.4$, $(1-\delta)/\delta$ ≈ -0.8 , c_1 is a constant which does not depend on λ^4 , and $c_2 \sim L_0 / \lambda^4$. As λ increases, the fluctuation scattering I_{t1} becomes the predominant contribution to Δ , as can in principle be explained by the singularity of the temperature and density (height) dependence of Δ in the region $q_0 r_c \ll 1$. In Ref. 39, Alekhin showed by processing the $\Delta(z)$ data of Ref. 38 that $I_{y,t1}^{xx}/I_y^{xx} = (\Delta_1(z^*)\lambda_1^4 - \Delta_2(z^*)\lambda_2^4)/(\lambda_1^4 - \lambda_2^4) \sim z^{*0.40\pm0.06}$, where $\Delta_i(z^*)$ are the values of the depolarization factor measured at $\lambda_1 = 435.8 \text{ nm}$ and $\lambda_2 = 632.8 \text{ nm}$. This result is in good agreement with both the theoretical predictions⁵⁹ and the experimental data⁸⁰ for the function $r_c(z^*)$, which determines the ratio $I_{y,f1}^{xz}/I_{y}^{xx} \sim r_{c}^{-1} \sim z^{*v/\beta\delta}$ along the critical isochore.

3) The dependence of Δ and I_2 on the linear dimensions of the scattering volume. The experimental data obtained to data are in agreement with the important consequences of the double-scattering theory²¹⁻²⁵: the dependence of the intensity on the fourth power of the linear dimensions $(I_2 \sim L_0^4)$ and the consequent proportionality of the depolarization factor to the linear dimension $(\Delta \sim L_0)$ in the region where $I_{y2}^{xx}/I_{y1}^{xx} \ll 1$. The character of the linear dimension of the scattering volume must be determined with the actual experimental geometry taken into account. For example, $L_0 = R$ for a spherical sample of radius R, $L_0 \approx a$ for a cube of side a, and for a cylindrical sample L_0 in general dependence of the base and the height.

The behavior $\Delta \sim L_0$ was observed experimentally even before the advent of the modern theory²¹⁻²⁵ of critical opalescence. Figure 8 shows data⁷⁸ on the dependence of Δ on the length L_0 of a cell containing a nitrobenzene-*n*-heptane solution of $\Delta T = 0.16$ °C. The growth of



FIG. 7. Height dependence of the depolarization factor in n-pentane for various wavelengths.³⁸



FIG. 8. Dependence of the depolarization factor on the length of the cell for a nitrobenzene-*n*-heptane solution on the $\Delta T = 0.16^{\circ}$ isotherm.⁷⁸

 Δ at small $L_0 < 5$ mm is attributed in that paper to growth of the scattering order, while the approximate constancy of Δ at $L_0 > 5$ mm is attributed to the establishment of a "deep" regime in which the multiple scattering has reached its maximum value.

After Ref. 21 appeared, measurements of $\Delta(L_0)$ began to be made with a definite goal in mind. A study²⁶ of the depolarized light-scattering in a nitrobenzene-hexane mixture near the critical point of stratification showed that at h=0 (the cylinders in Fig. 4 overlap) $\Delta \sim d$, where d is the diameter of the laser beam. At practically the same time as Ref. 26, measurements²⁷ of $\Delta(L_0)$ in Xe confirmed that Δ is proportional to the cylinder height L_0 (Fig. 9). In agreement with the theoretical predictions that $\Delta \sim L_0 \beta_T / \lambda^4$ for $q_0 r_c \ll 1$ (this inequality was satisfied in the experiment of Ref. 27, since $T - T_{e} \approx 0.5$ K), the slope of the curve $\Delta(L_{o})$ decreased with increasing λ . The theory predicts that the derivative $\partial \Delta / \partial L_0$ should grow $\sim \beta_T$, and this was manifested in the experiment²⁷ for T - T > 0.15 K. At smaller values of $T - T_e$ the theory²¹ and experiment²⁷ disagree. We note when the polarized double scattering is taken into account, 33 one obtains the observed 27 decrease in the slope of $\partial \Delta / \partial L_0$ as a function of $T - T_c$.

Trappeniers et al.^{35a} made detailed measurements of $\Delta(L_0)$ in CO₂ at $\rho \approx \rho_c$. In the experiments they varied the height $(L_{01} = 0.7 \text{ mm}, L_{03} = 2.1 \text{ mm}, L_{03} = 2.8 \text{ mm})$ of the scattering volume illuminated by a horizontal beam perpendicular to the direction of the gravitational field. The theoretical predictions for $\tau > 10^{-4}$ are compared with the experimental data in Table I.

A convenient variable for describing the distance from the critical point is the quantity $D = [k_0^4[(\varepsilon - 1)(\varepsilon + 2)/(12\pi)^2k_BT\beta_T]^{-1}$, which was introduced by Trappeniers *et al.*³⁶ and has units of length. When the connection between r_c and β_T in terms of the integral of the compressibility is taken into account, one obtains a universal relation between Δ and D for various materials at a fixed experimental geometry. In Ref. 36, Trappeniers *et al.* supplemented the measurements of Ref. 35



FIG. 9. Depolarization factor in Xe as a function of the height of a cylindrical sample for various wavelengths. 27

Material	Theory	Experiment				
$\Delta_{01}:\Delta_{02}:\Delta_{03}$	1:3:4	0.683: 1.803: 2.752 ($\Delta T = 0.2084^{\circ}$) 0.960: 3.139: 4.390 ($\Delta T = 0.1227^{\circ}$)				
$\Delta_{01}:\Delta_{02}$	1:3	$\begin{array}{ccc} 2,971:8.579 & (\Delta T = 0.0318^{\circ}) \\ 0.648:1.674 & (\Delta T = 0.0722^{\circ}) \end{array}$				

with a study of $\Delta(D)$ in Xe. For $L_0 = 1.69$ mm, double scattering plays a governing role in the region 0.1 m < D < 10 m; here $\Delta = (1/4)\pi D^{-1}h$, a result which agrees to within a factor $(D^{-1} = \sigma_0/2)$ with the results of Refs. 27 and 28. The correction for attenuation (see Sect. 4d) was neglibibly small all the way down to $D \ge 0.1$ m (corresponding to $T - T_c \ge 0.2$ K). For D > 10 m the main contribution to Δ was given by I_{aniso} , while for D < 0.1 m it is necessary to take higher-multiple scattering into account.

Let us conclude this section with a brief discussion of two questions.

The first question is still of a controversial nature and concerns the competition between the relative contributions I_{f1}^{xx}/I_1^{xx} and I_{aniso}^{xx}/I_1^{xx} on the one hand and I_{y2}^{xz}/I_1^{xx} on the other hand in the region of the minimum of the depolarization factor, where $q_0 r_c$ is still $\ll 1$. Using (3.3) for an elementary analysis of the line of minima $\tau_{\min} = \tau_{\min}(\lambda)$ on the critical isochore, one can study the following limiting cases: 1) $I_{aniso}^{xg} \ll I_{f1}^{xz}$, $\tau_{min}(\lambda) \sim \lambda^{-8/3r}$; 2) $I_{aniso}^{xg} \gg I_{f1}^{xg}$, $\tau_{min}(\lambda) \sim \lambda^{-4/(2\gamma-n)}$, where n is the exponent of the possible temperature dependence of $I_{aniso} \sim \varphi(\tau) \sim \tau^{-n}$. The experimental study of the spectral dependence of $\tau_{\min}(\lambda)$ is extremely useful for elucidating which of the contributions to the depolarized scattering $(I_{aniso}^{x_{\pi}}, I_{p}^{x_{\pi}}, or both)$ is competing with I_2^{xe} in the region of $\Delta = \Delta_{min}$. For the case in which I_{f1}^{xe} and I_{aniso}^{xe} are of the same order, one must make a more detailed analysis of the system of three equations (3.3) for different experimental values of $\Delta(\tau)$. An analogous study can be made for the line of minima τ_{min} $= \tau_{\min}(L_0): 1) I_{\min}^{x_{\pi}} \ll I_{f1}^{x_{\pi}}, \ \tau_{\min}(L_0) \sim L_0^{2/3\gamma}; 2) I_{\min}^{x_{\pi}} \gg I_{f1}^{x_{\pi}}, \\ \tau_{\min}(L_0) \sim L_0^{1/(2\gamma\gamma\eta)}.$ The experimental data²⁷ for $\Delta(L_0),$ which are shown in Fig. 5, indicate that it is most likely the second possibility that is realized (analysis of the curves gives $n \leq 0$).

_Yet another question concerns the use of the quantity $\Delta = I_x^x / I_y^x$, i.e., the ratio of the total scattered-light intensities observed in the directions parallel and perpendicular to the polarization direction of the incident light, to characterize the depolarization of the scattered light in experiments in dense gases⁸¹ and near the critical point.^{37b} In the region of τ and $\Delta \rho$ in which one may neglect scattering processes of order i > 2, one has $\Delta = \Delta(1 + \Delta_1)/(1 + \Delta)$. The polarization ratio³³ $\Delta_1 = I_x^{xx}/I_x^{xy} \text{ lies in the interval } \Delta_1(q_0^2 r_c^2 \rightarrow 0) = 1 < \Delta_1$ $<\Delta_1(q_0^2 r_c^2 \rightarrow \infty) = 1.589$. In the region $10^{-5} < \tau < 10^{-2}$ the value of Δ_1 is approximately equal to one. For example, at $q_0^2 r_c^2 = 1$, which corresponds to $\tau \approx 10^{-4}$ at $\lambda = 5 \cdot 10^{-5}$ cm, one has $\Delta_1 \approx 1.08$. Since one typically has $\Delta_{exp} \leq 0.1$, the value of Δ_{exp} should be about twice as large as Δ_{erv} . Comparison of the calculated values³³ of Δ with the measured values³⁷ of Δ shows that they agree

in order of magnitude, thereby confirming the indicated range of values of the polarization ratio Δ_1 .

4. HIGHER-MULTIPLE SCATTERING

a) Total coefficient of multiple scattering

Let us first discuss the critical behavior of the terms in (2.6) which are responsible for "interference" effects. The intensity of these terms depends on the following way on the characteristic dimension L_0 of the scattering volume⁴¹: $I_{inter} \sim \langle [\mathbf{E}_i, \mathbf{H}_j^*] \rangle \sim L_0^{2i^{-j+2}}, i \neq j$. It can be shown that $\langle [\mathbf{E}_2, \mathbf{H}_0^*] \rangle$ and $\langle [\mathbf{E}_0, \mathbf{H}_2^*] \rangle$ on the one hand, and $\langle [E_3, H_1^*] \rangle$ and $\langle [E_1, H_3^*] \rangle$ on the other, give the same contribution to the total multiple-scattering intensity as $\langle [E_1, H_1^*] \rangle$ and $\langle [E_2, H_2^*] \rangle$, which determine the "pure" single and double scattering, respectively. This assertion is based on the fact that $\langle [E_1, H_1^*] \rangle$, $\langle [E_2, H_0^*] \rangle$, and $\langle [E_0, H_2^*] \rangle$ are related to the correlation function G_2 , while $\langle [\mathbf{E}_2, \mathbf{H}_2^*] \rangle$, $\langle [\mathbf{E}_3, \mathbf{H}_1^*] \rangle$, and $\langle [E_1, H_3^*] \rangle$ are related to the correlation function G_4 . However, estimates^{21,22} show that both the "interference" effects enumerated above and the one-and-onehalf-fold scattering $I_{3/2} \sim \langle [E_2, H_1^*] \rangle, \langle [E_1, H_2^*] \rangle$, which contains the correlation function G_3 , give negligibly small contributions to the multiple-scattering intensity.

For studying higher-multiple scattering processes, we introduce in (2.6) the total coefficient of multiple scattering

$$R = \sum_{i \ge 1} R_i, \quad R_i = \frac{I_i L^2}{I_0 V}.$$
 (4.1)

The *i*-fold scattering coefficient R_i is defined here in analogy with the single-scattering coefficient.¹⁰ The general formulas (2.2) and (2.3) for the scattered fields in the static case give the following recursion relations⁴⁶ for R_i :

$$R_t(\sigma, \sigma_0) = L_0 \int_{\sigma_{i-1}} R_i(\sigma, \sigma_{i-1}) R_{i-1}(\sigma_0, \sigma_{i-1}) d\sigma_{i-1}, \qquad (4.2)$$

$$R_{i}(\sigma, \sigma_{i-1}) = \frac{\pi^{2}}{\lambda^{5}} \left(\rho \frac{\partial \varepsilon}{\partial \rho} \right)_{\mathrm{T}}^{2} G_{2}(q_{i}) \left(1 - \frac{(\mathbf{n}_{i} \mathbf{m}_{i-1})^{2}}{|\mathbf{m}_{i-1}|^{2}} \right).$$
(4.3)

In particular, (4.1) and (4.2) imply that $R_i \sim L_0^{i-1}$, $I_i \sim VL_0^{i-1}$.

When (4.2) is taken into account, it is readily apparent that expression (4.1) is the iterative solution of the integral equation

$$R(\sigma, \sigma_0) = R_1(\sigma, \sigma_0) + L_0 \int_{\sigma'} R_1(\sigma, \sigma') R(\sigma', \sigma_0) d\sigma', \qquad (4.4)$$

which has the following closed solution

$$R(\sigma, \sigma_0) = \sum_{n \ge 0} \frac{B_{0n} Y_n^0(\sigma)}{1 - L_0 B_{0n}} + \frac{1}{2} \sum_{n \ge 2} \frac{B_{2n} \{Y_n^*(\sigma) + Y_n^{-2}(\sigma)\}}{1 - L_0 B_{0n}}; \quad (4.5)$$

here

$$B'_{mn} = \left(\frac{4\pi}{2n+1}\right)^{1/2} B_{mn}, \quad B_{mn} = \int_{\sigma} R_1(\sigma, \sigma_0) Y_n^{*m}(\sigma) \, \mathrm{d}\sigma$$

are the coefficients of the expansion of R_1 [from (4.3)] in the spherical harmonics $Y_n^m(\sigma)$. Formula (4.5) enables one to find the various characteristics of the multiple scattering (the indicatrix, extinction coefficient, etc.) from a given correlation function G_2 for the orderparameter fluctuations. We note that a direct consequence of (4.5) is the following criterion for applying the iterative procedure to (4.4):

$$k_1 L_0 < 1 \quad (k_1 = B'_{00})$$
 (4.6)

b) Extinction coefficient for multiple scattering. The relationship of the various scattering orders

With allowance for (4.5), the extinction coefficient for multiple scattering

$$K = \int_{\sigma} R(\sigma, \sigma_0) \, \mathrm{d}\sigma \tag{4.7}$$

is given by the expression

$$K = \frac{k_1}{1 - k_1 L_0} \,. \tag{4.8}$$

This result can also be obtained directly from (4.7), (4.1), and (4.2), according to which

$$K = \sum_{i \ge 1} k_i = k_1 + k_1^* L_0 + k_1^* L_0^* + \dots$$
 (4.9)

Summation of the series (4.9) under condition (4.6) yields formula (4.8).

From (4.9) one obtains a relation between the contributions to K from scattering processes of successive orders:

$$\frac{k_{i+1}}{k_i} = k_i L_0, \quad i = 1, 2, \dots$$
(4.10)

For $k_1L_0 \ll 1$, it follows from (4.8) that what is determined in experiment is k_1 , the extinction coefficient for single scattering. In the general case it is not k_1 but K, the extinction coefficient for multiple scattering, that is found in experiment. From (4.8) and (4.10) we obtain the expression $k_{i \neq 1}/k_i = KL_0/(1 + KL_0)$, which enables one to determine the relative contributions of the successive scattering orders on the basis of the experimentally measured value of K.

For concrete calculations of the extinction coefficient K, we use the representation of the correlation function G_2 in the Ornstein-Zernike approximation. In this case we obtain for k_1 the well-known expression (see e.g., Refs. 19 and 82).

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

where $\tilde{a} \sim \beta_{\rm T}/\lambda^4$ and $\tilde{b} = q_0^2 r_c^2$. The coefficients $B_{\rm on}$ and B_{2n} appearing in formula (4.5) are evaluated in Ref. 46. The logarithmic singularity of k_1 at the critical point $(\tilde{b} \sim r_c^2 \rightarrow \infty)$ generally speaking leads to violation of criterion (4.6). Table II gives calculated⁴⁶ values of the quantity $k_1 L_0/s$, where s is the parameter introduced in (3.5), which show that at the realistic value s = 0.1 criterion (4.6) is violated $(k_1 L_0 = 1)$ at $q_0 r_c \approx 2$, corresponding to a temperature deviation $\tau \approx 10^{-4.9}$ on the critical isochore. At this same value of s the single-scattering contribution is comparable to the contribution of all the remaining scattering orders $(k_1 L_0 = 1/2)$ for $q_0 r_c \approx 1.1(\tau \approx 10^{-4.45})$ and, finally, the single-scattering approximation can be used with acceptable accuracy $(k_{i+1}/k_1 \leq 0.1, \Sigma_{i>2} k_i/k_1 \leq 11\%)$ for all $\tau \geq 10^{-3.7}$.

c) Experimental studies of higher-multiple scattering

In Ref. 35b, Trappeniers and co-workers reported the experimental observation of triple scattering along TABLE II.

$(q_0 r_c)^2$ $- \lg \tau$ $k_1 L_0/s$	10 ⁻³ 2.001 8.372·10 ⁻³		$ \begin{array}{c} 10^{-2} \\ 2.801 \\ 8.295 \cdot 10^{-2} \end{array} $		10~1 3.601 7.641.10 ⁻¹		2·10 ⁻¹ 3.842 1.412	3.10 ⁻¹ 3.982 1.976
$\frac{(q_0 r_c)^2}{-\log \tau} \frac{1}{k_1 L_0/s}$	1.0 4.401 4.601		2.0 4.642 7.008		3.0 4.782 8.604		3.0 4.0 .782 4.882 .604 9.834	
$(q_0 r_c)^2$ $- \frac{1}{k_1 L_0/s}$	4.082 2.476	5-10 ⁻¹ 4.160 2.926		5.10 ⁻¹ 4.160 2.926 3.3		7·10 ⁻¹ 4.227 3.713	8.10 ⁻¹ 4.323 4.061	9.10 ⁻¹ 4.364 4.386
$(q_{0}r_{c})^{2}$ $-\lg \tau$ $k_{1}L_{0}/s$	6,0 5.02 3 11.700	5 12	7.0 .077 . 43 9	8.0 5.12 13.09) 23 97	9.0 5.164 13.689	10.0 5.201 14.226	11.0 5.234 14.719

the critical isochore in Xe. In the region 0.02 K $< T - T_c < 0.1$ K the temperature dependence of the depolarization factor $\Delta(\tau)$ was described by the exponent -2.45 ± 0.05 , which agrees with the theoretical value -2γ for the exponent describing the temperature dependence of the ratio I_{y3}^{xx}/I_{y1}^{xx} . They also obtained a nonmonotonic dependence of Δ on the height L_0 of the scattering volume. With allowance for the triple scattering, for which $I_3 \sim L_0^5$, the L_0 dependence can be described by the formula³³

$$\Delta (\tau, L_0) \approx (a\tau^{-\nu}L_0 + b\tau^{-2\nu}L_0^*) / (1 + a_1\tau^{-\nu}L_0 + b_1\tau^{-2\nu}L_0^*)$$

$$(q_0^2 r_0^2 \ll 1),$$
(4.11)

where the last terms in the numerator and denominator represent I_{y3}^{xx}/I_{y1}^{xx} and I_{y3}^{xy}/I_{y1}^{xx} , respectively, Relation (4.11) implies, however, that detection of the triple-s scattering contribution on the basis of the temperature dependence of the depolarization factor $\Delta(\tau)$ requires special processing of the experimental data, since in addition to the growth of the depolarized component of the scattering intensity as the critical point is approached there is also growth in the fraction of the polarized component that is due to higher scattering orders.

A correct technique for separating the double and higher-multiple scattering from the total intensity of scattered light in critical opalescence was devised and applied by Adzhemyan et al. 29c In essence, this technique amounts to: 1) theoretically calculating the double-scattering intensity using the formulas of Ref. 29b, which take into account the actual experimental geometry (see Fig. 4), with the values of the critical exponents γ and ν and parameters a_0 and $B = R_1/(qr_c)^2$ obtained from the data on the single-scattering intensity $I_1(\tau, \theta)$; 2) using the experimental data on $I_{exp}(\tau, \theta)$ for each scattering angle to calculate the theoretical value of $I_2(\tau, \theta)$ and to discover thereby the intensity I_{\bullet} of all the scattering orders higher than two; 3) extrapolating $I_{0}(h)$ to h=0; 4) subtracting the contributions $I_{2}(h=0)$ and $I_{\rho}(h=0)$ from $I_{exp}(h=0)$ for all τ to obtain the corrected intensity $I_1(\tau, \theta, h=0)$; 5) finding a new set of values for γ , ν , a_0 , and B and reiterating the entire procedure until self-consistent values of the exponents and parameters are obtained. Table III illustrates how γ , ν , a_0 , and B depend on the number of iterations for the system studied in Ref. 19c: a nitrobenzene-hexane mixture near the critical state of stratification. AlTABLE III.

Number of iteration	a ₀ , Å	v	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 value	2.7±0.2	0.62±0.02	1.21±0.02	0.29 \pm 0.02

lowance for multiple scattering leads to lower values³⁾ of γ , a_0 , and B and to a higher value of ν . Figures 10 and 11 show the results of applying the procedure of Adzhemyan *et al.*^{29°} to separate I_2^{ee} and I_p^{ee} from I_{eep}^{ee} . At $k_0 r_e \approx 2$ the combined intensity of the double and higher-multiple scattering is comparable to the singlescattering intensity (Fig. 11). Adzhemyan *et al.*²⁹ also studied the angular dependence of $I_2^{ee}(\theta)$ and $I_p^{ee}(\theta)$ (Fig. 12). In addition to the fact that $I_2(\theta)$ is smoother than $I_1(\theta)$, as was noted in Refs. 19, 22, 23, and 83, it is interesting that the relative value of the multiple scattering increases with increasing scattering angle.

Sorensen *et al.*⁴³⁴ obtained estimates of the region in which multiple-scattering effects are important from an analysis of an experimental study of Δ in a methanol cyclohexane mixture. These estimates, which are similar to those obtained in Refs. 29c, 35b, and 46, are as follows: for $k_0 r_c < 0.6$ one may use the singlescattering approximation (at $k_0 r_c = 0.6$, $I_2/I_1 \approx 15\%$), for $0.6 \le k_0 r_c \le 0.8$ one should take into account both single and double scattering, and for $k_0 r_c > 0.8$ one should also take higher scattering orders into account.

d) Allowance for attenuation. The refractive index in the critical region

The standard method of taking into account the attenuation of the intensity of a light beam traversing a distance l in a medium is based on the familiar Bouguer-



FIG. 10. Measured intensity $\Gamma_{2\pi}^{exp}$, calculated intensities of double scattering $I_{2\pi}^{ex}$ and multiple scattering $I_{2\pi}^{ex}$ for the nitrobenzene-hexane system near the critical state of stratification, plotted as functions of the distance *h* between the illuminated and detected volumes²⁹ (see also Fig. 4).

FIG. 11. Relative content of double and multiple scattering in the measured intensity I_{sp}^{ss} for h = 0 (Ref. 29a).

Lambert law

$$I(l) = I_0 \exp(-k'l).$$
 (4.12)

The reciprocal attenuation length k' is usually, in the absence of intrinsic absorption, identified with the extinction coefficient for single scattering, k_1 . Equation (4.12) is based on the optical theorem, 4,17,18 which relates k_1 to the imaginary part of the refractive index n:

$$k_1 = 4\pi \operatorname{Im} n/\lambda. \tag{4.13}$$

The existence of an imaginary part of n and an estimate of its value near the critical point were adduced in Refs. 84 and 85 (a discussion of this question for the noncritical region is given, for example, in Refs. 2-4, 18, and 47). Those studies^{84, 85} obtained the corrections to the Lorentz-Lorenz expression for n that result from allowance for the two-particle and higher correlations. These contributions are expressed analytically in terms of integrals of the product of the electromagnetic field propagators \hat{T}_{ij} and the partial statistical distribution functions F_{i+j} . These integrals are analogous to those which arise in the microscopic approach to the description of multiple scattering.

A calculation incorporating the pair correlations, which is formally equivalent to the single-scattering approximation, yields the following expression for the refractive index near the critical point:

$$n = n_{LL} + F(kr_e); \qquad (4.14)$$

here n_{LL} is the Lorentz-Lorenz value of n, whose critical behavior is governed by the order parameter. For example, for a liquid-vapor system on the coexistence curve

$$n_{LL} = n_{c} \pm B_{0} |\tau|^{\beta} + B_{1} |\tau|^{1-\alpha} \pm B_{2} |\tau|^{\beta+\Delta^{*}} + o(|\tau|^{m}, m \ge 1),$$
(A 15)

where $a \approx 0.11$, the critical exponent $\Delta' \approx 0.5$, and the upper and lower signs correspond to $p > \rho_e$ and $\rho < \rho_e$, respectively. The correlation contribution $F(kr_e)$ has the asymptotic behavior:



FIG. 12. Angular dependence of various scattering orders in the polarized component. 294

³⁾The change in the parameter B, which is related to the scattering coefficient R_1 , reflects the decrease in the absolute intensity of the single scattering as the higher-multiple scattering processes are systematically taken into account. This same result follows directly from relations (4.1), (4.4), and (4.9).

$$\operatorname{Re} F(kr_{c}) \sim \begin{cases} a_{0}r_{c}k^{2} & \text{for } kr_{c} \ll 1, \\ a_{0}r_{c}^{-1} + a_{0}r_{c}^{-3}k^{-2} & \text{for } kr_{c} \gg 1, \end{cases}$$

$$\operatorname{Im} F(kr_{c}) \sim \int G_{2}(r) dr \sim \begin{cases} \tau^{-\gamma} & \text{for } kr_{c} \ll 1, \\ \text{const for } kr_{c} \gg 1. \end{cases}$$

$$(4.16b)$$

It follows from (4.14)-(4.16) that the refractive index is constant as the critical point is approached, whereas the derivative $\partial n/\partial \tau$ has a "weak" singularity of the type $|\tau|^{-\alpha}$. There should be an analogous singularity $(\partial n/\partial \rho)_{\rm T} \sim |\Delta \rho|^{-\alpha/\beta}$ on the critical isotherm. Formula (4.16b) determines Im*n* in accordance with the optical theorem.

The inclusion of higher-order (beyond pair) correlations leads to a refinement of the relation between Imn and k_1 given by the optical theorem (4.13). Here it becomes necessary to relate the experimental parameter in (4.12)—the reciprocal attenuation length k' to the multiple-scattering extinction coefficient K. For this purpose we write the following balance equation,⁴⁶ neglecting surface effects:

$$\sigma I_0 = \sigma I(l) + I_0 V K,$$

where σ is the cross section of the incident (transmitted) beam. Taking (4.12) into account, we find

$$k' = -l'^{-1} \ln \left(1 - \frac{VK}{\sigma} \right). \tag{4.17}$$

For $k'l \ll 1$ it by no means follows from (4.17) that $k' = k_1$. In fact, for $k'l \ll 1$ and $\sigma l/V = 1$, we find k' = K. It is only for $KL_0 \ll 1$ that (4.8) gives $K = k_1$ and the reciprocal attenuation length in (4.12) is the single-scattering extinction coefficient: $k' = k_1$. In the general case, however, when $\sigma l/V \neq 1$, one can use (4.10) and (4.17) to estimate the ratio k_{i+1}/k_i from the experimental value of k' and the geometric factors l, σ , V, and L_0 . We note that the fact that the reciprocal attenuation length k' depends not only on the thermodynamic variables but also on the geometric factors indicates that higher-multiple scattering is present.

In Ref. 21-23 and 27, the characteristics of the double scattering near the critical point were calculated without taking attenuation into account. The analogous calculations of Refs. 24, 25, and 29 included the attenuation factor in an approximation based on formula (4.12) with $k' = k_1$; as we have already mentioned, this approximation is equivalent to taking single scattering into account. It is clear that inclusion of the attenuation factor in this manner corresponds to an increase in the scattering order of the scattered light. For example, allowance for a factor $\exp(-k_1 l)$ in the single-scattering calculation requires simultaneous consideration of the unattenuated double scattering. Moreover, as was noted in Refs. 28, 47, and 86, it is consistent in this case to expand the exponential in series retaining the linear term. In other words, to write I_{exp} in the double-scattering approximation one should use the formula I_{exp} $= I_1 - k_1 l I_1 + I_2 (k' = k_1)$, which is valid for angles $\theta \neq 0$.

5. EFFECT OF MULTIPLE SCATTERING ON THE SPECTRUM OF CRITICAL OPALESCENCE

a) Single-scattering spectrum

The light-scattering spectrum contains extremely comprehensive information on the equilibrium and ki-

netic properties of a material. $^{10,87-89}$ The main feature of the dynamics of fluctuations in the critical region the growth of the relaxation time—governs the spectral features of the critical opalescence, which have been well studied theoretically and experimentally in the single-scattering approximation (Refs. 5, 6, 14–16, 53, and 90–94).

The hydrodynamic theory predicts that the widths $\Gamma_{\rm c}$ and $\Gamma_{\rm B}$ of the central (Rayleigh) and side (Brillouin) components of the single-scattering triplet and also the frequency shift $\Delta \Omega_{\rm B}$ depend on the thermal conductivity λ , the shear and bulk moduli $\tilde{\eta}$ and ζ , the specific heats $c_{\rm p}$ and $c_{\rm V}$, and the speed of sound v:

$$\Gamma_{c} = \frac{\lambda(q)}{\rho c_{p}(q)}q^{2}, \quad \Gamma_{MB} = \left[\left(\frac{4}{3}\widetilde{\eta}(q) + \zeta(q)\right)^{-1}\rho + \frac{\lambda(q)}{\rho c_{V}(q)} - \frac{\lambda(q)}{\rho c_{p}(q)} \right]q^{2}, \\ \Delta \Omega_{MB} = \nu(q) q. \quad (5.1)$$

In a binary mixture one has $\Gamma_c = \hat{L}(q)\chi^{-1}(q)q^2 = D(q)q^2$, where \tilde{L} is the Onsager coefficient, χ is the susceptibility, which is equal to $(\partial \rho / \partial p)_{T, \mu - \mu_1 - \mu_2}$ or to $(\partial x / \partial \mu)_{\rho, T}$ near a critical point of vaporization or stratification, and D is the diffusion coefficient.

Correct interpretation of the experimental data on the critical-opalescence spectrum requires that the background parts of the kinetic coefficients be taken into account.^{16,53,92,94} In the region in which the background parts λ^b and L^b exceed their singular parts $\lambda^{s}(q)$ and $ilde{L}^{s}(q), ext{ the increase in the relaxation time } t_{ ext{c}} ext{ (the nar-}$ rowing of $\Gamma_{\rm c} = t_{\rm c}^{-1}$) is completely determined by the strongly divergent equilibrium properties of c_{y} and χ : $\Gamma_{c}^{b} = \lambda^{b} q^{2} (1 + q^{2} r_{c}^{2}) / \rho c_{b} (q = 0)$ in a one-component fluid, and $\Gamma_c^b = \tilde{L}_c^b \chi^{-1} (q=0) q^2 (1+q^2 r_c^2)$ in a binary mixture. Extrapolation of the hydrodynamic formula for Γ_{e} to the critical point, where $\lambda^s \sim \tau^{-\nu} \gg \lambda^b$ and $\tilde{L}^s \sim \tau^{-\nu} \gg \tilde{L}^b$, leads to not so strong a narrowing of the central line: $\Gamma_{\rm e} \sim \tau^{\nu}$ for $\rho = \rho_{\rm e}$ and $\Gamma_{\rm e} \sim \Delta \rho^{\nu/\beta}$ for $T = T_{\rm e}$. This result follows from simple considerations based on the Stokes-Einstein relation: $D = k_{\rm B} T / 6\pi \tilde{n} r_{\rm e}$.

The behavior of the Brillouin component in the critical region is governed by singularities in the speed and damping of sound waves. The background part $v^{\flat}(\omega \rightarrow 0)$ $\sim (c_{\nu}^{b})^{-1/2}$ is regular. For the singular part we have $v^{s}(\omega \rightarrow 0) \sim \tau^{\alpha/2} f_{v}(\Delta \rho/\tau^{\beta})$, where $f_{v}(x \rightarrow 0) = \text{const.}$ The fall-off of the speed of sound, which leads to a decrease in the frequency shift $\Delta \Omega_{\rm B}$, should be seen only at frequencies $\omega \ll \omega_{b}$. The relaxation frequency $\omega_{b} = \lambda / \rho c_{p} r_{c}^{2}$ decreases rapidly as the critical point is approached; as a result, one should observe dispersion in the speed of sound $v(\omega)$. In close proximity in the critical point, where the contribution Γ_{B}^{b} is small, the growth of the acoustic damping and, accordingly, the broadening of the Brillouin component are governed predominantly by the singular part of the bulk viscosity: $\Gamma_{\rm B} \approx \Gamma_{\rm B}^s \sim \zeta^s \sim \tau^{-(3\nu+\alpha)} f_{\zeta}(\Delta \rho / \tau^{\beta})$, where $3\nu + \alpha$ =2, $f_{\xi}(x \rightarrow 0) = \text{const.}$ Here the dispersion $v(\omega)/v(0)$ $-1 = (\omega/2\rho v^2(0)) \operatorname{Im} \zeta^{s}(\omega)$ of the speed of sound and the damping $\alpha(\omega) = (\pi \omega / \rho v(0)) \operatorname{Re} \zeta^{s}(\omega)$ at the acoustic wavelength should be universal functions of the reduced frequency $\omega^* = \omega/2\omega_p$ (to within a factor which depends weakly on T and ρ). These features of the behavior of the Brillouin component were confirmed experimentally

by technqiues based on light-beating spectroscopy.^{16,95} Ultrasound studies are also promising.⁵³

Of primary interest in the study of the critical-opalescence spectrum is the rapidly growing central component. It can be seen from the Landau-Placzek relation $I_{\alpha}/2I_{\alpha} \sim \tau^{-\gamma+\alpha}(q \rightarrow 0, \Delta \rho \ll \tau^{\beta})$ that as the temperature is brought one decade (for example) closer to the critical point (in terms of the value of τ), the ratio $I_{\rm c}/2I_{\rm B}$ grows by an order of magnitude ($\gamma - \alpha \approx 1.1$). Naturally, allowance for the spatial dispersion of the fluctuations should lead to a large, but finite, value of $I_{\rm c}/2L_{\rm B}(q \neq 0)$ at the critical point. For studying the width $\Gamma_{\rm c}$, which characterizes the relaxation frequency of fluctuations of the order parameter, several versions of the dynamical theory of critical phenomena have been developed: the mode-mode coupling^{96,97} and decoupled-mode^{98,99} theories, modifications of these theories,¹¹⁰⁻¹⁰⁴ and the dynamic droplet model.^{105,106} Allowance for coupling between modes (the most important being the coupling of order-parameter fluctuations and the viscous mode) leads to the following result for Γ_{c}^{s} :

$$\Gamma_{c}^{s} = \frac{k_{\rm B}T}{6\pi \tilde{\eta}^{*} r_{c}^{s}} K_{0} (qr_{c}), \qquad (5.2)$$

where $\bar{\eta}^*$ is the "high-frequency" shear viscosity and $K_0(x) = (3/4)[1 + x^2 + (x^3 - x^{-1}) \operatorname{arctg} x]$. For $qr_c \ll 1$ we have $\lim_{x\to 0} K_0(x) = x^2$, and the result for $\Gamma_c^{\sigma} = Dq^2$ agrees with the hydrodynamic theory (see 5.1). In the nonhy-drodynamic region $(qr_c \gg 1)$ we have $\lim_{x\to\infty} K_0(x) = (3\pi/8)x^3$, which yields a value $\Gamma_c^{\sigma} = (k_B T/16\bar{\eta}^*)q^3$ which is independent of r_c and, hence, of τ and $\Delta\rho$.

In the modified mode-mode coupling theory¹⁰⁰⁻¹⁰² the following additional factors were taken into account: The relation $\tilde{\eta}^{*-1} = R(qr_c)\tilde{\eta}^{-1}$ between the "high-frequency" $\tilde{\eta}^*$ and macroscopic $\tilde{\eta}$ shear viscosities; a correction $C(qr_c) = \Gamma_c^s(G_{FB}, qr_c)/\Gamma_c^s(G_{OZ}, qr_c)$ describing the deviation of a correlation function¹⁰⁷ with $\eta \neq 0$ from the correlation function (2.8); a "vertex" correction $\tilde{V}(qr_c)$ arising from a more exact (than in Ref. 96) solution of the "Dyson" type equation for fluctuations of the order parameter. The factor $H(qr_c) = R(qr_c) \times$ $C(qr_c)\tilde{V}(qr_c)$ which arises in (5.2) grows smoothly from a value $H \approx 1.1$ at $qr_c = 0.1$ to $H \approx 1.3$ at $qr_c = 10$.

A similar, but not equivalent,^{96,97} approach to the dynamics of critical phenomena was taken by Ferrel and Perl in developing the decoupled-mode theory.^{98,99} Jointly solving the system of two equations for Γ_c and $\tilde{\eta}$ by an iterative method with a number of simplifying assumptions [factorization of the correlation functions of the stress tensors in using the fluctuation-dissipation theorem for the viscosity, introduction of a "Debye" cutoff wave vector q_D in evaluating the integrals over q, neglect of the "vertex" correction $\tilde{V}(qr_c)$], those authors obtained the following expression for Γ_c^s :

$$\Gamma_{c}^{s} = \frac{k_{\rm B}T}{6\pi\eta_{0}\phi\phi r_{c}^{2}} K_{0} (qr_{\rm c}) C (qr_{\rm c}), \qquad (5.3)$$

where $\tilde{\eta}_{eff} = \bar{\eta}^{b} + (8\bar{\eta}/15\pi^{2})[\ln(q_{D}r_{c}) - 1/2(1+q^{2}r_{c}^{2}) + \tilde{\tau}(qr_{c})]$ is the "effective" shear viscosity, $\bar{\tau}(qr_{c})$ is a tabulated function, and $\bar{\eta}$ is an adjustable parameter in the approximation formula^{5,99}

$$\Gamma_{\rm c}^{\rm s} = \frac{k_{\rm B}T}{16\bar{\eta}r_{\rm c}} q^2 \left(1 + q^2 r_{\rm c}^2\right)^{1/2},\tag{5.4}$$

which gives a good description of the experimental data and is used as a zeroth approximation for finding $\tilde{\eta}^s$.

A similar [to (5.4)] dispersion relation for Γ_c is used in the dynamic droplet model.^{105,106} according to which we have

$$\Gamma_{c} = \widetilde{\gamma} \frac{k_{\rm B}T}{6\pi \widetilde{\eta}^{b} r_{c}} q^{2} \sqrt{1 + q^{2} r_{c}^{2}}, \qquad (5.5)$$

where $\tilde{\gamma}$ is a factor of order of unity characterizing the non-Lorentzian (in contrast with the theory of Refs. 96-104) line shape of the central peak.

Figure 13 shows curves^{43a} of the dimensionless "scaling" width $\Gamma_c^{s*} = 6\pi \bar{\eta} \Gamma_c^s / k_B T q^3$ for the mode-mode coupling theory (curve 1), the decoupled-mode theory (curve 2), and the dynamic droplet model (curve 3). In the hydrodynamic region $(qr_{c} \ll 1)$ all the theories give practically the same result: $\Gamma_{c}^{s*} = 1/(qr_{c})$. A difference appears in the nonhydrodynamic region $(qr_s \gg 1)$. Experimental studies of Γ_{e} in individual fluids and liquid mixtures in the region $1 \leq qr_{e} \leq 10$ agree better in some cases (Xe, aniline-cyclohexane, 3-methylpentane-nitroethane) with the mode-mode coupling theory and in other cases (water-isobutyric acid) with the decoupledmode theory.^{16,92,94} The disparity between these theories, however, does not exceed 10% for $qr_{\rm e} \gg 1$. The predictions of the dynamic droplet model agree less with the experimental measurements of $\Gamma_{c}(qr_{c})$. For $\bar{\gamma} = 1$ the discrepancy between theory and experiment can reach tens of percent.¹⁰⁸ Nevertheless, by treating $\tilde{\gamma}$ as an adjustable parameter, one can obtain satisfactory agreement with experiment for this theory, too.

Let us discuss a number of important problems in dynamics of critical phenomena which continue to attract experimental and theoretical interest,

1) Dynamic critical exponent. In the dynamic scaling theory^{14,15,91} the width Γ_c is given by the formula $\Gamma_c = \tilde{q} \,{}^{s} f_{\Gamma}(qr_c)$. One of the main theoretical and experimental problems is to establish the value of the dynamic critical exponent \tilde{z} . In particular, it is important to answer the question of whether \tilde{z} is related to the exponents of the static theory of scaling or whether it is a new critical exponent. Far from the critical point, where $\Gamma_c^b \gg \Gamma_c^s$, one has $\tilde{z} = 2$ or $\tilde{z} = 2 - \eta$, depending on whether the Crnstein-Zernike approximation or a scale-invariant form of the correlation function G_2 is used. Close to the critical point, if Γ_c^b is neglected (in practice, the condition $\Gamma_c^b \ll \Gamma_c^s$ is not realized in experiments), it follows from (5.2)-(5.5) that $\tilde{z} = 3$. Such a value of \tilde{z} corresponds to the additional assumption



FIG. 13. Dependence upon qr_c of the "scaling" width $\Gamma_c^{\bullet*}$ of the central line in the various theories of critical dynamics.

that the viscosity $\tilde{\eta}^s$ has a weak logarithmic divergence (or no divergence at all) at the critical point. In reality (see Refs. 15. 94 and 104) the shear viscosity has a weak power-law singularity $\tilde{\eta}^{s} \sim r_{c}^{x\eta}$ for $x_{\tilde{n}} = 0.065$. This result is confirmed by experimental studies,^{94,109} according to which $x_{\tilde{e}} = 0.0635 \pm 0.0004$. Therefore, we have for the dynamic critical exponent \tilde{z} in fluids: $\vec{z}_{theo} = 3 + x_{\pi} = 3.065$ and $\vec{z}_{exp} = 3.063 \pm 0.024$ for the mixture 3-methylpentane-nitroethane.¹⁰⁹ The temperature dependence of \bar{z}_{eff} from Ref. 94, showing a smooth transition from $\tilde{z} = 2$ to $\tilde{z} \approx 3.06$, is shown in Fig. 14. In systems belonging to another universality class, \vec{z} can, of course, be different. Discussions of how \tilde{z} depends on the dimensionality of the order parameter and the spatial dimensionality, and also on whether the total order parameter is a conserved or nonconserved quantity, are found in Refs. 14 and 91.

2) Dynamic scaling function. The existing versions of the dynamical theory of critical phenomena predict different scaling functions $f_{\Gamma}(qr_c)$. According to the mode-mode coupling theory, $f_{\Gamma}(x) \sim x^{3}K_{0}(x)H(x)$. In the decoupled-mode theory $f_{\Gamma}(x) \sim (\tilde{\eta}/\tilde{\eta}_{ott})x^{-3}K_{0}(x)C(x)$ is generally not a universal function of $x = qr_c$, since $\tilde{\eta}_{ott}$ depends not only on the product qr_c , but also simply on r_c . In the dynamic droplet model $f_{\Gamma}(x) \sim (\tilde{\eta}/\tilde{\eta}^{b})x^{-1}(1+x^{2})^{1/2}$. The exact structure of the dynamic scaling function $f_{\Gamma}(qr_c)$ is needed in order to check the attractive hypothesis of the universality of kinetic phenomena near critical and second-order phase-transition points.

3) Renormalization group in critical dynamics. The diffusion coefficient D determined experimentally from the Rayleigh linewidth in binary mixtures satisfies the relation $D = \lim_{x \to 0} \Gamma_{c}(x)q^{-2} = Rk_{B}T/\tilde{\eta}r_{c}$, where the numerical coefficient R is equal to $1/6\pi$ in the mode-mode coupling and decoupled-mode theories. At the same time, renormalization group calculations¹¹⁰ of the critical dynamics have shown that $R \approx 1.2/6\pi = 1/5\pi$. Such a value of R corresponds to the Stokes-Einstein relation for a spherical droplet of radius r_{e} moving in a medium whose viscosity is the same as that of the field in the droplet.¹¹¹ An increase of 20% in the value of the constant R can be attributed to the factor H(x) which arises in formula (5.2) in the nonhydrodynamic region. In the hydrodynamic region, however, where $H(x \rightarrow 0)$ \approx 1, behavior of this sort becomes conspicuous and requires explanation. While a number of experiments have detected values $R \approx 1.2/6\pi$, more recent studies of Γ_c have given results which agree with the modemode coupling theory (see Ref. 94). In particular, Burstyn *et al.*¹⁰⁹ found $R = (1.02 \pm 0.06)/6\pi$ on the basis of their independent measurements of $\bar{\eta}$ and Γ_c (with allowance for the phonon contributions) and the data on r_{e} from measurements¹¹² of the integrated light-scattering



FIG. 14. Temperature dependence of the effective dynamical critical exponent. 94

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intensity in the mixture 3-methylpentane -nitroethane.

4) Crossover function for the shear viscosity. In order to find \tilde{z} , $f_{\Gamma}(x)$, and R, one faces the problem of determining the crossover function for the shear viscosity, which takes into account the relationship of the background and critical parts. Oxtoby and Gelbart¹⁰³ solved this problem in the framework of the mode-mode coupling theory, but with Γ_{c}^{b} included in the calculation. This term, which was not included in Refs. 96-102, should be taken into account, since the main contribution to the integral for $\tilde{\eta}^s$ is from large wave vectors q, for which $\Gamma_c^b \sim q^4$, while $\Gamma_c^s \sim q^3$. A refined crossover function for $\tilde{\eta}$ was recently determined¹⁰⁴ using the methods of the decoupled-mode theory, i.e., with the introduction of a cutoff wave vector q_n and simultaneous allowance for Γ_c^b in accordance with Ref. 103. The results of Ref. 104 are in good quantitative agreement with the experimental data for the viscosity of nitrogen¹¹³ and water vapor.¹¹⁴

5) Distorting influence. Factors causing distortion from ideal critical behavior (see part 2c) can also have a substantial effect on the critical-opalescence spectrum. In particular, the dependence Γ_c on the vertical coordinate z in a gravitational field was studied in Refs. 92, 108, 115, and 116. In Ref. 108 the function $\Gamma_c(z)$ was measured in CO₂ at $T - T_c = 10^{-3}$ °C (Fig. 15). The results are in best agreement with the decoupled-mode theory (the lower curve, with an rms error of 2.73%). The agreement with the mode-mode coupling theory is not as good (7.95% error). The origin of the "beak" in the calculations of $\Gamma_c(z)$ remains unclear. The disagreement with the dynamic droplet model is large (upper curve, with 33.95% error at $\tilde{\gamma} = 1$); for $\tilde{\gamma} = 0.8$, however, the error is reduced to 2.24%.

b) Calculations of the double scattering-spectrum

As in the static case, the properties of the higherorder space-time correlation functions for fluctuations of the order parameter, which determine the features of the multiple-scattering spectra, have been little studied in the critical region. Most of the calculations of the higher-multiple-scattering spectra to date^{40°43} have been done in the approximation that the successive reradiation processes are incoherent, i.e., have been done using asymptotic formulas which express the higher-order space-time correlation functions of even orders in terms of the pair correlation function



FIG. 15. Height dependence of the width $\Gamma_{c}(z)$ of the central line in a gravitational field. 108

 $G_2(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$. Most exact results, valid in the nonhydrodynamic region, can evidently be obtained with the aid of multiple-index fluctuation-dissipation theorems similar to that which establishes the connection between the three-index susceptibility and the ternary space-time correlation function.^{117,118} We note that the one-andone-half-scattering spectrum, which is related to the space-time correlation function G_3 and has the form of a triplet,^{24,41,119,120} gives a negligibly small contribution to the dynamic scattering.

In Ref. 41 the double-scattering spectrum in critical opalescence was studied in the hydrodynamic approximation, using the dynamic structure factor $G_{2}(\mathbf{k}, \mathbf{k}', \omega)$ obtained in Ref. 121 from hydrodynamic equations incorporating the inhomogeneity of the medium in an external field and all the necessary spatio-temporal dispersion effects in the critical region [the spatial dispersion^{122,123} of $(\partial p/\partial \rho)_{\rm T}$ and the spatio-temporal dispersion of the transport kernels¹²⁴]. The temperature and field anomalies of the coefficients in the hydrodynamic equations were assigned using the results of the dynamical theory of critical phenomena⁹¹⁻⁹⁹ and the theory of the gravitational effect. 60 If we neglect effects (temporal dispersion) in the transport kernels, the spatio-temporal pair correlation function has a three-pole structure with the roots

$$\omega^{(1)} = -i \operatorname{Im} \varphi(q), \quad \omega^{(2,3)} = \pm \operatorname{Re} f(q) - i \operatorname{Im} f(q), \quad (5.6)$$
$$\operatorname{Im} \varphi = q^{2} \left[\left(\frac{\partial p}{\partial \rho} \right)_{\mathrm{T}} + B_{\rho} q^{2} \right] \left[\left(\frac{\partial p}{\partial T} \right)_{\rho} \left(\left(\frac{\partial e}{\partial \rho} \right)_{\mathrm{T}} + h \right) (\lambda^{-1}(z, \tau) + B_{\lambda} q^{2}) \right]^{-1}, \quad (5.7a)$$

$$\operatorname{Re} f = q \, \sqrt{\left(\frac{\partial p}{\partial T}\right)_{\rho}} \, \sqrt{\left[\left(\frac{\partial e}{\partial \rho}\right)_{\mathrm{T}} + h\right] \left[c\overline{v}^{1}\left(z,\,\tau\right) + B_{c}q^{2}\right]}}, \quad (5.7b)$$

$$\operatorname{Im} f = \frac{1}{2} \, q^{2} \left[\left(\zeta^{-1}\left(z,\,\tau\right) + B_{\zeta}q^{2}\right)^{-1} + \left(\frac{3}{4\widetilde{\eta}}\left(z,\,\tau\right) + B_{\widetilde{\eta}}q^{2}\right)^{-1} - \frac{\operatorname{Im} \varphi}{q^{2}}\right]. \quad (5.7c)$$

We have used the standard notation¹⁰ in (5.7). To allow for spatial dispersion, terms of the form $B_i q^2$ are added to quantities which vanish at the critical point.

In Ref. 41, on the basis of the calculated spectral characteristics of the double scattering in the hydrodynamic approximation, it was shown that in comparison with Γ_{c1} , Γ_{B1} , and $\Delta\Omega_{B1}$, respectively, Γ_{c2} , Γ_{B2} , and $\Delta\Omega_{B2}$ have the same temperature dependence but a smoother angular dependence. For example, Γ_{c2} and Γ_{B2} go as $\sim q$, and in the limit of zero-angle scattering go to zero more slowly than Γ_{c1} and Γ_{B1} , which go as $\sim q^2$. The relation⁴¹

$$\frac{\Gamma_{c_1}}{\Gamma_{c_2}} = \frac{\Gamma_{MB1}}{\Gamma_{MB2}} = \frac{1}{V^2} \sqrt{1 - \cos\theta}$$
(5.8)

implies that the spectral components suffer an additional broadening in multiple-scattering processes. However, this broadening is insignificant: for example, $\Gamma_{c2} = \sqrt{2} \Gamma_{c1}$ at $\theta = \pi/2$. A relation analogous to (5.7) was obtained in Ref. 125 for point particles undergoing Brownian motion: $\Gamma_{c2}(\theta = \pi) = \Gamma_{c1}(\theta = \pi) = 2\Gamma_{c1}(\theta = \pi/2)$. This result has also been used^{43a} to obtain the estimate $\Gamma_{cn} = n\Gamma_{c1}(\pi/2)$ for the broadening of the central component in *n*-fold multiple light-scattering in such a system and to make qualitative arguments concerning the effect of multiple scattering on Γ_c in real media near the critical point.

On the basis of the dynamic scaling hypothesis, Kuz'min⁴⁰ compared the "pure-scattering" component of the double scattering with the contribution due to "interference" effects. In particular, if one takes into account all diagrams in which the space-time correlation function G_4 is represented as a product of two space-time correlation functions G_2 , the estimate obtained for the width Γ_{c2} of the central component is of the same order of magnitude as Γ_{c1} : $\Gamma_{c2} \sim q^2$ for $qr_c \gg 1$.

Beysens and Zalczer⁴² evaluated the spectral intensity $I_2(\omega)$ for double scattering with a central component $\Gamma_c(q_i, r_c)$ (i=1, 2) given by formula (5.2) for each independent (by assumption) scattering event. If the single-scattering spectrum is assumed to be Lorentzian, the contribution to the spectral intensity from two successive scattering events with wave-vector transfers q_1 and q_2 also has a Lorentzian shape:

$$L(q_1, q_2, \omega, r_c) = \frac{\Gamma_c(q_1, r_c) + \Gamma_c(q_2, r_c)}{[\Gamma_c(q_1, r_c) + \Gamma_c(q_2, r_c)]^2 + \omega^2}.$$
 (5.9)

The total spectral intensity of the double scattering is obtained by integrating (5.9) over the illuminated (V_1) and observed (V_2) scattering volumes:

$$I_{2}(\omega, r_{c}) = \int_{V_{2}} dV_{2} \int_{V_{1}} dV_{1} S(q_{1}, r_{c}) S(q_{2}, r_{c}) f(q_{1}, q_{2}) e^{-h_{1}t} L(q_{1}, q_{2}, \omega, r_{c}),$$
(5.10)

where $S(q_i, r_c) = r_c^2/(1 + r_c^2 q_i^2)$ is the static structure factor, $f(\mathbf{q}_1, \mathbf{q}_2)$ is a factor which characterizes the polarization of the incident and scattered light and is related to the dipole-scattering matrix, and h_1 is the extinction coefficient for single scattering in the Ornstein-Zernike approximation. The integration in (5.10) has been carried out for rectangular and cylindrical geometries of the scattering volume. One of the main results of the numerical calculation of $I_2(\omega, r_c)$ for nitrobenzene-*n*-hexane mixtures⁴² is that the spectrum of the polarized double scattering can be approximated to within 5% in a wide temperature interval $10^{-5} \leq \tau$ $\leq 10^{-2}$ by the formula

$$I_{s}(\omega, r_{c}) = I_{s}(r_{c}) L(\omega/\Gamma_{0}(r_{c})); \qquad (5.11)$$

here $I_2(r_c)$ is the integrated intensity and the function $L[\omega/\Gamma_0(r_c)]$ represents the sum of the two Lorentzians with respective half-widths of $(7/3)\Gamma_0$ and $(2/3)\Gamma_0$, indicating that the spectrum is non-Lorentzian.

Yet another confirmation of the non-Lorentzian character of the double-scattering spectrum was obtained by Ferrel and Bhattacharjee.⁴⁴ For the cylindrical geometry studied in Ref. 28, those authors, without using factorization of the four-point space-time correlation function G_4 , but assuming that the total double scattering at the critical point is small, showed that

$$\ln I(t) = \ln I_0 - (1 + \varepsilon C_1)\Gamma_{c_1}t + \varepsilon C_2 F(\Gamma_{c_1}t)(\Gamma_{c_1}t)^2;$$

here $\ln I_0 = \ln I_1 + I_2/I_1$ (I_2 is evaluated in Ref. 28), $\varepsilon = 4\pi r_0 B$, where r_0 is the radius of the cylinder and $B = \sigma_0 (k_0 r_c)^{-2}$, and the C_n are related to $(\Delta \Gamma/\Gamma_{c1})^n$, where $\Delta \Gamma = \Gamma_{c2} - \Gamma_{c2}$. Thus, the double-scattering effects were manifested in a change of the slope (the second term) and curvature (the third term) of the function $\ln I(t)$. The magnitude of these changes is determined by the specific values of ε , C_1 , C_2 , and F. At the critical point itself, for the case of incident light polarized along the height of the cylinder, we have $C_1 = C_1^1 = -0.07\gamma^{*-1}(\ln\gamma^* - 2.2)$ and $C_2 = C_2^1 = 1.12\gamma^{*-1}$ $\times (\ln\gamma^* + 0.13)$, where $\gamma^* = 2r_0/L_0$ and L_0 is the height of the cylinder. The function $F(\Gamma_{c1}t)$ differs only slightly from unity: $|F - 1| \le 0.25$. The technique proposed in Ref. 44 for taking into account the correction for double scattering in the critical-opalescence spectrum was recently used in Ref. 94.

c) Experimental studies of the multiple-scattering spectra

Let us first mention the studies of Velochine and Bergé¹²⁶ and Theil et al.,¹²⁷ who investigated the influence of multiple scattering on the critical-opalescence spectrum but failed to detect any. One of the reasons for this is that they had taken measures precisely to avoid an appreciable contribution from multiple scattering. In Ref. 127 these measures were to limit the approach to the critical temperature, thereby reducing the scattering power of the material (to be sure, at the expense of information needed for more exact determination of a_0 , ν , and η), and to decrease the path length of the beam in the medium and the aperture diameter of the detector. The role of the last factor was studied experimentally in Ref. 45. Measurements in CO₂ at $\Delta T = 2 \cdot 10^{-3}$ K showed that increasing the diameter of the receiving aperture from 0.2 to 1 mm caused the multiple-scattering percentage of the total scattered intensity to increase from 20% to 62%. Another, qualitative result of Ref. 45, which confirms the calculation of Ref. 41, is that the width of the central component of the multiple-scattering spectrum in CO₂ turns out to be less sensitive than $\Gamma_{c1}(\theta)$ to the scattering angle.

Studies devoted to investigating the role of multiple scattering in experimental studies of the dynamics of fluctuations near the critical point were undertaken by Beysens and Zalczer⁴² and Sorensen *et al.*⁴³⁴

The method of light-beating spectroscopy was used⁴² to study the critical behavior of a nitrobenzene-n-hexane mixture in a rectangular scattering volume (2R, L, z) with 2R = L = 2 cm and z = 0.125 cm $\ll R, L$. The results of the experiment were compared with the theoretical calculations for the following values of the parameters which appear in the integrand in (5, 10): $\lambda = 632.8 \text{ nm}, a_0 = 0.23 \text{ nm}, \nu = 0.63, \gamma = 1.22,$ $T_{\rm c} = 293.06 \text{ K}, \ \bar{\eta}^* = 0.67 \text{ sec} \cdot \text{Pa}, \text{ and } (\partial n^2 / \partial c) (\partial c / \partial \mu)_0$ = $2.36 \cdot 10^{-3}$ cm³/J; this last quantity is related to the amplitude of the susceptibility of the mixture. The main results of Ref. 42 are: 1) the Rayleigh component has a non-Lorentzian line shape, in accordance with (5.11); 2) the experimental data are in good agreement with the calculated results for the intensity I_2 of the double scattering down to $\tau \ge 10^{-4}$ and for the effective width Γ_0 of the double scattering throughout the entire temperature interval (Fig. 16). An unexpected finding is that the temperature dependence $\Gamma_{o}(\tau)$ is stronger than $\Gamma_{c1}(\tau)$ and that the value of Γ_{0} is lower than that of Γ_{e1} in the region $\tau < 10^{-4}$. There is no reasonable theoretical explanation for these facts. An attractive feature of the double-scattering spectra obtained for dif-





ferent τ is that they can be reduced to a common form with the aid of a single formula (5.11).

The results of Ref. 43a made it possible to explain the difficulty of experimentally detecting the influence of multiple scattering on the width Γ_c . It was shown in that paper that in the region $k_0 r_0 \gg 1$ the ratio of the decay times $t_2/t_1 = \Gamma_{c1}/\Gamma_{c2}$ of the correlation of the scattered fields for double and single scattering grows on approach to the critical point and tends toward a value close to unity. Figure 17 shows the ratios t_2/t_1 depend on $k_0 r_0$ for $\theta = 90^\circ$ in a methanol-cyclohexane mixture. The time t_2 was found from analysis of the time dependence of the correlation functions $\langle E_2^*(t)E_2(0)\rangle$ of the polarized and depolarized fields. With the aid of a cumulant analysis of the spectra, Koppel¹²⁸ established that the double-scattering spectra are almost exponential in the t representation (Lorentzian in the ω representation). The deviation from exponentiality is characterized by the small ratio of the first two cumulants $K_2/K_1^2 \approx 0.07$. The solid curves in Fig. 17 represent the ratios t_2/t_1 calculated with only the first cumulant taken into account. The dashed curve corresponds to the estimate of t_2 as the time by which the correlation function $\langle E_2^*(t)E_2(0)\rangle$ has decreased by a factor of e from its value at t=0. The growth of the ratio t_2/t_1 is particularly pronounced for the substantially more intense polarized component of the double scattering. The double scattering displays a greater broadening for smaller values of $k_0 r_e$. For $k_0 r_e \ge 9$ the growth of the ratio Γ_{c1}/Γ_{c2} is comparatively small and does not exceed 4% at $\theta = \pi/2$ and 40% at $\theta = \pi/6$. It is believed that this indicates that for $k_0 r_c \gg 1$ the width Γ_c in multiple scattering will be not much larger than Γ_{c2} (concrete estimates were not given in Ref. 43a).

Sorensen *et al.*^{43a} also studied the width of the depolarized component, which consists predominantly of double and multiple scattering for $k_0 r_c \ge 1$ (Fig. 18). The conversion to the scaling width $\Gamma_{c2}^* = 6\pi \tilde{\eta} \,{}^b \Gamma_{c2} /$



FIG. 17. Dependence upon $k_0 r_c$ of the ratio of the correlation decay times for doubly and singly scattered fields in the case of a methanol-cyclohexane mixture.^{43a}



FIG. 18. Dependence upon $k_0 r_c$ of the "scaling" width Γ_{2c}^* of the central line of the depolarized double scattering.^{43a}

 $k_{\rm B}Tk_0^3$ for double scattering is analogous to the introduction of Γ_{c1}^* for the single-scattering spectrum, the only difference being that one takes for the shear viscosity $\bar{\eta}$ the background value $\bar{\eta}^{b}$ (in accordance with the dynamic droplet model used in that paper). The experimental data on the width of the depolarized scattering for $k_0 r_c \gtrsim 1$ lies somewhat above the solid curve, which corresponds to the theoretical estimates of the same authors.^{43b} The deviation, which is due to multiple scattering effects, does not exceed 20%. Interestingly, for the smaller scattering angle $\theta = 30^{\circ}$ at which measurements of Γ_{c21}^* were made in Ref. 43a, the contribution from multiple scattering is lower. This result agrees with the conclusions of Refs. 29c and 41b concerning the angular dependence of the multiplescattering effects.

The experimental measurements^{43a} of the width Γ_c^* of all the scattered light (not just the depolarized component) are in good agreement with the values of Γ^* calculated in the dynamic droplet model in the single-scattering approximation for the following values of the variable parameters: $\nu = 0.652$ (this value of ν is higher than the most reliable value⁵³ $\nu = 0.63$), $a_0 = 0.241$ nm, and $\tilde{\gamma} = 1.037$. The problem of determining the doublescattering and multiple-scattering contributions to the width $\Gamma_{\alpha}^{*}(qr_{\alpha})$ is complicated by the difficulty of allowing for effects due to the nonexponential character of the spectrum in the close proximity of the critical point $(T - T_c < 0.008 \,^{\circ}\text{C}$ for the investigated methanol-cyclohexane mixture). The result $\Gamma_{c2} < \Gamma_{c1}$ for $k_0 r_c < 1$ obtained in Ref. 42 was not confirmed by the studies of Ref. 43a.

In the hydrodynamic region $(k_0 r_c < 1)$, as can be seen from Fig. 17, the ratio t_2/t_1 is given as ≈ 0.6 by the cumulant estimates and as ≈ 0.7 by estimates based on a strictly exponential spectrum. For comparison we note that in accordance with (5.8) the ratio Γ_{cl}/Γ_{c2} is ≈ 0.7 at $\theta = 90^{\circ}$ and decreases with decreasing θ , in qualitative agreement with experiment. ^{43a} The deviation of the ratio $t_2/t_1 = \Gamma_{cl}/\Gamma_{c2}$ from unity would seem to give reason to expect a large influence of double and multiple scattering on the critical-opalescence spectrum in the hydrodynamic region, but the absolute integrated intensity of higher-multiple scattering in this region is small.

So, despite the appreciable and growing contribution to the integrated intensity of the scattered light from higher-multiple scattering on approach to the critical point, the first exponential studies have shown that these effects play a relatively minor role in the measurement of Γ_c . At the same time, however, multiple scattering effects are the cause of the non-Lorentzian character of the spectral lines that is observed in experiment. These fundamental conclusions require new verification. Most importantly, a study is needed of the possible influence of multiple scattering on the value of the dynamic critical exponent \tilde{z} . If these effects do turn out to be important, one would expect a decrease in \tilde{z} as the critical point is approached $(\tilde{z}_{11m} \rightarrow 0)$, since the wave-vector dependence of all the characteristics of the scattered light becomes progressively less pronounced with increasing scattering order.

CONCLUSION

The phenomenon of critical opalescence, which has been known for over 100 years, is more and more widely used to study the anomalies of physical properties close to the critical point. This trend is promoted by the discovery of the basic behavior of highermultiple scattering, by reliable calculations of double scattering with allowance for the actual experimental conditions, and by the study of the effect of multiple scattering on the critical exponents. What we have just said is even more true of the integrated intensity and the depolarization of the scattered light. To clarify completely the role of double and multiple scattering in the critical-opalescence spectrum additional precision experiments and the corresponding calculations will be required. The most important such study will be to investigate the change due to multiple-scattering effects in the width $\Gamma_{\!_{\rm C}}$ of the central component and, hence, in the dynamic critical exponent \bar{z} . The growth of the multiple-scattering contribution in critical opalescence should evidently lead to a decrease in the effective value of \tilde{z} , since the dependence of Γ_c on q should become less pronounced (Lambertian) as the multiplicity of the scattering increases.

Finally, there is the fundamental question of how close to the critical point can one regard the single scattering contribution as primary, adequately describing the experimental data, and the double and multiple scattering as corrections. The analysis (see Sect. 4) of the convergence of the iterative series in the scattering orders for the extinction coefficient in the "ladder" approximation shows that this traditional situation breaks down at $qr_c \gtrsim 1$ and for the parameter value s = 0.1. For smaller values of s, which are attained, for example, by decreasing the linear dimension L_0 of the scattering volume or by decreasing the factor $(\partial \varepsilon / \partial \rho)_T^2$ (which in the case of a mixture is related to the difference between the refractive indices of the components), this conclusion remains valid, but only for large values of qr_c (which, in a number of cases, are not yet experimentally accessible). Because the original Born (Rayleigh) concept of scattering order loses meaning, in describing critical opalescence one must systematically apply the technique of resumming the initial series for the fields and intensity of the scattered light and also use functional methods of solving the electrodynamic problem when the

order-parameter fluctuations have non-Gaussian statistics.

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- ¹G. V. Rozenberg, Usp. Fiz. Nauk: a) **69**, 57 (1959); b) **91**, 569 (1967) [Sov. Phys. Usp.: a) **2**, 666 (1959); b) **10**, 188 (1967)].
- ²V. I. Tatarskii, Rasprostranenie voln v turbulentnoi atmosfere, Nauka, Moscow (1967) [Wave Propagation in a Turbulent Medium, McGraw-Hill, New York, 1961; reprinted Dover, New York (1968)].
- ³Yu. N. Barabanenkov, Usp. Fiz. Nauk 117, 49 (1975) [Sov. Phys. Usp. 18, 673 (1975)].
- ⁴S. M. Rytov, Yu. A. Kravtsov, and V. I. Tatarskii, Vvedenie v Statisticheskuyu Radiofiziku [Introduction to Statistical Radiophysics], Part II, Nauka, Moscow (1978).
- ⁵A. Z. Patashinskii, and V. L. Pokrovskii, Fluktuatsionnaya teoriya fazovykh perekhodov, Nauka, Moscow (1975) [Fluctuation Theory of Phase Transitions, Pergamon Press, Oxford (1979)].
- ⁶K. G. Wilson and J. Kogut, "The renormalization group and ε expansion," Phys. Rep. C 12, 75 (1974).
- ⁷M. Smoluchowski, Ann. Phys. (Leipzig) 25, 205 (1908).
- ⁸A. Einstein, Ann. Phys. (Leipzig) 33, 1275 (1910).
- ⁹L. Ornstein and F. Zernike, Proc. Acad. Sci. (Amsterdam):
- a) 17, 793 (1914); b) 18, 1520 (1916); c) 19, 1321 (1917).
- ¹⁰I. L. Fabelinskii, Molekuyarnoe rasseyaniye sveta, Nauka, Moscow (1965) [Molecular Scattering of Light, Plenum Press, New York (1968)].
- ¹¹V. L. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. 20, 1064 (1950).
- ¹²A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959) [Sov. Phys. JETP **9**, 571 (1959)].
- ¹³V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) 2, 2031 (1960) [Sov. Phys. Solid State 2, 1824 (1961)].
- ¹⁴A. Z. Patashinskii and V. L. Pokrovskii, Usp. Fiz. Nauk 121, 55 (1977) [Sov. Phys. Usp. 20, 31 (1977)].
- ¹⁵P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977)].
- ¹⁶H. L. Swinney, in: Photon Correlation and Light Beating Spectroscopy (H. Z. Cummins and E. R. Pike, eds.), Plenum Press, New York (1974), p. 331. [Russ. Transl. Mir. Moscow, 1978].
- ¹⁷L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred, Fizmatgiz, Moscow (1957) [Electrodynamics of Continuous Media, Pergamon Press, Oxford (1960)].
- ¹⁸R. G. Newton, Scattering Theory of Waves and Particles, McGraw-Hill, New York (1966) [Russ. Transl. Mir. Moscow, 1969].
- ¹⁹A. V. Chalyi, Ukr. Fiz. Zh. 13, 1159 (1968).
- ²⁰A. V. Chalyi, Fiz. Zhidk. Sostoyaniya, No. 8, 3 (1980).
- ²¹D. W. Oxtoby and W. W. Gelbart, J. Chem. Phys. 60, 3359 (1974).
- ²²E. L. Lakoza and A. V. Chalyi, Zh. Eksp. Teor. Fiz. 67, 1050 (1974) [Sov. Phys. JETP 40, 521 (1974)].
- ²³D. W. Oxtoby and W. M. Gelbart, Phys. Rev. A 10, 738 (1974).
- ²⁴V. L. Kuz'min, Opt. Spektrosk. : a) 38, 745 (1975); b) 39, 546 (1975) [Opt. Spectrosc. (USSR): a) 38, 423 (1975); b) 39, 306 (1975)].
- ²⁵H. M. J. Boots, D. Bedeaux, and P. Mazur, a) Physica Ser. A 79, 397 (1975); b) Chem. Phys. Lett. 34, 197 (1975).
- ²⁶L. V. Adzhemyan *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. 22, 11 (1975) [JETP Lett. 22, 5 (1975)].
- ²⁷L. A. Reith and H. L. Swinney, Phys. Rev. A 12, 1094

(1975).

- ²⁸A. J. Bray and R. F. Chang, Phys. Rev. A 12, 2594 (1975).
 ²⁹L. V. Adzhemyan *et al.*, a) Opt. Spektrosk. 46, 976 (1979)
- [Opt. Spectrosc. (USSR) 46, 545 (1979)]; b) Zh. Eksp. Teor.
 Fiz. 78, 1051 (1980) [Sov. Phys. JETP 51, 530 (1980)];
 c) Zh. Eksp. Teor. Fiz. 80, 551 (1981) [Sov. Phys. JETP 53, 278 (1981)].
- ³⁰V. L. Kuz'min, Opt. Spektrosk. : a) 40, 552 (1976); b) 44,
- 529 (1978) [Opt. Spectrosc. (USSR): a) 40, 313 (1976); b) 44, 307 (1978)].
- ³¹H. M. J. Boots, D. Bedeaux, and P. Mazur, Physica Ser. A **84**, 217 (1976).
- ³²H. M. J. Boots, Physica Ser. A 87, 185 (1977).
- ³³E. L. Lakoza and A. V. Chalyi, Zh. Eksp. Teor. Fiz. **79**, 1200 (1980) [Sov. Phys. JETP **52**, 607 (1980)].
- ³⁴D. Beysens, A. Bourgou, and H. Charlin, Phys. Lett. A 53, 236 (1975).
- ³⁵N. J. Trappeniers, A. C. Michels, and R. H. Huijser, Chem. Phys. Lett. : a) 34, 192 (1975); b) 48, 31 (1977).
- ³⁶N. J. Trappeniers, *et al.*, Chem. Phys. Lett. **62**, 203 (1979).
- ³⁷Y. Garrabos, R. Tufeu, and B. Le Neindre, a) C. R. Acad. Sci. Ser. B 282, 313 (1976); b) J. Chem. Phys. 68, 495 (1978).
- ³⁸A. D. Alekhin and V. I. Burak, Opt. Spektrosk. **49**, 749 (1980) [Opt. Spectrosc. (USSR) **49**, 410 (1980)].
- ³⁹A. D. Alekhin, Pis'ma Zh. Eksp. Teor. Fiz. 34, 108 (1981) [JETP Lett. 34, 102 (1981)].
- ⁴⁰V. L. Kuz'min, First All-Union Symposium on Acousto-Optical Spectroscopy [in Russian], Fan, Tashkent (1976), p. 216.
- ⁴¹E. L. Lakoza and A. V. Chalyi, a) First all-Union Symposium on Acousto-Optical Spectroscopy [in Russian], Fan, Tashkent (1976), p. 223; b) Zh. Eksp. Teor. Fiz. 72, 875 (1977) [Sov. Phys. JETP 45, 457 (1977)].
- ⁴²D. Beysens and G. Zalczer, Phys. Rev. A 15, 765 (1977).
- ⁴³C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, a) Phys. Rev. A 16, 365 (1977); b) Opt. Commun. 20, 140 (1977).
- ⁴⁴R. A. Ferrel and J. K. Bhattacharjee, Phys. Rev. A 19, 348 (1979).
- ⁴⁵D. M. Kim, J. P. Schroeter, and R. Kobayashi, in: Nelineinaya Optika: Trudy VI Vavilovskoi Konferentsii [Nonlinear Optics: Proceedings of Sixth Vavilov Conference], Novosibirsk (1979), p. 28.
- ⁴⁶E. L. Lakoza and A. V. Chalyi, Zh. Eksp. Teor. Fiz. 82, 441 (1982) [Sov. Phys. JETP 55, 252 (1982)].
- ⁴⁷B. Crosignani, P. Di Porto, and M. Bertolotti, Statistical Properties of Scattered Light, Academic Press, New York (1975).
- ⁴⁸N. A. Nemov, Opt. Spektrosk. 45, 617 (1978) [Opt. Spectrosc. (USSR) 45, 349 (1978)].
- ⁴⁹A. M. Polyakov, Pis'ma Zh. Eksp. Teor. Fiz. 12, 538 (1970) [JETP Lett. 12, 381 (1970)].
- ⁵⁰V. L. Pokrovskii, Pis'ma Zh. Eksp. Teor. Fiz. 17, 219 (1973) [JETP Lett. 17, 156 (1973)].
- ⁵¹J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1675 (1961).
- ⁵²F. M. Kuni, Dokl. Akad. Nauk SSSR 179, 120 (1968).
- ⁵³M. A. Anisimov, Usp. Fiz. Nauk 114, 249 (1974) [Sov. Phys. Usp. 17, 722 (1975)].
- ⁵⁴E. L. Lakoza, V. M. Sysoev, and A. V. Chalyi, Zh. Eksp.
- Teor. Fiz. 65, 605 (1973) [Sov. Phys. JETP 38, 298 (1974)]. ⁵⁵N. L. Tsyganov and A. V. Chalyi, Zh. Eksp. Teor. Fiz. 61,
- 1605 (1971) [Sov. Phys. JETP 34, 856 (1972)].
- ⁵⁶V. P. Skripov and Yu. D. Kolpakov, in: Sovremennye Problemy Fizicheskoi Khimii [Current Problems in Physical Chemistry], Vol. 5, Moscow University Press, Moscow (1970), p. 295.
- ⁵⁷A. D. Alekhin *et al.*, in; Sovremennye Problemy Fizicheskol Khimii [Current Problems in Physical Chemistry], Vol. 5, Moscow University Press, Moscow (1970), p. 372.

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- 1

- ⁵⁸A. Z. Golik *et al.*, in: Teplofizicheskie svoistva zhidkostei [Thermophysical Properties of Fluids], Nauka, Moscow (1976), p. 17.
- ⁵⁹A. V. Chalyi and A. D. Alekhin, Zh. Eksp. Teor. Fiz. 59, 337 (1970) [Sov. Phys. JETP 32, 181 (1971)].
- ⁶⁰A. D. Alekhin, N. P. Krupskii, and A. V. Chalyi, Zh. Eksp.
- Teor. Fiz. 63, 1417 (1972) [Sov. Phys. JETP 36, 751 (1973)].
- ⁶¹D. Yu. Ivanov and L. A. Makarevich, Dokl. Akad. Nauk SSSR 220, 1103 (1975).
- ⁶²D. Yu. Ivanov and V. K. Fedyanin, Preprint OIYaI R4-8429, Joint Institute of Nuclear Research, Dubna (1974).
- ⁶³B. N. Miller and O. Splittorff, a) J. Opt. Soc. Am. 62, 1291 (1972); b) Phys. Rev. A 9, 550 (1974).
- ⁶⁴E. L. Lakoza and A. V. Chalyi, Opt. Spektrosk. 37, 144 (1974) [Opt. Spectrosc. (USSR) 37, 79 (1974)].
- ⁶⁵H. K. Leung and B. N. Miller, Phys. Rev. A 12, 2162 (1975).
- ⁶⁶F. J. Wegner, Phys. Rev. A 5, 4529 (1972).
- ⁶⁷A. T. Berestov, Zh. Eksp. Teor. Fiz. 72, 348 (1977) [Sov. Phys. JETP 45, 184 (1977)].
- 68A. V. Chalyi, Fiz. Zhidk. Sostoyaniya, No. 10, 16 (1982).
- ⁶⁹M. A. Anisimov *et al.*, Zh. Eksp. Teor. Fiz. 76, 1661 (1979) [Sov. Phys. JETP 49, 844 (1979)].
- ⁷⁰E. T. Shimanskaya *et al.*, Zh. Eksp. Teor. Fiz. 80, 274 (1981) [Sov. Phys. JETP 53, 139 (1981)].
- ⁷¹M. A. Anisimov, E. E. Gordetskii, and V. M. Zaprudskii, Usp. Fiz. Nauk 133, 103 (1981) [Sov. Phys. Usp. 24, 57 (1981)].
- ⁷²A. M. Polyakov, Zh. Eksp. Teor. Fiz. 57, 271 (1969) [Sov. Phys. JETP 30, 151 (1970)].
- ⁷³N. P. Malomuzh, V. P. Oleřnik, and I. Z. Fisher, Zh. Eksp. Teor. Fiz. **63**, 2336 (1972) [Sov. Phys. JETP **36**, 1233 (1973)].
- ⁷⁴A. K. Atakhodzhaev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. 17, 95 (1973) [JETP Lett. 17, 65 (1973)].
- ⁷⁵V. S. Vikhrenko, Usp. Fiz. Nauk 113, 627 (1974) [Sov. Phys. Usp. 17, 558 (1975)].
- ⁷⁶W. M. Gelbart, Adv. Chem. Phys. 26, 1 (1974).
- ¹⁷A. F. Andreev, Pis'ma Zh. Eksp. Teor. Fiz. 19, 713 (1974) [JETP Lett. 19, 368 (1974)].
- ⁷⁸D. K. Beridze, in: Sovremennye Problemy Fizicheskoi Khimii [Current Problems in Physical Chemistry], Vol. 5, Moscow University Press, Moscow (1970), p. 323.
- ⁷⁹Yu. D. Dolpakov and V. P. Skripov, Opt. Spektrosk.: a) 24, 249 (1968); b) 29, 761 (1970) [Opt. Spectrosc. (USSR): a) 24, 128 (1968); b) 29, 405 (1970)].
- ⁸⁰A. D. Alekhin, Zh. Eksp. Teor. Fiz. 72, 1880 (1977) [Sov. Phys. JETP 45, 987 (1977)].
- ⁸¹A. Triki, B. Oksengorn, and B. Vodar, C. R. Acad. Sci. Ser. B 277, 411 (1973).
- ⁸²V. G. Puglielli and N. C. Ford, Jr., Phys. Rev. Lett. 25, 143 (1970).
- ⁸³M. J. Lavan, Opt. Commun. 26, 357 (1978).
- ⁸⁴S. Larsen, R. Mountain, and J. Zwanzig, J. Chem. Phys. 42, 2187 (1965).
- ⁸⁵A. Hocken and G. Stell, Phys. Rev. A 8, 887 (1973).
- ³⁶K. B. Tolpygo and A. V. Chalyi, Ukr. Fiz. Zh. 13, 1261 (1968).
- ⁸⁷M. F. Vuks, Rasseyanie Sveta v Gazakh, Zhidkostyakh i Rastvorakh [light Scattering in Gases, Liquids, and Solutions], Leningrad Univ. Press, Leningrad (1977).
- ⁸⁸S. Kelich, Molekulyarnaya nelineinaya optika [Molecular Nonlinear Optics], Nauka, Moscow (1981).
- ⁸⁹S. A. Akhmanov and N. I. Koroteev, Metody Nelineinoi Optiki v Spektroskopii Rasseyaniya Sveta [Methods of Nonlinear Optics in Light-Scattering Spectroscopy], Nauka, Moscow (1981).
- ³⁰H. E. Stanley, Introduction to Phase Transition and Critical Phenomena, Clarendon Press, Oxford (1971) [Russ. Transl. Mir. Moscow, 1973].
- ⁹¹S.-K. Ma, Modern Theory of Critical Phenomena, Benjamin-

Cummings, Reading, Mass. (1976) [Russ. Transl., Mir, Moscow, 1980].

- ⁹²H. L. Swinney and D. L. Henry, Phys. Rev. A 8, 2586 (1973).
- ⁹³V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyanin, Phys. Rep. 57, 152 (1980) [Russ. Transl., Usp. Fiz. Nauk 130, 615 (1980)].
- ⁹⁴ H. C. Burstyn and J. V. Sengers, Phys. Rev. A 25, 448 (1982).
- ⁹⁵I. L. Fabelinskii and I. D. Chistyi, Usp. Fiz. Nauk 119, 487 (1976) [Sov. Phys. Usp. 19, 597 (1976)].
- ⁹⁶K. Kawasaki, a) Phys. Rev. 150, 291 (1966); b) Ann. Phys. (N.Y.) 61, 1 (1970).
- 97 L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).
- ⁹⁸R. A. Ferrel, Phys. Rev. Lett. 24, 1169 (1970).
- ⁹⁹R. Perl and R. A. Ferrel, a) Phys. Rev. Lett. 29, 51 (1972); b) Phys. Rev. A 6, 2358 (1972).
- ¹⁰⁰K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29, 48 (1972).
- ¹⁰¹S. M. Lo and K. Kawasaki, Phys. Rev. A 8, 2176 (1973).
- ¹⁰²K. Kawasaki and J. Gunton, Phys. Rev. B 13, 4658 (1976).
- ¹⁰³D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. **61**, 2957 (1974).
- ¹⁰⁴J. K. Bhattacharjee et al., Phys. Rev. A 24, 1469 (1981).
- ¹⁰⁵B. J. Ackerson et al., Phys. Rev. Lett. 22, 1371 (1975).
- ¹⁰⁶C. M. Sorensen et al., Phys. Rev. A 13, 1539 (1976).
- ¹⁰⁷M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).
- ¹⁰⁸J. P. Schroeter, D. M. Kim, and R. Kobayashi, Phys. Rev. A 19, 2402 (1979).
- ¹⁰⁹H. C. Burstyn, I. V. Sengers, and P. Esfandiari, Phys. Rev. A 22, 282 (1980).
- ¹¹⁰E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B 13, 2110 (1976).
- ¹¹¹L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred, Gostekhizdat, Moscow (1953) [Fluid Mechanics, Pergamon Press, Oxford (1959)].
- ¹¹²R. F. Chang, H. C. Burstyn, and J. V. Sengers, Phys. Rev. A **19**, 866 (1979).
- ¹¹³V. N. Zozulya and Yu. P. Blagoi, Zh. Eksp. Teor. Fiz. 66, 212 (1974) [Sov. Phys. JETP 39, 99 (1974)].
- ¹¹⁴S. L. Ryvkin, A. Ya. Levin, and L. V. Izrailevskii, in: Teplofizicheskie Svoistva Veshchestv i Materialov [Thermophysical Properties of Matter and Materials], Izd. Standartov, Moscow (1976), Issue No. 10, p. 232.
- ¹¹⁵D. M. Kim, K. L. Henry, and R. Kobayashi, Phys. Rev. A 10, 1974 (1974).
- ¹¹⁶H. K. Leung and B. N. Miller, Phys. Rev. A 16, 406 (1977).
- ¹¹⁷G. F. Efremov, Zh. Eksp. Teor. Fiz. **55**, 2322 (1968) [Sov. Phys. JETP 28, 1232 (1969)].
- ¹¹⁸R. L. Stratonovich, Zh. Eksp. Teor. Fiz. 58, 1612 (1970) [Sov. Phys. JETP 31, 864 (1970)].
- ¹¹⁹I. M. Tkachenko and I. Z. Fisher, Zh. Eksp. Teor. Fiz.
- 69, 1092 (1975) [Sov. Phys. JETP 42, 556 (1975)].
- ¹²⁰I. M. Tkachenko, Fiz. Zhidk. Sostoyaniya, No. 5, 16 (1977).
- ¹²¹V. M. Sysoev and A. V. Chalyi, Teor. Mat. Fiz. : a) 18, 410 (1974); b) 26, 126 (1976).
- ¹²²V. V. Vladimirskii, Zh. Eksp. Teor. Fiz. 9, 1226 (1939).
- ¹²³V. U. Felderhof, J. Chem. Phys. 44, 602 (1966).
- ¹²⁴D. N. Zubarev and S. V. Tischenko, Physica (Utrecht) 59, 285 (1972).
- ¹²⁵C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A 14, 1520 (1976).
- ¹²⁶B. Volochine and P. Berge, J. Phys. (Paris) **31**, 819 (1970).
- ¹²⁷D. Theil et al., J. Chem. Phys. 62, 3689 (1975).
- ¹²⁸D. E. Koppel, J. Chem. Phys. 57, 4814 (1972).

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