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APPLICATION OF THE SCALING METHOD TO THE STUDY OF LIGHT SCATTERING WITH ALLOWANCE FOR THE GRAVITATIONAL EFFECT, AND THE DETERMINATION OF THE CRITICAL INDICES FROM LIGHT-SCATTERING DATA

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An experimental and theoretical investigation of light scattering near the critical point of a pure material with allowance for the gravitational effect has been carried out. An analysis of experimental data on critical opalescence in n-pentane has been used to show that the critical indices of isothermal compressibility are $\gamma^{\pm} = 1.2 \pm 0.1$. A method is put forward for the determination of the index δ of the critical isothermal, whose value has been found to be 4.9 ± 0.3. The scaling method is used to determine the density of the material and the scattered-light intensity in the immediate neighborhood of the critical point as functions of height.

IN the near-critical state of single-component systems, which is characterized by an unbounded increase in the isothermal compressibility as one approaches the liquid-vapor critical point, gravitational forces lead to a substantial spatial inhomogeneity of microscopic properties (fluctuations in various parameters, the corresponding correlation radii, and so on) as well as macroscopic parameters (density, scattered ability, and so on) of the medium. The most rapid variation in the distribution of these properties occurs in the thin layer which coincides with the level of the meniscus in the subcritical region, where the approach to the critical state is possible both in temperature and in density.

The gravitational field was investigated in [2-5] within the framework of the classical theory.[1] The results reported in these papers have been used to analyze the scattering of light by density fluctuations near the critical point of a pure material in the Rayleigh–Einstein approximation.[5-7] The density variation and the variation of the scattered-light intensity near the critical point predicted by the theory have been qualitatively confirmed by an experimental study of the gravitational effect and light scattering performed at the Kiev University.[4,5,7-9] We note that the use of the gravitational effect in measurements of the distribution of scattered intensity with height should enable us to approach the critical point in pressure much more closely than by other methods (in fact, closer by two orders of magnitude).

It must be noted, however, that a consistent analysis of critical opalescence with allowance for the gravitational effect in the immediate neighborhood of the critical point cannot be based on the classical theory of critical phenomena, which does not agree with model calculations and the experimental results obtained near the critical point.[10-16]

Moreover, owing to the recent development of scaling methods,[15-18] it has become possible to deduce correct predictions for the thermodynamic properties of matter at the critical point and in its immediate neighborhood.

These methods are used in the present paper in a theoretical and experimental study of the gravitational effect and the scattering of light in the immediate neighborhood of the critical point of a pure material.

DENSITY DISTRIBUTION IN THE IMMEDIATE NEIGHBORHOOD OF THE CRITICAL POINT

We shall use the theory of scaling transformations to find the variation of density (volume) with height under the influence of the gravitational field. If we proceed by analogy with the classical theory to calculate the gravitational effect we obtain the following equation for the variation of volume with height and temperature:

$$v^\delta + \delta \frac{a}{b} t^\gamma v = \frac{\delta}{h} h. \quad (1)$$

This expression is obtained by integrating the equation for the hydrostatic pressure dp = −dh in terms of the dimensionless variables defined in [3]:

$$p = \frac{P - P_c}{P_c}, \quad v = \frac{V - V_c}{V_c}, \quad t = \frac{T - T_c}{T_c}, \quad h = \frac{\rho_c g H}{P_c}$$

where P_c, V_c, T_c, and ρ_c are, respectively, the critical pressure, volume, temperature, and density in the system, and H is the height measured from the level with maximum density gradient. It is assumed in the derivation that

$$-(\partial p / \partial v)_T = a t^\gamma + b v^{\delta - 1}, \quad (2)$$

which is the analog of the expression for $(\partial p/\partial v)$ in the classical theory.[1] This means that the coefficients a and b do not change during the transition from the single-phase region (t > 0) to the two-phase region (t < 0). The indices γ and δ are the critical indices in the temperature dependence of the isothermal compressibility ($\beta_T \sim t \exp -\gamma$ for v = 0) and are used to describe the shape of the critical isothermal ($p \sim v \exp \delta$) for t = 0.

If we solve Eq. (1) by the method of successive approximations we obtain the following expressions:

a) when $t \approx 0$

$$v(h, t) = \left(\frac{\delta}{b}|h|\right)^{1/\delta} \operatorname{sign} h - \frac{a}{b}|t|^\gamma \operatorname{sign} t \Big/ \left(\frac{\delta}{b}|h|\right)^{(\delta-2)/\delta} \operatorname{sign} h, \quad (3)$$

b) when $h \approx 0$

$$v(h, t) = \frac{|h|}{a|t|^\gamma} \operatorname{sign} h \quad \text{for} \quad t > 0, \quad (4)$$

$$v(h, t) = \left[\left(\delta \frac{a}{b}|t|^\gamma\right)^{1/(\delta-1)} + \frac{|h|}{a(\delta - 1)|t|^\gamma}\right] \operatorname{sign} h \quad \text{for} \quad t < 0. \quad (5)$$

Analysis of Eqs. (3)–(5) shows that by studying the density distribution

$$\Delta\rho(h, t) = \frac{\rho(h, t) - \rho_c}{\rho_c} = -v(h, t)[1 + v(h, t)]^{-1}$$

in the immediate neighborhood of the critical point we can directly determine the critical index δ in the region where $|t|^\gamma/|h| \exp(\delta - 2)/\delta \ll 1$, and the critical exponents γ and $\beta = \gamma/(\delta - 1)$ (β is the index of the coexistence curve) in the region where $|h|/|t|^\gamma \ll 1$.

We note that in the classical case, when $\gamma = 1$ and $\delta = 3$, whereas $a = -(\partial^2 p/\partial t \partial v)_c$ and $b = -\tfrac{1}{2}(\partial^3 p/\partial v^3)_c$, the formulas given by Eqs. (3)–(5) become identical with the expressions obtained earlier for v(h, t) and Δ $\Delta\rho(h, t)$.[2–5]

CRITICAL OPALESCENCE WITH ALLOWANCE FOR THE GRAVITATION EFFECT

In the theory of scaling transformations the scattered-light intensity is given by

$$I = \frac{I_{RE}}{1 + (r_c k)^{2-\eta}}, \quad (6)$$

where I_{RE} is the intensity obtained in the Rayleigh–Einstein approximation, R is the correlation radius, $k = 4\pi/\lambda) \sin(\vartheta/2)$, and η is the critical index of the correlation function.

Equation (6) contains two quantities that vary in a singular fashion as we approach the critical point, namely,

1) isothermal compressibility

$$\beta_T \sim \frac{1}{a t^\gamma + b \Delta\rho^{\delta-1}}. \quad (7)$$

2) correlation radius which, when the gravitational effect is taken into account, is naturally assumed to depend not only on t but also on $\Delta\rho$, i.e.,

$$r_c \sim \begin{cases} t^{-\nu} & (\Delta\rho = 0) \\ \Delta\rho^{-\xi} & (t = 0), \end{cases} \quad (8)$$

where ν is the critical index in the temperature dependence of the correlation radius, and ξ is the critical index which must be introduced to characterize the approach of the system to the critical density along the critical isothermal.

Let us now establish the relation between the critical index ξ and the parameters of the theory of scaling transformations. The general solution of the well-known functional equation for the correlation function G(R, t, h)[17, 18] is

$$G(R, t, h) = |h|^{2(d-x)/x} g(R|h|^{1/x}, \; h/|t|^{x/y}), \quad (9)$$

where d is the dimensionality of the space, and x and y are the parameters of the theory of scaling transformations. Hence, $r_c(0, |h|) \sim |h| \exp 1/x$. On the other hand, if we use Eqs. (3) and (8), we find that $r_c(0, |h|) \sim |h| \exp -\xi/\delta$. Hence, if we use the expression $\delta = x/(d - x)$ we obtain

$$\xi = 1/(d - x). \quad (10)$$

Let us now consider the scattered intensity as we approach the critical height along the critical isothermal. From Eqs. (3), (6), (7), and (8) we have

$$I(0, |h|) \sim |h|^{[(2-\eta)\xi - \delta + 1]/\delta}, \quad (11)$$

where, in view of the above relation between δ and ξ and the parameter x, and the well-known formula $\eta = d + 2(1 - x)$, the exponent in Eq. (11) must be equal to zero.

A similar situation obtains at the h = 0 level:

$$I(t > 0, 0) \sim t^{(2-\eta)\nu - \gamma}. \quad (12)$$

Using the well-known formulas $\nu = 1/y$ and $\gamma = (2x - d)/y$, we can readily verify that the exponent in Eq. (12) is also zero.

Hence, we conclude that the scattered intensity at the critical point remains finite. In fact, the same relationships between the critical indices can be obtained from the physical hypothesis

$$0 < \lim_{\substack{t \to 0 \\ h \to 0}} I(h, t) < \infty. \quad (13)$$

Table I gives the values of $\xi = (\delta - 1)(2 - \eta)^{-1}$ and of the ratio ξ/δ, which characterizes the height dependence of the correlation radius for density fluctuations along the critical isothermal ($r_c(0, |h|) \sim |h| \exp -\xi/\delta$) for different theories of critical phenomena.

We note that, according to [19], the above relationships between the indices remain valid for scattering of arbitrary multiplicity.

Table I

Theory	Values of critical exponents	
	ξ	ξ/δ
Classical theory and Ornstein-Zernicke approximation	1	1/3
Two-dimensional Ising model	8	8/15
Three-dimensional Ising model	2.16±0.09	0.42±0.03

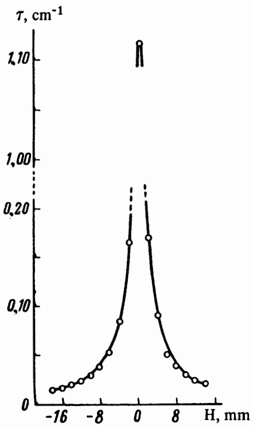


FIG. 1. Extinction coefficient τ of n-pentane as a function of height for λ = 546 nm and $t = 6 \times 10^{-5}$.

DETERMINATION OF CRITICAL INDICES BY LIGHT SCATTERING IN n-PENTANE

The apparatus described earlier in [5] 1) was used to investigate the height dependence of the scattering intensity in n-pentane at 25 different temperatures above and below the critical value (Table II summarizes some of these results). The height dependence of the scattered-light intensity is also given in [5]. The approach of the system to the critical state, i.e., the difference $T - T_c$, was measured with platinum resistance thermometers to within 0.1°. The anomalously high density gradients near the critical point complicated the visual determination of the temperature at which the meniscus disappeared. The critical temperature was therefore taken to be the temperature at which the scattering intensity in the region of the meniscus was a maximum.

Our measurements have shown that the critical temperature of n-pentane is 196.82°. The critical density of n-pentane was measured by Toepler's method and the microfloat method to within 0.5%, and was found to be $\rho_c = 0.232$ g/cm^3. The refractive index was determined at 20°C and was found to be n = 1.3575 for the yellow sodium line.

The properties of n-pentane near the critical point were analyzed by using measurements of the scattered intensity in a layer with maximum density gradient for $t > 0$ and $t < 0$ at two wavelengths, namely, $\lambda_1 = 436$ nm and $\lambda_2 = 546$ nm. To obtain the singly-scattered intensity, the experimental data were corrected for the attenuation of the incident radiation and the effect of secondary scattering. All these calculations were performed on a computer, using the formulas derived in [5]. It was found that the proportion of secondary scattering in the overall flux of scattered light at height h = 0 did not exceed 5% at λ = 546 nm throughout the temperature range which we investigated. This relatively small percentage is connected with the sharp inhomogeneity of the extinction coefficient τ as a function of the height H of the system (Fig. 1).

It is clear that the maximum extinction coefficient is reached at h = 0, but τ rapidly decreases on either side of this level. The overall error in the measured singly-scattered intensity was, on the average, 4–6%. The main contribution to this error was due to the uncertainty in the calculated intensity of secondary scattering, the uncertainty in the corrections for the attenuation of light in the system as a function of height, and the attenuation of scattered light along the path between the scattering volume and the lateral wall of the chamber, as well as the uncertainty in the photoelectric method of detection of the scattered light.

The accuracy with which the scattered intensity was measured was insufficient to enable us to determine experimentally the critical exponent η in Eq. (6) (numerical calculations based on the three-dimensional Ising model give $\eta \approx 0.06$,[17, 18]), so that we must use the Ornstein–Zernicke formula for the scattered intensity at 90°:[6]

$$I_{OR}^{-1} = I_{RE}^{-1} + 8\pi^2 f^* / k_1 \rho^2 \lambda^2, \qquad (14)$$

where $I_{RE} = k_1 \rho^2 \beta_t$ is the scattered intensity given by the Rayleigh–Einstein formula,

$$k_1 = I_0 \frac{\pi^2 V}{2\lambda^4 R^2} \left(\frac{\partial \varepsilon}{\partial \rho}\right)_T^2 k_B T,$$

and f* is a constant representing the contribution of correlation effects to the scattered intensity. We note that the use of the assumption that $\eta = 0$ will lead to an increase in the uncertainty in the subsequent determinations of the critical indices using Eq. (14) in the region where the correlation effects are important.

At the critical point itself the back-scattered intensity is known to be determined by the second term in Eq. (14), which corresponds to the intercept cut by curves 1 and 2 on the vertical axis at t = 0 (Fig. 2). The size of this intercept was determined by interpolation on a computer.

The height dependence of the intercept at t = 0 is of considerable interest. It should enable us to calculate the index ξ which determines the correlation radius r_c as a function of density in accordance with Eq. (8). However, reliable determination of this functional dependence encounters the following difficulties. It is clear from the form of the scattered-intensity isothermal which is closest to the critical temperature ($T - T_c$ = 0.03°; Table II) that the scattered intensity decreases rapidly with even small departures from the h = 0 level. This behavior of I(h) is connected with the fact that for h ≠ 0 the density is not equal to the critical value, and the compressibility falls sharply. The result is that the contribution of correlation effects to the scattered intensity is substantially reduced. For example, the contribution of the second term in Eq. (14) to the overall back-scattered intensity at h = 2 mm and $T - T_c$ = 0.03° is only 10–12%. On the other hand, for |h| < 2 mm this contribution increases and may even become predominant (it reaches 90% at h = 0 and the

1) A detailed description of the apparatus, the working chamber, the method of thermostating and temperature regulation (the temperature was kept constant to within 0.005°), the experimental method, and the method used to analyze the experimental results is given in [5].

Table II. Height Dependence of the Scattered Light Intensity in n-Pentane (λ = 546 nm) Expressed in Terms of Millimeters on the Scale of the Measuring Instrument

$t\cdot10^3$	H, mm														
	−14	−12	−10	−8	−6	−4	−2	0	2	4	6	8	10	12	14
2.61	107	128	147	164	193	230	260	280	270	245	210	166	135	109	85
2.25	105	126	150	174	212	255	310	328	322	284	235	182	140	108	84
1.81	96	116	144	180	230	302	375	430	390	326	255	180	137	106	82
1.21	86	102	132	170	244	370	480	670	500	372	253	175	126	98	78
0.87	77	90	106	145	199	334	620	910	670	360	235	151	118	88	72
0.47	63	75	93	121	163	295	650	1695	780	320	202	135	107	86	67
0.21	58	65	82	104	138	238	510	2620	590	265	175	115	92	74	62
0.06	57	63	78	98	130	216	380	3580	530	235	167	107	86	69	57
−0.06	58	66	78	95	122	183	320	2860	450	214	148	102	85	69	56
−0.19	57	65	75	97	120	167	275	1350	380	200	135	94	78	63	53
−0.49	55	63	72	86	110	146	230	640	310	173	120	90	73	60	51
−0.76	52	59	68	78	97	121	180	375	218	140	104	78	65	55	43
−1.12	47	53	62	73	87	110	133	208	155	108	83	65	54	45	38
−1.51	43	49	56	63	74	90	110	164	125	93	73	61	51	42	36
−1.94	38	40	47	51	59	72	84	110	89	72	58	48	41	36	30
−2.48	34	37	40	44	49	59	69	82	70	58	48	41	36	31	28

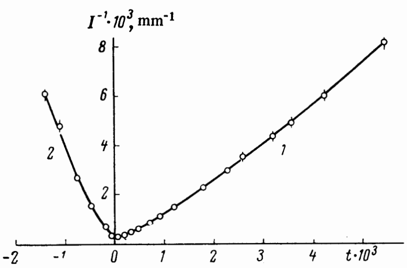
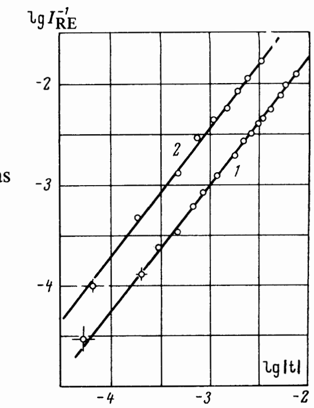


FIG. 2. Temperature dependence of the back-scattered intensity on the critical isochore for t > 0 (curve 1) and on the phase separation boundary for t < 0 (curve 2). I is the scattered intensity in millimeters on the scale of the measuring instrument.

FIG. 3. Back-scattered intensity as a function of temperature plotted on a double logarithmic scale for t > 0 (line 1) and t < 0 (line 2).



same temperature). Consequently, it is, in principle, possible to investigate the correlation radius as a function of height in a very small neighborhood of the critical density region. However, since the height resolution of our apparatus was 0.6 mm,[5] we did not succeed in establishing this dependence in any reliable way. To ensure reliable data the resolution would have to be increased by at least an order of magnitude.

If we subtract the intercept from the total backscattered intensity we can isolate the Rayleigh contribution and then use it to investigate the compressibility on the critical isochore for $t > 0$ and on the phase-separation boundary for $t < 0$. Near the critical point the pressure and density (volume) of the isothermal system are functions of the variable h (if special measures are not taken to eliminate the gravitational effect). Our experimental method corresponds to these conditions. Accordingly,

$$I_{RE} \sim \frac{\partial v}{\partial p} = \frac{\partial v}{\partial h} \Big/ \frac{\partial p}{\partial h}.$$

Next, in view of the obvious relation $\partial p/\partial h = -1$, we obtain the following relation between the scattered intensity and the density (volume) gradient: $I_{RE} \sim -\partial v/\partial h$. Using this, and differentiating Eqs. (4) and (5) with respect to h, we obtain the following expressions for the scattered intensity for $h \approx 0$:

$$I_{RE}(t>0) = \frac{k_1 \rho c^2}{P_c} \frac{1}{at^\gamma}, \qquad (15)$$

$$I_{RE}(t<0) = \frac{k_1 \rho_c^2}{P_c} \frac{1}{a(\delta-1)|t|^\gamma}. \qquad (16)$$

These formulas describe the temperature dependence of the scattered intensity at $h = 0$, which corresponds to the critical isochore for $t > 0$ and the coexistence curve for $t < 0$.

We must note that these formulas can also be obtained without using the gravitational effect. From the relationship between the scattered intensity and compressibility we have

$$I_{RE} = \frac{k_1 \rho_c^2}{P_c} \frac{1}{at^\gamma + bv^{\delta-1}}. \qquad (17)$$

On the critical isochore $v = 0$, which leads immediately to Eq. (15). Equation (16) follows by substituting in Eq. (17) the expression for the deviation of the volume (density) on the binodal $v = \pm(\delta|t|^\gamma a/b) \exp 1/(\delta-1)$, which can be obtained in a similar way by calculating this quantity on the basis of the classical theory[1] but with $(\partial p/\partial v)_t$ given approximately by Eq. (2).

It is clear from Eqs. (15) and (16) that experimental data on the scattered intensity can be used to determine the index γ which represents the temperature dependence of the isothermal compressibility. By plotting Eqs. (15) and (16) on a logarithmic scale, we find from the slope of the corresponding straight lines (Fig. 3) that $\gamma^+ \approx \gamma^- = 1.2 \pm 0.1$ (γ^+ and γ^- are, respectively, the temperature indices of the isothermal compressibility for $t > 0$ and $t < 0$).

Equations (15) and (16) can also be used to determine the critical index δ:

$$\delta = \frac{I_{RE}(t>0)}{I_{RE}(t<0)} + 1. \qquad (18)$$

The index δ was found from the data shown in Fig. 3 using the formula $\log(\delta - 1) = \log I_{RE}^{-1}(t < 0) - \log I_{RE}^{-1}(t > 0)$ and was shown to be $\delta = 4.9 \pm 0.3$.

The above calculations of the critical indices γ and δ show that, in the temperature range which we have investigated, the numerical values of these parameters are in agreement with the predictions of the three-dimensional Ising model.

CONCLUSION

We may thus conclude that light-scattering studies near the critical point have enabled us to determine the critical values of the isothermal compressibility index γ and the critical-isothermal index δ.

Moreover, by taking into account the influence of the gravitational effects on critical opalescence, it is found that the intensity of light scattered by density fluctuations depends also on the other critical indices ν, η, and ξ, which are introduced in the scaling theory to describe the temperature dependence of the correlation radius, the spatial dependence of the correlation function, and the dependence of the correlation radius on the closeness of the density to its critical value.

Experimental studies of the gravitational effect and its influence on light scattering near the critical point are thus capable of producing essential data for the determination of the range of validity of the classical theory of critical phenomena and the additional verification of the predictions of the theory of scaling transformations.

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[1] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964 [Addison-Wesley, 1960].

[2] A. V. Voronel' and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. **39**, 1162 (1960) [Sov. Phys.-JETP **12**, 809 (1961)].

[3] M. Sh. Giterman and S. P. Malyshenko, Zh. Eksp. Teor. Fiz. **53**, 2077 (1967) [Sov. Phys.-JETP **26**, 1176 (1968)].

[4] A. D. Alekhin, A. Z. Golik, N. P. Krupskiĭ, and A. V. Chalyĭ, Ukr. Fiz. Zh. **13**, 2067 (1968).

[5] A. D. Alekhin, A. Z. Golik, N. P. Krupskiĭ, A. V. Chalyĭ, and Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. **14**, 475 (1969).

[6] I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Scattering of Light), Nauka, 1965 [Consultants Bureau, 1968].

[7] A. D. Alekhin, A. Z. Golik, N. P. Krupskiĭ, A. V. Chalyĭ, and Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. **13**, 1570 (1968).

[8] E. T. Shimanskaya and A. Z. Golik, collection: Kriticheskie yavleniya i fluktuatsii v rastvorakh (Critical Phenomena and Fluctuations in Solutions), AN SSSR, 1960; E. T. Shimanskaya, Yu. I. Shimanskiĭ, and A. Z. Golik, ditto.

[9] Zh. P. Naumenko, E. T. Shimanskaya, and Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. **12**, 143 (1967).

[10] L. Onsager, Phys. Rev. **65**, 117 (1944).

[11] M. E. Fisher, J. Math. Phys. **5**, 944 (1965).

[12] Proceedings of the International Conference on Phenomena Near Critical Points, Washington, NBS Misc. Publications, 1965.

[13] M. Green, M. Vicentini-Missoni, and J. Levelt Sengers, Phys. Rev. Lett. **18**, 1113 (1967).

[14] M. E. Fisher, Nature of the Critical State, (Russ. Transl.) Mir, 1968.

[15] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Zh. Eksp. Teor. **46**, 944 (1964); **50**, 439 (1966) [Sov. Phys.-JETP **19**, 677 (1964); **23**, 292 (1966)].

[16] R. Griffiths, Phys. Rev. **158**, 176 (1967).

[17] L. Kadanoff, Rev. Mod. Phys. **39**, 395 (1967).

[18] V. L. Pokrovskiĭ, Usp. Fiz. Nauk **94**, 127 (1968) [Sov. Phys.-Uspekhi **11**, 66 (1968)].

[19] K. B. Tolpygo and A. V. Chalyĭ, Ukr. Fiz. Zh. **13**, 1261 (1968).

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