

Experimental investigation of the correlation function near the critical point

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An analysis of the angular and temperature dependences of the critical opalescence has revealed a deviation of the correlation function from the Ornstein-Zernike approximation. The obtained correlation function is of the form $G(k, r_c) \sim (r_c^{-2} + k^2)^{-(1-\eta/2)}$, where k is the wave number, r_c is the correlation radius and $\eta=0.055 \pm 0.010$.

To describe the correlation properties of liquids near critical points it is customary to use the following interpolation formula (see, e.g., [1])

$$G(k, r_c) = \rho r_c^{-(2-\eta)} (r_c^{-2} + k^2)^{-(1-\eta/2)}, \quad (1)$$

where $r_c = r_0[(T - T_c)/T_c]^{-\nu} = r_0 t^{-\nu}$ is the correlation radius, ρ is the density, and k is the wave number. In scattering experiments we have $k = 4\pi\lambda^{-1}n \sin(\theta/2)$ (λ is the radiation wavelength, n is the refractive index of the medium, and θ is the scattering angle). The exponent η characterizes the proposed deviation from the Ornstein-Zernike approximation, in which $\eta = 0$. [2]

Calculations for the three-dimensional Ising model yield $\eta = 0.041$ (numerical methods [3]) and $\eta = 0.037$ (analytic methods [4]). At the same time, the results of numerous experimental investigations of the correlation properties of liquids near the critical points (by the light-scattering method [1, 5-10]) are contradictory. For example, for one and the same object, namely a nitroethane + 3, methylpentane solution (a system similar to that investigated by us) they obtained $\eta = 0 \pm 0.01$ [5] and 0.2 ± 0.1 . [11] In fact, not a single experimental study has so far demonstrated convincingly enough that the Ornstein-Zernike approximation is inadequate. [6]

We can indicate the following main causes of these discrepancies. First, the proposed value of the exponent η differs little from zero, and its determination calls for a highly accurate measurement of the scattered-light intensity in as broad a range of measurement kr_c as possible. Second, the experiment near the critical point, in general, and investigation of the experiment critical opalescence, in particular, are accompanied by distorting factors that are difficult to eliminate (multiple scattering, attenuation of the light, parasitic light at small angles, etc.).

We measured the intensity of the scattered light near the critical liquid-liquid equilibrium point of a solution of nitroethane hexane ($T_c = 304.030 \pm 0.001$ °K, $x = x_c = 51.8 \pm 0.2$ wt. % hexane, difference between the re-

fractive indices of the components $\Delta n \approx 0.017$) at 24 scattering angles in the range $\theta = 12-150^\circ$ and in the temperature interval $t = 3 \times 10^{-2} - 10^{-5}$. We obtained approximately a thousand experimental points in the kr_c interval from 0.4 to 6.3. The thermostat system, which was somewhat improved in comparison with that described in [11], made it possible to maintain a given temperature with accuracy $\pm 2 \times 10^{-4}$ deg. The method of preparing the sample and the construction of the optical cell were similar to those described in [11]. The light source was an LG-55 helium-neon laser ($\lambda = 6328$ Å, power $\sim 10^{-3}$ W) with power stabilization ($\pm 0.1\%$ over one hour). The power of the exciting beam was decreased in the scattering volume near T_c to 2×10^{-6} W, which practically excluded the possibility of sample heating by the laser beam. The intensity of the scattered light was measured by the photon-counting method (FEU-79 photomultiplier - discriminator - ChZ-34 frequency meter). The range of measured intensities was $10^2 - 10^6$ counts/sec. The stability of maximum in-

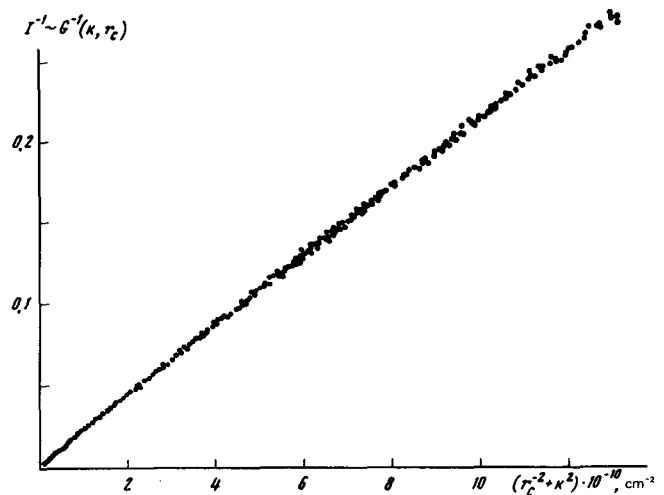


FIG. 1. Correlation function near critical point. The figure shows a fraction of the experimental points. The investigated interval of the argument $(r_c^{-2} + k^2)$ is $(0.18-54) \times 10^{10}$ cm⁻².

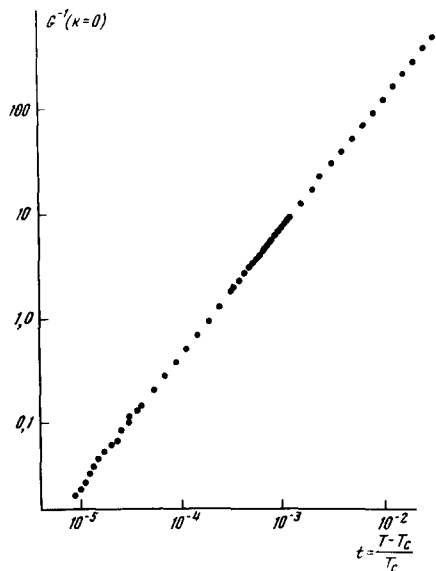


FIG. 2. Temperature dependence of the correlation function at $k=0$.

tensity was $\sim 0.5\%$ over one hour. The scattering intensity was calibrated against the intensity of the transmitted light, so that it was possible to take into account the attenuation effects, which depended on the proximity to T_c . We measured simultaneously the degree of depolarization of the scattered light (Δ), which is equal in order of magnitude to the contribution of the multiple scattering.^[12] At $t=10^{-4}$ – 10^{-5} we have $\Delta=0.1$ – 0.2% . The procedure employed made it possible to measure the relative intensity of singly-scattered light with accuracy not worse than 1% .

The result of the measurement of the correlation function $G(k, r_c)$, which is proportional to the relative intensity I , as a function of $(r_0^{-2} + k^2)$, is shown in Fig.

1, while Fig. 2 shows the temperature dependence of $G(k, r_c)$ at $k=0$, namely $G(0, r_c) \sim r_0^{2-\eta} \sim t^{-\gamma}$, where $\gamma = (2-\eta)\nu$. Approximation of the curve of Fig. 1 by expression (1) yielded the results $\eta=0.055 \pm 0.010$, $\nu=0.63 \pm 0.01$, $r_0=2.2 \pm 0.2 \text{ \AA}$. The slope of the line in Fig. 2 corresponds to $\gamma=1.22 \pm 0.02$.

In our opinion, the deviation of the correlation function near critical points of liquids from the Ornstein-Zernike approximation can now be regarded as experimentally proved.

We note that the results obtained for a liquid, on the one hand, and for the three-dimensional Ising model, on the other, turned out to be numerically close.

The correlation function should also contain terms of higher order in k ,^[3] but their observation calls for a much higher accuracy.

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