True and effective critical exponents of fluids

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A study is made of the relationship between the true (limiting) and effective (measured in actual experiments) thermodynamic critical exponents β, γ, and δ of a fluid. It is shown that the true critical exponents can differ appreciably from the effective exponents obtained in optical and p-ρ-T experiments without allowance for the averaging of the measured physical quantities (scattering intensity, compressibility, order parameter) over a layer whose dimensions are determined by the size of the entrance slit of the detector or by the vertical thickness of the working cell. Calculations of the effective critical exponents have revealed that optical experiments can yield values $\delta_{\rm eff} > \delta$ and $\gamma_{\rm eff} < \gamma$, while p-ρ-T experiments can give $\delta_{\rm eff} < \delta$ and $\beta_{\rm eff} < \beta$.

INTRODUCTION

The recent progress in the physics of critical phenomena and phase transitions is due, as we know, to our deeper understanding of the role of cooperative effects stemming from the correlation of strongly interacting fluctuations of the order parameter of the system at large distances and times. To a certain degree this progress has been promoted by the development of theoretical concepts based on fundamental notions of scale invariance (scaling)[1] and the renormalization group[2] and also by the many precision experiments that have been done.[3]

Obviously, it is important to determine the true, or limiting, critical exponents from an experiment and to compare them with the theoretical predictions. In a real experiment, however, there are always factors which distort the idealized critical behavior described by power-law monomials with the true critical exponents. It is sensible to distinguish two types of distorting factors, which might arbitrarily be called "physical" and "methodological." Factors of the first type might include external influences which give rise to a macroscopic inhomogeneity of the medium, multiple scattering effects in an optical experiment,[4] auxiliary thermodynamic variables and hidden parameters whose interaction with the critical order parameter can lead to a renormalization of the critical exponents and to crossover behavior,[5] etc. The second type includes the finite size of the detector slit, the limited precision of the temperature control, etc. Often the presence of methodological distorting factors makes it necessary to take factors of a physical nature into account. For example, to do an experiment in a rather wide neighborhood of the critical point (in the better experiments in classical fluids one cannot get closer to the critical temperature T_c than $\tau = (T - T_c)/T_c \approx 10^{-5}$) one must take into consideration the nonasymptotic and asymmetric scaling corrections.[6–9]

The influence of the distorting factors is manifested primarily in the fact that the critical exponents of the power-law monomials approximating the experimental data exhibit a dependence on the temperature variable τ, on the local value of the order parameter {for fluids in a gravitational field—on the density deviation $\Delta\rho = [\rho(H,\tau) - \rho_c]/\rho_c$ or the corresponding "field" variable $z = \rho_c gH/p_c$, where H is the height reckoned from the level at which the fluid has its critical density ρ_c, p_c is the critical pressure, and g is the acceleration due to gravity}, on the geometric dimensions of the volume under study, etc. In other words, a real experiment yields effective values of the critical exponents.

In this paper we determine the relationship of the true and effective critical exponents for a classical one-component fluid. We investigate in detail the role of a physical factor—the spatial inhomogeneity of the fluid in a gravitational field (the so-called gravitational effect)[10]—and a methodological factor—the finite size of the detector slit. We study the conditions under which an optical or p-ρ-T experiment can yield the true values of the critical exponents of a fluid.

OPTICAL EXPERIMENT

Let us consider the typical geometry of an optical experiment for the study of critical phenomena in fluids (see, e.g., Refs. 11 and 12). Suppose that we have monochromatic light propagating in the vertical direction in the working volume of the chamber, which is held at a temperature near the critical point, and that the scattered light is detected in the horizontal direction. Here the experimental information is taken from a layer of finite thickness ΔH whose size is determined by the width of the entrance slit of the detector. The minimum value of ΔH is typically $\Delta H = 6\cdot10^{-2}$ cm (Ref. 11) or $7\cdot10^{-2}$ cm (Ref. 12) (corresponding to $\Delta z = 6\cdot10^{-7}$ or $7\cdot10^{-7}$, respectively, at $\rho_c g/p_c = 10^{-5}$ cm^{-1}). Usually ΔH is larger. For example, in order to study the dependence of the depolarization factor on the linear dimensions of the scattering volume, Trappeniers *et al.*,[12] increased ΔH to $2.8\cdot10^{-1}$ cm. The finite size of the detector slit made it necessary to analyze the scattering intensity as averaged over a layer ΔH. In fact, the gravitational change in the density and fluctuational structure (and, hence, in the scattering power) of the material over a height interval ΔH becomes increasingly important as the temperature of the system approaches T_c and as the center of the layer ΔH approaches $H = 0$. A similar situation should in principle occur not only in optical experiments but also in other experiments which do not utilize some type of stirrer.

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Critical exponent δ. For a one-component fluid whose thermodynamic state lies in the vicinity of the critical isotherm the field and temperature variables are related by the inequality $|z| > |\tau|^{\beta\delta}$ ($\beta \approx 0.34$, $\delta \approx 4.5$ are the true critical exponents of the coexistence curve and critical isotherm). Generally speaking, this inequality should be satisfied by the dimensionless coordinates of the lower boundary z_1 and upper boundary z_2 and also by the coordinate ζ of the center of the plane-parallel layer from which the experimental information is taken.

On the critical isotherm the integrated single-scattering intensity averaged over the layer $\Delta z = z_2 - z_1$ is described in the Ornstein-Zernike approximation by the expression

$$\langle I\rangle = \frac{A}{\Delta z}\int_{z_1}^{z_2} \frac{dz}{az^{(\delta-1)/\delta} + f^* q^2}. \tag{1}$$

Here

$$A = I_0\left(\frac{k_0^2}{4\pi}\right)^2 \left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^2 \frac{1-(\mathbf{n}_1,\mathbf{m}_0)^2}{L^2 P_c} k_B T\sigma$$

is a quantity which is practically independent of the proximity to the critical point (the notation is standard[13,14]), a is the amplitude of the inverse compressibility $[\beta_T^{-1} = az^{(\delta-1)/\delta}]$, $f^* = r_c^2/\beta_T = ar_0^2 \approx 10^{-(11-12)}$ N is the nonlocality parameter of the fluctuations, r_0 is the amplitude of the correlation length r_c, and $q = 2\sqrt{2}\pi(1-\cos\vartheta)^{1/2}/\lambda$ is the change in the wave vector upon scattering through the angle ϑ. Integration of (1) yields

$$\langle I\rangle = \frac{A}{\Delta z f^* q^2}\Big\{ z_2 F\left(1, \frac{\delta}{\delta-1}; 1+\frac{\delta}{\delta-1}; -\frac{az_2^{(\delta-1)/\delta}}{f^*q^2}\right) - z_1 F\left(1, \frac{\delta}{\delta-1}; 1+\frac{\delta}{\delta-1}; -\frac{az_1^{(\delta-1)/\delta}}{f^*q^2}\right)\Big\}, \tag{2}$$

where $F(a_1,a_2;a_3;x)$ is a hypergeometric function. Since

$$x_{1,2} = az_{1,2}^{(\delta-1)/\delta}/f^*q^2 = 1/r_{c1,2}^2 q^2 > 1$$

(in the approximation of weak spatial dispersion, which is assumed in the Ornstein-Zernike theory, one has $r_c q < 1$), it is convenient to transform to hypergeometric functions containing $x_{1,2}^{-1}$ and then expand these functions in the small argument $x_{1,2}^{-1} < 1$. The final result of the calculation is of the form

$$\langle I\rangle = \frac{A}{a\Delta z}\Big\{\alpha_1\Big[z_2^{1/\delta} - z_1^{1/\delta} + \frac{q^2}{(\delta-1)(\delta-2)} \times (z_2^{1/\delta} r_c^2(z_2) - z_1^{1/\delta} r_c^2(z_1))\Big] + \alpha_2(-1)^{\delta/(\delta-1)} q^{2/(\delta-1)} (z_2^{1/\delta} r_c^{2/(\delta-1)}(z_2) - z_1^{1/\delta} r_c^{2/(\delta-1)}(z_1))\Big\}, \tag{3}$$

where

$$\alpha_1 = \Gamma\left(1+\frac{\delta}{\delta-1}\right)\Gamma\left(\frac{\delta}{\delta-1}-1\right)\Big/\Gamma^2\left(\frac{\delta}{\delta-1}\right) = \delta,$$

$$\alpha_2 = \Gamma\left(1+\frac{\delta}{\delta-1}\right)\Gamma\left(1-\frac{\delta}{\delta-1}\right) = \frac{\delta}{\delta-1}\frac{\pi}{\sin[\pi\delta/(\delta-1)]}.$$

Assuming in (3) that $z_1 = \zeta - \Delta z/2$ and $z_2 = \zeta + \Delta z/2$, expanding in the (assumed) small parameter $\Delta z/\zeta$, and taking the limit $\Delta z \to 0$, $q \to 0$, we easily arrive at an expression for the local intensity

$$I(\zeta) = (A/a)\zeta^{-1+1/\delta}$$

which contains the true value of the exponent δ of the critical isotherm. In the general case, by approximating the average intensity $\langle I\rangle$ from (3) by its local value $I(\zeta)$, we can find the effective value $\delta_{\rm eff}$, which depends on δ, Δz, ζ, and q, in accordance with the expression

$$\langle I\rangle = (A/a)\zeta^{-1+1/\delta_{\rm eff}}. \tag{4}$$

Let us analyze the function $\delta_{\rm eff}(\delta, \Delta z, \zeta)$ for $r_c q \to 0$. In this case we have from (3) and (4)

$$\zeta^{-1+1/\delta_{\rm eff}} = \frac{\delta}{\Delta z}\left\{\left(\zeta+\frac{\Delta z}{2}\right)^{1/\delta} - \left(\zeta-\frac{\Delta z}{2}\right)^{1/\delta}\right\}. \tag{5}$$

In expression (5) the slit width Δz is not assumed small in comparison with the coordinate ζ of its center; it is required only that $\zeta > \tau^{\beta\gamma}$. For small ratios $\Delta z/\zeta$ the expression for $\delta_{\rm eff}$ simplifies to

$$\delta_{\rm eff} = \delta + \frac{1}{6}(\delta-1)(2\delta-1)\left(\frac{\Delta z}{2\zeta}\right)^2 \frac{1}{|\ln\zeta|} + O\left(\frac{\Delta z^4}{\zeta^4}\right). \tag{6}$$

It follows from (5) and (6) that failure to average the scattering properties over the height of the detector slit results in a higher value of the effective critical exponent $\delta_{\rm eff}$. Table I gives the results of a calculation of $\delta_{\rm eff}$ as a function of ζ and Δz for $\delta = 4.5$. We note that two conditions which determine the choice of $\zeta_{\rm min}$ must be satisfied simultaneously: $r_c q < 1$ and $\zeta > \tau^{\beta\delta}$. For realistic values of the minimum temperature deviation from the critical point $\tau_{\rm min} \approx 10^{-5}$, the condition $r_c q < 1$ with $r_0 \approx 2\cdot 10^{-10}$ m, $\lambda = 6.28\cdot 10^{-7}$ m, and $\vartheta = \pi/2$ implies that $\zeta_{\rm min} > 6\cdot 10^{-7}$. At such a value of $\zeta_{\rm min}$ the second condition ($\zeta > \tau^{\beta\delta}$) is also satisfied. The values in the first row in Table I were calculated with formula (5), and the values in the second row were obtained with the approximate formula (6). In these calculations the slit width was taken to be $\Delta z = 2\cdot 10^{-6}$ ($\Delta H = 0.2$ cm).

As is seen in Table I, a decrease in the variable ζ at fixed τ leads to an increase in $\delta_{\rm eff}$. If the critical-isotherm condition $\zeta > \tau_{\rm min}^{\beta\delta} \approx 10^{-(7.5-8)}$ is violated, one can obtain still larger values of $\delta_{\rm eff}$ than are given in Table I. For example, for $\zeta = \Delta z/2 = 2\cdot 10^{-6}$, i.e., if one of the slit boundaries is at the level $z = 0$, one has $\delta_{\rm eff} = 6.572$.

Of course, formulas (5) and (6) can also be used to solve the inverse problem, which is of immediate theoretical and experimental interest: namely, to find the true value of the critical exponent δ from the experimentally determined value $\delta_{\rm eff}$ at known Δz and ζ. It should be stressed that for $\zeta \geqslant 4\Delta z$ (i.e., under the condition that the coordinate of the center of the detector slit, as reckoned from the level at which the density has its critical value, is four times as large as the slit width), the values of δ and $\delta_{\rm eff}$ agree up to the second decimal place.

Critical exponent γ. Let us turn now to the relationship between the true and effective values of the critical exponent γ for the temperature dependence of the susceptibility (the isothermal compressibility for a fluid) as measured in an optical experiment in the vicinity of the critical isochore. For this purpose, let us analyze the intensity of single scattering

TABLE I. Values of δ_{eff} (optical experiment).

Critical exponent	Ratio $\zeta/\Delta z$								
	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5
δ_{eff}, Eq. (5)	6,572	4.605	4.546	4.527	4,518	4,514	4.511	4.509	4.507
δ_{eff}, Eq. (6)	–	–	4.541	4.523	4.515	4,510	4.508	4.506	4.505

average over a layer $-z_0 \leqslant z \leqslant z_0$ whose center lies at the critical-density level and whose boundaries satisfy the inequality $|z_0| < \tau^{\beta\delta}$. In the Ornstein-Zernike approximation this quantity is given by

$$\langle I\rangle = \frac{1}{2z_0}\int_{-z_0}^{z_0} I(z,\tau,q)\,dz = \frac{A\,\mathrm{arctg}\,(B_1/B_0)^{1/2}z_0}{(B_0B_1)^{1/2}z_0}, \tag{7}$$

where

$$B_0 = b_0^{-1}\tau^{\gamma} + f^*q^2, \qquad B_1 = -b_1/b_0\tau^{2\beta\delta-\gamma},$$

and b_0 and b_1 are the constants appearing in the expression for the isothermal compressibility:

$$\beta_T = b_0\tau^{-\gamma}\left(1 + b_1\frac{z^2}{\tau^{2\beta\delta}} + O\left(\frac{z^4}{\tau^{4\beta\delta}}\right)\right). \tag{8}$$

In the present case the dimensionless coordinate $z_0 = \rho_c g H_0/p_c$ of the boundary of the layer is related to the width of the detector slit by the simple relation $z_0 = \Delta z/2$.

The experimental data on the intensity of scattered light (or on the compressibility determined in a conventional p-ρ-T experiment) in the vicinity of the critical isochore, for $q \to 0$ and $z < \tau^{\beta\delta}$, is usually approximated by a power law of the form

$$I(\tau, q\to 0) = A\beta_T(\tau) = A b_0\tau^{-\gamma} \tag{9}$$

and it is assumed that the critical exponent γ is the exact limiting exponent from scaling theory. In fact, as can easily be seen from (7), the critical exponent in (9) is some effective exponent γ_{eff} which in the general case depends on τ, z_0, and q. The value of γ_{eff} and its relation to the true value γ which appears in (7) is given by the formula

$$\frac{1}{(B_0B_1)^{1/2}z_0}\,\mathrm{arctg}\,(B_1/B_0)^{1/2}z_0 = b_0\tau^{-\gamma_{eff}}. \tag{10}$$

Hence, for $q \to 0$ and with allowance for the obvious inequality $b_1 < 0$ [the quantity β_T in (8) must fall off with distance from the $z = 0$ level] we have the following result:

$$\gamma_{eff} = \gamma - \beta\delta + (\ln\tau)^{-1}\ln\left\{\frac{|b_1|^{1/2}z_0}{\mathrm{arctg}\,\tau^{-\beta\delta}|b_1|^{1/2}z_0}\right\}. \tag{11}$$

For $z_0 \to 0$, this equation implies, of course, that $\gamma_{eff} \to \gamma$. Otherwise, $\gamma_{eff} < \gamma$. Keeping only the first two terms in the series expansion of arctan α in powers of the small argument $\alpha = |b_1|^{1/2}z_0/\tau^{\beta\delta}$, we obtain from (11) the expression

$$\gamma_{eff} = \gamma(|b_1|z_0^2/3\tau^{2\beta\delta}|\ln\tau|. \tag{12}$$

Table II gives the results of a calculation of the effective critical exponent γ_{eff} for various values of τ, according to formulas (11) and (12). The limiting value of the exponent γ was taken to be 5/4, and we used $\beta\delta = 5/3$, $|b_1| = 10$ (Ref. 15), and $H_0 = 10^{-1}$ cm ($z_0 = 10^{-6}$). The value of τ_{min} at fixed z_0 should be consistent with the inequality $z_0 < \tau^{\beta\delta}$ which defines what is meant by the vicinity of the critical isochore. For $z_0 \approx 10^{-6}$ we have $\tau_{min} \gtrsim 10^{-3.3}$.

The calculation shows that ignoring the finite size of the scattering volume and neglecting the averaging over height of the scattering properties of the fluid lead to a decrease in the critical exponent γ_{eff} for the temperature dependence of the light-scattering (compressibility) of the fluid. By increasing z_0 or decreasing τ (and violating the inequality $z_0 < \tau^{\beta\delta}$) one can, in principle, even get the "classical" value of the exponent $\gamma_{eff} \approx 1$. It can be shown that for $q \neq 0$ the exponent γ_{eff} becomes still smaller in comparison with the true value γ. The additional contribution to the difference $\gamma - \gamma_{eff}$, equal to $(r_c q)^2/|\ln\tau|$, amounts to a quantity of the order of 10^{-2} for $\tau \approx 10^{-3.3}$ ($r_c^2q^2 \approx 6\cdot 10^{-2}$).

As is seen from Table II, only for $n = -\log\tau < 3.0$ can the true and effective values of the critical exponent for the temperature dependence of the susceptibility along the critical isochore be considered equal (for the values of the parameters b_1 and z_0 used in the calculations).

p-ρ-T EXPERIMENTS

Let us now turn to the conventional p-ρ-T experiments for finding the thermodynamic critical exponents. Usually in such an experiment the cell containing the material in a near-critical state is positioned horizontally and made as thin as possible in order to avoid substantial gravitational effects. For convenience in comparing with the optical data,

TABLE II. Values of γ_{eff} (optical experiment).

Critical exponent	$n = -\log\tau$								
	2,9	3,0	3,1	3.2	3,3	3,4	3,5	3,6	3.7
γ_{eff}, Eq. (11)	1.249	1.246	1.242	1.233	1.214	1,194	1.174	1,147	1.110
γ_{eff}, Eq. (12)	–	–	–	–	1.221	1.197	1.170	1.140	1.106

in the numerical calculations below we shall take the vertical thickness of the cell to be the same as the width of the entrance slit of the detector, i.e., $\Delta H = 2\cdot 10^{-1}$ cm ($\Delta z = 2\cdot 10^{-6}$). Unlike the optical experiments, where the critical exponents are found from the density (height) dependence or temperature dependence of the light-scattering intensity, in the p-ρ-T experiments one obtains the critical exponents from an analysis of the order parameter.

Critical exponent β. Let us calculate the influence of gravity and the finite size of the detector slit on the order parameter in the vicinity of the coexistence curve. The main contribution to the local order parameter $\Delta\rho$ on the coexistence curve with the gravitational effect taken into account is given by the expression[10]

$$\Delta\rho(|\tau|,\ z) = C_0|\tau|^{\beta}(1+C_1 z|\tau|^{-\beta\delta})\,\mathrm{sign}\,\Delta\rho. \tag{13}$$

The averaged value of the order parameter $\langle|\Delta\rho|\rangle$ on the gas branch of the coexistence curve [in the approximation of a symmetric coexistence curve, when $\tau^{1-\alpha-\beta} \ll 1$ ($\alpha \approx 0.11$), the same result also holds for the liquid branch of the coexistence curve] is given by a relation of the form

$$\langle|\Delta\rho|\rangle = C_0|\tau|^{\beta}(1+{}^1\!/_2 C_1 z_0|\tau|^{-\beta\delta}). \tag{14}$$

On the other hand, we have $\langle|\Delta\rho|\rangle = C_0|\tau|^{\beta_{\rm eff}}$, from which we get

$$\beta_{\rm eff} = \beta - \ln(1+{}^1\!/_2 C_1 z_0|\tau|^{-\beta\delta})\,|\ln|\tau||^{-1}. \tag{15}$$

Since C_1 is always positive (the order parameter grows with increasing $|z|$), it follows from (15) that $\beta_{\rm eff} < \beta$. Assuming that $\frac{1}{2}C_1 z_0|\tau|^{-\beta\delta} < 1$, formula (15) can be written in the approximate form

$$\beta_{\rm eff} = \beta - {}^1\!/_2 C_1 z_0|\tau|^{-\beta\delta}|\ln|\tau||^{-1}. \tag{16}$$

Comparing (12) and (16), we easily see that by virture of the smallness of the ratio $z_0/\tau^{\beta\delta}$ in the neighborhood of the critical isochore and coexistence curve, the following inequality should hold:

$$\Delta\beta = \beta - \beta_{\rm eff} > \Delta\gamma = \gamma - \gamma_{\rm eff}.$$

Such a change in the exponents $\beta_{\rm eff}$ and $\gamma_{\rm eff}$, and also the growth in the exponent $\delta_{\rm eff}$, agree with the familiar identity $\beta = \gamma(\delta - 1)$. The results of the calculation of $\beta_{\rm eff}$ are given in Table III. For z_0 and $\beta\delta$ we used the same values $z_0 = 10^{-6}$ and $\beta\delta = 5/3$ that were used in the case of the critical isochore in the optical experiments. We assumed $C_1 \approx |b_1|/(\delta - 1) \approx 2.5$, since the difference in the coefficients is given by just such a difference of the isothermal compressibility β_T on the coexistence curve and on the critical isochore. The limiting value of the critical exponent β is 0.340.

The significant decrease in $\beta_{\rm eff}$ for $n \to 4$ is explained by (in addition to the main factors—gravity and the finite width of the detector slit) the fact that the inequality $z_0 < |\tau|^{\beta\delta}$, which defines what is meant by the vicinity of the coexistence curve, is violated in this region of $|\tau|$. As in the vicinity of the critical isochore, the exponents β and $\beta_{\rm eff}$ draw closer together with increasing temperature deviation $|\tau|$; at $n = 2.0$ we have $\beta_{\rm eff} = 0.3394$.

Critical exponent δ. It is of interest to compare the values of the effective critical exponent $\delta_{\rm eff}$ obtained in the optical and p-ρ-T experiments. In the latter case we must deal with the order parameter as averaged over the layer $\Delta z = z_2 - z_1$; on the critical isotherm this averaged value is given by

$$\langle|\Delta\rho|\rangle = \frac{z_2^{1+1/\delta} - z_1^{1+1/\delta}}{\Delta z d_0^{1/\delta}(1+1/\delta)}. \tag{17}$$

Here d_0 is the value of the scale function $G(x)$ of the equation of state $z = \Delta\rho^{\delta}G(x)\,\mathrm{sign}\,\Delta\rho$ on the critical isotherm ($x = \tau/z^{1/\beta\delta} \to 0$).

By equating $\langle|\Delta\rho|\rangle$ from (17) to the local value of the order parameter at the center of the layer, $|\Delta\rho| = (\zeta/d_0)^{1/\delta_{\rm eff}}$, we obtain the following equation for finding the relationship between δ and $\delta_{\rm eff}$ in a p-ρ-T experiment:

$$\zeta^{1/\delta_{\rm eff}} = \frac{(\zeta+\Delta z/2)^{1+1/\delta} - (\zeta-\Delta z/2)^{1+1/\delta}}{\Delta z(1+1/\delta)}. \tag{18}$$

For $\Delta z/\zeta < 1$, corresponding to a situation in which the average density of the material in the working cell is rather far from the critical value ρ_c, we have

$$\delta_{\rm eff} = \delta - \frac{1}{6}(\delta-1)\left(\frac{\Delta z}{2\zeta}\right)^2\frac{1}{|\ln\zeta|} + O\left(\frac{\Delta z^4}{\zeta^4}\right). \tag{19}$$

Equation (19) implies a somewhat unexpected result: p-ρ-T experiments give an understated value of the critical exponent $\delta_{\rm eff}$, rather than an overstated value as in the optical experiments. Comparing (6) and (19), we easily see that without allowance for the small corrections $O(\Delta z^4/\zeta^4)$ the differences between the effective and true values of the critical exponent δ in the experiments under discussion are connected by the simple relation

$$(\delta - \delta_{\rm eff})_{p-\rho-T} = \frac{1}{2\delta-1}(\delta_{\rm eff} - \delta)_{\rm opt}. \tag{20}$$

The values of the critical exponent $\delta_{\rm eff}$ for different values of the ratio $\zeta/\Delta z$ for $\delta = 4.5$ are given in Table IV. Rela-

TABLE III. Values of $\beta_{\rm eff}$ (p-ρ-T experiment).

Critical exponent	$n = -\lg|\tau|$								
	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
$\delta_{\rm eff}$, Eq. (16)	0.334	0.331	0.328	0.323	0.319	0.311	0.300	0.286	0.269
	3.6	3.7	3.8	3.9	4.0				
$\beta_{\rm eff}$, Eq. (16)	0.249	0.225	0.199	0.171	0.132				

TABLE IV. Values of δ_{eff} (p-ρ-T experiment).

Critical exponent	Ratio $\zeta/\Delta z$								
	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5
δ_{eff}, Eq. (18)	4.433	4.488	4.499	4.500	4.500	–	–	–	–
δ_{eff}, Eq. (19)	–	—	4.495	4.497	4.498	4.499	4.499	4.499	4.500

tion (20) and a comparison of the data in Table I and IV show that under otherwise similar conditions a p-ρ-T experiment can in principle yield a value of the exponent δ_{eff} that is closer to the true value δ than an optical experiment can.

The difference we have found between the values of δ_{eff} obtained in the optical and p-ρ-T experiments can be understood on the basis of the following considerations. Optical experiments for measuring the compressibility, which on the critical isotherm falls off (approximately as $\beta_T \propto |z|^{-0.8}$) with distance from the critical-density level $z = 0$, yield a value of the average intensity $\langle I \rangle$ over the width of the detector slit that is higher than the exact local value $I(\zeta)$ at the center of the slit. In other words, the averaged compressibility $\langle \beta_T \rangle \propto \zeta^{-1+1/\delta_{eff}}$ turns out to be larger than the exact local compressibility $\beta_T(\zeta) \propto \zeta^{-1+1/\delta}$, and it follows immediately that $\delta_{eff} > \delta$. In p-ρ-T experiments the situation is reversed. The order parameter increases in absolute value with distance from the $z = 0$ level along the critical isotherm (approximately as $\Delta\rho \sim |z|^{0.2}$). Therefore, the averaging of the order parameter over the layer Δz yields a value $\langle \Delta\rho \rangle \propto \zeta^{1/\delta_{eff}}$ that is smaller than the exact local value $\Delta\rho(\zeta) \propto \zeta^{1/\delta}$ at the center of the layer, and so $\delta_{eff} < \delta$.

Of course, if the p-ρ-T data are used to analyze not the order parameter $\Delta\rho$ but the compressibility $\beta_T \propto \partial\rho/\partial z$ on the critical isotherm, then, as can easily be seen by differentiating (18) and comparing the result with (5), both experiments for studying the compressibility give $\delta_{eff} > \delta$.

CONCLUSION

Our calculation of the critical exponents of fluids has shown that the values of these exponents observed in a real experiment depend to a substantial degree on effects due to the averaging of the physical properties (compressibility, order parameter) over a layer of dimensions determined by the width of the entrance slit of the detector or the thickness of the working cell. Neglect of the gravitational effect, even for small thicknesses of the order of 0.1–0.2 cm, can lead to noticeable changes in the effective values of the critical exponents from their true (limiting) values as given by the modern theory of phase transitions. For example, optical experiments can yield an overstated value $\delta_{eff} > \delta$ and an understated value $\gamma_{eff} < \gamma$. Conventional p-ρ-T experiments can lead to an understated value $\beta_{eff} < \beta$ and, in contrast to the optical experiments, to an understated value $\delta_{eff} < \delta$.

There is a certain amount of experimental support for the correctness of the conclusions of our theoretical calculations.

A decrease of γ_{eff} all the way to the "classical" value was obvserved in experimental studies[16] of the thermodynamic properties of SF_6 in close proximity to the critical point. Although it was a p-ρ-T experiment that was done in Ref. 16, the exponent γ was calculated by analyzing the compressibility, a situation which is equivalent to the results of an optical experiment in terms of the direction of the inequality $\gamma_{eff} < \gamma$. In Ref. 17 the "classical" value $\gamma_{eff} \approx 1$ in SF_6 was given a qualitatively correct explanation in terms of the influence of gravity. It should be stressed that, in agreement with the calculations of the present paper, the inequality $\gamma_{eff} < \gamma$ was observed in SF_6 in the region $\tau < 10^{-3}$.

A somewhat unusual situation in terms of the exponent δ_{eff} also occurs in experiment. In fact, experimental light-scattering studies along the critical isotherm in cyclopentane and n-pentane[11] gave $\delta = 5.0$ and $\delta = 4.9$, respectively. On the other hand, p-ρ-T measurements of the critical isotherm in He^3 (Ref. 18), N_2 (Ref. 19), and SF_6 (Refs. 16 and 17) have shown that the exponent δ is equal to 4.16, 4.28, and 4.30, respectively. The values of δ_{eff} found in the light-scattering experiments are obviously larger, and the values obtained in the p-ρ-T experiments, smaller, than the limiting value $\delta = 4.46$ given by the ε expansion to second order in $\varepsilon = 4 - d$ for a spatial dimension $d = 3$ and a scalar order parameter ($n = 1$).

In the modern picture of the phenomena occurring near critical and phase-transition points an important position is held by the so-called universality hypothesis, according to which a certain physical property in systems having the same dimensionality n of the order parameter, the same spatial dimensionality d, and the same radius r_0 of direct intermolecular interaction obey the same scaling laws, i.e., are described by the same limiting critical exponents. The above calculations of the effect of two (out of the many existing) factors which distort the idealized critical behavior give reason to hope that many differences in the values of the critical exponents obtained in different experiments can be eliminated, and that the intellectually attractive hypothesis of a universality of the diverse critical phenomena and phase transitions in the world around us will thus prove to be correct.

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