PHYSICAL REVIEW E **77**, 050103(R) (2008)

Ising-like criticality derived from the theory of fluids

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(Received 10 December 2007; published 16 May 2008)

It is shown that the conventional theory based on the integral equations for the correlation functions of fluid allows for a reasonable scaling analysis of the critical phenomena. The calculated critical exponents are in rather good agreement with the experimental data for real media, but some of the exponents (first of all, Fisher's exponent η) differ from the values predicted by the three-dimensional Ising model. The possibility to obtain Ising-like criticality from the statistical theory of fluids means that the latter does not disagree with the Kadanoff-Wilson-Fisher renormalization group approach.

DOI: 10.1103/PhysRevE.77.050103 PACS number(s): 05.70.Jk, 64.60.F−

The theory of critical phenomena in its modern form appeared after the connection between fluctuations and singularities of thermodynamic functions in the critical point was established [1–3], which led to the formulation of the universality and scaling hypotheses [4,5]. During recent decades, noticeable successes were achieved in the calculation of the critical exponents either with the help of the renormalization-group (RG) and the ϵ-expansion methods [6] (see also the review article [7]) or by means of numerical calculations for the three-dimensional (3D) Ising model (see, for example, [8]). This made it possible to predict, in close agreement with experiment, the critical behavior of real systems belonging to the $O(1)$ universality class, which besides the 3D Ising (or lattice-gas) model includes, in particular, the liquid-gas critical point and fluid mixture consolute points (see, for example, [9]).

However, it seems interesting to develop an approach that could describe the critical behavior not in the $(4-\epsilon)$-dimensions space (with the extrapolation $\epsilon \to 1$) but directly in the 3D space. Although, as long ago as in Ref. [10], such an approach was considered actual, at present the unsolved question is as follows: can we obtain nonclassical (of Ising-type) critical exponents starting from the integral equations of the theory of fluids [11]? Moreover, the lack of progress in attempts to derive the critical scaling characteristics from these equations led to the appearance of a surprising statement that the values of the critical exponents are determined by the behavior of the partition function at *small* distances [11].

In the present paper, we propose an approximate approach that allows, in principle, to derive the scaling characteristics of real fluid in the vicinity of its critical point starting from the equations of the statistical theory of liquids. Here, the critical exponents are obtained as rational fractions, and their values (except for Fisher's exponent η) are in rather good agreement with the experimental data and with the RG calculations. The results presented below should not be considered as a suggestion of a new type of critical behavior, but rather as an analytical investigation of the critical properties of the systems related to the $O(1)$ universality class that is sufficiently simple and works directly in 3D space.

As the basis, we shall use the equations (see, for example, [11])

$$\ln[h(r)+1] = h(r) - c(r) + B(r) - W(r)/T, \tag{1}$$

$$h(r) - c(r) = \rho \int d\mathbf{r}' c(r') h(|\mathbf{r}' - \mathbf{r}|), \tag{2}$$

which connect the total $h(r)$ and the direct $c(r)$ correlation functions of a one-component fluid; $W(r)$ is the pair potential (usually the Lennard-Jones one) of interaction between two atoms separated by the distance r, T is the temperature, and ρ is the atomic density of the fluid. The diagrammatic representation of the bridge function $B(r)$ by means of integrals containing the products of the total correlation functions was given by Morita and Hiroike [12]. Later on, a number of approximate expressions for $B(r)$ in a local form were proposed, for example Verlet's semiempirical closure $B(r) = -\gamma^2(r)/\{2[1+a\gamma(r)]\}$ [13], where a is some empirical parameter and $\gamma(r) \equiv h(r) - c(r)$ is the so-called indirect correlation function (see also, for example, [11]).

It is obvious, however, that forms of closure such as that shown above are too simplified. Moreover, even a possibility to present $B(r)$ near the critical point as a power series over $\gamma(r)$ is a rather essential assumption that is reminiscent of the Landau expansion with respect to the powers of the order parameter [14]. But the justification for this assumption is that by accepting it, we will calculate the nonclassical critical exponents, the values of which are in agreement with the experimental ones. Thus, let us represent $B(r)$ as

$$B(r) = a_2(T,\rho)\gamma^2(r) + a_3(T,\rho)\gamma^3(r) + a_4(T,\rho)\gamma^4(r) + \cdots, \tag{3}$$

where $a_n(T,\rho)$ $(n=2,3,4,\ldots)$ are assumed to be some functions of temperature and density.

Equations (1) and (2) together with representation (3) are enough to analyze the main singularities of the thermodynamic functions of a one-component fluid in the critical domain. When approaching the critical point, the asymptotic (at $r\to\infty$) behavior of $\gamma(r)$ and $h(r)$ [as well as $c(r)$] will be weakly dependent on $W(r)$ (see below). In this point itself, i.e., at $T=T_c$ and $\rho=\rho_c$ (here and below, we designate the values in the critical point by the subscript "c"), such a dependence turns out to be absolutely inessential [4,5]; in this

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case, the character of the asymptotic behavior of the correlation functions will be determined by the functional form (3).

To establish this behavior, let us use the Fourier representation $\tilde{h}(k)=(4\pi/k)\int_0^\infty dr r \sin(kr)h(r)$ [and, similarly, for $\tilde{c}(k)$ and $\tilde{\gamma}(k)$] in the Ornstein-Zernike equation (2),

$$\tilde{h}(k)=\frac{\tilde{c}(k)}{1-\rho\tilde{c}(k)}. \tag{4}$$

Now, take into account the fact (see, for example, [15]) that in the critical point itself $\tilde{h}_c(k)$ at $k\to 0$ diverges as

$$\tilde{h}_c(k)=\frac{1}{\rho_c^2[\tilde{c}_c(0)-\tilde{c}_c(k)]}, \tag{5}$$

whereas $\tilde{c}_c(k)$ at $k\to 0$ tends to the finite value $\tilde{c}_c(0)=1/\rho_c$. This means that $|c_c(r)|\ll|h_c(r)|$ at $r\to\infty$ [15], so that the asymptotic expansion (3) in the vicinity of the critical point will, in fact, be carried out upon the powers of $h(r)$.

Analyzing Eqs. (1)–(3) in the critical point, we come to the remarkable conclusion that the slowest—powerlike with the minimal exponent—asymptotic decay of the function $h_c(r)$ is achieved at quite definite values of the two coefficients,

$$a_2(T_c,\rho_c)=-1/2, \quad a_3(T_c,\rho_c)=1/3. \tag{6}$$

Two conditions (6) corresponding to the vanishing of the terms $\sim h^2(r)$ and $\sim h^3(r)$ in the asymptotic form of Eq. (1) allow us to locate, uniquely, the pair of critical values T_c and ρ_c (cf. [14], Sec. 143, about the conditions for the isolated points of a continuous transition in the Landau theory). An important feature of our theory is that it actually requires the coefficient $a_4(T_c,\rho_c)$ *not* to become $-1/4$, unlike the mean-spherical approximation where $B(r)=\ln[h(r)+1]-h(r)$ outside the hard-core region of the potential [16]. It is known [11] that the approximation [16] and others with the state-independent coefficients [for example, Verlet's closure, where $a_2(T,\rho)\equiv -1/2$ [13]] do not lead to the Ising-like critical behavior, whereas the theory developed here does.

Before we address the derivation of the critical exponents, note the following. The possibility of the realization of conditions (6) means that the form of the surfaces of the corresponding coefficients of expansion (3) in the ρ,T space cannot be absolutely arbitrary. In the opposite case, it could be that the equations of the theory no longer admit any solution at some temperature before the coefficients $a_2(T,\rho)$ and $a_3(T,\rho)$ reach the values required by conditions (6). Although such a case is not excluded, in principle, the experimental fact of the existence of the critical point seems to support the admissibility of Eq. (6).

Now, taking into account Eq. (6), from Eq. (1) one can easily find the asymptotic behavior,

$$c_c(r)=[a_4(T_c,\rho_c)+1/4]h_c^4(r), \tag{7}$$

which, as we shall see, is slower than the Lennard-Jones potential $W(r)\sim r^{-6}$ at large r. Now, assuming the powerlike asymptotic dependencies

$$h_c(r)\sim r^{-n}, \quad c_c(r)\sim r^{-m}, \tag{8}$$

we obtain the following from Eq. (7): $m=4n$ (with the supposed $m<6$, $n<3/2$; see below). On the other hand, at $k\to 0$ we have

$$\tilde{h}_c(k)\sim k^{n-3}, \quad \tilde{c}_c(0)-\tilde{c}_c(k)\sim k^{m-3} \tag{9}$$

and then Eq. (5) gives $m+n=6$ (cf. [15]). As a result, we find

$$n=6/5, \quad m=24/5, \tag{10}$$

which justifies the neglect of $W(r)/T$ when deriving the asymptotic form of $c_c(r)$.

Thus, the asymptotic behavior of the total correlation function in the critical point has the form (8) with the exponent n from Eqs. (10) corresponding to Fisher's critical exponent

$$\eta\equiv n-1=1/5, \tag{11}$$

which we have calculated based, in fact, on representation (3).

We emphasize once more that no other pair of values $a_i(T_c,\rho_c)$, $a_j(T_c,\rho_c)$ $(j>i=2,3,\ldots)$ leads to a slower asymptotic behavior of $h_c(r)$ than that corresponding to Eq. (11). This means that the pair of values (6) are exceptional because they must be taking into account the singular character of the critical point.

As is known (see, for example, [14]), using the relations between the critical exponents we can express any of them by means of only two "independent" ones. It is essential that our approach makes it possible to calculate, independently, more than two exponents. In order to show this, let us consider our equations at the critical isochore $\rho=\rho_c$. Introducing the designation $t\equiv T/T_c-1$ and assuming the analytical expansion of the coefficients in Eq. (3) on t (as in the Landau theory [14]), we have, to within the main terms,

$$a_2(t,\rho_c)=-1/2+\hat{a}_2 t, \quad a_3(t,\rho_c)=1/3+\hat{a}_3 t, \tag{12}$$

where $\hat{a}_2$ and $\hat{a}_3$ are some constants. Below, for definiteness, we shall consider the case $t>0$.

Let us calculate the critical exponent ν characterizing the temperature dependence of the correlation length $r_c\sim t^{-\nu}$. From Eqs. (1), (3), and (12) we find the next asymptotic form for $c(r)$ at the critical isochore (retaining the main terms on $t\to+0$),

$$c(r)=\hat{a}_2 t h^2(r)+[a_4(T_c,\rho_c)+1/4]h^4(r). \tag{13}$$

[Note that a general form of the coefficient at $h^2(r)$ in $c(r)$ had been proposed in Ref. [17]; the structure of the corresponding coefficient in Eq. (13) does not contradict, qualitatively, that found in [17].] Now, as in [14], we accept $h(r)=h_c(r)\exp(-r/r_c)$. Further, from Eq. (4) we have at the critical isochore for small t,

$$\tilde{h}(0)=-\frac{1}{\rho_c^2[\tilde{c}(0)-\tilde{c}_c(0)]}. \tag{14}$$

Because the singular parts of all thermodynamic quantities in the vicinity of the critical point will be determined by the

TABLE I. The values of the critical exponents.

	α	β	γ	δ	η	ν
This paper	(0.125)	(0.375)	1.125	(4)	0.2	0.625
Experiment	0.11–0.13[a]	0.325–0.377[b]	1.1–1.4[c]	4.0–4.8[d]	0.09–0.3[e]	0.62–0.63[f]
RG, 3D Ising	≈0.11	≈0.326	≈1.24	≈4.8	≈0.035	≈0.63
Classical	0	0.5	1	3	0	0.5

[a] References [9,10,19–22].
[b] References [9,10,23–30].
[c] References [9,10,28,29,31,32].
[d] References [10,23,28–30].
[e] References [10,23,27,28,31–37].
[f] References [9,18,22,28,32].

asymptotic behavior of the correlation functions, we obtain with the help of Eq. (13)

$$\tilde{c}(0) - \tilde{c}_c(0) = 4\pi \int_0^\infty dr\, r^2 \{\hat{a}_2 t h_c^2(r) e^{-2r/r_c} + [a_4(T_c,\rho_c) + 1/4] h_c^4(r)(e^{-4r/r_c} - 1)\}. \tag{15}$$

It is easy to see that the integral corresponding to the second term in the curly brackets of the integrand in Eq. (15) is $\sim 1/r_c$ when $r_c \to \infty$, because $\int_0^\infty dr\, r^3 h_c^4(r)$ converges at the upper limit. One can make sure that the integral of the first term is $\sim t r_c^{3/5}$. Besides, the explicit calculation gives $\tilde{h}(0) \sim r_c^{9/5}$. As a result, we have from Eqs. (14) and (15), to within the main terms at $t \to +0$,

$$r_c^{-9/5} = \hat{A}_2 t r_c^{3/5} + \hat{A}_4 r_c^{-1}, \tag{16}$$

where $\hat{A}_2$ and $\hat{A}_4$ are some constants. From here (assuming that these constants have opposite signs), at the critical isochore

$$r_c \sim t^{-5/8}, \tag{17}$$

i.e., the critical exponent $\nu = 5/8$ (the classical value is 1/2 [14]). Also, taking into account [15] that the isothermal compressibility at $t \to 0$ is $\kappa_T \sim \tilde{h}(0)$, we find

$$\kappa_T \sim t^{-9/8}, \tag{18}$$

from which the critical exponent $\gamma = 9/8$ (the classical value is 1 [14]).

Thus, starting from representation (3), we have calculated three critical exponents: η, γ, ν; in this case, we have not used any connections between them. The rest of the exponents can be found using the well-known relations [14]; moreover, our calculated values of η, γ, and ν, as can be verified, are consistent with these relations.

In principle, independent calculation of other exponents can be made within the framework of the approach developed. This task, however, requires more sophisticated actions (which will be presented later).

In Table I, we show the following in conventional notation: our calculated values of the exponents (those in parentheses are recovered using the well-known relations); the experimental values for one-component dielectric media (Ar, Xe, CO_2, etc.) and binary critical mixtures; the RG calculations and the numerical results for the 3D Ising model [8,18]; and the classical values of the exponents [14].

First of all, note that our value of η differs sharply from the value calculated in the framework of the RG approach [8,18], but it is within the bounds of the experimental measurements (Table I). Often, when processing the experimental data (see, for example, [9,18]), one uses, in particular, the exponents found for the 3D Ising model, whereas the numerical correction is realized by introducing the additional ("correction-to-scaling" [7]) terms [38]. In this connection, it is useful to give a quantitative description of the experimental data near the critical point of the fluid using only our values of the critical exponents. In Fig. 1, we show the experimental values of the light scattering intensity [18] and their processing by the formula $I(t) = I_0 t^{-\gamma}(1 + \tilde{k}^2 t^{-2\nu})^{-1+\eta/2}$ [18,36] with $\eta = 1/5$, $\gamma = 9/8$, $\nu = 5/8$; $I_0 = 1.986 \times 10^{-2}$, $\tilde{k}^2 = 1.012 \times 10^{-6}$ (solid line).

The analysis of other experiments for fluids [9,18] sometimes demonstrates a tendency to the deviation of the critical exponents β and γ from their values for the 3D Ising model (see, in particular, Refs. [25,26]).

Thus, in the present paper, based on the assumption that the bridge function of a fluid can be represented by the power series over the pair correlation function, we have

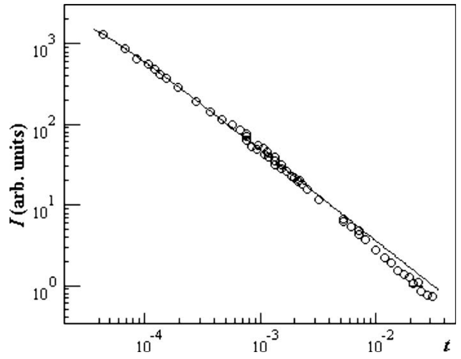

FIG. 1. The experimental (circles [18]) intensity of light scattered by ^{3}He near the critical temperature; the theoretical curve is constructed using our exponents η, γ, ν (see text).

demonstrated the calculation of *three* critical exponents. Some of the exponents, including those calculated with the help of the well-known relations, are in close agreement with the corresponding values for the 3D Ising model; others differ strongly. Although our calculated value of Fisher's exponent η deviates noticeably from the prediction of the RG approach, it is possible to give a good description of the critical light scattering experiments using the found η. On the other hand, the possibility to obtain the nonclassical critical scaling behavior from the theory of fluids means that the results of this theory do not disagree with the Kadanoff-Wilson-Fisher RG approach [4,6].

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