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Statistical theory of critical phenomena in fluids

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We show that there are two classes of the closure equations for the Ornstein-Zernike equation: The analytical equations for the bridge functional $B=B^{(an)}$ like hypernetted-chain approximation, Percus-Yevick approximation, etc., and nonanalytic equation $B=B^{(nan)}$, where $B^{(nan)}=B^{(rg)}+B^{(cr)}$ and $B^{(rg)}$ is the regular (analytical) component of the bridge functional, and $B^{(cr)}$ is the critical (nonanalytical) component of $B^{(nan)}$. The closure equation $B^{(an)}$ defines coordinates of the critical point and other individual features of critical phenomena, and $B^{(nan)}$ defines all the known relations between critical exponents. It is shown, that the necessary condition for existence of the nonanalytic solution of the OZ equation is the equality $5-\eta=\delta(1+\eta)$, where η,δ are the critical exponents, values of which can change in a narrow interval. We also show that the transition from the analytical solution to the nonanalytic one is accompanied by a break of the pressure derivative. The boundaries between the areas, where each of these solutions exists, are indicated on the phase diagram.

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I. INTRODUCTION

Actually, now the critical phenomena theory has been reduced to a scaling theory. The scaling theory states that in a vicinity of a critical point we have the following:

(1) The dependence of thermodynamic parameters a on the density ρ and the temperature $\theta=k_{Bl}T$ has the form as follows:

$$\text{(a)}\quad \Delta a = b\Delta x^{\chi},$$

where $\Delta a=a-a_c$, $\Delta x=\rho-\rho_c$ or $\Delta x=\theta-\theta_c$; ρ_c,θ_c are the coordinates of a critical point, and $\chi=\alpha,\beta,\ldots$ are the critical exponents, i.e., some fractional numbers.

(2) The relations of a type

$$\text{(b)}\quad \gamma=\nu(2-\eta),\quad 3\nu=2-\alpha,\ \text{etc.},$$

link the various critical exponents.

(3) The relations (a) and (b) are universal, i.e., they are identical for all fluids.

However, experiment shows that the dependence Δa on Δx is expressed by a more complicated formula (see [1]),

$$\text{(c)}\quad \Delta a = b\Delta x^{\chi}(1+b_1\Delta x^{\chi_1}+\cdots).$$

Furthermore, the critical exponents can slightly deviate from the values predicted by the scaling theory (see [2]). It is very important that the scaling theory contains only restricted information about the critical phenomena: In this theory it is impossible to determine the critical point coordinates ρ_c,θ_c, to calculate amplitudes b in relations (a), etc. Therefore, we must consider the scaling theory as the first approximation to the general theory of critical phenomena.

The scaling theory is a phenomenological theory because it deals only with the macroscopic characteristics of substance. A statistical theory is necessary to determine the microstructure of fluids. The attempts to build such a theory were made repeatedly. We can indicate two attempts that are more successful than the others: The hierarchical reference theory (HRT [3]) and SCOZA [4–6]. However, these theories are not consecutive statistical theories, as they are partially based on the scaling theory hypotheses. The theory of critical phenomenon, that is different from these approaches, was developed in [7]. It is based only on the fundamental equations of the statistical mechanics. The present paper develops this theory.

II. ASYMPTOTIC OF CORRELATION FUNCTIONS

All critical phenomena are accompanied by the appearance of gigantic fluctuations. In statistical mechanics, their values are determined by asymptotic behavior of correlation functions: The slower is the correlations attenuation, the greater is the characteristic size of fluctuation. The simplest method of investigation of the asymptotic of correlation functions is based on the analysis of the Ornstein-Zernike (OZ) equation, which expresses a condition of the chemical potential constancy (see [8]). In the Fourier components this equation becomes (see [8])

$$1+\rho\hat{h}(k;\rho,\theta)=\frac{1}{1-\rho\hat{C}(k;\rho,\theta)},$$

$$\rho\hat{h}(k;\rho,\theta)=\frac{\rho\hat{C}(k;\rho,\theta)}{1-\rho\hat{C}(k;\rho,\theta)},\tag{1}$$

where

$$\hat{h}(k)=4\pi\int_0^\infty h(r)\frac{\sin(kr)}{kr}r^2dr,$$

$$\hat{C}(k)=4\pi\int_0^\infty C(r)\frac{\sin(kr)}{kr}r^2dr,\tag{2}$$

and $h(r)=\exp[-\varphi(r)+w(r)]-1$ is the total correlation function, $\varphi(r)=\Phi(r)/\theta$ is the dimensionless interaction potential, $C(r)=h-w+B[h]$ is the direct correlation function, and $B[h(r)]$ is the bridge functional. The relations (1) and (2) are

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unambiguous consequences of the Gibbs distribution.

As far as we are interested in the distances $r \to \infty$, we should research the OZ equation (1) in a limit $k \to 0$. To do this we must take into account, that by definition (see [8])

$$\kappa_\theta(\rho,\theta) = \frac{\theta}{\partial P(\rho,\theta)/\partial\rho},$$

$$\kappa_\theta = 1 + \rho\hat{h}(0), \quad \frac{1}{\theta}\frac{\partial P(\rho,\theta)}{\partial\rho} = 1 - \rho\hat{C}(0), \tag{3}$$

where κ_θ is the isothermal compressibility and P is the pressure.

It is possible to show, that at $k \to 0$ the direct correlation function becomes (see the Appendix)

$$C(k) = C(0) + k^2 C^*(0) + k^3 4\pi a \int_0^\infty \zeta(x)\frac{dx}{x^4}, \tag{4}$$

where $\hat{C}(0) = 4\pi\int_0^\infty C(r)r^2 dr$ and $\hat{C}^*(0) = \frac{4\pi}{3!}\int_0^\infty C(r)r^4 dr$. Substituting Eq. (4) into Eq. (1) and omitting the term with k^3, we obtain

$$\rho\hat{h}(k) \to \frac{\rho\hat{C}(0) - k^2\rho\hat{C}^*(0)}{[1-\rho\hat{C}(0)] + k^2\rho\hat{C}^*(0)}.$$

By definition in the critical point $\partial P/\partial\rho = 0$ and, therefore, $\rho_c\hat{C}(0;\rho_c,\theta_c) \to 1$. Supposing

$$\hat{C}(0;\rho,\theta) = \hat{C}(0;\rho_c,\theta_c) + \Delta\hat{C}(0;\rho,\theta)$$

and taking into account that $\Delta\hat{C}(0) \to 0$ at $\Delta\rho, \Delta\theta \to 0$, we obtain

$$\rho\hat{h}(k) \to \frac{1 - \rho[\Delta\hat{C}(0) + k^2\hat{C}^*(0)]}{\rho[\Delta\hat{C}(0) + k^2\hat{C}^*(0)]}.$$

The expression in the square brackets in the numerator can be omitted, as far as with approach to the critical point $\Delta\hat{C}(0) \to 0$ and $k \to 0$. At the same time in the denominator nothing can be neglected, as far as $\Delta\hat{C}(0) \approx k^2\hat{C}^*(0)$. As the result we have

$$\rho\hat{h}(k) \to \frac{1}{\rho\hat{C}^*(0)}\frac{1}{\lambda^2 + k^2}, \quad \lambda = \sqrt{\Delta\hat{C}(0)/\hat{C}^*(0)}. \tag{5}$$

After the inverse Fourier transform we obtain

$$h(r) = A\frac{e^{-\lambda r}}{r}, \quad 4\pi\rho A = \frac{1}{\rho\hat{C}^*(0)} = \frac{6}{4\pi\rho\int_0^\infty C(r)r^4 dr}. \tag{6}$$

These are well-known formulas which were obtained by Ornstein and Zernike. Let us remark, that they are true only in the vicinity of the critical point where $\Delta\hat{C}(0) \to 0$; far from the critical point $\Delta\hat{C}(0)$ have a finite value and, therefore, here

$$\Delta\hat{C}(0) \gg k^2\hat{C}^*(0) \to 0 \quad \text{and } \rho\hat{h}(k) \to 1/\rho\Delta\hat{C}(0) = \text{const}.$$

From (3) and (6) follows, that the isothermal compressibility in the critical point is

$$\kappa_\theta = 1 + 4\pi\rho\int_0^\infty h(r)r^2 dr = 4\pi\rho\frac{A}{\lambda^2} \to \infty \quad \text{for } \lambda \to 0 \tag{7}$$

and that the pressure

$$\frac{1}{\theta}\frac{\partial P}{\partial\rho} = 1 - \rho\hat{C}(0;\rho,\theta) = \rho\Delta\hat{C}(0;\rho,\theta) \to 0,$$

$$\frac{1}{\theta_c}P(\rho_c,\theta_c) = \text{const}. \tag{8}$$

Both these predictions of the OZ theory were confirmed by experiment. Furthermore, if we make approximation of the bridge functional $B[h]$ by the closure equation $B(h)$, as it is done in the theory of fluids, we shall obtain the opportunity to calculate the coordinates of a critical point using (8). If the closure equation is selected successfully enough, the values ρ_c, θ_c obtained this way are sufficiently exact. Thus, for example, the equation of closure MSV[1] for the Lennard-Jones (LJ) potential gives $\rho_c \approx 0.28$, $\theta_c \approx 1.32$ (see [9]), which differs several percentages from the data of numerical experiment $\rho_c \approx 0.304$, $\theta_c \approx 1.312$. Probably, we can obtain more exact values of the coordinates if we use a more precise closure equation.

Despite of all this, now the OZ theory is considered as invalid because it gives rise to incorrect critical exponents (see [10]). However, the OZ equation is an unambiguous corollary of the Gibbs distribution and, therefore, an unambiguous corollary of the statistical mechanics postulates. On these grounds, I believe that the statement about an inaccuracy of the OZ equation and all formulas obtained from it, is too hasty.

III. TWO SOLUTIONS OF THE OZ EQUATION

Analytic solution. Usually it is supposed that the direct correlation function $C = C^{(an)}(r;\rho,\theta)$ is the analytical function of density ρ [index (an)]. If we expand this function into a series on $\Delta\rho$ and take into account, that in the critical point $\partial P/\partial\Delta\rho = \partial^2 P/\partial\Delta\rho^2 = 0$, we shall obtain

$$\frac{1}{\theta}\frac{\partial P}{\partial\rho} = \Delta\hat{C}(0) = \sum_{j=1}^{\infty} j\Delta\rho^{j-1}a_j(\theta), \quad \text{where } a_1(\theta_c) = a_2(\theta_c) = 0. \tag{9}$$

The classical critical exponents at once follow from this equation. However, the OZ equation belongs to the class of strongly nonlinear equations. The equations of this class may have many solutions. We shall show now, that the OZ equation aside from the analytical solution has also a nonanalytic solution [index (nan)].

Non analytic solution. We will begin the search of the nonanalytic solution with the postulate that exponential dependence $h(r) = Ae^{-\lambda r}/r$ from distance r [see Eq. (6)] should

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[1] In [9] these equations are referred to as the equation of Vompe-Martynov (VM). Historically they are more correctly named as equation of Martynov-Sarkisov-Vompe (MSV).

be the same in any case because it is an unambiguous consequence of the OZ equation (1) and three conditions, fulfilling of which is obligatory in the critical point vicinity,[2]

$$\Delta\hat{C}(0)\to 0, \quad k\to 0, \quad \text{and } \kappa_\theta\to\infty. \tag{10}$$

If this condition is true, the nonanalytic solution can differ from the analytical one only by a form of dependences $A=A(\rho,\theta)$, $\lambda=\lambda(\rho,\theta)$. This dependence is defined by the direct correlation function [see (5) and (6)]. Therefore, first we must define the direct correlation function $C^{(nan)}=C^{(nan)}(r;\rho,\theta)$.

The direct correlation function. Obviously, isothermal compressibility, which is determined by formula (7), can tend to infinity in the critical point not only if $\kappa_\theta \sim A/\lambda^2$, where $A=1/\rho\hat{C}^*(0)>0$, but also in the case of

$$A=A_0\lambda^\eta\to 0, \quad \kappa_\theta=4\pi\rho\frac{A_0\lambda^\eta}{\lambda^2}=4\pi\rho\frac{A_0}{\lambda^{2-\eta}}\to\infty, \tag{11}$$

where $0<\eta<2$ is a new critical exponent. However, formula $h=A_0\lambda^\eta\exp(-\lambda r)/r\equiv\psi(r)$ describes only the asymptotic of the total correlation function. A more general form of $h(r)$ is the expression $h(r)=\psi(r)+\Psi(r)$ (the proof of this statement is given in [7]). In this case, the bridge functional $B[h]=B[\psi+\Psi]$ can be expanded into a series of degrees $\psi\sim\lambda^\eta\to 0$. It gives

$$\begin{aligned} B &= B^{(rg)}[\Psi]-b\psi^\delta+\cdots = B^{(rg)}[\Psi]-b\left(A_0\lambda^\eta\frac{e^{-\lambda r}}{r}\right)^\delta+\cdots \\ &= B^{(rg)}[\Psi]+B^{(cr)}(\psi), \end{aligned} \tag{12}$$

where the regular component of the bridge functional $B^{(rg)}[\Psi]$ is an analytical function of ρ and θ, whereas the critical component $B^{(cr)}[\psi]\equiv C^{(cr)}(r)=-b(A_0\lambda^\eta\frac{e^{-\lambda r}}{r})^\delta$ is nonanalytic function of the same variables (here δ is one more critical index). We set $x=r$, where x is dimensionless distance, which is gauged in the correlation radii $R=1/\lambda$. In this case we obtain $C^{(cr)}=-bA_0^\delta\lambda^{\delta(1+\eta)}e^{-\delta x}/x^\delta$. Probably, it is necessary to take into account [in the expansion equation (12)] the high terms of a series, that possibly define the correction terms in the formula (C). However, here we shall restrict ourselves by the two first terms. Thus we assume that $B[h]=B^{(rg)}[\Psi]+B^{(cr)}(\psi)$. It is apparent, that $B^{(rg)}[\Psi]\neq B^{(an)}[h]$, as far as $B^{(an)}[h]$ depends on h, whereas $B^{(rg)}[\Psi]$ depends on Ψ. Besides it is necessary to take into account, that in a vicinity of a critical point the radius of correlation $R=1/\lambda\gg R_\Phi$, where R_Φ is that distance, on which the interaction potential $\Phi(r)$ practically turns into zero. Owing to this, the critical component $C^{(cr)}(r)$ cannot influence on the distribution of particles on small distances—here, all are determined by the regular component $C^{(rg)}[\Psi(r)]$. Because of this, let us assume that $C^{(cr)}(r)$ is equal to zero on distances $r<aR$, i.e., let us assume

$$b=\begin{cases} 0 & \text{at } x<a, \\ 1 & \text{at } x>a. \end{cases}$$

As will be shown below, $a\approx 2.29$.

So, we shall consider that

$$\begin{aligned} C^{(nan)}(r) &= (h-w+\rho^2B^{(rg)}[\Psi])-B^{(cr)}[\psi] \\ &= C^{(rg)}(r;\rho,\theta)+C^{(cr)}[\psi(r)] \\ &= \begin{cases} C^{(rg)} & \text{at } x<a,\ r<a/\lambda, \\ C^{(rg)}+C^{(cr)} & \text{at } x>a,\ r>a/\lambda. \end{cases} \end{aligned} \tag{13}$$

At $\lambda\to 0$ the interval of existence of the critical component $a/\lambda<r<\infty$ disappears. Consequently in the critical point, where $\lambda=0$, the state of the system is defined only by $C^{(rg)}$ on all intervals $0<r<\infty$. Simultaneously, the total correlation function takes the form $h=A(e^{-\lambda r}/r)_{\lambda=0}=A/r$. Due to this, the integrals into Eq. (2) are divergent at infinity.

Conditions of existence of nonanalytic solution. Substituting Eq. (13) into Eq. (8) for derivative pressures and expanding $C^{(rg)}(\rho_c+\Delta\rho,\theta_c+\Delta\theta)$ in a series on $\Delta\rho=\rho-\rho_c$, we obtain

$$\begin{aligned} \frac{1}{\theta}\frac{\partial P}{\partial\rho} &= 1-\rho\hat{C}(0;\rho,\theta)\equiv\left(1-4\pi\rho_c\int_0^\infty C^{(rg)}(r;\rho_c,\theta_c)r^2dr\right) \\ &\quad +\Delta\hat{C}^{(nan)}(0;\rho,\theta), \end{aligned} \tag{14}$$

where

$$\begin{aligned} \Delta\hat{C}^{(nan)}(0) &= \Delta\hat{C}^{(rg)}+\Delta\hat{C}^{(cr)} \\ &= \sum_{j=1}^{\infty} jb_j(\theta)\Delta\rho^{j-1} \\ &\quad +4\pi\rho A_0^\delta\lambda^{\delta(1+\eta)-3}\int_a^\infty e^{-\delta x}x^{2-\delta}dx. \end{aligned} \tag{15}$$

These formulas differ from Eq. (9) only by replacement of coefficients $a_j(\theta)$ on $b_j(\theta)$ in $\Delta\hat{C}^{(rg)}(0)=\Sigma_{j=1}^\infty j\Delta\rho^{j-1}b_j(\theta)$ and appearance of an integral term in Eq. (15). In the critical point, where $\lambda=0$, this integral must disappear. It is possible only if $\delta(1+\eta)-3>0$. We shall assume that this condition is fulfilled. In this case, at the critical point Eq. (14) takes the form

$$\frac{1}{\theta_c}\frac{\partial P(\rho_c,\theta_c)}{\partial\rho}=1-4\pi\rho_c\int_0^\infty C^{(rg)}(r;\rho_c,\theta_c)r^2dr=0. \tag{16}$$

In this equation $C^{(rg)}$ there is a known analytical function of ρ,θ, which is defined by the closure equation as it is done in the fluid theory. As a result, Eqs. (14) and (15) are reduced to

$$\begin{aligned} \frac{1}{\theta}\frac{\partial P}{\partial\Delta\rho} &= \Delta\hat{C}(0;\rho,\theta) \\ &= \sum_{j=1}^{\infty} jb_j(\theta)\Delta\rho^{j-1} \\ &\quad +4\pi\rho A_0^\delta\lambda^{\delta(1+\eta)-3}\int_a^\infty e^{-\delta x}x^{2-\delta}dx. \end{aligned} \tag{17}$$

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[2] I wish to remind the reader that the conditions $\Delta\hat{C}(0)=0$, $\kappa_\theta=\infty$ are a result of the condition $\partial P/\partial\rho=0$, whereas the condition $k=0$ is a result of gigantic fluctuations in the critical point vicinity.

Substituting (11) and (14) in the asymptotic OZ equation $\hat{h}(0)=1/[1-\rho\hat{C}(0)]$ and taking into account Eqs. (11) and (15), we obtain

$$4\pi\rho\frac{A_0}{\lambda^{2-\eta}}=\frac{1}{\Delta C^{(rg)}(0;\rho,\theta)+4\pi\rho A_0^{\delta}\lambda^{\delta(1+\eta)-3}\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx}. \tag{18}$$

In order to fulfill this equality for arbitrary $\lambda=\lambda(\rho,\theta)$, it is necessary, that $\Delta C^{(rg)}(0;\rho,\theta)$ tends to zero faster than an integral term with approach to the critical point. If this condition is fulfilled, this term in Eq. (18) can be neglected. After equaling exponents at λ in the left- and right-hand parts of Eq. (18), we obtain

$$2-\eta=\delta(1+\eta)-3, \quad 5-\delta(1+\eta)=\eta. \tag{19}$$

This equality is a necessary condition of existence for the nonanalytical solution. It is known in the critical phenomena theory for a long time. However, the physical meaning of this condition was unknown (see [10]).

One more necessary condition for the existence of a nonanalytic solution we can obtain from a condition $\Delta\hat{C}^{(rg)}(0)+\hat{C}^{(cr)}(0)\to\hat{C}^{(cr)}(0)$ at $\lambda\to 0$. As far as

$$\Delta\hat{C}^{(rg)}(0;\rho,\theta)=\sum_{j=1}^{\infty}jb_j(\theta)\Delta\rho^{j-1},$$

then the regular component disappears faster than the critical one only if

$$b_j(\theta_c)=0 \quad \text{at } j=1,\ldots,4 \tag{20}$$

[in the case of analytical solution the weaker condition $a_1(\theta_c)=a_2(\theta_c)=0$ was true; see (9)].

Definition of the constant a. If the conditions (19) and (20) are fulfilled, we obtain

$$4\pi\rho\frac{A_0}{\lambda^{2-\eta}}=\frac{1}{4\pi\rho A_0^{\delta}\lambda^{2-\eta}\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx}.$$

Canceling this equality on $\lambda^{2-\eta}$, we obtain the equation for the definition of the amplitude A_0,

$$4\pi\rho A_0=\frac{1}{4\pi\rho A_0^{\delta}\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx}. \tag{21}$$

At the same time substitution $\hat{C}^{(nan)}(r)=\hat{C}^{(rg)}(r)+\hat{C}^{(cr)}(r)$ into Eq. (6) gives

$$\begin{aligned}A=A_0\lambda^{\eta}&=\frac{6}{(4\pi\rho)^2\int_0^{\infty}C(r)r^4dr}\\&=\frac{6}{(4\pi\rho)^2\int_0^{\infty}[C^{(rg)}(r)+C^{(cr)}(r)r^4dr}\\&=\frac{6}{(4\pi\rho)^2\int_0^{\infty}C^{(rg)}(r)r^4dr+(4\pi\rho)^2\lambda^{-\eta}A_0^{\delta}\int_a^{\infty}e^{-\delta x}x^{4-\delta}dx}.\end{aligned} \tag{22}$$

At $\lambda\to 0$ the contribution of the regular component into the denominator (22) can be neglected, as $\lambda^{-\eta}\to\infty$. Canceling after this the left- and right-hand sides of this expression on λ^{η}, we will obtain one more formula for definition of amplitude A_0,

$$4\pi\rho A_0=\frac{6}{4\pi\rho A_0^{\delta}\int_a^{\infty}e^{-\delta x}x^{4-\delta}dx}. \tag{23}$$

Equating values A_0 from (21) and (23), we shall obtain the equation for definition of a constant a for a given value of an index δ,

$$\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx=\frac{1}{6}\int_a^{\infty}e^{-\delta x}x^{4-\delta}dx. \tag{24}$$

Index δ should be located always in an interval $4.0<\delta<5.0$, because for $\delta=4$ the nonanalytic solution becomes analytical, and for $\delta=5$ index $\eta=0$ [see Eq. (19)]. It follows from Eq. (24) that interval $4.0<\delta<5.0$ for δ correlates with interval $2.28<a<2.30$ for a. Supposing that $a\approx 2.29$, we shall obtain

$$A_0=\frac{13.3}{(4\pi\rho)^{0.344}}. \tag{25}$$

At last, from Eq. (5) it follows that

$$\begin{aligned}\lambda^2&=\frac{\Delta\hat{C}(0)}{\hat{C}*(0)}\\&=\frac{\int_0^{\infty}\Delta C^{(rg)}(r;\Delta\rho,\Delta\theta)r^2dr+A_0^{\delta}\lambda^{2-\eta}\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx}{\frac{1}{6}\int_0^{\infty}C^{(rg)}(r;\Delta\rho,\Delta\theta)r^4dr+\frac{1}{6}\lambda^{-\eta}A_0^{\delta}\int_a^{\infty}e^{-\delta x}x^{4-\delta}dx}.\end{aligned} \tag{26}$$

This formula determines the dependence $\lambda=\lambda(\Delta\rho,\Delta\theta)$ in the critical point vicinity; in the same critical point this expression degenerates into identity $0=0$.

IV. CRITICAL EXPONENT

Pressure. Let us expand $\lambda(\rho,\theta)=\lambda(\rho_c+\Delta\rho,\theta_c+\Delta\theta)$ into a series on $\Delta\rho,\Delta\theta$ and take into account the condition $\lambda(\rho_c,\theta_c)=0$. After this we obtain

$$\lambda(\rho,\theta)=\lambda_{\rho}\Delta\rho^{\mu}+\lambda_{\theta}\Delta\theta^{\nu}+\cdots, \tag{27}$$

where μ,ν are new critical exponents, and $\lambda_{\rho},\lambda_{\theta}$ are the amplitudes corresponding to them. At $\Delta\theta=0$ this relation is reduced to $\lambda(\Delta\rho,0)=\lambda_{\rho}\Delta\rho^{\mu}$. Substituting this expression into Eq. (17) and taking into account Eq. (20), we shall obtain

$$\frac{1}{\theta_c}\frac{\partial P(\Delta\rho,0)}{\partial\Delta\rho}=4\pi\rho_c A_0^{\delta}(\lambda_{\rho}\Delta\rho^{\mu})^{2-\eta}\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx+\sum_{j=5}^{\infty}jb_j(\theta_c)\Delta\rho^{j}.$$

After integration over $\Delta\rho$ it gives

$$\frac{1}{\theta_c}[P(\rho,\theta_c)-P_c]=\chi\Delta\rho^{\delta}+\sum_{j=5}^{\infty}b_j(\theta_c)\Delta\rho^{j}, \tag{28}$$

where

$$\chi=\frac{A_0^{\delta}\lambda_\rho^{2-\eta}}{(2-\eta)\mu+1}4\pi\rho_c\int_a^{\infty}e^{-\delta x}x^{2-\delta}dx=\text{const},$$

$$\delta=(2-\eta)\mu+1. \tag{29}$$

Substituting $\delta=4$, $\eta=0.2$ and $\delta=5$, $\eta=0$ into $\mu=(\delta-1)/(2-\eta)$, we obtain an inequality $1.7<\mu<2.0$. Approaching the critical point the sum $\Sigma_{j=5}^{\infty}jb_j(\theta_c)\Delta\rho^{j-1}$ decreases as $\Delta\rho^5$, whereas the nonanalytic term varies by the law $\Delta\rho^{\delta}$, where $4<\delta<5$. Therefore, near the critical point we can neglect this sum. After this, Eq. (28) turns into the following expression, which is well known in the scaling theory (see [8,10]):

$$P=P_c+\theta_c\chi\Delta\rho^{\delta}. \tag{30}$$

Coupled equations for critical exponents. Substituting λ from Eq. (27) into Eq. (11) we obtain

$$R=\frac{1}{\lambda}=\frac{1}{\lambda_\rho\Delta\rho^{\mu}+\lambda_\theta\Delta\theta^{\nu}}, \tag{31}$$

One can see that $R\sim 1/\Delta\rho^{\mu}$ at $\Delta\theta=0$ and that $R\sim 1/\Delta\theta^{\nu}$ at $\Delta\rho=0$. The last relation is well known in the scaling theory, where $\nu\approx 0.63$ (see [8,10]).

We can obtain, after substitution λ from Eq. (27) into Eq. (11),

$$\kappa_\theta=\frac{4\pi\rho_c A_0}{(\lambda_\rho\Delta\rho^{\mu}+\lambda_\theta\Delta\theta^{\nu})^{2-\eta}}. \tag{32}$$

At $\Delta\rho=0$ the relation (32) is reduced to $\kappa^{(cr)}\sim 1/\Delta\theta^{\gamma}$, where the critical exponent $\gamma=\nu(2-\eta)$. This relation is also well known in the critical phenomena theory (see [8,10]).

Until now, we considered behavior of thermodynamic parameters either at the critical isochors $\Delta\rho=0$, $\Delta\theta\neq 0$, or at the critical isotherm $\Delta\rho\neq 0$, $\Delta\theta=0$. Let us consider now their behavior in the case when we approach to a critical point along a ray $\Delta\rho=k\Delta\theta$. Substituting this expression into (27), we shall obtain $\lambda=\lambda_\theta\Delta\theta^{\nu}[1+(\lambda_\rho k^{\mu}/\lambda_\theta)\Delta\theta^{\mu-\nu}]$. As far as $\mu>\nu$, in this case the logarithmic decrement λ will tend to $\lambda=\lambda_\theta\Delta\theta^{\nu}$, and equalities (31) and (32) will transform into

$$R\sim\frac{1}{\Delta\theta^{\nu}},\quad \kappa_\theta\sim\frac{1}{\Delta\theta^{\gamma}}. \tag{33}$$

These relations appear in the scaling theory just in such form (see [8,10]).

Let us consider Eq. (17) for the pressure derivative. In the case of approaching to the critical point along the ray $\Delta\rho=k\Delta\theta$,

$$\frac{1}{\theta}\frac{\partial P}{\partial\Delta\rho}=\sum_{j=5}^{\infty}jb_j(\theta)\Delta\rho^{j-1}+\mathrm{A}\Delta\theta^{\gamma}=\sum_{j=5}^{\infty}jb_j(\theta)\Delta\rho^{j-1}+\mathrm{A}k^{\gamma}\Delta\rho^{\gamma}.$$

Integration of this expression on $\Delta\rho$ and setting $\lambda=\lambda_\theta\Delta\theta^{\nu}$ gives

$$P=P_c+\theta\sum_{j=5}^{\infty}b_j(\theta)\Delta\rho^{j}+\mathrm{A}\frac{\Delta\theta^{\gamma+1}}{\gamma+1}. \tag{34}$$

All relations, obtained in this section, do not depend on an interaction potential—they are an unambiguous consequence only of the condition of existence of the nonanalytic solution, Eq. (19) [and, certainly, the consequence of Eqs. (7) and (8), defining the pressure and the compressibility]. Therefore, they are universal, i.e., do not depend on the fluid nature.

Critical exponents. It is usually supposed, that the critical exponents δ,η,γ presented above are universal too. However, this point of view contradicts the statistical mechanics results. Really, the exact solutions for face-centered lattice of crystal and for volumetric-centered lattice give $\eta=0.297$ for the first case and $\eta=0.318$ for the second case (see [11]). As far as the crystal lattice is formed as a result of the particle interaction, apparently, the different lattices are matched by different interaction potentials. Although this dependence is rather feeble, it really exists. This conclusion is confirmed by the OZ equation. We show above that the index δ should lie in the interval $4<\delta<5$. To determine the more precise value of δ we must formulate a new condition, basing only on the statistical mechanics postulates. I was not able to find this condition. Besides the data of experiments unambiguously indicate, that the critical exponents of different fluids differ a little from each other. On these facts, I came to the conclusion, that the index δ is the individual characteristic of a given fluid. If my idea is right, it means, that in the theory of critical phenomena we must preset the value of δ as well as we preset the potential in the Gibbs theory.

All critical exponents are divided into two groups. The first group, including δ, η, and μ, determines the dependence of the thermodynamic parameters on the density. The values may be uniquely defined by the coupled equations $5-\delta(1+\eta)=\eta$ and $\mu=(\delta-1)/(2-\eta)$ if only the value of δ is known. The second group incorporates the critical exponents ν and $\gamma=\nu(2-\eta)$ defining the dependence of thermodynamic parameters on temperature $\Delta\theta$. For their definition it is necessary to know an index ν. Probably, they are also the individual characteristic of fluids. In any case, the fact that the temperature always appears in all statistical mechanics equations only as the ratio $\Phi(r)/\theta$, points to this. Therefore, different potentials (i.e., different fluids) must correspond to the different values of critical exponents. However, this dependence, most likely, will be feeble too, as far as the potential stands under the integral in $\Delta\hat{C}^{(rg)}(0;\rho,\theta)$.

Thus, I believe, that only the coupling equations, which determine the dependence of one index of a given fluid from another, are universal; absolute value of the critical exponents in these equations can vary at transitions from one fluid to another.

V. PHASE DIAGRAM OF FLUIDS

Two solutions. We have shown above that the OZ equation has only two solutions satisfying the condition of turning of the isothermal compressibility into infinity at the critical point; there are no other solutions that would satisfy this

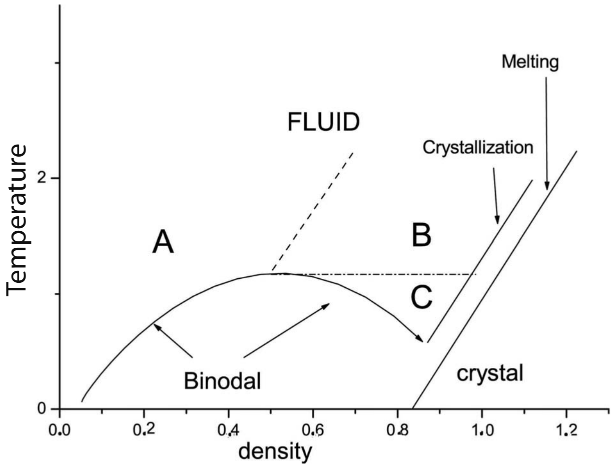

FIG. 1. The phase diagram of simple fluids. Dashed line is the line of the virial series divergence. Dashed-dotted line is the critical isotherm.

condition. From the formal point of view, both solutions are equivalent. However, at small densities the analytical solution must be true, because in the gas area of the phase diagram all thermodynamic parameters can be expanded into a series on the integer density degrees (proof of this is given in [12,13]. In its turn, the nonanalytic solution should be valid in the critical point vicinity, as from this solution follows the correct value of the critical exponents. The question arises: How does one solution transform into another? The trivial answer is the following: The critical component of direct correlation function $C^{(cr)}$ tends to zero with removal from the critical point. It is not appropriate obviously as far as $C^{(cr)} \sim \lambda^{2-\eta}$ and, hence, the critical component of the direct correlation function is also increasing with the increase of λ. Only one possibility is left: To suppose that the area of one solution's existence is separated from the area of the other solution's existence by a curve of singular points of the statistical sum. However, what is the nature of these points? It is necessary to search the answer to this question in the analysis of the pressure and its derivatives, as far as the OZ equation is closely related with P and $\partial P/\partial\rho$. It is a well-known fact, that the pressure is a continuous function of the density and the temperature on all phase planes. Therefore, the appearance of the singular points can be linked only with the behavior of the pressure derivatives, as far as they can vary by step (that always occurs on the phase equilibrium curve).

Regular area. At small densities the pressure always can be expanded in a virial series $P=\Sigma\rho^k B_k(\theta)$ (see [12,13]). Inside of the series existence interval $0\leqslant\rho<\mathrm{Re}(\theta)$ any singularities cannot exist; as the singular points can lay only on the curve $\rho=\mathrm{Re}(\theta)$, where this series diverges.

As shown in [14], below critical temperature the curve $\rho=\mathrm{Re}(\theta)$ coincides with the curve of the vapor condensation $\rho=\rho_{cnd}(\theta)$. In the critical point, the curve $\rho=\mathrm{Re}(\theta)$ has a point of inflection. After this, it goes to infinity with further rise of temperature (see Fig. 1). As it is known, on the curve of evaporation at $\theta<\theta_c$ the derivative of pressure is changed by the jump from $\frac{\partial P}{\partial\rho}\equiv\frac{\partial P^{(-)}}{\partial\rho}>0$ in gas area up to $\frac{\partial P^{(+)}}{\partial\rho}=0$ in two-phase area. Approaching the critical point the jump of derivatives becomes less and less, and in the critical point itself it becomes equal to zero. However, at $\theta>\theta_c$, the curve of a virial series divergence $\rho=\mathrm{Re}(\theta)$ also is a line of points, where the derivative $\partial P/\partial\rho$ is changing by a jump. It will be obvious in Fig. 2 that the derivatives are a smooth function of ρ at $\rho<\mathrm{Re}(\theta)$ and it becomes equal to infinity only in the points $\rho=\mathrm{Re}(\theta)$ (this jump becomes notable only at the consideration of a large number n of terms of a virial series). The reason of appearance of such jumps can be only the transition from the regular solution to the critical one. It is difficult to suggest another explanation.

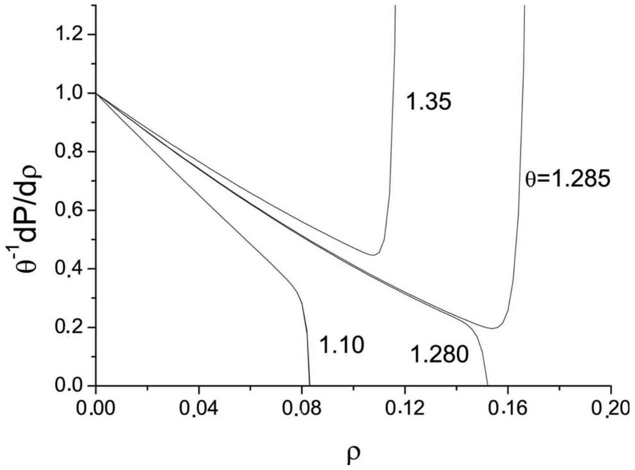

FIG. 2. Dependence $\partial P/\partial\rho$ on density ρ for the Lennard-Jones potential at isotherms θ=1.10, 1.280, 1.285, 1.30 (the data [14]. At subcritical temperature, $\theta<\theta_c\approx 1.283$, the derivative on the binodal turns into zero by jumping; at supercritical temperature, $\theta>\theta_c$ it turns into infinity. The curves are calculated with the use of 70 terms of a virial series. Reference [14] shows that the more terms of a series that are taken into account, the jump of the derivative becomes sharper.

Supercritical area. Let us consider now the area B in Fig. 1, which is located on the right-hand side from $\rho=\mathrm{Re}(\theta)$. This area is limited from below by the critical isotherm, where $\partial P^{(+)}/\partial\Delta\theta$ becomes equal to infinity. In order to confirm this assertion, we shall consider Eq. (17). Differentiating this equality on temperature, we shall receive

$$\frac{1}{\theta}\frac{\partial^2 P(\Delta\rho,\Delta\theta)}{\partial\Delta\rho\partial\Delta\theta}=\mathrm{const}(2-\eta)\lambda^{1-\eta}\frac{\partial\lambda}{\partial\Delta\theta}+\sum_{j=5}^{\infty} j\frac{\partial b_j(\Delta\theta)}{\partial\Delta\theta}\Delta\rho^{j-1}.$$

As $\lambda(\rho,\theta)=\lambda_\rho\Delta\rho^\mu+\lambda_\theta\Delta\theta^\nu$, where $\nu\approx 0.63$ [see (31)], the derivative $\partial\lambda/\partial\Delta\nu=0.63\lambda_\theta/\Delta\theta^{0.37}$. From this follows that $\partial\lambda/\partial\Delta\theta\to\infty$ at $\Delta\theta=\theta-\theta_c\to 0$. Therefore, at any $\lambda>0$,

$$\frac{\partial^2 P}{\partial\rho\partial\theta}=\infty,\quad \theta=\theta_c,\quad \rho_c<\rho<\rho_{cr}(\theta_c). \tag{35}$$

It is obvious that the critical isotherm is a line of singular points. This line, most probably, is ended on the crystallization curve $\rho_{cr}=\rho_{cr}(\theta)$, because there are not any indications that it can be ended somewhere between $\rho=\rho_c$ and $\rho=\rho_{cr}(\theta_c)$.

The hypothesis according to which the critical isotherm is the singular points line on an interval $\rho_c<\rho<\rho_{cr}$, was con-

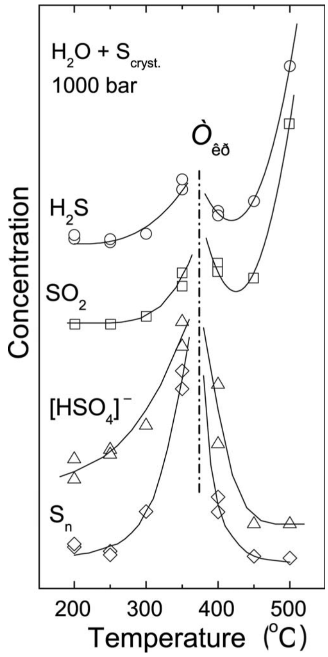

FIG. 3. The dependence of a solubility H_2S, SO_2, $[HSO^4_-$, S in water from temperature in a vicinity of a critical isotherm $T=3.74$ °C at pressure $P=1000$ atm. $\approx 5P_c$, where critical pressure $P=1000$ atm. $=5P_c$ and $P_c=218$ atm.. The reaction of dissolution is converted in Ref. [17]

firmed by Baxter for a system of sticky spheres (see [15]). By solving the Percus-Yevick equation, he found, that the analytical solution of this equation exists only at $\theta > \theta_c$. At the critical isotherm $\theta=\theta_c$ this solution disappears (see [15,16]). Until now, this result has been considered as an artifact. However, it follows from the formula (35) that it is true, because on the line of singular points the solution must change by a jump.

The experimental data also show that near the critical isotherm appears the area of anomalous behavior of fluids. For example, in water the derivative of the sound velocity on the temperature $\partial c_s/\partial\theta$ has a minimum at the critical isotherm for any density and the less the value of $\Delta\rho$ is, the more evident this minimum is. Simultaneously the parameter of water solubility has a rupture at the critical isotherm (see [1,17] and Fig. 3). It is interesting that the sizes of area of anomalous behavior of the water exceed many times the size of the region that we usually call "the vicinity of the critical point."

Thus, the area B in Fig. 1 is separated from all other areas by the lines of the hidden phase transitions, where $\partial^2 P/\partial\rho^2$ or $\partial^2 P/\partial\rho\partial\theta$ is changed by the jump.

I would like to make two remarks.

(A) In various fluids the area B can have various forms and distinct sizes, as the radius of convergence of a virial series $\rho=\mathrm{Re}(\theta)$ should be different for different fluids.

(B) We can distinguish inside B the area of similarity in which the inequality $C^{(cr)} \gg C^{(rg)}$ is true. In this area all thermodynamic parameters $a(\rho,\theta)$ are the functions of the logarithmic decrement $\lambda=\lambda(\Delta\rho,\Delta\theta)$. Therefore, selecting an appropriate scale of measurement λ and joining together the coordinates of the critical points of different fluids in one point of the phase diagram, we shall find out, that the values of thermodynamic parameters $a=a(\lambda)$ for different substances will be the same. This remark is a substantiation of van der Waals similarity law.

The area of the liquid states. As follows from Fig. 1, the area of liquid state is separated from the area of supercritical temperatures by the critical isotherm $\theta=\theta_c$. It is difficult to tell which solution dominates this area. It is likely, that the solution becomes analytical again.

VI. BINODAL AND THERMAL CAPACITY

The critical exponents η, δ, μ, ν and all relations obtained above are the consequences of nonanalyticity of the direct correlation function $C^{(cr)}$. But along with $C^{(cr)}$ the direct correlation function C includes also the analytical components $C^{(an)}(r)$ and $C^{(rg)}(r)$. We will show below that they determine the thermal capacity and the binodal form in the critical point vicinity.

Thermal capacity. Let us suppose, that we approach the critical point from the area A in Fig. 1 where the solution is analytical by definition. As we know, in statistical mechanics the specific heat at constant volume c_V is defined by the formulas

$$e = \frac{3}{2}\theta + \frac{1}{2}\rho\int_0^\infty \Phi(r)G(r)4\pi r^2 dr,$$

$$c_V = \frac{\partial e}{\partial\theta} = \frac{3}{2} + \frac{1}{2}\rho\int_0^\infty \Phi(r)\frac{\partial h(r)}{\partial\theta}4\pi r^2 dr, \qquad (36)$$

where e is the internal energy and $h=G-1$. According to the known thermodynamic identity the derivative (see [8]) is

$$\frac{\partial e}{\partial\rho} = -\frac{\theta^2}{\rho^2}\frac{\partial}{\partial\theta}\left(\frac{P}{\theta}\right).$$

After inserting $P=\rho\theta+\sum_{j=2}^{\infty}\rho^j B_j(\theta)$ into the right-hand side of this identity, integration over ρ and differentiation on θ we obtain

$$c_V = c_V^{(0)} - \theta\sum_{j=2}^{\theta}\frac{\rho^{j-1}}{j-1}\frac{\partial^2 B_j(\theta)}{\partial\theta^2}. \qquad (37)$$

Obviously, this series should diverge at the critical point because of divergence of the initial series for the pressure. However, the scaling theory makes a stronger statement: c_V changes as $c_V \sim \Delta\theta^{-\alpha}$ along the critical isochors. The experiment confirms this prediction in some cases. However, the coefficients of the virial series essentially depends on the interaction potential, which is different for different fluids. Correspondingly, the pressure derivative should be different for different $\Phi(r)/\theta$ and the assertion, that the law $c_V \sim \Delta\theta^{-\alpha}$ is true in all cases, has no theoretical basis.

Let us suppose now, that we are moving from area B in Fig. 1 to the critical point along a ray $\Delta\rho=k\Delta\theta$. As it was shown, in this case the nonanalytic component of pressure P has the form $A\Delta\theta^{\gamma+1}/(\gamma+1)$ [see Eq. (34)]. Differentiating this expression 2 times on $\Delta\theta$, we shall obtain, that the nonanalytic component of the thermal capacity is proportional to $\mathbb{A}\gamma\Delta\theta^{\gamma-1}$. As far as $\gamma-1\approx 0.3>0$, this term must tend to zero with approaching to the critical point. Therefore, the thermal capacity in the "B" area becoming equal to infinity at the critical point also should be the consequence of the behavior of the regular component of pressure. The form of the latter depends on the potential interaction. [I would like to remind the reader that this potential enters in $C^{(rg)}$ only as the ratio $\Phi(r)/\theta$]. Therefore, we have no basis to assert that in this case the law $c_V\sim\Delta\theta^{-\alpha}$ must be universal also.

Curve of two phases coexistence. The curve of two phases equilibrium (binodal) is located in the area of subcritical temperatures $\theta\leqslant\theta_c$. In this case the solution of the OZ equation is analytical in both areas A and C (see Fig. 1) and, therefore, we can always write [see formula (9)]

$$\frac{\partial\Delta P}{\partial\Delta\rho}=\Delta C(\Delta\rho,\Delta\theta)=3a_3\Delta\rho^2+4a_4\Delta\rho^3+\cdots+k_1\Delta\theta+\cdots,$$

where the coefficients a_i, k_i can have different values at $\Delta\rho<0$ and $\Delta\rho>0$. By definition, the binodal represents a line of singular points, on which the solution of the OZ equation with $\partial\Delta P/\partial\Delta\rho>0$ (one-phase area) transforms by a jump into the solution with $\partial\Delta P/\partial\Delta\rho=0$ (two-phase area; see Fig. 2). Therefore, on binodal $\partial\Delta P/\partial\Delta\rho=0$ or

$$3a_3\Delta\rho^2+4a_4\Delta\rho^3+\cdots=-k_1\Delta\theta+\cdots. \qquad (38)$$

If $\Delta\theta>0$, this equation does not have a solution, because the left-hand part is >0 and the right-hand part is <0. Therefore, at supercritical temperatures, phase transition fluid-vapor is impossible. But at $\Delta\theta<0$ (subcritical temperature) Eq. (38) has a solution.

In general, all a_i, k_i in (38) may differ from zero. In this case, the curve of the phase equilibrium $\Delta\rho=f(\Delta\theta)$ may have a rather complicated form. However, if the term $3a_3\Delta\rho^2$ is much greater than the others, Eq. (38) turns into the expression $\Delta\rho\sim\Delta\theta^{\beta}$, where $\beta=1/2$ is the classical critical exponent. If the term $4a_4\Delta\rho^3$ dominates, from Eq. (38) follows that $\beta=1/3=0.3333$, that is very close to the scaling index $\beta=0.3245$. But in the last case if a_3 is small, but not equal to zero, in the immediate vicinity of the critical point should appear a term with $\Delta\rho\sim\Delta\theta^{1/2}$. Generally it is possible that $\Delta\rho\sim\Delta\theta^{1/4}$. As follows from [1], all these variants actually are observed in the experiments.

Thus, the thermal capacity behavior and the binodal form in the critical point vicinity, the coordinates ρ_c, θ_c of critical point and the critical amplitudes are defined by the analytical components of correlation functions, which substantially depends on the interaction potential and can be different for different fluids. The values of these functions cannot be defined in the scaling theory.

VII. CONCLUSION

Let us summarize. All of the relations obtained above are based only on the Ornstein-Zernike equation, which has a meaning of the chemical potential constancy; not one of the scaling theory hypotheses was used. Nevertheless, we have obtained practically all the results of the scaling theory, but in the slightly changed form. Thus, the unambiguous statement of the scaling theory that "all critical exponents should be universal," is replaced by a somewhat weaker assertion that "these exponents can have slightly different value for different fluids;" strictly universal ones are only the coupling relations establishing the link between different indexes for the same fluid. In addition, we have shown, that the critical exponents cannot describe the heat capacity and the vapor-liquid coexistence curve and the critical point influence spreads on a very large area of the phase diagram. The lines of singular points of a statistical sum are the boundaries of these areas. The derivatives of the pressure on the density and on the temperature are divergent on these boundaries. It is very important that we have obtained the equations that permit us to calculate the coordinates of the critical point, the critical amplitudes, etc.

APPENDIX

Let us set

$$\frac{\sin(kr)}{kr}=1-\frac{1}{3!}(kr)^2+\left(\frac{\sin(kr)}{kr}-1+\frac{1}{3!}(kr)^2\right)$$
$$=1-\frac{1}{3!}(kr)^2+\zeta(kr).$$

Substituting this expression into $\hat{C}(k)$, we obtain

$$C(k)=C(0)+k^2C^{*}(0)+4\pi\int_0^{\infty}C(r)\zeta(kr)r^2dr, \qquad (A1)$$

where $C(0)$ and $C^{*}(0)$ is determined by Eq. (4). Let us suppose $x=kr$ and, therefore,

$$\int_0^{\infty}C(r)\zeta(kr)r^2dr=\frac{1}{k^3}\int_0^{\infty}C\left(\frac{x}{k}\right)\zeta(x)x^2dx. \qquad (A2)$$

At $k\to 0$, the argument of the direct correlation function $x/k\to\infty$. In this limit (see [8])

$$C(x/k)\to-\Phi(x/k)/\theta\to k^6a/x^6$$

and

$$\int_0^{\infty}C(r)\zeta(kr)r^2dr\to\frac{1}{k^3}\int_0^{\infty}\frac{k^6a}{x^6}\zeta(x)x^2dx=k^3\int_0^{\infty}\frac{a}{x^4}\zeta(x)dx. \qquad (A3)$$

The last integral converges because

$$\zeta(x)\to\begin{cases}x^4/5! & \text{at } x\to 0,\\ x^2/3! & \text{at } x\to\infty.\end{cases}$$

Substituting (A3) into (A1), we shall obtain Eq. (4).

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