INTRODUCTION

Scaling theory (renormalization group theory), which is based entirely on the Gibbs distribution, lies at the heart of the modern theory of critical phenomena. Its main achievements are the prediction of critical index values and the substantiation of the universal character of these indices (i.e., their independence on the nature of a liquid). Both were subsequently confirmed by experimental data. However, scaling theory is not flawless. Cyril Domb, one of the authors of the theory, writes “The renormalization group (RG) does not produce an exact solution (to the Gibbs distribution) of the Onsager type, and its application involves quite drastic approximations” [1]. I would add that the physical sense of these drastic approximations is by no means always clear. Thus, for example, it is not clear how the Gibbs theory can be generalized to systems of particles in d-dimensional space with fractional space dimensionality \(d > 3\). As was shown in [2], the Gibbs distribution is an unambiguous consequence of the motion equations of classical mechanics, which, in turn, are valid only at \(d = 3\). No generalization of motion equations exists for spaces with fractional dimensionality. Therefore, no Gibbs distribution exists in d-dimensional spaces either. Moreover, the mathematical apparatus of scaling theory is extremely complicated and hard to understand.

Sixty years before the emergence of scaling theory, Ornstein and Zernike (OZ) formulated their theory of critical phenomena [3]. Despite its extreme simplicity, it explains the basic features of critical phenomena while giving, of course, no full description of these phenomena. Unfortunately, when scaling theory was created in the 1970s, the prevailing opinion was that the OZ theory was semi-empirical. It was believed that a rigorous statistical theory must necessarily be based only on the Gibbs distribution. As far as I can judge, most scientists continue to adhere to this view. At practically the same time scaling theory was created, however, it was proved that the OZ equation can be derived from the Gibbs distribution through identical transformations [3–5]. It was shown in [6, 7] that the OZ equation is a convolution of the Bogolyubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy. (It should be remembered that the Gibbs distribution is the last equation of this hierarchy.) The above indicates that the OZ equation, as a basis for the derivation of statistical theory, must be as reliable as the Gibbs distribution.

It was hoped that the OZ theory would help create a simple and clear theory of critical phenomena. As a result, a number of papers on improving the OZ theory appeared in the literature [8, 9]. However, they were always based on the same idea: approximations such as those behind the scaling theory should be introduced into the OZ equation, thus bringing both theories into accordance. It should be noted that the rigorous results obtained in [3–7] were never considered. However, this turned out to be a dead-end: so far, no one has succeeded in calculating the values of critical indices with the same accuracy as the scaling theory.

In this work, we proceed only from the rigorous formulas that were derived in [3–7] as a result of transforming the Gibbs distribution into the OZ equation.
THE ORNSTEIN–ZERNIKE THEORY

Expansion around an Infinity Point

In 1914, Ornstein and Zernike proposed the integral equation [10]

\[ h(r_1) - C(r_2) - \rho \int C(r_3) h(r_3) \, dr_3 = 0, \tag{1} \]

which, as we now know, is as fundamental as the Gibbs distribution. The equation relates the direct correlation function \( C(r) \) to the general correlation function \( h(r) = G(r) - 1 \) (where \( G(r) \) is a two-particle distribution function, \( r \) is the distance between particles, and \( \rho \) is density). It is assumed in (1) that the function \( C(r) \) is defined, and the density distribution \( \rho(r_1 + r) \) around a given particle situated at arbitrary point \( r_1 \) is determined by the solution to this equation \( \rho(r) = \rho(r_1) G(r) = \rho(r_1) + \rho(r_1) h(r) \). It is evident that \( \rho(r_1) \) in this formula is the mean density of matter throughout the system, while \( h(r) \) describes the excess particle density distribution around point \( r_1 \), which emerges as a result of their interaction with particle 1. Since the appearance of particle 1 at a given point in the system is a random event, any change in the density around it is a fluctuation. This testifies to the close link between the OZ equation and the enormous density fluctuations that occur in the vicinity of a critical point.

Using the Fourier transform

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

the OZ equation can be written as

\[ 1 + \rho \hat{h}(k) = 1/1 - \rho \hat{C}(k). \tag{3} \]

Using an inverse Fourier transform, unity on the left side of the equation can be ignored, as it produces delta function \( \delta(r) \), which makes no contribution to the thermodynamic parameters of a liquid [11].

It is obvious that macroscopic fluctuations arising in the vicinity of a critical point must be described by the asymptotics of distribution functions. This asymptotic is fulfilled for the direct correlation function \( \hat{C}(k) \) values at \( k \to 0 \) (it should be remembered that point \( r = \infty \) in real space corresponds to the wave vector \( k = 0 \)). Assuming \( k \) to be a small parameter expanding \( \hat{C}(k) \) in power series of \( k \) around point \( k = 0 \), and ignoring terms on the order of \( k^4 \) and higher, Ornstein and Zernike obtained the asymptotic equation

\[ \rho \hat{h}(k) = \frac{1}{1 - \rho \hat{C}(k)} = \frac{1}{1 - (1 - \rho C_1) + k^2 \frac{1}{6} \rho C_4}, \tag{4} \]

in which the second and the fourth moments of the direct correlation function \( C(r) \) are equal to

\[ C_2 = \int_0^\infty C(r) r^2 \, dr, \quad C_4 = \int_0^\infty C(r) r^4 \, dr. \tag{5} \]

Asymptotic equation (4) can be written in a simpler form:

\[ 1 + \rho \hat{h}(k) = \frac{6}{\rho C_4} \frac{1}{\lambda^2 + k^2} = \frac{A}{\lambda^2 + k^2}, \tag{6} \]

where

\[ \lambda(\rho, \theta) = \left( \frac{6(1 - \rho C_2)}{\rho C_4} \right)^{1/2}, \quad A = 6/(\rho C_4). \tag{7} \]

The general correlation function can be found by performing an inverse Fourier transform in (6):

\[ h_n(r) = \frac{1}{4 \pi \rho C_4} \frac{6 e^{-\lambda r}}{r} = \frac{A e^{-\lambda r}}{4 \pi \rho r} \tag{8} \]

(here and below, index \( n \) is assigned to the functions obtained in the limit \( r \to \infty \), while index 0 denotes functions describing the state of a liquid at short distances).

In time, Bogolyubov showed [2, 9] that the isothermal compressibility of a liquid was

\[ \kappa_0 = \frac{\theta}{\partial P/\partial \rho} = 1 + \rho \hat{h}(0) \equiv 1 + \rho \int_0^\infty h(r) 4\pi r^2 \, dr, \tag{9} \]

where \( \theta = k_B T \) is temperature. Substituting (8) into (9) and integrating over \( r \), we obtain

\[ \kappa_\infty = \frac{\theta}{\partial P/\partial \rho} = 1 + \frac{A}{\lambda^2}. \tag{10} \]

1 It is easy to show that if the moment \( C_4 \) has a finite value, all other moments \( C_2n \) diverge at the upper limit for \( \Phi \to a/\rho^6 \). Therefore, formula (4) should be considered not as an expansion of \( C(k) \) in a power series of \( k^{2n} \), but rather as a formulation of the kernel of \( \sin(kr)/kr \) expansion in the form

\[ \frac{\sin(kr)}{kr} = 1 - \frac{1}{6}(kr)^2 + \zeta(kr), \]

where the function \( \zeta(kr) = \frac{\sin(kr)}{kr} - 1 + \frac{1}{6}(kr)^2 \) is not expanded into a series.

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