

The problem of phase transitions in statistical mechanics

G A Martynov

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Abstract. The first part of this review deals with the single-phase approach to the statistical theory of phase transitions. This approach is based on the assumption that a first-order phase transition is due to the loss of stability of the parent phase. We demonstrate that it is practically impossible to find the coordinates of the transition points using this criterion in the framework of the global Gibbs theory which describes the state of the entire macroscopic system. On the basis of the Ornstein–Zernike equation we formulate a local approach that analyzes the state of matter inside the correlation sphere of radius $R_c \approx 10 \text{ \AA}$. This approach is proved to be as rigorous as the Gibbs theory. In the context of the local approach we formulate a criterion that allows finding the transition points without calculating the chemical potential and the pressure of the second conjugate phase. In the second part of the review we consider second-order phase transitions (critical phenomena). The Kadanoff–Wilson theory of critical phenomena is analyzed, based on the global Gibbs approach. Again we use the Ornstein–Zernike equation to formulate a local theory of critical phenomena. With regard to experimentally established quantities this theory yields precisely the same results as the Kadanoff–Wilson theory; secondly, the local approach allows the prediction of many previously unknown details of critical phenomena, and thirdly, the local approach paves the way for constructing a unified theory of liquids that will describe the behavior of matter not only in the regular domain of the phase diagram, but also at the critical point and in its vicinity.

1. Introduction

There are many types of phase transitions in nature, and the more sophisticated the system, the more complex the phase transitions. In this review we confine our discussion to the simplest systems — one-component isotropic liquids which only exhibit the most common first- and second-order phase transitions (the latter are usually referred to as critical phenomena). What is the reason for such a choice?

The statistical theory of phase transitions has two principal tasks:

(1) to explain the mechanism of the phase transition onset, and

(2) to calculate the parameters of phase transitions from first principles. This assumes that we must at least be able to express from the given interaction potential Φ the curves of phase equilibrium $\rho = \rho(\Theta)$ (where ρ is the density, and $\Theta = kT$ the temperature), to calculate the heat of crystallization, etc. in the case of first-order phase transitions, and calculate the coordinates of the critical point ρ_c , Θ_c , the critical indices, etc. in the case of second-order phase transitions.

Now, while the first task may be considered more or less solved (at least on the qualitative level), the advances in calculating the parameters of phase transitions from first principles are rather modest. Obviously, the solution of this problem must start with the simplest systems.

There is yet another natural question: why is it that progress in the theory of phase transitions has been so slow in defiance of the efforts of many scholars?¹ What I am going

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¹ Some readers will disagree with this opinion, and perhaps for a rather good reason. Indeed, today we are able to calculate the curves of first-order phase equilibrium $\rho(\Theta)$ for simple fluids using the methods of numerical experiment, and the methods of the density functional; K Wilson was even awarded the Nobel prize (1982) for his theory of critical phenomena. I will try to demonstrate, however, that the two-phase approach used for calculating the $\rho(\Theta)$ curves has a number of important

to say now may sound blasphemous: this is because these scholars relied on the Gibbs distribution. By definition, a phase transition is a change in the structure of matter. At the same time, the concept of ‘structure’ is foreign to the global Gibbs theory which deals with the state of the entire macroscopic system. Because of this, it is impossible to formulate the criteria of phase transitions staying within the confines of the Gibbs theory. And without knowing these criteria it will be very difficult to find the coordinates of transition points and calculate the thermodynamic parameters of matter at these points.

In 1914, Ornstein and Zernike [1] formulated a local approach based on the assumption that the macroscopic parameters of matter at point \mathbf{r} only depend on the distribution of molecules in the immediate vicinity of this point (this neighborhood is known today as the correlation sphere, and its radius as the correlation radius R_c ; calculations indicate that usually $R_c \sim 10 \text{ \AA}$ [2]). Then in 1960, Morita and Hiroike [3] proved that the Ornstein–Zernike (OZ) equation can be derived from the same Gibbs distribution through identity transformations. Accordingly, as far as rigorousness and consistency are concerned, both approaches — the global Gibbs approach and the local OZ approach — are quite similar. However, the Gibbs distribution depends on the coordinates and momenta of all $N \approx \infty$ particles of the system, whereas the OZ equation defines the two-particle distribution function $G^{(2)}$ which only depends on the distance $r_{12} = |r_1 - r_2|$ between two arbitrarily selected particles 1 and 2. Obviously, this greatly simplifies the task. But there is something more than that. Within the framework of the OZ theory it is very easy to define the concept of ‘microstructure of matter’, which in turn makes it easy to identify those points on the phase diagram where this structure begins to change. I will try to show that these two advantages eventually open new possibilities in the theory of phase transitions.

Section 2 deals with the theory of first-order phase transitions, and Section 3 with the theory of critical phenomena. Both sections are formatted in the same way: first we consider the phase transitions from the standpoint of thermodynamics, then in the framework of the global Gibbs theory, and finally on the basis of the local OZ equation. Such presentation is best suited for unfolding the capabilities of each of these approaches.

2. First-order phase transitions

2.1 Statement of the problem

The physical cause of first-order phase transitions² is well known: it is the loss of stability by the parent phase. However, unless we can indicate precisely how this circumstance is reflected in the equations of statistical mechanics, this statement will remain an empty sound. And this is currently a much disputed point. Some authors hold that the transition points are singularities of the partition function [4, 5], others

believe that there are no singularities at the points of phase transformations, and that statistical mechanics therefore can equally well describe both equilibrium and metastable states [6, 7]; some authors argue that in Gibbs’ theory it is not possible to define the van der Waals loop, and hence one cannot use the Maxwell rule for identifying the transition points [8, 9], while others not only hold an opposite opinion, but actually find this loop in their calculations [10, 11]; some authors announce that “the curves of phase equilibrium can only be localized with the aid of thermodynamic conditions of equal pressures P , temperatures Θ and chemical potentials μ of the conjugate phases” [12] (such an approach has become known as the ‘two-phase approach’, since it is based on comparing the parameters of two phases in equilibrium with each other), while others successfully pursue the ‘one-phase’ approach that requires knowing the properties of only a single parent phase [13, 14].

Of special interest is the comparison between the one-phase and the two-phase approaches. From thermodynamics it does follow that phases A and B of the same substance may occur at equilibrium with one another only provided that

$$P_A = P_B, \quad \Theta_A = \Theta_B, \quad \mu_A = \mu_B. \quad (1)$$

These conditions, however, are by no means specific for phase transitions — they can equally well be realized in one-phase systems. Indeed, let us arbitrarily split a one-phase system in two, and call one part ‘phase A ’, and the other ‘phase B ’. Obviously, the condition of equilibrium of such virtual phases will again have the form of Eqn (1). As a matter of fact, in thermodynamics we simply enunciate that phase A is in some way different from phase B , and then start looking for those points on the phase diagram where our assumption is true. Since the conditions (1) do not give any indication of where such points are to be sought, the construction of curves of phase equilibrium in the two-phase approach implicitly suggests that all the calculations must be done by the trial and error method. Assume, for example, that we want to use the conditions (1) for constructing the curve of crystallization of a liquid. To do this, we must first use the given interaction potential to establish the structure of the crystal with which our liquid can be in equilibrium. This can only be done by trial and error: first find the free energy of one structure, then that of another, and so on, until such a structure is found that minimizes the free energy. This, however, is not enough: one must repeat all these calculations until the values of density and temperature are found for a given lattice that satisfy the conditions of equilibrium between the crystal and the liquid phase. In the case of complex systems (such as solutions), these essentially computational difficulties may become insuperable.

If, however, it is true that the phase transitions occur when the parent phase loses its stability, then it is not necessary to calculate the parameters of the second phase, since the parent phase will lose its stability irrespective of whether the other phase is or is not in equilibrium with it. This obviously makes the task much simpler. Because of this, the development of the one-phase approach is of great practical importance. In effect, this is what this section of our review is about; we shall only incidentally touch upon the two-phase approach. This circumstance is definitive for the way we present the material here.

Currently the two-phase approach is well validated, and the discussions are mainly concerned with the technical difficulties mentioned above. The situation is different with

drawbacks that severely limit its applicability, and Wilson’s theory cannot be regarded as a consistent statistical theory, because “its reasoning employs many approximations that cannot be verified” (quoted in back translation from the Russian edition of R Balescu’s monograph [11, p. 401]).

² Hereinafter we are going to omit the designation of the ‘first order’ whenever possible. Hopefully, this will not cause any confusion, since the entire section is devoted to these phenomena only.

the one-phase approach. There are very few practical results, the algorithm of its realization has not been developed, and even the very feasibility of this approach is much disputed by many authors (see, for example, Ref. [12]). So the first thing is to prove that the one-phase approach has the right to exist. This is the main purpose of Section 2 of this review.

As will be shown below, the first-order transition points are the singular points of the partition function. If only because of this, their description is one of the major problems in statistical mechanics. They are a concentration of the strengths and weaknesses of the contemporary theory. To sort out these problems would essentially amount to drawing the bottom line of the entire classical statistical mechanics. Hopefully, the reader will excuse my going into the general issues. Without such excursions it would be not possible to present a comprehensive treatment of the subject.

2.2 Phase transitions and thermodynamics

Validation of the one-phase approach ought to start with finding out what happens with the exact equations of statistical mechanics at the first-order transition points. Since we assume that at these points the system becomes unstable, it would be natural to try and investigate the role of stability in statistical mechanics.

We know that the Gibbs distribution only holds for stable systems. After all, this is quite natural, since it is only stable systems that can be at equilibrium for an indefinitely long time. By contrast, fluctuations in unstable systems will sooner or later cause deviations from the initial state. These deviations will grow, and eventually the system will leave the initial state.

Out of all possible criteria of stability of the Gibbs distribution we are only interested now in the criterion of mechanical stability $(\partial P/\partial V)_\Theta \leq 0$, where V is the volume of the entire system. Here the 'less than' sign

$$\left(\frac{\partial P}{\partial V}\right)_\Theta < 0 \quad (2)$$

corresponds to the state of absolute stability, and the equality sign

$$\left(\frac{\partial P}{\partial V}\right)_\Theta = 0 \quad (3)$$

corresponds to neutral equilibrium. Systems with $(\partial P/\partial V)_\Theta > 0$ are unstable (and therefore nonequilibrium), and are not described with the Gibbs distribution.

Now we would like to know how the density of a substance is distributed within the volume of the system in the cases of absolutely stable and neutral equilibrium? To answer this question we must first note that the concept of stability lies in essence beyond the framework of the equilibrium theory, since it admits the possible spontaneous deviation of the system from the initial equilibrium state. Because of this, we have to turn to the equations of hydrodynamics, which, like the Gibbs distribution, follow from the basic assumptions of the statistical mechanics [2]. These equations contain the gradient of pressure $P = P(\rho, \Theta)$, where the density of particles ρ and the temperature Θ are functions of the coordinate r and time t in nonequilibrium systems. At equilibrium, however, the pressure gradient must vanish, i.e.

$$\frac{\partial P(\rho, \Theta)}{\partial r} = \left(\frac{\partial P}{\partial \Theta}\right)_\rho \frac{\partial \Theta}{\partial r} + \left(\frac{\partial P}{\partial \rho}\right)_\Theta \frac{\partial \rho}{\partial r} = 0, \quad P(r) = \text{const}. \quad (4)$$

Since Θ and ρ are independent variables, each term in this expression must vanish independently of the other. To make the first term equal to zero, it will suffice to set

$$\frac{\partial \Theta(r)}{\partial r} = 0, \quad \Theta(r) = \Theta = \text{const}, \quad (5)$$

because the derivative $(\partial P/\partial \Theta)_\rho$ cannot be equal to zero. The situation is different with the second term. If the condition of absolute stability (2) is satisfied, then the derivative $(\partial P/\partial \Theta)_\rho$ is nonzero, and Eqn (4) can only be made to hold by setting

$$\frac{\partial \Theta(r)}{\partial r} = 0, \quad \rho(r) = \frac{N}{V} = \bar{\rho} = \text{const}, \quad (6)$$

where $\bar{\rho}$ is the mean (with respect to the entire volume V of the system) number density of particles. This means that equilibrium absolutely stable systems can only be spatially homogeneous (single-phase); if the equilibrium is indifferent, then $(\partial P/\partial \rho)_\Theta = 0$, and one cannot say anything about the distribution of density $\rho(r)$ over the volume of the system, based on Eqn (4). To find the form of the function $\rho(r)$ in this instance, one has to use the thermodynamic approach. Before doing this, however, we observe that equality $(\partial P/\partial \rho)_\Theta = 0$ may hold either over a certain finite interval of densities

$$\rho_A(\Theta) \leq \bar{\rho} \leq \rho_B(\Theta), \quad (7)$$

or at one point

$$\rho(\Theta) = \rho_c. \quad (8)$$

Here we shall only be interested in the former case. The latter situation will be discussed in the third section of this review, because it relates to critical phenomena.

To find out what happens within the interval (7), we integrate the known thermodynamic identity $dF = -P dV$ at $\Theta = \text{const}$, where F is the free energy of the entire system. Since, according to Eqn (4), we have $P = \text{const}$ in this identity, the integration from $\rho = \rho_A$ to $\bar{\rho}$ yields

$$F(\bar{\rho}) = F(\rho_A) - P(V - V_A), \quad (9)$$

where $V_A = N/\rho_A$. Setting in this equation $V = V_B = N/\rho_B$, we find that

$$P = \frac{F(\rho_A) - F(\rho_B)}{V_B - V_A}.$$

Substituting this equation into Eqn (9), and going over from the global free energy of the system F to the mean density $\bar{f} = F/V$ of free energy over the volume, we get

$$\bar{f}(\bar{\rho}) = \bar{\rho} \frac{f_A - f_B}{\rho_A - \rho_B} + \frac{\rho_A f_B - \rho_B f_A}{\rho_A - \rho_B}, \quad (10)$$

where $f_A = f(\rho_A)$, $f_B = f(\rho_B)$. Finally, introducing the parameter v such that

$$\bar{\rho} = v\rho_A + (1-v)\rho_B, \quad 1 \geq v \geq 0, \quad (11)$$

we finally arrive at

$$\bar{f}(v) = vf_A + (1-v)f_B, \quad 1 \geq v \geq 0. \quad (12)$$

Hence it follows that in the case of neutral equilibrium, the mean free energy of matter is a function of the parameter v rather than a function of the local density ρ , as in the case of stable one-phase states.

To clarify the meaning of parameter v , let us derive Eqn (11) in a different way. Assume that the system consists of two spatially homogeneous phases A and B separated by a clear boundary. Assume further that the densities of these phases are, respectively, $\rho_A = N_A/V_A$ and $\rho_B = N_B/V_B$, where $V_A = V - V_B$, $N_A = N - N_B$. Then the mean density over the entire system is

$$\bar{\rho} = \frac{N}{V} = \frac{N_A + N_B}{V} = \frac{N_A}{V_A} \frac{V_A}{V} + \frac{N_B}{V_B} \frac{V_B}{V} = v\rho_A + (1-v)\rho_B,$$

where $v = V_A/V$. Obviously, with v defined in this manner, this formula coincides with Eqn (11). In the same way one can derive the formula for the free energy, or for any other parameter of the system, and they all will be similar to Eqns (11) and (12).

Discussion. So, after a rather lengthy exercise we have arrived at results that are familiar at bottom: absolutely stable systems are spatially homogeneous (single-phase); the systems in which the state of neutral equilibrium is realized are always two-phase (in general, multiphase), and so on. In thermodynamics these results are usually postulated, whereas we deduced them from equations that can eventually be derived from the basic postulates of statistical mechanics. Now, however, something else is of greater importance. For any extensive parameter A we may set $A = Va$. Then from Eqn (12) it follows that in the range of densities $\rho_A \leq \bar{\rho} \leq \rho_B$ the values of

$$A = V[v a_A + (1-v) a_B] \quad (13)$$

do not depend on the local density of the relevant phase ρ ; this formula only involves the quantities $a_A = a(\rho_A)$, $a_B = a(\rho_B)$ defined at the ends of the interval. At the same time, outside of the two-phase interval (that is, for $\rho < \rho_A$, $\rho > \rho_B$), where the system is absolutely stable, all parameters of matter $A = A(\rho, \Theta)$ are functions of the local density $\rho = \bar{\rho}$. Because of this, if we plot the values of the local parameters a as a function of the local density ρ , we shall find that it is not defined over the interval $\rho_A \leq \rho \leq \rho_B$ — the values of $a(\rho, \Theta)$ do not enter any equation of equilibrium thermodynamics at the densities ρ within this interval (Fig. 1). At the same time, the functions A themselves are continuous functions of $\bar{\rho}$, since at the ends of the interval the parameter v assumes the values of 0 and 1. Of no less importance is the fact that the derivatives $\partial A / \partial \rho$ have discontinuities at the ends of the two-phase interval — outside they are nonzero, and zero inside, since within this interval the parameters of matter do not depend on ρ .

Finally, I would like to point out that the picture which follows from arguments developed above is in complete agreement with experiment. Indeed, assume that we take a cylinder filled with vapor and slowly drive a piston in, thus changing the mean density of matter. To do this, at first we need to increase steadily the force applied to the piston to raise the pressure of vapor in the cylinder. When the density of vapor reaches the point of vapor–liquid phase transition, however, the vapor will start to condense, and further compression will occur without any increase in the pressure. When finally all the vapor liquefies, further compression will require increasing the pressure.

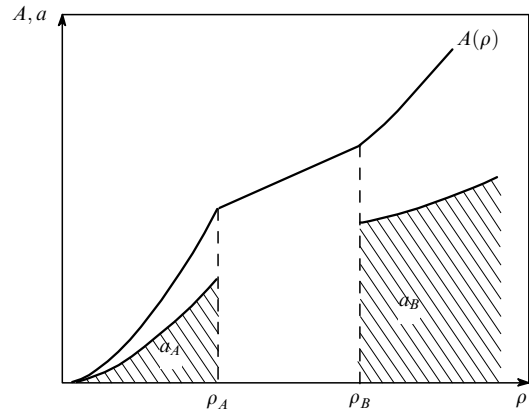


Figure 1. Global parameter A and local parameters a_A and a_B (hatched) vs. density ρ .

2.3 Phase transitions and the Gibbs distribution

Now we can see what happens with the Gibbs distribution

$$G = \exp \left[-\frac{1}{\Theta} (\Phi_{ij} - F) \right] \quad (14)$$

in the curves of phase equilibrium (here F is the normalization constant which has a meaning of free energy, and $\Phi_{ij} = \Phi(r_{ij})$ is the potential of pairwise interaction between particles). Accurate to the negligibly small fluctuations, we have $\sum \Phi_{ij} = E$, where E is the internal energy of the system. Because of this, in the domain of absolutely stable equilibrium we get

$$G = \exp \left[-\frac{1}{\Theta} (E - F) \right] = \exp \left[-\frac{V}{\Theta} (e - f) \right], \quad (15)$$

and in the domain of neutral equilibrium [see Eqn (13)] one obtains

$$G = \exp \left\{ -\frac{V}{\Theta} [v(e_A - f_A) + (1-v)(e_B - f_B)] \right\} = G_A G_B, \quad (16)$$

$$G_A(r; \rho, \Theta) = \begin{cases} G_A(r) & \text{at } 0 < \rho < \rho_A, \\ 1 & \text{at } \rho_A < \rho, \end{cases}$$

$$G_B(r; \rho, \Theta) = \begin{cases} 1 & \text{at } 0 < \rho < \rho_B, \\ G_B(r) & \text{at } \rho_B < \rho. \end{cases}$$

From Eqn (16) it follows that the Gibbs distribution in the two-phase region is broken up into the product of two single-phase distributions G_A and G_B , of which one is defined for the interval $\rho < \rho_A$, and the other for $\rho > \rho_B$. Each of these distributions is a one-valued function inside the single-phase interval; outside this interval the single-phase Gibbs distributions G_A and G_B do not depend on the local density of matter ρ . At the same time, the total Gibbs distribution G is a continuous function of the mean density $\bar{\rho}$ of the system (the latter equals the true density of matter $\rho = N/V$ on the single-phase portions, and is given by Eqn (11) on the two-phase portions). However, the derivatives of the total Gibbs distribution with respect to the local density have disconti-

nities at the ends of the two-phase interval, because

$$G^{[k]} \equiv \frac{1}{k!} \frac{d^k G}{d\rho^k} = \begin{cases} \frac{1}{k!} \frac{d^k G_A}{d\rho^k}, & 0 \leq \rho \leq \rho_A, \\ 0, & \rho_A \leq \rho \leq \rho_B, \\ \frac{1}{k!} \frac{d^k G_B}{d\rho^k}, & \rho_B \leq \rho \leq \rho_C, \end{cases} \quad (17)$$

since G here depends not on ρ , but on v (in Eqn (17), the operator is $[k] = (1/k!)(\partial^k/\partial\rho^k)$). In other words, the derivatives of the total Gibbs distribution behave like all other local parameters.

Then it remains to demonstrate that the pressure does not change in the interval of neutral equilibrium (this is necessary for satisfying the condition of equilibrium of phases (1)). For this we use the known formula of statistical mechanics that establishes the linkage between P and G [11]:

$$PV = N\Theta - \frac{1}{3} \int_V \sum_{ij} r_{ij} \frac{d\Phi_{ij}}{dr_{ij}} G d^3 r_1 \dots d^3 r_N. \quad (18)$$

Substituting here $G = G_A(v)G_B(1-v)$, and noting that integration in the two-phase domain must be carried out separately over the volumes V_A and V_B of each of the phases, and so the sum $\sum_{ij} r_{ij} (d\Phi_{ij}/dr_{ij})$ will also fall into two parts (the sum over all particles of phase A , and the sum over all particles of phase B), we find after some straightforward transformations that the pressure $P = vP_A + (1-v)P_B$ does not depend on v , since $P_A = P_B$. At the same time, from the thermodynamic identity $d\mu = dP/\rho$ follows the condition of the stability of chemical potential over the entire interval where $P = \text{const}$, $dP = 0$, which ensures that condition (1) $\mu_A = \mu_B$ is satisfied.

Discussion. So we have established that the single-phase Gibbs distributions defining all the local parameters of matter disappear in the phase equilibrium curves. As a result, for density $\rho > \rho_A$ (for phase A) and for density $\rho < \rho_B$ (for phase B) the local parameters of these phases turn out to be indeterminate and are nonexistent from the standpoint of the equilibrium theory. This alone is an indication that the curves of phase equilibrium of the first order correspond to the singularities of the partition function. Many years ago this was noted by Lee and Yang (see, for example, Refs [4, 5] which contain the proof of their theorem). Unfortunately, these authors failed to specify the nature of the singularity. As a result, this singularity up till now escaped detection, and the theorem of Lee and Yang was forgotten, but not refuted.

Another important result is the following: the spatially homogeneous metastable phases that develop inside the two-phase density interval $\rho_A < \bar{\rho} < \rho_B$ cannot be described by the Gibbs distribution, because the latter does not depend on the local density in this interval at all, whereas the state of the metastable phase must necessarily be a function of ρ . Accordingly, in the rigorous theory there is no place for the van der Waals loop as well.

2.4 Phase transitions and virial series

In this way, the pioneering problem in the theory of first-order phase transitions — understanding the mechanism of the phenomenon — is solved. It might seem that now it is not too hard to solve the next problem — finding the location of the phase equilibrium curves on the phase plane. This only requires learning how to calculate the Gibbs distribution

inside the single-phase domains, and then gradually increasing the density until it reaches the threshold where the appropriate solution disappears. In reality, however, the task is not that simple.

The most efficient present-day technique for calculating the Gibbs distribution inside the single-phase regions of the phase diagram is the numerical Monte Carlo method. On crossing the curves of phase equilibrium, however, the values of parameters found by this method do not generally vanish — the system easily overcools and goes from the absolutely stable equilibrium state into an unstable (metastable) state [15, 16]. There are several reasons for this. First, in numerical calculations the infinite system consisting of $N \approx 10^{23}$ particles is always replaced with a finite system consisting of a few hundreds (rarely thousands) of particles. At the same time, it is known that the macrophase always loses its stability because a nucleus of the new phase starts to grow. This nucleus in the phase equilibrium curve must be of infinite size and, consequently, must consist of an infinite number of particles. To describe the incipience of such a nucleus one needs to consider very large systems that defy the capabilities of even the most powerful modern computers. Secondly, in the case of phase transitions between condensed phases (for example, between liquid and crystal) there appear steric hindrances in matter — because of this the crystal, for instance, only melts from the surface; the transition from one structure to another in the crystal bulk is not possible because of the too close packing of atoms.

A second method for calculating the Gibbs distribution is based on the expansion in powers of density:

$$G = \sum_{k=0}^{\infty} \rho^k G^{[k]}, \quad (19)$$

where the operator $[k]$ is given by Eqn (17). Substituting this expression into Eqn (18), we get the sought virial series

$$Z \equiv \frac{PV}{N\Theta} = 1 + \sum_{k=0}^{\infty} \rho^k B_{k+1}(\Theta), \quad (20)$$

where Z is the so-called compressibility coefficient, and the virial coefficients are given by

$$B_{k+1}(\Theta) = -\frac{1}{3N\Theta} \int_V \sum_{ij} r_{ij} \frac{d\Phi_{ij}}{dr_{ij}} G^{[k]} d^3 r_1 \dots d^3 r_N. \quad (21)$$

Let us consider these equations in greater detail.

Discussion. Analysis of Eqns (20) and (21) leads to at least three curious conclusions that so far have been overlooked.

Firstly, from Eqn (17) it follows that the virial expansion is defined only inside the single-phase interval of densities $\rho \leq \rho_A$; at greater densities it ought to diverge (vanish?), since there we have $G^{[k]} = 0$. Analytical calculations done on the lattice systems lend credence to this conclusion [17]. The same thing, however, ought to happen in other systems. For example, in the case of one-component systems, expression (20) must diverge in the curves OAC and HP (see Fig. 2). Within the ‘liquid’ region $CBTEH$ it does not exist, because this region falls beyond the curve of divergence of the series OAC . Virial expansions are not equally defined in the crystal region to the right of the melting curve KDM (see Fig. 2). Because of this, virial expansions cannot be used for calculating the pressure and the chemical potential in the second conjugate phase. If only for this reason, virial

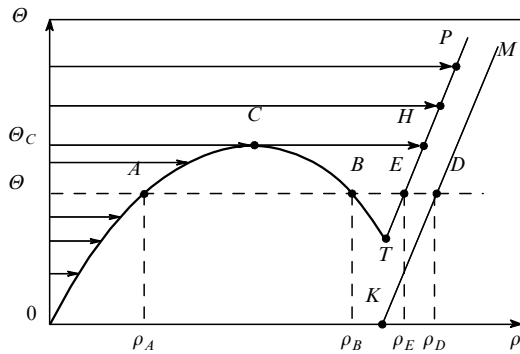


Figure 2. Schematic phase diagram of a one-component system: OAC — vapor condensation curve, CBT — liquid evaporation curve, $TEHP$ — liquid crystallization curve, KDM — crystal melting curve, C — critical point, T — triple point. Arrows indicate the region of convergence of virial expansions.

expansions cannot be used for finding the curves of phase equilibrium using the two-phase equilibrium condition (1).

But then could the virial expansions not be used for constructing the curves OAC and HP based on a different criterion — the divergence of virial expansion? Unfortunately, this is not possible either. In the theory of group expansions, specially developed for calculating the virial coefficients (see, for example, Refs [9, 11]), it is demonstrated that the number of different integrals entering into the k th coefficient B_k is approximately equal to $2^{k(k-1)/2}k!$ — in other words, this number increases incredibly fast with k . So it is usually possible to calculate the first two or three coefficients, five or six at best. A record number was found for the potential of rigid spheres

$$\Phi(r) = \begin{cases} \infty, & 0 \leq r \leq \sigma, \\ 0, & \sigma \leq r \leq \infty, \end{cases} \quad (22)$$

where σ is the diameter of the ball. Let us study this instructive example in greater detail.

Calculations indicate that the Taylor series for the compressibility coefficient in the system of rigid spheres has the form [18]

$$Z = 1 + 4\tilde{\rho} + 10\tilde{\rho}^2 + 18.365\tilde{\rho}^3 + 28.24\tilde{\rho}^4 + 39.5\tilde{\rho}^5 + 56.5\tilde{\rho}^6 + \dots,$$

where $\tilde{\rho} = (\pi/6)\rho\sigma^3$ (the leading coefficients are not known). Approximating this equation with the polynomial

$$Z = 1 + 4\tilde{\rho} + 10\tilde{\rho}^2 + 18\tilde{\rho}^3 + 28\tilde{\rho}^4 + 40\tilde{\rho}^5 + 54\tilde{\rho}^6,$$

Carnahan and Starling noticed that its coefficients can be expressed as $B_k = k^2 + k - 2$. Assuming that this holds for any k , they summed up the resultant series to get

$$Z = \frac{P}{\rho\Theta} = \frac{1 + \tilde{\rho} + \tilde{\rho}^2 - \tilde{\rho}^3}{(1 - \tilde{\rho})^3}. \quad (23)$$

This formula describes the pressure in a system of rigid spheres with exceptional accuracy — the error never exceeds 0.3%, and this over the entire range of densities $0 \leq \tilde{\rho} \leq \pi/6$, where the system of rigid spheres occurs in the fluid state. This formula, however, does not give any indication that at $\tilde{\rho} \approx \pi/6$ there happens a fluid–crystal phase transition in

the system. The reason is obvious: the Carnahan–Starling formula gives a good approximation to several first terms in the virial expansion that are definitive for all thermodynamic functions of the system, but does not carry any information regarding the behavior of the leading virial coefficients B_k with $k \rightarrow \infty$, which are responsible for the divergence of the virial series at the point of phase equilibrium. This example shows that the values of the first few coefficients are not sufficient for finding the point of divergence of the series; at the same time, it is impossible to calculate the leading coefficients that involve an immense number of integrals.

The third comment concerns the structure of virial coefficients. All integrals entering into the k th coefficients are taken with respect to coordinates of k particles. As follows from the above example, in order to calculate the compressibility coefficient to a very high accuracy it suffices to find a dozen (at worst, a hundred) of the first coefficients — that is, to take into account the interactions between a dozen (a hundred) particles not far away from each other (the virial coefficients are designed in such a way that the integrands tend to zero very fast as the distance between the particles increases). This implies that for calculating the local thermodynamic parameters α in a system consisting of approximately 10^{23} particles, it is sufficient to take into account the interactions between several tens or hundreds of particles; all the other particles of the system do not affect the values of the local parameters. This circumstance is used to advantage in the methods of numerical experiment (molecular dynamics and the Monte Carlo method) [15, 16], whereby the treatment of the entire macroscopic system is replaced with the treatment of a microscopic subsystem consisting of a few particles. The extensive experience gained with such studies testifies that the study of small subsystems permits calculating the thermodynamic parameters of matter to within 1 or 2%. This is good enough for calculating the curves of phase equilibrium in the context of the two-phase approach, but absolutely not sufficient for implementing the single-phase approach.

To summarize, we have to admit that neither numerical experiment nor the virial expansions are suitable for calculating the location of phase equilibrium curves by the single-phase method. And there are no other methods in the Gibbs theory.

2.5 Fundamental set of equations in the theory of liquids

Hence, we have found that the single-phase approach is not feasible within the framework of Gibbs's statistical mechanics. The only alternative is to go beyond the limits of this theory. But how? As a matter of fact, the answer has already been given above: one has to go over from a global to a local description of the system.

The Gibbs distribution is global in the sense that it describes the behavior of the entire macroscopic system consisting of $N \approx 10^{23}$ particles. At the same time, as soon as we tried to use the Gibbs distribution for calculating the pressure, we immediately saw that this only requires knowing the coordinates of a hundred or so of particles in the immediate neighborhood of the point where the pressure is to be calculated (this region is known in statistical mechanics as the correlation sphere). The result is quite universal: in order to find the value of *any* thermodynamic parameter of the equilibrium system at the given point, one only needs to know the density distribution of particles inside the correlation sphere around this point. Whatever falls outside this

sphere does not affect the values of the parameters. The approach based on studying the distribution of density of matter inside the correlation sphere we shall call the local approach.

Currently, the local approach is being developed under the modest appellation of the ‘theory of liquids’, although it can be equally well applied to the description of crystals (see, for example, Ref. [19]). At the same time, the Russian literature on statistical mechanics (see, for example, Refs. [20–22]) hardly contains any references to the local approach. Because of this I deemed it necessary to include a section dealing with the local theory, even though this topic, being closely related to the latter, may fall beyond the scope of our review.

Thermodynamic parameters and the Gibbs distribution. Let us look more closely at Eqn (18) which relates the pressure to the Gibbs distribution. Since the magnitude of the latter does not change when the numbering of particles is changed, Eqn (18) essentially reduces to the sum of $N(N-1)/2 \approx N^2/2$ identical integrals. We define the two-particle distribution function as

$$G^{(2)} = \frac{1}{V^{N-2}} \int_V G(r_1, \dots, r_N) d^3r_3 \dots d^3r_N, \quad (24)$$

and rewrite Eqn (18) in the form

$$P(\rho, \Theta) = \rho\Theta - \frac{1}{6}\rho^2 \int_0^\infty r \frac{d\Phi(r)}{dr} G^{(2)}(r) 4\pi r^2 dr \quad (25)$$

(here we have taken into account that, owing to the spatial homogeneity of the system, the two-particle distribution function $G^{(2)}$ only depends on the difference of coordinates $r_{ij} = |r_i - r_j| = r$). Similarly, the internal energy of the entire system [9, 23]

$$E(\rho, \Theta) = \frac{3}{2}N\Theta + \frac{1}{2} \int_V \sum_{ij} \Phi_{ij} G(r_1, \dots, r_N) d^3r_1 \dots d^3r_N \quad (26)$$

can be represented with the aid of Eqn (24) in the form

$$e(\rho, \Theta) \equiv \frac{E}{N} = \frac{3}{2}\Theta + \frac{1}{2}\rho \int_0^\infty \Phi(r) G^{(2)}(r) 4\pi r^2 dr. \quad (27)$$

If $P(\rho, \Theta)$ and $e(\rho, \Theta)$ are known, then all other parameters of substance can be calculated from thermodynamic identities. Therefore, the two-particle distribution function $G^{(2)}$ completely determines the state of matter. In this respect it is entirely similar to the Gibbs distribution G . At the same time, $G^{(2)}$ is a function of just one variable r , whereas G depends on the coordinates of $N \approx \infty$ particles.

Observe now that the interaction potential of particles $\Phi(r)$ in Eqns (25) and (27) usually decreases with the distance as r^{-6} — that is, very fast indeed. Because of this, the main contribution to the local thermodynamic parameters comes from small distances $r < R_c$, where $R_c \approx 5\sigma \approx 10 \text{ \AA}$ is the radius of the correlation sphere. At $r > R_c$, the integrands in Eqns (25) and (27) vanish. Hence it follows that the particles outside the correlation sphere do not affect the values of the parameters of matter.

Fundamental set of equations (FSE). We see that the problem of calculation of the thermodynamic parameters reduces to finding the two-particle distribution function $G^{(2)}(r)$. But how can one find it? For this purpose, Morita and Hiroike [3]

used a formula (24) which expresses $G^{(2)}$ in terms of the integral of the Gibbs distribution G , and a similar formula for the one-particle distribution function $G^{(1)}$. Expanding G in powers of the density ρ , they also constructed a virial series for the functions $G^{(i)} = \sum \rho^k G_{(i)}^{[k]}$, $i = 1, 2$. According to the Lee–Yang theorem, this series must be uniformly convergent [4, 5]. Therefore, its terms can be grouped in an arbitrary way without compromising the convergence of the series itself. Taking advantage of this circumstance, Morita and Hiroike regrouped the series for $G^{(1)}$ in such a way that it turned into the equation of constancy of chemical potential

$$\begin{aligned} \mu &= \Theta \ln(\rho a) = \Theta \ln \rho G^{(1)}(\mathbf{r}_1) \\ &- \Theta \rho \int_V G^{(1)}(\mathbf{r}_2) G^{(1)}(\mathbf{r}_1, \mathbf{r}_2) d^3r_2 = \text{const}, \end{aligned} \quad (28)$$

and the series for $G^{(2)}$ became the generalized OZ equation

$$h(r_{12}) = C^{(2)}(r_{12}) + \rho \int_V G^{(1)}(r_3) C^{(2)}(r_{13}) h(r_{23}) d^3r_3. \quad (29)$$

In the case of spatially homogeneous media, when $\rho(\mathbf{r}) = \rho_0 G^{(1)}(\mathbf{r}) = \rho_0 = N/V$, $G^{(1)} = 1$, the first equation degenerates into the definition of the logarithm of the activity coefficient $\ln a$, and the second into the conventional OZ equation

$$h(r_{12}) = G^{(2)}(r_{12}) + \rho \int_V C^{(2)}(r_{13}) h(r_{23}) d^3r_3. \quad (29a)$$

Subsequently we shall refer to the set of equations (28), (29) as the fundamental set of equations (abbreviated FSE). Here

$$h(r) = G^{(2)}(r) - 1 = \exp\left[-\frac{\Phi(r)}{\Theta} + \omega(r)\right] - 1 \quad (30)$$

is the so-called general correlation function, $\omega(r)$ is the thermal potential, and

$$C^{(1)}(r) = h(r) - \omega(r) - \frac{1}{2}h(r)[\omega(r) + B^{(1)}(r)], \quad (31)$$

$$C^{(2)}(r) = h(r) - \omega(r) + B^{(2)}(r) \quad (32)$$

are the direct correlation functions of the first ($C^{(1)}$) and the second ($C^{(2)}$) orders, which include the bridge functionals of the first ($B^{(1)}$) and the second ($B^{(2)}$) orders (the latter are the infinite series of integrals whose integrands involve the products of general correlation functions $h(r)$). The structure of bridge functionals is formally known [24], so the OZ equation may be considered as closed. However, it is not possible to make straightforward use of the exact series for $B^{(i)}$, since they contain too large a number of integrals, each of which is rather complicated. So in practice the bridge functionals are approximated to some kind of a simpler expression. On these grounds it is sometimes said that the local OZ approach is approximate, whereas the approach based on the Gibbs distribution is rigorous. This statement presents a misconception.

FSE and the Gibbs distribution. As noted above, the FSE was originally obtained from the convolution of the virial series. If we expand it again, we return to the expression from which it had been derived — that is, to the Gibbs distribution. So,

taken in their most general forms, the Gibbs distribution and the FSE are completely equivalent. In practical calculations, however, we never deal with *exact* expressions: we cut off the virial expansions that follow from the Gibbs distribution at the third or fifth term, being unable to calculate the terms that follow, and in the OZ equation we replace the exact values of bridge functionals with approximated. Both the procedures lead to *approximations* whose accuracy we, strictly speaking, cannot assess *a priori*.³

In this respect the two approaches differ little. There is, however, one important distinction. It is impossible to extend the domain of applicability of virial expansions by replacing the exact higher terms with approximations, because we know nothing of what these terms look like. By contrast, the form of bridge functionals is known at present sufficiently well from numerical experiments, and in principle it is not difficult to approximate it with an analytical expression. (Of course, it is not an easy thing to find a close practical approximation ensuring a good fit over a broad range of parameters.) Today there are several approximations, accurate within a few percent over the entire phase plane including the region *CBTEH* (see Fig. 2) of liquid phase [25–38]. This proves that the local approach based on the OZ equation is more flexible and better suited for practical calculations than the global Gibbs approach. After all, this ought to be expected, since the reduction of the OZ equation to the closed integral equation only requires approximating just a single bridge functional which depends on just one variable.

FSE and the condition of mechanical stability. In order to demonstrate that FSE yields the same exact results as the Gibbs distribution, let us consider the problem of mechanical stability of an equilibrium system. With this purpose we apply a Fourier transform to the OZ equation (29):

$$\begin{aligned}\hat{\psi}(k) &= \int_{V_k} \psi(r) \exp(-ikr) d^3r = 4\pi \int_0^\infty \psi(r) \frac{\sin kr}{kr} r^2 dr, \\ \psi(r) &= \frac{1}{(2\pi)^3} \int_{V_k} \hat{\psi}(k) \exp(ikr) d^3k \\ &= \frac{1}{(2\pi)^2} \int_0^\infty \hat{\psi}(k) \frac{\sin kr}{kr} k^2 dk,\end{aligned}\quad (33)$$

where by ψ we need to mean both $C(r)$ and $h(r)$. As a result, we get

$$1 + \rho \hat{h}(k) = \frac{1}{1 - \rho \hat{C}(k)}, \quad \hat{C}(k) = \frac{\hat{h}(k)}{1 + \rho \hat{h}(k)}. \quad (34)$$

Hence it follows that points $1 + \rho \hat{h}(k) = 0$ are singular. They divide the entire \mathbf{k} plane, over which the OZ equation is defined, into two half-planes not connected with one another. Since we are only interested in that part of the phase diagram where all functions entering into the OZ equation are regular, we obviously have to consider either the half-plane $\rho \hat{h}(k) > -1$, or the half-plane $\rho \hat{h}(k) < -1$. Only the upper half-plane, however, includes the points corresponding to the

³ This statement is not exactly true. In the case of virial expansions we can formally calculate the next term of the series and thus assess the accuracy of the resulting expression. In practice, however, this possibility cannot be realized, because we are incapable of calculating the higher terms in the expansion. In the case of bridge functionals, however, it is always possible to estimate the accuracy of the results by checking their thermodynamic consistency. This method is much more efficient than the calculation of leading terms of the virial expansion.

state of rarefied gas. Because of this, we must select the upper half-plane as a *physical* one. Observe that the isothermal compressibility κ_θ by definition is [23]

$$\kappa_\theta = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_\theta = \frac{1}{\rho \Theta} [1 + \rho \hat{h}(0)]. \quad (35)$$

Therefore, on the upper half-plane we have $\kappa_\theta > 0$, and $1/\kappa_\theta = \rho(\partial P/\partial \rho)_\theta$ is also always positive [since $\rho = N/V$, and hence $d\rho = -(N/V^2)dV$, this inequality reduces to $(\partial P/\partial V)_\theta < 0$; see Eqn (2)].

FSE and the structure of matter. Transferring from the global description of the system to the local approach, we can not only reproduce the known results, but also get a new insight into the physics of the phenomenon. Numerous examples will be given later; here I only want to discuss the concept of the ‘structure of matter’.

Obviously, one phase of a substance differs from another phase of the same substance only in structure. Because of this, the concept of ‘structure’ ought to be fundamental in the theory of phase transitions. Surprisingly, we do not find this concept altogether in the Gibbs theory. This does not mean, of course, that the Gibbs distribution does not actually describe a structure: one can, for instance, calculate this distribution by the Monte Carlo method and then process the results in an appropriate fashion. But what is the ‘appropriate fashion’? The Gibbs theory gives no indications to this effect. Nature, however, abhors vacuum, and the scientific literature abounds with recipes for processing the results of numerical experiments. Some authors identify the structure with the instantaneous set of coordinates of all particles [39], some other describe it with the Voronoï–Delone polyhedrons [40], yet others use the concept of the network of hydrogen bonds permeating the entire volume of liquid [41], etc. Widely acclaimed has become the so-called percolation theory of phase transitions, in which it is anticipated that a phase transition is associated with the formation of a macroscopically extended network of bonds at the transition point. Some of these theories are internally consistent and usable. The question is how constructive they are, and what they add to our understanding of the nature of the phenomenon?

Now let us see what the local approach tells us about the structure of matter. In the general case, the local approach leads to a system of two equations (FSE) in two unknown functions: the one-particle distribution function $G^{(1)}(\mathbf{r})$, and the two-particle distribution function $G^{(2)}(r_{12})$. The first of these describes the averaged distribution of the density of matter $\rho(r) = \rho_0 G^{(1)}(\mathbf{r})$ in the laboratory frame firmly nailed to the center of mass of the entire macroscopic system. Under such circumstances, the vector \mathbf{r} in $G^{(1)}$ can assume any value inside the volume of the system V , the function itself describing the structure of matter on the macroscopic scale. In the case of gaseous or liquid phases, this structure is the same at any point of the macroscopic system, and therefore $G^{(1)}(\mathbf{r}) = \text{const.}$ ⁴ In crystals, $G^{(1)}(\mathbf{r})$ is a periodic function of \mathbf{r} .

By contrast, the two-particle distribution function $G^{(2)}(r_{12})$ characterizes the averaged distribution of the

⁴ It is unforgettable that this constant changes abruptly upon transition from the gaseous to liquid phase. Since the physical meaning is ascribed not to the function $G^{(1)}$ itself, but rather to the product $\rho = \rho_0 G^{(1)}$, it is sometimes assumed that $G^{(1)} \equiv 1$, and then the jump is experienced by the constant ρ_0 , which is essentially the same thing.

density of matter in a moving frame rigidly bound, for instance, to the center of mass of particle I . In this frame we shall count how often other particles appear at the distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ from the center of particle I . Averaging the results obtained (over time or over the ensemble — which does not matter much, since these two methods of averaging are equivalent by dint of the ergodicity hypothesis), we find the two-particle distribution function $G^{(2)}(r_{12})$, whose values in the case of spatially homogeneous systems do not depend on the coordinate r_1 of the first particle. Obviously, the two-particle distribution function $G^{(2)}(r_{12})$ defined in this manner describes the structure of matter only within the correlation sphere. Outside of the latter, in accordance with the condition of correlation damping [23], we have

$$\omega \rightarrow 0, h \rightarrow 0, G^{(2)} \rightarrow 1 \text{ for } r_{12} \rightarrow \infty, \quad (36)$$

and the density of matter is $\rho(r) = \rho_0 G^{(2)}(r_{12}) \rightarrow \rho_0 = \text{const}$. The absence of correlations between the positions of particles located fairly far from one another indicates that no threading networks of hydrogen bonds, and no percolation throughout the entire macroscopic system, are possible on the microscopic level. This statement is not, however, precisely accurate. Of course, in the instant photograph obtained in numerical experiments one can always discern a solid network of bonds between all particles. This network, however, will change from one photograph to the next, whereas *the structure of matter, like any other parameter of the equilibrium system, cannot depend on time*. Accordingly, it can only be found by averaging all instantaneous (random) photographs. This is principally important, because all the physical methods for measuring the structure of matter *only* respond to the averaged values of coordinates of particles.

So, the state of matter in the local approach is described by two structures: macroscopic (function $G^{(1)}(\mathbf{r})$), and microscopic (function $G^{(2)}(r_{12})$). Since FSE simultaneously includes both distribution functions, and neither of them can be eliminated, this set of equations puts the macroscopic and microscopic structures into a one-to-one correspondence. Unfortunately, this linkage is often overlooked. For example, in the theory of gases and liquids, where $G^{(1)}(\mathbf{r}) \equiv 1$, everything reduces to finding the microstructure [that is, the function $G^{(2)}(r_{12})$]. Conversely, postulated in the theory of solids are usually the parameters of the crystal lattice (which is equivalent to setting the function $G^{(1)}(\mathbf{r})$), while the microstructure is often neglected at all. This does not mean, of course, that the interaction between particles is not taken into account in the treatment of certain problems in the solid-state theory. This interaction is taken into account, but not in terms of the distribution functions. In the long run this puts up an ideological barrier between the theory of liquids on the one hand, and the theory of solids on the other. This situation cannot be tolerated, because the nature of processes that occur in these objects is often the same. If, for example, one looks at the critical phenomena from the standpoint of the theory of liquids, and — independently — from the standpoint of the theory of solids, it is hard to explain why the critical indices have the same values in liquids and in solids. When we recall, however, that, according to statistical mechanics, the correlation sphere must be present in all bodies (including crystals), and that its radius goes to infinity at the critical point, then it is no wonder that the same cause (infinite correlation radius) has the same effect — identical values of critical indices.

The lack of clear conceptions of the two structures also leads to confusion in the theory of first-order phase transitions. Since the concept of microstructure is usually associated with gases and liquids, and the concept of macrostructure with solids, the gas (liquid)–solid phase transition is often interpreted as transformation of microstructure to macrostructure and vice versa. Now if macrostructure in solids is macroscopically extensive, why could not liquids feature networks of hydrogen bonds of infinite extent (or equally extended percolations)? The fact is that in the case of first-order phase transitions the macrostructure of a crystal described by a periodic one-particle distribution function $G^{(1)}(\mathbf{r})$ turns abruptly into the macrostructure of a liquid with $G^{(1)}(\mathbf{r}) = \text{const}$, whereas the microstructure of a solid body described by a two-particle distribution function $G^{(2)}(r_{12})$ transforms into the microstructure of a gas (liquid), which is also described by a two-particle distribution function.

Now one final remark. The two-particle distribution function is sometimes identified with the radial function which only depends on the distance $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ between the particles. This is only true for noble gases, whose particles are spherically symmetric. In the general case, the two-particle distribution function depends not only on the distance r_{12} between the particles, but also on the mutual orientation of particles described by five angular coordinates. As a result, the microstructure of substances comprised of asymmetric molecules will be described by a two-particle distribution function of six variables: the distance r and five angles. The problem is how to visualize such a structure. But this, as they say, is a different kettle of fish.

Discussion. We see that in statistical mechanics there are two approaches: the global approach based on the Gibbs distribution, and the local approach based on FSE. In terms of consistency and universality, these two approaches are equivalent. This does not mean, however, that they are identical: what cannot be formulated or justified in the framework of the Gibbs theory (for example, the concept of the structure of matter), can be validated in the context of the local approach; whatever cannot be calculated in the framework of the Gibbs theory (for example, the parameters of dense gases and liquids), can be calculated using FSE, etc. We shall prove these (and other) advantages of the local approach with concrete examples later on.

2.6 Phase transitions and the fundamental set of equations

Now let us return to the problem of phase transitions, and see how FSE can help us in moving forward in this direction.

Two-phase approach. Consider a system comprised of gas (A) and liquid (B) phases in equilibrium with each other. We fix the origin at the interface, and direct the z -axis perpendicularly to the latter. Then the one-particle distribution function $G^{(1)}$ will be a function of only the z coordinate. At $z = +\infty$ this function will define the density of the gas phase $\rho_A = \rho_0 G^{(1)}(+\infty)$, and at $z = -\infty$ the density of liquid $\rho_B = \rho_0 G^{(1)}(-\infty)$. Since each phase far enough from the interface is spatially homogeneous, equation (28) of constancy of chemical potential becomes

$$\ln \rho_A - \rho_A \int_V C_A^{(1)}(r) d^3r = \ln \rho_B - \rho_B \int_V C_B^{(1)}(r) d^3r, \quad (37)$$

and Eqn (29) for the two-particle distribution function falls into two equations — one for phase A , and the other for

phase B :

$$h_A(r_{12}) = C_A^{(2)}(r_{12}) + \rho_A \int_V C_A^{(2)}(r_{13}) h_A(r_{23}) d^3 r_3, \quad (38)$$

$$h_B(r_{12}) = C_B^{(2)}(r_{12}) + \rho_B \int_V C_B^{(2)}(r_{13}) h_B(r_{23}) d^3 r_3. \quad (39)$$

In the rigorous theory, Eqn (38) with the given ρ_A (and the given temperature Θ and interaction potential $\Phi(r)$) defines unambiguously the value of h_A , and thus the value of $C_A^{(1)}$ in Eqn (37), and ρ_B in Eqn (39) defines h_B and $C_B^{(1)}$ in Eqn (37). As a result, Eqn (37) reduces to

$$\mu_A(\rho_A, \Theta) = \mu_B(\rho_B, \Theta) \quad (40)$$

[see Eqn (1)]. At the same time, the pressure constancy condition

$$P_A(\rho_A, \Theta) = P_B(\rho_B, \Theta) \quad (41)$$

must be satisfied, where the pressures are calculated by Eqn (25):

$$P_A(\rho_A, \Theta) = \rho_A \Theta - \frac{1}{6} \rho_A^2 \times \int_0^\infty r \frac{d\Phi(r)}{dr} G_A^{(2)}(r; \rho_A, \Theta) 4\pi r^2 dr, \quad (42)$$

$$P_B(\rho_B, \Theta) = \rho_B \Theta - \frac{1}{6} \rho_B^2 \times \int_0^\infty r \frac{d\Phi(r)}{dr} G_B^{(2)}(r; \rho_B, \Theta) 4\pi r^2 dr. \quad (43)$$

It is clear that the two equations (40) and (41) uniquely define the values of the two densities ρ_A and ρ_B . Thus, the FSE lead to the same conditions of two-phase equilibrium as do the thermodynamic considerations [see Eqn (1)]. If one of the phases features a crystalline structure, the conditions of equilibrium (41), (42) remain the same, but this time $G^{(1)}$ at $z = \infty$ will be not a constant but a function of the coordinate \mathbf{r} .

The results of calculations using formulas (37)–(43) for the Lennard–Jones (LJ) potential

$$\Phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (44)$$

are shown in Fig. 3. We see a perfect fit between the numerical experiment and the calculations based on integral equations — at least for the vapor condensation curve for $\Theta/\epsilon \leq 1.15$ (the left-hand branch in Fig. 3). The fit is slightly worse for the liquid evaporation curve (the right-hand branch in Fig. 3), but the error still does not exceed a few percent. At $\Theta/\epsilon > 1.15$, the agreement is not as good, because we are approaching the critical point where both the numerical simulation and the calculations with integral equations are less reliable. And yet, the overall agreement is still there.

Single-phase approach (virial expansions). Now let us see what happens within the density range $\rho_A < \rho < \rho_B$. We set $\rho = \rho_A + \delta\rho$, and expand $P(\rho, \Theta)$ and $\mu(\rho, \Theta)$ in Eqns (40) and (41) in a power series of $\delta\rho$. As a result, we get

$$\left(\frac{\partial P(\rho_A, \Theta)}{\partial \rho} \right)_\Theta = 0, \quad \left(\frac{\partial \mu(\rho_A, \Theta)}{\partial \rho} \right)_\Theta = 0. \quad (45)$$

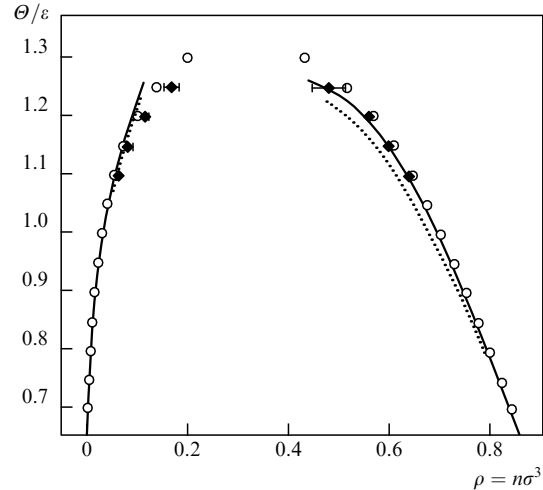


Figure 3. Curves of condensation and evaporation of an LJ liquid. Numerical experiment: ○ — results of Ref. [42], ◆ — results of Ref. [43]. Integral equations: — — results of Ref. [33], ⋯ — results of Ref. [32].

This means that inside the interval $\rho_A < \rho < \rho_B$ the quantities P and μ do not depend on the density ρ . However, this obviously is contrary to the initial OZ equation, which involves ρ as a literal parameter. The only way out of this complication is to assume that the OZ equation has no solution over the interval $\rho_A < \rho < \rho_B$. This assumption is in complete agreement with our conclusions based on the Gibbs distribution (see above). It is not surprising that the solution of the OZ equation vanishes: from the theory of integral equations we know that the eigenvalues (in our case the density ρ) of integral equations may feature breaks within the confines of which the equations admit no solutions (see any textbook on integral equations).

In this way, the points ρ_A and ρ_B are the points where the solution of the OZ equation *vanishes*. At these points the virial series must diverge. In the case of Gibbs distribution we were unable to identify these points, because this theory did not allow us to calculate the higher coefficients of the expansion that are responsible for the singularity. In the case of FSE, however, we can use the theory of integral equations for calculating the *approximate* values of the virial coefficients [44]. Let us reproduce here the argumentation of Ref. [44], which is a good illustration of the method for solving problems of this kind.

First, we need to get an approximation for the bridge functional (used for this purpose in Ref. [44] is the generalized Martynov–Sarkisov (MS) closure $B^{(2)} = -a(\rho, \Theta)\omega^2(r)$ [28]; of course, other approximations are also possible). The next step is to expand in the powers of density ρ both the OZ equation itself

$$h^{[k]}(r_{12}; 0, \Theta) = C^{[k]}(r; 0, \Theta) + \sum_{i=0}^{k-1} \int_V C^{[i]}(r_{13}; 0, \Theta) \times h^{[k-1-i]}(r_{23}; 0, \Theta) d^3 r, \quad k = 0, 1, \dots, \infty, \quad (46)$$

and the constant $a(\rho, \Theta) = \sum_{k=0}^{\infty} \rho^k a^{[k]}(\Theta)$, which gives

$$C^{[k]} = h^{[k]}(r; 0, \Theta) - \omega^{[k]}(r; 0, \Theta) - \sum_{i=0}^k a^{[i]}(0, \Theta) \{\omega^2(r; 0, \Theta)\}^{[k-i]} \quad (47)$$

(here the operator $[k]$ is defined by Eqn (17)). Starting with $k = 1$, these equations are linear in $C^{[k]}$ and $h^{[k]}$, and their successive solution does not pose any big problem. The constants $a^{[k]}(\Theta)$ are found in Ref. [44] from the conditions of thermodynamic consistency of the solution. The latter can be found from the obvious condition which states that the values of virial coefficients B_k found by substituting $h^{[k]}$ into the formula for the pressure (25) must coincide with the values of the same coefficients calculated from the expression for isothermal compressibility [23]

$$\frac{1}{\kappa_\Theta} = \rho \left(\frac{\partial P}{\partial \rho} \right)_\Theta = \rho \Theta \left(1 - \rho \int_0^\infty C^2(r) 4\pi r^2 dr \right). \quad (48)$$

Based on the above relations, several tens of the virial coefficients $B_k(\Theta)$ for the LJ potential were calculated in Ref. [44]. The comparison of the first four of them with the coefficients found by the method of group expansions indicates that the accuracy of the theory based on FSE is quite satisfactory (Fig. 4). Such a comparison cannot be performed for the higher coefficients, since the Gibbs theory does not allow their calculation. Unfortunately, the calculated coefficients were not yet sufficient for reliably locating the points of divergence of the virial series $\rho(\Theta)$. As we know, the latter can be found from the tests of convergence of Cauchy and d'Alembert:

$$\rho(\Theta) = \lim_{k \rightarrow \infty} \sqrt[k]{B_k(\Theta)}, \quad \rho(\Theta) = \lim_{k \rightarrow \infty} \frac{B_k(\Theta)}{B_{k+1}(\Theta)}. \quad (49)$$

However, the substitution of the calculated values of $B_k(\Theta)$ into these expressions always resulted in that the value of $\rho(\Theta)$ calculated from one test of convergence was different from the value of $\rho(\Theta)$ calculated from the other test. Because of this, in Ref. [44] an extrapolation technique was used, based on the principle illustrated in Fig. 5. The curve $\rho(\Theta)$ was plotted from the extrapolated data (Fig. 6). It was found that this curve lies close enough to the vapor condensation curve calculated by the two-phase method. The former is somewhat shifted to the right of this curve, which is explained by the fact that we are dealing with an approximate rather

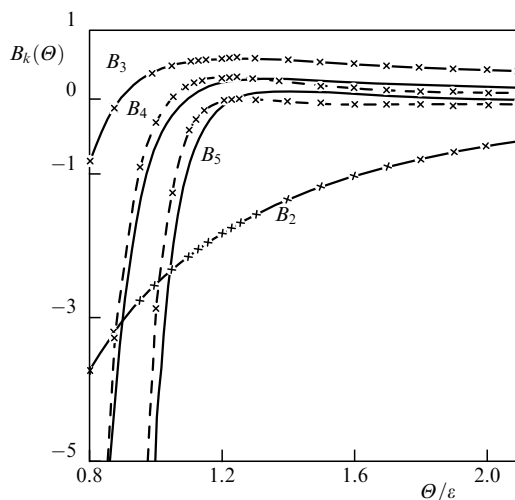


Figure 4. Temperature dependence of the first four virial coefficients $B_k(\Theta)$ for the LJ potential: — — results obtained with group expansions [45]; - - - results obtained with FSE [44].

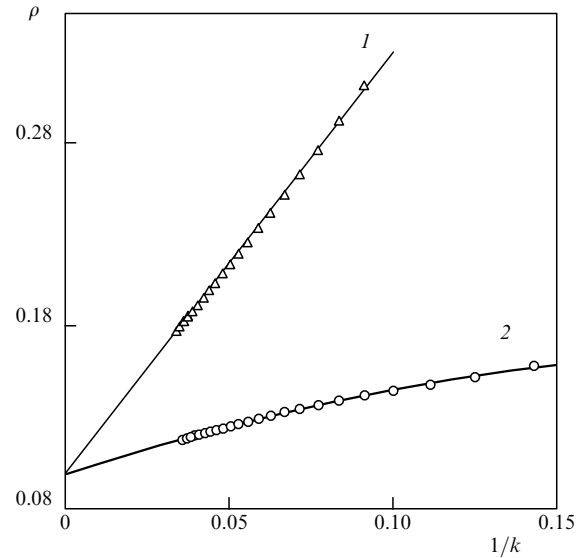


Figure 5. Extrapolation of virial coefficients $B_k(\Theta)$ to the limit $1/k \rightarrow 0$: 1 — Cauchy's test of convergence, 2 — d'Alembert's test of convergence [44].

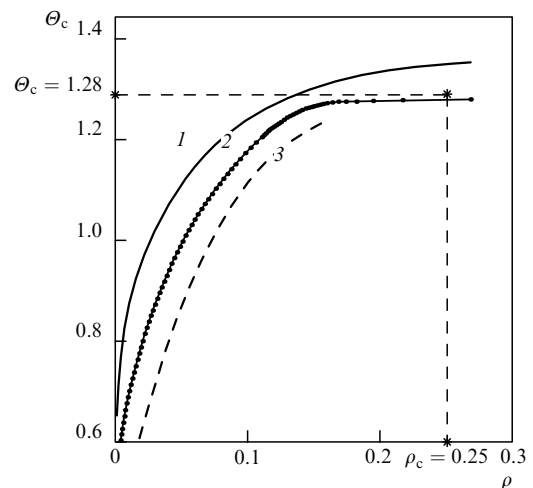


Figure 6. Vapor condensation curves obtained from numerical experiment (curve 1 [46]), and from divergence of the virial series (curve 2 [44]), and spinodal (curve 3 [46]).

than an exact solution. On approaching the critical point, the curve of divergence of the $\rho(\Theta)$ series levels out, in complete agreement with the predictions of the theory of critical phenomena.

General solution of the Ornstein–Zernike equation. Obviously, the solution of the OZ equation does not exist to the right of the curve of divergence of the virial series. The solution does not vanish, however, when the OZ equation is solved numerically — with the same closure but without series expansion. Instead, the solution always extends into the two-phase domain where, according to the arguments developed above, it does not exist. This is because the singularity appearing in the curve of phase equilibrium is very weak, and it is very difficult to detect it in numerical simulation without knowing in advance what it looks like. Here only analytical study of the problem can help, which we start with getting the general solution of the OZ equation [47]. Here we briefly describe the technique developed in Ref. [47].

From Eqn (33) it follows that, since $\hat{h}(k) \sin(kr)k$ is an even function of k , we have

$$\begin{aligned} rh(r) &= \frac{1}{(2\pi)^2} \int_0^{+\infty} \hat{h}(k) \sin(kr)k \, dk \\ &= \frac{1}{2} \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} \hat{h}(k) \sin(kr)k \, dk. \end{aligned} \tag{50}$$

Now, since $\sin(kr) \equiv -i[\exp(ikr) - \cos(kr)k]$, where $\cos(kr)k$ is an odd function, we can rewrite Eqn (50) using Eqn (34) in the form

$$\begin{aligned} rh(r) &= \frac{1}{2i} \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} \hat{h}(k) \exp(ikr)k \, dk \\ &= \frac{1}{2i} \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} \frac{\hat{C}(k)}{1 - \rho \hat{C}(k)} \exp(ikr)k \, dk. \end{aligned} \tag{51}$$

The integral on the right-hand side of Eqn (51) can be found with the theory of residues. To do this, we need to go over from the real values of k to the complex values $k = k' + ik''$, and close the real axis k' , over which the integral is taken in Eqn (51), in the complex plane with an arc of infinite radius. Then we find the locations of poles in the upper half of the complex plane, bounded from above by this arc, and by the real axis k' from below. Let the coordinates of poles of the integrand in Eqn (51) are given by $k_j = iz_j$, where $z_j = \alpha_j + i\beta_j$. Then, obviously, the poles of the integrand in Eqn (51) will be given by zeros of the denominator — that is, by the equation $1 = \rho \hat{C}(k_j)$ or, with due account for Eqn (33), by

$$1 = 4\pi\rho \int_0^{+\infty} C(r) \frac{\sin iz_j r}{iz_j r} r^2 \, dr$$

or

$$1 = 4\pi\rho \int_0^{+\infty} C(r) \frac{\text{sh}z_j r}{z_j r} r^2 \, dr \tag{52}$$

(first expressed in Ref. [48]). Since the integrand in Eqn (51) is the fraction $\xi(k)/\psi(k)$, where $\xi = k\hat{C}(k) \exp(ikr)$, $\psi = 1 - \rho\hat{C}(k)$, then from the theorem of residues we get

$$rh(r) = \frac{1}{2\pi} \sum_j R_j. \tag{53}$$

The residue is

$$R_j = \frac{\xi(k_j)}{\psi'(k_j)} = -\frac{k_j \hat{C}(k_j) \exp(ik_j r)}{\rho \hat{C}'(k_j)} = -\frac{iz_j \exp(-z_j r)}{\rho^2 \hat{C}'(iz_j)} \tag{54}$$

(here we have noted that $\hat{C}(k_j) = 1/\rho$). Finally, we find that

$$h(r) = -\sum_j \frac{iz_j}{2\pi\rho^2 \hat{C}'(iz_j)} \frac{\exp(-z_j r)}{r} = \sum_j A_j \frac{\exp(-z_j r)}{r}. \tag{55}$$

Since, by definition, the Fourier transform of the direct correlation function is (see Eqn (33))

$$\hat{C}(k) = 4\pi \int_0^{+\infty} C(r) \frac{\sin kr}{kr} r^2 \, dr, \tag{56}$$

its derivative with respect to k is

$$\tilde{C}'(k) = 4\pi \int_0^{+\infty} C(r) \left(\frac{\cos kr}{k} - \frac{\sin kr}{k^2 r} \right) r^2 \, dr. \tag{57}$$

Setting here $k = iz_j$, we get the sought expression for the amplitudes [47]

$$\begin{aligned} A_j &= -\frac{iz_j}{2\pi\rho^2 \hat{C}'(iz_j)} \\ &= \frac{z_j^2}{2(2\pi\rho)^2 \int_0^{+\infty} C(r) [\text{ch}(z_j r) - \text{sh}(z_j r)/z_j r] r^2 \, dr}. \end{aligned} \tag{58}$$

If z_j is a real number, then this formula does not require any modifications. If z_j is a complex number, in Eqns (55) and (58) one must set $A_j = A'_j + iA''_j$ and separate the real and imaginary parts in all expressions. This eventually leads to rather cumbersome equations which we do not reproduce here: the main idea is clear enough from the above results. The passage from the real roots of the transcendental equation (52) to the complex roots does not really change anything.

Vanishing of solutions of the Ornstein – Zernike equation. The transcendental algebraic equation (52), like any transcendental equation, has an infinite number of roots $z_j = \alpha_j + i\beta_j$, $j = 1, 2, 3, \dots$. We know very little of their behavior. As a matter of fact, they have only been studied in one paper [48], where these roots were examined in different approximations for a system of rigid spheres with the potential (22), without any reference whatsoever to phase transitions. Nevertheless, this work provides the basis for formulating a certain hypothesis concerning the mechanism of vanishing of the solution of the OZ equation in the curves of first-order phase transitions.

Table 1 gives the values of α_j, β_j found in the hypernetted-chain approximation (HNC) where we set $B^{(2)} = 0$, and in the MS approximation in accordance with whom $B^{(2)} = -\omega^2/2$. Calculations in Ref. [48] were done for different densities $\tilde{\rho} = \rho\sigma^3$, where $\rho = N/V$ is the mean number density of particles. We see that at all densities $\tilde{\rho}$ the majority of coefficients α_j fall within a rather narrow interval

$$\Delta\alpha = \alpha_{\max} - \alpha_{\min} \tag{59}$$

(we do not exclude the possibility that more accurate calculations will give $\Delta\alpha = 0$). At the same time, at high densities ($\tilde{\rho} > 0.2$) we can observe the appearance of individual ‘dropouts’ from the corridor $\Delta\alpha$, whose absolute value α_j^* quickly decreases with increasing density. In all likelihood, there is an infinite number of such dropouts. Judging by Table 1, every fifth root qualifies as a dropout, i.e.

$$\alpha_j^* = \alpha_{5j}, \tag{60}$$

and, curiously enough, this result does not depend on the approximation in which the OZ equation is being solved.⁵ What is more, the absolute values of α_j^* and the relevant imaginary parts β_j^* are approximately the same for the ‘dropouts’, whereas the values of regular roots α_j, β_j differ rather considerably in different approximations. As far as we can see, the following inequality always holds for the

⁵ The exception seems to be the Percus – Yevik approximation, where there are no dropouts at all. This assumption, however, has yet to be proved.

Table 1. Roots of the transcendental equation in HNC and MS approximations [48].

$\bar{\rho} = 0.1$		$\bar{\rho} = 0.5$		$\bar{\rho} = 0.9$	
HNC	MS	HNC	MS	HNC	MS
α_j	β_j	α_j	β_j	α_j	β_j
4.26	0.72	3.73	1.47	3.73	0.68
4.21	2.13	3.67	2.90	3.90	2.20
4.11	3.54	3.56	4.20	3.86	3.73
3.84	4.70	3.62	5.21	3.80	5.30
4.27	5.58	1.77	6.00	1.70	5.88
				2.70	1.68
				3.13	2.83
				2.83	4.60
				2.77	5.90
				0.80	6.92
					3.77
					1.44
					3.70
					2.93
					3.62
					4.48
					3.36
					6.00
					0.70
					6.82
					3.81
					7.83
					3.50
					9.41
					3.56
					10.9
					3.50
					12.5
					1.83
					12.7
					3.70
					14.3

Note: ‘Dropouts’ were marked with bold italic.

‘dropouts’:

$$\alpha_j^* < \alpha_{j+1}^* . \tag{61}$$

The general pattern of the distribution of poles is given in Fig. 7.

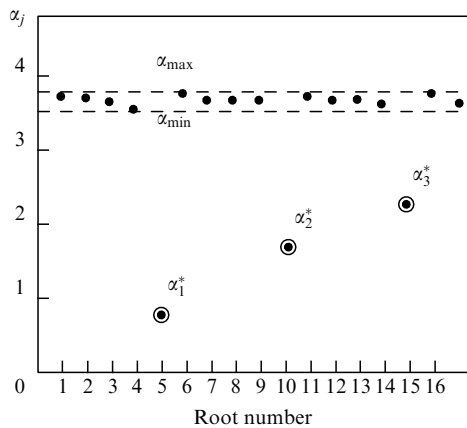


Figure 7. Schematic distribution of roots of the transcendental equation (52) for the system of rigid spheres with density $\bar{\rho} = 0.9$, calculated in the MS approximation [48].

Now let us turn to the transcendental equation (52), which we write out in the form

$$1 = 4\pi\rho \left[\int_0^R C(r) \frac{\text{sh}z_j r}{z_j r} r^2 dr + \int_R^\infty C(r) \frac{\text{sh}z_j r}{z_j r} r^2 dr \right] . \tag{62}$$

According to Eqn (32), in this expression we have $C = h - \omega + B^{(2)}$. In Eqn (62) we put R so large that at $r > R$ the potential $\Phi(r)$ can be regarded as equal to zero (recall that the potential varies as $\Phi \approx (\sigma/r)^6$ for $r \rightarrow \infty$, and at $r > (2-3)\sigma$ the condition $\Phi = 0$ is satisfied). In this approximation $h = \exp \omega - 1 = \sum_{j=1}^\infty \omega^j / j!$ and

$$C = \sum_{j=2}^\infty \frac{1}{j!} \omega^j - B^{(2)} . \tag{63}$$

Assume first that $B^{(2)} = 0$. Retaining in Eqn (63) only the principal term ω^j with the lowest power, we find that as

$r \rightarrow \infty$ the direct correlation function is

$$C \rightarrow \frac{1}{2} \omega^2 \approx \frac{1}{2} [A_1^* \exp(-\alpha_1^* r)]^2 . \tag{64}$$

In the second integral in Eqn (62) this expression is multiplied by $\text{sh}(\alpha_j r) / \alpha_j r \approx \exp(\alpha_j r) / 2\alpha_j r$, where α_j is a regular root from those falling within $\Delta\alpha$ (for simplicity, we disregard the imaginary part that describes oscillations of the distribution function). Obviously, the second integral in Eqn (62) will converge only if

$$2\alpha_1^* > \alpha_j ; \tag{65}$$

otherwise it diverges and goes infinite. Then, of course, the transcendental equation itself is no longer valid. Simultaneously, the integral in the denominator in Eqn (58) also goes to infinity, since it is also equal to

$$\int_0^\infty = \int_0^R + \int_R^\infty$$

and

$$\int_R^\infty \approx \int_R^\infty \frac{1}{2} (A^*)^2 \exp(-2\alpha_1^* r) \exp(\alpha_j r) r dr . \tag{66}$$

As a result, for the density at which

$$2\alpha_{\min}^* = \alpha_j , \tag{67}$$

the amplitude A_j becomes zero:

$$A_j = 0 , \tag{68}$$

and the corresponding term will disappear from the overall sum $h(r) = \sum_j A_j \exp(-\alpha_j r) / r$. This will happen very smoothly and insensibly, because the divergence occurs at the largest distances $r \approx 1/2\alpha_{\min}$, and develops gradually as we approach the point where condition (67) is satisfied.⁶ Obviously, in the regular group of roots the terms with $\alpha_j \approx \alpha_{\max}$ will be the first to disappear, then the roots with $\alpha_j \leq \alpha_{\max}$ will follow, and so on, all the way to the roots with $\alpha_j = \alpha_{\min}$. After that all the roots of the regular group will be

⁶The weak divergence of the virial series at the points of the first-order phase transition was also pointed out in Ref. [17], where the Gibbs distribution (not the OZ equation!) was used for getting the exact expressions for the virial coefficients $B_k(\Theta)$ of the lattice gas at $k \rightarrow \infty$.

gone, and $h(r)$ will only contain one term dominated by the ‘dropout’. Then, however, it will no longer be possible to satisfy the condition at $r = 0$, where $h = -1$. This means that the density at which all the regular roots disappear is the point where the solution vanishes — that is, the point of the phase transition.

So far we have assumed that $B^{(2)} = 0$. In the MS approximation, when the bridge functional $B^{(2)} = -\omega^2/2$ compensates the quadratic term in the expansion of h , the principal term in the expansion of C with respect to ω (the term that falls off at infinity at the slowest rate) is that with ω^3 . As a result, in place of Eqn (67) we get $3\alpha_1^* = \alpha_j$. If the bridge functional also compensates the cubic term in the expansion of h with respect to ω , then in this equality we shall have 4 in place of 3, and so on.

Discussion. In this section we have shown that the local theory based on FSE is capable of the following:

(a) in the context of the two-phase approach, calculating the curves of vapor condensation and liquid evaporation $\rho = \rho(\Theta)$ with good enough accuracy;

(b) calculating the leading terms of the virial expansion, and showing that this series diverges in the vapor condensation curve in complete agreement with the ideas of the single-phase approach;

(c) analyzing the asymptotic OZ equation and establishing the general criterion of vanishing the solution of the complete OZ equation [see Eqn (68)].

All this allows the guidelines for converting the single-phase approach into a working tool for calculation of the curves of phase equilibrium to be put forward. And, what is equally important, we have used this example to demonstrate that the theory based on FSE is capable of delivering fundamentally new results.

2.7 Metastable states

Strictly speaking, it is impossible to make any conclusions concerning the nonequilibrium metastable states, based on the results of the equilibrium theory. The only thing we can speak about is the peculiarities of the transition from the thermodynamically stable state to the metastable state.

Thermodynamic limit. From a macroscopic standpoint, there is no clear-cut distinction between equilibrium and metastable systems: the former last forever, and the latter (say, glasses) for hundreds of years. This is not a distinguishing feature. Compared with the only characteristic microscopic time parameter — the time of chaoticization of the system, $\tau \approx 10^{-12}$ s — a century is the same as eternity. At the same time, statistical mechanics has a way of telling one from the other, because it describes systems occurring at thermodynamic equilibrium, and does not describe a metastable system. How does this happen? What are the restrictions that automatically exclude metastable systems from consideration?

The matter is that statistical mechanics is formulated in the so-called thermodynamic limit

$$N \rightarrow \infty, \quad V \rightarrow \infty \quad \text{at} \quad \rho = \frac{N}{V} = \text{const}. \quad (69)$$

In other words, by definition it only deals with infinitely large bodies. The passage to the thermodynamic limit in statistical mechanics is necessary because it is only then that its predictions become unambiguous. In systems of finite size the distributions of particles, differing from the Gibbs distribution, may also be present (see Ref. [23]), and it is

impossible to decide which of the possible distributions is realized in each particular case, because this depends on the configuration of particles that has spontaneously sprung up in the system.

In order to understand why condition (69) is so important for the theory of phase transitions, let us consider a system in which the pressure and the temperature are maintained constant. The probability of occurrence of the system in the given phase state is $W \propto \exp(\Phi/\Theta)$, where $\Phi = N\mu$ is the thermodynamic potential of the system, N is the total number of particles, and μ is the chemical potential. Accordingly, the probabilities ratio for realization of phases A and B in such a system is

$$\frac{W_A}{W_B} = \exp\left[-\frac{1}{\Theta}(\Phi_B - \Phi_A)\right] = \exp\left[-\frac{N}{\Theta}(\mu_B - \mu_A)\right]. \quad (70)$$

For any finite N this ratio is also finite, which means that the system may, in principle, occur in either one of the two states. At $N = \infty$, however, the situation is different: with $\mu_B > \mu_A$ we have $W_A/W_B \approx 0$, and therefore the probability of realization of the phase A is zero (an impossible event), and that of the phase B is one (a certain event). Conversely, with $\mu_B < \mu_A$, the probability of realization of the phase A is one, and that of the phase B is zero. And only with $\mu_A = \mu_B$, the realizations of both the phases A and B are equiprobable (the two-phase state of the system).

The same conclusion can be reached in a different way. Let us mentally divide the entire system into N_0 identical volumes v_0 , so that $V = N_0 v_0$. Let the probability of the nucleus occurring in volume v_0 be W_0 . Then the probability $W = N_0 W_0$ of occurrence of at least one nucleus in the entire system (which is sufficient for starting a phase transition) for any arbitrarily small but finite W_0 is unity, because $N_0 \rightarrow \infty$ (a certain event). And only with $W_0 = 0$ (the state of stable thermodynamic equilibrium), the overall probability W of occurrence of the nucleus does not depend on N_0 — it is equal to zero as before.

We see that it is the passage to the thermodynamic limit in statistical mechanics (which deals with the discrete model of matter) that removes ambiguity from the problem of finding the points of phase transition. In this respect statistical mechanics is essentially different from thermodynamics which deals with the model of continuous medium. The concept of a ‘particle’ can only be introduced here by a *tour de force*. Usually this is accomplished by adding another postulate which states that the free energy F (or some other characteristic function of the system) depends not only on ρ and Θ , but also on several *macroscopic* parameters ξ_k . Let one of these parameters have the meaning of the total number of particles N . Then one can introduce the derivative $\mu = (\partial F/\partial N)_{\rho, \Theta}$ and call it the chemical potential. If, however, we turn to the BBGKY hierarchy⁷, which lies in the basis of the entire statistical mechanics, we find that after passage to the thermodynamic limit it only retains two independent literal parameters — ρ and Θ . Because of this, all other parameters ξ_k , including the number of particles N , are functions of density and temperature. This is easy to see if we look at the more general case of reacting systems. They obey the law of mass action, which states that the concentrations of individual components N_i (and, therefore, the total

⁷The Bogolyubov–Born–Green–Kirkwood–Yvon hierarchy of equations [49].

number of particles $N = \sum_l N_l$) are functions of ρ and Θ [20]. Another example is the order parameter, a concept widely used in the theory of critical phenomena (see Section 3). In the case of liquids, this parameter is identified with the length of the two-phase interval of densities $\Delta\rho = \rho_A(\Theta) - \rho_B(\Theta)$ (see Eqn (7)), a quantity that is by no means arbitrary in statistical mechanics — it has to be determined either from the Gibbs distribution or from the solution of FSE (the latter, as we know, do not involve any ζ_k ; they only include the interaction potential $\Phi(r)$ and the literal parameters ρ and Θ).

Thus we see that in statistical mechanics all the macroscopic parameters of the system, including ζ_k , depend on ρ and Θ , and this is a functional dependence. It is defined by the integrals of the distribution functions $G^{(i)} = G^{(i)}(r; \rho, \Theta)$, each of which is itself a function of ρ and Θ . Instead of this, in thermodynamics the parameters ζ_k are regarded as independent variables, like ρ and Θ . In most cases the introduction of these parameters gives a correct description of the phenomenon and does not lead to any significant mistakes or contradictions. It seems likely that the discrepancy between thermodynamics and statistical mechanics relates only to the metastable states: the former describes them, the latter does not.

Mechanism of the loss of stability. To understand the mechanism of the loss of stability we must return to the results of the preceding section. The solution disappears because just one root (out of the infinite set) becomes too small and thus violates condition (68), while all the other roots behave disciplined. Besides, the amplitude of the root that ‘violates an order’ vanishes at the time of breach, so the disappearance of the root occurs unnoticed. It is easy to overlook this event in numerical simulation — the more so because the smallest roots correspond to the largest distances, where all functions are practically equal to zero. That is the reason why attempts to find the point where the solution disappears usually fail, and the solution easily jumps over into the metastable region. The ‘weak’ divergence of the virial series at the transition point is also seen from the analytical solution obtained in Ref. [17] for the lattice model of liquid.

2.8 Summa summarum

Let us give the sum and substance of our discussion. Based on thermodynamics, we have shown that the single-phase approach has reason to exist. Further analysis revealed, however, that this approach cannot be realized within the framework of the global Gibbs approach. More promising is the local approach based on the fundamental set of equations (FSE). Using the latter, we established that the virial series diverge in the vapor condensation curve in full agreement with the Lee–Yang theorem. Besides, analyzing the asymptotic behavior of the OZ equation we found one of the possible mechanisms of the solution disappearance. It would be too early, however, to speak of having validated the single-phase approach. We must check thoroughly whether this mechanism allows defining the transition points, or there is an alternative mechanism by which the solutions may disappear. This, however, is a task for the future.

3. Critical phenomena

3.1 Statement of the problem

In 1982, K G Wilson won the Nobel Prize for development of the theory of critical phenomena. As I was told by one

celebrated theoretician: “This means that the problem is solved; nothing’s left to be done here”. I, however, dare to disagree with this opinion.

It is true that the classical Widom–Kadanoff–Wilson theory (WKW) permitted calculating the critical indices in full agreement with experiment [50]. The experimenters working, for example, with solutions are less interested in the critical indices than in the values of concentration and temperature at which the critical point will occur in the system under consideration, in how the system will behave in the neighborhood of this point, etc. These questions are not answered by the WKW theory — and cannot be, because this theory is based on the assumption that all properties of matter at the critical point are determined by the behavior of particles located far away from one another — at such distances for which the interaction potential is $\Phi(r) = 0$. We know, however, that it is the interaction potential that determines the distinctive properties of matter. Therefore, the neglect of the short interparticle distances, for which $\Phi(r) \neq 0$, automatically precludes the possibility of studying the individual features of critical phenomena.

Theoreticians have their own reasons to be disappointed — many concepts of this theory lack sufficient validation (see below). On top of that, almost all results of the classical theory of critical phenomena are based on *discrete* lattice models like the Ising model, for which the Gibbs distribution can be calculated exactly or almost exactly. At the same time, liquids belong to *continuous* media, and the results obtained with discrete lattice models can only be applied to them after careful analysis.

In the long run the WKW theory is based on the global Gibbs distribution (and on numerous additional assumptions). At the same time, as shown in the preceding section, passage to the local OZ equation gives extra insight into the mechanism of first-order phase transitions. It would be only natural to wonder what this approach could add to our understanding of second-order phase transitions (i.e. critical phenomena). This section of the review is devoted to this problem.

The first attempt to use the OZ equation for describing critical phenomena was undertaken by the authors of this equation themselves as early as 1914. Later, however, their so-called classical critical indices were found to be rather different from the experimental values [51]. At that time this was not much of a surprise, because the OZ equation was regarded as a definition of the direct correlation function rather than as an equation. If a definition does not apply to a particular case, so much the worse for it. As I said, however, in 1960 Morita and Hiroike proved that the OZ equation directly follows from the Gibbs distribution [3] (see also Refs [52, 53]). If so, then the OZ equation should yield precisely the same results as the Gibbs distribution. For a long time, however, this statement escaped proof: the OZ equation always led to the classical critical indices. Therefore, summarizing the current state of the theory of critical phenomena, M Fisher had all grounds to state that “... the integral equations cast essentially no light on the issue of Ising-type *versus* classical critical behavior”⁸ (from *Abstract* submitted to the NATO Advanced Study Institute “New Approaches to Old and New Problems in Liquid State Theory”, Patti Marina, Messina, Sicily, 7–17 July 1998).

⁸ The integral equations threw little light on the problem of the transfer from classical critical indices to Ising-type indices.

We shall shortly demonstrate that, with a more careful analysis, the OZ equation will yield not only all the results of the WKW theory, but also many previously unknown features of critical phenomena, practically without any additional hypotheses. As a matter of fact, the only additional assumption is the approximation of a bridge functional, without which the calculation of critical indices would have been impossible. As stated in Section 2, however, such an approximation is inevitable not only in the case of critical phenomena, but actually in the case of any attempt to go beyond the limits of the theory of rarefied gases. This is true irrespective of whether we are using the Gibbs distribution or the FSE.

3.2 Critical phenomena and thermodynamics

In Section 2 we studied a case when the condition of neutral equilibrium $(\partial P/\partial \rho)_\Theta = 0$ is satisfied over a finite interval $\rho_A < \rho < \rho_B$. Now we shall consider the case when

$$\left(\frac{\partial P}{\partial \rho}\right)_\Theta = 0 \quad (71)$$

at a single critical point

$$\rho = \rho_c, \quad \Theta = \Theta_c. \quad (72)$$

Since, by definition, we are only dealing with equilibrium systems, the latter condition implies that at any other values of ρ , Θ the system is absolutely stable. Accordingly, for all points that lie in the isotherm $\Theta_c = \text{const}$, with the exception of the critical point itself, we have $(\partial P/\partial \rho)_\Theta > 0$ (see Eqn (2)). This is compatible with Eqn (71) only provided that the critical point is the point of inflection of the isotherm $P(\rho, \Theta_c)$, and therefore

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_\Theta = 0 \quad (73)$$

at this point. Since at equilibrium we have $P = P(\rho, \Theta)$, the two conditions (71) and (73) uniquely define the coordinates of the critical point ρ_c, Θ_c (given, of course, that we know the equation of state $P(\rho, \Theta)$).

Now let us see what can be said about the properties of matter at the critical point, remaining in the framework of thermodynamics and phenomenological approach.

From the thermodynamic theory of fluctuations and Eqn (71) it follows that at the critical point the rms density fluctuation is [20]

$$\eta \propto \left[\frac{\rho}{\Theta} \left(\frac{\partial P}{\partial \rho}\right)_\Theta\right]^{-1/2} = \infty \quad \text{at } \rho = \rho_c, \quad \Theta = \Theta_c. \quad (74)$$

The latter means that the microscopic density fluctuations become macroscopic with the amplitude close to the mean density $\rho = N/V$. This conclusion is brilliantly confirmed by the experiment, since liquids at the critical point always feature opalescence.

The experiment also indicates that many parameters of a substance behave in a nonanalytical way in the neighborhood of the critical point (recall that, by contrast to this, in the regular part of the phase diagram all the macroscopic parameters can be expanded in the *analytical* Taylor series in powers of density [4]). For example, the heat capacities in the neighborhood of ρ_c, Θ_c vary as

$$C_P, C_V \propto \varepsilon_\Theta^{-\alpha}, \quad (75)$$

where $\alpha \approx 0.11$ is the critical index, and $\varepsilon_\Theta = (\Theta - \Theta_c)/\Theta_c$. The density difference between gas and liquid phases varies as

$$\Delta \rho = \rho_A - \rho_B \propto \begin{cases} 0, & \Theta > \Theta_c, \\ \varepsilon_\Theta^\beta, & \Theta < \Theta_c, \end{cases} \quad (76)$$

where $\beta \approx 0.33$ is another critical index. The isothermal compressibility varies as

$$\kappa_\Theta \propto \varepsilon_\Theta^{-\gamma}, \quad (77)$$

where $\gamma \approx 1.23$ is a third critical index. The pressure varies as

$$\Delta P = P - P_c \propto \varepsilon_\rho^\delta, \quad (78)$$

where $\delta \approx 4.6$ is a fourth critical index. In addition, we can define the critical index ν that describes the behavior of the correlation radius near the critical point:

$$R_c \propto \varepsilon_\Theta^{-\nu}, \quad (79)$$

where $\nu \approx 0.63$, and the critical index η that describes the asymptotic behavior of the two-particle distribution function

$$G^{(2)}(r) \rightarrow 1 + A \frac{\exp(-\lambda r)}{r^{1+\eta}}, \quad (80)$$

where $\eta \approx 0.05$. There may also be other critical indices (all the above values of critical indices were found experimentally [51]).

From purely thermodynamic considerations one can establish a number of *similarity relations* between the critical indices [11]:

$$\alpha + 2\beta + \gamma \geq 2, \quad (81)$$

$$\gamma \geq \beta(\delta - 1), \quad (82)$$

$$(2 - \eta)\nu \geq \gamma, \quad (83)$$

$$3 \frac{\delta - 1}{\delta + 1} \geq 2 - \eta, \quad (84)$$

and so on. The experiment reveals, however, that these relations are invariably realized as equalities rather than as inequalities [for instance, $(2 - \eta)\nu = \gamma$]. Thermodynamics cannot explain why this is so.

Calculation of critical indices with the aid of the van der Waals equation of state in this approximation (which is usually referred to as classical) gives $\alpha = 0$, $\beta = 0.5$, $\gamma = 1.0$, $\delta = 3$, $\eta = 0$. Although the classical values of critical indices are close to the experimental, there still is some difference.

The first attempt to construct a purely thermodynamic theory of critical phenomena was made by Landau [20, 54]. The pivotal concept in his theory is the *order parameter* ξ , which is defined as a macroscopic parameter of the crystal that is equal to zero in the symmetric crystalline phase, and is other than zero in the asymmetric phase. Obviously, in the case of liquids the order parameter ought to be identified with $\Delta \rho$, i.e. $\xi = \Delta \rho$; the symmetric phase with the liquid above the critical isotherm, where $\Delta \rho = 0$, and the asymmetric phase with the two-phase region of the phase diagram below the critical isotherm [see Eqn (76) and Fig. 2]. The next assumption is that the free energy of the system is a function of three parameters: ρ , Θ and ξ [that is, $F = F(\rho, \Theta, \xi)$],

whereupon the free energy is expanded in ξ :

$$F = F_0 + F_2\xi^2 + F_4\xi^4 + \dots \quad (85)$$

It can be proved that the odd terms in this expansion are equal to zero, and that the coefficients are $F_i(\Theta) = F_{i0} + F_{i1}\varepsilon_\Theta + \dots$. Hence we get the equation of state

$$\Delta P = \left(\frac{\partial F}{\partial \xi} \right)_\Theta = 2F_{21}\xi\varepsilon_\Theta + \dots + 4F_{40}\xi^3 + \dots \quad (86)$$

If we now set $\Delta P = 0$ in this expression, we immediately find that at the critical point $\xi = \Delta\rho \propto \varepsilon_\Theta^{1/2}$, which corresponds to the classical index. In a similar way one can prove that in Landau's theory all the indices assume their classical values [20, 11].

Seeking to improve Landau's theory, Widom [46] found that if the equation of state is written out in the form

$$\Delta P = \xi\psi(\Theta, \xi^{1/\beta}), \quad (87)$$

where ψ is a *homogeneous function of the power γ of the variables Θ and $\xi^{1/\beta}$* , satisfying the condition

$$\psi(\lambda\Theta, \lambda\xi^{1/\beta}) = \lambda^\gamma\psi(\Theta, \xi^{1/\beta}), \quad (88)$$

then, in complete agreement with experiment, we shall have an 'equality' sign in place of the 'greater than or equal to' sign in all similarity relations (81)–(84) considered above (for more details see Ref. [11]).

Discussion. Today the concept of the order parameter is used quite extensively. Therefore, it would be worthwhile to discuss this issue in greater detail.

As indicated above in Section 2.6, in a consistent statistical theory there is no place for the order parameter, because neither the Gibbs distribution, nor the FSE contain any macroscopic parameters other than ρ and Θ [and, of course, the interaction potential $\Phi(r)$].

Let us see now what happens with the liquid at the temperatures $\Theta < \Theta_c$, when the matter occurs in the two-phase state (region below curve ACB in Fig. 2). However narrow the two-phase interval $\xi = \Delta\rho$ might be, the mean pressure inside this interval remains constant ($P = \text{const}$) and therefore the free energy inside this interval is given by $F = V\bar{f}$, where the density of the free energy \bar{f} , according to Eqn (12), is a function of the volume fraction v of the system, occupied by one of the phases, and not a function of the order parameter $\Delta\rho$.

One might argue that there are always huge heterophase fluctuations in the two-phase region near the critical point, which add to the value of the free energy. This is true indeed, but the contribution of these fluctuations depends on the surface tension σ rather than the order parameter $\xi = \Delta\rho$. As a matter of fact, the smaller σ , the more vigorous is the process of splitting the continuous liquid phase into separate droplets, and the stronger are the heterophase fluctuations.⁹ Therefore, the initial postulate of Landau's theory (85) is hardly valid at $\Theta < \Theta_c$.

This means that Landau's theory does not apply to liquids: it does not describe altogether the homophase fluctuations occurring at $\Theta > \Theta_c$, and in all likelihood gives

a wrong description of the heterophase fluctuations in the two-phase system at $\Theta < \Theta_c$.

Quoting from R Balescu (see Ref. [11], p. 365), Widom's theory is a "...purely phenomenological thermodynamic theory based on assumptions that have no fundamental validation". The main advantage of this theory is that "the simplicity of the theory and successful predictions made on its basis have stimulated further investigations" (*ibid.*), this time on the statistical level. We are going to discuss these investigations now.

3.3 Critical phenomena and the Gibbs distribution (Kadanoff–Wilson theory)

In this presentation of the Kadanoff–Wilson (KW) theory I shall follow the scheme proposed by Balescu [11], skipping almost all of the equations. The majority of references in this section will also be to this book (its Russian translation).

Developing Widom's ideas on the microscopic level, Kadanoff put forward the hypothesis of universal similarity. According to this theory, the entire system near the critical point can be divided into separate blocks, assuming that the correlation between the particles in the block is approximately the same as the correlation between the blocks. Within the block, however, the correlation is mainly determined by the interaction potential, whereas this potential cannot affect the correlation between the blocks. Obviously, here we are dealing with a very strong (and unproven) assumption, which is fundamental for the entire theory, because it is needed for formulating the same similarity relations as those following from the Widom's similarity hypothesis.

The next step is Kadanoff's assumption that all substances can be divided into a number of classes, so that the substances of the same class behave in the same way near the critical point. As a matter of fact, this assumption postulates (without proof!) the universality of critical indices.

Kadanoff's formulas of the theory of universal similarity contain some functions whose form was simply guessed. To define these functions, Wilson constructed a set of differential equations. In fact, he used the same ideas of interaction between the blocks as suggested by Kadanoff. Subsequently, Wilson's system of equations became known as the renormalization-group (RG) equations. To solve this system, Wilson assumed that the functions entering these equations are analytical even at the critical point. As a result, he managed to demonstrate that a system of differential equations with analytical coefficients can naturally lead to critical singularities, which is of course an outstanding achievement. It turned out, however, that "the laws of similarity are very weakly related to the Hamiltonian" of the system, because they mainly "reflect the intrinsic characteristics of the RG equations" ([11], p. 386). On top of that, in order to solve the RG equations Wilson makes some assumptions which "are not always quite comprehensible" ([11], p. 392). In particular, he very boldly assumes that the dimensionality of space d can be used as small parameter of the theory when solving the RG equations. Nevertheless, all this train of assumptions eventually leads to surprisingly exact values of the critical indices. Summing up, Balescu very cautiously writes: "Wilson's theory may not be the last word in the theory of critical phenomena. His constructions use many approximations that sometimes cannot be proved. In addition, Wilson's similarity laws may be not universal, although a broad class of models and real systems seem to comply with them... The prospects offered by this theory for solving this difficult problem [*that*

⁹ Observe that neither thermodynamics nor the statistical mechanics of today can offer any more or less consistent theory of heterophase fluctuations.

is, the problem of construction of the theory of critical phenomena — Author] are esthetically so attractive that this theory ought to be at least partially true” ([11], p. 401).

Discussion. So, building on Widom’s phenomenological hypothesis, Kadanoff and Wilson were able to construct — with the aid of sometimes ‘very strong’ additional assumptions — a theory of critical phenomena that would not only establish the linkage between different critical indices, but also calculate the absolute values of these indices in good agreement with experiment. And since it is experiment that is the supreme judge of any theory, there is little doubt that the KW theory is correct. The concern is about something else: namely, whether this is a statistical theory? In other words, whether it is possible to deduce it from first principles (that is, from the Gibbs distribution) without any additional hypotheses? The answer to this question is negative.

Indeed, Kadanoff started with replacing the actual Hamiltonian of the system in the Gibbs distribution, that depends on the interaction potential of particles, with the ‘block Hamiltonian’ that does not depend on the interaction potential at all. Then Wilson changed the statement of the problem in such a way that “the laws of similarity are very weakly related to the Hamiltonian” (and hence with the Gibbs distribution). Instead, they mainly “reflect the intrinsic characteristics of the RG equations” — that is, those equations that were added by Wilson to the initial Gibbs distribution. This construction can hardly be called a consistent statistical theory.

Recall, however, that the KW theory was developed in the late 1960s–early 70s. The prevalent opinion at the time was that any statistical theory must necessarily be based on the Gibbs distribution. The FSE-based alternative was already known, but was still regarded as controversial — the more so because the rather numerous attempts to use the OZ equation for calculating the critical indices always ended up with the erroneous classical values [50]. As we have seen, however, the Gibbs distribution gives too broad (global) a description of the system. In particular, it does not explicitly define the concept of structure, which is pivotal for the theory of phase transitions of both the first and the second order. To make up for this shortfall, Kadanoff had to forcibly change the form of the Hamiltonian to take into account those changes of the structure that occur in the neighborhood of the critical point. This, however, was not enough and Wilson had to make further arbitrary assumptions, which eventually made the theory inconsistent. The desire to build only on first principles eventually led to a renunciation of them.

By contrast, the local approach based on FSE deals with the distribution functions that just define the structure of matter. Because of this, in the local theory one need not postulate the simple concept of, for instance, the correlation radius R_c — it arises in a natural way (the turning of R_c to infinity was one of the postulates of the KW theory). We shall see that the local approach (which, as I have stated more than once, is no less rigorous than the global Gibbs approach) allows the construction of a much simpler (both mathematically and physically) and much more consistent theory of critical phenomena.

3.4 Critical phenomena and virial expansions

The critical point C lies at the very top of curve $OACBT$ of the phase equilibrium of the first order (see Fig. 2) and, like all other points of this curve, is a singular point of the partition function. Because of this, the virial series in the critical

isotherm $\Theta = \Theta_c$ at $\rho = \rho_c$ must diverge. This divergence, however, has several salient features.

Calculating the fifth virial coefficient of Lennard–Jones (LJ) liquid by the methods of group theory, Barker et al. [45] found that the five-term equation of state $P = \sum_{k=0}^5 \rho^k B_k(\Theta)$, supplemented by conditions (71), (73) which define the coordinates of the critical point on the phase diagram, yields

$$\rho_c \equiv \frac{N}{V} \sigma^3 = 0.25 \pm 0.05, \quad \frac{\Theta_c}{\varepsilon} = 1.28 \pm 0.05 \quad (89)$$

[the parameters σ and ε are given by Eqn (44)] in very good agreement with the numerical experiment. This implies that the remaining terms of the virial expansion do not give any correction to the values of Eqn (89), which can only be if they are identically equal to zero. Because of the immense technical difficulties, however, it was impossible to check this hypothesis remaining within the framework of the Gibbs approach.

In Ref. [44], this problem was solved by the methods of the theory of liquids using the OZ equation [see Eqns (46)–(49)]. The results bore out the hypothesis by Barker et al., since at least the next 25 virial coefficients in the critical isotherm were equal to zero (see Fig. 8), and not only for the LJ potential, but also for the rectangular potential well

$$\Phi(r) = \begin{cases} +\infty, & 0 < r < r_1, \\ -\Phi_0, & r_1 < r < r_2, \\ 0, & r_2 < r < \infty. \end{cases}$$

A five-term polynomial, however, cannot diverge at the critical point, which seems to contradict the statement made above. As we can see from Fig. 8, however, as the number k of the virial coefficient increases, we have for the derivative $dB_k(\Theta)/d\Theta \rightarrow \infty$ at $\Theta = \Theta_c$. Accordingly, the condition of divergence of d’Alembert’s power series (49) can be written out in the form

$$\rho(\Theta_c) = \lim_{k \rightarrow \infty} \frac{B_k(\Theta)}{B_{k+1}(\Theta)} = \lim_{k \rightarrow \infty} \frac{dB_k(\Theta)/d\Theta}{dB_{k+1}(\Theta)/d\Theta} \rightarrow \frac{\infty}{\infty}.$$

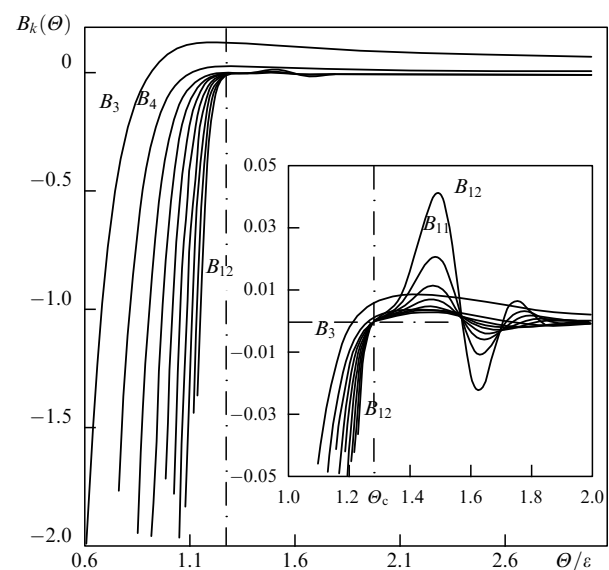


Figure 8. Leading virial coefficients $B_k(\Theta)$ with $k = 3, 4, \dots, 12$.

This relation may well define the coordinate ρ_c of the critical point (which, of course, cannot be rigorously proved by numerically solving the OZ equation).

Now we ought to pay attention to yet another feature of the results obtained in Ref. [44]. As follows from experiment, near the critical point the curve of phase transitions is described by the formula $\Delta\rho \sim \varepsilon_{\theta}^{0.33}$, that is a very flat parabola [see Eqn (76)]. The diagrams in Fig. 6 generally support this conclusion, although the accuracy is too poor to make any quantitative conclusions. At the same time, the coordinates of the critical point itself are very close to those given in Eqn (89). This and the good agreement between the shape of the curve and the experimental results bring one to the conclusion that the coordinates of the critical point calculated from the virial expansion [see Eqn (89)] are more accurate than those following from numerical experiment (which for an LJ liquid gives $\rho_c = 0.34 \pm 0.02$, $\Theta/\varepsilon = 1.34 \pm 0.02$ [49]).

3.5 Asymptotic Ornstein–Zernike equation

Starting with this section we embark on the local description of critical phenomena, based on the OZ equation. Since all phase transitions (including critical phenomena) are associated with the behavior of the two-particle distribution function $G^{(2)}(r)$ at large distances¹⁰, we shall start by deriving the asymptotic OZ equation. First, however, I would like to explain more precisely what I mean by the asymptotic behavior.

In the overwhelming majority of cases, the interaction potential $\Phi(r)$ at large distances decreases as $\Phi \sim (\sigma/r)^6$, where σ is the diameter of particles (with the exception of Coulomb systems, which we leave out of the consideration). Because of this, at $r > (2-3)\sigma$ we may safely set $\Phi = 0$. Given this, we assume that the asymptotics of the distribution functions start with $r = R$, where

$$\Phi(r) = \begin{cases} \Phi(r) & \text{for } r < R, \\ 0 & \text{for } r > R. \end{cases} \quad (90)$$

This condition does not impose any restrictions on subsequent results, because R can be made as large as desired (but finite).

This said, let us turn to the OZ equation (29a). We fix the origin at the point \mathbf{r} , direct the z axis along the vector \mathbf{r}_{12} , and go over to spherical coordinates. As a result, the OZ equation becomes

$$h(r) = C(r) + 2\pi\rho \int_0^\infty C(r_{13})r_{13}^2 dr_{13} \int_0^\pi h(r_{23}) \sin \vartheta_{13} d\vartheta_{13},$$

where ϑ_{13} is the polar angle between the z axis and the vector \mathbf{r}_{13} , and $r = r_{12}$ is the distance between particles 1 and 2. Solving the triangle formed by particles 1, 2, 3, we find

$$r_{23} = \sqrt{r^2 + r_{13}^2 - 2rr_{13} \cos \vartheta_{13}}, \quad \cos \vartheta_{13} = \frac{r^2 + r_{13}^2 - r_{23}^2}{2rr_{13}}.$$

Using these results, we rewrite the OZ equation in the form

$$h(r) = C(r) + \frac{2\pi\rho}{r} \int_0^\infty C(t)t dt \int_{|r-t|}^{r+t} h(\tau)\tau d\tau$$

¹⁰ For simplicity, we shall further on drop the superscripts ⁽²⁾ of the distribution function $G^{(2)}$, bridge functional $B^{(2)}$, and direct correlation function $C^{(2)}$.

(we have set $t = r_{13}$, $\tau = r_{23}$). To eliminate the modulus sign in the lower limit of the inner integral, we differentiate this equation with respect to r , getting

$$\frac{d}{dr} \{r[h(r) - C(r)]\} = 2\pi\rho \left[- \int_0^r C(t)h(r-t)(r-t)t dt \right] + \int_0^\infty [C(r+t)h(t) + C(t)h(r+t)](r+t)t dt. \quad (91)$$

Observe now that in the asymptotic region we have

$$h(r) = \exp[\omega(r)] - 1 = \omega(r) + \dots, \quad (92)$$

$$C(r) = h(r) - \omega(r) + B(r) = \frac{1}{2!}\omega^2(r) + \dots + B(r), \quad (93)$$

and, as follows from the diagram expansion of the bridge functional, the function $B(r)$ at large distances decreases at a rate not slower than that of $\omega^2(r)$. Currently, however, we are only interested in the terms linear in $h \approx \omega$, because they give the main contribution to the asymptotic behavior. Accordingly, the direct correlation function C on the left-hand side of Eqn (91) can be dropped.

Given Eqns (92), (93), we have

$$\int_0^\infty [C(r+t)h(t) + C(t)h(r+t)](r+t)t dt \approx \int_0^\infty C(t)h(r+t)(r+t)t dt.$$

Also, we rewrite the first integral on the right-hand side of Eqn (91) in the form

$$\int_0^r C(t)h(r-t)(r-t)t dt = \int_0^{r/2} + \int_{r/2}^r.$$

Setting in the second of these integrals $t' = r - t$, and going to the limit $r \rightarrow \infty$, we get

$$\int_0^r C(t)h(r-t)(r-t)t dt \rightarrow \int_0^\infty C(t)h(r-t)t dt + \int_0^\infty C(r-t)h(t)(r-t)t dt \approx \int_0^\infty C(t)h(r-t)(r-t)t dt.$$

Substituting these expressions into Eqn (91) and setting $\psi = rh(r)$, we obtain the sought asymptotic OZ equation [49]

$$\frac{d\psi(r)}{dr} = 2\pi\rho \int_0^\infty C(t)[\psi(r+t) - \psi(r-t)]t dt. \quad (94)$$

Discussion. Obviously, the solution of Eqn (94) has the form of $\psi = \exp(-\lambda t)$. Substituting this into Eqn (94), and cancelling out the exponential, we get the transcendental equation for finding the damping coefficient λ :

$$1 = 4\pi\rho \int_0^\infty C(t) \frac{\text{sh } \lambda_j t}{\lambda_j t} t^2 dt, \quad (95)$$

which exactly coincides with that obtained earlier from the analysis of the general solution of the OZ equation in the regular domain of the phase diagram [see Eqn (52); in Eqn (95) we replaced the complex root z_j with λ_j to emphasize that we shall be mainly interested in the real-valued roots]. Thus, it is the asymptotics of the OZ equation that determine the form of eigenfunctions $h_j = A_j \exp(-\lambda_j r)/r$ used in the expansion

of the general solution to the OZ equation [see Eqn (55)]. The amplitudes A_j of this expansion are given by Eqn (58), which we shall rewrite in the form

$$A_j = \frac{\lambda_j^5}{2(2\pi\rho)^2 \int_0^\infty C(t/\lambda_j) [\text{ch } t - \text{sh } t/t] t^2 dt}, \quad (96)$$

replacing r by $t = \lambda_j r$ in the integrand of Eqn (58).

3.6 Regular asymptotics of distribution functions¹¹ in the critical region

From Eqn (48) and definition of the critical point (71) it follows that the following equality is always satisfied at the critical point itself:

$$1 - 4\pi\rho \int_0^\infty C(t) t^2 dt = 0. \quad (97)$$

Obviously, it is compatible with the transcendental equation (95) only under the condition

$$\lambda = 0, \quad R_c = \frac{1}{\lambda} = \infty, \quad (98)$$

where R_c is the correlation radius. Since as $\lambda \rightarrow 0$ the width of the corridor $\Delta\lambda = \lambda_{\max} - \lambda_{\min}$ [see Eqn (59)] also tends to zero, the real parts of all exponentials in the general solution of the OZ equation (55) are practically the same, and can be factored out of the sum. Then the regular asymptotics of the general correlation function $h(r)$ become¹²

$$h^{(\text{rg})}(r) \approx \omega^{(\text{rg})}(r) = A \frac{\exp(-\lambda r)}{r} \quad \text{for } \lambda \rightarrow 0. \quad (99)$$

The next question is how the amplitude A of the degenerate regular asymptotics (99) behaves upon approaching the critical point? Since the latter is given by Eqn (96), we have to examine the behavior of the direct correlation function $C(r)$ in the critical region.

Observe now that the critical point C lies in the curve of phase equilibrium of the first order (see Fig. 2). So at this point, like at any other point that belongs to the curve of phase equilibrium of the first order, the regular component of the function $h(r)$ must turn to zero. From the OZ equation (29) it follows that the regular component of the direct correlation function $C(r)$ must vanish simultaneously. We know, however, that the pressure, chemical potential, and other parameters at the critical point remain finite and do not vanish. This can only be possible if the regular component in the neighborhood of the critical point is supplemented by the distinctive critical component of the distribution function. To take this into account, we set

$$\begin{aligned} h^{(\infty)} &\approx \omega^{(\infty)} = h^{(\text{rg})} + h^{(\text{c})}, & B^{(\infty)} &= B^{(\text{rg})} + B^{(\text{c})}, \\ C^{(\infty)} &= C^{(\text{rg})} + C^{(\text{c})} \end{aligned} \quad (100)$$

¹¹ Hereinafter by *regular asymptotics* we shall mean the asymptotics of distribution functions in the regular domain of the phase diagram — that is, in the domain where the absolutely stable single-phase states of the system are realized. The behavior of the asymptotics in the critical region will be referred to as *degenerate*. As we shall see, in the critical region the regular asymptotics are supplemented by the distinctive *critical asymptotics*.

¹² Broadly speaking, this expression must be multiplied by a certain function $\varphi(r)$ that describes oscillations of $h(r)$. In all likelihood, however, to a good accuracy one may assume that $\varphi(r) = 1$ (which has yet to be proved).

and assume that all the regular components vanish at the critical point:

$$h^{(\text{rg})} = \omega^{(\text{rg})} = B^{(\text{rg})} + C^{(\text{rg})} = 0 \quad \text{for } \rho = \rho_c, \quad \Theta = \Theta_c. \quad (101)$$

Observe now that in Eqn (96) we have $C(t/\lambda)$ in the integrand. Obviously, as $\lambda \rightarrow 0$ the argument of the direct correlation function is $t' = t/\lambda \rightarrow \infty$ for any finite t . Because of this, the main contribution to Eqn (96) comes from large distances, for which, as we have seen, $C^{(\infty)} \approx C^{(\text{c})}$, $B^{(\infty)} \approx B^{(\text{c})}$. Let

$$B^{(\text{c})} = Kh^\delta, \quad C^{(\text{c})} = Kh^\delta, \quad (102)$$

where K and δ are certain constants (the superscript (∞) on $h \approx \omega$ is dropped). At this stage these assumptions should be regarded as hypothetical. In the sections to follow, however, we shall give numerous proofs of this hypothesis, and find formulas for the constants in Eqn (102). Assuming that the problem has a unique solution, we may regard this as the proof of hypothesis (102).

Observing that in the nearest neighborhood of the critical point we have $h \approx A \exp(-\lambda r)/r$, and substituting this expression into Eqn (102), we get

$$C^{(\text{c})} \left(\frac{t}{\lambda} \right) = \lambda^\delta K \left[A \frac{\exp(-\lambda t)}{\lambda t} \right]^\delta. \quad (103)$$

Substituting Eqn (103) into Eqn (96) we arrive at

$$A^{1+\delta} = \lambda^{5-\delta} \left[2(2\pi\rho)^2 K \int_0^\infty \exp(-\delta t) \left(\text{ch } t - \frac{\text{sh } t}{t} \right) t^{2-\delta} dt \right]^{-1}.$$

To simplify this expression, we set

$$5 - \delta = \eta(1 + \delta), \quad (104)$$

where η is a new constant. As a result, we get

$$A = \lambda^\eta A_0, \quad (105)$$

where

$$\begin{aligned} A_0(\rho, \delta) &= \left[2(2\pi\rho)^2 K \right. \\ &\quad \left. \times \int_0^\infty \exp(-\delta t) \left(\text{ch } t - \frac{\text{sh } t}{t} \right) t^{2-\delta} dt \right]^{-1/(1+\delta)} \end{aligned} \quad (106)$$

is a constant independent of λ .

Discussion. Now let us closely inspect what we have learned. Using only the asymptotic OZ equation, the definition of isothermal compressibility (48) that is well known in statistical mechanics, and the purely thermodynamic definition of the critical point as a point where $(\partial P/\partial \rho)_\Theta = 0$, we

(a) demonstrated that the correlation radius at the critical point goes infinite (this fact is postulated in the Kadanoff–Wilson theory);

(b) proved that the amplitude of regular asymptotics upon approaching the critical point tends to zero as $A = \lambda^\eta A_0$, and

(c) corroborated the law of similarity (known actually from the time of J van der Waals), which states that all substances in the neighborhood of the critical point behave in a similar way. This follows from the fact that in the neighborhood of the critical point, where λ is small enough,

the asymptotics of the two-particle distribution function for all substances irrespective of their nature is $G \approx 1 + A \exp(-\lambda r)/r$.

Finally, I would like to draw attention to one curious feature of the results obtained. It is easy to show that in Eqn (106) the expression in square brackets goes to infinity as soon as the parameter δ becomes equal to 5; at $\delta \geq 5$, the amplitude of the regular asymptotics is zero. Can this be related to the fact that every fifth root in the general solution is a ‘dropout’ (see Table 1 above)?

3.7 Critical asymptotics of distribution functions

Now we need to find the form of the critical asymptotics, for which we have to go back to the asymptotic OZ equation. We shall seek its solution in the form

$$\psi(r) = D \frac{\exp(-\lambda r)}{r^\eta}, \tag{107}$$

where η and D are two new constants [we shall see that η coincides with the constant introduced in Eqn (104)]. Substituting Eqn (107) into Eqn (94), we get

$$\begin{aligned} & -\lambda \frac{\exp(-\lambda r)}{r^\eta} - \eta \frac{\exp(-\lambda r)}{r^{1+\eta}} \\ & = 2\pi\rho \int_0^\infty C(t) \left\{ \frac{\exp[-\lambda(r+t)]}{(r+t)^\eta} - \frac{\exp[-\lambda(r-t)]}{(r-t)^\eta} \right\} t dt, \end{aligned}$$

and, cancelling out $\exp(-\lambda r)$, we arrive at

$$\begin{aligned} & \frac{\lambda}{r^\eta} + \frac{\eta}{r^{1+\eta}} \\ & = 2\pi\rho \int_0^\infty C(t) \frac{(r+t)^\eta \exp(\lambda t) - (r-t)^\eta \exp(-\lambda t)}{(r^2 - t^2)^\eta} t dt \\ & = 2\pi\rho \int_0^\infty \frac{C(t)}{(r^2 - t^2)^\eta} \{ r^\eta [\exp(\lambda t) - \exp(-\lambda t)] \\ & + \eta r^{\eta-1} [\exp(\lambda t) + \exp(-\lambda t)] t + \dots \} t dt. \end{aligned}$$

Since $C(t)$ is a short-range function that practically turns to zero at $r > 2\sigma$ (where σ is the diameter of particles), the integral in this expression is taken over the range of short distances $0 \leq t \leq 2\sigma$. We, however, are currently interested in the domain of large distances $r \gg 2\sigma$, where we can safely set $(r^2 - t^2)^\eta \approx r^{2\eta}$. As a result, up to terms of the order of $1/r^{2+\eta}$, the above relation reduces to

$$\begin{aligned} \frac{\lambda}{r^\eta} + \frac{\eta}{r^{1+\eta}} & = \frac{\lambda}{r^\eta} 4\pi\rho \int_0^\infty C(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt \\ & + \frac{\eta}{r^{1+\eta}} 4\pi\rho \int_0^\infty C(t) \text{ch}(\lambda t) t^2 dt. \end{aligned}$$

Equating the terms containing the same powers of r , we get two conditions

$$1 = 4\pi\rho \int_0^\infty C(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt, \quad 1 = 4\pi\rho \int_0^\infty C(t) \text{ch}(\lambda t) t^2 dt, \tag{108}$$

which must be satisfied simultaneously in order that Eqn (107) be a solution of the asymptotic OZ equation. In the

critical region, where $\lambda \approx 0$, these conditions indeed coincide. In the regular domain of the phase diagram, however, where λ is nonzero, the solutions of type (107) with $\eta \neq 0$ are not possible, because the two conditions in Eqn (108) are not compatible with one another. Because of this, in the regular domain of the phase diagram the critical asymptotics as given by Eqn (107) must vanish, which presumes that the amplitude D must go to zero.

Since the asymptotic OZ equation is linear with respect to the unknown function ψ , its general solution, which holds in both the regular and critical domains of the phase diagram, can be written in the form

$$h^{(\infty)}(r) = \lambda^\eta A_0 \frac{\exp(-\lambda r)}{r} + D \frac{\exp(-\lambda r)}{r^{1+\eta}}, \tag{109}$$

where, according to the arguments developed above, one finds

$$\begin{aligned} & A = \lambda^\eta A_0 \rightarrow 0, D \neq 0 \text{ in the critical region, and} \\ & A \neq 0, D = 0 \text{ in the regular region.} \end{aligned}$$

Equation (109) defines the general form of the asymptotics of correlation function h over the entire phase diagram [in the regular region, the principal term $A \exp(-\lambda r)/r$ is broken up into numerous similar terms with different λ_k and A_k ; see Eqn (62)].

Discussion. In this section we have demonstrated that near the critical point the asymptotic OZ equation generates solutions different from those in the regular domain of the phase diagram. These solutions arise automatically, without making any additional assumptions. They follow from the OZ equation itself and the condition (71) that defines the coordinates of the critical point on the phase diagram. The solution, however, is not completely defined — we do not know the amplitude D in Eqn (107), the amplitude of the critical direct correlation function K in Eqn (102), and the values of the critical indices η and δ . To find them, we must turn to the second thermodynamic condition (73) that defines the location of the critical point on the phase diagram.

3.8 Implications of the condition $(\partial^2 P / \partial \rho^2)_\theta = 0$

First of all, let us demonstrate that all the expressions obtained in the preceding section automatically satisfy at $\lambda = 0$ not only the first thermodynamic condition (71) (with the aid of which they have actually been derived), but also the second thermodynamic condition (73), which we shall modify as follows.

Differentiating both parts of Eqn (48) with respect to ρ , we get

$$\rho \frac{\partial^2 P}{\partial \rho^2} = -\Theta \left[4\pi\rho \int_0^\infty C(t) t^2 dt + 4\pi\rho \int_0^\infty C_\rho(t) t^2 dt \right],$$

where $C_\rho = \rho(\partial C / \partial \rho)$ is a new unknown function. By virtue of the second thermodynamic condition (73) and Eqn (97), this equation at the critical point is reduced to

$$1 + 4\pi\rho \int_0^\infty C_\rho(t) t^2 dt = 0. \tag{110}$$

Obviously, this is completely equivalent to the original condition $(\partial^2 P / \partial \rho^2)_\theta = 0$.

Now let us prove that the same relation follows directly from the asymptotic OZ equation for $\lambda \rightarrow 0$. With this

purpose we differentiate Eqn (94) with respect to ρ :

$$\begin{aligned} \frac{d\psi_\rho(r)}{dr} - 2\pi\rho \int_0^\infty C(t) [\psi_\rho(r+t) - \psi_\rho(r-t)] t dt \\ = \frac{d\psi(r)}{dr} + 2\pi\rho \int_0^\infty C_\rho(t) [\psi(r+t) - \psi(r-t)] t dt, \end{aligned} \quad (111)$$

where $\psi_\rho = \rho(\partial\psi/\partial\rho)$, and the right-hand side contains the known function [see Eqn (109)]

$$\psi(r) = rh^{(\infty)}(r) = A \exp(-\lambda r) + D \frac{\exp(-\lambda r)}{r^\eta}. \quad (112)$$

Substituting the first term of this expression (that is, $\exp(-\lambda r)$) into the right-hand side of Eqn (111), we arrive at

$$\begin{aligned} \frac{d\psi_\rho(r)}{dr} - 2\pi\rho \int_0^\infty C(t) [\psi_\rho(r+t) - \psi_\rho(r-t)] t dt \\ = -\exp(-\lambda r) \left[\lambda + 4\pi\rho \int_0^\infty C_\rho(t) \text{sh}(\lambda t) t dt \right]. \end{aligned} \quad (113)$$

Obviously, in this case ψ_ρ must also be sought in the form of $\exp(-\lambda r)$. Substituting this solution into Eqn (113), and cancelling out by $\lambda \exp(-\lambda r)$, we get

$$1 - 4\pi\rho \int_0^\infty C(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt = - \left(1 + 4\pi\rho \int_0^\infty C_\rho(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt \right). \quad (114)$$

According to Eqn (61), the left-hand side of this equation is zero. Then the right-hand side should be zero too:

$$1 + 4\pi\rho \int_0^\infty C_\rho(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt = 0. \quad (115)$$

Substituting the second component of function ψ (that is, $\exp(-\lambda r)/r^\eta$) into the right-hand side of Eqn (111), we come to the conclusion that the asymptotic OZ equation is also satisfied, as long as

$$1 + 4\pi\rho \int_0^\infty C_\rho(t) \text{ch}(\lambda t) t^2 dt = 0. \quad (116)$$

As $\lambda \rightarrow 0$, equations (115) and (116) both reduce to the same equality (110), which is equivalent to the second thermodynamic condition (73). At the same time, condition (110) guarantees that the solution (109) of the asymptotic OZ equation (94), found in the preceding section, satisfies simultaneously equation (111) differentiated with respect to ρ . As ought to be expected, equations (115) and (116) can be derived directly from formulas (108) by differentiation with respect to ρ .

Now let us find the constants K and λ . Since $\psi(r)$ is a sum of two terms, the general solution of Eqn (111) must be a sum

$$\psi_\rho(r) = A_\rho \exp(-\lambda r) + D_\rho \frac{\exp(-\lambda r)}{r^\eta}, \quad (117)$$

where A_ρ and D_ρ are new constants. And since $\psi_\rho = \rho(\partial\psi/\partial\rho)$, the same expression can also be derived directly from Eqn (109), but under the condition $\lambda_\rho = \lambda(\partial\lambda/\partial\rho) = 0, \lambda = \lambda(\Theta)$. Setting $\lambda(\Theta) = \lambda(\Theta_c + \Delta\Theta) = \lambda(\Theta_c) + \lambda'(\Theta_c)\Delta\Theta^v$, and taking into account that $\lambda(\Theta_c) = 0$, we come to the known relation in the theory of critical

phenomena

$$\lambda(\Theta) = \text{const } \varepsilon_\Theta^v, \quad (118)$$

where v is a new critical index, and $\varepsilon_\Theta = (\Theta - \Theta_c)/\Theta_c$.

Setting $\lambda t = t'$, we rewrite Eqn (115) in the form

$$1 + \frac{4\pi\rho}{\lambda^3} \int_0^\infty C_\rho\left(\frac{t}{\lambda}\right) \frac{\text{sh}t}{t} t^2 dt = 0.$$

Hence it follows that as $\lambda \rightarrow 0$ the main contribution to the integral comes from the asymptotic values of $C_\rho(r)$ for $r \rightarrow \infty$. This allows us to replace in Eqn (115) C_ρ with $C_\rho^{(\infty)}$, and get

$$1 + 4\pi\rho \int_0^\infty C_\rho^{(\infty)}(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt = 0. \quad (119)$$

From similar considerations, we can also transform Eqn (95) into

$$1 - 4\pi\rho \int_0^\infty C^{(\infty)}(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt = 0. \quad (120)$$

Since both of these relations define the value of one and the same parameter λ , they must coincide with each other. This can only happen if either $C^{(\infty)}(t) = -C_\rho^{(\infty)}(t)$, or $C^{(\infty)} = -\rho(\partial C^{(\infty)}/\partial\rho)$. The solution of this equation gives us

$$C^{(\infty)}(r; \rho, \Theta_c) = \frac{\rho_c}{\rho} C^{(\infty)}(r; \rho_c, \Theta_c) \equiv \frac{\rho_c}{\rho} C_c^{(\infty)}(r). \quad (121)$$

Since $C^{(\infty)} = K\omega^\delta$, the same differential equation can be rewritten as

$$\rho \frac{\partial K}{\partial \rho} \omega^\delta + K \delta \omega^{\delta-1} \rho \frac{\partial \omega}{\partial \rho} = -K\omega^\delta. \quad (122)$$

Since, by definition, $\omega = \omega(r)$ is a function of r , and the constant K does not depend on r , equality (122) can only hold when $\omega_\rho = \rho(\partial\omega/\partial\rho) = \mu\omega$, where μ is a certain new constant (not to be confused with the chemical potential!). Substituting $\omega_\rho(r)$ into Eqn (122), and reducing the relation obtained by ω^δ , we get the equation

$$\rho \frac{\partial K}{\partial \rho} = -(1 + \mu\delta)K, \quad (123)$$

whose solution has the form $K = (\rho_c/\rho)^{1+\mu\delta}$. Substituting this expression into Eqn (106) for A_0 , we find that $A_0 \sim \rho^{(1-\mu\delta)/(1+\delta)}$. Therefore, one finds

$$A_\rho = \rho \frac{\partial A}{\partial \rho} = \lambda^\eta \rho \frac{\partial A_0}{\partial \rho} \sim -\frac{1 - \mu\delta}{1 + \delta} A_0 = \mu A_0. \quad (124)$$

This equality only holds when $\mu = -1$. As a result, we finally get

$$\omega_\rho = \rho \frac{\partial \omega}{\partial \rho} = -\omega(r; \rho, \Theta_c) = \frac{\rho_c}{\rho} \omega(r; \rho_c, \Theta_c) \equiv \frac{\rho_c}{\rho} \omega^c, \quad (125)$$

$$K = \left(\frac{\rho_c}{\rho}\right)^{1-\delta}, \quad A_0 = \frac{\rho_c}{\rho} A_0^c, \quad D = \frac{\rho_c}{\rho} D^c, \quad (126)$$

whence it follows immediately that

$$C^{(\infty)} = K\omega^\delta = \frac{\rho_c}{\rho} C^{(\infty)} \equiv \frac{\rho_c}{\rho} C_c^{(\infty)}$$

[see Eqn (121)].

Discussion. In this section, using only the asymptotic OZ equation and the second thermodynamic condition (73), we

(a) showed that when the correlation radius R_c goes to infinity, both conditions defining the location of the critical point on the phase diagram are satisfied simultaneously;

(b) established that the correlation radius $R_c = 1/\lambda$ at the critical point depends only on the temperature Θ ;

(c) found the value of the constant $K = (\rho_c/\rho)^{1-\delta}$ in the formula $C^{(\infty)} = K\omega^\delta$, which turned out to depend only on the density ρ , and

(d) defined the constants A_0 and D as functions of the density ρ (see the same Eqn (126)). So far, however, we have not found the values of the constants A_0^c and D^c in these formulas.

3.9 Similarity relations

Let us now demonstrate that similarity relations can be expressed directly from the OZ equation without any additional assumptions. With this purpose we consider the OZ equation written out in the space of wave vectors [see Eqns (33), (34)]

$$1 + 4\pi\rho \int_0^\infty h(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt = \left[1 - 4\pi\rho \int_0^\infty C(t) \frac{\text{sh}\lambda t}{\lambda t} t^2 dt \right]^{-1}. \tag{127}$$

Since large distances $r \rightarrow \infty$ correspond to $\lambda \rightarrow 0$, we expand $\sin \lambda t$ in λ and retain the first nonvanishing term to rewrite the left-hand part of Eqn (127) in the form

$$1 + 4\pi\rho \int_0^\infty h(t) \frac{\sin \lambda t}{\lambda t} t^2 dt \rightarrow 1 + 4\pi\rho \int_0^\infty h(t) t^2 dt \approx 4\pi\rho \int_0^\infty h^{(\infty)}(t) t^2 dt, \tag{128}$$

where we have dropped the 1 and replaced h with $h^{(\infty)}$, because the integral $\int_0^\infty h^{(\infty)}(t) t^2 dt$ diverges at the upper limit when $\lambda \rightarrow 0$ [the latter because the isothermal compressibility goes to infinity at the critical point; see Eqn (35)]. Since $h^{(\infty)}$ is given by Eqn (109), we can substitute this expression into the integrand in Eqn (128) and get

$$1 + 4\pi\rho \int_0^\infty h(t) \frac{\sin \lambda t}{\lambda t} t^2 dt \rightarrow 4\pi\rho_c [A_0^c + D^c \Gamma(2 - \eta)] \frac{\lambda^\eta}{\lambda^2}, \tag{129}$$

where $\Gamma(z) = \int_0^\infty \exp(-\xi) \xi^{z-1} d\xi$ is Euler's gamma-function. Then, going to the limit $\lambda \rightarrow 0$ in the right-hand side of Eqn (127), we can write

$$1 - 4\pi\rho \int_0^\infty C(t) \frac{\sin \lambda t}{\lambda t} t^2 dt \rightarrow \left[1 - 4\pi\rho \int_0^\infty C(t) t^2 dt \right] + \frac{1}{3!} \lambda^2 4\pi\rho \int_0^\infty C(t) t^4 dt + \dots$$

According to Eqn (97), the expression in square brackets here is equal to zero, and therefore

$$1 - 4\pi\rho \int_0^\infty C(t) \frac{\sin \lambda t}{\lambda t} t^2 dt \rightarrow \frac{\lambda^2}{3!} 4\pi\rho \int_0^\infty C(t) t^4 dt \approx \frac{\lambda^2}{3!} 4\pi\rho \int_0^\infty C^{(\infty)} t^4 dt + \dots$$

Here, with due account for Eqns (109) and (126), one finds

$$C^{(\infty)} = K\omega^\delta = \frac{\rho_c}{\rho} \lambda^{\delta(1+\eta)} \frac{\exp(-\delta t)}{t^{\delta(1+\eta)}} (t^\eta A_0^c + D^c)^\delta, \quad t' = \lambda t. \tag{130}$$

As a result, after some straightforward transformations we get

$$\left[1 - 4\pi\rho \int_0^\infty C(t) \frac{\sin \lambda t}{\lambda t} t^2 dt \right]^{-1} \rightarrow \frac{1}{4\pi\rho_c S_c} \frac{\lambda^{5-\delta(1+\eta)}}{\lambda^2}, \tag{131}$$

where

$$S_c = \int_0^\infty \exp(-\delta t) (t^\eta A_0^c + D^c)^\delta t^{5-\delta(1+\eta)} \frac{dt}{t} \tag{132}$$

and $5 - \delta(1 + \eta) > 0$. Equating expressions (129) and (131), and cancelling out the resultant expression by λ^{-2} , we obtain

$$4\pi\rho_c [A_0^c + D^c \Gamma(2 - \eta)] \lambda^\eta = \frac{1}{4\pi\rho_c S_c} \lambda^{5-\delta(1+\delta)}. \tag{133}$$

This equality will hold only if the powers of lambda are the same on both sides of Eqn (133) — that is, when $\eta = 5 - \delta(1 + \eta)$ or, in the more conventional form, when

$$2 - \eta = 3 \frac{1 - \delta}{1 + \delta}. \tag{134}$$

This last expression coincides with Eqn (84), with the replacement of the \geq sign by the = sign. This just confirms our earlier assumption that the constant η defined by Eqn (104) represents a critical index. In addition, from Eqn (133) it follows that

$$A_0^c + D^c \Gamma(2 - \eta) = \frac{1}{(4\pi\rho_c)^2 S_c}, \tag{135}$$

where, according to Eqns (106) and (126), we have

$$A_0^c = \left[2(2\pi\rho_c)^2 \int_0^\infty \exp(-\delta t) \left(\text{cht} - \frac{\text{sh}t}{t} \right) t^{2-\delta} dt \right]^{-1/(1+\delta)}. \tag{136}$$

Since $A_0^c = A_0^c(\delta)$, and the index η in $S_c = S_c(\delta, \eta)$ can be expressed via δ with the aid of Eqn (134), equation (135) represents a transcendental equation that defines the amplitude of the critical asymptotics D^c as a function of δ ; the amplitude $D^c = D^c(\delta)$ does not depend on Θ .

Apart from Eqn (134), the OZ equation can be used for expressing other similarity relations. Since, for example, the isothermal compressibility κ_Θ is given by Eqn (48), from Eqn (131) it follows that as $\lambda \rightarrow 0$ we have

$$\kappa_\Theta \rightarrow \frac{1}{4\pi\rho_c S_c \Theta} \lambda^{-(2-\eta)}. \tag{137}$$

By definition, however, $\kappa_\Theta \sim \varepsilon_\Theta^{-\gamma}$, where γ is a new critical index. But since $\lambda \sim \varepsilon_\Theta^v$ [see Eqn (118)], then $\kappa_\Theta \sim \lambda^{-(2-\eta)} \sim \varepsilon_\Theta^{-v(2-\eta)} \sim \varepsilon_\Theta^{-\gamma}$, and hence

$$\gamma = v(2 - \eta). \tag{138}$$

This is another well-known similarity relation. In a similar way one can obtain some other (possibly all) relations. There is, however, an alternative approach.

From first principles we have deduced at least two similarity relations (134) and (138), which precisely coincide with those following from Widom's similarity hypothesis (87) and Eqn (88). In this way we have proved the validity of this hypothesis. Now we can use this hypothesis for calculating all other similarity relations as was done by B Widom himself.

Discussion. In this section we established certain relations between the critical indices directly from the asymptotic OZ equation, thus confirming Widom's (but not Kadanoff's!) similarity hypothesis. In addition, we obtained Eqn (135) that defines the amplitude of the critical asymptotics $D = (\rho_c/\rho)D^c$ [see Eqns (109) and (126)], and found that the amplitude of isothermal compressibility in the neighborhood of the critical point depends not only on the amplitude of the regular asymptotics A , but also on the amplitude of the critical asymptotics D . This result is important so far as it indicates that, although the regular asymptotics degenerates in the neighborhood of the critical point, its contribution to the thermodynamic functions cannot be neglected.

3.10 The critical Ornstein–Zernike equation

If we now take a close look at the expressions obtained so far, we shall see that with the aid of the asymptotic OZ equation (94) and two conditions (71) and (73) defining the location of the critical point on the phase diagram we have expressed almost all the unknown parameters of the theory, *with the exception* of the critical index δ (and therefore all the critical indices expressible in terms of δ through the similarity relations). This source of information (that is, the asymptotic OZ equation) is exhausted and it is unlikely that we should get anything essentially new from this equation. Because of this, for calculating the values of critical indices we can only turn to the *complete* OZ equation (29a) that, unlike the asymptotic equation, describes the behavior of the distribution function at both short and long interparticle distances. In other words, we must assume that the concrete values of all critical indices are determined by the behavior of the distribution function at *small* distances. This statement is sacrilegious in itself, because it is common knowledge that the critical indices are determined by the long-range interactions [11, 50]. If, however, we look at the problem from the standpoint of local statistical mechanics, there is nothing preposterous in this statement. Indeed, from Eqns (52) and (58), which determine the shape of the asymptotics in the regular domain of the phase diagram, it follows that the values of λ and A are expressed in terms of the integrals of the direct correlation function $C(r)$, which is only defined at small distances $r < R_\phi$. It is these distances where the potential Φ is solely nonzero shape the asymptotic behavior at large distances $r > R$, where $\Phi = 0$. This result may be regarded as a consequence of the main postulate of Gibbs's statistical mechanics, which holds that the interaction potential Φ determines *all* the properties of matter, because

$$G \sim \exp \left[-\frac{1}{\Theta} \sum \Phi_{i,j} \right].$$

Obviously, this postulate must also work in the critical region. This implies, however, that the values of *all* the critical indices must be determined by the shape of the potential Φ — that is, by small distances $r < R$. This is why the values of the critical

indices in the local approach can only be found from the complete OZ equation (29a).

There are other reasons as well. The key role of small distances is visible in other equations of statistical mechanics. For example, according to Eqn (27), the internal energy e per particle is

$$e = \frac{E}{N} = \frac{3}{2}\Theta + \frac{1}{2}\rho \int_0^\infty \Phi(r) \exp \left[-\frac{\Phi(r)}{\Theta} + \omega(r) \right] 4\pi r^2 dr,$$

and hence the heat capacity at constant volume is

$$c_V = \left(\frac{\partial e}{\partial \Theta} \right)_\rho = \frac{3}{2} + \frac{1}{2}\rho \int_0^\infty \frac{\Phi(r)}{\Theta} \times \exp \left[-\frac{\Phi(r)}{\Theta} + \omega(r) \right] \left[\frac{\Phi(r)}{\Theta} + \Theta \frac{\partial \omega(r)}{\partial \Theta} \right] 4\pi r^2 dr. \quad (139)$$

The interaction potential in the integrand here is $\Phi(r) = 0$ at $r > R$. Accordingly, the integrals in Eqns (27) and (139) are only taken over the range of small distances $r < R$; the long-range distances does not give any contribution to c_V . At the same time we know that heat capacity c_V has a singularity at the critical point [see Eqn (75)]:

$$c_V \sim \varepsilon_\rho^{-\alpha}, \quad (140)$$

where $\alpha \approx 0.11$ is the critical index. Since Eqn (139) is a rigorous consequence of the postulates of statistical mechanics, the value of the critical index α is obviously determined by the behavior of the distribution function at small distances.

We can also give another example. We know that the pressure P is linked to the distribution function through Eqn (25):

$$P = \rho\Theta - \frac{1}{6}\rho \int_0^\infty r \frac{d\Phi(r)}{dr} G(r) 4\pi r^2 dr.$$

Here it is assumed that the value of P is determined by the short-range distances $r < R$. At the same time, in the critical region for the pressure we have the following expression

$$P(\rho, \Theta) = P(\rho_c, \Theta_c) + \text{const } \varepsilon_\rho^\delta, \quad (141)$$

where $\varepsilon_\rho = (\rho - \rho_c)/\rho_c$. Hence it follows that the index δ is also shaped at small distances. The classical theory of critical phenomena has no explanation for these facts. From the standpoint of the local approach, however, they are quite natural, since in this approach it is assumed that *all* the properties of matter are determined by the small distances $r < R$.

So, in order to calculate the concrete values of the critical indices, we must turn to the complete OZ equation (29a). As I indicated, however, it is *practically* unclosed, and must be supplemented with the equation of closure (which is generally typical for the theory of liquids). In this case the freedom of selecting the equation of closure is limited, because in accordance with condition (102) at the critical point itself the asymptotics of the direct correlation function are given by

$$C^{(\infty)}(r) = \omega^\delta(r) \quad (142)$$

[recall that, according to Eqn (126), we have $K = 1$ at $\rho = \rho_c$]. So the freedom only concerns the way in which this expression

is extended to small distances $r < R$. The simplest assumption is that Eqn (142) holds at all distances $0 \leq r \leq \infty$. Then the critical OZ equation becomes

$$h(r) = \omega^\delta(r) + \rho \int_V \omega^\delta(|\mathbf{r} - \mathbf{r}_3|)h(|\mathbf{r}_2 - \mathbf{r}_3|) d^3r_3. \quad (143)$$

This equation contains the unknown critical index δ , which can be determined from the expression

$$1 - 4\pi\rho \int_0^\infty \omega^\delta(r)r^2 dr = 0, \quad (144)$$

following from the thermodynamic condition (97) that defines the location of the critical point on the phase diagram, and the equation of closure (142). If it turns out that Eqn (144) holds only approximately, we shall have to slightly adjust the closure (142) at small distances. I would like to emphasize once again that this procedure is typical for the theory of liquids.

3.11 Summa summarum

Now we can compare two approaches: the global approach based on the Gibbs distribution, and the local approach based on the OZ equation. Observe first of all that whenever it was possible to use both approaches for finding the critical parameters of liquids, the results were the same. No difference could be detected, which once again proves that the two approaches are equivalent. There is, however, one fundamental distinction: everything that had to be *postulated* in the global approach (for example, the passage of the correlation radius to infinity, the universal properties of asymptotics of the distribution function, etc.), in the local approach was *inferred* from first principles (that is, from the OZ equation). In this way, the local approach provides a basis for the assumptions made by Kadanoff and Wilson in the construction of their theory. It also throws new light on some of these assumptions.

The central assumption is Kadanoff's hypothesis of universal similarity of all systems at the critical point. On these grounds, the real Hamiltonian which is a function of the interaction potential of particles, is replaced by the block Hamiltonian that does not depend on the form of the potential. We saw that at large distances the distribution functions of all substances *irrespective* of the potential form exhibit one and the same asymptotic behavior [up to the magnitudes of constants A_0 and D , which may differ for different substances; see Eqn (108)]. If the task is limited to describing only those effects that depend on the asymptotics of the distribution functions, then such a hypothesis is quite sound. Many things (including the concrete values of the critical indices), however, essentially depend on the behavior of the distribution functions at small distances (see Section 3.10). Then one certainly cannot use the block Hamiltonian. In the local approach, the postulate of universality of distribution functions is replaced by the much more lenient assumption of the universal asymptotics of the direct correlation function [see Eqn (142)]. The behavior of $C(r)$ at small distances is restricted here by only one additional condition (144) replacing the conditions of thermodynamic consistency of the solution. This is enough to ensure that the asymptotics of the distribution function are universal at large distances as well. At the same time, no restrictions are imposed on the general dependence of the distribution

functions on the potential (such dependence, as we have seen, can only arise at small distances).

The next major step relates to the calculation of critical indices. Since the original Hamiltonian in the Kadanoff–Wilson theory is replaced by the block Hamiltonian that does not depend on the interaction potential, it becomes necessary to introduce the RG equations that are lacking a statistical foundation (statistical mechanics does not admit the existence of equations that do not depend on the interaction potential — the only exception is the theory of an ideal gas). In the local approach, the RG equations are replaced by the OZ equation which obviously contains the interaction potential as one of its parameters. As a result, we come up against a new problem — since the RG equations do not depend on the potential, the resulting critical indices will automatically be universal. But the behavior of solutions of the OZ equation is not yet clear. The critical indices may show some kind of dependence on the potential; this issue, however, calls for further analysis.

It is well known that the critical indices are practically the same for liquids and for crystals (see Ref. [51]). In the Kadanoff–Wilson theory this fact is simply postulated (by using the same block description for both liquids and solids), while in the local approach it has to be clarified. Such clarification was actually given in Section 2.5, where we discussed the concept of structure. Briefly, it runs as follows. The crystalline state of matter is always described by the fundamental set of two equations (28), (29), which define two distribution functions $G^{(1)}$ and $G^{(2)}$. The former describes the symmetry of the crystal lattice, and the latter the mutual correlation of particles sitting at the adjacent lattice sites. Accordingly, $G^{(1)}$ is defined over the entire (infinite) volume of the crystal, while $G^{(2)}$ differs from unity only at small distances (since the correlation only exists between closest neighbors). At the critical point, the correlation radius of crystals goes up to infinity in exactly the same way as in liquids, and the same cause leads to the same effect — the onset of infinite fluctuations.

An important concept in the contemporary theory of critical phenomena is the Ginzburg criterion, which actually defines the boundary of the critical region as the region dominated by fluctuations [55]. In the local approach this criterion is naturally replaced by another one, wholly based on the results described above. Indeed, let us turn to Eqn (109), which describes the asymptotics of the correlation function in both the critical and regular regions. Assume that the boundary between these two regions lies at the value of $\lambda = \tilde{\lambda}$, when the two terms in Eqn (109) give the same contribution at $r = \sigma$ (where σ is the diameter of particles). Then we immediately find

$$\tilde{\lambda} = \left(\frac{D}{\sigma^\eta A_0} \right)^{1/\eta} \approx \left(\frac{D}{\sigma^\eta A_0} \right)^{20} \quad (145)$$

(here we have used the empirical value of $\eta \approx 0.05 = 1/20$; see Eqn (80)). Of practical interest is not so much the parameter $\tilde{\lambda}$ as the parameter $\varepsilon_\theta = (\Theta - \Theta_c)/\Theta_c$; taking into account that $\lambda \sim \varepsilon_\theta^v$ [see Eqn (118)] we get

$$\tilde{\varepsilon}_\theta \approx \left(\frac{D}{\sigma^\eta A_0} \right)^{1/v\eta} \approx \left(\frac{D}{\sigma^\eta A_0} \right)^{32}. \quad (146)$$

Here we have taken into account that $v \approx 0.63$ [see Eqn (79)]. Since $\sigma^{1/20} \approx 1$, the boundary between the regular and the

critical regions is mainly determined by the ratio D/A_0 . Obviously, the physical meaning of Eqn (146) is the same as that of the Ginzburg criterion.

The critical region defined by Eqn (146) is, as a rule, quite small. At the same time, it is known that the influence of the critical point extends over a fairly large portion of the phase diagram. This is explained by the fact that in this *quasi-critical* domain of the phase diagram the values of the parameter λ_{\max} are still small enough. So, even though the contribution from the critical asymptotics here can be disregarded, the corridor for the regular asymptotics

$$\Delta\lambda = \lambda_{\max} - \lambda_{\min}$$

remains quite narrow. As a result, all the constants are $\lambda_k \approx \lambda$. This allows us to factor $\exp(-\lambda r)$ out of the sum in Eqn (55) to find the *almost*-universal asymptotics

$$\omega^{(\infty)} \approx A \frac{\exp(-\lambda r)}{r}. \quad (147)$$

Presumably, as long as this relation gives a good approximation to the asymptotics of the correlation functions, the laws of similarity (the same for all liquids) hold in the regular domain of the phase diagram. But, of course, far from the critical point where the set of roots λ_k of transcendental equation can be different for each particular substance, one cannot expect to observe any similarity whatsoever. This probably explains the futility of all attempts to construct a universal equation of state good for all substances over the entire regular domain of the phase diagram, going back in time to the classical work of J van der Waals.

And one final remark. At a temperature $\Theta < \Theta_c$, the system is two-phase (see Fig. 2). Such states are not described either by the single-phase Gibbs distribution (see Section 2.3) or by the OZ equation, which admits no solution in the density range (see Section 2.5). So, the description of matter below the critical temperature cannot be based, strictly speaking, either on the Wilson theory or on the local approach using the OZ equation. New ideas are needed in these circumstances.

4. Conclusions

This review is devoted to the problem of phase transitions. So it is natural that phase transitions were the focus of our attention. There is something, however, that is of no less importance. We have demonstrated that the problem of phase transitions cannot be solved within the framework of the global Gibbs approach. It is necessary to go over to the local description based on the fundamental set of equations (FSE). In no way is this a departure from the main ideas of statistical mechanics, because the local approach follows from its postulates as rigorously as the global approach of Gibbs (although one may hear objections to this). To some extent I have proved this statement in Section 2.5; now I would like to summarize the discussion concerning the equivalence of the two approaches. I believe that this is an issue of major importance.

Classical statistical mechanics is based on the Newton equations that describe the motion of each separate molecule of matter. Through identical mathematical transformations this set of equations is first converted into the Liouville equation, and then into the hierarchy of BBGKY equations. In equilibrium systems the distribution function does not

depend on time, and the more general nonequilibrium BBGKY hierarchy degenerates into the equilibrium hierarchy. The Gibbs distribution is the solution of the last equation in this hierarchy, whereas FSE is a convolution of the entire equilibrium hierarchy into a system of two integral equations for the one-particle and two-particle distribution functions. In either case there are no approximations or simplifications, so both the Gibbs distribution and the FSE rigorously follow from the original Newton equations (I gave a comprehensive treatment of this issue in Ref. [2]). These facts support my argument in favor of the equivalence of the two approaches.

‘Equivalent’, however, does not mean ‘identical’. Each approach has its own advantages; it throws light on particular sides of the phenomenon, and each has its scope of applicability.

As a matter of fact, equilibrium statistical mechanics has to solve four main problems:

(1) to validate the laws of thermodynamics;

(2) to learn to calculate the structure and

(3) thermodynamic parameters of matter, as well as

(4) to find the location of curves of phase equilibrium on the phase diagram.

The first of these problems was brilliantly solved by W Gibbs with the aid of his distribution function that gives a global description of the system. The local approach can also be used for this purpose, but the relevant proof will be much less elegant and efficient.

The concept of the ‘structure of matter’ can only be defined within the framework of the local approach; in Gibbs’s theory there is no room for that. The structure of a particular substance can also be calculated in the context of the local approach based on FSE. However, the Gibbs distribution today allows this to be done much more efficiently (I refer to the Monte Carlo method). One should bear in mind, however, that the Monte Carlo method is concerned not strictly with the pure Gibbs approach, but rather with a kind of ‘hybrid’ approach. The calculations are always performed here not for the entire system of $N \approx \infty$ particles, but for small subsystems containing several hundreds or thousands of particles. In essence, this is a deviation from Gibbs’s global description. And, what is no less important, all calculations actually employ the concept of distribution functions that forms the basis of the local approach [see Eqns (18) and (25), as well as (26) and (27)].

The same can be said about the third problem: when the structure is known, the thermodynamic parameters of matter are found by simple integration.

Finally, the key role in solving the fourth problem belongs to the local approach, and there are several reasons for that. Firstly, the very concept of ‘phase transition’ implies that there is a change in the structure of matter — which is a natural part of the local approach, and completely foreign to Gibbs’s theory. Secondly, all phase transitions are associated with the onset of infinitely large fluctuations (recall that the nucleus of the new phase being in equilibrium with the parent phase must have an infinitely large radius). All this indicates that we have to study the behavior of a very large number of particles simultaneously, which is very hard to do in Gibbs’s theory. In the local approach this yet requires analyzing the asymptotic behavior of the distribution function, which does not pose any great difficulty.

Referring to the current situation with phase transitions, we may say that new prospects have been opened for the theory of first-order phase transitions, and for the theory of

critical phenomena. This is perhaps the most important achievement.

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