Molecular distribution functions of stable, metastable and amorphous classical models

G N Sarkisov

DOI: 10.1070/PU2002v045n06ABEH001003

Contents

1.	Introduction	597
2.	Two approaches to the investigation of the structure of the classical systems	599
	2.1 Method of integral equations for distribution functions; 2.2 Approximate thermodynamically consistent Ornstein-	
	Zernike equation; 2.3 Methods of computer simulations	
3.	Equilibrium states	602
	3.1 Equilibrium states of liquids and gases; 3.2 Equilibrium states of crystals	
4.	Equilibrium phase transitions	604
	4.1 Free energy, chemical potential and the density functional approach; 4.2 Vapor – liquid phase transition; 4.3 Liquid-	
	crystal phase transition; 4.4 Liquid near the phase interface	
5.	Metastable states	610
	5.1 Relationship between metastable states and Gibbs canonical distribution; 5.2 Spinodal decomposition	
6.	Amorphous states	614
	6.1 Nonequilibrium transition to amorphous state; 6.2 Structure of substance in amorphous state	
7.	Conclusion	616
	References	617

<u>Abstract.</u> This review is focused on the structure of stable, metastable and amorphous substances described by simple classical models of particles interacting through the central forces. A unified approach suitable for all states is used. The approach is based on the analysis of the molecular distribution functions obtained either by using integral equations for distribution functions, or by numerical computer experiments (Monte Carlo and molecular dynamics methods). One of the most difficult and still controversial problems of using equations obtained in the thermodynamic limit (and designed originally to describe thermodynamically stable equilibrium states) to predict and study the metastable and amorphous states is discussed.

1. Introduction

Recent progress in studying equilibrium classical systems, first of all gases and liquids, has been achieved as a result of the development of two powerful approaches. The first is the l-particle distribution functions theory, while the second is based on computer simulations. The main goal of these

G N Sarkisov Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, ul. Institutskaya 3, 142290 Pushchino, Moscow Region, Russian Federation Tel. (7-095) 923 96 68 E-mail: sarkisov@venus.iteb.serpukhov.su

Received 18 May 2001 Uspekhi Fizicheskikh Nauk **172** (6) 647–668 (2002) Translated by G N Sarkisov; edited by M I Zel'nikov approaches is the same, that is to utilize the Gibbs distribution discovered in 1902, to determine, in a general form, the probability of the spatial arrangements of molecules (that is the microstructure of a substance) and also the complete set of macroscopic characteristics following from this distribution. In both cases the problem is reduced to the examination of functions depending on a small number of variables. Indeed, when using the integral equation approaches both structural and thermodynamic properties are determined only by the lowest order one and two-particle distribution functions (in case the total energy of the system under consideration is written in the pair additive form). Moreover, all the higher distribution functions can be, at least as some expansion, unambiguously determined through those lowest functions.

On the other hand the computer simulation approaches make it possible to reduce the calculation of the Gibbs distribution of a system with a great number of particles $(N \sim 10^{23})$ to the calculation of the Gibbs distribution of a system with a small number of particles $(N \sim 100-1000)$, whose properties under some boundary conditions (periodic boundary conditions) unambiguously reflect the properties of the system with large N.

Note, that the integral equation approach not only reduces the problem to a reasonable number of variables but also opens a new way of analyzing and revealing the local properties of the system hidden originally in the total Gibbs distribution. Monte Carlo approaches make it possible to produce a chain of microstates of a system in the phase space and directly average dynamical quantities depending on the phase space coordinates according to either a canonical or grand canonical distribution. The molecular dynamic approaches allow one, in turn, to perform appropriate averaging directly along trajectories of molecules moving in correspondence with the equations of the classical mechanics. This extends the capabilities of the approach for studying the nonequilibrium states, particularly amorphous states.

In the last decade the integral equation theory approach for liquids has been significantly enriched with new approximate equations for correlation functions. This made it possible to advance greatly in studying both the gaseous and liquid states of the simple systems of particles interacting by the central forces. The progress is determined by the high accuracy of approximations found for the bridge-functionals appearing in the Ornstein–Zernike (OZ) equation. All these approximate integral equations of the theory of gases and liquids, being with rare exception semiempirical, agree well, however, with the thermodynamic consistence criteria and with the computer simulations. At the same time, one of the principal theoretical problems, of constructing the bridge functionals from analytical properties of series of irreducible diagrams forming the bridge functional, has not been solved completely yet.

Actual problems arise when describing the states in the critical point vicinity or near the phase equilibrium lines. Standing rigorously either in the framework of statistical theory, that is the Gibbs distribution, or in the framework of the distribution functions, it should be accepted that both the partition function and correlation functions should exhibit a singularity pointing to the onset of the phase change in the phase transition area. However, attempts to find this singularity have not been successful for it is impossible to sum up the partition function (except for the case of some special models, for example the Ising model) in the analytical form directly. Moreover, due to the general character of Gibbs distribution it is not clear how this singularity can be revealed.

The singularity in the correlation functions might be thought to be related to vanishing of the physical solutions to the OZ equation at the evaporation, condensation or the freezing lines. However, a large body of both analytical and numerical solutions to integral equations, obtained for a wide range of interaction potentials, revealed no vanishing of the solutions at the phase equilibrium lines. Moreover, the solutions to the OZ equation contain no features suggesting a difference between the metastable and stable regions. This fact can hardly be explained from the rigorous statistical mechanics point of view. As a matter of fact, the metastable states can only arise in constrained systems with a finite number of particles, that is the nonuniform case.

The OZ equation, that forms the basis for all current theories of gases and liquids, is rigorously justified only in the thermodynamic infinite limit case

$$N \to \infty$$
, $V \to \infty$, $n = \frac{N}{V} = \text{const}$

and has been designed to describe uniform stable states.

In the nonuniform case the Gibbs distribution does not correspond to the OZ equation for the two-particle correlation function. We will see below that the Gibbs distribution for the nonuniform systems corresponds to a coupled set of equations for one and two-particle distribution functions and that in this case the density becomes dependant on coordinate $n = n(\mathbf{r})$. At the same time solutions to the coupled set of equations should correspond to a two-phase stable state rather than to a one-phase uniform metastable state. Today, there are no rigorous theoretical explanations of this inconsistency.

The commonly accepted and used concept is the one which considers the OZ equation to be valid for describing the metastable states. In this review we formulate some hypotheses which justify this approach. Moreover, the feasibility for solutions to enter the region of the metastable states allows us, being based on the unified statistical background, to turn to the thermodynamic procedure for treating the first order phase transitions based on the thermodynamic equalities of pressures P, temperatures T and chemical potentials μ of the coexisting phases

$$\mu_{\rm g} = \mu_1, \quad P_{\rm g} = P_1, \quad T_{\rm g} = T_1.$$

This procedure can easily be performed for the vapor – liquid phase transitions. What is more, using solutions of the OZ equation in the metastable area, we can also determine the lines of the absolute stability of the homogeneous phases (spinodals).

The liquid-crystal phase transition, being similar in appearance to the vapor-liquid transition, is of a quite different physical character and is difficult to describe. There are fundamental structural differences lying in the physical nature of these transitions. The latter phase transition is determined mainly by the attraction part of the interactions between molecules (the first order vapor-liquid phase transition does not exist in the models of particles interacting with repulsive forces only, for example, a hard sphere fluid). Moreover, any two equilibrium states, one of which lies in the gaseous region of the phase diagram while the second one lies in the liquid part, can be connected by a curve of gradual transformations about the critical point. This means that there are no inherent features that may inhibit the gradual interconverting of structures. Theoretically it means that both of these states can be treated by the one and the same OZ equation. On the contrary, the properties of a crystal can not be described just by the OZ equation. To do this one should turn again to the complete set of coupled equations. This reflects a physical phenomenon that a thermodynamically stable state lying on the liquid side of the phase diagram can not be gradually connected to a thermodynamically stable state of a crystal. This reflects the fundamental discrepancy between structures of liquids and solids resulting in the fact that the critical point is nonexistent in the liquid-crystal phase transition region. The latter phase transition is determined solely by forces of repulsion acting between molecules, that is as a matter of fact, by the geometry of close packed molecules.

The uniform solutions to the OZ equation can be continued inside the region of parameters of a crystal. *This* gives rise to a new type of metastability, namely the metastability corresponding to one-phase parameters of a stable state.

Under some conditions absolutely new amorphous states can also arise in the crystalline region of parameters. These long-lived weakly nonequilibrium states are characterized by mixed properties. First of all note that the density of matter and its fluctuations in the amorphous state are very close to those in solids. On the other hand the correlation characteristics are close to what is seen in dense liquids having distinct short order and having no long-range order.

The change to a glassy state takes place either with an appropriate density increase or with a temperature decrease of the substance, being already in the dense metastable state. This change is not a thermodynamic one, it is localized neither in the density nor in the temperature and depends essentially on the rate of change of the density and temperature as well as on the other conditions of experiments. This transition is often characterized as kinetic, at the same time, as it will be shown below, it manifests structural changes. Making some approximations and assumptions we can consider the glassy state to be a quasistable one.

The problem now is to find out under what conditions the methods of the equilibrium statistical mechanics and, as in our case, the methods of the integral equation theory of liquids can be used for investigating amorphous states, and what the reliability and adequacy of the obtained results are.

A great number of calculations using molecular dynamics have been performed in order to find out if the amorphous change exists in simple models. The situation as it stands at present is very discrepant. The results to a great extent depend on the conditions under which computer experiments have been performed, for example on the number of test particles in calculations.

In this review we present a structural comparison of different states for the simple models from the unifying standpoint based on the analysis of distribution functions. This approach makes it possible to understand on a microscopic level the macroscopic features in different conditions.

2. Two approaches to the investigation of the structure of classical systems

2.1 Method of integral equations for distribution functions Let the Hamiltonian for the system have the form

$$H_N = \sum_i^N \frac{p_i^2}{2m} + \sum_i^N \sum_j^N \boldsymbol{\Phi}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i^N V(\mathbf{r}_i), \qquad (1)$$

where \mathbf{p}_i is the momentum of particle i, $\Phi(\mathbf{r}_i, \mathbf{r}_j)$ is the potential energy of interaction between two particles, and $V(\mathbf{r})$ is the external field potential at point \mathbf{r} .

In this nonuniform case the density, being also a function of \mathbf{r} , is determined in the canonical ensemble as a first functional derivative of the Helmholtz free energy with respect to the external field [1]

$$-\beta^{-1} \frac{\delta \ln Z[V(\mathbf{r})]}{\delta V(\mathbf{r})} \Big|_{V \to 0} = n^{(1)}(\mathbf{r}) = n(\mathbf{r}) = \langle n_m(\mathbf{r}) \rangle, \quad (2)$$

where $\beta = 1/(kT)$, k is the Boltzmann constant, Z is the partition function, $n_m(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$ is the microscopic density, and $\langle \rangle$ denotes the ensemble average. The average density may be found as

$$n = \frac{1}{V} \int_{V} n^{(1)}(\mathbf{r}) \,\mathrm{d}\mathbf{r} = \frac{N}{V} \,. \tag{3}$$

Similarly in the grand canonical ensemble we have [2]

$$-\frac{\delta\Omega}{\delta u(\mathbf{r})} = n(\mathbf{r}), \qquad (4)$$

where the grand potential $\Omega = F - G$; G is the Gibbs free energy, $u(\mathbf{r}) = \mu - V(\mathbf{r})$, and the average density now is $n = \overline{N}/V$.

Similarly the second functional derivative

$$\beta^{-1} \frac{\delta n(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)} = -\beta^{-1} \frac{\delta^2 \Omega}{\delta u(\mathbf{r}_2) \,\delta u(\mathbf{r}_1)} = K(\mathbf{r}_1, \mathbf{r}_2), \qquad (5)$$

or

$$-\beta^{-1} \frac{\delta n(\mathbf{r}_1)}{\delta V(\mathbf{r}_2)} = \beta^{-2} \frac{\delta^2 \ln Z[V]}{\delta V(\mathbf{r}_1) \,\delta V(\mathbf{r}_2)} = K(\mathbf{r}_1, \mathbf{r}_2) \,, \tag{5'}$$

yields the density — density correlation function

$$K(\mathbf{r}_1, \mathbf{r}_2) = \left\langle \left(n_m(\mathbf{r}_1) - n(\mathbf{r}_1) \right) \left(n_m(\mathbf{r}_2) - n(\mathbf{r}_2) \right) \right\rangle, \tag{6}$$

or

$$K(\mathbf{r}_1, \mathbf{r}_2) = n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1) n(\mathbf{r}_2) + n(\mathbf{r}_1) \,\delta(\mathbf{r}_1 - \mathbf{r}_2) \,.$$
(7)

The last term on the right hand side corresponds to correlation of a particle with itself and is of little importance. The first term is a two-particle distribution function. From the correlation function $K(\mathbf{r}_1, \mathbf{r}_2)$ it is possible to determine the total correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$:

$$n(\mathbf{r}_1) n(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) = n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1) n(\mathbf{r}_2).$$
(8)

A more usual expression is

$$g_1(\mathbf{r}_1) g_2(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) = g_{12}(\mathbf{r}_1, \mathbf{r}_2) - g_1(\mathbf{r}_1) g_2(\mathbf{r}_2), \qquad (9)$$

where

$$n_i(\mathbf{r}_i) = ng_i(\mathbf{r}_i), \quad n^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = n^2 g_{ij}(\mathbf{r}_i, \mathbf{r}_j).$$
(10)

We will also call the function $g_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ a *two-particle* distribution function, while $g_i(\mathbf{r}_i)$ is a one-particle function. Further functional differentiation yields *l*-particle distribution functions of any order [3]. Note that the given definition of the distribution functions is absolutely equivalent to that following directly from the Gibbs distribution [4, 5].

Let us consider the configurational part of the distribution

$$g_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = Q_N^{-1} \exp\left[-\beta \left(\sum_{i,j}^N \boldsymbol{\Phi}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i^N V(\mathbf{r}_i)\right)\right].$$
(11)

Then the one-particle distribution function is obtained by integrating g_N over all the variables except for the first one

$$g_{1}(\mathbf{r}_{1}) = \exp\left(-\beta V(\mathbf{r}_{1})\right) V \iiint_{V^{N-1}} Q_{N}^{-1}$$

$$\times \exp\left[-\beta \left(\sum_{i,j}^{N} \Phi(\mathbf{r}_{i},\mathbf{r}_{j}) + \sum_{i=2}^{N} V(\mathbf{r}_{i})\right)\right] d\mathbf{r}_{2} \dots d\mathbf{r}_{N}$$

$$= \exp\left(-\beta V(\mathbf{r}_{1})\right) \exp\left(\omega(\mathbf{r}_{1})\right)$$

$$= \exp\left(-\beta V(\mathbf{r}_{1}) + \omega(\mathbf{r}_{1})\right). \quad (12)$$

The one particle thermal potential $\omega(\mathbf{r}_1)$ emerges as an average interaction of a marked molecule with all the other molecules. The volume V has been introduced to make the distribution $g_1(\mathbf{r}_1)$ dimensionless.

By analogy the two-particle distribution function is obtained as [5]

$$g_{12}(\mathbf{r}_1, \mathbf{r}_2) = g_1(\mathbf{r}_1) g_2(\mathbf{r}_2) \left(1 + h_{12}(\mathbf{r}_1, \mathbf{r}_2) \right)$$

= $g_1(\mathbf{r}_1) g_2(\mathbf{r}_2) \exp\left(-\beta \Phi(\mathbf{r}_1, \mathbf{r}_2) + \omega_{12}(\mathbf{r}_1, \mathbf{r}_2)\right),$
(13)

where the two-particle thermal potential, that is the indirect part of the potential of mean force, depends both on density and temperature. Correlation functions $g_i(\mathbf{r}_i)$ and $g_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ are solutions to the coupled fundamental set of equations [5]

$$\omega_1(\mathbf{r}_1) = n \int g_2(\mathbf{r}_2) C_{12}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) \, \mathrm{d}\mathbf{r}_2 + \beta \mu^* \,, \tag{14}$$

$$h_{12}(\mathbf{r}_1, \mathbf{r}_2) = C_{12}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + n \int g_3(\mathbf{r}_3) C_{13}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) h_{23}(\mathbf{r}_2, \mathbf{r}_3) \, \mathrm{d}\mathbf{r}_3 \,, \qquad (15)$$

in which the direct two-particle correlation functions

$$C_{12}^{(1)} = (h_{12} - \omega_{12}) - \frac{1}{2} h_{12}(\omega_{12} + B_{12}^{(1)}), \qquad (16)$$

$$C_{12}^{(2)} = h_{12} - \omega_{12} + B_{12}^{(2)}$$
(17)

contain bridge-functionals $B_{12}^{(1)}$ and $B_{12}^{(2)}$, representing the infinite series of the irreducible diagrams built on the same unknown functions g_i and h_{ij} [5–7]. In the case of the spatially homogeneous system $\omega_i = 0$, $g_i = 1$.

If we take

$$\Phi(\mathbf{r}_i,\mathbf{r}_j) = \Phi(|\mathbf{r}_i - \mathbf{r}_j|) = \Phi(r_{ij}),$$

then equation (15) transforms to the usual OZ equation [8]

$$\gamma(r_{12}) = h(r_{12}) - C^{(2)}(r_{12}) = n \int C^{(2)}(r_{13}) h(r_{23}) \,\mathrm{d}\mathbf{r}_3 \,, \ (18)$$

and in this case equation (14) reduces to the definition of the excess chemical potential

$$\beta \mu^* = -n \int C^{(1)}(\mathbf{r}) \,\mathrm{d}\mathbf{r} \,. \tag{19}$$

This transformation is associated with transition to the thermodynamic limit. This factor gives rise, as we will see below, to very difficult problems when using the OZ equation in treating the metastable states.

Given distribution functions g_i and g_{ij} all the thermodynamic parameters can be calculated in approximation (1). The basic parameter characterizing the stability of the homogeneous phase is the isothermal compressibility

$$\chi_T = n^{-1} \left(\frac{\partial n}{\partial P} \right)_T.$$

It is known [1, 3] that the isothermal compressibility is proportional to fluctuations in the number of particles in the grand canonical ensemble

$$\varkappa = nkT\chi_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \,. \tag{20}$$

Then taking into account the normalizing conditions

$$\int n(\mathbf{r}) \, \mathrm{d}\mathbf{r} = \langle N \rangle \,, \tag{21}$$

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \, n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \left\langle N(N-1) \right\rangle = \left\langle N^2 \right\rangle - \left\langle N \right\rangle, (22)$$

we get a fundamental equation relating the distribution function to the compressibility which is a macroscopic quantity

$$\varkappa = nkT\chi_T$$

= 1 + $\frac{1}{\langle N \rangle} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left[n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1) n(\mathbf{r}_2) \right].$ (23)

In the homogeneous case formula (23) reduces to the known expression for compressibility

$$nkT\chi_T = 1 + n \int (g_{12}(r) - 1) \,\mathrm{d}\mathbf{r} \,.$$
 (24)

At the same time in the canonical ensemble we have

$$1 + \frac{1}{N} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left[n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1) n(\mathbf{r}_2) \right] = 0, \qquad (25)$$

or

$$1 + n \int (g_{12}(r) - 1) \,\mathrm{d}\mathbf{r} = 0\,, \tag{26}$$

that seemingly leads to the absurd conclusion that the compressibility is equal to zero.

This gap can be explained [9] if one takes into account that in the grand canonical ensemble we have

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \to n^2, \quad g^{GC}(r) \to 1, \quad r_{12} \to \infty,$$
 (27)

whereas in the canonical it should be

$$n^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \to n^{2} \left(1 + O(N^{-1}) \right),$$

$$g^{C}(r) \to 1 + O(N^{-1}), \quad r_{12} \to \infty.$$
(28)

This can be explained as follows. In the canonical ensemble the structure around some marked molecule is formed by the other N-1 molecules, whereas in the grand canonical ensemble this deficiency is covered through fluctuations of the number of particles. This means that $g^{GC} = g^C$ in the close vicinity about marked particle, whereas $g^{GC} \neq g^C$, $r \to \infty$ in the far region. For the canonical case, let us divide the volume V into volume v_0 corresponding to short range correlations and volume $V - v_0$ corresponding to long range correlations [10]. Then it follows that

$$nkT\chi_{T} = 1 + n \int_{v_{0}} \left(g^{\text{GC}}(r) - 1\right) d\mathbf{r}$$
$$= 1 + n \int_{v_{0}} \left(g^{\text{C}}(r) - 1\right) d\mathbf{r} .$$
(29)

On the other hand according to (26) we have

$$1 + n \int_{v_0} \left(g^{\mathbf{C}}(r) - 1 \right) d\mathbf{r} + n \int_{V - v_0} \left(g^{\mathbf{C}}(r) - 1 \right) d\mathbf{r} = 0, \quad (30)$$

or taking into account (29) and (30) we obtain

$$nkT\chi_T + n \int_{V-v_0} \left(g^{\mathbb{C}}(r) - 1\right) d\mathbf{r} = 0.$$
 (31)

Finally, supposing the difference $(g^{\mathbb{C}}(r) - 1)$ is constant in the volume $V - v_0$ due to the short range nature of correlations, as it occurs in liquids, we find that [10]

$$g^{\rm C}(r) \to 1 - \frac{nkT\chi_T}{N} + O(N^{-2}).$$
 (32)

Thus, correlation function g(r) behaves asymptotically differently in the two ensembles discussed above. Only in the thermodynamic limit case does the differences vanishes. In the case when correlations are of short range nature the correlation functions found for both ensembles as well as those corresponding to the thermodynamic limit are equivalent. This leads us to conclusion that, at least with respect to compressibility, the equations originally derived in the thermodynamic limit, are also able to describe states corresponding to finite size systems, for example the metastable states. Moreover, since amorphous states are also characterized by existence of short-range order and by absence of long-range order, the question arises whether the equations designed originally to describe thermodynamically stable states are valid for predicting and studying amorphous states where the relaxation time extends to infinity.

Note that compressibility can be also defined through the direct correlation function $C^{(2)}(r)$

$$nkT\chi_T = \left[1 - n\int (C^{(2)}(r) - 1) \,\mathrm{d}\mathbf{r}\right]^{-1}.$$
 (33)

Due to the specific short-range properties of the function C(r), equation (33) is very powerful in the case that the correlation radius of g(r) function is large, for instance in the vicinity of the critical point or near the spinodal line.

2.2 Approximate thermodynamically consistent Ornstein – Zernike equation

The infinite series of irreducible diagrams constituting the bridge-functional $B^{(1)}[g_i, g_{ij}]$, $B^{(2)}[g_i, g_{ij}]$ cannot be summed up completely, therefore, as a matter of fact, the formally exact equations (14), (15) or (18) are not closed. For example, single equation (18) relates two unknown functions h(r) and C(r). The search for closures C = f[h] is one of the fundamental theoretical problems. By now very accurate approximate closures comprising the body of the approximate equations theory of liquids and solutions have been elaborated for simple systems of particles interacting through the central symmetric short-range forces (hard sphere fluid, square well system, system with power potential of repulsion, Lennard-Jones liquid, Yukawa model and so on) [11].

Here, we base our consideration on the recently derived new OZ equation [12, 13], where an attempt to approximate the bridge- functional was made considering some analytical properties of diagrams entering this bridge- functional. In this work we have slightly modified this new equation to allow solutions to continue inside the region of densities and temperatures corresponding to the crystalline region of the phase diagram.

One of the simplest typical diagrams in the expansion of the bridge-functional has the form [5]

$$B_1^{(2)}(r_{12}) = n^2 \int h(r_{13}) h(r_{14}) h(r_{23}) h(r_{24}) h(r_{34}) \,\mathrm{d}\mathbf{r}_3 \,\mathrm{d}\mathbf{r}_4 \,.$$
(34)

The problem of finding the closures for the OZ equation is to approximate the nonlocal bridge-functional B = B[h(r)]by the local bridge-function B(r) = B(h(r)) or $B(r) = B(\gamma(r))$ or $B(r) = B(\omega(r))$. There are no rigorous theoretical arguments for changing to a local description, nevertheless overall contemporary approximate theories of liquids are built using this hypothesis. One of the most widely used classical equations is, for example, the Percus-Yevick (PY) equation

$$B^{(2)} = -\left[\exp(\omega) - 1 - \omega\right] = \ln(1 + \gamma) - \gamma,$$

$$\gamma = \exp(\omega) - 1,$$
(35)

$$g = \exp(-\beta\Phi)(\gamma+1).$$
(36)

New ideas have emerged after publications [14, 15], where it was shown that to obtain the best approximation, the pair potential $\Phi(r)$ should be explicitly taken into account in the bridge-functional. For the first time this idea was used in [16, 17], where a semiempirical closure, very accurately describing the Lennard-Jones fluid, was derived. Elaborating this idea in [12, 13] we proposed

$$B^{(2)} = -\frac{1}{2} \Omega^2 = \left[1 + 2(\gamma - n\beta\Phi_2)\right]^{1/2} + n\beta\Phi_2 - \gamma - 1,$$
(37)

$$g = \exp\left[-\beta\Phi + \left[1 + 2(\gamma - n\beta\Phi_2)\right]^{1/2} + n\beta\Phi_2 - 1\right], (38)$$

where

$$\Omega(r) = \omega(r) - n\beta\Phi_2 = -1 + \left[1 + 2(\gamma - \Phi_2)\right]^{1/2}; \quad (39)$$

 $\Phi_2(r)$ is the part of potential responsible for attraction and $\Phi(r) = \Phi_1(r)_{rep} + \Phi_2(r)_{att}$ in agreement with partitioning of the potential energy into reference repulsive and perturbation attractive terms [18].

A distinctive feature of the given closure is that it contains no empirical or adjustable parameters. Note also that for a hard sphere fluid $\Phi_2 = 0$ the closure (37) reduces to a simpler form [19]

$$B^{(2)} = -\frac{1}{2}\omega^2 = (1+2\gamma)^{1/2} - \gamma - 1.$$
(40)

Clearly, as follows from (39), the limiting values are

$$\Gamma = \gamma - \Phi_2 = -\frac{1}{2}, \quad \Omega = -1.$$
(41)

(The second solution in Eqn (39) with the minus sign before the square root does not satisfy the requirement of weakening the correlations $\Omega \to 0$, $\gamma \to 0$, $r \to \infty$ and therefore should be dropped).

These solutions determine the entire region of the existence of the gaseous and liquid phases. On this basis a hypotheses has been put forward that these limiting values might indicate the melting lines. From this an empirical criterion of melting has been formulated (see below). To extend the solutions inside the area of crystalline values of parameters the closure (37) is modified similarly to what has been used in [20, 21], where an approximation

$$\omega = \left[1 + s\gamma\right]^{1/s} - 1\,,\tag{42}$$

that is a generalized version of the closure (40), has been proposed. In the case s = 1 we arrive at another classical hypernetted chain approximation (HNC) $\omega = \gamma$, B = 0. In [20, 21] s was chosen either by comparison with some computer simulation values or from selfconsistent procedures. It was found that $s \cong 2$ always. To continue solutions inside the area of crystalline values of density and temperature, it is necessary to take s = 2A/B, where $A, B \to \infty$ as odd values. Thus we arrive at a modified closure

$$B^{(2)} = \text{sign} \left[\left[1 + 2(\gamma - n\beta\Phi_2) \right] \right]^{1/2} + n\beta\Phi_2 - \gamma - 1. \quad (43)$$

2.3 Methods of computer simulations

In this section these methods will be considered in a general but brief way for there exists exhaustive literature describing the modern approaches [22, 23]. As was noted, the main idea of the computer simulation methods is to use special periodic boundary conditions to make a system with a small number of variables equivalent to an infinitely large system. In their origin, computer simulation approaches represent the most rigorous way to realize the Gibbs distribution or, in this instance, the equations of classical mechanics. Monte Carlo methods make it possible to perform macroscopic averaging of dynamical quantities in exact correspondence with the Gibbs distribution due to the fact that it turns out to be possible to produce a chain of configurations in the phase space of the microstates with the probability of appearance of configurations proportional, for example in the canonical ensemble, to the Boltzmann factor. With Monte Carlo methods one can determine all the thermodynamic parameters.

Here we are interested in an analogue to the radial correlation function

$$g(|\mathbf{r}_i - \mathbf{r}_j|) = g(r) = \frac{V}{N4\pi \mathbf{r}^2} \frac{\mathrm{d}N(r)}{\mathrm{d}r}, \qquad (44)$$

where $N(r) = (1/N) \cdot \langle \sum_{1 \leq i \leq N} N_i(r) \rangle$ is the average number of particles separated by a distance *r*. The energy can be determined as

$$E = \frac{3}{2} NkT + \langle u_k \rangle , \qquad (45)$$

where u_k is the energy corresponding to the kth microstate.

Not every macroscopic quantity has its appropriate microscopic analogue, for example, the Helmholtz free energy F. We, however, can introduce some parameter λ so that

$$\frac{\partial F}{\partial \lambda} = -\beta^{-1} \frac{\partial}{\partial \lambda} \ln \iiint_{V^N} \exp\left[-\beta u(X)\right] dX$$
$$= \frac{\iiint (\partial u/\partial \lambda) \exp\left[-\beta u\right] dX}{\iiint \exp\left[-\beta u\right] dX} = \left\langle \frac{\partial u(\lambda, X)}{\partial \lambda} \right\rangle, \quad (46)$$

where $X = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. Then it follows that

$$F(\lambda) - F(\lambda_0) = \int_{\lambda_0}^{\lambda} \left\langle \frac{\partial u(\lambda, X)}{\partial \lambda} \right\rangle d\lambda .$$
(47)

If $\lambda = V$ then

$$F(V) - F(V_0) = -\int_{V_0}^{V} P \,\mathrm{d}V, \qquad (48)$$

and if $\lambda = T$ then

$$\frac{F(T)}{T} - \frac{F(T_0)}{T_0} = -\int_{T_0}^T \langle u \rangle \frac{\mathrm{d}T}{T^2} \,. \tag{49}$$

Formulae (47) and (48) will be especially analyzed in relation to the density functional approaches.

Methods of molecular dynamics have been developed to integrate directly the equations of motion and to average the dynamical quantities along calculated trajectories. The trajectories of each of the particles are treated as a sequence of linear steps, with length proportional to the period of time Δt . In the absence of the external field the following scheme is possible

$$\mathbf{r}_{i}(t+\Delta t) = \mathbf{v}_{i}\Delta t - \frac{1}{2m_{i}}\sum_{j}^{N-1}\nabla\Phi(i,j)(\Delta t)^{2} + \mathbf{r}_{i}(t), \qquad (50)$$

$$\mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) - \frac{1}{m_i} \sum_{j=1}^{N-1} \nabla \Phi(i,j)(\Delta t) \,. \tag{51}$$

3. Equilibrium states

3.1 Equilibrium states of liquids and gases

Figure 1 presents the full phase diagram of a simple system (in our case the Lennard-Jones fluid)

$$\Phi(\mathbf{r}) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right].$$
(52)



Figure 1. Complete phase diagram of the Lennard-Jones system. FCB is the vapor – liquid phase equilibrium line (binodal). LL_1 is the freezing line, MM_1 is the melting line. F_1CB_1 is the vapor-liquid boundary of the absolute stability of homogeneous phases (spinodal). KK1 is the melting spinodal. The freezing spinodal does not exist, the supercooled and overcompressed liquid can also be extended inside crystalline values of temperature and density. C is the critical point $\rho = n\sigma^3 \approx 0.31$, $T^* = kT/\varepsilon \approx 1.31$; B is the triple point $\rho \approx 0.85$, $T^* \approx 0.67$; T_m corresponds to the equilibrium freezing-melting phase transition, T_{g_1} , T_{g_2} are the temperatures of the amorphous transitions; CC_1 is the line of zero values in the first minimum of the total correlation function, while CC_2 corresponds to the maximum values of the reduced isothermal compressibility. These lines along with the Fisher-Widom one divide the whole vapor-liquid region of the phase diagram into three domains: vapor, fluid and liquid. The EE_2 line incorporates equilibrium liquid states; while Eg_1 and Eg_2 are lines of metastable states existing in the crystalline region of parameters. Glass 1 and Glass 2 denote the amorphous states.

The equilibrium phase states rigorously corresponding to the OZ equation (18) are those pointed in the figure as vapor, liquid or fluid found above the critical point C. General thermodynamic and structural properties of substances in these states are well known and widely described [5, 11]. The FCB line corresponds to vapor - liquid phase equilibrium and LL_1 is the freezing line. Here we consider those states only, in which specific structural features can be observed. As was noted, one can change gradually from point X_1 to point X_2 about the critical point. On the other hand, as is seen from Fig. 2, appropriate correlation functions are qualitatively different in these two states, and, as we will see, the difference is related to different asymptotic behavior of the correlation functions. This means that regardless of the path of changing from point X_1 to point X_2 above the critical point there should exist a line along which correlation functions exhibit qualitative changing. This line has been discovered and is known as the Fisher-Widom line.



Figure 2. Radial correlation functions in the vapor–liquid region of the phase diagram. Curve $1 - \text{`vapor': } T^* = 1.0; \ \rho = 0.01; \ P/(nkT) = 0.9470 (0.9473); u/(NkT) = -0.0932 (-0.0927); \beta\mu^* = -0.1061 (-0.1056). Curve <math>2 - \text{`critical point': } T^* = 1.31; \ \rho = 0.30; \ P/(nkT) = 0.2980 (0.3265); u/(NkT) = -1.7094 (-1.6810); \beta\mu^* = -1.5691 (-1.5070). Curve <math>3 - \text{`fluid': } T^* = 1.6; \ \rho = 0.55; \ P/(nkT) = 0.8503 (0.8172); u/(NkT) = -2.2502 (-2.2492); \ \beta\mu^* = -1.0153 (-0.9520). Curve 4 - \text{`liquid': } T^* = 1.0; \ \rho = 0.80; \ P/(nkT) = 1.5179 (1.2890); u/(NkT) = -5.5136 (-5.5234); \ \beta\mu^* = -2.2548 (-2.2716). R = r/\sigma. The results were obtained with the OZ equation and closure (37). The values extracted from the MBWR equation of state [45], approximating the computer simulation calculations are given in parentheses.$

Note that these changes in no way can be detected thermodynamically. As was shown in works [5, 24, 25], the total correlation function can be written in the form

$$h(r) = g(r) - 1 = \sum_{m=1}^{\infty} B_m \frac{\exp(i\lambda_m r)}{r} - (nkT\chi_T)^2 \frac{\Phi(r)}{kT} .$$
 (53)

The last term is an example of so called far asymptotics, whereas the sum determines the intermediate asymptotics of the function h(r). Here $\lambda = \pm \beta + i\alpha$, where α and β are determined by a set of two transcendental equations [24, 25]; λ can take both real and complex values. Supposing $\Phi(r) = 0$ at some large value $r = R_c$, the complete set λ_m in (53) will describe, in fact, the function h(r). As *r* increases, only terms with the smallest values of α_m remain in the competition. Then, depending on the thermodynamic conditions either a purely imaginary solution $\lambda_m = i\alpha_m$ with monotonically decreasing asymptotes or a pair of conjugated complex solutions $\lambda_m = \beta_m + i\alpha_m$ with an oscillating decay, will survive. At low and medium densities the monotonically decreasing term governed by cooperative effects of the attractive part of the potential dominates. As the density increases the packing effects controlled by the hard core result in dominating oscillations. At a certain density n_{FW} at the specified isotherm the α_m of monotonic decay becomes equal to the α_m of oscillatory decay resulting in change from one decay regime to another. This change is described in the (n, T)plane by the Fisher – Widom line [26].

In a hard sphere fluid there are no pure imaginary solutions $\lambda_m = i\alpha_m$, even for the smallest densities, which means that there are no asymptotes like

$$h(r) \to \frac{A \exp(-\alpha r)}{r}, \quad r \to \infty,$$
 (54)

and this means that the critical point and the spinodal lines are also absent [24, 25], that is, there is no evaporation – condensation phase transition in a hard sphere fluid.

Formula (54) was proposed by Ornstein and Zernike at the beginning of the past century to explain the critical phenomena. Upon approaching the critical point $\alpha \to 0$ and the correlation radius $R_k = 1/\alpha \to \infty$, which explains the experimentally detected enhancement of forward scattering. The understanding of the behavior of matter at the critical point has come a long way since that time, however the tendency of the correlation radius to approach infinity is still considered to be a determining structural indication for the critical point.

This property of correlation functions is unambiguously related to the zeroth value of the inverse compressibility $1/\varkappa \rightarrow 0$. Along with this both the analytical and numerical solutions to the OZ equation as well as the computer simulation results [13, 27, 28] show that there exists another unambiguous structural indication to the critical point, namely the minimum of the correlation function h(r)(curve 2, Fig. 2). This characteristic property of the total correlation function has escaped the attention of the researchers, most likely because it is difficult to find a link between this property and the behavior of a fluid in the vicinity of the critical point. However, the existence of this indication itself is beyond any doubt.

Thus along the critical isotherm we have

$$h_{\min}(r) > 0, \quad \frac{1}{\varkappa} > 0, \quad n < n_{\rm cr};$$

$$h_{\min}(r) = 0, \quad \frac{1}{\varkappa} = 0, \quad n = n_{\rm cr};$$

$$h_{\min}(r) < 0, \quad \frac{1}{\varkappa} > 0, \quad n > n_{\rm cr}.$$
(55)

In Fig. 1 we see that there is a line in the phase diagram originating from the critical point. Everywhere along this line

$$h_{\min}(r) = 0$$
, $g_{\min}(r) = 1$.

Furthermore, another line originates also from the critical point, which is very close to the first one. This line incorporates points at which the inverse compressibility $1/\varkappa$ takes its minimal values along appropriate isotherms. A

hypothesis has been put forward that the two lines may coincide with each other. However this hypothesis can hardly be proved because of inaccuracies caused by approximations themselves and difficulties in the physical interpretation of the minimum in h(r).

In general the whole phase region of the stable homogeneous (n = const) states, as a matter of fact, can be considered with respect to structure as comprised of three homogeneous domains. The first gaseous domain is characterized by having almost no order at all. The second domain containing states lying above the critical point is characterized by short-range order, having a few oscillations (curve 3, Fig. 2). Finally, the third domain represents liquid, which is characterized by both the short-range order and far oscillatory decaying order (curve 4, Fig. 2).

3.2 Equilibrium states of crystals

Equilibrium states of crystals are neither uniform nor isotropic, therefore to describe the structure of a crystal it is necessary to solve the coupled set of equations (14), (15) for the two lowest order functions. Today, however, there is no way to solve this problem. This problem is not so much a technical issue, but is rather related to how a solution is constructed.

To clarify this problem let us consider the hard sphere packing. There are two ways to arrange similar hard spheres in space in order to keep the remaining volume between particles minimal. One way corresponds to a face-centered cubic close packed structure, whereas the other structure displays a hexagonal symmetry [29] (as a matter of fact there exists one more crystalline structure displaying an interchanging packing). The fraction of the volume occupied by hard spheres is equal to 0.74 for all cases. Moreover, the nearest coordination numbers are also the same for all structures. Some subtle differences arise in the far coordination numbers, that is the differences are of weak entropic nature. It becomes absolutely unclear how solutions to the equations can distinguish these different states.

A similar situation also arises in the Lennard-Jones model. The cubic face-centered structure has been accepted to be correspondent to the stable state. On these grounds the correlation functions averaged over orientation

$$\tilde{g}(\mathbf{r}) = \frac{1}{4\pi V n^2} \int d\mathbf{r}_1 \int d\Omega n^2(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}), \qquad (56)$$

have been found with the Monte Carlo approach for a hard sphere system [30, 31], which can be related to solutions to the OZ equation extended inside the crystalline region.

We will see that solutions to the OZ equation obtained in the latter case, are not those corresponding to the averaged distribution function for crystal. As is seen from Fig. 3 the averaged crystalline correlation function for hard spheres is characterized by both short and long range nondecaying behavior. In the exact expressions (12) and (13) long-range nondecaying order is described by the $\omega_1(\mathbf{r}_1)$ function. It is governed by interaction with the external field $V(\mathbf{r})$ rather than by direct interaction between molecules comprising the pattern. For an infinite uniform solid the external field is formally absent. However, as a matter of fact, the external field is implicitly presented by introducing and fixing the origin of coordinates. The short and long-ranged decreasing order lies, as for liquids, in the properties of $\omega(\mathbf{r}_1, \mathbf{r}_2)$ function. What is specific for solids is the tendency, either with decreasing temperature or with increasing density, for g(r)



Figure 3. Hard sphere crystalline correlation function [31]: curve $1 - \rho = 1.0794$; curve $2 - \rho = 1.2987$.

function values to go to zero everywhere except in the small vicinity of some isolated r points. A specific feature is also a new additional maximum arising in g(r) between the first two maxima which are typical for liquids (Figs 3 and 4).



Figure 4. Lennard-Jones correlation functions near the melting line [30]: $T^* = 0.75$, $\rho = 1.0$.

4. Equilibrium phase transitions

4.1. Free energy, chemical potential and the density functional approach

The excess (nonideal) part of the Helmholtz free energy density at an arbitrary point in the liquid-vapor region of the phase diagram can be obtained on the basis of equations (49), (50)

$$\frac{f_{\rm ex}(n,T)}{kT} = \int_0^n \left(\frac{\beta P(n',T)}{n'} - 1\right) \frac{dn'}{n'},$$
(57)

$$\frac{f_{\text{ex}}(n,T)}{kT} = \frac{f_{\text{ex}}(n,T_0)}{kT_0} - \int_{T_0}^T \frac{u(n,T')}{kT'} \frac{\mathrm{d}T'}{T'} \,. \tag{58}$$

Having the problem of finding correlation functions solved, it is possible to connect gradually two points, for example X_1 and X_2 (Fig. 1) by alternating integration in (57), (58) along isotherms and isochores. Appropriate thermodynamic parameters are determined as

$$u = \frac{n}{2} \int_0^\infty \Phi(r) g(r; n, \beta) \,\mathrm{d}\mathbf{r} \,, \tag{59}$$

$$\frac{\beta P}{n} - 1 = -\frac{n}{6kT} \int_0^\infty r \, \frac{\mathrm{d}\Phi(r)}{\mathrm{d}r} \, g\left(r; n, \beta\right) \mathrm{d}\mathbf{r} \,. \tag{60}$$

Now, since, the chemical potential is $\mu = f + P$, it is possible to construct a thermodynamic procedure for comparing two phases in order to detect lines of phase equilibrium [32]. This approach being originally exact, hides, as a matter of fact, a great number of poorly identified sources of errors. They are inaccuracies caused by the huge amounts of computation when integrating numerically along isochores and isotherms. The errors are related to solving the OZ equation itself. But the major source of error is that caused by the so called thermodynamic inconsistency of the approximate OZ equation. By the following it is meant that a complete set of the thermodynamic parameters can be obtained starting from any of the formulae (24), (59) or (60). Had correlation functions been found from the exact OZ equation, the values of all three sets of thermodynamic parameters would have been the same. Using solutions to the approximate OZ equation makes formulae (59), (60) thermodynamically inconsistent. That leads to shifting values of the chemical potential under alternate integration.

Another possibility is to utilize directly the Kirkwood definition [33]

$$\beta \mu^* = n \int_0^1 \, \mathrm{d}\lambda \int_0^\infty \frac{\partial \beta \Phi(r,\lambda)}{\partial \lambda} \, g(r,\lambda) \, \mathrm{d}\mathbf{r} \,, \tag{61}$$

where $\beta\mu^*$ is the excess chemical potential, $\beta\mu = \beta\mu^* + \ln(n\Lambda^3)$, and $\Lambda = h/(2\pi mkT)^{1/2}$ is the thermal wavelength. The Kirkwood formula also implies repeated calculation of the correlation functions depending on the coupling parameter λ .

However, none of the described approaches can be utilized for investigating the liquid-crystal phase transitions. In the former case there is no continuous line connecting liquid to crystal. In the latter case possible solutions to the OZ equation no longer correspond to the solid structure.

At present, to describe the freezing phase transition, the density functional approach has been developed for equivalent descriptions of the states on each side of the lines of phase equilibrium [2, 3, 34]. The principles of the density functional theory are based on a theorem [35], according to which there exists a unique relation between the local density $n(\mathbf{r})$ and the external field $V(\mathbf{r})$. The external field localizes the physical system in space (for example fixing the boundary in liquids or fixing the origin of coordinates in solid). This means that thermodynamic potentials such as the Helmholtz free energy *F*, the Gibbs free energy *G* or potential $\Omega = F - G$ depending on thermodynamic variables are at the same time functions of the external field. Taking into account the theorem [35] we have

$$F = F[n(\mathbf{r})], \quad G = G[n(\mathbf{r})], \quad \Omega = \Omega[n(\mathbf{r})],$$

or

$$f[n] = \frac{F[n]}{V}, \quad \frac{\Omega[n]}{V} = -P[n], \quad \frac{G[n]}{V} = n\mu[n].$$
 (62)

It is possible as usual to define the ideal and the excess components of these functionals, for instance

$$F[n(\mathbf{r})] = F_{\rm id}[n(\mathbf{r})] + F_{\rm ex}[n(\mathbf{r})], \qquad (63)$$

where

$$F_{\rm id}[n] = \int f_{\rm id}(n(\mathbf{r})) \,\mathrm{d}\mathbf{r} \,, \tag{64}$$

$$f_{\rm id}(n) = kTn(\ln\Lambda^3 n - 1).$$
(65)

Along with the hierarchy of g_i , g_{ijk} , g_{ijk} functions a direct correlation function hierarchy C_i , C_{ij} , C_{ijk} can also be defined as

$$C_{(1)}(\mathbf{r}) = -\frac{\delta(\beta F_{\text{ex}}[n])}{\delta n(\mathbf{r})}, \qquad (66)$$

$$C_{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\delta^2 \left(\beta F_{\text{ex}}[n]\right)}{\delta n(\mathbf{r}_1) \,\delta n(\mathbf{r}_2)} \,. \tag{67}$$

Basing our consideration on [2] we find here two ways to build the free energy as the density functional in application to the phase transitions. The first one follows from the relation

$$\frac{\delta F[n]}{\delta \Phi(\mathbf{r}_1, \mathbf{r}_2)} = \frac{1}{2} n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) .$$
(68)

Let us take a system in which the interaction potential consists of the main term that is repulsion and an attractive term considered as a perturbation

$$\Phi_{\lambda}(\mathbf{r}_1, \mathbf{r}_2) = \Phi_1(\mathbf{r}_1, \mathbf{r}_2) + \lambda \Phi_2(\mathbf{r}_1, \mathbf{r}_2), \quad 0 \leq \lambda \leq 1.$$
 (69)

Integrating relation (68) we calculate an increment of the free energy, arising with charging of the perturbation term, to that corresponding to a reference system

$$F[n] - F_1[n] = \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 \int d\mathbf{r}_2 n^{(2)}(\Phi_\lambda; \mathbf{r}_1, \mathbf{r}_2) \,\Phi_2(\mathbf{r}_1, \mathbf{r}_2) \,.$$
(70)

The attractive potential $\lambda \Phi_2$ acts in this construction as an external field.

Note that this derivation is much like the Kirkwood method. It is applicable for describing the liquid and gaseous systems, however, additional assumptions need to be involved to consider the phase transitions. This is caused by a necessity to determine the properties of the reference system independently, as a rule, from computer simulations, that makes the approach, in spite of its apparent attractiveness, to a great extent semiempirical. Moreover, we will see that the results obtained with this approach are significantly less accurate than those calculated using equation (19).

Another construction is specifically adapted for describing the liquid-solid phase transition. To do this an original state with known properties and the density $n_0(\mathbf{r})$ found in advance, have to be involved. Let the final state taken at the same temperature T be of density

$$n_{\lambda} = n(\mathbf{r}; \lambda) = n_0(\mathbf{r}) + \lambda (n(\mathbf{r}) - n_0(\mathbf{r})) = n_0(\mathbf{r}) + \lambda \Delta n(\mathbf{r}),$$

$$0 \le \lambda \le 1.$$
(71)

Integrating expressions (66) and (67) we finally have [2, 34]

606

$$\beta F_{\text{ex}}[n] = \beta F_{\text{ex}}[n_0] - \int \Delta n(\mathbf{r}) C_{(1)}([n_0]; \mathbf{r}) \, \mathrm{d}\mathbf{r}$$
$$+ \int_0^1 d\lambda (\lambda - 1) \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Delta n(\mathbf{r}_1) \, \Delta n(\mathbf{r}_2) \, C_{(2)}([n_\lambda]; \mathbf{r}_1, \mathbf{r}_2) \,.$$
(72)

Given $F_{\text{ex}}[n_0]$, $C_{(1)}([n_0];\mathbf{r}) = \delta F_{\text{ex}}/\delta n_0(\mathbf{r})$ and the direct correlation function $C_{(2)}(\mathbf{r}_1, \mathbf{r}_2; [n(\mathbf{r})])$ as a local density functional, the potential *F* can in principle be reconstructed as

$$F[n] = kT \int n(\mathbf{r}) \left\{ \ln \left[\Lambda^3 n(\mathbf{r}) - 1 \right] \right\} d\mathbf{r}$$
$$+ \int n(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} + F_{\text{ex}}[n].$$
(73)

This problem is very difficult to solve and requires in fact making drastic simplifications, which cannot always be justified. In the absence of an external field the free energy is

$$f(n) = f_{\rm id}(n) + kTn^2 \int_0^1 d\lambda (\lambda - 1) \int d\mathbf{r} C_{(2)}(\lambda n; \mathbf{r}) \,.$$
(74)

4.2 Vapor-liquid phase transition

To determine the lines of the phase equilibrium, equation (70) can be utilized as follows [36]. The main approximation is

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \boldsymbol{\Phi}_2) \approx n(\mathbf{r}_1) n(\mathbf{r}_2); \qquad (75)$$

reflecting the neglect of correlations in $g(\mathbf{r}_1, \mathbf{r}_2)$. This so called *random phase approximation* is, as a matter of fact, not different from the Kirkwood superposition approximation made rather in the pair correlation function than in the three-particle one. A system of particles with an effective hard sphere diameter depending on temperature can be chosen as a reference in correspondence with the proposed partitioning in work [18] of the Lennard-Jones potential into the attractive and repulsive parts

$$\Phi_{1}(r) = \begin{cases}
\Phi_{LJ}(r) + \varepsilon, & r \leq r_{\min}, \\
0, & r \geq r_{\min},
\end{cases}$$

$$\Phi_{2}(r) = \begin{cases}
-\varepsilon, & r \leq r_{\min}, \\
\Phi_{LJ}(r), & r \geq r_{\min}.
\end{cases}$$
(76)

In the uniform limit we obtain

$$f(n) = f_{\text{h.s.}}(n) - \frac{1}{2} \alpha n^2$$
, (77)

from (70), (75), (76), where

$$\alpha = -\int \Phi_2(r) \,\mathrm{d}\mathbf{r} \,. \tag{78}$$

Then, taking into account that

$$\mu = \mu_{\text{h.s.}}[n(\mathbf{r})] + \int \Phi_2(|\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}') \,\mathrm{d}\mathbf{r}', \qquad (79)$$

we finally get

$$P = P_{\rm h.s.} - \frac{1}{2} \alpha n^2 \,, \tag{80}$$

$$\mu = \mu_{\text{h.s.}} - \alpha n \,. \tag{81}$$

The classical Carnahan-Starling results [37] can be used to describe the hard sphere reference fluid

$$P_{\rm h.s.}(\eta) = \frac{kT(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3}, \qquad (82)$$

where $\eta = (\pi/6) n\sigma^3$ is the hard sphere packing density



Figure 5. (a) Vapor-liquid equilibrium in the density functional approach (curve 1 — binodal, points are Monte Carlo data [38]; curve 2 — spinodal; curve 3 — Monte Carlo spinodal [28]; the critical temperature is $T^* = 1.488$). (b) Vapor-liquid phase equilibrium calculated by integration according to the equations (57), (58) [32]. Circles are Monte Carlo calculations [38], while triangles correspond to [39]. (c) Vapor-liquid phase equilibrium calculated with (84) and closure [17] — solid line, and that with (88) and closure (43) — crosses. Computer experiments [40] are marked by circles; Monte Carlo values [41] are marked by squares.

Figure 5a presents the vapor-liquid coexistence phase diagram found in this version of the density functional theory. Figure 5b presents the same phase diagram calculated by integrating equations (57), (58), and Fig. 5c exhibits the result found from equations for the chemical potential [42, 43], in which integration over the coupling parameter λ can be performed immediately, so that the resulting equations depend solely on the parameters of a single final state.

Note that the original equation is an exact analogue to the Kirkwood formula (61)

$$\beta \mu^* = n \int_0^\infty 4\pi r^2 \, \mathrm{d}\mathbf{r} \cdot \left[\left(\frac{1}{2} h^2 - \frac{1}{2} h C^{(2)} - C^{(2)} \right) + B^{(2)} + \int_0^1 h(r,\lambda) \, \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} \, \mathrm{d}\lambda \right], \tag{84}$$

where λ has the same coupling parameter meaning. The difference is that equation (84) can, with some assumptions on properties of the bridge-functional, be immediately integrated with respect to the coupling parameter. Note that according to formulae (16), (19)

$$\beta \mu^* = -\int_0^\infty \left\{ h - \omega - \frac{1}{2} h \big(\omega + B^{(1)} \big[(r) \big] \big) \right\} 4\pi r^2 \, \mathrm{d}\mathbf{r} \, ; \quad (85)$$

that means

$$B^{(1)}(r) = \frac{2}{h(r)} \int_0^1 h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} \,\mathrm{d}\lambda - B^{(2)}(r) \,. \tag{86}$$

Because of $\Phi(r, \lambda) = \lambda \Phi(r)$ one can also apply the linearly uniform approximation to the values

$$h(r, \lambda) = \lambda h(r), \quad C(r, \lambda) = \lambda C(r)$$

and

$$\Omega(r,\lambda) = \omega - n\beta \Phi_2 = \lambda \Omega(r) \,,$$

and after some transformations obtain [13]

$$\int_{0}^{1} h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} d\lambda = \frac{h(r)}{\Omega(r)} \int_{0}^{\Omega} \Omega \frac{\partial B^{(2)}(\Omega)}{\partial \Omega} d\Omega.$$
(87)

Substitution of closure (36) into (86), (87) gives a result

$$B^{(1)} = -\frac{1}{6} \,\Omega^2 = \frac{1}{3} \,B^{(2)} \,, \tag{88}$$

which can also be derived from direct analysis of the exact expansions of $B^{(1)}$ and $B^{(2)}$ [44].

Figure 6 presents the $\beta\mu^*$ dependence on the reduced density $\rho = n\sigma^3$ along different isotherms $T^* = kT/\epsilon$. Also presented are the results extracted from the modified Benedict–Webb–Rubin (MBWR) equation of state approximating a large body of computer simulation results [45]. We see a close agreement between the theory and numerical experiments; small deviations are found only in the critical point vicinity $T^* \approx 1.31$, $\rho \approx 0.31$, where very accurate values are difficult to obtain both in computer simulations and theory.

Note that the value of temperature found by the density functional approach for the critical point $T^* = 1.5$ is in



Figure 6. Chemical potential as a function of temperature T^* and density ρ . Solid circles are values extracted from the MBWR equation of state [45].

agreement neither with the computer simulation value nor with the result from approximate theory of liquids.

4.3 Liquid-crystal phase transition

Currently, the density functional theory is of considerable use for describing and predicting freezing of liquids [2, 34]. The basic equation is that presented by (72). Some additional comments are necessary.

As we have already seen, determination of the local density $n(\mathbf{r})$ of coexisting phases and analysis of the real complete two phase system are transformed into consideration of the properties of separated uniform bulk subsystems. In this case the properties of the interface are not taken into account. Once the chemical potential μ and the free energy F(n) have been calculated for the bulk uniform separated systems the comparison is performed. The problem, as in other approaches, is to prove that the density functional F(n)derived above is uniform both for stable states and for metastable ones [34]. On the other hand, changing to the thermodynamic limit, for instance in liquid, means the neglect of the external field (boundary with solid), which means replacing $g(\mathbf{r})$ for liquids in contact with crystal by g corresponding to bulk liquid. (Note that the condition $n_0(\mathbf{r}) = n_0$ underlies all the existent approximations of the density functional method.)

Another principal simplification lies in the approximation of the crystalline direct correlation function $C(\mathbf{r}_1, \mathbf{r}_2; [n_0 + \lambda \Delta n])$. The idea of the approach lies in expanding the functional about $\lambda = 0$. Then in the first approximation we have [see (72)]

$$\int_{0}^{1} (1 - \lambda) C(\mathbf{r}_{1}, \mathbf{r}_{2}; [n_{0} + \lambda \Delta n]) d\lambda$$

=
$$\int_{0}^{1} (1 - \lambda) \{ C(\mathbf{r}_{1}, \mathbf{r}_{2}; [n_{0}]) \} d\lambda + O(\lambda)$$

=
$$\frac{1}{2} C(\mathbf{r}_{1}, \mathbf{r}_{2}; [n_{0}]) + \dots$$
 (89)

Since n_0 is the reference liquid density in the homogeneous case, then $C(\mathbf{r}_1, \mathbf{r}_2; [n_0]) = C(r; n_0)$ can be determined from some approximate integral equation. The next terms which could be taken into account in the expansion would give corrections also found from the properties of liquid. What should also be noted is that there is one more principal problem to determine the crystalline density $n(\mathbf{r})$. It is not known in advance what crystalline structure (symmetry) the liquid crystallizes to. As a matter of fact, $n(\mathbf{r})$ is postulated in advance taking into account some additional arguments. To overcome this problem the solid is often considered as a liquid with the effective density n_{eff} determined from the condition of consistency with the real crystalline density $n(\mathbf{r})$.

The effective diameter can be determined, for instance, by the condition

$$F_{\rm ex}^{\rm cr}[n(\mathbf{r})] = F_{\rm ex}^{\rm liq}(n_{\rm eff})\,,$$

where $n_{\rm eff}$ is related to crystalline $n(\mathbf{r})$ by the weighting factor

$$n_{\rm eff} = n_{\rm eff} [n] = \int n(\mathbf{r}) \ W(\mathbf{r}; [n]) \,\mathrm{d}\mathbf{r} \,, \tag{90}$$

where W is a weighting function constructed in a special way [34].

From all the aforesaid it follows that a theory based on the density functional approach is, actually, a liquid based theory of freezing. Formally, the density functional theory allows us to construct the free energy both for liquids and solids based on uniform theoretical grounds, which are nothing more than equations of the theory of liquids. At present, however, there is no other theoretically more consistent theory of freezing, although, as we have seen, this approach is bound to numerous, often intuitive, approximations.

There are, however, some fundamental arguments casting doubts on the possibility of treating both the liquid and crystalline states from a uniform standpoint. The reason is that unlike the two state liquid-vapor case with no fundamental structural differences between states of incompatible nature, structural differences between liquids and solids are principal and lie in the existence of the elements of symmetry in liquids which are incompatible with those existing in solids. The inherent structure of liquids cannot be transformed into the crystalline structure by continuous changing. Change from liquid to crystal always occurs abruptly (this is a reason for the absence of an appropriate critical point). Therefore, although they are capable of provision reliable numerical values, the liquid based models of crystalline state cannot be accepted as physically well justified approaches. The functional density theory relates rather stable liquid states to metastable or amorphous ones, at least, with respect to structure.

As early as 60's Bernal performed some real experiments with a system of hard spheres [46], from which it might follow that the symmetry elements of order of 5 can exist even in liquids with simple central forces of interactions. Contrary to the earlier structural theories considering liquids as containing elements of gas disorder and also containing crystalline type features, today it is commonly accepted that liquids exhibit a unique structure, which can not be reduced to other structures [47]. This has been unambiguously confirmed in [48], when it was shown that even simple liquids can be overcooled below their freezing point with no crystallization. This is possible only if the liquid structure differs fundamentally from that of solid. On the other hand, crystals can be overheated or stretched inside the metastable states having still a crystalline structure. What is important is that the liquid metastable region overlaps with the crystalline metastable one. That is two different metastable states now correspond to the same values of the macroscopic parameters (this phenomena is absent in the liquid-vapor phase

transition). This once more underlines the fundamental structural disagreement between liquid and crystalline states.

A curious situation arises. In accordance with our concept the thermodynamic comparison procedure of two homogeneous phases should involve precisely crystalline metastable state described by the appropriate crystalline correlation function only (see Fig. 10 below). The density functional built on the liquid based approximations has no such crystalline features.

Along with the thermodynamic comparison procedure an attempt can be made to predict phase transition based on a concept of structural changes, as the system approaches the phase equilibrium point, regardless of whether the given phase is in contact with another phase. Therefore, the goal is to find out those one-phase microscopic or macroscopic criteria [34], which would point to these structural changes. Some such criteria are well known; for example, according to the Lindemann rule a crystal loses stability and melts when the root mean square displacement of atoms from their equilibrium position in the lattice reaches some definite value (approximately 15%).

Another one-phase criterion of freezing [32] is based on analyzing the fine structure of the entropy in terms of many particle correlations

$$S_{\rm ex} = \sum_{n=2}^{\infty} S_n \,. \tag{91}$$

For instance, the two-particle contribution is

$$S_2 = -\frac{n}{2} \int \left[g(r) \ln \left(g(r) \right) - g(r) + 1 \right] d\mathbf{r} \,. \tag{92}$$

The value of $\Delta S = (S_{ex} - S_2)$ is a very sensitive indicator to structural changes in liquids that occur as the density increases. In particularly, it was found that reversal of the sign of ΔS occurred at exactly the freezing point. This actually points to some mechanism of losing thermodynamic stability.

A direct but only qualitative criterion is given in work [49] where conclusions based on computer simulations treat the shoulder in the second peak of the correlation function as a structural precursor to freezing. This conclusion is, however, not in agreement with another treatment of the shoulder (see below). Most informative are those structural criteria that can be characterized by the value of some parameters of the correlation functions. One is the Hansen–Verlet criterion [50], which states that freezing occurs when the structure factor

$$S(k) = 1 + nh(k) \tag{93}$$

increases to a value of 2.85 at some wave number value k_0 in the Fourier transform of the total correlation function h(r). This criterion turned out to be in very close agreement with computer simulations and with the predictions given by the integral equation theory [13]. The existence of one-phase criteria unambiguously reflects the structural changes occurring in the system, however all of them are of semiempirical and approximate nature.

One of the goals of the theory is to find theoretical arguments justifying one or another criterion. As we have seen, the freezing criterion can be numerically related to properties of the correlation function.

A similar numerical criterion of melting has been proposed from the limiting form (41). This criterion, being Note that the condition

 $h(r_{\min}) = 0$ for $T = T_{cr}$, $n = n_{cr}$

may also be taken as a structural indication of the critical point. Tables 1 and 2 incorporate exhaustive and most reliable data for freezing and melting obtained by numerous computer experiments and by various theoretical approximations.

Table 1. Liquid-crystal phase transition in a hard sphere fluid.

Liquid density ρ_1	Crystal density $\rho_{c_{\rm cr}}$	Pressure $P^* = n_0 kT$ †	k_0	Reference
$0.911 \ S(k_0) = 2.85$	$1.032 \ \gamma = -1/2$	6.17	6.95	PY [13]
$0.928 \ S(k_0) = 2.85$	$1.018 \gamma = -1/2$	7.58	6.95	$B = -1/2 \cdot \omega^2 [13]$
0.943	1.041	8.27		MC [50]

 \dagger where n_0 is the close packing density.

4.4 Liquid near the phase interface

Several approaches can be used to determine the density profile near the model interface. The first one is that based on equations following from the free energy treated as the density functional. Another one is based on the first equations of the hierarchy of distribution functions or the hierarchy of the direct correlation functions. The third way is that utilizing the fundamental set of the coupled equations (14), (15), and final one is the so called 'blowing ball' approach based on the OZ equation for two-component homogeneous mixture.

The starting point in the density functional theory is the exact equation (72). Let us consider n_0 to be the density of a

Table 2. Liquid-crystal phase transition in the Lennard-Jones model.

uniform (bulk) reference fluid at the same chemical potential that corresponds to the given fluid $\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0$. Then the potential Ω_V is [2]

$$\Omega_{V}[n(\mathbf{r})] = \Omega_{V}[n_{0}] + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

+ $\beta^{-1} \int \left[n(\mathbf{r}) \ln \frac{n(\mathbf{r})}{n_{0}} - \Delta n \right] d\mathbf{r}$
+ $\beta^{-1} \int d\lambda (\lambda - 1) \int d\mathbf{r}_{1} \int d\mathbf{r}_{2} C^{(2)}([n_{\lambda}]; \mathbf{r}_{1}, \mathbf{r}_{2}) \Delta n(\mathbf{r}_{1}) \Delta n(\mathbf{r}_{2}).$
(94)

Using the singlet approximation

$$C^{(2)}([n_{\lambda}];\mathbf{r}_{1},\mathbf{r}_{2}) = C^{(2)}(n_{0};|\mathbf{r}_{1}-\mathbf{r}_{2}|)$$
(95)

and linearizing the functional $\Omega_V[n(\mathbf{r})]$ we arrive at an integral equation for the density profile in the external field $V(\mathbf{r})$

$$n(\mathbf{r}_{1}) = n_{0} \exp\left[-\beta V(\mathbf{r}_{1}) + \int C^{(2)}(n_{0}; r_{12}) (n(\mathbf{r}_{2}) - n_{0}) \,\mathrm{d}\mathbf{r}_{2}\right].$$
(96)

The meaning of the singlet approximation lies in setting the two particle correlation functions $C(\mathbf{r}_1, \mathbf{r}_2)$, $g(\mathbf{r}_1, \mathbf{r}_2)$ appearing in the equation for one particle distribution function, that is for the density profile, equal to their bulk equivalent $C(r_{12})$, $g(r_{12})$. The singlet approximation makes it possible to derive independently equations for the density profile.

From (96) we find

$$\omega_1(\mathbf{r}_1) = n \int C^{(2)}(r_{12}) \big(g_2(\mathbf{r}_2) - 1 \big) \, \mathrm{d}\mathbf{r}_2 \,, \tag{97}$$

which exactly coincides in appearance with equation (14), found also in the singlet approximation under condition (19). Thus, the functional density approach is equivalent to the first equation of the fundamental set (14), (15) in the singlet

T^* †	Liquid density ρ_1 , $S(k_0) = 2.85$	Crystal density $\rho_{c_{\rm cr}}$, $\Omega = -1$	Pressure $P^* = P\sigma^3/\varepsilon$	k_0	Reference
2.74	1.061 1.080 1.113	1.208 1.208 1.179	23.29 27.10 32.2	7.26 7.26	PY [13] $B = -1/2 \cdot \Omega^2$ [13] MC [50]
1.35	0.963 0.955 0.964	1.085 1.055 1.053	8.54 7.73 9.00	7.16 7.00	PY [13] $B = -1/2 \cdot \Omega^2$ [13] MC [50]
1.15	$\begin{array}{c} 0.947 \\ 0.930 \\ 0.936 \\ 0.960 \ \Delta S = 0 \end{array}$	1.060 1.021 1.024	6.57 5.37 5.68	7.10 6.95	PY [13] $B = -1/2 \cdot \Omega^2$ [13] MC [50] [51]
0.75	$\begin{array}{c} 0.910 \\ 0.871 \\ 0.875 \\ 0.856 \ \Delta S = 0 \end{array}$	0.998 0.938 0.973	3.23 1.07 0.67	7.05 6.85	PY [13] $B = -1/2 \cdot \Omega^2$ [13] MC [50] [51]
0.67	0.857 0.86	0.912	0.39	6.80	$B = -1/2 \cdot \Omega^2 [13]$ MC [32]

609

approximation. Note that function $C^{(2)}(r_{12})$ is found separately from the OZ equation. A small, but very important difference is that equation (14) deals with the function $C^{(1)}(r_{12})$. In the hypernetted chain approximation $B^{(1)} = B^{(2)} = 0$ both approaches are exactly equivalent.

From the given comparison it is evident that the functional density theory is principally not rigorous as not exactly corresponding to the fundamental set of equations.

One may choose as a basic equation either the first equation of the BBGKY (Bogolyubov – Born – Green – Kirk-wood – Yvon) hierarchy

$$\beta^{-1} \frac{\partial \omega_1(\mathbf{r}_1)}{\partial \mathbf{r}_1} = n \int_V g_2(\mathbf{r}_2) \exp\left[-\beta \Phi_{12}(r_{12}) + \omega_{12}(r_{12})\right] \\ \times \frac{\partial \Phi_{12}(r_{12})}{\partial \mathbf{r}_1} \, \mathrm{d}\mathbf{r}_2 \tag{98}$$

or the LMBW (Lovett-Mou-Buff-Wertheim) equation

$$\frac{\partial \omega_1(\mathbf{r}_1)}{\partial \mathbf{r}_1} = n \int_V C_{12}^{(2)}(r_{12}) \frac{\partial g_2(\mathbf{r}_2)}{\partial \mathbf{r}_2} \, \mathrm{d}\mathbf{r}_2 \,. \tag{99}$$

Equations (98), (99) can be used to solve some particular problems, however, they can not be applied directly in general. The question is that unknown functions $\omega_1(\mathbf{r}_1)$ or $g_1(\mathbf{r}_1)$ depend in general on three components of the \mathbf{r} vector (for instance, in the liquid – solid interface). Therefore, a single vectorial equation becomes equivalent to three coordinate ones. Without writing them in details note that they may have no unique solution [53]. And only in the one dimensional case are all restrictions removed, for instance in the case of a liquid near the ideal wall. Equations (98), (99) can be readily integrated [53, 54] resulting in

$$\omega_1(Z_1) = n \int_V g_2(Z_2) \, K(r_{12}, Z_1, Z_2) \, \mathrm{d}\mathbf{r}_2 + \beta \mu^* \,, \qquad (100)$$

where Z is the normal direction to the ideal wall plane (X, Y). According to equation (98) we have

$$K = h(r_{12}) + \int_{Z_1}^{\infty} \exp[-\beta \Phi_{12} + \omega_{12}] \frac{\mathrm{d}\omega_{12}(r'_{12})}{\mathrm{d}Z'_1} \,\mathrm{d}Z'_1, \ (101)$$

$$\beta \mu^* = \lim_{Z_1 Z_2 \to \infty} \int_V K(r_{12}, Z_1, Z_2) \,\mathrm{d}\mathbf{r}_2; \quad Z_{12} = \mathrm{const} \,. \quad (102)$$

whereas for (99) we obtain

$$K = C^{(2)}(r_{12}) = h(r_{12}) - \omega_{12}(r_{12}) + B^{(2)}(r_{12}), \qquad (103)$$

$$\beta \mu^* = -n \int C^{(2)}(r_{12}) \,\mathrm{d}\mathbf{r}_2 \,. \tag{104}$$

A more physically transparent way is applying the OZ equation directly to a two component mixture, letting the concentration of one species, say $n_a = N_a/V$, to approach zero. Then terms proportional to n_a can be omitted in the set of three OZ equations for mixture. We obtain [55]

$$\omega_{\rm as}(r_{12}) = B_{\rm as}^{(2)}(r_{12}) + n_{\rm s} \int_{V} C_{\rm ss}^{(2)}(r_{13}) h_{\rm as}(r_{23}) \,\mathrm{d}\mathbf{r}_{3} \,, \quad (105)$$

$$\omega_{\rm ss}(r_{12}) = B_{\rm ss}^{(2)}(r_{12}) + n_{\rm s} \int_{V} C_{\rm ss}^{(2)}(r_{13}) h_{\rm ss}(r_{23}) \,\mathrm{d}\mathbf{r}_{3} \,.$$
(106)

Here, the first equation determines the g_{as} correlation function describing the changing density of *s* molecules about molecule a, while the second one corresponds to the structure of the bulk liquid. To make the molecule *a* exhibit a plane surface, the diameter σ is allowed to grow to infinite size. Therefore the distance between centers of molecules *a* and *s* in (105) is set equal to $r_{12} = \sigma + Z_{12}$ then changing to the limit $\sigma \to \infty$, $Z_{12} = \text{const.}$ The solution of the equation thus derived $\omega_{as}(\sigma + Z_{12})$, $Z_{12} = Z$, is identified then with the potential $\omega_1(Z)$. Equation (105) takes the form

$$\omega_1(Z_1) - B^{(2)}(Z_1) = n \int g_2(\mathbf{r}_2) C^{(2)}(r_{12}) \,\mathrm{d}\mathbf{r}_2 + \beta \mu^* \,. (107)$$

The right hand side of this equation coincides exactly with that of equation (100), while an additional term $B^{(2)}$ appears in the left part.

We see that all the first order approximations produce one and the same equation for the density profile, having, however, different kernels K and different integration constants $\beta\mu^*$. In other words, the singlet approaches provide a number of versions depending on two approximations. The first one is determined by choosing the $C^{(1)}$ function in the equation for the density profile, while the second one is determined by choosing the bulk function $C^{(2)}$ or $\omega(r)$, which is determined by choosing the closure. For instance HNC/PY refers to the HNC singlet equation supplied with the bulk correlation function calculated with the PY OZ equation.

In Fig. 7 some density profiles calculated in different approximations for a hard sphere fluid in contact with an ideal wall are given. Some computer simulation data are also presented for comparison.

5. Metastable states

Let us turn to the phase diagram in Fig. 1. There we can find metastable states of a quite different nature. The gaseous branch FCF_1 of the metastable states corresponds either to supercooled or supercompressed vapor, whereas the liquid branch BCB_1 incorporates states corresponding either to overheated or stretched liquid. Spinodal F_1CB_1 restricts the region of existence of the homogeneous liquid and gaseous states. The region enclosed by the melting line MM_1 and the spinodal KK_1 is that of the metastable superheated and stretched crystals, whereas the region lying on the right beyond the freezing line LL_1 corresponds either to supercooled or overcompressed liquid. All the theoretical and experimental data available nowadays show that this side, having no spinodal line, covers a wide subregion of crystalline parameters values, changing farther in a nonlocal way to the region of amorphous states. A nontrivial case may occur inside the region KK_1MM_1 . Under the same conditions, two various metastable states, one of which is liquid and the second crystalline, can exist. Does it mean that there exists an equilibrium similar to that aimed to describe properties of supercooled water, where the low density liquid metastable water coexists with the high density metastable one [58]?

5.1 Relationship between metastable states and Gibbs canonical distribution

Let us first consider in detail arguments that may justify the idea that the OZ equation is not appropriate to describe



Figure 7. Density profile of a hard sphere: (a) fluid near the ideal wall [56]. Solid line is HNC/PY data, dashed line is HNC/MSA (mean spherical approximation). Points are Monte Carlo values (Snook, Henderson [57]), $\rho = 0.81$); (b) (*A* hard sphere density profile [53] *A* — fundamental set of equations (14), (19); *B* — equations (101), (102); *C* — equations (103), (104).

metastability. For instance in review [59] the idea is elaborated that the phase equilibrium boundary can be determined by vanishing the physical solutions to the OZ equation. The arguments are based on the van Hove theorem [60, 61], from which may follow that metastable states being in unstable equilibrium do not correspond to rigorous statistical mechanical equations derived in the thermodynamic limit to treat just stable equilibrium states.

The second argument incorporates the fact that, according to the Gibbs theorem, the phase distribution is not unique for a finite system [62, 63] where the metastability can arise, and therefore the system does not correspond to equations derived from the unique Gibbs canonical distribution valid rigorously in the thermodynamic limit only. The idea of disappearance of the solutions to the OZ equation has been discussed in papers [64, 65]. As has been already said, many years of experience showed that disappearance of the solutions at the stable-metastable boundary is not confirmed by theory and computer simulations. For instance, Monte Carlo calculations performed in the phase transition regions exhibit points that lie on the extension of branches of equation of state of appropriate phases. These points are assigned either to supercooled or overcompressed liquid, or to supercooled vapor [22].

One can suggest that the extension of solutions to the approximate equations inside the metastable area exists, because the approximation of the equation makes it not correspond to the exact partition function and therefore not correspond to the Gibbs distribution. Similarly, large scale fluctuations are not taken into account in computer simulations due to the small number of particles in calculations, which also leads to distortion of the partition function.

Indeed "The completely flat portion in P(n) is a consequence of the limiting process. The absence of a loop is due to the fact that the complete and rigorous configuration integral Z includes every possible configuration, including configurations associated with the simultaneous existence of two phases in the volume V. Approximate evaluations of Zinvariably introduce an implicit restraint of uniform macroscopic density throughout V in enumerating configurations, as well as other approximations. It is not possible under this restraint for the two phases to exist together in the container. Mathematically, the result is a loop." [66].

In the exact meaning the metastable states are not equilibrium states. On the other hand, the true nonequilibrium states are described by explicit time dependent equations and correlation functions, for instance by the nonequilibrium chain of the BBGKY equations. At the same time, metastable correlation functions do not depend on time. They remain constant until nuclei of appropriate size corresponding to a new phase arise by chance so that the new phase could grow.

We arrive at a paradoxical situation. As the metastable states are described neither by the equilibrium nor by the nonequilibrium chain of the BBGKY equations, how can these states be otherwise treated? In other words, how (if possible) can one introduce the random time of appearance of nuclei into the BBGKY hierarchy? On the other hand, if we are interested in finding distribution functions remaining constant for a finite period of time, is it not natural to find out whether the BBGKY equilibrium chain of equations can also, for some appropriate conditions, be used for treating metastability?

Such a hypothesis has been formulated in paper [13], where metastable states were supposed to be equivalent to some appropriate equilibrium states. Let us now consider for this purpose system A, consisting of a large but finite number N of particles placed in a volume V at temperature T.

The canonical distribution of the system is well known

$$f_N(X,T) = \frac{1}{Z_N(T)} \exp\left(-\beta H(X)\right), \qquad (108)$$

where H(X) is the Hamiltonian of our system. $Z_N(T)$ is the classical partition function

$$Z_N(T) = \frac{1}{N!} \int_X \exp\left(-\beta H(X)\right) dX, \qquad (109)$$

where *X* stands for the coordinate and momentum of all particles.

At the some time, another noncanonical distribution $f_N^*(X, T)$ [62, 63] may also exist in the finite case if some

$$\int f_N^*(X) \, \mathrm{d}X = \int f_N(X) \, \mathrm{d}X = 1 \,, \tag{110}$$

$$E = \int H(X) f_N^*(X) \, \mathrm{d}X = \int H(X) f_N(X) \, \mathrm{d}X.$$
 (111)

As follows from the Gibbs [62, 63] theorem, we have for the entropies

$$S^* = -k \int f_N^* \ln f_N^* \, \mathrm{d}X, \qquad S = -k \int f_N \ln f_N \, \mathrm{d}X \qquad (112)$$

the inequality $S \ge S^*$, that is the entropy which corresponds to the Gibbs distribution has a maximal value. The probabilities of canonical and noncanonical distributions in the phase space are interrelated as

$$\frac{P_N^*}{P_N} = \exp\left(-V\frac{s_n - s_n^*}{k}\right) \to 0 \quad \text{at} \quad V \to \infty \,, \tag{113}$$

where $S_N^* = V s_n^*$, $S_N = V s_n$, that is the probability of the noncanonical distribution tends to zero in the thermodynamic limit. In the finite case any distribution can be realized, however it is impossible to detect which one has arisen for it depends upon the appropriate conditions and random arrangements of particles. Two cases should be distinguished here.

As was shown in [62], the noncanonical distribution in the one phase case can be treated as $f_N^* = f_N(t)$ corresponding to nonequilibrium in the microcanonical ensemble with constant energy *E*. In another case, it was shown [67] that if a loop arises for those values of the thermodynamic parameters at which two phase states can exist then this unambiguously points to the bimodality of the statistical distribution. On the other hand the loop exhibits just the metastable case.

From all the aforesaid it follows that the canonical Gibbs distribution corresponds to the two phase equilibrium state, while the noncanonical one corresponds to the one phase metastable state.

The noncanonical distribution can be written as

$$f_N^*(X) = \frac{1}{Z_N^*} \exp\left[-\beta (H(X) + U(X))\right],$$
 (114)

where U(X) is an arbitrary function determined by the properties and form of the function $f_N^*(X)$,

$$Z_N^*(T) = \frac{1}{N!} \int \exp\left[-\beta \left(H(X) + U(X)\right)\right] \mathrm{d}X.$$
(115)

If the function $H(X) + U(X) = H^{\text{eff}}(X)$ is considered as a new effective Hamiltonian, then it would mean that the thermodynamic properties of a metastable one-phase state with the Hamiltonian H(X) are equivalent to those of a stable one-phase state with the effective Hamiltonian $H^{\text{eff}}(X)$. Thus, the entire metastable region can be reflected to the stable one-phase region, with the binodal being the line of reflection. But what is the way to do this?

Let us consider the canonical distribution (108) and the partition function (109). If we wanted to use these equations immediately to treat a two phase system then we could find no features in these equations pointing to the two phase character of the system. Such a global approach allows us to solve the phase separation problem only in a roundabout way calculating the thermodynamic parameters in advance with further thermodynamic comparison. The structure and the location of the transition layer are also not presented explicitly in the Gibbs distribution.

As was noted in book [61], "It seems to be questionable whether the condensation properties can be explained from the general expression of the partition function. From a mathematical standpoint it is difficult to understand how the apparently innocent expression (108) can produce that formula for the free energy $F = -kT \ln Z_N$, which ought to correspond to a nonsmooth function".

An immediate change to the thermodynamic limit does not alter the situation. Although the limiting function

$$\varphi(n,T) = \lim \frac{1}{N} F\left(\frac{N}{n}, T, N\right), \quad N \to \infty,$$
 (116)

can be proved to exist [61], it is not clear whether this expression would have discontinuities of its derivatives and how the construction of the theory can be made.

However, it is possible to change the global way of treating a system in general to a local treatment by using *S*-particle distribution functions. This makes it possible to advance further in understanding the bulk properties as well as those of microscopic structural character. As we have seen this change leads to a fundamental set of coupled equations (14), (15), which is an exact equivalent to the Gibbs distribution. In the one phase equilibrium state with

 $g_1 = \text{const} = 1$

the Gibbs distribution is equivalent to the OZ equation. In the stable two phase region, the Gibbs distribution ought to correspond to the complete set of equations (14), (15). The metastable one-phase state existing at values of parameters of two phase equilibrium state should correspond to some noncanonical distribution. On the other hand, from the aforesaid it follows that this case can be reduced to a canonical one. The only way this takes place is when the metastable state corresponds to the OZ equation taken at values of parameters that correspond now to the two phase case.

Note that there is no contradiction with the van Hove theorem which proved the existence of the limiting function (116). Note also that there is no contradiction with the condition proved also by van Hove that pressure

$$P = -\frac{\partial \varphi}{\partial (1/n)}$$

is a nondecreasing function as far as this condition is also fulfilled in the metastable region.

Let us underline once more the aforesaid. The noncanonical statistical distribution of the metastable states is equivalent to the canonical distribution of stable equilibrium states reflected at the phase equilibrium line and therefore when changing from the stable region to the metastable one, the OZ equation has no singularity related to the vanishing of the solutions. However, there is no answer yet as to whether solutions to the OZ equation found in the metastable region exhibit an analytical continuation of the solutions found in the equilibrium one.

Figure 8 presents correlation functions found in the close vicinity of the spinodal line in the liquid-vapor phase transition area. Points mark Monte Carlo results [28]. Note



Figure 8. Correlation functions in the metastable region of vapor – liquid transition near the spinodal line $T^* = 1.2$. I — gaseous region $\rho = 0.14$; P/(nkT) = 0.5069 (0.5277), $\beta\mu^* = -1.0069 (-0.9767)$. 2 — liquid region $\rho = 0.45$; P/(nkT) = 0.0351 (0.0516), $\beta\mu^* = -2.405 (-2.297)$. MBWR values [45] are given in parentheses. Solid lines — integral equation approach [13]; the points are Monte Carlo values [28].

that computer simulation points have some dispersion, which probably can be explained by the fact that accurate calculation in the metastable region is a difficult problem.

Let us now take metastable states in the liquid-solid phase transition area and those of the crystalline region.

We see in Fig. 9 that one phase metastable states can exist at those values of thermodynamic parameters that correspond to one phase crystalline equilibrium. Note that in the vapor-liquid phase diagram the metastable states could exist only within two state region of parameters. An explanation easily follows from the complete set of equations (14), (15). *Homogeneous metastable states can arise if and only if the*



Figure 9. Radial Lennard-Jones metastable correlation functions beyond the freezing line. Solid lines — Monte Carlo [28]. Lines with points — OZ equation with closure (88), $T^* = 1.0$; $\rho = 0.95$ (line *I*); $\rho = 1.2$ (line 2). At low density theoretical and computer simulation values are close to each other; at high density there is some discrepancy, broadening in the second peak indicating metastability.

equilibrium states are inhomogeneous and are described by the complete set of equations (14), (15). The stable one-phase crystalline states are indeed inhomogeneous and are described indeed by the complete set (14), (15). Therefore, the incomplete description with the simple OZ equation corresponds to liquid metastable states in the crystalline region.

In Fig. 9 we present Monte Carlo correlation functions [28] and those calculated with the theory. One point at $T^* = 1$ and $\rho = n\sigma^3 = 0.95$ corresponds to the area between freezing $\rho \approx 0.94$ and melting $\rho \approx 0.99$ [13], while another is placed in the crystalline part of the phase diagram $\rho = 1.2$.

In Fig. 10 we see two types of metastable states found for a hard sphere model, which can exist at the same density.



Figure 10. Two types of the metastable states for a hard sphere fluid at one and the same density $\rho = 0.9931$. Curve *1*: liquid metastable state – closure (88), curve *2*: crystalline metastable state — Monte Carlo [31]. The freezing density is $\rho = 0.943$; the melting density is $\rho = 1.041$.

5.2 Spinodal decomposition

The OZ equation (18) can be written in the Fourier variables

$$\hat{h}(k) = \frac{\hat{C}(k)}{1 - n\hat{C}(k)},$$
(117)

where for instance

$$\hat{h}(k) = \frac{4\pi}{k} \int_0^\infty h(r) \sin(kr) \, r \, \mathrm{d}\mathbf{r} \,, \tag{118}$$

$$h(r) = \frac{1}{2\pi^2 r} \int_0^\infty \frac{\hat{C}(k)}{1 - n\hat{C}(k)} \sin(kr) \, k \, \mathrm{d}k \,. \tag{119}$$

This means that solutions to the OZ equation will have no singularities until the denominator $1 - n\hat{C}(k)$ is equal to zero. At the same time according to (33) the isothermal compressibility

$$\chi_T \sim \left[1 - n\hat{C}(0)\right]^{-1};$$

that means that the quantity $1 - n\hat{C}(k)$ is always positive and is nowhere equal to zero. The only exception is point k = 0 at which $1 - n\hat{C}(0)$ can equal zero. That means that the isothermal compressibility becomes equal to an infinite value. On the phase diagram (Fig. 1) the points with the infinite compressibility value comprise the spinodal line. It is well known that condition $\chi_T \to \infty$ follows from general principles of stability of homogeneous phases [68–70]. In our case, this condition follows from the OZ equation directly and no other singularity can be found in the OZ equation. This means that the OZ equation also has no singularity on the phase equilibrium line.

The singularity which may exist at the point of the phase equilibrium should be attributed to solutions to the complete set of equations (14), (15). It is not clear however, how the equations (14), (15) can be applied to two-phase system description and how the solution to the set of equations (14), (15) can be derived in order to discover this singularity.

When analyzing metastability we noted that under some conditions, the metastable states remain stable. To disturb equilibrium, a fluctuation of the appropriate size should occur overcoming the barrier determined by the free energy relative minimum. The deeper the extension inside the metastable region is, that is closer to the spinodal, the lower the stability of the metastable states. In the latter case, even very small fluctuations have no time to disperse over the volume and the system has no way of recovering.

In the labile region beyond the spinodal, even the smallest fluctuations immediately cause decomposition of the system into two fractions. This stage is known as the spinodal *decomposition*. With this the isothermal compressibility χ_T changes sign to negative.

A system of particles interacting by the Yukawa potential has been studied in the so called mean spherical approximation (MSA) [27], where analytical solutions appropriate to stable, metastable and labile states have been found. For the former two cases the solutions were shown to be real, while in the latter case the solutions turned out to be complex. Along with this, numerical solutions have also been found for comparison, which coincide with those obtained analytically in the stable and metastable regions. In the labile region, numerical solutions have been found to be unstable with respect to the conditions of the iteration procedures. Of course, the physical instability corresponding to spinodal decomposition can in no way be attributed to the mathematical instability of solutions to the OZ equation; nevertheless, correlations between them do exist.

The OZ radial correlation functions found for the Lennard-Jones model in the labile region are given in Fig. 11. Of course, these solutions should be treated with care. Surprisingly, they qualitatively correspond to our concept of possible structures of the instantly decomposing system. For example, they reveal the existence of the longwave components in correlation functions possibly related to cooperative phenomena. When approaching the critical point from the labile region the correlation function transforms into the distribution function, specific for the critical point.

Table 3 presents the vapor – liquid spinodal values. Note that there is no need to involve a comparison procedure to find the spinodal line [16, 17, 71].

6. Amorphous states

6.1 Nonequilibrium transition to amorphous state

Let us consider once more the phase diagram (Fig. 1), where the lines Glass 1 and Glass 2 are given. These lines originate from the liquid region as one line of points of equilibrium and attain the point E at temperature T_m , where the equilibrium freezing phase transition may occur. From point E, the line incorporating now just metastable liquid states attains either

 $0.302(0.327); u/(NkT) = -1.726(-1.710); \beta \mu^* = -1.577(-1.516).$

Figure 11. Correlation functions for the labile vapor-liquid region. Curve

 $\rho = 0.31; P/(nkT) = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = -1.920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = 0.163 (0.181); u/(NkT) = 0.163 (0.181); u/(NkT) = 0.1920 (-1.958); \beta \mu^* = 0.163 (0.181); u/(NkT) = 0.1920 (0.181) (0.181); u/(NkT) = 0.1920 (0.181) (0$

-1.898(-1.836). Curve 3 — $T^* = 1.32$; $\rho = 0.31$; P/(nkT) =

 $T^* = 1.0; \quad \rho = 0.31; \quad P/(nkT) = -0.186 (-0.137); \quad u/(NkT) =$ $-2.666(-2.597); \quad \beta\mu^* = -2.694(-2.566). \quad \text{Curve} \quad 2 \quad - \quad T^* = 1.2;$

del
)

T^*	Vapor density $\rho_{\rm v}$	Liquid density $\rho_{\rm l}$	Reference
0.7	0.028	0.666	[16]
1.0	0.086	0.552	
1.2	0.161	0.446	
0.7	0.028	0.676	[17]
1.0	0.077	0.567	
1.2	0.141	0.470	
0.7	0.029	0.675	[13, 71]
1.0	0.086	0.550	
1.2	0.158	0.435	

point g_1 or g_2 . Then, the nonequilibrium transition to the amorphous (glassy) state may occur at points g_1 or g_2 at temperatures T_{g_1} and T_{g_2} . Glass transition from the supercooled or supercompressed metastable liquid to glass is not localized and depends upon the conditions of changing, meaning that there is no distinct transition point.

The glassy state is definitely unstable. Thermodynamically, the glass free energy takes no local minimum value. Glass, in contrast to a supercooled liquid, is continually relaxing. However, the relaxation time, unlike that for truly nonequilibrium cases, may be as long as thought to be infinite.

Amorphization can be considered as follows. As a supercooled liquid is cooled to a lower temperature, its viscosity swiftly increases and molecules comprising the system move more and more slowly. At some temperature, the molecules are moving so slowly that they have no chance to rearrange significantly before the temperature is lowered further. Thus, the random structure formed at that moment becomes 'frozen'. The momentary structure of this 'frozen' liquid is absolutely equivalent to some random momentary structure of the true liquid in usual conditions except that the amorphous structure is so squeezed that it prevents any diffusion motion.

Physics-Uspekhi 45 (6)







It is important to emphasize that the glass transition is not any kind of phase transition. It is to a great extent a kinetic event, which depends upon the experimental time scale and the time scale for molecular rearrangements. Furthermore, glasses are not crystals either; there is no long-range order, although some thermodynamic properties are similar to those of crystals. For instance, the thermal expansion coefficient

$$\alpha = \left[\frac{\mathrm{d}(\ln V)}{\mathrm{d}T}\right]_{P}$$

in the glass is significantly smaller than that in the liquids and supercooled liquids, and is close to α_{cr} .

Without discussing a great number of important properties of amorphous materials [69, 72], let us consider the appropriate distribution functions and the way they might be related to some solutions to the OZ equation.



Figure 13. Evolution of correlation functions with increasing density in a hard sphere fluid [73]; solid line — [73], dashed line — PY, dashed dotted line — HNC, dotted line — paper [78].

6.2 Structure of substance in amorphous state

The idea of formulating a problem on the possible existence of a link between nonequilibrium distribution functions of glass and equilibrium solutions to the OZ equation seems at the first glance to be physically unacceptable. Even attempts to describe the metastability with the OZ equation were considered, if not forbidden, at least, problematic, but could not be rejected due to the huge amount of theoretical and experimental results.

Paradoxically as it may seem, there are some arguments concerning glasses pertinent to this discussion. Some years ago, Malijevsky et al. [73] calculated the radial correlation function for a hard sphere fluid at crystalline densities using the OZ equation. A semiempirical closure $B^{(2)}$ was derived specifically in order to make the calculated values have high thermodynamic consistency close to the well known accurate results [74]. A split of the second peak into two subpeaks that occurs in the correlation function was taken as an indication of the transition to glassy state. Indeed, the splitting of the second peak has been generally accepted as a feature which is appropriate to the amorphous state [75, 76], as follows from real neutron and X-ray scattering experiments. Another example of the second peak splitting is that obtained with molecular dynamics for the Lennard-Jones model [77] (see Fig. 12).

Note that none of the known approximations of the theory of liquids predict a split in the second peak [78]. It was also noticed that the 'sign' of splitting in correlation functions already appears in the ordinary fluid at the reduced density $\rho = 0.94$ just before the freezing point ($\rho_{\rm cr} = 0.943$) as a small bend in the second maximum of g(r). With the density increasing, the bend develops and transforms into a split. Figure 13 presents the evolution of the second peak in the hard sphere model. Thus, a conclusion was made [73] that the OZ equation is capable of predicting the amorphous structure.

Further efforts by Gazzillo and Della-Valle [79] showed that the OZ equation also exhibits the second peak splitting in the Lennard-Jones liquid in the case where the MHNC approximation was applied (Fig. 14). Moreover, they concluded that the metastable liquid is also characterized by changes in the second peak, namely by broadening of the peak, which further transforms into a split.

Thus, the split in the second peak of the radial correlation function can serve as an indication of the onset of amorphous change.

The OZ results can be explained as follows. The fact that the relaxation time in a glassy material can be taken to be infinite means that correlation functions as a matter of fact, do not depend on time. On the other hand, with respect to structure, an amorphous state is just a frozen liquid structure. Does it not mean that under these conditions, the solution to the OZ equation for the dense system can at least qualitatively correspond to the glassy state? This hypothesis, however, may meet some objections. The molecular dynamics approach was used for investigating the structural features of the hard discs and hard spheres in the freezing-melting transition region [49]. After thorough crystallographic analysis, it was shown that splitting in the second peak exhibits a structural precursor pointing to the hexagonal close packed arrangement.

Note that a great number of studies give no clear outlines concerning this problem and contradict each other in many aspects.



Figure 14. Evolution of the correlation function with decreasing temperature for isochore $\rho = 0.95$ in the Lennard-Jones model [79]. Solid lines — modified hypernetted chain approximation (MHNC), points — molecular dynamics. The curves with $T^* > 0.233$ are vertically shifted.

7. Conclusion

In this review, all kinds of states within narrow limits of classical model systems described by simple central forces of interactions are treated from a unified structural standpoint. However, it turned out to be sufficient to reveal the one-toone correspondence between various states and the fine structural details of appropriate correlation functions. This makes it possible to discuss structural systematization of different states.

We have almost not touched the other aspects in the behavior of the system, for instance thermodynamics. The great variety of the real and model theoretical potentials of interaction between complex molecules exhibit a great variety of correlation functions, particularly in cases of multi-atom molecules described by atom-atomic correlation functions, or dipole molecules with correlation functions dependent on orientations.

Usually distribution functions are considered as a necessary basis for determining and analyzing macroparameters, while very important structural information is hidden. For example, the understanding of possible reasons of nonexistence of the freezing-melting critical point becomes possible only after fundamental structural differences between crystal and liquid have been revealed.

Another remarkable example is the Fisher–Widom line where correlation functions change their asymptotic decay, which in no way can be detected thermodynamically.

One more example is the behavior of correlation functions in the labile region, revealing possible mechanisms of the spinodal decomposition.

Particular attention should be given to those structural one-phase indications to phase transitions which, being of phenomenological nature, are nevertheless directly related to distribution functions. It is quite surprising that even very simple systems, that seemed to have been thoroughly studied, are so rich with respect to structure.

References

- Balescu R Equilibrium and Nonequilibrium Statistical Mechanics (New York: Wiley, 1975) [Translated into Russian (Moscow: Mir, 1978)]
- 2. Evans R, in *Fundamentals of Inhomogeneous Fluids* (Ed. D Henderson) (New York: M. Dekker, 1992) p. 85
- 3. Hansen J P, McDonald I R *Theory of Simple Liquids* 2nd ed. (London: Academic Press, 1986)
- Fisher I Z Statisticheskaya Teoriya Zhidkostei (Statistical Theory of Liquids) (Moscow: Fizmatgiz, 1961) [Translated into English (Chicago: Univ. of Chicago Press, 1964)]
- Martynov G A Fundamental Theory of Liquids: Method of Distribution Functions (Bristol: A. Hilger, 1992)
- 6. Morita T, Hiroike K Prog. Theor. Phys. 25 537 (1961)
- Stell G, in *The Equilibrium Theory of Classical Fluids* (Eds H L Frisch, J L Lebowitz) (New York: W.A. Benjamin, 1964) p. II-171
- 8. Ornstein L S, Zernike F Proc. Acad. Sci. Amsterdam 17 793 (1914)
- Münster A Statistical Thermodynamics (Berlin: Springer, 1969– 1974)
- Rascón C, Mederos L, Navascués G J. Chem. Phys. 105 10527 (1996)
- 11. Sarkisov G N Usp. Fiz. Nauk 169 625 (1999) [Phys. Usp. 42 545 (1999)]
- 12. Martynov G A, Sarkisov G N, Vompe A G J. Chem. Phys. 110 3961 (1999)]
- 13. Sarkisov G J. Chem. Phys. 114 9496 (2001)
- 14. Llano-Restrepo M, Chapman W G J. Chem. Phys. 97 2046 (1992)
- 15. Llano-Restrepo M, Chapman W G J. Chem. Phys. 100 5139 (1994)
- 16. Duh D-M, Haymet A D J J. Chem. Phys. 103 2625 (1995)
- 17. Duh D-M, Henderson D J. Chem. Phys. 104 6742 (1996)
- Weeks J D, Chandler D, Andersen H C J. Chem. Phys. 54 5237 (1971)
- 19. Martynov G A, Sarkisov G N Mol. Phys. 49 1495 (1983)
- 20. Gazzillo D J. Chem. Phys. 95 4565 (1991)
- 21. Gazzillo D Mol. Phys. 84 303 (1995)
- 22. Zamalin V M, Norman G É, Filinov V S *Metod Monte-Karlo v Statisticheskoĭ Termodinamike* (Monte Carlo Method in Statistical Thermodynamics) (Moscow: Nauka, 1977)
- Metod Molekulyarnoĭ Dinamiki v Fizicheskoĭ Chimii (Method of Molecular Dynamics in Physical Chemistry) (Ed. Yu K Tovbin) (Moscow: Nauka, 1996)
- 24. Leote de Carvalho R J F et al. J. Phys.: Condens. Mat. 6 9275 (1994)
- 25. Sarkisov G N Dokl. Ross. Akad. Nauk 359 326 (1998) [Dokl. Phys.
- **43** 157 (1998)]
- 26. Fisher M E, Widom B J. Chem. Phys. **50** 3756 (1969)
- 27. Cummings P T, Monson P A J. Chem. Phys. 82 4303 (1985)
- 28. Nicolas J J et al. Mol. Phys. **37** 1429 (1979)
- 29. Kittel C *Introduction to Solid State Physics* (New York: Wiley, 1976) [Translated into Russian (Moscow: Nauka, 1978)]
- 30. Weis J J Mol. Phys. 28 187 (1974)
- 31. Kincaid J M, Weis J J Mol. Phys. 34 931 (1977)
- 32. Caccamo C, Giaquinta P V, Giunta G J. Phys.: Condens. Mat. 5 B75 (1993)
- 33. Kirkwood J G J. Chem. Phys. 3 300 (1935)
- 34. Baus M J. Stat. Phys. 48 1129 (1987)
- 35. Mermin N D Phys. Rev. 137 A1441 (1965)
- 36. Zeng X C, Oxtoby D W J. Chem. Phys. 94 4472 (1991)
- 37. Carnahan N F, Starling K E J. Chem. Phys. 51 635 (1969)
- 38. Adams D J Mol. Phys. **32** 647 (1976)
- 39. Panagiotopulos A Z Mol. Phys. **61** 813 (1987)
- 40. Lotfi A, Vrabec J, Fischer J *Mol. Phys.* **76** 1319 (1992)
- 41. Panagiotopulos A Z Int. J. Thermophys. 15 1057 (1994)
- 42. Kjellander R, Sarman S J. Chem. Phys. **90** 2768 (1989)
- 43. Lee L L J. Chem. Phys. 97 8606 (1992)
- 44. Kiselyov O E, Martynov G A J. Chem. Phys. 93 1942 (1990)
- 45. Johnson J K, Zollweg J A, Gubbins K E Mol. Phys. 78 591 (1993)

- 46. Bernal J D Proc. R. Soc. London Ser. A 280 299 (1964)
- 47. Spaepen F *Nature* **408** 781 (2000)
- 48. Turnbull D J. Chem. Phys. 20 411 (1952)
- 49. Truskett T M et al. *Phys. Rev. E* **58** 3083 (1998)
- 50. Hansen J-P, Verlet L Phys. Rev. 184 151 (1969)
- 51. Giaquinta P V, Giunta G, Giarritta S P Phys. Rev. A 45 R6966 (1992)
- 52. Lovett R, Mou C Y, Buff F P J. Chem. Phys. 65 570 (1976)
- Tikhonov D A et al. Kolloid. Zh. 53 911 (1991) [Colloid J. 53 761 (1991)]
- 54. Tikhonov D A et al. J. Mol. Liq. 82 3 (1999)
- 55. Henderson D, Abraham F F, Barker J A Mol. Phys. 31 1291 (1976)
- 56. Quintana J, Henderson D, Plischke M J. Phys. Chem. 93 4304 (1989)
- 57. Snook I K, Henderson D J. Chem. Phys. 68 2134 (1978)
- 58. Mishima O, Stanley H E *Nature* **396** 329 (1998)
- Martynov G A Usp. Fiz. Nauk 169 595 (1999) [Phys. Usp. 42 517 (1999)]
- 60. Van Hove L Physica 15 951 (1949)
- Uhlenbeck G T, Ford G W, in Proc. of the 2nd Summer Seminar on Applied Mathematics, Boulder, Colorado, 1960 (Lectures in Applied Mathematics, Vol. 1, Ed. M Kac) (Providence: Am. Math. Soc., 1963)
- Klimontovich Yu L Statisticheskaya Fizika (Statistical Physics) (Moscow: Nauka, 1982) [Translated into English (Chur: Harwood Acad. Publ., 1986)]
- Martynov G A Classical Statistical Mechanics (Dordrecht: Kluwer Acad. Publ., 1997)
- 64. Martynov G A, Sarkisov G N Phys. Rev. B 42 2504 (1990)
- 65. Martynov G A, Sarkisov G N *Kristallogr*. **34** 541 (1989) [*Sov. Phys. Crystallogr*. **34** 322 (1989)]
- Hill T L Statistical Mechanics: Principles and Selected Applications (New York: McGraw-Hill, 1956)
- 67. Wales D J, Doye J P K J. Chem. Phys. 103 3061 (1995)
- Semenchenko V K Izbrannye Glavy Teoreticheskoĭ Fiziki (Selected Parts of Theoretical Physics) (Moscow: Uchpedgiz, 1960)
- 69. Debenedetti P G Metastable Liquids: Concepts and Principles (Princeton, N.J.: Princeton Univ. Press, 1996)
- Skripov V P Metastabil'naya Zhidkost' (Metastable Liquids) (Moscow: Nauka, 1972) [Translated into English (New York: J. Wiley, 1973)]
- Sarkisov G N Zh. Fiz. Khim. 75 1185 (2001) [Russ. J. Phys. Chem. 75 1068 (2001)]
- 72. Ediger M D, Angell C A, Nagel S R J. Phys. Chem. 100 13200 (1996)
- 73. Malijevský A, Labík S, Smith W R Mol. Phys. 72 193 (1991)
- 74. Malijevský A, Labík S Mol. Phys. 60 663 (1987)
- 75. Cheng Y-T, Johnson W L Science 235 997 (1987)
- 76. Cargill G S Solid State Phys. 30 227 (1975)
- 77. Rahman A, Mandell M J, McTague J P J. Chem. Phys. 64 1564 (1976)
- 78. Rogers F J, Young D A Phys. Rev. A **30** 999 (1984)
- 79. Gazzillo D, Della Valle R G J. Chem. Phys. 99 6915 (1993)