Approximate equations of the theory of liquids in the statistical thermodynamics of classical liquid systems

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<u>Abstract.</u> This review presents the fundamentals of the method of integral equations of the theory of liquids. One of the central problems of the theory, the definition of bridge-functionals, is analyzed. Some applications of the method of integral equations to simple liquid systems are discussed, and the problem of description of complex polyatomic classical systems is considered.

1. Introduction

After the publication of the excellent review of Barker and Henderson in 1976 [1], the impression could appear that the problems of the theory of at least simple liquids were solved. Indeed, by this time several approximate integral equations had been obtained for the binary distribution function, which have been used for qualitative and quantitative studies of many properties of simple liquids. The Percus–Yevick (PY) equation [2–4], which in many cases produces a good agreement with numerical experiment, was considered the most accurate. For this reason, it seemed that the method of integral equations developed at that time provided, in conjunction with the perturbation theory [1] and numerical experiments [1, 5-8], adequate studies of the macroscopic parameters and structural features of classical liquids.

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Received 16 June 1998; revised 3 February 1999 Uspekhi Fizicheskikh Nauk **169** (6) 627–642 (1999) Translated by M N Sapozhnikov; edited by S D Danilov The further systematic use of known approximate integral equations — PY, hypernetted-chain (HNC) [1, 9, 10], the middle-spherical approximation (MSA) [1, 11], and some other less known approximations showed, however, that their accuracy and predictability are inadequate for quantitative, and in some cases even qualitative description of liquids.

Of more importance is another circumstance: none of these equations were conclusively theoretically substantiated, although they are based on the exact but unrealizable systems of equations of Bogolyubov-Born-Green-Kirkwood-Ivone (BBGKI) [6]. For this reason, even after the publication of review [1] the search for more substantiated and exact approximations and procedures for finding the distribution function was continued [12-22]. Note that this theoretical problem is not completely solved even now and it represents one of the central problems of the theory of liquids. Nevertheless, recent achievements in this field form a good basis for real physicochemical studies of at least simple liquids.

In addition, after publication of review [1], all the most important and interesting parameters of simple systems seemed to have been described and understood. This impression was enhanced by a great number of calculations performed by the methods of molecular dynamics and Monte Carlo. However, the accumulation of the results of numerical experiments, which persists to the present, and attempts to construct various theoretical models of the behavior of classical liquids in specific situations, for example, upon phase transitions, critical phenomena, etc. show that we still are far from understanding many features in the behavior of simple liquids. Even such a simple and well-studied model liquid as a hard sphere system, remains enigmatic in many respects. For example, the process of crystallization of this system is not clear. Inert gases are known to crystallize in a cubic close-packed structure, whereas, according to calculations of the Lennard–Jones (LJ) liquid, they should crystallize in a hexagonal structure. It is assumed that this can be explained by the neglect of many-body interactions. But how can the crystallization of a hard sphere system be described, if it can occur, and what is the type of structure formed? How can this problem naturally be taken into account in the theory?

The possibility of the existence of metastable states in a hard sphere system remains unclear. Such problems as the behavior of liquid systems near a surface and within restricted volumes, the structure of long-range correlations, the structure of liquids in the transition region, etc., are open for studies.

Absolutely new problems appear in the description of properties of systems with nonspherical interaction potentials between molecules, such as, for example, systems with dipole– dipole interactions or systems of polyatomic molecules, including solutions. Here, in addition to conventional problems, new problems appear related to the description of interactions and the construction and solution of the corresponding systems of equations.

2. Approximate equations of the theory of liquids

2.1 Exact equations of the statistical mechanics of liquids

In the statistical mechanics of liquids, the system of linked integro-differential BBGKI equations [6] for a *l*-body distribution functions

$$\Theta \nabla_1 g(\mathbf{r}_1, ..., \mathbf{r}_l) + g(\mathbf{r}_1, ..., \mathbf{r}_l) \nabla_1 U(\mathbf{r}_1, ..., \mathbf{r}_l) + n \int \nabla_1 \Phi_{1,l+1} g(\mathbf{r}_1, ..., \mathbf{r}_l, \mathbf{r}_{l+1}) d\mathbf{r}_{l+1} = 0$$
(1)

is exact. Here, $g(\mathbf{r}_1, ..., \mathbf{r}_l) = g_{(l)} = g_{1,...,l}$ is the *l*-body distribution function $(l = 1, 2, 3...\infty)$; n = N/V is the density of particles in the system; $\Theta = kT$ is the temperature;

$$U(\mathbf{r}_{1},...,\mathbf{r}_{l}) = U_{(l)} = \sum_{1 \le i \le l} \Phi_{i} + \sum_{1 \le i,j \le l} \Phi_{ij}$$
(2)

is the potential energy of the group of l particles; $\Phi_i(\mathbf{r}_i)$ is the energy of a particle located at the point \mathbf{r}_i in an external field; and $\Phi_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ is the pair interaction energy of particles i and j. In the additive approximation (2), thermodynamic parameters of the system are completely determined under any conditions only by the unary $g_{(1)}$ and binary $g_{(2)}$ distribution functions. Their determination represents one of the central problems of the statistical mechanics of liquids. One can easily see that system (1) cannot be solved directly. One of the first suggested approximations is based on the superposition hypothesis of Kirkwood

$$g_{123} = g_{12}g_{23}g_{13} \tag{3}$$

resulting in the integral Bogolyubov–Born–Green equation for the binary distribution function. However, this equation proved to be inadequate for the description of liquid systems at middle and high densities [1, 6].

As was shown by Martynov [23, 24], a chain of the BBGKI equations under conditions (2) can be transformed to an exact system of two integral equations for the unary and binary distribution functions

$$\omega_1 = \omega(\mathbf{r}_1) = n \int g_2(\mathbf{r}_2) C_{12}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 + \ln a , \qquad (4)$$

$$h_{12}(\mathbf{r}_1, \mathbf{r}_2) = C_{12}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + n \int g_3(\mathbf{r}_3) C_{13}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) h_{23}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3,$$
(5)

where $g_i = \exp(-\Phi_i/\Theta + \omega_i), \omega_i$ is the unary thermal potential, $g_{ij} = g_i g_j (1 + h_{ij})$ is the binary distribution function, $h_{ij} = \exp(-\Phi_{ij}/\Theta + \omega_{ij}) - 1$ is the total correlation function, ω_{ij} is the binary thermal potential, and *a* is the activity. The direct correlation functions

$$C_{12}^{(1)} = (h_{12} - \omega_{12}) - \frac{1}{2}h_{12} \Big[\omega_{12} + B_{12}^{(1)}\Big], \qquad (6)$$

$$C_{12}^{(2)} = h_{12} - \omega_{12} + B_{12}^{(2)}$$
(7)

contain the bridge-functionals

$$B_{12}^{(1)} = \frac{1}{3}B_{12}^{(2)} + \frac{1}{6} \sqrt[6]{-1} - \frac{1}{12} \sqrt[6]{-1} \dots,$$
(8)

$$B_{12}^{(2)} = \frac{1}{2} \checkmark + \checkmark + \checkmark + \checkmark + + \frac{1}{2} \checkmark + \cdots,$$
(9)

which represent an infinite series of irreducible diagrams, in which each line denotes the multiplication of the integrand by $h(r_{ii})$, and each dark point indicates multiplication by ng_i and simultaneous integration over $d\mathbf{r}_i$. The open points determine the dependence of the diagrams on the moving coordinates \mathbf{r}_1 and \mathbf{r}_2 . Note that formally no other equations are required for the determination of the major distribution functions, because these function are completely expressed in terms of the unary and binary distribution functions and thermal potentials [24]. Although a new form of the exact equations for the distribution function contains an infinite series of diagrams, it is more convenient for the construction of various approximations. Note also that the possibility of obtaining the fundamental exact system of Eqns (4) and (5) was first pointed out by Morita and Hiroike as early as 1960 [25]. The same system was obtained in a less compact form by Arinshtein and Abrosimov [26].

2.2 General problem of the choice of bridge-functionals and thermodynamic consistency of approximate approaches

In the case of spatially homogeneous systems, $\omega_i = 0$, and $g_i = 1$, and all the functions entering Eqns (4) and (5) become dependent on the argument $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Equation (5) takes the form of the usual Ornstein–Zernike (OZ) equation

$$\gamma(r_{12}) = h(r_{12}) - C(r_{12}) = n \int C^{(2)}(r_{13})h(r_{23}) \mathrm{d}r_3 \,. \tag{10}$$

The required radial correlation function $g(r_{12})$ has the form

$$g(r) = h(r) + 1 = \exp\left[-\frac{\Phi(r)}{\Theta} + \omega(r)\right]$$
$$= \exp\left[-\frac{\Phi(r)}{\Theta} + \gamma(r) + B^{(2)}(r)\right]. \quad (11)$$

In this case, Eqn (4) reduces to the definition of $\ln a$ that is the excess chemical potential

$$\ln a = \beta \mu^* = -4\pi n \int C^{(1)}(r) r^2 \mathrm{d}r \,, \tag{12}$$

where $\beta = 1/kT$. Equation (10) is not closed, because it contains two unknown functions h(r) and $C^{(2)}(r)$. Taking into account Eqns (7) and (11), one can see that Eqn (10) becomes closed if the bridge-functional $B^{(2)}[h(r)]$ is defined. Because it is impossible to sum up an infinite series, the search for an adequate and physically substantiated approximation of the bridge-functional $B^{(2)}$ still remains one of the important problems in the construction of approximate theories of liquid.

After the determination of the distribution function, the thermodynamic parameters of the system can be calculated using the known expressions [1, 24]. The total internal energy is described by the expression

$$E = \frac{3}{2}NkT + \frac{nN}{2}\int_{0}^{\infty} \Phi(r)g(r;n,\Theta)4\pi r^{2}\mathrm{d}r, \qquad (13)$$

the compressibility factor (the equation of state), in accordance with the virial theorem, has the form

$$Z^{\text{vir}} = \frac{P}{nkT} = 1 - \frac{n}{6kT} \int_0^\infty r \frac{d\Phi(r)}{dr} g(r) 4\pi r^2 dr , \qquad (14)$$

and the reduced isothermal compressibility is

$$\chi = kT \left(\frac{\partial n}{\partial P}\right)_T = \frac{\kappa}{\kappa^{\rm id}} = 1 + 4\pi n \int_0^\infty h(r) r^2 dr$$
$$= \left[1 - 4\pi n \int_0^\infty C(r) r^2 dr\right]^{-1}, \tag{15}$$

where $\kappa = n^{-1} (\partial n / \partial P)_T$ is the isothermal compressibility and $\kappa^{id} = 1/nkT$ is the isothermal compressibility for an ideal liquid.

From Eqn (15), the compressibility factor can also be obtained:

$$Z^{\text{comp}} = \frac{1}{n} \int_0^n \chi \,\mathrm{d}n \,. \tag{16}$$

The compressibility factor can be determined in another way. Because [27]

$$E = -T^2 \left(\frac{\partial}{\partial T} \frac{F}{T}\right)_V,\tag{17}$$

where F is the Helmholtz free energy, we have

$$\frac{F - F_0}{T} = -\int_{1/T_0}^{1/T} E \,\mathrm{d}\left(\frac{1}{T}\right). \tag{18}$$

Here, F_0 is the free energy of the state chosen as the origin. Now, by integrating numerically Eqn (18) and differentiating with respect to the density, we can obtain the compressibility factor Z^E and other thermodynamic quantities. Such a procedure was used, for example, in papers [28, 29] for the determination of virial coefficients and the equation of state using the PY equation. In turn, F_0 can be found by integrating along isotherms of the compressibility factor:

$$\frac{F_0}{NkT} = \int_0^n Z \frac{\partial n}{n} \,. \tag{19}$$

Thus, the total set of thermodynamic parameters can be obtained using any of the three expressions (13)-(15) directly relating the distribution functions with thermodynamics. In the case of exact values of the distribution function, all the three methods are equivalent, i.e., the numerical values of the thermodynamic parameters should be the same to the accuracy of the rounding error. When the correlation functions are obtained from approximate equations, the situation is fundamentally different. The use of approximate functions g(r) in expressions (13)-(15) results in a mismatch between the thermodynamic parameters. Thus, now we have

$$Z^{\text{vir}} \neq Z^{\text{comp}} \neq Z^E \,. \tag{20}$$

The degree of closeness of the thermodynamic parameters (the thermodynamic consistency) is, as a rule, a criterion for the theory's quality. Another criterion for the theory's quality is the degree of agreement with the results of numerical experiments. Note, however, that the fulfillment of separate simple pair conditions

$$Z^{\text{vir}} = Z^{\text{comp}}; \ Z^{\text{vir}} = Z^{E}; \ Z^{\text{comp}} = Z^{E}$$
(21)

still does not mean that the approximate theory has an adequate accuracy leading to agreement with the results of computer simulations $Z^{c.s.}$. The question of the required number of independent relations yielding the criterion for thermodynamic consistency was discussed in papers [30, 31]. It was shown that only two relations can be independent. The definition of the isothermal compressibility establishes the thermodynamic consistency between the virial pressure and compressibility

$$\frac{1}{\kappa^{\text{comp}}}(n,T) = \left(\frac{\partial P^{\text{vir}}}{\partial n}\right)_T.$$
(22)

The second criterion is the Maxwell relation between the internal energy and pressure

$$\left(\frac{\partial E}{\partial V}\right)_T = T^2 \frac{\partial}{\partial T} \left(\frac{P}{T}\right)_V.$$
(23)

The final criterion is [30, 31]

$$I(n,\Theta) = \int_0^\infty \left\{ C(r) - \frac{r}{6\Theta} \frac{\partial \Phi(r)}{\partial r} \left[2g(r) + n \frac{\partial g(r)}{\partial n} \right] \right\} r^2 \mathrm{d}r = 0,$$
(24)

$$J(n,\Theta) = \int_0^\infty \left\{ \Phi(r) \left[g(r) + n \frac{\partial g(r)}{\partial n} \right] + \frac{r}{3} \frac{\partial \Phi(r)}{\partial r} \left[g(r) - \Theta \frac{\partial g(r)}{\partial \Theta} \right] \right\} r^2 dr = 0.$$
(25)

The derivatives $g_n = \partial g/\partial n$ and $g_\Theta = \partial g/\partial \Theta$ of the correlation functions can be found from the corresponding equations obtained by differentiating the OZ equation. The properties of these derivatives also will be determined by the

conditions of the closure of the OZ equation. Note that two fundamental criteria for the thermodynamic consistency can be also constructed using two other thermodynamic identities including E, P, κ . The functions g_n and g_T can be used for the calculation of thermodynamic parameters of a substance, which are not directly related to the radial correlation function g(r). For example, we have for the heat capacity

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_n = \frac{3}{2}kN + 2\pi nN \int_0^\infty \Phi(r)g_T(r)r^2 dr$$
(26)

or, since

$$\left(\frac{\partial g}{\partial T}\right)_{n} = \frac{g}{T} \left[\frac{\Phi}{T} + \Theta \frac{\partial \omega}{\partial \Theta}\right]$$
(27)

then [32]

$$\frac{C_V}{kN} - \frac{3}{2} = 2\pi n \int_0^\infty \frac{\Phi(r)}{\Theta} g(r) \left[\frac{\Phi(r)}{\Theta} + \Theta \frac{\partial \omega}{\partial \Theta} \right] r^2 \mathrm{d}r \,. \tag{28}$$

Such a method for determining the heat capacity is much more efficient and accurate than the numerical derivative $\partial E/\partial T$.

2.3 Local approximations of the method of integral equations

According to Eqns (8) and (9), the values of bridgefunctionals at point r_2 separated from point r_1 by the distance r_{12} are not only determined by the density at point r_2 but depend on the density distribution in its vicinity. For example, the first diagram in Eqn (9) can be written in the form

$$B_1^{(2)}(r_{12}) = n^2 \int_V h_{13} h_{14} h_{23} h_{24} h_{34} dr_3 dr_4 \,. \tag{29}$$

It is obvious that the integration over the coordinates of the third and fourth particles is equivalent to accounting for a change in the density in the vicinity of points 1 and 2, i.e., it is equivalent to accounting for nonlocal effects. The passage to approximate equations is based on the replacement of the nonlocal bridge-functional B(r) = B[h(r)] by the local bridgefunction B(r) = B(h(r)) [13] or local bridge-functions $B(\gamma(r))$ and $B(\omega(r))$. A rigorous theoretical substantiation of the possibility of the equivalent replacement of the bridgefunctional by bridge-functions is absent. Nevertheless, at present there is no other way to exploit the fundamental system of equations. In the HNC equation, which is most often used compared to other approximations, the bridgefunctional is altogether zero: B(r) = 0 [9, 10]. In this case,

$$g = \exp\left(-\frac{\Phi}{\Theta} + \gamma\right), \quad \gamma = \omega.$$
 (30)

The correlation function g can be expanded into an infinite series of diagrams [33], in which a series representing the bridge-functional B[h(r)] is a part of the total series. Diagrams corresponding to the bridge-functional are strongly coupled and, therefore, short-ranged [34]. For this reason, neglecting the bridge-functional results in the domination of the long-range terms in g. This explains a good results obtained for the long-range interaction potentials in the HNC approximation.

Another local equation, the PY equation

$$B = -[\exp(\omega) - 1 - \omega] = \ln(1 + \gamma) - \gamma, \quad \gamma = \exp(\omega) - 1,$$

$$(\Phi)$$
 (31)

$$g = \exp\left(-\frac{\star}{kT}\right)(\gamma + 1) \tag{32}$$

is also widely used. This equation describes the properties of systems with the short-range interaction potential in good agreement with numerical experiments. On the whole, however, the thermodynamic consistency of both the HNC and PY equations proves to be poor. Note that the PY equation can be obtained by a partial summation of the diagrams of a certain class in the expansion of the function g(r), however, it is impossible to estimate the value of the diagrams neglected [35].

It is known from the diagrammatic expansion of the direct correlation function C(r) that $C(r \to \infty) \to -\Phi/\Theta$ at large distances. This fact was used as an approximation at short distances as well. As a result, the MSA was formulated as [1, 11]

$$C(r) = -\frac{\Phi}{\Theta}, \quad r \ge \sigma; \quad h(r) = -1, \quad r \le \sigma,$$
(33)

where σ is the hard core diameter. This means that

$$B(r) = -h(r) + \omega(r) - \frac{\Phi(r)}{\Theta}.$$
(34)

The MSA equation is used in calculations of the properties of systems of particles with hard core. To expand the region of application to the case of particles with soft core, the potential is decomposed into the purely repulsive and purely attractive parts

$$\Phi(r) = \Phi_1(r) + \Phi_2(r) \,. \tag{35}$$

In one such decomposition suggested in Ref. [36], the attractive part Φ_2 is treated as a correction in the construction of the corresponding approximations of the perturbation theory

$$\Phi_{1}(r) = \begin{cases} \Phi(r) - \Phi(r_{\min}), & r \le r_{\min}, \\ 0, & r \ge r_{\min}, \end{cases}$$
(36)

$$\Phi_2(r) = \begin{cases} \Phi(r_{\min}), & r \le r_{\min}, \\ \Phi(r), & r \ge r_{\min}, \end{cases}$$
(37)

where r_{\min} is the coordinate of the potential minimum. By introducing the new function $\Gamma(r) = \gamma(r) - \beta \Phi_2(r)$, the MSA for soft spheres (SMSA) can be represented in the form [37]

$$B(r) = \ln[1 + \Gamma(r)] - \Gamma(r).$$
(38)

Such a representation resembles the PY approximation, with

$$g(r) = \exp(-\beta \Phi_1)(1+\Gamma).$$
(39)

For $r \ge r_{\min}$, we obtain the usual MSA equation (33).

By analyzing the first diagram in expansion (9), we can assume that the major contribution related to the distance r_{34} is provided by the values $h(r_{34}) = -1$. Based on this assumption, we obtain

At the same time, the expansion of the function $\omega(r)$ starts from the term [23]

$$\omega_{12} = n \int h_{13} h_{23} \mathrm{d}(3) + \dots \tag{41}$$

These considerations and also studies of the properties of bridge-functionals in the vicinity of the critical point allowed the MS closure to be formulated in the form [14, 15]

$$B(r) = -\frac{1}{2}\omega^2 = (1+2\gamma)^{1/2} - \gamma - 1, \qquad (42)$$

$$g(r) = \exp\left[-\frac{\Phi}{\Theta} + (1+2\gamma)^{1/2} - 1\right].$$
 (43)

As will be shown below, this closure not only provides high thermodynamic consistency in many cases but also possesses an internal criterion describing the boundaries of the existence of the liquid phase.

By introducing the new variable

$$\Omega(r) = \omega(r) - n\beta \Phi_2(r) \tag{44}$$

in Refs [38, 39], similarly to Eqn (38), a closure in the form

$$B = -\frac{1}{2}\Omega^{2} = \left[1 + 2(\gamma - n\beta\Phi_{2})\right]^{1/2} + n\beta\Phi_{2} - \gamma - 1, \quad (45)$$

$$g = \exp\left[-\frac{\Phi}{\Theta} + \left[1 + 2(\gamma - n\beta\Phi_2)\right]^{1/2} + n\beta\Phi_2 - 1\right] (46)$$

was suggested.

The necessity of the introduction of the potential term to the bridge-function in order to define the latter more adequately is governed by two circumstances. The representation of the bridge-function in the form B = B(h(r)) leads to uncertainty in the region where h(r) = -1, i.e., inside the particle core, and requires additional conditions. At the same time, according to Eqn (11), the quantities Φ/Θ and ω (or γ) enter into g(r) formally on equal grounds (in fact ω is the solution of the OZ equation for given Φ , n, and T, and thus implicitly depends on Φ). The numerical experiments [40, 41] on the determination of bridge-functionals also showed that it is impossible to construct bridge-functions adequate to the bridge-functionals using only functions ω or γ . This idea was realized using a phenomenological bridge-function in the form [42, 43]

$$B(\Gamma) = -\Gamma^2 \frac{1}{2} \left[1 + \left(\frac{5\Gamma + 11}{7\Gamma + 9} \right) \Gamma \right]^{-1}$$
(47)

by decomposing the potential into the repulsive and attractive parts in a different way. Despite a seemingly complex and not quite clear form of approximation, it rather accurately describes the LJ system, including the evaporation–condensation lines.

2.4 Self-consistent approximations

The local approximations described above are not versatile. Their thermodynamic consistency varies depending on the thermodynamic state of the system under study. For this reason, in a number of closures parameters were introduced into the bridge-function whose variations could provide the best thermodynamic consistency. These approximations represent in fact fittings and their theoretical value is low. However, they can yield reliable numerical results required for physicochemical calculations. The idea of self-consistency is well illustrated by the example of the Rogers-Young (RY) closure [44]

$$B(r) = \ln\left\{1 + \frac{\exp[f(r)\gamma(r)] - 1}{f(r)}\right\} - \gamma(r).$$
(48)

Here, $f(r) = 1 - \exp(-ar)$ is the function including the selfconsistent parameter *a*. For r = 0, we have f(r = 0) = 0 and, as one can see from Eqn (48), the PY closure is realized. For large distances, $f(r = \infty) = 1$, and closure (48) simulates the HNC closure. Thus, closure (48) realizes the advantages of the PY closure at small distances and of the HNC closure at large distances. In this case, the parameter *a* is chosen based on the thermodynamic consistency between the virial equation (14) and the compressibility equation (16). Closure (48) proved to be rather successful for the description of systems with a purely repulsive soft potential of the type $1/r^m$. In other cases, it is less adequate.

Another interpolation closure (Zerah–Hansen) relates the HNC approximation at large distances r to the SMSA equation at small distances [45]. In this case, the interpolation concept is used in combination with the decomposition of the potential according to Eqn (35)

$$g(r) = \exp\left[-\frac{\Phi_1(r)}{\Theta}\right] \left\{ 1 + \frac{\exp\left[f(r)\Gamma(r)\right] - 1}{f(r)} \right\},\tag{49}$$

where the function f(r) has the same meaning as in the closure (48).

One more popular closure (Verlet) has the form [46]

$$B = \frac{1}{2} \frac{\gamma^2}{1 + a\gamma} , \qquad (50)$$

where a is also an empirical parameter. Note that expression (50) forms the basis of approximation (47).

Another approach in the self-consistent procedures is based on the concept of the versatility and similarity of the bridge-functionals for all the potentials. Then, the bridgefunction determined for some of the potentials can be also used, in a renormalized (consistent) form, for the description of systems with other interaction potentials. As a reference system, a hard sphere system is chosen, for which reliable estimates of the bridge-functions exist obtained both in numerical experiments and from integral equations. This approach is formulated in the form of the modified hypernetted-chain equation (MHNC) [12]

$$B(r) = B_{\rm h.s}(r), \qquad (51)$$

$$g(r) = \exp\left(-\frac{\Phi}{\Theta} + \gamma + B_{\rm h.s}\right),$$
 (52)

where $B_{\rm h,s}$ is the bridge-function of a hard sphere system. An analytic expression for $B_{\rm h,s}$ was presented in a paper by Malijevsky and Labik [47] for all densities up to the density of close-packed hard spheres. In the earlier MHNC versions [12], the effective parameter σ was determined either from criteria of the thermodynamic consistency or using the procedure based on the principle of the minimum Helmholtz free energy [48]. In later papers [41, 49], σ was determined by the method based on the equality of the second derivative of the free energy for the system under study and the reference system. Closure (42) was modified [22] to the form

$$B(r) = [1 + a\gamma(r)]^{1/a} - \gamma(r) - 1.$$
(53)

For a = 1, this closure reduces to the HNC case; for a = 2, Eqn (42) is obtained.

Recently, a new self-consistent procedure [30] was suggested, in which

$$B = -a(\omega - \beta \Phi_2)^2,$$

$$g = \exp\left\{-\beta \Phi_1 - \frac{1 - [1 + 2(\gamma - \beta \Phi_2)]^{1/2}}{2a}\right\},$$
 (54)

where *a* was determined from the general principle (24), (25), taking into account the consistency of the correlation functions g(r) with their derivatives $g_n(r)$ and $g_T(r)$.

We considered above not all the available approximations and approaches used in the theory of liquids. Nevertheless, we can conclude that at present the theoretical basis of the approximate equations of the theory of liquids is developed insufficiently. Many of them are semi-phenomenological and often are even heuristic. At the same time, all the set of approaches and approximations provides a rather exact description of at least simple liquid systems and yields adequate structural and thermodynamic properties. On passing to more complex systems, many of these approaches are difficult to use. First of all this concerns the self-consistent procedures, which require the variation of a great number of fitting parameters. Restrictions also appear in the use of local approximations.

3. Thermodynamic and structural parameters of simple liquids

3.1 A hard sphere fluid

A hard sphere fluid has been studied very carefully. It represents a good object for comparison of different theories. The potential of hard spheres can be written in the form

$$\Phi(r) = \begin{cases} \infty, & r \le \sigma, \\ 0, & r \ge \sigma. \end{cases}$$
(55)

According to Carnahan and Starling (CS) [50], the relations

$$Z^{\rm CS} = \frac{R}{nkT} = \frac{1 + \eta + \eta^2 - \eta^3}{\left(1 - \eta\right)^3} \,, \tag{56}$$

$$\beta\mu^* = \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} , \qquad (57)$$

$$\frac{1}{\chi} - 1 = \beta \frac{\partial P}{\partial n} - 1 = \frac{8\eta - 2\eta^2}{(1 - \eta)^4} ,$$
 (58)

hold, which are considered the most exact. Here, $\eta = \pi n \sigma^3/6 = \pi \rho/6$ is the packing coefficient and $\rho = n \sigma^3$ is the reduced density. The virial equation of state takes the form

$$Z^{\text{vir}} = 1 - \frac{n}{6} \int_0^\infty r \frac{d\Phi(r)}{dr} g(r) 4\pi r^2 dr = 1 + \frac{2}{3}\pi n g(\sigma) \,.$$
(59)

Therefore, the equation of state is determined by the value of the correlation function at a single point $r = \sigma$. In this case, the danger appears that in the approximate theory the situation is realized when the values of the correlation function prove to be close to the real values only in the vicinity $r = \sigma$, being distorted in other regions of r. This may result in an erroneous estimate of the accuracy of the theory. At the same time, Z^{comp} is substantially determined by average and long distances. For this reason, the criterion for thermodynamic consistency means in fact the matching of different parts of the correlation functions.

Figure 1 shows the typical bridge-function for a system of rigid spheres calculated in the MS approximation (42), and Fig. 2 presents the typical correlation function. One can see minor differences from the results of numerical experiments. The MS equation is considered the thermodynamically most consistent equation for a hard sphere fluid in the class of local approximations, which is evident from the data presented in Tables 1 and 2.



Figure 1. Bridge-function B(R) for a hard sphere fluid ($\rho = 0.8$): (—) numerical experiment; (- -) $B = (-1/2)\omega^2 (\omega(R))$ is taken from Ref. [51]; here and in other figures, $R = r/\sigma$).



Figure 2. Radial correlation functions g(R) for a hard sphere fluid $(\rho = 0.884)$: — Eqn (42); (x) molecular dynamics data [52].

3.2 The well potential

The well potential is more realistic than that of hard spheres. It contains a short-range attractive part along with the repulsive part:

$$\Phi(r) = \begin{cases} \infty, & r \le \sigma, \\ -\varepsilon, & \sigma \le r \le \lambda \sigma, \\ 0, & r \ge \lambda \sigma. \end{cases}$$
(60)

_	~	1
_	~	
0	J	1

ρ	Closure	$Z^{ m vir}$	Z^{comp}	Z^{CS}
0.1	HNC PY MS	1.241 1.239 1.240	1.239 1.240 1.240	} 1.240
0.2	HNC PY MS	1.565 1.550 1.550	1.545 1.555 1.553	} 1.553
0.3	HNC PY MS	2.010 1.954 1.954	1.934 1.973 1.964	} 1.967
0.4	HNC PY MS	2.63 2.48 2.51	2.43 2.54 2.52	} 2.518
0.5	HNC PY MS	3.52 3.17 3.24	3.07 3.31 3.28	} 3.262
0.6	HNC PY MS	4.79 4.09 4.24	389 4.38 4.31	} 4.283
0.7	HNC PY MS	6.67 5.32 5.61	4.96 5.90 5.70	} 5.710
0.8	HNC PY MS	9.52 7.00 7.60	6.39 8.12 7.74	} 7.750
0.9	HNC PY MS	13.92 9.33 10.42	8.33 11.50 10.61	} 10.746

Table 1. Compressibility factor for a hard sphere fluid.

Table 2. Reciprocal compressibility $\frac{1}{kT} \left(\frac{\partial P}{\partial n} \right)_T$ for a hard sphere fluid.

ρ	CS [50]	MS (42)	HNC	PY	
0.1	1.513	1.513	1.509	1.513	
0.2	2.270	2.266	2.223	2.28	
0.3	3.392	3.381	3.250	3.42	
0.4	5.065	5.11	4.67	5.15	
0.5	7.591	7.73	6.66	7.82	
0.6	11.467	11.50	9.47	12.00	
0.7	17.539	17.53	13.58	18.70	
0.8	27.307	26.89	19.61	29.60	
0.9	43.546	41.65	28.67	48.30	

Here, σ is the diameter of the hard core, λ is a coefficient determining the range of attractive forces, and ε is the well depth. Then,

$$Z^{\text{vir}} = 1 + \frac{2}{3}\pi\rho \left[xy(\sigma) - (x-1)\lambda^3 y(\lambda\sigma) \right], \qquad (61)$$

$$\frac{E^*}{N\varepsilon} = -2\pi\rho \int_{\sigma}^{\lambda\sigma} g(r)r^2 \mathrm{d}r\,, \qquad (62)$$

where E^* is the excess (nonideal) part of the internal energy, $x = \exp(\varepsilon/kT)$, and $y = \exp[\omega(r)]$. Table 3 shows for comparison the results of calculations of the virial compressibility factor in the supercritical region. Note that, according to the numerical experiment, $T_{\rm cr}^* = kT_{\rm cr}/\varepsilon = 1.26$. The PY theory predicts $T_{\rm cr}^* = 1.20$, while according to Eqn (42), $T_{\rm cr}^* = 1.22$.

Fable 3. Virial com	pressibility factor Z^{v_1}	^r for the well potential.
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βε	Closure	ho=0.4	$\rho = 0.5$	$\rho = 0.6$	$\rho = 0.7$	$\rho = 0.8$	$\rho = 0.9$
0.0	HNC [53]	2.642	3.533	4.818	6.710	9.569	14.020
	PY [54]	2.481	3.173	4.091	5.323	7.001	9.330
	MS [55]	2.527	3.277	4.303	5.723	7.722	10.590
	Numerical		3.220	4.220	5.630	7.650	
	experiment						
	[53]						
0.1	HNC	2 3/3	3 1 5 3	1 373	6 777	0.063	13 531
0.1	PV	2.343	2 8 50	3 740	1 086	9.005 6.731	0 101
	MS	2.215	2.830	3 736	5.018	6 860	9.191
	WIS	2.205	2.839	5.750	5.018	0.809	9.374
0.3	HNC	1.749	2.397	3.486	5.252	8.069	12.566
	PY	1.684	2.217	3.050	4.304	6.124	8.703
	MS	1.602	2.033	2.706	3.744	5.326	7.719
0.5	UNC	1 169	1 655	2 608	4 202	7 099	11 617
0.5	DV	1.100	1.609	2.008	2 652	5 522	× 106
	MS	1.171	1 2 2 2	1 915	2.647	2.002	0.190
	Numerical	1.032	1.323	1.015	2.047	5.992	
	experiment		1.550	1.970	3.200	5.080	
	experiment						
0.7	HNC	0.619	0.944	1.749	3.346	6.122	10.684
	PY	0.680	1.027	1.756	3.019	4.939	7.654
	MS	0.548	0.702	1.085	1.721	_	

3.3 The Lennard – Jones potential

The Lennard-Jones potential

$$\Phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(63)

is quite close to a real potential. It was used in many papers for studying the properties of systems consisting of rare gas atoms and sometimes of more complex molecules, thus being in fact a central object of application of all theories of simple liquids. Figures 3–7 present some excess thermodynamic functions of the LJ liquid obtained in the MS approximation (42). The isolines of thermodynamic functions on the T, ρ plane include the lines of the ideal states, i.e., the lines where excess functions vanish: Z = 1; $\chi = 1$; and Gibbs free energy $G^* = 0$. The ideal curves describe the thermodynamic states in which the repulsive forces are compensated by the attractive forces. One can see from the figures that all the ideal curves are more or less close to straight lines. To study this question, we consider the van der Waals equation

$$P = \frac{nkT}{1 - bn} - an^2, \tag{64}$$

where *b* is a parameter taking into account the impermeability of particles, and *a* is a parameter responsible for attraction. Equation (64) written in terms of the dimensionless quantities $\tau = T/T_B$ and $v = n/n_B$, where $kT_B = a/b$; T_B is Boyle's temperature; $n_B = 1/b$ is the Boyle's density of particles, has the form

$$Z - 1 = \frac{\nu(\tau + \nu - 1)}{\tau(1 - \nu)} \,. \tag{65}$$

One can easily see from Eqn (65) that the compressibility factor Z = 1 is realized on the straight line $\tau = 1 - v$. The linear dependence of the ideal compressibility factor was found by Holleran [56] in many systems that can be described by the Lennard – Jones potential. Note that the van der Waals



Figure 3. Heat capacity $C^* = C_V/Nk - 3/2$ of the LJ system.





equation is insufficient for the description of many properties of liquids, but it confirms the experiment. Note also that neither of the effective and self-consistent approximations predicts a strict linear dependence of the ideal compressibility factor. Even accounting for many-body forces and quantum effects does not improve the situation. As for the linear behavior of other ideal lines, there are no theoretical considerations at all.

Table 4 summarizes the results of calculations of thermodynamic functions performed based on several most often used approximations and presents for comparison the results of numerical experiments. One can see that some theories predict close results, which are also close to the numerical data. Table 5 presents the results obtained using the local equation (45) [38, 39].



Figure 5. Isolines of the inverse compressibility $\chi^{-1} = 1 - \rho C(0) (\chi^{-1} = 0$ corresponds to the critical point).



Figure 6. Isolines of the excess Gibbs free energy $G^*/NkT = \text{const.}$

3.4 Long-range correlations in liquids

For a long time, the main problem of the theory of liquids was the search for distribution functions and the study of shortrange order features. It was assumed that the only region where the long-range order is responsible for the properties of liquid systems is the vicinity of the critical point. However, many other properties and phenomena in liquid systems are determined namely by the asymptotic properties of correlation functions. These are, for example, the properties of the systems at phase interfaces and within restricted volumes, solvation effects in colloidal systems, wetting, and many other phenomena. A remarkable feature of the asymptotes is their versatility. For example, in a binary solution consisting of molecules of the type A and B, the short-range order is characterized by three types of correlation functions AA, BB, and AB = BA. At the same time, the asymptotes of all the three correlation functions are the same. This surprising fact has a rigorous theoretical substantiation [24, 58].



Figure 7. Isolines of the excess enthalpy $H^*/NkT = \text{const.}$

Table 4. Thermodynamic parameters of the LJ liquid for different closures [30] ($T^* = 1.35$; $\rho = 0.85$).

Closure	$Z^{\rm vir}$	$1/\chi^{\rm vir}$	$1/\chi^{comp}$	$-E^*/N\varepsilon$
HNC (30) PY (31) SMSA (38) Zerah – Hansen (49) Vompe – Martynov (53) MS (42)	4.869 3.620 2.328 2.823 2.873 2.35	30.29 21.24 18.21 20.78 21.20	10.29 13.09 25.39 20.58 21.32	5.311 5.589 5.751 5.676 5.661
Monte Carlo [57]	2.864	_	_	5.67

Table 5. Thermodynamic parameters of the LJ liquid [39] obtained by the Monte Carlo method [57] and using Eqn (45).

ho	$E^*/N\varepsilon$		$Z^{ m vir}$		$eta\mu^*$	
	[57]	(45)	[57]	(45)	[57]	(45)
		1	At tempera	ture $T^* =$	3.0	
0.6	-3.37	-3.37	1.94	2.00	1.21	1.24
0.7	-3.81	-3.80	2.63	2.67	2.09	2.11
0.8	-4.10	-4.11	3.66	3.65	3.41	3.40
0.9	-4.17	-4.25	5.14	5.02	5.28	5.26
1.0	-3.95	-4.12	7.18	6.90	7.85	7.87
1.1	-3.33	-3.66	9.91	9.39	11.30	11.50
		1	At tempera	ture $T^* =$	2.0	
0.6	-3.73	-3.74	1.40	1.49	0.07	0.11
0.7	-4.29	-4.29	2.11	2.19	0.89	0.92
0.8	-4.74	-4.75	3.27	3.30	2.27	2.28
0.9	-5.02	-5.06	5.04	4.97	4.41	4.43
1.0	-5.03	-5.14	7.62	7.33	7.53	7.66
1.1	-4.68	-4.91	11.18	10.57	11.89	12.36
	At temperature $T^* = 1.0$					
0.6	-4.24	-4.21	-0.55	-0.33	-3.90	-3.83
0.7	-4.91	-4.87	0.00	0.24	-3.54	-3.49
0.8	-5.54	-5.50	1.25	1.53	-2.36	-2.24
0.9	-6.06	-6.03	3.57	3.79	0.12	0.37

As early as the beginning of the century, Ornstein and Zernike qualitatively explained the critical opalescence by means of the asymptotic form of the total correlation function

$$h(r) \to \frac{A \exp(-\alpha r)}{r}, \quad r \to \infty.$$
 (66)

They assumed that the Fourier transform of the direct correlation function C(k) can be expanded in a Taylor series at k = 0. Then, retaining only the first terms of the expansion

$$C(k) = C^{(0)}(0) + k^2 C^{(2)}(0) + \dots$$
(67)

and using the OZ equation in k-space

$$1 + nh(k) = \frac{1}{1 - nC(k)},$$
(68)

we obtain Eqn (66).

Upon approaching the critical point, $\alpha \to 0$ and the correlation radius $R_c = 1/\alpha \to \infty$, which explains the enhancement of forward scattering upon approaching the critical point.

One can see from analysis of the pair correlation function h(r) that for $n \to 0$ and $r \to \infty \omega(r) \to 0$. Then,

$$h(r) \to -\beta \Phi(r), \quad r \to \infty.$$
 (69)

At the same time, it was shown that for a hard sphere fluid (always) [59] and the well potential or another cut-off potential (for example, the cut-off Lennard-Jones potential), the asymptotic decrease of correlation functions at high densities is oscillatory [60]. It was also found that for the short-range (cut-off) potentials, there exists the Fisher– Widom (FW) line (named after the authors who first noted the possibility of the existence of such a line) on which the monotonic decrease in the correlation functions transforms to an oscillatory decrease [60]. The general approach based on the OZ equation allows one to predict the asymptotic behavior of correlation functions. The OZ equation can be written in the form

$$rh(r)2 = rC(r) + 2\pi n \int_0^\infty C(t)t \, \mathrm{d}t \int_{|r-t|}^{r+t} h(s)s \, \mathrm{d}s \,. \tag{70}$$

By differentiating in the inner integral and taking into account that $C(r) \rightarrow -\beta \Phi(r), r \rightarrow \infty$, we can obtain, after some transformations, the asymptotic form of the OZ equation

$$\frac{d(h(r)r)}{dr} - 2\pi n \int_0^\infty C(t)t [(r+t)h(r+t) - (r-t)h(r-t)] dt$$

= $-\frac{d(\beta \Phi(r)r)}{dr} - 2\pi n \int_0^\infty h(t)t \{\beta[(r+t)\Phi(r+t) - (r-t)\Phi(r-t)]\} dt.$ (71)

At low densities $(n \to 0)$, a solution is the correlation function (69). For short-range potentials, $r \ge R_c$, and $\Phi(r) = 0$, and the right-hand side in Eqn (71) vanishes. The equation itself becomes linear and homogeneous. The direct substitution of $rh(r) = B \exp(i\lambda r)$ and $\lambda = \pm \beta + i\alpha$ into the homogeneous equation (71) yields the solution

$$rh(r) = \sum_{m=1}^{\infty} B_m \exp(i\lambda_m r), \qquad (72)$$

$$\alpha = 4\pi n \int_0^\infty C(x) \operatorname{sh}(\alpha x) \cos(\beta x) x \, \mathrm{d}x \,, \tag{73}$$

$$\beta = 4\pi n \int_0^\infty C(x) \operatorname{ch}(\alpha x) \sin(\beta x) x \, \mathrm{d}x \,. \tag{74}$$

Now, it is necessary to add a particular solution of a linear inhomogeneous equation to the general solution (72) of the homogeneous system (71). As was shown in Ref. [61], it has the form

$$h(r) = -\chi^2 \beta \Phi(r) \,. \tag{75}$$

This expression is an example of the so-called long-range asymptotes [24, 60]. The total solution has the form

$$h(r) = \frac{\sum_{m=1}^{\infty} B_m \exp(i\lambda_m r)}{r} - \chi^2 \beta \Phi(r) .$$
(76)

One can easily see that a solution of Eqns (73) and (74) can be found only for C(r) = 0 in the region $r \ge R_c$, as follows from the condition $C \to -\beta \Phi$. This corresponds, however, to a search for the general solution (71), i.e., a search for solutions of the homogeneous equation means in fact a search for solutions in the region $r \ge R_c$. This means in essence that the direct correlation function can be represented in the form

$$C(r) = \begin{cases} C(r), & r \le R_{\rm c}, \\ -\beta \Phi(r), & r \ge R_{\rm c}. \end{cases}$$
(77)

Note that the direct correlation function is significant only within a rather short interval of r. For this reason, the total set $\lambda_m = \pm \beta_m + i\alpha_m$ describes in fact the function h(r) at medium distances as well. As r increases, only components with small values of α_m remain in the competition. In this case, depending on the thermodynamic state, either a purely imaginary solution with monotonically decreasing asymptotes of h(r) can be realized or a pair of conjugated complex solutions characterized by an oscillatory decrease. At low and medium densities, monotonically decreasing components dominate, which are governed by the cooperative effects of the short-range attractive potential. As the density increases, the packing effects controlled by a hard core result in dominating oscillations. At a certain density $n_{\rm FW}$ at the specified isotherm, the decrement α_m of the monotonic decay becomes equal to the decrement α_l of the oscillatory decay, resulting in the transition from one decay regime to another. The change in the decay regime is described in the n, T plane by the Fisher–Widom line. The action of the potential part of the asymptotes suppresses both types of exponential decay, exemplifying the long-range asymptotes (75).

Thus, the Lennard–Jones potential and other potentials of this type are characterized by three regions corresponding to different types of competitive asymptotic behavior, resulting in different asymptotes depending on the conditions. Note that at a critical point, cooperative effects are dominant. They also appear when $\Phi = 0$ and $r \ge R_c$. The condition of their existence is the presence of attractive forces at least within a finite region, for example, the presence of a potential well. Because the potential of hard spheres does not have such a region, the critical point and the evaporationcondensation phase transitions are absent in this system. Note that a crystallization type phase transition exists in a hard sphere fluid, because this transition is determined by the packing effects related to the hard core. It is for this reason that the crystallization-melting phase diagram does not contain a critical point, and the lines tend to infinity.

Table 6 presents the roots of Eqns (73) and (74) with the lowest values of α for a hard sphere fluid [59]. All the three approximations presented are qualitatively the same. At low densities, a fast decay is observed (α is large) with a random long-range order. Upon approaching the crystallization point, the decay of correlation functions becomes slow and the degree of long-range order increases.

Table 6. Roots of the $\lambda = \beta \pm i\alpha$ asymptotes for a hard sphere fluid with the minimum value of α .

Approximation	ho = 0.1		ho=0.5		ho=0.9	
	α	β	α	β	α	β
PY	4.07	4.76	1.67	5.89	0.68	6.80
HNC	3.84	4.70	1.77	6.00	0.80	6.99
MS	3.56	4.20	1.70	5.88	0.70	6.80

3.5 Definition of the chemical potential in approximate theories of liquids

A rigorous method of the definition of the chemical potential for liquid systems is based on the Kirkwood formula [61]

$$\beta \mu^* = \rho \int_0^1 d\lambda \int_0^\infty \frac{\partial \beta \Phi(r,\lambda)}{\partial \lambda} g(r,\lambda) 4\pi r^2 dr , \qquad (78)$$

where $\beta\mu^*$ is the excess (configuration) chemical potential corresponding to the work of transfer of a separated particle to some position in the system. The chemical potential is described by the expression

$$\beta \mu = \beta \mu^* + \ln(\rho \Lambda^3) \,. \tag{79}$$

Here, $\Lambda = h/(2\pi mkT)^{1/2}$ is the thermal wavelength. The definition of the chemical potential by expression (79) assumes, first, the repeated calculation of the radial correlation function $g(r, \lambda)$ depending on the parameter λ of the interaction switching; and, second, the numerical integration over the interaction parameter. The chemical potential can also be found using the known thermodynamic relations

$$\beta \mu = \beta \mu^0 - \int_0^\rho \frac{1}{\rho} \left(\frac{\partial \beta P}{\partial \rho} \right)_\beta \, \mathrm{d}\rho \,, \tag{80}$$

$$\beta \mu = \beta \mu^0 - \int_0^\beta \rho \left(\frac{\partial E}{\partial \rho} \right)_\beta \mathrm{d}\beta \,, \tag{81}$$

where μ^0 is the ideal part of the chemical potential.

Expressions (80) and (81), as well as expression (78), assume that the properties of the sequence of states are preliminarily determined. In addition to these problems, the problem of the thermodynamic consistency of pressure P and energy E exists. The fundamental system of Eqns (10) and (12)

allows one to reduce the problem to the determination of the parameters of a single state of the system. Indeed, according to Eqn (12), we have

$$\beta\mu^* = -\rho \int_0^\infty \left\{ h - \omega - \frac{1}{2}h(\omega + B^{(1)}[(r)] \right\} 4\pi r^2 \,\mathrm{d}r \,. \tag{82}$$

Here, the closure problem is related to the determination of the bridge-functionals $B^{(1)}$. It is obvious that the bridge-functional $B^{(1)}$ should be unambiguously determined by the closure of $B^{(2)}$. Below, this relation is determined explicitly.

The problem is solved simply and unambiguously in the case of the HNC closure $B^{(1)} = B^{(2)} = 0$, and we obtain the expression for the chemical potential [62]

$$\beta \mu_{\rm HNC}^* = \rho \int_0^\infty 4\pi r^2 \,\mathrm{d}r \left(\frac{1}{2}h\gamma + \gamma - h\right) \tag{83}$$

which is consistent with the HNC equation.

A comparative analysis of the diagrammatic expansions of $B^{(1)}(\omega)$ and $B^{(2)}(\omega)$ showed that, to a good approximation [63],

$$B^{(1)}(\omega(r)) = \frac{1}{3}B^{(2)}(\omega(r)).$$
(84)

An expression equivalent to Eqn (82), but permitting the selection of $B^{(1)}$ to be precisely linked with the selection of $B^{(2)}$, was found in the works [64, 65]

$$\beta \mu^* = \rho \int_0^\infty 4\pi r^2 dr \left[\left(\frac{1}{2} h^2 - \frac{1}{2} h C - C \right) + B^{(2)} + \int_0^1 d\lambda h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} \right].$$
(85)

Comparison of Eqns (82) and (85) shows that

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

Unlike relation (78), we can directly integrate expression (85) over the parameter λ . To do this, it is necessary to make some assumptions with respect to the properties of the bridge-functionals $B^{(2)}$ and the path of integration over the parameter λ . The basic requirement imposed on the bridge-functionals is the existence of the dependence in the form $B(r) = B(\gamma(r))$. We saw that many approximations, for example, (31), (42), (48), (50), and (52) possess this property. At the same time, the bridge-functional can be expressed in the form $B(r) = B(\omega(r))$. As we will see below, the estimate of the integral in expression (85) is affected by the choice of the approximate form and the integration path. In a linear homogeneous approximation,

$$h(r,\lambda) = \lambda h(r), \quad C(r,\lambda) = \lambda C(r).$$
 (87)

However, the dependence can be different, which is equivalent to a change in the integration path. The problem of the choice of the integration path is substantial namely for approximate equations. According to Refs [64, 65], in the case of the exact closure of the OZ equation, the problem disappears due to the independence of the integration path. However, as was already mentioned, an exact bridge-functional cannot be simply expressed by functions depending only on γ or ω [40, 41]. Consider the integral in Eqn (85)

$$\int_{0}^{1} \mathrm{d}\,\lambda h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} = \int_{0}^{1} \mathrm{d}\,\lambda h(r,\lambda) \frac{\partial B^{(2)}(\gamma(r,\lambda))}{\partial \gamma(r,\lambda)} \frac{\partial \gamma(r,\lambda)}{\partial \lambda} \,.$$
(88)

It follows from Eqn (87) that $\gamma(r, \lambda) = \lambda \gamma(r)$. Then, taking into account Eqn (86), we obtain, after simple transformations,

$$\int_{0}^{1} \mathrm{d}\,\lambda h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} = \frac{h(r)}{\gamma(r)} \int_{0}^{\gamma} \mathrm{d}\,\gamma\gamma \frac{\partial B^{(2)}(\gamma)}{\partial \gamma} \,. \tag{89}$$

If the form $B = B(\omega(r))$ is used under the condition $\omega(r, \lambda) = \lambda \omega(r)$, we obtain the similar but not equivalent expression

$$\int_{0}^{1} \mathrm{d}\,\lambda h(r,\lambda) \frac{\partial B^{(2)}(r,\lambda)}{\partial \lambda} = \frac{h(r)}{\omega(r)} \int_{0}^{\omega} \mathrm{d}\,\omega\omega \frac{\partial B^{(2)}(\omega)}{\partial \omega} \,. \tag{90}$$

Expressions (89) and (90) predict the results, which are closer to each other, the more exact the approximation used, so that the difference can also serve as a measure of the thermodynamic consistency. In the PY approximation, the results are

$$\beta \mu_{\mathrm{PY}(\gamma)}^{*} = \beta \mu_{\mathrm{HNC}}^{*}$$

$$+ 4\pi \rho \int_{0}^{\infty} r^{2} \, \mathrm{d}r \left\{ B^{(2)} + \frac{h}{\gamma} \left[\gamma - \ln(1+\gamma) \right] - \frac{\gamma^{2}}{2} \right\}, \qquad (91)$$

$$\theta \mu^{*} = -\theta \mu^{*}$$

$$\rho \mu_{\rm PY(\omega)} = \rho \mu_{\rm HNC} + 4\pi \rho \int_0^\infty r^2 dr \left\{ B^{(2)} + \frac{h}{\omega} \left(B^{(2)} \omega - \frac{\omega^2}{2} - B^{(2)} \right) \right\}.$$
 (92)

In the MS approximation, we have

$$\beta \mu_{\text{MS}(\gamma)}^* = \beta \mu_{\text{HNC}}^* + + 4\pi \rho \int_0^\infty r^2 \, \mathrm{d}r \left\{ B^{(2)} - h \frac{\omega^3/3 + \omega^4/8}{\omega + \omega^2/2} \right\}, \quad (93)$$

$$\beta \mu_{\text{MS}(\omega)}^* = \beta \mu_{\text{HNC}}^* + 4\pi \rho \int_0^\infty r^2 \, \mathrm{d}r \left\{ B^{(2)} - h \frac{\omega^2}{3} \right\}.$$
(94)

Because for the MS closure, $B^{(2)} = (-1/2)\omega^2$, we immediately obtain that $B^{(1)} = (1/3)B^{(2)}$, in accordance with the analysis performed in Ref [63]. Note that this correspondence is rigorously valid only for approximation (94), whereas in other cases the coefficient at $B^{(2)}$ changes between 1/2 and 1/3 [66].

Tables 7 and 8 present the results of calculations of the chemical potential for a hard sphere fluid and the LJ liquid [67]. The values of $\beta \mu^*_{MS(\omega)}$ for hard spheres virtually coincide with the reference values [50], although they are less accurate for the LJ fluid, which confirms the inadequacy of representation of bridge-functionals in the form neglecting the interaction potential. One can see from Tables 4 and 5 that accounting for Φ_2 allows one to adequately predict the values of the chemical potential, which is very important in studies of phase transitions.

ho	[50]	HNC	$\mathbf{PY}(\gamma)$	$\mathbf{PY}(\omega)$	$MS(\gamma)$	$MS(\omega)$
0.1	0.46	0.47	0.46	0.46	0.46	0.46
0.2	1.03	1.05	1.02	1.02	1.03	1.03
0.3	1.74	1.81	1.71	1.72	1.72	1.73
0.4	2.65	2.81	2.53	2.61	2.57	2.62
0.5	3.81	4.15	3.52	3.75	3.63	3.75
0.6	5.33	6.00	4.71	5.31	4.96	5.26
0.7	7.36	8.59	6.13	7.54	6.65	7.30
0.8	10.15	12.31	7.84	10.93	8.83	10.13
0.9	14.10	17.84	9.88	16.42	11.67	14.22

Table 7. Chemical potential $\beta \mu^*$ for a hard sphere fluid.

Table 8. Chemical potential $\beta \mu^*$ for the LJ system ($T^* = 3.0$).

ρ	Monte Carlo [57]	HNC	$\mathbf{PY}(\gamma)$	$\mathbf{PY}(\omega)$	$MS(\gamma)$	$MS(\omega)$
0.6	1.21	1.69	1.02	1.22	1.12	1.24
0.7	2.09	2.87	1.61	2.08	1.83	2.07
0.8	3.41	4.57	2.38	3.39	2.79	3.29
0.9	5.28	6.94	3.37	5.38	4.08	4.99
1.0	7.85	10.15	4.60	8.41	5.78	7.36
1.1	11.30	14.40	6.09	13.09	8.04	10.52

4. Phase diagram of the Lennard–Jones (LJ) system

In thermodynamics, the curves of the first-order phase transitions are usually determined by comparing the pressure P and chemical potentials μ of the two coexisting phases. But is such a comparison possible in reality? Indeed, for the density $n \le n_A$ (where n_A is the density on the phase equilibrium line), there are no nuclei of phase B inside phase A (density fluctuations in a stable one-phase region are not nuclei of a new phase, as can be the case in the metastable region) and, hence, molecules of phase A cannot be compared with molecules of phase B. Along with the procedure of comparison, the phase equilibrium can be described using a realistic mechanism of the loss of stability, which appears upon approaching the phase transition points, irrespective of whether or not the system is in contact with another system. This brings up the question: What are the features of the beginning of the loss of stability? But, of course, the phase equilibrium curves determined from the condition of the phase coexistence and from conditions of the loss of stability should coincide, otherwise the uniqueness theorem for the Gibbs distribution would be violated.

4.1 Two-phase approach to the problem of phase equilibrium

Figure 8 shows a typical phase diagram for the reduced temperature T^* and density ρ . Here, *C* is the critical point, *B* is the triple point, *AC* is the condensation curve, *CB* is the evaporation curve, *BN* and *KM* are the crystallization and melting curves. Curve *ACB* is called the binodal or the phase equilibrium (transition) curve. Curve *A'CB'* is the spinodal, in each point of which the condition

$$\frac{1}{\chi} = 1 - n \int C(r) \, \mathrm{d}r_3 = 0 \tag{95}$$

is satisfied, i.e., the compressibility on the spinodal and at the critical point tends to infinity. The region between curves



Figure 8. Phase diagram of the LJ system.

ACB and A'CB' represents a region of the metastable onephase states. According to the van Hove theorem [68], the region of metastable states is inaccessible in the thermodynamic limit $N \to \infty$, $V \to \infty$, $\rho = \text{const}$ and the limit of the one-phase states is the binodal. The region of two-phase states is located below the binodal. Finite systems can also have one-phase metastable states, whose region is limited by the spinodal. Note that the Gibbs distribution is absolutely valid only in the thermodynamic limit, so that the fundamental system of equations (4) and (5) or (10) and (12) is also rigorously valid only in the thermodynamic limit. Table 9 presents the results of the thermodynamic (two-phase) approach used for the prediction of vapor-liquid phase equilibrium, which proved to be in fact identical for closures (45) and (47) [39, 43]. Here, P^* is the reduced pressure: $P^* = P\sigma^3/\varepsilon$, $\bar{\mu}^*$ is the reduced chemical potential: $\bar{\mu}^* = \mu^* T^* + T^* \ln \rho$. Note that these results also completely agree with the numerical experiments [69, 70].

 Table 9. Parameters of the vapor–liquid phase equilibrium in the LJ system

 [43].

T^*	$ ho^{ m st}$	$ ho^{ m liq}$	$\bar{\mu}^*$	P^*
0.7	0.0026	0.8379	-4.200	0.0018
0.8	0.0071	0.7940	-4.045	0.0054
0.9	0.0158	0.7467	-3.915	0.0128
1.0	0.0305	0.6945	-3.812	0.0256
1.1	0.0535	0.6333	-3.739	0.0451
1.2	0.0870	0.5508	-3.698	0.0717

4.2 One-phase approach to the problem of phase transitions

As was mentioned above, the one-phase approach involves a search for features indicating the loss of thermodynamic stability of the one-phase system. Some such features are known, for example, the empirical Lindeman rule, according to which a crystal starts to melt when the root-mean-square deviations of an atom from its equilibrium position exceed 15%. Similarly, the empirical Hansen–Verlet rule [71] states that crystallization of simple liquids occurs when the structural factor S(k) = 1 + nh(k) reaches the value 2.85 for some k. The question is whether a consistent procedure for determining the phase equilibrium lines can be constructed on the basis of the fundamental equations and their approximations? According to the van Hove theorem, the rigorous

equation (10) should have a solution over the entire region of existence of the homogeneous stable phase, whereas the twophase region cannot be described by Eqn (10) only. From this, the so-called one-phase hypothesis follows [72, 73], according to which the lines of disappearance of the physical solution of the OZ equation should be the phase equilibrium lines. However, in the case of approximate equations the situation can be different. Indeed, in general, the approximate OZ equations can no longer correspond to the thermodynamic limit, which means the possibility of the existence of physical solutions in the metastable region as well. It is this circumstance that makes possible, however strange it may be, the existence of the two-phase transition in the case of the intersection of the $P-\mu$ -lines of one phase with the $P-\mu$ lines of another phase. These lines appear due to the existence of solutions in the metastable region as well.

The disappearance of physical solutions at the boundary of phase equilibria is not typical for most approximate equations and self-consistent procedures [29, 74-77]. At present, it is established that the solution of approximate equations in the region of stable one-phase states is unique and independent of the algorithms and procedures of searching for solutions. Upon the transition to the metastable region, solutions can depend on the conditions of searching for them, resulting in the appearance of many non-physical solutions. However, the region of confusion is so great that the possibility of the phase transition can be indicated only qualitatively. The situation is also aggravated by the fact that distribution functions obtained, as a rule, in the numerical form contain no features suggesting the difference between the metastable and stable regions.

Nevertheless, some closures, namely, (42) and (45) sometimes have physical solutions, which disappear in the region adjacent to the phase equilibrium lines [38, 39, 67, 73, 78]. For example, the solution of the OZ equation with the closure (42) is written in the form

$$\omega(r) = -1 + \sqrt{1 + 2\gamma(r)} \tag{96}$$

(the second solution corresponding to a minus sign in front of the root does not satisfy the condition of the correlation weakening $\omega \to 0$, $r \to \infty$, and, therefore, should be discarded). If we denote by r_{\min} the point on the *r*-axis at which γ takes the minimum value, then the limiting values are

$$\gamma_{\min} = -\frac{1}{2}, \quad \omega_{\min} = -1.$$
 (97)

Calculations for a hard sphere fluid [73] showed that, in accordance with the structural criterion (97), the disappearance of the physical solution occurs when the density $\rho = 1.02$. According to the data of various numerical experiments, the phase transition occurs in a hard sphere fluid at densities 0.95-0.98. It was shown in Ref. [79] that upon melting of a crystal of hard spheres, the value $\omega_{\min} = -1$ corresponds to the density 1.02.

5. Approximate equations for multicomponent polyatomic systems

Molecular polyatomic systems represent quite complicated objects for theoretical studies. When the interaction between molecules can be represented in the form of an additive scheme of atom-atom (site-site) interactions

$$U_{\alpha\beta} = \sum_{\alpha_i\beta_j}^{M_{\alpha}M_{\beta}} \Phi_{\alpha_i\beta_j}, \qquad (98)$$

the concept of the atom-atom correlation functions can be introduced to the theory. Here, α_i is the *i* th atom of molecule α , β_j is the *j* th atom of a molecule β , and M_{α} and M_{β} are numbers of atoms in each of the molecules. The Site–Site Ornstein–Zernike (SSOZ) equations or the Reference Interaction Site Model (RISM) developed by Chandler and Andersen [80] are the most useful in practice. The theoretical drawbacks of this method are well known. First of all, they stem from the fact that, unlike the OZ equation, which is rigorous for systems of monoatomic molecules, its SSOZ analog for polyatomic molecules is approximate itself [81]. Other, more rigorous systems of equations [82] based on exact virial expansions require substantial simplifications because of their great complexity, which makes them approximate as well.

5.1 Formulation of equations in the atom-atom approximation

The SSOZ equations can be conveniently written in k-space, in which they have the algebraic form (68), with

$$C(k) = \frac{4\pi}{k} \int_0^\infty C(r) \sin kr \, \mathrm{d}r \tag{99}$$

and, similarly, for h(r).

Consider now a two-component mixture of monoatomic molecules of type d and s. The OZ equations for such a system are still rigorous, and we obtain in k-space

$$h_{dd}(k) = C_{dd}(k) + n_d C_{dd}(k) h_{dd}(k) + n_s C_{ds}(k) h_{sd}(k) , (100)$$

$$h_{ds}(k) = C_{ds}(k) + n_d C_{dd}(k) h_{ds}(k) + n_s C_{ds}(k) h_{ss}(k) , \quad (101)$$

$$h_{ss}(k) = C_{ss}(k) + n_d C_{sd}(k) h_{ds}(k) + n_s C_{ss}(k) h_{ss}(k) , \quad (102)$$

where $n_d = N_d/V$ and $n_s = N_s/V$ are densities of particles of the type *d* and *s*, respectively. Note that $h_{ds} = h_{sd}$ and $C_{ds} = C_{sd}$. Equations (100)–(102) can be written in the matrix form

$$\hat{h}(k) = \hat{C}(k) + \hat{C}(k)n\hat{h}(k),$$
(103)

in which

$$\hat{h}(k) = \begin{pmatrix} h_{dd} & h_{sd} \\ h_{ds} & h_{ss} \end{pmatrix}, \quad n = \begin{pmatrix} n_d & 0 \\ 0 & n_s \end{pmatrix}.$$
 (104)

In the *m*-component atomic system, Eqns (103) will contain matrices C(k), h(k) and *n* of order $m \times m$. Formally, a molecular system can be treated as atomic one, in which atoms of different types are separated by fixed distances. Such an approach is implemented by introducing matrices of the intramolecular correlation functions [83, 84]

$$V_{ij}^{\alpha\beta}(k) = \delta_{\alpha\beta} \frac{\sin kR_{ij}}{kR_{ij}}, \qquad (105)$$

where R_{ij} is the intramolecular distance between atoms *i* and *j*. Now, a system of the SSOZ equations can be written in the general form

$$\hat{n}h\hat{n} = \hat{n}VC\hat{n}V + \hat{n}VC\hat{n}h\hat{n}.$$
(106)

If the distances R_{ij} are large, the matrix V transforms to the unit matrix I, and the system of equations (106) transforms to the system (103). In the case of an infinitely diluted solution, system (106) is decomposed into three systems of matrix equations

$$\gamma^{d}(k) = n^{-1} V^{d} n C^{d}(k) V^{d} \left[I - n C^{d}(k) V^{d} \right]^{-1} - C^{d}(k) , (107)$$

$$\gamma^{sd}(k) = V^{s}C^{sd}(k) [V^{d} + nh^{d}(k)] - C^{sd}(k), \qquad (108)$$

$$\gamma^{s}(k) = V^{s} \left[C^{s}(k) V^{s} + C^{sd}(k) n h^{ds}(k) \right] - C^{s}(k) \,. \tag{109}$$

The superscripts d and s refer to a solvent and a solute, respectively. As before, $\hat{\gamma}(k) = \hat{h}(k) - \hat{C}(k)$, V^d and V^s are structural matrices of a solvent and a solute. Now, the system (107)–(109) can be solved successively, first for γ^d of the pure solvent and then for the cross functions. The numerical solution of integral equations based on a combination of direct iterations and the Newton–Raphson method is described in papers [81, 84].

5.2 Water

The number of papers devoted to the study of the properties of water, hydration, and hydrophobic effects continues to increase. This is explained, on the one hand, by the necessity of explaining the well-known anomalous properties of water [85] and on the other, by the role that the water structure plays in a variety of physicochemical and biological processes.

The anomalous behavior of the thermodynamic functions of solvation (hydration) is manifested in the apparent discrepancy between the values of the chemical potential and thermodynamic solvation energy. Indeed, the experimental values of the thermodynamic solvation energy of nonpolar molecules are negative, suggesting that the dissolving process is energetically profitable. At the same time, the values of the chemical dissolving potential are strictly positive, indicating that dissolving of nonpolar molecules is thermodynamically unprofitable. The positive chemical potential and the negative thermodynamic energy result in the large negative values of the solvation entropy, and thus the dissolving of nonpolar molecules is related to the water structure, whose basic elements represent hydrogen bonds. For this reason, the description of water properties became one of the central problems of the theory of complex liquids.

Most models of water used in theoretical studies are models of rigid molecules with fixed charges Ze, i.e., they neglect vibrations of atoms in a molecule and polarization. These are the Simple Point Charge (SPC) [86], Transferable Intermolecular Potential with 3 Points (TIP3P) [87], TIP4P [88], MCY (after the authors' names) [89], SPC/E [90] models, and some others. The interaction of molecules is described by the *n*-center atom-atom potential in the form

$$\Phi_{\alpha_i\beta_j} = \frac{Z_{\alpha_i}Z_{\beta_j}e^2}{r} + \frac{A_{\alpha_i\beta_j}}{r^{12}} - \frac{C_{\alpha_i\beta_j}}{r^6} , \qquad (110)$$

where $A_{\alpha_i\beta_j}$ and $C_{\alpha_i\beta_j}$ are coefficients of the non-valence atomatom interactions. These models are based in fact on involved quantum-chemical calculations, which are approximated by simple expressions of the type (110). However, it is such approximations that allow one to use, on the one hand, the available theoretical models and, on the other hand, to obtain information on the thermodynamics and structure of complex systems in general. The scientific literature devoted to the numerous studies in this field may be a subject of special consideration.

Table 10 presents parameters of the water molecule for some models, and Table 11 lists the excess thermodynamic parameters of water at temperature 25° and a density of 0.997 g cm^{-1} calculated in the HNC approximation. Note that other closures have not been used in studies of water properties, because the HNC approximation predicts well the properties of systems with long-range interactions (the first term in Eqn (110) corresponds to the long-range Coulomb component of the potential). One can see from Table 11 that the scatter in the values of the chemical potential determined using different models is the largest compared to that for other thermodynamic parameters. This is explained by the fact that the chemical potential is very sensitive to the accuracy of the correlation function at small distances, whereas the HNC approximation is less accurate namely in this region. Here, we see once more that different thermodynamic functions are controlled by different ranges of the correlation functions. Thermodynamically consistent procedures for systems of polyatomic molecules have not been developed so far.

Table 10. Parameters of the water molecule [91] for some models.

Model	$R_{\rm O-H}, {\rm A}$	α_{H-O-H}, deg	Dipole moment (Debye)
Experiment	0.957	104.52	1.85
SPC	1.000	109.47	2.27
SPC/E	1.000	109.47	2.35
MCY	0.957	104.50	2.19
TIP3P	0.957	104.52	2.34

 Table 11. Thermodynamic parameters of water in the SSOZ-HNC approximation [91].

Model	Experiment	MCY	SPC	SPC/E	TIP3
-E, kcal mol ⁻¹	9.90 [7]	8.80	9.90	9.90	9.91
-F, kcal mol ⁻¹	5.74 [7]	3.74	5.15	4.93	5.22
$-\mu^*$, kcal mol ⁻¹	6.32 [92]	2.03	2.50	2.52	2.70

Table 12 presents two close variants of the potential of the SPC model of water, for which the atom-atom correlation functions h_{O-O} , h_{O-H} , and h_{H-H} are shown in Fig. 9 [93]. Analogous calculations based on other models of water were performed in papers [94, 95]. The largest difference in the behavior of the correlation functions is observed for O-H. Although the peaks of the correlation functions corresponding to the hydrogen bond are qualitatively similar, their amplitudes are different. The rearrangement of the water

Table 12. Parameters of the potential of the SPC model of water [91].

e _H	$C_{\text{O-O}},_{6}$ kcal A mol ⁻¹	$A_{0-0}, {}_{12}$ kcal A mol ⁻¹	$C_{\rm O-H},_{6}$ kcal A mol ⁻¹	$A_{\text{O-H}},$ kcal A mol ⁻¹
0.41	625.731	629624	0	225.18
0.41	625.000	624000	0	900.00



Figure 9. Total atom–atom correlation functions $h_{O-O}(a)$, $h_{O-H}(b)$, and $h_{H-H}(c)$. The solid and dashed curves are related to the water model corresponding to the first and second rows in Table 12. The distance *R* is given in A.

structure during the dissolving of molecules is characterized first of all by the rearrangement of hydrogen bonds in a hydrate shell. It is obvious that these effects related to the correlation function for O-H mainly determine the thermodynamics and structure of solvation. The contributions depending on the two other functions for O-O and O-Hare negligible.

Attempts have been made to use, along with rigid models of water, flexible models that describe the intramolecular and intermolecular interactions in the same way. In this case, water is treated as a mixture of hydrogen and oxygen atoms in the ratio 2:1, which interact with neighboring atoms in the molecule and atoms of other molecules in the same way [96, 97]. The empirical form of the potentials is chosen to provide the existence of stable molecules. The possible advantages of this model lie in its substantial simplification compared to other models and the passage from the SSOZ approximation to the exact OZ equations for mixtures. However, this approach has not found wide application because of the problems in the construction of adequate potential functions.

Note that even the potentials used for the description of simple systems, for example, the Lennard–Jones potential are the model ones. The degree of adequacy of such models is perpetually discussed in the literature. The problem of the theory of liquids mainly consists in the description of the systems with prescribed model potential functions.

5.3 Solvation of molecules

By 'solvation' (hydration) we mean the changes in a solution caused by transfer of an isolated molecule from a gaseous (ideal) medium to a fixed position in the solution. It is obvious that these changes mainly occur in the vicinity of a solute molecule. The type of the changes yields information on the properties and structure of the solvent itself. The excess chemical solvation potential in the atom–atom representation has the form

$$\beta\mu_s^* = n_d \sum_{i,j}^{M^d M^s} \int \mathrm{d}^3 r \left[\frac{1}{2} \left(h_{ij}^{sd} \right)^2 - \frac{1}{2} h_{ij}^{sd} - C_{ij}^{sd} + B_{ij}^{sd} \right] + n_d \sum_{i,j}^{M^d M^s} \int \mathrm{d}^3 r \frac{h_{ij}^{sd}}{\gamma_{ij}^{sd}} \int_0^{\gamma_{ij}^{sd}} \mathrm{d}\gamma\gamma \frac{\partial B_{ij}^{sd}}{\partial\gamma} , \qquad (111)$$

where the summation is carried out both over the number of atoms in the solvent molecule and the number of atoms in the solute molecule. The thermodynamic energy of interaction of the solute molecule with the solvent is described by the expression

$$E_s = n_d \sum_{i,j} \int_0^\infty 4\pi r^2 \, \mathrm{d}r \Phi_{ij}^{sd}(h_{ij}^{sd} + 1) \,. \tag{112}$$

Note that here we consider for simplicity the case of the one-component molecular solvent. In the case of the multicomponent solvent, the summation is performed over all the components of the solvent. Two cases should be distinguished for the excess solvation entropy. The first one corresponds to dissolving at a constant volume (density):

$$S_n = -\left(\frac{\partial \mu_s^*}{\partial T}\right)_n,\tag{113}$$

and the second one to dissolving at a constant pressure:

$$S_P = -\left(\frac{\partial \mu_s^*}{\partial T}\right)_P. \tag{114}$$

Then, the solvation energy is

$$E_{\text{solv}} = \frac{\partial(\mu_s^*/T)}{\partial(1/T)} = \mu_s^* + TS_n \,, \tag{115}$$

and the solvation enthalpy is

$$H_{\text{solv}} = \frac{\partial(\mu_s^*/T)}{\partial(1/T)} = \mu_s^* + TS_P \tag{116}$$

The solvation enthalpy and energy are related by the expression [91, 98]

$$H_{\text{solv}} - E_{\text{solv}} = T(S_P - S_n) = T\alpha_P n \left(\frac{\partial \mu_s^*}{\partial n}\right)_T, \quad (117)$$

where α_P is the thermal expansion coefficient of a pure solvent. Note that E_s is not equal to E_{solv} . One can easily see this by the example of the HNC closure. Indeed, by substituting Eqn (111), for B = 0, in Eqn (115) and taking into account (113), we obtain, after some transformations, [98]

Table 13. Thermodynamic parameters of solvation of hydrocarbons.

Hydro- carbon	Method	$H_{ m solv},$ kcal mol ⁻¹	$\mu_s^*,$ kcal mol ⁻¹	$-E_s$, kcal mol ⁻¹
Methane	Experiment	-3.30	2.01	_
	Numerical experiment	-5.02	2.3	2.89
	HNC	1.56	8.72	1.75
	MS	-2.27	1.21	2.60
	Equation (53)	-1.98	2.02	2.50
Ethane	Experiment	-4.72	1.84	_
	Numerical experiment	_	—	4.80
	HNC	1.33	12.30	3.49
	MS	-4.19	1.62	4.49
	Equation (53)	-4.02	1.83	4.47
Propane	Experiment	-5.38	1.96	_
	Numerical experiment	—		6.60
	HNC	2.20	17.50	4.46
	MS	-5.41	2.35	5.76
	Equation (53)	-5.61	1.98	5.79

Table 14. Thermodynamic parameters of solvation of molecules of rare gases [93].

$$E_{\text{solv}} = n \sum_{i,j} \int d^3 r \Phi_{ij} (h_{ij} + 1)$$

+ $\frac{Tn}{2\beta} \sum_{i,j} \int d^3 r (C_{ij} \delta_T h_{ij} - h_{ij} \delta_T C_{ij}).$ (118)

One can see from Eqn (118) that the thermodynamic energy E_s (the first term on the right-hand side) represents only a fraction of the solvation energy. The second term takes into account variations in the structure of the solvent itself during the dissolving process, δ_T meaning the derivative of functions C and h with respect to T.

It was shown in Ref. [91] that the MS closure (42) and the version (53) yield more correct results than the HNC equation in calculations of the solvation of nonpolar molecules. Table 13 presents the results of calculations of solvation of simple hydrocarbons under standard conditions at 25°C, and Table 14 lists the thermodynamic functions of solvation of molecules of rare gases [93] obtained in the SPC-MS approximation. One can see from these tables that the HNC equation inadequately describes the short-range order effects, to which solvation of nonpolar molecules belongs, whereas the MS closure and the version (53) yield more plausible results. Note that other approximations have not been used for these purposes. However, solvation of salts and polar molecules was adequately described in the HNC approximation [98, 99].

6. Conclusions

In this review, the possibilities of approximations used in the theory of liquids are shown and problems encountered using them in the description of classical liquids are considered. In combination with numerical experiments, these approximations form a reliable basis for solving problems related to simple liquids. Many interesting problems inherent in simple liquids, such as the behavior of

Gas	Method	$\mu_s^*,$ kcal mol ⁻¹	$H_{ m solv},$ kcal mol ⁻¹	$-S_P$, kcal (mol deg) ⁻¹	$-S_n$, kcal (mol deg) ⁻¹	$E_{\rm solv},$ kcal mol ⁻¹	$E_{\rm s},$ kcal mol ⁻¹
Neon	HNC	4.89	1.43	11.63	12.59	1.14	-0.003
		4.83	1.32	11.76	12.74	1.03	-0.03
	MS	1.54	-0.83	7.97	8.63	-1.03	-0.49
		1.73	-0.76	8.34	9.03	-0.96	-0.50
	Experiment [92]	2.67	-0.35	10.12	11.96	-0.89	
Argon	HNC	7.00	1.07	19.93	21.59	0.58	-1.51
		6.90	0.88	20.18	21.85	0.38	-1.55
	MS	0.78	-2.63	11.43	12.37	-2.91	-2.24
		1.08	-2.65	12.54	13.58	-2.96	-2.25
Krypton	Experiment	2.00	-2.38	14.71	16.55	-2.93	
	HNC	7.57	0.65	23.23	25.16	0.08	-2.39
		7.45	0.51	23.29	25.22	-0.07	-2.44
	MS	0.17	-3.77	13.22	14.32	-4.09	-3.20
		0.52	-3.69	14.13	15.30	-4.04	-3.22
	Experiment	1.66	-3.20	16.30	18.14	-3.75	
Xenon							
	HNC	9.69	0.42	31.11	33.69	-0.35	-3.72
		9.53	0.25	31.14	33.72	-0.52	-3.78
	MS	-0.63	-5.75	17.19	18.61	-6.18	-4.78
		-0.16	-5.48	17.84	19.32	-5.92	-4.81
	Experiment	1.33	-3.85	17.40	19.24	-4.40	

Note: two rows of values for the HNC equation and the MS closure are obtained for the two potentials of water (see Table 12).

systems in an external field and restricted volumes, etc. remained beyond the scope of this review. However, the basic theoretical and practical problems of the theory are related to the study of polyatomic liquid systems, which cannot be examined by means of the methods and approximations applied to simple liquid systems. The situation is additionally complicated by the fact that in this case the computing possibilities of numerical experiments are limited, which hinders the development of criteria of accuracy and likelihood for approximate approaches.

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