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Differential condition of thermodynamic consistency as a closure for the Ornstein-Zernike equation

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The differential condition of self-consistency relating the thermodynamic functions and their derivatives locally at a studied point of the phase diagram has been suggested as a closure for the Ornstein-Zernike (OZ) equation. This produces an infinite set of OZ-like equations together with functionals—these are conditions to determine exact values of correlation functions and bridge function. To solve the problem an efficient method was developed that allows one to obtain not only 14 virial terms for a hard-sphere fluid (low-density limit) but the equation of state at high density with good accuracy.

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INTRODUCTION

Gibbs's distribution is known to generate the infinite hierarchy of Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) equations for one-particle distribution functions which can be rigorously transformed into the Ornstein-Zernike (OZ) equation [1,2]. However, the OZ equation contains not only the radial distribution function $g(r)$ but also a bridge function $B(r)$ (r is the distance between the particles). The latter is given by an infinite sum of irreducible diagrams—the remainder of the senior distribution functions sequence removed from BBGKY. But in practice it is impossible to obtain $B(r)$ by means of calculating these diagrams. So, the OZ equation determines the relation between two unknown functions $g(r)$ and $B(r)$, which is why it can be solved only in combination with an additional equation, called the closure equation.

In the theory of liquids, the closure equation is defined as a function $B=B(g(r))$, and its concrete expression is selected on the basis of diagram analysis and partial summing of these diagrams. The closure equation incorporated into the OZ equation leads to the well-known integral equations of liquid-state Percus-Yevick (PY), hypernetted chain (HNC), or some other approximation. These approximations are quite satisfactory above the critical point, but hardly applicable for dense systems, lower temperatures, and phase equilibrium problems. Moreover, the replacement of real $B(r)$ by $B(g(r))$ involves an unknown error, and the accuracy of the integral equation can be verified only by means of comparison with the numerical experiment, which makes the theory semiempirical.

The approach called reference HNC (RHNC) was reported in [3]. According to this method [4], the condition of thermodynamic consistency in the form of a functional $I(\rho)=I[g,B]=0$ is taken instead of the closure function $B(g(r))$. The unknown bridge function $B(r,\rho,\Theta)$ (ρ is the density and Θ is the temperature) for studied systems is replaced by $B_{\mathrm{HS}}(r,\rho_{\mathrm{HS}})$ known from Monte Carlo hard-sphere (HS) simulations [5]. The reference system density ρ_{HS} is fitted to satisfy $I(\rho)=0$. The RHNC results are better than in the method of integral equations, but they are still insufficient [1]. It has been mentioned above that the uncertainty of the bridge function approximation is not *a priori* available.

Using B_{HS} instead of B means that the thermodynamic consistency functional $I(\rho,B)$ is always minimized in the restricted set of the unique basis function. To enlarge the supposed class of bridge functions we assume $B=\sum_i a_i(\rho)\varphi_i(\rho,r)$, where $\varphi_i(\rho,r)$ is a complete system of basis functions and $a_i(\rho)$ are unknown coefficients which are to be found using the condition of $|I(\rho,\sum_i a_i(\rho)\varphi_i(\rho,r))|$ as a minimum. Generally speaking, this procedure permits us to find the exact $g(r,\rho,\Theta)$ and $B(r,\rho,\Theta)$ values.

Total thermodynamic consistency demands not only the equality of virial and compressibility pressures, but all their derivatives with respect to ρ and Θ have to be equal at any point:

$$\frac{\partial^{k+l}p^{\mathrm{vir}}}{\partial\rho^k\partial\Theta^l}=\frac{\partial^{k+l}p^{\mathrm{compr}}}{\partial\rho^k\partial\Theta^l},\quad k,l=0,1,\ldots,\infty\ .$$

This condition brings us to an infinite sequence of thermodynamical consistency functionals $I_{k,l}=0$ and an infinite sequence of corresponding OZ equations (see Sec. I). In this paper we have derived the set of basic expressions (Sec. I) and have worked out a method of solving the problem at any density. The hard-sphere fluid was taken to demonstrate the efficiency for the examples of low (Sec. II) and high (Sec. III) densities. The method allowed us to evaluate up to 14 virial terms and the equation of state for dense fluids.

I. THERMODYNAMIC CONSISTENCY CONSTRAINT

Generally, three thermodynamic average values can be determined [6] if we know the correlation functions $C(r)$ and $h(r)$. The virial theorem gives pressure as

$$P(\rho)=\rho\Theta\left[1-\frac{\rho}{6\Theta}\int_0^\infty r\frac{d\Phi(r)}{dr}g(r,\rho)4\pi r^2dr\right] . \tag{1}$$

Isothermal compressibility is

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

Internal energy of a system is

$$E=\tfrac{3}{2}\Theta N+\frac{\rho N}{2}\int_0^\infty\Phi(r)g(r,\rho)4\pi r^2dr , \tag{3}$$

where $\rho=N/V$ is the density, N is the total number of particles in a system, $\Theta=kT$ is the temperature, $\Phi(r)$ is the pair interaction potential, $g(r)=\exp[-(\Phi/\Theta)+\omega]$ is the radial distribution function, $\omega(r)$ is the thermal potential, $h(r)=g(r)-1$ is the total correlation function, $C(r)=h(r)-\gamma(r)$ is the direct correlation function, and $\gamma(r)=\omega(r)+B(r)$, which does not have any special name.

It is obvious that any thermodynamic characteristic calculated from (1)–(3) should be the same independent of the evaluation formula. The coincidence among these three values can be estimated by two identities. The first one is the pressure compressibility consistency expression, which we get by differentiating (1) with respect to ρ and comparing the result with (2):

$$I(\rho)=\int_0^\infty\left[C(r)-\frac{r}{6\Theta}\frac{d\Phi(r)}{dr}\left[2g(r)+\rho\frac{\partial g(r)}{\partial\rho}\right]\right]r^2dr$$
$$=0 . \tag{4}$$

The second identity relates pressure to energy. It can be derived from the thermodynamic equation [7]:

$$\left[\frac{\partial E}{\partial V}\right]_\Theta=\Theta^2\frac{\partial}{\partial\Theta}\left[\frac{P}{\Theta}\right]_V . \tag{5}$$

Substituting for pressure and energy in terms of (1) and (3) we obtain the second condition,

$$J(\rho,\Theta)=\int_0^\infty\left[\Phi(r)\left[g(r)+\rho\frac{\partial g}{\partial\rho}\right]\right.$$
$$\left.+\frac{r}{3}\frac{d\Phi}{dr}\left[g(r)-\Theta\frac{\partial g}{\partial\Theta}\right]\right]r^2dr=0 . \tag{6}$$

It should be pointed out that Eqs. (4) and (6) are true at any density and temperature point where the equilibrium fluid exists. This means that all their higher derivatives with respect to ρ and Θ are also equal to zero. The correlative functions for examined HS fluids are independent of temperature, and (6) is always satisfied. For this reason we have omitted its further consideration.

Integral (4) contains three unknown functions C, h, and $\partial h/\partial\rho$. The first two satisfy the OZ equation:

$$h(r_{12})=C(r_{12})+\rho C(r_{13})\circ h(r_{23}) , \tag{7}$$

where $\circ$ is a convolution operator symbol. $\partial h/\partial\rho$ can be found by solving the OZ equation differentiated with respect to ρ [8]:

$$\frac{\partial h_{12}}{\partial\rho}=\frac{\partial C_{12}}{\partial\rho}+\rho\left[\frac{\partial C_{13}}{\partial\rho}\circ h_{23}+\frac{\partial h_{23}}{\partial\rho}\circ C_{13}\right]$$
$$+C_{23}\circ h_{31} . \tag{8}$$

In (8) we have another unknown function $\partial C/\partial\rho$, and the set of (4), (7), and (8) still remains unclosed. Differentiating (4) with respect to ρ we come to the second order-consistency constraint for (8):

$$\frac{\partial I(\rho)}{\partial\rho}=\int_0^\infty\left[\frac{\partial C(r)}{\partial\rho}\right.$$
$$\left.-\frac{r}{6\Theta}\frac{d\Phi(r)}{dr}\left[3\frac{\partial g(r)}{\partial\rho}+\rho\frac{\partial^2g(r)}{\partial\rho^2}\right]\right]r^2dr$$
$$=0 . \tag{9}$$

Here we see the same situation as in the previous stage [i.e., Eqs. (4) and (7)]. The constraint contains a higher derivative than the corresponding integral equation, so the next-order OZ must be included. By repeating this process we have obtained a sequence of equations

$$\gamma_{12}^{[k]}(\rho)=\rho\sum_{j=0}^{k}C_{13}^{[j]}\circ h_{23}^{[k-j]}$$
$$+\sum_{j=0}^{k-1}C_{13}^{[j]}\circ h_{23}^{[k-1-j]} \tag{10}$$

together with

$$I^{[k]}(\rho)=\int_0^\infty\left[C^{[k]}(r)-\frac{r}{6\Theta}\frac{d\Phi(r)}{dr}[(2+k)g^{[k]}(r)+\rho g^{[k+1]}(r)]\right]r^2dr=0,\quad k=0,\ldots,\infty . \tag{11}$$

Here and below the superscript symbol $[k]$ denotes the $[\partial^k/(k!\partial\rho^k)]$ operator.

The set of equations (10) and (11) becomes closed in an infinite limit $k\to\infty$. The physical idea of (11) is the application of total thermodynamical consistency to all derivatives of correlation functions. It is the same as the exact identity of curves $\kappa(\rho)$ found from (1) and (2). Equations (10) and (11) cannot be solved if we have not closed the OZ system by the suggested above $B(r)$ expression,

$$B(\omega)=\sum_{i=1}^{\infty} a_i(\rho)\varphi_i(\rho,r) \ . \tag{12}$$

In this case our closure is

$$C(\rho,r)=h(\rho,r)-\omega(\rho,r)-\sum_{i=1}^{\infty} a_i(\rho)\varphi_i(\rho,r) \ . \tag{13}$$

The differential closure form can be obtained by applying the $[k]$ operator to (13):

$$C^{[k]}(\rho,r)=h^{[k]}(\rho,r)-\omega^{[k]}(\rho,r) - \sum_{i=1}^{\infty}\sum_{j=0}^{k} a_i^{[j]}(\rho)\varphi_i^{[k-j]}(\rho,r) \tag{14}$$

and $\omega^{[k]}$ is found from the recurrence

$$C^{[k]}=\sum_{j=0}^{k-1}\left[1-\frac{j}{k}\right]h^{[j]}\omega^{[k-j]}-\gamma^{[k]} \ , \tag{15}$$

where for each k all $\omega^{[1]}\cdots\omega^{[k-1]}$ present in (15) are already known from the previous stage and the first, $\omega^{[0]}$, is defined by

$$\omega^{[0]}=\ln\{[h^{[0]}+1][f(r)+1]\} \ .$$

$f(r)$ is the Mayer function $\exp(-\Phi/\Theta)-1$.

To collect the complete system of (10), (14), (15), and (11) we have to rewrite them:

$$\gamma_{12}^{[k]}(\rho)=\rho\sum_{j=0}^{k} C_{13}^{[j]}\circ h_{23}^{[k-j]}+\sum_{j=0}^{k-1} C_{13}^{[j]}\circ h_{23}^{[k-i-j]} \ , \tag{16a}$$

$$\omega^{[k]}(\rho,r)=\gamma^{[k]}(\rho,r)+\sum_{i=1}^{\infty}\sum_{j=0}^{k} a_i^{[j]}(\rho)\varphi_i^{[k-j]}(\rho,r) \ , \tag{16b}$$

$$C^{[k]}=\sum_{j=0}^{k-1}\left[1-\frac{j}{k}\right]h^{[j]}\omega^{[k-j]}-\gamma^{[k]} \ , \tag{16c}$$

$$I^{[k]}(\rho)=\int_0^{\infty}\left[C^{[k]}(r)-\frac{r}{6\Theta}\frac{d\Phi(r)}{dr}[(2+k)g^{[k]}(r)+\rho g^{[k+1]}(r)]\right]r^2dr=0, \quad k=0,\ldots,\infty \ . \tag{16d}$$

To solve (16) we should fix a maximum number M instead of the infinite upper limit of sum (12) and organize an iteration process evaluating them step by step (16a)→(16b)→(16c)→(16a)$\cdots$ with $a_i^{[j]}$ values simultaneously satisfying (16d) for $k=0,1,2,\ldots,M$. Performing this process, we have noted that no approximations had been used and that the problem (16) is equivalent to the initial one. The choice of a suitable number of basis functions allows us to solve it with any required accuracy.

II. LOW DENSITIES

At lower density limits (16a) does not contain the first sum in the right-hand side and gives us simple expressions which can be solved consequently as a set of integral equations. Substituting density expansions for correlation functions (1) and (2), (16d) can be reduced to

$$B_{k+2}^{v}=-\frac{4\pi}{6}g^{[k]}(1) \qquad (\sigma=1 \text{ is a particle radius}) \ . \tag{17}$$

B_k^v are virial terms evaluated from the virial theorem and

$$B_{k+2}^{c}=-\frac{4\pi}{(k+2)}\int C^{[k]}r^2dr \ . \tag{18}$$

B_k^c are the same terms evaluated out of the compressibility expression. The correlation function derivatives are found from the corresponding (16a),

$$\gamma_{12}^{[k]}(\rho)=\sum_{j=0}^{k-1} C_{13}^{[j]}\circ h_{23}^{[k-1-j]} \ . \tag{19}$$

To close these equations we have to choose a basis function φ_i. For simplicity we take them in the form

$$B=a_2(\rho)\omega^2 \quad \text{and} \quad B=2a(\rho)\{\exp[\omega(\rho,r)]-1-\omega(\rho,r)\} \ . \tag{20}$$

This is the generalization of the Martynov-Sarkisov (MS) $B=\omega^2/2$ and the Percus-Yevick $B=\exp(\omega)-1-\omega$ approximations [1]. So, the differentiated closure is

$$\gamma^{[k]}(r)=\omega^{[k]}(r)+[a_2(\rho)\omega^2(\rho,r)]^{[k]} \ . \tag{21}$$

Using $C^{[k]}$ from (16c), we have substituted it in (18), satisfied $B_{k+2}^{v}=B_{k+2}^{c}$, and obtained B_{k+4} with $a_2^{[k]}$.

For $k=0$ and 1 solutions of the OZ equations are independent of (20) because the second term in (21) is equal to zero:

$$\begin{gathered} k=0, \quad \omega^{[0]}(r)=0, \quad \gamma^{[0]}(r)=0 \ , \\ h^{[0]}(r)=C^{[0]}(r)=f(r) \ . \end{gathered} \tag{22}$$

Next, $k=1$, $\gamma^{[1]}=f_{13}\circ f_{23}$, and

$$\omega^{[1]}(r)=\begin{cases}\dfrac{4\pi}{3}\left[\dfrac{r^3}{16}-\dfrac{3r}{4}+1\right] & \text{if } r\le 2\\ 0 \quad \text{if } r>2\,,\end{cases}$$

$$\gamma^{[1]}=\omega^{[1]},\quad h^{[1]}=[1+f(r)]\omega^{[1]}\,, \qquad (23)$$

$$C^{[1]}=f(r)\omega^{[1]}\,.$$

It gives exact consistent values for

$$B_2=\frac{2\pi}{3}\quad\text{and}\quad B_3=\frac{5}{8}\left[\frac{2\pi}{3}\right]^2\,.$$

For $k=2$, (19) is

$$\gamma_{12}^{[2]}=C_{13}^{[1]}\circ h_{23}^{[1]}\,. \qquad (24)$$

Substitution of (23) for (24) gives

$$\begin{aligned}\gamma^{[2]}(r)&=\left[\frac{2\pi}{3}\right]^2\left[\frac{15}{8}-\frac{15r}{8}-\frac{r^3}{4}\right],\quad 0\le r\le 1\\ &=\left[\frac{2\pi}{3}\right]^2\left[\frac{47}{16}-\frac{129r}{40}+\frac{9r^2}{16}+\frac{3r^3}{8}\frac{9r^4}{80}+\frac{r^6}{560}+\frac{81}{280r}\right],\quad 1\le r\le 2\\ &=\left[\frac{2\pi}{3}\right]^2\left[-\frac{81}{16}+\frac{162r}{40}-\frac{9r}{16}-\frac{r}{8}+\frac{9r}{80}-\frac{r}{560}+\frac{243}{280r}\right],\quad 2\le r\le 3\\ &=0,\quad 3\le r\le\infty\end{aligned}$$

$$\begin{aligned}&\omega^{[2]}=\gamma^{[2]}-a_2^{[0]}\omega^{[1]^2}\,,\\ &g^{[2]}=[1+f(r)][(\tfrac{1}{2}-a_2^{[0]})\omega^{[1]^2}+\gamma^{[2]}]\,,\\ &h^{[2]}=g^{[2]},\\ &C^{[2]}=[1+f(r)][(\tfrac{1}{2}-a_2^{[0]})\omega^{[1]^2}+\gamma^{[2]}]-\gamma^{[2]}\,.\end{aligned} \qquad (25)$$

Using (25) in $B_4^v=B_4^c$ we have found that $a_2^{[0]}=0.4172$ and $B_4=2.594$. The first two coefficients of the expansion $a_2(\rho)=\sum_i a_2^{[i]}\delta\rho^i$ are found numerically by the same procedure as shown in Table I. The procedure considered made it possible to find 14 virial terms, evaluating ten derivatives of correlation functions. One can see a close correspondence of our data and the diagram virial terms. The most important difference is the value of B_4. It is probably explained by the insufficiency of the $a_2\omega^2$ function. The value $a_2=0.437$ was reported by Herst [9].

TABLE I. Virial terms. $B_k^{(\text{dg})}$ denotes diagram virial terms.

		Martynov-Sarkisov		Percus-Yevic	
		$\varphi_i=-a\omega^2$		$\varphi_i=-2a(e^{\omega}-1-\omega)$	
k	$B_k^{(\text{dg})}$	B_k	$a^{[k-4]}$	B_k	$a^{[k-4]}$
4	2.6363	2.5929	0.4174	2.5929	0.4174
5	2.1242±0.001	2.0555	0.0298	2.0268	−0.0532
6	1.5555±0.016	1.4500	0.0308	1.4009	−0.0334
7	1.1647±0.034	1.0089	0.0129	0.9369	−0.0096
8	0.707–0.884	0.6955	0.0114	0.6307	0.0097
9		0.4143	−0.0013	0.4004	0.0038
10		0.2336	−0.0042	0.2336	−0.0285
11		0.0693	0.0156	0.0820	−0.0112
12		0.0780	0.0047		
13		0.0877	0.0578		
14		0.0866	0.0285		

However, obtained small values of $a_2^{[k]}$, good convergency of virial expansion, and agreement with MC data [10] make the suggested approximation rather attractive. On the other hand, independently of φ_i, absolute values of B_k coincide with the error range. One can see that the differences between modified MS and PY virial terms (see Table I) are less than the differences between any of them and the MC data. Thus, since $e^{\omega}-1-\omega\cong\omega^2$, the decisive role is played by the ω^2 term. This result has been obtained independently at $\rho\rightarrow 0$ and corresponds to consistent solution for dense HS fluid.

III. HIGH DENSITIES

The exact proof of convergency for virial sum in dense fluids is unknown [11]. Probably the convergency density is less than phase transition borders. In order to apply Eq. (19) for dense systems it is important to develop a method to avoid density expansions near $\rho=0$. An acceptable closure function should be expandable near $\rho=\rho_0$, $a_2(\rho)=\sum_i a_2^{[i]}\delta\rho^i$. We can select φ_i such that the unlinking procedure can be done by neglecting $a_2^{[i]}$. First-order expansion near ρ_0 is $a_2(\rho)=a_2(\rho_0)+a_2^{[1]}\delta\rho$. Thus the OZ equation must be solved in two close points: ρ_0 and $\rho_0+\delta\rho$, with simultaneous minimizing consistency functionals for both of them. Scanning through density from 0.2 to 1.0 we have found the result independent on $\delta\rho\le 0.02$. Exact consistency has been obtained. The corresponding function $a_2(\rho)$ is well fitted as

TABLE II. Equation of state. ρ is the density of HS fluid; $a_2^{[0]}$ is the coefficient in (25); $a_2^{[1]}$ is the derivative of $a_2^{[0]}$ under density (25); $Z_v = P/\rho\Theta$ is the evaluated compressibility factor (1) (according to the algorithm described in Sec. III); Z_{MC} is the compressibility factor from Monte Carlo [10] (for densities greater than 0.86, it is extrapolated); $Z_{\mathrm{vir}} = 1 + \sum_{k=2} B_k \rho^{k-1}$ is the compressibility factor from the virial equation of state (B_k are found by the algorithm described in Sec. II); κ_v is the compressibility derived from virial theorem (1); κ_c is the compressibility derived from expression (2).

ρ	$a_2^{[0]}$	$a_2^{[1]}$	Z_v	Z_{MC}	Z_{vir}	$\rho\Theta\kappa_v^{-1}$	$\rho\Theta\kappa_c^{-1}$
0.1	0.414	0.0965	1.239	1.240	1.240	1.512	1.512
0.2	0.422	0.0639	1.553	1.554	1.553	2.269	2.269
0.3	0.428	0.0568	1.966	1.968	1.966	3.388	3.388
0.4	0.435	0.0616	2.515	2.522	2.515	5.048	5.048
0.5	0.441	0.0763	3.253	3.269	3.254	7.534	7.534
0.6	0.449	0.0831	4.259	4.295	4.259	11.304	11.304
0.7	0.458	0.776	5.649	5.726	5.647	17.118	17.113
0.8	0.469	0.0773	7.606	7.768	7.593	26.259	26.246
0.9	0.478	0.0768	10.423	10.754	10.363	40.913	40.900
1.0	0.487	0.0757	14.583	15.256	14.356	65.075	65.141

$$a_2(\rho) = 0.4135 + 0.039\,47\rho + 0.036\,07\rho^2 \quad (0.2 < \rho < 0.95)\ . \qquad (26)$$

The small coefficient for the ρ^2 term confirms that first-order expansion for $a_2(\rho)$ is quite suitable. Here we see an important feature of the self-check. For example, usage of basis $\varphi_i = r^i$ ($\sigma \le r \le 1.4\sigma$) with the first-order density expansion for coefficients a_i gave results of insufficient quality. These results were not acceptable because of high values of coefficients $a_i^{[k]}$ derivatives. This is the reason why they cannot be neglected while unlinking.

With $\rho \to 0$, the a_2 value taken from the expression (26) (0.4135) is about the same for the virial terms evaluation (0.417). The compressibility factor $Z = P/\rho\Theta$ calculated in this way (see Table II) is about 0.5%, consistent with compressibility according to Eqs. (1) and (2). The absolute values are in excellent agreement with the virial equation of state.

IV. DISCUSSION

There are two ways to evaluate the thermodynamical functions of a liquid: the solution of integral equations and the minimizing of free-energy functional $F[g]$. We have already said that the first way is unsuitable to obtain an exact solution. The general expression for $F[g]$ is unknown. Therefore while realizing the second approach we have to involve an additional approximation [12]. Our method of thermodynamic consistency provides a set of exact equations (16a)–(16d) instead of the approximate expressions relating a radial distribution function and a bridge function. These expressions are derived *ab initio* and used in differential form, which makes possible local evaluation of disconsistency. Broadly speaking, the minimization of disconsistency makes it possible to find an exact solution of the problem.

The method contains a number of advantages. First, the higher the order of the derivatives in the initial equations that are taken into consideration, the more exact solution could be obtained. Comparing them, we can find out the accuracy of the results without using the numerical simulation data (MC or MD). Second, in our method we replace the integral of consistency

$$P^c(\rho_0) = \int_0^{\rho_0} [\rho\kappa(\rho)]^{-1} d\rho = P^v(\rho_0) \qquad (27)$$

with a set of local conditions (16d). In (27) $P^v(\rho)$ is determined by (1). To evaluate the integral (27) it is necessary to find $\kappa(\rho_i)$ for $0 < \rho_i < \rho_0$. In any of these points the compressibility is determined with an error, caused by the inexact consistency of the previous solution. While evaluating the integral this error is inherited from the previous points, which makes usage of (27) to obtain acceptable accuracy impossible. The equivalent expressions (16d) are free of this shortcoming.

The bridge function plays an important role in the theory of liquids, because it can provide information about the accuracy of the solutions. There are only two methods known for bridge function computation: the direct evaluation of elementary graphs and the simulation by means of numeric experiment. As far as we know, the technical problems preclude obtaining $B(r)$ by the first way. The second method was used successfully for HS fluid only [13]. It happened to be impossible to generalize this result for other potentials, because it would require time-consuming computations and accuracy of numerical experiment data that could not be achieved. The suggested method seems today the only one acceptable for bridge function evaluation. Our preliminary results [$B(r)$ for Lennard-Jones systems] have shown that there are no obstacles in principle. That is why we concentrated on the detailed study of HS fluid.

The improvement of accuracy depends on the basis functions selection. In order to check the working ability of our method we used a simple function taken from well-known liquid-theory approximations. However, we could take the complete basis of orthogonal polynomial functions $\varphi_i(r,\rho)$ in the interval [0.8;1.4], assuming $\varphi_i(r,\rho) = 0$ and $(d\varphi_i/dr) = 0$ for $1.4 \le r$. The latter seems to be promising due to its general form and the fact that the HS fluid distribution function $g(r)$ is determined by the values of a bridge function in the interval $\sigma \leq r \leq 1.4\sigma$ (for a Lennard-Jones fluid it would be $0.8\sigma \leq r \leq 1.3\sigma$). The values of the bridge function for lesser and greater distances do not influence the result. Probably expanding the bridge function in this interval to a Taylor series will give better accuracy.

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