

When $L = 1$, and $L = 1/2$, our results reduce to the results obtained in earlier work by Stell and Zhou (1989a); Zhou and Stell (1992a, 1992b); Lee and Rasaiah (1987); Baxter (1968a).

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ANALYTIC SOLUTION OF THE WERTHEIM'S PY APPROXIMATION FOR THE SHIELDED STICKY-POINT MODEL OF ASSOCIATING LIQUID

The analytical solution of the Wertheim's Ornstein — Zernike equation closed by the Percus — Yevick (PY)-like approximation for the shielded sticky-point model of associating liquid is presented. This model generalizes the one-site dimerizing Wertheim model for the case of associating liquids in which the bonding radius may be less than the core radius. Our numerical analysis leads to the conclusion that the present PY-like approximation provides satisfactory description of the system if the formation of associates does not change substantially an excluded volume of the system. In addition a simple approximation which relates the fraction of monomers (undimerized particles) and the strength of associative interaction is proposed. The predictions of this scheme agree well with nearly exact results of Zhou and Stell for all values of bonding radius.

1. Introduction

There has been considerable progress in the statistical — mechanical theory of associating liquids during the last decade [1—8]. Much of the effort has been focused on the development and application of the integral equation theory of associating systems. Two alternative versions of the integral equations theory have been proposed. In the series of papers by Cummings and Stell [1] the theory based on the Ornstein — Zernike (OZ) equation supplemented by common closure conditions, i. e., PY approximation, mixed PY and mean

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spherical (MSA) approximation have been used. In the studies of Wertheim [4] a new OZ-like integral equation supplemented by PY-like and hypernetted-chain (HNC)-like closure conditions has been proposed.

Most theoretical studies were carried out for so-called «primitive» models of associating liquids [1, 4, 6]. Such a models are simple enough for theoretical treatment and at the same time are able to reproduce the most important properties of this class of fluids, in particular — the formation of associates with a certain geometry. The structure of associates is provided by the special combination of the hardsphere repulsion and strong short-ranged attraction. The latter originates from the set of attractive sites embedded inside the hard core region. For a number of such a models i. e., for shielded sticky-shell model of chemical association introduced by Cummings and Stell [1], for one-site dimerizing model of Wertheim [4] and for Smith — Nezbeda model of associating liquid [6] the above mentioned integral equations were solved analytically [1, 7, 8].

The purpose of this study is to present an analytical solution of the Wertheim's OZ equation closed by PY-like condition for the model which generalizes one-site dimerizing model of Wertheim. This model has been proposed recently by Stell and Zhou [2] and corresponds to the associating liquid in which the formation of associates changes the excluded volume of the system. The paper is organized as follows. In Section 2 the model to under consideration is presented. Section 3 contains the Wertheim's OZ equation together with the PY-like closure condition and relation between the total and «monomer» densities. The Baxter functions for this system are obtained in Section 4. Numerical results, their analysis and conclusions are given in Section 5.

2. The model

Following [2] we consider the model with the pair potential that can be presented as a sum of two terms:

$$U(12) = U_{\text{ref}}(r) + U_{\text{ass}}(12), \quad (1)$$

where 1 and 2 denote the positions $\mathbf{r}_1, \mathbf{r}_2$ and orientations Ω_1, Ω_2 of the particles 1 and 2; $r = |\mathbf{r}_1 - \mathbf{r}_2|$. The reference part of the total potential is chosen to be:

$$U_{\text{ref}}(r) = \begin{cases} \infty, & r < L, \\ A, & L < r < \sigma, \\ 0, & r > \sigma \end{cases} \quad (2)$$

while the associative part appears due to the off center attractive site:

$$U_{\text{ass}}(x) = \begin{cases} \varepsilon, & x < a, \\ 0, & x > a, \end{cases} \quad (3)$$

where $A > 0, \varepsilon < 0, x$ is the distance between two attractive sites which belong to different particles

$$x = |\mathbf{r}_1 + \mathbf{d}(\Omega_1) - \mathbf{r}_2 - \mathbf{d}(\Omega_2)| \quad (4)$$

and d and a are subjected to the restriction $L < 2d + a < L - (2 - \sqrt{3})d$. This condition ensures that only dimers can be formed in the system.

To provide analytical treatment of the model we shall consider it within shielded sticky-point limit [2], i. e., we let $a \rightarrow 0, \varepsilon \rightarrow -\infty$ first and then take $A \rightarrow \infty$ under the restriction that the volume integral $K_0 = \int d(1) d(2) \times \times F(12)$ holds unchanged.

Here

$$\begin{aligned} F(12) &= e_{\text{ref}}(r) f_{\text{ass}}(x), & e_{\text{ref}}(r) &= \exp\{-\beta U_{\text{ref}}(r)\}, \\ f_{\text{ass}}(x) &= \exp\{-\beta U_{\text{ass}}(12)\} - 1, & \beta &= 1/kT. \end{aligned}$$

3. Integral equation and closure condition

Extension of the Wertheim theory to the model under consideration is straightforward and we shall therefore omit details. Similarly to [7], we consider an angle averaged version of the OZ-like integral equation which for the model presented takes form:

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_{lm} \rho_{lm} \int c_{il}(r_{13}) h_{mj}(r_{32}) dr_3, \quad (5)$$

where the functions h_{ij} and c_{ij} are the angle averaged analogues of the pair and direct correlation functions respectively; the lower indices in h_{ij} and c_{ij} take the values 0 and 1 and denote undimerized and dimerized states of the particle, respectively (see [4] for details). The matrix elements ρ_{ij} are defined as follows

$$\rho_{ij} = \delta_{i0}\delta_{j0}\rho + (\delta_{i0}\delta_{j1} + \delta_{i1}\delta_{j0})\rho_0, \quad (6)$$

where δ_{ij} is the Kronecker delta; ρ is the total number density and ρ_0 is the number density of «monomers» (undimerized particles).

The selfconsistent relation between the two densities and PY-like closure are given by:

$$\rho = \rho_0 + \rho_0^2 \int y_{00}(r) \bar{F}(r) dr \quad (7)$$

and

$$y_{ij}(r) = h_{ij}(r) + \delta_{0i}\delta_{0j}c_{ij}(r), \quad (8)$$

where \bar{F} is the angle average of F [2],

$$\bar{F}(r) = \begin{cases} 0, & r < L, \\ e^{-\beta A} (e^{-\beta B} - 1) (a + 2d - r)^2 (2a - 2d + r) / 24d^2 r, & L < r < 2d + a, \\ 0, & r > 2d. \end{cases} \quad (9)$$

The background correlation functions (BCF) y_{ij} are related to pair correlation functions h_{ij} as follows

$$h_{ij}(r) + \delta_{0j}\delta_{0i} = e_{\text{ref}}(r) y_{ij}(r) + \bar{F}(r) y_{00}(r) \delta_{i1}\delta_{j1}. \quad (10)$$

Relations (5), (7) and (8) form a closed set of equations for the «monomer» density ρ_0 and individual correlation functions h_{ij} . However, the structural quantity of main interest is the total pair correlation function. It can be calculated using the partial pair correlation functions $g_{ij} = h_{ij} + \delta_{0i}\delta_{0j}$

$$g(r) = g_{00}(r) + 2xg_{01}(r) + x^2g_{11}(r), \quad (11)$$

where x is the fraction of «monomers», $x = \rho_0/\rho$.

It turns out that the present PY-like approximation is not yet analytically solvable. An explicit analytical solution can be obtained within the shielded sticky-point limit [2], which leads to the following relation between the densities

$$\rho = \rho_0 + 4\pi BL^2 y_{00}(L) \rho_0^2, \quad (12)$$

and between the correlation functions h_{ij} and y_{ij}

$$h_{ij}(r) + \delta_{0i}\delta_{0j} = e_{\text{ref}}(r) y_{ij}(r) + \delta_{i1}\delta_{j1} B y_{00}(L) \delta(r - L). \quad (13)$$

Here the function \bar{F} containing the associative part of the pair potential has been substituted by the Dirac delta function: $\bar{F}(r) \rightarrow B\delta(r - L)$, where $B = K_0/(4\pi L^2)$.

4. Analytic solution of the Wertheim PY approximation

For the model under consideration the PY approximation (8) and (13) gives

$$c_{ij}(r) = 0 \text{ of } r > \sigma. \quad (14)$$

Hereafter, we shall assume that interparticle separation is measured in units of σ , i. e. $\sigma = 1$. Since all direct correlation functions are finite-ranged, the factorized version of the OZ equation (5) can be used

$$-rh_{ij}(r) = q'_{ij}(r) - 2\pi \sum_{lm} \rho_{ml} \int_0^1 q_{lm}(t) (r-t) h_{lj}(|r-t|) dt, \quad (15)$$

$$-rc_{ij}(r) = q'_{ij}(r) - 2\pi \sum_{lm} \rho_{ml} \frac{\partial}{\partial r} \int_0^1 q_{ml}(t) q_{lj}(r+t) dt, \quad (16)$$

where for $r > 1$ and $r < 0$ the Baxter functions q_{ij} are zero [7-9].

From (15), considered in the interval $0 < r < 1$, the set of differential equations for the functions q_{ij} follows

$$q'_{ij}(r) = \delta_{0j}(a_i r + b_i) - A \delta_{jl} [q_{i0}(r+L) - q_{i0}(r-L)] - \delta_{il} \delta_{jl} C L y_{00}(L) \delta(r-L), \quad (17)$$

where

$$a_i = \delta_{i0} - 2\pi \rho \int_0^1 q_{i0}(t) dt - 2\pi \rho_0 \int_0^1 q_{i1}(t) dt, \quad (18)$$

$$b_i = 2\pi \rho \int_0^1 q_{i0}(t) t dt + 2\pi \rho_0 \int_0^1 q_{i1}(t) t dt, \quad (19)$$

$$A = 2\pi \rho_0 L B y_{00}(L).$$

From this set of equations the functions q_{i0} are immediately obtained

$$q_{i0}(r) = \frac{1}{2} a_i r^2 + b_i r + c_i, \quad (20)$$

where c_i are the integration constants.

To find the functions q_{i1} one should consider equation (17) separately for $L < \frac{1}{2}$ and $L > \frac{1}{2}$. In both cases the total interval $0 < r < 1$ has to be divided into three subintervals

$$I_1 = [0, 1-L], \quad I_2 = [1-L, L], \quad I_3 = [L, 1] \text{ for } L > \frac{1}{2},$$

$$I_1 = [0, L], \quad I_2 = [L, 1-L], \quad I_3 = [1-L, 1] \text{ for } L < \frac{1}{2}$$

and (17) should be solved separately for each of this subintervals. We get

$$q_{i1}(r) = D_i^{(n)} r^3 + A_i^{(n)} r^2 + B_i^{(n)} r + C_i^{(n)} \text{ for } r \in I_n, \quad (21)$$

where the constant $D_i^{(n)}$, $A_i^{(n)}$ and $B_i^{(n)}$ at $n = 1$ and $n = 3$ for any L , are related to the parameters of the function q_{i0} by

$$D_i^{(n)} = A a_i \frac{n-2}{6}, \quad A_i^{(n)} = A \frac{2-n}{2} [(n-2) a_i L + b_i],$$

$$B_i^{(n)} = A(n-2) \left[\frac{1}{2} a_i L + (2-n) b_i L + c_i \right], \text{ for } L > \frac{1}{2} b y \quad D_i^{(2)} = A_i^{(2)} =$$

$$= B_i^{(2)} = 0, \text{ and for } L < \frac{1}{2} b y \quad D_i^{(2)} = 0, \quad A_i^{(2)} = -A L a_i, \quad B_i^{(2)} =$$

$$= -2A L b_i.$$

Here $C_i^{(n)}$ are the constants of integration. The expressions (20) and (21) for the Baxter functions q_{ij} involve the value of the BCF y_{00} for $r = L$, the «monomer» density ρ_0 and the set of twelve constants a_i , b_i , c_i , $C_i^{(n)}$. The problem of solving the OZ equation has thus been reduced to that of determining these parameters. Expression for y_{00} follows from the PY closure condition (8) in which the expressions (15) and (16) for the functions h_{ij} and c_{ij} have been used

$$y_{00}(L) = \frac{1}{L} (\xi + b_0) + a_0, \quad (22)$$

where

$$\xi = -2\pi \sum_{lm} \rho_{ml} \left\{ \frac{1}{8} a_m a_l (1-L)^4 + \frac{1}{3} \left[\frac{1}{2} a_m (a_l L + b_l) + a_l b_m \right] \times \right. \\ \left. \times (1-L)^3 + \frac{1}{2} [b_m (b_l + a_l L) + c_m a_l] (1-L)^2 + c_m (a_l L + b_l) (1-L) \right\}.$$

Expressions for a and b (18) and (19) form a set of four algebraic equations for the above fourteen unknown parameters. Additional equations needed arise from the conditions imposed on the functions q_{ij}

$$q_{i1}(L^-) - q_{i1}(L^+) = \delta_{i1} B L y_{00}(L),$$

$$q_{i1}(1-L^+) - q_{i1}(1-L^-) = 0,$$

$$q_{ij}(1^+) = 0.$$

We have now arrived at a closed set of fourteen nonlinear algebraic equations which after some algebra can be present as a set of twelve linear equations,

$$Z * M = R \quad (23)$$

and two algebraic equations

$$\rho_0 = \frac{-1 + \sqrt{1 + 16\pi B y_{00}(L) L^2 \rho}}{8\pi B y_{00}(L) L^2 \rho} \quad (24)$$

and (22). In (23)

$$Z = (a_{01}, a_{11}, b_{01}, b_{11}, c_{01}, c_{11}, C_{01}^{(1)}, C_{11}^{(1)}, C_{01}^{(2)}, C_{11}^{(2)}, C_{01}^{(3)}, C_{11}^{(3)})$$

and the elements of the matrices M and R along with details of the numerical solution are given in the Appendix.

Knowledge of q_{ij} enables one now to calculate g_{ij} . To obtain g_{ij} for $r > 1$ one may use the iterative scheme of Perram [10], but its direct application to (15) is not convenient. A form more appropriate for numerical calculations is obtain from (15) after carrying out some algebra:

$$r g_{ij}(r) = P_{ij}(r) + 2\pi \sum_{lm} \rho_{lm} \int_0^{r-1} q_{il}(t) g_{mj}(r-t) dt + \\ + B \rho_0 L \delta_{j1} q_{i0}(r-L) y_{00}(L), \quad (25)$$

where P_{ij} has the functional form of the function q_{ij} for $r \in I_3$.

Application of Perram's iterative scheme requires the knowledge of the contact values of g_{ij} . The latter follows from (25)

$$g_{ij}(1^+) = \delta_{0j}(a_i + b_i) + \delta_{j1} A q_{i0}(1-L). \quad (26)$$

5. Results and discussion

The main quantities of interest, obtained from the solution given in the proceeding section are the pair correlation functions $g_{ij}(r)$ and the fraction of «monomers» $x = \rho_0/\rho$ (or the fraction of «bonded» particles $\alpha = 1 - x$). The selfconsistent relation between the densities (7) contains the contribution from the pair correlations in the form of the integral with integrand involving the BCF y_{00} . In the shielded sticky-point limit this integral is substituted by the value of the function y_{00} at $r = L$ (12). Experience has shown that usual PY approximation give satisfactory prediction for the BCF of the hard sphere system only for $r \cong 1$, while in the rest of the overlap region the results appear to be unsatisfactory. One should expect therefore that the present PY-like approximation will give the BCF y_{00} with the same accuracy. To extend the applicability of the present PY approximation to the case of intermediate and small L we combine the integral equation theory with the thermodynamic perturbation theory (TPT) [4], appropriately modified. The latter is used to approximate the density of «monomers» $\rho_0 \simeq \rho_0^{(rel)}$. For this purpose $y_{00}(L)$

in (12) and (13) is substituted by the value of the BCF $y_{(\text{ref})}(L)$ of the correspondent reference system. In the usual TPT theory one should use as a reference system just the system of hard spheres with the density which is equal to the density of the original associating system. However such a reference system does not take into account the changes in the excluded volume due to the formation of associates. The importance of this effect increases with the decrease of the value of L . In the present study the hard sphere system with the total density $\rho_{(\text{ref})}$ which is related to the monomer density $\rho_0^{(\text{ref})}$ and L by

$$\rho_{\text{ref}} = \rho_0^{(\text{ref})} + \frac{3}{\pi} (\rho - \rho_0^{(\text{ref})}) V_d \quad (27)$$

is used as a reference system. Here Y_d is the volume of the dumbbell with elongation L .

The BCF of the reference system y_{ref} is calculated using the theory of Ballance and Speedy [11]

$$y_{\text{ref}}(r) = y_{\text{ref}}(0) \exp[-\Delta V(r)(\alpha_1 + \alpha_2 r)], \quad (28)$$

where $y_{\text{ref}}(0) = \exp(\Delta\mu_{hs}/kT)$, $\Delta\mu_{hs}$ is the excess chemical potential of the hard sphere system;

$$\Delta V(r) = \frac{1}{3} \pi \left[4 - 3 \left(1 - \frac{1}{2} r \right) \left(1 - \frac{1}{4} r^2 \right) - \left(1 - \frac{1}{2} r \right)^3 \right]$$

and the constants α_1 and α_2 are obtained from (28) and from the following two exact results

$$\left. \frac{\partial}{\partial r} \ln y_{\text{ref}}(r) \right|_{r \rightarrow 0} = -6\eta_{\text{ref}} y_{\text{ref}}(1), \quad P/(\rho_{\text{ref}} kT) = 1 + 4\eta_{\text{ref}} y_{\text{ref}}(1).$$

Here $\eta_{\text{ref}} = \frac{\pi}{6} \rho_{\text{ref}} \sigma^3$ and we have used the Carnahan — Straling equation of state [12].

We have now arrived at a closed set of two nonlinear equations (12) and (28) for two unknowns $\rho_0 = \rho_0^{(\text{ref})}$ and $y_{00}(L) = y_{\text{ref}}(L)$. Thus the initial problem of solving the coupled set of equations (5), (8) and (12) reduces to the solution of the OZ equation (5) closed by the closure condition (8) where the «monomer» density ρ_0 and BCF $y_{00}(L)$ are previously obtained as a solution of the set of equations (12) and (28).

In Fig. 1 and 2 we present the fraction of «dimerized» particles $\alpha = 1 - \rho_0/\rho$ as a function of total density ρ for different L and K_0 . We compare our results with those of Zhou and Stell [2], which were obtained using an exact relation between the usual BCF for associating system and α . The BCF for associating system was calculated from the very accurate Boublik equation of state [13]. Zhou and Stell [2] have considered the binary mixture of hard spheres of equal size and associative interaction only between the particles of different sort. As was shown in [14] description of such model reduces to the description of the model discussed in the present study but with the value of K_0 equal half of that used in [2]. One can see, that agreement between the results of the modified TPT and nearly exact results of Zhou and Stell is satisfactory for all L and for all K_0 . This demonstrates the importance of the correct accountment of the effects appearing due to the changes in the excluded volume of the system.

In Fig. 3—10 we show the pair correlation function for different values of L , K_0 and total density ρ predicted by the present PY-like approximation and by its combination with the modified TPT (MTPT). In all cases the labeling is the same: the results of Wertheim PY approximation are shown by the solid line, while the results of the PY/MTPT are given by the dashed line. To verify the theory we compare our results with those obtained from the numerical solution of the RISM equation (dotted line) for the mixture of hard spheres and dumbbells with elongation L . The hard sphere density $\rho_{h.sp}$ and the density of the dumbbells ρ_d of this two-component mixture follows from

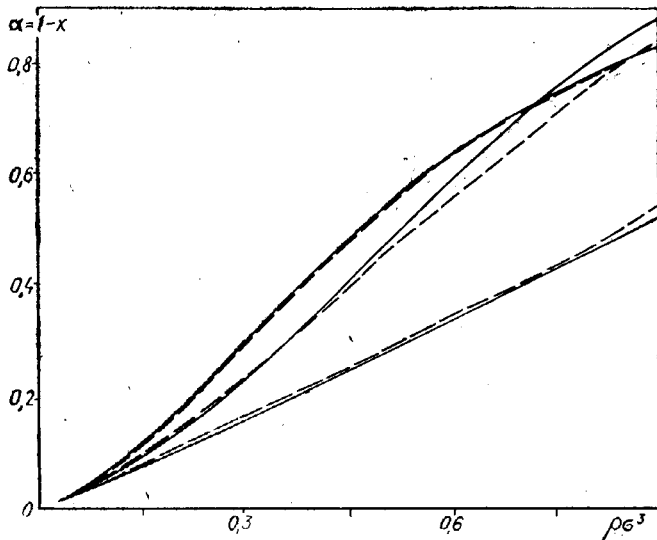


Fig. 1. The fraction of dimerized particles $\alpha = 1 - x$ as a function of the reduced density $\rho\sigma^3$ for $K_0 = 1$; $L = 1, 1/2$, and 0 from the bottom to the top at $\rho\sigma^3 = 0,6$. The solid line presents α obtained by using modified TPT of Wertheim, the dashed line shows the results of Zhou and Stell [2]. For $L = 0$ both theories gives indistinguishable results

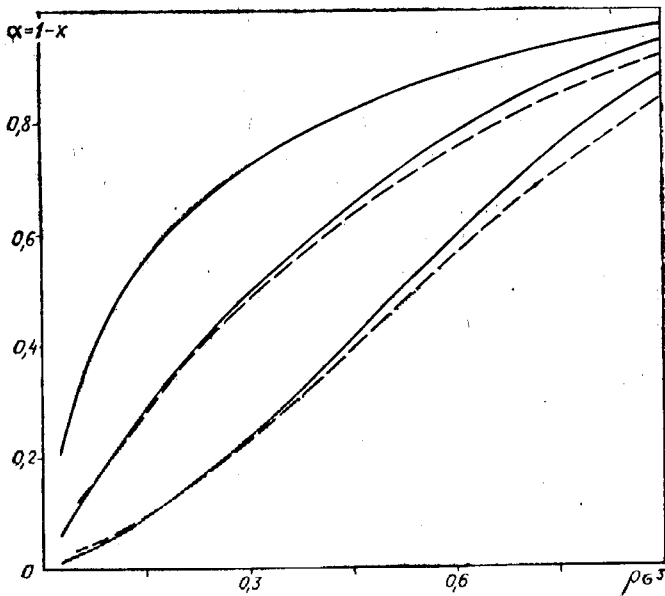


Fig. 2. The same as Fig. 1 for $L = 1/2$ and $K_0 = 1,5$ and 25 from the bottom to the top. Notations are the same as those used in Fig. 1.

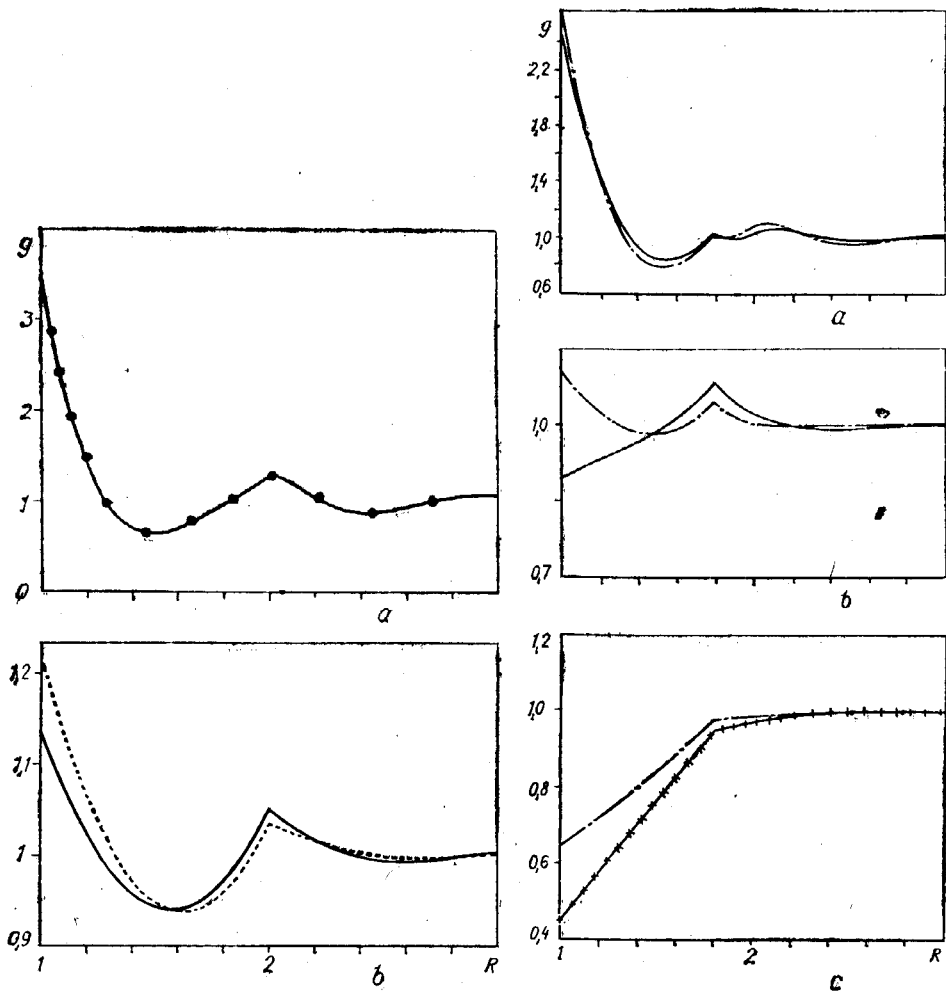


Fig. 3. Angle averaged pair correlation function for the shielded sticky-point model in the full associated limit ($K_0 \rightarrow \infty$) at $L = 1$ and $\rho\sigma^3 = 0,8$ (a), $0,4$ (b). The solid line represents the results of the Wertheim's PY approximation. The dotted line is the RISM results for correspondent system of dumbbells

Fig. 4. The same as Fig. 3 for $\rho\sigma^3 = 0,823$ (a), $0,412$ (b), 0 (c) and $L = 0,8$. In addition, the squares represent an exact results for the site-site pair correlation function for $\rho\sigma^3 \rightarrow 0$ (Ref. 16)

the MTPT

$$\rho_{h.sp} = \rho_0^{(ref)}, \quad \rho_d = \frac{1}{2} \rho_1^{(ref)}.$$

The pair correlation function, which is presented in the figures, is related to the set of the site-site correlation functions by $g(r) = (1-x)^2 g_{ss}(r) + 2x(1-x) g_{ms}(r) + x^2 g_{mm}(r)$, where s and m denote the site and the monomer (undimerized hard sphere), respectively. In addition to that in the case of the full association limit ($K_0 \rightarrow \infty$, Fig. 3—6) we compare our results with the predictions obtained from the computer simulation [15] by the Monte-Carlo (MC-squares) method.

We shall first analyze the case of full association limit. Since the present integral equation theory is based on the consistent diagrammatic analysis the PY approximation of Wertheim, in contrast to the RISM equation, correctly reproduces the low density behavior of the pair correlation function for all values of L (Fig. 4c, 6c). With the increase of the density the results of the present theory remains satisfactory for the elongation L close to the unity.

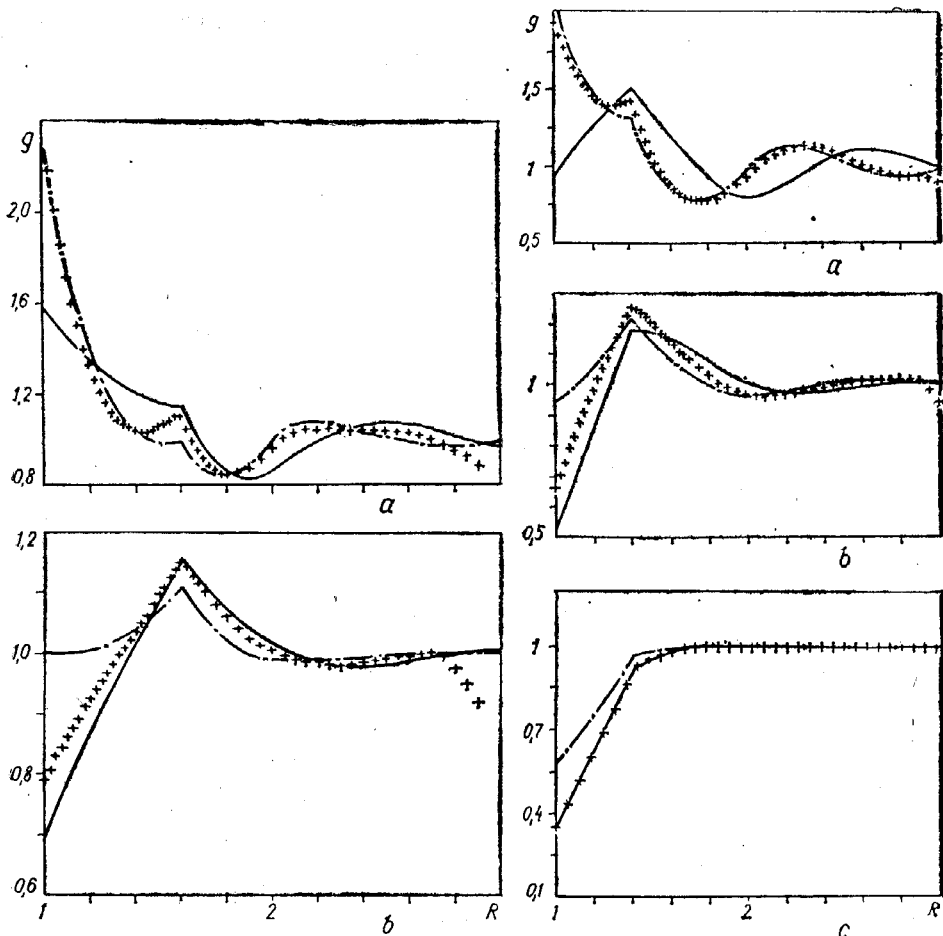


Fig. 5. The same as Fig. 3 for $\rho\sigma^3 = 0,893$ (a), $0,446$ (b) and $L = 0,6$. Here the squares is the results of the MC simulation (Ref. 15)

Fig. 6. The same as Fig. 5 for $\rho\sigma^3 = 0,765$ (a), $0,510$ (b), 0 (c) and $L = 0,4$. Here the squares in (c) denote an exact result for the site-site pair correlation function for $\rho\sigma^3 \rightarrow 0$ (Ref. 6)

The discrepancy between the predictions of Wertheim's PY approximation and MC results in the high density region increases with the decrease of L (Fig. 3—6). For all values of the density ρ and elongation L the pair correlation function, obtained from the present PY approximation, and that which follows from PY/MTPT in the full association limit coincide.

Similar as in the previous case in the case of partially associated system the predictions of PY and PY/MTPT remains satisfactory for all densities and all degrees of association at $L \cong 1$ (Fig. 7, 8). With the decrease of L the results of the PY approximation for the high and intermediate densities become unsatisfactory. At the same time the combination of PY and MTPT gives rather good prediction for the structure of the system at low degree of association (low K_0 , Fig. 9a, 10a).

The above analysis and short discussion lead to the conclusion that the present PY approximation gives satisfactory predictions for the structure of shielded stickypoint model of associated liquid if the formation of associates does not change substantially an excluded volume of the system. For the present model the excluded volume decreases as the parameter L decreases from unity and therefore for intermediate and small values of L one needs more sophisticated closures. Appropriate closures for that case are now under study and will be reported in due course.

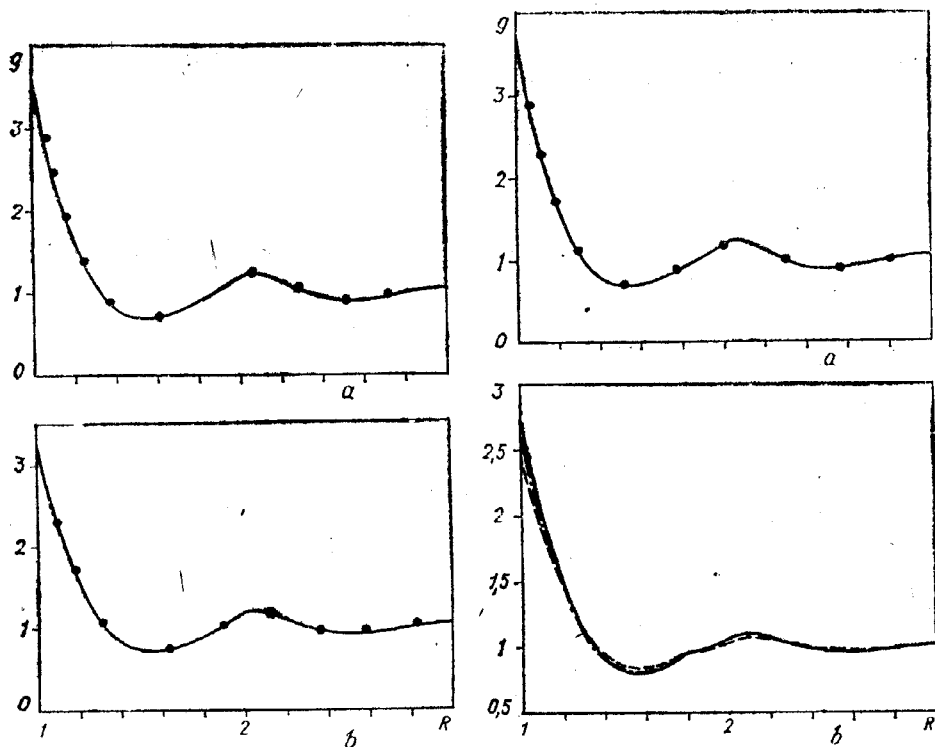


Fig. 7. Angle averaged pair correlation function for the shielded sticky-point model at $K_0 = 0,01$ (a), 1 (b), $\rho\sigma^3 = 0,8$ and $L = 1$. The solid line represents the results of the Wertheim's PY approximation. The dotted line is the RISM results for the correspondent mixture of hard spheres and dumbbells; the dashed line corresponds to the combination of Wertheim's PY and MTPT. On the scale of the figure the results of PY and PY/MTPT are indistinguishable

Fig. 8. The same as Fig. 7 for $\rho\sigma^3 = 0,829$ and $L = 0,8$

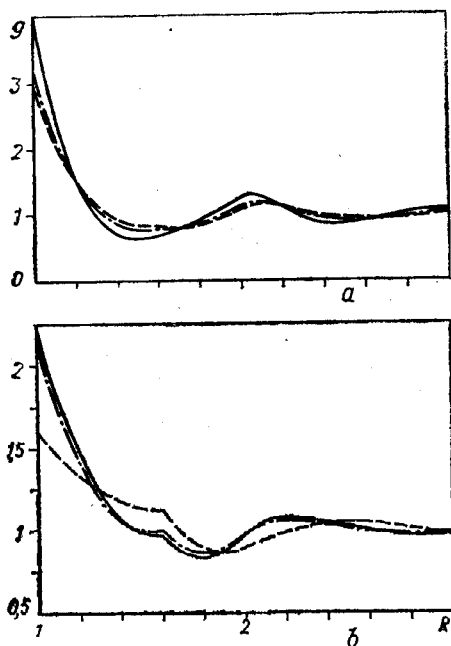


Fig. 9. The same as Fig. 7 for $\rho\sigma^3 = 0,893$ and $L = 0,6$

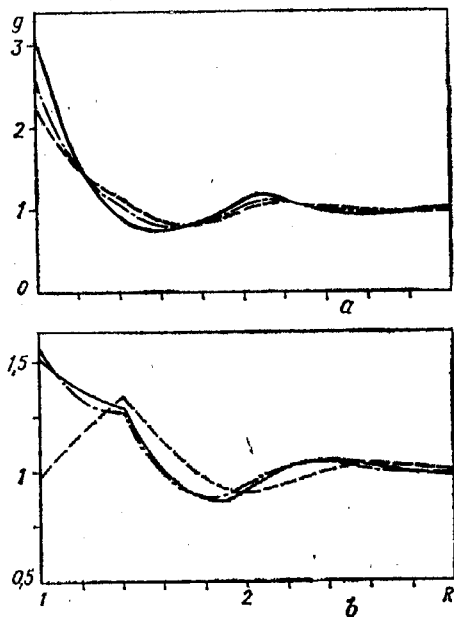


Fig. 10. The same as Fig. 7 for $\rho\sigma^3 = 0,765$ and $L = 0,4$

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It is a pleasure to express our gratitude to Professor M. Holovko for helpful discussion and criticism.

Appendix

The nonzero elements of the matrices M and R are

$$M_{1,1} = 1 + \frac{1}{3} \pi \rho + \pi A \rho_0 (1 - L^2) \left(\frac{1}{2} L - \frac{1}{3} \right) L,$$

$$M_{3,1} = \pi [\rho + A \rho_0 L (L - 1)],$$

$$M_{5,1} = 2\pi [\rho + A \rho_0 L (1 - L)], \quad M_{1,3} = \pi \left[\frac{1}{4} \rho + \frac{1}{3} A \rho_0 L (L^2 - 1) \times \right. \\ \left. \times \left(\frac{1}{2} - L \right) \right],$$

$$M_{3,3} = \frac{2}{3} \pi \rho - 1 + \pi \rho_0 A L \left(\frac{5}{6} L^3 - L^2 + \frac{1}{2} L - \frac{1}{3} \right),$$

$$M_{5,3} = \pi [\rho + 2A \rho_0 L (L - 1)],$$

$$M_{1,9} = \frac{1}{2},$$

$$M_{3,9} = 1, \quad M_{5,9} = 1, \quad M_{1,11} = \frac{1}{2} A \left(L^2 - L + \frac{1}{3} \right),$$

$$M_{3,11} = A \left(\frac{1}{2} - L \right), \quad M_{5,11} = A, \quad M_{11,11} = 1, \quad R_1 = 1;$$

(a) for $L \geq \frac{1}{2}$

$$M_{7,1} = 2\pi \rho_0 (1 - L),$$

$$M_{9,1} = 2\pi \rho_0 (2L - 1),$$

$$M_{11,1} = M_{7,1},$$

$$M_{7,3} = \pi \rho_0 (1 - L)^2,$$

$$M_{9,3} = \pi \rho_0 (2L - 1),$$

$$M_{11,3} = \pi \rho_0 (1 - L^2),$$

$$M_{1,5} = \frac{1}{6} A (L^3 - 1),$$

$$M_{3,5} = \frac{1}{2} A (L^2 - 1),$$

$$M_{5,5} = A (L - 1),$$

$$M_{7,5} = 1,$$

$$M_{9,5} = -1,$$

$$M_{1,7} = \frac{1}{6} A L^3,$$

$$M_{3,7} = -\frac{1}{2} A L^2,$$

$$M_{5,7} = A L,$$

$$M_{9,7} = -1,$$

$$R_6 = 0,$$

$$R_8 = -B L y_{00} (L),$$

(b) for $L < \frac{1}{2}$

$$M_{7,1} = 2\pi \rho_0 L,$$

$$M_{9,1} = -2\pi \rho_0 (2L - 1),$$

$$M_{11,1} = M_{7,1},$$

$$M_{7,3} = \pi \rho_0 L^2,$$

$$M_{9,3} = -\pi \rho_0 (2L - 1),$$

$$M_{11,3} = \pi \rho_0 L (2 - L),$$

$$M_{1,5} = \frac{1}{6} A L^3,$$

$$M_{3,5} = \frac{1}{2} A L^2,$$

$$M_{5,5} = A L,$$

$$M_{7,5} = -1,$$

$$M_{9,5} = 1,$$

$$M_{1,7} = \frac{1}{6} A (L^3 - 1),$$

$$M_{3,7} = \frac{1}{2} A (L^2 - 1),$$

$$M_{5,7} = A (L - 1),$$

$$M_{9,7} = 1,$$

$$R_6 = -B L y_{00} (L),$$

$$R_8 = 0.$$

We use an iterative method to solve the set (22), (23) and (24). The set is first turned into a set of linear equations using as an input estimates for ρ_0 and $y_{00} (L)$. We start from the high temperature limit which yields $\rho_0 = \rho$ and $y_{00} (L) = y_{PY} (L)$, where $y_{PY} (L)$ is the usual BCF obtained from the regular PY approximation.

Solution of the set of linear equations (23) is used then to get a new estimates of $y_{00} (L)$ from (22) and for ρ_0 from (24).

The convergence of this iteration scheme is rather fast: about 15 or 20 iteration loops are sufficient to obtain the solution with an accuracy up to 6 digits.

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TRIPLET CORRELATIONS IN FLUIDS

Six schemes for calculating the triplet correlation function of a fluid are considered. Four are based upon density expansions and their resummation. The other two approximations are based upon considering one or more of the particles to be the source of an inhomogeneity in the fluid and then using the formalism of the theory of inhomogeneous fluids. In contrast to the other approximations, the two approximations based on the theory of inhomogeneous fluids are inherently asymmetric, although they can be symmetrized easily. A few thoughts about the relative merits of the six schemes are given.

1. Introduction

Interest in the theory of fluids centers on the thermodynamic properties of the fluid and its structure, as described by the h -body correlation functions, $g_{1...h} = g(r_1...r_h)$, where $r_1...r_h$ are the positions of the h molecules. The greater the value of h , the greater the computational difficulty and the greater the difficulty in comprehending the results, if numerical, because of the increasing number of arguments of $g_{1...h}$ as h increases. For central forces, g_{12} is a function of one spatial variable while g_{123} and g_{1234} are functions of three and six variables, respectively. To this one must add the thermodynamic

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