Modification of the singlet equation for a molecular system of solid spheres near a solid surface in the Percus-Yevick approximation

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Abstract. An analysis of theoretical methods for studying the molecular structure of liquids bordering a solid surface was carried out. It was established that the currently existing nonlinear integral equations for partial distribution functions do not have an analytical solution for spatially inhomogeneous liquids. A linear integral equation having an analytical solution for a system of solid spheres near a solid surface was proposed.

1. Introduction
The microscopic description of close order in liquids, as a rule, is based on integral equations for one- and two-particle distribution functions. The core of such equations contains the infinite functional series of irreducible diagrams. Cut off of these infinite series, usually performed, produces various nonlinear integral equations. One of them is the Percus-Yevick (PY) equation for uniform spatial liquid [1] allows one to get an analytical solution for hard sphere system. Other similar equations don’t have analytical solution.

For space-heterogeneous systems, such as a liquid near a hard surface, two-particle distribution function is replaced by its value taken far from surface. We call such substitution as singlet approximation. In this approximation we obtain the equation for one-particle distribution function, which depends on single variable – distance from surface. This equation can be solved only numerically [2] and even for modern computers such calculations take much time.

We suggest to determine the contribution of PY approximation into irreducible diagrams so that other series terms will compensate all non-linear behavior. As a result, we obtain the linear Fredholm integral equation of the second kind, having an analytical solution for hard sphere system near hard surface. This equation can be generalized for molecular systems with realistic potentials, which is important for melting amorphization study.

2. Common equations

2.1. Common equations
Statistics considering molecular system is based on Born-Green-Yvon-equations system, known as BGY hierarchy, for l-particle functions \(G_{i_1 \ldots i_l}(r_1, \ldots, r_l)\) for ensemble of identical particles. The particles having diameter \(\sigma\) interact each other through potential \(\Phi_{ij}(r_{ij})\), where \(r_{ij} = |r_i - r_j| > \sigma\) is the distance between centers of particles \(i\) and \(j\).
The BGY-equations system may be transformed to equations for one- and two-particle distribution functions, which may be written as Ornstein-Zernike [3]:

$$\omega_i = n \int G_i C_{ij}^{(1)} d(2) + \ln a \quad ; \quad h_{12} = C_{12}^{(2)} + n \int G_j C_{ij}^{(2)} h_{ij} d(3)$$  \hspace{1cm} (1)

Here we integrating over coordinates of $i$-particle: $d(i) = d\mathbf{r}$, $n$ is density, $G_i$ is $\exp(-\Phi_i(kT)^{-1} + \omega_i)$ is one-particle distribution function, which describes particle position; $\Phi_i$ is potential energy in external field; $\omega_i$ is one-particle thermal potential; $a$ is activity coefficient, which is defined by condition of passing to isotropic system. Pair correlation function $h_{ij} = [\exp(-\Phi_j(kT)^{-1} + \omega_j) - 1]$ is connected with two particle distribution function by expression: $G_{ij} = G_j G_i (1 + h_{ij})$; $\omega_{ij}$ is two-particle thermal potential, which takes into account indirect interaction of two particles; $C_{ij}^{(k)}$ are direct correlation functions:

$$C_{ij}^{(1)} = h_{ij} - \omega_{ij} - \frac{1}{2} h_{ij} (\omega_{ij} + M_{ij}^{(1)}) \quad ; \quad C_{ij}^{(2)} = h_{ij} - \omega_{ij} + M_{ij}^{(2)}$$  \hspace{1cm} (2)

Functions $G_i(\mathbf{r}_1)$ and $G_{12}(\mathbf{r}_1, \mathbf{r}_2)$ describing internal structure are critical ones. Let’s obtain thermodynamic parameters of the system. Equations (1) and (2) are difficult to solve because $M_{ij}^{(1)}$ and $M_{ij}^{(2)}$ contains infinite series of distribution functions. To use the following equations in practice one should approximate these series by simple expressions (closures). In such a manner we can obtain approximated equations for high density systems.

Space-homogeneous systems (isotropic liquids in absence of external fields and surfaces) with $G_i(\mathbf{r}) = 1$, $\omega_i = 0$, $C_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = C_{ij}^{(1)(0)}(r_{12})$ are of special interest. In these systems the first equation in (1) can be used to evaluate chemical potential $\mu = \ln a = const$. The second one determines direct correlation function $C_{12}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = C_{12}^{(2)(0)}(r_{12})$, which can be evaluated by number of methods [3]. For PY equation (1) direct correlation function is $C_{12}^{(2)(0)}(r_{12}) = h_{12} - (\exp(\omega_{12}) - 1)$. As a result, an exponential non-linearity lowers to polynomial one for hard sphere system, i.e. the non-linearity becomes weaker. That provides possibility to get analytical solution.

For space-heterogeneous systems, such as a liquid near a hard surface, functions $G_i = G_i(\mathbf{r}_1)$, $C_{ij}^{(1)} = C_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$ describe microstructure of the substance and allow to obtain all thermodynamic parameters.

2.2. Singlet approximation

Direct solution of many variables’ equations (1-2) is possible only numerically [2]. It requires a lot of computational time. One can simplify this task using boundary value $C_{12}^{(1)(0)}(r_{12})$ for direct correlation function $C_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$. In this case, depending on closure to evaluate $M_{ij}^{(1)}$, we get different kinds of singlet equations, describing local density profile $n(\mathbf{r}_i) = nG_i(\mathbf{r}_i)$ near hard surface. All of them contain non-linear terms and have to be solved numerically. Review of solutions is presented in [2]. It should be stressed that analytical solution for one-particle distribution function is possible for special cases, for example, one- and two-dimension problem [4].
2.3. Molecular system of liquid near hard surface

Space-heterogeneous systems (liquid near a hard surface) are described by one- and two-particle distribution functions: \( G_1(\mathbf{r}_1) \) and \( G_{12}(\mathbf{r}_1, \mathbf{r}_2) \). Boundary conditions for these equations take into account a transition from a hard surface to a liquid.

Let’s form the equations for molecular system near hard surface. When solving first equation of (1) origin is located in the center of the particle, which contacts with hard surface. The \( z \) axis is perpendicular to the surface; thus, the whole liquid is placed in upper half-space (\( z \geq 0 \)). Bottom half-space (\( z < 0 \)) is unavailable for the particles. Such a system has axial symmetry,

\[
G_1(\mathbf{r}_1) = G_1 (z_i) = \exp(\omega_i (z_i)) \quad G_{12} (\mathbf{r}_1, \mathbf{r}_2) = G_{12} (z_i, z_2, r_{12})
\]

Here \( r_{12} \) is measured in particle diameter units, \( z_i \geq 0 \) – particle distance from the surface. Boundary conditions for \( G_1(\mathbf{r}_1) \) and \( G_{12}(\mathbf{r}_1, \mathbf{r}_2) \) are defined as follows

\[
\omega_i (z_i) \to 0 \quad G_i (z_i) \to 1 \quad G^{(0)}_{12} (r_{12}) = \lim_{\substack{z_i \to -\infty \quad z_2 \to \infty \quad r_{12} \to \text{const}}} G_{12} (z_i, z_2, r_{12})
\]

2.4. Modification of the singlet equation

We suggest modification of singlet approximation, which allows analytical solution for hard sphere system near hard surface.

In the first equation (1) for a single-particle distribution function, we combine the starting point with the center of the particle 1. After integration performed in a cylindrical coordinate system, \( d(\mathbf{r}_2) = \rho_{12} d \rho_{12} dz_{12} d\Phi_{12} \), \( r_{12}^2 = \rho_{12}^2 + z_{12}^2 \), \( z_{12} = z_2 - z_i \), we get

\[
\omega_i (z_i) = 2 \pi n \int_{-\infty}^{\infty} dz_{12} G(z_i + z_{12}) \int r_{12} dr_{12} C_i^{(1)}(r_{12}, z_i, z_{12}) - 2 \pi n \int_{-\infty}^{\infty} dz_{12} \int r_{12} dr_{12} C^{(1,0)}_{12}(r_{12})
\]

(5)

We determined the constant \( \ln a \) from the condition of spatial homogeneity (4). The boundary value of the function \( c_{12}^{(1)}(r_{12}, z_i, z_{12}) \) is \( C_{12}^{(1,0)} (r_{12}) \). The starting point in (5) we put on the surface, thus the distance from the surface to the particle 1 is equal to \( z_i \). After dividing the limits of integration in the second term into intervals \((-\infty, -z_i)\) and \((-z_i, +\infty)\), equation (5) takes the form

\[
\omega_i (z_i) = 2 \pi n \int_{-\infty}^{\infty} dz_{12} \int r_{12} dr_{12} G_i (z_i) C_i^{(1)}(r_{12}, z_i, z_{12}) - 2 \pi n \int_{-\infty}^{\infty} dz_{12} \int r_{12} dr_{12} C^{(1,0)}_{12}(r_{12})
\]

(6)

We modify equation (6). The unknown function in the first integral can be written as

\[
G_i (z_i) C_i^{(1)}(r_{12}, z_i, z_{12}) = C_{12}^{(1,0)} (r_{12}) + S_{12}^{(1)} (r_{12}, z_i, z_{12})
\]

(7)

where \( S_{12}^{(1)} (r_{12}, z_i, z_{12}) \) contains the contribution of all irreducible diagrams. We assume that all irreducible diagrams are compensated and can be represented as

\[
2 \pi n \int_{-\infty}^{\infty} dz_{12} \int r_{12} dr_{12} G_i (z_i) S_{12}^{(1)} (r_{12}, z_i, z_{12}) = \omega_i (z_i) - (e^{\alpha_i (z_i)} - 1)
\]

(8)

As a result, equation (6) takes the form

\[
(e^{\alpha_i (z_i)} - 1) - 2 \pi n \int_{-\infty}^{\infty} dz_{12} (e^{\alpha_i (z_{12})} - 1) \int r_{12} dr_{12} C_{12}^{(1,0)} (r_{12}) = -2 \pi n \int_{-\infty}^{\infty} dz_{12} \int r_{12} dr_{12} C_{12}^{(1,0)} (r_{12})
\]

(9)
This is the second kind of Fredholm equation. The core of the equation and its right hand side are known functions. In the Percus-Yevick approximation, we have

\[
C_{i2}^{(1,0)}(r_{i2}) = C_{i2}^{(2,0)}(r_{i2}) = -(\alpha + \beta r_{i2} + \gamma r_{i2}^3)\Theta(1 - r_{i2})
\]

\[
\alpha = \frac{(2\lambda + 1)^2}{(\lambda - 1)^4}, \beta = -\frac{3\lambda(2 + \lambda)^2}{2(\lambda - 1)^4}, \gamma = \frac{\lambda(2\lambda + 1)^2}{(\lambda - 1)^4}, \lambda = \frac{n}{12}
\]

where \(\Theta(1 - r_{i2})\) is the Heaviside function. The point corresponds to a physically unattainable state. The maximum value of a dense package is equal to. \(\lambda \approx 0.7\). At the interval \(0 \leq r_{i2} \leq 1\), the \(C_{i2}^{(2,0)}(r_{i2})\) function for dense packaging differs slightly from the maximum value \(\lambda = \frac{3}{2}\). Therefore, with a good degree of accuracy, we can assume

\[
C_{i2}^{(2,0)}(r_{i2}) = -\eta < 1
\]

where constant \(\eta < 1\). As a result, we get a system of equations for the function \(f(z_i) = (e^{\eta z_i^3} - 1)\)

\[
f(z_i) - \eta \int_0^{z_i} dz_2 f(z_2) (1 - (z_2 - z_i)^2) = \eta \int_{z_i}^{1} dz_2 (1 - (z_2 - z_i)^2) \quad z_i \leq 1
\]

\[
f(z_i) = \eta \int_{z_i}^{1} dz_2 f(z_2) (1 - (z_2 - z_i)^2) \quad z_i \geq 1
\]

3. Results and Discussion
As far as right part of equation (13) is 3-rd order polynome

\[
\eta \int_{z_i}^{1} dz_2 (1 - (z_2 - z_i)^2) = \eta \left(\frac{1}{3} z_i^3 - 3z_i + 2\right)
\]

we look for solution for (13) in Taylor series with the precision up to cubic terms

\[
f(z_i) = f(0) + \frac{f^{(1)}(0)}{1!} z_i + \frac{f^{(2)}(0)}{2!} z_i^2 + \frac{f^{(3)}(0)}{3!} z_i^3
\]

When evaluating left part of integral (13) the value of function \(f(z_i)\) and its 1st derivative \(f^{(1)}(z_i)\) at \(z_i = 1\) should be known. From (16) we get

\[
f(1) = f(0) + \frac{f^{(1)}(0)}{1!} + \frac{f^{(2)}(0)}{2!} + \frac{f^{(3)}(0)}{3!}
\]

Substituting decomposition (16) into (13), making equal expressions with the same \(z_i\) power and assuming (17), we obtain the algebraic equations system

\[
(1 - \frac{2}{3}\eta) f(0) - \eta \left(\frac{f^{(1)}(0)}{4} + \frac{f^{(2)}(0)}{15} + \frac{f^{(3)}(0)}{72}\right) = -\frac{2\eta}{3}
\]

\[
\eta f(0) - (1 - \frac{2}{3}\eta) f^{(1)}(0) + \eta \left(\frac{f^{(2)}(0)}{4} + \frac{f^{(3)}(0)}{15}\right) = -\eta
\]
\[ \eta f^{(3)}(0) - (1 - \frac{2}{3}\eta) f^{(2)}(0) + \eta \frac{f^{(3)}(0)}{4} = 0 \]  
(20)

\[ 2\eta f^{(0)} - \eta f^{(2)}(0) + (1 - \frac{2}{3}\eta) f^{(2)}(0) = -2\eta \]  
(21)

and get its solution as

\[ f(0) = \frac{1}{d(\eta)} (-1800 + 192\eta - 1481\eta^2 + 808\eta^3 - 1325\eta^4) \]  
(22)

\[ f^{(1)}(0) = \frac{60\eta}{9d(\eta)} (135 - 306\eta + 93\eta^2 + 124\eta^3) \]  
(23)

\[ f^{(2)}(0) = \frac{20\eta^2}{d(\eta)} (45 - 72\eta + 28\eta^2) \quad f^{(3)}(0) = \frac{3600\eta^3}{d(\eta)} (1 - \frac{4}{3}\eta) \]  
(24)

\[ d(\eta) = 1800 - 192\eta + 131\eta^2 - 520\eta^3 + 5\eta^4 \]  
(25)

Next, we find the solution of the equation (14) in the area \( z_i \geq 1 \) from its general form

\[ f(z_i) = e^{-ikz_i} (A \sin k_2 z_i + B \cos k_2 z_i) \quad i = 1,2 \]

Substituting this expression in (14) we get a system of equations for two amplitudes and two wave numbers

\[ A = \int_{-1}^{1} (1 - t^2) e^{-ik_2 t} (A \cos k_2 t - B \sin k_2 t) \quad (26) \]

\[ B = \int_{-1}^{1} (1 - t^2) e^{-ik_2 t} (A \sin k_2 t + B \cos k_2 t) \quad (27) \]

The amplitudes \( A,B \) are found from the condition of continuity of the desired function and its first derivative at the point \( z_i = 1 \), i.e. \( f(1 - 0) = f(1 + 0), f^{(1)}(1 - 0)f^{(1)}(1 + 0) \). As a result, we obtain a system of two linear inhomogeneous algebraic equations

\[ e^{-ik_2} (A \sin k_2 + B \cos k_2) = f(1) \quad (28) \]

\[ -e^{-ik_2} (k_2 A + k_2 B) \sin k_2 + e^{-ik_2} (k_2 A - k_2 B) \cos k_2 = f^{(1)}(1) \quad (29) \]

where the right parts are defined according to (17). Its solution is

\[ A = \frac{a}{k_2} \quad a = e^{ik_2} [(k_2 \cos k_2 + k_2 \sin k_2) f(1) + \cos k_2 f^{(1)}(1)] \quad (30) \]

\[ B = \frac{b}{k_2} \quad b = e^{ik_2} [(k_2 \cos k_2 + k_2 \sin k_2) f(1) - \sin k_2 f^{(1)}(1)] \quad (31) \]

where the wave numbers are found from the transcendental equations

\[ a \int_{-1}^{1} (1 - t^2) \sin k_2 t = 0 \quad (32) \]
\[-a \int_{-1}^{1} (1-t^2) e^{-kt} \sin kt dt + b \int_{-1}^{1} (1-t^2) e^{-kt} \cos kt dt = 0\]  

(33)

Numerical solution of this system allows us to fully define the function on the interval \(z_i \geq 1\). Solving equations (13), (14) with closure (12) gives qualitatively correct results on the interval \(0 \leq z_i < \infty\). To close Percus-Yevick (10) it is necessary to decompose the function of the desired function (16) up to the sixth-order summands. The result gives a slightly more complex analytical expression.

4. Conclusions
We have combined the Percus-Yevick closure relation (12) with OZ relations (1-2) to determine the one-particle function for a molecular system of liquid near hard surface. We have proposed a new approximation for irreducible diagrams of the direct correlation function in a single particle equation. This approximation leads to a linear Fredholm integral equation of the second kind. The right part and core of the integral equation are expressed in terms of a direct correlation function in the Percus-Yevick approximation. An analytical solution of the equation for a molecular system of solid spheres has been obtained. For realistic intermolecular interaction potentials, the numerical solution of a linear equation requires much less computational resources compared to nonlinear integral equations.

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