Close order in the molecular system near hard surface

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Abstract. Surface forces in boundary layers or thin films of classic molecular systems should be considered when describing different phenomena in near-surface layers. In this case a molecular system has axial symmetry. We obtained the solution for two-particle distribution function at low densities. It is shown that the solution describes the transition from axial to spherical symmetry while each particle goes to infinity.

1. Introduction
We should take into account surface forces boundary layers and thin films of classic molecular systems when describing phenomena (adsorption, wetting) in near-surface layers. In such cases a molecular system has axial symmetry, so we may apply a model of a liquid near a hard surface.

Far from the surface contact a molecular system is heterogeneous and isotropic so we should take into account the boundary condition for transition from axial to spherical symmetry. Moreover, properties of the system are described by pair molecular correlations, decreasing with the distance between particles as interaction potential $U(r)$.

In our work [1] the asymptotic behavior of pair distribution function was described for classic molecular system of liquid near hard surface. In this paper we get the particle distribution functions for arbitrary distance from surface. Interaction between particles is described by hard sphere potential.

2. Common equations
Statistics considering molecular system is based on Born-Green-Yvon-equations system (also known as BGY hierarchy) for l-particle functions $G_{i_1,...,i_l} (r_{i_1},...,r_{i_l})$ for ensemble of identical particles. These particles interact with each other through potential $\Phi_j (r_j)$, where $r_j = |r_i - r_j|$ is the distance between centers of particles $i$ and $j$. The diameter of each particle is $\sigma$.

The BGY-equations system may be transformed to equations for one- and two-particle distribution functions, which may be written as Ornstein-Zernike [2, 4, 5]:

$$\omega_i = n \int G_i C^{(1)}_{12} d(2) + ln a; \quad h_{12} = C^{(2)}_{12} + n \int C^{(2)}_{13} h_{23} d(3)$$  (1)

Here we integrating on coordinates of $i$-th particle: $d(i) = dr_i$, $n$ – density, $G_i = \exp(-\Phi_i (kT)^{-1} + \omega_i)$ one-particle distribution function, which describes particle position; $\Phi_i$

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- potential energy in external field; $\omega$ - one-particle thermal potential; $a$ – activity coefficient, which is defined by condition of passing to isotropic system. $h_y = [\exp(-\Phi_y(kT)^{-1} + \omega_y) - 1]$ is the pair correlation function, which is connected with two-particle distribution function by expression: $G_{ij} = G_xG_y(1 + h_y)$; $\Omega_y$ is the two-particle thermal potential, which takes into account indirect pair interaction; $C^{(k)}_{ijy}$ - direct correlation functions:

$$C^{(1)}_{ijy} = h_y - \omega_y - \frac{1}{2}h_y\left(\omega_y + M^{(1)}_{ijy}\right); \quad C^{(2)}_{ijy} = h_y - \omega_y + M^{(2)}_{ijy}$$

(2)

The functions $G_1(r_1)$ and $G_{12}(r_1,r_2)$ are most critical since they describe internal structure. Let us obtain thermodynamic parameters of the system. To use the equations (1) and (2) in practice one should approximate these series by simple expressions (closures). Most known of them are hyperchain, the Percus-Yevick and Martynov-Sarkisov approximations.

Isotropic systems, such as spatial liquids when far from surface, are of special interest. In these systems $G_1(r) \equiv 1$ and $\omega_1(r) \equiv 0$. As a result, the first equation of the system (1-2) simplifies to

$$\mu = \ln a = -n\int C^{(1)}_{12}(r_{12}) dr_{12}$$

(3)

Second equation may be formed as

$$h_{12} = C^{(2)}_{12} + n\int C^{(2)}_{13} h_{23} d$$

(4)

It defines the unknown function $h_{12} = G_{12}^{(0)}(r_{12}) - 1$. The structure and thermodynamic parameters are evaluated through two-particle distribution function $G_{12}^{(0)}(r_{12})$ depending on density $n = \sigma^3 NV^{-1}$.

Space-heterogeneous systems, such as a liquid near a hard surface, are described by one- and two-particle distribution functions: $G_1(r_1)$ and $G_{12}(r_1,r_2)$. Boundary condition for these equations is a transition from a hard surface to a liquid.

3. Singlet approximation

Equations (1-2) are very hard for direct solution. In order to simplify this problem we may substitute function $G_{12}(r_1,r_2)$ by its boundary value $G_{12}^{(0)}(r_{12})$ for spatial liquid. We call such substitution as singlet approximation. As a result we obtain the equation for one-particle distribution function $G_1(r_1)$, which describes local density profile $n(r_1) = nG_1(r_1)$ near a hard surface. Numerical solution for this equation is presented in [3].

We cannot directly estimate the precision of singlet approximation because of neglecting the close order change near surface but for indirect estimation we can compare the results of our calculation and numerical modeling (numeric experiment). Taking into account the close order change near surface for functions $G_1(r_1)$ and $G_{12}(r_1,r_2)$ we increase the precision of a singlet approximation.

When solving equation (1-2) the origin is located in the center of the particle contacting with hard surface. The $z$ axis is perpendicular to the surface, thus the whole liquid is placed in upper half-space ($z \geq 0$) and bottom one ($z < 0$) is unavailable for the particles (Fig. 1). Such a system has axial symmetry,

$$G_1(r_1) = G_1(z_1) = \exp(\omega_1(z_1)); \quad G_{12}(r_1,r_2) = G_{12}(z_1, z_2, r_{12})$$

(5)
where $r_{12}$ is measured in particle diameter units, $z_i \geq 0$ – particle distance from the surface. Boundary conditions for $G_i(r_1)$ and $G_{12}(r_1,r_2)$ are defined as follows

$$
\omega_i(z_i) \to 0, \quad G_i(z_i) \to 1
$$

$$
z_i \to \infty \quad z_i \to \infty \quad G_{12}(0) = \lim_{z_i \to \infty, r_{12} \to \text{const}} G_{12}(z_1, z_2, r_{12})
$$

(6)

System (1-2) with a singlet approximation takes the form

$$
\omega_i = n \int G_2 C_{12}^{(1,0)} d(2) + \ln a
$$

(7)

$$
l_{12}^{(0)} = C_{12}^{(2,0)} + n \int C_{13}^{(2,0)} l_{23}^{(0)} d(3)
$$

(8)

One-particle potential may be obtained from equation (7), where direct correlation function $C_{12}^{(1,0)}(r_{12})$ and pair correlation function $l_{12}^{(0)}$ are considered to be known.

4. Beyond singlet approximation

Close order in a molecular system changes even at low densities. Let’s take rarefied gas as an example. Thermal potential is obtained through series expansion by density powers. At the first order we get:

$$
\omega_i(z_i) = n\omega_i^{(1)}(z_i), \quad \omega_{12}(r_1, r_2) = n\omega_{12}^{(1)}(r_1, r_2)
$$

(9)

Substituting (9) into (7, 8) we obtain expression for factoring coefficients

$$
\omega_i^{(1)} = \int f_{12} d(2) + \mu^{(1)}
$$

(10)

$$
\omega_{12}^{(1)} = \int f_{13} f_{23} d(2)
$$

(11)

Here $f_{ij}$ – Mayer’s function. Integration is carried out through the whole upper half-space. Constants $\mu^{(1)}$ are derived from border condition at infinity. When evaluating the integral (10) we place the origin at the hard surface (Fig. 1). The surface normal goes through the center of the particle. All upper half-space is reachable for the second particle. By integrating in cylindrical system we get:

$$
\omega_i^{(1)}(z_i) = \frac{\pi}{3} \left( z_i^3 - 3z_i + 2 \right) \theta(1 - z_i)
$$

(12)

When integrating (11) the origin is placed at mass center. Through the centers of first and second particles we pass a plane normal to hard surface (Fig. 1). Intersection field of Mayer’s functions (11) is limited by two hemispheres with radii $A_1$ and $A_2$. Integrating at each quadrant, due to symmetry of particles exchange we obtain

$$
f_{13} f_{23} = \theta(1 - r_{23}^2) = \theta \left( 1 - \left( x_3^2 + z_3^2 + (R_{12} + y_3)^2 \right) \right)
$$

(13)

where $\theta(x)$ – Heavyside function. In particular, the integration range specified in Figure 1 is
Integrating for all $\Delta_1$ and $\Delta_2$ values, we get

$$\omega_1^{(1)} = \frac{\pi}{3} \theta(1 - R_{12}) \left[ \left( R_{12}^3 - 3R_{12} + 2 \right) \theta(\Delta_1 + R_{12} - 1) + \left( 3\Delta_1 (1 - R_{12}) - 3\Delta_1^2 - \Delta_1^3 \right) \right]$$

$$\omega_2^{(1)} = \left[ \left( 3\Delta_2 \left( 1 - R_{12}^2 \right) - 3\Delta_2^2 - \Delta_2^3 \right) \theta(1 - (\Delta_2 + R_{12})) \right]$$

$$\Delta_1 = \frac{z_0}{\cos \phi_{12}}, \quad \Delta_2 = \frac{z_0}{\sin \phi_{12}}, \quad z_0 = \frac{\bar{z}_1 + \bar{z}_2}{2}, \quad R_{12} = \frac{r_{12}}{2}$$

Where $z_1, z_2$ are the distances from the particles to the surface, $\phi_{12}$ – radius-vector angle to the z-axis, $\theta(x)$ – the Heavyside function. When $z_1, z_2$ go to infinity, $\omega_1^{(1)}(z_1)$ converges to zero, and $\omega_2^{(1)}$ to volume value

$$\theta(1 - R_{12}) \frac{2\pi}{3}(R_{12}^3 - 3R_{12} + 2)$$

Thus, as in [2] the solution obtained describes transition from axial to spherical symmetry while each particle goes to infinity. For all other $z_1, z_2$ values the equation (15) describes the close order change near surface.

### Acknowledgements

We are grateful to prof. A. P. Menushenkov and Dr. A. V. Kuznetsoov for their interest to our work. Following work is supported by Russian Basic Research Fund (grant No. 15-02-08204a).

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