Long-range oscillations of a single-particle distribution function for a molecular system of hard spheres near a solid surface in the Percus–Yevick approximation

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Abstract. The properties of molecular systems are defined by asymptotic behavior of distribution functions that have descending character with long-range oscillating order. We consider the molecular system of hard spheres near hard wall. The decrement and period of oscillation are calculated for the distribution function which defines the local density profile.

1. Introduction
In present work we consider the long-range oscillating correlations of the liquid’s local density near the hard surface. In our previous study we used the singlet approximation of statistical physics of liquids to consider the linear Fredholm equation of the second kind for the one-particle distribution function, which depends on the distance from the surface [1]. The boundary condition is defined by transition to macroscopic liquid far from the surface. The structure characteristics of the macroscopic liquid are determined by pair correlation function which depends on the distance between the particles [2]. The core and the right part of the Fredholm equation are also evaluated with this function.

The pair correlation function is related to the direct correlation function by the Percus–Yevick approximation [3]. The relationship (closure) between these two functions produces approximate nonlinear equation integral equation, which should be solved numerically. The Percus–Yevick approximation is the only exception, which has the analytical solution for the hard spheres system. The direct correlation function depends on the distance between particles as the third-degree polynomial function [4].

The Percus–Yevick closure allows to analytically evaluate the core and right part of the Fredholm equation. With this approach we get the analytical solution for the one-particle distribution function for the liquid near the hard surface. This solution can be generalized with statistical physics methods using Random First Order Transition Theory (RFOT) to describe the metastable conditions such as surface amorphization of supercooled liquids. For the last twenty years RFOT approach become popular to describe amorphization phenomena [5].

2. Common equations
2.1. Common equations
The Born–Green–Yvon (BGY) equations system may be transformed to equations for one- and two-particle distribution functions, which may be written [3] as Ornstein-Zernike equations:
\[ \omega_i = n \int G_i^2 \, d(2) + \ln a, \quad h^{(2)}_{ij} = C^{(2)}_{12} + n \int G_i C_{13}^2 h_{33} \, d(3) \]

Here we integrating on coordinates of \( i \)-particle: \( d(i) = dr_i \), \( n = \frac{N}{V} \) – density. The diameter of each particle is \( \sigma \). \( G_i = \exp(-\Phi_i (kT)^{-1} + \omega_i) \) – one-particle distribution function, which describes particle position; \( \Phi_i \) – potential energy in external field; \( \omega_i \) – one-particle thermal potential; \( a \) – activity coefficient, which is defined by condition of passing to isotropic system. The pair correlation function \( h_{ij} = [\exp(-\Phi_j (kT)^{-1} + \omega_j) - 1] \) is connected with two particle distribution function by the expression: \( G_{ij} = G_i G_j (1 + h_{ij}) \). The two-particle thermal potential \( \omega_{ij} \) takes into account indirect interaction of two particles; \( C^{(k)}_{ij} \) – direct correlation functions:

\[ C^{(1)}_{ij} = h_{ij} - \omega_{ij} - \frac{1}{2} h_{ij} \left( \omega_{ij} + M^{(1)}_{ij} \right) \]
\[ C^{(2)}_{ij} = h_{ij} - \omega_{ij} + M^{(2)}_{ij} \]

Functions \( G_i(r_i) \) and \( G_{12}(r_1, r_2) \) are critical ones since they describe internal structure. Let us obtain thermodynamic parameters of the system. Equations (1) and (2) are difficult to solve because \( M^{(1)}_{ij} \) and \( M^{(2)}_{ij} \) contain 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.

2.2. Molecular system of liquid near hard surface

Space-heterogeneous systems (liquid near a hard surface) are described by one- and two-particle distribution functions: \( G_i(r_i) \) and \( G_{12}(r_1, r_2) \). Boundary condition for these equations is 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. We assume that all irreducible diagrams in (1) are calculated in such way to compensate the nonlinearities. With this approach we get first equation of (1) as:

\[ (e^{\omega(z)} - 1) - 2\pi n \int_0^z dz_2 (e^{\omega(z_2)} - 1) \int r_{12} dr_{12} C^{(1,0)}_{12}(r_{12}) = -2\pi n \int_0^z dz_2 \int_{r_{12}}^{\infty} r_{12} dr_{12} C^{(1,0)}_{12}(r_{12}) \]

where \( r_{12} \) is measured in particle diameter units, \( z_i \geq 0 \) – particle distance from the surface. This is the second kind of Fredholm equation.

2.3. Percus–Yevick approximation

The internal integrals of equation (3) might be defined as follows:

\[ \Psi(|z|) = \int_0^1 r_{12} dr_{12} (\alpha + \beta r_{12} + \gamma r_{12}^3) \]
\[ K(|z|) = -\Theta(1-|z|)\Psi(|z|), \]

where \( \Theta(1-|z|) \) is the Heaviside function.
In our previous work [1] we have proposed that function $\hat{C}_{ij}^{(0)}(r_{ij})$ may be substituted with its mean value in the range $0 \leq r_{ij} \leq 1$. In this case $\Psi(z)$ will be the polynomial function of degree 2 and equation (3) has an analytical solution. In the present work we won’t use this approximation, and taking the direct definition of $\Psi(z)$ given in [4] write equation (3) in the form:

$$f(z_i) = -12\eta \int_{0}^{z_i} dz_z f(z_z) \Psi(|z_i - z_z|) + 12\eta \int_{z_i}^{z_{i+1}} dz_z \Psi(z_z) \quad z_i \leq 1$$ (6)

$$f(z_i) = -12\eta \int_{z_{i-1}}^{z_i} dz_z f(z_z) \Psi(|z_i - z_z|) \quad z_i \geq 1$$ (7)

where $\eta = \pi n / 6$ and $f(z_i) = \exp(\omega_1(z_i)) - 1$.

### 3. Results and Discussion

Here we evaluate the asymptotic behavior of $f(z_i)$ for large value of $z_i$. Differencing equation (7) by $z_i$ we get

$$\frac{d}{dz_i} f(z_i) = -\eta \int_{z_{i-1}}^{z_i} dz_z f(z_z) \Psi^{(i)}(z_i - z_z) - \int_{z_i}^{z_{i+1}} dz_z f(z_z) \Psi^{(i)}(z_z - z_i)$$ (8)

Solution of equation (8) can be presented as $f(z) = e^{-\eta z}(A\sin k_1 z + B\cos k_1 z)$. Substituting this expression to (8) we get the transcendent equations system, which defines the wave numbers $k_1, k_2$:

$$k_1 = 2\eta \int_{0}^{1} dt \Psi^{(i)}(t)(\cos k_1 t) \sin k_1 t, \quad k_2 = 2\eta \int_{0}^{1} dt \Psi^{(i)}(t)(\sin k_2 t) \cos k_2 t$$ (9)

The system of transcendent equations (9) was solved numerically. The values of the wave numbers $k_1, k_2$ for the high density in the interval $0.26 \leq n \leq 0.785$ are shown on Fig. 1.

**Figure 1.** Numerical solution of transcendent equations system for the wave numbers.
We will find the solution of equation (6) for the function \( f(z_i) \) into the interval \( 0 \leq z_i \leq 1 \) in the form of series by degrees of small parameter \( z_i \). Assuming that function \( f(z_i) \) and its first derivative are continuous at the point \( z_i = 1 \), we evaluate the amplitudes \( A, B \). In this case asymptotic descending of correlation functions for the high density becomes oscillating. However, we can estimate the qualitative behavior of \( f(z_i) \) without solving the equation (6). At the Fig. 2 we show the plot of \( f(z_i) \) for the amplitude values \( A=2, B=5 \).

\[ f'(z_1/\sigma) \]

\[ z_1/\sigma \]

\[ 2 \quad 4 \quad 6 \quad 8 \quad 10 \]

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\textbf{Figure 2.} Oscillation behaviour of one-particle distribution function for the densities \( n = 0.3141 \) (blue), \( n = 0.785 \) (green)

We should stress that the equations (6) and (7) allow the analytical solution if only the core and the right part have the analytical solution for the spatial liquid for Percus–Yevick approximation. The other approximations require the prior numerical solution of the corresponding equation [2]. Using the RFOT method we can consider the macroscopic metastable systems because it describes the transition from initial equilibrium state to the final metastable state avoiding study of the intermediate kinetic processes. In the previous studies the RFOT method was applied only for spatial systems [6]. In the present work we suggest to use it for the study the liquid near the hard surface by evaluating the core and the right part of the equations (6) and (7). This way we get linear integral equation which might be solved by well-known approaches [7]. Our approach allows to study surface layers of supercooled liquids by statistical physics methods.

4. Conclusions

In past years the distribution functions method using the several approximate integral equations is widely used to study the surface phenomena in liquids. The physical sense of such approximation remains unclear and the precision of the solutions can be evaluated only in comparison of the numerical simulation results with experimental data. We suggest an approach for statistical physics of surface phenomena: contribution of irreducible diagrams into infinite series for direct correlation functions may be evaluated in particular way to cancel nonlinearity. As the result we get linear equation – integral Fredholm equation of second kind. The parameters of the equation (the core and the right part) are expressed by direct correlation function of the macroscopic liquid, which in general should be evaluated numerically. However, in case of Percus–Yevick approximation these parameters can be evaluated analytically. We used the Percus–Yevick approximation to get the analytical solution of the integral equation for the one-
particle distribution function. We showed that this solution has descending and oscillating asymptotic behavior. The higher densities, the higher amplitude of the oscillations. The period of oscillations is defined by solution of transcendent equations. We suggest that equation (3) obtained in this study can be generalized to describe the metastable systems such as thin amorphous layers (or films).

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