

A Semi-Analytical Solution of the Mean Spherical Approximation: Application to Calculation of Structure Factors of Liquid Metals in the Square-Well Model

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We consider a one-component homogeneous model liquid with the following interatomic spherically symmetric pair potential:

$$\varphi(r) = \begin{cases} \infty, & r < \sigma, \\ \phi(r), & r \geq \sigma, \end{cases} \quad (1)$$

where σ is the hard-core (HC) diameter. Irrespective of the form of $\phi(r)$ for potential (1), the following equality is always valid:

$$g(r) = 0, \quad r < \sigma, \quad (2)$$

where $g(r)$ is the pair distribution function.

All structural characteristics of the system were analytically described only for the special case of potential (1) at $\phi(r) = 0$, which corresponds to the hard-sphere (HS) potential $\phi_{\text{HS}}(r)$, in [1, 2] in the Percus–Yevick approximation [3]. In this case, the direct correlation function $c_{\text{HS}}(r)$ of the HS system is written as follows [1, 2]:

$$c_{\text{HS}}(r) = \begin{cases} a_0 + a_1\left(\frac{r}{\sigma}\right) + a_3\left(\frac{r}{\sigma}\right)^3, & r < \sigma, \\ 0, & r \geq \sigma, \end{cases} \quad (3)$$

where a_0 , a_1 , and a_3 are the coefficients dependent on the packing density $\eta = \frac{\pi\rho\sigma^3}{6}$, and ρ is the average atomic density of the system.

In this work, we propose an analytical expression for the direct correlation function $c(r)$ of the system with potential (1) for $r < \sigma$ in the general form:

$$c(r) = \sum_m d_m \left(\frac{r}{\sigma}\right)^m, \quad r < \sigma, \quad (4)$$

where d_m are the coefficients, and $m = 0, 1, 2, \dots$.

With taking into account Eq. (3), Eq. (4) can be written as follows:

$$c(r) = c_{\text{HS}}(r) + \Psi(r), \quad r < \sigma, \quad (5)$$

where

$$\Psi(r) = \begin{cases} 0, & n = 0, \\ \sum_{m=1}^n b_{m-1} \left(\frac{r}{\sigma}\right)^{m-1}, & n > 0, \end{cases} \quad (6)$$

b_{m-1} are the coefficients, and n is the number of terms in the expansion $\Psi(r)$.

Proposed Eq. (5) together with Eq. (2) can be used instead of the Ornstein–Zerinke (OZ) equation in the direct space [4] when solving some of the approximated equations of the theory of liquid. The solution accuracy is determined by that of the approximated equation under use and the number of terms in the expansion of the direct correlation function inside the core. There is always an n at which the complete coincidence of the solution with the OZ numerical solution for this approximated equation is achieved.

We consider the application of this approach to the mathematically simplest of such equations—the mean spherical approximation (MSA) [5]. In this case, the direct correlation function of the system with potential (1) can be written as follows:

$$c(r) = \begin{cases} c_{\text{HS}}(r) + \Psi(r), & r < \sigma, \\ -\beta\phi(r), & r \geq \sigma, \end{cases} \quad (7)$$

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Isothermal compressibility χ_T and the internal energy E per atom for the system with the square-well potential for $\lambda = 1.5$

System parameters	Property	$n = 0$	$n = 2$	$n = 4$	$n = 6$	Data [10]
$\rho\sigma^3 = 0.1, \varepsilon\beta = -0.1$	$\frac{\beta}{\rho\chi_T}$	1.414	1.401	–	–	1.400
	$\frac{E}{\varepsilon}$	–0.572	–0.571	–	–	–0.571
$\rho\sigma^3 = 0.5, \varepsilon\beta = -0.1$	$\frac{\beta}{\rho\chi_T}$	7.320	6.955	6.971	–	7.030
	$\frac{E}{\varepsilon}$	–3.465	–3.383	–3.389	–	–3.388
$\rho\sigma^3 = 0.5, \varepsilon\beta = -0.5$	$\frac{\beta}{\rho\chi_T}$	5.330	3.609	3.960	4.068	4.032
	$\frac{E}{\varepsilon}$	–4.100	–3.595	–3.658	–3.657	–3.637

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, and T is the temperature.

For $n = 0$, Eq. (7) becomes

$$c(r) = \begin{cases} c_{\text{HS}}(r), & r < \sigma, \\ -\beta\phi(r), & r \geq \sigma. \end{cases} \quad (8)$$

Expression (8) is the random-phase approximation (RPA) [6, 7] applied to the HC potential. When using the RPA, the pair distribution function has large non-physical oscillations inside the HC; i.e., the fulfillment of condition (2) is violated within Eq. (8). In our approach, this condition is satisfied by selecting the values of coefficients in Eq. (6). We note that a solution coinciding like ours with the numerical OZ–MSA solution can be obtained also within the framework of the optimized random-phase approximation (ORPA) [8]. The ORPA was applied to a liquid with the square-well potential in [9].

From Eq. (7), we obtain the Fourier transform of the direct correlation function $c(q)$ in the analytical form:

$$c(q) = \begin{cases} c_{\text{HS}}(q) - \beta\phi(q), & n = 0, \\ c_{\text{HS}}(q) - \beta\phi(q) + \Psi(q), & n > 0, \end{cases} \quad (9)$$

$$\Psi(q) = \frac{4\pi}{q^3} \left\{ \sum_{m=1}^{n+1} x^{2-m} \frac{\partial^m \sin x}{\partial x^m} \sum_{l=0}^{n-1} b_l \prod_{k=0}^{m-2} (l+1-k) + \sum_{m=1}^{n/2} \frac{(-1)^{m+1} (2m)! b_{2m-1}}{x^{2m-1}} \right\}, \quad (10)$$

where $c_{\text{HS}}(q)$, $\phi(q)$, and $\Psi(q)$ are the Fourier transforms of the functions $c_{\text{HS}}(r)$, $\phi(r)$, and $\Psi(r)$, respectively, and $x = q\sigma$. Expression (10) is presented for even values of n (in the general form, it is not obtained).

In the long-wave limit, Eq. (9) becomes

$$c(q=0) = \begin{cases} c_{\text{HS}}(q=0) - \beta\phi(q=0), & n = 0, \\ c_{\text{HS}}(q=0) - \beta\phi(q=0) - 4\pi\sigma^3 \sum_{m=1}^n \frac{b_{m-1}}{m+2}, & n > 0. \end{cases} \quad (11)$$

The pair distribution function is calculated numerically from the known relation

$$g(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^\infty [S(q) - 1] \frac{\sin(qr)}{qr} q^2 dq, \quad (12)$$

where $S(q) = \frac{1}{1 - \rho c(q)}$ is the structure factor.

The fulfillment of condition (2) is achieved by minimizing the sum of squares of $g(r)$ taken in five points regularly distributed over r in the interval $r < \sigma$. During this procedure, the values of coefficients b_m are determined.

From the structural characteristics, we can calculate the thermodynamic properties of the chosen model liquid, in particular, the internal energy E per atom and the isothermal compressibility χ_T :

$$E = \frac{3}{2\beta} + 2\pi\rho \int_0^\infty \phi(r) g(r) r^2 dr, \quad (13)$$

$$\chi_T = \frac{\beta S(0)}{\rho}. \quad (14)$$

The proposed numerically analytical formalism is applied below to the square-well (SW) potential. Then

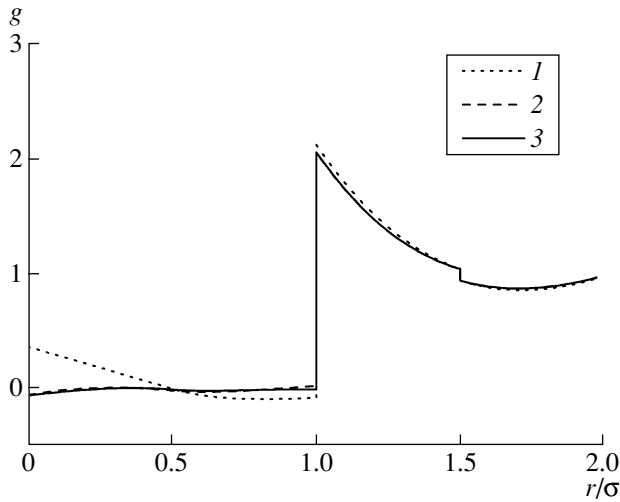


Fig. 1. Pair correlation function of the system with the square-well potential for $\lambda = 1.5$, $\rho\sigma^3 = 0.5$, and $\epsilon\beta = -0.1$ depending on the number of coefficients: $n = 0$ (1), 2 (2), 4 (3).

this MSA–SW approach is used for the calculation of structure factors of liquid metals by the example of liquid sodium.

CALCULATION OF MODEL-LIQUID PROPERTIES WITH A SQUARE-WELL POTENTIAL

The pair potential $\phi_{sw}(r)$ in the square-well model has the following form:

$$\phi_{sw}(r) = \begin{cases} \infty, & r < \sigma, \\ \epsilon, & \sigma \leq r < \lambda\sigma, \\ 0, & r \geq \lambda\sigma, \end{cases} \quad (15)$$

where σ , $\epsilon (< 0)$, and λ are the SW parameters: ϵ and $\sigma(\lambda - 1)$ are the well depth and width, respectively. For $\epsilon = 0$ or $\lambda = 1$, $\phi_{sw}(r)$ becomes identical to $\phi_{HS}(r)$.

Correspondingly, it follows from Eqs. (1) and (15) that

$$\phi_{sw}(r) = \begin{cases} \epsilon, & r < \lambda\sigma, \\ 0, & r \geq \lambda\sigma. \end{cases} \quad (16)$$

In the reciprocal space,

$$\phi_{sw}(q) = 4\pi\epsilon \left[\frac{\sin(\lambda x) - \sin x}{q} - \lambda x \cos(\lambda x) + x \cos x \right] \quad (17)$$

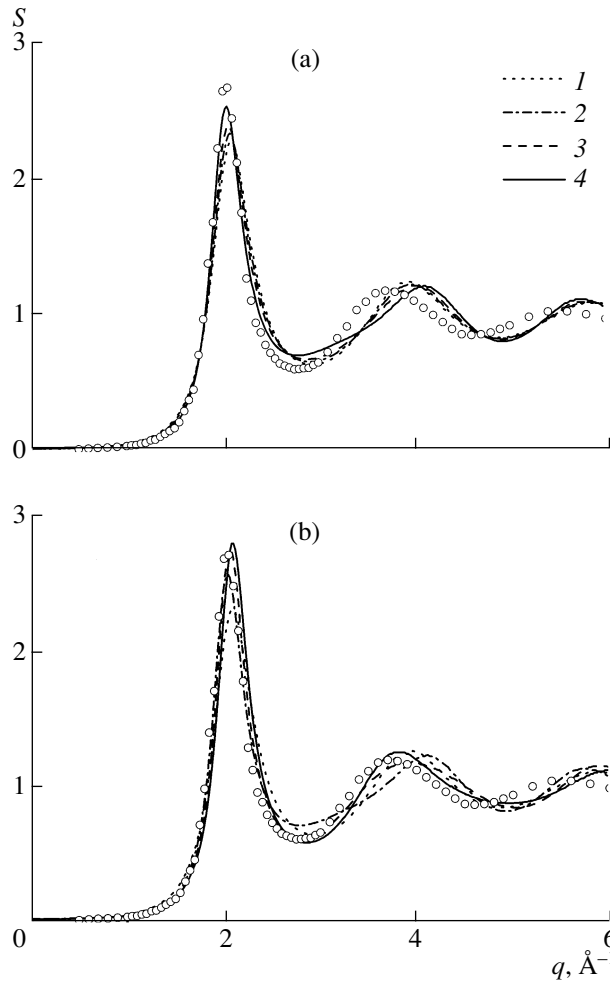


Fig. 2. Structure factor of liquid sodium at $T = 373$ K depending on (a) its depth for a constant SW width and (b) on its width for a constant depth in comparison with $S_{HS}(q)$ and with $S_{exp}(q)$: (a) (1) $S_{HS}(q)$; (2) $\lambda = 1.557$, $\epsilon = -0.00025$ au; (3) $\lambda = 1.557$, $\epsilon = -0.0005$ au; (4) $\lambda = 1.557$, $\epsilon = -0.001$ au. (b) (1) $S_{HS}(q)$; (2) $\lambda = 1.557$, $\epsilon = -0.001$ au; (3) $\lambda = 1.47$, $\epsilon = -0.001$ au; (4) $\lambda = 1.4$, $\epsilon = -0.001$ au. The dots correspond to $S_{exp}(q)$.

In the long-wave limit, $\phi_{sw}(q)$ is written as

$$\phi_{sw}(q = 0) = 4\pi\sigma^3\epsilon(\lambda^3 - 1). \quad (18)$$

It is convenient to investigate this model liquid in terms of dimensionless values of the reduced density $\rho\sigma^3$ and the reduced reciprocal temperature $\epsilon\beta$.

The calculation results for the thermodynamic properties show (see table) that the higher the values of $\rho\sigma^3$ and $|\epsilon\beta|$, the larger the number of terms in expansion (6) that should be used for achieving the coincidence of the obtained results with the results of numerical OZ–MSA integration [10]. In Fig. 1, we show the dependence $g(r)$ on the number of coefficients n for the SW liquid with $\rho\sigma^3 = 0.5$, $\epsilon\beta = -0.1$, and $\lambda = 1.5$. It can be seen that the

zero $g(r)$ is almost achieved inside the core for this set of values of parameters since $n = 2$.

CALCULATION OF THE STRUCTURE FACTOR OF LIQUID SODIUM IN THE SQUARE-WELL MODEL

Previously, the square-well model was used for quantitative study of liquid metals only within the RPA. For the first time, such an approach was proposed in [11] and applied to the calculation of structural characteristics of liquid mercury and aluminum. The structure factor and the transport properties of liquid sodium were calculated by this method in [12]. Silbert and Young [13] calculated the structure factors of liquid metals having a shoulder in the first peak of the structure factor (in this case, the values of ε were assumed positive).

In this work, we chose liquid sodium at the temperature of 373 K as the object of investigation. The values of σ (6.1027 au) and ρ (0.003621 au) are taken from [14], where they were obtained when calculating the thermodynamic properties of liquid sodium by the variational method with the reference HS system combined with the Animalu–Heine model pseudopotential. The number of coefficients in $c(r)$ expansion is taken as six.

In Fig. 2, we show the dependences of the structure factor (a) on the SW depth for the constant width $\lambda = 1.557$ and (b) on the SW width for the constant depth $\varepsilon = -0.001$ au. The results of calculation are compared with the experimental structure factor $S_{\text{exp}}(q)$ [15] and with $S_{\text{HS}}(q)$ obtained by us with the same input data. From Fig. 2a, it can be seen that the height of the first peak of the structure factor increases and approaches to experimental value with increasing the SW depth for constant λ . In this case, the position of the second peak of the structure factor moves away from the experimental value. At the fixed value $\varepsilon = -0.001$ au (Fig. 2b), the agreement with the experiment is improved for both the first and second peaks with decreasing the SW width to 1.4σ .

Thus, by varying the values of width and depth of the square well, it is possible to achieve good agreement of the calculated structure factor of liquid metal with the experimental value for finite nonzero values of these parameters. Therefore, it is expedient to use the

SW model further as the reference system for the calculations of structural and thermodynamic characteristics of metal melts in the approach of the joint use of the pseudopotential theory and the variational method of the thermodynamic perturbation theory.

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