

Structure factors of binary liquid metal alloys within the square-well model

Research Article

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Abstract:

The procedure suggested previously for the description of the square-well (SW) fluid within the framework of the mean spherical approximation is applied to calculate the structure factors of pure Na, pure K, and 0.5Na-0.5K alloy in liquid state. It is shown that our variations of the SW depth and SW width enable us to achieve a good agreement between calculated and experimental structure factors. The procedure under consideration gives more accurate results than the random phase approximation for the same values of the SW parameters.

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1. Introduction

Recently, for a model fluid with particles interacting by means of a pair potential with the hard-core (HC) repulsive part, we suggested to represent the direct correlation function, $c(r)$, inside the HC, as an expansion in polynomial series [1]. Then we applied this approach within the mean spherical approximation (MSA) [2] to the fluid with the square-well (SW) pair potential, $\varphi_{SW}(r)$. This approach allows the omission of the Ornstein-Zernike (OZ) integral equation in real space [3] because all characteristics can be expressed analytically by means of the expansion coefficients, which are defined numerically from

the condition that the pair correlation function, $g(r)$, must be equal to zero inside the HC. It was shown that with a sufficient number of terms in the expansion our results could achieve full agreement with the results of Smith, Henderson and Tago [4], which were obtained numerically by solving the OZ equation with the MSA closure (the necessary number of expansion terms is dependent on the input data: temperature, T , atomic density, ρ , and the SW parameters).

In the case of binary SW fluids, the OZ integral equation results for seven closures under consideration [5] show that the MSA closure gives the best agreement with the Monte Carlo computer simulation results given by Lee and Chao [6].

In Ref. [1], we expanded our SW-MSA approach to binary systems. Here, the binary liquid metal alloy is repre-

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sented as an SW mixture and the formalism under question is applied to calculate the structure of the equiatomic Na-K alloy at $T=373$ K.

Previously, descriptions of binary liquid metal alloys within the SW model [7–10] and the SW model with a repulsive SW barrier [11, 12] have been performed in the framework of the random phase approximation (RPA) [13, 14]:

$$c(r) = \begin{cases} c_{HS}(r), & r < \sigma, \\ -\beta\varphi(r), & r \geq \sigma, \end{cases} \quad (1)$$

where $c_{HS}(r)$ is the direct correlation function of the hard-sphere (HS) fluid obtained in the closed form by Wertheim [15] and Thiele [16] in the Percus-Yevick (PY) approximation [17]; $\varphi(r)$ - HC-based pair potential; σ - HC diameter; $\beta = (k_B T)^{-1}$; k_B - Boltzmann constant.

The RPA leads to an unphysical behaviour of $g(r)$ inside the hard core. Our procedure is more physically reasonable than the RPA. It gives a correction to the RPA similar to a correction arising in the optimized random phase approximation (ORPA) [18], which becomes equivalent to the MSA when it is applied to a fluid with a HC-based pair potential.

2. Theory

2.1. One-component SW fluid

The SW pair potential is being written as follows:

$$\varphi_{SW}(r) = \begin{cases} \infty, & r < \sigma, \\ \varepsilon, & \sigma \leq r < A\sigma, \\ 0, & r \geq A\sigma, \end{cases} \quad (2)$$

where $\varepsilon (< 0)$ is the SW depth; $\sigma(A - 1)$ - SW width.

The Fourier transform of $\varphi_{SW}(r)$ at $r \geq \sigma$ is

$$\tilde{\phi}_{SW}(q) = 4\pi\varepsilon [\sin(Ax) - \sin(x) - Ax \cos(Ax) + x \cos(x)] / q^3, \quad (3)$$

where $\phi(r)$ is the part of $\varphi(r)$ at $r \geq \sigma$; $x = q\sigma$.

In the long-wave limit, we have

$$\tilde{\phi}_{SW}(0) = \frac{4}{3}\pi\sigma^3\varepsilon(A^3 - 1). \quad (4)$$

The approach of Ref. [1] is

$$c(r) = \begin{cases} c_{HS}(r) + \sum_{m=0}^n b_m \left(\frac{r}{\sigma}\right)^m, & r < \sigma, \\ -\beta\varphi(r), & r \geq \sigma, \end{cases} \quad (5)$$

where $(n + 1)$ stands for the number of coefficients.

From Eq. (5), one can obtain the Fourier transform of the direct correlation function, $\tilde{c}(q)$, [1]:

$$\tilde{c}(q) = \tilde{c}_{HS}(q) - \beta\tilde{\phi}(q) + \left(\frac{4\pi}{q^3}\right) \left\{ \sum_{m=1}^{n+2} x^{2-m} \frac{\partial^m \sin(x)}{\partial x^m} \sum_{l=0}^n b_l \prod_{k=0}^{m-2} (l+1-k) + \sum_{m=1}^{(n+1)/2} \frac{(-1)^{m+1} (2m)! b_{2m-1}}{x^{2m-1}} \right\}, \quad (6)$$

(for odd n),

$$\tilde{c}(0) = \tilde{c}_{HS}(0) - \beta\tilde{\phi}(0) - 4\pi\sigma^3 \sum_{m=0}^n \frac{b_m}{m+3}, \quad (7)$$

where $\tilde{c}_{HS}(q)$ is the Fourier transform of $c_{HS}(r)$ given by Wertheim–Thiele [15, 16].

To satisfy the condition

$$g(r) = 0 \quad \text{at} \quad r < \sigma \quad (8)$$

we minimize the sum of squares of $g(r)$ taken in 5 points regularly distributed within the interval $r < \sigma$ at a finite n using the following expression:

$$g(r) = 1 + \frac{1}{2\pi^2\rho} \int_0^\infty [S(q) - 1] \frac{\sin(qr)}{qr} q^2 dq, \quad (9)$$

where $S(q)$ stands for the structure factor:

$$S(q) = \frac{1}{1 - \rho\tilde{c}(q)}. \quad (10)$$

As a result, the values of coefficients $b_m (m = 0, \dots, n)$ are defined.

2.2. Two-component SW fluid

The partial pair potentials, $\varphi_{ij}(r)$, for the SW mixture are

$$\varphi_{ij\text{SW}}(r) = \begin{cases} \infty, & r < \sigma_{ij}, \\ \varepsilon_{ij}, & \sigma_{ij} \leq r < A_{ij}\sigma_{ij}, \\ 0, & r \geq A_{ij}\sigma_{ij}, \end{cases} \quad (11)$$

where σ_{ij} , ε_{ij} , A_{ij} are the partial SW parameters. We use the additive binary SW mixture ($i, j = 1, 2$) [7–10], for which

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2,$$

$$\varepsilon_{12} = -\sqrt{\varepsilon_{11}\varepsilon_{22}} \quad \text{and} \quad \varepsilon_{ii} \leq 0, \quad (12)$$

$$A_{12} = (A_{11}\sigma_{11} + A_{22}\sigma_{22})/(\sigma_{11} + \sigma_{22}).$$

The Fourier transform of Eq. (11) at $r \geq \sigma_{ij}$ gives

$$\tilde{\phi}_{ij\text{SW}}(q) = 4\pi\varepsilon_{ij} [\sin(A_{ij}x_{ij}) - \sin(x_{ij}) - A_{ij}x_{ij} \cos(A_{ij}x_{ij}) + x_{ij} \cos(x_{ij})] / q^3, \quad (13)$$

The Fourier transforms of the partial direct correlation functions (15) and (16) are [1]

$$\tilde{c}_{ii}(q) = \tilde{c}_{ii\text{HS}}(q) - \beta\tilde{\phi}_{ii}(q) + \left(\frac{4\pi}{q^3}\right) \left\{ \sum_{m=1}^{n+2} x_{ii}^{2-m} \frac{\partial^m \sin(x_{ii})}{\partial x_{ii}^m} \sum_{l=0}^n b_{iil} \prod_{k=0}^{m-2} (l+1-k) + \sum_{m=1}^{(n+1)/2} \frac{(-1)^{m+1} (2m)! b_{ii(2m-1)}}{x_{ii}^{2m-1}} \right\}, \quad (\text{for odd } n), \quad (17)$$

$$\tilde{c}_{12}(q) = \tilde{c}_{12\text{HS}}(q) - \beta\tilde{\phi}_{12}(q) + \left(\frac{4\pi}{q^3}\right) \left\{ \sum_{m=1}^{n+2} q^{2-m} \frac{\partial^m \sin(x_{12})}{\partial x_{12}^m} \sum_{l=0}^n b'_{12l} \sigma_{11}^{l-m+2} \prod_{k=0}^{m-2} (l+1-k) + \sum_{m=1}^n \frac{(m+1)! b'_{12m}}{q^m} \frac{\partial^m \sin(y_{12})}{\partial y_{12}^m} \right\}, \quad (18)$$

$$\tilde{c}_{ii}(0) = \tilde{c}_{ii\text{HS}}(0) - \beta\tilde{\phi}_{ii}(0) - 4\pi\sigma_{ii}^3 \sum_{m=0}^n \frac{b_{iim}}{m+3}, \quad (19)$$

$$\tilde{\phi}_{ij\text{SW}}(0) = \frac{4}{3} \pi \sigma_{ij}^3 \varepsilon_{ij} (A_{ij}^3 - 1), \quad (14)$$

where $x_{ij} = q\sigma_{ij}$.

For the partial direct correlation functions, $c_{ij}(r)$, the approach of Ref. [1] is represented as follows:

$$c_{ii}(r) = \begin{cases} c_{ii\text{HS}}(r) + \sum_{m=0}^n b_{iim} \left(\frac{r}{\sigma_{ii}}\right)^m, & r < \sigma_{ii}, \\ -\beta\phi_{ii}(r), & r \geq \sigma_{ii}, \end{cases} \quad (15)$$

$$c_{12}(r) = \begin{cases} c_{12\text{HS}}(r) + b_{120}, & \lambda_{12} > r, \\ c_{12\text{HS}}(r) + \sum_{m=0}^n b'_{12m} (r - \lambda_{12})^{m+1} / r, & \lambda_{12} \leq r < \sigma_{12}, \\ -\beta\phi_{12}(r), & r \geq \sigma_{12}, \end{cases} \quad (16)$$

where $c_{ij\text{HS}}(r)$ are the HS partial direct correlation functions in the PY closed form [19]; $\lambda_{12} = (\sigma_{22} - \sigma_{11})/2$ at $\sigma_{22} > \sigma_{11}$; $b'_{ijm} = b_{ijm}/\sigma_{ij}^m$.

$$\begin{aligned} \tilde{c}_{12}(0) = & \tilde{c}_{12HS}(0) - \beta \tilde{\phi}_{12}(0) - 4\pi\sigma_{12}^3 \left[\frac{b''_{120}}{3} + \frac{b''_{121}}{12} (6\alpha^{-1} - 4 + \alpha - \delta\gamma^3) + \frac{b''_{122}}{20} (10\alpha^{-1} - 10 + 5\alpha - \alpha^2 \right. \\ & + \delta^2\gamma^3) + \frac{b''_{123}}{30} (15\alpha^{-1} - 20 + 15\alpha - 6\alpha^2 + \alpha^3 - \delta^3\gamma^3) + \frac{b''_{124}}{42} (21\alpha^{-1} - 35 + 35\alpha - 21\alpha^2 + 7\alpha^3 - \alpha^4 \\ & \left. + \delta^4\gamma^3) + \frac{b''_{125}}{56} (28\alpha^{-1} - 56 + 70\alpha - 56\alpha^2 + 28\alpha^3 - 8\alpha^4 + \alpha^5 - \delta^5\gamma^3) \right], \quad (\text{for } n = 5), \quad (20) \end{aligned}$$

where $y_{12} = q\lambda_{12}$; $\tilde{c}_{ijHS}(q)$ represent the Fourier transforms of the PYHS partial direct correlation functions in the analytical form [20, 21]; $b''_{12m} = b'_{12m}\sigma_{11}^m$; $\alpha = \sigma_{12}/\sigma_{11}$; $\delta = \lambda_{12}/\sigma_{11}$; $\gamma = \delta/\alpha$.

Condition (8) for the binary system is being rewritten as follows:

$$g_{ij}(r) = 0, \quad r < \sigma_{ij}. \quad (21)$$

Coefficients b_{ijm} are determined in a similar way to the case of the one-component fluid by means of

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2\rho\sqrt{c_i c_j}} \int_0^\infty [S_{ij}(q) - \delta_{ij}] \frac{\sin(qr)}{qr} q^2 dq, \quad (22)$$

where c_i is the concentration of the i -th component; $S_{ij}(q)$ - Ashcroft-Langreth (AL) partial structure factors [20]:

$$S_{ii}(q) = \frac{1 - c_i\rho\tilde{c}_{ij}(q)}{[1 - c_1\rho\tilde{c}_{11}(q)][1 - c_2\rho\tilde{c}_{22}(q)] - c_1c_2\rho^2\tilde{c}_{12}^2(q)}, \quad (23)$$

$$S_{12}(q) = \frac{\sqrt{c_1c_2\rho}\tilde{c}_{12}(q)}{[1 - c_1\rho\tilde{c}_{11}(q)][1 - c_2\rho\tilde{c}_{22}(q)] - c_1c_2\rho^2\tilde{c}_{12}^2(q)}. \quad (24)$$

3. Results and discussion

For the pure liquid Na and K at $T=373$ K we take values of σ obtained previously in Ref. [22] by the pseudopotential method in conjunction with the variational method with the HS reference system. The atomic densities are taken from experiment [23]. Input data for Na and K are given in Tab. 1. Our calculations are carried out for $n = 5$.

Table 2. Input SW parameters for the liquid equiatomic Na-K alloy at $T=373$ K.

	σ_{ii} (a.u.)	A_{ii}	ε_{ii} (a.u.)
Na	6.1027	1.400	-0.00100
K	7.7500	1.479	-0.00025

Table 1. Input data for liquid Na and K at $T=373$ K in atomic units (a.u.).

	σ (a.u.)	ρ (a.u.)
Na	6.1027	0.0036
K	7.7500	0.0019

In Fig. 1 it is shown how $S(q)$ of liquid Na is changed with the SW depth at the constant SW width (a) and with the SW width at the constant SW depth (b).

The results of varying the SW parameters for $S(q)$ calculations of liquid K are plotted in Fig. 2.

The hard-sphere structure factors, $S_{HS}(q)$, ($\varepsilon = 0$ or $A = 0$) demonstrated in Figs. 1 and 2 are obtained at the same σ and ρ as used for the corresponding SW calculations (Tab. 1).

To consider Na-K alloy we put $c_1 = c_2 = 0.5$, $T=373$ K, $\rho = 0.0024$ a.u. [23], and $n = 5$. Each partial SW parameter between atoms of the same kind is taken to be equal to the corresponding parameter in the pure metal. Among sets of parameters used for pure metals, values of A and ε that lead to better agreement with experimental structure factors (Figs. 1, 2) are chosen for the alloy calculations. Input values of the SW parameters are listed in Tab. 2. The values of coefficients b_m and b_{ijm} obtained at these parameters for pure metals and the alloy under consideration are summarized in Tabs. 3 and 4, respectively.

We calculate the AL partial structure factors and the

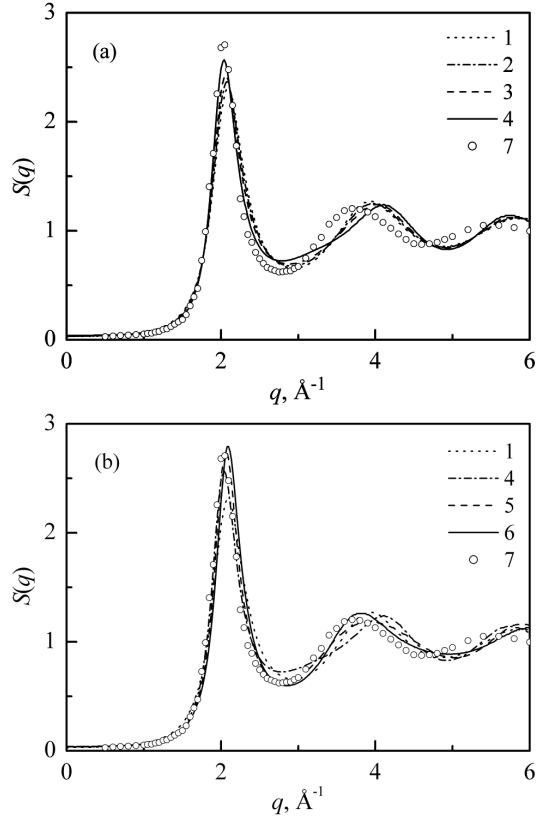


Figure 1. The structure factor of liquid Na at $T=373$ K for different values of A and ϵ (a.u.) (2: $A=1.557$, $\epsilon = -0.00025$; 3: $A=1.557$, $\epsilon = -0.0005$; 4: $A=1.557$, $\epsilon = -0.001$; 5: $A=1.47$, $\epsilon = -0.001$; 6: $A=1.4$, $\epsilon = -0.001$) in comparison with $S_{HS}(q)$ (1) and experiment (7) [24].

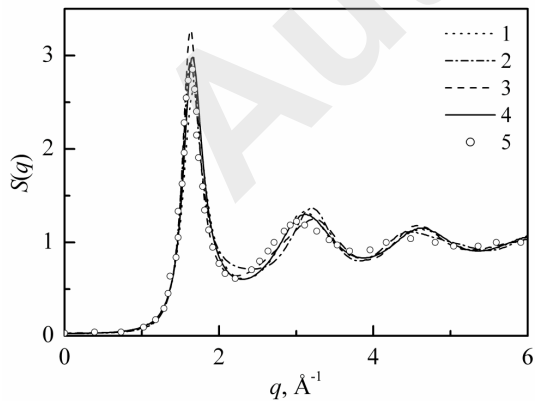


Figure 2. The structure factor of liquid K at $T=373$ K for different values of A and ϵ (a.u.) (2: $A=1.613$, $\epsilon = -0.001$; 3: $A=1.523$, $\epsilon = -0.001$; 4: $A=1.479$, $\epsilon = -0.00025$) in comparison with $S_{HS}(q)$ (1) and experiment (5) [25].

Table 3. Coefficients b_m (a.u.) obtained for pure Na and K employing the input data from Tabs. 1-2.

	b_0	b_1	b_2	b_3	b_4	b_5
Na	3.642	6.699	-46.031	42.457	8.877	-16.545
K	-0.277	10.767	-50.872	95.783	-81.597	26.011

Table 4. Coefficients b_{ijm} (a.u.) obtained for the equiatomic Na-K alloy at $T=373$ K.

	m	0	1	2	3	4	5
b_{ijm}							
b_{11m}		-0.079	-2.131	0.376	0.644	0.210	-0.002
b_{22m}		-1.111	1.291	-0.346	-0.489	0.135	0.307
b_{12m}		-0.989	-0.717	-0.572	1.941	-0.050	-0.118

Bhatia-Thornton (BH) [26] partial structure factors,

$$S_{NN}(q) = c_1 S_{11}(q) + c_2 S_{22}(q) + 2\sqrt{c_1 c_2} S_{12}(q), \quad (25)$$

$$S_{cc}(q) = c_1 c_2 [c_2 S_{11}(q) + c_1 S_{22}(q) - 2\sqrt{c_1 c_2} S_{12}(q)], \quad (26)$$

$$S_{Nc}(q) = c_1 c_2 \left[S_{11}(q) - S_{22}(q) + \frac{(c_2 - c_1) S_{12}(q)}{\sqrt{c_1 c_2}} \right], \quad (27)$$

and compare them (Figs. 3, 4) with the RPA results obtained for the same values of ρ and SW parameters.

The total structure factor for Na-K alloy is calculated from the partial structure factors by the standard way using atomic X-ray scattering factors for Na and K [27], and is presented in Fig. 5.

It is obvious from Figs. 3-5 that our MSA-SW formalism leads to a significant discrepancy with the RPA results.

4. Conclusion

From the results for pure liquid Na and K (Figs. 1, 2) it follows that variation of the SW parameters leads to a good agreement between calculated and experimental structure factors, but not in the case of the HS or infinite limits. This provides an option to use the SW model as a reference system in the framework of the variational method for liquid metal state calculations.

Fig. 5 shows that the results obtained in our approach are more accurate than those for the RPA.

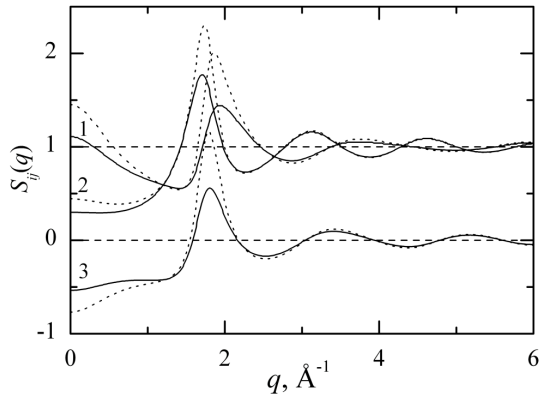


Figure 3. The Ashcroft-Langreth partial structure factors of the liquid equiatomic Na-K alloy at $T=373$ K (1: $S_{NaNa}(q)$; 2: $S_{KK}(q)$; 3: $S_{NaK}(q)$). Solid lines show our approach and dotted lines represent RPA.

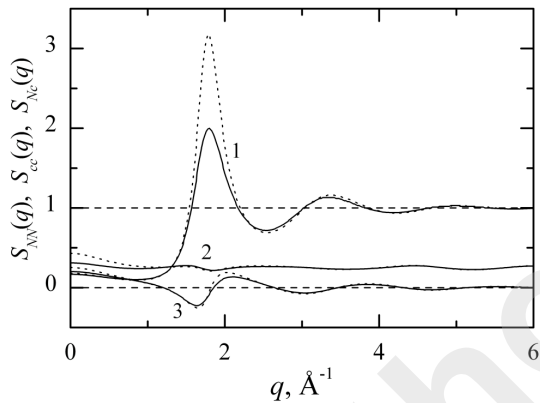


Figure 4. The Bhatia-Thornton partial structure factors of the liquid equiatomic Na-K alloy at $T=373$ K (1: $S_{NN}(q)$; 2: $S_{cc}(q)$; 3: $S_{Nc}(q)$). Solid lines show our approach and dotted lines represent RPA.

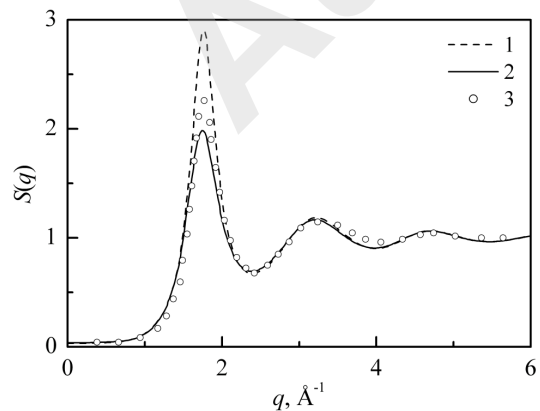


Figure 5. The total structure factor of the liquid equiatomic Na-K alloy (1: RPA; 2: our approach; 3: experiment [25]).

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