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Excess entropy of mixing for binary square-well fluid in the mean spherical approximation: Application to liquid alkali-metal alloys

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ABSTRACT

The expression for the entropy of binary square-well (SW) mixture is derived in the framework of the semi-analytical approach [J. Non-Cryst. Solids 353 (2007) 1798] for the mean spherical approximation. This expression is applied to calculate the concentration dependencies of the excess entropy of mixing for liquid Na-K and Na-Cs alloys at $T = 373$ K. It is shown that the SW model allows to achieve a better agreement with experiment than the hard-sphere model with the same values of hard-core parameters.

1. Introduction

Different types of fluids can be described by means of the square-well (SW) model: non-polar molecular fluids [1–3], colloids [4–7], aqueous electrolyte solutions [8,9], polymers [10–12] and polar and associating compounds, including water [13,14] and metal liquids [15–21] (for last, the SW model was used recently as a reference system also [22–24]).

For liquid metals, the SW model is able to describe the structure factor with low-lying shoulder on the high-angle side of the first peak [15]. In liquid metal binary alloys, this model can describe different deviations from the ideal mixing such as tendencies to chemical short-range ordering [18] or to phase separation [19].

In majority of works where the SW model is applied to metal state, the random phase approximation (RPA) [25–27] is used. Only recently, going beyond the framework of the RPA was implemented in this field [20,21] by using the mean spherical approximation (MSA) [28] for which the semi-analytical (SA) procedure suggested by Dubinin et al. [29] was conducted. Notice that the MSA-SA procedure reproduces explicitly the numerical MSA results obtained by solving the Ornstein–Zernike integral equation [30] both for a pure [31] and for binary [32] SW fluid at an appropriate number of coefficients in the expansion suggested by Dubinin et al. [29]. In the study of Dubinin et al. [21], the SW-MSA-SA was used to study the partial structure factors of liquid equiatomic Na-K alloy.

Here, we derive the MSA-SA expression for the entropy of binary SW mixture (earlier, expressions for the entropy of pure SW fluid were derived within the RPA [22] and within the MSA-SA [24]) and estimate its usefulness for liquid metal alloys on the example of Na-K and Na-Cs systems.

These systems are interesting for consideration since their entropies of mixing very little deviate from the entropy of the ideal solution, $S_{\rm id}$. In that case, the excess entropy of mixing, ΔS^{ex}, is very small and sensitive to the method of calculation. Consequently, this quantity namely is chosen here for investigation.

2. Theory

For a binary alloy, $\Delta S^{\rm ex}$ is expressed as follows:

$$\Delta S^{\rm ex} = S^{\rm bin} - \sum_{i=1}^{2} c_i S_i^{\rm pure} - S_{\rm id}, \qquad (1)$$

where $S^{\rm bin}$ is the entropy of binary alloy, $S_i^{\rm pure}$ is the entropy of the ith-kind pure substance at the same absolute temperature, T (further, we neglect indexes “pure” and “i,” denoting the thermodynamic quantities of pure substances) and c_i is the concentration of the ith component in the alloy. The entropy of the ideal solution is calculated as follows:

$$S_{\rm id} = -k_{\rm B}(c_1 \ln c_1 + c_2 \ln c_2). \qquad (2)$$

Consider a one-component SW fluid that is described by the following three-parameter model pair potential:

$$\varphi_{\rm SW}(r) = \begin{cases} \infty, & r<\sigma \\ \phi_{\rm SW}(r), & r\geq\sigma \end{cases}, \qquad (3)$$

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where σ is the diameter of the hard core (HC);

$$\phi_{SW}(r) = \begin{cases} 0, & r<\sigma \\ \varepsilon, & \sigma\le r<\lambda\sigma; \\ 0, & r\ge\lambda\sigma \end{cases} \tag{4}$$

ε and $\sigma(\lambda-1)$ are the depth and width of the square well, respectively.

The entropy of such a fluid can be expressed as follows:

$$S_{SW} = S_{HS} + \Delta S_{SW} = S_{IG} + \Delta S_{HS} + \Delta S_{SW}, \tag{5}$$

where S_{HS} is the entropy within the hard-sphere (HS) model, ΔS_{SW} is the contribution due to the difference between SW and HS entropies and S_{IG} is the entropy of the ideal gas (hereafter, all thermodynamic quantities will be written in atomic units (a.u.) per atom), calculated as follows:

$$S_{IG} = k_B\left[\frac{5}{2} + \ln\left(\frac{1}{\rho}\left[\frac{k_B T m}{2\pi}\right]^{\frac{3}{2}}\right)\right]. \tag{6}$$

Here, k_B is the Boltzmann constant, ρ is the mean number density and m is the atomic mass.

ΔS_{SW} in the framework of the MSA-SA was obtained by Dubinin et al. [24]:

$$\Delta S_{SW\text{-}MSA\text{-}SA} = \frac{k_B}{4\pi^2\rho}\int_0^\infty (\ln[(1-\rho\Delta c(q))\chi_{SW-MSA\text{-}SA}(q)] - (1-\rho\Delta c(q))\chi_{SW-MSA\text{-}SA}(q) + 1)q^2 dq \tag{7}$$

where $\chi(q)$ is the structure factor, calculated as follows:

$$\chi_{SW\text{-}MSA\text{-}SA}(q) = \frac{1}{1-\rho\Delta c(q) + \beta\rho\phi_{SW}(q)}; \tag{8}$$

$$\Delta c(q) = \left(\frac{4\pi}{q^3}\right)\left\{\sum_{m=1}^{n+2} x^{2-m}\frac{\partial^m \sin(x)}{\partial x^m}\sum_{l=0}^{n} b_l \prod_{k=0}^{m-2}(l+1-k) + \sum_{m=1}^{[(n+1)/2]}\frac{(-1)^{m+1}(2m)!b_{(2m-1)}}{x^{2m-1}}\right\}. \tag{9}$$

Here,

$$\phi_{SW}(q) = 4\pi\varepsilon[\sin(\lambda x) - \sin(x) - \lambda x\cos(\lambda x) + x\cos(x)]/q^3; \tag{10}$$

$\beta = (k_B T)^{-1}$, $x = q\sigma$, $[a]$ is the integral part of a, b_m is the coefficient determined numerically from the condition that the pair correlation function, $g(r)$, must be equal to zero inside the HC.

To obtain Eq. (7), we used the following thermodynamic relation:

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_\rho, \tag{11}$$

where E is the internal energy.

For the SW fluid, Eq. (11) leads to the following expression [24]:

$$\left(\frac{\partial(\Delta S_{SW})}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial U_{SW}}{\partial T}\right)_\rho, \tag{12}$$

where U_{SW} is the SW potential energy:

$$U_{SW} = 2\pi\rho\int_0^\infty \varphi_{SW}(r)g_{SW}(r)r^2 dr = 2\pi\rho\int_\sigma^{\lambda\sigma}\phi_{SW}(r)g_{SW}(r)r^2 dr. \tag{13}$$

For subsequent operations, U_{SW} within the MSA-SA form in the wave space will be used:

$$U_{SW\text{-}MSA\text{-}SA} = \frac{2}{3}\pi\rho\sigma^3\varepsilon\left(\lambda^3-1\right) + \frac{1}{4\pi^2}\int_0^\infty[\chi_{SW\text{-}MSA\text{-}SA}(q)-1]\phi_{SW}(q)q^2 dq. \tag{14}$$

For the binary SW mixture, Eqs. (3) and (4) are being transformed to the following expressions, respectively:

$$\varphi_{ijSW}(r) = \begin{cases} \infty, & r<\sigma_{ij} \\ \phi_{ijSW}(r), & r\ge\sigma_{ij} \end{cases}, \tag{15}$$

where σ_{ij}, ε_{ij} and λ_{ij} are the partial SW parameters ($i, j = 1, 2$);

$$\phi_{ijSW}(r) = \begin{cases} 0, & r<\sigma_{ij} \\ \varepsilon_{ij}, & \sigma_{ij}\le r<\lambda_{ij}\sigma_{ij} \\ 0, & r\ge\lambda_{ij}\sigma_{ij} \end{cases}. \tag{16}$$

The SW entropy of two-component fluid is written as follows:

$$S_{SW}^{bin} = S_{IG}^{bin} + S_{id} + \Delta S_{HS}^{bin} + \Delta S_{SW}^{bin}, \tag{17}$$

where

$$S_{IG}^{bin} = k_B\left[\frac{5}{2} + \ln\left(\frac{1}{\rho^{bin}}\left[\frac{k_B T m_1^{c_1} m_2^{c_2}}{2\pi}\right]^{\frac{3}{2}}\right)\right]. \tag{18}$$

To obtain ΔS_{SW}^{bin}, we use the way similar to that for the one-component case, i.e., rewrite Eq. (12) as follows:

$$\left(\frac{\partial\left(\Delta S_{SW}^{bin}\right)}{\partial T}\right)_{\rho^{bin}} = \frac{1}{T}\left(\frac{\partial U_{SW}^{bin}}{\partial T}\right)_{\rho^{bin}}, \tag{19}$$

where

$$U_{SW}^{bin} = \frac{2}{3}\pi\rho^{bin}\sum_{i,j=1}^{2} c_i c_j \sigma_{ij}^3\varepsilon_{ij}\left(\lambda_{ij}^3-1\right) + \frac{1}{4\pi^2}\sum_{i,j=1}^{2}\sqrt{c_i c_j}\int_0^\infty\left[\chi_{ijSW}(q)-\delta_{ij}\right]\phi_{ijSW}(q)q^2 dq. \tag{20}$$

Here, $\chi_{ij}(q)$ is the partial structure factor in the form of Ashcroft and Langreth [33]:

$$\chi_{ii}(q) = \frac{1-c_j\rho^{bin}c_{jj}(q)}{[1-c_1\rho^{bin}c_{11}(q)][1-c_2\rho^{bin}c_{22}(q)] - c_1c_2\rho^{bin2}c_{12}^2(q)}, \tag{21}$$

$$\chi_{12}(q) = \frac{\sqrt{c_1c_2}\rho^{bin}c_{12}(q)}{[1-c_1\rho^{bin}c_{11}(q)][1-c_2\rho^{bin}c_{22}(q)] - c_1c_2\rho^{bin2}c_{12}^2(q)}, \tag{22}$$

where $c_{ij}(r)$ is the partial direct correlation function. Within the SW-MSA-SA, this characteristic is written as follows:

$$c_{ijSW\text{-}MSA\text{-}SA}(q) = -\beta\phi_{ijSW}(q) + \Delta c_{ij}(q), \tag{23}$$