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Self-diffusion coefficients of liquid alkali metals described by the square-well model within the mean spherical approximation

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The square-well (SW) model in the semi-analytical modification of the mean spherical approximation (MSA) is used for calculating the self-diffusion coefficients of liquid sodium and potassium in the linear trajectory approximation. The results obtained are found to be in reasonable agreement with the available experimental data and show that a good quantitative description of diffusion properties for liquid metals in the SW-MSA approach can be achieved at the same values of the SW parameters that lead to a good description of their structure characteristics.

Keywords: Liquid alkali metals, Self-diffusion, Square-well model

1 Introduction

The square-well (SW) model is intensively studied and widely used for description of pair interactions in different real substances[1-5]. Starting from the work of Gopala Rao and Murthy[6] this model is actively applied to investigate liquid metals[7-11]. Recently, this model has been used also as a reference system[12-14] in liquid-metal variational calculations, which were successfully realized earlier with other reference systems[15-27].

Some years ago, the semi-analytical (SA) modification[28] of the mean spherical approximation[29] (MSA) was suggested to solve the SW model and then applied to calculate structure factors of liquid Na, K and their equiatomic alloy[9,10].In the present paper, the SW-MSA-SA approach is used to calculate the self-diffusion coefficients of liquid Na and K.

2 Theory

The pair potential of the SW fluid, $\varphi_{\rm SW}(r)$ is written as follows:

$$\varphi_{\rm SW}(r)=\begin{cases}\infty, & r<\sigma\\ \varepsilon, & \sigma\le r<\lambda\sigma\\ 0, & r\ge\lambda\sigma\end{cases} \quad \ldots(1)$$

where σ, ε and λ are the SW parameters: σ the diameter of the hard core (HC); ε and $\sigma(\lambda-1)$ are the depth and width of the square well, respectively.

Another way to express this characteristic is the following:

$$\varphi_{\rm SW}(r)=\begin{cases}\infty, & r<\sigma\\ \phi_{\rm SW}(r), & r\ge\sigma\end{cases} \quad \ldots(2)$$

where

$$\phi_{\rm SW}(r)=\begin{cases}0, & r<\sigma\\ \varepsilon, & \sigma\le r<\lambda\sigma\\ 0, & r\ge\lambda\sigma\end{cases} \quad \ldots(3)$$

The Fourier transform of $\phi_{\rm SW}(r)$ is:

$$\phi_{\rm SW}(q)=4\pi\varepsilon\left\{\begin{matrix}\sin(\lambda x)-\sin(x)\\ -\lambda x\cos(\lambda x)+x\cos(x)\end{matrix}\right\}/q^3 \quad , \quad \ldots(4)$$

where $x=q\sigma$.

For an arbitrary HC pair potential:

$$\varphi_{\rm HC}(r)=\begin{cases}\infty, & r<\sigma\\ \phi_{\rm HC}(r), & r\ge\sigma\end{cases} \quad \ldots(5)$$

Lebowitz and Percus[29] suggested the mean spherical approximation to describe the direct correlation function, *c*(*r*), outside the hard core:

$$c_{\text{MSA}}(r) = -\beta\phi_{\text{HC}}(r), \quad r \geq \sigma \qquad \ldots(6)$$

where $\beta = (kT)^{-1}$; k the Boltzmann constant; T is the absolute temperature.

Later, we suggested to represent $c(r)$ inside the hard core as analytical power series including coefficients determined numerically[28] (and named this approach as semi-analytical):

$$c_{\text{SA}}(r) = \sum_{m=0}^{n} b_m \left(\frac{r}{\sigma}\right)^m, \quad r < \sigma \qquad \ldots(7)$$

where b_m are the coefficients determined from the condition that the pair correlation function, $g(r)$ must be equal to zero inside the HC:

$$g(r) = 0, \quad r < \sigma \qquad \ldots(8)$$

The Fourier transform of $c_{\text{SA}}(r)$ was derived in Ref. (28):

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

where $[a]$ is the integral part of a.

The MSA in conjunction with the SA procedure for the case of the SW pair potential gives:

$$c_{\text{SW-MSA-SA}}(r) = \begin{cases} \sum_{m=0}^{n} b_m \left(\frac{r}{\sigma}\right)^m, & r < \sigma \\ -\beta\phi_{\text{SW}}(r), & r \geq \sigma \end{cases} \qquad \ldots(10)$$

$$c_{\text{SW-MSA-SA}}(q) = -\beta\phi_{\text{SW}}(q) + c_{\text{SA}}(q). \qquad \ldots(11)$$

To fulfill numerical calculations, the well-known relations must be used as :

$$S(q) = \frac{1}{1-\rho c(q)} \qquad \ldots(12)$$

$$g(r) = 1 + \frac{1}{2\pi^2\rho}\int_0^\infty [S(q)-1]\frac{\sin(qr)}{qr}q^2 \mathrm{d}q \qquad \ldots(13)$$

where $S(q)$ is the structure factor and ρ is the mean atomic density.

To calculate the self-diffusion coefficient, $D = (\beta\xi)^{-1}$ (where ξ is the friction coefficient), we use the linear trajectory (LT) approximation[30] applied to the HC fluids[30,31] :

$$\xi_{\text{LT}} = \xi_1 + \xi_2 + \xi_{12} \qquad \ldots(14)$$

where ξ_1 and ξ_2 are the contributions to the friction coefficient due to the repulsive and attractive parts of the pair interaction, respectively; ξ_{12} is the cross-correlation term:

$$\xi_1 = \frac{8}{3}\rho\sigma^2 g(\sigma)(\pi M/\beta)^{1/2} \qquad \ldots(15)$$

$$\xi_2 = -\frac{(\beta\pi M)^{1/2}}{12\pi^2}\int_0^\infty [S(q)-1]\phi_{\text{HC}}(q)q^3 \mathrm{d}q \qquad \ldots(16)$$

$$\xi_{12} = -\frac{1}{3}\rho\, g(\sigma)(\beta M/\pi)^{1/2}\int_0^\infty [x\cos(x) - \sin(x)]\phi_{\text{HC}}(q)\mathrm{d}q \qquad \ldots(17)$$

where M is the atomic mass. Here, we take:

$$\begin{aligned} \phi_{\text{HC}}(q) &= \phi_{\text{SW}}(q) \\ g(r) &= g_{\text{SW-MSA-SA}}(r) \\ S(q) &= S_{\text{SW-MSA-SA}}(q) \end{aligned} \qquad \ldots(18)$$

3 Results and Discussion

The SW-MSA-SA formalism is applied to calculate the self-diffusion coefficients of liquid Na and K at T = 373K. The values of SW parameters are taken from Ref. (10) (where they gave a good agreement with experiment for the structure factors of metals under consideration) and listed in Table 1. The value of n in Eqs. (10) and (11) is taken equal to 5. Experimental values of the mean atomic density are taken from Ref. (32) (0.0036 atomic units (a.u.) for Na and 0.0019 a.u. for K).

The results obtained for self-diffusion coefficients in comparison with experimental ones[33,34] are

Table 1 — SW parameters used for the calculation

Metal	σ(a.u.)	ε(a.u.)	λ
Na	6.1027	-0.00100	1.400
K	7.7500	-0.00025	1.479

Table 2 — Self-diffusion coefficient, $D*10^{-9}$ (m^2/s), of liquid Na and K at $T = 373$ K

Metal	Calculation	Experiment
Na	3.15	3.89 [33]
K	4.36	5.44 [34]

presented in Table 2. It is found that the calculated values are in a reasonable agreement with available experimental data.

4 Conclusions

The investigation fulfilled shows that the SW model is useful for description of diffusion properties in liquid metals. Besides, it is defined that a good quantitative description of self-diffusion coefficients can be achieved at the same values of the SW parameters that lead to a good description of structure factors in liquid metals.

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