The SW-MSA Calculation of Self-Diffusion Coefficients in Liquid Lithium and Rubidium

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Successfully used recently for liquid Na and K the approach combined the linear trajectory approximation with the square-well model in the semi-analytical representation of the mean spherical approximation to calculate the self-diffusion coefficients is applied here to liquid Li and Rb. As well as earlier for Na and K, the results obtained are found to be in reasonable agreement with the available experimental data and confirm previous conclusion that the square-well model within the mean spherical approximation is quite useful for description of diffusion properties in liquid alkali metals.

1. Introduction

Among different theoretical approaches applied to liquid metal state at last years (for example [1–3]) the square-well (SW) model remains actively used. This model in different modifications is widely studied by means of both theoretical and computer-simulation methods [4–6] and applied to investigate different-kind real substances, such as non-polar molecular fluids [7, 8], colloids [9–12], aqueous electrolyte solutions [13, 14], polymers [15, 16], polar and associating compounds [17], quasi-crystals [18]. To liquid metals the SW model is applied beginning with the work [19] up to now [20–24].

Recently, we applied the SW model in the semi-analytical (SA) representation [4] of the mean spherical approximation (MSA) [25] to calculate self-diffusion coefficients of liquid Na and K [26] within the linear trajectory approximation (LTA) [27, 28]. Here, this LTA-SW-MSA-SA formalism is used to calculate the same quantity for liquid Li and Rb near their melting temperatures.

2. Theory

The pair potential of the SW fluid, $\phi_{SW}(r)$, can be written as follows:

$$\phi_{SW}(r) = \begin{cases} \infty, & r < \sigma \\ \varphi_{SW}(r), & r \geq \sigma, \end{cases} \tag{1}$$

where

$$\varphi_{SW}(r) = \begin{cases} 0, & r < \sigma \\ \varepsilon, & \sigma \leq r < \lambda\sigma \\ 0, & r \geq \lambda\sigma. \end{cases} \tag{2}$$

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

To calculate the self-diffusion coefficient, $D = (\beta\xi)^{-1}$ (where ξ is the friction coefficient), we apply the linear trajectory approximation to the SW fluid. When the last is considered in the framework of the MSA-SA, ξ_{LTA} is expressed as follows:

$$\xi_{LTA}^{SW-MSA-SA} = \xi_1^{SW-MSA-SA} + \xi_2^{SW-MSA-SA}$$
$$+ \xi_{12}^{SW-MSA-SA}, \tag{3}$$

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

$$\xi_1^{SW-MSA-SA} = \frac{8}{3}\rho\sigma^2 g_{SW-MSA-SA}(\sigma)(\pi M/\beta)^{1/2}, \tag{4}$$

$$\xi_2^{SW-MSA-SA} = -\frac{(\beta\pi M)^{1/2}}{12\pi^2} \int_0^\infty (S_{SW-MSA-SA}(q)-1)$$
$$\times \varphi_{SW}(q)q^3 dq, \tag{5}$$

$$\xi_{12}^{SW-MSA-SA} = -\frac{1}{3}\rho g_{SW-MSA-SA}(\sigma)(\beta M/\pi)^{1/2}$$
$$\times \int_0^\infty (x\cos(x) - \sin(x))\varphi_{SW}(q)dq, \tag{6}$$

where ρ is the mean atomic density, M is the atomic mass, $\beta = (kT)^{-1}$, k is the Boltzmann constant, T is the absolute temperature, $g(\sigma)$ is the contact value of the pair correlation function, $g(r)$; $x = q\sigma$; $\varphi_{SW}(q)$ is the Fourier transform of $\varphi_{SW}(r)$, $S(q)$ is the structure factor.

Last two functions are expressed as follows:

$$\varphi_{SW}(q) = 4\pi\varepsilon \{\sin(\lambda x) - \sin(x) - \lambda x \cos(\lambda x)$$
$$+ x\cos(x)\}/q^3, \tag{7}$$

$$S_{\text{SW-MSA-SA}}(q) = \frac{1}{1 - \rho c_{\text{SW-MSA-SA}}(q)}, \qquad (8)$$

where $c(q)$ is the Fourier transform of the direct correlation function, $c(r)$.

The pair correlation function is connected with the structure factor by means of the Fourier transform

$$g_{\text{SW-MSA-SA}}(r) =$$

$$1 + \frac{1}{2\pi^2\rho} \int_0^\infty [S_{\text{SW-MSA-SA}}(q) - 1]\frac{\sin(qr)}{qr} q^2 \mathrm{d}q. \quad (9)$$

The semi-analytical representation of the mean spherical approximation is postulated as follows:

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

where $n \geq 3$; b_m are the coefficients determined numerically to satisfy the condition that $g_{\text{SW-MSA-SA}}(r)$ is equal to zero inside the hard core.

The Fourier transform of Eq. (10) gives the expression for $c_{\text{SW-MSA-SA}}(q)$:

$$c_{\text{SW-MSA-SA}}(q) = -\beta\varphi_{\text{SW}}(q)$$

$$+ \left(\frac{4\pi}{q^3}\right) \left\{ \sum_{m=1}^{n+2} x^{2-m} \frac{\partial^m \sin(x)}{\partial x^m} \sum_{l=0}^{n} b_l \prod_{k=0}^{m-2} (l+1-k) \right.$$

$$\left. + \sum_{m=1}^{[(n+1)/2]} \frac{(-1)^{m+1}(2m)!b_{(2m-1)}}{x^{2m-1}} \right\}, \quad (11)$$

where $[(n+1)/2]$ is the integral part of $(n+1)/2$.

3. Results and discussion

In this section, we apply the LTA-SW-MSA-SA formalism to calculate the self-diffusion coefficients of liquid Li and Rb near the melting temperatures.

The values of the SW parameters are found by fitting the calculated structure factors with respect to the experimental ones [29]. Experimental values of the mean atomic densities are taken from Ref. [30]. All input data are listed in Table I. The value of n is taken equal to 5.

TABLE I

Input data for calculations.

metal	T [K]	ρ [a.u.]*	σ [a.u.]	ε [a.u.]	λ
Li	463	0.0066	4.93	-0.00115	1.361
Rb	313	0.0015	8.63	-0.00028	1.495

*a.u. — atomic units

The calculated self-diffusion coefficients in comparison with experimental data [31–35] are presented in Table II. Results show that the calculated values of D for Li and Rb as well as obtained earlier for Na and K [26] are approximately by 20% less than corresponding experimental ones.

TABLE II

Self-diffusion coefficient, $D \times 10^{-9}$ [m^2/s].

metal	calculation	experiment		
Li	4.81	5.98 [31]	6.19 [32]	5.76 [33]
Rb	2.12	2.68 [31]	2.62 [34]	2.22 [35]

4. Conclusion

The present study confirms the conclusion of the work [26] that the SW model is quite useful for description of diffusion properties in liquid alkali metals at the same values of the SW parameters that lead to a good description of their structure functions.

Acknowledgments

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