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Determination of surface properties of liquid simple metals

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Certain surface properties of liquid simple metals are reported. Using the expression derived by Gosh and coworkers we investigated the surface entropy of liquid simple metals namely Na, K, Rb and Cs. We have also computed surface tensions of the metals concerned. The pair distribution functions are calculated from the solution of Ornstein-Zernike integral equation with Percus-Yevick closure using the individual version of the electron-ion potential proposed by Fioalhais and coworkers which was originally developed for solid state. The predicted values of surface tension and surface entropy are in very good agreement with available experimental data. The present study results show that the expression derived by Gosh and coworkers is very useful for the surface entropy by using Fiolhais pseudopotential and Percus-Yevick closure.

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1. Introduction

The surface properties of liquids have been a subject of interest to the physicist and metallurgists from the long past to the present day because of importance both from scientific and technological point of view [1-6]. The knowledge of surface properties of the liquid state is required during the soldering, brazing, sintering and dying. There are a large number of methods to measure the surface tension of liquids, but those suitable for liquid metals are limited by their chemical reactivity and high melting points. On the other hand, it is not fully understood how they depend on the structure and the thermodynamics of the liquids as well.

The surface properties have been studied by using different theories such as the statistical mechanical theory [1,2], density functional theory [3] and computer simulation [6,7]. The statistical mechanical theory involving surface tension which goes back to Fowler was analyzed and improved by different authors [2-4]. In ref. [4] the authors derived expressions for the surface entropy which is the negative derivative of surface tension, by describing the interaction within the pseudopotential approach. Itami and Shimoji have studied the surface entropy for liquid metals [8] by using the hard sphere model in the statistical theory. But they used a constant packing fraction (η=0.46) for all concerned systems. But experiments show that the values of packing fractions vary from metal to metal. In addition, the Hard Sphere theory for surface entropy involves temperature derivative of Hard sphere diameter. Gosh et al. [9] have described the interionic interaction by Bretonnet and Silbert pseudopotential [10] and derived the values of σ from it by using thermodynamic perturbation theory [11]. $d\sigma/dT$ was obtained from an analytic expression of which is taken from ref. [12].

In the present study, we have used the individual version of local pseudopotential proposed by Fiolhais and coworkers [13,14] which was developed for solid state and can be transferable to the liquid metals [15-20] as interaction potentials. The pair distribution function g(r) is determined from the solution of Ornstein-Zernike equation with Percus-Yevick closure As the hard sphere diameter σ is taken the value of r at the first maximum of g(r).

In order to check the reliability of analytical surface entropy formula derived by Gosh et al., we have chosen liquid alkali metals namely liquid Na, K, Rb and Cs metals near the melting point which have been investigated experimentally. We have calculated surface tensions using with diffusion coefficient taken from ref. [21] and surface entropy of the systems under consideration compared with the experimental values. To the best of our knowledge, previously no one has reported such a study to investigate surface entropy from this transferable pseudopotential and this closure.

The manuscript is organized as follows: In Section 2 we briefly describe the expressions the surface tension, γ and surface entropy S_V, of liquid metals. The results of numerical calculations are given and compared with the available experimental data in Section 3. Some concluding remarks are presented in the last section.

2. Theory

2.1. Surface tension and surface entropy

First expression for surface tension derived by Fowler [1] using the statistical mechanical theory given by

$$\gamma = \frac{\pi n^2}{8}\int_0^\infty \frac{du(r)}{dr} g(r) r^4 dr \,. \tag{1}$$

This theory was analyzed and improved by different authors [2-4]. Application of the hard sphere potential to equation (8) leads [2]

$$\gamma_{HS} = -\frac{1}{8}\pi n^2 k_B T \sigma^4 g(\sigma) \tag{2}$$

where $g(\sigma)$ represents the value of the pair distribution function $g(r)$ at contact distance σ is the hard sphere diameter which can be interpreted as the first maximum of $g(r)$.

Evans derived an expression for surface tension such a liquid by describing the interionic interaction within pseudopotential approach [4] as follows

$$\gamma = -\frac{1}{2} L_e n \frac{du(\rho)}{d\rho} + \gamma_{HS} \tag{3}$$

In Eq. (3) L_e and ρ are the length parameter and electron number density, respectively. As surface entropy is the negative derivative of surface tension S_V at constant volume, one can easily calculate this property once surface tension γ is known as

$$S_V = -\frac{d\gamma}{dT} = -\frac{dE_V}{dT} - \frac{\partial \gamma_{HS}}{\partial T} \tag{4}$$

Since the electrons number density varies very slowly with temperature, the first term on the right of equation (4) can be assumed to be much smaller than temperature dependence of γ_{HS}.. So it may be written

$$\frac{\partial \gamma}{\partial T} \cong \frac{\partial \gamma_{HS}}{\partial T} = -\frac{1}{8}\pi n^2 k_B \left[\sigma^4 g(\sigma) + T\frac{\partial(\sigma^4 g(\sigma))}{\partial T}\right] \tag{5}$$

If the value of $g(\sigma)$ can be obtained Carnahan and Starling's equation [22] and the temperature dependence of σ may be written as [12]

$$\sigma(T) = 1.126\sigma_m \left[1 - 0.112\left(\frac{T}{T_m}\right)^{1/2}\right]. \tag{6}$$

and therefore

$$\left(\frac{\partial \sigma}{\partial T}\right)_V = -0.063\frac{\sigma_m}{(TT_m)^{1/2}} \tag{7}$$

we have [9]

$$S_V = \frac{\pi n^2 k_B \sigma^4 (2-\eta)}{16(1-\eta)^3}\left[1 - 0.252\frac{\sigma_m}{\sigma}\left(\frac{T}{T_m}\right)^{1/2}\right] - \frac{0.189\pi n^2 k_B \sigma^3 \eta \sigma_m (5-2\eta)}{16(1-\eta)^4}\left(\frac{T}{T_m}\right)^{1/2}. \tag{8}$$

where subscript m denotes at melting temperature and $\eta = \pi n \sigma 3/6$ is the packing fraction. Equation (8) is the final formula for the surface entropy which we have used in the present calculation for the metals studied.

Recently, Yokoyama has presented simple but useful expressions for relations between the diffusion coefficient and the surface tension [23] as follows

$$\gamma = \frac{15\, k_B T (k_B T/m)^{1/2}}{(32\,\pi\,\sigma\,D)}\,. \tag{9}$$

3. Results and discussion

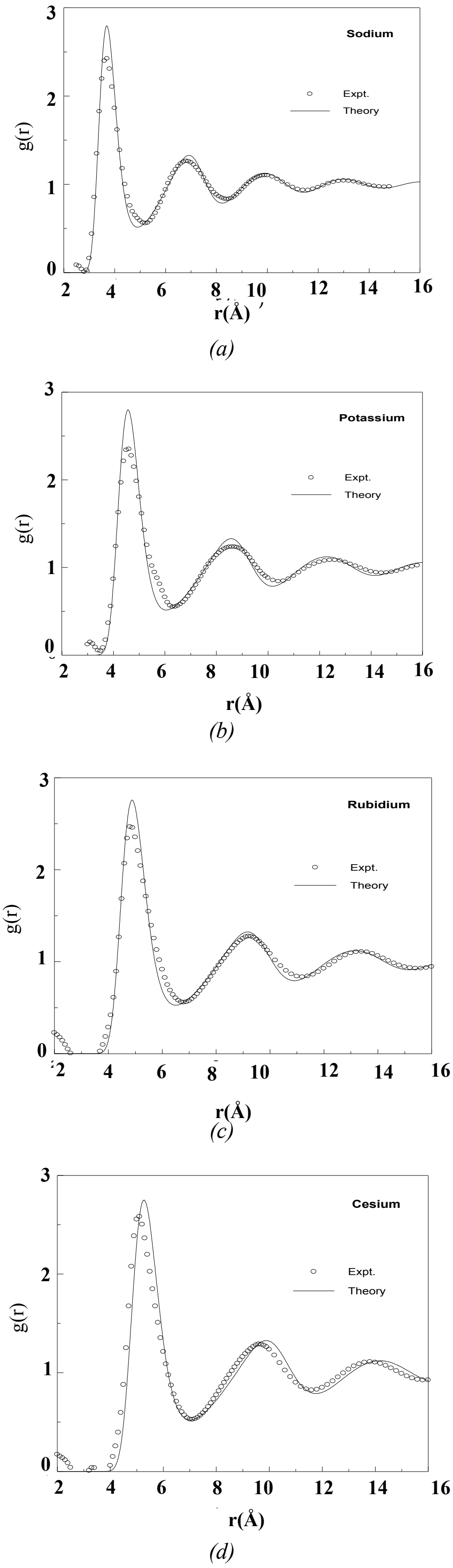
We have calculated the pair distribution function g(r) using Labik, Malijevsky and Vonka algorithm [24] for the numerical solution of the Ornstein Zernike equation in all cases. Each computation were carried out by using 2048 data points with a step size $\Delta r = 0.02$ Å. The computed pair distribution function obtained with Fiolhais pair potential is compared with the experimental data of Waseda [25] in Fig. 1. for the systems that are under consideration.

In the cases of Na, K, Rb, the position agreement between computed and experimental results for g(r) are reasonably well. For Cs, the position of the peak in the computed g(r) is shifted to the right of the experimental data but the amplitudes are at the same order.

As is seen Eq. (8), the main ingredients of the statistical theory for surface entropy at a particular temperature are the effective hard sphere diameter (HSD) and the ionic number density. The values of HSD for each element are listed Table 1.

Table 1. The values of HSD for each element.

Metal	T (K)	σ(Å)	σ_m(Å)
Na	378	3.680	3.685
K	343	4.560	4.566
Rb	313	4.880	4.883
Cs	303	5.280	5.283



(a)

(b)

(c)

(d)

Fig. 2. Computed pair distribution functions g(r) for (a) Na, (b) K, (c) Rb, (d) Cs. The empty circles correspond to the experimental data of Waseda [25]. Solid lines show integral equation results.

It is seen that the values of the HSD at temperature above melting are less than or equal to those of at melting temperature i.e. $\sigma < \sigma_m$. This is due to the fact that as the temperature increases the kinetic energy of the ions increases and consequently two ions get closer.

Then we have extended our calculations for surface properties of the systems that are under consideration. Predicted values of surface tension and surface entropy are summarized in Table 2.

We have calculated surface tensions using Eq. (9) with diffusion coefficient taken from ref. [21] and surface entropy of the systems under consideration using Eq. (8).

As is seen Table 2., the calculated surface tension and surface entropy values are in very good agreement with experimental values for each metal studied in this work.

Table 2. The calculated values of self diffusion coefficient D, surface tension γ and surface entropy S_V, of liquid Na, K, Rb and Cs are together with experimental data.

Metal	D ($10^{-9}m^2s^{-1}$)		γ (Nm^{-1})		S_V ($10^{-3}\ Nm^{-1}K^{-1}$)	
	Calc.*	Expt.♦	Calc.	Expt.♦	Calc.	Expt.#
Na	3.98	3.85-4.23	0.197	0.191	0.120	0.10
K	3.61	3.59-3.76	0.116	0.115	0.080	0.08
Rb	2.72	2.22-2.68	0.085	0.085	0.067	0.06
Cs	2.22	2.16-2.31	0.070	0.070	0.073	0.06

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*Taken from Ref. [21] # Taken from Ref. [8]
♦ Taken from Refs. [26] and [27]

4. Conclusions

We have investigated surface properties namely surface tension and surface entropy of liquid alkali metals. To calculate surface entropy, we have used an analytical expression derived by Gosh et al. following Itami and Shimoji. We have computed the pair distribution function using the individual version of pseudopotential proposed by Fioalhais and coworkers and Ornstein-Zernike integral equation with Percus-Yevick closure.

The Fiolhais potentials along with the Percus-Yevick thory provides reasonably good and reliable values for HSD σ for the study of surface properties of simple liquid metals. The calculated values of surface entropy and surface tension are in good agreement with experimental data. Therefore, we conclude that the the expression derived by Gosh and coworkers is very useful for the surface entropy by using Fiolhais pseudopotential and Percus-Yevick closure.

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