Calculation of surface entropy of liquid transition and noble metals

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ABSTRACT

The surface entropies of liquid transition and noble metals Fe, Co, Ni, Cu, and Ag have been investigated. Surface entropy expression involving hard–sphere (HS) interaction in closed form is used. Since the HS diameter depends on metallic properties and temperature, the temperature dependent effective HS diameter is determined from a well-known perturbation theory, linearized Weeks–Chandler–Andersen (LWCA) and integral equation theory, variational modified hypernetted chain (VMHNC). Theoretical calculations are compared with the available experimental data, and found good agreement for some concerned systems.

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1. Introduction

The surface properties of liquid attracted scientists, metallurgists and technologists from the long past to the present decade [1–6] for their multiple applications, such as soldering, brazing, sintering and dying. The knowledge of physics at the liquid surface is therefore required to understand such processes. The surface properties of a liquid metal is greatly influenced by its structural and thermodynamical properties [7]. Thus a theory which can best describe the liquid structure and thermodynamics of the system would be the most useful one for the effective investigation of the surface properties.

The surface properties can be studied using different theories, for example, the statistical mechanical theory [1,2], density functional theory [3] and computer simulation method [6]. Based on the statistical mechanical theory, Evans [4] studied surface properties of some metals where they described interionic interactions of metals within the pseudo-potential approach. Itami and Shimoji [8] derived an expression for surface entropy involving hard–sphere (HS) interaction, and calculated the surface entropies of concerned metals with a constant packing fraction of 0.46 for all systems. Since the packing fraction (PF) varies on metallic properties and temperature, the calculation of Itami and Shimoji is not theoretically self-consistent in this sense. To make it consistent theoretically, the present authors revised the expression of ref. [8] by introducing the temperature dependent HS diameter in the theory and,

applied it successfully on simple liquid metals [9]. Afterwards, this improved theory has proved to be successful for other liquid metals such as alkali metals [10]. Very recently, Korkmaz and Korkmaz [7] have applied the same theory to the liquid 3d transition metals and have apparently found good agreement with available experimental data, here the authors used an evanescent pseudopotential proposed by Fiolhais et al. [11]. Following them, we have applied same theory with their calculated HS diameters to evaluate surface entropy of their concerned systems. At the initial stage, we first attempted to reproduce the results those obtained by Korkmaz and Korkmaz [7], but unfortunately, we have not been able to do so. We should note here that, the values we obtained are exactly the same in magnitudes as the values of ref. [7] but opposite in sign (i.e. negative) which is physically unacceptable. This negative result of surface entropy particularly motivated us to examine whether the statistical mechanical theory with HS interaction can describe, at least qualitatively, the surface entropy of liquid transition metals. Furthermore, we test the applicability of the theory in case of liquid noble metals.

In order to make the theory self-consistent, we have derived the effective HS diameter or packing fraction from the knowledge of interionic interactions and, employing the thermodynamic perturbation theory as well as variational approach. Specifically, we have used the linearized Weeks–Chandler–Andersen (LWCA) thermodynamic perturbation theory [12] and the variational modified hypernetted chain (VMHNC) integral equation theory [13] in this regard. The VMHNC and LWCA theory have already proved to be successful in describing structure and thermodynamics of liquid transition metals [14–16]. Beside those, Bretonnet and Silbert (BS) proposed a model to describe interionic interactions suitable

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for liquid transition metals[17] as well. The model describes both nearly free electron contributions via the Ashcroft[18] empty core model and s–d mixing inside the core by an exponential term obtained from the d-band phase shift through an inverse scattering approach. As a result, BS pseudo-potential reduces to a simple local form which makes it simpler to evaluate properties of metals where the effect of hybridization is present. It has already proved to be successful in describing liquid structure[14,15], entropy and entropy mixing[19], and atomic transport properties[20] of simple and less simple metals. In the present study, we have therefore chosen BS pseudopotential to calculate surface entropies of liquid transition and noble metals.

We study the surface entropy for liquid transition and noble metals namely Fe, Co, Ni, Cu, and Ag. The first four of these elements lies at the end of the 3d series and the rest one, Ag, is at the end of 4d series. In our concerned metals, the tightly bound d electrons hybridize with nearly free s and p electrons. To incorporate this hybridization effect, the effective number of conducting s electrons per ion, Z_s, is taken as non-integer values following Moriarty[21] and afterwards Bhuiyan et al.[14].

The lay out of this paper is as follows: in Section 2 we describe theories relevant to the present calculation. Section 3 is devoted to the results and discussion. We summarize the report with some concluding remarks in Section 4.

2. Theories

2.1. Surface entropy

The surface entropy involving HS interaction can be written as[8]

$$S_V = \frac{\pi n^2 k_B \sigma^4 (2 - \eta)}{16(1 - \eta)^3} \left[1 + \frac{4T}{\sigma} \left(\frac{\partial \sigma}{\partial T} \right)_V \right]$$
$$+ \left(\frac{\partial \sigma}{\partial T} \right)_V \frac{3\pi n^2 \sigma^3 k_B T \eta (5 - 2\eta)}{16(1 - \eta)^4} \quad (1)$$

where n is the number density, η is the packing fraction, σ is the HS diameter and T is temperature above melting at which the desired properties are calculated.

Temperature dependent HS diameter as proposed by Protopapas et al.[22] is,

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

where σ and σ_m are the HS diameters at temperature T and melting temperature T_m, respectively. Differentiating Eq. (2) we have

$$\left(\frac{\partial \sigma}{\partial T} \right)_V = -0.063\sigma_m \frac{1}{(TT_m)^{1/2}} \quad (3)$$

Substitution of Eq. (3) into Eq. (1) yields the temperature dependent surface entropy[9]

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

This equation is finally used to calculate the surface entropy.

2.2. The effective pair potential

BS have proposed a model potential[17] for liquid transition metals. This model potential has the following form which is constructed by the superposition of the s–p and d-band contributions

$$w(r) = \begin{cases} \sum_{m=1}^{2} B_m \exp(-\frac{r}{ma}) & \text{for } r < R_c \\ -\frac{Z_s e^2}{r} & \text{for } r > R_c \end{cases} \quad (5)$$

where a, R_c and Z_s are the softness parameter, core radius and s-electron occupancy number, respectively. The unscreened form factor can be written as

$$w_0(q) = 4\pi n a^3 \left[\frac{B_1 J_1}{(1 + a^2 q^2)^2} + \frac{8B_2 J_2}{(1 + 4a^2 q^2)^2} \right] - \frac{4\pi n Z_s e^2}{q^2} \cos(q R_c) \quad (6)$$

where the expressions for B_m and J_m are given in ref. [17]. Now the effective interionic interaction is

$$v(r) = \frac{Z_s^2}{r} \left(1 - \frac{2}{\pi} \int F_N(q) \sin(qr) dq \right) \quad (7)$$

where $F_N(q)$ is the normalized energy wave number characteristic

$$F_N(q) = \left(\frac{q^2}{4\pi n Z_s e^2} \right)^2 w_0^2(q) \left[1 - \frac{1}{\epsilon(q)} \right] [1 - G(q)]^{-1}. \quad (8)$$

The dielectric screening function $\epsilon(q)$ is given by

$$\epsilon(q) = 1 - \left(\frac{4\pi e^2}{q^2} \right) \chi(q) [1 - G(q)]. \quad (9)$$

Here $\chi(q)$ is the Lindhard function and $G(q)$ is the local-field correction as developed by Ichimaru and Utsumi[23].

2.3. VMHNC integral equation theory

The VMHNC theory, originally proposed by Rosenfeld[13] belongs to a new generation of integral equation theories of liquids. Like most other integral equation theories the VMHNC solves the Ornstein–Zernike (OZ) equation with a closure relation

$$g(r) = \exp \left[h(r) - c(r) - \beta v(r) - B(r) \right] \quad (10)$$

where $g(r)$, $h(r)$, $c(r)$, $B(r)$ and β denote pair correlation function, total correlation function, direct correlation function, bridge function and inverse of temperature times Boltzmann constant, respectively. The bridge function $B(r)$ is approximated by using the analytic solution of the Percus–Yevick equation for HS namely $B(r) = B_{PY}^{HS}(r, \eta)$. Packing fraction (PF), η is the variational parameter which is determined by minimizing the VMHNC configurational Helmholtz free energy. Once η is fixed for a specific thermodynamic state, the static structure factor $S(q)$ and pair correlation function $g(r)$ may be evaluated.

2.4. LWCA theory

The starting point for the LWCA method as proposed by Meyer et al.[12] is the WCA[24]. The blip function in [24] is defined as

$$B(r) = y_\sigma(r) \left[\exp(-\beta u(r)) - \exp(-\beta u_\sigma(r)) \right] \quad (11)$$

where $u(r)$ and $u_\sigma(r)$ are the soft and the hard–sphere potentials, respectively. In Eq. (11), $y_\sigma(r)$ is the cavity function associated with hard–sphere distribution function. In order to evaluate $y_\sigma(r)$ we follow Mayer et al. [12]. The function $r^2 B(r)$, if plotted as a function of r, gives two sharp teeth (for detail see ref. [12]). In the LWCA the