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Investigation of surface entropy for liquid less simple metals

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Abstract. We have derived an efficient expression in closed form for the surface entropy of liquid metals from the statistical mechanical theory of zeroth order involving hard sphere model interaction. Using this expression we have investigated the surface entropy for liquid less simple metals namely Zn, Cd, In, Sn, Pb, Sb, Tl and Bi selfconsistently. The effective hard sphere diameters are obtained from the thermodynamic perturbation theory called the LWCA. The prediction of the selfconsistent calculation improves significantly for all concerned systems except for Zn and Cd. The underlying cause of discrepancy for Zn and Cd is also discussed.

PACS. 68.03.Cd Surface tension and related phenomena – 68.35.Md Surface thermodynamics, surface energies

1 Introduction

The surface properties of condensed matters have been a subject of interest to the metallergists and physicists from the long past to the present day [1–6]. The main reason of it is the technological importance of the surface properties such as soldering, brazing, sintering and dying. The surface properties may be studied by using different theories for example the statistical mechanical theory [1,2], density functional theory [3] and computer simulation [6,7].

The statistical mechanical theory involving surface tension and the intermolecular forces goes back to Fowler [1], and this theory was subsequently analyzed and improved by different authors [2,4]. In [4] the authors derived expressions for the surface entropy by describing the interionic interaction within the pseudopotential approach. The authors showed that the volume dependent (structure independent) term of the energy plays an important role in the case of surface tension. However, as the entropy is negative derivative of the surface tension one can easily study this property once surface tension γ is known. Regarding this we would like to mention here that the change of density of liquid metals with the change of temperature is very small near melting temperatures. So we assume that the contribution of the volume dependent term of the energy to the surface entropy would be negligibly small relative to the other one.

Surface entropy for some polyvalent metals specifically for Zn, Cd, Tl, Sn, Pb , Sb, and Bi, are studied in this paper. These elements lie at the end of the 3*d*, 4*d* and 5*d* series of transition metals. The *d*-bands of them are completely filled but the effect of $sp - d$ hybridization still exists and significant. In order to take the hybridization effect into account precisely, any concrete theoretical way has not been developed yet. So this effect is accounted for approximately by changing the relative occupancy of the $s(sp)$ and d bands. In doing this there is no restriction as such to use suitable values of the effective s-electron occupancy number, Z, provided the selfconsistent calculation of charge transfer supports it. Regarding this we should mention that Wills-Harison [8] used $Z = 1.5$ for all elements of the 3*d*, 4*d* and 5*d* series except for Au for which they used $Z = 2$. We further mention that the metals studied in [8] involved elements with completely empty, partially and completely filled *d*-bands. Following the same line Bhuiyan et al. used $Z = 1.4$ to describe structure for liquid 3*d* transition metals [9]. Sharmin et al. [10] in their study of electrical resistivity used different values of Z for different elements. In the present work we follow Sharmin et al. to choose the values of Z.

Bretonnet and Silbert (BS) have proposed a model [11] to describe interionic interactions, primarily for liquid transition metals. This model treats *sp* and *d*-bands separately within the well established pseudopotential formalism. The sp band is described via the empty core model and the *d*-band is described from the *d*-band scattering phase shift by using an inverse scattering approach.The resulting model pseudopotential thus reduces to a simple local form which appears similar to that of the well known Heine-Aberenkov model [12]. However, the BS model is simple to handle numerically. Moreover, the local form permits to extend this model to other liquid metals for which the effect of hybridization is important. In the mean time the BS model has already proved to be successful in describing liquid structure [13,14], electrical

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resistivity [10] and atomic transport properties [15] for the less simple metals and their alloys. Note that the norm-conserving non-local pseudopotentials are, in principle, to be preferred for accurate predictions. But there are evidences that local potentials describe physical properties, in some cases, even better [16] than former ones.

Itami and Shimoji have studied the surface entropy for liquid metals [17] by using the hard sphere model in the statistical theory. These authors used a constant packing fraction ($\eta = 0.46$) for all concerned systems. But experiment shows that the values of packing fractions varies from metal to metal. In addition, the hard sphere (HS) theory for surface entropy involves temperature derivative of HS diameter (HSD) $d\sigma/dT$ (see Eq. (8) below). In [17] the values of the $d\sigma/dT$ are extracted by fitting them to experimental values of thermal pressure coefficients. So, these values are not any way connected selfconsistently to the HSD or packing fraction used in the calculation. So in theoretical point of view Itami and Shimoji's calculation in [17] is not fully selfconsistent. In order to make the calculations more theoretical and selfconsistent one should obtain the HSD from the interionic interactions involved between different ions in the liquid. In addition, $d\sigma/dT$ in equation (8) should be connected with those σ which are derived theoretically. To this end we have described the interionic interaction by a model pseudopotential and derived the values of σ from it by using the thermodynamic perturbation theory [18]. Finally, $d\sigma/dT$ is obtained from these values of σ employing an analytic expression.

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

2 Theory

The statistical mechanical theory for surface tension in the zeroth order approximation for elemental liquids may be written as [1]

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

where n, v, and $g(r)$ denote ionic number density, interionic interaction and pair distribution function in the bulk, respectively. Application of the hard sphere potential to equation (1) leads [2]

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

where σ is the effective hard sphere diameter, k_B Boltzmann constant and T temperature.

A combination of a specific form of the electron density profile at the surface and the pseudopotential leads [4]

$$\gamma = E_V + \gamma_{HS} \tag{3}$$

where

$$E_V = -\frac{1}{2} L_e n \frac{du(\rho)}{d\rho}. \tag{4}$$

In equation (4) Le is the length parameter and ρ electron number density. Now the surface entropy of pure liquid at constant volume is

$$S_V = -\frac{\partial \gamma}{\partial T} = -\frac{dE_V}{dT} - \frac{\partial \gamma_{HS}}{\partial T}. \tag{5}$$

As the electrons number density is a very slowly varying function of temperature, the first term on the right of equation (5) may be assumed to be negligibly small relative to the second term. So we have

$$S_V = -\frac{\partial \gamma_{HS}}{\partial T}. \tag{6}$$

Carnahan and Starling's [19] equation gives

$$g(\sigma) = \frac{(2-\eta)}{2(1-\eta)^3} \tag{7}$$

where $\eta = \frac{1}{6}\pi n \sigma^3$, is the packing fraction. From equations (2, 6, 7) we have

$$S_V = \frac{\pi n^2 k_B \sigma^4 (2-\eta)}{16(1-\eta)^3} \left[1 + \frac{4T}{\sigma}(\frac{\partial\sigma}{\partial T})_V\right] + \left(\frac{\partial \sigma}{\partial T}\right)_V \frac{3\pi\ n^2 \sigma^3 k_B T \eta (5-2\eta)}{16(1-\eta)^4}. \tag{8}$$

The temperature dependence of the HSD may be written as [20]

$$\sigma(T) = 1.126\sigma_m \left[1 - 0.112\left(\frac{T}{T_m}\right)^{\frac{1}{2}}\right]. \tag{9}$$

Therefore

$$\left(\frac{\partial \sigma}{\partial T}\right) = -0.063 \frac{\sigma_m}{(T T_m)^{\frac{1}{2}}} \tag{10}$$

where subscript m denotes at melting temperature. Substitution of equation (10) into (8) yields

$$S_V = \frac{\pi n^2 k_B \sigma^4 (2-\eta)}{16(1-\eta)^3}\left[1 - \frac{4T}{\sigma} 0.252 \frac{\sigma_m}{\sigma}(\frac{T}{T_m})^{\frac{1}{2}}\right] - \frac{0.189 \pi n^2 \sigma^3 k_B \eta (5-2\eta)}{16(1-\eta)^4}\left(\frac{T}{T_m}\right)^{\frac{1}{2}}. \tag{11}$$

This is the final formula for the surface entropy which we have used in the present calculation.

2.1 The effective pair potential

The electron ion interaction for a metallic system may be written as [11]

$$w(r) = \begin{cases} \sum_{m=1}^{2} B_m \exp(-\frac{r}{ma}) & \text{for } r < R_c \\ -\frac{Ze^2}{r} & \text{for } r > R_c \end{cases} \tag{12}$$

where a, R_c and Z_s are the softness parameter, the core radius and the s electron occupancy number, respectively. The unscreened form factor is

$$w_0(q)=4\pi na^3\left[\frac{B_1J_1}{(1+a^2q^2)^2}+\frac{8B_2J_2}{(1+4a^2q^2)^2}\right]-\frac{4\pi nZ_se^2}{q^2\cos(qR_c)}. \tag{13}$$

Expressions for B_m and J_m are given in [11]. Now the effective interionic interaction is

$$v(r)=\frac{Z_s^2}{r}\left(1-\frac{2}{\pi}\int F_N(q)\sin(qr)dq\right) \tag{14}$$

where the normalized energy wavenumber characteristic is given by

$$F_N(q)=\left(\frac{q^2}{4\pi nZ_se^2}\right)^2 w_0^2(q)\left[1-\frac{1}{\epsilon(q)}\right][1-G(q)]^{-1}. \tag{15}$$

In equation (15) $\epsilon(q)$ denotes the dielectric function which incorporates the local field factor $G(q)$. The dielectric function is taken from Ichimaru and Utsumi [21] because it satisfies the compressibility sum rule and the short range correlation condition.

2.2 The LWCA theory

The starting point for the LWCA method as proposed by Meyer et al. [18] is the WCA [22]. The blip function in [22] is defined as

$$B(r)=y_\sigma(r)[\exp(-\beta u(r))-\exp(-\beta u_\sigma(r))] \tag{16}$$

where $u(r)$ and $u_\sigma(r)$ are the soft and the hard sphere potentials, respectively. β denotes the inverse temperature times Boltzmann constant. In equation (16) $y_\sigma(r)$ is the cavity function associated with hard sphere distribution function. In order to evaluate $y_\sigma(r)$ we follow Mayer et al. [18]. The function $r^2B(r)$, if plotted as a function of r, gives two sharp teeth (details are given in Ref. [18]). In the LWCA the teeth are approximated by right triangles. Then the Fourier transform of $B(r)$ gives

$$B(q)=4\pi\int_0^\infty B(r)r^2\frac{\sin(qr)}{qr}dr. \tag{17}$$

Now expanding the integral in-terms of Bessel's function and then taking $B(q=0)=0$ one gets

$$\beta u(\sigma)=\ln\left(\frac{-2\beta\sigma u'(\sigma)+Y+2}{-\beta\sigma u'(\sigma)+Y+2}\right) \tag{18}$$

where u' indicates the first derivative of u with respect to r. The graphical or numerical solution of this transcendental equation yields the effective hard sphere diameter σ.

Table 1. Input values for number densities ρ and ρ_m at temperature T and melting temperature T_m respectively, core radius R_c, softness parameter a and the effective s-electron occupancy number Z_s for concerned systems

Liquid	T (K)	T_m (K)	$\rho\,(\text{Å}^{-3})$	$\rho_m\,(\text{Å}^{-3})$	R_c (a.u.)	a (a.u.)	Z_s
Bi	573.0	544.0	0.0289	0.0290	1.49	0.317	1.7
Sb	933.0	903.5	0.0320	0.0321	1.06	0.193	1.5
Pb	613.0	600.0	0.0310	0.0310	1.47	0.307	1.6
Sn	523.0	505.0	0.0353	0.0355	1.30	0.273	1.7
Tl	588.0	575.0	0.0332	0.0332	1.13	0.218	1.5
In	433.0	429.6	0.0369	0.0369	1.32	0.278	1.6
Cd	623.0	594.0	0.0428	0.0429	1.23	0.253	1.8
Zn	723.0	692.0	0.0602	0.0605	1.27	0.285	1.4

3 Results and discussions

We have first derived the surface entropy formula by including an analytic expression for the temperature derivative of the HSD in the statistical theory of zeroth order. Then we have performed numerical calculations selfconsistently for the surface entropy of some liquid less simple metals (Bi, Sb, Pb, In, Tl, Cd, Zn). The results of these calculations are presented in this section.

In order to obtain the effective interionic interactions for less simple metals we require a model which can treat the *sp*-*d* hybridization effects adequately. The BS model is capable for taking this effect into account and so we used it in the calculations. The BS model has three parameters to be fixed before the effective calculations. These are the core radius R_c, the softness parameter a and the effective s-electron occupancy number Z. These values we choose in the following way. The value of R_c is generally determined by fitting to the physical properties of the system of interest, for example, bulk modulus, pressure and electrical resistivity etc. Since we are interested in the study of surface property the most reliable values of R_c are taken [23]. Regarding the choice of Z we follow the concept that the effect of $sp-d$ hybridization can be approximately accounted for by changing the relative occupancy of *sp*-band for elemental systems. Recently Sharmin et al. [10] studied the electronic transport properties of the same liquid less simple metals. We take the values for Z from their work [10]. Finally the values of the softness parameter a are determined by fitting the VMHNC results to the experimental static structure factor $S(q)$ at low q. The effective pair potentials obtained with these parameters are shown in the Figures 1 and 2. It is seen that the potential profiles, in particular the depth and position of the well are almost equal for all systems except for In. For the latter the depth is small. But from a closer look it is noticed that there is slight variation in the position of the minima for certain metals. The values of the input parameters for potentials are listed in Table 1.

The main ingredients of the statistical theory for surface entropy at a particular temperature are the effective hard sphere diameter (HSD) or packing fraction, and the ionic number density. The HSD is related to the effective

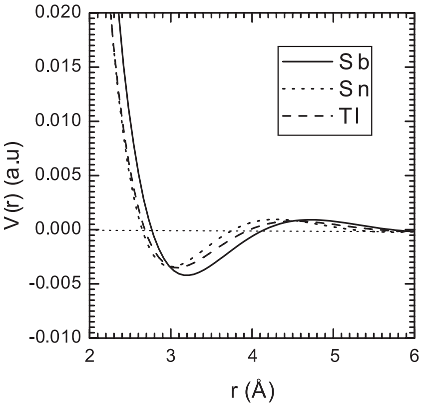

Fig. 1. Pair potentials for Sb, Sn, and Tl.

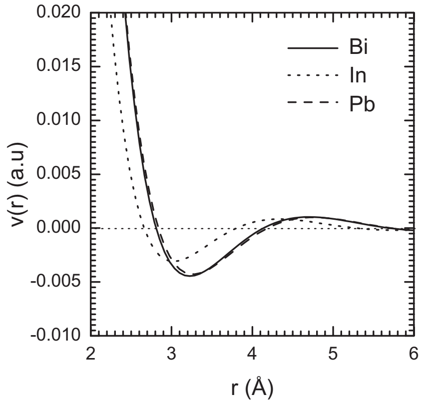

Fig. 2. Pair potentials for Bi, In and Pb.

interionic interaction and are derived by using a thermodynamic perturbation method, called the LWCA. The values of HSD for each element are listed in Table 2. It is seen that the values of the effective 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. The difference between the melting temperature and the temperature of calculation is very small in the case of Pb and In. Consequently, difference between σ and σ_m have not been observed for these two systems. A systematic study on the temperature dependence of the HSD [13] also lends support to the correctness of our results. These results also reflect the accuracy and internal consistency of our calculations.

Now we turn to the results for the surface entropy of liquid less simple metals namely for Bi, Sb, Pb, Sn, Tl, In, Cd and Zn. These are calculated by using equation (11) and presented in Table 2. From the Table 2 we see that the difference between the theoretical and experimental values for entropy lies in the range 0.008 to 0.063. But the overall agreement is good except for Cd. Now if our results are compared with those of reference [17], we notice that our values are closer to those of experiments for all systems except for Zn and Cd. However, in this view over all agreement of our results is much better than others.

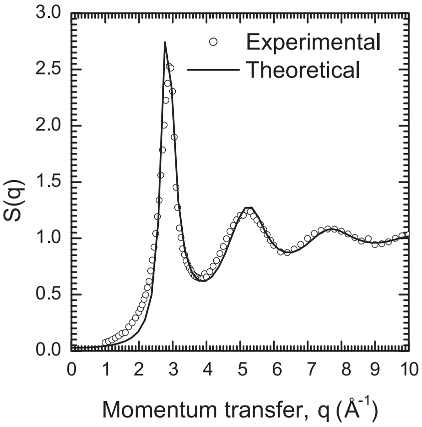

Fig. 3. Theoretical and experimental structure factor for Zn.

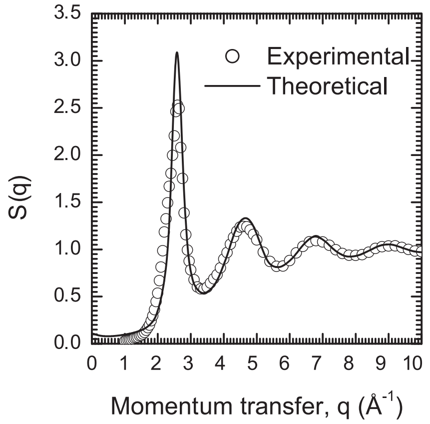

Fig. 4. Theoretical and experimental structure factor for Cd.

Table 2. Calculated values for surface entropies $S_V(\mathrm{N\,m^{-1}\,Kg^{-1}}(10^{-3}))$, HS diameters σ and σ_m at temperature T and melting temperature T_m respectively and temperature dependent packing fraction η of our concerned liquids. *A column represents surface entropies calculated by T. Itami and M. Shimoji.

Liquid	σ(Å)	σ_m(Å)	η	S_Ω (theo.)	S_Ω (expt.)	S_Ω(*A)
Bi	2.996	3.000	0.408	0.054	0.07	0.14
Sb	2.897	2.900	0.407	0.059	0.05	0.08
Pb	3.020	3.020	0.447	0.067	0.13	0.16
Sn	2.790	2.793	0.401	0.062	0.07	0.19
Tl	2.835	2.840	0.396	0.058	0.08	0.15
In	2.818	2.818	0.432	0.073	0.09	0.18
Cd	2.730	2.736	0.460	0.082	0.26	0.19
Zn	2.472	2.476	0.476	0.107	0.17	0.20

We note here that the experimental values for $d\gamma/dT$ are negative for all concerned systems except for Zn and Cd, for the latter two these are positive [24]. This anomalous behaviour may be the root cause of discrepancy in the case of Zn and Cd although calculated static structure factors are in good agreement with experimental data (see Figs. 3 and 4).

4 Conclusions

This paper reports the results of calculations for surface entropy of the polyvalent liquid less simple metals. In this work we have first derived an analytic expression for the surface entropy and then perform numerical calculations selfconsistently. From the above results and discussions we can draw the following concluding remarks.

(i) The Bretonnet-Silbert potentials along with the LWCA theory provides reasonably good and reliable values for HSD σ, for the study of surface properties of less simple liquid metals.
(ii) As far as agreement with the experimental data is concerned the present theoretically selfconsistent approach predicts the surface entropy better for all less simple polyvalent metals studied except for Cd and Zn. For the latter two systems the anomalous temperature dependence of surface tension hampers the agreement although theoretical static structure factors are in good agreement. Further study is required to understand the surface properties for Cd and Zn.
(iii) It is a conjecture that the results for surface entropy for Cd and Zn may be somewhat improved by employing a different but suitable set of parameters involved in the model for potential.
(iv) Finally, a theoretically selfconsistent approach gives better prediction for surface entropy of liquid less simple metals.

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