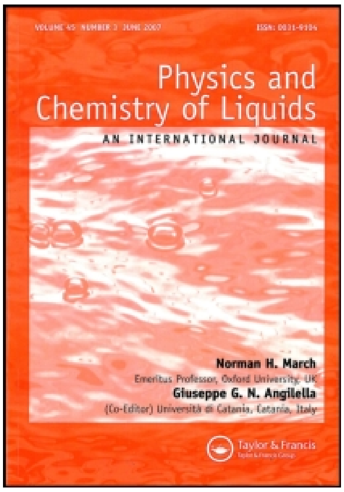

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Surface Energy of Liquid Transition Metals Related to Bulk Compressibility and Thickness

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Surface Energy of Liquid Transition Metals Related to Bulk Compressibility and Thickness

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Using recent data for the isothermal compressibility K_{T_m} of liquid transition metals near the melting temperature, we find that the product σK_{T_m}, where σ is the corresponding surface tension, gives a "length" L of near constant value. In consequence transition metals follow the same pattern as nontransition metals. That is, the width L of the liquid-vapour interface of all liquid metals is relatively sharp and varies little between different classes of metals. Furthermore, the small variations of L can be linked to an "effective valence" of the metal.

KEY WORDS: Liquid transition metals, surface tension, bulk compressibility, thickness.

1 INTRODUCTION

From the work of several authors[1–5] there is empirical evidence that the product σK_{T_m} of the surface tension σ and the isothermal compressibility K_{T_m} of liquid metals near the melting temperature Tm varies only by a factor between 2 and 3 over the range of liquid metals for which data on both σ and K_{T_m} exists. The range of metals on which this observation is based includes simple and polyvalent nontransition metals, and noble metals. This is interesting because the separate values of σ and K_{T_m} vary by as much as a factor of 30 through this range of liquid metals. The product σK_{Tm} has the units of length. Then the values of the length

$$L = \sigma K_{\mathrm{Tm}} \tag{1}$$

range from about 0.2 Å to 0.5 Å. This length was interpreted by Egelstaff and Widom[2] as a fundamental length, characteristic of a substance, proportional to the thickness of the liquid-vapour interface. The proportionality constant depends on the precise definition of this thickness but it is of order unity. In any case, the conclusion is that such an interface is very sharp.

Brown and March[6] have justified Eq. (1) from a simple density functional theory for a model of liquid metals strictly applicable, however, only the alkali group. On the other hand, Alonso and March[4] used some empirical correlations between surface tension, electron density, isothermal compressibility and molar volume, plus the fluctuation theory result[7]

$$S_{\mathrm{Tm}}(0) = \rho k_B T_m K_{\mathrm{Tm}}, \tag{2}$$

where $S_{\mathrm{Tm}}(0)$ is the long wavelength limit of the liquid structure factor $S(k)$, ρ is the atomic density and k_B is the Boltzmann constant, and they arrived at the conclusion that the width L involves the bulk liquid structure factor $S_{\mathrm{Tm}}(0)$ which reflects, in turn, the marked short-range ionic ordering in the liquid More specifically,

$$L = \alpha(S_{\mathrm{Tm}}(0)/Nk_B \mathrm{T}_{\mathrm{m}})^{1/2} \tag{3}$$

where the constant α, so far, is known from empirical considerations only, its value being $\alpha = 0.17 \times 10^{-7}\,\mathrm{mJ}^{1/2}$; N is Avogadro's number.

Very recently Waseda and Ueno[8] have deduced the compressibility of liquid transition metals of the 3d series. In the present paper we then analyse if liquid transition metals fit into the correlation embodied in Eqs (1) and (3). Not surprisingly we find that liquid transition metals behave just as other metals in this respect; in other words we find that the relatively sharp liquid-vapour interface (or the low value of L) appears to be a general property of liquid metals near the melting point.

2 EMPIRICAL CORRELATIONS

In Table 1 we give the experimental values of the surface tension and the isothermal compressibility for liquid 3d-metals, Pd and La, near the melting temperature. The compressibility was obtained by Waseda and

Table 1 Surface tension σ (from data collected by Miedema[11]), isothermal compressibility K_{Tm} (data for d-metals and La were obtained by Waseda and Ueno[8] from X-ray measurements; noble metals are from Ref. 10; Si and Ge are from Table 1 of Waseda[8]; the values in parenthesis for Fe, Co and Ni are from Tsu[9]), product of σ and K_{Tm} and product of atomic volume V_1 and electron density $n_b^1(V_1$ is from Miedema[11]; see Ref. 4 for details of the calculation of n_b^1).

Metal	σ (dyn cm_{-1})	K_{Tm} (10^{-12} dyn^{-1} cm^{-2})	$L = \sigma K_{\mathrm{Tm}}$ (Å)	$V_1 n_b^1$ (e)
Li	410	(11)	0.45	1.2
Na	200	18.6	0.37	1.3
K	110	38.2	0.42	1.2
Rb	85	49.3	0.42	1.2
Cs	70	68.8	0.48	1.1
Be	(1350)	(1.94)	0.26	2.2
Mg	570	5.06	0.29	2.1
Ca	350	11.0	0.38	1.8
Sr	295	13.1	0.39	1.9
Ba	255	17.8	0.45	2.2
Cu	1350	1.45	0.19	2.1
Ag	910	1.86	0.17	2.3
Zn	770	2.50	0.19	2.0
Cd	590	3.24	0.19	2.3
Hg	485	3.75	0.18	2.6
Al	865	2.42	0.21	2.4
Ga	715	2.19	0.16	2.7
In	560	2.96	0.17	2.5
Tl	465	3.83	0.18	2.3
Si	~ 800	3.96	0.32	2.3
Ge	640	3.22	0.21	2.0
Sn	570	2.71	0.15	2.1
Pb	460	3.49	0.16	2.7
Sb	390	4.90	0.19	3.1
Sc	(870)	3.64	0.32	2.9
Ti	1500	1.40	0.21	3.5
V	1900	1.31	<0.25	3.4
Cr	1700	1.10	0.19	3.5
Mn	1100	1.73	0.19	3.6
Fe	1830	1.05 (1.04)	0.19	3.6
Co	1830	0.96 (0.97)	0.18	3.2
Ni	1750	1.03 (0.98)	0.18	3.2
Pd	1480	1.32	0.20	2.7
La	720	4.29	0.31	3.6

Ueno from Eq. (2) above, using values of $S(0)$ deduced from small angle X-ray scattering data. We also report values of K_{Tm} for Fe, Co and Ni directly measured by Tsu *et al.*[9] These are in substantially good agreement with the values derived from X-ray diffraction experiments. To be complete, we have also included results for nontransition metals, taken from Ref. 4 (see also Reference 7). The values of K_{Tm} for the noble metals, taken from Filippov[10], differ a little, from those used in Ref. 4. In addition liquid Si and Ge are also reported in Table 1, with values of K_{Tm} for these two elements taken from Table 1 of reference 8.

The noticeable feature of Table 1 is that the values of $L = \sigma K_{\mathrm{Tm}}$ for liquid transition metals and La are perfectly in line with those of other metals. The average value of L for the transition metals is 0.21, whereas it is 0.43 for alkali metals, 0.35 for alkaline-earths, and 0.19 for the rest of the nontransition metals. Also the value for La is consistent with these. The value of L for Ge is consistent with those of polyvalent nontransition elements (there is some uncertainty, however, in the value of the surface tension of liquid Si, which could account for the value of L for this element).

To arrive at relation (3) Alonso and March[4] used two empirical relations borrowed from the work of Miedema[11,12,13.] The first one is a relation between σ and the electron density n_b^1 at the boundary of atomic cells in the bulk liquid metal (see Ref. 4 for details of the calculation of n_b^1)

$$\sigma = c_1^1 n_b^1, \tag{4}$$

and the other is a relation between n_b^1, the atomic volume V_1 and the isothermal compressibility,

$$n_b^1 = c_2^1 (K_{\mathrm{Tm}} N V_1)^{-1/2}. \tag{5}$$

The values of the empirical constants c_1^1 and c_2^1, determined in Ref. 4 are: $c_1^1 = 0.45\,\mathrm{Jm}^{-2}$ (d.u.) and $c_2^1 = 0.37 \times 10^{-7}\,\mathrm{m}^3$ (d.u.) $\mathrm{J}^{-1/2}$, where one density unit (d.u.) $= 6 \times 10^{22}$ electrons cm^{-3}. When equations (4) and (5) are combined one obtains

$$\sigma = c_1^1 c_2^1 / (K_{\mathrm{Tm}} N V_1)^{1/2} \tag{6}$$

and then, using Eqs (1), (2) and (6) one arrives at the result embodied in Eq. (3).

It is useful to notice that, in their test of Eq. (4) Alonso and March[4] considered nontransition as well as transition liquid metals. On the other hand Figure 1 shows that liquid transition metals are also well described by relation (5). This is not surprising since a similar relation

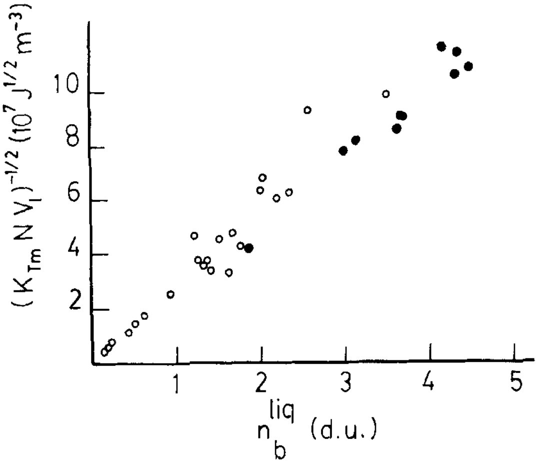

Figure 1 Correlation between the electron density at the boundary of atomic cells of liquid metals and $(K_{\mathrm{Tm}}NV_l)^{-1/2}$. K_{Tm} is the isothermal compressibility of the liquid metal at the melting temperature, V_l is the atomic volume and N is Avogadro's number. Empty circles: nontransition. Filled circles: transition metals.

holds for both nontransition and transition solid metals. Consequently (6) is also valid for liquid transition metals and we conclude that relation (3) is generally valid for both transition and nontransition liquid metals.

If we now calculate K_{Tm} from Eq. (5),

$$K_{\mathrm{Tm}} = \frac{(c_2^1)^2}{V_1 N (n_b^1)^2} \tag{7}$$

and then combine Eqs (4) and (7) with Eq. (1), the following expression for L is obtained

$$L = \frac{c_1^1 (c_2^1)^2}{N} \cdot \frac{1}{V_1 n_b^1} \tag{8}$$

This relation is very helpful in interpreting the variation of L through the different classes of metals. The product $V_1 n_b^1$ gives a charge Q that can be interpreted as an effective valence. Values of this product are given in Table 1. Since the conduction electron density in simple nontransition metals is almost constant, $V_1 n_b^1$ gives in such a case the usual valence, that is, 1 for alkalis and 2 for alkaline-earths. For the other nontransition metals Q is a number between 2 and 3, and it is between 3 and 4 for transition metals. So one can observe an inverse correlation between L and Q that is, large values of L correspond to small values of Q and vice versa.

Using nearly-free electron theory and the near constancy of L, March[5,14] has pointed out the relation existing between the vacancy formation energy E_v and the surface energy σ in the hot solid metal. We here just notice that the relation between E_v and σ also appears in Miedema's model[12]. Such a model provides, as shown above, much of the basis for the results of the present paper.

In conclusion, by using recent data for the isothermal compressibilities of liquid transition metals[8] we have shown that relations (1), (3) and (6) are generally valid for both transition and nontransition metals. Furthermore, insight has been provided about the small variation of L through the different types of metals. This can be ascribed mainly to the change of "effective valence," defined in the text.

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