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The Law of Corresponding States and Surface Tension of Liquid Metals[1]

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Empirical relationships for the surface tension of liquid metals (LM) are shown to follow from the principle of corresponding states. In order to relate the surface tension of LM to its bulk properties, a formula is derived by scaling with the melting point $T_m(0)$ at the atmospheric pressure, $p=0$ and the atomic volume $\Omega_m(0)$ at the melting point as macroscopic parameters for scaling ε and a characterizing the interatomic potential $\Phi(r)=\varepsilon\Phi^*(r/a)$. Correlation rules, derived for the surface tension and its temperature coefficient, are discussed and compared with experimental data.

KEY WORDS: corresponding states; empirical relationships; liquid metals; surface tension; temperature dependence.

1. INTRODUCTION

The surface tension, γ, of liquid metals (LM) is one of the fundamental and most important quantities in the theory and practice of materials processing (crystal growth, welding, sintering), and its temperature dependence governs the well-known Marangoni convection on the surface of melts. Although measurement methods of γ are sufficiently precise, there is still uncertainty regarding its absolute values and particularly its temperature coefficient mainly due to impurities, which affect strongly the results of measurements. The theoretical treatment from first principles is unwieldy and does not always enable one to calculate reliable values of γ as a function of temperature. Another active research field deals with semi-empirical

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predictions based on the correlation between the surface and bulk thermodynamic properties [1–5]. The Stephan rule [1], one of the first that links γ to the heat of evaporation L_e of the substance,

$$\gamma \propto \frac{L_e}{\Omega^{2/3}} \tag{1}$$

where Ω is the atomic volume, is widely used in processing experimental data on liquid and solid metals [2, 4–7]. Other empirical relations relate γ with bulk properties of metals (e.g., melting point, critical temperature, Young's modulus, isothermal compressibility) under different approaches [7–16].

We would like to point out a simple way of interpreting these relations as a consequence of the law of corresponding states (CS) [17], which implies the existence of a universal function of reduced surface tension versus reduced temperature. Scaling relations based on the CS principle provide a simple explanation for well-known empirical rules and permit establishment of new ones. As an example, a new CS rule for the surface tension and its temperature coefficient of LM is derived.

2. THEORETICAL BACKGROUND

To apply the law of CS to LM, two fundamental theoretical approaches should be emphasized. The first approach assumes that the total potential energy of atomic interaction is the sum of the interaction energies of pairs of atoms, and the second assumes that the potential energy of a pair interaction must be written in the form of a spherically symmetric function,

$$\Phi(r) = \varepsilon \Phi^*(r/a) \tag{2}$$

Here, $\Phi^*(r/a)$ is a universal function, equal to -1 when $r = a$, while the characteristic energy ε and the characteristic length a vary from one metal to another. If these conditions are satisfied, the partition function of a system of N atoms characterized by ε and a is a universal function of the reduced variables, temperature $T^* = \frac{kT}{\varepsilon}$, and volume $V^* = \frac{V}{Na^3}$, k being the Boltzmann constant. Any physical property derived from that partition function can be written as a function of these variables [17].

Although atomic interactions in metals cannot be introduced as pairwise, certain metallic ground-state energies obey the universal relationship, Eq. (2) [18]. Moreover, a total effective pair potential and pair correlation function in LM supports the existence of CS. We summarize these treatments with the structure model of LM recently discussed by Wallace [19] to find an equivalent approximation for the partition function of ion motion in LM with a free surface. In particular, far from the critical point, the reduced partition function for ion motion in the bulk can be written in classical quasi-harmonic approximation [19]

$$Z_I \approx w^N \exp\left(-\frac{N\Phi^*_{0l}}{T^*}\right) \prod_j^{3N} \frac{T^*}{\lambda^* v^*_j} \tag{3}$$

where the factor w^N accounts for the number of random liquid structures in the bulk; $\Phi^*_{0l} = \Phi_{0l}/N\varepsilon$ is the reduced liquid static structure potential per ion; and $\{v^*_j\}$ is the set of the reduced $3N$ harmonic normal modes, which are a universal functions of V^* only. Here, $\lambda^* v^*_j \ll T^*$, where $\lambda^* = h/(a\sqrt{M\varepsilon})$, h is Planck's constant, and M denotes the mass of ion. The error in writing Eq. (3) lies in the neglect of the anharmonic and "boundary" effects [19].

Using the reduced form of the thermodynamic relations $p = -(\frac{\partial F}{\partial V})_T$ and $F = -kT \ln Z$, where F is the Helmholtz free energy of the system, $F^* = F/N\varepsilon$, one obtains the reduced equation of state

$$p^* = -\left(\frac{\partial F^*}{\partial V^*}\right)_{T^*} = -\left(\frac{\partial \Phi^*_{0l}}{\partial V^*}\right)_{T^*} - \frac{T^*}{NV^*} \sum_{i=1}^{3N} \left(\frac{\partial \ln v^*_i}{\partial \ln V^*}\right)_{T^*} \tag{4}$$

which is a universal function connecting p^*, V^* and T^*. Since the existence of the liquid and solid phases reduces the variance of the system to unity on the line separating them, the reduced temperature depends only on p^*

$$T^*_m(p^*) = g^*(p^*) \tag{5}$$

where $g^*(p^*)$ means the universal function p^*. At normal pressure, $p^* \approx 0$, $T^*_m(0)$ is a universal constant and

$$T_m(0) = \frac{T^*_m(0)}{k}\,\varepsilon \tag{6}$$

i.e., $T_m(0)$ will serve as a good measure for the energy scale parameter ε. It should be noted that proportionality between experimental data cohesion energy and melting point is indeed observed.

On the other hand, V^* is a universal constant at $p^* = 0$ and T^*_m, (see Eq. (4))

$$V_m/N = \Omega_m = V^*_m a^3 \tag{7}$$

where Ω_m is the atomic volume at $p = 0$, and T_m.

3. SURFACE TENSION OF LM

The reduced surface tension can be written from simple dimensional considerations, using the scaling constants k, a, and ε or k, $\Omega_m^{1/3}$, and $T_m(0)$, as

$$\gamma^* = \gamma \frac{a^2}{\varepsilon} = \gamma \frac{\Omega_m^{2/3}}{kT_m(0)} \frac{T_m^*(0)}{V_m^{*2/3}} \tag{8}$$

and from the thermodynamic definition

$$\gamma^* = \left\{ \frac{\partial F^*}{\partial A^*} \right\}_{T^*, V^*, N} \tag{9}$$

where F^* is the reduced free energy of an LM with a free surface, A^* is the reduced surface area introduced as $A^* = A/a^2 = AV_m^{*2/3}/\Omega_m^{2/3}$, where $A = N_\omega \omega_m$, N_ω being the number of atoms on the surface, $\omega_m = f\Omega_m^{2/3}$ is the area occupied by one atom, and f is a factor which accounts for the "structure" of the LM; thus, $A^* = fV_m^{*2/3} N_\omega$ and we have

$$\gamma^* = \frac{1}{fV_m^{*2/3}} \left\{ \frac{\partial F^*}{\partial N_\omega} \right\}_{T^*, V^*, N} \tag{10}$$

The reduced free energy F^* can be evaluated from the reduced partition function for an LM with a free surface. To write it we use the structure model of an LM as discussed by Wallace [19], and the free surface is assumed as consisting of N_ω ions moving in the structure potential Φ_{ol}^{ω} within two atomic layers and forming $w_\omega^{N_\omega}$ random "surface structures." The latter differs from that of the bulk due to the breaking of bonds and the change symmetry. The reduced partition function of such an inhomogeneous system can be written as that of a system formed from $N - N_\omega$ volume and N_ω surface ions

$$Z \approx w^{N-N_\omega} w_\omega^{N_\omega} \exp\left(-\frac{(N-N_\omega)\,\Phi_{0l}^* + N_\omega \Phi_{0l}^{\omega *}}{T^*} \right) \prod_j^{3N-3N_\omega} \frac{T^*}{\lambda^* v_j^*} \prod_j^{3N_\omega} \frac{T^*}{\lambda^* v_{j\omega}^*} \tag{11}$$

where $\Phi_{0l}^{\omega *} = \Phi_{0l}^{\omega}/N_\omega \varepsilon$ is the reduced liquid surface structure potential per ion and $\{v_{j\omega}^*\}$ is the reduced set of $3N_\omega$ harmonic normal surface modes.

Introducing the reduced bulk and surface characteristic frequencies as

$$\ln \lambda^* \tilde{v}^* = \frac{\sum_j \ln \lambda^* v_j^*}{3(N - N_\omega)} \tag{12}$$

$$\ln \lambda^* \tilde{v}_\omega^* = \frac{\sum_j \ln \lambda^* v_{j\omega}^*}{3N_\omega} \tag{13}$$

and $F^* = -T^* \ln Z$, one obtains from Eq. (10) with Eq. (11)

$$\gamma^* = \left[(\Phi_{0l}^{\omega *} - \Phi_{0l}^{*}) + T^* \ln \frac{\tilde{v}_\omega}{\tilde{v}} - T^* \ln \frac{w_\omega}{w} \right] \Big/ f \cdot V_m^{*2/3} \tag{14}$$

At $p^* \approx 0$, γ^* is a universal function of T^* only, not of both T^* and V^* since the coexistence of the liquid and vapor phases reduces the variance of the system to unity. This statement can be easily proved also from simple dimensional considerations. The surface tension γ may be written in terms of the dimensionless group γ^*, which depends on p^*, T^*, k, M, a, and ε. Since no dimensionless combination of k, M, a, and ε exists, γ^* is independent of these parameters and at $p^* \approx 0$ depends on T^* only.

Now, combining Eqs. (14) and (8) we obtain the equation for the surface tension

$$\gamma(T) = \frac{kT_m}{\Omega_m^{2/3}} \left[c_1 + c_2 (T/T_m) \right] \tag{15}$$

Here, $c_1 = \frac{\Phi_{0l}^{\omega *} - \Phi_{0l}^{*}}{f T_m^*(0)}$ and $c_2 = (\ln \frac{\tilde{v}_\omega}{\tilde{v}} - \ln \frac{w_\omega}{w})/f$ are universal constants and $\Omega_m^{2/3}$ should be taken as temperature-dependent to account for the change in the surface area due to thermal expansion.

4. CALCULATIONS AND COMPARISION WITH EXPERIMENTAL DATA

Evaluation of c_1 and c_2 is not easy, but rough calculations are obtained with the nearest-neighbor interaction model [2–4, 8]. In the framework of this model the difference $\Phi_{0l}^{\omega *} - \Phi_{0l}^{*} = m$ is associated with a decrease of the number of nearest neighbors at the surface, where m is the fraction of broken atom bonds on the surface with respect to the bulk. Since the surface structure of LM is not known with certainty, we expect that the averaged expression, Eq. (15), over the low-index crystal faces of a hexagonal closed-packed fcc structure will be even closer to the description of the LM surface near the melting point. As a result, we have

$$\left\langle \frac{m}{f} \right\rangle = \frac{\sum_i m_i g_i / \omega_i^*}{\sum_i g_i} \tag{16}$$

Here, g_i is the statistical weight of the crystallographic face: $g_{100} = 6$; $g_{110} = 12$; $g_{111} = 8$; ω_i^* is the surface area of the crystal face per atom scaled to $\Omega_m^{2/3}$ and equal to f_i: $\omega_{100}^* = 1.54$; $\omega_{110}^* = 2.18$; $\omega_{111}^* = 1.33$; $m_{100} = 1/3$; $m_{110} = 5/2$ and $m_{111} = 1/4$. Using these data yields $\langle \frac{m}{f} \rangle = 0.196$ and with empirical constant $1/T_m^*(0) \approx 27$, obtained from Eq. (6) as coefficient proportionality between experimental data of the cohesion energy and the melting point of metals, we find $c_1 = 5.29$.

To calculate c_2 we use $\tilde{\nu}_\omega/\tilde{\nu} = \sqrt{1-m}$ from Madelung's consideration [8] and estimate $w_\omega^{N_\omega}$ as the number of virtual configurations from numbers of surface atoms N_ω plus nearest neighbors N_ν in the liquid phase and free sites N_0 (due to missing neighbors) in the complete configuration group from $N_\omega + N_\nu + N_0 = 13$ atoms, then

$$\ln w_\omega = \frac{1}{N_\omega}\left[13 \ln 13 - (N_\omega + N_\nu)\ln(N_\omega + N_\nu) - N_0 \ln N_0\right] \tag{17}$$

Using Eq. (16) for averaging over the faces with low indices, we obtain $c_2 = -0.73$.

The temperature dependence of the atomic volume $\Omega_m(T)$ is written under the assumption that the coefficient of thermal expansion α is constant

$$\Omega_m(T) = \Omega_m[1 + \alpha T_m(T/T_m - 1)] \tag{18}$$

Using the empirical rule $\alpha T_m \approx 0.09$ [20], which applies to all metals, we rewrite

$$\Omega_m^{-2/3}(T) \approx \Omega_m^{-2/3}[1 - 0.06(T/T_m - 1)] \tag{19}$$

Substituting Eq. (19) in Eq. (15) and using the calculated c_1 and c_2, we obtain

$$\gamma(T) = 4.56\,\frac{kT_m}{\Omega_m^{2/3}}\left[1 - 0.13\cdot\left(\frac{T}{T_m} - 1\right)\right]^{1.67} \tag{20}$$

Here, the expression preceding the square brackets is the surface tension at the melting point, γ_m, which is thus seen to be proportional to $T_m/\Omega_m^{2/3}$.

$$\gamma_m \approx 4.56\,\frac{kT_m}{\Omega_m^{2/3}} \tag{21}$$

Taylor [9] and subsequently Allen [10] discussed this proportionality in processing experimental data. Reynolds et al. [11] obtained empirically

$$\gamma_m = 4.77\,\frac{T_m}{r_0^2} \tag{22}$$

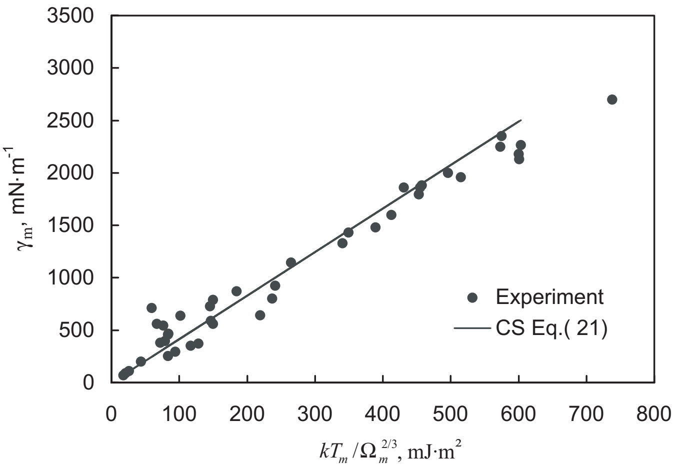

Fig. 1. Surface tension of LMs at their melting point, γ_m versus $kT_m/\Omega_m^{2/3}$. Dots: experimental data. Solid line: predicted by Eq. (21).

where r_0 is the nearest neighbor separation. When r_0 is expressed in terms of Ω_m, Eqs. (21) and (22) are essentially identical. Reynolds et al. justified Eq. (22) on the basis of a pair potential model. Here, we see that it is a CS relation, which is immediately apparent from Eqs. (14) and (8). The validity of Eq. (21) was tested on 45 reasonably reliable experimental data [12, 13]. For the molar volume $\Omega_m(0)$ at T_m, data from Ref. 14 were used. The plot of γ_m versus $T_m/\Omega_m^{2/3}$ does indeed fall on a straight line passing through the origin with a slope of 3.92 (see Fig. 1) which agrees within 16% with the one predicted by Eq. (21). Since γ_m is proportional to $T_m/\Omega_m^{2/3}$, it is possible to make use of γ_m and T_m to establish the scales γ and T. In this way an alternative expression, equivalent to Eq. (8) and due to Eq. (20), is obtained,

$$\gamma^* = \frac{\gamma(T)}{\gamma_m} = \left[1 - 0.13\left(\frac{T}{T_m} - 1\right)\right]^{1.67} \tag{23}$$

This equation was confirmed by experimental data for sodium recommended by Goldman [14], and lithium suggested by Keene [12] and Bohdansky et al. [15] (see Fig. 2). As can be seen, the agreement with experiment is excellent. Small deviations near the melting point may be related to the anharmonic effect, which is disregarded here. When the critical temperature is approached, one can expect considerable deviations above $4T_m$ due to the "boundary effect" [19], which we also disregard here.

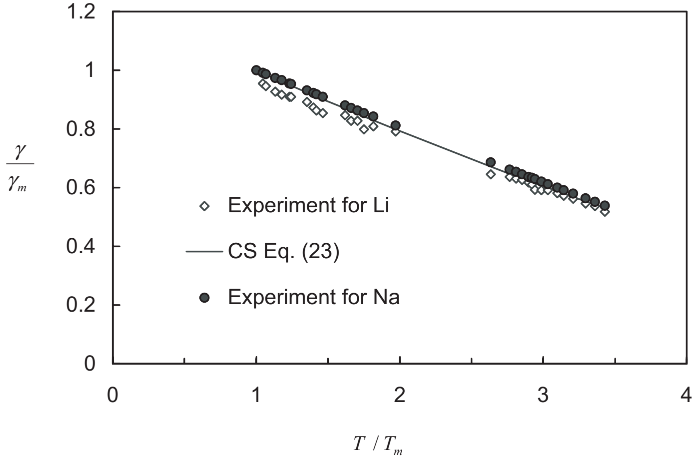

Fig. 2. Reduced surface tension of LM γ/γ_m versus T/T_m. Circles: experiment for Na [14]. Squares: experiment for Li [12, 15]. Solid line: present work with Eq. (23).

The temperature coefficient of γ is obtained by differentiation of Eq. (23) with respect to T

$$\frac{\partial\gamma}{\partial T} \approx -0.217\,\frac{\gamma_m}{T_m}\left[1-0.13\left(\frac{T}{T_m}-1\right)\right]^{0.67} \tag{24}$$

from which follows the CS rule for $\frac{\partial\gamma}{\partial T}$ at the melting point

$$\left.\frac{\partial\gamma}{\partial T}\right|_{T_m} \approx -0.217\,\frac{\gamma_m}{T_m} \tag{25}$$

This rule was tested for 25 LMs from different structure groups. The plot of $\frac{\partial\gamma}{\partial T}|_{T_m}$ versus $\frac{\gamma_m}{T_m}$ is shown in Fig. 3, from which it is seen that the proportionality coefficient 0.226 found empirically is in agreement with the prediction from Eq. (25) within 4%. Substitution of $\alpha T_m \approx 0.09$ [20] in Eq. (25) yields another rule,

$$\left.\frac{\partial\gamma}{\partial T}\right|_{T_m} \approx -2.4\alpha\gamma_m \tag{26}$$

recently reported by Tegetmeier et al. [16] under semi-empirical considerations for semiconductor melts with the coefficient 2.3, which as can be seen is a CS relation also.

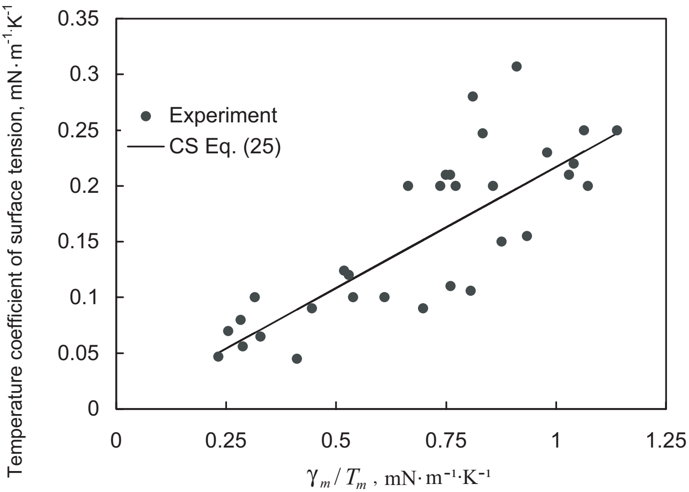

Fig. 3. Temperature coefficient of the surface tension of LMs at their melting point, $\frac{\partial\gamma}{\partial T}|_{T_m}$ versus γ_m/T_m. Dots: experimental data. Solid line: predicted by Eq. (25).

5. CONCLUSION

An analytical expression for the reduced surface tension of pure LM is derived in terms of Wallace's liquid dynamical theory and under the assumption of similarity of the static structure potential. The equation is a function of the reduced temperature only and applies to all normal melting metals, including semiconductors, and not for alloys below their critical temperatures. Well known empirical and semi-empirical relations between surface and bulk quantities of LM as well as new relations follow from this equation, which allows one to conclude that the connections between surface and bulk properties are a consequence of the law of CS.

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