

# Some theoretical considerations of the surface tension of liquid metals for metal matrix composites

JACQUES E. SCHOUTENS\*

*Metal and Ceramic Matrix Composites, Processing and Evaluation Center,  
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

This paper presents a model for calculating the surface tension of pure metals and their alloys. It is based upon the theory of Eyring *et al.* which uses classical statistical physics to describe the thermodynamic properties of metals in the liquid state. Calculations show the surface tension of pure aluminium to be nearly 9% greater than that measured for pure aluminium having a monolayer of oxide ( $\text{Al}_2\text{O}_3$ ), and within about 10% of measured values for Al-xMg and Al-xCu, where  $x$  is the weight percent of the alloying element. In the present calculations  $0 \leq x \leq 8$  wt% for magnesium and  $0 \leq x \leq 30$  wt% for copper were used. The values calculated are also in good agreement with results from other models. The model was also used to calculate the temperature coefficient. For pure aluminium the calculated values fall within experimental measurements, and exhibit a slight temperature dependence.

## 1. Introduction

Cast metal matrix composite (MMC) materials reinforced with unidirectional fibres will turn out to be a low cost alternative to MMC fabrication by diffusion bonding, cold and hot compaction, and other methods. In the development of this kind of casting technology, one of the most important problems to be solved is wetting of the fibres. From an experimental point of view, wettability is poorly understood. From the theoretical point of view there are a number of different approaches, and some of the sophisticated approaches have not been of use to experimentalists. There are a number of approaches for calculating the thermodynamic and surface properties of liquid metals, and they can be divided into macroscopic and microscopic models.

The macroscopic modelling approach is the most general and is based on equilibrium thermodynamics. It uses the classical Gibbs formulation for an interphase, and attempts to predict interfacial tension or adhesion and the surface free energy of liquid metal in equilibrium with its vapour, or another liquid, or a solid substrate. The Gibbs model is an energy balance between the Helmholtz free energy and the sum of entropy, mechanical work, surface tension and the chemical potential of the species involved. From this balance the surface free energy is related to the wettability of the liquid metal on a non-metallic substrate material, and wettability is then related to the contact angle using Young's equation. It is well known experimentally that the wetting of a ceramic by a liquid metal can be inferred from changes in the contact angle with changes in the parameters of the experiments. Consequently, this kind of modelling is used to

“estimate” the wettability of ceramics by liquid metals under specific conditions. What is most often the case is the Gibbs formulation is used *post facto* to explain what happened in an experiment, and, therefore, does not really possess much of what a good theory should possess: *predicting* the outcome of an experiment!

Various kinds of micro-models have been proposed which attempt to introduce an atomic or molecular “picture” into thermodynamic arguments. Included in this type of approach is the notion that the major contribution to adhesion forces arises from the instantaneous attraction among dipoles and among induced dipole interactions between the liquid and its substrate. This method has been fairly successfully applied to understand hydrocarbons wetting solid hydrocarbons and similar conditions in organic chemistry. These interactions are modelled variously with the well known Lennard-Jones, Devonshire or Morse potentials, and with the London formula which involves first ionization potentials of constituents. Another approach of the micro-model type argues that the basic parameter behind the empirical relationship between surface tension and heat of vaporization per unit atomic surface is the electron density at the boundary of the Wigner-Seitz atomic cell. It was shown by Miedema and coworkers [1–3] that the surface energy and the heat of vapourization are linearly related to the Wigner-Seitz cell by empirical scaling rules. These models then embody a combination of behaviours at the microscopic and at the macroscopic levels.

Finally, there are theories of liquid metals that are derived *ab initio*. These formal approaches are rigorous mathematically and generally elegant.

\* Permanent address: MMCIAC, Kaman Tempo, 816 State Street, Santa Barbara, California 93102, USA.

Approximations are introduced at the end, either in the form of simplified mathematics or over-simplified radial distribution functions and inter-molecular potentials. These theories are not really suitable for practical approaches to predict wettability or interfacial energies or for guiding experiments; they are tools to understand fundamental properties of liquid metals. The interested reader is referred to a review of the literature [4].

The approach taken in the work reported herein is intermediate between thermodynamic macro-models and detailed theoretical models.

## 2. Theory

The theory discussed here is based on classical statistical mechanics first developed by Eyring and coworkers [5, 6] to predict thermodynamic properties of liquids. Eyring's theory is founded on the assumption that the metal upon melting acquires vacancies that are moving freely through the melt and that there is short-range order in the liquid but no long-range order. These freely moving vacancies, called fluidized vacancies, have a volume fraction that is made to correspond to the volume change of the metal upon melting, or about 3 to 4% for transition and non-transition metals. Using statistical mechanics partition functions are written which account for the gas-like behaviour of the fluidized vacancies, and for the solid-like behaviour of the liquid metal. The relationship between the Helmholtz free energy and the partition functions make it possible to calculate the thermodynamic properties of the liquid metal. Eyring and coworkers have shown this approach to be quite successful in predicting the thermodynamic properties of a large number of liquids, including a number of pure metals. However, calculations of the surface tension of liquid metal alloys using this approach has not been reported. The work reported herein is a first attempt at calculating the surface tension of pure aluminium and binary alloys of aluminium such as Al-Cu and Al-Mg.

The relationship between the Helmholtz free energy and the partition function for a liquid is

$$A = -kT \ln f' \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $f'$  the partition function defined below. The surface tension is calculated from

$$\gamma = \left( \frac{\partial A}{\partial \Omega} \right)_{N, V, T} \quad (2)$$

where  $N$  is Avogadro's number,  $V$  the molar volume and  $\Omega$  is the surface area occupied by a monolayer of atoms on the liquid surface, which is given by

$$\Omega = \omega N_c \quad (3)$$

where  $\omega$  is the area occupied by one atom, and  $N_c$  is the total number of sites available for atoms on the liquid surface. To calculate the Helmholtz free energy, the partition function can be written as the product

$$f' = f_B f_{mL} \quad (4)$$

where  $f_{mL}$  is the partition function for the surface

atoms and  $f_B$  the partition function for the bulk liquid atoms. In general, any partition function can be written as the product of partition functions describing each process involved [7]. Therefore [5]

$$f_B^{N_B} = (f_s)^{N_B V_s / V} (f_g)^{N_B (1 - V_s / V)} \quad (5)$$

where  $V_s$  is the molar volume of the metal at its melting point, and

$$V = \frac{M}{\rho(T)} \quad (6)$$

is the molar volume of the liquid at temperature  $T$  when its density  $\rho(T)$  is a function of temperature, and  $M$  is the atomic weight of the metal under consideration. In Equation 5,  $f_s$  and  $f_g$  are the partition functions for the solid and gas-like behaviour of the bulk liquid respectively. The partition function can be further separated into the product of partition functions, thus

$$f_s = f_{\text{Einstein}} f_{\text{rot}} f_{\text{vib}} J(T) \quad (7)$$

and

$$f_g = f_{\text{trans}} f_{\text{rot}} f_{\text{vib}} \quad (8)$$

showing that rotation, vibration, and translation motion can be accounted for in this manner.  $J(T)$  is the partition function for internal degrees of freedom. The partition function for the oscillations of the atoms in the solid may be calculated from Einstein's theory, or

$$f_{\text{Einstein}} = \frac{\exp(E_s / RT)}{[1 - \exp(-\theta / T)]^3} \quad (9)$$

where  $\theta$  is the Einstein temperature [8]. For metals,  $\theta / T \ll 1$  so that Equation 9 reduces to

$$f_{\text{Einstein}} \simeq \exp(E_s / RT) \quad (10)$$

where  $E_s$  is the sublimation energy and  $R$  is the universal gas constant.

For pure liquid metals, the probability of diatomic modules is extremely small, and those formed with residual impurities in the metal is also very small. Consequently, the partition functions for rotation and vibration are unity.

A term must be included in the partition function given by Equation 7 to account for the total number of positions available to an atoms in the melt, or [5]

$$1 + n \left( \frac{V - V_s}{V_s} \right) \exp \left( - \frac{a E_s V_s}{(V - V_s) RT} \right) \quad (11)$$

where  $n$  and  $a$  are the parameters that can be calculated theoretically. It will be seen shortly that in the further development of the theory, these two parameters drop out.

The partition function for the bulk behaviour of the liquid is then written as

$$\begin{aligned} f_B^{N_B} = & \left\{ \frac{\exp(E_s / RT)}{[(1 - \exp(-\theta / T))]^3} \left[ 1 + n \left( \frac{V - V_s}{V_s} \right) \right. \right. \\ & \times \left. \left. \exp \left( - \frac{a E_s V_s}{(V - V_s) RT} \right) \right] \right\}^{N_B V_s / V} \\ & * \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} (V - V_s) J(T) \right]^{N_B (1 - V_s / V)} \\ & \times \left[ \left( \frac{N_B (V - V_s)}{V} \right) \right]^{-1} \end{aligned} \quad (12)$$

A similar reasoning gives the partition function for the monolayer or

$$f_{mL}^N = \left\{ \frac{\exp(E'_s/RT)}{[1 - \exp(-\theta'/T)]^3} \left[ 1 + n' \left( \frac{V - V_s}{V_s} \right) \times \exp \left( - \frac{a'E'_s V_s}{(V - V_s)RT} \right) \right] \right\}^{N'V_s/V} * \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} (V - V_s) J'(T) \right]^{N'(1-V_s/V)} \times \left[ \left( \frac{N'(V - V_s)}{V} \right) \right]^{-1} \quad (13)$$

The second brackets in Equations 12 and 13 can be simplified using Stirling's approximation  $x! = (x/e)^x$  so that

$$f_g^{N_B(1-V_s/V)} = \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \left( \frac{eV}{N} \right) \right]^{N_B(1-V_s/V)} \quad (14)$$

and

$$f_g^{N'(1-V_s/V)} = \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \left( \frac{eV}{N} \right) \right]^{N'(1-V_s/V)} \quad (15)$$

In Equation 13, the primed quantities refer to the surface atoms corresponding to the unprimed quantities. In the above derivation we must have conservation of the number of atoms, or

$$N = N_B + N' \quad (16)$$

where  $N_B$  is the number of atoms in the bulk and  $N'$  the number of atoms on the surface as a monolayer.

Now we write

$$\ln f' = \ln (f_B f_{mL}) = \ln f_B + \ln f_{mL} \quad (17)$$

and using Equations 12 to 15 gives

$$\ln f' = N' \frac{V_s}{V} \left( \ln \frac{f'_s \{1 + n'[(V/V_s) - 1] \exp[-a'E'_s V_s/(V - V_s)RT]\}}{f_s \{1 + n[(V/V_s) - 1] \exp[-aE_s V_s/(V - V_s)RT]\}} \right) + \ln f \quad (18)$$

where

$$f_s = \frac{\exp(E_s/RT)}{[1 - \exp(-\theta/T)]^3} \quad f'_s = \frac{\exp(E'_s/RT)}{[1 - \exp(-\theta'/T)]^3}$$

The Helmholtz free energy for a liquid involving its surface is

$$A = -kT \ln f' \quad (19)$$

and

$$\gamma = \left( \frac{\partial A}{\partial \Omega} \right)_{N,V,T} = \omega^{-1} \left( \frac{\partial A}{\partial N_c} \right)_{N,V,T} = \omega^{-1} \left( \frac{V_s}{V} \right) \left( \frac{\partial A}{\partial N'} \right)_{N,V,T} \quad (20)$$

In Equation 20, a random distribution of vacancies is assumed, that  $N_c$  is the total number of sites available for atoms on the surface, and

$$\frac{N'}{N_c} = \frac{V_s}{V} \quad (21)$$

Combining Equations 18, 19 and 20 gives after some algebra [9]

$$\gamma = \omega^{-1} \left( \frac{V_s}{V} \right)^2 kT \left[ \ln \left( \frac{f'_s}{f_s} \right) + \ln g_r \right] \quad (22)$$

where

$$\ln g_r = \frac{1 + n[(V/V_s) - 1] \exp[-aE_s V_s/(V - V_s)RT]}{1 + n'[(V/V_s) - 1] \exp[-a'E'_s V_s/(V - V_s)RT]} \quad (23)$$

As  $n' \simeq n$  and  $a' \simeq a$ ,  $g_r \simeq 1$ , hence  $\ln g_r = 0$  and Equation 22 reduces to

$$\gamma = \omega^{-1} \left( \frac{V_s}{V} \right)^2 kT \times \left( \frac{E_s - E'_s}{RT} + 3 \ln \frac{[1 - \exp(-\theta'/T)]}{[1 - \exp(-\theta/T)]} + \ln \frac{J(T)}{J'(T)} \right) \quad (24)$$

It can be shown that  $\ln [J(T)/J'(T)] = 0$ . Lu, Jhon, Ree and Eyring showed that

$$E'_s \simeq \frac{3}{4} E_s (1 + f) \quad (25)$$

and

$$\theta' = \theta \left( \frac{3}{4} + \frac{3}{4} f \right)^{1/2} \quad (26)$$

so that the second term in the bracket of Equation 24 reduces to

$$\frac{3}{2} \ln \frac{3}{4} (1 + f)$$

Then, we finally have

$$\gamma = \omega^{-1} \left( \frac{V_s}{V} \right)^2 kT \left( \frac{E_s}{4RT} (1 - 3f) + \frac{3}{2} \ln \frac{3}{4} (1 + f) \right) \quad (27)$$

In Equation 27, for close packing

$$\omega = \frac{\sqrt{3}}{2} \left( \frac{\sqrt{2} V_s}{N} \right)^{2/3} \quad (28)$$

### 3. Numerical results and discussion

We will now perform three calculations: one for pure aluminium, one for Al-Cu alloy and Al-Mg alloy.

#### 3.1. Pure aluminium

Table I presents the numerical values of the parameters used in the calculation of surface tension of

TABLE I Numerical values used for calculating the surface tension of pure aluminium with Equation 27.

Parameter	Numerical value	Reference
$f$	0.083	9
$V_s$ (cm <sup>3</sup> g-atom <sup>-1</sup> )	10.6327	9
$E_s$ (kcal mol <sup>-1</sup> )	64.5098	9
$M$ (g mol <sup>-1</sup> )	26.982	10
$k$ (erg K <sup>-1</sup> )	$1.3807 \times 10^{-16}$	
$R$ (erg K mol <sup>-1</sup> )	$8.314 \times 10^7$	
$N$ (atoms mol <sup>-1</sup> )	$6.023 \times 10^{23}$	

1 erg =  $10^{-7}$  J  
1 kcal = 4.184 kJ

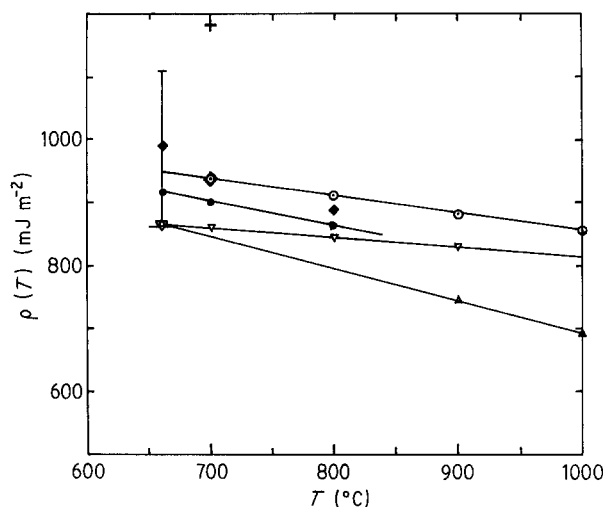


Figure 1 Calculated surface tension of pure aluminium as a function of temperature using Equation 27. (+ Calculated [13], ● Measured [9], ◆ Calculated [9], △ Measured [14], ▽ Calculated [15], I Garcia-Cordovilla *et al.* [16], ○ Equation 27).

pure aluminium. To calculate the surface tension of pure liquid aluminium the temperature dependent density values of Gebhardt *et al.* [11] were used. Between 933 and 1173 K, these values are well represented by

$$\rho(T) = 2.368 - 2.63 \times 10^{-4}(T - T_m) \quad (29)$$

where  $T_m = 933$  K is the melting temperature of pure aluminium and  $T$  is the temperature of interest in K. Compared with values obtained with a similar expression reported elsewhere [12], the values calculated from Equation 29 are 0.71% lower at the melting point and 0.56% lower at 1173 K. The molar volume,  $V_s$ , for pure aluminium given in Table I differs from that given by Shimoji [4] which is  $11.4 \text{ cm}^3 \text{ g-atom}^{-1}$ .

Fig. 1 shows the surface tension of pure aluminium as a function of temperature calculated with Equation 27. These values are compared with other calculated values [9, 13, 15] and measured values [9, 14, 16]. Also shown is a range of values at 660 C of the surface tension of pure aluminium measured by Garcia-Cordovilla and coworkers [13] using the method of maximum bubble pressure. They found that the surface tension of pure aluminium was as high as  $1122 \text{ mJ m}^{-2}$  [16] for an unoxidized bubble surface, decreasing to  $865 \text{ mJ m}^{-2}$  with a controlled increase in the bubble surface oxidation. The values calculated with Equation 27, are in good agreement with other computations using various modelling approaches, and measured values reported in the literature.

There is an interesting implication from the range of measured surface tension values shown in Fig. 1 and reported by Garcia-Cordovilla *et al.* [16]. These suggest that the values reported by others [9, 14, 17–26] are low because the surface was contaminated by oxides during surface tension measurements. Indeed, measurements of surface tension of aluminium requires great care that no oxygen is introduced into the system except under controlled conditions.

The surface tension value of  $1184 \text{ mJ m}^{-2}$  shown in Fig. 1 was calculated by Chacon *et al.* [13] for a free surface of pure aluminium. This value is still 5.2% greater than the highest value [16, 26] measured under conditions of ultra-high vacuum, or in a clean system

that has been purged with 99.9995% pure argon. Moreover, to attain such measured high surface tension values, high purity (99.999%) aluminium was used [26]. The drop in the surface tension from  $1122 \text{ mJ m}^{-2}$  to a mean value of  $868 \text{ mJ m}^{-2}$  [16, 26] has been established as caused by a monolayer of oxide, presumably  $\text{Al}_2\text{O}_3$  [26].

### 3.2. Aluminium–magnesium alloy

For the case of binary alloys, Equation 27 was modified by using rule-of-mixture types of scaling. If the alloy is designated as Al- $x$ Mg, where  $x$  is the weight percent, then the following rules of mixtures can be used. The area occupied by the atom,  $\omega$ , can now be assumed to have the value

$$\omega = (1 - x_1)\omega_{\text{Al}} + x_1\omega_{\text{Mg}} \quad (30)$$

where  $x_1$  is the fraction by volume. The molar volume of the alloy can be written similarly as

$$V_s = (1 - x_1)V_{s\text{Al}} + x_1V_{s\text{Mg}} \quad (31)$$

and the molar volume of the alloy as a function of temperature can be written

$$V = (1 - x_1) \frac{M_{\text{Al}}}{\rho_{\text{Al}}(T)} + x_1 \frac{M_{\text{Mg}}}{\rho_{\text{Mg}}(T)} \approx \left( (1 - x_1)M_{\text{Al}} + x_1M_{\text{Mg}} \frac{1}{\rho(T)} \right) \quad (32)$$

where  $x_1$  is of the order of a few percent in this calculation. For the density relation we used the following

$$\rho(T) = 2.376 - 2.8 \times 10^{-4}(T - T_m) - 0.9x_1 \quad (33)$$

where the last term is to account for the observation that the density of the alloy varies linearly with magnesium content [16]. The following equation was used to calculate the dissociation energy for the alloy [27]

$$E_s = (1 - x_1)^2 E_{s\text{Al}} + x_1^2 E_{s\text{Mg}} + 2x_1(1 - x_1)(E_{s\text{Al}}E_{s\text{Mg}})^{1/2} \quad (34)$$

These modifications were made to Equation 27, and the following values were used in addition to those

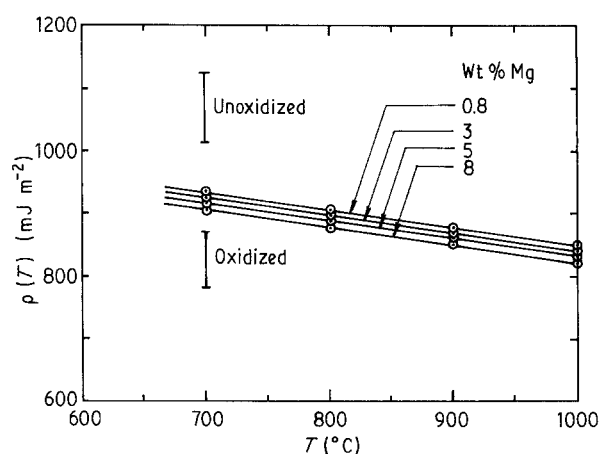


Figure 2 Calculated surface tension of Al- $x$ Mg, with  $0 \leq x \leq 8$  wt % Mg, as a function of temperature. (I measured range for 0.8–8 wt % Mg [16]).

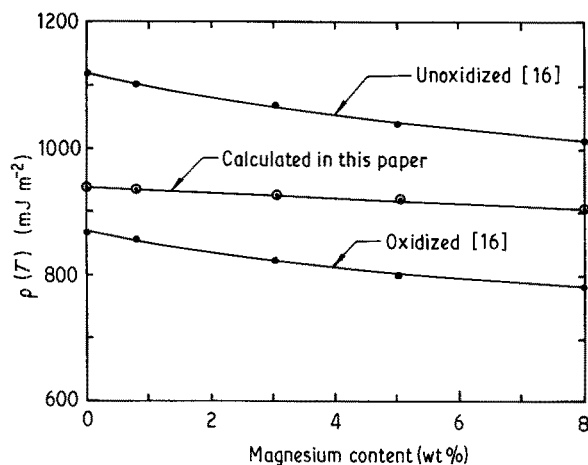


Figure 3 Calculated surface tension of Al-xMg, with  $0 \leq x \leq 8$  wt % Mg, as a function magnesium content at 973 K.

shown in Table I:  $E_{sMg} = 32.9498 \text{ kcal mol}^{-1}$ ,  $V_{sMg} = 14.821 \text{ cm}^3 \text{ g-atom}^{-1}$ ,  $M_{Mg} = 24.32 \text{ g mol}^{-1}$ .

Fig. 2 shows calculated values of surface tension for Al-xMg, where  $0 \leq x \leq 8$  wt % Mg. These results are compared with measured values reported by Garcia-Cordovilla and coworkers for the unoxidized and the oxidized state. The same data were replotted as a function of magnesium content at 973 K, and are shown in Fig. 3. The results of the present calculation fall between the results for unoxidized and oxidized measured values [16], the entire range being about 22%.

### 3.3. Aluminium-copper alloy

The calculation described for Al-xMg alloy were repeated for Al-xCu alloy, with  $0 \leq x \leq 30$  wt % copper. The results of these calculations are plotted in Fig. 4. These results are compared with measurements reported by Eremenko *et al.* [28] and Laty *et al.* [29]. It should be noted that the present results are about 6% higher than the values measured at 973 K for 20 wt % copper. Unlike the results for Al-xMg, the surface tension of this alloy increases with increasing weight percentage of copper. This is shown in Fig. 5 where the results of the present calculations are compared with the results of calculations performed by Poirier and Speiser [15]. In this calculation the

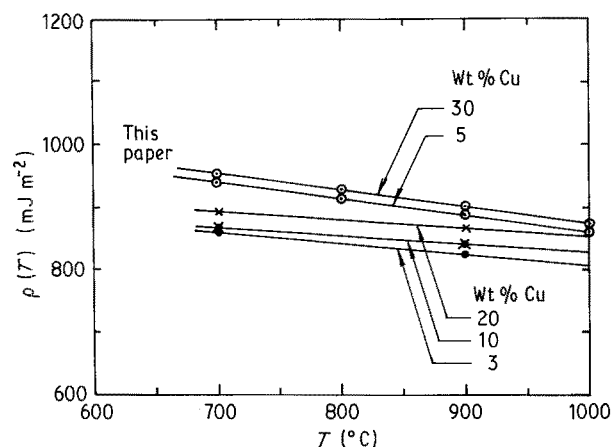


Figure 4 Calculated surface tension of Al-xCu, with  $0 \leq x \leq 30$  wt % Cu, as a function of temperature (x Eremenko *et al.* [28], ● Laty *et al.* [29]).

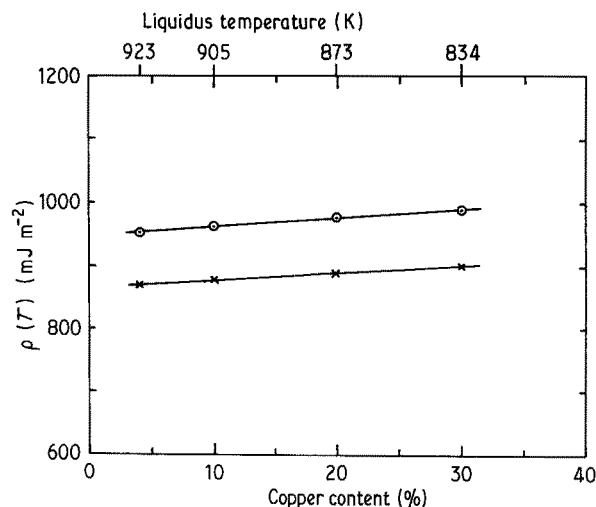


Figure 5 Calculated surface tension of Al-xCu, with  $0 \leq x \leq 30$  wt % Cu, as a function of copper content, along the liquidus of the Al-Cu binary. (○- present calculation, -x- Poirier and Speiser calculation [15]).

liquidus temperatures of Al-Cu binary corresponding to the wt % of copper were used. These results give a curve which is parallel to the curve calculated by Poirier and Speiser [15], who used a thermodynamic model to obtain their results. The present results give surface tension values for Al-xCu which are higher than Poirier and Speiser's result by approximately 8%.

### 3.4. Temperature coefficient

The temperature coefficient can be calculated directly from Equation 27 by differentiation with respect to  $T$ . This gives the following result

$$\frac{dy}{dT} = \frac{3k}{\omega} \left( \frac{V_s}{V(T)} \right) \ln \frac{3}{4} (1 + f) - 5.26 \times 10^{-4} \frac{\gamma(T)}{\rho(T)} \quad (35)$$

where the temperature dependence of the molar volume and density is shown to emphasize the fact that  $dy/dT$  has a temperature dependence. It is easily shown that the first term of Equation 35 is approximately 25% that of the second term. Calculated values of the temperature coefficient as a function of temperature for pure aluminium are shown in Table II. From these results, we note that the temperature coefficient has a weak dependence on temperature, decreasing by 5.8% over a temperature range of 300°.

It is worth noting that the calculated value of the temperature coefficient falls well within the

TABLE II Calculated values of the temperature coefficient for pure aluminium

$T$ (K)	$\gamma(T)^*$ (mJ m <sup>-2</sup> )	$V(T)$ (cm <sup>3</sup> g-atom <sup>-1</sup> )	$\rho(T)^\dagger$ (g cm <sup>-3</sup> )	$dy/dT$ (mJ m <sup>-2</sup> K <sup>-1</sup> )
973	938	11.448	2.357	-0.260
1073	911	11.574	2.331	-0.255
1173	884	11.706	2.305	-0.250
1273	858	11.842	2.279	-0.245

\* Calculated with Equation 27

† Calculated with Equation 29

experimentally determined range, this range varying from a minimum value of  $-0.12$  [24, 26] to a maximum value of  $-0.51$  [18] for pure aluminium, using various experimental methods. This wide range in measured values is attributable to the many difficulties encountered in making measurements of surface tension of liquid metal even though they are based on well known techniques in classical physics.

### Acknowledgements

The author is grateful to Dr James A. Cornie, Department of Materials Science and Engineering, MIT, for inviting him to spend the summer 1987 at MIT, and for his support and interest in this work.

### References

1. A. R. MIEDEMA, F. R. DE BOER, and P. F. DE CHATEL, *J. Phys. F* **3** (1973) 1558.
2. A. R. MIEDEMA, *Metallkd* **69** (1978) 287.
3. A. R. MIEDEMA and R. BOOM, *ibid.* **69** (1978) 183.
4. M. SHIMOJI, "Liquid Metals. An Introduction to the Physics and Chemistry of Metals in the Liquid State" (Academic Press, New York, 1977).
5. H. EYRING and M. S. JHON, "Significant Liquid Structures" (John Wiley and Sons, New York, 1969).
6. T. S. REE, T. REE and H. EYRING, *J. Chem. Phys.* **41** (1964) 524.
7. W. BAND, "An Introduction to Quantum Statistics" (Van Nostrand Company, New York, 1955) Chap. 4.
8. J. M. ZIMAN, "Principles of the Theory of Solids" (Cambridge University Press, Cambridge, 1965).
9. W. C. LU, M. S. JHON, T. REE and H. EYRING, *J. Chem. Phys.* **46** (1967) 1075.
10. "Handbook of Chemistry and Physics", 54th Edn. (CRC Press, Cleveland, Ohio, 1974).
11. E. GEBHARDT, M. BECKER and S. DORNER, *Aluminum* **31** (1955) 315.
12. "Metals Handbook Vol. I — Properties and Selection", 8th Edn. (American Society for Metals, Metals Park, Ohio 1985).
13. E. CHACON, F. FLORES and G. NAVASCUES, *J. Phys. F* **14** (1984) 1587.
14. M. UEKI, M. NAKA and I. OKAMOTO, *J. Mater. Sci. Lett.* **5** (1986) 1261.
15. D. R. POIRIER, and R. SPEISER, *Met. Trans.* **18A** (1987) 1156.
16. C. GARCIA-CORDOVILLA, E. LOUIS and A. PAMIES, *J. Mater. Sci.* **21** (1986) 2787.
17. S. K. RHEE, *J. Amer. Ceram. Soc.* **53** (1970) 386.
18. K. KÖRBER and K. LÖHBERG, *Giessereiforschung* **23** (1971) 173.
19. S. P. YATSENKO, W. I. KONONENKO and A. L. SCHUKMAN, *Tepl. Vysok. Temp.* **10** (1972) 66.
20. G. LANG, *Aluminum* **49** (1973) 231.
21. N. EUSTATHOPOULOS, J. M. HICTER, J. C. JOUD and P. DESRE, *J. Mater. Sci.* **9** (1974) 1233.
22. W. DAWIHL and J. FEDERMANN, *Aluminum* **50** (1974) 574.
23. G. LANG, P. LATY, J. C. JOUD and P. DESRE, *Z. Metallkd* **68** (1977) 113.
24. L. GOUMIRI, J. C. JOUD and P. DESRE, *Surf. Sci.* **83** (1979) 471.
25. L. GOUMIRI and J. C. JOUD, *Acta Metall.* **30** (1982) 1397.
26. A. PAMIES, C. GARCIA-CORDOVILLA and E. LOUIS, *Scripta Metall.* **18** (1984) 869.
27. S. W. KIM, H. EYRING and Y. T. LEE, *J. Chem. Phys.* **51** (1969) 3967.
28. V. N. EREMENKO, V. I. NISHENKO and Y. V. NAIDITSCH, *Izv. Akad. Nauk, SSSR, OTN* **3** (1961) 150.
29. P. LATY, J. C. JOUD and P. DESRE, *Surf. Sci.* **69** (1970) 508.

Received 22 February  
and accepted 9 September 1988