

# Calculation of surface tension and surface phase transition line in binary Ga–Tl system

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Received 15 April 2007; received in revised form 29 October 2007; accepted 31 October 2007

## Abstract

The surface phase transition (SPT) line has been calculated at the Ga-rich side of the binary Ga–Tl system. The liquid alloys at a given temperature can be divided into the following four different regions as a function of Tl-content of the alloy: (i) at very low Tl-content one bulk Ga-rich alloy is obtained not covered by any nano-layer, (ii) at a somewhat higher Tl-content one bulk Ga-rich liquid phase is obtained, covered by a Tl-rich nano-layer, (iii) at medium Tl-content two bulk liquids are obtained, (iv) at high Tl-content one Tl-rich liquid is obtained with no nano-layer on it. An improved version of the Ga–Tl phase diagram is offered, showing the equilibrium SPT line and the region of the Ga-rich bulk liquid, covered by a Tl-rich nano-layer. The presence of the latter changes some physical properties of the system. Particularly, the temperature coefficient of the surface tension changes from a low negative value to a high positive value when increasing the Tl-composition of the alloy and the SPT line is crossed. The position of the SPT line is essential to control Marangoni convection in liquid monotectic alloys.

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**Keywords:** Gallium; Thallium; Surface phase transition; Surface tension; Composition dependence; Temperature dependence; Marangoni convection

## 1. Introduction

It was theoretically predicted by Cahn [1] that a first order surface phase transition (SPT) might take place in monotectic systems. This SPT can be denoted by a new equilibrium line in monotectic phase diagrams, called SPT line. The SPT in liquid alloys was experimentally observed by ellipsometry in the Ga–Bi system [2], by Auger electron spectroscopy in the Ga–Pb [3,4], Ga–Tl [5] and Ga–Pb–Tl [6] systems and by measuring surface tension of the alloys in the Ga–Pb [7], Ga–Sn, Ga–Pb–Sn and Ga–Pb–Tl [8] systems.

Theoretical methods have been developed to predict the SPT line, using a single-surface-layer [9] (see also [10]) and a multi-surface-layer [11] regular solution model, with supposing the molar surface areas of both components being identical. The latter model was further extended to ternary alloys [8]. Based on the Butler equation a new method was developed to calculate the SPT line in monotectic systems [12]. The proposed new

method is free from the limitations of the previous models, i.e. the components can have different molar surface areas and any appropriate solution model (not only the simplified regular solution model) can be used to describe the excess Gibbs energy of the liquid solution.

In the present paper the above method [12] is applied to calculate surface tension and the SPT line in the Ga-rich side of the Ga–Tl system. It will be also demonstrated that the sign of the temperature coefficient of surface tension ( $d\sigma/dT$ ) changes from the normal negative value (valid for pure liquid metals, such as Ga) to a high positive value when the composition of the alloying component (Tl) crosses the SPT line. This finding is essential for understanding and controlling the Marangoni convection of alloys, being a key phenomenon in many technological processes, such as steelmaking [13–15], silicon crystal growth [16], arc welding [17–19] and others.

## 2. Basic equations

Reliable calculation of the concentration dependence of surface tension of liquid alloys from bulk thermodynamic data became possible when the Butler equation [20] was first combined with the model for the excess Gibbs energy in the surface

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Table 1  
The physical properties of pure Ga and Tl

Component	$T_{m,i}$ (K) [39]	$\sigma_i^o$ (mJ/m <sup>2</sup> )	$V_i^o$ (cm <sup>3</sup> /mol) [38]
Ga	302.92	708–0.064 ( $T-T_{m,Ga}$ ) [7]	11.4 ( $1 + 0.92 \times 10^{-4} (T-T_{m,Ga})$ )
Tl	577	464–0.08 ( $T-T_{m,Tl}$ ) [38]	18.00 ( $1 + 1.15 \times 10^{-4} (T-T_{m,Tl})$ )

phase by Hoar and Melford [21]. Since then this model (in a slightly corrected form) was successfully applied by the number of groups [22–32] to calculate the surface tension of liquid alloys. However, to the best of our knowledge, only in [12] the Butler equation was applied for the calculation of the SPT line. The basic equations to calculate the SPT line [12] are in accordance with [20–32] and can be summarized as follows.

The surface of a liquid solution will be in equilibrium with its bulk, if the partial surface tension values of the components A and B will equal. For a binary system:

$$\sigma_A = \sigma_B \quad (1)$$

If the concentration dependence of the molar volumes is ignored, the partial surface tensions of the components can be written as

$$\sigma_A = \sigma_A^o + \frac{RT}{f(V_A^o)^{2/3} N_{Av}^{1/3}} \ln \frac{x_A^*}{x_A} + \frac{\beta \Delta G_A^E(x_A^*) - \Delta G_A^E(x_A)}{f(V_A^o)^{2/3} N_{Av}^{1/3}} \quad (2)$$

$$\sigma_B = \sigma_B^o + \frac{RT}{f(V_B^o)^{2/3} N_{Av}^{1/3}} \ln \frac{1 - x_A^*}{1 - x_A} + \frac{\beta \Delta G_B^E(x_A^*) - \Delta G_B^E(x_A)}{f(V_B^o)^{2/3} N_{Av}^{1/3}} \quad (3)$$

where  $\sigma_A^o$  and  $\sigma_B^o$  are the surface tensions of pure components A and B,  $R$  the gas constant,  $T$  the absolute temperature,  $f$  a dimensionless geometrical constant ( $f \approx 1.06$ ),  $V_A^o$  and  $V_B^o$  the molar volumes of pure components A and B,  $N_{Av}$  the Avogadro number,  $x_A$  the bulk molar ratio of component A ( $x_A + x_B = 1$ ),  $x_A^*$  the surface molar ratio of component A ( $x_A^* + x_B^* = 1$ ),  $\beta$  the ratio of surface to bulk coordination numbers ( $\beta \approx 0.82$ ),  $\Delta G_A^E$  and  $\Delta G_B^E$  are the partial excess Gibbs energies of components A and B. The latter quantities can be described by any appropriate solution model. As literature data for the Ga–Tl system are expressed in the form of the Redlich–Kister polynomial [33–35], this semi-empirical model will be used in this paper (for a binary system in a 3-parameter version):

$$\Delta G_A^E = (1 - x_A)^2 [L_0 + L_1(4x_A - 1) + L_2(1 - 8x_A + 12x_A^2)] \quad (4)$$

$$\Delta G_B^E = x_A^2 [L_0 + L_1(4x_A - 3) + L_2(5 - 16x_A + 12x_A^2)] \quad (5)$$

where  $L_0$ ,  $L_1$  and  $L_2$  are temperature-dependent interaction energies (see Ref. [36] for more details). Although the self-aggregation model [37] would be more appropriate to describe the excess Gibbs energy of the liquid solution in this mono-

Table 2  
Interaction energies of the liquid Ga–Tl system (component A = Ga) [34]

$L_0$	15460.67 + 0.61255863 (J/mol)
$L_1$	1550.8555 – 0.65678765T (J/mol)
$L_2$	1966.550 + 0.4753241T (J/mol)

tectic system, this model is not used due to the lack of model parameters for the Ga–Tl system.

In the framework of a simplified model [9] the surface critical point  $T_{cr}^*$  can be estimated from the bulk critical point  $T_{cr}$  as:

$$T_{cr}^* \cong \beta T_{cr} \quad (6)$$

### 3. Physical properties of the Ga–Tl system needed for the calculations

The physical properties of pure Ga and Tl, the interaction energies of liquid Ga–Tl alloy and special points of the Ga–Tl phase diagram are given in Tables 1–3.<sup>1</sup>

#### 3.1. Calculation of the surface phase transition line

Substituting Eqs. (4) and (5) and parameters of Tables 1 and 2 into Eqs. (2) and (3) the partial surface tensions of components Ga (component A) and Tl (component B) can be calculated at given  $T$ ,  $x_{Tl}$  and  $x_{Tl}^*$ . Let us fix the temperature ( $T = 600$  K) and the bulk composition ( $x_{Tl}$ ) and show the dependence of the partial surface tensions of the two components as function of their surface content ( $x_{Tl}^*$ ) in Fig. 1. The following conclusions can be drawn from Fig. 1.

Fig. 1a at low bulk Tl-content (0.11 at.%) the two partial surface tension curves cross each other at a single point at the Ga-rich side of the diagram, and thus Eq. (1) has only one solution.

Fig. 1b at a higher bulk Tl-content (0.122 at.%) the two partial surface tension curves cross each other at 3 different points, and thus Eq. (1) has 3 mathematical solutions. The solution at the Ga-rich side provides the lowest partial surface tension and that is why this solution will be the real physical solution.

Fig. 1c at a somewhat higher, special bulk Tl-content (0.130 at.%) the two partial surface tension curves cross each other at 3 different points, and thus Eq. (1) has 3 mathematical solutions. However, the solutions at the Ga-rich and at the Tl-rich sides provide equal partial surface tension values, being

<sup>1</sup> Klingbeil and Schmid-Fetzer [35] performed the Calphad-assessment of the Ga–Tl system. However, due to a probable misprint their semi-empirical equation contradicts experimental facts collected in the same paper, and so data [35] are not used by us.

Table 3  
Special points of the Ga–Tl phase diagrams [39]

T (K)	Reaction type	Reaction	Tl (at.%)	Tl (at.%)	Tl (at.%)
302.66	Eutectic	$L_1 \leftrightarrow (\text{Ga}) + (\alpha\text{Tl})$	0.19	0	100
302.92	Melting	$\text{Ga} \leftrightarrow L_1$	–	0	–
496.4	Metatetic	$(\beta\text{Tl}) \leftrightarrow L_1 + (\alpha\text{Tl})$	99.82	1.39	100
503	Allotropic	$(\beta\text{Tl}) \leftrightarrow (\alpha\text{Tl})$	–	100	–
559.3	Monotectic	$L_2 \leftrightarrow L_1 + (\beta\text{Tl})$	96.32	2.39	99.67
577	Melting	$L_2 \leftrightarrow \beta\text{Tl}$	–	100	–
849	Critical	$L \leftrightarrow L_1 + L_2$	–	32	–

below that of the value of the middle solution. That is why at this special bulk composition of the alloy the surface of the alloy can co-exist in two different surface states: as the Ga-rich surface and as the Tl-rich surface.

Fig. 1d at a higher bulk Tl-content (0.14 at.%) the two partial surface tension curves cross each other at 3 different points, and thus Eq. (1) has 3 mathematical solutions. The solution at the Tl-rich side provides the lowest partial surface ten-

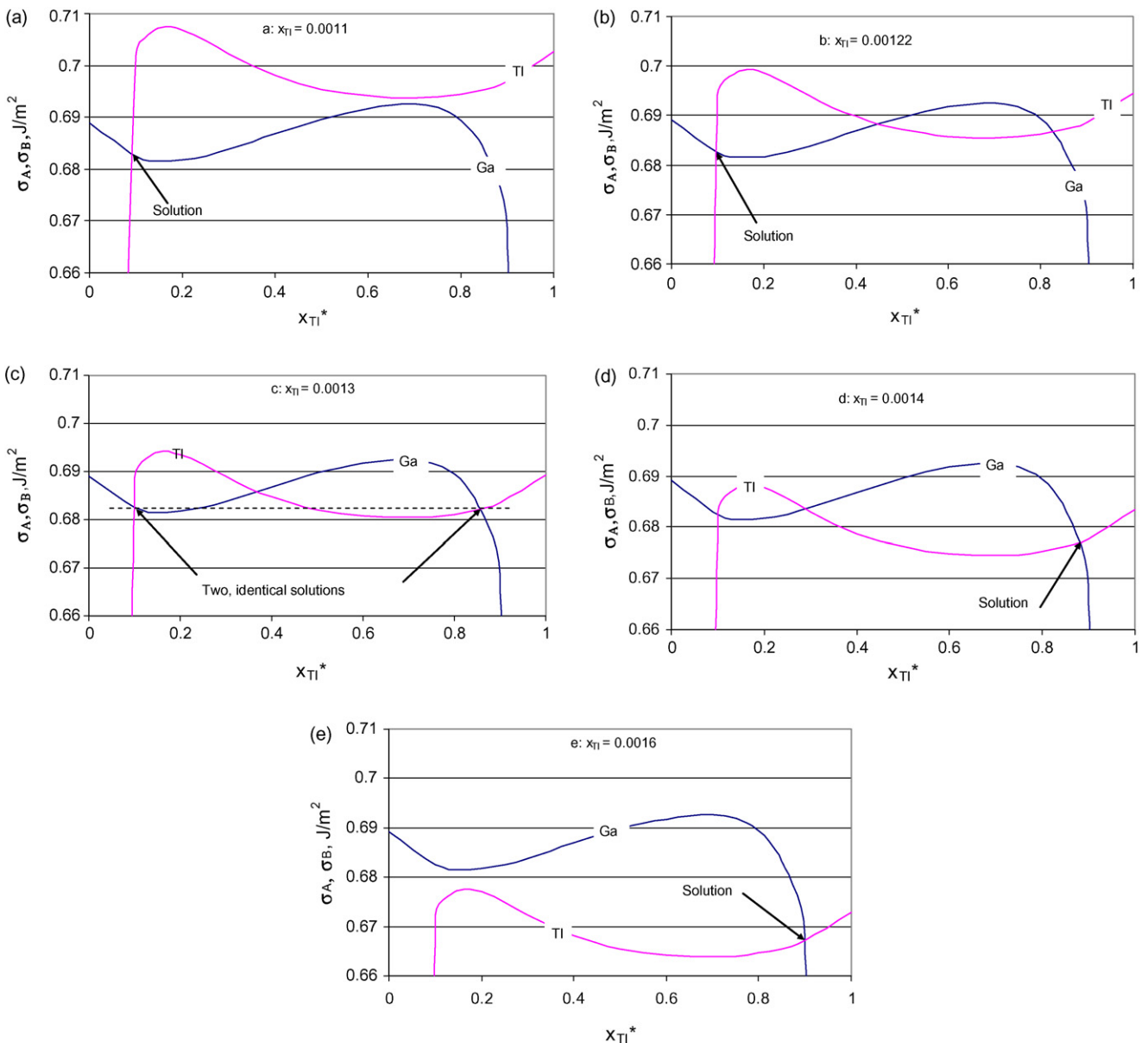


Fig. 1. The evolution of the calculated partial surface tension values as function of the surface concentration of Tl at its gradually increasing bulk concentration, calculated at  $T = 600\text{ K}$  (bulk mole fractions of Tl are given in the inset of each figure).

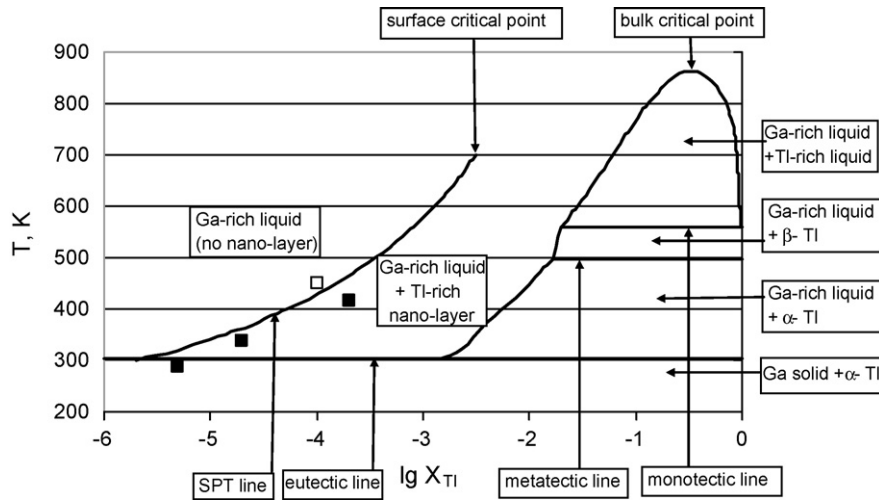


Fig. 2. The improved Ga–Tl equilibrium phase diagram with the calculated SPT line. Other lines are taken from the bulk phase diagram [39]. Points are experimental SPT points [5] (filled symbols: adsorption measurements, open symbol: surface tension measurement).

sion and that is why this solution will be the real physical solution.

Fig. 1e at a high bulk Tl-content (0.16 at.%) the two partial surface tension curves cross each other again at a single point, but now at the Tl-rich side of the diagram, and thus Eq. (1) has only one solution.

Summarizing the above, in the Ga–Tl system at 600 K and at 0.130 at.% of Tl bulk content the first order surface phase transition takes place (see Fig. 1c). Repeating the same procedure at different temperatures, the temperature–bulk composition line (i.e. the SPT-line) can be drawn. Using a home-made software this calculation has been performed and the calculated SPT line is shown in Fig. 2, together with the other lines of the phase diagram [39] (see Table 3). Also, the experimental points of Shim et al. [5] are shown in Fig. 2. One can see that our theoretical calculations (without any fitting parameter) match quite well the experimental data.

One can see from Fig. 2 that the SPT line terminates around  $T_{cr}^* = 709$  K and 0.332 at.% bulk Tl-content, what is the surface critical point. Using the approximated Eq. (6) with  $\beta \approx 0.82$  and  $T_{cr} = 849$  K (see Table 3) the approximated value of  $T_{cr}^* \approx 696$  K is obtained. Thus, the simplified theoretical equation [9] and our more accurate numerical method provide approximately the same results (the difference being only 1.9%).

If one compares the course of the SPT line with that of the liquid/liquid immiscibility line, they do not seem to approach each other in Fig. 2. As a consequence, these two lines seem to merge only in a deeply undercooled liquid, possibly even at 0 K. Thus, the wetting temperature, predicted by Cahn [1] is probably missing in the case of the Ga–Tl system as was generally predicted for metallic alloys [40] (the wetting temperature was estimated to be surely lower than 145 K [5]). In practice it means that the liquid/gas interface of liquid gallium will always be covered by at least a thin Tl layer at any composition within the miscibility gap and at any achievable (low) temperature. Further experiments are needed to accept or exclude this conclusion.

#### 4. Calculation of surface tension and its $T$ -coefficient

Eqs. (1)–(5) and physical properties in Tables 1 and 2 are used to calculate the surface tension in the Ga–Tl system. The concentration dependence of surface tension at three different temperatures is shown in Fig. 3. The lines are drawn till the compositions of the bulk liquid/liquid phase separation [39]. The calculated values are in good agreement with experimental data [41].

From Fig. 3 one can see that below the surface critical temperature of 709 K the concentration dependence is composed of two regions with different slopes separated by the break point (see curves of Fig. 3 at 600 and 700 K). The break points correspond to surface phase transition and their locations correspond to the SPT line in Fig. 2. Above the surface critical temperature of 709 K (see curve of Fig. 3 at 800 K) the transition between these two regions becomes gradual, with no break point and no surface phase transition.

The three isotherms shown in Fig. 3 cross each other. Thus, the temperature coefficient of surface tension changes its sign as the bulk Tl-content of the liquid alloy is increased. In Fig. 4 the temperature coefficient of surface tension ( $d\sigma/dT$ )

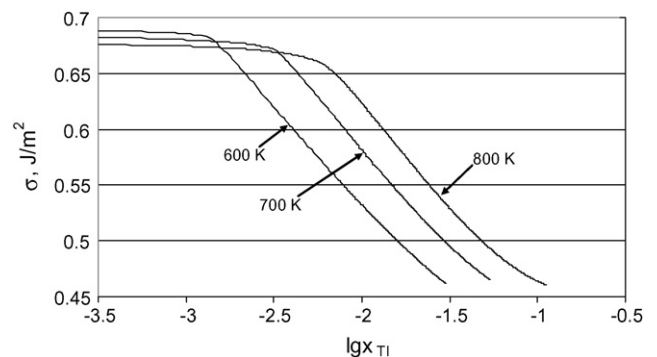


Fig. 3. Calculated values of surface tension of the Ga–Tl system at three different temperatures.

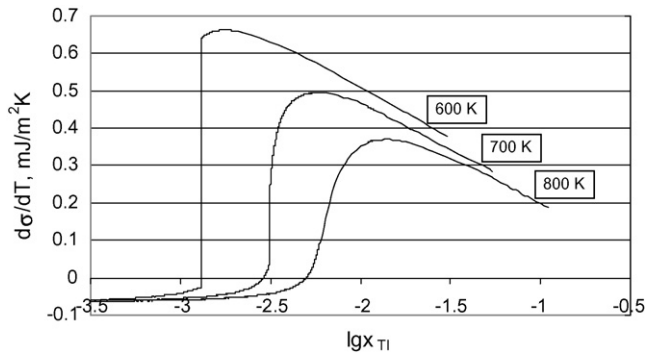


Fig. 4. Calculated temperature coefficients of the surface tension of the Ga–Tl system at three different temperatures.

is shown as function of bulk Tl-content at three different temperatures. At low concentrations of Tl (much below the SPT line)  $d\sigma/dT = -0.064 \text{ mJ}/(\text{m}^2 \text{ K})$ , corresponding to pure liquid Ga and being  $T$ -independent (see Table 1). In the vicinity and above the SPT line significant deviations from this initial value are observed in Fig. 4. At temperatures being below the surface critical temperature of 709 K (i.e. at 600 and 700 K of Fig. 4)  $d\sigma/dT$  abruptly changes from a negative to a positive value when the SPT line is crossed by gradual increase of the bulk Tl-content. During this abrupt change the absolute value of  $d\sigma/dT$  increases by about 1 order of magnitude. Thus, when the SPT line is crossed, not only the direction of the Marangoni flow changes but also its velocity increases significantly. With further additions of Tl to the bulk Ga-rich liquid the  $d\sigma/dT$  value gradually decreases but keeps its positive sign till the composition of the bulk liquid/liquid immiscibility.

## 5. Conclusions

The methodology [12], based on the Butler equation has been applied to calculate the surface phase transition line by a home-made software at the Ga-rich side of the monotectic Ga–Tl system. The calculated results are in good agreement with experimental findings [5], similarly to that of the Ga–Pb system [12]. Thus, the algorithm seems to be capable to predict surface phase transition lines in phase diagrams of monotectic metallic alloys. In future, all monotectic phase diagrams should be improved by adding the SPT line.

It was shown that when the bulk content of Tl is increased in a Ga-rich liquid at a constant temperature and the SPT line is crossed, the temperature coefficient of surface tension changes from a low negative value to a high positive value in an abrupt way. Thus, the knowledge of the position of the SPT line in all monotectic phase diagrams is necessary to control the

Marangoni convection in different high-temperature technologies.

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