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Model calculations of surface phase transitions in Ga–Bi alloys: adsorption, wetting, surface freezing and melting

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Abstract

Thermodynamic model calculations of the surface phase transitions in Ga–Bi alloys are performed, which account in particular for the finite thickness of the adsorption films. The excess chemical potential of bismuth in the films is calculated by employing a screened Coulomb potential. The calculated dependence of the liquid film thickness predicts adsorption and complete wetting transitions, which are in qualitative agreement with the experimental data. On the basis of surface tension calculations the surface freezing–melting transition is modelled and the results coincide with experimental observations via second harmonic generation and surface light scattering. Using an appropriate description of the nucleation mechanism in liquid films the line tension between the liquid and solid films is determined by a fit of experimental data. A complete diagram of the surface liquid–solid phase transitions on the vapour/liquid Ga–Bi interface is derived.

1. Introduction

Over the last two decades significant progress has been made in the study of phase transitions at fluid interfaces including phenomena such as wetting and surface freezing [1–6]. However, in contrast to simple dielectric fluids, little is known about these quasi-two-dimensional phase transitions at the fluid/vapour interface of metallic systems. Two major problems may explain this deficiency. A theoretical description of the interfacial properties of a liquid metal is complicated by the fact that a metal–nonmetal transition occurs across the liquid/vapour interface, i.e. the nature of the effective interatomic potential changes drastically [7]. On the experimental side, elevated temperatures are generally needed, which makes the investigation of fluid–metallic interfaces difficult.

First observations of a wetting transition in a metallic system at the fluid/vapour interface have been reported for the Ga–Bi [8] and Ga–Pb [9] alloys. The bulk phases of these alloys exhibit a liquid–liquid miscibility gap with characteristic critical, T_c , and monotectic, T_{mono} , temperatures of the phase diagrams [10, 11] (for Ga–Bi see figure 1). Approaching the

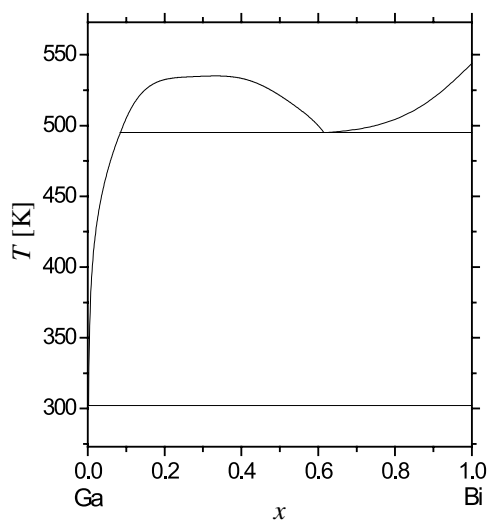


Figure 1. Ga–Bi bulk phase diagram.

monotectic point of the Ga-rich alloys a transition to complete wetting was found [8, 9]. In a more general way, this has been interpreted as wetting at a tetra-point of four-phase coexistence—vapour, Ga-rich liquid, Bi(Pb)-rich liquid and Bi(Pb) solid [12]. It is expected in this scenario that the temperature T_w of the complete wetting transition lies on the metastable extension of the liquid–liquid coexistence curve below T_{mono} . Thus, complete wetting should occur along this line and its observable part for $T_w \leq T \leq T_c$ [12]. For metallic interaction the wetting film thickness should increase as $-\ln \Delta\mu$, where $\Delta\mu$ is the chemical potential difference between loci in the one-phase liquid region and the metastable or stable parts of the liquid–liquid coexistence curve, respectively.

Surface freezing at the liquid/vapour interface of a metallic system has been observed only recently. Rice and co-workers [13, 14] studied the interface of a dilute alloy of Pb in Ga by x-ray reflectivity and grazing incidence x-ray diffraction in the temperature range 300–350 K. Up to 329 K a Pb monolayer in an ordered hexagonal phase exists which undergoes a first-order transition at 331 K to a hexatic phase. Surface freezing in Ga–Bi alloys has been studied by different techniques (optical second harmonic generation [15] and surface light scattering [16, 17]) at different compositions and temperatures up to the monotectic point. The results of both studies clearly indicate that surface freezing transitions occur at conditions slightly above the liquidus curve and that the line of these transitions merges the liquidus at the monotectic point. Freezing and melting of the surface films exhibit hysteresis behaviour, indicating a first-order interfacial phase transition. Assuming a strong undercooling of the Bi(Pb)-rich liquid wetting films, a simple model has been suggested to explain the surface freezing transition by classical nucleation theory [17].

In this study we present a simple model calculation of the interfacial phase transitions in Ga–Bi alloys. It is based on surface thermodynamics, taking into account a finite thickness correction of the wetting film chemical potential by the dominant repulsive part of the pseudo-potential. It is our aim to determine the correlation between the bulk and surface phase diagrams for a metallic binary liquid in detail. For simple binary liquid mixtures Dietrich and Lutz [18] first gave a systematic investigation of the dependence of interfacial wetting on the microscopic interaction potentials.

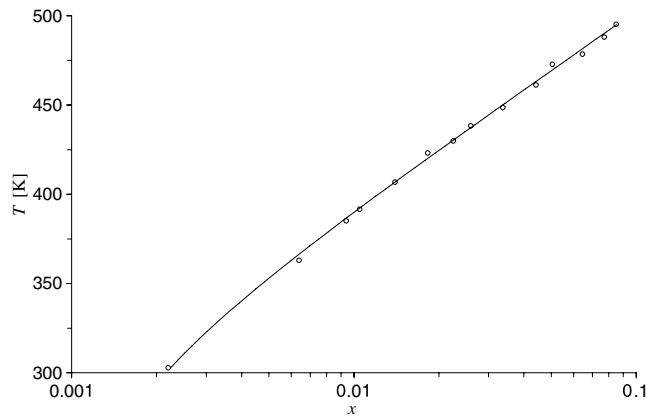


Figure 2. The experimental points [10] and the best fit by equation (2) of the Ga–Bi liquidus line.

2. Model calculations

2.1. Bulk thermodynamics of Ga–Bi alloys

The goal of the present investigation is to describe theoretically the surface phase transitions on a liquid/vapour interface of Ga–Bi alloys. Since the surface phases always reside in contact with the bulk ones, a quantitative modelling of the interfacial phase diagram requires first an appropriate description of the thermodynamics in the bulk. A favourable circumstance is the fact that all the phenomena, the subject of our present study, occur in dilute solutions where the Bi molar fraction does not exceed the monotectic composition 0.085. For this reason, in a first approximation the interaction among the Bi atoms in the bulk solution is neglected and the bismuth activity coefficient is assumed to be composition-independent. This assumption corresponds well to the experimental data [10], showing that the Bi activity obeys Henry's law for molar fractions up to 0.1. Hence, a reasonable approximation of the Bi chemical potential in the bulk in the considered region of concentrations is

$$\mu_{\text{B}}^{\text{L}} = \mu_0^{\text{L}} + RT \ln x + c_0 + c_1 T + c_2 T \ln T \quad (1)$$

where μ_0^{L} is the chemical potential in pure liquid bismuth, x is the Bi molar fraction in the bulk of the Ga–Bi liquid, T is the temperature and c_0 , c_1 and c_2 are unknown constants. The enthalpy and entropy of the interaction of Bi atoms with gallium are taken into account by the last three terms in equation (1). The unknown constants can be determined by fitting of the experimental data for crystallization of bismuth from the bulk solution, i.e. the liquidus line. In this case the chemical potential (1) is equal to the chemical potential in the pure solid bismuth:

$$\mu_{\text{B}}^{\text{L}}(x, T) = \mu_0^{\text{S}} = \mu_0^{\text{L}} + \Delta s_{\text{m}}(T - T_{\text{m}}) \quad (2)$$

where $\Delta s_{\text{m}} = 20.75 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T_{\text{m}} = 544.55 \text{ K}$ are the entropy and temperature of fusion of pure bismuth, respectively. The best fit by equation (2) of the experimental data of Predel [10] is presented in figure 2. It corresponds to the following values of the fitted constants: $c_0 = -511.79 \text{ J mol}^{-1}$, $c_1 = 1149.2 \text{ J mol}^{-1} \text{ K}^{-1}$ and $c_2 = -165.59 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus the chemical potential (1) is completely defined.

2.2. Liquid metal wetting film

Since the surface tension of the bismuth liquid/vapour interface is lower than that of the corresponding gallium interface, the bismuth atoms preferably adsorb on the Ga–Bi liquid/vapour interface. If x is very low, a Ga-rich liquid monolayer forms on the surface of the Ga-rich bulk liquid. Note that the Bi molar fraction in this monolayer is larger than x and thus the surface tension diminishes. By increasing the Bi molar fraction in the bulk the adsorption of bismuth increases as well and, at a certain point, the Ga-rich monolayer transforms into a Bi-rich liquid one. At this point the surface layer saturates and any further adsorption of Bi atoms increases mainly the film thickness but the molar fraction x_F of bismuth in the film remains nearly constant. A rigorous way to determine x_F is to balance the chemical potentials of Ga in the bulk and film, respectively. However, since the saturation value is nearly constant, its approximate value can be anticipated from the cryoscopy effect. It is known from the bulk phase diagram that the Bi-rich bulk phase freezes at the monotectic point. Hence, the saturation value of x_F can be estimated as

$$x_F = \exp[\Delta s_m(T_{\text{mono}} - T_m)/RT_{\text{mono}}] = 0.78 \quad (3)$$

where $T_{\text{mono}} = 495.15$ K is the Ga–Bi monotectic temperature. Since the present study is focused on the liquid film transitions, x_F will be further considered equal to the saturation value from equation (3).

The Bi chemical potential in the Bi-rich liquid film adsorbed on the Ga–Bi liquid/vapour interface can be presented in the form

$$\mu_F^L = \mu_0^L + RT \ln x_F - \Delta\mu_F^L \quad (4)$$

where $\Delta\mu_F^L$ is the chemical potential excess due to the finite thickness of the film. The contribution of the Bi–Ga interaction is neglected in equation (4) due to the low concentration of gallium in the film. To calculate the thickness-dependent part of the chemical potential (4), a model for the interatomic interaction potential is required. The film stability implies that this interaction is dominated by repulsion. DFT calculations [19] show that the repulsive part of the pseudo-potential in metals is described well by the screened Coulomb potential. In addition [20], the Friedel oscillations in bismuth are strongly damped. Hence, the potential acting on a Bi atom can be satisfactorily modelled as

$$\phi_{\text{Bi}}^X = \frac{Z_{\text{Bi}}Z_X e^2}{4\pi\epsilon_0 r} \cosh(k_{\text{TF}}R_c^{\text{Bi}}) \cosh(k_{\text{TF}}R_c^X) \exp(-k_{\text{TF}}r) \quad (5)$$

where Z_X and R_c^X are the charge and radius of an arbitrary atomic core, respectively, and k_{TF} is the wavevector of the Thomas–Fermi screening. The chemical potential $\Delta\mu_F^L$ can be approximated by the difference in the molar energy of the semi-infinite Bi-rich liquid and the corresponding film. This energy difference can be calculated via the integration of potential (5) along the part of the semi-infinite liquid replaced by vapour over the film, i.e.

$$\Delta\mu_F^L = N_A^2 \rho_F^L \int_{h_L}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [x_F \phi_{\text{Bi}}^{\text{Bi}} + (1 - x_F) \phi_{\text{Bi}}^{\text{Ga}}] dx dy dz \quad (6)$$

where the molar volume of the Bi-rich liquid is approximated by $1/\rho_F^L = x_F/\rho_{\text{Bi}}^L + (1 - x_F)/\rho_{\text{Ga}}^L$. The molar densities of the pure liquids, $\rho_{\text{Bi}}^L = 51\,600 - 6.46T$ mol m⁻³ and $\rho_{\text{Ga}}^L = 89\,900 - 8.89T$ mol m⁻³, are taken from the *CRC Handbook*. Substituting potential (5) in equation (6) and accomplishing the integration yields

$$\begin{aligned} \Delta\mu_F^L = & \frac{\rho_F^L Z_{\text{Bi}} F^2}{2\epsilon_0 k_{\text{TF}}^2} \cosh(k_{\text{TF}}R_c^{\text{Bi}}) [x_F Z_{\text{Bi}} \cosh(k_{\text{TF}}R_c^{\text{Bi}}) \\ & + (1 - x_F) Z_{\text{Ga}} \cosh(k_{\text{TF}}R_c^{\text{Ga}})] \exp(-k_{\text{TF}}h_L) \end{aligned} \quad (7)$$

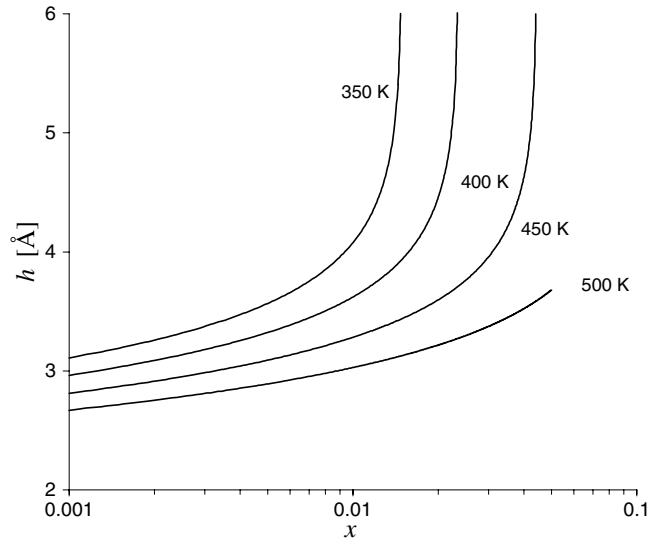


Figure 3. The x dependence of the thickness of an interfacial Bi-rich liquid film at different temperatures.

where F is the Faraday constant and h_L is the thickness of the liquid film. The application of equation (7) requires a knowledge of several specific parameters: some of them can be found in the literature [20] ($R_c^{\text{Bi}} = 0.488 \text{ \AA}$ and $R_c^{\text{Ga}} = 0.556 \text{ \AA}$), while others are general [21] ($Z_{\text{Bi}} = 5$ and $Z_{\text{Ga}} = 3$). Because of the electro-neutrality, the density of electrons in the Fermi gas is equal to the charge density of positive cores. Hence, the Thomas–Fermi wavevector can be calculated via the well-known relation [19]

$$k_{\text{TF}} = 0.251 \sqrt[6]{x_{\text{F}} \rho_{\text{F}}^{\text{L}} Z_{\text{Bi}} + (1 - x_{\text{F}}) \rho_{\text{F}}^{\text{L}} Z_{\text{Ga}}} \text{ \AA}^{-1} \quad (8)$$

adopted for the present case of a mixture of bismuth and gallium.

2.3. Adsorption and wetting transitions in liquid Ga–Bi alloys

Assuming that the Bi-rich liquid film and the Ga-rich bulk liquid are in equilibrium, the corresponding chemical potentials of bismuth should be equal to each other:

$$\mu_{\text{F}}^{\text{L}}(h_{\text{L}}, T) = \mu_{\text{B}}^{\text{L}}(x, T). \quad (9)$$

Here, since x_{F} is constant, it is not included as an argument in $\mu_{\text{F}}^{\text{L}}$. Substituting here the expressions (1), (4) and (7), one yields the equilibrium dependence of the film thickness on temperature and on the Bi molar fraction in the bulk. In figure 3 the dependence of h_L versus x is plotted at different temperatures. As seen, the thickness increases by increasing of the molar fraction of bismuth in the bulk, while h_L decreases with T increasing in the considered temperature interval. The x dependence of h_L shows a typical trend with complete wetting transition. The latter can be associated by the thickness divergence to infinity at larger x . This theoretical dependence of the temperature of complete wetting on x is plotted in figure 4 as well as the experimental points [10] of the Ga–Bi miscibility gap. The comparison shows again that the present model describes well the bulk thermodynamics up to $x = 0.12$. It is interesting to note that, below T_{mono} , the x values where h_L diverges lie well inside the two-phase region

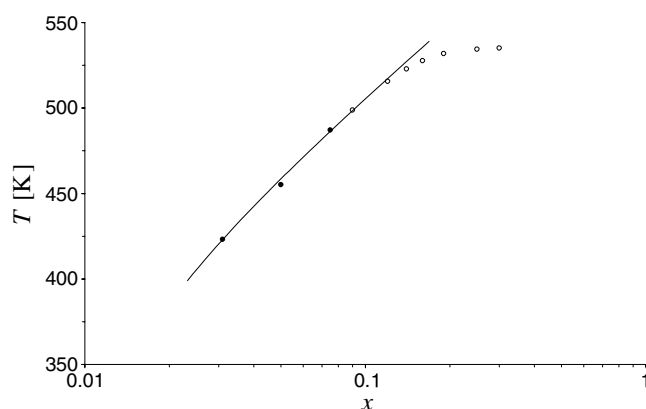


Figure 4. The theoretical complete wetting line compared to the experimental points (○) of the Ga–Bi miscibility gap [10] and its theoretical metastable extension [22] (●) below T_{mono} .

and qualitatively agree with the thermodynamic calculations of the metastable extension of the liquid–liquid coexistence curve [22].

Another peculiarity in figure 3 is that, at low x , the thickness drops below the atomic diameters. Of course, the validity of equation (9) ends at this point since the assumption $x_F = 0.78$ is violated. This indicates that the Bi-rich liquid film with saturation composition is no more realistic and the system transforms to another structure possessing lower bismuth composition, i.e. the Ga-rich liquid monolayer. This scenario possibly indicates the existence of a miscibility gap in the film phase diagram, which also corresponds to the bulk phase diagram. Indeed, measurements [16] of the Gibbs adsorption isotherms have shown that the surface excess density Γ_{Bi} jumps at low x and this discontinuity of Γ_{Bi} has been interpreted as a prewetting transition [17]. The rigorous description of this phase transition requires knowledge of the chemical potentials of Bi in the Bi-rich and Ga-rich phase separating films. The latter is, however, not known. Nevertheless, the temperature dependence of the composition, where this first-order demixing phase transition in an adsorbed monolayer on the surface appears, can be estimated via the relation

$$h_L(x, T) = [x_F d_{\text{Bi}} + (1 - x_F) d_{\text{Ga}}] (1 + a_1 T) (1 - a_2 T) \quad (10)$$

where $d_{\text{Bi}} = 3.2 \text{ \AA}$ is the Bi atom diameter, $d_{\text{Ga}} = 2.6 \text{ \AA}$ is the Ga atom diameter and the two unknown constants a_1 and a_2 are introduced to account for the temperature expansion of the Bi-rich liquid and the temperature dependence of the gallium solubility in the Bi-rich phase, respectively. The best fit by equation (10) of the experimental data for the adsorption transition obtained by surface light scattering experiments [16, 17] is presented in figure 5. The corresponding values of the fitted constants are $a_1 = 0.00187 \text{ K}^{-1}$ and $a_2 = 0.001 \text{ K}^{-1}$.

2.4. Surface freezing and melting

Another interesting phase transition on the Ga–Bi liquid/vapour interface is the melting of a solid film. The latter is composed from pure bismuth since there is no solubility of Ga in Bi in the solid state according to the bulk phase diagram. The chemical potential of bismuth in the solid film can be written in the form

$$\mu_F^S = \mu_0^L + \Delta s_m (T - T_m) - \Delta \mu_F^S \quad (11)$$

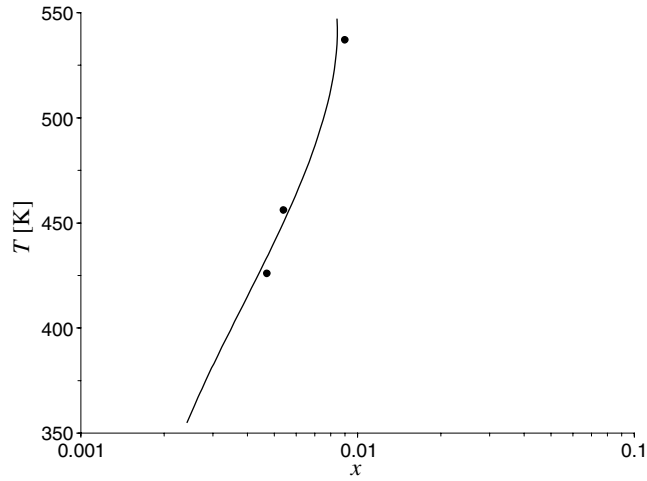


Figure 5. The theoretical surface demixing line compared to the surface light scattering experimental data [16, 17].

where $\Delta\mu_F^S$ accounts for the finite thickness of the film. The latter can be calculated analogously to the case of the liquid film to obtain

$$\Delta\mu_F^S = \frac{\rho_{\text{Bi}}^S Z_{\text{Bi}}^2 F^2}{2\varepsilon_0 k_{\text{TF}}^2} \cosh^2(k_{\text{TF}} R_c^{\text{Bi}}) \exp(-k_{\text{TF}} h_S). \quad (12)$$

Here the molar density $\rho_{\text{Bi}}^S = 47\,400 - 1.87T$ mol m⁻³ of the solid bismuth is taken again from the *CRC Handbook*, $Z_{\text{Bi}} = 5$ and the Thomas–Fermi wavevector is equal to

$$k_{\text{TF}} = 0.251 \sqrt[6]{\rho_{\text{Bi}}^S Z_{\text{Bi}}} \text{ \AA}^{-1}. \quad (13)$$

When the solid film and the Ga-rich bulk liquid are in equilibrium, the Bi chemical potentials in the two media should be the same:

$$\mu_F^S(h_S, T) = \mu_B^L(x, T). \quad (14)$$

In figure 6 the dependence of h_S versus x according to equation (14) is plotted at different temperatures. The dependence of the solid film thickness on x is quite similar to that of the liquid wetting film. The difference is that the wetting occurs at relatively lower values of the bismuth molar fraction. This effect, however, diminishes with temperature. The points of thickness divergence in figure 6 correspond to bulk freezing, i.e. to the liquidus line in figure 2.

A natural question now is which film forms at a given temperature and composition. The answer to this question can be found in the surface tension on the Ga–Bi liquid/vapour interface: the preferred film possesses lower surface tension. Using the Gibbs adsorption isotherm, one can calculate the difference between the surface tensions of an interface covered by liquid and solid films, respectively, to obtain

$$\Delta\sigma = \sigma_L - \sigma_S = -RT \int (\Gamma_{\text{Bi}}^L - \Gamma_{\text{Bi}}^S) d\ln x - c \quad (15)$$

where $\Gamma_{\text{Bi}}^L = x_F \rho_F^L h_L$ and $\Gamma_{\text{Bi}}^S = \rho_{\text{Bi}}^S h_S$ are the corresponding adsorptions of bismuth on the Ga–Bi liquid/vapour interface. Note that, according to equation (1), $d\mu_B^L = RT d\ln x$ at constant temperature. The integration constant c in equation (15) accounts for the phase-state

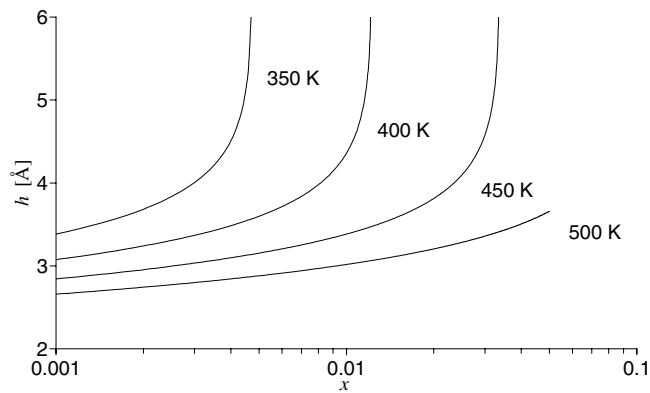


Figure 6. The x dependence of the thickness of an interfacial Bi solid film at different temperatures.

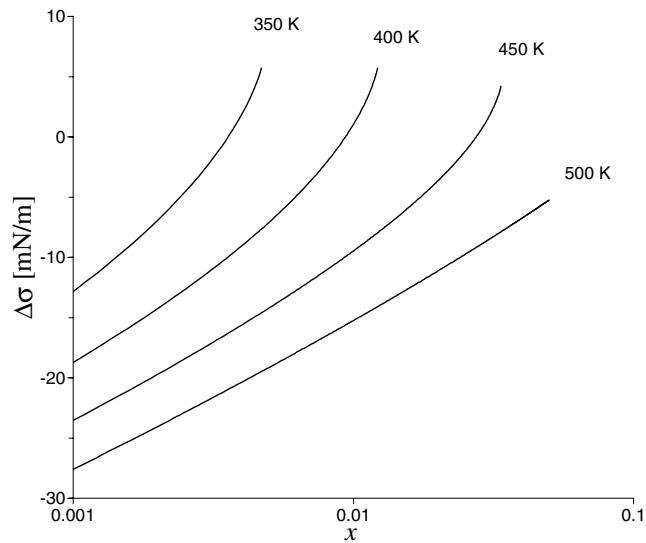


Figure 7. The x dependence of the surface tension difference $\Delta\sigma$ at different temperatures.

difference of the two bulk media composing the films. It can be estimated by the difference of the bulk chemical potentials per molar area of the Bi atoms in the solid, i.e.

$$c = (N_A \rho_{\text{Bi}}^{\text{S}})^{2/3} (\mu_0^{\text{L}} + RT \ln x_{\text{F}} - \mu_0^{\text{S}}) / N_A = (N_A \rho_{\text{Bi}}^{\text{S}})^{2/3} T_{\text{m}} \Delta s_{\text{m}} (1 - T / T_{\text{mono}}) / N_A. \quad (16)$$

Substituting c from equation (16) and using the expressions obtained for the thickness of the liquid and solid films, one can calculate the difference $\Delta\sigma$ from equation (15). It is plotted in figure 7 as a function of x at different temperatures. At low Bi fraction the surface tension of the interface covered by a solid film is larger than that of the liquid film. For this reason, a Bi-rich liquid film covers the Ga–Bi liquid/vapour surface. By increasing x , $\Delta\sigma$ becomes positive, which corresponds to coverage with a solid film. The point $\Delta\sigma = 0$ indicates the coexistence of liquid and solid films on the surface. Note that above the monotectic temperature the film can only be liquid since $\Delta\sigma$ is always negative. The equation $\Delta\sigma = 0$ defines a line on the T – x surface diagram corresponding to melting of the surface solid film. It is plotted in figure 8

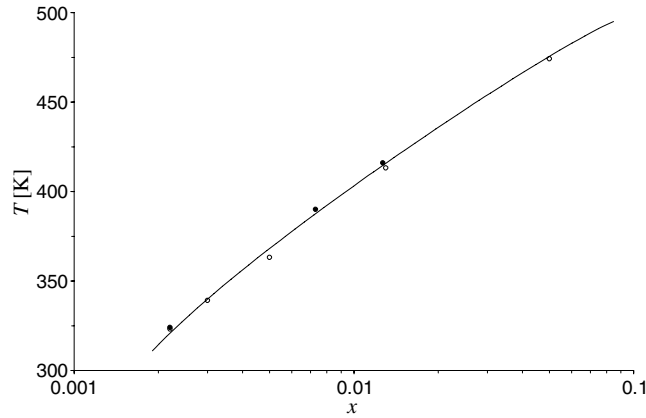


Figure 8. The theoretical surface melting line compared to the experimental points from second harmonic generation [15] (O) and surface light scattering [16, 17] (●).

as well as the data from second harmonic generation [15] and surface light scattering [16, 17] experiments. The juxtaposition of the results is remarkable.

2.5. Line tension

The points of surface freezing of the liquid film usually differ from the surface melting points due to an undercooling effect, which shows up in a clear temperature hysteresis [17]. Since the surface freezing occurs at constant temperature, chemical potentials, pressure and film area, the relevant thermodynamic characteristic function is the Ω potential. Hence the work for the creation of disc-like solid nuclei in the liquid film is equal to

$$\Delta\Omega = 2\pi a\tau - \pi a^2\Delta\sigma \quad (17)$$

where τ is the line tension and a is the nuclei radius. The maximum of this work corresponds to the radius $a^* = \tau/\Delta\sigma$ and its value equals

$$\Delta\Omega^* = \pi\tau^2/\Delta\sigma. \quad (18)$$

Since the nucleation is a thermally driven process, fast surface freezing will start if the maximum of the potential barrier is comparable to the thermal energy, i.e.

$$N_A\Delta\Omega^* = RT. \quad (19)$$

Substituting here the maximal work from equation (18) yields the following equation:

$$RT\Delta\sigma = \pi\tau^2N_A \quad (20)$$

which describes the surface freezing temperature as a function of the Bi molar fraction. The line tension can be determined from the best fit of the experimental results [15–17] by equation (20) together with equation (15), which is presented in figure 9. The fitted value of τ is 1.47 pN and it seems to be almost T -independent in the considered temperature interval. This value of the line tension is quite reasonable compared to the typical order of magnitude of τ in various systems [23], although data for metallic systems are not available to the best of our knowledge. Note that, in the present case, τ is the line tension on the border between four phases: interfacial Bi solid film, wetting Bi-rich liquid film, Ga-rich bulk liquid and vapour. Using equation (20) and the value of the line tension, the radius of the critical nuclei can be estimated as $a^* = 0.03T \text{ \AA}$. In the temperature interval considered a^* is in the range

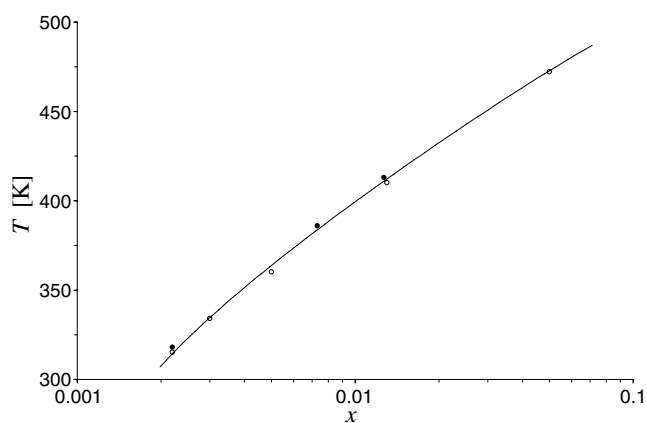


Figure 9. The theoretical fit by equation (20) of the surface freezing points obtained by second harmonic generation [15] (O) and surface light scattering [16, 17] (●).

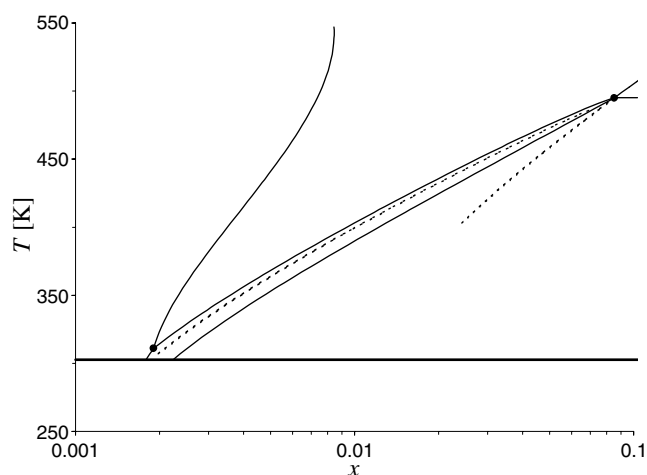


Figure 10. The phase diagram of the surface phase transitions on the liquid/vapour interface of the Ga-Bi alloys. From left to right: surface Ga-rich liquidus, surface demixing, surface Bi-rich liquidus, surface freezing, bulk liquidus and complete wetting lines.

of 10–15 Å, which is commensurable with previous estimations [17]. These numbers are reasonable, since they imply $N_A \rho_{\text{Bi}}^S h_S \pi a^{*2} = 10\text{--}40$ bismuth atoms in the critical nuclei. Of course, equation (20) corresponds to laterally homogeneous two-dimensional nucleation and any impurity, which lowers the line energy, will facilitate the surface freezing process.

3. Conclusions

Finally, the surface phase diagram, summarizing the present theoretical results, is presented in figure 10. As is seen, the bulk monotectic point appears to be quite a peculiar one, since it represents the coexistence of two interfacial and four bulk phases. The surface demixing and melting lines cross each other at a point corresponding to $x = 0.0019$ and $T = 311$ K. This surface monotectic point indicates the coexistence of three phases on the surface: Ga-rich

liquid, Bi-rich liquid and Bi solid films. The surface Ga-rich liquidus line can be approximated analogously to the demixing one via the relation

$$h_S(x, T) = d_{\text{Bi}}(1 + b_1 T). \quad (21)$$

Since the solid monolayer consists of pure Bi, only its temperature expansion is accounted for in equation (21) and the unknown constant here is accepted to be equal to $b_1 = 0.00008 \text{ K}^{-1}$ in order for the surface liquidus line to meet the surface demixing and melting ones at the surface monotectic point. Obviously, the surface freezing is observable only between the surface and bulk monotectic points, which corresponds well to the experimental failure [15] to detect surface freezing at $x = 0.0012$. In the surface phase diagram the complete wetting line is also presented, which is calculated at the points where $h_L \rightarrow \infty$. Below the bulk monotectic temperature it is located inside the bulk two-phase region and corresponds to the metastable extension of the coexistence curve as predicted for a tetra-point wetting scenario. On the other hand, the surface demixing line associated to the phase separation of the interfacial monolayer to Ga-rich and Bi-rich liquids can be considered as a prewetting line as well since the thickness of the film jumps due to the difference in the diameters of Bi and Ga atoms. The question about the corresponding critical temperature still remains open.

Acknowledgments

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