Wetting, prewetting and surface freezing transitions in fluid Ga-based alloys: a surface light scattering study

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Abstract
The surface energy and entropy of liquid Ga–Bi and Ga–Pb alloys have been studied by means of surface light scattering measurements at various compositions and temperatures between the respective eutectic and monotectic points. Analysis of these results using the Gibbs adsorption equation gives evidence for wetting and prewetting transitions in these alloys completely consistent with a tetra-point wetting scenario (Dietrich S and Schick M 1997 *Surf. Sci.* **382** 178). Surface freezing transitions are observed for conditions near the liquidus curves. In view of their viscoelastic properties and their relation with the wetting film characteristics, we suggest a simple explanation for the observed surface freezing phenomena in terms of nucleation of strongly undercooled wetting films.

1. Introduction

Phase transitions in two-dimensional systems have attracted special interest in theory for a long time—see e.g. [1–3] and further references therein. A rigorous solution of the thermodynamic functions for a rectangular two-dimensional lattice was first given by Onsager, from which he predicted an order–disorder transition at a specific temperature T_c [1]. In recent years a renewed and growing interest in this field emerged from research on interfacial phase transitions and wetting phenomena including peculiar wetting transitions such as surface melting or freezing; see e.g. [4–8].

However, for systems with metallic interactions only a few examples have been investigated so far. These include wetting and prewetting transitions at the fluid/wall interface of supercritical expanded Hg [9] and fluid K–KCl melts [10] and wetting and surface freezing transitions at the fluid/vapour interface of the binary alloys Ga–Bi [11–13] as well as Ga–Pb [14, 15]. In the latter, complete wetting was observed first by ellipsometry [11] and Auger spectroscopy [14] approaching the monotectic point—for the phase diagrams of these alloys, see [16]. It has been interpreted by tetra-point wetting (four-phase coexistence)

and consequently complete wetting has been predicted for conditions along the metastable extension of the liquid (ℓ_α)–liquid (ℓ_β) coexistence curve [17]. Surface freezing at the fluid/vapour interface in these systems was observed only recently by means of x-ray reflectivity [15] and SHG measurements [13]. Molecular dynamics simulations of the free surface of a liquid metal (Au) were first conducted by Tosatti and co-workers [18]. For the two-dimensional metal system they found a transition to hexatic ordering at a strong undercooling of $\sim$350 K below the melting point of Au.

In a previous publication we reported first measurements of the surface thermodynamic functions of the liquid Ga–Bi system obtained by means of surface light scattering [19]. By the same technique, we studied the surface freezing transition for a nearly eutectic composition of the Ga–Bi alloy [20]. In this paper we present further results for the Ga–Bi system, extending the composition and temperature range, and new measurements for the Ga–Pb system from light scattering studies. We focus on the Ga-rich alloys and discuss in more detail the experimental results with respect to the prewetting and surface freezing transitions in these systems.

2. Experiment and data analysis

Our experimental set-up for surface light scattering measurements on fluid metal systems at elevated temperatures under UHV conditions has been described previously [19]. In principle, laser light (He–Ne laser, $\lambda = 632$ nm) incident on the liquid surface is scattered by thermally excited capillary waves and is detected by the heterodyne technique. Light scattering measurements have been performed over a wavenumber range $200 \leqslant q \leqslant 645$ cm^{-1}. Spectra were fitted with a Lorentzian taking into account corrections for instrumental broadening. From these fits the peak frequency ω_0 and the damping constant κ_0 were determined. For further details of the experimental procedure and sample preparation, see [19].

The frequency $\omega = \omega_0 + i\kappa_0$ and the wavenumber q are related by the dispersion relations of surface waves which involve the surface tension σ, bulk (viscosity η, density ρ) and interfacial viscoelastic properties of the system—see e.g. [21]. For a bare liquid surface, the roots of the dispersion relation describing the propagation of capillary waves in first approximation are [21]

$$\omega_0 = (\sigma q^3/\rho)^{1/2}, \qquad \kappa_0 = 2\eta q^2/\rho. \tag{1}$$

The σ-results for the free liquid alloy surfaces have been determined from the measured capillary wave spectra according to equation (1). In general, relative errors $\Delta\sigma/\sigma < 1\%$ are found, which reflects the high precision of the ω-measurements and relatively low errors in q of $\sim$0.2–0.3%. Due to instrumental broadening corrections, the uncertainty in η is about one order of magnitude higher; see [22]. In the case of a structured interfacial film, Tejero and Baus [23] have calculated the dispersion equation for capillary waves and obtained the following solutions in the weakly damped domain:

$$\omega_0 = (\sigma q^3/\rho + \bar{\gamma}_s q^3/\rho)^{1/2}, \qquad \kappa_0 = 2\eta q^2/\rho + \bar{\eta}_t q^3/2\rho. \tag{2}$$

Here $\bar{\gamma}_s$ is the surface excess elastic modulus and $\bar{\eta}_t$ the surface excess shear viscosity, where the excess quantities are defined by $\bar{a} = \int_{-\infty}^{0} (a(x) - a)\,\mathrm{d}x$, with a denoting the bulk liquid value. The viscoelastic properties discussed below for surface freezing conditions have been evaluated according to equation (2)—see also [20].
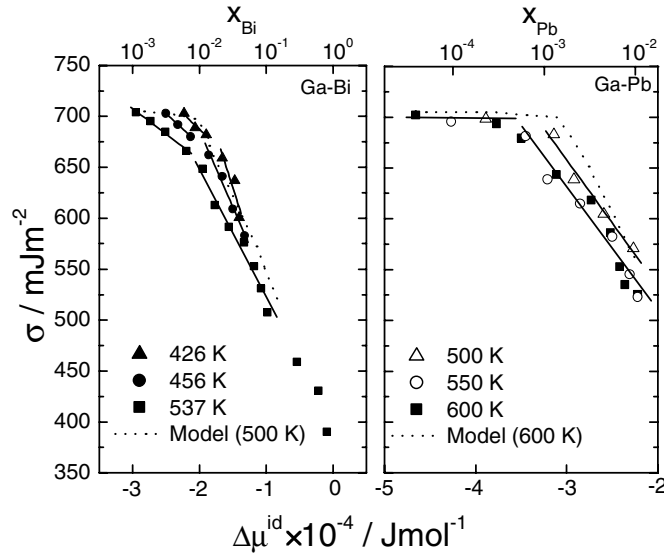
Figure 1. Gibbs adsorption isotherms of liquid Ga–Bi and Ga–Pb alloys; see the text.

3. Results and discussion

3.1. Wetting and prewetting transitions in liquid Ga–Bi and Ga–Pb alloys

The two alloy systems have similar phase diagrams with liquid miscibility gaps lying above the monotectic temperatures [16]. In the following we concentrate on the Ga-rich alloys at mole fractions x and temperatures T between the respective eutectic and monotectic points, i.e. $0.0022 \leqslant x_{Bi} \leqslant 0.085$, $302.6 \leqslant T/K \leqslant 495.2$ for Ga–Bi and $0.0006 \leqslant x_{Pb} \leqslant 0.024$, $302.6 \leqslant T/K \leqslant 588$ for Ga–Pb. From the capillary wave spectra we determined the surface energies σ and the surface entropies $S^{(\sigma)} = -\partial\sigma/\partial T$ according to equation (1). In discussing these surface thermodynamic quantities in relation with the wetting characteristics, the surface excess Γ of Bi or Pb is crucial—its magnitude and variation as a function of x and T. For a plane liquid surface at equilibrium and with the Gibbs dividing surface at $\Gamma_{Ga} \equiv 0$, Γ is given by the Gibbs adsorption equation:

$$\mathrm{d}\sigma = -S^{(\sigma)}\,\mathrm{d}T - \Gamma\,\mathrm{d}\mu. \tag{3}$$

Here $S^{(\sigma)}$ denotes the surface entropy per unit area and μ is the chemical potential of Bi or Pb in the liquid bulk phase. In view of the lack of detailed experimental data for μ, we approximate it by the ideal solution model. The corresponding Gibbs adsorption isotherms are plotted in figure 1. For both systems a clear break in slope of σ versus $\Delta\mu = RT \ln x$ is apparent at low mole fractions $x \leqslant x_{PW}$, which characterizes the prewetting transition from low to high adsorption. For the Ga–Bi alloys, $\Gamma_{Bi} = (1.6 \pm 0.2) \times 10^{-5}$ mol m^{-2} for $x > x_{PW}$ and $T = 426$ K which corresponds to a wetting film of pure liquid Bi. It drops by almost a factor of 3 for $x < x_{PW}$. On increasing the temperature up to 537 K, Γ_{Bi} is reduced by $\sim 20\%$ [22]. A qualitatively similar trend is observed for the Ga–Pb system (figure 1), although Γ is lower at high adsorption ($\Gamma_{Pb} = 1.2 \times 10^{-5}$ mol m^{-2}, $n_{Pb}^{(\sigma)} \sim 0.7$) and seems to be very low and temperature independent for $x < x_{PW}$. In both cases the change in the experimental adsorption isotherms is consistent with model calculations of the surface energy based on a layering model of the interfacial region and regular solution approximations—see also [24, 25].
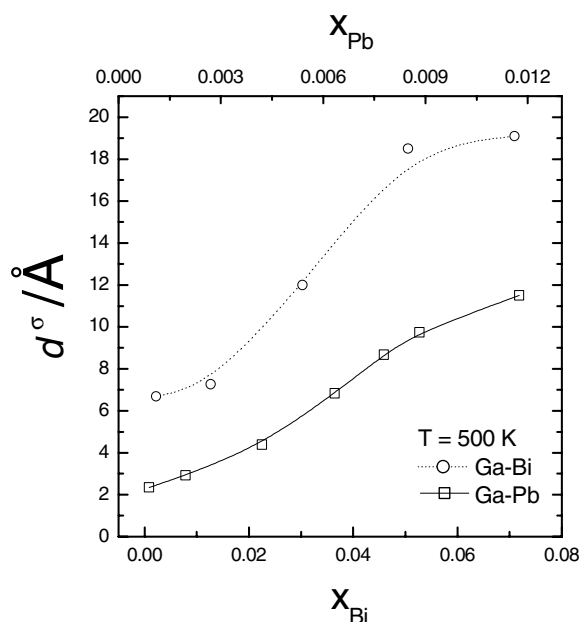
Figure 2. Thickness $d^{(\sigma)}$ of the interfacial region versus mole fraction x for the Ga–Bi and Ga–Pb systems; see the text.

The results for the Gibbs adsorption Γ clearly indicate a prewetting transition in the Ga-rich alloys—for the prewetting line, see figure 5. An interesting question now is: how does the thickness $d^{(\sigma)}$ of the Bi- or Pb-rich wetting film change as a function of x and T? This can be estimated with the multilayer model of Defay and Prigogine for the interfacial region of the liquid/vapour interface [25]. Within this model the surface entropy $S^{(\sigma)}$ is given by [25]

$$S^{(\sigma)} = S^{(S)} - d^{(\sigma)} S^{(l)}, \tag{4}$$

where $S^{(S)}$ is the entropy of the interfacial region which we derived from the model calculations of the surface energy (see above), and $S^{(l)}$ is the entropy of the liquid which we approximated by the ideal solution model. In this way we determined $d^{(\sigma)}$ from the measured temperature coefficients of σ according to equation (4). The results are shown in figure 2. An increase of $d^{(\sigma)}$ by roughly a factor of 4 occurs in both alloys moving from conditions near the eutectic towards the monotectic points.

3.2. Surface freezing transitions near the liquidus curves in Ga–Bi and Ga–Pb alloys

After equilibration of the alloys at temperatures above the monotectic, surface freezing was studied in different cooling and heating cycles with rates of 8 K h^{-1} approaching the liquidus curve at constant x. The surface freezing transition is recognized by a distinct drop of the capillary wave frequency ω_0 on cooling and a steep rise on heating, exhibiting hysteresis behaviour [20]. Very similar discontinuities have been observed for the damping constants κ_0. The variation of the surface energy $\sigma(T)$ at the surface freezing transition as determined from $\omega_0(T)$ according to equation (1) is plotted in figure 3 for two typical examples of Ga–Bi and Ga–Pb. The measurements were made with different samples at various q-values. Two observations are of special interest. Approaching surface freezing from above, a discontinuous change in slope of $\sigma(T)$ is indicated, i.e. the surface entropy $-\partial\sigma/\partial T$ jumps. This is indicative
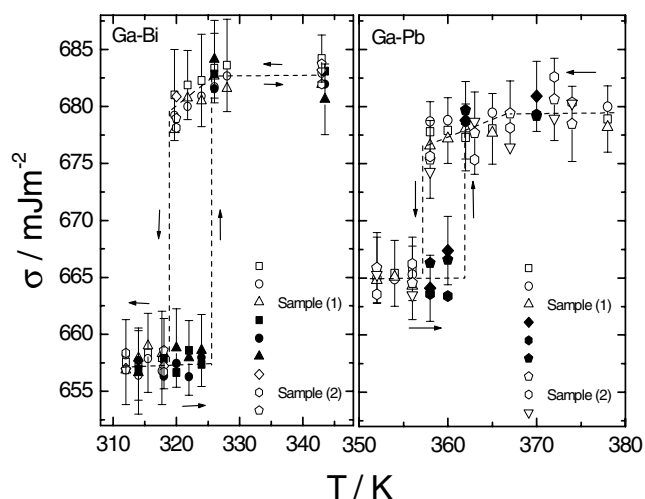
Figure 3. Surface energy σ versus temperature across the surface freezing transition in Ga–Bi ($x_{Bi} = 0.0022$) and Ga–Pb ($x_{Pb} = 0.000\,63$). Open symbols relate to cooling, full ones to heating; different symbols denote measurements at different q-values.
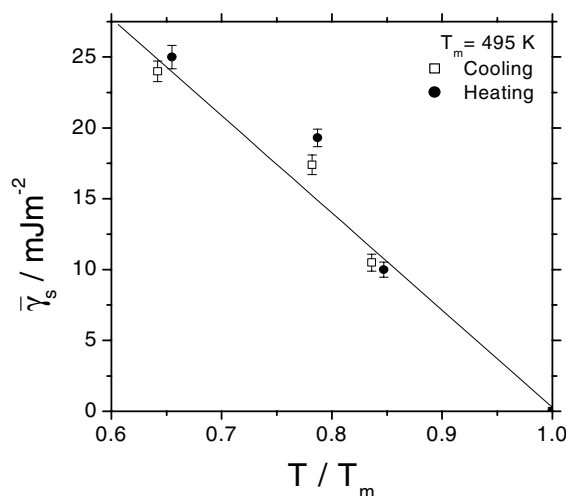

Figure 4. Surface excess elastic modulus of surface freezing films on top of Ga–Bi alloys plotted versus reduced temperature (T_m = monotectic temperature).

of a structural transition from a disordered, liquid-like to an ordered surface layer. A second feature of the plots in figure 3 concerns the pronounced hysteresis of $\sigma(T)$ of $\sim$5 K width between the surface freezing and the surface melting temperature, T_{sm}. This is in quantitative agreement with recent SHG results. Measurements at higher x and T moving towards the monotectic point show the following trend: the height and width of the hysteresis is reduced and the difference between T_{sm} and the liquidus temperatures gets smaller and approaches zero at the monotectic point (see figure 5).

In order to get information on the viscoelastic properties of the surface freezing films, we have analysed the $\omega(q)$ measurements according to equation (2); this analysis yielded the
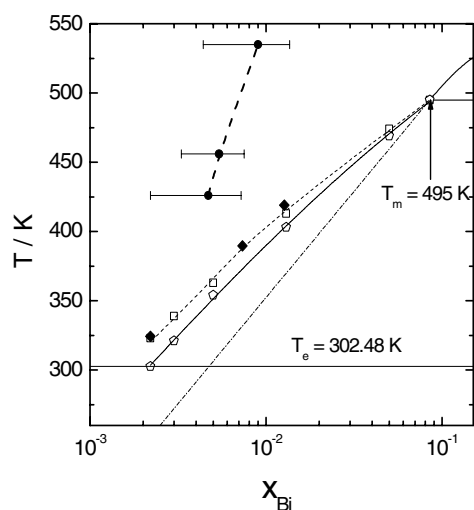
Figure 5. The surface phase diagram of Ga-rich liquid Ga–Bi alloys: prewetting line (line with bullets), surface freezing line (line with diamonds: this work; line with squares: from [13]), liquidus curve (line with pentagons) from [16], section of the liquid–liquid demixing gap (——), linear metastable extension of the latter (— · —); T_e = eutectic temperature, T_m = monotectic temperature.

surface excess elastic modulus $\bar{\gamma}_s$ and the surface excess shear viscosity $\bar{\eta}_t$. In comparison with surface freezing in liquid alkanes where measurements of $\bar{\gamma}_s$ and $\bar{\eta}_t$ by means of light scattering exist [26], we find one order-of-magnitude-higher values for the metallic surface freezing films. As an example, we present in figure 4 the surface excess elastic modulus of the Ga–Bi system plotted as a function of the reduced temperature T/T_m. The reduction of $\bar{\gamma}_s(T)$ reflects the decrease of the σ-drop on surface freezing. It obviously goes to zero at the monotectic point. A similar reduction with temperature is found for $\bar{\eta}_t$ [22]. With the definitions of $\bar{\gamma}_s$ and $\bar{\eta}_t$, the fall of the magnitude of these surface excess quantities with temperature indicates a decrease of the excess viscoelastic modulus governing shear normal to the surface plane. This may happen if with increasing temperature the surface freezing film gets thicker and more rigid. However, there is as yet no theory of the viscoelasticity of surface freezing films, so we refrain from drawing further conclusions. Instead we briefly discuss the relation between the surface freezing and wetting transitions in these alloys. In the light of the Γ values in figure 1 and the thickness variation of the wetting films in figure 2, we consider these wetting films along the liquidus curve as strongly undercooled Bi or Pb liquid films. At a given undercooling ΔT, freezing of these films may set in if their thickness $d^{(\sigma)}$ reaches the size of a critical nucleus, R_C, i.e. $d^{(\sigma)} \geqslant R_C$. Assuming homogeneous nucleation and taking $R_C = 2\sigma_{ls}/n\Delta\mu$, a first rough estimation for Bi yields: $R_C \sim 1$ nm for $\Delta T = 200$ K—see e.g. [27]. This is of the right order of magnitude, as seen by comparison with the $d^{(\sigma)}$-data in figure 2. Furthermore, since $R_C \propto \Delta T^{-1}$, we expect thicker surface freezing films approaching the monotectic point, which is in agreement with the merging of the liquidus curve and the T_{sm}-line at T_m. A fast freezing kinetics is also predicted, since the energy barrier $\Delta G_c = 0$ for $\Theta \to 0$ at complete wetting [4]. So this nucleation model explains the main features of the observed wetting and surface freezing transitions and is consistent with the bulk thermodynamics at T_m. We summarize the surface phase diagram for the example of the Ga–Bi system in figure 5.

Acknowledgments

References

[1] Onsager L 1944 *Phys. Rev.* **65** 117
[2] Kosterlitz J M and Thouless D J 1973 *J. Phys. C: Solid State Phys.* **6** 1181
[3] Nelson D R and Halperin B I 1979 *Phys. Rev.* B **19** 2457
[4] Dietrich S 1988 *Phase Transitions and Critical Phenomena* ed C Domb and J L Lebowitz (London: Academic)
[5] Schick M 1990 *Liquids at Interfaces* ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier)
[6] Bonn D and Ross D 2001 *Rep. Prog. Phys.* **64** 1085
[7] Van der Veen J F 1999 *Surf. Sci.* **433–435** 1
[8] Maeda N and Yaminski V V 2001 *Int. J. Mod. Phys.* B **15** 3055
[9] Hensel F and Yao M 1996 *J. Non-Cryst. Solids* **205** 231
      Kozhevnikov V F, Arnold D I, Naurzakov S P and Fisher M E 1997 *Phys. Rev. Lett.* **78** 1735
[10] Staroske S, Nattland D and Freyland W 2000 *Phys. Rev. Lett.* **84** 1736
      Staroske S, Freyland W and Nattland D 2001 *J. Chem. Phys.* **115** 7669
[11] Nattland D, Poh P D, Müller S C and Freyland W 1995 *J. Phys.: Condens. Matter* **7** L457
[12] Tostmann H, DiMasi E, Shpyrko O G, Pershan P S, Ocko B M and Deutsch M 2000 *Phys. Rev. Lett.* **84** 4385
[13] Turchanin A, Freyland W and Nattland D 2002 *Phys. Chem. Chem. Phys.* **4** 647
      Turchanin A, Nattland D and Freyland W 2001 *Chem. Phys. Lett.* **337** 5
[14] Chatain D and Wynblatt P 1996 *Surf. Sci.* **345** 85
      Chatain D and Wynblatt P 1998 *Ber. Bunsenges. Phys. Chem.* **102** 1142
[15] Yang B, Gidalevitz D, Huang Li and Rice S A 1999 *Proc. Natl Acad. Sci. USA* **96** 13009
[16] Predel B 1960 *Z. Phys. Chem., NF* **24** 206
[17] Dietrich S and Schick M 1997 *Surf. Sci.* **382** 178
[18] Celestini F, Ercolessi F and Tosatti E 1997 *Phys. Rev. Lett.* **78** 3153
[19] Ayyad A H and Freyland W 2002 *Surf. Sci.* **506** 1
[20] Ayyad A H, Mechdiev I and Freyland W 2002 *Chem. Phys. Lett.* **359** 326
[21] Langevin D (ed) 1992 *Light Scattering by Liquid Surfaces and Complementary Techniques* (New York: Dekker)
[22] Ayyad A H 2002 *PhD Dissertation* University of Karlsruhe
[23] Tejero C F and Baus M 1985 *Mol. Phys.* **54** 1307
[24] Wynblatt P, Saul A and Chatain D 1998 *Acta Mater.* **45** 2337
[25] Defay R and Prigogine I 1966 *Surface Tension and Adsorption* (London: Longmans Green)
[26] Earnshaw J C and Hughes C J 1993 *Prog. Colloid Polym. Sci.* **93** 108
[27] Adamson A W and Gast A P 1997 *Physical Chemistry of Surfaces* (New York: Wiley)