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Abstract. The temperature dependence of the surface tension $\gamma(T)$ of liquid gallium is studied theoretically and experimentally using light scattering from capillary waves. The theoretical model based on the Gibbs thermodynamics relates $\partial\gamma/\partial T$ to the surface excess entropy density $-\Delta S$. Although capillary waves contribute to the surface entropy with a positive sign, the effect of the dipole layer on ΔS is negative. Experimental data collected at a free Ga surface in the temperature range from 30 °C to 160 °C show that $\partial\gamma/\partial T$ changes sign near 100 °C.

1. Introduction

The temperature dependence of the surface tension of liquids is very important in applications such as Marangoni convection and crystal growth. However, little is known about the specific surface effects influencing this dependence in liquid metals.

Our previous works [1,2] were concerned with the surface tension of mercury as a function of temperature, which was studied using quasielastic light scattering from capillary waves [3]. Although the experimental data show a decrease in surface tension with T, the theoretical explanation of this fact seems to be non-trivial. The recent discovery of surface layering in liquid gallium and mercury indicates an ordered metal structure perpendicular to the surface which is a few atomic diameters thick [4,5]. This ordering can drastically influence the entropy-density profile in the surface zone, reducing the entropy density at the surface compared to the entropy density of the bulk. It was suggested [1] that a liquid-metal surface is a two-component system comprising quasi-free surface electrons and positive ions. In this case $\partial\gamma/\partial T$ would depend on the surface excess entropy as well as the chemical potential of the surface electrons [1]. However, the ionic and electronic profiles of any complicated shape should be approximated by the same right-angled profile [2] in order to preserve the electrical neutrality of the metal as a whole. Thus, the two-component model is inapplicable to a free metal surface, whose excess entropy should be evaluated in the framework of a one-component model [6,7]:

$$\Delta S = -\frac{\partial\gamma}{\partial T} \tag{1}$$

where ΔS is defined by

$$\Delta S = \int_{-\infty}^{\infty} dz\,(S(z) - S_b\theta(z)).$$

Here $\theta(z) = 0$ for $z > 0$ and $\theta(z) = 1$ for $z \leqslant 0$; $z = 0$ denotes the surface position and the integration is performed from the liquid bulk ($z = -\infty$) to a vapour phase ($z = \infty$), and S_b

denotes the entropy density in the liquid bulk. We split the surface excess entropy into three parts describing surface layering, capillary waves, and a surface double layer [2]. As expected, the contribution from surface layering to ΔS is negative [1], whilst that from capillary waves is positive. It was suggested [2] that the electric field in the double layer will contribute to the surface excess entropy with a positive sign if the layer thickness varies with T but the surface charge density does not. The present paper demonstrates that this is not the case; the thickness of the dipole layer remains insensitive to the temperature variations, and the contribution from the electric field to ΔS should be negative, indicating a decrease in the surface electron density on heating.

2. Theoretical estimates of ΔS

A liquid metal comprises two components: free electrons and positive ions. Free electrons behave as a quantum medium: even at zero temperature their energy is non-zero, and is usually written in terms of the Fermi energy E_f: $E = E_f N$, where N is the number of electrons. The spatial electron-density profile $\rho_e(z)$ has a non-zero width (even at 0 K), which leads to some redistribution of electrons between the bulk and the surface. In other words, some electrons are ejected from the bulk and concentrate on the vapour side of the interface. This charge separation leads to a surface double layer, as suggested by Frenkel [9].

Unfortunately, no theory describing the surface tension of liquid metals is well established. Numerical simulations of the electron- and ion-density profiles [11] predict oscillations of the density profile, but the driving force of these oscillations is not very clear. Only one paper, to the author's knowledge, treats this problem analytically [12]. Due to its importance for the present context, we repeat the main results of this paper.

A detailed analysis done by Samojlovich at 0 K ascertained that the electrostatic force $-\rho_e \nabla\phi$ leads to Maxwellian elastic stresses $\Pi_{zz} = -\Pi_{xx} = \epsilon_0 E^2/2$ (the z-axis is directed along the surface normal and the x-axis along the surface) or electrostatic pressure $P = \epsilon_0 E^2/2$ deforming the ionic fluid. This isotropic pressure acting on the topmost layer makes the atoms there over-compressed compared to atoms in the bulk. These considerations predict a non-monotonic density profile with a maximum in the topmost layer; this was demonstrated to be the case recently for the surfaces of liquid gallium and mercury.

The surface tension of any liquid can be expressed via the tensor of anisotropic stresses with the components Π_{zz} and Π_{xx} appearing as a result of the density gradient in the surface zone. The surface tension of a liquid metal at 0 K is given by

$$\gamma = \int_{-\infty}^{\infty} \mathrm{d}z \, (\Pi_{zz} - \Pi_{xx}) = \int_{-\infty}^{\infty} \mathrm{d}z \left[\chi_w \frac{1}{\rho} \left(\frac{\partial \rho}{\partial z} \right)^2 - \epsilon_0 E^2 \right] \tag{2}$$

where $\chi_w = \hbar^2/(4m)$ [12]. This expression is obtained from the balance between the electrostatic force $-\rho \nabla\phi$ and the quantum pressure of electron gas given by von Weizsacker's term

$$\chi_w \int \mathrm{d}z \, \frac{1}{\rho} (\nabla\rho)^2.$$

If only the electrostatic energy were taken into account, the surface tension would be negative [12]. In order to calculate the surface tension one should know the electron-density profile and the solution of Poisson's equation in the surface zone.

The temperature behaviour of the surface tension of a liquid metal is a most intriguing problem. While the changes in tension for nearly all liquid metals, as expected from the literature, are only by a few per cent over 100 K [13], the temperature derivative $\partial\gamma/\partial T$

should be extremely sensitive to the density profile [7]. In the following text we will give some basic relations connecting the surface excess entropy to other physical properties of the surface layer.

It is supposed that the surface entropy comprises different parts [7]: the first, pertinent to all fluids, is due to capillary waves. The second part is an orientational entropy ΔS_{or} determined by surface layering. As we discussed in [1], the variation of the entropy should have a minimum in the surface zone because the surface atoms are more ordered than atoms in the bulk. This would require $\Delta S_{or} < 0$, as shown schematically in [1]. There might be an orientational contribution to ΔS due to ordering in the surface plane. This ordering, which would appear in the form of a hexatic monolayer on an isotropic liquid substrate, is responsible for a change in sign of the temperature derivative of the surface tension of normal alkanes and some liquid crystals [7, 8]. For liquid metals, in-plane surface order has never been reported in experiments; only atomic ordering along the surface normal was detected [4, 5]. Also, from theory, this hexatic layer on a pure liquid metal is not to be expected: for the formation of the Wigner lattice one needs a very low electron density [10]. We show below that the impact of surface layering on ΔS is naturally linked to the surface anisotropic stresses and the dipole layer.

According to Frenkel's analysis, the surface excess entropy is [9]

$$\Delta S = n_s k_B \ln \frac{\bar{\omega}_p}{\bar{\omega}_c} \tag{3}$$

where n_s is the number of atoms per unit area, $\bar{\omega}$ is the mean frequency of capillary waves, defined as

$$\bar{\omega}_c = \frac{1}{n_s} \int_0^{q_{max}} dq\ \omega(q) 2\pi q$$

and $\bar{\omega}_p$ is the mean frequency of bulk phonons. ΔS is governed by the ratio of two mean frequencies, surface and bulk, and is positive because $\bar{\omega}_p > \bar{\omega}_c$. In order to calculate $\bar{\omega}_c$, one should know the dispersion relation $\omega(q)$ for the whole q-range: from long wavelengths to the shortest-wavelength limit. It should be borne in mind that the well-known relation $\omega \sim q^{3/2}$ derived from a linear theory of capillary waves is valid only for long wavelengths, i.e. relatively small q. For high wavenumbers, giving the main contribution to $\bar{\omega}_s$, this relation is not valid any longer because linear theory fails at some q such that the wavelength of the wave is of the same order as the amplitude. Hence it is not possible to calculate the contribution of capillary waves to ΔS correctly, at least in the framework of a phenomenological approach.

Now we discover the impact of the anisotropic surface stresses due to the electrostatic force and electron gas pressure on the entropy that is specific to all metals. The contribution of the electric field to the surface free energy is $F_s \propto -\epsilon_0 E^2\ \delta z$, as discussed above. We suggest that the structure of the expression for the free energy, equation (2), of a metal surface given at 0 K is valid for $T \neq 0$, but the two terms in equation (2) are supposed to be temperature dependent. Thus the surface excess entropy should be affected by the electrostatic energy and the gradient of the electron density; both are specific solely to the surface zone and are zero for the bulk metal. The standard expression $S = -\partial F/\partial T$ yields for the entropy

$$\Delta S_{es} = -\frac{\partial}{\partial T} \int_{-\infty}^{\infty} dz \left(\chi_W \left[\frac{1}{\rho} \left(\frac{\partial \rho}{\partial z} \right)^2 \right] - \epsilon_0 E^2 \right)$$

$$= -\delta z \frac{\partial}{\partial T} \left[\frac{\chi_W}{\rho} \left(\frac{\partial \rho}{\partial z} \right)^2 \right] + 2\epsilon_0 |E|\ \delta z\ \frac{\partial E}{\partial T}. \tag{4}$$

Here we make an essential assumption: that the characteristic length scale δz of the surface zone remains unchanged as T varies whereas the squared density gradient and electric field

should vary. This is so because the spatial density of surface electrons varies rapidly on the scale $\sim k_F^{-1}$, as the Fermi wavelength k_F is T-independent. By contrast, the amplitude of the first peak in the electronic density $\rho(z)$ is temperature sensitive, at least over the T-range from 30 to 200 °C [15]. The experiment data of the Harvard group clearly show that the typical length scale of oscillations of the electron density is T-independent, which confirms our suggestion regarding the thickness of the surface zone which is given by the length scale of these oscillations. According to Samojlovich's analysis [12], we associate the appearance of this maximum with the strength of a surface electric field, which should decrease on heating as the layering amplitude does [11, 15]. Put in other way, the density of over-compressed surface atoms decreases due to a decrease in the density gradient and electrostatic pressure, whilst the thickness of the double layer is nearly constant. The sign of ΔS_{es} depends on the interplay between the two terms in equation (4), whose numerical amplitudes remain essentially unknown in the present study. Since $\partial E/\partial T$ is negative, ΔS_{es} may be negative too. Due to the opposite effects produced by the density gradient and the electric field, the amplitude of ΔS_{es} is expected to be small; hence $\partial \gamma/\partial T$ is mainly affected by capillary waves, especially at elevated T. However, the theory outlined indicates a possible negative sign of the surface excess entropy in liquid metals when ΔS_{es} prevails over the capillary-wave entropy ΔS_{cap}.

3. Experimental methods

Our light scattering technique is described in detail elsewhere [3, 14, 16]. In brief, a beam from a 7 mW He–Ne laser (TEM$_{00}$, $\lambda = 632$ nm) impinged on the liquid surface. Small-angle-scattered light was optically mixed (on a photodetector) with a portion of the original beam, providing all of the necessary conditions for optical heterodyning. The output of a photomultiplier was modulated at the propagation frequency of a capillary wave with the selected wavenumber q. The spectral representation of the signal was recorded in the frequency domain with a spectrum analyser. The whole apparatus was placed on an optical table, vibration isolation being provided by four pressurized air cylinders in the legs.

The liquid-Ga surface was prepared in a high-vacuum chamber (10^{-7} to 10^{-8} Torr) by dripping Ga from a glass cylinder terminating in a capillary of diameter less than 1 mm. Liquid Ga (purity 99.999%, Alfa) was dripped in vacuum into a Ti trough having a diameter of 50 mm. The low melting rate ensures that a thick film of oxide remains on the glass walls while pure metal flows through the capillary. Usually it takes some hours to complete the layer, with strong curvature near the walls and a flat area in the middle part. Though no visible traces of contamination on the liquid surface were detected by eye, the laser beam displayed a halo caused by scattering from a transparent oxide film which had flowed through the capillary despite all precautions. This continuous oxide film was fired with an Ar-ion sputter gun having a beam energy of 2 keV at 10^{-5} Torr pressure of argon. Although the ion beam hits an area smaller than the whole surface, the film particles flow along the gradient of surface tension to the beam footprint. Hence a self-cleaning mechanism due to Marangoni flow works on the liquid surface sputtered in vacuum. The footprint of the laser beam on the sputtered gallium surface was hardly visible, indicating the mirror finish and the absence of particles on the liquid surface (apart from an island of oxide particles sticking to the wall). Note that the experimental $\omega(T)$ dependencies reported below were obtained with the sputter gun on. Switching off the ion source caused an increase in the visibility of the laser beam footprint due to enhanced scattering from an oxide layer formed either due to oxidation by the residual gas or due to redistribution of oxide particles on the Ga surface.

Due to the very high surface tension and the lack of wetting by gallium of the container, a Ga layer, usually 6–8 mm thick in the middle, easily supports the propagation of vibrations

in the liquid sample. Although the whole chamber was placed on an optical table, mechanical disturbances from a turbo-molecular pump caused such strong vibrations of the liquid sample that no wave spectra could be measured. We tried to obtain wetting by liquid Ga of the container in order to reduce the liquid depth. Wetting can easily be achieved by heating the sample in vacuum above 500 °C. At this temperature, Ga spreads over the container surface and thin layers can be prepared. However, the container material is very likely to dissolve in gallium at high temperature, as follows from our experiments. To keep the liquid sample clean, one should try to achieve wetting at room temperature.

In general, liquid gallium dripped in vacuum wets a polished container wall in some places, but it spreads neither along the wall nor along the bottom. Therefore a Ga drop should be rolled along the walls until a ring of liquid is formed. Then the layer can be completed by shaking the liquid sample. After the layer is completed its form is determined by the attraction potential between the Ga and the walls; usually the surface profile is highly non-symmetric (along the azimuth) with concave and convex parts. In our experiments, only partial wetting could be achieved: places that were wetted had a strong meniscus along the wall, upwards; where no wetting took place the liquid edge was directed downwards. The Ga layer prepared in such a way was about 3 to 4 mm thick in the middle. Due to a reduction in the amplitude of the vibrations, the wave spectra could be collected for such samples; wetting helps to achieve shallow layers under tension.

Capillary waves scatter light mainly at small angles about the reflected beam. The spectrum of the scattered light is the power spectrum of the capillary waves, which is approximately Lorentzian [3]. The data were fitted with a theoretical function that incorporates the effects of instrumental broadening [17, 18]. The spread δq in the wavenumbers gives a corresponding broadening $\Delta\omega$ in the spectrum. For the Gaussian beam the instrumental function is also a Gaussian [17, 18]. The convolution of an ideal Lorentzian and the Gaussian instrumental function of width β yields [18]

$$P(\omega) = \int_{-\infty}^{\infty} \frac{(\Gamma/\beta)\exp[-(\omega - \omega')^2/\beta^2]}{\Gamma^2 + (\omega' - \omega_0)^2}\, d\omega'. \tag{5}$$

This integral can be evaluated in terms of a complementary error function with a complex argument [17, 19]:

$$S(\omega) = A\,\Re[\exp(-\{i\Gamma/\beta + (\omega - \omega_0)/\beta\}^2)\,\mathrm{erfc}(-i\{i\Gamma/\beta + (\omega - \omega_0)/\beta\})] + B \tag{6}$$

where A is the scaling amplitude and B the background. Thus, five properties were extracted from the fit of the experimental spectra: frequency ω_0, damping constant Γ, instrumental width β, amplitude A, and background B. In the present context, we concentrate just on the peak frequencies ω_0.

4. Results

The temperature behaviour of the peak frequencies ω_0 of the capillary waves at the free gallium surface is shown in figure 1. To first order, the roots of the dispersion relation describing the propagation of a capillary wave with a particular wavenumber q are [3]

$$\omega_0 = \sqrt{\gamma q^3/\rho} \tag{7}$$
$$\Gamma = 2\eta q^2/\rho \tag{8}$$

where γ, η, and ρ are the surface tension, bulk viscosity, and density, respectively. Equation (7) serves as a basis for evaluation of the tension. The data in figure 1 are fitted by assuming a
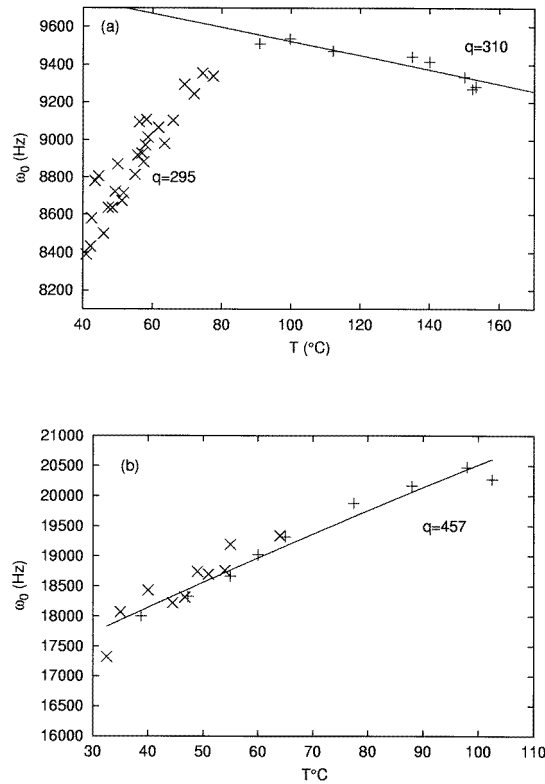
Figure 1. Temperature variations of the peak frequencies of the capillary waves of different wave-numbers given in each plot in cm^{-1} at the free surface of gallium. The errors in ω_0 are less than the size of the data points. The solid lines are the best-fit solutions to the form of equation (9). The experimental points in (b) were collected on heating (+) and cooling (×).

linear temperature dependence of the surface tension, $\gamma = \alpha(T - T_0) + \gamma_0$, where T_0 is the melting point:

$$\omega_0(T) = \sqrt{(\alpha(T - T_0) + \gamma_0)q^3/\rho}. \tag{9}$$

The best-fit estimate of the slope of the temperature dependence in the temperature interval from 100 °C to 160 °C is $\alpha = \mathrm{d}\gamma/\mathrm{d}T = -0.57 \pm 0.09$ mN m^{-1} K^{-1}. The best estimate of γ_0 corresponding to the tension at the melting point (30 °C) is $\gamma_0 = 766 \pm 17$ mN m^{-1}.

In the temperature range from 30 to 100 °C the temperature dependence is anomalous, and the best estimate of the slope is $\alpha = 4.18 \pm 0.2$ mN m^{-1} K^{-1} and the tension at the melting point is $\gamma_0 = 690 \pm 6$ mN m^{-1}. The two data sets, at temperatures above 100 °C and below, were collected for the same sample but at two different values of q (295 and 310 cm^{-1}); this was dictated by the necessity of optical adjustment of the reference beam. Theoretically, there is no limitation for a negative slope (at T far away from the critical point) but there is one for a positive α. The point is that a negative excess entropy indicates that the entropy density at the surface is less than that in the bulk. We do not know how much this density changes; however, we can estimate a maximum variation of the entropy, whose spatial profile cannot fall below zero in the surface zone (for a graphical interpretation, see [1]). For liquid Ga at 303 K we find the bulk entropy per mole $S = 9.82 + 4.4 = 14.2$ cal mol^{-1} K^{-1} [20]. Then the entropy

density is $S_b = S\rho/M_{Ga} = 59.7 \times 6.1/69.7 = 5\,\text{MJ}\,\text{m}^{-3}\,\text{K}^{-1}$, where M_{Ga} is the molar weight of Ga. In order to obtain the surface entropy density, this value should by multiplied by the thickness of the surface zone: $(S_s)_{max} = S_b\,\delta z = 5 \times 10^6 \times 10 \times 10^{-10} = 5\,\text{mJ}\,\text{m}^{-2}\,\text{K}^{-1}$, where $\delta z \sim 10\,\text{Å}$ was suggested to be the characteristic length scale of the oscillations of the atomic density [4]. This value confirms that the variations of the entropy occur in a relatively thick surface zone of about 10 Å, indicating that the electrostatic interactions penetrate deeper than the topmost atomic layer. $\alpha = 4.18\,\text{mN}\,\text{m}^{-1}\,\text{K}^{-1}$ extracted from experimental data at $q = 295\,\text{cm}^{-1}$ is in accord with $\alpha = 3.87\,\text{mN}\,\text{m}^{-1}\,\text{K}^{-1}$ obtained from peak frequencies at $456\,\text{cm}^{-1}$ for the surface of another sample (figure 1(b)), demonstrating that the increase in surface tension on heating is real and not due to vibration-induced changes in ω. The damping constants inferred from the fit were strongly influenced by vibrations: the dispersions of Γ were up to 100 per cent of the mean values. Therefore no quantitative predictions of the magnitude and the temperature behaviour of Γ could be made in the present experiment.

The $\gamma(T)$ behaviour can be discussed now. The effect of capillary waves on ΔS is positive and ΔS_{cap} is very probably T-independent. On the other hand, ΔS_{es} becomes negative according to equation (4) when the condition

$$\epsilon_0 E\left|\frac{\partial E}{\partial T}\right| > \chi_W \frac{\partial}{\partial T}\left[\frac{1}{\rho}\left(\frac{\partial\rho}{\partial z}\right)^2\right]$$

is fulfilled. This means that both the density gradient and the electric field decrease on heating (because a proportion of the surface electrons are injected into the bulk), setting up $\partial\gamma/\partial T < 0$ until $|\Delta S_{el}| > \Delta S_{cap}$ becomes valid. Of course, this mechanism drives the magnitude of ΔS until the Fermi distribution of electrons becomes T-independent; for metals it is valid up to 1000 K.

The light scattering experiment does not directly yield the surface tension; only the peak frequency is directly measurable. In order to obtain additional information on the sign of $\partial\gamma/\partial T$, the following experiment was carried out. A temperature gradient imposed along the sample causes a liquid-metal flow (usually called thermocapillary convection) driven by the gradient of the surface tension. The surface tension gradient is indirectly related to the liquid velocity v_x via the boundary condition for the tangential stress at the free surface [21]:

$$\frac{\partial\gamma}{\partial T}\,\nabla T = \eta\frac{\partial v_x}{\partial z}. \tag{10}$$

The direction of flow on the liquid surface is expected to be from hot to cold if the temperature derivative of the tension is negative. In the opposite case, the surface flow should be directed toward the hot end. Gallium was solidified and transferred to another vacuum enclosure having better conditions for creating a temperature gradient along the water-cooled flange. This chamber was not an UHV one: only a vacuum of about 5×10^{-6} Torr could be achieved.

After sputtering the liquid surface, we observed the surface flow to be always directed from the cold to the hot end in the middle of the surface. The flow was visible by means of light scattered from the beam footprint on the surface. Due to the extremely small scattering cross-section, such observations are only possible when oxide particles occasionally flow through the beam footprint. This explains why γ *increases* with T in the temperature range 15 to 35 °C. Further heating caused deterioration of the vacuum, with the subsequent oxidation of the sample and quick suppression of the convective flow. Thermocapillary convection usually couples to buoyancy convection; therefore this reverse direction of the surface flow was observed only on shallow liquid samples. For deeper layers, buoyancy convection takes over and surface flow is directed from hot to cold regardless of the temperature behaviour of the tension.

To summarize, we studied the free Ga surface using light scattering from capillary waves. The peak frequency of the waves exhibits a temperature-dependent behaviour $\omega(T)$ that corresponds to an increase in surface tension up to 100 °C and a decrease in γ upon heating to 160 °C. This phenomenon clearly indicates that the surface excess entropy switches from negative to positive at a temperature near 100 °C. The present study shows a clear difference in the temperature behaviour of the tension between liquid gallium and mercury. $\partial\gamma/\partial T$ for mercury, studied with the light scattering technique, is continuously negative in the T-range from 0 to 100 °C; this is probably due to a stronger effect of capillary waves on the surface excess entropy in mercury compared to the same contribution for liquid gallium.

Acknowledgment

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