

## TEMPERATURE DEPENDENCE OF SURFACE TENSION AND CAPILLARY WAVES AT LIQUID METAL SURFACES

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The temperature dependence of the surface tension  $\gamma(T)$  is treated theoretically and experimentally. The theoretical model based on the Gibbs thermodynamics of a one-component fluid relates  $\partial\gamma/\partial T$  to the surface excess entropy density  $-\Delta S$ . All specific surface effects, namely ordering, capillary waves, and double layer influence the surface entropy, which in turn governs the sign and the magnitude of  $\partial\gamma/\partial T$ . Experimental data collected at a free Hg surface in the temperature range from 0° C to 30° C show that  $\partial\gamma/\partial T$  is negative.

### 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 forces influencing this dependence in liquid metals.

Our previous work [1] was concerned with the surface tension of mercury as a function of temperature, which was studied using quasielastic light scattering from capillary waves [2]. 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 highly ordered metal structure perpendicular to the surface which is about a few atomic diameters thick [3, 4]. 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. If this were the case then the surface excess entropy  $\Delta S$  defined by

$$\Delta S = \int_{-\infty}^{\infty} dz [S(z) - S_b\theta(z)] \quad (1)$$

would be negative [1]. Here  $\theta(z) = 0$  for  $z > 0$  and  $\theta(z) = 1$  for  $z \leq 0$ ;  $z = 0$  denotes the surface position and the integration is performed from the liquid bulk ( $z = -\infty$ ) to a vapor phase ( $z = \infty$ ). Insofar as the surface tension derivative of a one-component liquid is related to  $\Delta S$  by [5, 6]

$$\Delta S = -\partial\gamma/\partial T, \quad (2)$$

the temperature dependence is expected to be an increasing function of  $T$ , as demonstrated at surfaces of normal alkanes over a certain  $T$  range [7]. However, the experimental data

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collected at a Hg-vapor interface contradict this expectation. In order to reconcile experiment and theory, we suggested that a liquid metal surface is a two-component system comprising quasi-free surface electrons and positive ions. In this case  $\partial\gamma/\partial T$  is not given by Eq. (2) but depends on the chemical potential of electrons as well [1]. However, the ionic and electronic profiles of any complicated shape should be approximated by the same right-angled profile in order to preserve the electrical neutrality of 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. It will be shown that the effect of surface ordering is not a single contribution on the surface entropy. Other specific surface effects opposing layering tend to increase the entropy of the interface.

## 2. THEORETICAL ANALYSIS

As noted in Ref. [6] the interface thickness of van der Waals liquids is determined by thermal fluctuations, which take the form of thermally excited capillary waves. The r.m.s. amplitude of these waves is usually slightly greater than an atomic diameter [2]. One would thus expect the interface thickness at zero temperature to vanish, and the density profile to be a discontinuous step function dropping from the bulk density  $\rho_b$  to zero. In such a situation it is natural to suppose that the location of the Gibbs surface coincides with the step profile at 0 K. The real surface profile varies with  $T$  in such a way that the surface excess density given by

$$\Gamma_s = \int_{-\infty}^{\infty} dz [\rho(z) - \theta(z)\rho_b] \quad (3)$$

remains zero for all  $T$ .

Consider now a liquid metal comprising two components: free electrons and positive ions. Free electrons behave as a quantum medium: even at zero temperature their energy is nonzero, and is usually written in terms of the Fermi energy  $E_f$ :  $E = E_f N$ , where  $N$  is the number of electrons. It is instructive to consider the profiles of both components, electronic and ionic, at  $T = 0$ . Due to nonzero wavelength the electronic density profile has a nonzero width, which leads to some redistribution of electrons between bulk and the surface. In other words, some electrons are ejected from the bulk and concentrate on the vapor side of the interface. This charge separation leads to a surface double layer with an electric field  $E = Q_s/\epsilon_0$ , where  $Q_s$  is the surface charge density and  $\epsilon_0$  is the dielectric constant. The existence of such a double layer, suggested by Frenkel [8], leads to significant changes in the surface interactions. We consider first the conditions that must be satisfied even in the presence of charge separation. The first is electrical neutrality: the total electric charge of a metal must be zero,

$$\int_{-\infty}^{\infty} dz [\rho_i(z) - \rho_e(z)] = 0, \quad (4)$$

where  $\rho_i$  and  $\rho_e$  are the ionic and electronic densities.

The second quantity that must be taken into account is the surface excess density. In general this quantity is a relative one; it depends on the choice of the Gibbs surface. If this

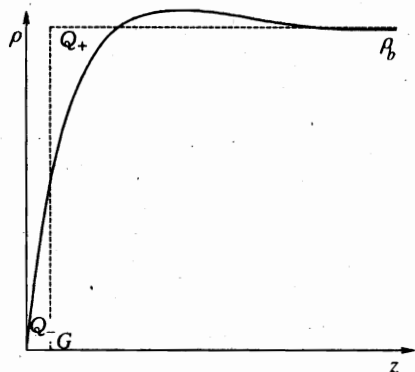


Fig. 1. Schematic variations of the electron density (solid line) and positive ionic jellium represented as a step function which coincides with the Gibbs surface, denoted by  $G$ . Friedel oscillations of small amplitude are shown in the electron density profile. Surface double layer comprises a negative electrode formed by the area to the left to the step function (labeled with  $Q_-$ ) and a positive electrode formed by the area to the right of  $G$  labeled with  $Q_+$ .

surface coincides with the step ionic profile, the surface excess mass density of electrons can be written via Eq. (3):

$$\Gamma_e = \int_{-\infty}^{\infty} dz [\rho_e(z) - \theta(z)\rho_b].$$

From a comparison with Eq. (4) it is clear that  $\Gamma_e = 0$  in our choice of Gibbs surface.

We concentrate first on changes in the electronic density with  $T$  dictated by the surface concentration of electrons in the double layer. This concentration is temperature dependent, although this dependence can be different from the temperature dependence of the bulk electron concentration. This means that the area under the tail on the vapor side (to the left of the Gibbs surface) would vary with  $T$  (see Fig. 1). If we anticipate that the positive ions do not follow these changes, then the ionic profile will have a shorter tail but a higher amplitude in order to satisfy Eq. (4). However, an ionic density profile of any complicated shape is approximated by a step function that drops from  $\rho_b$  to zero at some  $z$ . If this step function deviates from the step function that approximates the electronic distribution, electrical neutrality of the metal as a whole will be violated. Although the electronic and ionic profiles do not necessarily coincide, they can be approximated by the same right-angled profile as the Gibbs surface in Fig. 1. We have shown that the surface excess density of a metal surface should be zero, according to Eqs. (4) and (3).

Unfortunately, no theory describing the surface tension of liquid metals is well established. Numerical simulations of the electronic and ionic density profiles [9] do not provide clear insight into the different forces acting in the surface zone. Only one paper, to the author's knowledge, treats this problem analytically [10]. Due to its importance for the present context we repeat the main results of this paper.

The electronic density  $\rho_e$  at a metal surface varies upon an ionic jellium that approximates the real profile of the ionic density. Following the ideas of Kirkwood and Buff-Bakker (see Ref. [6] for example), the surface tension of any liquid can be expressed via the tensor of anisotropic stresses ( $\Pi_{\parallel} \neq \Pi_{\perp}$ ) and results from the density gradient in the surface zone:

$$\gamma = \int_{-\infty}^{\infty} dz (\Pi_{\perp} - \Pi_{\parallel}), \quad (5)$$

where integration is taken from  $-\infty$  to  $\infty$  in order to take into account the effect of free electrons on the vapor side of the interface. The forces acting at the surface at 0 K are nothing more than the quantum pressure of the electron gas and electrostatic force stemming from the potential drop in the double layer. A detailed analysis done by Samojlovich ensures that the long-range electrostatic force  $-\rho_e \nabla \phi$  leads to Maxwellian elastic stresses  $\Pi_{zz} = -\Pi_{xx} = \epsilon_0 E^2/2$  that deform the ionic fluid. This deformation is impossible for the rigid ionic continuum suggested by the jellium model. Therefore some external pressure  $P = \epsilon_0 E^2/2$  must be introduced in order to provide the equilibrium of the whole system. This isotropic pressure acting on the topmost layer makes the ions there over-compressed compared to the ions in the bulk. These considerations confirm some increase of the ionic density in the surface layer, which was demonstrated recently on the surface of liquid gallium and mercury. Unfortunately, this conclusion was not drawn by Samojlovich, who used a simple monotonic profile to calculate the surface tension. However, his analysis helps to understand surface layering, which is closely related to electrostatic pressure due to a surface double layer.

The temperature behavior of the surface tension of a liquid metal is a most intriguing question. While the tension changes only by a few percent over 100 K, the temperature derivative  $\partial\gamma/\partial T$  is extremely sensitive to the density profile. Here Eq. (2) is considered to be a basic thermodynamic equation relating the temperature derivative  $\partial\gamma/\partial T$  to the surface excess entropy. It is plausible to suppose that the surface excess entropy comprises different parts [6]: the first is responsible for surface ordering, and the second is pertinent to all fluids, due to capillary waves. The third part is determined by the electric field in the double layer.

We first concentrate on the orientational part. The recent discovery of surface layering in liquid gallium and mercury shows that surface atoms are more ordered than bulk atoms (along the surface normal) [3, 4]. Hence the orientational part of the entropy in the surface zone might be less than that part of the bulk entropy if the surface atoms exhibit long-range order in the surface plane. Only order along the surface normal was reported at the Hg surface; in-plane surface order has not been confirmed experimentally [3, 4]. Therefore we cannot make any definitive predictions about the orientational part of the entropy in the surface zone.

As we already noted, the surface excess entropy should split into different parts; the orientational part describing the effect of surface layering remains beyond our simplified approach. The other surface effect that can be treated quantitatively is the effect of capillary waves. Following Frenkel's ideas, the surface free energy due to thermal motion in the form of capillary waves is given by [8]

$$F_s = F_{s0} - n_s k_B T \ln \frac{k_B T}{\hbar \bar{\omega}_c}, \quad (6)$$

where  $n_s$  is the number of atoms per unit area,  $F_{s0}$  is the surface free energy at 0 K, and  $\hbar$  is Planck's constant;  $\bar{\omega}_c$  is the mean frequency of capillary waves, defined as

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

Using the usual thermodynamic relation  $S = -\partial F/\partial T$ , we find the part of the surface entropy associated with capillary waves [8]

$$S_{cap} = n_s k_B \ln \frac{k_B T}{\hbar \bar{\omega}_c}. \quad (7)$$

The surface excess entropy density is given by the difference between the densities at the surface  $S_s$  and in the bulk  $S_b$ :  $\Delta S \simeq [S(z) - S_b] \delta z$ . The part of the bulk entropy associated with thermal motion is defined by the number of modes of sound waves (or phonons) propagating in the bulk at any  $T \neq 0$ :

$$S_b = n_b k_B \ln \frac{k_B T}{\hbar \bar{\omega}_p},$$

where  $\bar{\omega}_p$  is the mean frequency of bulk phonons [5]. Combining the last two equations, we obtain for the surface excess entropy

$$\Delta S = n_s k_B \ln \frac{\bar{\omega}_p}{\bar{\omega}_c}. \quad (8)$$

We see that  $\Delta S$  is governed by the ratio of two mean frequencies surface and bulk.

This theory can be applied only to relatively long surface waves whose frequencies are much less than the inverse relaxation time  $\tau_0$  typical of each liquid [8]. If the frequency of capillary waves is such that  $\omega \geq 1/\tau_0$ , then vibrations in the liquid propagate as in a solid body. Hence capillary waves should be replaced by Rayleigh surface waves, which propagate at the surface of a liquid or solid body with a velocity  $u_s = 0.9\sqrt{G/\rho}$ , where  $G$  is the shear modulus and  $\rho$  is the density. The high-frequency part (with  $\omega \geq 1/\tau$ ) makes the main contribution to the spectrum of surface waves [8]. Therefore the question of the number of modes at the liquid surface reduces to a calculation of these modes at a solid surface. The situation is complicated by the influence of surface waves on the bulk modes [8]. A thorough analysis by Frenkel shows that the surface excess entropy is

$$\Delta S_s = \frac{3}{4} \left( \frac{3\pi}{2} \right)^{1/3} \frac{k_B n_s}{(u_l/u_t)^2 \left[ (2 + \sqrt{G/Y})^{2/3} \right]}, \quad (9)$$

where  $Y$  is Young's modulus and  $u_l$  and  $u_t$  are the velocities of longitudinal and transverse sound waves, respectively. The surface tension derivative evaluated using this model is negative, and is in good agreement with the tabulated  $\partial\gamma/\partial T$  for mercury.

The second mechanism contributing to the surface excess entropy is the electric field in the surface double layer. The impact of this field on the surface free energy is given by  $F_s \propto \epsilon_0 E^2 \delta z$ . However this term appears in the free surface energy with a negative sign, due to the specific distribution of electric stresses in the double layer. As we discussed above, the effect of electric fields is expressed via the Maxwell stress tensor  $S_{ij}$ , with components  $-S_{zz} = S_{xx} = \epsilon_0 E^2/2$ . The change in the surface free energy due to the electric field is [8]

$$F = \int_0^\infty dz (S_{zz} - S_{xx}) = - \int_0^\infty dz \epsilon_0 E^2. \quad (10)$$

It is clear that the surface excess entropy should have a term stemming from electrostatic energy that is specific solely to the surface zone and is zero in the bulk metal. The standard expression  $S = -\partial F/\partial T$  yields for the entropy

$$\Delta S_{el} = \epsilon_0 E^2 \frac{\partial \delta z}{\partial T}, \quad (11)$$

where the derivative is taken at constant surface charge  $Q_s$ . This electric part of the surface excess entropy is positive, as the thickness of the surface zone increases with  $T$ . To the author's knowledge, no analytical predictions exist about the temperature dependence of the intrinsic length scale for the surface electrostatic interactions in liquid metals. Therefore the amplitude of capillary waves will be used as an approximate width of the interface. The r.m.s value of the interface thickness can be found from the theory of capillary waves [2]:

$$\delta z = \sqrt{\frac{k_B T}{2\pi\gamma} \ln \frac{q_{min}}{q_{max}}}. \quad (12)$$

The upper cutoff of capillary waves can be estimated in terms of a molecular size  $a$ :  $q_{max} = 1/a$ . The minimum wavenumber is usually related to the capillary length:  $l_c = \sqrt{\gamma/(\rho g)}$ . Bearing this in mind, the part of the surface excess entropy due to the double layer can be written

$$\Delta S = \frac{1}{2} \epsilon_0 \left( \frac{\phi}{\delta z} \right)^2 \sqrt{\frac{k_B}{2\pi\gamma T} \ln \frac{l_c}{1/a}}. \quad (13)$$

Simple estimates based on the values  $\delta z \sim 1 \text{ \AA}$  and  $\phi \sim 1 \text{ V}$ ,  $\epsilon_0 = 10^{-11} Q^2/(N \text{ m}^2)$ ,  $l_c \sim 1 \text{ mm}$  yield  $\Delta S = 10^{-4} \sqrt{\ln(10^{-3}/10^{-10})} = 0.4 \text{ mN}/(\text{m}\cdot\text{K})$ . Note that Eq. (13) describes a nonlinear dependence of  $\Delta S(T)$  and consequently of  $\partial\gamma/\partial T(T)$ . It should be stressed that near 0 K the interface thickness in Eq. (11) cannot be given by the r.m.s. amplitude of capillary waves but is equal to the wavelength of quasi-free surface electrons possessing the Fermi energy. Our Eq. (13) does not contain a term  $\propto (k_B T/E_f)^2$  typical of the  $T$ -dependence of the energy of a free electron fluid. This is possibly due to our phenomenological approach to the electric field of the double layer.

These estimates are based on the assumption that capillary waves survive up to the upper cutoff of  $q$ , i.e., on an atomic scale. From the discussion above we know that at higher frequencies liquid surfaces are similar to solid ones, so capillary waves must be replaced by Rayleigh waves propagating along the surface without dispersion. The surface elastic energy per unit area associated with this mode is

$$F_s = \int_0^\infty dz \frac{1}{2} G (\nabla_s u)^2, \quad (14)$$

where  $G$  is the elastic (or shear modulus),  $u$  is the displacement and  $\nabla_s$  is the differential operator in the surface plane. Then the squared wave amplitude in the  $q$ -domain can be written analogously to that of capillary waves [2],

$$\langle \chi_q \rangle^2 = \frac{k_B T}{A G_s q^2}, \quad (15)$$

where  $A$  is the surface area. In order to calculate the r.m.s. displacement of the surface using Eq. (12) one should replace  $\gamma$  with the shear modulus  $G_s$  whose magnitude can be estimated using data on the bulk modulus:  $G_s \approx G_b \delta z = 10^{11} \cdot 10^{-8} = 10^3 \text{ dyn/cm}$ . The surface excess entropy density of the Hg surface calculated using Eqs. (15) and (11) is 0.7 times lower than  $\Delta S$  estimated from Eq. (12).

### 3. EXPERIMENTAL METHODS

A liquid mercury surface was prepared by distillation in vacuum (about  $10^{-4}$  Torr) from a batch of 10 ml Hg (99.998%, Merck). The quartz glass distillation apparatus consisted of a compartment filled with Hg in the open air and a condenser (water cooled) connected by a U-tube to a stainless steel capillary mounted in the wall of the working chamber. The chamber had a vacuum flange and an optical window for laser access. Mercury dropped through the capillary to the working chamber and formed a layer about 2 mm deep. The working trough was rectangular with dimensions of  $60 \times 60$  mm<sup>2</sup>, and was machined from stainless steel. Prior to the experiment, the working trough and capillary were cleaned with chromic acid and carefully rinsed in double-distilled water. Distillation was carried out at 200°C and about 2 hours were necessary to complete the continuous layer. While no efforts were made to achieve wetting, the Hg surface was relatively flat, as confirmed by the minimal divergence of a reflected beam. Heating or cooling was carried out from below through a copper plate. This plate was heated with a resistive heater or cooled using liquid nitrogen. The temperature was measured with a thermocouple glued to the thin bottom of the working chamber.

Our light scattering technique is described in detail elsewhere [2, 11, 12]. In brief, a beam from a 5 mW He-Ne laser (TEM<sub>00</sub>,  $\lambda = 632$  nm) fell on the liquid surface. Small-angle scattered light was optically mixed (on a photodetector) with a portion of the original beam, providing all the necessary conditions for optical heterodyning. The output of an avalanche photodiode 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 analyzer. The whole apparatus was placed on an optical table, vibration isolation being provided by four pressurized air cylinders in the legs.

Capillary waves, present on all liquid surfaces up to the critical point, scatter light mainly at small angles about the reflected beam. The spectrum of the scattered light is the power spectrum of capillary waves, which is approximately Lorentzian [2]. The data were fitted with a theoretical function that incorporates the effects of instrumental broadening [13, 14]. The latter arises from illumination of the detector by light scattered by more than one wave-vector  $q$  on the surface. The spread  $\delta q$  in the wave numbers gives a corresponding broadening  $\Delta\omega$  in the spectrum. For the Gaussian beam the instrumental function is also a Gaussian [13, 14]. The convolution of an ideal Lorentzian and the Gaussian instrumental function of width  $\beta$  yields [14]

$$P(\omega) = \int_{-\infty}^{\infty} \frac{(\Gamma/\beta) \exp[-(\omega - \omega')^2/\beta^2]}{\Gamma^2 + (\omega' - \omega_0)^2} d\omega'. \quad (16)$$

This integral can be evaluated in terms of the complementary error function of the complex argument [13, 15]:

$$S(\omega) = A \operatorname{Re} \left\{ \exp \left[ - \left( \frac{i\Gamma}{\beta} + \frac{\omega - \omega_0}{\beta} \right)^2 \right] \operatorname{erfc} \left[ -i \left( \frac{i\Gamma}{\beta} + \frac{\omega - \omega_0}{\beta} \right) \right] \right\} + B, \quad (17)$$

where  $A$  is the scaling amplitude and  $B$  the background. Thus, five properties were extracted from the fit of experimental spectra: frequency  $\omega_0$ , damping constant  $\Gamma$ , instrumental width  $\beta$ , amplitude  $A$ , and background  $B$ . In the present context we concentrate only on peak frequencies  $\omega_0$ .

4. RESULTS

The temperature behavior of peak frequencies  $\omega_0$  of capillary waves at the free Hg surface is shown in Fig. 2. To first order, the roots of the dispersion relation describing the propagation of a capillary wave with a particular wavenumber  $q$  are [2]

$$\omega_0 = \sqrt{\gamma_0 q^3 / \rho}, \tag{18}$$

$$\Gamma = 2\eta q^2 / \rho, \tag{19}$$

where  $\gamma_0$ ,  $\eta$ , and  $\rho$  are the surface tension, bulk viscosity, and density, respectively. Equation (18) serves as a good basis for evaluation of the tension. The data in Fig. 2 are fit by assuming a linear temperature dependence of the surface tension,  $\gamma_0 = C_1(T - T_0) + C_2$ , where  $T_0$  is the melting point:

$$\omega_0(T) = \sqrt{[C_1(T - T_0) + C_2] q^3 / \rho}. \tag{20}$$

The best-fit estimate of the slope  $C_1$  of the temperature dependence is:  $d\gamma/dT = C_1 = -0.27 \pm \pm 0.07$  mN/(m·K). The best estimate of  $C_2$  corresponding to the tension at the melting point ( $-39^\circ\text{C}$ ) is  $C_2 = 526 \pm 7$  mN/m, which is slightly greater than the tension (497 mN/m) extrapolated to the melting point using the tabulated slope  $d\gamma/dT = -0.2$  mN/(m·K) [16, 17].

The light scattering experiment does not directly yields 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 was imposed along the bottom of our cell. In this case a liquid metal flow (usually called thermocapillary convection) driven by the gradient of the surface tension is expected. The surface tension gradient is indirectly related to the liquid velocity  $v_x$  via the boundary condition at the free surface, which for the tangential stress is [18]:

$$\frac{\partial\gamma}{\partial T} \nabla T = \eta \frac{\partial v_x}{\partial z}. \tag{21}$$

Thermocapillary convection usually couples to buoyancy-driven convection. However, thermocapillary flow dominates buoyancy convection for a 2-mm deep Hg layer (see Ref. [1]). 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. The flow was made visible by means of light scattered from the beam footprint on the surface. We observed the surface flow always to be directed from hot to cold in the middle of the trough, with a characteristic velocity of a few mm/s, which ensures a decreasing dependence  $\gamma(T)$ .

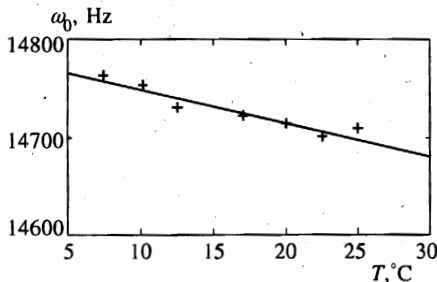


Fig. 2. Temperature variations of peak frequencies of capillary waves of wave number  $q = 619 \text{ cm}^{-1}$  at the free surface of mercury. The errors in  $\omega_0$  are less than the size of the data points. The solid line is the best-fit solution in the form of Eq. (20)



## 5. CONCLUSIONS

Surface light scattering from a free mercury surface exhibits the temperature-dependent behavior  $\omega(T)$  that corresponds to a decrease in surface tension upon heating. This phenomenon clearly indicates that the surface excess entropy is positive, as it should be in a one-component fluid. The present theoretical treatment ensures that a liquid metal surface is a one-component substance, despite its comprising two components: positive ions and delocalized free electrons. The surface excess entropy  $\Delta S$  splits into three parts, describing surface layering, capillary waves, and a surface double layer. Since the capillary waves contribution is proportional to  $k_B T$ , it is expected that this effect is smallest near the melting point. Since surface layering is most pronounced there,  $\Delta S$  might become negative in some  $T$ -range. Unfortunately, it is not possible to estimate the contribution of surface layering to  $\Delta S$  in the framework of our simple model. However, we hope that surface light scattering is sensitive enough to detect a possible change in the temperature dependence of the surface tension.

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