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Temperature-dependent behaviour of capillary waves at Hg–vapour and Hg–HgO interfaces

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Abstract. Free and oxidized surfaces of liquid mercury have been studied by means of light scattering from thermally excited capillary waves. The temperature dependence of the wave peak frequency at the free Hg surface reveals a negative derivative of the surface tension $d\gamma/dT$. This phenomenon is related to the spatial distribution of quasi-free electrons being much more strongly temperature dependent than the local surface ordering recently revealed at the Hg–vapour interface. The frequency $\omega(T)$ observed at the Hg–HgO interface displayed two essentially different tendencies, according to the thickness of the oxide film.

1. Introduction

Oxidation of liquid metal surfaces is an important phenomenon for many technical applications, such as in metallurgy, and crystal growth. However, little work has been done with the aim of explaining the basic surface properties of the liquid metal–oxide interface.

Our previous work [1] was concerned with the surface tension of mercury as a function of temperature, studied using quasielastic light scattering from capillary waves [2]. Extreme precautions were taken against the oxidation of the liquid surface: the liquid surface was prepared in a small chamber which was evacuated down to 10^{-2} Torr and then pressurized with an Ar/H₂ mixture. Then mercury was dropped from the upper compartment, terminating in a capillary leading to the working trough. The main result of that study was that the temperature dependence of the peak frequency of the waves $\omega(T)$ was steadily *increasing* over the whole accessible temperature range. The surface tension was evaluated from the peak frequency of the waves using the first-order solution of the dispersion equation [3]. It was assumed that the temperature derivative of the tension is just the surface excess entropy density, as it usually is for one-component systems [4]. We expected that the surface ordering recently discovered for liquid gallium and mercury [5, 6] would turn out to be the reason for the positive slope of $d\gamma/dT$.

However, it was erroneously suggested that the mercury surface was oxide-free. The present study demonstrates that this is not the case, and much more stringent conditions have to be met to prepare a surface which is really oxide-free. The present paper concentrates upon two parallel studies: that of the free Hg surface obtained under high vacuum (about 10^{-6} Torr), and that of oxidized surfaces prepared at higher residual pressure (from 10^{-2} to 10^{-1} Torr). We will show that for the free Hg surface the temperature dependence of the wave frequency $\omega(T)$ decreases on heating. In contrast, the dependence $\omega(T)$ detected for oxidized samples reveals different characters according to the thickness of the oxide film.

2. Experimental methods

The liquid mercury surface was prepared by distillation in vacuum (about 10^{-6} Torr) from a batch of 10 ml of Hg (99.998%, Merck). The distillation apparatus, made from quartz glass, comprised a compartment filled with Hg in the open air, and a condenser (water cooled) connected via a polyethylene U-tube to the stainless steel capillary mounted in the wall of the working chamber. The chamber had a vacuum flange, and an optical window for the laser access. Mercury dropped through the capillary to the working chamber, and formed a layer of about 2 mm depth. The working trough had a rectangular form with dimensions of 60×60 mm, 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. The distillation was carried out at a temperature of 200 °C, and about two hours was 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 the reflected beam.

Heating or cooling was carried out from below, through a copper plate. This plate can be heated with a resistive heater or cooled using liquid nitrogen. The temperature was measured with a thermocouple (diameter: 0.2 mm) glued to the thin bottom of the working chamber.

The free mercury surface was oxidized by increasing the residual pressure during the distillation, so oxide layers of various thicknesses could be obtained. In nearly all cases, the liquid surface was mirror reflecting, without any visible traces of contamination except for in the case of a rough HgO film of macroscopic thickness. A laser beam reflected from such a surface displays a halo, caused by scattering from the roughness of the oxidized surface.

The light scattering technique was described in detail elsewhere [2, 7, 8]; in brief, a beam from a 5 mW He–Ne laser (TEM_{00} , $\lambda = 632$ 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 of the necessary conditions for optical heterodyning [9]. The output of an avalanche photodiode was modulated at a frequency pertinent to the propagation frequency of a capillary wave with the selected wave-vector q . The spectral representation of the signal was registered in the frequency domain with a spectrum analyser. The whole apparatus was placed on an optical table, vibration isolation being supplied by four air-pressurized cylinders mounted into the legs.

Capillary waves, present on all liquid surfaces up to the critical point, scatter light mainly at small angles around the reflected beam. The spectrum of the scattered light is the power spectrum of the capillary waves, which is approximately Lorentzian in shape [2]. The data were fitted with a theoretical function including the effects of instrumental broadening [11, 12]. This arises from the illumination of the detector by light scattered by more than one wave-vector q on the surface. The spread δq in the wavenumbers gives a corresponding broadening $\Delta\omega$ in the spectrum. For the beam having a Gaussian profile, the instrumental function is a Gaussian [11, 12]. A convolution of an ideal spectrum having the Lorentzian shape and the Gaussian instrumental function of width β gives the form [12]

$$P(\omega) = \int_{-\infty}^{\infty} \frac{(\Gamma/\beta) \exp[-(\omega - \omega')^2/\beta^2]}{\Gamma^2 + (\omega' - \omega_0)^2} d\omega'. \quad (1)$$

This integral can be solved in terms of a complementary error function of complex argument [11, 13]:

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

where A is the scaling amplitude and B the background. Thus five properties were extracted from the fit of the experimental spectra: the frequency ω_0 , the damping constant Γ , the instrumental width β , the amplitude A , and the background B . Note that neglecting the instrumental term leads to significant overestimation of the damping constant Γ .

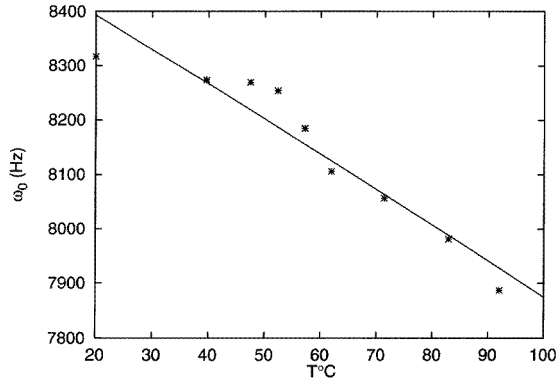


Figure 1. Temperature variations of the peak frequencies of the capillary waves of wavenumber $q = 423.8 \text{ cm}^{-1}$ at the free surface of mercury. The errors in ω_0 are less than the size of the data points. The solid line is the best-fit solution to the form of equation (5).

3. Results

The mercury surface prepared at a residual pressure of about 10^{-6} Torr will be considered here as the free surface. The temperature behaviour of the peak frequencies ω_0 of the capillary waves at the free Hg surface is shown in figure 1. In the first-order approximation, the roots of the dispersion equation describing the propagation of a capillary wave with a particular wavenumber q are given by [3]

$$\omega_0 = \sqrt{\gamma_0 q^3 / \rho} \quad (3)$$

$$\Gamma = 2\eta q^2 / \rho \quad (4)$$

where γ_0 , η , and ρ are the surface tension, the bulk viscosity, and the density, respectively. Equation (3) serves as a good basis for evaluation of the tension. The data in figure 1 are fitted with a function 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:

$$\omega_0(T) = \sqrt{(C_1(T - T_0) + C_2)q^3 / \rho} \quad (5)$$

where density dependence $\rho(T)$ is taken from [15]. The best-fit estimate of the temperature derivative C_1 is $d\gamma/dT = -0.7 \pm 0.07 \text{ mN m}^{-1} \text{ K}^{-1}$ which is about three times higher than the tabulated value. The best estimate of C_2 corresponding to the tension at the melting point ($-39 \text{ }^\circ\text{C}$) is $C_2 = 538 \pm 7 \text{ mN m}^{-1}$, which is slightly above the tension (497 mN m^{-1}) extrapolated to the melting point using the tabulated slope $d\gamma/dT = -0.2 \text{ mN m}^{-1} \text{ K}^{-1}$ [15, 16]. The linear form is the only existing theoretical prediction of temperature variations of the tension of liquid metals (see for example [16]); therefore we are forced to use this form in the data fit. Note that the poor quality of the fit at low T probably indicates inadequacy of the objective function in its present form.

The surface tension $\gamma = 481 \text{ mN m}^{-1}$ at $20 \text{ }^\circ\text{C}$ evaluated using equation (3) is in good accord with the tabulated data: from 475 to 489 mN m^{-1} depending on the literature source (see [16] and references therein). The main result of our previous study [1] was the finding of an *increasing* $\omega(T)$ dependence of the mercury surface, which was wrongly believed to be oxide-free. The present study on pure Hg shows that lowering the residual pressure leads to the more usual *decreasing* $\gamma(T)$ dependence.

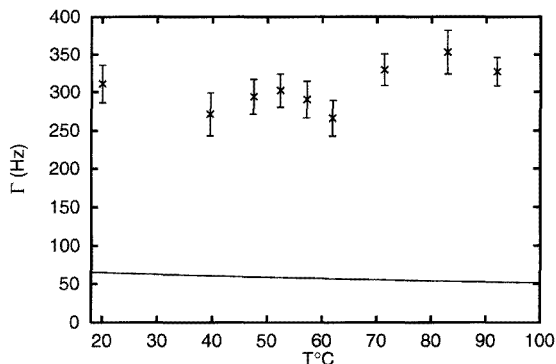


Figure 2. The damping constants collected at $q = 423.8 \text{ cm}^{-1}$ as functions of temperature. The solid line is the theoretical prediction for the wave damping based on equation (4) and the tabulated temperature variation of the bulk viscosity of mercury.

The damping constant data are plotted in figure 2 together with the theoretical expectation $\Gamma(T)$ deduced from equation (4) on the basis of the temperature dependence of the bulk viscosity of mercury $\eta(T) = A \exp(E/k_B T)$ [15]. The difference between the theoretical curve and the experimental observation is explained by the elasticity of a surface layer of ‘double-state’ atoms [17], which was inferred from the multiparametric fit at room temperature in [18].

Incorporation of surface viscoelasticity into the dispersion equation (see the discussion in section 4) leads to drastic changes of Γ but only minor changes in ω_0 . The dilational modulus ϵ_0 has the strongest influence on Γ due to the intrinsic coupling between the transverse and longitudinal waves at the liquid–monolayer interface (see for example [2]). Unfortunately there is no analytical dependence connecting the wave damping Γ and the surface elastic modulus ϵ : the variations $\Gamma(\epsilon)$ can be obtained only from numerical solutions of the dispersion equation. These solutions are well known (see [2, 14]); they can be presented in a dimensionless form which is independent of the type of fluid [2]. The main essence of this theoretical approach is that near the point $\epsilon/\gamma_0 \sim 0.16$ there is a resonance of the surface modes, increasing the value of Γ by about a factor of four over that for the free liquid surface [2, 14]. The effect of the two surface viscosities on the wave damping is less pronounced than that of the elastic modulus, although the surface dilational viscosity ϵ' reduces the variations of Γ near the point of resonance. The influence of the surface viscoelasticity on the peak frequency of the waves will be discussed below.

We turn now to the data obtained on the oxidized mercury surface prepared at a residual pressure of 10^{-2} Torr. The dependence $\omega_0(T)$ shown in figure 3 for the waves at the HgO–Hg interface was found to be monotonically *increasing* on heating the sample and the opposite on cooling. Such anomalous behaviour has been observed over the entire experimentally accessible temperature range from $-30 \text{ }^\circ\text{C}$ to $150 \text{ }^\circ\text{C}$. Note that this tendency is identical to that observed in our previous study [1], where the mercury surface was

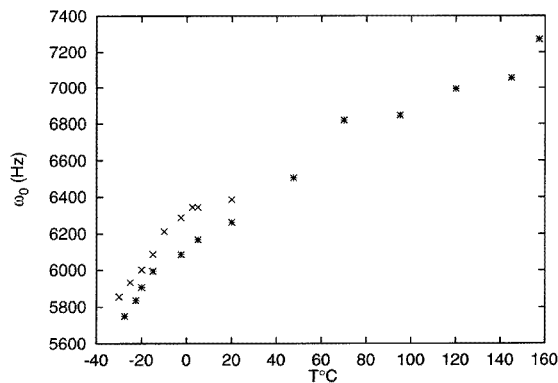


Figure 3. Temperature variations of the peak frequencies of the capillary waves at $q = 382.6 \text{ cm}^{-1}$ at the Hg–HgO interface. The errors in ω_0 are less than the size of the data points. Two data sets were obtained, on heating (*) and on cooling (x).

prepared at nearly the same residual pressure but without distillation. As we noted in [1], such a dependence *cannot* be attributed to either instrumental effects or variations in the scattering angle due to the thermal expansion of the sample. Using equation (3), one can extract the increasing $\gamma(T)$ dependence. Unfortunately such a dependence contradicts the theoretical concept of the surface tension at the Hg–HgO interface (see the discussion in section 4). We conclude that equation (3) fails to give correct estimates of γ , and that higher-order solutions are necessary for establishing the $\gamma(T)$ behaviour.

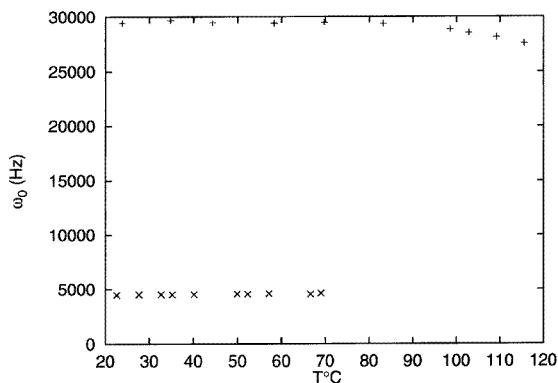


Figure 4. Temperature variations of the peak frequencies of the capillary waves at $q = 353 \text{ cm}^{-1}$ (x) and $q = 1140 \text{ cm}^{-1}$ (+) at the Hg surface covered with the polymolecular thick oxide film.

The third data set was obtained at a residual pressure about 10^{-1} Torr. The data in figure 4 show a nearly constant $\omega(T)$ dependence for a relatively thick oxide film, which is visible to the unaided eye. In every case, $\omega(T)$ displayed a hysteresis between the data collected on heating and on cooling, which indicates irreversible changes in the film structure.

Because the ω -data are collected at different values of q , it is instructive to compare the surface tensions of HgO films of different thicknesses. In general we cannot extract the tension from the first-order solution; therefore we use the ‘apparent tension’ evaluated using

equation (3) from raw data in order to compare the properties of interfaces formed from different HgO layers. This apparent tension evaluated from the data collected at the Hg/HgO monolayer interface at $T = 20\text{ }^\circ\text{C}$ is 364 mN m^{-1} , while the tension which corresponds to the macroscopically thick film is 290 mN m^{-1} for $q = 353\text{ cm}^{-1}$ and 302 mN m^{-1} for $q = 1140\text{ cm}^{-1}$. The difference between these data and the tension at the Hg–vapour interface (481 mN m^{-1}) ensures that the surface tension is lowered by oxidation of the Hg surface.

4. Discussion

The discussion is structured as follows: first, we consider the wave behaviour at the free Hg surface, and, second, we review the $\omega(T)$ dependence at the Hg–HgO interface.

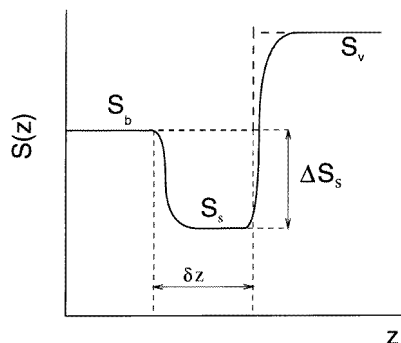


Figure 5. A schematic diagram of the variation of the entropy $S(z)$ of a structured Hg surface compared to that of an idealized fluid exhibiting a discontinuous jump of the entropy (from the bulk value S_b to vapour value S_v) shown with the thick dashed line. ΔS_s denotes the real variation of S in the surface zone δz .

4.1. The free Hg surface

It is well known that for a single-component fluid the temperature derivative of the tension is equal to the surface excess entropy density ΔS_s [4]:

$$\Delta S_s = -\frac{d\gamma}{dT}. \quad (6)$$

The surface layering recently discovered at the free Hg surface [6] implies that surface atoms are more ordered than those in the bulk. Thus it is clear that the variation of the entropy $S(z)$ should have a minimum upon transition through the surface zone, which indicates that the surface atoms are in a crystalline rather than in a liquid state. The surface excess of the entropy is the difference between the variations of entropy from the bulk liquid through the real surface and that of an idealized liquid with an infinitely sharp surface. Figure 5 shows schematically the variations of the entropy through the liquid–vapour interface. It is clear that ΔS_s ($\Delta S_s = (S_s - S_b)\delta z$) should be negative for a liquid surface possessing some local ordering. Hence equation (6) predicts a positive slope of $d\gamma/dT$ for the correlated Hg surface, while our experiment on the free Hg surface clearly demonstrates that $d\gamma/dT < 0$. Using the surface thermodynamics, we must establish a correct equation for $d\gamma/dT$.

Remembering that a liquid metal surface comprises strongly delocalized free electrons and positive ions [19], we see that such a surface *cannot* be treated as that of a one-component fluid. We should use the thermodynamic relation written in the form for a fluid comprising two components [20]:

$$d\gamma = -\Delta S_s dT - \sum_i \Gamma_i d\mu_i \quad (7)$$

where Γ_i and μ_i are the surface excess of density and the chemical potential (of each component) respectively. In general, the Γ_i are relative properties: they are defined according to the idealized surface plane (or a dividing surface) [20]. This dividing surface can be chosen in such a way that the surface excess density of the ions is zero. Then we expect that the surface excess of electrons (Γ_e) is essentially positive. Equation (7) can be rewritten as follows:

$$\frac{d\gamma}{dT} = -\Delta S_s - \Gamma_e \frac{d\mu_e}{dT}. \quad (8)$$

The effect of the second term on the RHS should work oppositely to the first one for $d\gamma/dT < 0$ to be satisfied. It is well known that the chemical potential of free electrons in the bulk is independent of the temperature (at least up to 200 °C) [21]. However, the surface electrons are influenced strongly by the electric field in a double layer created by these electrons and the positive ions [19], which causes a jump in the electric potential [22]. Therefore the chemical potential of surface electrons μ_s is connected to that in the bulk μ_b as follows:

$$\mu_s - \mu_b = e \delta\phi \quad (9)$$

where e is the electronic charge, and $\delta\phi$ is the potential drop connected with the electric field inside the double layer: $\delta\phi = Ez$. Since the electric field depends on the surface charge density which is nearly independent of T , the chemical potential should be very sensitive to variations in the thickness of the double layer. On heating, this thickness should increase, which leads to an increase in the chemical potential of the surface electrons, which in turn provides $d\mu_s/dT > 0$. Note that equation (9) is written for a classical electron gas, without taking into account specific quantum effects which may complicate the situation. Unfortunately, it is impossible to estimate the slope $d\gamma/dT$, due to the lack of data showing temperature variations of the spatial profile of the electronic density at the free Hg surface.

We note that the main conclusion of the outlined analysis is that the spatial distribution of electrons in the surface layer is broadened with increasing T . This distribution does not repeat that of the ionic component: surface electrons are essentially delocalized, creating an electric double layer whose thickness is strongly temperature dependent.

4.2. The Hg–HgO interface

The most surprising tendency has been obtained in the wave behaviour at the monolayer HgO–Hg interface. We will try to explain this phenomenon by considering the surface tension at the film-covered mercury surface. Irrespective of the thickness, the surface pressure p caused by the film is given by

$$\gamma_{\text{HgO}} = \gamma_{\text{Hg}} - p \quad (10)$$

where γ_{Hg} and γ_{HgO} are the surface tensions of pure and oxide-covered mercury respectively.

When the surface concentration is appreciably high, the surface pressure can be written as [22]

$$p = nkT - \frac{a'/A_s - b'nkT}{A_s} = -\frac{a'}{A_s^2} + (1 + b')nkT \quad (11)$$

where n is the surface concentration of HgO molecules, and A_s is the surface area. The constant b' represents the minimum area per molecule, and the constant a' characterizes the mutual interaction between the molecules of the film and the pure liquid.

We address the question of whether the surface pressure might decrease on heating, and hence provide an increasing γ_{HgO} . Analysis of equation (11) shows that this cannot be the case, since $b' > 0$. Therefore the derivative $dp/dT > 0$, and the surface tension of the mercury–oxide interface can only be a *decreasing* function of T . The surface tension is not directly measurable in the present experiment, and can only be evaluated from the solution of a dispersion equation in the form of equation (3). The analysis outlined shows that, in the case of a film-covered surface, the first-order approximation to the solution of the dispersion equation is not valid. This means that the influence of the elastic moduli (dilatational and transverse shear) must be accounted for. Surface light scattering provides information on the two viscoelastic surface moduli: transverse to the interfacial plane, and the uniaxial dilation in this plane. In the case of a liquid/monolayer interface, possessing viscoelastic properties, the surface tension γ_0 and the shear viscosity γ' normal to the interface are combined into a shear modulus [23]:

$$\gamma = \gamma_0 + i\omega\gamma' \quad (12)$$

The dilatational modulus can be written as the superposition of the surface elasticity and the dilatational viscosity [23]:

$$\epsilon = \epsilon_0 + i\omega\epsilon' \quad (13)$$

We examine the effects of each of these moduli separately.

The propagation of a capillary wave at a liquid surface covered with a monolayer is affected by its viscoelastic properties. The dispersion equation reflecting the dependence $\omega(q)$ explicitly has been given in [25, 2]:

$$[\epsilon q^2 + i\omega\eta(m + q)][\gamma q^2 + i\omega\eta(m + q) - \omega^2\rho/q] - [i\omega\eta(q - m)]^2 = 0 \quad (14)$$

where $m = \sqrt{q^2 + i\omega\eta/\rho}$ and $\text{Re}(m) > 0$.

The surface film definitely possesses a dilatational elastic modulus, which influences the capillary waves via their coupling to the longitudinal modes [2, 14]. Since the theory outlined does not predict temperature dependences of ω and Γ , we can only suppose that these variations arise from the temperature dependences of the complex moduli, $\epsilon(T)$ and $\gamma(T)$. Numerical solutions of the dispersion equation highlight the effect of ϵ on the capillary-wave frequency ω_0 . Figure 6 shows the variation of ω_0 with ϵ for $q = 383 \text{ cm}^{-1}$ (this corresponds to the wavenumber used in our experiment). Although ω_0 increases by 1.5% when ϵ grows from 0 to about 20 mN m^{-1} , the experimentally observed effect on ω_0 (from figure 3) constitutes about 20% over the whole T -range. Moreover, ω_0 falls off after $\epsilon \approx 20 \text{ mN m}^{-1}$, which does accord with the experimental observations. Hence, we are compelled to search for another explanation for the $\omega_0(T)$ behaviour.

The second possible source is the shear modulus, which is dominant in the transverse plane. The classical theory of the wave propagation at the liquid–film interface [3, 25] was formulated for isotropic liquid films. However, for amorphous or quasi-crystallized layers on top of a liquid substrate, no adequate theoretical description has been found; therefore we may only propose some phenomenological forms. Such a layer possesses both

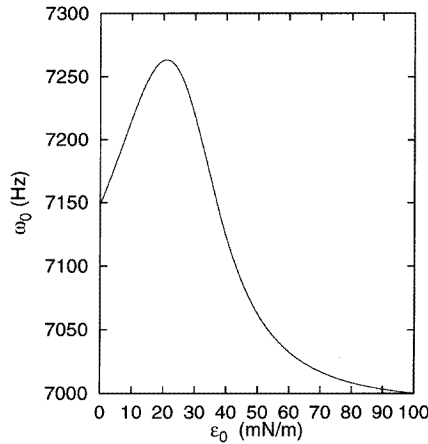


Figure 6. The theoretical variation of ω_0 with ϵ_0 for $q = 383 \text{ cm}^{-1}$ at a liquid surface with the surface tension $\gamma_0 = 485 \text{ mN m}^{-1}$ and bulk properties that are the same as those for mercury. The transverse shear and the dilational surface viscosities are assumed to be zero.

transverse and longitudinal elastic moduli. The transverse shear modulus γ_t together with the surface tension act in the same plane normal to the surface, and may be introduced as a superposition with γ_0 [24]:

$$\omega_0 \approx \sqrt{\frac{(\gamma_0 + \gamma_t(\omega))q^3}{\rho}}. \quad (15)$$

Another possibility for introducing γ_t is to use the Maxwell model, including both the elastic and the viscous part of the monolayer [18]:

$$\gamma(\omega) = \gamma_0 + \frac{-i\omega\gamma_t\gamma'}{\gamma_t - i\omega\gamma'} \quad (16)$$

where γ' is the transverse surface viscosity. A capillary wave (at fixed q) provides an intrinsic modulation frequency ω_0 . For liquids without surface structure, the time-dependent part of the tension seems to be always zero. For liquid mercury covered with a thin oxide layer, the time-dependent modulus shows relaxations with some characteristic time $\tau = \gamma'/\gamma_t$ responsible for the relaxation of the oscillatory shear stresses.

In order to find out what the impact of γ_t is on ω_0 , we may substitute equation (16) into the Lamb–Levich dispersion equation describing the propagation of pure capillary waves:

$$(i\omega + 2\eta q^2/\rho)^2 + (q^3/\rho)\left(\gamma_0 + \frac{-i\omega\gamma_t\gamma'}{\gamma_t - i\omega\gamma'}\right) = 4(\eta/\rho)^2 q^4 \sqrt{1 + i\omega\rho/(q^2\eta)}. \quad (17)$$

In this case there is no analytical solution for the wave peak frequency: the modified dispersion equation can only be solved numerically [18]. It is worth establishing the solutions of equation (17) in the form of $\omega(\gamma_t)$ dependencies, which suggest variations of $\omega(T)$ via the temperature-dependent modulus γ_t .

Figure 7 demonstrates clearly the increasing of ω_0 with γ_t obtained at $q = 383 \text{ cm}^{-1}$ for a structured Hg surface having $\gamma_0 = 485 \text{ mN m}^{-1}$ and $\gamma' = 5 \times 10^{-6} \text{ mN s m}^{-1}$. This effect explains the $\omega_0(T)$ behaviour: if the frequency-dependent modulus $\gamma_t(\omega)$ rises with the temperature, the peak frequency of the capillary waves will follow the same trend. Note that such behaviour of the elastic modulus can arise from the change in concentration of

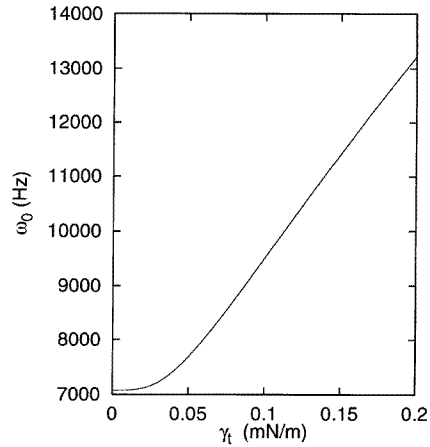


Figure 7. The variation of the capillary-wave frequency ω_0 with the transverse shear elastic modulus γ_t for $q = 383 \text{ cm}^{-1}$ at a liquid surface having the surface tension $\gamma_0 = 485 \text{ mN m}^{-1}$ and the surface transverse viscosity $\gamma' = 5 \times 10^{-6} \text{ mN s m}^{-1}$, and bulk properties that are the same as those for mercury.

HgO molecules on heating. We expect that the oxidation of the Hg surface on heating, caused by residual oxygen, will alter the surface packing of the HgO molecules, and that the transverse elastic modulus will vary with T . These continuous changes in the surface concentration are believed to induce a smooth transition in the HgO film from a gaseous to a condensed state on heating. This conclusion is supported by the fact that the thermocapillary flow on an oxidized surface is suppressed gradually during the heating of the sample (see below).

In order to obtain additional information on the sign of $d\gamma/dT$, 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 gradients of the surface tension is expected. The surface tension gradients couple to the liquid velocity v_x indirectly, via the boundary condition on the free surface, which for tangential stress is [3]

$$\frac{dp}{dx} = \frac{d\gamma}{dT} \nabla T = \eta \delta v_x. \quad (18)$$

Usually, the thermocapillary convection couples to the buoyancy-driven convection. Dimensionless Reynolds and Grashof numbers (Re and Gr) are defined in this case as [26]

$$Re = \frac{d\gamma}{dT} \frac{\delta T H^2}{L \rho \nu^2} \quad (19)$$

$$Gr = g\beta \frac{\delta T H^4}{L \rho \nu^2} \quad (20)$$

where δT is the temperature difference, and H and L are the depth and length of the liquid layer respectively. Re and Gr represent the relative importances of the effects of thermocapillarity and buoyancy [3]. For a layer of infinite length, the dimensionless surface velocity is [26, 27]

$$u = -Re/4 + Gr/48. \quad (21)$$

This equation cannot be used for precise evaluation of the surface velocity, but order-of-magnitude estimates of the velocities developed in both buoyancy, u_{Gr} , and thermocapillary, u_{Re} , convections can be made:

$$\frac{u_{Re}}{u_{Gr}} = 12 \frac{Re}{Gr} = \frac{d\gamma/dT}{g\beta H^2} \quad (22)$$

where β is the coefficient of thermal expansion. This ratio of the melt velocities due to thermocapillarity and due to buoyancy is $u_{Re}/u_{Gr} \approx 80$ (if $|d\gamma/dT| = 0.7 \text{ mN m}^{-1} \text{ K}^{-1}$), which means that thermocapillary flow dominates over buoyancy convection for a Hg layer of depth 2 mm.

The direction of the 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 towards the hot end. The flow was made visible by means of graphite particles placed in the chamber prior to the start of the experiment. Convective flow was detected on the oxidized surface only for the samples with $d\omega/dT > 0$ (from light scattering data). This serves as an additional indication that HgO films exhibiting an anomalous $\omega(T)$ dependence were in a gaseous or liquid state, instead of a condensed, solid state, which would have too high an elasticity, which would completely suppress the surface flow. We observed the surface flow to be directed always from hot to cold in the middle of the trough, with a characteristic velocity of a few mm s^{-1} , and a recirculating flow near the side walls which ensures that the dependence $\gamma(T)$ is a decreasing function. Note that the velocity of the thermocapillary convection was very sensitive to the temperature range: on heating one end above 80°C , convection decayed quickly with time, indicating the changes of the film state on oxidation. The flow with a characteristic velocity about two to four times higher than that for the oxidized surface (for the same δT) was observed at the free Hg surface, in the direction towards the cold end, confirming our prediction of $d\gamma/dT < 0$ for the free surface.

The $\omega_0(T)$ dependence for the macroscopically thick film appeared to be nearly constant. The thickness of a polymolecular film does not change with temperature, providing a linear dependence of the surface pressure. Such a film possesses both dilational and transverse elastic moduli. We assume that the transverse shear elastic modulus does not vary with temperature (in contrast with that for the monolayer), while the surface pressure, being proportional to T , affects $\omega_0(T)$ according to equation (10). Note that there was never any thermocapillary flow detectable on the surface of the macroscopically thick HgO film, proving that the film was in a condensed solid state.

5. Conclusions

Surface light scattering from the free mercury surface shows a temperature-dependent behaviour, $\omega(T)$, which corresponds to a decrease in the surface tension on heating. This phenomenon is supported by a theoretical treatment of the liquid metal surface as comprising two components: positive ions, and delocalized free electrons. The spatial profile of the density of the electronic component should be shifted relatively to that of the ionic component in order to provide a positive surface excess of electrons. Thus the effect of the negative excess entropy (due to surface layering) is exceeded by that of the temperature variations of the excess density of electrons.

The $\omega(T)$ dependence obtained for the oxidized surface reveals different tendencies, according on the film thickness: it is increasing for microscopically thin films, but for HgO films of macroscopic thickness, $\omega(T)$ is nearly constant. Theoretical analysis has

shown that the increasing $\omega(T)$ can be explained in terms of the impact of the frequency-dependent transverse shear modulus, which should grow with T . An additional experiment on thermocapillary flow induced by the temperature difference imposed along the length of the cell was carried out. The surface flow, being directed in all cases from the hot to the cold end, confirmed our prediction of a positive sign for $d\gamma/dT$.

While the macroscopically thick film also ‘perceives’ the transverse shear modulus, it seems to be independent of T . $\omega(T)$ observed for such a surface is nearly constant, which indicates that the surface pressure of the film increases proportionally to the temperature. This effect acts oppositely to the surface tension of pure liquid mercury, provided that the tension of the Hg–HgO interface is nearly independent of the temperature.

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