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Wetting of mercury on sapphire

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Abstract. Reflectivity experiments on fluid mercury against an optically transparent sapphire window at high temperatures and high pressures close to the liquid–vapour critical point ($T_c = 1478$ °C, $p_c = 1673$ bar, $\rho_c = 5.8$ g cm⁻³) reveal clearly the existence of a prewetting transition of mercury on the sapphire substrate. The prewetting line intersects the coexistence curve at the wetting temperature $T_w = 1310$ °C, and terminates at the prewetting critical temperature $T_{pw}^c = 1468$ °C and prewetting critical pressure $p_{pw}^c = 1586$ bar lying close to the bulk critical point.

1. Introduction

The closest example in common experience of a non-wetting substance is liquid mercury at room temperature on solid non-metallic substances. It forms drops with contact angles far beyond 90° on glass, quartz and sapphire. For such a situation a wetting transition is expected [1, 2] to take place at a ‘wetting temperature’, T_w ($T_w < T_c$), when mercury is heated to the region of its liquid–vapour critical point, which is located at $T_c = 1478$ °C, $p_c = 1673$ bar, and $\rho_c = 5.8$ g cm⁻³ [3]. In this paper we report the first experimental results which we regard as evidence that mercury adsorption on sapphire displays characteristic features of a first-order wetting transition: a wetting transition temperature $T_w = 1310$ °C and a prewetting line terminating in a prewetting critical point at $T_{pw}^c = 1468$ °C and $p_{pw}^c = 1586$ bar.

2. Results and discussion

Because of the severe experimental problems connected with the high critical temperature of mercury, we used the conventional technique of reflecting light from a vertical sapphire–mercury–vapour interface to study the wetting behaviour. In order to locate the prewetting line, reflectivity measurements at various wavelengths were performed at constant temperature T by increasing p , the pressure of the vapour, towards its value at bulk saturation p_{sat} or alternatively at constant p by decreasing T towards T_{sat} . The line of the first-order prewetting transition $p_{pw}(T)$ ($< p_{sat}(T)$) extends from the point of the (first-order) wetting transition (T_w, p_{sat}) to a prewetting critical point (T_{pw}^c, p_{pw}^c). Three representative isotherms are shown in figure 1. The shape of the curve at 1300 °C is characteristic for isotherms below T_w . The measured reflectivity R for $p < p_{sat}$ (solid curve) coincides with that calculated (dotted curve) employing Fresnel’s formula for normal incidence at the sapphire–mercury–vapour interface. There is no indication of a precursor of

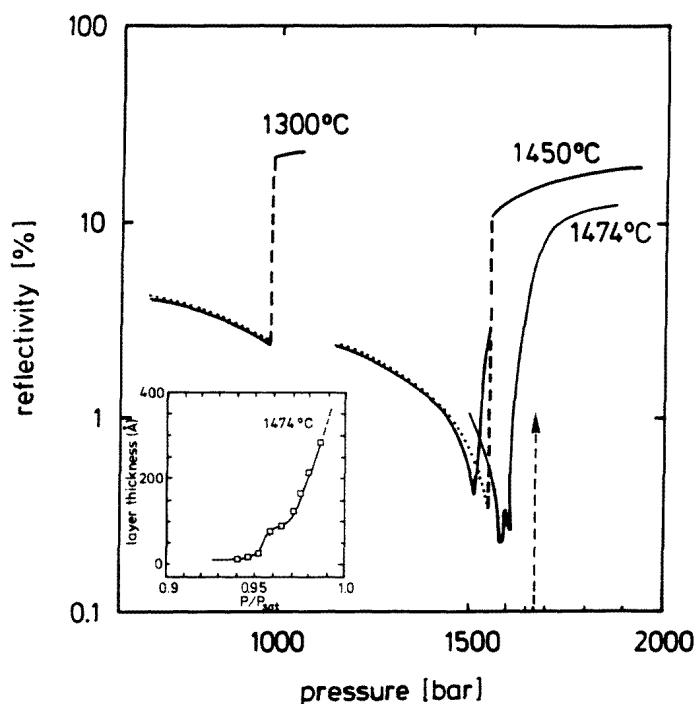


Figure 1. Reflectivity of mercury vapour against an optically transparent sapphire substrate at constant temperature T as a function of pressure near the vapour-liquid coexistence line for $T = 1300\text{ }^{\circ}\text{C} < T_w$, $T_w < T = 1450\text{ }^{\circ}\text{C} < T_{pw}^c$, and $T = 1474\text{ }^{\circ}\text{C} > T_{pw}^c$. The inset shows the estimated thickness of the wetting film for $T > T_{pw}^c$ as a function of p/p_{sat} .

wetting. The sudden increase in reflectivity (broken curve) indicates bulk phase separation—that is, condensation to the liquid state.

Unlike the isotherms at $T < T_w$, the measured reflectivity curve at $1450\text{ }^{\circ}\text{C}$ deviates markedly from the calculated dotted curve. The slope of the R - p -curve discontinuously changes its sign distinctly before condensation sets in (broken curve). A purely bulk description of the anomalous change in reflectivity seems to be inadequate because it requires a discontinuous change in the unsaturated mercury-vapour refractive index. An alternative more likely explanation is that the reflectivity anomaly is an interface phenomenon. In all ways, the features displayed by the $1450\text{ }^{\circ}\text{C}$ isotherm are completely consistent with the abrupt formation of a wetting film. By assuming that the intruding film has the density and optical properties of the coexisting liquid at the corresponding pressure p_{sat} , the reflectivity data can be reduced to layer thicknesses by employing the theory of optical reflectance properties of thin absorbing multilayer films [4]. To calculate the wetting-film thickness, we used the experimentally determined complex dielectric constants for liquid mercury [5, 6]. The density (pressure) dependence of the refractive index n_v of mercury vapour was determined from reflectivity data at temperatures T far above T_c or below T_w , respectively. In these regimes, there should be only a small contribution from adsorption. It is found that n_v can be reasonably well approximated by the Lorentz-Lorenz equation in the density region of interest. A selection of wetting-layer thicknesses estimated in this way are displayed in figure 2.

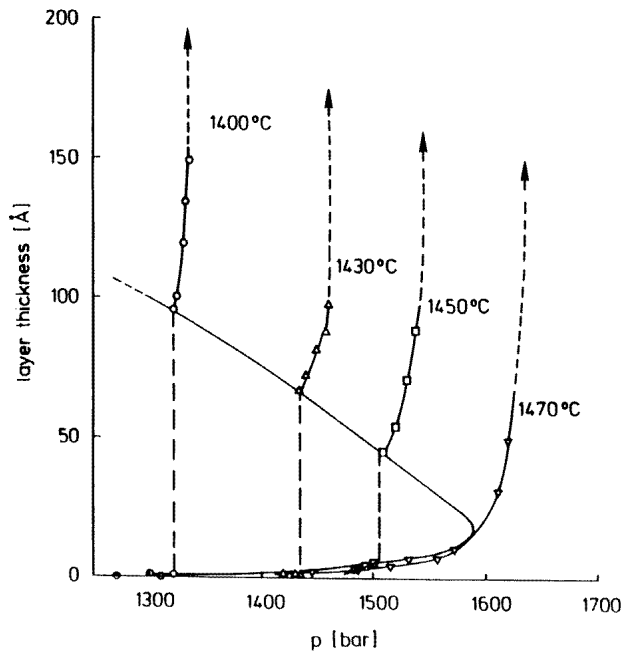


Figure 2. The wetting-layer thickness estimated with a slab model employing the theory of the reflectance of the absorbing films.

All of the isotherms show a rapidly thickening film at $p/p_{sat} = 1$ (p_{sat} is indicated by the arrows in figure 2). The isotherms at $T < 1470$ °C have an additional jump in the film thickness at the prewetting line for $p/p_{sat} < 1$. The jump becomes smaller as the prewetting line is crossed farther from coexistence and vanishes at a temperature of 1468 °C. We identify this temperature as the prewetting critical temperature T_{pw}^c .

It is immediately evident from a glance at figure 1 that the reflectivity isotherms slightly above T_{pw}^c , as shown for the curve at $T = 1474$ °C, are qualitatively different from those at lower temperatures. Two, now slightly rounded minima occur in the R - p -curve. The changes in sign seem to be no longer discontinuous. However, it must be pointed out that in practice making the distinction between continuous and discontinuous can be very difficult. We believe that the R - p -curve above is caused by two competing effects: an increase in the thickness of the wetting film and the mercury vapour refractive index n_v . This assumption results in the wetting-layer thicknesses as a function of p/p_{sat} displayed in the inset of figure 1. There is no thin-thick-film coexistence region, but the isotherm nevertheless has a small, rounded step that occurs far from p_{sat} . Adopting arguments used by Rutledge and Taborek [7] we assume that the step marks the maximum in the 2D compressibility of the prewetting supercritical one-phase region.

Quantitative analysis of the different isotherms and isobars allows one to construct the prewetting phase diagram in the p - T -plane as displayed in figure 3. The prewetting line, which terminates at high temperatures at the prewetting critical point CPW lying below the bulk critical point CP and at low temperatures at the wetting transition temperature T_w lies close to the bulk vapour-pressure coexistence curve. In order to determine T_w we plot in the inset of figure 3 the values of p_{jump}/p_{sat} , i.e. the minimum in the R - p -curves. T_w can be estimated by extrapolating the values of p_{jump}/p_{sat} to the coexistence

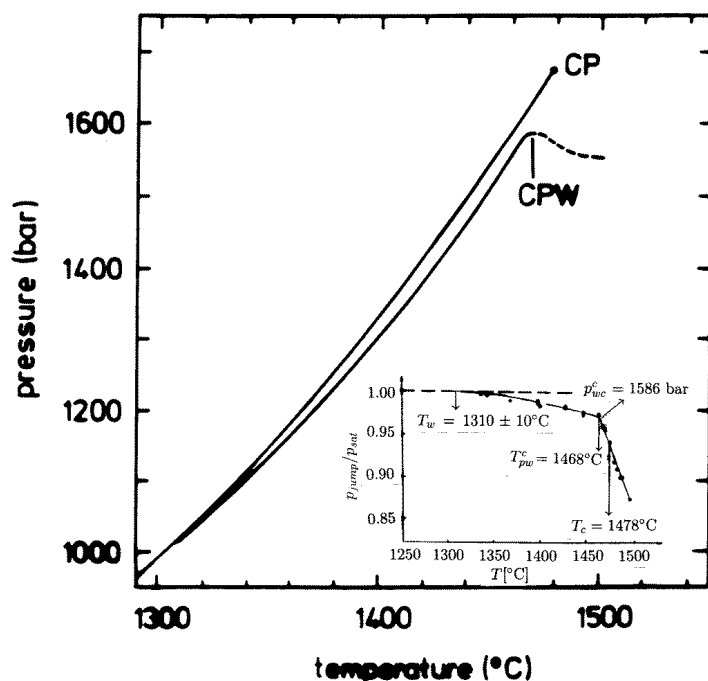


Figure 3. The bulk vapour-pressure curve of mercury terminated by the critical point CP together with the prewetting line which terminates at high temperature at the prewetting critical point CPW and at low temperature at the wetting temperature T_w . The dashed extension of the prewetting line is a line of maximum 2D compressibility in the prewetting supercritical one-phase region. The inset shows p_{jump}/p_{sat} (the location of the minima in the R - p -curves) versus T . The intersection of this curve with the line $p/p_{sat} = 1$ locates the prewetting temperature.

curve, represented by the horizontal dashed line $p/p_{sat} = 1$. p_{jump} and p_{sat} become experimentally indistinguishable at temperatures smaller than 1330 °C. The extrapolation is suggestive of a wetting temperature T_w of about 1310 °C.

An additional interesting observation is that T_{pw}^c divides the curve in the inset in figure 3 into two parts: for $T_w < T < T_{pw}^c$ the curve defines the prewetting thick–thin coexistence region; while for $T > T_{pw}^c$ the curve marks the location of the dashed extension of the prewetting line (figure 3) which we identified above as the line of maximum 2D compressibility in the prewetting supercritical one-phase region.

A noteworthy observation is that T_w lies in the range where the gradual metal–non-metal transition occurs in liquid mercury at coexistence [8]. At the highest density $\rho = 13.6 \text{ g cm}^{-3}$, corresponding to the liquid range near room temperature, Hg is essentially a free-electron metal and the frequency-dependent conductivity $\sigma(\omega)$ shows Drude-like behaviour. But with decreasing density if the liquid is heated to the region of its critical point a gradual diminution of metallic properties occurs. The frequency dependence of $\sigma(\omega)$ clearly shows that for temperatures higher than 1300 °C, i.e. densities smaller than 9 g cm^{-3} , either a true energy gap opens or a range of energy exists that is so thinly populated with states that the contribution to the optical properties is small. The coincidence of the wetting transition and the metal–non-metal transition is an indication for the intimate interplay between the changes in interparticle forces and the changes in the electronic structure associated with the metal–non-metal transition.

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