Wetting Phenomena Near the Bulk Critical Point of Fluid Mercury

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We have studied the adsorption of mercury on sapphire at temperatures and pressures close to the liquid-vapour critical point ($T_c = 1478\,°C$, $p_c = 1673$ bar, $\rho_c = 5.8$ g/cm^3) of mercury. The mercury film undergoes a first-order phase transition known as prewetting. At low temperatures, the prewetting line meets the bulk coexistence curve tangentially at the wetting temperatures $T_w = 1310\,°C$. At high temperatures the prewetting line terminates at the prewetting critical point $T_{pw}^c = 1468\,°C$ and the prewetting pressure $p_{pw}^c = 1586$ bar lying close to the bulk critical point. In analogy with the line of compressibility maxima extending above the liquid-vapor critical point, we can identify an extension of the prewetting phase line for $T > T_{pw}^c$ which marks the maximum in the two-dimensional compressibility of the prewetting supercritical phase.

1. Introduction

As first noted by Cahn [1], a substrate in contact with a vapour near vapour-liquid coexistence which is incompletely wet at low temperatures is expected to become completely wet as the critical temperature T_c of the bulk fluid system is approached. The change from one condition to the other is denoted the wetting transition and the corresponding temperature the wetting temperature T_w. This transition is defined only at bulk coexistence. The wetting transition can be either continuous or first order. If the transition is first order, with a discontinuous jump in the film thickness on the coexistence curve, thermodynamics requires that it is accompanied by a line of prewetting transitions [2]. These are transitions from a thin to a thick liquid layer induced, for example, by increasing p, the pressure of the vapour, towards its value on bulk saturation $p_{sat}(T)$ at a fixed temperature T above the wetting temperature T_w. The line of first-order prewetting transitions extends smoothly from the point of the first order wetting transition (T_w, p_{sat}) into the region of unsaturated films with $p < p_{sat}$. It is expected to terminate at a prewetting critical point (T_{pw}^c, p_{pw}^c) the location of which must depend upon the properties of the substrate as well as on the interparticle interaction of the fluid system.

Since the initial prediction of wetting transitions in 1977 [1] a large amount of theoretical and experimental work has been done in an effort to determine the conditions under which wetting transitions take place, the order of the transitions, and associated phase diagrams and critical properties [2]. In spite of this effort, convincing experimental evidence for prewetting transitions at solid wall-vapour interfaces had to wait until 1992, when they were finally seen in experiments with helium on cesium [3], [4] and hydrogen on rubidium [5]. The observation of the wetting transition in the quantum fluids helium and hydrogen was soon followed by evidence from fluid mercury on sapphire [6]. The latter system was an obvious candidate for a wetting transition because as a result of their low surface free energies, most nonmetallic solids are not wetted by nonreactive liquid metals like mercury. Indeed the closest example in common experience of a nonwetting substance is liquid mercury on glass. On the other hand, the subsequent report of the existence of a wetting transition in mercury [7] on the walls of molybdenum and niobium was a sursprise because most pure liquid metals (including mercury) wet completely a perfectly clean solid metal surface. One must be extremely careful, however, when considering the apparent nonwetting of metallic solids by liquid metals. Thin layers of oxide or sulfide are sufficient to prevent wetting by most liquid metals even when, as is usually the case, the layer is extremely thin.

Be that as it may, as mentioned before an obvious candidate for a wetting transition is mercury on a nonmetallic substrate when it is brought by heating near its liquid-vapour critical point. Unfortunately, making such measurements is technically very demanding because high pressures and high temperatures are needed to reach the critical point of mercury which is located at the temperature $T_c = 1478\,°C$, the pressure $p_c = 1673$ bar and the density $\rho_c = 5.8$ g/cm^3 [8]. A major experimental problem encountered in working with mercury at high temperatures and pressures is its containment in uncontaminated form. Materials found to be chemically inert in contact with the fluid sample are pure molybdenum, the sintered nonmetal aluminium oxide, and sapphire single crystals. However, cells from these materials cannot be constructed in such a way that they can withstand a high internal pressure. At conditions near the critical point of mercury, an arrangement must therefore be used in which the sample cell, together with the necessary furnaces, are placed in larger high pressure autoclaves filled with the pressure transmitting argon gas under the same pressure as the mercury sample inside the cell. This avoids any mechanical stress on the cell, but at the necessary high pressures severe problems of temperature measurement and control arise.

Over the past two decades a great variety of experiments (9) have contributed to improve the experimental techniques in a way which permits relatively precise mea-

surements of the electrical, optical and thermophysical properties of mercury with sufficiently accurate temperature control in the region of the critical point. This new experimental information is accurate enough to allow one to study the complete wetting phase diagram for mercury on sapphire.

2. Experimental Procedure

In the experiments reported here, we have studied the wetting behaviour of mercury by reflecting light from a vertical sapphire mercury vapour interface. Successful measurements with optimal elimination of temperature gradients were achieved with a long optical reflectivity cell (Fig. 1) consisting of a molybdenum cylinder, with an inner diameter of 5 mm which is closed at one end by an 80 mm long synthetic sapphire window with optically polished upper and lower surfaces. The cell was mounted in a specially constructed autoclave with high-pressure windows and an internal electric resistance furnace which is thermally insulated from the steel walls. The furnace consisted of two independently controlled heating elements made of molybdenum wire. The pressure medium was argon. The cell was connected to a reservoir maintained at the same pressures as the autoclave. The sample temperature was measured with two W-Re thermocouples in close contact with the hot part of the cell where the mercury sample was located. We calibrated the sample temperature by employing the most accurate vapour pressure data. For temperature lower than the wetting temperature T_w the vaporization temperature at a given pressure could easily found as an abrupt change in the reflectivity when the mercury sample is vaporized (Fig. 2 a). The reproducibility of this procedure was checked over numerous experimental runs and was found to be better than $\pm 1\,°C$. Pressures were measured to ± 1 bar with calibrated commerical Bourdon-type manometers. A standard optical set-up was employed to measure the reflectivity. The optical system consisted of a pulse tunable dye laser pumped by an excimer laser and a commercial optical detection system. The reflectivity data have been measured for the incident light nearly normal (about $1°$ off from normal incidence) to a surface between mercury vapour and sapphire. The entire optical system was calibrated by use of reflection at the sapphire liquid mercury interface [10]. A small error due

to temperature-dependent absorption in sapphire was corrected for.

3. Results and Discussion

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 increasing T towards T_{sat}. Figs. 2 a–c display three representative isotherms. The shape of the curve at 1300 °C in Fig. 2 a is characteristic for isotherms below T_w. The measured reflectivity R for $p < p_{sat}$ (solid curve, and experimental points) coincides with that calculated (dotted curve) employing Fresnel's formula for normal incidence at the sapphire(s)-mercury-vapour(v) interface. There is no indication of a precursor of wetting. The sudden increase in reflectivity (broken curve) indicates bulk phase separation – that is condensation to the liquid state, i.e. R is then for normal incidence at the sapphire (s)-mercury-liquid (L) interface.

Unlike the isotherms at $T < T_w$, the measured reflectivity curve at 1450 °C (Fig. 2 b) deviates markedly from the calculated dotted curve. The slope of the curve of reflectivity changes sign discontinuously within a certain temperature range. The pressure is below that needed for bulk condensation. The latter is again readily detected by the abrupt increase in the reflectivity (broken curve). To attribute the anomalous change in reflectivity to bulk phase behaviour would require an unphysical, discontinuous change in the refractive index of the unsaturated mercury vapour. Much more likely is that the reflectivity anomaly is due to abrupt formation of a wetting film.

On the assumption that the film formed on the sapphire window has the density and optical properties known for the coexisting liquid, one can employ the theory of the reflectance of thin absorbing slabs [11] to estimate the layer thicknesses from the reflectivity data (see Fig. 2 b). The density dependence of the refractive index n_v of mercury vapour was determined from reflectivity data at temperatures far above T_c, or below T_w. The wetting layer thickness for the 1450 °C isotherm estimated in this way is displayed in the inset of Fig. 2 b. The film thickens rapidly as p approaches coexistence, i.e. at $p/p_{sat} = 1$. In principle, for complete wetting the film thickness should become infinitely thick at $p/p_{sat} = 1$. However the latter applies only to the hypothetical case of zero gravity. In terrestial experiments gravity limits the film thickness to a few hundred Angström at saturation.

In addition there is a jump in the film thickness at intermediate values of p/p_{sat}. The location of these jumps for different isotherms can be mapped by the reduced pressure at the reflectivity anomaly, p_{jump}/p_{sat}. The positions of the reflectivity anomalies measued in a series of isotherms such as that in Fig. 2 b define the solid curve in the p-T plane, shown in Fig. 3. This is the line of first-order phase transitions between thin and thick films called
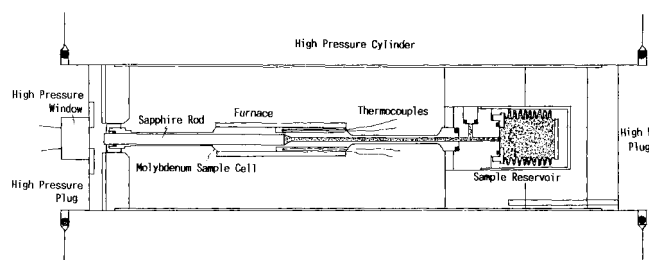

Fig. 1
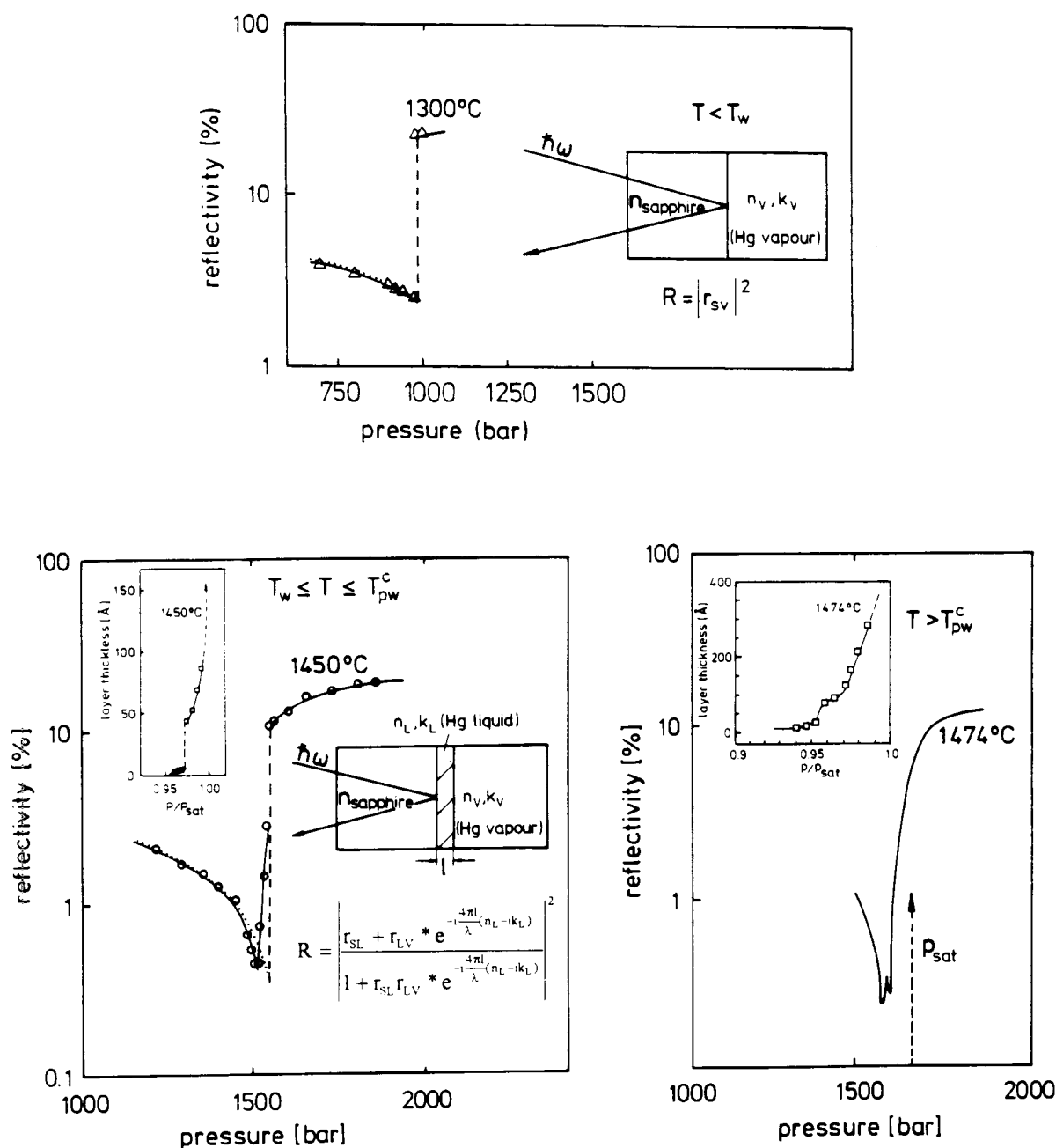Autoclave with optical access for reflectivity measurements on fluid mercury

Fig. 2
Typical experimentally observed reflectivity curves of mercury vapour against an optically transparent sapphire substrate at constant temperature T. Fig. 2a displays an example for the pattern observed for $T<T_w$. The sudden increase in reflectivity indicates codensation to the liquid state

$$r_{\alpha\beta} = \frac{(n_\alpha - ik_\alpha) - (n_\beta - ik_\beta)}{(n_\alpha - ik_\alpha) + (n_\beta - ik_\beta)}$$

where n and k are the usual optical constants. Fig. 2b shows an example for the pattern observed for $T_w < T < T_{pw}^c$. The wetting layer thickness estimated with the slab model illustrated on the right part of the Figure is displayed in the inset of Fig. 2b. The prewetting step at $p/p_{sat} = 0977$ represents a coexistence region in which the thick phase is growing at the expense of the thin phase. Fig. 2c shows the isotherm at 1474 °C. It is a typical example for the pattern observed for $T > T_{pw}^c$. The inset shows the estimated thickness of the wetting film for $T > T_{pw}^c$ as a function of p/p_{sat}

the prewetting line. The wetting transition temperature T_w which is the temperature at which the prewetting line meets the bulk liquid-vapour coexistence curve tangentially, is determined by extrapolating the values of p_{jump}/p_{sat} shown in Fig. 3 to the coexistence curve, represented by the horizontal line $p/p_{sat} = 1$. The extrapolation is suggestive of a wetting temperature T_w of about 1310 °C.

The prewetting critical point at which the distinction between thin and thick films disappears must lie on the p_{jump}/p_{sat} versus T curve in Fig. 3. To find the prewetting

Fig. 3

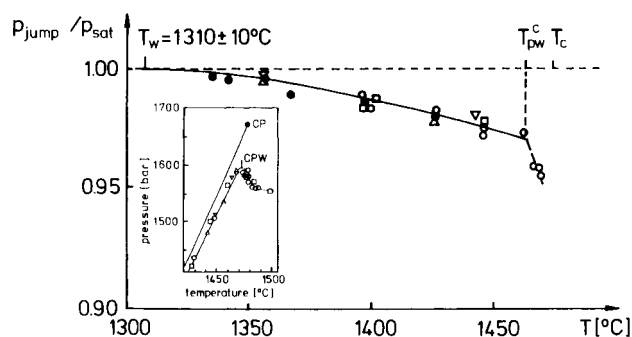P_{jump}/p_{sat} as a function of temperature T. The tangential approach of this curve to the line $p/p_{sat}=1$, i.e the coexistence curve, locates the wetting temperature T_w. The critical temperature T_{pw}^c marks the end of the two-phase thick-thin-film coexistence. The inset shows the prewetting line in the p-T-plane near the prewetting critical point

critical temperature T_{pw}^c the anomalies in the reflectivity isotherms at higher temperatures must be examined.

Above T_{pw}^c, there should be no coexistence region, and the wetting film should thicken over a range of pressure, which should result in a continuous (but probably very steep) increase in an isotherm for $T \geq T_{pw}^c$. It is indeed evident from a glance at Fig.2c 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 reflectivity versus pressure cuve. The changes in sign of the slopes seem to be no longer discontinuous. The film, calculated from the reflectivity curve in Fig.2c (see inset) thickens indeed over a range of pressure which results in a nonvertical step in the isotherm. The rounded step occurs far below p_{sat}. The position of the rounded steps in a series of isotherms such as that in Fig.2c define the dashed curve in Fig.3. It is obvious that the location of T_{pw}^c divides the curve in Fig.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 maximum in the 2D compressibility of the prewetting supercritical one-phase region.

Quantitative analysis of reflectivity anomalies for isotherms above T_{pw}^c show that steps although progressively rounded, persists in isotherms far above the bulk critical temperature T_c (see inset in Fig.3).

In summary, the features observed in the pressure and temperature dependence of the reflectivity at the mercury-sapphire interface display all of the characteristics of a first-order wetting transition: a wetting temperature T_w, a prewetting line terminating in a prewetting critical point at T_{pw}^c as well as maxima in the compressibility in the prewetting supercritical single-phase region. A combination of the data presented in Fig.3 with the known p-ρ-T-data for fluid mercury [11] allows one to construct the complete prewetting phase-diagram in the density ρ-temperature T plane as illustrated in Fig.4. The prewetting line, lies close to the bulk liquid-vapour coexistence curve which is also shown in Fig.4 along with the line of symmetry, i.e.
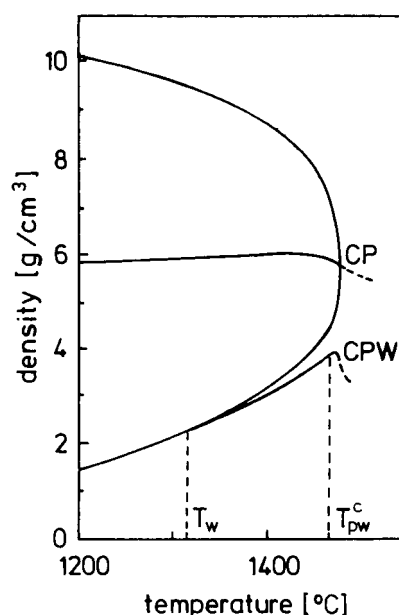

Fig. 4

The bulk coexistence curve of mercury, along with the mean of the densities ρ_L and ρ_v, the so-called diameter. The prewetting line terminates at high temperatures at the prewetting critical temperature T_{pw}^c and at low temperatures at the wetting temperature T_w. The dashed extension of the prewetting line is a line of maximum 2D compressibilities in the prewetting supercritical one-phase region. It bears analogy to the line of compresssibility maxima extending above the liquid-vapour critical point CP

the mean of the density ρ_L and ρ_v of coexisting liquid and vapour phases, the so-called diameter. The prolongation of the line of symmetry (dashed line) beyond the critical point CP into the supercritical fluid marks the location of the maxima of the isothermal compressibility $\chi_T = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$ determined from the condition $\left(\frac{\partial \chi_T}{\partial \rho}\right)_T = 0$. It is noteworthy that in analogy with the line of compressibility maxima extending above the liquid-vapour critical point, we can identify the extension of the prewetting phase line (dashed curve) as the line of maximum two-dimensional compressibility in the prewetting supercritical single-phase region. This interpretation is supported by a recent Monte Carlo simulation investigation of the prewetting supercritical phase [12].

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