Prewetting Transitions in a Near-Critical Metallic Vapor

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Velocity of sound measurements at 10 MHz in near-critical liquid and vapor mercury up to supercritical temperatures and pressures of 1900 K and 1800 bars, respectively, demonstrate the existence of a wetting transition on the walls of molybdenum and niobium cells at $T_W \simeq 1250$ K, together with an associated first-order *prewetting line* in the dense mercury vapor that terminates at a prewetting critical point $(T_{c,\mathrm{pre}}, p_{c,\mathrm{pre}}) \gtrsim$ (1860 K, 1830 bars) lying *above* the bulk mercury critical point at $(T_c, p_c) =$ (1764 K, 1670 bars). [S0031-9007(97)02507-6]

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When a bulk fluid system in the vapor phase near the gas-liquid coexistence pressure $p_\sigma(T)$ approaches a critical point T_c, rather general arguments [1,2], following the initial predictions in 1977 [3], demonstrate that the walls of the container, if not already wet at low temperatures [4], should undergo a first-order *wetting transition* at a temperature $T_W < T_c$. Below T_W the walls, even just at coexistence $p = p_\sigma(T)-$, are covered with at most a microscopically thin layer of the liquid phase; at T_W the thickness $l(T, p)$ of the adsorbed layer jumps discontinuously and, thereafter, becomes *macro*scopically thick when the coexistence curve is approached, $p \to p_\sigma(T)-$ (the actual thickness being determined by gravity and other large-scale constraints). Theory then dictates [1,2] that the first-order wetting transition at coexistence must be associated with a *prewetting line,* $T_{\mathrm{pre}}(p) \geq T_W$ [or $p_{\mathrm{pre}}(T) \geq p_\sigma(T_W)$], that lies wholly in the vapor phase $[p < p_\sigma(T)]$ and terminates in a *prewetting critical point* at $(T_{c,\mathrm{pre}}, p_{c,\mathrm{pre}})$ that is quite distinct from the bulk critical point at $T = T_c, p = p_c \equiv p_\sigma(T_c)$. When the prewetting line is crossed, the equilibrium thickness of the adsorbed layer jumps from a low value "below" the prewetting line to a higher value "above" the line (i.e., closer to coexistence). Since this thin-to-thick film transition is of first order, hysteresis effects are to be anticipated. The analogous phenomena should arise in fluid mixtures and many other systems.

Although wetting transitions in single-component fluids and liquid mixtures were observed soon after the original predictions [3], the prewetting line itself proved elusive for many years. However, in 1992 it was found at low temperatures using a quartz microbalance in helium adsorbed on a cesium substrate [5] and in 1993 in hydrogen on rubidium [6]. Also in 1993 it was observed at room temperatures by ellipsometric techniques in the adsorption of the methanol-rich phase of a methanol-cyclohexane mixture on the vapor-liquid interface [7].

Here we report the first observation, by a technique not previously used, of wetting transitions and prewetting lines at high temperatures in a metallic vapor on metallic substrates. Specifically, by direct velocity of sound measurements a wetting transition has been found at $T_W \simeq 1250$ K in mercury vapor contained in molybdenum and in niobium cells. The metallic nature of both the dense fluid and the solid substrates preclude the usual optical techniques [7,8]. The associated prewetting lines extend *above* the critical point of mercury (located at $T_c \simeq 1764$ K and $p_c \simeq 1670$ bars [9]); see Fig. 1, which summarizes our observations in a molybdenum cell. The *prewetting critical point* is located at $T_{c,\mathrm{pre}} \gtrsim 1860$ K and $p_{c,\mathrm{pre}} \gtrsim 1830$ bars; the corresponding bulk density, $\rho_{c,\mathrm{pre}} \simeq 3.8$ g/cm^3, lies well below the critical density $\rho_c \simeq 5.8$ g/cm^3 [10].

As regards the *bulk* (or wall-independent) features of the phase diagram shown in Fig. 1, note that the $\rho = 9.0$ g/cm^3 isochore may be identified as the locus of the metal-nonmetal transition—actually a steep, but smooth and continuous crossover—as traced by electronic and other properties [11,12]. Near the *critical isochore* above T_c one finds anomalies in thermopower [13] and other features [9,14].

Our own study of the wall-dependent features originates in observations [15] of abnormal behavior of the velocity of sound in mercury vapor near saturation at high pressures. Anomalies in the thermopower [10(b),13] and optical reflectivity against a sapphire window [8] had been seen previously in the same region of the phase diagram. The sound velocity data [15] suggested a *second locus* of first-order transitions occurring in the bulk vapor for pressures $p \gtrsim 1000$ bars and at temperatures 50–60 K above the true vapor pressure line $p_\sigma(T)$. It was proposed

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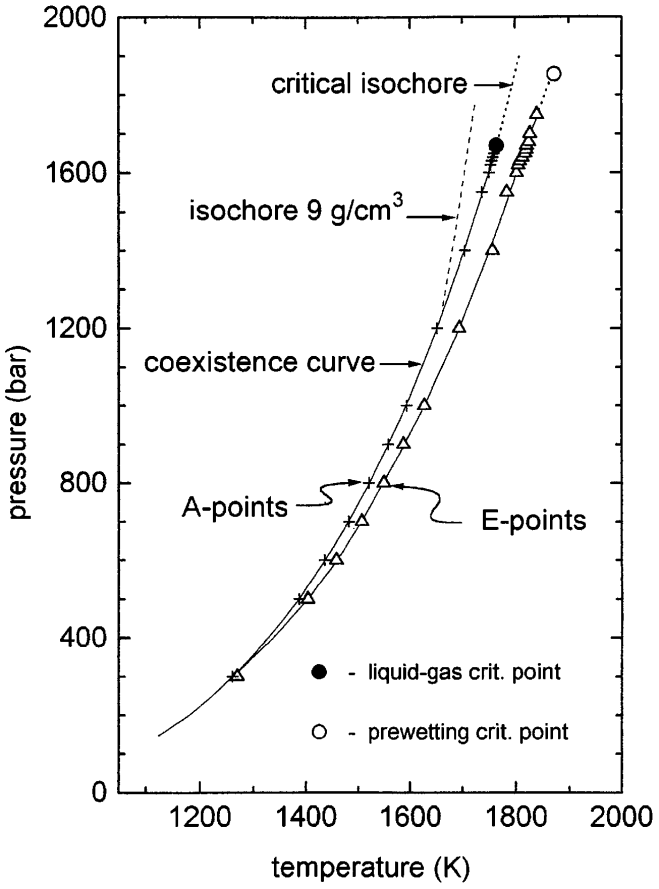

FIG. 1. The phase diagram of mercury in contact with a molybdenum wall: The locus of A points represents the bulk gas-liquid phase boundary $p_\sigma(T)$ or vapor pressure curve; the locus of E points marks the *prewetting line* which meets the phase boundary at $T_W \simeq 1250$ K (see Fig. 2).

tentatively [15] that this second locus might represent the sharp, first-order, so-called plasma phase transition predicted by Norman and Starostin [16]. Essentially the same interpretation had been offered previously for the optical data [8]. However, despite earlier suggestions to the contrary [17], there are no longer serious theoretical grounds for believing that, in a metallic vapor or simple ionic model, this "plasma transition" can be anything other than the bulk gas-liquid transition itself [18,19] (which is not directly related to the metal-insulator crossover).

If the second transition locus is not a property of bulk mercury it is most naturally associated with the walls of the container, in particular, with the *inner faces* of the two 18 cm long, 1 cm diameter, coaxial, cylindrical *buffer rods* that, with the cylindrical side walls, form the sample cell of height about 2.1 mm [9,15]. These buffer rods serve to transmit, reflect, and receive the 10 MHz pulses used in the precision phase-sensitive sound-velocity measurements [9,15]. The original [15] and recent, more extensive experiments [9] used *molybdenum* buffer rods and cell walls, but if wetting phenomena are involved, some dependence on the walls/substrate should be seen. Indeed, following further experiments and analysis, Yao and Hensel [20] have recently reinterpreted their reflectivity data [8] as demonstrating wetting and prewetting of mercury on *sapphire* with $(T_{c,\mathrm{pre}}, p_{c,\mathrm{pre}}) \simeq (1741\ \mathrm{K},\ 1586\ \mathrm{bars})$ lying *below* the bulk critical point [21,22]. Correspondingly, as reported here, we have undertaken new sound-velocity experiments in a *niobium* cell. The data, presented in Figs. 2 and 3, strongly support the wetting scenario, resembling the molybdenum experiments [9], but with slight changes as expected. Furthermore, in the extended Mo study [9] a smooth coalescence of the A and E points was found as the pressure dropped to $p \simeq 300$ bars; see Fig. 1, where the data for $p = 500$, 700, and 900 bars have not been previously reported. This observation accords with the theoretical requirement that a prewetting line must meet the bulk gas-liquid phase boundary *tangentially* at the wetting transition point $T = T_W$ [2,21].

Our new Nb cell was held vertically and had the same design used previously [9,15]; in particular, the upper buffer rod and cell body were made of one piece. The lower rod was inserted into the cell body and sealed in place. The vertical orientation and absence of clearance between cell body and upper rod are important. Preliminary studies employed Mo cells of standard construction with two inserted buffer rods, held both horizontally and vertically. In the interesting (p, T) region strong instabilities arose which precluded precise data taking. (Possibly related variations have been seen in a horizontal sapphire cell with two inserted rods [14].) We believe these effects

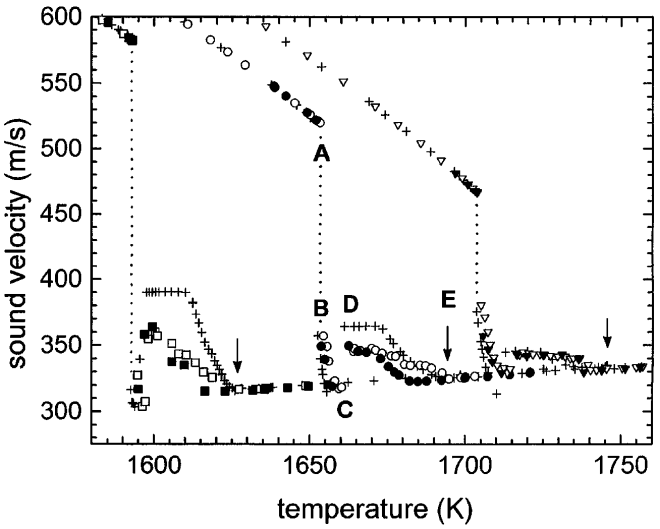

FIG. 2. The sound velocity of mercury observed in a niobium cell at pressures of 1000, 1200, and 1400 bars (squares, circles, and triangles) on heating (open symbols) and cooling (solid symbols). The crosses represent corresponding data for a molybdenum cell. Characteristic points seen on most isobars have been named $A, \ldots, E$ but, for clarity, are marked only on the 1200 bars isobar. The E points (see arrows and text for further details) locate the prewetting transition.

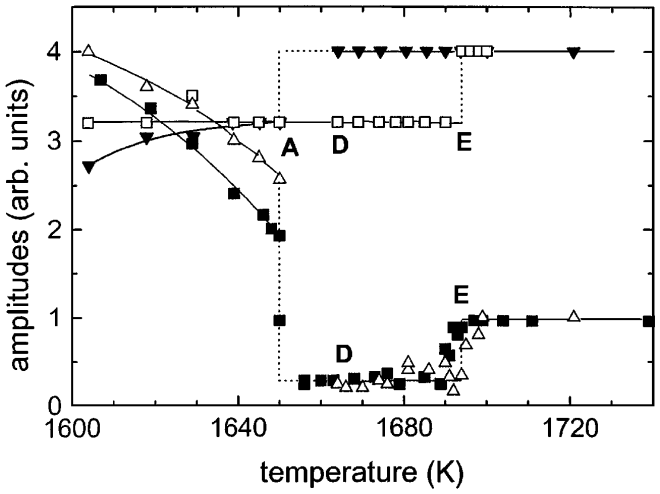

FIG. 3. Amplitudes of the acoustical signals on heating at $p = 1200$ bars: (a) *transmitted* through the Mo cell (solid squares) and Nb cell (open triangles) and (b) *reflected* in the upper (solid triangles) and lower (open squares) Nb buffer rods. Points *A*, *D*, and *E* correspond to Fig. 2.

reflect convective flows arising near the boiling (i.e., vaporization) points and, possibly, instabilities of the dense prewetting layer on the vertical walls.

The cell was surrounded by a sectioned Mo wire heater and mounted in a high-pressure bomb filled with argon as the pressurizing fluid. Although the outer faces of the buffer rods (which carry the sound transducers) must be kept relatively cool, the temperature variation measured vertically across the sample amounted to no more than 2–8 K and correlated well with the observed $(T_C - T_B) \simeq (T_C - T_A)$ intervals (see Fig. 2); no more than 2 or 3 K radial variation was seen. Further details of the design and measurement techniques are given in [9]. The Hg impurity levels ($\sim 10^{-4}$ wt %) were not changed by the experiments.

The present Nb data were collected by both heating and cooling at fixed pressures of 1000, 1200, and 1400 bars. About 5–10 min were spent on each measurement; thermal time constants of <10 s were observed. Typical results for the sound velocity (of optimal precision 0.4%) are shown in Fig. 2 together with corresponding Mo data (crosses) [9]. The isobars at 1000 and 1200 bars were measured twice: Reproducibility is within 1 K for the bulk boiling points, named "*A*" in the figures. Beyond *A* the data display features labeled *B*, *C*, *D*, and *E*.

To obtain further information about the state of the sample, the amplitudes of the reflected and transmitted signals in the buffer rods have now also been recorded (with moderate precision) [23]; the data in Fig. 3 are typical. Marked variations imply changes in the sound impedance of the sample media and/or of layer thicknesses. Data for the *BC* intervals (see Fig. 2) are absent in Fig. 3 because the signals become unstable, oscillating erratically in strength. Correspondingly, the velocity data in this region have lower precision, say $\pm 3\%$.

Now, in Fig. 3, note that the reflected amplitude in the lower buffer rod (open squares) jumps sharply at *E;* the *E* points are thus located rather precisely as recorded by the arrows in Fig. 2 and triangles in Fig. 1. Furthermore, for $T > T_E(p)$ all data vary smoothly up to the highest temperatures studied ($T \simeq 2060$ K; see [15]). This behavior must characterize bulk mercury vapor beyond (or below) any prewetting line with, one may presume, only a *thin* liquidlike layer on the walls of the cell. But, as we will see, interpreting the *A*-*E* data convinces one that $T_E(p)$ actually represents the *prewetting line* on which a *thick* wetting layer can coexist with the thin layer.

Consider, first, the *ABC* section where we believe the sample consists of liquid and vapor at saturation pressure but not in full equilibrium, the extent and variability of this region being due to the temperature gradients across the sample mentioned above. Near the *C* points the last, more-or-less compact drops of saturated liquid evaporate and a thick wetting layer grows, becoming established at *D*. The change in effective sound velocity from *C* to *D* accords with this picture [24]. Vapor then makes up the bulk of the sample.

On heating above *D*, the thick wetting layer should, at equilibrium, thin down continuously. This agrees with (i) the decrease in the observed velocity, (ii) the steady reflected amplitudes, and (iii) the much smaller transmitted signal, attributable to enhanced wetting layer losses (see Fig. 3). If the velocity of sound in the wetting layer is similar to that observed in the bulk liquid [7(b)], the data suggest a thickness of order 0.1 mm on the face of the lower buffer rod. However, this is likely to represent a major overestimate of the true equilibrium layer thickness $l(T, p)$; rather, such a thick layer probably results from a *dynamic* equilibrium established by thermal inhomogeneities and driven by gravitationally induced shedding of the wetting layer off the relatively warmer vertical cell walls to accumulate on the lower buffer-rod face where it then boils off. On the other hand, the signal amplitudes in the upper buffer rod are consistent with wetting layer thicknesses of order 100 Å [25].

Finally, in an interval of 5 K or so, on approach to the *E* point, the sound velocity drops more abruptly (Fig. 2), while the transmitted amplitude becomes erratic (Fig. 3) and then rises to a steady value; the reflected amplitude in the lower buffer rod jumps sharply, as noted, but that in the upper rod changes little. We believe these signals, observed in similar form up to supercritical pressures, mark the nucleation of the thin wetting layer on heating through the prewetting transition. On cooling the high-temperature vapor through the transition from *E* to *A* some hysteresis is seen (Fig. 2) which supports the first-order nature of the prewetting transition: Its near absence when

$p = 1400$ bars may be a consequence of the temperature inhomogeneities.

In conclusion, while various aspects of the acoustical anomalies remain to be understood in fuller detail [7(b)], the experiments in the niobium and molybdenum cells provide convincing evidence of wetting phenomena in near-critical mercury vapor with, in particular, a well defined prewetting line leaving the bulk vapor pressure boundary around $T_W \simeq 1250$ K and terminating in a prewetting critical point at $T_{c,\mathrm{pre}} \gtrsim 1860$ K. More precise estimates of the prewetting critical point require further high-T experiments (where the niobium cell presents technical problems). Future studies should also address other substrates although, owing to the extreme conditions, the options are limited.

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