Nonwetting of Cesium by Neon near Its Critical Point

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We report quartz crystal microbalance measurements of the adsorption of neon on surfaces of cesium and rubidium at temperatures up to the critical point of neon. In the case of Ne/Rb there is little adsorption until the temperature approaches 0.97 of T_c, where a wetting transition occurs. In the case of Ne/Cs no adsorption is seen all the way to $T = T_c$. Instead our data suggest the presence of a vapor film adjacent to the Cs surface when the sample cell is filled with liquid. This may indicate a crossover from wetting to drying. [S0031-9007(97)02427-7]

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In 1977 Cahn [1] predicted that wetting transitions should be a general phenomenon in systems which are not wet at low temperature. In 1991 the first observation in a physisorption system of a wetting transition not tied to a bulk phase transition [2], and the associated prewetting transition [3,4], was made in the system ^{4}He on Cs, following the explicit prediction of Cheng *et al.* [5]. Taborek and Rutledge [4] determined the wetting temperature T_w of ^{4}He on Cs to be 1.95 K. When the cesium layer deposited on the gold electrode of their quartz crystal microbalance was reduced to a few atomic layers, these authors found a significant reduction of T_w [6]. The calculated potential well depth of such a composite substrate is intermediate between that of Cs and Au [7]. This result, and the finding that $T_w = 0.31$ K for ^{4}He/Rb [8], confirms the expectation that a stronger substrate tends to move T_w towards $T = 0$ and a weaker substrate will push T_w toward T_c, the liquid-vapor critical point of the adsorbate. Cahn [1] showed that, in mean field treatment of a model with short-range interactions, wetting always occurs at some temperature below T_c, or alternatively, if the substrate is sufficiently weak, a symmetrical "drying" transition occurs on the liquid side of the coexistence line, in which a vapor layer of diverging thickness is interposed between the substrate and the bulk liquid. More recent theoretical treatments which include long-range interactions have found that wetting and especially drying behavior near T_c depends on a subtle interplay between short-range and long-range interactions [9–11].

One way to quantify the strength of a substrate/adsorbate pair is to compare the well depth D of the adsorbate molecule-substrate potential with the well depth ε of the molecule-molecule potential. For ^{4}He/Cs the ratio D/ε is 0.40 [12], which may be compared to the value 8.4 for ^{4}He/Au [13], for which wetting occurs from $T = 0$. The systems Ne/Rb and Ne/Cs are estimated to have ratios D/ε of 0.30 and 0.25, respectively, making them the weakest substrate cases available [13]. Thus they are promising systems for investigation of wetting behavior near T_c.

In this Letter we report measurements of the adsorption of neon on cesium and rubidium, using the quartz crystal microbalance (QCM) technique [14]. The sensor is a beveled plano-convex AT-cut quartz crystal designed for and used in the third-overtone thickness shear mode near 10 MHz. The crystal is 1.41 cm in diameter, with a 0.80-cm-diam gold electrode deposited in the center of each side. Adsorption is indicated by a reduction in resonant frequency due to mass loading, with a sensitivity of approximately -5 Hz per monolayer of liquid neon near the triple point. Our crystal is mounted in a vertical plane in the center of a thick-walled copper cell. In this configuration, gravity will smear critical singularities within 0.04 K of T_c. For our principal measurements, a layer of cesium approximately 1.9 μm thick was evaporated over the gold electrodes.

Because adsorption in the neighborhood of the critical point is of interest, the ambient vapor may approach liquid density, and its effect in loading the crystal vibration must be taken into account. Motion of the surface drives a damped shear wave with viscous decay length $\delta = (2\eta/\rho\omega)^{1/2}$, where ρ is the density and η is the viscosity of the ambient fluid and $\omega = 2\pi f$ is the angular frequency. With nonslip boundary condition, this leads to a shear stress on the solid surface with equal components of inertial and dissipative loading. These cause a reduction in resonant frequency and a reduction in Q of the resonator, respectively, which are given by [15–17]

$$-\Delta f = (f/2)\Delta Q^{-1} = (2f/n\pi R_q)(\pi f\eta\rho)^{1/2}, \quad (1)$$

where $R_q = 8.86 \times 10^6$ kg m^{-2} s^{-1} is the acoustic impedance of quartz and $n = 3$ is the overtone number.

If there is adsorption of a liquid film on the surface of the microbalance, then there will be an additional frequency shift, given by

$$-\Delta f = (4f^2/nR_q)\sigma\,, \quad (2)$$

where σ is the mass per unit area adsorbed on each side of the crystal.

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A frequency synthesizer is locked to the series resonance of the crystal by a high-frequency lock-in amplifier, which monitors the reactive component of the electrical transmission of the crystal and shifts the synthesizer frequency to null this component, after an offset is applied to cancel the contribution of shunt capacitance. During measurement of an adsorption isotherm, the resonant frequency and transmitted amplitude (hence the Q of the resonance) are monitored, together with the cell temperature and the pressure. The rf power input to the crystal was typically 60 nW or less.

The cell is cooled by a closed-cycle refrigerator and is temperature regulated using a silicon diode thermometer. The cell temperature is monitored by a separate platinum resistance thermometer, which is calibrated against the saturated vapor pressure of neon. Pressure is measured at the room temperature end of the 0.16-cm-i.d. filling tube by a quartz pressure transducer, which has a precision of 0.01 psi and an accuracy better than 1 psi (7 kPa). Gas is admitted to (or withdrawn from) the cell in measured doses, after which the perturbation to the cell temperature is allowed to relax. All measured frequencies are corrected for a hydrostatic shift of 0.99 Hz/psi (0.144 Hz/kPa), determined by measurements in helium gas with allowance for the viscous drag effect.

Figure 1(A) shows a QCM isotherm at 36.6 K for neon on the gold electrodes before evaporation of an alkali film. Both the (negative) frequency shift and the quantity $(f/2)\Delta Q^{-1}$, which we will call the "loss," are plotted. The solid line is the homogeneous fluid contribution to the frequency shift and the loss, calculated with Eq. (1), using interpolated density and viscosity data from Ref. [18]. It is apparent that the loss is in good agreement with Eq. (1), while the frequency shift is larger, showing the effect of adsorption, Eq. (2). This adsorption contribution extrapolates to 58 ± 5 Hz at saturation. Considering the difference between liquid and vapor density at this temperature, this corresponds to a film thickness of 7.6 nm (14 layers). For comparison, the viscous decay length for saturated liquid (vapor) at this temperature is $\delta = 37$ nm (53 nm). Thus the adsorbed layer is effectively localized at the surface and should contribute almost solely to inertial loading, as assumed.

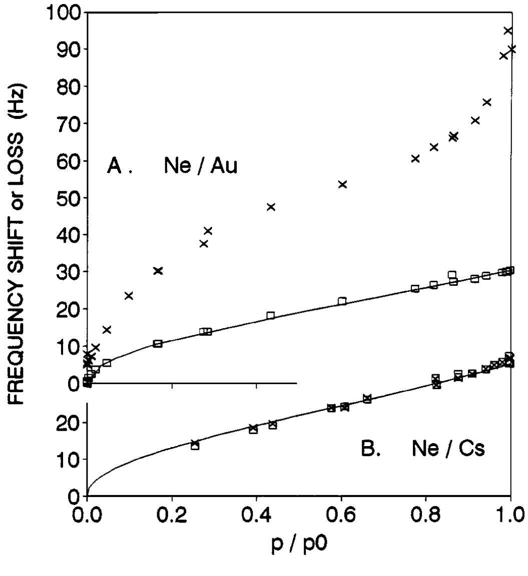

FIG. 1. Isotherms for (A) Ne/Au at 36.6 K, and (B) Ne/Cs at 38.5 K. The symbol × represents the (negative) frequency shift and □ represents the quantity $(f/2)\Delta Q^{-1}$, which we call "loss." The solid line is the expected contribution to each due to uniform ambient vapor, as calculated from Eq. (1). For Ne/Cs, the near equality of frequency shift and loss indicates the absence of any adsorption. For Ne/Au, the excess negative frequency shift is a measure of the amount of neon adsorbed, by Eq. (2). p_0 is the saturated vapor pressure.

Figure 1(B) shows a QCM isotherm at 38.5 K for neon on cesium, where the symbols have the same meaning as in Fig. 1(A). In this case the frequency shift as well as the loss is consistent with Eq. (1), which represents the ambient vapor contribution alone. That is, there is no measurable adsorption at any pressure up to saturation. The effective zero of frequency shift is uncertain by about 5 Hz, due to anomalous behavior at very low pressures where the vapor mean free path is large. Including this uncertainty, the upper limit to the adsorption at this temperature is one layer. Computer simulations by Bojan *et al.* [13] using realistic potentials for Ne on Cs and Rb find negligible adsorption at all temperatures below $T_c - 2$ K.

In order to look for a wetting (or drying) transition, we measured isotherms at several higher temperatures approaching the critical temperature (44.4 K). These are shown in Fig. 2, where now the difference between the measured frequency shift and the measured loss is plotted. This difference should represent the excess mass localized near the surface due to adsorption. The data in Fig. 2 show

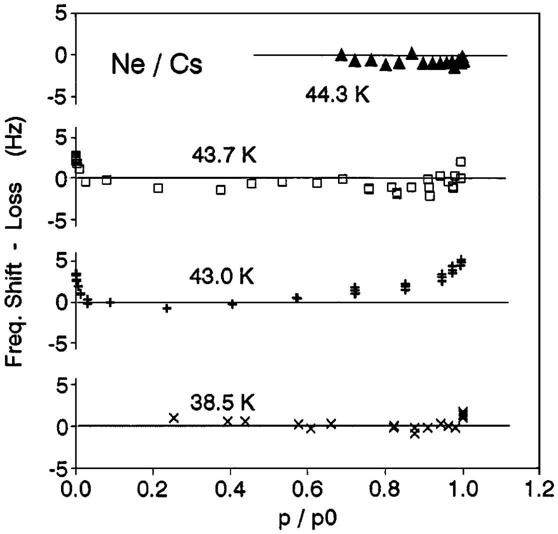

FIG. 2. Adsorption of Ne on Cs (measured by the difference between frequency shift and loss) as a function of reduced pressure. p_0 is the saturated vapor pressure. These plots show the continued absence of adsorption as T is increased toward the critical temperature on neon, $T_c = 44.4$ K.

no evidence of any significant adsorption at 43.0, 43.7, or even at 44.3 K (0.998 of T_c).

We have also studied neon adsorption on rubidium by the same technique. The rubidium evaporation (of 340 nm mean thickness) apparently formed a granular film, as indicated by a pattern left on the gold after warmup and by a large excess loading when immersed in liquid neon, which we attribute to roughness. The contributions of random roughness to frequency shift and to loss depend on the root-mean-squared height h and the lateral correlation length ℓ to the roughness and on the ambient fluid properties [19]. We assumed a value for h to fit our loading data for the cell filled with liquid and used this to correct the data in the vapor region. If ℓ is large compared to δ, this amounts to scaling the roughness contribution to loading in proportion to the ambient bulk density. We interpret the remaining surface-excess mass as adsorption, as in the case of gold. Portions of some of the corrected isotherms showing the approach to saturation are shown in Fig. 3. It appears that wetting begins between 42.96 and 43.44 K, i.e., 1.2 ± 0.3 K below T_c. We cannot identify prewetting steps.

Several isotherms for neon on gold and cesium were extended beyond the liquid-vapor coexistence pressure, where the cell is completely filled with liquid. Figure 4 shows such isotherms at 43.0 K for neon on gold and on cesium. The solid line is the calculated uniform fluid contribution to the frequency shift and to the loss, given by Eq. (1). For gold the measured frequency shift in the liquid region is about 35 Hz larger and the loss about 17 Hz larger than predicted. A frequency shift of about 11 Hz is expected due to compression of the liquid by substrate attraction [17,20], while roughness should contribute less than 1 Hz. Any surface-normal motion associated with the resonant mode would radiate short-wavelength longitudinal sound and contribute predominantly to loss. We have not identified the cause of the remaining deviations.

For liquid neon on cesium the frequency shift is about 50 Hz *below* the uniform fluid prediction, and the loss is about 16 Hz below. Very similar results were obtained at 38.5, 43.7, and 44.3 K. This implies a partial decoupling of the liquid neon from the cesium surface, which could be due to a slip boundary condition or to slip across a (partial) drying layer.

In a partial drying situation, a layer of neon of vapor density, favored by the short-range interaction, intervenes between the cesium wall and the liquid neon. This will reduce the frequency shift from its uniform-liquid value because of the reduced density of the vapor layer and because its lower viscosity reduces the coupling to the liquid beyond. We have evaluated the expected frequency shift with a uniform slab of vapor adjacent to the substrate of thickness equal to the critical correlation length, which we take to be $(0.16\ \mathrm{nm})t^{-\nu}$, where $t = |T - T_c|/T_c$ and $\nu = 0.63$. The result is not strongly temperature dependent over the experimental range, due to competing effects of vapor density and layer thickness, but the reduction is about twice as large as is observed (see Fig. 4). If there

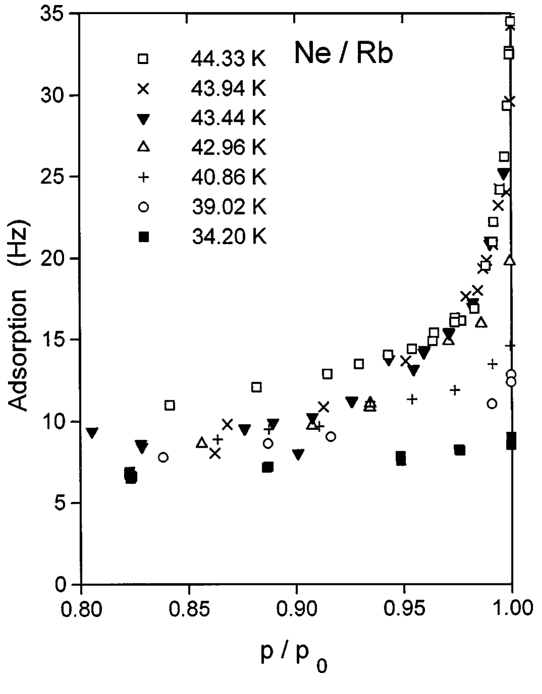

FIG. 3. Adsorption isotherms of Ne on Rb at several temperatures. The ordinate is the difference between frequency shift and loss, with a correction for the contribution due to surface roughness. These plots indicate incomplete wetting for $T \leq 42.96$ K and wetting growth for $T \geq 43.44$ K.

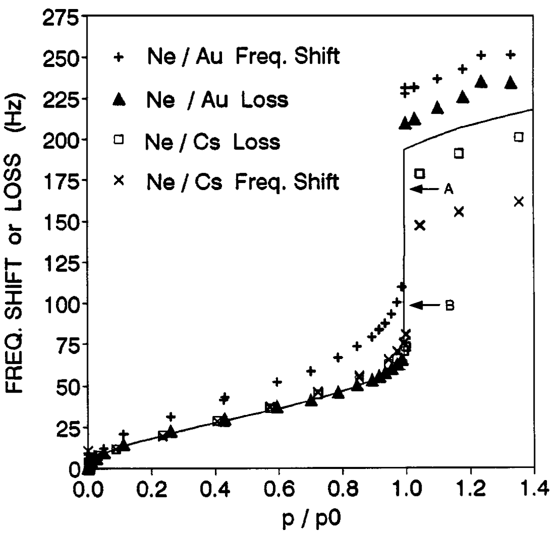

FIG. 4. Frequency shift and loss as functions of reduced pressure, for Ne on Au and Ne on Cs at 43.0 K. The solid line is the expected contribution due to homogeneous ambient fluid, which is vapor on the left and liquid on the right. The frequency shift and loss data for the liquid Ne/Au system lie above the solid line, while for liquid Ne/Cs they lie below. Compression of the liquid by attraction to Au accounts for part of the positive deviation. The negative deviation suggests the presence of a vapor layer adjacent to the Cs surface. Arrows (*A*) and (*B*) indicate the loss and frequency shift calculated for a simple model of a drying layer, described in the text.

is an anomalous contribution as for gold, this would reduce the discrepancy. The calculated reduction in loss is comparable to the experimental reduction. Below about 44.0 K this model is equivalent to a slip boundary condition with a temperature-dependent slip length of order 11 nm. A slip boundary condition might be appropriate at a microscopically smooth interface even in the absence of a drying layer [21]. However, the appropriate theoretical treatment is a matter of current controversy [22]. A hydrodynamic experiment cannot easily distinguish whether slip is due to drying. However, if the slip is unrelated to drying, it will be necessary to understand why it should set in rather sharply as the density is increased in the neighborhood of the critical density.

In conclusion, while neon wets rubidium approximately as predicted by simple models [13,23], there is no measurable adsorption of neon on cesium at any temperature up to the critical temperature. Neon/cesium is the weakest known physisorption system, in terms of well depth ratio D/ε [13]. Although the long-range van der Waals force favors wetting, a sufficiently small D/ε can lead instead to partial drying on the liquid side of the coexistence line; then the diverging correlation length will produce complete drying exactly at T_c [10]. For the cesium surface in liquid neon we found a negative surface excess mass, which may be plausibly understood as decoupling from the ambient liquid by slip across a partial drying layer. The relatively small difference in interaction with neon between rubidium and cesium surfaces leads to a dramatic change in adsorption behavior and suggests a possible crossover from wetting to drying. Nonhydrodynamic experiments may be necessary to confirm the occurrence of drying.

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