Triple-Point Wetting of Light Molecular Gases on Au(111) Surfaces

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Wetting characteristics of Ar, Kr, Xe, N_2, O_2, methane, and ethane adsorbed on Au(111) have been determined with a high-frequency microbalance. All gases form incompletely wet films below their bulk triple points and completely wet films above. The transitions to complete wetting are continuous, the maximum thicknesses of the layered films below T_t varying as $(T_t - T)^{-1/3}$.

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The growth characteristics of multilayer films adsorbed on solid surfaces are exciting considerable interest. Two basic forms of growth are observed: In "type-1" systems the film thickens monotonically as the pressure increases, remaining uniformly flat up to infinite thickness, reached at the pressure P_0 of coexistence with the bulk phase. Such films are "completely wet" at coexistence. In "type-2" systems the film is uniform only up to a finite thickness at $P < P_0$, bulk phase forming abruptly at P_0. These films are "incompletely wet" at coexistence. If type-2 growth occurs, its domain is expected to be at relatively low temperature. A transition to type-1 growth may then occur at a "wetting temperature" T_W lower than the bulk critical temperature. Systematics of wetting behavior and the theoretical dependence on relative magnitudes of molecule-molecule and molecule-substrate interactions are described by Pandit, Schick, and Wortis,[1] where discussions of earlier work are presented. The low-temperature wetting characteristics of several gases on graphite substrates have been reported.[2,3] Crossovers between complete and incomplete wetting on graphite have been observed in ethylene[4] and carbon tetrafluoride.[5] Some observations have been made of type-2 behavior in molecular films on substrates other than graphite,[6] but little is known about their wetting temperatures or the nature of their wetting transitions. The present study reports the behavior of several gases on Au(111) surfaces, incuding the type of low-temperature growth, wetting temperatures, and nature of the transitions.

Recent high-energy electron-diffraction studies on a series of light molecular gases by Sequin *et al.*[2] and Bienfait *et al.*[3] discovered that complete wetting on graphite at low temperature is restricted to Ar, Kr, and Xe, whose relative interaction strengths fall within a limited range, and that type-2 behavior is reentrant at weaker and stronger potentials. Reentrant wetting is predicted by Ebner, Rottman, and Wortis[7] on the basis of a lattice gas model, and by Gittes and Schick[8] and Muirhead, Krim, and Dash[9] for molecular gases. The generality of the proposed wetting diagram[3] can be tested by studying growth in a series of gases on surfaces with substrate-molecule potentials appreciably different from that of graphite. If the dominant parameter determining low-temperature growth is the ratio of interaction strengths and the type-1 region is very narrow, then adsorption on weaker or stronger substrates should cause most or all of the gases, including Ar, Kr, and Xe, to shift into one or the other of the type-2 regions. Such a test was the primary motivation for this study.

High-frequency microbalances have been used as thickness monitors in the preparation of evaporated metal films and in adsorption studies.[10,11] The resonant frequency of a crystal oscillating in its thickness shear mode is lowered by mass loading, the frequency shift Δf being proportional to the mass deposited, for $\Delta f \ll f$. Previous applications to physisorption have shown sensitivities adequate to detect coverage changes of less than a monolayer of light molecules. In our study the frequency of 10-MHz AT-cut quartz was compared with a similar reference crystal held at constant temperature. Isotherms were obtained from continuous recordings of frequency and vapor pressure as gas was slowly admitted to the crystal chamber. The flow rates could be adjusted to give total isotherm times from a few minutes to several hours: Except for the shortest times we observed no transitory effects due to nonequilibrium conditions. The cell temperatures were controlled between 4 and 170 K to within 0.01 K by a thermal link to cooling baths and by a cell heater. Frequency drift at constant coverage and pressure ranged from 0.01 to 0.1 Hz/h, equivalent to a coverage change of less than 3 $\times 10^{-3}$ monolayer of Kr during the typical time required to complete an isotherm. High excitation voltages produced noticeable crystal heating, but operating conditions were always set well below these levels.

The Au adsorption substrates also served as the oscillator electrodes. The Au(111) surface is technically convenient, being chemically inert and preferred as the exposed facet. This surface is also extremely smooth, molecular scattering measurements showing that the effective corrugation is $\ll 10^{-2}$ Å.[12] The Au was evaporated from 99.999+% purity sources, deposited directly on the quartz at rates 1–2 Å/s to thicknesses of about 1500 Å at residual gas pressures $\sim 10^{-9}$ Torr. This procedure can produce polycrystalline Au films with (111) faces parallel to the substrate.[13,14] We confirmed the orientation by x-ray diffraction. Cleanliness was checked by Auger spectroscopy, and grain size estimated from x-ray diffraction and electron microscopy. An estimate of surface uniformity was obtained from isotherm step sharpness (see below). After evaporation the plated crystals were quickly transferred to the cryostat cell, pumped to 10^{-9} Torr, and baked at 300 °C for several hours. After installation a crystal could be kept for several weeks and used for many isotherms without evidence of surface degradation.

The gases were high-purity Ar, Kr, Xe, N_2, O_2, C_2H_6, and CH_4. Isotherms were taken over a range of temperatures for each, below and above their bulk triple points T_t. The experiments were repeated on numerous crystals and Au platings. On the most carefully prepared surfaces, rounded steps could be observed at low temperatures, indicating the formation of two successive solid layers. The nonverticality of the steps, amounting to a half-width of 15% of P in the second step of Xe at $T = 0.6T_t$, may be due to the limited terrace width on the Au surface. On this basis we estimate the mean terrace width to be 140 Å.[15] Although step rounding can obscure important features of the phase changes in the layered films, we saw no evident differences of wetting characteristics of films on any of the Au substrates: Even on evidently poor platings, where no isotherm steps could be discerned, the growth types, thicknesses, and wetting temperatures agreed with those on the best surfaces. Typical isotherms are shown in Fig. 1, presenting a series for Kr below its triple point. Several features are significant. The layer steps indicate that the critical thickness is two layers at low T. The film thickens gradually with P up to P_0, where it increases abruptly, indicating condensation of bulk phase. Isotherms at higher

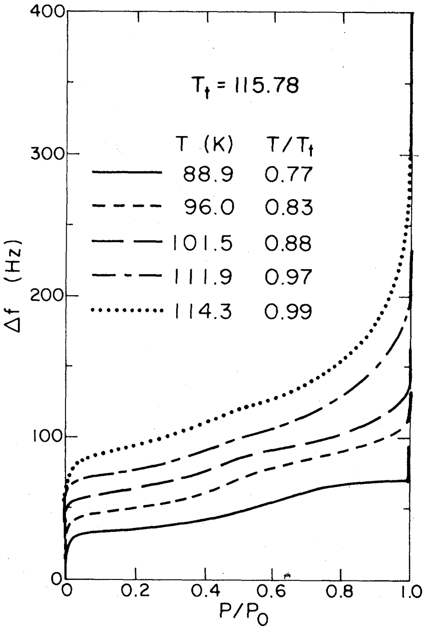

FIG. 1. Adsorption isotherms of Kr on Au(111) below its triple point. For clarity, successive curves have been shifted upward by 13 Hz.

temperatures have progressively more rounded steps and higher intercepts at P_0. Near T_t there is little remanence of steps but the frequency always rises abruptly at P_0, even at $T/T_t = 0.992$.

The character of all isotherms above T_t is qualitatively different from those below. There is no indication of finite intercepts, n tending to infinite thickness at P_0. We observed similar behavior throughout this domain, with measurements to $T/T_t = 1.003$.

The high-temperature data were compared to the expected relation $n = [(kT/\alpha)\ln(P_0/P)]^a$ for the thickness n of a uniform-density structureless film on a substrate with long-range attraction characterized by α.[1] In Fig. 2 we see that the empirical exponent $a = -\frac{1}{3}$, which is ascribed to the z^{-3} long-range dependence of van der Waals potentials. The asymptotic trend of the data to infinite thickness at P_0 shows that all of the films are completely wet at $T > T_t$. Values for α are appreciably above those for adsorption on graphite, ranging up to a factor of 2 for Xe.

The data show that the transition is at or very close to the triple point for all of the gases. More precise measures of T_W and a determination of the nature of the transitions are made by examining the maximum thickness n_c of uniform film at coexistence, as a function of $T_t - T$. Figure 3 presents a semilogarithmic plot, showing

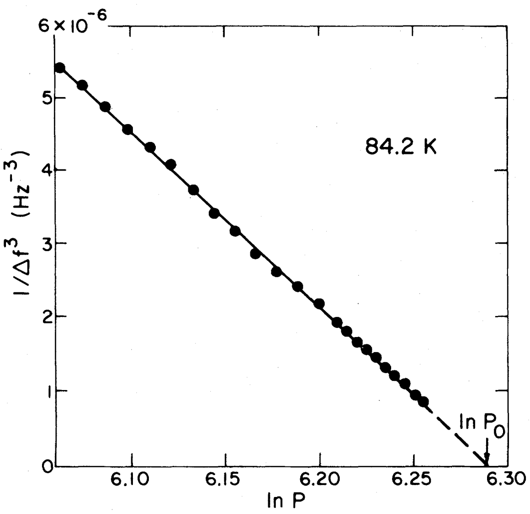

FIG. 2. Adsorption of argon on Au(111) above its triple point.

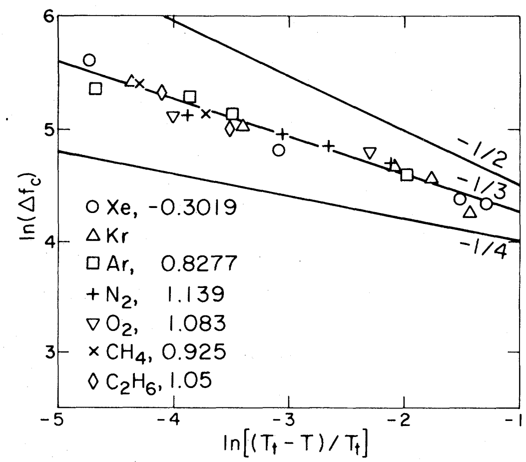

FIG. 3. Temperature dependence of the frequency shifts at critical thickness of type-2 films on Au(111). T_t is the triple point temperature of each adsorbate. For illustration, the data set for each gas was shifted vertically by a constant. The data are compared with power-law exponents $-\frac{1}{2}$, $-\frac{1}{3}$, and $-\frac{1}{4}$.

that n_c for all of the gases follows a power law

$$n_c = A[(T_t - T)/T_t]^{-1/3}, \qquad (1)$$

where A is a constant specific to each gas. This analysis shows that $T_w = T_t$ generally, and that the transitions are continuous.

The exponent of the temperature factor arises directly from the range dependence of the substrate potential. The empirical Eq. (1) can be derived from thermodynamics and simple assumptions as to the nature of the film and the bulk phase diagram. The substrate potential is assumed to vary as z^{-3}, as in the type-1 films. The bulk solid phase does not wet the substrate, but the liquid does. The disappearance of layer steps near T_t indicates that the film is liquidlike; hence coexistence is approached through a wetting phase. The isotherms in this range of T should then begin as in type-1 adsorption, with virtual saturation pressures P_0' corresponding to bulk liquid. The actual saturation $P_0(T)$ is reached before P_0', causing the abrupt formation of solid. We obtain $P_0'(T)$ by extending the liquid vapor pressure line below T_t, by a first-order expansion in T. The result is Eq. (1), with coefficient

$$A = \left[\frac{\alpha/kT}{(d\ln P_0/dT)_{\rm sol} - (d\ln P_0/dT)_{\rm liq}}\right]^{1/3}. \qquad (2)$$

Experimental values of A for the rare gases are within 15% of the values computed from Eq. (2), the phase boundary slopes, and the measured α's, the others being within 30%.

Several authors have presented theoretical arguments concerning triple-point wetting transitions.[1,16-18] The possibility of a continuous triple-point wetting transition was first noted by Schick,[16] in a comment on lattice-gas calculation by Ebner.[17] Pandit and Fisher[18] have also discussed this possibility, together with other effects of the triple point.

The universal type-2 low-temperature growth in the experimental gases supports the conjecture that complete wetting is restricted to a very narrow range of relative interaction potentials. The transition to complete wetting of all of the films at their bulk triple points shows that structural mismatch is a significant factor in low-temperature growth. At low temperature, both film and bulk are solids, with presumably different structures. Above the triple point the bulk phase is liquid, and hence structural mismatch cannot exist. The present experiments, together with those on graphite and other surface, show that complete wetting at low temperature is a rare and accidental occurrence and indicates why this is so.

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