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Wetting transition of CF_2Cl_2 on graphite

U. G. Volkmann and K. Knorr
Institut für Physik, Universität Mainz, 6500 Mainz, Germany

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Adsorption isotherms of CF_2Cl_2 on graphite have been measured by ellipsometry. In the vicinity of the first-order wetting transition, nonequilibrium states including irregular fluctuations of the adsorbate thickness have been observed.

The study of adsorption isotherms gives access to the wetting phenomenon.[1,2] When the pressure of the gas is increased towards the saturated vapor pressure p_0 for a wetting adsorbate/substrate system, the number of adsorbed monolayers on the substrate will diverge. In a nonwet system the number will stay finite. The behavior might change from one to the other type at the wetting temperature T_w. In many adsorbate/substrate combinations for which a wetting transition has been observed, the transition is of first order and occurs at the triple point of the bulk system T_t (Refs. 1 and 2).

Conventional volumetric measurements of adsorption isotherms rely on large-area powdered substrates, for which capillary condensation will inevitably interfere with the multilayer growth, thus making the study of wetting difficult. High quality multilayer adsorption isotherms have been, however, obtained on substrates of pyrolytic graphite crystals using ellipsometry as a monitor of the adsorbate thickness.[3,4] This method measures the change of the polarization state of light reflected from the adsorbate covered substrate. The results are condensed into the changes $\delta\Delta, \delta\psi$ of the ellipsometric quantities Δ, ψ upon adsorption. For adsorbate films thin compared to the wavelength of the light used for ellipsometry, $\delta\Delta$ and $\delta\psi$ are proportional to the coverage, averaged over the light dot on the surface (some mm^2). Experimental details of the optical, vacuum, and cryogenic setup have been given elsewhere.[4] We recall that $\delta\Delta$, the gas pressure p in the vacuum chamber and the stray light in an off-specular direction are recorded with time t, while gas flows into the vacuum chamber through a needle valve, leading to a slow increase of p with t. Typically the isotherm is completed in some thousand seconds. This rate is a compromise between the intention to grow the layers as slowly as possible in order to give nonequilibrium states time to relax and to keep the overall time of exposure of the cold substrate to the gas short in order to avoid the accumulation of contaminants on the substrate. (At low T where the pressures of interest are low, the rate furthermore depends on the experimenter's skill in adjusting a minimum opening of the leak valve.) A temperature stability of the Cu plate, to which the substrate is mounted, of 0.001 K is obtained by using an ac resistance bridge in combination with a controller (Linear Research, models 130 and 110) and a Pt resistor. The time constant

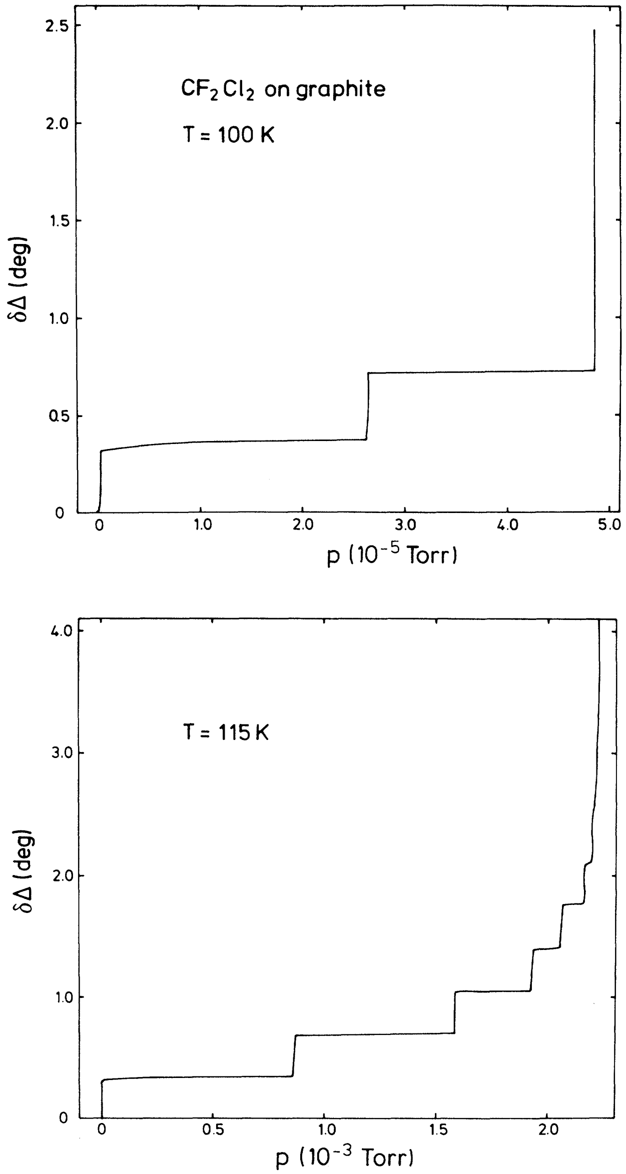

FIG. 1. Two ellipsometric isotherms showing incomplete wetting behavior at low T and the complete wetting at high T.

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of the stabilization feedback loop is 4 sec. For the measurement of the gas pressure a number of gauges are available (capacitance, ionization and cold cathode Penning gauge, mass spectrometer and rotating ball viscosimeter). The p values given in the figure are taken from the viscosimeter; in the p range of interest here its resolution is 0.1%. Our design of the vacuum chamber and the cryostat minimizes the problem of a "cold spot"; see Fig. 1 of Ref. 4. From the study of Ar, Kr, and Xe multilayer adsorption isotherms,[4,5] we can estimate that the Cu plate is less than 0.01 K colder than the graphite surface. Note that the gas is not in contact with the liquid He leading parts of the cryostat. It is, however, clear that the gas adsorbed on the Cu plate does participate in the adsorption process. CF_2Cl_2 gas is commercially available with a purity of 99%. For further purification the gas passes through a cold trap, held at 260 K, before entering into the chamber. The structure of the bulk solid is unknown, but dielectric measurements[6] propose that the bulk solid is electrically ordered and that there are no further structural phase transitions in the solid state. The coverage-temperature phase diagram and the structures of the monolayer adsorbate on graphite have been established recently.[7] The bulk triple point temperature T_t is 116 K.

Ellipsometric absorption isotherms have been measured for $90\ \mathrm{K} < T < 190\ \mathrm{K}$. We distinguish three T ranges of different growth behavior.

$T < 100$ K. See Fig. 1 for a representative isotherm. In this range the growth behavior is as expected for the nonwet case. Two monolayers form at lower pressures. At some well-defined p value, which we regard as the saturated vapor pressure p_0, the $\delta\Delta$ readings and the stray light increase strongly. Eventually the ellipsometer readings are lost, at stray-light levels of the order of some volts of photomultiplier output, because of an ill-defined polarization state of the reflected light. We ascribe these effects to the growth of an optically rough overlayer of bulk CF_2Cl_2 crystallites on top of two monolayers.

$T > 106$ K. In this range the growth is as expected for the wet case. The isotherm shows a sequence of several resolved monolayer steps and approaches asymptotically a vertical line. We read this p value as p_0 (Fig. 1). The stray-light intensity starts exceeding the noise level above thicknesses larger than the equivalent of about ten monolayers, at the equivalent of 20 monolayers the intensity is of the order of some hundred mV. From the p,T values of the monolayer steps the $(\mu-\mu_0)-T$ phase diagram was derived, $\mu-\mu_0=kT\ln(p/p_0)$. Above 116 K the diagram is of the type observed for other wet

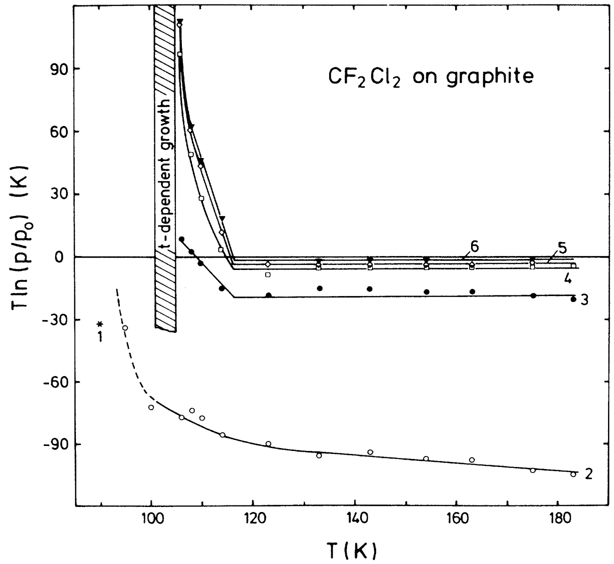

FIG. 2. The $\mu-\mu_0=T\ln(p/p_0)$ vs T phase diagram showing the layering transitions of the second up to the fifth layer. For $T < 100$ K and for $T > T_t = 116$ K the values of the saturated vapor pressure p_0 used for the construction of the diagram are directly read from the asymptotic pressure of the isotherms. For $106\ \mathrm{K} < T < T_t$ adjustments have been made which are described in the text.

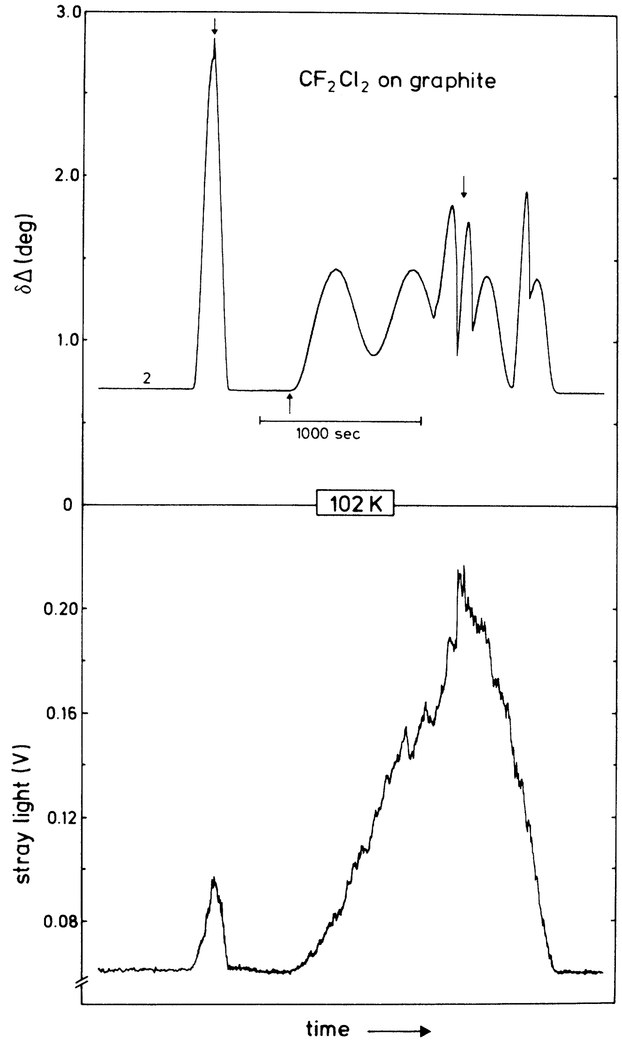

FIG. 3. The time evolution of the ellipsometric thickness $\delta\Delta$ and of the stray-light intensity at 102 K. Two monolayers had been adsorbed already previously. The openings (↑) and closures (↓) of the gas inlet are marked.

adsorbate/substrate systems with a sequence of about horizontal layering transition lines; Fig. 2. Problems arise for temperatures below 116 K. In this regime the length of the second plateau (between p_2 and p_3) of the adsorption isotherms is unusually large and grows with decreasing T. In the $(\mu-\mu_0)-T$ phase diagram of Fig. 2, this feature would lead to a bending down of the layering transition to the first and to the second monolayer. Such a diagram does not seem realistic, we rather suspect that the identification of the asymptotic pressure with p_0 is incorrect. Therefore we have introduced adjusted $p_0(T)$ values for 106 $\mathrm{K}<T<116$ K, in such a way that $kT\ln(p_1/p_0)$ is a linear function of T for all T, with $T>106$ K. The resulting diagram for the higher layers is shown in Fig. 2; it suggests that for $T<116$ K the fourth and higher layers grow under supersaturated conditions only. Thus this view suggests that the wetting transition is at about T_t, with $T_t=116$ K.

100 $\mathrm{K}<T<106$ K. The first two monolayers form at characteristic pressures, but the subsequent growth behavior is different from run to run. A typical example is shown in Fig. 3. There is one growth mode where at some stage the ellipsometric thickness shoots up at some pressure value in very much the same way as observed at p_0 for the nonwet case. In the other mode the ellipsometric thickness fluctuates in a quasiperiodic fashion. There are no corresponding fluctuations of the gas pressure; p always changes monotonically with time. The excursions to thicknesses larger than two-monolayer equivalents are accompanied by moderate values of stray-light intensity (Fig. 3). The stray-light level is comparable to that observed for $T>116$ K at film thickness of several monolayers. Hence we are confident that $\delta\Delta$ is still a reasonably faithful measure of the average film thickness and reject the idea that the excursions are due to macroscopically thick (and presumably rough) films, for which the ellipsometric signal would have gone through multiple periods.[8] After stopping the gas inlet by closing the leak valve the thickness eventually comes back to the two-monolayer level, either monotonically or with oscillations. Thus the two-monolayer level presumably represents the equilibrium state, correspondingly excursions to higher coverages are nonequilibrium states of some extra, moderately rough layers. Since there is no marker for p_0 in this T range, we cannot decide how the onset pressure p_{on} of these excursions compares to p_0 (but think that $p_{\mathrm{on}}>p_0$). Even the values of p_{on} are to a large degree nonreproducible, they vary by a factor of almost 2 from run to run and appear to shift to larger values for higher gas inlet rates. Higher inlet rates also seem to favor the abrupt growth mode with respect to the oscillatory mode. Unfortunately these observations could not be studied systematically, since the inlet rate cannot be controlled with sufficient accuracy.

As mentioned above we favor the idea of a wetting transition at $T_w\approx T_t\approx 116$ K. (For a lower T_w it would be difficult to imagine how the hexagonal structure of the monolayer solid can grow into an orientationally ordered bulk solid.) Triple point wetting is considered a first-order transition[1,2] which necessarily involves metastable states. It is likely that the anomalous adsorption behavior slightly away from the $p_0(T)$ coexistence line is connected with a hysteresis on the coexistence line. If this view is correct, the hysteresis would only extend to below T_w, but not to above, similar to the situation encountered for melting in three dimensions.

For thicker adsorbates the layering transition lines are closely spaced in the μ-T phase diagram and bunch at a wetting transition. In this situation a small stimulus will lead to large changes of the film thickness. The first thought is that the erratic time dependence of $\delta\Delta$ is induced by small variations of the thermodynamics variables p and T. Within the resolutions given above, we can rule out such variations of p and T.

A hint for the understanding of the erratic fluctuations may come from the observation that the fluctuating film is moderately rough. Correspondingly the thermodynamic variables and potentials will vary across the surface. Note that p_0 and the layering pressures p_i depend on the curvature (and in the case of facetting on the orientation) of the gas-adsorbate interface and that then the flow of sublimation heat will lead to lateral T variations. This scenario is favorable for growth instabilities including the appearance of self-sustained oscillations, but we still cannot specify the nature of the feedback mechanism which is responsible for this effect, let alone explain why it occurs in a small T range, well below the presumed wetting temperature, only.

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