

Multilayer phase diagram of CF₄ adsorbed on graphite

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Layer transitions in CF₄ adsorbed on graphite are studied by vapor-pressure isotherm measurements in the range one to eight layers and 52 K < T < 104 K, using an ellipsometric technique to measure the coverage on a single surface. A maximum of two layers adsorb below 71 K. Above 71 K we observe for the first time the condensation of a double-layer (third and fourth), which splits into separate layers above a triple point at 75 K. The fifth layer appears at 80 K, the sixth at 87 K, and at least eight discrete layers are seen over several kelvin above the bulk melting point at 89.5 K. The slopes of the layer chemical potentials versus temperature yield estimates of the locations of phase transitions and of entropy differences.

In recent years a rich variety of two-dimensional phases and phase transitions has been found in monolayer physisorbed systems.¹ There is evidence of a similar richness in multilayer systems.²⁻⁴ Attention has focused particularly on wetting, that is, the stability of uniform thick films with respect to bulk condensed phases,⁵ on melting of wetting films and its relation to bulk melting,⁶ and on layering in wetting films and the relation of the layer critical points to roughening of the bulk phase surface.⁷ At intermediate thicknesses the topology of the phase diagrams may involve layer appearance transitions at finite temperatures,²⁻⁴ prewetting,⁸ melting of individual layers or of multilayer phases,^{9,10} layer critical points,^{4,11} and layer coalescence or splitting transitions.¹² The last has not been observed previously experimentally. If a particular layer is stable over an appreciable temperature range, there may be additional phase transitions involving changes in structure or molecular orientation.¹³

The system CF₄ on graphite exhibits many of the phenomena just mentioned. X-ray¹⁴ and neutron¹⁵ diffraction measurements have been reported, but so far only for the first layer. Zhang, Kim, and Chan (ZKC) have made an extensive heat-capacity study covering the monolayer,^{10,16} bilayer,¹⁰ and multilayer¹⁷ regimes. Volumetric isotherm measurements have been reported by Dolle, Matecki, and Thomy,¹⁸ including two isotherms below the bulk melting temperature at 89.5 K. Gay, Bienfait, and Suzanne¹⁹ have studied CF₄ on graphite below 50 K by reflection high-energy electron diffraction and interpret their results as showing a wetting transition at 37 K. They also report stepwise attenuation of substrate low-energy electron diffraction intensity, which indicates condensation of a third and possibly fourth layer in isotherms between 51 and 58 K.

In this paper we report extensive adsorption measurements for CF₄ on a single surface of highly oriented pyrolytic graphite.²⁰ The CF₄ coverage on a 0.1 × 0.2-mm² area of graphite is measured by a phase-modulation ellipsometric technique.²¹ The ellipsometer output I_1 at the modulation frequency is directly proportional to coverage, in the range of interest. For very thick uniform films, I_1 and the output at twice the modulation frequency I_2 should vary periodically with film thickness (with period of

order half the wavelength of light) and in quadrature with each other. Deposition of a bulk phase on the substrate is indicated by a decrease in the dc reflectance signal I_0 due to scattering. The apparatus and procedure have been described elsewhere.²²

Our pressure gauge does not provide useful resolution for CF₄ at temperatures below about 68 K. Nevertheless we can monitor the ellipsometric signal as a function of time as gas is admitted to the cell. Such measurements have been made down to 52 K. In all cases we see abrupt steps in I_1 corresponding to condensation of the first and second layers, followed by a large continuous rise which is the start of an oscillatory pattern. This is accompanied by an oscillation in I_2 , which indicates that thicknesses of hundreds of layers are involved, and by a decrease in I_0 , suggesting scattering by bulk crystallites. Thus it appears that from 52 to 71 K the bilayer film coexists with bulk crystallites, and no further layers are stable. This is contrary to the results reported by Gay *et al.*¹⁹ However, ZKC¹⁷ also find no heat-capacity signature of third- or higher-layer appearance between 18 and 71 K.

Figure 1 shows a series of isotherms above 72 K, in a range of pressures beyond second-layer completion. The step seen in the isotherms between 72 and 75 K is twice as high as a monolayer step, and corresponds to a direct transition from a two-layer to a four-layer film. Above 75 K this double step splits, the third layer continuing to move down in reduced pressure, while the fourth layer moves up. The fifth layer appears at 80 and the sixth just above 87 K.

The loci of these steps in the temperature-chemical potential plane are shown in Fig. 2. Chemical potentials are measured relative to the bulk phase which occurs at the same temperature, indicated at the top of the figure. Data from 97 isothermal scans are included. Each layer line is a first-order phase transition between two-dimensional vapor and a two-dimensional condensed phase in the top layer, and may also involve changes in underlying layers.

Some information about the nature of the two-dimensional phases can be inferred from entropy considerations. The partial entropy of the film is related to the slope of a layer locus by the Maxwell relation

$$(\partial S/\partial N)_T = -(\partial \mu/\partial T)_N, \quad (1)$$

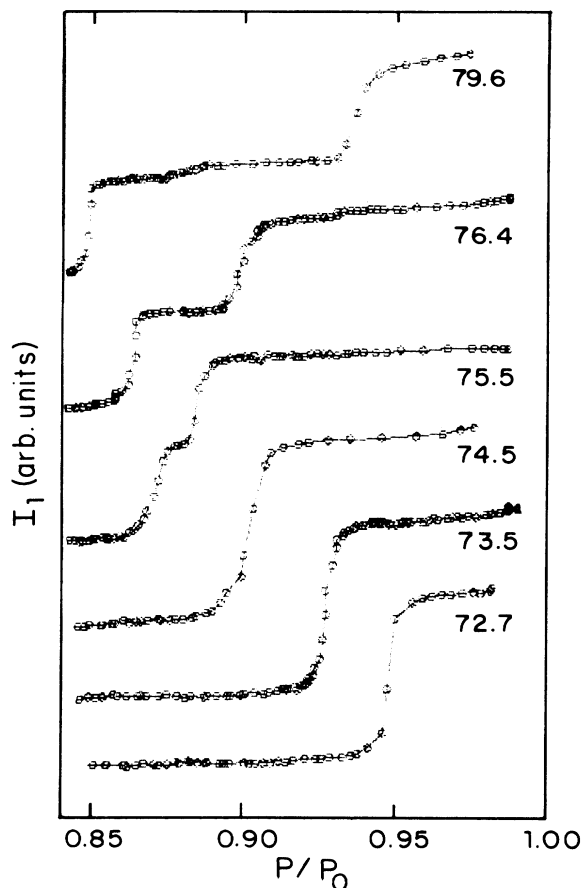


FIG. 1. Isotherms between 72 and 80 K in the region of third- and fourth-layer condensation. I_1 is proportional to coverage, and the zero is offset between traces. P_0 is the saturated vapor pressure. The film thickness is two layers at the left end of each trace.

where N is the number of molecules of adsorbate in the film, S is the entropy of the adsorbate, and μ is the chemical potential per molecule. The terms in Eq. (1) are independent of coverage over the range of the vertical part of a layer step. In this range, the film consists of coexisting patches of a phase of n condensed layers and a phase of n' condensed layers, whose respective thermodynamic states are unchanged along the isotherm (neglecting heterogeneity and finite-size effects) until the coexistence boundary is reached. In this situation

$$(\partial S/\partial N)_T = (S_2 n_2 - S_1 n_1)/(n_2 - n_1), \quad (2)$$

where S_2 and n_2 are the entropy per molecule and areal density of the n -layer phase, and subscript 1 refers similarly to the n' -layer phase.

Between 71 and 75 K, for mean coverage between two and four layers, the film breaks up into coexisting patches of two layers and of four layers. Thus the structure of the third-fourth bilayer is sufficiently energetically favorable compared to that of a separate third layer that it overcomes the difference of about 11 K in substrate potential between the third and fourth layers, as well as the reduced entropy. The slope of this transition is about -2.2 . If the

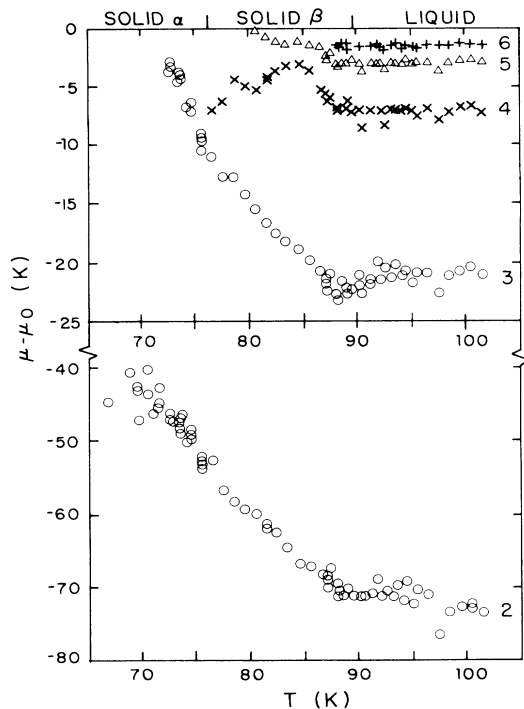


FIG. 2. Loci of layer steps 2 through 6 in the temperature-chemical potential plane. The symbols indicate steps in individual isotherms, or in some cases averages of two or three isotherms. The step numbers are given on the right. The third and fourth layers appear together as a double-height step at 71 and separate at a triple point at 75 K.

first and second layers are assumed to be passive, the entropy of the third-fourth bilayer is thus larger by $2.2k_B$ per molecule than that of the bulk α solid. This probably means the film is orientationally disordered: The entropy increase associated with the bulk α - β transition is $2.7k_B$, and this is thought to be associated mostly with loss of molecular orientational order.²³ It has been suggested that molecular orientation is lost in submonolayer and in bilayer films at 57 and about 59 K, respectively.¹⁰

Between 76.2 and about 83 K, the slope of the third layer is about -1.1 and that of the fourth about $+0.6$. Half the difference between these slopes should equal the entropy increase per molecule in going from third-fourth bilayer to third monolayer, as in warming through the layer-separation triple point at 75 K. This, as well as the double-layer appearance at 71 K, should produce heat-capacity peaks. The 71-K peak, which results from transformation of bulk α solid into third-fourth bilayer, should appear at a coverage of two layers, with an area of $(155 \text{ K})k_B$ per molecule from two layers through the fourth layer, and constant area at higher coverage. The peak at 75 K also should appear at two layers, with an area of $(63 \text{ K})k_B$ per molecule from two statistical layers through three, then decline linearly to zero at completion of the fourth layer. Peaks at nearly these temperatures and coverages are reported by ZKC,¹⁷ but they are much smaller than predicted. This could be due to long equilibrium times associated with mass transport between separated

phases, which would attenuate the peaks in an ac heat-capacity experiment. In particular, complete cycling of the 71-K transition at coverages below four statistical layers would require nucleation of α -phase crystallites each cycle.

The entropy of transition at 75 K calculated above is comparable to that of bulk melting. This suggests that the third layer, as long as it is the top layer, remains liquid down to 75 K. The average slope of the third layer over the whole β -solid range is -0.9 , which is comparable to the entropy difference between β solid and bulk liquid (-0.96).

Above the bulk melting temperature at 89.5 K, the layer condensation lines in Fig. 2 are very nearly parallel to the bulk liquid-vapor coexistence line, indicating that the partial entropy at condensation of each layer from the second to at least the sixth is nearly equal to the entropy of bulk liquid. Figure 3 is a representative series of isotherms over this region, showing condensation of layers two through eight. The choice of abscissa is intended to expose the higher layers. If the chemical potential of the film differed from that of bulk liquid only by a potential of van der Waals form $V(z) = -C/z^3$ and each layer had the same density, then isotherms plotted in this way would be uniform staircases.

The above conjecture has been tested by a numerical comparison. Because of the layer structure of graphite,

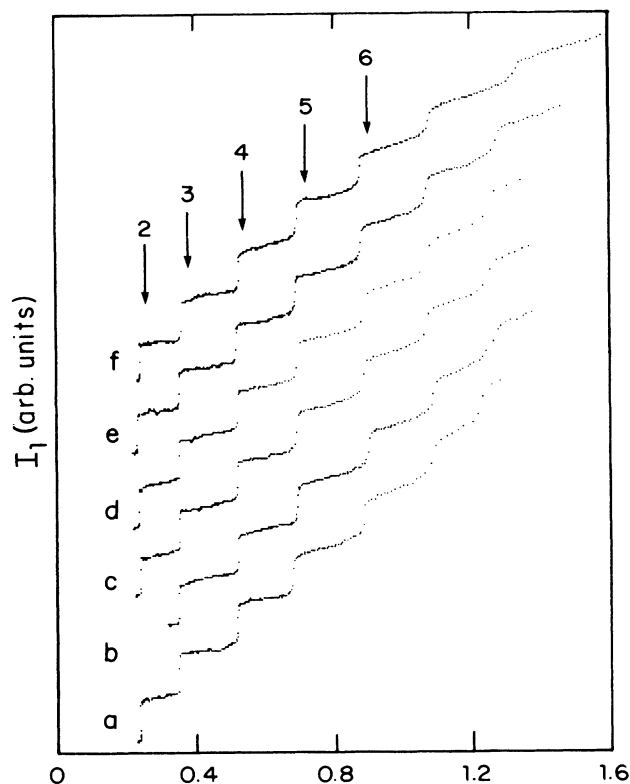


FIG. 3. Isotherms between 88 and 94 K, where thick, liquid-like films are observed. Layer step numbers are given at the top. The temperatures are a, 88.0 K; b, 89.0 K; c, 90.1 K; d, 91.2 K; e, 92.1 K; f, 94.1 K.

TABLE I. Relative chemical potential of the film above 89.5 K at condensation of the n th layer and fit of theory as described in the text. The chemical potentials are in temperature units. This fit yields $C_3/d_1^3 = 322 \pm 7$.

| n | $\mu_n - \mu_\infty$ (K) Expt. | $\mu_n - \mu_\infty$ (K) Fit | Residual | Slope, $d(\mu_n - \mu_\infty)/dT$ |
|------|-----------------------------------|---------------------------------|----------|--------------------------------------|
| 2 | -71.57 ± 0.55 | -73.05 | +1.48 | -0.16 ± 0.14 |
| 3 | -22.08 ± 0.54 | -18.08 | -4.00 | $+0.08 \pm 0.16$ |
| 4 | -7.30 ± 0.09 | -6.98 | -0.32 | 0.00 ± 0.05 |
| 5 | -3.37 ± 0.06 | -3.42 | +0.05 | 0.00 ± 0.02 |
| 6 | -1.84 ± 0.04 | -1.95 | +0.11 | 0.00 ± 0.02 |
| 7 | -1.21 ± 0.03 | -1.23 | +0.02 | -0.01 ± 0.02 |
| 8 | -0.90 ± 0.03 | -0.84 | -0.06 | $+0.02 \pm 0.02$ |
| Bulk | (-0.43 ± 0.14) | | | $(+0.02 \pm 0.02)$ |

the attractive potential of the substrate is represented more appropriately by a sum over layers²⁴

$$V(z) = -3C_3d_0 \sum_{m=0}^{\infty} (z + md_0)^{-4}, \quad (3)$$

where $d_0 = 3.348 \text{ \AA}$ is the layer spacing of graphite and C_3 is an effective van der Waals coefficient. The Frankel-Halsey-Hill form for the chemical potential of the film during condensation of the n th layer is

$$\mu_n = \mu_\infty + V(nd_1), \quad (4)$$

where μ_∞ is the chemical potential of a semi-infinite slab of adsorbate and d_1 is the thickness of an adsorbate monolayer. In Eq. (4), $V(z)$ represents the difference between the attraction of the graphite and the (weaker) attraction of continued adsorbate replacing the graphite. The data tested are the 12 isotherms above 89.5 K from our last run.

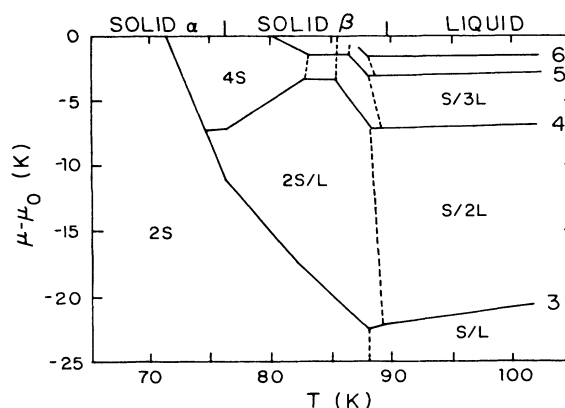


FIG. 4. Proposed phase diagram, based on this study and previous work. Solid lines are first-order layer condensation transitions. To the right of layer critical points, which are not well determined, these lines become loci of inflection points of the isotherms. The dashed lines are possible locations of melting transitions, probably of individual layers. These transitions are not directly observed, but are inferred from changes in slope of layer lines. The proposed phases are labeled as follows: 2S = bilayer solid; 2S/L = bilayer solid plus liquid monolayer, etc. Layers above the sixth are not shown.

Because the saturated vapor pressure is determined with less precision than the step pressures, we made a preliminary fit to each isotherm to determine μ_∞ , and averaged $\mu_n - \mu_\infty$. These averages are listed in Table I, together with their standard deviations and the results of a weighted least-squares fit of Eqs. (3) and (4). The fit is good beyond the third layer, but the data for the second and third layers deviate significantly. The chemical potential μ_0 of the bulk liquid is lower than the fit extrapolated to films thicker than ten layers, indicating that thicker films are unstable and wetting is not quite complete. This is similar to the behavior observed previously for oxygen and ethylene films on the same substrate.²² It is not clear why this should happen for a liquid film, but it is evident from Fig. 3 that films of at least eight layers retain significant layer modulation, and thus differ structurally somewhat from bulk liquid.

If it is accepted that the film above 89.5 K (except possibly the bottom layer) is liquid, differing in chemical potential and entropy from bulk liquid only by amounts comparable to the entries in the "Residual" and "Slope" columns, respectively, of Table I, then one can examine Fig. 2 to locate phase changes at lower temperatures. In Fig. 4 we propose a phase diagram for CF₄ films. The dashed lines are possible locations of phase transitions not involving large coverage changes, such as melting, based on changes in slope of layer lines and on heat-capacity results.¹⁷ The main conjecture on which identification of

phases in this diagram is based is that the relevant phase transitions in the film are layer-by-layer melting, as suggested by the behavior of the third and fourth layers above 75 K. Heat-capacity measurements suggest that the bilayer film melts at 88–89 K;¹⁰ therefore, the region below this is labeled (2S). It is not certain whether both layers melt near 89 K or only the top layer.¹⁰ We label the bilayer phase above 89 K (S/L), corresponding to the second possibility.²⁵ Higher coverage phases can then be identified, consistent with this scheme, according as the slope of the intervening layer line suggests addition of a liquid or a solid layer. The large slope of the second layer in the β solid region implies that the bilayer has considerably greater entropy per molecule than not only the β solid but also the monolayer.

X-ray or neutron diffraction measurements in the coverage range between two and four layers would be most valuable for clarifying the structures of the postulated phases, including the occurrence of layer-by-layer melting.

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