PHASES AND PHASE TRANSITIONS IN THE FIRST FEW LAYERS OF METHANE, ARGON AND KRYPTON ADSORBED ON GRAPHITE

DAVID GOODSTEIN*, P. DAY*, M. LaMADRID*, AND M. LYSEK**

*California Institute of Technology, 114-36, Pasadena, CA 91125

**Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109

ABSTRACT

The equilibrium phase diagrams of monolayers of many substances adsorbed on graphite have long been studied as examples of 2-dimensional (2D) matter. One typically observes 2D gas and liquid phases, and solid phases that may be commensurate or incommensurate with the substrate lattice. Many experimental techniques have been used, but thermodynamic measurements are generally the most useful for tracing out phase boundaries.

Recent advances in technique have made it possible to use thermodynamic measurements to study the phase diagrams of the second and higher layers, up to the fifth or sixth. These advances include ultra high resolution scanning calorimetry, and a detailed understanding of the role of capillary condensation in corners and pores of the graphite foam substrate. We find a rich array of phases and phase transitions in multilayer methane, argon and krypton. The second and third layers typically have distinct 2D gas, liquid and solid phases evidenced by 2D triple points and critical points. We observe phase transitions between solid phases that are commensurate and incommensurate with the layer below. We also observe melting of the first layer at higher temperatures, even when one to five additional layers are adsorbed on top of it.

In argon and krypton, but not in methane, a strange new phenomenon is observed at temperatures above the gas-liquid critical point of the n th layer for $n \gtrsim 3$. Below that temperature, n th layer gas coexists with a condensed n th layer. At some temperature above it, a new coexistence region is observed in which a partial n th layer coexists with a partial $n+1$ st layer. This behavior is thought to be evidence for a theoretically predicted phase transition of the bulk interface, called the preroughening transition.

INTRODUCTION

Films of matter adsorbed on solid surfaces simulate two dimensional (2D) matter in the laboratory. The substrate of choice for adsorbed monolayers has generally been graphite, because atomically pure graphite surfaces are relatively easy to prepare. Thus, the general scheme is to prepare a submonolayer film of the substance of interest adsorbed on graphite, and to study its properties as a function of temperature and coverage. A wide variety of experimental techniques have been applied to this problem, including vapor pressure and heat capacity measurements, x-ray, neutron and atomic scattering, ellipsometry, nuclear magnetic resonance, and others [1]. Since phase transitions often show up as peaks in the heat capacity, calorimetric measurements have proved most useful for tracing out phase boundaries, while diffraction data are often essential for identifying phases.

An example is shown in Fig. 1, a schematic phase diagram of the first layer of methane adsorbed on graphite in the 2D-density-temperature plane [2,3]. As one would find in the analogous plot in 3D, there are solid, liquid and gas phases, separated by coexistence regions indicating that the phase transitions between those states are first order (i.e., the phases coexist at different 2D densities). Just as in 3D, the liquid-gas coexistence region ends in a critical point. Above the critical point temperature, $T_c(1)$ there is no distinction between the two phases. Also like 3D, there is a triple point T_t , at which solid, liquid and gas phases all coexist.

Unlike 3D matter, however, there is a solid phase called CS for Commensurate Solid.

In this state, the methane lattice is commensurate with the underlying graphite basal plane, one methane molecule nestled in the center of every third carbon hexagon, forming a triangular close-packed array. It is separated by thermodynamically observable phase transitions from two other 2D solid states, ES for Expanded Solid, i.e., less dense than commensurate, and DS for dense solid, i.e., denser than commensurate. These phases are incommensurate with the substrate, although their crystal axes are thought to be oriented at a preferred angle with respect to the substrate axes. With minor variations, Fig. 1 is typical of the many adsorbate/graphite systems whose monolayer phase diagrams have been studied.

In this paper we turn our attention to the study of the second, third and higher adsorbed layers of CH_4 , Ar and Kr adsorbed on graphite [4]. We understand now in retrospect that multilayer studies have been hindered in the past by two factors. First, phase transitions tend to be weaker—involving smaller signals—than in the first layer, and hence require higher resolution calorimetry to detect. Second, capillary condensation plays a more important role than previously suspected. Both of these difficulties had to be overcome to obtain the results we present in the following sections.

Figure 1: Schematic phase diagram of the first layer of methane on graphite.

NEW MEASUREMENTS

Figure 2 shows part of the calorimetric data for methane, in the form of 18 heat capacity scans at nominal fillings of the calorimeter ranging from 0.87 to 5.27 equivalent layers [2]. The tall narrow peaks between 100 and 110K are due to melting of the first layer, even when higher layers are adsorbed on top of it. About 8K below each of those peaks is a smaller peak due to a dense solid-commensurate solid transition in the first layer, which then melts at high temperature directly from the commensurate phase as shown in Fig. 1. The peaks in the higher coverages at around 90K are not due to adsorbed film. They are due to melting of matter capillary condensed in pores, cracks, corners, etc. in the graphite foam substrate. The complicated set of wriggles in the range 75–85K are all real features that will be analyzed below. They could not be resolved at all in previous measurements.

To make these measurements we constructed an Adiabatic Scanning Ratio Calorimeter [5], shown schematically in the inset of Fig. 2. The calorimetric cell is in vacuum, surrounded by two nested radiation shields inside a cryogenic bath. The fill tube, which may be sealed off by means of a cryogenic valve, enters the shielded region first through an upper thermal platform, at which all incoming electric feeds are also thermally anchored. It then passes successively through an isolation thermal mass and a comparison thermal mass (CTM) before reaching the cell. Active, computer controlled feedback is used to

Figure 2: Heat capacity scans, methane on grafoam, adsorption branch, cryogenic valve open, uncorrected for desorption. Fillings in nominal layers: 0.87, 0.94, 1.03, 1.12, 1.25, 1.55, 1.70, 1.85, 2.06, 2.44, 2.67, 3.00, 3.30, 3.66, 4.00, 4.43, 4.87, 5.27. Inset: Calorimeter assembly: (a) Fill tube (b) isolation vacuum tube, (c) upper thermal platform, (d) outer radiation shield, (e) inner radiation shield, (f) isolation thermal mass, (g) comparison thermal mass, (h) cell.

keep all these elements (three thermal masses, the cell, and two shields) at essentially the same temperature at all times during the measurement. To measure the heat capacity, heat is supplied to the CTM such that its temperature rises linearly at 1-2K/h. The signal is the power required to keep the cell at the same temperature, which is proportional to the heat capacity. The resolution achieved by this scheme is a few hundred ppm at $\sim 100\text{K}$.

The features (peaks, bumps, steps, etc.) in the heat capacity seen in Fig. 2 are plotted in the number-adsorbed-versus-temperature plane in Fig. 3, with likely phase boundaries indicated by solid curves. In the range 90-110K, the first layer dense solid-commensurate solid transition and first layer melting are seen. The nearly vertical curve at 85-90K is the melting of capillary condensate. In the region between 75 and 85K, the second, third and fourth layers are formed. Each appears to have a 2D gas-liquid coexistence region ending in a critical point, $T_c(n)$ where layer number $n = 2, 3, 4$. Each also exhibits a 2D triple point T_{tr} , followed by what appears to be melting of the top layer at higher coverage and temperature. In the second layer, for which the first layer seems to provide an inert, solid substrate, there is also evidence of a commensurate-incommensurate transition, (unlike the first layer, the solid is incommensurate with the layer below when it melts) and there are peaks at the highest coverage (data not shown in Fig. 2) that may indicate second layer melting above the bulk triple point temperature. The third and fourth layer phase diagrams have begun to be intertwined in a way that hints at an approach to bulk crystal interface formation. The fourth layer especially seems stretched out vertically because

Figure 3: Methane on graphite, probable phase boundaries, 2nd-4th layers. Symbols mark heat capacity features as described in text. Phases: G,L,S gas, liquid, solid; DS,ES,CS, IC-dense, expanded, commensurate, incommensurate solid; CC-capillary condensate. $nA+B$ means phase B in the uppermost layer on top of n layers of phase A. A/B means phases A and B coexist in the uppermost layer.

the number adsorbed includes not only film but also capillary condensate.

The data shown in Fig. 2 are plotted in Fig. 3 as open circles. These data are taken with the cryogenic valve closed, and the sample is prepared by adsorption (adding matter to the substrate). Adsorption data with the cryogenic valve open (x's) permit simultaneous measurement of 3D gas pressure, and hence the chemical potential, μ , of the film. In samples prepared by adsorption, capillary condensation begins to be significant for films of more than about 3 layers. The crosses in Fig. 3 mark features in samples prepared by desorption (removing matter from an initially saturated sample). In desorption samples, capillary condensation is observed to persist until only 1.1 layers remain adsorbed [6]. However, the adsorption and desorption data in Fig. 3 agree with one another because the difference in amount adsorbed has been measured and corrected in the desorption data. Capillary condensate is an independent state of matter that coexists with the film without interacting significantly with it. Figure 2 illustrates that film behavior may be studied in spite of capillary condensation if the latter is properly understood and corrected for.

In addition to methane, we have also studied multilayer argon [7,8] and krypton [9] on graphite by these same techniques. The phases of the first few layers of argon in the N-T

plane are shown in Fig. 4. A number of phase boundaries are seen to extend to above T_t , the bulk argon triple point. In the region between T_t and 90K, starting at low coverage and adding argon, one observes the following states: fluid first layer (F); commensurate solid first layer (CS) with second layer fluid (+F) adsorbed on top of it (thus, the boundary separating F from CS+F is the melting of the first layer); high density first layer (DS)

Figure 4: First 3 layers of Argon on graphite, number adsorbed *versus* temperature. All symbols mark heat capacity features. Same notation of phases as in Fig.3.

with F on top (this boundary is the incommensurate-commensurate transition in the first layer); coexistence between second layer incommensurate solid and second layer fluid (DS+(ES/F)); the DS first layer is now an inert solid substrate with which the second layer solid is incommensurate); a uniform DS+ES phase (meaning DS first layer, ES second layer); bilayer mutually commensurate solid (2DS) with third layer fluid on top of it, and finally three mutually commensurate solid layers with fourth layer fluid on top (3DS+F). The last phase boundary is the melting of the third layer.

At low T , below 70K, one sees the now familiar signatures of 2D gas-liquid coexistence, and 2D triple points in the second and third layers. Each of these triple points is the start of a melting transition curve that proceeds to higher temperature. However, something new is seen on the third layer melting curve that is a precursor of things to come in yet thicker films. It is the broad coexistence region between 70 and 80K marked 2DS+F/3DS+F. This region separates two solid layers plus a fluid partial third layer (2DS+F) from 3DS+F. In other words, not only does the third layer melt here, but a new kind of layering transition also takes place.

The data for the second and third layers of krypton are remarkably similar to those in argon, differing from Fig. 4 only in minor topological detail, and in the relevant temperature range (for krypton it is roughly 90-120K) [10].

For films thicker than those discussed above, capillary condensation becomes a serious problem, not only for samples created by desorption, but also for those prepared by adsorption. It is still possible to study 4, 5 and perhaps 6 layer films, although the amount in the film phase can no longer be known with precision. Beyond about the sixth layer, virtually all the matter in the system is consumed by capillary condensation.

To analyze data up to the sixth layer in a way that is not affected by capillary condensation, we make use of a well known approximation for the chemical potential of a film,

$$\mu - \mu_0 = -\frac{C}{Z^3} \quad (1)$$

where μ_0 is the chemical potential of the bulk at the same temperature, C is a constant that depends on the adsorbate/substrate system and Z is the film thickness. To the extent

that Eq.(1) is correct, the film thickness, which is otherwise unknown, is proportional to $(\mu_o - \mu)^{-1/3}$, which is measured independently in our work. Thus, a plot with $(\mu_o - \mu)^{-1/3}$ instead of N as abscissa will at least give roughly equal space to each layer regardless of how much matter is capillary condensed.

Figure 5 shows where heat capacity features have been observed, in the $(\mu_o - \mu)^{-1/3}$

Figure 5: Krypton on graphite, multilayer phase diagram, showing low temperature layering transitions, and the new intermediate coverage layering at higher temperature.

versus T plane, for krypton on graphite. This kind of plot bears some superficial resemblance to the $N - T$ plots shown earlier, but there is an important topological difference: since phases that coexist have the same μ , phase coexistence shows up as a single curve rather than an extended region on this plot. In Fig. 5, coexistence regions are indicated by double lines.

At low temperature ($T \lesssim 95\text{K}$) there is a series of coexistence curves just like those in methane and argon, called layering transitions, that mark layer-by-layer growth of the film. Thus 2 solid layers, plus some gas in the third (2DS+G) coexists with three solid layers plus gas in the fourth (3DS+G) and so on. Transitions of this kind at low T have been observed in many film systems. The second layer has a triple point, a melting transition, and separately, a critical point $T_c(2) \approx 98\text{K}$. The third layer does not have separate triple and critical points (in this property krypton differs from argon) nor do the fourth and higher layers (this is true in argon too). Instead a new set of layering transitions is observed at film thicknesses intermediate between the old ones and at higher temperatures. These new transitions were originally discovered in ellipsometry experiments by Youn and Hess (YH) [11]. As indicated in the figure, we observe not only the new layering transitions in agreement with YH, but also heat capacity peaks around 96K (indicated by filled circles) that connect the new layering transitions to the old ones. This whole set of phenomena occurs also in argon, but we have not observed it to occur in methane. We believe these layering transitions and the peaks around 96K to be related to crystal surface phase transitions, theoretically expected on the basis of model calculations, known as Roughening and Preroughening.

Roughening is a phenomenon associated with the surfaces of bulk crystals [12]. Below the roughening temperature, T_R , the equilibrium shape of the surface is flat, or faceted. Microscopic kinks or steps do occur, but they cost energy, E_k , so they are thermally suppressed. However, because they can occur anywhere on the surface they also have entropy S_k , so the step free energy, $F_k = E_k - TS_k$ becomes equal to zero at $T_R = E_k/S_k$. In the region $T_R < T < T_i$, the equilibrium shape of a crystal is area-minimizing like a liquid droplet, rather than faceted. In adsorbed films, roughening was expected to

manifest itself the low temperature layering transitions, which tend toward a crystal facet. These end in critical points, $T_c(n)$, and it was expected that as $n \rightarrow \infty$, $T_c(n) \rightarrow T_R$.

More refined model calculations have led to a new picture, in which a new surface phase occurs at $T < T_R$ [13]. Here kinks are once again thermally favored, but each up-kink is balanced by a nearby down-kink. Thus the overall crystal surface remains flat or faceted, but the topmost layer becomes disordered. The transition into this phase is known as preroughening (PR), occurring at $T_{PR} < T_R$. In films, the PR phase is manifested by regions where the topmost layer prefers to be partially populated. Thus, one expects coexistence between films of $n - \frac{1}{2}$ layers (approximately) and $n + \frac{1}{2}$. That is the behavior we observe.

If this interpretation of these results is correct, then in krypton, $T_{PR} \approx 96\text{K}$. This is the common temperature that $T_c(n)$ and onset of the new layering transitions seem to tend toward at high n . In argon, where the new layering transitions are observed up to the 5th layer, $T_{PR} \approx 69\text{K}$. The roughening temperature is the high temperature end point of the new layering transitions, $T_R \approx 110\text{K}$ in krypton, 80K in argon. Table 1 compares argon and krypton.

Table I.

	$T_t(\text{K})$	T_R/T_t	T_{PR}/T_t
Argon	83.6	.96	.82
Krypton	115.8	.95	.83

CONCLUSIONS

Up until very recently, there was what might be called a standard model of multilayer film growth. At low T , a series of layering transitions led to a faceted crystal surface in the limit of thick films. These layering transitions ended in critical points, $T_c(n)$, which tended toward the roughening temperature of the bulk crystal interface, $T_c(\infty) = T_R$ [14]. At slightly higher temperature, $T_R < T < T_t$, a new phenomenon, called surface melting in the bulk, or stratified melting in films, was thought to occur in many materials [15]. Depending on a delicate balance of surface tensions, a stratum of liquid might intersperse itself between the solid and vapor phases. Then as T approached T_t from below, the liquid-solid interface would propagate downward, consuming the solid phase. This was thought to be the mechanism of melting, in both films and bulk solids. At $T > T_t$, the reverse phenomenon, called substrate induced freezing, might stabilize a stratum of solid at the substrate interface [16].

The data we have presented here suggest a more subtle and complex picture. The critical end points of the low temperature layering transition seem, at least for argon and krypton, to tend not to roughening but to preroughening, $T_c(\infty) = T_{PR}$. Preroughening is evidenced by new layering transitions at fractional layer coverages. The endpoints of these transitions tend to T_R . The older picture may, however, continue to be valid in methane. On the other hand, we see no evidence in any of our data for surface melting or stratified melting. We believe that evidence previously ascribed to those phenomena may be completely accounted for by the melting of capillary condensate, and by the 2D melting of the uppermost layer of film. We do confirm previous observations that the first few layers may persist in solid form to $T > T_t$, a phenomenon that may be identified with substrate freezing.

Since methane behaves in a manner qualitatively different from argon and krypton, it is clear that there is more than one kind of approach to bulk behavior. Whether there are yet other kinds remains to be determined from future observations. These measurements also fail to shed very much light on the melting of thick films, since the signal is overwhelmed

by melting of capillary condensate in the relevant temperature range. We hope future experiments will provide new insights into this problem.

ACKNOWLEDGEMENT

This work was supported by DOE grant # DE-FG03-85ER45192.

REFERENCES

1. For a review see M.H.W. Chan, in *Phase Transitions in Surface Films 2*, edited by H. Taub et al., (Plenum Press, New York, 1991), p. 1.
2. M.J. Lysek, M. LaMadrid, P.K. Day and D.L. Goodstein, Phys. Rev. B to be published.
3. H.K. Kim, Q.M. Zhang and M.H.W. Chan, Phys. Rev. B **34**, 4699 (1986).
4. For a review of multilayer films prior to this work, see G.B. Hess, "Multilayer Physisorbed Films on Graphite" in *Phase Transitions in Surface Films 2*, edited by H. Taub et al., (Plenum Press, New York, 1991).
5. M.J. Lysek, P.K. Day, M. LaMadrid and D.L. Goodstein, Rev. Sci. Instr. to be published.
6. M.J. Lysek, M. LaMadrid, P.K. Day and D.L. Goodstein, Langmuir **8**, 898 (1992).
7. Peter Day, Mark Lysek, Marissa LaMadrid and David Goodstein, Phys. Rev. B to be published (Argon: 1st 3 layers).
8. Peter Day, Mark Lysek, Marissa LaMadrid and David Goodstein, Phys. Rev. B to be published (Argon: reentrant layering).
9. Peter Day, Mark Lysek, Marissa LaMadrid and David Goodstein, submitted to Phys. Rev. B (Krypton multilayers).
10. Krypton multilayers have recently been studied by R. Gangwar and R.M. Suter, Phys. Rev. B **42**, 2711 (1990) and R.F. Hainsey, R. Gangwar, J.D. Shindler and R.M. Suter, Phys. Rev. B **44**, 3365 (1991). Some 2nd and 3rd layer features may be explained by W.F. Saam, Surf. Sci. **125**, 253 (1983). Argon multilayers were studied by D.M. Zhu and J.G. Dash, Phys. Rev. Lett. **60**, 432 (1988) and Phys. Rev. B **38**, 11673 (1988).
11. H.S. Youn and G.B. Hess, Phys. Rev. Lett. **64**, 918 (1990).
12. J.D. Weeks in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste, (Plenum, New York, 1979), p. 293.
13. M. den Nijs in *Phase Transitions in Surface Films 2*, edited by H. Taub et al., (Plenum Press, New York, 1991), p. 247.
14. R. Pandit, M. Schick and M. Wortis, Phys. Rev. B **26**, 5112 (1982).
15. J.G. Dash, Contemp. Phys. **30**, 89 (1989).
16. M.S. Pettersen, M.J. Lysek and D.L. Goodstein, Phys. Rev. B **40**, 4938 (1989).