Phase transitions of ethylene on graphite

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The results of an extensive thermodynamic study of the phase transitions of monolayer and multilayer ethylene on graphite are presented. In the submonolayer and near-monolayer completion regions, the melting transition is found to be continuous. Heat-capacity anomalies indicative of orientational and structural transitions of monolayer solid phases are found. Our result indicates the existence of a third monolayer solid phase in addition to the low- and high-density phases defined according to the orientation of the carbon-carbon axis of the molecule with respect to the substrate surface. In the multilayer region, our result is consistent with the interpretation that the wetting transition is pinned at T_t , the bulk triple-point temperature, and it is approached via a sequence of layering transitions. Liquidlike ethylene film is found to be layered by the graphite substrate well above T_t . The layer critical point $T_c(m)$, the high-temperature limit where a film of m-1 layers coexists with that of m layers, is found to decrease towards T_t with increasing m. The monolayerbilayer layer-critical-point transition is found to be two-dimensional Ising-like. The isotopic effects in two-dimensional orientational, melting, and liquid-vapor transitions were also studied in this experiment.

I. INTRODUCTION

Ethylene on graphite is a prototype physisorption system exhibiting many interesting phase transitions in the monolayer and multilayer regions. To date, ethylene on graphite has been studied via vapor-pressure isotherm,¹ NMR,^{2,3} neutron,^{4,5} x-ray⁶ scattering, ellipsometric isotherm,⁷ and isoteric heat of adsorption⁸ techniques. In this introduction, we shall briefly compare the results of these studies to our own experiment.

A NMR study² found the two-dimensional melting transition temperature remains constant at 68 K below a certain (n=0.800; this coverage scale will be defined below) coverage and increases rapidly above this coverage. The diffraction results confirm this finding.⁴⁻⁶ These studies interpret the transition in the submonolayer coverages to occur at a triple point and to be first-order-like. In contrast, our heat-capacity results clearly show that the melting in the submonolayer and monolayer completion region is continuous. These results will be discussed in Sec. IV.

Structural transitions between different twodimensional solid phases were found in the neutrondiffraction study.⁴ Below 70 K, a low-density (LD) solid phase was found below n=0.83 and a high-density (HD) solid phase above n=1.05. A coexistence region of (LD + HD) was found between these two phases. It is thought that the C=C bond in the C₂D₄ molecule is perpendicular to the graphite basal plane in the HD phase and parallel in the LD phase. The lattice constants of HD and LD phases are slightly dependent on temperature, having roughly the values of 4.22 and 4.65 Å, respectively.⁴⁻⁶

The neutron-diffraction study⁴ also found evidence for a third monolayer solid phase, the intermediate density (ID) solid phase, above 72 K. The C=C bond of the C_2D_4 molecules in the ID phase is postulated to be also parallel to the surface, similar to LD. It is thought that in the ID phase the inclination angle between the substrate and the C_2D_4 molecule, as defined by the C—D bonds, may be larger than that in the LD phase. The xray study,⁶ however, did not find any evidence for a distinct ID phase. Our heat-capacity results, to be presented in Sec. II, appear to support the existence of a distinct ID phase. Our results in the monolayer to bilayer coverage region also clearly indicate that the structural transition in the monolayer coverage is strongly coupled with layering transition in the bilayer.

In addition to melting and structural transitions, another transition was found near 35 K in submonolayer coverages in a more recent NMR study.³ This transition was though to be related to the orientational ordering of the molecular axes in the LD phase. We labeled the orientationally ordered (low temperature) phase as OLD and the orientationally disordered (high temperature) phase as DLD. In contrast, the neutron-diffraction study⁴ failed to find evidence of such a transition. Heatcapacity evidence for such a transition is discussed in Sec. III.

Ethylene on graphite is also a prototype multilayer physisorption system, exhibiting clear examples of layering, layer critical-point, and wetting transitions. We shall briefly define these terms.

An interface separating two different phases, e.g., solid and liquid, solid and vapor, and liquid and vapor, is said to be rough if the distance the interface wanders diverges. The interface is said to be smooth if the distance it wanders is on the order of its own width.⁹ The temperature separating these two regimes is the roughening temperature T_R . For $T > T_R$ the interface is rough, and for $T < T_R$ the interface is smooth. It should be noted that the liquid-vapor interface is always rough and the value of T_R for a solid-liquid and solid-vapor interface is dependent on the particular crystal (solid) facet.⁹⁻¹³ These observations allow one to conclude that the triplepoint temperature T_t is the upper limit of all T_R . In a physisorption system, the roughening transition is meaningful only in the limit of infinitely thick film and the crystal (solid) facet to be considered is, of course, that determined by the substrate.

There are two basic processes for a multilayer film to grow on an attractive surface, namely wetting and nonwetting growth. ^{10,11,14} When the adsorbed film grows uniformly to an infinite number of layers as bulk coexistence is approached, it is called wetting growth. In nonwetting growth, the maximum thickness of the adsorbed film coexisting with bulk is finite. A layering transition is said to occur at a particular temperature when the thickness of the adsorbed film coexisting with bulk increases by one layer. Under variation of temperature, a (wetting) transition from nonwetting to wetting growth can occur at the wetting temperature T_w . This transition can be approached from below either via a sequence of layering transitions if $T_w < T_R$, or via a thinfilm-to-thick-film transition if $T_R < T_w$. Here T_R is the bulk roughening temperature of the adsorbate.^{10,12}

The vapor-pressure-isotherm study of Menaucourt, Thomy, and Duval¹ found a single step below 80 K, indicating that only a single layer can form on graphite. Between 80 and 98 K, two steps, and above 98 K, three steps, were found. Isotherms taken above 104 K, the bulk triple point (T_t) of solid, liquid, and vapor, showed the coverage diverged as the pressure was brought close to the saturated value. These results suggest a wetting transition at T_t .

X-ray measurement⁶ of multilayer C_2H_4 on graphite provided evidence of a layering transition from monolayer to bilayer at 78 K, in agreement with the vaporpressure-isotherm study.¹ Above bilayer coverages, the wetting transition at the triple point is interpreted to proceed via a prewetting or thin-film to thick-film transition immediately below T_t after a bilayer film is formed.⁶

This interpretation is not consistent with two recent In repeating the volumetric vapor-presstudies. sure-isotherm study, Bassignana and Larher found a fourth step above 102 K.¹⁵ Drir, Nham, and Hess⁷ performed an ellipsometric isotherm study of ethylene on graphite and they were able to resolve four discrete steps at 102.1 K, five steps at 103.2 K, six steps at 103.3 K, and eight steps at 104.6 K. The total film coverage is limited to the total number of resolved steps for isotherms taken below 104 K, the value taken to be T_t in their study. Above T_t , although only eight distinct steps were resolved, the total film coverage on graphite increased to more than 50 layers. This study shows clearly that the layering transition near 98 K is not a prewetting transition and there are many layering transitions compressed in the narrow temperature range between 102 and 104 K. The ellipsometry results therefore are suggestive of a wetting transition at the triple point approached via a sequence of layering transitions. It should be noted, however, that Drir, Nham, and Hess⁷ observed bulklike droplets of liquid $T > T_t$ when total film coverage is above 10 layers, prompting the authors to suggest that the wetting growth above T_t may not be complete. Since the isotherm was measured by changing the pressure continuously, it is also possible, as noted by the authors, that the bulklike droplets are a result of slow kinetics in a thickfilm system. We shall discuss our results in Sec. VI in light of these interesting possibilities.

The boundary of the monolayer liquid-vapor coexistence region of ethylene on graphite is also mapped out in this study. The coexistence boundary is found to be similar to that of the CH₄ on graphite system and it is described by the 2D Ising model.¹⁷ This result and the isotopic effect on the 2D critical point are discussed in Sec. V. The details of the experimental techniques and arrangements used in this study were described previously¹⁶ and will not be repeated here. The resolution in heatcapacity determination is about 0.2%.¹⁶ This resolution allows us to detect heat-capacity anomalies with the peak height of $0.3k_B$ per molecule for a film of monolayer coverage. Heat-capacity scans of 49 surface coverages of C_2D_4 and six surface coverages of C_2H_4 , were made from 25 to 120 K. The coverage region studied ranges from n=0.15 to n=6. Three different calorimeters were used in this study. We define n=1 to be the coverage at the completion of the substep of a 74-K N_2 isotherm. This is the coverage corresponding to the formation of a $\sqrt{3} \times \sqrt{3}$ solid. The surface area of the calorimeters based on this definition is found to be, respectively, 2.1 m^2 , 1.4 m^2 , and 1.2 m^2 . Our data are normalized to those of the 2.1 m² calorimeter. In our coverage scale, n=1 corresponds to 1.33×10^{19} molecules. Although the ethylene molecules do not form a $\sqrt{3} \times \sqrt{3}$ solid, this coverage scale is used to measure the number of ethylene molecules on the surface. Similar coverage scales are used in other experimental studies, for example, n=1 is defined against a 77.4-K N₂ isotherm in the NMR and neutron-diffraction studies and a 95-K Kr isotherm in the x-ray study. These coverage scales, according to the respective phase diagrams, appeared to be consistent within 5%.

The relative surface coverage from one scan to another in our study is reliable to 0.3% up to n=2. At higher coverages, a number of difficulties set in. In a multilayer $(n \ge 4)$ experiment, the equilibrium vapor pressure in the sample cell is very close to the bulk saturated vapor pressure. A small temperature gradient between the (colder) sample cell wall and the (warmer) calorimeter will cause preferential condensation of the adsorbate gas on the cell wall. Since in our experimental arrangement the calorimeter is maintained at a temperature of about 2 K higher than the sample cell, preferential condensation onto the wall is difficult to avoid for $n \ge 4$. Preferential condensation at these coverages may also occur if the sample cell was cooled down rapidly after dosage of the adsorbate gas. In order to minimize this problem, the sample cell was cooled down at the rate of 1 K/h. Because of the preferential adsorption problems, we estimate that our reported coverage for $n \ge 4$ is reliable to 15%. Since the substrate used is exfoliated graphite foam, capillary condensation is also expected to be important for a multilayer film. As we shall see below, our heat-capacity scan found a merged broad signal where a sequence of transitions is expected for n > 4. Another problem related to the correct surface coverage is that of desorption of the

adsorbate molecules into the volume surrounding the calorimeter. Comparing with other adsorbates, this is a less serious problem for ethylene on graphite. This is the case because the saturated vapor pressure P_0 of ethylene is quite low, for example, at the triple point (104 K), $P_0 = 0.85$ Torr. At this pressure, desorption correction corresponds to a decrease in coverage of $\Delta n = 0.04$. At 115.2 K, near the layer critical point $T_c(2)$, $P_0 = 5.05$ Torr, desorption correction becomes more significant and causes a decrease in coverage of $\Delta n = 0.24$. Vapor-pressure isotherms performed at 108 and 115.2 K in this study, as well as those by Menaucourt, Thomy, and Duval, ¹ are used to calculate the true, effective surface coverage.



FIG. 1. Phase diagram of C_2D_4 on graphite in terms of coverage vs temperature. HD, ID, OLD, DLD are monolayer solid phases; their meanings are explained in the text. 1V, 1L, 2L, 3L, 4L represent first layer vapor, and first layer, bilayer, trilayer, and quadlayer liquids. 2S is bilayer solid. B stands for bulk solid. Black dots are locations of heat-capacity peaks. Solid lines represent first order and dashed lines represent continuous transitions. Dash-dot lines represent more speculative phase boundaries. A narrow (ID + 2S) region, not labeled, is proposed to exist between the (ID + bulk) and (2S + DLD) region. Layering transitions for adsorbed film thicker than trilayer cannot be resolved in this experiment. For the sake of clarity, details above $n \sim 3$ and temperature between 101 and 104 K, the triple point temperature, are not shown. The ellipsometry study (Ref. 7) found at least four additional layering transitions in this region. T_t at 104 K is denoted by an arrow. This is defined against a triplet-point-like melting peak at $n \sim 6$.



FIG. 2. Chemical potential vs temperature phase diagram. Chemical potential relative to that of bulk liquid (μ_l) is shown in schematic scale. The phase boundaries, connecting the ID, DLD, 2S, and B phases are tentative. Our data are not of sufficient resolution to exclude other possibilities, e.g., there may be a (DLD + bulk) coexistence line that separates the ID and 2S phases.



FIG. 3. Vapor pressure adsorption isotherms of C_2D_4 on graphite at 108 K (a) and at 115.2 K (b). P_0 , the saturated vapor pressures, are 1.80 Torr (108 K) and 5.05 Torr (115.2 K), respectively. Note that the second step (near $P/P_0=0.45$) for the 108-K isotherm is more "vertical" than that of the 115.2-K isotherm.

In the multilayer region, the heat-capacity value related to a transition is shown in units of mJ/K rather than in terms of k_B per molecules. Our choice is due to the fact that in some of the transitions, such as layering, the layer critical point and melting transition of the monolayer with a coexisting bilayer, the fraction of the molecules on the graphite surface participating in the transition, is dependent on the specific transition.

Our proposed coverage-temperature (n-T) and chemical potential-temperature $(\mu - T)$ phase diagrams are shown in Figs. 1 and 2. Phase boundaries shown in these figures are based on our heat-capacity and vapor pressure isotherm studies (Fig. 3), as well as other experimental studies discussed above. We shall show below the differences between our phase diagram and that due to other studies.

Since our results on continuous melting in the monolayer¹⁸ and layer-critical-point transitions in a multilayer¹⁹ have already been published, the discussions here concerning these two topics are intended to be complementary. The organization of the remainder of this paper is as follows: In Sec. II structural and layering transitions are discussed; in Sec. III the result of the orientational ordering transition is presented; in Sec. IV we describe the melting transition in the first few layers; and in Secs. V and VI we discuss, respectively, the twodimensional liquid-vapor transition in the monolayer and the multilayer layer-critical-point transitions. Since measurements were made with both C_2H_4 and C_2D_4 , isotopic effects observed in some of these transitions are also presented.

II. STRUCTURAL AND LAYERING TRANSITIONS

A. Structural transitions in monolayer solids and layering transition to a two-layer film

In Fig. 4, seven heat-capacity traces from n=0.92 to n = 1.33 are shown. A broad peak (full width at half maximum, FWHM=6 K) is found for coverages n=0.92 and n = 0.98 and two peaks [labeled (1) and (2)] separated by 4 K are found for coverages above n=1. Both heatcapacity peaks are interpreted as signals of structural transitions in the solid phases. We identify peak (1) to be the signal due to the HD-to-ID transition and peak (2), the ID-to-LD transition. The identification of peak (1) is consistent with the published result of neutron diffraction.⁴ Both peaks (1) and (2) extend far into multilayer coverages, supporting our interpretation as shown in Figs. 1 and 2, that above n = 1.25 this ID phase coexists with bulk. We shall return to this point. The broad anomaly at n=0.92 and n=0.98 is probably the merged signal of peaks (1) and (2). Since heat-capacity scans are not sensitive to phase boundary parallel, or nearly parallel to the temperature axis of an n-T phase diagram, we cannot be certain whether the ID phase terminates near n=0.9 and T=65 T or extends below 65 K as a sliver parallel to the temperature axis. Figures 1 and 2 are drawn assuming ID terminates near 65 K.

In Fig. 5, six out of the 11 heat-capacity scans taken



FIG. 4. Heat-capacity traces related to the structural transitions from HD to ID (1) and from ID to LD (2) in the monolayer solid. The coverage shown at each scan is the lowtemperature value, desorption is not important up to T_t . Dashed lines are drawn to guide the eye. All scans were done in the warming process except the top scan which was done during cooling.



FIG. 5. Heat-capacity traces related to the structural transition from HD to ID in the monolayer solid (1) and the layering transition from monolayer to bilayer solid with and without coexisting bulk (2). All scans were made during warming except the top scan which was done during cooling. Dashed lines are drawn to guide the eye.



FIG. 6. Heat of transitions vs coverage of the structural transition from HD to ID [peak (1)] and the structural transition from ID to LD and the layering transition between monolayer and bilayer [peak (2)].

between n = 1.48 and $n \sim 6$ are shown. Peaks (1) and (2) are smoothly connected to those shown in Fig. 4. The temperature of peak (2) is consistent with the layering transition from monolayer to bilayer found by vaporpressure¹ and x-ray⁶ studies. The temperature of peak (1), on the other hand, is consistent with that of the structural transition from the coexistence region of HD and bulk, i.e., (HD + B) to (LD + B) reported in the xray study. However, we shall show below that peak (1) is actually due to a transition between (HD + B) and (ID + B) regions.

The heat of transition as a function of coverage for peaks (1) and (2) are shown in Fig. 6. The heat of transition of peak (2) shows a rapid increase from n=1.0 to n = 1.15, decreases monotonically from n = 1.15 to n = 1.88, and stays at 1.5 mJ for *n* above 2. These results suggest possible phase boundaries parallel to the temperature axis near n=1.15 and n=2. In particular, we propose the DLD phase completes near n = 1.25 and the bilayer completes near n=2. Therefore, we identify peak (2) to be a signal of the ID-to-LD transition for n < 1.25and (ID + bulk)-to-(DLD + 2S) transition for n > 1.25. The (ID + bulk)-to-(DLD + 2S) transition is likely to occur as a two-step process going through a narrow (ID + 2S) region. This region is proposed to avoid thermodynamic (Gibbs phase rule) inconsistency. Heatcapacity anomalies related to the melting of the monolayer DLD and bilayer solid and the crossing of the monolayer and bilayer liquid coexistence region (to be discussed below) and the vapor-pressure isotherm at 108 K (Fig. 3) provide evidence for a boundary near n = 1.61separating the monolayer-bilayer coexistence and the pure bilayer (2S or 2L) phases for T > 80 K. Therefore, peak (2) is a signature of layering transition for (ID + bulk) to (2S) between n = 1.61 and n = 2 and a transition from (ID + bulk) to (2S + bulk) for n > 2.

Above n=1.33, the position of peak (1) is independent of coverage and as shown in Fig. 6, there is an abrupt drop in the heat of transition between n=1.33 and n=1.48. We interpret these results as suggestive of a parallel boundary separating the HD and (HD + bulk) regions near n=1.35 below peak (1). The location of this parallel boundary is consistent with the x-ray result.⁶

We shall now present our argument for a distinct third monolayer solid, the ID phase. Instead of a distinct ID phase, one might interpret peak (1) below n=1.35 to be due to a transition from HD to (HD + LD) and peak (2) as leaving this coexistence region. However, this inter-

Coverage n	T_p (K)	Height (mJ/K)	FWHM (K)	$\Delta H \ ({ m mJ})$
1.10 C_2D_4	68.3±1.0	0.5±0.2	5.0±1.0	1.83±0.5
$1.15 C_2 D_4$	71.4±0.5	1.1 ± 0.2	$3.3 {\pm} 0.5$	3.80±1.0
$1.26 C_2 D_4$	73.9±0.5	$2.0 {\pm} 0.2$	$2.8{\pm}0.5$	3.70±1.0
1.33 C_2D_4	74.3±0.5	1.7±0.2	1.4±0.5	3.60±1.0
1.48 C_2D_4	76.0±0.2	0.8±0.2	1.6±0.2	2.00±0.4
$1.56 C_2 D_4$	76.0±0.2	1.1±0.2	$2.0{\pm}0.2$	1.77±0.4
$1.60 C_2 D_4$	76.0±0.2	0.8±0.2	1.8±0.2	1.93±0.4
1.88 C_2D_4	76.5±0.5	$1.4{\pm}0.2$	1.0±0.2	1.87±0.4
2.14 C ₂ D₄	77.0±0.1	2.0±0.3	0.30±0.05	1.53±0.2
2.32 C_2D_4	77.1±0.1	2.8±0.3	$0.20{\pm}0.05$	1.71 ± 0.2
2.63 $C_2 D_4$	77.1±0.1	3.2±0.3	$0.15 {\pm} 0.05$	$1.59 {\pm} 0.2$
2.92 C_2D_4	77.2±0.1	3.2±0.3	$0.15 {\pm} 0.05$	$1.64 {\pm} 0.2$
$3.32 C_2 D_4$	77.2±0.1	2.9±0.3	$0.15 {\pm} 0.05$	$1.68{\pm}0.2$
4.15 $C_2 D_4$	77.2±0.1	3.1±0.3	$0.15 {\pm} 0.05$	$1.58{\pm}0.2$
$\sim 6 C_2 D_4$	77.3±0.1	3.6±0.3	$0.15 {\pm} 0.05$	1.68±0.2

TABLE I. Structural transition between HD and ID [peak (1)]. T_p , FWHM, and ΔH represent the position, full width at half maximum, and the heat of transition. n=1 correspond to 1.33×10^{19} molecules

Coverage n	T_p (K)	Height (mJ/K)	FWHM (K)	$\Delta H (mJ)$
0.92 C_2D_4	71.0±2.0	0.1±0.02	~7.0±2	~0.85±0.3
$0.98 C_2 D_4$	72.5±2.0	0.1±0.02	\sim 5.5 \pm 2	$\sim 0.90 \pm 0.3$
1.10 $C_2 D_4$	73.7±0.5	1.3±0.2	2.5±1	$2.26{\pm}0.5$
1.15 C ₂ D ₄	76.4±0.3	2.3±0.2	1.50±0.2	4.88±1.0
$1.26 C_2 D_4$	77.5±0.3	3.4±0.2	0.85±0.2	3.59±1.0
1.33 $C_2 D_4$	78.1±0.3	3.2±0.2	0.55±0.2	$3.38 {\pm} 1.0$
1.48 $C_2 D_4$	79.0±0.1	3.0±0.2	$0.60 {\pm} 0.1$	2.07±0.4
$1.56 C_2 D_4$	79.0±0.1	3.2±0.2	0.50±0.1	2.07±0.4
$1.60 C_2 D_4$	79.0±0.1	3.1±0.2	0.45±0.1	2.15±0.4
1.88 C_2D_4	79.4±0.1	2.5±0.2	$0.50{\pm}0.1$	1.88±0.3
2.14 C ₂ D₄	79.6±0.1	2.9±0.2	$0.30 {\pm} 0.05$	1.47±0.2
2.32 $C_2 D_4$	79.6±0.1	2.9±0.2	$0.25 {\pm} 0.05$	1.39±0.2
2.63 C_2D_4	79.6±0.1	2.7±0.2	$0.20 {\pm} 0.05$	1.37±0.2
2.92 C_2D_4	79.7±0.1	2.7±0.2	$0.30 {\pm} 0.05$	1.48±0.2
3.32 $C_2 D_4$	79.7±0.1	2.7±0.2	$0.25{\pm}0.05$	$1.44 {\pm} 0.2$
4.15 C_2D_4	79.8±0.1	1.9±0.2	0.50±0.1	$1.64{\pm}0.2$
$\sim 6 C_2 D_4$	79.4±0.2	1.1±0.2	1.00 ± 0.2	1.57±0.2
1.33 ^a C ₂ D ₄	76.2±0.5	0.9±0.2	1.7±0.2	3.50±0.4
2.92 ^a $C_2 D_4$	77.9±0.5	1.4±0.2	1.7±0.2	3.28±0.4

TABLE II. Structural transition between ID and LD phases and layering transition from monolayer to bilayer [peak (2)].

^aCooling process, peaks (1) and (2) are merged together.

pretation requires the existence of three different phases (bulk, HD and LD) in the temperature interval between 76 K and 79 K above n=1.35. This is not allowed by the Gibbs phase rule. Therefore, it is more likely that between 76 K and 79 K and between n=0.90 and n=1.25, a pure solid phase ID distinct from HD and LD exists; above n=1.25 a coexisting region of (ID + bulk) is present.

In order to examine thermal hysteresis of the structural and layering transitions, scans were made during cooling as well as warming for coverages n = 1.33 and n = 2.92 (all other scans were made by warming the sample cell). While two well-defined peaks at both coverages are observed during warming, only one broad peak is observed during the cooling process. The heat of transition seen in the cooling process is equal to the sum of the two peaks in the warming process. Since peak (2) in Figs. 4 and 5 are smoothly connected from monolayer to multilayer and that only a merged heat-capacity peak of structural and layering transitions is observed during cooling, it is reasonable to conclude that the structural transition in monolayer solid and the layering transition from monolayer to bilayer are strongly coupled. Tables I and II show the characteristics of peaks (1) and (2).

B. Layering transitions in films thicker than two layers

Figure 7 shows seven heat-capacity traces for coverages between n=2.14 and $n \sim 6$ in the temperature range 85 K < T < 110 K. In this figure, three heat-capacity peaks for each trace are found. Two peaks labeled (5) at 95 K and (3) at 98 K are found on the low-temperature side of a broad asymmetric peak (6). Whereas peak (6) grows with coverage, peaks (3) and (5) appear to be coverage independent. Peak (5) is due to the melting of the bilayer solid. This identification is consistent with the result of x-ray diffraction; ⁶ we shall discuss this melting peak of the bilayer solid in Sec. IV.



FIG. 7. Heat-capacity traces of multilayers between 80 and 110 K. See the text for the interpretation of each anomaly. Dashed lines are drawn to represent, according to our interpretation, the contribution of peak (6).

The heat-capacity peak (3) is identified as due to the lavering transition between two- and three-laver films. This identification is consistent with other experiments of ethylene on graphite. The vapor pressure isotherm study reported a bilayer-trilayer layering transition at 98 K. The x-ray-diffraction study⁶ also found a transition from the bilayer to a thicker film at 98 K. They suggested, however, that this is not a simple layering transition but a thin-film to thick-film transition. In other words, they suggest that at 98 K the two-layer thin-film changes to a thick film whose thickness is larger than two but not limited to three layers. In addition to its size, the shape of peak (3) also appears to be coverage independent up to $n \sim 6$ (height ~ 2 mJ/K, width ~ 1.5 K). This indicates that the number of molecules involved in this transition are limited to a finite number, probably the equivalent of a single layer. This result favors the interpretation of a layering transition between a two-layer and three-layer film over that of a thin-film to thick-film transition.

The highest temperature heat-capacity peak (6) is related to the sequence of layering transitions forming layered film thicker than three layers. As discussed in the Introduction, the ellipsometry study found a series of layering transitions compressed in the narrow temperature range between 99.5 K and the triple point at 104 K.⁷ The pronounced asymmetry of peak (6) that rises gradually from the low-temperature side and drops off rapidly above 104 K is consistent with the ellipsometry result. Since the sequence of layering transitions are nearby and the heatcapacity peaks for each transition are of finite width in temperature, a merged broad signal is seen. Since the substrate used in this study is exfoliated graphite, capillary condensation of thicker adsorbed film in the crevices is also expected. It should be noted that if this peak is due only to the melting of bulk clusters, the shape should be more symmetric and should resemble a broadened (due to finite size) δ function. Even at n=6, the signature still does not resemble completely the signature of bulk triple-point melting. FWHM for this signal at n = 4.15 is 5 K and at $n \sim 6$ is 1 K, whereas a value of less than 0.15 K is found for 2D triple-point melting of methane on graphite. The rapid sharpening of the peak between n=4.15 and n=6 and the abrupt drop on the hightemperature side of the n=6 peak indicates melting of a substantial amount of bulk clusters in addition to the sequence of layering transitions, and the peak position at 103.9 K is fairly close to the true bulk triple-point temperature. Due to the problem of preferential adsorption of ethylene molecules on the walls of the calorimeter, we did not extend our scans to higher coverages. There is, however, some difficulty with this interpretation, namely the presence of this peak for coverages n=2.14 and n=2.32; at these coverages layering transition to a fourlayer film is not possible. It is tempting to interpret this as due to the melting of a trilayer film near 102.5 K, indeed, we chose such an interpretation in presenting the phase diagram in an earlier Letter¹⁹ reporting this work. However, an ellipsometry isotherm²⁰ at 97.5 K, not shown in Ref. 7, clearly confirmed the x-ray result that the trilayer film is liquidlike upon its formation. Therefore, the most reasonable and simple interpretation is that the presence of peak (6) at coverages less than n=3 are a result of capillary condensation. In the crevices of the graphite foam substrate, the effective film thickness could be significantly higher than the average value and the aforementioned layering transition to a four-layer film or the melting of a capillary condensed bulk cluster is reflected in peak (6). For an ideal substrate with no capillary condensation we would expect heat-capacity signatures due only to layering transitions at finite coverage. The triple-point δ -function heat-capacity peak should be present only for an adsorbed film of infinite thickness.

III. MONOLAYER ORIENTATIONAL ORDERING TRANSITION

Figure 8 shows heat-capacity traces between 30 and 45 K. A broad heat-capacity maximum is found near 39 K for C_2D_4 and near 36 K for C_2H_4 in submonolayer coverages. The peak near 36 K for C_2H_4 is consistent with the NMR result³ where a broad and symmetric minimum in spin-lattice relaxation time (T_1) is found at n=0.65 and n=0.74. Since the T_1 and heat-capacity signals are observed far below the melting temperature, they are probably related to transition of the orientation of the axes of the ethylene in the two-dimensional solid.

The size of this low-temperature heat-capacity anomaly (in per molecule, reduced unit) remains constant up to n=0.8, decreases with coverages up to n=0.9, and disappears for n > 0.9. This result suggests that this transition exists only in the LD phase and that there is a (HD + LD) or (ID + LD) coexisting region between n=0.8 and n=0.9. As stated in Sec. II, our phase diagram (Figs. 1 and 2) are drawn with the interpretation that there is no ID solid below 65 K.

Since this transition exists only in the LD phase where the C = C bond of the ethylene is parallel to the graphite surface,^{4,6} it is suggestive that the transition is probably related to an ordering transition of the orientation of the molecular axes, rather than that related to the rotation



FIG. 8. Heat capacity related to the orientational ordering transition in the LD phase (bottom two scans for C_2H_4 , others for C_2D_4). Dashed lines are drawn to guide the eye.

Coverage	T_p (K)	Height (units of C/Nk_B)	FWHM (K)	$\Delta H/Nk_B$ (K)
0.35 C ₂ D₄	37.6±1	2.3±0.5	4.0±1	14±3
0.45 $C_2 D_4$	38.4±1	2.5±0.5	5.0±1	18±3
0.55 $C_2 D_4$	39.2±1	3.0±0.5	4.5±1	15±3
0.76 $C_2 D_4$	39.2±1	2.3±0.5	6.0±1	20±3
0.80 $C_2 D_4$	39.0±1	1.5±0.5	4.5±1	9±3
0.84 $C_2 D_4$	39.0±1	1.3±0.5	6.0±1	9±3
$0.88 C_{2}D_{4}$	40.0±1	1.3±0.5	8.0±1	11±3
0.36 $C_2 H_4$	36.0±1	1.3±0.5	6.0±1	8±3
0.56 C ₂ H ₄	36.0±1	1.5 ± 0.5	7.0±1	10±3

TABLE III. Orientational transition in the LD phase.

TABLE IV. Melting transitions.

Monolayer					
Coverage n	T_p (K)	Height (units of C/Nk_B)	FWHM (K)	$\Delta H/Nk_B$ (K)	
	N	Ionolayer and submonolayer cov	/erages		
$0.45 C_2 D_4$	67.8±0.2	4.0±0.5	2.7±0.3	19±3	
$0.55 C_2 D_4$	67.7±0.2	5.0±0.5	2.5 ± 0.3	19±3	
$0.65 C_2 D_4$	67.8±0.2	5.0±0.5	2.7±0.3	19±3	
$0.70 C_2 D_4$	67.8±0.2	5.5±0.5	2.2 ± 0.3	17±3	
$0.78 C_2 D_4$	67.8±0.2	6.0±0.5	2.4±0.3	18±3	
0.80 C_2D_4	70.5±0.5	2.5±0.5	4.0±0.5	12±3	
$0.84 C_2 D_4$	71.0±0.5	4.5±0.5	4.0±0.5	17±3	
$0.88 C_2 D_4$	79.0±1.0	2.0±0.5	3.6±0.5	6±2	
$0.92 C_2 D_4$	85.0±1.0	$3.0 {\pm} 0.5$	5.0±0.5	11±2	
$0.98 C_2 D_4$	87.5±1.0	2.0±0.5	4.0±0.5	7±2	
1.10 C_2D_4	93.5±1.0	2.5±0.5	3.0±0.5	7±2	
0.30 C ₂ H ₄	67.5±0.5	2.5±0.5	3.3±0.5	8±2	
$0.47 C_2 H_4$	68.2±0.2	4.5±0.5	2.6±0.3	14±3	
$0.58 C_2 H_4$	68.1±0.2	6.0±0.5	2.2±0.3	18±4	
$0.61 C_2 H_4$	68.2±0.2	5.0±0.5	2.2 ± 0.3	18±4	

Beyond monolayer coverage

Coverage n	T_p (K)	Height (mJ/K)	FWHM (K)	$\Delta H (mJ)$
	Melting of the r	nonolayer (with a coexisting	bilayer solid), peak (4)	
$1.26 C_2 D_4$	88.5±1	0.4±0.1	4.5±0.5	$1.70 {\pm} 0.3$
1.33 C_2D_4	89.0±1	0.4±0.1	$3.0{\pm}0.5$	$1.20 {\pm} 0.2$
1.48 C_2D_4	88.2±1	0.3±0.1	2.0 ± 0.4	1.17±0.2
1.56 C_2D_4	87.5±1	0.3±0.1	2.0 ± 0.4	$1.10{\pm}0.2$
$1.60 C_2 D_4$	87.6±1	0.3±0.1	2.0±0.4	$0.93{\pm}0.2$
	Melting of the b	ilayer (with a coexisting mon	olayer liquid), peak (5)	
1.15 C_2D_4	95.1±1	0.5±0.2	3.0 ± 0.5	$1.50 {\pm} 0.3$
$1.26 C_2 D_4$	93.8±1	0.5±0.2	$2.0{\pm}0.4$	$1.30 {\pm} 0.3$
1.33 C_2D_4	92.5±1	0.7±0.2	2.5 ± 0.4	2.15±0.4
1.48 C_2D_4	94.2±1	0.7±0.2	3.5 ± 0.5	3.51 ± 0.5
$1.56 C_2 D_4$	94.5±1	0.8 ± 0.2	3.5 ± 0.5	$3.00 {\pm} 0.5$
$1.60 C_2 D_4$	94.7±1	0.7±0.2	4.0±0.5	3.35 ± 0.5
$1.88 C_2 D_4$	94.7±1	1.5±0.2	3.0±0.5	4.50±0.5
	Melting of	of the bilayer (with coexisting	bulk), peak (5)	
2.14 C_2D_4	94.8±1	0.6±0.2	1.0 ± 0.2	1.1 ± 0.2
2.32 C_2D_4	94.9±1	0.4±0.2	1.2 ± 0.2	1.0 ± 0.2
2.63 C_2D_4	94.9±1	0.8±0.2	1.4 ± 0.2	1.4 ± 0.2
2.92 C_2D_4	96.0±1	0.5 ± 0.2	1.2 ± 0.2	1.4 ± 0.2
$3.32 C_2 D_4$	96.0±1	0.5±0.2	1.0 ± 0.2	$1.0 {\pm} 0.2$
4.15 C_2D_4	96.0±1	0.9±0.2	1.2 ± 0.2	1.7 ± 0.3
$\sim 6 C_2 D_4$	97.5±1	0.8 ± 0.2	1.2 ± 0.2	1.6±0.3

about the C = C axis. This interpretation is supported by the study of Prenzlow, Beard, and Brundage²¹ which suggested that the C—H axis of the C_2H_4 molecule in the LD phase is inclined at 35° with respect to the graphite surface, and the C = C axis is parallel to the surface. For submonolayer N_2 and CO on graphite,²² the molecular axes form an ordered herringbone structure below the transition temperature and the high-temperature phase is orientationally disordered. It is likely that the low temperature, ordered phase in ethylene on graphite also forms a herringbone structure.²³ The heat-capacity anomaly in ethylene on graphite is broad (FWHM about 5 K) and weak (peak height is on the order of $2k_B$ per molecule). For N_2 and CO on graphite, the FWHM and peak heights are, respectively, 1 K and 3 K and $5k_B$ and $0.5k_B$ per molecule.^{24,25} In the nitrogen and CO cases, the two-dimensional solid overlayer is commensurate $(\sqrt{3} \times \sqrt{3})$ with the substrate in both the herringbone and disordered phases.

As stated above, the neutron-diffraction study⁴ did not find any evidence for the orientational ordering transition down to 10 K, however, a more recent neutron study found evidence for a slight structural transition in the LD phase near 40 K.²⁶ It is possible that the orientational ordering transition is accompanied by a structural transition as suggested in a molecular-dynamics simulation study.²³ It is not clear whether the broad and weak heat-capacity signal is consistent with such a picture of orientational ordering transition. Table III summarizes the heat-capacity peak of the orientational ordering transition of the monolayer.

IV. THE MELTING OF ETHYLENE ON GRAPHITE

Verification of a 2D continuous and, in particular, Kosterlitz-Thouless-Nelson-Halperin-Young (KTNHY) type of melting transition²⁷ is one of the most interesting possibilities in physisorbed systems. Since our result of the melting transition in monolayer region has already been reported in a recent paper,¹⁸ only a summary will be given here. Ethylene on graphite is unique among all physisorption systems showing continuous melting behavior in submonolayer as well as monolayer completion region. The peak height of the heat-capacity anomaly related to melting for submonolayer as well as monolayer completion region is on the order of 20 times smaller but the width is 20 times broader than that found for systems such as O₂,²⁸ Ne,²⁹ Xe,³⁰ and CH₄ (Ref. 17) on graphite. These systems, just as ethylene on graphite, melt from an incommensurate solid phase. The absence of any sharp heat-capacity peak allows us to conclude that there is no abrupt density jump larger than 0.05% between the solid and liquid phases throughout the melting process. The lack of singularity in heat capacity is consistent with the prediction of KTNHY.

The characteristics of the melting transition, i.e., peak temperature, full width at half maximum, peak height, and heat of transition are shown in Table IV from submonolayer to multilayer coverages.

At this point we do not understand why ethylene on graphite is the only system that exhibits continuous melting transition in the entire monolayer coverage. In Table V, the ratio of 2D triple temperature to a 2D critical temperature, T_t^{2D}/T_c^{2D} , is compared for a number of adsorbates that melt from incommensurate 2D solid phases. This ratio turns out to be between 0.82 and 0.86 for Xe, Ne, Ar, and methane. Ethylene, however, has a much lower value of 0.62. This might indicate that the solid ethylene overlayer is not as stable as that of the other overlayer systems mentioned earlier. However, this may not be a relevant observation since the ratio for O₂ on graphite is even smaller and the melting transition of O₂ on graphite was found to be clearly first order. A comparison of the T_t^{2D}/T_c^{3D} , where T_c^{3D} is a 3D critical temperature, also shows anomalously low values for O₂ and C₂H₄ on graphite.

The simulation study of Saito³⁴ shows that the melting of a two-dimensional overlayer can change from firstorder-like, with dislocations of small core energy, to continuous for sufficiently large core energy. Assuming an activation model³⁵ for the melting transition, the value of E_c/k_bT_m for ethylene is almost four times Saito's critical value.³⁴ Here E_c is the core energy of dislocation and T_m is the melting transition temperature. If an activation model of dislocation unbinding is appropriate to understand our data, then it would be interesting to determine why the ethylene on graphite system shows large core energy of dislocation. A recent simulation study³⁶ found that the melting of ethylene on graphite involves the standing up of the ethylene molecule for the LD phase, and the simulation indicates that the molecules stand up gradually. It is not clear to us whether this mechanism is related to the dislocation unbinding model.

Figure 9 shows heat-capacity traces related to the melting transition of monolayer film [peak (4)] and bilayer

TABLE V. Ratios of the two-dimensional triple point to the two-dimensional and three-dimensional critical-point temperature for various adsorbates on graphite.

Adsorbate	T_t^{2D} (K)	$T_c^{2\mathrm{D}}$ (K)	T_c^{3D} (K)	$T_t^{2\mathrm{D}}/T_c^{2\mathrm{D}}$	T_t^{2D}/T_c^{3D}
Ne	13.6 (Ref. 29)	15.8 (Ref. 29)	44.5 (Ref. 31)	0.87	0.31
O ₂	25.5 (Ref. 28)	65.0 (Ref. 28)	154.3 (Ref. 31)	0.39	0.17
Xe	99.0 (Ref. 30)	117.0 (Ref. 30)	289.8 (Ref. 31)	0.85	0.34
Ar	47.0 (Ref. 16)	55.0 (Ref. 16)	150.9 (Ref. 31)	0.86	0.31
CH₄	56.5 (Ref. 17)	68.8 (Ref. 17)	191.0 (Ref. 32)	0.83	0.30
C_2H_4	67.8ª	110.0ª	283.0 (Ref. 33)	0.62	0.24

^aPresent work.



FIG. 9. Heat-capacity anomalies related to (4) first layer melting and (5) bilayer melting transitions.

film [peak (5)] between n = 1.10 and n = 1.88. This assignment is consistent with the x-ray-diffraction result⁶ which found a loss of long-range order in the monolayer before the bilayer film. The monolayer melting peak was found to decrease in size with coverage above n=1.15 and disappear for n = 1.88 and above. This result suggests that between n = 1.15 and n = 1.65 the adsorbed film consists of a monolayer (LD) and a coupled bilayer (2S) rather than a decoupled top and bottom layer. Above the coexistence region, a pure bilayer film is found. For 1.10 < n < 1.15 the melting temperature of monolayer appears to bend downwards from 94 to 88 K. The monolayer melting temperature remains constant near 88 K in the monolayer and bilayer coexisting region. The heatcapacity peaks related to the melting of monolayer and bilayer in Fig. 9 are comparable in height ($\sim 2k_B$ per molecule) and width (~ 3 K) with each other. These peaks are also comparable to the melting peak in submonolayer coverages. The similarity suggests that the nature of melting of the bilayer is similar to that of monolayer, namely it is also continuous.

V. LIQUID-VAPOR CRITICAL POINT OF MONOLAYER ETHYLENE ON GRAPHITE

Figure 10 shows five traces showing the heat-capacity anomaly related to crossing the liquid-vapor coexistence region for various submonolayer coverages. The height and the half-width of the peak are similar to those found for two-dimensional liquid-vapor transition of other ad-



FIG. 10. Heat-capacity anomaly related to liquid-vapor transition of the monolayer film.

sorbate systems.^{16,17,37} The fact that the peak temperature is essentially coverage independent between n=0.35and n=0.55, indicating a coexistence boundary that is perpendicular to the temperature axis over a wide coverage range. In the methane system, ¹⁷ where an exhaustive study was made, the critical exponent β which characterized the liquid-vapor coexistence boundary, was determined to be 0.127 ± 0.02 in good agreement with the value of 0.125 expected for a 2D Ising model system.³⁸ Here β defined by the power law $(n_1 - n_c) = (n_c - n_v)$ is $=B[(T_c-T)/T_c]^{\beta} \text{ where } n_l, n_v, \text{ and } n_c \text{ are, respectively,}$ the two-dimensional liquid, vapor, and critical coverages, and T_c is the critical temperature. Although the twodimensional liquid-vapor coexistence region in ethylene on graphite, as that in Ar, ¹⁶ and CF₄, ³⁷ was not mapped out to the extent to yield a reliable value for β , the qualitative shape of the coexistence boundary found in these systems is similar to that found in the methane on graphite system. This similarity is indeed expected as a consequence of principle of universality.

Figure 10 shows that the two-dimensional critical temperature of C_2H_4 on graphite at 110 K is 2.3 K higher than that of C_2D_4 on graphite. A similar isotopic effect is found in the methane or graphite system³⁹ [68.7 K (CH₄) and 68.4 K (CD₄), respectively]. The sign of the isotopic effect is also consistent with that found for three-dimensional liquid-vapor transition in methane.³² The isotopic effect in ethylene is much larger than that for methane. We are not able to locate the critical temperature of bulk C_2D_4 for comparison.

Our critical temperature at 110 K is substantially lower than the value found by vapor pressure isotherm experiments at 114.2 K (Ref. 1) and 120 K (Ref. 8). We believe our result is more reliable because in our experi-

Coverage n	T_p (K)	Height (units of C/Nk_B)	FWHM (K)	$\Delta H/Nk_B$ (K)
0.15 $C_2 D_4$	73.0±1.0	4.0±0.5	4.0±1.0	12±5
$0.35 C_2 D_4$	107.0±0.5	7.0±1.0	3.6±0.5	25±5
$0.45 C_2 D_4$	107.7±0.5	8.0±1.0	3.2 ± 0.5	23±5
$0.55 C_2 D_4$	107.7±0.5	7.0±1.0	2.6±0.5	17±4
0.70 $C_{2}D_{4}$	95.0±0.5	6.4±1.0	2.6±0.5	13±3
$0.47 C_2 H_4$	110.0±0.5	7.0±1.0	3.6±0.5	23±5

TABLE VI. 2D liquid-vapor transition.

ment scans were made along a path that is perpendicular to the phase boundary of the coexistence region. In contrast, vapor pressure isotherms are performed along a path that is parallel and therefore less sensitive to the phase boundary.⁴⁰

The peak temperature, height, half-width, and heat of transition of heat-capacity peak due to two-dimensional liquid-vapor transition of ethylene on graphite are tabulated in Table VI.

VI. LAYER-CRITICAL-POINT TRANSITIONS

Since the result of the layer-critical-point transitions of ethylene on graphite has already been reported, ¹⁹ only a brief discussion will be given here.

The study of Menaucourt, Thomy, and Duval¹ found a "vertical" step, representing a coexistence region of monolayer and bilayer films for a number of vapor-

pressure isotherms performed above T_t . This vertical step becomes washed out for isotherms taken above 119 K. Similarly, the "vertical" second step evident in our 108-K isotherm in Fig. 3 becomes less vertical at 115.2 K. As discussed above, the ellipsometry study⁷ also found a number of vertical steps in isotherms measured below as well as above T_t . Isotherms taken at higher temperatures (e.g., 112.5 K) also show rounding of the higher layer (m > 4) steps. The vertical steps in the isotherm show that the growth of the adsorbed film proceeds layer-by-layer that passes through successively coexisting regions; namely regions where a film of m-1layers coexist with that of m layers with m = 2, 3, 4, ...At higher temperatures, the verticality of the isotherm disappears signifying that the growth is no longer layerby-layer, i.e., the film thickness increases continuously with the addition of adsorbate molecules. The critical

TABLE VII. Layer-critical-point transition. Here n and n_e represent the coverage corresponding to total number of molecules in the sample cell and the effective surface coverage with desorption correction at the transition temperature.

	Coverage	<i>T</i> .	Height	FWHM	۸ <i>H</i>
Coverage n	n _e	(K)	(mJ/K)	(K)	(mJ)
1.20	1.095	108.5±1.5	0.32±0.03	4.2±0.5	1.3±0.3
1.27	1.145	114.5 ± 1.5	$0.24{\pm}0.03$	6.4±1.3	1.5±0.5
1.30	1.165	115.0 ± 1.5	$0.37 {\pm} 0.05$	7.1 ± 1.0	2.6±0.7
1.33	1.190	115.0±1.5	$0.54{\pm}0.03$	7.7±1.0	4.2±0.8
1.36	1.220	115.0 ± 1.5	0.72 ± 0.05	8.0 ± 1.0	6.4±1.2
1.44	1.30	115.5 ± 1.5	$0.56 {\pm} 0.06$	6.5 ± 1.0	3.6 ± 1.0
1.47	1.32	116.0 ± 1.5	0.88 ± 0.5	6.9±1.0	6.0 ± 1.2
1.52	1.38	116.0±1.5	0.48 ± 0.05	5.9 ± 1.0	2.8 ± 0.8
1.57	1.43	114.7±1.5	0.64 ± 0.03	4.6±1.0	2.9 ± 0.8
1.59	1.46	113.8 ± 1.5	0.60 ± 0.02	3.0 ± 1.5	1.9+1.6
1.61	1.46	115.0 ± 1.5	0.64 ± 0.05	4.1±1.0	2.6 ± 0.8
1.61	1.54	109.0 ± 1.5	0.45 ± 0.03	3.9 ± 1.0	1.7+0.6
1.62	1.47	115.0 ± 1.5	0.32 ± 0.03	2.6 ± 1.0	0.8 ± 0.4
1.62	1.53	110.0 ± 1.5	0.32 ± 0.03	3.2 ± 1.0	1.0 ± 0.4
1.63	1.54	111.1±1.5	$0.45 {\pm} 0.05$	5.0±1.0	2.2±0.7
2.43	2.28	110.5±1.5	0.72 ± 0.08	4.2±1.0	3.0 ± 1.1
2.52	2.35	111.0 ± 1.0	0.64 ± 0.05	4.2+1.0	27+09
2.56	2.39	111.0 ± 1.0	0.88 ± 0.05	4.6±0.5	30+0.7
2.63	2.46	111.0 ± 1.0	0.64 ± 0.16	3.9 ± 0.5	2.5 ± 0.9
2.72	2.60	108.5±1.0	0.88 ± 0.08	4.2±0.5	3.7±0.8
3.50	3.25	108.5 ± 1.0	0.88 ± 0.08	3 3+0 5	2 9+0 7
3.76	3.50	108.5 ± 1.0	1.04 ± 0.08	25+05	2.5 ± 0.7
4.03	3.35	108.5 ± 1.0	1.0120.00	2.5 ±0.5	2.0±0.7
	4.5	105 ±1			

temperatures separating the discontinuous or layer-bylayer and continuous growth regimes is called the layercritical-point $T_c(m)$. $[T_c(m)$ is not expected to be the same for all *m*'s.] Following the discussion in the Introduction, as the film thickness diverges, i.e., $m \to \infty$, $T_c(m)$ approaches towards the roughening transition temperature T_R .

Heat-capacity scans, performed along constant (or quasiconstant) coverage path, as in the case of twodimensional liquid-vapor transition, is a suitable technique to locate the boundaries of coexistence and the layer-critical-point temperatures. As discussed in the Introduction, the vapor pressure of ethylene, by comparison to other adsorbates, is exceedingly low, so that vapor desorption correction is not a serious obstacle for such a study. The characteristics of the heat-capacity peaks related to the layer-critical-point transition are summarized in Table VII.

For scans taken between n=1 and 2, heat-capacity signals related to the crossing of the coexistence boundary of monolayer and bilayer liquid films are found. At higher coverages, heat-capacity peaks corresponding to the crossing of the coexistence boundaries of the bilayer and trilayer, and that of the trilayer and quadlayer liquid films are also found (see Fig. 3 of Ref. 19). These results locate the respective layer-critical-point temperatures at $T_c(2)=115.3$ K, $T_c(3)=111$ K, $T_c(4)=108.4$ K, and $T_c(5) \sim 105$ K.

These values are striking that they showed liquid ethylene is layered by the graphite substrate. We know the adsorbed film is liquidlike since the melting temperature of the monolayer and bilayer are well below T_t and $T_c(2)$ and $T_c(3)$ and we know from x-ray and ellipsometry results that adsorbed film equal and thicker than three layers are liquidlike upon their formation. The monotonic decrease in $T_c(m)$ with m is quite reasonable since the graphite substrate, responsible in layering the liquid film, is expected to be less effective with increasing m. These results ought to be considered together with the ellipsometric isotherm results;⁷ namely layering transitions for the four-, five-, and six-layer films were found near 102.1 K, 103.2 K, and 103.3 K, respectively. For film coverage above six layers and for temperatures inside (both below and above) 1 K of T_t , reliable experimental information is not available. Based on available results, it is tempting and reasonable to speculate that under more ideal experimental conditions, for example, improved precision and stability in pressure and temperature control and measurement under equilibrium rather than varying pressure, Drir, Nham, and Hess⁷ might resolve even more steps as T approaches T_t above 103.3 K, leading to a wetting transition at T_t . If a much more sensitive heat-capacity study can be made with a graphite substrate with no capillary condensation, one might also observe the continued decrease in $T_c(m)$ towards T_t with increasing *m*. Since the sequence of layering transitions is proposed to end at T_t , $T_c(m)$ will not assume a value below T_t for any *m*. Such a scenario of film growth on a solid surface resembles Fig. 4(b) in the paper of Pandit and Fisher.¹¹

The only other physisorbed system exhibiting layered liquid is multilayer O_2 on graphite.⁴¹ In this system, isotherm study found coexistence regions of the monolayer and bilayer films, and the bilayer and trilayer films up to 60 K, and diffraction experiment⁴² clearly indicates that the melting temperature of the various multilayer are all below T_t (50.4 K). However, the isotherm result indicates that $T_c(m)$ might be constant at 60 K for the first few layers.⁴¹

The layer critical point has been observed in a number of other systems, namely, CF_4 , ³⁷ Kr, ⁴³ and CH_4 (Ref. 44) on graphite. In these systems, $T_c(m)$ was found to be below T_t and the adsorbed films are solid layers. CF_4 on graphite may be an exception, i.e., the layer critical point $T_c(2)$ was found at 93 K, above its triple point 89.5 K and the coexistence region is proposed to be that of a monolayer solid and bilayer fluid. ³⁷ However, $T_c(m)$ for $m \ge 3$ are found to lie below T_t .³⁷

Heat-capacity scans made at 13 coverages in the monolayer-bilayer coexistence region allow us to determine that the critical exponent β characterizing the coexistence phase boundary lies between 0.08 and 0.17 where β is defined according to $(n_2 - n_c) = (n_c - n_1) = B [(T_c - T)/T_c]^{\beta}$. Here n_2 , n_1 , and n_c are, respectively, the bilayer, monolayer, and critical coverages. A vapor pressure isotherm experiment⁴⁵ studying the condensation of the second layer of Ar on CdCl₂ (i.e., the coexistence region of the monolayer and bilayer) found a value of 0.16 for β with an upper limit of 0.21. These results are consistent with the theoretical predictions^{9,13} that the layer-critical-point transition, at least for that between m=2 and m=1, does belong to the two-dimensional Ising universality class.

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