RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 7 1 SEPTEMBER 1988

Layer critical points of multilayer ethane adsorbed on graphite

H. S. Nham and G. B. Hess
Department of Physics, University of Virginia, Charlottesville, Virginia 22901

(Received 20 May 1988)

The physisorption system ethane on graphite was investigated by an ellipsometric technique. We report layer condensation critical temperatures for layers 2–9. $T_c(2)$ is 120.8 ± 0.3 K, somewhat lower than previously reported. $T_c(n)$ decreases with increasing layer number n until for $n = 8$ and 9 the extrapolated critical temperatures are below the bulk melting point (90.3 K), where these layers have been preempted by bulk solid. The coefficient of the compressibility above T_c increases strongly with n. This phenomenon is not predicted in a theory based on the two-dimensional Ising model, and probably reflects the importance of a second interaction parameter related to the substrate holding potential.

When a uniform substrate surface at low temperature is exposed to an adsorbate gas, in some cases adsorbate condensates on the surface layer by layer, and each layer in the neighborhood of its condensation can be regarded as a two-dimensional system. The formation of the nth layer on top of $(n-1)$ layers is in this case a first-order phase transition. This means, for an ideal substrate, the coverage of the adsorbate in the film increases abruptly at a particular pressure of the gas surrounding the substrate. As T increases, the first-order phase transition may terminate at a layer critical temperature $T_c(n)$, beyond which the step in coverage is no longer vertical. In practice, the shape of the step in the coverage-pressure plane always has a finite slope because of the nonideality of the substrate. The number of layers which can be formed in this manner depends mainly on the relative strength of the interaction between adsorbate and substrate and that between adsorbate molecules themselves.[1] If the film thickness becomes infinite as the pressure approaches the vapor pressure of the bulk phase, the case of the strong substrate, the behavior is called "wetting" or "complete wetting." Otherwise, it is called "nonwetting" or "incomplete wetting." A system which does not wet at low temperature may wet above some temperature T_w.[1,2] As the layer number increases, $T_c(n)$ must either fall below T_w or converge to a roughening temperature T_R.[3] The roughening transition at T_R is a bulk interfacial phase transition. A solid-gas interface will be atomically flat for $T < T_R$ and will be rough for $T > T_R$. A liquid-gas interface is expected always to be rough because of long-wavelength capillary waves. The roughening temperature must then be, if not zero, at least below the bulk melting temperature and inaccessible.

The system of ethane adsorbed on graphite has been studied by various groups using volumetry,[4] neutron diffraction,[5] quasielastic neutron scattering,[6] low-energy electron diffraction[7-10] (LEED), reflection high-energy electron diffraction[10] (RHEED), and inelastic neutron scattering.[11] Most experiments are in the monolayer region and only Refs. 4, 7, and 10 deal with multilayers. Only Regnier, Menaucourt, Thomy, and Duval[4] (RMTD) report layer critical temperatures. They used a volumetric adsorption isotherm technique and found both $T_c(1)$ and $T_c(2)$ to be about 130 K, which is nearly 40 K above bulk melting. For comparison, the second-layer critical temperature of ethylene[12] and CF_4 (Ref. 13) are approximately 12 and 10 K above their bulk melting points, respectively. In this sense ethane provides an extreme case of a layered liquid film.

Multiple-layer critical temperatures have been reported for several other systems. Maynard and co-workers[14] studied layered solid ^{4}He films on graphite under bulk liquid and reported that $T_c(n)$ increases with increase of n. Zhang, Feng, Kim, and Chan,[12] using a heat-capacity technique, found that $T_c(n)$ is decreasing toward the bulk melting point with the increase of n from two to five in the case of the layered liquid-ethylene film. Hamilton and Goodstein[15] reported that $T_c(n)$ is around 78 K from the first to sixth layer for solid methane films.

The heat-capacity technique has an advantage in determining layer critical temperatures in that the path of the experiment is generally perpendicular to the boundary which separates the homogeneous fluid region from the two-dimensional liquid-vapor coexistence region in the coverage-temperature plane. In the case of adsorption isotherms, one observes a change of slope of the step in the coverage-chemical potential $(N-\mu)$ plane as the temperature increases above T_c. One of the difficulties in determining the layer critical temperature by this technique is that, unless the quality of the substrate is very good, background width in the two-phase coexistence region can obscure the slope change near the layer critical temperature. Dash and Puff[16] analyzed the effects of heterogeneity, which they described by a convolution in μ of the ideal $(\partial N/\partial\mu)_T$ with a binding-energy-width function $g(\mu-\mu_2)$. Ecke and co-workers[17] applied the model of Dash and Puff with a Gaussian binding energy distribution of width σ to a two-dimensional Ising equation of state. For our substrate the width σ, normalized by k_BT_c, is about 5×10^{-4}. This low heterogeneity is possible because the ellipsometric technique requires only a small patch of the substrate surface.

In this paper we report measurement of adsorption isotherms for ethane on highly oriented pyrolytic graphite (HOPG) above and in the neighborhood of the bulk ethane melting point at 90.3 K. An ellipsometric signal

I_1, which is proportional to the coverage, is recorded as a function of time along with the pressure of the adsorbate gas, as the pressure is increased to saturation at fixed temperature. The technique will be described in detail elsewhere.[18] In the ethane experiment we covered the temperature range from 79 to 132 K with 67 complete isotherms, extending from the second layer to saturation, and 35 partial isotherms. In this paper we will report primarily results relating to the layer critical temperatures. When the film is in equilibrium with the surrounding gas, the chemical potential of the film is equal to that of the gas. This allows us to calculate the chemical potential of the film from the measured vapor pressure. From this we construct the phase diagram given in Fig. 1.

Chemical potentials are plotted relative to bulk liquid-vapor coexistence. The solid line represents bulk solid-III phase,[19] relative to a simple extrapolation of the bulk liquid chemical potential. Different symbols indicate our data for the condensation of the second through the sixth layers. These layer lines have negative slopes, decreasing in magnitude from 0.83 for the second layer to 0.31 for the third and 0.15 for the fourth. This implies that the partial entropy (in units of k_B) is larger than the entropy of bulk liquid by these amounts. This probably reflects an increase in entropy per molecule on going from monolayer to bilayer, and to successively higher layers, due to reduced constraints on molecular orientation. Also shown are the layer critical points, as determined below.

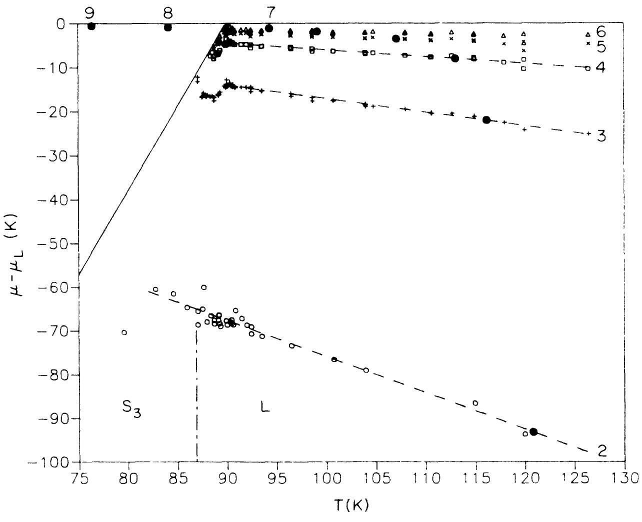

FIG. 1. Chemical potential at layer condensation (relative to bulk liquid) vs temperature. Different symbols are used for layers two through six, which are labeled at the right. Dashed lines are fits to the data for three of the layers; in fitting the second layer, the point near 80 K is excluded, and for the third and the fourth, only data at $T > 90$ K are used in the fits. The solid circles are layer critical points (see text). The solid line represents bulk solid-III phase-vapor coexistence. The dot-dashed line represents melting of the monolayer solid phase S_3 (from Ref. 6).

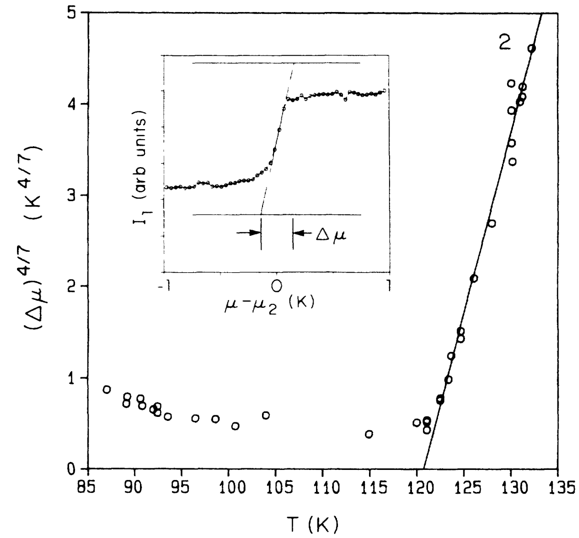

FIG. 2. Width $\Delta\mu$ of the second-layer condensation step, raised to the $\frac{4}{7}$ th power, as a function of temperature. The solid line is a fit to the data above 122 K. Inset: A portion of a 120 K isotherm near the second-layer step. The width $\Delta\mu$ is taken from the intercept of the tangent drawn at the inflection point with the horizontal lines, which represent the height of a complete layer.

The inset of Fig. 2 shows a small portion near the second-layer condensation step of an isotherm at 120 K, from which we determine the width $\Delta\mu$ of the step. In the one-phase region of hypercritical fluid, scaling theory predicts the two-dimensional compressibility K_T to diverge as $[(T-T_c)/T_c]^{-\gamma}$, where $\gamma=\frac{7}{4}$ for the two-dimensional Ising model. $\Delta\mu$ is related to K_T by

$$\Delta\mu=(4/\Delta N)K_T^{-1} \tag{1}$$

where ΔN is the full coverage in the layer.

Therefore, above but near T_c,

$$\Delta\mu=\Gamma\left(\frac{T-T_c}{T_c}\right)^{\gamma}. \tag{2}$$

When $\Delta\mu$ for the second layer is graphed against temperature, it is clear that the width of the step increases rapidly for temperatures higher than about 121 K, but the onset is not very well defined, because the plot is curved near the beginning of the rise. Below T_c, in the two-dimensional gas-liquid coexistence region, $\Delta\mu$ does not vanish completely because of the heterogeneity of the substrate. The background value $\Delta\mu_B$ is given in Table I.

If Eq. (2) applies with $\gamma=\frac{7}{4}$, then, if we take $\frac{4}{7}$th power of $\Delta\mu$, we should get a straight line in the high-temperature region. This is done in Fig. 2. The layer critical temperature is determined by reading the intersection between the extrapolated line of the fit and the horizontal axis $\Delta\mu=0$. When the data are corrected for the heterogeneity as in Ref. 13, we find very little difference between corrected and uncorrected data above T_c, so we can neglect the effect of heterogeneity when smaller than the intrinsic width. Therefore we present here raw data which are not corrected for heterogeneity, except for layers eight and nine.

From Fig. 2 we find the second-layer critical temperature to be 120.8 ± 0.3 K, which is about 9 K lower than the value estimated by RMTD. Much of the difference may be due to the effect of curvature of $\Delta\mu$ as a function

TABLE I. Experimental quantities for layers 2–9, all in kelvin temperature units. $T_c(n)$ is the nth layer critical temperature, $\Delta\mu_B$ is the transition width below T_c, Γ is the critical width coefficient defined by Eq. (2), and $\mu_c(n)-\mu_L$ is the chemical potential at the nth layer critical point relative to saturated bulk liquid.

n	$T_c(n)$	$\Delta\mu_B$	Γ	$\mu_c(n)-\mu_L$
2	120.8 ± 0.3	0.21	878.4	−93.2
3	116.1 ± 0.6	0.14	301.7	−22.1
4	113.0 ± 1.1	0.07	106.4	−8.1
5	107.1 ± 0.8	0.08	30.1	−3.6
6	99.1 ± 1.6	0.06	8.3	−1.9
7	94.3 ± 1.9	0.05	4.4	−1.2
8	84.1 ± 2.8	(0.05)	1.3	−0.9
9	76.4 ± 10.2	(0.05)	0.7	−0.65

of T. We have determined in the same way the critical temperatures of the higher layers up to the seventh layer. In Fig. 3, which shows data for the fifth to seventh layers, we clearly see a constant background in two-phase region, which we assume to be due to heterogeneity of the surface, and an increase at higher temperatures. The critical temperatures determined from these plots are listed in Table I. In the eighth- and ninth-layer widths there is no evident two-phase region. We therefore assume that the background width is the same as for the seventh layer and we correct our data for this background, assuming it adds in quadrature.[13] The corrected widths are given in Fig. 4 and then fit in the same way as the other layer steps.

Up to this point, we have assumed a critical exponent γ of $\frac{7}{4}$, taken from the two-dimensional Ising model. We can estimate the critical exponent γ for the second layer from our data. We varied γ and computed the goodness of the fit χ^2 for the 16 data points at $T > T_c$ as a function of γ. The χ^2 is normalized so that its minimum value is 14 with 14 degrees of freedom. The minimum is at $\gamma = 1.76$, which is fortuitously close to the theoretical value. The value of χ^2 remains below 15 for γ between 1.38 and 2.50, which is then an estimate of the range consistent with our data. If the second-layer critical temperature is reevaluated with different values of the exponent, $T_c(2) = 118.1$ K for $\gamma = 1.38$ and $T_c(2) = 122$ K for $\gamma = 2.5$.

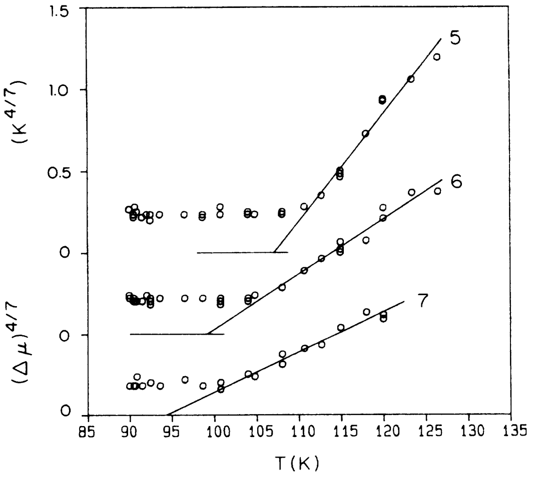

FIG. 3. Same as Fig. 2, for layers five, six, and seven. The zeros are offset. Fits (solid line) include data above 112 K for the fifth, above 110 K for the sixth, and above 107 K for the seventh layer.

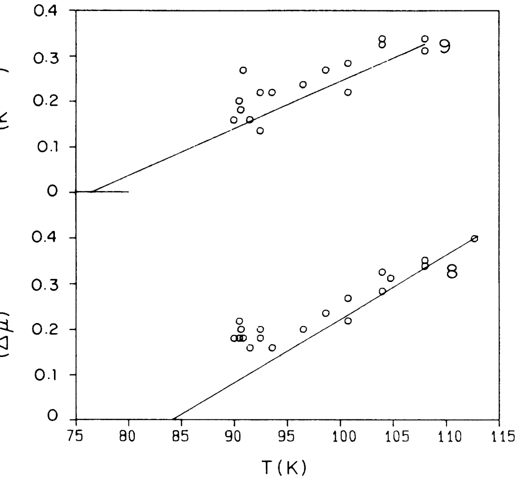

FIG. 4. Same as Fig. 3, for layers eight and nine, except data are corrected for substrate heterogeneity. Fits include data above 98 K for the eighth and above 96 K for the ninth layer. The zero is offset for the ninth layer.

The Ising model also predicts the coefficient of the compressibility (susceptibility) near T_c. The value is given by Fisher[20] for several two-dimensional (2D) lattices. The prediction for the coefficient in Eq. (2) is

$$\Gamma = 4T_c/C_T^+ \,, \tag{3}$$

where $C_T^+ = 0.9627$ for a square lattice or 0.9244 for a triangular lattice and $\Delta\mu$ is in temperature units. For $T_c = 120.8$ K the coefficient Γ then is about 500 K. Griffith's[21] equation of state also results in about the same value, from the leading term in his function $h(x)$. Therefore, based on the two-dimensional Ising model, we might expect $\Gamma(n)$ to be constant, and independent of the layer number. The coefficients $\Gamma(n)$ from the slopes of fits such as those shown in Figs. 2–4 are given in Table I. We find that they decrease very strongly with the layer number.

When the layer critical temperatures are located in the chemical potential-temperature phase diagram (Fig. 1), $T_c(2)$ through $T_c(7)$ are above the bulk melting temperature in the 3D vapor region, and decrease approximately linearly with n. Similar behavior has been reported for ethylene.[12] However the extrapolated eighth- and ninth-layer critical points are above the bulk solid line. These are therefore virtual critical points, and there is no real phase transition. The corresponding steps are nevertheless quite sharp because the compressibility coefficient is large for these high layers.

This is different from the behavior calculated by Huse[22] for a lattice gas model, and by Nightingale, Saam, and Schick[23] for the solid-on-solid (SOS) model, for which $T_c(n)$ increases with the increase of film thickness, with the dependence

$$T_R - T_c(n) \propto (\ln n)^{-2} . \qquad (4)$$

In the lattice gas model and in the SOS model there is only one condensed phase, which has solid characteristics. Decreasing $T_c(n)$ is consistent with qualitative expectations for a liquid film, as discussed above. Very recently, Chernov and Mikheev,[24] and Ball and Evans,[25] have studied layering in liquids near a wall and layer critical points, using density functional theory. The first paper[24] includes a renormalization-group treatment of capillary waves, and predicts critical temperatures consistent with our results if the bulk-liquid correlation length is about two times the layer thickness.

The behavior of the compressibility coefficient is also not predicted by available model calculations, but is responsible in part for the striking persistence of layering in certain liquid films. In the two- (or three-) dimensional Ising model, both T_c and Γ scale with a single interaction parameter. In the present problem, where the substrate potential is responsible for the existence of layer condensation, there is evidently an additional parameter, strongly dependent on distance from the substrate, which controls $\Gamma(n)$. For comparison with $\Gamma(n)$, we have also listed in Table I the chemical potentials at the layer critical points, relative to bulk liquid at the same temperature, a quantity which is expected to be dominated by the substrate potential.

We have benefited from discussions with M. H. W. Chan, W. F. Saam, M. Schick, and J. G. Dash. This work was supported by the National Science Foundation, Low Temperature Physics, Grant No. DMR 8617760.

[1] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

[2] C. Ebner, in *Chemistry and Physics of Solid Surfaces VI*, edited by R. Vanslow and R. Howe (Springer-Verlag, Berlin, 1986), p. 581ff; S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, London, 1988), Vol. 12.

[3] M. J. de Oliveira and R. B. Griffiths, Surf. Sci. **71**, 687 (1978).

[4] J. Regnier, J. Menaucourt, A. Thomy, and X. Duval, J. Chim. Phys. **78**, 629 (1981).

[5] J. P. Coulomb *et al.*, Phys. Rev. Lett. **43**, 1878 (1979); H. Taub *et al.*, in *Ordering in Two Dimensions*, edited by S. K. Sinha (North-Holland, New York, 1980), p. 91ff.

[6] J. P. Coulomb and M. Bienfait, J. Phys. (Paris) **47**, 89 (1986).

[7] J. M. Gay, J. Suzanne, and R. Wang, J. Chem. Soc. Faraday Trans. 2, **82**, 1669 (1986); J. M. Gay, J. Suzanne, and R. Wang, J. Phys. (Paris) Lett. **46**, L425 (1985).

[8] J. W. Osen and S. C. Fain, Jr., Phys. Rev. B **36**, 4074 (1987).

[9] J. Suzanne, J. L. Sequin, H. Taub, and J. P. Biberian, Surf. Sci. **125**, 153 (1983).

[10] J. M. Gay, J. Suzanne, G. Pepe, and T. Meichel (unpublished).

[11] F. Y. Hansen *et al.*, Phys. Rev. Lett. **53**, 572 (1984).

[12] Q. M. Zhang, Y. P. Feng, H. K. Kim, and M. H. W. Chan, Phys. Rev. Lett. **57**, 1456 (1986).

[13] H. S. Nham and G. B. Hess, Phys. Rev. B **37**, 9802 (1988).

[14] S. Ramesh, Q. Zhang, G. Torzo, and J. D. Maynard, Phys. Rev. Lett. **52**, 2375 (1984).

[15] J. J. Hamilton and D. L. Goodstein, Phys. Rev. B **28**, 3838 (1983).

[16] J. G. Dash and R. D. Puff, Phys. Rev. B **24**, 295 (1981); R. E. Ecke, J. G. Dash, and R. D. Puff, *ibid.* **26**, 1288 (1982).

[17] R. E. Ecke, J. Ma, A. D. Migone, and T. S. Sullivan, Phys. Rev. B **33**, 1746 (1986).

[18] H. S. Nham, M. Drir, and G. B. Hess (unpublished).

[19] T. Atake and H. Chihara, Chem. Lett. 683 (1976).

[20] M. E. Fisher, J. Math. Phys. **4**, 278 (1963).

[21] R. B. Griffiths, Phys. Rev. **158**, 176 (1967).

[22] D. A. Huse, Phys. Rev. B **30**, 1371 (1984).

[23] M. P. Nightingale, W. F. Saam, and M. Schick, Phys. Rev. B **30**, 3830 (1984).

[24] A. A. Chernov and L. V. Mikheev, Phys. Rev. Lett. **60**, 2488 (1988).

[25] P. C. Ball and R. Evans (unpublished).