

## Preroughening and Reentrant Layering Transitions on Triangular Lattice Substrates

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Recent ellipsometric and calorimetric studies of argon and krypton adsorbed on triangular lattice graphite substrates have found a novel sequence of apparent reentrant layering transitions between integer-plus-one-half coverages. Related behavior has been demonstrated in a Monte Carlo study by Phillips, Zhang, and Larese. In contrast to arguments made by these authors, however, we use solid-on-solid models that include a substrate potential to demonstrate that this behavior should be expected to arise out of the physics that produces roughening and preroughening of a bulk crystal surface, which then provides a unified picture of both the experiments and the simulation results.

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Controversy has recently arisen over the nature of a new series of apparent phase transitions first observed by Youn and Hess (YH) [1] in ellipsometric studies of multilayers of argon, krypton, and xenon films adsorbed on graphite. The discovery, which YH called *reentrant layering*, was confirmed and extended into richly detailed phase diagrams by means of high resolution calorimetry and volumetric measurements [2,3] in argon and krypton on graphite. Both YH and the authors of the calorimetric studies speculated that the new phase transitions might be associated with the disordered flat (DOF) phase [4–7] of bulk crystal interfaces that has been discovered in lattice gas-type models. Such phases are normally thought to arise from the disordering of a corresponding *reconstructed phase*. No obvious candidate for the latter exists in a half-filled layer on a triangular substrate, so the origin of a triangular lattice DOF phase is puzzling. In addition, in a recent Letter Phillips, Zhang, and Larese (PZL) [8] have used the results of a Monte Carlo simulation to argue that the observations of YH are instead due to the melting and resolidification of each layer at constant temperature, driven by the addition of higher layers. PZL see no need for a DOF phase interpretation, and they doubt the phenomenon could occur in thin films.

In this Letter we report the results of a new analysis of the restricted-solid-on-solid (RSOS) model, including next nearest neighbor (nnn) interactions, in the presence of a binding triangular lattice substrate. We demonstrate that the DOF phase still exists on the bulk interface. We show, first via general arguments and then by explicit calculation using a mean field formalism sophisticated enough to describe all relevant phases, that many of the observed phenomena are accounted for in a semiquantitative way. We conclude that all known evidence, including the results of PZL, is consistent with the physics of the DOF phase.

Figure 1 shows the phase diagram in the second to sixth layers of argon on graphite, as deduced from calorimetry [2], in the  $(\Delta\mu)^{-1/3} - T$  plane, where  $\Delta\mu = \mu_0(T) - \mu$  is the difference between the chemical potential of the bulk and that of the film at the same temperature. The quantity  $(\Delta\mu)^{-1/3}$  is roughly proportional to the thick-

ness of the film. At low  $T$ , the double lines correspond to layer-by-layer growth of mutually commensurate solid films.

The second layer [at  $(\Delta\mu)^{-1/3} \approx 0.25$ ] has a triple point at  $T \approx 67$  K, followed by a melting transition that extends to above  $T_t$  and a critical point,  $T_{c,2} \approx 70$  K. The third layer [ $(\Delta\mu)^{-1/3} \approx 0.37$  at low  $T$ ] also has a triple point, a melting curve, and a critical point ( $T_{c,3} \approx 68$  K). However, the melting curve turns into a new coexistence regime, shown by the double lines in the region 70–80 K. This is the first appearance of the YH reentrant phase transition. Above 80 K, the new coexistence regime once again becomes an ordinary melting transition that extends above  $T_t$ . Evidence of the new coexistence regions are also seen for the fourth and fifth layers. The strongest calorimetric evidence is in the form of a series of zig-zagging heat capacity peaks connecting the low temperature layering transitions to the new (and controversial) higher temperature transitions. Essentially identical behavior is observed in krypton on graphite [3].

Surface critical phenomena are most conveniently described using solid-on-solid (SOS) models. These are lattice models in which the surface is defined by an integer valued column height  $h(\mathbf{r})$ , above a two-dimensional

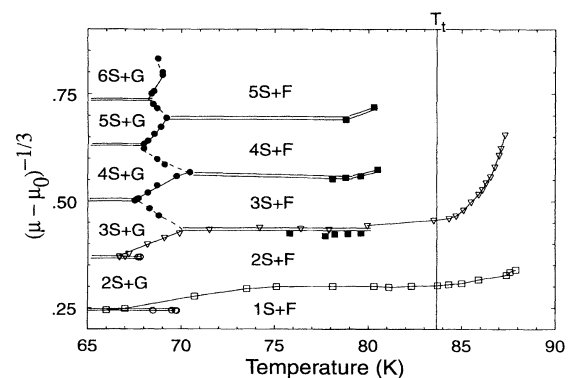


FIG. 1. Phase diagram of the second to sixth layers of argon on graphite, as deduced from calorimetry measurements, Ref. [2].  $T_t$  is the triple point temperature.

lattice, which we take to be triangular (as appropriate to a graphite substrate) spanned by the index  $\mathbf{r}$ . The bulk solids considered here are fcc crystals, so that successive lattice planes should actually be displaced horizontally with respect to one another. The experiments also make it clear that 2D melting effects in the layers, which cannot be described by lattice models, play some role as well. In order to simplify the calculations we shall ignore these complications, leaving their proper inclusion for later work. We consider, therefore, Hamiltonians of the form [4]

$$\mathcal{H} = \frac{1}{2} J_1 \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} [h(\mathbf{r}) - h(\mathbf{r}')]^2 + \frac{1}{2} J_2 \sum_{\langle \mathbf{r}, \mathbf{r}'' \rangle} [h(\mathbf{r}) - h(\mathbf{r}'')]^2 + \sum_{\mathbf{r}} V[h(\mathbf{r})], \quad (1)$$

where the first sum is over nearest neighbors (nn) and the second is over nnn's. The nn values of  $h$  are allowed to differ by at most one (the R in RSOS). The substrate is represented by  $V(h) = h\Delta\mu + v(h)$  with  $v(h) = c(h+1)^{-a}$ ,  $c > 0$ , and  $a = 2$  for a van der Waals substrate, and we restrict  $h$  to be positive. Then at  $T = 0$ , if  $J_1, J_2 > 0$  the equilibrium value of  $h$  is  $h_0(\Delta\mu) \sim (\Delta\mu)^{-1/3}$ .

In the absence of  $V(h)$ , (1) describes the ordinary RSOS model. Depending on the choice of parameters, at low  $T$  it may give rise to a *flat* phase (all  $h$  the same) or various *reconstructed* phases where the surface layer forms a periodic structure with a rational filling factor  $\theta_R$ . At high  $T$ , entropy favors a *rough* phase, in which the height-height correlation function diverges logarithmically at large distance. The transition into this phase, called the roughening transition, is in the Kosterlitz-Thouless universality class [9].

The DOF phase exists in an intermediate range of  $K \equiv J_1/k_B T$ ,  $L \equiv J_2/k_B T$ . In this phase, the surface is flat, but the top layer is only partly occupied and is disordered. If the top layer of a reconstructed phase is only weakly stable, one way of entering this phase would be to have it disorder *without roughening* via, for example, an Ising transition. This is possible only if  $L$  is large enough to maintain second neighbors the same height, preventing full roughening. The result is a DOF phase in which the top layer has  $\theta_{\text{DOF}} \approx \theta_R$ . The DOF phase may also be entered from the flat phase *without the corresponding reconstructed phase ever being stable*. This is crucial for a triangular lattice, since the analog of an "antiferromagnetic" checkerboard phase does not exist due to frustration. The idea is that although a *macroscopically* flat interface is preferred, entropy may be gained from the *microscopic* roughness associated with a disordered top layer. A perfectly flat interface will then phase separate into two DOF domains with roughly unit height difference between them. The phase transition, called *preroughening*, occurs on a critical line,  $K_{\text{pr}}(L)$ ,  $L^- \leq L \leq L^+$ , and belongs to a new universality class [6]. On a square lattice, the transition turns first order for  $L > L^+$  and the low temperature phase converts from

DOF to checkerboard reconstructed. The corresponding behavior on a triangular lattice will be discussed in a future publication [10].

The question we now address is the following: Given the above understanding of the possible phases on a *bulk* crystalline interface, what behavior do we expect, for the *same values* of the bulk parameters  $J_1$  and  $J_2$ , in the presence of the substrate potential  $V(h)$ ? A full analysis covering all possible values of  $J_1$  and  $J_2$  will be presented elsewhere [10]. Here we discuss only those results relevant to the present controversy. We first address in general terms why the existence of a preroughening transition on the bulk surface should lead to reentrant layering in the film. The main effect of the substrate potential is to define the preferred film thickness,  $h_0(\Delta\mu)$ , that minimizes  $V(h)$  (over integer  $h$ ). If  $K$  and  $L$  are sufficiently large to stabilize a bulk flat phase, then the film will also be flat, with height  $h_0$ . To study fluctuations about this value, suppose, for simplicity, that only heights  $h_0$  and  $h_0 \pm 1$  are important. We may then define a spin variable  $s(\mathbf{r}) = h(\mathbf{r}) - h_0$  which takes values  $0, \pm 1$ . Ignoring all other values of  $h$  we then obtain the classical spin-1 Ising Hamiltonian

$$\mathcal{H} \approx \mathcal{H}_1 = \frac{1}{2} J_1 \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} [s(\mathbf{r}) - s(\mathbf{r}')]^2 + \frac{1}{2} J_2 \sum_{\langle \mathbf{r}, \mathbf{r}'' \rangle} [s(\mathbf{r}) - s(\mathbf{r}'')]^2 - H \sum_{\mathbf{r}} s(\mathbf{r}) + H_2 \sum_{\mathbf{r}} s(\mathbf{r})^2, \quad (2)$$

where  $H = \frac{1}{2}[V(h_0 - 1) - V(h_0 + 1)]$ ,  $H_2 = \frac{1}{2}[V(h_0 + 1) + V(h_0 - 1) - 2V(h_0)] > 0$ , and we have dropped an overall constant term,  $C = V(h_0)N$ , where  $N$  is the number of sites per layer. The effective magnetic field  $H$  measures the deviation of  $\Delta\mu$  from the value at which  $V(h)$  most closely approximates a parabola centered at  $h_0$ , so that  $H = 0$  corresponds to greatest energetic stability of  $h = h_0$ . This implies that the ground state of  $\mathcal{H}_1$  yields a flat surface. The stable height switches from  $h_0$  to  $h_0 \pm 1$  at  $T = 0$ , when  $H = \pm H_2$ , with first order transitions between. These transitions extend out into the usual set of layering transitions at low temperatures. When  $K$  becomes sufficiently small, these end in Ising critical points  $T_{c,n}$  [11]. If  $J_2 = 0$ , the film grows continuously for all higher  $T$ , and as  $n \rightarrow \infty$  the  $T_{c,n}$  accumulate at the roughening temperature  $T_r$  [11]. In effect, then, at large  $n$  where the minimum in  $V(h)$  becomes very broad, the disordering of the layers is a precursor to roughening in a weak localizing external potential. However this picture can change drastically if  $J_2 > 0$ . The point is that  $J_2$  will then also prefer a macroscopically flat interface, but is less sensitive to microscopic roughness which is controlled mainly by  $J_1$ . This should allow the layers to disorder and gain entropy, but bulk roughening need not follow immediately. Thus if  $L$  remains sufficiently large near  $T_{c,n}$ , one will have a DOF phase on the bulk interface,

and, plausibly, a nearly identical phase on the surface of the film.

To establish the existence of reentrant layering we now argue that the entropy gain associated with the DOF phase will reflect itself in the film as a preference for partially filled layers,  $h = h_0 \pm \theta$ , with  $\theta \approx \frac{1}{2}$ . Full layers may be energetically favorable, but they have very high free energy due to their low entropy, and the surface layer of the film should phase separate into two partially filled domains, with  $h \approx h_0 - \theta$  and  $h \approx h_0 + \theta$ , in order to lower the free energy. The key to understanding why half-layers are preferred even for a triangular lattice is to realize that entropy will “repel” the filling fraction *nearly equally* away from both  $h_0$  and  $h_0 \pm 1$  filled layers, even without a reconstructed phase to “attract” the filling to  $h_0 \pm \frac{1}{2}$ . In terms of the Ising model (2) this means that even if  $H = 0$  and  $J_1$ ,  $J_2$ , and  $H_2$  are all positive, we expect a *spontaneously broken symmetry*,  $\langle s(\mathbf{r}) \rangle = \theta \neq 0$ , over some temperature range. At low temperatures these new layering transitions end in critical points  $T_{2,n}^-$ . Both these and the critical points  $T_{c,n}$  should accumulate at the preroughening temperature  $T_{pr}$ . At higher temperatures the tendency towards roughening finally overcomes both  $J_1$  and  $J_2$ , and the new layering transitions end in high temperature critical points  $T_{2,n}^+$ . These then must accumulate at the true roughening temperature  $T_r$ . The reentrant coexistence regions then become the DOF phase.

To demonstrate the validity of this picture we shall exhibit this broken symmetry state using a self-consistent mean field calculation. Because it is only the nature of the phases, not the phase transitions, that is in question, mean field theory is an adequate tool. Since, as we have argued, nnn interactions are crucial, the usual single-spin mean field theory is insufficient. We use instead a plaquette of six independent spins (i.e., column heights; the minimum required to represent both nn and nnn interactions) interacting with a mean field of all other spins (columns) of (continuously varying) magnetization  $\theta$  (i.e., mean height  $h_0 + \theta$ ; see the inset to Fig. 2). The mean field Hamiltonian  $\mathcal{H}_{MF}$  constructed from (1) has interaction terms that couple the central spins,  $s_i$ ,  $i = 1, \dots, 6$ , to each other and to the mean field via couplings  $\lambda_1 J_1$  and  $\lambda_2 J_2$ , where  $\lambda_1$  and  $\lambda_2$  are free parameters that may be used to account partially for fluctuation effects (we will take  $\lambda_1 = \lambda_2 = \frac{1}{2}$ , which gives best agreement with bulk interface results of the RSOS model [4]). The free energy,  $\mathcal{F}_{MF} = -\frac{1}{6} \ln[\text{tr}(e^{-\mathcal{H}_{MF}/k_B T})]$ , is obtained by summing over all permitted configurations of the six central spins with fixed mean field  $\theta$ , which is then determined by minimizing  $\mathcal{F}_{MF}$  with respect to  $\theta$ . This yields the self-consistency condition required, namely  $\langle s_i \rangle = \theta$  (i.e.,  $\langle h_i \rangle = h_0 + \theta$ ). As  $H$  and  $T$  are varied, phase transitions occur in the usual way when different local minima of  $\mathcal{F}_{MF}$  versus  $\theta$  become degenerate and then exchange stability. The expression for  $\mathcal{F}_{MF}$  is rather

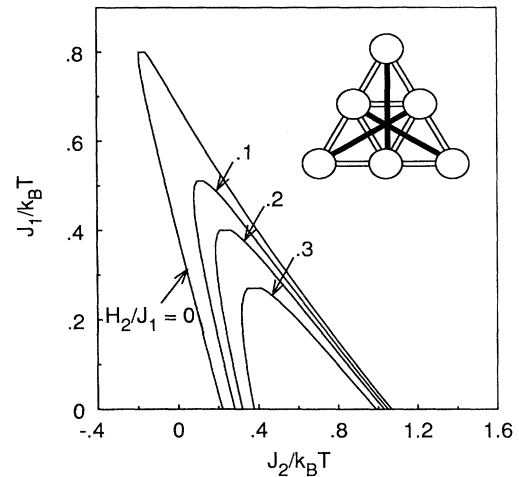


FIG. 2. Spin-1 phase diagram for  $H = 0$  and various  $H_2$  (see text). The reentrant layering analog of the disordered flat phase (interior regions) shrinks as  $H_2$  increases. An experimental trajectory for fixed  $J_1$ ,  $J_2$ , and  $H_2$ , with temperature  $T$  as the only variable, corresponds to a straight line through the origin and will lead to reentrant behavior if the slope,  $J_2/J_1$ , and curvature,  $H_2/J_1$ , are sufficiently small. The inset shows the plaquette of six spins used to define the mean field theory. This plaquette is also connected to the surrounding mean field (not shown).

long, and we do not reproduce it here [10] but quote only the results. We find that the broken symmetry at  $H = 0$  is indeed reentrant and exists over a substantial region of parameter space. This is shown in Fig. 2. The boundary of this region corresponds to a second order Ising transition. This region is even larger than that which we have observed in similar calculations for a square lattice. The reason is that for a triangular substrate the second neighbor interaction divides the lattice into three independent triangular sublattices. This actually *increases* the tendency toward reentrant layering since the greater choice of sublattices further enhances the entropy of a partially filled layer. In addition, with the tendency toward reconstruction now completely eliminated, the DOF phase is stabilized over an even *broader* range of parameters.

Having demonstrated existence, we now seek to improve the theory to reproduce better the experimental results. In order to model multilayer growth, we also relax the assumption that only three column heights are important. It is straightforward to extend mean field theory to allow for a much larger range of the  $h_i$ . The phase diagram shown in Fig. 3 was produced using  $h_{max} = 20$ , for  $J_2/J_1 = 1$  with substrate parameter,  $c/J_1 = 0.1$ . The ordinate is the parameter that counts the steps in the film thickness at  $T = 0$ ,  $h_0 = (\Delta\mu/2c)^{-1/3} - 1$ . At low  $T$  the double lines mark regions where  $n$  (integer) complete layers coexist with  $n + 1$ , i.e., the familiar low  $T$  layering behavior that approaches a flat interface at infinite thickness. These end in a series of critical points  $T_{c,n}$  at

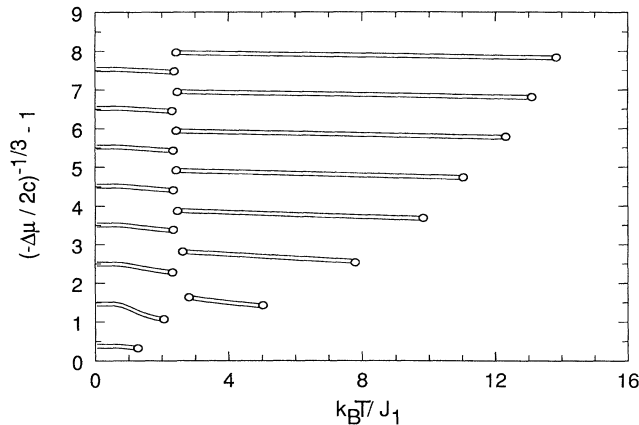


FIG. 3. Mean field phase diagram with substrate potential parameter  $c/J_1 = 0.1$ , tuned to qualitatively reconstruct Fig. 1. The choice  $J_1/k_B \approx 30$  K yields the correct preroughening temperature. Other features, such as the roughening temperature, fare poorly due to the lack of a bulk triple point in our model. The vertical axis corresponds to the position,  $h_0(\Delta\mu)$ , of the minimum of  $V(h)$ .

$k_B T_{c,n}/J_1 \approx 0.3$ . As shown in Fig. 3, at higher  $T$  a new set of coexistence regions appear at intermediate coverages,  $n + \theta$ , coexisting with  $n - \theta$ , where  $\theta \approx \frac{1}{2}$ . As advertised, these new (reentrant) coexistence regions each have upper and lower critical points,  $T_{2,n}^-$  and  $T_{2,n}^+$ , and both  $T_{c,n}$  and  $T_{2,n}^-$  appear to converge to the same temperature  $T_{pr}$  at increasing layer thickness. The similarity of the phase diagrams in Figs. 1 and 3 is striking, even including the fact that the reentrant layering transitions are suppressed entirely in the first few layers.

The observations (although not the interpretation) reported by PZL are in agreement with the picture shown in Fig. 3. For a simulation of the argon on graphite system they report an increase in occupation of the fourth layer at the expense of the third layer just before third layer completion as film thickness is increased at  $T = 70$  K. As shown in Fig. 1, that is precisely what is expected to signal the onset of the coexistence between  $3 - \theta$  and  $3 + \theta$  layers (marked  $2S + F$  and  $3S + F$  in the figure). Radial distribution functions from the PZL simulations at 70 and 75 K, and x-ray scans at 75 K show two ordered lower layers plus disordered upper layers when the nominal coverage is close to three layers and three ordered layers when it is closer to four, i.e., above and below the first reentrant coexistence region. In other words, their observations are perfectly consistent with Fig. 3 and its experimental counterpart. We believe PZL have observed, but misinterpreted, important evidence for the DOF phase.

The phase transitions that have been observed in films are not preroughening and roughening, phenomena that can only occur at the interface of a semi-infinite crystal.

However, we have found that the existence of such transitions on the bulk interface may be expected to manifest themselves in films of just a few layers, and this expectation is borne out by the real data in argon and krypton adsorbed on graphite.

From the data shown in Fig. 1, and from similar data for krypton on graphite [3], it is easy to extract accurate values for  $T_{pr}$  and  $T_r$ . The results are 69 and 80 K, respectively, in argon, and 96 and 110 K, respectively, in krypton. When these values are normalized to the respective bulk liquid-vapor critical point temperatures,  $T_c = 150.7$  K of argon and  $T_c = 209.5$  K of krypton, the ratios are in striking agreement with one another: One finds  $T_{pr}/T_c \approx 0.46$  and  $T_r/T_c \approx 0.53$  in both cases. This is good evidence that the phenomena expected from our theory and observed in Fig. 1 are properties of the bulk interface (which should be essentially the same for argon and krypton owing to their chemical similarity).

In summary, we believe theory, simulation, and experiment combine to make a convincing argument that the phase diagram of argon and krypton films show the onset of behavior to be expected when the bulk interface has a flat phase, a DOF phase and a rough phase as  $T$  increases towards  $T_r$ . Our model also suggests that there are many possible phase diagrams that have not yet been seen. There appears to be much interesting new physics to be explored in multilayer films [10].

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