Phase transitions in monolayers adsorbed on uniaxial substrates

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The phase diagram of a $p\times1$ uniaxial adsorbed layer is investigated theoretically, including the possibility of incommensurate phases. For $p=3$ and 4 we determine the incommensurability crossover exponents at the commensurate-fluid multicritical point. We then argue that due to a strong renormalization of the dislocation core energy the incommensurate phase should be stable up to the multicritical point for $p\geq3$. Possible phase diagrams for general p are discussed.

Monolayers adsorbed on substrates of uniaxial symmetry exhibit various types of phase transitions: Examples are the commensurate (C)–incommensurate (IC) transition in Xe-Cu(110) (Ref. 1) and H-Fe(110) (Ref. 2), the C-fluid (disordered) transition in H-Fe(110) (Ref. 2) and Ba-Mo(112) (Ref. 3), or the IC-fluid transition in Pb-Cu(110).[4] Theoretically, the uniaxial C-IC transition can be understood in terms of domain-wall creation.[5–7] For an IC phase of higher density than the C phase, walls are local compressions and are called "heavy." In the opposite case one has light walls. C-fluid transitions are often described by lattice gas models.[8,9] The IC phase has a continuous translational symmetry (i.e., it is a floating solid), and therefore the transition to the fluid state should occur by the unbinding of dislocation pairs.[10,11] In the present paper we investigate the structure of the C-IC-fluid phase diagram in the vicinity of a $p\times1$ C phase ($p=2$, 3, and 5 in the above examples). Our results are also relevant to the currently much studied chiral Potts models.[12–15]

We consider a two-dimensional sine-Gordon model with a misfit parameter δ which favors an IC structure:

$$F=\int d^2r\left[\frac{\mu}{2}\left(\frac{\partial u}{\partial x}-\delta\right)^2+\frac{\nu}{2}\left(\frac{\partial u}{\partial y}\right)^2+\lambda\cos(pu)\right]\ . \tag{1}$$

Here u is the x component of the atomic displacement field, and $u=2\pi/p$ corresponds to a shift by one lattice constant of the substrate. The cosine term is the substrate potential, and the layer is assumed to be commensurate in the y direction. The statistical mechanics of the model (1) has been treated previously, using the equivalence to a one-dimensional quantum problem.[5–7] In those papers, dislocations are not included, so that a fluid phase cannot occur. Allowing for dislocations, the Hamiltonian describing the statistical mechanics of F at temperature T is

$$H=\int dx\left[\frac{T^2}{2\nu}v^2(x)+\frac{\mu}{2}\left(\frac{\partial u}{\partial x}-\delta\right)^2+\lambda\cos(pu)+\frac{2Tz}{\alpha^2}O_D(x)\right]\ ,\quad O_D(x)=\cos\left[2\pi\int^x v(x')\,dx'\right]\ . \tag{2}$$

Here v is the momentum density conjugate to u, $z=e^{-\beta\epsilon_c}$, ϵ_c is the dislocation core energy, and α is a short-distance cutoff. The constant z determines the probability of thermal creation of dislocations.

In the fermion representation[5,7] of H, the dislocation operator O_D creates or destroys p fermions, as derived previously.[16] On the other hand, O_D is the quantum representation[17] of the vortex operator of the XY model.[18] Consequently, for $\delta=0$ the model (1) exhibits the phase transitions of the XY model with p-fold anisotropy[18]: For $p=1$ there is no ordered state; for $p=2$, 3, and 4 there is a C-fluid transition of Ising, three-state Potts, and nonuniversal types, respectively. From a fermion equivalent[19] of H, the correlation length exponent for $p=4$ is $\nu=(32\pi^2\alpha^2\lambda z/T)^{-1/2}$. For $p\geq5$ and not too large λ and z there is a transition from the C to a floating phase at $T=T_0$, and only at a higher temperature T_m the floating solid melts into a fluid. For $\lambda,z\to0$ one has $T_m=\pi\sqrt{\mu\nu}/2$, $T_0=16T_m/p^2$. On the other hand, for sufficiently strong λ and z the two transitions may merge into a single first-order C-fluid transition, as occurs[20] in the general five-state model ($\lambda\to\infty$). In the notations of Ref. 20 one has $z=(x_1x_2)^2$, so that z decreases along the first-order line $x_2=(\sqrt{5}-1)/2-x_1$ from its maximum value at $x_1=x_2$ (Potts model) towards the point where the first-order line splits into two Kosterlitz-Thouless lines.

Let us now consider the possibility of IC phases for $\delta\neq0$. A direct C-IC transition is only possible[11] for $p^2>8$. For $p=1$ there is no ordered C state at all, but at $T=0$ an IC phase occurs[6] for $|\delta|>4/\pi\sqrt{\lambda/\mu}$. For large $|\delta|$ the substrate potential is unimportant, so that dislocation unbinding leads to an IC-fluid transition which is of the Kosterlitz-Thouless[10] type as are all IC-fluid transitions below (Figs. 1 and 3) (Ref. 21).

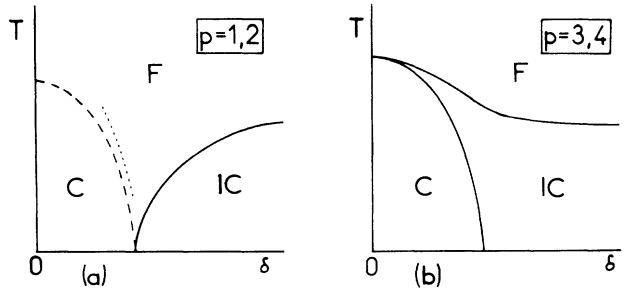

FIG. 1. Phase diagram for (a) $p=1,2$ [the dashed and dotted lines are the C-fluid (F) and disorder lines, respectively, and do not exist for $p=1$]; (b) $p=3$ and 4 with the multicritical point at $\delta=0$. Near $\delta=0$ one has $T_c(0)-T_c(\delta)\propto\delta^{1/\phi_p}$ [cf. Eqs. (4) and (6)].

For $p=2$ there is always a fluid phase between the C and IC states,[11] with an Ising-type C-fluid transition,[11,22] as for $\delta=0$ [Fig. 1(a)]. In the fluid phase there exists a disorder line[23]: The correlations develop an oscillatory component, and the position of the structure factor maxima changes with increasing δ as $(\delta-\delta_{\rm dis})^{1/2}$. Note that the power law is the same as at a C-IC transition[5-7]; however, the disorder line is not a phase transition.

For $p\geq 3$ and $\delta\neq 0$ a direct C-IC transition is possible.[11] We first consider the behavior near the C-fluid transition at $\delta=0$. The XY model with fourfold anisotropy is in the same universality class as the Ashkin-Teller model.[24] In that model a finite δ is represented by a chirality operator $H_c=\delta\Sigma_r O_c(r)$, where r are the sites of a square lattice,

$$O_c(r)=S(r)T(r')-T(r)S(r') \ ,$$

$S,T=\pm 1$ are spin variables, and r' is the nearest neighbor of r in the positive x direction. To assess the relevance of H_c we evaluate the long-range behavior of the correlation function of $O_c(r)$. Under the transformations of Kohmoto, den Nijs, and Kadanoff,[25] O_c translates into an operator,

$$O_c=(\sigma^y_{2j+3}\sigma^y_{2j+2}-\sigma^x_{2j+3}\sigma^x_{2j+2})\exp\left(i\frac{\pi}{2}\sum_{n=1}^{2j+1}\sigma^z_n\right) \ , \quad (3)$$

in an XXZ spin chain. In the language of Ref. 17, the most relevant part of O_c is $O_{-1,1}$, so that at $T_c(\delta=0)$

$$\langle O_c(r)O_c(s)\rangle\propto|r-s|^{-2x_c} \ ,$$

$$x_c=1/x_T+x_T/4 \ ,$$

and x_T is the thermal exponent. From crossover scaling,[26] the incommensurability crossover exponent for $p=4$ follows:

$$\phi_4=(2-x_c)/(2-x_T)=3\nu/2+\tfrac{1}{4}-\nu^2/(2\nu-1) \ . \quad (4)$$

To obtain results for $p=3$ we first consider the p-state Potts model with chirality operator

$$O_c\simeq\delta_{n_r,n_{r'}+1}-\delta_{n_r,n_{r'}-1} \ ,$$

where the n_r $(=0\cdots p-1)$ are Potts variables at site r. After some manipulations with the Kronecker symbols, and using the permutation symmetry of the Potts model, one finds

$$\langle O_c(r)O_c(s)\rangle=\langle\delta_{n_r n_{s'}}+\delta_{n_{r'}n_s}-\delta_{n_r n_s}-\delta_{n_{r'}n_{s'}}\rangle$$
$$+q(\langle\delta_{n_r n_s}\delta_{n_{r'}n_{s'}}\rangle-\langle\delta_{n_r n_s}\delta_{n_{r'}n_s}\rangle) \ . \quad (5)$$

The first term is the second derivative of the spin correlation function, and decays as $|r-s|^{-2x_c}$, $x_c=1+x_H$, with x_H the magnetic exponent. We have not been able to evaluate the second term for general p. Assuming the first term in Eq. (5) to be dominant, from the known value[27,28] of x_H we obtain the crossover exponent for $p=3$ as

$$\phi_3=\tfrac{13}{18}=0.7222\ldots \ . \quad (6)$$

The results (4) and (6) show that a nonzero δ is a *relevant* perturbation for $p=3$ and 4, i.e., the C-fluid transition at $\delta=0$ is multicritical, as predicted by Huse and Fisher[13] from qualitative arguments. Their estimated crossover exponents are close, albeit not equal, to our above results.

We now consider the stability of the IC phase against dislocation unbinding.[10,11] From Ref. 16, near the C-IC transition the potential energy of an isolated dislocation pair of distance $\vec{r}=(x,y)$ is

$$e^{-\beta V(\vec{r})}=C^2 l^{-p^2}[1+(x/l)^2+(l_0 y/l^2)^2]^{-p^2/4} \ , \quad (7)$$

where l is the mean distance between walls, and C and l_0 are constants independent of l and $\vec{r}$. Short-distance effects, coming from walls of the unfavored type and neglected by the cutoff at $x\simeq l$ in (7), are important on length scales $\xi_0\ll l$ (ξ_0 is the correlation length of the C state at $\delta=0$), and may be included in C. The partition function can be obtained by integrating over all possible dislocation configurations,[10] and after the scale change $x'=x/l$, $y'=l_0 y/l^2$ becomes

$$Z=\sum_n\frac{C^{2n}l_0^{-2n}}{(n!)^2}e^{-2n\beta\epsilon_c}l^{-n(p^2-6)}\int\prod_{\nu=1}^{2n}d^2r_\nu\exp\left(-\frac{p^2}{4}\sum_{j=1}^{2n}\sum_{i=j+1}^{2n}s_i s_j\ln(1+r_{ij}^2)\right) \quad (s_1,\ldots,s_n=1,s_{n+1},\ldots,s_{2n}=-1) \ , \quad (8)$$

where n is the number of dislocation pairs and s_i is the sign of the Burger's vector of a dislocation. All l dependence has disappeared from the exponent in Eq. (8), and the system can be described as a dislocation "gas" with a *renormalized core energy,*

$$\tilde{\epsilon}_c=\epsilon_c+\tfrac{1}{2}T(p^2-6)\ln l \ , \quad (9)$$

which becomes very large near the C-IC transition ($l\to\infty$) for $p^2>6$. The origin is quite easy to understand: Near a dislocation p, domain walls come very close to each other,[11,16] and consequently loose a large amount of "meandering entropy,"[29] leading to an increase of the effective core energy (Fig. 2). In the Kosterlitz-Thouless scaling analysis,[10,11] Eq. (9) implies that the IC phase should *always* be stable near the C state for $p^2>8$.

The analysis of Ref. 16 relies on the fact that near the C-IC transition only one type of walls (heavy or light) is important. Whether this is still true in the vicinity of the multicritical point ($\delta=0$) is not clear *a priori.* However, it has been argued[13] that for *any* finite δ the important fluctuations near the boundary of the C state involve only one type of walls, as assumed in Ref. 16. The above arguments then suggest that for any nonzero δ (and $p^2>8$) the disordering of the C state occurs in two stages: C-IC-fluid [Fig. 1(b)]. For small δ the IC region is quite narrow: From the variation of the correlation exponent of the IC state[7] with δ the IC state is unstable as soon as $l\simeq\xi_0$. Crossover scaling[26] implies $T_c(0)-T_c(\delta)\propto\delta^{1/\phi_p}$ for both the C-IC and IC-fluid transitions. Figure 1(b) disagrees with previous results[12-15] for the chiral Potts model. In Refs. 12 and 13 the renormalization of ϵ_c is neglected. Monte Carlo[14] and series expansion[15] may miss a very narrow IC strip between the fluid and C phases. However, for ϵ_c smaller than some critical value the analysis of Ref. 16 may be inapplicable, and we

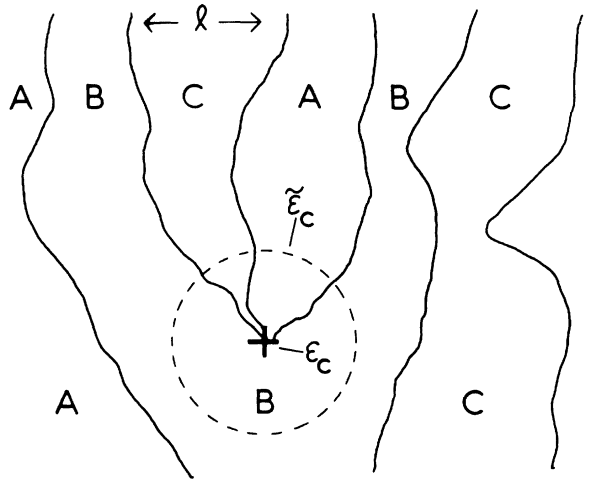

FIG. 2. Near a dislocation (cross) p walls ($p=3$) come close to each other, leading to the renormalization $\epsilon_c \to \tilde{\epsilon}_c$. Different domains are labeled A, B, and C.

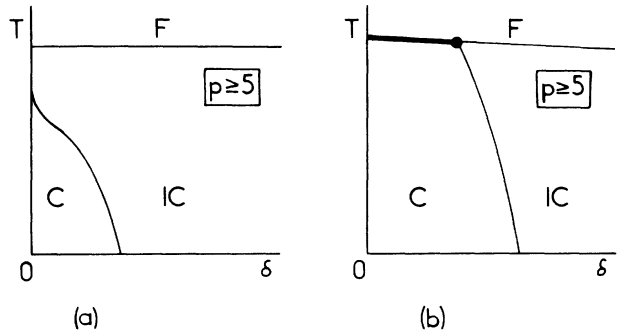

FIG. 3. Phase diagram for $p \geq 5$ for (a) weak substrate potential; (b) strong potential (tentative). The heavy line is of first order.

cannot therefore exclude a direct C-fluid transition for $\delta \neq 0$ in that case.

Finally, for $p \geq 5$, dislocation pairs are bound as long as a C state is stable,[11] leading to the C-IC transition described previously[5-7] [Fig. 3(a)]. However, finite-energy configurations involving only one type of walls may occur if dislocations are present. This will lead to next-to-leading singularities, which may be observable on the C side where the amplitude of the leading singularity vanishes[7] for $z=0$. If λ and z are sufficiently large, so that the C-fluid transition is of first order at $\delta=0$, we expect the first-order transition to persist for small δ, and a phase diagram like Fig. 3(b) may be anticipated, though we do not have any detailed results near the C-IC-fluid triple point.

In conclusion, we have investigated theoretically the phase diagram of a $p \times 1$ adsorbed layer in the vicinity of commensurability. Most notably, we have found the crossover exponents at the multicritical point for $p=3$ and 4. We have argued that the IC phase should be stable up to the multicritical point for $p \geq 3$. Strictly speaking, the model (1) applies for weak substrate potentials. However, universality implies that the same critical behavior should also occur for stronger substrates (i.e., chemisorbed phases[2-4]), where usually lattice gas models are used.[8,9] Some of our results apply directly to experimental systems: An IC-fluid transition, apparently of Kosterlitz-Thouless type, occurs in Pb-Cu(110) ($p=5$).[4] For the $p=2$ system Xe-Cu(110) (Ref. 1) the apparent C-IC line may rather be a disorder line. However, more experiments with high-resolution techniques, especially on $p=3$ and 4 systems, seem desirable.

After finishing this paper we received a report of work prior to publication by Haldane, Bohr, and Bak, who argue for a phase diagram similar to our Fig. 1(b)—however, on the basis of arguments for $z=0$ only.

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