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Melting of a physisorbed commensurate phase

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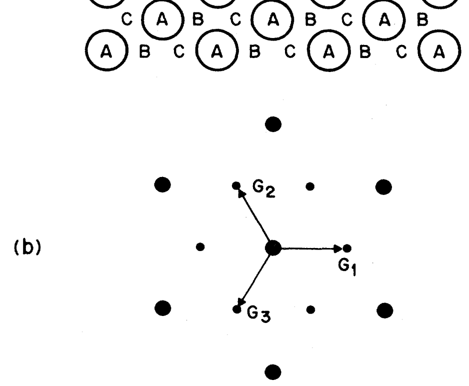
The general Landau-Ginzburg-Wilson Hamiltonian for the melting of a physisorbed $\sqrt{3}\times\sqrt{3}$ commensurate phase on a substrate of triangular lattice symmetry is examined. Two limits in which it simplifies are considered: first, the lattice-gas limit resulting from infinite substrate potential, and second, a decoupling limit in which the Hamiltonian reduces to three independent chiral clock models. Universality classes of melting transition with various degrees of symmetry might occur; evidence exists for two. It is argued that the "chiral" transition which may have been observed for Kr on graphite cannot be modeled by a simple lattice gas. Possible phase diagrams are examined and a new spin model with the appropriate symmetry is proposed. The general approach should be applicable to other commensurate surface phases.

I. INTRODUCTION

Atoms or molecules adsorbed on a face of a crystal may form commensurate ordered phases, in which the atoms preferentially occupy one (or more) sublattices of the full array of lowest-energy adsorption sites. Some experimental systems in which the melting of such phases has been studied in some detail are He on graphite,[1] Kr on graphite,[2–4] and O on Ni(111).[5] For low temperatures and intermediate vapor pressures, both He and Kr on graphite order in a $\sqrt{3}\times\sqrt{3}$ commensurate phase where one of $p=3$ equivalent sublattices of adsorption sites is preferentially occupied,[1–4] as illustrated in Fig. 1(a). The symmetry that relates the three sublattices (A,B,C in Fig. 1) is spontaneously broken when the adsorbate freezes into the commensurate phase.

It was Alexander[6] who first suggested that this $\sqrt{3}\times\sqrt{3}$ commensurate ordering transition should be in the same universality class as the ordering transition of the three-state Potts model, where the symmetry relating the three equivalent states of the Potts spins is broken. Bretz[1] then measured the specific-heat exponent α for the transition in He on graphite and found a result consistent with the Potts model exponent, $\alpha=\frac{1}{3}$.[7] Domany, Schick, Walker, and Griffiths[8] have formalized and greatly extended Alexander's idea, examining the melting transitions of many commensurate phases on substrates of triangular, square, and rectangular lattice symmetry. They predicted the universality class of each transition on the basis of rules due to Landau and Lifshitz, renormalization-group ideas, and a lattice-gas approximation.[8]

More recently, however, a high-resolution x-ray scattering study of Kr on graphite by Moncton and co-workers[4] found a continuous melting transition of the $\sqrt{3}\times\sqrt{3}$ commensurate phase that does not appear to be in the Potts universality class. Specifically, the apparent scaling function for the structure factor was not found to be symmetric about the first Bragg point. Huse and Fisher[9] interpreted this asymmetry as indicating a phase transition in a new "chiral" universality class. An examination of domain walls demonstrates that the adsorbate-substrate system actually has a lower symmetry than the three-state Potts model.[9,10] The spin model with the appropriate symmetry for modeling $\sqrt{3}\times\sqrt{3}$ melting in a simple *lattice gas,* where all adatoms are assumed to sit *at* lowest-energy adsorption sites, is a Potts model with additional



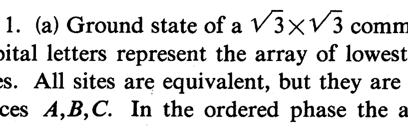


FIG. 1. (a) Ground state of a $\sqrt{3}\times\sqrt{3}$ commensurate phase. The capital letters represent the array of lowest-energy adsorption sites. All sites are equivalent, but they are labeled as three sublattices A,B,C. In the ordered phase the adatoms (circles) preferentially occupy one of the three sublattices. (b) Reciprocal lattice of the substrate (large solid circles) and the $\sqrt{3}\times\sqrt{3}$ commensurate overlayer (small solid circles). The three basic reciprocal-lattice vectors of the overlayer are shown explicitly.

"triaxially chiral" symmetry-breaking terms present in the Hamiltonian (see Refs. 9 and 10 and Sec. II of this paper).

The lattice-gas approximation, which has been either explicitly or implicitly used in most previous studies,[6,8–10] is certainly suspect when applied to physisorbed systems such as Kr on graphite. This is because many atoms may sit well away from the lowest-energy adsorption sites in a typical equilibrium configuration, since the variations in the substrate potential are on a scale smaller than or of the same order as those defined by the experimental temperatures and the krypton-krypton interactions. In this paper the lattice-gas approximation is therefore not made. As originally pointed out by Bak and Mukamel,[11] the commensurate phase then has three independent complex scalar order parameters, namely the Fourier transforms of the density at the three basic reciprocal-lattice vectors of the commensurate overlayer. For a simple lattice gas these three order parameters are precisely equal for all configurations, so there is really only one order parameter. The general Landau-Ginzburg-Wilson (LGW) Hamiltonian for the melting of a physisorbed $\sqrt{3}\times\sqrt{3}$ commensurate phase is functional of the three *local* order-parameter fields and has various symmetries corresponding to the symmetries of the substrate-adsorbate system.[11] A relatively simple spin model with the same symmetries is proposed at the end of this paper; further study of this model, which consists of three coupled chiral clock models, may be useful for understanding phase-transition behavior near $\sqrt{3}\times\sqrt{3}$ commensurate phases.

The scaling behavior of the structure factor near continuous fluid-to-$\sqrt{3}\times\sqrt{3}$ commensurate transitions is considered in Sec. III. The scaling function for the structure factor may, in principle, have at least four possible symmetries, each corresponding to a different universality class of phase transition. One possibility is, of course, the Potts universality class, for which the scaling function has a very high symmetry. The transition in the exactly solved hard-hexagon model, a simple lattice gas with continuous $\sqrt{3}\times\sqrt{3}$ melting,[12] is apparently in this universality class, as was suggested by Alexander's[6] argument. The other likely possibility is a universality class for which the scaling function for the structure factor has no additional symmetry beyond that of the adsorbate-substrate system itself. This would be a chiral transition that *cannot* be modeled by a simple lattice gas because the simple lattice gas has a symmetry in momentum space that is not present in real systems. The transition in Kr on graphite observed by Moncton *et al.*[4] appears to be in this latter universality class, as is argued in Sec. III below.

The types of arguments used here and in Refs. 9 for $\sqrt{3}\times\sqrt{3}$ commensurate phases may be applied equally well to other commensurate phases. Therefore, evidence for new universality classes might be also looked for in the melting of other commensurate phases. Likely candidates are those transitions classified by Domany *et al.*[8] as being in the universality classes of the four-state Potts model and the X-Y model with cubic anisotropy. Those transitions that Domany *et al.*[8] have assigned to the Ising universality class, on the other hand, do indeed have the full Ising symmetry, so new types of transitions seem much less likely to occur.

II. LGW HAMILTONIAN FOR $\sqrt{3}\times\sqrt{3}$ COMMENSURATE MELTING

Let us consider a physisorbed monolayer that is ordered in a $\sqrt{3}\times\sqrt{3}R\,30^\circ$ commensurate phase on a substrate with triangular lattice symmetry, such as Kr on graphite.[2–4] Upon freezing into such a commensurate phase, the adsorbate selects one of the three equivalent sublattices [A,B,C in Fig. 1(a)] of lowest-energy adsorption sites to preferentially occupy. A ground state of this phase is shown in Fig. 1(a). The order parameters of this commensurate phase are the Fourier transforms of the adsorbate density at the basic reciprocal-lattice vectors of the overlayer. There are three such basic reciprocal-lattice vectors, namely $\vec{G}_1$, $\vec{G}_2$, and $\vec{G}_3$ in Fig. 1(b), and therefore three corresponding complex scalar order parameters.

The Landau-Ginzburg-Wilson (LGW) Hamiltonian appropriate for modeling a continuous order-disorder transition from this commensurate phase should be a functional of the fluctuating *local* order-parameter fields. The three complex scalar ordering fields may be defined by a coarse-graining scheme as

$$\psi_\alpha(\vec{r})=\int d\vec{r}\,'K(\vec{r},\vec{r}\,')e^{i\vec{G}_\alpha\cdot\vec{r}\,'}\rho(\vec{r}\,')\ , \tag{2.1}$$

where $K(\vec{r},\vec{r}\,')$ is a finite-ranged coarse-graining kernel and $\rho(\vec{r})$ is the local density. For each symmetry of the substrate there is a corresponding symmetry that the LGW Hamiltonian must have. There are four basic symmetries. First, there is global translation of the adsorbate relative to the substrate by a substrate-lattice vector; this has the effect of multiplying each of the three fields $\psi_\alpha(\vec{r})$ by

$$\omega=\exp(2\pi i/3)\ , \tag{2.2}$$

or by ω^*, depending on the lattice vector. Second, there is rotation of the adsorbate by 180° about a lattice point (taken to be the origin); this has the effect

$$\psi_\alpha(\vec{r})\to\psi_\alpha^*(-\vec{r})\ . \tag{2.3}$$

Third, there is rotation of the adsorbate by 120° about the origin; this has the effect

$$\psi_\alpha(\vec{r})\to\psi_{\alpha+1\,(\mathrm{mod}3)}(A\vec{r})\ , \tag{2.4}$$

where A is the rotation operator. And fourth, there is reflection of the adsorbate about the x axis [which is chosen parallel to $\vec{G}_1$; see Fig. 1(b)]; this has the effect

$$\begin{aligned}&\psi_2(x,y)\to\psi_3(x,-y)\ ,\\&\psi_3(x,y)\to\psi_2(x,-y)\ ,\\&\psi_1(x,y)\to\psi_1(x,-y)\ .\end{aligned} \tag{2.5}$$

The general Hamiltonian that is invariant under these symmetry operations is

$$H=\int d^2r \left\{ u_1 \sum_\alpha |\psi_\alpha(\vec{r})|^2 + u_2 \left| \sum_\alpha \psi_\alpha(\vec{r}) \right|^2 + \mathrm{Re} \left[w_1 \sum_\alpha \psi_\alpha^3(\vec{r}) + w_2 \left[\sum_\alpha \psi_\alpha(\vec{r}) \right]^3 + w_3 \psi_1(\vec{r}) \psi_2(\vec{r}) \psi_3(\vec{r}) \right] + s\, \mathrm{Im} \left[\sum_\alpha \psi_\alpha(\vec{r}) \nabla_\alpha \psi_\alpha^*(\vec{r}) \right] + \cdots \right\}, \tag{2.6}$$

where

$$\nabla_\alpha \equiv \vec{G}_\alpha \cdot \vec{\nabla} , \tag{2.7}$$

and all terms of higher order in the field or gradient than those shown have not been exhibited (although some of schematic form $|\nabla\psi|^2$ and ψ^4 are certainly essential to the physics). Bak and Mukamel[11] have written an essentially identical Hamiltonian, although they have neglected some unimportant terms, such as that proportional to w_2 above. This Hamiltonian is rather complicated; one limit in which it simplifies is the infinite-substrate potential or lattice-gas limit. In this limit all the adatoms sit *at* sites in the triangular array of lowest-energy adsorption sites $\{\vec{R}\}$, for all of which

$$e^{i\vec{G}_1\cdot\vec{R}} = e^{i\vec{G}_2\cdot\vec{R}} = e^{i\vec{G}_3\cdot\vec{R}} . \tag{2.8}$$

The local ordering fields are therefore equal,

$$\psi_1(\vec{r}) = \psi_2(\vec{r}) = \psi_3(\vec{r}) , \tag{2.9}$$

and thus there is just *one* local ordering field, which we shall call $\psi(\vec{r})$. To order ψ^4 and $\psi\nabla^3\psi^*$, the general LGW Hamiltonian for $\sqrt{3}\times\sqrt{3}$ melting in such a lattice gas (which will be referred to as a "simple" lattice gas) is[9]

$$H_l = \int d^2r \{ \tilde{u}_2 |\psi(\vec{r})|^2 + \tfrac{1}{2} |\vec{\nabla}\psi(\vec{r})|^2 + w\, \mathrm{Re}[\psi^3(\vec{r})] + u_4 |\psi(\vec{r})|^4 + \tilde{s}\, \mathrm{Im}[\psi(\vec{r}) \nabla_1 \nabla_2 \nabla_3 \psi^*(\vec{r})] + \cdots \} . \tag{2.10}$$

In some previous treatments,[6,8,11] the final term shown explicitly in (2.10) was ignored in constructing the lattice-gas LGW Hamiltonian. The resulting Hamiltonian is precisely that of a three-state Potts model. However, the three-state Potts model Hamiltonian is invariant under the transformation

$$\psi(\vec{r}) \rightarrow \psi^*(\vec{r}) . \tag{2.11}$$

The term proportional to $\tilde{s}$ in (2.10) is not invariant under this transformation, and thus the lattice gas actually has a lower symmetry than the three-state Potts model.[9,10] Such symmetry-breaking terms have been dubbed chiral[9] because they discriminate between configurations in which $\psi(\vec{r})$ moves clockwise around the origin in the complex ψ plane as one moves through real space and configurations in which the motion is counterclockwise. The chiral symmetry-breaking term in (2.10) is invariant under rotation by 120° in real space. It has therefore been termed *triaxially* chiral to discriminate it from the *uniaxially* chiral terms that arise in the LGW Hamiltonian for 3×1 commensurate phase melting.[9]

The scaling exponent of the *triaxially chiral field* $\tilde{s}$ at the Potts-model critical point (at which $\tilde{s}=0$) may be estimated by naive power counting[9] or by low-temperature expansions similar to those carried out for the *uniaxially* chiral field by Huse, Szpilka, and Fisher.[13] Both approaches indicate that the triaxially chiral field is *irrelevant*, with a renormalization-group eigenvalue of approximately -1.[9] Thus the melting transition of a $\sqrt{3}\times\sqrt{3}$ lattice-gas phase should remain in the three-state Potts-model universality class (as originally suggested by Alexander[6]) as long as the triaxially chiral symmetry breaking is sufficiently weak. Crossover to a chiral transition[9] for strong symmetry breaking cannot be ruled out, although there is no evidence that such crossover can occur in lattice gases. Baxter's[12] exact solution of the hard-hexagon model is consistent with these conclusions. The melting transition of the $\sqrt{3}\times\sqrt{3}$ phase of this lattice gas has critical behavior that appears to be in the three-state Potts-model universality class. One possible interpretation of the nonanalytic corrections to scaling present in the exact solution is that they are due to an irrelevant triaxially chiral field with a renormalization-group eigenvalue of precisely -1.[12,14]

The Hamiltonian (2.6) of a real adsorbate without the lattice-gas symmetry (2.9) may be viewed as a generalization of the lattice gas where two new nonordering fluctuating fields are introduced, namely the *differences* between the fields $\psi_\alpha(\vec{r})$. Since these are nonordering fields (in the $\sqrt{3}\times\sqrt{3}$ phase their expectation values vanish), they should not change the critical behavior, at least when their amplitudes are small. Thus one might argue that the critical behavior of an adsorbate with very strong, but finite, relief in the substrate potential should be in the same universality class as that of a lattice gas. This is probably the case for most chemisorbates. However, for physisorbates the energy scale of the substrate relief can be small relative to, for instance, the ordering temperature. The system can then be quite far from a lattice gas, with many atoms sitting well away from the lowest-energy adsorption sites. This is the situation in Kr on graphite, as illustrated, for example, by the molecular-dynamics simulation of Abraham, Koch, and Rudge.[15] Thus, to understand physisorbates it is useful to consider a limit of the general Hamiltonian (2.6) that is far from the lattice-gas limit. In the lattice-gas limit the three fields $\psi_\alpha(\vec{r})$ are rigidly coupled by (2.9). Thus let us consider the opposite limit, in which all couplings between the different fields vanish. Exactly what type of adsorbate-substrate system this limit corresponds to is not obvious, but it is certainly one in which the adatoms are permitted to sit away from the lowest-energy adsorption sites. Thus this *decoupling limit*, in which a certain simplification of (2.6) occurs, is in a sense closer to physisorbate systems than is the lattice-gas limit.

In the decoupling limit, $u_2 = 0 = w_2 = w_3$, etc., the general Hamiltonian (2.6) reduces to

$$H_d=\sum_{\alpha}\int d^2r\{u_1\,|\,\psi_\alpha(\vec{r})\,|^2+\tfrac{1}{2}\,|\,\vec{\nabla}\psi_\alpha(\vec{r})\,|^2+v\,|\,\nabla_\alpha\psi_\alpha(\vec{r})\,|^2$$
$$+w_1\,\mathrm{Re}[\psi_\alpha^3(\vec{r})]+u_4\,|\,\psi_\alpha(\vec{r})\,|^4+s\vec{G}_\alpha\cdot\mathrm{Im}[\psi_\alpha(r)\vec{\nabla}\psi_\alpha^*(\vec{r})]+\cdots\}\,, \tag{2.12}$$

which is simply the Hamiltonian of three independent *uni*axially chiral clock models.[9] Each chiral clock model, $\alpha=1,2,3$, consists of a three-state Potts model with additional uniaxially chiral symmetry-breaking terms, proportional to s in (2.12), that break the invariance under (2.11). The uniaxially chiral field in each model is $s\vec{G}_\alpha$ and thus is of the same magnitude as and oriented at mutual angles of 120° to the chiral fields of the other two models. The chiral term is *first* order in the gradient, in contrast to the lattice-gas limit where it is third order and thus irrelevant. In this decoupling limit the chiral field s is actually relevant at the Potts ($s=0$) critical point, as indicated by scaling arguments,[9,16] series expansions,[13] and as confirmed by den Nijs's recent exact analysis of related models.[17] Thus it appears that chiral symmetry breaking can become more important as the substrate relief is weakened, making new, intrinsically chiral classes of phase transitions[9] more likely for physisorbed systems than for chemisorbed systems and lattice gases. The evidence for a chiral transition in Kr on graphite is discussed in the following section. A more detailed examination of the decoupling limit of the LGW Hamiltonian (2.6) and a related spin model is then undertaken in the remainder of this paper.

III. STRUCTURE FACTOR AND SCALING

The structure factor of an adsorbate is

$$S(\vec{q})=L^{-2}\int d\vec{r}\,d\vec{r}\,'e^{i\vec{q}\cdot(\vec{r}-\vec{r}\,')}\langle\rho(\vec{r})\rho(\vec{r}\,')\rangle\,, \tag{3.1}$$

where L^2 is the total area of the substrate over which the integrals run. Let us examine the structure factor of an adsorbate on a substrate of triangular lattice symmetry for $\vec{q}$ near a Bragg point of the $\sqrt{3}\times\sqrt{3}$ overlayer such that

$$\vec{q}=\vec{G}_\alpha+\vec{k}\,, \tag{3.2}$$

where $|\,\vec{k}\,|$ is small compared to the inverse of the range of the coarse-graining kernel in (2.1). Then the structure factor may be written in terms of the complex scalar order-parameter field (2.1) as

$$S(\vec{G}_\alpha+\vec{k})\approx L^{-2}\int d\vec{r}\,d\vec{r}\,'e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\langle\psi_\alpha(\vec{r})\psi_\alpha^*(\vec{r}\,')\rangle\,, \tag{3.3}$$

when the kernal $K(\vec{r},\vec{r}\,')$ is appropriately normalized.

If the adsorbate undergoes a <u>continuous</u> transition from the disordered fluid phase to the $\sqrt{3}\times\sqrt{3}$ commensurate phase, then the structure factor in the near critical disordered phase should scale as

$$S(\vec{G}_\alpha+\vec{k})\approx\xi^{\gamma/\nu}D_\alpha(\vec{k}\xi)\,, \tag{3.4}$$

where ξ is the correlation length. The scaling functions $D_\alpha(\vec{z})$ and the exponents γ and ν will be determined by the universality class of the transition. One can imagine universality classes for which the $D_\alpha(\vec{z})$ have at least four possible symmetries, although there is evidence for the existence of only two of these. Assuming that there is no orientational ordering, the structure factor of a general adsorbate on a substrate of triangular lattice symmetry is invariant under rotations by 60° about the origin and reflections about lines through the origin parallel to the $\{\vec{G}_\alpha\}$ in momentum space. These symmetries dictate that the scaling functions may all be written as

$$D_\alpha(\vec{z})=D(z,\theta_\alpha)\,, \tag{3.5}$$

where $z=|\,\vec{z}\,|$ and θ_α is the angle between $\vec{z}$ and $\vec{G}_\alpha$. The only symmetry that the scaling function $D(z,\theta)$ *must* have is

$$D(z,\theta)=D(z,-\theta)\,. \tag{3.6}$$

There are two other symmetries which the scaling function may or may not have. If the chiral symmetry [invariance under $\psi_\alpha(\vec{r})\rightarrow\psi_\alpha^*(\vec{r})$] is restored in the scaling limit due to irrelevance of chiral symmetry breaking, then the scaling function will have the symmetry

$$D(z,\theta)=D(z,\theta+\pi)\,. \tag{3.7}$$

If the system is a simple lattice gas with all adatoms sitting *at* sites of the substrate triangular lattice, then the structure factor has a discrete translational invariance in momentum space, namely

$$S(\vec{q})=S(\vec{q}+\vec{K})\,, \tag{3.8}$$

where $\vec{K}$ is any reciprocal-lattice vector of the underlying triangular lattice. The resulting symmetry of the scaling function is

$$D(z,\theta)=D(z,\theta+2\pi/3)\,. \tag{3.9}$$

For a real adsorbate system this lattice-gas symmetry may be restored in the scaling limit.

If the melting transition of a $\sqrt{3}\times\sqrt{3}$ phase is in the universality class of the three-state Potts model, as originally suggested by Alexander,[6] and as appears to be the case for the hard-hexagon model,[12] then the scaling function must be identical to that of the Potts model and therefore have both chiral [Eq. (3.7)] and lattice-gas [Eq. (3.9)] symmetries. This means the system attains a high degree of symmetry in the scaling limit which is not present in the original Hamiltonian. One should expect a second possible universality class of melting transition for which the scaling function does *not* have any symmetry beyond that dictated by the Hamiltonian (2.6). For such a transition both the chiral and lattice-gas symmetries remain broken in the scaling limit. Thus this chiral transition could not be modeled by a simple lattice gas or by the one-field LGW Hamiltonian (2.10). A more general lattice gas in which adatoms are also permitted to "sit" at certain positions away from the lowest-energy adsorption sites might exhibit this type of chiral transition. The melting transition of the commensurate phase of Kr on graphite near 97 K as observed by Moncton and coworkers[4] appears to be a chiral transition[9] of this minimal-symmetry type. They measured the location, relative to the Bragg point of the ordered phase, of the maximum in $S(\vec{q})$ in the fluid phase. The product of this "incommensurability" and the correlation length appears to approach a constant of order unity at the commensurate-phase boundary. This admittedly preliminary data is consistent with a scaling function $D(z,\theta)$ which is *not* symmetric about the Bragg point, having a maximum at $\theta=0$, $z=z_0=O(1)$. Further study of this transition, perhaps at higher temperatures where the critical region may be larger, is certainly needed to check this interpretation of the experimental results.

The melting transition will be in the Potts universality class if *both* the chiral and the lattice-gas symmetries are restored in the scaling limit. One may also postulate two other universality classes, in each of which only one of these symmetries is attained. No evidence for the existence of either type of transition has appeared. One would be a chiral transition in a simple lattice gas and the other a nonchiral, non-Potts transition that cannot be modeled by a simple lattice gas.

IV. DECOUPLING LIMIT

Let us now return to consideration of the decoupling limit (2.11) of the general adsorbate Hamiltonian (2.6). The uniaxially chiral clock models into which the model separates here are relatively well understood,[18,19,13,9] although agreement on some details does not yet exist.[9,16,20] Since physisorbed systems such as Kr on graphite are in some sense closer to this decoupling limit than to the lattice-gas limit, it is worth asking what behavior we might expect near the decoupling limit. The most straightforward, and probably the most important, term in the general Hamiltonian (2.6) that couples the different ordering fields, $\psi_\alpha(\vec{r})$, is the local pairwise ferromagnetic coupling term, proportional to u_2 in (2.6). Thus we should examine the consequences of adding such a coupling to (2.12).

A schematic phase diagram of the uniaxially chiral clock models (2.12) is shown in Fig. 2(a). There is a ferromagnetically ordered phase at low temperatures and small chiral fields s. This phase represents the commensurate phase of the adsorbate-substrate system and is therefore labeled as such in Fig. 2. At decoupling the three models order independently, each into one of three possible ordered states, making the commensurate phase 27-fold degenerate. As the chiral field s, which corresponds roughly to the pressure or chemical potential in the physical system,[9] is increased, this commensurate phase becomes unstable at $s_c(T)$, undergoing a commensurate-to-incommensurate transition for sufficiently low temperatures.[18,9] If the temperature is then increased, this "striped" incommensurate phase[21,22] will melt into the fluid phase which exists at high temperatures. Precisely how these phase boundaries join up is presently a controversial point,[9,16,20] but it is clear that the commensurate phase melts *directly* into the fluid phase via a transition in the Potts universality class for zero chiral field ($s=0$). Thus the commensurate-incommensurate and incommensurate-fluid phase boundaries must meet at some $s\geq 0$. Of course, for a general model first-order transitions may preempt any of the continuous phase transitions shown in Fig. 2.

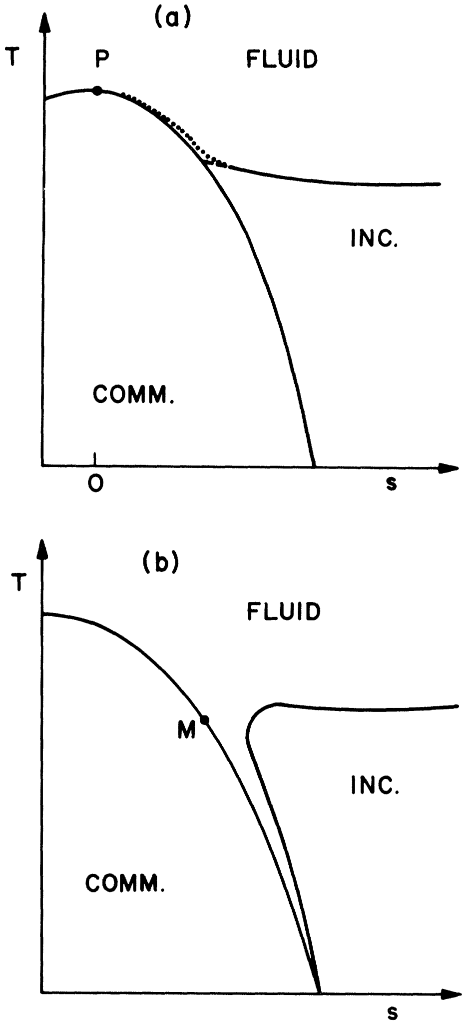


FIG. 2. (a) Schematic phase diagram of the uniaxially chiral clock model. Commensurate, incommensurate, and fluid or disordered phases are indicated. Precisely how the phase boundaries meet is not known: The fluid-incommensurate boundary may (dotted line) or may not (dashed line) extend to the Potts point P at $s=0$. (b) Possible phase diagram when the three chiral clock models are coupled, with the fluid phase intruding between commensurate and incommensurate phases. The commensurate-fluid transition will probably be in the Potts universality class for a small chiral field s, but may cross over at a possible multicritical point M to a chiral class for larger s. A first-order commensurate-incommensurate transition (not shown) might also occur, particularly at low temperatures.

A possible schematic phase diagram for a small but finite coupling between the three models is illustrated in Fig. 2(b). In the commensurate phase all three models must now order the same way so that the degeneracy is reduced to threefold. The coupling between the models represents a relevant (in the renormalization-group sense of the word) perturbation of the decoupled Potts point P in Fig. 2(a). General scaling arguments affirm that the crossover is $\phi=\gamma=\frac{5}{3}$.[23,7] The phase transition at $s=0$ presumably crosses over to a new transition in the Potts universality class, but with the three models coupled in the scaling limit. Since chiral symmetry breaking is irrelevant at this coupled Potts fixed point, a finite segment of the commensurate phase boundary should be in the Potts universality class when the models are coupled.

In order to understand what may happen to the commensurate-incommensurate transition when the models are coupled, we must first examine the incommensurate phase. In the decoupling limit, the weakly incommensurate phase of each uniaxially chiral clock model may be viewed as consisting of roughly parallel fluctuating domain walls separating the three types of domain, say A, B, and C.[9,21,22] The domain walls run, on average, normal to the chiral field, and as one moves along the direction specified by the chiral field one finds the domain sequence $ABCABC\ldots$. The domain-wall spacing diverges at the commensurate-incommensurate transition[21,22] as $(s-s_c)^{-1/2}$. When the three models are then considered together, the incommensurate phase consists of fluctuating domain walls running in three different directions and separating a total of 27 types of domain, with a given domain sequence, as illustrated in Fig. 3. When the three models are coupled, the degeneracy of the 27 domain types is broken, with those domains in which all three models are ordered the same way becoming favored; these domains are labeled AAA, BBB, and CCC in Fig. 3. The coupling therefore produces a periodic transverse force on each domain wall, tending to modulate each wall in order to enlarge the favored domains, producing the pattern shown in Fig. 4. This requires bending the domain walls, and thus is opposed by the domain-wall "stiffness."[9,22,24] The resulting susceptibility to the coupling, namely $\partial^2 f/\partial J^2$, where f is the free-energy density and J is the coupling, is proportional to the wall spacing as the commensurate-incommensurate transition is approached in the decoupling limit. This divergent susceptibility indicates that the coupling is relevant at the transition and thus will cause crossover to a new type of phase transition for nonzero coupling.

The coupling between the models produces a somewhat more orderly incommensurate phase, with three domains in the pattern being favored over the other 24. The resulting pattern, Fig. 4, is the "hexagonal" or "honeycomb" incommensurate phase, as discussed by Bak *et al.*[25] and Coppersmith *et al.*[26] For weak coupling, the bending of the domain walls will be large only near the commensurate-incommensurate transition. In terms of the physisorbate system this means that for relatively weak substrates a distinct honeycomb domain-wall pattern will be present only near the transition. Well away from the transition, only a small fraction of the adatoms sit very near the lowest-energy absorption sites (represented by the domains AAA, BBB, and CCC in Fig. 3), and a description in terms of domains and domain walls is not appropriate.

Coppersmith *et al.*[26] have argued that a continuous commensurate-to-honeycomb incommensurate transition cannot occur. Thus the continuous transition that occurs in the decoupling limit should cross over either to a first-order transition or to a sequence of two transitions (either of which could also be first order), with the fluid phase intruding between the two ordered phases, when the cou-

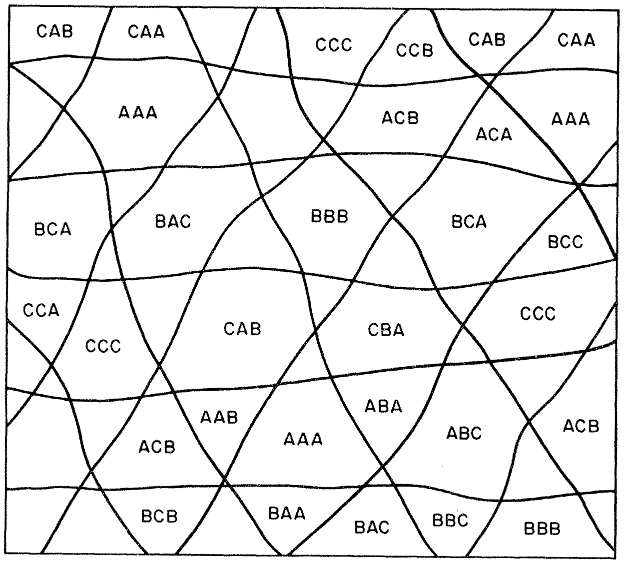


FIG. 3. Weakly incommensurate phase in the decoupling limit. The fluctuating domain walls separate the 27 different types of domains. The three letters in the labeled domains represent the domain type for each of the three decoupled chiral clock models.

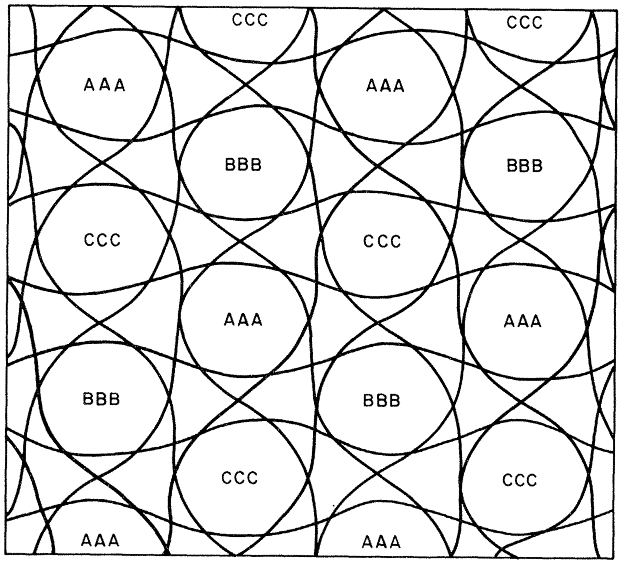


FIG. 4. Weakly incommensurate phase with a weak coupling between the models. Three of the 27 domain types in Fig. 3 are now favored, namely AAA, BBB, and CCC. Each domain wall in Fig. 3 is now deformed in order to enlarge the area of the favored domains. The resulting pattern is the honeycomb incommensurate phase.

pling is added. The intrusion of the fluid phase is due to the instability of the weakly incommensurate honeycomb phase to dislocation-mediated melting.[26] This is a thermal effect and thus is most likely to be important at higher temperatures. At lower temperatures a first-order commensurate-to-incommensurate transition appears to be more likely [not shown in Fig. 2(b)].[25,26] If the fluid phase intrudes between the commensurate and incommensurate phases, and the commensurate-fluid transition is continuous, then this transition occurs in the presence of a strong chiral field and may well be in a chiral universality class.[9] If so, the chiral portion of the commensurate-phase boundary would be separated from the portion in the Potts universality class by a new type of multicritical point,[9] labeled M in Fig. 2(b). The experiments on Kr on graphite[3,4] suggest a phase diagram that is qualitatively similar to Fig. 2(b), with a narrow interval of fluid phase and a chiral commensurate melting transition near 97 K. Precisely what happens at lower and higher temperatures is not yet known.

In order to explore the phase diagrams and phase transitions we might expect near $\sqrt{3}\times\sqrt{3}$ commensurate phases, it may be useful to have a simple spin model with the same LGW Hamiltonian (2.6). Our examination of the decoupling limit makes it clear that any such model may be viewed as three separate uniaxially chiral clock models, with additional couplings between the models. The symmetries of the system dictate that the model should be defined on a triangular lattice with three spins n_i^α, $\alpha=1,2,3$, at each site i. Each spin may take on the possible states $n_i^\alpha=0,1,2$. The chiral field[18,9] in each model, $\alpha=1,2,3$, must be oriented at 120° to those in the other two; let us choose the fields to be perpendicular to nearest-neighbor directions. Then the minimum couplings needed to construct a physical model are chiral bonds coupling nearest-neighbor spins whose separation is not normal to the chiral field and on-site ferromagnetic coupling between the different spins. The resulting Hamiltonian is

$$H_s=-J_0\sum_{\alpha\neq\beta}\sum_i \cos\frac{2\pi}{3}(n_i^\alpha-n_i^\beta) -J_1\sum_\alpha\sum_{\langle ij\rangle}^{\alpha}\cos\frac{2\pi}{3}(n_i^\alpha-n_j^\alpha+\Delta)\ , \tag{4.1}$$

where the sum $\sum_{\langle ij\rangle}^{\alpha}$ runs over those nearest-neighbor pairs for which the vector from i to j points in a direction 30° to either side of the chiral field for the α spins. Of course, one may also add couplings between nearest-neighbor spins whose separation vector is normal to the chiral field, as well as any other couplings consistent with the symmetry of (2.6), but these are not essential to the basic physics of the system. Simulation or other study of this model, especially in the commensurate-incommensurate transition region for weak coupling J_0, may be useful in illuminating the behavior of Kr on graphite and other $\sqrt{3}\times\sqrt{3}$ ordered physisorbates.

V. CONCLUSIONS

The general LGW Hamiltonian (2.6) appropriate for modeling the continuous melting of a $\sqrt{3}\times\sqrt{3}$ commensurate phase is a rather complicated functional of the three complex scalar ordering fields that has a given set of symmetries (2.2)–(2.5). The LGW Hamiltonian of the three-state Potts model is a special case of (2.6) with higher symmetry. Those perturbations allowed in the general Hamiltonian (2.6) that break the Potts-model symmetry all appear to be irrelevant at the critical point of the Potts model. Thus a general class of possible $\sqrt{3}\times\sqrt{3}$ melting transitions will be in the Potts-model universality class, as was originally suggested by Alexander.[6] In these cases the system attains the full Potts-model symmetry in the scaling limit, a symmetry not present in the original Hamiltonian (2.6). This will be reflected in the scaling function for the structure factor, which will be highly symmetric about the Bragg point in momentum space. On the other hand, we might expect that other $\sqrt{3}\times\sqrt{3}$ melting transitions might occur for which the system has no additional symmetries in the scaling limit. In fact, universality classes of $\sqrt{3}\times\sqrt{3}$ melting transitions with at least four possible symmetries are conceivable; in each case the scaling function for the structure factor will exhibit a corresponding symmetry (or lack of symmetry) about the Bragg point in momentum space.

One might expect to be able to model a general $\sqrt{3}\times\sqrt{3}$ melting transition using a simple triangular lattice gas where all adatoms are assumed to sit *at* lowest-energy adsorption sites. However, such a lattice gas has the symmetry (3.8) in momentum space, which dictates a symmetry of the structure factor about the Bragg points of the $\sqrt{3}\times\sqrt{3}$ phase (the Brillouin-zone corners) which is not present in a general adsorbate-substrate system. Thus such a lattice gas will be inadequate for modeling $\sqrt{3}\times\sqrt{3}$ melting transitions for which the lattice-gas symmetry is not attained in the scaling limit. The x-ray scattering data of Moncton *et al.*[4] for Kr on graphite suggest that the scaling function for the structure factor at the commensurate melting transition near 97 K is *not* symmetric about the Bragg point. Thus this transition appears to be in a chiral universality class that cannot be modeled by a simple lattice gas. The spin model (4.1) introduced above is a relatively simple model which, unlike a simple lattice gas, has the appropriate symmetry for modeling the melting of $\sqrt{3}\times\sqrt{3}$ physisorbed commensurate phases.

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