the velocity of crystallization recovers, and layering is reestablished [see Fig. 2(d) at 333 psec]. At the end of the process (~500 psec) the total number density profile is identical to that in Fig. 1(a), and the impurity profile is shown in Fig. 1(d)(f). A certain amount of impurity segregation to the free surface is evident.

In this study we demonstrated the use of MD in an investigation of a complex nonequilibrium material process. Of interest is the "liquid layering" which, as we observed, precedes the solidification front, preparing the liquid for formation of perfect crystalline planes, and significantly affects impurity segregation and transport (see also Wood, Ref. 3), while in turn being affected by interfacial conditions that it, in part, brings about. MD studies can be instrumental in analyzing the dynamic interrelationship between the structure and properties of the interface and the solidification process. Investigations continue in our laboratory on the relationship between the time scale of interface processes (such as layering) and the nature of the resulting solid (crystalline versus amorphous) under various solidification rates, the effect of crystal face, crystallization on amorphous substrates, the role of "liquid layering" in solute trapping or expulsion, and the dependence on host and impurity interaction potentials and mass ratios.

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Domain Walls and the Melting of Commensurate Surface Phases

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Commensurate adsorbed surface phases, particularly $p \times 1$ rectangular and $\sqrt{3} \times \sqrt{3}$ hexagonal phases, exhibit two (or more) classes of domain wall, reflecting a lower than ideal symmetry; these compete statistically and undergo wetting transitions. Scaling arguments and model calculations indicate that new types of continuous melting transitions, possibly already seen in Kr on graphite, can thereby arise.

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Many ($d = 2$)-dimensional systems are now known in which an adsorbed, commensurate surface phase, with the adsorbate atoms or molecules in ordered registry with the substrate solid, *melts* under variation of the temperature, T, or chemical potential, ζ (controlled by the vapor pressure). Such melting may be discontinuous (i.e., first order) in nature but theory suggests,[1] and experiments confirm,[2,3] that *continuous transitions* may also occur. We focus here on such continuous $d = 2$ commensurate melting and ask "What types of transition may occur?" We argue that a class of asymmetric or chiral transitions —distinct from the previously identified symmetric Ising, Potts, and p-state clock universality classes—should arise in real systems and may already have been seen in studies of krypton on graphite.[3] The existence of *different types of domain walls* plays a significant role in the phenomena.

Our analysis addresses systems where, in the commensurate phase, one of $p=2,3,\ldots$ distinct sublattices, A, B, C, ..., of substrate adsorption "sites" is preferentially occupied while, in the melted phase, the sublattices are no longer physically distinguished. The sublattices display an abstract "internal" or "global" symmetry, say Y_p, which permutes them. In particular, we consider $p\times 1$ *rectangular phases*, in which an adsorbate on a rectangular substrate has an x-axis lattice constant p times the corresponding substrate lattice constant, and $p=3$ *hexagonal phases* on hexagonal substrates, such as the $\sqrt{3}\times\sqrt{3}$ phase of He or Kr on graphite.[2-4]

Since the commensurate ordered phases display the internal, global symmetry, Y_p, it is not unnatural to expect that the corresponding melting transitions should be in the universality classes represented by the Ising ($p=2$), Potts ($p\geq 3$), or symmetric clock ($p\geq 3$) models[1,5] which exhibit matching symmetry. These models can be realized with "spin" variables $n_i=0,1,\ldots,(p-1)$ at sites $i,j,\ldots$ of some lattice and nearest-neighbor "ferromagnetic" couplings: The clock form $-J\cos[2\pi(n_i-n_j)/p]$, which favors pairs $00,11,\ldots$ equally over $01,10,12,21$, etc., is general for $p=2$ or 3. On this basis one thus predicts *continuous* melting for $p=3$ systems; further, the specific heat should diverge with the Potts exponent $\alpha=\frac{1}{3}$, a conclusion apparently confirmed, for a least one coverage, in studies of He on graphite.[2]

Now the full symmetry of these simple p-state models on a given lattice is the direct product of the internal symmetry, Y_p, and the independent lattice symmetry, say L. Some inspection reveals, however, that this model symmetry does *not* in general match the real physical symmetry, say G, which is, at best, a subgroup of $Y_p\times L$. This can be seen in a physically informative way by considering an ideal, single-domain sample and examining the heterodomain fluctuations which, ultimately, are responsible for its melting. Figure 1 illustrates, for $p=3$, some such fluctuations, first, topologically and, below, as microscopic subdomains of an adsorbate (shown *schematically* with neglect of small displacements around the adsorption sites which do not affect the disordering directly[6]). In the standard three-state Potts/clock model the subdomain free energy is $l\Sigma_0(T)$, where l is the total length of domain wall and $\Sigma_0(T)$ is the wall tension: this is the *same* between any pair of domains. But microscopically, as evident from Fig. 1, for both rectangular and hexagonal phases there are (at least) two configurationally distinct types of wall, say "heavy" and "light." [Topologically, there are $(p-1)$ types of wall.] Furthermore, because of the asymmetric, repulsive-versus-attractive nature of interactions between real atoms, different walls will, in general, have *different tensions*, say $\Sigma_+(T,\zeta)$ and $\Sigma_-(T,\zeta)$. In particular, heavy walls will, normally, be favored (i.e., $\Sigma_+<\Sigma_-$) by an "overpressure," while an "underpressure" favors light walls; for some chemical potential, say $\zeta_0(T)$, one should find $\Sigma_+=\Sigma_-$.

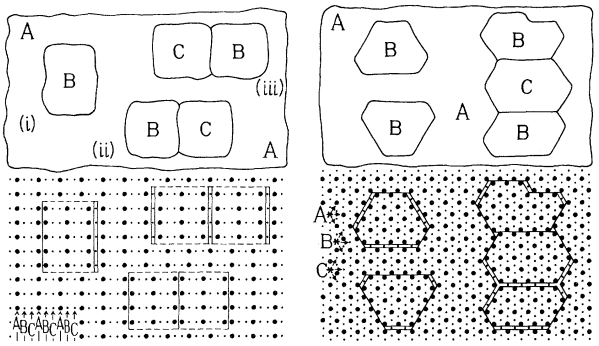

FIG. 1. Heterodomain fluctuations in $p=3$ rectangular and hexagonal commensurate phases illustrating, in the lower part of the figure, the occurence of "heavy" (single line) and "light" (double line) domain walls. The labels A, B, and C correspond, in the upper part, to occupation of one of the three equivalent sublattices illustrated in the lower part.

It follows that subdomains which differ only in their lattice orientation can have quite different free energies (see Fig. 1). Thus in a rectangular phase, a domain sequence $A|B|C|A$, with walls predominantly parallel to the y axis, will be distinguished from the mirror sequence $A|C|B|A$.[7] Likewise in a hexagonal phase the heavy wall junction (A,B,C) has a different free energy from (A,C,B). These examples demonstrate the "chiral" character of the heterodomain fluctuations in real adsorbed phases and establish that appropriate model Hamiltonians should embody a symmetry lower than $Y_p\times L$.[5]

The presence of a lowered symmetry suggests transitions of a new, chiral character: But "Does the breaking of the full $Y_p\times L$ symmetry in real systems represent a *relevant* perturbation of pure Potts or clock criticality?" If the symmetry breaking is relevant, pure Potts behavior should appear,[7] e.g., as in Fig. 2(a), only at an isolated multicritical point, P (where $\zeta=\zeta_0$), lying on a chiral transition line whose chirality switches at P.[8] Conversely, if the perturbation is *irrelevant*,

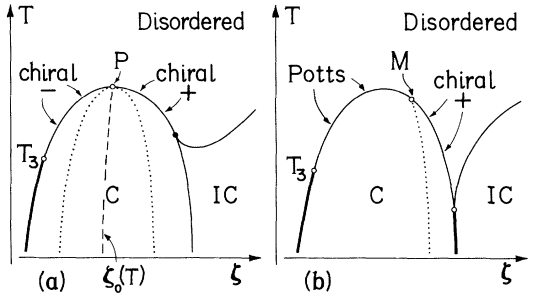

FIG. 2. Schematic phase diagrams for the melting of a commensurate $p = 3$ surface phase (C) when the chiral perturbation is (a) *relevant* and (b) *irrelevant*. Bold lines denote (possible) first-order transitions; thin lines, continuous transitions; dotted lines, domain wall wetting; IC indicates an incommensurate solid phase (Ref. 4); T_3 denotes a tricritical point; P a multicritical point of three-state Potts character; and M a (possible) new multicritical point.

Potts-like behavior should be maintained along the critical line, at least for a range of ζ near ζ_0. Nevertheless, as in Fig. 2(b), a tricritical point, T_3, and first-order segment may appear and, possibly, also a new multicritical point, M, and a *subsequent* chiral transition region.[8] We believe that phase diagrams like Fig. 2 can be realized in physical systems. To distinguish the possibilities we present, first, a scaling argument, applicable to the disordered, melted phase, which suggests that chiral melting may already have been seen in Kr on graphite[3]; second, we discuss calculations for a *uniaxial chiral Potts* or *asymmetric* $p = 3$ *clock model*,[5,9] which indicate an isolated Potts multicritical point and a new chiral transition.

Consider the structure factor, $S(\vec{q}; T, \zeta)$, in the disordered phase for wave vectors $\vec{q} = \vec{G} + \hat{x}\Delta q$, where $\vec{G}$ locates a Bragg peak of the commensurate adsorbate. Let $t(T, \zeta) > 0$ be a smooth function vanishing linearly on the commensurate melting line. Now $S(\vec{q})$ displays a maximum at an incommensurability $\Delta q = \bar{q}(T, \zeta)$ which is, in general, nonzero but which vanishes, say, as $t^{\bar{\beta}}$ when the commensurate phase is approached. The peak width, $\kappa_x(T, \zeta)$, standardized say at "half height," measures the inverse correlation length and so vanishes as t^{ν}/a. Asymptotically, as $t \to 0$, scaling asserts $S(\vec{q}) \approx t^{-\gamma} D(\Delta q a / t^{\nu})$ with $D(w)$ a universal function. Now for pure Potts universality[7] we expect $D(w)$ to attain its maximum at $w = 0$, which in turn implies $\bar{\beta} > \nu$ and $\bar{q}/\kappa_x \to 0$. This conclusion is supported by exact calculations[10] for the hard hexagon model—thought to be Potts-like—which yield $\bar{\beta} = \frac{5}{3}$ and $\nu = \frac{5}{6}$: The incommensurability, $\bar{q}$, thus appears only as a correction to scaling. On the other hand, the prefreezing, critical fluctuations at a chiral transition should reflect the preference for, say, heavy domain walls in an *intrinsic* scaling manner. These walls resemble ordinary discommensurations[4] and thereby force a nonzero $\bar{q}$ corresponding to $D(w)$ being maximal at $w = w_c \neq 0$. Thus in the disordered phase a chiral transition should be *signaled* by the ratio $\bar{q}/\kappa_x$ approaching a *universal* nonzero limit (which also implies $\bar{\beta} = \nu$). The experiments of Moncton *et al.*[3] on the "fluid" phase of Kr on graphite at $T \simeq 97$ K find that this ratio approaches $w_c = 1.0 \pm 0.4$ at the boundary of the $\sqrt{3} \times \sqrt{3}$ phase. Further experiments could check the universality of the ratio and decide if the phase diagram resembles, say, Fig. 2(b) (see below).

Note that the usual $T \gtrless T_c$ symmetry implies the equality of ν', the correlation length exponent *in* the commensurate phase, and ν. At a continuous commensurate-incommensurate transition $\bar{q}$ and $\bar{\beta}$ are well defined in the incommensurate, floating solid[4,11] although κ_x and ν are not; but scaling implies $\bar{\beta} = \nu'$, generally.

The symmetric p-state coupling quoted above is generalized in the uniaxial chiral (or asymmetric) clock models[5,9] to $-J \cos[2\pi(n_i - n_j + \vec{\Delta} \cdot \hat{R}_{ij})/p]$, where $\hat{R}_{ij}$ is a nearest-neighbor vector. Then for a small chiral field, $\vec{\Delta} = \hat{x}\Delta$, like pairs, 00,11,..., are still preferred to unlike pairs *but*, along the x axis, the + pairs, 01,12,..., are favored over the − pairs, 10,21,..., when $\Delta > 0$; likewise, as has been confirmed by low-temperature expansions, there are two distinct wall tensions, which satisfy $\Sigma_+ < \Sigma_-$ for $\Delta > 0$. On a square lattice these models can thus reasonably describe $p \times 1$ adsorbates with Δ corresponding to $\zeta - \zeta_0$.[5] Now Δ is relevant if and only if the corresponding crossover exponent, ϕ_p, is positive.[12] Scaling arguments supplemented by a plausible assumption[13] identify the exponent for the field-theoretic chiral term, $\int d^d r\, \psi \nabla \psi$, as $\phi_p = \mu_p - 2\beta_p$, where β_p is the standard, pure symmetric order parameter exponent, while μ_p describes the wall tension via $\Sigma_0 \sim t^{\mu_p}$. This result checks in mean field theory, which should be valid for $d \geq 4$, where it yields $\phi_p = \frac{1}{4}(p - 2)$ when $p \geq 4$. (For $p = 3$ mean field theory predicts a first-order transition.) For $p = 4$, where the model decomposes into two disjoint Ising models when $\Delta = 0$, an exact analysis[14] agrees for all d, giving $\phi_4 = 1$, $\frac{3}{4}$, 0.61, and $\frac{1}{2}$ for $d = 1$ to 4. In the limit $d \to 1$ the Migdal-Kadanoff (MK) approximate renormalization group,

which should then be exact, confirms $\phi_p = 1$ for all $p > 2$. For $p = 3$ we have no further exact results, but for a Berker or fractal lattice, where the MK method is again exact, one obtains[9] $\phi_3 = \frac{1}{2}$ when $d_{\text{eff}} = 2$. Finally, the scaling relation with accepted Potts exponent values yields $\phi_p = \frac{11}{18} \simeq 0.61$ for $d = 2$ which, even if not exact, is probably a good estimate. Thus we conclude that a chiral term is always relevant in the uniaxial models. Hence the symmetric point, P, should be *multicritical*, as in Fig. 2(a), for all $p \times 1$ phases ($p > 2$) and the phase boundaries $T_c(\zeta)$ near P should have a contribution varying as $(\zeta - \zeta_0)^{1/\phi_p}$.

Even granted chiral crossover from symmetric, Potts behavior, it is not obvious that the resulting transition has an intrinsically new character. (Thus in a two-layer Ising model Ising-to-Ising crossover occurs when the layers are coupled.[14]) To address this, consider, for $p = 3$, the heterodomain fluctuations in the chiral regime and note, first, that the tension, $\Sigma_+(T, \zeta)$, of a favored, +, domain wall must vanish on the melting line. Conversely the unfavored tension, $\Sigma_-(T, \zeta)$, ought to approach zero only *beyond* the transition. However, when Σ_+ falls to $\frac{1}{2}\Sigma_-$ a *wetting transition* must occur after which any wall, say $A \| C$, lowers its free energy by decomposing into *two* + walls and forming an $A|B|C$ structure by insertion of a B domain. In the chiral clock model at $T = 0$ this wetting transition occurs at $\Delta = \frac{1}{4}$, well inside the commensurate phase (which extends to $\Delta = \frac{1}{2}$); for $T > 0$ it can be studied by series expansions, etc. In a "solid-on-solid" limit we find that the wetting transition is continuous with $(\Sigma_- - 2\Sigma_+) \sim (T - T_w)^2$. Generally, the wetting line, $T_w(\zeta)$, should resemble the dotted curves in Fig. 2. It follows that the long boundaries of large heterodomain fluctuations should, near chiral melting, all be of the + type. For a given length, the boundaries of the most probable subdomains in the neutral limit, $\zeta = \zeta_0$, form simple loops [e.g. (i) in Fig. 1]; but for $\zeta \neq \zeta_0$ these entail unfavored wall segments and hence, in the wetting region, must decompose into two-loop form [e.g., (ii) in Fig. 1] of lower entropy. Similarly, all two-loop subdomains [e.g., (ii) and (iii)] contribute equally when $\zeta = \zeta_0$, but half are suppressed and half are enhanced when $\zeta \neq \zeta_0$. In short, the nature of the dominant fluctuations driving melting changes so drastically in the chiral regime that it seems unlikely that the symmetric melting exponents are preserved. Similar considerations apply for $p > 3$ and for hexagonal chiral melting.

In summary, we have argued that the behavior of domain walls yields new types of commensurate melting transitions which may be observable in surface phases. Further experiments are desirable, especially on 3×1 rectangular phases[15] where the predicted features should show most clearly.

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[6]At least for "narrow" domain walls.

[7]Here, as at places above, we take $p = 3$ for simplicity.

[8]For $p \times 1$ phases with $p > 4$ (and, possibly, $p = 4$) the incommensurate phase should extend up to P. Note also that Fig. 2 is consistent with the analysis of Domany (Ref. 1) for $p \times 1$ phases since these violate the Lifshitz condition; but for $\sqrt{3} \times \sqrt{3}$ phases both Figs. 2(a) and 2(b) contradict Domany and, if correct, mean that neglected triaxial terms in the Landau-Ginzburg-Wilson Hamiltonian, like $\nabla^3\psi^2$ and $(\nabla\psi)^3$, although irrelevant near $d = 4$, may play a crucial role when $d = 2$.

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