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Dislocations and the Commensurate-Incommensurate Transition in Two Dimensions

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The incommensurate adsorbed solid is found to become unstable to dislocations when the lattice period approaches that of a sufficiently low-order commensurate phase such as a 2×1 rectangular overlayer or the $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal structure which occurs for krypton on graphite. In these cases, a fluid phase is expected between the commensurate and incommensurate solids.

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There are many two-dimensional (2D) systems in which a transition occurs from a registered phase, where the lattice constant of the "adsorbate" solid is commensurate with that of the "substrate," to a phase where it is incommensurate. Theoretical descriptions of the commensurate-incommensurate (C-I) transition in 2D systems have been given by several authors.¹⁻³ In this paper, however, we show that near the lowest-order commensurate structures, the incommensurate solid becomes unstable to the formation of dislocations, and the description of the C-I transition must be revised accordingly. While the results may apply to other systems, such as charge-density waves in layered compounds, we will for

clarity work in terms of atoms adsorbed on a substrate.

We will consider three types of adsorbate phases which can be distinguished by nature of singularities in the structure function $S(\vec{q})$. In the *fluid* phase, the only singularities in $S(\vec{q})$ are of the form $\delta(\vec{q} - \vec{Q})$, where $\{\vec{Q}\}$ is the set of *substrate* reciprocal-lattice vectors. For the *floating* ("incommensurate") *solid*, in addition to Bragg peaks at $\{\vec{Q}\}$, there are power-law singularities characteristic of a 2D solid of the form

$$S(\vec{q}) \sim |\vec{q} - \vec{G} - \vec{Q}|^{-2 + \eta_{\vec{G}}(T)},$$

where $\eta_{\vec{G}}(T) \propto G^2 T$ independent of \vec{Q} . The set $\{\vec{G}\}$ is the set of reciprocal-lattice vectors of the *ad-*

orbate which vary continuously with temperature T and with the adsorbate chemical potential ζ . For the *registered commensurate solid*, the sets $\{\vec{Q}\}$ and $\{\vec{G}\}$ have elements in common and there are δ function Bragg peaks at all $\vec{Q}+\vec{G}$. Two possible phase diagrams containing these states are shown in Fig. 1.

We shall first discuss the case of a *rectangular adsorbate solid on a rectangular substrate*. We assume that the commensurate phase is a $(p \times 1)$ structure; i.e., the adsorbate lattice constant in the x direction is p times the lattice constant a of the substrate, while the substrate and adsorbate have identical lattice constants c in the y direction. (Later we shall discuss the C-I transition for a $\sqrt{3} \times \sqrt{3}$ hexagonal adsorbate on a hexagonal substrate, such as occurs for krypton on graphite.²) The *incommensurate solid* in the rectangular case is assumed to have a lattice constant $pa(1-\delta)$ along x , where δ is small (with $\delta > 0$ for definiteness), while the y lattice constant remains locked to the substrate. The incommensurate solid in this case can be obtained from the commensurate phase by the addition of a small density of *domain walls*, parallel to the y axis, with spacing $l = a/\delta \gg pa$. (The domain walls separate commensurate regions shifted relative to each other by one unit of the substrate spacing a , and therefore, they produce on average a fractional change $-a/l$ in the adsorbate lattice constant.) A single wall has a characteristic width, w , and a free energy per unit length, f_w , which includes the entropy from the wall meandering [see Fig. 2(a)]. The interaction energy between two walls falls off as $e^{-l/w}$ and hence is negligible if l is sufficiently large. When the chemical potential $\zeta \geq \zeta_0 = pcf_w$ the registered phase will be unstable to the formation of domain walls and will become incommensurate. As shown by Pokrovsky and co-workers,¹ there is an effective repulsion between the walls due to the loss of meandering entropy

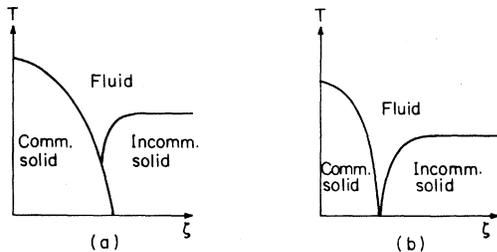


FIG. 1. Two possible phase diagrams in the temperature-chemical-potential (T - ζ) plane.

caused by walls approaching to within w of one another. This gives rise to a term in the free energy per unit area, f , proportional to l^{-3} , which for $T \neq 0$ dominates the exponential wall-wall interaction energy as $l \rightarrow \infty$. The resulting effective interaction stabilizes the wall density at a finite value $l^{-1} \propto (\zeta - \zeta_0)^{1/2}$. We are thus led to consider the long-wavelength elastic properties of the incommensurate adsorbate in the limit $l \rightarrow \infty$.

In the registered phase, long-wavelength strains will cost an energy linear (rather than quadratic) in the strain; the effective elastic constants are therefore infinite because of the presence of the substrate. This is also true for displacements u_y in the incommensurate phase, because of registry in the y direction. We thus need only consider displacements parallel to x , $u(\vec{r}) \equiv u_x(\vec{r})$, about the average incommensurate positions of the atoms; the elastic constants associated with these strains will be finite.

On scales much larger than l , the elastic free energy in the incommensurate phase can be written (in the absence of free dislocations)

$$F = \frac{1}{2} \int d^2r [K_x (\partial_x u)^2 + K_y (\partial_y u)^2]. \quad (1)$$

Alternatively, we could instead consider the displacements $\tilde{u}(\vec{r})$ of the *walls* from their average positions and write a long-wavelength elastic free energy for the walls,

$$F = \frac{1}{2} \int d^2r [\tilde{K}_x (\partial_x \tilde{u})^2 + \tilde{K}_y (\partial_y \tilde{u})^2]. \quad (2)$$

At long wavelengths, a wall-displacement \tilde{u} will produce an adsorbate displacement $u = \tilde{u}a/l$, so that the elastic constants are related by $\tilde{K}_{x,y} = a^2 l^{-2} K_{x,y}$. The elastic coefficient \tilde{K}_y arises from the bending energy of the walls and $\tilde{K}_x \propto T^2 / \tilde{K}_y l^4$ from the loss of meandering entropy due to the collisions between walls discussed above. It

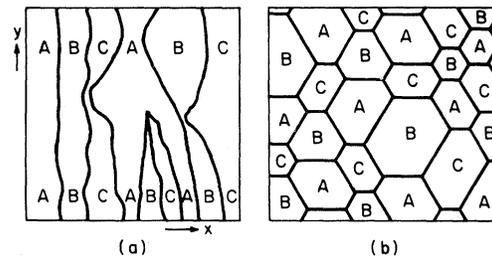


FIG. 2. Configurations of domain walls: (a) "Parallel array" for the 3×1 structure, including a dislocation; (b) "Honeycomb array" for a $\sqrt{3} \times \sqrt{3}$ hexagonal phase. Domains A , B , and C correspond to the three possible occupied sublattices of adsorption sites.

can be shown that $K_x \propto l \rightarrow \infty$; and thus $K_x \propto l^{-1} \rightarrow 0$ as $l \rightarrow \infty$.

Schulz³ has studied the correlation function for the translational order parameter $\tilde{\rho}(\vec{r}) \equiv \exp[2\pi i \tilde{u}(\vec{r})/l]$ and has found $\langle \tilde{\rho}(\vec{r}) \tilde{\rho}(0) \rangle \sim (1/r)^\eta$, for large r , with $\eta \rightarrow 2$ in the limit $l \gg w$. Since $\tilde{\eta} = 2\pi l^2 T / (\tilde{K}_x \tilde{K}_y)^{1/2}$, it follows that

$$p^2 a^2 (K_x K_y)^{1/2} / 8\pi T \rightarrow p^2 / 8, \quad (3)$$

as $\xi \rightarrow \xi_0$.

The Kosterlitz-Thouless criterion⁴ for stability of the solid against formation of free dislocations with the minimum Burgers vector $b = pa$ requires that the left-hand side of Eq. (3) be no less than 1. Since this criterion is violated for $p = 2$, we see that there cannot be a direct second-order transition from the 2×1 structure to an incommensurate solid, at any $T > 0$. This suggests the phase diagram sketched in Fig. 1(b), where a fluid intervenes between the commensurate and incommensurate structures at all $T > 0$. Interactions between the domain walls will stiffen the elastic constants and resolidify the incommensurate phase as l^{-1} increases. The width in ξ of the fluid phase will decrease exponentially for $T \rightarrow 0$.

For $p = 3$, the Kosterlitz-Thouless criterion is consistent with a second-order transition from the commensurate to incommensurate solid. However, if the dislocation core energy is low, the presence of bound dislocation pairs at moderately high temperatures may cause the elastic constants to drop below the value calculated from the domain walls above, and might lead to a dip in the fluid-phase boundary near the C-I transition, as indicated in Fig. 1(a).

We could also have reached the above conclusions by considering the instability of the array of walls to a group of p half-walls terminating at a point, as shown (for $p = 3$) in Fig. 2(a). [Microscopically, this is exactly a dislocation with Burgers vector $b = (pa, 0)$ considered above.] The free energy of this configuration and the resulting instability for $p^2 < 8$ could be calculated from the wall elastic free energy [Eq. (2)] without reference to the microscopic structure at all; this method will be useful in considering the hexagonal system.

We now turn to the second case to be considered: a hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbate phase on a hexagonal substrate. The C-I transition may again proceed by the formation of domain walls, but now there will be three types of walls having different preferred orientations. It is hence necessary to consider the free energy f_1 associated

with wall intersections. If $f_1 < 0$, the transition is presumably strongly first order and not of interest here.

At first it appears that $f_1 > 0$ implies that the lowest free-energy configuration with a small density of walls is an array of parallel walls with no intersections, yielding an anisotropic lattice or "striped" phase. However, Villain² has pointed out that a honeycomb array of all three types of walls has large configurational entropy per unit area arising from various possible positions of the wall intersections. Neglecting terms of order l^{-3} , where l is the average length of a hexagon side, we have (following Villain)

$$f = \frac{2l^{-2}}{3\sqrt{3}} \left[\frac{l}{a'} (\xi_0 - \xi) + 2f_1 - BT \ln \left(\frac{l}{a'} \right) \right], \quad (4)$$

where the expression in square brackets is the free energy per hexagon, a' is a length of order a , and ξ has been conveniently normalized. The quantity $B \ln(l/a')$ is the entropy per hexagon of a honeycomb array of walls, when the walls are constrained to be parallel to the three 120° axes, and the number of hexagons and total area are specified, but the positions of the vertices are otherwise free.^{5,6} A typical configuration of this type is shown in Fig. 2(b). It can be shown analytically that $B = 1$, and Monte Carlo computer simulations confirm this result.⁶ The equilibrium value of l is obtained by minimizing f .

According to the Villain picture, there will be a first-order transition from the commensurate phase to the honeycomb incommensurate phase at a chemical potential $\xi_c = \xi_0 - Ta'/l_c$, where $l_c \equiv a' \exp(1 + 2f_1/T)$ is the value of l at the transition. The free energy of the honeycomb lattice remains smaller than that of the striped phase until $\xi = \xi_{\max} = \xi_0 + O(l_c^{-4/3})$, at which point $l \approx l_c / e^{1/2}$. If f_1/T is large and positive, the transition will be very weakly first order and l_c will be large. In this limit, we are thus justified in ignoring terms in f of order l^{-3} and can calculate the long-wavelength elastic properties of the system in terms of the superlattice. The honeycomb-superlattice elastic-free energy ignoring dislocations will be of the form⁵

$$F = \frac{1}{2} \int d^2r \left[\frac{1}{2} \tilde{u} (\partial_i \tilde{u}_j + \partial_j \tilde{u}_i)^2 + \tilde{\lambda} (\nabla \cdot \tilde{u})^2 + \tilde{\gamma} (\nabla \times \tilde{u})^2 \right], \quad (5)$$

where $\tilde{u}(\vec{r})$ is the displacement of the superlattice hexagon at \vec{r} from its average position and $\tilde{\mu}$ and $\tilde{\lambda}$ are the Lamé coefficients. The third term of Eq. (5) with elastic coefficient $\tilde{\gamma}$ is the free ener-

gy of rotation of the superlattice. It can be shown that $\bar{\gamma}$ is infinite relative to $\bar{\mu}$ and $\bar{\lambda}$ in the limit $l \rightarrow \infty$. The "bulk modulus" ($\bar{\mu} + \bar{\lambda}$) is equal to $\frac{1}{4} l^2 d^2 f / dl^2$, and one finds that $l^2(\bar{\mu} + \bar{\lambda})/T$ increases monotonically from the value $1/6\sqrt{3}$, for $\xi = \xi_c$, to $1/3\sqrt{3}$, for $\xi = \xi_0$. The value of $\bar{\mu}$ has been obtained from a Monte Carlo simulation, and we find that $l^2 \bar{\mu}/T \approx 0.21$ independent of ξ .⁶ We note the unusual result that the system has a negative Poisson's ratio (i.e., $\bar{\lambda} < 0$).

Any 2D solid with an elastic free energy of the form Eq. (5) will be unstable to the presence of free dislocations with Burgers vector b if⁷

$$\bar{b}^2[\bar{\mu}(\bar{\mu} + \bar{\lambda})/(2\bar{\mu} + \bar{\lambda}) + \bar{\mu}\bar{\gamma}/(\bar{\mu} + \bar{\gamma})] < 4\pi T. \quad (6)$$

For the $\sqrt{3} \times \sqrt{3}$ overlayer under consideration, the minimum Burgers vector consistent with the labeling of the hexagons A , B , and C [see Fig. 2(b)] has $\bar{b} = 3l$; this corresponds to a dislocation in the adsorbate lattice with minimal Burgers vector $b_0 \approx a\sqrt{3}$. With $\bar{\gamma} = \infty$ and the calculated values of $\bar{\mu}$ and $\bar{\lambda}$ for $\xi = \xi_c$, the left-hand side of Eq. (6) is equal to $2.5T$ which is considerably less than the right-hand side, and we find that the slightly incommensurate phase is unstable to dislocations and hence is a fluid.

We thus conclude that the incommensurate phase sufficiently close to the C-I transition of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal overlayer will be a fluid at all temperatures, provided that the C-I transition is weakly first order, i.e., the superlattice period l_c is large. The phase diagram in this region will be similar to that for the 2×1 C-I transition discussed above [see Fig. 1(b)]. Implications of the results obtained here on systems of experimental interest will be discussed in a longer paper, in particular with reference to recent x-ray scattering experiments on kryp-

ton on Grafoil,⁸ which stimulated this work.

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²J. Villain, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980), p. 221.

³H. J. Schulz, *Phys. Rev. B* **22**, 5274 (1980).

⁴See J. M. Kosterlitz and D. J. Thouless, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1978), Vol. VIIb. The anisotropic case considered here may be mapped onto the isotropic case by a scale change in one direction.

⁵Actually, in many cases, the domain walls will be rotated by an angle relative to the substrate axes. (See Villain, Ref. 2). This makes the description more complicated but does not appear to affect our final conclusion.

⁶Details will be given elsewhere.

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