Quasicrystallinity in Twist-Grain-Boundary Phases

T. C. Lubensky and Tetsuji Tokihiro[a]
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

S. R. Renn
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501
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We present a simplified polymer model for twist-grain-boundary phases in liquid crystals. The thermodynamic phases of this model are characterized by an angle $2\pi\tilde{\alpha}$. There are incommensurate phases with $\tilde{\alpha}$ an irrational number and commensurate phases with $\tilde{\alpha}=P/Q$, with P and Q relatively prime integers. The latter have quasicrystalline symmetry for $Q=5$ or $Q>6$. Equilibrium phases with all values of $\tilde{\alpha}$ can be produced by varying a control parameter α. The curve $\tilde{\alpha}(\alpha)$ is an incomplete devil's staircase with finite locking intervals about every rational $\tilde{\alpha}$.

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The nematic-to-smectic-A transition in liquid crystals is strongly analogous [1] to the normal-to-superconducting transition in metals, with the unit vector $\mathbf{n}$ specifying the direction of molecular alignment (the Frank director) playing the role of the vector potential $\mathbf{A}$. The analog in liquid crystals of an external magnetic field in superconductors is molecular chirality, which induces a nonvanishing twist, $\mathbf{n}\cdot(\nabla\times\mathbf{n})$, in the nematic phase. Superconducting order tends to expel magnetic fields (i.e., $\nabla\times\mathbf{A}$). Nevertheless, in type-II superconductors, superconducting order and magnetic fields coexist in an Abrikosov phase containing a regular lattice of vortices. The analogy between smectic liquid crystals and superconductors suggests that there should be the analog of the Abrikosov phase in liquid crystals in which there is a regular array of twist grain boundaries consisting of screw dislocations and an associated nonzero twist, $k_0=\mathbf{n}\cdot(\nabla\times\mathbf{n})$. A theoretical analysis [2] based on the de Gennes model [1] indicates that this new twist-grain-boundary (TGB) phase in liquid crystals should consist of a stack of twist grain boundaries each consisting of a lattice of parallel screw dislocations whose axes precess in a helical fashion from one grain boundary to the next. Independently of the above theoretical investigations, a material exhibiting the properties of a TGB phase (e.g., x-ray diffraction indicating the existence of smectic lamellae and optical properties of a twisted nematic [3]) was discovered. Subsequently, other materials exhibiting this remarkable new phase have been found [4].

If $2\pi\tilde{\alpha}$ is the average angle between dislocations in adjacent grain boundaries separated by a distance l_b, then $k_0=2\pi\tilde{\alpha}/l_b$. Thus, $\tilde{\alpha}$ is a winding number which can be rational or irrational. In the former, rotationally commensurate (C) case, $\tilde{\alpha}=P/Q$ for relatively prime integers P and Q, and the system has quasicrystalline symmetry [5,6] for $Q=5$ and $Q>6$. In this Letter, we wish to investigate some of the properties of these quasicrystalline TGB phases and the nature of the phase transitions from them to the rotationally incommensurate (I) phases. Ideally, one would like to study these phases using the de Gennes model [1] for the smectic phase. Unfortunately, interactions among dislocations in real smectics are quite complicated. We, therefore, introduce a simple model system, in which dislocations are treated as interacting nearly straight polymers [7]. This model exhibits C and I phases analogous to those in real TGB phases. Though our analysis will focus on ground-state properties (temperature $T=0$), its qualitative results are valid at finite temperature and thus applicable to real TGB phases. In our model, polymers are confined to lie in a series of equally spaced planes perpendicular to the x axis. Polymer displacements parallel to the x axis could easily be included, but they will not lead to any significant modification of our results. In the absence of interplane interactions, polymers in a given plane p are in their lowest-energy configuration if they form a grating, which we will call the reference grating, of N parallel lines of length L separated by a distance l and aligned along $\mathbf{n}_p=(0,\sin\theta_p,\cos\theta_p)$. There is a harmonic energy cost for deviations from this configuration. Thus, we parametrize the position of the kth polymer in plane p with the two-dimensional vector

$$\mathbf{X}_{p,k}(w)=\mathbf{R}_{p,k}(w)+u_{p,k}(w)\mathbf{e}_p\,,$$

where $\mathbf{e}_p=(0,\cos\theta_p,-\sin\theta_p)$ is the unit vector perpendicular to $\mathbf{n}_p$ and $\mathbf{R}_{p,k}(w)=w\mathbf{n}_p+(kl+u_p^0)\mathbf{e}_p$, with $w=\mathbf{x}\cdot\mathbf{n}_p$ $(0<w<L)$ a coordinate measuring distance along $\mathbf{n}_p$. When $u_{p,k}(w)$ is zero, the polymers lie on the reference grating with positions $\mathbf{R}_{p,k}(w)$. The variable u_p^0 determines the translation of the whole grating parallel to $\mathbf{e}_p$, whereas the displacement variable $u_{p,k}(w)$ measures inhomogeneous distortions of the regular grating. The latter has Fourier components $\mathbf{q}\neq 0$ in the first Brillouin zone of the reference grating $(-\pi/l<\mathbf{q}\cdot\mathbf{e}_p<\pi/l$, $-\infty<\mathbf{q}\cdot\mathbf{n}_p<\infty)$:

$$u_{p,k}(w)=\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_{p,k}(w)}u_p(\mathbf{q})\,.$$

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The harmonic Hamiltonian for layer p is

$$H_p = \tfrac{1}{2}\sigma\sum_k \int dw\{[du_{p,k}(w)/dw]^2 + 2l^{-2}[u_{p,k}(w) - u_{p,k+1}(w)]^2\}.$$

The parameter σ can be viewed as a line tension. When $\sigma=\infty$, the polymers are forced to be straight.

We now consider interactions between planes. We wish polymer lattices to rotate relative to each other like the director in a chiral nematic, and we introduce

$$H_\theta = \tfrac{1}{2} NLK\sum_p (\theta_{p+1} - \theta_p - 2\pi\alpha)^2,$$

which is clearly minimized when the winding number $\tilde{\alpha} = (\theta_{p+1} - \theta_p)/2\pi$ is equal to α. The bare winding number α is the parameter that forces twist; it is the analog of the external magnetic intensity in a superconductor or the chiral potential (controlled by molecular chirality) in a chiral nematic liquid crystal. There is an explicit factor of NL in H_θ to make it extensive. Alternate, more microscopic formulations in terms of the local unit tangent vectors to polymers are also possible but unnecessary for our present purposes. Finally, we introduce an interaction among polymers in nearest-neighbor planes similar to that among vortices in superconductors:

$$H_{\rm int} = -\sum_p \int d^2x\, d^2x'\, \mathbf{m}_p(\mathbf{x})\cdot\mathbf{m}_{p+1}(\mathbf{x}')U(\mathbf{x}-\mathbf{x}') = -A\sum_{\mathbf{q}} \mathbf{m}_p(-\mathbf{q})\cdot\mathbf{m}_{p+1}(\mathbf{q})U(\mathbf{q}),$$

where $A = NLl$ is the area in the y-z plane,

$$\mathbf{m}_p(\mathbf{x}) = \sum_n \int dw \left[\mathbf{n}_p + \frac{du_{p,k}(w)}{dw}\mathbf{e}_p\right]\delta(\mathbf{x} - \mathbf{X}_{p,k}(w))$$

is the directed polymer density, and $\mathbf{m}_p(\mathbf{q}) = A^{-1}\int d^2x \times e^{-i\mathbf{q}\cdot\mathbf{x}}\mathbf{m}_p(\mathbf{x})$ is its Fourier transform. $H_{\rm int}$ favors parallel alignment (i.e., ferromagnetic) of adjacent grain boundaries if $U(\mathbf{x})$ is positive and antiparallel alignment if $U(\mathbf{x})$ is negative. For real dislocations, $U(\mathbf{x})$ is negative. The total Hamiltonian is thus $H = H_\theta + H_{\rm int} + \sum_p H_p$. When $\sigma=\infty$ and $u_{k,p}(w)=0$, $\mathbf{m}_p(\mathbf{x}) = \mathbf{m}_p^0(\mathbf{x})$ is the polymer density associated with the reference grating parallel to $\mathbf{n}_p$, with

$$\mathbf{m}_p^0(\mathbf{q}) = l^{-1}\sum_n e^{-in\phi_p}\mathbf{n}_p\delta_{\mathbf{q},n\mathbf{G}_p},$$

where $\mathbf{G}_p = G\mathbf{e}_p$ with $G = 2\pi/l$ and $\phi_p = Gu_p^0$. The vector $\mathbf{G}_p$ is the basis for the one-dimensional reciprocal lattice of the reference grating, and ϕ_p is the phase of the fundamental density wave of that grating. When $\sigma\neq\infty$, $\mathbf{m}_p(\mathbf{x}) = \mathbf{m}_p^0(\mathbf{x}) + \delta\mathbf{m}_p^0(\mathbf{x})$ has contributions arising from a nonzero $u_{p,k}(\mathbf{x})$, with

$$\delta\mathbf{m}_p(\mathbf{q}) = -(i/l)(\mathbf{e}_x\times\mathbf{q})u_p(\mathbf{q}) + O(u_p^2). \quad (1)$$

There are, of course, terms in $\delta\mathbf{m}_p(\mathbf{x})$ of arbitrary order in $u_{p,k}(\mathbf{x})$.

We now turn to equilibrium configurations of the total Hamiltonian. If $\sigma=\infty$, $\mathbf{m}_p(\mathbf{x}) = \mathbf{m}_p^0(\mathbf{x})$ and

$$H_{\rm int} = Al^{-2}\sum_p \cos(\theta_p - \theta_{p+1})U(\mathbf{q}=0),$$

and one can easily verify that $\tilde{\alpha} = \alpha - \beta\sin 2\pi\tilde{\alpha}$ in equilibrium, where $\beta = U(\mathbf{q}=0)/2\pi Kl$. Thus, the average winding number $\tilde{\alpha}$ is a monotonic increasing function of α for $\beta < 1$. When $\sigma < \infty$, $u_{p,k}(w)$ will be nonzero in equilibrium. The contribution to $H_{\rm int}$ linear in $u_{p,k}(w)$ is

$$\delta H_{\rm int} = -A\sum_{\mathbf{q}} [\mathbf{m}_{p+1}^0(\mathbf{q}) + \mathbf{m}_{p-1}^0(\mathbf{q})]\cdot\delta\mathbf{m}_p(-\mathbf{q})U(\mathbf{q}). \quad (2)$$

Thus coupling between nearest-neighbor planes will induce modulations in $u_{p,k}(w)$ at wave vectors $n\mathbf{G}_{p\pm1}$ of the reference gratings in layers $p\pm1$. Minimization of $\sum H_p + \delta H_{\rm int}$ with respect to $u_p(\mathbf{q})$ yields

$$u_p(n\mathbf{G}_{p\pm1}) = i2\pi nl\left[\frac{U(nG)}{\epsilon_p(n\mathbf{G}_{p\pm1})l^3}\right]e^{-in\phi_{p\pm1}},$$

where

$$\epsilon_p(\mathbf{q}) = \sigma\{(\mathbf{q}\cdot\mathbf{n}_p)^2 + 2l^{-2}[1 - \cos(\mathbf{q}\cdot\mathbf{e}_p l)]\}.$$

The phase of $-iu_p(\mathbf{G}_{p\pm1})$ is equal to the phase $n\phi_{p\pm1}$ of $\mathbf{m}_{p\pm1}^0(n\mathbf{G}_{p\pm1})$. Once modulations at $n\mathbf{G}_{p+2}$ develop in layer $p+1$, they will induce modulations in layer p at $n\mathbf{G}_{p+2}$ because of couplings in the $\delta\mathbf{m}_p\cdot\delta\mathbf{m}_{p\pm1}$ part of $H_{\rm int}$. Thus, there will be modulations in each layer at the

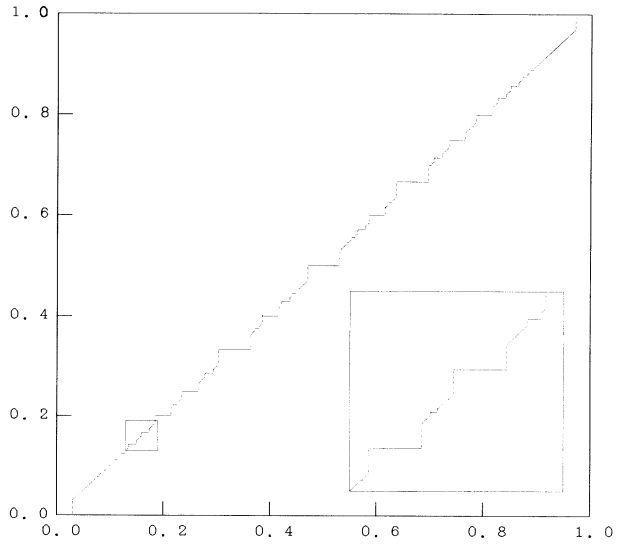

FIG. 1. Schematic representation of the curve $\tilde{\alpha}(\alpha)$. There are commensurate states where $\tilde{\alpha}$ is equal to a rational number P/Q for a finite range of values of α followed by first-order transitions to incommensurate states.

fundamentals of all other layers, with $u_p(n\mathbf{G}_{p\pm s})/l \sim (U/\epsilon l^3)^s$ if there are only nearest-neighbor interactions. The phase of each $u_p(n\mathbf{G}_{p+s})$ is determined uniquely in terms of the reference grating phases $\phi_p = Gu_p^0$ provided $\tilde{\alpha}$ is irrational. To lowest order in $U/\epsilon l^3$, the phase of $-iu_p(n\mathbf{G}_{p+s})$ is simply $n\phi_{p+s}$. It is straightforward to verify that the local minimum to the free energy in which $\tilde{\alpha}$ is a monotonic increasing function of α continues to exist for $\sigma < \infty$. This minimum competes with minima in which $\tilde{\alpha}$ locks in to a rational value P/Q. The lowest-order locking terms can be calculated using $u_p(\mathbf{q}) = \sum_{s,n} u_p(n\mathbf{G}_{p+s})\delta_{\mathbf{q},n\mathbf{G}_{p+s}}$ in Eqs. (1) and (2). If $\tilde{\alpha} = P/Q$, then there will be terms in $H_{\rm int}$ of order $Ul^{-2}(U/\epsilon l^3)^{Q+1}$ that are not present when $\tilde{\alpha}$ is irrational. For $U(\mathbf{x}) > 0$, these terms favor $\phi_p = \phi_{p\pm Q}$ if Q is odd and $\phi_p = -\phi_{p\pm Q} + \pi$ if Q is even; for $U(\mathbf{x}) < 0$, they favor $\phi_p = \phi_{p\pm Q/2}$ for Q odd, $\phi_p = -\phi_{p\pm Q/2} + \pi$ for Q and $Q/2$ even, and $\phi_p = \phi_{p\pm Q/2}$ for Q even and $Q/2$ odd.

Lock-in to a local isomorphism class for $Q = 2M+1$ a prime is brought about by couplings between displacements at all wave vectors $\mathbf{G}_s$ in the Q-fold star of $\mathbf{G}$. Terms of the form $\prod_{i=1}^{Q} u_{p_i,k_i}(\mathbf{q}_i)$ in $H_{\rm int}$ are nonzero provided the sum of the Q wave vectors $\mathbf{q}_i$ is zero. If $\tilde{\alpha} = P/Q$, then the sum of the Q basis vectors $\mathbf{G}_p$, $p = 0, \ldots, Q-1$ is zero, and there are nonzero terms in $H_{\rm int}$ of the form

$$H_{\rm int}^{P/Q}(p) \sim Cl^{-2-Q}U(G)u_p(\mathbf{G}_{p-M})u_p(\mathbf{G}_{p+1})u_{p+1}(\mathbf{G}_p) \times \prod_{s=1}^{M-1}[u_p(\mathbf{G}_{p-s})u_{p+1}(\mathbf{G}_{p+s-1})], \quad (3)$$

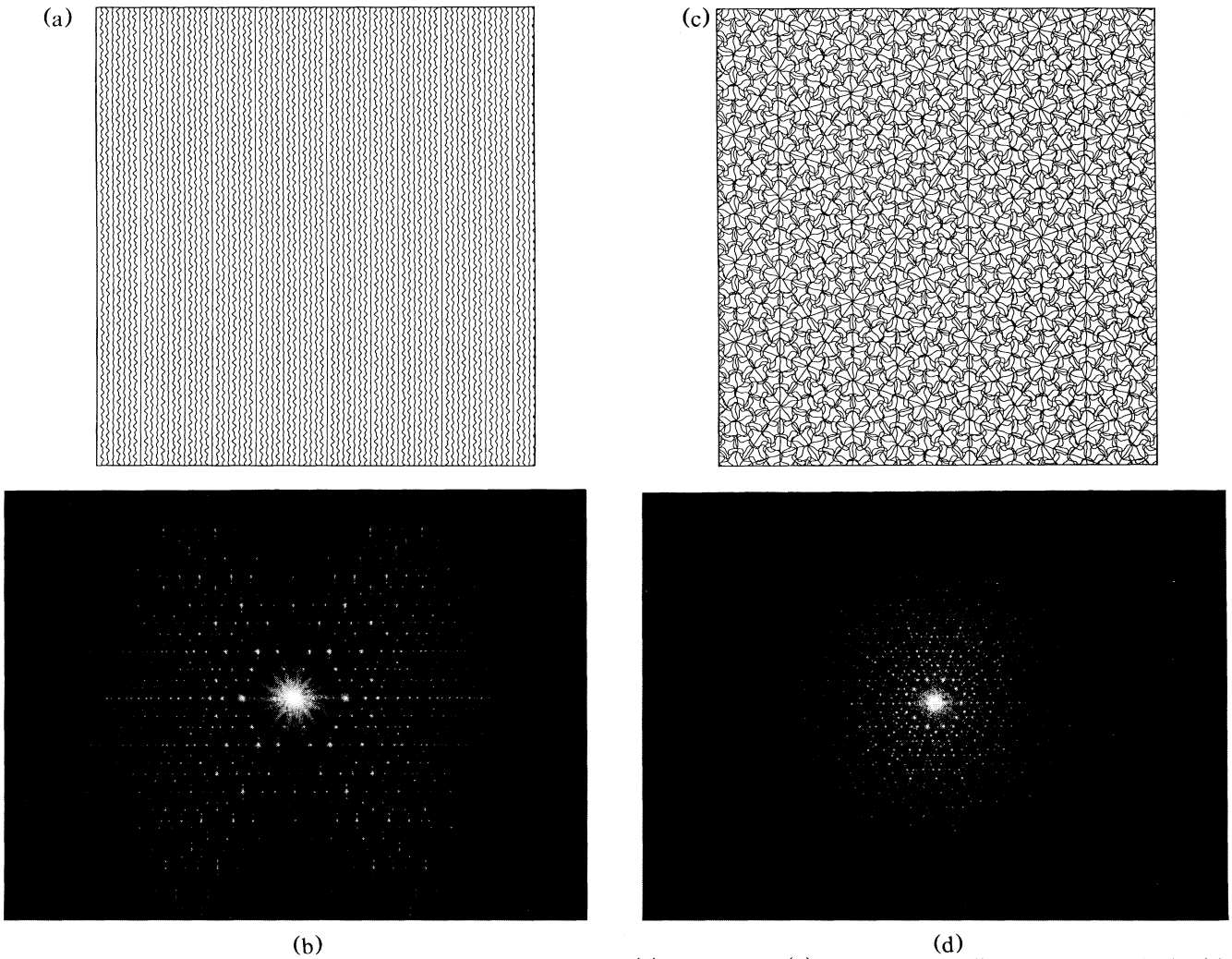

FIG. 2. (a) A polymer grating with displacements given by Eq. (4) with $Q = 5$. (b) Experimental diffraction pattern obtained by scattering laser light from the pattern in (a). The positions of the Bragg peaks in this pattern have fivefold symmetry as can be seen, for example, by local pentagonal patterns of spots. The intensities, however, have only twofold symmetry. (c) Polymer configurations obtained by superposing five patterns shown in (a) at relative angles $2\pi n/5$ with $n = 0, \ldots, 4$. (d) Experimental diffraction pattern for (c).

and another with $u_p(\mathbf{G}_{p-M})$ replaced by $u_{p+1}(\mathbf{G}_{p+M+1})$. As discussed above, the phase of $u_p(\mathbf{G}_{p'})$ is equal to $\phi_{p'}$ independent of p. Thus the phase of $H_{\rm int}^{P/Q}$ in Eq. (1) is $\gamma_p = \sum_{s=-M}^{M} \phi_{p+s}$. It can be shown that $H_{\rm int}^{P/Q}(p) \equiv (-1)^M \cos\gamma_p$ for $U(\mathbf{x}) > 0$ and that the lock-in energy is minimized when $\gamma_p = \gamma$ independent of p, with $\gamma = \pi$ for M even and $\gamma = 0$ for M odd. The angle γ is simply the sum of phases of the mass density waves associated with the vectors $\mathbf{G}_p$ that generate the lattice with Q-fold symmetry. The value of γ determines the local isomorphism class [5,8] of a quasicrystalline structure if Q is a prime. The lock-in energy $H_{\rm int}^{P/Q}$ is of order $Al^{-2}U(U/\epsilon l^3)^{\nu_Q}$, where $\nu_Q = 2 + (Q-1)^2/4$. When $U(\mathbf{x}) < 0$, $\gamma_{p+1} = \gamma_p + \pi$, $\cos\gamma_{p+1} = -\cos\gamma_p$, and higher-order terms are needed to establish a local isomorphism class.

What can be said about the phase diagram of our model, or more specifically about the curve $\tilde{\alpha}$ as a function of α? In equilibrium, there will be a finite region around each rational value of $\alpha = P/Q$ for which $\tilde{\alpha} = P/Q$. If $U/\epsilon l^3$ is sufficiently small, there will be transitions from these rotationally commensurate states to rotationally incommensurate states with $\tilde{\alpha}$ irrational, with the fraction of any interval in α for which $\tilde{\alpha}$ is rational less than 1; i.e., the curve $\tilde{\alpha}$ vs α will be a sort of incomplete devil's staircase [9]. Much of our insight into commensurate-incommensurate transitions is obtained from the discrete Frenkel-Kontorova (FK) model [10] in which these transitions are continuous and occur via the formation of a soliton lattice. In our model, the interactions favoring lock-in are extremely nonanalytic, contributing only when the angle between neighboring planes is a rational multiple of 2π. There are, therefore, no solitons of the sort that occur in the FK model, and we expect the C-I transition to be first order. We can estimate the width $\delta\alpha_{P/Q} = |\alpha - \alpha_{P/Q}|$, where $\alpha_{P/Q}$ is the value of α for which $\tilde{\alpha} = P/Q$, of the lock-in regions by comparing the lock-in energy with the strain energy in $H_\theta \sim (NLK/2) \times (2\pi\delta\alpha_{P/Q})^2$. The result is $\delta\alpha_{P/Q} \sim (\epsilon l^2/K)^{1/2}(U/\epsilon l^3)^{1+Q/2}$. A schematic representation of the curve $\tilde{\alpha}(\alpha)$ is shown in Fig. 1.

At finite temperature [11], fluctuations in u diverge logarithmically with L in the I phase but are bounded in the C phase. Nevertheless, one can calculate the difference ΔF in free energy between the C and I phases as a power series in T to obtain $\delta\alpha_{P/Q}(T)$. To leading order in T, $\delta\alpha_{P/Q}(T)$ remains nonzero for all P/Q. We expect this result to apply to real finite-temperature TGB phases. The width $\delta\alpha_{P/Q}(T)$ may, however, be unobservably small.

The patterns of wiggles and the x-ray intensities predicted by the above analysis are quite remarkable. If there is Q-fold rotational symmetry, then $u_{p,k}(w)$ will have Fourier components at all reciprocal-lattice vectors in a quasicrystalline lattice with that symmetry. For Q odd, the lowest-order contributions to $u_{p,k}(w)$ can be expressed as

$$u_{p,k}(w) = \sum_{s=1}^{M} \{u_s \cos[\mathbf{G}_s \cdot \mathbf{R}_{p,k}(w)] + (s \rightarrow -s)\}, \qquad (4)$$

where the coefficients u_s are proportional to $(U/\epsilon l^3)^s$. A similar expression applies to Q even. The polymer pattern for $Q = 5$ produced by Eq. (4) is shown in Fig. 2(a), and its associated optical transform (diffraction pattern), obtained by direct diffraction of laser light, in Fig. 2(b). The polymer density, and thus the scattering intensity, has Fourier components at every point in the fivefold reciprocal lattice generated by the vectors $\mathbf{G}_p$, $p = 0, \ldots, 4$. The polymer density, however, clearly does not have fivefold symmetry, and the intensities in the Bragg peaks only have twofold symmetry. The scattering intensity at $q_x = 0$ from the entire set of rotated planes does have fivefold symmetry as shown in Fig. 2(d). We have obtained similar patterns for sevenfold and ninefold symmetry.

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[a]Present address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan.

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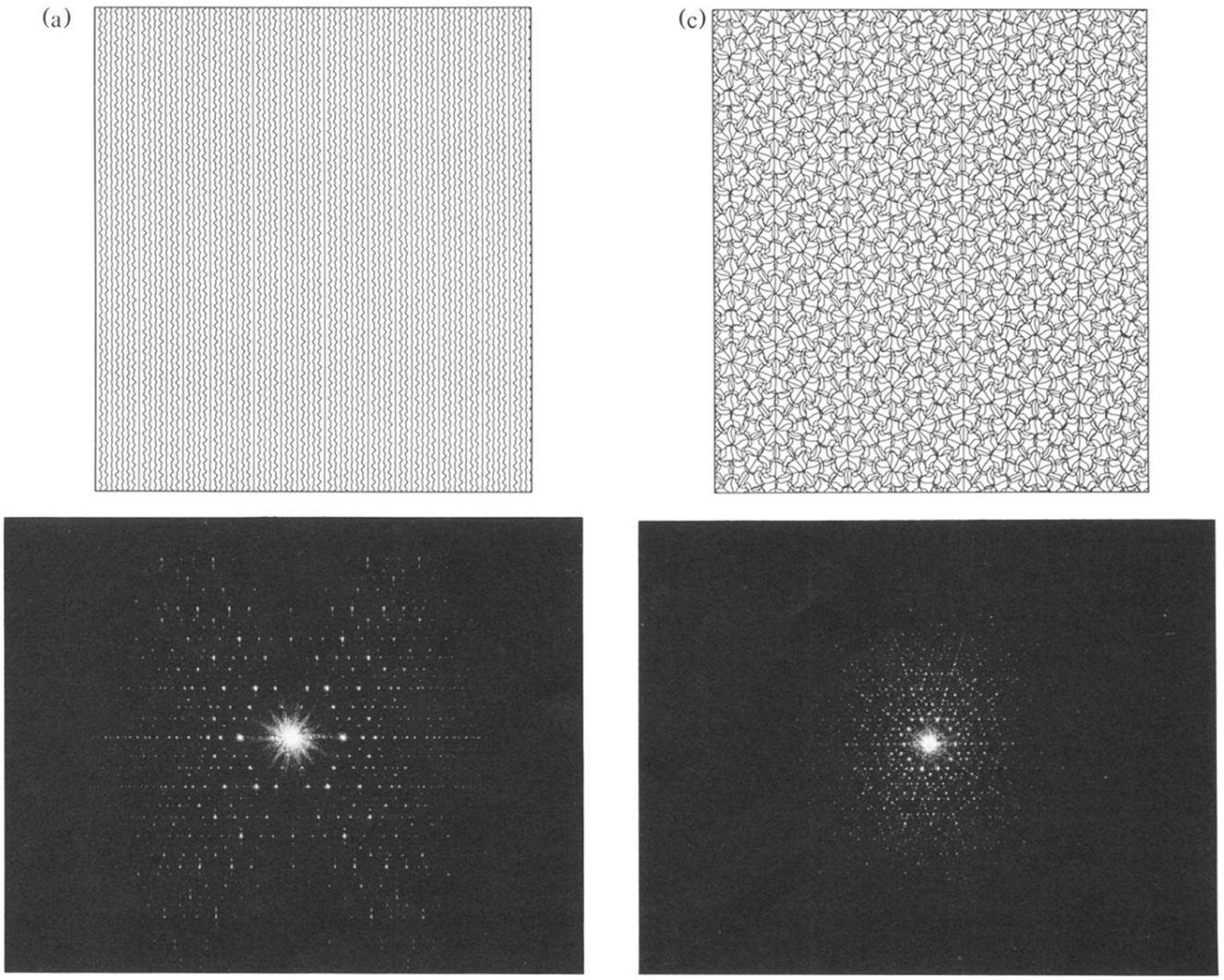

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