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INVITED ARTICLE

Twist penetration in single-layer smectic A discs of colloidal virus particles

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de Gennes first pointed out, in the 1970s, the geometric analogy between the layers of a smectic liquid crystal and the phase structure of the wave function of a superconductor. He showed that a layered structure expels twist deformations just as a superconductor expels a magnetic field, with twist penetrating only at the edges of a layer. We calculate how twist penetrates the edge of a small circular disc of a single isolated smectic A layer composed of chiral *fd* virus particles subjected to a depletion interaction. We find that under certain conditions small discs with a twisted edge are at least metastable, relative to large discs and other possible structures. We see samples in which such small discs appear to be stable for long periods of time.

Keywords: smectic; monolayer; twist; penetration

1. Introduction

In a smectic A liquid crystal system composed of layers of rod-like molecules, with the molecules oriented perpendicular to the layers, there are geometric constraints on the possible curvature deformations of the layers, which preserve the system of parallel layers of fixed thickness. In terms of a unit vector director field, $\hat{n}$, that is parallel to the local molecular alignment, the geometric constraints can be expressed as $\nabla \times \hat{n} = 0$. Even for a single smectic A layer, for which bend, $\hat{n} \times \nabla \times \hat{n}$, is undefined, the twist of the director, $\hat{n} \cdot \nabla \times \hat{n}$, is forbidden. In the first edition of *The Physics of Liquid Crystals*, de Gennes pointed this out (*1*). Describing the slowly varying deformation of an initially flat layer by a displacement function $u(x, y)$, for small tilts of the layer, $n_x = -\partial u/\partial x$ and $n_y = -\partial u/\partial y$. Then the twist of the director field, $t = (\partial n_y/\partial x - \partial n_x/\partial y) = -(\partial^2 u/\partial y \partial x - \partial^2 u/\partial x \partial y) = 0$.

However, as discussed in de Gennes's seminal paper of 1972, on the analogy between the smectic A phase and a superconductor, by allowing local tilting of $\hat{n}$ relative to the smectic layer normal by an angle θ, both twist and bend re-enter the structure locally, as spatial variations of the direction and magnitude of the tilt angle (*2*). This local tilting occurs with a cost to the free-energy density of $\frac{1}{2} C \sin^2(\theta)$, so it only occurs when there is a force driving it.

For a liquid crystal composed of chiral molecules, which are not superposable on their mirror image, the molecular packing tends to produce a twisted local structure as the lowest free-energy state. In the smectic A phase, this tendency is generally suppressed by the geometric constraints described above, but twist, and perhaps some accompanying bend, can penetrate at the edges of a layer, in the form of local molecular tilting, in analogy with magnetic flux penetration at the edge of a superconductor. For the systems studied here, experience has shown that the characteristic penetration length of twist at the layer edge, λ_t, is much longer than the intrinsic ordering coherence length scale of the smectic layer, so this system is analogous to a type II superconductor.

In this paper, as in previous work, we base our analysis on the study of single smectic layers, composed of chiral rod-like *fd* virus particles, which form when subjected to a depletion force in a solution of water-soluble polymer molecules (*3*). As the virus particles are 880 nm long, the twist penetration length is on an optical length scale, and we can observe the twist penetration structure in detail by optical microscopy. We observe these single layers as circular discs, with a band of twist around their edge. In the optical microscope, the molecular tilt at the edge of a disc makes the twist visible as a birefringent region, whereas in the absence of tilt the sample appears isotropic. We were able to compare theory with quantitative optical retardance data taken with the LC-PolScope (LC-PolScope, Cambridge Research and Instrumentation, Woburn, MA; http://www.cri-inc.com) (*4*, *5*), and extract the twist penetration length for this material. The twisting tendency is weak, so this system is analogous to a type II superconductor in a magnetic field below its lower critical

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field. In the previous paper, we focused our attention on the edges of large discs, for which an analytic expression for the twist profile is available. In this paper, we focus on the structure of small diameter discs, in which twist is accompanied by bend, due to the small radius of curvature of the disc edge. We analyse the energy of these discs, and find that under some circumstances there is a certain small radius that minimises the mean free-energy density of the disc, so that if discs could dynamically change their size, discs of this radius would be stable.

2. Theory

For this problem, we simplify the general form of the smectic A free energy presented by de Gennes in analogy with superconductors. First, since the smectic layer is flat, and only director tilt occurs, the smectic order parameter is simply a constant. We ignore any change in the order parameter very near the edge of the single smectic layer, in effect ignoring the possible existence of a small but finite coherence length, and focus only on the spatial variation of the director. In our previous paper we considered the twist penetration profile in a semi-infinite smectic layer and found that we could obtain good fits, using this analytic solution, to the experimental data for the tilt angle profile in discs of radii approximately 2 μm and larger (*3*). Here we carry out a theoretical analysis of the tilt angle profile and energetics of discs of finite radii R to assess their stability and gain an understanding of the range of validity of the semi-infinite approximation. We assume that the director tilts by an angle θ tangential to the edge of the disc and assume circular symmetry, so that the tilt angle θ is a function of the radial coordinate r only. The free energy is then given by

$$\begin{aligned} F &= \int_0^R \left[\frac{1}{2}K_2(\hat{n}\cdot\nabla\times\hat{n}-q)^2+\frac{1}{2}K_3(\hat{n}\times\nabla\times\hat{n})^2 + \frac{1}{2}C\sin^2(\theta)\right]2\pi r\,dr+2\pi\gamma R \\ &= \int_0^R\left[\frac{1}{2}K_2\left(\frac{\sin(2\theta)}{2r}+d\theta/dr-q\right)^2 + \frac{1}{2}K_3\left(\frac{\sin^4(\theta)}{r^2}\right)+\frac{1}{2}C\sin^2(\theta)\right]2\pi r\,dr+2\pi\gamma R. \end{aligned} \quad (1)$$

The K_2 and K_3 terms are the twist and bend energy densities, respectively. The term proportional to C is the tilt energy density and q is the spontaneous twist wave vector. The edge energy per unit length is denoted by γ. The Euler–Lagrange equation for this energy is given by

$$K_2\left[r^2d^2\theta/dr^2+r\,d\theta/dr-2qr\sin^2(\theta)-\frac{1}{2}\sin(2\theta)\cos(2\theta)\right] - K_3\sin^2(\theta)\sin(2\theta)-\frac{C}{2}r^2\sin(2\theta)=0 \quad (2)$$

We have solved this equation numerically using a finite element boundary value problem solver with boundary conditions:

$$\theta=0, \quad r=0, \quad (3)$$

$$\frac{d\theta}{dr}+\frac{\sin(2\theta)}{2r}=q, \quad r=R, \quad (4)$$

and have assumed that $K_2=K_3$. We use dimensionless units where we measure lengths in units of the twist penetration length $\lambda_t=(K_2/C)^{1/2}$ and γ in units of K_2/λ_t. Results for θ are shown in Figure 1(a)–(d) for several values of disc radii with $q\lambda_t=0.71$, a value derived from experiments reported in our previous paper (*3*). A comparison with the results of the semi-infinite geometry considered in (*3*) is also shown in the figure. We see that for disc radii $R\gtrsim 5\lambda_t$ the tilt profile is well fit by the semi-infinite result

$$\theta(x)=2\arctan[\tan(\theta_0/2)\exp(-x/\lambda_t)], \quad (5)$$

with $x=R-r$ and $\theta_0=-\arcsin(q\lambda_t)$

To assess the stability of finite-sized discs we have calculated the free energy per unit area relative to the uniformly untilted state ($\theta=0$ for all r):

$$\Delta f \equiv F/\pi R^2-\frac{1}{2}K_2q^2. \quad (6)$$

Stable discs correspond to the minimum value of Δf with $\Delta f\leq 0$, although this criterion does not rule out the possibility that the discs are only metastable, with other structures such as twisted ribbons having lower energy. In Figure 2 we plot the value of the radius of stable discs as a function of $\gamma^*\equiv\gamma\lambda_t/K_2$, the dimensionless edge energy per unit length, with $q\lambda_t=0.71$. Note that for sufficiently large γ finite-sized discs are no longer stable.

We have also explored the stability of finite-sized discs as a function of $q\lambda_t$ as shown in Figure 3. The phase boundary between finite-size and infinite discs is a line of continuous transitions, i.e. $R\to\infty$ as the phase boundary is approached from below. An equation for the phase boundary can be derived using the results for the semi-infinite case which is relevant here because the transition occurs at infinite radius.

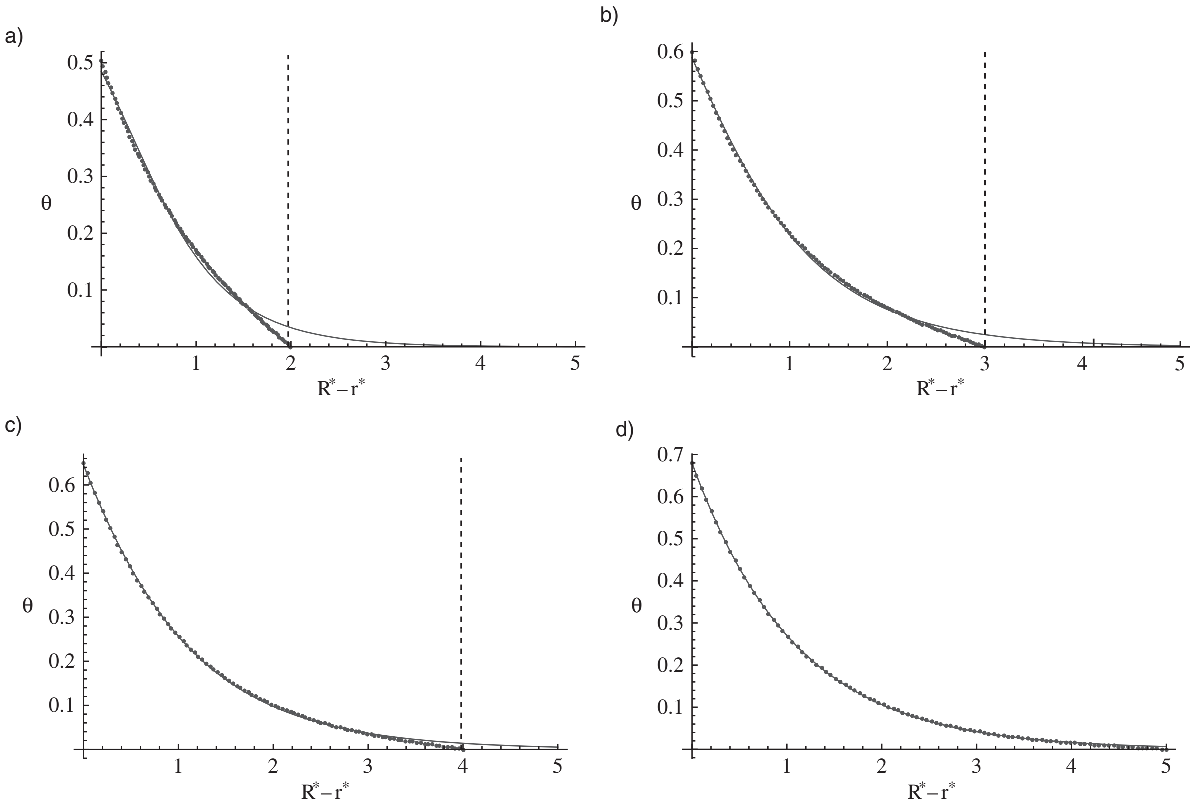

Figure 1. Plots of the tilt angle θ as a function of the shifted dimensionless radial coordinate $R^* - r^*$, where $R^* \equiv R/\lambda_t$, $r^* \equiv r/\lambda_t$ for discs of dimensionless radii: (a) $R^* = 2$; (b) $R^* = 3$; (c) $R^* = 4$; (d) $R^* = 5$; in all four cases $q\lambda_t = 0.71$. Using a shifted coordinate allows comparison of the data points obtained from the Euler–Lagrange equation (2), with the analytic semi-infinite solution (solid line) obtained from (5) with θ_0, the tilt angle at the edge, chosen to match the finite radius data in each case. The edge of the disc is located at the origin of the shifted coordinate. In (a)–(c) the vertical dashed line indicates the centre of the disc. Coordinate values to the right of this line do not correspond to points on the disc but provide an indication of how the semi-infinite tilt profile overshoots the boundary condition $\theta = 0$ at the centre of the disc for discs of radii $R^* \lesssim 5$.

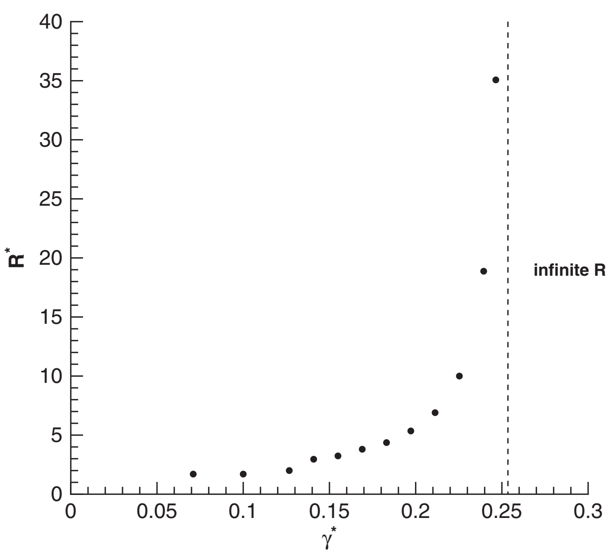

Figure 2. Plot of the radii of stable discs (measured in units of λ_t) as a function of the dimensionless edge energy per unit length $\gamma^* \equiv \gamma\lambda_t/K$ for $q\lambda_t = 0.71$. For $\gamma^* \gtrsim 0.25$ (the vertical dashed line) there are no stable discs of finite radius.

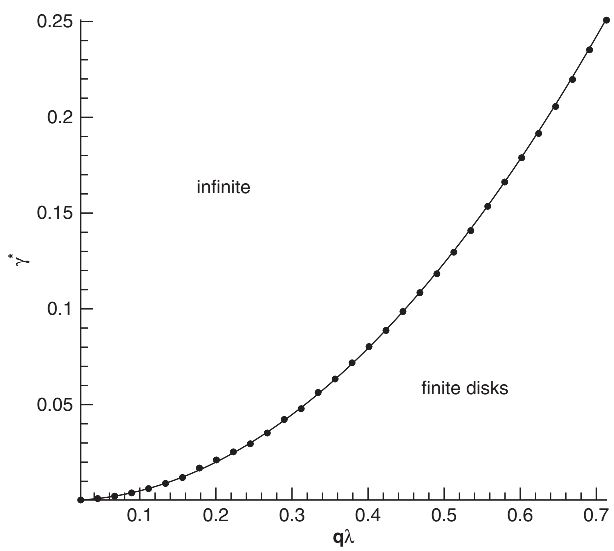

Figure 3. Plot of the phase boundary separating discs of finite and infinite radius. The data points are computed numerically, each point corresponding to the critical value of γ^* as obtained, e.g., in Figure 2 for $q\lambda_t = 0.71$. The solid curve is a power-law fit to the data with $\gamma^* \approx 0.49(q\lambda_t)^2$.

Evaluating Δf using the semi-infinite tilt profile (5) and setting $\Delta f = 0$ we find for the phase boundary

$$\gamma = K_2 q \sin^{-1}(q\lambda_t) - \frac{2K_2}{\lambda_t}\ln\left[\frac{2(1-\sqrt{1-(q\lambda_t)^2})}{(q\lambda_t)^2}\right] \approx \frac{1}{2}K_2\lambda_t q^2, \ q\lambda_t \ll 1. \quad (7)$$

In dimensionless units, the small q limit of this expression is given by $\gamma^* \approx \frac{1}{2}(q\lambda_t)^2$. As can be seen from the figure, the quadratic approximation fits the numerical data remarkably well.

3. Results and analysis

It is important to note that the twist penetration length is independent of the intrinsic twist wave vector q of a liquid crystalline material, depending only on the twist elastic constant K_2 and the value of the tilt energy parameter C. The prediction of the theoretical model is that the value of the parameter q only enters into determining the maximum tilt at the disc edge. In the semi-infinite smectic layer model, the value of q is given by $q = \sin(\theta_0)/\lambda_t$. For the curved edge of a finite diameter disc, the relationship between the maximum tilt angle and q is not so simple. In general, higher curvature leads to lower values of maximum tilt, as shown in Figure 1. To verify this experimentally, along with the detailed shape of the twist penetration profile, we need to analyse discs of different diameters quantitatively. This analysis will be published elsewhere.

We find that the penetration of twist at the edge of a disc effectively contributes a negative term to the overall edge energy. If the ordinary edge energy γ is small enough, then the net edge energy can become negative, and the energy of a disc is minimised by maximising the role of the edge, i.e. by breaking the membrane up into an array of small discs rather than keeping one large one. The value of γ is reduced by lowering the polymer concentration in the solution, since most of the edge energy is actually a property of the polymer solution, not of the disc itself, as is usual in a system controlled by the depletion interaction. Although we do not yet have a definitive experimental test of the relative stability of small discs, as samples are prepared with increasingly lower polymer concentration, we have a number of qualitative observations of samples containing many very small discs that appear to be stable. However, the annealing of the disc size by the transport of virus particles through the background polymer solution is a very slow process, so we cannot be sure that these small discs are actually in equilibrium. On the other hand, the dynamics of the initial formation of the discs, which we have not yet been able to observe microscopically, do apparently lead to the formation of many small discs under certain solution conditions, suggesting their stability, relative to large discs. This question remains the subject of further experimentation. At still lower polymer concentrations, with the net edge energy becoming increasingly negative, another structure in which edges dominate replaces discs; long twisted ribbons become the dominant structure observed. The study of these ribbons will be reported elsewhere.

In conclusion, de Gennes long ago presented a clear theoretical understanding of how twist is expelled from layered systems such as the smectic A phase, and of how, for a weakly chiral smectic A phase, twist penetrates only at sample edges. We are now able to confirm his insights with direct observations of twist penetration in a single smectic layer, and to measure the important twist penetration length in this system. We can also see how chirality frustrates long-range order, disfavouring large discs, and making small discs minimise the mean free-energy density. In the future we will explore the variation of the twisting strength in our materials, to examine the fascinating regime of strong chirality, in which twist penetrates our two-dimensional single-layer smectic samples as quantised π-twist-wall defects, in analogy with the flux-lattice phase of a type II superconductor, and with the twist grain boundary phase of three-dimensional smectics.

Acknowledgments

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