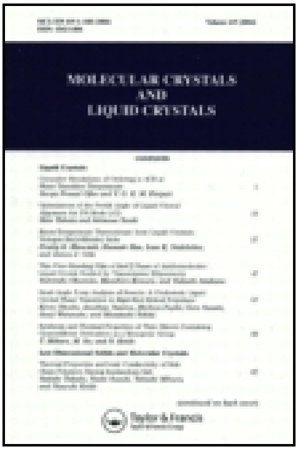

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Chiral Fluctuations and Structures

T. C. Lubensky [a] , Randall D. Kamien [a] & Holger Stark [a]
[a] Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA, 19104, USA

Version of record first published: 24 Sep 2006.

To cite this article: T. C. Lubensky , Randall D. Kamien & Holger Stark (1996): Chiral Fluctuations and Structures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 15-23

To link to this article: http://dx.doi.org/10.1080/10587259608034580

Mol. Cryst. Liq. Cryst., 1996, Vol. 288, pp. 15–23
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CHIRAL FLUCTUATIONS AND STRUCTURES

T.C.LUBENSKY, RANDALL D.KAMIEN AND HOLGER STARK
Department of Physics and Astronomy,University of Pennsylvania,Philadelphia, PA 19104, USA

Abstract Chiral molecules form a number of non-chiral structures, the simplest being an isotropic fluid phase. In a mesophase of achiral molecules the fluctuations will on an average be achiral as well: left-handed twists and right-handed twists will occur with the same probability. In a system composed of chiral molecules, however, the fluctuations will be biased in one direction or the other, and there will be optical effects such as a non-zero fluctuation induced rotary power in addition to the molecular rotary power of the individual molecules. We discuss this effect in a number of contexts, including lyotropic lamellar phases. When the tendency to twist is strong enough or the line energy of having an exposed edge is small enough,a new, defect riddled ground state of a lyotropic lamella, akin to the Renn-Lubensky twist-grain-boundary phase of thermotropic smectics, can occur.

INTRODUCTION

Since the discovery of rotary power by Biot in the early 19^{th} century, we have expanded our understanding of the form and function of chiral molecules with almost reckless abandon. The microscopic origin of macroscopic chiral structures is still not very well understood. Chiral molecules have no reflection planes as shown in Figure 1. We also show achiral molecules from which chiral molecules can be formed by chemical changes. A fundamental feature of all chiral molecules is that they are three dimensional: a planar molecule is invariant with respect to reflections through the plane in which it lies. The loss of reflection symmetry causes energetic and entropic preference for axes of neighboring molecules to rotate relative to each other. This leads to a new length scale (the inverse of the rotation angle per unit distance) normally much larger than any molecular length and to a spectacular array of equilibrium spatially modulated chiral phases, including the cholesteric (or chiral nematic N^*) phase, the blue phases, the TGB phases, and the smectic-C^* phase. These equilibrium phases, like the molecules of which they are comprised, have no reflection planes.

Chiral molecules can also form phases which do not exhibit macroscopic chiral order, *i.e.*, phases that do have reflection planes. Examples of non-chiral phases composed of chiral molecules are the isotropic phase and the smectic-A phase. Even though the structure of these phases is achiral, they nevertheless exhibit chiral properties if they are composed of chiral molecules. In particular, there will chiral fluctuations, the most familiar manifestation of which is optical rotary power of a precholesteric isotropic phase of chiral nematogens.[1] Of course the individual molecules have a non-zero rotary power (*e.g.* a solution of sugar molecules rotates light) as well. Since the optical chirality of the molecules need *not* be the same as the chirality of the resulting mesophase, the chiral fluctuations can lead to either a reduction or enhancement of the rotary power over that of a very dilute solution.

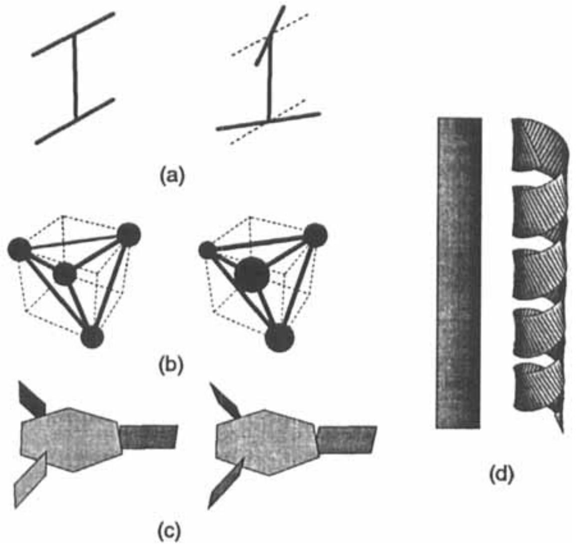

FIGURE 1: This figure shows a series of achiral molecules and the chiral molecules they become after an appropriate transformation. (a) left, a planar achiral H-shaped molecule; right a chiral molecule obtained by rotating one leg of the H relative to the other through an angle between 0 and $\pi/2$. (b)left: a tetrahedral molecule like CH_4 with identical molecules at all four vertices; right a chiral molecule with different atoms at each vertex. (c) left: an achiral discotic molecule with three propeller blades; right: a chiral discotic molecule obtained from the molecule at the right rotating through an angle between 0 and $\pi/2$. (d) left: a planar "strip" molecule; right: a chiral helical ribbon obtained by wrapping the strip at the right around a cylinder. This is a model for DNA.

This talk will explore possible new structures produced by chirality and fluctuations in achiral phases of chiral molecules.

CHIRAL FLUCTUATIONS IN ACHIRAL PHASES

The isotropic and smectic-A phases are achiral liquid crystal mesophases that can be, nonetheless, composed of chiral molecules. Residual chiral fluctuations can lead, however, to optical rotary power. Other achiral states exist at isolated points of the phase diagram of smectic-C^* phases and cholesterics. Some of these mesophases have the remarkable property of twist inversion,[2] where the mesoscopic pitch changes sign without a concomitant microscopic change in the molecular structure.

The Smectic-A Phase

The smectic-A phase, like the isotropic phase, has an achiral structure. Its periodic layering expels molecular twist.[3] Thus, chiral molecules can and often do form an achiral smectic-A phase. Around the achiral ground state there will be chiral fluctuations. To study these fluctuations, we use the low-temperature elastic free energy of a smectic, expressed in terms of the layer displacement variable u and the Frank director $\mathbf{n}=\mathbf{n}_0+\delta\mathbf{n}$ with $\mathbf{n}_0=\hat{\mathbf{z}}$:

$$F = F_u + F_n + F_{Ch}, \tag{1}$$

where

$$F_u = \frac{1}{2}\int d^3x[B(\nabla_{\|}u)^2 + D(\nabla_{\perp}u + \delta\mathbf{n})^2] \tag{2}$$

is the strain energy,

$$F_n = \frac{1}{2}\int d^3x\{K_1(\nabla\cdot\mathbf{n})^2 + K_2[\mathbf{n}\cdot(\nabla\times\mathbf{n})]^2 + K_3[\mathbf{n}\times(\nabla\times\mathbf{n})]^2\} \tag{3}$$

is the Frank free energy, and

$$F_{Ch} = K_2 k_0 \int d^3x\mathbf{n}\cdot(\nabla\times\mathbf{n}) \tag{4}$$

is the chiral energy. In the last equation $k_0=2\pi/P$, where P is the cholesteric pitch.

From this free energy, we can calculate the correlation function of the displacement and director fields. We find in the special case that $B = D$ and $K = K_1 = K_2 = K_3$ (with $q^2 = q_\perp^2 = q_z^2$) [4]

$$G_{\delta n_i \delta n_j}(q_\perp, q_z) = k_B T \frac{(B + Kq^2)q^2\delta_{ij} - iKk_0 q_z q^2 \epsilon_{ij}}{(B + Kq^2)^2 q^2 - K^2 k_0^2 q_z^2 q^2 - B(B + Kq^2)q_\perp^2} \tag{5}$$

The terms linear in k_0 represent chiral fluctuations since they multiply the two-dimensional antisymmetric tensor. It should be possible to measure these quantities via light scattering and to distinguish between a smectic composed of chiral molecules and one that is not.

The chiral director fluctuations are nearly frozen out: they are only correlated on the scale of the twist penetration depth $\lambda = \sqrt{K/B}$. Nevertheless, these short range correlations lead to a fluctuation induced rotary power, which for light travelling along the z direction is

$$R = \lambda k_0 \left[\frac{\omega}{c}\right]^2 \frac{k_B T}{48\pi K} \frac{(\epsilon_\perp - \epsilon_\parallel)^2}{\epsilon_\perp} \frac{radians}{cm} \tag{6}$$

where ω is the frequency of the polarized light beam, c is the speed of light in vacuum and $\epsilon_\perp$ and $\epsilon_\parallel$ are the perpendicular and parallel dielectric constants of the mesogens. Putting in typical numbers we get rotations between 5×10^{-2} and 0.5 *radians/cm* deep in the smectic phase. As the smectic phase melts and forms a cholesteric, $B \to 0$ and thus the rotary power will grow as $1/\sqrt{B}$. At the transition the fluctuation induced rotary power will grow larger than the molecular rotary power (roughly 10^{-1}*radians/cm*). This effect could also be quite large in colloidal liquid crystals which have penetration depths on the order of microns.

Compensated Cholesterics

There are a number of molecules[5] whose cholesteric phases exhibit the phenomenon of twist inversion. Their pitch wavenumber k_0 passes through zero and changes sign as a function of temperature or other external parameters. At the point where $k_0=0$, the pitch is ∞, and the resultant "cholesteric" phase has the same macroscopic symmetry as an achiral nematic. The molecules, however, are still chiral, and this nematic phase will exhibit chiral fluctuations not present in the achiral nematic phase. The microscopic origin of twist inversion is not totally understood. Any microscopic mechanism will, however, eventually lead to a phenomenological free energy for the director $\mathbf{n}$ and some other variable whose variation can lead to a vanishing of k_0. A simple model for a cholesteric that displays twist inversion can be constructed from $\mathbf{n}$ and S, the Maier-Saupe order parameter, which measures the magnitude of the nematic order parameter:

$$F = F_n + \int d^3x f(S) - \int d^3x (aS^2 - bS^4)\mathbf{n}\cdot(\nabla\times\mathbf{n}), \tag{7}$$

where $f(S)$ is a free energy density depending only on S. Compensation occurs when the coefficient of $\mathbf{n}\cdot(\nabla\times\mathbf{n})$ is zero, i.e., when $S^2=a/b$. Near this point, we can write $S = (\mathrm{a/b})^{1/2} + \delta S$ and

$$F = F_n + F_0 + \frac{1}{2}\int d^3x A(\delta S)^2 - \alpha \int d^3x \delta S \mathbf{n}\cdot(\nabla \times \mathbf{n}), \tag{8}$$

where $A = f''(\sqrt{a/b})$ and $\alpha{=}2a^2/b$.

While there will be, on an average, no net chiral fluctuations in the director, there is still a fundamental asymmetry. Fluctuations with one handedness (or one sign of $\mathbf{n}\cdot(\nabla \times \mathbf{n})$) are coupled to a decrease in S while fluctuations of the other handedness go with an increase of S. Since fluctuations in both S and n contribute to fluctuations in the dielectric tensor, the chiral terms in the above correlation functions will lead to a nonzero fluctuation-induced rotary power of a compensated cholesteric.

Compensated Smectic-C^* Phases

The chiral smectic-C^* phase, like the cholestetic phase can exhibit twist inversion. A simple model free energy producing this phenomenon can be constructed from the magnitude and phase of the **c**-director: $\mathbf{c}{=}c(\cos\theta,\sin\theta,0)$:

$$F = \int d^3x \frac{1}{2} K(\nabla\theta)^2 - \int d^3x (ac^2 - bc^4)\nabla_z\theta + \int d^3x f(c), \tag{9}$$

where $f(c)$ is a free energy density. The chiral wavenumber is zero when $c^2{=}a/b$. Expanding about this point, we obtain

$$F = \frac{1}{2}\int d^3x \{A(\delta c)^2 + K(\nabla\theta)^2 - 2\sqrt{a^3/b}\,\delta c \nabla_z\theta\}, \tag{10}$$

This leads to

$$G_{ab} = \frac{1}{AKq^2 - (a^3/b)q_z^2}\begin{pmatrix} Kq^2 & i\sqrt{a^3/b}q_z \\ -i\sqrt{a^3/b}q_z & A \end{pmatrix} \tag{11}$$

The rotary power will again scale as

$$R \sim \lambda\sqrt{\frac{a^3}{b}}\left[\frac{\omega}{c}\right]^2 \frac{(\epsilon_\perp - \epsilon_\parallel)^2}{2\epsilon_\perp + \epsilon_\parallel} \tag{12}$$

Equation (9) is the simplest model free energy for a compensated smectic-C^* phase. It can be made more realistic and considerably more complicated by including such things as the anisotropy of the Frank elastic constants and the couplings to the electric dipole moment, which is always present in chiral ferroelectric liquid crystals.

The chiral term proportional to $\nabla_z\theta$ arises from a $\mathbf{c}\cdot(\nabla \times \mathbf{c})$ term in the free energy. There are also other chiral terms such as $\mathbf{N}\cdot(\nabla \times \mathbf{c})$. The latter term is present in $2D$ films whereas the former is not. It is responsible for two-dimensionally modulated structures in smectic-C films.[6,7] In three-dimensional smectic-C^* phases, the $\mathbf{c} \cdot (\nabla \times \mathbf{c}) \sim \nabla_z \theta$ term is dominant, and the second term can often be ignored. When, however, the coefficient of $\nabla_z \theta$ is small or zero, the other term becomes important and can lead to interesting two-dimensional structures similar to those predicted for films and to slowly rotating versions of these structures. Indeed such structures have recently been observed.[8]

CHIRAL MEMBRANES AND LYOTROPIC PHASES

Membrane Model and Chiral Fluctuations

Aliphatic molecules with polar heads and oily tails form membranes to protect the oily tails from contact with water. DMPC is a chiral molecule that can form a variety of lamellar and vesicular structures. In the fluid, or L_α, phase of these membranes, the molecular axes, aligned along a unit director $\mathbf{n}$, are parallel to the local membrane normal $\mathbf{N}$, and there is no macroscopic manifestation of chirality. Indeed, if $\mathbf{n}$ is *constrained to be parallel to* $\mathbf{N}$, the phenomenological energy describing a membrane with chiral molecules is identical to that[9] describing a membrane with achiral molecules. This is because the curl of a vector normal to a surface is always zero. When $\mathbf{n}$ tilts relative to $\mathbf{N}$, as it does in the $L_{\beta'}$ phases, there is a component of $\mathbf{n}$ in the membrane's tangent plane, and there are chiral surface terms that have been discussed extensively.[7,10] The L_α phase of a membrane is similar to the smectic-A phase of a thermotropic liquid crystal: it expels twist, but it does not destroy the underlying forces tending to produce twist. There are chiral fluctuations in the L_α phase produced by fluctuations of the director into the tangent plane. To describe these fluctuations, we treat the molecular director and the membrane shape as independent parameters. Then the phenomenological free energy for a membrane can be written as

$$F = F_h + F_n + F_{Ch} + F_c, \tag{13}$$

where

$$F_h = \frac{1}{2}k \int dS \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 = \frac{1}{2}k \int dS (\nabla \cdot \mathbf{N})^2 \tag{14}$$

is the Helfrich-Canham energy[9] for an isolated membrane,

$$F_c = -\gamma \int dS (\mathbf{n} \cdot \mathbf{N})^2 \tag{15}$$

favors **n** parallel to **N**, and F_n and F_{Ch} are, respectively, the membrane versions of the Frank director free energy and the chiral free energy:

$$F_n = \frac{1}{2}\int dS\{K_1(\nabla_\perp \cdot \mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla_\perp \times \mathbf{n})^2 + K_3[\mathbf{n}\times(\nabla_\perp \times \mathbf{n})]^2\} \tag{16}$$

and

$$F_{Ch} = K_2 k_0 \int dS \mathbf{n}\cdot(\nabla_\perp \times \mathbf{n}), \tag{17}$$

where $\nabla_{\perp,i}=(\delta_{ij} - N_i N_j)\nabla_j$ is the gradient restricted to the tangent plane. Note that if γ is large locking **n** parallel to **N**, then the effective Helfrich bending rigidity is $\kappa + K_1$. In the Monge gauge, we specify points on a membrane by their height $h(\mathbf{x})$ above a two-dimensional plane with coordinates **x**. Then to linear order in h, we have $\mathbf{N}=(-\nabla_\perp h, 1)$, and

$$\begin{aligned} F = \frac{1}{2}\int d^2x\{\kappa(\nabla_\perp^2 h)^2 + K_1(\nabla_\perp \cdot \delta\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla_\perp \times \delta\mathbf{n})^2 + [\mathbf{n}\times(\nabla_\perp \times \mathbf{n})]^2\} \\ + \frac{1}{2}\gamma\int d^2x(\nabla_\perp h + \delta\mathbf{n})^2 + K_2 k_0 \int d^2x(\nabla_\perp \times \delta\mathbf{n})_z \end{aligned} \tag{18}$$

This free energy yields chiral fluctuations similar to those of the smectic-A free energy of (5).

Since there are fluctuations in lamellae that contribute to the rotary power, it is reasonable to believe that an isotropic vesicular phase will have a fluctuation rotary power as well. Since each vesicle will undergo chiral fluctuations, the rotary power should, again, be greater than the sum of microscopic contributions from individual molecules. It would be interesting to study the rotary power of chiral amphiphiles as a function of their concentration. The lamellar L_α will have a chiral fluctuation and a rotary power similar in form to those of a thermotropic smectic-A phase. While it is typically believed that there is no in-plane order in lyotropic phases, the chiral fluctuations may still lead to static chiral interactions which cause a tendency for cholesteric-like twisting between neighboring ellipsoidal vesicles.

Lyotropic Cholesteric Phase

In the L_α phase, membranes allow no average molecular twist if they form only closed surfaces or lamellae extending from one end of the sample to the other. The only way to introduce twist into the membrane is to tear it: it is possible to gain twist energy at the expense of edge energy in configurations that have the form of a lamellar screw dislocation. By adding a cosurfactant, such as alcohol, the line energy will be reduced. Then, as in the analysis of all defect phases, there will be a trade-off between the energy of destroying the integrity of the membrane and allowing chirality into it. As shown in Figure 2, the core of the dislocation is a tube filled with water, wrapped helically by the edges of lamellar planes. The molecular director exhibits a double twist configuration near the core that has negative chiral energy.

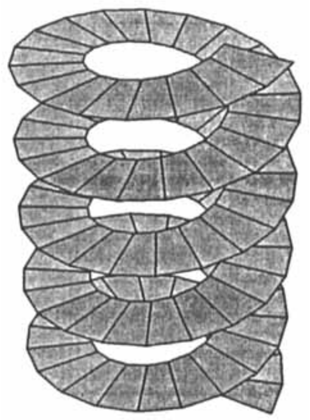

FIGURE 2: This figure shows the structure of a chiral, screw dislocation type defect in a lyotropic phase. Note that the center of the defect is filled with the solvent and there are exposed edges around the center tube.

Using (18) and the usual methods to calculate the strain field of a dislocation, one can show that the energy per turn of a membrane with a single screw dislocation with pitch P and height profile $h(x,y) = (P/2\pi)\tan^{-1}(y/x)$ is

$$E = \gamma \frac{P^2}{2\pi} ln(\lambda/\xi) - \mid K_2 k_0 \mid P + \tau P, \tag{19}$$

where ξ is the core radius, $\lambda = (K_2/\gamma)^{1/2}$ is the membrane twist penetration depth, and τ is the line tension of the exposed edge. Thus, if $\mid K_2 k_0 \mid - \tau$ is sufficiently large, it is energetically favorable for a membrane to create a screw dislocation with an exposed edge rather than to maintain only flat or closed structures.

In a lamellar phase, the pitch P is identical to the layer spacing, which is set by a balance between a negative membrane-water surface tension and either Helfrich entropic or by electrostatic forces. Then, the energy per unit length $\epsilon -$ E/P is identical to the energy per unit length of a dislocation in a thermotropic smectic with τ playing the role of the core energy. As in thermotropic smectics, when ϵ becomes negative, it becomes favorable for screw dislocations to penetrate the lamellar phase and to create a lamellar TGB phase. Local thermal fluctuations in dilute lamellar phases are more violent than they are in thermotropic phases, and one might expect the lamellar TGB phase to be more susceptible to thermal melting than its thermotropic cousin.[11] A melted TGB phase is a chiral line liquid that is indistinguishable from a cholesteric phase.[12] We can thus speculate that there should exist a lyotropic cholesteric phase composed of a melted lattice of twist grain-boundaries and possessing local lamellar ordering similar to that of the lamellar smectic-A phase.

ACKNOWLEDGEMENTS

It is pleasure to acknowledge stimulating discussions with R.Meyer, S.Milner, P.Nelson, T.Powers, J.Prost, D.Roux, C.Safinya and especially D.Walba, who brought these problems to our attention. This work was supported by NSF Grants DMR94-23114 and DMR91-22645.

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