

Something New Emerging: Tetrahedric Order

Patricia E. CLADIS^{*)}

Cladis Foundation, POB 162, Summit, NJ 07902-0162, USA

Nematic order conserves parity while tetrahedric order does not. We found that parity conservation allows free energy gradient terms in uniaxial quadrupolar (Q_{ij}) and tetrahedral (T_{ijk}) order parameters to couple at lower order than spatially homogenous ones thereby accounting for the spontaneous appearance of traveling birefringent objects with a length scale in achiral (no preferred sense of rotation) banana liquid crystals. Here we present one of our first solutions, the twisty wrap, using a braid construction to highlights its topology. In the twisty wrap, one of the fields rotates with one hand, right hand say, while the other field rotates with the other hand, left hand, say, leading to an over all structure with no hand. This analysis implies that the observed isotropic liquid is tetrahedric, T_d , an isotropic non-parity conserving liquid rather than $O(3)$, the usual isotropic liquid. A non-parity conserving liquid in contact with a parity conserving anisotropic entity could account for why the anisotropic entities always travel in the banana liquid crystal phase known as $B7$.

Up until about 5 years ago, the only way we knew how to get a length scale in nematic liquid crystals was to take away all its mirrors. That is, couple the nematic order parameter, Q_{ij} belonging to the symmetry group $D_{\infty h}$ to the symmetry group $SO(3)$, the group with no mirrors, to get a cholesteric liquid crystal (Fig. 1).

Cholesteric liquid crystals are in the group D_{∞} and have a length scale, a helical pitch. The helical pitch has a rotation sense. There are right handed cholesterics

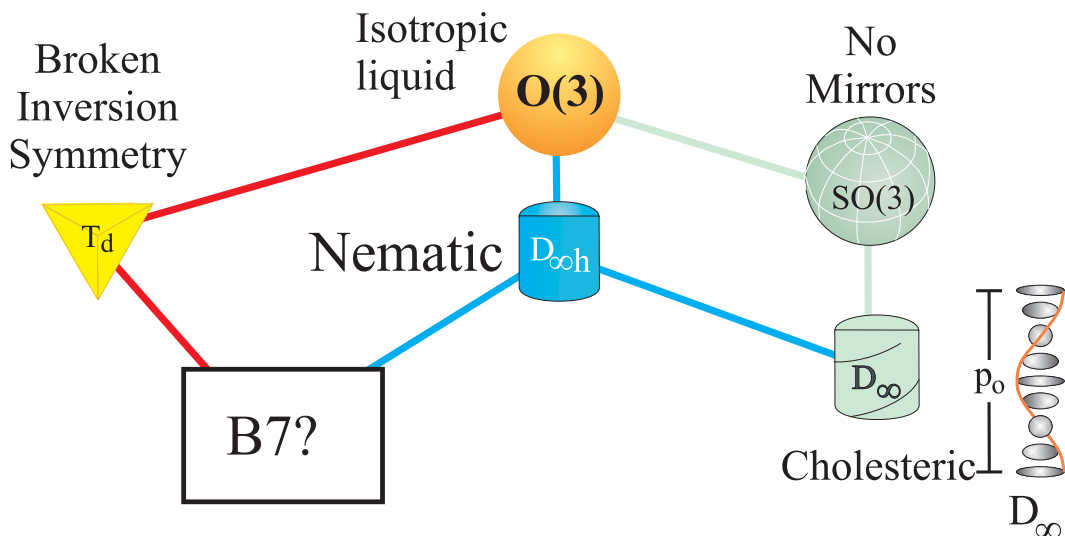


Fig. 1. Cholesteric liquid crystals with a length scale arise when $D_{\infty h}$ couples to $SO(3)$, the group with no mirrors. Length scales can also arise by coupling tetrahedric octupolar order with broken inversion symmetry to gradients in the parity conserving nematic quadrupolar order.

^{*)} E-mail: cladis.research@gmail.com

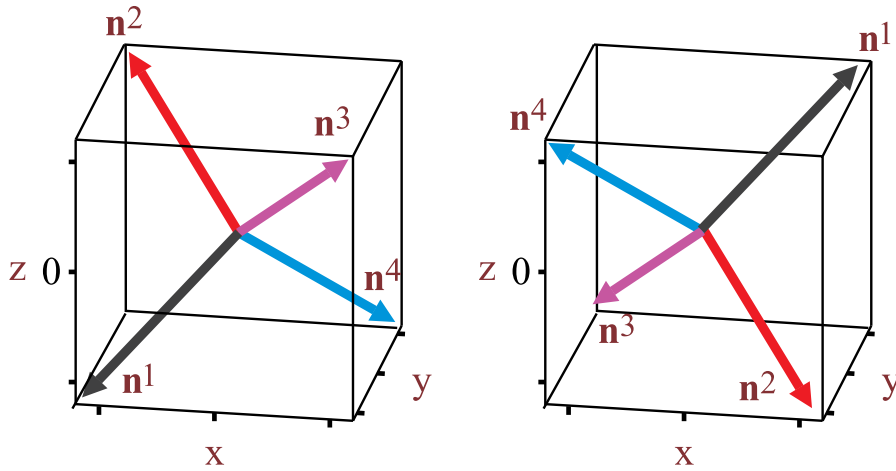


Fig. 2. Tetrahedra have broken inversion symmetry. Two tetrahedra of opposite parity inside a cube.

and left handed cholesterics. Without mirrors, only one hand can exist at a time. Fig. 1.

How is it then that achiral banana liquid crystals^{1),2)} have a length scale³⁾⁻⁵⁾?

We found that coupling the gradient of Q_{ij} , written as $Q_{ij,k}$, which does not conserve parity, to the tetrahedric order parameter, T_{ijk} which also does not conserve parity, Fig. 2, gave rise to a length scale.^{6),7)} The first structure we found was a nematic rotating in one sense with a regular tetrahedron rotating in the opposite sense. The combined construction $Q_{ij,k}T_{ijk}$ conserves parity, has a lower energy than the uniform state and is not chiral.⁶⁾

The topology of this solution is shown using the braid construction as $Q_{ij,k}$ wrapping around the rotating T_{ijk} 's. Indeed, Fig. 3 shows such an object observed in the polarizing microscope of one of the time dependent but long lived anisotropic objects traveling in an isotropic liquid in Weissflog's $B7$ phase in an achiral banana liquid crystal.⁵⁾

We need the braid construction because tetrahedra are 3-dimensional objects and braids are a neat way to highlight their topology enabling contact with observations. The tetrahedron has 4 vertices, call them, 1, 2, 3 and 4. Call the director strand 0. Associate a strand of the braid for each vertex of the tetrahedron and one for the director. Then order the strands in descending values of the x -coordinates given in the graphs. If two strands have the same x -value, order their y -coordinates in descending value. Then draw how the strands connect from graph to graph. There is one rule: for strands going towards positive \hat{z} , less positive x are on top of the more positive x strand(s) they cross and underneath for more positive to less positive. In Fig. 4, strand zero wraps around the outside of the counter-rotating tetrahedron bundle. As mentioned above, Fig. 3 is a snapshot of just such an object observed in Weissflog's $B7$ phase.⁵⁾

The twisty wrap has the following characteristics. It's localized and travels. As long as at least one of its ends can travel, the twisty wrap can get to be quite

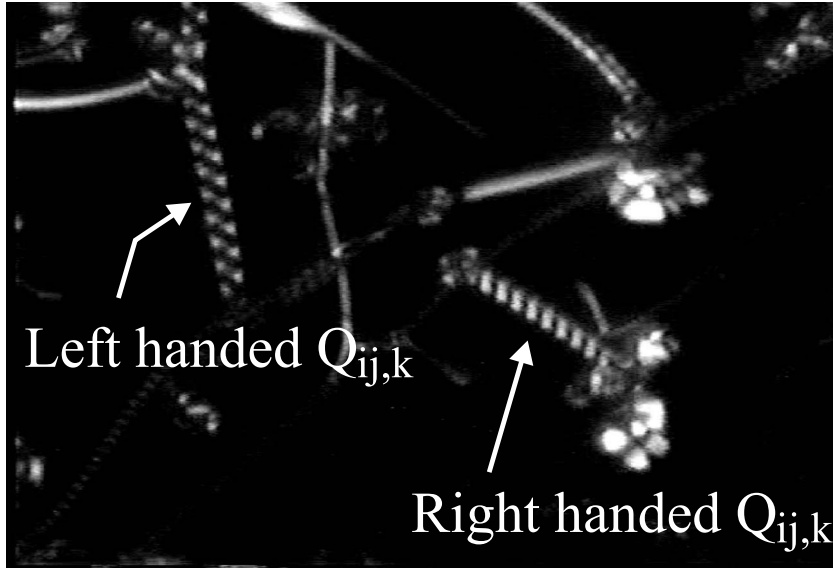


Fig. 3. Left and right handed twisty wraps where the nematic director wraps an isotropic tetrahedric bundle. The nearly transparent bundle for the left handed twisty wrap shows just one wrapping strand, strand 0.

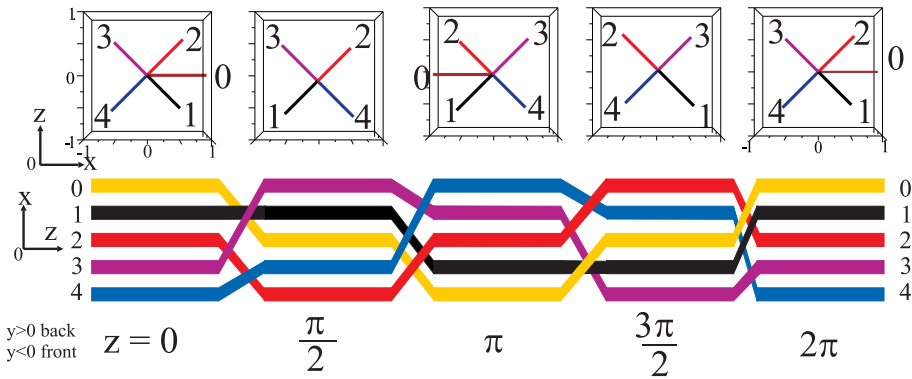


Fig. 4. Top are the graphs for the braid (bottom) including strand 0 for $Q_{ij,k}$, the nematic director, $\mathbf{n} = (\cos(z), \sin(z), 0)$. Strand 0 twists with a right handed sense around the left handed twisting bundle of tetrahedron vertices, 1, 2, 3 and 4. Strand 0 is under the bundle for $0 \leq z \leq \pi$ and on top of the bundle for $\pi \leq z \leq 2\pi$. Strands 2,3 rotate together as do strands 1,4.

long. When it slows down, the twisty wrap becomes a long wave length undulating twisty wrap that can locally coil up into a super-twisty wrap that grows with renewed vigor into available isotropic liquid space. Our theory does not predict this. A better understanding of braid topology will be important to address instabilities in *B7*.

We used a similar analysis to account for another birefringent object, a myelin pattern known as a biaxial Bouligand arceau that was also observed in Weissflog's *B7* phase⁷⁾ and gave it a braid representation.⁸⁾ The conclusion is that our coupling analysis is robust and has applications in the mysterious *B7* phase of Weissflog. Its topological implications can be elucidated with braids.

What is this mysterious *B7* phase? The answer to that is still under construction. What we can say is that it has a complicated x-ray pattern, is stable and always has isotropic liquid co-existing with traveling anisotropic objects even as much as 20–30K away from a transition temperature to an $O(3)$ isotropic liquid.⁹⁾ Currently we think of the isotropic liquid in *B7* as a tetrahedric liquid. A homogeneous broken parity liquid would explain why the observed less energetic parity conserving anisotropic objects must travel to survive. When they slow down, they die. They never take over even though they are less energetic than uniform states.

Tetrahedral, or octupolar order was introduced to liquid crystals by Fel.¹⁰⁾ While tetrahedral order has long been of interest to chemists, mathematicians, computer scientists, cryptographers as well as artists such as da Vinci and Escher, its importance to banana liquid crystals is only now emerging.⁸⁾ With recent advances in the synthesis of banana liquid crystals,¹¹⁾ we now have a means to check theories of novel mechanisms for anisotropy to emerge from isotropy. Indeed, coupling an isotropic liquid with broken inversion symmetry to a liquid with orientational order impacts descriptions of natural phenomena at length scales ranging from microscopic to cosmological. Closer to home, we can think of the recent conjecture¹²⁾ that such a coupling could be a way to understand long lived transient micro-ordered states in glass-forming systems. Tetrahedral order may even improve our understanding of the interplay between frozen-in orientational order in liquid crystalline elastomers and orientational order in low molecular weight liquid crystals.¹³⁾

Acknowledgements

I thank Professor Shoichi Kai, Kyushu University for supporting my participation in this International Symposium.

References

- 1) H. R. Brand, P. E. Cladis and H. Pleiner, *Macromolecules* **25** (1992), 7223.
- 2) H. R. Brand, P. E. Cladis and H. Pleiner, *Eur. Phys. J. B* **6** (1998), 347.
- 3) T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.* **6** (1996), 1231.
- 4) T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi and H. Takezoe, *J. Mater. Chem.* **7** (1997), 1307.
- 5) G. Pelzl, S. Diele and W. Weissflog, *Adv. Mat.* **11** (1999), 707.
- 6) H. R. Brand, H. Pleiner and P. E. Cladis, *Physica A* **351** (2005), 189.
- 7) H. Pleiner, P. E. Cladis and H. R. Brand, *Eur. Phys. J. E* **20** (2006), 257.
- 8) P. E. Cladis, *C. R. Chimie.* **11** (2008), 207.
- 9) Y. Yusuf, Y. Hidaka, S. Kai, H. R. Brand, P. E. Cladis, W. Weissflog and G. Pelzl, *Ferroelectrics* **276** (2002), 171.
- 10) L. G. Fel, *Phys. Rev. E* **52** (1995), 702; *Phys. Rev. E* **52** (1995), 2692.
- 11) R. A. Reddy and C. Tschierske, *J. Mater. Chem.* **16** (2006), 907.
- 12) H. R. Brand and K. Kawasaki, *Physica A* **324** (2003), 484.
- 13) D.-U. Cho, Y. Yusuf, P. E. Cladis, H. R. Brand, H. Finkelmann and S. Kai, *Jpn. J. Appl. Phys.* **46** (2007), 1106.