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Chiral Interactions and Structures

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The chiral structure of liquid crystalline phases arises due to the intrinsic chirality of the constituent mesogens. While it is seemingly straightforward to quantify the macroscopic chirality by using, for instance, the cholesteric pitch or the optical rotatory power, it is not as simple to quantify the chirality of a single molecule. I will discuss a systematic quantification of molecular chirality and show how the resulting chiral parameters may be used to predict macroscopic chiral structure.

SUMMARY

Liquid crystal physics is a useful and fruitful proving ground for ideas based on symmetry. The entire apparatus and formalism of spontaneous symmetry breaking can be used to accurately model and predict behavior at phase transitions between the host of liquid crystalline phases as well as inside the phases themselves¹. In addition, many of the phenomenological parameters can be estimated rather well through dimensional analysis. To illustrate, we consider the nematic phase. The nematic is a phase with a spontaneously chosen direction, which we can take to be the \hat{z} -axis. There are two Goldstone modes associated with infinitesimal rotations away from this preferred axis, δn_x and δn_y , the deviation of the unit nematic director \mathbf{n} away from $\mathbf{n}_0 = \hat{z}$. The free energy dictated by the nematic symmetry ($\mathbf{n} \rightarrow -\mathbf{n}$) and rotational invariance is the Frank free energy²:

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

The elastic constants have the dimensions of energy per unit length. Since typical nematic phases exist within an order-of-magnitude of room temperature, the

relevant energy scale is $k_B T \sim 4 \times 10^{-14}$ erg. The lengthscale is simply the molecular size, roughly 10\AA . Put together, we can estimate the three Frank constants, K_1 , K_2 and K_3 to be on the order of 1 microdyne. Indeed, this simple estimate is remarkably good for typical nematics². When the constituent molecules are chiral, a new term is allowed in (1) which is not invariant under inversion:

$$\delta F^* = \int d^3x K_2 q_0 [\mathbf{n} \cdot (\nabla \times \mathbf{n})] \quad (2)$$

where the new parameter q_0 is a pseudoscalar, reflecting the chirality of the molecules. However, it is clear that this new parameter introduces a *lengthscale*, q_0^{-1} . Indeed, though the ground state of (1) is simply a constant director field, the ground state of $F + \delta F^*$ is not nematic, but *cholesteric*, with $\mathbf{n} = [\cos(q_0 z), \sin(q_0 z), 0]$, corresponding to a helical structure with a pitch $P = 2\pi/q_0$ which is typically on the order of microns. Thus the presence of chirality introduces a *new* lengthscale into the problem which leads to a number of macroscopic, periodic structures, of which the cholesteric is only one example. It is a theoretical challenge to predict and explain these new lengthscales. While the elastic constants of the cholesteric can be estimated on dimensional grounds, the micron-sized pitch is not comparable to any molecular scale.

We have found a systematic approach to calculate macroscopic chiral properties from the microscopic character of the constituents. A chief result is an expression for the cholesteric wavenumber q_0 . While dimensional analysis predicts something too large, we have shown³ that any consistent mean-field treatment predicts $q_0 = 0$. This is a straightforward consequence of group theory: in a uniaxial phase, there is no long range ordering of the molecular orientation *perpendicular* to the nematic director. It follows that the average electron and nucleon density of the molecules has a C_∞ axis along the director. However, there are no symmetry groups that have a C_∞ axis which do not contain the inversion element⁴. Thus the uniaxial averaging “washes out” the chirality of the molecules and hence q_0 must vanish.

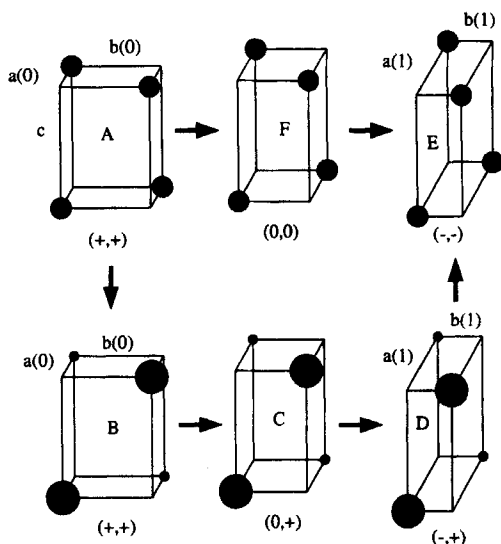


FIGURE 1. Path I (AFE) and path II (ABCDE) between chiral enantiomers (mirror images) **A** and **E** for a molecule consisting of 4 atoms at the tetrahedral vertices of a cube. Below each configuration we give (σ, σ') , where σ and σ' are respectively the signs or zero value of the chiral parameters ψ_0 and ψ'_0 . (From reference 5).

We have argued that it is therefore necessary to include correlations between the orientations of the molecules and found that³:

$$K_2 q_0 = \psi \langle g_B(R) V(R) \rangle \quad (3)$$

where $g_B(R)$ is the biaxial-orientation correlation function, $V(R)$ is a function of the interatomic potentials, $\langle \cdot \rangle$ in (3) is the fluid average of the intermolecular separation R and ψ is a chiral parameter depending only on a single molecule. Thus, if the biaxial correlations are absent $q_0 = 0$.

It is interesting that this result also depends on a pseudoscalar molecular parameter ψ . Being a pseudoscalar, $\psi \rightarrow -\psi$ under inversion. Thus this parameter can only be non-zero for chiral molecules. However, this parameter also quantifies

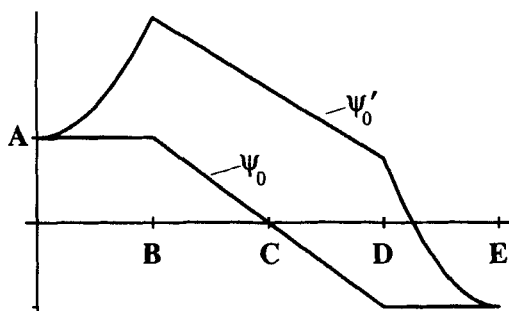


FIGURE 2. Plot of two chiral measures ψ_0 and ψ'_0 along the path **ABCDE**. Note that both parameters pass through zero on this path, but they do not pass through zero at the same place. On the Path **AFE** both parameters vanish simultaneously. (From reference 5)

the chirality at a molecular level and makes a *direct connection* between the microscopics and the macroscopic parameter q_0 . However, when calculating other macroscopic quantities other than q_0 (or when calculating higher-order corrections to q_0) other chiral parameters appear which are not equal to ψ . In fact, they may not even have the same sign as ψ ! To make this concrete, we have considered “rubber glove molecules” which can be transformed into their enantiomer through a chiral pathway ⁵. Figure 1 illustrates the chiral pathway and Figure 2 shows the development of two different chiral parameters ψ_0 and ψ'_0 . Notice that they vanish at different places and thus need not have the same sign over the entire range of deformation of the molecule. Even though “left” and “right” are a matter of convention, our construction shows that even a chosen convention cannot be defined globally since continuous deformations can change “left” to “right” without an achiral intermediate state. Thus the handedness of an object depends on the property of interest.

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References

- [1] See, for instance, R.D. Kamien and D.R. Nelson, *Phys. Rev. E*, **53**, 650 (1996); *Phys. Rev. Lett.*, **74**, 2499 (1995).

- [2] P.-G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Second Edition, (Oxford University Press, New York, 1993).
- [3] A.B. Harris, R.D. Kamien and T.C. Lubensky, *Phys. Rev. Lett.*, **78**, 1476 (1997); 2867 (1997).
- [4] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, Third Edition (Pergamon Press, Oxford, 1977).
- [5] A.B. Harris, R.D. Kamien and T.C. Lubensky, *Rev. Mod. Phys.*, **71**, in press (1999).