High- and Low-Pitch Helical Structures of Tilted Chiral Lipid Bilayers

Shigeyuki Komura* and Ou-Yang Zhong-can[†]

*Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology,
Iizuka 820-8502, Japan
[†]Institute of Theoretical Physics, Academia Sinica, P.O. Box 2735 Beijing 100080, China

Tubular and helical structures are rather commonly observed in nature [1]. For example, many authors found various helical structures of chiral lipid bilayers (CLBs) in recent experiments. Among several theoretical approaches, a fundamental basis which is consistent with the experiments is that the molecular packing interaction is chiral as in cholesteric liquid crystals (ChLCs). According to the early theories, the pitch angle of the helix (ϕ_0 in Fig. 1(a)) have been predicted to be 45° which was in good agreement with the previous experimental observations.

Although the concept of molecular packing interaction in ChLCs has been experimentally confirmed and theoretically extended, a recent challenge is to understand the new findings in cholesterol crystallization (ChC) in native and model biles [2]: Micellar model biles composed of bile salt sodium taurocholate, lecithin, and cholesterol in a molar ratio of 97.5:0.8:1.7 were initially prepared and contained both micelles and vesicles. Within 2-4 hours of dilution, filamentous structures were observed. A few days later, the filaments were bent to form high-pitch helices ($\approx 54°$). These helices grew laterally while maintaining the pitch angle to form tubules. Within a few weeks, high-pitch helices and tubules disappeared, while new helices with low-pitch angle ($\approx 11°$) appeared and grew to form new tubules. Eventually only plate-like cholesterol monohydrate crystals (ChMs) remained. One of their interesting findings is the existence of helical ribbon structures with two distinctive pitch angles: high- (54°) and low-pitch (11°) helices.

In order to explain these experimental observations, we investigate the molecular packing on a helical ribbon of CLBs as ChLCs by using the complete free energy density per unit area of ChLC

$$g_{LC} = \frac{k_{11}}{2}(\nabla \cdot \mathbf{d})^2 + \frac{k_{22}}{2}\left(\mathbf{d} \cdot \nabla \times \mathbf{d} - \frac{k_2}{k_{22}}\right)^2 + \frac{k_{33}}{2}(\mathbf{d} \times \nabla \times \mathbf{d})^2. \tag{1}$$

In the above, $\mathbf{d}$ is a unit vector parallel to the long axis of the molecules (Fig. 1(b)), k_{ii} ($i = 1, 2, 3$) are the splay, twist, and bending elastic constants, respectively, k_2 characterizes the chirality of ChLC, and ∇ is the three-dimensional gradient
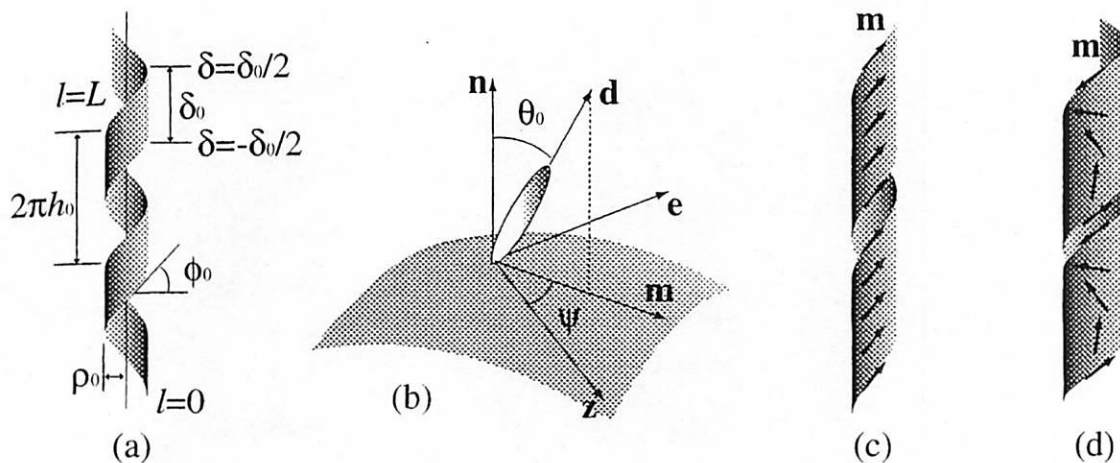
FIGURE 1. Schematic illustration of a helical ribbon: (a) the geometric parameters characterizing the ribbon, (b) local coordinate system of TCLB, (c) helical ribbon with "parallel packing" of molecules, (d) helical ribbon with "anti-parallel packing" of molecules.

operator. To view (1) as an energy per unit area, we regard k_{ii} and k_2 as the corresponding elastic constants of ChLC multiplied by the thickness of the CLB, and thence the total free energy of the CLB is given by $F = \oint g_{LC} dA$, where dA is the area element of the CLB surface.

We allow the molecular tilt direction to vary on the bilayer, but keep the boundary condition that the tilt direction is aligned with the helical direction at the ribbon edges. Especially, we obtained the tilt direction field exactly by solving the Euler-Lagrange equation derevid from g_{LC}. With these refinements, we have revealed that for the high-pitch helices, molecules at the two edges of bilayers tilt parallel with each other (Fig. 1(c)), whereas for the low-pitch helices, they tilt anti-parallel with each other (Fig. 1(d)). Helix formation takes place through a transition from a fluid CLB (chain-melted L_α) phase to a tilted CLB (chain-frozen $L_{\beta*}$) phase under cooling or dilution. The observed sequence of structures from filaments to ChMs by way of two types of helices can be shown as a decreasing succession of free energy of the metastable intermediate structures and regarded as a quench-like cooling process of the molecular tilt.

Details of our results are given in Ref. [3].

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