Chiral Symmetry Breaking in Crystals of Achiral Polymers

Yashodhan Hatwalne[1] and M. Muthukumar[2]

[1]*Raman Research Institute, Bangalore—560 080, India*
[2]*Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA*

Many achiral polymers crystallize into spherulites with gigantic chirality, as is evident from spectacular images of periodic banding observed in a polarized optical microscope, arising from the twisting of the lamellae making up the spherulites. We present a new mechanism of the spontaneous chiral symmetry breaking, by accounting for topological defects in finite crystalline ribbons made of achiral molecules in equilibrium. We show that disclinations stabilize a twisted helicoidal ribbon, with spontaneous selection of its width and chiral period, which are proportional to each other, as a universal law.

When a collection of interpenetrating and entangled long flexible polymer molecules in a molten state is cooled to low enough temperatures, crystallinity develops in the form of spherulites with radiating and space filling branched lamellae [1–5]. Spherulites from many polymers, both achiral and chiral in their molecular conformations, exhibit spectacular concentric bands in a polarized optical microscope, which are manifestations of the twisting of polymer lamellae constituting these "banded spherulites." These helicoidal lamellar ribbons consist of multiply folded chains and are typically about 10 nm thick, $\sim$1 μm wide, and have a remarkably uniform pitch of the order of 1 μm. Right- and left-handed helicoids are observed in roughly equal numbers. It is remarkable that even the simplest polymer, polyethylene, which is achiral, leads to such gigantic chirality in the crystallized state. Starting from the initial recognition of this phenomenon many decades ago [1], an understanding of the mechanism behind the spontaneous formation of gigantic chirality in polymeric spherulites continues to be a stubborn challenge [6–18] imposing intense research and discussion [5].

There have been four major approaches to explain the banding period in spherulites from polymers. Keith and Padden [6,7] proposed that unbalanced stresses can develop at the opposite fold surfaces of individual lamellae, due to local variations in the congestion of chain folds, which then result in lamellar twisting. Bassett *et al.* [8–11] proposed that isochiral screw dislocations can occur sequentially resulting in an essentially cumulative reorientation of the lamellae. Instead of structural origins, Kyu *et al.* [17] introduced a model of rhythmic crystallization arising from nonlinear diffusion of the molecules during spherulite growth. Another kinetic model was introduced by Schultz [3,18], where self-induced compositional or mechanical fields are generated at the growth fronts. In addition to the generic features of the banded spherulites mentioned above, there are also additional hints from experiments. Lamellae grown in even dilute solutions of achiral polyethylene chains exhibit spontaneous

twisting [19]. There is no one-to-one correspondence between the chirality of the polymer and that of the lamellar twist [5]. The lamellar twist is not restricted to only polymers. This phenomenon is of common occurrence in a wide variety of materials [1,5]. As a specific recent example, solution-grown lamellar crystals of achiral 1,3 diynes [20] twist with pitch as large as 2 mm, and with an equal number of right- and left-handed helicoids. The various models of banding in spherulites and their relative positions against the known experimental facts have been substantively reviewed by Lotz and Cheng [5], who have emphasized that the understanding of lamellar twist remains as one of the major challenges in polymer morphology and that a "universal" explanation is not yet reached.

In this Letter we propose a new general model of spontaneous selection of chirality in lamellae, independent of the configurational chirality of the constituent molecules, based on topological disclination defects on the lamellae. Our model does not deal with the nucleation-growth process, but instead addresses the role of disclinations in the chiral symmetry breaking of equilibrium, finite-sized lamellae. Although the interior of the lamellae is ordered (for example, with orthorhombic crystal symmetry for polyethylene), the surfaces have considerable disorder [Fig. 1(a)] arising from the conformational changes (from trans- to gauche- and reverting back to trans-) associated with the obligatory requirement for chain folding [21]. As a result, we treat the lamellae as deformable thin crystalline plates in equilibrium, and use the Föppl–von Kármán theory of large deflection of thin plates [22], modified to include topological defects [23].

Let us first consider qualitatively the stability of a thin crystalline ribbon of uniform thickness. Bending of the ribbon midplane, as well as stretching of the ribbon material contribute to the elastic free energy of a crystalline ribbon. The bending free energy density has a part proportional to the square of the local mean (extrinsic) curvature H and a part proportional to the local Gaussian (intrinsic) curvature K [22,23]. Whereas the coefficient κ of the mean
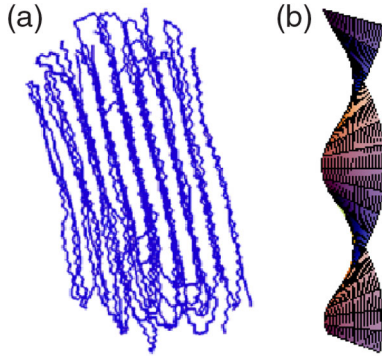
(a)   (b)

FIG. 1 (color online).   (a) A typical configuration of a multiply folded chain in a lamella. (b) One full pitch $p = 2\pi b$ is shown for a helicoid.

curvature term has to be positive for stability, there is no such restriction on the sign of the coefficient κ_G of the Gaussian curvature term—Gaussian curvature is a total divergence, integrates to the boundary (Gauss's theorem), and does not affect bulk stability. If κ_G is positive, an elastic ribbon prefers to buckle into a locally saddlelike shape which has negative Gaussian curvature. Nonzero K is usually (but not always) associated with nonzero H, which costs energy. Shapes with $K < 0$; and $H = 0$ everywhere (minimal surfaces) are therefore favored for ribbons with $\kappa_G > 0$. The natural choice for such a shape is the simple helicoid [Fig. 1(b)], which is a minimal surface: $\mathbf{R} = (\rho \cos\phi, \rho \sin\phi, b\phi)$, where $\mathbf{R}$ is a three-dimensional Cartesian position vector of a point on the ribbon midplane, $0 \le \phi \le 2\pi$, $| \rho | \le r$, $p = 2\pi | b |$ is the pitch of the helicoid, and the sign of b determines the handedness of the helicoid. For large deflections of the ribbon (relative to a flat configuration), bending also leads to stretching of the ribbon midplane. The energy cost of stretching can be overwhelmingly large, unless we allow for topological defects in the ribbon. The "stretching" stress produced in twisting the ribbon can be partially relieved if we allow for topological defects in the ribbon material [23]. The negative Gaussian curvature of the ribbon acts as the source of negative disclination density s, and mitigates the stress. Moreover, this compensation is such that the stretching, or "Hooke's law" stress is reduced to zero if the local disclination density is equal to the local Gaussian curvature of the ribbon (i.e., if $s = K$ everywhere), and amounts to adding just the right quantity of "extra material" to the ribbon so that it buckles into a helicoidal shape. We believe that the growth process makes this imbibition of disclinations possible; lamellae take in the extra material at the growth front itself so that s balances K. We assume a continuous distribution of disclination density in order to match the Gaussian curvature. In addition to the bend and stretch contributions to the total energy, we have to account for the surface tension of the ribbon and the line tension at the edges of the ribbon. In what follows, we solve the modified Föppl–von Kármán

equations for this variational problem subject to free boundary conditions. The free boundary conditions amount to balancing forces at the edge of the ribbon, and impose strong restrictions on the radius as well as the pitch of the helicoidal structure.

A note on κ_G is in order before we present the calculations. For a stable homogeneous and isotropic body, κ_G can never be positive [22]; consequently a ribbon of a homogeneous, isotropic material would not twist spontaneously. However, we believe that the "cilia" shown in Fig. 1(a) play a major role in determining the sign of the effective κ_G (in principle renormalized, so that the effects of the cilia are integrated out), which is a phenomenological parameter. A single polymer with one end (or a loop with two ends) either adsorbed or attached onto one of the sides of a flexible membrane (which, in our context is the lamellar crystal) can bend the membrane so as to gain entropy [24]. The efficacy and the nature of this "curvature effect" depends upon the solvent, the stiffness of the polymer, polymer-membrane interactions, the strength of adsorption or anchoring, and in the case of loops, the distance between the adsorbing or anchoring points. We note that in the case of lamellar polymer crystals, both the surfaces of the lamellae have cilia. In the absence of a detailed analysis of this problem, we will content ourselves with a description which uses the phenomenological parameter κ_G, which can have either sign. Further, the fold surfaces of these lamellae are disordered in the tilt angles of the stems [2–5,21]. We therefore believe that it is easier to form topological defects in polymer lamellae. Thus polymer lamellae are particularly good candidate systems to assess the validity of the proposed mechanism.

For large deflections, the elastic free energy of a ribbon can be cast in the form $F = F_b + F_s + F_i + F_l + F_{gc}$. The bending energy is given by

$$F_b = \int \left(\frac{\kappa}{2} H^2 + \tilde{\kappa}_G K \right) d^2 S, \tag{1}$$

where H and K are, respectively, the mean and the Gaussian curvatures of the surface, and the integral is over the curved surface.

The stretching energy of the ribbon material is

$$F_s = \frac{1}{2} \int u_{ij} \sigma_{ij} d^2 S', \tag{2}$$

where u_{ij} is the nonlinear Lagrangian strain tensor [22], σ_{ij} is the stress tensor, and $d^2 S' = \rho d\rho d\phi$ in polar coordinates.

The energy cost due to the surface tension σ is given by

$$F_i = \sigma \int d^2 S, \tag{3}$$

and the energy cost from the line tension γ:

$$F_l = \gamma \int dl, \tag{4}$$

where the integral is taken over the boundary of the surface.

In addition, there is a contribution from the geodesic curvature k_g of the boundary of the surface

$$F_{gc} = \alpha \int k_g dl. \tag{5}$$

For an orientable surface with a boundary, (5) merely renormalizes the coefficient of the Gaussian curvature term in (1) to $\kappa_G = \tilde{\kappa}_G - \alpha$ (Gauss-Bonnet theorem).

We now show that the above ansatz for the shape is in fact a solution to the equations of equilibrium with free boundary conditions and that the Hookean stress is zero if $s = K$. The variational problem of minimizing the total free energy F subject to free boundary conditions is formidable. We therefore use the parametrization $\mathbf{R} = (\rho\cos\phi, \rho\sin\phi, b\phi)$, for the twisted ribbon of radius r, and find the conditions under which it is energetically favored over a flat, distortion-free surface. For this helicoidal shape, $H = 0$, $K = -b^2/(\rho^2 + b^2)^2$, $k_g = r/(r^2 + b^2)$, and the components of the curvature tensor are $K_{\rho\rho} = 0$, $K_{\rho\phi} = K_{\phi\rho} = -b/\sqrt{\rho^2 + b^2}$, $K_{\phi\phi} = 0$. The fact that this is a minimal surface leads to great simplifications in the equations of stability (the Euler-Lagrange equations) as well as the free boundary conditions, and makes the problem tractable.

Setting the variational derivatives of F_b and F_s with respect to the height of the midplane of the surface and the displacement u respectively to zero gives the "shape equation" [22,23]

$$K_{ij}\epsilon_{ik}\epsilon_{jl}\partial_k\partial_l\chi = 0, \tag{6}$$

where the Airy stress function χ is related to the components of the stress tensor via $\sigma_{ij} = \epsilon_{ik}\epsilon_{jl}\partial_k\partial_l\chi$. The stress function is so defined that it identically satisfies the Euler-Lagrange equation $\delta F/\delta u_i = \partial_j\sigma_{ij} = 0$ for the displacement field. However, χ cannot be chosen arbitrarily; the requirement that the stress should be compatible with a displacement field [23] leads to the "compatibility condition"

$$\frac{1}{K_0}\nabla^4\chi = s - K, \tag{7}$$

where K_0 is the (two-dimensional) Young's modulus, the disclination density $s = \epsilon_{ij}\partial_i\partial_j\theta$, and $\theta = (1/2)\epsilon_{ij}\partial_i u_j$ gives the local rotation of the ribbon material. These constitute the modified Föppl–von Kármán equations, which are coupled, nonlinear partial differential equations. The Gaussian curvature of the ribbon is the source of disclination density, and screens the elastic stress [25,26].

In order to address the energetics of the twisted ribbon we need to solve (6) and (7) for χ with free boundary conditions. Free boundary conditions arise naturally from the variational problem [27,28]. At the edge of the ribbon, i.e., $\rho = r$, for all ϕ,

$$\kappa_G K + \gamma k_g + \sigma = 0. \tag{8}$$

Further, the normal components of the stress tensor

$$\sigma_{\rho\rho} = \sigma_{\phi\rho} = 0 \tag{9}$$

at the edge. In polar coordinates, $\sigma_{\rho\rho} = (1/\rho)\partial_\rho\chi + (1/\rho^2)\partial_\phi^2\chi$ and $\sigma_{\phi\rho} = -\partial_\rho((1/\rho)\partial_\phi\chi)$ [22].

For the twisted ribbon, the shape equation dictates that $\sigma_{\phi\rho} = 0$ in the bulk. Thus χ is of the form $a_1\rho f(\phi) + a_2$, where a_1 and a_2 are constants. The allowed solutions are either $f(\phi)$ is a constant or $a_1 = 0$ (i.e., χ is a constant). From the boundary condition (9), $\sigma_{\rho\rho} = 0$, the only allowed solution is $\chi = $ const. This result, in combination with the compatibility condition (7), yields $s = K$. Thus all components of the stress tensor are identically zero (with no stretching energy).

The free energy density follows from (1), (3), and (4) in the helicoidal gauge of the twisted ribbon as

$$f = -\frac{\kappa_G}{b}\frac{r}{\sqrt{r^2 + b^2}} + \frac{\sigma r}{b}\sqrt{r^2 + b^2}$$
$$+ \sigma b \ln\frac{r + \sqrt{r^2 + b^2}}{b} + \frac{\gamma}{b}\sqrt{r^2 + b^2}, \tag{10}$$

where $f \equiv (F_b + F_i + F_l)/(4\pi b)$. The boundary condition (8) in the helicoidal gauge is

$$-\frac{\kappa_G b^2}{(r^2 + b^2)^2} + \frac{\gamma r}{(r^2 + b^2)} + \sigma = 0. \tag{11}$$

Thus the boundary condition (8) establishes a relation between b and r in terms of the material parameters κ_G, σ, and γ. For the sake of analytical tractability (facilitating physical insight) we have ignored the line tension term in (8), and we have checked that our results (see below) do not change qualitatively if this term is included. With $\gamma = 0$, the solution is

$$\tilde{r}^2 = -\tilde{b}^2 \pm \tilde{b}, \tag{12}$$

where $\tilde{r} \equiv r/\lambda$ and $\tilde{b} \equiv b/\lambda$, with the characteristic length in the problem being $\lambda \equiv \sqrt{\kappa_G/\sigma}$. For physical situations ($\tilde{r} > 0$), $|\tilde{b}| < 1$. If $\tilde{b} > 0$, the positive sign in (12) is valid and we refer this situation as the right-handed helicoid, and the other solution for $\tilde{b} < 0$ as the left-handed helicoid. The relation between b and r as stipulated by the boundary condition on a finite right-handed helicoid is given in Fig. 2 and has two branches given by $\tilde{b} = (1/2)(1 \pm \sqrt{1 - 4\tilde{r}^2})$.
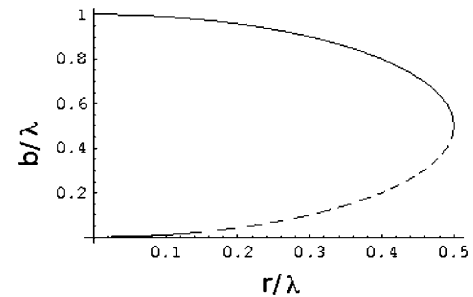

FIG. 2.   The relation between b/λ and r/λ.
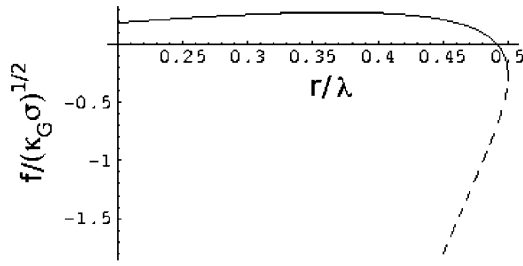
FIG. 3.   Energy per unit length f, in units of $(\kappa_G \sigma)^{1/2}$ as a function of r/λ.

The free energy density $f/\sqrt{\kappa_G \sigma}$ from (10), after substituting the above relation for $\tilde{b}$ in terms of $\tilde{r}$, is given in Fig. 3. There are two branches. The lower branch (dashed curve) leads to the unphysical result that $F \to -\infty$ as $r \to 0$. We discard this "melting" branch for crystallizing ribbons. The upper branch (solid curve) shows that the free energy per unit length of the twisted ribbon becomes negative in comparison with a flat ribbon and that the global free energy minimum occurs at $\tilde{r} = 1/2 = \tilde{b}$ with the value $[\log(1 + \sqrt{2}) - \sqrt{2}]/2 \approx -0.2664$.

The main conclusions of the above calculations are the following. The lamellar width $W \equiv 2r$ and the pitch $p = 2\pi b$ of a helicoidal thin ribbon are both finite, and are spontaneously selected in equilibrium. Remarkably, b is equal to r and is related to the nonuniversal material parameters κ_G and σ through the relation $b = r = \lambda/2$, with the characteristic length of the system $\lambda = \sqrt{\kappa_G/\sigma}$. Both the right- and left-handed helicoids cost the same energy. The recent experimental results [15,16] on the lamellar width (W) and the ring period (P_{ring}) of the banded spherulites from polyethylene and poly (vinylidene fluoride) support our theoretical result $P_{\text{ring}} = (\pi/2)W$.

The present treatment, based on a combination of the topological defects of disclinations and the finite size of the ribbon, is a universal model independent of whether the constituent molecules are of lower molar mass or polymeric, organic or inorganic, or chiral or achiral. There is considerable discussion on the relation between the molecular chirality and the macroscopic chirality of their assembled bundles [5,29–31]. It would be of interest to investigate the interference between the topological-defects-driven chiral symmetry breaking treated here and the molecular conformational chirality. Our present model uses a continuous distribution of disclinations. It would also be of interest to extend it to localized defects to address other morphological forms such as tents, chairs, and scrolls as also seen in polymer crystals [5].

[1] A. Keller, Nature (London) **169**, 913 (1952).
[2] P. H. Geil, *Polymer Single Crystals* (John Wiley, New York, 1963).
[3] J. M. Schultz, *Polymer Crystallization* (Oxford University Press, New York, 2001).
[4] *Progress in Understanding of Polymer Crystallization*, edited by G. Reiter and G. R. Stobl (Springer, Berlin, 2007).
[5] B. Lotz and S. Z. D. Cheng, Polymer **46**, 577 (2005).
[6] H. D. Keith and F. J. Padden, Polymer **25**, 28 (1984).
[7] H. D. Keith and F. J. Padden, Macromolecules **29**, 7776 (1996).
[8] D. C. Bassett and A. M. Hodge, Polymer **19**, 469 (1978).
[9] D. C. Bassett and A. M. Hodge, Proc. R. Soc. A **359**, 121 (1978).
[10] D. C. Bassett and A. M. Hodge, Proc. R. Soc. A **377**, 61 (1981).
[11] D. Patel and D. C. Bassett, Polymer **43**, 3795 (2002).
[12] A. Toda, T. Arita, and M. Hikosaka, Polymer **42**, 2223 (2001).
[13] A. Toda *et al.*, Polymer **46**, 8708 (2005).
[14] H. Kajioka *et al.*, Polymer **46**, 8717 (2005).
[15] A. Toda *et al.*, Macromolecules **41**, 2484 (2008).
[16] A. Toda *et al.*, Polym. J. **40**, 905 (2008).
[17] T. Kyu *et al.*, Phys. Rev. Lett. **83**, 2749 (1999).
[18] J. M. Schultz, Polymer **44**, 433 (2003).
[19] M. Kunz, M. Dreshsler, and M. Möller, Polymer **36**, 1331 (1995).
[20] W. E. Lindsell, P. N. Preston, J. M. Seddon, G. M. Rosair, and T. A. J. Woodman, Chem. Mater. **12**, 1572 (2000).
[21] P. Welch and M. Muthukumar, Phys. Rev. Lett. **87**, 218302 (2001).
[22] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Butterworth and Heinenann, Oxford, 1995).
[23] H. S. Seung and D. R. Nelson, Phys. Rev. A **38**, 1005 (1988).
[24] R. Lipowsky, H.-G. Döbereiner, C. Hiergeist, and V. Indrani, Physica (Amsterdam) **249A**, 536 (1998).
[25] M. W. Deem and D. R. Nelson, Phys. Rev. E **53**, 2551 (1996).
[26] J.-M. Park and T. C. Lubensky, Phys. Rev. E **53**, 2648 (1996).
[27] D. H. Boal and M. Rao, Phys. Rev. A **46**, 3037 (1992).
[28] R. Capovilla, J. Guven, and J. A. Santiago, Phys. Rev. E **66**, 021607 (2002).
[29] J. V. Selinger, M. S. Spector, and J. M. Schnur, J. Phys. Chem. B **105**, 7157 (2001).
[30] R. L. B. Selinger *et al.*, Phys. Rev. Lett. **93**, 158103 (2004).
[31] C. Y. Li *et al.*, Phys. Rev. Lett. **83**, 4558 (1999).