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A case of mistaken identity: spontaneous formation of twisted bipolar droplets from achiral nematic materials

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New observations of the structure of nematic droplets containing material with a low K_{33}/K_{11} ratio indicate that these droplets adopt a twisted bipolar, rather than concentric, orientation. The data supporting this new interpretation are presented and discussed. These data provide verification for a prediction of Williams regarding the relative stabilities of bipolar, twisted bipolar, and concentric droplets. Nematic liquid crystals confined to spheres and cylinders form a general class of structures in which achiral molecules can form chiral structures due to the combination of external boundary conditions and the minimization of the free energy near defect structures.

1. Introduction

Liquid crystals confined to droplets can adopt a variety of internal structures, depending on the balance of elastic constants and anchoring properties [1]. In 1988 the observation of a droplet configuration found in liquid crystals with a K_{33}/K_{11} ratio less than 1.0 was reported [2]. Out of 28 nematic mixtures tested, the 9 mixtures with K_{33}/K_{11} less than 1.0 possessed the new structure, while the 17 mixtures with K_{33}/K_{11} greater than 1.0 possessed the more common bipolar structure (table 1).

The primary method for tracking the director field in the earlier work was by doping the liquid crystal with a high order parameter dichroic dye, and then observing the extinction of the droplet as a function of the orientation of a single polarizer. This probe indicated that the bulk of the nematic director field was oriented at an angle that appeared nearly perpendicular to the obvious two-fold symmetry axis of the droplet. On the basis of these observations, it was suggested that the droplets adopted a concentric (then named axial) orientation, with the director field forming circular alignment around a central

Table 1. A listing of the liquid crystal mixtures, K_{33}/K_{11} ratio, and droplet configuration assigned to 28 different liquid crystal mixtures examined in the 1988 study.

Nematic	K_{33}/K_{11}	Droplet structure	Nematic	K_{33}/K_{11}	Droplet structure
ZLI 1691	2.05	Bipolar	ZLI 2116-000	1.19	Bipolar
ZLI 3039	1.86	Bipolar	ZLI 2788-000	1.16	Bipolar
ZLI 3201-000	1.80	Bipolar	ZLI 1957/5 (20 C)	1.14	Bipolar
ZLI 1840	1.78	Bipolar	ZLI 2116-100	1.10	Bipolar
ZLI 3219	1.67	Bipolar	ZLI 1957/5 (25 C)	0.99	Bipolar
ZLI 1800-000	1.63	Bipolar	ZLI 2977	0.94	Concentric
ZLI 3021-000	1.40	Bipolar	ROTN 3848	0.87	Concentric
ZLI 2903	1.38	Bipolar	ZLI 2975	0.84	Concentric
ZLI 2452	1.34	Bipolar	ZLI 2974-000	0.82	Concentric
ZLI 1565	1.27	Bipolar	ZLI 2583-000	0.81	Concentric
ZLI 3347-000	1.27	Bipolar	ZLI 2974-100	0.75	Concentric
ZLI 2950	1.26	Bipolar	ZLI 2583-100	0.75	Concentric
ZLI 3282	1.20	Bipolar	ZLI 2620	0.73	Concentric
ZLI 2116-000	1.19	Bipolar			

ZLI prefix refers to nematic from E. Merck; ROTN prefix for nematic from Hoffman-La Roche. Data at 20 C, unless otherwise noted. From Drzaic, *Mol. Cryst. Liq. Cryst.* (1988), **154**, 289.

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core defect. It was argued that this structure relieves the costly splay energy found in nematic droplets with a low K_{33}/K_{11} ratio. This structure, however, does assume the existence of a high energy $S = +1$ line defect along the centre core (figure 1).

One difficulty with this interpretation is that the existence of an $S = +1$ line defect is problematic. It has been argued by Meyer [3] and by Cladis and Kléman [4] that $S = +1$ line defects should not exist in volumes of liquid crystals with length scales greater than a few tens of nanometers, as the director can 'escape' by twisting into the third dimension and forming one or more point defects. As such, the concentric configuration should not be stable in micron-sized droplets. This problem was noted in the earlier work but not reconciled [5].

One shortcoming with the earlier work is that an alternative droplet configuration, the twisted bipolar configuration (figure 2), was not considered. In this work, those earlier experiments and new observations are combined to determine that the internal structure of nematic droplets with low K_{33}/K_{11} ratio are indeed consistent with a twisted bipolar structure. Furthermore, the dependence of droplet structure on K_{33}/K_{11} ratio can be accommodated with the theoretical work of Williams [6], who predicted that a twisted bipolar structure would spontaneously form when the liquid
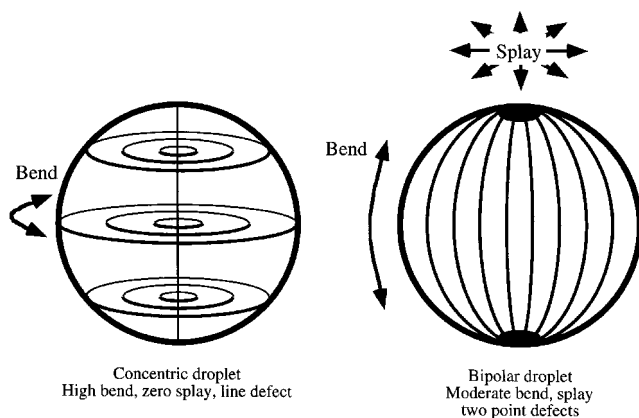
crystal elastic constants met the stability criterion $K_{11} \geqslant K_{22} + 0.431 K_{33}$. It is shown here that the relationship noticed in the earlier work is consistent with the prediction by Williams.

2. Experimental

Liquid crystals were obtained from E. Merck. A suspension of 5% liquid crystal in glycerine was created by stirring. Several drops of this suspension were placed under a microscope slide supported by $100 \, \mu m$ spacers. Droplet sizes ranged from approximately 4 to $100 \, \mu m$ in diameter. Droplets were observed using polarized narrowband illumination $(600 \pm 10 \, nm)$ at magnifications up to $630 \times$. Care was taken to make sure that droplets were freely suspended and not wetted onto the bounding cell plates. Only droplets with their symmetry axis perpendicular to the observation direction were measured, although it is possible that for many of these droplets their symmetry axis did not lie exactly along this perpendicular.

3. Results

For the purposes of this study, the droplet twist angle α is defined as the angle between the orientation of the droplet symmetry axis (defined by the bipolar defects) and the relative orientation of the director field at an equatorial position on the surface of the droplet (figure 2). To determine the twist angle α, the procedure of Volovik and Lavrentovich [7] was used. These large (supramicron) droplets are within the Maugin limit, so polarized light entering the droplet will be rotated by the twisted nematic structure by an angle 2α. As such, light passing through a twisted bipolar droplet observed by a polarizing microscope will be extinguished if the following conditions are met: (1) the droplet symmetry axis lies (nearly) perpendicular to the incident light direction; (2) the polarizer is oriented parallel to the director orientation at the droplet entrance; and (3) the analyser is perpendicular to the director orientation at the droplet exit. Measurement of the angle γ between the polarizer and analyser leading to this extinction condition can be used to determine α, as they are related by the equation

$$2\alpha = \pi/2 - \gamma. \tag{1}$$

The equation assumes that the twist orientation angle varies smoothly and uniformly from α at the droplet surface to zero near the interior axis.

The procedure to determine α was as follows. Using crossed polarizers, the droplet was rotated so that the droplet symmetry axis (as defined by the bipolar defects) was oriented along the polarizer direction, figure 3(a). The droplet orientation (stage) and the analyser were then rotated empirically until maximum extinction of

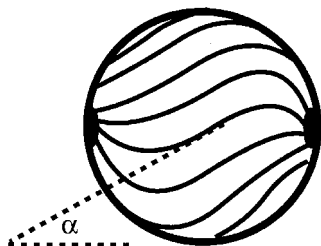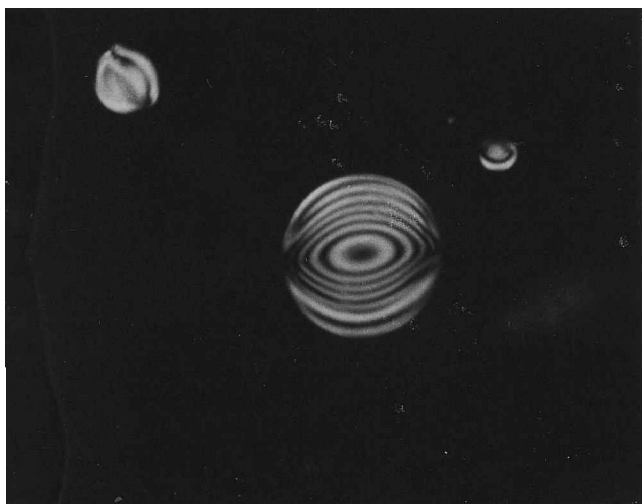Figure 1. Director fields for bipolar and concentric droplet configurations.

Figure 2. Director field for a twisted bipolar structure. The angle α is defined by the angle of the director field on the droplet surface relative to the droplet symmetry axis.

(a)
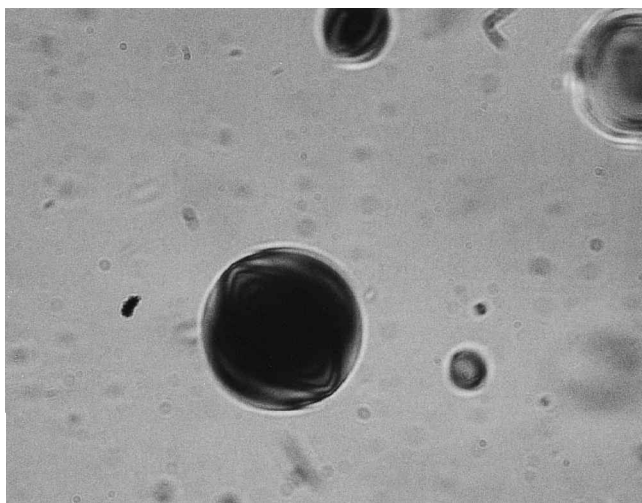
(b)

Figure 3. Twisted bipolar droplet suspended in glycerine (31 μm droplet of ZLI 2583-100). (*a*) Droplets examined under crossed polarizers with symmetry axis along polarizer; (*b*) polarizers and droplet rotation adjusted for maximum extinction. Defining the entrance polarizer angle as 0°, the droplet symmetry axis was oriented at 120° and the analyser at 151° (− 29°). These observations, plus the observation of the interference fringes relative to the droplet symmetry axis, put the droplet twist angle α at 60°.

the droplet centre was observed, figure 3 (*b*). The relative orientations of the polarizer and analyser by themselves define two possible rotation angles, γ and $\pi - \gamma$, depending on whether the angle used for the analyser orientation is θ or $\theta - \pi$ (e.g. 151° degrees is equivalent to − 29°). For the droplets in figure 3, this leads to uncertainty whether the angle α is actually 30° or 60°. This uncertainty can be resolved by examining the orientation of the interference rings within the droplet relative to the droplet centre in the original image, figure 3 (*a*). In all cases the

retardation was greater (more fringes) along the direction perpendicular to the droplet symmetry axis, indicating that the director field was preferentially aligned in this direction. This indicates that the droplets are twisted more towards the perpendicular (60° twist angle in figure 3) rather than along the symmetry axis (30°). A combination of the polarizer and analyser positions, coupled with observations of the interference fringes within the droplet, led to a determination of the internal twist angle of each droplet.

Figure 4 shows the patterns exhibited by bipolar droplets (in this case ZLI 1840) at 21 μm and 45 μm. When the symmetry axis of the droplet is aligned along either orientation of two crossed polarizers, the centre of the droplet and the horizontal and vertical axes are extinguished. These droplets exhibit no internal twist.
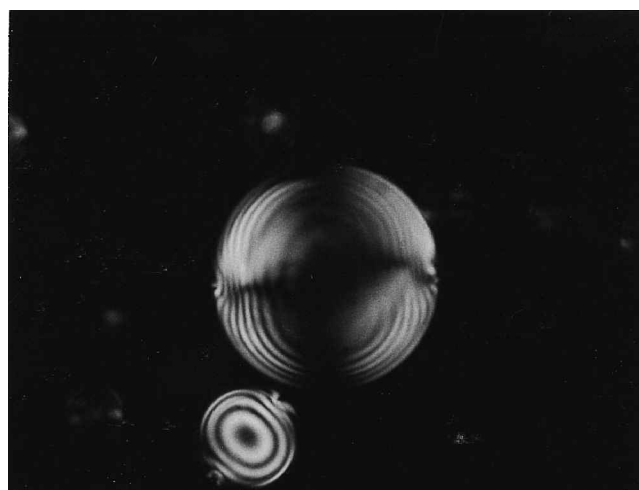
(a)
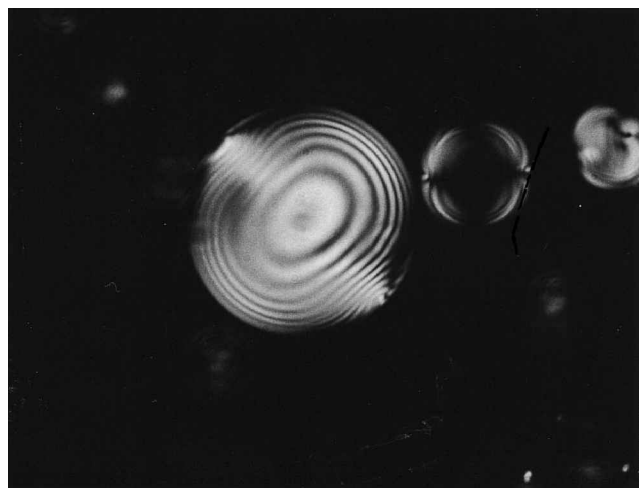
(b)

Figure 4. Bipolar droplets, oriented relative to crossed polarizers to provide extinction of the centre of the droplets: (*a*) 21 μm and (*b*) 45 μm droplets of ZLI 1840.

A number of droplets from four different nematic mixtures with low K_{33}/K_{11} were examined under narrowband illumination, and the appropriate polarizer positions determined to provide extinction of the droplet. These results are summarized in table 2. It is readily seen that the twist for all the droplets is relatively constant ($60° \pm 5°$) for nearly all the droplets. The twist angle has no obvious dependence on the droplet size or on the K_{33}/K_{11} ratio, although a bipolar configuration was seen in a few cases in systems that were otherwise predominantly twisted bipolar.

4. The Williams prediction

In 1985 Williams [8] predicted that the twisted bipolar structure would become stable in nematic droplets with a large splay constant. He then analysed numerically the relative stability of bipolar and twisted bipolar droplets [6], and arrived at the conclusion that the twisted bipolar state would be preferred over the bipolar structure when the liquid crystal elastic constant met the stability criterion of $K_{11} \geqslant K_{22} + 0.431 K_{33}$.

The ability of a large splay constant to induce a transition from a bipolar to twisted bipolar structure was verified by Lavrentovich and Sergan in 1990 [9]. They used the temperature dependence of the elastic constants in 8CB and 8OCB to cross the stability threshold into the twisted bipolar regime. The twist angles in both cases were relatively small ($\pm 5°$). They found good agreement with the stability criterion predicted by Williams.

Table 2. Measured internal twist angles for 18 different nematic droplets across four different eutectic mixtures. In systems with K_{33}/K_{11} near 1.0 bipolar droplets were occasionally seen.

	K_{33}/K_{11} ratio	Droplet diameter (μm)	Twist angle
ZLI 1957/5	0.99	14	57
		16	60
		107	Bipolar
ZLI 2977	0.94	4	Bipolar
		20	53
		45	50
ZLI 2583-100	0.75	16	59
		31	59
		80	59
ZLI 2620	0.73	4	62
		9	64
		9	63
		17	55
		28	60
		28	60
		32	65
		64	62
		65	59

Twist elastic constants are not available for the mixtures used here. Still, these data can be compared with the Williams data by making some reasonable assumptions. The present and earlier results show that for 9 different nematic mixtures with $K_{33}/K_{11} < 1.0$, the twisted bipolar structure is observed. These data can be rationalized with the Williams equation by noting that for a large number of nematic mixtures [10] the elastic constant $K_{22} \approx 0.6 K_{11}$. Substituting this approximation into the Williams equations leads to a stability criterion of $K_{33}/K_{11} < 0.93$, remarkably close to the transition criterion found in this and the earlier study.

5. Chiral structures from achiral materials

There has recently been an increasing interest in the formation of chiral structures from otherwise achiral materials. For example, chiral helices within achiral polyisocyanates have been described by Green and coworkers [11]. Achiral bent-core ('banana') molecules have been found to form local chiral domains of ferro-electric smectic C liquid crystal [12, 13]. While the local molecular structure in these systems is achiral, there are additional symmetry-lowering packing considerations for these structures (helix formation for the polyisocyanate, the bent core for the smectic C materials) which allow for the formation of chiral structures as the systems arrange themselves to minimize their elastic free energy. These systems have also been shown to demonstrate interesting 'sergeants and soldiers' type of behaviour [11], in which a small energetic preference for one chirality over another can have a profound effect on the overall chirality of the system. In systems which prefer to form a chiral structure of one form or another, but in which both chiral forms are initially of equal energy, a small amount of chiral material is sufficient strongly to tip the balance of one chiral form or another.

It has long been known that a variety of confined achiral nematics structures can spontaneously adopt twisted structures [1]. Besides the twisted bipolar droplets described here, twisted (chiral) structures have also been observed in 'escaped' structures in cylinders [3, 4], twisted radial droplets [14, 15], and lens-shaped twisted radial droplets [16]. The twisted curvature of the nematic director field near the structural centre not only reduces strong splay or bend deformations with weaker twist deformations, but in some cases also avoids the formation of line defects. The external boundary conditions (spheres or cylinders with strong anchoring) demand that some sort of defect structure is formed along the structural centre. As such, the symmetry-lowering element that allows for the formation of spon-taneous chirality is the spherical or cylindrical shape of the nematic volume.

To date, examination of these twisted nematic structures invariably shows equal numbers of both chiral senses. It is expected that these chiral structures should show a similar 'sergeants and soldiers' behaviour, in that a small amount of chiral material will be sufficient to give a strong preference for one twist sense over another.

6. Conclusions

In retrospect, the use of a single polarizer and dichroic dye-doped nematic led to a faulty conclusion regarding the assignment of the droplet structures in 1988. The large twist angle in these droplets, coupled with the wave-guiding effect of light passing through the droplet, made the assignment of a structure based on the absorbance of light by the dye problematic. The fact that the twisted bipolar structure was not considered was also a significant shortcoming. The twisted bipolar structure allows relaxation of the splay deformation in droplets with a low K_{33}/K_{11} without creation of a $S = +1$ line defect.

The present work is certainly not the first observation of twisted bipolar droplets. Besides the previously mentioned work of Volovik, Lavrentovich, and Sergan, twisted bipolar droplets have been observed in achiral nematics by Xu, Kitzerow, and Crooker [17], and in chiral-doped nematics by Lu and Yang [18].

Besides correcting the earlier error, the present work further establishes the general prediction made by Williams, that the twisted bipolar structure becomes favoured when the splay energy is high. The crossover point of $K_{33}/K_{11} < 1.0$ is consistent with his calculations. Additionally, it is worth noting that nematic droplets and cylinders provide another example of chiral structures formed from achiral materials, an area of currently increasing research interest.

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