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Undulating paired disclinations (oily streaks) in lyotropic liquid crystals

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Résumé. — Des observations au microscope optique révèlent la présence d'ondulations de la position latérale des axes de disclinations appariées ou « stries huileuses » dans la phase L_α (smectique A) de minces cristaux liquides lyotropes, totalement hydratés, de dimyristoyl phosphatidylcholine (DMPC). Ces ondulations expliquent les bandes sombres caractéristiques traversant les disclinations appariées, qui sont observées à l'aide de polariseurs croisés. Lorsque les disclinations appariées sont adjacentes, les périodes de leurs ondulations deviennent égales et le déphasage s'annule. Les ondulations apparaissent spontanément dans toutes les disclinations appariées dès que des échantillons alignés homéotropiquement sont formés dans la phase L_α .

Abstract. — Optical microscopy reveals regular periodic undulations of the lateral position of the axes of paired disclinations or « oily streaks » in thin, fully hydrated lyotropic liquid crystals of dimyristoyl phosphatidylcholine (DMPC) in the L_α (smectic A) phase. These undulations explain the characteristic dark bands that traverse the paired disclinations on observation with crossed polarizers. When paired disclinations are adjacent, their undulation periods become equal and lock in phase. The undulations appear spontaneously in all paired disclinations on formation of homeotropically aligned specimens in the L_α phase.

1. Introduction.

Defect structures in liquid crystals provide important clues to understanding the symmetry of perfect crystals and their mechanical properties. Paired disclinations, or « oily streaks », with transverse striations are observed in thermotropic smectic [1-3], cholesteric [4-5], lyotropic (smectic) liquid crystals [6-10] and most recently in liquid crystalline polymers [11-13] and polymeric liquid crystals [14, 15] and in lamellar phases of mixtures which also have a micro-emulsion phase [16]. The basic structure of the oily streak is a pair of positive disclinations of strength $1/2$ [9-10]. This structure suggests a straight, smooth form which does not explain the dark transverse striations always observed in disclination pairs between crossed polarizers [1-16]. In thermotropic smectic A's, the observed striations have been attributed to a row of focal conics [1, 3] which form from the two disclinations [17]. It has recently been found that the permeation coefficient in lyotropic smectics is extremely small [18-19]. Since the relaxation of disclination pairs to focal conics requires permeation, we were motivated to look for an alternative origin for the transverse striations. Using optical microscopy to

observe thin specimens of lyotropic liquid crystals composed of water and the phospholipid dimyristoyl phosphatidylcholine, (DMPC), in the L_α (smectic A) phase, we find that the transverse striations are due to transverse undulations of the disclination cores.

2. Experimental methods.

2.1 SPECIMEN PREPARATION AND CHARACTERIZATION. — Fully hydrated, homoeotropic specimens (molecular layers parallel to glass slides) in the L_α phase are prepared from a 5 mg/ml mixture of DMPC (Applied Science, State College, Pa., U.S.A.) in 2 : 1 v/v chloroform-methanol solution. A fluorescent dye, 3,3' dihexadecylindocarbocyanine iodide [20] (a gift from Dr. Alan S. Waggoner) is sometimes added from a stock solution in ethanol (0.1 mg/ml) to obtain a lipid to dye molar ratio of about 5 000 to 1. The dye is a lipid-like molecule, composed of two 16 chain hydrocarbon tails joined by a head group which is fluorescent. It is highly soluble in all phases of DMPC and appears to serve as an effective fluorescent lipid analog [21]. Fifty microliters of the mixture are dried down on a glass slide which has been cleaned in hot chromic-sulfuric acid (to insure homeotropic alignment [10])

and rinsed with distilled water. The specimen is slightly heated (to about 40 °C) to evaporate the solvent and then left for 2 h. at 30 °C. For best results, the cover glass is treated in the same manner. The slide (and cover glass) are wet slightly with steam from hot distilled water and the cover glass is placed on the slide. A 7 gm weight is placed on top and the specimen is left in a water saturated atmosphere for several days at 30 °C. Before use, the cover glass is attached to the slide with Torr Seal (Varian Associates) or Pyseal wax (Fisher Scientific Co.) and then the weight is removed. Just prior to sealing, some additional water is sometimes added to assure the availability of free water in a second phase. The specimens are stored in a water saturated atmosphere above the DMPC phase transition temperature of 23 °C.

This method produces a fully hydrated specimen of fairly uniform thickness that can be adjusted from 4 to 10 μm . To obtain thicker (13-18 μm) specimens, a more concentrated solution (50 mg/ml) of lipid in chloroform-methanol is used.

2.2 OBSERVATIONS AND STRUCTURE OF PAIRED DISCLINATIONS. — Optical observations by phase contrast, fluorescence and polarization microscopy use a Zeiss Universal microscope and (usually) a 40 $\times$ microscope objective. (See Ref. 22 for optical setup.) With fluorescence microscopy, it is seen that the lipid is not uniformly spread over the area of the slide but is aggregated in some uniform areas which may contain holes (areas free of lipid). The lipid-free areas contain water, as indicated by the presence of liposomes (mul-

tilayer lipid vesicles). The thickness of the specimen is estimated by using the calibrated fine focus movement of the microscope to measure the distance between the two glass-lipid interface reflections of a focused laser beam [22].

On examination between crossed polarizers, the defects seen (Fig. 1) closely resemble the typical paired disclinations described in the previous literature [6-10]. The unusual thinness of our specimen and the use of high magnification microscope objectives (40 $\times$ - 100 $\times$) allows the undulating structure of the paired disclinations to be discovered. The essential optical properties of a particularly visible example are shown in the photomicrographs of figures 2a-d. Although the overwhelming majority of observable paired disclinations are smaller and less easily photographed than this example, they do conform with all of the properties illustrated by this example.

Asher and Pershan [10] have shown that the paired disclinations have the basic structure shown by the schematic in figure 3, as first suggested by Kléman *et al.* [9]. The drawing shows the pattern of the intersection of the smectic layers and a plane normal to the mean axis of the paired disclinations; the two + 1/2 disclinations centred around P and P' include the same number of layers. The structure of figure 3 can be regarded as a pair of dislocations [9] with equal magnitude of the burgers vector, b , but opposite signs. A dislocation in smectics is composed of a + 1/2 and a - 1/2 disclination [23]. In figure 3, the distance between the - 1/2 disclinations has been shrunk to 0;



Fig. 1. — Typical appearance of an isolated disclination pair (centre field) observed with plane polarized light and a crossed analyser (arrows show their orientations). The bar is 10 μm long.

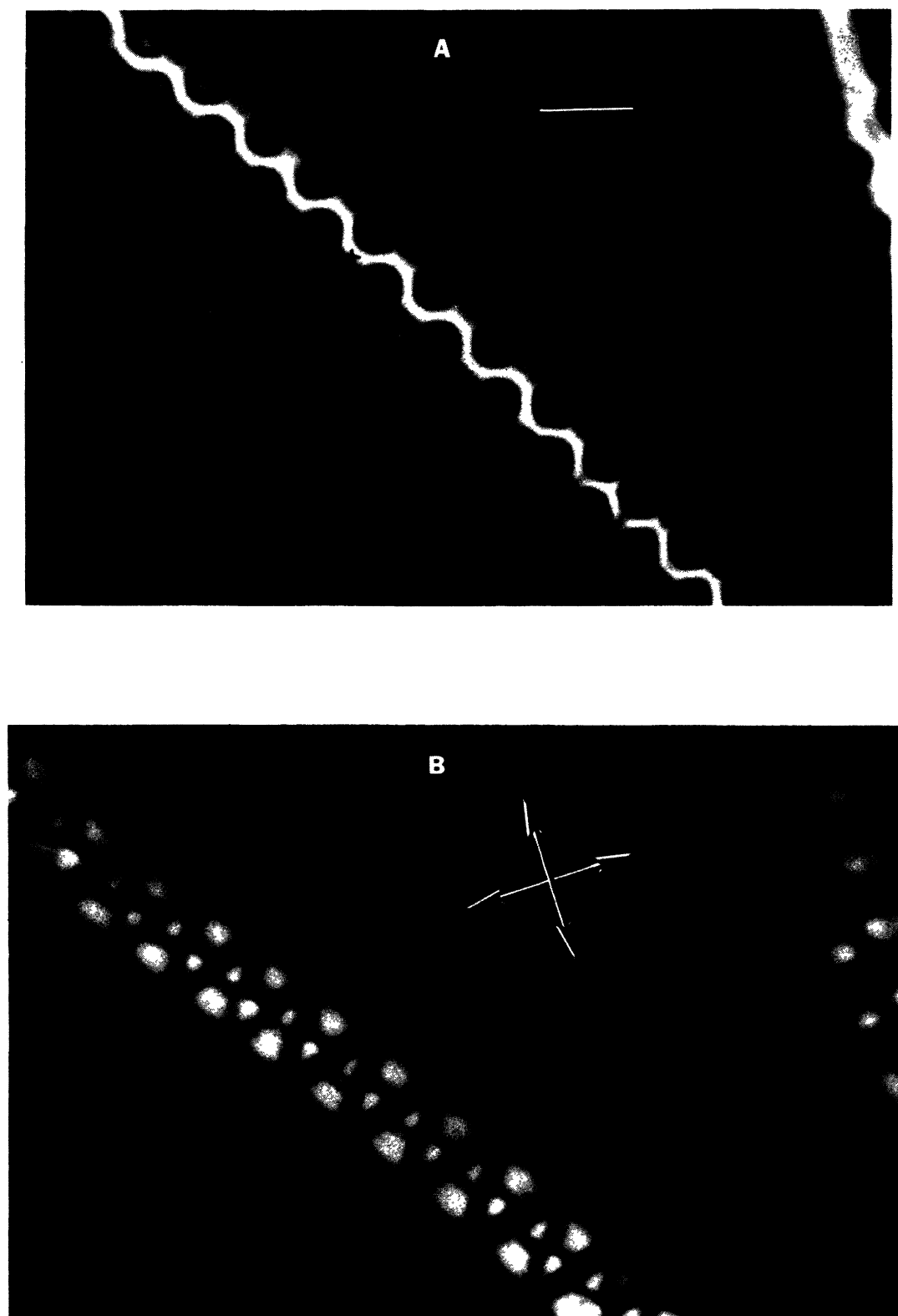


Fig. 2. — A large disclination pair in a homeotropically aligned specimen. *a*) phase contrast; (The bar is 10 μm long.) *b*) crossed polarizers, oriented as marked. See figure 5*b*. (Residual asymmetry is due to optical system birefringence.) *c*) and *d*) fluorescence excited by incident light polarized as indicated. Compare with figures 5*c* and *d*. The thin line of missing fluorescence along the undulating centre line *L* of the defect is attributed to the absence of the cusped smectic layers above and below the paired disclinations. The cross marks the same point in all 4 frames. The specimen is about 10 μm thick.

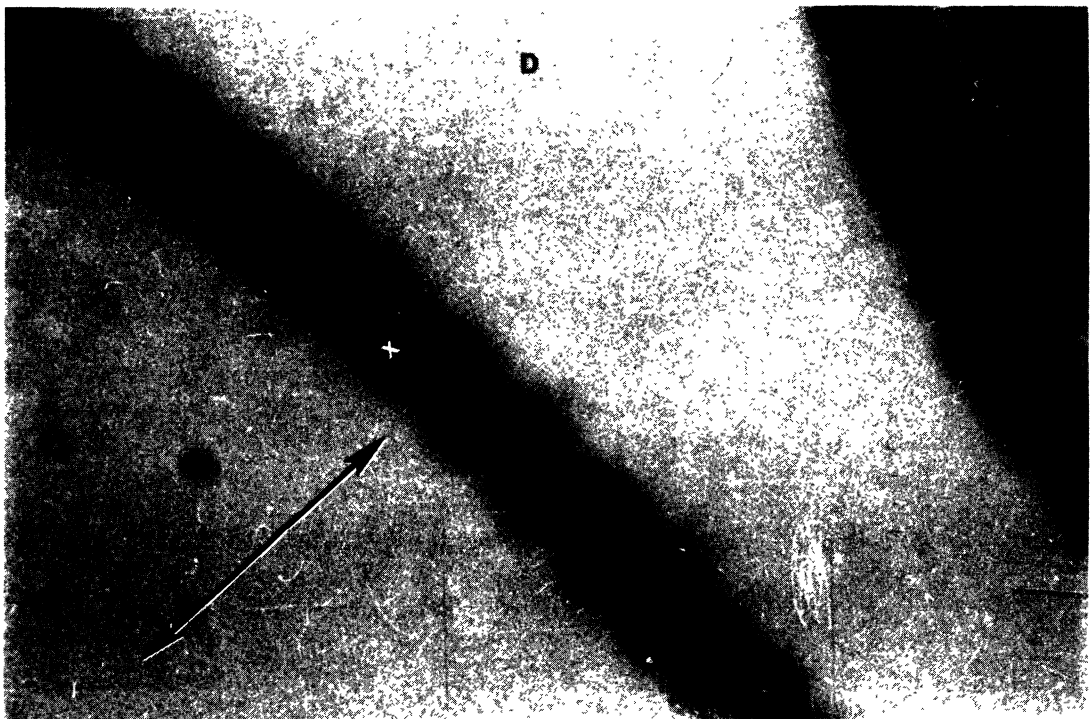
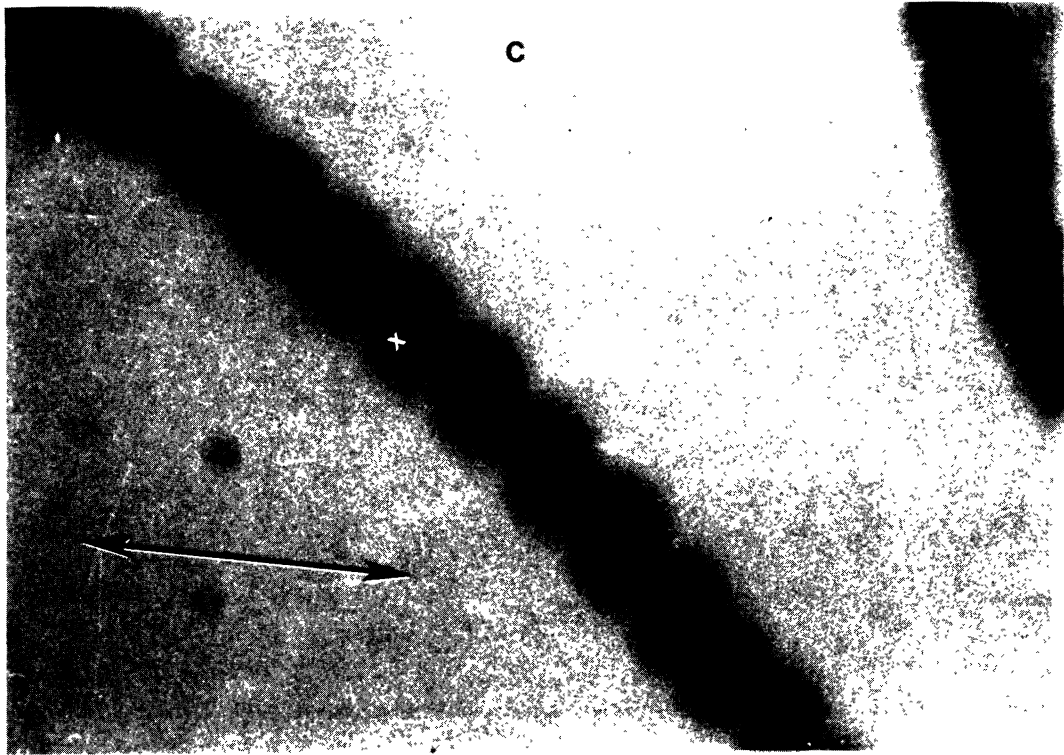


Fig. 2 (continued).

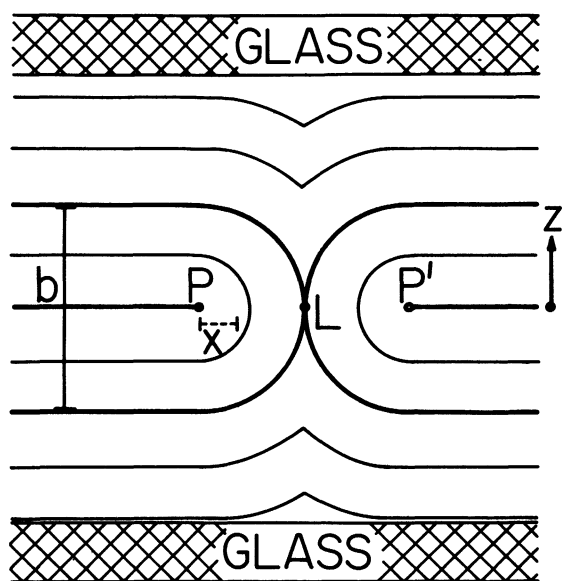


Fig. 3. — Established structure of paired disclinations depicted in section perpendicular to the nominal disclination axes. The intersection of the edges of the molecular layers with the plane of the drawing is indicated by the solid lines. P, P' are the intercepts of the pair of $+1/2$ disclination lines, which lie in the xy plane, with the plane of the drawing. x is the distance from P along PL. L denotes the intercept, with the plane of the drawing, of the line at which the outmost layers involved with each disclination meet. b is the magnitude of the burgers vector. Sometimes, as in figure 2, the cusped layers surrounding the paired disclinations are absent.

they are both centred around L, leaving the $+1/2$ disclinations centred around P and P'.

Microscopic observations perpendicular to the midplane of the paired disclinations suggest that the central line L undulates in the plane of the disclination cores. Thus the intersection of the smectic layers with the midplane (at $z = 0$) resembles figure 4 which is actually based on a tracing of a brightness contour made from figure 2a. L is drawn as a sinusoidal curve. Lines P, P' are drawn with cusps, although the cusps might be slightly rounded. Figure 3 is then the intersection of the smectic layers with a plane normal to line L at any point along the undulation.

The structure in figures 3 and 4 explains the appearance of the paired disclinations in photomicrographs recorded with plane polarized light using a crossed analyser (Fig. 1, 2b). Consider the propagation of a light ray normally incident on the undistorted smectic layers and polarized at an angle $\pi/2 - \alpha$ with respect to the tangent to line L (or polarized at an angle α with respect to the plane of Fig. 3). Since the crystal is optically uniaxial with the optic axis normal to the smectic layers, in the defect region, the light will be split into an ordinary component (perpendicular to the plane of Fig. 3) and an extraordinary component (in the plane of Fig. 3) [24] which travel at different speeds through the crystal. The optic axis changes direction

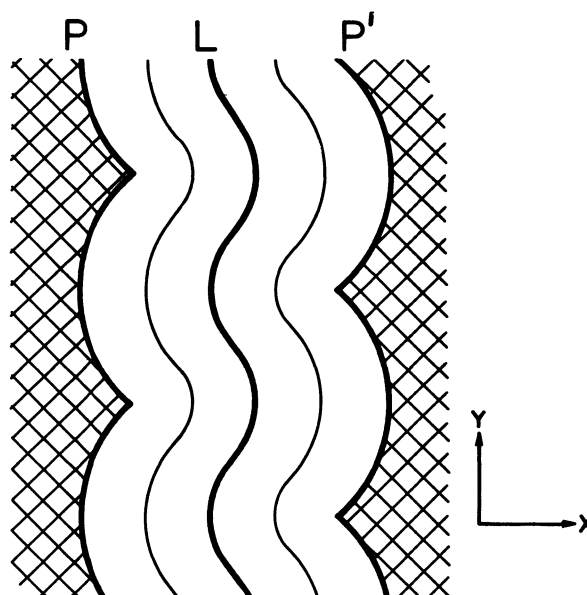


Fig. 4. — Schematic diagram of the undulating paired disclination structure shown in longitudinal section through the $z = 0$ plane. The cross-hatched areas mark the two central layers of each disclination.

gradually through the defect but it always remains in the plane of figure 3, that is, perpendicular to the local axis of the defect (line L). Since the ratio of the ordinary to extraordinary index of refraction is very close to 1.0 [24], the ordinary and extraordinary rays will follow the same straight path [25-26] through the crystal [27]. The light intensity emerging from the defect region will be elliptically polarized, and will not be totally extinguished by a crossed analyser. The only exceptions appear where the incident electric field is polarized parallel or perpendicular to the tangent to L, in which case the light polarization is all ordinary or extraordinary and thus remains linearly polarized. The light intensity passing through the crossed analyser is proportional to $\cos^2(2\alpha) \sin^2(\delta/2)$, where δ is the phase difference between the ordinary and extraordinary rays. The magnitude of δ is given by Asher and Pershan [10] as a function of x , the distance from P along PL in figure 3. Thus, as indicated schematically in figures 5a-b there will be two dark « pie slices » per period along the polarizer or analyser direction, perpendicular to the appropriate line segment of L; they are centred at the cusps in line P (P') and spread out to line P' (P). In figure 1, these « pie slices » are visible only where the polarizer or analyser are parallel or perpendicular to the mean axis of the paired disclinations in the center. In figure 2b the polarizer and analyser are crossed at 45° to the mean axis of the paired disclinations resulting in bright « cones ».

Fluorescence microscopy independently verifies the proposed structure of the undulations (Fig. 2c, d). The fluorescent dye molecule has a transition dipole lying in the plane of the smectic layers [20]; fluorescence is

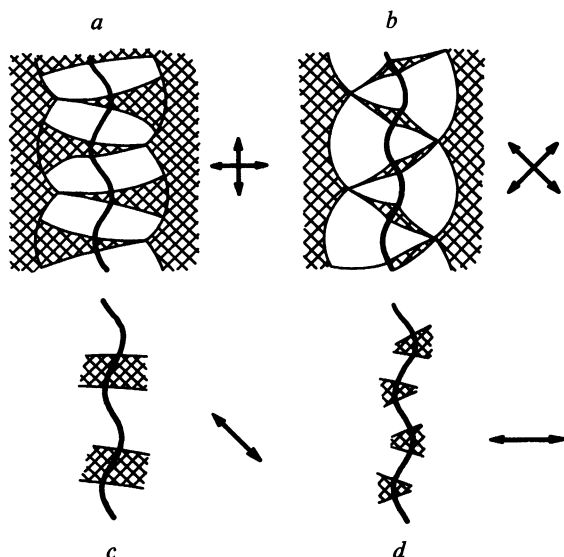


Fig. 5. — Optical properties of the structure of figures 3 and 4. Cross hatching indicates areas with little light intensity. *a)* and *b)* crossed polarizers, oriented as marked. Compare figure 1 with 5*a*) and figure 2*b* with 5*b*. *c)* and *d)* fluorescence, the polarization of the exciting light is indicated by the arrow. Compare figure 2*c* with 5*c* and figure 2*d* with 5*d*.

not excited if the plane polarized incoming excitation light has no component locally parallel to the tangent of line L (Fig. 4), as is schematically shown in figures 5*c*-*d*.

We observe that neighbouring paired disclinations interact. This is seen in the photomicrograph of figure 6, where the adjacent paired disclinations have the same periodicity and their undulations are in phase. The coupling between the periodicities of adjacent paired disclinations disappears where they separate (Fig. 7). Paired disclinations at different heights in thick specimens can also interact.

3. Discussion.

The undulations of the paired disclinations always exist in our homeotropically aligned fully hydrated specimens of DMPC-water in the L_α phase. Straight paired disclinations are seen in the P_β phase [28], a low temperature phase of DMPC-water. Upon heating, the undulations appear spontaneously at the phase transition to the L_α phase.

The undulations occur irregardless of the presence (Fig. 1, 6-7) or absence (Fig. 2) of cusped smectic layers (Fig. 3) enveloping the molecular planes involved in the paired disclinations. There is no deliberately applied pressure normal to the smectic layers. We believe that the adventitious macroscopic stress associated with the formation of undulations is negligible because there is ordinarily no long term flow of the liquid crystals, and, if stress is applied to move the oily streaks, the undulations remain.

Macroscopic flow is allowed because the multilayers are unsupported at their edges, being surrounded with water.

If large multilayer vesicles (composed of concentric smectic layers about a water core) are forced into a homeotropic (planar) configuration by the loss of water from the core, undulations appear spontaneously as the edges of the flattening multilayer vesicles flow toward each other. Undulations usually appear while some free water remains inside the flattened vesicles and before contact between vesicles occurs. Thus it is apparently not necessary for the surface of the inner bilayer to reach its limit for undulations to occur. This process takes place as the water level outside of the vesicle is lowered below the original height of the vesicle and excess water drains out probably through flaws in the layer structure. The layers do remain fully hydrated. The edge of a flattened vesicle is a $+1/2$ disclination. We have recorded this process on video tape using a silicon intensified television camera (SIT) attached to the microscope. The undulations between two $15\ \mu\text{m}$ long vesicle edges that are initially straight can appear in less than 100 ms.

We have measured the geometrical properties of about twenty paired disclinations using crossed polarizers and a micrometer eyepiece. The paired disclinations varied in width from 2 to $10\ \mu\text{m}$. We find that the periodicity of isolated paired disclinations is about 0.9 ± 0.1 times the apparent optical width of the paired disclinations as seen between a crossed polarizer and analyser oriented at 45° to the mean defect axis (Fig. 2*b*). The amplitude of the undulations is more difficult to determine because the central line L is observable only in the paired disclinations with large burgers vector. In these, the period to amplitude ratio is observed to vary from 1.3 to 4.

The driving energy for the undulations of the paired disclinations is not clear to us. We have considered qualitatively various contributions to the energy of paired disclinations without finding evidence that the undulations should reduce it relative to a straight structure. There are four terms that contribute to the energy of a disclination in a smectic: (1) a surface energy, (2) a core energy and two elastic energy terms (3) dilatational energy and (4) splay energy.

The surface energy term seems to be negligible because the occurrence and geometry of the undulations is observed to be independent of whether the paired disclinations are sandwiched between other smectic layers (whether or not there is a lipid-water interface).

The core of a disclination is described by a core radius, which is probably a few molecular lengths, and a core energy per unit length [29]. The observed bending of the core due to the undulations should not affect the core energy per unit length very strongly but it would increase the core's contribution to the total energy due to the increase in core length.

Outside of the core radius, the usual linear elastic

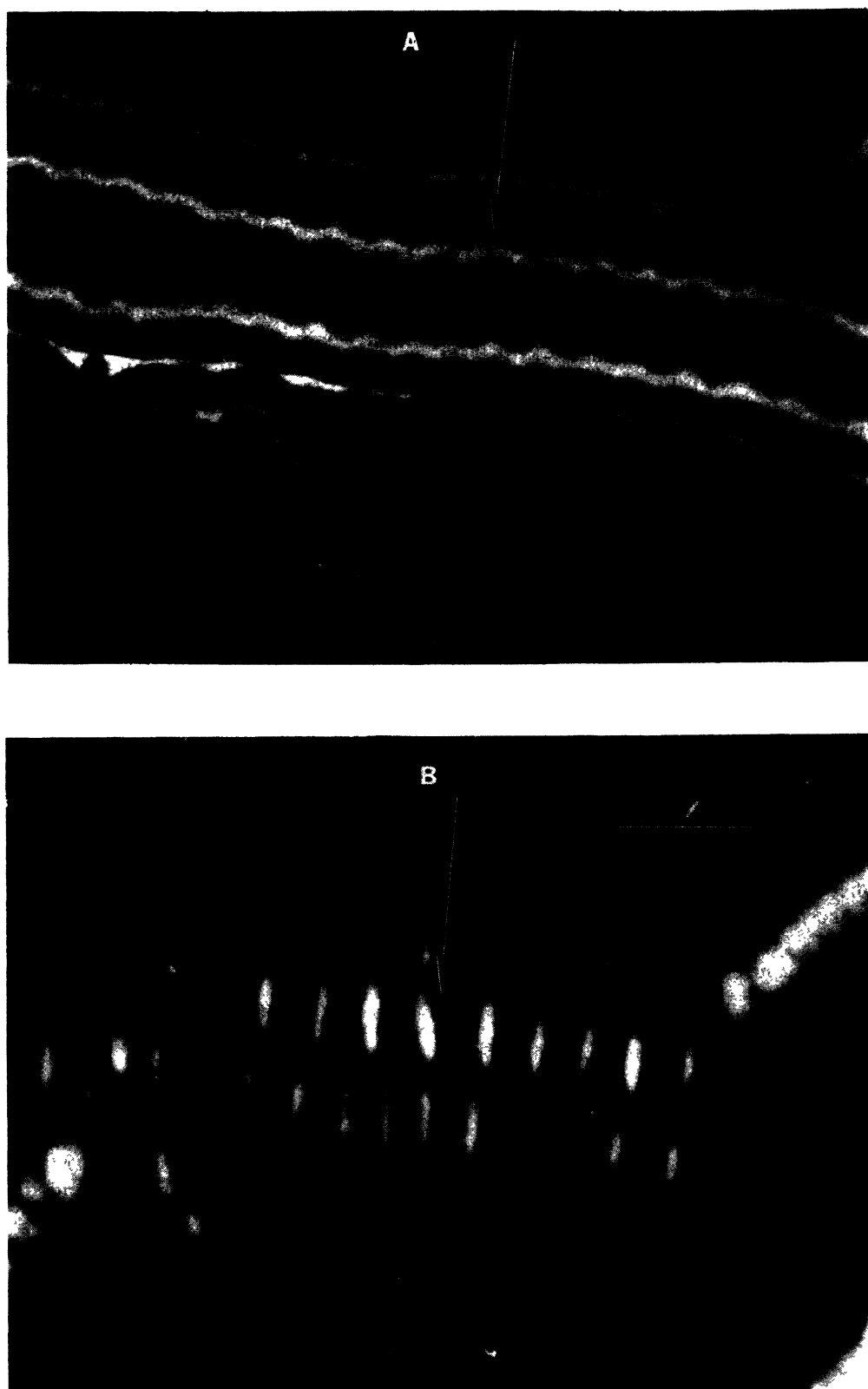


Fig. 6. — Photomicrographs of interacting paired disclinations *a*) phase contrast *b*) crossed polarizers oriented parallel and perpendicular to the edges of the paper. The long arrow indicates the same point in both illustrations. In *b*) the undulation phase is made visible by placing a birefringent material, with its axes aligned at a small angle to the axis of the polarizer, between the specimen and the analyser. This makes the parts of the defect separated by half an undulation period optically inequivalent. The undulations of adjacent defects are in phase. The specimen is about $10\ \mu\text{m}$ thick. The bar in *b*) is $10\ \mu\text{m}$ long.

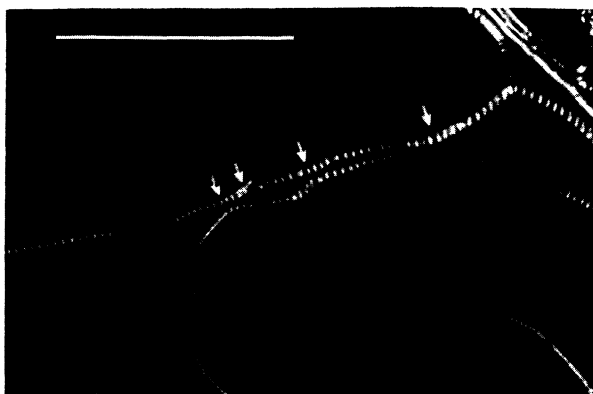


Fig. 7. — Dependence of the interaction of paired disclinations on their spacing. As the paired disclinations diverge their periodicities lose synchronization. Crossed polarizers are oriented parallel and perpendicular to the edges of the paper. The specimen is about 4 μm thick. The bar is 10 μm long.

theory for smectics dominates. The elastic energy consists of a dilation energy term (described with elastic modulus $\bar{B}$) and a splay energy term (described with elastic modulus K_1) [30]. In general, the distance between smectic layers in a disclination must remain nearly constant because $\bar{B}$ is very large compared with K_1/R^2 where R is radius of the layer. We calculated the splay energy of the crystal with the undulations and find that it is about one third larger than the splay energy of the crystal with a straight structure. Thus it seems that the undulations should increase the energy of the crystal.

Several other undulation phenomena observed in smectics have been described by the linear elasticity theory. Kléman [31] has suggested that the bead-like modulations at the centre of cylindrical layer patterns observed by Cladis [32] near the smectic to nematic phase transition may be understood in terms of a reduction of splay energy by modulations that form one minimal surface (radii of curvature at each point are equal but opposite in direction) near the defect core. The surrounding layers are placed smoothly around this surface at the expense of dilation energy. This model implies modulations only on the spatial scale of $\lambda = (K_1/\bar{B})^{1/2}$ which is about 100 Å [24] for our crystals.

The elasticity theory is used to explain the periodic corrugation instability introduced in homeotropically aligned smectic A liquid crystals by tension perpendicular to the molecular planes. The theory finds the fundamental period depends on the crystal thickness, t , as well as on λ leading to a macroscopic period $P \sim (t\lambda)^{1/2}$ [33-36]. We performed the analogous calculation for smectic A layers oriented in concentric cylinders under a radial tension and found that an undulation of the layers is induced with a period $P \sim (b\lambda)^{1/2}$ where b is the diameter of the outermost layer, contrary to our observation that $P \sim b$. Thus we have not accounted for the undulations using the traditional linear elasticity theory of liquid crystals and we are now investigating an alternative theory in which each layer is treated as an independent two dimensional liquid.

We note that no relaxation of the undulations occurs on annealing.

4. Conclusion.

We tend to think that the undulations are probably inherent properties of the structure of the paired disclinations in these materials. We suspect that the paired disclinations with transverse striations previously reported elsewhere [1-16] are complicated patterns of the isolated and the interacting paired disclinations like those we have described rather than rows of focal conics as previously suggested [1, 17]. We have not understood the true cause of the observed undulations of disclination pairs in smectic A lyotropic liquid crystals, but we believe that we have identified the gross features of these defect structures. There may well be other distinctive features not visible at the resolution of the light microscope.

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