Preferred equilibrium structures of a smectic-A phase grown from an isotropic phase: Origin of focal conic domains

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Preferred equilibrium structures of a smectic-A phase grown from an isotropic phase have been investigated theoretically and experimentally. The surface-integral equation reported in our recent paper [H. Naito, M. Okuda, and Z. Ou-Yang, Phys. Rev. Lett. **70**, 2912 (1993)] and a surface-differential equation are derived from the Euler-Lagrange equations for the variation of the nucleation energy of the smectic-A phase. Toroidal structures of the smectic-A phase are shown to be solutions of both equations and are observed experimentally in binary mixtures of octyloxycyanobiphenyl with dodecyl alcohol. It is also shown that focal conic domains are developed from such structures.

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Focal conic domains (FCD's) in a smectic-A liquid crystal (Sm-A LC) have been extensively studied ever since the discovery of FCD's by Friedel and Grandjean in 1910 [1]. FCD's are certainly represented in terms of a family of Dupin cyclides [2–4] where the Sm-A layers preserve the interlayer spacing. However, as Bragg has questioned [3], why the cyclides are preferred to other geometrical structures under the preservation of the interlayer spacing is still open. Kleman has evaluated the energy of an isolated FCD on the basis of a pure elastic energy theory [5] and concluded that the eccentricity of the elliptic disclination line in the FCD is one at the minimum of the energy [6]. However, Nakagawa [7] has pointed out that this conclusion contradicts the experimental results, which are that certain values of the eccentricity have been observed [3,4]. The theoretical approach to the FCD problem in Ref. [7] was that the uniaxial Sm-A theory was changed to the so-called biaxial Sm-A theory but still within the framework of the elastic energy theory. On the other hand, Bragg has suggested the importance of the thermodynamic generation of the geological structures such as contortions of strata in the Sm-A phase. FCD's are undoubtedly thermally generated; FCD's are formed by cooling a LC from the isotropic (I) or nematic (N) phase to the Sm-A phase [3,4]. Thus, efforts have been made to understand the development of FCD's [8,9] by means of nucleation and growth theories [10]. In these studies, however, the preference for FCD's (or Dupin cyclides) has not been discussed theoretically from the energetic point of view. For this reason, we stress that Bragg's question mentioned above is still open.

Recently, we have investigated the equilibrium shapes of a Sm-A phase grown from an I phase [11]; we have derived the integral equation that describes the equilibrium condition of the Sm-A–I interface, and have successfully explained the equilibrium cylinder structures with or without beaded configurations observed in the growth of the Sm-A phase [12]. Unfortunately, the integral equa-

tion in Ref. [11] gives only the necessary condition of the equilibrium structures of the Sm-A phase and does not predict the shapes of the preferred structures.

In this paper, we derive the general shape equation of the Sm-A phase in an I phase for the prediction of the preferred equilibrium shapes and confirm the theoretical prediction experimentally in the binary mixture of octyloxycyanobiphenyl (8OCB) with dodecyl alcohol (DODA). We find that the toroidal structures of the Sm-A nucleus are equilibrium shapes and show that FCD's are developed from such structures.

The Sm-A nucleus grown from an I phase can be described as a layer whose inner and outer surfaces are parallel surfaces [13]; the inner and outer surfaces are represented by $\vec{Y}(u,v)$ and $\vec{Y}(u,v) + D\vec{n}(u,v)$, respectively, where u and v are parametric coordinates of the surface, D is the thickness of the layer, and $\vec{n}(u,v)$ is the unit outward normal vector of both surfaces. As described in our previous paper [11], the net difference in the energy between the Sm-A and the I phase is the sum of the three terms: (1) the volume free energy change due to the I–Sm-A transition [11]

$$F_V = -g_0 V = -g_0 \oint (D - D^2 H + \tfrac{1}{3}D^3 K) dA, \qquad (1)$$

where $g_0 (>0)$ is the difference in the Gibbs free energy density between Sm-A and I phases, V is the volume of the Sm-A phase, and H and K are the mean and Gaussian curvatures of the inner surface, respectively, (2) the surface energy of the inner and outer Sm-A–I interfaces [13]

$$F_A = \gamma \oint [1 + \epsilon(1 - 2DH + D^2 K)] dA, \qquad (2)$$

where ϵ is equal to $+1$ or -1 according as $1 - 2DH + D^2 K$ is positive or negative [11], and (3) the curvature elastic energy of the Sm-A nucleus [14]

$$F_c = \frac{k_{11}}{2} \oint 2\sqrt{H^2 - K} \ln\left(\frac{1 - DH + D\sqrt{H^2 - K}}{1 - DH - D\sqrt{H^2 - K}}\right) dA$$

$$+ (2k_{11} + k_5)D \oint K dA, \tag{3}$$

where k_{11} is the splay elastic constant of the Sm-A, and k_5 is defined as $2k_{13} - k_{22} - k_{24}$, k_{ij} are the Oseen-Frank elastic constants. All the surface integrals are carried out over the inner surface $\vec{Y}(u,v)$. Then, the total free energy of the Sm-A layer in the I phase is

$$F = F_V + F_A + F_c = \oint \psi(H, K, D)dA, \tag{4}$$

where $\psi(H, K, D)$ is the sum of the integrands of Eqs. (1)–(3). Thus, the preferred equilibrium structures of the Sm-A nucleus are obtained from the solutions of the variation problem, $\delta F = 0$.

Since the nucleation energy is a function of $\vec{Y}(u,v)$ and D, we can derive the two Euler-Lagrange (EL) equations from the variation of F with respect to D and $\vec{Y}(u,v)$. The first EL equation is

$$\oint (2k_{11}\bar{H}^2 + k_5\bar{K} - g_0 - 2\gamma\bar{H})d\bar{A} = 0, \tag{5}$$

obtained from the straightforward calculation, $\partial F/\partial D = \oint \psi_D dA = 0$, where $\psi_D = \partial\psi/\partial D$, $\bar{H} = \epsilon(H - DK)/(1 - $

$2HD + D^2K)$, $\bar{K} = K/(1 - 2HD + D^2K)$, and $d\bar{A} = \epsilon(1 - 2HD + D^2K)dA$. Note that Eq. (5) is identical to the equilibrium condition of the outer surface, $\vec{Y}(u,v) + D\vec{n}(u,v)$ [13], which has been reported in our recent paper [11].

The second EL equation is calculated from $\delta F/\delta \vec{Y}(u,v) = \vec{0}$ and is the general shape equation of the Sm-A nucleus [15],

$$(2H^2 - K + \tfrac{1}{2}\nabla^2)\psi_H + (2HK + \bar\nabla^2)\psi_K - 2H\psi = 0, \tag{6}$$

where $\psi_H = \partial\psi/\partial H$, $\psi_K = \partial\psi/\partial K$, ∇^2 is the Laplace-Beltrami operator defined as $(1/\sqrt{g})\partial_i(g^{ij}\sqrt{g}\partial_j)$, $\bar\nabla^2$ is a new operator that we define as $(1/\sqrt{g})\partial_i(KL^{ij}\sqrt{g}\partial_j)$, $\partial_1 = \partial_u$, $\partial_2 = \partial_v$, $g = \det(g_{ij})$, $L^{ij} = (L_{ij})^{-1}$, and g_{ij} and L_{ij} are associated with the first and second fundamental forms of the surface, respectively. Equation (6) is identical to the equilibrium condition of bilayer vesicles derived in Ref. [16] for $\psi_K = 0$. This condition is a simple extension of the shape equation of bilayer vesicles at mechanical equilibrium [17], but Eq. (6) is a more general expression and hence the derivation of Eq. (6) requires more laborious calculation [15]. As an example of the generality, we show that Eq. (6) is also identical to the Gauss-Bonnet theorem, $\delta \oint K dA = 0$, for $\psi = K$.

Substituting ψ into Eq. (6), we have

$$\frac{k_{11}}{2}\left\{(\nabla^2 H - \bar\nabla^2)\frac{1}{\sqrt{H^2 - K}}\ln\left(\frac{1 - DH + D\sqrt{H^2 - K}}{1 - DH - D\sqrt{H^2 - K}}\right) + 2D\left[\nabla^2(H - DK) - \bar\nabla^2(1 - DH)\right]\frac{1}{1 - 2DH + D^2K}\right\}$$

$$+ k_{11}\frac{2D(H^2 - K)(2H - DK)}{1 - 2DH + D^2K} - (2H - KD)(2\gamma - g_0D) = 0. \tag{7}$$

It is evident that spheres and cylinders [11,12] are always the solutions of Eq. (7) when their H and K satisfy $k_{11}\frac{2D(H^2 - K)(2H - DK)}{1 - 2DH + D^2K} - (2H - KD)(2\gamma - g_0D) = 0$. We show that the equilibrium condition of the inner surface, $\oint(2k_{11}H^2 + k_5K - g_0 + 2\gamma H)dA = 0$, in Ref. [11] can be derived from Eqs. (5) and (7). These findings indicate that our previous results are consistent with the present analysis.

Our next interest is in formation processes of FCD's; we believe that FCD's are developed from one of the solutions of Eq. (7). At the early stage of the growth of the Sm-A nucleus, D increases from zero to $2\gamma/g_0$ with decreasing temperature at an optimum cooling rate. Indeed, there exist such optimum cooling rates from the N or I phase to observe FCD's [9]. It is, therefore, reasonable to write $D = 2\gamma/g_0$ at a constant temperature in the Sm-A phase (D is temperature dependent because of $g_0 \simeq \frac{\Delta H(T_c - T)}{T_c v_m}$ [9], where ΔH is the transformation enthalpy, T_c is the transition temperature, and v_m is the molar volume of the LC). D is expected to be much smaller than the geometrical size of the nucleus and thereby Eq. (7) can be linearized with respect to D. The linearized equation is

$$\nabla^2 H + 2H(H^2 - K) = 0. \tag{8}$$

This equation is a well-known surface equation and is satisfied by minimal surfaces and spheres [16]. We should note that a Clifford torus expressed as $\vec{Y}(u,v) = ((\sqrt{2} + \cos v)\cos u, (\sqrt{2} + \cos v)\sin u, \sin v)$ ($0 \leq u,v \leq 2\pi$) and its conformal transformation [18] are the solution of Eq. (8) as well. Such toroidal nuclei can be regarded as seeds of FCD's as illustrated in Ref. [19] because it has been shown that a spherical Sm-A nucleus is unstable [11,12]. The conformal invariability of Eq. (8) provides an explanation for the key characteristics of FCD's, which the size of FCD's is distributed even in the same sample [1–3] and which FCD's are described by Dupin cyclides. We consider the following two possible reasons why toroidal structures are preferred: (i) a Gaussian-curvature elastic modulus k_5 is positive (this means that the Gaussian-curvature elastic energy of the toroidal structures is lower than that of spherical structures) [18] and (ii) genus-1 surfaces like a Clifford torus and its conformal transformation are at the absolute minimum of the curvature energy, $\oint H^2 dA$, known as the Willmore conjecture [20] [$\frac{k_{11}D}{2} \oint (2H)^2 dA$ is the approx-

imated form of Eq. (3) in case where $k_5 D \oint K dA$ is neglected and $D \ll$(the size of the Sm-A nuclei)].

We demonstrate this prediction concerning the origin of FCD's experimentally. The LC material used here was the binary mixture of 8OCB and DODA whose phase diagram has been reported by Pratibha and Madhusudana [12]. In this system, the N phase is suppressed for a molar concentration ($> 20\%$) of DODA and the I and Sm-A phases coexist in a fairly wide temperature range. The LC cells of dimensions 10×10 mm^2 and of thickness 50 μm bounded by glass plates were prepared. The sample temperature was controlled in a hot stage (Mettler FP82HT) with a processor (Mettler FP90). The growth processes and the equilibrium shapes were observed with a polarizing microscope (Nikon) equipped with a video camera (Sony DXC-151A). The images were recorded and fed into an image processor (Shimadzu Nexus600).

The cells with 40% of 8OCB were cooled from the I phase at -0.1 °C/min and the cooling was stopped at a temperature in the coexisting region for the observation of equilibrium Sm-A shapes. The Sm-A appears initially in the form of a number of spherical droplets that grow in size and then start elongating into a cylindrical structure. The cylinders rapidly grow and become long and entangled threads [12]. The threads suddenly collapse forming compact domains at the LC-glass interfaces (Fig. 1). Figure 2 shows a representative domain observed with the analyzer and polarizer crossed (a) and with the polarizer only (b). We can see that the domain has a toroidal structure as predicted theoretically.

In order to confirm our observation further, we simulated polarizing-microscope images of the toroidal structures by means of a method described in Ref. [21]. The cross sectional area of the toroidal structure in this simulation is schematically illustrated in the inset of Fig. 3, where R and r are the radii of the two generating circles of the inner toroidal surface of the Sm-A nucleus and have been demonstrated to have the relation $R/r = \sqrt{2}$ [18], and $\bar{D}$ [$= 2(R + r + D)$] and $\bar{d}$ [$= 2a = 2(r + D)$] represent the outer diameter and the width of the ring of the outer toroidal surface, respectively. The transmitted light intensity I_T through the polarizer, the LC slab, and
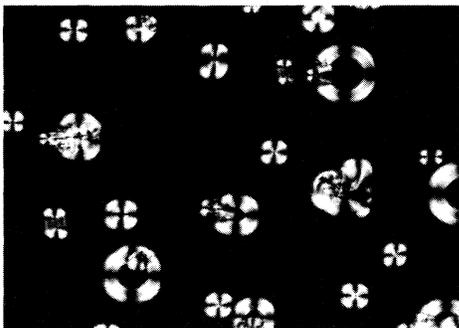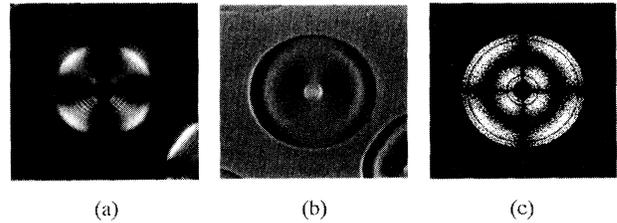
(a)   (b)   (c)

FIG. 2. Equilibrium shape of a toroidal structure observed with the analyzer and polarizer crossed (a) and with the polarizer only (b). The picture is about 70 μm wide. Simulated texture for a toroidal structure under crossed polarizers (c). The width of the ring of the simulated structure is 20 μm.

finally the analyzer is calculated to be [15]

$$I_T = \cos^2 u \sin^2(u)\| - 1$$
$$+ \exp[i2\pi\{n_e(v) - n_0\}\ell(v)/\lambda_0]\|^2, \quad (9)$$

where $0 \le u \le 2\pi$ and $0 \le v \le \pi$, $n_e(v) = n_0 n_e / \sqrt{n_0^2 \cos^2 v + n_e^2 \sin^2 v}$, $\ell(v) = \{\sqrt{x^2 - (x - 1)^2 \cos^2 v} - (x - 1)\sin v\}D$, $x = \sqrt{2}/\{1 + \sqrt{2} - (\bar{D}/\bar{d})\}$, $D = \bar{d}/(2x)$, λ_0 is the wavelength of the incoming light, and n_e and n_0 are the principal refractive indices for extraordinary and ordinary ray, respectively. In this calculation, we use values of $n_0 = 1.5$ and $n_e = 1.7$ typical of cyanobiphenyl liquid crystals, and ignore diffraction effects and the tilt of the LC molecules [21]. Figure 2(c) shows the simulated texture for $\bar{d} = 20$ μm. We can see that there is a good resemblance between the observed texture and the computer generated texture, especially in the concentric patterns near the outer and inner edges of the toroidal structure.

It is expected that the range of the values of $\bar{D}/\bar{d}$ is
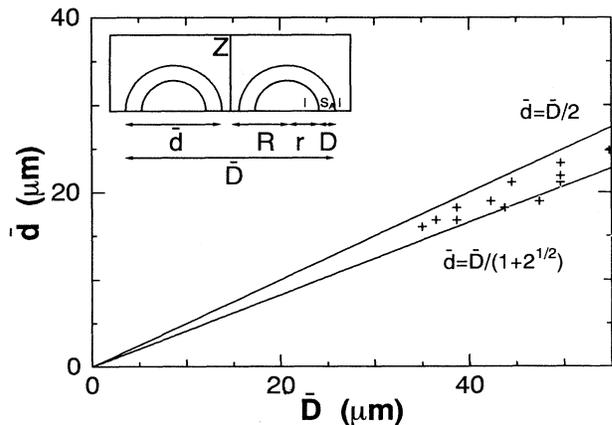
$$2 \le \bar{D}/\bar{d} \le 1 + \sqrt{2}. \quad (10)$$

FIG. 1. Equilibrium shapes of Sm-A domains grown from the I phase at 40 °C in the mixture of 8OCB and DODA observed under crossed polarizers (the molar concentration of 8OCB is 40%). The picture is about 385 μm wide.

FIG. 3. A plot of the outer diameter $\bar{D}$ vs the width of the ring, $\bar{d}$ of the equilibrium toroidal structures observed at 40 °C in the mixture of 8OCB and DODA. The molar concentration of 8OCB is 40%. Two solid lines represent $\bar{d} = \bar{D}/2$ and $\bar{d} = \bar{D}/(1 + 2^{1/2})$. The inset shows the schematic illustration of the cross sectional area of the toroidal structure. The z axis is the axis of rotational symmetry.

We measured $\bar{D}/\bar{d}$ values for various toroidal structures and indeed find that the values are in the range of Eq. (10) as shown in Fig. 3. In this figure, we show the toroidal structures with $\bar{D}$ less than the cell thickness, because the equilibrium structures of Sm-A nuclei change as shown in Fig. 1 when $\bar{D}$ reaches a critical value close to the cell thickness. The size of the Sm-A nucleus is determined by γ, g_0, and k_{11}. Since $a = xD$, we obtain

$$\sqrt{x^2 - 4x + 2}(8x^2 - 4x) = q(x - 1) \qquad (11)$$

from Eq. (5) [15], where $q = \sqrt{2}k_{11}g_0/\gamma^2$ is a dimensionless quantity. Using $k_{11} = 10^{-6}$ dyn [5], $\gamma = 10^{-2}$ dyn/cm [9,11], and $g_0 \approx 10^4(T_c - T)$ ergs cm^{-3} [9], we have $q = 0 \sim 10^2$ and thereby $x = 2 + \sqrt{2} \sim 10$ [15]. This corresponds well to the relation in Eq. (10). Furthermore, the value of D ($= 2\gamma/g_0$) is in the order of μm. These results are consistent with the observation shown in Figs. 1–3.

Finally, we mention that FCD's are not always generated from axisymmetric toroidal nuclei as is evident from the conformal invariability of Eq. (8). For non-axisymmetric toroidal structures of the Sm-A nucleus such as Dupin cyclides, the geometrical restriction, Eq. (11), derived from Eq. (5) becomes very complex (all kinds of elliptic integrals are involved) but can determine the eccentricity of the elliptic disclination line in the FCD's [15].

In summary, we have derived the two shape equations for Sm-A nuclei grown from the I phase by the variation of the Sm-A nucleation energy with respect to D and $\vec{Y}(u, v)$; one is Eq. (5), which is identical to the surface-integral equation in Ref. [11] and the other is Eq. (6). A toroidal structure is shown to be a solution of these shape equations and are observed in the binary mixture of 8OCB and DODA. The thermal generation of the toroidal structure is controlled by the difference in the Gibbs free energy between the Sm-A and I phases, the curvature elastic energy of the Sm-A nucleus and the interface energy, and plays a key role of the formation of FCD's because of the conformal invariability of Eq. (8). We stress that the shape equation, Eq. (6) has significance in the nucleation and growth theory for other complex fluids or soft matters.

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[15] The details will be described in a future publication by the current authors.

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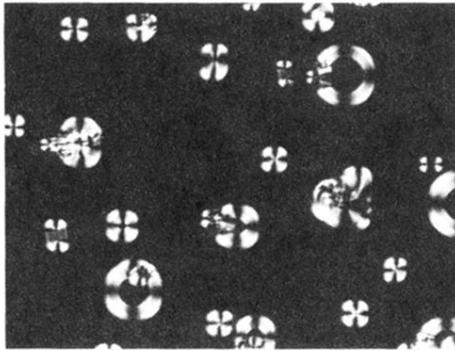FIG. 1. Equilibrium shapes of Sm-A domains grown from the I phase at 40 °C in the mixture of 8OCB and DODA observed under crossed polarizers (the molar concentration of 8OCB is 40%). The picture is about 385 μm wide.
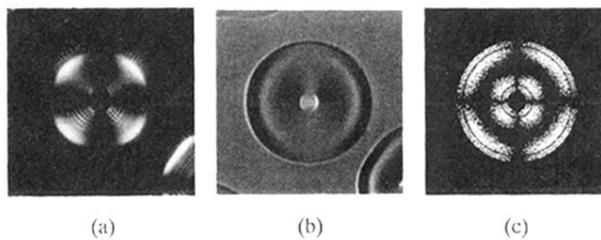
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