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STABILITY OF UNDULOIDLIKE SHAPES OF SMECTIC-A PHASE GROWN FROM ISOTROPIC PHASE

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Abstract Stability of unduloidlike shapes of a smectic A (Sm-A) phase grown from an isotropic (I) phase has been studied. An equilibrium shape equation for smectic A phase is derived by taking account of the difference in a Gibbs free energy between the smectic A and the isotropic phase, a curvature elastic energy of the smectic A phase, and an interface energy. The stability of unduloidlike shapes has been experimentally examined in the binary mixture of octyloxycyanobiphenyl with dodecyl alcohol. The experimental results can be theoretically explained in case where the experimentally observed surfaces are unduloid of Delaunay's surfaces.

INTRODUCTION

Smectic A (Sm-A) phase grown from isotropic (I) phase exhibits a variety of shapes as temperature is lowered.[1–5] For instance, the shapes of the Sm-A phase grown from the I phase in the binary mixtures of smectogenic and non-mesomorphic aliphatic compounds such as mixtures of octyloxycyanobiphenyl (8OCB) and dodecyl alcohol (DODA) have been studied, and are batonnets, spheres, cylinders and undulated cylinders.[1] However, the theoretical treatment for the stability of undulated cylinders of Sm-A phase is still an open question.[6]

In this paper, we derive the general shape equation and the stability condition for equilibrium Sm-A phase grown from the I phase.[5,6] The stability of unduloidlike shapes of Sm-A phase in I phase observed in the mixtures of 8OCB and DODA is discussed in terms of the present theory.

EXPERIMENT

The liquid crystal material used here was the binary mixture of 8OCB and DODA whose phase diagram has been reported by Pratibha and Madhusudana.[1] 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 liquid crystal 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 CCD video camera (Sony DXC-151A). The images were recorded and fed into an image processor (Shimadzu Nexus600).

THEORY

We consider the outward growth by adding a Sm-A layer of the thickness d on the surface of the outermost equilibrium Sm-A nucleus, and will derive the expressions for the corresponding net increase in the interfacial area and volume for the Sm-A domain. Then, we will derive the general shape equation and the stability condition for the growth of Sm-A domain.

If segments of constant length are laid off along the normals to a surface S of the outermost equilibrium Sm-A nucleus, the locus of their end points in general is a surface S' which is called a parallel surface of S. Obviously if $\underline{Y}(u^1, u^2)$ is a representation of S,

$$\underline{Y'}(u^1, u^2) = \underline{Y}(u^1, u^2) + d\underline{n}, \tag{1}$$

is a representation of S', where $\underline{n}$ is the unit normal vector to S. We choose the curvature coordinates as $g_{12} = 0$ and $L_{12} = 0$, where g_{ij} and L_{ij} are the first and second fundamental forms of the surface S. From the Weingarten equation,[8] $\partial_i \underline{n} = -L_{ij} g^{jk} \underline{Y}_k$, we have the relation,

$$\partial_1 \underline{Y'} = \underline{Y'_1} = \underline{Y_1} + d\partial_1 \underline{n} = (1 - dc_1)\underline{Y_1}, \tag{2}$$

where c_1 $(= L_{11} g^{11})$ is one of the principal curvatures. We also have

$$\underline{Y'_2} = (1 - dc_2)\underline{Y_2}. \tag{3}$$

Thus, the first fundamental form of S' are

$$\begin{aligned} g'_{11} &= (1 - dc_1)^2 g_{11}, \\ g'_{12} &= 0, \\ g'_{22} &= (1 - dc_2)^2 g_{22} \end{aligned} \tag{4}$$

and

$$g' = (1 - dc_1)^2 (1 - dc_2)^2 g. \tag{5}$$

The outerward unit normal vector, $\underline{n'}$, to S' is given by

$$\sqrt{g'}\underline{n'} = \underline{Y_1'} \times \underline{Y_2'} = (1 - dc_1)(1 - dc_2)\sqrt{g}\underline{n}. \tag{6}$$

It is evident from the above expression that the surfaces, S and S', have the same normals:

$$\underline{n'} = \epsilon \underline{n}, \tag{7}$$

where ϵ is equal to ± 1 according as

$$(1 - dc_1)(1 - dc_2) = (1 - 2dH + d^2K) \tag{8}$$

is positive or negative, where H and K are the mean curvature and the Gaussian curvature of the outer surface of the equilibrium Sm-A nucleus, respectively.

From Equations (2), (3), and (7), we have

$$L_{11}' = \underline{n'} \cdot \underline{Y_{11}'} = \epsilon \underline{n}[(1 - dc_1)\underline{Y_{11}} + \underline{Y_1}\partial_1(1 - dc_1)] = \epsilon(1 - dc_1)L_{11} \tag{9}$$

$$L_{12}' = \underline{n'} \cdot \underline{Y_{12}'} = \epsilon \underline{n}[(1 - dc_1)\underline{Y_{12}} + \underline{Y_1}\partial_2(1 - dc_1)] = \epsilon(1 - dc_1)L_{12} = 0 \tag{10}$$

$$L_{22}' = \epsilon(1 - dc_2)L_{22}. \tag{11}$$

Since $g_{12}' = 0$ and $L_{12}' = 0$, the surfaces have the same parametric coordinate. Thus, the difference in the area between the surfaces is

$$\begin{aligned} \delta A &= \oint \sqrt{g'}dudv - \oint \sqrt{g}dudv \\ &= \oint(-2dH + d^2K)dA, \end{aligned} \tag{12}$$

for the case where d is much smaller than the size of the Sm-A surface and hence ϵ is equal to 1.

We define

$$p = \underline{Y} \cdot \underline{n} \tag{13}$$

and the difference in the volume between the two surfaces, δV is obtained as

$$\begin{aligned} \delta V &= \frac{1}{3}[\oint p'dA' - \oint pdA] \\ &= \frac{1}{3}\oint[(d - 2d^2H + d^3K) + p(-2dH + d^2K)]dA. \end{aligned} \tag{14}$$

We further reduce the above expression to

$$\delta V = \oint(d - d^2H + \frac{1}{3}d^3K)dA. \tag{15}$$

using the following two equations[7]:

$$\oint pHdA = -\oint dA \tag{16}$$

and

$$\oint pKdA = -\oint HdA. \tag{17}$$

The bulk energy variation is given by $\delta F_V = -g_o \delta V$, where g_o is the difference in the Gibbs free energy densities between I and Sm-A phases. Since the isotropic phase is metastable, while the Sm-A phase is stable, g_o is positive. The extra interface energy is $\delta F_A = \gamma dA$, where γ is the I–Sm-A interfacial tension. In addition to these energies, the extra growth costs a curvature elastic energy[9]

$$\delta F_C = \frac{1}{2} k_{11} d \oint (2H)^2 dA + k_5 d \oint KdA, \tag{18}$$

where k_{11} is the splay elastic constant of the Sm-A, and k_5 is defined as $2k_{13} - k_{22} - k_{24}$, which are the Oseen-Frank elastic constants. Then, the net energy of the growth has the form,

$$\begin{aligned} F &= \delta F_C + \delta F_A + \delta F_V \\ &= \oint [-\frac{1}{3} g_o K d^3 + (g_o H + \gamma K) d^2 + (2k_{11} H^2 + k_5 K - g_o - 2\gamma H) d] dA. \end{aligned} \tag{19}$$

This expression can be seen as a third-order function of d. In case of the shapes having spherical topology, the coefficient of d^3 in Equation (19) is negative because of $g_o > 0$ and $\oint KdA = 4\pi$ (the Gauss-Bonnet theorem). The absolute minimum of F of the equilibrium shapes must be located at $d = 0$, requiring that the coefficients of d^2 and d in Equation (19) are positive and zero, respectively. From the requirement we have the general shape equation for the outermost layer of the Sm-A domain,

$$\oint [2k_{11} H^2 + k_5 K - g_o - 2\gamma H] dA = 0, \tag{20}$$

and the stability condition,

$$\oint [g_o H + \gamma K] dA > 0. \tag{21}$$

The equilibrium shape equation and the stability condition for the inner growth can be obtained by simply replacing H with $-H$.[6]

RESULTS AND DISCUSSION

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 which grow in size and then start elongating into a cylindrical structure. The cylinders rapidly grow and become long and entangled threads.[1,2,5] In rare cases the cylinders having beaded configuration (unduloidlike shape) were found (Figure 1(a)). The threads suddenly collapse forming compact domains at the LC/glass interfaces. It is obvious from the experimental results that the unduloidlike shape is unstable.

We have discussed the stability of spherical and cylindrical Sm-A domains in I phase, but have not discussed the stability of unduloidlike Sm-A domains.[6] Since the experimentally observed unduloidlike shape can be expressed as unduloid of Delaunay's surfaces, we examine the stability using the mathematical expression for Delaunay's surfaces. In 1841 Delaunay[10] has shown that the surfaces of revolution with constant mean curvature in Euclidean space are catenoids ($H = 0$), unduloids, nodoids, circular cylinders, and spheres. These surfaces are called Delaunay's surfaces. Delaunay's surfaces can be constructed by rolling a given conic section on a line in a plane, and rotating about that line the trace of a focus. The surfaces are expressed as[11]

$$\sin\psi(\rho) = a\rho + d\rho^{-1}, \tag{22}$$

where the two parameters, a and d determine the types of the surfaces: (i) the unduloids: $0 < ad < 1/4$ and (ii) the nodoids: $ad < 0$. The spheres and the circular cylinders are corresponding to the two limiting cases: when $d \to 0$ the unduloids become the spheres, and when $ad \to 1/4$ the unduloids degenerate to the cylinders. The contour $z(\rho)$ can be obtained from an integration

$$z(\rho) - z(\rho') = \int_{\rho'}^{\rho} \tan\psi(\rho'')d\rho''. \tag{23}$$

where $\psi(\rho)$ is the angle ψ between the surface tangent and the plane perpendicular to the axisymmetric axis (z axis) and ρ is the distance from the z axis. We fitted Equations (22) and (23) to the texture in Figure 1(a), we obtained $a = 1.67\times 10^{-2}$ μm^{-1} and $d = 5.00$ μm.

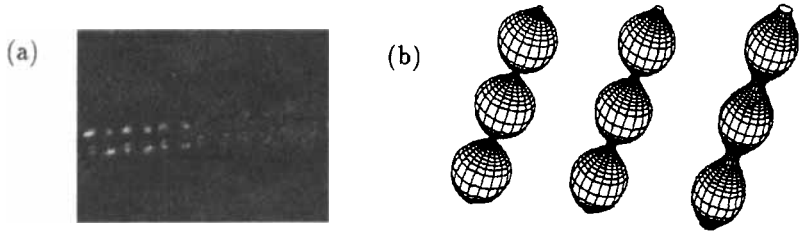

FIGURE 1 (a) An undulated cylinder of Sm-A phase observed in the binary mixture of 8OCB and DODA. The picture is about 200 μm wide. (b) Unduloids of the Delaunay's surfaces for $a = 1.67\times 10^{-2}$ μm^{-1} $d = 5.00$ μm, $a = 1.67\times 10^{-2}$ μm^{-1} $d = 6.67$ μm, and $a = 1.67\times 10^{-2}$ μm^{-1} $d = 10.0$ μm.

We examine the stability of the experimentally observed unduloidlike shape by substituting $H(= -a)$ and $K(= a^2 - d^2/\rho^4)$ for unduloid of Delaunay's surfaces into Equation (20) and (21). From the numerical analysis of Equation (20) and (21) for the values of k_{11}=10^{-6} dyn, k_5=$10^{-8}\sim 10^{-6}$ dyn, g_0=$1\sim 100$ ergs/cm^3 and γ=10^{-2} dyn/cm.[6] We find that the outward growth ($a > 0$) of the unduloid is unstable.

This is consistent with the experimental observation. On the other hand, the inward growth ($a < 0$) is always stable. These experimental and theoretical results are those of similar to those of spheres.[1,6]

CONCLUSIONS

We have derived the general shape equation and the stability condition for the equilibrium Sm-A domains by taking account of the I–Sm-A interface energy, the difference in Gibbs free energy between I and Sm-A phases, and the Sm-A curvature elastic energy.We apply the present theory to the analysis of the stability of experimentally observed unduloidlike shapes in the mixture of 8OCB and DODA. It is found that the unduloidlike shapes are unstable, consistent with the experiment, in case where the unduloidlike shapes are presented by unduloid of Delaunay's surfaces.

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