

## Equilibrium Shapes of Smectic-*A* Phase Grown from Isotropic Phase

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Equilibrium shapes of a smectic-*A* phase grown from an isotropic phase have been investigated. An integral equation which describes the equilibrium shapes is derived by taking account of the difference in Gibbs free energy between the smectic-*A* and the isotropic phase, a curvature elastic energy of the smectic-*A* phase, and an interface energy. It is shown that a popular family of solutions of the equation are given by some Weingarten surfaces. The equilibrium cylinder structures with and without beaded configurations observed in the growth of a smectic-*A* phase can be well explained in terms of such surfaces.

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A number of mesomorphic compounds exhibit the phase-transition sequence isotropic (*I*)-nematic (*N*)-smectic *A* (*S<sub>A</sub>*) as the sample is cooled, while some others go over directly to *S<sub>A</sub>* from the *I* phase. Normally, the shapes of the *S<sub>A</sub>* phase surrounded by the *N* or the *I* phase are batonnets, which are elongated structures consisting of focal conic domains [1]. However, the *S<sub>A</sub>* phase grown directly from the *I* phase can also form long cylindrical structures and some of these structures develop a beaded configuration. Investigators, captivated by the symmetry of the shapes, have made efforts to understand the formation mechanisms of such shapes [2-5].

The equilibrium shapes of a *S<sub>A</sub>* phase grown from an *I* phase are undoubtedly determined by the competition between the bulk and the interfacial energies. For the bulk energy, the *S<sub>A</sub>* phase has a lower Gibbs free energy than the *I* phase, but possesses an extra curvature elastic energy. The determination of the *S<sub>A</sub>* nucleus shape is, therefore, a puzzling theoretical problem. Recently Pratibha and Madhusudana have experimentally investigated the structures of the *S<sub>A</sub>* phase grown from the *I* phase in binary mixtures of smectogenic and nonmesomorphic aliphatic compounds such as mixtures of octyloxycyanobiphenyl (8OCB) and dodecyl alcohol (DODA), and have given a theoretical explanation for such structures [5]. However, their treatment of the problem is still insufficient, because the curvature mechanism of the interface between the *S<sub>A</sub>* and *I* phases has not been determined yet. In Ref. [5] the cylinder formation was explained by a spontaneous curvature due to the concentration gradients of the mixture of smectogenic and nonmesomorphic compounds, but the same structures have been found in some single-component systems [4]. Thus, the general questions which arise are as follows: What is the shape of the *S<sub>A</sub>* nucleus in the isotropic phase, and how can we describe it?

In this Letter we try to provide clear answers to these questions. We analytically obtain the general equilibrium-shape equation of the *S<sub>A</sub>* phase grown from the *I*

phase [6] and find that the shapes can be described by one of the Weingarten surfaces, which are extensively studied problems in differential geometry [7]. Some exact solutions of the equation are found and are in excellent agreement with the experimental findings [1-4], especially the recent observation in Ref. [5].

First, let us consider the outward growth by adding a *S<sub>A</sub>* layer of thickness *d* on the top of the outermost equilibrium *S<sub>A</sub>* nucleus. The corresponding net increase in the interfacial area and volume for the *S<sub>A</sub>* domain can be exactly expressed as

$$\delta A = \oint (-2dH + d^2K) \epsilon dA \quad (1)$$

and

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

respectively, where *H* and *K* are the mean curvature and the Gaussian curvature of the outer surface of the equilibrium *S<sub>A</sub>* nucleus, respectively, and  $\epsilon$  is equal to +1 or -1 according to whether  $1 - 2dH + d^2K$  is positive or negative [6]. The value of  $\epsilon$  is +1, because the layer thickness *d* is much smaller than the size of the nucleus and thereby  $1 - 2dH + d^2K$  is positive. The bulk energy variation is given by  $\delta F_V = -g_0 \delta V$ , where  $g_0$  is the difference in the Gibbs free energy densities between the *I* and *S<sub>A</sub>* phases. Since the isotropic phase is metastable, while the *S<sub>A</sub>* phase is stable, the free energy density difference  $g_0$  is positive. The extra interfacial energy is  $\delta F_A = \gamma dA$ , where  $\gamma$  is the *S<sub>A</sub>*-*I* interfacial tension. In addition to these energies, the extra growth costs a curvature elastic energy [8,9]

$$\delta F_C = (k_{11}d/2) \oint (2H)^2 dA + k_5 d \oint K dA, \quad (3)$$

where  $k_{11}$  is the splay elastic constant of the *S<sub>A</sub>*, 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

$$\begin{aligned}
 F &= \delta F_C + \delta F_A + \delta F_V \\
 &= \oint [(-g_0/3)Kd^3 + (g_0H + \gamma K)d^2 \\
 &\quad + (2k_{11}H^2 + k_5K - g_0 - 2\gamma H)d]dA. \quad (4)
 \end{aligned}$$

This expression can be seen as a third-order function of  $d$ . If we restrict ourselves to the study of the shapes having spherical topology, the coefficient of  $d^3$  in Eq. (4) is certainly negative because  $g_0 > 0$  and  $\oint K dA = 4\pi$  according to the Gauss-Bonnet theorem. By the definition of the equilibrium shape, the absolute minimum of  $F$  must be located at  $d=0$ , requiring that the coefficients of  $d^2$  and  $d$  in Eq. (4) are positive and zero, respectively. From these requirements we have the general equilibrium-shape equation for the outermost layer of the  $S_A$  domain,

$$\oint [2k_{11}H^2 + k_5K - g_0 - 2\gamma H]dA = 0, \quad (5)$$

and the stability condition

$$\oint [g_0H + \gamma K]dA > 0. \quad (6)$$

We illustrate the behavior of  $F$  as a function of  $d$  in Fig. 1. It is clearly seen that Eqs. (5) and (6) form the energy barriers which prevent the  $S_A$  nucleus at  $d=0$  from growing and dissolving.

It is now obvious that the equation of surface

$$2k_{11}H^2 + k_5K - g_0 - 2\gamma H = 0 \quad (7)$$

can always satisfy Eq. (5). A surface described by Eq. (7) is just one of the so-called Weingarten surfaces, on which there exists a functional relation between  $H$  and  $K$  [7]. For the examination of the shapes found in the experiments, we consider two kinds of obvious solutions of Eq. (7): One is a sphere and the other is a cylinder. Although both surfaces satisfy Eq. (7), the behavior in stability is completely different. For a sphere of radius  $r_0$ , we have  $H = -r_0^{-1}$  and  $K = r_0^{-2}$  and the unique solution calculated from Eq. (7) is

$$r_0 = \frac{k}{(\gamma^2 + g_0k)^{1/2} - \gamma}, \quad (8)$$

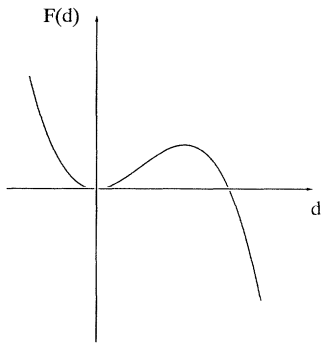


FIG. 1. Illustration of the net energy function  $F(d)$  which has the form of  $Ad^3 + Bd^2$  with  $A < 0$  and  $B > 0$ .

where  $k = 2k_{11} + k_5$ . Substituting the above solution into the integral in Eq. (6), we obtain

$$\begin{aligned}
 \oint [g_0H + \gamma K]dA &= 4\pi(\gamma - g_0r_0) \\
 &= -4\pi(\gamma^2 + g_0k)^{1/2} < 0, \quad (9)
 \end{aligned}$$

which states that Eq. (6) is not satisfied; in other words, a sphere is not stable. This theoretical prediction is supported by the observation at high concentration of DODA in the mixtures of 8 OCB and DODA [5]: At a sample cooling rate of  $0.1^\circ\text{C}/\text{min}$ , the  $S_A$  appears initially in the form of a number of spherical droplets which grow in size. This instability is consistent with the above results. After the droplets attain a radius of  $3\text{--}4\ \mu\text{m}$ , they start elongating and finally form cylinders with a constant radius of  $\sim 3\ \mu\text{m}$ .

The experimental evidence that a cylinder is a stable shape is also predicted by the present theory. The Weingarten equation, Eq. (7), with  $H = -(2\rho_0)^{-1}$  and  $K = 0$ , gives the expression for the radius of the cylinder  $\rho_0$ ,

$$\rho_0 = \frac{k_{11}}{(\gamma^2 + 2k_{11}g_0)^{1/2} - \gamma}. \quad (10)$$

If we assume that the influence of the caps at both ends is negligible (i.e.,  $L \gg \rho_0$ , with  $L$  the length of the cylinder) and  $L < 4\gamma/g_0$ , then the stability condition, Eq. (6), is satisfied,

$$\oint (g_0H + \gamma K)dA \cong \pi(4\gamma - g_0L) > 0. \quad (11)$$

Substituting the experimentally obtained values of  $\rho_0 = 3\ \mu\text{m}$  [5],  $k_{11} = 10^{-6}\ \text{dyn}$  [1], and  $\gamma = 10^{-2}\ \text{dyn}/\text{cm}$  [10] into Eq. (10), we have  $g_0 = 40\ \text{ergs}/\text{cm}^3$ . Using these values and Eq. (11), we find  $L < 10\ \mu\text{m}$ . These short and stable cylinders are just the feature of batonnets found in the early stage of the study of liquid crystals [1] as well as in the recent observation at low DODA concentration (Fig. 2 of Ref. [5]). On the other hand, if  $L > 4\gamma/g_0$ , the integral of Eq. (11) is negative. The cylindrical structures are, thereby, unstable and will rapidly elongate as found in the experiment; the cylinders with high DODA concentration rapidly grow to lengths  $\cong 500\ \mu\text{m}$  or more at a temperature which is  $2\text{--}3^\circ\text{C}$  below that at which they form [5].

It is evident from Eqs. (8) and (10) that the radius of the sphere and the cylinder is determined by the difference in the Gibbs free energy densities between the  $I$  and  $S_A$  phases, the  $S_A$  curvature elastic energy, and the  $S_A$ - $I$  interfacial tension. In other words, the spontaneous curvature is controlled by these quantities.

Second, we analyze the inward growth by adding a  $S_A$  layer onto the inner surface of the equilibrium nucleus of  $S_A$ . Here, we assume that the inside of the innermost  $S_A$  layer of the cylinders is filled with the  $I$  phase, and is called the core region hereafter, and that the equilibrium shape discussed below is defined at the inner surface. A

calculation similar to that mentioned above [6] has shown that we can obtain the equilibrium-shape equation and the stability condition for the inner growth by simply replacing  $H$  with  $-H$ . Indeed, Eqs. (6) and (7) are transformed into

$$\oint (-g_0 H + \gamma K) dA > 0 \quad (12)$$

and

$$2k_{11}H^2 + k_5K - g_0 + 2\gamma H = 0, \quad (13)$$

respectively. For the case of the spherical inner surface, the inner radius and the stability condition are

$$r'_0 = \frac{k}{(\gamma^2 + g_0 k)^{1/2} + \gamma} \quad (14)$$

and

$$\oint (-g_0 H + \gamma K) dA = 4\pi(\gamma + g_0 r'_0) > 0, \quad (15)$$

respectively. For the case of the cylindrical inner surface, the inner radius and the stability condition are

$$\rho'_0 = \frac{k_{11}}{(\gamma^2 + 2k_{11}g_0)^{1/2} + \gamma} \quad (16)$$

and

$$\oint (-g_0 H + \gamma K) dA \cong \pi(4\gamma + g_0 L') > 0, \quad (17)$$

respectively. It is evident that the inequalities, Eqs. (15) and (17), are always valid. Note from these results that unlike the outer-growth problem the spherical and cylindrical inner interfacial surfaces of the  $S_A$  domain are always stable. The above results also predict that a nucleus of a sphere or a cylinder whose radius is smaller than  $r'_0$  or  $\rho'_0$ , respectively, dissolves in the isotropic phase. It is observed that all the long cylinders at equilibrium have the core region [5]. Using the same values of  $\gamma$  and  $g_0$  as mentioned above we obtain from Eq. (16) the inner radius  $\rho'_0 = 0.43 \mu\text{m}$ , which is in excellent agreement with the experimental observation [5].

We mention here the shape transformation of cylinders filled with the  $S_A$  phase, i.e., without the core region. If the cylinders are unstable when they are bent these cylinders may grow and then form focal conic defects, which are the most common structures in the  $S_A$  phase. We speculate that this is a possible origin of the formation process of the defects. The detailed analysis of the formation process is, however, beyond the scope of the present Letter and will be published elsewhere.

Finally, we explain the undulated cylinder structures, which consist of successive beads, in terms of the present theory, i.e., Weingarten surfaces satisfying Eq. (7). These structures have been observed in the experiment on the growth of the  $S_A$  nucleus (see, for example, Fig. 8 in Ref. [5]). For simplicity, we neglect the  $k_5$  term in Eq. (7). In this case, Eq. (7) can be modified to

$$\left[ H - \frac{\gamma + (\gamma^2 + 2k_{11}g_0)^{1/2}}{2k_{11}} \right] \left[ H - \frac{\gamma - (\gamma^2 + 2k_{11}g_0)^{1/2}}{2k_{11}} \right] = 0. \quad (18)$$

Equation (18) indicates that the solution of the surface can be constructed by linking two kinds of hypersurfaces with constant mean curvature. In 1841, Delaunay [11] developed the following beautiful way of constructing a rotationally symmetric hypersurface with constant mean curvature: By rolling a given conic section on a straight line in a plane, and then rotating the trace of a focus about that line, one obtains a surface. As indicated in Fig. 2, the conic section is assumed to be an ellipse with the lengths of semiaxes  $a$  and  $b$ , where  $a > b$  and

$$a = \frac{k_{11}}{(\gamma^2 + 2k_{11}g_0)^{1/2} - \gamma}. \quad (19)$$

We obtain a periodically and rotationally symmetric surface with  $H = [\gamma - (\gamma^2 + 2k_{11}g_0)^{1/2}] / 2k_{11}$ , which satisfies Eq. (18), by Delaunay's method. The maximum and minimum radii of the surface are  $\rho_{\max} = a + (a^2 - b^2)^{1/2}$  and  $\rho_{\min} = a - (a^2 - b^2)^{1/2}$ , respectively, where the parameter  $b$  can be determined from the stability condition [Eq. (6)]. The detailed calculation for this is based upon the analysis of elliptic integrals, but we do not show the results here [6]. The pitch of the undulation  $p$ , which corresponds to the perimeter of the rolling ellipse, is also calculated from the elliptic integrals,

$$p = 4a \int_0^{\pi/2} (1 - k^2 \sin^2 \theta)^{1/2} d\theta = 4aE(k^2), \quad (20)$$

where  $k = (a^2 - b^2)^{1/2} / a$ . The threshold radii for the undulation are  $\rho_{\max} = \rho_{\min} = a$ , which lead to  $k = 0$ . In this case, the threshold pitch is given by

$$p = 2\pi a = 2\pi(\rho_{\max} + \rho_{\min}) / 2. \quad (21)$$

This pitch is different from that obtained by Pratibha and Madhusudana; their expression is

$$p = 2\pi(\rho_{\max} \rho_{\min})^{1/2}. \quad (22)$$

It is obvious from the properties of the elliptic integral [ $1.35 \leq E(k^2) \leq \pi/2$ ] that Eq. (21) is always a good approximation for Eq. (20), whereas Eq. (22) does not always give a reasonable result. For example, when  $\rho_{\min} \rightarrow 0$ , Eq. (21) gives a definite pitch which is exactly

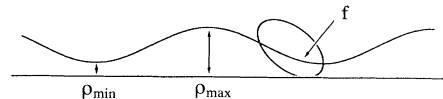


FIG. 2. Illustration of constructing a rotationally symmetric and periodic surface with constant mean curvature by Delaunay's method.  $f$  is the focus of an ellipse.  $\rho_{\max}$  and  $\rho_{\min}$  are the maximum and minimum radii of the surface.

equal to half of the perimeter of the sphere with the radius  $\rho_{\max}$ . A beaded structure which appears as a string of spheres is often found in lyotropic liquid crystals [12]. On the other hand, Eq. (22) gives  $p=0$ ; the undulated structure is a *string of coins*, which has never been observed in experiments.

A sphere of radius  $2a$  is the solution of  $H = [\gamma - (\gamma^2 + 2k_{11}g_0)^{1/2}]/2k_{11}$  as well, and is 2 times as large as the average radius of the cylinder with the undulated configuration  $[(\rho_{\max} + \rho_{\min})/2 = a]$ . We expect the existence of the structures which consist of the sphere and the undulated cylinder. Indeed, such structures have been found in the experiment and the observed radius of the sphere is just 2 times as large as the average radius of the undulated cylinder [see Fig. 8(b) in Ref. [5]]. We feel that these observations are strong evidence for the validity of the present theory. The structure generated by the other solution of Eq. (18) is not acceptable as a nucleus of the  $S_A$  phase, because the locus of the focus of the solution forms the nodary [11], and thereby inscribed hollow rings to the surface of the structure are formed periodically.

In summary, we have derived an equation, not found before, to describe the equilibrium shape of the growth of the  $S_A$  layer from the  $I$  phase. We show that a popular family of shape solutions is described by the Weingarten surfaces. The cylindrical structures with and without undulated configurations found in the experiment can be completely explained by the present theory. This indicates that these shapes are determined by the competition among the  $I$ - $S_A$  interface energy, the difference in  $I$  and  $S_A$  Gibbs free energies, and the  $S_A$  curvature elastic energy, and hence the spontaneous curvature of the  $S_A$  layers is governed by these quantities. To our knowledge a

surface equation which has an integral form has never been presented in either mathematics or physics before our present theory. The surface-integral equation [Eq. (5)] derived for the study of the  $S_A$ -nucleus shape has, therefore, general significance.

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