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Shape of The Cross Section in Freely Suspended Discotic Strands

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A free energy expression including surface terms is given for a freely suspended discotic strand near a phase transition. By means of symmetry considerations and the theory used in discussing the equilibrium shapes of crystals (ECS), the changes of the shape of the cross section and the Wulff plot structure through the phase transition are investigated.

Keywords: liquid crystal, phase transition, shape, surface

Freely suspended discotic strands can be formed in columnar liquid crystals with a two dimensional order in the plane perpendicular to the strand axis.[1,2] For HAT (triphenylene hexa-*n*-dodecanoate) materials, two different columnar (D_1 and D_2) phases and the phase transition from one to the other have been observed by either optical[1] or high resolution X-ray experiments.[2] In the low temperature D_1 phase, different orientational states (see the definition in Ref. 3 and 4) may separately exist along the strands, each of which corresponds to a single domain in the strand.[1] The symmetry analysis and suitable order parameter for the $D_2 - D_1$ transition in an infinite bulk system have been presented by the present authors.[5,6] Here, we will focus on the existence of a surface in the freely suspended strand system and related properties which may have significant changes through the $D_2 - D_1$ transition, *e.g.*, the surface free energy, shape of the cross section etc. These changes should be dominated by the symmetry change through the $D_2 - D_1$ transition, and therefore should be closely related to the order parameter.

The freely suspended discotic strand will be treated as an infinitely long system. The diameter of the strand is supposed to be large

enough as compared with the internal column spacing so that one can consider it to be composed of an infinitely long strand-like bulk system and a surrounding dividing surface, both of which are uniform along the strand. The total free energy per unit length, F, can then be written as $F = F_b + F_s$ (b means bulk and s, surface). We assume the system is in equilibrium with its environment.

For the sake of simplicity, we will ignore the molecular tilt and spontaneous strain effects[4,6] in the D_1 phase *i.e.* we will discuss a model system similar to that of Ref. 5.

The macroscopic properties of a crystal system depend on the symmetry of its crystal class[7] which is described by a suitable point group. In this sense, the change of the symmetry through the transition in our system can be considered from the C_{6v} point group to C_{2v} without loss of generality (see the arguments in Ref. 4). We will choose the coordinate system of Figure 1 of Ref. 4, so that the edges of the rectangular unit cell in the [1, 0, 0] state of the low temperature phase are parallel to the x and y axes.

Suppose the shape of the cross section in the high temperature phase is described by the equation

$$\Phi_0(x, y) = 0. \tag{1}$$

From the viewpoint of symmetry considerations, Eq. (1) should be invariant under C_{6v}. Of course this requirement can be simply satisfied if $\Phi_0(x, y)$ as a function of x and y is invariant under C_{6v} (this happens to be the case in the following). For a second order phase transition or a first order transition with small latent heat, in the low temperature phase near the transition point, a slight change of the shape of the cross-section from Eq. (1) is expected. The shape in the low temperature phase then described by

$$\Phi_0(x, y) + \delta\Phi(x, y) = 0 \tag{2}$$

where $\delta\Phi(x, y)$ is small.

We further expand $\delta\Phi(x, y)$ in Eq. (2) according to the irreducible representations (IR) of C_{6v}. The equilibrium form of $\delta\Phi(x, y)$, which minimizes the total free energy, $F = F_b + F_s$, should keep Eq. (2) invariant under C_{2v}. This requirement restricts the number of the permitted IRs of C_{6v} in the expansion of $\delta\Phi(x, y)$. The allowable IRs are τ_1 (the unit representation which preserves all the symmetry operations in C_{6v}) and τ_6 (the one which may lead to C_{2v} symmetry in

the low temperature phase) of C_{6v} in Zak's table.[8] So, we expand $\delta\Phi(x,y)$ as

$$\delta\Phi(x,y) = \epsilon_0\psi_0(x,y) + \epsilon_1\psi_1(x,y) + \epsilon_2\psi_2(x,y) \tag{3}$$

where ψ_0 is invariant under C_{6v}; and $\psi_1(x,y)$ and $\psi_2(x,y)$ transform according to IR of τ_6.

$\psi_1(x,y)$ and $\psi_2(x,y)$ give the possible modes of changes of the shape (ψ_0 is added to keep the area constant) and ϵ_1 and ϵ_2 are the amplitudes of the modes. Eq. (2) can be put in a form

$$y = y(x, \epsilon_0, \epsilon_1, \epsilon_2). \tag{4}$$

Now, we add the condition that the area of the cross-section is unchanged through the transition, *i.e.*

$$\int y dx = \text{const.} \tag{5}$$

Condition (5) means that only two of the three parameters (ϵ_0, ϵ_1, and ϵ_2) are independent; say ϵ_1 and ϵ_2 in the following. Now ϵ_1 and ϵ_2 may be regarded as order parameters in the density function,[7] and transform in the same way as $\psi_1(x,y)$ and $\psi_2(x,y)$ respectively. Further, any term in the free energy expression should be an invariant of C_{6v}. The total free energy per unit length of the strand can be written as

$$F = F_0 + \delta F \tag{6}$$

where

$$\delta F = \left(\frac{1}{2}r\eta^2 + u\eta^4 + v\sum_{i=1}^{3}\eta_i^4\right)A + \left(\frac{J}{2}\sum_{i=1}^{2}\epsilon_i^2 + \mu\sum_{i=1}^{2}\epsilon_i f_i(\{\eta_j\})\right)L \tag{7}$$

and where δF is the change of the free energy associated with the symmetry breaking through the transition; $f_1(\{\eta_j\})$ and $f_2(\{\eta_j\})$ are the lowest order possible homogeneous functions of $\{\eta_j\}$ which transform in the same way as ϵ_1 and ϵ_2. Thus, $f_1(\{\eta_j\}) = 2\eta_1^2 - \eta_2^2 - \eta_3^2$ and $f_2(\{\eta_j\}) = \sqrt{3}(\eta_2^2 - \eta_3^2)$ (See Eqs. (6a) and (6b) of Ref. 4). Also A is the area of the cross-section; and L, its boundary length. In the following, we choose the unit of length so that A is equal to unity. Then we have

$$\delta F = \frac{1}{2}r\eta^2 + u\eta^4 + v\sum_{i=1}^{3}\eta_i^4 + \frac{J}{2}L\sum_{i=1}^{2}\epsilon_i^2 + \mu L\sum_{i=1}^{2}\epsilon_i f_i(\{\eta_j\}). \tag{8}$$

If we neglect the last two terms, which represent the change of surface free energy, Eq. (8) reduces to Eq. (12) of Ref. 5. The stable values of $\{\eta_j\}$ and $\{\epsilon_i\}$ which minimize δF should be obtained from $\partial\delta F/\partial\eta_i = 0$, and $\partial\delta F/\partial\epsilon_i = 0$. Several sets of solutions are available. However the one which gives the extreme minimum value of δF should lead to the correct orientational states in the low temperature phase as observed experimentally.[1] This is the same as obtained in the bulk system.[4] For this reason, we minimize δF by the following steps:

(1) determine the orientation of $\{\eta_j\}$, $[\gamma_1, \gamma_2, \gamma_3]$ ($\eta_i = \gamma_i\eta$, $\gamma_1^2 + \gamma_2^2 + \gamma_3^2 = 1$) by neglecting the last two terms in Eq. (8),

(2) determine ϵ_1 and ϵ_2 in the given orientational state.

The results from step (1) are familiar. There are three orientational states in the low temperature phase, corresponding to $[\gamma_1^0, \gamma_2^0, \gamma_3^0] = [1, 0, 0]$, $[0, 1, 0]$, and $[0, 0, 1]$[5] respectively. Step (2) gives

$$\epsilon_1^0 = -\frac{\mu\eta^2}{J}[2\gamma_1^{02} - \gamma_2^{02} - \gamma_3^{02}] = \frac{1}{2}[2\gamma_1^{02} - \gamma_2^{02} - \gamma_3^{02}]\Delta \tag{9a}$$

$$\epsilon_2^0 = -\frac{\sqrt{3}\mu\eta^2}{J}[\gamma_2^{02} - \gamma_3^{02}] = \frac{\sqrt{3}}{2}[\gamma_2^{02} - \gamma_3^{02}]\Delta \tag{9b}$$

with $\Delta = -2\mu\eta^2/J$.

In either case, we have

$$\delta F|_{eq} = \frac{1}{2}r\eta^2 + (u + v)\eta^4 - \frac{2\mu^2}{J}L\eta^4. \tag{10}$$

where the subscript eq means that $\{\eta_i\}$ and $\{\epsilon_i\}$ in Eq. (8) take the values which minimize δF. The last term in Eq. (10) represents the change of the surface free energy and can be expressed as

$$\delta F_s|_{eq} = -\frac{2\mu^2}{J}L\eta^4 \tag{11}$$

So far we have not given the detailed form of the shape of the cross-section (*i.e.* that of $\Phi_0(x, y)$, $\psi_0(x, y)$, $\psi_1(x, y)$, and $\psi_2(x, y)$). The exact shape of the cross-section can only be obtained when the model system is solved by statistical mechanics with the given internal column interactions.[9] This is beyond our present knowledge. What we can do in the following is (1) give the approximate forms of $\Phi_0(x, y)$,

$\psi_0(x,y)$, $\psi_1(x,y)$ and $\psi_2(x,y)$ according to symmetry considerations (the shape of the cross-section is then given); (2) give the expression of the surface free energy per unit area from the given shape, from which the Wulff plot can be constructed; (3) calculate the change of total surface free energy through the transition and compare the results with Eq. (11) in order to determine the coefficient J in Eq. (8). This turns out to be associated with the detailed form of the shape of the cross-section, not just the symmetry.

Let us consider the [1, 0, 0] state in the low temperature phase. From Eqs. (9a) and (9b), we have

$$\epsilon_1^0 = -\frac{2\mu\eta^2}{J} = \Delta. \tag{12a}$$

$$\epsilon_2^0 = 0. \tag{12b}$$

The shape of the cross-section is now given by Eqs. (2), (3), and (12). *i.e.*

$$\Phi_0(x,y) + \epsilon_0\psi_0(x,y) + \Delta\psi_1(x,y) = 0 \tag{13}$$

with ϵ_0 being determined by Eq. (5). We expect that there no faceted surfaces and sharp corners appear in our system. The arguments are as following. In ECS problems, faceted surfaces corresponding to the low index planes stem from the existence of cusps in the Wulff plot,[7,9,10] which is closely related with the appearance of steps when the surface is oriented slightly differently from low index planes. As the temperature increases these cusps will be blunted by the thermodynamic fluctuations of the steps and finally disappear at the roughing transition temperature. Above the roughening temperature the shape of the equilibrium crystal will be totally rounded and close to a sphere as the melting point is approached. Now in columnar liquid crystals, the measured D_2 – Isotropic transition temperature (melting point) in HAT materials is 118°C (or 391°K), and the temperature range we are interested (near $D_2 - D_1$ transition) is around 105°C (or 378°K) which is fairly close to the melting point. In this case, we expect that the shape of the cross-section of the strand is everywhere rounded without facets and sharp corners, and even that the difference between the real shape and a circle is tiny. We suppose that the shape of the cross-section in the high temperature phase is a circle. So, we take

$$\Phi_0(x,y) = x^2 + y^2 - R^2 = 0. \tag{14}$$

As we mentioned above, $\psi_0(x,y)$, $\psi_1(x,y)$, and $\psi_2(x,y)$ are the basis of the relevant IRs of C_{6v}. Each of them can be formed by summing various homogeneous polynomials in different orders, and is generally a power series. We will limit these functions to include up to the quadratic polynomials and ignore the higher order corrections. Then we have

$$\psi_0(x,y) = C_1 + C_2(x^2 - y^2) \tag{15}$$

and

$$\psi_1(x,y) = x^2 - y^2 \tag{16a}$$

$$\psi_2(x,y) = 2xy\,. \tag{16b}$$

Substituting Eqs. (14) through (16) into Eq. (13), the shape of the cross-section in [1, 0, 0] state is given by

$$x^2 + y^2 - R^2 + \epsilon_0[C_1 + C_2(x^2 + y^2)] + \Delta(x^2 - y^2) = 0\,. \tag{17}$$

The term $\epsilon_0[C_1 + C_2(x^2 + y^2)]$ in Eq. (17) can further be written as $\epsilon_0(C_1 + C_2R^2) + C_2\epsilon_0(x^2 + y^2 - R^2)$. Near the transition ϵ_0 and Δ are small. We will see that ϵ_0 is in order of Δ^2 (see Eq. (19)), and $x^2 + y^2 - R^2$ is in order of Δ. So, $C_2\epsilon_0(x^2 + y^2 - R^2)$ is in order of Δ^3 and will be ignored in Eq. (17). We rename $\epsilon_0(C_1 + C_2R^2)$ as ϵ_0. Finally, Eq. (17) can be simplified to

$$x^2 + y^2 - R^2 + \epsilon_0 + \Delta(x^2 - y^2) = 0\,. \tag{18}$$

As a result of Eq. (5), we have

$$\epsilon_0 = (1 - \sqrt{1 - \Delta^2})R^2\,. \tag{19}$$

Putting Eq. (19) back into Eq. (18), we obtain

$$\frac{x^2}{\left[\left(\frac{1-\Delta}{1+\Delta}\right)^{1/4} R\right]^2} + \frac{y^2}{\left[\left(\frac{1+\Delta}{1-\Delta}\right)^{1/4} R\right]^2} = 1\,. \tag{20}$$

Eq. (20) is nothing but the equation of an ellipse with its two axes along x and y axes respectively. The Wulff plot structure, which can be constructed from the known surface free energy per unit area as

a function of the orientation of the interface, and the shape of the cross-section are connected by a Legendre transformation.[9,11] So, we can give the Wulff plot structures of our system in the high and low temperature phases from Eqs. (14) and (20) respectively. For the high temperature phase, the Wulff plot is apparently a circle because we assumed that the shape of the cross-section is a circle. Then the surface free energy per unit area $\alpha(\theta)$ as a function of the orientation of the interface should be

$$\alpha(\theta) = \alpha_0 = \text{Const.} \tag{21}$$

where the exact value of α_0 depends on the internal interactions among different columns. For the low temperature [1, 0, 0] state, we obtain from the Legendre transform

$$\alpha(\theta) = \bar{\alpha}\sqrt{1 - \Delta \cos 2\theta}\,. \tag{22}$$

Eq. (22) can easily be put in a more general form which fits all three orientational states:

$$\alpha(\theta) = \bar{\alpha}\sqrt{1 - \epsilon_1^0 \cos 2\theta - \epsilon_2^0 \sin 2\theta} \tag{23}$$

It can be proved that the Wulff plots constructed by Eq. (21) and Eq. (22) will give the shapes of the cross-section in high and low temperature phases exactly the same as described by Eqs. (14) and (20) respectively, by following the procedures in Andreev's paper.[11] Generally, $\bar{\alpha}$ in Eq. (23) may depend on ϵ_i^0, but it will not change the Wulff plot structure and the shape of the cross-section.

To see how the constant J in Eq. (7) depends on the shape of the cross section in the following, we will consider $\bar{\alpha}$ to be independent of ϵ_i^0. Then $\bar{\alpha}$ and α_0 will be the same because they should be equal when ϵ_i^0 approach to zero. The total surface free energy per unit length of the strand can be calculated by

$$F_s = \int \alpha(\theta) d\Sigma\,. \tag{24}$$

The intregral in Eq. (24) is over the whole surface area Σ. In the high temperature phase

$$F_s = 2\pi R \alpha_0 \tag{25}$$

and in the low temperature phase

$$F_s = 2\pi R\alpha_0(1 - \Delta^2)^{1/4} \approx 2\pi R\alpha_0\left(1 - \frac{1}{4}\Delta^2 + \cdots\right). \quad (26)$$

The change of the surface free energy through the transition is

$$\delta F_s = -\frac{\pi R\alpha_0}{2}\Delta^2 = -\frac{2\pi R\alpha_0\mu^2\eta^4}{J^2}. \quad (27)$$

On the other hand, Eq. (11) gives

$$\delta F_s = -\frac{2\mu^2}{J}L\eta^4 \approx -\frac{4\pi R\mu^2\eta^4}{J}. \quad (28)$$

Comparing Eq. (27) with (28), we find

$$J = \frac{\alpha_0}{2}. \quad (29)$$

If the corrections from the higher order polynomials are added to Φ_0, ψ_0, ψ_1, and ψ_2. The calculations after Eq. (14) should be reperformed. The results obtained for J can be expected to be different from Eq. (28). This means that the constant J depends on the details of the shape of the cross-section.

In this paper, we gave a free energy expression for a freely suspended discotic strand system in discussing the changes of the surface properties through a phase transition; An approximate shape of the cross-section in the low temperature phase and its dependence on order parameter were given; The Wulff plot structure was also obtained from the given shape; Finally, we indicated the dependence of the coefficients J on the detailed shape of the cross-section.

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References

1. D. H. Van Winkle and N. A. Clark, *Phys. Rev. Lett.*, **48**, 1407 (1982).
2. C. R. Safinya, K. S. Liang, W. A. Varady, N. A. Clark and G. Andersson, *Phys. Rev. Lett.*, **53**, 1172 (1984).
3. K. J. Aizu, *J. Phys. Soc. Japan*, **27**(2), 387 (1969).
4. Y. F. Sun and J. Swift, *Mol. Cryst. Liq. Cryst.*, **131**, 91 (1985).
5. Y. F. Sun and J. Swift, *J. Physique*, **48**, 1801 (1984).
6. Y. F. Sun and J. Swift, *Phys. Rev. A*, **33**, 2735, and 2740 (1986).
7. L. D. Landau and E. M. Lifshitz, "*Statistical Physics*," 3rd Edition (Pergamon Press, Oxford (1980)).
8. J. Zak, "*The Irreducible Representations of Space Groups*," (W. A. Benjamin, Inc., New York) 1969.
9. C. Rottman and M. Wortis, *Phys. Rep.*, **103**, 59 (1984).
10. C. Herring, "*The Use of Classical Macroscopic Concepts in Surface-Energy Problems*," in *Structure and Properties of Solid Surface*, eds. R. Gomer and C. S. Smith (University of Chicago Press, Chicago, 1953) pp. 5–72.
11. A. F. Andreev, *Sov. Phys. JETP*, **53**, 1063 (1981).