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Y. F. Sun [a] & J. B. Swift [a]
[a] Department of Physics, The University of Texas at Austin, Austin, Texas, 78712

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Trigger First Order Phase Transitions in Liquid Crystal Systems

Y. F. SUN and J. B. SWIFT

Department of Physics, The University of Texas at Austin, Austin, Texas 78712

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The experimentally observed D_{hd} (disordered hexagonal)—four sublattice $P321$ and D_{hd}—two sublattice $P2_1/a$ phase transitions in columnar liquid crystals are treated in a unified manner by means of the Laudau theory of phase transitions. They can be understood as a trigger first order phase transition associated with two coupled irreducible representations in an asymmetric model. Details of the symmetry analysis are also given.

Keywords: columnar liquid crystals, phase transitions

1. INTRODUCTION

The polymorphism of columnar liquid crystals and the vast number of various phase transitions among them were widely recognized in the last decade. For some discotic mesogens (e.g. HAT materials), the higher temperature phase is disordered hexagonal (D_{hd}). Two of the experimentally observed lower temperature phases from this D_{hd} phase through a phase transition are a 2 sublattice $P2_1/a$ phase[1,2] and a 4 sublattice $P321$ phase[3] depending on the materials. Both of these transitions are first order and the symmetry groups of the lower temperature phases ($P2_1/a$ and $P321$) can not be simply associated with only one irreducible representation of the higher temperature symmetry group ($P6/mmm$). This is different from the usual second order phase transition according to Landau theory.[4] A model associated with two irreducible representations was then suggested by the present authors[5] to explain the D_2–D_1 (i.e., D_{hd} $P6/mmm$ – 2 sublattice $P2_1/a$) phase transition and its first order property. In this paper, a similar technique is invoked to investigate the D_{hd} – 4 sublattice $P321$ phase transition which has not been discussed yet. Comparing with our previous work,[5] instead of a primitive derivation we directly generalize Gufan and Larin's results[6] to determine the required conditions that the phenomenological coefficients should be satisfied. In such a way, the D_{hd} – 2 sublattice $P2_1/a$ phase transition is also reconsidered, and the conclusions are more complete. We classify both of these transitions as a trigger first order phase transition in the sense of Gufan and Larin. In Section 2, we give a brief review of the asymmetric model for the systems associated with two one-dimensional irreducible representations and the main conclusions given by Gufan and Larin; details of the

symmetry analysis and a generalization of the two one-dimensional irreducible representations to two multi-dimensional irreducible representations are presented in Section 3; and a brief discussion is finally given in Section 4.

2. ASYMMETRIC MODEL

Phenomenological models applicable to the description of the phase transitions associated with two one-dimensional (1-D)irreducible representations (IR) have been investigated by several authors (e.g. Gufan and Larin[6]) within the framework of Landau theory. A review of this subject is now available in Tolédanó's book.[7] For our purpose, we will only consider their asymmetric models.[6,7] The results can be easily used to discuss P6/mmm-P321 ($D_{6h}^1 - D_3^2$) and P6/mmm-P2_1/a ($D_{6h}^1 - C_{2h}^5$) phase transitions in columnar liquid crystals, so that these transitions can be treated in a unified manner. According to Gufan and Larin,[6] the free energy may be expanded as a power series of the two order parameters and in their asymmetric model is

$$F = \frac{1}{2} r\eta^2 + \frac{1}{4} b\eta^4 + \frac{1}{6} w\eta^6 + \frac{1}{2} r'\xi^2 + \frac{1}{4} b'\xi^4 + \frac{1}{2} c\eta^2\xi^2. \tag{1}$$

In Equation 1, η and ξ transform according to two different 1-D IRs of the symmetry group for the original high temperature phase (O phase); also r, r', b, b', c, and w are phenomenological coefficients which are functions of the temperature T and pressure P. If no other higher order terms beyond Equation 1 need to be added to the free energy, one may assume a linear dependence of r, r', and c on T and P.[1] The possibility of the existence of a stable phase according to Equation 1 requires a positive definite condition of F for large ξ and η. This can only be guaranteed when both w and b' are greater than zero. Three kinds of low temperature ordered phases can then be obtained by minimizing F with respect to ξ and η, corresponding to phase I ($\eta \neq 0$, $\xi = 0$), phase II ($\eta = 0$, $\xi \neq 0$), and phase III ($\eta \neq 0$, $\xi \neq 0$). In some temperature and pressure range, a large value of the primary order parameter η will bring about an instability with respect to ξ and give rise to the direct O-III phase transition, through a first order transition line in the $r - r'$ plane. This has been called a trigger first order transition in Reference 6. It only appears in the first quadrant of the $r - r'$ plane when $c < -\sqrt{|b|b'}$ (remember $b' > 0$). With these restrictions on the coefficients ($b > 0$, $w > 0$, and $c < -\sqrt{|b|b'}$) and the stability condition (*i.e.* positive definiteness of the second derivatives of F with respect to η and ξ), the two possible phase diagrams in $r - r'$ plane which include the trigger first order transition line were plotted in Figure 1 c) and d) of Reference 6 corresponding to $b > 0$ and $b < 0$, respectively. Of course, the free energy expression for the trigger first order phase transition in columnar liquid crystals may not have the exactly same form as given in Equation 1. For example, we usually need to deal with multi-component order parameter in D-dimensional irreducible space ($D > 1$). However the asymmetric model still makes sense if the orientation of the order parameter in its irreducible space can be

determined first in the process of minimizing the free energy. The P6/mmm-P321 and P6/mmm-$P2_1/a$ transitions in columnar liquid crystals are selected in this paper as two examples to demonstrate such an approach.

To handle a symmetry breaking phase transition following Landau theory,[7,8] one should first identify the symmetry group of the high temperature phase.

3. P6/mmm-P321 AND P6/mmm-$P2_1/A$ PHASE TRANSITIONS

Although the correct symmetry group of the D_{hd} columnar system has been classified as a semi-direct product of a translational subgroup $T_H = R \times Z^2$ and a point group D_{6h},[8] it can often be suitably treated as a space group P6/mmm if the continuous translational symmetry along the column axis is frozen through the transition. This will limit our discussion so that we are unable to include some special phases (e.g. helicoidal structure).

As in Reference 10, we first introduce a tensor density function $\mathbf{Q}(\mathbf{r})$. Near the transition in the low temperature phase

$$\mathbf{Q}(\mathbf{r}) = \mathbf{Q}_o(\mathbf{r}) + \delta\mathbf{Q}(\mathbf{r}), \tag{2}$$

where $\mathbf{Q}_o(\mathbf{r})$ is invariant under G_o (P6/mmm). $\delta\mathbf{Q}(\mathbf{r})$ can be expanded as

$$\delta\mathbf{Q}_{ij}(\mathbf{r}) = \sum_{n,\alpha} T_{ij}^{n,\alpha}\Phi_{n\alpha}(\mathbf{r}), \tag{3}$$

where $\Phi_{n,\alpha}(\mathbf{r})$ is the αth basis function of the nth irreducible representation of G_o. The subscripts i and j in $T_{ij}^{n,\alpha}$ correspond to its transformation properties in real space. Also $T_{ij}^{n,\alpha}$ is a "vector" in the nth irreducible space of G_o spanned by $\{\Phi_{n\alpha}(\mathbf{r})\}$. Under a symmetry operation $g_i \in G_o$, the transformation properties of $\delta\mathbf{Q}_{ij}(\mathbf{r})$ in the irreducible space can be equivalently considered by rotating either the basis or the vector $T_{ij}^{n,\alpha}$. If one takes the latter view, $T_{ij}^{n,\alpha}$ will transform according to the direct product of the tensor representation $\Gamma_T^{(6)}$ (which is a 6-D representation) and the nth IR $\Gamma^{(n)}$.[10] The entire independent set $\{T_{ij}^{n,\alpha}\}$ will support a reducible representation of G_o, $\Gamma_R^{(n)}$, *i.e.*,

$$\Gamma_R^{(n)} = \Gamma_T^{(6)} \otimes \Gamma^{(n)}. \tag{4}$$

For a space group, the nth IR should be assigned by two indices, a wave vector $\mathbf{k}$ (which may generate a star contribution) and an IR $\tau_\rho(\mathbf{k})$ for the group of $\mathbf{k}$. When $\mathbf{k}$ is given, we take the following $\tau_\rho(\mathbf{k})$ to have the meaning given in Kovalev's table.[11] For simplicity, we will use τ_ρ in stead of $\tau_\rho(\mathbf{k})$ hereafter. Then

$$\delta\mathbf{Q}_{ij}(\mathbf{r}) = \sum_{\mathbf{k},\rho,\alpha} T_{ij}^{\mathbf{k}\tau\rho,\alpha}\,\Phi_{\mathbf{k}\tau_\rho,\alpha}(\mathbf{r}). \tag{5}$$

So far we have not neglected anything yet in expanding $\delta\mathbf{Q}_{ij}(\mathbf{r})$. According to the Landau theory of phase transitions, not all the IRs of G_o are relevant to a

given transition. For the problems under the considerations, at least the low temperature phase should continue to have a periodic structure. So only these wave vectors located at some high symmetry points in the first Brillouin zone are of interest. For example, to obtain the low temperature phase with the unit cell doubled ($P2_1/a$ phase) or quadrupled (P321 phase), we just need to take into account $\mathbf{k} = \mathbf{k}_o \equiv 0$ and $\mathbf{k} = \mathbf{k}_1 \equiv \mathbf{b}_1/2$ ($\mathbf{b}_1$ is the primitive vector of the reciprocal lattic[5]).

Therefore the summation over $\mathbf{k}$ in Equation 5 leaves two terms only, *i.e.*

$$\delta \mathbf{Q}_{ij}(\mathbf{r}) = \sum_{\rho,\alpha} T_{ij}^{\mathbf{k}_o\tau_\rho,\alpha}\, \Phi_{\mathbf{k}_o\tau_\rho,\alpha}(\mathbf{r}) + \sum_{\sigma,\beta} T_{ij}^{\mathbf{k}_1\tau_\sigma,\beta}\, \Phi_{\mathbf{k}_1\tau_\sigma,\beta}(\mathbf{r}). \tag{6}$$

However the summation over ρ (or σ) still involves too many irrelevant IRs. For the P6/mmm-P321 transition, we find that the related IRs come from $T_{ij}^{\mathbf{k}_o\tau_5,\alpha}$ and $T_{ij}^{\mathbf{k}_1\tau_6,\alpha}$. So, the final expansion of $\mathbf{Q}_{ij}(\mathbf{r})$ is of the form

$$\mathbf{Q}_{ij}(\mathbf{r}) = T_{ij}^{\mathbf{k}_o\tau_5}\, u_{\mathbf{k}_o}^{\tau_5}(\mathbf{r}) + \sum_{\alpha=1}^{3} T_{ij}^{\mathbf{k}_1\tau_6,\alpha}\, u_{\mathbf{k}_\alpha}^{\tau_6}(\mathbf{r}) \cos(\mathbf{k}_\alpha \cdot \mathbf{r}). \tag{7}$$

In Equation 7, the base function Φ has been put into a more explicit form: $\Phi_{\mathbf{k}_0}{}^{\tau_5}(\mathbf{r}) \equiv u_{\mathbf{k}_o}^{\tau_5}(\mathbf{r})$, $\Phi_{\mathbf{k}_\alpha\tau_6,\alpha} \equiv u_{\mathbf{k}_\alpha}^{\tau_6} \cos(\mathbf{k}_\alpha \cdot \mathbf{r})$, where $u_{\mathbf{k}_\alpha}^{\tau_6}(\mathbf{r}) = h_\alpha u_{\mathbf{k}_1}^{\tau_6}(\mathbf{r})$; $u_{\mathbf{k}_0}^{\tau_5}(\mathbf{r})$ and $u_{\mathbf{k}_1}^{\tau_6}(\mathbf{r})$ are the basis of the IRs for the group of $\mathbf{k}_o$ and $\mathbf{k}_1$ respectively, and they are invariant under the translational sub-group of G_o; $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ represent the three wave vector star; and $h_\alpha(\alpha = 1,2,3)$ has the meaning of Reference 11. We dropped the α index in $T_{ij}^{\mathbf{k}_o\tau_5}$ because $\Gamma^{\mathbf{k}_o\tau_5}$ is a 1-D IR. The non-equilibrium free energy now is totally determined by $\{T_{ij}^{\mathbf{k}_o\tau_5}\}$ and $\{T_{ij}^{\mathbf{k}_1\tau_6,\alpha}\}$, which span a 6-D and an 18-D reducible representation space, respectively. For the P6/mmm space group, these two spaces are automatically block diagonalized if we group T_{ij} as (T_{11}, T_{22}, T_{12}); (T_{13}, T_{23}); and T_{33}. In other words, each of the original reducible spaces is divided into several independent sub-spaces. Thus all the possible IRs of P6/mmm constructed by $\{T_{ij}^{\mathbf{k}\tau_\rho,\alpha}\}$ can be relatively easy to obtain by a linear combination of $T_{ij}^{\mathbf{k}\tau_\rho}$ within each sub-space. To select the IRs relevant to the P6/mmm-P321 transition, we focus on two of the sub-spaces. One is spanned by $\{T_{13}^{\mathbf{k}_1\tau_6,\alpha}, T_{23}^{\mathbf{k}_1\tau_6,\beta}\}$ ($\alpha,\beta = 1,2,3$), and the other, by $T_{11}^{\mathbf{k}_o\tau_5}$, $T_{22}^{\mathbf{k}_o\tau_5}$, and $T_{12}^{\mathbf{k}_o\tau_5}$. The projected IRs and the corresponding basis from these two sub-spaces are

$$\Gamma^{\mathbf{k}_o\tau_5}\colon\ \eta^{\mathbf{k}_o\tau_5} = \frac{1}{\sqrt{2}}\left(T_{11}^{\mathbf{k}_o\tau_5} + T_{22}^{\mathbf{k}_o\tau_5}\right) \tag{8}$$

$$\Gamma^{\mathbf{k}_o\tau_9}\colon\ \eta_1^{\mathbf{k}_o\tau_9} = \frac{1}{6}\left(T_{11}^{\mathbf{k}_o\tau_5} - T_{22}^{\mathbf{k}_o\tau_5} + i2T_{12}^{\mathbf{k}_o\tau_5}\right) \tag{9a}$$

$$\eta_2^{\mathbf{k}_o\tau_9} = \frac{1}{6}\left(T_{11}^{\mathbf{k}_o\tau_5} - T_{22}^{\mathbf{k}_o\tau_5} - i2T_{12}^{\mathbf{k}_o\tau_5}\right) \tag{9b}$$

$$\Gamma^{\mathbf{k}_1\tau_2}\colon\ \xi_1^{\mathbf{k}_1\tau_2} = \frac{1}{2}\left(\sqrt{3}T_{13}^{\mathbf{k}_1\tau_6,1} + T_{23}^{\mathbf{k}_1\tau_6,1}\right) \tag{10a}$$

$$\xi_2^{\mathbf{k}_1\tau_2} = T_{23}^{\mathbf{k}_1\tau_6,2} \tag{10b}$$

$$\xi_3^{\mathbf{k}_1\tau_2} = \frac{1}{2}(\sqrt{3}T_{13}^{\mathbf{k}_1\tau_6,3} - T_{23}^{\mathbf{k}_1\tau_6,3}) \tag{10c}$$

$$\Gamma^{\mathbf{k}_1\tau_4}\colon\ \xi_1^{\mathbf{k}_1\tau_4} = \frac{1}{2}(T_{13}^{\mathbf{k}_1\tau_6,1} - \sqrt{3}T_{23}^{\mathbf{k}_1\tau_6,1}) \tag{11a}$$

$$\xi_2^{\mathbf{k}_1\tau_4} = T_{13}^{\mathbf{k}_1\tau_6,2} \tag{11b}$$

$$\xi_3^{\mathbf{k}_1\tau_4} = \frac{1}{2}(T_{13}^{\mathbf{k}_1\tau_6,3} + \sqrt{3}T_{23}^{\mathbf{k}_1\tau_6,3}) \tag{11c}$$

Among the four IRs, $\Gamma^{\mathbf{k}_0\tau_5}$ and $\Gamma^{\mathbf{k}_1\tau_2}$ will be seen later to be responsible for the P6/mmm-P321 phase transition. Another of the two IRs ($\Gamma^{\mathbf{k}_0\tau_9}$ and $\Gamma^{\mathbf{k}_1\tau_2}$) and the IRs from the other sub-spaces are assumed to be irrelevant to the transition and are discarded in constructing the non-equilibrium free energy. Thus we have

$$F = \frac{1}{2}r\eta^2 + \frac{1}{4}b\eta^4 + \frac{1}{6}w\eta^6 + \frac{1}{2}r'\xi^2 + \frac{1}{4}u'\xi^4 + \frac{1}{4}v'(\xi_1^4 + \xi_2^4 + \xi_3^4) + \frac{1}{2}c\xi^2\eta^2 \tag{12}$$

where $\xi^2 = \xi_1^2 + \xi_2^2 + \xi_3^2$, and the simplified notation η for $\eta^{\mathbf{k}_0\tau_5}$ and ξ_i for $\xi_i^{\mathbf{k}_1\tau_2}$ have been adopted. The fact that no cubic invariants appear in F and that the only lowest order coupling term is $\frac{1}{2}\eta^2\xi^2$ are based on the symmetry analysis for P6/mmm group. These conclusion therefore possess a rigorous meaning. The term $\frac{1}{4}v'(\xi_1^4 + \xi_2^4 + \xi_3^4)$ in F uniquely determines the orientation of the order parameter, $\{\xi_i\}$, in its irreducible space, and can further be rewritten as $\frac{1}{4}v'\xi^4(\gamma_1'^4 + \gamma_2'^4 + \gamma_3'^4)$ if one introduces $\xi_i = \xi\gamma_i'$. The orientation parameters γ_1', γ_2', and γ_3' can be first determined by minimizing F with respect to γ_i' subject to the condition $\gamma_1'^2 + \gamma_2'^2 + \gamma_3'^2 = 1$. The results are (1) $(\gamma_1'^2, \gamma_2'^2, \gamma_3'^2) = (1, 0, 0)$, $(0, 1, 0)$, or $(0, 0, 1)$ if $v' < 0$. (2) $(\gamma_1'^2, \gamma_2'^2, \gamma_3'^2) = (1/3, 1/3, 1/3)$, if $v' > 0$. Apparently in either case, when we substitute these results to Equation 12, the free energy will have the same form as that in Equation 1 if one notices $b' = u' + v'$ in case (1) and $b' = u' + v'/3$ in case (2). When b', $w > 0$, and $c < -\sqrt{|b|b'}$ a trigger first order (O-III) phase transition line will be allowed to exist (see Figure 1 c) and d) in Reference 6). In either case, phase I is always the $P\bar{3}m1$ phase with the unit cell size unchanged. However the symmetry pattern of phase II (and therefore of phase III) is different for case (1) and case (2). To reach the 4-sublattice P321 phase through the trigger first order transition, one must take case (2). Then phase II has a 4-sublattice structure with P622 symmetry. Now the symmetry group for phase III (4-sublattice P321 phase) is merely the intersection of P622 and $P\bar{3}m1$. The criterion for checking these conclusions is to explicitly give the equilibrium form of $\delta\mathbf{Q}(\mathbf{r})$ and to determine the surviving subgroup of G_o under which $\delta\mathbf{Q}(\mathbf{r})$ is invariant. The equilibrium tensor density functions for phases I, II, and III can

be easily solved for by putting

$$\eta^{\mathbf{k}_o\tau_5} = \eta, \qquad \eta_i^{\mathbf{k}_o\tau_9} = \xi_j^{\mathbf{k}_1\tau_2} = \xi_k^{\mathbf{k}_1\tau_4} \equiv 0 \qquad \text{Phase I}$$

$$\eta^{\mathbf{k}_o\tau_5} = \eta_i^{\mathbf{k}_o\tau_9} = \xi_j^{\mathbf{k}_1\tau_4} \equiv 0, \qquad \xi_1^{\mathbf{k}_1\tau_2} = \xi_2^{\mathbf{k}_1\tau_2} = \xi_3^{\mathbf{k}_1\tau_2} \equiv \frac{1}{\sqrt{3}}\xi \qquad \text{Phase II}$$

$$\eta^{\mathbf{k}_o\tau_5} = \eta, \qquad \xi_1^{\mathbf{k}_1\tau_2} = \xi_2^{\mathbf{k}_1\tau_2} = \xi_3^{\mathbf{k}_1\tau_2} \equiv \frac{1}{\sqrt{3}}\xi, \qquad \eta_i^{\mathbf{k}_o\tau_9} = \xi_j^{\mathbf{k}_1\tau_4} \equiv 0 \qquad \text{Phase III}$$

into Equations (8) through (11). Substituting each set of the solution into Equation (7), we have

$$\delta\mathbf{Q}^I(\mathbf{r}) = \sqrt{2}\eta \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} u_{\mathbf{k}_o}^{\tau_5}(\mathbf{r}) \tag{13}$$

$$\delta\mathbf{Q}^{II}(\mathbf{r}) = \xi \begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2\sqrt{3}} \\ \frac{1}{2} & \frac{1}{2\sqrt{3}} & 0 \end{pmatrix} u_{\mathbf{k}_1}^{\tau_6}(\mathbf{r}) \cos(\mathbf{k}_1 \cdot \mathbf{r})$$

$$+ \xi \begin{pmatrix} 0 & 0 & -\frac{1}{2} \\ 0 & 0 & \frac{1}{2\sqrt{3}} \\ -\frac{1}{2} & \frac{1}{2\sqrt{3}} & 0 \end{pmatrix} u_{\mathbf{k}_2}^{\tau_6}(\mathbf{r}) \cos(\mathbf{k}_2 \cdot \mathbf{r}) \tag{14}$$

$$+ \xi \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{3}} \\ 0 & \frac{1}{\sqrt{3}} & 0 \end{pmatrix} u_{\mathbf{k}_3}^{\tau_6}(\mathbf{r}) \cos(\mathbf{k}_3 \cdot \mathbf{r})$$

$$\delta\mathbf{Q}^{III}(\mathbf{r}) = \delta\mathbf{Q}^I(\mathbf{r}) + \delta\mathbf{Q}^{II}(\mathbf{r}) \tag{15}$$

In Equations (13), (14), and (15), we did not insert the explicit expressions for the equilibrium values of ξ and η. These do not matter if we are only interested in the symmetry properties of $\delta\mathbf{Q}^I(\mathbf{r})$, $\delta\mathbf{Q}^{II}(\mathbf{r})$, and $\delta\mathbf{Q}^{III}(\mathbf{r})$. However one should understand that Equation (15) can only be formally written as the sum of $\delta\mathbf{Q}^I(\mathbf{r})$ and $\delta\mathbf{Q}^{II}(\mathbf{r})$, and the expressions for the equilibrium values of η and ξ in Equation (15) are different from that in Equation (13) and Equation (14).[6] Acting with all

the symmetry operations $g_i \in G_o$ (P6/mmm) on $\delta\mathbf{Q}^I(\mathbf{r})$, $\delta\mathbf{Q}^{II}(\mathbf{r})$, and $\delta\mathbf{Q}^{III}(\mathbf{r})$, and following the rule given by Equation (1) of Reference 5, it is not difficult to check that the surviving sub-group in these three cases is P$\bar{3}$m1, P622, and P321 respectively.

As for the P6/mmm-P2_1/a phase transition in columnar liquid crystals, we do not present the details because it has been previously discussed by the authors.[5] Here we just show how this phase transition may be put into the same frame work as a trigger first order phase transition for an asymmetry model. This approach will solve the problem in a more complete way. We directly read off the non-equilibrium free energy from Equation (2.5) of Reference 5:

$$F = \frac{1}{2}r\eta^2 + \frac{1}{4}u\eta^4 + \frac{1}{4}v\sum_{i=1}^{4}\eta_i^4 + \frac{1}{6}w\eta^6 + \frac{1}{2}r'\xi^2 + \frac{1}{4}u'\xi^4 + \frac{1}{4}v'\sum_{i=1}^{3}\xi_i^4 + \frac{1}{2}c_1\sum_{i,j=1}^{3}\eta_i^2\xi_j^2 + \frac{1}{2}c_2\sum_{i=1}^{3}\eta_i^2\xi_i^2 \tag{16}$$

where $\{\eta_i\}$ and $\{\xi_i\}$ transform according to the IRs $\Gamma^{\mathbf{k}_1\tau_3}$ and $\Gamma^{\mathbf{k}_1\tau_5}$; and $\mathbf{k}_1$ generates a three arm wave vector star. Due to the coupling term $c_2\Sigma_{i=1}^3\eta_i^2\xi_i^2$, we now can not independently determine the orientation of each order parameter set in its own irreducible space, but have to adjust their orientations simultaneously by minimizing $v\eta^4(\gamma_1^4 + \gamma_2^4 + \gamma_3^4) + v'\xi^4(\gamma'^4 + \gamma_2'^4 + \gamma_3'^4) + c_2\eta^2\xi^2(\gamma_1^2\gamma_1'^2 + \gamma_2^2\gamma_2'^2 + \gamma_3^2\gamma_3'^2)$ with respect to $\{\gamma_i\}$ and $\{\gamma_i'\}$ subject to the conditions $\gamma_1^2 + \gamma_2^2 + \gamma_3^2 = 1$ and $\gamma_1'^2 + \gamma_2'^2 + \gamma_3'^2 = 1$. The problem may turn to be complicated if there exist several stable solutions. Considering the 2-sublattice structure of the P2_1/a herringbone phase, it requires v, v', and $c_2 < 0$. Fortunately, under this condition the only stable orientations for both $\{\eta_i\}$ and $\{\xi_i\}$ are $(\gamma_1^2, \gamma_2^2, \gamma_3^2; \gamma_1'^2, \gamma_2'^2, \gamma_3'^2) = (0, 0, 1; 0, 0, 1)$, $(0, 1, 0; 0, 1, 0)$, and $(0, 0, 1; 0, 0, 1)$.[5] Putting these solutions back into Equation (16), F will again have the same form as that in Equation (1) if we denote $u + v = b$, $u' + v' = b'$, and $c_1 + c_2 = c$. Then if b', $w > 0$, and $c < -\sqrt{|b|b'}$,† a trigger first order phase transition line will exist in the first quadrant in the $r - r'$ plane (*i.e.* r, $r' > 0$). In our previous paper,[5] we assumed $b < 0$, this corresponds to Figure 1 c) in Reference 6. In fact, for $b > 0$ but $c < -\sqrt{bb'}$, a trigger first order phase transition from phase O to phase III is still available as shown in Figure 1 d) of Reference 6. Phase I and Phase II in this model are Figure 2a and Figure 3a in Reference 10. Phase III is the P2_1/a herringbone phase. The details of the symmetry analysis for the P6/mmm-P2_1/a ($D_2 - D_1$) transition can be found in Reference 5.

4. DISCUSSIONS

(1) For either the D_{hd}-4 sublattice $P321$, or D_{hd}-2 sublattice $P2_1/a$ phase transition, our model free energy (Equation 12 or Equation 16) supplies a reasonable first order transition mechanism and a perfect fit to the low temperature symmetry

†The condition $c < 0$ given in Reference 5 should be replaced by the condition given here.

patterns. However the theoretical approach given in the text predicts two possible phase diagrams corresponding to Figure 1 c) and d) in Reference 6 which can not be uniquely determined according to the experimental results reported so far.[1-3] In some temperature range, these phase diagrams also predict direct O-I and O-II phase transitions. For the materials to have the trigger transition behavior observed, a significant difference will be seen if their direct O-I and O-II transitions can be found. For the case of Figure 1 c) in Reference 6, both O-I and O-II transitions are the second order. On the other hand, for the case of Figure 1 d), the O-II transition is the second order, while the O-I transition is the first order. This can be used as the criterion to determine the sign of the coefficient b in Equation (12) and Equation (16).

(2) The technique developed in Reference 5, Reference 10, and this paper can also be invoked to discuss a number of possible low temperature phases reached through a second order phase transition if the transition stems from orientational symmetry breaking and is associated with only one IR of the high temperature symmetry group. For example, the in-plane symmetry breaking of the D_{hd} phase associated with IR $\Gamma^{\mathbf{k}_1\tau_3}$ due to the orientational order of the disc-like molecules will lead to either the 2-sublattice Pbam phase[9] or 4-sublattice P6/m phase depending on the coefficients u and v. For $v < 0$, $u + v > 0$, the stable low temperature phase is 2-sublattice Pbam phase (see Figure 2 in Reference 9). The relative molecular orientation in the two different sublattices are perpendicular to each other. If a spontaneous strain effect is allowed for, we predict a change of the relative molecular orientation (see Equation (16) in Reference 9). Following the same procedure as in Reference 9 and in section 3 of this paper, it is not difficult to deduce the equilibrium low temperature tensor density function for $v > 0$, and $u + \frac{1}{3} > 0$:

$$\delta\mathbf{Q}(\mathbf{r}) = \eta \begin{pmatrix} \frac{1}{2} & -\frac{1}{2\sqrt{3}} & 0 \\ -\frac{1}{2\sqrt{3}} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \cos(\mathbf{k}_1 \cdot \mathbf{r}) + \eta \begin{pmatrix} 0 & \frac{1}{\sqrt{3}} & 0 \\ \frac{1}{\sqrt{3}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \cos(\mathbf{k}_2 \cdot \mathbf{r}) + \eta \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2\sqrt{3}} & 0 \\ -\frac{1}{2\sqrt{3}} & \frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \cos(\mathbf{k}_3 \cdot \mathbf{r}). \tag{17}$$

Apparently, we have $\delta\mathbf{Q}(\mathbf{r}) = 0$ at $\mathbf{r} = 0$, *i.e.*, the molecular orientation at $\mathbf{r} = 0$ remains the same as that in the high temperature P6/mmm phase. The relative orientations of the six nearest neighbours around the origin can be easily determined from Equation (17). It will give the same symmetry pattern as Figure 3 in Reference 12, which gives 4-sublattice P6/m phase. To date no such second order phase transition has actually been observed in the D_{hd} columnar liquid crystals.

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