

## de Vries behavior in smectic liquid crystals near a biaxiality-induced smectic-A–smectic-C tricritical point

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We show that a generalized Landau theory for the smectic-A–smectic-C (Sm-A–Sm-C) phases exhibits a biaxiality induced Sm-A–Sm-C tricritical point. Proximity to this tricritical point depends on the degree of orientational order in the system; for sufficiently large orientational order the Sm-A–Sm-C transition is three-dimensional XY-like, while for sufficiently small orientational order, it is either tricritical or first order. We investigate each of the three types of Sm-A–Sm-C transitions near tricriticality and show that for each type of transition, small orientational order implies de Vries behavior in the layer spacing, an unusually small layer contraction. This result is consistent with, and can be understood in terms of, the “diffuse cone” model of de Vries. Additionally, we show that birefringence grows upon entry to the Sm-C phase. For a continuous transition, this growth is more rapid the closer the transition is to tricriticality. Our model also predicts the possibility of a nonmonotonic temperature dependence of birefringence.

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### I. INTRODUCTION

Since its discovery in the 1970s [1], the nature of the smectic-A–smectic-C (Sm-A–Sm-C) transition has been a topic of great interest. Early work showed that many systems exhibit a continuous Sm-A–Sm-C transition which could be described by a mean-field model near tricriticality [2]. A tricritical point, with associated neighboring second-order and weakly first-order transitions was later found [3,4]. The origin of a Sm-A–Sm-C tricritical point has been of significant interest, with two main mechanisms having been proposed. The first is the coupling of the tilt to biaxiality, which in chiral systems are related to the size of spontaneous polarization [3,4]. The second is the width of the Sm-A phase [5]. Another mechanism, involving a coupling between tilt and smectic elasticity, has also been proposed [6], but this seems less likely. Until now, a comprehensive theory that addresses the effect of biaxiality on the nature of the Sm-A–Sm-C transition has not been produced.

More recently, much attention has been given to de Vries materials, which exhibit a Sm-A–Sm-C transition with an unusually small change in layer spacing and a significant increase in birefringence (associated with an increase in orientational order) upon entry to the Sm-C phase [7]. Some de Vries materials exhibit another unusual feature, namely, a birefringence that varies nonmonotonically with temperature [8,9]; in particular, the birefringence decreases as the Sm-A–Sm-C transition is approached from within the Sm-A phase. de Vries materials generally seem to have unusually small orientational order and follow the phase sequence isotropic (I)–Sm-A–Sm-C. In several de Vries materials, the Sm-A–Sm-C transition seems to occur close to tricriticality [12,13].

Separate theoretical models [10,11] have been developed, each of which predicts the possibility of a continuous Sm-A–Sm-C transition with the two main signatures of de

Vries behavior: small layer contraction and increase in birefringence upon entry to the Sm-C phase. There are differences between the assumptions used in the models, the most significant of which is the treatment of the temperature dependence of the layering order parameter; the model of Gorkunov *et al.* [11] does not take this into account while that of Saunders *et al.* does [10]. Given the absence of a nematic phase in de Vries materials, incorporating the temperature variation of the layering order parameter is of crucial importance in the modeling of de Vries materials. It seems most likely that the I–Sm-A transition in de Vries materials is primarily driven by the development of layering order, with orientational order being secondarily induced by the layering order. This is consistent with the general observation [7] that de Vries materials have unusually strong layering order and unusually weak orientational order. Additionally, only by including temperature-dependent layering, does one predict [10] the unusual, yet experimentally observed [8,9], possibility of a nonmonotonic temperature dependence of birefringence.

Neither model considers the effect of biaxiality on the Sm-A–Sm-C transition. The model of Gorkunov *et al.* investigates the possibility of an Sm-A–Sm-C transition that has signatures of tricriticality, but does not predict a tricritical point or the possibility of a first-order Sm-A–Sm-C transition.

In this article, we present and analyze a new generalized nonchiral Landau theory, based on that developed in Ref. [10], which includes orientational, layering, tilt, and biaxial order parameters. The model naturally produces a coupling between tilt and biaxiality and we show that this coupling leads to a Sm-A–Sm-C tricritical point. We show that the effect of biaxiality is stronger in systems with small orientational order  $M_0$  so that a tricritical point and associated neighboring first-order transition can be accessed by systems with sufficiently small orientational order,  $M_0 \leq M_{TC}$ . Here  $M_{TC}$  is the value of the orientational order at which the system exhibits a tricritical Sm-A–Sm-C transition. This means that the two mechanisms that have been proposed as leading

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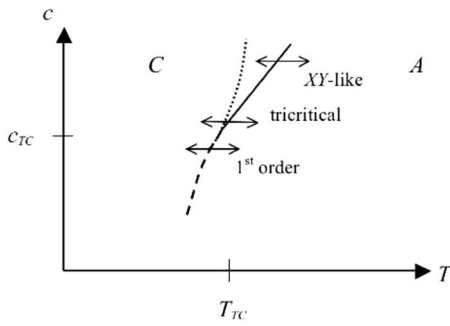


FIG. 1. Phase diagram in temperature- ( $T$ -) concentration ( $c$ ) space. For materials with excluded volume interactions, increasing the concentration would lead to an increase in the orientational order. The solid line represents the continuous Sm-A-Sm-C boundary while the dashed line represents the first-order Sm-A-Sm-C boundary. These two boundaries meet at the tricritical point: ( $T_{TC}, c_{TC}$ ). The dotted line indicates the region in which the behavior in the Sm-C phase crosses over from XY-like to tricritical. The region in which the behavior is XY-like shrinks to zero as the tricritical point is approached. Also shown as double ended arrows, are the three distinct classes of transitions (at fixed concentration): XY-like, tricritical, and first order.

to tricriticality, the coupling of tilt to biaxiality and the width of the Sm-A phase, may in fact be two sides of the same coin. Systems with a narrow Sm-A phase, which are thus close to the  $I$  phase, will have small orientational order which according to our model, leads to an enhanced effect of the biaxiality on the nature of the Sm-A-Sm-C transition. For materials with excluded volume interactions, a decrease in orientational order could be achieved by decreasing concentration.

Figure 1 shows the phase diagram for our model near the tricritical point in temperature- ( $T$ -) concentration ( $c$ ) space, along with the three different types of transitions: XY-like, tricritical, and first order. In each case the transition from the Sm-A phase to the Sm-C phase implies a tilting of the optical axis away from the normal to the smectic layers by an angle  $\theta$ , as shown schematically in Fig. 2. Our model gives the expected temperature dependence of  $\theta$  for each type of transition, as summarized in Fig. 3. For both the XY-like and tricritical transitions the growth of  $\theta$  with decreasing temperature is continuous, although with different scaling for each transition. It should be noted that here, and throughout the article, exponents are calculated within mean-field

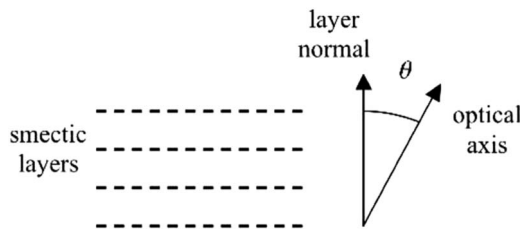


FIG. 2. A schematic showing the layer normal and optical axis. The layers are shown as dashed lines. The transition from the Sm-A to -C phase occurs via a tilting, by angle  $\theta$ , of the optical axis away from the layer normal.

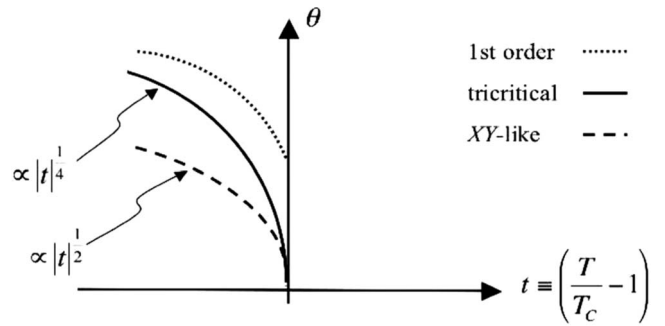


FIG. 3. The tilt angle  $\theta$  as a function of reduced temperature  $t \equiv (1 - \frac{T}{T_C})$  near the Sm-A-Sm-C transition temperature  $T_C$ , i.e., for  $t \ll 1$ . Upon entry to the Sm-C phase the growth of the tilt angle scales as  $|t|^{1/2}$  for a mean-field XY-like transition. For a tricritical transition it scales as  $|t|^{1/4}$  and is thus more rapid. For a first-order transition there is a jump in the tilt angle upon entry to the Sm-C phase.

theory, and do not include the effects of fluctuations. For example, it is known that when fluctuation effects are included in analysis of the three-dimensional (3D) XY transition,  $\theta$  scales as  $(1 - \frac{T}{T_C})^\beta$ , with  $\beta \approx 0.35$ , whereas in mean-field theory  $\beta = 0.5$ . The use of mean-field theory is justified by the fact that virtually all continuous Sm-A-Sm-C transitions are observed to be mean-field-like.

For the first-order transition the tilt angle  $\theta$  jumps discontinuously at the transition. Our model also leads to the expected [2] temperature dependence of specific heat  $c_V$  near the continuous Sm-A-Sm-C transition. This temperature dependence is shown in Fig. 4. For an XY-like transition  $c_V$  jumps by an amount  $\Delta c_V$  as the system enters the Sm-C phase. If the transition becomes tricritical ( $M_0 \rightarrow M_{TC+}$ , via decreasing concentration), the size of this jump diverges. Our model predicts that the divergence should scale as

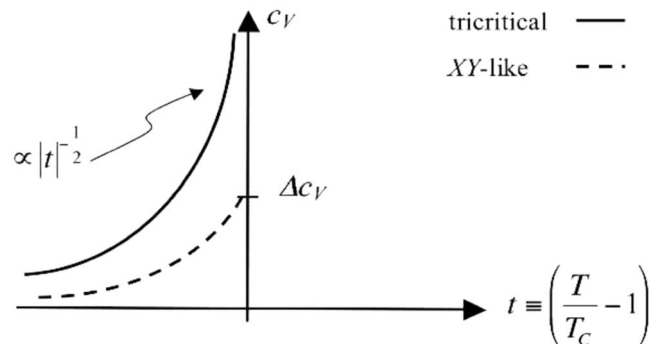


FIG. 4. The specific heat  $c_V$  as a function of reduced temperature  $t \equiv (1 - \frac{T}{T_C})$  near the continuous Sm-A-Sm-C transition temperature  $T_C$ , i.e., for  $t \ll 1$ . As the transition is approached from the Sm-C phase, the specific heat grows as  $c_V \propto (1 - \frac{T}{T_m})^{-1/2}$ , where  $T_m > T_C$ . This growth is cut off at  $T = T_C$ , where it reaches a maximum value  $\Delta c_V$ . If the transition becomes tricritical  $T_m \rightarrow T_C$  and  $c_V$  diverges at the transition. Note that the specific heat shown here only includes the contribution from the piece of the free energy density associated with the ordering as the system moves into the Sm-C phase. For a first-order transition there will be a latent heat absorbed in going from the Sm-C phase to the Sm-A phase.

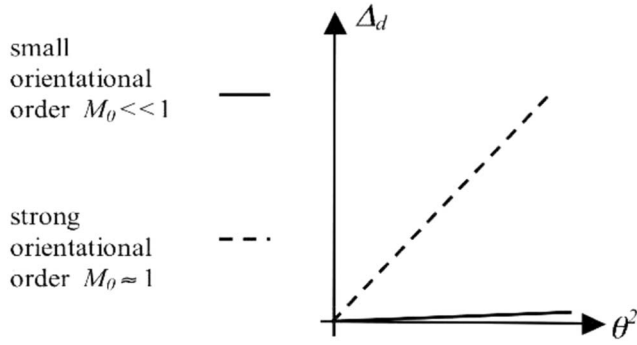


FIG. 5. The layer contraction  $\Delta_d \equiv (d_{AC} - d_C)/d_{AC}$  as a function of  $\theta^2$  near the Sm-A-Sm-C transition. For any type of transition the contraction will scale as  $M_0\theta^2$ . Thus, the slope of  $\Delta_d$  versus  $\theta^2$  is proportional to the orientational order  $M_0$  in the system. Near tricriticality, the orientational order is small and  $M_0 \ll 1$  and so the contraction is also small. Also shown is the layer contraction for a system with strong orientational order  $M_0 \approx 1$ , for which the contraction will be sizable. For a first-order transition there will be a jump in the tilt angle  $\theta$  at the transition and, thus, the  $\Delta_d$  vs  $\theta^2$  line does not extend all the way to zero.

$$\Delta_{CV} \propto \frac{1}{M_0 - M_{TC}}. \tag{1}$$

For a first-order Sm-A-Sm-C transition there is an associated latent heat  $l$ . We show that if the transition becomes tricritical ( $M_0 \rightarrow M_{TC}$ , via increasing concentration) then the latent heat vanishes as

$$l \propto (M_{TC} - M_0). \tag{2}$$

The model is also used to examine the behavior of the layer spacing and birefringence for the three possible transitions (XY-like, tricritical, first order). We show that, for all three types of transitions, an unusually small layer contraction can be directly attributed to unusually small orientational order  $M_0$ . Specifically, we find that for any of the three possible types of transitions

$$\Delta_d \propto M_0[1 - \cos(\theta)] \approx \frac{1}{2}M_0\theta^2, \tag{3}$$

where the tilt angle  $\theta$  is small near a continuous or weakly first-order transition. We define the layer contraction as  $\Delta_d \equiv (d_{AC} - d_C)/d_{AC}$ , where  $d_{AC}$  and  $d_C$  are the values of the layer spacing in the Sm-A phase (right at the Sm-A-Sm-C boundary) and in the Sm-C phase, respectively. Schematic plots of  $\Delta_d$  vs  $\theta^2$  are shown in Fig. 5 for two types of systems: one “de Vries-like” and the other “conventional.” The de Vries-like system has small orientational order  $M_0 \ll 1$  and thus has a small slope of  $\Delta_d$  vs  $\theta^2$ , which corresponds to small layer contraction. The “conventional” system has strong orientational order  $M_0 = O(1)$ , and thus has a larger slope, which corresponds to significant layer contraction. It should be noted that for a first-order transition there will be a jump in the tilt angle  $\theta$  at the transition and thus, the  $\Delta_d$  vs  $\theta^2$  line would not extend all the way to zero.

This result of our rigorous theory complements the simple geometric diffuse cone argument of de Vries [14], which is shown in Fig. 6. The conventional, but oversimplified, relationship between layer contraction and tilt angle  $\Delta_d = [1 - \cos(\theta)]$  is obtained geometrically by assuming a liquid crystal with perfect orientational order, as shown in Fig. 6(a).

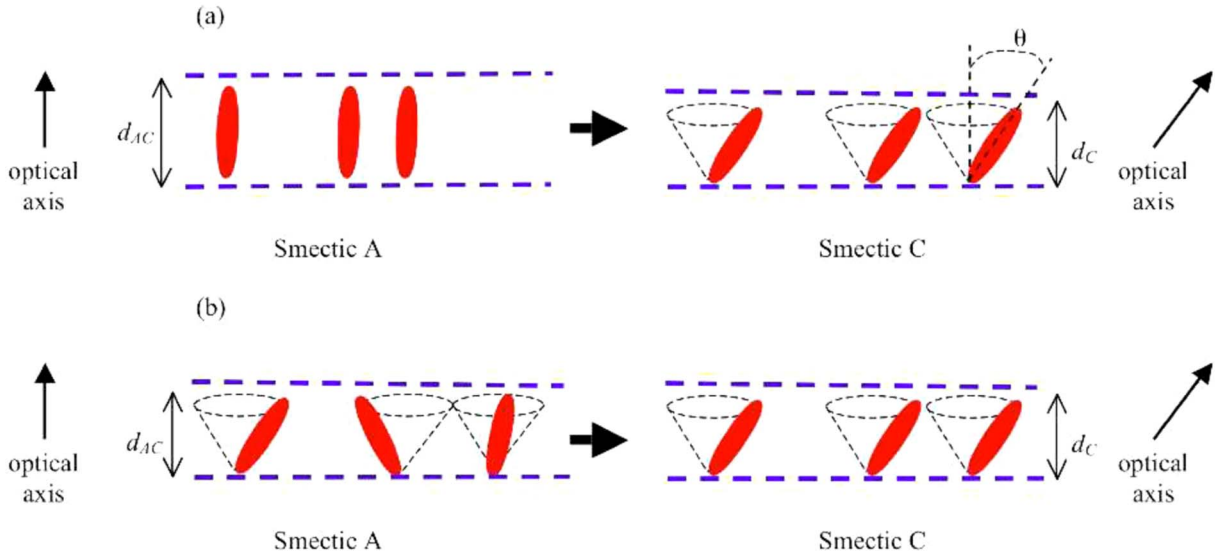


FIG. 6. (Color online) (a) An oversimplified schematic showing the arrangement of molecules in the Sm-A phase, in which the orientational order is perfect. Such a model predicts that, as the system moves into the Sm-C phase, the layer spacing should contract according to  $\Delta_d \equiv [1 - \cos(\theta)]$ , where  $\Delta_d = (d_{AC} - d_C)/d_{AC}$ . (b) A more realistic arrangement of the molecules in which the molecular axes are tilted away from the optical axis, but in azimuthally random directions. The more that the molecules are tilted, the smaller the orientational order. As the system moves into the Sm-C phase, the “pretilted” molecules do not need to tilt but rather need only to order azimuthally, thus leading to an unusually small layer contraction. Thus, the smaller the orientational order in the Sm-A phase, the more pretilted the molecules will be and the smaller the layer contraction will be, an interpretation consistent with our result, Eq. (3). The figure also shows that, as a result of the azimuthal ordering as the system moves into the Sm-C phase, it should become more orientationally ordered.

However, it has long been known that the orientational order in liquid crystals is far from perfect. The schematic in Fig. 6(b) shows a more realistic arrangement of the molecules in the Sm-A phase. The molecular axes are tilted away from the optical axis, but in azimuthally random directions. One can see that the more the molecules are tilted, the smaller the orientational order in the Sm-A phase. The diffuse cone model argues that, upon entry to the Sm-C phase, the “pretilted” molecules do not need to tilt but rather need only to order azimuthally, thus leading to an unusually small layer contraction. Thus, the smaller the orientational order in the Sm-A phase, the more pretilted the molecules will be and the smaller the layer contraction will be. As shown in Eq. (3), our rigorous theoretical analysis predicts a small contraction for systems with small orientational order, which agrees with this geometric argument. It also correlates well with the general experimental observation [7] that de Vries materials have small orientational order.

From Fig. 6(b) one also expects a growth of orientational order, and hence birefringence  $\Delta n$ , as the system moves into the Sm-C phase. It is useful to define a fractional change in birefringence  $\Delta_{\Delta n} \equiv \frac{\Delta n - \Delta n_{AC}}{\Delta n_{AC}}$ , where  $\Delta n_{AC}$  is the value of the birefringence in the Sm-A phase right at the Sm-A–Sm-C boundary. Our model predicts that upon entry to the Sm-C phase, for any of the three types of transitions (XY-like, tricritical, first order),  $\Delta_{\Delta n}$  of a de Vries type material will grow according to  $\Delta_{\Delta n} \propto \theta^2$ . While the dependence of  $\Delta_{\Delta n}$  on  $\theta$  is the same for all three types of transitions, its dependence on temperature is not the same because, as shown in Fig. 3,  $\theta$  scales differently with temperature for each type of transition. Thus,

$$\Delta_{\Delta n} \propto \theta^2 \propto \begin{cases} \left(1 - \frac{T}{T_C}\right) & \text{XY-like,} \\ \left(1 - \frac{T}{T_C}\right)^{1/2} & \text{tricritical,} \\ \text{jump} & \text{first order.} \end{cases} \quad (4)$$

The growth of  $\Delta_{\Delta n}$  as a function of reduced temperature  $t \equiv \left(\frac{T}{T_C} - 1\right)$  is shown in Fig. 7. For an XY-like transition the growth will be linear  $\propto |t|$ , while for a transition at tricriticality it scales as  $\propto |t|^{1/2}$  and is thus more rapid. For a first-order transition there will be a jump in the tilt angle and thus an associated jump in  $\Delta_{\Delta n}$ , although near tricriticality, where the transition is only weakly first order, the jump will be small.

Our model also predicts (for materials with excluded volume interactions) the possibility of birefringence that decreases as the Sm-A–Sm-C transition is approached from the Sm-A phase, which, as discussed above, is an unusual feature that has been observed experimentally [8,9]. For any of the three types of transitions  $\Delta_{\Delta n}$  decreases linearly with temperature as the transition is approached from the Sm-A phase, as shown in Fig. 7. The decrease in birefringence is particularly unusual, as it indicates that the system is becoming less ordered (orientationally) as a lower symmetry (Sm-C) phase is approached. To the best of our knowledge, this is the first example of such a phenomenon.

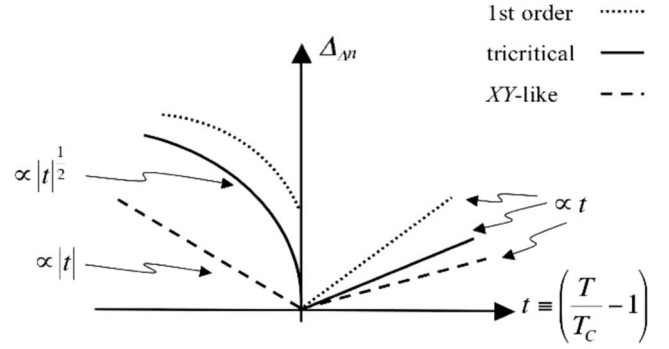


FIG. 7. The fractional change in birefringence  $\Delta_{\Delta n} \equiv \frac{\Delta n - \Delta n_{AC}}{\Delta n_{AC}}$  as a function of reduced temperature  $t \equiv \left(1 - \frac{T}{T_C}\right)$  near the Sm-A–Sm-C transition temperature  $T_C$ , i.e., for  $t \ll 1$ . For materials with excluded volume interactions, we expect the birefringence  $\Delta n$ , and thus  $\Delta_{\Delta n}$ , to decrease as the Sm-A–Sm-C transition is approached from within the Sm-A phase. For all three types of transitions (XY-like, tricritical, first-order) this decrease will scale linearly  $\propto t$  with reduced temperature. Upon entry to the Sm-C phase the birefringence  $\Delta n$ , and thus  $\Delta_{\Delta n}$ , will grow. The growth is linear  $\propto |t|$  for a mean-field XY-like transition. For a tricritical transition the growth scales as  $\propto |t|^{1/2}$  and is thus more rapid. For a first-order transition there will be a jump in birefringence as the system enters the Sm-C phase.

It should be emphasized that our analysis is only made tractable, and thus is only valid, in the limit of weak coupling between order parameters. This means that our results do not imply that all materials with small orientational order will have Sm-A–Sm-C transitions close to tricriticality or will exhibit de Vries behavior. Similarly, not all materials exhibiting de Vries behavior must have Sm-A–Sm-C transitions near tricriticality. In other words, the conclusions that our model leads us to are generic but not ubiquitous. The remainder of this article is organized as follows. In Sec. II we introduce our model and in Sec. III we locate and analyze the biaxiality induced tricritical point. We then analyze the nature (XY-like, tricritical, first order) of the Sm-A–Sm-C transition near this tricritical point in Sec. IV. In Sec. V we examine the thermodynamic nature of each type of transition. Specifically, we calculate the specific and latent heats for the continuous and first-order transitions, respectively. Last, we study the behavior of the layer spacing and birefringence near the Sm-A–Sm-C transition in Sec. VI. We briefly summarize our results in Sec. VII. The Appendix includes details of the analysis from Sec. VI.

## II. MODEL

The starting point for our analysis is a generalized version of the free energy density introduced in Ref. [10], which includes orientational, tilt (azimuthal), biaxial, and layering order parameters. The complex layering order parameter  $\psi$  is defined via the density  $\rho = \rho_0 + \text{Re}(\psi e^{i\mathbf{q}\cdot\mathbf{r}})$  with  $\rho_0$  constant and  $\mathbf{q}$  the layering wave vector, the arbitrary direction of which is taken to be  $z$ . The remaining order parameters are embodied in the usual second rank tensor orientational order parameter  $\mathcal{Q}$ , which is most conveniently expressed as

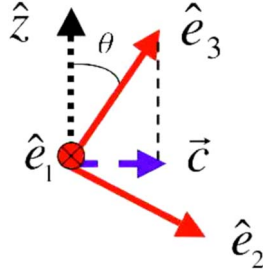


FIG. 8. (Color online) The unit eigenvectors  $\hat{e}_1$ ,  $\hat{e}_2$ ,  $\hat{e}_3$  of the orientational order tensor  $\mathcal{Q}$ . These are shown as solid arrows, with  $\hat{e}_1$  pointing into the page. Also shown, as a dotted arrow, is the layering direction  $\hat{z}$ , which is normal to the plane of the layers. The eigenvector  $\hat{e}_3$  corresponds to the average direction of the molecules' long axes. The order parameter  $\mathbf{c}$  for the Sm-C phase is the projection of  $\hat{e}_3$  onto the plane of the layers, and is shown as a dashed arrow. The angle  $\theta$ , by which the optical axis tilts, is also shown.

$$\begin{aligned} Q_{ij} = M \{ & [-\cos(\alpha) + \sqrt{3} \sin(\alpha)] e_{1i} e_{1j} \\ & + [-\cos(\alpha) - \sqrt{3} \sin(\alpha)] e_{2i} e_{2j} + 2 \cos(\alpha) e_{3i} e_{3j} \}, \end{aligned} \quad (5)$$

where  $\hat{e}_3 = \mathbf{c} + \sqrt{1 - c^2} \hat{z}$  is the average direction of the molecules' long axes (i.e., the director). Here, in either smectic phase,  $\hat{z}$  is normal to the plane of the layers. The projection  $\mathbf{c}$  of the director onto the layers is the order parameter for the Sm-C phase. The other two principal axes of  $\mathcal{Q}$  are given by  $\hat{e}_1 = \hat{z} \times \hat{c}$  and  $\hat{e}_2 = \sqrt{1 - c^2} \hat{c} - c \hat{z}$ . These unit eigenvectors are shown in Fig. 8. The amount of orientational order is given by  $M \propto \sqrt{\text{Tr}(\mathcal{Q}^2)}$ , which is thus proportional to the birefringence. The degree of biaxiality is described by the parameter  $\alpha$ . The Sm-A phase is untilted ( $\mathbf{c} = \mathbf{0}$ ) and uniaxial ( $\alpha = 0$ ), while the Sm-C phase is tilted ( $\mathbf{c} \neq \mathbf{0}$ ) and biaxial ( $\alpha \neq 0$ ). From Fig. 8 it can be seen that the angle  $\theta$ , by which the optical axis tilts, can be related to  $c$  via  $c = \sin(\theta)$ . Taking both  $\psi$  and  $\mathcal{Q}$  to be spatially uniform allows the use of a Landau free energy density  $f = f_Q + f_\psi + f_{Q\psi}$ , with the orientational ( $f_Q$ ), layering ( $f_\psi$ ), and coupling ( $f_{Q\psi}$ ) terms given by

$$f_Q = \frac{t_n \text{Tr}(\mathcal{Q}^2)}{12} - \frac{w \text{Tr}(\mathcal{Q}^3)}{18} + \frac{u_n [\text{Tr}(\mathcal{Q}^2)]^2}{144}, \quad (6)$$

$$f_\psi = \frac{1}{2} t_s |\psi|^2 + \frac{1}{4} u_s |\psi|^4 + \frac{1}{2} K (q^2 - q_0^2)^2 |\psi|^2, \quad (7)$$

$$\begin{aligned} f_{Q\psi} = \frac{q_i q_j |\psi|^2}{2} \left\{ & - [a(q^2) - b(q^2) |\psi|^2] Q_{ij} + g(q^2) Q_{ik} Q_{jk} \right. \\ & \left. + \frac{h(q^2)}{2} q_k q_l Q_{kl} Q_{ij} - \frac{s(q^2)}{4} (q_k q_l Q_{kl})^2 Q_{ij} \right\}, \end{aligned} \quad (8)$$

where the Einstein summation convention is implied and  $q_i \equiv q \delta_{iz}$ . As usual in Landau theory, the parameters  $t_n$  and  $t_s$  are monotonically increasing functions of temperature and control the “bare” orientational and layering order parameters  $M_0$  and  $\psi_0$ , respectively. By “bare” we mean the values the order parameters would take on in the absence of the

coupling term  $f_{Q\psi}$ . Similarly, the constant  $q_0$  is the bare value of the layering wave vector. From Eq. (7) above, we immediately find  $|\psi_0| = \sqrt{-t_s/u_s}$ . The remaining parameters in  $f_Q$  and  $f_\psi$  ( $w, u_n, u_s, K$ ) are positive constants.

The coupling piece of the free energy  $f_{Q\psi}$  includes the lowest order (in fields  $\psi$  and  $\mathcal{Q}$ ) terms necessary to obtain an Sm-A–Sm-C transition with tricriticality. The dependence on  $q^2$  of each of the coupling parameters,  $a, b, g, h$ , and  $s$ , takes into account all other possible terms that have the same tensorial form, but with higher powers of  $q^2$ , which is not an order parameter and is therefore not assumed to be small. For weak coupling  $q \approx q_0$  we can Taylor expand each coupling parameter, e.g.,  $a(q^2) \approx a_0 + a_1(q^2 - q_0^2)$ , where  $a_0 \equiv a(q_0^2)$  and  $a_1 \equiv \frac{da}{dq^2} \big|_{q^2=q_0^2}$ . For all but one of the couplings it is sufficient to use the zeroth order approximation, e.g.,  $g(q^2) \approx g_0$ . It will be seen below that  $a_1$ , the first-order correction to  $a_0$ , is necessary for layer contraction at the Sm-A–Sm-C transition. For notational convenience, we will, for the remainder of the article, write  $a(q^2)$  as  $a$  with the  $q^2$  dependence implied. To render the analysis tractable, the coupling parameters are all assumed to be small and are treated perturbatively throughout.

The relatively large number of parameters in  $f$  is inevitable given the fact that the theory incorporates four types of order, layer spacing, and also allows for continuous, first-order, and tricritical Sm-A–Sm-C transitions. Additionally, it will be shown that proximity to tricriticality and the signatures of de Vries behavior can be interpreted simply in terms of the size of the orientational order.

### III. BIAxIALITY-INDUCED Sm-A–Sm-C TRICRITICAL POINT

To investigate the nature of the Sm-A–Sm-C transition, we expand the part of the free energy density involving orientational order,  $f_Q + f_{Q\psi}$  in powers of the biaxial and tilt order parameters  $\alpha$  and  $\mathbf{c}$ . This expansion is done near the continuous Sm-A–Sm-C transition temperature  $T_C$  [i.e., for  $(T - T_C)/T_C \ll 1$ ] and to lowest order in  $M$  and  $\psi$ . We find  $f_Q + f_{Q\psi} \approx f_M + f_{\text{coup}}$ . The piece  $f_M$  only involves the orientational order parameter  $M$  and is given by

$$f_M = \frac{1}{2} t_n M^2 - \frac{1}{3} w M^3 + \frac{1}{4} u_n M^4. \quad (9)$$

From  $f_M$  we immediately find the bare value of orientational order  $M_0(t_n) = (w + \sqrt{w^2 - 4u_n t_n})/2u_n$ . It is useful to write the orientational order as a combination of the bare value and a correction:  $M = M_0(1 + \Delta_M)$ , where the correction  $\Delta_M$  is due to the coupling piece  $f_{\text{coup}}$ . The correction  $\Delta_M$  can be thought of as an augmentation of the bare orientational order  $M_0$  due to the presence of layering order. As discussed in Ref. [10], de Vries behavior is implied by a virtually athermal  $t_n$  (and thus an athermal  $M_0$ ), so that for a given material  $M_0$  can be thought of as a fixed quantity. This would correspond to almost perfect excluded volume short range repulsive molecular interactions. This means that the temperature variation in orientational order  $M$  is effectively due to its coupling to the temperature-dependent layering, i.e., via  $\Delta_M$ . We as-

sume and verify *a posteriori* that in the limit of weak coupling  $\Delta_M \ll 1$ . Similarly, we express the wave vector as  $q^2 = q_0^2(1 + \Delta_q)$  and the layering order as  $|\psi|^2 = |\psi_0|^2(1 + \Delta_\psi)$ . The bare wave vector  $q_0$  is also taken to be athermal but the bare layering order parameter  $\psi_0$  is not.

The coupling piece can be broken up into three pieces:  $f_{\text{coup}} = f_{M\psi} + f_c + f_{ac}$ . The piece  $f_{M\psi}$  involves a coupling between layering and orientational order that is nonzero in both Sm-A and -C phases, and is given by

$$f_{M\psi} = q^2 |\psi|^2 M (-a\tau + g_0 M - h_0 q^2 M), \quad (10)$$

where

$$\tau = 1 - \frac{b_0 |\psi|^2 + (g_0 + 2h_0 q^2) M}{a}. \quad (11)$$

The piece  $f_c$  involves the tilt (azimuthal) order parameter  $c$  and is given by

$$f_c = \frac{1}{2} r_c c^2 + \frac{1}{4} u_c c^4 + \frac{1}{6} v_c c^6. \quad (12)$$

The coefficients  $r_c$ ,  $u_c$ ,  $v_c$  are given by

$$r_c = 3aq^2 |\psi|^2 M \tau, \quad (13)$$

$$u_c = 9h_0 q^4 |\psi|^2 M^2, \quad (14)$$

$$v_c = \frac{81}{4} s_0 q^6 |\psi|^2 M^3. \quad (15)$$

At the continuous Sm-A–Sm-C transition the parameter  $\tau$  (and thus also  $r_c$ ), changes sign. Close to the transition  $\tau \propto (T - T_C)/T_C \ll 1$  and can be considered small. From Eq. (11) we see that to lowest order in the corrections  $\Delta_{M,q,\psi}$  and for athermal  $M_0$ , this transition occurs due to layering order increasing as temperature decreases. The transition temperature  $T_C$  is defined via  $|\psi_0(T_C)| = \sqrt{[a_0 - (g_0 + 2h_0 q_0^2) M_0]/b_0}$  or, equivalently,

$$t_s(T_C) = - \frac{u_s [a_0 - (g_0 + 2h_0 q_0^2) M_0]}{b_0}. \quad (16)$$

This continuous phase boundary is shown as a solid line in Fig. 9, the phase diagram in  $t_s$ - $M_0$  space. For a given material, decreasing the temperature would, in the phase diagram of Fig. 9, correspond to moving horizontally from right to left. The size of the orientational order  $M_0$  should increase with concentration. Thus, the topology of the corresponding phase diagram, Fig. 1, in temperature-concentration space should essentially be the same as that shown in Fig. 9.

The coupling between tilt and biaxiality appears in the final piece are

$$f_{ac} = A_\alpha \alpha c^2 + \frac{1}{2} B_\alpha \alpha^2, \quad (17)$$

where, to lowest order in  $\tau$ ,

$$A_\alpha = \frac{3\sqrt{3}}{2} g_0 q^2 |\psi|^2 M^2, \quad (18)$$

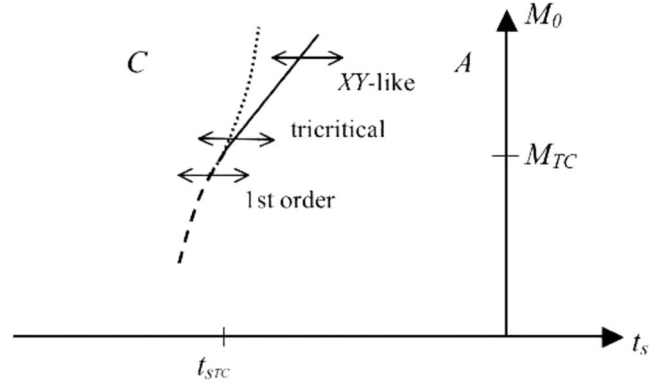


FIG. 9. The phase diagram in  $t_s$ - $M_0$  space near the tricritical point ( $t_{sTC}, M_{0TC}$ ). The quantity  $M_0$  is a measure of how much bare orientational order the system possesses and for de Vries materials is effectively athermal. Increasing concentration should increase  $M_0$ . The quantity  $t_s$  is a monotonic function of temperature so that for a given material, decreasing the temperature corresponds to moving horizontally from right to left. The topology of the corresponding phase diagram in temperature-concentration space should essentially be the same. The solid line represents the continuous Sm-A–Sm-C boundary while the dashed line represents the first-order Sm-A–Sm-C boundary. These two boundaries meet at the tricritical point ( $t_{sTC}, M_{0TC}$ ). The dotted line indicates the region in which the behavior crosses over from XY-like to tricritical. The region in which the behavior is XY-like shrinks to zero as the tricritical point is approached. The slopes of the first-order and continuous Sm-A–Sm-C boundaries are equal at the tricritical point. Also shown as double ended arrows are the three distinct classes of transitions: XY-like, tricritical, and first order.

$$B_\alpha = 3M^2 (wM - g_0 q^2 |\psi|^2). \quad (19)$$

From Eq. (17) we see that biaxiality is induced by tilt order. Minimization gives

$$\alpha = -\chi_\alpha c^2, \quad (20)$$

where  $\chi_\alpha$  can be thought of as a biaxial susceptibility and is given by

$$\chi_\alpha = \frac{\sqrt{3}}{2} \left( \frac{wM}{g_0 q^2 |\psi|^2} - 1 \right)^{-1}. \quad (21)$$

Keeping in mind the weak-coupling regime of our analysis, i.e.,  $g_0 \ll 1$ , we see that the systems with small orientational order  $M$  will have large biaxial susceptibility. Thus, large biaxiality (and for chiral materials, an associated large spontaneous polarization) can be directly attributed to small orientational order. In fact, Eq. (21) predicts that the biaxial susceptibility will be largest in systems that have a combination of weak orientational order ( $M$ ) and strong layering order ( $|\psi|$ ). It has been observed [7] that this combination may be common in de Vries materials. It should be noted that the expression for  $\chi_\alpha$  is only valid for  $M > M_L \equiv g_0 q^2 |\psi|^2 / w$ , below which terms we have neglected become important. However, we will see that the tricritical point we predict occurs at a value of  $M > M_L$ .

The effect of the biaxiality on the Sm-A–Sm-C transition is to renormalize the quartic coefficient in Eq. (12), giving

$$u'_c = u_c \left( 1 - \frac{g_0}{\sqrt{3}h_0q^2} \chi_\alpha \right). \quad (22)$$

For small biaxial susceptibility  $\chi_\alpha$  (corresponding to strong orientational order), the renormalized quartic coefficient  $u'_c > 0$  and the Sm-A–Sm-C transition is continuous. For large  $\chi_\alpha$  (corresponding to weak orientational order),  $u'_c < 0$  and the transition is first order. The tricritical point occurs at  $\tau = u'_c = 0$ , which, to lowest order in the corrections  $\Delta_{q,\psi}$ , corresponds to  $M = M_{TC}$  with

$$M_{TC} = \frac{a_0 g_0 q_0^2}{b_0 w} \left( 1 + \frac{g_0}{2h_0 q_0^2} \right), \quad (23)$$

which is larger than  $M_L$ . For small coupling ( $a_0, b_0, g_0, h_0 \ll 1$ ) the value of orientational order  $M_{TC}$  at tricriticality will also be small. In obtaining Eq. (23) we have used Eq. (11) at tricriticality to find  $|\psi_{0,TC}|^2 \approx a_0/b_0$ , an approximation that is valid for small  $M_{TC}$ . Equivalently,  $t_{s,TC} \approx -u_s a_0/b_0$ .

#### IV. Sm-A–Sm-C TRANSITION NEAR THE TRICRITICAL POINT

Having found the biaxiality induced tricritical point, we now investigate the nature of the Sm-A–Sm-C transition in the vicinity of the tricritical point. We analyze both the continuous Sm-A–Sm-C transition and the first-order Sm-A–Sm-C transition.

##### A. Continuous Sm-A–Sm-C transition near tricriticality

For sufficiently large orientational order,  $M > M_{TC}$ , the renormalized quartic coefficient  $u'_c > 0$  and the Sm-A–Sm-C transition is continuous. As discussed in Sec. III, the phase boundary is defined via  $\tau = 0$  or, equivalently,  $t_s = t_s(T_C)$ . Upon entry to the Sm-C phase,  $\tau$  becomes negative and, minimizing the effective  $f_c$  (i.e., with  $u_c \rightarrow u'_c$ ) with respect to  $c$  we find that the tilt order parameter grows continuously with increasing  $|\tau|$  as

$$c = \left[ \frac{2h'_0}{9s_0q^2M} \left( -1 + \sqrt{1 + \frac{3as_0}{(h'_0)^2} |\tau|} \right) \right]^{1/2}, \quad (24)$$

where the effect of the coupling between biaxiality and tilt is incorporated via a renormalized  $h'_0$ , which by expanding  $\chi_\alpha$  close to tricriticality (i.e.,  $M \approx M_{TC}$ ) can be shown to be

$$h'_0 = h_0 \left( 1 + \frac{2h_0q^2}{g_0} \right) \left( \frac{M - M_{TC}}{M_{TC}} \right). \quad (25)$$

Similar to  $u'_c$ ,  $h'_0$  changes sign at  $M = M_{TC}$ . It is straightforward to show that sufficiently close to the transition ( $|\tau| \ll |\tau_*|$ ), the dependence of  $c$  on  $\tau$  is effectively XY-like and that sufficiently far from the transition ( $|\tau| \gg |\tau_*|$ ) it is tricritical, i.e.,

$$c \approx \begin{cases} c_{XY} = \sqrt{\frac{a}{3h'_0q^2M}} (|\tau|)^{1/2} & |\tau| \ll |\tau_*|, \\ c_{TC} = \left( \frac{4a}{27s_0q^4M^2} \right)^{1/4} (|\tau|)^{1/4} & |\tau| \gg |\tau_*|. \end{cases} \quad (26)$$

The crossover from XY-like to tricritical behavior occurs in the region  $\tau = O(\tau_*)$  where  $\tau_*$  is the value of  $\tau$  where  $c_{XY} = c_{TC}$ ,

$$|\tau_*| = \frac{4(h'_0)^2}{3as_0}. \quad (27)$$

Near tricriticality where  $M$  is small, the corresponding  $t_{s^*}$  is given by  $t_{s^*} = t_s(T_C)(1 + |\tau_*|)$  and is shown as a dotted line in Fig. 9. The width of the region in which the behavior is XY-like shrinks to zero as the tricritical point is approached. Near the transition, the tilt angle  $\theta \approx c$ , and its scaling with temperature is shown in Fig. 3 for both an XY-like and a tricritical transition. Of course, the XY behavior of Eq. (26) is that of a mean-field theory and incorporating fluctuation effects would yield  $c \propto \tau^\beta$  with  $\beta \approx 0.35$ .

##### B. First-order Sm-A–Sm-C transition near tricriticality

When the orientational order is small enough ( $M < M_{TC}$ ) the quartic coefficient ( $u'_c$ ) changes sign. The free energy now has two local minima, one at  $c=0$  and another at

$$c_{1st} = \left[ \frac{2|h'_0|}{9s_0q^2M} \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right) \right]^{1/2}. \quad (28)$$

The first-order Sm-A–Sm-C transition, and the jump from  $c=0$  to  $c=c_{1st}$  occur when the free energy at  $c_{1st}$  becomes smaller than the free energy at  $c=0$ . The location of the first-order boundary can thus be obtained by finding where the two free energies are equal or, equivalently, where the difference  $\Delta f$  between them is zero. To lowest order in corrections  $\Delta_{M,q,\psi}$  this difference is just the effective  $f_c$  (i.e., with  $u_c \rightarrow u'_c$ ) evaluated at  $c_{1st}$  and is given by

$$\Delta f = \frac{|h'_0|^3}{27s_0^2} \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right)^2 \left( 1 - 2 \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right), \quad (29)$$

which when set to zero yields an expression for the location of the first-order Sm-A–Sm-C boundary

$$\tau_{1st} = \frac{3}{16} |\tau_*|. \quad (30)$$

This boundary is shown as a dashed line in Fig. 9. At the transition the tilt order parameter jumps from zero to a value  $c_{1st,AC} = \sqrt{|h'_0|/(3s_0q^2M)}$ . Close to tricriticality, where the transition is weakly first order,  $c_{1st}$  is small and  $\approx \theta$ . The corresponding temperature dependence of  $\theta$  is shown in Fig. 3. The size of the jump in  $c$  (and thus  $\theta$ ) goes to zero at the tricritical point, where  $h'_0 \rightarrow 0_-$ .

#### V. THERMODYNAMIC NATURE OF THE Sm-A–Sm-C TRANSITION NEAR TRICRITICALITY

We next investigate the thermodynamic nature of the Sm-A–Sm-C transition near tricriticality. First we analyze the

specific heat near the continuous transition and then the latent heat at the first-order transition.

### A. Specific heat near the continuous Sm-A–Sm-C transition

It is well established [2] that the specific heat will exhibit a jump at the continuous Sm-A–Sm-C transition and that the thermodynamic signature of a continuous transition close to tricriticality is a divergence of this jump [3]. We obtain the specific heat for our model using  $c_V = -T \frac{d^2 f'_c}{dT^2}$ , where the prime indicates the use of the biaxiality renormalized  $u'_c$ , as given by Eq. (22), in  $f'_c$ . In using  $f'_c$  instead of the full free energy density  $f$ , we are focusing on the contribution to the specific heat associated with the onset of ordering as the system moves into the Sm-C phase. It is this contribution that is responsible for the specific heat jump. As discussed above, following Eq. (15), in a material with athermal  $M_0$  the transition from the Sm-A to -C phase is driven by the layering order which increases with decreasing temperature. Near tricriticality, where the orientational order is small, the value of the layering order at the transition is  $|\psi_0(T_C)| \approx \sqrt{a_0/b_0}$ , and the dimensionless parameter  $\tau$  can be expressed as

$$\tau = 1 - \frac{|\psi_0(T)|^2}{|\psi_0(T_C)|^2} \approx \gamma_c \left( \frac{T}{T_C} - 1 \right), \quad (31)$$

where we have Taylor expanded  $|\psi_0(T)|$  near  $T=T_C$  and the dimensionless parameter  $\gamma_c > 0$  is given by  $\gamma_c$

$$c_V = \begin{cases} 0 & \tau > 0, \\ T \left( \frac{\gamma_c}{T_C} \right)^2 \frac{a^2 |\psi_0(T_C)|^2}{2h'_0} \left[ \frac{1 + |\tau|}{\sqrt{1 + \frac{4|\tau|}{|\tau_*|}}} + |\tau_*| \left( \sqrt{1 + \frac{4|\tau|}{|\tau_*|}} - 1 \right) \right] & \tau < 0. \end{cases} \quad (33)$$

Close to tricriticality, where  $\tau_*$  is small, the specific heat in the Sm-C phase near the transition is dominated by the first term. Substituting  $|\tau| = \gamma_c (1 - \frac{T}{T_C})$  (valid in the Sm-C phase where  $T < T_C$ ) into the first term, we find that  $c_V$  scales as

$$c_V \propto \left( 1 - \frac{T}{T_m} \right)^{-1/2}, \quad (34)$$

where  $T_m = T_C (1 + \frac{|\tau_*|}{4\gamma_c}) > T_C$ . This scaling is shown in Fig. 4, where it can be seen that specific heat grows as the Sm-A–Sm-C transition is approached from the Sm-C phase. This growth is cut off at  $T=T_C$  (or equivalently  $\tau=0$ ), where it reaches a maximum value. This maximum value is the size of the specific heat jump at the Sm-A–Sm-C transition and is found to be

$$\Delta c_V = T \left( \frac{\gamma_c}{T_C} \right)^2 \frac{a^2 |\psi_0(T_C)|^2}{2h'_0}. \quad (35)$$

If the transition becomes tricritical then  $T_m \rightarrow T_C$  and  $c_V$  diverges at the transition. Equivalently, at tricriticality  $h'_0 = 0$

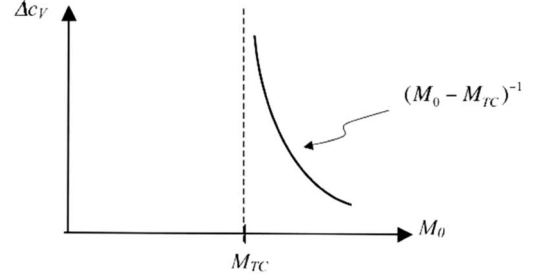


FIG. 10. The size of the specific heat jump  $\Delta c_V$  as a function of the system's orientational order  $M_0$ . As  $M_0 \rightarrow M_{TC}$  the transition becomes tricritical and the specific heat jump diverges. For systems with athermal  $M_0$  it should be experimentally possible to drive the system to tricriticality by varying the concentration.

can be expressed as

$$c_V = -T \left( \frac{\gamma_c}{T_C} \right)^2 \frac{d^2 f'_c}{dT^2}. \quad (32)$$

In the Sm-A phase, where  $f'_c = 0$ , the specific heat is zero. Using Eq. (24) for  $c$  and Eq. (12) (with  $u_c \rightarrow u'_c$ ) for  $f'_c$  we can find the specific heat in the Sm-C phase. Thus we find

and size of the jump  $\Delta c_V$  diverges. Using Eq. (25) we can relate a system's bare orientational order  $M_0$  to its proximity to tricriticality (where  $M_0 = M_{TC}$ ) which gives

$$\Delta c_V \propto \left( \frac{M_0}{M_{TC}} - 1 \right)^{-1}. \quad (36)$$

This relationship, shown in Fig. 10, allows us to see how the size of the jump in specific heat would diverge if the orientational order in the system could be tuned to approach  $M_{TC}$ . For systems with athermal  $M_0$  it should be experimentally possible to drive the system to tricriticality by varying the concentration.

### B. Latent heat at the first-order Sm-A–Sm-C transition

For a first-order Sm-A–Sm-C transition there will be a latent heat absorbed in going from the Sm-C phase to the Sm-A phase. This latent heat vanishes when the transition becomes tricritical. We obtain the latent heat  $l$  for our model using  $l = -T_C \frac{df_c}{dT}$  evaluated at the first-order boundary, where



for  $f_c$  we use the expression given in Eq. (29). Using the relationship between  $\tau$  and  $T$ , as given in Eq. (31), we find

$$l = \gamma_c \frac{df_c}{d\tau} \Big|_{\tau=\tau_{1st}} = \gamma_c \frac{a|h'_0|}{2s_0}. \quad (37)$$

As the transition becomes tricritical  $h'_0 \rightarrow 0_-$  and the latent heat vanishes. Relating the system's bare orientational order  $M_0$  to its proximity to tricriticality (where  $M_0 = M_{TC}$ ) gives

$$l \propto \left(1 - \frac{M_0}{M_{TC}}\right). \quad (38)$$

This relationship allows us to see how the latent heat would vanish if the orientational order in the system could be tuned to approach  $M_{TC}$ . For systems with athermal  $M_0$  it should be experimentally possible to drive the system to tricriticality, and the latent heat to zero, by varying the concentration.

## VI. BEHAVIOR OF THE LAYER SPACING AND BIREFRINGENCE NEAR THE Sm-A–Sm-C TRANSITION

We next analyze the behavior of the orientational order (which is proportional to the birefringence) and the layering wave vector (which is inversely proportional to layer spacing  $d$ ) close to the Sm-A–Sm-C transition. As discussed following Eq. (9) above, for athermal  $M_0$  and  $q_0$ , the temperature variation of  $M = M_0(1 + \Delta_M)$  and  $q^2 = q_0^2(1 + \Delta_q)$  comes from the corrections  $\Delta_M$  and  $\Delta_q$ , respectively. We thus seek the temperature dependence of the corrections  $\Delta_{M,q}$  near the Sm-A–Sm-C transition. Assuming, and verifying *a posteriori*, that the corrections are small, we Taylor expand the free energy to order  $(\Delta_{M,q})^2$  and minimize with respect to  $\Delta_{M,q}$ , keeping only terms to lowest order in coupling coefficients. This is done both within the Sm-A phase and within the Sm-C phase. Details of the analysis are given in the Appendix.

### A. Orientational order near the Sm-A–Sm-C transition

For the orientational order correction within the Sm-A phase we find

$$\Delta_{M_A} = |\Delta_M^0| \left( -1 + \frac{a_0}{3g_0 M_0} \tau_0 \right), \quad (39)$$

where  $\tau_0$  is just the bare value of  $\tau$ , i.e.,  $\tau$  evaluated at  $M = M_0$ ,  $\psi = \psi_0$ , and  $q = q_0$ . To zeroth order in corrections  $\Delta_{M,\psi,q}$ ,  $\tau = \tau_0$ . The quantity  $\Delta_M^0 = -3g_0 q_0^2 |\psi_0(T_C)|^2 / \gamma_M < 0$  and for a continuous transition is just the value of the correction at the continuous Sm-A–Sm-C boundary, i.e., where  $\tau_0 = 0$ . At the first-order Sm-A–Sm-C boundary near tricriticality, at which  $\tau_0 = \tau_{1st} > 0$ , the correction is a little bit larger than  $\Delta_M^0$  [15]. Last,  $\gamma_M = d^2 f_M / dM^2|_{M=M_0}$ .

From Eq. (39) we see that as the Sm-A–Sm-C transition is approached from the Sm-A phase, i.e., as  $\tau_0 \rightarrow 0_+$ , the correction  $\Delta_{M_A}$  will decrease. For materials with sufficiently athermal  $M_0$ , this means that the orientational order will decrease as the transition is approached from above. Using the fact that birefringence  $\Delta n$  is proportional to orientational order

$M$ , the fractional change in birefringence  $\Delta_{\Delta n} \equiv \frac{\Delta n - \Delta n_{AC}}{\Delta n_{AC}}$  (where the reader is reminded that  $\Delta n_{AC}$  is the value of the birefringence in the Sm-A phase right at the Sm-A–Sm-C boundary) can be related to  $\Delta_M$ . It is straightforward to show that, to lowest order in  $\Delta_M$ ,  $\Delta_{\Delta n} \approx \Delta_M - \Delta_M^0$ . Thus, in the Sm-A phase  $\Delta_{\Delta n} \propto \tau_0$  will decrease as the transition is approached from above, as shown in Fig. 7. This is a feature that has been experimentally observed in some de Vries materials [8,9]. We find this feature particularly interesting, as it is the first example that we know of in which the order of a phase decreases as a transition to a lower symmetry phase is approached. It should be noted that in materials with a sufficiently strongly temperature dependent  $t_N$ , the growth of the “bare” (i.e., coupling-free) orientational order  $M_0(t_n)$  as  $T$  is lowered swamps the effects due to the correction term  $\Delta_{M_A}$ . In this case, the orientational order would grow as the transition is approached from above.

To find the correction near the transition within the Sm-C phase one must separately analyze the three distinct regions of the phase diagram, corresponding to XY, tricritical, and first-order behavior. As one might expect, the dependence of  $\Delta_M$  on  $\tau_0 \propto (T - T_C) / T_C \ll 1$  is different in each region. However, near tricriticality the dependence on the tilt order parameter  $c$  in each respective region (i.e.,  $c_{XY}$ ,  $c_{TC}$ , and  $c_{1st}$ ) is identical and is given by

$$\Delta_{M_C} = |\Delta_M^0| \left[ -1 + \frac{1}{2} \left( 1 + \frac{2h_0 q_0^2}{g_0} \right) c^2 \right], \quad (40)$$

where  $\Delta_M^0$  is equal to the value of the correction in the Sm-A phase right at the transition [15]. In each of the three regions the orientational order grows as one moves into the Sm-C phase, consistent with birefringence measurements of de Vries materials. Using the fact that the optical axis tilt angle  $\theta \approx c$  near the transition, we predict that the fractional change in birefringence will grow as  $\Delta_{\Delta n} \propto \theta^2$ . It is important to note that while the dependence of the growth of  $\Delta_{\Delta n}$  on  $\theta$  is the same in each of the three distinct regions of the phase diagram, the dependence on  $\tau_0$  is not. This is because the dependence of  $c$  (and thus  $\theta$ ) on  $\tau_0$  differs in each of the three regions. For sufficiently large orientational order, away from the tricritical point  $c \propto |\tau_0|^{1/2}$  and the growth of  $\Delta_{\Delta n}$  near the continuous transition will scale as  $(T_C - T)$ . For smaller orientational order, near the tricritical point  $c \propto |\tau_0|^{1/4}$  and the growth of  $\Delta_{\Delta n}$  will scale as  $(T_C - T)^{1/2}$ . These scalings are shown in Fig. 7. Thus, our model predicts that for continuous transitions near tricriticality one will see a particularly rapid growth of birefringence as one moves into the Sm-C phase. For a first-order transition there will be a jump in  $c$  and thus an associated jump in the birefringence. Close to the tricritical point, where the transition is weakly first order, this jump will be small.

### B. Layer spacing near the Sm-A–Sm-C transition

For the layering wave vector (which is inversely proportional to the layer spacing) within the Sm-A phase we find that

$$\Delta_{q_A} = \Delta_q^0 + \frac{a_0 M_0}{K q_0^2} \tau_0, \quad (41)$$

where  $\Delta_q^0 = a_1 M_0 / K$  is the value of the correction at the continuous Sm-A–Sm-C boundary and the reader is reminded that  $a_1 = \left. \frac{da}{d(q^2)} \right|_{q^2=q_0^2}$ . At the first Sm-A–Sm-C boundary near tricriticality, at which  $\tau_0 = \tau_{1st} > 0$ , the correction is a little bit larger than  $\Delta_q^0$  [16]. From the above equation we see that as the Sm-A–Sm-C transition is approached, i.e., as  $\tau_0 \rightarrow 0_+$ , the layering wave vector decreases. This corresponds to the layer spacing increasing, a feature which is generally observed experimentally.

As with the orientational order, it is necessary to separately analyze the three distinct regions (*XY*, tricritical, and first order) of the phase diagram to obtain the correction near the Sm-A–Sm-C boundary in the Sm-C phase. Similarly, while the dependence of this correction on  $\tau_0$  differs within each region, the dependence on the respective tilt order parameter  $c$  in each region (i.e.,  $c_{XY}$ ,  $c_{TC}$ , and  $c_{1st}$ ) is identical. It is given by

$$\Delta_{q_C} = \Delta_q^0 + \frac{3|a_1| M_0}{2K} c^2, \quad (42)$$

where  $\Delta_q^0$  is equal to the value of the correction in the Sm-A phase right at the transition [16] and for a layer contraction (as opposed to dilation) to occur we have required  $a_1 < 0$ . Using the above equation and the relationship between layer spacing ( $d$ ) and wave vector ( $q = 2\pi/d$ ) we next seek the contraction in the layer spacing. This contraction is defined as  $\Delta_d = (d_{AC} - d_C) / d_{AC}$ , where  $d_{AC}$  and  $d_C$  are the values of the layer spacing in the Sm-A phase (right at the Sm-A–Sm-C boundary) and in the Sm-C phase, respectively. We find that this contraction is given by

$$\Delta_d = \frac{3|a_1| M_0}{4K} c^2. \quad (43)$$

Near the transition  $\theta \approx c$  and the fractional contraction scales as  $\theta^2$ , as one would expect from the simple geometric argument discussed in the Introduction. However, our theory predicts that this fractional contraction is also proportional to the size of the orientational order  $M \approx M_0$ . Thus, systems with unusually small orientational order will exhibit an unusually small layer contraction, as shown in Fig. 5. Given the fact that the tricritical point predicted by our model also occurs for small orientational order, it would not be surprising for some de Vries materials to exhibit Sm-A–Sm-C transitions close to tricriticality. It should also be noted that for the first-order transition, the contraction will be discontinuous, although the size of the discontinuity will nonetheless be proportional to the orientational order, which if small will make the contraction small.

## VII. SUMMARY

In summary, we have shown that our generalized Landau theory exhibits a biaxiality induced Sm-A–Sm-C tricritical point. The effect of the biaxiality is larger in systems with small orientational order, which would correspond to sys-

tems with narrow Sm-A phases. This means that the two mechanisms that have been proposed as leading to tricriticality in a system, the coupling of tilt to biaxiality and the width of the Sm-A phase, can both be attributed to the system possessing sufficiently small orientational order. For materials with excluded volume interactions, one could reduce the orientational order, and thus access a tricritical point, by reducing concentration. We have shown that the optical tilt, specific heat, and latent heat all exhibit the expected behavior near tricriticality. In addition, we have explored the effect of proximity to tricriticality on these quantities, and we have quantified the effect in terms the degree of orientational order in the system.

We have also analyzed the behavior of the birefringence (via the orientational order) and the layer spacing (via the wave vector) for each of the three possible types of transitions (*XY*-like, tricritical, and first order) near tricriticality. For de Vries material the birefringence has been shown to increase upon entry to the Sm-C phase and for a continuous transition this increase is more rapid the closer the transition is to tricriticality. It was also shown that for materials with excluded volume interactions, birefringence will decrease as the Sm-A–Sm-C transition is approached from the Sm-A phase, implying a nonmonotonic temperature dependence of birefringence, a very unusual feature. We have used our model to obtain a relationship between the layer contraction and the tilt of the optical axis as a system moves into the Sm-C phase, for any of the three possible types of transitions. This relationship predicts that systems with small orientational order in the Sm-A phase will exhibit a corresponding small layer contraction. Our result correlates well with the diffuse cone geometric argument of de Vries.

Our future work in this area will involve further generalizing our model to include chirality. Having done so, we will analyze the electroclinic effect in materials near the Sm-A–Sm-C transition. Of particular interest will be how the size of electro-optical response depends on orientational order and proximity to a tricritical point.

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## APPENDIX: CORRECTIONS TO THE BARE ORIENTATIONAL ORDER AND TO THE BARE LAYERING WAVE VECTOR

In this appendix we outline the procedure by which we obtain the corrections  $\Delta_M$  and  $\Delta_q$  to the bare orientational order and to the bare layering wave vector, respectively. This is done near the Sm-A–Sm-C boundary for both the Sm-A phase and the Sm-C phase. Near the Sm-A–Sm-C boundary within the Sm-C phase, we analyze separately the three regions of interest (*XY*-like, tricritical, and first order).

### 1. Correction to the bare orientational order

In this section we find the correction  $\Delta_M$  to the bare orientational order  $M_0$ , where  $\Delta_M$  is defined via the full orien-

tational order  $M=M_0(1+\Delta_M)$ . This is done by expanding the free energy to order  $(\Delta_M)^2$  in the phase of interest and then finding the  $\Delta_M$  that minimizes the free energy.

### a. Correction in the Sm-A phase

We begin our analysis of the correction in the Sm-A phase by expanding  $f_M$ , given by Eq. (9),

$$f_M \approx f_M(M_0) + \frac{1}{2} \gamma_M M_0^2 (\Delta_M)^2, \quad (\text{A1})$$

where  $\gamma_M = d^2 f_M / dM^2|_{M=M_0}$ . In both the Sm-A and -C phases, a nonzero  $\Delta_M$  is due to the coupling parts of the free energy. In the Sm-A phase only the piece  $f_{M\psi}$ , given by Eq. (10), is nonzero. Expanding  $f_{M\psi}$ , which requires the expansion of  $\tau$ , yields

$$f_{M\psi} \approx f_{M\psi_0} + q_0^2 |\psi_0|^2 M_0 (3g_0 M_0 - a_0 \tau_0) \Delta_M, \quad (\text{A2})$$

where  $f_{M\psi_0}$  and  $\tau_0$  are the bare values of  $f_{M\psi}$  and  $\tau$ , i.e., evaluated at  $M=M_0$ ,  $\psi=\psi_0$ , and  $q=q_0$ . We have ignored order  $(\Delta_M)^2$  terms, which are higher order in the coupling than the  $(\Delta_M)^2$  term in Eq. (A1) and are thus subdominant. Minimizing  $f_M + f_{M\psi}$  with respect to  $\Delta_M$  gives

$$\Delta_{M_A} = \frac{q_0^2 |\psi_0(T_C)|^2}{M_0 \gamma_M} (-3g_0 M_0 + a_0 \tau_0), \quad (\text{A3})$$

where we have replaced  $\psi_0 \approx \psi_0(T_C)$  near the Sm-A–Sm-C transition. The above expression can be rearranged to give Eq. (39). From the above expression we see that the correction  $\Delta_M$  is on the order of the coupling parameters  $a_0$  and  $g_0$  and is thus small as was assumed in expanding the free energy.

### b. Correction in the Sm-C phase

In finding the corrections in the Sm-C phase near the Sm-A–Sm-C boundary we first follow the same procedure as for the Sm-A phase, namely, the expansion of  $f_M$  and  $f_{M\psi}$  as given by Eqs. (A1) and (A2) above. We must also expand the piece of coupling  $f'_c$  that is nonzero in the Sm-C phase. The prime indicates the use of the biaxiality renormalized  $u'_c$ , as given by Eq. (22), in  $f_c$ , which is given by Eq. (12). For each separate region of interest (XY, tricritical, and first order) we use the appropriate expression for  $c$  in  $f'_c$ .

In the XY-like region we find

$$f'_{c_{XY}} = -\frac{r_c^2}{4u_c'} = -\frac{|\psi|^2 a^2 \tau^2}{4h_0'}. \quad (\text{A4})$$

Expanding  $\tau$  and  $h_0'$  in powers of  $\Delta_M$ , keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{XY}} \approx f'_{c_{XY_0}} + \frac{|\psi_0(T_C)|^2 M_0 a_0 \tau_0}{2h_{00}'} (g_0 + 2h_0 q_0^2) \Delta_M, \quad (\text{A5})$$

where  $f'_{c_{XY_0}}$  and  $h_{00}'$  are the bare values of  $f'_{c_{XY}}$  and  $h_0'$ .

Minimizing  $f_M + f_{M\psi} + f'_{c_{XY}}$  with respect to  $\Delta_M$  gives

$$\Delta_{M_{c_{XY}}} = \frac{q_0^2 |\psi_0(T_C)|^2}{M_0 \gamma_M} \left( -3g_0 M_0 + \frac{a_0 |\tau_0|}{2h_{00}' q_0^2} (g_0 + 2h_0 q_0^2) \right), \quad (\text{A6})$$

where, in neglecting the  $\tau_0$  dependent contribution from  $f_{M\psi}$  we have used the fact that close to tricriticality  $h_{00}'/h_0 \ll 1$ . Using the bare version of  $c=c_{XY}$  as given by Eq. (26) this expression can be rearranged to give Eq. (40).

For the tricritical region where  $u'_c$  is effectively zero, one must use  $f'_c$  evaluated at  $c=c_{TC}$  which yields

$$f'_{c_{TC}} = -\frac{1}{3} \sqrt{\frac{-r_c^3}{v_c}} = -\frac{2|\psi|^2}{3\sqrt{3}} \sqrt{\frac{-a^3 \tau^3}{s_0}}. \quad (\text{A7})$$

Expanding  $\tau$  in powers of  $\Delta_M$  while keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{TC}} \approx f'_{c_{TC_0}} - |\psi_0(T_C)|^2 M_0 \sqrt{\frac{a_0 |\tau_0|}{3s_0}} (g_0 + 2h_0 q_0^2) \Delta_M, \quad (\text{A8})$$

where  $f'_{c_{TC_0}}$  is the bare value of  $f'_{c_{TC}}$ .

Minimizing  $f_M + f_{M\psi} + f'_{c_{TC}}$  with respect to  $\Delta_M$  gives

$$\Delta_{M_{c_{TC}}} = \frac{q_0^2 |\psi_0(T_C)|^2}{M_0 \gamma_M} \left( -3g_0 M_0 + \sqrt{\frac{a_0 |\tau_0|}{3s_0 q_0^4}} (g_0 + 2h_0 q_0^2) \right), \quad (\text{A9})$$

where, in neglecting the  $\tau_0$  dependent contribution from  $f_{M\psi}$  we have used the fact that  $\sqrt{\tau_0} \gg \tau_0$  close to tricriticality, i.e., where  $\tau_* \ll 1$ . Using the bare version of  $c=c_{TC}$  as given by Eq. (26) this expression can be rearranged to give Eq. (40).

Lastly we obtain the correction in  $\Delta_M$  in the Sm-C phase (where  $h_0' < 0$ ) near the first-order Sm-A–Sm-C boundary. We do this by expanding  $f'_c$  near the first-order Sm-A–Sm-C boundary, the expression for which is given by Eq. (29). Expanding  $\tau$ ,  $h_0'$  and  $\tau_*$  (which depends on  $h_0'$ ) in powers of  $\Delta_M$  while keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{1st}} \approx f'_{c_{1st_0}} - \frac{|\psi_0(T_C)|^2 M_0 |h_{00}'|}{3s_0} \times \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right) (g_0 + 2h_0 q_0^2) \Delta_M, \quad (\text{A10})$$

where  $f'_{c_{1st_0}}$  is the bare value of  $f'_{c_{1st}}$ .

Minimizing  $f_M + f_{M\psi} + f'_{c_{1st}}$  with respect to  $\Delta_M$  gives

$$\Delta_{M_{c_{1st}}} = \frac{q_0^2 |\psi_0(T_C)|^2}{M_0 \gamma_M} \left[ -3g_0 M_0 + \frac{|h_{00}'|}{3s_0 q_0^2} \times \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right) (g_0 + 2h_0 q_0^2) \right], \quad (\text{A11})$$

where  $\tau_{*0}$  is the bare value of  $\tau_*$  and, in neglecting the  $\tau_0$ -dependent contribution from  $f_{M\psi}$  we have used the fact that close to tricriticality  $h_{00}'/h_0 \ll 1$ . Using the bare version

of  $c=c_{1st}$  as given by Eq. (28) this expression can be rearranged to give Eq. (40).

## 2. Correction to the bare wave vector

In this section we find the correction  $\Delta_q$  to the bare wave vector  $q_0$ , where  $\Delta_q$  is defined via the full wave vector  $q^2 = q_0^2(1 + \Delta_q)$ . As with the orientational order, this is done by expanding the free energy to order  $(\Delta_q)^2$  in the phase of interest and then finding the  $\Delta_q$  that minimizes the free energy.

### a. Correction in the Sm-A phase

We begin our expansion of the free energy in powers of  $\Delta_q$  by expanding  $f_\psi$  given by Eq. (7),

$$f_\psi \approx \frac{1}{2} K |\psi_0|^2 q_0^4 \Delta_q^2. \quad (\text{A12})$$

In both the Sm-A and -C phases, a nonzero  $\Delta_q$  is due to the coupling parts of the free energy. In the Sm-A phase only the piece  $f_{M\psi}$  given by Eq. (10), is nonzero. Expanding  $f_{M\psi}$  yields

$$f_{M\psi} \approx f_{M\psi_0} - q_0^2 |\psi_0|^2 M_0 (a_1 q_0^2 + a_0 \tau_0) \Delta_q, \quad (\text{A13})$$

where we have used the fact that  $M$  is small near tricriticality. We have ignored order  $(\Delta_q)^2$  terms, which are higher order in the coupling than the  $(\Delta_q)^2$  term in Eq. (A12) and are thus subdominant. Minimizing  $f_M + f_{M\psi}$  with respect to  $\Delta_q$  gives

$$\Delta_{qA} = \frac{M_0}{K q_0^2} (a_1 q_0^2 + a_0 \tau_0). \quad (\text{A14})$$

The above expression can be rearranged to give Eq. (41). From the above expression we see that the correction  $\Delta_q$  is on the order of the coupling parameters  $a_0$  and  $a_1$  and is thus small as was assumed in expanding the free energy.

### b. Correction in the Sm-C phase

In finding the corrections in the Sm-C phase near the Sm-A–Sm-C boundary we follow the same procedure as for the orientational order. To obtain the correction within the XY-like region we use  $f'_{c_{XY}}$  as given by Eq. (A4). Expanding  $\tau$  and  $h'_0$  in powers of  $\Delta_q$ , keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{XY}} \approx f'_{c_{XY_0}} - \frac{|\psi_0(T_C)|^2 a_1 q_0^2 a_0 \tau_0}{2 h'_{00}} \Delta_q, \quad (\text{A15})$$

where we have used the fact that  $M$  is small near tricriticality.

Minimizing  $f_M + f_{M\psi} + f'_{c_{XY}}$  with respect to  $\Delta_q$  gives

$$\Delta_{q_{c_{XY}}} = \frac{a_1}{K q_0^2} \left( M_0 q_0^2 - \frac{a_0 |\tau_0|}{2 h'_{00}} \right), \quad (\text{A16})$$

where, in neglecting the  $\tau_0$ -dependent contribution from  $f_{M\psi}$ , we have used the fact that close to tricriticality  $h'_{00}/h_0 \ll 1$ . Using the bare version of  $c=c_{XY}$  as given by Eq. (26) this expression can be rearranged to give Eq. (42).

For the tricritical region we use  $f'_{c_{TC}}$  as given by Eq. (A7). Expanding  $a$  and  $\tau$  in powers of  $\Delta_q$  while keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{TC}} \approx f'_{c_{TC_0}} + |\psi_0(T_C)|^2 q_0^2 a_1 \sqrt{\frac{a_0 |\tau_0|}{3 s_0}} \Delta_q, \quad (\text{A17})$$

where we have used the fact that  $M$  is small near tricriticality.

Minimizing  $f_M + f_{M\psi} + f'_{c_{TC}}$  with respect to  $\Delta_q$  gives

$$\Delta_{q_{c_{TC}}} = \frac{a_1}{K q_0^2} \left( M_0 q_0^2 - \sqrt{\frac{a_0 |\tau_0|}{3 s_0}} \right), \quad (\text{A18})$$

where, in neglecting the  $\tau_0$ -dependent contribution from  $f_{M\psi}$ , we have used the fact that  $\sqrt{\tau_0} \gg \tau_0$  close to tricriticality, i.e., where  $\tau_* \ll 1$ . Using the bare version of  $c=c_{TC}$  as given by Eq. (26) this expression can be rearranged to give Eq. (42).

We conclude by obtaining the correction in  $\Delta_q$  in the Sm-C phase (where  $h'_0 < 0$ ) near the first-order Sm-A–Sm-C boundary. We do this by expanding  $f'_c$  near the first-order Sm-A–Sm-C boundary, the expression for which is given by Eq. (29). Expanding  $\tau$  and  $h'_0$  in powers of  $\Delta_q$ , keeping terms to lowest order in  $\tau_0$  and coupling coefficients gives

$$f'_{c_{1st}} \approx f'_{c_{1st_0}} + \frac{|\psi_0(T_C)|^2 a_1 q_0^2 h'_{00}}{3 s_0} \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right) \Delta_q, \quad (\text{A19})$$

where we have used the fact that  $M$  is small near tricriticality.

Minimizing  $f_M + f_{M\psi} + f'_{c_{1st}}$  with respect to  $\Delta_q$  gives

$$\Delta_{M_{c_{1st}}} = \frac{a_1}{K q_0^2} \left[ M_0 q_0^2 - \frac{|h'_{00}|}{3 s_0} \left( 1 + \sqrt{1 - \frac{4\tau}{|\tau_*|}} \right) \right], \quad (\text{A20})$$

where, in neglecting the  $\tau_0$ -dependent contribution from  $f_{M\psi}$ , we have used the fact that close to tricriticality  $h'_{00}/h_0 \ll 1$ . Using the bare version of  $c=c_{1st}$  as given by Eq. (28) this expression can be rearranged to give Eq. (42).

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- [16] As with the orientational order [15], it is straightforward to show that at the first-order Sm-A–Sm-C transition the value of the correction  $\Delta_{q_A} = |\Delta_q^0|(-1 + \frac{a_0}{16|a_1q_0^2}\tau_{*0})$ , which near the tricritical point is  $\approx -|\Delta_q^0|$ .