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A Twist on the Electroclinic Critical Point: Type I and Type II Smectic C^* Systems

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We conduct an in-depth analysis of the electroclinic effect in chiral, ferroelectric liquid crystal systems that have a first order Smectic- A^* -Smectic- C^* (Sm- A^* -Sm- C^*) transition, and show that such systems can be either Type I or Type II. In temperature-field parameter space Type I systems exhibit a macroscopically achiral (in which the Sm- C_M^* helical superstructure is expelled) low-tilt (LT) Sm- C_U^* -high-tilt (HT) Sm- C_U^* critical point, which terminates a LT Sm- C_U^* -HT Sm- C_U^* first order boundary. Notationally, Sm- C_M^* /Sm- C_U^* denote the Sm- C^* phase with/without a modulated superstructure. This boundary extends to an achiral-chiral triple point at which the macroscopically achiral LT Sm- C_U^* and HT Sm- C_U^* phases coexist along with the chiral Sm- C_M^* phase. In Type II systems the critical point, triple point, and first order boundary are replaced by a Sm- C_M^* region, sandwiched between LT and HT Sm- C_U^* phases, at low and high fields respectively. Correspondingly, as the field is ramped up, the Type II system will display a reentrant Sm- C_U^* -Sm- C_M^* -Sm- C_U^* phase sequence. Moreover, discontinuity in the tilt of the optical axis at each of the two phase transitions means the Type II system is tristable, in contrast to the bistable nature of the LT Sm- C_U^* -HT Sm- C_U^* transition in Type I systems. Whether the system is Type I or Type II is determined by the ratio of two length scales, one of which is the zero-field Sm- C^* helical pitch. The other length scale depends on the size of the discontinuity (and thus the latent heat) at the zero-field first order Sm- A^* -Sm- C^* transition. We note that this Type I vs Type II behavior in this ferroelectric smectic is the Ising universality class analog of Type I vs Type II behavior in XY universality class systems. Lastly, we make a complete mapping of the phase boundaries in all regions of temperature-field-enantiomeric excess parameter space (not just near the critical point) and show that a variety of interesting features are possible, including a multicritical point, tricritical points and a doubly reentrant Sm- C_U^* -Sm- C_M^* -Sm- C_U^* -Sm- C_M^* phase sequence.

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I. INTRODUCTION: CHIRAL SMECTIC- C^* PHASES AND THE ELECTROCLINIC CRITICAL POINT

In the 1970s Meyer[1] used an elegant symmetry argument to predict that the application of an electric field to a chiral Smectic- A^* (Sm- A^*) phase would induce a transition to the Smectic- C^* (Sm- C^*) phase, along with an associated tilt of the optical axis. This electroclinic effect was subsequently confirmed experimentally[2]. This in turn led to the development of electro-optic devices using ferroelectric (chiral) liquid crystals and also to the synthesis of many new ferroelectric liquid crystals possessing Sm- A^* and Sm- C^* phases. These ferroelectric liquid crystals, and their behavior in an electric field, have been the subject of much experimental and theoretical study in the decades since the discovery of the electroclinic effect[3].

It is worth briefly reviewing the basics of the smectic phases. As shown schematically in Fig. 1(a), smectics have a modulated density along one direction (\hat{z}). The elongated molecules tend to align their long axes along a common direction (\hat{n}) known as the director or optical axis. In the Sm- A phase, $\hat{n} = \hat{z}$, while in the lower temperature Sm- C phase, \hat{n} lies at an angle θ relative to \hat{z} . The order parameter of the Sm- C phase is c , the projection of \hat{n} onto the xy layering plane. For nonchiral smectics, the transition from the Sm- A to the Sm- C phase is typically induced by lowering temperature, but can also be induced by compressing the smectic layers or by varying concentration. For a chiral Sm- A^* phase, the transition can also be induced via the electroclinic effect, i.e., by applying an electric field \mathbf{E} perpendicular to \hat{z} . Application of a field to a system already in the Sm- C^* phase will increase the degree of tilt. It is important to note that the direction of the induced tilt (c) is determined by the direction of \mathbf{E} . For the schematic shown in Fig. 1(a), $\mathbf{E} = E\hat{y}$ (into the page) induces $c = c\hat{x}$ (to the right). Switching the field, i.e., $\mathbf{E} = -E\hat{y}$ (out of the page) would switch the direction of the induced tilt, i.e., $c = -c\hat{x}$ (to the left). This switching behavior is a key feature in the operation of surface stabilized ferroelectric LCDs[4].

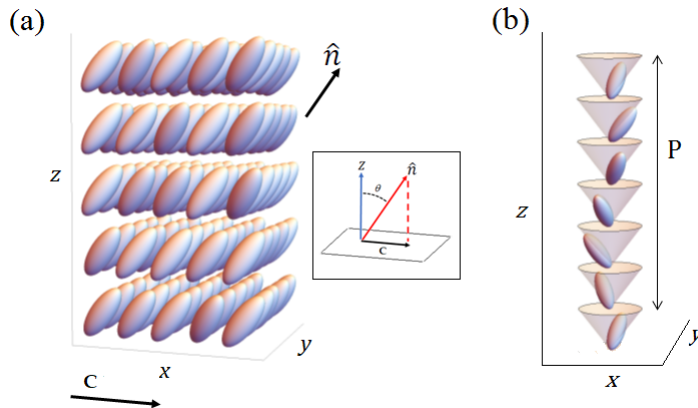


FIG. 1. A schematic representation of (a) the Sm- C_U^* phase and (b) the Sm- C_M^* phase. The inset shows the tilt angle θ of the director \hat{n} relative to the layer normal \hat{z} , and also c , the Sm- $C_{U/M}^*$ order parameter. In the Sm- C_M^* phase the average molecular direction precesses from layer to layer. This modulation along z has period P . For zero field the modulation is perfectly helical, as shown here. For sufficiently large electric field the modulation is expelled, and the average molecular direction is uniform, as shown for the Sm- C_U^* phase.

The simple situation described above is complicated by the fact that in the Sm- C^* phase, the director \hat{n} is not uniform. Instead, it precesses around \hat{z} with a periodicity that is larger than the layer spacing. In the absence of a field, this precession is helical, as shown schematically in Fig. 1(b). This Sm- C^* chiral superstructure is a macroscopic manifestation of the microscopic chirality of the constituent molecules[5]. As discussed above, the electroclinic effect both increases the magnitude of the tilt *and* selects a direction for the tilt. This means that the field tends to expel the Sm- C^* chiral superstructure, and for a sufficiently large field, there is a transition from the Sm- C_M^* phase to the Sm- C_U^* phase in which the director \hat{n} is uniform, as shown in Fig. 1(a). Notationally, we use Sm- C_M^* for the phase in which \hat{n} is modulated and precesses around \hat{z} , while we use Sm- C_U^* for the phase in which \hat{n} is uniform and the macroscopic chiral superstructure has been expelled. Of course, the Sm- C_U^* phase is still microscopically chiral and is thus responsive to the electroclinic effect. We will often refer to this Sm- C_M^* –Sm- C_U^* transition as a modulated–uniform transition. It is important to remember that modulated–uniform refers to the director \hat{n} and

not to the density. In both the $\text{Sm-}C_M^*$ and $\text{Sm-}C_U^*$ phases the density is modulated. The critical field $E_c(T)$ for the transition between the $\text{Sm-}C_M^*$ and $\text{Sm-}C_U^*$ phases depends on temperature T , and the corresponding E - T phase diagram has been investigated (both experimentally [6–8] and theoretically [9–11]) for materials with a *continuous* zero-field $\text{Sm-A-Sm-}C_M^*$ transition, i.e., a continuous growth of the order parameter magnitude $|\mathbf{c}|$ upon entry to the $\text{Sm-}C_M^*$ phase. The history of this work is well summarized by Ghoddoussi et al, [7].

In this article we present T - E phase diagrams for systems with a *first order* $\text{Sm-A}^*-\text{Sm-}C_M^*$ transition, in which $|\mathbf{c}|$ jumps to a non-zero value upon entry to the $\text{Sm-}C_M^*$ phase, with an associated non-zero latent heat. We will see that the phase diagrams for such systems are rich, including the possibility of reentrance, as well as distinct Type I and Type II behaviors.

One motivation for studying systems with a first order $\text{Sm-A}^*-\text{Sm-}C_M^*$ transition is that the first order nature of the transition leads to a more dramatic electroclinic effect discovered by Bahr and Heppke[12], as shown in Fig. 2(a). For materials with a continuous $\text{Sm-A}^*-\text{Sm-}C^*$ transition, the induced tilt grows continuously with increasing field, whereas for materials with a first order $\text{Sm-A}^*-\text{Sm-}C^*$ transition, there is a temperature window within which the induced tilt jumps discontinuously with increasing field. This high-tilt–low-tilt phase boundary is shown in Fig. 2(b). According to a theoretical model by Bahr and Heppke[13], if one ignores the possibility of helical modulation, the high-tilt–low-tilt phase boundary extends from the (zero field) $\text{Sm-A}^*-\text{Sm-}C_U^*$ transition temperature and terminates at a critical point, where the size of the high-tilt–low-tilt discontinuity shrinks to zero. This critical point is basically Ising-like and analogous to the liquid–gas critical point[14]. The theoretical analysis[13] of the critical point assumed

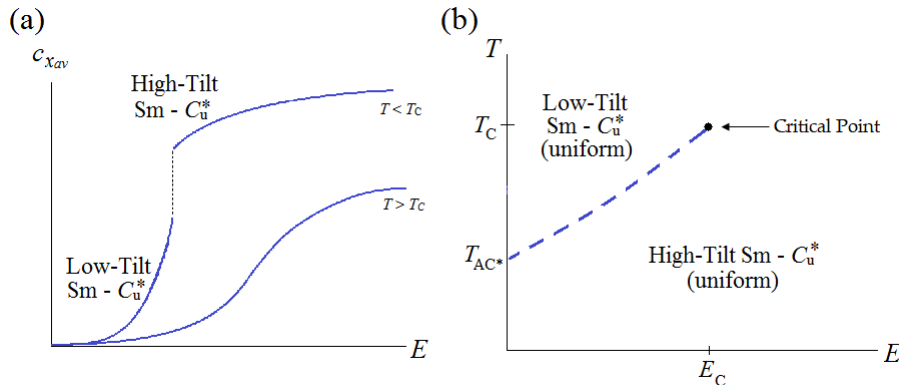


FIG. 2. (a) The electroclinic effect, i.e., average tilt ($c_{x,av}$) vs electric field (E) for fixed temperatures for a material with a first order $\text{Sm-A}^*-\text{Sm-}C^*$ transition. For $T \lesssim T_c$ there is a discontinuous jump between low tilt and high tilt states, and the system is bistable. (b) The first order phase boundary separating uniform low-tilt from uniform high-tilt $\text{Sm-}C_U^*$ phases. The phase boundary terminates at an Ising-like critical point at T_c , as found in [12]. The phase diagram assumes zero modulation.

a $\text{Sm-}C^*$ phase without any modulation of the director which, using our notation, means that the analysis considered the electroclinic effect in only the uniform $\text{Sm-}C_U^*$ phase. This was justified by the fact that the critical point was at a field larger than the field required to expel the modulated superstructure. However, there is no reason, a priori, to assume that this is true in all systems.

II. SUMMARY OF RESULTS

In mapping out the T - E phase diagrams for systems with a first order $\text{Sm-A}^*-\text{Sm-}C^*$ transition we are also able to carry out a more complete analysis of the electroclinic effect in such systems, i.e., an analysis that, unlike [13], does not assume a uniform $\text{Sm-}C_U^*$ phase. We find that for some systems, which we categorize as Type I, the critical point does indeed exist within the uniform ($\text{Sm-}C_U^*$) region, as found by [12, 13]. However, we show that for other systems, which we categorize as Type II, the critical point no longer exists, and that the high-tilt–low-tilt line is replaced by a modulated region. Phase diagrams for these two classes of systems are shown in Fig. 3.

Whether a system with a first order $\text{Sm-A}^*-\text{Sm-}C^*$ transition is Type I or Type II depends on a ratio of length scales, which we denote m . One of these is the helical pitch at the zero field $\text{Sm-A}^*-\text{Sm-}C^*$ transition. The other length scale is the correlation length (at the critical point) for fluctuations of the tilt director away from the direction imposed by the electric field. Systems with long helical pitch (corresponding to small chirality) will be Type I, while

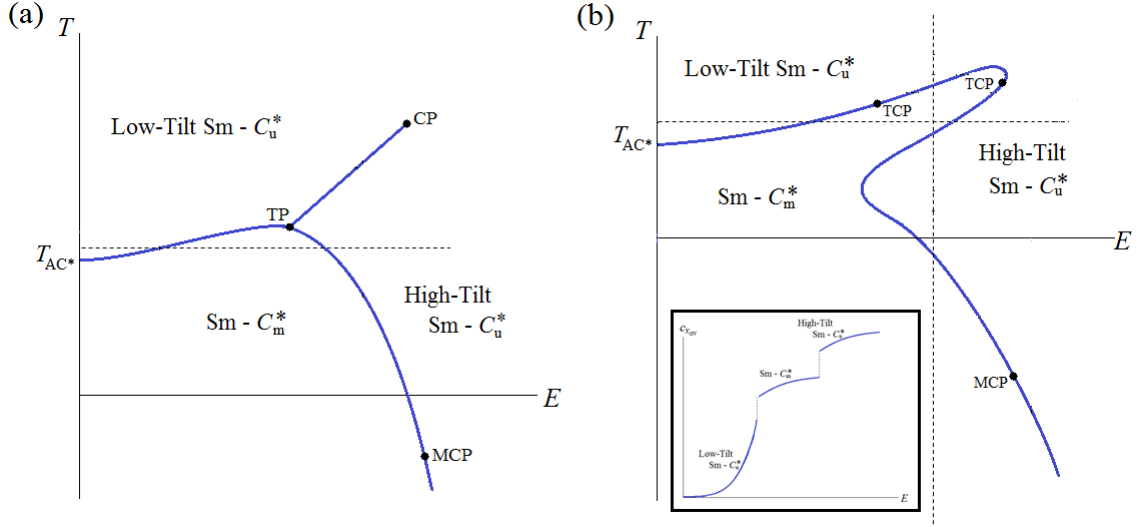


FIG. 3. T - E phase diagrams for (a) Type I systems and (b) Type II systems. The smectic A phase exists for $E = 0$ and $T > T_{AC}^*$. CP denotes critical point, TP denotes triple point, MCP denotes multicritical point, and TCP denote tricritical points. Each figure shows a fixed temperature path that will exhibit the reentrant phase sequence: $Sm-A^*-Sm-C_U^*-Sm-C_M^*-Sm-C_U^*$, as E is ramped up. The inset shows the corresponding average tilt vs E , which is tristable. The fixed E path shown on the Type II phase diagram will exhibit the doubly reentrant phase sequence: $Sm-C_U^*-Sm-C_M^*-Sm-C_U^*-Sm-C_M^*$.

those with short helical pitch (corresponding to large chirality) will be Type II. Thus, a system could be tuned via varying enantiomeric excess to be Type I or Type II. Of course, the length scale ratio also depends on other system parameters, including, as we shall see, the size of the tilt discontinuity at the first order transition. We will show that systems with weakly first order transitions can be Type II, even with relatively low chirality. In Section IV we present a more detailed discussion of the length scale ratio m , and also how Type I vs Type II behavior may be accessed experimentally. In addition, we present a complete 3D phase diagram in temperature-field-chirality parameter space, from which one can see how the system can be tuned between Type I and Type II.

The Type I vs Type II behavior in $Sm-C^*$ phases is reminiscent of Type I vs Type II behavior in superconductors[15]. In Type I superconductors there are two phases, the high- T normal phase and low- T superconducting phase. In Type II superconductors there is an intermediate, modulated phase, the Abrikosov flux lattice. Type I vs Type II behavior is determined by the Ginzberg parameter, a ratio of the London penetration depth to the superconducting correlation length. There is also Type I vs Type II behavior in another type of chiral liquid crystal, near the cholesteric (N^*)-smectic- A^* transition[16]. For Type I systems there is a high- T (N^*)-low- T ($Sm-A^*$) transition. For Type II systems there is an intermediate, modulated phase known as the Twist Grain Boundary (TGB) phase, a set of $Sm-A^*$ domains separated by a modulated, periodic array of twist grain boundaries. In this case the Ginzburg parameter is the ratio of the twist penetration depth to the smectic correlation length. For the Type I vs Type II behavior in $Sm-C^*$ systems that we present here, the high- T phase is the low tilt $Sm-C_U^*$ while the low- T phase is the high tilt $Sm-C_M^*$. Thus, the intermediate modulated $Sm-C_M^*$ phase is analogous to the Abrikosov flux lattice or the TGB phase.

It should be pointed out that our Type I vs Type II analogy is only appropriate for temperatures near the critical point. For sufficiently low temperatures the phase will always be modulated. For a Type I system the phase boundary between low tilt and high tilt uniform states intersects the boundary for the modulated phase at a triple point as shown in Fig. 3(a). At this uniform-modulated triple point the uniform low-tilt phase, the uniform high-tilt phase, and the modulated phase are all energetically equivalent, and thus the system is equally likely to be found in any of the three phases.

Another notable result of our model is the possibility of uniform-modulated reentrance within Type I or Type II systems, for which there is no analogous behavior in systems with normal-superconducting or N^* - $Sm-A^*$ transitions[17]. This makes reentrance possible. In Figs. 3(a) and (b) the fixed T path will exhibit the reentrant phase sequence $Sm-A^*-Sm-C_U^*-Sm-C_M^*-Sm-C_U^*$, while in Fig. 3(b) the fixed E path will exhibit the *doubly reentrant* phase sequence $Sm-C_U^*-Sm-C_M^*-Sm-C_U^*-Sm-C_M^*$. Fig. 3(b) we also show the field (E) dependence of the average tilt for the $Sm-A^*-Sm-C_U^*-Sm-C_M^*-Sm-C_U^*$ sequence. The average tilt exhibits *two* discontinuities, one at the $Sm-C_U^*-Sm-C_M^*$ transition, and the other at the $Sm-C_M^*-Sm-C_U^*$ transition, and the system is *tristable*. Of course, the tilt in the $Sm-C_M^*$ phase is modulated, but has a non-zero average (over one modulation period).

The remainder of the paper is organized as follows. In Section III we establish the model and free energy. In

Section IV we estimate the length scale ratio that delineates Type I and Type II behavior, and also discuss ways to experimentally access each type of behavior. In Section V, we map out the small E and low T phase boundaries. For both Type I and Type II systems these parts of phase boundaries are similar. We analyze the most interesting region of the phase diagrams, near the uniform low tilt – high tilt critical point in Sections VI and VII, mapping out the Type II region in Section VI and the Type I region in Section VII. We discuss the crossover between Type I and Type II phase diagrams in Section VIII. Numerical results are presented in Section IX and we conclude with some discussion and future plans in Section X. The Appendices contain some technical details of our analyses as well as a rescaling prescription for comparing how experimental results could be compared with our theoretical predictions.

III. MODEL AND FREE ENERGY

As shown in Fig. 1 the order parameter for the tilted phases (either the uniform $\text{Sm-}C_U^*$ phase or the modulated $\text{Sm-}C_M^*$ phase) is the two-component vector, $\mathbf{c}(\mathbf{r})$ that describes the local tilt of the molecular director relative to the layers. The vector \mathbf{c} is perpendicular to the layer normal $\hat{\mathbf{z}}$. As shown in Fig. 1(a) the magnitude of the order parameter $|\mathbf{c}(\mathbf{r})| = \sin \theta$, where θ is the tilt angle between the molecular director $\hat{\mathbf{n}}$ and the layer normal $\hat{\mathbf{z}}$. The molecular director $\hat{\mathbf{n}}$ can be expressed in terms of \mathbf{c} as $\hat{\mathbf{n}} = \mathbf{c} + \sqrt{1 - |\mathbf{c}|^2} \hat{\mathbf{z}}$, or equivalently as $\hat{\mathbf{n}} = \sin \theta \hat{\mathbf{c}} + \cos \theta \hat{\mathbf{z}}$. In the untilted Sm-A^* phase $\theta = \mathbf{c} = 0$. In the uniform $\text{Sm-}C_U^*$ phase, $\mathbf{c}(\mathbf{r}) = \mathbf{c}$, independent of position \mathbf{r} . In the modulated $\text{Sm-}C_M^*$ phase, the precession of the optical axis around the layer normal $\hat{\mathbf{z}}$ shown in Fig. 1(b) corresponds to periodic, z -dependent $\mathbf{c}(\mathbf{r}) = \mathbf{c}(z)$. Our analysis is restricted to the ground states of the different phases, and does not consider thermal fluctuations of the order parameter $\mathbf{c}(\mathbf{r})$ or the layers. Previous analyses of the *non-chiral* $\text{Sm-A}^* \text{--} \text{Sm-}C_U^*$ transition have included fluctuation effects due to both layers and molecular tilt[18, 19]. Interestingly, at a $\text{Sm-A}^* \text{--} \text{Sm-C}$ tricritical point (where a first order phase boundary meets a second order phase boundary) the stronger, tricritical fluctuations of the molecular tilt can be shown to destroy the smectic layering[19]. An analysis of the fluctuation effects near the *chiral* $\text{Sm-A}^* \text{--} \text{Sm-}C_M^*$ transition will be carried out at a later date [20].

Having established the order parameter $\mathbf{c}(\mathbf{r})$, we employ standard Landau theory[21], expanding the free energy in powers of the order parameter and its spatial gradients. The validity of such an expansion is predicated on a small $|\mathbf{c}(\mathbf{r})|$, or equivalently a small tilt angle θ . Carrying out the expansion results in a free energy per unit volume:

$$\frac{F}{V} = \frac{q}{2\pi} \int_0^{2\pi/q} dz \left[\frac{r(T)}{2} |\mathbf{c}|^2 + \frac{u}{4} |\mathbf{c}|^4 + \frac{v}{6} |\mathbf{c}|^6 + \frac{K_b}{2} (\partial_z \mathbf{c})^2 - e\eta (c_x \partial_z c_y - c_y \partial_z c_x) - eg E c_x \right], \quad (1)$$

with $r(T) = \alpha(T - T_0)$ the temperature dependent parameter that drives the transition. The constants α and T_0 are system dependent. In Appendix A we detail the procedure for experimentally mapping from T to $r(T)$, but for now it is enough to know that $r(T)$ is a monotonically increasing function of temperature. Both u and v are temperature independent constants, and stability of the system requires that $v > 0$. The elastic constant K_b is the standard elastic constant for bend distortions of the molecular director $\hat{\mathbf{n}}$, and, results from inserting $\hat{\mathbf{n}} = \mathbf{c} + \sqrt{1 - |\mathbf{c}|^2} \hat{\mathbf{z}}$ into the standard Frank elastic energy density [22] and expanding to order $|\mathbf{c}(\mathbf{r})|^2$. The remaining terms break chiral symmetry, and are only appropriate for chiral smectics. The term proportional to η favors a helical modulation of \mathbf{c} with pitch $P_0 = \frac{2\pi}{q_0} = \frac{2\pi K_b}{e\eta}$. The second term is responsible for the well-known electroclinic effect[1, 2], whereby a coupling between the tilt and polarization of the molecules allows an electric field $\mathbf{E} = E\hat{\mathbf{y}}$, to break the inversion symmetry within the plane of the layers, and thus causing the molecules to uniformly tilt along a direction perpendicular to the field, i.e., $\mathbf{c} = c\hat{\mathbf{x}}$. The constant g is proportional to the electric susceptibility. Thus, the two chiral terms compete, with the first favoring a modulated state and the second favoring a uniform state. We include a common, dimensionless factor, e , which represents the degree of chirality, and is thus a monotonically increasing function of enantiomeric excess. In a racemate, $e = 0$ and neither of the chiral terms is present. Since \mathbf{c} is periodic along z , the integral over the length of the smectic has been converted into one over a single period $2\pi/q$.

We note that a more fundamental free energy would include a bilinear coupling ($\propto \hat{\mathbf{z}} \cdot (\mathbf{p} \times \mathbf{c})$) between polarization (\mathbf{p}) and tilt (\mathbf{c}), and also a bilinear coupling ($\propto \mathbf{p} \cdot \mathbf{E}$) between polarization and field. Elimination (via energy minimization) of the polarization would result in the bilinear coupling ($\propto \hat{\mathbf{z}} \cdot (\mathbf{E} \times \mathbf{c})$) between tilt and field that is presented above. Also, past theoretical treatments[10, 11] of the transition for the compound DOBAMBC have used a model[23] that included higher order terms in their Landau expansion. This model was developed with the express purpose of modeling a nonmonotonic temperature dependence of the $\text{Sm-}C_M^*$ helical pitch near the *continuous* zero-field $\text{Sm-A}^* \text{--} \text{Sm-}C_M^*$ transition for that compound[23]. However, as pointed out by Ghoddoussi et al[7] not all higher order terms of equivalent order were included, just those needed to fit the experimental data for that compound. In this work, we are not modeling this specific compound (or *any* compound with a continuous zero-field $\text{Sm-A}^* \text{--} \text{Sm-}C_M^*$ transition) and therefore do not a priori need to include any higher order terms in our Landau expansion. Indeed, as we will soon show, the above model given by Eq. (1) can be rescaled so that it depends on only three independent parameters. We find the relative simplicity of the model and the richness of its predictions to be appealing.

IV. ESTIMATING THE LENGTH SCALE RATIO AND EXPERIMENTAL PARAMETERS THAT DETERMINE TYPE I VS TYPE II BEHAVIOR

As discussed in Section II, we find that systems with a first order Sm- A^* -Sm- C_M^* transition can be categorized as Type I or Type II. Type I systems have a first order uniform low-tilt uniform high-tilt (Sm- C_U^* -Sm- C_U^*) phase boundary that terminates in an Ising-type critical point. In Type II systems the critical point is absent and there is a modulated (Sm- C_M^*) phase between the uniform low-tilt and uniform high-tilt phases. Whether the system is Type I or Type II depends on a ratio of length scales. We calculate this ratio more carefully using an instability analysis in Section VI A, but here we use a heuristic energetic argument that better illustrates *why* there are distinct Type I and Type II systems, and also results in an estimate that is accurate to within a factor of order one. To determine whether a system is Type I we employ a length scale estimate to determine whether the uniform, tilted phase (Sm- C_U^*) is energetically favorable compared to the modulated, tilted state. As discussed in the above section, for $\mathbf{E} = E\hat{\mathbf{y}}$, the lowest energy uniform state has $\mathbf{c} = c_u\hat{\mathbf{x}}$. The equation of state for c_u is found by minimizing the free energy of Eq. (1), which gives

$$E = (rc_u + uc_u^3 + vc_u^5)/eg. \quad (2)$$

The energetic *cost* of a deviation away from this uniform state can be estimated by inserting a non-uniform $\mathbf{c} = c_u\hat{\mathbf{x}} + \sigma_y(z)\hat{\mathbf{y}}$ into the free energy of Eq. (1), in which $\eta = 0$. By setting $\eta = 0$ we intentionally omit the energetic gain for a chiral deviation $\sigma_y(z)$. To $\mathcal{O}(\sigma_y^2)$, the energetic cost is

$$\Delta f_\sigma = \frac{1}{2}\chi_y^{-1}\sigma_y^2 + \frac{1}{2}K_b(\partial_z\sigma_y)^2, \quad (3)$$

where the susceptibility χ_y is given by

$$\chi_y^{-1} = r + uc_u^2 + vc_u^4 = \frac{egE}{c_u}. \quad (4)$$

The second equality is obtained using the equation of state Eq. (2). Equation (3) then gives a correlation length which can be interpreted as the length scale above which deviations away from the uniform ground state come at a significant energetic cost:

$$\xi_y = \sqrt{\frac{K_b}{\chi_y^{-1}}} = \sqrt{\frac{K_b c_u}{egE}} = \sqrt{\frac{K_b}{(r + uc_u^2 + vc_u^4)}}, \quad (5)$$

Now we remind ourselves that the $\eta \neq 0$ term favors a chiral modulation along z with a length scale $P_0 = \frac{2\pi}{q_0} = \frac{2\pi K_b}{e\eta}$, and argue (heuristically) that such a modulation will *not* be energetically favorable if it occurs on a length scale large compared to ξ_y . In other words, the uniform state is favorable if $\frac{\xi_y}{P_0} < 1$. To determine when a system is Type I, we apply this criterion at the uniform low-tilt uniform high-tilt (Sm- C_U^* -Sm- C_U^*) critical point. The location of this critical point in r - E space is found by solving $E'(c_u) = E''(c_u) = 0$ which yields the critical point values:

$$c_{uc} = \sqrt{\frac{-3u}{10v}}, \quad r_c = \frac{9u^2}{20v}, \quad E_c = \frac{6u^2 c_{uc}}{25egv}, \quad (6)$$

so that at the critical point the correlation length is

$$\xi_{y_c} = \sqrt{\frac{25K_b v}{6u^2}}. \quad (7)$$

Thus the length scale ratio that determines whether the system is Type I or Type II is

$$\frac{\xi_{y_c}}{P_0} \sim e\eta \sqrt{\frac{v}{K_b u^2}}. \quad (8)$$

where we have omitted constants of order one. We note that the sign of the length scale is determined by the sign of the chirality, and simply corresponds to the handedness of the chiral modulation. For $\frac{\xi_{y_c}}{P_0} < 1$ the chiral modulations are too energetically costly at the critical point, and the system will be Type I, while for $\frac{\xi_{y_c}}{P_0} > 1$ they are energetically favorable and the system will be Type II. That $\frac{\xi_{y_c}}{P_0}$ is a monotonically increasing function of enantiomeric excess e makes sense, since modulated states are favored in systems with larger enantiomeric excess. Of course, $\frac{\xi_{y_c}}{P_0}$ also

depends on other parameters, including K_b the bend modulus, as well as v and u , with the latter two controlling the discontinuity of the first order ($u < 0$) transition. We suggest that the above equation could be used as a guide towards identifying a Type II Sm- C_M^* system, e.g., a material with a combination of large chirality (large e) and/or a weakly first order transition (small $u < 0$). Perhaps such a combination could be obtained through synthesis or mixing. The variation of enantiomeric excess (e) by mixing isomers of opposite handedness is well-established [22] and variation of $u < 0$ has also been achieved through mixing [24].

From the ratio in Eq. (8) we also see that for a system with a tricritical Sm- A^* -Sm- C_M^* , i.e., with $u = 0$, the ratio $\frac{\xi_{yc}}{P_0}$ will diverge, and Type II behavior will always result. However, such a system will *not* have a first order uniform low-tilt uniform high-tilt (Sm- C_U^* -Sm- C_U^*) phase boundary, nor the associated Ising type critical point. If we again consider a model with $\eta = 0$, i.e., one in which we intentionally omit the energetic gain for a chiral deviation, any system with $u \geq 0$ will have a Heisenberg type critical point at $r = E = 0$. Since $E = 0$, no special direction is picked out for \mathbf{c} , i.e., the symmetry is *spontaneously* broken at the continuous transition to the Sm- C_U^* phase. The associated Goldstone mode means that deviations away from the spontaneously chosen direction of \mathbf{c} cost no energy, so that an infinitesimal amount of chirality will result in a modulated state. This differs from the $u < 0$ critical point at $E_c \neq 0$, which is Ising like and does not have a Goldstone mode, meaning that the chirality must exceed a finite threshold for a modulated state to be energetically favorable.

Having discussed the delineation of Type I vs Type II behavior in terms of experimental parameters, it is useful to now rescale our model. Doing so allows us to work with a non-dimensionalized model with only three parameters. We rescale by letting:

$$\mathbf{c} = c_{uc} \mathbf{C}, \quad r(T) = r_c R(T), \quad E = E_c \epsilon, \quad z = \frac{Z}{q_0}. \quad (9)$$

\mathbf{C} is the rescaled tilt, $R(T)$ is the rescaled temperature dependent parameter, ϵ is a dimensionless field, and Z is the dimensionless length scale. The zero field helical wavevector $q_0 = e\eta/K_B$ and Eq. (6) gives c_{uc} , r_c and E_c . Inserting the above rescalings into Eq. (1) gives the following rescaled free energy density:

$$\begin{aligned} \frac{F}{V} = \frac{q}{2\pi q_0} \left(\frac{-27u^3}{200v^2} \right) \int_0^{\frac{2\pi q_0}{q}} dZ & \left[\frac{R(T)}{2} |\mathbf{C}|^2 - \frac{1}{6} |\mathbf{C}|^4 + \frac{1}{30} |\mathbf{C}|^6 + \frac{m^2}{15} \left((\partial_Z \mathbf{C})^2 - 2(C_x \partial_Z C_y - C_y \partial_Z C_x) \right) \right. \\ & \left. - \frac{8}{15} \epsilon C_x \right], \end{aligned} \quad (10)$$

where

$$m \equiv \pm \frac{e\eta}{u} \sqrt{\frac{50v}{3K_b}} \sim \frac{\xi_{yc}}{P_0}, \quad (11)$$

is equivalent (up to a constant of order one) to the length scale ratio $\frac{\xi_{yc}}{P_0}$ that determines Type I versus Type II behavior. In Section VI we will use an instability analysis to show that for $|m| < 1$ the system is Type I while for $|m| > 1$ it is Type II. We note that since $u < 0$, the overall coefficient is positive. The above rescaled free energy density only has three parameters: $R(T)$, ϵ , m . For a given system (characterized by m) we can then map out the phase diagram in $R(T)$ - ϵ space. In Appendix A we outline how one can convert an experimental phase diagram from T - E space to $R(T)$ - ϵ space, and also how one can quantitatively determine the experimental m value that characterizes the system.

V. COMMON FEATURES OF TYPE I AND TYPE II PHASE DIAGRAMS

From the Type I and Type II phase diagrams shown in Fig. 3 we see that the uniform-modulated phase boundaries are qualitatively similar in two regions: **(A)** for temperatures far below the Sm- A^* -Sm- C_M^* transition temperature, i.e., $T \ll T_{AC^*}$ and **(B)** for small electric fields, i.e., $E \approx 0$. We begin our analysis by considering the phase boundary in these two regions.

A. Uniform-Modulated Phase Boundary Far Below the Sm- A^* -Sm- C_M^* Transition Temperature

Deep within the Sm- C_M^* phase, i.e., far below the Sm- A^* -Sm- C_M^* transition temperature, ramping up the electric field (ϵ) will cause the helical modulation to unwind. Eventually, at finite critical field $\epsilon_{q \rightarrow 0}$ the pitch diverges, or

equivalently, the modulation wave vector q vanishes. Determining $\epsilon_{q \rightarrow 0}(R)$ thus gives the location of the $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ (uniform-modulated) phase boundary. The calculation of $\epsilon_{q \rightarrow 0}(R)$ for systems with $u < 0$ [9] is not very different from those with $u > 0$, and also results in a phase boundary $\epsilon_{q \rightarrow 0}(R)$ with negative slope as shown in Figs. 3 (a) and (b). The reason for this similarity between $u < 0$ and $u > 0$ systems is that deep within the $\text{Sm-}C_M^*$ phase there is only a single energetic minimum for the uniform phase regardless of the sign of u . This is *not* the case for temperatures near or above the $\text{Sm-}A^* \text{--} \text{Sm-}C_M^*$ transition temperature, which leads to significantly different and more interesting behavior for systems with $u < 0$, e.g., the possibility of Type I or Type II systems, and reentrance.

B. Uniform-Modulated Phase Boundary for Small Electric Field

In the absence of an electric field the system will transition from the uniform $\text{Sm-}A^*$ phase to modulated $\text{Sm-}C_M^*$ as temperature is lowered. In the $\text{Sm-}C_M^*$ phase, the tilt director $\mathbf{c}(z)$ has a perfectly helical modulation with wave vector $q_0 = \frac{e\eta}{K_b}$. For small finite field $\epsilon \approx 0$ the perfect helix will be distorted slightly and we approximate the rescaled tilt director $\mathbf{C}(z)$ with the following ansatz:

$$\begin{aligned} C_x(Z) &= C_u + s\sigma \sin\left(\frac{qZ}{q_0}\right), \\ C_y(Z) &= s\sqrt{1-\sigma^2} \cos\left(\frac{qZ}{q_0}\right), \end{aligned} \quad (12)$$

where C_u the magnitude of the tilt along $\hat{\mathbf{x}}$ in the high temperature uniform state, and q is the wave-vector of the lowest energy chiral modulation. The positive amplitudes $s\sigma$ and $s\sqrt{1-\sigma^2}$ describe the shape of the helical modulation, with $0 \leq \sigma \leq 1$. In the uniform $\text{Sm-}C_U^*$ phase $s = 0$ and $C_u \neq 0$, while for the modulated $\text{Sm-}C_M^*$ phase at finite field ϵ , $s \neq 0$ and $C_u \neq 0$. The first order $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ phase boundary is found by determining the locus in R - ϵ space where the energy of the phases are equal. We relegate details of the process to Appendix B and quote the result for the locus of the phase boundary, which we denote as $R_{1\text{st}}(\epsilon)$.

$$R_{1\text{st}}(\epsilon) = R_{1\text{st}}^0(m) + G(m)\epsilon^2 + \mathcal{O}(\epsilon^4). \quad (13)$$

where $R_{1\text{st}}^0(m) = \frac{5}{12} + \frac{2m^2}{15}$ is the location of the zero-field, first order $\text{Sm-}A^* \text{--} \text{Sm-}C_M^*$ boundary. In Appendix B we show that the constant $G(m)$ is positive and so we see that the curvature of the 1st order $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ phase boundary is positive, opposite to that of systems with a continuous $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ phase transition. This means that, as shown in Figs. 3(a) and (b), if we start with a system in the $\text{Sm-}A^*$ phase (close to the $\text{Sm-}A^* \text{--} \text{Sm-}C_M^*$ transition temperature) and ramp up the field then the system will eventually jump from a uniform ($\text{Sm-}C_U^*$) to modulated ($\text{Sm-}C_M^*$) state. Of course, for sufficiently large fields the system must eventually transition back to a uniform ($\text{Sm-}C_U^*$) state. Thus, the system displays a reentrant $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^* \text{--} \text{Sm-}C_U^*$ phase sequence. The average tilt exhibits *two* discontinuities, one at the $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ transition, and the other at the $\text{Sm-}C_M^* \text{--} \text{Sm-}C_U^*$ transition, and the system is *tristable*, as shown in the inset of Fig. 3(b).

VI. DETERMINATION OF THE UNIFORM-MODULATED PHASE BOUNDARY FOR TYPE II SYSTEMS

Next we consider the most interesting region of the phase diagram, near the uniform low-tilt-high tilt critical point. We will show that there is a length scale ratio m which determines whether the system is Type I or Type II. For $m > 1$ the uniform phase at the critical point is unstable to modulation, and the system is Type II. In this case a $\text{Sm-}C_U^* \text{--} \text{Sm-}C_M^*$ phase boundary surrounds the *unstable* uniform critical point as shown in Fig. 4(a). The modulated region shrinks as m is reduced towards 1. For $m < 1$ we show that the critical point is stable, and that there is a first order phase boundary between the uniform high and low tilt states. This first order line meets the modulated region at a triple point as shown in Fig. 4(b), where uniform low-tilt phase, the uniform high-tilt phase, and the modulated phase are all energetically equivalent. We map out the phase boundaries for Type I systems in Section VII.

A. Model for Type II Behavior and Determination of the Critical Length Scale Ratio

Since we are interested in the phase diagram near the critical point ($\epsilon_c = 1, R(T_c) = 1$), we expand $\mathbf{C} = C_u \hat{\mathbf{x}}$, ϵ , and R near their critical point values:

$$\mathbf{C}(z) = C_u \hat{\mathbf{x}} = (1 + \gamma) \hat{\mathbf{x}}, \quad R(T) = 1 + \rho(T), \quad \epsilon = 1 + \delta, \quad (14)$$

where γ , ρ and δ are each $\ll 1$. We also express the field deviation δ in terms of ρ and a new effective field h

$$\delta = \frac{15}{8}(h + \rho). \quad (15)$$

We will see that this results in the critical point being located at $\rho = h = 0$ and a first order low tilt–high tilt phase boundary for $\rho < 0$ located along $h = 0$. Inserting the change of variables of Eqs. (14) and (15) into the free energy density of Eq. (10) results in the following uniform free energy near the critical point:

$$\frac{F_u}{V} = -\frac{27u^3}{200v^2} \left[\frac{\rho}{2}\gamma^2 + \frac{1}{3}\gamma^4 - h\gamma + \mathcal{O}(\gamma^5) \right]. \quad (16)$$

Again, since $u < 0$, the overall coefficient is positive. The expression inside the brackets is the standard dimensionless Ising model free energy, which describes the Ising paramagnetic–ferromagnetic transition or the gas–liquid transition [21]. In this case it describes the low tilt ($\gamma < 0$)–high tilt ($\gamma > 0$) Sm- C_U^* transition. The critical point, where $\gamma = 0$, is located at $\rho = h = 0$ and the first order low tilt–high tilt phase boundary exists for $\rho < 0$ along $h = 0$. Note that the γ^4 term is required to stabilize the system when $\rho \leq 0$. Near the critical point the equation of state is found by minimizing F_u with respect to γ , i.e.,

$$h(\gamma, \rho) = \rho\gamma + \frac{4}{3}\gamma^3. \quad (17)$$

Next we analyze the stability of the uniform state at and near the $\rho = h = 0$ critical point. We again consider the ansatz of Eq. (12), but near the critical point, i.e.,

$$\begin{aligned} C_x(Z) &= C_{u_c}(1 + \gamma) + s\sigma \sin\left(\frac{qZ}{q_0}\right), \\ C_y(Z) &= s\sqrt{1 - \sigma^2} \cos\left(\frac{qZ}{q_0}\right). \end{aligned} \quad (18)$$

We insert this ansatz into the free energy density of Eq. (10) and minimize the free energy with respect to q and σ . This is the same process used in the preceding section, but with C_u replaced by $C_{u_c}(1 + \gamma)$. This free energy is then expanded in powers of γ and s to yield

$$F = F_u - \frac{27u^3}{200v^2} \left[A(\gamma, \rho)s^2 + B(\gamma)s^4 + \mathcal{O}(s^6) \right]. \quad (19)$$

The quartic coefficient $B(\gamma)$ is,

$$B(\gamma) = \frac{1}{240m^4} \left[4 + 18m^2 + 8m^4 + (36m^4 + 18m^2 + 10)\gamma + (18m^4 - 135m^2 - 75)\gamma^2 \right] + \mathcal{O}(\gamma^3). \quad (20)$$

As discussed in Section IV, the dimensionless quantity m is basically the ratio of length scales $\frac{\xi_{yc}}{P_0}$ which grows with enantiomeric excess. Note that B is positive at the critical point where $\gamma = 0$. Thus, it is the coefficient $A(\gamma, \rho)$ that determines whether the uniform state is unstable to the modulated state, in which $s \neq 0$. In terms of m it is

$$A(\gamma, \rho) = \frac{1}{30m^2} \left[-(m^2 - 1)^2 + \frac{15}{2}\rho m^2 - 2(m^2 - 1)\gamma + (17m^2 + 12)\gamma^2 + \mathcal{O}(\gamma^3) \right]. \quad (21)$$

We also note that both A and B are even in m , confirming that the results are the same for opposite handedness. Before we use the above expression to find the uniform-modulated boundary, it is illustrative to consider the system at the critical point, where $\rho = h = 0$. If the system is in the uniform state, then $\gamma = 0$ at the critical point and

$$A(\gamma = 0, \rho = 0) = -\frac{(m^2 - 1)^2}{30m^2} < 0. \quad (22)$$

Since A is negative at the critical point for all $m \neq 1$ it would initially appear that the uniform state at the critical point is always unstable to the modulated state. However, one must check to make sure that the corresponding modulated ansatz of Eq. (18) is physically reasonable. In particular $q_{\min} = 2q_0\sigma\sqrt{1 - \sigma^2}$ must be real, which means that σ_{\min} must be less than 1. The expression for σ_{\min} is given in Eq. (B2) and involves both C_u and s . At the critical point $C = C_{u_c} = 1$, and we find s_{\min} by minimizing the free energy of Eq. (19) with respect to s , i.e.,

$$s_{\min_c} = \sqrt{\frac{-A(\gamma = 0, \rho = 0)}{2B(\gamma = 0)}}. \quad (23)$$

Setting $s = s_{\min_c}$ and $C = C_{u_c} = 1$ in the expression for σ_{\min} yields a purely m dependent expression for σ_{\min} ,

$$\sigma_{\min}(m) = \sqrt{1 - (m^2 - 1)w(m)}, \quad (24)$$

where $w(m) > 0$ for all m :

$$w(m) = \frac{3m^{10} + 107m^8 + 362m^6 + 294m^4 + 118m^2 + 16}{2m^2(3m^{10} + 68m^8 + 310m^6 + 328m^4 + 167m^2 + 24)}. \quad (25)$$

Note that if $|m| < 1$ then $\sigma_{\min}(m) > 1$, and q_{\min} is imaginary. Thus, the modulated ansatz of Eq. (18) is only physically reasonable for $|m| > 1$, e.g., for sufficiently large enantiomeric excess. Thus, systems with $|m| < 1$ are Type I and those with $|m| > 1$ are Type II. We also note that at $m = 1$, $\sigma_{\min} = 1$ and the modulation wavevector $q_{\min} = 0$, corresponding to a uniform phase. We will come back to this point when we further discuss how a system evolves between Type I and II behavior and vice versa. If $m < 1$ then q_{\min} of the modulated ansatz of Eq. (18) is imaginary, then the ansatz no longer oscillates sinusoidally, but instead exhibits exponential growth or decay. While such an ansatz is not physically reasonable, it does give a hint of what sort of modulated structure may exist near the critical point when $|m| < 1$, namely one with large scale uniform domains periodically broken up by regions of short scale (exponential) twist. Before we analyze the system for $|m| < 1$, we find the second order phase boundary of the “nose” of the modulated state for $|m| > 1$ in Type II systems.

B. Mapping the Second Order Uniform-Modulated Phase Boundary for Type II Systems

Next we determine the second order phase boundary in ρ - h space for the continuous uniform-modulated (Sm-C_U^* – Sm-C_M^*) transition where the modulation amplitude $s_{\min} = \sqrt{\frac{-A(\gamma, \rho)}{2B(\gamma)}}$ grows continuously from zero. We consider Type II systems with enantiomeric excess just larger than the critical value, i.e., $m^2 \gtrsim 1$. For such systems the phase boundary is close to the critical point and the expansion in powers of γ (Eqs. (19) – (21)) is valid. The uniform modulated phase (U-M) phase boundary $\rho_{U-M}(h)$ is found by solving the pair of equations: $A(\gamma_{U-M}, \rho_{U-M}) = 0$ and the equation of state $h = h(\gamma_{U-M}, \rho_{U-M})$ given by Eq. (17). Solving this equation for γ_{U-M} and inserting the solution into the equation of state $h = h(\gamma_{U-M}, \rho_{U-M})$, Eq. (17), yields the following uniform-modulated phase boundary $\rho_{U-M}(h)$

$$\rho_{U-M}(h) = \rho_v - \frac{\lambda}{(m^2 - 1)^4} (h - h_v)^2, \quad (26)$$

where $\rho_v \equiv \frac{2(m^2-1)^2}{435}$, $h_v \equiv \frac{26(m^2-1)^3}{121,945}$ give the location of the vertex of the parabola, and the constant $\lambda = \frac{307,667,235}{111,392} \approx 2,762$. We remind the reader of our sequence of rescaling and shifting of the temperature dependent parameter ($r(T) \rightarrow R(T) \rightarrow \rho(T)$) and the electric field ($E \rightarrow \epsilon \rightarrow h$). In Appendix A we outline the way in which one can convert an experimental phase diagram from T - E space to $R(T)$ - ϵ space and $\rho(T)$ - h space so that experimental results can be directly compared with the theoretical results, e.g., Eq. (26) and Fig. 4.

We emphasize that the above phase boundary is second order, i.e., only valid for continuous uniform-modulated phase transitions. Numerical analysis also reveals the existence of two tricritical points on either side of the nose, also shown in Fig. 4. Below each tricritical point the phase boundary becomes first order, corresponding to a discontinuous uniform-modulated phase transition, whereby there is a jump in the modulation amplitude s . Thus the above, parabolic, expression for the phase boundary is only valid *between* the tricritical points. As $|m| \rightarrow 1$, these two tricritical points approach each other and seem to merge at $m = 1$. In other words, as $|m| \rightarrow 1$, the second order phase boundary shrinks to zero, resulting in a phase boundary that is purely first order. Moreover, as $|m| \rightarrow 1$ and the two tricritical points approach each other, the curvature of the continuous phase boundary increases rapidly due to the $(m^2 - 1)^4$ in the denominator of Eq. (26), as shown in Fig. 4(a). Thus, modulated “nose” of the phase boundary becomes sharper and approaches a cusp-like point at the transition to Type I behavior.

We close this section by noting that location of the tricritical points analytically requires the use of an ansatz with higher wave vector harmonics[9]. This is a cumbersome process so we instead rely on the numerical analysis discussed in Section IX. Lastly, in Appendix B we further analyze the modulated state just inside the nose, and show that there is no discontinuity of spatially averaged tilt within the modulated region.

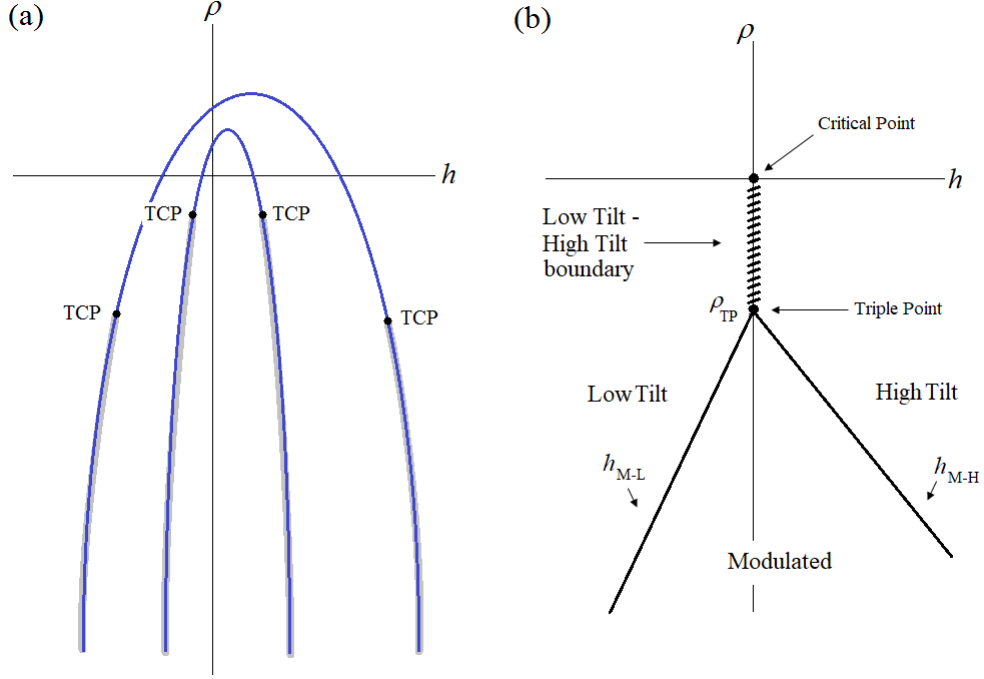


FIG. 4. (a) The uniform-modulated phase boundary for two Type II systems, near the unstable critical point at $\rho = h = 0$. As Type I behavior is approached, the modulated region (below the phase boundary) shrinks. Between the two tricritical points (TCP) the uniform-modulated transition is continuous. The parabolic shape of the phase boundaries, i.e., $\rho - \rho_v \propto -(h - h_v)^2$, is only valid between the two TCPs. The narrower modulated region corresponds to smaller m . Note that for smaller m the tricritical points are closer together. (b) The Type I phase diagram near the high tilt - low tilt - modulated triple point. Note the different slopes of the phase boundary between the low tilt - modulated states and the phase boundary between the high tilt - modulated states.

VII. MAPPING THE MODULATED PHASE BOUNDARY FOR TYPE I SYSTEMS

As we prepare to move onto analysis of the Type I phase boundary, we recall from Section VIA that the breakdown of the sinusoidally oscillating ansatz (i.e., imaginary q) suggests that the nature of the modulated state for $|m| < 1$ changes to one with large scale uniform domains periodically broken up by regions of short scale (exponential) twist. This suggests that for $|m| < 1$ we should consider a modified modulated ansatz with finite amplitude, and that we should also anticipate a first order transition to the uniform state, which is consistent with the vanishing of the second order boundary discussed above. Thus, we consider an ansatz near the *stable* uniform critical point where $\mathbf{C}_{u_c}(z) = \hat{\mathbf{x}}$:

$$\begin{aligned} C_x(z) &= 1 + |\gamma| \sin \phi(Z), \\ C_y(z) &= |\gamma| \cos \phi(Z), \end{aligned} \quad (27)$$

where we take $|\gamma|$, the magnitude of the deviation of the tilt from critical value, to be independent of position. Both $\phi(Z)$ and $|\gamma|$ are now to be determined via minimization of the free energy. Unlike Eq. (18) we have not constrained the functional form of $\phi(z)$, which allows us to consider modulations more general than sinusoidal. Insertion of the above ansatz into the free energy Eq. (1) and following the standard unwinding analysis of [9] results in an equation for the modulation period in terms of the system parameters h, ρ, m :

$$P(h, \rho, m) = \frac{mP_0}{4\pi} \int_0^{2\pi} d\phi \left[W_{\min} - \frac{15h}{4|\gamma_M|} \cos(\phi) + \sin^2(\phi) \left(1 - |\gamma_M| \cos(\phi) - \frac{3|\gamma_M|^2}{2} \right) \right]^{-\frac{1}{2}}, \quad (28)$$

where W_{\min} and $|\gamma_M|$ are constants that depend on system parameters h, ρ, m . In the standard unwinding analysis of [9] the term “unwinding” refers to the divergence of the modulation period P at the transition. However, we show that this standard unwinding analysis does not work in this case because the free energy of the modulated state becomes smaller than that of the uniform state while the period is still finite. In other words, the continuous unwinding transition is preempted by a first order transition between the modulated and uniform states. To find the

corresponding phase boundary $\rho_{1st}(h, m)$ one must instead determine where the uniform and modulated free energies are equal.

A. Locating the Modulated-Uniform Triple Point

We begin by locating the phase boundary at $h = 0$, i.e., we find $\rho_{1st}(h = 0, m)$, and we will see that $\rho_{1st}(h = 0, m) < 0$. Since the first order uniform low tilt–high tilt phase boundary lies along $h = 0$ and $\rho < 0$ [25], the fact that $\rho_{1st}(h = 0, m) < 0$ means that the two first order uniform–modulated phase boundaries must meet at a triple point, as shown in Fig. 4(b). Thus we denote $\rho_{1st}(h = 0, m)$ as $\rho_{TP}(m)$. The process of finding $\rho_{TP}(m)$ is somewhat tricky and we relegate the details to Appendix B and instead quote the result:

$$\rho_{TP}(m) = \frac{8\pi}{19}(m - m_1), \quad (29)$$

where $m_1 \equiv 4/\pi$. In Appendix B we show that the above result is only valid for $m \leq m_1$, i.e., $\rho_{TP} \leq 0$, implying that for a Type I system the triple point will always lie below the critical point as shown in Fig. 4(b). As $m \rightarrow m_1 \equiv 4/\pi$, the triple point approaches the critical point, ultimately merging at $m = m_1$. Thus, the system is Type I for $m < m_1$. We remind the reader that in Section VI we showed that the system is Type II for $m > m_2 \equiv 1$. Of course, the system must be either Type I or Type II, so there must be a single value, m_c that delineates Type I and Type II behavior. Our analysis yields $m_1 = 4/\pi \neq m_2 = 1$. However, it would be quite surprising if our analysis yielded $m_1 = m_2 = m_c$, given that each regime required a fundamentally different ansatz. Nonetheless, it is reassuring that m_1 and m_2 are relatively close, and we would expect that the true m_c is near m_1 and m_2 . Indeed, the numerical analysis of Section IX predicts a critical value $m_c \approx m_1 = 4/\pi$.

In Section VIII we will further discuss the crossover between Type I and Type II behavior, but first we locate the first order phase boundaries that meet at the triple point. The boundary between the low (L) and high (H) tilt uniform states has already been found and lies along $h = 0$ for $\rho < 0$. The other two boundaries separate the modulated (M) and uniform high (H) tilt phases, and the modulated (M) and uniform low (L) tilt phases. Notationally we refer to the three phase boundaries as $L - H$, $M - H$, and $M - L$. The $M - H$ and $M - L$ phase boundaries are found by expanding near the triple point, i.e., for $\rho \lesssim \rho_{TP}$. We again relegate the details of the expansion to Appendix B and move directly to defining the phase boundaries:

$$\rho_{M-H/M-L}(h, m) = \rho_{TP}(m) \mp \frac{19}{24} \frac{1}{\sqrt{W_{TP}(m)}} h, \quad (30)$$

with $W_{TP}(m)$ given by Eq. (B26). The $M - H$ expression is valid for $h > 0$ so the $M - H$ boundary has negative slope, whereas the $M - L$ expression is valid for $h < 0$ so the $M - L$ boundary has positive slope. In Appendix B, we show that higher order corrections to the expressions for $\rho_{M-H/M-L}$ imply that the $M - L$ boundary is steeper than the $M - H$ boundary, as shown in Fig. 4(b). In the Appendix we show that $W_{TP} \rightarrow 0$ as $m \rightarrow m_1$, so we see that the boundaries become increasingly steep, as the transition to Type II behavior is approached.

B. Structure of the Modulated Phase Near the Triple Point in Type I Systems

The pitch of the modulated phase at the triple point can be found by setting $h = 0$, $W = W_{TP}$ and $\gamma_M = |\gamma_{TP}|$ in Eq. (28). Expanding for small W_{TP} (valid for $m \lesssim m_1$) gives;

$$P_{TP} \approx -\frac{mP_0}{2\pi} \ln(W_{TP}). \quad (31)$$

which, as one would expect, diverges as $m \rightarrow m_1$. Thus, at $m = m_1$ where the Type I triple point and critical point merge, the modulation wavevector q vanishes, corresponding to a uniform system. We recall that for $m = m_2$, where the two Type II tricritical points merged, the modulation wavevector q also vanishes. As discussed above, there must be a single m_c at which the system crosses over from one Type to the other, and it is reasonable to assume that the wavevector q vanishes as this m_c is approached from either the Type I or Type II side.

The structure $\phi(z)$ of the modulated phase at the triple point can be found using Eq. (B17). Doing so at the triple point results in the $\phi(z)$ shown in Fig. 5(a). This corresponds to equally long high and low tilt ($\approx \frac{P_{TP}}{2}$) domains separated by narrow domain walls, as shown schematically in Fig. 5(b). For $\rho \lesssim \rho_{TP}$ the variation of L_L and L_H with h is shown schematically in the inset of Fig. 5(a).

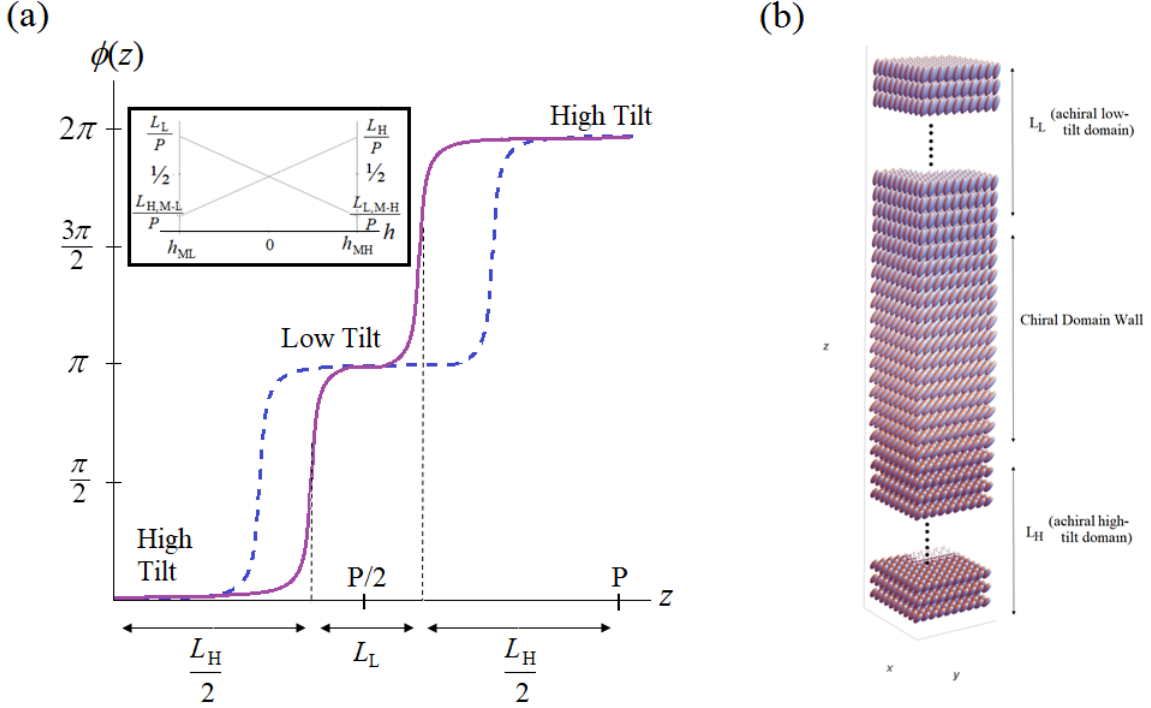


FIG. 5. (a) The dashed curve shows $\phi(z)$ for the modulated phase at the triple point, i.e., $\rho = \rho_{TP}$ and $h = 0$. The low and high tilt domains are the same size ($\approx P/2$). The solid curve shows $\phi(z)$ for the modulated phase below the triple point, $\rho \lesssim \rho_{TP}$ and $h \gtrsim 0$. The high tilt domains are larger than the low tilt domains. The inset shows the variation of fractional low and high tilt domain sizes, L_L/P and L_H/P , as well as $L_{H,M-L}/P$ and $L_{L,M-H}/P$. (b) Schematic illustration of the modulated Sm-C_M^* structure in a Type I system close to the triple point. The structure consists of long domains ($L_L \approx P/2$ and $L_H \approx P/2$) of achiral low tilt and high tilt, with the domains separated by short $\ll P$ chiral domain walls in which the system rapidly twists from low to high tilt (or vice versa).

As ρ is lowered from ρ_{TP} , while keeping $h = 0$, the modulation period becomes shorter. The relative length of the high and low tilt domains remains equal. For $h > 0$, the high-tilt domains become longer than the low-tilt domains, and vice versa for $h < 0$. As shown in Fig. 5(a), one can define a low-tilt domain length:

$$L_L = \frac{mP_0}{4\pi} \int_{\pi/2}^{3\pi/2} d\phi' \left[W - \frac{15h}{4|\gamma_M|} \cos(\phi') + \sin^2(\phi') \left(1 - |\gamma_M| \cos(\phi') - \frac{3|\gamma_M|^2}{2} \right) \right]^{-\frac{1}{2}}, \quad (32)$$

which depends on ρ via W and $|\gamma_M|$, each of which would be found by solving Eqs. (B18)–(B20). The corresponding high-tilt domain length is simply $L_H = P - L_L$, and for $h = 0$, $L_L = L_H \approx P/2$. While one can use the above equation to find L_L as a function of ρ , h , and m , it is rather tedious and not particularly illuminating. In particular, since the $M-H$ and $M-L$ transitions are first order, L_L and L_H will remain finite at the $M-H$ and $M-L$ boundaries, as shown in the inset of Fig. 5(a).

The transition to the modulated phase can be thought of as occurring via the nucleation of a periodic array of domain walls, as shown schematically in Fig. 5(b). For example, as h is lowered through h_{M-H} the system transitions to the modulated phase from the high-tilt phase, where there is a nucleation of a periodic array of low-tilt domains, each of length $L_{L,M-H}$. This is analogous to the transition to the modulated Abrikosov flux lattice in Type II from the superconducting phase. This Abrikosov flux lattice can be thought of as a superconducting phase containing a periodic array of normal domains or defects. As h continues to be lowered, the density (L_L/P) of the low-tilt domains grows, and eventually the system transitions to the low-tilt phase at h_{M-L} . Similarly the transition from the low-tilt phase to the modulated phase at h_{M-L} occurs via the nucleation of an array of periodic array of high-tilt domains of length $L_{H,M-L}$.

We note that the periodic arrangement of defects in the Abrikosov flux lattice (and the TGB phase) is two dimensional, whereas the periodic defects (chiral domain walls) in the modulated Sm-C_M^* phase is one dimensional. This difference in the defect structure of the two modulated phases can be ascribed to a difference in symmetry between the two systems. The order parameter that distinguishes the normal and superconducting phases (or the cholesteric

and smectic A phases) systems has two components with a transition that can be loosely [26] categorized in the XY universality class. The order parameter distinguishing the low and high tilt $\text{Sm-}C_U^*$ phases has one component, and the transition is thus in the Ising universality class. The number of components in the order parameter distinguishing the low T and high T phases thus matches the dimensionality of the defect periodicity in the modulated phase between the low T and high T phases.

VIII. CROSSOVER BETWEEN TYPE I AND TYPE II BEHAVIOR

Now that we have obtained separate $\rho(T)$ - h phase diagrams (shown in Fig. 4) for Type I and Type II systems, we discuss the crossover from one Type to the other. As discussed in Section VII our analysis for each Type of system employs a different ansatz. We have shown that the system will be Type I for $m < m_1 \equiv 4/\pi$ and Type II for $m > m_2 \equiv 1$. Of course, the system must be either Type I or Type II, so there must be a single value, m_c that delineates Type I and Type II behavior. The numerical analysis of Section IX predicts a critical value $m_c \approx m_1 = 4/\pi$.

Based on the evolution with m of the phase diagram for each Type, we can infer how the crossover from one Type to the other occurs. Consider a Type I system, i.e., with $m < m_c$, with phase diagram shown in Fig. 4(b). At each of the two uniform-modulated first order phase boundaries, the modulation wave vector q changes discontinuously (zero in the uniform phase, finite in the modulated phase). There will also be a jump in $|\gamma|$, and thus the tilt. These two phase boundaries (and the uniform low-uniform high tilt boundary) meet at a triple point. At the triple point, q_{TP} is finite and will jump discontinuously to zero as one crosses the triple point in transitioning to the uniform state. If one crosses the triple point to the right of the uniform low-uniform high tilt boundary, the system will jump to the high tilt state, whereas crossing to the other side will take the system to the low tilt state. Either way, there is jump in $|\gamma|$.

As $m \rightarrow m_c$, the triple point approaches and merges with the critical point into what we term a critical triple point located at $\rho = 0$, $h = 0$ and $m = m_c$. As discussed following Eq. (31), the modulation period diverges at the triple point, i.e., $q_{TP} \rightarrow 0$ as $m \rightarrow m_c$. Thus, at $m = m_c$, the transition, via the critical triple point, from the modulated to uniform phase will be accompanied by a *continuous* vanishing of q . Moreover, at the critical point the discontinuity between the uniform low and high tilt states vanishes. This means that at the critical triple point, the uniform-modulated transition is continuous in *both* wavevector q and tilt $|\gamma|$. In other words, at the critical triple point, the three phases (modulated, uniform low tilt, uniform high tilt) are energetically *and* symmetrically equivalent. Of course, this is only true *at* the critical triple point. On either side of it there is a first order modulated-uniform phase boundary where both wavevector and tilt jump discontinuously. Thus, the critical triple point can be thought of as a second order phase boundary of infinitesimal (point-like) extent.

As m exceeds m_c the system becomes Type II. Now the critical triple point splits into two tricritical points, in between which there is a second order modulated-uniform phase boundary as shown in Fig. 4(a). In other words the infinitesimal (point-like) second order boundary at $m = m_c$ now grows in extent as m exceeds m_c . In addition, as m exceeds m_c the cusp-like modulated-uniform phase boundary becomes parabolic, with continuously decreasing curvature. On this second order phase boundary it is the amplitude of the finite q modulation that grows continuously as one crosses to the modulated phase. This is sometimes referred to as an “instability” type transition, as opposed to the “unwinding” type transition discussed in Section V A that occurs via the continuous growth of the modulation wave vector. Thus, the critical triple point located at $\rho = 0$, $h = 0$ and $m = m_c$ can be thought of as a point where the transition is simultaneously instability type *and* unwinding type.

In Fig. 6 we show the phase diagram in ρ - h - m space, which incorporates both the Type I and Type II ρ - h phase diagrams. The modulated phase lies below the curved surface, while the uniform phase lies above the curved surface. Crossing the green region of the surface (lower region of surface, beneath solid line) corresponds to a first order uniform-modulated transition, while crossing the gold region of the surface (upper region of surface, above solid line) corresponds to a continuous uniform-modulated transition. These two regions meet at a line of tricritical points represented by the solid line bounding the yellow (upper) region. The vertical $h = 0$ plane separates the low and high tilt uniform phases, and crossing the plane corresponds to the first order uniform low tilt-uniform high tilt phase transition. The dotted line at the top of the vertical plane is a line of uniform low tilt-uniform high tilt critical points, while the dashed line at the bottom of the plane is a line of uniform low tilt-uniform high tilt-modulated triple points. These lines meet at $\rho = 0$, $h = 0$, $m = m_c$, at a critical triple point. For $m < m_c$ the system has a uniform low tilt-uniform high tilt phase transition and is thus Type I. For Type I systems the transition to the modulated state is first order. Taking a ρ - h cross-section at $m < m_c$ will yield a ρ - h phase diagram like that shown in Fig. 4(b). For $m > m_c$ there is no longer a phase transition between the uniform phases. Instead there is an intermediate modulated phase, and the system is Type II. For $m > m_c$ the uniform-modulated transition can be first order (across the green (lower) surface) or continuous (across the gold (upper) surface). These two distinct regions meet at a line of tricritical points. Taking a ρ - h cross-section at $m > m_c$ will yield a ρ - h phase diagram with two tricritical points, as shown in

Fig. 4(a).

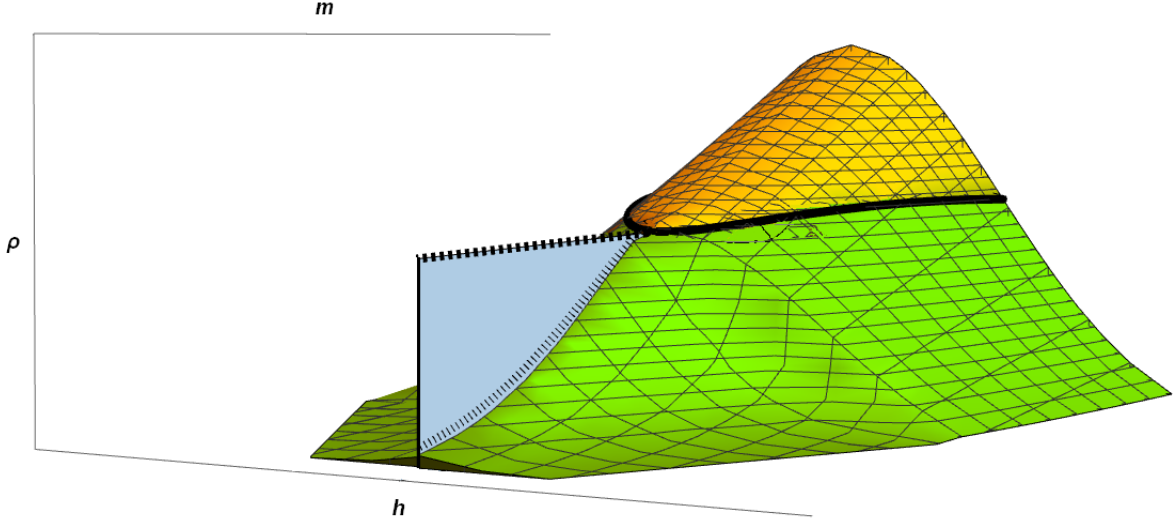


FIG. 6. The phase diagram in ρ - h - m space near the critical triple point. The modulated phase lies below the curved surface, while the uniform phase lies above the curved surface. The green region of the surface (lower region of surface, beneath solid line) and gold region of the surface (upper region of surface, above solid line) correspond to first order and continuous uniform-modulated phase boundaries respectively. The gold (upper) surface is bounded by a line of tricritical points. The vertical $h = 0$ plane separates the low and high tilt uniform phases, and crossing the plane corresponds to the first order uniform low-uniform high phase transition. The dotted line at the top of the vertical plane is a line of uniform low-uniform high critical points, while the dashed line at the bottom of the plane is a line of uniform low-uniform high-modulated triple points. These lines, and the line of tricritical points, all meet at $\rho = 0$, $h = 0$, $m = m_c$ at what we term a critical triple point. For $m < m_c$ the system is Type I and for $m > m_c$ it is Type II.

IX. NUMERICAL ANALYSIS OF PHASE DIAGRAMS

The analyses of the preceding sections have relied on the use of ansatz solutions, due to the non-harmonic nature of the free energy density, Eq. (10). Next we use brute force numerics to check that the results are reasonable. We do this by minimizing the free energy density which we represent in polar form, i.e., $C_x(z) = C(Z) \cos \phi(Z)$ and $C_y(z) = C(Z) \sin \phi(Z)$,

$$\frac{F}{V} = \frac{q}{2\pi q_0} \left(\frac{-27u^3}{200v^2} \right) \int_0^{\frac{2\pi q_0}{q}} dZ \left[\frac{R(T)}{2} C^2 - \frac{1}{6} C^4 + \frac{1}{30} C^6 + \frac{m^2}{15} \left((\partial_Z C)^2 + C^2 (\partial_Z \phi)^2 - 2C^2 (\partial_Z \phi) \right) - \frac{8}{15} \epsilon C \cos(\phi) \right], \quad (33)$$

Minimization with respect to $C(Z)$ and $\phi(Z)$ gives:

$$R(T)C - \frac{2}{3} C^3 + \frac{1}{5} C^5 - \frac{8}{15} \epsilon \cos \phi + \frac{2m^2}{15} \left(C (\partial_Z \phi)^2 - 2C (\partial_Z \phi) - \partial_Z^2 C \right) = 0, \quad (34)$$

and

$$\frac{8}{15} \epsilon C \sin \phi - \frac{2m^2}{15} \left(2C (\partial_Z C) (\partial_Z \phi) + C^2 (\partial_Z^2 \phi) - 2C (\partial_Z C) \right) = 0. \quad (35)$$

These two second-order, coupled, nonlinear equations are then numerically solved as a boundary value problem (BVP). We use the built-in routines in Matlab [27], `bvp4c` or `bvp5c` as needed. Each utilizes the Lobatto IIIa formula, an implicit Runge-Kutta formula with a continuous extension [28].

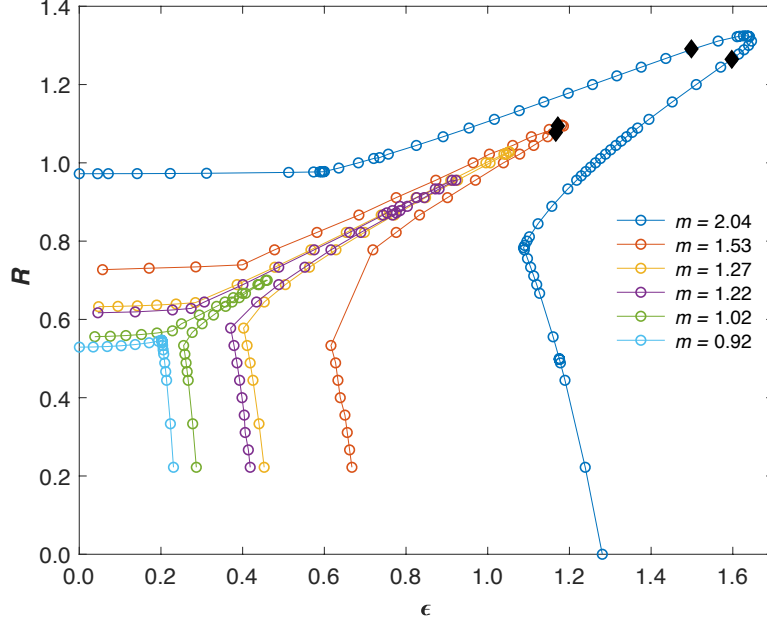


FIG. 7. The modulated phase boundary for systems with different m values (rightmost being largest). For $m > 1.27$ each phase boundary has two tricritical points, shown as diamonds. For $m < 1.27$ the tip of each “nose” is a triple point. There is a uniform low tilt–high tilt first order boundary (not shown) that extends from each triple point to a critical point located at $R = \epsilon = 1$.

These solutions are then used to map out the phase diagram in R - ϵ space for a given m value. Specifically, we loop through a set of different R values, and for each R value find the ϵ location of the phase boundary. Lowering R from high to low, one will first locate the top of the modulated “nose” region, where the phase boundary is second order, i.e., where the modulated-uniform transition is continuous. The $\epsilon(R)$ location of the boundary was found by determining where the amplitude of the modulation vanishes continuously with ϵ , i.e., where the modulated solution continuously becomes uniform. Of course, the nonmonotonic “nose” shape of the phase boundary means that two such ϵ values are found for each R value. Care must be taken to compare the energies of the modulated and uniform solutions near the phase boundary. Eventually, at sufficiently low R value, the energy of the uniform solution becomes smaller than the modulated solution *within* the modulated region. In other words the uniform phase becomes energetically preferable before the modulation vanishes, and the modulated-uniform phase transition becomes first order. The evolution from a continuous to first order transition occurs at a specific location on the phase boundary, namely at a tricritical point. Two such tricritical points are found on the “nose,” but not at the same R value. For R values below each tricritical point the first order boundary between the uniform and modulated phases is found by determining where the energies of the uniform and modulated solutions are equal.

Figures 7 and 8 show phase diagrams for a variety of m values in R - ϵ space and ρ - h space respectively. These two phase diagrams are related by a simple shift and rotation, i.e., $\rho = R - 1$ and $h = \frac{8}{15}(\epsilon - 1) - \rho$. We note that the numerically obtained ρ - h phase diagrams shown in Fig. 8 compare qualitatively well with those predicted analytically in Sections VIB and VII. Also, looking at Fig. 8 one can see that the transition from Type I to Type II occurs at approximately $m_c \approx 1.22$, which compares well with the value of $m_c = 4/\pi = 1.27$ estimated in Section VII. The phase diagrams in R - ϵ space will most resemble those in T - E space, while those in ρ - h space focus on the nose region and more clearly show the evolution from Type I to Type II behavior. In Appendix A we describe how one can convert an experimental phase diagram from T - E space to $R(T)$ - ϵ space and $\rho(T)$ - h space so that experimental results can be directly compared with the theoretical phase diagrams of Figs. 7 and 8.

X. CONCLUSION

In summary, we have carried out an in-depth analysis of the electroclinic effect in ferroelectric liquid crystal systems that have a first order Smectic- A^* –Smectic- C^* (Sm- A^* –Sm- C^*) transition, and have shown that such systems can

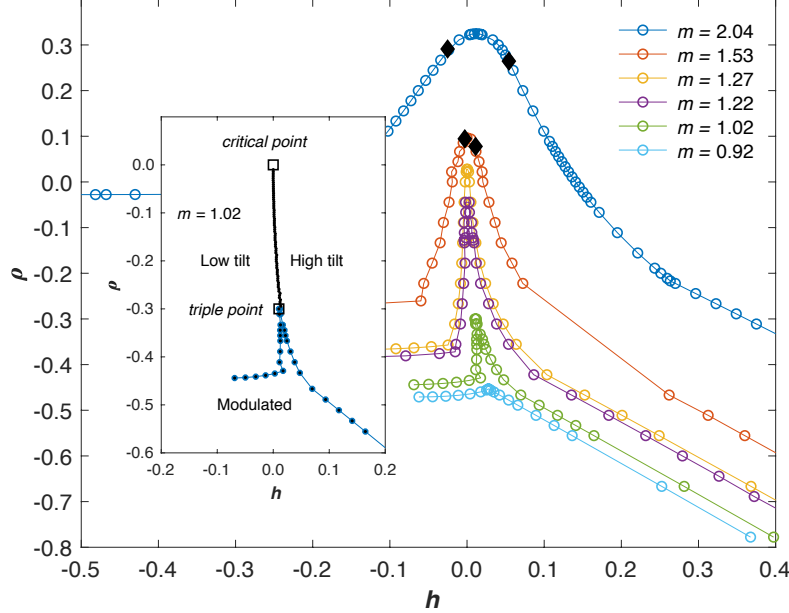


FIG. 8. The modulated phase boundary for systems with different m values (topmost being largest). For $m > 1.27$ each phase boundary has two tricritical points, shown as diamonds. For $m < 1.27$ the tip of each “nose” is a triple point. There is a uniform low tilt–high tilt first order boundary (only shown in inset for $m = 1.02$) that extends from each triple point to a critical point located at $\rho = h = 0$.

be either Type I or Type II. In temperature–field parameter space Type I systems exhibit a macroscopically achiral (in which the modulated $\text{Sm-}C_M^*$ helical superstructure is expelled) uniform low-tilt (LT) $\text{Sm-}C_U^*$ –high-tilt (HT) $\text{Sm-}C_U^*$ critical point, which terminates a LT $\text{Sm-}C_U^*$ –HT $\text{Sm-}C_U^*$ first order boundary. This boundary extends to an achiral-chiral triple point at which the achiral LT $\text{Sm-}C_U^*$ and HT $\text{Sm-}C_U^*$ phases coexist along with the chiral $\text{Sm-}C_M^*$ phase. In Type II systems the critical point, triple point, and first order boundary are replaced by a $\text{Sm-}C_M^*$ region, sandwiched between LT and HT achiral $\text{Sm-}C_U^*$ phases, at low and high fields respectively.

Whether the system is Type I or Type II is determined by the ratio of two length scales, one of which is the zero-field $\text{Sm-}C_M^*$ helical pitch. The other length scale depends on the size of the discontinuity (and thus the latent heat) at the zero-field first order $\text{Sm-}A^*$ – $\text{Sm-}C_M^*$ transition. We have proposed ways in which a system could be experimentally tuned between Type I and Type II behavior, e.g., by doping a low chirality $\text{Sm-}C^*$ system with a high chirality, tight-pitch $\text{Sm-}C^*$ compound. We have also shown that this Type I vs Type II behavior is the Ising universality class analog of Type I vs Type II behavior in XY universality class systems. Specifically, the LT and HT achiral $\text{Sm-}C_U^*$ phases are analogous to normal and superconducting phases, while the 1D periodic $\text{Sm-}C_M^*$ superstructure is analogous to the 2D periodic Abrikosov flux lattice.

We have made (analytically and numerically) a complete mapping of the phase boundaries in temperature–field parameter space and show that a variety of interesting features are possible, including a multicritical point, tricritical points and a doubly reentrant $\text{Sm-}C_U^*$ – $\text{Sm-}C_M^*$ – $\text{Sm-}C_U^*$ – $\text{Sm-}C_M^*$ phase sequence. In addition we have shown how the system crosses over between Type I and Type II behaviors.

Interestingly, at first sight the phase diagram for the compound CE8, proposed by Ghoddoussi et al. [7], resembles the Type I phase diagram of Fig. 3(a). However, there are some important, fundamental differences. For example, the transition on the uniform $\text{Sm-}C_U^*$ – $\text{Sm-}C_U^*$ phase boundary for CE8 is continuous (and without a critical point) whereas that of Fig. 3(a) is discontinuous and does have a critical point. Additionally, the sign of the curvature of the phase boundary at zero-field differs for each system. The fundamental reason for these differences is that the compound CE8 exhibits a *continuous* zero field $\text{Sm-}A^*$ – $\text{Sm-}C_M^*$ transition, whereas the phase diagram of Fig. 3(a) only applies to systems with a discontinuous zero field $\text{Sm-}A^*$ – $\text{Sm-}C_M^*$ transition.

There is however another theoretical model [29] that does predict phase diagrams with striking similarities to Figs. 3(a) and (b), namely a model for a quantum system capable of displaying ferromagnetic (FM), antiferromagnetic (AFM) and paramagnetic (PM) phases. Loosely speaking, the AFM phase is analogous to the modulated, $\text{Sm-}C_M^*$ phase, while the FM and PM phases are analogous to the low and high tilt uniform $\text{Sm-}C_U^*$ phases. In some regions

of parameter space, the quantum phase diagram exhibits a FM-PM quantum critical point, and a FM-PM-AFM quantum triple point, like our Type I system. In other regions of parameter space the quantum critical and triple points are replaced by a region of AFM phase, with a *single* tricritical point. In future work, we will investigate the analogies between the mesoscopic smectic and quantum systems. In other future work, we plan to expand our model to consider thermal fluctuations about the ground states, particularly in the region of parameter space where the Type I – Type II crossover occurs, i.e., at the critical triple point. We also plan to consider the effect of electric field terms that are higher order than the linear term considered here.

Appendix A: Rescaling Experimental Data for Comparison with Theory

To compare experimental results with our theoretical predictions, it is necessary to convert experimental phase diagrams in T - E space to $R(T)$ - $\epsilon(E)$ space. The process of doing so differs depending on whether the phase diagram is Type I or Type II.

1. Rescaling Experimental Data for Comparison with Theory: Type I

We remind the reader that $\epsilon = E/E_c$, so that for a Type I system (one with a critical point at T_c, E_c) one only need know the experimental value of E_c to rescale from E to ϵ . The conversion from T to R is slightly more involved. We recall that $R(T) = r(T)/r(T_c)$ and that $r(T) = \alpha(T - T_0)$, where the constants α and T_0 are system dependent. Thus

$$R(T) = \frac{T - T_0}{T_c - T_0}, \quad (\text{A1})$$

and we see that converting from T to $R(T)$ requires knowing T_0 and T_c . The experimental value of T_c can be obtained directly from the location of the critical point. To obtain the value of T_0 , one can use the experimental values of T_{AC}^* , the temperature of the zero field Sm- A^* -Sm- C_M^* transition, and T_{TP} , the temperature of the triple point. Converting $R_{1st}^0 = \frac{5}{12} + \frac{2m^2}{15}$ to T_0, T_c , and T_{AC}^* gives

$$\frac{T_{AC}^* - T_0}{T_c - T_0} = \frac{5}{12} + \frac{2m^2}{15}. \quad (\text{A2})$$

Converting Eq. (29) to T_0, T_c , and T_{TP} gives

$$\frac{T_{TP} - T_0}{T_c - T_0} = 1 + \frac{8\pi}{19} \left(m - \frac{4}{\pi} \right). \quad (\text{A3})$$

The above two equations can then be solved for T_0 and m . The T_0 value, along with T_c can be used to convert T to $R(T)$ as per Eq. (A1). This conversion along with $\epsilon = E/E_c$ then allows one to produce an R - ϵ phase diagram for comparison with Fig. 7. To produce a ρ - h diagram for comparison with Fig. 8 one simply uses R and ϵ along with

$$\begin{aligned} \rho &= R - 1, \\ h &= \frac{8}{15} (\epsilon - 1) - \rho. \end{aligned} \quad (\text{A4})$$

2. Rescaling Experimental Data for Comparison with Theory: Type II

Unlike the phase diagram for a Type I system which has three special points (critical point, triple point and zero field Sm- A^* -Sm- C_M^* transition), Type II lacks a critical point and thus only has two special points: the vertex of the parabolic modulated region and the zero field Sm- A^* -Sm- C_M^* transition. The relationship between T_0, T_c, T_{AC}^* , and m is given in Eq. (A2). The vertex T_v, E_v of the parabola can be related to T_0, T_c, E_c and m using the expressions for ρ_v and h_v after Eq. (26) giving:

$$\frac{T_v - T_c}{T_c - T_0} = \frac{2(m^2 - 1)^2}{435}, \quad (\text{A5})$$

and

$$\frac{8}{15} \left(\frac{E_v - E_c}{E_c} \right) = \left(\frac{T_v - T_c}{T_c - T_0} \right) + \frac{26(m^2 - 1)^3}{121,945}. \quad (\text{A6})$$

Together the three Eqs. (A2), (A5), (A6) contain four unknowns: T_0 , T_c , E_c and m so a fourth relationship is required. An extra relationship can be obtained using the experimental curvature at the vertex of the parabolic modulated region and the parabolic equation Eq. (26):

$$\left| \frac{d^2 T}{dE^2} \right|_v = \frac{2,946}{(m^2 - 1)^4} \frac{(T_c - T_0)}{E_c^2}. \quad (\text{A7})$$

One can now solve Eqs. (A2), (A5), (A6) and (A7) to obtain T_0 , T_c , E_c , and m , and to subsequently convert $T \rightarrow R \rightarrow \rho$ and $E \rightarrow \epsilon \rightarrow h$ as described above in the subsection for Type I.

Appendix B: Details of Phase Boundary Calculations

1. Details of Calculation of Sm- C_U^* -Sm- C_U^* Boundary for Small Electric Field

Inserting the ansatz of Eq. 14 into the free energy, and performing the integral results in a free energy that depends on C_u , s , σ , and q . Minimizing with respect to q yields

$$q_{\min} = 2q_0\sigma\sqrt{1 - \sigma^2}. \quad (\text{B1})$$

Inserting $q = q_{\min}$ back into F , and minimizing with respect to σ yields

$$\sigma_{\min} = \frac{1}{\sqrt{2}} \sqrt{\frac{3s^4 - 10s^2 + 16m^2 - 24C_u^4 + 40C_u^2}{3s^4 - 10s^2 + 16m^2 + 18C_u^2 s^2}}. \quad (\text{B2})$$

At zero field, the uniform piece of \mathbf{C} is zero, i.e., $C_u = 0$, and Eqs. (B1) and (B2) rightly yield $\sigma_{\min} = 1/\sqrt{2}$ and $q_{\min} = q_0$. The remaining zero field free energy density is

$$\frac{F_{\epsilon=0}}{V} = -\frac{27u^3}{800v^2} \left[\left(R - \frac{2}{15}m^2 \right) s^2 - \frac{1}{6}s^4 + \frac{1}{60}s^6 \right]. \quad (\text{B3})$$

The negative s^4 coefficient means that the Sm- A^* -Sm- C_M^* transition is first order, and upon entry to the Sm- C_M^* phase the tilt magnitude jumps to a nonzero value $s_{1\text{st}}^0$, where the superscript 0 indicates the zero field result. The transition temperature $R_{1\text{st}}^0 \equiv R(T_{1\text{st}}^0)$ can be found by equating the Sm- A^* and Sm- C_M^* minima of $F_{\epsilon=0}(s)$, i.e., solving the simultaneous equations

$$\begin{aligned} \frac{dF_{\epsilon=0}}{ds_{1\text{st}}^0} &= 0, \\ F_{\epsilon=0}(s=0) &= F_{\epsilon=0}(s_{1\text{st}}^0), \end{aligned} \quad (\text{B4})$$

for $R = R_{1\text{st}}^0$ and $s_{1\text{st}}^0$. This yields

$$\begin{aligned} R_{1\text{st}}^0 &= \frac{5}{12} + \frac{2m^2}{15}, \\ s_{1\text{st}}^0 &= \sqrt{5}. \end{aligned} \quad (\text{B5})$$

For nonzero field $\epsilon \neq 0$, $C_u \neq 0$ and the system is no longer in the untilted, Sm- A^* phase. Instead it is either in the uniform Sm- C_U^* phase or the modulated Sm- C_M^* phase. To determine the Sm- C_U^* -Sm- C_M^* boundary near $\epsilon = 0$, we expand the free energy in powers of C_u , which will be small for small ϵ . Inserting $q = q_{\min}$ and $\sigma = \sigma_{\min}$ (given by Eqs. (B1) and (B2)) into the free energy and expanding to quadratic order in C_u we find

$$\frac{F_{\epsilon \approx 0}(s, C_u)}{V} = \frac{F_{\epsilon=0}(s)}{V} - \frac{27u^3}{200v^2} \left[\beta(s, R)C_u^2 - \frac{8}{15}\epsilon C_u \right], \quad (\text{B6})$$

where

$$\beta(s, R) = \frac{R}{2} - \frac{1}{3}s^2 + \frac{3}{40}s^4. \quad (\text{B7})$$

The above free energy density has a minimum C_u :

$$C_{u_{\min}} = \frac{4\epsilon}{15\beta(s)} . \quad (\text{B8})$$

Inserting $C_{u_{\min}}$ back into Eq. (B6) results in a purely s dependent free energy density

$$\frac{F_{\epsilon \approx 0}(s)}{V} = \frac{F_{\epsilon=0}(s)}{V} + \frac{6u^3}{625v^2} \frac{\epsilon^2}{\beta(s, R)} . \quad (\text{B9})$$

This time we equate the Sm- C_U^* and Sm- C_M^* minima of $F_{\epsilon \approx 0}(s)$, i.e., solving the simultaneous equations

$$\begin{aligned} \frac{dF_{\epsilon \approx 0}}{ds_{1\text{st}}(\epsilon)} &= 0 , \\ F_{\epsilon \approx 0}(s=0) &= F_{\epsilon=0}(s_{1\text{st}}(\epsilon)) . \end{aligned} \quad (\text{B10})$$

This results in a modified $s_{1\text{st}}(\epsilon) = s_{1\text{st}}^0 + \mathcal{O}(\epsilon^2)$ and a Sm- C_U^* -Sm- C_M^* boundary in $R - \epsilon$ space:

$$R_{1\text{st}}(\epsilon) = R_{1\text{st}}^0 + \frac{8\epsilon^2}{15\beta(s_{1\text{st}}^0, R_{1\text{st}}^0)\beta(0, R_{1\text{st}}^0)} + \mathcal{O}(\epsilon^4) , \quad (\text{B11})$$

from which we identify $G(m)$ in Eq.13 as $G(m) = \frac{8}{15\beta(s_{1\text{st}}^0, R_{1\text{st}}^0)\beta(0, R_{1\text{st}}^0)} > 0$.

2. Showing that the Tilt is Continuous in the Modulated Phase for Type II Systems.

As shown in Section VI, for Type II systems the uniform low tilt – high tilt critical point is unstable to a modulated phase. We recall that this critical point terminated the uniform low tilt – high tilt first order phase boundary, and that the tilt changed discontinuously across the boundary. We now show that the average tilt in the modulated phase remains continuous, i.e., both the critical point and tilt discontinuity are absent. Our starting point is the spatially averaged tilt, i.e, the tilt averaged over one period:

$$\langle \mathbf{c} \rangle = \frac{q}{2\pi} \int_0^{\frac{2\pi}{q}} \mathbf{c}(z) dz = c_u \hat{\mathbf{x}} = c_u (1 + \gamma) \hat{\mathbf{x}} . \quad (\text{B12})$$

Near the phase boundary given by Eq. (26), the system is close to the unstable uniform critical point, so as in the previous section, we work with the small deviation γ . Of particular interest is whether the discontinuous behavior of γ , and thus the average tilt, still exists despite the modulation. Looking at the expression for F_u , the free energy of the uniform state (when $s = 0$), given by Eq. (16), it is useful to recall that for $\rho < 0$, the γ^2 coefficient is negative and discontinuous behavior of γ is possible.

To determine whether this discontinuous behavior of γ is possible in the modulated state, we must determine the γ^2 coefficient when $s \neq 0$. We do so by inserting $s_{\min} = \sqrt{\frac{-A(\gamma, \rho)}{2B(\gamma)}}$ back into the free energy of Eq. (19). Expanding for $m^2 \gtrsim 1$ gives a purely γ dependent energy within the modulated phase, to $\mathcal{O}(\gamma^3)$:

$$\begin{aligned} F_M(\gamma) &= F_u - \frac{27u^3}{200v^2} \left[\left(\frac{29}{30}(\rho_c - \rho) + \frac{26}{225}(m^2 - 1)^2 \right) \gamma^2 - \left(\frac{1}{15}(\rho_c - \rho)(m^2 - 1) + \frac{56}{6525}(m^2 - 1)^3 \right) \gamma \right] \\ &= -\frac{200v^2}{27u^3} \left[\left(\frac{7}{15}(\rho_c - \rho) + \frac{729}{6525}(m^2 - 1)^2 \right) \gamma^2 - \left(h + \frac{1}{15}(\rho_c - \rho)(m^2 - 1) + \frac{56}{6525}(m^2 - 1)^3 \right) \gamma \right] \end{aligned} \quad (\text{B13})$$

Remembering that within the modulated phase, $\rho < \rho_c$, we see that the γ^2 coefficient in $F_M(\gamma)$ is always positive, implying that there is no discontinuous behavior of γ in the modulated phase.

3. Locating the Triple Point in Type I Systems

Insertion of the ansatz Eq. (27) into the free energy Eq. (1) yields

$$\begin{aligned} \frac{F_M}{V} &= \frac{q}{2\pi q_0} \left(\frac{-27u^3}{200v^2} \right) \int_0^{\frac{2\pi q_0}{q}} dZ \left[-h \cos(\phi) |\gamma| + \left(\frac{\rho}{2} + \frac{4}{15} \sin(\phi) \right) |\gamma|^2 + \frac{4}{15} \cos(\phi) \sin^2(\phi) |\gamma|^3 + \right. \\ &\quad \left. \left(\frac{2}{5} \cos^2(\phi) - \frac{1}{15} \right) |\gamma|^4 + \frac{m^2}{15} \left((\partial_Z \phi)^2 - 2(\partial_Z \phi) \right) |\gamma|^2 + \mathcal{O}(|\gamma|^5) \right] . \end{aligned} \quad (\text{B14})$$

where $q_0 = 2\pi/P_0$ is the wave vector of the perfectly helical modulation with pitch P_0 , and q is the wave vector of the actual modulation, and is still to be determined. For a uniform state $\partial_Z\phi = 0$ and the energy is minimized by $\phi = 0$ for $h > 0$ and $\phi = \pi$ for $h < 0$, corresponding to the high and low tilt states. In contrast to Section IV these states are distinguished by the value of the angle ($\phi = 0$ for high tilt and $\phi = \pi$ for low tilt) and not by the sign of $|\gamma| \geq 0$ which is positive by definition. The corresponding energy of the uniform state for either the $\phi = 0$ or $\phi = \pi$ states is

$$\frac{F_U}{V} = -\frac{27u^3}{200v^2} \left[\frac{\rho}{2} |\gamma_U|^2 + \frac{1}{3} |\gamma_U|^4 - |h| |\gamma_U| \right], \quad (\text{B15})$$

which when minimized with respect to $|\gamma_U|$ agrees with the uniform equation of state Eq. (17), as it should.

For the modulated state, minimizing with respect to $\phi(Z)$, and employing the Beltrami identity gives:

$$\frac{d\phi}{dZ} = \frac{2}{m} \left[W - \frac{15h}{4|\gamma_M|} \cos(\phi) + \sin^2(\phi) \left(1 - |\gamma_M| \cos(\phi) - \frac{3|\gamma_M|^2}{2} \right) \right]^{\frac{1}{2}}, \quad (\text{B16})$$

where W is a dimensionless constant of integration that (along with $|\gamma_M|$) is determined by further minimization. In Eq. (B16), and the analysis to follow, we take $m > 0$ corresponding to positive enantiomeric excess. We note that carrying out the analysis with $m < 0$ (corresponding to enantiomeric excess of opposite handedness) results in the same phase boundary, i.e., the results are independent of the handedness of the enantiomeric excess, as they should be. The above equation can be integrated to obtain $Z(\phi)$ and thus the modulated structure $\phi(Z)$.

$$Z = \frac{m}{2} \int_0^{\phi(z)} d\phi' \left[W - \frac{15h}{4|\gamma_M|} \cos(\phi') + \sin^2(\phi') \left(1 - |\gamma_M| \cos(\phi') - \frac{3|\gamma_M|^2}{2} \right) \right]^{-\frac{1}{2}}, \quad (\text{B17})$$

where we remind the reader that the actual, unrescaled position $z = Z/q_0 = ZP_0/2\pi$.

Inserting the above expression for $\partial_Z\phi$ back into the free energy given by Eq. (B14), and by minimizing with respect to W gives

$$m\pi = I(W_{\min}, h, |\gamma_M|) \equiv \int_0^{2\pi} d\phi \left[W_{\min} - \frac{15h}{4|\gamma_M|} \cos(\phi) + \sin^2(\phi) \left(1 - |\gamma_M| \cos(\phi) - \frac{3|\gamma_M|^2}{2} \right) \right]^{\frac{1}{2}}. \quad (\text{B18})$$

Using Eqs. (B16) and (B18), the free energy density of Eq. (B14) can be simplified to

$$\frac{F_M}{V} = \frac{-27u^3}{200v^2} \left[\frac{\rho}{2} |\gamma_M|^2 + \frac{1}{3} |\gamma_M|^4 - \frac{4}{15} W_{\min} |\gamma_M|^2 \right], \quad (\text{B19})$$

which when minimized with respect to $|\gamma_M|$ gives:

$$\rho |\gamma_M| + \frac{4}{3} |\gamma_M|^3 - \frac{8}{15} W_{\min} |\gamma_M| - \frac{4}{15} \frac{dW_{\min}}{d|\gamma_M|} |\gamma_M|^2 = 0. \quad (\text{B20})$$

The coupled equations (B18) and (B20) could in principle be solved to obtain $W_{\min}(h, \rho, m)$ and $\gamma_M(h, \rho, m)$ for the modulated state, which could in turn be used to find the modulation period in terms of the system parameters h, ρ, m . This modulation period is given by Eq. (28).

To obtain $\rho_{1st}(h = 0, m) \equiv \rho_{TP}(m)$ we begin by setting $h = 0$ in Eq. (B18) and expanding the right hand side for small $|\gamma_M|$ and small W . Doing so yields a relationship between $|\gamma_M|$, W and m :

$$|\gamma_M|^2 \approx G(W, m) \equiv -\frac{3}{4} \rho_m + \frac{6}{19} [4 \ln(2) + 1 - \ln(W)] W, \quad (\text{B21})$$

where $\rho_m = \frac{8}{19}(\pi m - 4)$. The condition that the modulated and uniform free energies (given by Eqs. (B15) and (B19)) are equal implies that

$$\frac{\rho_{TP}}{2} |\gamma_M|^2 + \frac{1}{3} |\gamma_M|^4 - \frac{4}{15} W_{TP} |\gamma_M|^2 = \frac{\rho_{TP}}{2} |\gamma_U|^2 + \frac{1}{3} |\gamma_U|^4. \quad (\text{B22})$$

We then use Eq. (B21) to eliminate $|\gamma_M|$ and reexpress Eq. (B20) and Eq. (B22) purely in terms of m and W_{TP} (the value of W at the triple point):

$$\rho_{TP} + \frac{4}{3} G(W_{TP}, m) - \frac{8}{15} W_{TP} - \frac{8}{15} G(W_{TP}, m) \left(\frac{dG(W_{TP}, m)}{dW_{TP}} \right)^{-1} = 0, \quad (\text{B23})$$

and

$$\frac{\rho_{TP}}{2} G(W_{TP}, m) + \frac{1}{3} G(W_{TP}, m)^2 - \frac{4}{15} W_{TP} G(W_{TP}, m) = -\frac{3}{16} \rho_{TP}^2, \quad (\text{B24})$$

where we have used $\gamma_U = \sqrt{-\frac{3}{4}\rho_{TP}}$ at the triple point. The above two equations can then be used to solve for ρ_{TP} and W_{TP} in terms of m , yielding

$$\rho_{TP}(m) = \frac{8}{19} [\pi m - 4 - W_{TP}(m) \ln(W_{TP}(m))] , \quad (\text{B25})$$

where $W_{TP}(m)$ is given by

$$W_{TP}(m)(\ln(W_{TP}(m)))^2 = \frac{19}{15} (4 - \pi m) . \quad (\text{B26})$$

Together these two equations give ρ_{TP} as a function of m . We note that Eq. (B26) implies that $m \leq m_1 \equiv 4/\pi$, and that both $W_{TP}(m) \rightarrow 0$ and $\rho_{TP}(m) \rightarrow 0$ as $m \rightarrow m_1$. For $m \lesssim m_1$ Eqs. (B25) and (B26) can be approximated to give ρ_{TP} explicitly in terms of m , i.e., Eq. 29.

4. Locating the Phase Boundaries Near the Triple Point in Type I Systems

Next we locate the first order phase boundaries that meet at the triple point. The boundary between the low (L) and high (H) tilt uniform states has already been found and lies along $h = 0$ for $\rho < 0$. The other two boundaries separate the modulated (M) and uniform high (H) tilt phases, and the modulated (M) and uniform low (L) tilt phases. Notationally we refer to the three phase boundaries as $L-H$, $M-H$, and $M-L$. The $M-H$ and $M-L$ phase boundaries are found by expanding near the triple point, i.e., for $\rho \lesssim \rho_{TP}$. Specifically, expanding Eq. (B18) for $W \approx W_{TP}$, $h \approx h_{TP} = 0$ and $|\gamma| \approx |\gamma_{TP}|$ gives:

$$m\pi = I(W_{TP}, h_{TP} = 0, |\gamma_{TP}|) + I_W(m)\omega + I_\gamma(m)\nu + I_h(m)h, \quad (\text{B27})$$

where $\omega = W - W_{TP}$, $\nu = |\gamma| - |\gamma_{TP}|$ and $|\gamma_{TP}|$

$$I_W(m) = \left. \frac{dI}{dW} \right|_{TP}, I_\gamma(m) = \left. \frac{dI}{d\gamma_M} \right|_{TP}, I_h(m) = \left. \frac{dI}{dh} \right|_{TP}. \quad (\text{B28})$$

$I_W(m)$, $I_\gamma(m)$, and $I_h(m)$ depend on m via $W_{TP}(m)$ and $|\gamma_{TP}|(m)$. We recall that $W_{TP}(m)$ is given by Eq. (B26) and $|\gamma_{TP}|$ is obtained from Eq. (B21)

$$|\gamma_{TP}|^2 = -\frac{3}{4}\rho_m + \frac{6}{19} [4 \ln(2) + 1 - \ln(W_{TP})] W_{TP}. \quad (\text{B29})$$

Since $m\pi = I(W_{TP}, h_{TP} = 0, |\gamma_{TP}|)$, Eq. (B27) gives ω in terms of ν and h :

$$\omega = -\frac{I_\gamma\nu + I_h h}{I_W}. \quad (\text{B30})$$

Using this ω we insert $W = W_{TP} + \omega$ into Eq. (B20) to obtain ν_{\min} :

$$\nu_{\min} = f_\rho(m)(\rho - \rho_{TP}) + f_h(m)h, \quad (\text{B31})$$

where $f_\rho(m)$ and $f_h(m)$ are constants of order one. Inserting ν_{\min} back into Eq. (B30) gives the corresponding ω_{\min} . The free energy near the triple point is then found by setting $W = W_{TP} + \omega_{\min}$ and $|\gamma_M| = |\gamma_{TP}| + \nu_{\min}$ into Eq. (B19). To lowest order in $\rho - \rho_{TP}$ and h this gives

$$\frac{F_M}{V} = \frac{-27u^3}{200v^2} \left[-\frac{3}{16}\rho_{TP}^2 + \frac{1}{2}[(\rho - \rho_{TP}) - h]|\gamma_{TP}|^2 \right]. \quad (\text{B32})$$

We also minimize the uniform free energy of Eq. (B15) for small h and $\rho - \rho_{TP}$:

$$\frac{F_U}{V} = \frac{-27u^3}{200v^2} \left[-\frac{3}{16}\rho_{TP}^2 - \frac{3}{8}\rho_{TP}(\rho - \rho_{TP}) \mp \frac{\sqrt{-3\rho_{TP}}}{2}h \right]. \quad (\text{B33})$$

where the \mp refers to $h > 0$ (high tilt) and $h < 0$ (low tilt) respectively. Setting $F_M = F_U$ gives the location of the first order phase boundaries. The modulated-high ($M-H$) tilt boundary and the modulated-low ($M-L$) tilt first order boundaries are:

$$\rho_{M-H/M-L} = \rho_{TP} + \frac{(|\gamma_{TP}|^2 \mp \sqrt{-3\rho_{TP}})}{(|\gamma_{TP}|^2 + \frac{3}{4}\rho_{TP})} h. \quad (\text{B34})$$

We note that the magnitude of the boundaries' slopes are different, with the modulated-high tilt boundary being steeper. As m is raised towards m_1 , $W_{TP} \ll 1$, and the boundaries can be approximated by Eq. (30).

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