Disordering to Order: de Vries Behavior from a Landau Theory for Smectic Phases

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We show that Landau theory for the isotropic (I), nematic (N), smectic-A, and smectic-C phases generically, but not ubiquitously, implies "de Vries" behavior: i.e., a continuous A-C transition can occur with little layer contraction while the birefringence increases significantly once the system moves into the C phase. Our theory shows that 1st order A-C transitions are also possible. These transitions can be de Vries-like, but in general need not be. Generally, de Vries behavior occurs in models with unusually small orientational order and is preceded by a first order I-A transition. These results correspond well with experimental work to date.

Recently, an unusual new class of liquid crystals known as "de Vries smectic liquid crystals" [1] has drawn interest. They possess two defining features. First, there is little change with temperature T of the layer spacing $d(T)$ upon entry to the C phase, in contrast to the rapid geometrical contraction $d(T) \propto \cos\theta(T)$ expected if the molecules tilt by a strongly temperature dependent angle $\theta(T)$. Second, the birefringence increases significantly upon entering the C phase from the A phase. In fact, for de Vries materials with a 2nd order A-C transition, the birefringence is seen [2,3] to *decrease* with decreasing temperature as the A-C transition as approached, reaching a minimum at the A-C transition. This is the first example known to us of *decreasing* order as a lower symmetry phase is approached. For de Vries materials with a 1st order transition, the birefringence increases moderately as the A-C transition is approached and then jumps significantly at the transition [4]. Generally, de Vries smectic liquid crystals exhibit the phase sequence I-A-C, without a nematic phase. First order A-C transitions are not always de Vries-like [4], contrary to some recent speculations.

In de Vries' "diffuse cone model" [5] of these materials, the molecules "pretilt" in the A phase as the A-C transition is approached, but in azimuthally random directions (hence reducing orientational order), so that there is no long range order in the tilting. Upon entering the C phase, the molecules azimuthally order (hence increasing orientational order) without the significant layer contraction that occurs in conventional smectics whose molecules tilt at the A-C transition.

In this Letter, we show that in a complete, nonchiral Landau mean field theory for the isotropic (I), nematic (N), A and C phases, in which all three order parameters (orientational, layering, azimuthal tilt) and the layer spacing are coupled, de Vries behavior occurs in a finite fraction of parameter space, while other regions exhibit conventional behavior. The mean field phase diagram for our model is shown in Fig. 1. Here, t_s and t_n are Landau theory parameters that control layering and orientational order, respec-

tively. We find that two main features are necessary for de Vries behavior— an unusually weak coupling between layering and orientational order and a virtually temperature independent t_n. This latter feature would correspond to almost perfect excluded volume short range repulsive molecular interactions. Our theory also predicts that materials exhibiting de Vries behavior will almost always follow the phase sequence I-A-C. For 2nd order A-C transitions, we show that systems with an athermal t_n will exhibit the unusual feature of a decreasing birefringence as the transition is approached from the A phase. In fact, we predict
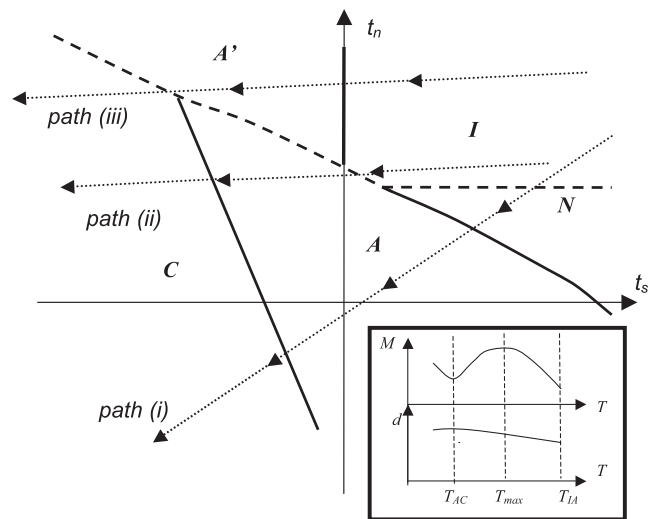

FIG. 1. The phase diagram in t_s-t_n space for the I, N, A, and C phases. 1st and 2nd order phase boundaries are shown as dashed and solid lines, respectively. Three decreasing temperature paths from the I to C phase are shown. Path (i) corresponds to a conventional material that does not exhibit de Vries behavior. Path (ii) corresponds to a material exhibiting de Vries behavior and a 2nd order A-C transition. Path (iii) leads to a 1st order A-C transition with de Vries behavior. The inset shows a possible temperature dependence of birefringence (M) and layer spacing (d) for path (ii).

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that in the A phase, some systems will exhibit a birefringence that has a nonmonotonic dependence on temperature, as shown in the inset of Fig. 1 [6]. Lastly, we also show that 1st order A-C transitions can (but generally need not) be de Vries-like.

Another result of our theory, unrelated to de Vries behavior, is that this phase diagram predicts *two* distinct smectic-A phases of identical symmetry, denoted A and A', separated by a first order phase transition. While 1st order transitions between two smectic-A phases due to competition between two different layer spacings [7] have been predicted, our result shows that even without such competition, A-A transitions occur quite naturally and should be far more common than was previously thought.

Any experiment in which temperature is varied at fixed concentration traces a path through this phase diagram. As usual in Landau theory, we assume throughout this Letter that t_s and t_n are monotonically increasing functions of temperature; hence, as temperature is lowered, one moves monotonically from upper right to lower left in Fig. 1. Three qualitatively distinct paths of this type are shown. Path (i) is a typical path for a material that does *not* display de Vries behavior; along it, t_s *and* t_n both depend strongly on temperature. Paths (ii) and (iii) correspond to de Vries behavior with 2nd and 1st order A-C and A'-C transitions, respectively. Both paths have strongly varying t_s and weakly varying t_n; i.e, t_n is virtually athermal. This would be the case if the I-N transition is driven by a steric mechanism for which t_n depends strongly on concentration and weakly on T. We find that de Vries behavior occurs in this case, for sufficiently weak coupling between layering and orientational orders. It should also be pointed out that a path above (iii), away from the A-A'-C critical end point (CEP), would exhibit a 1st order A'-C transition *without* de Vries behavior.

This restriction to nearly horizontal paths implies that de Vries systems should very rarely exhibit an N phase between the A and C phases, since to cross the I-N boundary, a nearly horizontal path in Fig. 1 would have to be "fine tuned" to start very close to the boundary. The most likely paths to see de Vries behavior are those like (ii) or (iii), showing phase sequence I-A-C or I-A'-C, in good agreement with experimental work to date.

In this Letter, we focus on path (ii) and briefly discuss path (iii) at the end. The inset in Fig. 1 shows predictions for the layer spacing $d(T)$ and birefringence $M(T)$ as T is varied along path (ii). The *increase* of the layer spacing in the A phase as the A-C transition is approached, though contrary to the de Vries picture of "pre-tilting" in the A phase, is seen experimentally [2]. In the A-phase, our Landau theory predicts

$$M_A(T) = M_{\max} - M_2\left[\frac{t_s(T) - t_s(T_{\max})}{t_s(T_{\max})}\right]^2, \qquad (1)$$

where $M_{\max}$, M_2, and $T_{\max}$ are positive constants. We have shown that if t_n is completely athermal, $T_{AC} < T_{\max}$, where

T_{AC} is the A-C transition temperature, so that in systems that follow a path like (ii), $M_A(T)$ will *decrease* as the A-C transition is approached. A subset of such systems will have $T_{\max} < T_{IA}$, where T_{IA} is the I-A transition temperature, so that M_A has a maximum *within* the A phase, as shown in the inset in Fig. 1. If t_s is linear in T in the A-phase (as expected for small $T_{IA} - T_{AC}$), then $M_A(T)$ will be *perfectly* parabolic in T.

In the C phase near the A-C transition, the critical temperature dependences of M and the tilt angle $\theta(T)$ predicted by our Landau theory are as follows: M linear in T, and $\theta \propto (T_{AC} - T)^{1/2}$. When fluctuation effects are included, we expect [8] $\theta \propto (T_{AC} - T)^{\beta}$, where $\beta \approx 0.35$ is the order parameter critical exponent for the 3D XY model. The layer spacing scales with temperature in our Landau theory according to

$$d = d_0 + a(T_{AC} - T) + b(T_{AC} - T)^3, \qquad (2)$$

where d_0 is the value of the layer spacing *at* the A-C transition and a and b are constants that depend on the Landau theory parameters . Clearly, if a is sufficiently small, which we find is the case in the C phase for sufficiently weak coupling between layering and orientational order, the layer spacing shows very little variation with temperature near T_{AC}. Significantly, we find that in cases like path (ii), the criterion for de Vries behavior of $d(T)$ differs from that for $M(T)$. Hence, we predict that some systems will exhibit de Vries behavior of the birefringence, but *not* de Vries behavior of the layer spacing.

How do fluctuations affect our mean field Landau theory? While our theory predicts that the I-A' transition is continuous, it is known [9] that fluctuations *always* drive the I-A' transition first order, albeit only weakly so if fluctuations are small. Fluctuation effects will also shift the positions of *all* of the transitions we have found. We expect, however, that the topology and essential geometry of the phase diagram Fig. 1 should occur in real systems. The only qualitative difference we expect is that the I-A-A' critical end point (CEP) predicted by Landau theory will be replaced by an I-A-A' *triple* point.

In other regions of parameter space, our model has an N-A-C point; we will discuss this elsewhere [10].

In summary, de Vries behavior emerges quite naturally from our Landau theory. Equally importantly, conventional behavior (for both 1st and 2nd order transitions) also generically occurs for different Landau parameters. Thus, the model can accommodate all observed behaviors in *all* systems, and also predicts new behaviors not yet seen experimentally, like the first order A-A' transition.

We will now briefly describe the formulation and analysis of our theory. A Landau theory for all four phases (I, N, A, C) must include order parameters for three types of order: uniaxial orientational order, tilt (azimuthal) order, and layering order. The first two are embodied in the usual second rank tensor orientational order parameter $\mathcal{Q}$. The complex layering order parameter ψ is defined via the

density $\rho = \rho_0 + \mathrm{Re}(\psi e^{i\mathbf{q}\cdot\mathbf{r}})$ with ρ_0 constant and $\mathbf{q}$ the layering wave vector. Taking both ψ and $\mathcal{Q}$ to be spatially uniform implies the Landau free energy density $f = f_Q + f_\psi + f_c$, with the orientational (f_Q) [11], layering (f_ψ), and coupling (f_c) terms given by

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

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

$$f_c = \frac{1}{2}[-g_1(q^2)q_iq_jQ_{ij} + g_2q_iq_jQ_{ik}Q_{jk}]|\Psi|^2$$
$$+ \frac{h}{4}(q_iq_jQ_{ij})^2|\Psi|^4, \quad (5)$$

where q_i is the component of the layering wave vector in the ith direction, and the Einstein summation convention is implied. The constant q_0 is the magnitude that the layering wave vector would have in the absence of coupling between layering and orientational order. For weak coupling, $q \approx q_0$, and we Taylor expand $g_1(q^2) \approx g_{1_0} + g_1'(q^2 - q_0^2)$, where $g_{1_0} \equiv g_1(q_0^2)$ and $g_1' \equiv \frac{dg_1}{d(q^2)}|_{q^2=q_0^2}$. The relatively large number of parameters in f is inevitable given the fact that the theory incorporates three types of order. Furthermore, this theory allows for the possibility of conventional or de Vries behavior. However, we will show that in general, any of the five possible phases shown in Fig. 1 can be accessed by allowing, at most, two of the above parameters (t_n and t_s) to vary (with temperature). The presence or absence of the two defining features of de Vries behavior, small change in layer spacing and decreasing birefringence, depend only on the size of g_1' and the athermal nature of t_n, respectively. The remaining fixed positive parameters are required to stabilize the phases [12–14].

Choosing the arbitrary direction of the layer normals to be z, we seek the configuration of ψ, $\mathcal{Q}$, and $\mathbf{q} = q\hat{\mathbf{z}}$ that minimizes f. The form of $\mathcal{Q}$ that does so [10] is given by

$$Q_{ij} = (-S + \sqrt{3}\eta)e_{1i}e_{1j} + (-S - \sqrt{3}\eta)e_{2i}e_{2j}$$
$$+ (2S)e_{3i}e_{3j}, \quad (6)$$

where $\hat{\mathbf{e}}_3 = \mathbf{c} + \sqrt{1 - c^2}\hat{\mathbf{z}}$ is the average direction of the molecules' long axes (i.e., the director). Here, in either smectic phase, $\hat{\mathbf{z}}$ is normal to the layers; in the N and I phases, the direction of $\hat{\mathbf{z}}$ is arbitrary. The projection, $\mathbf{c}$, of the director onto the layers is the order parameter for the C phase. The other two principal axes of $\mathcal{Q}$ are given by $\hat{\mathbf{e}}_1 = \hat{\mathbf{z}} \times \hat{\mathbf{c}}$ and $\hat{\mathbf{e}}_2 = \sqrt{1 - c^2}\hat{\mathbf{c}} - c\hat{\mathbf{z}}$. S and η are proportional to the birefringence and biaxiality of the system, respectively. The A phase is untilted ($\mathbf{c} = \mathbf{0}$) and uniaxial ($\eta = 0$), while the C phase is tilted ($\mathbf{c} \neq \mathbf{0}$) and biaxial ($\eta \neq 0$). It is convenient to make the change of variables $S = M\cos(\alpha)$ and $\eta = M\sin(\alpha)$. In the A phase, M is proportional to the birefringence.

We next minimize the free energy f over the variables M, α, c, $|\Psi|$, and q. Four qualitatively different types of minima are possible, corresponding to the four different symmetry phases (I, N, A, C). Specifically, the I phase has $M = 0$; $\Psi = 0$; the N phase has $\Psi = 0$, $\mathbf{c} = \mathbf{0}$, and $\alpha = 0$, but $M \neq 0$; the A phase has $\Psi \neq 0$ and $M \neq 0$, but $\mathbf{c} = \mathbf{0}$ and $\alpha = 0$; and the C phase has all of the variables M, α, $\mathbf{c}$, and $\Psi \neq 0$. We render minimization analytically tractable by assuming that the coupling term Eq. (5) is small and by treating it perturbatively. Standard phase transition analysis [15] leads to the phase diagram shown in Fig. 1. Equations for the loci of the phase boundaries are given in [16]. The minimization of our Landau free energy also leads to predictions for the temperature dependences of M and q. We find, in the A-phase,

$$M_A = M_0(t_n) + \frac{q_0^2\Psi_0^2}{\gamma}[-3g_2M_0(t_n) + \delta], \quad (7)$$

$$q_A^2 = q_0^2 + \frac{M_0(t_n)}{K}[-g_2M_0(t_n) + g_1'q_0^2 + \delta], \quad (8)$$

where $\gamma \equiv wM_0(t_n) - 2t_n > 0$ and $M_0(t_n) = (w + \sqrt{w^2 - 4u_nt_n})/2u_n$ is the "bare" value of M, i.e., its value in the absence of coupling. Likewise, $\Psi_0 = \sqrt{-t_s/u_s}$ is the bare value of Ψ. For strongly T dependent t_s and athermal t_n, the quantity δ is most usefully expressed as

$$\delta(t_s, t_n) \equiv \zeta(t_s - t_s^{AC}), \quad (9)$$

where $\zeta = (2hq_0^2M_0)/u_s$, and $t_s^{AC} = -(g_{1_0} - g_2M_0)/\zeta$ is the value of t_s where δ vanishes and the 2nd order A-C transition occurs. In the A phase, $\delta > 0$ and in the C phase $\delta < 0$. In the C phase, we find

$$M_C = M_0(t_n) + \frac{q_0^2\Psi_0^2}{\gamma}\left(-3g_2M_0(t_n) - \frac{g_2}{2hq_0^2\Psi_0^2}\delta\right), \quad (10)$$

$$q_C^2 = q_A^2(t_s^{AC}) + \frac{g_1'}{2Kh\Psi_0^2}\delta, \quad (11)$$

where a decrease in layer spacing requires $g_1' < 0$. Finally, in the A'-phase, we find

$$M_A' = \frac{q_0^2\Psi_0^2g_{1_0}}{t_n}, \quad (12)$$

$$q_A'^2 = q_0^2\left(1 + \frac{2g_{1_0}^2\Psi_0^2}{Kt_n}\right). \quad (13)$$

These results imply de Vries behavior for both birefringence and layer spacing. For a nearly horizontal experimental locus like path (ii) through the A phase, the T dependence of M (and hence birefringence) in Eq. (7) comes from the linear t_s- dependence of each of Ψ_0^2 and δ in the correction due to the coupling of layering and orientational orders. From Eq. (7), we see that nonmonotonicity of M_A is due to a competition between the layering

order, Ψ_0^2 and the coupling δ which increase and decrease, respectively, as the A-C transition is approached. This happens because, as the system moves deeper into the A phase, the layering order increases, thereby augmenting the weak orientational order due to the coupling between the two. However, as the A-C transition (where at the director tilts away from the layer normal) is approached, this coupling necessarily decreases and, hence, so does M_A, which means the birefringence *decreases* as the A-C transition is approached. Once in the C phase, the birefringence begins to *increase* with decreasing t_s. It is straightforward to show that if $g_{1_0} > 4g_2M_0$, then M_A exhibits a maximum inside the A phase, as shown in the inset in Fig. 1.

As the A-C transition is approached within the A phase, q_A monotonically decreases and hence d monotonically increases. This is typical of both conventional *and* de Vries smectics although, as discussed above, it is somewhat contrary to the diffuse cone picture. The T dependence of the layer spacing at the transition depends crucially on the size of the parameter g_1'. In systems where the coupling of the layering and orientational order depends weakly on layer spacing and $|g_1'|$ is unusually small, the T-dependence of q is almost flat. We have shown that if $g_1' = 0$, then the change in layer spacing scales like $(T_{AC} - T)^3$ and hence varies very weakly in the C phase near the A-C transition. Systems with larger values of $|g_1'|$ will have conventional behavior of the layer spacing.

Since this de Vries behavior of q has a different criterion than the de Vries behavior of M (which relies on t_n being athermal), it should be possible to find systems which exhibit de Vries behavior of the birefringence, but *not* de Vries behavior of the layer spacing.

For systems that approach the C phase from the A' phase, along path (iii), the birefringence will increase monotonically before jumping substantially (on the order of M_0) at the transition. From Eq. (13), we see that the T dependent piece of q_A' is second order in the coupling g_{1_0} which we treat perturbatively in our analysis. Thus, this T dependent piece is very small in the A phase. Upon entry into the C phase, the T dependence of the layering spacing will be weak if g_1' is small. At the A'-C transition, there will be a jump in q but Eqs. (8), (11), and (13) can be used to show that this jump will be small when g_1' and g_2 are small. For such a system, a transition just above the CEP will exhibit an almost continuous change in tilt angle, a weakly varying layer spacing, a substantial jump in birefringence, and a latent heat. Systems entering the C phase well above this CEP will exhibit jumps in all of the above quantities and thus not be de Vries-like.

The requirement of near T-independence of t_n for de Vries behavior severely restricts the possible experimental loci in Fig. 1 that can display such behavior: namely, nearly horizontal ones. A significantly sloped path like (i) will *not* exhibit de Vries behavior. In this case, the growth of the bare (i.e., coupling-free) birefringence $M_0(t_n)$ as T is lowered swamps the effects due to the coupling terms, and makes the behavior of both the birefringence and the layer spacing conventional. Thus, our model can accommodate *either* conventional behavior or de Vries behavior, if t_n is thermal or athermal, respectively.

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[1] For an excellent review of de Vries smectics, see J. P. F. Lagerwall and F. Giesselmann, Chem. Phys. Chem. **7,** 20 (2006).

[2] J. P. F. Lagerwall, F. Giesselmann, and M. D. Radcliffe, Phys. Rev. E **66,** 031703 (2002).

[3] Y. Panarin (private communication).

[4] N. Hayashi, A. Kocot, M. J. Linehan, A. Fukuda, J. K. Vij, G. Heppke, J. Naciri, S. Kawada, and S. Kondoh, Phys. Rev. E **74,** 051706 (2006).

[5] A. de Vries, Mol. Cryst. Liq. Cryst. Lett. **41,** 27 (1977); A. de Vries, A. Ekachai, and N. Spielberg, *ibid.* **49,** 143 (1979).

[6] Unfortunately, published data on birefringence of these materials within the A phase seems only to focus very near the A-C transition, although such nonmonotonicity has been seen in DSi3-MR11 [3].

[7] P. Barois, J. Prost, and T. C. Lubensky, J. Phys. (Paris) **46,** 391 (1985).

[8] G. Grinstein and R. A. Pelcovits, Phys. Rev. A **26,** 2196 (1982).

[9] S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. **69,** 979 (1975) [Sov. Phys. JETP **42,** 497 (1976)].

[10] K. Saunders and J. Toner (to be published).

[11] P. G. De Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1995).

[12] It should be noted that for the system to exhibit an N-A-C multicritical point, a term $(q_iq_jQ_{ij})^2|\Psi|^2$ must be included.

[13] We have for simplicity dropped some terms (e.g., $\mathrm{Tr}(\mathcal{Q}^2)|\Psi|^2$) that are actually lower order in the presumed small fields Ψ and $\mathcal{Q}$ than the terms we have kept. We have verified that keeping such terms with small, but nonzero, coefficients has no qualitative effect on our results. In contrast, dropping any one of the terms we *have* kept is unphysical.

[14] A free energy similar to ours was used by P. K. Mukherjee *et al.*, J. Chem. Phys. **117,** 7788 (2002) to investigate first order I-A and I-C transitions. However, they ignored the biaxiality of the orientational order parameter and incorrectly claimed that the C phase is stabilized by the g_2 term. This last mistake led them to exclude the h term, which is necessary to stabilize the C phase.

[15] See, for example, P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995).

[16] See EPAPS Document No. E-PRLTAO-98-078718 for equations for the phase boundaries. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.