Phase Transitions in Smectic Liquid Crystal Systems

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Abstract

Liquid crystal systems show strong responses to small changes in both temperature and electric field. Changing these conditions can result in phase shifts and other similar behaviors. We study several theoretical models of smectic liquid crystals. The ideas and notation are first developed in basic polynomial models used to describe liquid crystal systems dependent only on temperature. Specifically, smectic-C to smectic-A phase transitions are examined in a fourth-order polynomial model. The bifurcations in the nonlinear equations are shown to correspond to the phase transitions in the system. Similar analytic techniques are then applied to a more complex model, based on the work of Schaub and Mukamel[1]. This model, which includes terms for electric field dependance and chirality, describes smectic-C* liquid crystal molecules wound into helixes. Increasing temperature and electric field strength tends to "unwind" the helixes into the smectic-A or smectic-C state. The phase transition from the smectic-C* phase to smectic-A phase is identified analytically in the special case of zero electric field. Numeric analysis of the system in general is undertaken with `bvp5c`, a Matlab boundary value problem solver. The region of transition from smectic-C* to smectic-C is mapped using numeric solutions, and specific areas of interest wherein the phase transition changes in nature are highlighted.

1 Introduction to Liquid Crystals

Liquid crystals form a state of matter sharing properties of both solids and liquids. Solids have position and orientation order: all molecules are slotted into a defined lattice structure. Liquids, while still having strong intermolecular attractive forces, lack any structural order. Liquid crystals fall in between. The long, thing molecules that form liquid crystal states tend to arrange themselves parallel to one another (Figure 1).

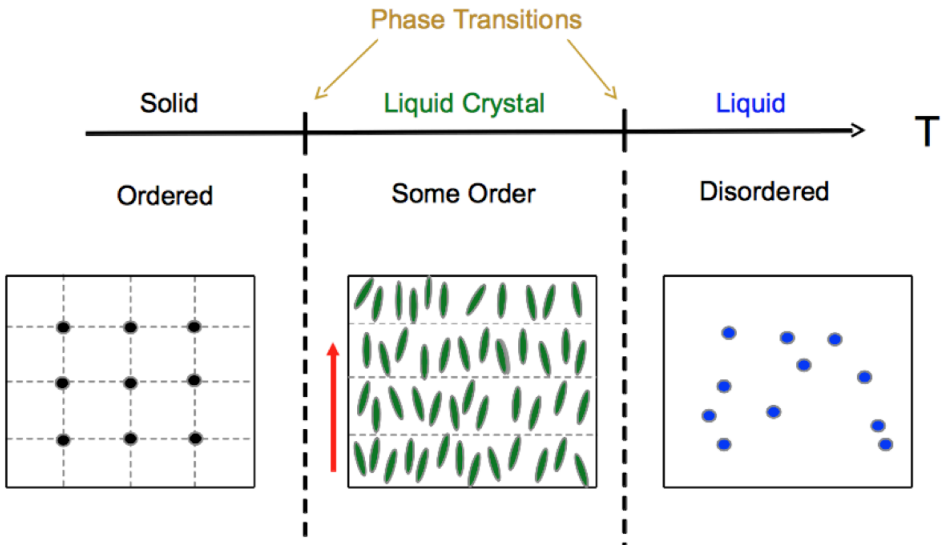


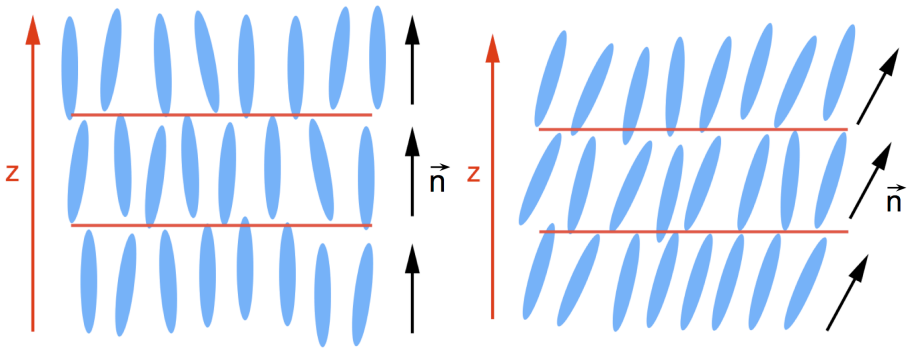
Figure 1: Liquid crystals have orientation order but lack positional order, giving them properties of both liquids and solids.

Many patterns of molecular arrangement are possible, yielding a plethora of different behaviors from liquid crystal systems. Our research focuses on smectic liquid crystals, wherein the molecules stack themselves in discrete layers. The simplest case of this is called a smectic-A system (Figure 2a). In this phase, the layer tilt vector $\vec{n}$, called the director, is aligned in the same direction as the layer vector, $\vec{z}$. If the director was instead tilted at an angle relative to the layer vector, as in Figure 2b, the system would be in the smectic-C phase.

Some liquid crystal molecules are chiral: they are not identical to their mirror image. Such molecules can form a special smectic-C* phase. Like the smectic-C phase, the molecules are tilted compared to the layer vector. However, the direction of the tilt changes from layer to layer (Figure 3). Each successive layer tilts in a different direction in the x-y plane. The result is a helical structure to the liquid crystal system, with layers winding around the z axis.

Cylindrical coordinates provide a convenient coordinate system to describe smectic liquid crystal systems. In these coordinates, we use z to represent the height of the layer, $\vec{c}$ to represent the projection of the (idealized) liquid crystal molecules onto the x-y plane, and ϕ to represent the angle of rotation around the x-y plane (Figure 4).

The system's overall structure will be periodic in z. The periodicity can be expressed using a wavevector $\vec{p}$ and its inverse, $\vec{q} = 1/\vec{p}$.



(a) *Smectic-A* (b) *Smectic-C*

Figure 2: Smectic liquid crystals are classified according to the tilt of the molecules within layers.

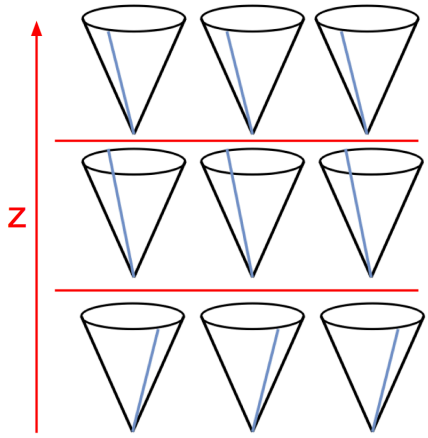


Figure 3: Smectic-C* molecules tilt at in different directions depending on the layer they are in. As depicted here, the light blue line is the molecule, the cone is simply a visual aid to help show their three dimensional behavior.

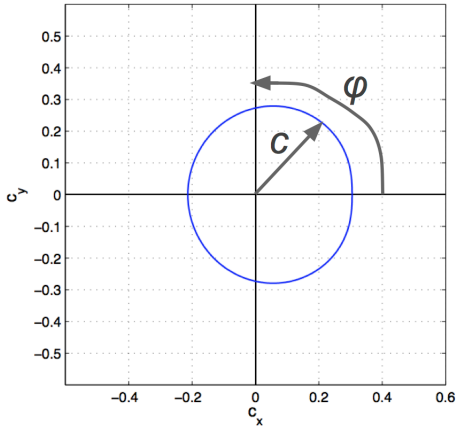


Figure 4: Parametric plot of $\vec{c}$. Over a single period in z (out of the page), the molecules will trace a closed orbit.

2 Analytic Solutions of a Basic Polynomial Model

We can analytically solve several simplified models for smectic liquid crystals. For example, a straightforward polynomial model gives the following Hamiltonian, where r is the temperature dependence, c is the tilt projection, and u and v are parameters of the system. Here, c is a scalar—the system has no angular variance.

$$H = \int dxdydz \left[\frac{1}{2}rc^2 + \frac{1}{4}uc^4 + \frac{1}{6}vc^6\right] = Vh \tag{1}$$

The parameters u and v are intrinsic to a system based on the details of the molecules themselves. By changing their values and sign, we can model liquid crystal systems of various types. Even this basic model exhibits different behaviors depending on the sign of u, so each case must be examined separately.

2.1 Behavior when $u > 0$

Our goal is to minimize the interior of the integral, and consequently the energy of the system,

$$h = \frac{1}{2}c^2 + \frac{1}{4}uc^4 + \frac{1}{6}vc^6$$

We can arbitrarily scale this such that $v = 1$ and use basic calculus to locate the extrema:

$$\frac{dh}{dc} = rc + uc^3 + c^5 = 0$$

There are five solutions:

$$c = 0 \tag{2}$$

$$c^2 = \frac{-u \pm \sqrt{u^2 - 4r}}{2} \tag{3}$$

Since c^2 must be positive, only the positive solution of Equation 3 is valid. Factoring out a u^2 from the root and rearranging, we obtain

$$c^2 = \frac{u}{2}\left(\sqrt{1 - \frac{4r}{u^2}} - 1\right) \tag{4}$$

When u is positive, r must be negative to have real solutions. If c^2 is also close to zero, meaning $4r/u^2$ is small, we can use a binomial approximation $(1+x)^\alpha \approx 1 + \alpha x$ to simplify further:

$$c^2 \approx \frac{u}{2}\left(1 - \frac{1}{2}\left(\frac{4r}{u^2}\right) - 1\right)$$

$$c = \sqrt{\frac{-r}{u}} \tag{5}$$

The two solutions for c (Equation 2 and Equation 5) describe the system's behavior as the temperature r is increased. For $r < 0$, Equation 5) will be energetically favorable. But at $r = 0$, that solution disappears, leaving only $c = 0$ as a valid solution (Figure 5).

We have just shown a phase transition mathematically. Below $r = 0$, the system must be in the smectic-C phase, since the tilt c has a positive value. For $r > 0$, the system is in the smectic-A phase, with untilted molecules. Note that this is a continuous phase transition, with no discontinuities in c.

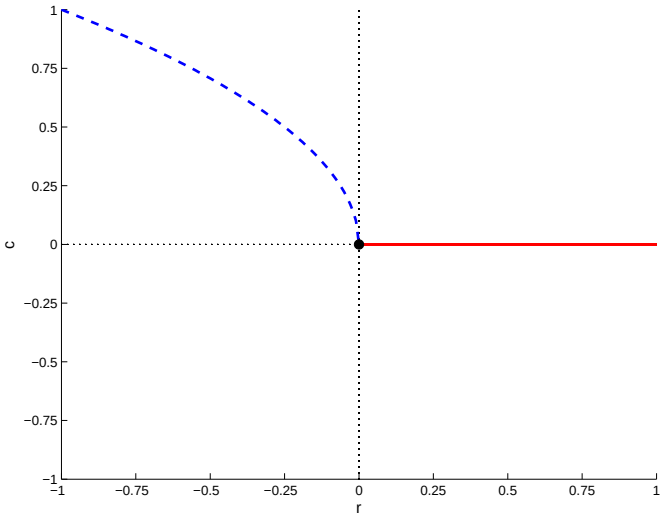


Figure 5: A bifurcation occurs at $r = 0$ where the energetically favorable Equation 5 becomes non-real. Units in all figures are arbitrary.

2.2 Behavior when $u < 0$

We proceed in a similar manner for $u < 0$. Replacing u with $|u|$ to avoid sign confusion, we can rewrite Equation 3:

$$c^2 = \frac{|u| \pm \sqrt{|u|^2 - 4r}}{2}$$

Factoring out the u^2 from the root, as done previously, we get

$$c^2 = \frac{|u|}{2}\left(1 \pm \sqrt{1 - \frac{4r}{|u|^2}}\right) \tag{6}$$

Again, c^2 must be positive. Starting with the positive solution of Equation 6,

$$c^2 = \frac{|u|}{2}\left(1 + \sqrt{1 - \frac{4r}{|u|^2}}\right) \tag{7}$$

The only requirement is that the root be positive:

$$1 - \frac{4r}{|u|^2} > 0$$

$$r < \frac{|u|^2}{4} \tag{8}$$

Next, we consider the negative solution of Equation 6,

$$c^2 = \frac{|u|}{2}\left(1 - \sqrt{1 - \frac{4r}{|u|^2}}\right) \tag{9}$$

There are two conditions. First, the inside root must be real, $r < |u|^2/4$. The total c^2 must also be positive:

$$1 - \sqrt{1 - \frac{4r}{|u|^2}} > 0$$

$$1 > 1 - \frac{4r}{|u|^2} \tag{10}$$

This can only be true if r is positive. Combining the two conditions, we see this solution is only possible when $0 \leq r \leq |u|^2/4$.

Putting these three solutions together and setting $u = 1$ for convenience, we construct Figure 6. For $r > |u|^2/4$, only the $c = 0$ solution is real. Likewise, for $r < 0$, the positive solution of Equation 6 is required. In the intermediate region, $0 < r < |u|^2/4$, two solutions are possible, but the negative branch of Equation 6 will be energetically favorable. In physical terms, this describes another smectic-C to smectic-A transition as the temperature r is increased.

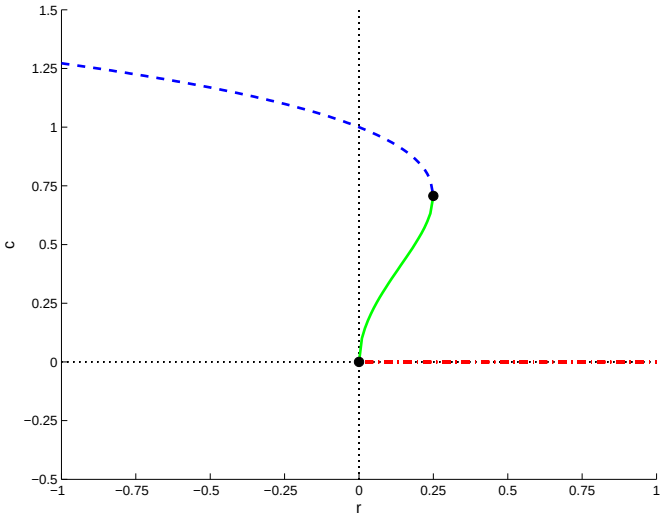


Figure 6: c undergoes two transitions, one at $r = 0$ and one at $r = .25$.

3 Analytic Solutions for the Schaub-Mukamel Model

A much more sophisticated model from Schaub and Mukamel [1] includes terms for chirality and electric field dependance. We seek to describe the behavior of a smectic-C* system as temperature and electric field are changed. The Hamiltonian is expressed as

$$H = \int dxdydz \left[\frac{1}{2}rc^2 + uc^4 + vc^6 - Ec\cos\phi + \frac{1}{2}c^2\left(\frac{\partial^2\phi}{\partial z^2} + \frac{\partial\phi}{\partial z}\right) + \frac{1}{2}\frac{\partial^2 c}{\partial z^2}\right] \tag{11}$$

where r is again the temperature dependance, u and v are system parameters, E is the field strength, and c and ϕ have a z dependance. The electric field acts such that $\vec{E}$ in the $\hat{y}$ direction will cause $\vec{c}$ to tilt in the $\hat{x}$ direction.

We approach this difficult problem with three different methods. First, removing the electric field by setting $\vec{E} = 0$ greatly simplifies the equation, allowing an analytic solution similar to that found for the previous polynomial model. When the electric field is instead very strong, we can eliminate the z dependance and again find an analytic solution. Finally, in the intermediate region, where $\vec{E}$ causes complex behavior, we use numeric methods in Matlab to compute solutions.

3.1 Zero Electric Field

Our first simplification is to consider the region where there is no electric field, $\vec{E} = 0$. In r-E space, this naturally corresponds to the vertical axis. To begin with, we treat the $dxdy$ element of Equation 11 as a constant area A and set $u = 1$. For notational simplicity, we also change all ∂z terms to primes terms, i.e. $\partial\phi/\partial z = \phi'$.

$$\frac{H}{A} = \int dz \left[\frac{1}{2}rc^2 + uc^4 + \frac{1}{2}c^2(\phi'^2 + \phi') + \frac{1}{2}c'^2\right]$$

We will again work with the interior of the integral,

$$h = \frac{1}{2}rc^2 + c^4 + \frac{1}{2}c^2(\phi'^2 + \phi') + \frac{1}{2}c'^2 \tag{12}$$

Next, we use the Euler-Lagrange equations to minimize the Hamiltonian,

$$\frac{d}{dz}\left(\frac{\partial h}{\partial c'}\right) = \frac{\partial h}{\partial c}\ ,\ \frac{d}{dz}\left(\frac{\partial h}{\partial \phi'}\right) = \frac{\partial h}{\partial \phi}$$

First in c:

$$c'' = rc + 4c^3 + c(\phi'^2 + \phi') \tag{13}$$

Now ϕ:

$$\frac{d}{dz}\left(c^2\phi' + \frac{1}{2}c^2\right) = 0$$

$$2cc'\left(\phi' + \frac{1}{2}\right) + c^2\phi'' = 0 \tag{14}$$

Looking back at Equation 12, we see that c' is isolated in a lone c'^2 term. Since this term will always be positive, and we seek to minimize Equation 12, we can assert that $c' = 0$ is the only possible minimum for this term. Putting this simplification into Equation 14, we get a simple differential equation,

$$c^2\phi'' = 0$$

Solutions to this are in the form

$$\phi(z) = Az + B \tag{15}$$

Equation 15 describes a helix: the helically wound structure of a smectic-C* system is revealed here mathematically. We can arbitrarily choose B to equal π and set A to be negative. Furthermore, we can relate A to the helical period by $A = -\frac{2\pi}{p}$, with p as a free parameter. Now we can write the solution set in a more convenient notation,

$$\phi(z) = \frac{-2\pi}{p}z + \pi$$
$$\frac{d\phi}{dz} = \phi' = \frac{-2\pi}{p} \tag{16}$$

Substituting ϕ' back into Equation 12:

$$h = \frac{1}{2}rc^2 + c^4 + \frac{1}{2}c^2\left(\frac{4\pi^2}{p^2} - \frac{2\pi}{p}\right) + \frac{1}{2}c'^2 \tag{17}$$

Here, h is a function of both c and p, but they are decoupled, so we can treat each variable independently. First minimizing h with respect to p:

$$\frac{\partial h}{\partial p} = 0$$
$$c^2\left(\frac{-4\pi^2}{p^3} + \frac{\pi}{p^2}\right) = 0$$
$$\frac{\pi}{p^2} = \frac{4\pi^2}{p^3} \tag{18}$$

The minimum is reached when $p = 4\pi$. Now we substitute this result back into Equation 17 and minimize with respect to c:

$$\frac{\partial h}{\partial c} = 0$$
$$rc + 4c^3 - \frac{1}{4}c = 0 \tag{19}$$

The three roots are $c = 0$ and $c = \pm\sqrt{\frac{1}{16} - \frac{r}{4}}$. For $r > \frac{1}{4}$, only the $c = 0$ solution exists. Once again, this represents a phase transition as r is increased, this time from the smectic-C* phase to the smectic-A phase (Figure 7).

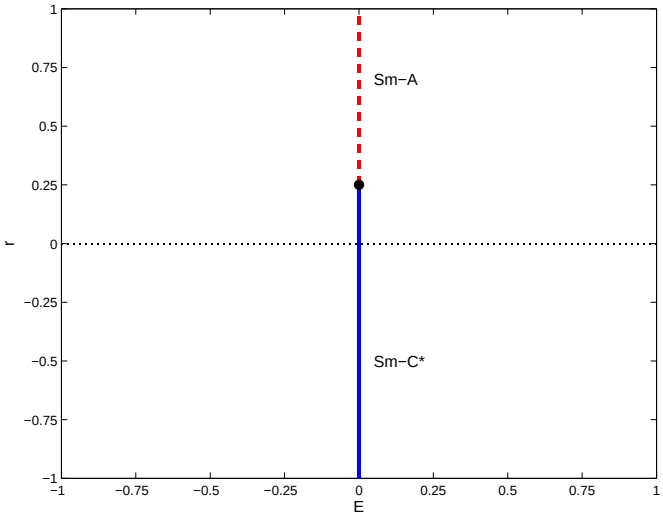


Figure 7: Transition from smectic-C* to smectic-A occurs at $r = .25$ when $\vec{E} = 0$.

3.2 Large Electric Field

If we assume $\vec{c}$ is uniform—valid when $\vec{E}$ is large—all the ∂z terms in Equation 11 will be zero. We can also replace $\int\ dxdydz$ with the volume, V.

This project focuses primarily on systems where $u > 0$. In these cases, the vc^4 term becomes irrelevant to the system and can be discarded. In turn, this allows us to again make the simplification $u = 1$. After also replacing $\vec{c}$ with c_u (to denote the uniformity of c in the strong field), we get a much more tractable Hamiltonian:

$$H = V(\frac{1}{2}rc_u^2 + uc_u^4 - Ec_u \cos\phi) \tag{20}$$

Since the $Ec_u \cos(\phi)$ term is subtracted, the energy must be minimized when $\phi = 0$. Consequently,

$$\frac{H}{V} = \frac{1}{2}rc_u^2 + c_u^4 - Ec_u \tag{21}$$

Taking the derivative of this with respect to c_u and setting it to zero results in critical points at

$$E = 4c_u^3 + rc_u \tag{22}$$

Large electric fields will force the liquid crystal molecules to align in the smectic-C state, and this equation provides the energy for such a system. It will later allow us to compare the system energy of a smectic-C state with that of a smectic-C* state.

4 Numeric Solutions for the Schaub-Mukamel Model

While analytic methods can provide insight into specific regions, a numeric boundary value problem (BVP) solver is necessary to fully map the system's behavior over all r-E space. For this, we turn to Matlab's `bvp5c` function. A collocation algorithm, `bvp5c` solves BVPs by dividing the region in question into mesh points. Each point is treated as a function composed of polynomials whose coefficients are unknown. The boundary conditions directly provide equations for the edge meshes. By solving the resulting system of equations and unknowns, in a manner similar to the generation of an interpolating curve, a solution for the BVP is formed.

To help the algorithm, we rescale Equation 11 in the following manner, with partial derivatives in subscripts: $q = \frac{1}{p}$, $\phi_\eta = \frac{d\phi}{d\eta}$, $c_\eta = \frac{dc}{d\eta}$. The Hamiltonian for the smectic-C* phase is thus rewritten as:

$$H = 2\int_0^{\frac{1}{2}} d\eta \left[\frac{1}{2}rc^2 + c^4 - Ec\cos\phi + \frac{1}{2}c^2q^2\left(\frac{d\phi}{d\eta}\right)^2 + \frac{1}{2}c^2q\frac{d\phi}{d\eta} + \frac{1}{2}q^2\left(\frac{dc}{d\eta}\right)^2\right] \tag{23}$$

The associated Euler-Lagrange equations are then

$$\phi_{\eta\eta} = \frac{1}{q^2c^2}\left(-2q^2cc_\eta\phi_\eta - qcc_\eta + Ec\sin\phi\right) \tag{24}$$

$$c_{\eta\eta} = \frac{1}{q^2}\left(rc + 4c^3 - E\cos\phi + q^2c\phi_\eta^2 + qc\phi_\eta\right) \tag{25}$$

Once again, we seek to find values for c and ϕ over a single loop of the helix it forms in z. Due to symmetry in the periodicity, it is only necessary to consider a half period, $0 \leq z \leq .5$. The numeric method is able to provide solutions of c and ϕ over this interval. However, it is important to note that the solutions generated only indicate the possible system values for the smectic-C* case. They do not indicate whether this state is actually energetically favorable. To find the region in r-E space where the transition from smectic-C* to smectic-C occurs, it is necessary to compare the respective energies for each state. We accomplish this by feeding the solution values back into the corresponding Hamiltonians, Equation 20 for smectic-C and Equation 23 for smectic-C*. Since the lower energy will be the physically realized state, an energy difference of zero identifies the phase transition's location.

A further complication arises from the wavenumber q, the length of the unwinding in z. The numeric solver does not accept q as an arbitrary parameter, so we have to repeatedly run iterations of `bvp5c` over a range of q values. Once again, we make the assumption that the molecules will arrange themselves to minimize overall energy, and that the q value yielding the minimum energy is correct.

Although it would be tempting to simply iterate over all q, r, and E space in this manner, generating solutions everywhere before any analysis, this proved impossible. `bvp5c` will fail to converge if solutions are not fairly close to initial guesses, and so care must be exercised in traversing the parameter space. We focused our efforts on specific regions along the smectic-C* to smectic-C transition manifold. By fixing an r value and plotting the difference in energy between these phases, $H_m - H_u/|H_u|$, for different E values, we can identify the exact point in q-r-E space where the phase transition occurs (Figure 8).

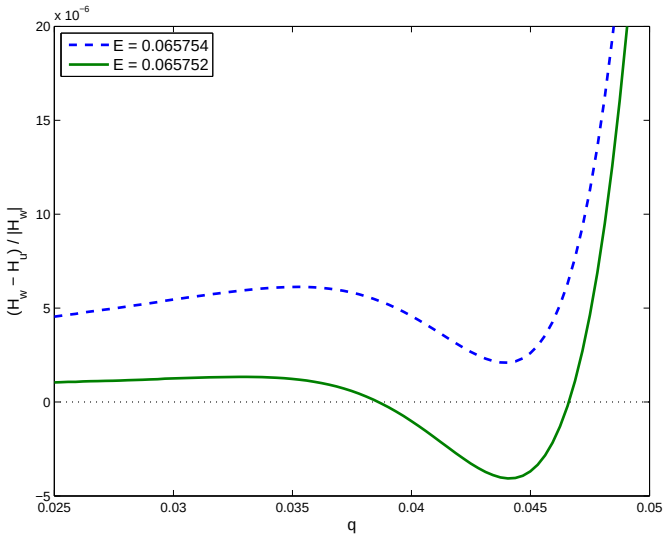


Figure 8: Two different values of E for a fixed $r = .5$. Since the minima in each curve straddle the zero difference in energy line ($H_w - H_u/|H_w| = 0$), the phase transition must occur between the two values of E, $.065754$ and $.065752$.

4.1 Multicritical Point

We expect to find a *multicritical* point M around $r = -.75$ [1]. This is a change in the *type* of phase transition between smectic-C* and smectic-C phases. For values of $r < M$, the system will unwind with the spatial period going to infinity and the wave number q going to zero. In contrast, for $r > M$, the system will still have a finite period and nonzero wave number when the phase transition occurs. Since the unwound smectic-C state is analogous to an infinite period ($q = 0$), this difference in q implies the phase transition will be first order.

Evidence for the multicritical point is shown in a comparison of Figure 9 and Figure 8. For values of r above the multicritical point, as in figure Figure 9, q is nonzero during the phase transition near $E = .065753$. Therefore, when this transition occurs, the system will undergo a sudden jump from $q \approx .44$ to $q = 0$. For values below, such as $r = -.9$ in Figure 8, there is no local minimum in q: it approaches zero as the phase transition occurs. Therefore, the phase transition in this regime is continuous.

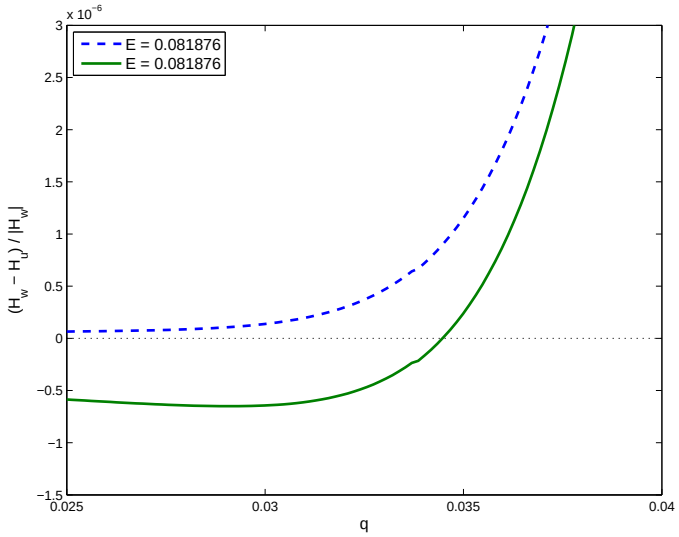


Figure 9: Below the multicritical point. At $r = -.9$, the value of q minimizing the system's energy approaches zero as increasing E unwinds the smectic-C* phase to the smectic-C phase.

4.2 Wound and Rocking Solutions

For values of $r > 0$, two different types of solutions are possible for the smectic-C* phase. The wound case found for $r < 0$ is still possible. Additionally, the system may enter a regime wherein its helical structure tilts away from the z-axis. Instead of $\vec{c}$ forming spirals around the z-axis, it will rock back and forth, offset from the axis. Accordingly, we call this the *rocking* case. Different boundary conditions in $\phi(z)$ are required for the wound and rocking solutions. The wound solution still uses conditions of $\phi(0) = \pi$ and $\phi(.5) = 0$, but the rocking solution requires $\phi(0) = 0$ and $\phi(.5) = 0$. With these changes, we can generate complete solutions for each boundary value problem separately (Figure 10, Figure 11).

Both wound and rocking solutions can be found on the boundary between the smectic-C* and smectic-C phases. Rocking solutions occur at higher values of r. The continuous transformation

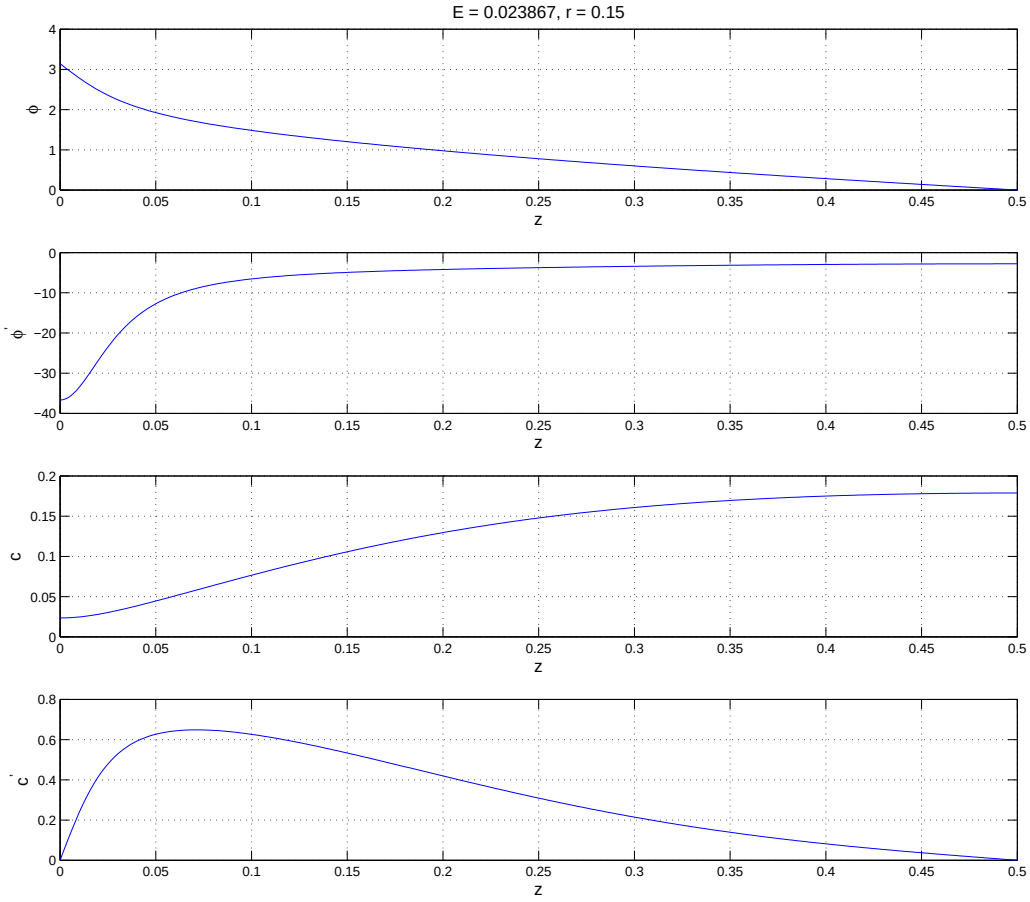


Figure 10: Complete wound solutions of $\vec{c}$ and ϕ across a half period of z. Note the boundary conditions in ϕ require it to start at π and end at 0.

of the wound solution into the rocking solution is most clearly seen on parametric plots of $\vec{c}$ (Figure 12). As r is increased, the circular region depicting the path of $\vec{c}$ simultaneously shrinks and shifts away from the origin. At $r = .165$, the system is at the edge of the two solutions, and no distinction is possible between wound and rocking. Further increases in r bring the system completely into the rocking mode. Therefore, the transition between smectic-C* and smectic-C phases for $.165 < r < .25$ will be between a rocking state and an unwound state.

Figure 12 also shows the order of the phase transition. The wound/unwound transition in Figure 12a is first order, since $\vec{c}$ has a nonzero magnitude, as discussed in subsection 4.1. Likewise, the rocking/unwound transition is also first order: the path in Figure 12d has a nonzero radius. However, since the radius of the rocking in Figure 12 shrinks with increasing r, we expect that at some r value between .17 and .25 a *tricritical* point is reached. At this point, the rocking/unwound boundary will switch from first order to continuous, just as it switches at the multicritical point. Unfortunately, our solver was unable to compute the solutions necessary to conclusively verify this

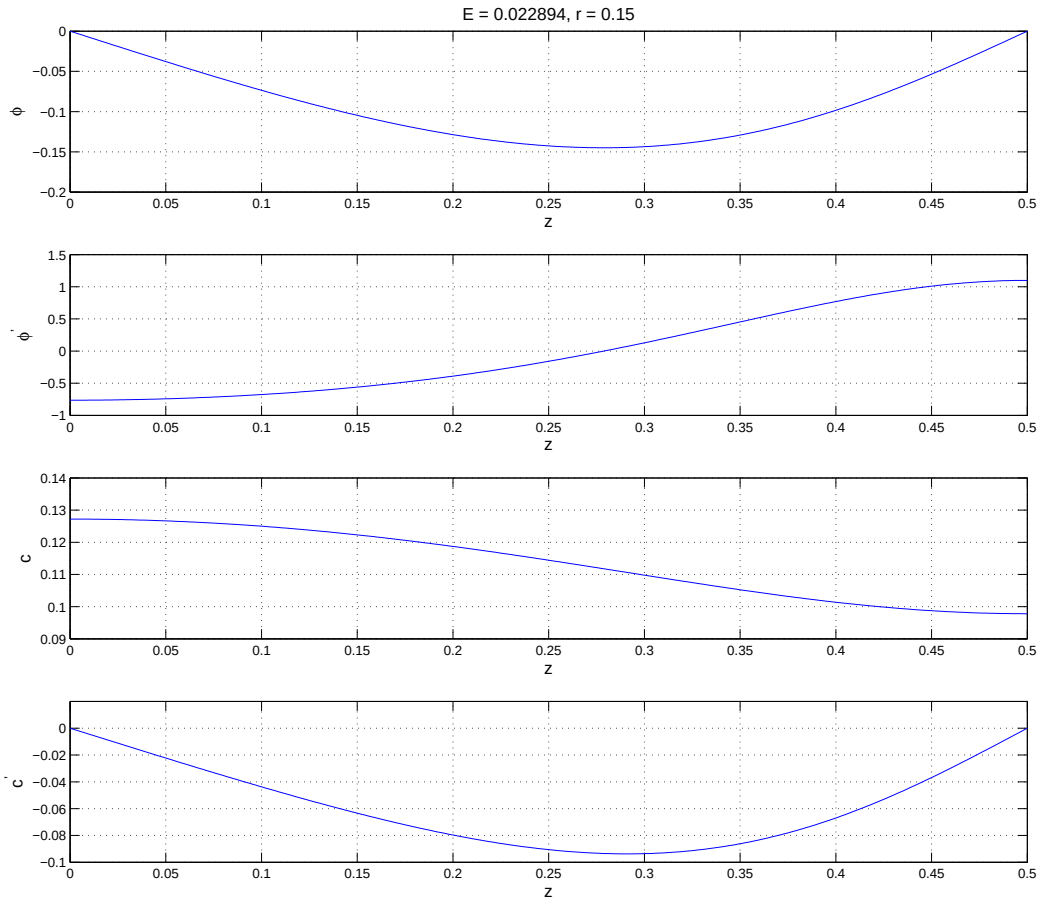
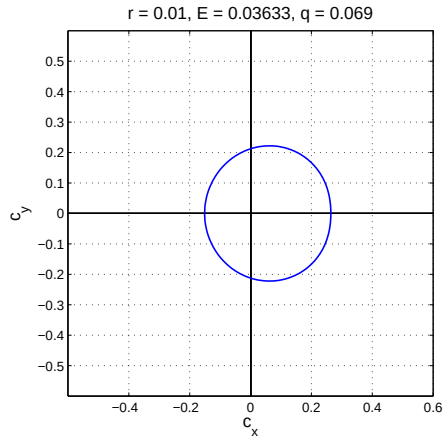
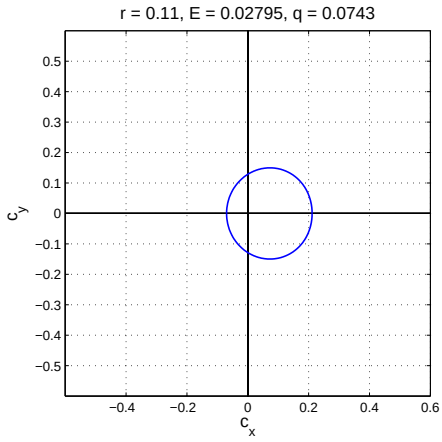


Figure 11: Complete rocking solutions of $\vec{c}$ and ϕ across a half period of z. The boundary conditions in ϕ now require it to both start and end at zero.

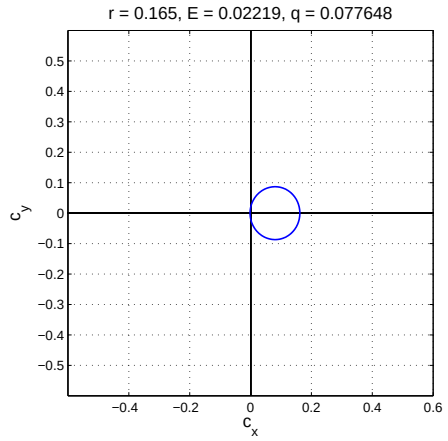
behavior.



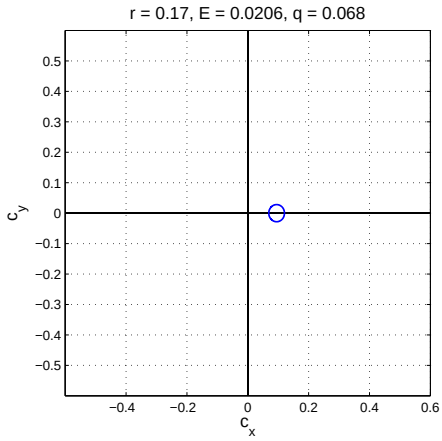
(a) $r = .01$



(b) $r = .11$



(c) $r = .165$



(d) $r = .17$

Figure 12: Parametric plots of $\vec{c}(\phi)$ with increasing r show the transition from the wound solution to the rocking solution. The helix of liquid crystal molecules tilts further and further towards the right until it eventually cross the y-axis completely. All these solutions are found on the boundary between the wound/rocking and unwound state.

5 Summary

Combining these results allows us to present a complete diagram of the system's behavior for all values of r and E. Several points of interest on the transition curve between the wound smectic-C* state and unwound smectic-C state are annotated on Figure 13. At point A, on the $\vec{E} = 0$ axis, the transition is not to smectic-C but to smectic-A, as described in subsection 3.1. The dashed transition region between point A and point R indicates the region where the system's transition is from a rocking state instead of a wound state (subsection 4.2). Point R itself indicates the junction of wound and rocking states. Continuing down the curve, point M marks the multicritical point, where the state transition changes from first order to continuous (subsection 4.1). We expect the continuous transition to remain unchanged for all r values below M so long as the liquid crystal phase itself holds.

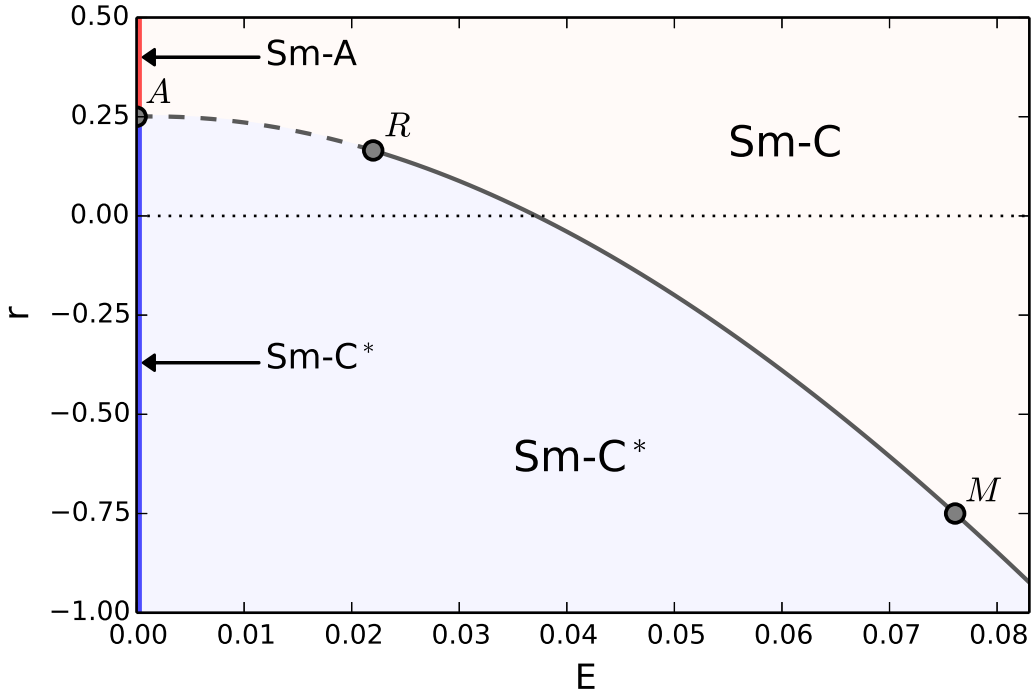


Figure 13: Phase diagram for all r-E space.

6 Addendum: Code Outline

The Matlab code is procedural and self-contained. Solutions to the boundary value problems for different parameter values are found using the built-in `bvp5c` function. As long as the initial guesses approximate the solution, the solver is able to work quickly. However, in regions far away from the wound/unwound transition, the solver will either converge on a spurious solution or fail to converge on any solution at all.

Loop for all r values in a given range:
Loop for all E values in a given range:
-Use each E value to calculate c_u, as described in subsection 3.2.
Loop for all q values in a given range:
-Set up the Matlab collocation mesh. A suitable initial guess is generated with a polynomial function, or can be loaded from a previous working solution.
-Use `bvp5c` to generate a solution for this r-E-q point.
-Use the previous solution's mesh as the starting guess for the next mesh.
As long as the changes between the q values is small, the solutions will be similar.
-Save the found solutions of c, c', ϕ, ϕ' over a half period of z.
End q loop.

The physically realizable solution will be the one with a q such that energy is minimized.
-Calculate wound state energy by substituting the found solutions into Equation 23 and integrating over the half period (0 to .5) of z.
-Calculate unwound state energy by Equation 21, also integrated over a half period of z.

Plot the following figures:
-Solutions of c, c', ϕ, ϕ' over a half period of z.
-The difference between wound and unwound energy, H_w and H_u.
-c plotted parametrically in ϕ as it goes through a half period of z.
End E and r loops.

Functions:
`dydz`: Equation 24 and Equation 25
`res_neg`: Boundary conditions, $r < 0$
`res_pos`: Boundary conditions, $r > 0$
`zinit_neg`: Initial guess function (used if no other initial solutions available), $r < 0$
`zinit_pos`: Initial guess function (used if no other initial solutions available), $r > 0$

References

[1] Schaub, B., Mukamel, D. 1983, Physical Review B., 32. Phase diagrams of systems exhibiting incommensurate structures.