Transitions through critical temperatures in nematic liquid crystals

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We obtain estimates for critical nematic liquid crystal (LC) temperatures under the action of a slowly varying temperature-dependent control variable. We show that biaxiality has a negligible effect within our model and that these delay estimates are well described by a purely uniaxial model. The static theory predicts two critical temperatures: the supercooling temperature below which the isotropic phase loses stability and the superheating temperature above which the ordered nematic states do not exist. In contrast to the static problem, the isotropic phase exhibits a memory effect below the supercooling temperature in the dynamic framework. This delayed loss of stability is independent of the rate of change of temperature and depends purely on the initial value of the temperature. We also show how our results can be used to improve estimates for LC material constants.

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I. INTRODUCTION

Nematic liquid crystals (LCs) are complex anisotropic liquids with a degree of long-range orientational ordering [1,2]. Of key importance is the concept of a "scalar order parameter" that can distinguish between a disordered isotropic phase and an ordered nematic phase [3,4]. Order parameters are of prime importance in various branches of condensed matter physics, e.g., superconductivity [5] and active systems [6], and are used to describe transitions between different admissible equilibria. We focus on thermotropic LCs wherein the degree of orientational ordering is dictated by the temperature [1]. The isotropic-nematic phase transition has been extensively studied for thermotropic LCs [2,3,7], without paying attention to the effects of spatial and temporal variations in the temperature profile. In this paper, we study the nonequilibrium dynamics of the scalar order parameter when the temperature is not a constant but rather a time-dependent control variable.

We work within the Landau-de Gennes (LdG) theory for thermotropic nematic phases [2,3,7]. A thermotropic phase is classified as being *biaxial* or *uniaxial* according to the symmetry of the nematic phase and the degree of orientational ordering. A *biaxial* phase typically has a primary direction and a secondary direction of preferred molecular alignment, say **n** and **m**, and we need at least two scalar order parameters to quantify the degree of ordering about both directions. A uniaxial sample has greater symmetry and is characterized by two macroscopic variables: (i) the director, **n**, which represents the unique preferred direction of molecular alignment, and (ii) an order parameter, S, which is a measure of how well the molecules align with **n**. In particular, the isotropic phase has an identically vanishing order parameter whereas nonzero order parameters correspond to an ordered nematic phase.

The LdG theory is a variational theory and equilibrium states correspond to minimizers of an appropriately defined LdG energy functional [1,2,8]. The isotropic-nematic phase transition is driven by the LdG thermotropic energy that contains a temperature-dependent parameter, denoted by A throughout this paper; more details are given in Sec. II. The equilibrium order parameters at a given temperature, or equivalently for a given value of A, are given by the thermotropic energy minimizers [8]. We work with a simple quartic form of the thermotropic energy such that all thermotropic energy minimizers are necessarily either uniaxial or isotropic, for all temperatures. These thermotropic energy minimizers are fully characterized by the uniaxial scalar order parameter, S, and roughly speaking, the minimizer is an ordered nematic phase, with $S > 0$, for "low" temperatures, and is isotropic, with $S = 0$, for "high" temperatures [1,8].

There are two *static critical values* of A, associated with a bifurcation in the (A,S)-phase plane, or an exchange of stability between ordered nematic and isotropic states, in the LdG framework. The first critical temperature is the *supercooling temperature* below which the isotropic phase loses stability. The second critical temperature is the *superheating temperature* above which the nematic phases do not exist and the isotropic phase is the unique thermotropic energy minimizer. The supercooling and superheating temperatures are associated with a transcritical and a saddle-node bifurcation in the (A,S)-response diagram, respectively (see, e.g., [9] for definitions of bifurcation points). The static critical temperatures are computed by treating the temperature-dependent variable, A, to be a constant. However, in many practical applications, A is a function of a time and we study the evolution of the scalar order parameter, S, as A slowly passes through the static critical values. In what follows, *static* refers to a *constant value of A* and *dynamic* refers to a time-dependent A variable.

We assume a simple gradient-flow model for the evolution of the order parameters [3,7] and mathematically describe how the (A,S)-response diagram in Fig. 1 is modified by the slow time modulations of A. In particular, we show that biaxiality is negligible for physically realistic initial conditions and that a purely uniaxial model suffices for the dynamic estimates, at least within our relatively simple framework. Our most striking result concerns the critical supercooling value.

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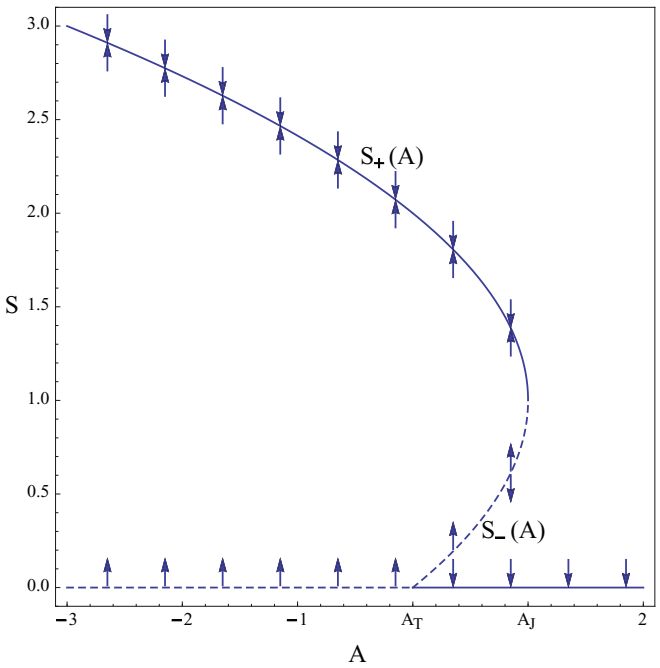

FIG. 1. (Color online) The static equilibria plotted in the $(\tilde{A},\tilde{S})$ plane. Unstable branches are marked with dashed curves and the arrows indicate the sign of $d\tilde{S}/d\tau$. The tildes have been removed from the dimensionless variables for brevity.

There is a marked difference between a monotonic increase and a monotonic decrease through this critical value which implies that experimental measurements can be sensitive to the direction of temperature change. More precisely, the static theory predicts that the isotropic state is unstable for all temperatures below the critical supercooling temperature but the dynamic approach shows that the unstable isotropic branch exhibits a memory effect in the low-temperature regime, far below the predicted static supercooling value, and this delayed loss of stability is also observed in boundary-value LC problems for confined systems. This is indeed our central result: critical LC temperatures can be strongly dependent on spatial and temporal variations in the temperature profile. We also show how our dynamic delay estimates can be used to measure material-dependent LC constants and this could potentially lead to new experimental investigations.

The study of bifurcations with a time-dependent bifurcation parameter has a long history; the reader is referred to [9–14]. In general, the phenomenon of dynamic stability exchange depends on multiple factors such as the nature of the bifurcation point, the initial value of the control variable, the presence of imperfections, etc. Of particular importance is the rate at which the control variable crosses its critical value, which we assume to be slow compared to the response time of the sample.

In Sec. II, we review the LdG theory for thermotropic nematics and present the governing equations. In Sec. III, we study the dynamic exchange of stability between distinct static equilibria when the control variable, A, slowly crosses the static critical values. Our study is presented in stages. In Sec. III A, we examine the effect of biaxiality and show that it suffices (for our purposes in this paper) to consider a purely uniaxial model. In Sec. III B, we present analytic solutions for an isothermal model with constant A, and in Secs. III C and III D, we state our main dynamic estimates and present numerical results. The technical details are deferred to the appendices to avoid distraction from the main text. In Sec. III E, we suggest applications for the measurements of material-dependent LC constants, and in Sec. IV, we discuss delay estimates for confined LC systems and outline directions for future work.

II. THE MODEL

The LdG theory describes the state of a nematic LC by a physical state variable: the LdG $\mathbf{Q}$ tensor defined in terms of anisotropic macroscopic quantities [1,7,8]. The LdG $\mathbf{Q}$ tensor is a macroscopic measure of orientational anisotropy in the nematic sample and can be written as

$$\mathbf{Q} = S\cos\alpha\left(\mathbf{n}\otimes\mathbf{n} - \frac{\mathbf{I}}{3}\right) + \frac{S\sin\alpha}{\sqrt{3}}(\mathbf{m}\otimes\mathbf{m} - \mathbf{p}\otimes\mathbf{p}), \quad (1)$$

where $S = \sqrt{\frac{3}{2}\mathbf{Q}_{ij}\mathbf{Q}_{ij}} \geqslant 0, \alpha \in [0,2\pi)$ is a measure of the degree of biaxiality and $\mathbf{n},\mathbf{m},\mathbf{p} \in S^2$ constitutes an orthonormal triad of eigenvectors. The eigenvectors represent the preferred directions of molecular alignment and the pair (S,α) contains quantitative information about the degree of orientational ordering. In (1), S is proportional to the norm or magnitude of $\mathbf{Q}$ and the eigenvalues of $\mathbf{Q}$ can be expressed in terms of the pair (S,α). For the biaxial case, $\mathbf{Q}$ has three distinct eigenvalues, and for the uniaxial case, $\mathbf{Q}$ has a pair of degenerate nonzero eigenvalues. In the uniaxial case, the $\mathbf{Q}$ tensor reduces to

$$\mathbf{Q} = S\left(\mathbf{n}\otimes\mathbf{n} - \frac{\mathbf{I}}{3}\right), \quad (2)$$

where S is the uniaxial order parameter and $\mathbf{n}$ has been defined above.

We work with a simple form of the LdG energy functional on a three-dimensional (3D) domain, $\Omega \subset \mathbb{R}^3$, given by

$$I[\mathbf{Q}] := \int_\Omega \frac{L}{2}|\nabla\mathbf{Q}|^2 + f_B(\mathbf{Q})dV, \quad (3)$$

where $L > 0$ is an elastic constant, $|\nabla\mathbf{Q}|^2 = \sum_{i,j,k=1}^3 \frac{\partial\mathbf{Q}_{ij}}{\partial\mathbf{x}_k}\frac{\partial\mathbf{Q}_{ij}}{\partial\mathbf{x}_k}$, and $f_B(\mathbf{Q})$ is the thermotropic energy density [3,8]. We work with the simplest, physically reasonable form of f_B proposed in [1,7], namely,

$$f_B(\mathbf{Q}) := \frac{A(T)}{2}\mathrm{tr}\,\mathbf{Q}^2 - \frac{B}{3}\mathrm{tr}\,\mathbf{Q}^3 + \frac{C}{4}(\mathrm{tr}\,\mathbf{Q}^2)^2. \quad (4)$$

In fact, (4) is the minimal polynomial that can reproduce a first-order isotropic-nematic phase transition [1]. In (4), $A(T)$ is a linear function of the absolute temperature, T, given by $A(T) = \beta(T - T^*)$; $\beta,B,C > 0$ are positive material-dependent constants and T^* is a characteristic temperature below which the isotropic phase loses stability. In what follows, we refer to A as temperature even though it is the rescaled temperature.

One can explicitly show that all stationary points of the quartic f_B in (4) are either *uniaxial or isotropic* [1,2,7,8]. In particular, there are no biaxial stationary points and one can, thus, intuitively argue that biaxiality may not be significant for the dynamics of $\mathbf{Q}$, for this choice of f_B in (4). We demonstrate

the negligible role of biaxiality in the **Q**-tensor dynamics in the next section. We note that there are higher-order polynomial forms of f_B, e.g., sixth-order polynomials, that do admit biaxial equilibria [1,2], but (4) is a popular choice in the LC literature and suffices for our purposes in this paper.

For $A < 0$, the stable thermotropic equilibria are uniaxial nematic states given by

$$\mathbf{Q} = \left\{ S_+(A)\left(\mathbf{n}\otimes\mathbf{n} - \frac{\mathbf{I}}{3}\right); S_+(A) = \frac{B + \sqrt{B^2 - 24AC}}{4C} \right\}, \tag{5}$$

where $\mathbf{n} \in S^2$ is an arbitrary constant unit vector. For $0 < A < \frac{B^2}{24C}$, $f_B(\mathbf{Q})$ has two distinct families of stable equilibria: (i) the isotropic phase with $\mathbf{Q} = 0$ and (ii) the uniaxial nematic branch in (5). For $A > \frac{B^2}{24C}$, the ordered nematic states do not exist and the isotropic branch is the unique thermotropic energy minimizer. We point out that there is a third uniaxial stationary branch given by

$$\mathbf{Q}= \left\{ S_-(A)\left(\mathbf{n}\otimes\mathbf{n} - \frac{\mathbf{I}}{3}\right); S_-(A) = \frac{B - \sqrt{B^2 - 24AC}}{4C} \right\},$$

but this branch is always unstable with respect to biaxial perturbations and, hence, is not a competing stable equilibrium [1,7,8]. We do not refer to this unstable uniaxial stationary branch in this paper.

As stated in the Introduction, there are two static critical values in the theory of thermotropic nematics. The supercooling temperature is simply $A = 0$ and is associated with a transcritical bifurcation in the (A,S)-response diagram, i.e., the isotropic branch $S = 0$ is stable for $A > 0$ and unstable for $A < 0$. The superheating temperature is denoted by $A_J = \frac{B^2}{24C}$; $A = A_J$ is associated with a saddle-node bifurcation such that the nematic equilibrium, $S_+(A)$, ceases to exist for $A > A_J$ and the isotropic state is the unique equilibrium for $A > A_J$.

As in [3,7], we assume a simple gradient-flow model to describe the evolution of the **Q**-tensor order parameter. Gradient-flow models are effectively reaction-diffusion equations describing the evolution of a macroscopic quantity (**Q** tensor in this case) along a path of decreasing free energy [15]. Our main dynamic equation is given below:

$$\mu\frac{\partial \mathbf{Q}_{ij}}{\partial t} = L\nabla^2\mathbf{Q}_{ij} - A\mathbf{Q}_{ij} + B\left(\mathbf{Q}_{ip}\mathbf{Q}_{pj} - (\mathrm{tr}\,\mathbf{Q}^2)\frac{\delta_{ij}}{3}\right) - C(\mathrm{tr}\,\mathbf{Q}^2)\mathbf{Q}_{ij}, \tag{6}$$

where $\mu > 0$ is a rate constant, $i,j,p = 1\ldots3$, and the remaining coefficients have been defined in (3). In most of what follows, we assume that **Q** does not depend on the spatial variables; the eigenvectors in (1) are constant unit-vectors; and the pair, (S,α), only depends on time. We refer to such systems as being *spatially homogeneous* systems and our assumptions are justified for samples with untreated boundaries, wherein we are interested in the temporal response of (S,α) to temperature variations. We further assume that A varies linearly with time. In the spatially homogeneous case, the model (6) reduces to two ordinary differential equations (ODEs) for (S,α) with a slowly varying time-dependent bifurcation parameter, $A(t)$, as given below in (7)–(9):

$$\mu\frac{dS}{dt} = -\frac{S}{3}[2CS^2 - BS\cos 3\alpha + 3A(t)], \tag{7}$$

$$\mu\frac{d\alpha}{dt} = -\frac{BS}{3}\sin 3\alpha, \tag{8}$$

$$\frac{dA}{dt} = \pm q, \tag{9}$$

where $q > 0$ is a positive constant and the initial conditions are $S(0) = S_0$, $\alpha(0) = \alpha_0$, and $A(0) = A_0$.

III. SLOW PASSAGE THROUGH CRITICAL VALUES

A. Effect of biaxiality

We make some basic assumptions throughout the paper, namely, (i) the initial temperature $A_0 \neq 0$ and $A_0 \neq A_J$, i.e., A_0 is bounded away from the static critical values, and (ii) we only consider initial conditions that are almost in *thermal equilibrium* at $A = A_0$. In other words, the initial condition (S_0,α_0) is "close" to a locally stable equilibrium of the thermotropic energy at $A = A_0$. In particular, if $A_0 < 0$, then the initial condition must be close to the nematic branch (5), and if $0 < A_0 < A_J$, then the initial condition can be either close to $S_+(A_0)$ in (5) or close to the isotropic branch.

It is straightforward to check that solutions of the dynamical system (7)–(9) cannot cross the lines $\alpha = 0, \frac{\pi}{3}, \frac{2\pi}{3}$ and we can, without loss of generality, assume that $\alpha \in (0, \frac{\pi}{3})$. This corresponds to assuming that **n** is the principal axis with the largest positive eigenvalue. Recalling that $S \geqslant 0$ from (1), it is then immediate from (8) that α decreases monotonically with time. For a physically realistic initial condition as described above, α_0 is small and, therefore, $\alpha(t) \leqslant \alpha_0$ for all times. This justifies a detailed study of the purely uniaxial case with $\alpha = 0$, as is presented in the subsequent sections.

We introduce the following rescalings:

$$S = \frac{B}{4C}\tilde{S}, \quad A = \frac{B^2}{24C}\tilde{A}, \quad t = \frac{B^2}{24Cq}\tau,$$

so that (7) and (9) become

$$\epsilon\frac{d\tilde{S}}{d\tau} = -\tilde{S}[\tilde{S}^2 - 2\tilde{S} + \tilde{A}(\tau)], \tag{10}$$

$$\frac{d\tilde{A}}{d\tau} = \pm 1, \tag{11}$$

where $\tilde{S}(0) = \tilde{S}_0$, $\tilde{A}(0) = \tilde{A}_0$, and

$$\epsilon = \frac{576C^2}{B^4}\mu q = \left(\frac{\mu}{A_J}\right)\left(\frac{q}{A_J}\right) \ll 1 \tag{12}$$

is a dimensionless parameter which measures the ratio of the viscous relaxation time, μ/A_J, which from the data in [16] is of $O(10^{-7}$ s), to the time scale, A_J/q, over which the temperature is changed. We require ϵ to be small in this paper. The static critical values are $\tilde{A} = 0$ (the supercooling value) and $\tilde{A} = +1$ (the superheating value), and the nematic equilibrium is given by $\tilde{S}_+ = 1 + \sqrt{1 - \tilde{A}}$, for $\tilde{A} \leqslant 1$.

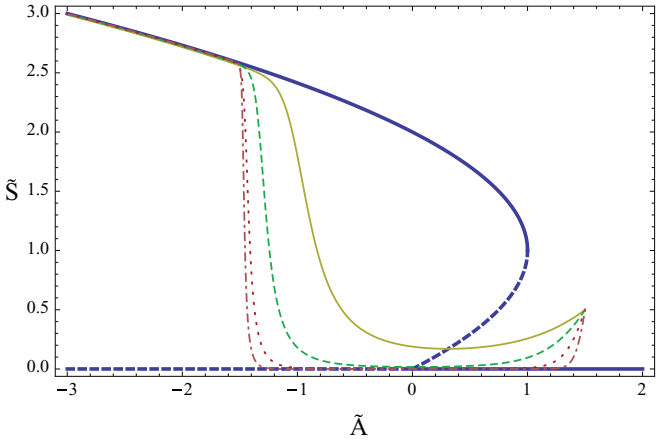

FIG. 2. (Color online) Numerical solutions of the differential Equation (10) plotted in the $(\tilde{A},\tilde{S})$ plane with $\tilde{A}(\tau) = 1.5 - \tau$, $\tilde{S}(0) = 0.5$, and $\epsilon = 0.5$ (yellow, solid), 0.25 (green, dashed), 0.125 (red, dotted), and 0.0625 (pink, dot-dashed). The equilibrium solution is plotted as a thick blue curve.

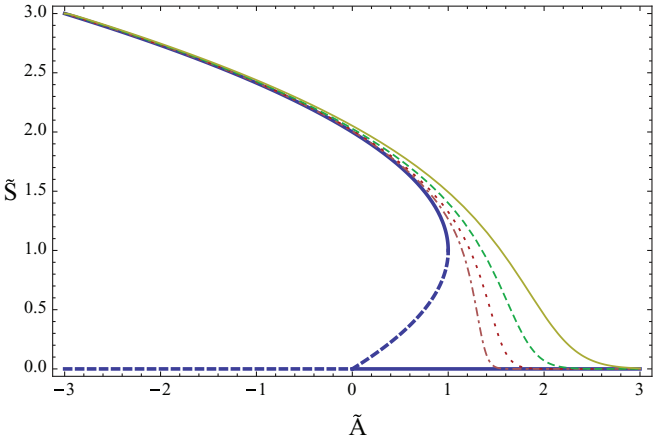

FIG. 3. (Color online) Numerical solutions of the differential Equation (10) plotted in the $(\tilde{A},\tilde{S})$ plane with $\tilde{A}(\tau) = -3 + \tau$, $\tilde{S}(0) = 3$, and $\epsilon = 0.5$ (yellow, solid), 0.25 (green, dashed), 0.125 (red, dotted), and 0.0625 (pink, dot-dashed). The equilibrium solution is plotted as a thick blue curve.

B. The isothermal model

The isothermal model corresponds to a constant $A = A_0$, in which case the ODE (10) has a unique monotonic solution $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$, provided that $\tilde{S}_0 \neq 0$ and $\tilde{S}_0 \neq \tilde{S}_+(\tilde{A}_0)$, where $\tilde{S}_+$ has been defined above. One can check that for $\tilde{A}_0 < 1$, $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$ is given by

$$\exp\left[-\frac{\tau}{\epsilon}\right] = \left(\frac{\tilde{S}}{\tilde{S}_0}\right)^{1/\tilde{A}_0} \left(\frac{\tilde{S}-\tilde{S}_+(\tilde{A}_0)}{\tilde{S}_0-\tilde{S}_+(\tilde{A}_0)}\right)^{\frac{1}{2\tilde{S}_+\sqrt{1-\tilde{A}_0}}} \times \left(\frac{\tilde{S}_0-\tilde{S}_-(\tilde{A}_0)}{\tilde{S}-\tilde{S}_-(\tilde{A}_0)}\right)^{\frac{1}{2\tilde{S}_-\sqrt{1-\tilde{A}_0}}}. \quad (13)$$

We cannot write down explicit analytic solutions for the fully time-dependent problem (10)–(12). Hence, in the next sections, we use asymptotic methods and differential inequalities to describe the evolution of $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$ as $\tilde{A}$ slowly crosses the critical values, $\tilde{A} = 0$ and $\tilde{A} = 1$. We state our main results below and defer the technical details to the appendices.

C. Backward transition through $\tilde{A} = 0$

Let the temperature decrease slowly through the critical value $\tilde{A} = 0$, i.e., $\tilde{A} = \tilde{A}_0 - \tau$ for some $\tilde{A}_0 > 0$. Let $\tilde{S}_0$ be within the basin of attraction of the isotropic branch at $\tilde{A} = \tilde{A}_0$. Our main result is that the solution descends towards the isotropic branch over a temperature range of width $O(\epsilon)$ and remains within an exponentially small neighborhood of $\tilde{S} = 0$ for $\tilde{A} \in (-\tilde{A}_0,\tilde{A}_0)$, followed by a rapid ascent towards the nematic branch, $\tilde{S}_+(\tilde{A})$ for $\tilde{A} < -\tilde{A}_0$. Therefore, the isotropic phase does not lose stability immediately after crossing $\tilde{A} = 0$ as suggested by the static theory. The isotropic phase persists over the interval $\tilde{A} \in (-\tilde{A}_0,0)$ and the delay in stability exchange is independent of ϵ and proportional to the initial temperature. In particular, we do not recover the predictions of the static theory in the $\epsilon \to 0$ limit.

In Fig. 2, we numerically solve (10) with $\tilde{S}_0 = 0.5$ and $\tilde{A}_0 = 1.5$, with different values of ϵ. The delayed loss of stability of the isotropic phase is evident in the plots, as stated above, and the mathematical proofs are given in Appendix A.

D. Forward transition through $\tilde{A} = 1$

We want to capture the solution dynamics as $\tilde{A}$ slowly increases through the critical value $\tilde{A} = 1$. Let $\tilde{A} = \tilde{A}_0 + \tau$ for some $\tilde{A}_0 < 1$. Then all physically realistic initial conditions must be within the basin of attraction of the nematic branch, $\tilde{S}_+(\tilde{A})$. It can be rigorously demonstrated that the solution will closely follow $\tilde{S}_+(\tilde{A})$ until we approach the critical value $\tilde{A} = 1$ [9,10,17], followed by a descent towards the isotropic branch for $\tilde{A} > 1$. Our main result here is that the transition from the ordered nematic branch, $\tilde{S}_+(\tilde{A})$, to $\tilde{S} = 0$ takes place within a layer of width $O(\epsilon^{2/3})$ around $\tilde{A} = 1$; i.e., the dynamic transition overshoots the static value $\tilde{A} = 1$ but this overshoot smoothly vanishes as $\epsilon \to 0$, so that we recover the static solutions in the $\epsilon \to 0$ limit. In Appendix B, we derive this delay estimate using asymptotic methods.

In Fig. 3, we plot numerical solutions of (10) with $\tilde{A}_0 = -3$, $\tilde{S}_0 = 3$, and different values of ϵ. It is clear that the solution rapidly approaches the isotropic branch for $\tilde{A} > 1$ and the width of the transition layer shrinks as $\epsilon \to 0$. We analyze the scaling of the transition layer width versus ϵ by numerically computing the value of τ for which $\tilde{S}(\tau) = \epsilon$. We then measure the width of the transition layer by the following quantity:

$$\delta\tilde{A} = \tilde{A}_0 + \tilde{S}^{-1}(\epsilon) - 1. \quad (14)$$

In Fig. 4, we plot δA versus ϵ using the same parameter values as in Fig. 3. We find that δA is well approximated by the following relation:

$$\delta\tilde{A} \sim C_1\epsilon^{2/3} + \frac{4}{3}\epsilon\log\left(\frac{1}{\epsilon}\right) - (1+C_2)\epsilon, \quad (15)$$

where $C_1 \approx 2.338$ and $C_2 \approx 0.509$, in agreement with the asymptotic estimates in Appendix B.

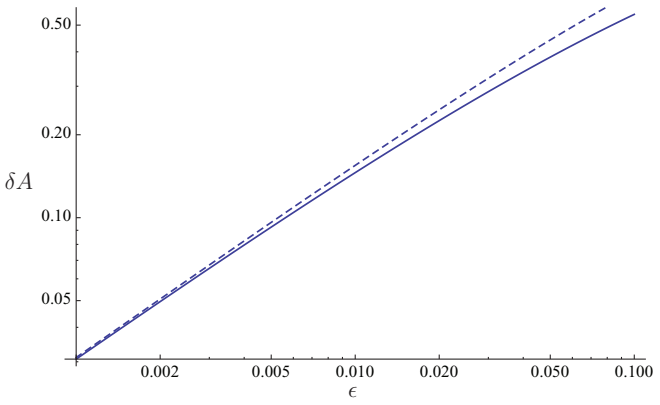

FIG. 4. (Color online) The interval δA over which $S(\tau)$ transitions to an ϵ neighborhood of $S = 0$. The dashed curve shows the asymptotic prediction (15).

E. Measurements of LC constants

We present some preliminary ideas on how these delay estimates can be used to measure characteristic temperatures and material-dependent LC constants in experiments. Our methods assume some *a priori* knowledge of the critical temperature T^* and the magnitudes of B and C in (4). In particular, we require the variable ϵ defined in (12) to be small in magnitude, which in turn requires the rate of change of temperature, q, to be much smaller than the material-dependent constant, $\frac{B^4}{C^2\mu}$, in (12). Our methods can then be used to refine previous estimates or they can provide a check on parallel experimental work.

In Proposition IV, we show that the isotropic phase persists over the range $\tilde{A} \in [-\tilde{A}_0, \tilde{A}_0]$ for $\tilde{A}_0 > 0$, when $\tilde{A}$ is monotonically decreased through $\tilde{A} = 0$; see Fig. 2. Let T_I be the initial temperature (with $\tilde{A} = \tilde{A}_0$) and we assume that we can accurately measure T_D (with $\tilde{A} = -\tilde{A}_0$). Recalling that

$$\tilde{A}(T) = 24\beta(T - T^*)C/B^2,$$

where B, C, and β have been defined in (4), we obtain

$$T_I + T_D = 2T^*. \tag{16}$$

Equation (16) requires some *a priori* knowledge of T^*, so that we do not initiate the experiment "too close" to T^* in the first place. However, this knowledge need not be accurate and rough estimates of T^* can be refined using (16), since T_I and T_D are both experimentally controlled quantities.

Similarly, in Sec. III D, we show that the transition from the ordered nematic branch to the isotropic branch overshoots the critical value $\tilde{A} = 1$ by the amount $\delta\tilde{A} = 2.338\epsilon^{2/3}$, where ϵ is directly proportional to the rate of temperature change; also see Fig. 3. We assume that we can measure the temperature T_D corresponding to $\tilde{A}^* = 1 + \delta\tilde{A}$. Recalling the definition of $\tilde{A}$ above, we obtain

$$T_D - T^* \sim \frac{B^2}{24\beta C}(1 + 2.338\epsilon^{2/3}). \tag{17}$$

Thus, having computed T^* from (16), it is possible to compute the characteristic constant, $\frac{B^2}{24\beta C}$, from measurements of T_D versus ϵ.

IV. CONCLUSION AND DISCUSSION

This paper focuses on delay estimates for the exchange of stability across bifurcation points in thermotropic nematics, with a slowly varying control variable. We have adopted a simple gradient-flow model to describe the evolution of the nematic scalar order parameters in space and time, and in the simple case of a spatially homogeneous system, our model falls within the well-studied framework of first-order algebraic bifurcation problems [9,10]. With reference to Fig. 1, we are primarily interested in two critical values: (i) the supercooling value, $A = 0$, and (ii) the superheating value, $A_J = \frac{B^2}{24C}$. The superheating value corresponds to a saddle-node bifurcation and $A(\epsilon t)$ regularizes the exchange of stability between the ordered nematic equilibria and the isotropic branch over a region of width, $O(\epsilon^{2/3})$, centered around $A = A_J$. In this case, we do not expect any marked changes in macroscopic measurements of A_J.

Our most striking observation concerns the supercooling value, $A = 0$. As the temperature is slowly decreased through $A = 0$, the exchange of stability between $S = 0$ and the nematic branch, $S_+(A)$, takes place within a region of width, $O(2A_0)$, around $A = 0$, where A_0 is the initial temperature. In particular, we do not recover the static value in the $\epsilon \to 0$ limit.

The results in Sec. III are restricted to spatially homogeneous systems. Some of our results can be easily generalized to confined LC systems where the order parameters vary on spatial and temporal scales. As an illustrative example, consider the partial differential Equation (6) for the uniaxial order parameter, S, on a one-dimensional interval, $0 \leqslant x \leqslant D$, as shown below

$$\mu\frac{\partial S}{\partial t} = \frac{2L}{3}\frac{\partial^2 S}{\partial x^2} - \frac{2S}{9}[2CS^2 - BS + 3A(x,t)], \quad 0 \leqslant x \leqslant D, t \geqslant 0. \tag{18}$$

For simplicity, we impose homogeneous boundary conditions, $S(0,t) = S(D,t) = 0$, and the initial condition can be any arbitrary function "sufficiently close" to the isotropic equilibrium. The temperature profile, $A(x,t)$, depends on both the spatial coordinate and the time coordinate. One can rigorously prove that if

$$\min_{x\in[0,D];t\geqslant 0} A(x,t) > A_T = -\pi^2\frac{2L}{3D^2}, \tag{19}$$

then the isotropic branch is stable in the sense that initial conditions within a small neighborhood of the isotropic equilibrium generate dynamic solutions of (18) that remain within a small neighborhood of the isotropic equilibrium for all times [18,19]. In particular A_T is strictly less than the static critical value $A = 0$, implying that the isotropic phase does not lose stability immediately for $A < 0$ but persists at least over the range $A \in (A_T, 0)$. This delayed loss of stability, compared to the supercooling value $A = 0$, is purely a consequence of the boundary effects. The technical details of this stability result are given in Appendix C.

The preceding discussion shows that measurements of the supercooling temperature can be sensitive to spatial and temporal variations in the temperature profile. In Sec. III E, we indicate how these delay estimates can be potentially used to

measure material-dependent constants. The "inhomogeneous" estimate (19) may yet be another crude method of computing the elastic constant in prototype LC experiments. Of course, the evolution of the LC phase with temperature depends on a combination of factors, not all of which are included in our simplistic model. For example, we assume a constant director field **n** in (2) and, in practice, **n**, surface anchoring, and elastic anisotropy effects couple to the LC scalar order parameter. Also, preliminary investigations suggest that noise can play a crucial role in stability exchange phenomena and there is a delicate balance between the relative magnitudes of noise and ϵ in our model. Nevertheless, although our model represents an idealized situation, it draws attention to a hitherto neglected effect, namely, the sensitivity of critical LC temperatures to the temperature distribution itself.

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APPENDIX A: BACKWARD TRANSITION THROUGH $\tilde{A} = 0$

Proposition 1. Let $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$ denote a solution of the initial-value problem (10), with $\tilde{A}(\tau) = \tilde{A}_0 - \tau$ for some $0 < \tilde{A}_0 < 1$ and $0 < \tilde{S}_0 = \delta \ll 1$. For $\epsilon > 0$ sufficiently small and for $\tilde{A}_0 > 0$ independent of ϵ, we have

$$0 < \tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0) \leqslant \delta \tag{A1}$$

for $\tilde{A} \in [-\tilde{A}_0 + 2\delta, \tilde{A}_0]$.

Proof. From qualitative solution properties (see Fig. 1), the solution $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$ descends towards the isotropic branch for $\tilde{A} \in (0,\tilde{A}_0]$, followed by a monotonic increase for $\tilde{A} < 0$.

One can verify that, for $\tilde{S} \in (0,\delta)$, we have the following inequalities:

$$(-\tilde{A} - 2\delta)\tilde{S} \leqslant \epsilon\frac{d\tilde{S}}{d\tau} \leqslant (-\tilde{A} + 2\delta)\tilde{S}. \tag{A2}$$

The ordinary differential equation

$$\epsilon\frac{d\tilde{S}}{d\tau} = (-\tilde{A} \pm 2\delta)\tilde{S} \tag{A3}$$

can be solved explicitly with $\tilde{A}(\tau) = \tilde{A}_0 - \tau$ and the initial condition $\tilde{S}_0 = \delta$. The corresponding solutions are $\tilde{S}^{\pm}(\tau,\tilde{A}_0,\epsilon)$, where

$$\ln\left(\frac{\tilde{S}^{\pm}}{\delta}\right) = \frac{1}{2\epsilon}\left[\tilde{A}^2 - \tilde{A}_0^2 \pm 2\delta(\tilde{A}_0 - \tilde{A})\right]. \tag{A4}$$

The upper curve, $\tilde{S}^{+}$, reintersects the line, $\tilde{S} = \delta$, again at

$$A_{+} = 2\delta - \tilde{A}_0,$$

and the lower curve, S^{-}, reintersects the line, $S = \delta$, again at

$$A_{-} = -2\delta - \tilde{A}_0.$$

Let $A_*(\tilde{A}_0,\epsilon)$ denote the first point of reintersection between the solution, $\tilde{S}(\tau,\tilde{S}_0,\tilde{A}_0)$, and the line, $\tilde{S} = \delta$. From the inequalities (A2) and the values $A_{\pm}$ above, we deduce that $-2\delta - \tilde{A}_0 \leqslant A_*(\tilde{A}_0,\epsilon) \leqslant 2\delta - \tilde{A}_0$. In the limit $\delta \to 0$, we obtain

$$A_*(\tilde{A}_0,\epsilon) = -\tilde{A}_0 < 0. \tag{A5}$$

The conclusion of Proposition IV now follows. ■

Proposition IV gives a coarse picture of the delay phenomenon. We can get more detailed information by an asymptotic analysis as shown below. The asymptotic analysis not only captures the delay but also the final approach from the isotropic to the nematic equilibrium as the temperature is decreased. The delay only depends on $\tilde{A}_0$ but the final approach depends on both $\tilde{A}_0$ and $\tilde{S}_0$, as illustrated in (A11).

We take $\tilde{A}(\tau) = \tilde{A}_0 - \tau$ for some $0 < \tilde{A}_0 < 1$ and the initial condition $\tilde{S}_0$ to be within the basin of attraction of the isotropic equilibrium at $\tilde{A} = \tilde{A}_0$. This is in contrast to Proposition IV where we only consider initial conditions within a small δ-neighborhood of the isotropic branch.

From the $(\tilde{A},\tilde{S})$-phase plane, the solution descends towards the isotropic branch, in a layer of width $O(\epsilon)$, for $\tilde{A} > 0$, and the leading-order equation in this region is

$$\frac{d\tilde{S}}{d\tau'} = -\tilde{S}[\tilde{S}^2 - 2\tilde{S} + \tilde{A}_0], \tag{A6}$$

where $\tau' = \frac{\tau}{\epsilon}$. The leading-order solution is implicitly given by

$$\tau' = \frac{\log\left(\frac{\tilde{S}_0^2(\tilde{A}_0+\tilde{S}^2-2\tilde{S})}{\tilde{S}^2(\tilde{A}_0+\tilde{S}_0^2-2\tilde{S}_0)}\right)}{2\tilde{A}_0} + \frac{\tanh^{-1}\left(\frac{\sqrt{1-\tilde{A}_0}(\tilde{S}_0-\tilde{S})}{\tilde{A}_0-\tilde{S}+(\tilde{S}-1)\tilde{S}_0}\right)}{\tilde{A}_0\sqrt{1-\tilde{A}_0}}. \tag{A7}$$

As $\tau' \to +\infty$, we have $\tilde{S} \sim B_0\exp[-\tilde{A}_0\tau']$, where

$$\log(B_0) = \frac{1}{2}\log\left(\frac{\tilde{A}_0\tilde{S}_0^2}{\tilde{S}_0^2 - 2\tilde{S}_0 + \tilde{A}_0}\right) + \frac{\tanh^{-1}\left(\frac{\sqrt{1-\tilde{A}_0}\tilde{S}_0}{\tilde{A}_0-\tilde{S}_0}\right)}{\sqrt{1-\tilde{A}_0}}. \tag{A8}$$

Thereafter, $\tilde{S}$ becomes small for $\tilde{A} < \tilde{A}_0$ and the subsequent behavior may be found by linearizing (10) about $\tilde{S} = 0$,

$$\epsilon\frac{d\tilde{S}}{d\tau} + (\tilde{A}_0 - \tau)\tilde{S} = 0,$$

with the matching condition $\tilde{S} \sim B_0\exp[-\tilde{A}_0\frac{\tau}{\epsilon}]$, as $\tau \to 0^+$. The leading-order solution for $\tau > 0$ is given by

$$\tilde{S}(\tau) \sim B_0\exp\left[\frac{-\tilde{A}_0\tau + \frac{\tau^2}{2}}{\epsilon}\right], \tag{A9}$$

which is exponentially small for $0 < \tau < 2\tilde{A}_0$, or for $\tilde{A} \in (-\tilde{A}_0,\tilde{A}_0)$, and is consistent with the lower and upper solutions computed in (A4).

Near $\tilde{A} = -\tilde{A}_0$, we set $\tau = 2\tilde{A}_0 + \epsilon\tau'$ to get the leading-order equation

$$\frac{d\tilde{S}}{d\tau'} = -\tilde{S}(\tilde{S}^2 - 2\tilde{S} - \tilde{A}_0) \tag{A10}$$

with the matching condition $\tilde{S}(\tau') \to B_0 \exp[+\tilde{A}_0\tau']$ as $\tau' \to -\infty$. As in (A7), we obtain

$$\tau' = -\frac{\log\left(\frac{B_0^2(\tilde{A}_0 - \tilde{S}^2 + 2\tilde{S})}{\tilde{A}_0\tilde{S}^2}\right)}{2\tilde{A}_0} - \frac{\tanh^{-1}\left(\frac{\sqrt{1+\tilde{A}_0}\tilde{S})}{\tilde{A}_0+\tilde{S}}\right)}{\tilde{A}_0\sqrt{1+\tilde{A}_0}}, \tag{A11}$$

where B_0 has been defined in (A8) and this describes the isotropic-nematic ascent, in a layer of width $O(\epsilon)$, for $\tilde{A} < 0$.

APPENDIX B: FORWARD TRANSITION THROUGH $\tilde{A} = 1$

Let $\tilde{A}(\tau) = \tilde{A}_0 + \tau$ for some $\tilde{A}_0 < 1$ and let the initial condition, $\tilde{S}_0$, be within an ϵ neighborhood of the nematic branch, $\tilde{S}_+(\tilde{A}_0)$. It can be rigorously proven that the solution remains within an ϵ neighborhood of $\tilde{S}_+(\tilde{A})$ provided that $\tilde{A}$ is bounded away from $\tilde{A} = 1$ [10,14]. Indeed, the solution may be expanded asymptotically in the form

$$\tilde{S} \sim 1 + \sqrt{1-\tilde{A}} + \frac{\epsilon}{4(1-\tilde{A})(1+\sqrt{1-\tilde{A}})} + O(\epsilon^2),$$

and we infer that there is a nonuniformity when $1 - \tilde{A} = O(\epsilon^{2/3})$ and $\tilde{S} - 1 = O(\epsilon^{1/3})$.

We, therefore, define $\bar{\tau} = \epsilon^{-2/3}(1 - \tilde{A}_0 - \tau)$ and seek an asymptotic expansion for $\tilde{S}(\bar{\tau})$ from (10) as follows:

$$\tilde{S}(\bar{\tau}) = 1 + \epsilon^{1/3}S_1(\bar{\tau}) + \epsilon^{2/3}S_2(\bar{\tau}) + \cdots. \tag{B1}$$

The first-order term is a solution of the Riccati equation

$$\frac{dS_1}{d\bar{\tau}} = -\left(S_1^2 + \bar{\tau}^2\right), \tag{B2}$$

and therefore,

$$S_1(\bar{\tau}) = -\frac{\mathrm{Ai}'(-\bar{\tau})}{\mathrm{Ai}(-\bar{\tau})},$$
$$S_2(\bar{\tau}) = \frac{\int_{-\bar{\tau}}^{\infty}\mathrm{Ai}'(z)^3/\mathrm{Ai}(z)dz}{\mathrm{Ai}(-\bar{\tau})^2} + \frac{\mathrm{Ai}'(-\bar{\tau})^2}{2\mathrm{Ai}(-\bar{\tau})^2}, \tag{B3}$$

where Ai denotes the Airy function [9].

This expansion becomes nonuniform as $\bar{\tau} \to \tau^*$, where $-\tau^*$ denotes the first zero of the Airy function, i.e., $\tau^* = +2.338$. In this limit,

$$\tilde{S}(\bar{\tau}) \sim 1 - \frac{\epsilon^{1/3}}{\tau^* - \bar{\tau}} - \epsilon^{2/3}\frac{C_1 + \log(\tau^* - \bar{\tau})}{(\tau^* - \bar{\tau})^2} + \cdots, \tag{B4}$$

where $C_1 \approx 0.5085$ is an explicitly computable positive constant. This motivates the scaling, $\tilde{A} = 1 - \tau^*\epsilon^{2/3} + \frac{1}{3}\epsilon\log(\frac{1}{\epsilon}) + \epsilon\tilde{\tau}$, which results in the leading-order Equation (B5) below,

$$\frac{d\tilde{S}}{d\tilde{\tau}} \sim -\tilde{S}(\tilde{S}-1)^2, \tag{B5}$$

with the matching condition

$$\tilde{S} \sim 1 + \frac{1}{\tilde{\tau}} - \frac{C_1 + \log(-\tilde{\tau})}{\tilde{\tau}^2} + \cdots \tag{B6}$$

as $\tilde{\tau} \to -\infty$. The leading-order inner solution is then implicitly given by

$$\tilde{\tau} = -C_1 - \frac{1}{1-\tilde{S}} + \log\left(\frac{1-\tilde{S}}{\tilde{S}}\right). \tag{B7}$$

Thus, the temperature overshoots the critical value $\tilde{A} = 1$ by a distance of

$$\Delta\tilde{A} \sim \tau^*\epsilon^{2/3} + \frac{1}{3}\epsilon\log\left(\frac{1}{\epsilon}\right) \tag{B8}$$

before transitioning down to the isotropic branch over a temperature range of order ϵ.

APPENDIX C: DELAY ESTIMATES FOR BOUNDARY-VALUE PROBLEMS

Consider the partial differential Equation (18) with homogeneous boundary conditions and initial conditions close to the isotropic equilibrium, i.e., $\max_{x\in[0,1]} S(x,0) \ll 1$. To demonstrate dynamic stability of the isotropic equilibrium, we need to show that the following integral,

$$\|S\|^2(t) = \int_0^D \left(\frac{\partial S}{\partial x}\right)^2 + S^2 dx, \tag{C1}$$

remains small for all times, given that $\|S\|(0) \leqslant \sigma \ll 1$ [18]. The integral (C1) can be viewed as a measure of the deviation from the isotropic equilibrium, $S(x,t) = 0$.

Following the methods in [18], the key step is to compute the second variation of the one-dimensional LdG energy below,

$$I[S] := \int_0^D \frac{L}{3}\left(\frac{\partial S}{\partial x}\right)^2 + \frac{A}{3}S^2 - \frac{2B}{27}S^3 + \frac{C}{9}S^4 dx, \tag{C2}$$

around the isotropic equilibrium, $S(x,t) = 0$. We consider small variations around $S = 0$, given by $S_\eta(x,t) = \eta\theta(x,t)$, where θ is an arbitrary continuously differentiable function vanishing at the end points (consistent with the homogeneous boundary conditions). The second variation of the associated LdG energy (C2), around $S = 0$, is given by

$$\left.\frac{d^2 I[S_\eta]}{d\eta^2}\right|_{\eta=0} = \int_0^D \frac{2}{3}L\left(\frac{\partial\theta}{\partial x}\right)^2 + A\theta^2(x,t)dx. \tag{C3}$$

Recalling Wirtinger's inequality [19], i.e.,

$$\int_0^D \left(\frac{\partial\theta}{\partial x}\right)^2 dx \geqslant \frac{\pi^2}{D^2}\int_0^D \theta^2(x,t)dx,$$

we deduce that the second variation is necessarily positive if

$$\min_{x\in[0,D];t\geqslant 0} A(x,t) > A_T = -\pi^2\frac{2L}{3D^2}. \tag{C4}$$

Having demonstrated the strict positivity of the second variation of the LdG energy around $S(x,t) = 0$ for $A > A_T$, one can straightforwardly demonstrate that the integral in (C1) remains small for all times leading to dynamic stability for $A > A_T$, by an immediate application of Liapounov's direct method [18].

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