Structure and shape of nematic liquid-crystal microdroplets

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We calculate the continuous dependence of structure and shape of tangentially anchored nematic liquid-crystal microdroplets on the parameters of anchoring strength w_0 and radius r, at fixed temperature, using a numerical relaxation method and Landau–de Gennes theory. The structure is characterized by spatially varying order parameter and director fields S and $\hat{\mathbf{n}}$, and the shape of a free droplet is assumed to be a prolate ellipsoid. For droplets of fixed spherical shape, we find discontinuous and discontinuous order-disorder and uniform-distorted transitions of S induced by r and by w_0, respectively, and uniform-distorted transitions of $\hat{\mathbf{n}}$ induced by both r and w_0. For free droplets, we show that the surface interactions can indeed induce prolateness, which increases toward a limiting value as the volume becomes smaller, and which is nearly proportional to w_0/σ, where σ is the director-independent part of the surface tension.

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I. INTRODUCTION

In recent years keen interest has surrounded the behavior of liquid crystals in confined geometries (droplets, films, and capillaries) due to present and potential applications. In such situations, surface and bulk effects may be comparable, and both the order parameter and the director field may show large spatial variations at equilibrium. The case of nematic droplets is particularly interesting because of their use in polymer-dispersed liquid-crystal (PDLC) devices that act as field-actuated shutters.

Theoretical treatments of nematic droplets have an extensive history. Chandrasekhar [1] in 1964 pointed out that the competition of elastic and surface energies might render their shapes elongated rather than spherical. Dubois-Violette and Parodi [2] were the first to model in detail the effect of an external (magnetic) field on the director configuration of a spherical droplet, in the limit of strong anchoring. For homeotropic anchoring, they found a first-order transition from the radial to the axial configuration with increasing external field. The order parameter, and therefore the elastic constants, were considered to be fixed and uniform. Sheng showed that the temperature-driven isotropic-nematic transition, which in the bulk is first order (discontinuous), could become continuous in confined geometries due to the order-enhancing effects of surface anchoring, both strong [3] and weak [4]. The isotropic-to-radial-nematic transition in droplets with strong homeotropic anchoring was then shown by Žumer, Vilfan, and Vilfan [5] to become continuous or disappear entirely, for sufficiently small radius, a picture later confirmed by experiment [6], and analyzed [7] in greater detail using a picture in which spatial variations of the nematic order parameter are permitted. Vilfan, Vilfan, and Žumer [8] found similar behavior in the case of strong tangential anchoring, where the transition is from isotropic to bipolar nematic.

Transitions between various configurations within the nematic phase have been examined more recently. For example, Erdman, Žumer, and Doane [9] have studied the axial-to-radial transition as a function of external field, temperature, and radius in the approximation of a spatially uniform order parameter and equal splay and bend constants, and have tested their predictions against experimental results obtained on micrometer-sized droplets of the liquid crystal E7 dispersed in a polyurethane matrix. A more thorough study of this transition [10] has delineated a region of the phase diagram in which the configuration is axial with an equatorial line defect for anchoring strengths that are large compared to the external field. For strong tangential anchoring and uniform order parameter, Williams [11] has demonstrated the existence of a twisted bipolar phase for a splay elastic constant that is large compared to the sum of twist and bend constants.

Still lacking to this point is a complete and integrated picture of the combined effects of droplet size, anchoring strength, elastic constants, field, and temperature on the structure of nematic droplets, including the spatial configurations of both the order parameter and the director fields. In this paper we begin such a program by describing the interrelated effects of droplet radius (from hundreds of angstroms to hundreds of micrometers) and anchoring strength, from weak to strong. We use a single-elastic-constant approximation in which the bend and splay constants are set equal and the twist constant assumed very large (i.e., no twisted configurations are allowed). A mean field or Landau–de Gennes approach is employed, and both the order parameter and the director fields are allowed to vary spatially. We focus on the case of tangential anchoring, so that the competing configurations in the nematic regime are uniform and bipolar, as shown in Fig. 1.

In a second and related portion of this work, we examine Chandrasekhar's original prediction concerning the shapes of free droplets. This issue may be approached in a qualitative way by noting that both the elastic and surface anchoring terms tend to produce an elongated shape. The surface tension counters this tendency, and the two

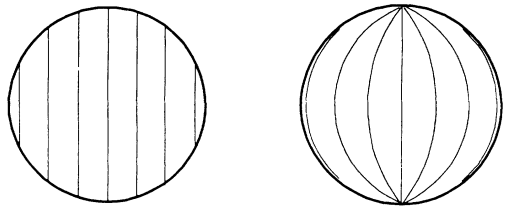

FIG. 1. Bipolar and uniform director configurations in a spherical droplet.

surface terms may be comparable in size. The bulk elastic energy of the nematic is associated with the squares of gradients of $\hat{\mathbf{n}}$, and so is proportional to the radius r of the droplet, while the surface energy is proportional to r^2. Thus for small radius, the bulk energy dominates and may also play a role in determining the droplet shape. With the same model free-energy and calculational approach that we use for the fixed-shape case, we consider droplets of fixed volume whose surfaces are allowed to assume prolate ellipsoidal configurations and find the equilibrium (minimum-total-free-energy) shape.

In what follows we first briefly review the model free energy used in our calculations, including approximations. We also outline the numerical procedure used to find the minimum-free-energy configurations. This involves a direct minimization of the discretized free energy, rather than the usual Euler-Lagrange equation approach. In Sec. III we discuss our findings for both the fixed-shape and the free-shape parts of our work.

II. MODEL DEFINITION AND COMPUTATIONAL METHOD

The model free-energy density used in this work is of the Landau–de Gennes type [12], consisting of contributions from both the bulk and the surface, and is a function of both the nematic scalar order parameter $S(\mathbf{r})$ and the director field $\hat{\mathbf{n}}(\mathbf{r})$. Following Ref. [8], we take the expression for the bulk free-energy density f_b to be of the form

$$f_b = f_0 + \frac{a}{2}(T-T^*)S^2 - \tfrac{1}{3}BS^3 + \tfrac{1}{4}CS^4 + \tfrac{3}{4}L(\nabla S)^2 + \tfrac{9}{4}S^2L[(\nabla\cdot\hat{\mathbf{n}})^2 + (\nabla\times\hat{\mathbf{n}})^2] \ . \quad (1)$$

The terms involving S alone are responsible for driving the first-order isotropic-nematic transition. The temperature T^* represents an ideal bulk supercooling limit, while in the absence of elastic distortions, surface effects, or inhomogeneities, the first-order transition would occur at $T^*+2B^2/9aC$. Terms involving the director field describe the splay, bend, and twist elastic energy density, specialized to the case of equal elastic constants; the usual Frank elastic constant K in this approximation is given by $K=9LS^2/2$. In fact, we treat only configurations in which twist is excluded, so that the contribution of $(\nabla\times\hat{\mathbf{n}})^2$ arises entirely from bend distortions.

The areal free-energy density at the surface is modeled by a general expression for weak anchoring:

$$f_s = \sigma - \tfrac{1}{2}w_0(\hat{\alpha}\cdot\hat{\mathbf{n}})^2 \ , \quad (2)$$

where α is a unit vector in the "favored" direction—the surface normal in the homeotropic case or a surface tangent in the cases discussed here in which bipolar configurations arise. The quantities σ and w_0 describe, respectively, the surface tension and anchoring strength. The anchoring is here assumed to be independent of S, although we have recently also studied [13] the effects of allowing w_0 to be S dependent.

The total free energy F is obtained by integrating f_b over the volume of the droplet and f_s over its surface. To find equilibrium configurations, we minimize directly [14–16] a discretized version of F. The discretization is most simply discussed in the case of the droplets of fixed shape. We introduce a square mesh covering a single quadrant of the drop's axial cross section and at each node (i,j) define local variables S_{ij} and θ_{ij} for the order parameter and the angle between the director and the polar axis. Note that in the no-twist case, $\hat{\mathbf{n}}$ has no azimuthal component. F is then a sum involving the set $\{S_{ij},\theta_{ij}\}$, and the simultaneous minimization equations $\{\partial F/\partial S_{ij}=0, \partial F/\partial\theta_{ij}=0\}$ are solved numerically: We repeatedly sweep through the mesh and adjust the variables at each point with a single iteration of a Gauss-Seidel over-relaxation method, using the most current values for the node variables at adjacent points in the calculation of the spatial derivatives. To take account of the droplet boundary efficiently [14], we assign to each mesh point a fixed weight factor of 1 or 0, depending on whether the point is inside or outside the surface, and use these factors to calculate the contribution of a unit cell of the mesh to the free-energy integral. Using this technique, variables at both bulk and surface points may be updated in the same sweep.

For our investigation of droplet shape, we describe the prolateness by a single additional variable $x \geq 1$. We deform the unit cell of our mesh from square to rectangular through contraction of the lateral dimension by a factor $1/x$ and extension of the vertical dimension by x^2. Thus, x is simply the cube root of the ratio of the ellipse principal axes. Mesh points outside the droplet before the deformation remain outside, those inside remain inside, and the droplet volume is conserved. This allows us to compute the free energy as a function of x and adds very little complexity to the code.

III. RESULTS

For the results described here we used the bulk coefficients of the nematic liquid crystal 4-n-pentyl-4′-cyanobiphenyl (5CB), as given by Ref. [4]: $a=0.13$ J/K cm^3, $B=1.605$ J/cm^3, $C=3.9$ J/cm^3, and $L=10^{-13}$ J/cm. The corresponding bulk supercooling limit $T^*=317.14$ K is 1.129 K below the bulk nematic-isotropic transition temperature, and we fix the temperature at a point just below the transition: $T-T^*=0.001$ K.

As either r or w_0 is varied in a spherical droplet, we find that the director configuration can show a distortion

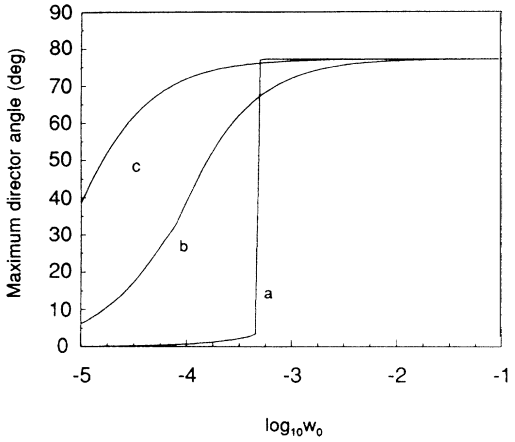

FIG. 2. Maximum polar director angle as a function of the log of the anchoring strength parameter w_0 (in J/m^2) for droplets of radius (a) 0.01, (b) 1, and (c) 10 μm. Because of the use of a finite-spaced mesh, the maximum angle is less than 90° even in the bipolar phase.

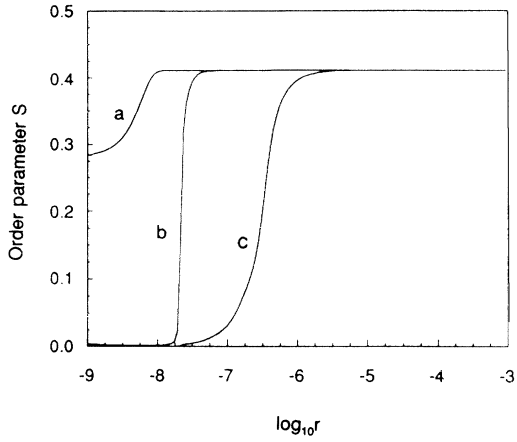

FIG. 4. Order parameter as a function of radius, for fixed anchoring parameter w_0: (a) $w_0=3\times10^{-5}$ J/m^2, a case for which the order parameter is uniform; (b) maximum value of S, for $w_0=0.01$ J/m^2; (c) minimum value of S for $w_0=0.01$ J/m^2.

transition, as measured by θ_{max}, the maximum value of the director angle (Figs. 2 and 3). The transition with respect to w_0 can become virtually discontinuous for small droplets, a situation that we describe as "first-order" by analogy to usual phase transitions in bulk systems. It is possible that the first-order character of the transition here and in the following is due to our assumption of an anchoring parameter independent of S, but we believe that the qualitative trends shown here are reasonable. For droplet radius larger than 10^3 μm, or anchoring strength greater than 2×10^{-2} J/m^2 the configuration is always highly distorted (bipolar). Thus for large droplets, there is always effectively strong anchoring, even if the anchoring parameter is small, as proposed in Ref. [11] and confirmed by photographs [17]. On the other hand, for small droplets and not extremely strong anchoring, the director field can become completely undistorted. This is also consistent with our earlier arguments, which indicated that for small droplets, the bulk elastic energy term dominates; a reduction in size is virtually equivalent to a reduction in anchoring strength.

The result of uniform director field for small droplets is of particular interest since Ref. [8] used the condition of fixed tangential surface director (in analogy to Sheng's proposal for a planar surface) to discuss the experimental observation (Ref. [6]) of a nematic-isotropic transition with temperature. However, the same findings can be explained if S dependence is introduced into w_0, and in this case the uniform state is still retained for small droplets [13].

The behavior of the order-parameter field under these conditions is equally interesting but somewhat more complex. Viewed as a function of droplet size, the order parameter decreases from its bulk value as r decreases, as noted in experiment [6]. For small values of the anchoring parameter w_0 (e.g., $w_0=3\times10^{-5}$ J/m^2, shown in curve *a* of Fig. 4), the order-parameter field remains

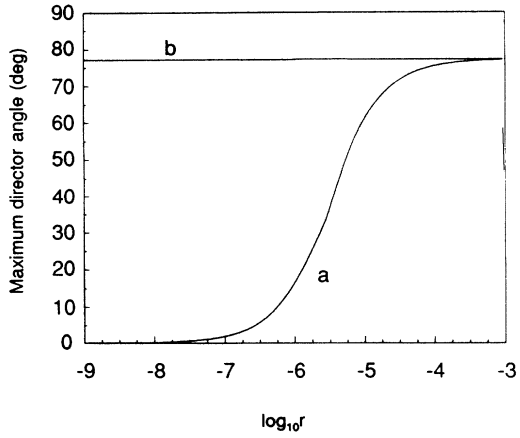

FIG. 3. Maximum polar director angle as a function of the log of the radius (in m) for anchoring strength parameters w_0 of (a) 3×10^{-5} J and (b) 0.1 J/m^2.

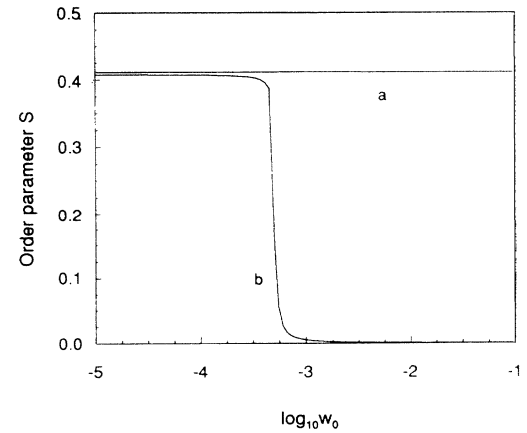

FIG. 5. Order parameter S as a function of anchoring strength w_0: (a) Value of uniform S for 10-μm droplet and maximum value of S for 0.1- μm droplet; (b) minimum value of S for 0.1-μm droplet.

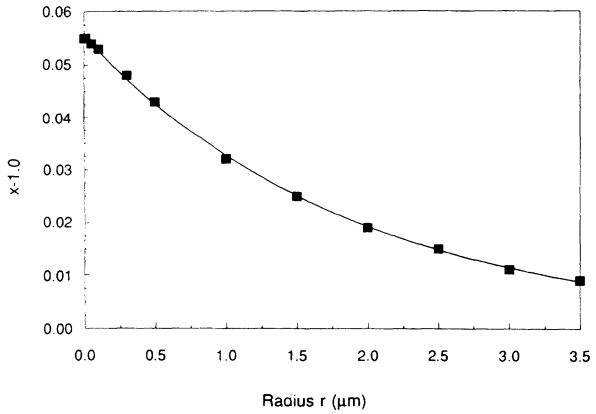

FIG. 6. Prolateness parameter x versus radius (of a spherical droplet of equal volume) for anchoring strength parameter $w_0 = 3 \times 10^{-5}$ J/m^2 and surface tension $\sigma = 10^{-4}$ J/m^2.

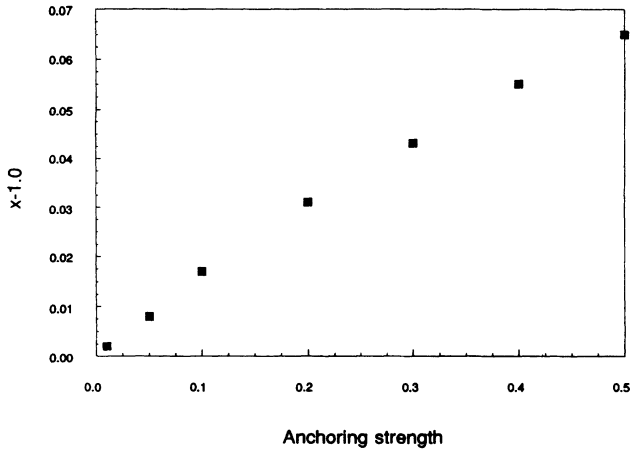

FIG. 7. Prolateness parameter x versus anchoring strength w_0 for a 0.5-μm droplet and $\sigma = 10^{-4}$ J/m^2.

roughly uniform over the volume of the droplet as it decreases in size. For larger w_0, the decrease is a two-stage process: S rapidly falls to near zero in the pole regions (around the director singularity), while in the rest of the volume it remains at its bulk value until yet smaller values of radius are reached, whereupon it abruptly goes to zero everywhere. That is, the anchoring can force the director to remain distorted and therefore the elastic energy rises until order is destroyed. There is a size regime in which S is distinctly nonuniform, as illustrated by the difference in curves b (the maximum value of S) and c (the minimum value of S) in Fig. 4.

For the droplet size that is fixed and small, an increase in w_0 can induce sudden nonuniformity in the S field, as shown in Fig. 5. Large droplets remain in the bipolar phase for all values of w_0, with S virtually constant and uniform.

If the droplet shape is allowed to become ellipsoidal, we find that the change of the bulk free energy under a shape variation is always smaller than that of the surface energy. In consequence, the shape depends only on the director configuration and the ratio w_0/σ. Figure 6 shows that large drops become spherical; the director near the surface is perfectly tangential and no decrease of surface energy is possible under elongation. For a small droplet the shape becomes prolate, approaching a limiting value as the radius shrinks. For the surface tension to anchoring strength ratio shown in Fig. 6, the limiting value of x is near 1.06, giving a structure with a ratio of major to minor axes of 1.19. The nearly linear dependence of shape on the ratio w_0/σ is demonstrated in Fig. 7 for a droplet of radius 0.5 μm.

In summary, we have obtained several results unavailable from earlier work that assumed fixed anchoring or uniform order parameter. These include the uniform director configuration for small droplets, an order-disorder transition for small droplets with very strong anchoring, and a range of size and anchoring strength in which a nonuniform S field appears. In addition, we have shown that moderate prolateness does indeed exist under certain conditions for a free droplet. Since these effects appear at the micrometer level, light-scattering methods on aerosols, electron microscopy, or shape-analysis techniques routinely used in microbiological studies may prove applicable in developing experimental tests of our results.

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