



Structure and shape of nematic liquid crystal microdroplets  
by Wei Huang

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Physics

Montana State University

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Abstract:

With a numerical relaxation method and Landau-de Gennes theory, we have calculated the continuous dependence of structure and shape of tangentially anchored liquid crystal microdroplets on the parameters of anchoring strength  $W_0$  and radius  $r$ , at fixed temperature. The structure is characterized by order parameter field  $S$  and director field  $n$  and the shape is described by a prolateness parameter  $x$ . For structure, we find that there exists an order/disorder first-order transition induced by  $r$ , a distortion/uniform first-order transition of  $S$  induced by  $w_0$ , and a distortion/uniform continuous transition of  $n$  induced by both  $W_0$  and  $r$ . For shape, we find that the change of bulk free energy due to deviations from spherical shape can never compete with that of the surface energy. The surface interaction itself can induce prolateness, which becomes greater and approaches to a limiting value as the size gets smaller, and which is almost proportional to  $W_0/\zeta$ . None of the above predictions have been reported before. Our physical explanations show they are reasonable and not the outcomes of approximations made in the work.

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A thesis submitted in partial fulfillment  
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Master of Science

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Physics

MONTANA STATE UNIVERSITY  
Bozeman, Montana

April 1993

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency and is ready for submission to the College of Graduate Studies.

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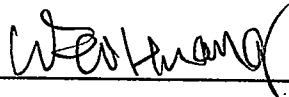
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## ABSTRACT

With a numerical relaxation method and Landau-de Gennes theory, we have calculated the continuous dependence of structure and shape of tangentially anchored liquid crystal microdroplets on the parameters of anchoring strength  $w_0$  and radius  $r$ , at fixed temperature. The structure is characterized by order parameter field  $S$  and director field  $\mathbf{n}$  and the shape is described by a prolateness parameter  $x$ . For structure, we find that there exists an order/disorder first-order transition induced by  $r$ , a distortion/uniform first-order transition of  $S$  induced by  $w_0$ , and a distortion/uniform continuous transition of  $\mathbf{n}$  induced by both  $w_0$  and  $r$ . For shape, we find that the change of bulk free energy due to deviations from spherical shape can never compete with that of the surface energy. The surface interaction itself can induce prolateness, which becomes greater and approaches to a limiting value as the size gets smaller, and which is almost proportional to  $w_0/\sigma$ . None of the above predictions have been reported before. Our physical explanations show they are reasonable and not the outcomes of approximations made in the work.



## CHAPTER 1

### INTRODUCTION

There has been continuous interest in liquid crystals (LC) over the past several decades due to their importance in the electro-optic industry. Studies of a LC microdroplet have been stimulated recently by the appearance of a new generation of LC shutters and displays based on the use of polymer-dispersed liquid crystals (PDLC) [1]. A PDLC is a solid polymer in which a large number of LC droplets, whose radii vary from the submicrometer region up to 100  $\mu\text{m}$ , are embedded.

#### Basic Knowledge about LCs

A liquid crystal is one of the intermediate phases between phases of crystalline solid and isotropic liquid. These intermediate phases are called mesophases. We can briefly say that LCs are ordered fluid mesophases, compared to plastic crystals which are disordered solid mesophases. A liquid crystal can flow like an ordinary liquid, while other properties, for example the birefringence, are reminiscent of those of a crystalline phase. Liquid crystals are characterized by the fact that the molecular translational order has disappeared, while some degree of orientational order is still present. (By contrast, plastic

crystals have translational order but not orientational order.) Usually the molecules of LC are greatly elongated ones, and their long axes, except for the influence of thermal fluctuations, are parallel to each other.

There are two types of LC, thermotropic and lyotropic. The term "thermotropic" arises because transitions involving these mesophases are most naturally effected by changing temperature. This type is of interest both from the standpoint of basic research and for applications in electro-optic displays, etc. We deal with this type in our work. Solutions of rod-like entities in a normally isotropic solvent often form LC phases for sufficiently high solute concentration. These anisotropic solution mesophases are called "lyotropic" LC. The natural parameter inducing phase transitions of this type is the solute concentration. Lyotropic LCs are of interest in polymer and biological studies.

Liquid crystals can be classified as nematic and smectic according to molecular order, as Fig.1 shows. Under each type there are several subtypes, e.g., cholesteric nematic, smectic A, smectic B, etc. The essential difference between a nematic LC and a smectic LC is that the smectic phase has some degree of positional order, i.e., layering.

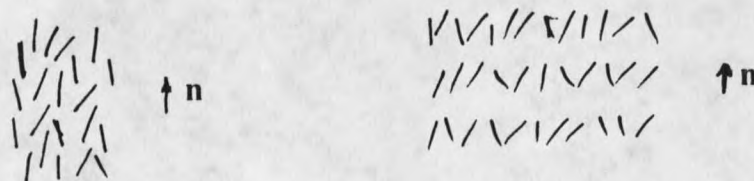


Figure 1. Schematic picture of the nematic (a) and smectic A (b) phase.

Molecular statistical theory and macroscopic continuum theory are used to describe the structures and properties of LC. Macroscopically in most cases we use two structural quantities, a unit vector  $\mathbf{n}$  (the director) and a scalar  $S$  (the order parameter).  $\mathbf{n}$  is the local average direction of molecular axes.  $S$  measures the local average deviation of directions of molecular axes from  $\mathbf{n}$ . More general quantities will be described in Chapter 2.

In the commonly used macroscopic elastic continuum theory which embeds the order parameter into temperature dependent elastic constants, there are three independent distortion modes of director field (Fig. 2), and the free energy density is

$$f = \frac{1}{2} [K_{11} (\nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33} (\mathbf{n} \times \nabla \times \mathbf{n})^2] \quad (1)$$

where the so-called Frank elastic constants  $K_{11}$ ,  $K_{22}$ , and  $K_{33}$  are, respectively, the splay, twist, and bend elastic constants.

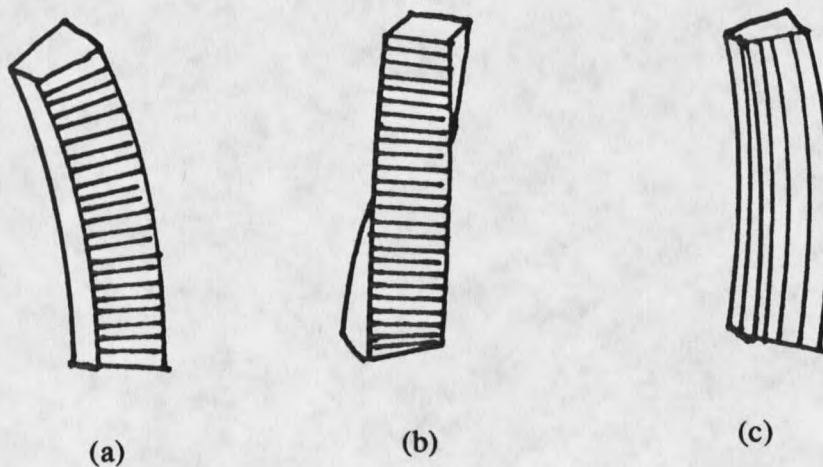


Figure 2. The three basic deformations of a uniaxial nematic: (a) splay, (b) twist, (c) bend.

At the interface between a LC and other phase, anchoring always occurs, even if the other phase is vacuum. Anchoring means there is a preferable direction for the director  $\mathbf{n}$  at the interface. The simplest way to describe anchoring is shown by equation (2) for the surface energy density:

$$f_s = \sigma - \frac{1}{2} w_0 \cos^2(\alpha \cdot \beta) \quad (2)$$

$\alpha$  and  $\beta$  are respectively, the favorable direction unit vector and the actual surface director. Depending on the materials,  $\alpha$  can vary from tangential to the surface to normal to the surface.  $\sigma$  and  $w_0$  are the surface tension constant and the anchoring strength parameter, respectively.

There are several types of structures for nematic LC droplets which reflect two typical boundary anchoring condition: tangential and normal (Fig.3). The characterization of these types is by the different distortion patterns of director  $\mathbf{n}$  field.

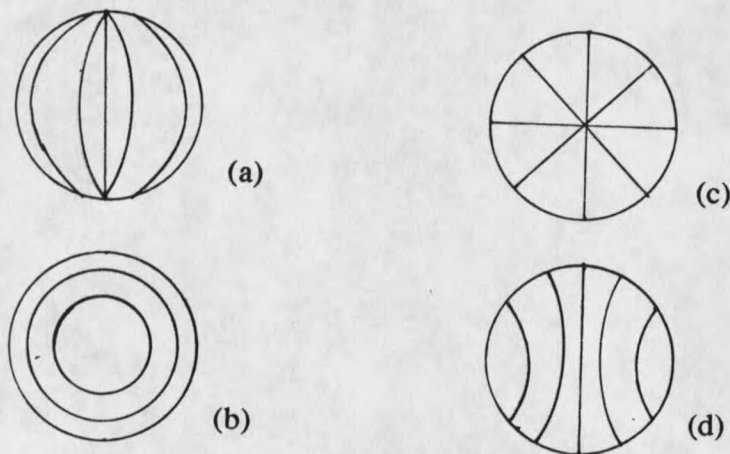


Figure 3. Director configurations in nematic microdroplets:

(a) bipolar, (b) toroidal, (c) radial, and (d) axial structures.

### Review of Other Work

The previous theoretical work on the subject can be divided into following categories.

- (1) Obtaining one of the above structures [2][3].
  
- (2) Studying the nematic/isotropic transition of certain structures for the LC droplets as the temperature varies [4][5]. For example, in [5] Zumer et al. showed the director and order parameter configuration for a bipolar droplet near the nematic/isotropic phase transition, with a strong anchoring condition.
  
- (3) Studying the transition between two of these structures, as external field or ratio of elastic constants varies [6][7]. For example, in [7] R.D.Williams calculated the transition of the bipolar/twist-bipolar configuration, occurring when  $K_{11} > K_{22} + 0.431K_{33}$ .

Computational relaxation methods and Landau-de Gennes theory are the common tools of these works. The agreement between experiment and theoretical calculation [9][10] stand as the support for the appropriateness of the theory.

However, a clear and integral picture of LC droplet structure's continuous dependence

on various parameters is still missing, especially for submicrometer droplets and for droplets with three different elastic constants. Furthermore until this thesis no work on the shape of LC microdroplets has been carried out.

### Introduction of this Work

In this thesis, we study with a numerical relaxation method, the structure and shape of tangentially anchored droplets with one-elastic-constant and no-twist approximations, probing their continuous dependencies on radius, anchoring strength, etc., followed by physical explanations.

## CHAPTER 2

## LANDAU-DE GENNES THEORY AND THE PROBLEM OF THIS STUDY

Tensor Order Parameter

A nematic LC state is characterized by an macroscopic second rank tensor order parameter  $\mathbf{Q}$ . A macroscopic approach can be used in constructing  $\mathbf{Q}$ , i.e., the construction is independent of any assumption regarding the molecules. Consider the application of some field  $\mathbf{X}$  on the system with a response  $\mathbf{Y}$  given by:

$$Y_{\alpha} = T_{\alpha\beta} X_{\beta} \quad (3)$$

where  $T_{\alpha\beta}$  is a symmetric tensor. As an example  $\mathbf{X}$  and  $\mathbf{T}$  may represent respectively the external magnetic field  $\mathbf{B}$  and the susceptibility tensor  $\chi$ , and  $\mu_0^{-1}\mathbf{Y}$  is the magnetization  $\mathbf{M}$ .

In a properly chosen coordinate system,  $\mathbf{T}$  is diagonal:

$$\mathbf{T} = \begin{bmatrix} T_1 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_3 \end{bmatrix} \quad (4)$$

A tensor order parameter is obtained by extracting the anisotropic part of  $\mathbf{T}$ . This can be accomplished by putting  $\sum T_i = T$ , then letting the diagonalized order parameter tensor  $\mathbf{Q}$

be:

$$\mathbf{Q} = \begin{bmatrix} -1/3(Q_1 - Q_2) & 0 & 0 \\ 0 & -1/3(Q_1 + Q_2) & 0 \\ 0 & 0 & 2/3Q_1 \end{bmatrix} \quad (5)$$

where  $Q_1$  and  $Q_2$  are determined by:

$$T_1 = 1/3T (1 - Q_1 + Q_2) \quad (6)$$

$$T_2 = 1/3T (1 - Q_1 - Q_2) \quad (7)$$

$$T_3 = 1/3T (1 + 2Q_1) \quad (8)$$

$Q_1$  and  $Q_2$  have values between 0 and 1. The isotropic liquid is described by  $Q_1 = Q_2 = 0$ .

The anisotropic liquid with uniaxial symmetry is described by only one order parameter.

In this case the unique axis is conventionally chosen along the basis vector  $e_3$  and the

medium is described by  $Q_1 \neq 0$  and  $Q_2 = 0$ . (A perfectly aligned medium has  $Q_1 = 1$ .)

Changing the uniaxial symmetry into a biaxial one requires the introduction of the second

independent order parameter  $Q_2$ . Clearly the order parameter  $\mathbf{Q}$  depends on the

temperature.



The general expression for the tensor order parameter is obtained by an arbitrary rotation of the coordinate system.

$$Q_{\alpha\beta} = -\frac{1}{3}(Q_1 - Q_2)(e_\alpha \cdot e'_1)(e_\beta \cdot e'_1) - \frac{1}{3}(Q_1 + Q_2)(e_\alpha \cdot e'_2)(e_\beta \cdot e'_2) + \frac{2}{3}Q_1(e_\alpha \cdot e'_3)(e_\beta \cdot e'_3) \quad (9)$$

where  $e'_\alpha$  is the cartesian coordinate system giving rise to a diagonal representation of  $Q$ , and  $e_\alpha$  is the new coordinate system.

### Induction of S and n from Q

For nematics with uniaxial symmetry, the direction of the unique axis, which is given by the director  $n$ , coincides with one of the basis vectors belonging to the cartesian coordinate system in which  $Q$  is diagonal. And diagonalized  $Q$  is written as

$$Q = S \begin{pmatrix} -1/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & 2/3 \end{pmatrix} \quad (10)$$

where  $S$  is the scalar order parameter and is equal to  $Q_1$  of equation (5). In an arbitrary external coordinate system,

$$Q_{ij} = \frac{1}{3}S(3n_i n_j - \delta_{ij}) \quad (11)$$

Relationship Between Macroscopic Order Parameter and Microscopic Orientational  
Order of Molecules

It can be shown for a nematic LC composed of rod-like molecules [11],

$$n(r) = \langle a(r) \rangle \quad (12)$$

$$S(r) = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \quad (13)$$

where  $a$  is direction of an individual molecule,  $\theta$  is the angle between  $a$  and  $n$ , and  $\langle \dots \rangle$  represents a local thermal average.

If the distribution of the long molecular axes is random, as in the isotropic phase, we have  $\langle \cos^2\theta \rangle = 1/3$ , and  $S=0$ . The value  $S=1$  corresponds to the case of perfectly aligned molecules.

Landau-de Gennes Theory of Free Energy and Phase Transition

In 1937 Landau speculated that near a first or second-order phase transition point the free energy density function can be expanded as a power series in the order parameter and its spatial derivatives, with temperature-dependent coefficients. He further argued that only the leading terms of the series are important, so that the expansion of the free energy density function becomes a simple low order polynomial in the order parameters. Landau's theory of phase transitions has proven to be as good as mean field theory in

providing a semi-quantitative description of the specific heat, the order parameter, and the entropy in the vicinity of phase transition. De Gennes was the first to successfully apply Landau's theory to first-order LC phase transitions.

The Landau free energy density expression for a nematic LC, constructed with order parameter tensor  $Q$  is:

$$f = f_0 + \frac{1}{2}a(T - T_c^*)Q_{ij}Q_{ji} + \frac{1}{3}BQ_{ij}Q_{kl} + \frac{1}{4}C_1(Q_{ij}Q_{ji})^2 + \frac{1}{4}C_2Q_{ij}Q_{jk}Q_{kl}Q_{li} + \frac{1}{2}L_1\partial_i Q_{jk}\partial_i Q_{jk} + \frac{1}{2}L_2\partial_i Q_{ij}\partial_k Q_{kj} \quad (14)$$

where  $f_0(T)$  is the free energy density of the isotropic phase;  $T_c^*$  is a temperature slightly below the bulk sample transition temperature  $T_c$ . ( $T_c^*$  can be interpreted physically as that temperature below which supercooling becomes impossible.) The parameters  $a, B, C_1, C_2, L_1, L_2$  are temperature-independent bulk material constants. With substitution of equation (10), constants  $C_1$  and  $C_2$  can be combined to  $C = C_1 + C_2/2$ .  $L_1$  and  $L_2$  are two independent elastic constants. It should be noted that in the nematic phase there are known to be three independent elastic constants, and the Landau expansion to the second order gives rise to two of them.

### Our Problem

In our work we use equal-elastic constant approximation, and  $f$  becomes:

$$f_b(r,T) = f_0 + \frac{1}{2}a(T-T^*)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \frac{3}{4}L_1(\nabla S)^2 + \frac{9}{4}S^2L_1[(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2] \quad (15)$$

The relationship between  $L_1$  and the Franck elastic constant  $K$  is  $L_1 = 2K/(9S^2)$ .

The droplet we are studying has cylindrical symmetry, so, assuming no twist,  $\mathbf{n}$  can be expressed by the scalar angle  $\theta$  (Fig.4), and  $f$  becomes,

$$f(\rho,z,T) = f_0 + \frac{1}{2}a(T-T^*)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \frac{3}{4}L_1[(\partial S/\partial \rho)^2 + (\partial S/\partial z)^2] + \frac{9}{4}S^2L_1\left[\frac{1}{\rho^2}\sin^2\theta + (\partial\theta/\partial\rho)^2 + (\partial\theta/\partial z)^2 + \frac{2}{\rho}\sin\theta\cos\theta(\partial\theta/\partial\rho) + \frac{2}{\rho}\sin^2\theta(\partial\theta/\partial z)\right] \quad (16)$$

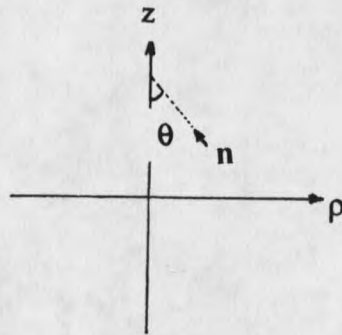


Figure 4. Description of the local director  $\mathbf{n}$  in the droplet.

$z$  is the axis of cylindrical symmetry of the droplet.

The problem is that of the minimization of the total free energy, which is the sum of the integrals of the above bulk term, and the surface term of equation (2).

An open question is the shape of a freely suspended LC droplet. Here "free" means the environment is an isotropic fluid. We can approach the problem qualitatively in the following way. The first consideration is dimensional analysis. Since the bulk elastic energy density is associated with the squares of gradients of  $\mathbf{n}$ , the elastic energy of a volume of nematic is proportional to the linear dimension  $L$  of the droplet. On the other hand, the surface energy is proportional to  $L^2$ . Thus the internal energy of a large drop is dominated by the surface energy, and the drop is spherical. For small drops, the bulk energy can dominate, and due to preference of an elongated shape of the bulk, the shape may be nonspherical. The other consideration is that, for weak surface anchoring, the surface energy itself may tend to be smaller for an elongated shape.

There are experimental optical photographs of free LC droplets bigger than  $1 \mu\text{m}$ , which are spherical, but no experiment or theory on the shapes for smaller droplets exists in the literature, to our knowledge. Since computational results show that the effect of deviation from sphere is small, through our work we can simply study prolate shapes, of course including the sphere.

## CHAPTER 3

## NUMERICAL METHOD

Usual Method

Usually when one solves a minimization problem, one uses a variational method to get a set of Euler-Lagrange partial differential equations. In this problem, for a fixed shape, from equation (15)&(2), we would have two partial differential equations plus two mixed boundary equations (not pure Dirichlet or Neumann boundary conditions). The numerical solution of this is a rather complicated one.

An alternate approach which has been used in some papers [13] on LC was first suggested in Adler's paper on gauge field equilibrium equations [8]. The spirit of the method is direct differentiation. We use this method in our problem.

Reducing the Continuous Total Free Energy into Discrete Form

We first introduce a two-dimensional ( $\rho$ - $z$ ) computational square lattice, replace the continuous variables  $\rho$  and  $z$  by discrete ones, and rewrite the free energy in this discrete coordinate system. Due to symmetry we can limit the region of our study to a single quadrant of a circle. There are three kinds of unit cells (Fig. 5), corresponding to the three kinds of terms in the bulk free energy density. We use the corresponding unit cell in summing that term to get the total free energy.

An  $h$ -factor is assigned to each mesh point to take account of the boundary. Briefly speaking,  $h$ -factors of mesh points outside or inside boundary are 0 or 1, respectively;  $h$ -















































































