Theoretical Estimates for Elastic Properties of Biaxial Nematics

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Abstract
Using theoretical analysis based on Landau theory, it is shown that only five phenomenological parameters are necessary to describe the twelve bulk elastic constants of a biaxial nematic phase. Further, a simple method for determining the values of these five parameters experimentally is given. Comparison with the values of the well-known splay, twist, and bend elastic constants of the uniaial nematic is made.

1. Introduction
Recent reports [1-3] of the observation of a biaxial nematic phase in thermotropic liquid crystals have renewed interest in the properties and possible applications of this novel liquid crystal phase. The systems studied in these reports incude two classes of molecules: certain bent core (commonly called banana shaped) molecules [1,2] and some branched molecules described as tetrapods [3]. Analagous to the case for unixial nematic systems, the key for applications is to demonstrate the ability to align both axes of the biaxial phase by means of surfaces and fields, and to elastically switch or re-orient them. Therefore the elastic properties of biaxial phases are of central importance and they are the subject of the research presented in this paper.

The basic theory of elasticity of the biaxial nematic phase was worked out by several independent research groups back in the early 1980's. They each found that the phase has twelve different bulk elastic constants, and three so-called surface elastic constants. In this work, we will ignore the surface constants and focus only on the bulk constants. Further, we will adopt the notation used by Saupe [4] to label and define them. In the next section, the twelve bulk elastic constants will be discussed, and the distortions of the liquid crystal that are associated with them are shown. Section 3 presents the Landau theory that will be used to make predictions for the values and temperature dependence of the elastic constants and shows how measurements on a uniaxial nematic phase can determine all the adjustable parameters. Finally the last section examines how the elastic constants depend on the biaxial order parameter and reduce to the well-known splay, twist, and bend elastic constants of the uniaxial nematic in the limit the biaxial order goes to zero.

2. Bulk Elastic Constants
Using the treatment given by Saupe [4], the local elastic behavior of a biaxial nematic is described by means of terms quadratic in the spatial derivatives of a tripod of orthogonal unit vectors **a**, **b**, and **c**. Applying symmetry considerations, he showed that the bulk elastic free energy density consists of twelve terms. Six of them are of the form

(1) $$K_{ab}\,([(\mathbf{a}\bullet \mathrm{grad})\mathbf{a}]\bullet\mathbf{b})^2$$

where the first subscript on the K corresponds to the first two unit vectors in the expression, and the second subscript refers to the final unit vector. The six constants are then K_{ab}, K_{ac}, K_{ba}, K_{bc}, K_{ca}, and K_{cb}. The orientation of **a**, **b**, and **c** that will contribute only to the K_{ab} term is easily visualized. An example is to use cylindrical coordinates and have **a** bending to follow the θ direction, **b** splaying to be along **r**, and **c** being uniform along **z**, as illustrated in Fig. 1.

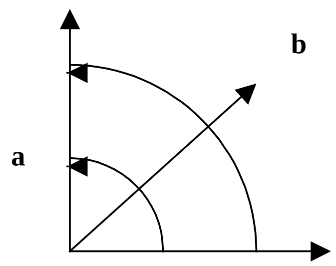

Figure 1. A distortion involving K_{ab} is shown. There is a bend of a and a splay of b.

Another three terms in the elastic free energy density are of the form:

(2) $K_{aa}([(\mathbf{a}\bullet \text{grad})\mathbf{b}]\bullet\mathbf{c})^2$.

This term is non-zero for a distortion in which **b** and **c** rotate about the **a** axis and the rotation angle is proportional to the translation distance along the axis, i.e. a twist about the **a** axis. A cyclic permutation of **a**, **b**, and **c** gives the three terms K_{aa}, K_{bb} and K_{cc}.

The last three terms in the elastic free energy density are coupling terms, and they have the form:

(3) $2C_{ab}([\mathbf{a}\bullet \text{grad}]\mathbf{a})\bullet([\mathbf{b}\bullet \text{grad}]\mathbf{b})$.

As with the other terms, cyclic permutation of the unit vectors and C subscripts leads to the three constants C_{ab}, C_{ac}, and C_{bc}. Unfortunately no simple distortion exists for which only one C term is non-zero. However, a configuration in which the **a-b-c** tripod is aligned with the tripod of unit vectors of the spherical coordinate system will have one non-zero C term.

All twelve bulk elastic constants have now been discussed.

3. Landau Theory

A standard method of estimating values of the elastic constants of both uniaxial and biaxial nematic phases is the phenomenological Landau theory. It is based on an expansion of the free energy density in terms of scalar invariants of powers of a traceless second rank tensor, $Q_{\alpha\beta}$, and its spatial derivatives $\partial_\alpha Q_{\beta\gamma}$. The local principal axes of the tensor are the **a-b-c** tripod of unit vectors, and the eigenvalues of the tensor are determined by the anisotropic values of any chosen tensor property, such as the magnetic susceptibility or the indices of refraction. For example, suppose a biaxial nematic has three indices of refraction $n_1 > n_2 > n_3$ and their average value is n. If $n_2 < n$, we may take $Q_{cc} = n_1 - (n_2 + n_3)/2$ and $Q_{aa} - Q_{bb} = n_2 - n_3$. (If $n_2 >$ n, interchange n_1 and n_3 in these expressions.) Q_{cc} is the uniaxial order parameter and will be called S in the rest of this work, while $n_2 - n_3$ is the biaxial order parameter, which will be called P. Referenced to a Cartesian coordinate system, $Q_{\alpha\beta}$ may be taken to be

(4) $Q_{\alpha\beta} = S(3\mathbf{c}_\alpha\mathbf{c}_\beta - \delta_{\alpha\beta})/2 + P(\mathbf{a}_\alpha\mathbf{a}_\beta - \mathbf{b}_\alpha\mathbf{b}_\beta)/2$.

Monselesan and Trebin [5] showed that the terms in the Landau expansion that are relevant for determining the elastic constants are the invariants of the form $(\partial Q)(\partial Q)$, $Q(\partial Q)(\partial Q)$, and $QQ(\partial Q)(\partial Q)$. There are three invariants of the first type, six of the second type and thirteen of the third type. Unfortunately each invariant introduces a phenomenological coefficient, so the theory contains 22 adjustable coefficients, which is far too many to be of much practical use. The need for the three types of terms is due to the fact that if only the first type is kept, one finds the bend and splay uniaxial elastic constants to be identical (which contradicts experiment), but the expansion is unstable against large deformations if only the second type of term is included but not the third type.

The approach that is taken in this work to overcome the dilemma noted above is to reformulate the problem by not treating the eigenvalues of Q as spatial variables. They are instead assumed to be given functions of temperature. This approach is clearly an approximation that is not always valid because it is known from wetting and defect studies that the eigenvalues *do* change with position in regions near surfaces and in the cores of defects. However these effects seem to *always* be limited to very small length scales. Therefore they will be neglected. When S and P are not functions of position, the expansion is stable if only the first two types of terms are kept. Thus we may discard all thirteen terms of the form $QQ(\partial Q)(\partial Q)$.

The final simplification that has been made is to neglect the surface elastic terms, as was mentioned previously. This simplification is not necessary, but is made because it is convenient and because in most situations the surface terms are unimportant. If they are kept, an additional two terms appear in the free energy density given below.

Under these assumptions, the free energy density reduces to only five terms.

(5) $$2F = L_1(\partial_\alpha Q_{\beta\gamma})(\partial_\alpha Q_{\beta\gamma}) + L_2(\partial_\alpha Q_{\alpha\beta})(\partial_\gamma Q_{\gamma\beta}) + L_4 Q_{\alpha\beta}(\partial_\alpha Q_{\mu\nu})(\partial_\beta Q_{\mu\nu}) + L_5 Q_{\alpha\beta}(\partial_\mu Q_{\mu\alpha})(\partial_\nu Q_{\nu\beta}) + L_6 Q_{\alpha\beta}(\partial_\mu Q_{\nu\alpha})(\partial_\mu Q_{\nu\beta}).$$

Specifically, $(\partial_\alpha Q_{\beta\gamma})(\partial_\beta Q_{\alpha\gamma})$ differs from the term multiplying L_2 by only a surface term, and $Q_{\alpha\beta}(\partial_\mu Q_{\nu\alpha})(\partial_\nu Q_{\mu\beta})$ differs from the term multiplying L_6 by only a surface term. Furthermore, $Q_{\alpha\beta}(\partial_\alpha Q_{\beta\mu})(\partial_\nu Q_{\nu\mu}) = \{Q_{\alpha\beta}(\partial_\alpha Q_{\mu\nu})(\partial_\beta Q_{\mu\nu}) -$

$2\, Q_{\alpha\beta}(\partial_\mu Q_{\mu\alpha})(\partial_\nu Q_{\nu\beta}) + 2\, Q_{\alpha\beta}(\partial_\mu Q_{\nu\alpha})(\partial_\mu Q_{\nu\beta})\}/4$ and

$Q_{\alpha\beta}(\partial_\alpha Q_{\mu\nu})(\partial_\mu Q_{\nu\beta}) = \{Q_{\alpha\beta}(\partial_\alpha Q_{\mu\nu})(\partial_\beta Q_{\mu\nu}) +$

$2\, Q_{\alpha\beta}(\partial_\mu Q_{\nu\alpha})(\partial_\mu Q_{\nu\beta}) - 2\, Q_{\alpha\beta}(\partial_\mu Q_{\nu\alpha})(\partial_\nu Q_{\mu\beta})\}/4$.

This accounts for all six of the terms of the form $Q(\partial Q)(\partial Q)$ and all three of the form $(\partial Q)(\partial Q)$. For the familiar uniaxial nematic phase, this expression for F and Eq. (4) yields the following expressions for the splay, bend and twist elastic constants.

$K_1 = (3S/2)^2(2L_1+L_2)+(3S/2)^3(-2L_4+2L_5+L_6)/3$,

$K_2 = (3S/2)^2(2L_1)+(3S/2)^3(-2L_4+L_6)/3$, and

$K_3 = (3S/2)^2(2L_1+L_2)+(3S/2)^3(4L_4-L_5+L_6)/3$.

Dividing these expressions by S^2 , one expects

K_j/S^2 to be linearly dependent on S with a non-zero intercept. As pointed out in the work of Berreman and Meiboom [6], experimental data on the splay, twist, and bend constants can be fit to the form $K_j/S^2 = b_j + m_j S$ for j = 1,2,3 to obtain values for the five parameters $b_1=b_3$, b_2, m_1, m_2, and m_3. For the materials analyzed in ref.[6], m_1 and m_2 were negative but m_3 was positive. The five L's are then given by $L_1=2b_2/9$, $L_2=4(b_1-b_2)/9$, $L_4=2(m_1-3m_2+2m_3)/27$, $L_5=4(m_1-m_2)/9$, and $L_6=4(m_1+3m_2+2m_3)/27$.

Thus all five phenomenological parameters can in principle be determined from data on the uniaxial elastic constants, i.e. the b's and m's.

4. Results for Biaxial Elastic Constants

In this section, the results of the Landau theory for estimating all twelve bulk biaxial phase elastic constants are given. It is useful to simplify the expressions by making the following notational definitions: $x = 3S/2$, $y = P/3S$, $D_1 = 2L_1+L_2$, and $D_2 = 2L_1$. The variable y represents the biaxial order parameter P.

$$K_{aa} = x^2D_2(1+y)^2 + x^3(-2L_4+L_6)(1+y)^2(1-3y)/3$$

$$K_{bb} = x^2D_2(1-y)^2 + x^3(-2L_4+L_6)(1-y)^2(1+3y)/3$$

$$K_{cc} = x^2D_2(4y^2) - x^3(-2L_4+L_6)(8y^2)/3$$

$$K_{ab} = x^2D_1(4y^2) - x^3[2L_4(1-3y)+L_5(1+3y)+2L_6](4y^2)/3$$

$$K_{ac} = x^2D_1(1-y)^2 - x^3[2L_4(1-3y)-2L_5-L_6(1+3y)](1-y)^2/3$$

$$K_{ba} = x^2D_1(4y^2) - x^3[2L_4(1+3y)+L_5(1-3y)+2L_6](4y^2)/3$$

$$K_{bc} = x^2D_1(1+y)^2 - x^3[2L_4(1+3y)-2L_5-L_6(1-3y)](1+y)^2/3$$

$$K_{ca} = x^2D_1(1-y)^2 + x^3[4L_4-L_5(1-3y)+L_6(1+3y)](1-y)^2/3$$

$$K_{cb} = x^2D_1(1+y)^2 + x^3[4L_4-L_5(1+3y)+L_6(1-3y)](1+y)^2/3$$

$$C_{ab} = x^2L_2(1-y^2) + x^3[2L_5](1-y^2)/3$$

$$C_{ac} = x^2L_2[2y(1+y)] - x^3[2L_5][y(1+y)(1+3y)]/3$$

$$C_{bc} = -x^2L_2[2y(1-y)] + x^3[2L_5][y(1-y)(1-3y)]/3$$

At a second order transition between uniaxial and biaxial nematic phases, y goes to zero, so taking the limit y goes to zero in the preceding equations, one finds the values of the constants at the transition.

The values are $K_{aa} = K_{bb} = K_2$, $K_{ac} = K_{bc} = K_1$, $K_{ca} = K_{cb} = K_3$, $C_{ab} = K_1 - K_2$, and the other five constants are zero. As temperature is reduced and y(P) increases, the degeneracy is destroyed and each constant has a distinct value.

5. Conclusions

Motivated by the recent experimental observations of thermotropic biaxial nematic phases, this work has analyzed their elastic properties. The important new result presented here is the demonstration of a practical method to characterize all twelve bulk elastic constants in terms of only five adjustable parameters, and to indicate how these parameters can be experimentally determined.

6. References

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