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Tensor representation of Oseen-Frank strain energy in uniaxial cholesterics

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de Gennes gave a three-parameter representation of strain energy in a cholesteric liquid crystal that is second order on the Q tensor, and hence in order parameter. He discarded a term involving an elastic constant K_{24} which is relevant at surfaces and disclinations. The splay and bend elastic constants K_{11} and K_{33} are alike in the second-order theory. The complete Oseen-Frank expression in terms of a director has five parameters, including K_{24}. If uniaxiality, which is implicit in the director theory, is imposed on the Q tensor, five independent third-order tensor functions are found. These differentiate between K_{11} and K_{33} and show the third-order dependence of the Oseen-Frank elastic constants on order parameter. Numerical values of these second- and third-order elastic coefficients of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA), *p*-azoxyanisole (PAA), and E-7 (British Drug House designation of a cyano-biphenyl mixture) are obtained from published values of the dependence of Oseen-Frank elastic constants and various anisotropies on temperature, and from a relation of Nehring and Saupe.

BACKGROUND

In order to unify the representation of strain and thermal free energy in cholesteric or nematic liquid crystals, de Gennes[1] wrote a second-order Landau-tensor representation of strain energy density. The Landau tensor Q is symmetric and has zero trace. If Q corresponds to a uniaxial liquid crystal its diagonalized form is

$$\begin{aligned} Q_{11}&=-S/3\ ,\\ Q_{22}&=-S/3\ ,\\ Q_{33}&=2S/3\ . \end{aligned} \tag{1}$$

S is the directional order parameter of the uniaxial liquid crystal. de Gennes's expression for the combined thermal and strain free energy of a cholesteric in the absence of an electric or magnetic field may be written

$$\begin{aligned} F=F_0&+A^{(2)}(T)Q^2+A^{(3)}(T)Q^3+A^{(4)}(T)Q^4+\cdots\\ &+C_1^{(2)}Q_{ij,k}Q_{ij,k}+C_2^{(2)}Q_{ij,j}Q_{ik,k}\\ &+C_4^{(2)}e_{ijk}Q_{il}Q_{jl,k}=F_T+F_s\ . \end{aligned} \tag{2}$$

In this and succeeding expressions a subscript after a comma represents differentiation with respect to the corresponding rectangular coordinate. Also, e_{ijk} is the perfect antisymmetric tensor, which is 0 if two or more subscripts are alike, 1 if they are in the order 123, 231, or 312, and -1 otherwise. Summation over repeated indexes is to be understood when not stated explicitly.

In de Gennes's approximation there are three parameters related to elastic energy, which we have called $C_1^{(2)}$, $C_2^{(2)}$, and $C_4^{(2)}$. The Oseen-Frank expression in terms of director variation contains five parameters: the helicity q_0 and four elastic constant K_{11}, K_{22}, K_{33}, and K_{24} (see Refs. 2–4). The last constant K_{24} goes with a divergence term that de Gennes discarded from his simplified Landau theory. Static equilibrium configurations surrounded by boundaries of predetermined orientation are not affected by the omission of that term but it has an effect on configurations bounded by free or elastically attached surface layers, including some theories of the blue phase.[5,6]

As pointed out by de Jeu,[7] a second-order expansion yields the same value for K_{11} as for K_{33}, so that the two should approach one another as temperature rises and order parameter decreases. This accounts for the second missing parameter in de Gennes's expansion.

Schiele and Trimper[8] recently extended the tensor theory to third order in Q for nematics. They showed that one of the third-order terms will remove the degeneracy between K_{11} and K_{33} but they followed de Gennes in discarding K_{24} and the associated divergence term. In this paper we will show the relation between all five of the Oseen-Frank terms and all of the second- and third-order terms in the Landau expansion of the strain energy for a uniaxial cholesteric.

DIRECTION REPRESENTATION OF STRAIN ENERGY

The Oseen-Frank strain energy of a uniaxial cholesteric may be represented by a sum of five vector functions V_1 to V_5 multiplied by material parameters K_1 to K_5 that are functions of q_0 and the four K_{ij}, as follows:

$$F_s=\sum_{i=1}^{5}K_iV_i\ , \tag{3}$$

where

$$\begin{aligned} V_1&=(\mathrm{div}\vec{n})^2/2\ ,\\ V_2&=(\vec{n}\cdot\mathrm{curl}\vec{n})^2/2\ ,\\ V_3&=(\vec{n}\times\mathrm{curl}\vec{n})\cdot(\vec{n}\times\mathrm{curl}\vec{n})/2\ ,\\ V_4&=(n_{i,j}n_{j,i}-n_{i,i}n_{j,j})/2\ ,\\ V_5&=-\vec{n}\cdot\mathrm{curl}\vec{n}\ . \end{aligned} \tag{4}$$

$\vec{n}$ is the local unit vector in the direction of the principal axis of the uniaxial liquid crystal.

The parameters K_i of Eq. (3) are related to the Oseen-Frank elastic constants and helicity as follows:

$$\begin{aligned} K_1 &= K_{11} , \\ K_2 &= K_{22} , \\ K_3 &= K_{33} , \\ K_4 &= K_{22} + K_{24} , \\ K_5 &= q_0 K_{22} . \end{aligned} \tag{5}$$

The term $K_4 V_4$ is often omitted because its contribution to total energy may be changed from a volume to a surface integral by the application of Gauss's theorem. Consequently, if the surface orientation is predetermined the equilibrium configuration does not depend on V_4. This argument does not apply if the surface orientations are not fixed.

TENSOR REPRESENTATION OF STRAIN ENERGY

In a uniaxial region of a cholesteric or nematic liquid crystal when a director $\vec{n}$ has its ordinary meaning, the order tensor elements may be expressed as

$$Q_{ij} = S \left[n_i n_j - \frac{\delta_{ij}}{3} \right] . \tag{6}$$

de Gennes made the theory simple by discarding terms higher than second order in Q in the strain, and also by omitting a term that would contribute to V_4. In the notation we shall adopt, de Gennes's strain terms are

$$G_1^{(2)} = Q_{ij,k} Q_{ij,k} , \tag{7.1}$$

$$G_2^{(2)} = Q_{ij,j} Q_{ik,k} , \tag{7.2}$$

and

$$G_4^{(2)} = e_{ijk} Q_{il} Q_{jl,k} . \tag{7.3}$$

The order of the first two indexes on Q is irrelevant since Q and its derivatives are symmetric.

The second-order expression in Q that de Gennes discarded is

$$G_3^{(2)} = Q_{ij,k} Q_{ik,j} . \tag{7.4}$$

$G_3^{(2)}$ makes possible the separation of the divergence term from the rest of the energy but it still does not differentiate between splay energy $K_1 V_1$ and bend energy $K_3 V_3$.

By algebraic manipulation or by comparing of numerical values for various strains it can be shown that if the order parameter S is invariant and the Q tensor is uniaxial,

$$\begin{aligned} G_1^{(2)} &= 4S^2[(V_1 + V_3) + V_2 + V_4] , \\ G_2^{(2)} &= 2S^2(V_1 + V_3) , \\ G_3^{(2)} &= 2S^2[(V_1 + V_3) + V_4] , \\ G_4^{(2)} &= S^2 V_5 . \end{aligned} \tag{8}$$

Note that there is no way to separate V_1 and V_3 among Eqs. (8). Conversely,

$$\begin{aligned} V_2 &= (G_1^{(2)} - 2G_3^{(2)})/4S^2 , \\ V_4 &= (-G_2^{(2)} + G_3^{(2)})/2S^2 . \end{aligned} \tag{9}$$

THIRD-ORDER TERMS IN THE Q TENSOR

In the preceding section we listed the four independent second-order functions $G_j^{(2)}$. To extend the series to third order, we have made an exhaustive search of all nondegenerate third-order scalar contractions of the general form $Q_{ij} Q_{kl,m} Q_{no,p}$, with the restriction of uniaxiality. Each subscript appears twice in the contractions, as they do in Eqs. (7). As shown by Schiele and Trimper,[8] the Oseen-Frank elastic constants K_{11} and K_{33} are not degenerate in such third-order terms.

There are six different third-order expressions that are not identically zero and that are second order in derivatives of Q. They are

$$G_1^{(3)} = Q_{ij} Q_{ik,j} Q_{kl,l} , \tag{10.1}$$

$$G_2^{(3)} = Q_{ij} Q_{ik,k} Q_{jl,l} , \tag{10.2}$$

$$G_3^{(3)} = Q_{ij} Q_{ik,l} Q_{jk,l} , \tag{10.3}$$

$$G_4^{(3)} = Q_{ij} Q_{ik,l} Q_{jl,k} , \tag{10.4}$$

$$G_5^{(3)} = Q_{ij} Q_{ik,l} Q_{kl,j} , \tag{10.5}$$

$$G_6^{(3)} = Q_{ij} Q_{kl,i} Q_{kl,j} . \tag{10.6}$$

There is also a helicity term that is third order in Q,

$$G_7^{(3)} = e_{ijk} Q_{il} Q_{jm} Q_{kl,m} . \tag{10.7}$$

The algebraic derivation of the relation between $G_j^{(3)}$ and of the vector terms V_i is extremely tedious. We originally obtained them by computing numerical values of V_i with Eqs. (4) for several independent forms of strain, then computing values of $G_j^{(3)}$ for the same strains with Eqs. (7), and finally solving the resulting set of linear equations. Results were further verified by numerical evaluation of V_i and $G_j^{(3)}$ with other, different strain fields.

We find that if the order parameter S is invariant and the Q tensor is uniaxial,

$$\begin{aligned} G_1^{(3)} &= 2S^3(-V_1 + 2V_3) , \\ G_2^{(3)} &= 2S^3(V_1 - 2V_3) , \\ G_3^{(3)} &= 2S^3(V_1 + V_2 + V_3 + V_4) , \\ G_4^{(3)} &= 2S^3(2V_1 - V_3 + 2V_2) , \\ G_5^{(3)} &= 2S^3(-V_1 + 2V_3 - V_4) , \\ G_6^{(3)} &= 4S^3(-V_1 - V_2 + 2V_3 - V_4) , \\ G_7^{(3)} &= S^3 V_5 / 3 . \end{aligned} \tag{11}$$

Since there are seven tensor functions, $G_j^{(3)}$, and only five vector functions, V_i, the tensor functions are not all independent for uniaxial liquid crystals with invariant order parameter. We need use only the first four tensor functions to give the inverse relations

$$\begin{aligned} V_1&=(G_1^{(3)}+2G_2^{(3)})/2S^3\ ,\\ V_2&=3(-2G_1^{(3)}-G_2^{(3)}+2G_3^{(3)}-G_4^{(3)})/4S^3\ ,\\ V_3&=(2G_1^{(3)}+G_2^{(3)})/2S^3\ ,\\ V_4&=3(-G_2^{(3)}+G_4^{(3)})/4S^3\ . \end{aligned} \tag{12}$$

We may also show that for uniaxial tensors,

$$\begin{aligned} G_5^{(3)}&=G_1^{(3)}+(G_2^{(3)}-G_4^{(3)})/2\ ,\\ G_6^{(3)}&=4G_1^{(3)}+2G_2^{(3)}-2G_3^{(3)}\ . \end{aligned} \tag{13}$$

The last two relations would not apply in a theory that did not make the liquid crystal strictly uniaxial. Two more elastic constants would appear in such a more general third-order Landau theory.

Schiele and Trimper[8] give three rather than only two relations among the first six third-order expressions. Their expressions for $G_1^{(2)}$, $G_2^{(2)}$, $G_1^{(3)}$, and $G_2^{(3)}$ are equivalent to ours. Their expressions for $G_6^{(3)}$ would be equivalent to ours if we were to assert that V_4 is zero. They actually use only $G_1^{(2)}$, $G_2^{(2)}$, and $G_6^{(3)}$, which suffice to lift the degeneracy between K_{11} and K_{33}, in their final discussion.

CONSTANTS FOR THE THIRD-ORDER LANDAU THEORY

We have shown that the Landau expansion for the strain energy of a strictly uniaxial cholesteric liquid crystal may be expressed in the form

$$F_s=\sum_{j=1}^{4} C_j^{(2)}G_j^{(2)}+\left[\sum_{j=1}^{4} C_j^{(3)}G_j^{(3)}+C_7^{(3)}G_7^{(3)}\right]+\cdots\ . \tag{14}$$

Comparing this with Eq. (3) we may conclude that

$$K_i=S^2K_i^{(2)}+S^3K_i^{(3)}+\cdots\ . \tag{15}$$

By turning Eqs. (9) and (12) around it can be shown that the constants $C_j^{(n)}$ of Eq. (14) are related to the constants $K_i^{(n)}$ of Eq. (15) as follows:

$$\begin{aligned} C_1^{(2)}&=K_2^{(2)}/4\ ,\\ C_2^{(2)}&=(K_1^{(2)}-K_4^{(2)})/2=(K_3^{(2)}-K_4^{(2)})/2\ ,\\ C_3^{(2)}&=(-K_2^{(2)}+K_4^{(2)})/2\ ,\\ C_4^{(2)}&=K_5^{(2)}\ . \end{aligned} \tag{16}$$

Also,

$$\begin{aligned} C_1^{(3)}&=0.5K_1^{(3)}-1.5K_2^{(3)}+K_3^{(3)}\ ,\\ C_2^{(3)}&=K_1^{(3)}-0.75K_2^{(3)}+0.5K_3^{(3)}-0.75K_4^{(3)}\ ,\\ C_3^{(3)}&=1.5K_2^{(3)}\ ,\\ C_4^{(3)}&=-0.75K_2^{(3)}+0.75K_4^{(3)}\ ,\\ C_7^{(3)}&=3K_5^{(3)}\ . \end{aligned} \tag{17}$$

PARAMETERS ESTIMATED FROM PUBLISHED DATA

Published data for MBBA and PAA (see Ref. 9) and for E-7 (see Ref. 10) will now be analyzed to obtain estimates of the elastic constants associated with the third-order tensor theory. Since these liquid crystals are nematic the chirality constant K_5 is 0. Unfortunately there are no published measurements of K_i for cholesterics so we are unable to give examples of the complete theory. The data for PAA, MBBA, and E-7 include the first three Oseen-Frank elastic constants K_1, K_2, and K_3, and the magnetic anisotropy or, for E-7, the dielectric anisotropy, as functions of temperature. The nematic-to-isotropic transition temperature is also given.

We may reasonably assume that magnetic or dielectric anisotropy is nearly proportional to order parameter in these materials. In order to get the constant of proportionality we have assumed that the order parameter at the highest temperature for which the data were tabulated is given by the Maier-Saupe theory.[11,12] The data are probably not precise enough to warrant a correction for thermal expansion.

We wish to determine the coefficients in a power series of the form shown in Eq. (15). We have plotted the ratio of the three known elastic constants to the square of the order parameter versus the order parameter in Figs. 1—3. We should obtain horizontal lines if there were no term of higher order than second, $K_i^{(2)}$, or straight sloping lines if there were no term of higher order than third, $K_i^{(3)}$, in the Landau expansion of the terms in a particular elastic constant.

In fact, nearly all the curves show unmistakable upward curvature. We could simply add a second-order polynomial term to fit this upward curvature. Instead, we have chosen to use a function for the last term that diverges when the order parameter, S, approaches unity. The particular form we have chosen is

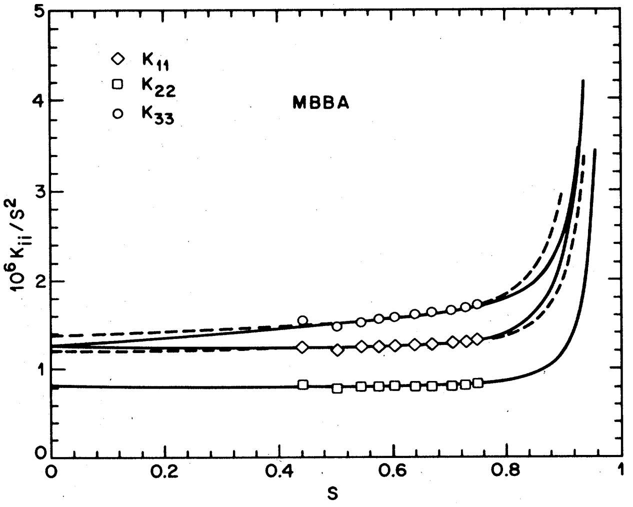

FIG. 1. Variation of K_{ii}/S^2 with S for MBBA (see Ref. 9).

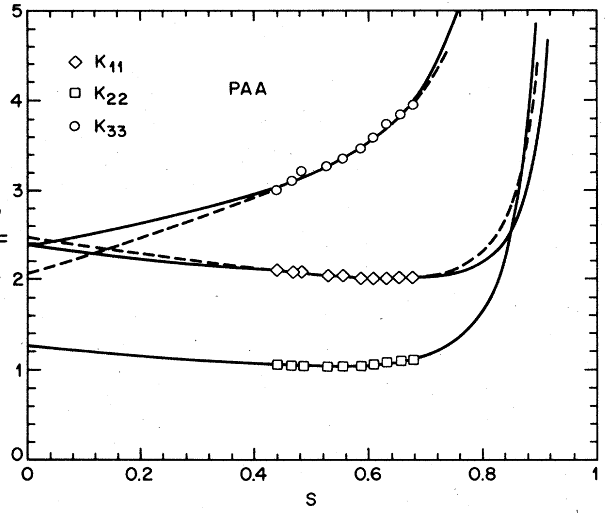

FIG. 2. Variation of K_{ii}/S^2 with S for PAA (see Ref. 9).

$$\frac{K_{ii}}{S^2}=K_i^{(2)}+K_i^{(3)}S+K_i^{(4)}\left[\frac{S}{1-S}\right]^2$$

$$=K_i^{(2)}+K_i^{(3)}S+K_i^{(4)}(S^2+2S^3+3S^4+\cdots)\ . \qquad (18)$$

The liquid crystal elastic constants should diverge and the order parameter should approach unity simultaneously if the nematic crystallizes directly into a solid. If a smectic phase lies between the nematic and the solid phases, the bend constant, K_{33}, should diverge at higher temperature or lower order parameter than the splay constant, K_{11}. A "virtual" smectic state may account for the greater curvature in the K_{33} curves than in the K_{11} curves for most of the materials listed. However, we do not think either the data or our choice of divergent function are sufficiently accurate to warrant using different low-temperature transition temperatures in our curve fitting.

Figures 1—3 show curves of this form that are least-squares fitted to the data. The solid curves are obtained from a least-squares fit with the condition that K_{11} and K_{33} must converge at $S=0$. The dashed curves are least-square fits without that condition. The data for K_{11} and K_{33} are weighted in inverse proportion to the rms error in the fit on the dashed curves before getting the solid curves. The result of this weighting is that the rms error of each curve is increased in the same proportion. The increase in rms error in the solid curves is well within the uncertainty of the fit in each case. The parameters determined by the fitting are listed in Table I.

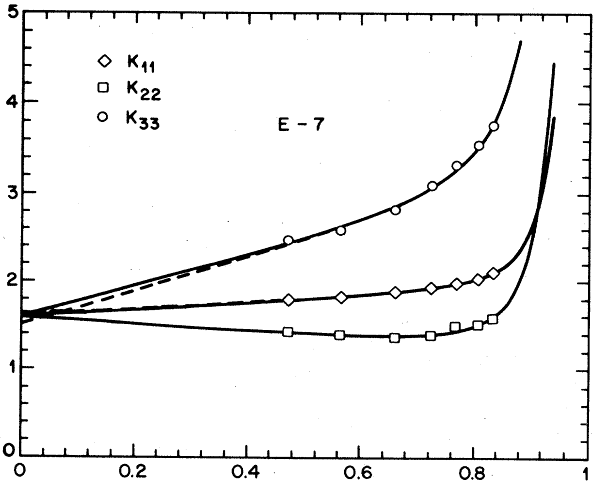

FIG. 3. Variation of K_{ii}/S^2 with S for E-7 (see Ref. 10).

In all the examples we have studied K_{11}/S^2 and K_{33}/S^2 tend to move toward move toward one another as order parameter approaches zero. Although the data do not demonstrate that the curves for K_{11}/S^2 and K_{33}/S^2 converge at zero order parameter, they are consistent with such a hypothesis in each case.

Since there are no measurements of K_{24} we shall resort to the assumption that

$$K_{24}=(K_{11}-K_{22})/2\ . \qquad (19)$$

This relation was derived by Nehring and Saupe[4] using a model involving only nearest-neighbor interactions. If this model is accurate to third order in Landau theory then

$$K_4^{(n)}=(K_1^{(n)}+K_2^{(n)})/2\ , \qquad (20)$$

where n is 2 or 3.

Finally we note that the constants $C_j^{(n)}$ in Eqs. (2) and (14) could depend on temperature as the constants $A^{(n)}(T)$ do. We hope that this temperature dependence is small enough that the estimation of the constants $C_j^{(n)}$ from data at different temperatures will be approximately correct.

TABLE I. Elastic constants and fitting errors. Units are 10^{-6} dyn.

	MBBA	PAA	E-7
Fit with $K_{11}=K_{33}$ at $S=0$:			
$K_1^{(2)}$	1.272	2.381	1.608
$K_1^{(3)}$	−0.072	−0.687	0.379
rms error	0.0013	0.0010	0.000 56
Best fit:			
$K_1^{(2)}$	1.213	2.468	1.622
$K_1^{(3)}$	0.046	−0.886	0.355
rms error	0.0012	0.0009	0.000 54
$K_2^{(2)}$	0.821	1.267	1.594
$K_2^{(3)}$	−0.041	−0.560	−0.389
rms error	0.0014	0.0008	0.0026
Fit with $K_{11}=K_{33}$ at $S=0$:			
$K_3^{(2)}$	1.272	2.381	1.608
$K_2^{(3)}$	0.485	1.280	1.740
rms error	0.0026	0.0035	0.0039
Best fit:			
$K_3^{(2)}$	1.388	2.081	1.514
$K_3^{(3)}$	0.253	1.960	1.740
rms error	0.0024	0.0032	0.0038
From equation (20), assuming $K_{11}=K_{33}$ at $S=0$:			
$K_4^{(2)}$	1.046	1.824	1.576
$K_4^{(3)}$	−0.056	−0.624	−0.045

CONCLUSIONS

We have written a Landau expansion for strain energy in uniaxial cholesteric liquid crystals that is complete to third order in strains. We have verified that the Landau theory predicts no difference between $K_1^{(2)}$ and $K_3^{(2)}$, and that it predicts five independent third-order terms if the tensor is uniaxial.

The phase transitions of cholesteric and nematic liquid crystals are rather strongly first order. The order parameter is usually more than 0.4 just below the isotropic transition. Consequently a Landau expansion to third order is not a very precise description of their behavior. However, it is our hope that a better qualitative understanding of their behavior near disclinations and in other regions of high strain can be achieved through the merging of thermal and strain energies in one unified theory. We believe that it will prove helpful to have the elastic parameters listed here, imprecise as they may be, in such an endeavor. In the neighborhood of a disclination, particularly, the restriction that the tensor Q be uniaxial is also a severe limitation. However, there are no data at present that would hint at the magnitude of the two additional constants that would be required in more general theory with all seven third-order terms.

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