Cholesteric energies

By JAMES T. JENKINS

Department of Mechanics, The Johns Hopkins University†

Repeated observations of a uniformly twisted director field in cholesteric liquid crystals are used to motivate an expression for a free energy which is obtained as an expansion about this state. Terms quadratic in the director perturbation and the gradients of this perturbation are retained. Utilizing invariance arguments, it is possible to obtain significant simplification of the coefficients which appear in the expansion. A properly invariant form of the free energy is produced which agrees with the expansion for small excursions about a twisted state, and which assigns arbitrary values to the non-vanishing coefficients.

The consequences of requiring that a free energy achieve a minimum at a twisted state are explored. A commonly used form of the free energy for cholesteric liquid crystals is seen to be rather severely restricted by this requirement. An alternative to this form is proposed which is a special case of the free energy previously produced. The particular form suggested attains a unique absolute minimum at a characteristic uniform twist.

1. Introduction

Liquid crystals are fluids composed of large, relatively rigid, rod-like molecules. At a point the molecules tend to align parallel to one another. The direction of this parallel will generally vary smoothly from point to point. The existence of this preferred direction gives rise to the anisotropic behaviour typical of these materials. For two common types of liquid crystals, nematic and cholesteric, the molecules are free to translate in any direction, and the material may flow. In the continuum theory of liquid crystals, as reviewed by Ericksen (1967 a), the preferred direction is described by a vector field $\mathbf{n}(\mathbf{x}, t)$. The vector $\mathbf{n}$ is called the director.

The nematic and cholesteric types of liquid crystals are distinguished by characteristic director orientations which are observed in static equilibrium. For nematic liquid crystals this characteristic pattern is a uniform parallel orientation. In liquid crystals of cholesteric type, the equilibrium configuration often observed is that of a uniform twist. Here, the directors are everywhere perpendicular to a single direction. In any plane with this direction as a normal parallel orientation obtains. However, as this normal is traversed, the orientation changes in an uniform fashion. These ideal orientations, or recognizable distortions of them, are reported to occur in various materials of the same type; and, apparently, persist in samples of varying size and shape (Robinson, Ward &

† Present address: Faculté des Sciences, Laboratoire de Physique des Solides, 91-Orsay, France.

Beevers 1958). As remarked by Ericksen (1966*a*, 1967*a*), these considerations suggest that these configurations are, for the particular type of material considered, of relatively low energy, and represent states which are, in some sense, stable.

To solve problems in the static theory for these liquid crystals one frequently employs a simple form for the free energy proposed by Frank (1958). This form is essentially obtained as an expansion about a uniform parallel orientation. Terms linear and quadratic in the director gradient are retained. While this procedure appears reasonable for liquid crystals of nematic type, it is not apparent that a free energy derived in this fashion applies to cholesteric liquid crystals. Here, we use the observations of the twisted equilibrium state in cholesteric liquid crystals as the basis for developing a quadratic free energy governing small excursions from this state. The occurrence of the basic twist and this quadratic energy are together used to motivate a general form of the free energy which may characterize liquid crystals of cholesteric type.

2. Governing equations

We consider the hydrostatic theory of liquid crystals as presented by Ericksen (1962*a*) and Leslie (1968*a*, *b*). We assume that the director $\mathbf{n}(\mathbf{x})$, which describes the orientation of the liquid crystal, is of fixed length and satisfies the normalization condition

$$\mathbf{n} \cdot \mathbf{n} = 1. \tag{2.1}$$

Also, the liquid is considered to be incompressible. In the static theory, the energy density W, interpreted as the Helmholtz free energy per unit volume, is of the form,

$$W = W(\mathbf{n}, \nabla\mathbf{n}). \tag{2.2}$$

It is required that this energy remain unchanged when the material is rigidly rotated. Thus,

$$W(\mathsf{R}\mathbf{n}, \mathsf{R}\,\nabla\mathbf{n}\mathsf{R}^T) = W(\mathbf{n}, \nabla\mathbf{n}) \tag{2.3}$$

where

$$\mathsf{R}^T = \mathsf{R}^{-1} \quad \text{and} \quad \det \mathsf{R} = 1. \tag{2.4}$$

Then, derivatives of W with respect to $\mathbf{n}$ and $\nabla\mathbf{n}$ transform as tensors of the appropriate order.

As Ericksen (1961) indicates, a consequence of (2.3) is

$$B_{ij} \equiv n_i \frac{\partial W}{\partial n_j} + n_{i,k} \frac{\partial W}{\partial n_{j,k}} + n_{k,i} \frac{\partial W}{\partial n_{k,j}} = B_{ji}. \tag{2.5}$$

For liquid crystals of cholesteric and nematic type, $\mathbf{n}$ and $-\mathbf{n}$ are physically indistinguishable; thus,

$$W(\mathbf{n}, \nabla\mathbf{n}) = W(-\mathbf{n}, -\nabla\mathbf{n}). \tag{2.6}$$

For liquid crystals of nematic type W is further restricted to remain invariant under both proper and improper rotations.

Using Leslie's work, we may write down expressions for the stress $\mathbf{t}$ and the couple stress $\mathbf{l}$ which apply in a static isothermal state:

$$t_{ik} = -p\,\delta_{ik} - w_{jk}n_{j,i} + (\mu\epsilon_{juk}n_u n_i)_{,j}, \tag{2.7}$$

$$l_{ik} = \epsilon_{iuv}n_u(w_{vk} + \mu\epsilon_{vkp}n_p), \tag{2.8}$$

where

$$w_{ik} \equiv \partial W/\partial n_{i,k}, \tag{2.9}$$

μ is a material constant, and the pressure p is an arbitrary function of position. At material boundaries, the surface force **F** is given, in terms of **t** and the outward normal to the boundary **ν**, by

$$F_i = t_{ik}\nu_k; \tag{2.10}$$

and **L**, that portion of the surface moment which is independent of the surface force, is, in terms of **l** and **ν**,

$$L_i = l_{ik}\nu_k. \tag{2.11}$$

When external influences are absent, the equilibrium equations are

$$t_{ik,k} = 0 \tag{2.12}$$

and

$$w_{ik,k} - \left(\frac{\partial W}{\partial n_i}\right) = \lambda n_i. \tag{2.13}$$

Here, the director tension λ, is an arbitrary function of position. Equation (2.12) is satisfied if **n** is a solution of (2.13) and the pressure is given by

$$p + W = a = \text{const.} \tag{2.14}$$

3. A quadratic free energy

Ericksen (1967 *b*) has proved that the director field

$$n_i = N_i \equiv (\cos\theta, \sin\theta, 0), \tag{3.1}$$

with

$$\theta = bx_3 + c, \tag{3.2}$$

and b and c arbitrary constants, is a general solution of (2.13). That is, for some choice of λ, the field (3.1) is a solution of (2.13) for any W which satisfies (2.3).

Motivated, then, by the natural occurrence in cholesteric liquid crystals of equilibrium configurations resembling the field (3.1), we propose a free energy F obtained by expanding W about this uniformly twisted state. We write

$$n_i = N_i + u_i \tag{3.3}$$

and

$$n_{i,k} = N_{i,k} + u_{i,k}, \tag{3.4}$$

where **N** is given by (3.1).

Then, in terms of **N** and **u**, the constraint (2.1) is

$$2N_k u_k + u_k u_k = 0. \tag{3.5}$$

In the expansion we retain only terms linear and quadratic in **u** and ∇**u**. Thus

$$F = A^{(0)} + A_i^{(1)}u_i + A_{ik}^{(2)}u_{i,k} + A_{ik}^{(3)}u_i u_k + A_{ijk}^{(4)}u_i u_{j,k} + A_{ijkp}^{(5)}u_{i,j}u_{k,p}. \tag{3.6}$$

Here, for example,

$$A_{ik}^{(3)} = \frac{1}{2}\frac{\partial^2 W}{\partial N_i \partial N_k} = A_{ki}^{(3)} \tag{3.7}$$

and

$$A_{ijkp}^{(5)} = \frac{1}{2}\frac{\partial^2 W}{\partial N_{i,j} \partial N_{k,p}} = A_{kpij}^{(5)}, \tag{3.8}$$

where derivatives shown with respect to $\mathbf{N}$ and $\nabla\mathbf{N}$ indicate derivatives taken with respect to $\mathbf{n}$ and $\nabla\mathbf{n}$ evaluated at the state (3.1). For the remainder, we assume, without loss of generality, that

$$A^{(0)} = 0. \tag{3.9}$$

4. Invariance arguments

We use the invariance arguments of Ericksen (1967b) to determine the non-vanishing coefficients in the expansion (3.6).

For the field (3.1), W reduces to a function of

$$\theta = bx_3 + c \tag{4.1}$$

and

$$\theta' = \frac{d\theta}{dx_3} = b. \tag{4.2}$$

We assume $b \neq 0$.

Changing c in (4.1) amounts to a rigid rotation (2.4) of the material about the x_3-axis. Because by (2.3) W is invariant under these rotations, it must be independent of θ; hence,

$$W = W(\theta') = W(b). \tag{4.3}$$

The quantity

$$N_{i,k}\frac{\partial W}{\partial N_{i,k}} = N_i'\frac{\partial W}{\partial N_{i,3}} \tag{4.4}$$

transforms as a scalar under rotations about the x_3-axis; then, by the same argument,

$$N_i'\frac{\partial W}{\partial N_{i,3}} = M(b). \tag{4.5}$$

Obviously, similar results obtain for combinations of $\mathbf{N}$, $\nabla\mathbf{N}$ and the higher derivatives of W which transform as scalars under rotations about the x_3-axis. However, an immediate simplification occurs for those combinations in which the index 3 is repeated an odd number of times.

Consider a 180° rotation about the x_3-axis; then, for example,

$$\partial W/\partial N_3 = k(\mathbf{N}, \mathbf{N}') = k(-\mathbf{N}, -\mathbf{N}'). \tag{4.6}$$

However, a 180° rotation about $\mathbf{N}'$ gives

$$k(\mathbf{N}, \mathbf{N}') = -k(\mathbf{N}, \mathbf{N}'), \tag{4.7}$$

so

$$\frac{\partial W}{\partial N_3} = A_3^{(1)} = 0, \tag{4.8}$$

$$N_i'A_i^{(1)} = 0, \tag{4.9}$$

$$N_iA_{i3}^{(2)} = N_iA_{3i}^{(2)} = 0, \tag{4.10}$$

$$N_i'A_{ik}^{(3)}N_k = 0, \tag{4.11}$$

$$N_iA_{i3}^{(3)} = 0, \tag{4.12}$$

$$N_iN_jN_k'A_{ijk}^{(4)} = N_iN_jN_k'A_{ikj}^{(4)} = N_iN_jN_k'A_{kij}^{(4)} = 0, \tag{4.13}$$

$$N_i N_j N_k' A_{jik}^{(4)} = N_i N_j N_k' A_{jki}^{(4)} = N_i N_j N_k' A_{kji}^{(4)} = 0, \tag{4.14}$$

$$N_i N_j A_{ij3}^{(4)} = N_i N_j A_{i3j}^{(4)} = N_i N_j A_{3ij}^{(4)} = 0, \tag{4.15}$$

$$N_i' N_j' A_{ij3}^{(4)} = N_i' N_j' A_{i3j}^{(4)} = N_i' N_j' A_{3ij}^{(4)} = 0, \tag{4.16}$$

$$N_i' A_{i33}^{(4)} = N_i' A_{3i3}^{(4)} = N_i' A_{33i}^{(4)} = 0, \tag{4.17}$$

$$A_{333}^{(4)} = 0, \tag{4.18}$$

$$N_i N_j N_k N_p' A_{ijkp}^{(5)} = N_i N_j N_k N_p' A_{ijpk}^{(5)} = 0, \tag{4.19}$$

$$N_i N_j' N_k' N_p' A_{ijkp}^{(5)} = N_i N_j' N_k' N_p' A_{jikp}^{(5)} = 0, \tag{4.20}$$

$$N_j N_k N_p A_{3jkp}^{(5)} = N_i N_j N_k A_{i3jk}^{(5)} = 0, \tag{4.21}$$

$$N_i N_j' N_k' A_{3ijk}^{(5)} = N_i N_j' N_k' A_{i3jk}^{(5)} = 0, \quad N_i N_j' N_k' A_{3jik}^{(5)} = N_i N_j' N_k' A_{j3ik}^{(5)} = 0, \tag{4.22}$$

$$N_i N_j' A_{ij33}^{(5)} = N_i N_j' A_{i3j3}^{(5)} = N_i N_j' A_{i33j}^{(5)} = 0, \tag{4.23}$$

$$N_i' N_j A_{ij33}^{(5)} = N_i' N_j A_{i3j3}^{(5)} = N_i' N_j A_{i33j}^{(5)} = 0, \tag{4.24}$$

$$N_i A_{i333}^{(5)} = N_i A_{3i33}^{(5)} = 0. \tag{4.25}$$

Another of Ericksen's (1967*b*) arguments yields additional information about the remaining coefficients. The vector

$$v_i \equiv \epsilon_{ijk} \frac{\partial W}{\partial N_{m,k}} N_{m,j} = \epsilon_{i3k} \frac{\partial W}{\partial N_{m,k}} N_m' = v_i(\mathbf{N}, \mathbf{N}') \tag{4.26}$$

is, according to (2.6), unaffected if the signs of **N** and **N**' be reversed. Such a change, combined with a 180° rotation about the x_3-axis, leaves **N** and **N**' unaltered, but should take $\mathbf{v} \to -\mathbf{v}$. Thus,

$$\mathbf{v}(\mathbf{N}, \mathbf{N}') = -\mathbf{v}(\mathbf{N}, \mathbf{N}') = 0; \tag{4.27}$$

so
$$\epsilon_{i3k} N_m' A_{mk}^{(3)} = 0. \tag{4.28}$$

A repetition of the argument gives

$$\epsilon_{i3k} N_m A_{mk}^{(3)} = 0. \tag{4.29}$$

A consequence of (4.28) and (4.29) is

$$A_{\alpha\beta}^{(3)} = 0, \tag{4.30}$$

where Greek subscripts take the values 1 and 2.

In the same fashion, we obtain

$$\epsilon_{pk3} N_i N_j' A_{ijk}^{(4)} = 0, \tag{4.31}$$

and
$$\epsilon_{pk3} N_i N_j A_{ijk}^{(4)} = 0. \tag{4.32}$$

Repeating the argument as often as necessary gives

$$A_{\alpha\beta\gamma}^{(4)} = 0. \tag{4.33}$$

Finally, the observation that
$$\epsilon_{3km} N_i' N_j' A_{ij3k}^{(5)} = 0, \tag{4.34}$$

and
$$\epsilon_{pk3} N_i' N_j A_{ij3k}^{(5)} = 0, \tag{4.35}$$

leads to
$$A_{3\alpha\beta}^{(5)} = A_{\alpha3\beta}^{(5)} = 0. \tag{4.36}$$

Still further restrictions on the coefficients may be obtained by utilizing the identity (2.5) or the identity differentiated with respect to $\mathbf{n}$ or $\nabla\mathbf{n}$. Thus, (2.5) combined with (4.8) and (4.30) gives

$$A_{33}^{(2)} = 0. \qquad (4.37)$$

Differentiating (2.5) with respect to $\mathbf{n}$ and using (4.8), (4.18) and (4.33), we find that

$$\epsilon_{3\alpha\beta}\left(N_\alpha \frac{\partial^2 W}{\partial N_3 \partial N_\beta} + N_\alpha' \frac{\partial^2 W}{\partial N_3 \partial N_{\beta,3}}\right) = 0, \qquad (4.38)$$

$$\epsilon_{3\beta\gamma}\left(\delta_{\alpha\beta}\frac{\partial W}{\partial N_\gamma} + N_\beta \frac{\partial^2 W}{\partial N_\alpha \partial N_\gamma} + N_\beta' \frac{\partial^2 W}{\partial N_\alpha \partial N_{\gamma,3}}\right) = 0, \qquad (4.39)$$

$$N_\beta \frac{\partial^2 W}{\partial N_\alpha \partial N_3} + N_\beta' \frac{\partial^2 W}{\partial N_\alpha \partial N_{3,3}} = 0, \qquad (4.40)$$

and

$$\frac{\partial W}{\partial N_\alpha} - N_\alpha \frac{\partial^2 W}{\partial N_3 \partial N_3} + N_\beta' \frac{\partial^2 W}{\partial N_3 \partial N_{\beta,\alpha}} = 0. \qquad (4.41)$$

From (3.1) it follows that

$$b\epsilon_{3\beta\alpha}N_\beta = N_\alpha', \qquad (4.42)$$

$$\epsilon_{3\beta\alpha}N_\alpha' = bN_\beta, \qquad (4.43)$$

and

$$N_\alpha'' = -b^2 N_\alpha, \qquad (4.44)$$

with (4.42) and (4.43), (4.38) and (4.39) are

$$2N_\beta' A_{3\beta}^{(3)} - b^2 N_\beta A_{3\beta3}^{(4)} = 0 \qquad (4.45)$$

and

$$b\epsilon_{3\alpha\beta}A_\beta^{(1)} + 2N_\beta' A_{\alpha\beta}^{(3)} - b^2 N_\beta A_{\alpha\beta3}^{(4)} = 0. \qquad (4.46)$$

Equation (4.40) implies that

$$A_{\alpha3}^{(3)} = 0 \qquad (4.47)$$

and

$$A_{\alpha33}^{(4)} = 0, \qquad (4.48)$$

with (4.47), (4.45) gives

$$N_\beta A_{3\beta3}^{(4)} = 0. \qquad (4.49)$$

Upon taking the inner product of (4.46) with $\mathbf{N}'$, we find

$$-b^2 N_\beta A_\beta^{(1)} + N_\alpha' N_\beta' 2A_{\alpha\beta}^{(3)} - b^2 N_\alpha' N_\beta A_{\alpha\beta3}^{(4)} = 0. \qquad (4.50)$$

The inner product of (4.41) with $\mathbf{N}$ is

$$N_\beta A_\beta^{(1)} - 2A_{33}^{(3)} + N_\alpha N_\beta' A_{3\beta\alpha}^{(4)} = 0. \qquad (4.51)$$

Differentiating the identity (2.5) with respect to $\nabla\mathbf{n}$, and utilizing the information already determined, we obtain

$$N_\beta' N_\alpha A_{3\alpha\beta}^{(4)} - 2b^2 N_\beta N_\alpha A_{3\alpha\beta3}^{(5)} + N_\beta' A_{3\beta}^{(2)} = 0, \qquad (4.52)$$

$$N_\alpha' N_\beta A_{\beta3\alpha}^{(4)1} + N_\alpha' A_{\alpha3}^{(1)} - 2b^2 N_\beta N_\alpha A_{\beta3\alpha3}^{(5)} = 0, \qquad (4.53)$$

$$-2N_\gamma' A_{\alpha\beta33}^{(5)} - \delta_{\gamma\alpha}A_{3\beta}^{(2)} + 2N_\mu' A_{\alpha\beta\mu\gamma}^{(5)} - N_\gamma A_{\alpha\beta3}^{(4)} - \delta_{\gamma\beta}A_{\alpha3}^{(2)} = 0, \qquad (4.54)$$

$$-N_\beta A_{3\alpha3}^{(4)} - 2N_\beta' A_{\alpha3\alpha3}^{(5)} = 0, \qquad (4.55)$$

$$-N_\beta A_{33\alpha}^{(4)} - 2N_\beta' A_{3\alpha33}^{(5)} = 0, \qquad (4.56)$$

and

$$A_{\alpha3}^{(2)} + A_{3\alpha}^{(2)} - 2N_\alpha' A_{3333}^{(5)} + 2N_\beta' A_{33\beta\alpha}^{(5)} = 0. \qquad (4.57)$$

Equations (4.55) and (4.56) require

$$A^{(4)}_{3\alpha 3} = 0, \quad A^{(5)}_{\alpha 333} = 0, \tag{4.58}$$

and
$$A^{(4)}_{33\alpha} = 0, \quad A^{(5)}_{3\alpha 33} = 0, \tag{4.59}$$

respectively.

Last, the equation of motion (2.13) is, with the restrictions already obtained,

$$N'_\beta A^{(4)}_{\beta \alpha 3} - 2b^2 N_\beta A^{(5)}_{\alpha 3 \beta 3} - A^{(1)}_\alpha = \lambda N_\alpha. \tag{4.60}$$

Respecting the identities

$$b^2 \delta_{\alpha\beta} = b^2 N_\alpha N_\beta + N'_\alpha N'_\beta \tag{4.61}$$

and
$$b\epsilon_{3\alpha\beta} = N_\alpha N'_\beta - N'_\alpha N_\beta, \tag{4.62}$$

we find that the most general forms for the coefficients which are compatible with the restrictions (4.8)–(4.25), (4.30), (4.33), (4.36), (4.37), (4.47)–(4.51), (4.52)–(4.54), (4.57)–(4.59) and (4.60), are

$$A^{(1)}_\beta = \alpha N_\beta, \quad A^{(1)}_3 = 0, \tag{4.63}$$

$$A^{(2)}_{\alpha\beta} = 0, \quad A^{(2)}_{\alpha 3} = \beta_1 N'_\alpha, \quad A^{(2)}_{3\alpha} = \beta_2 N'_\alpha, \quad A^{(2)}_{33} = 0, \tag{4.64}$$

$$2A^{(3)}_{\alpha\beta} = \gamma_1 N'_\alpha N'_\beta + \gamma_2 N_\alpha N_\beta, \tag{4.65}$$

$$A^{(3)}_{\alpha 3} = 0, \quad A^{(3)}_{3\alpha} = 0, \quad 2A^{(3)}_{33} = b^2 \gamma_3, \tag{4.66}$$

$$A^{(4)}_{\alpha\beta} = 0, \tag{4.67}$$

$$A^{(4)}_{3\beta\alpha} = \delta_1 N_\beta N'_\alpha + \delta_2 N'_\beta N_\alpha, \tag{4.68}$$

$$A^{(4)}_{\alpha 3\beta} = \delta_3 N_\alpha N'_\beta + \delta_4 N'_\alpha N_\beta, \tag{4.69}$$

$$A^{(4)}_{\alpha\beta 3} = \delta_5 N_\alpha N'_\beta + \delta_6 N'_\alpha N_\beta, \tag{4.70}$$

$$A^{(4)}_{\alpha 33} = 0, \quad A^{(4)}_{3\alpha 3} = 0, \quad A^{(4)}_{33\alpha} = 0, \quad A^{(4)}_{333} = 0, \tag{4.71}$$

$$
\begin{aligned}
2A^{(5)}_{\alpha\beta\gamma\mu} = {} & \epsilon_1 N_\alpha N_\beta N_\gamma N_\mu + \epsilon_2 N'_\alpha N'_\gamma N_\beta N_\mu + \epsilon_3 N_\alpha N_\gamma N'_\beta N'_\mu \\
& + \epsilon_4 (N_\alpha N_\beta N'_\gamma N'_\mu + N_\gamma N_\mu N'_\alpha N'_\beta) + \epsilon_5 (N'_\alpha N'_\mu N_\beta N_\gamma + N'_\beta N'_\gamma N_\alpha N_\mu) \\
& + \epsilon_6 N'_\alpha N'_\beta N'_\gamma N'_\mu,
\end{aligned}
\tag{4.72}
$$

$$A^{(5)}_{3\beta\gamma\mu} = 0, \quad A^{(5)}_{\alpha 3\gamma\mu} = 0, \tag{4.73}$$

$$2A^{(5)}_{\alpha 3\beta 3} = \epsilon_7 N'_\alpha N'_\beta + \epsilon_8 N_\alpha N_\beta, \tag{4.74}$$

$$2A^{(5)}_{\alpha 33\beta} = \epsilon_9 N'_\alpha N'_\beta + \epsilon_{10} N_\alpha N_\beta, \tag{4.75}$$

$$2A^{(5)}_{3\beta 3\alpha} = \epsilon_{11} N'_\alpha N'_\beta + \epsilon_{12} N_\alpha N_\beta, \tag{4.76}$$

$$2A^{(5)}_{\alpha\beta 33} = \epsilon_{13} N'_\alpha N'_\beta + \epsilon_{14} N_\alpha N_\beta, \tag{4.77}$$

and
$$A^{(5)}_{\alpha 333} = 0, \quad A^{(5)}_{3\alpha 33} = 0, \quad A^{(5)}_{3333} = \epsilon_{15}. \tag{4.78}$$

Here,
$$\alpha - b^2 \gamma_1 + b^2 \delta_6 = 0, \tag{4.79}$$

$$\alpha - b^2 \gamma_3 + b^2 \delta_2 = 0, \tag{4.80}$$

$$-b^2 \delta_6 + b^2 \epsilon_8 + \alpha + \lambda = 0, \tag{4.81}$$

$$\delta_4 - \epsilon_{10} + \beta_2 = 0, \tag{4.82}$$

$$\delta_6 - \epsilon_8 + \beta_1 = 0, \tag{4.83}$$

$$\beta_1 + \delta_2 - b^2 \epsilon_2 = 0, \tag{4.84}$$

$$\beta_2 + \delta_1 - b^2 \epsilon_5 = 0, \tag{4.85}$$

$$\varepsilon_{14} - b^2\varepsilon_4 = 0, \tag{4.86}$$

$$\beta_1 + \beta_2 + b^2\varepsilon_{13} - b^4\varepsilon_6 = 0, \tag{4.87}$$

and

$$\beta_1 + \beta_2 + b^2\varepsilon_{13} - \varepsilon_{15} = 0. \tag{4.88}$$

The coefficients $\alpha, \beta., \gamma., \delta.,$ and $\varepsilon.$ are functions of b.

If the representations (4.63)–(4.78) are used in (3.6), the relations (4.79)-(4.88) taken into account, and the constraint (3.5) utilized, after rearrangement and simplification, we may write the expansion for F, in an arbitrary Cartesian co-ordinate system, as

$$
\begin{aligned}
F = {} & \beta_1 N_{i,k} u_{i,k} + \beta_2 N_{k\,i} u_{i,k} + \tfrac{1}{2}\delta_2 N_{m,i} N_{m,k} u_i u_k + \delta_2 N_{j,i} N_k u_i u_{j,k} \\
& + \tfrac{1}{2}[b^{-2}(\beta_1 + \delta_2)\,N_{i,m} N_{k,m} N_j N_p + \varepsilon_6 N_{i,m} N_{k,m} N_{j,s} N_{p,s} \\
& + \varepsilon_7 N_{i,j} N_{k,p} + \beta_1 b^{-2} N_i N_k N_{m,j} N_{m,p} + \varepsilon_9 (N_{i,k} N_{p,j} + N_{k,i} N_{j,p}) \\
& + \beta_2 b^{-2}(N_i N_p N_{m,j} N_{m,k} + N_k N_j N_{m,p} N_{m,i}) + \varepsilon_{11} N_{j,i} N_{p,k} \\
& + \varepsilon_{12} b^{-2} N_j N_p N_{m,i} N_{m,k} + (b^2\varepsilon_6 - \beta_1 - \beta_2)\,(N_{i,k} N_{j,p} + N_{k,i} N_{p,j}) \\
& + \varepsilon_6 N_{m,i} N_{m,k} N_{s,j} N_{s,p}]\, u_{i,j} u_{k,p}. \tag{4.89}
\end{aligned}
$$

In order to establish that we have exhausted the arguments limiting the coefficients which appear in (4.89), it is necessary to produce an energy W which assigns arbitrary values to the coefficients which remain. Such an energy is, for example,

$$
\begin{aligned}
\overline{W} = {} & B_1 \epsilon_{ijk} n_i n_{k,j} + B_2(\epsilon_{ijk} n_i n_{k,j})^2 + B_3 n_{i,k} n_k n_{i,p} n_p \\
& + B_4(n_{k,k})^2 + B_5 G_{kp} G_{pk} + B_6 G_{kp} G_{pk} \epsilon_{rst} n_r n_{t,s} \\
& + B_7 G_{kp} \epsilon_{pst} n_{t,s} G_{ki} \epsilon_{iuv} n_{v,u} + B_8(G_{kp} G_{pk})^2, \tag{4.90}
\end{aligned}
$$

where

$$G_{kp} = \tfrac{1}{2}(n_{k,p} + n_{p,k}). \tag{4.91}$$

5. A general energy

Here we explore the consequences of requiring that the energy W achieve a minimum at the twisted state. This requirement is consistent with stability criteria which result, by arguments analogous to Ericksen's (1966b), from the dynamical equations and the entropy inequality.

The attainment of a minimum necessitates that, at this state, the first variation of W vanish

$$\delta W = \frac{\partial W}{\partial N_i}\delta n_i + \frac{\partial W}{\partial N_{i,k}}\delta n_{i,k} = 0. \tag{5.1}$$

Here, the allowed variations $\delta\mathbf{n}$ and $\delta\nabla\mathbf{n}$ are, according to the constraint (2.1), those for which

$$n_i \delta n_i = 0 \tag{5.2}$$

and

$$n_{i,k}\delta n_i + n_i \delta n_{i,k} = 0. \tag{5.3}$$

We satisfy (5.2) and (5.3) by introducing the infinitesimal rotation vector $\boldsymbol{\Omega}$, so that

$$\delta n_i = \epsilon_{ipq}\Omega_p N_q \tag{5.4}$$

and

$$\delta n_{i,k} = \epsilon_{ipq}(\Omega_{p,k} N_q + \Omega_p N_{q,k}). \tag{5.5}$$

Utilizing (5.4), (5.5) and the identity (2.5), we may write the condition (5.1) for an extremum of W in the form,

$$\delta W = \epsilon_{jki} \frac{\partial W}{\partial N_{p,k}} N_{p,i} \Omega_j + \epsilon_{jki} N_k \frac{\partial W}{\partial N_{i,p}} \Omega_{j,p} = 0. \tag{5.6}$$

Because $\boldsymbol{\Omega}$ and $\nabla \boldsymbol{\Omega}$ are arbitrary, (5.6) requires that both

$$\epsilon_{jki} \frac{\partial W}{\partial N_{p,k}} N_{p,i} = 0 \tag{5.7}$$

and

$$\epsilon_{jki} N_k \frac{\partial W}{\partial N_{i,p}} = 0. \tag{5.8}$$

In terms of the coefficients in the expansion (3.6), the restrictions (5.7) and (5.8) are

$$\epsilon_{jpi} A^{(2)}_{ki} N_{k,p} = 0 \tag{5.9}$$

and

$$\epsilon_{jpq} N_p A^{(2)}_{qk} = 0, \tag{5.10}$$

which necessitate that

$$\beta_1 = \beta_2 = 0. \tag{5.11}$$

It might be pointed out here, that for a form of the free energy for cholesteric liquid crystals proposed by Frank (1958),

$$\hat{W} = k_{11}(n_{k,k})^2 + k_{22}(\epsilon_{ijk} n_i n_{k,j} + t_0)^2 + k_{33}(n_{i,k} n_k n_{i,p} n_p)$$
$$- (k_{22} + k_{24})[(n_{k,k})^2 - n_{i,k} n_{k,i}], \tag{5.12}$$

the conditions (5.7) and (5.8) are fulfilled only if

$$b = t_0 \tag{5.13}$$

and

$$(k_{22} + k_{24}) = 0. \tag{5.14}$$

Although, for reasons given by de Gennes (1968a) and Ericksen (1962b), the term multiplied by $(k_{22} + k_{24})$ in (5.12) does not affect the equilibrium equations (2.13), the restriction (5.14) seems sufficiently severe to motivate an attempt to obtain an alternative to (5.12).

Resuming consideration of the general case, in order that the extremum achieved at the twisted state be a minimum, it is necessary that the inequality

$$\epsilon_{ipq} \epsilon_{kuv} \{ [N_q (N_v A^{(3)}_{ik} + N_{v,j} A^{4}_{ikj}) + N_{v,j} N_{q,s} A^{(5)}_{kjis}] \Omega_p \Omega_u$$
$$+ 2N_v (N_q A^{(4)}_{ikj} + N_{q,s} A^{(5)}_{kjis}) \Omega_p \Omega_{u,j} + N_q N_v A^{(5)}_{kjis} \Omega_{p,s} \Omega_{u,j} \} \geqslant 0 \tag{5.15}$$

obtain. Thus, we may employ the inequality (5.15) and the representations (4.63)–(4.78) to restrict the quantities $\alpha, \gamma., \delta.$, and $\epsilon..$. Here, however, we use an equivalent method which seems more direct.

At a point, we choose a co-ordinate system so that

$$N_i = (1, 0, 0) \tag{5.16}$$

and

$$N'_i = (0, b, 0). \tag{5.17}$$

Then $\mathbf{u}$ is arbitrary; but, as a consequence of (3.5),

$$u_{i,k} = \begin{vmatrix} 0 & 0 & -bu_2 \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{vmatrix}, \tag{5.18}$$

with an error that is quadratic in $\mathbf{u}$ and $\nabla\mathbf{u}$. Using (5.16), (5.17), (5.18) with (5.11) in (4.89) we obtain

$$2F = \delta_2(bu_3 + u_{21})^2 + b^4\varepsilon_6(u_{22} + u_{33})^2 + b^2(\varepsilon_7 u_{23}^2 + 2\varepsilon_9 u_{23}u_{32} + \varepsilon_{11}u_{32}^2) + \varepsilon_{12}u_{31}^2. \quad (5.19)$$

Hence, W is a minimum at the twisted state if and only if

$$\beta_1 = \beta_2 = 0, \quad (5.20)$$

with
$$\delta_2 \geqslant 0, \quad \varepsilon_6 \geqslant 0, \quad \varepsilon_{12} \geqslant 0, \quad (5.21)$$

and
$$\varepsilon_7 \geqslant 0, \quad \varepsilon_{11} \geqslant 0, \quad \varepsilon_9^2 - \varepsilon_7\varepsilon_{11} \leqslant 0. \quad (5.22)$$

Consider a particular form of the free energy $\overline{W}$ given by (4.90):

$$\begin{aligned}
2\overline{\overline{W}} = {} & \alpha_1(\epsilon_{ijk}n_i n_{k,j} + t)^2 + \alpha_2 n_{i,k}n_k n_{i,p}n_p + \alpha_3(n_{k,k})^2 \\
& + 2\alpha_4(G_{kp}G_{pk} - \tfrac{1}{2}t^2)(\epsilon_{ijk}n_i n_{k,j} + t) \\
& + \alpha_5 G_{pi}\epsilon_{ijk}n_{k,j}G_{pl}\epsilon_{trs}n_{s,r} + \alpha_6(G_{pk}G_{kp} - \tfrac{1}{2}t^2)^2. \quad (5.23)
\end{aligned}$$

If the material functions $\alpha.$ in (5.23) obey

$$\alpha_2 \geqslant 0, \quad \alpha_3 \geqslant 0, \quad \alpha_5 \geqslant 0, \quad (5.24)$$

$$\alpha_6 + \alpha_1 > 0, \quad \alpha_4^2 - \alpha_1\alpha_6 < 0, \quad (5.25)$$

then the energy $\overline{\overline{W}}$ achieves a unique absolute minimum in a twisted state (3.1) with characteristic twist $t = b$. Also, if we calculate the appropriate derivatives of $\overline{\overline{W}}$ and evaluate them at this minimum, we find

$$\delta_2 = \alpha_2, \quad \varepsilon_6 = \alpha_3, \quad \varepsilon_{11} = \alpha_1 t^{-2}, \quad (5.26)$$

$$\varepsilon_7 = \alpha_1 t^{-2} - 2\alpha_4 t^{-1} + 4\alpha_6, \quad (5.27)$$

$$\varepsilon_9 = -\alpha_1 t^{-2} + 2\alpha_4 t^{-1}, \quad (5.28)$$

$$\varepsilon_{12} = \alpha_2 + \alpha_5 t. \quad (5.29)$$

Notice that, as is to be expected, (5.24)–(5.25) and (5.26)–(5.29) ensure (5.21) and (5.22). Comparison of (5.23) with (5.12) indicates that $\overline{\overline{W}}$ contains those parts of $\hat{W}$ which are consistent with the attainment of an extreme in the twisted state. Furthermore, with the identification (5.26)–(5.29), the free energy (5.23) is a properly invariant generalization of the expansion (3.6) when that expansion is performed about the characteristic, stable twisted state of the material. Finally, it should be noted that the presence of the term multiplied by the coefficient α_4 allows this free energy to distinguish, for example, between increasing and decreasing the twist about the characteristic state.

These features of the free energy (5.23) suggest that it is a general form of free energy applicable to cholesteric liquid crystals. We present it here as an alternative to the form (5.12) proposed by Frank. The analysis of de Gennes (1968*b*) and the experiments of Durand *et al.* (1969) indicate that, in one case, the use of (5.12) will yield predictions consistent with observation. However, when more detailed experimentation is performed, the need for such an alternative may become apparent.

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