TEMPERATURE DEPENDENCE OF THE PITCH IN CHOLESTERIC LIQUID CRYSTALS: A MOLECULAR STATISTICAL THEORY

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Abstract. — A molecular statistical theory is given which describes the temperature dependence of the pitch in cholesteric liquid crystals in terms of all order parameters relevant to the untwisted nematic phase.

1. Introduction. — Some years ago a molecular statistical theory was proposed which explained the helical structure of the cholesteric phase, however with a temperature independent pitch [1]. The model has been extended to account for the temperature dependence of the pitch in terms of hindered rotation of the molecules around the long principal axes [2, 3]. The temperature dependence is then determined by an order parameter which describes biaxiality on a microscopic scale [3]. The distribution of the long molecular axes themselves with respect to the local axis of alignment, i.e. the director, was considered to be uniaxial. Consequently any influence of hindered rotation of the long molecular axes around the director was disregarded. This hindered rotation, generated by the above mentioned microscopic or molecular biaxiality, give rise in a nematic liquid crystal to a macroscopic or phase biaxiality. In cholesteric liquid crystal, where the director rotates smoothly around the helix axis, this biaxiality should manifest itself on a local scale, i.e. intermediate between molecular and pitch dimensions, the helix axis still being an axis of uniaxial symmetry.

It is the purpose of this paper to review and extend the above mentioned theory [1] and to show how local biaxiality may play a significant role in the temperature dependence of the pitch. A different, rather phenomenological model has been proposed by Priest and Lubenski [4]. They introduced a model Hamiltonian in terms of the order parameters of a biaxial nematic phase, having the proper symmetry for producing a twisted nematic phase. General symmetry arguments then allowed them to arrive at similar conclusions, albeit with no physical background and interpretation as to the molecular aspects and origin of the twist.

2. General formulation. — The theory of the cholesteric phase presented in reference [1] can be viewed as an extension of the Maier-Saupe theory for the nematic phase. The dispersion energy between two anisotropic, optically active molecules was calculated, taking into account not only the dipole-dipole interaction, but also the dipole-quadrupole interaction. These respective energies are defined as

\[ V^{ij}_{pp} = \sum_{r,r'} \left( \frac{P_i \cdot P_j}{P_p \cdot P_p} \right) \cdot \left( \frac{P_i \cdot P_j}{P_p \cdot P_p} \right) \cdot \frac{C^{ij}_{rr'} C^{il}_{rr'}}{(r^{ij})^6} \]

\[ V^{ij}_{pq} = \sum_{r,r'} \frac{(p_i \cdot q_j)}{E_{rr'}^{ij}} \cdot \frac{C^{ij}_{rr'} D_{rr'}^{ij}}{(r^{ij})^5} + \sum_{r,r'} \frac{(p_i \cdot q_j)}{E_{rr'}^{ij}} \cdot \frac{C^{ij}_{rr'} (r^{ij})}{(r^{ij})^5} + \text{c.c.} \]
where $(P_\alpha^g | p_\beta^g)_v = \langle 0 | p_\alpha^g | v \rangle \langle v | p_\beta^g | 0 \rangle$ and $(p_\alpha^g | q_{\beta\gamma}^g)_v = \langle 0 | p_\alpha^g | v \rangle \langle v | q_{\beta\gamma}^g | 0 \rangle$ are products of molecular matrix elements of the dipole moment operator $p$ and quadrupole moment operator $q$.

Repeated indices $\alpha$, $\beta$, $\gamma$, etc., which refer to the coordinates $X$, $Y$, $Z$ of a macroscopic, fixed, Cartesian coordinate system, indicate a summation over the corresponding components. Besides one has to sum over all excited states $v$ and $v'$ with energies $E_v$ and $E_{v'}$ such that $E_{v'} - E_v = (E_{0'} + E_0') - (E_0 + E_0) \neq 0$.

The scalar $r^{ij}$ is the absolute value of the vector $r^{ij} = (r_{i1}^{ij}, r_{i2}^{ij}, r_{i3}^{ij})$, pointing from the centre of mass of molecule $i$ to that of molecule $j$. The quantities $C^{ij}_{ab}$ and $D^{ij}_{ab}$ are tensor elements depending only on the relative positions of the molecules, not on their orientations; they are defined by:

$$C^{ij}_{ab} = \delta_{ab} - \frac{3 r^{ij}_a r^{ij}_b}{(r^{ij})^2}$$

$$D^{ij}_{ab} = \frac{3 r^{ij}_a r^{ij}_b}{2 r^{ij}} \left(2 \delta_{ab} - \frac{5 r^{ij}_c r^{ij}_c}{(r^{ij})^2}\right).$$

The matrix elements for the electric dipole moment operator $p$ and electric quadrupole moment operator $q$ transform under rotations like the corresponding components of $p$ and $q$ respectively. For convenience we will therefore use the following abbreviations:

$$\sum_{v, v'} \left( \frac{P_\alpha^g | p_\beta^g}_v \frac{P_\alpha^g | p_\beta^g}_v \right) \frac{E^{ij}_{v,00}}{E^{ij}_{v',00}} = (\alpha \beta)_i (\alpha' \beta')_j.$$  

(6)

$$\sum_{v, v'} \left( \frac{P_\alpha^g | p_\beta^g}_v \frac{P_\alpha^g | q_{\beta\gamma}^g}_v \right) \frac{E^{ij}_{v,00}}{E^{ij}_{v',00}} = (\alpha \beta)_i (\alpha' \beta' \gamma)_j.$$  

(7)

which clearly reflect the symmetry properties. Besides $(\alpha \beta)_i = (\beta \alpha)_i$, $(\alpha \beta \gamma)_i = (\alpha \gamma \beta)_i$, etc.

The above pair potential $V^{ij}$ will be used for an internal field approximation in which the precise interaction $V^i = \sum_V V^{ij}$ of one molecule with all the others will be approximated by a suitable averaged interaction. In order to do so we will use the following symmetry arguments.

a) The helix axis, which we identify with the macroscopic $y$-axis, is an axis of twofold rotational symmetry. Therefore only those dipole-dipole transitions contribute to the interaction energy that transform like $XX, YY, ZZ$ and $XZ$. With regard to the dipole-quadrupole transitions only those contribute to the interaction energy that transform like $XYY, YYY, ZZY$ and $XYZ$.

b) The helix axis is an axis of screw symmetry. There is thus a correlation between orientation and translation along the $y$-axis. The easiest way to account for this correlation is to first average over the positions of the molecules with regard to their $r_x$ and $r_z$ dependence, keeping $r_y$ fixed; we then assume that all molecules with the same $r_y$ have on the average the same orientation. The distribution of the centres of mass of the molecules with regard to the helix axis can be taken as having rotational symmetry. Then only those combinations $C_{ab} C_{ap} \beta \gamma, C_{ap} D_{ab} \gamma, \text{ and } C_{ab} r_y$ have an averaged value different from zero that are not odd in $r_x$ and $r_z$, i.e.

$$C_{XX} C_{XY} = 0, C_{XX} D_{XY} = 0,$$

$$C_{XX} r_y \neq 0, C_{XX} C_{ZZ} \neq 0, C_{XY} D_{XXXX} \neq 0,$$

etc. Taking these arguments into account the dipole-dipole and dipole-quadrupole interaction averaged over $r_x^{ij}$ and $r_z^{ij}$ can then be written as

$$V^{ij}_{pp} = V^{ij}(4(XX + YY + ZZ), (YY)_i + 4(YY)_i (XX + YY + ZZ)_i +$$

$$+ 2(XX + ZZ)_i (XX + ZZ)_i + (XX - ZZ)_i (XX - ZZ)_i + 4(XZ)_i (XZ)_i).$$

(8)

$$V^{ij}_{pq} = \frac{2 V^{ij}}{r^{ij}} \left(2(XX + 2 YY + ZZ)_i ((\Sigma^{(+)} X, YY)_i + (Y, YY)_i) +$$

$$+(XX - ZZ)_i (\Sigma^{(-)} X, YY)_i + 2(XZ)_i (\Sigma X, ZZ)_i)$$

where

$$\Sigma^{(+)} X, YY)_i = (X, XY - \frac{1}{2} Y, XX)_i + (Z, ZY - \frac{1}{2} Y, ZZ)_i$$

$$\Sigma^{(-)} X, YY)_i = (X, XY - \frac{1}{2} Y, XX)_i - (Z, ZY - \frac{1}{2} Y, ZZ)_i$$

$$\Sigma X, ZZ)_i = (X, YZ - Y, ZX + ZZ)_i.$$  

(10)

The common factor $V^{ij} = 3/(b 4(r^{ij})^4)$ arises from the averaging over the various combinations of the tensor elements $C_{ab}$ and $D_{ab\gamma}$.

3. Order parameters and molecular properties. — We shall now consider the molecular aspects in more detail. According to equations (6) and (7) $(XX)_i, (XX, YYZ)$ etc. refer to products of matrix elements for the electric dipole and electric quadrupole moments. These moments were defined with respect to the fixed macroscopic coordinate system $X, Y, Z$.

In order to define these quantities in terms of molecular properties and of the order parameters describing the phase, we have to project the tensor components $p_{\alpha\gamma}, q_{\beta\gamma}$ upon a molecular fixed coordinate system $X, Y, Z$. Quite generally we may write

$$[X] = \begin{bmatrix} X_x & X_y & X_z \end{bmatrix} [X] = \begin{bmatrix} x \end{bmatrix}$$

$$[Y] = \begin{bmatrix} Y_x & Y_y & Y_z \end{bmatrix} [y] = \begin{bmatrix} y \end{bmatrix}$$

(11)
where \( x, X = a, a, x, Y = a, a, \) etc. Here \( a, a, a, \) etc. are unit vectors along the corresponding coordinate axes. The order parameters then appear as the averaged values \( \langle \xi_1, \xi_2, \xi_3 \rangle \) ; \( \xi, \xi = x, y, z \) and \( \alpha, \beta = X, Y, Z, \) whereas the brackets denote an ensemble average. It is convenient to have an explicit representation of these order parameters in terms of Euler angles. Therefore we use the following representation for \( \mathbf{A} \), which specifies the orientation of the molecular coordinate system \( x, y, z \) with respect to the macroscopic coordinate system \( X, Y, Z \) [5],

\[
\mathbf{A} = \begin{bmatrix}
\cos \psi \cos \varphi \cos \theta - \sin \psi \sin \varphi, & -\sin \psi \cos \varphi \cos \theta - \cos \psi \sin \varphi, & \cos \varphi \sin \theta \\
\cos \psi \sin \varphi \cos \theta + \sin \psi \cos \varphi, & -\sin \psi \sin \varphi \cos \theta + \cos \psi \cos \varphi, & \sin \varphi \sin \theta \\
-\cos \psi \sin \theta, & \sin \psi \sin \theta, & \cos \theta
\end{bmatrix}.
\] (12)

Here \( \varphi \) is an angle that describes a rotation around the macroscopic \( Z \)-axis, \( \theta \) an angle that describes a rotation around an axis perpendicular to the \( Z \)-axis, i.e. the angle between the molecular \( z \)-axis and the macroscopic \( Z \)-axis, and \( \psi \) describes a rotation around the molecular \( z \)-axis.

In addition to the macroscopic symmetry elements already mentioned and used, there is also twofold rotational symmetry around the molecular \( z \)-axis (the \emph{long axis}) and around any axis perpendicular to that axis. The order parameters describing the nematic phase can then be defined as the ensemble averages of the following invariants [6] (in fact these invariants appear in this form quite naturally, as will be seen below) which are normalized to unity:

\[
\begin{align*}
F_1 &= \frac{1}{2}(z^2_x - \frac{1}{2}) = \frac{1}{2}(\cos^2 \theta - \frac{1}{4}) \\
F_2 &= x^2_y - y^2_x = \cos 2 \psi \sin^2 \theta \\
F_3 &= z^2 - z^2_x = \cos 2 \varphi \sin^2 \theta \\
F_4 &= \frac{1}{2}(x^2_z - x^2_y) - \frac{1}{2}(y^2_x - y^2_z) = \frac{1}{2} \cos 2 \varphi \cos 2 \psi (1 + \cos^2 \theta).
\end{align*}
\] (13)

The ensemble average \( \langle F_1 \rangle \) is the basic order parameter to describe the nematic phase; the ordering corresponds to uniaxial alignment of the molecular \( z \)-axes along the macroscopic \( Z \)-axis. In this uniaxial phase there may be biaxial order on a molecular scale described by \( \langle F_2 \rangle \). When both \( \langle F_3 \rangle \) and \( \langle F_4 \rangle \) are non-zero, for which it is necessary that both \( \langle F_1 \rangle \) and \( \langle F_2 \rangle \) are non-zero, the nematic ordering is biaxial [6]. This phase biaxiality is due to molecular biaxiality. Doing the transformations for \((XX)_h\), \((YY)_h\) and \((ZZ)_h\), one finds:

\[
\begin{align*}
(XX)_h &= f_1 - (\delta F_1 + \frac{1}{2} \varepsilon F_2)_h + (\frac{1}{6} \delta F_3 + \varepsilon F_4)_h \\
(YY)_h &= f_1 - (\delta F_1 + \frac{1}{2} \varepsilon F_2)_h + (\frac{1}{6} \delta F_3 + \varepsilon F_4)_h \\
(ZZ)_h &= f_1 + 2(\delta F_1 + \frac{1}{2} \varepsilon F_2)_h.
\end{align*}
\] (14)

The quantities \( \delta \) and \( \varepsilon \) are molecular anisotropies formally introduced as \( \delta_1 = \frac{1}{3}((zz) - \frac{1}{3}(xx + yy))_h \) and \( \varepsilon_1 = \frac{1}{2}(xx + yy)_h \), reflecting their symmetry properties. Analogous to equation (6) the precise definition is

\[
\begin{align*}
\delta_1 \delta_2 &= \sum_{\nu\omega} \left[ (p^\nu_\nu/p^\nu_\nu)_\nu - \frac{1}{4}(p^\nu_\nu/p^\nu_\nu)_\nu + (p^\nu_\nu/p^\nu_\nu)_\nu \right][(p^\nu_\nu/p^\nu_\nu)_\nu - \frac{1}{4}(p^\nu_\nu/p^\nu_\nu)_\nu + (p^\nu_\nu/p^\nu_\nu)_\nu] \\
\delta_1 \varepsilon_1 &= \sum_{\nu\omega} \left[ (p^\nu_\nu/p^\nu_\nu)_\nu - \frac{1}{4}(p^\nu_\nu/p^\nu_\nu)_\nu + (p^\nu_\nu/p^\nu_\nu)_\nu \right][(p^\nu_\nu/p^\nu_\nu)_\nu - (p^\nu_\nu/p^\nu_\nu)_\nu].
\end{align*}
\] (15, 16)

The quantity \( f_1 = \frac{1}{2}(xx + yy + zz) \), is defined similarly. Next we calculate the transforms of \((XX)_h\), and of the dipole-quadrupole transition moments \((X, YZ)_h\), etc. After some lengthy calculations one finds:

\[
\begin{align*}
(XZ)_h &= (3 \delta - \varepsilon \cos 2 \psi) \cos \varphi \sin 2 \theta, \\
(XX)_h &= \frac{1}{3}(y, y)_h = - (\xi + \frac{1}{2} \zeta) \cos 2 \psi \sin^2 \varphi \cos \varphi \sin 2 \theta, \\
(XY)_h &= (2 \gamma + (\zeta - (\xi + \frac{1}{2} \zeta) \sin^2 \varphi) \cos 2 \psi) \cos \varphi \sin 2 \theta, \\
(YY)_h &= 2 \gamma (F_1 - \frac{1}{2} F_3)_h - (\xi - \zeta) (F_3)_h + (\xi^2 \zeta - \xi \zeta^2), \\
(YZ)_h &= (X, YZ)_h = 2 \gamma_1 (F_1 - \frac{1}{2} F_3)_h - (\xi - \zeta) (F_3)_h + (\xi^2 \zeta - \xi \zeta^2)_h
\end{align*}
\] (17)

where \( F_4^1 = \cos 2 \psi \cos 2 \varphi \cos^2 \theta \), \( F_4^2 = \cos 2 \psi \cos 2 \varphi \sin^2 \theta \) and \( 2 F_4^1 + F_4^2 = F_4 \) as defined in equation (13). The molecular quantities \( \gamma, \zeta \) and \( \xi \) are introduced for their symmetry properties as:

\[
\begin{align*}
\gamma &= (x, y, z)/(2, \quad \zeta = (x, y)_h, \quad \xi = (x, y, z)_h/2).
\end{align*}
\]
The precise definition is analogous to equation (7) given by:

$$\delta_{ij} \gamma_1 = \sum \frac{[(p_i^j/p_i^j)_{12} - \frac{1}{2}(p_i^j/p_i^j)_{12} + (p_i^j/p_i^j)_{12}] \left[(p_i^j/q_i^j)_{12} - (p_i^j/q_i^j)_{12}\right]}{6 E_{11,12}}$$  \( (18) \)

and similar equations for \( \xi \) and \( \xi \) in combination with \( \beta \) and \( e \). The molecular quantities \( \gamma, \xi \) and \( \xi \) are only non-zero in the case of molecules possessing neither a plane nor a centre of symmetry, i.e. optically active molecules.

The important thing to observe is the appearance of some new invariants all proportional to \( \cos \phi \sin 2 \theta = 2 z_X z_Z \).

These clearly demonstrate the overall planar symmetry of the cholesteric phase. Twofold rotational symmetry around the fixed macroscopic \( X \) or \( Z \)-axis destroys the asymmetric interaction which, as will be shown below, gives rise to the twist.

4. Calculation of the twist. — In order to illustrate the physical meaning of the odd terms in the dipole-dipole and dipole-quadrupole interaction we first consider the rather simple case of a purely planar structure in which the molecular \( z \)-axes are confined to the \( X-Z \) planes \([1,7]\); then \( z_Y = 0 \), i.e. \( \phi = 0 \).

Consequently we take \( \psi = 0 \pm \pi \). One easily finds that \((XX + ZZ)\) and \((YY)\) are constants, that \((Y, YY)\) = 0 and

\[
(ZZ - XX) = (3 \delta_1 - \epsilon_1) \cos 2 \theta, \\
(XX - ZZ) = (3 \delta_1 - \epsilon_1) \sin 2 \theta, \\
(SX, YZ) = (2 \gamma_1 + \xi) \cos 2 \theta, \\
(2^{(-)} X, YX) = (2 \gamma_1 + \xi) \sin 2 \theta
\]

leading to

\[
V_{pp}^{ij} = \text{const} + V_{pp}^{ij}(3 \delta_1 - \epsilon_1)(3 \delta_1 - \epsilon_1) \cos 2 \theta_{ij}, \\
V_{pi}^{ij} = \frac{2 V_{pi}^{ij}}{r^2}(3 \delta_1 - \epsilon_1)(2 \gamma_1 + \xi) \sin 2 \theta_{ij}.
\]

The twist angle, which can be defined as the average rotation \( \langle \alpha \rangle \) of the projection of the \( z \)-axis upon the \( X-Z \) plane (see Fig. 1) is then given by:

$$2 \langle \alpha \rangle = \theta_{ij} = \frac{1}{2} \left( \frac{2 \gamma + \xi}{(3 \delta - e)} \right) \cos \theta_{ij}$$  \( (19) \)

where \( \alpha \) is a molecular dimension. The order of magnitude of \( \langle \alpha \rangle \) has been discussed in reference [1].

Now we return to the general case. From figure 1 we see that now \( \alpha \) is not identical with \( \theta \) but determined by

$$\sin \alpha = z_X/(z_X^2 + z_Z^2)^{1/2}, \quad z_X^2 + z_Z^2 = 1 - z_Y^2. $$

So we find

$$2 \alpha = 2 z_X z_Z/(1 - z_Y^2) = \cos \phi \sin 2 \theta/(\cos^2 \phi \sin^2 \theta + \cos^2 \theta).$$

If we introduce instead of \( \theta \) and \( \phi \) the new variables \( \alpha \) and \( z_Y^2 \) defined by

$$\cos \phi \sin 2 \theta = (1 - z_Y^2) \sin 2 \alpha \equiv 2 z_X z_Z$$
$$\cos^2 \theta - \cos^2 \phi \sin^2 \theta = (1 - z_Y^2) \cos 2 \alpha \equiv z_Z^2 - z_X^2 = F_4 - \frac{1}{2} F_3$$  \( (23) \)

FIG. 1. — Orientation of the molecular \( z \)-axis, i.e. the long molecular axis, with respect to the macroscopic coordinate system \( X, Y, Z \) in terms of the angles \( \theta \) and \( \varphi \) and in terms of the angle \( \alpha = \arctan(z_y/z_x) \) and the scalar \( z_Y \), where \( z_X^2 + z_Y^2 + z_Z^2 = 1 \); \( \Psi \) denotes a rotation around the molecular \( z \)-axis.
where

\[ \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \int_0^1 d(\cos \theta) = \int_0^{2\pi} d\theta \int_0^\theta d\gamma \int_0^{2\pi} dx , \]

the dipole-dipole and dipole-quadrupole interaction can be written as

\[ V_{pp} = \sum_{n=0}^{\infty} V_n^p(\psi, z_{1y}, r_y) \cos 2nx \]

(24)

\[ V_{pq} = \sum_{n=1}^{\infty} V_n^q(\psi, z_{1y}, r_y) \sin 2nx . \]

(25)

The potential in this form is similar to the potential proposed in reference [7] for a purely planar configuration in which only the variables \( \phi \equiv x \) and \( r_z \equiv r_y \) enter and where \( z_{1y} = 0 \). In view of the limit discussed above for a purely planar configuration, this model seems rather artificial as the appearance of the higher harmonics is in fact due to the three-dimensionality of the problem; we find that \( \langle V_{pp} \rangle \sim 2 \cos \frac{2\pi}{3} \). Using equation (24) and (25) all moments of \( \sin 2x \) can be calculated from which \( \langle x \rangle \) can be obtained. This method is rather cumbersome and tedious.

It is far more practical to use the fact that the cholesteric can be considered as a continuous rotating nematic phase [3, 4, 7]. The corresponding rotating coordinate system \( X', Y', Z' \) can be defined by:

\[ X' = X \cos Qr_y + Z \sin Qr_y \]

\[ Y' = Y \]

\[ Z' = -X \sin Qr_y + Z \cos Qr_y \]

(26)

where the \( y \)-axis is the helix axis and \( Q = 2\pi/p \), with \( p \) being the pitch of the helix. We now apply this transformation to the matrix elements \( V_{pp} \), etc. occurring in equation (8) and equation (9). Since these elements transform like the corresponding coordinates, one finds:

\[ \langle XX - ZZ \rangle' = \langle XX - ZZ \rangle \cos 2Qr_y - 2\langle XX \rangle \sin 2Qr_y \]

\[ 2\langle XX \rangle' = \langle XX - ZZ \rangle \sin 2Qr_y + 3\langle XX \rangle \cos 2Qr_y \]

\[ \langle \Sigma^{(i)} X, XY \rangle' = \langle \Sigma^{(i)} X, XY \rangle \cos 2Qr_y - \langle \Sigma X, YZ \rangle \sin 2Qr_y \]

\[ \langle \Sigma X, YZ \rangle' = \langle \Sigma^{(i)} X, YY \rangle \sin 2Qr_y + \langle \Sigma X, YZ \rangle \cos 2Qr_y \]

(27)

all other terms being independent of \( Q \).

We now substitute these expressions for the corresponding matrix elements in equations (8) and (9) for \( V_{pp}^{ij} \) and \( V_{pq}^{ij} \) respectively. For the \( Q \) dependent part of \( V_{pp}^{ij} \) one finds:

\[ V_{pp}^{ij}(Q) = \langle (ZZ - XX)^{ij} \rangle (ZZ - XX)^{ij} + 4\langle XX \rangle (XX)^{ij} V^{ij} \cos 2Qr_y^{ij} + \]

\[ + \langle (ZZ - XX)^{ij} \rangle (2XX)^{ij} - (2XX)^{ij} (ZZ - XX)^{ij} \rangle V^{ij} \sin 2Qr_y^{ij} . \]

(28)

Here the primed quantities are defined with respect to the rotating coordinate system. The local equilibrium configuration with respect to this coordinate system corresponds to nematic ordering, for which

\[ \langle (ZZ - XX)^{ij} \rangle = \langle (ZZ - XX)^{ij} \rangle , \]

independently of position. In this case one also may demand that the averaged value of the odd terms vanish identically, i.e. \( \langle \Sigma^{(i)} X, XY \rangle^{ij} \rangle = 0 \). Hence the averaged value of \( V_{pp}^{ij}(Q) \) in a molecular field approximation can be defined by:

\[ \langle V_{pp}(Q) \rangle = \langle (ZZ - XX)^{ij} \rangle^2 \int dr_y V(r_y) \cos 2Qr_y . \]

(29)

The prime on the integral restricts \( r_y \) to values not running over the mutually excluded volume of two molecules. Proceeding in the same way we can define the averaged value of \( V_{pq} = V_{pp}^{ij} + V_{pq}^{ij} \) by:

\[ \langle V_{pq}(Q) \rangle = 4 \langle (ZZ - XX)^{ij} \rangle \langle (XX, YZ)^{ij} \rangle \int dr_y V(r_y) \cos 2Qr_y . \]

(30)

Since in a molecular field approximation the entropy does not depend on the spatial variation of the direction of alignment [4, 7], the value of \( Q \) that minimizes the free energy can be found by minimizing the average potential energy. Expanding the sine and cosine up to order \( Q^2 \) one finds:

\[ Q = \frac{\langle \Sigma X, YZ \rangle }{\langle ZZ - XX \rangle} \frac{1}{a^2} \]

(31)
where \( a \) is a molecular dimension defined by
\[
a^2 = \int dr_y V(r_y) r_y^2 \int dr_y V(r_y).
\]

Using equations (14) and (17), the equation for \( Q \) can finally be written as:
\[
Q = \frac{2 \gamma (\langle F_1 \rangle - \frac{1}{2} \langle F_3 \rangle) - (\xi - \zeta) \langle F_2 \rangle + (\zeta \langle F_4 \rangle - \xi \langle F_2 \rangle) + \xi \langle F_2 \rangle)}{3 \delta (\langle F_1 \rangle - \frac{1}{2} \langle F_3 \rangle) - \delta (\langle F_4 \rangle - \frac{3}{2} \langle F_2 \rangle)} \frac{1}{a^2}. \tag{32}
\]

5. Discussion. — Our final result is an equation for \( Q = 2 \pi/p \), where \( p \) is the pitch which is characteristic of the cholesteric or twisted nematic phase, in terms of molecular quantities and of the order parameters \( \langle F_1 \rangle \) which are characteristic of the corresponding untwisted nematic phase. For a purely planar configuration the above equation reduces to equation (22) with \( \theta_{31} = 2 aQ \). When both \( \langle F_3 \rangle \) and \( \langle F_4 \rangle \) are zero the result of reference [3] is retained, which accounts for biaxiality on a molecular scale described by \( \langle F_2 \rangle \). When the local nematic ordering is biaxial we have to use the full expression given by equation (32). To our knowledge no macroscopic biaxiality in nematic phases has been reported. Local biaxiality in cholesteric phases is rather difficult to observe directly because of the overall uniaxial symmetry. Nevertheless cholesteric phases are biaxial on a local scale, at least of the order of \( (Qa)^2 \), due to the dipole-quadrupole interaction [4]. It seems quite plausible that this biaxiality can be reinforced by the dipole-dipole interaction since the constituting molecules can be considered to be planar, i.e. \( \varepsilon \neq 0 \). Since cholesterics do not have a corresponding untwisted nematic phase, it seems worthwhile to make a kind of corresponding untwisted nematic phase by making a compensated mixture of two natural cholesteric compounds. Whether phase biaxiality exists or not can then be detected directly. This point is not only interesting in itself but can be important for the understanding of the temperature dependence of the pitch. As to the magnitude of the order parameters \( \langle F_3 \rangle \) and \( \langle F_4 \rangle \) nothing is known except for the results of the model calculations given in reference [6]. There it is was found that when there is biaxiality, \( \langle F_4 \rangle \) and therefore also \( \langle F_2 \rangle \) are large compared to both \( \langle F_2 \rangle \) and \( \langle F_3 \rangle \) and consequently also \( \langle F_2 \rangle \). The temperature dependence of the pitch should then be governed by the ratios \( \langle F_4 \rangle/\langle F_1 \rangle \) and \( \langle F_2 \rangle/\langle F_1 \rangle \). However since we have no knowledge of the relative magnitude and sign of the molecular quantities \( \gamma, \zeta \) and \( \xi \) it seems almost impossible to make any prediction. As a function of temperature the pitch may increase, decrease or do both successively, depending on the relative magnitude of the various biaxial order parameters. We hope that systematic experiments on the temperature dependence of the pitch will give more conclusive results that will enable us to interpret and test the theoretical description.

References