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Tilt and temperature dependence of the pitch in the chiral smectic C phase

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The chirality of the constituent molecules in the chiral smectic phase induces a helical structure with a pitch, p_0. Because of the tilt and chirality there is a spontaneous polarization and a bend deformation which act upon the induced helix. The resulting pitch is described as a function of p_0 using the phenomenological theory of a chiral smectic C phase. The pitch, p_0, is then calculated using a molecular theory of the cholesteric phase. The results obtained explain the experimental observations, at least qualitatively.

1. Introduction

The smectic C phase has two specific features; the director is tilted with respect to the layer normal and the phase is optically biaxial [1]. Whether the biaxiality results from the tilt or vice versa is not well understood. None the less it can be shown that both go together in the same way as chirality and biaxiality in the cholesteric phase, however small the biaxiality may be [2]. When the smectic C phase is composed of chiral molecules the tilted director rotates from plane to plane around the layer normal, creating a helical structure much like that in cholesterics [3]. Because of the reduction of symmetry the chiral smectic C phase can sustain a spontaneous polarization in each smectic plane perpendicular to the plane of the tilt in that plane [4]. Much experimental work has been done to elucidate the properties and the nature of these phases, especially with regard to the tilt and temperature dependence of the pitch and spontaneous polarization. The theoretical descriptions of the phase properties up to now are mostly phenomenological, based upon a Landau type of approach using macroscopic symmetry arguments. Many of these aspects are discussed in [5–8]. The molecular theories put to the fore in [9, 10] are of no interest. The unspecified temperature dependence of the twist in [9] associated with the smectic A–smectic C phase transition in [11] is based on the unjustified multiplication of some coupling constants with $(1 + T/T_p)$ l.c., which has no physical significance; cf. [12, 13]; $T_p^{-1} \propto \Delta S_{tr.}$ is a measure for the orientation-dependent translational entropy $\Delta S_{tr.}$ in the nematic phase. The outcome of the theory in [10] is that both the calculated twist and the calculated expansion coefficient α_{20}, claimed to describe the S_A–S_C phase transition and to be compared with the coefficient a in equation (1), where $a \propto T - T_{S_CS_A}$, are almost temperature independent which does not correspond with physical reality; cf. also [12]. In this paper we shall therefore focus attention on the molecular aspects of the chirality in the smectic C phase, especially with regard to the tilt and temperature dependence of the pitch of the helix. In §2 we first recapitulate and reformulate, in brief, the usual description of the chiral smectic C phase. There it is shown that the actual pitch p, observed experimentally and determined by the ground state pitch p_0 and the spontaneous bend deformation, depends on the tilt angle. In §3 we show how the existing theory for cholesterics can be adapted to calculate the ground state pitch p_0 for the chiral smectic phase. The results of §2 and §3 are discussed in §4.

2. Phenomenological description

In the smectic C phase the molecules are arranged in layers; the director, **n**, is tilted with respect to the layer normal which is chosen along the Z axis of a fixed macroscopic coordinate system X, Y, Z. Because of the tilt there is a non-vanishing component of **n** in the smectic planes which can be described by the vector

$$\mathbf{c} = \mathbf{i}n_x + \mathbf{j}n_y;$$

here

$$c^2 = 1 - n_z^2 = \sin^2\theta,$$

where θ is the macroscopic tilt angle. The specific order in the smectic C phase can be described by the vector invariant

$$\mathbf{n} \wedge \mathbf{c} = -\mathbf{i}n_y n_z + \mathbf{j}n_z n_x;$$

the length of this vector determines the magnitude of the tilt and its direction fixes the two-fold symmetry axis C_2 in each smectic plane. The free energy associated with this order is then written as [14–16]

$$F_c = \frac{a}{2}(\mathbf{n} \wedge \mathbf{c})^2 + \frac{b}{4}(\mathbf{n} \wedge \mathbf{c})^4,$$

$$= \frac{a}{2}n_z^2 c^2 + \frac{b}{4}n_z^4 c^4. \qquad (1)$$

When the smectic C phase is composed of chiral molecules, **c** rotates around the Z axis, creating a helical structure with

$$n_x = \cos\phi(z)\sin\theta, \quad n_y = \sin\phi(z)\sin\theta.$$

Since the spontaneous twist induces a bend deformation there is an additional elastic free energy which, in the usual notation, is given by

$$F_{\mathrm{el}} = \frac{K_{22}}{2}(\mathbf{n}\cdot\operatorname{rot}\mathbf{n} + q_0)^2 + \frac{K_{33}}{2}(\mathbf{n} \wedge \operatorname{rot}\mathbf{n})^2. \qquad (2)$$

Here q_0 is the wave number of the pitch of the helix due to the chirality of the constituent molecules. Since

$$\operatorname{rot}\mathbf{n} = \operatorname{rot}\mathbf{c} = -q\mathbf{c},$$

where $q = \partial\phi/\partial z$,

$$F_{\mathrm{el}} = \frac{K_{22}}{2}(qc^2 - q_0)^2 + \frac{K_{33}}{2}q^2 n_z^2 c^2. \qquad (3)$$

It has been argued theoretically [4, 5, 8, 16] and shown experimentally [6, 17, 18] that in a chiral smectic C phase there is a spontaneous polarization **P** along $\mathbf{n} \wedge \mathbf{c}$. The corresponding contribution to the free energy can be written as [8, 16]

$$F_{\mathrm{p}} = -(\mu_{\mathrm{p}}(\mathbf{n} \wedge \mathbf{c}) - \mu_{\mathrm{f}}(\mathbf{n} \wedge \operatorname{rot}\mathbf{c}))\cdot\mathbf{P} + \frac{1}{2\chi}\mathbf{P}\cdot\mathbf{P}. \qquad (4)$$

Here μ_p and μ_f are the piezo-electric and flexo-electric moduli, which describe the coupling between the polarization on the one hand and the tilt and the bend on the other; χ is the dielectric susceptibility, which is of the order unity. Minimizing F_p with respect to $\mathbf{P} = (P_x, P_y, 0)$ yields

$$\begin{aligned} \mathbf{P} &= \chi(\mu_p(\mathbf{n} \wedge \mathbf{c}) - \mu_f(\mathbf{n} \wedge \operatorname{rot} \mathbf{c}), \\ &= \chi(\mu_p + q\mu_f)(\mathbf{n} \wedge \mathbf{c}), \\ &= P_0 \cdot \mathbf{n} \wedge \mathbf{c} \end{aligned} \tag{5}$$

and

$$F_p = \tfrac{1}{2}\chi(\mu_p + q\mu_f)^2 n_z^2 c^2. \tag{6}$$

Summing equations (1), (3) and (6) gives the total free energy F, which can be written as

$$\begin{aligned} F = {} & \tfrac{1}{2}(a - \chi\mu_p^2) n_z^2 c^2 + \frac{b}{4} n_z^4 c^4 + \tfrac{1}{2} K_{22}(qc^2 - q_0)^2 \\ & + \tfrac{1}{2}(K_{33} - \chi\mu_f^2) q^2 n_z^2 c^2 - \chi\mu_p\mu_f q n_z^2 c^2. \end{aligned} \tag{7}$$

Here q is the actual wavenumber of the helix, which can be found by minimizing F with respect to q. Thus for $c^2 \neq 0$,

$$q = \frac{K_{22} q_0 + \chi\mu_p\mu_f n_z^2}{K_{22}c^2 + (K_{33} - \chi\mu_f^2) n_z^2} \tag{8}$$

which relates the wavenumber q of the actual pitch with the coefficients q_0, μ_p and μ_f appearing in the phenomenological description of the chiral smectic C phase, equation (7). Since both c^2 ($= \sin^2 \theta$) and n_z^2 ($= 1 - c^2$) have to be non-zero, this relation clearly depends on the tilt angle θ, which has not been shown or noticed before [8, 14, 15, 16]. Compared with the twisted nematic phase for which c^2 is unity and $q = q_0$ there is, in the chiral smectic C phase, an additional contribution to q due to the spontaneous bend and proportional to $\chi\mu_p\mu_f$ [4, 5, 8]. A molecular theory of q for the chiral smectic C phase given a finite θ, that is given orientational order with respect to a tilted director, requires a calculation of q_0, μ_p and μ_f in terms of molecular properties. In §4 however it is shown that for all practical purposes the influence of the terms determined by μ_p and μ_f is negligibly small. It suffices therefore to calculate q_0, the wavenumber of the unperturbed helix in the smectic C phase caused by the molecular chirality; this is done in the following section.

3. Microscopic theory

It has been shown that the interplay between the induced molecular dipole–dipole interaction, V^{pp}, and the dipole–quadrupole interaction, V^{pq}, results in the helical structure of the cholesteric phase [19]. The helical twist in the ground state of the chiral smectic C phase can be described along the same lines. In order to do so we recapitulate the basic features to show the similarity of and the difference between the twist in these two phases. Consider therefore the interaction energies V_{ij}^{pp} and V_{ij}^{pq} between two molecules i and j, which can be written quite generally as

$$V_{ij}^{pp} = (\alpha\beta)_i(\alpha'\beta')_j C_{\alpha\alpha'} C_{\beta\beta'} r_{ij}^{-6}, \tag{9}$$

$$\begin{aligned} V_{ij}^{pq} = {} & (\alpha\beta)_i(\alpha', \beta'\gamma')_j C_{\alpha\alpha'} D_{\beta\beta'\gamma'} r_{ij}^{-7} \\ & + (\alpha\beta)_i(\alpha', \beta'\beta')_j C_{\alpha\alpha'} r_\beta^{ij} r_{ij}^{-8}. \end{aligned} \tag{10}$$

Here $(\alpha\beta)$ and $(\alpha, \beta\gamma)$ are shorthand notations for products of molecular matrix elements of the dipole and quadrupole moment operators p_α and $q_{\beta\gamma}$ respectively. The precise definition in the language of quantum mechanics is [19]

$$(\alpha\beta)_i(\alpha'\beta')_j = \sum_{v,v'} \langle 0|p_\alpha|v\rangle_i \langle v|p_\beta|0\rangle_i \langle 0|p_{\alpha'}|v'\rangle_j \langle v'|p_{\beta'}|0\rangle_j / E_{vv',00}, \tag{11}$$

$$(\alpha\beta)_i(\alpha', \beta'\gamma')_j = \sum_{v,v'} \langle 0|p_\alpha|v\rangle_i \langle v|p_\beta|0\rangle_i \langle 0|p_{\alpha'}|v'\rangle_j \langle v'|q_{\beta'\gamma'}|0\rangle_j / E_{vv',00}. \tag{12}$$

Repeated indices $\alpha\beta\gamma$, which refer to the coordinates XYZ of a fixed macroscopic coordinate system, indicate a summation over the corresponding components. The notation used in equations (9) and (10) and defined in equations (11) and (12) is employed because it reflects clearly the transformation properties of these quantities, which are the same as those of the corresponding coordinates. The scalar r_{ij} is the absolute value of the vector $\mathbf{r}_{ij} = (r_\alpha^{ij}, r_\beta^{ij}, r_\gamma^{ij})$ pointing from the centre of mass of molecule i to that of molecule j. The quantities $C_{\alpha\beta}^{ij}$ and $D_{\alpha\beta\gamma}^{ij}$ in equations (9) and (10) are tensor elements depending on the relative positions of the molecules i and j, i.e. on $\mathbf{r}_{ij}$; they are defined by

$$C_{\alpha\beta}^{ij} = \delta_{\alpha\beta} - 3r_\alpha^{ij} r_\beta^{ij} / r_{ij}^2, \tag{13}$$

$$D_{\alpha\beta\gamma}^{ij} = (2\delta_{\alpha\beta} - 5r_\alpha^{ij} r_\beta^{ij} / r_{ij}^2)(3r_j^{ij} / 2r_{ij}). \tag{14}$$

The pair potential

$$V_{ij} = V_{ij}^{pp} + V_{ij}^{pq} + V_{ij}^{qp}$$

has been used for an internal field approximation in which the precise interaction $V_i = \Sigma_j V_{ij}$ of one molecule with all the others is approximated by a suitably averaged interaction. This averaged interaction can be reduced to a tractable form by considering the distribution of the centres of mass of the constituting molecules as cylindrically symmetrical with respect to the helix axis. This symmetry is reflected in the averaged values of the products $C_{\alpha\beta}C_{\alpha'\beta'}$ and $C_{\alpha\beta}D_{\alpha'\beta'\gamma'}$. When the averaging is performed as prescribed in [19] only those combinations of $C_{\alpha\beta'}C_{\alpha'\beta'}$ and $C_{\alpha\beta'}D_{\alpha'\beta'\gamma'}$, survive that are even in r_α^{ij} and r_β^{ij} where α and β are the coordinates of the plane perpendicular to the helix axis. In [19] the helix axis was chosen along the Y axis, because in cholesterics the helix axis is perpendicular to the director which is usually chosen along the Z axis. It was found in a straightforward way that the wavenumber q_0 ($=2\pi/p_0$), with p_0 being the pitch of the helix, is given by

$$q_0 = \frac{\langle (X, YZ)' - (Y, ZX)' + (Z, XY)' \rangle}{\langle (ZZ)' - (XX)' \rangle \overline{r_y^2}}, \tag{15}$$

where the brackets $\langle\ \rangle$ denote a statistical average of the corresponding quantities. The prime on these quantities denotes the fact that they are defined with respect to a coordinate system X', Y', Z' continuously rotating around the helical axis, i.e. the $Y = Y'$ axis over an angle $q_0\overline{r_y}$ ensuring that the local director is everywhere along the Z' axis. This enables the quantities $(\alpha\beta)'$, etc., and therefore q_0, to be expressed in terms of molecular quantities and of the orientational order parameters describing the local nematic order; $\overline{r_y}$ is the average distance of closest approach of two molecules along the helical axis. All the approximations made and calculations performed in order to obtain equation (15) apply equally to chiral smectics with the following provisos.

(i) In chiral smectics the helix axis is along the normal to the smectic planes, usually denoted as the Z axis. Making therefore an appropriate change of coordinates,

$Y \to Z$, $Z \to X$, $X \to Y$ (equally the coordinate system may be rotated over $\pi/2$ around the X axis) equation (15) reads

$$q_0 = \frac{\langle (X, YZ)' + (Y, ZX)' - (Z, XY)' \rangle}{\langle (XX)' - (YY)' \rangle \overline{r_z^2}}. \tag{16}$$

(ii) The primed quantities in equation (16) refer to a coordinate system X', Y', $Z' = Z$, with X' and Y' rotating from layer to layer over an angle $q_0\overline{r_z}$ around the layer normal Z, i.e. the helix axis. Neither of the axes of this coordinate system is along the local director, which is tilted with respect to the layer normal. We therefore define a rotating tilted coordinate system X'', Y'', Z'' by

$$X' = X'',\ Y' = Y''\cos\theta + Z''\sin\theta,\ Z' = -Y''\sin\theta + Z''\cos\theta$$

with θ being the tilt angle of the director in the smectic C phase. Then the Z'' axis is along the local director whereas the X'' axis coincides with the two-fold symmetry axis in each smectic plane. Applying this transformation to the primed quantities in equation (16) gives

$$q_0 = \frac{A\sin^2\theta + B\cos^2\theta}{\Delta\alpha\sin^2\theta - \delta\alpha\cos^2\theta}\frac{1}{l^2(\theta)}, \tag{17}$$

where

$$\left.\begin{aligned} A &= \langle (X, YZ + Z, XY - Y, XZ)'' \rangle, \\ B &= \langle (Z, XY - X, YZ - Y, ZX)'' \rangle, \\ \Delta\alpha &= \langle (ZZ)'' - \tfrac{1}{2}(XX + YY)'' \rangle \approx \langle (ZZ - XX)'' \rangle, \\ \delta\alpha &= \langle (XX - YY)'' \rangle \end{aligned}\right\} \tag{18}$$

and

$$l^2(\theta) = l^2(1 - \lambda\sin^2\theta),\quad \lambda = 1 - d^2/l^2 < 1, \tag{19}$$

with l the length and d the diameter of the molecules. Here we have not considered the existence of a non-vanishing $\langle (YZ)'' \rangle$ [12], which does not interfere with the results described in §4. Now we express the macroscopic quantities in equation (17) as defined in equation (18) in terms of molecular quantities and the order parameters describing the local orientational order in the X'', Y'', Z'' coordinate system. This can be achieved by means of the transformation

$$\begin{bmatrix} X'' \\ Y'' \\ Z'' \end{bmatrix} = \begin{bmatrix} X_x'' & X_y'' & X_z'' \\ Y_x'' & Y_y'' & Y_z'' \\ Z_x'' & Z_y'' & Z_z'' \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \tag{20}$$

where $X_x'' = x_{X''} = \cos\chi_{x,X''}$, etc.—$\chi_{x,X''}$ is the angle between the molecular x axis and the macroscopic X'' axis, which can be written as a function of the Euler angles ϕ, ϑ, ψ [19]. The order parameters describing the orientational order in the X'', Y'', Z'' coordinate system come to the fore quite naturally as [20–22]

$$\left.\begin{aligned} S_1 &= \tfrac{1}{2}\langle 3z_{Z''}^2 - 1 \rangle = \tfrac{1}{2}\langle 3\cos^2\vartheta - 1 \rangle, \\ S_2 &= \langle x_{Z''}^2 - y_{Z''}^2 \rangle = \langle \cos 2\psi, \sin^2\vartheta \rangle, \\ S_3 &= \langle z_{X''}^2 - z_{Y''}^2 \rangle = \langle \cos 2\phi \sin^2\vartheta \rangle, \\ S_4 &= \tfrac{1}{2}(\langle x_{X''}^2 - x_{Y''}^2 \rangle + \langle y_{Y''}^2 - y_{X''}^2 \rangle) \approx \langle \cos 2\phi \cos 2\psi \rangle. \end{aligned}\right\}. \tag{21}$$

For the macroscopic anisotropy $\Delta\alpha$ and the macroscopic biaxiality $\delta\alpha$ we then find

$$\Delta\alpha = \alpha_a S_1 + \tfrac{3}{4}\alpha_b S_2, \tag{22}$$

$$\delta\alpha = \alpha_a S_3 + \alpha_b S_4, \tag{23}$$

whereas the quantities A and B can be written as

$$A = \gamma(S_1 - \tfrac{1}{2}S_3) - (\zeta - \tfrac{1}{2}\xi)S_2 + \zeta S_4, \tag{24}$$

$$B = (\zeta - \tfrac{1}{2}\xi)S_4 - \gamma S_3. \tag{25}$$

Here α_a, α_b, γ, ζ and ξ are molecular quantities formally defined as

$$\alpha_a = (zz) - \tfrac{1}{2}(xx + yy), \quad \alpha_b = (xx - yy), \tag{26}$$

$$\gamma = (x, yz) - (y, zx), \quad \zeta = (z, xy), \quad \xi = (x, yz) + (y, zx). \tag{27}$$

reflecting their symmetry properties on a molecular scale. The precise definitions of all the separate terms in these quantities is given by equations (11) and (12) for $(\alpha\beta)$ and $(\alpha, \beta\gamma)$ respectively, where α, β and γ then refer to the molecular coordinates z, x and y.

The definitions given in equation (21) clearly reflect the uniaxial symmetry of the order described by S_1 and S_2, being defined with respect to the Z'' axis only. In order that S_3 and S_4, which are defined with respect to the X'' and Y'' axes, are non-zero, the orientational distribution function must be biaxial; then in addition there is a macroscopic biaxiality, whatever its magnitude [21, 22, 24].

4. Discussion

Before discussing the tilt and temperature dependence of the pitch we shall show that the influence of the spontaneous polarization on the pitch, as described in equation (7), is rather small. From the experimental data we may conclude that an upper limit to P_0, defined in equation (5), is 10 nC/cm^2 [6, 7, 16–18]. In [16] it is concluded that the flexo-electric contribution to P_0, cf. equation (5), is at best 10 per cent; the accepted order of magnitude of μ_f is 10^{-5} dyne [6, 16]. With $q \simeq 10^4\,\mathrm{cm}^{-1}$ we have, $q\mu_f \simeq 10^{-1(0)}\,\mathrm{dyne}^{1/2}/\mathrm{cm}$. From the definition of P_0 we then find an upper limit for μ_p, i.e. $\mu_p \lesssim 10^{1(0)}$ dyne/cm. Comparing $\chi\mu_p\mu_f \lesssim 10^{-4}\,\mathrm{dyne\,cm}^{-1}$ with $K_{22}q_0 \gtrsim 10^{-7} \times 10^4\,\mathrm{dyne\,cm}^{-1} = 10^{-3}\,\mathrm{dyne\,cm}^{-1}$ and $\chi\mu_f^2 \simeq 10^{-10(9)}$ dyne with $K_{33} > 10^{-7}$ dyne we may indeed conclude that the influence of the spontaneous polarization on q is negligible. Equation (8) can then be written as

$$q = \frac{K_{22}q_0}{K_{22}c^2 + K_{33}n_z^2},$$

$$= \frac{q_0}{\kappa - (\kappa - 1)\sin^2\theta}, \tag{28}$$

where $\kappa = K_{33}/K_{22}$ and q_0 is given by equation (17), i.e.

$$q_0 = \frac{A\sin^2\theta + B\cos^2\theta}{\Delta\alpha\sin^2\theta - \delta\alpha\cos^2\theta}\,\frac{1}{l^2(1 - \lambda\sin^2\theta)}. \tag{29}$$

The anisotropy $\Delta\alpha$ and biaxiality $\delta\alpha$, defined in equations (22) and (23), are well-known quantities. The few experimental data indicate that $\delta\alpha \lesssim 10^{-2}\Delta\alpha$; with $\theta > 10^{-1}$ rad the denominator can be written as $\Delta\alpha\sin^2\theta$. The quantities A and B are defined, in equations (24) and (25) respectively, in terms of the orientational order parameters S_i, $i = 1, 2, 3, 4$, and the molecular quantities γ, ζ and ξ. Though information regarding the order parameters S_2, S_3 and S_4 is scarce, it seems fair to state that they are of the order of 10^{-2}. Then with $\theta > 10^{-1}$ rad the numerator can be written as $\gamma S_1 \sin^2\theta$. Collecting these results we find, with $\Delta\alpha \simeq \alpha_a S_1$, see equation (22), that equation (28) can be written as

$$q = \frac{\gamma}{l^2 \alpha_a} \frac{1}{(1 - \lambda \sin^2\theta)(\kappa - (\kappa - 1)\sin^2\theta)}, \tag{30}$$

valid for $\theta > 10^{-1}$ rad, i.e. $T < T_{S_C S_A} - 1$ K where $T_{S_C S_A}$ is the smectic C–smectic A transition temperature. The tilt dependence of the pitch is then determined by the tilt dependence of the bend deformation and the layer thickness. Accordingly the temperature dependence of the pitch is determined by the temperature dependence of the tilt angle θ; with increasing temperature θ decreases, q decreases and p increases, which is indeed the general trend reported [6, 7].

Finally we want to discuss the behaviour of p when T approaches the transition temperature, $T_{S_C S_A}$. Experimentally we know that in a very small temperature region near $T_{S_C S_A}$, p decreases very strongly [6, 7]. We propose a tentative explanation which is hard to prove but seems plausible. There is experimental evidence that the biaxiality $\delta\alpha$ near $T_{S_C S_A}$ is proportional to $\sin^2\theta$ [22, 24]. Then the denominator, $\Delta\alpha \sin^2\theta - \delta\alpha \cos^2\theta$, in equation (29) is in its entirety proportional to $\sin^2\theta$, which for $T \to T_{S_C S_A}$ goes to zero as $\theta^2 \propto (T_{S_C S_A} - T)^{2\beta}$; here $0{\cdot}5 > \beta > 0{\cdot}35$ [24]. There is also experimental evidence that the spontaneous polarization $P = P_0 \sin\theta$, cf. equation (5), near $T_{S_C S_A}$ goes to zero as θ, indicating that $P_0 \propto \langle x_{X''} \rangle$ remains finite up to $T_{S_C S_A}$ [6, 7, 17]. Here $\langle x_{X''} \rangle$ is the polar order parameter which describes the averaged orientation of the x component of the molecular dipole with respect to the macroscopic X'' axis, i.e. the two-fold symmetry axis. As a non-vanishing polarization requires a coupling of the transverse dipole with the chiral centre [4, 6, 7] we may then expect that the bipolar order parameter

$$S_4 = \tfrac{1}{2}(\langle x_{X''}^2 - x_{Y''}^2 \rangle + \langle y_{Y''}^2 - y_{X''}^2 \rangle)$$

for the chiral centre, though small, also remains finite up to $T_{S_C S_A}$. Since the numerator in equation (29) then remains finite,

$$B = (\zeta - \tfrac{1}{2}\xi) S_4$$

we find that close to $T_{S_C S_A}$,

$$p = \kappa/(2\pi q_0) \propto \theta^2$$

and approaches zero as $(T_{S_C S_A} - T)^{2\beta}$. The physical idea is that the chiral interaction, trying to stiffen up the helical structure, remains finite whereas the resistance against it, i.e. the biaxiality $\langle (XX - YY)' \rangle$, vanishes at the transition. At the same time it should be kept in mind that with $\theta \to 0$ the concept of a helical structure ceases to be meaningful, because the length of the rotating c director, being proportional to $\sin\theta$, also goes to zero: in fact equation (8) is only valid for $c^2 \neq 0$. In conclusion we have shown that the tilt dependence of the pitch in the chiral smectic C phase well below $T_{S_C S_A}$ is quite different from that close to $T_{S_C S_A}$. This quite different dependence on θ in combination with the temperature dependence of θ itself explains at least qualitatively the quite different behaviour of the pitch as a function of temperature well below and close to $T_{S_C S_A}$.

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