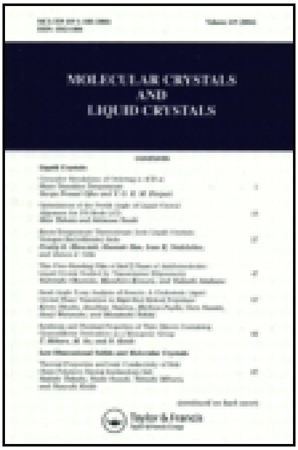

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Smectic A and the Smectic C Phase: A Coherent Molecular Picture

W. J. A. Goossens [a]

[a] Philips Research Laboratories, P. O. Box 80.000, 5600, JA, Eindhoven, The Netherlands

Version of record first published: 13 Dec 2006.

To cite this article: W. J. A. Goossens (1987): The Smectic A and the Smectic C Phase: A Coherent Molecular Picture, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 150:1, 419-445

To link to this article: http://dx.doi.org/10.1080/00268948708074813

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 419–445
Photocopying permitted by license only

Printed in the United States of America

The Smectic A and the Smectic C Phase: A Coherent Molecular Picture†

W. J. A. GOOSSENS

Philips Research Laboratories, P. O. Box 80.000, 5600 JA Eindhoven, The Netherlands

(*Received September 1, 1986; accepted May 27, 1987*)

A molecular field theory of the smectic A and smectic C phase is presented which is based on an interaction derived in terms of the molecular polarizability, its anisotropy and the components of the static molecular quadrupole tensor. It is shown that this attractive interaction strongly depends on the anisotropy of the excluded molecular volume. The results obtained explain the stability of the A phase, the appearance of the tilt in the C phase and the A–C phase transition, without resource to adjustable parameters which indeed have no molecular significance.

Keywords: liquid crystal, phase transition, molecular theory, mean field approximation, smectic A phase, smectic C phase

I. INTRODUCTION

In the molecular theory of Maier and Saupe for the nematic phase,[1] the orientation–dependent interaction is described in terms of a well defined molecular property, i.e. the anisotropy of the molecular polarizability. The interaction derived however only depends on the relative orientation of two molecules and not on their relative position. Such interaction, appropriate indeed for orientational order only, cannot account for a coupling between orientational and translational order as does exist in the smectic phase. A molecular theory for the smectic phase therefore requires an additional interaction that

---

†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, June 30–July 4, 1986.

accounts in a natural way for such coupling again in terms of well defined molecular properties. Usually however a model interaction is proposed, which prescribes the relative orientation and position of the molecules without resource to their properties except for some relationship with the Maier-Saupe interaction. As such an approach cannot be classified as a molecular theory we show in Section II that a proper molecular interaction can still be derived according to the procedure of Reference 1, with due regard however to the symmetry of the distribution of the centres of mass of the molecules. In the smectic phase this symmetry is reflected by the one-dimensional layered structure, which is shown to be strongly dependent on the shape anisotropy of the molecules. In section III we demonstrate the stability of the smectic A phase with respect to a tilt of the director. In section IV we show that the interaction between the molecules in terms of their static quadrupole moments may give rise to an A–C phase transition according to the rules.[2] Finally, in section V we discuss the results in connection with existing "molecular" theories.

II. THE SMECTIC A PHASE

The description of the attractive forces between the anisotropic molecules constituting the various liquid crystal phases is based on a multipole expansion of the electrostatic energy $v^{i,j}$ of the charge distributions $\Sigma_\nu e^i_\nu$ of these molecules. Quite generally one has with $\Sigma_\nu e^i_\nu = 0$ and $\mathbf{R}^i_\nu = \mathbf{R}^i + \mathbf{r}^i_\nu$:

$$\begin{aligned} V^{i,j} &= p^i_\alpha p^j_\beta \frac{\partial}{\partial R^i_\alpha}\frac{\partial}{\partial R^i_\beta}\left(\frac{1}{R}\right) + \frac{1}{2} p^i_\alpha q^j_{\beta\gamma} \frac{\partial}{\partial R^i_\alpha}\frac{\partial}{\partial R^j_\beta}\frac{\partial}{\partial R^j_\gamma}\left(\frac{1}{R}\right) \\ &\quad + \text{transpose} + \frac{1}{4} q^i_{\alpha\beta} g^j_{\gamma\delta} \frac{\partial}{\partial R^i_\alpha}\frac{\partial}{\partial R^i_\beta}\frac{\partial}{\partial R^i_\delta}\frac{\partial}{\partial R^j_\delta}\left(\frac{1}{R}\right) \qquad (1) \\ &= V^{i,j}_{pp} + V^{i,j}_{pq} + V^{i,j}_{qp} + V^{i,j}_{qq} \end{aligned}$$

Here $p^i_\alpha = \Sigma_\nu e^i_\nu (r^i_\nu)_\alpha$ and $g^i_{\alpha\beta} = \Sigma_\nu e^i_\nu (r^i_\nu)_\alpha (r^i_\nu)_\beta$ are the dipole moment and the quadrupole moment respectively of the charge distribution of the i-th molecule; $(r^i_\nu)_\alpha$ is the α-component of the radius vector of the charge e^i_ν with respect to the origin of a molecular fixed coordinate system x, y, z. The position of that origin, defined as centre of mass, with respect to the origin of a fixed macroscopic coordinate system X, Y, Z is described by the radius vector $\mathbf{R}^i = (R^i_X, R^i_Y, R^i_Z)$. The relative position of two molecules i and j is described by the vector $\mathbf{R}^{ij} = \mathbf{R}^i - \mathbf{R}^j = (R^{ij}_X, R^{ij}_Y, R^{ij}_Z)$.

For ease of notation $R^{ij} = |\mathbf{R}^{ij}|$ and R^{ij}_α will be denoted as R and R_α respectively. Repeated subscripts α, β etc., which all refer to the macroscopic coordinates X, Y, Z, indicate a summation over the corresponding components. The theory of the isotropic–nematic phase transition in terms of attractive forces is based on the second-order perturbation energy $V(pp)$ of the dipole–dipole interaction, i.e. $V(pp) \propto -(V^{i,j}_{pp}, V^{i,j}_{pp})$.[1] The theory of the spontaneous twist occurring in the cholesteric, i.e. twisted nematic phase, is based on the second-order perturbation energy $V(pq)$ of the dipole–dipole and dipole–quadrupole interaction, i.e. $V(pq) \propto -(V^{i,j}_{pp}\ V^{i,j}_{pq})$.[3] The way in which $V(pq)$ can be incorporated to describe the twist in the chiral C phase will be presented in App. B. In order to explore the properties of $V(pp)$ exhaustively we recall that using Eq. (1) the dipole–dipole interaction can be written as[3]

$$V^{i,j}_{pp} = p^i_\alpha p^j_{\alpha'} \left(\delta_{\alpha\alpha'} - \frac{3R_\alpha R_{\alpha'}}{R^2} \right) \frac{1}{R^3} = p^i_\alpha p^j_{\alpha'} C_{\alpha\alpha'} \tag{2}$$

The second-order perturbation energy $V(pp)$ is accordingly obtained as[1,3,4]

$$V(pp) = -(\alpha\beta)(\alpha'\beta') C_{\alpha\alpha'} C_{\beta\beta'} \tag{3}$$

where $(\alpha\beta)(\alpha'\beta')$ is a shorthand notation for a long expression, that is,

$$(\alpha\beta)(\alpha'\beta') = \sum_{\nu,\mu} \langle o|p_\alpha|\nu\rangle_i \, \langle \nu|p_\beta|o\rangle_i \, \langle o|p_{\alpha'}|\mu\rangle_j \, \langle \mu|p_{\beta'}|o\rangle_j / E^{ij}_{\nu\mu,oo} \tag{4}$$

In Eq. (4) the summation is over all excited states ν and μ with energies E^i_ν and E^j_μ such that $E^{ij}_{\nu\mu} = E^i_\nu + E^j_\mu - E^i_o - E^j_o \neq 0$. A useful approximation for Equation (4) which shows at once the relationship of Equation (3) with the isotropic v/d Waals interaction is[4]:

$$(\alpha\beta)(\alpha'\beta') = \mathrm{I}\alpha^i_{\alpha\beta}\alpha^j_{\alpha'\beta'} \tag{5}$$

Here I is an average molecular ionization potential and $\alpha_{\alpha\beta}$ is the $\alpha\beta$-component of the molecular polarizability tensor $\bar{\bar{\alpha}}$ defined with respect to the macroscopic coordinates X, Y, Z. The notation used in Equation (3) and defined in Equations (4) and (5) is not only very tractable but also clearly reflects the transformation properties of the quantities $(\alpha\beta)$, which are the same as those of the corresponding coordinates $\alpha\beta$. The orientation dependence of $(\alpha\beta)$ is defined accordingly; considering for instance the component (ZZ) one may write:

$$(ZZ) = (xx)\, x_Z^2 + (yy)\, y_Z^2 + (zz)\, z_Z^2 \tag{6}$$

where x_Z, y_Z and z_Z are the direction cosines of the molecular x, y and z-axes respectively with respect to the macroscopic Z-axis. The quantities (xx) etc. are still defined by Eqs. (4) and (5) where, however, α, β then refer to the molecular coordinates x, y, z. The orientation of the molecular coordinate system with respect to the macroscopic coordinate system in terms of the direction cosines can also be described by the Euler angles φ, ϑ, ψ; in the following this orientation will be denoted by the one symbol $\Omega = (\varphi, \vartheta, \psi)$. The relation between the direction cosines and the Euler angles is given in Appendix A.

An important feature of Equation (3) is the coupling of the orientation-dependence of the interaction to the relative position of the molecules through the matrix elements $C_{\alpha\alpha'}$ and $C_{\beta\beta'}$ defined as a function of R_X,R_Y and R_Z.

In order to reduce Equation (3) to a tractable form $V_{(pp)} = V(\Omega^i, \Omega^j, \mathbf{R})$ will be used for a mean field approximation in which the precise interaction $V^i = \Sigma_{j \neq i}\, V(\Omega^i, \Omega^j, \mathbf{R})$ of one molecule with all others will be approximated by a suitable averaged interaction. This approximate interaction, called mean field interaction, is written as

$$V(\Omega^i, \mathbf{R}^i) = -\rho \int d\mathbf{R}^j \int d\Omega^j\, f(\Omega^j, \mathbf{R}^j)(\alpha\beta)^i(\alpha'\beta')^j C_{\alpha\alpha'} C_{\beta\beta'} \tag{7}$$

where ρ is the density and where the normalized one-particle distribution function in turn is defined in terms of the mean field, that is

$$f(\Omega, \mathbf{R}) = \exp(-V(\Omega, \mathbf{R})/\mathrm{kT}) \Big/ \int d\Omega d\mathbf{R}\, \exp(-V(\Omega, \mathbf{R})/\mathrm{kT}) \tag{8}$$

In the smectic phase the distribution of the centres of mass of the molecules is periodic along the layer normal once and for all to be along the Z-axis. The distribution of the centres of mass, being a function of R_Z only, can be considered as rotationally symmetric with respect to that axis. So we have[5]

$$f(\Omega, \mathbf{R}) = f(\Omega, R_Z) = f_0(\Omega) + f_1(\Omega) \cos qR_Z + \ldots \tag{9}$$

where $f_0(\Omega) = 1/d. \int_0^d dR_Z\, f(\Omega, R_Z)$, $f_1(\Omega) = 2/d. \int_0^d dR_Z\, f(\Omega, R_Z) \cos qR_Z$, $q = 2\pi/d$ and d is the layer thickness. We also change the variables, that is $R_X = r \cos \phi$, $R_y = r \sin \phi$, $R^2 = r^2 + R_Z^2$, $d\mathbf{R}_j \Rightarrow d\mathbf{R} = dR_Z.\, rdr.\, d\phi$ and $C_{\alpha\beta} = C_{\alpha\beta}(R_Z, r, \phi)$. The integration over ϕ in Equation (7) is elementary; the result can be written as

$$\int_0^{2\pi} d\phi\; C_{\alpha\alpha'} C_{\beta\beta'}\; (\alpha\beta)^i(\alpha'\beta')^j = \sum_{n=0,2,4} A_n(\Omega^i,\Omega^j)\, \frac{2\pi P_n(R_Z/R)}{R^6} \tag{10}$$

where $P_n(R_Z/R)$ is the n-th order Legendre polynomial. The corresponding orientation-dependent contributions A_n are found to be

$$A_0(\Omega^i, \Omega^j) = \tfrac{2}{3}\, \alpha_Z(\Omega^i)\alpha_Z(\Omega^j) + \tfrac{2}{15}\, \delta_Z(\Omega^i)\delta_Z(\Omega^j) + \tfrac{1}{10}\, \epsilon_Z(\Omega^i)\epsilon_Z(\Omega^j)$$
$$+ \tfrac{1}{10}\, (\chi_{XY}(\Omega^i)\chi_{XY}(\Omega^j) + \chi_{YZ}(\Omega^i)\chi_{YZ}(\Omega^j) + \chi_{ZX}(\Omega^i)\chi_{ZX}(\Omega^j)) \tag{11}$$

$$A_2(\Omega^i, \Omega^j) = \tfrac{2}{3}\, (\alpha_Z(\Omega^i)\delta_Z(\Omega^j) + \delta_Z(\Omega^i)\alpha_Z(\Omega^j))$$
$$- \tfrac{4}{21}\, \delta_Z(\Omega^i)\delta_Z(\Omega^j) + \tfrac{1}{7}\, (\epsilon_Z(\Omega^i)\epsilon_Z(\Omega^j) + (\chi_{YX}(\Omega^i)\chi_{YX}(\Omega^j) \tag{12}$$
$$- \tfrac{1}{14}\, (\chi_{YZ}(\Omega^i)\chi_{YZ}(\Omega^j) + \chi_{ZX}(\Omega^i)\chi_{ZX}(\Omega^j))$$

$$A_4(\Omega^i,\Omega^j) = \tfrac{72}{35}\, \delta_Z(\Omega^i)\delta_Z(\Omega^j)$$
$$+ \tfrac{9}{35}\, (\epsilon_Z(\Omega^i)\epsilon_Z\, (\Omega^j + \chi_{XY}(\Omega^i)\chi_{XY}(\Omega^j))$$
$$- \tfrac{36}{35}\, (\chi_{YZ}(\Omega^i)\chi_{YZ}(\Omega^j) + \chi_{ZX}(\Omega^i)\chi_{ZX}(\Omega^j)) \tag{13}$$

where the following abbreviations have been used

$$\begin{array}{ll} \text{a) } \alpha_Z = (XX + YY + ZZ) & \text{d) } \chi_{XY} = 2(XY) \\ \text{b) } \delta_Z = (ZZ) - \tfrac{1}{2}(XX + YY) & \text{e) } \chi_{YZ} = 2(YZ) \\ \text{c) } \epsilon_Z = (XX - YY) & \text{f) } \chi_{ZX} = 2(ZX) \end{array} \tag{14}$$

After substitution of Eqs. (9) and (10) in Eq. (7) and putting $\cos qR^{ij}_Z = \cos qR_Z \cos qR^i_Z + \ldots$ the latter can be written as

$$\begin{aligned} V(\Omega^i, R^i_Z) &= V_N(\Omega^i) + V_{S_A}(\Omega^i, R^i_Z) \\ &= -\sum_n \overline{P}_n \int d\Omega^j f_0(\Omega^j)\, A_n(\Omega^i, \Omega^j) \\ &\quad - \cos qR^i_Z \sum_n \overline{cP}_n \int d\Omega^j f_1(\Omega^j)\, A_n(\Omega^i, \Omega^j) \end{aligned} \tag{15}$$

where

$$\overline{P}_n = 2\pi\rho \int dR_Z \int r\,dr\, P_n(R_Z/R)\, R^{-6} \tag{16}$$

$$\overline{cP}_n = 2\pi\rho \int dR_Z \int r\,dr\, P_n(R_Z/R) R^{-6} \cos qR_Z \tag{17}$$

The first part of the r.h.s. of Equation (15), determined by $f_0(\Omega)$, describes orientation–dependent interaction only and is typical of the nematic phase; the first term $\int d\Omega^j f_0(\Omega^j) A_0(\Omega^i, \Omega^j)$ in $V_N(\Omega^i)$ corresponds to the interaction derived in Reference 1. In the second part of the r.h.s. of Equation (15), determined by $f_1(\Omega) = 2/d. \int_0^d dR_Z f(\Omega, R_Z) \cdot \cos qR_Z$, the orientation–dependence of the interaction is coupled to the translational dependence. This interaction denoted as $V_{S_A}(\Omega, R_Z)$ is typical of the smectic phase and will be our main concern. To have an easy start we first consider uniaxial orientational order with respect to the layer normal. Quoting the results from Appendix A we have

$$\begin{aligned} &a)\ (XX) = (YY) = \alpha I^{1/2} - \tfrac{1}{3}\delta I^{1/2} P_2(\cos\vartheta) \\ &b)\ (ZZ) = \alpha I^{1/2} + \tfrac{2}{3}\delta I^{1/2} P_2(\cos\vartheta) \\ &c)\ (XY) = (YZ) = (ZX) = 0 \end{aligned} \tag{18}$$

and according to Equation (14)

$$\begin{aligned} &a)\ \alpha_Z = 3\alpha I^{1/2} \\ &b)\ \delta_Z = \delta I^{1/2} P_2(\cos\vartheta) \\ &c)\ \epsilon_Z = \chi_{\alpha\beta} = 0 \end{aligned} \tag{19}$$

where $\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and $\delta = \alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy})$ are the molecular polarizability and the anisotropy thereof respectively.

Introducing the order parameters,[5]

$$\eta = \int d\Omega \int dR_Z\, f(\Omega, R_Z)\, P_2(\cos\vartheta) \tag{20}$$

$$\tau = \int d\Omega \int dR_Z\, f(\Omega, R_Z) \cos qR_Z \tag{21}$$

$$\sigma = \int d\Omega \int dR_Z\, f(\Omega, R_Z)\, P_2(\cos\vartheta) \cos qR_z \simeq \eta\tau \tag{22}$$

the averaged mean field $\langle V_{S_A} \rangle = \int d\Omega \int dR_Z\, f(\Omega, R_Z)\, V_{S_A}(\Omega, R_Z)$ is after substitution of Equation (19) in Equations (11), (12), and (13) and subsequent substitution in Equation (15) obtained as

$$\langle V_{S_A} \rangle = -\mathrm{I}\left(6\left(\alpha^2\tau^2 + \frac{\delta^2\sigma^2}{45}\right)\overline{cP}_0 + 4\left(\alpha\delta\sigma\tau - \frac{\delta^2\sigma^2}{21}\right)\overline{cP}_2 + \tfrac{72}{35}\,\delta^2\sigma^2\,\overline{cP}_4\right) \tag{23}$$

which, despite the easy start, is quite an expression. In order to show the relevance of the various contributions we have to consider the quantities $\overline{cP}_n$ in more detail. From the definition of the mean field it may be clear that the integration in Equation (7) and consequently in Equation (17) is over all space with the exclusion of the volume denied by the central molecule to all others[6,7]: the molecules are impenetrable. This excluded volume can in a first approximation be described as an ellipsoid of revolution around the common direction of alignment, i.e. the director; see Figure 1. With the director along the Z-axis the ellipsoid is described by

$$\frac{r^2}{b^2} + \frac{R_Z^2}{a^2} = 1 \tag{24}$$

where a and b are the semi-axes. So we find that for $|R_z| \leq a = d$ there is a lower bound r_0 for r given by $r_0^2 = b^2 - b^2R_z^2/a^2$, whereas for $|R_Z| \geq a$ one has $0 \leq r \leq \infty$. Eq. (17) can then be written as

$$\overline{cP}_n = 4\pi\rho \int_a^\infty dR_Z \cos qR_z \int_0^\infty rdr\, P_n(R_Z/R)\, R^{-6}$$

(25)

$$+ 4\pi\rho \int_0^a dR_Z \cos qR_Z \int_{r_0}^\infty rdr\, P_n(R_Z/R)\, R^{-6} \tag{25}$$

where the integration over r is elementary. With the notation $\overline{cP}_n = \pi\rho C_n/a^3$ the numbers C_n come to the fore as

$$\begin{aligned} &a)\ C_0 = c_0 + c(0) \\ &b)\ C_2 = \frac{1}{2}(c_0 - c(0) + 2c(1)) \qquad (26) \\ &c)\ C_4 = \frac{1}{16}(c_0 + 6c(0) - 40c(1) + 35c(2)) \end{aligned}$$

where

$$c_0 = a^3 \int_a^\infty dR_Z\, R_Z^{-4} \cos qR_Z = \int_1^\infty dx\, x^{-4} \cos 2\pi x = 0.064 \qquad (27)$$

$$\begin{aligned} c(m) &= a^3 \int_0^a dR_Z \left(b^2 + \left(1 - \frac{b^2}{a^2}\right)R_Z^2\right)^{-(2+m)} R_Z^{2m} \cos qR_Z \\ &= \left(\frac{a}{b}\right)^{2(m+2)} \int_0^1 dx \left(1 + \left(\frac{a^2}{b^2} - 1\right)x^2\right)^{-(2+m)} x^{2m} \cos 2\pi x \qquad (28) \end{aligned}$$

with $q = 2\pi/a$ and $a = d$.

The importance of the anisotropy of the excluded volume is apparent when we consider the dependence of the C_n on the ratio a/b. The results of the numerical calculations are shown in Table I.

Striking are the strong increase of C_4 and the corresponding decrease of C_2, which indeed becomes increasingly negative with increasing a/b; the dependence of C_0 on a/b is moderate. To appreciate the magnitude of these numbers we quote the fact that $\overline{P}_0$ in Eq. (15) which determines the main contribution to V_N, that is $\langle V_N \rangle \simeq -2\mathrm{I}/15\ \overline{P}_0\delta^2\eta^2$, is equal to $4\pi\rho/3a^3$; the C_n are then compared with 4/3.

Using $\overline{cP}_n = \pi\rho C_n/a^3 = 3\rho\nu_{\mathrm{sp.}} C_n/4a^6$, $\nu_{\mathrm{sp.}} = 4\pi a^3/3$, and rearranging terms, Equation (23) can finally be written as

$$\begin{aligned} \langle V_{S_A} \rangle = -\rho\nu_{\mathrm{sp.}}\mathrm{I}\Bigg(&\frac{9C_0}{2}\left(\frac{\alpha}{a^3}\right)^2 \tau^2 + 3C_2 \frac{\alpha\delta}{a^6}\sigma\tau \\ &+ \left(\frac{C_0}{10} - \frac{C_2}{7} + \frac{54}{35}C_4\right)\left(\frac{\delta}{a^3}\right)^2 \sigma^2\Bigg) \qquad (29) \end{aligned}$$

TABLE I

a/*b*	C_0	C_2	C_4
1	0.064	0.083	0.082
1.1	0.046	0.066	0.133
1.2	0.035	0.034	0.197
1.3	0.037	−0.014	0.275
1.4	0.056	−0.081	0.368
1.5	0.10	−0.168	0.473

Now we note that $\langle V_{S_A}\rangle$ contains contributions proportional to τ^2, $\tau\sigma$ and σ^2 respectively; the necessity to have all these various terms together has indeed been recognized.[5,8,9,10,11] One may also infer from Table I that the absolute and relative weights of the various contributions strongly depend on the ratio a/b; the preponderance of $C_4\sigma^2$ over $C_0\sigma^2$, usually considered only, is nevertheless apparent. A further discussion will be given in Section V.

III. THE STABILITY OF THE SMECTIC A PHASE

To discuss the stability of the smectic A phase with respect to a tilt of the director we consider again Eq. (15) for the mean field. In deriving that equation it was assumed that the distribution of the centres of mass of the molecules is rotationally symmetric around the layer normal, without specifying the direction of average alignment. In the previous section the director was assumed to be along the layer normal. Now we consider orientational order with respect to a tilted director.

In addition to the X, Y, Z coordinate system we then introduce a rotated coordinate system X', Y', Z' defined by

$$\begin{aligned} X &= X' \\ Y &= Y' \cos\omega + Z' \sin\omega \\ Z &= Z' \cos\omega - Y' \sin\omega \end{aligned} \tag{30}$$

where the Z'-axis is considered to be along the director. Applying this transformation to the tensor components ($\alpha\beta$) in Equation (14), it is easily verified that

$$\begin{aligned}
&\text{a) } \delta_Z + \tfrac{1}{2}\epsilon_Z = (\delta_{Z'} + \tfrac{1}{2}\epsilon_{Z'})\cos 2\omega - \chi_{Z'Y'} \sin 2\omega \Rightarrow \delta_{Z'} \cos 2\omega \\
&\text{b) } \chi_{YZ} = (\delta_{Z'} + \tfrac{1}{2}\epsilon_{Z'}) \sin 2\omega + \chi_{Y'Z'} \cos 2\omega \Rightarrow \delta_{Z'} \sin 2\omega \\
&\text{c) } \chi_{ZX} = \chi_{Z'X'} \cos \omega - \chi_{X'Y'} \sin \omega \Rightarrow 0 \qquad (31) \\
&\text{d) } \chi_{XY} = \chi_{X'Y'} \cos \omega + \chi_{Z'X'} \sin \omega \Rightarrow 0
\end{aligned}$$

and

$$\alpha_Z = \alpha_{Z'},\ \delta_Z - \tfrac{3}{2}\epsilon_Z = \delta_{Z'} - \tfrac{3}{2}\epsilon_{Z'} \Rightarrow \delta_{Z'} \qquad (32)$$

Here $\delta_Z' = (Z'Z') - \frac{1}{2}(X'X' + Y'Y')$ etc. The arrows in Eqs. (31) and (32) apply when we assume that the orientational order is uniaxial with respect to the director; this assumption, generally accepted but not essential, keeps the formalism tractable. The transformation properties of the A_n defined in Eqs. (11), (12) and (13) come to the fore when these quantities are rewritten as

$$A_0 = \tfrac{2}{3}\,\alpha_Z^2 + \tfrac{1}{30}(\delta_Z - \tfrac{3}{2}\,\epsilon_Z)^2 + \tfrac{1}{10}((\delta_Z + \tfrac{1}{2}\,\epsilon_Z)^2 + \chi_{YZ}^2) \qquad (33)$$

$$\begin{aligned}
A_2 = {} & \tfrac{1}{3}\,\alpha_Z(\delta_2 - \tfrac{3}{2}\,\epsilon_Z) + \tfrac{1}{42}(\delta_Z - \tfrac{3}{2}\,\epsilon_Z)^2 \\
& - \tfrac{1}{14}((\delta_Z + \tfrac{1}{2}\,\epsilon_Z)^2 + \chi_{YZ}^2) + (\alpha_Z - \tfrac{1}{7}(\delta_Z \\
& - \tfrac{3}{2}\,\epsilon_Z))(\delta_Z + \tfrac{1}{2}\,\epsilon_Z) \qquad (34)
\end{aligned}$$

$$\begin{aligned}
A_4 = {} & \tfrac{27}{140}(\delta_Z - \tfrac{3}{2}\,\epsilon_Z)^2 - \tfrac{36}{35}((\delta_Z + \tfrac{1}{2}\,\epsilon_Z)^2 + \chi_{YZ}^2) \\
& + \tfrac{9}{14}(\delta_Z - \tfrac{3}{2}\,\epsilon_Z)(\delta_Z + \tfrac{1}{2}\,\epsilon_Z) + \tfrac{9}{4}(\delta_Z + \tfrac{1}{2}\,\epsilon_Z)^2 \qquad (35)
\end{aligned}$$

showing that only A_0 is rotationally invariant. Substitution of Eqs. (31) and (32) and putting $\cos 2\omega = 1 - 2\sin^2\omega$ indeed yields

$$A_0 = A_0' \qquad (36)$$

$$A_2 = A_2' - 2(\alpha_{Z'} - \tfrac{1}{7}\delta_{Z'}) \sin^2\omega \qquad (37)$$

$$A_4 = A_4' - \tfrac{72}{7}\,\delta_{Z'}^2 \sin^2\omega + 9\delta_{Z'}^2 \sin^4\omega \qquad (38)$$

where the A_n' are defined according to Eqs. (11), (12) and (13) in terms of $\alpha_{Z'}$, $\delta_{Z'}$ etc. with respect to X', Y' and Z'; $\alpha_{Z'} = 3\alpha I^{1/2}$ and $\delta_{Z'} = \delta I^{1/2} P_2(z_{Z'})$ where $z_{Z'} = \cos\vartheta$ is the direction cosine of the molecular z-axis with respect to the director along the Z'-axis. The translational order $\tau = \langle \cos qR_Z \rangle$ however, and consequently the coefficients C_n, c.f. Eqs. (25), (26), (27) and (28), remain defined with respect to the layer normal along the Z-axis. Since the excluded volume v_{ex} is defined as an ellipsoid of revolution around the director, Eq. (24) now reads

$$\frac{r^{2\prime}}{b^2} + \frac{R_{Z'}^2}{a^2} = 1. \tag{39}$$

Transformation of this equation yields the approximate result

$$R_Z^2 + r^2(R_Z^2) = b^2\left(1 + x^2\left(\frac{a^2}{b^2} - 1\right) + \frac{bx}{a}(1 - x^2)^{1/2}\left(\frac{a^2}{b^2} - 1\right)\sin\omega + \frac{1}{2}\left(\frac{b^2}{a^2} - x^2\left(3 - \frac{b^2}{a^2}\right)\right)\left(\frac{a^2}{b^2} - 1\right)\sin^2\omega\right) \tag{40}$$

where in the r.h.s. the variable R_Z/d has been changed into the variable x, that is

$$R_Z^2 = \frac{R_Z^2}{d^2} \cdot d^2 = x^2 \cdot d^2 = x^2 \cdot a^2\left(1 - \left(1 - \frac{b^2}{a^2}\right)\sin^2\omega\right) \cdot \tag{41}$$

Upon substitution of Eqs. (40) and (41) in Eqs. (27) and (28), respectively, c_0 and $c(m)$ become functions of sin ω. In App. C it is shown that the final result for the C_n can be written as

$$C_n(\omega) = C_n - S_n \sin^2\omega. \tag{42}$$

The numerically calculated values of S_n are presented in Table II. Proceeding as before, the additional contribution to the averaged mean field energy for the tilted configuration, denoted as $\langle \delta V_{S_A}(\omega) \rangle$, is obtained from the Eqs. (36), (37), (38) and (42) as

$$\langle \delta V_{S_A}(\omega) \rangle = \tfrac{9}{2}\rho v_{\text{sp.}} I\left(S_0 \frac{\alpha^2}{\delta^2}\frac{\tau}{\sigma} + \left(C_2 + \frac{2}{3}S_2\right)\frac{\alpha}{\delta} + \left(\tfrac{12}{7}C_4 + \tfrac{12}{35}S_4\right)\frac{\sigma}{\tau}\right)\left(\frac{\delta}{a^3}\right)^2 \sigma\tau \sin^2\omega \tag{43}$$

TABLE II

a/b	S_0	S_2	S_4
1	0	0	0
1.1	−0.02	−0.04	+0.06
1.2	−0.01	−0.11	+0.11
1.3	+007	−0.20	+0.16
1.4	+0.22	−0.31	+0.19
1.5	+0.46	−0.48	+0.22

where, as a reminder, τ and σ are the order parameters and α, c.q. δ are the molecular polarizability and its anisotropy respectively: c.f. Eqs. (22), (21), (19b) and (19a). To keep this equation within bounds we have neglected the contribution $(-\frac{1}{21}\ C_2 + \frac{1}{45}\ S_0 - \frac{2}{63}\ S_2)\ \sigma/\tau$ within the brackets which, indeed being small compared to $(\frac{12}{7}\ C_4 + \frac{12}{35}\ S_4)\ \sigma/\tau$, does not noticeably influence the sign and magnitude of that term. The values of the coefficients multiplying σ/τ, α/δ and $\alpha^2/\alpha^2\tau/\delta^2\sigma$ respectively are presented in Table III.

From the above we cannot leave out of account that for small values of a/b the coefficient of $\sin^2\omega$ in Eq. (43) becomes negative; this is for instance the case for $1 < a/b < 1.3$ when we take $\sigma/\tau \simeq \eta = 0.5$ and $\alpha/\delta = 3$. However, disregarding such unlikely extreme values one may conclude that with $\sigma/\tau \simeq \eta \gtrsim 0.7$ and $\alpha/\delta < 3$ the coefficient of $\sin^2\omega$ in Eq. (43) is positive. Then the A phase is stable against a tilt of the director whatever the sign of the $\sin^4\omega$ term, which has not been considered. It should be noted that the contribution of the $(\frac{2}{3}\ S_2 + C_2)\ \alpha/\delta$ term in Eq. (43), positive or negative dependent on a/b, is of minor importance. This casts serious doubt on the validity of the models proposed in [11], [12] and [13], to be discussed in Section V.

TABLE III

a/b	S_0	$\frac{2}{3} S_2 + C2$	$\frac{12}{35} S_4 + \frac{12}{7} C_4$
1	0	0 0.08 = 0.08	0 + 0.12 = 0.12
1.1	−0.02	−0.03 + 0.07 = 0.04	0.02 + 0.23 = 0.25
1.2	−0.01	−0.07 + 0.03 = −0.04	0.04 + 0.34 = 0.38
1.3	+0.07	−0.13 + 0.01 = −0.14	0.05 + 0.48 = 0.53
1.4	+0.22	−0.20 + 0.08 = −0.28	0.06 + 0.63 = 0.69
1.5	+0.46	−0 30 = 0.17 = −0.37	0.07 + 0.81 = 0.88

IV. THE SMECTIC C PHASE

It has been shown that the interaction between the permanent molecular dipoles as described in Eq. (1) by $V^{i,j}_{pp}$ is not adequate to produce an A–C phase transition.[2] The same applies to the interaction in terms of the inductive effect of the permanent dipoles; this interaction, denoted in[12] as $V_{\alpha\mu}$ and proportional to $\alpha\mathbf{p}^2$, is in fact part of the interaction $\alpha_Z\delta_Z$ described in Eq. (12). This point will be discussed in section V. Therefore we will consider the perturbation of the A phase due to the interaction between the static molecular quadrupole moments, in Eq. (1) denoted as $V^{i,j}_{qq}$. This interaction can be written as

$$V^{i,j}_{qq} = q^i_{\alpha\beta} q^j_{\gamma\delta} T_{\alpha\beta\gamma\delta} \tag{44}$$

where $T_{\alpha\beta\gamma\delta}$, the definition of which can be inferred from Eq. (1), describes the coupling of the orientation-dependent interaction to the relative position. To reduce this rather lengthy expression to a tractable form we proceed as in section II. According to Eqs. (7–10) we define the mean field energy $V_{S_C}(\Omega^i, R^i_Z)$ by

$$V_{S_C}(\Omega^i, R^i_Z) = \rho \int d\Omega^j \int dR^j_Z\, f(\Omega^j, R^j_Z) \int r\,dr \int d\phi\; q^i_{\alpha\beta}\cdot\, q^j_{\gamma\delta\; T_{\alpha\beta\gamma\delta}}. \tag{45}$$

The integration over ϕ of all separate terms, yielding nonzero only if these are even in both R_X and R_Y, is easily done. Collecting the results we find

$$\begin{aligned}\int_0^{2\pi} d\phi\; q^i_{\alpha\beta} q^j_{\gamma\delta\, T_{\alpha\beta\gamma\delta}} = \Big(&\sigma\Delta_Z(\Omega^i).\ \Delta_Z(\Omega^j) + E_Z(\Omega^i).\ E_Z(\Omega^j) \\ &+ \Gamma_{XY}(\Omega^i).\ \Gamma_{XY}(\Omega^j) - 4(\Gamma_{YZ}(\Omega^i).\ \Gamma_{YZ}(\Omega^j) \\ &+ \Gamma_{ZX}(\Omega^i).\ \Gamma_{ZX}(\Omega^j))\Big)\,\frac{3\pi P_4(R_Z/R)}{2R^5}\end{aligned} \tag{46}$$

where

$$\begin{aligned} &\text{a) } \Delta_Z = q_{ZZ} - \tfrac{1}{2}(q_{XX} + q_{YY}) \\ &\text{b) } E_Z = q_{XX} - q_{YY} \\ &\text{c) } \Gamma_{\alpha\beta} = 2q_{\alpha\beta},\ \alpha \neq \beta = X, Y, Z. \end{aligned} \tag{47}$$

Here again, we consider orientational order with respect to a tilted director. The transformation of the tensor components in Eq. (47) according to Eq. (30) yields in lowest order of sin ω.

$$\begin{aligned}
&\text{a) } \Delta_Z = \Delta_{Z'} - \tfrac{3}{2}\Gamma_{Y'Z'}.\ \sin\omega \\
&\text{b) } E_Z = E_{Z'} - \Gamma_{Y'Z'}.\ \sin\omega \\
&\text{c) } \Gamma_{YZ} = \Gamma_{Y'Z'} + 2(\Delta_{Z'} + \tfrac{1}{2}E_{Z'}).\ \sin\omega \qquad (48) \\
&\text{d) } \Gamma_{ZX} = \Gamma_{Z'X'} - \Gamma_{Y'X'}.\ \sin\omega \\
&\text{e) } \Gamma_{XY} = \Gamma_{X'Y'} + \Gamma_{Z'X'}.\ \sin\omega
\end{aligned}$$

where $\Delta_{Z'}$, $E_{Z'}$, and $\Gamma_{\alpha'\beta'}$ are defined according to Eqs. (47a–c) in terms of $q_{Z'Z'}$ etc. To reduce the number of terms in Eq. (48) we first express the tensor components $q_{Z'Z'}$ etc. in terms of the corresponding tensor components q_{ZZ} etc., defined with respect to the molecular coordinate system x, y, z. The molecular model for the interaction is depicted in Figure 1, from which one derives

$$\begin{aligned}
&\text{a) } q_{zz} = 2p\cos\alpha(c + d\cos\alpha) \qquad &&\text{c) } q_{yy} = 2pd\sin^2\alpha \\
&\text{b) } q_{yz} = p\sin\alpha(c + 2d\cos\alpha) \qquad &&\text{d) } q_{xx} = q_{xy} = q_{xz} = 0.
\end{aligned} \qquad (49)$$

Retaining only the essential rotational invariants we then find

$$E_{Z'} = \Gamma_{X'Y'} = \Gamma_{X'Z'} = 0 \qquad (50)$$

and

$$\begin{aligned}
&\text{a) } \Delta_{Z'} = (q_{zz} - \tfrac{1}{2}q_{yy})(\tfrac{3}{2}z_{Z'}^2 - \tfrac{1}{2}) = \Delta.\ P_2(\cos\vartheta) \\
&\text{b) } \Gamma_{Y'Z'} = (2q_{yz})(y_{Y'}.\ z_{Z'}) = \Gamma.\ Q(\Omega)
\end{aligned} \qquad (51)$$

where, as a reminder, $z_{Z'} = \cos\vartheta$ and $y_{Y'} = \sin\varphi\sin\psi\cos^2\vartheta - \cos\varphi\cos\psi$ are the direction cosines of the molecular $z(y)$-axis with respect to the macroscopic $Z'(Y')$-axis. Here we want to stress the appearance of a new rotational invariant $y_{Y'}z_{Z'}$ denoted as $Q(\Omega)$;

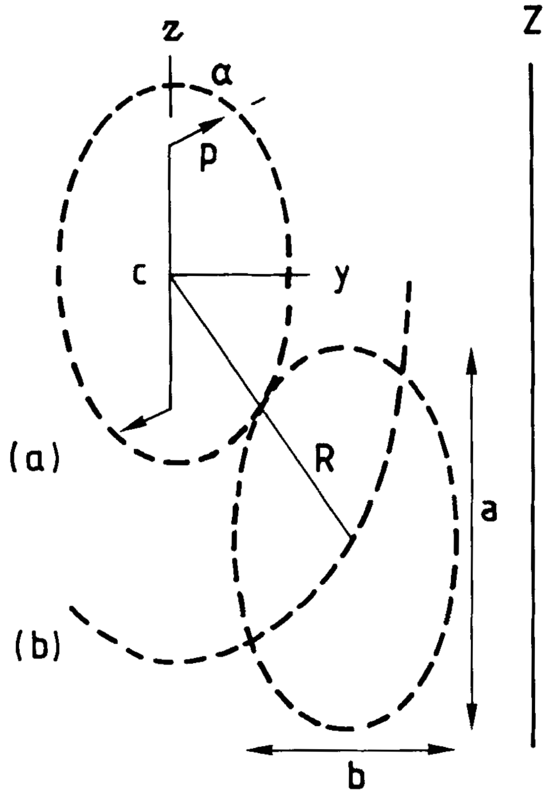

FIGURE 1 (a) The molecular quadrupole moment in terms of two eccentric dipoles of magnitude p = ed, the angle α and the distance c; (b) Part of the anisotropic excluded molecular volume described by $R^2 = b^2 + (1 - b^2/a^2)R_Z^2$, $-a \le R_Z \le +a$.

c.f. Eq. (51b). Substitution of Eqs. (50) and (51) in Eqs. (48a–c) and subsequent substitution in Eq. (46) yields:

$$\int_0^{2\pi} d\phi\, q^i_{\alpha\beta} q^j_{\gamma\delta} T_{\alpha\beta\gamma\delta} = -\Big(3\Theta^2 Q(\Omega^i).\ Q(\Omega^j) - 6\Delta^2 P_2(\cos\vartheta^i).\ P_2(\cos\vartheta^j) + 15\,\Gamma\Delta\,(P_2(\cos\vartheta^i).\ Q(\Omega^j) + P_2(\cos\vartheta^j).\ Q(\Omega^i))\sin\omega\Big)\frac{2\pi P_4(R_Z/R)}{R^5} \qquad (52)$$

From Eqs. (52), (45) and (9) the averaged mean field $\langle V_{Sc}(\omega)\rangle = \rho$

$\int dR_Z \int d\Omega\, f_1(\Omega)\; V_{S_C}(\Omega, R_Z, \omega)$. $\cos qR_Z$ is obtained as

$$\langle V_{S_C}(\omega)\rangle = -(3\Gamma^2 \langle cQ\rangle^2 + 30\Gamma\Delta\sigma \langle cQ\rangle.\ \sin\omega)\ \overline{cP_4}' \qquad (53)$$

where, analogous to Eq. (17) and Eq. (22) respectively,

$$\overline{cP_4}' = 2\pi\rho \int dR_Z \int r dr\, \frac{P_4(R_Z/R)}{R^5} \cos qR_Z = \frac{\pi\rho}{a^2} C_4' \qquad (54)$$

and

$$\langle cQ\rangle = \langle Q(\Omega).\ \cos qR_Z\rangle = \int dR_Z \int d\Omega f(\Omega, R_Z)\, Q(\Omega)\, \cos qR_Z. \qquad (55)$$

Here $f(\Omega, R_Z)$ is according to Eq. (8) defined in terms of the mean field $V(\Omega, R_Z) = V_{S_A}(\Omega, R_Z, \omega) + V_{S_C}(\Omega, R_Z, \omega)$; in Eq. (53) we have not considered the contribution due to Δ^2 which, being proportional to σ^2, can be absorbed in $\langle V_{S_A}\rangle$. Minimizing the corresponding averaged mean field energy $\langle V(\omega)\rangle = \langle \delta V_{S_A}(\omega)\rangle + \langle V_{S_C}(\omega)\rangle$ with respect to ω one obtains from Eqs. (43) and (53)

$$\omega = \frac{5C_4'(\Gamma\Delta/a^5)\ \langle cQ\rangle}{2\left[s_0 \frac{\alpha^2}{\delta^2}\frac{\tau^2}{\sigma} + (C_2 + \frac{2}{3}S_2)\frac{\alpha\tau}{\delta} + (\frac{12}{7}C_4 + \frac{12}{35}S_4)\sigma\right]\left(\frac{\delta}{a^3}\right)^2 I} \qquad (56)$$

So we find that the tilt angle ω, defined in terms of molecular properties, $\Gamma\Delta \simeq 2q_{yz}q_{zz}$, depends on the existence of the new order parameter $\langle cQ\rangle$.

An approximate solution for $\langle cQ\rangle$, which demonstrates in a simple way the existence of a second-order phase transition, can be obtained in the usual way by expanding the free energy $F = F(V_{S_A}, V_{S_C})$ defined by[2,5]

$$F = -\tfrac{1}{2}N\,\langle V_{S_A} + V_{S_C}\rangle + \mathrm{NkT}\ \ln \int \exp(-(V_{S_A} + V_{S_C})/\mathrm{kT})\, d\Omega\, dR_Z \qquad (57)$$

in powers of V_{S_C}.[10,13,14] The procedure is straightforward and yields $F = F(V_{S_A}) + \mathrm{F}_{S_C}$, where F_{S_C} is obtained as

$$F_{S_C} = \tfrac{1}{2}\,\mathrm{N}\,\langle cQ\rangle^2 \left(C - \mathrm{kT}\left[\frac{uC^2}{(\mathrm{kT})^2} - \frac{vC^4\,\langle cQ\rangle^2}{4(\mathrm{kT})^4} + \cdots \right] \right). \tag{58}$$

For ease of notation we have used the abbreviation

$$C = \frac{3\pi\rho\, C_4'\,\Gamma^2}{a^2} = 9\rho v_{\mathrm{sp.}} C_4'\,\frac{q g_{yz}^2}{a^5} \tag{59}$$

The numbers u and v in Eq. (58) come to the fore as $u = \tfrac{1}{2}\langle Q^2(\Omega)\rangle_A = \tfrac{1}{8}\,(\langle \cos^4\vartheta\rangle_A + \langle \cos^2\vartheta\rangle)$ and $\upsilon = \tfrac{3}{8}\,(\langle Q^2(\Omega)\rangle_A^2 - \tfrac{1}{3}\langle Q^4(\Omega)\rangle_A) \simeq \tfrac{3}{64}$ $\langle \cos^2\vartheta\rangle_A\,\langle \cos^4\vartheta\rangle_A$, where the averages are defined with respect to $f(V_{S_A})$; c.f. Eq. (8). Minimizing F_{S_C} with respect to $\langle cQ\rangle$ yields, apart from $\langle cQ\rangle = 0$,

$$\langle cQ\rangle^2 = \left(\frac{uC}{\mathrm{kT}} - 1\right)\frac{2}{v}\left(\frac{\mathrm{kT}}{C}\right)^3 \tag{60}$$

which shows a phase transition at $T = T_{S_{A,C}} = uC/\mathrm{k}$, that is

$$T_{S_{A,C}} = 9\rho v_{\mathrm{sp.}} u C_4'\,\frac{q_{yz}^2}{ka^5}. \tag{61}$$

At this stage it is important to note that C_4', defined in Eq. (54) and given by

$$C_4' = \tfrac{1}{2}\,(c'(0) - 6c'(1) + 5c'(2)) \tag{62}$$

where, analogous to Eq. (28),

$$c'(m) = \left(\frac{a}{b}\right)^{2m+3} \int_0^1 dx \left(1 + \left(\frac{a^2}{b^2} - 1\right)x^2\right)^{-(m+3/2)} \cdot x^{2m} \cdot \cos 2\pi x, \tag{63}$$

is nonzero and positive, whereas $\int dR_Z \int r dr\; P_4(R_Z/R).\; R^{-5}$, which determines V_{qq} in the nematic phase, is zero. This shows that the quadrupole–quadrupole interaction is only effective once smectic order is established. The dependence of C_4' on (a/b) has been calculated numerically; the results are given in Table IV. Here again, the strong increase of C_4' with increasing a/b is remarkable.

TABLE IV

a/b	1	1.1	1.2	1.3	1.4	1.5
C_4'	0,064	0,112	0,164	0,236	0.308	0,384

V. DISCUSSION

The molecular field derived in section II on the basis of the dipole–dipole interaction contains all terms that can possibly contribute to the attractive dispersion energy in the smectic A phase. Apart from the spherically symmetric contribution determined by A_0, we have found additional contributions determined by A_2 and A_4 which, not being rotationally invariant, are essential to the stability of the A phase. The possible role of the permanent dipoles in the dispersion energy is apparent from Eq. (4) where the summation is over all excited states $\nu\mu\rangle$ of the combined system of two interacting molecules such that $E_{\nu,\mu} \neq E_{0,0}$. Then indeed $0\mu\rangle$ and $\nu 0\rangle$ are excited states of the system, which implies that for instance $\alpha_Z\delta_Z$ in Eq. (12) contains contributions like $(\mathbf{p})^2\delta_Z$ and $\alpha_Z p_Z^2$ where $\mathbf{p}$ c.q. p_Z, defined by $\langle 0|\mathbf{p}|0\rangle$ and $\langle 0|p_Z|0\rangle$ respectively, refer to the permanent molecular dipole. All terms in Eqs. (11), (12) and (13) contain similar contributions in terms of the corresponding components of the permanent dipoles; a separate derivation as presented in [12] seems superfluous. The effect of an anisotropic excluded volume on the mean field has been taken into account by imposing a lower bound to the intermolecular distance, depending on the relative position of the molecules. The numerical results obtained for the $C_n \propto \overline{cP_n}$ demonstrate the great influence of the anisotropy of this excluded volume on the strength of the various contributions determined by these coefficients. The preponderance of the term determined by $\delta^2 C_4$ over the term determined by $\delta^2 C_0$, which indeed is apparent from Eq. (29) and Table I, has not been recognized up to now. This contribution greatly enhances the stability of the smectic A phase with respect to the nematic phase. This contribution is also the main source for the stability of the A phase with respect to a tilt of the director; this can be inferred from Eq. (43) and Table III.

Despite the important role of the anisotropy of the excluded volume, this anisotropy is not the cause of the existence of the various contributions to the mean field. As shown in section II, the terms $A_n P_n(R_Z/R)$, $n = 0, 2, 4$ come to the fore quite naturally as a consequence of the symmetry of the complete pair interaction $V(p,p)$, Equation (3), in connection with the cylindrical symmetry of the distribution of the centres of mass of the molecules.

The fact that the original theory of the smectic A phase in Ref. 15, being based on the spherically symmetric interaction $A_0P_0(R_Z/R) = A_0$ only, is not adequate to that purpose has been recognized before[10,11,12]; indeed the absence of a coupling between the relative orientation and position of two molecules, leaves the relative orientation between the director and the layer normal totally undetermined. The construction, however, of model interactions without a proper derivation from the very beginning is not the appropriate way to improve the situation. In Ref. 11 for instance a model has been proposed to include steric effects. The mere addition to $A_0P_0(R_Z/R)$, however, of an interaction proportional to $(P_2(\cos \vartheta^i) + P_2(\cos \vartheta^j))$ $P_2\,(R_Z/R)$ cannot possibly, as discussed above, be considered as a steric effect in a mean field theory. The requirement that this additional term in the pairwise interaction has a positive sign has no physical basis and is in conflict with the result derived in Section II. The way in which steric effects can be accounted for in the translational entropy, not considered here, is discussed in Ref. 16.

In Ref. 12 excluded volume effects are taken into account by considering the pairwise interaction of two molecules in contact for three discrete relative orientations defined with respect to the direction of the intermolecular distance vector. The way in which these three discrete orientations are used to define the continuum of allowed orientations in the model interaction is rather unusual and cannot be justified.

The formal expansion of the molecular interaction in spherical harmonic functions of **R**/R proposed in Ref. 10 is in principle correct and in agreement with the symmetry of the A phase. However, since the interaction strengths A, B, C and D, l.c., poorly defined and not calculated at all, are given the sign and weight that suit the purpose, the discussion of the results has no physical significance.

The A–C phase transition described in section IV is thermodynamically consistent; at the transition the entropy changes due to the onset of a new element of order described by $\langle y_Y, z_{Z'}\rangle = \langle Q\rangle$. The tilt of the director, proportional to $q_{yz}q_{zz} \propto c^2p^2 \sin\alpha \cos\alpha$, $q_{zz} - \frac{1}{2}\, q_{yy} \simeq q_{zz}$, depends on the existence of this order parameter, which determines the temperature dependence of the tilt. The quadrupole–quadrupole interaction, considered to be responsible for the phase transition, is only effective in the layered structure of the smectic phase. This interaction accounts for the interaction of all dipoles of one molecule with all dipoles of another, regardless of their relative position; there is no selective interaction and no need for perfect smectic and orientational order. To estimate the order of magnitude of the interaction energies involved we take $\rho v_{\mathrm{sp.}} = \rho v_0(a/b)^2 \simeq 0.6 * 10 = 6$, $\mathrm{I} \simeq 10$ eV $= 6^{-1}. 10^{-10}$ erg, that is $\rho v_{\mathrm{sp.}}\mathrm{I} \approx 10^{-10}$ erg.

With $(\alpha/a^3)^2 \approx 2 \cdot 10^{-4}$ and $(\delta/\alpha)^2 \approx 1/3$ we find that $\langle V_{S_A}\rangle \approx (qC_0\tau^2 + C_4\sigma^2)\ 10^{-14}$ erg. With $\Gamma = 2q_{YZ} = 2p \sin\alpha\ (c + 2d \cos\alpha) \approx p(c + d) \approx p.a \approx q_{zz}$, $p = 2D$ and $a \approx 20$Å we find that $\langle V_{S_C}\rangle \approx C_4' \langle cQ\rangle^2. 10^{-14}$ erg. Both values are physically acceptable and reasonable. It has been shown already that a number of the existing theories of the A–C phase transition are not adequate to that purpose.[2] One of the reasons is that in a mean field approach the tilt angle ω cannot be considered as an order parameter, responsible for the phase transition: the entropy is independent of ω. Consequently the theory of the A–C phase transition in Ref. 13 cannot be correct either, which indeed is easily demonstrated. The expansion coefficient α_{20} being proportional to $\langle \cos qR_Z\rangle \cdot \langle \cos qR_Z p_2(\cos\vartheta)\rangle = \tau\sigma$ cannot possibly, despite the claim, be identified with the coefficient $\alpha = a°((T/T_1) - 1\rangle$, $T_1 = T_{S_{A,C}}$- of the Landau expansion of the free energy of the smectic C phase; c.f. Eqs. (64), (72) and (73) l.c. Moreover there is the remarkable fact that the underlying interaction ϕ^{SB}, introduced in [11] to stabilize the A phase, is taken over with the opposite sign to produce a tilt of the director with no stable A phase at the base.

The introduction of the translational entropy $S_{\mathrm{tr.}}(\omega)$ in Ref. 17, albeit in a rather simple way, the pair excluded volume being represented by an area in a perfectly organized smectic layer with $\tau = \sigma = \eta = 1$, at least guarantees the stability of the A phase within the model. The driving force for the A–C phase transition, named $(\frac{1}{2}J_{10} + 5J_{20})\sigma^2\omega^2$ and originating from the unspecified interaction in Ref. 10, has not been shown to be negative, a necessary prerequisite; c.f. Eqs. (4.5), (4.10) and (4.11) l.c. This term, however, is the equivalent of the additional contribution $\langle \delta V_{S_A}(\omega)\rangle$ defined in Eq. (43), which, being positive, stabilizes the A phase; there is no A–C phase transition.

Finally the translational entropy $S_{\mathrm{tr.}}(\omega)$ mentioned above was first introduced in Ref. 18 not to stabilize the A phase but to drive an A–C phase transition. The gain of translational entropy, however, is defined with respect to an assembly of ellipsoidal molecules, restricted to moving on one plane, with no common direction of average alignment; the director is apparently everywhere identical with the unit vector $\mathbf{e} = \pm\ \hat{z} \cos\epsilon + (\hat{x}\cos\phi + \hat{y}\sin\phi) \cdot \sin\epsilon$ along the long axis of each individual molecule; the fixed angle ϵ describes a random tilt of the molecules with $\langle \cos\phi \rangle = \langle \sin\phi \rangle = 0$. The discussion of a phase transition then only makes sense when it is shown that this exotic picture of an A phase, with no properly defined degree of orientational order, corresponds to a thermodynamically stable phase.

Acknowledgment

We gratefully acknowledge the contribution of Dr. H. A. van Sprang who performed the numerical calculations, part of which we have presented in the tables.

References

1. W. Maier and A. Saupe, *Naturforschg*, **14a**, 882 (1959).
2. W. J. A. Goossens, *J. Physique*, **46**, 1411 (1985).
3. W. J. A. Goossens, *J. Physique Colloq.*, **40**, C3-150 (1979).
4. H. Eyring, J. Walter and G. E. Kimball, *Quantum Chemistry* (J. Wiley and Sons, New York, London) 1949.
5. E. Priestley, P. J. Wotjowiez and Sheng Ping, Introduction to Liquid Crystals (Plenum Press, New York, London) 1975.
6. W. H. de Jeu, W. J. A. Goossens and P. Bordewijk, *J. Chem. Phys.*, **61**, 1985 (1974).
7. W. M. Gelbart and A. Gelbart, *Mol. Phys.*, **33**, 1387 (1977).
8. F. T. Lee, H. T. Tan, Y. M. Shy and C. W. Woo, *Phys. Rev. Lett.*, **31**, 1117 (1973).
9. F. T. Lee, H. T. Tan and C. H. Woo, *Phys. Lett.*, **48A**, 68 (1974).
10. R. G. Priest, *Mol. Cryst. Liq. Cryst.*, **37**, 101 (1976); *J. Physique*, **36**, 437 (1975).
11. L. Senbetu and C. W. Woo, *Phys. Rev.*, **A17** 1529 (1978).
12. B. W. v/d Meer and G. Vertogen, *J. Physique Colloq.*, **40**, C3-222 (1979).
13. M. Nakagawa, *Mol. Cryst. Liq. Cryst.*, **130**, 349 (1985).
14. L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, London, Paris) 1959.
15. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
16. W. J. A. Goossens, *Phys. Rev.*, **A35**, 1043 (1987).
17. M. Matsushita, *J. Phys. Soc. Jpn.*, **50**, 1351 (1981).
18. A. Wulf, *Phys. Rev.*, **A17**, 2077 (1978).
19. W. J. A. Goossens, *Liq. Cryst.*, **1**, 521 (1986).

Appendix A

The orthogonal transformation of the macroscopic coordinates X, Y, Z to the molecular coordinates x, y, z is quite generally described by

$$\begin{bmatrix}X\\Y\\Z\end{bmatrix} = \begin{bmatrix}X_x & X_y & X_z\\ Y_x & Y_y & Y_z\\ Z_x & Z_y & Z_z\end{bmatrix} \sqrt{= [A_{ij}]}\begin{bmatrix}x\\y\\z\end{bmatrix} \tag{A1}$$

Here $X_x = x_X = \mathrm{A}_{11}$, $X_y = y_X = \mathrm{A}_{12}$, etc. are the direction cosines of the X-axis with respect to the $x(y)$-axis. Since

$$\sum_i \mathrm{A}_{ij}\mathrm{A}_{ik} = \sum_i \mathrm{A}_{ji}\mathrm{A}_{ki} = \delta_{jk} \tag{A2}$$

there are three independent elements, which indeed corresponds with the description of the A_{ij} in terms of the Euler angles φ, ϑ and ψ that is

$$[\mathrm{A}_{ij}]$$

$$= \begin{bmatrix}\cos\psi\cos\varphi\cos\vartheta \;-\sin\psi\sin\varphi, & -\sin\psi\cos\varphi\cos\vartheta \;-\cos\psi\sin\varphi, & \cos\varphi\sin\vartheta\\ \cos\psi\sin\varphi\cos\vartheta \;+\sin\psi\cos\varphi, & -\sin\psi\sin\varphi\cos\vartheta \;+\cos\psi\cos\varphi, & \sin\varphi\sin\vartheta\\ -\cos\psi\sin\vartheta \qquad , & \sin\psi\sin\vartheta & ,\cos\vartheta\end{bmatrix} \tag{A3}$$

In order to express the tensor components (XX) etc. in terms of the (xx) etc., it is convenient to use for A_{ij} the representation given in Eq. (A1). Then for instance the transformation

$$\begin{aligned}(XX) &= (xx)\,x_X^2 + (yy)\,y_X^2 + (zz)\,z_X^2\\ &= \tfrac{1}{2}(xx + yy)(x_X^2 + y_X^2) + \tfrac{1}{2}((xx) - (yy))(x_X^2 - y_X^2) + (zz)\,z_Z^2\\ &= \tfrac{1}{3}(xx + yy + zz) + (zz)(z_X^2 - \tfrac{1}{3}) + \tfrac{1}{2}(xx + yy)(x_X^2 + y_X^2 - \tfrac{2}{3})\\ &\qquad + \tfrac{1}{2}(xx - yy)(x_X^2 - y_X^2)\end{aligned} \tag{A4}$$

can, using the relations

$$\begin{aligned}&x_X^2 + y_X^2 = 1 - z_X^2\\ &2z_X^2 = z_X^2 + 1 - z_Y^2 - z_Z^2 \qquad\qquad (\mathrm{A5})\\ &2x_X^2 - 2Y_X^2 = (x_X^2 + 1 - x_Y^2 - x_Z^2) - (y_X^2 + 1 - y_Y^2 - y_Z^2)\end{aligned}$$

, which follow from Eq. (A2), and the definitions, c.f. Eq. (5),

$$\tfrac{1}{3}(xx + yy + zz) = \alpha \mathrm{I}^{1/2}$$

$$(zz) - \tfrac{1}{2}(xx + yy) = \delta \mathrm{I}^{1/2} \qquad \text{(A6)}$$

$$(xx - yy) = \epsilon \mathrm{I}^{1/2}$$

be written in the physically appealing form

$$\begin{aligned}(XX) = {} & \alpha \mathrm{I}^{1/2} - \tfrac{1}{2}\delta \mathrm{I}^{1/2}([z_Z^2 - \tfrac{1}{3}] - [z_X^2 - z_Y^2]) \\ & + \tfrac{1}{4}\epsilon \mathrm{I}^{1/2}([x_Z^2 - y_Z^2] - [x_X^2 - x_Y^2 + y_Y^2 - y_X^2])\end{aligned} \qquad \text{(A7)}$$

The bracketed terms are rotational invariants which correspond to the various symmetries of the orientational order; these symmetries are clearly reflected by the definitions in terms of the corresponding direction cosines. The invariants

$$z_Z^2 - \tfrac{1}{3} = \cos^2\vartheta - \tfrac{1}{3} = \tfrac{2}{3} P_2(\cos\vartheta) = \tfrac{2}{3} S_1, \qquad \text{(A8)}$$

$$x_Z^2 - y_Z^2 = \cos 2\psi \sin^2\vartheta = S_2, \qquad \text{(A9)}$$

being defined with respect to the Z-axis only, correspond to uniaxial orientational order with respect to that axis; the local biaxiality $x_Z^2 - y_Z^2$ is compatible with this symmetry. The additional invariants

$$z_X^2 - z_Y^2 = \cos 2\varphi \sin^2\vartheta = S_3 \qquad \text{(A10)}$$

$$x_X^2 - x_Y^2 + y_Y^2 - y_X^2 = \cos 2\varphi \cos 2\psi(1 + \cos^2\vartheta) = 2\, S_4, \qquad \text{(A11)}$$

being defined with respect to the X- and Y-axes, are only relevant when the orientational order is biaxial on a macroscopic scale. The procedure for the transformation of (XX) as shown in Eqs. (A4-7) can equally be used for all other tensor components. Considering only the relevant ones we find

$$(YY) = \alpha \mathrm{I}^{1/2} - \tfrac{1}{3}\delta \mathrm{I}^{1/2}(S_1 + \tfrac{3}{2}S_3) - \tfrac{1}{4}\epsilon \mathrm{I}^{1/2}(S_2 + 2\, S_4) \qquad \text{(A12)}$$

$$(ZZ) = \alpha \mathrm{I}^{1/2} + \tfrac{2}{3}\delta \mathrm{I}^{1/2} S_1 + \tfrac{1}{2}\epsilon \mathrm{I}^{1/2} S_2 \qquad \text{(A13)}$$

yielding

$$\alpha_Z = (XX + YY + ZZ) = 3\alpha \mathrm{I}^{1/2} \qquad \text{(A14)}$$

$$\delta_Z = (ZZ) - \tfrac{1}{2}(XX + YY) = \delta I^{1/2}S, + \tfrac{3}{4}\epsilon I^{1/2}S_2 \qquad (A15)$$

$$\epsilon_Z = (XX - YY) = \delta I^{1/2}S_3 + \epsilon I^{1/2}S_4 \qquad (A16)$$

and

$$(YZ) = (yz)\, y_Y z_Z + \delta I^{1/2} z_X z_Y \qquad (A17)$$

Appendix B

The second-order perturbation energy $V(pq) \propto V^{i,j}_{pp}.\, V^{i,j}_{pq}$, where $V^{i,j}_{pp}$ and $V^{i,j}_{pq}$ are defined in Eq. (1), can be written as[3]:

$$V(pq) = -(\alpha\beta)(\alpha', \beta'\, \gamma').\, C_{\alpha\alpha'}\, (D_{\beta\beta'\gamma'} + \tfrac{3}{2}\delta_{\beta'\gamma'}R_\beta R^{-5}) \qquad (B1)$$

where

$$(\alpha\beta)(\alpha'\beta'\gamma') = \sum_{\nu,\mu} \langle 0|p_\alpha|\nu\rangle_i\, \langle \nu|p_\beta|0\rangle_i\, \langle 0|p_{\alpha'}|\mu\rangle_i\, \langle \mu|q_{\beta'\gamma'}|0\rangle_j\, E_{\nu\mu,00} \qquad (B2)$$

and

$$D_{\beta\beta'\gamma'} = \tfrac{3}{2}R_{\gamma'}(2\delta_{\beta\beta'} - 5R_\beta R_{\beta'} R^{-2})R^{-5}. \qquad (B3)$$

The molecular field $V^*(\Omega^i, \mathbf{R}^i) = \rho \int d\mathbf{R}^j \int d\Omega^j f(\Omega^j, \mathbf{R}^j) V_{(pq)}$ is then determined by the integral

$$\int_0^{2\pi} d\phi\, (\alpha\beta)(\alpha', \beta'\gamma')(D_{\beta\beta'\gamma'} + \tfrac{3}{2}\delta_{\beta'\gamma'}R_\beta R^{-5}) \qquad (B4)$$

which is the analogue of Eq. (10). The integration of all separate terms yields after a lengthy calculation the result that in Eqs. (11), (12) and (13) $\epsilon_Z^2 + \chi_{XY}^2$ is effectively replaced by

$$\epsilon_Z^2 + \chi_{XY}^2 + [\epsilon_Z((X, XZ - Y, YZ) - \tfrac{1}{2}(Z, ZX - Z, ZY))$$
$$+ \chi_{XY}(X, YZ + Y, ZX - Z, XY)]\, 2R_Z \cdot R^{-2} \qquad (B5)$$

The additional terms in Eq. (15) due to this replacement are then determined by the average value of the $P_n(R_Z/R)$, $n = 0, 2, 4$, defined according to Eqs. (16) and (17) with however R^{-6} replaced by $R_Z R^{-8}$.

Then the third-order tensor elements (X, YZ) etc. can be transformed to the corresponding tensor elements (x, yz) etc. as prescribed in Appendix A, yielding the results presented in Refs. 3 and 19.

Appendix C

To show the ω dependence of the C_n in a tilted configuration we use Eqs. (41) and (40) for R_Z^2 and $R_Z^2 + R^2(R_Z)$ respectively to recalculate c_0 and $c(m)$.

To start with Eq. (27) for c_0 one easily finds using Eq. (41)

$$\begin{aligned} c_0(\omega) &= a^3 \int_d^\infty dR_Z R_Z^{-4}.\ \cos(2\pi R_Z/d) \\ &= \int_1^\infty dx\ (1 - \epsilon \sin^2\omega)^{-3/2}.\ x^{-4}.\ \cos 2\pi x \\ &\simeq (1 + \tfrac{3}{2}\epsilon \sin^2\omega)c_0 \end{aligned} \tag{C1}$$

Here we have used the abbreviation $\epsilon = (1 - b^2/a^2)$ and neglected higher order terms. For the calculation of $c(m, \omega)$ it is convenient to write Eq. (40) in the form

$$R_Z^2 + r^2(R_Z) = (1 + \alpha + \beta\epsilon S^2 + \gamma\epsilon S)b^2 = R_+^2 \tag{C2}$$

and to define

$$R_-^2 = (1 + \alpha + \beta\epsilon S^2 - \gamma\epsilon S)b^2 \tag{C3}$$

where $S = \sin^2\omega$ and

$$\begin{aligned} 1 + \alpha &= 1 + \left(\frac{a^2}{b^2} - 1\right)x^2 \\ \beta &= \tfrac{1}{2}\left(1 - \left(\frac{3a^2}{b^2} - 1\right)x^2\right) \\ \gamma &= \frac{a}{b}x(1 - x^2)^{1/2} \end{aligned} \tag{C4}$$

Then we have

$$c(m, \omega) = \tfrac{1}{2}a^3 \int_{-d}^{+d} dR_Z \, \frac{R_Z^{2m}.\ \cos(2\pi R_Z/d)}{R_+^{2(m+2)}}$$

$$= \tfrac{1}{2}a^3 \int_0^d dR_Z \left(\frac{R_+^2 + R_-^2}{R_+^2 \cdot R_-^2} \, R_Z^{2m}.\ \cos(2\pi R_Z/d) \right.$$

$$= \left(\frac{a}{b}\right)^{2(m+2)} . \, (1 - \epsilon s^2)^{(2m+1)/2} . \int_0^1 dx \, x^{2m}.\ \cos 2\pi x$$

$$* \frac{(1+\alpha)^{m+2} + \binom{m+2}{1}(1+\alpha)^{m+1}\beta\epsilon S^2 + \binom{m+2}{2}(1+\alpha)^m \gamma^2\epsilon^2 S^2}{(1+\alpha)^{2(m+2)}\left(1 + \binom{m+2}{1}\left(\frac{2\beta}{1+\alpha} - \frac{\gamma^2\epsilon}{(1+\alpha)^2}\right)\epsilon S^2\right)}$$

$$= \left(\frac{a}{b}\right)^{2(m+2)} \cdot \left(1 - \left(\frac{2m+1}{2}\right)\epsilon S^2\right) c(m) \qquad \text{(C5)}$$

$$+ \int_0^1 dx \left(- \frac{(m+2)\beta}{(1+\alpha)^{m+3}} + \frac{(m+2) + \binom{m+2}{2}}{(1+\alpha)^{m+4}} \gamma^2\epsilon \right) \epsilon S^2 \cos 2\pi x$$

After substitution of Eq. (C1) and (C5) in Eq. (26) it is easy but tedious to show that the S_n, $n = 0, 2, 4$ introduced in Eq. (42) are given by

$$S_0 = \left(1 - \frac{b^2}{a^2}\right) \left[-0.096 + \left(\frac{a}{b}\right)^4 (\tfrac{1}{2}\, b(0, 2) + b(0, 3) \right.$$
$$\left. + 4b(2,3)) - 3\left(\frac{a}{b}\right)^6 (b(2, 3) + b(2, 4)) \right] \qquad \text{(C6)}$$

$$S_2 = \left(1 - \frac{b^2}{a^2}\right) \left[-0.048 - \left(\frac{a}{b}\right)^4 (\tfrac{1}{4}\, b(0, 2) + \tfrac{1}{2}\, b(0, 3) \right.$$
$$+ 2b(2, 3)) + 3\left(\frac{a}{b}\right)^6 \left(b(2, 3) + b(2, 4) + \tfrac{5}{2}\, b(4, 4) \right.$$
$$\left. - 3\left(\frac{a}{b}\right)^{\delta} \left(\tfrac{3}{2}\, b(4, 4) + 2b(4,5)\right) \right] \qquad \text{(C7)}$$

$$S_4 = \left(1 - \frac{b^2}{a^2}\right)\left[-\,0.006 + \tfrac{3}{8}\left(\frac{a}{b}\right)^4 \left(\tfrac{1}{2}\, b(0, 2) + b\,(0, 3)\right.\right.$$

$$\left. + \, 4b\,(2, 3)\right) - \tfrac{39}{8}\left(\frac{a}{b}\right)^6 \left(b(2, 3) + b\,(2, 4) + \tfrac{150}{39}\, b(4, 4)\right)$$

$$+ \, \tfrac{1}{32}\left(\frac{a}{b}\right)^8 \left(535\, b(4, 4) + 620\, b(4, 5) + 840\, b(6, 5)\right)$$

$$\left. - \, \tfrac{1}{8}\left(\frac{a}{b}\right)^{10} \left(105\, b\,(6, 5) + 175\, b(6, 6)\right)\right] \tag{C8}$$

Here $b\,(n, m)$ is a shorthand notation for the integral

$$b(n, m) = \int_0^1 dx \, \frac{x^n \cos 2\pi x}{\left(1 + \left(\left(\frac{a^2}{b^2}\right) - 1\right)x^2\right)^m}. \tag{C9}$$