A molecular theoretical derivation of the Landau free energy of chiral smectic C liquid crystals

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A molecular theoretical derivation of the Landau free energy of chiral smectic C liquid crystals

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A molecular theoretical derivation of the Landau free energy of chiral smectic C liquid crystals is presented on the basis of a molecular theoretical approach. The excess free energy concerned with the ferroelectric helicoidal structure is derived within a mean field approximation. Several material constants such as the Curie temperature, the elastic constant, the helical pitch, the piezo- and flexoelectric constants and the dielectric susceptibility are expressed in terms of some effective intermolecular interaction parameters between molecules. A molecular theoretical consideration of the chiral smectic C–smectic A transitions is given in comparison with a few previous works. By comparing with some available experimental data for DOBAMBC, effective interaction parameters are numerically estimated.

1. Introduction

Several theoretical studies of ferroelectric chiral smectic C (S_C^*) liquid crystals have been so far developed as well as many experimental ones [1–15, 19, 27]. Pikin and Indenbom first formulated a phenomenological theory on the basis of symmetry consideration of the S_C^* macroscopic structure [4]. Some phenomenological approaches have been successfully applied to explaining such macroscopic properties as thermo-dynamic and elastic properties of S_C^* liquid crystals [5–11]. On the basis of the phenomenological theories, several material constants have been experimentally obtained [19]. Therefore, in practice, such phenomenological approaches are considered to be very useful in the study of macroscopic properties of S_C^* liquid crystals.

On the other hand, it seems also to be important to clarify the macroscopic nature of these liquid crystals from a molecular theoretical aspect. For example, from the view point of the molecular structural design for S_C^* materials applicable to fast electro-optical switching light valves, we must know the correspondence between the molecular structures and the macroscopic properties. In this respect, it seems to be worthwhile to derive the Landau free energy accompanied by the S_C^* structure at a molecular level. As a first step for this purpose, van der Meer and Vertogen formulated a molecular theory of S_C^* liquid crystals within a molecular field treatment [12, 20]. They pointed out that the entropy of the molecular packing plays an important role in driving the S_C^*–S_A transition. But they did not evaluate accurately the excluded volume between molecules in the S_C^* phase on the basis of the molecular theory but merely introduced a phenomenological packing temperature so as to take account of the molecular packing effect. In consequence, the steric effect through the intermolecular repulsion could not be studied in detail. Later Matsushita suggested that the molecular packing effect might induce the S_C (or S_C^*)–S_A transitions [13]. Similar to the implication by van der Meer and Vertogen [12, 20], he also concluded

that while the molecular packing effect has a tendency to align the S_C^* molecules along the layer normal, the attractive interaction tends to incline them with respect to it, and that the S_C^*–S_A transition is not of the order–disorder type. In his approach, however, since the centres of the molecules were assumed to be completely fixed in the planes isolated from each other with a layer spacing, the molecular packing effect was not treated as accurately as in the above-mentioned analogous approach by van der Meer and Vertogen [12, 20].

Previously, based on a molecular theory of S_A [16] and cholestric liquid crystals [17], we proposed a concise molecular theory of S_C^* liquid crystals [15]. Therein, only the effective attractive interaction was taken into account; anisotropic steric effects were not included. We explained the S_C^*–S_A transition as being of an order–disorder type in contrast to the above-mentioned explanations by van der Meer and Vertogen and Matushita [12, 13, 20]. Therefore one may conclude that both the energetic contribution in the previous work and the entropy contribution considered by van der Meer and Vertogen play an important role in driving the S_C^*–S_A transition. The latter contribution in particular should be significant for the S_C^*–S_A transition where the S_C^* molecules have an almost saturated orientational order, free from any thermal fluctuation, of the long molecular axis.

As was mentioned above, several types of theories have been proposed by assuming a uniaxial molecular ordering about the long molecular axes. However, in order to study the S_C^* ferroelectric nature, we have to take account of the biaxial interactions between molecules. Osipov and Pikin proposed a theoretical model of S_C^* liquid crystals to explain the strong temperature dependence of the helical pitch near the S_C^*–S_A transition point of p-(n-decylobenzylidene)-p-amino-(2-methylbutyl)-cinnamate (DOBAMBC) [14]. In their approach, however, since the intermolecular interaction concerned with the driving force of the S_C^*–S_A transition was not included, the thermodynamic properties of the S_C^*–S_A transition could not be discussed at a molecular level. In addition, an intermolecular interaction concerned with the flexo-electric effect in the S_C^* phase was not included. As far as we are aware, the ferroelectric coupling between molecules and the steric effect concerned with the driving force of the S_C^*–S_A transitions have not been simultaneously involved in any molecular statistical theory. Moreover, such material constants as the Curie temperature, the elastic constant, the piezo- and the flexoelectric coefficients, etc., have not been derived at a molecular level.

The purpose of the present paper is to derive the Landau expansion coefficients of S_C^* liquid crystals on the basis of a molecular theory of S_C^* liquid crystals and to investigate the mechanism of S_C^*–S_A transitions. In this work, the ferroelectric interactions between S_C^* molecules are taken into account through the intermolecular attraction alone and not through the repulsion. In addition, a saturated molecular orientational order or completely aligned hard rods along the local director denoting the S_C^* helicoidal structure is assumed for the evaluation of an excess free energy accompanied by the S_C^* structure. This simplification for the saturation orientational order is suggested by the experimental finding by Doane *et al.*, who observed that the orientational order in the S_A phase is almost saturated for S_A liquid crystals with a relatively wide S_A mesomorphic temperature range [18]. Therefore this situation may also be the case for the S_C^* and S_A phases of a DOBAMBC sample which has a relatively wide S_A temperature range. Neglecting the correlations between molecules, we shall resort to a mean field approximation analogous to the previous approaches [14, 15]. A molecular statistical approach and the Landau expansion of the excess free

energy accompanied by the S_C^* structure are formulated in §2. The dependences of the expansion coefficients on the molecular length-to-breadth ratio and a few phase diagrams for the volume fraction and the temperature are provided in §3. A comparison with the available experimental data by Carlsson and Dahl [19] is also given. Finally, §4 gives several remarks on the present study as well as the microscopic consideration of the S_C^*–S_A transitions.

2. Theory
2.1. *Intermolecular potential*

The pairwise intermolecular potential Φ_{int} composed of the repulsive part Φ^{rep} and the attractive part Φ^{att} can be written as

$$\Phi_{int}(\mathbf{Q}_1, \mathbf{Q}_2) = \Phi^{rep}(\mathbf{Q}_1, \mathbf{Q}_2) + \Phi^{att}(\mathbf{Q}_1, \mathbf{Q}_2), \tag{1}$$

where $\mathbf{Q}_i$ is the set of variables $(\mathbf{r}_i, R_i)$; here $\mathbf{r}_i$ and R_i are the position and the eulerian angles of the i th molecule with respect to the laboratory frame, respectively. In this work, the S_C^* molecule is assumed to be non-polar along the long axis, whose molecular shape is modelled into a cylinderical one with the length L and the diameter D as shown in figure 1. In addition the intermolecular repulsive potential Φ^{rep} is assumed to be hard core. Because of the uniaxiality of the molecular shape, the peizo- and flexoelectric effects related to the ferroelectric coupling between molecules are attributed to only the intermolecular attraction but not to the repulsion.
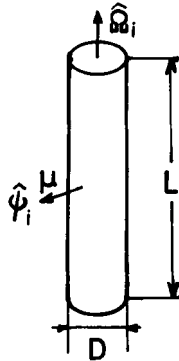
Figure 1.   A cylindrical rod-like molecule. Here $\hat{\boldsymbol{\Omega}}_i$ and $\hat{\boldsymbol{\psi}}_i$ are the unit vectors along the long and the short molecular axes, respectively. μ denotes the permanent dipole attached along $\hat{\boldsymbol{\psi}}_i$.

Now we shall assume that Φ^{att} consists of the following six components:

$$\Phi^{att}(\mathbf{Q}_1, \mathbf{Q}_2) = \Phi^S(\mathbf{Q}_1, \mathbf{Q}_2) + \Phi^{SB}(\mathbf{Q}_1, \mathbf{Q}_2)$$
$$+ \Phi^C(\mathbf{Q}_1, \mathbf{Q}_2) + \Phi^P(\mathbf{Q}_1, \mathbf{Q}_2)$$
$$+ \Phi^F(\mathbf{Q}_1, \mathbf{Q}_2) + \Phi^D(\mathbf{Q}_1, \mathbf{Q}_2), \tag{2}$$

which are put into the following forms:

$$\Phi^S(\mathbf{Q}_1, \mathbf{Q}_2) = A_{00}(r_{12}) + A_{22}(r_{12})P_2(\hat{\boldsymbol{\Omega}}_1 \cdot \hat{\boldsymbol{\Omega}}_2), \tag{3}$$

$$\Phi^{SB}(\mathbf{Q}_1, \mathbf{Q}_2) = A_{20}(r_{12})P_2(\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_1) + A_{02}P_2(\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_2)$$
$$+ A_{40}(r_{12})P_4(\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_1) + A_{04}P_4(\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_2), \tag{4}$$

$$\Phi^{C}(\mathbf{Q}_1, \mathbf{Q}_2) = B(r_{12})(\hat{\mathbf{\Omega}}_1 \times \hat{\mathbf{\Omega}}_2) \cdot \hat{\mathbf{u}}_{12}(\hat{\mathbf{\Omega}}_1 \cdot \hat{\mathbf{\Omega}}_2), \tag{5}$$

$$\Phi^{P}(\mathbf{Q}_1, \mathbf{Q}_2) = C_{P}(r_{12})\{(\hat{\mathbf{\Omega}}_2 \times \hat{\mathbf{\psi}}_1) \cdot \hat{\mathbf{u}}_{12}(\hat{\mathbf{u}}_{12} \cdot \hat{\mathbf{\Omega}}_1)$$
$$+ (\hat{\mathbf{\Omega}}_1 \times \hat{\mathbf{\psi}}_2) \cdot \hat{\mathbf{u}}_{12}(\hat{\mathbf{u}}_{12} \cdot \hat{\mathbf{\Omega}}_2)\}(\hat{\mathbf{\Omega}}_1 \cdot \hat{\mathbf{\Omega}}_2) \tag{6}$$

$$\Phi^{F}(\mathbf{Q}_1, \mathbf{Q}_2) = C_{F}(r_{12})\{(\hat{\mathbf{u}}_{12} \times \hat{\mathbf{\psi}}_1) + (\hat{\mathbf{u}}_{12} \times \hat{\mathbf{\psi}}_2)\} \cdot (\hat{\mathbf{\Omega}}_1 \times \hat{\mathbf{\Omega}}_2)(\hat{\mathbf{\Omega}}_1 \cdot \hat{\mathbf{\Omega}}_2), \tag{7}$$

$$\Phi^{D}(\mathbf{Q}_1, \mathbf{Q}_2) = C_{D}(r_{12})(\hat{\mathbf{\psi}}_1 \cdot \hat{\mathbf{\psi}}_2), \tag{8}$$

where $P_l(x)$ is the Legendre polynomial of the lth order, $r_{12} = r_2 - r_1$, $r_{12} = |r_2 - r_1|$, $\hat{\mathbf{u}}_{12} = r_{12}/r_{12}$, and $\hat{\mathbf{\Omega}}_i$ and $\hat{\mathbf{\psi}}_i$ denote the unit vectors along the long and the short molecular axes, respectively. The direction of the unit vector $\hat{\mathbf{\psi}}_i$ is assumed to be coincident with the transverse permanent dipole. Consistent with the non-polar assumption along the long molecular axis, all these potential components are invariant under such orientational inversions as $\hat{\mathbf{\Omega}}_1 \rightarrow -\hat{\mathbf{\Omega}}_1$ and/or $\hat{\mathbf{\Omega}}_2 \rightarrow -\hat{\mathbf{\Omega}}_2$. Now let us mention the property of each component of Φ^{att}. Firstly, since Φ^{S} depends only on the relative angle between two long molecular axes, it possesses spherical symmetry and is invariant under full rotations of the relative position vector r_{12}. For most rod-like liquid-crystalline molecules, this component originates from the van der Waals, or the induced dipole–induced dipole, interaction. Of course, the anisotropic part of Φ^{S}, $A_{22}P_2(\hat{\mathbf{\Omega}}_1 \cdot \hat{\mathbf{\Omega}}_2)$, stabilizes the parallel alignment of molecules, or nematic order, and corresponds with to so to speak the Maier–Saupe potential [31]. Secondly the next component Φ^{SB} is related to the rod-like molecular shape [21, 24, 25]. This type of potential has no spherical symmetry with respect to r_{12} different from Φ^{S} and therefore will hereafter be called the symmetry-breaking component. As will be shown later, Φ^{SB} affects the thermodynamic stability of the phases with a layer structure as seen in the S_C^* or S_A phase, whereas its effect completely vanishes in the N^* or I phase. The effect of an analogous symmetry-breaking component on the thermodynamic stability of the S_A layer structure was first discussed by Senbetu and Woo [16].

Recently Kimura and Nakano [21] studied the effect of a somewhat elaborated potential corresponding to equation (4) on the surface tension of nematogens. In previous work [15] it was shown that the driving force of the S_C^*–S_A phase transition comes from the symmetry-breaking component, Φ^{SB}, but not from the spherically symmetric component, Φ^{S}. As can be easily seen from equation (4), $A_{20} (= A_{02})$ and $A_{40} (= A_{04})$ may have positive values for an elongated molecule as was assumed by Senbetu and Woo [16] and by us [15]. On the other hand, van der Meer and Vertogen pointed out that A_{20} may become negative because of the interaction between a transverse permanent dipole and transversely induced dipole [12, 20]. Therefore A_{20} may become positive or negative depending on the microscopic molecular structure. As will be shown later, the S_C^* molecules tend to align along the layer normal for $A_{20} > 0$, whereas they may incline with respect to the layer normal for $A_{20} < 0$. Of course $A_{40} > 0$ has a tendency to incline the S_C^* molecules whether A_{20} is greater than or less than zero. One purpose of this study is to show that such symmetry-breaking components of the attractive interaction, A_{20} and A_{40}, play an important role in making a tilted molecular alignment in the S_C^* phase. The third component, Φ^{C}, is a pseudo-scalar and represents the chiral interaction which results from the second-order perturbation energy of the dipole–quadrupole interaction between the uniaxial molecules without centrosymmetry, and it contributes to the twisting power of the helical S_C^* or N^* structure [15, 17, 22, 23, 32]. As can be easily seen from equation (5), no twisting power exists in the S_A phase, where the average of $\hat{\mathbf{\Omega}}_1 \times \hat{\mathbf{\Omega}}_2$ has to vanish.

The sign of B determines the sense of the helix in the S_C^* or N* phase. That is, $B > 0$ prefers the left-hand helix, whereas $B < 0$ prefers the right-handed one.

Now we shall consider the other three components in the right-hand side of equation (2), which are concerned with the ferroelectric coupling between molecules and are not included in the previous work [15]. First, Φ^P corresponds to the interaction between the chiral and the banana-like molecules and is essentially the same as that introduced by Osipov and Pikin [14]. This component reflects a polarity along the short molecular axis. As will be shown in the next subsection, this energy is concerned with the coupling between the molecular tilt and ferroelectric alignment of the transverse permanent dipoles, and results in the so-called piezoelectric effect. The second component Φ^F is a pseudo-scalar and also related to the coupling energy between the molecular tilt and the dipole alignment as well as Φ^P. As will be shown in §2.4, this component bears on the flexoelectric effect related to the natural bend deformation in the helicoidal S_C^* structure. Of course, as can be easily seen from equation (7), this term does not affect the molecular ordering in the S_A or N* structure because the average of $\hat{\Omega}_1 \cdot \hat{\psi}_2$ or $\hat{\Omega}_2 \cdot \hat{\psi}_1$ has to vanish. The above two components, Φ^P and Φ^F, result of course from the biaxial and non-centrosymmetric molecular structure as is briefly derived in the Appendix. Finally the component Φ^D represents the dipole–dipole interaction between the transverse dipoles attached along the short molecular axes. Like Φ^S, this is also assumed to have spherical symmetry with respect to r_{12}. The potential coefficient C_D should be positive to assure non-ferroelectric ordering of the transverse dipoles in the S_A or N* phase.

The above-mentioned components have to be closely related to the molecular structure and might be in principle expanded as an infinite series in terms of the spherical harmonics or the Wigner rotation matrices [24–26]. In practice, this problem is quite interesting but very troublesome and beyond the scope of the present work. According to the result of the previous work [15] and the experimental finding that the difference in the transition temperatures between chiral DOBAMBC and a racemic mixture of it is sufficiently small [1], we may regard the contributions of the latter four interactions in equation (2) to the free energy as perturbations compared with those of the former two interactions. Therefore, in this work, we shall regard the Landau free energy accompanied with the inclined, helical and ferroelectric ordering of molecules in S_C^* phase as perturbation free energy compared with the free energy concerned with the layer structure in the SmA phase. Assuming the above-mentioned molecular geometry and making use of the intermolecular attractive interactions, the Landau free energy in the S_C^* phase will be derived in the following subsections on the basis of a molecular theory.

2.2. *Thermodynamic quantities and order parameters*

Making use of the intermolecular potentials presented in the previous subsection, we shall derive here the excess free energy in the thermal equilibrium system composed of N similar cylinders with absolute temperature T and the total volume V. Throughout the following we shall restrict ourselves to the thermodynamic properties of S_C^* near the S_C^*–S_A transition point. Moreover we assume here that the S_C^* liquid crystals have relatively wide S_A temperature ranges. Therefore, as was previously mentioned, the orientation fluctuation of the long molecular axes about the local director may be neglected in the derivation of the excess free energy concerned with the S_C^* helicoidal structure. The similar approximation for such a saturated molecular orientation was accepted as accounting for the S_A–N phase transition by Wadati and

Isihara [28] and Hosino *et al.* [29]. The validity of this assumption may be confirmed by N.M.R. measurements for the orientational order of S_A liquid crystals with relatively wide S_A temperature ranges [18]. This assumption seems also to be valid in the case of such S_C^* liquid crystals as DOBAMBC and its homologous series with relatively wide S_A mesomorphic temperature ranges.

As is well appreciated [30, 33], within the second virial approximation for the intermolecular repulsion the Helmholtz free energy of the N-body system, F_N, is given by

$$F_N = \frac{\varrho^2}{2} \int d\mathbf{Q}_1 d\mathbf{Q}_2 f(\mathbf{Q}_1) f(\mathbf{Q}_2) \{g^{rep}(\mathbf{Q}_1, \mathbf{Q}_2) \Phi^{att}(\mathbf{Q}_1, \mathbf{Q}_2) - \kappa T f^{rep}(\mathbf{Q}_1, \mathbf{Q}_2)\}$$
$$+ \varrho \kappa T \int d\mathbf{Q}_1 f(\mathbf{Q}_1) \log\{\varrho f(\mathbf{Q}_1)\}, \tag{9}$$

where κ is the Boltzmann constant, $\varrho = N/V$ the average number density, $f(\mathbf{Q}_i)$ the one-body distribution function of the ith molecule, g^{rep} the pair correlation function in the system interacting through only intermolecular repulsion Φ^{rep} but not the attraction Φ^{att}, and f^{rep} the Mayer function defined by

$$f^{rep}(\mathbf{Q}_1, \mathbf{Q}_2) = \exp[-\Phi^{rep}(\mathbf{Q}_1, \mathbf{Q}_2)/\kappa T] - 1. \tag{10}$$

As a consequence of the hard-core approximation for Φ^{rep}, f^{rep} takes -1 for the intersecting pair of molecules and otherwise 0. In equation (9) $f(\mathbf{Q}_i)$ of course has to satisfy the following constraint:

$$\int d\mathbf{Q}_i f(\mathbf{Q}_i) = V, \quad i = 1, 2, \ldots, N. \tag{11}$$

Then the internal energy U_N and the entropy S_N are given by

$$U_N = \frac{\varrho^2}{2} \int d\mathbf{Q}_1 d\mathbf{Q}_2 f(\mathbf{Q}_1) f(\mathbf{Q}_2) g^{rep}(\mathbf{Q}_1, \mathbf{Q}_2) \Phi^{att}(\mathbf{Q}_1, \mathbf{Q}_2), \tag{12}$$

and

$$S_N = \frac{\varrho^2}{2} \kappa \int d\mathbf{Q}_1 d\mathbf{Q}_2 f(\mathbf{Q}_1) f(\mathbf{Q}_2) f^{rep}(\mathbf{Q}_1, \mathbf{Q}_2) - \varrho \kappa \int d\mathbf{Q}_1 f(\mathbf{Q}_1) \log\{\varrho f(\mathbf{Q}_1)\}, \tag{13}$$

respectively; here the first integral denotes the packing entropy which is not involved in our previous work [15]. The second term corresponds to the orientational or mixing entropy. By minimizing F_N under the constraint of equation (11), we readily obtain the minimized free energy

$$F_N = -U_N - \kappa T I^{rep} - N\kappa T \log\{Z_1/\varrho\}, \tag{14}$$

where I^{rep} and Z_1 are defined by

$$I^{rep} = -\frac{\varrho^2}{2} \int d\mathbf{Q}_1 d\mathbf{Q}_2 f(\mathbf{Q}_1) f(\mathbf{Q}_2) f^{rep}(\mathbf{Q}_1, \mathbf{Q}_2), \tag{15}$$

and

$$Z_1 = \frac{1}{V} \int d\mathbf{Q}_1 \exp[-\Phi_1(\mathbf{Q}_1)/\kappa T], \tag{16}$$

respectively; here $\Phi_1(\mathbf{Q}_1)$ is the mean field potential defined by

$$\Phi_1(\mathbf{Q}_1) = \varrho \int d\mathbf{Q}_2 f(\mathbf{Q}_2)\{g^{\mathrm{rep}}(\mathbf{Q}_1,\mathbf{Q}_2)\Phi^{\mathrm{att}}(\mathbf{Q}_1,\mathbf{Q}_2) - \kappa T f^{\mathrm{rep}}(\mathbf{Q}_1,\mathbf{Q}_2)\}. \quad (17)$$

In the next subsection we introduce the macroscopic and microscopic order parameters to represent the S_C^* structure.
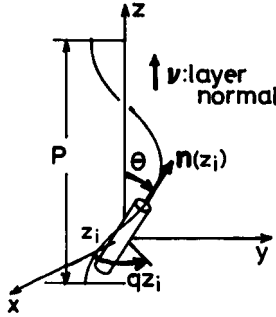

Figure 2. The macroscopic structure in the S_C^* phase. Here θ and P are the tilt angle and helical pitch, respectively. $\mathbf{n}(z_i)$ and v are the local director and the layer normal unit vector, respectively. The z axis in cartesian coordinates is taken to be the layer normal.

2.3. *Order parameters*

The macroscopic order parameters of the molecular tilt angle θ and the helical pitch P are shown in figure 2. Taking the z axis to be normal to the smectic layer in the cartesian coordinate system fixed in the laboratory frame, the local director $\mathbf{n}(z_i)$ at $z = z_i$ may be expressed by assuming the uniform helicoidal structure as

$$\mathbf{n}(z_i) = (\eta\cos qz_i, \eta\sin qz_i, \xi), \quad (18)$$

where the macroscopic order parameters, η, ξ, and q are defined by

$$\eta = \sin\theta \quad (19)$$

$$\xi = \cos\theta \quad (20)$$

$$q = 2\pi/P, \quad (21)$$

respectively. Neglecting the thermal fluctuation of the long molecular axes about the spatially varying local director $\mathbf{n}(z_i)$ [12, 14, 28], we may approximate the one-body distribution function of the ith molecule, $f(\mathbf{Q}_i)$, as follows:

$$f(\mathbf{Q}_i) = \delta(\hat{\boldsymbol{\Omega}}_i - \mathbf{n}(z_i))g(z_i)h(\psi_i), \quad (22)$$

where ψ_i is defined as the angle between the transverse dipole of the ith molecule and $v \times \mathbf{n}(z_i)$, and the distribution functions, $g(z_i)$ and $h(\psi_i)$, have to satisfy the following constraints:

$$\int_0^d dz_i g(z_i) = d, \quad (23)$$

and

$$\int_0^{2\pi} d\psi_i h(\psi_i) = 1. \quad (24)$$

respectively; here d denotes the layer spacing. In the distribution function (22), the correlation between z_i and ψ_i was assumed to be negligible near the S_C^*–S_A phase transition point of S_C^* liquid crystal with a relatively wide S_A temperature range. In such a case, while the magnitude of the spontaneous polarization or the orientational order of ψ_i appreciably changes near the S_C^*–S_A transition point, the translational order of z_i is not drastically affected by the temperature change but remains almost constant throughout the transition. Therefore the correlation between z_i and ψ_i may be neglected as was assumed above.

To introduce the microscopic order parameters, $g(z_i)$ and $h(\psi_i)$ may be expanded in terms of the appropriate orthogonal functions as follows:

$$g(z_i) = \sum_k \frac{2}{1 + \delta_{k_0}} \langle \cos kz \rangle \cos kz_i, \quad k = 0, k_0, 2k_0, \ldots, \tag{25}$$

$$\langle \cos kz \rangle = \frac{1}{d} \int_0^d dz_i g(z_i) \cos kz_i, \tag{26}$$

and

$$h(\psi_i) = \frac{1}{2\pi} \sum_m \frac{2}{1 + \delta_{m_0}} \{\langle \cos m\psi \rangle \cos m\psi_i + \langle \sin m\psi \rangle \sin m\psi_i\}, \quad m = 0, 1, 2, \ldots,$$

$$\left. \begin{array}{l} \langle \cos m\psi \rangle = \displaystyle\int_0^{2\pi} d\psi_i h(\psi_i) \cos m\psi_i, \\[2mm] \langle \sin m\psi \rangle = \displaystyle\int_0^{2\pi} d\psi_i h(\psi_i) \sin m\psi_i, \end{array} \right\} \tag{28}$$

respectively, where k_0 is the fundamental wave number of the one-dimensional density wave equal to $2\pi/d$. Making use of equations (22), (25) and (27), we will derive U_N of equation (12) and I^{rep} of equation (15) below. Throughout the following the calculation concerned with the free energy, the internal energy and the entropy will be accomplished within the same order of approximation as the following expression for the Pikin–Indenbom free energy of S_C^* phase:

$$f_{\text{LD}} = \alpha(T)\eta^2 + \beta\eta^4 - \frac{K_e}{2}\eta^2 q^2 + \Lambda_c\eta^2 q - \mu_P\eta\xi P_S + \mu_F\eta\xi Q P_S + \frac{P_S^2}{2\chi}, \tag{29}$$

where α and β are appropriate constants, K_e an elastic constant, Λ_c the Lifshitz invariant and μ_P and μ_F the piezo- and flexoelectric constants.

For simplicity, in the calculation of the internal energy, we approximate the correlation function by the spherically symmetric one, viz.

$$g^{\text{rep}}(\mathbf{Q}_1, \mathbf{Q}_2) \simeq g^{\text{rep}}_{(r_{12})}. \tag{30}$$

Within the above-mentioned approximation, making use of equations (22), (25) and (27), the spherical component of the internal energy, U^S, corresponding to Φ^S can be written as

$$U^S = \frac{N}{2} \sum_{k,l} \frac{2}{1 + \delta_{k0}} \langle \cos kz \rangle^2 \varrho \int d\mathbf{r}_{12} \cos kz_{12} \{g^{\text{rep}}_{(r_{12})} A_{ll}(r_{12}) P_l(\mathbf{n}_1 \cdot \mathbf{n}_2)\}, \tag{31}$$

where $\mathbf{n}_i$ is the abbreviation for $\mathbf{n}(z_i)$ and will be used hereafter.

Making use of the following approximations:

$$\mathbf{n}_1 \cdot \mathbf{n}_2 = 1 + \eta^2 (\cos q z_{12} - 1)$$

$$\simeq 1 - \tfrac{1}{2}\eta^2 q^2 z_{12}^2, \tag{32}$$

$$P_l(1 - \varepsilon) \simeq 1 - \frac{l(l+1)}{2}\varepsilon, \quad 0 \leqslant \varepsilon \ll 1, \quad l = 0 \text{ and even.} \tag{33}$$

and utilizing Rayleigh's formula [35],

$$\cos k z_{12} = \sum_{L = 0 \text{ and even}} i^L (2L + 1) j_L(k r_{12}) P_L(\hat{\mathbf{u}}_{12} \cdot \mathbf{v}), \tag{34}$$

where $j_L(x)$ is the spherical Bessel function of the Lth order, one can readily obtain

$$U^S = \frac{N}{2} \sum_{k,l} \frac{2}{1 + \delta_{k0}} \langle \cos kz \rangle^2 \varrho 4\pi \int_0^\infty r_{12}^2 dr_{12} g_{(r_{12})}^{\text{rep}} A_{ll}(r_{12})$$

$$\times \left\{ j_0(k r_{12}) - \frac{l(l+1)}{12} \eta^2 q^2 r_{12}^2 (j_0(k r_{12}) - 2j_2(k r_{12})) \right\}. \tag{35}$$

Then, restricting the attractive interactions to nearest neighbours, we can derive approximately

$$U^S = \frac{N}{2} \sum_{k,l} \frac{2}{1 + \delta_{k0}} \langle \cos kz \rangle^2 \tilde{a}_{ll} \left\{ j_0(k r_0) - \frac{l(l+1)}{12} \eta^2 q^2 r_0^2 (j_0(k r_0) - 2j_2(k r_0)) \right\}, \tag{36}$$

where $\tilde{a}_{ll}$ is the effective attractive interaction defined by

$$\tilde{a}_{ll} = 4\pi \varrho \int_0^\infty r_{12}^2 dr_{12} g_{(r_{12})}^{\text{rep}} A_{ll}(r_{12}), \tag{37}$$

and r_0 is the average intermolecular distance between nearest-neighbour molecules and may be evaluated as

$$\left. \begin{aligned} \varrho \frac{4\pi}{3} \left(\frac{r_0}{2} \right)^3 &\equiv 1, \\ r_0 &= \left(\frac{3\lambda}{2c} \right)^{1/3} D \equiv \Lambda D. \end{aligned} \right\} \tag{38}$$

Here the volume fraction c and the length-to-breadth ratio λ are defined by

$$c = \varrho \frac{\pi}{4} D^2 L = \varrho v_{\text{mol}}, \tag{39a}$$

and

$$\lambda = L/D, \tag{39b}$$

respectively. Consequently we can derive the following result:

$$U^S = \frac{N}{2} \sum_k \{ a_S^{00}(k) + a_S^{22}(k) \eta^2 Q^2 \} \langle \cos kz \rangle^2, \tag{40}$$

where $Q = (2\pi/P)D \quad (\ll 1)$ and a_S^{00} and a_S^{22} are defined by

$$a_S^{00}(k) = \frac{2}{1 + \delta_{k0}} \left\{ \sum_l \tilde{a}_{ll} \right\} j_0(k r_0), \tag{41a}$$

and

$$a_S^{22}(k) = -\frac{1}{1 + \delta_{k0}} \tilde{a}_{22} \Lambda^2 (j_0(kr_0) - 2j_2(kr_0)), \tag{41 b}$$

respectively. Here the first and the second numbers of the superscripts represent the power indices of η and Q, respectively.

Similarly, with the aids of the above-mentioned approximations, U^{SB} and U^C can be written as

$$U^{SB} = \frac{N}{2} \sum_k \{a_{SB}^{00}(k) + 2a_{SB}^{20}(k)\eta^2 + 2a_{SB}^{40}(k)\eta^4\} \langle \cos kz \rangle^2, \tag{42}$$

$$a_{SB}^{00}(k) = \frac{2}{1 + \delta_{k0}} \{-2\tilde{a}_{20} j_2(kr_0) + 2\tilde{a}_{40} j_4(kr_0)\}, \tag{42 a}$$

$$a_{SB}^{20}(k) = -\frac{1}{1 + \delta_{k0}} \{-3\tilde{a}_{20} j_2(kr_0) + 10\tilde{a}_{40} j_4(kr_0)\}, \tag{42 b}$$

$$a_{SB}^{40}(k) = \frac{2}{1 + \delta_{k0}} \frac{35}{8} \tilde{a}_{40} j_4(kr_0), \tag{42 c}$$

$$U^C = \frac{N}{2} \sum_k b^{21}(k)\eta^2 Q \langle \cos kz \rangle^2, \tag{43}$$

$$b^{21}(k) = \frac{2}{1 + \delta_{k0}} \tilde{b} \frac{\Lambda}{3} (j_0(kr_0) - 2j_2(kr_0)). \tag{43 a}$$

Here the effective interaction coefficients, $\tilde{b}$ and $\tilde{a}_{40}\ (=\tilde{a}_{04})$, are defined in similar manner as in equation (37). Next, we shall consider the internal energies concerned with the polar effects which are not involved in the previous work [15]. For convenience, let us first define the following two unit vectors, $\hat{\mathbf{v}}_i$ and $\hat{\mathbf{w}}_i$, at $z = z_i$:

$$\hat{\mathbf{v}}_i = (\mathbf{v} \times \mathbf{n}_i)/|\mathbf{v} \times \mathbf{n}_i| \tag{44}$$

and

$$\hat{\mathbf{w}}_i = \mathbf{n}_i \times \hat{\mathbf{v}}_i, \tag{45}$$

where $\mathbf{v}$ is the unit vector along the z axis or the layer normal.

Introducing these two unit vectors, we can express the unit vector along the transverse dipole of the ith molecule, $\hat{\psi}_i$, as

$$\hat{\psi}_i = \cos \psi_i \hat{\mathbf{v}}_i + \sin \psi_i \hat{\mathbf{w}}_i; \tag{46}$$

here ψ_i is defined as the angle between $\hat{\mathbf{v}}_i$ and the transverse permanent dipole of the ith molecule. Making use of this expression, after some straightforward calculations we can find the internal energies concerned with the dipolar interactions as follows:

$$U^P = N \sum_k c_P^{10}(k)\eta\xi \langle \cos \psi \rangle \langle \cos kz \rangle^2, \tag{47}$$

$$c_P^{10}(k) = -\frac{2}{1 + \delta_{k0}} \tilde{c}_P j_2(kr_0), \tag{47 a}$$

$$U^F = N \sum_k c_F^{11}(k)\eta\xi Q \langle \cos \psi \rangle \langle \cos kz \rangle^2, \tag{48}$$

$$c_{F(k)}^{11} = \frac{2}{1 + \delta_{k0}} \tilde{c}_F \frac{\Lambda}{3} (j_0(kr_0) - 2j_2(kr_0)), \tag{48 a}$$

$$U^D = \frac{N}{2} \sum_k c_D^{00}(k)\{\langle \cos\psi \rangle^2 + \langle \sin\psi \rangle^2\}, \tag{49}$$

$$c_D^{00}(k) = \frac{2}{1 + \delta_{k0}} \tilde{c}_D j_0(kr_0). \tag{49 a}$$

Here the definitions for the averaged interaction parameters, $\tilde{c}_P$, $\tilde{c}_F$ and $\tilde{c}_D$, are also the same as equation (37). From equation (47), one finds that $U^P \propto \langle \cos kz \rangle^2$. This result just corresponds to that found by Osipov and Pikin (see equation (20) in [14]).

Now the total internal energy can be separated into two parts as

$$U_N = U^0(\langle \cos kz \rangle) + U^1(\langle \cos\psi \rangle, \langle \sin\psi \rangle, \eta, Q; \langle \cos kz \rangle), \tag{50}$$

where $U^0(\langle \cos kz \rangle)$ and $U^1(\langle \cos\psi \rangle, \langle \sin\psi \rangle, \eta, Q; \langle \cos kz \rangle)$ are defined by

$$U^0(\langle \cos kz \rangle) = \frac{N}{2} \sum_k \{a_S^{00}(k) + a_{SB}^{00}(k)\}\langle \cos kz \rangle^2. \tag{51}$$

and

$$
\begin{aligned}
U^1(\langle \cos\psi \rangle, \langle \sin\psi \rangle, \eta, Q; \langle \cos kz \rangle) = \frac{N}{2} \sum_k \{ & a_S^{22}(k)\eta^2 Q^2 + 2a_{SB}^{20}(k)\eta^2 + a_{SB}^{22}(k)\eta^2 Q^2 \\
& + 2a_{SB}^{40}(k)\eta^4 + b^{21}(k)\eta^2 Q + 2c_P^{10}(k)\eta\xi\langle \cos\psi \rangle + 2c_F^{11}(k)\eta\xi Q\langle \cos\psi \rangle \\
& + c_D^{00}(k)(\langle \cos\psi \rangle^2 + \langle \sin\psi \rangle^2)\}\langle \cos kz \rangle^2,
\end{aligned} \tag{52}
$$

respectively.

As the next stage, let us consider the repulsive or molecular packing contribution which was not included in the previous work [15]. The internal energy has been calculated in the spatial structure expressed by equation (18). Since the steric hindrance between molecules is short range, the local director may be reasonably approximated in terms of the somewhat simplified

$$\mathbf{n}'(z) = (\eta \cos\phi, \eta \sin\phi, \xi), \quad \phi = \text{constant}. \tag{53}$$

Then making use of equation (53) and assuming that the molecules are relatively elongated, we can easily integrate equation (15) and obtain the following results within the approximation up to the order of η^2 (see figure 3):

$$
\begin{aligned}
I^{rep} &= \frac{N}{2} \sum_k \frac{2}{1 + \delta_{k0}} \langle \cos kz \rangle^2 \varrho \int_{-L\xi}^{+L\xi} dz_{12} \cos kz_{12} \frac{\pi D^2}{\xi} \\
&= \frac{N}{2} \sum_k \frac{2}{1 + \delta_{k0}} \langle \cos kz \rangle^2 8\varrho v_{mol} j_0(kL\xi) \\
&\simeq \frac{N}{2} \sum_k c\{v^{00}(k) + 2v^{20}(k)\eta^2\}\langle \cos kz \rangle^2,
\end{aligned} \tag{54}
$$

where $v^{00}(k)$ and $v^{20}(k)$ are defined by

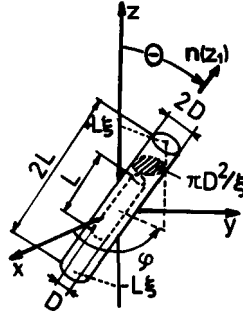$$v^{00}(k) = \frac{2}{1 + \delta_{k0}} 8j_0(kL), \tag{55}$$

Figure 3. The excluded volume between two molecules. S_C structure is supposed for simplicity, and therefore the two molecules are parallel one another.

and

$$v^{20}(k) \;=\; \frac{2}{1 + \delta_{k0}} \, 2kL j_1(kL), \tag{56}$$

respectively; here the superscript numbers represent the power indices of η and Q as before. As will be shown later, since $v^{20}(k)$ takes a positive value for an appropriate value of $k \simeq 2\pi/L$, the molecules tend to orient along the layer normal due to the packing effect. In addition, it should be borne in mind here that such η^2 dependence of I^{rep} is assured by the existence of the one-dimensional density wave in the S_C^* state. Such η^2 dependence of equation (54) is essentially equivalent to that pointed out by Matsushita as the explanation of the S_C^* (S_C)–S_A transitions [13]. Of course, since he restricted the positions of molecules in the planes separated by d, the dependence of the packing effect on η was overestimated. Now I^{rep} can be written as

$$I^{rep} \;=\; I^0(\langle \cos kz \rangle) + I^1(\eta; \langle \cos kz \rangle), \tag{57}$$

where $I^0(\langle \cos kz \rangle)$ and $I^1(\eta; \langle \cos kz \rangle)$ are defined by

$$I^0(\langle \cos kz \rangle) \;=\; \frac{N}{2} \sum_k c v^{00}(k) \langle \cos kz \rangle^2 \tag{58}$$

and

$$I^1(\eta; \langle \cos kz \rangle) \;=\; N \sum_k c v^{20}(k) \eta^2 \langle \cos kz \rangle^2, \tag{59}$$

respectively. Finally the total free energy expressed by equation (14) leads to

$$F_N \;=\; -U^0 - U^1 - \kappa T I^0 - \kappa T I^1 - N\kappa T \log Z_1. \tag{60}$$

2.4. Landau expansion of the excess free energy

In this subsection, we use a perturbation method to derive the excess free energy accompanied by the SmC* structure. As was previously mentioned regarding the excess free energy in S_C^* phase as a perturbation energy compared with the free energy concerned with the S_A phase, we shall resort to the following approximation for the one-body partition function Z_1:

$$Z_1 \;\simeq\; Z_1^0 \exp[-\langle \Phi^1 \rangle^0 / \kappa T], \tag{61}$$

where

$$\langle \Phi^1 \rangle^0 = \left\{ \frac{1}{d} \int_0^d dz \, \Phi^1(z) \exp\left[-\Phi^0(z)/\kappa T\right] \right\} \Big/ Z_1^0, \qquad (62)$$

$$Z_1^0 = \frac{1}{d} \int_0^d dz \exp\left[-\Phi^0(z)/\kappa T\right]; \qquad (63)$$

here $\Phi^0(z_1)$ and $\Phi^1(z_1)$ are defined by

$$\Phi^0(z_1) = \sum_k \{a_S^{00}(k) + a_{SB}^{00}(k) + c\kappa Tv^{00}(k)\} \langle \cos kz \rangle \cos kz_1, \qquad (64)$$

and

$$\begin{aligned}
\Phi^1(z) = \sum_k \{&a_S^{22}(k)\eta^2 Q^2 + 2a_{SB}^{20}(k)\eta^2 + a_{SB}^{22}(k)\eta^2 Q^2 + 2a_{SB}^{40}(k)\eta^4 + b^{21}(k)\eta^2 Q \\
&+ 2c_P^{10}(k)\eta\xi\langle \cos\psi \rangle + 2c_F^{11}(k)\eta\xi Q\langle \cos\psi \rangle + c_D^{00}(k)(\langle \cos\psi \rangle^2 + \langle \sin\psi \rangle^2) \\
&+ 2v^{20}(k)c\kappa T\eta^2\} \langle \cos kz \rangle \cos kz,
\end{aligned} \qquad (65)$$

respectively. While $\Phi^0(z_1)$ is the mean field potential concerned with only the S_A layer structure with $\theta = 0$ and $Q = 0$, $\Phi^1(z_1)$ is the mean field potential concerned with the ferroelectric helicoidal structure with $\theta \neq 0$ and $Q \neq 0$ as well as the S_A layer structure.

Consequently, the total free energy F_N can be separated into two parts similar to that of $\Phi_1(z_1)$,

$$F_N = F^0(\langle \cos kz \rangle) + F^1(\langle \cos\psi \rangle, \langle \sin\psi \rangle, \eta, Q; \langle \cos kz \rangle), \qquad (66)$$

where F^0 and F^1 are defined by

$$F^0 = -U^0 - \kappa TI^0 - N\kappa T \log(Z_1^0/\varrho), \qquad (67)$$

and

$$F^1 = U^1 + \kappa TI^1 = \frac{N}{2} \langle \Phi^1 \rangle^0, \qquad (68)$$

respectively. Consequently the excess free energy per volume f^1 can be written as

$$\begin{aligned}
f^1 = F^1/V = \varrho\{&(\bar{a}_{SB}^{20} + c\kappa T\bar{v}^{20})\eta^2 + \tfrac{1}{2}(\bar{a}_S^{22} + \bar{a}_{SB}^{22})\eta^2 Q^2 + \tfrac{1}{2}\bar{b}^{21}\eta^2 Q \\
&+ \bar{c}_P^{10}\eta\xi\langle \cos\psi \rangle + \bar{c}_F^{11}\eta\xi Q\langle \cos\psi \rangle + \tfrac{1}{2}\bar{c}_D^{00}(\langle \cos\psi \rangle^2 + \langle \sin\psi \rangle^2)\}.
\end{aligned} \qquad (69)$$

Here the bars on these coefficients denote the summation over k, for example

$$\bar{a}_{SB}^{20} = \sum_k a_{SB}^{20}(k)\langle \cos kz \rangle^2. \qquad (70)$$

Equation (69) is the Landau free energy based on the molecular statistical aspect. From equation (67), the translational order parameter, $\langle \cos kz \rangle$, may be approximately determined by minimizing F^0 ($\simeq F_N$) instead of F_N with respect to itself, as follows:

$$\langle \cos kz \rangle = \left\{ \frac{1}{d} \int_0^d dz \cos kz \exp\left[-\Phi^0(z)/kT\right] \right\} \Big/ Z_1^0. \qquad (71)$$

Making use of the microscopic order parameter $\langle \cos kz \rangle$ for given T and ϱ, the rest order parameters, η, Q, $\langle \cos\psi \rangle$ and $\langle \sin\psi \rangle$, can be determined by minimizing

equation (69) with respect to them. From the fact that C_D must be positive, as was previously noted, we can immediately confirm $\langle \sin \psi \rangle = 0$ from $\partial f^1/\partial \langle \sin \psi \rangle = 0$. Therefore the average orientation of the transverse dipoles attached along $\hat{\psi}_i$ is collinear to $\hat{v}_i$, consistent with considerations of symmetry [4]. Comparing f^1 with the Landau free energy, equation (29), phenomenologically derived by Pikin and Indenbom [4], and putting

$$P_S = \mu \langle \cos \psi \rangle, \tag{72}$$

where μ means the transverse dipole moment, one finds the following correspondences:

$$\alpha(T) = \varrho(c\kappa T \bar{v}^{20} + \bar{a}_{SB}^{20}), \tag{73}$$

$$\beta = \varrho \bar{a}_{SB}^{40}, \tag{74}$$

$$K_e^* = K_e/D^2 = \varrho(\bar{a}_S^{22} + \bar{a}_{SB}^{22}), \tag{75}$$

$$\Lambda_c^* = \Lambda_c/D = \frac{\varrho}{2} \bar{b}^{21}, \tag{76}$$

$$\mu \mu_P = -\varrho \bar{c}_P^{10}, \tag{77}$$

$$\mu \mu_F = \varrho \bar{c}_F, \tag{78}$$

$$\chi/\mu^2 = 1/(\varrho \bar{c}_D^{00}) \tag{79}$$

These are the Landau expansion coefficients derived by making use of a molecular statistical method. Next, from equation (71), truncating the Fourier series within $k = 0$ and $k = k_0$, the critical temperature corresponding to the S_A–N^* transition point where the translational order $\langle \cos k_0 z \rangle$ vanishes with increasing temperature can be analytically derived by the following expression:

$$\kappa T_{SN} = \frac{|A| j_0(K_0\Lambda) - \frac{2}{3}\tilde{e} j_2(K_0\Lambda) - 2\tilde{a}_{40} j_4(K_0\Lambda)}{1 + 8cj_0(K_0\lambda)}, \tag{80}$$

where we put $\tilde{e} = -3\tilde{a}_{20}$ for convenience and A is defined by

$$A = \sum_l \tilde{a}_{ll}, \tag{81}$$

and K_0 and γ are defined by

$$K_0 = k_0 D = 2\pi\gamma/\lambda, \tag{82}$$

and

$$\gamma = L/d, \quad \gamma < 1, \tag{83}$$

respectively. Here, γ corresponds to the molecular packing along the layer normal and must be determined by minimizing the free energy $F_N \simeq F^0$, or maximizing T_{SN} determined by equation (80), for given c and T. At the same time, the critical value of γ at the S_A–N^* phase transition point, γ_c, can be determined by maximizing T_{SN} of equation (80). Next, from equation (73), the Curie temperature T_c can be evaluated as

$$\kappa T_c = \frac{\tilde{e} j_2(K_0\Lambda) + 10\tilde{a}_{40} j_4(K_0\Lambda)}{4cK_0\lambda j_1(K_0\lambda)}, \tag{84}$$

where we again put $\tilde{e} = -3\tilde{a}_{20}$ for convenience. Therefore, in this work, the S_C^*–S_A phase transition is driven by the competition between one of the symmetry-breaking

components A_{40} and the other component A_{20}, together with the repulsive or the packing contribution through v^{20}. This conclusion may be of course reduced to that in the previous work [15] apart from the effect of packing and the thermal fluctuation of the long molecular axes. In this aspect, the attractive symmetry-breaking component A_{40} tends to incline the molecules with respect to v, whereas the other component A_{20} and the repulsive interaction tend to align them parallel to v. It is therefore confirmed that the effect of the molecular packing may contribute to the driving force of S_C^*–S_A transition.

3. Results and discussions

3.1. *The dependence of* μ_P, μ_F, χ, T_c *and* T_{SN} *on the molecular length-to-breadth ratio* λ

Let us introduce the following reduced quantities for convenience:

$$\mu_P^* = \frac{\mu\mu_P}{\varrho\tilde{c}_P} = 2j_2(K_0\Lambda)\langle\cos k_0 z\rangle^2, \tag{85}$$

$$\mu_F^* = \frac{\mu\mu_F}{\varrho\tilde{c}_F} = \frac{\Lambda}{3}\{1 + 2(j_0(K_0\Lambda) - 2j_2(K_0\Lambda))\langle\cos k_0 z\rangle^2\}, \tag{86}$$

$$\chi^* = \frac{\varrho\tilde{c}_D\chi}{\mu^2} = \frac{1}{1 + 2j_0(K_0\Lambda)\langle\cos k_0 z\rangle^2}, \tag{87}$$

$$T_{SN}^* = \frac{kT_{SN}}{|A|} = \frac{j_0(K_0\Lambda) - \frac{2}{3}e^*j_2(K_0\Lambda) - 2a_{40}^*j_4(K_0\Lambda)}{1 + 8cj_0(K_0\lambda)}, \tag{88}$$

$$T_C^* = \frac{kT_C}{|A|} = \frac{e^*j_2(K_0\Lambda) + 10a_{40}^*j_4(K_0\Lambda)}{4cK_0\lambda j_1(K_0\lambda)}, \tag{89}$$

with e^* and a_{40}^* defined by $\tilde{e}/|A|$ and $\tilde{a}_{40}/|A|$, respectively. As was previously noted in §2.1, while a_{40}^* must be positive, $e^* = -3\tilde{a}_{20}/|A|$ may be positive or negative. Roughly assuming $\langle\cos k_0 z\rangle \simeq 1$, the dependences of the above quantities on λ are shown in figure 4 (a)–(c) for various volume fractions c. γ is set to γ_c in equations (85)–(89). According to van der Meer and Vertogen [12, 20], we assume $e^* > 0$ in the following numerical calculation. In addition a_{40}^* may be positive but such a higher order contribution may be expected to be relatively small. Then we put $e^* = 3$ and $a_{40}^* = 0$ and denote τ as T_c/T_{SN}. Even though we put a_{40}^* into a certain positive value, the qualitative properties of T_c^* and T_{SN}^* were not found to be drastically affected. As a whole, we found numerically that an increase in a_{40}^* tends to decrease T_{SN}^* and increase T_c^*.

From figure 4 (a)–(c), one finds that while μ_f^* increases with the increasing λ, μ_p^* decreases. Both T_c^* and T_{SN}^* tend to increase with increasing λ. Therefore we may confirm that the anisotropic steric effect arising from the intermolecular repulsion stabilizes the layer structure and becomes more appreciable with increasing c. As was previously expected, we confirmed numerically that $v^{20}(K_0\lambda)$ defined by equation (56) has a positive value, viz. that the steric effect concerned with the layer structure has a tendency to align molecules along the layer normal. As can be found from equation (88), when $\lambda \to \infty$ with a finite c, T_{SN}^* asymptotically approaches a certain value determined by

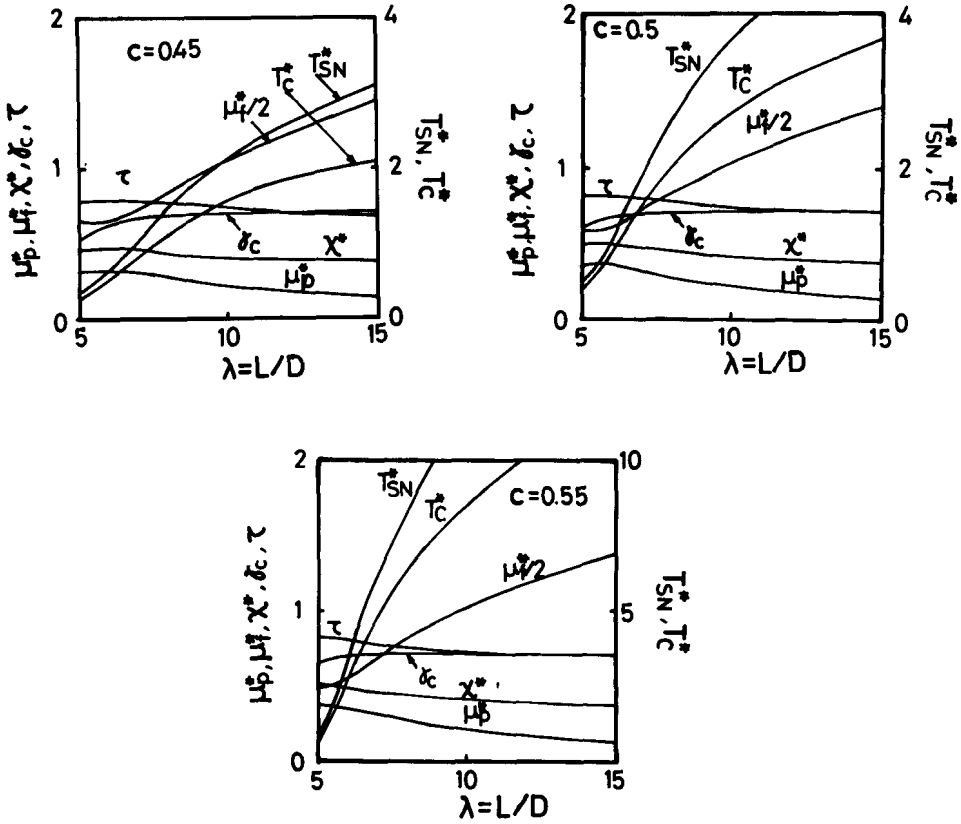$$T_{SN}^*(\lambda \to \infty) = \frac{1}{1 - 1\cdot74c}. \tag{90}$$

Figure 4.   The dependences of the material constants on the molecular length-to-breadth ratio for various volume fractions. Here e^* and a_{40}^* are set to 3 and 0, respectively. τ is defined by T_c/T_{SN}. (a) $c = 0.45$; (b) $c = 0.5$; (c) $c = 0.55$.

Of course, this trend seems to be qualitatively in agreement with experimental findings for S_A or certain S_C^* homologous series [16, 34]. That is, T_{SN} appears to saturate with increasing molecular length for a homologous series.

3.2. c–T phase diagram

In this subsection, we shall give the c–T phase diagrams obtained by equations (88) and (89), and discuss the dependence of them on the symmetry-breaking potential coefficient e^*. For the moment, a_{40}^* is set to 0 as before. In figure 5 (a)–(c), the c–T^* ($T^* = \kappa T/|A|$) phase diagrams are shown for various e^*. From these results, the increase in e^* is found to stabilize the S_C^* mesophase and destabilize S_A as can be deduced from equations (88) and (89). From this finding, as was previously noted in §2.1, one may confirm that e^* or the interaction between the dipole and the induced dipole has a tendency to incline the molecules with respect to the layer normal. Moreover, the increase in c stabilizes both the S_A and S_C^* mesophases. As can be seen from equation (88), one finds in figure 5 (a)–(c) that no thermotropic S_A–N* phase transition occurs for $c > 0.575$, because in such cases T_{SN^*} diverges for a certain γ such that $0 < \gamma < 1$ and only the lyotropic S_A–N* transition may occur.
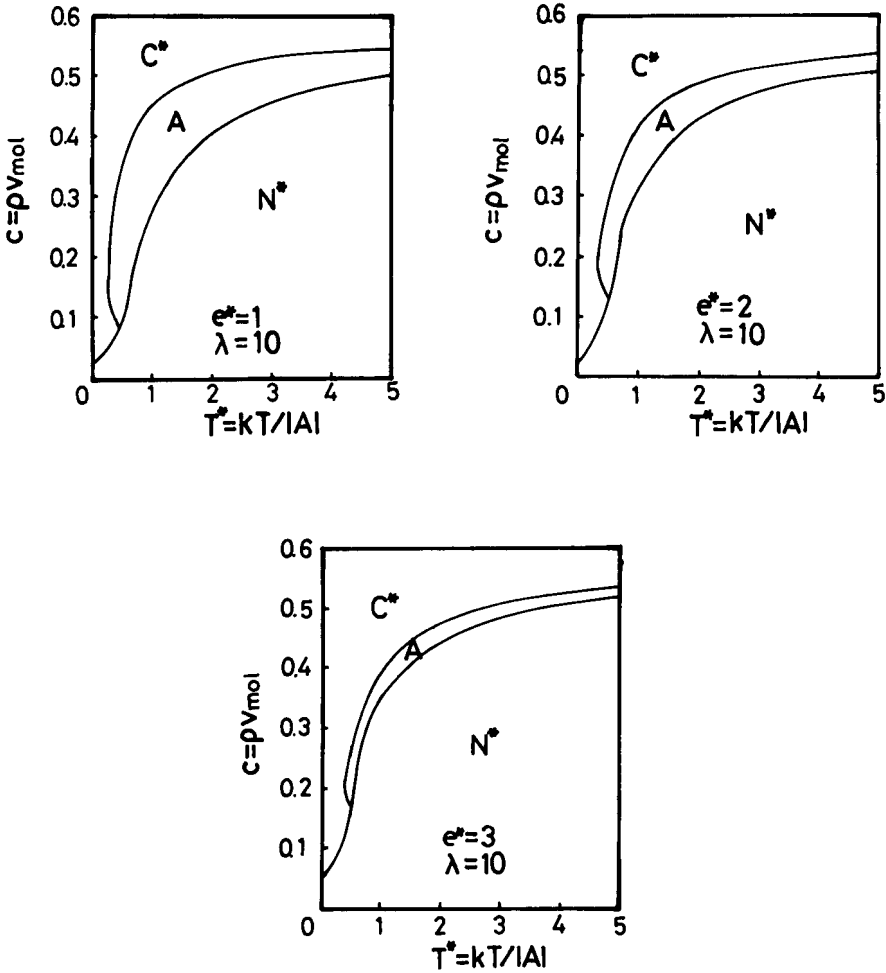
Figure 5. The $c–T^*$ phase diagram. Here $T^* = \kappa T/|A|$ and λ and a_{40}^* are set to 10 and 0, respectively. (a) $e^* = 1$; (b) $e^* = 2$; (c) $e^* = 3$.

3.3. *Numerical estimation of the interaction parameters between DOBAMBC molecules*

Throughout the following, we roughly assume that $P = 2 \times 10^{-6}$ m, $D = 5 \times 10^{-10}$ m, $\varrho = 2 \times 10^{27}$ m^{-3}, $c = 0.5$ and $\langle \cos k_0 z \rangle = 0.9$ for DOBAMBC liquid crystal [4]. T_c is evaluated as 368·3 K [19]. The molecular length-to-breadth ratio, λ, is set to 5 according to Osipov and Pikin [14]. In this case, from figure 4 (b), we can estigate γ as 0·6. Putting $\alpha(T) = \alpha^0(T - T_c)$ in equation (73), we have

$$
\begin{aligned}
\alpha^0 &= \varrho c \kappa \bar{v}^{20}, \\
&= \varrho c \kappa 4 K_0 \lambda j_1(K_0 \lambda) \langle \cos k_0 z \rangle^2,
\end{aligned}
\tag{91}
$$

and

$$
\begin{aligned}
\varrho \bar{a}_{\mathrm{SB}}^{20} &= -\alpha^0 T_c, \\
&= -\varrho \tilde{e} j_2(K_0 \Lambda) \langle \cos k_0 z \rangle^2.
\end{aligned}
\tag{92}
$$

From equation (91), we can evaluate $\alpha^0 \simeq 2\cdot8 \times 10^4\,\mathrm{J/m^3\,K}$. This result is in fairly good agreement with the experimental result, $2\cdot5 \times 10^4\,\mathrm{J/m^3\,K}$, experimentally obtained by Carlsson and Dahl [19]. Then from equation (92) we can estimate $\tilde{e}/\kappa$ as 2300 K. Next, we shall evaluate $\tilde{a}_{40}$ below. From equation (74) we have

$$\beta = \tfrac{3\cdot5}{4}\varrho\tilde{a}_{40}j_4(K_0\Lambda)\langle\cos k_0 z\rangle^2. \tag{93}$$

Using the experimental data by Carlsson and Dahl, $\beta = 21\cdot25 \times 10^4\,\mathrm{J/m^3}$ [19], we can evaluate $\tilde{a}_{40}/\kappa$ as 100 K from equation (93). Now, from the above results, we can roughly evaluate $\tilde{a}_{20}/\tilde{a}_{40} \simeq -7\cdot7$.

Next let us consider $\tilde{a}_{22}$ by using equation (75). K_c^* is evaluated from equation (75) as

$$K_c^* = \varrho(\bar{a}_S^{22}),$$
$$\simeq \varrho(-8\cdot6\tilde{a}_{22}). \tag{94}$$

By making use of the experimental data $K_c^* \simeq 4 \times 10^8\,\mathrm{J/m^3}$ [19], we can find $|\tilde{a}_{22}|/\kappa \simeq 1700\,\mathrm{K}$. For the nematic liquid crystal, PAA [31], $|\tilde{a}_{22}|/\kappa \simeq 1800\,\mathrm{K}$. Therefore the present result seems to be qualitatively accepted. Finally, let us estimate the chiral component b. From the experimental data by Carlsson and Dahl [19] we can estimate Λ_c^* as $-2 \times 10^5\,\mathrm{J/m^3}$. From equation (76), Λ_c^* is reduced to

$$\Lambda_c^* = \frac{\varrho}{2}\bar{b}^{21},$$
$$\simeq 1\cdot1\varrho\tilde{b}. \tag{95}$$

Then $|\tilde{b}|/\kappa$ is estimated as 10 K. From the above discussion, $\tilde{a}_{22}$, $\tilde{a}_{20}$, $\tilde{a}_{40}$ and $\tilde{b}$ may be evaluated as $1700\,\kappa$, $-770\,\kappa$, $100\,\kappa$ and $-10\,\kappa$, respectively. Some further data may be required to examine these parameters in more detail. However this point will not be discussed further in this paper.

4. Conclusion

We presented a molecular theoretical derivation of the Landau free energy of $\mathrm{S_C^*}$ liquid crystals taking account of certain ferroelectric interactions. In this work, it was found that the steric effect tends to align to molecules along the layer normal, whereas one of the symmetry-breaking components caused by the dipole-induced dipole interaction may have a tendency to incline them, and that the competition between such two symmetry-breaking components and the steric effects determines the Curie temperature. This conclusion is simply a generalization of that derived by van der Meer and Vertogen [12, 20], who concluded theoretically that the competition between the intermolecular repulsion and the attraction determined the tilt angle of the $\mathrm{S_C^*}$ molecules.

From the Curie temperature expressed by equation (89), one may see that while the increase of a_{40}^* (> 0) stabilizes the inclined molecular alignment in $\mathrm{S_C^*}$ phase, the steric effect may destabilize it. Of course, in agreement with the previous conclusion [15], the increase of $e^* > 0$ (or $A_{20} < 0$) stabilizes the inclined molecular alignment, whereas $e^* < 0$ (or $A_{20} > 0$) may destabilize it. We also found that both the $\mathrm{S_C^*}$–$\mathrm{S_A}$ and $\mathrm{S_A}$–$\mathrm{N^*}$ transition temperatures increase with the increasing molecular length-to-breadth ratio λ, or that the anisotropic steric effect stabilizes the smectic layer structure for the relatively long molecules. In this case, $\tau = T_c/T_{\mathrm{SN}}$ was found to

slightly decrease with increasing λ. It was found that the flexoelectric constant increases with increasing λ, while the piezoelectric constant decreases. Therefore, for relatively long S_C^* molecules, the flexoelectric effect may become dominant compared with the piezoelectric effect. Since hard-core intermoelcular repulsion was assumed in the present work, such a steric effect between cylindrical molecules might be overestimated. Nevertheless, the above-mentioned qualitative properties of material constants still seem to be valid. The present results remain to be compared with available experimental data of S_C^* homologous series in the future.

To conclude the present work, we must mention the driving mechanism of the S_C^*–S_A transition in connection with the previous work [15]. As can be seen from equation (89), if $e^* > 0$ and $a_{40}^* > 0$, then T_c^* increases or the S_C^* structure with the inclined molecules may be stabilized. Therefore in such a case the S_C^*–S_A transition is not, so to speak, of the order–disorder type as noted by van der Meer and Vertogen [12, 20]. On the other hand, even though $e^* < 0$ or $A_{20} > 0$ in equation (89), the S_C^*–S_A transition may be driven by the contribution of $a_{40}^* > 0$ such that $10a_{40}^* j_4(K_0\Lambda) > -e^* j_2(K_0\Lambda)$. In the latter case, if the orientational fluctuation of the long molecular axes had been concerned in the present approach, the S_C^*–S_A transition temperature T_c might of course have been lower than that predicted by equation (89) as can be deduced from the conclusion in the previous work [15]. According to the above-mentioned aspect, it may be concluded that the order–disorder type S_C^*–S_A transition found in the previous work [15] seems to occur for S_C^* liquid crystals with a relatively large thermal fluctuation near the S_C^*–S_A transition point or with a relatively narrow S_A mesomorphic temperature range above the S_C^* range. On the other hand, the S_C^*–S_A transition driven by the molecular packing effect also seems to occur for S_C^* liquid crystals (e.g. DOBAMBC) with an almost saturated orientational order near the S_C^*–S_A transition point or with a relatively wide S_A mesomorphic temperature range above the S_C^* range. According to the previous [15] and the present considerations, we may conclude that v^{20} and $a_{40}^* > 0$ tend to align the S_C^* molecules along the layer normal and to incline them with respect to it, respectively, whereas a_{20}^* has a tendency to align them along the layer normal or to incline them depending on $a_{20}^* > 0$ or $a_{20}^* < 0$, respectively.

From the numerical estimation of the interaction coefficients in §3.3, one may deduce $a_{20}^* < 0$ for DOBAMBC molecules because of the existence of a relatively strong dipole moment along the short molecular axis.

Appendix

Let us evaluate herein the piezo-potential of equation (6) and the flexo-potential of equation (7) by considering the biaxiality of an attractive chiral interaction similar to the Osipov and Pikin's approach [14]. As shown in figure 6, let us consider a pair of S_C^* molecules. Here $2w$ stands for the distance between two induced dipoles in a molecule and the directions of the induced dipoles denoted by the unit vectors $\hat{L}_1^{(r)}$ and $\hat{L}_2^{(r)}$ ($r = 1, 2$), which are defined by

$$\hat{L}_1^{(1)} = \cos\alpha\,\hat{\Omega}_1 + \cos\beta\,\hat{\psi}_1 + \cos\gamma\,\hat{e}_1, \tag{A 1}$$
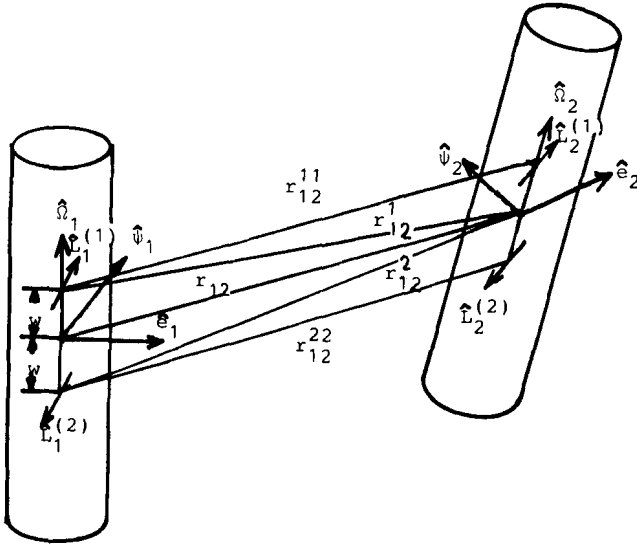
Figure 6. The two interacting S_C^* molecules. $\hat{\mathbf{L}}_i^{(r)}$ ($i = 1, 2; r = 1, 2$) denote the directions of the induced dipoles concerned with the biaxial chiral interaction. Here if we assume that the induced dipoles have no component with respect to $\hat{\mathbf{e}}_i = \hat{\boldsymbol{\psi}}_i \times \hat{\boldsymbol{\Omega}}_i$, then the interaction we are concerned with is reduced to that introduced by Osipov and Pikin [14].

$$\hat{\mathbf{L}}_1^{(2)} = -\cos\alpha\hat{\boldsymbol{\Omega}}_1 + \cos\beta\hat{\boldsymbol{\psi}}_1 - \cos\gamma\hat{\mathbf{e}}_1, \tag{A 2}$$

where $\cos\alpha$, $\cos\beta$ and $\cos\gamma$ are the direction cosines of the unit vector $\hat{\mathbf{L}}_1^{(1)}$ with respect to $\hat{\boldsymbol{\Omega}}_1$, $\hat{\boldsymbol{\psi}}_1$ and $\hat{\mathbf{e}}_1 = \hat{\boldsymbol{\psi}}_1 \times \hat{\boldsymbol{\Omega}}_1$, respectively.

The second order perturbation energy between the induced dipole and the quadrupole interaction can be written as

$$\Phi_{int}^{DQ} = \frac{1}{4}\sum_{rr'} A(r_{12}^{rr'})(\hat{\mathbf{L}}_1^{(r)} \times \hat{\mathbf{L}}_2^{(r')}) \cdot \hat{\mathbf{r}}_{12}^{rr'}(\hat{\mathbf{L}}_1^{(r)} \cdot \hat{\mathbf{L}}_2^{(r')}), \tag{A 3}$$

where A denotes the interaction coefficients, $r_{12}^{rr'}$ is the relative position vector between $\hat{\mathbf{L}}_1(r)$ and $\hat{\mathbf{L}}_2(r')$, and $\hat{\mathbf{r}}_{12}^{rr'}$ is defined by $\mathbf{r}_{12}^{rr'}/|\mathbf{r}_{12}^{rr'}|$. Then assuming $r_{12} \gg w$ and making use of the following approximations:

$$A(r_{12}^1) \simeq A(r_{12}) - (\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_1)w\frac{dA}{dr_{12}}, \tag{A 4}$$

$$A(r_{12}^2) \simeq A(r_{12}) + (\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_1)w\frac{dA}{dr_{12}}, \tag{A 5}$$

$$\hat{\mathbf{r}}_{12}^1 = \frac{r_{12} - w\hat{\boldsymbol{\Omega}}_1}{|r_{12} - w\boldsymbol{\Omega}_1|} \simeq \hat{\mathbf{u}}_{12} - \frac{w}{r_{12}}\hat{\boldsymbol{\Omega}}_1 + \frac{w}{r_{12}}(\hat{\mathbf{u}}_{12} \cdot \boldsymbol{\Omega}_1)\hat{\mathbf{u}}_{12}, \tag{A 6}$$

$$\hat{\mathbf{r}}_{12}^2 = \frac{r_{12} + w\hat{\boldsymbol{\Omega}}_1}{|r_{12} + w\boldsymbol{\Omega}_1|} \simeq \hat{\mathbf{u}}_{12} + \frac{w}{r_{12}}\hat{\boldsymbol{\Omega}}_1 - \frac{w}{r_{12}}(\hat{\mathbf{u}}_{12} \cdot \hat{\boldsymbol{\Omega}}_1)\hat{\mathbf{u}}_{12}, \tag{A 7}$$

one can readily find the following result accompanied with a few leading terms:

$$\Phi_{\text{int}}^{\text{DQ}} \simeq A(r_{12})(\hat{\Omega}_1 \times \Omega_2) \cdot \hat{u}_{12}(\hat{\Omega}_1 \cdot \hat{\Omega}_2)\cos^2\alpha$$

$$+ w\left(\frac{A(r_{12})}{r_{12}} - \frac{dA(r_{12})}{dr_{12}}\right)\{(\hat{\psi}_1 \times \hat{\Omega}_2) \cdot \hat{u}_{12}(\hat{u}_{12} \cdot \hat{\Omega}_1)$$

$$+ (\hat{\psi}_2 \times \hat{\Omega}_1) \cdot \hat{u}_{12}(\hat{u}_{12} \cdot \hat{\Omega}_2)\}\ (\hat{\Omega}_1 \cdot \hat{\Omega}_2)\cos\alpha\cos\beta$$

$$+ A(r_{12})\{(\hat{\psi}_1 \cdot \hat{\Omega}_2)(\hat{\Omega}_1 \cdot \hat{u}_{12}) - (\hat{\psi}_2 \cdot \hat{\Omega}_1)(\hat{\Omega}_2 \cdot \hat{u}_{12})\}(\hat{\Omega}_1 \cdot \hat{\Omega}_2)\cos\alpha\cos\gamma.$$

$$(A\,8)$$

Here the first term in the right-hand side represents the chiral interaction and corresponds to equation (5). The second represents the piezo-potential first introduced by Osipov and Pikin [14] and leads to equation (6). Finally the third leads to the flexo-potential and just corresponds to equation (7). It should by borne in mind that the last component was not involved in Osipov and Pikin's approach because they restricted themselves to the case of $\gamma = \pi/2$ [14], and in their approach the flexo-electric contribution was not involved.

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