Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Invited Lecture. Order-parameter theories of phase diagrams for antiferroelectric smectic-A phases

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To cite this Article Longa, Lech(1989) 'Invited Lecture. Order-parameter theories of phase diagrams for antiferroelectric smectic-A phases', Liquid Crystals, 5: 2, 443 — 461

To link to this Article: DOI: 10.1080/02678298908045395

URL: http://dx.doi.org/10.1080/02678298908045395

LIQUID CRYSTALS, 1989, VOL. 5, NO. 2, 443–461

Invited Lecture

Order-parameter theories of phase diagrams for antiferroelectric smectic-A phases

Role of orientational degrees of freedom

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Using exact relations between Landau and molecular approaches, the symmetry-induced topologies of phase diagrams are studied for antiferroelectric smectic-A phases. In particular, the tricritical points are found for a large class of order-parameter theories of nematic–smectic A (-A$_1$, -A$_d$) and -A$_2$ (NA) phase transitions. These include generalizations to antiferroelectric smectic-A phases of McMillan and Meyer–Lubensky mean-field theories and the Ramakrishnan–Youssouff (RY) density-functional approach. The use of these different approaches allows study of influence of various couplings between nematic (orientational) and smectic (translational) degrees of freedom and polarization field, $P_1(\cos\theta)$, on various NA and AA phase transitions. From the results, it is of interest that the coupling between orientational degrees of freedom ($P_4(\cos\theta)$) and density waves can destabilize the smectic-A phase at low temperatures—pointing to the existence of a nematic–smectic-A–reentrant-nematic phase transition. A possible relation of this result to A$_d$, C$_2$, C$_d$ and $\tilde{\mathrm{C}}$ phases is discussed. Some relations between Fourier components of correlation functions and order parameters at tricritical points are derived from the RY density-functional theory. Despite some limitations, the theory presented here seems to provide the simplest approach to study topologies of phase diagrams in molecular theories.

1. Introduction

The nematic state of liquid crystals is characterized by long-range orientational order of constituent elongated molecules [1], which are on average aligned with their long axis parallel to a certain common direction, say $\hat{\mathbf{z}}$, which is called the director. Additionally, at the nematic–smectic-A (NA) phase transition the continuous translational symmetry is spontaneously broken, resulting in a one-dimensional density modulation parallel to $\hat{\mathbf{z}}$. Thus a weak layer structure is observed in the smectic-A phase with a periodicity $d \approx l$, where l is the length of a molecule.

One of the attractive features of the NA transition is that it may be first- or second-order. This interesting possibility was predicted theoretically by McMillan [2, 3] and de Gennes [4], who took the effect of coupling between orientational and translational degrees of freedom into account. They showed that close to the nematic–isotropic phase transition ($T_{\mathrm{NA}}/T_{\mathrm{NI}} \approx 1$, where T_{NI} is the nematic–isotropic transition temperature) the character of the NA transition is governed by the nematic order

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parameter, which results in the transition being first order. On the other hand, for small values of T_{NA}/T_{NI} ($T_{NA}/T_{NI} \ll 1$), the orientational order saturates and as a result the character of the transition is governed by a purely translational order parameter, leading to a second-order phase transition. Consequently, a tricritical point is predicted at an intermediate value of T_{NA}/T_{NI}. In the McMillan theory [2, 3] this was found to occur at $T_{NA}/T_{NI} \approx 0{\cdot}87$.

Another mechanism for the NA tricritical point was suggested by Meyer and Lubensky [5]. They discussed the effect of higher-order Fourier components of the one-particle distribution function on the character of the transition, while assuming perfect orientational order in both the smectic-A and nematic phases. By studying various forms of interlayer potentials and solving the mean-field Euler equations for the one-particle distribution function numerically, they showed that the nature of the NA transition is governed by the ratio V_2/V_1 of the two lowest-order Fourier components of the pair potential. For $V_2/V_1 < \frac{1}{2}$ the transition is second-order, occurring at a temperature $T = V_1/k_B$ (k_B being Boltzmann's constant), while for $V_2/V_1 > \frac{1}{2}$ the transition is first-order. Thus the tricritical point is predicted for $V_2/V_1 = \frac{1}{2}$. They concluded that higher-order harmonics of the potential are irrelevant in determining the character of the NA transition. Their analysis implies that for smectic interactions localized in the centre of the layer the transition should be first-order, and that with increasing delocalization the character of the transition should finally change to second-order.

Following the development of the ideas discussed above, a great deal of experimental effort has been spent in attempting to determine the character of the NA phase transition in real systems [6–12]. In general, the McMillan–de Gennes suggestion has been confirmed, showing that the tricritical point occurs when the McMillan ratio T_{NA}/T_{NI} is larger than 0·99. Furthermore, the topology of the phase diagrams obtained resembles those of McMillan [12]. Also, detailed studies of the tricritical exponents, in particular of the nematic and smectic order parameters, yield mean-field tricritical values [12]. This indicates that a description of the corresponding phase diagrams using a Landau-type expansion should lead to correct qualitative predictions. Finally, there is no experimental evidence on the *classical* NA phase transition to support the mechanism proposed by Meyer and Lubensky.

In summary, the experimental data existing at present favour the McMillan–de Gennes mechanism for the NA tricritical point and simple molecular models.

The analysis as given raises the question of whether the model proposed by Meyer and Lubensky is relevant at all for NA tricritical behaviour. With small modifications, a positive answer to this question is provided by the recent discovery of a new class of antiferroelectric smectic-A phases by the Bordeoux group [13]. More precisely, it has been shown [13–23] that liquid crystals consisting of molecules with a strongly polar end group such as CN and NO_2 give rise to other types of smectic-A phases. Among these, we can distinguish the A_d, A_2 and A_1 phases:

> smectic-A_d is similar to smectic-A, but with a layer spacing d incommensurate with the molecular length l. Typically one finds $d \approx 1{\cdot}4\,l$;
>
> smectic-A_2 is an antiferroelectric double-layer phase with two commensurate layer spacings $d_1 \approx 2l$, $d_2 \approx l$;
>
> smectic-A_1 is antiferroelectric like A_2, but with only one characteristic layer spacing $d \approx 1$.

There are other antiferroelectric smectic-A phases that develop an additional modulation parallel to the layer, but these will not be considered here. Interestingly, no ferroelectric smectic-A phase, as suggested by Photinos and Saupe [24], has been found.

A phenomenological model based on a general Landau free-energy expansion was developed by Prost [25] to account for the variety of antiferroelectric smectic-A phases. In this theory it is assumed that strong dipolar interactions introduce a new order parameter to the problem, i.e. the polarization field with overall antiferroelectric symmetry, which, in general, does not need to be commensurate with the smectic-A density wave. Owing to the coupling between four order parameters (nematic, smectic-A, antiferroelectric and layer periodicity), the Prost theory qualitatively explains the experimental observations and predicts a large number of multicritical points.

A possible molecular origin of the A_d, A_1 and A_2 phases has been discussed in our recent paper [26] (see also [27, 28]). The important mechanism that stabilizes various phases was identified as the competition between dispersive and dipolar interactions in connection with steric repulsion. It was also found from estimates of these interactions in various phases that the ferroelectric smectic-A phase with non-zero global polarization is strongly destabilized. An alternative molecular description has been proposed by Guillon and Skoulios [29] and Indekeu and Berker [30].

The evidence as given clearly demonstrates the relevance of a study of molecular mechanisms, leading to both qualitative and quantitative understanding of differences between the behaviour of 'classical' and strongly polar liquid crystals. In particular, the role of orientational degrees of freedom and higher-order harmonics on the character of these phase transitions has not yet been studied systematically. Clearly, there is a need for a relatively simple method of calculating the phase diagrams and tricritical points for a given molecular theory. The commonly used direct method is rather inefficient and difficult. It is based on solving the self-consistency equations for the order parameters and comparing the free energies of various allowed solutions (see e.g. [2, 3, 5, 10, 24, 31, 32]). In the vicinity of a tricritical point this method is sensitive to the accuracy of the order parameters and of the corresponding free energies. As shown by Kloczkowski and Stecki [33], a relative accuracy better than 10^{-8} is required for the free energy in order to describe the tricritical point in the McMillan theory correctly.

To overcome these difficulties, Kloczkowski and Stecki [33] showed yet another way of solving this problem. They found approximate relations between the coefficients of the Landau theory and the molecular parameters of the McMillan model. Using these relations, they calculated the tricritical parameters of the model. The calculations were much easier than those of McMillan [2, 3] (see also [10]), since only information on the orientational order parameters in the nematic phase was required. Furthermore, the method was found to be less sensitive to the accuracy of various intermediate results.

In our recent papers [34, 35] we generalized this method by incorporating some symmetry properties of low- and high-temperature phases into the formalism. More precisely, our line of approach was to seek the minimum information necessary to solve the problem of a tricritical point in order-parameter theories *exactly*. By 'exact', we mean here all steps that must be performed to locate a multicritical point in a molecular theory, which is analytical in the order parameters. In particular, we found equations for the NA tricritical temperature in terms of derivatives of the free energy with respect to the order parameters taken in the nematic phase. The relations derived in [33] appeared as special cases of those discussed in [34, 35].

The main purpose of the present paper is to demonstrate the wider applicability of this method. In particular, we concentrate on a molecular description of the phase diagrams of antiferroelectric smectic-A phases that generalizes the model calculations [26]. After deriving equations for the tricritical temperatures of NA, NA_n ($n = 1, d, 2$) and A_1A_2 transitions, we shall discuss universal properties of these transitions in terms of competition between McMillan–de Gennes and Meyer–Lubensky mechanisms. Some specific mean-field models will also be solved. In studying possible topologies of phase diagrams, the role of orientational degrees of freedom will be emphasized.

This paper is organized as follows. In §2 we outline the main results of [34, 35]. In §3 the general formulae of §2 are applied to the problem of antiferroelectric smectic-A phases. The free energy is defined in §4 in terms of the order parameters. Model calculations of tricritical points are found in §5, which also includes some discussion. Final remarks are given in §6.

2. Comments on the order-parameter theories of multicritical points

In [34, 35] we reported on exact calculations of tricritical temperature for some molecular models of the NA phase transition. It is the purpose of this section to outline and comment on the main results of these papers; some of them will be used in the next section.

The starting point of our discussion is the Landau expansion of the free energy in powers of an order parameter **x** [36, 37]:

$$F = F_0 + \sum_{i=1}^{2N} a_i \mathbf{x}^i, \quad a_{2N} > 0, \tag{1a}$$

where F_0 is the regular part of the free energy. The coefficients of this expansion depend, in general, on the temperature, the pressure and the other thermodynamic variables. When performing the expansion (1 *a*) it is implicitly assumed that the system undergoes a phase transition from a state of thermodynamic equilibrium with symmetry $\mathbf{G}_0$ to another state of thermodynamic equilibrium with symmetry $\mathbf{G}_1$, where $\mathbf{G}_1$ is a subgroup of $\mathbf{G}_0$, and that the phase transition is described by a *single* order parameter **x**.

By definition, the transition point is said to be an Nth-order multicritical point if $2N$ Landau coefficients (including the order parameter) vanish simultaneously. In particular, at a critical point we have

$$\mathbf{x} = a_1 = a_2 = a_3 = 0, \quad a_4 > 0. \tag{1b}$$

while a tricritical point requires

$$\mathbf{x} = a_1 = a_2 = a_3 = a_4 = a_5 = 0, \quad a_6 > 0. \tag{1c}$$

The relations (1 *b*,*c*) simplify considerably at the tricritical points of antiferroelectric smectic-A phases. In this case all the phases have different symmetries, which implies that $a_1 \equiv 0$. Next, the existence of a line of second- and first-order phase transitions rules out a_3 and a_5 ($a_3 \equiv a_5 \equiv 0$). Consequently, the calculations of the tricritical temperatures for a given molecular model of the A phases are reduced to finding the coefficients a_2, a_4 and a_6 in the Landau expansion (1 *a*).

On the other hand, in molecular theories of phase transitions the free energy can be considered as functional of the one particle distribution function $P(1)$, itself a function of the 'relevant' degrees of freedom '1'. For example, $P(1) \equiv P(\mathbf{r}, \hat{\Omega})$ for liquid crystals. The equilibrium distribution function is obtained by the minimization of the free energy with respect to the variation of $P(1)$. The necessary condition is

$$\frac{\delta F}{\delta P(1)} = 0. \tag{2}$$

As the symmetry of the low-temperature phase is known, we can expand $P(1)$ in terms of the basic functions $\{\Psi_\mu^m(1)\}$ of irreducible representations of $\mathbf{G}_1$:

$$P(1) = \sum_{m,\mu} \mathbf{x}_\mu^m \Psi_\mu^m(1), \tag{3a}$$

where

$$\int d(1)\, \Psi_\nu^n(1) \Psi_\mu^{m*}(1) = \delta_{nm}\delta_{\nu\mu} \tag{3b}$$

and where $\mathbf{x}_\mu^m = \int d(1)\, P(1)\, \Psi_\mu^{m*}(1)$; here n parametrizes irreducible representations while μ labels all functions belonging to the same n. Now the symmetry of high- and low-temperature phases allows identification of non-vanishing invariant combinations of the coefficients $\{\mathbf{x}_\nu^n\}$ in the expansion (3 *a*). These combinations provide us with the definition of the order parameters $\{\mathbf{x}, \mathbf{x}_\alpha\}$ for our problem. Again we assume that the phase transition is driven by a single order parameter $\mathbf{x}$, i.e. $\mathbf{x} \neq 0$ implies that all secondary order parameters $\mathbf{x}_\alpha \neq 0$. As the $\{\Psi_\mu^m(1)\}$ are known functions, the free energy depends effectively on $\{\mathbf{x}, \mathbf{x}_\alpha\}$, and the integral equation (2) can be written as a set (in general infinite) of nonlinear equations

$$\frac{\partial F}{\partial \mathbf{x}} \equiv F_x = 0, \tag{4a}$$

$$\frac{\partial F}{\partial \mathbf{x}_i} \equiv F_{x_i} = 0, \quad i = 1, 2, \dots . \tag{4b}$$

Now choosing $\mathbf{x}$ as an independent variable and noting that $\{\mathbf{x}_i\}$ are implicit functions of $\mathbf{x}$, determined by the self-consistency equations (4 *b*), we can construct the Landau expansion for F around $\mathbf{x} = 0$. It reads

$$F = F^0 + \sum_{n=1} \frac{1}{n!} \frac{d^n F^0}{d\mathbf{x}^n} \mathbf{x}^n, \tag{5a}$$

where [34, 35]

$$\frac{dF^0}{d\mathbf{x}} = \partial_x F^0 \equiv F_x^0, \tag{5b}$$

$$\frac{d^2F^0}{d\mathbf{x}^2} = \mathbf{D}^2 F^0 = F_{xx}^0 + \mathbf{D}_1 F_x^0, \tag{5c}$$

$$\frac{d^3F^0}{d\mathbf{x}^3} = \mathbf{D}^3 F^0, \tag{5d}$$

$$\frac{d^4F^0}{d\mathbf{x}^4} = \mathbf{D}^4 F^0 - 3\mathbf{D}_2^2 F^0, \tag{5e}$$

$$\frac{d^5F^0}{d\mathbf{x}^5} = \mathbf{D}^5 F^0 + 10\mathbf{D}^3\mathbf{D}_2 F^0 + 15\mathbf{D}_2^2\mathbf{D} F^0, \tag{5f}$$

$$\frac{d^6F^0}{d\mathbf{x}^6} = \mathbf{D}^6 F^0 + 15\mathbf{D}^4\mathbf{D}_2 F^0 + 45\mathbf{D}_2^2\mathbf{D}^2 F^0 - 10\mathbf{D}_3^2 F^0 + 15\mathbf{D}_2^3 F^0, \tag{5g}$$

and where superscript zero denotes that all derivatives are taken in the high-temperature phase ($\mathbf{x} = 0$). Here $\mathbf{D}$ and $\mathbf{D}_m$ are differentiation operators, defined by

$$\mathbf{D} = \partial_{\mathbf{x}} + \mathbf{D}_1, \quad \mathbf{D}_m = \sum_{i=1} \frac{d^m \mathbf{x}_i^0}{d\mathbf{x}^m} \partial_{x_i}, \tag{6a}$$

$$\mathbf{D}_m^n = \underbrace{\mathbf{D}_m \mathbf{D}_m \cdots \mathbf{D}_m}_{n\text{-times}} \tag{6b}$$

where $d^m \mathbf{x}_k^0 / d\mathbf{x}^m$ are the solutions of the linear equations

$$\mathbf{D}_m F_{\mathbf{x}_j}^0 = -\mathbf{A}_m F_{x_j}^0, \tag{6c}$$

and where

$$\mathbf{A}_1 = \partial_x, \quad \mathbf{A}_2 = \mathbf{D}^2, \quad \mathbf{A}_3 = \mathbf{D}^3 + 3\mathbf{D}_2\mathbf{D}, \ldots .$$

Equations (5) and (6) allow the calculation of critical and tricritical temperatures provided that the derivatives of the free energy with respect to the order parameters, taken in the high-temperature phase ($\mathbf{x} = 0$), are known. These are given by various molecular theories.

Note that (5) and (6) display a hierarchical structure with respect to the derivatives $\{d^m \mathbf{x}_k^0 / d\mathbf{x}^m\}$. As a rule, only derivatives of order not exceeding n are necessary for calculating the coefficient $d^{2n} F^0 / d\mathbf{x}^{2n} \equiv n!\, a_{2n}$. Interestingly, further simplification of (5) and (6) is achieved by studying the symmetry properties of the derivatives $F_{x_m x_n \ldots x_p}^0$. Clearly, these must satisfy relations that follow from the Clebsch–Gordan couplings of $\mathbf{G}_1$ in $\mathbf{G}_0$:

$$\begin{aligned} F_{x_m x_n \ldots x_p}^0 &\sim \int d(1)\, \Psi_\alpha^a(1) \Psi_\beta^b(1) \ldots \Psi_\gamma^c(1) \\ &\sim \left(\begin{array}{cc|c} a & n_1 & n_2 \\ \alpha & \nu_1 & \nu_2 \end{array} \right) \left(\begin{array}{cc|c} b & n_2 & n_3 \\ \beta & \nu_2 & \nu_3 \end{array} \right) \cdots \left(\begin{array}{cc|c} c & n_3 & n_0 \\ \gamma & \nu_3 & \nu_0 \end{array} \right), \end{aligned} \tag{6d}$$

where $\{n_0, \nu_0\}$ are $\mathbf{G}_0$-invariant states.

The proportionality (6 *d*) implies that many of the coefficients in (6 *a*) must vanish by symmetry. Some examples are given in [36]. Typical examples of molecular theories to which the above formalism applies are finite-order virial, cluster, *Y* expansions or standard mean-field theories.

Some features and restrictions of this method are immediately clear. First, it applies to a molecular theory that is analytical in the order parameters. Secondly, the orthogonality relations (6 *d*) between functions belonging to irreducible representations of $\mathbf{G}_1$ are *crucial* here. They allow solution of the infinite set of equations (6 *c*). More precisely, only for $\{\Psi_\mu^m(1)\}$ does the set (6 *c*) effectively reduce to a small number of equations (see §§ 3–5). This last statement does not hold for other (inequivalent) parametrizations of $P(1)$.

Finally, the equation $a_2 = 0$ determines the critical temperature, if the phase transition is of second order, or the supercooling temperature, if the phase transition is of first order. The higher-order coefficients determine the character of the phase transition (relations (1 *b*, *c*)). Obviously, the method may not work too well in determining the first-order transition temperature, where the equilibrium value of $\mathbf{x}$ is finite and the convergence of the series can be questionable. In this case an alternative procedure, such as that suggested by Katriel *et al.* [37], may work better.

3. Theory of the smectic-A tricritical points

In this section we apply the formulae (5) and (6) to a particular case of the NA, NA_n ($n = d$, 1, 2) and A_1A_2 phase transitions. More precisely, we find exact forms of the operators $\mathbf{D}_m$ for these cases.

As already discussed in § 1, the A_1 and A_d phases appear to be similar to the classical smectic-A phase in that they show a single quasi-Bragg spot in X-ray scattering experiments. In the A_2 phase a doubling of periodicity is observed compared with the A_1 phase, i.e. an additional quasi-Bragg spot appears at a wave vector $q \approx 2\pi/2l$. This observation can be interpreted in terms of long-range antiferroelectric ordering of neighbouring single layers. Thus in the general NA problem the relevant degrees of freedom '1' are θ and z, where θ is the angle between $\hat{\mathbf{z}}$ and the long molecular axis. Additionally, the one-particle distribution function should described antiferroelectric double layers at low temperatures, which implies [26] that

$$\left.\begin{aligned} P(\cos\theta, z) &= P(\cos\theta, z + 2d), \\ P(\cos\theta, z) &= P(-\cos\theta, z + d), \end{aligned}\right\} \tag{7a}$$

where $2d$ is the double-layer spacing ($d \approx 1$) of the A_2 phase. In our description we shall keep the layer spacing d constant. This assumption corresponds to one of the cases obeyed by the Prost model [25].

With the symmetry restrictions (7 *a*) fulfilled, we find it physically useful to introduce an order-parameter expansion of $P(1)$ in terms of Legendre polynomials and Fourier series:

$$\begin{aligned} P(\cos\theta, z) = {} & 1 + 2\sum_{L,n=0} (4L + 3)\zeta_{2L+1,2n+1} P_{2L+1}(\cos\theta)\cos[(2n+1)qz] \\ & + \sum_{L=1} (4L+1)\eta_{2L} P_{2L}(\cos\theta) + 2\sum_{n=1} \tau_{2n}\cos(2nqz) \\ & + \sum_{L,n=1} (4L+1)\sigma_{2L,2n} P_{2L}(\cos\theta)\cos(2nqz), \end{aligned} \tag{7b}$$

where P satisfies the normalization condition

$$\frac{1}{4d}\int_{-1}^{1} d(\cos\theta)\int_{0}^{2d} dz\, P(\cos\theta, z) = 1 \tag{7c}$$

and where $\{\zeta_{L,n}, \eta_L, \tau_n, \sigma_{L,n}\} \equiv \{\mathbf{x}_{L,n}\}$ are the order parameters

$$\mathbf{x}_{L,n} = \frac{1}{4d}\int_{-1}^{1} d(\cos\theta)\int_{0}^{2d} dz\, P(\cos\theta, z) P_L(\cos\theta)\cos(nqz). \tag{7d}$$

In the ideal nematic-order approximation, which will also be discussed in the next section, the expansion (7 *b*) reads

$$P(s, z) = 1 + 2\sum_{n=0} \zeta_{2n+1} s \cos[(2n+1)qz] + 2\sum_{n=1} \tau_{2n}\cos(2nqz), \tag{7e}$$

where the pseudospin variable $s = \pm 1$ is introduced instead of $\cos\theta$. The integration over $\cos\theta$ is reduced to a summation over s. The choice of the point of reference for the density modulation in the geometrical centre of the molecules ensures that no terms of the form $\sin(mqz)$ appear in (7 *b*, *e*).

Four different phases are described by the distributions (7 *b*, *e*):

(i) isotropic: $\zeta_{2L+1,2n+1} = \eta_{2L} = \tau_{2n} = \sigma_{2L,2n} = 0$;

(ii) nematic: $\eta_{2L} \neq 0$,
$\zeta_{2L+1,2n+1} = \tau_{2n} = \sigma_{2L,2n} = 0$;

(iii) smectic-A, -A_1 or -A_d (if $l < d < 2l$): $\eta_{2L} \neq 0$, $\tau_{2n} \neq 0$, $\sigma_{2L,2n} \neq 0$, $\zeta_{2L+1,2n+1} = 0$;

(iv) smectic-A_2: $\eta_{2L} \neq 0$, $\tau_{2n} \neq 0$, $\sigma_{2L,2n} \neq 0$, $\zeta_{2L+1,2n+1} \neq 0$;

The order parameter **x** is identified for the A_2 phase with $\zeta_{1,1} \equiv \zeta$. for A, A_1 and A_d phases, $\mathbf{x} \equiv \tau_2 \equiv \tau$ or $\sigma_{2,2}$. As the exact results must be independent of the choice of **x**, we assume that $\mathbf{x} = \tau$.

The relations (6 *d*) now express either the momentum conservation of the smectic order-parameter interactions in the nematic phase or the Clebsch–Gordan relations between Legendre polynomials. They reduce the number of non-vanishing coefficients in the formulae for the operators $\mathbf{D}_m$. More specifically, the following exact relations hold.

Nematic–smectic-A_2 and isotropic–smectic-A_2 transitions

With $\mathbf{x} = \zeta_{1,1} \equiv \zeta$, the equations (5) yield

$$\mathbf{D} = \partial_\zeta + \mathbf{D}_1 = \partial_\zeta + \sum_{l=1} \frac{d\zeta^0_{2l+1,1}}{d\zeta} \partial_{\zeta_{2l+1,1}}, \tag{8 a}$$

$$\mathbf{D}_2 = \frac{d^2\tau^0_2}{d\zeta^2} \partial_{\tau_2} + \sum_L \frac{d^2\sigma^0_{2L,2}}{d\zeta^2} \partial_{\sigma_{2L,2}} + \sum_L \frac{d^2\eta^0_{2L}}{d\zeta^2} \partial_{\eta_{2L}}, \tag{8 b}$$

where the numerical coefficients in **D** and $\mathbf{D}_2$ satisfy linear equations similar to those in [35] and where superscript zero refers to the nematic phase.

Only the two lowest-order wave vectors are necessary to determine the character of the NA_2 transition. The third-order wave vector is responsible for the stability of the NA_2 tricritical point. Similar formulae are found for the isotropic–smectic-A_2 transition.

Smectic-A_l–smectic-A_2 transition

In this case the order parameter **x** may be identified as ζ, leading to the formula (8 *a*) for the operator **D**. However, the operator $\mathbf{D}_2$ differs from (8 *b*) is the presence of terms depending on τ_{2m}. It reads

$$\mathbf{D}_2 = \sum_m \frac{d^2\tau^0_{2m}}{d\zeta^2} \partial_{\tau_{2m}} + \sum_{L,m} \frac{d^2\sigma^0_{2L,2m}}{d\zeta^2} \partial_{\sigma_{2L,2m}} + \sum_L \frac{d^2\eta^0_{2L}}{d\zeta^2} \partial_{\eta_{2L}}. \tag{9}$$

Again the coefficients in the formulae for $\mathbf{D}_1$ and $\mathbf{D}_2$ satisfy linear equations similar to those given in [35]. But now the superscript zero refers to the A (A_1) phase.

The above formulae allow practical calculations of tricritical temperatures in theories where the orientational part of the two-particle interactions is expanded in Legendre polynomials. If this is not the case then an alternative would be to replace (6) by an equivalent formulation in terms of Fredholm integral equations of the first kind [34].

The formulae for the operators **D** for the nematic–smectic-A transition are given in [35].

4. Specification of the free energy

In this section we apply the formulae derived in the previous section to a general mean-field model of the antiferroelectric smectic-A phases.

Let us consider a system of axially symmetric rigid molecules, interacting through the two-particle potential

$$V = -V(r_{12}, \hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{u}}_1, \hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{u}}_2, \hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2). \tag{10}$$

Here $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ are unit vectors defining the orientation of the elongated molecules while $\hat{\mathbf{r}}_{12}$ is the unit vector pointing from the centre of mass of molecule 1 to the centre of mass of molecule 2. After expanding (10) in a spherical-harmonic basis [38, 39] and averaging the resulting expression over the degrees of freedom of the particle '2', weighted with the distribution function (7 *b*), we arrive at the potential of the mean torque felt by molecule '1':

$$V_{\text{eff}}(\cos\theta_1, z_1) = -\sum_{L,N,m}(2-\delta_{m,0})(2L+1)V_{LNm}\mathbf{x}_{N,m}P_L(\cos\theta_1)\cos(mqz_1), \tag{11 a}$$

where $V_{LNm} = 0$ if L and N are of different parity and

$$V_{LNm} = \lim_{\mathcal{V}\to\infty}\frac{1}{4\pi}(2N+1)\int_{\mathcal{V}} d^3r\prod_{i=1}^{2}\left[\int_0^{2\pi}d\phi_i\int_{-1}^{1}d(\cos\theta_i)\right]$$
$$\times V(r_{12}, \hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{u}}_1, \hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{u}}_2, \hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2)P_L(\cos\theta_1)P_N(\cos\theta_2)\cos(mqz) \tag{11 b}$$

otherwise.

The symmetry of the two-particle interaction influences the final form of the operators $\mathbf{D}_n$, (5), (6). For example, a substantial difference is expected between **D**s for separable (i.e. independent of $\hat{\mathbf{r}}_{12}$) and non-separable potentials; this is connected with the different nature of the orientational part of the interaction (10). For separable potentials, only the parameters V_{LLm} are non-zero which means that all two-particle configurations with a fixed distance between centres of mass of the molecules and a fixed relative angle between $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ give the same contribution to the interaction energy in the nematic phase. A similar statement holds true for the antiferroelectric smectic-A phases, provided that the distance between centres of mass of molecules is a multiple of the basic layer spacing. Finally, in the ideal nematic-order approximation only the potential parameters $V_{00m} \equiv V_m$ are relevant.

Formula (11 *a*) is a direct generalization of that proposed by Kuzma and Allender [32]. Note, however, that, in order to get (11 *b*), it is not necessary to perform the additional average over a plane, perpendicular to $\hat{\mathbf{z}}$, as postulated in [32]. the formula (11 *a*) is obtained by projecting out this part of the interaction (10), consistently with the antiferroelectric symmetry (7 *b*).

Now, combining (7 *b*) and (11 *a*), we write down the mean-field free energy per particle as

$$\frac{F}{\varrho} = -\frac{1}{8d}\int_0^{2d}dz_1\int_{-1}^{1}d(\cos\theta_1)\,V_{\text{eff}}(\cos\theta_1, z_1)P(\cos\theta_1, z_1) - t\ln Z, \tag{11 c}$$

where

$$Z = \frac{1}{4d}\int_0^{2d}dz_1\int_{-1}^{1}d(\cos\theta_1)\exp\left[-t^{-1}V_{\text{eff}}(\cos\theta_1, z_1)\right] \tag{11 d}$$

and where $t = k_B T/\varrho$ and $\varrho = N/V$. As (11 *c,d*) define the free energy in terms of the order parameters $\mathbf{x}_{L,n}$, (7 *d*), it is now a straightforward matter to calculate the Landau coefficients (5) and consequently the tricritical temperature.

Another very interesting type of order-parameter theory was proposed by Ramakrishnan and Youssouff (RY) [40] to describe liquid–solid transition. It was later generalized by Sluckin and Shukla [41] and Lipkin and Oxtoby [42] to treat the isotropic–nematic and nematic–smectic-A transitions respectively. In this approach the free energy is related to direct correlation functions of the high-temperature liquid phase at constant temperature and chemical potential. These can be measured experimentally or found from independent theoretical calculations. Interestingly, in the simplest non-trivial approximation the resulting free energy is a functional of the one-particle distribution function and of the direct correlation function $C(1, 2)$. The latter is defined in terms of the molecular pair-distribution function $g(1, 2)$ by the Percus–Yevick equation. Under the additional assumption that the isotropic liquid is incompressible, the RY free energy of the antiferroelectric smectics, divided by $Nk_B T$, is identical with (11 *c*) if ϱ is replaced by 1, $V(1, 2)$ by $k_B TC(1, 2)$ and V_{LNm} by $k_B TC_{LNm}$. Additionally, the one-particle distribution function must be normalized to N.

Consequently, the mean-field parameters can be interpreted in terms of the structural parameters C_{LNm}. Thus, using the formalism of §2, we find relations at the tricritical point between the order parameters $\mathbf{x}_{Lm}$ and some ratios of the C_{LNm}.

It is worth mentioning that the neglect of higher-order correlations is equivalent to the assumption that, close to a phase transition, the differences between pair correlations in the high-temperature liquid phase and in the low-temperature liquid phase are very small.

5. Model calculations and discussion

Our purpose now is to apply the formalism discussed in the previous sections to some models of the antiferroelectric smectic-A phases. Though the results will be interpreted in terms of the parameters V_{NLm}, the same conclusions hold true for the C_{NLm}.

As follows from (8) and (10), the tricritical properties of the system (11) are independent of the details of the translational part of the pair potential. Only the orientational part of (11), which is responsible for the nematic background, must be specified. Below, we list the necessary approximations in each case. We start by discussing the classical NA transition. Some of the results will also serve as a direct test of the validity of the equations (5) and (6).

5.1. *Generalized James–Humphries–Luckhurst model of the nematic–smectic-A transition* (only $L = N = 2, 4$ terms are retained in (11 *a*))

There are already several theories of formation of the classical smectic-A phase [1–5, 10, 32–35]—some of which have been described in §1. Here we concentrate on a generalization of those results. Our purpose here is to give a partial answer to the question of what happens when the McMillan–de Gennes and the Mayer–Lubensky mechanisms compete. In order to make the analysis feasible, we must decide on how many terms with different L to retain in the pseudopotential (11 *a*). Since the terms with $P_4(\cos\theta)$ lead to qualitatively new results, the series (11 *a*) is truncated after the terms with $L = 4$.

The above model is a generalization to smectic-A phases of that proposed by James, Humphries and Luckhurst (see [43]) for nematics and that of Kuzma and Allender (KA) [32]. The *exact* analysis of the mean-field properties of this model was presented in our recent paper [35]. Here we shall concentrate on the effect of the P_4 terms in (11 *a*). As shown by KA, the negative values of the V_{442} coupling cause the molecules to *tilt*, on average, with respect to the direction perpendicular to the layer. However, the molecules are placed in each layer in such a way as to preserve the uniaxial symmetry of the smectic-A phase. This means that the maxima of the distribution function $P(\cos\theta, z)$ shift from $\cos\theta = \pm 1$ positions to cones around the director.

The concept of molecular tilting discussed here was proposed some time ago by deVries [44]. It is consistent with experimental measurements of smectic layer spacing in classical-A phases, which show that d is less than the molecular length l.

In the mean-field calculations the tilting of the molecules follows directly from the mathematical structure of the Legendre polynomial $P_4(y)$, which has maxima at $y = \pm 1, 0$. Thus, for negative values of V_{442} in the pseudopotential (11 *b*), a barrier develops between the states parallel and perpendicular to the director, which effectively shifts the maxima of the distribution function at $y = \pm 1$ towards the state $y = 0$.

Guided by this last observation, we performed more general calculations of the NA critical temperature by solving the equation $d^2F^0/d\tau^2 = 0$. We showed that at low temperatures all maxima of the distribution function are well separated and that the states around $y = 0$ may help to destabilize the A phase. Typical results of numerical calculations are shown in figure 1. Interestingly, in the case of extreme competition between various maxima of the distribution function there is a possibility of nematic–smectic-A–reentrant-nematic phase transitions, which are stabilized by higher-order couplings V_{224} and V_{444}. These couplings were disregarded in the KA theory. Furthermore, each of the phase transitions NA and AN$_{\mathrm{re}}$ can be tricritical, since the stability of the tricritical points is governed by still-higher-order terms V_{226} and V_{446} (figure 2). Note that the equations $a_4 = 0$ and $a_6 = 0$ can be analysed independently, since they are polynomials in the different coupling constants, like V_{224}, V_{444} and V_{226}, V_{446} respectively.

The results as given seem to indicate the importance of the orientational degrees of freedom in the problem of the re-entrant phase transitions in liquid crystals [44–46]. We may expect that a broadening at low temperatures of dominant, side maxima of the orientational part of the smectic-A distribution function would help to destabilize the A phase. If the dimer model [47] correctly describes the mechanism of the AN$_{\mathrm{re}}$ transition then the increase of the dimer concentration when the temperature is lowered will give rise to such an effect. This, in turn, can help to destabilize the smectic-A phase at low temperatures as indicated by our calculations.

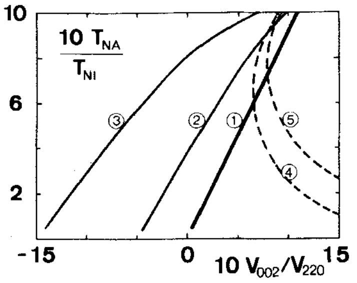


Figure 1. Theoretical phase diagrams $T_{\mathrm{NA}}/T_{\mathrm{NI}}$ as a function of V_{002}/V_{220} for $(V_{222}/V_{220}, V_{442}/V_{220}) = (0,0)$ (1), $(0{\cdot}1, 0)$ (2), $(0{\cdot}3, 0)$ (3), $(0{\cdot}2, -\frac{1}{3})$ (4), $(0{\cdot}2, -\frac{1}{2})$ (5), and for $V_{440}/V_{220} = 0$.

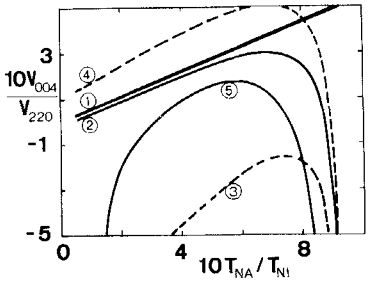


Figure 2. The tricritical boundaries in the (V_{004}/V_{220}, T_{NA}/T_{NI}) plane for (V_{222}/V_{220}, V_{224}/V_{220}, V_{442}/V_{220}, V_{444}/V_{220}) = (0, 0, 0, 0) (1), (0·3, 0, 0, 0) (2), (0·3, 0·1, 0, 0·05) (3), (0·3, −0·1, 0, 0·05) (4), (0·2, 0, 1/6, 0) (5), and for $V_{440}/V_{220} = -\frac{1}{6}$.

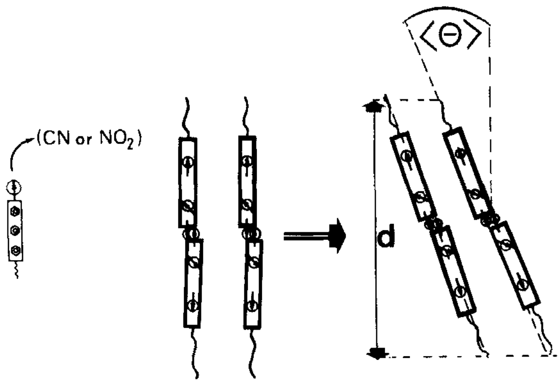


Figure 3. Monomer and dimers in the Goullon–Skoulios model [29]. The arrows indicate positions and orientations of dipole moments.

An alternative interpretation may be proposed in terms of a modified version of the Goullon–Skoulios (GS) model [29].

According to GS, the antiferroelectric phases are attributed to the formation of head-to-head dimers in combination with single molecules (monomers) (figure 3). In this picture the A_1 symmetry is recovered provided that there is disorder of the dipoles inside the layer. An additional transverse interaction between the dimers may stabilize the A_2 order.

Suppose now that the preferred direction $\langle\theta\rangle$ for the dimers to align is tilted with respect to the layer normal in the A_d phase (figure 3), where $\langle \ldots \rangle$ denote the thermal average and where $0 \leqslant \theta \leqslant \frac{1}{2}\pi$. This effect could account for the layer periodicity $1{\cdot}6 \leqslant d/l < 2$. At low temperatures it could help to destabilize the A_d phase towards reentrant nematic, smectic-C_2, -C_d or -$\tilde{C}$ phases.

Finally, let us concentrate on the importance of the mechanisms proposed by McMillan and deGennes and by Meyer and Lubensky by solving the tricritical condition $a_4 = 0$ for different values of V_{NNm}. The characteristic tricritical boundaries are obtained as shown in figure 2. The results are presented so as to emphasize the differences with the Meyer–Lubensky model.

Notable features of these diagrams are

(*a*) a strong dependence of the topology of the diagrams on higher-order couplings between orientational and translational degrees of freedom; and (*b*) a strong nonlinear dependence of the tricritical parameters on orientational degrees of freedom at both low and high critical temperatures.

5.2. *The smectic-A_2 phase and related phase transitions*

The simplest type of antiferroelectric-A phase is probably the bilayer A_2 phase. In our model it is described by the order parameters $\zeta_{M,n}$, (9 *a*,*b*). For non-zero values of $\zeta_{M,n}$ this implies an antiferroelectric symmetry of the distribution function (7 *b*). Thus we may expect a qualitatively different behaviour of the phase diagrams compared with the classical NA phase transition. Using the results of the previous sections, we show that this is indeed the case. More precisely, we concentrate on the description of isotropic(I)–A_2, NA_2 and A_1A_2 transitions. In particular, we shall discuss how orientational degrees of freedom and higher-order harmonics influence the topology of phase diagrams.

Isotropic–smectic-A_2 transition

Interestingly, the antiferroelectric symmetry (7 *a*) allows both first- and second-order phase transition to occur between isotropic and A_2 phases. In this case the equation $a_2 = 0$ yields

$$t = V_{111}, \tag{13}$$

which is valid for the general interaction potential (11 *a*). In order to study the tricritical condition $a_4 = 0$, we shall additionally assume that the interactions between particles are separable. Now, combining the critical and tricritical conditions yields

$$\frac{108}{25}\frac{V_{222}/V_{111}}{1 - V_{222}/V_{111}} + \frac{V_{002}/V_{111}}{1 - V_{002}/V_{111}} + \frac{V_{220}/V_{111}}{1 - V_{220}/V_{111}} = 1, \tag{14}$$

which must be satisfied at the tricritical point. From equation (14) it follows that the IA_2 phase transition is of second order for small or negative values of the parameters V_{220}, V_{222} and V_{002}. This possibility would imply very strong intensity of the [001] Bragg spot of double layer compared to the [002] one. A first-order phase transition is expected when the opposite holds. As far as we know, the direct phase transition IA_2 has not yet been observed experimentally.

Nematic–smectic-A_2 transition

In the ideal nematic-order approximation the NA_2 transition is described by the Meyer–Lubensky theory. When the molecular orientations are allowed to fluctuate, the Meyer–Lubensky theory is modified in a very simple way. More specifically, for pair potentials that are separable in the antiferroelectric degrees of freedom, i.e. $V_{2L+1,2N+1,m} = \delta_{LN} V_{2L+1,2L+1,m}$, the condition $a_2 = 0$ yields

$$t = (2\langle P_2(\cos\theta)\rangle + 1)V_{111}, \tag{15 a}$$

here $\langle \ldots \rangle$ denotes the thermal average over translational and orientational degrees of freedom. Importantly, (15 *a*) is independent of the description of the nematic state that is employed. A general pair interaction leads to very complicated relations between t and the effective coupling constants.

Equation (15 *a*) shows that the influence of orientational degrees of freedom on the critical temperature is to reduce the effect of V_{111} coupling. In general, the critical

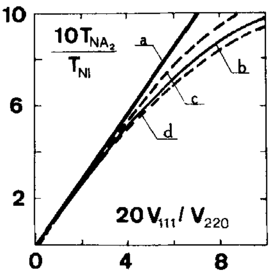


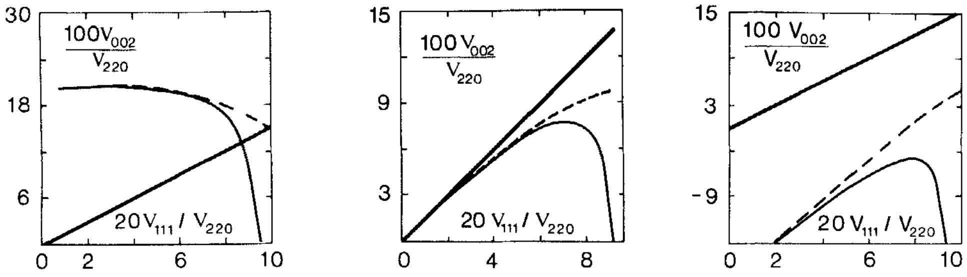
Figure 4. Critical temperature for the NA_2 transition in the ideal nematic-order approximation (a) and for the James–Humphries–Luckhurst model [43] with $V_{440}/V_{220} = 0$ (b), $\frac{1}{9}$ (c), $-\frac{1}{9}$ (d).

temperature is lower than that calculated in the ideal nematic-order approximation ($\langle P_2 \rangle = 1$). In contrast with what is found for the classical NA transition, the NA_2 phase diagrams should be characterized by a high degree of universality. This is shown in figure 4, where the nematic phase is described by means of the James–Humphries–Luckhurst potential.

The tricritical conditions $a_2 = a_4 = 0$ lead to a rather complicated relation between the model parameters (see (A 1) in Appendix A). Although complicated, this relation depends only on $\langle P_2 \rangle$ and $\langle P_2^2 \rangle$. At intermediate temperatures, where $\langle P_2^2 \rangle \approx \langle P_2 \rangle^2$, the formula (A 1) simplifies considerably, yielding

$$10V_{002} = (2\langle P_2 \rangle + 1)V_{111} - 10V_{222}\langle P_2 \rangle^2. \qquad (15b)$$

The solutions of (A 1) and (15b) are illustrated in figures 5 (a–c).



(a) (b) (c)

Figure 5. Tricritical boundaries for the NA_2 transition as found from (A 1) (continuous line) and from the approximate relation (15b) (broken line) for $V_{222}/V_{220} = -0{\cdot}2$ (a), 0 (b), 0·2 (c). The straight line on the diagrams corresponds to the ideal nematic-order solution.

Smectic-A_1–smectic-A_2 transition

In this case we expect a rather small influence of orientational degrees of freedom on the transition temperature. Because of this, we shall restrict our analysis to the case when nematic order is saturated.

In the ideal nematic-order approximation the A_1A_2 phase transition may be viewed as an antiferroelectric condensation of pseudospin degrees of freedom in the well-developed layer structure of the A_1 phase. Since the A_1 order forms a background for the A_2 phase, we expect the higher-order harmonics of the one-particle distribution function (7e) to be important. Indeed, a resolution-limited (003) Bragg peak has been observed experimentally in the A_2 phase [18]. In agreement with this observation, we retain in the pseudopotential (11b) the terms $V_{00l} \equiv V_l$ with $l \leqslant 3$. The forms of the

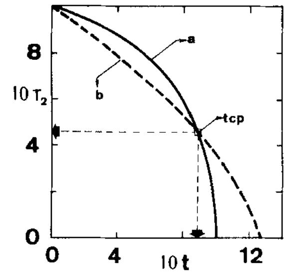
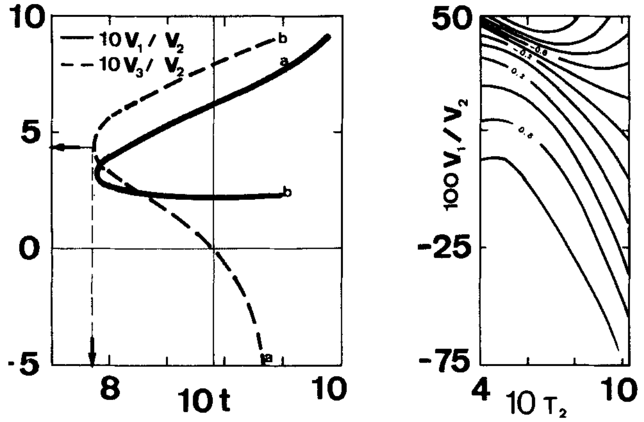


Figure 6. The A_1A_2 tricritical point for $V_3 = 0$ shown as the intersection of two curves: (*a*) τ_2 found from the self-consistency equations (B 3); and (*b*) τ_2 calculated from the system of equations (B 1), (B 2).



(*a*) (*b*)

Figure 7. (*a*) Solutions of the equations (B 1) (continuous line) and (B 2) (broken line). Corresponding branches are indicated by the same letter. (*b*) Tricritical surface (B 2). Curves are parametrized by V_3/V_2. The self-consistency equation (B 3) has not been taken into account.

Landau relations $a_2 = a_4 = 0$ that result from (5) after a fair amount of algebra are given in Appendix B. As expected, these are polynomials in V_1, V_2, V_3, t and τ_2, where t and τ_2 are related via the self-consistency equations (B 3). After choosing the energy scale, $V_2 = 1$, the equations (B 1) and (B 2) only depend on three parameters. The numerical solutions to these equations are easily found (see figures 6 and 7). In figure 6 the simpler case $V_3 = 0$ is shown, with a tricritical point occurring at $t = 0{\cdot}889$, $V_1 = 0{\cdot}612$ and $\tau_2 = 0{\cdot}453$. The tricritical point appears here as a result of coupling between ζ and τ_2. The mechanism generating the tricritical point is similar to that proposed by McMillan and de Gennes. More precisely, close to the NA transition the smectic order parameter τ_2 varies strongly with temperature, resulting in the A_1A_2 phase transition being first-order. For $\tau_2 > 0{\cdot}453$ the variation of τ_2 becomes less important, and the transition is continuous.

A qualitatively new solution is obtained for $V_3 > V_3^* \approx 0{\cdot}45$ (see figures 7 (*a*,*b*)). In this case coupling between ζ, ζ_3 and the smectic-A order parameters τ_i ($i \leqslant 6$) becomes relevant (branches (b) in figure 7 (*a*)). This situation is only expected to be important in cases where many Bragg reflections are observed at the transition. Again, for $V_3 < V_3^*$ the tricritical mechanism is the same as in the case of $V_3 = 0$ (branches (a) in figure 7 (*a*)). By taking higher-order couplings into account ($V_{2n+1} > 0$), the second-order A_1A_2 phase transition may be eliminated.

Finally, in figure 7 (*b*) we show the structure of the tricritical surface $a_4 = 0$. The results can be correlated with the structure parameters C_1/C_2, C_3/C_2 and τ_2.

6. Final remarks

In this paper we have extended our earlier work [26] on antiferroelectric smectic-A phases to include the effect of orientational degrees of freedom on the topology of phase diagrams. In particular, we have considered the influence of breaking the up–down symmetry of mesogenic molecules on the occurrence of the A phases in molecular theories. The molecules are represented by axially symmetric rigid rods with soft angle-dependent interactions (dipolar, dispersive, etc.).

It should be emphasized that the minimum ingredients have been sought for in order to study exactly the influence of orientational degrees of freedom and higher-order harmonics on the topology of the phase diagrams.

More precisely, we have derived the conditions for the tricritical points in a large class of order-parameter theories. These conditions are found by 'projecting out' a molecular theory onto the Landau expansion. In this way a minimal set of conditions can be identified, allowing the calculation of tricritical temperatures (for a detailed discussion see §5). Interestingly, the hierarchical structure of the Landau coefficients allows general predictions to be made without the necessity of performing numerical calculations. For example, from the formulae for the operators **D** it follows that the phase diagrams may exhibit not only tricritical points separating first- and second-order transition regions but also triple point N–A_1–A_2 or multicritical points like I–N–A_1–A_2.

We believe that this analysis is attractive for at least three reasons. First, we expect the smectic-A tricritical points to be classical tricritical points. This is supported by experimental measurements of tricritical indices for the nematic and smectic order parameters [12]. Thus we expect that the molecular theories can be used to classify phase diagrams and correlate their features with molecular properties. Secondly, a large number of recent papers have been devoted to the topology of phase diagrams in mixtures of strongly polar liquid crystals. In these studies the role of orientational degrees of freedom has not yet been taken into account. The third reason is that the tricritical conditions, when interpreted in terms of generalized RY theory, only depend on structural parameters. These may be checked experimentally or theoretically from independent molecular calculations. Some very simple relations of this type have been derived from generalized RY theory. These relations become very complicated when higher-order correlations are included in the free-energy functional. In this case the tricritical conditions depend on couplings between all coefficients C_{LMn}.

Finally, we should point out that the Landau coefficients were obtained with the help of the algebraic computing processors MACSYMA and REDUCE.

The author wishes to thank Professors H. Stegemeyer and H.-R. Trebin for the kind hospitality extended to him at the Universities of Paderborn and Stuttgart. It is also a pleasure to thank S. Picken for carefully reading the final version of the manuscript.

This work was partially supported by the Alexander von Humboldt Foundation and by the Polish Project C.P.B.P.01.03.

Appendix A

The Landau relation $a_4 = 0$ at the NA_2 tricritical point implies

$$b_2 V_{002}^2 + b_1 V_{002} + b_0 = 0, \tag{A 1}$$

where

$$
\begin{aligned}
b_2 = {} & 18U^3(48P^5 + 104P^4 - 16P^3Q + 92P^3 - 24P^2Q + 42P^2 - 12PQ + 10P \\
& - 2Q + 1) + 108U^2W(20P^6 + 36P^5 - 24P^4Q + 25P^4 - 40P^3Q + 8P^3 \\
& + 4P^2Q^2 - 26P^2Q + P^2 + 4PQ^2 - 8PQ + Q^2 - Q) + 54U^2 \\
& \times (8P^6 + 24P^5 + 22P^4 - 16P^3Q + 8P^3 - 8P^2Q^2 - 20P^2Q + P^2 \\
& - 8PQ^2 - 8PQ - 2Q^2 - Q) + 162UW^2(8P^7 + 12P^6 - 16P^5Q + 6P^5 \\
& - 24P^4Q + P^4 + 8P^3Q^2 - 12P^3Q + 12P^2Q^2 - 2P^2Q + 6PQ^2 + Q^2) \\
& + 324UW(2P^7 + 9P^6 + 2P^5Q + 6P^5 - 15P^4Q + P^4 - 10P^3Q^2 \\
& - 12P^3Q + 3P^2Q^2 - 2P^2Q + 6PQ^3 + 6PQ^2 + 3Q^3 + Q^2) + 486W^2 \\
& \times (4P^7 + 4P^6Q + P^6 - 12P^5Q - 12P^4Q^2 - 3P^4Q + 12P^3Q^2 \\
& + 12P^2Q^3 + 3P^2Q^2 - 4PQ^3 - 4Q^4 - Q^3), \\
b_1 = {} & 3U^4(-320P^6 - 832P^5 + 128P^4Q - 912P^4 + 256P^3Q - 544P^3 \\
& + 192P^2Q - 188P^2 + 64PQ - 36P + 8Q - 3) + 18U^3W \\
& \times (-64P^7 - 144P^6 + 160P^5Q - 128P^5 + 352P^4Q - 56P^4 - 32P^3Q^2 \\
& + 312P^3Q - 12P^3 - 48P^2Q^2 + 140P^2Q - P^2 - 24PQ^2 + 32PQ \\
& - 4Q^2 + 3Q) + 9U^3(-32P^7 - 144P^6 - 32P^5Q - 192P^5 + 48P^4Q \\
& - 112P^4 + 64P^3Q^2 + 144P^3Q - 30P^3 + 96P^2Q^2 + 104P^2Q - 3P^2 \\
& + 48PQ^2 + 30PQ + 8Q^2 + 3Q) + 27U^2W^2(64P^6Q + 4P^6 + 128P^5Q \\
& + 4P^5 - 64P^4Q^2 + 88P^4Q + P^4 - 128P^3Q^2 + 24P^3Q - 92P^2Q^2 \\
& + 2P^2Q - 28PQ^2 - 3Q^2) + 54U^2W(-24P^7 - 16P^6Q - 28P^6 \\
& + 64P^5Q - 10P^5 + 64P^4Q^2 + 92P^4Q - P^4 + 8P^3Q^2 + 36P^3Q \\
& - 48P^2Q^3 - 52P^2Q^2 + 4P^2Q - 48PQ^3 - 26PQ^2 - 12Q^3 - 3Q^2) \\
& + 81UW^2(2P^7 + 32P^6Q + P^6 + 32P^5Q^2 + 18P^5Q - 48P^4Q^2 + P^4Q \\
& - 64P^3Q^3 - 42P^3Q^2 - 5P^2Q^2 + 32PQ^4 + 22PQ^3 + 16Q^4 + 3Q^3), \\
b_0 = {} & U^5(256P^7 + 768P^6 - 128P^5Q + 992P^5 - 320P^4Q + 720P^4 - 320P^3Q \\
& + 320P^3 - 160P^2Q + 88P^2 - 40PQ + 14P - 4Q + 1) \\
& + 3U^4W(-256P^6Q - 16P^6 - 704P^5Q - 32P^5 + 64P^4Q^2 - 800P^4Q \\
& - 24P^4 + 128P^3Q^2 - 480P^3Q - 8P^3 + 96P^2Q^2 - 160P^2Q - P^2 \\
& + 32PQ^2 - 28PQ + 4Q^2 - 2Q) + 3U^4(64P^7 + 64P^6Q + 144P^6 \\
& + 64P^5Q + 128P^5 - 64P^4Q^2 - 48P^4Q + 56P^4 - 128P^3Q^2 - 96P^3Q \\
& + 12P^3 - 96P^2Q^2 - 52P^2Q + P^2 - 32PQ^2 - 12PQ - 4Q^2 - Q) \\
& + 9U^3W^2Q(64P^5Q + 8P^5 + 160P^4Q + 12P^4 + 152P^3Q + 6P^3 \\
& + 68P^2Q + P^2 + 14PQ + Q) + 9U^3W(-8P^7 - 96P^6Q - 12P^6
\end{aligned}
$$

$$
\begin{aligned}
&- 96P^5Q^2 - 152P^5Q - 6P^5 - 48P^4Q^2 - 84P^4Q - P^4 + 96P^3Q^3 \\
&+ 88P^3Q^2 - 18P^3Q + 144P^2Q^3 + 84P^2Q^2 - P^2Q + 72PQ^3 + 24PQ^2 \\
&+ 12Q^3 + 2Q^2) + 27U^2W^2Q(4P^6 + 32P^5Q + 4P^5 + 32P^4Q^2 + 32P^4Q \\
&+ P^4 + 8P^3Q - 32P^2Q^3 - 28P^2Q^2 - 32PQ^3 - 12PQ^2 - 8Q^3 - Q^2)
\end{aligned}
$$

and

$$U = V_{111}, \quad W = 5V_{222}, \quad P = \langle P_2 \rangle, \quad Q = \langle P_2^2 \rangle.$$

Appendix B

The Landau relations $a_2 = a_4 = 0$ for the A_1A_2 phase transition in the ideal nematic order approximation lead to the following relationships.

The solution of the equation $a_2 = 0$ is

$$V_1 = \frac{V_3(\tau_2^2 + \tau_2 + 2t^2 - 2t) - \tau_2 t}{V_3(2\tau_2^2 + \tau_2 t + 2t - 2) - \tau_2(\tau_2 + 1)} \tag{B 1}$$

The equation $a_4 = 0$ gives

$$
\begin{aligned}
&3V_3^4[24\tau_2^8 + 8\tau_2^7(10 - 7t) + 2\tau_2^6(123t^2 - 140t + 28) + 16\tau_2^5(-4t^3 \\
&+ 11t^2 - 2t - 5) + \tau_2^4(320t^4 - 507t^3 - 42t^2 + 348t - 120) + 8\tau_2^3(8t^4 \\
&- 10t^3 - 7t^2 + 11t - 2) + 4\tau_2^2(4t^6 + 61t^5 - 247t^4 + 319t^3 - 151t^2 \\
&+ 4t + 10) + 16\tau_2(-2t^6 + 12t^5 - 29t^4 + 34t^3 - 18t^2 + 2t + 1) \\
&+ 4t(3t^6 - 6t^5 - 19t^4 + 76t^3 - 99t^2 + 58t - 13)] + 4\tau_2 V_3^3 t[-52\tau_2^6 \\
&+ 4\tau_2^5(29 - 41t) + 2\tau_2^4(50 - 57t^2 + 7t) + \tau_2^3(-152t^3 + 109t^2 \\
&+ 190t - 144) + 2\tau_2^2(22 - 2t^4 - 88t^3 + 213t^2 - 145t) + 2\tau_2 \\
&\times (14 - 49t^4 + 151t^3 - 141t^2 + 25t) + 4(2t^5 - 25t^4 + 86t^3 \\
&- 128t^2 + 88t - 23)] + 6\tau_2^2 V_3^2 t[36\tau_2^5 + 2\tau_2^4(33t - 16) + 16\tau_2^3(3t^2 \\
&+ t - 4) + 3\tau_2^2(4t^3 + 27t^2 - 56t + 24) + 4\tau_2(8t^3 - 12t^2 \\
&- 3t + 7) + 2(t^4 + 11t^3 - 45t^2 + 53t - 20)] + 12\tau_2^3 V_3 t[-8\tau_2^4 \\
&- 8\tau_2^3 t + 2\tau_2^2(8 - t^2 - 7t) + \tau_2\tau(8 - 7t) + 2(-3t^2 + 7t - 4)] \\
&+ \tau_2^4 t[16\tau_2^3 + 2\tau_2^2(t + 8) + 16\tau_2(t - 1) - t^2 + 14t - 16] = 0
\end{aligned}
$$

In deriving (B 1) and (B 2), use has been made of (*a*) the self-consistent equations for τ_2 in the A_1 phase,

$$\tau_2 = \frac{I_1(2\tau_2/\bar{t}}{I_0(2\tau_2/\bar{t})}, \quad \bar{t} = \frac{t}{V_2}, \tag{B 3}$$

where I_n $(n = 0, 1)$ are the modified Bessel functions of integer order; and (*b*) the standard recurrence relations between I_n.

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