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Revisiting McMillan's theory of the smectic A phase

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Abstract

We consider the full solution of McMillan's molecular model of the smectic A phase within the mean-field approximation, expressing the free energy (or the effective one-particle mean-field energy) of the model in terms of an infinite set of orientational and translational order parameters. The general formalism reduces to the usual McMillan theory (hereafter referred to as McMillan's approximation) when second- and higher-order harmonics in the Fourier expansion are neglected, which leads to a description of the smectic phase in terms of the leading order parameters. The effects of such a truncation on the location of the tricritical nematic–smectic A point have been previously considered by Longa (1986 *J. Chem. Phys.* **85** 2974). A quantitative analysis to assess the relative importance of the neglected terms in the description of the smectic phase and its various transitions is reported. It is shown that McMillan's approximation underestimates both orientational and translational order, and leads to values of the transition entropies smaller than those resulting from the full expansion.

1. Introduction

Smectic liquid crystals are known to be condensed phases of matter characterized by some degree of translational order in addition to the long-range orientational order. The simplest type is the smectic A (SmA) phase, where the molecules are arranged in liquid layers in which the long molecular axes are, on average, normal to the layers. Hence, the centres of mass of the molecules form a well-defined one-dimensional density wave along the layer normal while the system remains fluid-like in the smectic planes.

One of the earliest and simplest molecular-based theories of the SmA phase was given by McMillan [1, 2], based on the assumption that smectic ordering is promoted by the anisotropic attractive interactions. The theory is formulated in terms of a specific phenomenological molecular model, which is an extension of the Maier–Saupe model [3] for nematics. For axially

symmetric molecules located at positions \mathbf{r}_1 and \mathbf{r}_2 , with orientations defined by the axial unit vectors $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$, the pair interaction is assumed to be of the form

$$u(1, 2) = u_0(r_{12}) + u_2(r_{12})P_2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2), \quad (1)$$

where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ is the distance between the centres of mass of the molecules, and P_2 is the second-order Legendre polynomial. In his seminal papers [1, 2], McMillan adopted a simple Gaussian form for the distance dependence of the interactions:

$$u_0(r_{12}) = -\epsilon_0\delta \exp[-(r_{12}/r_0)^2], \quad (2a)$$

$$u_2(r_{12}) = -\epsilon_0 \exp[-(r_{12}/r_0)^2], \quad (2b)$$

where r_0 is the range of the interactions, ϵ_0 is the strength of the anisotropic term, and δ is the (dimensionless) strength of the isotropic term (2a) relative to the anisotropic term (2b). Different versions of McMillan's model have been proposed by a number of authors [4–12]. For a recent account, see [13] and references therein. In all cases, the theory is formulated within the mean-field approximation, and an approximate solution is obtained considering a truncated Fourier–Legendre expansion of the intermolecular interaction, the effective (mean-field) energy, or the one-particle distribution function (see, however, [11]). Such a truncation involves a description of the SmA phase in terms of a limited number of order parameters. Typically, only the first-order term in the Fourier–Legendre expansion is considered, which leads to a description of the SmA phase in terms of the leading order parameters η , τ , and σ (orientational, translational, and mixed translation–orientation order parameters, respectively, to be defined later). Within this approximate scheme the theory is seen to depend on η and σ when $\delta = 0$ in (2a), whereas in the most general case ($\delta \neq 0$), the theory depends additionally on τ .

For most smectics, a description based on this truncated scheme appears to be justified considering that the intensity of the first peak in typical x-ray measurements is orders of magnitude larger than the intensity associated with higher-order harmonics [14]. However, exceptions where the intensity of successive peaks is not negligible are not rare (for example, lyotropic smectics which are less compressible than typical thermotropic smectics [15]). Moreover, as pointed out by Gunther *et al* [16], even the absence of higher-order peaks in the scattering pattern does not necessarily imply the absence of higher-order Fourier components in the density.

The purpose of this work is to go beyond the truncation scheme at the level of the first-order harmonic (hereafter, referred to as McMillan's approximation), obtaining an essentially exact numerical solution of McMillan's model within the mean-field approximation. A quantitative comparison between the results so obtained and those obtained within McMillan's approximation will allow us to gauge the relative importance of higher-order harmonics in the description of the SmA phase. This question has been partly addressed by Longa [11], who analysed the effect of including higher-order components on the critical and tricritical behaviour of McMillan's model. As shown by Longa [11], the nature of the smectic A–nematic transition and the location of the tricritical temperature are fully determined by the two lowest-order terms in the Fourier expansion for a broad class of molecular models. As for the tricritical parameters, the contribution of the second-order terms—neglected in McMillan's approximation—is found to be small, the relative difference between the exact [11] and the approximate values [17] being about 2%. While the nature of the transitions involving the smectic A phase is not significantly affected by the truncation scheme assumed in McMillan's approximation, it is not obvious whether the predicted values of the transition properties (e.g. degree of order or transition entropy) and the thermodynamic properties of the smectic phase are sensitive to the approximation. In particular, it is known that the experimental magnitudes of the entropy

changes at the (first-order) smectic A–nematic and smectic–isotropic transitions are grossly overestimated within McMillan's approximation [1]. Though this discrepancy is most likely due to the use of a mean-field approximation, it is unknown to what extent the differences between theoretical predictions and experimental values are due to the use of a truncated approximation.

We organize this paper as follows. In section 2 we outline a general description of McMillan's model within the mean-field approximation. Expressions are obtained for the effective (mean-field) energy and the Helmholtz free energy in terms of an infinite set of translational and orientational order parameters. In section 3 we derive general equations for the critical and tricritical smectic A–nematic transition parameters from a Landau-type expansion of the free energy [11, 17, 18]. We present our numerical results in section 4, focusing on the differences between the approximate and exact treatments of McMillan's model. We summarize our conclusions in section 5.

2. Theoretical background

2.1. Mean-field description

We consider a system of N axially symmetric molecules in a volume V at temperature T . The thermodynamic and structural properties of the system can be analysed in terms of the Helmholtz free energy F , which depends functionally on the one-particle density $\rho(1) \equiv \rho(\mathbf{r}_1, \omega_1)$. The latter is defined as the density of particles at position \mathbf{r}_1 with orientations $\omega_1 = (\theta_1, \phi_1)$. At given thermodynamic conditions, the equilibrium one-particle density follows from minimization of the free energy functional $F[\rho]$. Considering the form of the intermolecular interactions given in (1), (2a), and (2b), the free energy can be expressed as an ideal term, plus a contribution arising from the (attractive) intermolecular interactions. Using the notation $d1 = d\mathbf{r}_1 d\omega_1$,

$$F[\rho] = kT \int d1 \rho(1) \ln[4\pi\rho(1)/\rho_0] + \frac{1}{2} \int d1 d2 u(1, 2) \rho^{(2)}(1, 2), \quad (3)$$

where k is Boltzmann's constant, $\rho_0 = N/V$ is the average number density, and $\rho^{(2)}(1, 2)$ is the two-particle density. We assume, in keeping with the mean-field approximation, that short-range correlations can be ignored and consider $\rho^{(2)}(1, 2) \approx \rho(1)\rho(2)$. At any temperature, the equilibrium $\rho(1)$ follows from the stationary condition $\delta F/\delta\rho(1) = 0$. Minimizing the free energy functional under the constraint $\int d1 \rho(1) = N$ yields

$$\rho(1) = \frac{\rho_0}{4\pi} \frac{1}{Z} \exp[-\beta u_{\text{eff}}(1)], \quad (4)$$

where $\beta = (kT)^{-1}$, and u_{eff} is the one-body effective potential defined as

$$u_{\text{eff}}(1) = \int d2 \rho(2) u(1, 2). \quad (5)$$

Z ensures the normalization of the one-particle density and is explicitly given by

$$Z = \frac{1}{4\pi V} \int d1 \exp[-\beta u_{\text{eff}}(1)]. \quad (6)$$

Further simplifications can be introduced after considering the symmetry properties of the phases to be described. The most general one-particle density appropriate for a description of isotropic (I), nematic (N), and SmA phases is of the form $\rho(z, \cos\theta)$, where the z axis is taken

along the average direction of alignment (director), and θ is the angle between the molecular axis and the director. Equation (4) now reads

$$\rho(z, \cos \theta) = \frac{\rho_0}{4\pi} \frac{1}{Z} \exp[-\beta u_{\text{eff}}(z, \cos \theta)], \quad (7)$$

where

$$u_{\text{eff}}(z_1, \cos \theta_1) = \int d2 \rho(z_2, \cos \theta_2) u(1, 2). \quad (8)$$

The solution of the integral equation (7) provides the equilibrium one-particle density at each input temperature. The I phase is characterized by a constant $\rho(z, \cos \theta) = \rho_0/(4\pi)$, the N phase by $\rho(z, \cos \theta) = \rho(\cos \theta)$, and the SmA phase by $\rho(z, \cos \theta)$ with periodicity d in the space variable z . It is straightforward to show that, after substitution of the (equilibrium) $\rho(z, \cos \theta)$ into (3), the free energy can be expressed in terms of the average of the effective potential. Explicitly, we obtain

$$\frac{F}{NkT} = -\frac{1}{2} \langle \beta u_{\text{eff}} \rangle - \ln Z. \quad (9)$$

Similarly, the energy per particle can be written as

$$\frac{U}{NkT} = \frac{1}{2} \langle \beta u_{\text{eff}} \rangle, \quad (10)$$

and the entropy follows from the thermodynamic relation $F = U - TS$.

2.2. The effective potential

In order to obtain the exact solution of McMillan's model the integral equation (7) has to be solved numerically. This is not a trivial task particularly for the smectic phase: due to the periodicity of the one-particle density, the evaluation of u_{eff} from (8) implies numerical integration of a function that can be a very slowly decaying function of z . Alternatively, one can use the symmetry properties of the smectic phase and expand the one-particle density in terms of Legendre polynomials (for the angular variable) and Fourier series (for the spatial variable):

$$\rho(z, \cos \theta) = \frac{\rho_0}{4\pi} \sum_{n=0} \sum_{m=0} \frac{2(2m+1)}{1+\delta_{0n}} \rho_{nm} \cos(nqz) P_m(\cos \theta), \quad (11)$$

where $q = 2\pi/d$ is the wavevector of the density modulation. Owing to the axial symmetry of the molecules, $\rho(z, \cos \theta)$ is an even function of $\cos \theta$, and so the above expansion is restricted to even values of m . The expansion coefficients ρ_{nm} are order parameters and are given by

$$\rho_{nm} = \langle \cos(nqz) P_m(\cos \theta) \rangle \quad (12)$$

where the angular brackets denote an statistical average. In the following, we consider the full expansion of the one-particle density and express the effective potential (8) in terms of the (infinite) set of order parameters ρ_{nm} . Considering the form of the intermolecular interactions (see (1), (2a), and (2b)) it is convenient to write $u_{\text{eff}} = u_{\text{eff}}^{(0)} + u_{\text{eff}}^{(2)}$, with

$$u_{\text{eff}}^{(0)}(z_1, \cos \theta_1) = \int d\mathbf{r}_2 d\omega_2 \rho(z_2, \cos \theta_2) u_0(r_{12}), \quad (13a)$$

$$u_{\text{eff}}^{(2)}(z_1, \cos \theta_1) = \int d\mathbf{r}_2 d\omega_2 \rho(z_2, \cos \theta_2) u_2(r_{12}) P_2(\cos \theta_{12}), \quad (13b)$$

where $d\omega = d\phi d\cos \theta$, and $\cos \theta_{12} = \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2$. Inserting (2a) into (13a) and integrating with respect to ϕ_2 gives

$$u_{\text{eff}}^{(0)}(z_1, \cos \theta_1) = -4\pi\epsilon_0\delta \int d\mathbf{r}_2 \exp[-(r_{12}/r_0)^2] \int_0^1 d\cos \theta_2 \rho(z_2, \cos \theta_2).$$

Substituting here the Fourier–Legendre expansion of $\rho(z, \cos \theta)$ given in (11) and using the relation $\int_0^1 dx P_m(x) = \delta_{m0}$ (for m even), we find

$$u_{\text{eff}}^{(0)}(z_1, \cos \theta_1) = -\epsilon_0 \rho_0 \delta \sum_{n=0} \frac{2}{1 + \delta_{0n}} \rho_{n0} I_n(z_1), \quad (14)$$

where

$$I_n(z_1) = \int d\mathbf{r}_2 \exp[-(r_{12}/r_0)^2] \cos(nqz_2). \quad (15)$$

After integration with respect to $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ ($d\mathbf{r}_{12} = d\mathbf{r}_2$), $I_n(z_1)$ is found to be given by

$$I_n(z_1) = (\pi)^{3/2} r_0^3 \left(\frac{\alpha}{2}\right)^{n^2} \cos(nqz_1), \quad (16)$$

where $\alpha = 2 \exp[-(\pi r_0/d)^2]$ coincides with the parameter α introduced by McMillan [1]. From its definition, $0 \leq \alpha \leq 2$. The isotropic contribution to the effective potential is then given by

$$\beta u_{\text{eff}}^{(0)}(z, \cos \theta) = -\frac{\delta}{t} \sum_{n=0} \frac{2}{1 + \delta_{0n}} \left(\frac{\alpha}{2}\right)^{n^2} \tau_n \cos(nqz), \quad (17)$$

where we have used the notation $\tau_n \equiv \rho_{n0}$ for the set of translational order parameters and defined the reduced (dimensionless) temperature t as

$$t = \frac{kT}{\epsilon^* \rho_0^*}, \quad (18)$$

with $\epsilon^* = (\pi)^{3/2} \epsilon_0$, and $\rho_0^* = \rho_0 r_0^3$. Note that $\tau_0 = \rho_{00} = 1$. Similarly, we can express the anisotropic contribution to the effective potential (13b) in terms of the order parameters. Making use of the addition theorem of the Legendre polynomials for $P_2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)$ and integrating with respect to the azimuthal angle, one obtains

$$u_{\text{eff}}^{(2)}(z_1, \cos \theta_1) = -4\pi \epsilon_0 P_2(\cos \theta_1) \int d\mathbf{r}_2 \exp[-(r_{12}/r_0)^2] \int_0^1 d \cos \theta_2 P_2(\cos \theta_2) \rho(z_2, \theta_2).$$

Substituting the expansion of $\rho(z, \cos \theta)$ (11) and using the orthogonality relation $\int_0^1 dx P_2(x) P_m(x) = \delta_{m2}/(2m+1)$ (for m even), we find

$$u_{\text{eff}}^{(2)}(z_1, \cos \theta_1) = -\epsilon_0 \rho_0 P_2(\cos \theta_1) \sum_{n=0} \frac{2}{1 + \delta_{0n}} \rho_{n2} I_n(z_1). \quad (19)$$

Denoting the set of mixed order parameters by $\sigma_n \equiv \rho_{n2}$, and using the value of $I_n(z)$ obtained in (16), it follows that

$$\beta u_{\text{eff}}^{(2)}(z, \cos \theta) = -\frac{1}{t} P_2(\cos \theta) \sum_{n=0} \frac{2}{1 + \delta_{0n}} \left(\frac{\alpha}{2}\right)^{n^2} \sigma_n \cos(nqz). \quad (20)$$

The final expression of the effective potential in terms of the set of order parameters τ_n and σ_n reads

$$\beta u_{\text{eff}}(z, \cos \theta) = -\frac{1}{t} \sum_{n=0} \frac{2}{1 + \delta_{0n}} \left(\frac{\alpha}{2}\right)^{n^2} [\delta \tau_n + \sigma_n P_2(\cos \theta)] \cos(nqz). \quad (21)$$

Summarizing, the mean-field solution of McMillan's model in terms of the order parameters σ_n, τ_n is given by

$$\rho(z, \cos \theta) = \frac{\rho_0}{4\pi Z} \exp[-\beta u_{\text{eff}}(z, \cos \theta)], \quad (22)$$

with

$$Z = \frac{1}{d} \int_0^d dz \int_0^1 d \cos \theta \exp[-\beta u_{\text{eff}}(z, \cos \theta)]. \quad (23)$$

The effective potential u_{eff} is given in (21), and the order parameters are given by

$$\begin{aligned} \sigma_n = \langle P_2(\cos \theta) \cos(nqz) \rangle &= \frac{1}{Z} \left\{ \frac{1}{d} \int_0^d dz \right. \\ &\times \left. \int_0^1 d \cos \theta P_2(\cos \theta) \cos(nqz) \exp[-\beta u_{\text{eff}}(z, \cos \theta)] \right\} \end{aligned} \quad (24)$$

$$\tau_n = \langle \cos(nqz) \rangle = \frac{1}{Z} \left\{ \frac{1}{d} \int_0^d dz \int_0^1 d \cos \theta \cos(nqz) \exp[-\beta u_{\text{eff}}(z, \cos \theta)] \right\}. \quad (25)$$

Equations (21)–(25) must be solved self-consistently. At each input temperature, three different solutions are possible depending on the model parameters α and δ : solutions with $\sigma_n = \tau_n = 0$ represent the I phase; solutions with $\sigma_0 \equiv \eta \neq 0$, $\sigma_n = \tau_n = 0$ for all $n \geq 1$ correspond to the N phase; and solutions with $\sigma_n \neq 0$, $\tau_n \neq 0$ correspond to the SmA phase. If the self-consistent equations accommodate more than one solution at a given temperature, the thermodynamic stable solution corresponds to the phase with lowest free energy.

2.3. Free energy

As shown in (9), the free energy can be expressed in terms of the average of the effective potential. From the final expression for u_{eff} given in (21), and using (24) and (25), one obtains the following expression for the free energy of McMillan's model in terms of the order parameters:

$$\frac{F}{NkT} = \frac{1}{2t} \sum_{n=0} \frac{2}{1 + \delta_{0n}} \left(\frac{\alpha}{2}\right)^{n^2} (\delta \tau_n^2 + \sigma_n^2) - \ln Z. \quad (26)$$

As expected, the free energy in the original McMillan's model ($\delta = 0$) only depends on the set of order parameters σ_n . In the most general case ($\delta \neq 0$), the free energy depends additionally on the order parameters τ_n . The free energy in McMillan's approximation is recovered by neglecting terms $n \geq 2$ in the above expansion. Recalling that $0 \leq \alpha \leq 2$, one may anticipate that these higher-order terms are likely to make a non-negligible contribution to the free energy for large values of the model parameter α .

3. The smectic A–nematic transition

As shown by McMillan [1, 2], the SmA–N transition may be either first order or continuous depending on the particular choice of the potential parameters. These two regimes are separated by a tricritical point, the exact location of which depends on the model parameters α and δ . In order to locate the line of continuous SmA–N transitions, as well as the tricritical point, we follow Meyer and Lubensky [18] and consider a Landau expansion of the free energy of the SmA phase f_A around that of the nematic phase f_N in powers of the order parameters, where $f \equiv F/NkT$. For simplicity, we present our derivation in some detail for the simplest original McMillan's model ($\delta = 0$) and outline the derivation for the more general case ($\delta \neq 0$) in the appendix.

According to (26), the free energy for $\delta = 0$ only depends on the set of mixed order parameters $\sigma = (\sigma_0, \sigma_1, \dots)$. If $\Delta \sigma = \sigma - \sigma_N$ are the deviations of the order parameters from

their values in the nematic phase, the expansion of the free energy reads

$$f_A(\boldsymbol{\sigma}) = f_N(\boldsymbol{\sigma}_N) + \frac{1}{2!} \sum_{ij} f_{\sigma_i \sigma_j} \Delta \sigma_i \Delta \sigma_j + \frac{1}{3!} \sum_{ijk} f_{\sigma_i \sigma_j \sigma_k} \Delta \sigma_i \Delta \sigma_j \Delta \sigma_k + \frac{1}{4!} \sum_{ijkl} f_{\sigma_i \sigma_j \sigma_k \sigma_l} \Delta \sigma_i \Delta \sigma_j \Delta \sigma_k \Delta \sigma_l + \dots, \quad (27)$$

where we have used the notation

$$f_{\sigma_i \sigma_j} = (\partial^2 f / \partial \sigma_i \partial \sigma_j),$$

$$f_{\sigma_i \sigma_j \sigma_k} = (\partial^3 f / \partial \sigma_i \partial \sigma_j \partial \sigma_k),$$

etc. All these derivatives are taken in the nematic phase. No linear terms appear in the above expansion as a result of the condition that f must be a minimum with respect to variations in the order parameters. From the stationary conditions $\partial f / \partial \sigma_n = 0$ it can be shown that the deviations of the order parameters in the neighbourhood of the SmA–N transition follow the asymptotic relations

$$\Delta \sigma_0 = \sigma_0 - \sigma_{0N} = \eta - \eta_N \sim \sigma_1^2,$$

$$\Delta \sigma_n = \sigma_n \sim \sigma_1^n \quad n \geq 2,$$

where we employ the usual convention of denoting the orientational order parameter (σ_0) by η . Considering these relations, and using the leading smectic order parameter σ_1 as an independent variable, the only terms in (27) that contribute to the free energy up to fourth order in σ_1 are

$$f_A = f_N + \frac{1}{2} f_{\sigma_1 \sigma_1} \sigma_1^2 + \frac{1}{2} f_{\sigma_0 \sigma_0} (\Delta \sigma_0)^2 + \frac{3}{3!} f_{\sigma_0 \sigma_1 \sigma_1} \Delta \sigma_0 \sigma_1^2 + \frac{1}{4!} f_{\sigma_1 \sigma_1 \sigma_1 \sigma_1} \sigma_1^4 + \frac{1}{2} f_{\sigma_2 \sigma_2} \sigma_2^2 + \frac{3}{3!} f_{\sigma_2 \sigma_1 \sigma_1} \sigma_2 \sigma_1^2 + \frac{2}{2!} f_{\sigma_0 \sigma_2} \Delta \sigma_0 \sigma_2. \quad (28)$$

The stationary conditions $(\partial f / \partial \sigma_0) = 0$ and $(\partial f / \partial \sigma_2) = 0$ allow expressing $\Delta \sigma_0$ and σ_2 , respectively, in terms of σ_1 . It is straightforward to show that $\Delta \sigma_0 = a_0 \sigma_1^2 + O(\sigma_1^4)$, and $\sigma_2 = a_2 \sigma_1^2 + O(\sigma_1^4)$ with

$$a_0 = -(1/2) f_{\sigma_0 \sigma_1 \sigma_1} / f_{\sigma_0 \sigma_0},$$

$$a_2 = -(1/2) f_{\sigma_2 \sigma_1 \sigma_1} / f_{\sigma_2 \sigma_2}.$$

After substitution in the expansion of the free energy (27), one finally obtains

$$f_A(\sigma_1) = f_N + A_2 \sigma_1^2 + A_4 \sigma_1^4 + O(\sigma_1^6), \quad (29)$$

where the Landau coefficients A_2 and A_4 are given in terms of the derivatives of the free energy as

$$A_2 = \frac{1}{2} f_{\sigma_1 \sigma_1},$$

$$A_4 = \frac{1}{2} f_{\sigma_0 \sigma_0} a_0^2 + \frac{1}{2} f_{\sigma_0 \sigma_1 \sigma_1} a_0 + \frac{1}{4!} f_{\sigma_1 \sigma_1 \sigma_1 \sigma_1} + \frac{1}{2} f_{\sigma_2 \sigma_2} a_2^2 + \frac{1}{2} f_{\sigma_2 \sigma_1 \sigma_1} a_2 + f_{\sigma_0 \sigma_2} a_0 a_2. \quad (30)$$

The line of continuous SmA–N transitions follows from the solution of the equation $A_2 = 0$ (with $A_4 > 0$); on the other hand, the tricritical point satisfies the set of equations $A_2 = 0$, $A_4 = 0$. The stability of the tricritical point requires the sixth-order coefficient in the expansion (29) to be positive. This coefficient was not calculated here. It is important to note that A_2 does not depend on terms $n \geq 2$, whereas A_4 does not depend on terms $n \geq 3$. As a consequence, differences are to be expected between the approximate and exact solutions for the tricritical point, and for the loci of the SmA–N critical points through the stability condition $A_4 > 0$. This has been previously noted by Longa [11]. After calculating the derivatives of the

free energy appearing in (30) in terms of the reduced temperature and model parameters, the equations for the continuous SmA–N transition line ((31) below) and the tricritical point ((31) and (32) below) are

$$A_2 = \frac{1}{2} \left(\frac{\alpha}{t} \right) \left[1 - \left(\frac{\alpha}{t} \right) \frac{S_2}{2} \right] = 0, \quad (31)$$

$$A_4 = \frac{1}{32} \left(\frac{\alpha}{t} \right)^4 \left[S_2^2 - \frac{1}{2} S_4 - \frac{(S_3 - \eta_N S_2)^2}{t - S_2 + \eta_N^2} - \frac{(\alpha/2)^4 S_3^2 / 2}{t - (\alpha/2)^4 S_2} \right] = 0, \quad (32)$$

where we have defined, following Kloczkowski and Stecki [17],

$$S_n = \langle [P_2(x)]^n \rangle_N \quad (33)$$

where the subscript N indicates that the average is taken over the nematic state (i.e., considering $\sigma_n = 0$ for $n \geq 1$). Equations (31) and (32) coincide with the corresponding equations obtained by Kloczkowski and Stecki [17] within McMillan's approximation, except for the last term on the left-hand side of (32), which is the contribution to A_4 due to the second-order terms ($n = 2$) not included in McMillan's approximation.

4. Numerical results

In the following, we consider the numerical solution of the molecular field theory based on McMillan's model formulated in section 2, focusing on the differences between predictions based on the approximate and exact mean-field solutions of the model. We recall that the latter solution follows from the full expansion of the effective potential keeping as many terms as necessary to obtain the desired numerical accuracy.

In practice, we make use of an iterative scheme to minimize the free energy and to obtain the corresponding values of the order parameters and thermodynamic properties for various combinations of the model parameters α and δ . Using a maximum of five ($n = 5$) terms in the Fourier–Legendre expansion of the effective potential ensures a numerical accuracy in the free energy better than a part in 10^8 for the values of model parameters considered here. For values of α close to its maximum value (i.e. $\alpha = 2$), the series converges rather slowly and more terms are required to achieve the above-mentioned accuracy; however, we did not consider the numerical solution of the model for these extreme values of α . The numerical scheme involves the following steps. For selected values of the model parameters α and δ , and for each input value of the temperature t , we consider an input guess for the set of order parameters $\sigma_0, \dots, \sigma_n$ and τ_1, \dots, τ_n . The corresponding effective potential and one-particle density are then obtained from (21) and (22) for a discrete set of values of the spatial and angular variables. Here, we use a grid of 10 points for each variable in the corresponding integration range $0 \leq z/d \leq 1$, and $0 \leq \cos \theta \leq 1$. The one-particle density allows us to calculate a new set of order parameters from (24) and (25). All integrations are performed using a 10-point Gauss–Legendre quadrature [19]. This process is repeated until two successive distributions $\rho(z, \cos \theta)$ are found to differ by less than 10^{-10} for all values of z and $\cos \theta$. When convergence is so achieved, the resulting $\rho(z, \cos \theta)$ corresponds to the equilibrium one-particle density, which in turn allows us to determine the values of the order parameters, and therefore the nature of the most stable phase, as well as the corresponding thermodynamic properties at the prescribed temperature.

The variation of the leading order parameters ($\eta \equiv \sigma_0$, $\sigma \equiv \sigma_1$, and $\tau \equiv \tau_1$) with temperature is shown in figure 1 for the choice of model parameters $\alpha = 0.85$, and $\delta = 0$. For this choice the SmA–N transition is first order. According to the approximate scheme, the value of the transition temperature is $t_{AN}/t_{NI} = 0.9406$, a value slightly lower than the exact

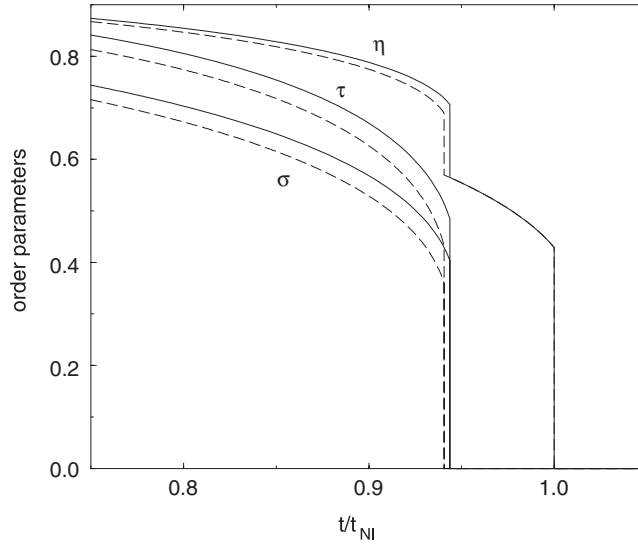


Figure 1. Variation of the leading order parameters η , σ , and τ (see the text for their definition) with reduced temperature t in McMillan's model with parameters $\alpha = 0.85$, and $\delta = 0$. The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation. The temperature is expressed in units of the reduced N–I transition temperature t_{NI} .

value ($t_{\text{AN}}/t_{\text{NI}} = 0.9436$). Here, $t_{\text{NI}} = 0.22019$ corresponds to the N–I transition temperature, which coincides with the value obtained within the Maier–Saupe theory. The effects of the neglected harmonics become more apparent when the variation with temperature of the degree of order and thermodynamic properties of the SmA phase is analysed. From figure 1 we infer that the approximate solution underestimates the values of the order parameters in the SmA phase at all temperatures $t < t_{\text{NA}}$. The effect of the truncation at the first-harmonic level on the thermodynamic properties of the SmA phase is illustrated in figure 2, where we display the variation of the internal energy $U/(NkT)$ and entropy $S/(Nk)$ with temperature for the same set of model parameters ($\alpha = 0.85$, and $\delta = 0$). According to figure 2, the absolute magnitudes of both thermodynamic properties are systematically underestimated at all temperatures in the SmA phase within McMillan's approximation.

We now turn to analysing the effect of neglecting higher-order harmonics on the stabilization of the smectic phase and on the nature of the SmA–N and SmA–I transitions. The phase diagram of McMillan's model as a function of α is shown in figure 3 for selected values of the model parameter δ . Also included for comparison are the corresponding transition lines obtained within McMillan's approximation. The SmA–N transition is continuous for $\alpha < \alpha_{\text{tc}}$ and turns first order for $\alpha_{\text{tc}} < \alpha < \alpha_{\text{tp}}$. Here, α_{tc} locates the tricritical point (tc) and α_{tp} the triple point (tp) for each value of δ . For $\alpha > \alpha_{\text{tp}}$, the N phase is no longer stable and the SmA phase melts directly into the I phase upon heating, the transition being first order. Values for the tricritical and triple point parameters are included in table 1 for selected values of δ . As t_{NI} does not depend on the model parameters α and δ , it follows that $t_{\text{tp}}/t_{\text{NI}} = 1$. The tricritical points are obtained by solving numerically the set of equations $A_2 = 0$, and $A_4 = 0$, where the Landau coefficients A_2 and A_4 are given in (A.2) and (A.3). Our numerical results for the tricritical parameters are found to be in full agreement with those reported by Longa [11]. It is found that the relative difference between the approximate and exact values of the tricritical temperatures is small and decreases with increasing δ , which indicates that the second-order

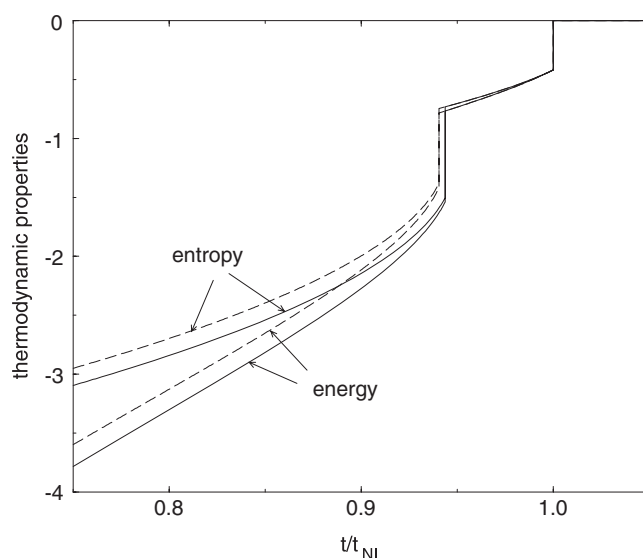


Figure 2. Variation of the entropy $S/(Nk)$ and the internal energy $U/(NkT)$ with reduced temperature t in McMillan's model with parameters $\alpha = 0.85$, and $\delta = 0$. The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation. The reduced temperature is expressed in units of the N–I transition temperature t_{NI} .

harmonic has little effect in the tricritical region. The lines of continuous SmA–N transitions for $t < t_{tc}$ are obtained by solving $A_2 = 0$. This equation contains no contributions from harmonics $n > 1$ and therefore no differences between the exact and approximate solutions are to be expected, as can be observed in figure 3. The lines of first-order SmA–N (for temperatures $t_{tc} < t < t_{tp}$) and SmA–I transitions (for temperatures $t > t_{tp}$) are calculated by equating the free energy of the corresponding phases according to (26). As can be seen in figure 3, the explicit consideration of the terms neglected in McMillan's approximation does not bring about qualitative changes in the topology of the phase diagram of the model. Whenever the SmA–N transition is continuous, the neglected harmonics are proportional to order parameters which vanish at t_{NA} and, as a result, including these new terms does not give rise to shifts in the transition temperatures. However, this is no longer the case when the transition from the SmA to the I or N phases happens to be first order. In this case, a description based on the truncation scheme at the level of $n = 1$ is seen to underestimate the values of the transition temperatures: the relative difference between the exact and approximate predictions becomes increasingly important with increasing α or decreasing δ .

We include in table 2 numerical results for a number of properties at the first-order SmA–N and SmA–I transitions for selected values of the parameter α with $\delta = 0$. For this value of δ , we find $\alpha_{tc} = 0.6951$ and $\alpha_{tp} = 0.9659$ (see table 1). An inspection of the data included in table 2 shows that the order parameters, excess orientational order, and entropy change at the transitions are systematically underestimated within the truncated scheme. Differences between the approximate and exact values are seen to become increasingly large with increasing value of the model parameter α .

Numerical results are presented in figures 4 and 5 for the values of the leading order parameters at the SmA–N and SmA–I transitions, respectively, in McMillan's model for different values of δ . In all cases, it is observed that neglecting harmonics $n \geq 2$ underestimates the degree of order at both transitions, the effect being increasingly noticeable for decreasing

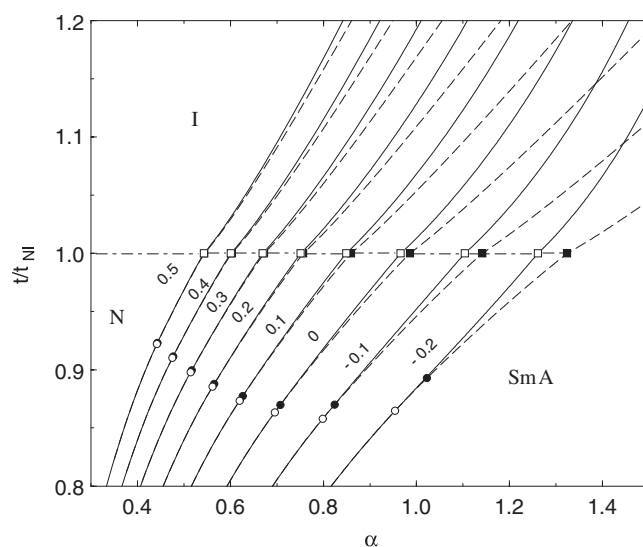


Figure 3. Phase diagram of McMillan's model in terms of the model parameter α and different values of δ shown as labels on the curves. The lines separate the regions of stability of the isotropic (I), nematic (N) and smectic A (SmA) phases. The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation; the dashed-dotted line is the N-I transition line. The circles locate the tricritical points on the SmA-N transition lines and the squares the triple points. Open symbols are for the exact solution, and filled symbols are for the approximate solution.

Table 1. Comparison between the approximate and exact locations of the SmA-N tricritical (tc) and the triple (tp) points for selected values of the model parameter δ in McMillan's model. t is the reduced temperature and $t_{NI} = 0.22019$ is the reduced N-I transition temperature. Note that $t_{tp}/t_{NI} = 1$ for all values of δ .

δ	Approximate			Exact		
	α_{tc}	t_{tc}/t_{NI}	α_{tp}	α_{tc}	t_{tc}/t_{NI}	α_{tp}
-0.2	1.0222	0.8927	1.3241	0.9542	0.8647	1.2611
-0.1	0.8239	0.8698	1.1414	0.7985	0.8578	1.1039
0.0	0.7070	0.8696	0.9858	0.6951	0.8632	0.9659
0.1	0.6261	0.8772	0.8592	0.6196	0.8733	0.8488
0.2	0.5650	0.8878	0.7564	0.5612	0.8852	0.7508
0.3	0.5165	0.8995	0.6721	0.5141	0.8977	0.6691
0.4	0.4766	0.9113	0.6022	0.4750	0.9101	0.6005
0.5	0.4428	0.9229	0.5436	0.4417	0.9219	0.5426

values of δ . The difference between the exact and approximate results becomes particularly large at the SmA-I transition, as the transition temperature—and correspondingly, the model parameter α —increases.

Finally, we show in figure 6 the model predictions of the transition entropy at the first-order SmA-N and SmA-I transitions versus transition temperature. The solid lines correspond to the exact values and the dashed lines correspond to the predictions within McMillan's approximation. Though the experimental trend (increasing absolute values of the transition entropy with increasing temperature ratio t_{AN}/t_{NI}) is correctly predicted, it is known that

Table 2. Comparison between the approximate and exact numerical results for properties at the first-order SmA–N and SmA–I transitions for selected values of the model parameter α in McMillan’s model with $\delta = 0$. The transition temperatures are expressed in terms of the reduced N–I transition temperature $t_{NI} = 0.22019$, $\Delta\eta$ is the excess orientational order at the transition, σ and τ are the mixed and translational order parameters at the SmA side of the transition, respectively. $\Delta S_{AN} = S_A - S_N$ is the entropy change at the SmA–N transition, and $\Delta S_{AI} = S_A - S_I$ is the corresponding change at the SmA–I transition in units of Nk .

α	Approximate					Exact				
	t_{AN}/t_{NI}	$\Delta\eta$	σ	τ	ΔS_{AN}	t_{AN}/t_{NI}	$\Delta\eta$	σ	τ	ΔS_{AN}
0.85	0.9406	0.119	0.359	0.432	−0.628	0.9436	0.142	0.404	0.485	−0.770
0.90	0.9634	0.170	0.407	0.488	−0.844	0.9683	0.201	0.458	0.548	−1.033
0.95	0.9852	0.231	0.447	0.534	−1.069	0.9925	0.277	0.505	0.602	−1.323
α	t_{AI}/t_{NI}	$\Delta\eta$	σ	τ	ΔS_{AI}	t_{AI}/t_{NI}	$\Delta\eta$	σ	τ	ΔS_{AI}
1.00	1.0044	0.723	0.487	0.580	−1.719	1.0131	0.754	0.557	0.660	−1.994
1.05	1.0207	0.739	0.525	0.623	−1.859	1.0342	0.770	0.599	0.707	−2.167
1.10	1.0380	0.749	0.552	0.653	−1.916	1.0575	0.783	0.632	0.742	−2.315
1.20	1.0744	0.762	0.589	0.693	−2.108	1.1107	0.802	0.684	0.780	−2.577
1.50	1.1916	0.779	0.646	0.752	−2.349	1.3497	0.845	0.792	0.906	−3.320

McMillan’s approximation overestimates the experimental values [1]. As follows from earlier discussion, when the terms neglected in McMillan’s approximation are explicitly considered the transition to the SmA phase is found to be more strongly first order, which in turn results in values for the transition entropy larger than those resulting in McMillan’s approximation. This is clearly illustrated in figure 6. We then conclude that the lack of quantitative agreement is not to be attributed to the truncation scheme. One of the reasons for this discrepancy is probably related to the use of a mean-field approximation [1, 2] in which contributions to the free energy arising from fluctuations of the order parameters are neglected. Additionally, any molecular theory aiming for quantitative accuracy should include the packing effects of anisotropic hard cores, an ingredient that is lacking in McMillan’s model.

5. Conclusion

McMillan’s model is arguably the simplest molecular model for the SmA liquid crystalline phase. Smectic ordering in the model is due to the anisotropic attractive intermolecular interactions: hard-core repulsions are not explicitly considered, although their effects are obviously expected to be of importance in a more general description of real smectics. An approximate solution of the model can be obtained within the framework of the mean-field approximation. It is common practice to consider a further simplification that implies truncation of the one-particle density (or, similarly, of the effective one-particle potential) at the level of the first harmonic in the Fourier expansion. This is what has been referred to here as McMillan’s approximation, which leads to a formulation of the properties of the smectic A phase in terms of the dominant order parameters η , σ , and τ . Here, we have solved McMillan’s model—still within the mean-field approximation—with explicit consideration of higher-order harmonics. A comparison with the numerical calculations obtained within McMillan’s approximation has allowed us to assess the relative importance of these (neglected) terms in the description of the properties of the SmA phase.

According to our results, including additional harmonics does not affect the predictions of t_{NA} for those combinations of model parameters for which the SmA–N transition is

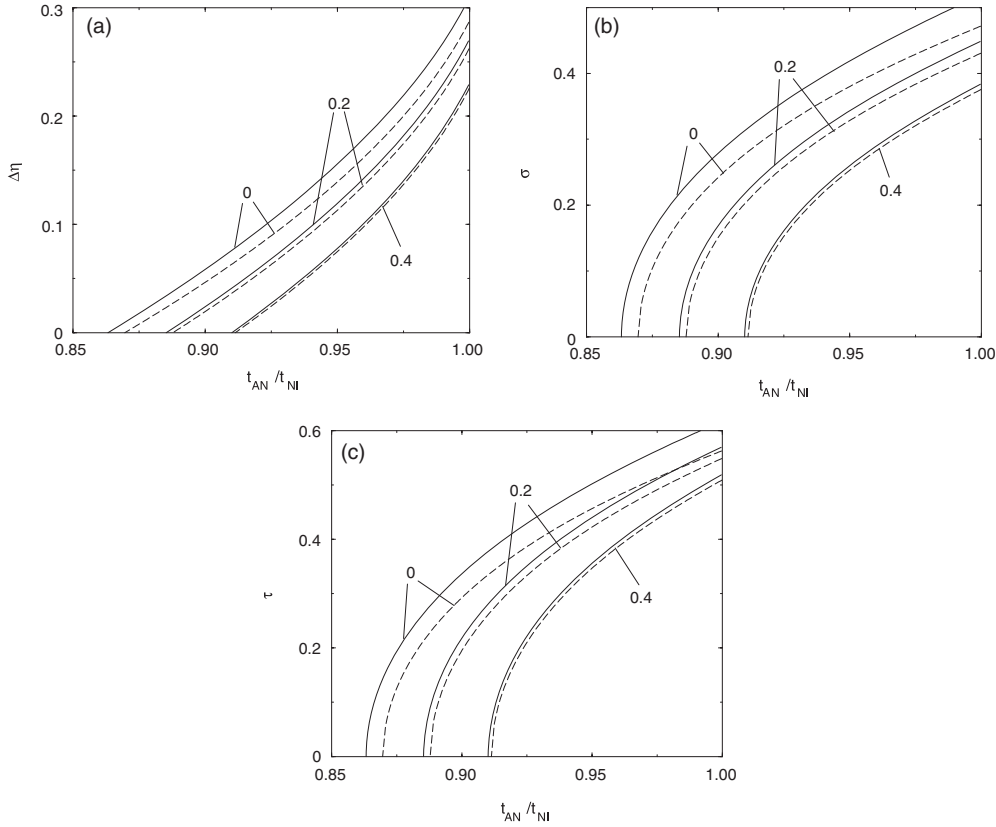


Figure 4. The values of the leading order parameters at the SmA–N transition for different values of the model parameter δ , shown as labels on the plot: (a) the excess orientational order parameter $\Delta\eta = \eta_A - \eta_N$, (b) the mixed order parameter σ , and (c) the translational order parameter τ . The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation. The temperature t_{AN} at the SmA–N transition is expressed in units of the reduced N–I transition temperature t_{NI} .

continuous: in agreement with previous findings [11], the truncation scheme implicit in McMillan's approximation has no effect on the location of the continuous SmA–N transition whatsoever. The tricritical temperature is fully determined by terms involving the first and second harmonics: the latter are not included in McMillan's approximation, but their explicit consideration essentially brings about only small corrections to the tricritical temperature. Whenever the transition involving the SmA phase is first order, a theoretical description based on the dominant order parameters (McMillan's approximation) is seen to shift the transition temperatures to slightly lower values: this shift becomes quantitatively important with increasing values of α and decreasing values of δ . Additionally, McMillan's approximation is seen to systematically underestimate the degree of orientational and translational order in the SmA phase at all temperatures, and at the SmA–I and SmA–N transitions. Also, a formulation based on the truncated expansion underestimates the absolute magnitude of thermodynamic properties, such as the free energy, entropy, energy, and specific heat (not shown here) of the SmA phase at all temperatures, as well as their changes at the first-order SmA–N and SmA–I transitions. In general, these differences are seen to grow with increasing values of the model parameter α , i.e., as the corresponding transition turns more strongly first

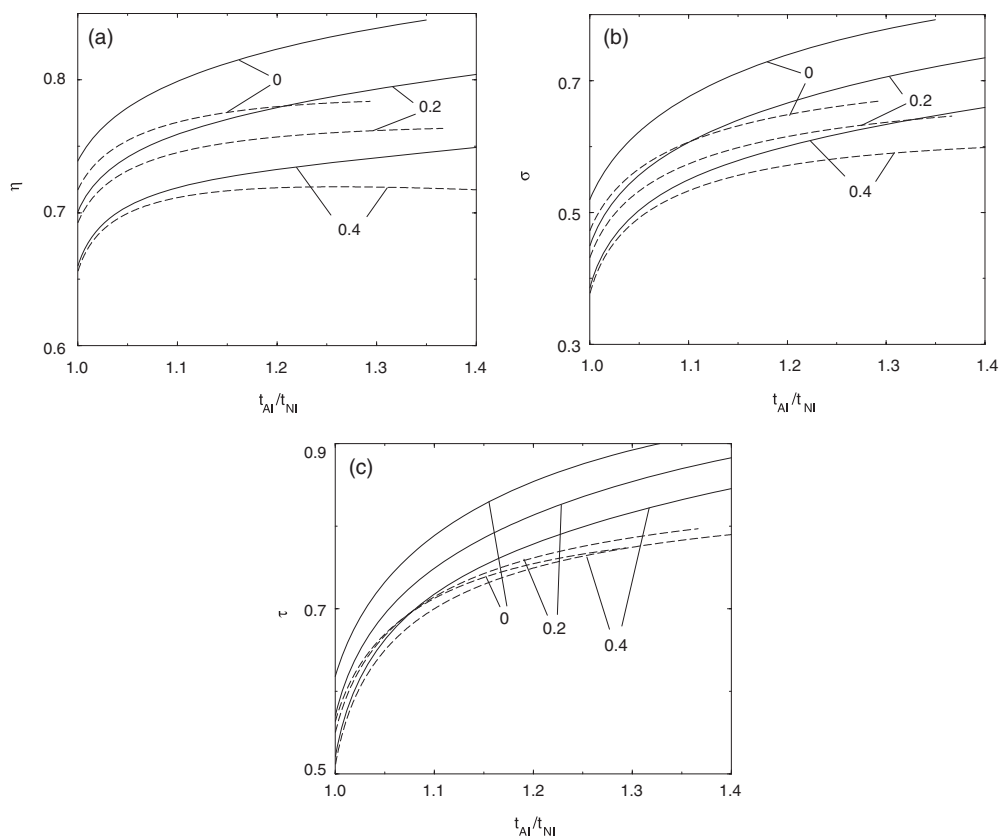


Figure 5. The values of the leading order parameters at the SmA–I transition for different values of the model parameter δ , shown as labels on the plot: (a) the orientational order parameter η , (b) the mixed order parameter σ , and (c) the translational order parameter τ . The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation. The temperature t_{AI} at the SmA–I transition is expressed in units of the reduced N–I transition temperature t_{NI} .

order. One should bear in mind that it is standard practice to correlate model parameters and molecular structure in smectic compounds from measurements of transition properties, such as the transition temperature, entropy of transition, and changes in order parameters, when the transition involving the smectic phase is first order [10]. According to our results, the lack of quantitative agreement between theoretical predictions and experimental data for the transition entropy (and, presumably, for other quantities) is not a consequence of the truncation assumed in McMillan's approximation. Among other factors, these differences are likely to be due to the oversimplified form of the interactions and the use of the mean-field approximation.

We finally remark that a truncated approximation has also been used in closely related problems involving McMillan's model. For example, this approximation was considered by Hama [20] to investigate the effects of an orienting (magnetic or electric) field on the (first-order) SmA–N transition. As shown by Hama, a field-induced tricritical point is predicted as the intensity of the external field is increased. This prediction remains valid when the full mean-field treatment considered here is carried out. Quantitatively, however, the truncated approximation is found to underestimate the values of the tricritical field by as much as 30–70%, depending on the model parameters. Similarly, one might anticipate that quantitative discrepancies between the truncated approximation and the full treatment will occur in the

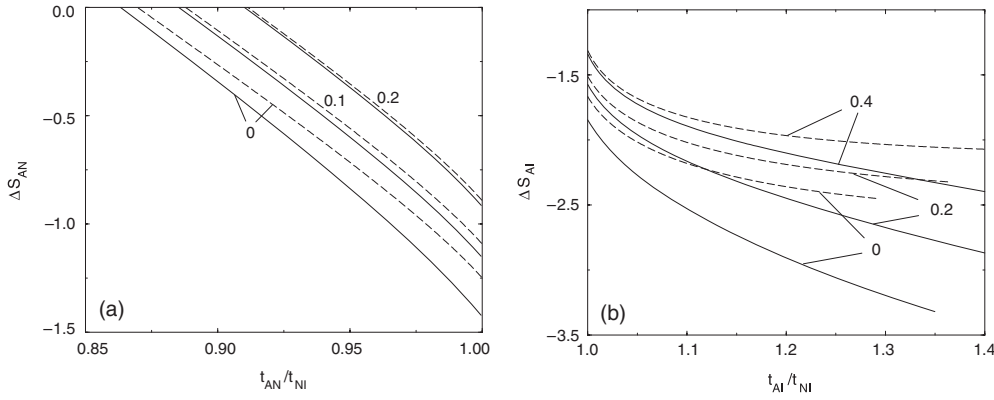


Figure 6. The entropy change at the (a) SmA–N transition $\Delta S_{AN} = S_A - S_N$, and (b) SmA–I transition $\Delta S_{AI} = S_A - S_I$, as a function of the transition temperatures (in units of the reduced N–I transition temperature t_{NI}) for several values of the model parameter δ shown as labels on the plot. The solid lines correspond to the exact solution; the dashed lines correspond to McMillan's approximation.

description of the properties of the first-order nematic–columnar transition within the extension of McMillan's model to discotic liquid crystals [21].

Acknowledgments

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Appendix

Here we outline the derivation of the equation of the critical lines and tricritical points arising in McMillan's model with $\delta \neq 0$ (general case). In this case, the free energy depends not only on the set of order parameters σ but also on the set of translational order parameters $\tau = (\tau_1, \tau_2, \dots)$. An expansion of the free energy of the SmA phase in terms of the order parameters contains, in addition to the terms appearing in (28), contributions from τ , as well as contributions coupling σ and τ . From the stationary conditions $(\partial f / \partial \tau_n) = 0$ one can show that the following asymptotic relations hold in the neighbourhood of the SmA–N transition:

$$\Delta \tau_n = \tau_n \sim \sigma_1^n \quad n \geq 1.$$

Using these asymptotic relations, the extra terms up to fourth order in σ_1 appearing in the free energy given in (28) are

$$\begin{aligned} & \frac{1}{2} f_{\tau_1 \tau_1} \tau_1^2 + \frac{1}{2} f_{\tau_2 \tau_2} \tau_2^2 + f_{\sigma_0 \tau_2} \Delta \sigma_0 \tau_2 + f_{\sigma_1 \tau_1} \sigma_1 \tau_1 + f_{\sigma_2 \tau_2} \sigma_2 \tau_2 \\ & + \frac{3}{3!} f_{\sigma_0 \tau_1 \tau_1} \Delta \sigma_0 \tau_1^2 + \frac{3}{3!} f_{\tau_2 \sigma_1 \sigma_1} \tau_2 \sigma_1^2 + \frac{3}{3!} f_{\sigma_2 \tau_1 \tau_1} \sigma_2 \tau_1^2 \\ & + \frac{3}{3!} f_{\tau_2 \tau_1 \tau_1} \tau_2 \tau_1^2 + \frac{6}{3!} f_{\sigma_0 \sigma_1 \tau_1} \Delta \sigma_0 \sigma_1 \tau_1 + \frac{6}{3!} f_{\sigma_1 \sigma_2 \tau_1} \sigma_1 \sigma_2 \tau_1 \\ & + \frac{6}{3!} f_{\sigma_1 \tau_1 \tau_2} \sigma_1 \tau_1 \tau_2 + \frac{4}{4!} f_{\sigma_1 \sigma_1 \sigma_1 \tau_1} \sigma_1^3 \tau_1 + \frac{6}{4!} f_{\sigma_1 \sigma_1 \tau_1 \tau_1} \sigma_1^2 \tau_1^2 \\ & + \frac{4}{4!} f_{\sigma_1 \tau_1 \tau_1 \tau_1} \sigma_1 \tau_1^3 + \frac{1}{4!} f_{\tau_1 \tau_1 \tau_1 \tau_1} \tau_1^4. \end{aligned} \quad (\text{A.1})$$

The stationary conditions can be solved for the order parameters $\Delta\sigma_0$, σ_2 , τ_1 , and τ_2 in terms of σ_1 . After substitution in the expansion of the free energy we obtain a Landau free energy (see (29)) with coefficients

$$A_2 = A_2^{\text{app}} + A_2^{\text{new}}, \quad (\text{A.2})$$

$$A_4 = A_4^{\text{app}} + A_4^{\text{new}}, \quad (\text{A.3})$$

where the superscript ‘app’ indicates the corresponding value obtained within McMillan’s approximation ($\sigma_n = \tau_n = 0$ for all $n \geq 2$) and ‘new’ refers to the extra contribution arising from higher-order ($n = 2$) terms. After some algebra, one finds

$$A_2^{\text{app}} = \frac{1}{2} \left(\frac{\alpha}{t} \right) \left[1 - \left(\frac{\alpha}{t} \right) \frac{S_2}{2} - \frac{(\alpha/t)^2 \eta_N^2 \delta / 4}{1 - (\alpha/t) \delta / 2} \right] \quad (\text{A.4})$$

$$A_2^{\text{new}} = 0 \quad (\text{A.5})$$

where η_N is the orientational order parameter in the nematic phase, and S_2 is defined in (33); the Landau coefficient A_4 is given by

$$A_4^{\text{app}} = \frac{1}{32} \left(\frac{\alpha}{t} \right)^4 \left\{ S_2^2 - \frac{1}{2} S_4 + 2(2S_2 \eta_N - S_3) X + (4\eta_N^2 - S_2) X^2 + 2\eta_N X^3 + \frac{1}{2} X^4 - \frac{[(S_3 - S_2 \eta_N + 2(S_2 - \eta_N^2) X)]^2}{t - S_2 + \eta_N^2} \right\} \quad (\text{A.6})$$

$$A_4^{\text{new}} = \frac{-1}{32} \left(\frac{\alpha}{t} \right)^4 B \{ [t - (\alpha/2)^4 \delta] (S_3 + 2S_2 X + \eta_N X^2)^2 + [t - (\alpha/2)^4 S_2] (S_2 + 2\eta_N X + X^2)^2 \delta + 2(\alpha/2)^4 \eta_N (S_3 + 2S_2 X + \eta_N X^2) (S_2 + 2\eta_N X + X^2) \delta \} \quad (\text{A.7})$$

where we have defined X and B as

$$X = \frac{(\alpha/t) \eta_N \delta}{2 - (\alpha/t) \delta}, \quad (\text{A.8})$$

$$B = \frac{(\alpha/2)^4 / 2}{[t - (\alpha/2)^4 S_2] [t - (\alpha/2)^4 \delta] - (\alpha/2)^8 \eta_N^2 \delta}. \quad (\text{A.9})$$

The lines of SmA–N critical points follow from the solution of the equation $A_2 = 0$, and the tricritical points from the solution of the set of equations $A_2 = 0$, $A_4 = 0$. These equations reduce to (31) and (32) for the case $\delta = 0$. As shown in section 3, higher-order harmonics make no contribution to A_2 ($A_2^{\text{new}} = 0$), but they do contribute to A_4 ($A_4^{\text{new}} \neq 0$). If these contributions are neglected, one recovers the corresponding equations obtained by Kloczkowski and Stecki [17] within McMillan’s approximation.

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