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NEMATIC SMECTIC-A TRICRITICAL POINTS FOR NONSEPARABLE INTERACTIONS.

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Abstract Realistic interactions in liquid crystals depend not only on the relative orientation of the molecules but also on the orientation of the radius vector connecting molecular centers. The last feature of the interactions is commonly referred to as nonseparability. In this presentation we address the question how nonseparability influences the nematic-smectic A tricritical behaviour in classical and strongly polar liquid crystals. We study the influence of this effect on the classical nematic-smectic A and the nematic-smectic A2 phase transitions. Detailed calculations are presented for some mean-field free energies.

INTRODUCTION

In microscopic theories of liquid crystal phases the molecules are usually described as axially symmetric, rigid rods. Although these assumptions certainly are not correct, in the rigid rod model a minimal number of relevant degrees of freedom is present. Namely, a molecule can be specified by the position of its centre of mass and by the unit vector R describing the orientation of the long molecular axis with respect to a laboratory-fixed coordinate system [1-3].

Consequently, a general pair interaction, V(1,2), between axially symmetric, rigid molecules depends only on the intermolecular separation $\vec{r}$ and on the orientations R_1 and R_2 of the molecules 1 and 2, respectively. It can be written as[3]

$$V_{soft}(1,2) = \sum_{LL'J} V_{LL'J}(r) \sum_{m,m'M} \begin{pmatrix} L & L' & J \\ m & m' & M \end{pmatrix} Y^{L}_{m}(R_1) Y^{L'}_{m'}(R_2) Y^{J}_{M}(\hat{r}) \qquad (1)$$

where $\begin{pmatrix} L & L' & J \\ m & m' & M \end{pmatrix}$ are the 3j-symbols and where Y_m^L are the spherical harmonics. For the nonchiral molecules L + L' + J must be even. Identical molecules additionally satisfy $V_{LL'J} = V_{L'LJ}$.

Simpler forms of the intermolecular interactions that depend on the relative orientation between the molecular long axes only, have intensively been studied so far [4-7]. In this case of so-called separable potentials, the intermolecular interaction is independent of the orientation of the radius vector connecting molecular centers. Formally it corresponds to J = M = 0 in the expansion (1).

Our purpose here is to investigate the influence of nonseparability of the dispersive interactions on the nematic-smectic A tricritical behaviour within the frame of the mean field approach. In the lowest order the nonseparability is described by the terms (L,L',J) = (2,0,2), (0,2,2) in (1). While these terms are not necessarily directly responsible for the stability of various smectic-A phases, they may influence the character of the phase transitions.

THEORY

In orthogonal smectic A phases one-dimensional density wave of the molecular centers is formed in the nematic background, parallel to the director, say $\hat{z}$-direction of a cartesian coordinate system [2,8]. Among these we distinguish the classical smectic A (S_A) and antiferroelectric smectic A2 (S_{A2}) phases. In the S_A phase the layer thickness is (nearly) equal to the length l of the free molecule in the all-trans-conformations while in the S_{A2} phase a doubling of periodicity is observed compared with the S_A. This observation is interpreted as a long-range, antiferroelectric ordering of neighbouring single layers.

An attractive feature connected with S_A and S_{A2} phases is that the associated phase transitions to nematic phase may be of the first or the second order. Furthermore, at the tricritical point many characteristics are similar to those observed for classical tricritical points[9]. Thus, mean

field theories can be used to, at least, classify phase diagrams and correlate their features with molecular properties.

An important ingredient of such theories is the one-particle distribution function P(1). For smectic A phases P(1) can be parametrized using θ and z only, where θ is the angle between $\hat{z}$ and the long molecular axis. The antiferrroelectric symmetry additionally implies that [7]

$$P(\cos\theta,z) = P(\cos\theta,z + 2d)$$
$$P(\cos\theta,z) = P(-\cos\theta,z + d); \qquad (2a)$$

where 2d is the double layer spacing ($d\approx l$) of A_2 phase

The restrictions (2a) lead to the order parameter expansion of P(1) in terms of Y_m^L and Fourier series

$$P(\cos\theta,z) = 1 + 2\sum_{L,n=0} \zeta_{2L+1,2n+1} Y_0^{2L+1}(\cos\theta)\cos((2n+1)qz) + \sum_{L=1} \eta_{2L} Y_0^{2L}(\cos\theta) + 2\sum_{n=1} \tau_{2n}\cos(2nqz) + \sum_{L,n=1} \sigma_{2L,2n} Y_0^{2L}(\cos\theta)\cos(2nqz) \qquad (2b)$$

where P satisfies standard normalization condition and where $\{x_{L,n}\} \equiv \{\zeta_{L,n},\eta_L,\tau_n,\sigma_{L,n}\}$ are the order parameters [7].

Four different phases are described by the distribution (2): A. Isotropic : all order parameters vanish ; B. Nematic : only $\eta_{2L} \neq 0$; C. Smectic-A: only $\zeta_{2L+1,2n+1} = 0$; and D. Smectic-A_2: all order parameters are nonzero. Only these phases can minimize a free energy functional when the restrictions (2a) are imposed.

The calculations of tricritical points from such theories require the use of advanced computer techniques. These can considerably be simplified by utilizing the method proposed elsewhere[6,7]. By substituting the expansion (1) into the mean-field free energy [7] with the soft part of the interaction approximated by the terms (LL'J) = (110), (000), (220), (202), and (022) and by using the method described

in[7], we find the resulting topologies of the nematic-smectic phase diagrams. They depend on four effective model parameters V_0, V_2, V_1 and V_n, and on reduced temperature $t = k_BT/(\rho|V_{2200}|)$, where $V_{LL',Jm} = -\int d^3\vec{r}\ V_{LL',J}(r)\cos(2\pi zm/2d)$ and where $V_0 = V_{0002}/|V_{2200}|$, $V_2 = V_{2202}/|V_{2200}|$, $V_1 = V_{1101}/|V_{2200}|$, $V_n = V_{2022}/|V_{2200}| = V_{0222}/|V_{2200}|$. The above parameters can be interpreted as the averaged energies of the system, associated with the pure states described by τ_2, $\sigma_{2,2}$, and $\zeta_{1,1}$, respectively, relative to the state associated with η_2. The parameter V_n is a measure of nonseparability of dispersive interactions. It allows to distinguish between 2-particle configurations with fixed distance between centers of mass of the molecules and with fixed relative angle R_{12} between the long molecular axes.

In order to study the effect of V_n on the stability of the smectic-A ordering, we performed more general calculations of the nematic-smectic critical temperatures using the formalism discussed in[7]. It yields

$$V_0 = \frac{\eta_{22}V_2 t + (\eta_{22} - \eta_2^2)V_n^2 + 2\eta_2 V_n t - t^2}{(\eta_{22} - \eta_2^2)V_2 - t} \quad (NS_A \text{ transition}) \qquad (3a)$$

$$V_1 = 3t/(2\eta_2 + 1) \qquad (NS_{A2} \text{ transition}^{7}) \qquad (3b)$$

where $\eta_2 \equiv \eta_2(t) \equiv \langle Y_0^2 \rangle^0$ is the nematic order parameter calculated in the nematic phase and where $\eta_{22} = \langle (Y_0^2)^2 \rangle^0$. Typical results of the numerical calculations for the NS_A phase transition are shown in Figure 1. In general, the critical temperature is lowered as compared with the case $V_n = 0$. Contrary to what was found for the classical NS_A transition , the NS_{A2} critical temperature is independent of V_n and is characterized by a high degree of universality, Eq.(3b) .The tricritical values of model parameters are illustrated in Figures 2-3 (for comparison see also [7]).

The results as given indicate the importance of the nonseparability of dispersive interactions on the character of the NS_A phase transition. As seen from Figures 2-3 the general trend is that nonzero, positive value of V_n shift

the tricritical temperature to higher values.

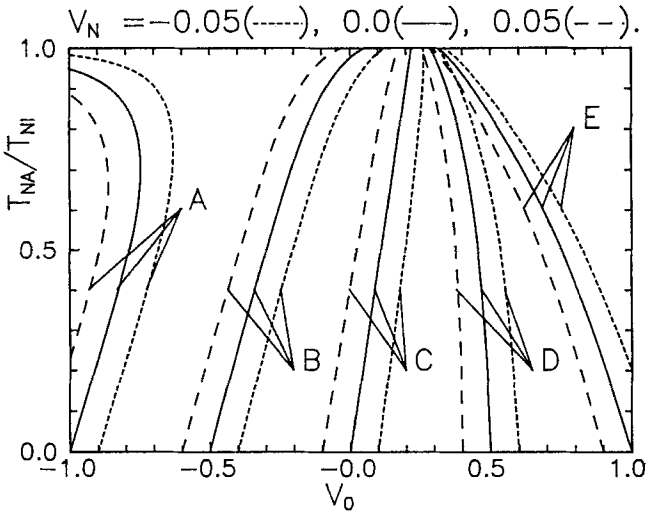

FIGURE 1. Nematic-smectic A critical temperature for nonseparable interactions. Curves labeled A, B, C, D, and E correspond to V_2= 1.0, 0.50, 0.0, -0.50, and -1.0 respectively.

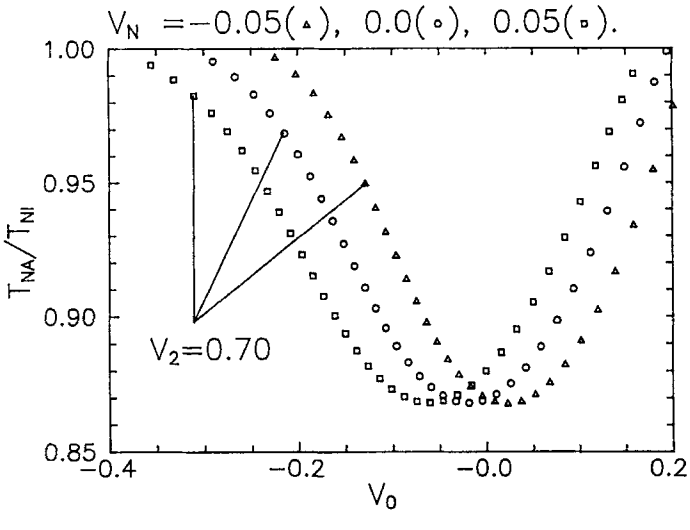

FIGURE 2. Nematic-smectic A tricritical temperature for nonseparable interactions for different values of V_N and V_2. Values of V_2 decrease from left to right and two adjacent points differ in V_2 by 0.02.

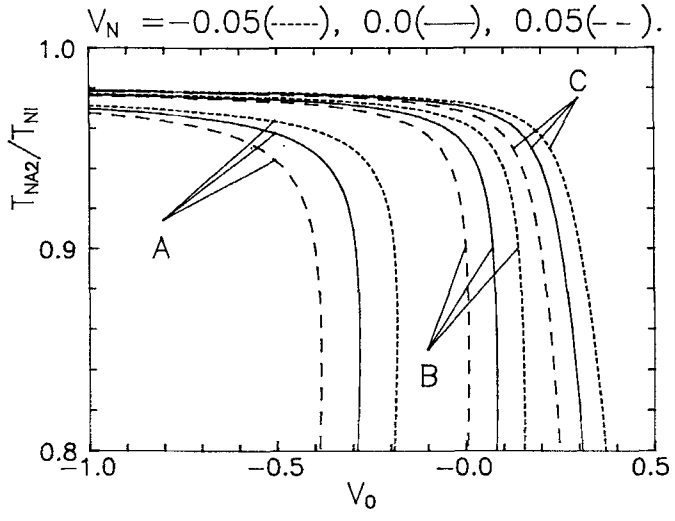

FIGURE 3. Nematic-smectic A2 tricritical temperature for nonseparable interactions for different values of V_N and V_2. Curves labeled A, B, and C correspond to V_2= 0.5, 0.0, and -0.5 respectively.

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