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Microscopic one-particle description of reentrant behavior in nematic liquid crystals

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Reentrant behavior in nematic liquid crystals is described by the treatment of the system as a mixture of monomers and dimers interacting through attractive induced soft interactions as well as hard-core repulsions. It is shown that the induced forces between dimers, monomers, and between monomers and dimers, respectively, under suitable conditions of temperature and density lead to a smectic layer structure with a period equal to the length of the dimer. However, with decreasing temperature or increasing density, repulsive steric forces, due to the unfavorable packing of the dimers in the smectic planes, may take over and thus favor the nematic phase again. In agreement with experiment the best conditions to get a reentrant nematic phase are predicted for the ratio of the length of the dimer to that of the monomer between 1.3 and 1.4. The predictions of the model are in good agreement with currently available experimental data. In principle, the model applies also to discotic liquid crystals.

I. INTRODUCTION

A considerable amount of evidence has become available that liquid crystals consisting of molecules with a strongly polar end group (usually CN, but also NO_2) differ in many aspects from the more classical liquid crystals. These differences refer to the physical properties, or even to the very existence of the liquid-crystalline phases. The most spectacular effect is the occurrence with decreasing temperature of the phase sequence nematic—smectic-*A*—reentrant nematic, first observed by Cladis in a mixture of two *para*cyano substituted compounds.[1] Later, it was also observed in a pure compound[2] at high pressure and, finally, even in pure compounds at atmospheric pressure.[3] In the cases studied up to now, the period of the density wave of the intermediate smectic-*A* phase is not commensurate with the molecular length d (as is usually the case for classical liquid crystals), but varies for different compounds from $1.1d$ up to $1.6d$.[4]

A phenomenological Landau theory has been given to account for the reentrant behavior.[5] This involves the notion of an optimum density for stabiliziation of the S_A phase. However, in this way no explanation is offered for the microscopic origin of the effect, which also can not be obtained from some thermodynamic arguments.[6] It is the purpose of this paper to present a microscopic model for the two subsequent phase transitions nematic—smectic-*A* and smectic-*A*—reentrant nematic. The first transition can be understood from a simple extension of McMillan's theory of the nematic—smectic-*A* phase transition,[7] in combination with the effect of association of the polar molecules with antiparallel dipole moments. This latter effect restores, in a sense, the symmetry of the molecules and makes McMillan's theory applicable again. The phase transition is percolationlike; above a certain concentration of associated molecules a smectic phase can be formed. The second phase transition is caused by the unfavorable packing of the bulky paired units in the smectic planes. With decreasing temperature or increasing pressure (increasing pairing) the associated packing entropy makes the smectic-*A* phase unstable again towards the nematic state. A preliminary, qualitative description of this model has been given earlier by one of the authors.[8] Some elements of the model can be found in early work by Cladis.[2(a)]

The observed anomalous phase behavior is related to association between the strongly polar molecules. In these compounds, the induced polarization contributes much less to dielectric permittivity ϵ than the orientation polarization. One would thus expect ϵ in the isotropic phase and

$$\bar{\epsilon}=(\epsilon_{\parallel}+2\epsilon_{\perp})/3$$

in the nematic phase to be proportional to μ^2/k_BT. Here, μ is the permanent dipole moment, k_B is Boltzmann's constant, and T is the absolute temperature. Hence, the normal behavior would be that $\bar{\epsilon}$ increases with decreasing temperature. In practice, either the slope is much smaller than expected for a large dipole moment ($\sim$4.4 D in the case of a CN group), or even has the opposite sign.[9] This indicates that μ is not constant but decreases with decreasing temperature (antiparallel association of the dipole moments). One can describe this association as a monomer-dimer equilibrium

$$D \leftrightarrows 2M\ , \tag{1}$$

where M and D denote a monomer and a dimer, respectively (higher n-mers will not be taken into account). We emphasize that the associated pairs or dimers need not exist on a human time scale, but that a dynamic equilibrium is involved. This behavior of $\bar{\epsilon}$, illustrated in Fig. 1(a), has been observed through all phases, including the isotropic phase. Near the transition smectic-reentrant nematic some form of saturation occurs.[10,11] In some cases in the reentrant nematic phase a maximum is reached followed by a strong decrease.[11] This latter effect is related to the occurrence at lower temperatures of a second smectic-A phase with a layer spacing commensurate with the molecular length.[12] This latter phase transition will not be our concern here. A molecular model for this type of smectic-A phase will be given elsewhere.

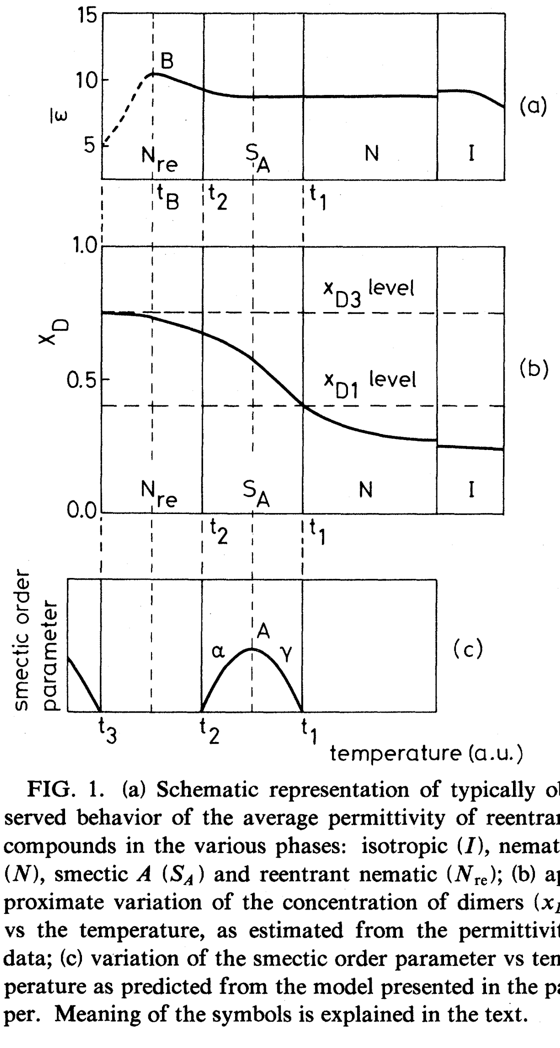
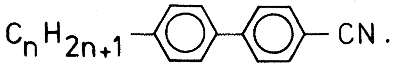


FIG. 1. (a) Schematic representation of typically observed behavior of the average permittivity of reentrant compounds in the various phases: isotropic (I), nematic (N), smectic A (S_A) and reentrant nematic (N_{re}); (b) approximate variation of the concentration of dimers (x_D) vs the temperature, as estimated from the permittivity data; (c) variation of the smectic order parameter vs temperature as predicted from the model presented in the paper. Meaning of the symbols is explained in the text.

From the dielectric permittivity data, one can derive reasonable estimates concerning the temperature variation of x_M and x_D, the concentration of monomers and dimers, respectively. As a model example, we consider the well-studied series of p,p'-alkylcyanobiphenyls (nCB)



Similar molecules with an alkoxy chain are denoted as nOCB. For 7CB, dipole correlation factors have been reported.[13] Though 7CB has no smectic phase, we can combine these results with the permittivity data of 8CB [Ref 9(a)] to obtain the estimate $x_D \approx 0.3-0.4$ at the NS_A phase transition. Combining the information available from various compounds, we arrive at a curve for x_D as sketched in Fig. 1(b). As we shall see, the results of our model do not depend on the details of the shape of the curve of x_D versus temperature.

The layer structure in the bilayer smectic-A phases is rather weak. This is evident from the absence of weakness of higher-orders of the (001) reflection in x-ray experiments.[14] What usually is called a layer is, in fact, only a small density modulation. The layer spacing varies for various substances from 1.1d to 1.6d, depending on the amount of overlap of the molecules when forming a dimer, and on the length of the aliphatic chain.[15] Typical values are in between 1.3d and 1.4d. Throughout the smectic phase, only minor variations of this parameter with temperature[1(b),16] or pressure[2(b),17] are observed. For both 8CB (Ref. 18) and 8OCB (Ref. 19), the transition nematic—smectic is observed to be of second order. As far as information is available, this seems to be so in most relevant cases, and also for the transition smectic-reentrant nematic.[20] In such a situation, the smectic order parameter increases relatively strongly from a zero value at the phase transition, as indicated in Fig. 1(c).

Summarizing, we can state that a microscopic theory of the phase behavior under consideration has to account for the following observations:

(1) The occurrence of a transition nematic—smectic *A*, for which the smectic layer spacing is typically 1.4*d*. The model must be applicable to strongly asymmetric molecules and compatible with other observations about smectic phases (for example, that quite generally smectic phases can be observed with nonpolar molecules; see Ref. 8).

(2) The occurrence with decreasing temperature or increasing pressure of a reentrant nematic phase.

(3) The model should be compatible with an approximately constant layer spacing throughout the intermediate smectic phase, and account for the observed behavior of the dielectric permittivity.

In Sec. II we disuss the main elements of our theoretical model. In Sec. III the results of the model calculations are given, while Sec. IV contains a concluding discussion.

II. THEORETICAL MODEL

A. Main elements and assumptions of the theory

We focus our attention on the study of the stability of the smectic-*A* phase: regimes α and γ in Fig. 1(c). We show that under certain conditions, to be described below, the smectic-*A* phase loses its stability, leading to the reentrant-nematic phase.

In McMillan's theory of the nematic—smectic-*A* transition[7] a parameter

$$\alpha=2\exp[-(\pi r_0/d)^2]$$

is introduced, where d is the length of a molecule [Fig. 2(a)] and r_0 a length of the order of the dimension of the central aromatic core. For $0.98<\alpha<2$ (small values of r_0/d), no nematic phase is predicted and the smectic-*A* phase clears directly into the isotropic liquid. For $\alpha<0.98$ a smectic-*A* —nematic phase transition is obtained, which becomes second order for $\alpha<0.70$. In this model, implicit reference is made to approximately symmetrically substituted molecules, and the question arises how these ideas can be extended to asymmetric molecules. As long as the molecules have no preference to be "up" or "down", it seems reasonable to take for r_0 an average over these two situations. In the case of extreme asymmetry, as for the *n*CB and *n*OCB series, we thus have $r_0\approx d$, and only nematic behavior is predicted. However, if some pairing of the molecules occurs, the dimers again have the possibility to fulfill the condition of large α. A smectic-*A* phase is again possible if two conditions are fulfilled: (a) sufficient pairing (low temperature or high pressure) and (2) long alkyl chains (small r_0/d for the dimers). In this case the spacing of the resulting phase will be larger than d. As to be discussed below in some detail, the induction forces between dimers, monomers, and monomers and dimers are thus responsible for the formation of the smectic phase with a period d', equal to the length of the dimers [see Fig. 2(b)].

The concentration of dimers will depend strongly on the (thermodynamic) forces governing the dimer formation, i.e., on the actual equilibrium conditions. In that situation, one may expect within the smectic temperature range an appreciable change in x_D. The reentrant-nematic phase is proposed to result as an escape from the problems associated with the packing of paired molecules in layers, to be understood in the following way: Owing to the decrease of temperature and to the associated increase of x_D, initially the smectic order parameter increases (γ regime in Fig. 1). Now the "packing capacity" of the

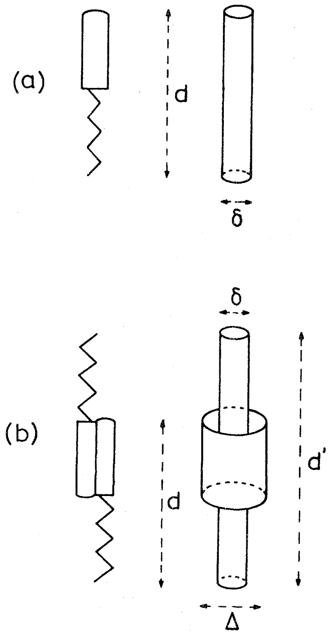


FIG. 2. Definition of the model particles used to represent a monomer (a) and a dimer (b). Four important lengths enter into the reentrant-nematic problem: d the length of a monomer, d' the length of the dimer, δ the breadth of the molecules, Δ the breadth of the central bulky part of the dimer.

smectic plane (the number of dimers per unit area) will depend on the actual equilibrium conditions. Taking models for the monomers and dimers as pictured in Fig. 2, for example, the excluded volume of the bulky central cores of the paired molecules will be important. In the low-temperature part of the γ regime, too many dimers are being produced. Monomers can fill the rest of space outside the smectic planes, but dimers that cannot be packed centrally anymore are too long to do so without disturbing the smectic order. This creates "destructive" steric forces, described by a packing entropy in the expression for the free energy, that destabilize the smectic phase. At point A in Fig. 1(c) the increase of the smectic order parameter due to the decreasing temperature is just balanced by the steric forces due to too abundant dimers that tend to decrease its value. In the α regime these steric forces become more important until, at the temperature t_2, the reentrant nematic phase is produced. We shall now describe these effects more quantitatively within the framework of a detailed thermodynamic model.

B. Model potential

Let us consider a system of axially symmetric monomers and dimers, interacting through the general two-particle potential

$$\tilde{V}_{AB}(\Omega_A,\Omega_B;\vec{r}_{AB})=\begin{cases}\infty & \text{if } r_{AB}<\xi_{AB}\\ -V_{AB}(\Omega_A,\Omega_B;\vec{r}_{AB}) & \text{if } r_{AB}\geq\xi_{AB}\,.\end{cases} \quad (2)$$

Here ξ_{AB} is the distance of closest approach of A,B, while $A,B=M,D$, and $\Omega_A\equiv(\theta_A,\phi_A)$ are the the angles defining the orientation of the long axis of a molecule A with respect to a given Cartesian coordinate system. Where no confusion arises we shall denote the degrees of freedom of a particle simply by the subscript A, with $A\equiv(\Omega_A,\vec{r}_A)$, $\vec{r}_A$ denoting the position of the center of mass, while

$$r_{AB}=|\vec{r}_{AB}|=|\vec{r}_A-\vec{r}_B|\ .$$

The potential (2) is composed of a hard-core interaction for $r_{AB}<\xi_{AB}$ and an attractive soft part

$$-V_{AB}(\Omega_A,\Omega_B,\vec{r}_{AB})\ .$$

This soft part of the interaction will be shown to be responsible for the stability of the smectic phase in the α,γ regime (see Fig. 1). The hard-core structure of the dimers will cause the destabilization of the smectic phase at t_2.

The soft part of the potential consists of three different parts, namely, (a) dispersion forces, in the lowest order of perturbation theory given by induced dipole-induced dipole forces

$$V_1\sim\bar{\alpha}^2r^{-6}\ ,$$

$\bar{\alpha}$ being the average polarizability of the molecules, and r the separation of the centers of mass. These forces are, in McMillan's model, responsible for the occurrence of the smectic phase. (b) Dipole-induced dipole interactions:

$$V_2\sim\bar{\alpha}\mu^2r^{-6}\ ,$$

μ being the permanent dipole of the molecules. These forces have the same symmetry as the former ones. However, they are weaker, but still can have some influence on the effective coupling constants. (c) Dipole-dipole interactions between the polar end groups

$$V_3\sim\mu^2r^{-3}\ .$$

These forces are of long-range order. They are assumed to be responsible for the dimer formation and as such for the symmetry of the one-particle distribution functions. Only in this way these forces contribute to the stability of the smectic phase. This exclusion of any direct effect of dipoles on the stability of the smectic phase is probably not true in general. However, from the occurrence of smectic phases with nonpolar molecules we may conclude that the influence of permanent dipoles is not a primary effect.

A full thermodynamic description of the system interacting through the potential of Eq. (2) is extremely difficult. Nevertheless, some general trends (especially for the critical temperatures) can be obtained from a calculation of the equilibrium properties of the system within the mean-field approximation.

C. Mean-field description

In the mean-field approximation the soft- and the hard-core contributions to the potential can be discussed, to some extent, independently. The hard-core part of the interaction influences the free energy in two ways. First it leads to a packing entropy term which is simply the measure of the phase space which cannot be penetrated by the center of mass of a given particle in the presence of another particle. Secondly, it modifies the soft part of the interaction, multiplying this part by $\Theta(r_{AB}-\xi_{AB})$, where Θ is the step function (Gelbart-type coupling).[21] More precisely, let N_M and N_D be the number of monomers and dimers, respectively. Then $N_M+2N_D=N$ is constant at all temperatures, N being the total number of monomers for $x_D=0$. The concentrations x_M and x_D are defined by

$$x_M=\frac{N_M}{N^*}=\frac{N_M}{N-N_D},\quad N_M+N_D=N^*$$

$$x_D=\frac{N_D}{N-N_D},\quad x_M+x_D=1\ .$$

In the mean-field approximation, the orientational free energy F is given by (including steric effects)

$$F=U-TS_r-TS_p\ , \tag{3}$$

where U is the internal energy, S_r the orientational entropy, and S_p the packing entropy from the hard-core repulsions. The quantities U, S_r, and S_p are given by

$$U=-\tfrac{1}{2}(N^*)^2\left[\sum_{A,B} x_A x_B \mathop{\mathrm{Tr}}_{(A,B)}[f_A(A)V_{AB}(A,B)\Theta(r_{AB}-\xi_{AB})f_B(B)]\right]\ , \tag{4a}$$

$$S_r=-k_B N^*\left[\sum_{A} x_A \mathop{\mathrm{Tr}}_{(A)}[f_A(A)\ln f_A(A)]\right]\ , \tag{4b}$$

$$S_P=-\tfrac{1}{2}(N^*)^2 k_B\left[\sum_{A,B}\mu_{AB} x_A x_B \mathop{\mathrm{Tr}}_{(A,B)}[f_A(A)\Theta(\xi_{AB}-r_{AB})f_B(B)]\right]\ . \tag{4c}$$

Here, μ_{AB} is a factor, which depends in general on the packing fraction[22(a)];

$$\mathop{\mathrm{Tr}}_{(A)}=(4\pi\mathscr{V})^{-1}\int d\Omega\int d^3\vec{r}_A=\int_{-1}^{1}\int_0^{2\pi}\int_{\mathscr{V}}\frac{d\cos\theta_A}{2\pi}\frac{d\phi_A}{2}\frac{d^3\vec{r}_A}{\mathscr{V}}\ ;$$

$f_A(A)$ is the one-particle distribution function for molecule A, $\mathscr{V}$ is the volume of the system. An exact derivation of formulas (3)—(4c), based on a generalization of the Lebowitz-Penrose theory[23] will be given elsewhere.[24] In formula (3) we keep only terms which couple to the one-particle distribution functions $f_A(A)$. As the concentration of dimers is treated as a free parameter, any other contribution, like entropy of mixing, kinetic energy, and pair association-dissociation energy can be neglected. In the further calculations we make the approximation $\mu_{AB}=1$.[22(b)]

The free energy as defined in Eq. (3) contains two unknowns, the one-particle distribution functions f_M and f_D. These can be found variationally from the minimum of the free energy under the normalization constraints imposed on f_A. The necessary conditions are

$$\frac{\delta F}{\delta f_A}=0,\quad \mathop{\mathrm{Tr}}_{(A)} f_A(A)=1,\quad A=M,D\ . \tag{5}$$

After standard variational calculations, we finally obtain the following self-consistent equations:

$$f_A(A)=Z_A^{-1}\exp\left[\beta N^*\sum_{B=M,D}\left(x_B \mathop{\mathrm{Tr}}_{(B)}\{f_B(B)[V_{AB}(A,B)\Theta(r_{AB}-\xi_{AB})-\beta^{-1}\Theta(\xi_{AB}-r_{AB})]\}\right)\right]\ , \tag{6}$$

where $\beta=1/k_BT$ and Z_A is the normalization constant. The system of Eq. (6) is a set of nonlinear integral equations that is still far too complicated for numerical treatment. Further simplifications can be introduced using the symmetry properties of the phases we want to describe and from some experimental facts.

D. Approximate one-particle distribution functions

Our purpose now is to investigate the stability of the smectic phase against changes in the number of dimers. To do so we seek the simplest possible mean-field expressions to account for both the attractive and repulsive forces. The problem is then to find an appropriate approximation for the one-particle distribution functions $f_A(A)$, $A=M,D$, in accordance with the experiments.

From the symmetry of the nematic and smectic phase, we know that the most general form of the one-particle distribution function depends only on one space variable, for example, z, describing the one-dimensional smectic modulation, and on one angle variable $\cos\theta$ describing the orientation of the long axis of the molecules with respect to the director $\vec{n}$ (where $\vec{n}\,||\,z$ axis):

$$f_A(A)=f_A(\cos\theta,z),\quad A=M,D\ . \tag{7}$$

The second-order character of the phase transitions suggests that the orientational order varies only slowly with temperature and, thus, will be relatively high. Therefore, we shall apply the approximation of ideal orientational order. This leads to the following expression for f_A (Ref. 25):

$$f_A(A)=1+\tilde{f}_A(z)g(\Omega)\ , \tag{8a}$$

where

$$g(\Omega)=\tfrac{1}{2}\delta(\cos^2\theta-1)$$

and where $\delta(x)$ is the Dirac δ function. We shall denote these types of distribution as the saturated-McMillan (SM) model. Additionally, as the smectic density modulation is rather weak, we can keep in a Fourier expansion of f_A with respect to z only the lowest harmonic, i.e.,

$$\tilde{f}_A(z)\sim\cos(2\pi z/\bar{d}+\phi_A)+\cdots\ . \tag{8b}$$

Here, $\bar{d}$ is the period of the density wave of the smectic-A phase and ϕ_A is a phase shift. For the dimers, ϕ_D specifies the origin of the coordiante system, for which we take $\phi_D=0$. The meaning of ϕ_M will become clear later. The density of dimers (normalized to unity) can now be described as

$$f_D(\cos\theta,z)=1+2\tau_D\cos(2\pi z/\bar{d})g(\Omega)\cdots\ , \tag{8c}$$

where

$$\tau_D=(4\pi\mathscr{V})^{-1}\times\int d^3\vec{r}\,d\Omega f_D(\cos\theta,z)\cos(2\pi z/\bar{d})$$

is the smectic dimer order parameter.

Now one can think of several ways to distribute the polar monomers in the smectic-A phase. The overall symmetry of this phase dictates that it is not ferroelectric, so that there are equal numbers of monomers oriented in opposite directions. The smectic layer of period $\bar{d}$ could, apart from the dimers, comprise two overlapping sublayers with the monomers all up in one sublayer and all down in the other. Or all sublayers could be identical, with each containing equal numbers of molecules up and down. The second possibility seems to be more probable, because no evidence from dielectric data exists for any kind of long-range antiferroelectric or ferroelectric order. In the lowest order of the Fourier analysis the one-particle distribution function of the monomers will then have the form

$$\begin{aligned}f_M(\cos\theta,z)&=1+\tau_M[\cos(2\pi z/\bar{d}-\phi_M)+\cos(2\pi z/\bar{d}+\phi_M)]g(\Omega)/\cos\phi_M+\cdots\\&=1+2\tau_M\cos(2\pi z/\bar{d})g(\Omega)+\cdots\ ,\end{aligned} \tag{8d}$$

where the connection between the smectic monomer order parameter, denoted by τ_M^*, and the order parameter τ_M introduced in Eq. (8d), is given through the relation

$$\begin{aligned}\tau_M^*&=(4\pi\mathscr{V})^{-1}\int d^3\vec{r}\,d\Omega\,f_M(\cos\theta,z)\cos(2\pi z/\bar{d}\pm\phi_M)\\&=\cos\phi_M(4\pi\mathscr{V})^{-1}\int d^3\vec{r}\,d\Omega\,f_M(\cos\theta,z)\cos(2\pi z/\bar{d})=\tau_M\cos\phi_M\ ,\end{aligned}$$

and where ϕ_M describes the equlibrium position of the centers of mass of the monomers with respect to that of the dimers. The advantage of using τ_M instead of τ_M^* in practical calculations is that it eliminates the parameter $\cos\phi_M$ from the self-consistency equations. This means that the critical temperature is independent of $\cos\phi_M$. As $\bar{d}$ is not commensurate with the length of the molecule, it seems natural to identify $\bar{d}$ in the SM model with the length of the dimer d'. An alternative would be to take for $\bar{d}$ some weighted average of the length of the monomer and dimer, respectively. However, then one would expect this average to shift with decreasing temperature in the direction of the length of the dimer, which is not in agreement with the observed constancy of the period of the density modulation. This constant period can be explained if we assume that the monomers fit into a smectic phase with a spacing determined by the dimers, which means $\bar{d}=d'$ and $\phi_M\simeq\pi(1-d/d')$.

The use of the SM approximation leads to a considerable simplification of the self-consistency equations, Eq. (6). After all necessary integrations we finally arrive at the following system of integral equations for the smectic order parameters:

$$
\begin{aligned}
\tau_A = (4\pi Z_A)^{-1} \int d^3\vec{r}_A d\Omega_A g(\Omega_A) \cos(2\pi z_A/d') \\
\times \exp\Bigg[\beta\rho \Bigg\{ 2\cos(2\pi z_A/d') \sum_{B=M,D} x_B \tau_B (4\pi)^{-1} \int d\Omega_B d^3\vec{r}_{AB} \cos(2\pi z_{AB}/d') g(\Omega_B) \\
\times \Bigg[V_{AB}(\Omega_A, \Omega_B, \vec{r}_{AB}) \Theta(r_{AB} - \xi_{AB}) \\
- k_B T \Theta\left[\xi\left[\Omega_A, \Omega_B, \frac{\vec{r}_{AB}}{r_{AB}} \right] - r_{AB} \right] \Bigg] + \cdots \Bigg\} \Bigg] ,
\end{aligned}
\tag{9}
$$

where $A = M,D$ and $\rho = N^*/V$ is the number density. The normalization constant Z_A can be calculated by using the integral at the right-hand side of Eq. (9) with the first factor $\cos(2\pi z_A/d')$ replaced by 1.

There are always trivial solutions of Eq. (9) given by $\tau_A = 0$ $(A = M,D)$. Nonzero solutions occur for $A = M,D$ simultaneously (provided, of course, that x_M and x_D are nonzero). This is due to the fact that the monomer and the dimer one-particle distribution function have the same symmetry. These solutions, which can be found by numerical analysis of Eq. (9), are not immediately connected with the experimentally measured smectic order parameter. This is because we are not able to separate the monomer and the dimer contributions. The connection with experiment can be made by introducing the weighted order parameter τ:

$$\tau = x_M \tau_M^* + x_D \tau_D . \tag{10}$$

Among all the possible solutions of Eq. (9) for the temperature variation of τ, Eq. (10), there is one which is interesting from the point of view of reentrance. This solution has been sketched in Fig. 1(c). On decreasing the temperature at t_1 we get the first smectic phase with the period of the density modulation equal to d'. In between the temperatures t_2 and t_3, there exists a reentrant nematic phase, and for temperatures below t_3 the smectic-*A* phase with period d' reenters. This last reentrant smectic phase, again with period d', should not be confused with the usually observed second smectic phase with monolayers. However, recently a reentrant smectic phase with, again, a layer spacing around $1.3d$ has been observed experimentally.[26] The existence of the temperature t_3 provides a very convenient criterion for discussing the experimentally observed reentrant nematic phase (the dimensionless temperatures t_1, t_2, and t_3 are defined in Sec. III).

E. Critical temperatures

Although the complete solution of the self-consistency equations, Eq. (9), requires much numerical effort, the finding of the critical temperatures is more straightforward. First, we note that the self-consistency equations are always fulfilled by zero solutions $\tau_A \equiv 0$. The nonzero solutions, which can exist for sufficiently low temperatures are always symmetric with respect to the zero one, i.e., the solutions occur in pairs

$$\tau_A = \pm |\tau_A| \neq 0 .$$

In the language of the mean-field approach, this means that the transitions are of second order. Consequently, the critical temperature can be identified with the bifurcation point of the system described by Eq. (9), i.e., with the point on the temperature scale where the nonzero solution bifurcates from the zero one. One can find this point by solving Eq. (9) to the first order with respect to the order parameters τ_A $(A = M,D)$. Such linearized self-consistency equations have the following form:

$$\hat{A}(t) \begin{bmatrix} \tau_M \\ \tau_D \end{bmatrix} = 0 \tag{11}$$

with

$$\hat{A}(t) = \begin{bmatrix} x_M(\tilde{V}_{MM} - t\kappa\eta\tilde{\Theta}_{MM}) - t & x_D(\tilde{V}_{MD} - t\kappa\eta\tilde{\Theta}_{MD}) \\ x_M(\tilde{V}_{MD} - t\kappa\eta\tilde{\Theta}_{MD}) & x_D(\tilde{V}_{DD} - t\kappa\eta\tilde{\Theta}_{DD}) - t \end{bmatrix} ,$$

and where

$$t = \frac{k_B T}{\rho V_{MM}} ,$$

V_{MM} being the monomer-monomer attractive soft-interaction coupling constant, and where

$$\eta = v_M/(x_M v_M + x_D v_D) \simeq v_M/(x_M v_M + 2x_D v_M) = 1/(1+x_D) ,$$

v_M, v_D being the molecular volumes of the monomer and of the dimer, respectively ($v_D \simeq 2v_M$); $\kappa = \rho v_M/\eta$ is the packing fraction. Furthermore,

$$\tilde{V}_{AB} = (16\pi^2 V_{MM})^{-1} \int d^3\vec{r}_{AB} \cos(2\pi z_{AB}/d') \int d\Omega_A d\Omega_B g(\Omega_A) V_{AB}(\Omega_A, \Omega_B, \vec{r}_{AB}) g(\Omega_B) \Theta(r_{AB} - \xi_{AB}) , \tag{12a}$$

$$\tilde{\Theta}_{AB} = (16\pi^2 v_M)^{-1} \int d^3\vec{r}_{AB} \cos(2\pi z_{AB}/d') \int d\Omega_A d\Omega_B g(\Omega_A) \Theta \left[\xi_{AB} \left[\Omega_A, \Omega_B, \frac{\vec{r}_{AB}}{r_{AB}} \right] - r_{AB} \right] g(\Omega_B) . \tag{12b}$$

The critical temperature connected with the appearance of the nonzero solution is determined by

$$\det \hat{A}(t_c) = 0 . \tag{13}$$

Equation (13) can be rewritten in a more convenient (fixed point) form as

$$t_c = \frac{\bar{V} + \overline{\Theta V} + [(\bar{V} + \overline{\Theta V})^2 + 4(1 + \bar{\Theta} + \overline{\Theta\Theta})\overline{VV}]^{1/2}}{2(1 + \bar{\Theta} + \overline{\Theta\Theta})} , \tag{14a}$$

where

$$\begin{aligned} \bar{\Theta} &= \kappa\eta(x_M \tilde{\Theta}_{MM} + x_D \tilde{\Theta}_{DD}) , \\ \bar{V} &= x_D \tilde{V}_{DD} + x_M \tilde{V}_{MM} , \\ \overline{\Theta\Theta} &= (\kappa\eta)^2 x_M x_D (\tilde{\Theta}_{MM} \tilde{\Theta}_{DD} - \tilde{\Theta}_{MD}^2) , \qquad (14b) \\ \overline{\Theta V} &= \kappa\eta x_M x_D (\tilde{V}_{DD} \tilde{\Theta}_{MM} + \tilde{V}_{MM} \tilde{\Theta}_{DD} - 2\tilde{V}_{MD} \tilde{\Theta}_{MD}) , \\ \overline{VV} &= x_M x_D (\tilde{V}_{MD}^2 - \tilde{V}_{MM} \tilde{V}_{DD}) . \end{aligned}$$

All the parameters in Eq. (14a) are temperature dependent because the concentration of dimers x_D is temperature dependent. Furthermore, all solutions of Eq. (14a) depend on the effective potential parameters $\tilde{V}_{AB}$, and on the effective steric parameters $\tilde{\Theta}_{AB}$, defined by Eqs. (12a) and (12b). Some general properties of these parameters can be found without any numerical effort.

Let us first discuss the parameters $\tilde{V}_{AB}$. The dominant contribution to this effective parameter is coming from the interactions of orientationally ordered particles located in the smectic planes. This is due to the fact that the interaction stabilizing the smectic phase is (i) located in the central part of the molecule and (ii) is of short-range character. Now $\tilde{V}_{AB}$ is a function of the dimensionless parameters built from all the characteristic lengths in the model potential. In agreement with all previous approximations, it is enough to consider only two most important characteristic lengths. The first one r_0^{AB} measures the "dispersion" of the interaction along the molecule. The second one is d', and our dimensionless parameter is r_0^{AB}/d'. Thus, we find

$$\tilde{V}_{AB} = (V_{AB}/V_{MM}) I(r_0^{AB}/d') > 0 , \tag{15}$$

where V_{AB} is the pair-interaction coupling constant between A and B. In the McMillan-type of description we expect for overlapping of the central aromatic core

$$I(r_0^{MM}/d') \simeq I(r_0^{MD}/d') \simeq I(r_0^{DD}/d') . \tag{16}$$

If, in addition, we assume that the dimer-dimer and the dimer-monomer interactions can be approximated by that of two monomers-two monomers and two monomers-monomer, respectively, we get a set of inequalities

$$4 \gtrsim \frac{V_{DD}}{V_{MM}} \gtrsim 2 \gtrsim \frac{V_{MD}}{V_{MM}} > 1 . \tag{17}$$

By combining the relations (16) and (17) we arrive at

$$4 \gtrsim \frac{\tilde{V}_{DD}}{\tilde{V}_{MM}} \gtrsim \frac{\tilde{V}_{MD}}{\tilde{V}_{MM}} \gtrsim 1 . \tag{18}$$

Because our description is not exactly equivalent to that of McMillan, we expect deviations from these inequalities. The upper limit in inequalities (18) gives only the order of magnitude of the ratio's $\tilde{V}_{DD}/\tilde{V}_{MM}$ and $\tilde{V}_{MD}/\tilde{V}_{MM}$. In our further analysis these two ratios will be treated as independent parameters.

A first analysis of the steric parameters $\tilde{\Theta}_{AB}$ can also be done very easily. To do so, let us consider a molecule centered at z_{AB} with $0 \le z_{AB} \le d'$. We divide the volume of this layer into two parts:

$$\text{(I)}\ \ 0 \le z_{AB} \le \tfrac{1}{4}d' \ \text{ and }\ \tfrac{3}{4}d' \le z_{AB} \le d' \,,$$

$$\text{(II)}\ \ \tfrac{1}{4}d' < z_{AB} < \tfrac{3}{4}d' \,.$$

This division is given according to the sign of the function $\cos(2\pi z_{AB}/d')$. This function is positive in region (I) and negative in region (II). Now the quantity $\tilde{\Theta}_{AB}$ can be decomposed into the contributions coming from the two regions:

$$\tilde{\Theta}_{AB} = 2[\tilde{\Theta}_{AB}(\mathrm{I,I}) + \tilde{\Theta}_{AB}(\mathrm{I,II})] \,.$$

The first contribution can be thought of as the mean excluded volume of two particles, both being in region (I). The second one similarly for the particles being in a different region. In our SM model the value of $\tilde{\Theta}_{AB}$ depends mainly on the geometry of the molecules along the z axis. If the central part of the molecule is broad enough and if the central, broad part is (well) localized in area (I) then $\tilde{\Theta}_{AB}(\mathrm{I,I}) \gtrsim |\tilde{\Theta}_{AB}(\mathrm{I,II})|$. Otherwise this inequality changes sign.

F. Conditions for reentrance

The easiest way of formulating the condition for reentrance is with the help of two critical temperatures t_1 and t_3. The temperatures t_1 and t_3 are defined in the following way: Let us assume first that the concentration x_D is constant as a function of temperature and that it is equal to x_{D1} [x_{D1} level in Fig. 1(b)] and let us find from Eq. (14a) the corresponding critical temperature $t_1 = t_c(x_{D1})$. Next, let us find in the same way the critical temperature t_3, corresponding to the concentration $x_{D3} > x_{D1}$. In that situation the necessary condition to obtain reentrant nematic behavior is that the critical temperatures t_1 and t_3 must fulfill the following relation [see Fig. 1(c)]:

$$\frac{t_3}{t_1} = \frac{t_c(x_{D3})}{t_c(x_{D1})} < 1 \,. \tag{19a}$$

If this inequality is reversed there will only be a single transition NS_A at t_1. Now we assume that condition (19a) is fulfilled and we consider a continuous, monotonic function $x_D(t)$ with

$$x_{D3} \ge x_D(t) \ge x_{D1} \,,$$

and with $dx_D/dt \lesssim 0$ in the region around both t_3 and t_1 [as shown in Fig. 1(b)]. Then the critical temperatures t_1 and t_3 still remain solutions of Eq. (14a) and, additionally, there exists a third solution for the critical temperature t_2 with $t_3 < t_2 < t_1$ [see Fig. 1(c)].

We can now impose the following constraints on the concentrations x_{D1} and x_{D3}:

$$1 \ge x_{D3} > x_{D1} \gtrsim 0.4 \,, \tag{19b}$$

The last number comes from our estimate of the concentration of dimers at the first nematic–smectic transition as obtained from the dielectric permittivity data. In the absence of more detailed information on the (x_D, t) curve, the conditions [(19a) and (19b)] are, in practice, the only ones that have to be fulfilled to obtain the reentrant nematic phase.

III. RESULTS OF MODEL CALCULATIONS

A. Steric interaction

Our aim is now to solve the SM model for particles as shown in Figs. 2(a) and 2(b). For this particular choice of the form of the particles $\tilde{\Theta}_{AB}$, defined in Eq. (12b), can be calculated very easily. Quite generally we can write

$$\begin{aligned}\tilde{\Theta}_{AB} &= v_M^{-1} \int d^3\vec{r}_{AB} \cos(2\pi z_{AB}/d')\Theta(\xi_{AB}(|z_{AB}|) - r_{AB}) \\ &= \pi v_M^{-1} \int_0^{\max} dz_{AB} \cos(2\pi z_{AB}/d')\Theta(\xi_{AB}^2(z_{AB}) - z_{AB}^2) \,,\end{aligned} \tag{20}$$

where $\max = \max\limits_{(z_{AB})}[\xi_{AB}(z_{AB})]$. For our specific choice of the geometry of the particles we find

$$\xi_{DD} = \begin{cases} (\Delta^2 + z_{DD}^2)^{1/2} & \text{if } 0 \le |z_{DD}| < 2d - d' \\ [\tfrac{1}{4}(\Delta+\delta)^2 + z_{DD}^2]^{1/2} & \text{if } 2d - d' < |z_{DD}| < d \\ (\delta^2 + z_{DD}^2)^{1/2} & \text{if } d < |z_{DD}| < d' \end{cases} \tag{21a}$$

$$\xi_{MD}=\begin{cases}[\frac{1}{4}(\Delta+\delta)^2+z_{MD}^2]^{1/2} & \text{if } 0\le |z_{MD}|<\frac{1}{2}(3d-d') \\ (\delta^2+z_{MD}^2)^{1/2} & \text{if } \frac{1}{2}(3d-d')<|z_{MD}|<\frac{1}{2}(d+d')\end{cases} \tag{21b}$$

$$\xi_{MM}=(\delta^2+z_{MM}^2)^{1/2} \text{ for } 0\le |z_{MM}|<d\ . \tag{21c}$$

Inserting these results into Eq. (20) we obtain

$$\widetilde{\Theta}=\frac{4}{\pi}b\frac{d'}{d}\{(2+3b)\sin[2\pi(2d/d'-1)]+(2+b)\sin(2\pi d/d')\}\ , \tag{22a}$$

$$\widetilde{\Theta}_{MD}=\frac{4}{\pi}b\frac{d'}{d}\{(2+b)\sin[\pi(3d/d'-1)]+(1/b)\sin[\pi(d/d'+1)]\}\ , \tag{22b}$$

$$\widetilde{\Theta}_{MM}=\frac{4}{\pi}\frac{d'}{d}\sin(2\pi d/d')\ , \tag{22c}$$

where we have used $b=\frac{1}{2}(\Delta/\delta-1)$ and $v_M=\pi(\delta/2)^2d$. The geometrical parameters, d, d', δ, and Δ are defined in Fig. 2.

The dependence of the steric parameters $\widetilde{\Theta}_{AB}$ on d'/d for some values of Δ/δ is shown in Fig. 3. Negative values of $\widetilde{\Theta}_{AB}$ indicate that the smectic phase is stabilized. Optimal conditions are from the purely steric point of view (see Fig. 3): $1.0\lesssim d'/d\lesssim 1.5$. It is worth noting that the purely monomer part $\widetilde{\Theta}_{MM}$ always helps to stabilize the smectic phase in spite of the fact that the layer spacing d' corresponds to the dimer. This tendency is strongest for $1.3\lesssim d'/d\lesssim 1.6$.

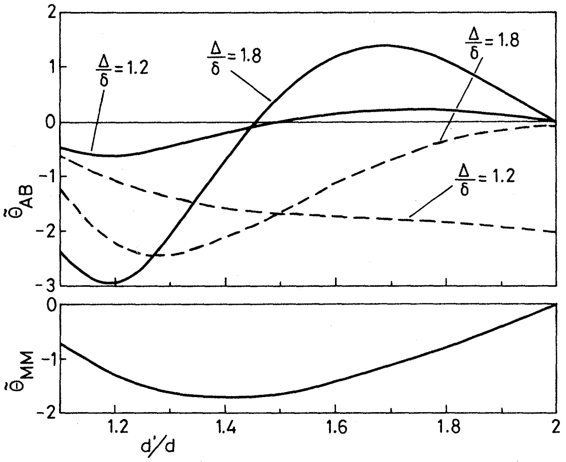


FIG. 3. Dependence of steric parameter $\widetilde{\Theta}_{AB}$ $(A,B=M,D)$ on d'/d for a few values of the parameter Δ/δ. Broken lines (top picture) give values for $\widetilde{\Theta}_{MD}$ while full lines represent the case $\widetilde{\Theta}_{DD}$. Purely monomer part $\widetilde{\Theta}_{MM}$ (bottom picture) is independent of Δ/δ.

B. Choice of parameters

The calculation of the concentration dependence of the nematic—smectic-*A* critical temperatures requires values for the three intermolecular energy parameters $\widetilde{V}_{MM}$, $\widetilde{V}_{MD}$, and $\widetilde{V}_{DD}$. In the calculations, these quantities are [in agreement with the inequalities (18)] assumed to be related by $\widetilde{V}_{MD}^2=\widetilde{V}_{MM}\widetilde{V}_{DD}$ or

$$\widetilde{V}_{MD}/\widetilde{V}_{MM}=(\widetilde{V}_{DD}/\widetilde{V}_{MM})^{1/2}\ . \tag{23}$$

As far as the anisotropy in the intermolecular potential is determined by the dispersion forces, this geometric mean approximation is exact in the dominant, lowest-order approximation. Any other reasonable restriction imposed on the parameters $\widetilde{V}_{AB}$, and including other, secondary terms to the intermolecular potential does not lead to qualitative changes in the final picture.

To carefully formulate the conditions for reentrance, we have to consider the restrictions coming from experiments imposed on the various parameters at the right-hand side of Eq. (14a). As we shall see, there is in fact, not that much freedom.

(a) For the critical temperature ratio [see Eq. (19a)] we take

$$0<\frac{t_c(x_{D3})}{t_c(x_{D1})}\lesssim\frac{t_B}{t_1}\approx 0.7\ ,$$

where t_B and t_1 are defined in Fig. 1(a). As noted before, the reentrant smectic phase with period d' occurring at t_3, which is inherent to the model, is usually not observed experimentally. Therefore, we require $t_3\lesssim t_B$, where t_B is the temperature where we see from the dielectric data that other effects, probably associated with some form of long-range antiferroelectricity, take over. From the available experimental information we locate t_B somewhat below t_2 in the reentrant nematic phase. From the data for various homologous series we estimate $t_B/t_1 \approx 0.7$. We shall treat this value as a threshold above which reentrant behavior cannot be observed.

(b) For the soft-core potential parameters we take

$$1 \lesssim \tilde{V}_{DD}/\tilde{V}_{MM} \lesssim 4 \ .$$

Both limits are discussed below Eq. (18).

(c) The ratio of the length of dimer to monomer we take somewhat wider than the experimentally observed spacings as

$$1.1 \lesssim d'/d \lesssim 1.9 \ .$$

(d) The ratio of the diameter of the central part of the dimer to the diameter of the monomer is taken as

$$1 < \Delta/\delta < 2 \ .$$

If we take the effective area of the central part of the dimer equal to twice that of the monomer, we arrive at the optimal value $\Delta/\delta = \sqrt{2} \approx 1.4$. The physically most acceptable values will be less than 1.4 as follows from density measurements.[5b]

(e) For the concentrations x_{D1} and x_{D3} we choose

$$0.4 \lesssim x_{D1} < x_{D3} \lesssim 0.8 \ .$$

The lower limit has been discussed in Sec. I. The higher limit is somewhat arbitrary and will be kept as a variable.

(f) For the packing fraction κ we take

$$0.65 \lesssim \kappa \lesssim 0.8 \ .$$

Actual packing fractions of liquid crystals at atmospheric pressure are of the order of the lower limit. To account for the fact that our model does not consider the orientational degrees of freedom and because of the assumption $\mu_{AB} \equiv 1$ in Eq. (6), we should also include higher values. This is also useful for a comparison with experiments at increased pressure.

We note that the chosen set of parameters is the minimal one to be considered in the case of a complicated thermodynamic system as the present two-component mixture. Any freedom to adjust the parameters to account for the experimental results is rather small, and is, in fact, limited to the points mentioned under (a) and (e). As we shall see, any reasonable variation of these parameters does not affect the general predictions of our model.

C. Results

All qualitative predictions of the model depend on the assumptions with respect to the variation of x_D. Therefore, we shall discuss the properties which are independent of the detailed temperature variation of x_D. This is especially true for the critical temperatures t_1 and t_3 or, more precisely, $t_1/\tilde{V}_{MM}$ and $t_3/\tilde{V}_{MM}$. It can be checked that all variations of t_1 as a function of d'/d, Δ/δ, or κ are much more important than the corresponding variations of t_3. This means we can simplify the further analysis by looking only at the ratio t_3/t_1. An increase (decrease) of t_3/t_1 when one of the parameters mentioned changes, means that t_1 decreases (increases) and also that $(t_1-t_3)/t_1$ decreases (increases). With x_{D1} and x_{D3} as parameters, the only condition to get reentrant nematic behavior is that given by inequality (19a). The lower values of t_3/t_1 correspond to better conditions for reentrant behavior. As mentioned before, from the permittivity data one would like to see $t_3/t_1 \lesssim 0.7$, but the actual value taken is not of great importance.

The predictions of our model are gathered in Figs. 4–8. All of them show the condition for reentrance, thus the dependence of the ratio t_3/t_1 on various sets of parameters. In all cases sets of two curves are given (full and broken lines) corresponding to two choices for $\tilde{V}_{DD}/\tilde{V}_{MM}$. Furthermore, several ranges are chosen for the concentration change from x_{D1} to x_{D3}. An impression of the results for other values can be obtained by simple interpolation. Some general features of the model are the following:

(i) the ratio t_3/t_1 increases with increasing value x_{D1} (the rest of the parameters being fixed).

(ii) the ratio t_3/t_1 decreases with increasing value of x_{D3} (the rest of the parameters being fixed).

Figure 4 shows the dependence of t_3/t_1 on the

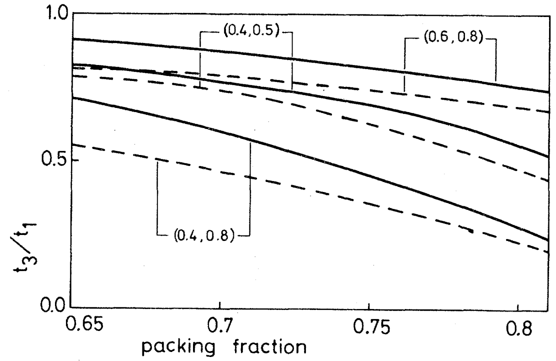


FIG. 4. Ratio of the two critical temperatures t_3/t_1 vs the packing fraction for fixed values $\Delta/\delta = 1.4$ and $d'/d = 1.35$. Broken lines denote the case $\tilde{V}_{DD}/\tilde{V}_{MM} = 2$ and the full lines are given for $\tilde{V}_{DD}/\tilde{V}_{MM} = 4$. Values of x_{D1} and x_{D3} are given in brackets.

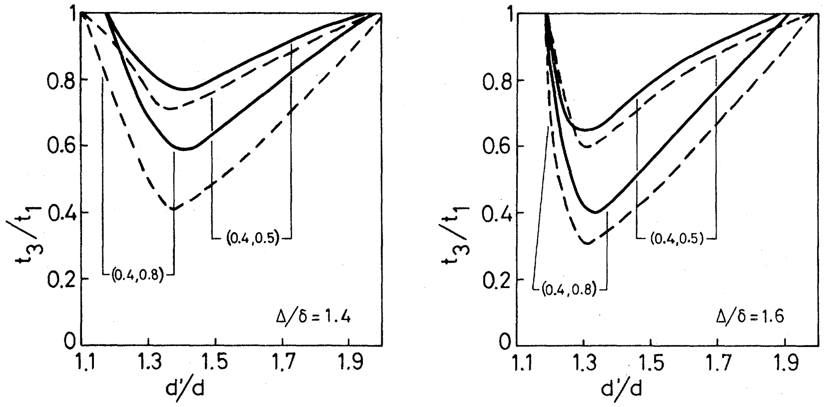


FIG. 5. Ratio of the two critical temperatures t_3/t_1 vs the d'/d ratio for fixed packing fraction $\kappa=0.7$ and for different values of $\tilde{V}_{DD}/\tilde{V}_{MM}$, x_{D1}, and x_{D3} (see caption of Fig. 4).

packing fraction. Here, Δ/δ is taken equal to the optimal value 1.4, while d'/d is chosen in such a way that the lowest value of t_3/t_1 is obtained (the rest of the parameters being fixed). As we see, an increase in the packing fraction leads to conditions more favorable for reentrance. This prediction of the possibility to obtain the reentrant nematic phase by increasing the pressure is in agreement with the experimental observations. Figure 5 then shows how the optimum value of d'/d was obtained. It shows that the best conditions for reentrant behavior are reached for

$$1.3 \lesssim d'/d \lesssim 1.4 .$$

Because the overlap of two monomers forming a dimer should not depend on the length of the alkyl chains, the variation with d'/d also serves as an indication for the change of t_3/t_1 along a homologous series.

Figure 6 gives boundaries of regions for which $t_3/t_1 \leq 0.7$ on a $(d'/d,\kappa)$ plane. In principle, the same trends are observed as demonstrated in Figs. 4 and 5. If we stick to this particular requirement for t_3/t_1, we see that reentrant behavior is not possible for all values of d'/d. This, in turn, depends on the range chosen for (x_{D1}, x_{D3}) and the packing fraction. This is shown once more in Fig. 7, but now with Δ/δ as a variable for a constant packing fraction. Figs 7 and 8 also show another somewhat unexpected thing. For a high enough difference $x_{D3}-x_{D1}$ and specific values of the interaction parameter $\tilde{V}_{DD}/\tilde{V}_{MM}$, the function t_3/t_1 has two distinct minima within the physical regime of the $(\Delta/\delta, d'/d)$ plane. One corresponds to $\Delta/\delta=1$; the second one is connected with higher values of Δ/δ (see Fig. 8).

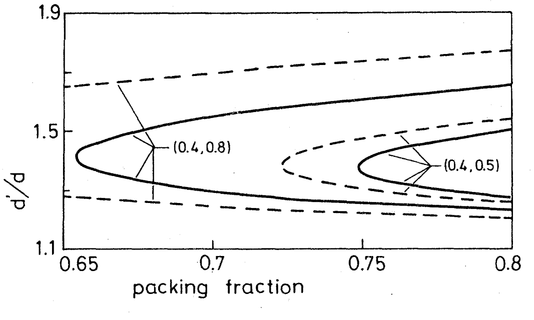


FIG. 6. Boundaries of regions for which $t_3/t_1 \leq 0.7$ on the (packing fraction, d'/d) plane for different values of $\tilde{V}_{DD}/\tilde{V}_{MM}$, x_{D1}, and x_{D3} (see caption of Fig. 4). Additionally, $\Delta/\delta=1.4$ is assumed.

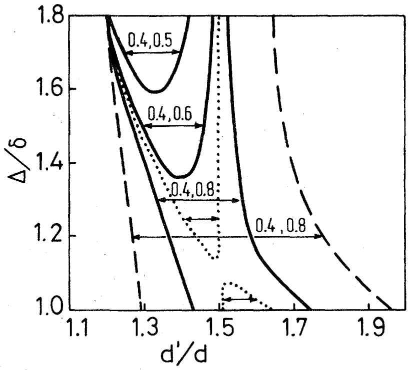


FIG. 7. Boundaries of regions for which $t_3/t_1 \leq 0.7$ on the $(d'/d,\Delta/\delta)$ plane for different values of $\tilde{V}_{DD}/\tilde{V}_{MM}$, x_{D1}, x_{D3}, and for $\kappa=0.7$ (see caption of Fig. 4). Dotted lines indicate the special case $\tilde{V}_{DD}/\tilde{V}_{MM}=5$, $(x_{D1},x_{D3})=(0.4,0.8)$.

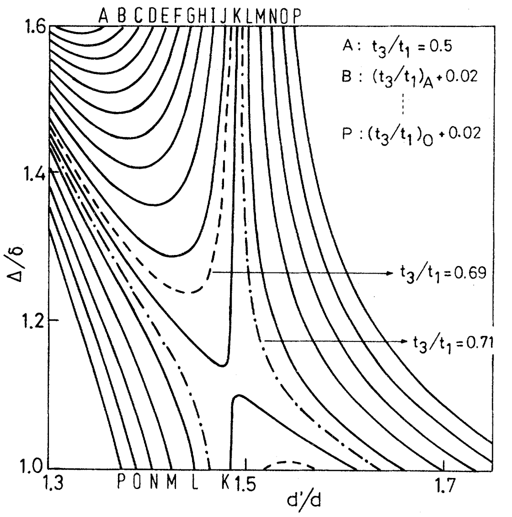


FIG 8. Lines of constant t_3/t_1 ratio on the $(d'/d,\Delta/\delta)$ plane for $\kappa=0.7$, $\tilde{V}_{DD}/\tilde{V}_{MM}=5$, $(x_{D1},x_{D3})=(0.4,0.8)$.

IV. DISCUSSION

First we shall compare the predictions of our model in somewhat more detail with experimental results. It is clear from the basic assumptions that the packing effects causing the transition to the reentrant nematic phase become less effective for values of d'/d close to 1 or close to 2. Now this, in turn, will depend on the degree of delocalization of the CN dipole over the molecule. Experimentally, for substances with two benzene rings, often d'/d values of the order of 1.4 are observed. This is in agreement with the predictions of Fig. 5. For substances with three rings, usually somewhat smaller values for d'/d are found, still in agreement with the theory. No reentrant behavior should occur if the CN dipole is strongly localized, and consequently the overlap of two monomers forming a dimer is small. This is the case if the CN group is directly attached to a cyclohexane ring. As far as we know, indeed no reentrant phases with such types of compound have been observed. There are some details such as the temperature dependence of the layer spacing that are beyond the scope of the model.

If we consider the reentrant behavior of homologous series, one finds experimentally that an increase of the length of the alkyl chains stabilizes the intermediate smectic phase.[3(e),12] This again is predicted by Figs. 3 and 5, as one expects in such a situation of an increase of d'/d. But for the larger d'/d ratio associated with longer chains, the conditions for reentrant behavior become less favorable. Another effect, not incorporated in the model, might help here. The longer the alkyl chains, the more possibilities for *gauche-trans* conformations which make the chain effectively bulkier and shorter. In this way the alkyl chains are able to fill the available space better, in agreement with the basic assumptions of the model.

The model also accounts for the effect of pressure on the phase behavior. The increase of the packing fraction with pressure will shift t_3/t_1 to lower values (Fig. 4), which means a shift of the transition to the reentrant-nematic phase to higher temperatures. The effect of pressure on the high-temperature nematic—smectic phase transition is much smaller, and above a certain pressure the smectic phase is not stable anymore, as observed experimentally.[3]

Inherent to the model is a reentrant smectic phase below t_3, again with the period d' of the dimer. In several cases, a smectic phase has been observed below the reentrant-nematic phase but with a period equal to the length of the monomer. Therefore, we do not like to call this behavior reentrant. However, recently real reentrant smectic behavior, again with spacings around $1.3d$, has been observed,[26] as predicted by the model. In addition, a second reentrant-nematic phase has been found.

Finally, we note that the model also allows for the possibility of a reentrant-nematic phase in the case $\Delta/\delta=1$ (Figs. 7 and 8). It means that, for certain values of the interaction parameters, the difference between the length of the monomer and that of the dimer is more important for reentrant-nematic behavior than the possible central bulky part of the dimer. In this situation, we could replace monomer and dimer by two different molecules of suitable dimensions and of appropriate distribution of induced forces. Then the theory predicts induced smectic behavior (or reentrant-nematic behavior versus concentration, because this is now the only way to vary x_D) even for a mixture of nonpolar molecules. This possibility will be discussed in some detail elsewhere, in combination with attempts to verify it experimentally.

Now we come to a more detailed discussion of the model itself. The process of dimer formation is a consequence of antiferroelectric interactions between the dipole moments of the molecules in combination with a liquid structure. Higher-order n-mers occur with a low probability because of the existence of the frustration effect.[27] By this is meant that when we put three molecules on, for example, a triangle, two can orientate their dipoles antiparallel, but then the direction of the third one is undetermined. In combination with the liquid structure, this will break up higher-order *n*-mers, and the most efficient way to lower the free energy is the formation of dimers.

In the model the dimer concentration x_D is used as an input parameter, and we do not propose here any self-consistent calculation for x_D. This means that the quantitative aspects of the results should be treated with some caution. Such self-consistent calculations would be much more difficult than the simple analysis given here and, moreover, would introduce additional parameters to the model. Nevertheless, no really new elements would be added to the theory as presented here, as the results are independent of the details of the shape of the $x_D(t)$ function. This can be tested using, for example, the simplified form

$$x_D(t)=\begin{cases} x_{D1}, & t\geq t_1-\omega \\ x_{D1}+(t-t_1+\omega)(x_{D3}-x_{D1})/(t_3-t_1+2\omega), & t_3+\omega\leq t\leq t_1-\omega \\ x_{D3}, & t\leq t_3+\omega \end{cases}$$

where $0<\omega<(t_1-t_3)/2$. The full phase diagram, however, depends on the detailed temperature variation of x_D in equilibrium. In principle, when there is a coupling between x_D and the smectic order parameter that is strong enough, one can expect that the picture presented here can repeat itself on the temperature scale. This implies a situation where several reentrant nematic phases will be separated by the same type of smectic phases, as recently observed in Bordeaux.[26] This seems to us a more probable explanation of this particular phase sequence than the occurrence of the two minima in Figs. 7 and 8.

The high-temperature nematic—smectic-*A* phase transition, as calculated in the model, has some analogy with the percolation problem observed in magnetic systems doped with annealed nonmagnetic impurities.[28] In our system we need a sufficient number of dimers (percolation threshold) to obtain a stable smectic-*A* modulation. From the point of view of packing, however, the monomers are still necessary to stabilize the smectic phase because they are better able to fill the space than when a dimer is surrounded by only dimers. When the percolation threshold is passed (sufficient value of x_D by decreasing the temperature or increasing the pressure), the tendency towards the smectic-*A* phase formation increases abruptly. Once the smectic phase has been formed, a further decrease of temperature (or increase of pressure) leads to a further increase of x_D, which due to the unfavorable packing of the dimers, finally destabilizes the smectic phase again.

Finally, we mention that the results of the model depend only on two characteristic lengths, namely, d'/d and Δ/δ. This means that the predictions of reentrant-nematic behavior remain true also for disklike molecules. In fact, in these types of systems reentrant nematics have also been observed.[29]

Next we come to a comparison with some other models. Berker and Walker[30] have proposed what is called a frustrated spin-glass model for reentrant behavior. The high-temperature nematic—smectic transition is attributed to the formation of "an infinite network ('polymer') of positionally disordered, but antiferroelectrically ordered molecules. Each layer, consecutively along the *z* direction, will have its own network, ... The result is the density modulation along the *z* axis." As discussed above, in our opinion such an infinite network will probably be unstable in connection with a liquid structure. More importantly, one would expect from such a long-range ordering some influence on both the static and dynamic behavior of the dielectric permittivity. Such effects have not been observed in the relevant temperature range.[9,11,31] In fact, experimentally $\bar{\epsilon}$ is approximately constant through all three phases: isotropic, nematic, and smectic *A*.

In a recent lattice model of reentrant behavior by Hida[32] it is assumed that all molecules form dimers ($x_D=1$) and occupy a face-centered-cubic lattice. Additionally empty spaces (vacancies) between the dimers are introduced. It is assumed that every lattice site is occupied by a dimer or not, double occupancy being inhibited. For a given pair potential, the model is solved within the mean-field approximation. We have done the same for the continuous version of Hida's model, which takes the full symmetry of the one-particle distribution function into account. Then the model is equivalent to a modified version of McMillan's theory with an approximation for the steric forces, from which, however, no reentrant phase transition is predicted. On the other hand, from the steric point of view there might be no essential difference between Hida's vacancies and the monomers. The decrease of the density of vacancies might then be somewhat related to the decrease of the monomer concentration which, in turn, would lead to reentrant behavior. An essential difference remains that in Hida's model necessarily $\tilde{V}_{MD}=\tilde{V}_{MM}=0$.

Luckhurst and Timimi[33] have shown that reentrant behavior can be obtained within McMillan's model by assuming the parameter

$$\alpha=2\exp[-(\pi r_0/d)^2]$$

to decrease with decreasing temperature. In fact, our model gives a physical interpretation to the model exercise of Luckhurst and Timimi. As we can see from Eq. (14a), the packing effects introduced in our model lead to changes in the same direction as obtained by the variation of α used.

Finally, we note that Prost has discussed reentrant behavior within the framework of a Ginzburg-Landau model.[34] In his view the reentrant behavior results from a competition between smectic ordering and antiferroelectric ordering. In our model the antiferroelectric interactions do only influence the phase behavior in an indirect way, via the dimer concentration x_D. Therefore, we can conclude that reentrant behavior is possible without the mechanism proposed by Prost. Of course, this does not necessarily exclude a possible influence of such effects.

Finally, we note that several other remarkable effects have been observed in connection with terminally polar liquid crystals. As already noted in Sec. I, the reentrant nematic phase may give way at lower temperatures to a second smectic-A phase, with a layer spacing commensurate with the molecular length. A direct phase transition between the two types of smectic phase is also possible.[16c] Secondly in mixtures of a terminally strongly polar compound and an "ordinary" compound an induced smectic phase may appear.[35] By ordinary we mean a nonpolar or relatively weakly polar compound. Cladis[36] has attributed this induced smectic phase to the decrease of association of the terminally polar compound due to the dilution with the less polar compound. However, the real situation is much more complicated because the existence of charge-transfer complexes between the terminally strongly polar compound and the ordinary compound has been demonstrated.[37] In principle, one could treat these mixtures along similar lines as discussed here, but with two equilibria involved (charge-transfer complex between ordinary and terminally polar compound, monomer-dimer for the polar compound only). This problem will be treated in more detail elsewhere.

All the effects described above indicate that the association between polar mesomorphic compounds has a profound influence on both the phase behavior and the physical properties. In analogy with the situation in the physics of ordinary liquids, we propose to call them *associated liquid crystals* to distinguish them from the more classical liquid-crystalline systems.

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