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► **To cite this version:**

Ioannis Lelidis, Geoffroy Durand. Landau Model of Electric Field Induced Smectic Phases in Thermotropic Liquid Crystals. *Journal de Physique II*, 1996, 6 (10), pp.1359-1387. 10.1051/jp2:1996136 . jpa-00248375

**HAL Id: jpa-00248375**

**<https://hal.science/jpa-00248375v1>**

Submitted on 4 Feb 2008

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# Landau Model of Electric Field Induced Smectic Phases in Thermotropic Liquid Crystals

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(Received 22 April 1996, received in final form 24 June 1996, accepted 3 July 1996)

PACS.61.30.Gd – Orientational order of liquid crystals; electric and magnetic field effects on order  
 PACS.64.60.Kb – Solid-solid transitions  
 PACS.64.70.Md – Transitions in liquid crystals

**Abstract.** — We extend the Landau-de Gennes phenomenological model of the electric field induced isotropic-nematic phase transition to describe electric field induced smectic A phase transitions, for varying coupling between orientational and positional order parameters. Increasing the field, first order nematic-smectic A transition becomes second order at a tricritical point. The electric field induced non spontaneous nematic phase, can be metastable close enough to the isotropic-smectic A spontaneous transition temperature. For strong enough nematic-smectic coupling, when reentrant nematic is favored, a new non spontaneous smectic phase exists. Another new field induced paranematic-parasmectic phase transition is expected followed by a first order parasmectic-smectic A transition which disappears above a critical point.

## 1. Introduction

Liquid crystal materials present a rich variety of order-disorder phase transitions [1] characterized by the onset of one or more order parameters of various symmetry, coupled between them and with external fields (electric or magnetic). Because of this coupling, phase transitions between the isotropic, nematic, and smectic A phases induced by external fields have been predicted, using mostly microscopic models. In this work, we develop a phenomenological Landau-de Gennes (LdG) model to unify previous predictions and to describe phase diagram topologies. The present model describes electric field induced smectic transitions whose systematic experimental study began recently [2].

Nematic liquid crystals (NLC) present orientational order with the mean molecule parallel to the director  $\mathbf{n}$  ( $\mathbf{n}^2 = 1$ ). The quadrupolar nematic ordering is described by the traceless tensor [1]:  $\mathbf{Q}_{ab} = S(3\mathbf{n}_a\mathbf{n}_b - \delta_{ab})/2$ , where  $0 \leq S \leq 1$  is the order modulus. In the isotropic phase, orientational order is lost ( $S = 0$ ). Because  $\mathbf{Q}_{ab}$  and  $-\mathbf{Q}_{ab}$  are physically different, the isotropic-nematic (I – N) phase transition is of first order with a critical point above which it disappears, as for the liquid-gas transition. An I – N field induced transition was indeed predicted by Hanus [3] in the frame of the Maier-Saupe [4–6] molecular theory and recalculated later with microscopic models [7–10] and phenomenological LdG models [11–13]. The nematic

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critical point has been observed by applying an electric field [14], which couples directly with the nematic order *via* the dielectric anisotropy of the material.

In the smectic A ( $S_A$ ) phase the molecules form layers perpendicular to  $\mathbf{n}$  [1]. An additional one-dimensional translational order exists. The smectic order is described by a complex order parameter  $\Psi(\mathbf{r}) = |\Psi|e^{-i\Phi}$  that specifies the amplitude and phase of the density modulation. The average attraction between molecules in the smectic layers becomes stronger with  $S$ , *i.e.*, the positional order is coupled with the orientational order [15–18]. This coupling was introduced by Kobayashi [15, 16] and McMillan [17, 18] to investigate the nematic-smectic A ( $N-S_A$ ) phase transition in a molecular theory frame. Kobayashi has extended the solid-liquid transition theory of Kirwood and Monroe [19]. McMillan has extended the Maier-Saupe model of the transition I–N [4–6]. According to their results the  $N-S_A$  transition could be either first or second order. The order of the transition changes at a tricritical point (TCP). de Gennes has shown [20] that the coupling between the two order parameters plays a crucial role in the appearance of the TCP. The tricritical point of the  $N-S_A$  phase transition has been observed by: (i) changing the length of the alkyl end chains [21], (ii) varying the concentration in binary mixtures [22], (iii) increasing the pressure [23] and (iv) applying a strong electric field [2].

The effects of magnetic field on the  $N-S_A$  and the  $I-S_A$  phase transitions were investigated by Hama [24] and Rosenblatt [25, 26]. The first has introduced the magnetic field in McMillan's model while the second has used a previously developed [27, 28] lattice model. These models predict that a strong enough magnetic field could induce the  $N-S_A$  and the  $I-S_A$  phase transitions at higher temperature than the *spontaneous* (without external field) transition temperature. The expected magnetic field to attain the TCP is  $\sim 6 \times 10^6$  G. For LC materials which spontaneously transit from the isotropic phase to the smectic A phase, a field induced *non-spontaneous nematic* (NSN) phase could arise [26] at a field of  $\sim 7.5 \times 10^6$  G. It is difficult to achieve such strong magnetic fields. Instead of a magnetic field one can use an electric field which couples more strongly with the system. Recently [2] we have induced by an electric field, the paranematic-non spontaneous nematic-smectic A ( $pN-NSN-S_A$ ) phase transitions. We localised the TCP of the field induced  $NSN-S_A$  transition. For the interpretation of the existing experimental data [2, 29], we need a general phenomenological model which does not exist yet. The aim of the present paper is to extend the LdG model of the electric field induced  $pN-N$  transition to describe the  $pN-NSN$ , the  $NSN-S_A$ , the  $N-S_A$ , the  $I-S_A$  and the smectic A-reentrant nematic ( $S_A-RN$ ) [30–33] phase transitions in a simple and unified way.

In Section 2 we define the model. In Section 3 we recall the electric field induced  $I-N$  phase transition model. Section 4 describes the electric field induced phase transition to a smectic A phase, the non-spontaneous nematic phase, and a new field induced *parasmectic* phase. Section 5 is devoted to the field induced reentrant nematic transition where a new non spontaneous smectic A phase is predicted. In Section 6, we show the free energy *versus* order diagrams of the phases. In Section 7, we present the final temperature, coupling, electric field phase diagram of the isotropic-nematic-smectic A transitions. A preliminary report of the electric field induced NSN phase was given in reference [2].

## 2. Model

2.1. THE FREE ENERGY. — In what follows, we discuss only the behaviour of uniform systems. The normalized strength of the smectic order parameter  $|\Psi|$  is defined as [1]:

$$\frac{\delta\rho}{\rho_0} \approx \text{Re} \left\{ \frac{1}{\sqrt{2}} \Psi(\mathbf{r}) \exp [i(\mathbf{q}_s \cdot \mathbf{r})] \right\}, \quad (1)$$

where  $\rho_0$  is the average density,  $\delta\rho$  its oscillating amplitude, and  $2\pi/q_s = d$  is the smectic layer spacing. We imagine (see later) that there exist a “stabilizing electric field”  $\mathbf{E}||\mathbf{n}$ , which decreases the free energy density  $f$  of the system.  $f$  writes as:

$$f = f_N(T, S) + f_A(T, \Psi) + f_{AN}(S, \Psi) + f_E(S, \Psi, E), \quad (2)$$

where  $f_N(T, S)$  is the free energy density of the nematic phase,  $f_A(T, \Psi)$  corresponds to the translational ordering,  $f_{AN}(S, \Psi)$  is the contribution from the coupling between  $S$  and  $\Psi$ , and  $f_E(S, \Psi, E)$  is the free energy density associated to the coupling of the electric field with the order parameters. In the frame of the LdG formulation each term of  $f$  is expanded in powers of  $S$  and  $\Psi$  as follows [1]:

$$f_N = f_0 + \frac{1}{2}A_N S^2 + \frac{1}{3}b_N S^3 + \frac{1}{4}c_N S^4 + \dots, \quad (3a)$$

where:

$$A_N = a_N(T - T_{NI}^*). \quad (3b)$$

$f_0$  is the free energy density of the I-phase ( $S = \Psi = 0$ ).  $T$  is the absolute temperature.  $T_{NI}^*$  is the isotropic supercooling temperature.  $a_N, b_N, c_N$ , are supposed constants. As the I – N transition is first order, one chooses:  $a_N > 0$ ,  $b_N < 0$ , and  $c_N > 0$  [1]. The term  $f_A(T, \Psi)$  describing the one dimensional uniform positional order contains only even powers [1] of  $|\Psi|$ .  $f_A$  writes as:

$$f_A = \frac{1}{2}A_A |\Psi|^2 + \frac{1}{4}c_A |\Psi|^4 + \dots, \quad (4a)$$

where :

$$A_A = a_A(T - T_{AN}^*). \quad (4b)$$

$T_{AN}^*$  is the supercooling temperature limit of the nematic phase for the uncoupled system ( $f_{AN} = 0$ ) in absence of electric field ( $E = 0$ ).  $a_A, c_A$ , are supposed constants.  $a_A$  is chosen positive because  $f_A(T, 0)$  must have a minimum for  $T > T_{AN}^*$  and a relative maximum for  $T < T_{AN}^*$ . The coefficient  $c_A$  is chosen positive to provide stability. In absence of coupling, equation (4) describes a second order transition. From  $f_A$  one could think that the smectic order could appear at  $T_{AN}^*$  without nematic order. But if the system builds layers in one direction from isotropic objects, *i.e.*, *without* nematic order, then layers should appear also along other directions of space and one should get a three-dimensional crystal. To obtain one-dimensional smectic order only, one must introduce a coupling between  $S$  and  $\Psi$  so that nematic order exists as soon as positional order appears. At lowest order the coupling term  $f_{AN}(S, \Psi)$  can be written as follows:

$$f_{AN} = \gamma S |\Psi|^2 + \frac{1}{2}\lambda S^2 |\Psi|^2 + \dots, \quad (5)$$

$\gamma, \lambda$ , are the coupling constants. An  $S\Psi$  term does not appear in  $f_{AN}(S, \Psi)$  because  $\Psi$  is modulated and  $S$  is uniform.  $\gamma$  is chosen negative to favor the  $S_A$  phase when the nematic order exists. The second coupling term represents a saturation ( $\lambda > 0$ ). It allows reentrant effects [30–33]. As previously explained  $\gamma$  cannot be zero. This restriction does not exclude that  $f_{AN}(S, \Psi)$  could become zero for  $S \neq 0$  from the superposition of other coupling terms. Because of the  $(S, \Psi)$  coupling, the spontaneous N –  $S_A$  phase transition can be of second or first order [20]. For weak enough  $(S, \Psi)$  coupling the N –  $S_A$  transition remains of second order, and it is of first order for strong enough coupling. In the development (5), we suppose that higher order terms in the coupling can be neglected. In fact, one guesses that, at a first order

transition, these terms would be important and should not be neglected. For sake of simplicity, we keep only these lowest order terms. The situation is the same for the nematic phase: the development of  $f_N$  should contain higher order terms, especially far from the I – N transition temperature [29, 34] but for simplicity we do not take them into account.

We discuss now the effect of a “stabilizing” field. This leads to describe the coupling of the order parameters with an uniform external electric field. From symmetry arguments, the lowest order terms of  $f_E(S, \Psi, E)$  the development writes as:

$$f_E = \mu E^2 S + \dots + \frac{1}{2} \mu' E^2 |\Psi|^2 + \dots, \quad (6)$$

where  $\mu$  and  $\mu'$  are constants. The first term, called dielectric term in what follows, comes from the direct coupling of the electric field  $E$  with  $S$  *via* the dielectric anisotropy  $\varepsilon_a$ .  $\mu = -\varepsilon_{a0}/12\pi$ ;  $\varepsilon_{a0} = \varepsilon_a/S$  is the dielectric anisotropy for  $S = 1$ . For typical materials,  $\varepsilon_{a0} \sim 10 - 20$ . For  $\varepsilon_a > 0$ , the electric field is stabilizing when orienting  $\mathbf{n}$  along its direction. When the smectic order is present, the dielectric term gives also an indirect coupling of the electric field with  $\Psi$  *via* the  $(S, \Psi)$  coupling (Eq. (5)) between the two order parameters. The second term of equation (6) describes a direct coupling between  $\Psi$  and the electric field *via* what could be called “smectic electrostriction”. It is well-known [35] that the volume  $V$  of a compressible fluid (and consequently its density  $\rho$ ) changes when subjected to the electrostatic pressure  $p = \varepsilon_{\text{iso}} E^2 / 8\pi$ , where  $\varepsilon_{\text{iso}}$  is the isotropic dielectric constant. Typically,  $\varepsilon_{\text{iso}} \sim \varepsilon_{a0}$ . Taking as positive the external applied pressure, the free energy density varies as  $p dV/V = -p \Delta\rho/\rho$ . By symmetry,  $\Delta\rho/\rho$  is proportional to  $|\Psi|^2$ , as:  $\Delta\rho/\rho = \kappa |\Psi|^2$ .  $\kappa$  can be estimated from the measured increase of density at an I –  $S_A$  phase transition [36], typically of  $\Delta\rho/\rho \sim +10^{-2}$ . Assuming  $|\Psi| \sim 0.6$ , one estimates  $\kappa \sim 3 \times 10^{-2}$ . The smectic electrostriction term  $\mu'$  is then comparable to  $\kappa \sim 10^{-2}$ . In the isotropic phase, the electrostatic pressure would result in a relative change of density  $\sim (\varepsilon_{\text{iso}} E^2 / 8\pi) / K_{\text{iso}}$ , where  $K_{\text{iso}} \sim 10^{10}$  dyn/cm<sup>2</sup> is the bulk liquid rigidity. For fields  $E$  lower than  $E_{\text{elastic}} = \sqrt{\kappa K_{\text{iso}}} \sim 10^4$  in cgs units, the smectic electrostriction dominates over the conventional one. As  $E_{\text{elastic}} \sim 300$  V/ $\mu\text{m}$ , one order of magnitude larger than the largest typically obtained field [2, 29], the conventional direct effect is negligible. In what follows, we assume the smectic to be incompressible ( $K_{\text{iso}} \sim \infty$ ).

We can now compare the direct  $E^2 |\Psi|^2$  coupling of the applied field  $E$  on the smectic order with the indirect coupling through  $E^2 S$  and  $S |\Psi|^2$ . For strong  $S |\Psi|^2$  coupling  $\gamma$ ,  $\Psi^2$  and  $S$  compare (see later). As  $\mu \sim 1$  and  $\mu' \sim 10^{-2}$ , the direct electric coupling is usually much less efficient than the indirect one and can be neglected. We describe later the one situation (weak coupling  $\gamma$ ) where the direct electric coupling should be considered.

2.2. STATES OF EQUILIBRIUM. — The minimization of  $f$  with respect to  $S$ , and to the amplitude  $|\Psi|$  (the phase is here irrelevant) gives the following two equilibrium conditions:

$$\begin{cases} \frac{\partial f}{\partial |\Psi|} = f'_{|\Psi|} = |\Psi| (A_A + c_A |\Psi|^2 + 2\gamma S + \lambda S^2) = 0 \\ \frac{\partial f}{\partial S} = f'_S = A_N S + b_N S^2 + c_N S^3 + \gamma |\Psi|^2 + \lambda S |\Psi|^2 + \mu E^2 = 0 \end{cases} \quad (7)$$

For thermodynamic stability,  $f$  must always increase for small deviations of  $S$ ,  $|\Psi|$  around equilibrium. The following stability conditions must be fulfilled:

$$\frac{\partial^2 f}{\partial S^2} = A_N + 2b_N S + 3c_N S^2 + 2\lambda |\Psi|^2 > 0 \quad (8a)$$

$$\frac{\partial^2 f}{\partial |\Psi|^2} = A_A + 3c_A |\Psi|^2 + 2\gamma S + \lambda S^2 > 0, \quad (8b)$$

with the Hessian:

$$\frac{\partial^2 f}{\partial S^2} \frac{\partial^2 f}{\partial |\Psi|^2} > \left( \frac{\partial^2 f}{\partial S \partial |\Psi|} \right)^2 = [2(\gamma + \lambda S)|\Psi|]^2 \quad (8c)$$

With the previously discussed point that the  $S|\Psi|^2$  coupling  $\gamma$  can never be zero, the system (7) with the conditions (8) could be satisfied by solutions ( $S_0|\Psi_0|$ ) corresponding to the three following situations in absence of external field:

- i) ( $S_0 = 0, |\Psi_0| = 0$ ), total absence of order.
- ii) ( $S_0 \neq 0, |\Psi_0| = 0$ ), only orientational order exists.
- iii) ( $S_0 \neq 0, |\Psi_0| \neq 0$ ), both kinds of order exist.

The first case corresponds to the isotropic phase; the second one to the nematic phase alone; the last case corresponds to a smectic phase. Note that even for  $T_{AN}^* > T_{NI}^*$ , nematic order is always induced when positional order appears.

Let us write now the existence condition of the  $S_A$  phase. From (7) we find:

$$|\Psi|^2 = \begin{cases} -\frac{A_A + 2\gamma S + \lambda S^2}{c_A} & \text{if } A_A + 2\gamma S + \lambda S^2 < 0 \\ 0 & \text{if } A_A + 2\gamma S + \lambda S^2 > 0 \end{cases} \quad (9)$$

The equation:

$$A_A + 2\gamma S + \lambda S^2 = 0 \quad (10)$$

defines the limits of the smectic A phase existence. In what follows where we discuss ( $S, T$ ) phase diagrams, this limit is called "smectic line". From (10) we see that the transition to the smectic A phase depends on the temperature  $T_{AN}^*$  and on the ratio  $\gamma/a_A$ . The transition is favored by a large enough nematic order. The saturation coupling term  $\lambda S^2$  is important for reentrance phenomena, discussed later.

### 3. The Nematic Phase

We recall here well-known properties of the I – N transition. The nematic phase has only orientational order and no positional order. Equation (7) simplifies to:

$$f'_S = f'_N + f'_E = A_N S + b_N S^2 + c_N S^3 + \mu E^2 = 0. \quad (11a)$$

The stability condition (8a) gives:

$$f''_S = A_N + 2b_N S + 3c_N S^2 > 0. \quad (11b)$$

The spinodal line  $f''_S = 0$  defines the stability region: inside the spinodal the system is completely unstable. Equation (11a) describes the first order I – N transition at the temperature  $T_{NI}$  in absence of external field and the pN – N first order transition under a stabilizing electric field. We do not give here a detailed description of these transitions extensively described in the literature [3, 7–13]. Under the electric field  $E$  action, the minimum of  $f$  corresponding to the isotropic state is no more  $S = 0$ . It is shifted to a small but non zero value, proportional to  $E^2$  (Kerr effect). The field induced pN phase appears. The second minimum corresponding to the nematic phase shifts also to a higher order value. A critical point exists for  $f'_S = f''_S = f'''_S = 0$ .

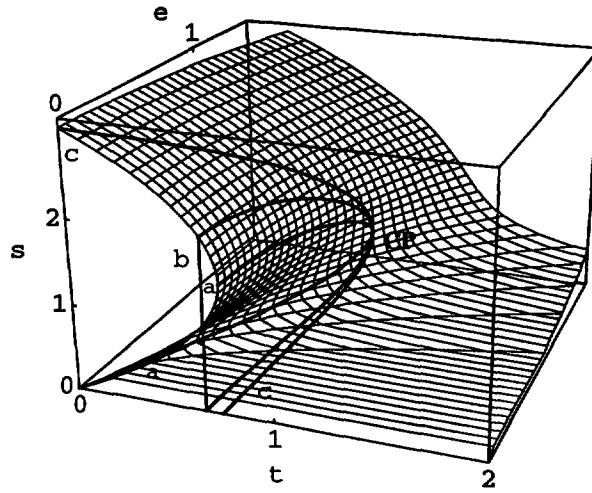


Fig. 1. — Paranematic-nematic transition surface in the space  $(T, S, E)$ .  $t = (T - T_{NI}^*) / (T_C - T_{NI}^*)$ ,  $s = S / S_C$ , and  $e = E / E_C$ . a: spinodal; b: binodal; c: conjugate of the spinodal; CP: critical point.

The coordinates of the critical point, *i.e.*, the critical order  $S_C$ , the critical field  $E_C$ , and the critical temperature  $T_C$  are:

$$\begin{cases} S_C = -\frac{b_N}{3c_N} \\ E_C^2 = \frac{b_N S_C^2}{3\mu} \\ T_C = T_{NI}^* + \frac{b_N^2}{3a_N c_N} \end{cases} \quad (12)$$

Above the critical point the two phases pN and N are indistinguishable, as for the liquid-gas transition. In Figure 1 we present the  $(T, S, E)$  phase diagram of the I – N transition under a stabilising electric field for a liquid crystal of positive dielectric anisotropy. We used the values of the coefficients of equation (11a) for the compound 4'-n-pentyl-cyanobiphenyl (5CB) [14]:  $a_N = 0.11 \times 10^7 \text{ erg/cm}^3$ ,  $b_N = 1.56 \times 10^7 \text{ erg/cm}^3$ ,  $c_N = 3.47 \times 10^7 \text{ erg/cm}^3$ ,  $T_{NI} = 306.8 \text{ K}$ . The coordinate axes are the reduced temperature  $t = (T - T_{NI}^*) / (T_C - T_{NI}^*)$ , the reduced nematic order parameter  $s = S / S_C$  and the reduced electric field  $e = E / E_C$ . The curve a is the spinodal line. The curve c is the conjugate of the spinodal line, *i.e.*, the line representing the value of the other minimum of  $f$  for the same  $E, t$ . The curve b is the coexistence line (binodal) of the transition and it defines the transition temperature under electric field. Let us follow an isofield from the pN-phase. When we intersect the spinodal, the system transits towards the N-phase on the conjugate of the lower spinodal. Let us follow an isofield from the N-phase. When we intersect the spinodal, the system transits towards the pN-phase on the conjugate of the upper spinodal. This process is responsible for the hysteresis of the first order transition.

#### 4. The Smectic Phase

The smectic phase has orientational and positional order:  $S \neq 0$  and  $|\Psi| \neq 0$ . One has to consider the full equation (2). As the two kinds of order are coupled we can eliminate the

orientational or the positional order parameter to write the free energy as function of only one order parameter. Here we choose to keep the orientational order parameter  $S$  because existing experimental data measured only orientational order [2, 29]. For  $|\Psi| \neq 0$ ,  $f$  can be written as function of  $S$  alone, by substituting  $|\Psi(S)|^2$  from equation (9) in equation (2). We obtain:

$$f = f_0 - \frac{A_A^2}{4c_A} + (\mu E^2 - A_A \gamma / c_A) S + \frac{1}{2} A S^2 + \frac{1}{3} b S^3 + \frac{1}{4} c S^4, \quad (13)$$

where the renormalized coefficients are:  $A = A_N - (\lambda A_A + 2\gamma^2) / c_A$ ,  $b = b_N - 3\lambda\gamma / c_A$ , and  $c = c_N - \lambda^2 / c_A$ . The equilibrium conditions (7) write as:

$$f' = (\mu E^2 - A_A \gamma / c_A) + A S + b S^2 + c S^3 = 0 \quad (14)$$

To ensure stability, we suppose that  $c_N > \lambda^2 / c_A$ . If it were not the case, higher order terms should be included. The spinodal of the coupled system which defines its stability is given by  $f'' = 0$ , *i.e.*:

$$f'' = A + 2bS + 3cS^2 = 0 \quad (15)$$

The spinodal is independent of  $E$ .

Let us now repeat de Gennes' argument [20] for the order of the N – S<sub>A</sub> transition. One writes for the free energy  $f$  of the smectic phase:

$$f \approx f_N(S_0) + \frac{1}{2} f''_{S_0} (S - S_0)^2 + \frac{1}{2} \mu E^2 S + \frac{1}{2} A_A |\Psi|^2 + \frac{1}{4} c_A |\Psi|^4 + \gamma S |\Psi|^2, \quad (16)$$

where  $f_N(S_0)$  is the free energy of the nematic phase at the N – S<sub>A</sub> phase transition temperature,  $S_0$  is the nematic order parameter value at the transition, and  $f''_{S_0}$  is its second derivative at the same point. After minimisation and eliminating  $S$ , one finds:

$$f \approx f_N(S_0, E) + \frac{1}{2} a_A (T - \tilde{T}_{AN}^*) |\Psi|^2 + \frac{1}{4} \tilde{c}_A |\Psi|^4, \quad (17)$$

where:  $\tilde{T}_{AN}^* = T_{AN}^* + \frac{2\gamma}{a_A} \left( \frac{\mu}{f''_{S_0}} E^2 - S_0 \right)$  and  $\tilde{c}_A = c_A - 2\gamma^2 / f''_{S_0}$ . One observes a renormalization of the transition temperature due to the  $(S, \Psi^2)$  coupling and the electric field effect. One also sees a renormalization of the saturation term  $\tilde{c}_A$  with the addition of a negative quantity. For strong enough  $(S, \Psi^2)$  coupling,  $\tilde{c}_A$  can become negative, *i.e.*, the transition becomes first order. In this case, one should add in (16) a positive  $|\Psi|^6$  term to ensure stability. If the coupling is weak enough,  $\tilde{c}_A$  remains positive and the transition is of second order.

One can classify the transitions between the isotropic, nematic and smectic A phases using as parameter either  $T_{AN}^*$  or the reduced coupling  $\gamma / a_A$  between the two order parameters. We choose the last way. When the spontaneous N – S<sub>A</sub> phase transition is of second order, we call the coupling *vanishingly weak* if under electric field the smectic electrostriction becomes dominant, and *very weak* if the indirect coupling is dominant. If the N – S<sub>A</sub> phase transition is of first order, we call the coupling *weak*. When the TCP appears at the transition, the coupling is called *tricritical*. When the LC material exhibits spontaneously the I – S<sub>A</sub> phase transition, we call the coupling *medium* if a NSN-phase is induced by the field, and *strong* if the electric field does not induce a NSN-phase. All these situations were already discussed independently in various microscopic models [24–26]. In the following we examine the different possibilities in presence of electric field in our LdG phenomenological model.

Typical values for the model coefficients are given in the Table I. The coefficients are chosen of the same order of magnitude as the experimental values of 5CB [14] in the nematic case,



Table I. — *Model parameters used for nematic-smectic coupling ranged between very weak and medium.*

$a_N$	$(10^7 \text{ erg/Kcm}^3)$	0.1
$b_N$	$(10^7 \text{ erg/cm}^3)$	-2.0
$c_N$	$(10^7 \text{ erg/cm}^3)$	5.0
$a_A$	$(10^7 \text{ erg/Kcm}^3)$	0.05
$c_A$	$(10^7 \text{ erg/cm}^3)$	0.4
$\lambda$	$(10^7 \text{ erg/cm}^3)$	0.7
$T_{NI} - T_{NI}^*$	(K)	1.8
$T_{AN}^* - T_{NI}^*$	(K)	-8.7

and of a mixture of 25% in 8CB and 10CB which transits spontaneously from the isotropic phase to the smectic A one [2]. In what follows, we keep these coefficients constants and we allow only the reduced coupling  $\gamma/a_A$  to vary, typically from -10 to -70. For each value of the coupling, we draw the  $(S, T)$  phase diagram calculated numerically. We show later the  $f(S)$  diagrams as function of temperature, field, and the reduced  $\gamma/a_A$  coupling.

4.1. VANISHINGLY WEAK COUPLING. — When the  $(S, \Psi)$  coupling is vanishingly weak the only influence of the electric field on the smectic order comes from the direct smectic electrostriction coupling.  $f$  can be approximated as:

$$f \approx f_N(S_0) + \frac{1}{2}f''_{S_0}(S - S_0)^2 + \frac{1}{2}\mu E^2 S + \frac{1}{2}A_A|\Psi|^2 + \frac{1}{4}c_A|\Psi|^4 + \frac{1}{2}\mu' E^2|\Psi|^2. \quad (18)$$

After minimisation and eliminating  $S$ ,  $T_{AN}^*$  is renormalized to:

$$\tilde{T}_{AN}(\gamma = 0) = T_{AN}^* - \frac{\mu'}{a_A}E^2. \quad (19)$$

In absence of coupling, as  $\mu'/a_A < 0$ , smectic electrostriction provokes an increase of the transition temperature proportional to the square of the applied electric field. Smectic electrostriction does not influence the order of the transition. In presence of coupling, smectic electrostriction renormalizes the coefficient of the field dependent part of the  $T_{AN}^*$  variation. Although simple, this result is new, since direct coupling was never discussed. In what follows, we do not consider smectic electrostriction any more. This approximation does not change qualitatively the results of the model.

4.2. VERY WEAK COUPLING. — In the absence of coupling, the two transitions in  $S$  and  $\Psi$  have been chosen stable. For very weak coupling, they stay stable. The N -  $S_A$  transition is of second order. In Figure 2 we give the  $(S, T)$  phase diagram for different values of the field  $E$ . The ordinate scale represents the temperature  $t = T - T_{NI}$ . This phase diagram is calculated with  $\gamma = -0.65 \times 10^7 \text{ erg/cm}^3$  and  $\gamma/a_A = -13.0$ . The curve a is the zero field equilibrium line.  $S(T)$  is calculated from (11a) in the nematic phase and from (14) in the smectic phase. At  $T_{NI}$  appears the nematic phase with a jump of  $S$  from zero to  $S_{NI} = 2S_C$ . When cooling,  $S$  changes continuously with the temperature while at the N -  $S_A$  transition temperature ( $T_{AN}$ ) appears a slope  $\partial S/\partial T$  discontinuity. This slope discontinuity is due to the continuous onset of positional order as it is shown at the bottom of the same figure (curve a').  $|\Psi(T)|^2$  is calculate from (9).  $T_{AN}$  is defined from (7) and the supplementary condition of equal energy of the two

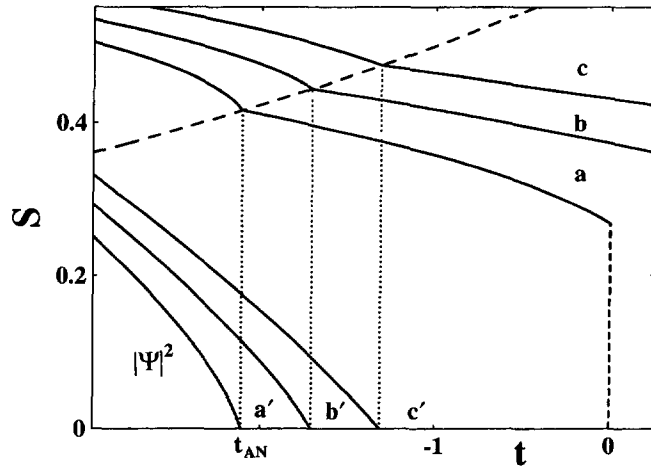


Fig. 2. —  $S, t = T - T_{NI}$  phase diagram for very weak coupling. The dashed line is the smectic line. a is the equilibrium curve for zero field. b, c are isofields. The lines a', b', c' show  $|\Psi|^2$  for the a, b, c isofields. The  $T_{AN}$  upshifts with the field.

phases,  $f(T_{AN}) = f_S(T_{AN})$ . The smectic line (dashed curve) intersects the  $S(T)$  line at  $T_{AN}$ . In absence of field, one finds:

$$S_{AN}^{\pm} = -\frac{b_N - 2\gamma a_N/a_A}{2(c_N - \lambda a_N/a_A)} \pm \sqrt{\left(\frac{b_N - 2\gamma a_N/a_A}{2(c_N - \lambda a_N/a_A)}\right)^2 - \frac{a_N(T_{AN}^* - T_{NI}^*)}{c_N - \lambda a_N/a_A}}. \quad (20)$$

The  $S_{AN}^-$  root corresponds to a non physical unstable nematic. The order  $S_{AN}$  at the  $N - S_A$  transition is given by the  $S_{AN}^+$  solution. The transition temperature  $T_{AN}$  is calculated from the condition  $|\Psi(T_{AN})| = 0$  which writes as:

$$T_{AN} = T_{AN}^* - \frac{[2\gamma S_{NA}^+ + \lambda(S_{NA}^+)^2]}{a_A} \quad (21)$$

Let us now see the effect of the electric field on the  $N - S_A$  transition. The field induced  $N - S_A$  transition temperature  $T_{AN}(E)$  and the order  $S_{AN}(E)$  at the transition are calculated numerically from the system (10, 11a) using the coefficients of Table I. The isofield b (Fig. 2) is calculated for  $E = 2E_C$ .  $T_{AN}(E)$  is displaced at higher temperatures. The slope discontinuity at  $T_{AN}(E)$  is smaller than at zero field. This happens because the smectic order increases slower from zero (curve b'). The isofield c is calculated for  $E = 3E_C$ . The slope discontinuity is even smaller while  $T_{AN}(E)$  has increased more. One concludes that  $T_{AN}(E)$  is increasing with the field as expected while the slope  $\partial S/\partial T$  discontinuity at  $T_{AN}(E)$  decreases. As the nematic order  $S_0$  at the  $N - S_A$  transition increases with the field:  $S_0 \rightarrow S_0 - \mu E^2/f''_{S_0}$ , the appearance of the smectic order at the transition has smaller influence on the nematic order because this later is saturated by the field.

4.3. TRICRITICAL COUPLING. — We increase  $|\gamma|$  keeping the other parameters constants. For  $E = 0$ , when the transition point coincides with the TCP at  $T_{AN}$  for  $\gamma = \gamma_{TC}$ , the Hessian (8) becomes equal to zero. The  $N - S_A$  transition appears with infinite slope just before the first order transition. The TCP is found at the intersection of the smectic line (10) and the smectic

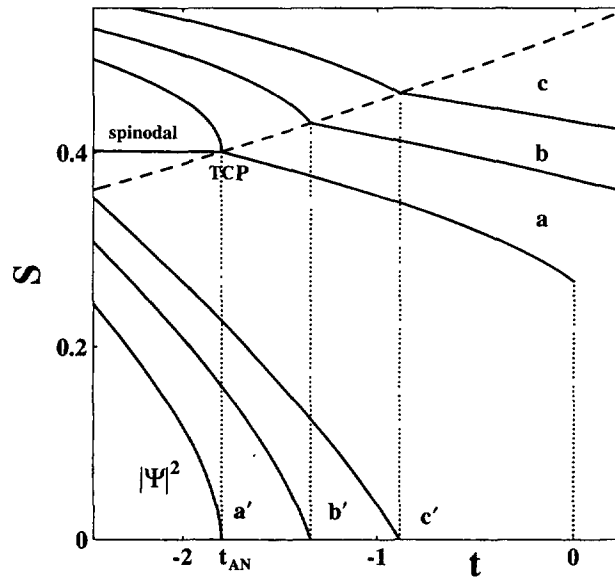


Fig. 3. — Same as Figure 2 for tricritical coupling. TCP: tricritical point.

spinodal (15). When this point appears at the  $N - S_A$  transition, it belongs also to the nematic equilibrium curve (11a) in absence of field. These conditions define the value of  $\gamma_{TC}$  as:

$$\gamma_{TC} = -\lambda S_{TC} \pm \left[ (\lambda S_{TC})^2 + c_A S_{TC} \frac{(b_N + c S_{TC})}{2} \right]^{1/2} \quad (22)$$

where  $S_{TC}$  is the orientational order at the transition. Using the values of Table I, we calculate  $\gamma_{TC} = -0.683 \times 10^7$  erg/cm<sup>3</sup> and  $\gamma_{TC}/a_A = -13.67$ . The corresponding  $(S, t = T - T_{NI})$  phase diagram is shown in Figure 3. For  $E = 0$  (curve a),  $S$  appears at the transition point with an infinite slope from the smectic side, and a finite slope from the nematic side. The isofields b, c are calculated for  $E = 2E_C$  and  $E = 3E_C$  correspondingly. On the isofield b one remarks that the electric field changes the infinite slope of  $S$ , from the smectic side, to a finite one. At  $T_{AN}(E)$ , the slope of the isofields is decreasing with the field from both sides of the transition. The slope decrease is more rapid from the  $S_A$  side. The slope discontinuity at  $T_{AN}(E)$  is decreasing with the field while  $T_{AN}(E)$  increases. The field induced transition could become of first order when changing the sign of the dielectric term while keeping the orientation. This situation has no simple physical meaning.

4.4. WEAK COUPLING. — In the absence of electric field, the  $N - S_A$  transition is of first order when  $|\gamma| > |\gamma_{TC}|$ . At  $T_{AN}$ , the Hessian (8c) is negative. With  $\gamma = -0.72 \times 10^7$  erg/cm<sup>3</sup> and  $\gamma/a_A = -14.4$ , we obtain the  $(S, t = T - T_{NI})$  phase diagram shown in Figure 4. In the absence of field, the  $N - S_A$  transition at  $t_{AN}$  is of first order and shows a jump of  $S$  (curve a) because positional order (curve a') appears discontinuously. The electric field effect (isofields b, c) is difficult to show on this scale. In Figure 5 we show a magnification of the region around the  $N - S_A$  transition. The lower dashed line  $S - sp$  is the smectic line and the upper dashed line is its conjugate. The solid line is the upper spinodal. The curve  $S - sp - conjugate$  is the conjugate of the upper spinodal. In the region between the coupled spinodal line and the

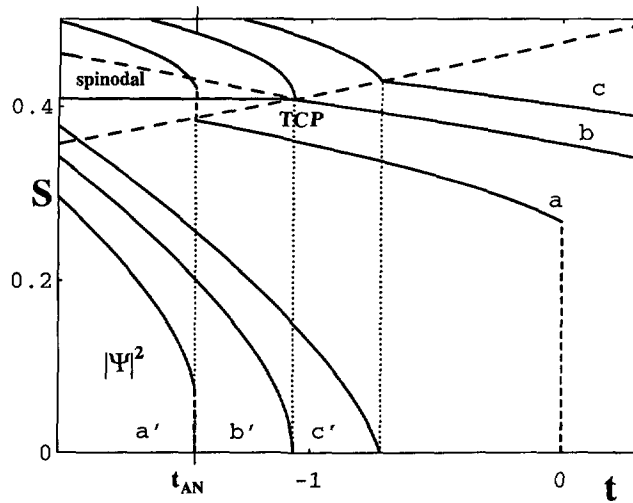


Fig. 4. — Same as Figure 2 for weak coupling. TCP: tricritical point.

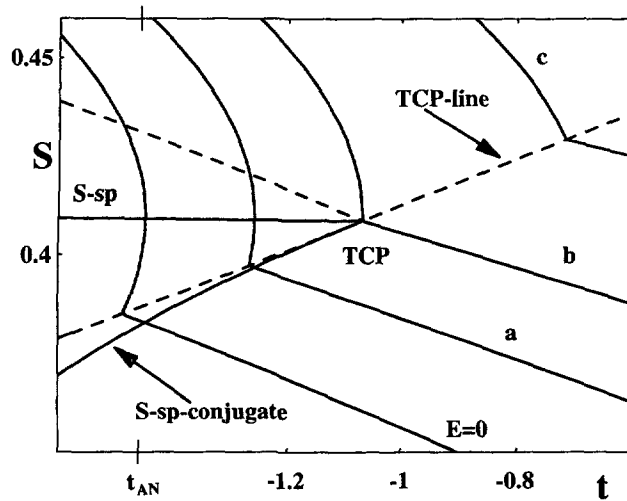


Fig. 5. —  $S, t = T - T_{NI}$  phase diagram for weak coupling around the spontaneous ( $E = 0$ ) nematic-smectic A phase transition temperature  $t_{AN}$ . The lower branch of the dashed line is the smectic line, the upper branch is its conjugate. S - sp: smectic spinodal; S - sp - conjugate is its conjugate line. TCP: tricritical point.  $E = 0$ , a, b, c are isofields.

smectic line, the smectic phase is unstable. The transition temperature  $T_{AN}(E)$  is defined from the supplementary condition:

$$f(S \neq 0, |\Psi| \neq 0) = f(S \neq 0, |\Psi| = 0). \tag{23}$$

The intersection of the smectic spinodal with the equilibrium line  $S(T, E = 0)$  (curve  $E = 0$ ) gives the superheating limit  $T_{AN}^{**}$  of the first order  $N - S_A$  transition in absence of external field.

The intersection of the spinodal with the smectic line defines the TCP where the transition becomes of second order with coordinates  $(S_{TC}, T_{TC})$  given by:

$$\begin{aligned} S_{TC}^{\pm} &= -\frac{b - a_C \gamma / a_A}{3c - a_C \lambda / a_A} \pm \sqrt{\left(\frac{b - a_C \gamma / a_A}{3c - a_C \lambda / a_A}\right)^2 - \frac{a_C (T_{AN}^* - T^*)}{3c - a_C \lambda / a_A}} \\ T_{TC}^{\pm} &= T_{AN}^* - S_{TC}^{\pm} (2\gamma + \lambda S_{TC}^{\pm}) / a_A, \end{aligned} \quad (24a)$$

where  $a_C = a_N - \lambda a_A / c_A$  and  $T^* = a_N T_{NI}^* / a_C + (2\gamma^2 - \lambda a_A T_{AN}^*) / c_A a_C$ . The spinodal and the smectic lines intersect in two points which should present tricritical behaviour. For this coupling, the spontaneous N – S<sub>A</sub> transition appears before  $T_{TC}^-$ , and the  $(T_{TC}^-, S_{TC}^-)$  point is not visible. The tricritical point is the  $(T_{TC}^+, S_{TC}^+)$  point. Note that the TCP does not depend on the field, in our model approximation. The “tricritical field” to attain the TCP is given by:

$$E_{TC}^2 = \frac{1}{\mu} \left[ \frac{A_A (T_{TC}) \gamma}{c_A} - A(T_{TC}) S_{TC} - b S_{TC}^2 - c S_{TC}^3 \right]. \quad (24b)$$

For the given coefficient in Table I, we calculate:  $E_{TC} = 35.06 \text{ V}/\mu\text{m}$ . The curves a, b, c in Figure 5 are isofields. The isofield a corresponds to the field  $E = E_{TC} / \sqrt{2}$ . One remarks that the transition happens at a higher  $S$  than for zero field and the order discontinuity at the transition temperature decreases with the field, while  $T_{AN}$  has increased. For  $E = E_{TC}$  the TCP appears and the transition becomes second order (isofield b). At the tricritical point, the curve  $S(T, E_{TC})$  has a finite slope on the nematic side and an infinite slope on the smectic side. The isofield c is calculated for  $E = \sqrt{2} E_{TC}$ . The transition remains of second order and the slope discontinuity is smaller than at the TCP. The part of the smectic line on the right of the TCP is a critical points line.

**4.5. TRIPLE POINT COUPLING.** — When the nematic-smectic coupling becomes stronger, in absence of external field, the region of the nematic phase shrinks out and disappears for high enough coupling. When the temperatures of the I – N and of the N – S<sub>A</sub> transitions coincide ( $T_{NI} = T_{AI} = T_{TP}$ ), a triple point appears, for the corresponding triple point coupling  $\gamma_{TP}$ . The nematic phase disappears for values of coupling higher than  $|\gamma_{TP}|$  and an I – S<sub>A</sub> phase transition takes place.  $\gamma_{TP}$  is the solution of the system:

$$\begin{cases} f(T_{NI}, E = 0) = f_N(T_{NI}, E = 0) = 0 \\ f'(T_{NI}, E = 0) = f'_N(T_{NI}, E = 0) = 0, \end{cases} \quad (25)$$

(the free energy is normalized with  $f_0 = 0$ ) where  $T_{NI} = T_{NI}^* + 2b_N / 9a_N c_N$ .  $\gamma_{TP}$  is given by:

$$\gamma_{TP} = \frac{2c_A [A_A^2 / 4c_A + \frac{1}{6} b_N S_{NA}^3 + \frac{1}{4} c S_{NA}^4]}{\lambda S_{NA}^3 - A_A S_{NA}} \quad (26)$$

Using the values of Table I we find  $\gamma_{TP} = -0.983 \times 10^7 \text{ erg}/\text{cm}^3$  and  $\gamma_{TP} / a_A = -19.66$ . The corresponding  $(S, t = T - T_{NI})$  phase diagram is shown in Figure 6. The dashed line is the smectic line. The curve n-binodal is the nematic binodal and curve ns-binodal is the nematic-smectic binodal, *i.e.*, the two lines, one in the nematic phase, below the smectic line, and the other in the smectic phase, which represent the nematic and smectic phases of equal energy. The two branches of the ns-binodal join at the TCP above which they coincide with the smectic line. When cooling from the isotropic phase in absence of electric field, the order is zero for  $T > T_{NI}$ . At  $T_{NI}$  the lower branch of the nematic binodal crosses the temperature axis

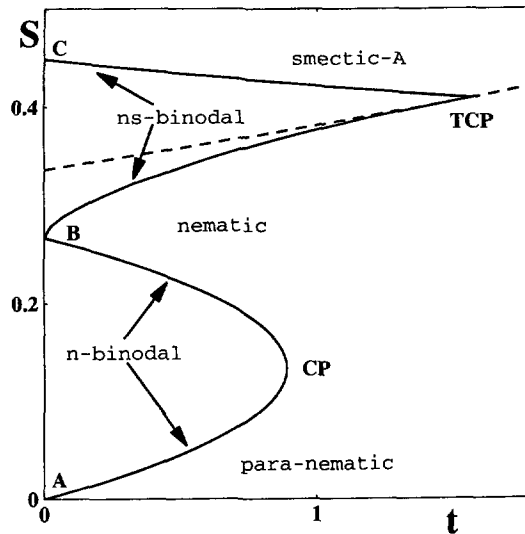


Fig. 6. — Nematic binodal (n-binodal), and nematic-smectic binodal (ns-binodal), showing the three phases coexistence ABC. CP: critical point. TCP: tricritical point.

at a zero order point A and the energy of the nematic phase, point B conjugate of A, becomes equal to the one of the isotropic phase. We remark also that at  $T_{NI}$ , the upper branch of the n-binodal crosses the lower branch of the ns-binodal at the point B. The conjugate of point B is the point C on the upper branch of the ns-binodal. From the definition of the binodal line, we conclude that the conjugate points A, B, C representing the isotropic, nematic and smectic phases correspondingly, have the same energy at  $T_{TP}$ . We conclude that in absence of field, for  $\gamma = \gamma_{TP}$  the isotropic, nematic and smectic phases coexist at  $T_{TP}$ , *i.e.*, the system is at its triple point. The application of an external electric field brings the system far from the triple point and it favors the nematic phase which becomes the stable phase. We shall see later (Sect. 7) how varies the triple point *versus* field and coupling. Increasing the field value, the smectic phase becomes the stable phase of the system. This situation will be analyzed in the next paragraph.

4.6. MEDIUM COUPLING. — In absence of field  $E$ , the  $I-S_A$  phase transition takes place at the temperature  $T_{AI}$  defined from the supplementary condition  $f(S, |\Psi| \neq 0) = 0$ . The spontaneous  $I-S_A$  phase transition can be considered as an  $I-N$  transition, which forces immediately, because of the  $(S, \Psi)$  coupling, the onset of positional order. If one would be able to create a nematic phase with a lower ordering, smectic order could disappear. One could eventually observe such a non spontaneous nematic (NSN) phase when applying a field on the isotropic phase, through for example a sequence of separated  $pN \rightarrow NSN \rightarrow S_A$  phase transitions. The analysis of the NSN phase does not differ from that of a material which spontaneously presents the  $I-N$  transition discussed previously. A critical point exists between the pN and the NSN phase. Its coordinates are given from (12). As long as  $T_C \geq T_{AI}$  a NSN could be induced by a high enough external stabilizing electric field  $E$  before the  $S_A$  phase is induced for higher fields. Increasing  $E$  above the NSN induction field,  $S(E)$  should increase continuously. If  $E$  becomes strong enough,  $S$  should attain a value for which equation (9) has a solution  $|\Psi| > 0$  and the  $S_A$  should appear. Figure 7 shows the  $(S, t = T - T_{NI})$  phase diagram for the case

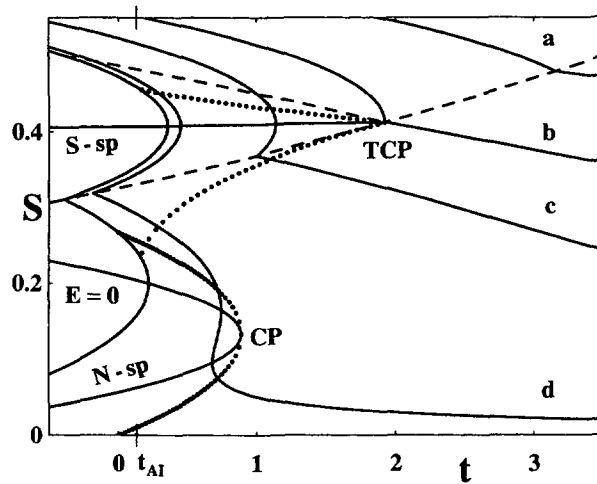


Fig. 7. —  $S, t = T - T_{NI}$  phase diagram of the field induced paranematic-non spontaneous nematic-smectic A (pN-NSN- $S_A$ ) phase transitions. The liquid crystal shows a spontaneous isotropic-smectic A transition at  $t_{AI}$ . The nematic phase is metastable at  $t_{AI}$ . The lower branch of the dashed line is the smectic line, the upper branch is its conjugate. N-sp is the NSN spinodal with its dotted coexistence line. S-sp : smectic spinodal.  $E = 0$  is the zero field equilibrium line. a, b, c, d are isofields. TCP: tricritical point; CP: critical point.

of medium coupling. To obtain this phase diagram we have increased the coupling up to  $\gamma = -1.0 \times 10^7$  erg/cm<sup>3</sup> and  $\gamma/a_A = -20.0$ . We have also increased the value of the second coupling constant at  $\lambda = 1.2 \times 10^7$  erg/cm<sup>3</sup>. This allows to visualize better the situation and does not alter qualitatively the results. At the lower part of the diagram the solid line N-sp is the spinodal of the field induced NSN phase with its dotted binodal line. In the upper part of the phase diagram, the lower dashed line is the smectic line. The upper dashed line is the conjugate of the smectic line. The smectic line and its conjugate coincide at the TCP with coordinates given from (24). At the TCP comes also the smectic spinodal line (S-sp).  $t_{TC}$  corresponds to the tricritical temperature. The two upper dotted curves represent the nematic-smectic binodal. If the system crosses the smectic line at  $t < t_{TC}$  it enters an unstable region ( $f'' < 0$ ) and transits with a discontinuous increase of  $S$  towards a state in the  $S_A$  phase. As  $t$  approaches  $t_{TC}$  from below, the jump of order becomes smaller, and at  $t_{TC}$  the transition becomes of second order. For  $t \geq t_{TC}$ , the tricritical points line appears. The line  $E = 0$  is the zero field equilibrium line. The full lines a, b, c, and d correspond to different isofields: a,  $E = \sqrt{2}E_{TC}$ ; b,  $E = E_{TC}$ ; c,  $E = E_{TC}/\sqrt{2}$ ; and d,  $E = 0.9E_C$ . The isofield d is calculated for an electric field lower than the NSN critical one. As the system is cooled from the isotropic phase, when it crosses the NSN spinodal, it transits from the pN to the NSN phase with a jump of order. Cooling more, the system crosses the smectic line and undergoes a second first order transition from the NSN to the  $S_A$  phase. For  $E > E_C$  the system goes continuously from the pN to the NSN without any transition (isofields a, b, c). When the isofield lines a, b, c cross the smectic line, either they show a first order NSN- $S_A$  transition at the left of the TCP (isofield c) or a second order transition at the right of the TCP (isofield a and b). The isofield b is the tricritical one.

In absence of field, the NSN phase can be metastable or unstable at  $T_{AI}$ . If  $T_{NI}^{**} > T_{AI}$ , the nematic phase is metastable at  $T_{AI}$  and it could be supercooled. Increasing the coupling,

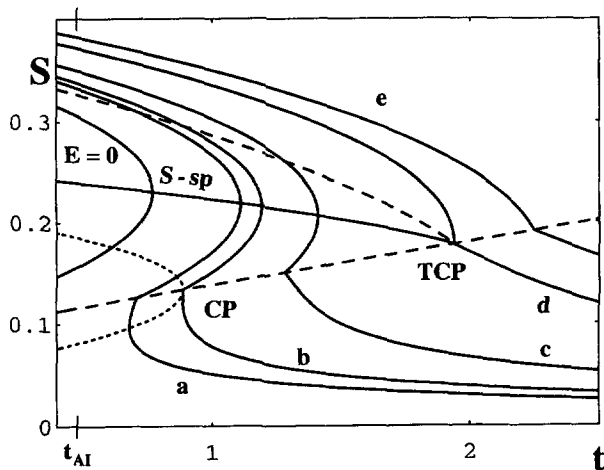


Fig. 8. — Same as Figure 7, when the smectic line goes through CP: the NSN critical point.

$T_{AI}$  approaches  $T_{NI}^{**}$  and for  $T_{AI} = T_{NI}^{**}$  the nematic phase becomes unstable. This means that it is not possible to supercool the nematic phase without a favorable external field. Under external field, the NSN-phase can be supercooled at  $T_{AI}$  if  $T_{NSN}^* < T_{AI}$ , where  $T_{NSN}^*$  is the supercooling limit of the NSN-phase given from the intersection of the smectic line (10) and the upper nematic spinodal. A phase diagram corresponding to this last situation is shown in Figure 1 of [2].

4.7. CRITICAL COUPLING . — As the coupling increases,  $T_{AI}$  approaches  $T_C$  of the NSN-phase. When  $T_{AI}$  and  $T_C$  coincide the NSN phase degenerates at its critical point. For stronger coupling the transition is the pN –  $S_A$  one. However the metastable NSN-phase can be supercooled under field. Increasing the coupling, the NSN-phase becomes unstable under field when the smectic line passes through the NSN-critical point, *i.e.*, when the coordinates of the NSN-critical point satisfy the smectic line equation. We call the corresponding coupling constant critical coupling  $\gamma_C$ .  $\gamma_C$  is given by:

$$\gamma_C = -\frac{a_A(T_C - T_A^*) + \lambda S_C^2}{2S_C} \tag{27}$$

$S_C$  and  $T_C$  are given from (12). We calculate  $\gamma_C = -2.11 \times 10^7 \text{ erg/cm}^3$  and  $\gamma_C/a_A = -44.23$ . To better visualize this topology, we give a  $(S, t = T - T_{NI})$  phase diagram (Fig. 8) using a different set of parameters ( $\gamma_C = -0.6 \times 10^7 \text{ erg/cm}^3$ ,  $\lambda = 0.1 \times 10^7 \text{ erg/cm}^3$  and  $T_{NA}^* - T_{NI}^* = 0.5 \text{ K}$ ). The spontaneous transition is a first order I –  $S_A$  phase transition at  $t_{AI}$ . The lower part of the dashed line is the smectic line while the upper part is its conjugate line. S – sp is the smectic spinodal. The pointed line is the NSN spinodal. The smectic line crosses the nematic spinodal at the nematic critical point CP. The NSN has disappeared. TCP is the tricritical point of the I –  $S_A$  transition. The curves a, b, c, d, e are isofields. The curve  $E = 0$  gives the equilibrium line  $S(T)$  of the smectic phase in absence of field. The isofield e is calculated for a field  $E > E_{TC}$ . The transition is a second order pN –  $S_A$  one. The isofield c is calculated for a field  $E_{TC} > E > E_C$ . The transition is a first order pN –  $S_A$  one accompanied by a jump of order. For  $E = E_C$ , the critical isofield b gives also a first order pN –  $S_A$  transition. When cooling, the slope of the critical isofield when crossing the smectic line is infinite because this



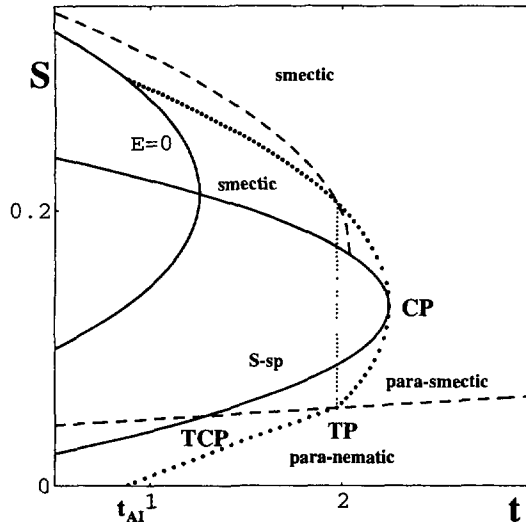


Fig. 9. —  $S, t = T - T_{NI}$  phase diagram of the field induced paranematic-parasmectic-smectic A phase transitions. The liquid crystal shows a spontaneous isotropic-smectic A transition at  $t_{AI}$ . Lower branch of the dashed line: smectic line; upper branch: its conjugate. S - sp: smectic spinodal. The dotted curve is the binodal, smectic above the smectic line and nematic below.  $E = 0$ : zero field equilibrium line. TCP: tricritical point; CP: critical point; TP: triple point.

point is critical for the NSN phase. For  $E > E_C$ , the slope is always finite. The last isofield is calculated for  $E < E_C$ . When cooling, a first order pN -  $S_A$  transition takes place when the isofield crosses the nematic spinodal and not at the crossing point of the isofield with the smectic line.

4.8. STRONG COUPLING. — We increase the reduced coupling at  $\gamma/a_A = -60.0$  and we calculate the corresponding phase diagram. This phase diagram presents a very large critical region in temperature. To make more compact the phase diagram scale, we use another set of parameters (Tab. II) for the smectic phase while keeping the same for the nematic one (Tab. I). We keep the reduced coupling at  $\gamma/a_A = -60.0$ . The phase diagram is shown in Figure 9. The ordinate scale represents the temperature  $t = T - T_{NI}$ . In zero field, the spontaneous transition is a first order I -  $S_A$  one. The dashed line is the smectic line. Below the smectic line, the order is purely orientational and one gets under field the pN phase. The curve S - sp is the spinodal of the smectic phase.

Table II. — Model parameters used for strong nematic-smectic coupling.

$a_A$	( $10^7$ erg/Kcm $^3$ )	0.01
$c_A$	( $10^7$ erg/cm $^3$ )	5.0
$\lambda$	( $10^7$ erg/cm $^3$ )	-0.6
$\lambda$	( $10^7$ erg/cm $^3$ )	0.1
$T_{NI} - T_{NI}^*$	(K)	1.8
$T_{AN}^* - T_{NI}^*$	(K)	-0.5

At high enough temperature, when applying a high enough field  $E$ , the system crosses the smectic line from the pN phase and a smectic phase of small positional order is induced which

Table III. — *Model parameters used in the case of a field induced pN – pS – N.*

$a_A$ ( $10^7$ erg/Kcm <sup>3</sup> )	0.03
$c_A$ ( $10^7$ erg/cm <sup>3</sup> )	5.0
$\gamma$ ( $10^7$ erg/cm <sup>3</sup> )	-0.2
$\lambda$ ( $10^7$ erg/cm <sup>3</sup> )	-4.0
$T_{NI} - T_{NI}^*$ (K)	1.8
$T_{AN}^* - T_{NI}^*$ (K)	-0.5

we call “parasmectic” (pS) phase. The smectic line crosses the smectic spinodal at the point TCP which is tricritical because in the left of this point the transition is a first order pN – S<sub>A</sub> transition and in the right of the TCP the transition is a second order pN – pS<sub>A</sub> transition. The apex CP of the coupled spinodal is now allowed, since it appears above the smectic line. This point is a *smectic critical point*. Below this critical point, a first order pS<sub>A</sub> – S<sub>A</sub> phase transition takes place between two phases of the same symmetry. This transition becomes of second order at the critical point and disappears above it as for the liquid-gas transition. The pointed line in Figure 9 is the nematic-smectic binodal. The smectic line crosses the binodal at a point TP where the energy of the pN, pS and S<sub>A</sub> phases are the same. TP is a triple point. The curve  $E = 0$  is the zero field equilibrium line. The coordinates of the smectic critical point, critical order  $S_C^{sm}$ , field  $E_C^{sm}$ , and temperature  $T_C^{sm}$ , satisfy the condition  $f' = f'' = f''' = 0$  and one finds:

$$\begin{cases} S_C^{sm} = -\frac{b}{3c} \\ (E_C^{sm})^2 = \frac{b^3}{27c^2\mu} \\ T_C^{sm} = T^* + \frac{b^2}{3a_Cc} \end{cases} \quad (28)$$

In the present strong ( $S, \Psi$ ) coupling case, the tricritical point is somewhat different from the tricritical point for weaker ( $S, \Psi$ ) coupling discussed previously. In the latter case when the system approaches the TCP from the left the jump of order at the transition becomes infinitely small. In the former case the jump of order remains finite at the TCP.

When increasing the reduced coupling  $T_{AI} > T_{TC}$ , the field induced first order pN – S<sub>A</sub> transition disappears. For temperatures lower than the critical one, the system goes to the S<sub>A</sub> phase *via* a second order pN – pS transition and a first order pS – S<sub>A</sub>.

In the Table III, we summarize the reduced coupling constant ( $\gamma/a_A$ ) for all cases already studied, with the reduced  $\gamma/a_A$  coupling always increasing (in absolute values) when the system goes from a second order N – S<sub>A</sub> transition to a first order I – S<sub>A</sub> transition.

## 5. Reentrant Nematics

5.1. REENTRANT NEMATIC TRANSITION. — As previously explained in [30–33], reentrance phenomena, *i.e.*, the further appearance of a nematic phase below the smectic phase, is produced when a high value of the orientational parameter  $S$  disfavors the smectic positional ordering  $\Psi$ . This is represented in the LdG model by the presence of a large and positive coefficient  $\lambda$  for the  $S^2|\Psi|^2$  coupling term in the free energy. The smectic line  $|\Psi|^2 = 0$  (Eq. (10)) is the parabola:

$$S_{\psi=0}^{\pm} = -\frac{\gamma}{\lambda} \pm \sqrt{\left(\frac{\gamma}{\lambda}\right)^2 - \frac{A_A}{\lambda}}. \quad (29)$$

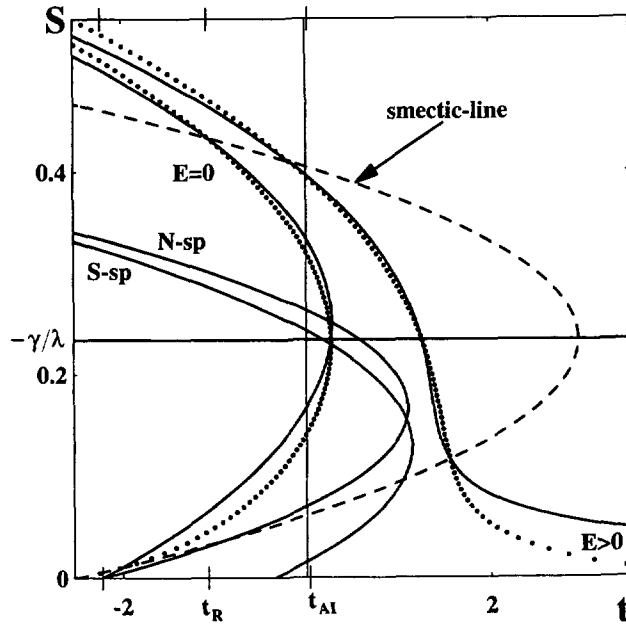


Fig. 10. —  $S, t = T - T_{NI}$  phase diagram for smectic A-reentrant nematic phase transition. Under field the transition shifts towards higher temperature. N-sp: nematic spinodal; S-sp: smectic spinodal. Solid  $E = 0$  curve: nematic equilibrium curve in zero field. Pointed  $E = 0$  curve: smectic equilibrium curve in zero field.  $t_R$  corresponds to the reentrance temperature.  $E > 0$  curves: isofields.

$S_{\psi=0}^{\pm}$  are real for:  $T \leq T_{AN}^* + (\gamma^2/a_A \lambda)$ . The smectic phase can exist inside the parabola defined by equation (29). For large and favorable  $\gamma$  and weak  $\lambda$ , this parabola in practice is just a straight line, its apex  $S_{\text{apex}} = -\gamma/\lambda$  being larger than 1. For reentrant systems, the whole parabola has now a physical meaning, defining  $(S, T)$  the region where the  $S_A$ -phase can exist.

One can make a general remark on the reentrant  $S_A \rightarrow N$  transition. Let us consider the smectic and nematic isofield equilibrium curves (Eqs. (11a) and (14)). Both curves are cubic in  $S$ . They intersect in three points. Two of these points are obviously located on the  $|\Psi|^2 = 0$  smectic line since there one cannot distinguish between  $S_A$  and N. The third intersection happens on the  $S = -\gamma/\lambda$  line, independent of the temperature, which goes through the apex of the  $|\Psi|^2 = 0$  parabola (see Fig. 10). An immediate consequence of this behaviour is that the reentrant  $S_A \rightarrow N$  transition is predicted as a second order transition in the present model (one has to add higher order than  $S^4$  terms, in the nematic free energy, to permit a first order reentrant  $S_A \rightarrow N$  transition). The reentrant  $S_A \rightarrow N$  transition takes place at the intersection of the nematic (solid  $E = 0$  curve) and smectic (pointed  $E = 0$  curve) zero field equilibrium curves with the smectic line. Under electric field (isofields  $E > 0$ , the solid one is the nematic isofield, and the pointed one is the smectic isofield at the same field  $E$ ), the  $S_A - RN$  transition is induced at a temperature higher than the spontaneous one  $T_R$ . Another interesting prediction from Figure 10 is the following: close to the phase transition, in the smectic phase, the positional order is given by equation (9) as:  $|\Psi|^2 = -A_A + 2\gamma S + \lambda S^2/c_A$ . One calculates  $\partial|\Psi|^2/\partial S = -2(\gamma + \lambda + \lambda S)/c_A$ . For small  $S$  and favorable  $\gamma S|\Psi|^2$  coupling,  $\gamma$  is negative, and the onset of the smectic order *increases* the orientational order (see in Fig. 10,

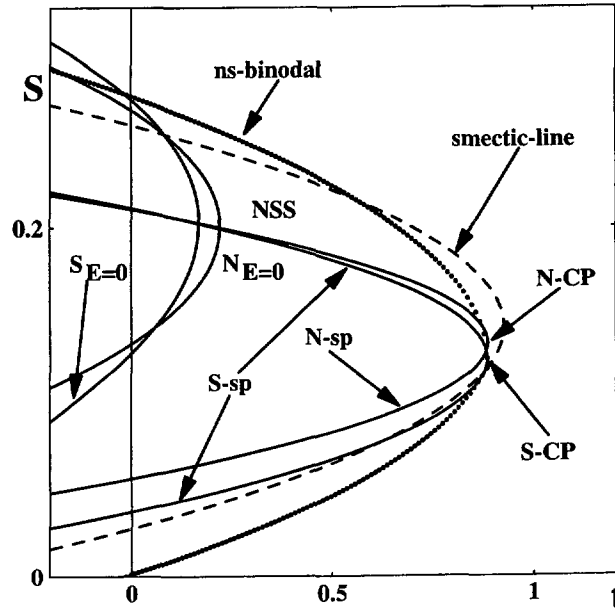


Fig. 11. —  $S, t = T - T_{NI}$  phase diagram when a non spontaneous smectic phase appears under field. Pointed line: nematic-smectic binodal; N-CP: nematic critical point; S-CP smectic critical point; N-sp: nematic spinodal; S-sp: smectic spinodal;  $N_{E=0}$ : nematic equilibrium curve in zero field;  $S_{E=0}$ : smectic equilibrium curve in zero field.

the lower intersection of the smectic line with the nematic and smectic isofields with  $E > 0$ ). On the contrary, close to the reentrant  $S_A \rightarrow N$  transition, the onset of smectic order *decreases* the orientational order. Both  $S$  orders of the nematic and smectic phases would coincide on the apex line  $S = -\gamma/\lambda$ .

We now discuss in more details some interesting reentrant situations.

5.2. THE NON SPONTANEOUS SMECTIC PHASE. — When the non favorable coupling constant  $\lambda$  becomes larger, a new situation could arise: the  $S_A$ -phase could disappears completely in zero field. This happens when the orientational smectic order  $S_{AI}$  at the transition temperature  $T_{AI}$  is equal to or larger than the  $S_{\psi=0}^+$  value of the smectic line for the same temperature. From (29), one obtains the condition:

$$S_{\psi=0}^+(T_{AI}) = -\frac{\gamma}{\lambda} + \sqrt{\left(\frac{\gamma}{\lambda}\right)^2 - \frac{A_A(T_{AI})}{\lambda}} \leq S_{AI} \quad (30)$$

$S_{AI}, T_{AI}$  can be calculated numerically. The condition (30) can be fulfilled for large  $\lambda$ . A too large value of  $\lambda$  will shift down the smectic parabola too much for a smectic phase to appear under field. This situation will be discussed later.

In Figure 11, we have shown a situation where there exists in zero field a direct  $I - N$  transition, towards a large  $S$  value, and no  $S_A$  phase. We have chosen the values  $\gamma = -0.1 \times 10^7$  erg/cm<sup>3</sup> and  $\lambda = 0.7 \times 10^7$  erg/cm<sup>3</sup>. In presence of field, one allows a nematic phase with lower  $S$  value, *i.e.*, a non spontaneous  $S_A$  phase (NSS) is expected. A way to produce the NSS phase is to start from the nematic phase at  $T_{NI}$  and to apply an electric field. One heats now the system at constant field. The nematic order  $S$  decreases, along the corresponding isofield

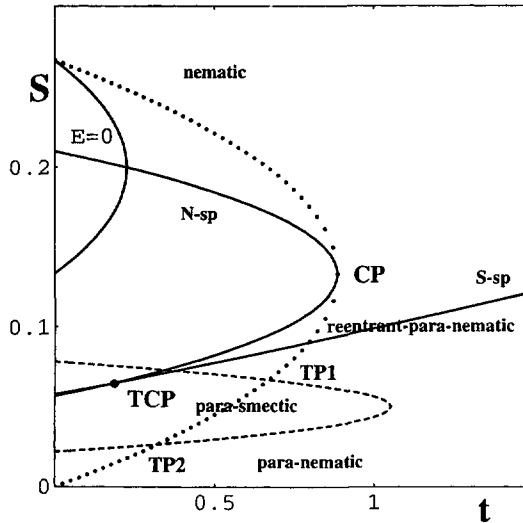


Fig. 12. —  $S, t = T - T_{NI}$  phase diagram of the field induced parasmectic-reentrant paranematic-smectic A phase transitions. The liquid crystal shows a spontaneous isotropic-nematic transition. Dashed line: smectic line; N-sp: nematic spinodal; pointed line: binodal;  $E = 0$ : zero field equilibrium line; S-sp: smectic spinodal. There are two triple points TP1 and TP2. CP: critical point; TCP: tricritical point.

(such isofields are shown in Fig. 10). When the isofield crosses the smectic line, the NSS is induced, with even smaller  $S$ . The  $N \rightarrow NSS$  transition is second order in the present model approximation.

5.3. A PARASMECTIC-REENTRANT PARANEMATIC TRANSITION. — When both nematic-smectic coupling terms  $\gamma$  and  $\lambda$  are strong and  $\lambda \gg |\gamma|$ , the transition in absence of external field is an I-N one while no  $S_A$  phase appears. In this case the system could give under the action of an external field a pS phase separated from the pN phase by a second order phase transition as it is shown in Figure 12. This field induced second order pN-pS phase transition can be followed either by a first order transition to a nematic phase or from a second order transition to a reentrant paranematic (RpN) phase while for higher fields a transition to the nematic phase happens with a critical point given from (12). The two regimes should be separated by a tricritical point (TCP) at the intersection of the smectic spinodal S-sp and the smectic line. In fact, above the smectic spinodal, no smectic phase is allowed. The transition is now a second order parasmectic  $\rightarrow$  reentrant paranematic. This transition has in fact its tricritical point at the intersection of the two smectic and nematic spinodal. This TCP point can appear at a temperature lower than  $T_{NI}$  and it is not attained under field, or higher than  $T_{NI}$  and it is attainable under field. The intersection of the nematic binodal (pointed line) with the smectic line gives two triple points (TP1, TP2) between the pS, RpN, and N phases (TP1) and the pN, pS, and N phases (TP2).

## 6. The Free Energy Density of the Phases

In this paragraph, we present the diagrams of  $f(S)$  to better explain the complicated phase dependence on the nematic-smectic coupling, on the temperature and on the electric field.

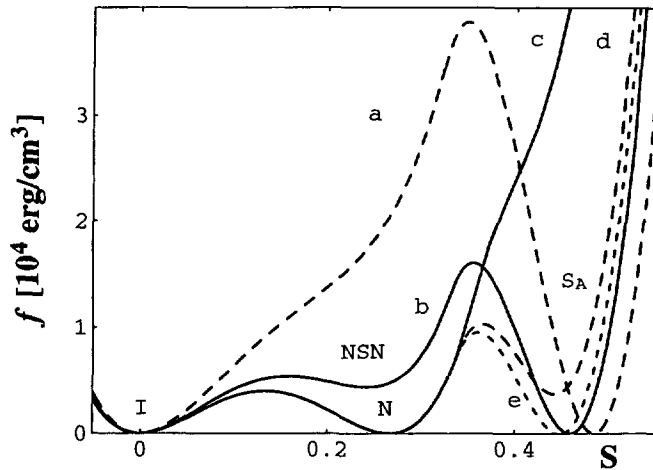


Fig. 13. — Free energy density *versus* orientational order for coupling ranging between weak and medium, in the absence of electric field. Curve b (medium coupling) shows the existence of a metastable nematic phase. Curve d (weak coupling) shows the existence of a metastable smectic.

6.1. EFFECT OF THE NEMATIC-SMECTIC COUPLING. — The influence of the nematic-smectic coupling on the I –  $\tilde{N}$  or  $S_A$  transition in absence of electric field is shown in the free energy *versus* orientational order diagram in Figure 13. Curve a is calculated with  $\gamma = -1.05 \times 10^7$  erg/cm<sup>3</sup> (medium coupling) while the other parameters are the same as in the case of medium coupling (Tab. I). The transition is a I  $\rightarrow$   $S_A$  phase transition. At the transition temperature  $T_{AI}$ ,  $f$  has two minima at  $S = 0$  and at  $S \neq 0$  corresponding to the isotropic and the smectic phase. No nematic minimum appears. Curve b is calculated for a lower coupling  $\gamma = -1.0 \times 10^7$  erg/cm<sup>3</sup>. The transition is always a I  $\rightarrow$   $S_A$  one. Now at  $T_{AI}$ , it appears a third relative minimum corresponding to a metastable nematic phase. This minimum will give under field the NSN phase. Reducing again  $|\gamma|$  down to  $\gamma = -0.983 \times 10^7$  erg/cm<sup>3</sup> (curve e) the system arrives at the isotropic-nematic-smectic A triple point TP. The three phases coexist at the transition temperature and  $f(S)$  has three minima with the same energy. For  $\gamma = -0.98 \times 10^7$  erg/cm<sup>3</sup> (curve d), the transition is a I  $\rightarrow$  N one.  $f(S)$  has three minima. The minimum of higher order is metastable and corresponds to the  $S_A$  phase. For a lower  $\gamma = -0.95 \times 10^7$  erg/cm<sup>3</sup> (curve c), the transition is always a I  $\rightarrow$  N one. Only two minima appear corresponding to the isotropic and the nematic phase while the relative minimum of the  $S_A$  phase has disappeared.

6.2. EFFECT OF THE TEMPERATURE. — To better visualize the case of a non spontaneous nematic phase, we present in Figure 14 some isotherms of  $f(S, E = 0)$  around  $T_{AI}$  for a liquid crystal with a spontaneous I  $\rightarrow$   $S_A$  phase transition. The orientational order is modified by the positional order *via* the coupling between them.

We first consider the case without metastable nematic phase at  $T_{AI}$  ( $T_{NI}^{**} < T_{AI}$ ) obtained with  $\gamma/a_A = -21.0$ . At  $T_{AI}$  in absence of field (isotherm d), there are two minima: at  $S = 0$ , the isotropic phase, and for  $S \neq 0$  the smectic phase. For temperatures far in the smectic phase  $T < T_{AI}^*$  there is only one minimum (curve j) for  $S > 0$ , corresponding to the smectic phase. At  $T_{AI} > T \geq T_{AI}^*$ , the isotropic phase appears as a metastable phase (curve h) while the absolute minimum is the smectic phase. The lower temperature for which the I phase remains

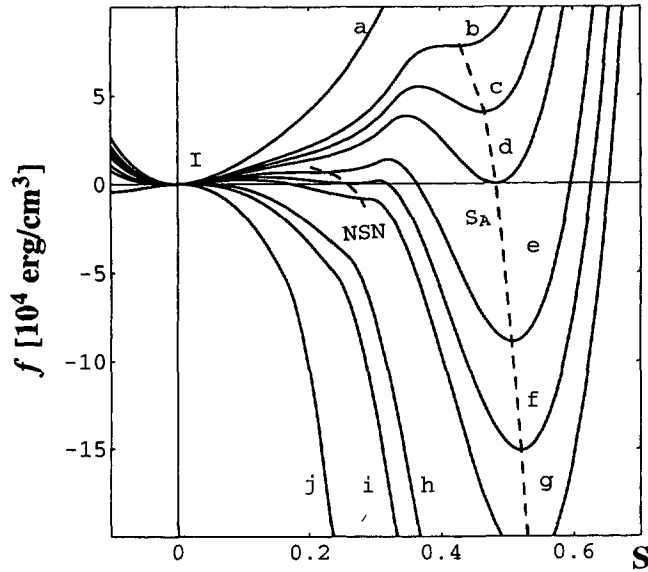


Fig. 14. — Free energy density *versus* orientational order for medium coupling without metastable nematic phase at the isotropic-smectic A temperature. All isotherms are calculated for zero electric field: isotherm a at  $T > T_{AI}^{**}$ ; isotherm b at  $T_{AI}^{**}$ ; isotherm c at  $T_{NI}$ ; isotherm d at  $T_{AI}$ ; isotherm e at  $T_{NI}^{**}$ ; isotherm f at  $T_{NI}$ ; isotherm g at  $T_{AI}$ ; isotherm h at  $T < T_{AI}$ .

metastable is  $T_{AI}^*$  (curve i). Approaching  $T_{AI}$  from below there is a temperature  $T_{AN}^*(\gamma)$  above which it appears a local minimum (curve g) with  $S > 0$ , corresponding to a metastable nematic phase. Increasing the temperature the free energy of the nematic minimum increases and at  $T_{NI} < T_{AI}$  becomes equal to the energy of the isotropic phase (curve f) while the absolute minimum is that of the smectic phase. At  $T_{NI}^{**}$  the nematic phase becomes unstable (curve e). At  $T_{AI}$  (curve d), the free energy of the smectic and of the isotropic phases become equal. The local minimum corresponding to the nematic phase has already disappeared. Increasing the temperature, the absolute minimum is that of the I phase while the  $S_A$  phase is a local minimum (curve c). The smectic phase becomes completely unstable at  $T_{AI}^{**}$  (curve b). For  $T > T_{AI}^{**}$  only one minimum exists with  $S = 0$  corresponding to the isotropic phase (curve a).

We decrease the coupling at  $\gamma/a_A = -20.0$  and  $T_{AI}$  decreases at  $T_{AI}^{**} \geq T_{AI}$  then at  $T_{AI}$  it exists a third minimum corresponding to a metastable nematic phase (Fig. 15, curve d). Varying the temperature the evolution is similar to the one of the previous case (isotherms a, b, c, e, f, g).

### 6.3. EFFECT OF THE ELECTRIC FIELD

**6.3.1. The Non Spontaneous Nematic.** — We remain in the case of medium coupling ( $\gamma/a_A = -20.0$ ). In absence of electric field, the transition is a I –  $S_A$  one. With the LC material in the isotropic phase, at  $T = T_{AI} + 0.15$  K,  $f(S)$  has a local minimum (Fig. 16) corresponding to the smectic phase ( $T < T_{AI}^{**}$ ). We apply a stabilizing electric field. A second local minimum appears, at lower order than the order of the smectic phase, corresponding to a metastable nematic phase (curve a). Increasing the field, the local minimum of this nematic phase becomes the absolute minimum (curve b) and consequently the NSN phase appears. At  $E_{trans}$  (curve c,

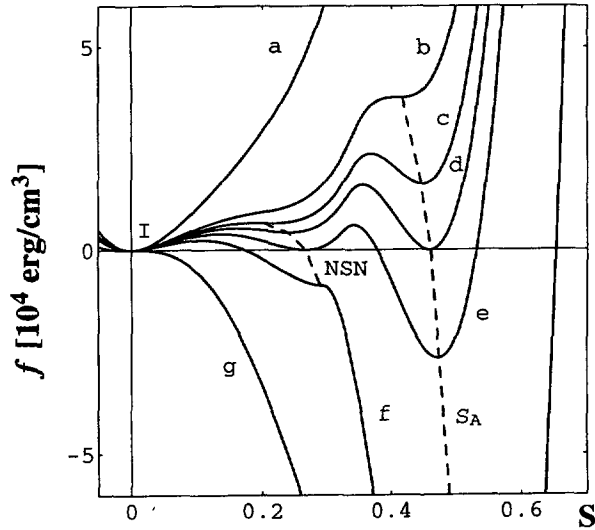


Fig. 15. — Same as Figure 14 for medium coupling with a metastable nematic phase at the isotropic-smectic A temperature (curve c).

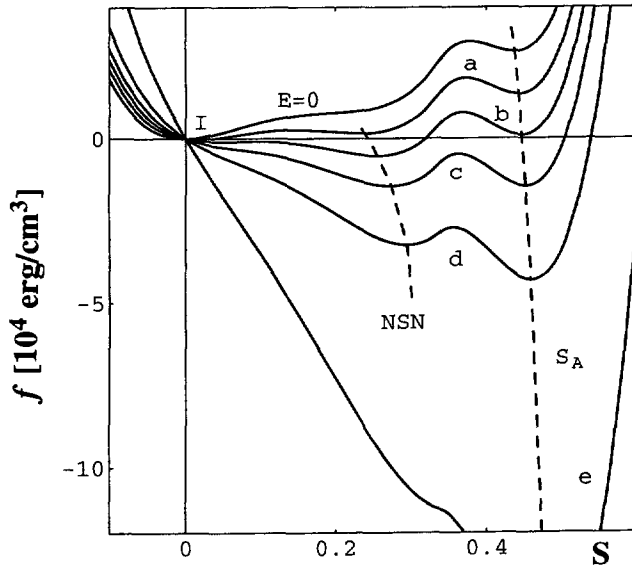


Fig. 16. — Free energy density *versus* orientational order for medium coupling, at  $T = T_{AI} + 0.15$  K.  $E = 0$  is  $f(S, E = 0)$ . Curves a, b for  $E < E_{trans}$ , ( $E_{trans}$  is the electric field inducing the NSN -  $S_A$  phase transition), c for  $E = E_{trans}$ , and d, e for  $E > E_{trans}$ .

$E_{trans}$  is the electric field inducing the NSN -  $S_A$  phase transition), both NSN and smectic minima have the same energy. For  $E > E_{trans}$  the absolute minimum corresponds to the smectic phase (curve d), while the NSN-phase is a local minimum. Increasing the field, the NSN-phase local minimum disappears and only the minimum of the smectic phase exists. When



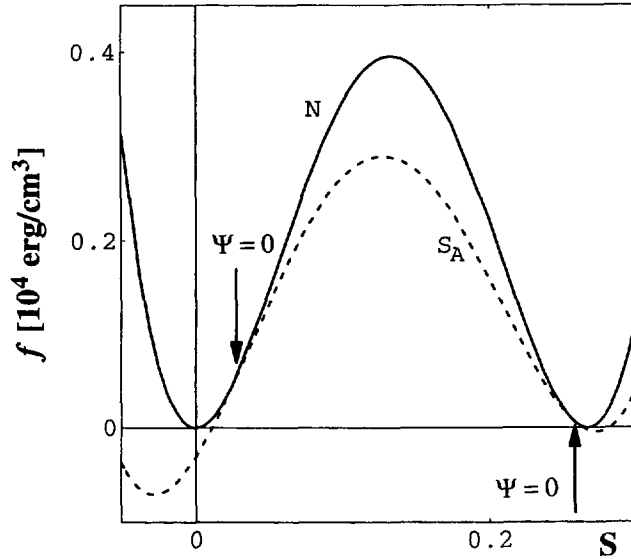


Fig. 17. — Free energy density *versus* orientational order for the non spontaneous smectic case, in absence of field. The transition is a I – N (solid line). The smectic phase (dashed line) minima are in the  $|\Psi|^2$  region.

the smectic phase is not a local minimum in absence of field ( $T > T_{AI}^{**}$ ), it becomes metastable under the action of a sufficiently high field. For higher values of the field it follows the same evolution as in the previous case.

**6.3.2. The Non Spontaneous Smectic.** — We choose  $\gamma = -0.1 \times 10^7 \text{ erg/cm}^3$  and  $\lambda = 0.7 \times 10^7 \text{ erg/cm}^3$ . We plot in Figure 17 the free energy  $f$  *versus* the orientational order  $S$  in absence of field. The spontaneous transition is an I – N one. The full curve has two minima of the same energy, one at  $S = 0$  and a second one at  $S_{NI}$ . The dashed curve would correspond to a smectic phase. The arrows indicate the crossing points with the smectic line. Between the arrows  $|\Psi|^2$  is positive. We remark that both minima are in the region  $|\Psi|^2 < 0$  and no smectic phase is permitted. This is visible from the shift of the  $S$  minima: for large  $S$ , the smectic minimum appears at a larger  $S$  than for the nematic, although for  $|\Psi|^2 > 0$ , it should be smaller, and conversely for the small  $S$  minimum values. In Figure 18, we plot  $f(S)$  at  $T = T_{NI} + 0.25 \text{ K}$ , under a field  $E = 8 \text{ V}/\mu\text{m}$ . The full curve shows two minima, one close to  $S = 0$ , the paranematic phase, and one for larger  $S$ , the non spontaneous smectic phase. The dashed line is the pure nematic free energy, larger than the smectic one in between the two arrows corresponding to  $\Psi = 0$ . Outside the arrows, the dashed line would correspond to the smectic phase.

## 7. The $\gamma$ , $T$ , $E$ Phase Diagram

We have made the above analysis in the space: temperature or electric field and orientational order. One is usually interested in the three-dimensional phase diagram in the space: nematic-smectic coupling, temperature, and electric field ( $\gamma, T, E$ ). The diagram in Figure 19 was calculated in the one coupling constant approximation, in absence of saturation ( $\lambda = 0$ , *i.e.*, no reentrant nematic). We allow the variation of the nematic-smectic coupling and we fix

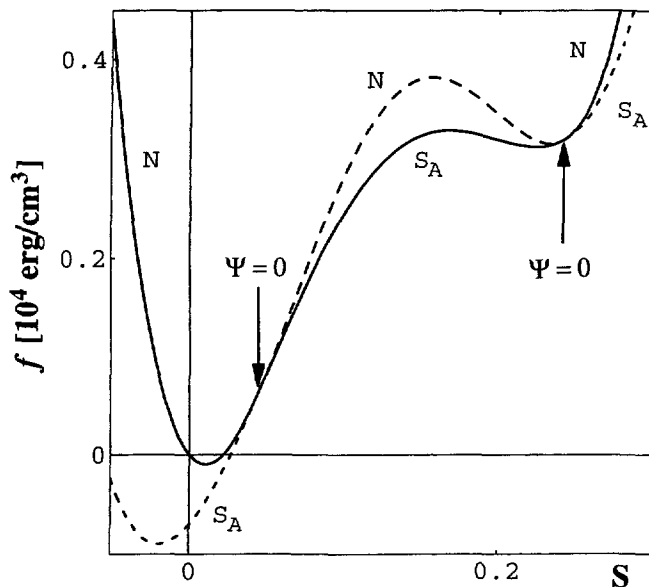


Fig. 18. — Same as Figure 17, at  $T = T_{NI} + 0.25$  K, but under field  $E = 8$  V/ $\mu$ m. The smectic minimum at  $S > 0$  is now permitted and has lower energy than the nematic minimum.

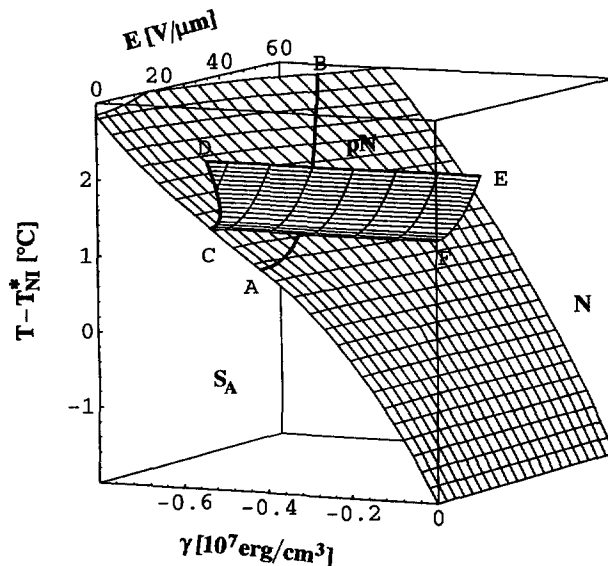


Fig. 19. — Three dimensional phase diagram in the space “coupling, temperature, and electric field”.

$T_{AN}^*$ . The values of the model coefficients, we used to calculate this phase diagram are given in Table IV. The grid surface separates the smectic phase under the surface from the higher symmetry phases, above the grid surface. The solid line, AB, is a *line of tricritical points*. On the left of the tricritical line the isotropic-smectic A ( $E = 0$ ) or the electric field induced

Table IV. — *Model parameters used for the phase diagram in the space coupling, temperature, and electric field (one coupling constant approximation).*

$a_N$	( $10^7$ erg/Kcm <sup>3</sup> )	0.1
$b_N$	( $10^7$ erg/cm <sup>3</sup> )	-1.5
$c_N$	( $10^7$ erg/cm <sup>3</sup> )	3.5
$a_A$	( $10^7$ erg/Kcm <sup>3</sup> )	0.1
$c_A$	( $10^7$ erg/cm <sup>3</sup> )	1.0
$T_{NI} - T_{NI}^*$	(K)	1.43
$T_{AN}^* - T_{NI}^*$	(K)	-2.0

Table V. — *The different kinds of coupling with their coupling force.*

Coupling	$\lambda/\alpha_A$
very weak	-13.0
tricritical	-13.67
weak	-14.4
triple point	-19.66
medium	-20.0
critical	-44.23
strong	-60.0
pN - pS - N	-66.7

nematic either paranematic-smectic A phase transition are of first order. On the right of the tricritical line these transitions are of second order. One remarks that the isotropic-smectic A transition is always at the left of the tricritical line and the transition is always of first order.

In absence of external field the nematic phase is localized in the "triangle" OCF (Fig. 19). The smectic-nematic phase transition for very weak coupling is of second order. The range of the nematic phase shrinks out with increasing coupling. The nematic phase disappears for coupling higher than  $|\gamma_{TP}|$  corresponding to the triple point C and the transition is the I - S<sub>A</sub> one.

Under the action of the electric field, the I - N transition becomes a pN - N one while  $T_{NI}$  rises with the field. Above the critical point this transition disappears. As the pN - N transition does not depend on the nematic-smectic coupling, the transition line is perpendicular to the temperature-electric field plane. Its intersection with the grid surface, the CD line, is a *line of triple points*. The ED line is a *line of critical points*. Their intersection, the point D, is a "triple-critical" point where the line of triple points disappears. This point appears at the nematic critical field and it corresponds to a coupling  $\gamma_{TPC}$  defined by:

$$\begin{cases} f(T_C, E_C, S, \gamma_{TPC}) = f_S(T_C, S_C, E_C) = -\frac{b_N^4}{324c_N^3} \\ f'(T_C, E_C, S, \gamma_{TPC}) = 0. \end{cases} \quad (31)$$

Using the values of the model coefficient (Tab. V), we calculate  $\gamma_{TPC} = -0.65 \times 10^7$  erg/cm<sup>3</sup>, while  $\gamma_{TP}(E = 0) = -0.53 \times 10^7$  erg/cm<sup>3</sup>. The necessary coupling to obtain the triple point increases, in absolute value, with the applied field.

We present a magnification of the region around the triple point line (Fig. 20) in order to visualize better the NSN phase. We choose the point *K* corresponding to a system with no

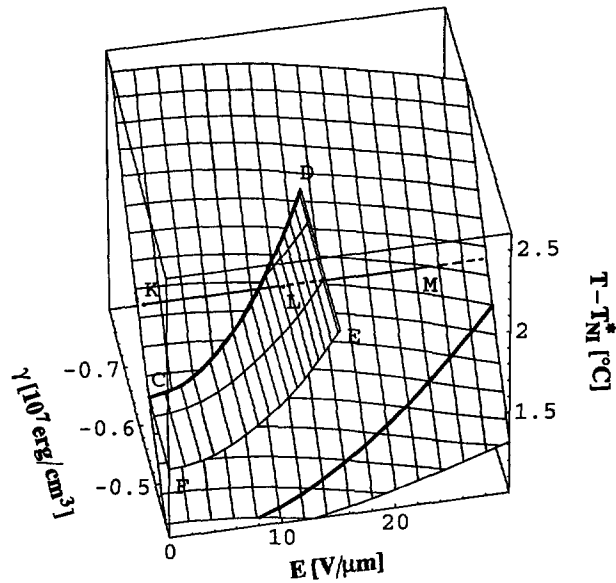


Fig. 20. — Magnification of Figure 19 around the non spontaneous nematic phase region.

nematic phase in absence of field. At  $K$  the system is in the isotropic phase. Increasing the field, the system goes from the isotropic to the paranematic phase and for a certain strength of the field it crosses the paranematic-nematic transition surface: the system transits to the NSN phase. Increasing the field, the system crosses the grid surface and transits to the smectic phase. The NSN phase can be reached under field for liquid crystals with a coupling constant higher than  $|\gamma_{\text{TP}}|$ , the zero field triple point coupling, and smaller than  $\gamma_{\text{TCP}}$ , the coupling constant of the triple-critical point  $D$ .

With our simplifying hypothesis  $\lambda = 0$ , we cannot show on this diagram the NSS phase, which is connected with reentrance phenomena.

## 8. Conclusion

We have developed a phenomenological model in the Landau de Gennes formulation to describe the field induced phase transitions between isotropic, nematic, and smectic A. We use as relevant parameter the reduced nematic-smectic coupling  $\gamma/a_A$ . The typical values of these coupling are described in Table V. Increasing  $|\gamma/a_A|$  the zero field transition changes from a second order nematic-smectic A ( $N-S_A$ ) to a first order isotropic-smectic A ( $I-S_A$ ) transition. The effect of a field on a second order  $N-S_A$  transition is to increase the transition temperature as the square of the applied field. In presence of field, a zero field first order  $N-S_A$  transition can become of second order above a tricritical point (TCP). The coordinates of the TCP are field independent. The tricritical field values have been calculated. A material which undergoes in zero field a spontaneous  $I-S_A$  transition, can give under field a non spontaneous nematic (NSN) phase and a smectic A phase or directly the smectic A phase. The NSN phase disappears above a critical point. Furthermore we have found that the NSN phase is either metastable in absence of electric field and stable under electric field or unstable in absence of field and stable under field. We have also predicted a new parasmectic phase which could be induced

by the electric field under certain conditions depending on the material constants. Increasing the amplitude of the non favorable coupling, we can describe second order reentrant  $S_A \rightarrow N$  transitions. Another new topology is the field induced parasmectic-reentrant paranematic phase transition in the case of a material which transits spontaneously from the isotropic to the nematic phase. In the reentrant case, one can find a situation where a non spontaneous smectic (NSS) exists, visible only under electric field. The NSS and parasmectic phases have never been observed experimentally. It would be interesting to look for their existence. Our model predicts also some new interesting topologies, *e.g.*, a critical smectic point. We have also constructed the phase diagrams of these field induced transitions. Our model reproduces in a unified way the known results from different microscopical models [24–26]. It predicts two new phases: the parasmectic and the non spontaneous smectic, and some new transition topologies. On the experimental ground, there exist unpublished data [29] of the electric field induced transition in smectogenic materials, for most of the coupling parameters values. Only part of these data, for medium coupling, have been presented in a letter [2]. The present model will help us to analyze all these experimental data. This analysis will be presented in a forthcoming paper [37]. We also hope the model to stimulate further experimental studies.

### Acknowledgments

We thank J. Prost and T. Sluckin for useful discussions and suggestions.

### References

- [1] de Gennes P.G. and Prost J., *The Physics of Liquid crystals* (Clarendon, Oxford, 1993).
- [2] Lelidis I. and Durand G., *Phys. Rev. Lett.* **73** (1994) 672.
- [3] Hanus J., *Phys. Rev.* **178** (1969) 420.
- [4] Maier W. and Saupe A., *Z. Naturforsch.* **13a** (1958) 564.
- [5] Maier W. and Saupe A., *Z. Naturforsch.* **14a** (1959) 882.
- [6] Maier W. and Saupe A., *Z. Naturforsch.* **15a** (1960) 287.
- [7] Wojtowicz P.J. and Sheng P., *Phys. Lett. A* **48** (1974) 235.
- [8] Shen J. and Woo C.-W., *Phys. Rev. A* **24** (1981) 493.
- [9] Savithramma K.L. and Madhusudana N.V., *Mol. Cryst. Liq. Cryst.* **103** (1983) 99.
- [10] de Bruyn J.R., *Liq. Cryst.* **11** (1992) 269.
- [11] Fan C. and Stephen M., *Phys. Rev. Lett.* **25** (1970) 500.
- [12] Hornreich R.M., *Phys. Lett. A* **109** (1985) 232.
- [13] Vause C.A., *Phys. Lett. A* **114** (1986) 485.
- [14] Lelidis I. and Durand G., *Phys. Rev. E* **48** (1993) 3822.
- [15] Kobayashi K., *J. Phys. Soc. Jpn* **29** (1970) 101.
- [16] Kobayashi K., *Mol. Cryst. Liq. Cryst.* **13** (1971) 137.
- [17] McMillan W.L., *Phys. Rev. A* **4** (1972) 1238;
- [18] McMillan W.L., *Phys. Rev. A* **6** (1972) 936.
- [19] Kirkwood J. and Monroe E., *J. Chem. Phys.* **9** (1941) 514.
- [20] de Gennes P.G., *Mol. Cryst. Liq. Cryst.* **21** (1973) 49.
- [21] Doane J.W., Parker R.S., Cvikel B., Johnson D.L. and Fishel D.L., *Phys. Rev. Lett.* **28** (1972) 1694.
- [22] Johnson D.L., Maze C., Oppenheim E. and Reynolds R., *Phys. Rev. Lett.* **34** (1975) 1143.

- [23] McKee T.J. and McColl J.R., *Phys. Rev. Lett.* **34** (1975) 1076.
- [24] Hama H., *J. Phys. Soc. Jpn* **54** (1985) 2204.
- [25] Rosenblatt C., *J. Phys. Lett.* **42** (1981) L-9.
- [26] Rosenblatt C., *Phys. Lett. A* **83** (1981) 221.
- [27] Ronis D. and Rosenblatt C., *Phys. Rev. A* **21** (1980) 1687.
- [28] Rosenblatt C. and Ronis D., *Phys. Rev. A* **23** (1981) 305.
- [29] Lelidis I., thèse de doctorat, Orsay, n°3492 (1994).
- [30] Cladis P.E., *Phys. Rev. Lett.* **35** (1975) 48.
- [31] Pershan P.S. and Prost J., *J. Phys. Lett. (Paris)* **40** (1979) L-27.
- [32] Prost J., *Liquid Crystal of one and two dimensional order* (Springer Verlag, 1980) p. 125.
- [33] Prost J. and Toner J., *Phys. Rev. A* **36** (1987) 5008.
- [34] Lelidis I., Nobili M. and Durand G., *Phys. Rev. E* **48** (1993) 3818.
- [35] See, for instance, Böttcher C.J.F., *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973).
- [36] Kelker H. and Hats R., *Handbook of Liquid Crystals* (Verlag Chemie, 1980).
- [37] Lelidis I. and Durand G., to be submitted.