

Direct Transitions from Isotropic to Smectic Phases

Harald Pleiner¹, Prabir K. Mukherjee^{2,3}, and Helmut R. Brand²

¹ *Max-Planck-Institut für Polymerforschung, 55021 Mainz, Germany*

² *Theoretische Physik III, Universität Bayreuth, 95440 Bayreuth, Germany*

³ *Dept. of Physics, Haldia Govt. College, P.O.-Debhog, Dist.-Midnapur, Pin-721657, India*

Proceedings Freiburger Arbeitstagung Flüssigkristalle, 29 (2000) P59

Introduction

Although the nematic-isotropic (NI) phase transition has been a topic of active theoretical and experimental studies over the past few decades [1], reports on the smectic *A* - isotropic (AI) transition are comparatively scarce [2–5]. This is even more applicable for direct transitions to more complex smectic phases, like smectic C, F, I, C_M or the recent family of banana phases. These transitions are characterized by the fact that more than one type of ordering is involved. We will discuss the AI transition within a phenomenological Ginzburg-Landau approach in greater detail and comment briefly on other direct transitions.

All the experimental observations show that the AI transition is more strongly first order than the NI transition, which is known to be rather weakly first order. This indicates that the orientational order in the smA phase is much higher than that in the nematic phase. The vicinity of a smA phase has a noticeable influence on the pretransitional phenomena in the isotropic phase. However, there is as yet no systematic theoretical study on the AI transition that takes into account all the key features of this transition.

Isotropic to smectic A transition

The starting point of our approach is to write down the Ginzburg-Landau free energy functional F [6]. The nematic order parameter originally proposed by de Gennes [1] is a symmetric, traceless tensor described by $Q_{ij} = \frac{1}{2}S(3n_i n_j - \delta_{ij})$. The quantity S defines the strength of the nematic ordering (the modulus of the nematic order parameter) and is zero (one) for complete disorder (order). Thus in the isotropic phase $S = 0$ and in the nematic phase $S \neq 0$. The smectic order parameter $\psi(\mathbf{r}) = \psi_0 \exp(-i\phi)$ is a complex scalar quantity whose modulus ψ_0 , is defined as the amplitude of a one dimensional density wave characterized by the phase ϕ . The wave vector $\nabla_i \phi$ is parallel to the director n_i in the smectic A phase. The layer spacing is given by $d = 2\pi/q_0$ with $q_0 = |\nabla \phi|$.

Keeping homogeneous terms up to quartic and gradients only to the lowest relevant order, the total free energy near the AI transition can be written as:

$$F = F_0 + \int \left[\frac{1}{2} A Q_{ij} Q_{ij} - \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C_1 (Q_{ij} Q_{ij})^2 + \frac{1}{4} C_2 Q_{ij} Q_{jk} Q_{kl} Q_{li} + \frac{1}{2} \alpha |\psi|^2 \right] \quad (1)$$

$$+\frac{1}{4}\beta|\psi|^4 + \frac{1}{2}\delta|\psi|^2Q_{ij}Q_{ij} + \frac{1}{2}d_1|\nabla_i\psi|^2 + \frac{1}{2}d_2|\Delta\psi|^2 + \frac{1}{2}e_1Q_{ij}(\nabla_i\psi)(\nabla_j\psi^*)]dV$$

where F_0 is the free energy of the isotropic phase, $A = a(T - T_{NI}^*)$ and $\alpha = \alpha_0(T - T_{AI}^*)$. T_{NI}^* and T_{AI}^* are the critical temperatures for a hypothetical second order transition to the nematic and the smectic state, respectively, in the absence of any cross coupling. All other coefficients, as well as a and α_0 , are assumed to be constants near the transition point. There is a direct, bi-quadratic coupling between the nematic and smectic order governed by the coupling coefficient δ . As we shall see, a negative value of δ favors the smA phase over the nematic phase, whereas a positive δ favors the nematic phase over the smA phase. We assume C_1 , C_2 , β and $\beta C - \delta^2$ (with $C = C_1 + C_2/2$) and d_2 to be positive to guarantee the stability of the isotropic, homogeneous phase at high temperatures and $B > 0$ to get $S > 0$ in the nematic phase. Some higher gradient terms involving Q_{ij} as well as second order derivatives of ψ , which have been disregarded in eq.(1), do not qualitatively change the physical picture.

There is no direct linear coupling term $\sim |\psi|^2 S$ [7] in the free energy (1), since such a term cannot exist in the isotropic phase: Written in the full order parameter Q_{ij} it would read $\xi_{ij}|\psi|^2 Q_{ij} = 0$, since $\xi_{ij} = \xi\delta_{ij}$ in the isotropic phase and Q_{ij} is traceless. However, such a coupling term is possible near the nematic - smectic A transition, since one has uniaxial symmetry on both sides of the transition. The isotropic gradient terms in (1) govern q_0 , while the one with Q_{ij} give the relative direction of the layering with respect to the director.

Here we consider phases in which the nematic and smectic order are spatially invariant, $S = \text{const.}$ and $\psi_0 = \text{const.}$ and for the smectic A phase a spatially constant wave vector q_0 with the layering along the director. In that case eq.(1) reads

$$F - F_0 = \int \left[\frac{3}{4}AS^2 - \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 + \frac{3}{4}\delta\psi_0^2S^2 + \frac{1}{2}d_1\psi_0^2q_0^2 + \frac{1}{2}e_1\psi_0^2Sq_0^2 + \frac{1}{2}d\psi_0^2q_0^4 \right] dV \quad (2)$$

Note that there is now a nematic-smectic coupling term linear in S . However it comes with a q_0^2 factor and is zero in the isotropic phase. The presence of the cubic term describes the first order character of the NI and AI transition. We note that a Landau energy of the same structure as the first line in eq.(2) has been used to describe the reentrant behavior in liquid crystals in [8] and for $B \equiv 0$ in [9]. Minimization of Eq.(2) with respect to S , ψ_0 and q_0 yields the following three phases:

$$\text{Isotropic phase : } S = 0, \quad \psi_0 = 0, \quad q_0 = 0 \quad (3)$$

$$\text{Nematic phase : } S_N = \frac{1}{6C} \left[B + (B^2 - 24AC)^{1/2} \right] > 0, \quad \psi_0 = 0, \quad q_0 = 0 \quad (4)$$

$$\text{Smectic A phase : } S_A > 0, \quad \psi_0^2 = -\frac{1}{\beta} \left(\alpha^* - e^*S_A + \frac{3}{2}\delta^*S_A^2 \right), \quad q_0^2 = -\frac{1}{2d_2}(d_1 + e_1S_A) \quad (5)$$

with S_A given by $0 = 6AS_A - 3BS_A^2 + 9CS_A^3 + 6\delta\psi_0^2S_A + 2e_1\psi_0^2q_0^2$. We use the abbreviations $\alpha^* = \alpha - d_1^2/(4d_2)$, $\delta^* = \delta - e_1^2/(6d_2)$, and $e^* = d_1e_1/(2d_2)$. Necessary conditions for the different phases to be stable include

$$\frac{\partial^2 f}{\partial \psi_0^2} > 0, \quad \frac{\partial^2 f}{\partial S^2} > 0, \quad \frac{\partial^2 f}{\partial q_0^2} > 0 \quad (6)$$

The derivatives in (6) have to be taken at the values (3-5) for the appropriate phases. Among others these conditions are $\alpha^* + \frac{3}{2}\delta^*S_A^2 < e^*S_A$, $A - BS_A + \frac{9}{2}CS_A^2 + \delta\psi_0^2 > 0$ and $6d_1 + e_1S_A < 0$ for the smectic A phase. These three (and the other) conditions determine the stability of the smA phase somewhat implicitly. For the isotropic phase the stability conditions are $\alpha > 0$ and $A > 0$.

Although the stability conditions are involved, some important qualitative features can be extracted already at this stage. First, it is obvious that a continuous AI transition ($S_A = 0 = \psi_0$) is not possible (except for the very special case $B = 0$ and $T_{NI}^* = T_{AI}^* - d_1^2/(4d)$). In the general case there is a jump in S_A and ψ_0 at some temperature $T_{AI} > T_{AI}^*$. Layering can take place for $d_1 < 0$, only.

The smectic A phase is in competition with possible isotropic and nematic phases. The existence range of all three phases generally overlap. That phase with the lowest free energy is the stable one. A (first order) transition takes place, when 2 free energies are identical. In order to study the direct AI transition in more detail, we substitute the solution (5) for the smectic order parameter ψ_0 and for q_0^2 into the free energy (2). We get a free energy expression for the smectic A phase as a function of S alone, which can be written as

$$F = F_0 - \frac{\alpha^{*2}}{4\beta} + \frac{\alpha^*e^*}{2\beta}S + \frac{3}{4}A^*S^2 - \frac{1}{4}B^*S^3 + \frac{9}{16}C^*S^4 \quad (7)$$

where $C^* \equiv C - \frac{\delta^{*2}}{\beta}$, $B^* \equiv B - \frac{3e^*\delta^*}{\beta}$, and $A^* \equiv A - \frac{\delta^*\alpha^*}{\beta} - \frac{e^{*2}}{3\beta}$ and α^* , δ^* and e^* are defined after (5). Since $\delta^* < \delta < 0$, we can infer $C^* > 0$ from $\beta C > \delta^2$ and $B > 0$ leads to $B^* > 0$. Of the 3 extrema ($\frac{\partial F}{\partial S} = 0$) of eq.(7) that exist within the stability range of the smectic A phase, two are minima (large and small S) with a maximum in between. The minimum at the larger $S = S_A$ is the deeper one, since $B^* > 0$.

At the AI transition the isotropic minimum at $S = 0$ and the smectic A minimum at S_A have equal free energies, but the two phases are separated by a barrier height. These conditions, $F(S_A) = F_0$ and $\delta F/\delta S|_{S_A} = 0$, fix the transition temperature T_{AI} and give the jump in S as $\Delta S = S_A(T_{AI})$. Some implicit formulas for these quantities are

$$f_1g_2 + f_2(g_1^2 - f_1h_1)^{1/2} = f_2g_1 + f_1(g_2^2 - f_2h_2)^{1/2} \quad (8)$$

with $f_1 = 3(-18A^*C^* + B^{*2})$, $g_1 = -3(A^*B^* + 9\alpha^*e^*\beta^{-1}C^*)$, $h_1 = (2\alpha^*/\beta)(18\alpha^*C^* - e^*B^*)$, $f_2 = 18\alpha^*C^* - e^*B^*$, $g_2 = 3(A^*e^* - \alpha^*B^*)$, $h_2 = 6\alpha^*(2A^* + e^{*2}/\beta)$, where α^* and A^* (or rather α and A) have to be taken at $T = T_{AI}$. Thus, eq.(8) is an implicit equation for T_{AI} . In terms of T_{AI} the jump ΔS is given by

$$\Delta S = f_2^{-1}(-g_2 + [g_2^2 - f_2h_2]^{1/2}) \quad (9)$$

Having calculated T_{AI} and ΔS we can go back to eq.(5) and calculate the finite smectic order $\psi_0(T_{AI})$ and the layer wavelength $q_0(T_{AI})$ at the transition temperature. Of course, one has to check that T_{AI} is within the existence range (6) of the smectic phase, e.g. that the resulting quantities ψ_0^2 and q_0^2 are positive. In that case there is always a direct AI transition possible within the framework and assumptions of our mean-field model. Of course, the NI transition could come first before T_{AI} is reached. To prevent this, T_{AI} has to be larger than $T_{NI} = T_{NI}^* + B^2/(27Ca)$.

For $T < T_{AI}$ the smectic A minimum represents the stable state. The isotropic state is then a metastable one, and at even lower temperatures, it becomes unstable (a local energy maximum).

Other transitions

For the direct transition to the biaxial, orthogonal C_M phase [10] the full biaxial Q_{ij} is needed to describe orientational order in addition to the smectic order parameter. Thus eq.(1) can be used with $Q_{ij} = \frac{1}{2}S(3n_in_j - \delta_{ij}) + \frac{1}{2}\eta(m_im_j - l_il_j)$ and η is another quantity to be determined by minimizing the Ginzburg-Landau free energy. Concerning the polar untilted C_P phase [11] made-up by banana-shaped molecules, the in-plane polarization \mathbf{P} is another order parameter involved (in the $C_{P'}$ phase the polarization is across the layers [12]). The appropriate free energy is of the form

$$F = F_{AI} + \int \left[\frac{1}{2}a\mathbf{P}^2 + \frac{1}{4}c\mathbf{P}^4 + \frac{1}{2}b_1(\nabla_i P_j)^2 + \frac{1}{2}b_2(\text{div}\mathbf{P})^2 + f_1\text{div}\mathbf{P} + f_2\mathbf{P}^2\text{div}\mathbf{P} \right. \\ \left. + \frac{1}{2}\delta_2|\psi|^2\mathbf{P}^2 + \frac{1}{2}\delta_3P_iP_jQ_{ij} + g_1Q_{ij}\nabla_iP_j + g_2|\psi|^2\text{div}\mathbf{P} \right] dV \quad (10)$$

where F_{AI} is the free energy of eq.(1). Some higher order gradient terms have been omitted. If orthogonal dolphin phases C_Q and $C_{Q'}$ are considered [13, 14], there are two (orthogonal) polarizations that order at the direct phase transition (instead of one for C_P and $C_{P'}$).

With respect to direct transitions from isotropic to tilted smectic phases (e.g. smectic C) one has to take into account additionally the tilt order parameter describing the tilting of the nematic preferred direction off the layer normal. This involves the tilt angle and tilt direction as quantities entering the appropriate free energy. For the tilted (polar) banana phases C_{B1} and C_{B2} [15] as well as the tilted dolphin phases C_{D1} and C_{DG} [16], in addition the polarization(s) have to be taken onto account in a Ginzburg-Landau functional.

P.K.M. thanks the Alexander von Humboldt-Foundation for the award of an Alexander von Humboldt Fellowship. H.R.B. acknowledges partial support of this work through the Sonderforschungsbereich 481: 'Polymere und Hybridmaterialien in inneren und äußeren Feldern' of the Deutsche Forschungsgemeinschaft.

References

- [1] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford, Clarendon Press) 1993.
- [2] H.J. Coles H.J. and C. Strazielle, *Mol. Cryst. Liq. Cryst. Lett.*, **49** (1979) 259.
- [3] B.M. Ocko, A. Braslau, P.S. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev. Lett.*, **57** (1986) 94.
- [4] M. Olbrich, H.R. Brand, H. Finkelmann and K. Kawasaki, *Europhys. Lett.*, **31** (1995) 281.
- [5] A. Drozd-Rzoska, *Liq. Cryst.*, **24** (1998) 835.
- [6] P.K. Mukherjee, H. Pleiner, and H.R. Brand, submitted for publication.
- [7] I. Lelidis and G. Durand, *J. Phys. II*, **6** (1996) 1359.
- [8] N.A.P. Vaz and J.W. Doane, *Mol. Cryst. Liq. Cryst.*, **101** (1983) 35.
- [9] P.E. Cladis, *Mol. Cryst. Liq. Cryst.*, **67** (1981) 177.
- [10] H.R. Brand and H. Pleiner, *Makromol.Chem., Rapid Commun.*, **12** (1991) 539.
- [11] H.R. Brand, P.E. Cladis and H. Pleiner, *Macromol.*, **25** (1992) 7223.
- [12] H. Pleiner, H.R. Brand and P.E. Cladis, *Proc. Freiburger Arbeitstagung Flüssigkristalle*, **28** (1999) 16.
- [13] H.R. Brand, P.E. Cladis and H. Pleiner, *Int. Journal of Engin. Science*, **39** (2000) 1099.
- [14] H. Pleiner, H.R. Brand and P.E. Cladis, *Ferroelectrics*, .. (2000) in print.
- [15] H.R. Brand, P.E. Cladis and H. Pleiner, *European Physical Journal B*, **6** (1998) 347.
- [16] P.E. Cladis, H.R. Brand and H. Pleiner, *Ferroelectrics*, .. (2000) in print.