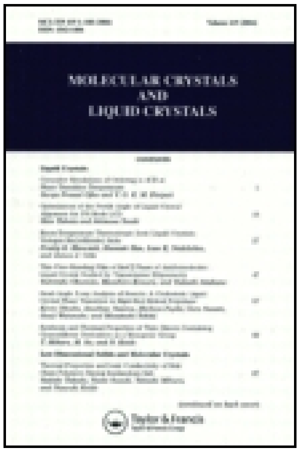

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ORDER ELECTRICITY AND THE NEMATIC, SMECTIC A, SMECTIC C PHASE TRANSITIONS

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Abstract Smectic liquid crystal are quadrupolar oriented systems, with a spatial modulation across layers. This modulation creates an order electric antiferroelectric polarization. The associated dielectric depolarization energy, originating from long range forces, creates a new non analytic term, which must be added to the usual Landau-de Gennes expansion. This new term can physically explain the molecular tilt inside the layers and the smectic A-Nematic reentrance. The tilt appears as an intrinsic property of well ordered quadrupolar layered systems.

Smectic liquid crystals are layered systems, constituted of one dimensional piling of two dimensional liquids(1). In each layer, the rod like molecules are aligned normal to the layers (smectic A or A), or tilted (smectic C or C). The transition between A and C can be continuous(2), although direct first order transitions from the ordered liquid (nematic or N) to the C phase are also observed(3). The tilting (A → C) transition is also observed in most lamellar system, like lyotrope soaps and membranes(4,5) so that it was a challenge to explain its physical origin. Of course, phenomenological Landau model have been build to describe the tilting transition(6-9).

But, as usual in this approach, the free energy expansion in term of tilt and smectic order parameter was constructed with "ad hoc" terms which could hardly explain the physics of the transition. More physical molecular models have been proposed, based on electric dipolar, quadrupolar or steric interactions(10-14). Reviews and criticism of these models are given in ref. 15,16. Some models seem unphysical, assuming for instance frozen rotations around the long molecular axis(10). Other models seem to predict results inconsistent with the assumed hypotheses(12), or lack essential features like packing entropy(13). Finally a very recent model(17) of the A → C transition based on quadrupolar interactions seems also to have problems, predicting that the tilt is identically zero for a perfectly ordered A phase. Recently, order electricity (i.e. the electric polarization connected with a gradient of the orientational N order parameter) was introduced(18). The dielectric energy associated with this polarization, originating from electric macroscopic long range forces, gives a non-analytic term(19) which must be added to the usual Landau-de Gennes free energy. This procedure is standard, when dealing with electric forces in elastic problems(20). This new non-analytic term can force a molecular tilt at a N-isotropic (I) interface. In this letter, we generalize this idea to layered systems, by considering the layers as a piling of interfaces, with internal orientational gradient of order. The tilting transition appears then as a general property of quadrupolar layered systems.

Let us assume the existence of a nematic material of director $\hat{n}$ ($\hat{n}^2 = 1$), inside which external forces impose a macroscopic modulation of order in form of a layered texture, of wave number k. The size of the "layers" is assumed much larger than a molecular size m, i.e. km<1. The amplitude of the layer modulation can be defined by a normalized parameter ψ ($0 < |\psi| < 1$), i.e. is assumed proportional to exp(i k r).

$$\overleftrightarrow{Q} = - e\, S\, (3/2)\, (\hat{n}\, \hat{n} - \overleftrightarrow{I}/3) \quad . \qquad (1)$$

$S(3/2)\,(\hat{n}\ \hat{n} - \overleftrightarrow{I}/3)$ is the usual orientational N order parameter for our non-polar ($<\hat{n}> = 0$) oriented system, of modulus $S(0 < S < 1)$. e, of the order of $qm^2/m^3 = q/m$ (q electric charge) is the usual flexo-electric coefficient of nematics. In the presence of the layered ordering the density $\overleftrightarrow{Q}$ is modulated across the layers. As a result, there appears in the layers a gradient of the quadrupolar moment giving rise to an electric polarization:

$$\vec{P} = - \vec{\nabla}\, \overleftrightarrow{Q} \quad . \qquad (2)$$

$\vec{P}$ is the order electric polarization associated with the layer ordering. Each layer must present an antiferroelectric ordering. In an arbitrary layered system, the quadrupolar density $\overleftrightarrow{Q}(z)$ across the layers is

$$\overleftrightarrow{Q}(z) = \overleftrightarrow{Q}_0 + \delta\overleftrightarrow{Q}(z) \qquad (3)$$

where $\hat{z}$ ($\hat{z}.\hat{z} = 1$) is the coordinate normal to the layers. $\overleftrightarrow{Q}_0$ is the uniform part. $\delta\overleftrightarrow{Q}(z)$ is a periodic function of z, related to the layer ordering ψ, and proportional to $\overleftrightarrow{Q}_0$, as:

$$\delta\overleftrightarrow{Q}(z)=\overleftrightarrow{Q}_0\,\psi\,\exp(i\,k\,z)=-e\,S\,(3/2)(\hat{n}\,\hat{n}\,-\overleftrightarrow{I}/3)\psi\exp(i\,k\,z) \qquad (4)$$

which is the first Fourier component of the quadrupole modulation at k. Using (2), the modulated polarization writes as:

$$\vec{P} = e\,S\,(3/2)\,i\,k\,\left[(\hat{z}.\hat{n})\,\hat{n} - (1/3)\,\hat{z}\right]\psi\exp(i\,k\,z) \quad , \quad (5)$$

where we assume $\hat{n}$ uniform. Using $D_z = 0 = \varepsilon_{zz}E_z + 4\pi P_z$ ($\vec{E}$, $\vec{D}$ electric and displacement fields), the new dielectric energy associated with $\vec{P}$ writes as$^{(13)}$:

$$2\pi P_z^2/\,\varepsilon_{zz} = (1/2)\,r^2\,S^2\,|\psi|^2\,(\cos^2\theta-1/3)^2 \quad , \quad (6)$$

where $r^2 = (3ke/2)^2\,(2\pi/\,\varepsilon_{zz})$. ε_{zz} is the zz component of the dielectric tensor, and $\theta = (\hat{n}, \hat{z})$ the tilt angle.

Note that this non-analytic P_z^2 term cannot be reduced to the corresponding Landau term P^2. Eq.6 shows that $\hat{n}$ will tend to orient at the "magic" angle, $\cos^2\theta = 1/3$ ($\theta \simeq 54°$) to suppress this dielectric contribution.

To apply these considerations to a real smectic phase, for which $km \sim 2\pi$, we must be careful.

We can empirically define now the electric monopoles, dipoles, and quadrupoles on a bond scale a, rather them a molecular scale m. As in the microscopic model of Priest $^{(14)}$, we restrict to the special case of purely quadrupolar systems, whithout dipoles.

Practically, this means that the systems contains only isotropic electric quadrupoles (most of the electron clouds around C or H atoms) or anisotropic quadrupoles along $\hat{n}$, from say double bonds. We also assume steric forces to have a shorter range than m, as practially most thermotropic smectics molecules present flexible end chains. We call now "macroscopic" any observable on the whole system, which can be measumed on a size much larger than a, then on the layer m, since m $>$ a. Of course, the use of localized quantities P(z), $\delta Q(z)$ is not correct, in this macroscopic description. Only the Fourier components of these quantities are observables, corresponding to thermodynamical averages over the whole sistem.

Following de Gennes procedure, we consider now as the Fourier component of the smectic modulation of electron density $\rho(z)^{(1,21)}$ i.e. the smectic order parameter. There exist now modulations of $\vec{P}(k)$ and $\overleftrightarrow{\delta Q}(k)$ whith Fourier components proportional to $\rho(k)/(ik)$ and $\rho(k)/k^2$. As $\rho(k)$ itself, $\vec{P}(k)$ and $\overleftrightarrow{\delta Q}(k)$ are proportional to ψ . Eq. 6 remains valid in term of Fourier components.

This energy term is similar to one already introduced$^{(22)}$ to explain reentrance phenomena, with a new angular dependence. The physical origin of the $\rho(k)$, and then $\overleftrightarrow{\delta Q}(k)$, modulation can be naively related to the rod-like structure of molecules constituent of smectic phases. They possess generally a central rigid core, with high electron density and flexible alkylchains with low electron density.

It is now a simple matter to describe the N → C and A → C transitions, combining a classical Landau model(1) for smectic ordering with our order electric source of tilt. The smectic free energy density F, compared to the N phase, developped for small $|\psi|$, is

$$F= (1/2)a(T-T_C)\ |\psi|^2 +(1/4)b|\psi|^4 -(1/2)c|\psi|^2 S(\cos^2\theta -1/3)$$
$$+(1/2)\ r^2\ |\psi|^2\ S^2\ (\cos^2\theta-1/3)^2 \quad . \tag{7}$$

T is the temperature, T_C the assumed N → C transition temperature in absence of order electricity, $b > 0, c > 0$.

The third term in $|\psi|^2 S$, written as in ref.21, is the usual stabilizing term coming from the smectic-nematic coupling, which forces the molecules to align normal to the layers. Usually it is written as $(1/2)B\ \theta^2$ (1). Here we understand it as the equivalent of the Rapini-Papoular(23) interaction at an interface, which justifies the $\cos^2\theta$ angular dependence. The important parameter is the ratio $S(T)r^2/c = S(T)\ \beta$ of the destabilizing order electric energy compared to the stabilizing one. Whatever may be the initial value of the molecular parameter β, the increase of nematic ordering S(T), when cooling down, will change the balance between these two terms and will induce the C phase.

We call $t = (1-T/T_{NI})^{1/2}$ the reduced temperature. T_{NI} is the N→I transition temperature. We also note $y = c/a$. By minimizing F compared to ψ and θ, we have calculated(24) the NAC phase diagram in the (t, β) plane (Fig.1), assuming for S(t) a classical law $S(t)=S_0 t$. The line aa' represents the stability domain of the A phase, in the absence of tilt

$(\partial^2F/\partial\psi^2 = 2\,b^2\,\psi^2 > 0$ for $\theta=0)$ a' would give the transition temperature of a reentrant N phase if θ were blocked to zero. The reentrant phenomenon is due to the built up of the order electric energy, which eventually suppresses the A ordering. The line bb' is the line along which a tilt θ, if it has any meaning, decreases F

$$(\partial^2F/\partial\psi^2)\ (\partial^2F/\partial\theta^2) - (\partial^2F/\partial\psi\,\partial\theta)^2 > 0 \quad \text{for } \theta = 0\ .$$

The line cc' defines the stability domain of the C phase $(\partial^2F/\partial\psi^2 = 2b\,\psi^2 > 0$ for the optimal tilt θ_{op}, given by $\cos^2\theta_{op} = (1/3)+(1/2\,\beta\,S(t))$. These three lines intersect at the gathering point G. The phase sequence is now easy to describe.

Assume a material with a small molecular quadrupole modulation $(\beta<1)$. It undergoes, when cooling down a second order N $\rightarrow$ A transition across a, at $T_S > T_C$, then a continuous A $\rightarrow$ C transition across b. For a larger β parameter, the system undergoes a direct N $\rightarrow$ C transition across c. Along the c line, θ_{op} goes continuously from zero (at G) up to the magic angle for infinite β, at $t = t_s$ $(T = T_S)$. Along C, despite the finite value of θ_{op}, the N $\rightarrow$ C transition remains continuous in our simple model, since ψ^2 goes continuously to zero. One can give a gradual first order character across c, starting from G, by adding higher order terms in F, for instance the one describing that the smectic wave number k minimizes F around k_o. Its shape is $S^2(k^2 - k_o^2)^2\,\psi^4$. In the rotation θ inside the layers, with rigid rod molecules, k would change, resulting in a $S^2\,\psi^4\,tg^4\theta$ term. These details(24) are irrelevant for

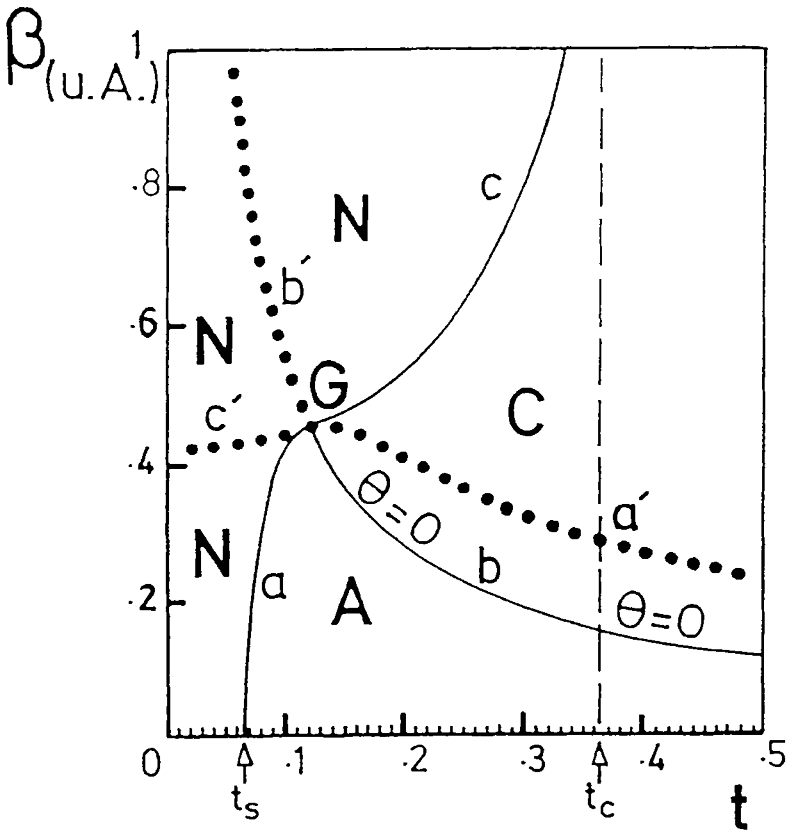

FIG. 1

Phase diagram of the N A C equilibrium, from the order electric mechanism. t, reduced temperature; β, reduced order electric parameter, y = 500. t = 0 corresponds to the N-I transition.

The N-C and A-C transitions are induced by the increase in nematic ordering when cooling down.

our present purpose.

To understand what happens across the b' line, we write the thermal fluctuations $<|\psi|^2>_{th}$ with the equipartition theorem, as:

$$<|\psi|^2>_{th} = (k_B T/aV)\,[\,T-T_C -(1/4)(y/\beta)+ \beta y\, S^2(T)\,(\cos^2\theta -\cos^2\theta_{op}(T))^2\,]^{-1}, \qquad (8)$$

$k_B T/V$ being the Boltzmann free energy density. θ is the assumed $\hat{n}$ tilt inside the fluctuating layer ψ, at fixed $|k| = k_o$. On the high temperature side of the b' line, because $\cos^2\theta_{op} > 1$, the largest fluctuations correspond to $\theta=0$, i.e. represent smectic A fluctuations. When crossing b', the largest $<|\psi|^2>_{th}$ corresponds to the real tilt θ_{op}, i.e. represents smectic C fluctuations. These biaxial fluctuations, far from an eventual uniaxial → biaxial nematic transition, cannot induce long range biaxial order. The phase remains N. b' is a disorder line(25). The line c' has no physical meaning. G, at the intersection of a, b and c, is the tricritical point of the N,A,C equilibrium. Note that the N → A and the N → C lines are tangent in G, and that the disorder line b' is just the extrapolation of the A → C transition line. Note finally that G tends toward the maximum of the aa' line for large y, i.e. G. tends toward the reentrant N - A - N point, as recently suggested(26).

Another way, other than tilt or A-N reentrance to escape the order electric depolarizing energy, would be for polar molecules to readjust the layer spacing to partially overlap to decrease $\overleftrightarrow{\delta Q}$, as in the $A_2 \rightarrow A_d$ transition for instance. Infact, this point has already been discussed in ref. 21. An extension of this model to molecules possessing dipoles will be presented later(24).

We can make a rapid check of our theory of the NAC transition. It is well known first that molecules with a large quadrupole modulation give rise to a strong first order N $\rightarrow$C transition, with $\theta \simeq 50°$ as shown for instance by the alkoxybenzoicacid series(27). The $\hat{n}\rightarrow-\hat{n}$ symmetry of the molecule in the layers tends to decrease $\delta\overleftrightarrow{Q}(k)$, except when the quadrupole distribution is localized at the centre or at the ends of the molecule. Indeed, it is known(15) that non-polar dialkylazobenzenes have N and A phases only, when the same alkoxy compounds, with an outboard dipole moment and then a larger quadrupole modulation, show a tendency to the C phase. Note that in this case, contrary to ref. 10, the dipoles are used only to build quadrupoles, allowing for free molecular rotations.

To conclude, nematic liquid crystals are uniform quadrupolar oriented systems. Cholesterics are a first example of a spatially modulated quadrupolar system, with constant modulus of the quadrupoles, but a modulated orientation. Smectic liquid crystals could be considered as nematics with a fixed orientation, and a spatial modulation of the quadrupolar modulus. The Fourier amplitude $\delta\overleftrightarrow{Q}(k)$ of this modulation can be considered a thermodynamical variable, as the density modulation itself, since it is obtained by an average on the whole system. This modulation of $\overleftrightarrow{Q}$ creates a modulated order electric polarization, and a new dielectric depolarizing energy, which must be added to the usual Landau-de Gennes expansion. It is a geometrical property of quadrupoles that a tilt at the magic angle suppresses this dielectric energy, by aligning the dipoles normal to the order gradient.We have shown that this order electric effect can explain the physics of the N-C or A-C tilt transition, and if the tilt is frozen the N-A reentrance. This mechanism could also explain the tilt of any quadrupolar oriented lamellar system, like the one of the L_β and P_β , phases of lyotropic liquid crystals . Of course, other quasi-macroscopic models can also predict the tilting transition, using steric quadrupoles, as recently, demonstrated(28,29,30). It will be important in the future to correlate the observed tilt transition in smectics with their molecular structure, to understand which mechanism is dominant.

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