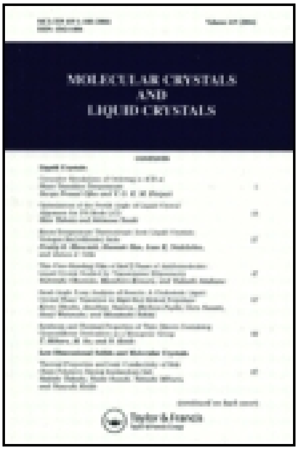

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MOLECULAR ORIENTATIONAL ORDER IN REENTRANT NEMATIC LIQUID CRYSTALS

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ABSTRACT

The predictions of orientational order parameter in reentrant nematic liquid crystals using a Landau-type theory are compared with those from the McMillan-type molecular theory. Recent experimental results from birefringence, NMR and ESR studies are discussed.

Since the first discovery of reentrant phenomenon in liquid crystals by Cladis[1], numerous experiments[2-9] have been carried out in order to elucidate structural and dynamical properties of the reentrant mesophases in binary liquid crystalline mixtures and in pure compounds at normal and elevated pressures. Nuclear magnetic resonance (NMR) spectroscopy appears to be most suitable in probing the orientation order[10] in liquid crystals. The measured orientational order parameter Q can be used to test the validity of molecular theory[11] and/or phenomenological theory[2,12] of reentrant polymorphism. A molecular theory based on the McMillan-type has been proposed by Luckhurst and Timimi[11]. The single particle potential involves a cross term between the smectic order and orientational order parameters whose strength is governed by a positive coupling constant α'. The model predicts a reentrant nematic (RN) below a smectic A (S_A) phase as α' is decreased with decreasing temperature. We reproduce in the figure their proposed temperature dependence of α' and Q. One can clearly identify an enhancement in the Q value within the S_A phase in comparison with the high temperature nematic (N) and the low temperature RN phases. Recent measurements of the anisotropy of the index of refraction by a birefringence study[3] appear to support the model. However both NMR[7] and ESR[8] studies of probe molecule in binary mixtures show contrasting results.

A Landau-type theory has also been proposed[2] to account for the reentrant nematic phase in 6OCB/8OCB mixtures on one hand and the enhancement of S_A phase over the nematic in 40.8/8OCB mixtures on the other hand. Cladis has assumed that both the nematic to isotropic transition (at T_{NI}) and nematic to smectic A (at T_{NS}) transition are of second order and that a quadratic coupling (with coupling constant η) between Q and the smectic order parameter ψ exists. The free energy density ΔF ($\Delta F = F-F_I$, F_I is the isotropic liquid value) is written without a cubic term in Q as:

$$\Delta F = \frac{1}{2}\alpha Q^2 + \frac{1}{4}\gamma Q^4 + \frac{1}{2}a\psi^2 + \frac{1}{4}b\psi^4 + \frac{\eta}{2}Q^2\psi^2 \qquad (1)$$

where $\alpha = \alpha_o\,(T-T_{NI})$, $a = a_o\,(T-T_{NS})$, and a_o, α_o, b and γ are positive constants. The determination of Q and ψ are easily achieved by minimizing ΔF to give

$$Q = \left(\frac{a\eta-\alpha b}{b\gamma-\eta^2}\right)^{\frac{1}{2}} \quad ; \quad \psi = \left(\frac{\alpha\eta-\gamma a}{b\gamma-\eta^2}\right)^{\frac{1}{2}} \qquad (2)$$

where $b\gamma-\eta^2>o$. In particular, $\psi = 0$ at the renormalized N to S_A transition ($T_{NS}^{\dagger}$) which yields

$$T_{NS}^{\dagger} = \frac{T_{NS} - \frac{\eta}{\eta_o}T_{NI}}{1 - \frac{\eta}{\eta_o}} \qquad (3)$$

where $\eta_o = \gamma a_o/\alpha_o$. Hence it is obvious that T_{NS}^{+} can either be larger or smaller than T_{NS} depending on the sign of η. For nematic to be more stable than S_A phase, η must be greater than zero[2]. But this does not apply to the RN to S_A transition since RN is the low temperature phase. In fact we will show below that η cannot be larger than zero once a S_A phase is formed. Chen et al.[3] have discarded the model of Cladis because they used $\eta>o$. Instead a linear coupling between the order parameters, proposed by de Gennes[13], was used to explain their birefringence data. Recently Vaz et al.[7] have extended the Landau theory by including the term $\frac{1}{3}\beta Q^3$ in eq. (1) with β being negative. By further assuming weak coupling (η small), they write $Q = Q_o + \delta Q$ where Q_o is the orientational order parameter with $\eta = o$. Again by minimizing ΔF w.r.t. Q and ψ, one obtains

$$\alpha + \beta Q + \gamma Q^2 + \eta\psi^2 = o \qquad (4)$$

$$a + b\psi^2 + \eta Q^2 = o \qquad (5)$$

from which Q and ψ can be solved[14] exactly. From eq. (4), one obtains[7]

$$\delta Q = -\frac{\eta\psi^2}{\beta+2\gamma Q_o}\left[1 + \frac{\gamma\eta\psi^2}{(\beta+2\gamma Q_o)^2} + \frac{2\gamma^2\eta^2\psi^4}{(\beta+2\gamma Q_o)^4} + ..\right] \qquad (6)$$

where $\beta+2\gamma Q_o>o$ for $T<T_{NI}$. To explain their ^{2}H NMR data of a probe molecule dissolved in a 6OCB/8OCB mixture, they also use $\eta>o$ and obtain a negative δQ in the S_A phase just above the RN phase. The prediction of a negative perturbation in Q is in contradiction with the molecular theory. The apparent disagreement between the Landau theory and the McMillan-type theory results from taking $\eta>o$. Two reasons why η should not be positive in the S_A phase of reentrant nematic liquid crystals are: (i) one obtains from eq. (5)

$$\eta = -\left(\frac{a+b\psi^2}{Q^2}\right) \qquad (7)$$

which is negative since quantities within brackets are positive within the S_A phase; (ii) at the renormalized transition ($T_{NS}^{\dagger}$) between RN and S_A phases, ψ is again zero and $T_{NS}^{\dagger} = T_{NS} - \eta Q^2/a_o$. To make RN more stable than S_A, $T_{NS}^{\dagger} > T_{NS}$ which implys $\eta < o$. Consequently $\delta Q > o$ in the S_A phase just above the RN phase as in the figure. Since $\eta \geq o$ in the high temperature N phase[2], it must however become negative for a stable S_A phase to form. The temperature dependence of η will be required to exactly predict the variation of Q with temperature. The enhancement of Q is expected to be small just below the N to S_A transition since both η and ψ would be relatively small. This does not seem to be borne out by the molecular theory (see figure) and the birefringence study. As temperature decreases, η becomes increasingly more negative until its magnitude is sufficient to render S_A phase less favorable. This is how the S_A phase is being driven into a RN phase. The positive δQ has been detected by the birefringence study[3] and should be detectable at the RN to S_A transition by NMR. Both spin probe study of Q by NMR and ESR give similar results which are in contrast with the above theories. The discrepancy cannot be understood unless one can blame on some peculiar behaviors of the probe molecule. It may well be that the solvation sites of the probe molecules vary with temperature, particularly near the phase transitions. We are currently using ^2H NMR to study the orientational order of partially deuterated solvent molecule in the 6OCB/8OCB mixtures with the hope of eliminating such possible difficulty.

In conclusion, the Landau theory predicts a positive enhancement of Q in the S_A phase of reentrant nematic liquid crystals in agreement with the molecular theory of Luckhurst and Timimi. These theories appear to support the reported changes in birefringence at the N to S_A and RN to S_A phase transitions.

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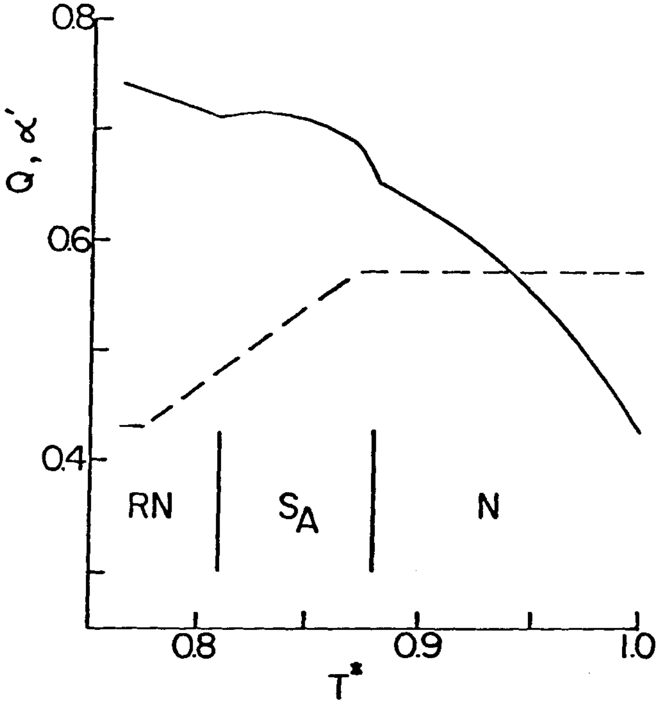

Figure The proposed temperature dependence of the parameter α' (dashed line) and the resulting variation in orientational order parameter Q by Luckhurst and Timimi[11]. T* is T/T_{NI}, the reduced temperature.

REFERENCES

1. P.E. Cladis, *Phys. Rev. Lett.* 35, 48 (1975); P.E. Cladis, R.K. Bogardus, W.D. Daniels and G.N. Taylor, *Phys. Rev. Lett.* *39*, 720 (1977)
2. P.E. Cladis, *Mol. Cryst. Liq. Cryst.* *67*, 177 (1981)
3. N.R. Chen, S.K. Hark and J.T. Ho, *Phys. Rev. A* *24*, 2843 (1981)
4. D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, *Mol. Cryst. Liq. Cryst. Lett.* *56*, 289 (1980); 295 (1980)
5. R.Y. Dong, *J. Chem. Phys.* *76*, 5659 (1982)
6. C.W. Garland, G.B. Kasting and K.J. Lushington, *Phys. Rev. Lett.* *43*, 1420 (1979)
7. N.A.P. Vaz, Z. Yaniv and J.W. Doane, *Chem. Phys. Lett.* *98*, 354 (1983)
8. G.R. Luckhurst, K.J. Smith and B.A. Timimi, *Mol. Cryst. Liq. Cryst. Lett.* *56*, 315 (1980)
9. A.R. Kortan, H.V. Känel, R.J. Birgeneau and J.D. Litster, *Phys. Rev. Lett.* *47*, 1206 (1981)
10. J.W. Doane, in *Magnetic Resonance of Phase Transitions*, edited by F.J. Owens, C.P. Poole, Jr. and H.A. Farach, (Academic, N.Y., 1979) pp. 171-246
11. G.R. Luckhurst and B.A. Timimi, *Mol. Cryst. Liq. Cryst. Lett.* *64*, 253 (1981)
12. P.S. Pershan and P. Prost, *J. Physique Lettres* *40*, L-27 (1979) N.A. Clark, *J. Physique Colloq.* *40*, C3-345 (1979)
13. P.G. de Gennes, *Mol. Cryst. Liq. Cryst.* *21*, 49 (1973)
14. N.A.P. Vaz and J.W. Doane, to be published