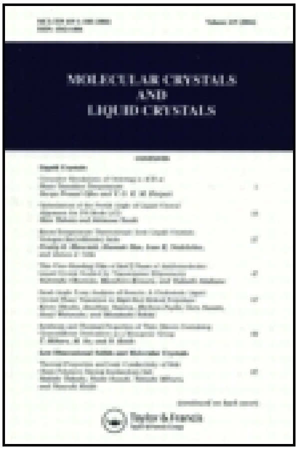

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A MOLECULAR THEORY OF RE-ENTRANT POLYMORPHISM IN PURE LIQUID CRYSTALS

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Abstract: Here we develop a molecular theory for the re-entrant nematic and smectic A mesophases by extending McMillan's treatment of the smectic A phase.

One of the more fascinating discoveries in the realm of liquid crystals was made by Cladis when she found that it is possible to obtain a nematic phase on either heating or cooling a smectic A phase.[1] This observation is of particular interest for it shows that the order of the system apparently decreases on lowering the temperature, in marked contrast with the behaviour of most mesogens. The discovery of the low temperature or re-entrant nematic phase was made for a binary mixture of mesogens. However it was soon shown that a pure liquid crystal could possess a re-entrant nematic, albeit at high pressures.[2] This limitation was also removed[3] and many re-entrant nematics are known to exist at atmospheric pressure. In addition the mesogen 4-n-octyloxybenzoyloxy-4'-cyanostilbene was found to possess re-entrant nematic and smectic A phases;[3,4] the transition temperatures are

$$\mathrm{C} \xleftrightarrow{95^{\circ}\mathrm{C}} \mathrm{S_A} \xleftrightarrow{96^{\circ}\mathrm{C}} \mathrm{N} \xleftrightarrow{138.9^{\circ}\mathrm{C}} \mathrm{S_A} \xleftrightarrow{247^{\circ}\mathrm{C}} \mathrm{N} \xleftrightarrow{283^{\circ}\mathrm{C}} \mathrm{I}.$$

A Landau theory[5] and thermodynamic model[6] of the re-entrant nematic-smectic A transition have been published and the phenomenological theories appear to be in excellent accord with experiment. However, a molecular theory of re-entrant polymorphism does not seem to have been developed and we present such a theory here.

It occurred to us that, in view of its considerable success in describing the smectic A phase, it should be possible to extend the McMillan theory[7] to provide an account of re-entrant polymorphism and this has proved to be the case. To understand this extension we first sketch the essential elements of the McMillan theory which is founded on the molecular field approximation. The single particle potential is given by

$$U(\zeta,\cos\beta) = -u_0\{\overline{P}_2P_2(\cos\beta) + \alpha\sigma\cos\zeta P_2(\cos\beta) + \delta\alpha\tau\cos\zeta\}, \quad (1)$$

where β is the angle between the assumed or effective molecular symmetry axis and the director. ζ is $2\pi z/d$ where z is the position of the molecular centre of mass with respect to its mean position and d is the layer spacing. The parameter u_0 reflects the strength of the intermolecular potential while δ gives the relative weight of the scalar to the anisotropic component. Three order parameters enter naturally into the theory; they are

$$\overline{P}_2 = \overline{P_2(\cos\beta)}, \quad (2)$$

$$\sigma = \overline{\cos\zeta P_2(\cos\beta)} \quad (3)$$

and

$$\tau = \overline{\cos\zeta}. \quad (4)$$

The various transitions are located by evaluating the

Helmholtz free energies for the isotropic ($\bar{P}_2 = \sigma = \tau = 0$), nematic ($\bar{P}_2 \neq 0$, $\sigma = \tau = 0$) and smectic A ($\bar{P}_2 \neq 0$, $\sigma \neq 0$, $\tau \neq 0$) phases from

$$A/RT = (u_0/2kT)(\bar{P}_2^{\,2} + \alpha\sigma^2 + \delta\alpha\tau^2) - \ln Z. \tag{5}$$

The partition function Z is given by

$$Z = \int_{-1}^{1} d\cos\beta \, \exp\{(u_0/kT)\bar{P}_2 P_2(\cos\beta)\} \, I_0(\lambda), \tag{6}$$

where $I_n(\lambda)$ is an nth order modified Bessel function with argument[8]

$$\lambda = (u_0/kT)\{\delta\alpha\tau + \alpha\sigma P_2(\cos\beta)\}. \tag{7}$$

The order parameters needed to determine the free energy and to ensure that it is a minimum are evaluated from[8]

$$\bar{P}_2 = \int_{-1}^{1} d\cos\beta \, P_2(\cos\beta) \exp\{(u_0/kT)\bar{P}_2 P_2(\cos\beta)\} \, I_0(\lambda)/Z, \tag{8}$$

$$\sigma = \int_{-1}^{1} d\cos\beta \, P_2(\cos\beta) \exp\{(u_0/kT)\bar{P}_2 P_2(\cos\beta)\} \, I_1(\lambda)/Z, \tag{9}$$

and

$$\tau = \int_{-1}^{1} d\cos\beta \, \exp\{(u_0/kT)\bar{P}_2 P_2(\cos\beta)\} \, I_1(\lambda)/Z. \tag{10}$$

The predicted behaviour of the mesogen is controlled by the two quantities α and δ, with α being the primary variable; indeed the original version of the McMillan theory set δ equal to zero.[7] When δ is held constant it is found[7] that increasing α causes the smectic A-nematic transition temperature T_{S_AN} to increase while the nematic-isotropic transition T_{NI} is fixed at $u_0/4.542k$. For real mesogens it is observed that the reduced smectic A-nematic transition temperature $T^*_{S_AN}(=T_{S_AN}/T_{NI})$ increases along an homologous series as the number of methylene units in the alkyl chain attached to the rigid core is increased. Empirically therefore α is seen to be related to the fraction of the chain in the mesogenic molecule.

The particles in the McMillan theory are assumed to be rigid; consequently the parameters in the pair potential and hence α are taken to be temperature independent. However, this may not be the case for those mesogens which exhibit re-entrant polymorphism. For example one of the major requirements for re-entrant behaviour is the possession of a strongly polar head group such as cyano. This polar group is known to result in the formation of loose dimers whose structure may well change with temperature.[9] As a consequence the particles in McMillan's theory should be identified as the dimers and so we expect α to be weakly temperature dependent for such mesogens. Now if α decreased with temperature then the smectic A-nematic transition temperature will be reduced. An appropriate choice for the temperature dependence of α could result in a situation where lowering the temperature would still produce the usual smectic A-nematic transition. However further decrease in temperature could reduce α to such an extent that the smectic A phase becomes unstable and reverts to a nematic phase; in other words a re-entrant nematic is formed. In addition further decrease in temperature could lead to the formation of a re-entrant smectic A phase from the re-entrant nematic as observed for 4-n-octyloxybenzoyloxy-4'-cyanostilbene.[3,4]

To test our molecular theory of re-entrant polymorphism we have calculated the three order parameters $\overline{P}_2$, α and τ from equations (8 - 10) using various assumed temperature dependences for α. We find that we are able to obtain re-entrant nematic and smectic A phases by employing an essentially linear variation of α with temperature; a typical dependence is shown in the figure. Using this variation of α and setting δ equal

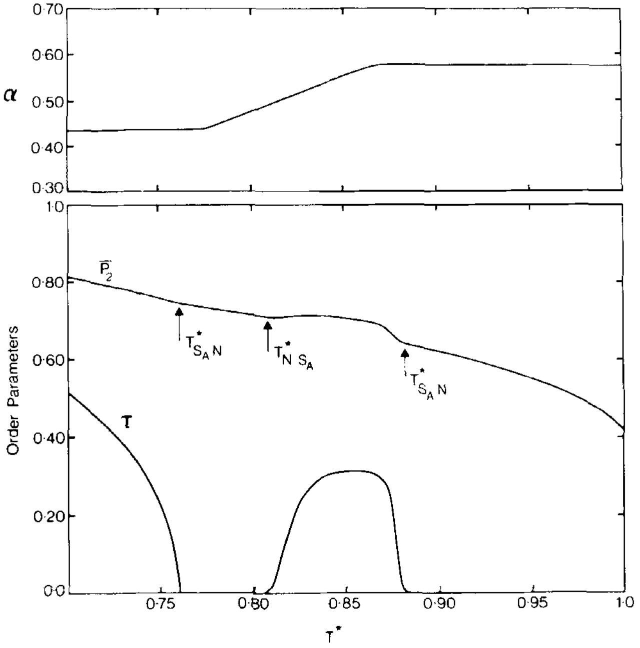

FIGURE The proposed temperature dependence of the parameter α and the resulting variation in the orientational ($\overline{P}_2$) and spatial (τ) order parameters. The system clearly exhibits re-entrant nematic and and smectic A phases.

to 0.16 we obtain the dependence of the orientational ($\overline{P}_2$) and spatial (τ) order parameters on reduced temperature also sketched in the figure. The changes in the nature of the phases are indicated by the spatial order parameter τ which vanishes for the nematic and re-entrant nematic phases but is non-zero for the smectic A and re-entrant smectic A phases. The results in the figure also show that whereas the spatial order varies dramatically with temperature the orientational order parameter $\overline{P}_2$ increases with decreasing T^* in a manner almost independent of the smectic A-nematic transitions. This behaviour is in good accord with experimental studies of orientational order in such systems using the anisotropy in the diamagnetic susceptibility[4] and electron resonance spectroscopy.[10] Both smectic A-nematic transitions are predicted to be second order by our model and this prediction is also in agreement with the very small entropies of transition observed for 4-n-octyloxybenzoyloxy-4'-cyanostilbene.[4]

Finally we note that the total change in α needed to obtain both re-entrant phases is about 0.14 over a reduced temperature range of approximately 0.1. We can gauge what change in molecular structure would produce such a variation in the following way. The value of $T^*_{S_AN}$ increases along a homologous series and for a given $T^*_{S_AN}$ we may evaluate the corresponding value of α from the McMillan theory. We find that α varies almost linearly with the length of the alkyl chain and that a change of 0.1 in α is equivalent to approximately one methylene group. An equivalent change in the structure of the loose dimer over the temperature range studied does not seem unreasonable. It would appear therefore that our simple extension of the McMillan theory does provide a molecular interpretation of re-entrant polymorphism.

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REFERENCES

1. P.E. Cladis, Phys. Rev. Letters 35, 48 (1978).

2. P.E. Cladis, R.K. Bogardus and W.B. Daniels, Phys. Rev. Letters 39, 720 (1977).
3. F. Hardouin, G. Sigaud, M.F. Achard and H. Gasparoux, Phys. Letters 71A, 347 (1979).
4. F. Hardouin, G. Sigaud, M.F. Achard and H. Gasparoux, Solid State Commun. 30, 265 (1979).
5. P.S. Pershan and P. Prost, J. Physique Lettres 40, L-27 (1979).
6. N.A. Clark, J. Physique Colloq. 40, C3-345 (1979).
7. W.L. McMillan, Phys. Rev. A 4, 1238 (1971); ibid 6, 936 (1972).
8. R.L. Humphries and G.R. Luckhurst, Molec. Phys. 35, 1201 (1978).
9. A.J. Leadbetter, J.L.A. Durrant and M. Rugman, Molec. Cryst. Liq. Cryst. Letters, 34, 231 (1977).
10. G.R. Luckhurst, K.J. Smith and B.A. Timimi, Molec. Cryst. Liq. Cryst. Letters 56, 315 (1980).