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SMECTIC C MODEL WITH SEPARATE ORDER PARAMETERS FOR THE LAYER THICKNESS AND THE OPTICAL TILT ANGLE: VARIATION OF THE LAYER THICKNESS IN THE SMECTIC C PHASE

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ABSTRACT. Recently a model for the smectic A to smectic C transition has been proposed with separate order parameters for the optical tilt angle α and the quantity d/l, where d is the layer thickness and l the molecular length. Within the simplest Landau Theory for this type of model, and with the assumption that the system is near the smectic A - smectic C tricritical point, we find the simple result

$$\alpha \simeq 2^{1/2}(1+\sigma^2/4)\cos^{-1}d/d_A,$$

where $\sigma=\alpha/\varepsilon$, $\varepsilon=\cos^{-1}d/l$ and d_A is the layer thickness in the A phase ($0\leq\sigma<1$). This relation between α and $\cos^{-1}d/d_A$ is approximately linear.

Based on results of X-ray studies[1] which suggest that the long molecular axes are tilted with respect to the layer normal in the smectic A phase of (especially) compounds having a smectic A to smectic C transition, it has been proposed that the essential feature of this phase transition is the onset of long range order in the tilt directions of the individual molecules.[2,3] Some properties of this type of smectic A - smectic C transition have been studied in the Landau approximation by means of the following simple form for the thermodynamic potential G at given pressure and temperature:[3]

$$G/NkT = (w/2)(\varepsilon^2-\varepsilon_A^2)^2-c\varepsilon^2\sigma^2+A\sigma^2+B\sigma^4+D\sigma^6, \qquad (1)$$

where the angle ε is defined in terms of the layer thickness d and molecular length l by $d=l\cos\varepsilon$, and the order parameter $\sigma=\alpha/\varepsilon$, α = optical tilt angle, measures the degree of orientational order of the molecular tilt directions (N=number of molecules, k=Boltzmann constant, T=absolute temperature).

In the smectic A phase $\sigma=0$ and G is minimized by $\varepsilon=\varepsilon_A$, i.e., $d=d_A=l\cos\varepsilon_A$ ($\varepsilon_A>0$). The last three terms on the right hand side of Eq.(1) account for the loss of orientational entropy when $\sigma>0$; the molecular model[2] presented previously gives A=1, B=1/4, D=5/36.[3] The parameters w and c are functions of the temperature and pressure (p). The molecular model[2] suggests that the coupling term $-c\varepsilon^2\sigma^2$ (which favours alignment of the tilt directions when $\varepsilon\neq 0$) arises mainly from the translational entropy of the molecules and their intralayer Van der Waals attractions.[4] It is assumed in Eq.(1) that ε and ε_A are fairly amall angles ($\varepsilon,\varepsilon_A \lesssim \pi/9$ radians).

In this note we develop the implications of Eq.(1) for the relation between α and $\cos^{-1}d/d_A$. First, a condition for the tricritical point of the model is determined.

Minimization of Eq.(1) with respect to ε leads to:

$$\varepsilon^2 = \varepsilon_A^2+\varepsilon_1^2\sigma^2 \ , \ \varepsilon_1^2 = c/w. \tag{2}$$

On substituting (2) into (1), one obtains the thermodynamic potential as a function of σ:

$$G/NkT = \text{const} + (A-c\varepsilon_A^2)\sigma^2 + (B-c\varepsilon_1^2/2)\sigma^4 + D\sigma^6. \tag{3}$$

The tricritical point for this model (the point on the transition curve in the p,T plane dividing the second order and first order transitions) occurs where the coefficients of σ^2 and σ^4 in Eq.(3) vanish simultaneously.[5,3] Using A=1 and B=1/4, this condition gives, at the tricritical point,

$$\varepsilon_1^2/\varepsilon_A^2 = 1/2. \tag{4}$$

The fractional change Δ in the layer thickness is given by

$$\Delta = (d-d_A)/d_A \approx -(\varepsilon^2 - \varepsilon_A^2)/2, \tag{5}$$

for not too large ε and ε_A. (The error in Eq. (5) is less than 4% for $\varepsilon, \varepsilon_A < 25\pi/180$ radians.) Combining Eqs.(5) and (2), and using the approximation $\cos^{-1}x \approx \left[2(1-x)\right]^{1/2}$ (accurate to better than 1% for $0 \le \cos^{-1}x \le 25\pi/180$ radians) one finds

$$\cos^{-1}d/d_A = \cos^{-1}(1-|\Delta|) \approx 2^{1/2}|\Delta|^{1/2} = \varepsilon_1\sigma. \qquad (6)$$

Since $\sigma = \alpha/\varepsilon$, Eqs.(6) and (2) give the result

$$\alpha = (\varepsilon/\varepsilon_1)\cos^{-1}d/d_A = (\varepsilon_A/\varepsilon_1)(1+\varepsilon_1{}^2\sigma^2/2\varepsilon_A{}^2)\cos^{-1}d/d_A + O(\sigma^4). \qquad (7)$$

The quantity $\varepsilon_1/\varepsilon_A$ varies much slower than σ and α near the transition[3] and may be taken as constant in Eq.(7). In particular, for systems near the tricritical point Eq.(4) can be used as an estimate for $\varepsilon_1/\varepsilon_A$; then Eq.(7) becomes

$$\alpha \approx 2^{1/2}(1 + \sigma^2/4)\cos^{-1}d/d_A. \qquad (8)$$

(Weakly first order, as well as second order, A to C transitions have been observed,[6] and this, together with the failure[7] of the smectic A - smectic C superfluid analogy,[8] suggests that in many cases the transition may be taking place near the tricritical point.)

Eq.(8) exhibits two interesting features. First, the relation between α and $\cos^{-1}d/d_A$ is approximately linear - especially near the A to C transition where $\sigma \ll 1$ - and, secondly, $\alpha/\cos^{-1}d/d_A \approx 2^{1/2} > 1$.[9] Of course, the relation between α and $\varepsilon = \cos^{-1}d/l$ is <u>not</u> linear in the present model (see Eq.(2)) because an increase in the orientational order of the molecular tilt directions means an increase in $\sigma = \alpha/\varepsilon$.

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