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Phenomenological Model for Smectic C Phases With Separate Tilt Angles for the Layer Thickness and the Optical Axis

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A simple, phenomenological model is given which may describe the smectic A-smectic C transition in the case where the molecules make an appreciable angle with the layer normal in both the A and C phases. X-ray experiments by several workers on a number of compounds indicate that this case may be quite common. The model is based on an earlier suggestion that the essential feature in these A to C transitions is the onset of long range order in the molecular tilt directions. The free energy is expressed as a function of the layer tilt angle ε (which determines the layer thickness) and the ratio $r = \alpha/\varepsilon$, where α is the optical tilt angle. The quantity r $(0 \leq r \leq 1)$ is a measure of the order of the molecular tilt directions. When ε is eliminated (which corresponds to considering the system at fixed pressure instead of fixed layer thickness), it is found that the transition can be either first or second order, depending on the model parameters. For the first order transition the approximate temperature variation $r \sim (\gamma\Delta T/D')^{1/4}$, for r^2 in the range $(\Delta r)^2 \ll r^2 \lesssim \frac{1}{4}$, is obtained—where Δr is the discontinuity in r, $D' \approx \frac{5}{12}$, γ is a parameter, $\Delta T = T_0 - T$, and T_0 is the transition temperature. The $\frac{1}{4}$ power in this result leads to a very rapid increase of r and α near the transition. Data of Johnson and Saupe suggests $\gamma \sim \frac{1}{10}{}^\circ\mathrm{K}^{-1}$. For the second order transition we obtain $r \sim (\gamma\Delta T/2\psi)^{1/2}$ for $r^2 \ll \psi$, and $r \sim (\gamma\Delta T/D')^{1/4}$ for $r^2 \gg \psi$, where ψ is a parameter. The model predicts a strong discontinuity in the dilation modulus, with the ratio:

$$\frac{\text{modulus in C phase}}{\text{modulus in A phase}} \sim \begin{cases} (\Delta r)^2, & \text{first order transition} \\ \psi, & \text{second order transition} \end{cases}$$

Such a discontinuity has been deduced by Johnson and Saupe for two compounds from experimental data on undulations. The latent heat per mole L for the first order transition is given by $L = \gamma T_0(\Delta r)^2 R T_0$ (R = gas constant). Assuming $\varepsilon \sim 15^\circ$, $T_0 \sim 350^\circ\mathrm{K}$ and $\gamma \sim \frac{1}{10}{}^\circ\mathrm{K}^{-1}$, the discontinuity $\Delta\alpha$ in the optical tilt angle can be estimated from this relation as $\Delta\alpha \sim 0.5 \times (L/20)^{1/2}$, where $\Delta\alpha$ is in degrees and L in cal/mol.

1. INTRODUCTION

Some years back Diele, Brand and Sackman[1] observed a rather surprising phenomenon in an X-ray study of smectic liquid crystals. They found strong evidence that in many cases the layer thickness in the smectic A phase is considerably less than the molecule length, so that the molecules could not be normal to the layers as generally assumed. In particular, this effect is quite clearly marked in all of the compounds they investigated (six of them) which have a smectic A–smectic C phase transition. Further, the layer thickness changed little with temperature in both the A and C phases.

More recently, de Jeu and De Poorter[2] and, independently, De Vries[3] have confirmed these results. De Jeu and De Poorter investigated the smectic phase of heptyloxybenzylidene-pentylaniline ($\bar{7}$BA5), a new compound not among those studied in Ref. 1. This is a particularly interesting case as the layer thickness is approximately constant, at 27.7 Å, in the A and C phases, and jumps discontinuously to 28.9 Å at the C to B transition.[2] This shows rather convincingly that the layer thickness in the A and C phases cannot be the result of a shortening of the molecules due to flexibility of the terminal hydrocarbon chains.

De Vries suggested that in these compounds the smectic A phase consists of tilted layers stacked in random fashion with respect to the direction of tilt, and that the A to C transition results from a coupling of the direction of tilt of adjacent layers.[4] Recently, it has been pointed out that this interpretation cannot explain a sharp thermodynamic A to C transition, and an alternative interpretation of the X-ray data was given.[5] In this interpretation the individual molecules are tilted with respect to the layer normal in both the A and C phases, but their directions of tilt within the layers are disordered in the A phase and ordered in the C phase. This interpretation is substantiated by a simple molecular model which exhibits a second order transition between phases with and without long range order in the molecular tilt directions.[5] This model shows the usual optical behaviour associated with the smectic A smectic C transition.

In Ref. 5 the transition was considered for fixed layer thickness. In this paper we employ a simple, phenomenological free energy—motivated by the molecular model of Reference 5—to consider the transition at fixed pressure. We find that in this case the transition can be either first or second order, depending on the model parameters. (The smectic A–smectic C transition in the compounds studied in References 2 and 3 is weakly first order, as shown by latent heats of the order of 100 cal/mol.) Several interesting consequences of the model are derived in Sections 2 and 3. The results are consistent with the scarce data available for making comparisons.

The present phenomenological model is based on the assumption that the essential feature in (at least a class of) A to C transitions is the onset of long range order in the molecular tilt directions. The case of smectic C with the layer thickness directly proportional to cos α, where α is the optical tilt angle, does not seem to fit into this type of theory. This may mean that there are at least two basically different kinds of smectic A–smectic C transitions, as suggested by De Vries[3] (however, see also remarks in Section 4).

2 PHENOMENOLOGICAL MODEL FOR SMECTIC A-SMECTIC C TRANSITION

For convenience, we imagine the smectic layers stacked up in a cylinder, of fixed cross-section, which is closed off by a piston exerting a fixed pressure p on the layers. Let a denote the area per molecule in a layer. Then the volume V of the system is

$$V = Nal \cos \varepsilon, \tag{1}$$

where N is the total number of molecules, l is the (effective) length of the molecules and ε is the tilt angle for the layer thickness t ($t = l \cos \varepsilon$). At fixed cross-section a, the Helmholtz free energy $\mp$ of the system is a function of ε, the temperature T and an appropriate order parameter r for the molecular tilt directions.

At constant p the angle ε is determined by the pressure equation

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{1}{al \sin \varepsilon}\right) \frac{\partial(F/N)}{\partial \varepsilon},$$

or

$$\frac{\partial}{\partial \varepsilon} [(F/N) + pal \cos \varepsilon] \tag{2}$$

Since we are dealing with a condensed phase, the second term in Eq. (2) is very much less than kT (at room temperatures) and can be neglected to a good approximation. Thus the condition determining ε reduces approximately to

$$\frac{\partial(F/N)}{\partial \varepsilon} = 0. \tag{3}$$

For the order parameter r for the tilt directions we choose the ratio

$$r = \frac{\alpha}{\varepsilon}, \tag{4}$$

where α is the optical tilt angle. Clearly $0 \leq r \leq 1$. The simplest form for F

which gives $\varepsilon > 0$ in the A and C phases—at fixed p—and a second order transition in r at fixed ε, is

$$\frac{F}{NkT} = \frac{F_{00}}{NkT} - \left(\frac{W_2}{kT}\right)\varepsilon^2 + \left(\frac{W_4}{kT}\right)\varepsilon^4 - C\varepsilon^2 r^2 + Ar^2 + Br^4 + Dr^6, \quad (5)$$

where the coefficients W, C, A, B, D are positive (k is Boltzmann's constant). The term in r^6 in Eq. (5) becomes necessary when the transition is considered at fixed p.

The various terms in Eq. (5) are interpreted as follows. The first term is the free energy for the smectic A phase with $\varepsilon = 0$. The second and third terms give the free energy minimum for the smectic layer structure at $\varepsilon = (W_2/2W_4)^{1/2}$. These terms presumably arise from several competing effects. One expects that the interlayer van der Waals attraction favours $\varepsilon > 0$, while translational entropy and the intralayer van der Waals attraction favour $\varepsilon = 0$.[6] The term in $\varepsilon^2 r^2$ is a coupling term which causes the tilt directions of the molecules to order (at sufficiently low temperatures) if $\varepsilon > 0$. The previous molecular model[5] suggests that this term results mainly from the translational entropy of the molecules and the intralayer van der Waals attractions. The coefficient C increases with decreasing T. The last three terms in Eq. (5) represent the loss in orientational entropy associated with an increase in order of the molecular tilt directions. The coefficients A, B, D are independent of T. It is expected that Eq. (5) is adequate for ε and r not too large.

Values for the coefficients A, B, D can be obtained from the model of Ref. 5. This model gives, for the orientational entropy S_{or} of the tilt directions,

$$\frac{S_{\text{or}}}{Nk} = x^2 - \tfrac{3}{4}x^4 + \tfrac{5}{9}x^6 - \cdots, \quad (6)$$

where $x = p/2$ and p is a mean field variational parameter. As $p \to \infty$, the order of the tilt directions becomes perfect, $r \to 1$.[5] This suggests that r is a better expansion parameter than p. In the limit $\varepsilon \to 0$, we also have from Ref. 5

$$r = \frac{\alpha}{\varepsilon} = x - \tfrac{1}{2}x^3 + \tfrac{1}{3}x^5 - \cdots.$$

Inversion of this series gives

$$x = r + \tfrac{1}{2}r^3 + \tfrac{5}{12}r^5 + \cdots.$$

Substituting this in Eq. (6) we obtain

$$\frac{S_{\text{or}}}{Nk} = r^2 + \tfrac{1}{4}r^4 + \tfrac{5}{36}r^6 + \cdots.$$

Therefore we take

$$A = 1, \quad B = \tfrac{1}{4}, \quad D = \tfrac{5}{36}. \tag{7}$$

We now consider the transition at fixed pressure. Eqs. (3) and (5) give

$$-W_2\varepsilon + 2W_4\varepsilon^3 - kTC\varepsilon r^2 = 0, \tag{8}$$

i.e., $\varepsilon = 0$, or

$$\varepsilon^2 = \frac{W_2}{2W_4} + \left(\frac{CkT}{2W_4}\right)r^2 \equiv \varepsilon_0^2 + \varepsilon_1^2 r^2. \tag{9}$$

The quantities ε_0 and ε_1 are real since W_2, W_4 and C are positive. Using Eq. (8), the first three terms of Eq. (5) reduce to $-W_4\varepsilon^4/kT$, so that the lower free energy corresponds to Eq. (9) and not $\varepsilon = 0$.

In the smectic A phase $r = 0$ and $\varepsilon = \varepsilon_0$. We expect the energy $W_4\varepsilon_0^4$ to be of the same order of magnitude as the latent heat for the nematic–smectic A transition. For compound $7BA5$ this is about 700 cal/mol $\approx RT|_{T=350}$ (R = gas constant).[2] Thus we have the estimate

$$W_4\varepsilon_0^4 = \frac{W_2\varepsilon_0^2}{2} \sim kT_0, \tag{10}$$

where T_0 is the smectic A–smectic C transition temperature.

Eliminating ε from Eq. (5) by means of Eq. (9) we obtain

$$\frac{F}{NkT} = \frac{F_0}{NkT} + (A - C\varepsilon_0^2)r^2 + \left(B - \frac{C\varepsilon_1^2}{2}\right)r^4 + Dr^6. \tag{11}$$

With the values $A = 1$, $B = \frac{1}{4}$ from Eqs. (7), it is clear that the transition $r = 0$ to $r > 0$ is first order if $\varepsilon_1^2 > \varepsilon_0^2/2$ and second order if $\varepsilon_1^2 \leq \varepsilon_0^2/2$. We assume that near the transition point Eq. (11) can be written

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \gamma(T - T_2)r^2 + [\gamma'(T - T_2) \pm \psi]r^4 + Dr^6, \tag{12}$$

where γ, γ', ψ, T_2 are positive constants independent of T. The upper and lower signs correspond to the second and first order transitions respectively.

The quantities C, ε_1 and ε_0 vary with T. (ε_0 is, however, quite insensitive to T in the cases studied in Refs. 1–3.) In particular, these quantities may be expected to depend on the squares of order parameters σ—characterizing the smectic layer structure—and η—characterizing the orientational distribution function for the long axis of the molecules. Now suppose, for example, that $C\varepsilon_0^2 \sim w\sigma^2$, where w depends only weakly on temperature and

$w\sigma^2 \approx A = 1$ near $T = T_2$. Then

$$\frac{\partial}{\partial T}(A - C\varepsilon_0^2) \sim -2w\sigma\frac{\partial \sigma}{\partial T} \approx \frac{2}{\sigma}\left|\frac{\partial \sigma}{\partial T}\right|$$

$$\sim 4\left|\frac{\partial \sigma}{\partial T}\right| \sim \frac{4}{100},$$

where we have taken $|\partial\sigma/\partial T| \sim \frac{1}{100}$.[7] A similar estimate may be made for the temperature variation of $C\varepsilon_0^2$ with η. Therefore, values of γ and γ' of order $10^{-1}\,°\mathrm{K}^{-1}$ may be expected ($\gamma \sim \frac{1}{10}\,°\mathrm{K}^{-1}$ is required to fit data given in Ref. 8—see below).

The smectic A–smectic C transitions studied in Refs. 2 and 3 are (weakly) first order. Hence we concentrate on this case (ε_1^2 slightly greater than $\varepsilon_0^2/2$).

The transition temperature T_0 is attained when

$$f(y) = \gamma(T - T_2)y + [\gamma'(T - T_2) - \psi]y^2 + Dy^3$$

has two coincident zeros $y = y_0 > 0$. The condition for $T = T_0$ is therefore

$$[\gamma'(T - T_2) - \psi]^2 - 4D\gamma(T - T_2) = 0, \tag{13}$$

and the corresponding value of y is

$$y_0 = \frac{\psi - \gamma'(T_0 - T_2)}{2D}. \tag{14}$$

Now, $y_0 = (\Delta r)^2$, where Δr is the discontinuity in r at the transition, related to the discontinuity $\Delta\alpha$ in α by $\Delta\alpha \approx \varepsilon_0 \Delta r$. Johnson and Saupe[8] estimate $\Delta\alpha < 1°$ for pentyloxybenzylidene-heptylaniline (5BA7). Therefore we take $\Delta r \lesssim \frac{1}{17}$, so that y_0, ψ, $\gamma'(T_0 - T_2)$ are all quite small ($\lesssim 10^{-2}$). (Since 5BA7 is clearly similar to the compound 7BA5 of Ref. 2, we assume in this paper that both compounds have similar smectic A and C phases.) The smaller root of Eq. (13) is given approximately by

$$T_0 - T_2 \approx \frac{\psi^2}{4D\gamma}. \tag{15}$$

Since $\psi/2D \sim y_0 \sim 10^{-2}$ and $\gamma \sim 10^{-1}\,°\mathrm{K}^{-1}$, it follows from Eq. (15) that $T_0 - T_2 \lesssim 10^{-2}\,°\mathrm{K}$ is quite small. The expansion (12) therefore remains valid near $T = T_0$.

Below T_0, $f(y)$ has two distinct positive roots and between these a minimum at which $f(y) < 0$. Therefore, the smaller root of Eq. (13), given by Eq. (15), is indeed the first order transition temperature T_0. The value of y at the minimum is determined by the condition $\partial f/\partial y = 0$; this reduces, for $y \neq 0$, to a quadratic equation in y. The smaller root of the quadratic equation corresponds to a maximum of $f(y)$, the larger root to the required minimum. Expanding the latter about $T = T_0$, for $T < T_0$, we obtain

$$y = r^2 \approx \frac{2y_0}{3} + \frac{\gamma'\Delta T}{3D} + \frac{1}{3}\left[y_0^2 + \frac{3\gamma}{D}\Delta T\right]^{1/2}, \tag{16}$$

where $\Delta T = T_0 - T$. (A term $4y_0\gamma'\Delta T$ has been neglected inside the square brackets.) Eq. (16) is the general formula for r in the first order case. For $3\gamma\Delta T/D \gg y_0^2$, or $r^2 \gg (\Delta r)^2$, Eq. (16) becomes

$$r^2 \approx \gamma'\Delta T/D' + (\gamma\Delta T/D')^{1/2}, \tag{17}$$

where $D' = 3D$ and terms of order $(\Delta r)^2$ are neglected. With $\gamma \sim \frac{1}{10}\,^\circ\mathrm{K}^{-1}$ $y_0 \sim 10^{-2}$, the form (17) becomes valid for $\Delta T \gtrsim 10^{-2}\,^\circ\mathrm{C}$. For $r^2 \lesssim \frac{1}{4}$ the second term in Eq. (17) dominates; hence we have

$$r \approx \left(\frac{\gamma\Delta T}{D'}\right)^{1/4} + \left(\frac{\gamma'}{2\gamma}\right)\left(\frac{\gamma\Delta T}{D'}\right)^{3/4}, \tag{18}$$

in the range $(\Delta r)^2 \ll r^2 \lesssim \frac{1}{4}$. The dominating term with the $\frac{1}{4}$ power leads to a very rapid increase of r and α near T_0. Taking into account the variation of ε with r, Eq. (9), we have

$$\alpha = r\varepsilon \approx r\varepsilon_0\left\{1 + \frac{1}{2}\left(\frac{\varepsilon_1}{\varepsilon_0}\right)^2 r^2\right\}. \tag{19}$$

With $(\varepsilon_1/\varepsilon_0)^2 \approx \frac{1}{2}$, $D' = \frac{5}{12}$ and the estimates $\gamma'/\gamma \sim 1$, $\varepsilon_0 \sim 17^\circ$, we find from Eqs. (18) and (19) that to fit the value $\alpha = 12^\circ$ at $\Delta T = 0.4^\circ\mathrm{C}$, given in Ref. 8, $\gamma \sim \frac{1}{10}$ is required.

In the second order case (upper sign in Eq. (12)), $T_0 = T_2$ and

$$D'r^2 = (\gamma'\Delta T - \psi) + [(\gamma'\Delta T - \psi)^2 + D'\gamma\Delta T]^{1/2} \tag{20}$$

for $T < T_0$. For $\psi^2 \gg \gamma\Delta T$ (or $r^2 \ll \psi$) Eq. (20) gives

$$r \approx (\gamma\Delta T/2\psi)^{1/2},$$

while for $\gamma\Delta T \gg \psi^2$ (or $r^2 \gg \psi$) it gives

$$r \approx (\gamma\Delta T/D')^{1/4}.$$

3 SOME FURTHER PROPERTIES OF THE MODEL

In the following no distinction is made between layer thickness and layer separation. We assume that these two quantities are, to a sufficient approximation, directly proportional.

The layer tilt angle ε is defined in terms of the layer thickness t by

$$t = l\cos\varepsilon, \tag{21}$$

where l is the (effective) length of the molecules. Hence the fractional change $\delta t/t$ can be written

$$\frac{\delta t}{t} = -\tan \varepsilon\, \delta\varepsilon \approx -(\varepsilon_0 \tan \varepsilon_0)\frac{\delta\varepsilon}{\varepsilon_0}. \tag{22}$$

Using Eqs. (18), (19) and (22) with $\varepsilon_0 \sim 17°$, $(\varepsilon_1/\varepsilon_0)^2 \approx \frac{1}{2}$ and $\gamma \sim \frac{1}{10}$, we obtain

$$|\delta t/t| \sim \begin{cases} 3 \times 10^{-3}, & \Delta T = 0.1°C \\ 10^{-2}, & \Delta T = 1°C \\ 1.4 \times 10^{-2}, & \Delta T = 2°C \end{cases}$$

with t equal to the layer thickness just above T_0. (At $\Delta T = 1°\mathrm{C}$ already $r \sim 0.7$, so that results for $\Delta T \gtrsim 1°\mathrm{C}$ should be taken with some caution—see also Section 4.) There are two points worth noting here. The first is that $|\delta t/t|$ remains small within several degrees of T_0, in agreement with Refs. 1–3. The second is that $|\delta t/t|$ at $\Delta T = 1°\mathrm{C}$ is greater than the linear expansion coefficient of metals ($\sim 20 \times 10^{-6}\,°\mathrm{C}^{-1}$) by a factor of about 500. Therefore the explanation given in Ref. 8 for the formation of undulations in the smectic C phase by stepwise cooling should still be applicable.

We now consider the discontinuity at the transition of the dilation modulus K. The modulus K is defined by the expression[8]

$$F = \tfrac{1}{2}K\left(\frac{t - \bar{t}}{\bar{t}}\right)^2 = \tfrac{1}{2}K \tan^2 \bar{\varepsilon}(\varepsilon - \bar{\varepsilon})^2,$$

where $\bar{t}$ and $\bar{\varepsilon}$ are the equilibrium values of t and ε at given temperature and pressure. (The symbol B is used in Ref. 8 for the above quantity K.) We can write

$$K = \left(\frac{1}{\tan^2 \bar{\varepsilon}}\right)\left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_{\varepsilon = \bar{\varepsilon}}, \tag{23}$$

where it is understood that F is expressed as a function of ε, the order parameter r being eliminated by means of the condition $\partial F/\partial r = 0$.

The calculation is presented for the first order case. The second order case is somewhat simpler and we merely give the result at the end. The notation $\tilde{F} = F/NkT$, $\tilde{W}_i = W_i/kT$ and $\tilde{K} = K/kT$ will be used.

First we note some simple results. It is immediate from the definition of ε_0^2 and ε_1^2, Eq. (9), that

$$\frac{\varepsilon_1^2}{\varepsilon_0^2} = \frac{C}{\tilde{W}_2}. \tag{24}$$

Putting

$$\varepsilon_1^2 = (1 + \delta)\frac{\varepsilon_0^2}{2}, \tag{25}$$

it follows, from the equivalence of Eqs. (11) and (12), that

$$\delta \approx 4\psi \approx 8D(\Delta r)^2, \tag{26}$$

at $T = T_0$. (Noting, from Eq. (15), that $\gamma(T_0 - T_2) \sim \psi^2 \ll \psi$.) Also, we have, at $T = T_0$,

$$A - C\varepsilon_0^2 \approx \psi^2/4D > 0, \tag{27}$$

and, with $\bar\varepsilon^2 = \varepsilon_0^2 + \varepsilon_1^2(\Delta r)^2$,

$$A - C\bar\varepsilon^2 \approx \psi^2/4D - C\varepsilon_0^2(\Delta r)^2/2 \approx -(\Delta r)^2/2 < 0. \tag{28}$$

We carry out the calculation of K just below T_0 to order $(\Delta r)^2$ only.

The equilibrium value of r for given ε is given by $r = 0$, if $A - C\varepsilon^2 \geq 0$, and by

$$\begin{aligned} r^2 &= \frac{-B}{D'} + \left(\frac{B}{D'}\right)\left[1 + \left(\frac{D'}{B^2}\right)(C\varepsilon^2 - A)\right]^{1/2} \\ &\approx \frac{(C\varepsilon^2 - A)}{2B} - \left(\frac{D'}{8B^3}\right)(C\varepsilon^2 - A)^2, \end{aligned} \tag{29}$$

if $A - C\varepsilon^2 < 0$. Further,

$$\tilde F(\varepsilon) = \tilde F_0 + \tilde W_4\varepsilon^4 - \tilde W_2\varepsilon^2 + \begin{cases} 0 & \text{if } A - C\varepsilon^2 \geq 0 \\ -Br^4 - 2Dr^6, & \text{if } A - C\varepsilon^2 < 0, \end{cases} \tag{30}$$

where r is given by Eq. (29). We have,

$$-Br^4 - 2Dr^6 \approx -\frac{(C\varepsilon^2 - A)^2}{4B} + \left(\frac{D}{8B^3}\right)(C\varepsilon^2 - A)^3. \tag{31}$$

By Eqs. (30) and (27) it follows that for $T > T_0$ and ε close to the equilibrium value $\varepsilon = \varepsilon_0$, the free energy $\tilde F(\varepsilon)$ is given by

$$\tilde F(\varepsilon) = \tilde F_0 + \tilde W_4\varepsilon^4 - \tilde W_2\varepsilon^2.$$

Therefore, K_A, the modulus K in the smectic A phase just above T_0, is given by

$$\tilde K_A = \left.\frac{\partial^2\tilde F}{\partial\varepsilon^2}\right|_{\varepsilon = \varepsilon_0} = 4\tilde W_2, \tag{32}$$

where the relation $W_2 = 2W_4\varepsilon_0^2$ from the definition of ε_0^2, Eq. (9), has been used. Similarly, from Eqs. (30), (28) and (31) it follows that in the smectic C phase

$$\tilde{F}(\varepsilon) \approx \tilde{F}_0 + \tilde{W}_4 \varepsilon^4 - \tilde{W}_2 \varepsilon^2 - \frac{(C\varepsilon^2 - A)^2}{4B} + \left(\frac{D}{8B^3}\right)(C\varepsilon^2 - A)^3.$$

Therefore, the modulus $\tilde{K}_C$ just below T_0 is (with $\bar{\varepsilon}^2 = \varepsilon_0^2 + \varepsilon_1^2(\Delta r)^2$)

$$\begin{aligned} \tilde{K}_C = \left.\frac{\partial^2 \tilde{F}}{\partial \varepsilon^2}\right|_{\varepsilon = \bar{\varepsilon}} &\approx 4\tilde{W}_2 + 12\tilde{W}_4 \varepsilon_1^2(\Delta r)^2 \\ &\quad - \frac{(C\bar{\varepsilon}^2 - A)C}{B} - \frac{2C^2\bar{\varepsilon}^2}{B} + 3D(C\bar{\varepsilon}^2 - A)C^2\bar{\varepsilon}^2 \\ &\approx -4\delta\tilde{W}_2 + 48D\tilde{W}_2(\Delta r)^2 \\ &\approx 16D\tilde{W}_2(\Delta r)^2, \end{aligned} \tag{33}$$

where Eqs. (7) and Eqs. (24)–(28) have been used. Finally, from Eqs. (32) and (33) we have

$$\frac{K_C}{K_A} \approx 4D(\Delta r)^2 = \tfrac{5}{9}(\Delta r)^2. \tag{34}$$

In the second order case, $\Delta r = 0$ and $\delta = -4\psi$, so that $K_C = 16\psi W_2$ and

$$\frac{K_C}{K_A} \approx 4\psi.$$

Assuming $\Delta r \lesssim \frac{1}{17}$ for $\overline{5}$BA7 (see Section 2) we obtain from Eq. (34)

$$\frac{K_C}{K_A} \lesssim \tfrac{1}{500},$$

which is consistent with the rough estimate given by Johnson and Saupe.[8] The above calculation of K_C/K_A is, of course, of the mean field variety. Hence it is possible that the results exaggerate the strength of the discontinuity in K.

To end this section, we consider the latent heat associated with the first order smectic A–smectic C transition. By Eq. (12) the entropy, S/N, per molecule is

$$\begin{aligned} -\frac{S}{N} = \frac{\partial(F/N)}{\partial T} = -\frac{S_0}{N} &+ \gamma kTr^2 + \gamma k(T - T_2)r^2 \\ &+ \gamma' kTr^4 + [\gamma'(T - T_2) - \psi]kr^4 + Dkr^6. \end{aligned}$$

Therefore, the entropies just above and below T_0 are given by

$$-\left(\frac{S}{N}\right)_A = -\frac{S_0}{N},$$

and

$$-\left(\frac{S}{N}\right)_C = -\frac{S_0}{N} + \gamma k T_0(\Delta r)^2,$$

to order $(\Delta r)^2$. The latent heat L is

$$L = T_0(S_A - S_C) \approx [\gamma T_0(\Delta r)^2]NkT_0. \tag{35}$$

For $\overline{7}$BA5 we have $L \sim 40$ cal/mol, $T_0 \approx 340°\mathrm{K}$ (Ref. 9) so that Eq. (35) gives

$$\Delta r \sim \tfrac{4}{100},$$

on using $\gamma \sim \frac{1}{10}°\mathrm{K}^{-1}$ from Section 2. Hence we have the estimate for the discontinuity of α for $\overline{7}$BA5 (with $\varepsilon_0 \approx 17°$)

$$\Delta\alpha \approx \varepsilon_0 \Delta r \sim 0.7°. \tag{36}$$

Johnson and Saupe give the experimental bound $\Delta\alpha < 1°$ for $\overline{5}$BA7.[8]

4 COMMENTS

Equation (5) is not the most general free energy expansion to third order in ε^2 and r^2. In particular, there are no coupling terms higher order than $\varepsilon^2 r^2$. This can make the theory inaccurate, especially at larger values of r; e.g., the model defined by Eqs. (5) and (12) shows no saturation of r for $r \leq 1$.

Any theory like the present one, which is centred on the order parameter $r = \alpha/\varepsilon$ for the molecular tilt directions, necessarily predicts that α grows more rapidly with ΔT than ε. However, it has been seen that r can grow to a value of order 1, say $\frac{1}{2}$, rather quickly, within a degree or less of the transition. Hence it is conceivable that in cases with fairly small ε_0 the parameter r quickly begins to saturate but ε continues to grow strongly as ΔT increases (e.g., ε might depend on r^4 and higher order terms in r). Then one would have α approximately proportional to ε, for $\Delta T \gtrsim 1°\mathrm{C}$. Of course, to study this possibility, a free energy expression with higher order terms than those included in Eq. (5) would have to be considered.

References

1. S. Diele, P. Brand, and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **16**, 105 (1972). I am indebted to A. De Vries for pointing out this reference to me.
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3. A. De Vries, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 27 (1977).
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6. Also, the interaction between the longitudinal dipole moments of the molecules, considered by D. Cabib and L. Benguigui (*J. Phys.*, **38**, 419 (1977)), favours $\varepsilon > 0$ even if the molecular tilts are disordered. Still another, possibly very important, effect favouring $\varepsilon > 0$ might be a steric one. Molecules which have alkyl chains at their ends and rotate freely about their long axes have an effective dumb-bell-like shape. Therefore, when confined to layers such molecules may have a minimum average diameter for some $\varepsilon > 0$.
7. E.g., see molecular model calculations in W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
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