Pramāṇa, Suppl. No. 1, pp. 225–236

Experimental determination of the twist elastic constant of nematic liquid crystals

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Abstract. The Freedericksz transition associated with a twist distortion in a nematic liquid crystal cannot be detected optically when viewed along the twist axis. Because of this difficulty, there have not been any direct determinations of the twist elastic constant k_{22} as a function of temperature except for the well-known studies of Freedericksz and Tsvetkov who used a total internal reflexion technique.

Optical theory shows that an important parameter in determining the behaviour of such a medium is the ratio of the retardation ($=\pi\ \Delta n/\lambda$, where Δn is the birefringence of the untwisted medium) to the twist per unit length. For light propagation along the twist axis, Δn is large and it can be shown that with the usual experimental geometry in which the director is anchored to the walls at either end, the twist does not reveal itself in transmitted light. On the other hand, when Δn is small the optical properties of the medium are very sensitive to distortions. To reduce the effective Δn, observations were made in a direction inclined at a large angle to the twist axis. The Freedericksz transition could then be detected easily.

Experimental values of k_{22} determined by this method are presented for a few compounds. The critical divergence of k_{22} in the vicinity of the smectic A–nematic transition point in *p*–cyanobenzylidene–*p'*–octyloxyaniline has been studied and is discussed in the light of de Gennes's theory.

Introduction

There has been considerable interest of late in the measurement of the elastic constants of nematic liquid crystals as it is recognised that short range order has a profound influence on the magnitudes of some of these constants. In simple nematics, the elastic constants can be related directly to the long range orientational order parameter by using the mean field approximation[1, 2, 3]: the ratios of the elastic constants should then be essentially temperature independent. This is in fact found to be nearly so for *p*–azoxyanisole and *p*–azoxyphenetole[4]. But if the short range order is sensitive to temperature, as is the case in a nematic which exhibits a smectic phase at lower temperatures, the ratio of the bend to the splay

constants varies considerably in the nematic range[4,5]. This effect is particularly pronounced when the smectic A–nematic transition is quasi-second order. The bend and twist constants are then expected to increase rapidly as the temperature approaches the smectic A–nematic point[6,7], whereas the splay constant is expected to show normal behaviour throughout. Direct measurements of the bend and splay constants have confirmed these conclusions[8,9].

A simple and direct method of determining the elastic constants is to measure the critical field corresponding to the Freedericksz transition[10,11]:

$$H_c = \frac{\pi}{x_0} \left(\frac{k_{11}}{\Delta\chi}\right)^{\frac{1}{2}}$$

where x_0 is the thickness of the sample, $\Delta\chi$ is the anisotropy of the volume magnetic susceptibility of the medium. By using a suitable optical arrangement for detecting the deformation, the splay and bend constants, k_{11} and k_{33}, have been determined by this technique[11,12]. However, under normal conditions of observation this method is not suitable for determining the twist constant k_{22} for reasons which will be discussed below.

The usual experimental geometry for producing twist is shown in figure 1*a*. The maximum deformation φ_m takes place in the mid-plane and at a field H slightly above H_c[4],

$$\frac{H}{H_c} = 1 + \tfrac{1}{4}\varphi_m^2 + \frac{11}{196}\varphi_m^4 + \cdots$$

If the error in determining H_c is not to exceed about 1%, the maximum value of $\varphi_m \simeq 0{\cdot}2$ raidans. Now, consider thin sections of the deformed medium parallel to the glass plates, each section being of thickness 10^{-7} cm. If $x_0 = 20 \times 10^{-4}$ cm, then, as a rough order of magnitude, the average

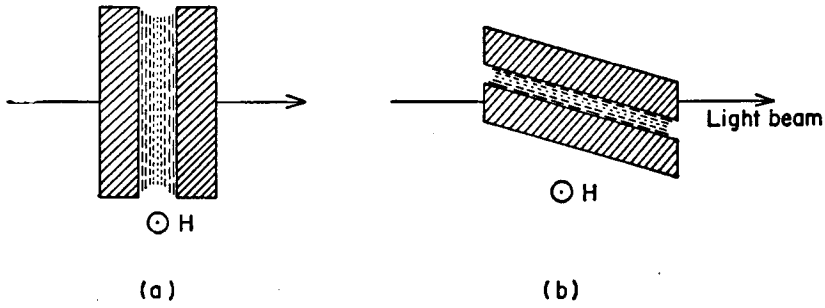

Figure 1 The geometry of the experimental set up for observing twist deformation. (*a*) the conventional geometry and (*b*) the present set up. The magnetic field H is perpendicular to the plane of the paper in both cases.

twist per layer $\beta \simeq 2 \times 10^{-5}$ rad. If the birefringence of the nematic is 0·2, the phase retardation γ between the ordinary and the extraordinary rays per layer $\simeq 2 \times 10^{-3}$, so that $\gamma/\beta \simeq 10^2$. Optical theory[13–15] shows that under these circumstances the normal waves are linearly polarized, and that the directions of polarization rotate with the director. This behaviour can be readily appreciated in terms of the Poincare sphere (figure 2 a).

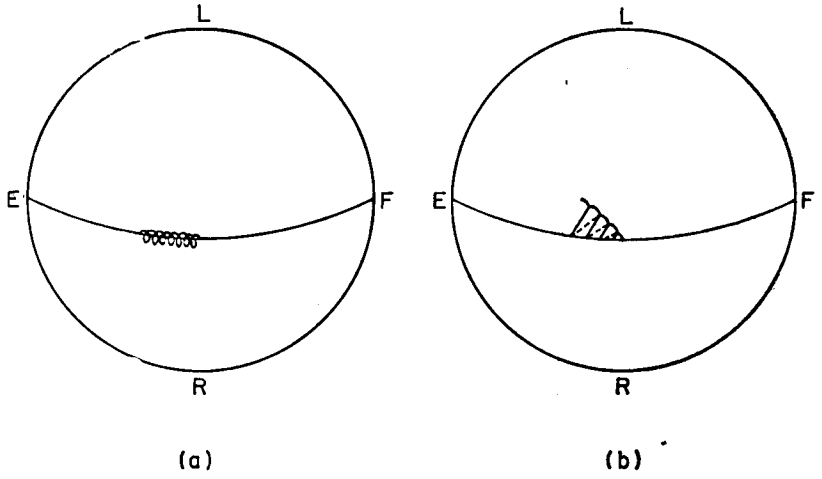

Figure 2 Illustration on the Poincare sphere of the propagation of linearly polarized light through the sample corresponding to (*a*) the set up in Figure 1 *a* and (*b*) that in figure 1 *b*. Changes in the state of polarization of the light beam are traced as follows : The point on the equator representing linearly polarized incident light is rotated in the proper sense through an angle γ about the equatorial axis corresponding to the azimuth of the first birefringent layer. This operation is repeated for the next layer where longitude is greater by 2β compared to that of the previous layer and so on.

If the incident light beam is linearly polarized along the director axis of the first section, we can see that the polarization state of the beam remains very close to the equator as it traverses the medium, *i.e.*, the light beam remains linearly polarized, and that the director is 'dragging' the polarization state along with it. Thus with the usual experimental geometry in which the director is anchored to the walls at either end, the state of polarization of the emergent beam is exactly the same as for the untwisted medium, and the twist deformation cannot be detected optically.

Because of this difficulty, Freedericksz and Tsvetkov[16] employed a total internal reflection technique using a beam incident at a suitable angle on the specimen contained between a convex lens and a prism. More recently, following a suggestion by de Gennes, Cladis[17] has made use of

the rotation of the conoscopic interference figure when the specimen gets deformed. Other methods which have been investigated are :

by studying the light scattering in an appropriate geometry[18]

by producing a cholesteric using a chiralic impurity and then untwisting the sample using an external field[19]

by determining the threshold field for a twisted nematic, the field being parallel to the twist axis (in this case, one needs to know the other two elastic constants[20] ; however, it should be pointed out that the γ / β problem discussed earlier will be important in this case also.)

by observing the rotation in the electrohydrodynamic flow pattern under the action of an external magnetic field[12].

However, none of these methods has been widely employed because of various difficulties inherent in each of them. We shall now discuss a simple technique which can be used with the sample taken in the usual configuration.

The Method

In order to be able to detect the twist deformation in transmitted light with the configuration shown in figure 1 a, γ / β has to be small, say about 4 or 5. Obviously, β can never be large near the threshold field, but it can be increased to some extent by applying very high fields. However, even with the highest fields normally attainable ($\simeq$ 25 kG) there will not be sufficient sensitivity to measure the deformation. An alternative method is to reduce the effective γ by viewing the index ellipsoid obliquely, say at $\sim 5°$ to the director. In such a case the extraordinary index is given by the well-known equation[21]

$$\frac{1}{n_{\text{eff}}^2} = \frac{\sin^2 \theta}{n_e^2} + \frac{\cos^2 \theta}{n_o^2}$$

where θ is the angle between the director and the direction of observation which should be in the plane containing the director and the normal to the glass plates. Under these circumstances, γ / β is reduced to ~ 4 or 5 even though the effective layer thickness is increased because of the obliquity. The effect of this on the polarization state of the emerging beam is to introduce an additional large phase difference between the ordinary and extraordinary rays as will be clear from figure 2 *b*. The deformation can therefore be easily detected by optical methods.

Experimental arrangement

The specimen was contained between two flat polished glass plates, the rim of which was cut and polished at an oblique angle to avoid refraction effects at the glass-air interface (figure 1 *b*). Standard mylar spacers, or at higher temperatures, mica spacers were used. The actual thickness of the sample was always measured by means of a channelled spectrum obtained by focussing white light on an air gap left deliberately unfilled for this purpose. The sandwich was mounted in a massive copper block which had a groove at the proper angle. The block in turn was slid inside an electrically heatable oven which itself was evacuated and filled with nitrogen during the experiment. The temperature was controlled by heating the oven with a stabilized DC supply and could be measured to $\pm$ 0·02° C by means of a copper-constantan thermocouple. The orientation of the sample was ensured by a previous rubbing of the glass plates. For the Freedericksz transition to occur, the director must be truly oriented at 90° to the external field. Even a small deviation of the order of 1–2° will give a long tail at lower fields and there is no critical field*. In order to ensure this exact alignment, the whole oven was mounted on a specially constructed platform whose alignment with respect to the field could be adjusted to an accuracy of 1–2′ of arc. Further, the platform itself rested on levelling screws so that the alignment of the sample could be varied in every possible manner. When the sample is aligned at exactly 90°, there should be no particular preference for the tilt of the director one way or the other in the field. Hence walls are formed in the field of view. The sample orientation was achieved by fixing the field at a value higher than the critical field and adjusting the alignment till the maximum number of threads could be observed.

The magnetic field was measured using a Hall-probe fluxmeter which was calibrated against an NMR unit. The accuracy of the field measurement was $\sim$ 1—2%. The observations were made using sodium light. The specimen was observed through a low power microscope and a well-aligned area was selected for observations. The incident beam was polarized at 45° to the vertical. The emergent beam passed through a $\lambda/4$ plate whose principal axes were at 45° to the vertical and then through an analyser which could be rotated. The deformation was detected visually. The critical field was taken to be the lowest field which when switched off did not produce any change in the field of view.

Results

(a) p-*Azoxyanisole (PAA):*

This is one of the few compounds for which the anisotropy of volume susceptibility $\Delta\chi$ has been measured in the nematic range[23, 24]. The value

* *See*, for instance, the calculations by Papoular and Rapini[22] which bring out this effect.

of $\Delta\chi$ were taken from the recent measurements of Gasparoux *et al*[24]. The density data of Maier and Saupe[25] were used in the calculations. The results are shown in figure 3. Our values are somewhat lower (by 6–8%) compared to the data of Freedericksz and Tsvetkov[16] as recalculated by Saupe[11] mainly because the $\Delta\chi$ values that we have used are lower than those of Foex[23] which were used by Saupe. When one allows for this difference, the agreement between the two sets of data is quite good.

(b) p-*Azoxyphenetole (PAP)*:

No susceptibility data are available for this compound. However, since the anisotropy of magnetic susceptibility arises essentially from the aromatic rings, we assumed that the molar susceptibility of PAA and PAP are the same. Using the values of the order parameter[26] and density[27], we have calculated the twist elastic constant. The results are shown in figure 3. The only other measurement for this compound is that due to

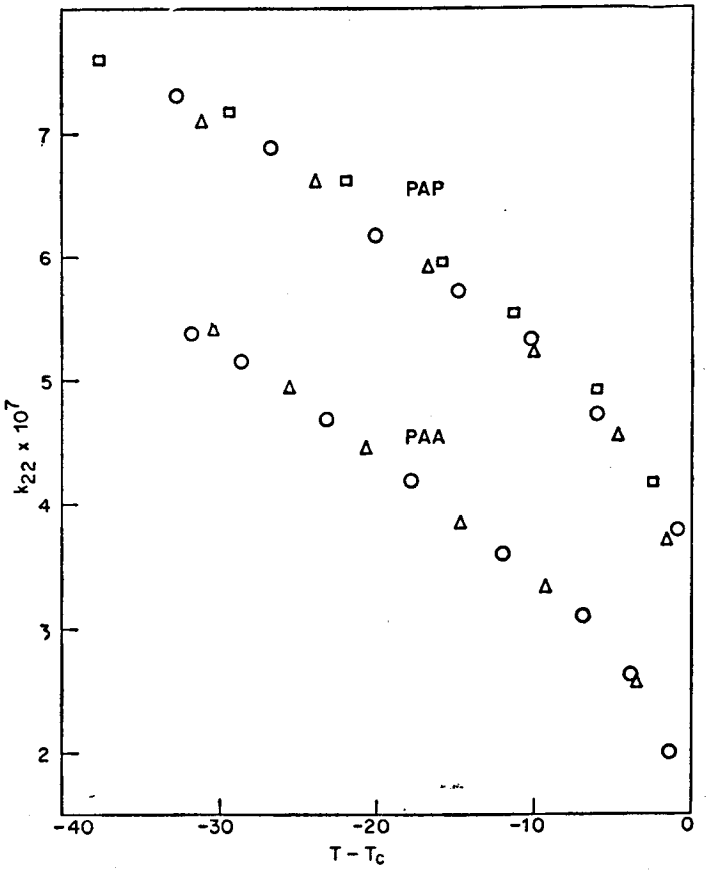

Figure 3 The twist elastic constants of PAA and PAP *versus* the relative temperature. Squares, circles and triangles represent independent measurements on different samples.

the Orsay group[28] carried out by dissolving a small quantity of a chiralic impurity and untwisting the mixture by means of a magnetic field. Again our measured value at that temperature is lower, but as we do not know the value of $\Delta\chi$ used in the earlier measurement, we merely point out that the Orsay measurement at one temperature on PAA also yielded a value higher than that reported by Saupe.

The ratio of k_{22} values of PAP and PAA agree approximately with the theoretical ratio given in our earlier paper. However the ratio is not independent of temperature but decreases somewhat at lower temperature (from $\sim$ 1·6 near T_c to $\sim$ 1·4 near T_c–30). Further the ratio is lower than that found in the case of k_{11} (1·8–2·0), which exhibits a maximum at a few degrees below T_c.

(c) N-p-*Cyanobenzylidene*-p-n-*octyloxyaniline (CBOOA)*

This is an interesting compound as it exhibits both the smectic A and nematic phases. The smectic A–nematic transition has generally been assumed to be second order—no heat of transformation could be detected within experimental limits. However, the recent investigation by Cladis on a highly purified specimen shows that this may not be true[17]. Moreover, from theoretical considerations Halperin and Lubensky[29] have claimed that this transformation should be at least weakly first order.

de Gennes[6] has drawn an analogy between this transition and the superconductor – normal transition and has suggested that the pre-transitional increase in k_{22} and k_{33} should follow the relation

$$\Delta k \propto \xi \propto \frac{1}{(T - T^*_{AN})^{\gamma}}$$

where Δk is the excess value of the elastic coefficient and ξ the coherence length of the smectic-like regions, and T^*_{AN} is the hypothetical second order phase transition point if the transition is weakly first order, or the actual transition point itself if it is truly second order. The mean field value for γ is 0·5, but de Gennes argued that the behaviour might not correspond to the mean field description and in such a case $\gamma = 0{\cdot}66$. Following this suggestion, there have been several measurements of the bend elastic constant[8,9] which have been claimed to agree with the latter result. The only determination of the twist elastic constant of CBOOA has heen that of Durand *et al.*[18] who studied the light scattering and they too obtained the result $\gamma = 0{\cdot}65$. However, recently Cladis has measured k_{33} of CBOOA with varying amounts of dissolved impurity and by using a least square analysis of the data. She has shown that $\gamma \simeq 0{\cdot}5$ for CBOOA and increases to 1 as the impurity content increases.

We have determined the bend and twist elastic constants of CBOOA (figures 4 and 5). The smectic-nematic transition point of our sample was

(83° C.) (The purest sample used by Cladis had a transition temperature of 83·4° C). The bend constant k_{33} was studied with a homeotropically aligned sample and the twist k_{22} with a homogeneously aligned sample using the technique described earlier. We may express k_{22} in the form

$$k_{22} = C_1 S^2 + C_2 (T - T^*_{AN})^{-\gamma} \quad (1)$$

where $C_1 S^2$ is the pure nematic contribution, S is the order parameter and C_1, C_2 are constants. A similar relation holds good in the case of k_{33}. We took the order parameter from the NMR measurements of Cabane and Clark[30]. The mass susceptibility of CBOOA have been reported recently[31] but since the density data are not yet known, they could not be converted to volume susceptibility. Therefore, in actual calculations we used the relation $\Delta \chi \propto S$. A graphical procedure for determining γ has been employed by a number of investigators but since the reliability of this procedure is doubtful, we used a least squares fitting programme which involved scanning the transition temperature and treating the other three constants as free parameters. Ideally, one should have an independent estimate of the pure-nematic contribution, *i. e.*, the value of the coefficient C_1. However, since there is no method of estimating this, we treated C_1 also as a free parameter. Figure 6 shows the minimum in r.m.s. error as a function of T^*_{AN}. The computations yielded

$$\gamma\,(k_{33}) = 0{\cdot}55$$

$$\gamma\,(k_{22}) = 0{\cdot}54$$

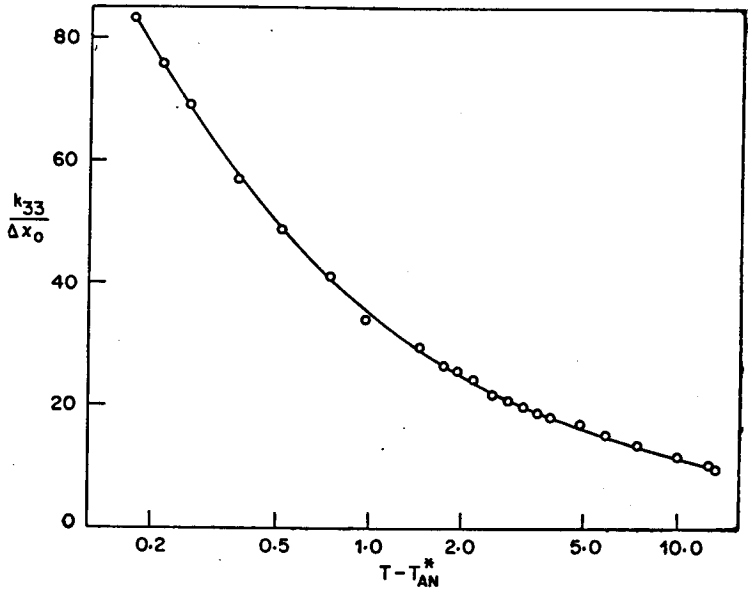

Figure 4 Bend elastic constant of CBOOA *versus* the relative temperature ($T - T^*_{AN}$)

The experiment on k_{22} was repeated on a commercial sample of CBOOA (Eastman Kodak). The A–N transition point was 82·7°C, and the value of γ for two independent sets of measurements found to be 0·52 and 0·49. However it was observed that C_2 was significantly less for this material

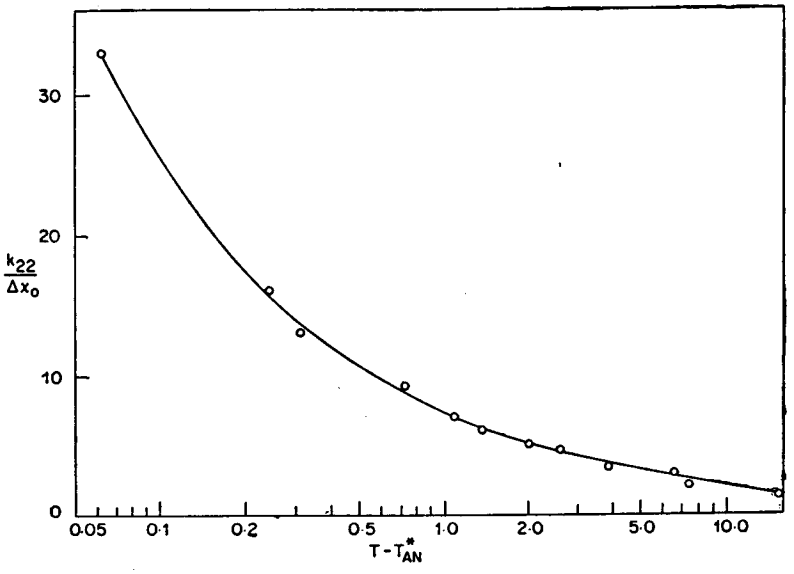

Figure 5 Twist elastic constant of CBOOA *versus* the relative temperature ($T-T^*_{AN}$)

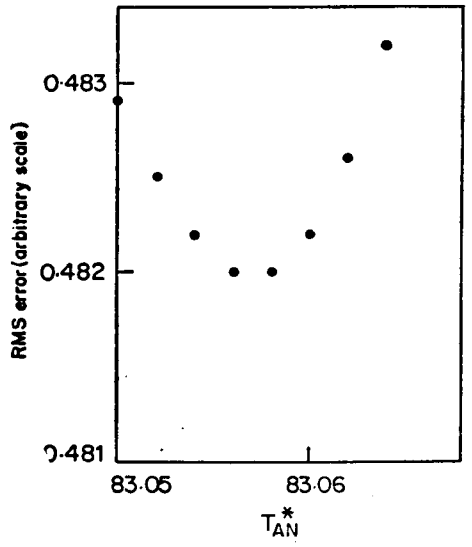

Figure 6 Least squares analysis of data using eq. (1): RMS error *versus* T^*_{AN}.

suggesting that impurities do influence the short range order effects. Thus our preliminary values of the critical exponents for both elastic constants are closer to the mean field value and in fair agreement with the recent measurements of Cladis[17]. It therefore appears reasonable to conclude that the mean field description of this transition is valid in the present case.

Twist viscosity

It is in principle possible to estimate the twist viscosity coefficient γ_1 using the present set-up. If we have a *small* twist deformation and switch off the magnetic field suddenly, the deformation relaxes to zero with a characteristic time constant τ given by

$$\tau = \left(\frac{\gamma_1}{\Delta\chi}\right)\frac{1}{H_c^2}$$

Hence τH_c^2 is a measure of γ_1. Theoretically, it has been suggested[7] that the excess viscosity due to fluctuations of the smectic-order parameter should show a divergence as $(T - T^*_{AN})^{-0.33}$ while $\Delta k_{22} \propto (T - T^*_{AN})^{-0.66}$.

Hence we should expect

$$\tau \propto (T - T^*_{AN})^{0.33}$$

i.e., the relaxation time should *decrease* near the nematic–smectic A point. The relaxation time was estimated by switching off a field $H \simeq 1{\cdot}1\ H_c$ and then noting the time taken for the sample to return to the undistorted state. It was observed that the relaxation time initially increased as the temperature was lowered, and very near T_{AN}, it *decreased* in value. This is in agreement with the expected trend.

Acknowledgements

We are grateful to Dr Ribotta and to Dr Durand for giving us the sample of CBOOA used in the experiments. Our thanks are also due to Dr Saupe for useful discussions and to Dr Khetrapal for the least squares fitting program.

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DISCUSSION

Rustichelli : What is the minimum twist that you could measure ?

Madhusudana : We estimated that a twist angle of $\sim 1/5$ radian could be detected for a typical sample thickness of $\sim 20\mu$. This is at the middle of the specimen where the deformation is maximum. In other words a twist per unit length of $\sim 0{\cdot}02$ radian per micron could be detected.

Mishra : Cladis's value of the critical exponent is 0·5. Can you comment on that ?

Madhusudana : Cladis has made a detailed study of the value of γ as a function of the purity of the sample. She finds that γ is 0·5 for very pure samples and goes up to 1 when impurities are added.

de Gennes : I am very sorry that the theory came first. I think that some of the earlier work, that of the Harvard group and also that of the Orsay group, has been influenced by the theoretical work. You might have smectics which obey the mean field and this would give $\gamma = \frac{1}{2}$ as Cladis says, and you might have smectics which are helium-like which would give 2/3. There may be further complications like what Lubensky is studying in which the fluctuations of the director may be reduced and can act on the system as radiation pressure would act on superconductors and can change the nature of the transition. The force or pressure required for the formation of the layers of the ordered state is singular and it has not been taken into account by any of the theories.