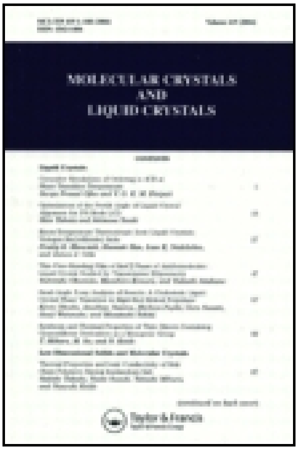

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Field-Induced Alignment of the Directors in the Smectic A Phase. Experiment and Simulation

Geoffrey Roger Luckhurst [a]

[a] Department of Chemistry and Southampton Liquid, Crystal Institute, University of Southampton, Southampton, SO17 1BJ, UK

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Field-Induced Alignment of the Directors in the Smectic A Phase. Experiment and Simulation

GEOFFREY ROGER LUCKHURST

Department of Chemistry and Southampton Liquid Crystal Institute,
University of Southampton, Southampton SO17 1BJ, UK

In contrast to nematics far less is known about the alignment of the directors in a smectic A phase by an external field. To characterise this process, which necessarily involves the flow of the molecules, we have undertaken an NMR investigation of the smectic A phase of 4-octyl-4′-cyanobiphenyl. The results of these experiments have revealed that, as expected, the alignment of the directors is a complex process strongly influenced by the nature of the containing surface for the smectic A phase. To assist in understanding the alignment process we have used computer simulations to study the field induced alignment of the directors in the smectic A phase formed by the Gay-Berne mesogen GB(4.4,20.0,1,1).

Keywords: smectic A; director alignment; NMR; computer simulation

1. INTRODUCTION

One of the many fascinating properties of the liquid crystal phase is the ability of relatively weak fields to align the director [1]. This field-induced alignment of the director in a nematic is a well understood process. Thus for materials with a positive diamagnetic anisotropy, $\Delta\tilde{\chi}$, the director orientation, β, with respect to the field is predicted and found to change according to

$$\tan\beta(t) = \tan\beta(0)\exp(-t/\tau), \tag{1}$$

where $\beta(0)$ is the initial value of the angle between the field and the director [2]. The relaxation time τ is given by

$$\tau = \mu_0\gamma_1/\Delta\tilde{\chi}B^2, \tag{2}$$

where μ_o is the magnetic constant, B is the magnetic flux density and γ_1 is the rotational viscosity coefficient. This expression is obtained by assuming that the nematic rotates as a monodomain and that interactions with the surface of the container are negligible in comparison with the magnetic energy.

The analogous alignment process for a smectic A phase is necessarily more complicated because if the layers are to remain intact as the director is aligned then the molecules must translate as well as change their orientations. A first step in this process is expected to be the creation of undulating smectic layers as predicted by Helfrich and Hurault [3]. In order to characterise this process we have chosen to use deuterium NMR spectroscopy, employing the magnetic field of the spectrometer to align the director of the smectic A phase. In addition we have used the technique of computer simulation to help understand the unusual results of these experiments. The following section describes briefly the NMR experiment while a selection of the results for the smectic A phase of specifically deuteriated 4-octyl-4′-cyanobiphenyl-d_2 (8CB-d_2) are described in section 3. The Gay-Berne model mesogen is presented in section 4 together with the results of the analogous computer simulation study of the director alignment experiments. Our conclusions are in section 5.

2. DEUTERIUM NMR SPECTROSCOPY

NMR spectroscopy in general and deuterium NMR spectroscopy in particular has proved to be an especially powerful technique for studying liquid crystal behaviour [4]. Many of these investigations have been concerned with the order and dynamics at the molecular level. However, it is also finding an increasing use to study the macroscopic behaviour of a liquid crystal, again both dynamic and static. One of the advantages of the technique results from the simplicity of the deuterium NMR spectrum of a liquid crystal and its relation to the director distribution. For a material containing a set of equivalent deuterons the NMR spectrum for a monodomain sample contains a doublet resulting from the partially averaged quadrupolar interaction of the deuterons. The magnitude of the splitting depends on several factors including the orientational order of the molecule. However this is not of interest to us here, what is important is the variation of the quadrupolar splitting with the angle, β; this is given by

$$\Delta\tilde{\nu}(\beta) = \Delta\tilde{\nu}(0)P_2(\cos\beta), \tag{3}$$

where $\Delta\tilde{\nu}(0)$ is the quadrupolar splitting when the director is parallel to the magnetic field and $P_2(\cos\beta)$ is the second Legendre function. Knowledge of the splitting $\Delta\tilde{\nu}(\beta)$ then allows the director orientation to be determined.

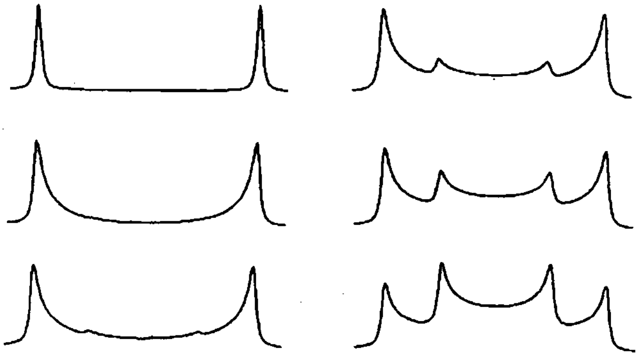


Fig. 1 Simulated deuterium NMR spectra showing their dependence on the director distribution function, ranging from a monodomain to a random two dimensional distribution.

The lineshape also contains valuable information concerning the distribution of the director with respect to the field. This situation obtains because the observed spectrum is a weighted sum of spectra from all director orientations. For a monodomain sample with the director parallel to the field the spectrum contains two symmetric lines as we can see in Fig. 1. As the director begins to be distributed in a plane containing the magnetic field so the spectral lines are broadened and become asymmetric. On further increase in the width of the director distribution two weak peaks appear in the spectrum with a splitting corresponding to the director aligned perpendicular to the magnetic field. These peaks increase in intensity at the expense of the quadrupolar doublet associated with the director parallel to the field. This change in the relative intensities of the parallel and perpendicular peaks continues until they have approximately the same intensity corresponding to a random distribution of the director in two dimensions.

3. EXPERIMENTAL STUDIES

The majority of studies of the magnetic field alignment of the directors in a smectic A phase were made with the mesogen 4-octyl-4′-cyanobiphenyl, using a magnetic flux density of 4.7T [5]. This mesogen has a nematic phase so that a monodomain sample of the smectic A phase can be prepared by first aligning the director in the nematic phase and then slowly lowering the temperature. The process is facilitated by the weakness of the SmA – N transition. The high quality of the director alignment in the smectic A phase is apparent from the deuterium NMR spectrum labelled 0^- in Fig. 2. This consists of a single quadrupolar doublet with symmetric lineshapes and relatively sharp lines. This spectrum corresponds to the director aligned parallel to the magnetic field which is the stable state of the system. On rotating the sample by 41° about an axis orthogonal to the magnetic field, to a non-equilibrium state, the quadrupolar splitting is reduced significantly, as we can see from spectrum 0^+ in Fig. 2, and as expected from Eq. (3). The spectral lines remain sharp which is further evidence for the high quality of the uniformity of director alignment. If, as in a nematic, the director was realigned parallel to the magnetic field as a monodomain, then the quadrupolar splitting should simply grow with increasing time until it reached the value observed at 0^-.

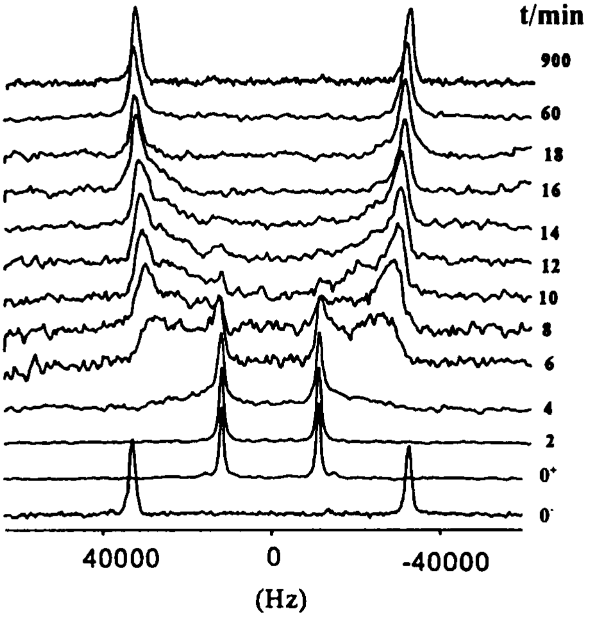


Fig. 2 The time dependence of the deuterium NMR spectrum of the smectic A phase of 8CB-d_2 just before and after the rotation of the director by 41° with respect to the magnetic field of the spectrometer.

Such behaviour is clearly not found for the smectic A as the spectra, shown as a function of time in Fig. 2, demonstrate. Thus after 2 min the quadrupolar splitting has not changed, although there is a slight reduction in the overall intensity, which suggests that some of the directors have moved to new orientations although these are not apparent in the spectrum. Four minutes following the rotation of the sample there is still an intense doublet associated with director at 41° to the field but the lines have broadened, there is also an increase in the spectral intensity with a range of splittings where the angle between the director and the field is less than 41°. After 6 min there has been a profound change in the spectrum with the introduction of two very broad lines with a splitting slightly less than that found at 0⁻. It would seem, therefore, that the orientations of many of the directors with respect to the field are now close to 0° although there are still a range of orientations between this value and the rotation angle. The field-induced alignment continues with time as is evidenced by the increase in intensity of the quadrupolar doublet with the large splitting. In addition, the asymmetry in the spectral lineshape decreases as the sample is reformed, by the magnetic field, as a monodomain. However, even after 900 min the linewidth is not quite as small as that before the sample is rotated, indicating that the director distribution is not so narrow. It would seem, therefore, that immediately following the rotation of the sample there is a short induction period when the director does not move. Then the director does start to move although there is a variation in the rate of its motion that results in a significant broadening of the director distribution. Subsequently this distribution begins to narrow as the director is realigned parallel to the magnetic field, although the narrowing process is not quite complete even 900 min after the sample has been rotated.

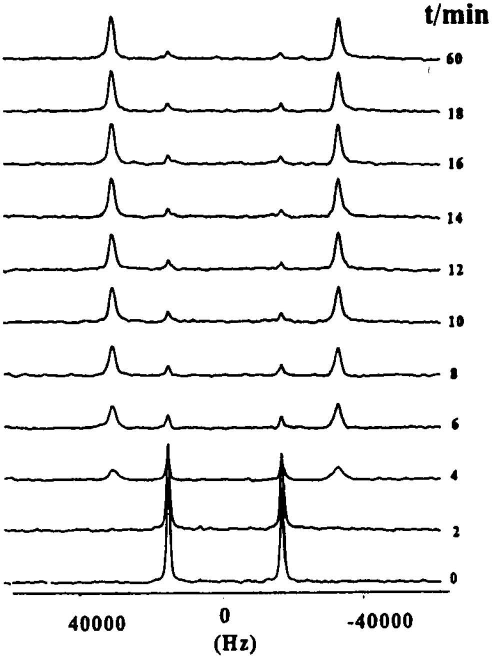


Fig. 3 The time dependence of the deuterium NMR spectrum of $8CB\text{-}d_2$ in its smectic A phase following rotation of the director through 90°.

This behaviour proves to be quite different to that observed when the director starts perpendicular to the magnetic field. The spectrum recorded immediately after the sample had been rotated is seen in Fig. 3, and has a quadrupolar splitting one half that before rotation in accord with Eq. (3). The spectral lines are symmetric and sharp which again shows the uniform alignment of the director. As for the sample rotated by the smaller angle, there is an induction period just greater than 2 min. However, the time-dependent changes in the spectra are quite different; what is observed is that the quadrupolar doublet associated with the director perpendicular to the field decreases in intensity, while that corresponding to the director parallel to the field increases. It is of interest to note that this four line spectrum differs quite significantly from that for a planar distribution of director orientations shown in Fig. 1 where the lineshapes are asymmetric and there is considerable intensity between them. After 60 min the alignment process has not gone to completion for the spectrum shown in Fig. 3 still contains weak features coming from the director perpendicular to the field. It is important to note that integration of the spectrum shows that the signal intensity decreases and then increases again. However, there is no indication as to why the intensity is reduced and what director orientations the missing intensity corresponds to.

In these two experiments the results suggest that the director alignment by the field of the NMR spectrometer is accompanied by reorganisation of the smectic A phase. This could be associated with decoupling of a region from the bulk layer structure, possibly via the migration of defects. The magnetic field is then able to align this part of the smectic A phase, that could be nematic-like, without disturbing the remainder of the smectic layers. This would account for much of the behaviour that is observed when the director is initially at 41° to the field. The situation is quite different when the director is initially orthogonal to the magnetic field, for now the NMR spectra suggest that the director distribution is bimodal with narrow components parallel and perpendicular to the field. It is clear, however, that there must be director orientations not revealed by the experiment. In both experiments the field-induced alignment of the director does not proceed as a monodomain and some reorganisation of the smectic A structure must be occurring.

There is, in principle, another pathway by which the director can be aligned and that is for the sample to be rotated as a rigid body.

However, this does not play a major role presumably because of the interaction between the surface of the smectic A phase and that of the glass tube. One way by which the friction between the two surfaces could be reduced would be to suspend a droplet of the smectic A phase in an isotropic liquid. A liquid for which this has proved to be possible is glycerol in which 8CB-d_2 is essentially insoluble; in addition the densities of the two phases are similar so that the droplet of the smectic A phase remains suspended in the glycerol for a reasonable time [6].

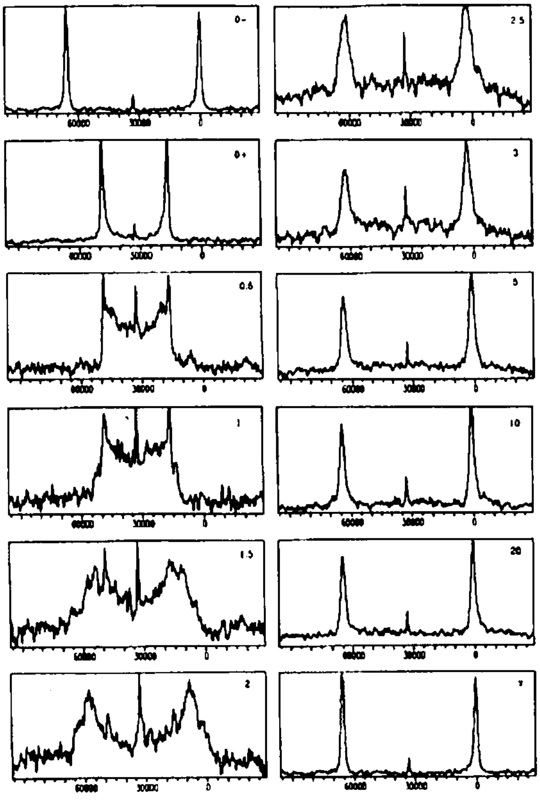


Fig. 4 The variation with time, shown in seconds, of the deuterium NMR spectrum of a droplet of 8CB-d_2 in its smectic A phase suspended in glycerol prior to and following the rotation of the director by 90° with respect to the magnetic field.

The NMR spectrum of the droplet of 8CB-d_2 prior to rotation, at $t = 0^-$, is shown in Fig. 4, it consists of a quadrupolar doublet with sharp lines which shows that the director is well-aligned parallel to the magnetic field. Immediately following rotation by 90^0 at $t = 0^+$ the spacing is reduced to approximately one half its original value (see Eq. (3)). Then within 0.5s the director begins to move, as we can see from the broad pair of lines shown in Fig. 4. The spacing between these lines continues to decrease and then to increase once the angle between the director and the magnetic field passes 54.74^0 at which point $P_2(\cos\beta)$ vanishes. After only about 2.5s the director is essentially parallel to the magnetic field with a fairly narrow director distribution. This distribution continues to reduce in width for about 7s before reaching its limiting form with a width of approximately 2^0. The NMR experiment has shown, therefore, that there is no induction period following the rotation of the sample, and that the director takes just a few seconds to be aligned parallel to the magnetic field. This suggests that the major pathway by which the director moves is via rotation of the droplet as a rigid body. The relaxation time for this to occur is given by

$$\tau = \mu_0\eta/6\Delta\tilde{\chi}\,B^2, \tag{4}$$

that is analogous to the expression in Eq. (2) but with the dynamic viscosity, η, of glycerol replacing the rotational viscosity of the nematic [6]. The value predicted for this is found to be of the order of several seconds, in agreement with experiment.

Although the NMR experiments cast some significant light on the complexity of the pathways by which the director of a smectic A phase is aligned by a magnetic field our understanding is far from complete. One way by which the alignment process can be investigated further is with the aid of computer simulation. Some of the results obtained in this way are described in the following section.

4. COMPUTER SIMULATION STUDIES

The model potential used in the simulation studies of the field-induced alignment process is that developed by Gay and Berne [7]. This is a single site or Corner potential, namely

$$U(R) = 4\varepsilon(R^{-12} - R^{-6}) \tag{5}$$

where

$$R = (r - \sigma + \sigma_0)\sigma_0. \tag{6}$$

The parameters, ε and σ, controlling the potential depend on the orientations of the two molecules and the vector joining them. The distance dependence of the potential is shown in Fig. 5 for a selection of orientations of the molecules and the intermolecular vector. The anisotropy in both the attractive and repulsive forces is clearly apparent and these represent, in a generic sense, the essential features needed for the formation of a liquid crystal. Just as there are many mesogenic molecules so there are many parametrisations of the Gay-Berne potential which are denoted by GB(κ,κ′,μ,ν) where κ denotes the anisotropy in the contact distance σ and κ′ is that in the well-depth ε [8]. The parameters μ and ν control the form of the angular variation in the well-depth. The Gay-Berne mesogen which has been studied is GB(4.4,20.0,1,1); at a scaled pressure P* of 2.0 this forms isotropic, nematic, smectic A and smectic B phases [8].

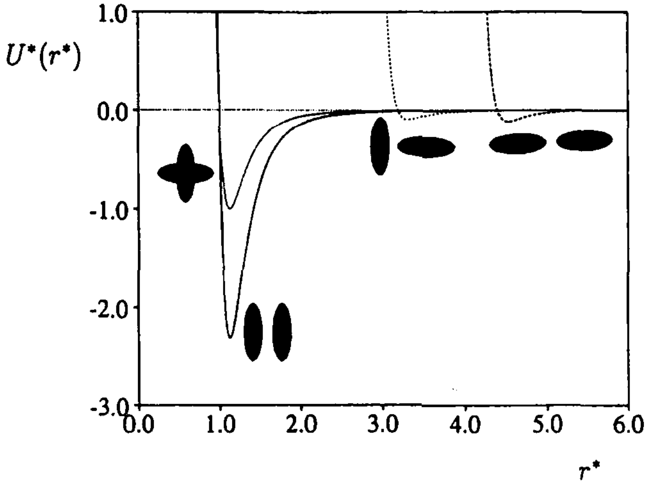


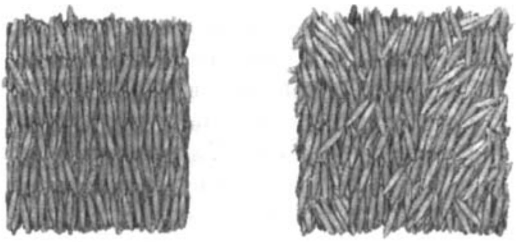
Fig. 5 The distance dependence given by the Gay-Berne potential for the mesogenic molecules GB(4.4,20.0,1,1) in a selection of relative orientations. Here r^* is r/σ_0 and U^* is U/ε_0.

In addition to the intermolecular interactions each molecule interacts with a magnetic field according to

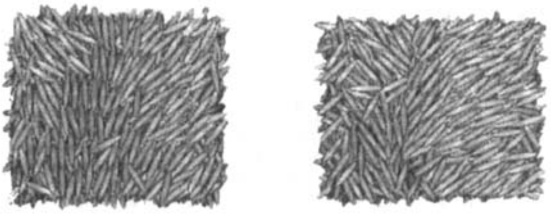
$$U_f = -\lambda\varepsilon_0 P_2(\cos\theta), \tag{7}$$

where θ is the angle between the molecular symmetry axis and the field [9]. The relative strength of the field is determined by the parameter λ. As in the NMR experiments a monodomain sample of the smectic A phase is prepared, then the angle between the field and the director is changed to its initial value of zero. The subsequent behaviour of the system as it returns to equilibrium is then followed by the Monte Carlo simulation technique. Although this does not provide the time dependent behaviour in the same way as a molecular dynamics simulation it does have certain convenient features [10]. The validity of the Monte Carlo methodology in such studies has been demonstrated by an analogous investigation of the field-induced director dynamics in the nematic phase formed by GB(4.4,20.0,1,1). This is found to be in good agreement with the behaviour predicted by Eqs. (1) and (2) [11]. As we had anticipated the alignment of the smectic A phase proved to be more complex. This process can be followed using a variety of properties and correlation functions, however one of the best approaches is to visualise configurations of the system since they invariably illustrate the basic physics.

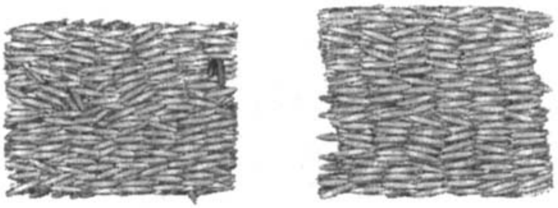
As an example we show in Fig. 6 pictures of configurations taken from simulations for the alignment of the smectic A phase by a field originally applied orthogonal to the director. Prior to rotation of the field the layered structure of the smectic A phase is clearly apparent as is the interdigitation of the layers and the relatively high orientational order. After 21k cycles, where a cycle corresponds to an attempt to move each of the 2000 molecules in this sample, the uniform layer structure is no longer apparent. At the centre of sample the molecules have not moved but in the regions on either side the molecular orientations with respect to the field have changed but in opposite senses. Such changes are clearly visible after 25k cycles and the resultant spatial variation in the director orientation is reminiscent of that found during the field-induced alignment of the director in a nematic phase [12]. After 30k cycles a disclination line is seen separating two regions where the director has moved in opposite senses to be parallel to the field. In addition only remnants of the smectic layers are apparent in the system showing that a nematic-like structure has been induced by the field. This change in the structure continues and after another 10k cycles the layers are essentially destroyed and the director is aligned parallel to the magnetic field. It then takes a long time for the smectic layers to be reformed, thus after 100k cycles the layer structure is clearly observed although the layers are tilted slightly with respect to the director.



Start Cycle # 21000



Cycle # 25000 Cycle # 30000



Cycle # 40000 Cycle # 100000

Fig. 6 Pictures of the molecular organisation in the Gay-Berne mesogen, GB(4.4,20.0,1,1), both before and after rotation of the magnetic field through 90° with respect to the director in the smectic A. The images are shown for different numbers of cycles during the Monte Carlo simulation.

The visualisation of configurations taken from the Monte Carlo simulation clearly provide a considerable insight into the nature of the changes in the structure induced by the field. However, to complete this view it is also important to consider how average properties such as the ordering tensor, the density and the director components change during the course of the simulation. These are shown in Fig. 7 as a function of the number of cycles [11]. We begin with the components of the director, **n**; the z axis is parallel to the layer normal in the initial SmA phase and the field defines the x axis.

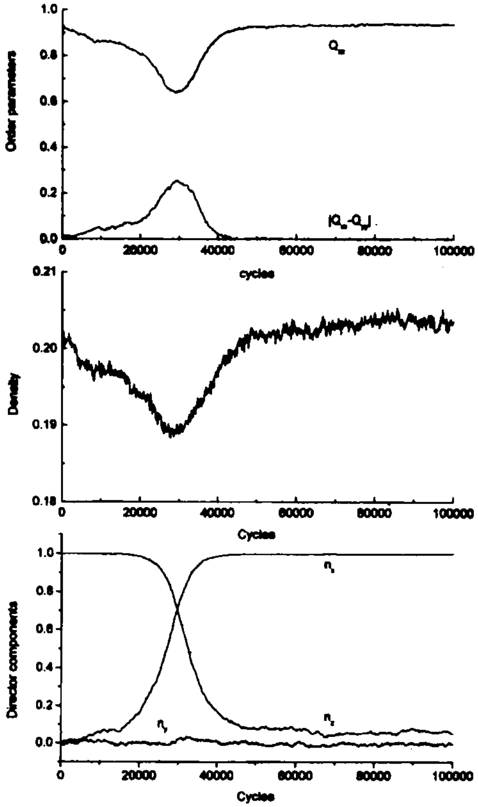


Fig. 7 The variation, with the number of cycles, of the ordering matrix, **Q**, the number density and the components of the director, **n**, following rotation of the field through 90° with respect to the director.

We see that there is a period of about 20k cycles during which n_z is unity, indicating that the director orientation does not change. Then this component decreases rapidly almost to zero and at the same time n_x increases to unity indicating the alignment of the director parallel to the field after about 40k cycles. The third component n_y is essentially zero for all of the time showing that the director remains in the xz plane. During the rotation of the director other changes in the phase structure occur. These are apparent from the density which decreases, passes through a minimum and then increases again but does not reach its initial value until 100k cycles. This reduction in the density is consistent with the formation of a nematic phase and the eventual reformation of the smectic A phase. The principal elements of the ordering tensor, **Q**, also change, thus the major order parameter, Q_{zz}, decreases significantly passes through a minimum and then increases rapidly before regaining its original value. At its minimum the order parameter is typical of that expected for a nematic. The biaxial order parameter, $Q_{xx} - Q_{yy}$, which reflects the phase symmetry is of interest, initially it is zero as required for a smectic A phase with its uniaxial symmetry. It then increases and passes through a maximum at the point at which the director orientation is changing most rapidly. This non-zero value does not indicate that a biaxial phase has been formed by the field but that the system is non-uniform with essentially three regions having different director orientations in the xz plane. It is this inhomogeneity which is responsible for the observed biaxiality. Consequently as the directors are aligned parallel to the magnetic field so the biaxiality in **Q** falls rapidly to zero.

5. CONCLUSIONS

One of the distinct advantages in using NMR spectroscopy to investigate the macroscopic behaviour of liquid crystals is its ability to determine the director distribution. The value of this is clearly apparent in the studies of the magnetic field induced alignment of the directors in a smectic A phase. Here, the sample is not realigned as a monodomain and the nature of the alignment process varies significantly with the initial orientation of the director with respect to the field. The pinning of the smectic A phase at the surface of the glass tube has a profound influence on the pathway by which the director is rotated. Replacing the tube with a liquid interface seems to allow the smectic A droplet to rotate more or less as a rigid body, which is a relatively fast process. Our understanding of the field-induced alignment of a smectic A phase has been further enhanced by the use of computer simulation studies of a Gay-Berne mesogen, These reveal, amongst other things, an induction period prior to the movement of the director. In addition the layer structure is destroyed during the alignment process and then reformed. Both observations are consistent with the NMR results and our interpretation of them.

Acknowledgements

Here it is a pleasure for me to acknowledge the contributions of my colleagues who were involved in these investigations; they are Dr. C. Bacchiocchi, Dr. M. A. Bates, Professor J. W. Emsley, Dr. P. Pedrielli and Dr. G. Saielli.

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