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Incoherent Neutron Quasi-Elastic Scattering (NQES) as a Tool to Study Molecular Ordering in Liquid Crystals

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It is shown that high resolution incoherent neutron quasi-elastic scattering (NQES) may be used, via the measurement of the elastic incoherent structure factor (EISF), as a new tool to study molecular ordering in liquid crystals. The EISF is a bilinear combination of all the order parameters $\langle P_l \rangle$ and its experimental value can be deduced from an intensity measurement. As an example, we measure from the NQES spectra, the EISF of powder smectic A TBBA at 184°C. These data are analysed in terms of two microscopic models (molecules rotating around their long axis and (i) fluctuating about the director: model 1, (ii) precessing on a cone about the director: model 2). It is shown that from the powder results only, we cannot discriminate between these two models, but that model 2 can explain other published experimental results (in particular some Raman scattering of light data) whereas model 1 cannot. Some conjectures about model 2 are made.

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1 INTRODUCTION

The liquid crystalline mesophases[1] are characterized by the existence of a long range molecular ordering, superimposed on the short range order which already exists in the higher temperature isotropic phase. The study of such ordering has been the subject of considerable work, both theoretical and experimental. Molecular theories for the nematics[2] and the (numerous) smectic[3] mesophases have been developed which predict the values of suitably defined translational and orientational order parameters. A number of experimental methods are available to study this problem. Light scattering is certainly the most convenient means to study the long range orientational order and it is in fact the most widely used technique.[1] X-ray[4] or neutron[5] diffraction yield information on both long and short range correlations between molecules. Moreover, from data obtained at high momentum transfer, it is possible to extract information on the orientational order.[5] Other techniques are sensitive to the properties of individual molecules, distinct from the collective properties described above. The most important ones are nuclear magnetic resonance (NMR),[6] electron spin resonance (ESR),[7] Raman scattering of light[8,9] and infra-red (IR) absorption.[10] In all these cases, the information on the order is contained in the average value of quantities associated with the molecules. For example, from a NMR splitting one deduces the average value $\langle P_2 \rangle$ of $P_2(\cos \lambda) = \frac{1}{2}(3 \cos^2 \lambda - 1)$ where λ is the angle between the vector joining two nuclear spins and the applied magnetic field. It is seen that this information is not very direct since what is predicted theoretically is the average value of the same quantity but where λ is the angle between the molecular axis and some suitable direction (e.g. the director in a nematic). A model must be made to connect them. The situation is similar with the other techniques. In fact, the full information on the molecular ordering is contained in the distribution function $q(\lambda, \phi)$ of the molecular axes. This function can be expanded in Legendre functions P_l^m so that in principle at least, all the $\langle P_l^m \rangle$ are required for a complete knowledge of q. If the medium is uniaxial, q is independent of ϕ and only the average values of the usual Legendre polynomials $P_l^0 \equiv P_l$ are needed. So far, due to the very nature of the physical quantities which are measurable by the above spectroscopic techniques, information is mainly available for $\langle P_2 \rangle$. It is thus of importance to develop methods which can reach the higher order parameters. So far only $\langle P_4 \rangle$ can be estimated from Raman scattering of light[8] and ESR line-widths measurements[7a,c] Unfortunately, in both these cases, we are concerned with the ordering of molecules in solution.

The aim of this paper is to show that high resolution incoherent neutron quasi-elastic scattering (NQES) is an alternative new method to approach this problem. Incoherent NQES has already been used in the past to study liquid crystals.[11] However, due to relatively bad experimental conditions (low neutron fluxes and poor energy resolution), the results were not accurate and the analysis sometimes incorrect. With new high flux reactors (e.g. that of the I.L.L., Grenoble), cold neutron sources and high resolution spectrometers, the situation has greatly improved and it is now possible to perform measurements with precision. Some such experiments have already been made.[12] Another will be described here, as a typical example of the NQES method. The paper will be organized as follows. First, we present the basic concepts of incoherent NQES, aimed at the study of molecular ordering in liquid crystals. Then, as an illustration, we describe experimental results obtained on a powder sample of TBBA in its smectic A phase. These results are then discussed in terms of two possible microscopic models, (hereafter referred to as model 1 and 2). Finally, in the appendixes, some conjectures about model 2 are made.

2 INCOHERENT NEUTRON QUASI-ELASTIC SCATTERING: THEORETICAL BACKGROUND

In this section, we only present the main results of incoherent NQES relevant to the present purposes. For more details, the reader is referred to standard textbooks.[13]

We consider first the idealized case of a hydrogeneous molecular compound containing only one proton per molecule. Such a system scatters neutrons almost entirely incoherently. Due to the molecular motions, the position $\mathbf{r}$ of the proton varies with time. The self-correlation function (s.c.f.) relevant to NQES is the so-called intermediate (incoherent) scattering law $I_s(\mathbf{Q}, t)$ defined by[13]

$$I_s(\mathbf{Q}, t) = \langle\langle \exp i\mathbf{Q}[\mathbf{r}(t) - \mathbf{r}_0]\rangle\rangle_{\mathbf{r}_0} \tag{1}$$

where $\mathbf{Q}$ is the neutron momentum transfer, $\mathbf{r}(t)$ and $\mathbf{r}_0$ picture the positions of the proton at time t and time zero respectively, the inner brackets indicate a suitable ensemble average while the outer brackets indicate an average over all the possible initial positions. The neutron spectra are then directly proportional to the (incoherent) scattering law $S_s(\mathbf{Q}, \omega)$ given by

$$S_s(\mathbf{Q}, \omega) = \frac{1}{2\pi}\int I_s(\mathbf{Q}, t)\exp(-i\omega t)\,\mathrm{d}t \tag{2}$$

Note that we have

$$\int S_s(\mathbf{Q}, \omega)\,\mathrm{d}\omega = I_s(\mathbf{Q}, 0) = 1 \tag{3}$$

Let us assume that the motion of the proton is characterized by the propagator $G_s(\mathbf{r}, \mathbf{r}_0, t)$ (also called the Van Hove self-correlation function), which is the probability to find the proton at $\mathbf{r}$ at time t if it was at $\mathbf{r}_0$ at $t = 0$. This function obeys a rate equation which, in the case of diffusive motions, is of the Fokker-Planck type. If this equation can be solved exactly and if the distribution of initial positions is known, the averages in (1) can be calculated. The scattering law given by (2) can then be derived and compared to the actual neutron spectra line shapes. This would in principle be the best way to analyse neutron data. However, in general G_s is not known, hence this procedure fails. We shall show now that, with some weak assumptions, valuable information can in practice be extracted from intensity measurements only. The first assumption we make is that the molecular centre of mass (c.o.m.) is fixed (no translational motion). In this case, the proton remains always on the sphere of radius r (the c.o.m. is taken as origin). Thus at infinite time, $G_s(\mathbf{r}, t = \infty)$ is still finite in space, not zero as would have been the case for diffusive translational motion. Consequently $I_s(\mathbf{Q}, t = \infty) \neq 0$, i.e. the s.c.f. $I_s(\mathbf{Q}, t)$ does not decay to zero but to some constant value $A_0(\mathbf{Q})$.

We can write:

$$I_s(\mathbf{Q}, t) = I_s(\mathbf{Q}, t = \infty) + [I_s(\mathbf{Q}, t) - I_s(\mathbf{Q}, t = \infty)] \tag{4}$$

The quantity in brackets now decays to zero, generally as a sum of exponential functions for stochastic processes.[14] Assuming such a functional form, we have:

$$I_s(\mathbf{Q}, t) = A_0(\mathbf{Q}) + \sum_{n>0} A_n(\mathbf{Q})\exp(-t/\tau_R^n) \tag{5}$$

Using Eq. (2), we finally get:

$$S_s(\mathbf{Q}, \omega) = A_0(\mathbf{Q})\delta(\omega) + \sum_{n>0} A_n(\mathbf{Q})L_n(\omega) \tag{6}$$

where the $L_n(\omega)$ are Lorentzian functions of half width $(\tau_R^n)^{-1}$. Consequently, the incoherent scattering law of a purely rotational model is the sum of a sharp $\delta(\omega)$ function and a broad component, composed by Lorentzians, whose width is of the order of $(\tau_R^n)_{\mathrm{Av}}^{-1}$. Moreover, using Eq. (3), it is seen that $A_0(\mathbf{Q})$ *is the fraction of the total (quasi-elastic) intensity contained in the purely elastic term.* $A_0(\mathbf{Q})$ is by convention, the Elastic Incoherent Structure Factor (EISF) of the model. Finally, from Eq. (1), since the initial and final distributions of the protons are the same, dropping the index 0, we have:

$$A_0(\mathbf{Q}) = |\langle \exp i\mathbf{Q} \cdot \mathbf{r} \rangle|^2 \tag{7}$$

Let θ be the angle between $\mathbf{Q}$ and $\mathbf{r}$. Expanding the exponential, we can write:

$$A_0(\mathbf{Q}) = 16\pi^2 \left| \sum_{l=0}^{\infty} i^l j_l(Qr) \langle P_l(\cos\theta) \rangle \right|^2 \tag{8}$$

where the j_l are the spherical Bessel functions.

It is seen that from the measurement of an intensity, one can get information on the quantities $\langle P_l \rangle$ as explained above. But, as in the case of the other techniques, the $\langle P_l \rangle$ do not concern the molecular axis and the director, but some other molecular vector (here that joining the c.o.m. to the proton) and the "external" vector **Q**. This is valid if the molecule contains only one proton. If there are many protons, the right hand sides of Eq. (7) and (8) should be further averaged over all these protons.

3 INCOHERENT NEUTRON QUASI-ELASTIC SCATTERING: AN ACTUAL EXPERIMENT

In an actual experiment, the EISF is a useful practical concept only if in the neutron spectra, the above mentioned sharp peak is well separated from the broadened line. This will occur in practice if the energy width $\Delta\omega$ of the instrumental resolution function $R(\omega)$ is (much) smaller than the width of the broadened line. The actual spectra will then appear as the superposition of a sharp line reproducing $R(\omega)$ and a (much) broader component. These two components can then be separated,[12a–12e] the intensities I_e and I_q measured (e for elastic and q for quasi-elastic) and an experimental value for the EISF deduced from the ratio $I_e/(I_e + I_q)$. This has assumed that the sharp peak is not broadened by some much slower motion of the c.o.m. of the molecules. One of these motions is translational self-diffusion. In this case, the extra broadening of the sharp line is $2D_tQ^2$ where D_t is the self-diffusion coefficient.[13] If then $2D_tQ^2$ is much smaller than $\Delta\omega$ (and this is always the case at sufficiently low Q values), then the structure of the spectra remains essentially unchanged, the only difference in identifying the sharp component is to replace the resolution function $R(\omega)$ by an effective resolution function $R'(\omega) = R(\omega) \otimes T(\omega)$, where $T(\omega)$ is the Lorentzian function given by:

$$T(\omega) = \frac{1}{\pi} \frac{D_tQ^2}{(D_tQ^2)^2 + \omega^2} \tag{9}$$

and where $\otimes$ symbolizes the convolution product.

At high Q ($Q \approx 1$ Å^{-1}), it is not clear that the concept of self-diffusion is still meaningful (since then $Ql > 1$, where l is a molecular length) and this extra broadening may become constant with Q. This broadening then reflects a residence time between two successive jumps of the c.o.m.[13,15] Other mechanisms such as the undulation modes in smectics[16] may also contribute to this broadening. Since many mechanisms may broaden the sharp component, it is important to measure it accurately in order to make a reliable separation. This can be done by means of the neutron back-scattering technique.[12f–12h] In what follows, we use these concepts to analyse NQES data on smectic A terephtal-bis-butyl-aniline (TBBA).

4 INCOHERENT NEUTRON QUASI-ELASTIC SCATTERING ON SMECTIC A TBBA: EXPERIMENTAL RESULTS

In a series of papers, we have presented NQES results on the solid and smectic VI, H and C phases of TBBA.[12a–12d] The present results concern the smectic A phase at 184°C. The specimen studied was the partially deuterated derivative of TBBA (completely deuterated on the butyl chains and called DTBBA in References 12), in powder form. The experimental set-up and conditions were the same as in previous work,[12a] except that the incident wavelength was 7.52 Å yielding an elastic instrumental resolution of 67 μeV FWHM (1 $\mu\text{eV} = 1.52 \times 10^9$ rd/sec). Figure 1 shows three typical spectra together with the resolution function. It is seen that they have the structure described above. The broadening of the sharp component was measured by the back-scattering technique[16b] and it was found that its width Δ varies like Q^2 up to $Q = 0.45$ Å^{-1}. The relation $\Delta = 2D_tQ^2$ yields $D_t \approx 2.8 \times 10^{-6}$ cm^2/sec in good agreement with NMR results,[17] showing that up to

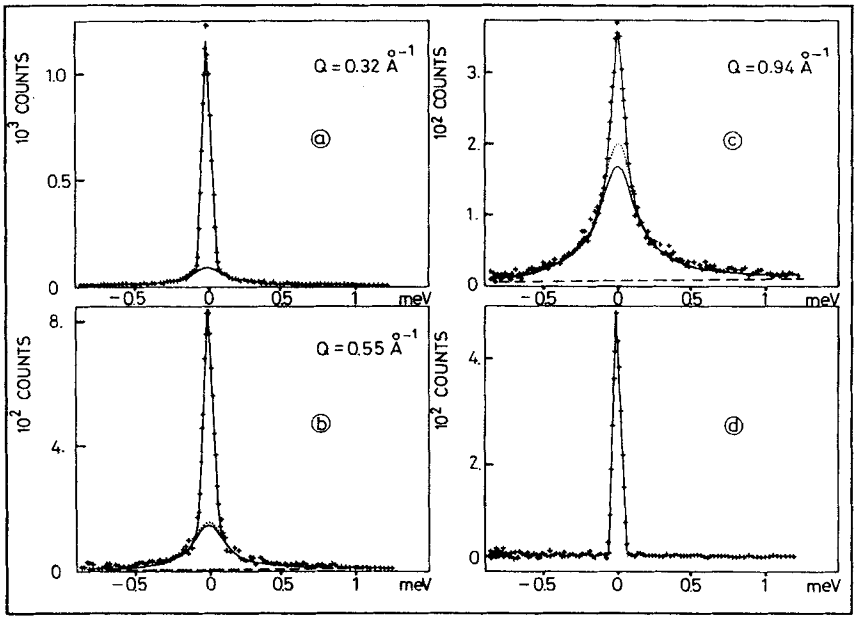

FIGURE 1 ⓐ, ⓑ, ⓒ: examples of corrected NQES spectra obtained with a powder sample of DTBBA at 184°C (Sm A phase), for a few values of the elastic momentum transfer Q; ⓓ instrumental resolution function. The separation between the sharp and broad components, determined by the method described in Ref. 12d is shown for the two hypothesis labelled (i) and (ii) in Section 4—(i) the broadening of the sharp component varies like $2D_tQ^2$ up to 1 Å^{-1} (the full line), (ii) same law up to 0.45 Å^{-1} and then the broadening is constant and equal to 7 μeV (the dashed line). The fitted background is also shown.

0.45 Å^{-1} at least, the broadening of the sharp component is dominated by translational self-diffusion. For $Q = 0.45$ Å^{-1} we get $2D_t Q^2 \approx 7$ μeV, which is rather small compared to the width of the resolution ≈ 67 μeV and the width of the broad component ≈ 250 μeV. The problem occurs at the higher Q values, between 0.45 and 1 Å^{-1}, where similar results do not at present exist. However, we can estimate two limits to this broadening; (i) we assume that the Q^2 law is still valid. This yields a maximum broadening of 35 μeV at 1 Å^{-1}, (ii) we assume that the broadening is constant and equal to its value at 0.45 Å^{-1}, i.e. 7 μeV. With these assumptions, the experimental EISF was determined using the computer method described in Reference 12d and the results are shown in Figure 2. The circles and the squares are the results

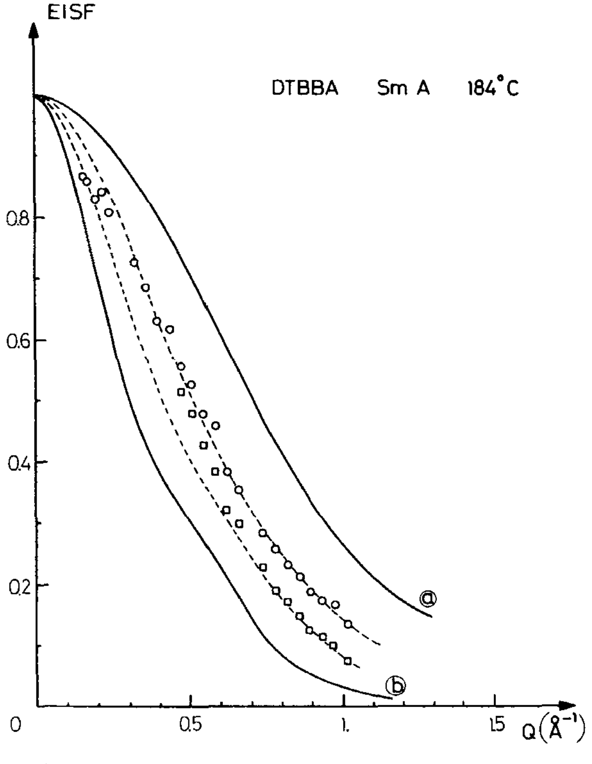

FIGURE 2 Experimental EISF as a function of Q for powder DTBBA at 184°C in the smectic A phase. The circles and the squares correspond to hypothesis (i) and (ii) of Section 4 respectively —(i) the broadening of the sharp component varies like $2D_t Q^2$ up to 1 Å^{-1} and (ii) same law up to 0.45 Å^{-1} and then the broadening is constant and equal to 7 μeV. The best fit of the circles corresponds to either model 1 with $\delta' = 9.0$ or model 2 with $\delta' = 70.0$ and $\lambda_m = 23°$. The best fit of the squares corresponds to either model 1 with $\delta' = 3.5$ or to model 2 with $\delta' = 11.$ and $\lambda_m = 32°$. In each case, the differences between the two models is less than 0.002 in the whole Q range.

obtained using assumptions (i) and (ii) respectively. It is seen that the differences between the two analysis increase with Q and reach a factor of about 2 at $Q = 1$ Å^{-1}. This shows the great importance of the precise knowledge of the true broadening of the sharp component for obtaining a reliable value for the experimental EISF. Clearly, this is not sufficient since the method involves other parameters such as the level of the flat background and the actual shape of the broad component. Any systematical error in these will also affect the results by 10 to 30% (c.f. Figure 4 of Reference 12d).

5 ANALYSIS

The problem is now to find out the meaning of the points in Figure 2 in terms of molecular ordering. The approach we choose is to conceive a model, calculate the theoretical EISF and compare the results to the experiment.

In a Smectic A phase, the molecules are usually pictured as pointing on average towards the normal to the planes. They can rotate around their long axis, this axis can fluctuate about its average position and sometimes flip by π around a short axis. All these motions have certainly occurred many times after a sufficiently long time. However, in the present case, the time scale of the method is a few $(\Delta\omega)^{-1} \sim 10^{-10}$ sec. This means that all the motions whose characteristic time is much longer than 10^{-10} sec are not seen and should be excluded from the analysis. In the present case, the existence of a broad component whose width is significantly greater than $\Delta\omega$ means that at least one of these motions occurs on a shorter time scale $\sim 10^{-11}$ sec. It is reasonable to assume that these are the rotation around the long axis and the axis fluctuations, but that the flip by π should be excluded since the corresponding time scale is expected to be in the radiofrequency region.[18] The distribution $q(\lambda, \phi)$ of the axis should thus be of symmetry 2π in λ since if at time $t = 0$, the axis is pointing near say $\lambda = 0$, after $\sim 10^{-10}$ sec it will still be pointing to about the same direction. The choice of a function with symmetry π would merely mean that the molecule have flipped many times in 10^{-10} sec, an hypothesis we reject for the Sm A phase of TBBA.

At this point it is interesting to discuss why these kinds of considerations are not made in relation with the other techniques. Consider for example NMR or ESR. As with the neutron technique, there exists also a time scale, given by $(\gamma\Delta H)^{-1}$ where γ is the gyromagnetic ratio of the spin in question and ΔH the observed splitting. This corresponds to $\sim 10^{-5}$ sec for NMR and $\sim 10^{-8}$ sec for ESR, in both cases much longer than for neutrons. With these methods, the basic hypothesis done to interpret the measured splitting is that all the motions are rapid on this time scale (extreme narrowing).

The question of flipping by π of the molecule is thus "a priori" important (in particular for ESR) since it is expected to be slow. In fact, it is not relevant. What is measured by these two techniques are quantities involving only the average values of *even* Legendre polynomials (P_2, P_4) and it is known that changing λ to $\lambda + \pi$ does not affect their value. With the neutron method, the situation is quite different since the *odd* Legendre polynomials also play a role (Eq. 8). The calculated EISF will thus be completely different according to the symmetry chosen for the axis distribution function, while the calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ will be essentially the same. This last point will be discussed further in Appendix 1.

Let us now return to our present problem. To calculate the EISF of smectic A TBBA, we therefore assume uniform rotation around the long axis and fluctuations of this axis about its average position taken as polar axis, the symmetry of the corresponding distribution $q(\lambda, \phi)$ being 2π in λ (no flipping). Moreover, since the medium is uniaxial we assume that q is independent of the azimuthal angle ϕ so that we finally take:

$$q(\lambda, \phi) = \frac{1}{2\pi} f(\lambda) \tag{10}$$

With these ingredients, the EISF can now be calculated. The details are given in Reference 12d and the result for DTBBA in a power form is (Eq. 7 of Reference 12d):

$$\overline{A_0(Q)} = \frac{1}{5} \sum_{i=1}^{5} \sum_{l=0}^{\infty} (2l + 1) j_l^2(Qr_i) S_l^2 P_l^2(\cos \mu_i) \tag{11}$$

with

$$\sin \mu_i = a_i / r_i \tag{12}$$

The quantities r_i and a_i are the distances of the five different kinds of protons i of the DTBBA molecule, to the centre of the central ring (the c.o.m.) and to the axis passing through the centres of the three phenyl rings of the molecule in its trans conformation (the body axis), respectively. The quantities S_l are the average values of the P_l calculated with Eq. (10), namely:

$$S_l = \langle P_l \rangle = \int_0^\pi P_l(\cos \lambda) f(\lambda) \sin \lambda \, d\lambda \tag{13}$$

Since all the distances are known (they are given in Reference 12d), the only parameters of the problem are those contained in the function $f(\lambda)$. In what follows, we have chosen two functional forms for $f(\lambda)$, which correspond to models we shall refer to as model 1 and 2, and which have been proposed in Reference 12d.

Model 1

This model corresponds exactly to the conventional textbook picture, where the maximum probability for the axis orientation is along the normal to the smectic planes. To describe the fluctuations, we choose the (normalized) function:[12d]

$$f(\lambda) = f_1(\lambda) = \frac{\delta'}{2sh\delta'}\exp(\delta' \cos \lambda) \tag{14}$$

which is peaked at $\lambda = 0$. The S_l can then be calculated from Eq. (13) and the result is:[12d]

$$\begin{aligned} S_0 &= 1 \\ S_1 &= \coth \delta' - \frac{1}{\delta'} \\ S_{l+1} &= -\frac{2l+1}{\delta'} S_l + S_{l-1} \end{aligned} \tag{15}$$

This model contains only one parameter δ'. Since the relation between δ' and the S_l is univocal, one can choose as parameter any of the S_l, for example S_1, or the more popular S_2. For each value of δ', introducing relations (15) into Eq. (11), one obtains one curve $\overline{A_0(Q)}$. The two extreme cases are $\delta' = \infty$ (i.e. $S_l = 1$) (uniaxial rotation, but no fluctuation) and $\delta' = 0$ (i.e. $S_l = \delta_{l0}$) where in addition to uniaxial rotation, the molecules tumble isotropically. The two corresponding curves labelled ⓐ and ⓑ are shown in Figure 2. (The sums in Eq. (12) were calculated by computer and limited to $l = 14$). It is seen that the experimental points fall between these two curves, as they should. By varying continuously δ' one can thus find a curve which best fits the data. In the present case, we find that the best fit lies certainly between the two dashed curves corresponding to $\delta' = 9$. (i.e. $S_1 = 0.89$; $S_2 = 0.70$) and $\delta' = 3.5$ (i.e. $S_1 = 0.71$; $S_2 = 0.39$). It is seen that the lack of the exact knowledge of the broadening of the sharp component leads to a rather important imprecision on the order parameters, within the framework of the present model.

Model 2

As the above (standard) model 1 appears to be sufficient to explain the data, we could well terminate our analysis here. However, in some circumstances it has been questioned. Firstly, on the basis of NMR line-shapes, it has been suggested,[19] that at least in some smectic A phases "all the molecules are arranged in layers and their axes *tilted* to the normal of the latter and are rotating very fast around this normal direction." Secondly, from X-ray diffraction pattern analysis it has been claimed[20] that smectic A EPAB and TLST "share the common feature of molecular tilt within one smectic layer" and that "the smectic A and C forms must be distinguished on the basis of some property other than tilt within any one layer." Finally, a recent Raman light scattering experiment on a nematic[8b] has shown that the order parameter $\langle P_4 \rangle$ could be negative, a result which indicates that the "molecules have a stronger tendency to be tipped away from the nematic axis than predicted by mean field theory." These three examples share the common feature that, although the studied systems are uniaxial, the molecules appear to be tilted with respect to this axis. This feature can easily be included in a model by choosing for $f(\lambda)$ a function which is no more peaked at $\lambda = 0$, but at some angle $\lambda_m \neq 0$. We thus choose the function:

$$f(\lambda) = f_2(\lambda) = A_2 \exp[\delta' \cos(\lambda - \lambda_m)] \tag{16}$$

with

$$A_2^{-1} = \int_0^\pi \exp[\delta' \cos(\lambda - \lambda_m)] \sin \lambda \, d\lambda \tag{17}$$

The difference with model 1 is now that it is a two parameter model, namely the apex angle λ_m which defines a cone and the quantity δ' which describes the "width" of this cone. Since the angle λ is always around λ_m (at least for sharp, i.e. $\delta' \gg 1$, cones) the molecular axes can be pictured as precessing on this cone. No closed expression is available for the S_l so that they must be calculated numerically from Eqs. (17), (16) and (13). Then using this result in Eq. (11), the EISF can be calculated for each set of values δ', λ_m. It is easily seen that the two extreme cases ($\delta' = \infty$, $\lambda_m = 0$) and ($\delta' = 0$, λ_m arbitrary) are identical to those of model 1 (curves ⓐ and ⓑ in Figure 2). The experimental points can a priori be approached in many ways by adjusting the two parameters. For example, we find that a sharp cone ($\delta' = 70.0$) of apex angle $\lambda_m = 23°$ yields an as good fit to the circles as model 1 with $\delta' = 9.0$, with similar values for the order parameters ($S_1 = 0.90$; $S_2 = 0.72$), while a flatter cone ($\delta' = 11.0$) with an apex angle $\lambda_m = 32°$ (the tilt angle in the Sm H phase) yields a fit to the squares of equal quality than model 1 with $\delta' = 3.5$, with similar order parameters ($S_1 = 0.74$; $S_2 = 0.36$). In fact, the theoretical EISF for the two models differs by less than 0.002 between 0 and 1 Å^{-1}, for the two best fits, and it is thus hopeless to discriminate between these two models from the present results alone. Clearly, more data (e.g. similar measurements on (well) aligned samples at higher resolution) are needed. It is not sure that the neutron data only will be sufficient to solve this problem, but they will certainly be of great value.

negative. However, this would correspond to very open cones ($\lambda_m > 54°$), a situation which is probably not realistic. For comparison, we have also shown in dashed line the theoretical curve predicted by model 1, calculated from Eqs. (A.1 and A.2) where f_2 is replaced by f_1 given by Eq. (14). It is seen that the fit is now rather bad. In particular such a model cannot explain negative values for the order parameters. In this context, it is interesting to compare Figure 3 with Figure 4 of Reference 7a showing the $\langle P_2 \rangle$, $\langle P_4 \rangle$ plot predicted by a Maier–Saupe type theory (i.e. the function $f_1(\lambda)$ is of symmetry π in λ). This curve and ours on Figure 3 are very similar, showing that the even order parameters are insensitive to the symmetry of the distribution function used to calculate them, as mentioned in the text.

Appendix 2

The aim of this appendix is to comment more on model 2. We have seen that our NQES data cannot rule it out for Sm A TBBA. Secondly, from Appendix 1 where we analyse the Raman data of Reference 8b, we have shown that (i) a model type 1 can be excluded, (ii) model 2 explains surprisingly well the data, and (ii) in this case, the apex angle found for the cone is in the range 20–40°. The fact that in the examples considered here, the apex angle of the cone is always found in the same range is perhaps related to some common property of these compounds. Which one? We conjecture that the indication must be sought in the solid crystalline phase. It is indeed remarkable that at least for the few cases where the structure is known[21] (i) the symmetry is found to be low (generally monoclinic), (ii) one of the dimensions of the elementary cell (say the **a** axis) is (much) greater than the two others and (iii) the molecules are generally tilted with respect to the normal **a*** to the corresponding crystallographic plane by an angle whose value is in the range 20–40°. If we thus accept model 2 for the liquid crystalline mesophases, the transition from the solid to a uniaxial mesophase may be pictured as the onset of rotation around the long axis superimposed on a precession of this axis around the **a*** axis, this axis being thus a principal axis of the system (the normal to the planes for a smectic A, the director for a nematics). For a biaxial mesophase such as a smectic C, this picture should be slightly modified by assuming that the precession around **a*** is no longer uniform. Expressed mathematically, this would mean that the azimuthal part $g(\phi)$ of the distribution function $q(\lambda, \phi)$ is not constant, but peaked at some direction[12d] (corresponding to the C-director in a smectic C phase). In this case, the precession should be pictured rather as overdamped librations about the azimuthal maximum position and if the ampiltude of these librations is not too large, translational order may still be maintained in the smectic planes, as for example, in the smectic H phase.

Clearly, these kinds of considerations are conjectural since they apparently contradict presently accepted pictures, and consequently many of the existing microscopic mean field theories. Moreover, it is difficult to imagine the necessarily collective precessional motion implied by the model. However, this model has the virtue of accounting simply for a few results which cannot be explained in terms of the classical pictures and not in contradiction with results which can be explained "classically" (e.g. our present NQES data). In any case, much more accurate experiments involving the high order parameters (Raman scattering of light, ESR, incoherent NQES on aligned samples, diffraction...) are required to confirm or refute this proposition.

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