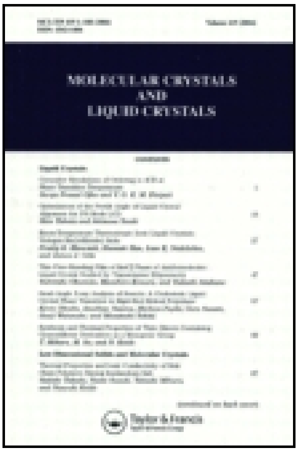

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Bayesian Analysis of Quasielastic Neutron Scattering Data in Liquid Crystalline Phases of 7S5

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BAYESIAN ANALYSIS OF QUASIELASTIC NEUTRON SCATTERING DATA IN LIQUID CRYSTALLINE PHASES OF $\bar{7}$S5.

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Abstract QENS data for the $\bar{7}$S5 liquid crystal (both hydrogenous and chain-deuterated samples) have been analysed from a probabilistic (Bayesian) point of view. When a physical model cannot be proposed for a given reorienting system, it is appropriate to use probability theory to assess how many quasi-elastic components there is most evidence for in the data. A "component" can be thought of both as a single Lorentzian or as a more complex, non-Lorentzian lineshape.

INTRODUCTION

Reorientation motions in liquid crystals of the homologous series of 4-n-pentylphenyl-4'-alkoxythiobenzoates, frequently referred to as $\bar{n}$S5, have been extensively studied for many years, using a variety of experimental techniques (see [1] and references therein). Dielectric relaxation methods, which measure response coming from molecular dipole moments, are mainly sensitive to the reorientation of whole molecules. Fast intramolecular motions, as well as conformational changes within the terminal chains, show as a distribution of dielectric correlation times, and as distortion to the Cole–Cole plots in the high frequency region.

It seemed interesting to get a closer look at this picosecond range reorientation in liquid crystalline phases of $\bar{n}$S5, although a large variety of motions within this time scale made us feel skeptical about possibility of getting any definitive answers [2].

One of the most widely exploited methods to investigate stochastic picosecond-range motions of hydrogen containing objects is the Quasielastic Neutron Scattering (QENS), where purposeful deuteration of selected parts of the molecule can be used to hide them from being seen by the neutrons (incoherent scattering).

Many years of the usage of this method have resulted in a good knowledge of both its power and limitations (cf. e.g. [3]). In our case, the latter come from inability to distinguish among many reorientation processes. Even selective deuteration does not help too much, since: (i) it does not eliminate the contribution from the "unwanted" nuclei to the scattering intensity, but makes it 40 times smaller (for $\bar{7}$S5-d_{26}, incoherent scattering from deuterium contributes 7.5% to the total incoherent scattering from both hydrogen isotopes present in the molecule), and deuteration is never perfect, (ii) mechanical and dynamical couplings are there, so that e.g. motion of deuterated terminal chains will indirectly affect quasielastic scattering from non-deuterated benzene rings.

The "correct" approach to QENS data is to assume a theoretical model of the expected motions, then to least-squares fit its free parameters, and finally to test the hypothesis of it being the right model. An interesting question arises: Does inability to put forward such a model (due to complexity of reorientation and a distribution of conformations) necessarily mean that doing a QENS experiment is a waist of precious beam time? This paper aims at contributing to the answer to the above question.

THE SUBSTANCE

Schematic structure of the molecule is presented in Fig. 1.

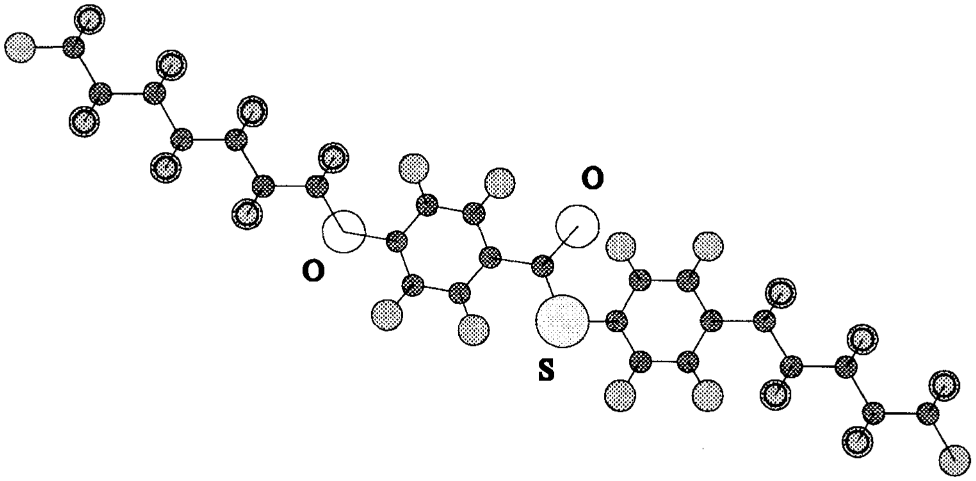

FIGURE 1 Schematic structure (projection) of the $\bar{7}$S5 molecule

$\bar{7}$S5 is known to form two liquid crystalline phases: nematic (N), and monotropic smectic C (S_C). The phase diagram of is shown in Fig. 2 The S_C phase easily transforms into the solid one.

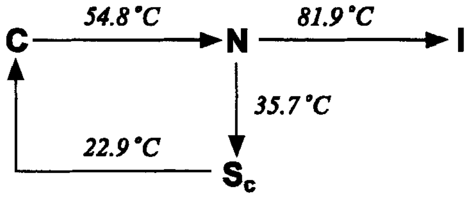

FIGURE 2 Phase diagram of $\bar{7}$S5–d_0 as obtained from DSC.

Both fully hydrogenous $\bar{7}$S5–d_0, and chain-deuterated $\bar{7}$S5–d_{26}, have been synthesized at the Institute of Chemistry of the Agricultural and Pedagogical University at

Siedlce (Poland). Detailed description of the synthesis, as well as the mesomorphic properties of these liquid crystals are given in [4].

THE EXPERIMENT.

Quasielastic neutron scattering was carried out on the IRIS spectrometer at the ISIS Pulsed Neutron Source, Rutherford Appleton Laboratory, England. The inverted geometry spectrometer was configured to use the (002) reflection of pyrolytic graphite crystal analysers, giving a roughly symmetrical resolution line with FWHM of about 15 μeV (as measured on a vanadium standard). With this configuration the recorded spectra covered momentum transfer range (Q) of 0.33 $Å^{-1}$ — 1.87 $Å^{-1}$. The neutron scattering spectra spanned the energy transfer range of ca. ±300 μeV

The IRIS spectrometer collected simultaneously 51 QENS spectra at different scattering angles. These spectra were summed up in groups of three to obtain 17 data sets, each corresponding to their mean scattering angle, or to their mean momentum transfer at $\omega=0$. Standard data reduction was then applied to obtain the $S(Q,\omega)$ dependencies (ω is the energy transfer).

The $\bar{7}$S5 sample was first heated up to the nematic phase (70°C), and then a number of measurements were taken at different temperatures, as shown on the following schematic scenario:

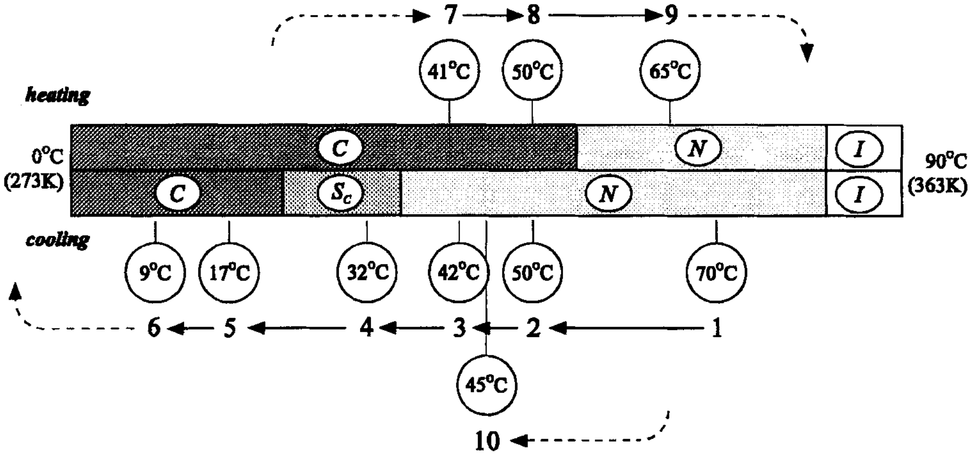

FIGURE 3. Flow diagram of the QENS measurements on $\bar{7}$S5

Chain-deuterated $\bar{7}S5\text{–}d_{26}$ was measured in three temperatures: 70°C (nematic), 45°C (nematic close to the N→S_C transition), and 32°C (smectic C).

DATA ANALYSIS

From a large volume of QENS data published so far for various liquid crystals, especially those with rod-like liquid molecules, it follows that we cannot propose a simple theoretical model, and to reduce the job to obtaining the best estimate for its free parameters. This is due to a large number of intramolecular motions involved, and to the mechanical complexity of the 7S5 molecule, leading to inter– and intramolecular dynamical couplings, whose theoretical treatment is extremely difficult, if at all possible.

In order to treat such cases, a probabilistic approach has been proposed by D.S. Sivia and co., and appropriate algorithm implemented.[5]

Quasielastic spectrum is believed to be a convolution of a certain number of Lorentzian components with the instrumental resolution function, plus some background $b(\omega)$ and noise $\sigma(\omega)$.:

$$d(\omega) = \left[A_0 \delta(\omega) + \sum_{j=1}^{N} A_j \frac{w_j}{\pi(\omega^2 + w_j^2)} \right] \otimes R(\omega) + b(\omega) + \sigma(\varepsilon\omega) \tag{1}$$

where $d(\omega)$ denotes experimental data

The problem we face is:

- To tell how many components there is most evidence for in the data, and
- To provide the best estimates for their parameters

The "best" number of components N is the one that maximizes the conditional probability prob(N) given experimental data (prob(N|d)) To estimate the latter, we first apply the Bayes' theorem:

$$prob(N|d) = prob(d|N) \times prob(N) \tag{2}$$

Assuming no prior knowledge as to the number N, the second term in (2) can be taken as a uniform distribution. Ref [5] estimates prob(N|d) as:

$$prob(N|d) \propto \frac{N!}{(w_{\max} A_{\max})^N} \times \frac{(4\pi)^N \exp(-0.5\chi^2_{\min})}{\sqrt{Det(\nabla\nabla\chi^2)}}, \tag{3}$$

where χ^2 is the best-fit chi-squared given N Lorentzians, and Det($\nabla\nabla\chi^2$) is the Hessian determinant calculated at $\chi^2_{\min}$. $A_{\max}$ and $w_{\max}$ are the estimates of the maximum amplitude and width of any Lorentzian.

This approach in an underlying concept of the actual implementation in the Quasi Lines 2D programme by D.J. Sivia, which was used in this paper. The programme produces the probabilities (3) for 0, 1, 2, or 3 components, and gives the best estimates for the parameters of each Lorentzian involved. The chi-squared minimization is unconstrained in the sense that A_j's and w_j's in (1) are allowed to take on any values.

The above implementation has been tested and proved correct for simulated data [5]. We therefore believe that it is correct, provided the unknown scattering function indeed is a sum discrete Lorentzians. This is the case where e.g. a proton jumps among several sites on a circle.

We would prefer not to use the outlined method without some prior knowledge as to the shape of the scattering function. In [5] the authors assume Lorentzian lineshapes, thus limiting themselves to those physical cases where such an assumption is justified.

There do, however, exist non-Lorentzian lineshapes (quite frequently). Very often they can be expanded into an infinite series of Lorentzians, or they appear as a limiiting case (uniaxial rotational diffusion scattering function can be obtained from a sequence of functions decribing a proton jumping among n equidistant sites on a circle when $n \to \infty$) An attempt to express such shapes in terms of a few (usually very few) Lorentzians can lead to unphysical solutions of e.g. negative amplitudes in (1), and the Loretzians obtained in this way can by no means be called "physical components" and assign physical meaning.

This approach, assuming single Lorentzian components, for simplicity, will be further referred to as "SL".

In $\bar{7}$S5, we have a good reason to assume that some kind of rotational diffusion of the two parts of the molecule (cf. [2]) will largely contribute to the QENS spectrum. By "some kind" we mean anything from uniaxial diffusion to diffusion inside a conical volume. This is why relying on (1) only would be a weak point in our case. Indeed, as we look at the results of Quasi Lines 2D run on all data sets shown in flow diagram in Fig. 3, we discover more than 50% of negative amplitudes. We feel that they cannot be called "quasi-elastic components", although they remain correct expansion terms of unknown scattering functions. Solutions with negative amplitudes have been excluded from further discussion on the grounds that piror probability for such values equals zero.

We therefore decided to try a second approach assuming that the "components" are not single Lorentzians, but rotational diffusion lineshapes. For an unoriented sample, the corresponding scattering function (for a single scattering nucleus undergoing uniaxial rotational diffusion) can be written down as follows: (see e.g. [6])

$$S(Q,\omega) = A_0(Q)\delta(\omega) + \frac{2}{\pi}\sum_{l=1}^{\infty} A_l(Q)\frac{l^2 D_r}{\left(l^2 D_r\right)^2 + \omega^2} \tag{4a}$$

where:

$$A_l(Q) = \frac{1}{\pi}\int_0^{\pi} j_0(2Qr\sin x)\cos(2lx)\,dx\,, \tag{4b}$$

r is the gyration radius for scattering nucleus in question, and D_r is the rotational diffusion constant. Here the quasielastic part is an infinite series of Lorentzians with decreasing amplitudes and increasing widths. A weak point of this approach is our inability to provide a reasonable estimate for the gyration radius of each proton. For the following calculations we assumed values between 2.15Å (benzene ring rotating around its para axis), and 2.5 Å. There is, however, an indication for much greater gyration radii.

Least squares fitting was carried out by means of the CERN MINUIT package, version 94.1. Free parameters (amplitudes and diffusion constants) were allowed to vary within physically acceptable limits (constraint LSQ). Minuit provides a good estimate of the Hessian matrix, which could be used to calculate probabilities (3). This realisation of the concept of finding the most probable number of components hidden in the QENS spectrum, lacks the elegance of D. Sivia's Quasi Lines 2D, and also is very time consuming: Many hours of CPU time had to be spent in order to treat all the spectra in this paper. As a reward, one profits from being able to invest some prior knowledge as to the line shape, and to impose limits on fitted parameters. And last, but not least, one can fine-tune the minimization process by fixing or releasing parameters, choosing the method, and requesting a very detailed error analysis.

For simplicity, this approach will be henceforth referred to as "RD".

Within both approaches, we do not aim at estimating any quantitative physical characteristics of the reorientation observed (such as the rotational diffusion constant). This would be a dubious activity since spectra for different momentum transfers (scattering angles) were processed individually, and no attempt was made to correlate them (as it is the case when a theoretical model is being verified). The resulting amplitudes are scattered and so are the pseudo-EISF values. In some cases LSQ fits gave very narrow or very wide components. Such extreme results lead to high values of correlation coefficient between the corresponding amplitudes and the amplitude of the elastic line (narrow components) or background parameters (wide components). A further consequence is a poor estimate of the EISF.

RESULTS AND DISCUSSION

Chain-deuterated sample.

We begin the analysis with the chain-deuterated sample. In the nematic phase, which is the most "mobile" liquid crystalline one, we are unable to determine the number of quasi-elastic components. In the SL approach, we can see that above $1.4Å^{-1}$, one component is most likely, whereas below $1.4Å^{-1}$ we have evidence for either one or two. In the RD approach, the picture is blurred, and nothing can be said about the number of components. This is a consequence of the complexity of reorientation motions in that phase. A preference of just one Lorentzian component for higher momentum transfers, is an interesting yet easily explainable feature. In this region, smaller gyration radii can be "seen", and more terms have to be taken into account in the expansion of the rotational diffusion scattering function. All such contribution get eventually averaged out to an effective single Lorentzian. Assumption of a non-Lorentzian line shape in the RD approach fails to provide a consistent description in this case, and cannot be considered superior.

As we get closer to the $N \rightarrow S_C$ transition, some motions slow down, and the picture becomes clearer. Within the RD approach, there is most evidence for two components in the QENS data. The SL approach gives the results similar to those obtained at 70°C, but this time the region of the "effective" single Lorentzian at higher Q is clearly smaller. The two-component region grows and seems to dominate.

This tendency is preserved in the smectic C phase, where we can see most evidence for two components in both approaches.

In order to illustrate the kind of information produced within both approaches in Fig. 4 we compare the results obtained for $\overline{7}S5\text{-}d_{26}$ at 45°C, before the $N \rightarrow S_C$ transition. Some probabilities involved are very small indeed. This is why the quantity being usually referred to is base 10 logarithm: $\log_{10}(\text{prob}(N|d))$. In both Figures: 4 and 5, the low Q results are either awkward or missing whatsoever. This is due to the "shadow" produced by a flat sample oriented under the angle of 45° with respect to the beam.

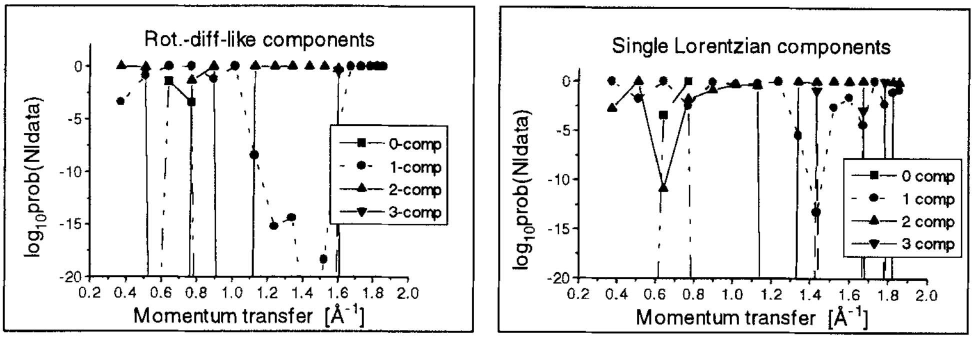

FIGURE 4. Sample $\log_{10}$(prob(N|data)) plots for $\overline{7}$S5-d_{26} within both approaches: "RD" and "SL". Spectra taken at 45°C (318K)

Non-deuterated sample.

Although in the non-deuterated sample we receive much more complex information (most of the quasi-elastic broadening originates from the terminal chains), the main logic of changes remains similar to that discussed above for $\overline{7}$S5-d_{26}.

In the nematic phase, at 70°C we generally have just one RD component, and one, two or three SL components. At 50°C we still receive one RD component, and generally two SL ones. Three SL components are preferred at 42°C, and one or two RD lines. This can be repeated for the smectic C phase, at 32°C. The N→S_C transition, however, can be easily noticed in the pseudo-EISF pictures (see Fig. 4). Similarly, pseudo-EISF witnesses the S_C→Cr transition. In the solid phase, there is an obvious preference for one RD component (but not 0, however!), but the SL approach gives one, or sometimes two. This can be an artifact. A fitted Lorentzian is sometimes very narrow, contributing to the elastic part, of the spectrum, rather than inelastic.

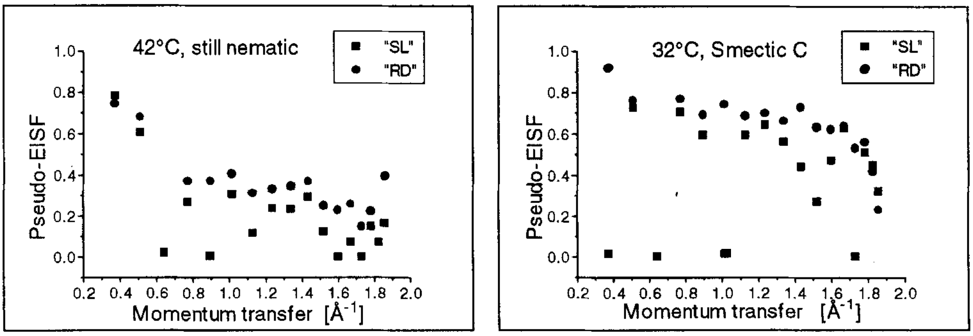

FIGURE 5. Pseudo-EISF as obtained within both approaches before and after the N→S_C transition

Two more measurements were taken in the solid phase: at 9°C (302K), and 7°C (300K), the latter not shown in Fig. 3 in order to preserve clarity. The corresponding $\log_{10}$(prob(N|data)) indicate that the reorientation motions continue to freeze down, with a noticeable difference between the data for 302K and 300K. This can be explained in view of the detailed study of the phase situation in $\bar{7}$S5 [7]. Adiabatic calorimetry measurements indicates that in the solid there are two modifications with distinctly different thermodynamical properties: a stable and metastable ones. The metastable phase can spontaneously transform into a stable one between 294 and 302K, if appropriately triggered by initiating centres of nucleation. If this explanation is correct, then we have a really powerful tool in the probabilistic approach to the QENS data.

When heated up again, the sample regains reorientation mobility, although a kind of hysteresis can be noticed. It is likely that if kept in a given temperature long enough, the transition processes would have more time to complete.

CONCLUSIONS

Both SL and RD approaches are equally arbitrary, since the actual line shapes are probably neither Lorentzian nor exactly RD-like. Comparison of the two sets of results lets us conclude:

1. We are inclined to give a slight preference to the RD approach, as the "best" numbers of components obtained sometimes makes more physical sense than that resulting from SL.
2. We find it difficult to accept that free parameters are allowed to vary from $-\infty$ to $+\infty$. Any number of Lorentzians can be fitted to an unknown lineshape. Solution with negative amplitudes have to be rejected by setting their corresponding prior probability to zero. Consequently, we are unable to assess the "correct" number of components. The problem of "negative amplitudes" is very well known in linear least-squares problems, and received much attention in literature.
3. The RD approach gives much smoother and more reliable results for pseudo-EISF. This is probably caused by the issue discussed in 2. above.

The complexity of the molecule and a multitude of its reorientational degrees of freedom makes the high temperature range of the nematic phase less attractive for further investigation. Some interesting features, however, have been noticed close to the phase transition temperatures, and these regions may still attract some attention in further investigation.

The probabilistic approach to the neutron scattering data, as proposed by D.S. Sivia in [5] and related papers, seems to be a very important tool in the investigation of complex systems, such as polymer chains, or biological macromolecules. The method requires, however, that the collected neutron scattering spectra be of very good quality. Poor signal-to-noise ratio does not allow one to obtain consistent and reliable values for parameters that may be of physical meaning such as line widths.

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