

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Neutron scattering by liquid crystals. A new analysis

J. A. Janik^a; J. M. Janik^b; K. Otnes^c; T. Stanek^b

^a Institute of Nuclear Physics, Kraków, Poland ^b Faculty of Chemistry, Jagiellonian University, Kraków, Poland ^c Institute for Energy Technology, Norway

To cite this Article Janik, J. A. , Janik, J. M. , Otnes, K. and Stanek, T.(1989) 'Neutron scattering by liquid crystals. A new analysis', *Liquid Crystals*, 5: 3, 1045 – 1051

To link to this Article: DOI: 10.1080/02678298908026408

URL: <http://dx.doi.org/10.1080/02678298908026408>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Neutron scattering by liquid crystals

A new analysis

by J. A. JANIK†, J. M. JANIK‡, K. OTNES§ and T. STANEK‡

†Institute of Nuclear Physics, 31-342 Kraków, Poland

‡Faculty of Chemistry of the Jagiellonian University, 30-060 Kraków, Poland

§Institute for Energy Technology, Kjeller, Norway

This paper presents a new analysis of all (old and new) quasi-elastic neutron scattering results obtained for seven members of the PAA series ($n = 1, \dots, 7$). The analysis is based upon a discussion of the parameter p , which is the deviation of the intensity of the elastic component from the intensity demanded by a reorientational model. If the value of this parameter is negative, it may be interpreted as an indication of an additional motion which has not been taken into account in the model. The first model analysed in this way for all seven substances in the nematic phase was that of the rotational diffusion of the whole molecule in its stretched (*trans*) conformation, around the long axis. A very large negative values of p ($p \approx -60$ per cent) was obtained, clearly showing that some motions have been neglected. The second model was that of the rotational diffusion of moieties consisting of benzene rings plus alkoxy side-chains. The diffusion occurs around the benzene para-axes, and the alkoxy side-chains are assumed to be in their *trans* conformations. Less negative values of p ($p \approx -10$ per cent) were obtained, indicating that other motions still exist. Since these must take place in the alkyl chains, we make a third step in the analysis, in which we retain the second model but now take substances which are alkyl-deuterated (which means masking for the neutron incoherent scattering method). Now values of p which are nearly zero are obtained which means that the motions previously ignored indeed exist in the alkyl chains. An even-odd effect observed in the dependence of p on n indicates that even molecules are more mobile than odd ones, probably due to less steric hindrance in more ordered, even substances.

A critical discussion on reorientational correlation times is also presented.

1. Introduction

In a series of papers published in the past 15 years we have tried to derive information on molecular motions in nematic phases of the seven members ($n = 1, \dots, 7$) of the PAA series from incoherent, quasi-elastic neutron scattering (QNS) measurements [1-7]. It should be remembered that, for a system of molecules containing hydrogen which perform stochastic reorientations, the QNS spectrum consists of two components—the elastic one and the quasi-elastic one (see, for example [8]). From the shape of the quasi-elastic component one may, in principle, obtain the reorientational correlation time through model fitting. In our previous works mentioned above such an approach dominated. In this paper we present a critique of this approach. However, we must emphasize that at least the order of magnitude of the correlation times previously obtained was probably valid and lies, for the seven members of the PAA series (in their nematic phases), in the region of several picoseconds. Since this differs markedly from the reorientational correlation times

obtained from dielectric relaxation, which lie in the region of 100 ps, the conclusion that each method detects a different type of reorientational motion is probably valid [9]. We use this conclusion in this paper when discussing the adequacy of one of the models.

Now, let us stress our belief that putting too much significance on the exact value of the correlation time is certainly doubtful and probably meaningless. This is because, if the molecular fragment in question contains several hydrogen atoms (which dominate in the neutron incoherent scattering response), with several gyration radii, then the quasi-elastic component is a complicated superposition of subcomponents. Moreover, the unknown status of the distribution of conformations leads to the practical impossibility of evaluating the subcomponents.

Many authors express an opinion that the most valuable information is obtained from the QNS method by analysing the so-called elastic scattering form factor, i.e. the ratio of the elastic to total (elastic plus quasi-elastic) scattering intensities. In this paper we are going to propose a modification of this approach, as applied to the PAA series.

2. Concept of the 'excess elasticity'

Normally one tries to describe the QNS results for liquid crystals by means of the rotational diffusion model. The fitted function (or the model scattering function) is proportional to (for references, see for example [8])

$$\sigma_{\text{inc}} \frac{k_f}{k_i} \exp\left(\frac{\hbar\omega}{k_B T}\right) S(\boldsymbol{\kappa}, \omega) * G(\omega),$$

with

$$S(\boldsymbol{\kappa}, \omega) = f_0(\boldsymbol{\kappa})\sigma(\omega) + \frac{2}{\pi} \sum_{k=1}^{\infty} f_k(\boldsymbol{\kappa}) \frac{\Gamma_k}{\Gamma_k^2 + (\hbar\omega)^2},$$

where σ_{inc} is the incoherent neutron scattering cross-section for hydrogen, \mathbf{k}_f and \mathbf{k}_i are the scattered and initial neutron wave vectors, $\hbar\omega = E_f - E_i$ and $\hbar\boldsymbol{\kappa} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$ are the neutron energy and momentum transfers, respectively, $G(\omega)$ is the spectrometer instrumental function, $\Gamma_k = \hbar k^2 / \tau_1$, τ_1 is the correlation time connected with reorientation around an axis,

$$f_k(\boldsymbol{\kappa}) = \frac{1}{2} \sum_i a_i \int_0^{\pi} J_k^2(\kappa d_i \sin \beta) d(\cos \beta),$$

a_i is the fraction of hydrogen atoms in the molecule whose radius of reorientation is d_i and the J_k are cylindrical Bessel functions. The parameter β in the integral is connected with various molecular orientations, and the formula for f_k includes averaging over orientations, since our nematic samples were not oriented.

In our modification of this procedure the fitted function contains a $[p\delta(\omega) + (1-p)S(\boldsymbol{\kappa}, \omega)]$ term instead of only $S(\boldsymbol{\kappa}, \omega)$. In this way we are extracting the p -parameter, which (for a given $\boldsymbol{\kappa}$) represents the 'excess elasticity' compared with the model, which includes only the scattering function $S(\boldsymbol{\kappa}, \omega)$.

If the 'excess elasticity' is positive for all reasonable models, it means that reorientation is accompanied by large angle overdamped librations. It is then probably better to analyse the data by using an approach suggested by Dianoux and Volino [10] which corresponds to a motion in a cosine type of potential.

In our case, however, we have to deal with the situation in which p is negative, i.e. instead of an *excess* we have a *lack* of elasticity. Such negative 'excess elasticity' (compared with a model) means simply that in the model some motions have been ignored. Hence, we can try other models until we reach the situation in which p is nearly zero, which corresponds to the model which is in agreement with experiment.

3. QNS results and their discussion for the PAA series

In this study we have reanalysed the old QNS data and, in order to ensure that small differences in experimental conditions which occurred over the years did not affect the results, we performed new QNS measurements in strictly standardized conditions pertaining to sample holders, scattering angle, resolution, etc. For one of the substances (hexyloxyazoxybenzene) the new measurements were the only ones available. After analysis the old data and the standardized new data gave identical results. All (old and new) QNS measurements were carried out on the neutron time-of-flight spectrometer (TOF) installed at the cold source of the JEEP II reactor in the Institute for Energy Technology, Kjeller, Norway. In the new measurements the incident neutron energy was 4.66 meV. The energy resolution of the spectrometer was 0.137 meV. In the new measurements the 30° scattering angle was used, which corresponded to momentum transfer of about 0.8 Å⁻¹. The time-of-flight spectra were converted to an energy scale.

The sample was mounted in an oven with a temperature control. The inelastic background was estimated and drawn as a smooth line through the ends of the quasi-elastic wings of the spectra. The values of this line were subtracted in order to obtain the isolated quasi-elastic plus elastic components. For each sample measurements were made for at least two temperatures in the nematic phase. Moreover, they were made at room temperature for the solid sample in order to determine the resolution.

As was mentioned in §2, the model spectra were convoluted with the resolution function when fitted. The model fittings were made on the CYBER 72 computer using the program MINUIT from the C.E.R.N. Computer Library [11]. All old and new QNS spectra were newly processed. The parameters which had to be adjusted were the 'excess elasticity' p and the reorientational correlation time τ_1 . The best-fit values of the adjustable parameters for the models were obtained by using a χ^2 test.

Before showing the results, it will be useful to present the molecule and to suggest which reorientational motions (external and internal) are likely to occur. Figure 1 shows the molecule. The external motion, which can be considered as a candidate for

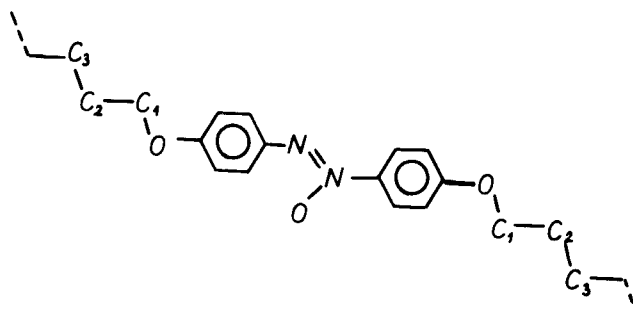


Figure 1. View of the 4,4'-di-*n*-alkoxyazoxybenzene molecule. Hydrogen atoms are omitted.

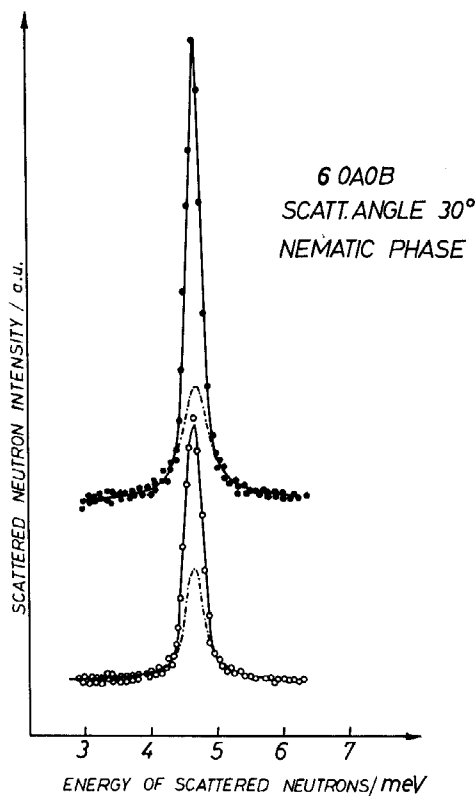


Figure 2. QNS (quasi-elastic plus elastic) spectrum of normal (○) and alkyl side-chain deuterated (●) 6-OAOB. Both spectra are normalized so that their quasi-elastic components are nearly equal (—). The higher elastic component for the side-chain deuterated substance corresponds to a larger 'excess elasticity' value of p , compared with the normal substance. Temperature +120°C, nematic phase.

showing up in the QNS 'time window', is (a) the reorientation around the long axis. The internal motions, which can be considered as such candidates are: (b) reorientations of moieties composed of benzene rings plus alkoxy side-chains, around the C_{ar} -N axes, (c) reorientations of alkoxy side-chains, around the C_{ar} -O axes, and some conformation changes in the side-chains.

Figure 2 shows an example (hexyloxyazoxybenzene) of the QNS results. Figure 3 shows the 'excess elasticity' parameter p versus the number of carbon atoms in the side-chains, n , as derived from model (a), which assumes a rotational diffusion of the whole molecule (in its *trans* conformation) around the long axis. It should be noted that values of p in the figure correspond to clearing temperatures. Such values of p were obtained from those measured at somewhat lower temperatures by using extrapolated temperature dependences.

We interpret the results in the following manner. Let us initially ignore the even-odd effect (which will be discussed separately). The picture shows a systematic increase of the negative value of p , when going from PAA to heptyloxyazoxybenzene (7-OAOB). For PAA the value of p is about -11 per cent, whereas for 7-OAOB it is about -64 per cent. The increasing negative tendency is shown by the broken line in figure 3. That the values of p are negative demonstrates that we have ignored an

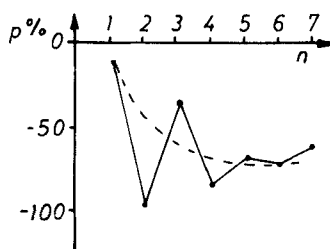


Figure 3. 'Excess elasticity' p versus alkyl side-chain length n as derived from model (a), i.e. that of rotational diffusion of the whole molecule around its long axis of inertia. Normal substances. The broken line shows the average tendency of decrease in p . Values of p correspond to the clearing temperatures T_c . The figure corresponds to the scattering angle of 30° .

additional motion in our model in which the side-chains take part. The increasing negative tendency with n is natural, since the number of hydrogen atoms involved in this additional motion increases with n . Hence, we reject model (a). It must also be noted that this model gives reorientational correlation times of the order of several picoseconds, whereas it is generally accepted that the dielectric relaxation times (which are of the order of 100 ps) are correct for the reorientation of the molecule as a whole.

Figure 4 shows the 'excess elasticity' parameter p versus n for model (b), which assumes a rotational diffusion of the benzene rings plus alkoxy side-chains moieties around the $C_{ar}-N$ axes. When interpreting this, let us again ignore for the moment the even-odd effect. We now observe much lower negative values of p which are about -8 per cent for PAA and about -11 per cent for 7-OAOB. The increase of the negative tendency with n has practically disappeared. We are now ignoring whole-molecule rotations since the dielectric relaxation times, which we believe are nearly correct, lead to QNS broadenings which are invisible at the resolution used. (In other words, the whole molecule reorientation is outside of the 'time window' of our QNS method.) We conclude that model (b) is much closer to reality than model (a), but some additional motions have still been ignored.

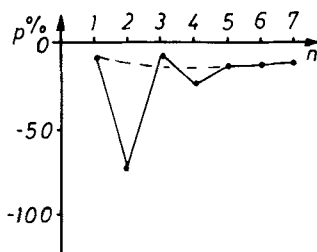


Figure 4. 'Excess elasticity' p versus n as derived from model (b), i.e. that of rotational diffusion of moieties composed of benzene rings plus alkoxy side-chains around the $C_{ar}-N$ axes. Normal substances. The broken line shows that the average tendency of decreasing p almost disappeared. Values of p correspond to the clearing temperatures T_c . The figure corresponds to a scattering angle of 30° .

It now would be logical to try a model which takes into account, in addition, the motions in the alkyls. However, it is very difficult to suggest which fragments rotate around which axes, etc. Therefore, we decided to eliminate the additional motions of

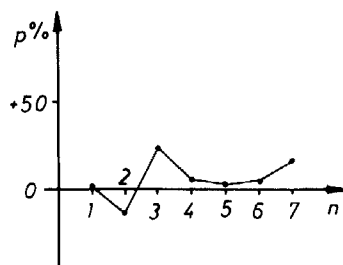


Figure 5. 'Excess elasticity' p versus n as derived from the same model as in figure 4, but for the alkyl side-chain deuterated substances. Values of p are near to zero. They correspond to the clearing temperatures T_c . The figure corresponds to a scattering angle of 30° .

the (c) type empirically by making QNS measurements with side-chain deuterated samples. (We remind the reader that deuteration means masking for incoherent neutron scattering.) Figure 5 shows p versus n values obtained under these circumstances. The moieties rotation was assumed to be the same as in model (b). Again ignoring the even-odd effect for the time being, we see that the values of p are near to zero, which may be interpreted as an adequate description of the facts by the model.

Let us now make some remarks in connection with the observed even-odd effect in p . First it must be remembered that quite a number of physical quantities show such an effect, when measured against n for an homologous series of liquid crystals. Among such quantities are, for instance, the melting and the clearing points. The translatory diffusion coefficients also show a similar alternation, as measured by Noack for the PAA-series [12]. As stated by Marčelja [13], 'the addition of carbon atoms C_2 increases the anisotropy of the molecule and helps the ordering process, subsequent addition of atoms C_3 hinders the ordering, atoms C_4 help again, and so on. As the chains become longer, their flexibility makes the effect progressively smaller until, for long end chains, it becomes unnoticeable'. By means of this mechanism Marčelja obtains theoretically the alternation of the nematic order parameter, which indeed was observed experimentally [14].

When we first noticed the effect of p alternation in our experimental results, we thought that it may be a secondary effect connected with the fact that the temperatures of the measurements differed from the clearing points by various amount. This possibility was eliminated by extrapolating all results to the clearing points. Another possibility was that our effect is caused by not taking into account the translational diffusion in our model calculations. We therefore corrected our calculations for translational diffusion, using the Noack data quoted above [12]. Again the correction happened to be very small. Thus, we must conclude that the p alternation is real and must be connected with the rotational properties. We think that in the even members of the PAA series (especially for $n = 2$) the higher degree of nematic order causes less steric hindrance to all kinds of motions in the alkyls. The odd members (especially $n = 3$) show large steric hindrance. In this way we interpret the p alternation via the nematic order parameter alternation, or (more specifically) via the alternation of rotational hindrance in the side-chains. It should be noted that the even-odd effect can be seen not only in Figures 3 and 4, corresponding to normal substances, but also in figure 5, corresponding to the side-chain deuterated substance. We believe that all motions occurring in the side-chains, which for a side-chain deuterated sample should

be invisible for neutrons, cause fluctuations of the long molecular axis and hence affect the dynamics of the hydrogen atoms in benzene rings.

Two of us (J.A.J. and J.M.J.) express our gratitude to the Institute for Energy Technology at Kjeller for the financial assistance during stay in Norway. Our thanks are also due to Professor A. Suszko-Purzycka, Dr D. Chruściel and Dr J. Chruściel for obtaining the normal and side-chain deuterated samples. We also thank Dr J. Krawczyk for his help in the computer calculations.

References

- [1] JANIK, J. A., JANIK, J. M., OTNES, K., and ROŚCISZEWSKI, K., 1976, *Physica B + C Amsterdam*, **83**, 259.
- [2] ROŚCISZEWSKI, K., 1972, *Acta phys. pol. A*, **41**, 549
- [3] JANIK, J. A., JANIK, J. M., OTNES, K., KRAWCZYK, J., and ROŚCISZEWSKI, K., 1977, *Physica B + C, Amsterdam*, **92**, 351.
- [4] CHŁĘDOWSKA, K., JANIK, B., KRAWCZYK, J., JANIK, J. A., JANIK, J. M., and OTNES, K., 1986, *Liq. Crystals*, **1**, 127.
- [5] JANIK, J. A., JANIK, J. M., KRAWCZYK, J., and OTNES, K., 1982, *Molec. Crystals liq. Crystals*, **89**, 171.
- [6] NGUYEN, X. P., KRAWCZYK, J., CHRUSCIEL, D., CHRUSCIEL, J., JANIK, J. A., JANIK, J. M., OTNES, K., KRESSE, H., NATKANIEC, I., URBAN, S., and WRÓBEL, S., 1986, *Liq. Crystals*, **1**, 561.
- [7] CHŁĘDOWSKA, K., CHRUSCIEL, D., JANIK, J. A., JANIK, J. N., KRESSE, H., STETTIN, H., OTNES, K., STANEK, T., URBAN, S., and WRÓBEL, S., 1988, *Liq. Crystals*, **3**, 1339.
- [8] JANIK, J. A., and RISTE, T., 1987, *Methods of Experimental Physics*, edited by K. Sköld and D. D. Price (Academic Press), Vol. 23, Chap. 17, Part B.
- [9] JANIK, J. A., JANIK, J. M., 1986, Report No. 1305/PS, Institute of Nuclear Physics, Kraków. JANIK, J. A., JANIK, J. M., 1986, *Zehn Arbeiten über Flüssige Kristalle*, Vol. 52, edited by Martin-Luther-Universität Halle), p. 4.
- [10] DIANOUX, A. J., and VOLINO, F., 1967, *Molec. Phys.*, **34**, 1263.
- [11] JAMES, F. and ROSS, M., MINUIT, C.E.R.N. Computer Library.
- [12] NOACK, F., 1984, *Molec. Crystals liq. Crystals*, **113**, 247.
- [13] MARČELJA, S., 1974, *J. chem. Phys.*, **60**, 3599.
- [14] LIPPMANN and WEBER, 1957, *Annln Phys.*, **20**, 265.