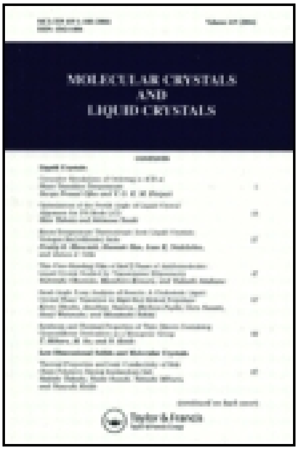


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Molecular Dynamics in a Partial Bilayer Smectic A Phase by Proton NMR Relaxation

A. C. Ribeito [a]
[a] Centro de Fisica da Matéria Condensada, Av. Gama Pinto, 2, 1699, LISBOA Codex, Portugal

Version of record first published: 17 Oct 2011.

To cite this article: A. C. Ribeito (1987): Molecular Dynamics in a Partial Bilayer Smectic A Phase by Proton NMR Relaxation, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 151:1, 261-271

To link to this article: http://dx.doi.org/10.1080/00268948708075336

Mol. Cryst. Liq. Cryst., 1987, Vol. 151, pp. 261-271
Photocopying permitted by license only

Printed in the United States of America

MOLECULAR DYNAMICS IN A PARTIAL BILAYER SMECTIC A PHASE BY PROTON NMR RELAXATION

A.C. RIBEIRO
Centro de Física da Matéria Condensada, Av. Gama Pinto, 2, 1699 LISBOA Codex, Portugal

Abstract The dynamics of a partial bilayer smectic A phase is studied for the p-|(p-dodecyloxybenzylidene) --amino| benzonitrile by the NMR technique. The proton spin relaxation rate $1/T_1$ has been measured as a function of the Larmor frequency between 5.6 and 84 MHz and as a function of the temperature for the whole domain of the smectic A phase. The relaxation measurements are discussed in terms of potential contributions of different molecular motions, namely translational self diffusion, rotations/reorientations and order director fluctuations. In the high frequency limit the relaxation is dominated by rotations/reorientations while translational self diffusion is dominant in the low frequency region. For all the frequencies of work it seems that order director fluctuations have a small contribution to the relaxation. This unsual result for a S_A phase must reflect the particular distribution of the polar asymmetric molecules in the smectic layers and also the molecular structure.

1 - INTRODUCTION

Many papers concerning the study of molecular dynamics by Nuclear Magnetic Resonance in monolayer smectic A phases of liquid crystals are reported in literature. However the molecular dynamics in partial bilayer and bilayer smectic A phases is not very known. In this paper we present new results obtained with a liquid crystal of asymmetric molecules with a strong polar terminal group (CN) that exhibits a partial bilayer smectic A phase[1].

Systematic measurements of the proton spin-lattice relaxation time T_1 were performed as a function of temperature and Larmor frequency in the isotropic and smectic A phase of p-|(p-dodecyloxybenzylidene)-amino| benzonitrile (hereafter abbreviated 12CN).

As it will appear below, in the smectic A phase of 12CN the frequency dependence of the spin lattice relaxation rate is rather peculiar in confrontation with the usual behaviour detected in other S_A phases[8-13].

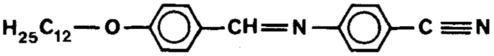
In section 2 we mention the techniques used in this work and we present the experimental data with a brief comment. In section 3 we analyse the experimental data relative to the smectic A phase in terms of different mechanisms which are expected to contribute to the relaxation. The results we have so obtained are discussed in section 4 where we also contrast our conclusions about the molecular dynamics in the S_A phase to those different structural models[3-6] proposed to explain the partial bilayer behaviour of some smectic phases.

An extension of this research work including results obtained with other similar compounds with the same molecular core but with a different chain length will be presented in a forthcoming paper[18].

Preliminar results of this paper[17] were presented at I Simpósio Ibérico de Física da Matéria Condensada.

2 - EXPERIMENTAL TECHNIQUES AND EXPERIMENTAL DATA

The synthesis of 12CN was described in[2]. Its molecular structure is given below:



After purification, the sample (0.5 cm^3) used in our NMR experiment was degassed and sealed in an evacuated glass tube (∅ = 10mm). The degassing pressure was less than 10^{-4} mbar. This compound shows the following sequence of phases:

$$K \xrightarrow{62,2\,^{\circ}C} S_A \xleftrightarrow{103\,^{\circ}C} I$$

Measurements of the spin lattice relaxation time were performed at eight frequencies f between 5.6 and 84 MHz. For each frequency the temperature was varied over the whole smectic A phase and at least up to 17°C above the clearing point. T_1 was measured by the $\pi-\tau-\pi/2$ pulse sequence with a Bruker SXP/4-100 MHz spectrometer. The temperature of the sample was controlled to within ±0.3°C and the experimental error in the value of T was less than 1 °C.

Figure 1 shows the experimental results of T_1 as a function of the temperature for two working frequencies. One paramount feature of our experimental results is evident in figure 2, where the obtained values of $1/T_1$ are represented as a function of $f^{-1/2}$ for two temperatures in the S_A phase, namely the strong deviation of the classical dominant behaviour ($1/T_1 \simeq Bf^{-1/2}$) usually detected in conventional smectic A phases[8-13]. In fact this

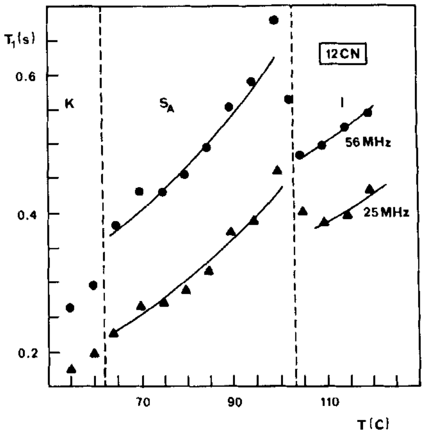


FIGURE 1. Temperature dependence of the proton spin lattice relaxation time T_1.

representation seems to show that order fluctuations are not the dominant mechanism of relaxation in the S_A phase of 12CN; by the other hand for each working temperature the representation of $1/T_1$ as a function of $f^{1/2}$ gives with a

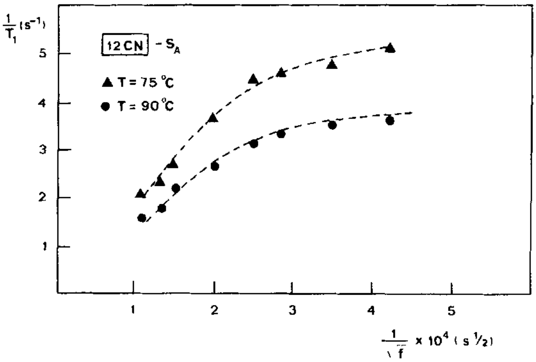


FIGURE 2. Experimental results of $1/T_1$ as a function of $f^{-1/2}$ for two temperatures in the S_A phase. The curves are simply guides for the eye, they have not a theoretical origin.

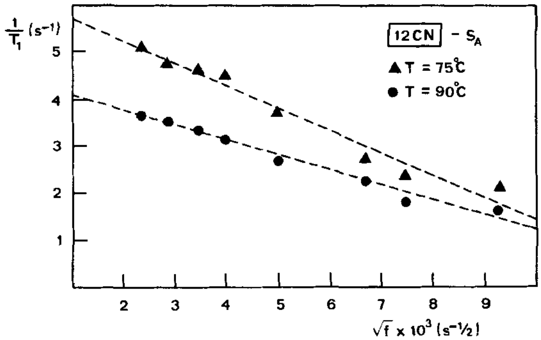


FIGURE 3. Experimental results of $1/T_1$ as a function of $f^{1/2}$ for two temperatures in the S_A phase.

reasonable approximation a straight line, as evidenced in figure 3, and this result agrees with the possibility of a strong contribution of self-diffusion to the relaxation[7]. Figure 4 shows two possible fits of our experimental results at T≈90 °C and the contributions of different mechanisms to the overall relaxation as described in section 3 of this paper.

3 - ANALYSIS OF THE DATA RELATIVE TO THE S_A PHASE

In the smectic A phase the experimental results were analysed in terms of three mechanisms of relaxation namely translational self diffusion, rotations/reorientations and order director fluctuations.

To describe self diffusion we have used, as proposed by Vilfan and Zumer for S_A phases[11,13], the classical corrected Torrey's theory[14] with a reduction factor of 1.4[11] with $\tau_{Torrey} = \tau_\perp$ and $< r_\perp^2 > = d^2$ being $\tau_\perp$ the average time between flights within layers ($D_\perp$ is the associated diffusion coefficient), $< r_\perp^2 >$ the mean squared flight distance within layers and d the closest approach distance of molecules within layers. The value of 5Å has been imposed for d[1].

To describe order director fluctuations we have used the classical contribution[9] $Bf^{-1/2}$ taking in account the recent results of Vilfan et al[15] that confirm this behaviour in smectic A phases for frequency domains in which our measurements are clearly included.

The rotations of molecules around their long molecular axes, nearly isotropic motions of aliphatic chains and orientational fluctuations of the long molecular axes, are described by superposition of Lorentzians, but in our domain of frequency measurements this contribution must be reduced to a constant term A dependent only on temperature[8,9].

For each temperature the experimental results are then fitted with:

$$1/T_1 = (1/T_1)_{SD} + (1/T_1)_{OF} + (1/T_1)_R =$$
$$(1.4)^{-1} \cdot (1/T_1)_{Torrey} + Bf^{-1/2} + A \qquad (1)$$

being A and B free parameters and varing $\tau_\perp$, in the Torrey's expression between values with physical meaning for a smectic A phase[16]. As an example, the parameters associated with two of the best fits for T = 90°C are described in the table I. These fits and the different contributions to the overall relaxation are represented in figure 4 (the value of the spin density is $n=5.09 \times 10^{22}$ spins/cm^3).

TABLE I. Parameters associated to fits represented in figure 4.

FIT	$\tau_\perp$(s)	$D_\perp$ (cm^2 s^{-1})	B(s$^{-3/2}$)	A(s^{-1})
———	1.89×10^{-9}	3.30×10^{-7}	202	1.19
— — —	1.54×10^{-9}	4.06×10^{-7}	1601	1.02

Concluding the section 3 we must say that we also have fitted the experimental results using Vilfan and Zumer theory[11] to describe self diffusion instead of Torrey's expression. However the fits obtained by the two theories are very similar in their behaviour and also in the values of the obtained physical constants. Therefore we present here only the results obtained by Torrey's theory used as a first approximation to describe the contribution of diffusion to the relaxation in a smectic A phase whose structural details are not very well known; however we must remark once again that Torrey's theory seems to describe very well the diffusion contributions in S_A phases[11,13].

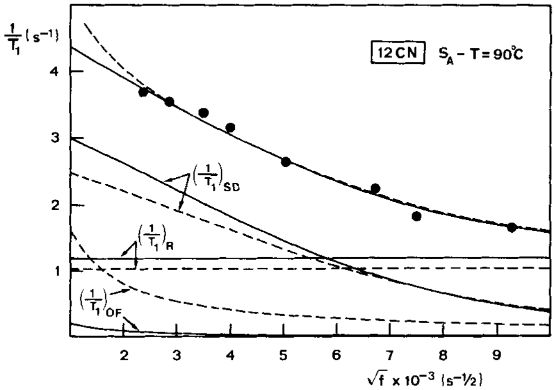


FIGURE 4. Fits of the experimental results of $1/T_1$ as a function of $f^{1/2}$ for T=90°C and contributions of different mechanisms to the relaxation.

4 - DISCUSSION AND CONCLUSIONS

The fit on continuous black represented in figure 4 is the best one (minimum error) however only measurements in a very low region of frequencies, not available in our spectrometer, could clarify the selection between one of the two represented fits. In any case the conclusions obtained from the two fits are essentially the same, namely:

- self-diffusion is the predominant contribution in the low frequency domain (in fact for five of the eight explored frequencies).
- the value of the constant A associated with rotations/reorientations is clearly elevated in confrontation with other published results[8-13] obtained with conventional smectic A phases. Our estimation gives for the correlation times of these motions values $\tau_R > 3.10^{-11}$ s.
- the contribution $Bf^{-1/2}$ associated with order fluctuations is very low and this contribution is not predominant in any region of our explored frequency domain.

All the conclusions presented above are very unusual in smectic A phases but these conclusions must be correlated with the particular structure of this partial bilayer phase and also with the proton distribution in the molecules. Usually in S_A phases order fluctuations are the predominant mechanism of relaxation in large frequency domains, but our experimental results and the proposed interpretation seem to deny that in the case of 12CN. In fact, recent theoretical results by Vilfan et al[15] confirm once again that order fluctuations in S_A phases would give a dependence of the type $1/T_1 \simeq Bf^{-1/2}$ for frequencies above the MHz. In our case the deviation of this law takes place at 16MHz (see figure 2) and this result and also the representation evidenced in figure 3 would be good arguments to understand the proposed low contribution of order fluctuations to the relaxation. By the other side, this result must also be correlated with the proton distribution in the molecule of 12CN. In fact, we are observing molecules with only 9 protons in the core and 25 in the chain and we remind that the most important contribution to order fluctuations comes from the core protons (26% of the total).

The results presented here and the proposed interpretation make possible to do some comments about those models proposed to explain the structure of partial bilayer smectic phases of asymmetric and highly polar molecules[3-6], namely:

- the strong contribution of self-diffusion to the relaxation is compatible with Leadbetter model[6] in which an important longitudinal diffusion of molecules is described as responsible for the partial bilayer behaviour. Nevertheless we don't know how to justify with this model the high value of the term A associated to rotations/reorientations.
- the model of Cladis[5], with the aromatic cores of molecules overlapped one another in antiparallel pairs within the layers, could probably justify the high value of A because the motions of rotation/ /reorientation of coupled pairs would occur slower in a theoretical confrontation with motions of isolated

molecules.

- the model of Guillon and Skoulios[3-4] with single molecules and pairs of molecules associated polar head to polar head within the smectic layers could justify very well the strong contribution of self-diffusion to the relaxation because this model predicts the dissociation/reassociation of pairs and also the diffusion of single molecules and pairs of molecules within layers and between layers. From the local motions of pairs could probably come the most important contribution of term A.

In conclusion, our results show that the relaxation in the smectic A phase of 12CN is interpreted in terms of self-diffusion, rotations/reorientations and order fluctuations.

In the high frequency limit the relaxation is dominated by rotations/reorientations while translational self--diffusion is dominant in the low frequency region. For all the frequencies of work it seems that order fluctuations have a small contribution to the relaxation. This unusual result for a S_A phase must reflect the particular distribution of the polar asymmetric molecules in the smectic layers and also the proton distribution in the molecules.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. A. Skoulios and Dr. D. Guillon (CNRS - Strasbourg) who supplied the sample. I thank Dr. A. F. Martins for his helpful suggestions. I also thank M. I. Sampaio for the careful typing.

REFERENCES

1. P.Seurin,D.Guillon and A.Skoulios, Mol.Cryst.Liq.Cryst, 71,37(1981)
2. P.Seurin,D.Guillon and A.Skoulios, Mol.Cryst.Liq.Cryst, 65,85(1981)
3. D.Guillon and A.Skoulios, Mol.Cryst.Liq.Cryst.,91,341 (1983)
4. D.Guillon and A.Skoulios, J.Physique,45,607(1984)
5. P.E.Cladis,R.K.Bogardus and D.Aadsen, Phys.Rev.A,18,2292 (1978)
6. A.J.Leadbetter,J.C.Frost,J.P.Gaughan,J.Phys.,40,375 (1979)
7. M.Vilfan,R.Blinc and J.W.Doane, Solid State Commun.,11, 1073(1972).
8. R.Blinc,M.Luzar,M.Vilfan and M.Burgar, J.Chem.Phys., 63,3445(1975)
9. R.Blinc,M.Vilfan,M.Luzar,J.Seliger and V.Zagar, J.Chem. Phys.,68,303(1978)
10. M.Vilfan,Dissertation,University of Ljubljana(1978)
11. M.Vilfan and S.Zumer, Phys.Rev.A,21,672(1980)
12. R.Y.Dong, J.Mag.Res.,48,280(1981)
13. M.Vilfan,R.Blinc and V.Rutar,Mol.Cryst.Liq.Cryst.,114, 271(1984)
14. H.C.Torrey, Phys.Rev.,92, 962(1953)
15. M.Vilfan,M.Kogoj and R.Blinc,J.Chem.Phys.,86,1055(1987).
16. G.J.Krüger, Phys.Rep.,82,229(1982)
17. A.C.Ribeiro and A.F.Martins,Actas do I Simpósio Ibérico de Física da Matéria Condensada,Lisboa(1984)
18. A.C.Ribeiro and P.Sebastião, to be published