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QENS AND NMR INVESTIGATION OF MOLECULAR DIF FUSION IN THE NEMATIC PHASE OF EBBA

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Abstract In this paper we present a combined Quasi Elastic Neutron Scattering and ^{13}C magnetic relaxation study of the molecular dynamics in the nematic phase of EBBA. Attention has been focused on the relatively rigid biphenylic core of the molecule. In both cases a global model dependent fit of the obtained data has been performed. We were able to separate the rotational and translational contributions to QENS. The translational broadening displays an anomalous behavior in the high Q region which has been discussed against different diffusional mechanisms. The values of the rotational diffusion around the long molecular axis has been extracted as a function of temperature and compared to those measured with ^{13}C magnetic relaxation of the orthophenylic

carbons. Finally, the flexibility of the considered molecular fragment has been taken into account in interpreting the ^{13}C relaxation data.

Keywords: nematics, molecular diffusion, QUENS, NMR

INTRODUCTION

The molecular dynamics in the nematic phase and especially in the smectic phases has been extensively studied with quasi elastic neutron scattering (QENS)[1-11] as well as with magnetic relaxation[12-17]. Nevertheless, these two different techniques have never been combined probably due to the fact that, quite often, the obtained results did not agree. The situation is particularly difficult in the nematic phase, where translational and rotational time scales are not too separated. In a previous preliminary work[18], we used the high resolution, high momentum transfer IRIS spectrometer at RAL to study QENS in the nematic phase of EBBA (ethoxybenzylidene-bis-butyl-anyline). Although we succeeded in separating the translational and rotational (spinning) contributions to the quasi elastic broadening, the temperature behavior of the spinning diffusion coefficient derived from our data still disagreed with similar data obtained by NMR relaxation. In this work we demonstrate that a good agreement of the measured dynamical parameters can be obtained if all the relevant dynamical processes, including molecular flexibility, influencing the broadening of the quasi elastic line in QENS and the relaxation time in NMR are taken into account adopting a model dependent global fit of the data for both the techniques. The comparison of the QENS and NMR results leads to a more precise picture of the molecular diffusion in the nematic mesophase.

Due to the 15 μeV energy resolution of the neutron spectrometer we expect that both the translational diffusion of the molecules and their rotational diffusion around the long axis (*spinning*) will contribute to the quasi elastic

broadening of the elastic line while the diffusion around the short axis (*tumbling*) is expected to be too slow to produce observable effects.

The pure orientational dependence of the dipolar interaction, on the contrary, guarantee that the reorientation of the molecule is the only dynamical process responsible for the relaxation of the ^{13}C nuclei. In this case both the spinning and the tumbling motion are expected to contribute, while the slow collective fluctuations of the nematic director are supposed to have a negligible effect at the observed Larmor frequencies[17]. In both cases, the flexibility of the probed molecular fragment should be taken into account.

NEUTRON SCATTERING

Experiment

The inverse geometry, time of flight spectrometer IRIS combines a resolution of 15 μeV to a exchanged momentum (Q) ranging from 0.25 $Å^{-1}$ to 1.85 $Å^{-1}$; the incident energy is 1.82 meV [19]. EBBA was selectively deuterated along the alkyl chains in order to "blind" the measurement of their motion, spectra were taken at four temperatures within the nematic phase (T= 308K, 317K, 327K and 337K) and in the isotropic phase (T= 346.5K). The sample was contained in a slab-shaped cell (50 × 50 mm) made of thin boronless glass. Its inner surfaces have been treated with surfactants in order to get a homogeneous alignment in the nematic phase. In order to enhance the scattering due to spinning dynamics the nematic director was aligned perpendicular to the scattering plane. The sample thickness was 250 μ which yielded a transmission coefficient of 0.87. 29 spectra have been recorded covering an angular range from 15° to 165°. Standard programs have been used to correct data for: absorbtion, self shielding, sample holder absorbtion, detectors efficiency, empty cell subtraction, monitor normalization, background subtraction. The energy integrated inten-

sity has been checked to follow a regular Debye-Waller behavior with respect to Q in order to rule out possible coherent scattering from the sample.

Theory and data analysis

The observed quantity in a neutron scattering experiment is the double differential cross section $\frac{d^2\sigma}{d\Omega dE'}$ where Ω is the solid angle and E' is the final energy. It can be expressed as the time Fourier trasform of the scattering law $S(\mathbf{Q},t)$:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\ exp\{-i\omega t\}S(\mathbf{Q},t) \qquad (1)$$

where $\hbar\omega$ is the exchanged energy $E'-E=\hbar\omega$ and $\mathbf{Q}$ is the exchanged momentum $\mathbf{k}'-\mathbf{k}=\mathbf{Q}$. Due to the very high incoherent scattering length of hydrogen (referred to as b), the observed scattering can be assumed to be entirely due to this nucleus. As a consequence the scattering law can be expressed as an ensemble average of the following self correlation function of the position of the scattering nucleus $\mathbf{R}$:

$$S_{incoh}(\mathbf{Q},t) = \sum_l |b_l|^2 \langle exp\{i\mathbf{Q}\cdot\hat{\mathbf{R}}_l(0)\}exp\{i\mathbf{Q}\cdot\hat{\mathbf{R}}_l(t)\}\rangle \qquad (2)$$

which, in the classical limit, is proportional to the space Fourier trasform of the self correlation function of $\mathbf{R}$[20].

All the different motions of the molecules (translation, rotation, flexibility, vibrations) contribute in principle to the quasi elastic broadening. If we assume that all these movements are completely decoupled, the scattering law can be expressed as the product of the such contributions, so that the differential cross section results as the convolution of those originating from the different dynamical processes.

As it is well known[20], the vibrations contribute to a scattered intensity in the inelastic region with a consequent decrease of the intensity in the quasi

a Mayer-Saupe form) of the rotation axis around the nematic director. The average for such a distribution has been performed numerically. The calculation of the elastic and quasielastic structure factors for the two rotational models was based on the molecular structure determined by X-ray diffraction on the solid fully protonated compound[23].

Results

The 29 energy spectra have been analyzed simultaneously using the Minuit (Cernlibrary) fitting program for all the investigated temperatures. Due to the presence of the translational broadening, the identification of the elastic and quasielasic intensity is not straightforward. In order to identify the different contributions all the components have to be fitted and, in order to reduce the fitting parameters, the fit has to be model dependent. The rotational elastic and quasi elastic lines have been convoluted with a translational lorentzian broadening and with the experimental resolution line (obtained from a vanadium slab run). The parameters of the fit were the intensity of the elastic line, that of the quasielastic rotational part, the rotational broadening (the same for all the energy spectra), and the translational broadening. No reasonably good fit of the data can be obtained in the nematic phase by letting the translational broadening follow a $\mathbf{Q^2}$ law which instead was found to follow in the isotropic liquid phase. Letting this broadening to vary with respect to $\mathbf{Q}$ a good fit of the energy spectra at all the $\mathbf{Q}$ values can be obtained as is shown in fig.1.

A self consistency model test can be performed by comparing the EISF of the assumed model with the one calculated from the fitted intensities.

Fig. 2 displays the result of this comparison for the continuous rotational diffusion model and for the 180° jumps model. The former seems to fit quite well the predicted behavior while the former seems to diverge from it expe-

elastic region whose **Q** dependence follows a Debye-Waller behavior. In the case that a continuous translational diffusion holds, the expected quasi elastic broadening consists of a single lorentzian whose width is proportional to $\mathbf{Q}^2$. The rotational contribution consists of the sum of a purely elastic part and many (virtually infinite) quasi elastic components.

The energy resolution of the spectrometer set a lower limit to the rate of the observed processes under which the motion has to be considered static from the neutron spectroscopy point of view.This pseudo static motion contributes to the **Q** dependence of the Elastic Incoherent Structure Factor (EISF) which yields information about the geometry of the rotational diffusion. In the observable time window of our experiment we see the spinning and the translational diffusion while, as shown by other techniques[21,16], the tumbling motion is too slow to be resolved by the spectrometer so that it has to be considered as contributing to a static distribution. Two different spinning mechanisms have been tested in our experiment: uniaxial continuous rotational diffusion on a circle and 180° jump reorientation very often assumed for the reorientation of aromatic rings. In the former case the expected differential cross section is[22]:

$$\frac{d^2\sigma_{inc}^{rot}}{d\Omega dE'} = \frac{k'}{k}\frac{N}{2\pi\hbar}|b|_{inc}^2\{J_0^2(Qrsin\theta)\delta(\omega)+\frac{2}{\pi}\sum_{l=1}^{\infty}J_l^2(Qrsin\theta)\frac{D_r l^2}{(D_r l^2)^2+\omega^2}\} \quad (3)$$

where r is the rotation radius, θ is the angle between the **Q** vector and the rotation axis, $J_n^2(x)$ are Bessel functions of the first kind of order n and D_r is the diffusion coefficient. In the latter case, only one quasi elastic component is expected[22]:

$$\frac{d^2\sigma_{inc}^{rot}}{d\Omega dE'} = \frac{k'}{k}\frac{N}{2\pi\hbar}|b|_{inc}^2\{\frac{1}{2}[1+cos\mathbf{Q}\cdot\mathbf{r}]\delta(\omega)+\frac{1}{2}[1-cos\mathbf{Q}\cdot\mathbf{r}]\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}\}. \quad (4)$$

These equations decribe the case in which the axis of rotation are fixed in space while in the case of the real system we must include a distribution (we chose

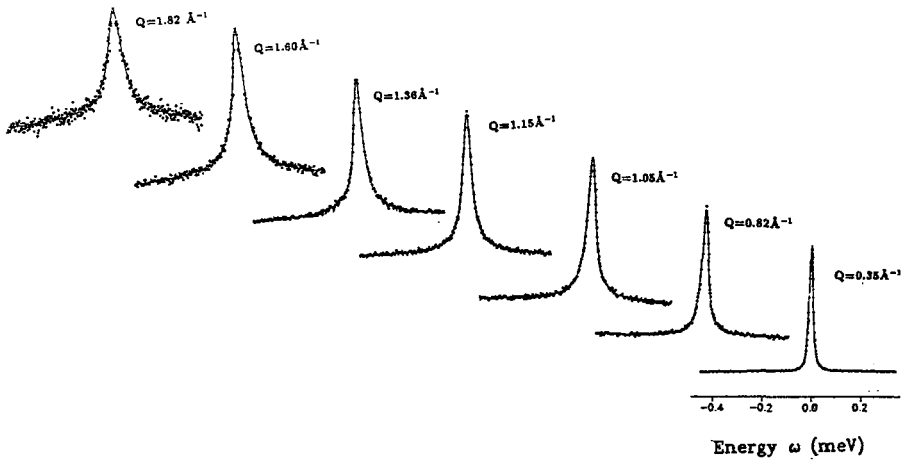

Fig. 1 Quasi elastic scattering law at several exchanged wave vectors, obtained for the aligned nematic phase of EBBA (T=65°C).

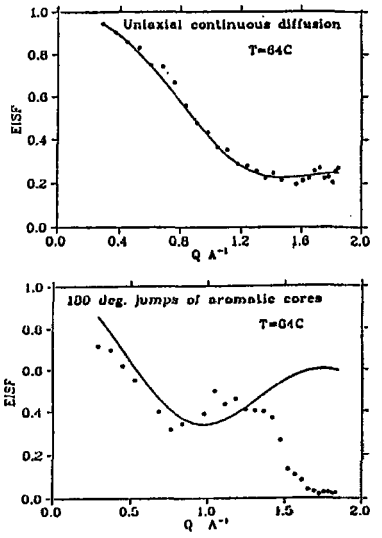

Fig. 2 Experimental (dots) and calculated (solid line) EISF for two rotational diffusion models for the nematic phase.

cially at the higher **Q** values where probably the adoption of a sigle quasielastic component (as predicted by eq. 4) seems to be totally inadequate.

At low **Q**'s ($\mathbf{Q} \leq 1\mathring{A}^{-1}$) the translational broadening is proportional to Q^2. From such behavior a translational diffusion coefficient D_{tr} can be deduced; it

is plotted in fig. 3 as a function of reciprocal temperature. It does not follow a quantitative Arrhenius behavior probably due to the different mixing of the parallel and perpendicular translational coefficients at different temperatures.

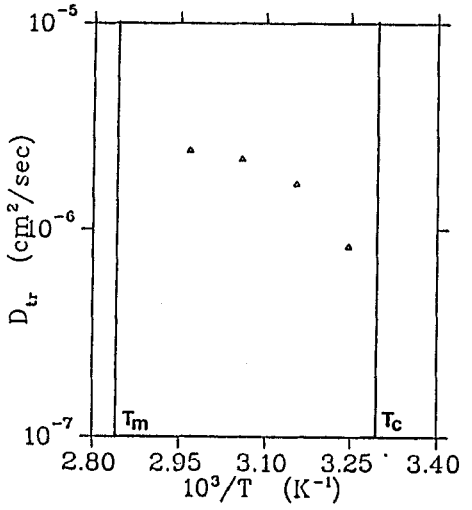

Fig. 3 Temperature dependence of the microscopic translational diffusion coefficient.

At higher Q's the linear dependence on Q^2 saturates. This effect was observed also by Bee et al[24] in the nematic phase of 2-OAOB. A more dramatic departure from the $\mathbf{Q^2}$ law is observed at still higher 'Q's where a dip at about 2 Å^{-2} appears. This anomalous behavior was already reported by us for hydrogenated EBBA[18] and its detailed analysis will be published elsewhere[25].

The rotational diffusion coefficient for the spinning motion is also (as it is evident from eq. 3) a product of the fit. It is presented in fig. 4 as a function of temperature and it seems to follow a regular Arrhenius behavior.

This behavior is remarkably different from that found for $D_{\|}$ in the fully hydrogenated EBBA[18], which was instead similar to the results obtained by IR dicroism bandshape analysis[21]. We believe that the origin of the discrepancy is the extra disordered motion of the alkyl tails which dominated the QENS

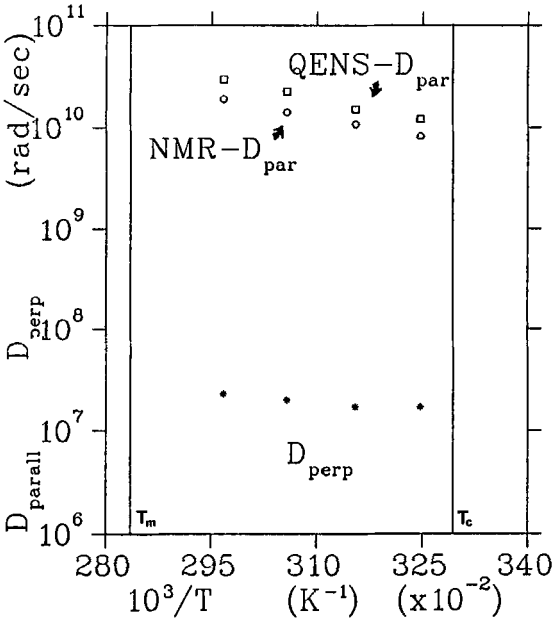

Fig. 4 Spinning and Tumbling diffusion coefficients as determined by QENS (D_{par})and NMR (D_{par} and D_{perp}) in the nematic phase of EBBA.

of h-EBBA and also the IR results (for a detailed analysis see our forthcoming review[26]).

NUCLEAR MAGNETIC RELAXATION

Experiment

The ^{13}C relaxation mesurements have been performed on the commercial spectrometers Bruker AC100, CPX200 and AMX400. The fully protonated EBBA samples have been purified by recrystallization. They were subsequently sealed under vacuum after several freeze-pump-thaw cycles.

The measurements of the spin lattice relaxation times (T_1) has been done with a conventional full inversion recovery experiment under proton irradiation. The power of the decoupler was increased during the acquisition period (gated decoupling). In some instances a composit pulse decoupling technique (MLEV16[27]) was adopted to avoid sample heating from the decoupler radio

frequency.

Theory

As discussed in the introduction paragraph, unlike the neutron scattering technique, the magnetic relaxation is expected to be sensitive also to the slower reorientation around the short molecular axis (*tumbling*) so that, the interpretation of the data has to be done on the basis of a more complex model which takes into account both the dynamics. As is suggested by neutron scattering results, a continuous diffusion model seems to be more suitable. We adopted a small step rotational diffusion model according to which the conditional probability for the reorientation of the molecule (assumed to be a rigid round ellipsoid in an anisotropic restoring potential $V(\theta)$) is given by the following Smoluchowski equation:[28]

$$\frac{\partial P(\Omega_0,\Omega,t)}{\partial t} = -\{\mathbf{L}\cdot\mathbf{D}\cdot[\mathbf{L}+\mathbf{L}\frac{V(\theta)}{kT}]\}P(\Omega_0,\Omega,t). \tag{6}$$

In the case that the heteronuclear dipolar relaxation with the bonded hydrogen be the only relaxation mechanism, the relaxation rate can be expressed in terms of the spectral densities $J_n(\omega)$ by the following[29]:

$$\frac{1}{T_{1D}} = \frac{1}{2}(\frac{\gamma_C\gamma_H\hbar}{r_{CH}^3})^2[J_0(\omega_C-\omega_H)+3J_1(\omega_C)+6J_2(\omega_C+\omega_H)] \tag{7}$$

where γs are the gyromagnetic ratios, $\hbar$ is Planck's constant divided by 2π, the ωs are the resonance frequencies and r_{CH} is the $C-H$ bond length. The calculation of spectral densities from eq. 6 in terms of the diffusion coefficients $D_{\|}$ and $D_{\perp}$ have been made by P. L. Nordio et al.[28,30] and J. H. Freed[31].

Unfortunately the heteronuclear dipolar mechanism is not the only one inducing the relaxation of the ^{13}C nucleus, other mechanisms like the chemical shift anisotropy, spin-rotation interaction direct coupling anisotropy etc. are

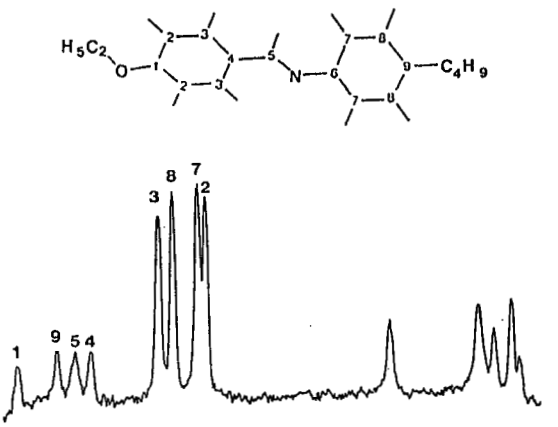

Fig. 5 ^{13}C spectrum of EBBA in the nematic phase; the line assignements follow those of ref. 16.

modulated by the molecular reorientation. The pure dipolar part of the relaxation can be isolated by measuring the Nuclear Overhauser Enhancement (η_{sp}) factor. It implies that the extraction of the dynamical parameters from the measured relaxation times has to be performed using an iteration procedure which has proven to be quickly convergent for the orthophenyl carbons in usual nematogens[32].

Results

Figure 5 represents the ^{13}C spectrum of EBBA in the nematic phase together with the assignment of the lines.

We focused our attention on the relaxation of the orthophenylic carbons (the four highest peaks in the spectrum) because the collective director fluctuations can be proven to be quite ineffective in inducing relaxation of these carbons[33] thanks to the fact that the angle through the $C-H$ bond and the molecular axis is very close to the magic angle ($\sim 55°$). As a consequence this contribution can be totally neglected in the analysis of the relaxation times and it greatly simplifies the treatment of the data.

The relaxation time measured at a single Larmor frequency does not allow the determination of the two model parameters and, in order to perform a also model test, at least three Larmor frequency T_1 data are necessary. Our experiments have been performed at 2.35 T, 4.7 T and 9.4 T and the measured relaxation times within the nematic phase are displayed in Fig. 6 as a function of temperature.

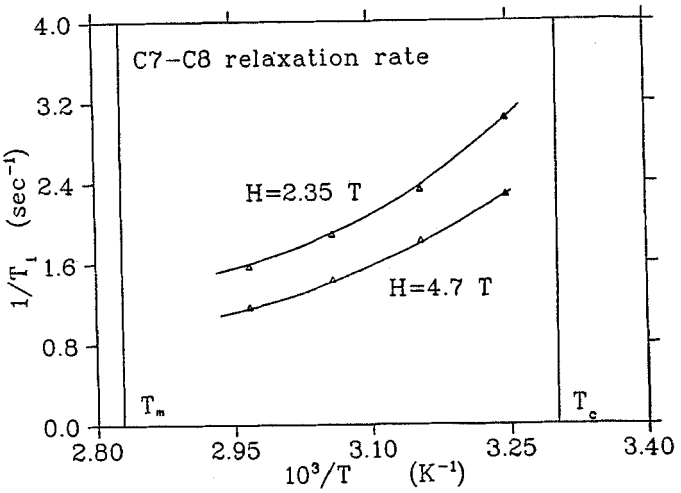

Fig. 6 Measured ^{13}C spin lattice relaxation times at two different values of the applied field. The lines are a guide to the eye.

The values of the diffusion coefficients are plotted against inverse temperature in fig. 4 together with the values of $D_{\|}$ measured in the QENS experiment. The agreement between the values extracted with the two different techniques looks quite good.

The very high ratio of the two different diffusion coefficients ($\sim 10^3$) much higher of what is predicted by classical hydrodynamic theories (~ 10) suggests the presence of an internal rotation of the aromatic rings around their para axis. This internal rotation can be easily taken into account in the developement of the theory of the magnetic relaxation[34] but, as a consequence of the relatively small angle (6°)[23] between the phenyl para axis and the long axis

of the molecular core, the fit cannot distinguish between internal and overall rotation. The investigation of the interphenyl carbon (referred to as nr. 5 in fig. 5) will hopefully allow the distinction of the two different dynamical processes.

CONCLUSIONS

Our coupled QENS-NMR measurements clarify considerably the complexities of stochastic dynamics in nematic phases. The good separation between translational and rotational broadening in QENS allows an unambiguous fit of the EISF with the small step rotational diffusion model for the spinning fluctuations. The measured values of $D_{\|}$ and its temperature dependence obtained by QENS and NMR agree, and this gives selfconsistency to the data and our interpretation. The role of internal degrees of freedom corresponding to molecular fragments is clearly evidenced, and this in turn may lead to a definitive explanation of the anomalies observed with fluctuation IR spectroscopy.

Questions which remain to be answered are just how coupled are the "separate" motions of the diphenylic core and the alkyl tails, and how far the decoupling approximation for rotational and translational diffusion may be pushed. We feel that more detailed parallel measurements by NMR, QENS and fluctuation spectroscopy should definitely clarify these issues.

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