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S. Kralj[a]; M. Vilfan[a]; S. ŽKumer[b]

[a] J. Stefan Institute, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia [b] Physics Department, E. Kardelj University of Ljubljana, Ljubljana, Yugoslavia

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Proton N.M.R. lineshape in nematic microdroplets

by S. KRALJ, M. VILFAN and S. ŽUMER†

J. Stefan Institute and †Physics Department, E. Kardelj University of Ljubljana,
Jamova 39, 61111 Ljubljana, Yugoslavia

The dependence of the proton N.M.R. absorption spectrum on nematic director configuration and molecular self-diffusion in nematic submicrondroplets is analysed. The lineshape is evaluated numerically for radial and bipolar director configuration. The motional averaging is taken into account by means of a numerical simulation of the molecular diffusion which induces slow molecular reorientations due to non-uniform orientational ordering in the droplet. This diffusion process strongly affects the absorption spectra of the radial configuration, whereas spectra of the bipolar configuration are only slightly influenced. The possibility of determinating the submicrometre nematic droplet structures using the proton N.M.R. lineshape is discussed.

1. Introduction

Materials consisting of a random dispersion of nematic liquid crystal microdroplets in a solid polymer matrix (PDLC) have recently been developed for use in electro-optical devices [1, 2]. The intensity of the light, scattered from a thin film of a PDLC material, depends strongly on the ordering of nematic molecules in the droplets [3]. The nematic structure depends on the elastic properties of the liquid crystal, the surface interaction and external electric or magnetic field, and can therefore be easily controlled [1, 3, 4].

For the nematic liquid crystal free energy the following approximations are used: the surface and external field contributions are neglected [5], a single elastic constant approximation is introduced, the nematic order parameter is assumed to be constant throughout the droplet, and a strong surface anchoring is assumed. The equilibrium nematic configuration, corresponding to the minimum free energy, can be calculated by solving the partial differential equation [3, 5]

$$\frac{\partial^2\theta_n}{\partial\varrho^2}+\frac{\partial^2\theta_n}{\partial z^2}+\frac{\partial\theta_n}{\partial\varrho}\frac{1}{\varrho}=\frac{\sin(2\theta_n)}{2\varrho^2}. \qquad (1)$$

Here θ_n, which denotes the angle between the symmetry axis of the droplet (**N**) and the local nematic director $\mathbf{n}(\mathbf{r})$, depends on the positional cylindrical coordinates z and ϱ. For the parallel molecular anchoring (at the liquid crystal–polymer interface **n** is parallel to the boundary) on the droplet surface, equation (1) results in the bipolar configuration, and for the normal anchoring in the radial configuration [3]. The radial alignment (see figure 1 (*a*)) is spherically symmetric and has a point disclination in the centre. On the other hand, the bipolar configuration (see figure 1 (*b*)) is cylindrically symmetric and has two point disclinations at opposite ends of the droplet diameter. In liquid crystals with a low ratio between the bend and the splay elastic constants the toroidal configuration (see figure 1 (*c*)) occurs [6]. The nematic director field is concentric around a central disclination line. Several other possible configurations are predicted theoretically, as for example the axial [7] and the twisted arrangement [8].

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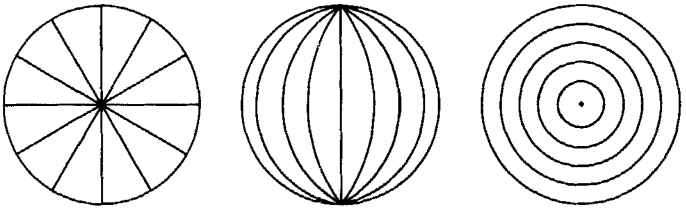

(*a*) (*b*) (*c*)

Figure 1. Schematic illustration of (*a*) radial, (*b*) bipolar and (*c*) toroidal director configuration. In (*b*) the symmetry axis of the droplet is in the plane of the paper, and in (*c*) it is normal to it.

The existence of the radial and bipolar configuration has been proved by microscopic observations [7], and deuterium N.M.R. methods [9].

We present here proton N.M.R. lineshapes calculated for the radial and bipolar molecular structure in submicrometre droplets in order to analyse the possibility of studying indirectly the droplet configuration and its effect on molecular diffusion. The broad line proton N.M.R. spectrum in bulk nematic liquid crystals [10–12] usually shows three lines with linewidths of about 10 kHz. It has been established [12] that the splitting and line broadening in the nematic phase is predominantly due to partially averaged dipolar interactions. The external line doublet corresponds to rigid parts of the molecule (benzene rings, etc.) and the internal central line to highly mobile proton groups like methyl groups. The absence of the central line in some nematic liquid crystals indicates more-rigid structures [13].

In §2 we calculate, following the approach developed for deuteron N.M.R. in microdroplets [9], the static lineshape appropriate for the slow diffusion case. In §3 the molecular translational diffusion which induces reorientations of nematic molecules due to non-uniform spatial ordering is taken into account. Numerical simulation calculations are made for a simple isotropic random jump diffusion. Conclusions are given in the final section.

2. Static lineshape

Here we evaluate the nematic proton N.M.R. lineshape for the case when the averaging effects of molecular translational diffusion in microdroplets are neglected, the averaging of dipolar interactions due to all faster motions (i.e. rotation around the long molecular axis, etc.) being taken into account. We first assume that we have a single proton pair at the ith position in the molecule. The corresponding averaged dipolar interaction can be described by an effective interproton vector parallel to the nematic director. The N.M.R. linesplitting $\omega_d^{(i)}$ due to this residual dipolar interaction depends on the bulk nematic splitting parameter $A^{(i)}$ [14] and on the position $\mathbf{r}$ of the molecule which carries the proton pair. $\omega_d^{(i)}(\mathbf{r})$ can be then written as [15]

$$\omega_d^{(i)}(\mathbf{r}) = 2\pi\nu_d^{(i)}(\mathbf{r}) = \pm\tfrac{1}{2}A^{(i)}[3\cos^2\theta(\mathbf{r}) - 1], \qquad (2)$$

where $\theta(\mathbf{r})$ is the angle between the magnetic field $\mathbf{B}$ and the local director $\mathbf{n}(\mathbf{r})$. As in the bulk nematic phase, $A^{(i)}$ is proportional to the nematic orientational order parameter. The additional line broadening $\delta\omega = 2\pi\,\delta\nu$ due to residual interactions with other nuclei will, for simplicity, be described by a gaussian distribution. The absorption spectrum $I(\omega, \mathbf{r})$ of a nematic molecule with m independent proton pairs can thus be presented as

$$\begin{aligned} I(\omega, \mathbf{r}) &= I_0 \sum_{i=1}^{m} (\exp\{-4[\omega - \omega_Z - \omega_d^{(i)}(\mathbf{r})]^2/\sigma^2\} \\ &\quad + \exp\{-4[\omega - \omega_Z + \omega_d^{(i)}(\mathbf{r})]^2/\sigma^2\}). \end{aligned} \tag{3}$$

Here ω_Z is the Zeeman frequency, $\sigma^2 = \delta\omega^2/\ln 2$, I_0 is a normalization constant and $\omega_d^{(i)}(\mathbf{r})$ are given by equation (2). To obtain the absorption spectrum $I(\omega)$ of the whole nematic droplet, equation (3) is integrated over the droplet volume V:

$$I(\omega) = \frac{1}{V} \int d\mathbf{V}\, I(\omega, \mathbf{r}). \tag{4}$$

The integration is performed numerically for the radial and bipolar droplet configurations [3, 5]. The effect of magnetic field on ordering is neglected as the typical N.M.R. magnetic fields are too weak to change significantly the director configurations in submicrometre droplets. For instance, the radial alignment in a droplet with strong normal surface anchoring remains stable if $R/\xi < 4$, where ξ is the magnetic coherence length [14]. Its typical value for nematic liquid crystals for $B = 5$ T is about 0·5 μm.

The calculated spectrum of the bipolar molecular configuration depends strongly on the relative orientation of the magnetic field **B** and the symmetry axis of the droplet **N**. In a perfect spherical droplet **N** is always parallel to the magnetic field, but even a small distortion can favour practically any direction of **N**. A particular alignment of **N** can be also obtained by an additional external electric field. For a general orientation of **N** we express $\theta(\mathbf{r})$ in terms of the angles θ_N, φ_n and θ_n defined in figure 2:

$$\cos\theta(\mathbf{r}) = \cos\theta_n \cos\theta_N + \sin\theta_n \sin\theta_N \cos\varphi_n. \tag{5}$$

Values of θ_n are obtained by solving equation (1).

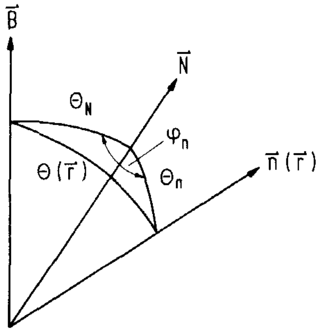

Figure 2. Presentation of angles used in the text.

In figure 3 (*a*) the radial and oriented bipolar configuration (**N** ∥ **B**) static absorption spectra are presented for $A^{(i)} = A$. This situation corresponds to the case where all chain protons are deuteriated and all core proton pairs are equivalent but not coupled. The ratio between the linewidth and linesplitting in the proton spectrum is

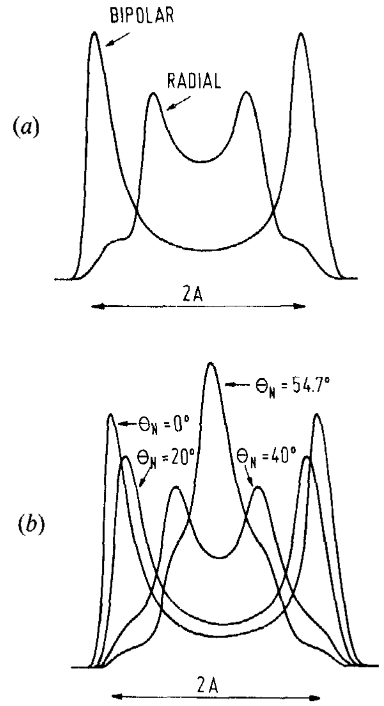

Figure 3. Simulated static spectra of nematic microdroplets with the assumption $A^{(i)} = A$ for: (*a*) bipolar ($\mathbf{N} \parallel \mathbf{B}$) and radial configuration, and (*b*) bipolar configurations for different angles between the droplet director **N** and the magnetic field **B**. Data used in calculations are $\delta\omega/2A = 1/10$.

chosen to be 1 : 10. In the radial case the spectrum has a typical powder-like shape with singularities at $\omega_d = \pm A/2$. For the bipolar configuration the average value of $\theta(\mathbf{r})$ is close to zero and so the major contributions to the spectrum arise at $\omega_d \approx \pm A$. Figure 3 (*b*) shows the dependence of $I(\omega)$ on the angle θ_N between **N** and **B** for the bipolar orientation. With increasing θ_N the separation between the two lines in the spectrum is reduced until a single line is observed at $\theta_N \approx 54{\cdot}7°$. For $\theta_N > 54{\cdot}7°$ the absorption spectrum again shows two lines. The splitting at $\theta_N = 90°$ equals A. For a PDLC sample where all droplets have the same size but randomly oriented symmetry axes **N**, the resultant spectrum is a powder spectrum again (as in the radial case).

Next we consider the case when in addition to benzene proton pairs a molecule contains mobile methyl proton groups (for instance, the PAA molecule [12]). In the bulk spectrum an additional central line is observed which corresponds to methyl protons with strongly averaged dipolar interactions. For the simulation of the proton lineshape we assume that 3/7 of the protons (methyl group) have $A = 0$ and that for 4/7 of the protons (benzene ring) $A^{(i)} = A \neq 0$. This case is illustrated by the broken curve in figure 4 (*a*) for the bipolar structure and in figure 4 (*b*) for the radial structure. For comparison, the simulated bulk nematic liquid crystal line is also presented (chain-broken curves). Comparing figures 3 and 4, it can be seen that in the case where both ring and methyl protons contribute to the spectrum a lot of information about droplet structure is lost.

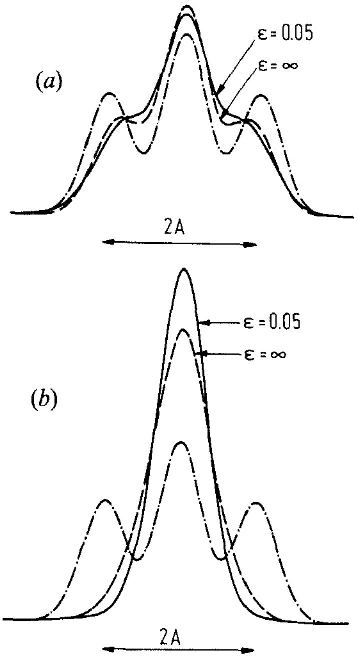

Figure 4. Simulated absorption spectra of (*a*) the bipolar and (*b*) the radial structure for nematic liquid crystal molecules with 4/7 of the protons having the splitting parameter A and 3/7 of the protons having splitting parameter zero. $\delta\omega/2A$ is 1/3. Static ($\varepsilon = \infty$) spectra are shown as broken curves and dynamic ($\varepsilon = 0{\cdot}05$) as full curves. For comparison the bulk nematic spectra are shown as chain-broken curves.

3. Dynamic lineshape

The 'static' spectra described in §2 could be observed in nematic droplets with radius R if the molecular diffusion is slow, i.e. the diffusion time $R^2/6D$ is much longer than $1/A$. In submicrometre nematic droplets with diffusion constant D of the order 10^{-10}–$10^{-12}\,\mathrm{m^2\,s^{-1}}$, motional narrowing must be taken into account.

To calculate the proton N.M.R. spectra including the motional narrowing we use the semiclassical approach, where the molecular translational diffusion is introduced via a time dependent dipolar hamiltonian. The frequency spectrum $I(\omega)$ for a single proton pair case is then given by [15]

$$I(\omega) = \int_{-\infty}^{\infty} \exp\left[i(\omega_Z - \omega)t\right] G(t)\,dt, \tag{6a}$$

where

$$G(t) = \left\langle \exp\left(i \int_0^t \omega_d^{(i)}[\mathbf{r}(t')]\,dt' \right) \right\rangle. \tag{6b}$$

Here $\omega_d^{(i)}[\mathbf{r}(t)]$ is the instantaneous value of the dipolar frequency shift and $\langle \cdot\cdot\cdot \rangle$ denotes the ensemble average. We take into account the residual line broadening by convolving $I(\omega)$ with a gaussian distribution curve.

The non-uniformity of the director field on the molecular scale is small except in defects, so we assume that details about molecular motions do not affect motional averaging. This enables us to use a simple random jump model to simulate the diffusion process [9]. In the nematic droplet we introduce a square lattice with a lattice constant a, which is chosen so that the director field does not change appreciably when a molecule is displaced a distance a. Nematic molecules are allowed to jump with the same probability to one of the six nearest lattice sites. The relatively small anisotropy of the diffusion tensor in nematic phase is neglected [9]. The jump time τ is then given roughly by $a^2/6D$. Diffusive reflection is assumed at the liquid crystal–polymer interface. According to this model the autocorrelation function $G(t)$ defined by equation (6*b*) is

$$G(t = p\tau) = \langle \exp\{i[\omega_d^{(i)}(\mathbf{r}_1) + \omega_d^{(i)}(\mathbf{r}_2) + \cdots + \omega_d^{(i)}(\mathbf{r}_p)]\tau\}\rangle_r, \qquad (7)$$

where p is the number of jumps and $\langle\cdot\cdot\cdot\rangle_r$ denotes an average over different initial points $\mathbf{r}_1$ and possible trajectories.

Simulations were made on Vax 8650 computer for the 60 × 60 lattice. The results for $A^{(i)} = A$ and different values of the parameter $\varepsilon = AR^2/6D$ are shown in figures 5 (*a*) and 5 (*b*). The ratio between the linesplitting $2A$ and the linewidth due to residual broadening is again chosen to be 1 : 10. The line narrowing is more pronounced for the radial structure, where the distribution of orientations of nematic director $\mathbf{n}$ is isotropic. For $\varepsilon = 50$ the diffusion is so slow that the absorption spectra are only slightly affected by the motion. For faster diffusion and consequently a smaller value of ε, the spectra gradually narrow. For $\varepsilon = 0{\cdot}05$ the spectrum of the radial configuration is represented by a single line, whereas for the bipolar arrangement no qualitative difference is observed except a small (about 15 per cent) reduction of the linesplitting.

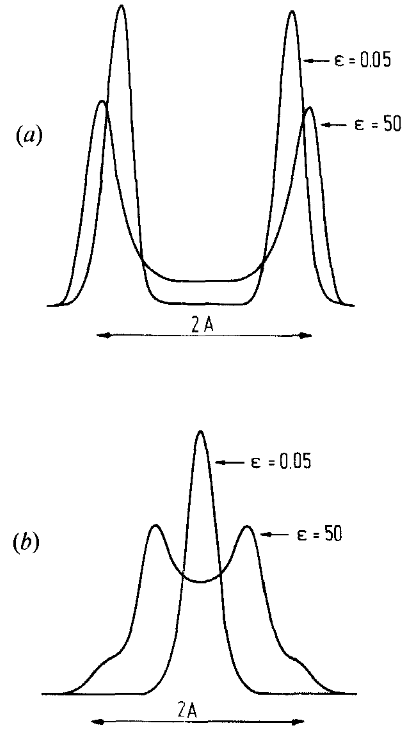

Figure 5. Dynamic spectra for (*a*) the bipolar and (*b*) the radial director configuration for different values of ε in the case of $A^{(i)} = A$ and $\delta\omega/2A = 1/10$. For the bipolar configuration $\mathbf{N}$ is parallel to $\mathbf{B}$.

The simulation of a simple non-equivalent proton case (model for PAA, introduced in § 2) is presented by full curves ($\varepsilon = 0{\cdot}05$) in figures 4 (*a*) and 4 (*b*). The differences between static (broken curves) and averaged dynamic (full curves) spectra are much less pronounced than in the equivalent proton case illustrated in figure 5.

4. Conclusions

We calculated the proton N.M.R. spectrum of a nematic liquid crystal confined to small spherical droplets, and analysed the effect of molecular orientational order and molelcular self-diffusion on the proton lineshape. In view of the assumptions used (viz. neglecting the effects of the magnetic field and constant order parameter approximation) the validity of our treatment is limited to droplets with $2\,\mu\text{m} > R > 0{\cdot}2\,\mu\text{m}$ [16] and temperatures far from the N–I transition. It is shown that a proton N.M.R. study can be used to discriminate between different droplet structures only if the corresponding bulk spectrum has two relatively well defined lines. Also, in the slow diffusion limit one cannot discriminate between the system of radial droplets and the system of randomly oriented bipolar droplets. The difference shows up in the fast diffusion limit where the radial line is motionally narrowed. It should be mentioned that the effect of diffusion can be partially masked if there is a distribution of droplet sizes.

An example with two types of protons demonstrates that in a common nematic case, where molecules have several non-equivalent hydrogen sites, proton lineshape study cannot be used for determination of the droplet structure. The problem could be by-passed by the deuteriation of non-equivalent hydrogen sites so that the residual protons would have a bulk spectrum with two sharp lines only.

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