Confinement of a liquid crystal to small droplets and its effect on nuclear magnetic relaxation

S. Žumer[a]; M. Vilfan[b]; I. Vilfan[b]

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

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Confinement of a liquid crystal to small droplets and its effect on nuclear magnetic relaxation

by S. ŽUMER†, M. VILFAN‡ and I. VILFAN‡

Physics Department† and J. Stefan Institute‡, E. Kardelj University of Ljubljana,
61000 Ljubljana, Yugoslavia

The spatial dependence of the orientation of the molecular director and of the nematic order parameter is obtained by minimization of the Landau–de Gennes free energy of the nematic liquid crystal confined in a spherical droplet. Special attention is given to the vicinity of the nematic–isotropic transition. The influence of the resulting nematic structure, large liquid crystal–polymer interface and restricted molecular diffusion on the nuclear magnetic relaxation is analysed. The translationally-induced molecular reorientation and the liquid crystal–polymer cross relaxation are discussed in particular. The possibility of an indirect study of the molecular anchoring on the polymer surface is demonstrated.

1. Introduction

Materials consisting of nematic liquid crystal microdroplets embedded in a solid polymer matrix have been developed recently for use in electro-optical shutters [1, 2]. These devices are based on a controllable light scattering cross-section of the nematic structure in the droplets. Such a structure, i.e. the spatial dependence of the orientation of the nematic director and of the degree of orientational order, results as an interplay of nematic elastic forces and surface interactions. In addition, the structure is strongly affected by temperature, droplet shape (for example, stress-induced distorsion), and external electric or magnetic fields. In the case of equal elastic constants and strong anchoring of molecules on the polymer surface two equilibrium configurations occur [3]: a bipolar structure for tangential surface alignment, and a radial structure for normal surface alignment. In addition to this some other structures [4–6] can result when the elastic constants are not equal or the surface anchoring is weak.

The nematic structures obtained in the constant orientational order parameter approximation [3] agree rather well with optical microscopy experiments on supramicron droplets formed in liquids [4, 7]. Using the same approximation the light scattering cross-sections for submicron [8] and supramicron [9] droplets have been estimated recently. Experimental studies of the light attenuation [10] and deuterium N.M.R. lineshape [11], performed on submicron nematic droplets with bipolar structures, are in agreement with theoretical predictions. However, in small droplets (radius $R \ll 1\,\mu$m) or near the nematic–isotropic phase transition the spatial dependence of the degree of orientational order should be taken into account. Preliminary studies of the radial structure even indicate a change in the nature of the phase transition [12].

In this contribution we first extend earlier studies of the nematic structure in microdroplets by taking into account the spatial dependence of the nematic order parameter. Further, we discuss the possibilities for the determination of molecular structure and dynamics in droplets by nuclear magnetic relaxation. We analyse

nuclear magnetic relaxation mechanisms specific for droplets and, in particular, point out what kind of information about molecular self-diffusion and molecular anchoring on the droplet surface could be obtained.

2. Nematic structures

The equilibrium nematic structure of a spatially confined liquid-crystalline phase can be determined by the minimization of its free energy. If the temperature is far from the nematic–isotropic transition and the diameter of the droplets is close to one micron or larger, the orientational order parameter can be considered constant everywhere in the droplet. The director configuration can be obtained simply by minimization of the elastic part of the free energy [3] and of the coupling to the external field [8] if it is present.

We have improved this approach by using the Landau–de Gennes formalism for a non-uniform nematic phase [13–15] where the orientational order parameter depends on the position in the droplet. Neglecting the distorsion and surface induced biaxiality [16, 17] we use a scalar orientational order parameter $S(\mathbf{r})$. Further we assume a spherical shape for the droplet and strong anchoring [12, 18] of molecules at the polymer surface; this simplifies the minimization procedure. The effect of an external field, which is usually measured in terms of the correlation length ζ of the surface-induced order [19], is also neglected. In magnetic field $\mathbf{B}$ the correlation length ζ_M is given by

$$\zeta_M = (\mu_0 K/\Delta\chi)^{1/2}/B, \tag{1}$$

where K can be either equal to one of the elastic constants K_1, K_2 or K_3 or a combination of them, depending on geometry; $\Delta\chi$ denotes the anisotropy of the magnetic suscep-tibility. In magnetic fields used in N.M.R., ζ_M is larger than $0.5\,\mu$m and so our treatment, where the effect of the field is neglected, applies to the situation when $R < 0.5\,\mu$m.

The expansion of the free energy density in terms of the orientational order parameter S, nematic director $\mathbf{n}$ and their spatial derivatives is then given by

$$f = f_0 + \tfrac{1}{2}a(T - T^*)S^2 - \tfrac{1}{3}BS^3 + \tfrac{1}{4}CS^4 + \tfrac{3}{4}L_1(\nabla S)^2$$
$$+ \tfrac{9}{4}S^2 L_1\left[(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2\right], \tag{2a}$$

with

$$L_1 = 2K/9S^2, \tag{2b}$$

where K $(= K_1 = K_2 = K_3)$ is the Frank elastic constant in the single constant approximation. Here the additive constant f_0 and the coefficients a, B and C in the expansion are temperature independent. T^* stands for the supercooling limit [19]. The minimization of the total free energy results in the coupled set of non-linear second order partial differential equations

$$S^2\nabla^2\theta = \frac{S^2}{2\varrho^2}\sin 2\theta - 2S\left[\frac{\partial S}{\partial\varrho}\frac{\partial\theta}{\partial\varrho} + \frac{\partial S}{\partial z}\frac{\partial\theta}{\partial z} + \frac{\sin 2\theta}{2\varrho}\frac{\partial S}{\partial\varrho} + \frac{\sin^2\theta}{\varrho}\frac{\partial S}{\partial z}\right], \tag{3a}$$

and

$$\nabla^2 S = \frac{2a}{3L_1}S(T - T^*) - \frac{2}{3}\frac{B}{L_1}S^2 + \frac{2C}{3L_1}S^3 + 3S\left[\frac{1}{\varrho^2}\sin^2\theta + \left(\frac{\partial\theta}{\partial\varrho}\right)^2 + \left(\frac{\partial\theta}{\partial z}\right)^2\right.$$
$$\left. + \frac{2}{\varrho}\sin\theta\cos\theta\frac{\partial\theta}{\partial\varrho} + \frac{2}{\varrho}\sin^2\theta\frac{\partial\theta}{\partial z}\right], \tag{3b}$$

for an order parameter S and a tilt angle θ of the local nematic director $\mathbf{n}$ (See figure 1). Here ϱ and z are cylindrical coordinates in the system fixed by the symmetry axis of the droplet structure, i.e. arbitrary direction for the radial structure or polar axis for the bipolar structure. According to our assumption of strong molecular anchoring on the spherical surface we have the boundary conditions $S(\mathbf{r} = \mathbf{R}) = S_0 = \text{constant}$ and $\mathbf{n} \cdot \mathbf{R} = \text{constant}$. Equation (3) is solved numerically by a relaxation method [20] for two simple cases, $\mathbf{n} \cdot \mathbf{R} = \mathbf{r}$ (radial structure) and $\mathbf{n} \cdot \mathbf{R} = 0$ (bipolar structure).
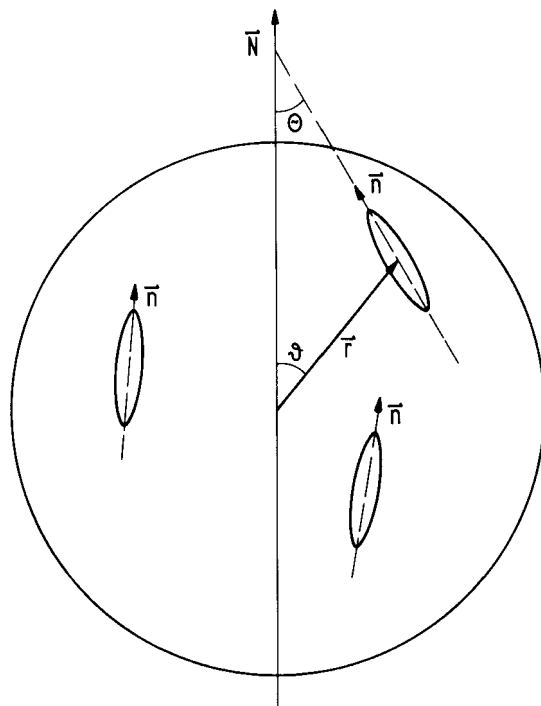
Figure 1. Schematic presentation of nematic director $\mathbf{n(r)}$ in the droplet. ϑ is the polar angle describing the orientation of $\mathbf{r}$ with respect to the droplet axis $\mathbf{N}$. $\theta(\mathbf{r})$ denotes the angle between the director and the droplet axis.

2.1. *Radial structure*

In this case the director field $\mathbf{n}$ is orthogonal to the spherical surface of the droplet. Because we neglect the symmetry breaking effect of the magnetic field, the solution is spherically symmetric with $\mathbf{n} \cdot \mathbf{r} = r$ everywhere except at the point defect in the centre of symmetry. The system of differential equations (Equation (3)) reduces to a single equation for S. Its solutions are treated in detail in [12]. For the following set of material constants (typical for 4-n-pentyl-4'-cyanobiphenyl): $a = 1 \cdot 3 \times 10^5 \, \text{J/m}^3 \text{K}$, $B = 1 \cdot 6 \times 10^6 \, \text{J/m}^3$, $C = 3 \cdot 9 \times 10^6 \, \text{J/m}^3$, $L_1 = 1 \cdot 0 \times 10^{-11} \, \text{N}$, $T^* = 306 \, \text{K}$ and a fixed value of the surface order parameter S_0 we find a critical droplet radius $R_c(S_0)$ where the nematic–isotropic phase transition becomes second order. For $S_0 = 0 \cdot 5$ the critical radius is $0 \cdot 16 \, \mu\text{m}$. In droplets with radius smaller than R_c there is no nematic–isotropic transition. In figure 2 the radial dependence of the orientational order parameter $S(r)$ is shown for the radius $0 \cdot 25 \, \mu\text{m} > R_c$ and several temperatures. Curves A and B correspond to temperatures below the phase transition. Curves C

Figure 2.   Radial dependences of the orientational order parameter $S(r)$ in a droplet with a
radial structure, $S_0 = 0.5$ and radius $0.25\,\mu m > R_c$. Different curves correspond to the
following values of $(T - T^*)/K$: A, 1·000; B, 1·083; C, 1·166; D, 1·249; and E, 1·332.

represent high and low temperature solutions in the narrow biphasic region around
the first order phase transition. Solutions D and E correspond to temperatures above
the phase transition where the surface-induced nematic order is restricted to a thin
layer. In figure 3 low and high temperature nematic structures are presented schemati-
cally. The degree of the local orientational order is represented by the length of the
bars. The solutions for the same set of temperatures as in figure 2 but for the radius
$0.1\,\mu m < R_c$, presented in figure 4, show the spatial dependence of the orientational
order parameter in very small droplets where the nematic–isotropic transition is absent.

(a)   (b)

Figure 3.   The configuration of director in the droplet ($R = 0.25\,\mu m$) with a radial structure
(a) below the nematic–isotropic transition at $(T - T^*) = 1.0\,K$, and (b) above the
transition at $(T - T^*) = 1.3\,K$. The local orientational order is represented by the
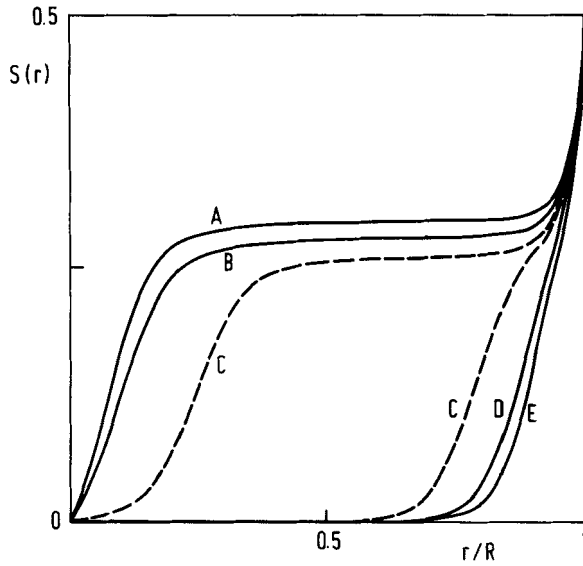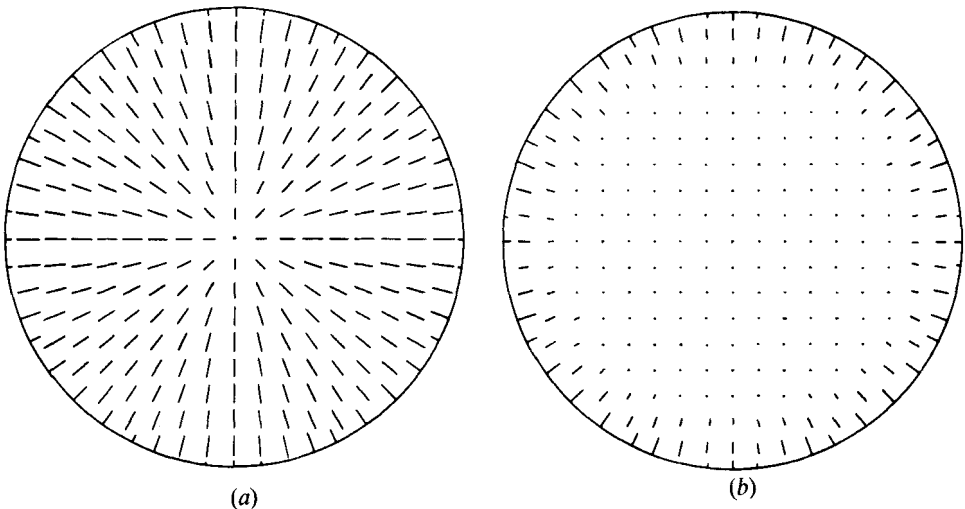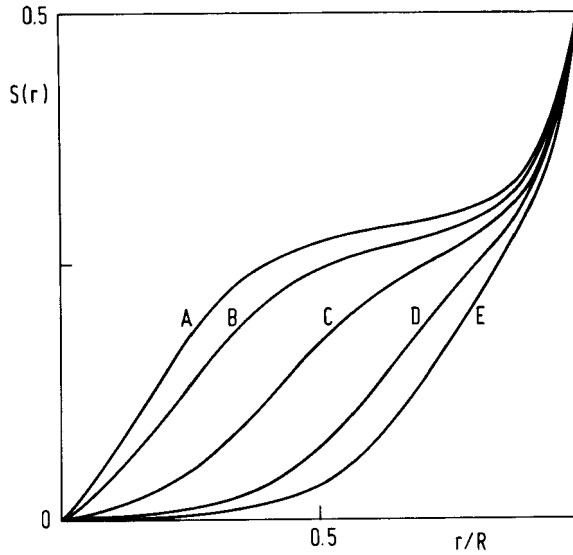length of the bars.

Figure 4. The radial dependence of the orientational order parameter $S(r)$ in a droplet with a radial structure, $S_0 = 0.5$ and radius $0.1 \, \mu m < R_c$. Different curves correspond to the following values $(T - T^*)/K$: A, 1.000; B, 1.083; C, 1.166; D, 1.249; and E, 1.332.

2.2. *Bipolar structure*

In the case of strong parallel anchoring of the liquid crystal molecules on the spherical surface the nematic structure corresponding to the minimum free energy has two point defects on the axis of cylindrical symmetry and is therefore called bipolar. In general, the behaviour of the bipolar system is the same as in the radial case. In figure 5 the low and high temperature bipolar structures are presented schematically for $S_0 = 0.5$. At both temperatures there is a narrow region ($< 0.1 \, R$) with a relatively
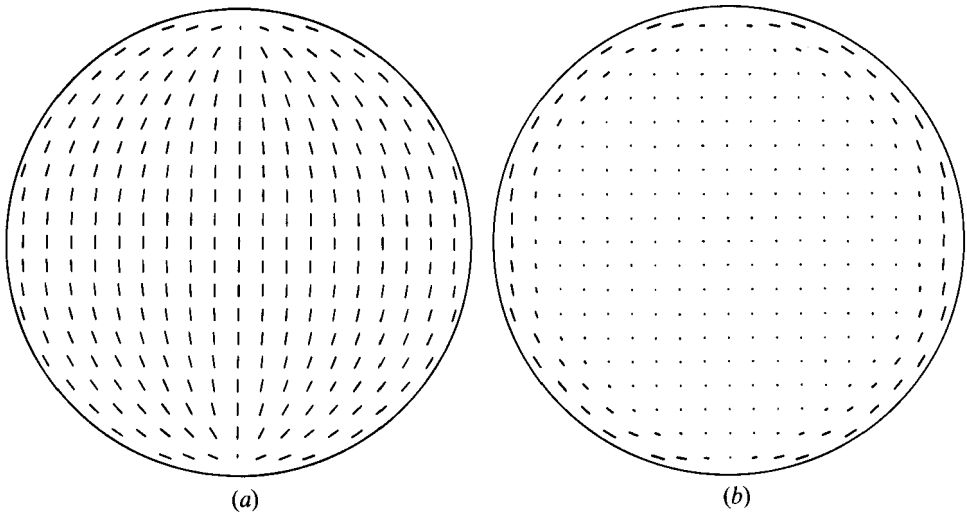

(a)   (b)

Figure 5. The configuration of the director in the droplet with a bipolar structure (a) below the nematic–isotropic transition at $(T - T^*) = 1.1 \, K$ and $R = 1 \, \mu m$, and (b) above the transition at $(T - T^*) = 1.2 \, K$ and $R = 0.3 \, \mu m$. The local orientational order is presented by the length of the bars.

high surface-induced order while in the rest of the droplet the order parameter is constant.

3.   Nuclear magnetic relaxation

Nuclear magnetic relaxation studies have given valuable information on molecular dynamics in nematic liquid crystals. In the following we wish to show what kind of information about the nematic structure, molecular anchoring and molecular dynamics can be obtained from nuclear magnetic relaxation data for microdroplets.

The main nuclear relaxation mechanisms in droplets are: internal molecular motions; local molecular reorientation and translation; order director fluctuations (ODF); molecular self-diffusion via translationally-induced modulation of the intermolecular coupling and translationally-induced rotation modulating intramolecular coupling; and cross relaxation on the liquid crystal–polymer interface. The relative importance of different relaxation mechanisms varies depending on the nuclei observed and the resonant frequency ω. For instance, when choosing deuterium all intermolecular dipolar couplings can be neglected. By selecting the experimental method (observation of T_{1z}, T_{1Q}, $T_{1\varrho}$ etc.) the various spectral densities [21]

$$J^{(k)}(\omega) \quad = \quad \mathrm{Re} \int_{-\infty}^{\infty} \langle F^{(k)}(0)F^{(k)*}(t) \rangle \exp{(i\omega t)} dt \tag{4}$$

can be determined. Here $F^{(k)}$ is the kth spatial component of either dipolar or quadrupolar coupling [21]. We shall focus our attention on two relaxation mechanisms, translationally-induced rotation and cross relaxation on the polymer boundary, which are specific for the confined nematic phase.

3.1.   *Translationally induced rotation*

Translational self-diffusion of molecules in non-uniformly oriented nematic liquid crystals induces relatively slow rotation of the molecules as they adjust to the local direction of $\mathbf{n}$. The corresponding time scale can be estimated roughly from the relation $\tau_{\mathrm{TR}} \sim R^2/6D$ where R is the droplet radius and D is the average diffusion coefficient. Assuming that other molecular motions are much faster we can write

$$G^{(k)}(t) \quad = \quad \langle \overline{F^{(k)}(0)} \ \overline{F^{(k)*}(t)} \rangle$$

$$= \quad \frac{3}{4\pi R^3} \iint \overline{F^{(k)}(\mathbf{r}_0)} P(\mathbf{r}_0, \mathbf{r}, t) \overline{F^{(k)*}(\mathbf{r})} \ dV dV_0, \tag{5}$$

where the motionally averaged interaction $F^{(k)}$ given by

$$\overline{F^{(k)}(\mathbf{r})} \quad = \quad \alpha^k S(\mathbf{r}) Y_2^k(\theta, \phi). \tag{6}$$

Here α^k is the strength of the interaction depending on its type [21], and $S(\mathbf{r})$ is the local orientational order parameter. Y_2^k are the second order spherical functions with angles θ and ϕ describing the orientation of the local director (See figure 1) with respect to the droplet symmetry axis which is chosen parallel to the magnetic field. The probability $P(\mathbf{r}_0, \mathbf{r}, t)$, that a molecule diffuses within a sphere from position $\mathbf{r}_0$ to $\mathbf{r}$ in time t, is given by

$$P(\mathbf{r}_0, \mathbf{r}, t) \quad = \quad \frac{3}{4\pi R^3} \sum_{l,s,m} b_{ls} Y_l^m(\vartheta, \varphi) Y_l^{m*}(\vartheta_0, \varphi_0) j_l(\beta_{ls} r_0/R)$$

$$\times \ j_l(\beta_{ls} r/R) \exp{(-\beta_{ls}^2 Dt/R^2)}, \tag{7}$$

with

$$
b_{ls} = \begin{cases} 4\pi, & l = 0,\, s = 1, \\ 0, & l > 1,\, s = 1, \\ \dfrac{8\pi}{3[1 - l(l+1)]/\beta_{ls}^2] j_l^2(\beta_{ls})}, & \text{for the rest of } l,\, s. \end{cases}
$$

Here j_l are spherical Bessel functions and β_{ls} the corresponding zeros of their first derivatives. ϑ and φ are the polar and azimuthal angles corresponding to the position **r** in the droplet. Expression (7) is a solution [2] of the continuous diffusion equation where the small anisotropy of the self-diffusion tensor [23] is neglected. It should be mentioned that the continuous diffusion approach used here ia appropriate for the description of the translationally-induced rotation mechanism where the details on the molecular scale are not important. Introducing the Fourier transform of $\overline{F^{(k)}}$,

$$
f^{(k)}(l,\, s,\, m) = \frac{3\alpha^k}{4\pi R^3} \int S(\mathbf{r}) Y_2^k(\vartheta,\, \varphi) Y_l^m(\vartheta,\, \varphi) j_l(\beta_{ls} r/R) dV, \tag{8}
$$

we find

$$
G^{(k)}(t) = \sum_{l,s,m} |f^{(k)}(l,\, s,\, m)|^2 b_{ls} \exp(-\beta_{ls}^2 Dt/R^2), \tag{9}
$$

and finally

$$
J^{(k)}(\omega) = \sum_{l,s} A_{ls}^{(k)} \frac{2\tau_{ls}}{1 + (\omega\tau_{ls})^2}, \tag{10}
$$

where

$$
\tau_{ls} = R^2/\beta_{ls}^2 D. \tag{11}
$$

The coefficients $A_{ls}^{(k)}$ and τ_{ls} were calculated numerically for radial and bipolar structures. The results show that only a few terms in this series are relevant. The dominant term corresponds to the correlation time $\approx R^2/10D$ for the radial case and $\approx R^2/40D$ for the bipolar case. For droplets with $0.3\,\mu\text{m} < R < 1.0\,\mu\text{m}$ the correlation times are thus in the ms range. Therefore the translationally-induced rotation relaxation mechanism is expected to be important and easily observable either in the kHz regime in micron size nematic droplets or at higher frequencies in very small droplets ($R < 0.1\,\mu\text{m}$). This relaxation mechanism can also be important in the isotropic phase near the nematic–isotropic phase transition where a surface nematic layer of thickness δ exists [12]. The characteristic translationally-induced rotational correlation time here is about δ^2/D. The effect is more pronounced in small droplets where the relative volume of the surface layer is larger.

3.2. *Cross relaxation*

This relaxation mechanism includes the exchange of nuclear (proton for instance) Zeeman energy between nuclei on the polymer surface and nuclei in the liquid crystal molecules in the droplet. It becomes important when there is a strong, not motionally averaged, dipolar interaction between these two systems of nuclei. In addition there must be a fast exchange of molecules between the surface layer and the rest of the droplet. Introducing τ_s as a surface interaction time for which a molecule is rather firmly

attached to the polymer, we can specify the *fast molecular exchange* limit, where a single relaxation time is expected, by the requirement

$$\tau_s \ll (T_1, T_{1\varrho})_{\text{l.c. surface layer}}; \quad \tau_D, \tau_s/x \ll (T_1/T_{1\varrho})_{\text{free l.c. molecules}}$$

Here x is the relative number of molecules in the surface layer and $\tau_D (\approx R^2/6D)$ a typical time required for a molecule to reach the surface.

The characteristic time for the magnetization exchange on the liquid crystal-polymer interface τ_{cross} can be estimated according to the relations [21] for *strong cross relaxation* when $\tau_{\text{cross}} \ll \tau_s$:

$$\tau_{\text{cross}} \approx \langle \overline{H_{\text{int}}}^2 \rangle^{-1/2}, \tag{12}$$

and

$$\tau_{\text{cross}} \approx \langle \overline{H_{\text{int}}}^2 \rangle \tau_s \tag{13}$$

for *weak cross relaxation* where $\tau_{\text{cross}} \gg \tau_s$. $\overline{H_{\text{int}}}$ is the interfacial dipolar interaction per resonant nucleus on the liquid-crystalline molecule averaged over all molecular motions which are faster than τ_s. The degree of this motional averaging and the length of the interaction time τ_s are expected to be qualitative measures of the strength of molecular anchoring on the polymer surface.

In the presence of cross relaxation the experimental relaxation rate T_1^{-1} is an effective average between the value T_{1f}^{-1} of the free liquid crystal molecules in the droplet and the value corresponding to the molecules bound on the surface [22]. The latter is governed by the polymer relaxation rate and the cross relaxation rate. Comparing relaxation times of the free liquid crystal T_{1f} and of the polymer T_{1p} to the times τ_{cross} and τ_s we find three simple limiting cases:

(*a*) $T_{1p} > \tau_{\text{cross}}/x, \tau_s/x$: here the relaxation rate of the resonant nuclei is given by the average

$$\frac{1}{T_1} = \frac{1-y}{T_{1p}} + \frac{y}{T_{1f}}, \tag{14}$$

where y denotes the ratio between the number of resonant nuclei in liquid-crystalline molecules and their total number in the sample.

(*b*) $T_{1p}, \tau_s < \tau_{\text{cross}}$: T_1^{-1} is, in this limit, the weighted average the relaxation rate of the free liquid crystal T_{1f}^{-1} and the relaxation rate of the liquid crystal molecules attached to the polymer surface, which here is approximately equal to τ_{cross}^{-1}:

$$\frac{1}{T_1} = \frac{1-x}{T_{1f}} + \frac{x}{\tau_{\text{cross}}}. \tag{15}$$

Here the cross relaxation is caused by the modulation of interfacial dipolar interactions due to molecular exchange on the polymer surface. The corresponding τ_{cross}^{-1} is given approximately by $\langle \overline{H_{\text{int}}}^2 \rangle \tau_s$ plus some BPP-type terms [21].

(*c*) $T_{1p}, \tau_{\text{cross}} < \tau_s$: due to the relatively slow molecular exchange in this limit the contribution of the molecules attached to the polymer surface is limited to τ_s^{-1}. We can write, therefore,

$$\frac{1}{T_1} = \frac{1-x}{T_{1f}} + \frac{x}{\tau_s}. \tag{16}$$

Both situations (*b*) and (*c*) are expected to be realized at low resonant frequencies where T_{1p} becomes shorter. The measured values T_1^{-1} can be used to study indirectly

τ_s and $\overline{H_{int}}$. A partial deuteriation of protons on the liquid crystal molecule can reduce $\overline{H_{int}}$ and thus bring us from the limit (*c*) to the limit (*b*). In this way τ_s and $\overline{H_{int}}$ can be determined separately giving a better insight into molecular anchoring on the polymer surface.

4. Conclusions

In this contribution we have analysed nematic structures and the spatial dependence of the orientational ordering near the nematic–isotropic phase transition in small liquid crystal droplets. It was shown that in the case of strong surface anchoring the orientational order changes from the surface-dictated value to the bulk value (nematic or isotropic, depending on the temperature) within a thin layer close to the surface. For micron size droplets the thickness of the layer is about $0{\cdot}1\,R$. Approaching the point defects the degree of the orientational order decreases both for radial and bipolar structures. If the radius of the droplet is reduced, a critical value is reached where the nematic–isotropic transition becomes second order and then disappears.

In the second part of the paper the influence of the molecular confinement on nuclear spin relaxation is considered. It is shown that the translationally-induced rotation relaxation mechanism is expected to be rate determining only in very small droplets ($R < 0{\cdot}1\,\mu m$), where an indirect determination of the translational diffusion constant is possible therefore. On the other hand, cross relaxation between nuclei of the same kind in the droplet and in the surrounding medium is a strong relaxation mechanism in the whole submicron range. By choosing a proper resonant nucleus the surface interaction time for which a liquid crystal molecule is rather firmly attached to the polymer surface can be estimated. The value of the cross relaxation rate gives information of the firmness of molecular anchoring.

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