### Supporting Information for paper

# Magnetic field effects in nematic and smectic liquid crystals probed by time resolved observation of orientation relaxation of the spin probe.

Alexey V. Bogdanov, Gleb I. Proniuk, Andrey Kh. Vorobiev.

# Appendix A. Simulation of angular dependence of EPR spectrum of radical A5 in nematic liquid crystal HOPOOB.

In the present work, the sample of liquid crystal is assumed to have a hierarchic orientation organization. There is the "internal" orientation order, which relates to uniformly aligned areas of liquid-crystalline material (domains), and the "external" orientation order, caused by non-uniform angular distribution of domain directors. This "external" orientation distribution of domain directors is present even in the aligned sample of liquid crystal, due to equilibrium director fluctuations, defects and disclinations of the material. The experimentally observed angular dependence of EPR spectrum is due to the convolution of the both orientation effects. For the purpose of spectra simulation, the "internal" orientation distribution was modeled in the approach of mean-field potential developed by Freed et al [1, 2]. In this approach, the orientation distribution is given by equilibrium Maxwell–Boltzmann type exponent:

$$\rho_{\text{int}}(\theta) = Q^{-1} \cdot \exp\left(\lambda_{20} \cdot \frac{3\cos^2 \theta - 1}{2}\right) \tag{A.1}$$

where  $\lambda_{20}$  is the mean-field potential anisotropy magnitude,  $\theta$  is the angle between the probe molecule orientation axis and domain director, and  $Q = \int_{0}^{\pi} \exp\left(\lambda_{20} \cdot \frac{3\cos^2 \theta - 1}{2}\right) \sin \theta d\theta$  is normalization term.

The domains, which possess the internal order according to orientation distribution function (A.1), are aligned within the material with orientation distribution function of domain directors  $\rho_D(\Theta)$  defined by a set of order parameters  $\langle \mathcal{D}_{00}^{j*} \rangle$ :

$$\rho_D(\Theta) = \sum_{j=0}^{\infty} \frac{2j+1}{8\pi^2} \left\langle \mathcal{D}_{00}^{j*} \right\rangle \cdot \mathcal{D}_{00}^{j}(0,\Theta,0)$$
(A.2)

where now  $\Theta$  is the angle between the sample preferential orientation axis and domain director. The resulting orientation distribution function of the probe molecules in a sample is thus given by the convolution of orientation distribution functions (A.1) and (A.2).

For the spectra simulation, a number of basis spectra for different domain orientations  $\Theta$  was calculated with the approach described in [2]. A joint simulation of angular dependence of EPR spectrum, was carried out, i. e., a series of spectra recorded at different angles  $\beta$  between the sample director and EPR spectrometer magnetic field. The weight function of basis spectrum corresponding to director orientation  $\Theta$  for the spectrum of angular dependence corresponding to angle  $\beta$  between the sample director and EPR spectrometer magnetic field, was calculated using the expression:

$$\rho_{\beta}\left(\Theta\right) = \sum_{j=0,2...}^{J_{\max}} \frac{2j+1}{8\pi^{2}} \left\langle \mathcal{D}_{00}^{j*} \right\rangle \cdot \mathcal{D}_{00}^{j}\left(0,\beta,0\right) \cdot \mathcal{D}_{00}^{j}\left(0,\Theta,0\right)$$
(A.3)

where  $\langle \mathcal{D}_{p0}^{j^*} \rangle$  are order parameters for the "external" orientation distribution function and  $J_{\text{max}}$  is the truncation value. The value  $J_{\text{max}} = 16$  was found to be sufficient for simulation of EPR spectra of A5 in nematic phase of HOPOOB.

It has been found that for successful simulation of radical A5 in HOPOOB it is necessary to account for fast stochastic reorientations of the probe molecule within the solvent cage. This was accounted for by quasi-libration approach [3].

The simulation was carried out using nonlinear-least-squares approach, the varied parameters being: rotation diffusion coefficients, quasi-libration amplitudes, orientation order parameters for "external" ordering, as well as Gaussian and Lorentzian linewidths

The results of spectra simulation are presented in Fig. A1 and Table A1. In Fig. A1 the experimental spectra (black lines) and optimum simulated spectra (red lines) are compared. It is seen that the quantitative agreement between experiment and simulation is achieved. In Table A1 the principal parameters obtained in the course of simulation, are listed.

Table A1. Principal parameters used for simulation of angular dependence of EPR spectra of radical A5 in liquid crystal HOPOOB in the nematic phase.

g-tensor*	2.0097; 2.0068; 2.0023
hfs-tensor*	7.1; 4.9; 34.17
rotation diffusion	$R_x = R_y = R_z = 1.8 \cdot 10^9 \text{ s}^{-1}$
tensor	
Diffusion tilt,	0; 90°; 90°
$\Omega_{d \to m}^{**}$	
Mean field	13.9 $k_B T$
potential	
coefficient $\lambda_{20}$ for	
"internal"	
orientation order	
Quasi-libration	51°; 0; 66°
amplitudes	
Order parameters	$\left\langle \mathcal{Z}_{00}^{0^*} \right\rangle = 1.000  \left\langle \mathcal{Z}_{00}^{6^*} \right\rangle = 0.6113  \left\langle \mathcal{Z}_{00}^{12^*} \right\rangle = 0.2030$
for orientation	$\langle \mathcal{R}_{22}^{2*} \rangle = 0.8849 \langle \mathcal{R}_{22}^{8*} \rangle = 0.4647 \langle \mathcal{R}_{22}^{14*} \rangle - 0.1085$
distribution of	$\begin{pmatrix} 200 \\ -0.100 \end{pmatrix}$
domain directors	$\left\langle \mathcal{Z}_{00}^{4^*} \right\rangle = 0.7504  \left\langle \mathcal{Z}_{00}^{10^*} \right\rangle = 0.3235  \left\langle \mathcal{Z}_{00}^{16^*} \right\rangle = 0.038$

<sup>\*</sup> determined from the separate experiment, not varied during simulation

\*\* Euler angles that transform diffusion reference frame into magnetic reference frame



Fig. A1. Experimental spectra of the angular dependence of A5 in HOPOOB (black lines) and results of their quantitative simulation (red lines).

The obtained order parameters relate to the preferential orientation of domains along z-axis of the reference frame:

$$\rho_D^0\left(\theta,0\right) = \sum_{j=0}^{\infty} \frac{2j+1}{8\pi^2} \left\langle \mathcal{D}_{00}^{j*} \right\rangle \cdot \mathcal{D}_{00}^j\left(0,\theta,0\right) \tag{A.4}$$

Orientation distribution function of domain directors  $\rho_D(\theta, \varphi)$  is substituted in the model of magnetic field reorientation described in the text:

$$\frac{d\rho_D(\theta,\varphi)}{d\tau} = 3 \frac{\int \left(\cos^2\theta - \cos^2\theta'\right) \rho_D^{2/3}(\theta,\varphi) \rho_D^{2/3}(\theta',\varphi') \sin\theta' d\theta' d\varphi'}{\int \rho_D^{2/3}(\theta',\varphi') \sin\theta' d\theta' d\varphi'}$$
(A.5)

To account for the turn of sample by 90° prior to observation its reorientation in magnetic field, the rotation of orientation distribution function was carried out using the equation [4]:

$$\rho_{D}^{90}(\theta,\varphi) = \sum_{j=0}^{J_{\max}} \sum_{m=-j}^{j} \frac{2j+1}{8\pi^{2}} \left\langle \mathcal{D}_{00}^{j*} \right\rangle \cdot \mathcal{D}_{0m}^{j} \left(90^{\circ}, 90^{\circ}, -90^{\circ}\right) \cdot \mathcal{D}_{m0}^{j} \left(\varphi, \theta, 0\right) =$$

$$= \sum_{j=0}^{J_{\max}} \sum_{m=-j}^{j} \frac{2j+1}{8\pi^{2}} \left\langle \mathcal{D}_{00}^{j*} \right\rangle \cdot \left(-\frac{1}{4}\right)^{j/2} \cdot \frac{\sqrt{(j+m)!(j-m)!}}{\left(\frac{j+m}{2}\right)! \left(\frac{j-m}{2}\right)!} \cdot \mathcal{D}_{m0}^{j} (\varphi, \theta, 0)$$
(A.6)

The obtained orientation distribution  $\rho_D^{90}(\theta, \varphi)$  was used as a starting point for simulation of magnetic field reorientation according to eq. (A.5). In the course of modeling of the evolution of domain orientation distribution, the orientation distribution functions at different moments of time are obtained. These are used as the orientation distribution functions of "external" order to simulate EPR spectra of the sample in the course of reorientation (cf. Fig. 5b of the manuscript).

#### Appendix B. Model of reorientation of smectic C phase.

In this section, the model of reorientation of smectic C liquid crystal in the magnetic field, is described. Geometric constructions and vector designations used for the simulation of smectic C reorientation, are illustrated in Fig. B1.



Fig. B1. A sketch illustrating geometry of the smectic C sample.

Let us consider the sample-fixed reference frame xyz, with the initial director be defined by unit vector  $\mathbf{n}_0$ , directed along z-axis. Then the normals to smectic planes N are distributed on the cone with the axis along z and aperture of  $2\Psi$ , where  $\Psi$  is the tilt angle of molecules within the smectic layer:

$$N(\varphi) = (\sin \Psi \cos \varphi, \sin \Psi \sin \varphi, \cos \Psi)$$
(B.1)

where  $\varphi$  goes from 0 to  $2\pi$ .

For each domain (i. e., for a fixed value of  $\varphi$ ), the reorientation of director tilt gives a continuum of new possible directors distributed on a cone with generatrix  $\mathbf{n}_0$  and aperture of  $2\Psi$ . The reorientation of tilt director by angle  $\alpha$  produces the new director  $\mathbf{n}_1$ :

$$\mathbf{n}_{1}(\varphi, \alpha) = N \cos \Psi + \mathbf{p} \cos \alpha + \mathbf{q} \sin \alpha =$$

$$= (\sin \Psi \cos \Psi \cos \varphi - \sin \Psi \cos \Psi \cos \varphi \cos \alpha + \sin \Psi \sin \varphi \sin \alpha,$$

$$\sin \Psi \cos \Psi \sin \varphi - \sin \Psi \cos \Psi \sin \varphi \cos \alpha - \sin \Psi \cos \varphi \sin \alpha,$$

$$\cos^{2} \Psi + \sin^{2} \Psi \cos \alpha)$$
(B.2)

Here  $N \cos \Psi$  is the cone height, and p and q are two mutually perpendicular base radii, p being directed from the base center towards z-axis, and q being perpendicular to z-axis:

$$\boldsymbol{p} = \left(-\sin\Psi\cos\Psi\cos\varphi, -\sin\Psi\cos\Psi\sin\varphi, \sin^2\Theta\right),$$
$$\boldsymbol{q} = \left(\sin\Psi\sin\varphi, -\sin\Psi\cos\varphi, 0\right)$$

Before the sample turn the magnetic field vector is directed along  $\mathbf{n_0}$ . Let the sample turn around *y*-axis. Then, after the turn of the sample by angle  $\pi/2$ , the unit vector of magnetic field **h** is directed along *x* axis:

$$\mathbf{h} = (1, 0, 0)$$
.

In the case of unconstrained reorientation of layer tilt direction, the energy of interaction of the director with magnetic field is given by

 $u = -\mathcal{M} \left( \mathbf{n}_1 \cdot \mathbf{h} \right)^2 = -\mathcal{M} \left( \sin \Psi \cos \Psi \cos \varphi - \sin \Psi \cos \varphi \cos \alpha + \sin \Psi \sin \varphi \sin \alpha \right)^2$ (B.3) where  $\mathcal{M}$  is a dimensional constant, which defines the magnetic anisotropy magnitude (see text).

In Fig. B2a the shape of the potential defined by eq. (B.3) for different domains (i. e. different values of  $\varphi$ ) is illustrated. One can see that the potential has two minima, and care should be taken for minimization procedure to converge to the deeper minimum. Figure B2b shows the optimum values of angle  $\alpha$  of tilt direction reorientation depending on the domain orientation  $\varphi$  obtained as the result of minimization of corresponding potentials (B.3). This figure also shows the values of angle  $\xi$  between the new domain director and the magnetic field for the optimum director orientations.



Fig B2. (a) Shapes of potentials in the model of unconstrained tilt direction reorientation, according to eq. (B.3), defining the energy of the domain in the magnetic field, for different domains (different values of angle  $\varphi$ ); (b) dependence of the optimum values of angles  $\alpha$  and  $\xi$  on domain orientation.

In the modification of this model, described in the paper text, the elastic constraint of tilt direction rotation is considered. In this case, the potential has the form:

$$u = -\mathcal{M} \left( \mathbf{n}_{1} \cdot \mathbf{h} \right)^{2} + K_{el} \cdot \alpha^{2}$$
(B.4)

In this case, the shape of the potential is illustrated in Fig. B3a (mind different  $\alpha$  scales in Figs. B2a and B3a). It can be seen that in this case large changes of tilt direction become infavorable, due to the quadratic elastic term. The optimum values of angle  $\alpha$  of tilt direction turn and of angle  $\xi$  between the new domain director and the magnetic field, are presented in Fig. B3b. It is seen that for domains, for which  $\varphi$  is in the vicinity of 0 and  $\pi$ , no reorientation of tilt direction takes place. Comparison with Fig. B2 shows that these are the domains for which larger the optimum values of  $\alpha$  correspond to large reorientations.



Fig. B3. (a) Shapes of potentials in the model of constrained tilt direction reorientation, according to eq. (B.4), defining the energy of the domain in the magnetic field, for different domains (different values of angle  $\varphi$ ); (b) dependence of the optimum values of angles  $\alpha$  and  $\xi$  on domain orientation.

In summary, by minimizing potential (B.3) or (B.4), one obtains the optimum tilt reorientation angle  $\alpha$  for a set of domains with different layer normal directions  $N(\varphi)$ . The resulting distribution of optimum angles between the liquid crystal director and the new direction of magnetic field ( $\xi$ ) gives the orientation distribution function of smectic domains  $\rho_D(\xi)$  in the relaxed smectic sample (cf. Fig. 6a of the manuscript).

# Appendix C. Calculation of theoretical EPR spectra for smectic C reorientation.

To calculate EPR spectra of the radical in the smectic C phase in the course of its reorientation in magnetic field, the orientation distribution function of smectic domains  $\rho_D(\xi)$  (obtained in the previous section) is used. The spectrum is calculated as superposition of individual spectrum for each orientation multiplied by the fraction of domains at this orientation:

$$f(H) = \int_{0}^{\pi/2} f_{ind}(H,\xi) \rho_D(\xi) d\xi$$
(C.1)

where f(H) is the shape of resulting EPR spectrum,  $\xi$  is the angle between the domain director and magnetic field of EPR spectrometer,  $f_{ind}(H,\xi)$  are individual spectra for each orientation.

As it has been shown in the paper, partial reorientation of liquid crystal takes place upon the sample turn in the magnetic field. Due to this partial relaxation process, the experimentally observed EPR spectra of angular dependence in the smectic phase are not the true spectra of individual orientations. This angular dependence obtained in the present work (cf. Fig. 2b) could not be successfully simulated, as each spectrum of angular dependence relates to a different orientation distribution function.

In this paper, the theoretical spectra of the smectic phase are used only for qualitative illustration of smectic C reorientation models. For the sake of this illustration, a very simplified approach is used for spectra calculation. The spectra are approximated by a sum of three Lorentzian lines, of which the positions and linewidths are interpolated from the experimental angular dependence. The line positions and widths are illustrated in Fig. C1.



Fig. C1. Experimentally measured component positions (a) and linewidth (b) for the spectra of angular dependence of radical A5 in liquid crystal HOPOOB in the smectic phase.

Simple interpolation formulas for line positions  $H_i$  and linewidths  $\Delta H_i$  were obtained on the basis of experimental data:

$$H_{1} = 3344.16 + 3.68 \cdot \cos^{2} \xi$$

$$H_{2} = 3361.08 - 1.11 \cdot \cos^{2} \xi$$

$$H_{3} = 3378.23 - 6.27 \cdot \cos^{2} \xi$$

$$\Delta H_{1} = 2.000 - 0.423 \cdot \cos^{2} \xi - 0.4 \cdot \cos^{2} (2\xi)$$

$$\Delta H_{2} = 1.558 - 0.473 \cdot \cos^{2} \xi$$

$$\Delta H_{3} = 2.781 - 0.548 \cdot \cos^{2} \xi - 0.9 \cdot \cos^{2} (2\xi)$$
(C.2)

The lineshape function used was as follows:

$$f_{ind}(H; H_i, \Delta H_i) = -\frac{16(H - H_i)\Delta H_i}{\pi \left(4(H - H_i)^2 + (\Delta H_i)^2\right)^2}$$
(C.4)

Thus, the EPR spectra of relaxed samples were calculated by eq. (C.1) with the use of the orientation distribution functions obtained on the basis of the reorientation models and lineshapes for individual spectra given by (C.4).

Appendix D. Comparison of experimental and modeled spectra for magnetic field reorientation of nematic and smectic C phases of HOPOOB.



Fig. D1. EPR spectra of the spin probe A5 liquid crystal HOPOOB in nematic phase during the process of magnetic field reorientation; experimental spectra (black lines), theoretical spectra (red lines). Numbers in seconds denote the time after the turn of the sample corresponding to the experimental spectra; numbers in parentheses denote dimensionless time  $\tau$  corresponding to the theoretical spectra.



Fig. D2. EPR spectra of the spin probe A5 liquid crystal HOPOOB in smectic C phase during the process of magnetic field reorientation; experimental spectra (black lines), theoretical spectra (red lines). The spectra before the sample turn, immediately after the sample turn and after orientation relaxation, are presented.

### **References:**

1. J.H. Freed. Stochastic-molecular theory of spi-relaxation for liquid crystals // J. Chem. Phys. 1977. V. 66. No 9. P. 4183-4199.

2. E. Meirovitch, D. Inger, E. Inger, G. Moro, J.H. Freed. Electron-spin relaxation and ordering in smectic and supercooled nematic liquid crystals // J. Chem. Phys. 1982. V. 77. No 8. P. 3915.

3. D.A. Chernova, A.K.H. Vorobiev. Molecular Mobility of Nitroxide Spin Probes in Glassy Polymers. Quasi-Libration Model // J. Polym. Sci. B: Polym. Phys. 2009. V. 47. No 1. P. 107-120.

4. D.A. Varshalovich, A.N. Moskalev, A.K. Khersonskii. Quantum theory of angular momentum: Irreducible tensors, Spherical harmonics, Vector coupling coefficients, 3Nj symbols. : World Scientific, 1988. 514.