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Simulations of flow-induced director structures in nematic liquid crystals through Leslie-Ericksen equations. II. Interpretation of NMR experiments in liquid crystal polymers

Assis F. Martins* and Alexandre E. Gomes
Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2825-114 Monte de Caparica, Portugal

Antonino Polimeno and Laura Orian
Department of Physical Chemistry, University of Padova, Via Loredan 2, 35131 Padova, Italy

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Computationally exact and approximate solutions of the Leslie-Ericksen equations for nematic liquid crystals in two dimensions are employed to calculate director distributions in cylindrical samples, rotating under the influence of a magnetic field. In particular, the time evolution of systems prepared initially in metastable states with respect to the magnetic field is investigated, and calculated director distributions are used to interpret rheo-NMR experiments in nematic liquid crystal polymers.

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I. INTRODUCTION

In the preceding paper (hereafter referred to as I) [1], a computational methodology for the treatment of Leslie-Ericksen (LE) equations [2–4] in two dimensions was presented, and a number of significant dynamical behaviors were described for a classical experimental setup, in which the nematic fluid is contained in a cylindrical vessel and subjected to magnetic torques and/or mechanical stresses induced by spinning, either with a constant rotational speed or according to a start-and-stop speed profile. In this work it is our intention to complement the discussion presented in I by illustrating a restricted application of the LE equations to the interpretation of combined rheological and nuclear magnetic resonance (NMR) experiments performed on nematic polymers [5–7]. We shall introduce additional approximations that take into account specific features of the experimental setup and we shall compare simulated spectra with experimental results. Our purpose is mainly to demonstrate that a qualitative interpretation of the dynamical behavior of a nematic polymer under mechanical stress, detected by NMR spectroscopy, can be reached within the Leslie-Ericksen approach, at a modest computational effort.

Magnetic resonance experiments, both nuclear magnetic resonance and electron spin resonance (ESR) [8,9], can be used to monitor the time evolution of nematic director patterns, which evolve according to the hydrodynamics of the fluid and the influence of magnetic and mechanical forces and in principle are obtainable from numerical solutions of LE equations. The complexity of the computational treatment of LE equations, even in two dimensions, is essentially due to the algebraically involved form of the coupling terms between the director vector field $\mathbf{n}(\mathbf{r},t)$, which specifies the orientation of the local director at time t and position $\mathbf{r}$, and the velocity vector field $\mathbf{v}(\mathbf{r},t)$, which describes the local flux of the fluid [1]. By introducing suitable functions related to the primary variables, like the vorticity and stream functions of the fluid and the angle made by the director with the magnetic field, one can significantly reduce the complexity of the equations, without introducing any additional approximation. An exact computational treatment, which takes into account the spatial dependence of the director field and its coupling with the velocity field, is required when low viscosity nematics (0.1–10 Pa s) are subject to fast mechanical perturbations (e.g., start-and-stop rheo-NMR and ESR measurements), particularly if one is interested in determining the director field behavior during the mechanical solicitation [1]. Suitable approximate treatments can be introduced if the system is under the influence of the magnetic field only, and for nematic liquid crystals characterized by much larger viscosities (10^2–10^3 Pa s), since in this case it is permissible to simplify the treatment of the velocity field (or related functions) considerably, as it relaxes faster than the director field and can be treated adiabatically.

We shall concentrate in the following on a particular experimental setup combining rheology and NMR, performed on a nematic liquid crystal polymer, as an example of the application of nematodynamics to the semiquantitative interpretation of magnetic resonance experiments in liquid crystal samples. The system will be initially prepared assuming that the director is aligned perpendicularly to a strong magnetic field. We shall assume that the initial distribution of the director field is subjected to thermal fluctuations, whose time evolution will be treated in the following as determined purely by nematodynamics equations. For metastable initial distributions, for instance, if the director is aligned perpendicularly to the magnetic field, fluctuations are the main source of symmetry breaking, which allows the director field to start realigning with the magnetic field in the absence of mechanical stress. Approximate solutions of the LE equations will be used to calculate theoretical spectra to be compared with experimental data.

This paper is organized in the following way. In the next section a brief summary is given of the computational methodology described in I; next, additional approximations suitable for highly viscous nematics are illustrated. Comparison

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*Corresponding author. Email address: asfm@mail.fct.unl.pt of calculated and experimental spectra is discussed in Sec. III. Finally, a short summary of our work is provided.

II. METHODOLOGY

Let us first summarize the main equations derived in I and the computational methodology employed for their treatment. For a generic nematic, characterized by an average elastic constant K and Leslie viscosities α_i $(i=1,\ldots,6)$, the LE equations in their vorticity-stream function form in two dimensions can be written in the following way [1]:

$$\frac{\partial \phi}{\partial \tau}+\frac{\partial(\psi,\phi)}{\partial(x_1,x_2)}-\frac{1}{2}\xi=\varsigma, \tag{1}$$

$$\begin{aligned}\frac{\partial \xi}{\partial \tau}+\frac{\partial(\psi,\xi)}{\partial(x_1,x_2)}={}&a_K\frac{\partial(\phi,\hat{\nabla}^2\phi)}{\partial(x_1,x_2)}\\ &+a_1\left[-\frac{\partial^2}{\partial x_1\partial x_2}\mu\cos 2\phi\right.\\ &\left.+\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}-\frac{\partial^2}{\partial x_2^2}\right)\mu\sin 2\phi\right]\\ &+a_2\left[\frac{\partial^2}{\partial x_1\partial x_2}\varsigma\sin 2\phi\right.\\ &\left.+\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}-\frac{\partial^2}{\partial x_2^2}\right)\varsigma\cos 2\phi\right]\\ &+a_3\hat{\nabla}^2\varsigma+a_4\hat{\nabla}^2\xi+a_5\hat{\nabla}^2\nu,\end{aligned} \tag{2}$$

$$\xi=\hat{\nabla}^2\psi, \tag{3}$$

$$\varsigma=\lambda\eta+b_1\sin 2\phi+b_2\hat{\nabla}^2\phi, \tag{4}$$

$$\eta=\frac{1}{2}\cos 2\phi\left(\frac{\partial^2\psi}{\partial x_1^2}-\frac{\partial^2\psi}{\partial x_2^2}\right)+\sin 2\phi\frac{\partial^2\psi}{\partial x_1\partial x_2}, \tag{5}$$

$$\mu=\frac{1}{2}\sin 2\phi\left(\frac{\partial^2\psi}{\partial x_1^2}-\frac{\partial^2\psi}{\partial x_2^2}\right)-\cos 2\phi\frac{\partial^2\psi}{\partial x_1\partial x_2}, \tag{6}$$

$$\nu=\frac{1}{2}\cos 2\phi\left(\frac{\partial^2\psi}{\partial x_1^2}-\frac{\partial^2\psi}{\partial x_2^2}\right)-\sin 2\phi\frac{\partial^2\psi}{\partial x_1\partial x_2}, \tag{7}$$

choosing as unknowns the scaled vorticity $\xi=\Xi/\Omega$ and the stream function $\psi=\Psi/\Omega R^2$, and scaled time and coordinates $\tau=t\Omega$, $x_1=r_1/R$, $x_2=r_2/R$, where Ω has the dimension of a rotational velocity, for instance, the rotational velocity imposed on the tube; ϕ is the angle made by the director with the magnetic field. Coefficients a_K, a_i $(i=1,\ldots,5)$, λ, and b_j $(j=1,2)$ are written explicitly in terms of the viscoelastic constants: $a_K=K/s^2\rho$, $a_1=\alpha_1/s\rho$, $a_2=\gamma_2/s\rho$, $a_3=-\gamma_1/2s\rho$, $a_4=(\alpha_4/2+\gamma_3/4)/s\rho$, and $a_5=-\gamma_2/2s\rho=-a_2/2$, where $s=\Omega R^2$; and $\lambda=-\gamma_2/\gamma_1$, $b_1=-\chi_a H^2/2\gamma_1\Omega$, and $b_2=K/\gamma_1 s$. The coefficients γ_i $(i=1,\ldots,3)$ are defined according to Parodi's relation:

$$\gamma_1=\alpha_3-\alpha_2, \tag{8}$$

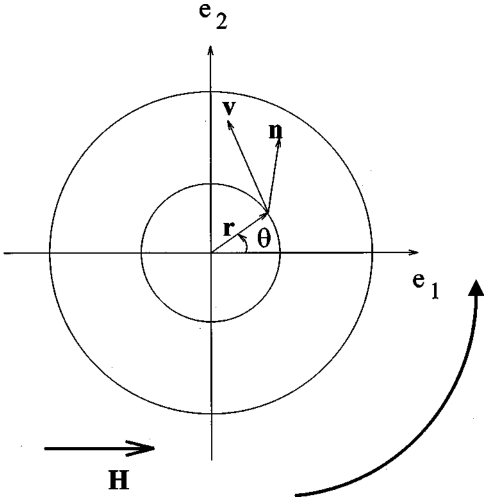

FIG. 1. Sketch of a rheo-NMR start-and-stop experimental geometry.

$$\gamma_2=\alpha_3+\alpha_2=\alpha_6-\alpha_5, \tag{9}$$

$$\gamma_3=\alpha_6+\alpha_5. \tag{10}$$

Notice that the coefficients a_i are essentially Ekman numbers and b_2 is the inverse of a rotational Ericksen number. The influence of the aligning magnetic field is contained in b_1, for the experimental setup illustrated in Fig. 1; the average elastic constant appears in a_K and b_2, which quantify the elastic effect in the vorticity equation (2) and in the director equation (1), respectively. The computational treatment adopted in I was based on a straightforward finite-difference algorithm. Simplified boundary conditions were imposed, assuming that in the neighborhood of the internal cylindrical walls of the sample container (NMR tube), the LE equations are satisfied without significant changes of the director orientation due to the walls [1].

A. Highly viscous nematics

Applications of the full equations (1) and (2) discussed in I were mainly concerned with low viscosity nematics, i.e., nematic fluids with Leslie coefficients of the order of 0.1–10 Pa s. The main object was the study of director dynamical behavior in the presence of an imposed magnetic field, which was assumed to be of the order of 10^3 G, typical of an ESR experiment. Finally, the outcome was the description of spatial time-dependent distributions of the director field under fast rotation (Ω of the order of $10^2\ \mathrm{s}^{-1}$) for short periods (milliseconds) or slow rotation (Ω of the order of $1\ \mathrm{s}^{-1}$) for long periods (seconds). The purpose was to investigate backflow effects arising from the coupling between director and velocity fields, which are especially important for low viscosity nematic fluids, and the long time behavior of a nematic fluid under stationary conditions. It was then essential to simulate the complete development of the system by fully solving the constitutive equations in their bidimensional form (1) and (2). Such calculations are necessarily cumbersome [1], especially because one needs to calculate the director response during the fast rotation regime, in which the system is rapidly accelerated, and the following long time relaxation to a realigned state with respect to the magnetic field. However, a number of interesting phenomena inferred from the analysis of ESR spectra collected during step-rotation experiments were rationalized, like (i) initial spreading and subsequent refocusing of the director distribution, (ii) the ''overshooting'' effect, i.e., partial orientation of the director field above the angle of rotation of the sample, and (iii) weak backflow resulting from coupling with the velocity field [9]. In this work our scope is different and more limited. First of all, we shall shift our interest from low viscosity to high viscosity systems, having in mind, essentially, a typical NMR experiment performed on a nematic polymer, combined with rheological measurements. Classical rheo-NMR experiments [5,6,10] are usually performed by imposing a sudden rotation on the NMR tube containing the nematic, in a time which is essentially instantaneous compared to the time scale of the director response. It is important, however, to define the initial state carefully, in order to describe the possible amplification of long wavelength distortions of imperfectly aligned initial director distributions. This is especially true if the starting distribution is in an *unstable* configuration, corresponding, for instance, to an alignment perpendicular to the magnetic field resulting from an initial rotation of the tube of 90°. During the subsequent realignment to the magnetic field, the director orientation is, for all practical purposes, separated from the fast adjustment of the velocity flux, which is not caused by any mechanical torque but just by the local reorientation of the director itself. This allows a simplified treatment of the coupled LE equations. In the following, then, we shall propose a simplified form for Eqs. (1) and (2), working for an effective albeit approximate interpretation of rheo-NMR experiments performed on high viscosity nematics, and we shall compare simulated NMR spectra with available experimental data.

B. Approximate treatment

The following experimental setup will be considered throughout the paper (cf. Fig. 1). A highly viscous nematic (Leslie coefficients of the order of 10^2–10^3 Pa s) is subjected to a constant magnetic field of the order of a few tesla, in a tube having the diameter of a typical NMR probe, 0.5–1 cm. The director is initially aligned with the magnetic field. A very fast rotation of 90° is imposed on the system, which can be considered instantaneous compared to the total time scale of the experiment (the *rotation step*), to prepare the system in a configuration perpendicular to the magnetic field (*initial configuration*). The system then realigns with the magnetic field, on a time scale of the order of 10^3 s (*realignment*). Let us analyze the rotation-step regime in detail. For a low viscosity nematic it has been shown [1] that the director is unable to rigidly follow the sudden change in orientation. Indeed, for viscosities of the order of 0.1–10 Pa s and for relatively large tubes, i.e., those with diameters of the order of 1 cm, and for a duration of the rotation step of the order of tens of milliseconds, the director field in the bulk of the system is never actually rotated [1]. For increasingly viscous nematics, keeping the tube dimension and rotation time constant, the system behaves increasingly according to a rigid-like behavior, i.e., the director field is rotated in the whole sample in a homogeneous way, by an angle close to the cylinder rotation angle. To illustrate this phenomenon, we have simulated the director behavior for a series of hypothetical nematic liquid crystal samples of increasing viscosities, through the complete numerical solution of Eqs. (1) and (2). In Fig. 2 we show snapshots of the director orientation, represented via a false color convention: from blue (0°) to green (90°) and finally red (180°), the colors represent the local director orientation ϕ, for a sudden rotation of 90°. The diameter of the tube is 0.75 cm and the rotational speed is 100 s^{-1}, while the rotation time is 15 ms. In Fig. 2(a) we show the director patterns for a low viscosity nematic (see Table I): the system dimension is large enough and the rotation time is fast enough that essentially no realignment is reached perpendicular to the magnetic field. On increasing all the viscosity numbers tenfold the director rotates inhomogeneously, lagging behind in the bulk [see Fig. 2(b)]; further increase of the viscosity [Figs. 2(c) and 2(d)] causes the director to rotate rigidly and homogeneously in the whole sample. We can thus safely assume in the following that, when one analyzes a highly viscous nematic, the rotation step can be assimilated into a rigid rotation of the director, which is confirmed by experimental observations. Thus our starting configuration for analyzing step-rotation NMR experiments performed in polymers will be based on the assumption that immediately before rotation (time 0^-) the director is homogeneously aligned with the magnetic field, except for the possible existence of long wavelength thermal fluctuations; immediately after rotation (time 0^+) the director is homogeneously perpendicular to the magnetic field. The initial velocity field at 0^+ is taken to be zero everywhere in the field, i.e., a sudden and complete stop of the tube is assumed to spread instantaneously to the fluid: this is confirmed by experimental NMR lines which are identical in shape immediately before and after rotation (see Sec. III).

The assumed distribution of the director at time 0^+ is intrinsically unstable, i.e., it corresponds to a maximum of the free energy of the system. The director can realign parallel to the magnetic field by rotating in two opposite directions, which are energetically equivalent. Thermal fluctuations are the source for an imperfect alignment of the director, causing the initial symmetry to be broken. Following Veron *et al.* [11], we shall represent initial fluctuations in terms of Fourier components, retaining the first few wavelength components, corresponding to the lower elastic modes.

It is not our purpose here to discuss thoroughly the treatment of thermal fluctuations in nematics. Rather, we are mostly interested in the evolution of slightly perturbed initial states, assuming implicitly that on the long time scale of the process of realignment to the magnetic field, purely hydrodynamic and deterministic behavior is to be expected, at least for highly viscous nematics. Also, we are neglecting in our study any relaxation processes characteristic of the polymer (conformational motions, etc.), assuming that the Leslie-Ericksen hydrodynamic equations suffice to describe the main features of the director relaxation.

We are now in the position of evaluating the dynamical evolution of the director under the restoring pull of the magnetic field. The complete numerical solution of Eqs. (1) and (2) is possible, but very cumbersome because of the large difference in the time scales of the director orientation ϕ and the velocity-related quantities ξ and ψ. On the other hand, for

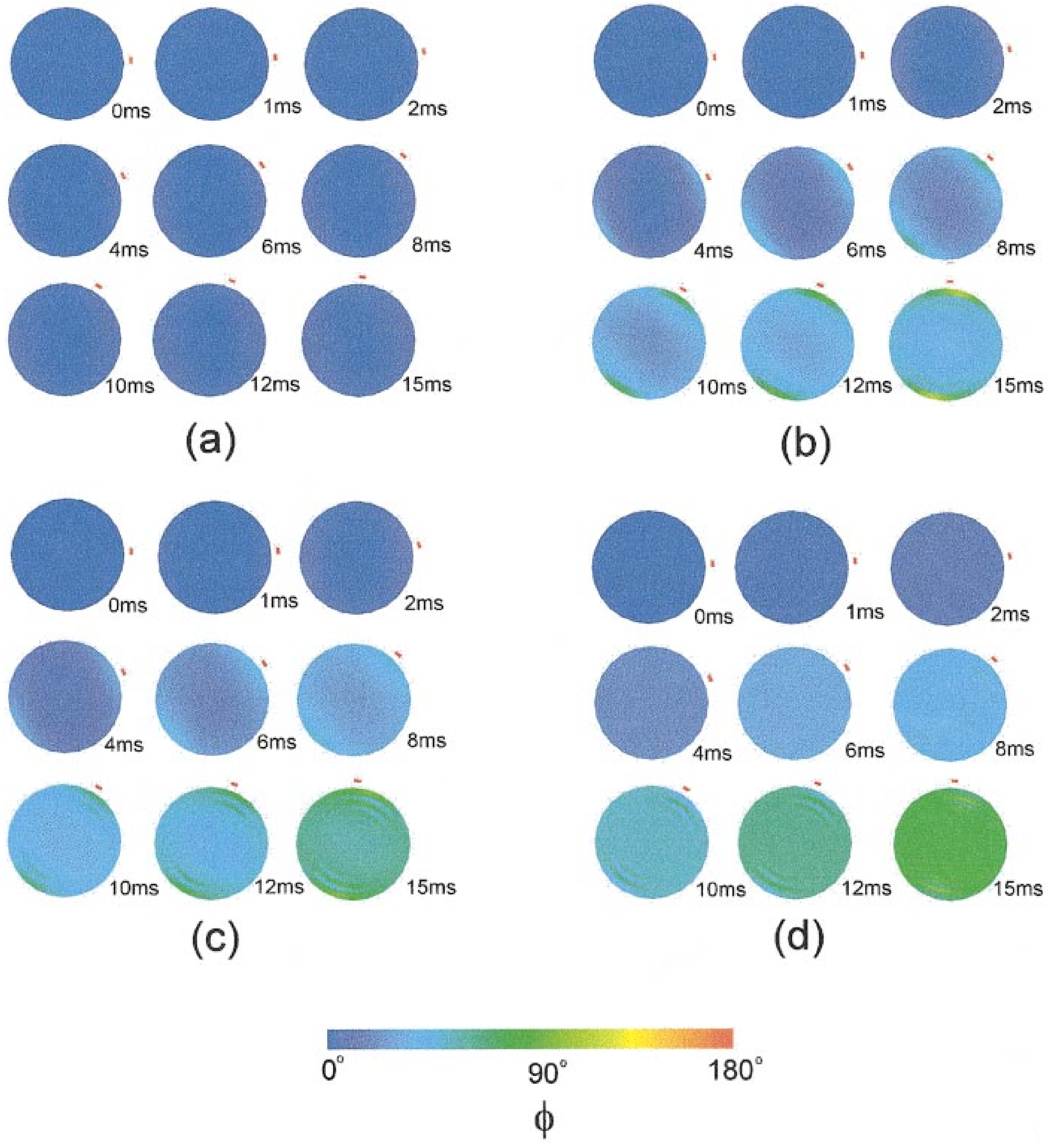

FIG. 2. (Color) Snapshots of the director patterns obtained for a 90° step rotation in a low viscosity nematic (a) and in a system with viscosities increased 10 times (b), 50 times (c), and 100 times (d). See Table I for the complete parametrization and Ref. [1] for a guide to the false color interpretation. Times are 0, 1, 2, 4, 6, 8, 10, 12, and 15 ms.

a highly viscous system such as a nematic polymer, we may safely assume that the velocity flux of the fluid in the absence of externally imposed mechanical stresses is relatively small and adiabatically determined by the director reorientation. In the following we shall thus consider the treatment of the realignment regime using a simplified version of Eqs. (1) and (2), which are essentially obtained from them by (1) neglecting entirely the material time derivative of the vorticity in Eq. (2), to take into account the adiabatic variation of the velocity field; (2) simplifying the material time derivative of the director orientation in Eq. (1) by neglecting the convective term, i.e., $\partial/\partial\tau \approx D/D\tau$; and (3) considering the spatial dependence of the velocity-related functions only upon the x_2 coordinate, i.e., assuming that the velocity flux along

TABLE I. Low viscosity nematic liquid crystal: MBBA (4-methoxybenzylidene-4-n-butilaniline) 10 K below clearing point.

Density	ρ	10^3 kg m^{-3}
Susceptibility	χ_a	1.62×10^{-7}
Field	H	7.065 T
Average elastic constant	K	1×10^{-11} N
Leslie coefficients	α_i	$-0.0087,\ -0.052,\ -0.002,\ 0.058,\ 0.038,\ -0.016$ Pa s

the direction parallel to the magnetic field is dominant:

$$\frac{\partial\psi}{\partial x_1}\propto v_2=0. \tag{11}$$

The approximate equation for the director can be written, according to point (1), simply as

$$\frac{\partial\phi}{\partial\tau}=\tfrac{1}{2}\,(1-\lambda\cos2\phi)\xi+b_1\sin2\phi+b_2\hat{\nabla}^2\phi, \tag{12}$$

and the scaled vorticity ξ can be obtained as a function of ϕ taking into account that the ancillary functions η, μ, and ν which appear in Eq. (2) can be simplified according to point (2):

$$\eta=\nu=\tfrac{1}{2}\xi\cos2\phi,\qquad \mu=\tfrac{1}{2}\xi\sin2\phi. \tag{13}$$

Since ζ is immediately expressed in terms of ξ and ϕ as $\varsigma=\partial\phi/\partial\tau-\xi/2$, we can write a second order partial differential equation in ξ from Eq. (2) in the form

$$\frac{\partial^2}{\partial x_i\partial x_j}\left(A_{ij}(\phi)\xi+B_{ij}(\phi)\frac{\partial\phi}{\partial\tau}\right)=0, \tag{14}$$

where Einstein's notation is used and matrices **A** and **B** are defined, whose elements $A_{ij}(\phi)$ and $B_{ij}(\phi)$ are functions of the director angle ϕ:

$$\mathbf{A}=\frac{1}{4}\begin{pmatrix} a_1\sin^2 2\phi-2a_2\cos2\phi-2a_3+4a_4 & -a_1\sin2\phi\cos2\phi-2a_2\sin2\phi\\ -a_1\sin2\phi\cos2\phi-2a_2\sin2\phi & -a_1\sin^2 2\phi-2a_3+4a_4\end{pmatrix}, \tag{15}$$

$$\mathbf{B}=\frac{1}{2}\begin{pmatrix} a_2\cos2\phi+2a_3 & a_2\sin2\phi\\ a_2\sin2\phi & -a_2\cos2\phi+2a_3\end{pmatrix}. \tag{16}$$

The elastic term in a_K [cf. Eq. (1)] has been neglected, since it is at least three orders of magnitude smaller than the viscous terms. The complete solution can be obtained numerically and substituted back into Eq. (12), or a simplified solution can be recovered by retaining only the dominant term, which corresponds to $i=j=2$. Under the condition that ξ is periodic [5,10,11] along the direction perpendicular to the magnetic field, we get

$$\xi=-\frac{B_{22}(\phi)}{A_{22}(\phi)}\frac{\partial\phi}{\partial\tau}. \tag{17}$$

Substituting in Eq. (12) we get the final approximate equation for the director time evolution:

$$\frac{\partial\phi}{\partial\tau}=\frac{b_1\sin2\phi+b_2\hat{\nabla}^2\phi}{1+\dfrac{(1-\lambda\cos2\phi)(-a_2\cos2\phi+4a_3)}{-a_1\sin^2 2\phi-2a_3+4a_4}}. \tag{18}$$

Equation (18) is of limited, but clearly defined, value: it is applicable for high magnetic fields, absence of mechanical stresses, and large viscosities.

III. INTERPRETATION OF RHEO-NMR SPECTRA

We shall consider in this section the application of the procedure summarized above to interpret rheo-NMR data obtained for a solution of 14% of poly-l-benzylglutamate (PBLG) in *m*-cresol [11], a model lyotropic polymer liquid crystal (PLC).

The combined rheological and NMR experiment [5,11] consists in putting the PLC sample in a strong magnetic field and allowing enough time for the director to become fully aligned with the magnetic field direction. Then the sample is suddenly rotated by an angle of 90° and deuterium NMR (D-NMR) spectra are collected during the following director relaxation process. Let us first summarize the experiment in more detail. In the initial state the polymer sample is at rest in the strong magnetic field **H** of the NMR spectrometer. At equilibrium, the molecules become aligned parallel to **H**, at least on average, and the nematic director field becomes homogeneous in space. The D-NMR spectrum then shows a symmetric doublet. The separation between doublet peaks reflects the macroscopic alignment of the director and the order parameter of the nematic phase. Once the equilibrium situation is obtained, the sample tube is rotated suddenly around its long axis, perpendicular to the magnetic field. The spectrum recorded immediately after rotation (which is sup-

TABLE II. High viscosity nematic liquid crystal: PBLG in *m*-cresol at 302 K. Data shown here are from Ref. [11].

Density	ρ	10^3 kg m^{-3}
Susceptibility	χ_a	0.94×10^{-8}
Field	H	7.046 T
Average elastic constant	K	1×10^{-11} N
Order parameter	S	0.74
Leslie coefficients	α_i	-463, -602, 8, 160.7, 429.3, -164.7 Pa s

posed to be instantaneous; see Sec. II) maintains the same shape, but the doublet splitting is reduced to half its equilibrium value due to homogeneous alignment of the director perpendicular to the magnetic field. Under the restoring pull of the magnetic field the director then relaxes back to being aligned to the magnetic field; during the realignment, inhomogeneous distributions of the director are generated. The time scale of the process is dictated by nematodynamics equations, which can be used to calculate transient director distributions as explained in Sec. II. Details of the strength of magnetic field, temperature, estimated viscoelastic constants, order parameter, and so forth are reported in Table II for the case under investigation. Further information on the experimental procedure and apparatus can be found in [5,11].

Once the time distributions of the director orientation are available, we can calculate the D-NMR spectrum as a superposition of spectra, each characterized by a director orientation, taking into account that the separation of the doublet peaks for a director orientation is proportional to the second Legendre polynomial of the director orientation angle with respect to the magnetic field. Further details of this procedure, which is straightforward since it is based on the Redfield approximation [12] and allows for the inclusion of inhomogeneous broadening, are described in [5,10,11]. In Fig. 3 we show a set of experimental NMR spectra, for a sample of diameter 0.75 cm. The whole set of data is referred to a period of 700 s. The director is initially aligned perpendicular to the field; then it starts relaxing, aligning to the magnetic field. The doublet splitting first decreases, going through zero at the magic angle, and then increases progressively while the director is realigning with the magnetic field, and finally it is stabilized to a maximum value corresponding to the aligned configuration. In order to reproduce correctly the time evolution of the director distribution, and of the corresponding NMR spectra, we start by defining a suitable initial distribution which is assumed to be of the form [5,11]

$$\phi_{t=0}=\phi_0+A_1\sin qr_2+A_3\sin 3qr_2, \qquad (19)$$

in terms of the largest Fourier components of thermal fluctuations. Here $\phi_0=90°$, and A_1,A_3 are assumed to be small perturbation terms ($A_1\ll10^{-3}$), and q is taken as 50 μm; the ratio A_1/A_3 has been fixed to 3. These values are based on a rough estimate of the characteristic thermal fluctuations of the director orientation in the polymer. It should be noted that qualitative changes in the calculated director distributions can be observed by changing the initial configuration (19): however, the time scale of the transient director patterns predicted by the LE equations is rather independent of such a choice. In Fig. 4 we present snapshots of the director distribution in the sample assuming an initial distribution characterized by Eq. (19): for the first 10 s (a), 100 s (b), and 700 s (c); the same false color representation used in Fig. 2 is adopted but only a small area, corresponding to 0.5 mm in radius, is shown. The system evolves by deepening the initial minima and maxima of the director. Afterward, the patterns are slightly complicated by competition with elastic effects and nonhomogeneous flow induced by the director reorientation. Finally, the liquid crystal polymer is aligned to the field, maintaining a characteristic wall structure, i.e., the director is oriented alternately in two opposite directions, as predicted by Martins and co-workers in a simplified analysis of LE equations [5,11]. Our treatment fully confirms this prediction, and allows a satisfactory interpretation of experimental data. From the spatial distributions shown in Fig. 4, one can obtain the probability distribution of the director angle, which describes the director behavior quantitatively at each time. In Fig. 5 we show the time evolution of the probability distribution of the director, which is essentially peaked around 90° at short times ($t<5$ s); it spreads homo-

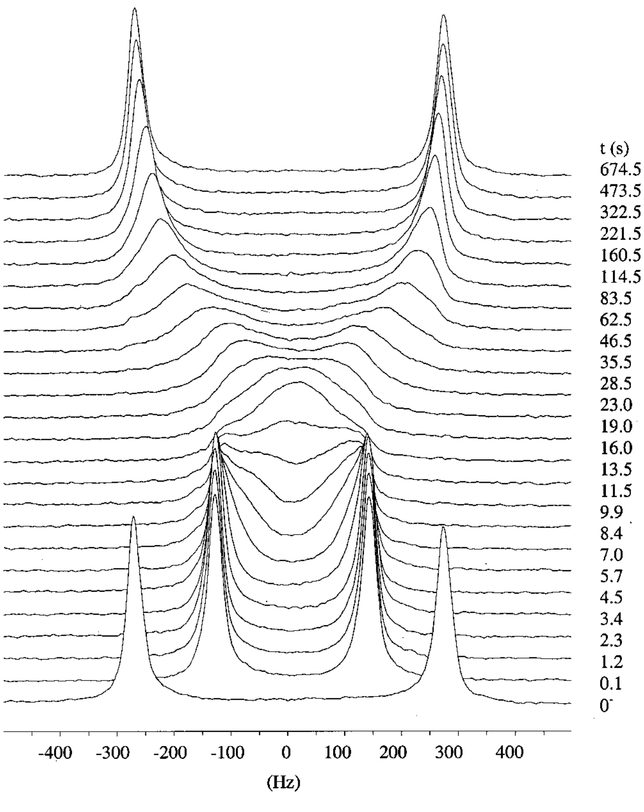

FIG. 3. Experimental NMR spectra for the system defined by the set of parameters in Table II. The spectra are collected in a range of times going from 0 to 700 s. Data are taken from Ref. [11].

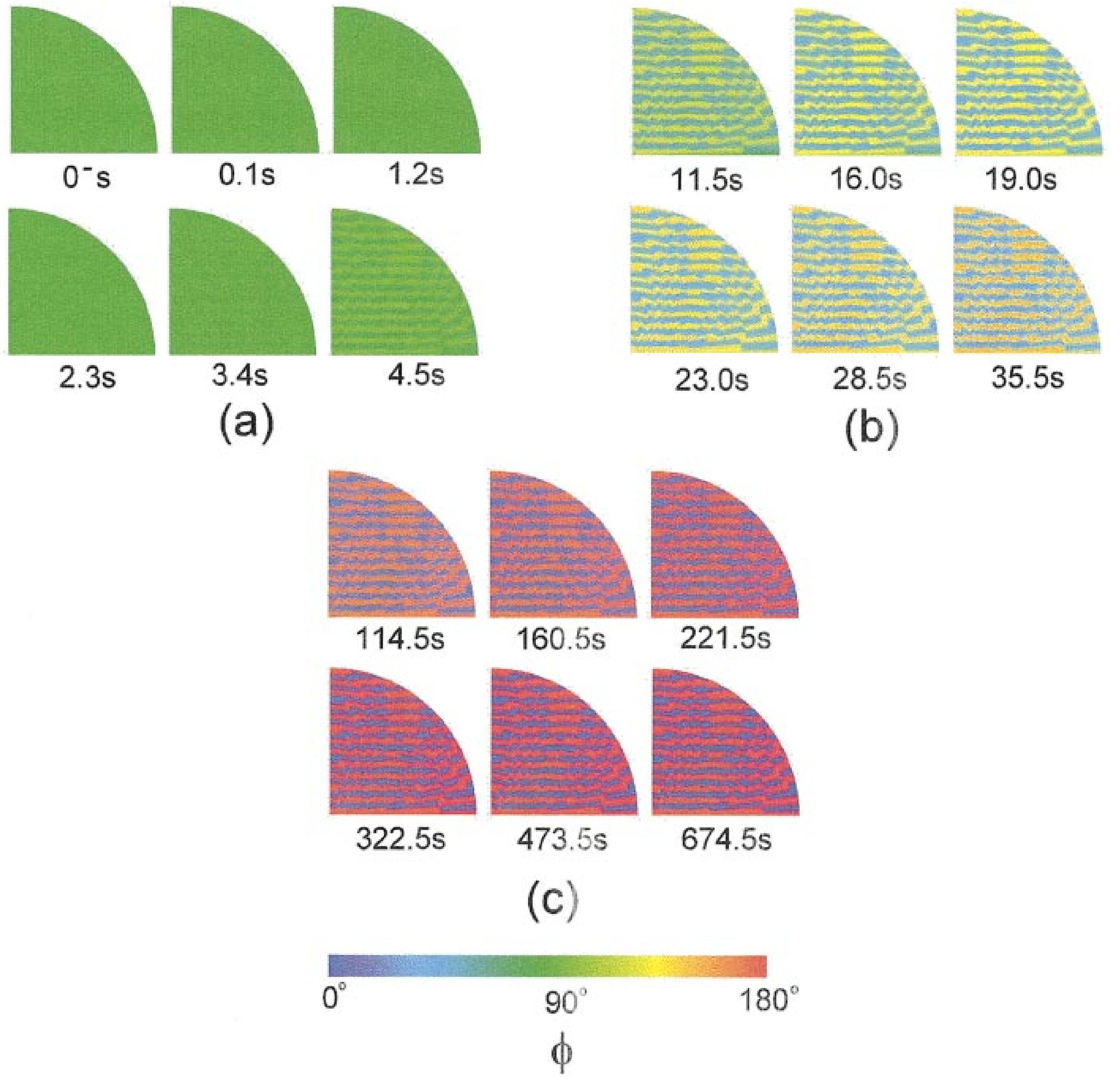

FIG. 4. (Color) Snapshots of the director patterns obtained for the realignment to the magnetic field of a high viscosity nematic; see Table II for the complete parametrization. Only a region corresponding to 0.5 mm in radius is shown. Times are 0, 0.1, 1.2, 2.3, 3.4, and 4.5 s (a); 11.5, 16, 19, 23, 28.5, and 35.5 s (b); 114.5, 160.5, 221.5, 322.5, 473.5, and 674.5 s (c).

geneously at intermediate times ($50<t<100\,\mathrm{s}$), and it is aligned to the magnetic field for longer times ($t>100\,\mathrm{s}$). Finally, using the calculated director distributions we can calculate the NMR spectra, shown in Fig. 6, to be compared with the experimental ones shown in Fig. 3. The agreement is rather good, especially since the time scale of the experiment is reproduced by the simulation in a reasonable way, taking into account also that no fitting procedure was employed. We have simply used the viscoelastic parameters reported in Table II, previously determined from rheo-NMR measurements [11], without further adjustment.

IV. SUMMARY AND CONCLUSIONS

We have presented in this work an application of nematodynamics equations, in the Leslie-Ericksen formulation, to the interpretation of the reorientation process following the rotation by 90° of a nematic monodomain sample of a lyotropic nematic liquid crystal polymer. The methodology for treating numerically the LE equations in two dimensions that was discussed in I has been adapted to the case of highly viscous nematics (i.e., with viscosity coefficients α_i of the order of 10^2-10^3 Pa s), in the absence of external mechanical forces and in the presence of a strong magnetic field.

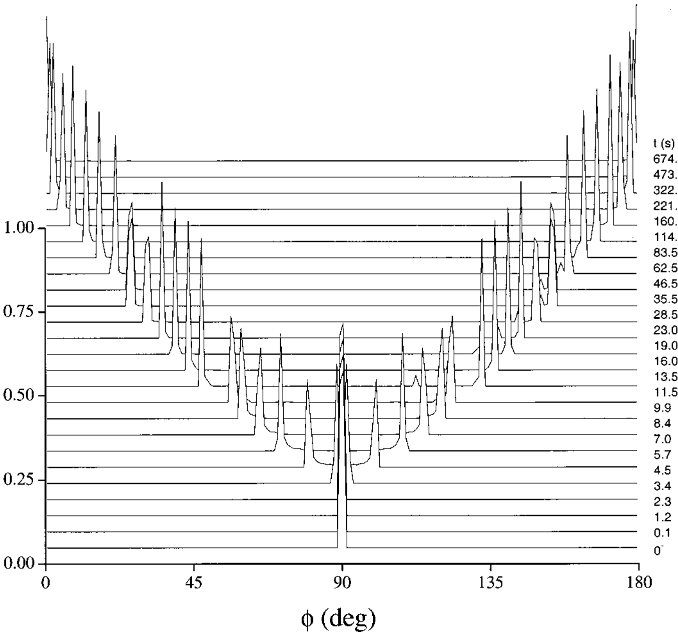

FIG. 5. Distributions of the director, calculated for the times reported in Fig. 3.

First, by exactly solving the LE equations for increasing viscosities of a hypothetical nematogen we have shown that in a reorientation experiment the initial rotation step is equivalent to a rigid rotation of the director, for viscosities of the order of 10^2 Pa s and tube diameters of the order of 1 cm. Next we have assumed that the initially metastable state, with the director perpendicular to the magnetic field, is perturbed by thermal fluctuations, in the form of a periodic bend distortion along the direction of alignment of the director. Assuming an initial distortion less than 0.001%, we have shown by solving the LE equations approximately that the director field realigns to the magnetic field on increasing the initial distortion amplitude, as was previously predicted [5]. Simulated NMR spectra have been calculated from the director distributions at different times, and they have been found to compare favorably with available experimental data. No attempt at actually fitting calculated NMR spectra to experimental ones has been made, our purpose here being mainly to illustrate that (i) the rheological behavior predicted by the LE equations for a model nematic liquid crystal polymer is in accordance with available nuclear magnetic resonance experiments; and (ii) an initial aligned configuration of the director, perturbed by thermal fluctuations, coupled to a purely deterministic description based on the LE equations, is necessary to predict the correct time evolution of the nematic director.

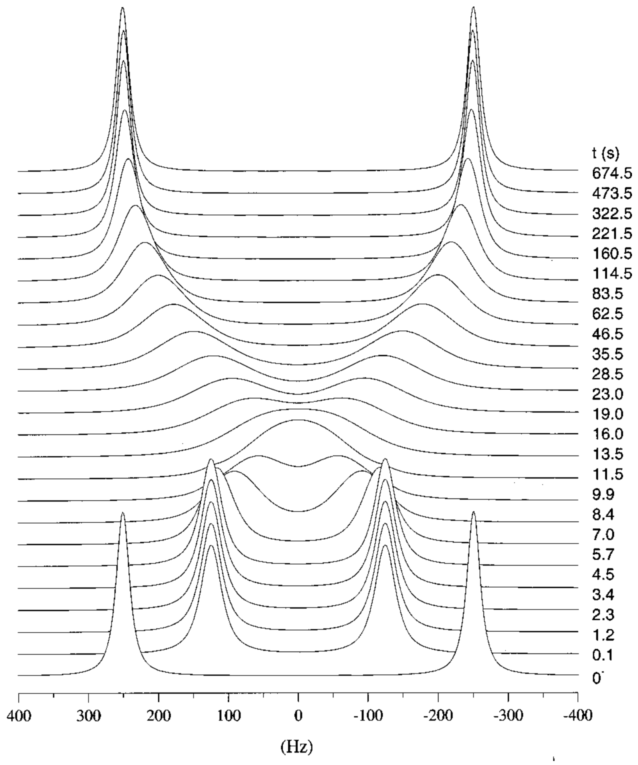

FIG. 6. Calculated NMR spectra, obtained from the director distributions illustrated in Fig. 5.

Nematic liquid crystal polymers, in spite of their intrinsically more complex microscopic dynamics compared to ‘‘simple’’ low viscosity nematogens, can still be well described qualitatively in the present limit by basic nematodynamics theory. However, there are a number of experimental observations, especially pertaining to shear rate dependence of viscosity and shear flow experiments in general, performed on liquid crystal polymers that still are hardly explained by the theoretical framework of the LE equations. Molecular aspects may have to be included in the description of the director dynamics [13,14]. Nevertheless, a clearly defined treatment of the LE approach can be very useful for determining the capabilities and limitations of standard theory. The exact computational tool developed in [1] and approximate treatments like the one developed here can be employed satisfactorily in the description of director patterns both for the comprehension of the general rheological behavior of nematics and for interpreting a number of experimental results, obtained in purely rheological, optical, ESR, and NMR measurements.

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