Linear Viscoelasticity of Leslie-Ericksen Liquid Crystal Polymers

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Abstract

The linear viscoleasticity of seven lyotropic and thermotropic liquid crystalline polymers is characterized using the Leslie-Ericksen equations of defect-free nematodynamics for small amplitude oscillatory capillary Poiseuille flow, and using analytical, numerical and scaling methods. The experimental data sets used in this study correspond to the six Leslie viscosities coefficients for seven nematics liquid crystal polymers, that include shear flow-aligning and non-aligning materials. The predicted equivalent rheological responses between the shear flow-aligning and shear non-aligning polymers demonstrate the universality of nematodynamics. In this work the principles of superposition are developed, applied, and shown to be accurate in collapsing the data sets for both classes of polymers. The scaled resonance peak in the loss tangent (tan δ=G"/G') as a function of the oscillation frequency shown to be a universal constant for monodomain nematics.

Introduction

The Leslie-Ericksen liquid crystal (LELC) is a mathematical material model for rod- or disk-like uniaxial incompressible isothermal nematic liquid crystals widely used to describe anisotropic viscoelastic behavior [1]. A common rheological classification scheme for nematic liquid crystal polymers (LCPs) is based on their shear flow aligning characteristics, which is set by the sign and magnitude of the reactive order parameter λ [1,2,3]. Lyotropic LCPs are usually non-aligning at low shear rates and aligning at high shear rates [3]. On the other hand, main-chain thermotropic LCPs with flexible spacers are likely to be flow-aligning at all shear rates, while main-chain thermotropic LCPs without flexible spacers are apparently non-aligning. A data set of viscoelastic parameters for seven thermotropic and lyotropic LCPs was recently presented [4]; it shows the rheological differentiation between lyotropic and thermotropic LCPs.

Small amplitude oscillatory flows (SAOFs) are a main rheological tool used to characterize viscoelasticity in terms of the storage G'(ω,T) and loss G"(ω,T) moduli as a function of frequency (ω) and temperature (T) [5]. This paper uses small-amplitude pressure driven Poiseuille capillary flow, and characterizes the linear viscoelasticity of seven LCPs [4] using the Leslie-Ericksen equations of defect-free nematodynamics that is useful to understand the nematics liquid crystals materials rheology. [1,2,6]. This paper also demonstrates that flow-aligning and non-aligning materials can exhibit identical viscoelastic responses, thus showing features of universality in the nematodynamics of lyotropic and thermotropic materials.

Governing Equations

In flowing liquid crystal systems, elastic and viscous stresses are usually both important. The governing equations of the Ericksen and Leslie theory consists of the linear momentum balance, director torque balance, and constitutive equations for the stresses, viscous and elastic torques, that takes into account external forces that distort the spatially uniform equilibrium configurations of liquid crystals [1,2,6].

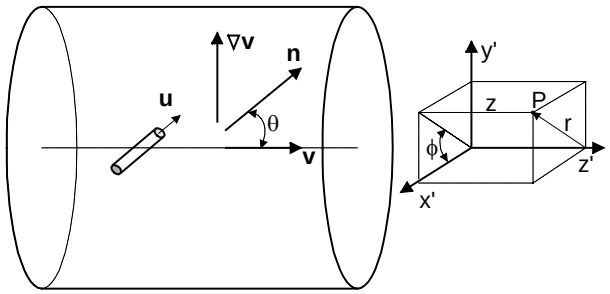

Figure 1. Schematic representations of the flow in a capillary showing an uniaxial rod-like molecules with unit normal vector (**u**), director vector (**n**), velocity vector (**v**), velocity gradient (∇**v**), alignment angle (θ) and the cylindrical (r,ϕ,z) coordinate system used to describe a generic point P.

Uniaxial NLC are characterized by an average molecular orientation represented by the director vector **n** collinear with the average molecular orientation direction. For small-amplitude oscillatory Poiseuille capillary flow of a NLC, the flow is described by an axisymmetric oscillatory planar director field ($\mathbf{n}(r,t)=(\sin\theta(r,t),0,\cos\theta(r,t))$) and a purely axial oscillatory velocity field ($\mathbf{v}(r,t)=(0,0,v(r,t))$) with finite velocity gradient at the centerline. Linearizing the orientation equation, resulting from the angular moment balance, around the axial direction (i.e., $\sin\theta\cong\theta$, $\cos\theta\cong 1$), the dimensionless governing equations for the director tilt angle $\theta(\tilde{r},\tilde{t})$ and the axial velocity $\tilde{v}(\tilde{r},\tilde{t})$ simplify to [7,8]:

$$\frac{\partial\theta}{\partial\tilde{t}}=\frac{\partial}{\partial\tilde{r}}\left(\frac{1}{\tilde{r}}\frac{\partial}{\partial\tilde{r}}(\tilde{r}\theta)\right)+\frac{\tilde{\alpha}_3}{2\ \tilde{\eta}_l}E\,\tilde{r} \tag{1}$$

$$\frac{\partial\tilde{v}}{\partial\tilde{r}}=-\frac{E\ \tilde{r}}{2\tilde{\eta}_l}-\frac{\tilde{\alpha}_3}{\tilde{\eta}_l}\frac{\partial\theta}{\partial\tilde{t}} \tag{2}$$

$$\tilde{\gamma}_1=\tilde{\alpha}_3-\tilde{\alpha}_2\ ;\qquad \tilde{\gamma}_2=\tilde{\alpha}_6-\tilde{\alpha}_5=\tilde{\alpha}_3+\tilde{\alpha}_2 \tag{3a,b}$$

$$\lambda=-\frac{\tilde{\gamma}_2}{\tilde{\gamma}_1}=-\frac{\tilde{\alpha}_6-\tilde{\alpha}_5}{\tilde{\alpha}_3-\tilde{\alpha}_2}=-\frac{\tilde{\alpha}_3+\tilde{\alpha}_2}{\tilde{\alpha}_3-\tilde{\alpha}_2} \tag{4}$$

where $\tilde{\alpha}_i$ are the dimensionless Leslie viscosities ($\tilde{\alpha}_i=\alpha_i/\eta_{splay}$), η_{splay} is the splay viscosity ($\eta_{splay}=\gamma_1-\alpha_3^{\,2}/\eta_l$), η_l is the Miesowicz viscosity when the director is parallel to the velocity direction ($\eta_l=(\alpha_3+\alpha_4+\alpha_6)/2$), $E(\tilde{\omega}\tilde{t})=R^3\left[-dp(\tilde{\omega}\tilde{t})/dz\right]/K_{11}$ is the ratio of viscous flow effects to long-range elasticity effects known as the Ericksen number, $\tilde{r}=r/R$ is the dimensionless radius, R is the capillary radius, $\tilde{t}=K_{11}t/(R^2\eta_{splay})$ is the dimensionless time, $\tilde{v}=\eta_{splay}R\,v/K_{11}$ is

the scaled axial velocity, $-dp(\tilde{\omega}\tilde{t})/dz$ is the given small amplitude oscillatory pressure drop in the capillary per unit length, $\tilde{\omega}=\omega\left(R^2\eta_{splay}\right)/K_{11}$ is the dimensionless frequency, $K_{11,}$ is the splay Frank elastic constants, γ_1 is the rotational viscosity, and γ_2 is the irrotational torque coefficient. The second term in the right hand side of Eq.(2) is the dimensionless backflow ($\tilde{B}$) [7,8]. The Ericksen number (i.e. dimensionless pressure drop) for small amplitude oscillatory capillary Poiseuille flow oscillates as follows:

$$E = E_0 \sin \tilde{\omega}\tilde{t} \qquad (5)$$

where E_o is the infinitesimal dimensionless amplitude. The boundary conditions for the director orientation angle represent strong planar anchoring, $\theta(0,\tilde{t}) = \theta(1,\tilde{t}) = 0$, and for the axial velocity the no slip condition at the surface, $\tilde{v}(1,\tilde{t}) = 0$. The director oscillates around the velocity (z) direction, and the undistorted director field is: $\mathbf{n}_o=(0,0,1)$.

The viscoelastic material properties needed to characterize the small amplitude oscillatory Poiseuille flow of NLCs aligned along the capillary axis include the Miesowicz viscosities η_l, the reactive parameter λ, the torque coefficient α_3, and the re-orientation viscosity η_{splay} [2,7].

Here the viscoelastic material parameters of aligning ($\lambda>1$), neutral ($\lambda=1$) and non-aligning ($\lambda<1$) LCPs are used [4], (see Table 1): (i) Aligning LCPs: (1) PSi4 (poly[(2,3,5,6-tetradeuterio-4-methoxyphentl-4'-butanoxybenzoate)-methylsiloxane]), (2) AZA9 (poly(4,4'-dioxy-2,2'-dimethylazoxybenzene-dodeccanediyl)), and (3) DDA9 (poly(4,4'-dioxy-2,2'-dimethylazoxybenzene-dodeccanediyl)). (ii) Neutral LCP: (4) TPB10 (poly[1,10-decylene-1-(4-hydroxy-4'-biphenylyl)-2-(4-hydroxyphenyl)butane]). (iii) Non-aligning LCPs: (5) PBLG (poly(γ-benzyl-L-glutamate)) 17% in m-cresol, (6) PPTA 8.8% (poly(p-phenylene terephthalamide)) in SO_4D_2, and (7) PBLG 12% in m-cresol.

Table 1: Parameter values [4]

Set	1	2	3	4	5	6	7
	PSi4	AZA9	DDA9	TPB10	PBLG 17% in m-cresol	PPTA 8.8% in SO_4D_2	PBLG 12% in m-cresol
T (K)	348	393	394	360	302	300	302
Leslie viscosities coefficients (Pa.s)							
α_1	-960.0	-1320	-162.0	-1.793×10^5	-1212	-1.177×10^6	-193.0
α_2	-2000	-1595	-170.0	-1.810×10^5	-1328	-2.136×10^6	-390.0
α_3	-127.0	-25.00	-2.000	0.000	4.000	6.972×10^4	29.00
α_4	3066	208.9	16.01	7.838×10^3	113.7	2.415×10^5	59.83
α_5	1534	1470	162.0	1.752×10^5	1208	1.767×10^6	291.6
α_6	-593.2	-149.9	-10.01	-5.838×10^3	-115.7	-2.992×10^5	-69.43
Reactive parameter							
λ	1.1356	1.0318	1.0238	1.0000	0.9940	0.9368	0.8616

Analytical results and discussion

Imposing pressure oscillations on the NLCs will produce spatially non-homogeneous director oscillations. Since NLCs are viscoelastic materials, the director oscillations will not be in-phase with the applied pressure drop. Thus the total director angle $\theta\left(\tilde{r},\tilde{t},\tilde{\omega}\right)$ is given by the sum of the following in-phase and out-phase components:

$$\theta\left(\tilde{r},\tilde{t},\tilde{\omega}\right)=\theta_{i}\left(\tilde{r},\tilde{\omega}\right)\sin\left(\tilde{\omega}\tilde{t}\right)+\ \theta_{o}\left(\tilde{r},\tilde{\omega}\right)\cos\left(\tilde{\omega}\tilde{t}\right) \tag{6}$$

Since the director field **n** is coupled to the velocity field **v**, imposing an oscillatory pressure drop to the NLC will produce a velocity field with in-phase and out-of-phase components. Thus the total dimensionless velocity field $\tilde{v}\left(\tilde{r},\tilde{t},\tilde{\omega}\right)$ is given by the sum of the following in-phase and out-phase components:

$$\tilde{v}\left(\tilde{r},\tilde{t},\tilde{\omega}\right)=\tilde{v}_{i}\left(\tilde{r},\tilde{\omega}\right)\sin\left(\tilde{\omega}\tilde{t}\right)\ +\ \tilde{v}_{o}\left(\tilde{r},\tilde{\omega}\right)\cos\left(\tilde{\omega}\tilde{t}\right) \tag{7}$$

Using the in-phase and out-of-phase dimensionless components in Eqs.(6) and (7) the following expressions were obtained for the dimensionless storage modulus ($\tilde{G}'$), loss modulus ($\tilde{G}''$), and loss tangent ($\tan\delta=\tilde{G}''/\tilde{G}'$) [8]:

$$\tilde{G}'=\frac{M_{1}\left[\tilde{\omega}F_{2}-1\right]}{\left(1+\frac{F_{1}}{M}\right)^{2}+\left(\frac{F_{2}}{M}-\frac{1}{\tilde{\omega}M}\right)^{2}} \tag{8}$$

$$\tilde{G}''=\frac{M_{2}\left[\frac{\tilde{\omega}F_{1}}{M}+\tilde{\omega}\right]}{\left(1+\frac{F_{1}}{M}\right)^{2}+\left(\frac{F_{2}}{M}-\frac{1}{\tilde{\omega}M}\right)^{2}} \tag{9}$$

$$\tan\delta=\frac{M+F_{1}\left(\tilde{\omega}\right)}{F_{2}\left(\tilde{\omega}\right)-\frac{1}{\tilde{\omega}}} \tag{10}$$

where

$$F_{1}\left(\tilde{\omega}\right)=\frac{\mathrm{ber}_{1}\sqrt{\tilde{\omega}}\left(\mathrm{bei}_{0}\sqrt{\tilde{\omega}}-\mathrm{ber}_{0}\sqrt{\tilde{\omega}}\right)-\mathrm{bei}_{1}\sqrt{\tilde{\omega}}\left(\mathrm{ber}_{0}\sqrt{\tilde{\omega}}+\mathrm{bei}_{0}\sqrt{\tilde{\omega}}\right)}{2\sqrt{2\tilde{\omega}}\left(\mathrm{ber}_{1}^{\ 2}\sqrt{\tilde{\omega}}+\mathrm{bei}_{1}^{\ 2}\sqrt{\tilde{\omega}}\right)} \tag{11}$$

$$F_{2}\left(\tilde{\omega}\right)=\frac{\mathrm{bei}_{1}\sqrt{\tilde{\omega}}\left(\mathrm{ber}_{0}\sqrt{\tilde{\omega}}-\mathrm{bei}_{0}\sqrt{\tilde{\omega}}\right)-\mathrm{ber}_{1}\sqrt{\tilde{\omega}}\left(\mathrm{bei}_{0}\sqrt{\tilde{\omega}}+\mathrm{ber}_{0}\sqrt{\tilde{\omega}}\right)}{2\sqrt{2\tilde{\omega}}\left(\mathrm{ber}_{1}^{\ 2}\sqrt{\tilde{\omega}}+\mathrm{bei}_{1}^{\ 2}\sqrt{\tilde{\omega}}\right)} \tag{12}$$

$$\mathrm{ber}_{\nu}\,x=\sum_{k=0}^{\infty}\frac{\cos\left(\frac{3\pi}{4}\nu+\frac{\pi}{2}k\right)}{k!\,\Gamma\left(k+1+\nu\right)}\left(\frac{x}{2}\right)^{2k+\nu} \tag{13}$$

$$\mathrm{bei}_{\nu}\,x=\sum_{k=0}^{\infty}\frac{\sin\left(\frac{3\pi}{4}\nu+\frac{\pi}{2}k\right)}{k!\,\Gamma\left(k+1+\nu\right)}\left(\frac{x}{2}\right)^{2k+\nu} \tag{14}$$

The functions $bei_\nu(x)$ and $ber_\nu(x)$ are the Kelvin functions of order ν [9]. Note that these results have the same pattern of the results presented for simples shear flow of NLCs [10]. The main viscoelastic parameter ratios that controls the dimensionless storage modulus (G'), the loss modulus (G") and the loss tangent (tan δ) are respectively M_1, M_2, and M, given by:

$$M_1 = 8 \underbrace{\left(\frac{\tilde{\alpha}_3}{\tilde{\gamma}_1}\right)^2}_{(\text{viscous torque}/\text{rotation})^2} = 2(1-\lambda)^2 \tag{15}$$

$$M_2 = \underbrace{\frac{\tilde{\eta}_1}{\tilde{\gamma}_1}}_{\text{translation}/\text{rotation}} \tag{16}$$

$$M = \frac{1}{8} \underbrace{\left(\frac{\tilde{\eta}_1}{\tilde{\alpha}_3}\right)}_{\text{translation /viscous torque}} \cdot \underbrace{\left(\frac{\tilde{\gamma}_1}{\tilde{\alpha}_3}\right)}_{\text{rotation/viscous torque}} \tag{17}$$

The storage modulus ($\tilde{G}'$) increases with M_1 since as this ratio increases the viscous torques create more elastic storage and less rotational dissipation; when λ=1 viscous torques are absent and no elastic storage is possible (G'=0). The loss modulus ($\tilde{G}''$) increases with M_2 since as this ratio increases translation dissipation is larger than rotational dissipation; when $\tilde{\gamma}_1 \to \infty$ rotational dissipation dominates (G"=0). The ratio M is the product of the two dissipation to torque ratios, and can be rewritten in terms of λ as:

$$M = \frac{1}{2}\frac{\tilde{\eta}_1}{\tilde{\gamma}_1} \cdot \frac{1}{(1-\lambda)^2} \tag{18}$$

By using the known asymptotic behavior [9] of the Kelvin functions the frequency dependence of the viscoelastic moduli for $\tilde{\alpha}_3 \neq 0$ is as follows: the loss modulus is always greater than the storage modulus, the low frequency (terminal) regime is classic of a viscous fluid, and the characteristic slopes are:

$$\text{as} \quad \tilde{\omega} \to 0, \quad \tilde{G}' \sim \tilde{\omega}^2, \quad \tilde{G}'' \sim \tilde{\omega}; \qquad \text{as} \quad \tilde{\omega} \to \infty, \quad \tilde{G}' \sim \tilde{\omega}^{1/2}, \quad \tilde{G}'' \sim \tilde{\omega} \tag{19}$$

It follows from Eq.(15) that for $\tilde{\alpha}_3 = 0$, M_1=0, as a result, the behavior is Newtonian and $\tilde{G}'$=0. In addition, at frequencies larger than resonance the dependency on material properties simplifies; resonance is found at $\tilde{\omega}_r = 18.6522$, and the large frequency regime results in this section hold for $\tilde{\omega} \geq 10\tilde{\omega}_r$. The factorization of material properties from frequency dependent functions is obtained by direct order of magnitude analysis. At frequencies larger than the resonance ($\tilde{\omega}_r$), the terms F_1/M and $F_2/M - 1/\tilde{\omega}M$ in Eqs. (8) and (9) are very small compared with one; in addition in the numerator of Eq.(9) F_2/M is very small compared with one; therefore, the asymptotic expressions for the viscoelastic functions for frequencies larger than $\tilde{\omega}_r$ are:

$$\frac{\tilde{G}'}{M_1} = \tilde{\omega}F_2 - 1 = \Phi'(\tilde{\omega}) \tag{20}$$

$$\frac{\tilde{G}''}{M_2} = \tilde{\omega} = \Phi''(\tilde{\omega}) \tag{21}$$

$$\frac{\tan\ \delta}{M} = \left(F_2\left(\tilde{\omega}\right) - \frac{1}{\tilde{\omega}} \right)^{-1} = \Phi\left(\tilde{\omega}\right) \tag{22}$$

These equations show the origin of the vertical (amplitude) scaling of all data sets. The horizontal scaling (frequency) is obtained by plotting the dimensionless storage modulus ($\tilde{G}'$), loss modulus ($\tilde{G}''$), and loss tangent ($\tan\delta$) as functions of $\tilde{\omega}$.

Figure 2 shows the scaled storage modulus (G'/M_1) and scaled loss modulus (G''/M_2) as a function of the dimensionless frequency ($\tilde{\omega}$) for the data sets. The figure shows for storage modulus that a collapse of the curves is essentially perfect for $\tilde{\omega} > 30\tilde{\omega}_r$. For PTB10 the storage modulus is zero. The figure also shows a collapse of the curves of loss modulus is essentially perfect for $\tilde{\omega} > 16\tilde{\omega}_r$.

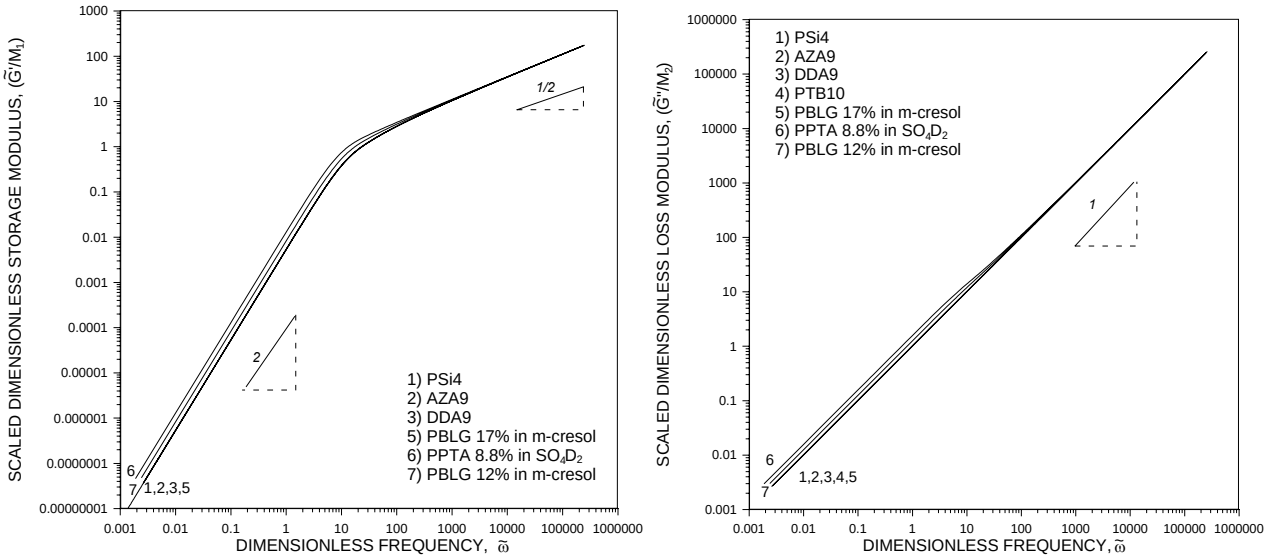

Figure 2. Scaled dimensionless storage ($\tilde{G}'/M_1$) and loss ($\tilde{G}''/M_2$) moduli as a function of the dimensionless frequency ($\tilde{\omega}$) for PSi4, AZA9, DDA9, PBLG 17%, PPTA 8.8%, and PBLG 12%.

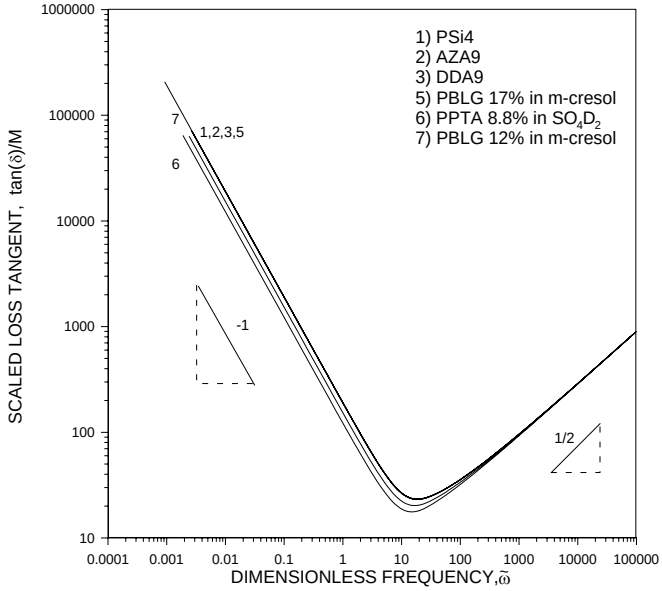

Figure 3. Scaled loss tangent ($\tan\delta/M$) as a function of the dimensionless frequency ($\tilde{\omega}$) for PSi4, AZA9, DDA9, PBLG 17%, PPTA 8.8%, and PBLG 12%.

Figure 3 shows the scaled loss tangent ($\tan\delta/M$) as a function of the dimensionless frequency ($\tilde{\omega}$) for the data sets. These results show a collapse of the plots is almost perfect especially to high frequencies.

Conclusions

The rheological responses of defect-free liquid crystal polymers subjected to small-amplitude oscillatory pressure-driven Poiseuille flow show superposition and universality. In general the degree of superposition is almost perfect at frequencies above resonance. Although liquid crystals are usually differentiated into shear aligning and non-aligning materials, the results presented here shows that under certain flow conditions, linear viscoelasticity only depends on the dimensionless factor $(1-\lambda)^2$, and hence rheological equivalence between aligning and non-aligning materials exists if $\lambda_{NA}=2-\lambda_A$. Morover, the resonance is also shown to be independent of flow-alignment.

Acknowledgments

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References

[1] A.D. Rey, M.M. Denn, “Dynamical phenomena in liquid-crystalline materials”, Annual Reviews in Fluid Mechanics, **34**, 233-266 (2002).

[2] P.G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, (2nd edn., Oxford University Press, London, 1993).

[3] R.G. Larson, *The Structure and Rheology of Complex Fluids*, (Oxford University Press, New York, 1999).

[4] A.F. Martins, “Measurament of viscoelastic coefficients for nematic mesophases using magnetic resonance”, In: *Physical Properties of Liquid Crystals: Nematics*, edited by D. A. Dunmur, A. Fukuda, and G. Luckhurst (IEE Publishing, London, 2001), p. 405-413.

[5] R.B. Bird R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids*, (John Wiley & Sons, New York, 1989).

[6] F. R. S. Chandrasekhar, *Liquid Crystals*, (2nd edn., Cambridge University Press, 1992).

[7] L.R.P. de Andrade Lima, A.D. Rey, “Linear and nonlinear viscoelasticity of discotic nematics under transient Poiseuille flows”, Journal of Rheology, **47**(5), 1261-1282 (2003).

[8] L.R.P. de Andrade Lima, A.D. Rey, “Linear viscoelasticity of discotic mesophases”, Chemical Engineering Science, **59**(18), 3891-3905 (2004).

[9] M. Abramowitz, I.A. Stegun, *Handbook of Mathematical Functions*, (Dove Publications, New York, 1972).

[10] W.R. Burghardt, “Oscillatory shear flow of nematic liquid crystals”, Journal of Rheology, **35**, 49-62 (1991).