SIMULATION OF FLOW–INDUCED TEXTURE FORMATION IN MESOPHASE PITCH

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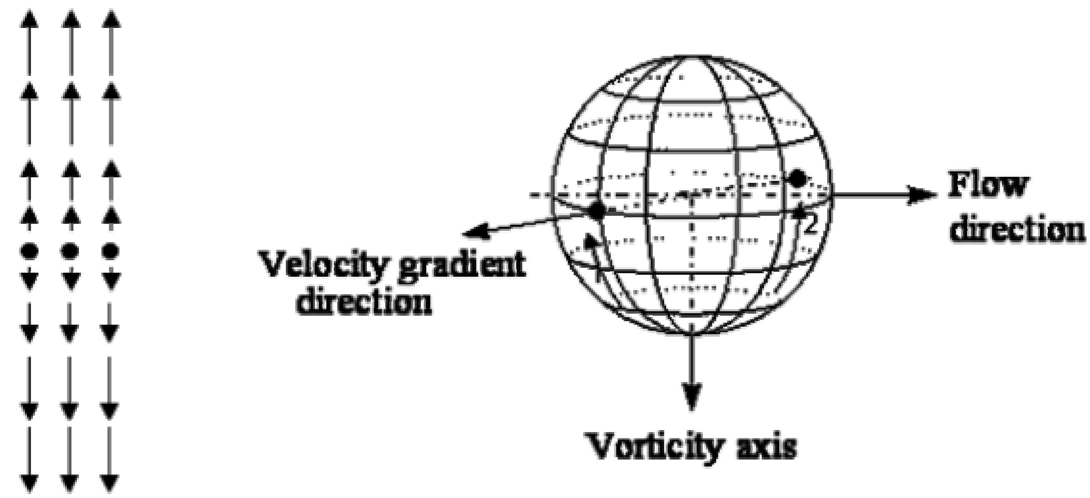
Introduction

Carbon fibers produced from mesophase pitch exhibit high stiffness and thermal conductivity and are used in satellite structures and other thermal management applications. The internal structure and therefore the final properties of pitch-based carbon fibers are highly dependent on the flow-induced microstructure developed during the melt-spinning process.

Mesophase pitches are multicomponent discotic nematic liquid crystals (DNLCs), whose characteristic molecular weight is intermediate between low molar mass and polymeric nematic liquid crystals. The distinguishing features of the mechanical behavior can be summarized by stating that LC materials exhibit anisotropic, non-linear, viscoelastic behaviour quite distinct from Newtonian viscous materials and from isotropic flexible-chain polymers. These differences arise because liquid crystals display various degrees of orientational order and because their elasticity has short and long range contributions, the latter arising from spatial gradients of the orientational order.

This work uses a very well established mesoscopic model for liquid crystalline materials is based on the Landau-de Gennes free energy [1,2]. This model takes into account all the three major effects (short and long range order elasticity and viscous flow) and can capture general and complex phenomena of liquid crystals behavior (e.g. banded texture, defect generation and coarsening phenomena) which are not captured by the classical theories.

The shear flow behaviour and rheology of DNLCs depend on the sign and magnitude of the reactive parameter λ, which is the ratio of the flow aligning effect of the deformation rate and the tumbling (rotational) effect of the vorticity. For DNLCs, $\lambda < -1$ and hence they display the flow-aligning mode. At present there is strong evidence that carbonaceous mesophases are flow-aligning systems, since mesophase fibers show clearly ordered macroscopic orientation [3]. Experimental observations [4] have characterized microstructural development in mesophase pitch during shear flow. When observed under cross-polarized light, the typical schlerien texture for nematics is observed in mesophase pitch [3].



a) b)

Figure 1. a) Schematic of a splay-bend inversion wall in which the director rotates by π radians when traversing the wall; b) Schematic of the unit sphere description of the director field with respect to rectilinear simple shear flow. The director trajectory for two splay-bend inversion walls.

Textures are spatial distributions of defects. Defects are classified according to dimensionality (D) in terms of points (D=0), disclination lines (D=1), and inversion walls (D=2). Inversion walls are 2D non-singular defects, in which spatially localized director gradients occur. Inversion walls are classified according to the elastic (i.e., splay, bend, and twist) modes of deformation [1]. In this paper we use shear-induced generation of splay-bend inversion walls as a model for texture generation. Figure 2(a) shows an schematic of a splay-bend wall [5] in which the director rotates by π radians when traversing the wall. Figure 2(b) is an schematic of the unit sphere description of the director field [6], where the x-axis is the flow direction, the y-axis the velocity gradient direction, the z-axis (out of the plane of the paper) the vorticity axis. The equator lies in the shear (x-y) plane and the north pole and the south pole are located on the vorticity (z) axis. The figure shows the director trajectory for two splay-bend inversion walls, of charge C= –1/2 (1), and C= +1/2 (2), according to the rotation sense in going from the vorticity axis to the velocity gradient.

The aim of this paper is to model and simulate the flow-induced texture generation in sheared, flow-aligning, disk-like, nematic liquid crystals, under isothermal conditions, and constant shear rate.

Theory and governing equations

A Landau-de Gennes model that takes into account short range and long range energy, and flow-induced orientations has been adapted to describe the flow behavior of flow-aligning, thermotropic, discotic, nematic, liquid crystals as models of carbonaceous mesophases [7]. The dynamics of the tensor order parameter is given by the following sum of flow **F**, short range $\mathbf{H}^{sr}$, and long range $\mathbf{H}^{lr}$ contributions [8]:

$$\hat{\mathbf{Q}} = \mathbf{F}(\mathbf{Q},\nabla\mathbf{v}) + \mathbf{H}; \quad \mathbf{H} = \mathbf{H}^{sr}\left(\mathbf{Q},\overline{D}_r(\mathbf{Q})\right) + \mathbf{H}^{lr}(\nabla\mathbf{Q}) \tag{1}$$

(i) flow contribution **F**:

$$\begin{aligned}\mathbf{F}(\mathbf{Q},\nabla\mathbf{v}) = {} & \tfrac{2}{3}\beta\mathbf{A} + \beta\left[\mathbf{A}\cdot\mathbf{Q} + \mathbf{Q}\cdot\mathbf{A} - \tfrac{2}{3}(\mathbf{A}:\mathbf{Q})\mathbf{I}\right] - \\ & \tfrac{1}{2}\beta\left[(\mathbf{A}:\mathbf{Q})\mathbf{Q} + \mathbf{A}\cdot\mathbf{Q}\cdot\mathbf{Q} + \mathbf{Q}\cdot\mathbf{A}\cdot\mathbf{Q} + \mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{A} - \{(\mathbf{Q}\cdot\mathbf{Q}):\mathbf{A}\}\mathbf{I}\right]\end{aligned} \tag{2}$$

(ii) short-range elastic contribution $\mathbf{H}^{sr}$:

$$\mathbf{H}^{sr}\left(\mathbf{Q},\overline{D}_r(\mathbf{Q})\right) = -6\overline{D}_r\left[\left(1-\tfrac{1}{3}U\right)\mathbf{Q} - U\mathbf{Q}\cdot\mathbf{Q} + U\left\{(\mathbf{Q}:\mathbf{Q})\mathbf{Q} + \tfrac{1}{3}(\mathbf{Q}:\mathbf{Q})\mathbf{I}\right\}\right] \tag{3}$$

(iii) long-range elastic contribution $\mathbf{H}^{lr}$:

$$\mathbf{H}^{lr}(\mathbf{Q}) = 6\overline{D}_r\left[\frac{L_1}{2ckT}\nabla^2\mathbf{Q} + \frac{1}{2}\frac{L_2}{c\kappa T}\left[\nabla(\nabla\cdot\mathbf{Q}) + \{\nabla(\nabla\cdot\mathbf{Q})\}^T - \tfrac{2}{3}\mathrm{tr}\{\nabla(\nabla\cdot\mathbf{Q})\}\mathbf{I}\right]\right] \tag{4}$$

$$\overline{D}_r = \frac{Dr}{\left(1-\frac{3}{2}\mathbf{Q}:\mathbf{Q}\right)} \tag{5}$$

Here **A**, L_i (i=1,2), U and β are the rate of deformation tensor, the Landau coefficients, the nematic potential and the molecular shape parameter, respectively. The dimensionless numbers Er (Ericksen number) and energy ratio R [2]:

$$Er = \frac{\dot{\gamma}H^2ckT^*}{2L_1D_r} \qquad R = \frac{3H^2ckT^*}{L_1} \tag{6a,b}$$

give the ratio of viscous flow effects to long-range order elasticity, and short-range order elasticity to long-range order elasticity, respectively (H is the characteristic distance between the two plates (see figure 5) , V is the constant velocity of the top plate and T^* is the isotropic-nematic transition temperature).

The Deborah number De commonly used in the rheological literature [2] to characterize flow-induced molecular elasticity is the ratio of flow time scale to molecular (short range order) time scale:

$$De = \frac{Er}{R} \tag{7}$$

Numerical results and discussion

The model equations are a set of five coupled non-linear parabolic partial differential equations. The equations are solved using Galerkin Finite Elements for spatial discretization and a forth order Runge-Kutta time adaptive method. The selected adaptive time integration scheme is able to efficiently take into account the stiffness that rises due to the disparity between time scales and length scales.

In this work we study a rectilinear simple start-up shear flow with Cartesian coordinates, fixed boundary conditions are used, such that the director **n** is anchored along the vorticity direction, as shown in figure 2. The initial director field is oriented in x-z plane, with $80<\phi<100$ degrees (ϕ is the twist angle and $\phi=90$ degrees corresponds to the vorticity direction) with random variation. In the present work the parametric values are set at: U=3.5, β =-1.2 (flow aligning system), and the simulations are performed for a range: $10^4<Er<3x10^5$ (0.01<De<0.3) and for $R=10^6$.

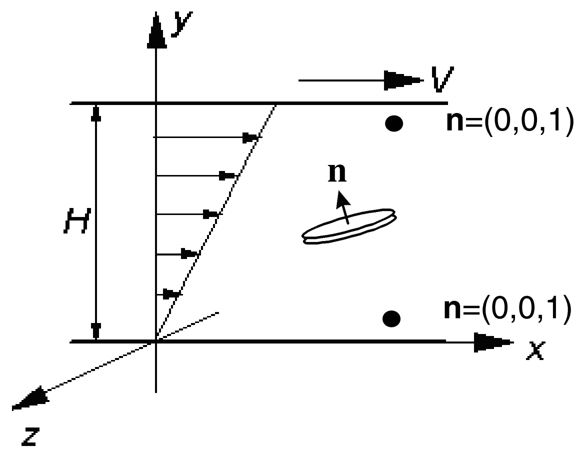


Figure 2. Definition of the flow geometry and coordinates system for simple shear flow. The lower plate is at rest and the upper plate moves in the x- direction with a constant velocity V. H is the gap separation.

In this work we present results only for shear rates (Ericksen numbers) corresponding to Deborah number De<1. In this case the orientation processes dominate the rheology [9].

It is found that as the shear-rate increases, the pathway between an oriented non-planar state and an oriented planar state is through texture formation and coarsening. The shear-rate dependent dimensionless numbers that control the texture formation and coarsening process is Ericksen Er as Deborah number, De <1. The emergence of texture is independent of the Deborah number, and occurs at $Er=10^4$.

The nucleation of the parallel array of splay-bend inversion walls is due to the degeneracy in reorientation towards the shear plane. Increasing the Ericksen number, the number of the splay-bend walls increases (see figure 4b). Here the spatial variations of the director occur over length scales much smaller than the thickness of the sample H and number of walls is high and time dependent, so they can be described in a statistical manner.

Figure 3a shows a computed gray scale visualization of director component n_z ($0\leq y^*\leq 1$) as a function of strain for Er=10000. The figure shows a typical example of two splay-bend inversion walls in the bulk. Figure 3b shows the steady state director components (n_x, n_y and n_z) [9] as a function of dimensionless distance y*, corresponding to figure 3a. At these relatively low Er no coarsening takes place and the director is periodic.

By increasing the shear rate (Ericksen number), the number of splay-bend walls increases (see figure 4). The steady state texture of a liquid crystal is given by the balance of nucleation and coarsening processes. Coarsening events limit the lifetime of an inversion wall, and a texture can be viewed as a balance between birth-death events.

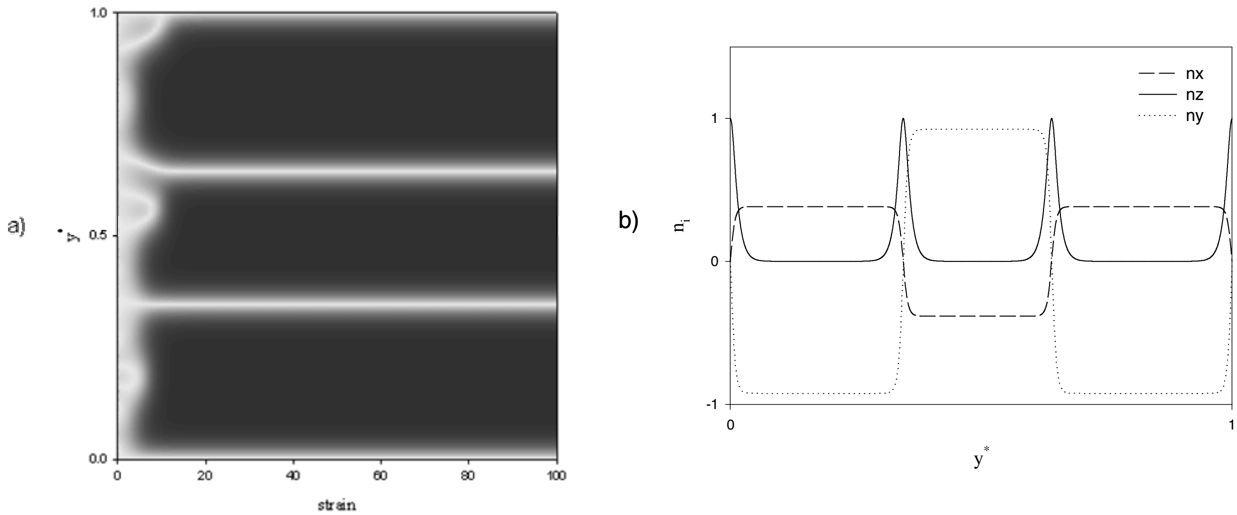


Figure 3. a) Computed gray scale visualization of director component n_z ($0 \leq y^* \leq 1$) as a function of strain (γ). Black -in plane orientation (n_z=0) and light - orientation along the vorticity (n_z=1) for Er=10000; b) Steady state director components (n_x, n_y, n_z) as a function of dimensionless distance y*.

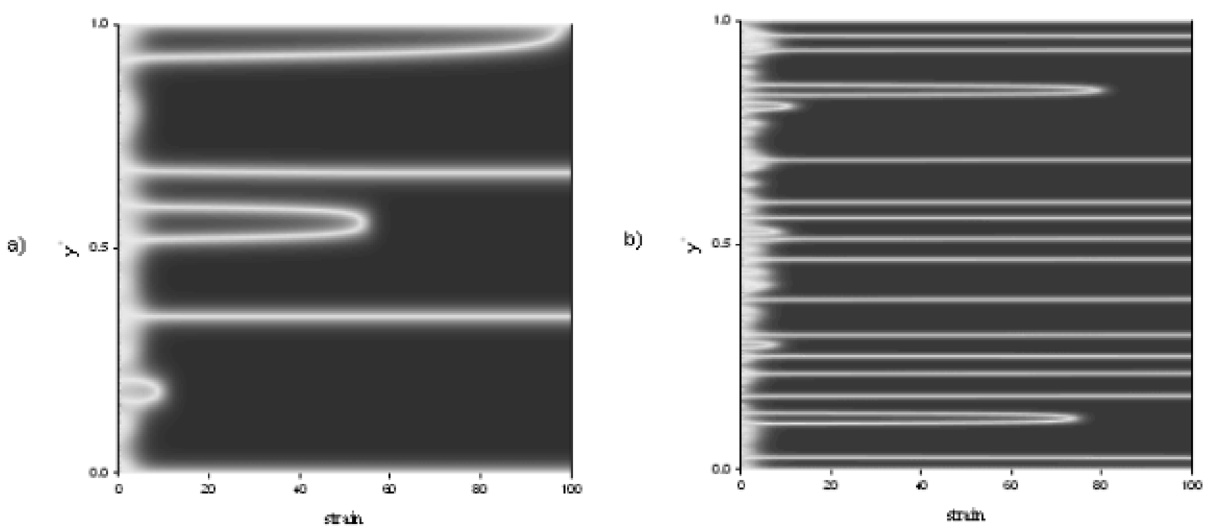


Figure 4. Computed gray scale visualization of director component n_z ($0 \leq y^* \leq 1$) as a function of strain (γ). Black -in plane orientation (n_z=0) and light- orientation along the vorticity (n_z=1): a) Er=4×10^4; b) Er=2.4×10^5.

Figure 4 represents computed gray scale visualizations of director component n_z ($0 \leq y^* \leq 1$) as a function of strain for a) Er=4×10^4 (De=0.04) and b) Er=2.4×10^5

(De=0.24). At this relatively low Ericksen numbers, splay-bend walls can annihilate by two mechanisms: wall-wall annihilations (figure 4a,b) and wall-bounding surface reaction (figure 4a) .

Conclusions

This paper shows that the Landau-de Gennes model for flow-aligning discotic mesophases captures the experimentally observed shear flow-induced texture generation. The texture is given by a balance between nucleation and annihilation events. The shear-rate dependent dimensionless number that control the texture formation and coarsening process is the Ericksen number Er (for Deborah De<1). The emergence of texture occurs at $Er=10^4$. Our results are consistent with experimental observations [4] showing that sheared mesophase pitches are textured and flow aligning materials.

Acknowledgements

This work was supported primarily by the ERC program of the National Science Foundation under Award Number EEC-9731680 and of the Natural Science and Engineering Research Council of Canada.

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