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Brownian dynamics simulation of external magnetic field effect on director tumbling in liquid-crystalline polymers under shear flow

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We have made the first investigation of the external magnetic field effect on director dynamics and flow instability in liquid-crystalline polymers subjected to shear flow by Brownian dynamics simulation and Lebwohl-Lasher nematogen model. According to our simulation, the static magnetic field can, depending on the field strength and orientation, enhance or inhibit the flow instability. The corresponding state diagram for director tumbling and shear aligning is presented. The tumbling period in a magnetic field does not obey the conventional scaling relation. In addition, a novel phenomenon about the first normal stress difference vs shear rate has been found in a magnetic field. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid-crystalline polymer; Brownian dynamics simulation; Lebwohl-Lasher model)

Introduction

Liquid-crystalline polymers (LCPs) provide an excellent system to study flow instability besides their importance of technical application. Different from flexible polymers, LCPs show many unusual rheological properties such as the negative first normal stress difference at the moderate shear rate and the pronounced oscillations of stress and dichroism with time[1-10]. Complicated spatial pattern formation has also been observed[11]. These phenomena have been attributed to a kind of flow instability in the LCP, director tumbling, i.e., the periodic rotation of the averaged molecular orientation about the vorticity axis under simple shear flow[12-25]. In addition to that, a nematic liquid crystal in a continuously rotating magnetic field has also been studied experimentally and novel non-linear dynamic spatial structures have been found[26,27]. However, the external magnetic field effect on director tumbling of LCP under shear flow is still an open question at the present time. It is even unknown whether a static magnetic field can inhibit or enhance the director tumbling of LCP.

In this communication, we present the state diagram of flow instabilities obtained by Brownian dynamics simulation based on the Langevin equation. In particular, we find that the shear-rate dependence of the first normal stress difference can be altered by external magnetic field. It is emphasized that apart from the magnetic strength, the orientation of the magnetic field is also crucial to the occurrence of director tumbling and the frequency of the stress oscillation. We would like to promise that the variability of dynamic instabilities will, together with the possibility to control them in the experiment, stimulate further extensive experimental and theoretical studies on this system.

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Simulation formalism

For simplicity, the simulation is performed on two-dimensional square lattices. Our algorithm distinguishes itself in that the rotation of the local director at each lattice is described by the Langevin equation written as

$$\xi \frac{d\theta_i}{dt} = f_{s,i} + f_{n,i} + f_{h,i} + f_{l,i} \qquad (1)$$

where θ_i is the orientation angle of the local director at the ith lattice with the zero angle defined along the plates or the horizontal direction; $f_{s,i}, f_{n,i}, f_{h,i}$ and $f_{l,i}$ arise from the flow field, the anisotropic interaction between the nearest-neighbour (NN) lattices, the external magnetic field and the Langevin stochastic torque, respectively; ξ is the friction coefficient and reads $\xi = kT/D$. Here, kT is the Boltzmann constant times the absolute temperature; D is the effective rotational diffusivity and is, for simplicity, assumed to be a constant.

For a simple steady shear flow with a constant shear rate $\dot{\gamma}$,

$$f_{s,i} = -\xi \dot{\gamma} \sin^2 \theta_i \qquad (2)$$

The nematic interaction can be described by the well-known Lebwohl-Lasher (L-L) nematogen model[22-25,28-33]. The two-dimensional L-L potential at position i, $E(\theta_i)$, can be written as

$$E(\theta_i) = \frac{1}{4} kTU \sum_{j \in NN} \sin^2(\theta_i - \theta_j) \qquad (3)$$

where U designates the dimensionless strength of the nematic interaction. The summation is made over the four nearest-neighbour sites. This potential is, therefore, free of the mean-field approximation. The corresponding elastic torque is readily expressed as $f_{n,i} = -dE(\theta_i)/d\theta_i$. Through this model, not only the nematic interaction is considered, but also the spatial correlation of the local directors is introduced.

Along the plate direction, the system is divided into 50 lattices and the periodic boundary condition is applied. The perpendicular dimension is restricted by upper and lower plates and divided into 20 lattices. The surface-anchoring potential at position i near the plates, $E_s(\theta_i)$, reads

$$E_s(\theta_i) = kTU_s \sin^2(\theta_i - \theta_a) \quad (4)$$

where U_s represents the dimensionless strength of the anchoring energy and is tentatively set to equal to U in this paper; θ_a is the anchoring angle with $\theta_a = 0$ for the parallel anchoring and $\theta_a = \pi/2$ for the homeotropic anchoring. The parallel anchoring is assumed in this communication. The slippage periodic boundary condition[22–25,34] is employed along the direction of velocity gradient.

The interaction energy between the magnetic field and the local director can be described as

$$E_h(\theta_i) = -kTU_h \cos^2(\theta_i - \theta_h) \quad (5)$$

where U_h is the reduced dimensionless magnetic field strength and reads

$$U_h = \epsilon_h/(kT), \quad \epsilon_h = 0.5\chi_a H^2 \quad (6)$$

Hear, H, is the field strength; χ_a is the anisotropy of the magnetic susceptibility and is, without loss of generality, assumed to be positive; the term ϵ_h refers to the maximum magnetic energy under a given magnetic field strength. The magnetic torque can also be easily obtained by $f_{h,i} = -dE_h(\theta_i)/d\theta_i$.

The Langevin torque results from the Brownian thermal fluctuation. Its effect on the time evolution of director rotation at position i can be realized by a white noise, W_i[22–25,29,30]. As a result, the Langevin equation, equation (1), can be rewritten as

$$d\theta_i = -D\{\Gamma \sin^2\theta_i + \frac{1}{4}U \sum_{j \in NN} \sin[2(\theta_i - \theta_j)] + U_h \sin[2(\theta_i - \theta_h)]\}dt + \sqrt{2D}dW_i \quad (7)$$

where Γ is the dimensionless shear rate defined as $\dot{\gamma}/D$, the ratio of shear rate and diffusivity. The director dynamics can, hence, be described by a Wiener process. In a computer simulation, it is inevitable to discretize time. The time step, $\Delta(Dt)$, is taken to be 0.03, which is reasonable[22–25].

It has been revealed that the L–L model implies equal Frank constants[30–33] and reflects the elastic interaction in the nematic system. Both splay and bend Frederiks transitions take place at $U_h(\text{crit}) \sim 0.1$ in the simulated system with $U = 15$ and the depth $d = 20$[30]. The time-dependent orientational distribution function and hence the director and order parameter can be obtained by statistics[22–25]. The shear stress and the first normal stress difference can be calculated with the formulae derived by us following the same procedure as that of Doi[35]. The derivation process will be published in a full paper. The statistic formulae without magnetic field have been published by the authors[22–24]. It is necessary to mention that despite unrealistic dimensionality, the simulation based on equation (1) has caught the essential actual behaviour of director tumbling under simple shear flow, according to our previous research in zero magnetic field[22–25].

Results and discussion

The state diagram is obtained by Brownian dynamics simulation and presented in *Figure 1*. There are two characteristic states existing in LCP subjected to simple shear flow and external static magnetic field. Outside the closed loop is the shear aligning state, i.e., a kind of steady state with the system director, namely, the average

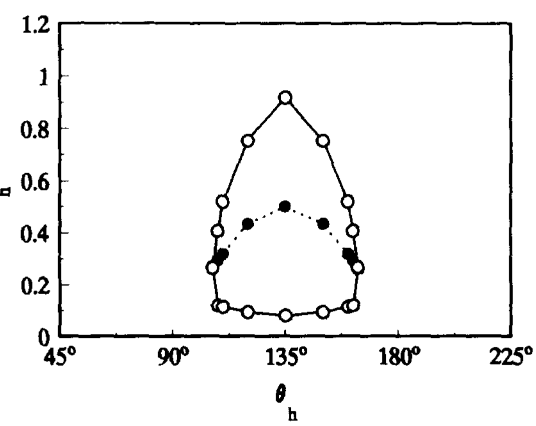


Figure 1 State diagram for the external state magnetic field effect on LCP subjected to shear flow. (–O–) Tumbling-aligning transition points obtained from Brownian dynamics simulation with $U = 15$ and $\Gamma = 15$; (···●···) fastest-tumbling points with respect to the corresponding magnetic strength or orientation

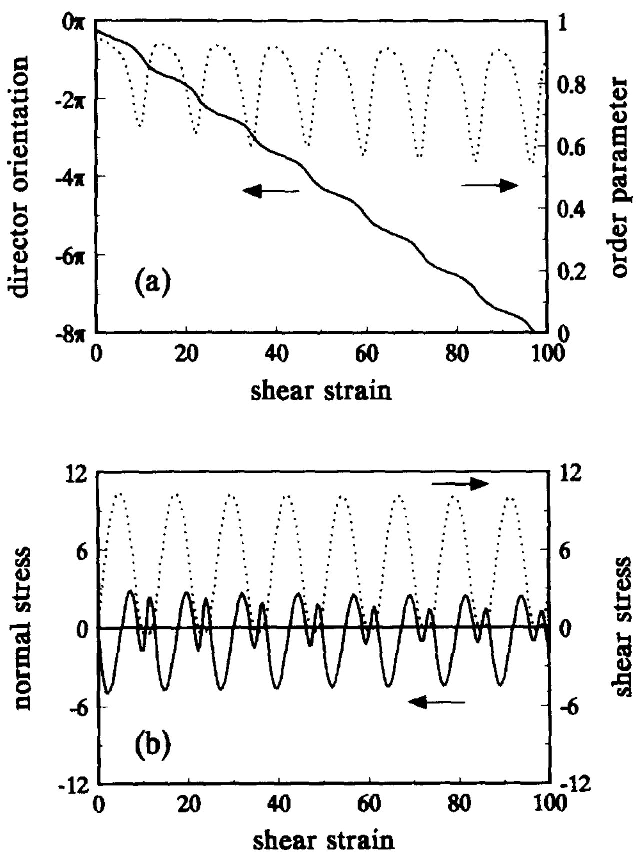


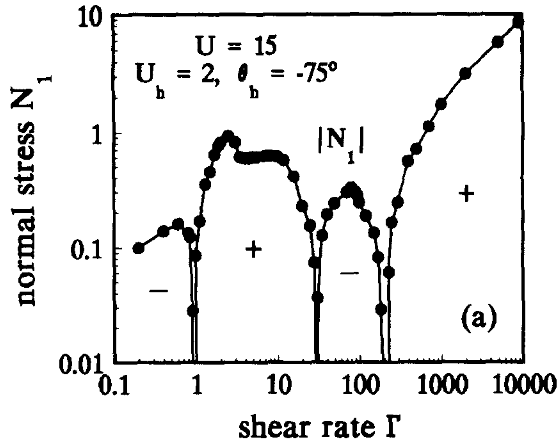
Figure 2 A typical dynamic process in an appropriate static magnetic field: (a) showing director tumbling by the transient director orientation and order parameter vs shear strain, and (b) showing stress oscillation by the transient dimensionless first normal stress difference and dimensionless shear stress vs shear strain. The data are obtained from Brownian dynamics simulation with $U = 15$, $\Gamma = 15$, $U_h = 12$, and $\theta_h = -\pi/4$. The initial state is the equilibrium state in the magnetic field but without shear flow

orientation of the local directors, finally aligning along the Leslie angle near the shear direction. Correspondingly, inside the closed loop, the system director rotates periodically about the vorticity axis, which is just the director tumbling. Simultaneously, the macroscopic stresses behave as periodic oscillations. Typical results of the director tumbling and stress oscillation are shown in *Figure 2*. The transient values in *Figure 2* are obtained by statistics with the similar procedures to those in references 22–25. The difference is that the magnetic contribution to the stresses must be taken into account in the case of an external field.

The magnetic field effect on the director tumbling can be comprehended physically. For occurrence of director tumbling, a necessary condition is to make the local directors pass through the deadlock *clockwise* (from shear direction to the negative direction of velocity gradient). In zero magnetic field, the deadlock is along the shear direction, where the total torque is zero. The only mechanism to pass through this deadlock is the thermal fluctuation in this case. However, the deadlock may be eliminated when an external magnetic field is imposed. Thus, the director tumbling may, in principle, take place or even be enhanced, if the magnetic field has an appropriate direction and strength. Since the magnetic field with the direction in the second or fourth quadrant will make the molecules with the orientation near the shear direction rotate clockwise also, such a magnetic field will, again with an appropriate magnetic strength, enhance the director tumbling. It will be mentioned in the following paragraph that the fastest tumbling of all cases must occur when $\theta_h = -\pi/4$, just because in this direction, the magnetic torque exerted on LCPs with $\theta = 0$ is maximal for a given magnetic strength. Similarly, the magnetic field with the direction in the first or third quadrant will inhibit tumbling. It is not difficult to understand that the magnetic strength should also be appropriate: an over-strong field (for instance, with $U_h > \Gamma$) will lock the director near the field direction and suppress the director tumbling; on the other hand, an over-weak field (for instance, below the Frederiks transition point) cannot overcome the nematic interaction and the flow field effect, and thus cannot drive the director to rotate. In fact, the director dynamics and the corresponding dissipative structures in this system are determined by the subtle balance among the viscous, elastic, and magnetic effects. Therefore, the employment of the statistical theory and simulation is absolutely necessary for us to deal with this non-linear dynamic system and to interpret the complicated rheological phenomena extensively.

In experiment, Grabowski and Schmidt have studied LCP subjected to both shear slow and magnetic field[36]. Unfortunately, the director tumbling was not observed by them because the magnetic field for n.m.r. was very strong and the field orientation was just beyond the tumbling regime. So, the state diagram given in the present paper might be helpful for later experiments.

The tumbling period in terms of shear time, t_p or of shear strain, γ_p, follows, in zero magnetic field, the scaling relation: $\gamma_p = \dot{\gamma} t_p = \text{constant}$, with changing shear rate, which has been repeatedly observed experimentally[4–10] and reproducted theoretically[12–25]. We discovered, however, this simple scaling relation is never satisfied when the external magnetic field exists.



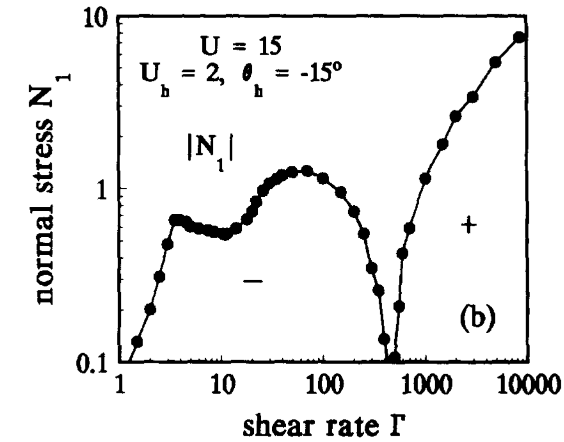


Figure 3 Dimensionless first normal stress difference N_1 as a function of dimensionless shear rate Γ in a magnetic field obtained from Brownian dynamics simulation with two typical external magnetic fields showing (a) four and (b) two regimes in the N_1 vs Γ curves

The tumbling period is, to the contrary, sensitive to the shear rate as well as to the field strength and orientation. For instance, with the field orientation fixed and the field strength and the shear rate changed, we can find the fastest tumbling points (*Figure 1*). Especially, when $\theta_h = -\pi/4$ and $U_h = 0.5\Gamma$, the tumbling is fastest in all of cases with $\gamma_p(\min) = 2\pi$, which indicates that there is an upper limitation of tumbling velocity.

Outside the tumbling regime, the shear aligning will occur. Our simulated aligning angles or Leslie angles are found to have good agreement with the experimental observations by Grabowski and Schmidt[36]. The simulated results about the state diagram, tumbling period and aligning angle have been further analysed by the Ericksen–Leslie (EL) continuum theory. All these studies will be reported in another paper[37].

In zero magnetic field, double sign-changes of the first normal stress difference (positive to negative, then to positive again) take place with increasing shear rate and three regimes in N_1 vs Γ are observed experimentally[2–10] and explained theoretically[12–25]. Surprisingly, more or less than three regimes can be predicted in the magnetic field (*Figure 3*) besides three regimes. With the same procedure as for the experimental data processing[2,3] the first normal stress differences given here are either the steady-state values in the aligning state or the averaged values of many integral cycles in the tumbling state. The subtle effect of the magnetic field, especially the great change of the shear-rate regime with negative N_1 might be applied to improve LCP processing, and the detailed studies will be published elsewhere in a full paper.

Conclusions

We have, for the first time, explored the external static magnetic field effect on the flow instability of LCP by the Brownian dynamics simulation and the L–L nematogen model. The magnetic field can enhance or inhibit the director tumbling, depending on the field strength and orientation as well as the shear rate. The state diagram is obtained and the dynamic processes are described. The tumbling period in a magnetic field does not obey the conventional scaling relation. Hence, this communication affords a novel model system for studying the hydrodynamic instability of anisotropic fluids. We even find out that the magnetic field can alter the shear-rate dependence of the first normal stress difference, which might be meaningful for LCP processing. This simulation algorithm can be readily extended into three dimensions, and therefore, the out-of-plane rotation of local directors during tumbling orbit[16] can also be dealt with. The experimental confirmation of the magnetic field effect on the director tumbling is absolutely necessary. Further theoretical and experimental research is thus desired, which will be very interesting and challenging.

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