Destabilization of a Layered System by Shear Flow

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I. Introduction

Shear experiments performed on a variety of layered systems have revealed a strong coupling between the orientation of the layers and the applied shear flow. Independent of the significant differences between the system under investigation, shear turns out to influence both the orientation and the arrangement of the layers. The experiments were carried out on polymeric and low molecular weight (LMW) lyotropic systems [1–4], liquid crystalline polymers [5], LMW thermotropic smectic A [6] and lamellar phases of block copolymer melts [7–10]. Starting with a well aligned state of layers parallel to the plates ("parallel" alignment, see Fig. 1), by increasing the applied shear rate, the layers become unstable and either layers within the xz-plane ("perpendicular" alignment) [7] or multilamellar vesicles ("onions") [1, 3] form. In some systems a second parallel alignment of the layers is observed at high shear rates [10]. If a statistical distribution of layer orientation is chosen as initial condition, no parallel alignment is observed at low shear rates and reorientation phenomena seem to be governed by the applied strain rather than the applied shear rate [4, 8].

In this contribution we present a simple model to explain the destabilization of originally parallel layers by an applied shear [11]. In contrast to other approaches we derive the macroscopic hydrodynamic equations of our model and perform a linear stability analysis of these equations. This procedure allows us a straight forward inclusion of dissipative effects. To derive the macroscopic equations we follow the standard procedure of irreversible hydrodynamics [12–14]. In our simple picture all mentioned layered systems are isomorphic to smectic A liquid crystals (LCs), i.e. we neglect polymeric degrees of freedom and the coupling of thermal layer fluctuations to the shear flow. Within this simple model of a layered structure we show that parallel layers are unstable above a certain critical shear rate.

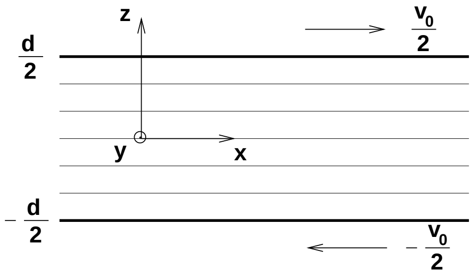

Figure 1: *We consider an idealized geometry of a shear experiment. Between two parallel plates we assume a defect-free well aligned lamellar phase. The upper plate moves with the velocity $\frac{v_0}{2}$ in positive x-direction, the lower plate moves with the same velocity in negative x-direction.*

II. Physical Mechanism

We consider an infinite layer of a mono-domain smectic A liquid crystal of thickness d as shown in Fig. 1. Both plates move with a velocity of $\frac{v_0}{2}$ along the x-axis but in opposite direction, thus giving rise to an average shear rate of $\dot{\gamma} = \frac{v_0}{d}$.

Similar to LMW nematics one can easily define a director $\hat{n}$ in layered systems via averaging over the axes of the molecules. A second axis of the system is given by the normal to the layers $\hat{p}$. In the usual picture of a smectic A LC $\hat{n}$ and $\hat{p}$ are parallel since the director is perpendicular to the layer *by definition.* The underlying nematic order is thus totally governed by the smectic layering. In our model we drop the assumption that $\hat{n}$ is parallel to $\hat{p}$. Both directions are dealed as independent variables which are coupled elastically. This elastic coupling guarantees that $\hat{n}$ and $\hat{p}$ are parallel in equilibrium.

The motivation for this generalized model of a smectic A lies in the well known coupling between the shear flow and the nematic order: Exposed to a shear flow a homeotropically aligned nematic feels a torque on the director. Depending on the material parameters this torque leads —in the simplest case— to a flow alignment of $\hat{n}$. Our key assumption is that this torque is also present

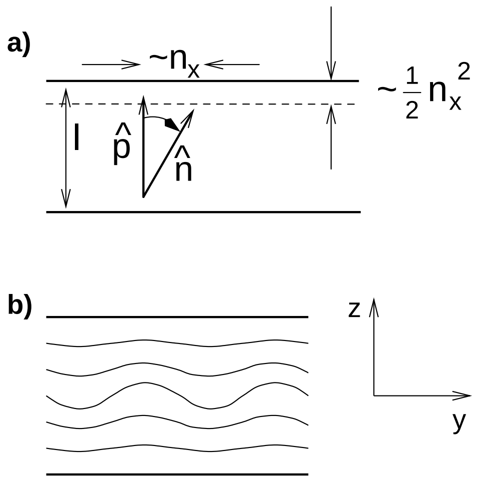

Figure 2: *A finite angle between the layer normal $\hat{p}$ and the director $\hat{n}$ induces a tendency of the layers to reduce their thickness (a). Supposing the total number of layers is constant, the system tries to accommodate this tendency by rotating the layers. Global rotations are not possible due to the boundary conditions, so the system rotates the layers locally as show in (b). The amplitude of the undulations is highly exaggerated in this figure. Note the difference in the directions: $\hat{n}$ is tilted in the x-direction, whereas the wave vector of the undulations points in the y-direction.*

in a smectic A LC and that it is balanced by the elastic coupling between $\hat{n}$ and $\hat{p}$.

Under shear the balance between this torque and the elastic coupling of $\hat{n}$ and $\hat{p}$ leads to a finite angle between these two directions, which we call flow alignment. As illustrated in Fig. 2a this flow alignment is equivalent to an effective dilatation of the layers. As in the case of dilated thermotropic smectic A LCs, above a certain threshold the system answers to this effective dilatation by developing undulations [15, 16] (see Fig. 2b).

III. Set of Macroscopic Equations

In the following we will discuss briefly the terms entering the energy density due to the symmetry of the system. Besides $\hat{n}$ and $\hat{p}$ it is very convenient to introduce the variable u which is the layer displacement along the z-axis (u is connected to $\hat{p}$ via $\hat{p} = \frac{\nabla(z-u)}{|\nabla(z-u)|}$). The director $\hat{n}$ does not distinguish between head and tail, thus it must occur quadratically in this energy density. Furthermore the energy density of the system is invariant under rigid rotations. In this paper we adopt the standard notation $\frac{1}{2}K_1(\nabla\cdot\hat{n})^2+\frac{1}{2}K_2[\hat{n}\cdot(\nabla\times\hat{n})]^2$ $+\frac{1}{2}K_3[\hat{n}\times(\nabla\times\hat{n})]^2$ which represent splay, twist and bend deformations respectively [17].

Similarly, in the part representing the layering of the system, terms corresponding to rigid rotations or translations must not occur. Since parity requires that u occurs quadratically in the energy density, the lowest order terms can be written as $\frac{1}{2}K\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right)^2+\frac{1}{2}B_0\left(\frac{\partial u}{\partial z}\right)^2$, describing the curvature of the layers and their dilatations.

As mentioned above rigid rotations of $\hat{n}$ together with $\hat{p}$ do not contribute to the energy density due to rotational invariance, but relative rotations of $\hat{n}$ versus $\hat{p}$ may contribute to the energy. Assuming a small angle between $\hat{n}$ and $\hat{p}$ we write this term as $\frac{1}{2}B_1(\hat{n}\times\hat{p})^2$. We note that this term is non-hydrodynamic, since it does not vanish in the limit of small wave number excitations (i.e. $q\to 0$). It thus leads dynamically to a relaxation and not to diffusive behavior in the long wavelength limit.

In the following we make several simplifications: 1) Since bend deformations are rather higher order gradient corrections to dilatations, if the angle between $\hat{n}$ and $\hat{p}$ is small, we will neglect bend. 2) In the hydrodynamics of smectics twist deformations are forbidden. Thus, for $\hat{n}$ close to $\hat{p}$, any twist of $\hat{n}$ has to be very small and we will neglect it. 3) A curvature of the layers is very similar to a splay deformation of the director, so we only keep the latter one.

To derive the set of macroscopic equations describing our model we follow the standard procedure [12–14]. In addition to the energy density discussed above, other key ingredients in this procedure are the Gibbs relation, balance equations for the macroscopic variables and the dissipation function R. In the spirit of our model, we also assume $\hat{n}$ and $\hat{p}$ to be independent variables in the above relations. For details of the derivation of the macroscopic equations see [11].

We find that the conditions for stationary solutions of $\hat{n}$ and u are given by

$$0 = -\frac{1}{2}\lambda_{ijk}\nabla_j v_k + \frac{1}{\gamma_1}\delta^{\perp}_{ik}h_k \tag{1}$$

$$0 = \nabla_i\Psi_i \tag{2}$$

with the flow alignment parameter $\lambda_{ijk} = (\lambda-1)\delta^{\perp}_{ij}n_k + (\lambda+1)\delta^{\perp}_{ik}n_j$, the conjugated variables $\vec{h}$ and $\vec{\Psi}$ (related to $\hat{n}$ and ∇u), the rotational viscosity γ_1^{-1} and the transverse Kronecker symbol $\delta^{\perp}_{ij} = \delta_{ij} - n_i n_j$.

The macroscopic description of our model contains elements of both, nematic and smectic A hydrodynamics. Their usual descriptions are included as limiting cases in our model, provided we suppress the approximations made in the energy density mentioned above. This implies, that our model does not describe the nematic–smectic A phase transition. To include the phase transition one has to take into account the nematic and smectic order parameters as additional dynamic macroscopic variables.

IV. Flow Alignment and its Consequences

We analyze the set of equations in two steps: First we determine the flow field and the director assuming that the layers are unchanged by the shear flow. In a second step we investigate undulations of $\hat{n}$ and $\hat{p}$ with a wave vector parallel to the y-direction.

Throughout our analysis the density ρ and the temperature T are taken to be constant. We assume weak anchoring at the boundaries in the sense that the director is free to rotate around its equilibrium homeotropic orientation *without* any energy barrier. This implies that the boundaries have no orienting effect on the director field.

Under the assumption that $\hat{n}$ and u are constant the linear velocity profile $\vec{v} = \dot{\gamma} z \hat{e}_x$ satisfies linear momentum conservation. Inserting this velocity profile in Eq. (1) and supposing an unchanged layered structure leads to the equation

$$\left[\frac{\lambda+1}{2} - \lambda n_x^2\right] \dot{\gamma} = \frac{B_1}{\gamma_1} n_x n_z + \frac{B_0}{\gamma_1} n_x (1-n_z), \quad (3)$$

with $n_z = \sqrt{1-n_x^2}$ and $n_y = 0$. For a small angle between $\hat{n}$ and $\hat{p}$, we find[1] (to linear order in n_x) $n_x = \dot{\gamma} \frac{\gamma_1}{B_1} \ \frac{1+\lambda}{2}$.

As shown in Fig. 2a this result has important consequences: The non-vanishing projection of $\hat{n}$ on the flow direction directly leads to a z-component of the director $n_z = 1 - \frac{1}{2} n_x^2 + O(n_x^4)$ less than unity. Following the discussion in Sect. II, this tilt of $\hat{n}$ is equivalent to an effective *dilatation* of the layers.

To analyze the effect of this dilatation we perform a linear stability analysis of Eqs. (1–2), assuming that the undulations of $\hat{n}$ and $\hat{p}$ do *not* couple to the velocity field. In accordance with the results of [18] we suppose the wave vector of the undulation to point in the vorticity direction (Fig. 2b) $\vec{q} = q_y \hat{e}_y$.

Undulating lamellae lie no longer in the xy-plane, so their dilatation can no longer be measured along the z-axis. To take this into account we use the well known replacement [15, 16] $\frac{\partial u}{\partial z} \to \frac{\partial u}{\partial z} - \frac{1}{2}\left(\frac{\partial u}{\partial y}\right)^2$ in the energy density of the system. The undulation amplitude must vanish at the plates, so our ansatz for the layer displacement is (see also Fig. 2) $u = A\cos(\frac{\pi}{d}z)\cos(q_y y) + \frac{1}{2} n_x^2 z$, where A is the small amplitude of the undulations, leading to a layer normal of the form

$$\hat{p} = q_y A \cos(\frac{\pi}{d} z) \sin(q_y y)\ \hat{e}_y + \hat{e}_z + O(A^2) \quad (4)$$

and similar ansatz for $\hat{n}$

$$\begin{aligned} \hat{n} \ &= \ n_x \hat{e}_x + q_y \tilde{A} \cos(\frac{\pi}{d} z) \sin(q_y y) \hat{e}_y \\ &\quad + (1 - \frac{1}{2} n_x^2) \hat{e}_z + O(\tilde{A}^2, n_x^4). \end{aligned} \quad (5)$$

In linear order the x- and z-components of (1) lead to the same result as equation (3). From the y-component of (1) we find that the ratio of the undulation amplitudes contained in $\hat{n}$ and $\hat{p}$ is close to unity $\tilde{A} = \frac{B_1}{B_1 + K q_y^2}\ n_z\ A$. Inserting this result in (2) we find for the critical values:

$$q_{y,c}^2 \ = \ \frac{\pi}{d}\sqrt{\frac{B_0}{K}} \quad (6)$$

$$n_{x,c}^2 \ = \ 4\frac{\sqrt{B_0 K}}{B_0 - 2B_1}\ \frac{\pi}{d} \quad (7)$$

$$\dot{\gamma}_c \ = \ \frac{4}{1+\lambda}\ \frac{B_1}{\gamma_1}\sqrt{\frac{\sqrt{B_0 K}}{B_0 - 2B_1}\ \frac{\pi}{d}} \quad (8)$$

Before discussing numerical values, we want to point out some important implications of our model [Eq. (8)]. The critical shear rate increases with increasing B_1. No undulation instability is possible if $2B_1$ exceeds B_0. This result could explain why some layered systems do not show a destabilization of the layers parallel to the plates under shear flow (e.g. most thermotropic smectic A LCs far from the phase transition to the nematic phase).

For smectic A LCs it is known [15, 16] that the critical dilatation is of the order of 10^{-5}, so we expect $n_{x,c}$ to be of the order of 10^{-2}. Thus, there would be only a comparatively small change to the uniaxial nature of a layered system even just below the onset of the undulation instability. To give a numerical value for the critical shear rate appears rather difficult, because neither the elastic constant B_1 nor the rotational viscosity γ_1 are used for the hydrodynamic description of the smectic A phase. Therefore, the only possibility appears to find measurements in the vicinity of the nematic-smectic A phase transition. Measurements on LMW LCs made in [19] in the vicinity

[1] Note that this stationary solution also occurs for $|\lambda| < 1$. The tumbling solution found for nematics for $|\lambda| < 1$ above the nematic-smectic A transition cannot occur in smectic A due to the layering.

of the nematic-smectic A transition indicate that B_1 is approximately one order of magnitude less than B_0. As for γ_1 we could not find any measurements which would allow an estimate of its value in the smectic A phase. In the nematic phase γ_1 increases drastically towards the nematic-smectic A transition.

V. Concluding Remarks

In this paper we have shown that a modification of the usual smectic hydrodynamics (layer normal and director are no longer parallel) leads to a flow aligning behavior and thus to an effective dilatation of the smectic layers. A linear stability analysis shows, that above a critical shear rate the flow alignment is strong enough to cause an undulation instability and thus to destabilize the layered structure. We point out, that the linearized analysis presented here does not allow to predict which structure will be stable at shear rates above the critical shear rate. To overcome this problem two strategies can be followed. Either one expands the governing equations in small, but non-vanishing amplitudes (in the vicinity of the threshold). Or one attacks the full non-linear equations by direct numerical integration. Following the lines proposed above will allow to give a prediction of the pattern formed above onset.

For a transition from undulating lamellae to reorientated lamellae or to multilamellar vesicles, defects have to be created for topological reasons. Since the order parameter varies spatially in the vicinity of the defect core, a description of such a process must include the full (tensorial) nematic order parameter as macroscopic dynamic variables. Both types of refinements (non-linear analysis and inclusion of defects) are beyond the scope of the present paper.

Using molecular dynamics computer simulations Soddemann, Kremer and Dünweg recently confirmed several features of the above model [20]. Namely they identified a flow alignment of the director and undulations developing above a critical shear rate. Furthermore Noirez [21] found in shear experiment on a smectic A liquid crystalline polymer in a cone-plate geometry, that the layer thickness reduces slightly with increasing shear. This result is compatible with the model presented here as well. In addition, recent experiments by Müller et al. [2] on the lamellar phase of a lyotropic system (a LMW surfactant) under shear suggest, that multilamellar vesicles develop via an intermediate state characterized by a distribution of director orientations in the plane perpendicular to the flow direction. These results are compatible with an undulation instability of the type proposed here, since undulations lead to such a distribution of director orientations. Nevertheless further investigations on these points are highly desirable.

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