

## MECHANICS OF ANISOTROPIC FLUIDS

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### ABSTRACT

The microstructure of anisotropic fluids affects the flow development, and the microstructure itself evolves with the flow. The result is velocity and stress distributions that can differ greatly from those associated with solutions of the Navier-Stokes equations under the same conditions, leading to unusual flow instabilities and "textures."

### INTRODUCTION

Many materials used in structural and electronic applications are processed in the liquid state, and the microstructure developed during liquid-phase processing affects the flow and the properties of the final shaped object. We are concerned here with liquids in which the microstructure is inherently anisotropic; this includes suspensions of high-aspect ratio particles, such as might be used in fiber-reinforced composite materials, and liquids made up of rigid high-aspect ratio molecules. The latter, which can form a liquid crystalline phase, are used in optical devices (low molar mass liquid crystals) and in high-performance materials applications (liquid crystalline polymers). The macroscopic rheology of such liquids is dependent on the developing orientation, leading to field equations that are far more complex than the Navier-Stokes equations for fluids consisting of low molar mass, low aspect ratio molecules. As a result, unexpected flow and stress distributions can result, and unusual flow instabilities and "textures" are observed.

This paper is a general overview of major issues in the mechanics of anisotropic fluids. References are limited to recent papers, from which relevant earlier literature can be found.

### FIBER SUSPENSIONS

The simplest anisotropic liquid to analyze is a dilute suspension of rigid fibers. Let  $r$  be the aspect ratio of the fiber and  $\phi$  be the fiber volume fraction. Geometrical arguments can then be used to classify suspensions of rigid fibers into three categories of fiber interaction, as follows:

$$\begin{array}{ll} \text{dilute} & \phi r^2 < 1 & (1a) \\ \text{semidilute} & 1/r < \phi r < 1 & (1b) \\ \text{concentrated} & 1 < \phi r & (1c) \end{array}$$

Dilute systems consist of isolated particles which have a negligible probability of interacting. Semidilute systems (called semiconcentrated by some authors) involve occasional particle-particle interactions, and the excluded volume must be considered. Coordinated particle-particle motions need not be taken into account in semidilute systems, however, whereas they dominate the motion of concentrated systems.

The macroscopic continuum rheology of dilute suspensions of macroscopic (i.e., too large to experience Brownian effects) rigid particles has been developed by a number of authors (c.f. Evans, 1975a; Dinh and Armstrong, 1984; Lipscomb et al., 1988) through statistical averaging of Jefferey's (1922) solution for the motion of ellipsoids in a Newtonian fluid. The stress is a function of the local statistical orientation distribution dyadic,  $\langle nn \rangle$ , where the unit vector  $n$  represents the instantaneous orientation of a particle and  $\langle \cdot \rangle$  denotes an ensemble average; the orientation distribution dyadic itself evolves with the motion. The constitutive equations are as follows:

$$\sigma = -pI + 2\eta_0 \Delta + \phi \langle \Sigma \rangle \quad (2)$$

$$\begin{aligned} \langle \Sigma \rangle = & 2\mu_0 \Delta + \mu_1 \langle nn \rangle + \mu_2 \Delta : \langle nn \rangle \langle nn \rangle \\ & + 2\mu_3 [\Delta \cdot \langle nn \rangle + \langle nn \rangle \cdot \Delta] \end{aligned} \quad (3)$$

$$\begin{aligned} D\langle nn \rangle / Dt = & \Omega \cdot \langle nn \rangle - \langle nn \rangle \cdot \Omega \\ & + \lambda [\Delta \cdot \langle nn \rangle + \langle nn \rangle \cdot \Delta \\ & - 2\Delta : \langle nn \rangle \langle nn \rangle] \end{aligned} \quad (4)$$

$\sigma$  is the total (Cauchy) stress and  $p$  is an isotropic pressure.  $\Delta$  and  $\Omega$  are the rate-of-deformation and vorticity tensors, respectively. Equations 3 and 4 include a closure approximation to remove the fourth moment  $\langle nnnn \rangle$ ; this approximation is not required in the integral equation formulation of Dinh and Armstrong (1984).  $\eta_0$  is the viscosity of the Newtonian suspending fluid, and the parameters  $\{\mu_i\}$  and  $\lambda$  are completely determined by the aspect ratio and  $\eta_0$ . For purely extensional flow a theory by Batchelor (1971) is recovered, which predicts extensional stresses that can exceed those of the suspending fluid by orders of magnitude; Batchelor's theory has been verified experimentally by Mewis and Metzner (1974). Batchelor has shown how the functional form appropriate to dilute suspensions can be



rescaled for application in the semidilute region, and this scaling has been used by Evans (1975a,b) and Dinh and Armstrong (1984).

The dilute fiber suspension equations have been solved numerically by Lipscomb and co-workers (1988) for flow through a contraction, and by Papanastasiou and Alexandrou (1987) for free-jet extrusion. Lipscomb and co-workers found a substantial increase in the size of the recirculating corner eddy with increasing fiber concentration, and the results were in quantitative agreement with experiments. (This result is not surprising in terms of qualitative dissipation arguments, given the high dissipation in the extensional flow along the centerline. There is, however, no variational principle to support this qualitative approach, but it is consistent with experiments by van de Griend and Denn (1989) on coaxial flow of fluids of greatly differing viscosities through expansions and contractions.) Papanastasiou and Alexandrou made no direct comparisons with experiment, but the predicted reduction in extrudate swell is consistent with experience. Recent experiments by Milliken and coworkers (1989) on low-Reynolds number motion of a sphere through a suspension of rods offers an excellent test of the theory.

There is no continuum theory for concentrated suspensions of non-Brownian high-aspect ratio particles. Some concentrated suspensions appear to form a low-viscosity "slip layer" near a confining wall, possibly because of particle migration away from the wall. In many cases this will lead to a flow of the suspension that approximates a potential flow. Potential flows are highly orienting, and high-aspect ratio particles will align rapidly with one of the principal axes of the motion. This behavior is predicted by the dilute-suspension theory described above, and an equivalent theory has been used successfully in the design of extrusion dies for reinforced pipe (Goettler et al., 1979, 1981). Clearly no theory is required for flows in which both kinematics and orientation are known a priori, and the dilute (or semidilute) theories should not be expected to apply in other situations for concentrated suspensions.

#### NEMATIC LIQUID CRYSTALS

When rigid molecules are packed beyond a critical concentration, free volume considerations require that there be a high degree of local alignment. Such a "mesophase," or intermediate phase, between an ordered solid and a randomly-ordered liquid is known as a liquid crystal. If the local order is uni-directional then the liquid crystalline phase is called nematic. The high-aspect ratio molecules which form liquid crystalline phases are typically para-substituted aromatic compounds. While we shall not be concerned with chemical composition in this discussion, it is important to keep in mind that subtle changes in composition are known to have a profound effect on the phase behavior and transitions in liquid crystalline systems; for applications, therefore, chemical composition is an overriding concern. Lyotropic liquid crystals are formed when mesogenic molecules exceed a critical concentration in a solution; thermotropic liquid crystals occur in a homogeneous melt of rigid molecules when the temperature drops below a critical value and orientation induced by entropic effects overcomes randomization by Brownian motion.

There is a well-developed theory by Leslie and Ericksen for the dynamics of low molar mass nematic liquid crystals (DeGennes, 1975; Leslie, 1979). The Leslie-Ericksen theory contains terms which are quite similar to those in Equation 3, but with six scalar coefficients (five of which are independent) because the stress is anisotropic, and with an important addition. The molecular orientation induces a purely entropic contribution to the system free energy, as follows:

$$2F = K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 |\mathbf{n} \times \nabla \times \mathbf{n}|^2 \quad (5)$$

The three terms in Equation 5 represent splay, twist, and bend deformations of the local director, respectively. This free energy term causes a contribution to the stress of the form  $(\delta F / \delta \mathbf{v}_n) \cdot \mathbf{v}_n$ . The director gradient contribution to the stress is purely elastic because of its entropic origins. Because the mesogenic molecules typically have anisotropic magnetic susceptibilities they can be oriented in electromagnetic fields; the elastic strain should therefore be completely recoverable upon removal of an electromagnetic torque.

The presence of (recoverable) entropic elasticity in the constitutive equation for a Leslie-Ericksen nematic liquid introduces interesting microstructural gradients. A rod-like particle will rotate in a shear field, but the entropic elasticity, when "anchored" at a bounding surface, will resist rotation and cause the director to align at a fixed angle to the shear flow. This induces an orientation boundary layer for rearrangement between the angle induced at the wall and the angle induced by the shear flow; the presence of such a boundary layer introduces a new length measure, and scaling that is quite different from that expected for an isotropic material of the same viscosity level determines the flow (Tseng et al., 1976; Rey and Denn, 1988). The orientation effect of an elongational flow (along the center line in a converging region, for example) will cause a different alignment, and hence a different boundary layer scaling (Rey and Denn, 1988). There is an interesting series of flow-induced orientation transitions in radial laminar flow (Hiltrop and Fischer, 1976) which has recently been predicted by Rey (1989) with the Leslie-Ericksen theory.

For certain values of the six Leslie viscosities (the analogs of the  $\{\mu_i\}$  in Equation 3) a phenomenon known as "tumbling" can occur. Contrary to the name, tumbling is not a dynamic process but is rather a cascade-like phenomenon in which steady solutions can exhibit rotations of the director over very small spatial distances, producing textures known as "walls" (Carlsson, 1984a,b; Rey and Denn, 1989a). Similar textures induced by the symmetry-breaking action of magnetic fields produce orientation distributions that can be unstable to out-of-plane perturbations, leading to orientations that are transverse to the plane of motion (Rey and Denn, 1989b). (Such out-of-plane orientations are frequently observed in molded parts of macromolecular liquid crystals and of fiber-filled composites, and the inherent instability of in-plane regions with large orientation gradients is a likely cause.) The dynamics of Leslie-Ericksen fluids in all but the simplest flow fields is essentially unexplored, and is a fruitful area for research.



## LIQUID CRYSTALLINE POLYMERS

Liquid crystalline polymers for high-performance applications have been known for only two decades; the history of development is described by Economy (1989) and Jackson (1989). There is no complete theory for the rheology of liquid crystalline polymers (LCPs). The dynamics of some lyotropic systems may be approximated by the Leslie-Ericksen theory, but it appears that in general the flexibility of the macromolecules must be considered; in addition, the theory is unlikely to apply at the high deformation rates experienced in polymer processing. A theory by Doi (1981) does not contain an analog of the entropic free energy (Eq. 5) and hence cannot be applied to systems with large director gradients. Relaxation experiments following orientation in a magnetic field (Moore and Denn, 1988) have shown that the orientational elasticity in nematic polymers decreases in time, hence cannot be purely entropic. The rheology of liquid crystalline polymers must therefore account for two different types of viscoelasticity: that normally encountered in flexible polymers because of the relaxation of macromolecules, and a new type resulting from the relaxation of director elasticity. The elastic coefficients governing the recoverable portion of the latter are believed to be small, in which case the effects on the flow will be induced through small boundary layers.

Optical microscopy of LCPs shows the presence of micron-scale "domains;" these are regions of high local orientation, separated by sub-micron regions of rapid changes in director orientation. The regions containing large director gradients might be analogs of either the "walls" or "disclinations" (line singularities) present in the theory for low molar mass liquid crystals; in either case the effect on the fluid mechanics of the LCPs has not been elucidated. Nuclear magnetic resonance spectroscopy has shown some liquid crystalline polymers to be biphasic in the melt, containing both nematic and isotropic phases (Moore and Stupp, 1987; Nicely, et al, 1987; Amundson, et al, 1987; Amundson, 1989). High-melting crystallites have been identified at melt temperatures in the two most-studied fully-nematic thermotropic LCPs (Lin and Winter, 1988; Kalika, et al, 1989a), and more than one dispersed immobile phase may be present at melt processing temperatures (Amundson, 1989). There are unusual effects of the size of the channel in both torsional and capillary flow, and the results are inconsistent in independent studies (Wissbrun et al, 1987; Kalika et al, 1989b), perhaps as a result of subtle compositional or structural changes in samples. The rheology of a fully-nematic thermotropic melt exhibits a power-law viscosity over eight decades of shear rate (Kalika et al, 1989a), which is most unusual for any material and inconsistent with any available rheological theory.

Clearly, prediction of the fluid mechanics of this class of anisotropic materials is beyond our ability at present because of the absence of any appropriate rheological description. (An unpublished theory by Edwards and coworkers (1989) appears to be a promising step in resolving this problem.) Several theoretical studies of the fluid mechanics and orientation development in liquid crystalline polymers have been published, but these cannot be taken seriously as quantitative (or even qualitative) descriptions of molding and extrusion flows

because they use the Leslie-Ericksen theory and neglect the entropic elastic terms. The orientation distributions observed in parts molded from LCPs contain boundary layers, textures, and transverse orientations that cannot be explained in the absence of something like the director gradient terms in Eq. 5.

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