

EQUILIBRIUM MICROSTRUCTURE OF COMPLEX FLUIDS

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EXTENDED ABSTRACT

Predictions of the microstructure of complex fluids, such as liquid crystalline polymers or concentrated rigid rod suspensions, are often based on a moment equation for the orientation dyad $\langle \underline{p}\underline{p} \rangle$ that requires a closure model for the orientation tetrad $\langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle$ (see Doi and Edwards, 1986). Here the unit vector \underline{p} represents the instantaneous orientation of a constituent component of the dispersed phase, such as a rigid rod. Unfortunately, the widespread use of the method of moments to characterize the microstructure has been limited by the absence of a practical and accurate closure model that relates the dispersed phase orientation tetrad (fourth-order moment) to the dispersed phase orientation dyad (second-order moment).

The fraction of the dispersed phase having orientation coordinates on the unit sphere in the range $0 \leq \theta \leq \theta + \Delta\theta$ and $0 \leq \phi \leq \phi + \Delta\phi$ is given by

$$P\{0 \leq \theta \leq \theta + \Delta\theta, 0 \leq \phi \leq \phi + \Delta\phi\} = \Psi(\theta, \phi, t) \sin(\theta) d\theta d\phi . \quad (1)$$

The orientation distribution function $\Psi(\theta, \phi, t)$ in the above definition is governed by Smoluchowski's equation:

$$\frac{D\Psi}{Dt} + \frac{\partial}{\partial \underline{p}} \cdot \left[(\underline{p} \cdot \nabla \underline{u} - \underline{p}\underline{p}\underline{p} : \nabla \underline{u}) \Psi \right] = \bar{D}_R \frac{\partial}{\partial \underline{p}} \cdot \left[\frac{\partial \Psi}{\partial \underline{p}} + \Psi \frac{\partial}{\partial \underline{p}} \left(\frac{\Delta U_{MS}}{k_B T} \right) \right], \quad (2)$$

subject to the condition that

$$\int_0^{2\pi} \int_0^\pi \Psi(\theta, \phi, t) \sin\theta d\theta d\phi = 1. \quad (3)$$

Here \bar{D}_R represents the rotary diffusion coefficient (1/time) and ΔU_{MS} is the Maier-Saupe potential for the excluded volume,

$$\Delta U_{MS} = -\frac{3}{2} U k_B T \underline{p} \underline{p} : \left(\langle \underline{p}\underline{p} \rangle - \frac{1}{3} \underline{I} \right). \quad (4)$$

The Maier-Saupe (MS-) potential depends explicitly on the microstructure and implicitly on the volume fraction of the dispersed phase through the phenomenological coefficient U .

Low-order moments of the orientation distribution function are used to characterize the microstructure of fiber suspensions and complex fluids such as liquid crystalline polymers. The second moment, or orientation dyad, is defined as follows:

$$\langle \underline{p}\underline{p} \rangle = \int_0^{2\pi} \int_0^\pi \underline{p}\underline{p} \Psi(\underline{p}, t) \sin(\theta) d\theta d\phi. \quad (5)$$

An equation for $\langle \underline{p}\underline{p} \rangle$ can be written as

$$\begin{aligned} \frac{D \langle \underline{p}\underline{p} \rangle}{Dt} = & +(\nabla \underline{u})^T \cdot \langle \underline{p}\underline{p} \rangle + \langle \underline{p}\underline{p} \rangle \cdot \nabla \underline{u} - 2 : \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle : \underline{S} \\ & - 6 \bar{D}_R \left[(\langle \underline{p}\underline{p} \rangle - \frac{1}{3} \underline{I}) - U (\langle \underline{p}\underline{p} \rangle \cdot \langle \underline{p}\underline{p} \rangle - \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle : \langle \underline{p}\underline{p} \rangle) \right] \end{aligned} \quad (6)$$

In the above equation, $\nabla \underline{u}$ is the velocity gradient. For liquid crystalline polymers, it is noteworthy that the orientation tetrad directly impacts the microstructure by coupling with both the orientation dyad and the strain rate,

$$\langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle : \langle \underline{p}\underline{p} \rangle \quad \text{and} \quad \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle : \underline{S}.$$

Recently, a new closure for the orientation tetrad has been developed that retains the six-fold symmetry and six-fold projection properties of the exact fourth order moment (see Petty *et al.*, 1999; Nguyen *et al.*, 2001; Kini *et al.*, 2003). A preclosure for the orientation tetrad (FSQ-preclosure) is given by

$$\langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle = (1 - C_2) \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle_1 + C_2 \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle_2 \quad \text{where} \quad (7)$$

$$\langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle_1 = -\frac{1}{35} S[\underline{I}, \underline{I}] + \frac{1}{7} S[\underline{I}, \langle \underline{p}\underline{p} \rangle], \quad \text{and} \quad (8)$$

$$\begin{aligned} \langle \underline{p}\underline{p}\underline{p}\underline{p} \rangle_2 = & \frac{2}{35} \langle \underline{p}\underline{p} \rangle : \langle \underline{p}\underline{p} \rangle S[\underline{I}, \underline{I}] \\ & + S[\langle \underline{p}\underline{p} \rangle \cdot \langle \underline{p}\underline{p} \rangle, \langle \underline{p}\underline{p} \rangle \cdot \langle \underline{p}\underline{p} \rangle] - \frac{2}{7} S[\underline{I}, \langle \underline{p}\underline{p} \rangle \cdot \langle \underline{p}\underline{p} \rangle] \end{aligned} \quad (9)$$

In the above equations, the result of the operation $S[\underline{A}, \underline{B}]$ is a fully symmetric tetradic-valued operator formed from the two indicated symmetric dyadic-valued operators. In this research, \bar{D}_R and U are independent of the local microstructure. In general, the closure coefficient C_2 depends on the invariants of the structure tensor $\text{II}_b \equiv \text{tr}(\underline{b} \cdot \underline{b})$ and $\text{III}_b \equiv \text{tr}(\underline{b} \cdot \underline{b} \cdot \underline{b})$, where

$$\underline{b} \equiv \langle \underline{p}\underline{p} \rangle - \frac{1}{3} \underline{I} \quad (10)$$

If the relaxation of *planar anisotropic states* is controlled by Brownian motion, then the coefficient C_2 is given by

$$C_2 = \frac{8 + 45 \text{III}_b}{18(1 + 9 \text{III}_b)}. \quad (11)$$

In this research, Eq.(11) is extended to all realizable states of the microstructure.

The foregoing theory seeks a balance between the flow alignment process and the rotary diffusion process in orientation space. U is a dimensionless measure of the strength of the Maier-Saupe potential and accounts for the excluded volume self-alignment process on the rotary diffusive flux. In the absence of flow and for $U > 5$, the equilibrium states predicted by the above theory are anisotropic. Although an isotropic microstructure satisfies the steady-state moment equation for all values of U , a dynamic analysis of the orientation dyad shows that the isotropic state is stable for $U < 4.656$ and unstable for $U > 5.000$. For $4.654 < U < 5.000$, three steady states are predicted: a conditionally stable isotropic state, an unstable anisotropic state, and a conditionally stable anisotropic state. The quadratic form associated with the anisotropic microstructure has a prolate shape. The theory is consistent with the qualitative behavior of lyotropic liquid crystalline polymers and other theories for LCP microstructure. For example, at high concentration of the dispersed phase and in the absence of an external field, the theory together with Eq.(11) predicts that all *realizable microstructures* relax to multiple equilibrium realizable states.

KEYWORDS: Liquid crystalline polymers, composites, microstructure, orientation statistics, closure approximation, equilibrium states, self-alignment, flow induced alignment, simple shear

ACKNOWLEDGMENT

This research was partially funded by the National Science Foundation (CTS-9986878). The authors are grateful for this financial support.

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