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A molecular theory of flow alignment and tumbling in sheared nematic liquid crystals

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A molecular theory is presented for the dynamics of small-molecule nematic liquid crystals in shear flow. The flow-alignment angle is predicted to depend on the aspect ratio of the liquid crystal molecules, as well as the second and fourth moments, P_2 and P_4 of the distribution of molecules about the nematic director. This theory also predicts a transition from flow alignment to tumbling well away from any nematic-smectic-A phase transitions. © 1995 American Institute of Physics.

In the absence of other orienting fields, the dynamics of nematic liquid crystals in shearing flows depend strongly on the relative orientation of the direction of preferential molecular alignment, the director, and the flow direction. If the director is aligned in the shear plane (the plane defined by the direction of relative motion of the shearing surfaces and the normal to these surfaces) prior to flow, a simple torque balance shows that the net torque acting on the director vanishes when it aligns at an angle $\theta_0 = 0.5 \cos^{-1}(1/\lambda)$ to the flow direction. Here $\lambda = (-\gamma_2/\gamma_1)$ and γ_1 and γ_2 are phenomenological volume torque coefficients having dimensions of viscosity. It is therefore apparent that if $|\lambda| < 1.0$, i.e., $|\gamma_2| < |\gamma_1|$, no steady-state solution for the flow-alignment angle exists, and the director rotates continuously (tumbles) in the shear plane.

It had long been thought that for prolate nematogens $|\lambda|$ is always greater than unity and the director therefore flow aligns at a small angle to the flow direction except when pre-translational fluctuations, which may result from a nearby nematic-smectic-A phase transition,¹ are present. Gähwiler, however, determined the flow-alignment angle from simple birefringence measurements on nematic liquid crystals in plane-Poiseuille flow and found that not all nematics flow align, even at temperatures far from a nematic-smectic-A phase transition.² Specifically, he observed that while 4-methoxy-benzylidene-4'-*n*-butylaniline (MBBA) flow-aligns over its entire nematic range, another nematic, *p*-*n*-hexyloxybenzylidene-*p*'-aminobenzonitrile (HBAB), undergoes a transition from flow alignment to tumbling at a reduced temperature, $T_r = (T/T_{NI})$, of 0.97; where T is the absolute temperature in Kelvin and T_{NI} is the absolute temperature at the isotropic-nematic phase transition. This transition from flow alignment to tumbling in HBAB has since been confirmed by others.^{3,4}

Such a dramatic difference in the flow dynamics of HBAB and MBBA is unexpected because, apart from a difference in the sign of their respective dielectric anisotropies, these molecules are very similar.^{5,6} Indeed Gähwiler has contended that the positive dielectric anisotropy of HBAB should make side-to-side molecular association more likely in HBAB than in MBBA. He therefore speculated that tumbling in HBAB results from molecular association; the

“bumpy” contour of the resulting flow units causes the director to experience disorienting torques even in the flow-aligned state, making this state unstable.

In what follows a general molecular theory is presented that shows a transition from flow alignment to tumbling in the flow dynamics of small-molecule nematic liquid crystals. We begin by considering the behavior of an isolated ellipsoid of revolution in simple shear flow. In such a flow, fluid elements experience local deformations that range from pure rotation to pure straining. The velocity gradient tensor, $\partial v/\partial x$, therefore consists of a symmetric part, \underline{A} (the rate of strain tensor), and an antisymmetric part, $\underline{\omega}$ (the vorticity tensor). If such an ellipsoidal particle, with an aspect ratio a and orientation characterized by a unit vector \mathbf{u} that points in the direction of its symmetry axis, is subjected to shear flow, it can be shown that its orientation at any moment in time satisfies the equation,⁷

$$\frac{\partial \mathbf{u}}{\partial t} = L(a)[\underline{A} \cdot \mathbf{u} - \underline{A} : \mathbf{u} \mathbf{u} \mathbf{u}] + \underline{\omega}^T \cdot \mathbf{u}, \quad (1)$$

where $L(a) = (a^2 - 1)/(a^2 + 1)$.

If this particle is now surrounded by other similar ellipsoidal particles and, as before, subjected to shear flow, its transient orientation will be altered by collisions with other particles. In the absence of flow or other orienting forces, these collisions will cause the particles to adopt random orientations with respect to each other. Such a randomizing force can be modeled as a stochastic Brownian force, and the probability distribution of particle orientations $\psi(\mathbf{u}, t)$ that result from flow in the presence of this force is governed by a Fokker-Planck equation of the form,

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial \mathbf{u}} \left(\psi \frac{\partial \mathbf{u}}{\partial t} \right) - \bar{D}_r \frac{\partial^2 \psi}{\partial R^2} = 0, \quad (2)$$

where \bar{D}_r is an effective Stokes-Einstein rotary diffusion coefficient that characterizes the transient evolution of particles in the stochastic field,

$$\frac{\partial}{\partial R} = \mathbf{u} \times \frac{\partial}{\partial \mathbf{u}},$$

and the term $\partial \mathbf{u}/\partial t$ describes the convection of particles by flow [Eq. (1)].

At sufficiently high volume densities, nematic interactions between particles become significant, and at appropriate temperatures may even exceed the Brownian forces. Under such conditions, the ensemble of particles can undergo a transition from a random orientation distribution to a nematic state in which they align about a specific direction, the director, at equilibrium. To account for the nematic interactions in this model, we follow Hess⁸ and Doi⁹ by including an orientation-dependent nematic potential $V_{\text{nem}}(\mathbf{u})$ in the evolution equation for the orientation distribution,

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial \mathbf{u}} \cdot \psi \frac{\partial \mathbf{u}}{\partial t} - \overline{D_r} \frac{\partial}{\partial R} \left(\frac{\partial \psi}{\partial R} + \psi \frac{\partial}{\partial R} \frac{V_{\text{nem}}(\mathbf{u})}{k_B T} \right) = 0, \quad (3)$$

where k_B is the Boltzmann constant. This final form of the governing Fokker–Planck equation should be easily recognizable since it has been highly successful in describing the orientation dynamics of the nematic director in lyotropic nematic polymers.^{10,11}

A variety of expressions for $V_{\text{nem}}(\mathbf{u})$ suitable for describing small-molecule nematics have been presented in the literature.^{12,13} For simplicity, we choose the so-called Maier–Saupe form,¹⁴ $V_{\text{nem}}(\mathbf{u}) = K - (3/2)U\mathcal{S}:\mathbf{u}\mathbf{u}$, where K and U are constants and $\mathcal{S} = \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\delta \rangle$ is the tensor order parameter; δ being the unit tensor. The evolution equation for the second moment, $\langle \mathbf{u}\mathbf{u} \rangle = \int \mathbf{u}\mathbf{u} \psi(\mathbf{u}) d\mathbf{u}$, of the orientation distribution of ellipsoids is easily found from Eq. (3) to be,

$$\begin{aligned} \frac{\partial}{\partial t} \langle \mathbf{u}\mathbf{u} \rangle &= L(a) (\langle \mathbf{u}\mathbf{u} \rangle \cdot \mathbf{A} + \mathbf{A} \cdot \langle \mathbf{u}\mathbf{u} \rangle - 2\mathbf{A} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle) \\ &+ \langle \mathbf{u}\mathbf{u} \rangle \cdot \boldsymbol{\omega} + \boldsymbol{\omega}^T \cdot \langle \mathbf{u}\mathbf{u} \rangle - 2\overline{D_r} (3\langle \mathbf{u}\mathbf{u} \rangle - \delta) \\ &- 6\overline{D_r} \frac{U}{k_B T} (\mathcal{S} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle - \mathcal{S} \cdot \langle \mathbf{u}\mathbf{u} \rangle). \end{aligned} \quad (4)$$

For slow flows, an approximate analytical expression for λ can be easily derived from Eq. (4) by neglecting shear-induced distortions from uniaxiality in the molecular orientation distribution (we will consider the effect of such distortion shortly). The orientation dynamics of the director and the flow dynamics of the liquid crystal molecules can then be related through the following expressions for the second and fourth moments of $\psi(\mathbf{u})$,

$$\begin{aligned} \langle u_i u_j \rangle &= P_2 (n_i n_j - \frac{1}{3} \delta_{ij}) + \frac{1}{3} \delta_{ij}, \\ \langle u_i u_j u_k u_l \rangle &= \frac{1}{105} (7 - 10P_2 + 3P_4) (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} \\ &+ \delta_{il} \delta_{kj}) + \frac{1}{7} (P_2 - P_4) G_{ijkl} + P_4 n_i n_j n_k n_l. \end{aligned}$$

Here the second and fourth moments ($\langle \mathbf{u}\mathbf{u} \rangle$ and $\langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle$) are written in their respective index notation forms ($\langle u_i u_j \rangle$ and $\langle u_i u_j u_k u_l \rangle$), δ_{ij} , etc. are unit tensors, P_2 and P_4 are the second and fourth order Legendre functions, respectively, and

$$\begin{aligned} G_{ijkl} &= \delta_{ij} n_k n_l + \delta_{ik} n_j n_l + \delta_{il} n_j n_k + \delta_{jk} n_i n_l + \delta_{jl} n_k n_i \\ &+ \delta_{kl} n_i n_j. \end{aligned}$$

The dot product of Eq. (4) with \mathbf{n} yields the evolution equation for the director,

$$\begin{aligned} \frac{\partial \mathbf{n}}{\partial t} &= \boldsymbol{\omega}^T \cdot \mathbf{n} + L(a) \frac{(15P_2 + 48P_4 + 42)}{105P_2} \{ \mathbf{A} \cdot \mathbf{n} - \mathbf{A} : \mathbf{n}\mathbf{n}\mathbf{n} \} \\ &- 4\overline{D_r} \left(1 + \frac{U}{35k_B T} (24P_4 - 5P_2 - 7) \right) \mathbf{n} \\ &+ \text{other terms parallel to } \mathbf{n}. \end{aligned} \quad (5)$$

The “other terms parallel to \mathbf{n} ” serve to keep the magnitude of the director fixed at unity.

A phenomenological counterpart to Eq. (5) may be derived from the Leslie–Ericksen continuum theory. In the absence of magnetic fields, conservation of angular momentum yields the following equation for the director:^{15,16}

$$\mathbf{n} \times \left(\gamma_1 \frac{\partial \mathbf{n}}{\partial t} + \gamma_2 \mathbf{A} \cdot \mathbf{n} - \gamma_1 \boldsymbol{\omega}^T \cdot \mathbf{n} \right) = 0. \quad (6)$$

Applying the constraint $\mathbf{n} \cdot \mathbf{n} = 1$ to Eq. (6), the evolution equation for the director is found to be

$$\frac{\partial \mathbf{n}}{\partial t} = \boldsymbol{\omega}^T \cdot \mathbf{n} + \lambda \{ \mathbf{A} \cdot \mathbf{n} - \mathbf{A} : \mathbf{n}\mathbf{n}\mathbf{n} \}, \quad (7)$$

where, as before, $\lambda = (-\gamma_2/\gamma_1)$. Comparing Eqs. (5) and (7), it is apparent that,

$$\lambda = L(a) \frac{(15P_2 + 48P_4 + 42)}{105P_2}; \quad (8)$$

the Brownian and nematic interaction terms simply combine to define the relationship between P_2 and P_4 for the Maier–Saupe potential. Therefore, provided that the orientation distribution of molecules about the director is uniaxial, the specific form of the nematic potential does not affect Eq. (8). From this equation, flow alignment or, alternatively, tumbling is seen to be controlled by the molecular aspect ratio and the second and fourth moments of the orientation distribution of molecules about the director. Thus, the flow behavior of nematics is by no means universal; it depends on the shape of the liquid crystal molecules as well as their orientation distribution with respect to the director.

For small-molecule nematics away from critical points, the orientation distribution of molecules about the director is assumed to be largely unperturbed by flow, except at unusually high shear rates, and P_2 and P_4 will be close to their equilibrium values. It is therefore possible to determine λ from measurements of P_2 and P_4 made in the absence of flow. λ values determined using Eq. (8) with P_2 and P_4 measurements on the liquid crystal trans-4-pentyl-(4-cyano phenyl)-cyclohexane (PCH-5), using polarized laser Raman scattering,¹⁷ are presented at a variety of reduced temperatures in Fig. 1. This plot shows that at a reduced temperature of 0.95, λ becomes less than unity. PCH-5 should therefore undergo a transition from flow aligning to tumbling at this temperature. For this liquid crystal, the measured P_2 and P_4 values are not far from those predicted by the Maier–Saupe theory. Therefore, λ determined using the Maier–Saupe values of P_2 and P_4 is in good agreement with λ determined using experimental P_2 and P_4 values; see Fig. 1. All λ 's are calculated for $L(a) = 1.0$.

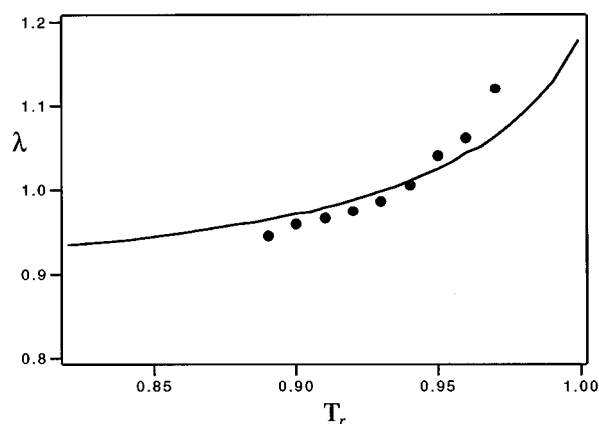


FIG. 1. λ vs reduced temperature using P_2 and P_4 data from polarized Raman scattering measurements on PCH-5 (solid circles), and from P_2 and P_4 obtained from the Maier-Saupe theory (solid line). Both sets of results λ 's are obtained using Eq. (8).

As shown earlier, λ may also be determined from either viscosity measurements or from measurements of the flow-alignment angle. λ values for the liquid crystals 4-*n*-pentyl-4'-cyanobiphenyl (5CB), 4-methoxy-4'-*n*-butylazoxybenzene (N4), and the eutectic mixture of 4-*n*-pentyl-phenyl-4-methoxybenzoate and 4-*n*-pentyl-phenyl-4-*n*-hexyloxybenzoate (EM) determined from the viscosity measurements of Knepe *et al.*^{18,19} and λ values from Gähwiller's flow-alignment angle measurements on HBAB and MBBA (Ref. 2) are presented in Fig. 2. Figure 2 includes theoretical λ values for large, ($a \rightarrow \infty$), and small, ($a = 5.0$), molecular aspect ratios. Estimates of the molecular aspect ratios from tabulated bond length and bond angle data²⁰ yield values that range from 4 to about 10 for the liquid crystals considered here. Note that an aspect ratio of only 7 corresponds to a value of $L(a)$ of 0.96, almost unity.

It is apparent from Fig. 2 that very good agreement is observed between the λ 's calculated using Eq. (8) and their

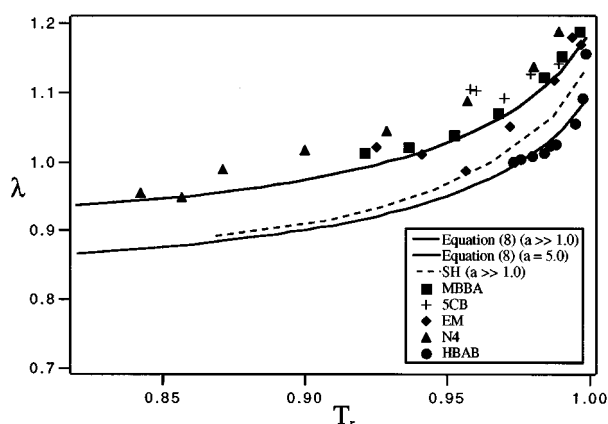


FIG. 2. λ vs reduced temperature from various sources. Dashed line: values determined from numerical solution of Eq. (3) using a spherical harmonics expansion of the orientation distribution function (SH). Solid lines: λ values calculated using Eq. (8) for two molecular aspect ratios. Symbols: values obtained from viscosity and flow-alignment angle measurements for various liquid crystals.

experimental counterparts. Particularly good agreement between theory and experiment is observed for MBBA. Unfortunately, however, this material crystallizes before the predicted transition from flow-alignment to tumbling could be observed. As stated earlier, a material for which this transition is known to occur is HBAB. In Fig. 2 it is clear that the theoretical λ values computed from Eq. (8) using a high aspect ratio disagree with those determined from Gähwiller's flow-alignment angle measurements for HBAB. However, for a lower molecular aspect ratio, namely 5.0, the theoretical and experimental values of λ are observed to agree rather well. Furthermore, for this lower aspect ratio, the theory predicts tumbling at a reduced temperature of 0.975, which is almost exactly the temperature at which a transition from flow alignment to tumbling has been reported for this material.

This result is important because to this point this transition from flow aligning to tumbling with decreasing temperature has gone largely unexplained. Moreover, it shows that Gähwiller's speculation that the difference in the flow behavior of MBBA and HBAB is due entirely to side-to-side molecular aggregation in HBAB, is very likely correct. Such aggregation will lower the effective aspect ratio of the liquid crystal flow units, and, according to the theory, push the flow-aligning-to-tumbling transition to higher temperatures.

Finally, we consider the effect of shear-induced distortions from uniaxiality on λ by solving Eq. (3) numerically using an expansion of ψ in terms of spherical harmonic functions, as described in Ref. 11. At low shear rates, this numerical solution gives a second moment tensor \mathcal{S} , the time evolution of which can be matched to that of the Leslie-Ericksen equation by adjusting λ . This procedure gives λ to within ± 0.002 . Figure 2 shows that although this "exact" value of λ for $a \gg 1$ is about 7% lower than that given by Eq. (8), it shows a similar dependence on the reduced temperature; in particular, flow aligning is replaced by tumbling as T_r decreases. Surprisingly, the "approximate" λ 's obtained by neglecting shear-induced distortions of the molecular distribution function are in better agreement with the experimental values of λ than are the "exact" λ 's for all the liquid crystals except the anomalous HBAB.

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