Comment on "Measurement of the Viscoelastic Coefficients of Main-Chain Nematic Polymers by an NMR Technique"

Martins, Esnault, and Volino[1] (MEV) have proposed a NMR technique and a theoretical model for determining the viscosities and the ratio of the bend to splay elastic constants in polymer liquid crystals. Although their analysis contains some of the right qualitative features, we seriously doubt its quantitative validity for the following reasons. First, the crucial assumption for the form of distortion employed in their model was not supported by direct microscopic observation. Second, the actual initial response depends on the exact geometry and boundary conditions. We argue that the neglect of them both, as done by MEV, is quantitatively incorrect. Third, twist distortions, which play an important role in the initial response, play an increasing role as the pattern evolves at intermediate times to an array of twist walls which thin and slowly recombine. This evolution of twist structure is entirely absent from MEV's model. Fourth, we experimentally verified in the same geometry and on a similar system that the response to the external field was far more complex than assumed by MEV. We see this in detail below.

The initial response for systems driven far from equilibrium is dominated by the fastest-growing distortion mode.[2] The mode selected is determined by material parameters and sample geometry. For a complex system with unknown material parameters, in the absence of a general theory, the only reliable way to determine the geometry of the selected mode is by direct observation. This was not done by MEV. Instead, they assumed a simple geometry involving pure splay-bend distortion and a one-dimensional flow field. Our experience with polymer nematics is that at high driving fields the mode-selection process is dominated by elongational flow avoidance and splay avoidance, which dictate a twist-bend oblique stripe pattern, involving a three-dimensional flow field, and quite different combinations of material parameters than those dictated by MEV's oversimplified model.

Second, wavelength selection for the fastest mode is sensitive to boundary conditions, especially for velocities which must go to zero at solid surfaces. Ignoring boundary conditions, as done by MEV, leads to large quantitative errors. Their model actually has no consistent mechanism for the selection of wavelength, but leaves it as a fitting parameter. With MEV's model, the fitted wavelength will always be shorter than the correct one.

Third, the intermediate-time response that we observe in similar systems involves conversion of undulations to almost pure twist walls which thin to a steady-state thickness. Structures evolve towards pure twist because of its very low energy. The walls then slowly recombine over a much larger time scale. This is entirely different from MEV's splay-dominated picture.

Our interest in the subject led us to try some experiments on a similar system, a tobacco mosaic virus colloidal nematic in a 5-mm-diam cylindrical tube. When an initially well aligned sample was rotated 90°, as in MEV, oblique undulating stripes appeared, which would quickly break up into closed, football-shaped domains, randomly distributed throughout the whole sample. We could not detect any semblance of parallel stripes.

We agree that NMR is potentially an important tool for the measurement of viscoelastic properties of polymer liquid crystals, but only if it is combined with the correct analysis. The theoretical model of MEV contains enough of the right kind of features, and enough parameters to give a good fit. However, this does not mean it is a unique analysis or the correct one. The observed pattern of a fast initial response followed by a longer-term slow response (and a final extremely slow decay) is generally seen in many situations, and is not sufficient to justify a particular geometric model. Therefore, the quantitative conclusions reached by MEV must be doubted.

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George Srajer, Seth Fraden, and Robert B. Meyer
The Martin Fisher School of Physics
Brandeis University
Waltham, Massachusetts 02254

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[1] A. F. Martins, P. Esnault, and F. Volino, Phys. Rev. Lett. **57**, 1745 (1986).

[2] A. J. Hurd, S. Fraden, F. Lonberg, and R. B. Meyer, J. Phys. (Paris) **46**, 905 (1985), and Refs. 1, 2, and 5 therein.