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Pretransitional Phenomena in the Viscoelastic Parameters of Micellar Lyotropic Nematic Liquid Crystals

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Although thermotropic and lyotropic liquid crystals (LCs) share a common state of matter, their macroscopic behavior can differ significantly. One important distinction concerns their bulk elastic response to external perturbations, which is characterized by three elastic constants associated with splay (K_{11}), twist (K_{22}) and bend (K_{33}) director deformations. Since the elastic moduli are material parameters, their values strongly depend on thermodynamic variables of the state, such as temperature and concentration [1].

For low molar mass thermotropic nematic LCs, the temperature dependence of the elastic coefficients has been studied extensively over many decades, and the three constants are typically found to be in the same range, monotonically decreasing with increasing temperature [2]. In contrast, the elasticity of lyotropic nematic LCs is far less understood, and various studies [3] have revealed exceptions from the well-known one-constant approximation ($K_{11} \approx K_{22} \approx K_{33}$) [1], with K_{22} being at least an order of magnitude smaller than K_{11} and K_{33}.

Searching the literature, we recognize that very little is known about the elastic constants and their related viscosities for nematics composed of micellar aggregates. Although these systems represent by far the most ubiquitous class of lyotropic LCs, comprehensive measurements of their viscoelastic parameters, in which temperature and/or concentration are varied systematically, are extremely rare and provide information only on the splay and bend elastic constants or only ratios thereof [4].

By means of light scattering we have recently reported the first systematic measurements of director fluctuations in a lyotropic nematic LC, formed by disk-shaped micelles (N_D phase) [5]. Interestingly, our results highlight not only differences, but also some notable similarities in the viscoelasticity between lyotropic and thermotropic systems. In particular, we find that in the vicinity of the nematic-lamellar phase transition, the twist and bend viscoelastic coefficients diverge critically, as twist and bend deformations become energetically unfavorable for a layered structure. This pretransitional behavior in the micellar N_D phase resembles that theoretically predicted and experimentally observed in thermotropic nematic LCs as a function of temperature [2], but in this case concentration acts as the main thermodynamic control variable. In direct analogy to smectic cybotactic clusters in thermotropic nematics, the pretransitional fluctuation phenomena observed in the lyotropic N_D phase can be attributed to the presence of short-range pseudo-lamellar order of the micelles, which we were able to confirm via X-ray diffraction. In this contribution, these new findings on the viscoelasticity of micellar LCs, are compared with experimental results on both thermotropic and other classes of lyotropic LCs and will be discussed in light of existing theoretical concepts.

References

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