Molecular Origins of Higher Harmonics in Large-Amplitude Oscillatory Shear Flow: Shear Stress Response

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Recent work has focused on understanding the molecular origins of higher harmonics that arise in the shear stress response of polymeric liquids in large-amplitude oscillatory shear flow. These higher harmonics have been explained using only the orientation distribution of a dilute suspension of rigid dumbbells in a Newtonian fluid, which neglects molecular interactions and is the simplest relevant molecular model of polymer viscoelasticity [R.B. Bird et al., *J Chem Phys*, 140, 074904 (2014)]. We explore these molecular interactions by examining the Curtiss-Bird model, a kinetic molecular theory that accounts for restricted polymer motions arising when chains are concentrated [Fan and Bird, *JNNFM*, 15, 341 (1984)]. For concentrated systems, the chain motion transverse to the chain axis is more restricted than along the axis. This anisotropy is described by the link tension coefficient, $\epsilon$, for which several special cases arise: $\epsilon = 0$ corresponds to reptation, $\epsilon > 1/8$ to rod-climbing, $1/2 \geq \epsilon \geq 3/4$ to reasonable shear-thinning predictions in steady simple shear flow, and $\epsilon = 1$ to a dilute solution of chains. We examine the shapes of the shear stress versus shear rate loops for the special cases, $\epsilon = (0, 1/8, 3/8, 1)$, of the Curtiss-Bird model, and we compare these with those of rigid dumbbell and reptation model predictions.