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**Molecular Origins of Higher Harmonics in Large-Amplitude Oscillatory Shear Flow: Shear Stress Response** PETER GILBERT, A. JEFFREY GIACOMIN, Chemical Engineering Department, Queen's University, ANDREW SCHMALZER, Chemical Diagnostics and Engineering, Los Alamos National Laboratory, R. B. BIRD, Chemical Engineering Department, University of Wisconsin - Madison — 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.

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