Unraveling Dynamics of Entangled Polymers in Strong Extensional Flows

Soroush Moghadam¹, Indranil Saha Dalal², Ronald G. Larson³

¹Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI.
²Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India.
³Department of Chemical Engineering and Mechanical Engineering, University of Michigan, Ann Arbor, MI.

Supporting Information

Chain conformation and stress evolution: kink dynamics vs. affine motion

The difference between the evolution of the end-to-end distance \( R_{EE} \) and stress \( \sigma_{xx} \) under three different conditions (1. Affine kink motion; 2. Unentangled kinks; and 3. EKD with \( \rho_{EK}^0 = 0.8 \)) for three different chain lengths \((L = 25, 50, 100)\) were shown in Figure 6 of the main text. To study how initial entanglement density affects the evolution of stress and configuration, we add the results for three other initial entanglement densities, \( \rho_{EK}^0 = 0.5, 0.25, 0.05 \), to that of Figure 6. As explained in the main text, the end-to-end distance in multiple chain entangled systems evolves almost identically to that of the dilute unentangled solution. The stress follows the same trend except for the starting stress which depends on initial entanglement fraction. The higher \( \rho_{EK}^0 \) is, the higher the value of \( \sigma_{xx} (\epsilon = \epsilon_t) \) will be. For all cases, \( \zeta' = \dot{\epsilon} = \nu = 1 \) and periodic boundary conditions have been applied for multiple chain systems. Results are obtained by taking an ensemble average over stress and end-to-end distance of 400 chains. Note that for either affine kink motion or for unentangled (i.e., dilute) chains, the dynamics of each chain is uncoupled from that of the other chains, and one can solve the equation of motion for a single chain without pairwise interactions with other chains. Hence, in each of these two limits, the results presented here were obtained from single-chain simulations.
Figure S1. Evolution of stress (main figure) and end-to-end distance (inset) for chains with contour length $L = 25$ under different conditions: affine kink motion (black dotted line), free or unentangled kinks (green dashed line) and entangled kinks (solid lines) with $\rho_{\text{EK}}^0 = 0.8$ (purple), $\rho_{\text{EK}}^0 = 0.5$ (yellow), $\rho_{\text{EK}}^0 = 0.25$ (orange), and $\rho_{\text{EK}}^0 = 0.05$ (blue).

Figure S2. The same as Fig. S1, except for $L = 50$. 

S2
Figure S3. The same as Fig. S1, except for $L = 100$. 