129a Ergodicity-Breaking and Conformational Hysteresis in Polymer Dynamics near a Surface Stagnation Point

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We study the dynamics of long chain polymeric molecules tethered to a plane wall and subjected to a stagnation point flow. Using a combination of theory and numerical techniques, including Brownian dynamics (BD), we demonstrate that a chain configuration hysteresis exists even for freely draining (FD) chains. We also perform BD simulations including hydrodynamic interactions (HI) between the polymer and the wall. We find qualitative agreement between the FD and HI simulations, with both exhibiting simultaneous coiled and stretched states for a wide range of fixed flow strengths. The range of state coexistence is understood by considering an equivalent projected equilibrium problem of a two state reaction. Using this formalism, we construct a Kramer's rate theory for the hopping transition from coil-to-stretch and vice versa. The activation energy for this rate is found to scale proportionately with chain size, and in the thermodynamic limit of infinite chains the states are “frozen.” We present results that demonstrate this “ergodicity breaking” and generalize these results to other non-linear flows and driving forces. The consequences for polymer dynamics and solution rheology in microscale flows will also be discussed.