Collective effects on activated segmental relaxation in supercooled polymer melts

STEPHEN MIRIGIAN, KENNETH SCHWEIZER, University of Illinois at Urbana-Champaign — We extend the polymer nonlinear Langevin equation (NLE) theory of activated segmental dynamics in supercooled polymer melts in two new directions. First, a well-defined mapping from real monomers to a freely-jointed chain is formulated that retains information about chain stiffness, monomer volume, and the amplitude of thermal density fluctuations. Second, collective effects beyond the local cage scale are included based on an elastic solid-state perspective in the “shoving model” spirit which accounts for longer range contributions to the activation barrier. In contrast to previous phenomenological treatments of this model, we formulate an explicit microscopic picture of the hopping event, and derive, not assume, that the collective barrier is directly related to the elastic shear modulus. Local hopping is thus renormalized by collective motions of the surroundings that are required to physically accommodate it. Using the PRISM theory of structure, and known compressibility and chain statistics information, quantitative applications of the new theory to predict the temperature and chain length dependence of the alpha time, shear modulus, and fragility are carried out for a range of real polymer liquids and compared to experiment.