Slow dynamics and the glass transition in anisotropic polymer liquids

Folusho Oyerokun, Kenneth Schweizer, University of Illinois, Urbana-Champaign — A microscopic theory has been developed at the coarse-grained segment level for the onset or crossover temperature ($T_c$) to highly activated dynamics in deeply supercooled anisotropic polymer liquids. A generalization of a simplified mode coupling theory is employed which utilizes structural and thermodynamic information from anisotropic PRISM theory. Conformational alignment or deformation modifies equilibrium properties thereby inducing anisotropic segmental dynamics. For liquid crystalline polymers a suppression of $T_c$ with increasing nematic or discotic orientational order is predicted. The underlying mechanism is reduction of the degree of coil interpenetration and intermolecular repulsive contacts due to chain alignment. For supported thin films on neutral substrates a significantly larger suppression of $T_c$ is found which emerges due to the presence of both segmental alignment and deformation. Reasonable agreement with experiment has been demonstrated. The theory can also be applied to brush-like systems and rubber networks where chain deformation results in more intermolecular contacts, an enhanced bulk modulus and an elevation of $T_c$. Extension to treat directionally-dependent collective barrier formation and hopping is also possible.

Folusho Oyerokun
University of Illinois

Date submitted: 23 Nov 2004

Electronic form version 1.4