Theory of Relaxation, Physical Aging and Nonlinear Mechanical Properties of Polymer Glasses KANG CHEN, KENNETH SCHWEIZER, University of Illinois at Urbana-Champaign — The theory of Saltzman and Schweizer for collective dynamic barriers, segmental relaxation and the kinetic glass transition of deeply supercooled polymer melts has been generalized to the nonequilibrium glass. The critical idea is that the structural component of density fluctuations become frozen below T_g, which results in a crossover of the thermal dependence of the relaxation time to an Arrenhius form. Physical aging is modeled based on a first order kinetic equation for the time evolution of the dimensionless amplitude of density fluctuations. On intermediate time scales after a quench, the relaxation time grows with aging time as a power law with a temperature dependent exponent. The theoretical approach has been generalized to treat the consequences of applied stress which modifies the confining nonequilibrium free energy and accelerates relaxation. A constitutive equation has been developed and applied to compute stress-strain curves and yield points as a function of temperature and strain rate. The coupling of mechanical deformation and aging has also been studied to address the phenomenon of stress-induced "rejuvenation". It is possible to generalize the theory to treat the consequences of large amplitude chain deformation and strain hardening. Comparisons of the theoretical results with multiple experiments are encouraging.

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