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Glassy Dynamics and Pressure Effects in Polymer Melts ERICA J. SALTZMAN, Department of Polymer Science, University of Massachusetts at Amherst, KENNETH S. SCHWEIZER, Department of Materials Science, University of Illinois at Urbana-Champaign — A statistical mechanical theory of collective dynamic barriers, slow segmental relaxation and the glass transition in polymer melts has been developed by combining and extending methods of mode coupling, density functional and activated hopping transport theories. Previously, atmospheric pressure results were obtained for the crossover and glass transition temperatures, collective barrier and segmental relaxation time. A cooperativity parameter is introduced based on dynamic consequences of local chain stiffness, and its effects on dynamic fragility are discussed. The theory is extended to elevated pressures, which are found to broaden the deeply supercooled regime and reduce the dynamic fragility while retaining a universal Rossler-Sokolov scaling law for the temperature dependence of the alpha relaxation time. The ratio of the dynamic crossover temperature (ideal mode coupling critical temperature) and kinetic glass transition temperature plays an essential role in the dynamics at all pressures.

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