Mobility of Glass-Forming Liquids

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In glass-forming liquids, there is a dramatic decrease in mobility as the temperature is decreased toward the glass transition temperature, where the mobility decrease can exceed by ten or more orders-of-magnitude than would be expected from the Arrhenian response exhibited at temperatures well above T_g . Determination of the origin of the super-Arrhenian behavior of super-cooled liquids is perhaps the key challenge in developing a fundamental understanding of glass-forming materials. One model that has been proposed to describe this super-Arrhenian behavior is due to Adam and Gibbs (J. Chem. Phys., 1965), where the logarithm of the relaxation time is postulated to be proportional to $1/TS_c$ where S_c is the configurational entropy. Alternatively, in order to describe the nonlinear viscoelastic behavior of glassy polymers, constitutive models have been developed (Caruthers, et al., Polymer, 2004; Medvedev and Caruthers, J. Rheology, 2013) where the logarithm of the relaxation time is postulated to be proportional to $1/U_c$ where U_c is the configurational internal energy. In this talk, we will critically compare the ability of $1/TS_c$, $1/U_c$ and other configurational and excess thermodynamic quantities to quantitatively describe the mobility of small molecule and polymer equilibrium liquids above T_g as a function of temperature and pressure. In addition, molecular dynamics simulations of selected small molecule glass formers will be used to provide understanding of what molecular processes are captured by the excess thermodynamic properties.