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Theory of Spatially Heterogeneous Activated Relaxation, Vitrification and Elasticity in Confined Polymer and Molecular Liquids

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Building on the Elastically Collective Nonlinear Langevin Equation theory of structural relaxation in deeply supercooled bulk liquids, a force-level description is constructed of how confinement and interfaces in free standing thin films introduces spatial mobility and shear modulus gradients as a function of temperature, film thickness and location in the film. The key idea is that relaxation speeds up due to the reduction of both the local cage barrier near the surface due to loss of neighbors, and the dynamical softening and cutoff of the longer range collective elastic barrier near the vapor interface. Quantitative predictions under isothermal conditions are made for the apparent glass transition temperature as a function of film thickness, the emergence of a two-step decay and mobile layers in time domain measurements, film-averaged relaxation times, surface diffusivity, role of a nonzero liquid-vapor interfacial width, and the relationship between kinetic and pseudo-thermodynamic measurements. Dynamical behavior under non-isothermal conditions can be qualitatively different. For example, mobile layers near the vapor surface can coexist with strongly vitrified regions in the film interior, resulting in a glassy shear modulus that increases as the film thins (despite a Tg reduction) and possible large implications for chain scale viscoelasticity. Extension of the theoretical approach to the droplet geometry and systems confined by condensed phase boundaries (liquids, solids) of variable mechanical stiffness has been achieved, and initial results will be presented. The new approach can also address activated glassy dynamics in quenched porous media, polymer nanocomposites and phase-separated polymer blends.