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Effects of Substrate Interaction on Slow Dynamics and Vitrification in Confined Thin Films STEPHEN MIRIGIAN, KENNETH SCHWEIZER, University of Illinois at Urbana-Champaign — The nanoscopic confinement of a glass-forming liquid can have major effects on its slow dynamics which depend on the nature of the confining surface in a nonuniversal manner. We generalize our force-level theory for free-standing films [1] to incorporate the effects of solid surfaces in supported and capped films. A solid surface is treated as locally modifying the liquid density as a consequence of packing-induced layering and/or physical adsorption. For films supported on a neutral surface where the former densification mechanism is dominant, the theory predicts that the physical behavior is akin to a free-standing film but with one interface behaving in a nearly unperturbed bulk manner, in agreement with experiment. With increasing interfacial attraction, the relaxation near the solid surface slows down dramatically and a very large local mobility gradient emerges. The competition between the dynamical effects of the adsorbed layer and the mobile layer near the vapor interface results in a rich behavior of an apparent vitrification temperature. Representative calculations of the full spatial gradient of the relaxation time as a function of temperature, film thickness, and interfacial densification will be presented.

[1] J.Chem.Phys.-Comm., 141, 161103 (2014).

Stephen Mirigian University of Illinois at Urbana-Champaign

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