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Slow Relaxation, Vitrification, and Mobility Gradients in Free Standing Thin Films KENNETH SCHWEIZER, STEPHEN MIRIGIAN, University of Illinois at Urbana-Champaign — Glass forming molecular and polymeric liquids confined by free surfaces experience major changes of their slow dynamics beginning at relatively large film thickness. We have constructed a predictive, quantitative, force-level theory of relaxation in free-standing films that addresses the nature of the spatial mobility gradient [1]. The theory predicts a generic speed up of relaxation near a free surface due to two coupled effects: a local, direct surface reduction of caging forces near the vapor interface, and a weakening of the spatially long ranged component of the activation barrier associated with collective elasticity. Effective vitrification temperatures, dynamic length scales and mobile layer thicknesses naturally follow. At low temperatures in the vicinity of the thickness-dependent Tg, highly mobile and immobile regions are predicted to coexist near the surface and in the film interior, respectively. The latter can result in mechanical stiffening which can commence at a large film thickness. Our results provide a theoretical basis for reconciling a variety of experimental results (e.g., probe mobility, dielectric relaxation, particle embedding, ellipsometry, creep) within a single framework.

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

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