Effect of density and structure on dynamics within self-assembled monolayers

DERRICK STEVENS, MARY SCOTT, JASON BOCHINSKI, LAURA CLARKE, NC State University Dept. of Physics — Previously, we have observed interacting dynamics within self-assembled alkylsiloxane monolayers, and characterized this motion via sensitive dielectric spectroscopy (along with more traditional techniques such as ellipsometry, contact angle, and force microscopy). In these monolayers, molecules are covalently bound to the surface and thus cannot spontaneously change density, as in an adsorbate system. We identified this relaxation as akin to the polyethylene-like glass transition observed in polymers with phase-segregated alkyl side chains [1]. As a next step, we deliberately manipulated the physical structure of the monolayers (via different film growth procedures and/or post-deposition heat treating) and the monolayer density (from ~10% to full coverage), and observed the resultant changes in dynamics. This experimental system may prove a useful model for more complex materials, such as glassy polymers or traditional molecular glasses, where density cannot be explicitly tuned. As density increases, the steepness index increases, indicating a more complex or fragile relaxation. At low densities, the motion has an almost-Arrhenius dependence on temperature. [1] M.C. Scott, D.R. Stevens, J.R. Bochinski, L.I. Clarke, ACS Nano. DOI: 10.1021/nn800543j.