Correlation between the interfacial bond orientational order and the shift in $T_g$ upon confinement

SIMONE NAPOLITANO, Université Libre de Bruxelles — The two-order-parameter (TOP) model rationalizes the interfacial slower dynamics in terms of enrichment in bond orientational order (BOO), near the wall [1]. Recently, we verified that the dielectric strength, $\Delta \epsilon$, is a robust parameter for measuring the BOO, as $\Delta \epsilon = g <\mu^2>/k_B T$, where $\mu$ is the dipole moment, and $g$ accounts for the correlation among neighbor dipole moments. We obtained interfacial values of the dielectric strength, $\Delta \epsilon_{int}$, analyzing the thickness dependence of all the polymers for which $\Delta \epsilon$ was measured upon confinement in ultrathin films. Although for all the investigated systems $\Delta \epsilon$ decreases in proximity of a solid interface due to the reduction in $<\mu^2>$ upon adsorption [3], we identified a striking correlation between $\Delta \epsilon_{int}$ and the shift in $T_g$ upon confinement. Increases in $T_g$ were univocally correlated to nonzero positive values of $\Delta \epsilon_{int}$, implying a larger BOO near the wall, in line with the predictions of the TOP model. [1] Watanabe, Kawasaki, Tanaka, Nature Materials 2011, 10, 512 [2] Capponi, Napolitano, Wuebbenhorst, Nature Comm. 2012, accepted [3] Napolitano, Wuebbenhorst, Nature Comm. 2011, 2, 260