Nanoscale Confinement in Single-Layer and Multilayer Supported Polymer Films: Effects on Glass Transition Temperature and Surface Capillary Wave Dynamics near the Glass Transition
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A number of studies have reported major differences in the effects of confinement on the glass transition temperature, $T_g$, of polymers as determined by (pseudo-)thermodynamic methods and on cooperative segmental dynamics as probed by techniques such as dielectric spectroscopy. While substantial $T_g$-confinement effects are often observed, the effects on cooperative mobility are often muted or absent. Here, we describe studies employing single-layer films and multilayer films of immiscible polymers in which both $T_g$ and dynamics, related to surface capillary wave relaxation characterized by x-ray photon correlation spectroscopy, are strongly affected by confinement and neighboring polymer layer species. Regarding $T_g$, we show that a key parameter governing the effect of confinement is polymer fragility – that of the polymer being characterized for $T_g$ in single-layer films and that of the neighboring layer for multilayer films. Similarly, at temperature near $T_g$, surface capillary wave dynamics of a top layer of a bilayer film can be strongly affected by the neighboring underlayer, with underlayer modulus and confinement itself being important factors governing the dynamics. Both factors are negligible at $T_g + 40$ K in the case of polystyrene top layers, demonstrating the importance of temperature in tuning the effects of confinement and substrates on dynamics.