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Cloaking the Effects of Strongly Interacting Substrates in Thin Polymer Films[1] WENGANG ZHANG, Wesleyan University, JACK DOUGLAS, National Institute of Standards and Technology, FRANCIS STARR, Wesleyan University — It is widely appreciated that the glass transition of thin polymer films can be strongly altered compared to bulk polymers. Furthermore, it is generally agreed that attractive substrate interactions slow relaxation and increase the glass-transition temperature T_g. However, there is evidence that the magnitude of T_g changes for strong substrate interactions are much smaller are expected, a phenomenon that also occurs in polymer-nanoparticle composites. Here, we use molecular simulations to reproduce this effect in supported polymer thin films; we explain the lack of sensitivity of T_g to strong substrate interactions as a result of the emergence of a layer of "bound" polymer at the substrate. This bound polymer effectively cloaks the remainder of the film from the strong interfacial interactions. This bound layer manifests itself by an additional relaxation process in self-intermediate scattering function. We further characterize the temperature and substrate interaction strength dependence of the bound layer relaxation time from the overall relaxation, as well as the relaxation from polymer chains near the film center.

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