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Molecular simulation of the dynamics in thin polymer films

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After more than 15 years of study since the original article by Keddie et al. demonstrating the effects of confinement on the glass transition temperature (Tg) in nanoscopic polymer films supported on a silicon substrate, there is not yet a consensus on the origins of the Tg shift. Understanding and controlling the effects of confinement on glass-forming polymers is essential to further development of photolithography and semiconductor manufacturing, as well as several emerging technologies that will depend on the properties of confined glasses, such as stable glasses, flexible displays, and responsive materials. A growing body of experimental literature exists that suggests that the dynamics near a free surface are not only enhanced but are fundamentally different in their nature compared to a bulk glass-forming material. However, despite the fact that the experimentally-relevant length scales can be easily captured by molecular simulation, there are comparatively few simulation studies examining the dynamics of glass-forming polymers in confined geometries relative to the extensive experimental work. In this talk, I will describe some of our recent efforts to understand how the dynamics of glass-forming polymers change under nanoscale confinement. First, I will describe our results on the changes in the entanglement network of an entangled polymer under both planar and cylindrical confinement, where we find that the density of entanglements is strongly decreased. Second, I will describe our work examining the nature of the dynamics near the free surface at temperatures close to the simulated glass transition and below. Finally, I will describe some of our work trying to understand how the view of confinement effects found in model systems studied with molecular dynamics compares with recent experiments.