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Confinement and Interfacial Effects on the Dynamics of Polymer Nanocomposites and Ultra-Thin Films FRANCIS STARR, Wesleyan Univ

Changes in the dynamics of confined polymer materials relative to the bulk polymer involve a complex convolution of effects, including the form and scale of confinement, as well as the interfacial interaction strength and surface roughness, leading to a seemingly intractable degree of complexity in describing these changes. In this talk, we review the results of molecular dynamics simulations of confinement effects on polymer dynamics in both ultra-thin films and nanocomposites. We show that all observed changes to the polymer dynamics can be understood in a unified way. In particular, we quantitatively describe the change in dynamics based on how the collective motion is perturbed. These changes are ultimately parameterized in terms of the high-temperature activation free energy, leading to the almost paradoxical finding that changes in glass formation are controlled by the changes to activation barriers in the high temperature limit. We also consider the peculiar case of strongly interacting interfaces, where experiments often report small or no changes in the glass transition temperature, T_g . We find that when interfacial interactions exceed the polymer-polymer interactions, a distinct relaxation that is slower than the main α -relaxation emerges, arising from an adsorbed "bound" polymer layer near the interface. This bound layer "cloaks" the interfacial interactions, so that the dynamics of the matrix polymer is largely unaffected. Consequently, T_g defined from the temperature dependence of the routinely measured thermodynamics or the polymer matrix relaxation can nearly independent of interfacial interaction strength.