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Cooperative Motion as a Unifying Principle to Understand Confinement Effects on Glass Formation

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We examine how confinement scale and interfacial interactions affect polymer glass formation, studied via molecular dynamics simulations. We consider both thin supported polymer films and polymer-nanoparticle composites. By varying the film thickness, nanoparticle loading fraction, or polymer-interfacial interactions, we can significantly alter both T_g and the fragility of glass formation, leading to a seemingly intractable degree of complexity. However, we find that all our observations can be described in unified way by using the scale of collective motion as a measure of "cooperatively rearranging regions" in the Adam-Gibbs (AG) description of glass formation. For thin films, we show how the scale of cooperative motion relates to the scale of enhanced interfacial dynamics at the free surface, offering a promising route to experimentally determine the scale of cooperative motion. These string-like motions can further be described as a living polymerization. Combining polymerization theory with the AG approach, we theoretically predict the relaxation time at much lower T, which suggests a return to Arrhenius behavior that avoids a Kauzmann "entropy crisis." Finally, we consider the applications of these ideas to ultra-stable polymer films formed by vapor deposition.