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Molecular Dynamics Simulations of Glass-forming Polymer Films

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We employ molecular dynamics simulations to explore structure and dynamics of freely standing and supported polymer films as they are cooled toward the glass transition. Our simulations are concerned with the features of a coarse-grained bead-spring model in a temperature regime above the critical temperature T_c of mode-coupling theory. We find that the film dynamics is spatially heterogeneous. Monomers at the free surface relax much faster than they would in the bulk at the same temperature T. The fast relaxation of the surface layer continuously turns into bulk-like relaxation with increasing distance y from the surface. This crossover remains smooth for all T, but its range grows on cooling. We show that it is possible to associate a gradient in critical temperatures $T_\mathrm{c}(y)$ with the gradient in the relaxation dynamics. This finding is in qualitative agreement with experimental results on supported polystyrene (PS) films. Furthermore we show that the y-dependence of $T_\mathrm{c}(y)$ can be expressed in terms of the depression of $T_\mathrm{c}(h)$—the global T_c for a film of thickness h—if we assume that $T_\mathrm{c}(h)$ is the arithmetic mean of $T_\mathrm{c}(y)$ and parametrize the depression of $T_\mathrm{c}(h)$ by $T_\mathrm{c}(h) = T_\mathrm{c}/(1 + h_0/h)$, a formula suggested in the literature for the reduction of the glass transition temperature in supported PS films. We demonstrate the validity of this formula by comparing our simulation results to results from other simulations and experiments.