

PRF Grant Number: 57405

Grant Title: Influence of Strongly Attractive Polymer-Substrate Interactions on Polymer Conformations and Chain Dynamics under Rigid Confinement

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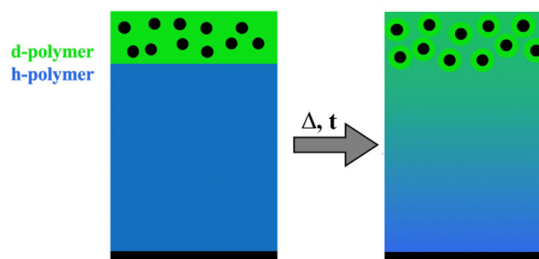
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Synopsis: Strongly attractive interactions between polymers and substrates are known to distort the polymer conformations that in turn alter the polymer dynamics. In the first year of this grant, we constructed two rigid confinement geometries: cylinders and thin films. The most interesting case has been cylindrical confinement wherein phase separation is observed for high molecular weight polymers in small pores. This phase separation has profound slowing on center-of-mass diffusion, as detailed below. Interestingly, there is little evidence of phase separation in thin film confinement and consequently the center-of-mass polymer diffusion increases monotonically with confinement. Also during the first year of the grant, the importance of strong interactions between polymers and nanoparticles became apparent, and we discovered we had a unique opportunity to study these systems. A stable nanoparticle dispersion within polymer nanocomposites often relies on strong adsorption of the polymer onto the nanoparticle surface. In a new direction of research, we are exploring the conformation and the multiscale dynamics of polymers strongly adsorbed to nanoparticles.

Polymer Conformation and Diffusion in Cylindrical Confinement: The behavior of polymer melts under cylindrical confinement was investigated using molecular dynamics simulations. A range of polymer chains, from unentangled to highly entangled, were confined in cylindrical pores with radii ranging from smaller to larger than the polymer size. These simulations were used to measure polymer chain conformation, entanglement density, and center-of-mass diffusion. The conformational anisotropy is well-described by a confined random walk model, although excluded volume effects cause slight differences in the radius of gyration. The number of entanglements per chain in confinement is accurately described using a simple volume fraction model consisting of a zero-entanglement region near the pore wall and a bulk-like entanglement region in the pore center. Finally, the diffusion along the pore axis exhibits non-monotonic behavior with the pore radius, **Figure 1** (next page). As the pore radius decreases, the diffusion coefficient, D , initially increases due to increasing chain disentanglement, though for small pores D eventually decreases as a result of confinement-induced chain segregation, **Figure 2** (next page).

Polymer Conformation and Diffusion in Symmetric Thin Film Confinement: An approach similar to that described above was applied to thin film confinement. This one-dimensional rigid confinement has a more subtle impact on the polymer conformations. Moreover, while there is some evidence of chain segregation, polymer diffusion increases monotonically with decreasing film thickness indicating that chain disentanglement is the primary influence.

Direct Separation and Quantification of Bound Polymer in Melt Polymer Nanocomposites: This new research direction involves silica nanoparticles and poly(2-vinyl pyridine), which are known to be attractive. We construct a bilayer sample with a polymer nanocomposite layer ($\sim 150\text{nm}$) composed of deuterated polymer (green) on top of a thick layer ($\sim 1\ \mu\text{m}$) of regular polymer (blue). The nanoparticle size and the polymer molecular weights are selected such that the unbound polymer diffuses into the polymer matrix two orders of magnitude faster than the nanoparticles. Upon annealing the nanoparticles and the bound polymer remain at the top of the sample, with the unbound deuterated polymer diffusing into the matrix, as determined by Rutherford backscattering and elastic recoil detection methods that measure the concentration depth profiles of silicon and deuterium, respectively. Our early results are quite promising and plans are underway



to measure the bound layer as a function of polymer molecular weight, annealing temperature, nanoparticle size, and the strength of the polymer-particle interactions.

Impact on my career and that of the students: The most important teaching moment of this first year was when we decided to redirect the project from strongly attractive substrates to strongly attractive nanoparticles. By developing a unique combination of experimental tools, we have quantified the amount of bound polymer and in future studies, we expect to be able to measure the lifetime of this bound layer.

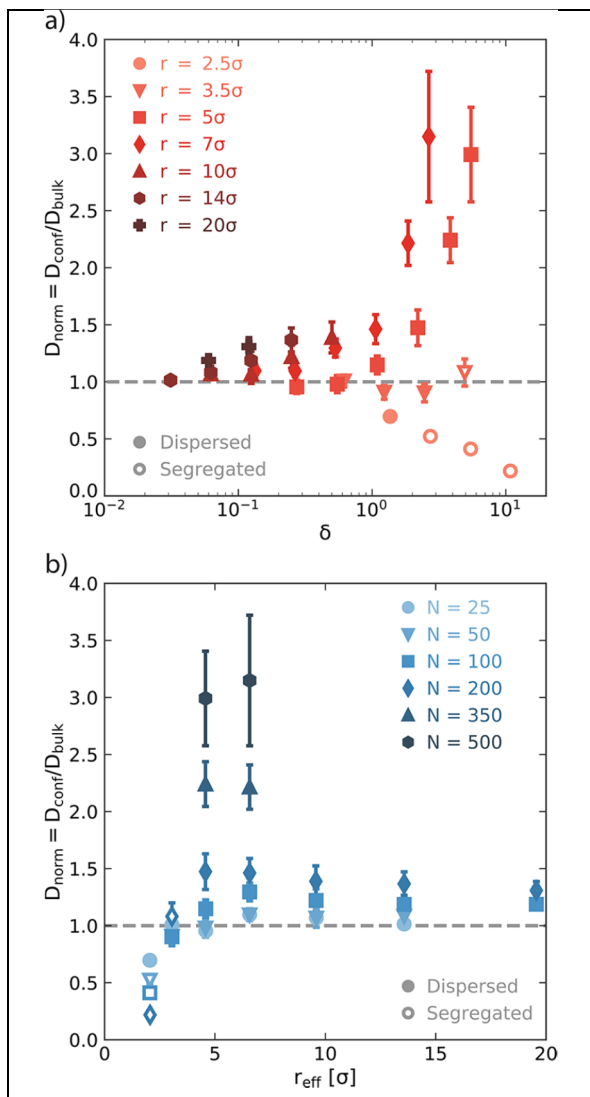


Figure 1. Normalized diffusion coefficients plotted (a) as a function of confinement, δ , and (b) as a function of effective pore size. Filled and open markers indicate dispersed and segregated systems, respectively. For $r_{\text{eff}} = 6.57$ and 9.59σ the data points for $N = 25$ and 50 overlap.

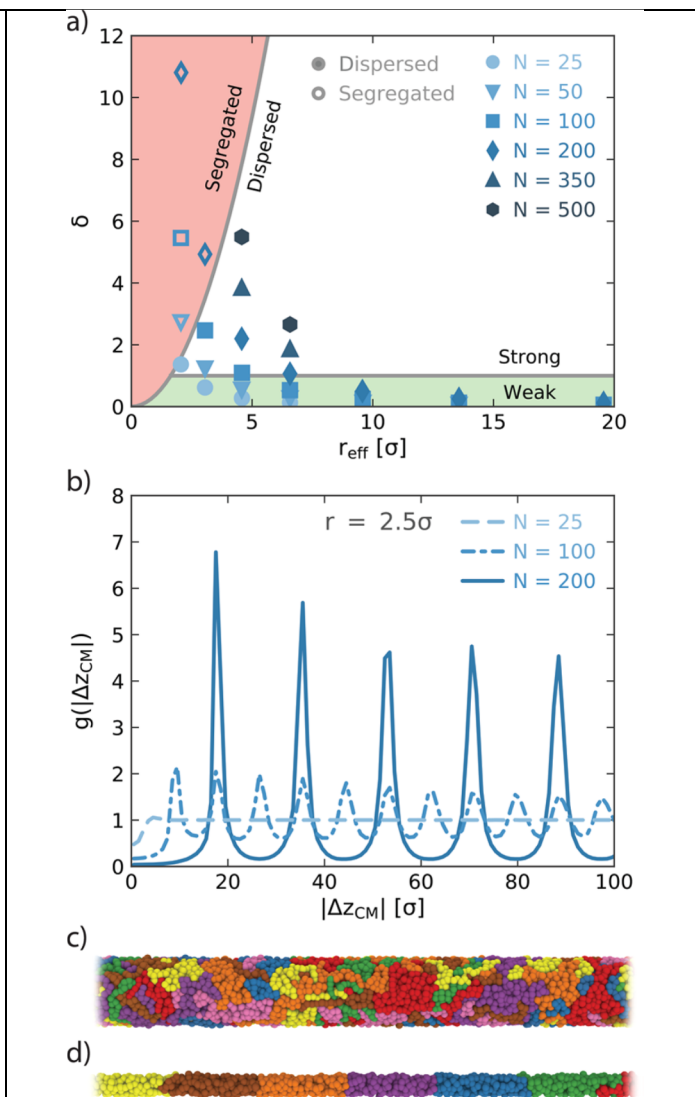


Figure 2. (a) Confinement parameter, δ , versus effective pore radius, r_{eff} . The colored domains indicate different confinement regimes. Simulations cover weak and strong confinement with dispersed chains (filled) and segregated chains (open). (b) Pair distribution functions between the polymer chain centers of mass along the z-axis distinguish dispersed and segregated chain distributions. Visualizations of confined polymers (c) dispersed: $N = 200$, $r = 7 \sigma$, $\delta = 1.06$, and (d) segregated: $N = 200$, $r = 2.5 \sigma$, $\delta = 10.81$.