

Chain Size Effects on Surface Depletion Layer Formation in a Dilute Polymer Solution

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Introduction

There has been an increase in interest over the last few years in ultra-thin polymer films for use as coatings or functional membranes, whose typical thicknesses range from 50nm up to 100 microns. At these dimensions, surface contributions to the free energy become important, so it is of practical interest to understand how polymer chains behave near hard surfaces. The primary tool for studying equilibrium properties in polymer materials is referred to as Polymer Self-Consistent Field Theory (SCFT), which exploits the fact that chains occupy large coarse-grained volumes while sampling conformations to access mesoscopic length scales. One subtle feature of the theory is that the Fokker-Planck equation describing how the distribution of polymer segments in space changes as you move along the contour, is derived by assuming an infinite volume from the perspective of each segment - an assumption which is violated in close proximity to hard walls. This is typically treated in the field theory by imposing an absorbing boundary condition at the hard wall surface, so that any transition that “sees” the wall is not counted when propagating the segment distribution.

Given these assumptions, SCFT predicts the development of a depletion layer near the wall where the segment density transitions from the bulk value to zero continuously. This behavior has interesting implications for copolymer ordering near walls, as it implies an entropic repulsion that grows with chain length. If we consider an asymmetric copolymer as a short and long chain bound together, we might expect a net entropic affinity of the short block for the hard wall. It is difficult to determine the effect that finite chain size and thermal fluctuations has on this phenomenon in the field theory language since it is valid in the infinite chain-length limit and it is difficult to properly sample fluctuations. In this study, the effect that chain length has on the form of the depletion layer near a hard wall is investigated using Molecular Dynamics simulations of a Lennard-Jones chain in an explicit solvent.

1 Simulation Details

In order to maximize the information obtained from simulations, dilute solution conditions were chosen so that the slowing down of relaxation times due to entanglements was not a factor. The simulations included 300 total particles, M of which were bonded together in a linear chain with stiff harmonic potentials. Periodic boundary conditions were used in the x and y directions, while a truncated Lennard-Jones interaction was used to model hard walls at $z = \pm L$.

The purpose of the calculations is to determine the potential of mean force as a function of distance along the z-axis from the wall. From the ground-state approximation to the SCFT equations, we anticipate an exponential decay of density towards the wall with a characteristic length $\approx 1R_g$. In order to obtain good statistics in regions near the wall, Umbrella sampling was used to bias the center-of-mass position of the chain to sample regions around a given set of positions with a standard harmonic bias potential:

$$\eta(\mathbf{r}^M; z^{target}) = -\beta \frac{k^w}{2} \left(\frac{1}{M} \sum_i^M r_{i,z} - z^{target} \right)^2 \quad (1)$$

where $r_{i,z}$ is the z-component of the i th bead position along the chain. This results in a restoring force that acts on all beads in the chain equally to translate the center of mass towards the target value.

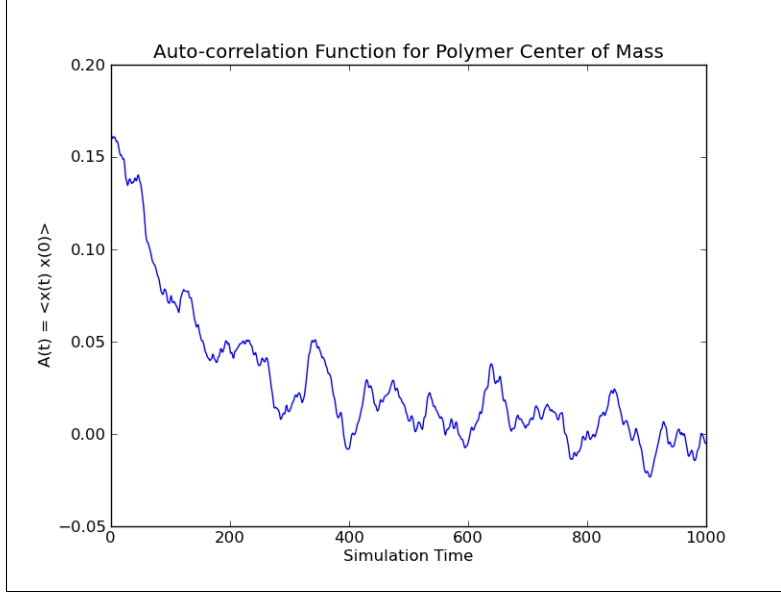


Figure 1: Autocorrelation function averaged over 4 independent runs from random initial conditions. Runs were equilibrated for 10000 MD steps before recording $x(t)$. The correlation time was estimated to be around 400 MD time units.

Velocity rescaling was used to equilibrate the set temperature for 5000 MD steps, followed by a final rescaling of the kinetic energies and subsequent equilibration run for 10000 MD steps. Finally, a production run was performed where the z-component of the polymer chain’s center of mass is recorded every 4000 MD steps. This sample frequency was chosen by calculating the autocorrelation function $\langle z(t)z(0) \rangle$ for the chain center of mass, averaged over 4 simulations (Figure 1). When multiple runs at multiple positions were performed, a histogram was computed using 20 bins spanning $z=-0.5$ to $z=4.0$. From this histogram, the underlying potential of mean force was computed by iteration (WHAM).

1.1 Interaction Potentials

Lennard-Jones interactions were used to model the beads representing solvent and comprising the polymer chain:

$$U_{LJ}(\mathbf{r}) = 4\epsilon \left(\left(\frac{\mathbf{r}}{\sigma} \right)^{-12} - \left(\frac{\mathbf{r}}{\sigma} \right)^{-6} \right) \quad (2)$$

The bonded interactions between polymer beads is described by a harmonic potential:

$$U_{bonded}(\mathbf{r}_{ij}) = \frac{k}{2} |\mathbf{r}_{ij}|^2 \quad (3)$$

The wall interactions were modelled as the repulsive part of the Lennard-Jones potential above:

$$U_{wall}(\mathbf{r}) = 4\epsilon \left(\frac{r_z}{\sigma} \right)^{-12} \quad (4)$$

where r_z is the z-component of the distance between the particle and the walls.

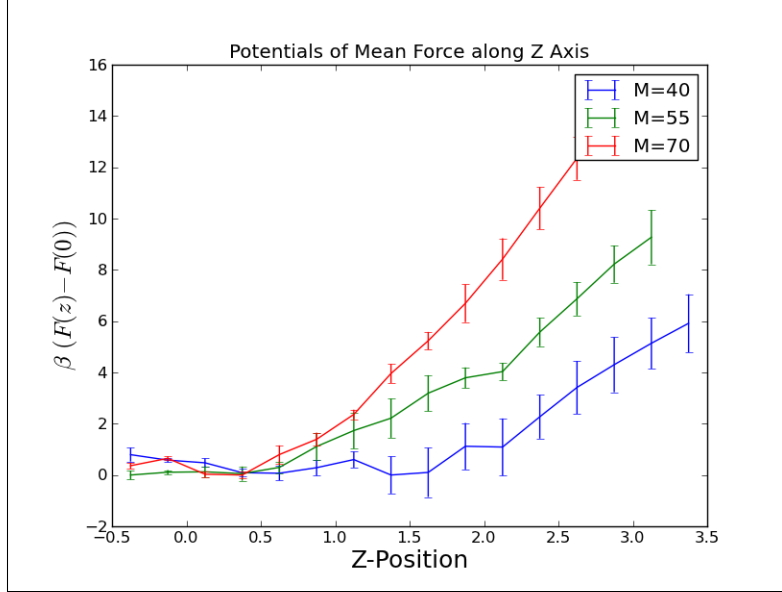


Figure 2: Potentials of mean force along a path perpendicular to the hard wall in the simulations. Various chain lengths were simulated at 4 distances: 0.0, 1.0, 2.0, and 3.0 (in reduced LJ units). Shown is the average of 5 simulations (with each minimum subtracted from the whole curve so that the difference from bulk behavior is plotted). Error bars indicate a standard deviation of the error in the calculated mean at each point.

2 Results

The results show a surprisingly weak cut-off dependence on chain length. While the basic structure of the curves is expected, that is an increase in the potential of mean force near the walls as a result of coil deformation, the curves seem to meet at approximately the same distance from the wall. This implies that the bulk-like, undisturbed behavior isn't solely determined by the chain being within a single hydrodynamic radius of the wall. Instead, there seems to be some effect either repelling shorter chains or attracting larger chains towards the wall in the vicinity of the cut-off distance. Potential of mean force curves are provided in Figure 2. Ideal chain statistics would anticipate a scaling of $\frac{1}{\sqrt{N}}$ in the effective coil radius and, therefore, depletion layer thickness. It is important to recognize, however, that this scaling is appropriate for $N \rightarrow \infty$. It is likely that these results are reflecting a finite chain length effect where ideal scaling is being approached as the chain lengths increase.

There was an additional feature that came up in the simulations which I was unable to reproduce, but was physically reasonable so I wanted to include it here. At higher fluid density, a local minimum in the free energy appeared around $z=2.0$, the result of what I imagine to be a depletion effect as solvent is pushed out of the wall region. Unfortunately, the simulations take longer for denser fluids and I was unable to find the parameters that led to the adsorption behavior again to perform a more comprehensive sweep.

3 Future Work

In many systems, there are some near-wall attractive forces that could easily be implemented by adding back in the attractive well to the Lennard-Jones potential. The effect of this attractive potential on the potential of mean force would be simply additive for simple polymers, but the non-local effects resulting from the bonded interactions in block copolymers should result in an interesting secondary effect. As the chains orient to favor one block resting near the preferential wall, a correlation in density would develop which the nearby chains would “see” and respond to (for sufficiently large interactions between the blocks). The frequency and amplitude of these density correlations as a function of block fraction and interaction strength would be very interesting to investigate. Since this effect is essentially a spinodal wave phenomenon as you approach the order-disorder temperature, fluctuations are important and can only be reliably applied in a particle-based simulation.