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Dynamic Properties of an Amorphous Polyethylene Nanofiber

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Introduction

The structures and properties of polymers at various surfaces and interfaces have been the subject of numerous recent studies due to the critical role interfaces play in many important applications of polymers.¹ The equilibrium and dynamic characteristics of the macromolecule in the vicinity of a free surface can depart significantly from those of the unconstrained bulk.² The local density, conformation, and mobility vary with distance from the free surface, on the length scale comparable to chain dimensions.

Mansfield and Theodorou reported the first look at the free surface of an amorphous polymer in atomistic detail using molecular dynamics, thus providing new quantitative information on the local structure and mobility in such a system.³ They showed that the local mobility on the nanosecond time scale was enhanced at the free surfaces of a glassy atactic polypropylene film. The length scale for this enhancement in mobility was larger than the radius of gyration of the polymer chains. Dynamic Monte Carlo studies of a confined, coarse-grained polymer melt,⁴ as well as a free-standing polymer thin film,⁵ showed the displacement of monomers and the center of mass increased in the parallel direction and decreased in the perpendicular direction, relative to the normal to the surface.

Most of the polymer systems in the previous simulation studies are flat, with no curvature at the surface. An interesting question is to ask how polymer molecules will behave when the surface geometry becomes strongly curved, as in a nanofiber with a cross-section only a few multiples of the root-mean-square radius of gyration, $\langle s^2 \rangle^{1/2}$, of the polymer molecules. Polymer nanofibers with such small dimensions can be prepared by an electrospinning method.⁶

A coarse-grained molecular model of an amorphous polyethylene nanofiber was recently formed on a high coordination lattice, and the static properties of the equilibrated fibers were determined.⁷

Major findings of this study were (i) fibers of different sizes, i.e., consisting of different numbers of parent chains, exhibit almost identical hyperbolic density profiles at the surfaces, (ii) the end beads are predominant and the middle beads are depleted at the free surfaces, (iii) there is anisotropy in the orientation of bonds and chains at the surface, and (iv) the center of mass distribution of the chains exhibits oscillatory behavior across the fibers. These static properties are qualitatively similar to the properties deduced from the simulation, by the same technique, of a free-standing thin film, where there is no curvature at the surface.⁸ In this paper we report the dynamics of the nanofiber using two local properties (acceptance rate and randomization of chord vectors) and two chain properties (diffusion of the center of mass and randomization of the end-to-end vector). The results are compared to the dynamics in the bulk and in thin films.

Model and Simulation Methodology

Generation, equilibration, and analysis of the static properties of the polyethylene nanofibers were reported recently.⁷ The simulation employs a bridging technique⁹ that allows interconversion between a fully atomistic representation of a structure in continuous space and a coarse-grained version of the same structure in the discrete space of a high coordination lattice.¹⁰ The coarse-grained representation retains every second carbon atom on a lattice with $10i^2 + 2$ sites in shell i .¹¹ Each chain of $C_{100}H_{202}$ is represented by 50 beads. The models contain either 36 (system f36) or 72 (system f72) independent parent chains.

The short-range intramolecular interactions are treated using the rotational isomeric state model,¹¹ and the intermolecular interactions are treated using a discretization of a Lennard-Jones potential energy function appropriate for the interaction of a pair of two-carbon fragments.¹² The dynamics is assessed by using single-bead moves, which have been described previously in detail.¹⁰ Each single-bead move corresponds to the displacement of two or three carbon atoms in the fully atomistic representation of the chain. A Monte Carlo step (MCS) is the length of simulation which would move a number of beads equal to the total in all of the independent parent chains, if every attempted move was accepted. The actual acceptance of a move is based on the Metropolis criteria, evaluated at 509 K. The same method was used recently for the study of the dynamics of free-standing thin films.^{5,13} The general method employed in the simulation has been reviewed.¹⁴ Additional details specific to the nanofiber can be found in a recent Ph.D. dissertation.¹⁵ The Supporting Information contains five relevant figures taken from this dissertation.

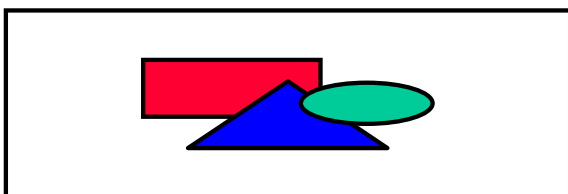
Results and Discussion

The periodic boundary conditions produce a fiber with infinite length and an internal density of 0.7 g/cm^3 at 509 K .⁷ The region of constant internal density has a diameter of about 2.5 nm (f36, which has 36 independent parent chains) or 4.0 nm (f72, which has 72 independent parent chains), followed by a hyperbolic decay of the density to zero over an additional 2.5 nm . The root-mean-square radius of gyration of the chains, $\langle s^2 \rangle^{1/2}$, is 1.3 nm . Therefore, the diameter of the fibers is a few multiples of $\langle s^2 \rangle^{1/2}$.

Since the dynamics of the nanofibers is similar to the dynamics of the planar free-standing thin films described earlier,⁵ we will not present the raw data for the nanofibers as figures (which would appear similar to the equivalent figures reported previously for the thin films), but will instead focus on the comparison with the dynamics in the bulk and in the thin films. The figures describing the raw data for the nanofibers are available in a recent Ph.D. dissertation.¹⁵

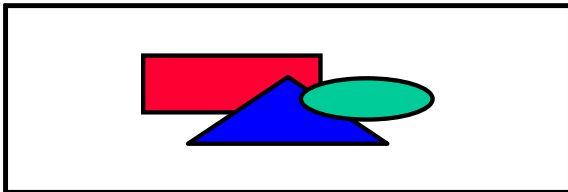
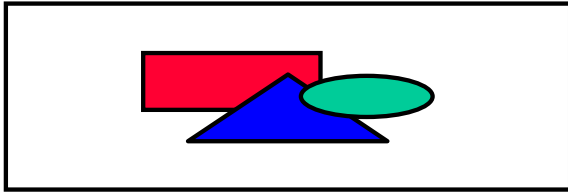
Movement of Single Beads. Acceptance rates at 509 K are about 17.5% in the internal region of the nanofibers, where the density reaches its plateau value of 0.7 g/cm^3 . This acceptance rate is very close to the one achieved in simulations of bulk melts (with no surfaces) at this density and temperature. The acceptance rates increase to values around 22% in the outer region of the nanofiber, where the density decreases from 0.7 g/cm^3 to zero over a distance of about 2.5 nm . This increase in acceptance rate in the low-density surface region was seen earlier in the simulation of free-standing thin films, where the surface has no curvature.^{5,13} The increased mobility in the surface region is also evident in the residence times for individual beads at a distance r from the axis of the nanofibers.

Reorientation of Chord Vectors. A vector connecting two beads in a coarse-grained chain corresponds to a chord vector between next-nearest-neighbor carbon atoms in the fully atomistic description of the chains. The reorientation of these chord vectors was measured with the



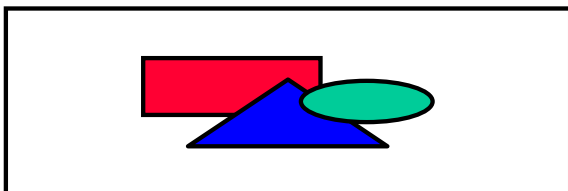
autocorrelation function, $P(t)$, defined using the unit vector along the chord at time t , $\mathbf{m}(t)$:

Angular brackets denote an average over all chains and time origins. The short-time portion of this autocorrelation function was fitted to the empirical Williams-Watts expression:

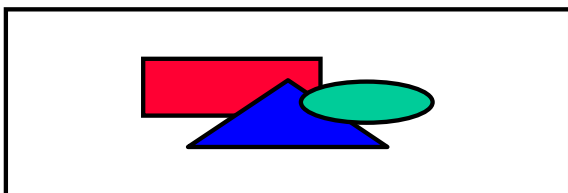


Here τ_1 is the relaxation time and β is a factor accounting for the deviation from Debye behavior. The values of τ_1 and β are summarized in Table 1 [1a991633yt00001a991633yt00001](#). The relaxation times for the chord vectors are shorter in the nanofibers than in the bulk, and they are somewhat shorter for the thinner nanofiber (f36) than for the thicker one (f72). The value of β is less sensitive than the value of τ_1 to the differences in these systems.

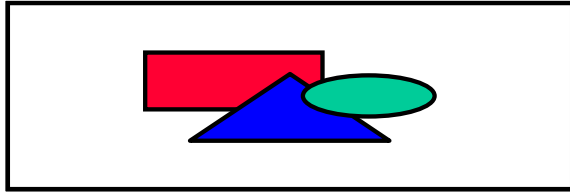
Rotational Diffusion of the Chains. Chain relaxation was monitored using the decay of the orientation of the end-to-end vector:



Here $\mathbf{r}(t)$ is the end-to-end vector of a chain at time t . The decay of $C(t)$ was fitted to the Rouse

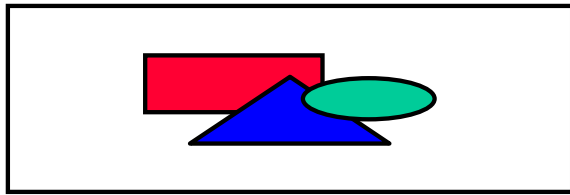


model using eq 4.

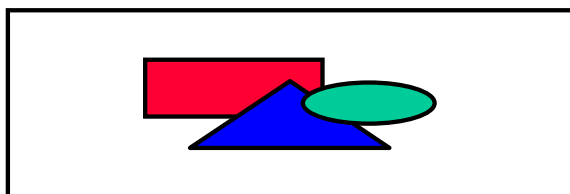


The longest relaxation time, or Rouse time, τ_r , is the only adjustable parameter. The sum in eq 4 extends over all odd values of the index p . In our analysis, the range was truncated at $p = 7$, which is reasonable, on the basis of previous work in the bulk with a similar simulation.¹⁶ The values of τ_r are given in Table 1. Randomization of the end-to-end vector is faster in the nanofibers than in the bulk, and it is slightly faster in the narrower nanofiber (f36) than in the thicker one (f72). A slightly greater effect of the surface on τ_r was seen in the simulations of the free-standing thin films.

Translational Diffusion of the Center-of-Mass of the Chains. The translational diffusion coefficient of the chains, D , is determined by the long-time limit of the mean-square displacement of the center of mass, using the vector to the center of mass of a chain at time t , $\mathbf{r}_{\text{com}}(t)$:



In the nanofibers, the long-time limit for this displacement is unbounded only in the direction parallel with the axis of the fiber. In the two directions perpendicular to the fiber axis, the magnitude of this displacement is limited by the diameter of the fiber. When expressed in a Cartesian coordinate system in which the z axis is parallel with the fiber axis, the z component of the diffusion coefficient,



D_z , is finite:

However, D_x and D_y are zero, when evaluated in the long-time limit. Focusing on D_z , the values for

the narrower (f36) and thicker (f72) nanofiber are $5.6 \cdot 10^{-6}$ and $4.4 \cdot 10^{-6} \text{ nm}^2/\text{MCS}$, respectively.

Diffusion of the chains along the fiber axis is faster in the narrower fiber.

Conclusion

The mobility of the chain in a nanofiber, defined at the level of individual beads, individual chords, or the entire chain, is greater than in the bulk, and the mobility increases as the diameter of the nanofiber decreases. These trends in the nanofiber, with its strongly curved surface, are similar to the results seen in simulations of free-standing thin films, where the surface is flat. The region of low density at the surface facilitates the increased mobility in the nanofibers and in the free-standing thin films.

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Supporting Information Available

Five figures (density profile, acceptance rates, orientation autocorrelation function for chord vectors, orientation autocorrelation function for the end-to-end vector, mean square displacement of the center of mass) from the Ph.D. Dissertation by V.V.-s.¹⁵ This material is available free of charge via the Internet at <http://pubs.acs.org>.

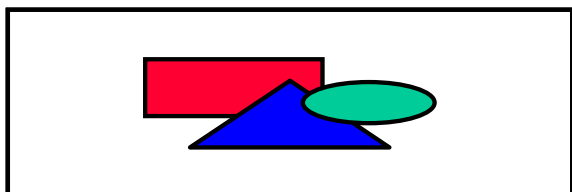
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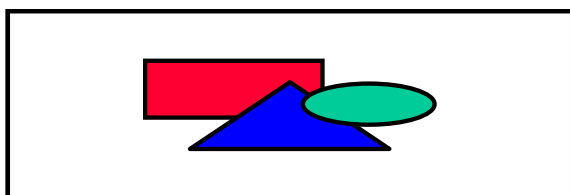
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the Orientation Autocorrelation Function for the Chord
for the End-to-End Vector to the Rouse Expression



system	τ_1 (10^3 MCS)		τ_r (10^5 MCS)
f36 nanofiber	3.17	0.280	1.63
f72 nanofiber	3.50	0.260	1.66
bulk	5.12	0.245	3.13