Effect of chain shape on the diffusion of star polymers in solution

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Polymer chains dissolved in a solvent take random conformations due to large internal degrees of freedom and are characterized by their average shape and size. The diffusive dynamics of such large macromolecules play an important role in many engineering applications[1]. The influence of the size of the chain on its diffusion is well known[2]. But the same is not the case for the chain shape. In the present work, we have used Molecular Dynamics simulation to investigate the influence of shape on center-of-mass diffusion of a polymer chain dissolved in a good solvent at infinite dilution [3]. The bead-spring model and Finitely Extensible Non-linear Elastic (FENE) potential are used to model the polymer chains. The solvent is modeled using Multi-particle Collision Dynamics (MPCD)[4]. We study star-shaped polymer chains of varying degrees of functionality (number of arms). Star-shaped chains with five different functionality (f) are selected. To eliminate the effect of size, their radius of gyration (R_g) is maintained constant, i.e., $R_g \sim 5\sigma_p$ (σ_p is the size of a monomer bead). Asphericity (b) and relative shape anisotropy (κ^2) are used to calibrate the shape of the chains [5]. From Figure 1(a), it is clear that star-shaped chains with higher functionality have less value of asphericity (normalized by R_g^2) and relative shape anisotropy. For the diffusion study, we calculate the center-of-mass mean square displacement of the chains and find the diffusion coefficient (D). From Figure 1(b), it is clear that, for star-shaped chains of the same R_g, the value of D decreases with an increase in functionality. Hence, the higher the values of asphericity and anisotropy of the star-shaped chains in a solvent, the faster it diffuses.

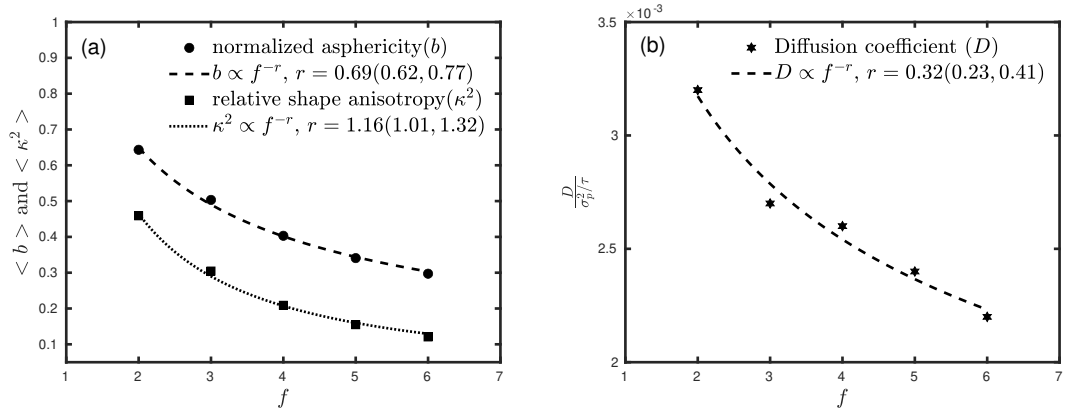

Figure 1: (a) Variation of normalized asphericity (b) and relative shape anisotropy (κ^2) with functionality (f) of star-shaped chains. The angle brackets ($< b >$ and $< \kappa^2 >$) represent time and ensemble average over five replicas for each system. (b) Variation of the center-of-mass diffusion coefficient (D) with functionality (f) of star-shaped chains. Here, σ_p is the size of a monomer bead, and τ is the Lennard-Jones unit of time. The values within the parentheses are the confidence intervals for the exponent (r) calculated from power law fits.

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