Solvent effects on the dynamics of polyelectrolyte chains near a charged wall: Molecular dynamics simulations with explicit solvent

GOVARDHAN REDDY, University of Wisconsin-Madison, RAKWOO CHANG, University of Utah, ARUN YETHIRAJ, University of Wisconsin-Madison — The effect of solvent quality on the behavior of salt-free dilute and semi-dilute polyelectrolyte chains near a charged wall is studied using molecular dynamics simulation. The polyions are modeled as a chain of charged spherical beads, counter ions to the polyion and the surface are charged spheres, and solvent molecules are uncharged spheres. The wall is atomically smooth with a uniform charge density. For dilute solutions, the chain radius of gyration decreases monotonically with decreasing solvent quality but shows a non-monotonic dependence on surface charge density. As the surface charge density is increased, the polyions orient in a direction parallel to the surface. The diffusion constant of the centre of mass and the characteristic rotational relaxation time of the polyions show explicit dependence on the solvent quality: The diffusion constant increases and the rotational relaxation time decreases as solvent quality is decreased. As the surface charge density is increased, the rotational correlation function does not decay in good solvents, contrary to what is seen in poor solvents. In semidilute solutions the thickness of the adsorbed layer increases as solvent quality is decreased suggesting that solvent effects play an important role in polyelectrolyte adsorption.

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