518e Monte Carlo Simulations and Self-Consistent Mean Field Theory of Polyelectrolyte Brushes

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In this study, we investigate the structure of polyelectrolyte brushes using two different approaches: Monte Carlo simulations and self-consistent mean-field theory. In particular, we investigate the effect of grafting density, surface charge density, distribution of charges on the polyelectrolytes, salt concentration, monomer-counterion charge ratio and polymer chain length on the distribution of the polyelectrolyte brushes, salt and counterions. Our model system consists of charged polymer chains end-tethered to a charged surface surrounded by a solvent containing both salt and counterions associated with the brush/surface. The polymer is modeled as a chain of N coarse-grained beads occupying consecutive sites on an underlying lattice having a coordination number of $z = 26$, where some of the beads may be charged. The dissociated salt ions and counterions, which are included explicitly in our approach, are also modeled in a coarse-grained way whereby each ion bead occupies a single lattice site. The solvent molecules are not included explicitly in our calculations. The polymer and free-ion beads interact with each other through Coulombic and excluded volume interactions. The two main advantages of our approach over previous approaches are that (a) the different configurations of the polymer are explicitly included into our calculations without resorting to any assumptions about the configuration of the polymer chains, and (b) the counterions are included explicitly, thus obviating the use of a Debye-Hückel type approximations. In our canonical Monte Carlo simulations, the polymer configurations are sampled using a Rosenbluth-biased chain regrowth procedure while the associated counterion and salt positions are sampled using a distance-biased displacement algorithm. For the self-consistent mean field calculations of polyelectrolyte brushes, we employ a novel computational scheme based on the Fang and Szleifer theory [1] for obtaining the self-consistent monomer and counterion density profiles, This scheme first involves enumerating all the possible single-chain polymer configurations and their associated Boltzmann weights according to the electrostatic energy associated with inserting a single polymer chain in a mean field of the polymer and counterions. The next step involves an iterative procedure for obtaining the monomer and counterion density profiles which self-consistently agree with the probability of occurrence of individual polymer and counterion configurations within the polyelectrolye brushes.

[1] F. Fang and I. Szleifer, J. Chem. Phys. 119, 1053 (2003).