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Electronic Supplementary Information

Hybrid particle-field molecular dynamics simulation for polyelectrolyte systems

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(a) The structure of electric double layers

To validate the method, the structure of electric double layers for a salt solution near a charged planar surface has been checked in particle-field (PF) simulations. And the results are compared with reference particle-particle (PP) simulations. The charged surface is constructed by a two-dimensional wall with a layer of fixed particles in hexagonal lattice at a density of 4.62/nm^2. Some of wall particles carry a positive charge. The salt solution consists of monovalent cations and anions, and neutral solvents, which are all modeled as a single particle. The system is electrically neutral and treated as a dielectric continuum. The short-range interactions between those particles are described by Lennard-Jones (LJ) potential $V_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ in PP simulation, which are characterized with ε = 1.0 kJ/mol, σ = 0.47 nm, and a cut-off radius of 1.4 nm. The box size is 14.0×13.9×14.0 nm^3. The bulk number density of the system is 7.55/nm^3. The symbols ε_r, d, z, $\rho(z)$, and ρ_0 denote, respectively, relative dielectric constant, surface charge number density, the distance from the wall center, ion concentration in normal direction of the wall, and average salt concentration.

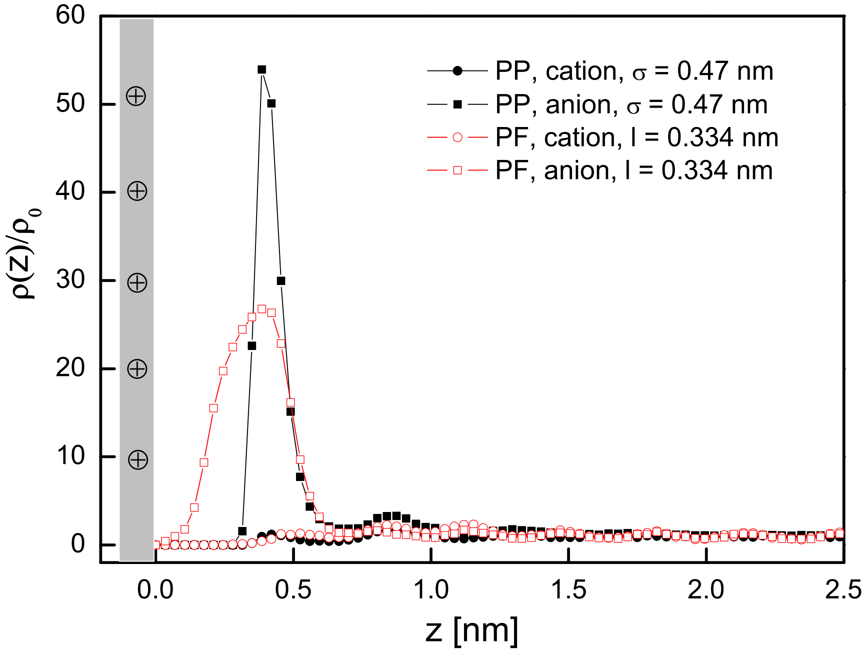

Figure S1: Ion density profiles at ε_r = 20.0, ρ_0 = 0.1 M, and d = 0.45/nm^2.

The structure of electric double layers is influenced by salt concentrations and surface charge densities, etc.[1] We analyzed the density profiles of ions in normal direction of charged wall at lower values of salt concentration and charge density. In both PF and PP simulations, electric double layers are formed, as shown in **Figure S1**. In the first layer, the surface charge comprises cations which are anchored into the wall. The second layer is composed of anions attracted by the surface charge via the Coulomb force, electrically screening the first layer. As shown in **Figure S1**, the density of anions monotonically decreases after the peak, which is in accordance with the theoretical prediction.[1] The density profiles of ions from PF simulations qualitatively agree with the ones from PP simulations. However, the data of PP simulations show a vacancy of anions near the cation layer, while the data of PF simulations do not. In PF framework, there are no strict volume exclusions, which can provide core repulsions to empty the anions in short distance ($< \sigma$) from the wall as PP model does. Thereby, the difference of results between PP and PF simulations can be ascribed to the "soft" nature of interactions in PF simulations.

(b) The phase behaviors of polyelectrolyte-surfactant complex

Electrostatic interactions play an important role in the phase behaviors of mixtures of polyelectrolyte and surfactant.[2] Dissipative particle dynamics (DPD) incorporating electrostatics has been employed to study these systems.[3,4] To conveniently compare with previous results obtained by DPD simulations, we employ DPD-type soft interaction in MD-SCF simulations in this study. Here, we use the DPD model of the polyelectrolyte-surfactant system and the corresponding parameters (including compressibility κ and Flory-Huggins χ-parameters) which have been introduced in Refs.[3,4] in our hybrid PF simulations directly.

For completeness, we describe the DPD model as follows. The system consists of a total number of $N = 10,125$ DPD particles. A single polyelectrolyte chain of 50 CG particles (P), 75 surfactant molecules each modeled by a head-tail dimer with a head CG particle (H) and a tail CG particle (C), and 9825 CG particles (W) of water are allocated in a cubic box of volume V* = 15

$\times$ 15 $\times$ 15. Each particle in the polyelectrolyte carries a charge of $e/2$ and each head particle of surfactant molecule carries a charge of $-e$. To preserve the charge neutrality of the system, 25 counterions for polyelectrolyte each with a charge of $-e$ and 75 counterions for surfactants each with a charge of e are added and they have the same χ-parameters of water. The pairwise Flory-Huggins parameters are χ_{PH} = χ_{WH} = 0, χ_{CP} = χ_{CH} = 6, χ_{PW} = 0.65, and χ_{CW} =18. The spring constant of the harmonic force between bonded particles is $K = 4.0$.

To illustrate the effect of electrostatic interactions intuitively, we construct an uncharged "polyelectrolyte" and surfactant system by removing the charges. The typical equilibrium conformations of the charged and uncharged systems are shown in **Figure S2**. In the case of the uncharged system, the polymer chain distributes near the micelle formed by surfactants, but there is no compact interaction between them. However, for the charged system, the polymer chain closely wraps around the micelle due to the electrostatic attractions between positive charges of the polymer and negative charges of the surfactants. The difference of structure of the charged and uncharged system can be quantitatively presented by comparing their radial distribution functions (RDF). In **Figure S3**, the RDF between the head particles of surfactants and polymer particles are shown. The RDF of *H*-*H* and *P*-*P* of the charged system are lower than those of the uncharged system, while the RDF of *P*-*H* of the charged system is higher than that of the uncharged system. This is clearly due to the repulsion between the particles with the same charge and the attraction between the particles with the opposite charges.

The formulation of the hybrid MD-SCF method employed here is based on the interactions of molecules with external density fields while DPD simulations involve the evaluation of forces between particle pairs. This implies that, although the equilibrium structures of polyelectrolyte-surfactant complex in PF and PP simulations are in good agreement, pair correlations between particles can be different. The initial regime with $r < 1$ nm, in which the correlation is dominated by particle-particle repulsion in the DPD simulations, has not been found in our PF simulations due to the continuous nature of mean field in PF method. However, the correlation function for the polyelectrolyte in the PF simulations gives similar slope to that in the DPD simulations. We

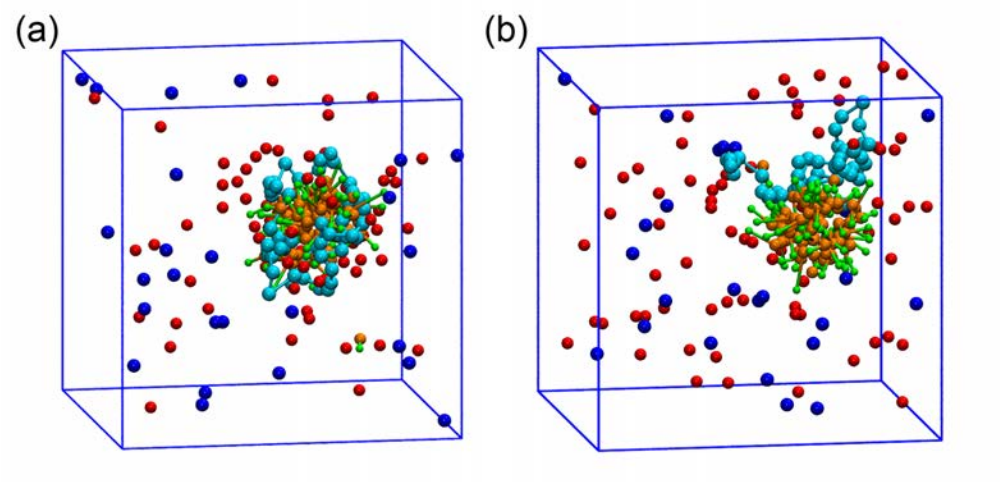

Figure S2: The snapshots of the charged (a) and uncharged (b) polyelectrolyte-surfactant system. The polyelectrolyte, head and tail of surfactants, polyelectrolyte counterions, and surfactant ions are shown in cyan, green, orange, blue, and red, respectively.

draw a line of slope -1.18, which was observed in DPD simulations, in **Figure S3** to guide eyes. As we can see, the slope of *P*-*P* RDF curve in the PF simulations is close to the line. A little difference from DPD simulations in which single micelle or two discrete micelles are wrapped by the polymer chain[3] is that the equilibrium structures are always a single, complete micelle wrapped by the polymer chain in our PF simulations. This little difference can be analyzed by the RDF of *H*-*H* which reflects the size of the micelle. The RDF of *H*-*H* in the PF simulations start with much higher value and decays faster for $r > 3$ nm than that in the DPD simulations, which reflects the more intact micelles formed in the PF simulations. Hence, the structural properties obtained in the PF simulations qualitatively agree with those in the DPD simulation and the small discrepancy can be understood by the different nature between PF interactions and PP interactions.

For this system, we measure the performances of DPD and PF simulations both running on a GTX 980 Ti. To be specific, the performances of DPD and PF are 408 and 2290 time steps per second, respectively. The DPD simulation uses the Ewald summation based on the Non-Uniform fast Fourier transform,[5] which is also implemented in GALAMOST. The number of grid points of electrostatic field in these two methods is identically $32 \times 32 \times 32$.

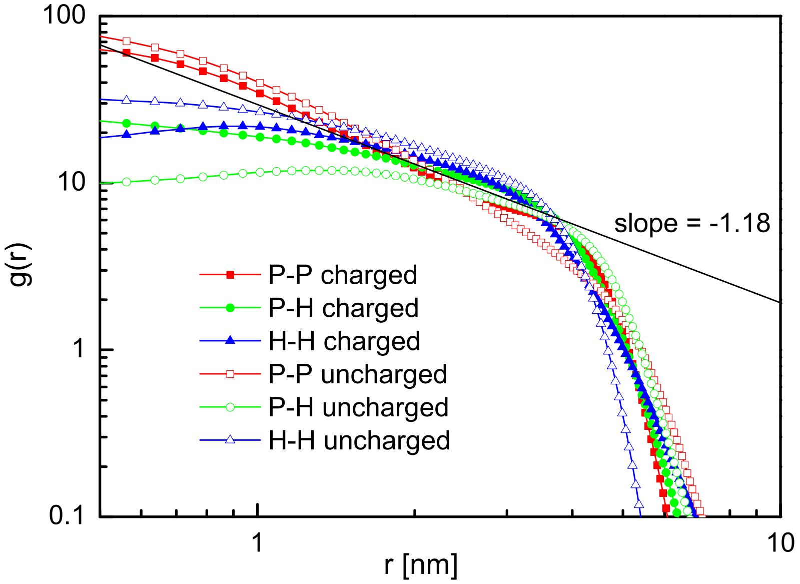

Figure S3: The radial distribution functions for polymer-polymer, polymer-head group, and head group-head group.

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