§20. Molecular Dynamics Simulation of Strongly Coulomb Coupled System: Effects of Salt and Polymer Ions on the Charge Inversion

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The charge inversion phenomenon takes place due to strong correlations of a macroion with small salt ions in solution, which has recently been studied for the physiochemical and bio-engineering systems [1]. Particularly interesting application is the possibility of facilitating the delivery of genes through negative cell walls.

By molecular dynamics simulation we have studied here the charge inversion of a rod macroion in the presence of polyelectrolyte counterions [2]. We take the system of one rod-shaped macroion, many counterions, coions and neutral particles to represent viscous solvent. In order to separate aggregated ions to the macroion from free counterions, we simulate electrophoresis of the macroion under an applied electric field as we did before [3].

When the macroion is rod-shaped and both counterions and coions are polyelectrolytes (charged polymers), charge inversion occurs if the line charge density of the counterions is larger than that of the coions. This is because the counterions must dominate the macroion aggregate for charge inversion to take place.

For the macroion whose surface charge density is equal to that of the DNA, the reversed mobility is realized either with adsorption of the multivalent counterion polyelectrolyte or the combination of electrostatics and other mechanisms including the short-range attraction potential or the mechanical twining of polyelectrolyte around the rod axis.

Figure 1 shows that the DNA, which is a rod-shaped charged polymer, can be charge inverted by the influence of polymer counterions where counterions are polymers of trivalent Z-ions (filled circles). However, the same macroion is not charge inverted if counterions are all isolated spheres (open circles). Massive condensation of counterion polyelectrolyte, which is a source of charge inversion, is clearly seen in Fig.2.

Fig.1 The electrical mobility of a rod-shaped macroion against the ionic strength (salt concentration) of polyelectrolyte counterions (filled circles). By contrast, charge inversion does not occur for isolated spherical counterions (open circles).

Fig.2 Charge inversion of DNA with (a) polyelectrolyte cations of trivalent ions, and (b) polyelectrolyte of monovalent ions. External electric field points horizontally rightward.


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