Molecular Dynamics Study of Charge Inversion of a Rod-Shaped Macroion by Polyelectrolyte Counterions

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Charge inversion is the phenomenon in which the net charge of macroions (large ions) reverses its sign due to adsorption of many counterion (and coions). It occurs under strong electrostatic correlations of the macroion with other small ions and salts in solution. The phenomenon was known for half a century and has recently been studied in the physiochemical and bio-engineering contexts [1-7]. Particularly, it can be a decisive means in modern gene therapy to facilitate the delivery of genes through predominantly negative cell walls [8,9]. In our previous studies of charge inversion [6,7], we adopted the static (immovable) and dynamic (moving) macroions in molecular dynamics simulations, and showed that a charge inverted complex drifts under the external electric field in the direction determined by its inverted charge [7]. The net charge of the macroion complex was estimated by the force balance, $Q^* \sim \nu\mu$, where μ is the electrophoretic mobility and ν is the solvent friction.

In the present simulation, we take the system of a rod-shaped macroion, polyelectrolyte counterions, coions, and neutral particles. The system is maintained in overall charge neutrality, $Q_0 + N^+Z^+e - N^-Z^-e = 0$. The simulation domain is a periodic cubic box. We solve the Newton equations of motion for each particle with the electrostatic (Coulombic) and Lennard-Jones potential forces under a uniform applied electric field E ($E > 0$). A large number of neutral particles are used to model the viscous solvent of given temperature and to treat the interactions among the finite-size macroion, counterions, coions and solvent. The temperature is $k_BT = e^2/5\epsilon a$, or in the Bjerrum length $\lambda_B = e^2/\epsilon k_BT = 5a$ (we assume spatially homogeneous dielectric constant ϵ). The Joule heat produced by the external electric field on ions is drained safely by a heat bath for neutral particles, as the hydrodynamic interactions in the electrolyte solvent are screened at short distances comparable to the Debye length λ_D [7,10,11].

The surface charge density of the *infinite rod* macroions in Fig.1 are $\sigma_{rod} = |Q_{rod}|/2\pi R_{rod}L \sim 0.08e/a^2$ (filled circles), $0.06e/a^2$ (open circles) and $0.04e/a^2$ (0.33 C/m^2, filled squares). The surface charge density of the DNA is 0.19 C/m^2. The number of Z-ions is adjusted

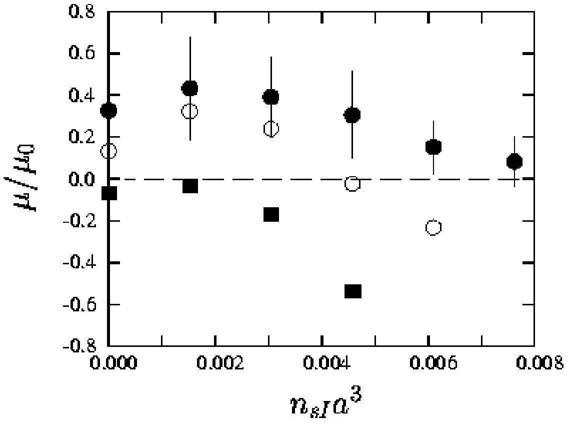

Figure 1: The electrophoretic mobility of the rod-shaped macroion is shown against ionic strength of monovalent salt n_{sI} for strongly charged (filled circles; 0.66 C/m^2), mediumly charged (open circles), and weakly charged (square; 0.33 C/m^2) macroions.

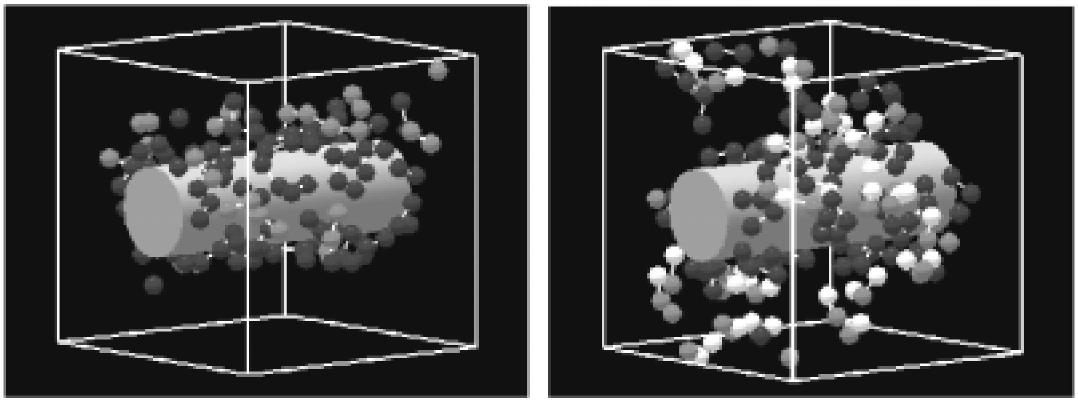

Figure 2: The rod-shaped macroions under polyelectrolyte counterions and coions, with [left] equal and [right] larger line charge density of counterion polyelectrolyte (dark gray spheres) than that of coion polyelectrolyte (light gray spheres; white spheres are neutral monomers).

as $N^{+3} \approx |Q_{rod}|/eZ + 30$. The normalization of the mobility is $\mu_0 \approx 21(\mu\mathrm{m/sec})/(\mathrm{V/cm})$. The Manning parameter $\xi_M = \lambda_B Q_{rod}/eL$ [12] for these rods is between 3.9 and 7.8, and counterion condensation is expected which, however, does not affect the shape of the rigid-rod macroion. We see that the mobility for the cylindrical macroion is reversed and enhanced by the addition of small amount of monovalent salt, similarly to the strongly charged spherical macroion [13]. It is found that the rod-shaped macroion is more persistent to monovalent salt than the spherical macroion of the same radius and surface charge density.

Figure 2 shows the charge inversion when both the counterions and coions are polyelectrolytes. For simplicity, all chains consist of four monomers. The number of counterion polyelectrolyte chains is 30 where all the monomers are charged unity e (dark gray monomers). As for the coions, there are (a) 10 polyelectrolyte chains of four unit charges ($-e$) (light gray), and (b) 20 chains consisting of two unit charges and two neutral monomers (white). In the case (a) in which the line charge densities of the counterion and coion polyelectrolytes are the same, charge reversal is small $\mu \sim 0.02\mu_{0r}$. When the line charge density of the coion polyelectrolyte is reduced to a half in (b), significant revered mobility is obtained $\mu \sim 3.1\mu_{0r}$.

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