Density Functional Study on the Osmotic Coefficient for DNA-Electrolyte Solutions

K. Wang, Y.X. Yu,[C, S] and G.H. Gao
Department of Chemical Engineering, Tsinghua University, Beijing, China
yangxyu@mail.tsinghua.edu.cn

A density functional approach and canonical Monte Carlo simulations are presented for describing the ionic microscopic structure around DNA molecules immersed in mixed-size counterion solutions. The DNA molecules are modeled as charged cylinders, while the ions are represented as charged hard spheres. In the density functional approach, the hard-sphere (HS) contribution to the Helmholtz energy functional is obtained from the modified fundamental measure theory, and the electrostatic contribution is evaluated through a quadratic functional Taylor expansion.

The new theory is suitable for systems containing ions of arbitrary sizes and valences. In the established canonical Monte Carlo simulation, an iterative self-consistent method is used to evaluate the long-range energy, and another iterative algorithm is adopted to obtain desired bulk ionic concentrations. The ion distributions from the density functional theory (DFT) are in good agreement with those from the corresponding MC simulations. It is found that the ratio of bulk concentrations of two species of counterions (cations) makes significant contributions to the ion distributions in the vicinity of DNA. A comparison with the electrostatic potential profiles from the MC simulations shows that the accuracy of the DFT becomes low when small divalent cations exist.

Both the DFT and MC simulation results illustrate that the electrostatic potential at the surface of DNA increases as the anion diameter or the total cation concentration is increased, and decreases as the diameter of one cation species is increased. The calculation of the electrostatic potential using real ion diameters shows that the accuracy of DFT predictions for divalent ions is also acceptable. When combining the established density functional theory with the cell model, the osmotic coefficients of aqueous DNA-electrolyte solutions are predicted, and a good agreement between the calculated results and experimental data is achieved.