

Modelling polyelectrolytes: coupling of conformational and ionization equilibria in solution





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Introduction

The role of polymer chemical structure in its properties has been a topic of research in the development of new materials. Theoretically and computationally, conformational properties have been mainly rationalized by means of ideal chains like the Freely Rotating chain or the Worm-Like chain.

The conformational and protonation properties of linear polyelectrolytes are studied by means of accurate Statistical Mechanics models and Monte Carlo Simulations. A classical technique, the <u>Rotational Isomeric State (RIS)</u> model proposed by Flory [1], has been used to study a wide range of such physical properties of neutral polymers.



However, many polyelectrolytes of interest are able to regulate their charge depending on the conformational state. Here it is shown that the RIS model can be coupled with the <u>Site Binding</u> (SB) model. The resulting combined scheme, the <u>SBRIS model</u>, allows analysing conformational and ionization properties of polyelectrolytes on the same time [2].



Monte Carlo (MC) approach

Excluded volume (EV) interactions:

Long range electrostatic interactions:



Hard spheres interaction between chain atoms *i* and *j*.

 $r_{ii} \equiv distance$ $E_{ij}^{EV}(r_{ij}) = \begin{cases} \infty & \text{if } r_{ij} \le R_i + R_j \\ 0 & \text{if } r_{ij} > R_i + R_j \end{cases}$ between i and j $R_i \equiv \text{Radius of i}$

Debye-Hückel (DH) interaction between charged non-neighbour atoms

$$E^{DH} = \frac{q_1 q_2 e^2}{4\pi\varepsilon_0 \varepsilon_r} e^{-\kappa r} \qquad \kappa = \sqrt{\frac{2N_A e^2 I}{\varepsilon_0 \varepsilon_r k_B T}}$$



Conclusions

- Monte Carlo simulations complement SBRIS model to include long range interactions.
- Long range interactions have a major contribution to polyelectrolytes radius of gyration, specially for long chains. For polyethylenimine, this effect increases when the chain is charged (low pH) even at a high ionic strength .
- Polyelectrolyte global charge is regulated by polymer mechanical stretching. High forces increase polymer global charge.
- Long range interactions have only a minor role on polymer titration at high ionic strength.
- Even at low ionic strength, pH does not change polyethylenimine mechanical response
- In low force regime, low ionic strength show higher L_z values. Thus, ionic strength enhance folded polymer conformations.

Bibliography

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