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Solvent Effect on the Mean Dimensions of Model Polyelectrolytes

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SUMMARY: The influence of the polarisation of the solvent on the mean dimensions of model polyelectrolytes is incorporated by solving numerically the Poisson equation for each conformation of the chain embedded in a continuous dielectric media. The mean squared end to end distance reveals the screening effect introduced by the charges induced within the dielectric. The highest departure from continuous dielectric models occurs at intermediate values of the Coulomb coupling strength.

Introduction

The size of polyelectrolyte chains has been studied by a number of methods as a tool to understand the basic interactions that determine the configurational statistics of charged macromolecules. The simplest mean field theories describe the water soluble polyelectrolytes as elastic chains immersed in a medium with dielectric permitivity ε close to that of water with charges interacting through an effective Debye Huckel potential. Numerical simulations of Monte Carlo type incorporate more realistic short range interactions, finite sized monomers, etc, but the solvent is treated as a continuous whose dielectric permitivity is that of the bulk, independently on the presence of the macromolecule 1).

Description of the model

Our flexible polyelectrolyte model is described by a freely linked chain of N identical spherical monomers (beads) each one carrying the same charge Q, with fixed link distance l (unit length scale) between nearest neighbour beads.

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The solute molecule is represented here by a cavity of low dielectric permitivity ε_i (~ 2-5 ε_o characteristic of proteins, for instance) embedded in a continuum solvent medium of high dielectric permitivity ε_s . For each configuration of the solute molecule, the cavity surface is traced by inward-facing part of a spherical probe as it rolls over the beads surface of the polymer solute $^{2)}$.

The beads interact each other through unscreened Coulomb forces and the energy is written as: Ecoul / k_BT = u / ε_i r $_{ij}$, where the adimensional parameter u = $Q^2 / 4\pi\varepsilon_o k_BT$, k_B is the Boltzmann constant, T is the absolute temperature, r $_{ij}$ is the distance between monomers i and j and ε_o is the permitivity of vacuum.

The solvation free energy is the work to transfer the solute molecule from the vacuum to solvent and represents the additional electrostatic contribution to the total energy as consequence of solvent polarisation effect. The electrostatic solvation potential was computed by solving the Poisson equation in finite difference form using iterative numerical techniques with the DelPhi package $^{3-5)}$. Following this approach, the solute/solvent system was first mapped onto a three-dimensional lattice where each lattice point is assigned a value for the charge and each lattice bond a value of the dielectric permitivity. The dimension of the chosen cubic grid was 65x65x65 such that half of the box was occupied by the solute. An ionic strength zero was assumed in this work.

The solution yields the electrostatic potential at every grid points. The electrostatic solvation free energy is:

$$E_{solv} = \frac{1}{2}\sum_i q_i(\Phi_i^{\varepsilon=80} - \Phi_i^{\varepsilon=1})$$

where q_i and Φ_i are the charge and the computed potential at ith grid point.

Results

In order to test the influence of the solvent polarisation effect on model polyelectrolyte systems we analyse in detail the minimal model to capture the underlying physical effect. In addition, we report some preliminary results on longer polymer chains.

The minimal model for the polyelectrolyte is that with only one degree of freedom, i.e. N=3. Their configurational properties depend on the single bond angle θ and the partition function is obtained analytically when the beads are point charges in a continuous dielectric. In particular, the mean squared end to end distance $<R^2>$ grows continuously between $<R^2> = 2$ (uncharged) and $<R^2> = 4$ (fully charged).

To quantify the effect of the parameters of the model on the solvation free energy we choose a fixed probe sphere radius $R_p = 0.3$ and several bead radius R_b from 0.5 to 4. The dielectric permitivity were chosen $\varepsilon_i = \varepsilon_o$ within the cavity and $\varepsilon_s = 80\ \varepsilon_o$ outside. It is expected a decreasing influence of the solvent polarisation with increasing bead radius, approaching the limiting case of uniform dielectric permitivity ε_i. In this work we assume that the second bead is uncharged. The solvation free energy was computed numerically with DelPhi as a function of the bond angle, every 10 degrees. The Fig.1 depicts our results for $R_b = 0.5$.

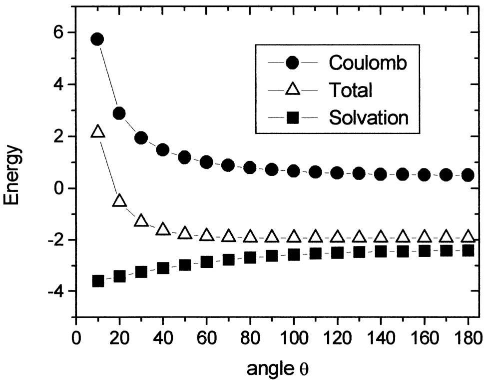

Fig.1. Solvation energy (in $k_BT \cdot u$ units) of the minimal model as a function of angle θ. The Coulomb and total energies are included for comparison.

The solvation free energy was fitted according to:

$$E_{solv} / k_BT\,u = A + B / (C + \cos\ \theta)^{1/2} \qquad (1)$$

which resembles a shifted Coulomb energy. The unscreening Coulomb energy corresponds to: A = 0, B=0.707, C = 1. The parameters A, B, C are found to depend on the bead radius, as shown in the Table 1. As $R_b = 4$ the solvent effect is negligible and the interaction is that of two charges in a medium of dielectric permitivity ε_i.

Table 1. Dependence of parameters with bead radius.

R_b	0.5	1.0	2.0	4.0
A	- 1.86	- 1.10	- 0.762	- 0.1
B	- 0.856	- 0.52	- 0.095	- 0.04
C	1.232	1.55	1.35	1.02

The probability density functions $P_m(\theta)$ of occupation of the angle θ are defined as

$$P_m(\theta) = Z^{-1} \sin\theta \; \exp(-E_m(\theta) / k_B T u)$$

where E_m is the Coulomb (m=1) and total (i.e. Coulomb plus solvation, m=2) energies, respectively, and Z is the partition function. They are plotted on Fig.2 as a function of θ for $R_b = 0.5$. In the weakly charged limit ($u \ll 1$), $P_1(\theta)$ is symmetric around 90 degrees, since $P_1(\theta) \approx \sin\theta$. In a uniform dielectric medium with dominant Coulomb forces ($u \gg 1$) the chain elongates and a maximum of the corresponding $P_1(\theta)$ is depicted at large θ angles, as expected. On the other side, the addition of the solvation energy compensates this stretching: a sharper probability distribution $P_2(\theta)$ is obtained, with a maximum around 90 degrees and lower weights at small or large angles.

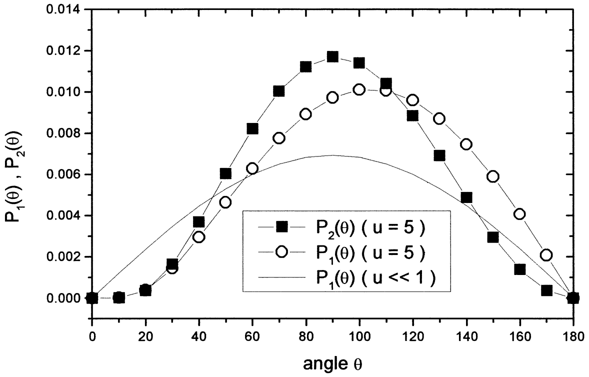

Fig.2. Probability density functions versus angle θ

The mean squared end to end distance of the model chain was calculated as a function of the interaction parameter u by Monte Carlo simulation. The total energy includes the solvation free energy as given by Eq.(1). The results are shown in Fig. 3 for the case $R_b = 0.5$, $R_p = 0.3$. It is evident that the mean size of the molecule is overestimated or underestimated when uniform dielectric mediums with $\varepsilon_s = 80\ \varepsilon_o$ or $\varepsilon_s = \varepsilon_o$, respectively, are assumed.

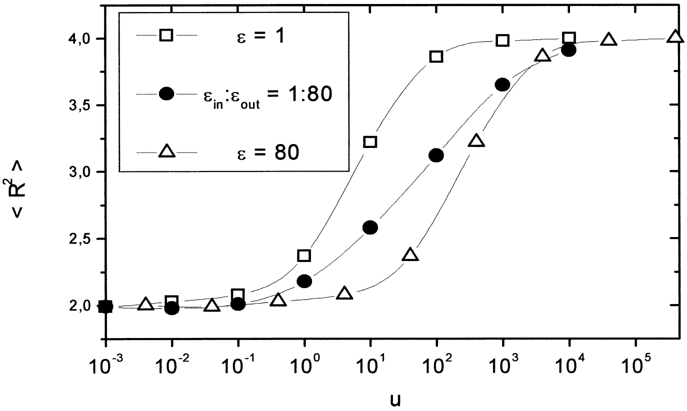

Fig. 3: Mean squared end to end distance of the minimal model as a function of the Coulomb interaction parameter u.

It is worth to note that $< R^2 >$ derived from a non uniform dielectric medium cannot be fitted in the whole range of u with an effective dielectric permitivity.

Whether these effects are present or not in longer polymer chains remains to be proved. Hence, longer polyelectrolyte chains were generated on a computer assuming that all the beads carry the same charge. The pivot algorithm was used to sample the conformational and the calculation of the configurational properties of these polyelectrolyte chains was performed by solving the Poisson equation *at each step of the Monte Carlo simulation.* The mean squared end to end distance of a chain with 11 beads ($R_b = 0.5$, $R_p = 0.3$) is depicted in Fig.4. The chain is highly expanded over the unperturbed state in a range (u ~ 0.1) where the continuous dielectric model ($\varepsilon_s = 80\ \varepsilon_o$) still gives approximately the unperturbed dimensions ($< R^2 > \sim 10$). At higher u values, the chains with contributions of solvent polarisation expands more rapidly than those in a continuous dielectric. This fact demonstrates that the solvent polarisation effect cannot be described by an effective dielectric permitivity. Details of the scaling behaviour of the mean dimensions of longer polyelectrolytes chains with the chain length will be reported elsewhere.

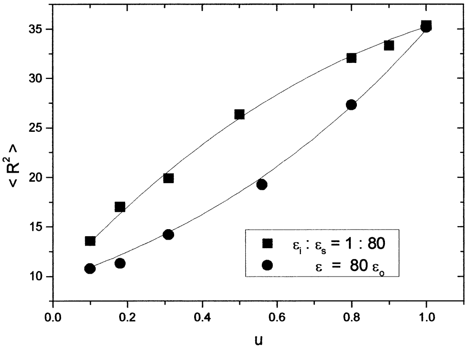

Fig.4. Mean squared end to end distance of chains with N=11 beads ($R_b = 0.5$, $R_p = 0.3$). A restricted range of values of u is shown for comparision.

Conclusion

The discontinuity of the value of the dielectric permitivity between the cavity representing the solute molecule and the liquid environment is responsible of an effect on the mean dimensions of the polyelectrolyte that cannot be accounted for by an uniform effective dielectric model. Departures from the predictions of uniform dielectric models are enhanced at intermediate values of the Coulomb coupling constant u.

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