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BACHELOR THESIS



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Study of persistence length of linear polyelectrolytes in solutions

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I declare that I have written my bachelor work by myself and that all the sources of information used are listed in the bibliography. I agree that this work may be lent and published.

In Prague

Petra Bačová

Contents

Abstract	2
List of Symbols	3
1 Introduction	6
2 State of the art	8
2.1 Models of polymer chains	8
2.1.1 Freely jointed chain (FJC)	8
2.1.2 Freely rotating chain (FRC)	9
2.1.3 Worm-like chain (WLC)	10
2.2 Theory of the persistence length	10
2.2.1 Persistence length of neutral polymers	10
2.2.2 Persistence length of polyelectrolytes	12
3 Simulation method	14
3.1 Molecular dynamics	14
3.2 Bead-spring model	15
3.3 Interaction potentials	16
3.3.1 Short range potentials	16
3.3.2 Long range potentials	17
3.4 Reduced units	18
3.5 Simulation details	18
4 Results and discussion	20
4.1 Persistence length of neutral polymers	20
4.2 The end-effects of polyelectrolytes	21
4.3 Persistence length of polyelectrolytes	22
5 Conclusions	25
Bibliography	25

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Abstract:

The presented bachelor thesis deals with the study of the persistence length of semi-flexible polyelectrolytes. The polymer solution was simulated using Molecular dynamics. The dependence of the persistence length on intrinsic stiffness of the chain was investigated. The obtained results were compared to the several theoretical models, in particular to the approach of Manghi and Netz which predict different behaviour on two different length scales. It was found that only the approach of Manghi and Netz can describe the behaviour of the polymers reasonably well.

Also the effect of finite chain length of the simulated polymers was studied and a method how to avoid undesired systematic errors when simulating relatively short chains was suggested.

Keywords: polyelectrolyte, persistence length, Molecular dynamics, end-effects

List of Symbols

α	degree of ionization of the polyelectrolyte
ΔE_{bend}	bending energy of a short elastic rod
Δt	time step
ϵ_{LJ}	parameter of Lennard-Jones potential
Γ	friction coefficient
κ^{-1}	Debye screening length
κ_b	bending modulus per unit length of polymer
ν	scaling exponent
ϕ	bond angle
σ	diameter of the bead
τ	simulation time
θ	complementary angle to bond angle
ϵ_0	vacuum permittivity
ϵ_r	relative dielectric constant of the medium
B	parameter in expression of Manghi and Netz for the tangent-tangent correlation function
d	number of degrees of freedom
e	unit charge
I	ionic strength
k_{bend}	bending constant
k_{FENE}	parameter of bonding potential
l	bond length
l_b	Bjerrum length
l_p	total persistence length

l_p^*	persistence length of the null isomer of the polyelectrolyte
l_p^n	persistence length of neutral polymer
$l_p^{(1)}$	persistence length defined in eq. 2.12
$l_p^{(2)}$	persistence length defined in eq. 2.13
l_p^0	intrinsic persistence length
l_p^e	electrostatic persistence length
m_i	mass of particle i
N	number of particles
R	radius of cross section of polymer
R_e	end-to-end distance
r_{cut}	cut-off distance in Lennard-Jones potential
R_{FENE}	maximum bond stretching
r_{ij}	distance between particle i and j
s	length of the chain segment between two positions in the chain
T	temperature
t	time
T_k	kinetic temperature
$U(\theta)$	bending potential
$U(\mathbf{R}^N)$	potential energy of particles
$U_{\text{Coul}}(r_{ij})$	Coulomb potential
U_{FENE}	attractive finitely-extensible non-linear elastic (FENE) potential
$U_{\text{LJ}}(r_{ij})$	Lennard-Jones potential
V	volume
z_c	valence of counterions
$\mathbf{F}_i^r(t)$	stochastic force
\mathbf{F}_i	force on a particle
\mathbf{R}_e	end-to-end vector
\mathbf{R}_i	position vector
\mathbf{r}_i	bond vector

\mathbf{v}_i	velocity of particle i
R_{\max}	contour length
FJC	freely jointed chain
FRC	freely rotating chain
OSF	Odijk and Skolnick and Fixman
PEs	polyelectrolytes
WCA	Weeks-Chandler-Andersen potential
WLC	worm-like chain

1. Introduction

It is nearly impossible to find a part of everyday life that is not affected by polymers. The polymers play an important role in modern society. Polymer materials have found their application ranging from food packaging, production of clothes and children toys to advanced products as contact lenses, mobile phones, medical implants etc.[1] Naturally occurring polymers have been used by humans for centuries and biopolymers like proteins and nucleic acids are essential to life existence.

Polymer is a molecule which is made up of many repeating molecular units called monomers. They are covalently bonded together forming a long chain. General properties of polymers are influenced by very large number of structural units, which comprise the chain. Due to their flexibility polymers can take up huge amounts of different conformations. Therefore some physical properties related to the conformations can be adequately described only by statistical approaches. The shape of a polymer in solution is strongly influenced by interactions with solvent.[2]

In recent years the interest in polymers with special properties has increased. Polyelectrolytes (PEs) belong to this group under investigation. They are bearing ionizable groups, which can dissociate in a polar solvent such as water. After the dissociation, a macroion with many small charges along the chain is formed and an equivalent amount of counterions is released into the solution.[3] One of the favourable properties of PEs is their good solubility in water. It is possible to vary their solution behaviour by adjusting the pH or ionic strength, which is not feasible in non-charged polymer species. The presence of long-ranged Coulomb interactions causes that behaviour of PEs differs from that of neutral polymers and the understanding of their properties is still relatively poor.[4] The repulsive electrostatic interactions between charged monomer units force the chain to elongate. The more the charges repel along the backbone, the more stretched is the chain.

Thanks to their unusual properties, PEs are used in various technical applications like viscosity modifiers, for heavy metals ion precipitation in water cleaning, as superabsorbers for baby diapers etc.[5] Many biopolymers are polyelectrolytes and they behave as semiflexible chains due to steric constraints. Study of their conformational changes with varying degree of ionization or investigation of their bending rigidity can help to understand how stiffness is important to their biological function.[6]

The chain flexibility can be characterized by the persistence length. It is a property which determines the distance along the chain over which orientation becomes uncorrelated. [7] Over the years several different definitions and theories of persistence length have been formulated (see [8, 9] and references therein) and many experimental methods [10, 11, 12] have been used to investigate this characteristic of polymers.

Computer simulations bridge the gap between theoretical models and experiments. Simulation can mimic an experiment at the molecular scale under well defined conditions based on a model provided by theoreticians. Nowadays the most disputable theory of

polyelectrolyte persistence length was worked out by Odijk [13] and Skolnick and Fixman (OSF) [14]. For stiff polyelectrolytes in solutions with added salt this approach brings a concept called electrostatic persistence length. In addition to the intrinsic rigidity of the chain, the electrostatic persistence length accounts for the contribution of electrostatic interactions to the chain stiffness. The significance of this contribution should depend inversely on ionic strength of solution. The OSF theory has been extended to chains with variable intrinsic stiffness [15] and its validity was tested by many simulations and experimental methods (e.g.[16, 17, 18]). The basic assumption of OSF is based on several approximations which can be applied only in a certain range of ionic strength (Debye-Hückel approximation) and only for a certain model of polyelectrolyte chain (deviations for flexible chains [16]). According to many studies, the OSF theory is not a universal way of explaining the changes of polyelectrolyte rigidity in solution.

Recently, a new approach towards the persistence length of polyelectrolytes appeared. The Manning model relates the persistence length of polyelectrolyte to persistence length of an uncharged chain called the null isomer and should be independent on the used polymer model.[19] This assumption puts together results of his previous studies about deformation of polymers [20] and condensation of counterions [21]. However, the Manning approach has not yet been confirmed by other works and remains only a hypothesis for the present study. Both approaches mentioned above deal with polyelectrolytes in solution, they consider the presence of a salt and hence the screening of electrostatic interactions.

The aim of this work is to investigate the conformational behaviour of semiflexible polyelectrolytes in a salt-free aqueous solution. The relationship between persistence length of a semiflexible polyelectrolytes and neutral polymers is studied.

2. State of the art

2.1 Models of polymer chains

Polymer chains are composed of a large number of monomer units and most of their properties are influenced by this fact. Simulation of a macromolecular system at the molecular scale is computationally demanding and such detailed description is often unnecessary. Some macroscopic properties of polymers can be studied without considering the detailed chemical structure. The universal polymer behaviour can be described by simplified models of polymers. The simplification comprises representation of the chain by jointed linear parts (segments) and/or neglecting the finite size effects etc.

The simplest polymer model is the ideal chain. This model does not take into account the excluded volume of monomers, nor the interactions between monomers along the chain or between monomers and solvent molecules.[2] The ideal chain forms a basis for more advanced theories of polymer chains.

2.1.1 Freely jointed chain (FJC)

Consider a chain consisting of $N + 1$ backbone monomer units described by position vectors \mathbf{R}_i ($0 \leq i \leq N$). It is schematically depicted in Fig. 2.1. The conformation of the chain is represented by a set of bond vectors $\{\mathbf{r}_i\}=(\mathbf{r}_1 \dots \mathbf{r}_N)$ [22], where the bond vector is defined as $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_{i-1}$ $i = 1, 2, 3 \dots N$.

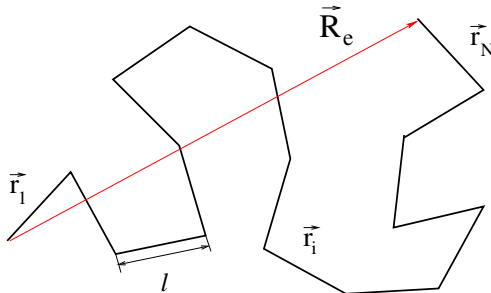


Figure 2.1: Freely jointed chain

In the FJC model, the orientations of bond vectors are fully random and all bonds vector have the same length l :

$$|\mathbf{r}_i| = l.$$

The vector \mathbf{R}_e connecting the ends of a linear polymer chain in a particular conformation is called the end-to-end vector [2]:

$$\mathbf{R}_e = \sum_{i=1}^N \mathbf{r}_i. \quad (2.1)$$

The maximum end-to-end distance of a linear chain is referred to as the contour length R_{\max} . The contour length is equal to the product of the number of bond vectors N and their projected length along the contour. The freely jointed chain can be extended to a fully straight conformation with R_{\max} :

$$R_{\max} = lN. \quad (2.2)$$

The mean-square end-to-end vector can be used as a characteristic size of the chain:

$$\langle \mathbf{R}_e^2 \rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \sum_{i=1}^N \langle \mathbf{r}_i^2 \rangle + 2 \sum_{i>j} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle. \quad (2.3)$$

Because there are no correlations between the directions of different bond vectors \mathbf{r}_i and \mathbf{r}_j , $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = l^2 \delta_{ij}$. Inclusion of condition $\langle \mathbf{r}_i^2 \rangle = l^2$ gives:

$$\langle \mathbf{R}_e^2 \rangle = \langle R_e^2 \rangle = Nl^2. \quad (2.4)$$

2.1.2 Freely rotating chain (FRC)

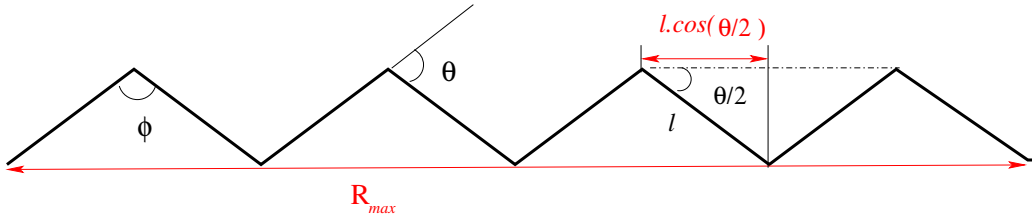


Figure 2.2: Contour length of FRC

A more complex model than FJC is the freely rotating chain. This model assumes that all bond lengths and bond angles are fixed, but the rotation around single bonds is unrestricted. The complementary angle, θ , to the bond angle is defined as the angle between successive bond vectors (see also Fig. 2.2):

$$\theta = 180^\circ - \phi,$$

where ϕ is the bond angle. The projected length of a bond vector along the chain contour is $l \cos(\theta/2)$, so the contour length of FRC is given by:

$$R_{\max} = Nl \cos \frac{\theta}{2}. \quad (2.5)$$

The formula for the mean-square of the end-to-end vector of the FRC is analogous to equation 2.3,

$$\langle \mathbf{R}_e^2 \rangle = \left\langle \left(\sum_{i=1}^N \mathbf{r}_i \right) \cdot \left(\sum_{j=1}^N \mathbf{r}_j \right) \right\rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle, \quad (2.6)$$

however, $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$ does not vanish for $i \neq j$. [22] It can be shown that the correlation between the bond vectors along FRC decays with increasing distance $|j - i|$ along the polymer chain [2]:

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = l^2 (\cos \theta)^{|j-i|}. \quad (2.7)$$

After the substitution of (2.7) to (2.6) and several approximations the expression for the mean-square of the end-to-end vector of FRC can be obtained:

$$\langle \mathbf{R}_e^2 \rangle = \langle R_e^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta}. \quad (2.8)$$

The root-mean-square end-to-end distance $\sqrt{\langle R_e^2 \rangle}$ of the freely jointed (eq. 2.4) and freely rotating chain (eq. 2.8) scales with $N^{1/2}$

$$\sqrt{\langle R_e^2 \rangle} \propto N^{\frac{1}{2}}. \quad (2.9)$$

The $N^{1/2}$ scaling is a typical feature of ideal linear chains.[2] For real chains, the excluded volume and interactions with solvent have to be taken into account. If these effects are not ignored, a more general scaling for the root-mean-square end-to-end distance is:

$$\sqrt{\langle R_e^2 \rangle} \propto N^\nu. \quad (2.10)$$

Excluded volume effects of monomer units cause the chain expansion and the value of the scaling exponent ν increases:

$$\nu \geq \frac{1}{2}.$$

If the attractive interactions among chain segments are stronger than those between chain and solvent, the value of the scaling exponent ν becomes smaller

$$\nu \leq \frac{1}{2}$$

and the chain is more collapsed than the ideal chain. For a given polymer-solvent pair and a certain temperature these two effects cancel each other. This special case is called the Θ state. In the Θ state the polymer behaves effectively as an ideal chain and its scaling exponent equals exactly 0.5 (eq. 2.9). This state can be fulfilled simply by suitable choice of solvent (Θ solvent) and temperature (Θ temperature).[23]

2.1.3 Worm-like chain (WLC)

The worm-like chain, also known as the Kratky-Porod chain, is the model of a linear macromolecule consisting of an infinitely thin chain of continuous curvature. It is defined as the limiting case of FRC for $l \rightarrow 0$ and $\theta \rightarrow 0$ under the restriction of constant contour length

$$R_{\max} = Nl \cos \frac{\theta}{2} \cong Nl \quad (2.11)$$

and constant persistence length (see next section).[23] The mean-square of the end-to-end distance can be evaluated from $\langle \mathbf{R}_e^2 \rangle$ of discrete chain (eq. 2.6), but with correction for continuous chain.[2] The chains with various degrees of stiffness can be described by this model.

2.2 Theory of the persistence length

2.2.1 Persistence length of neutral polymers

The persistence length, l_p , is a characteristic of chain flexibility. It is the distance over which the polymer chain "forgets" the orientation of the segments, which are further than

this distance.[24] This concept of l_p is intuitive but when one tries to find a more exact definition s/he can encounter problems. There are a few well established definitions of the persistence length. In the limiting case of the ideal chain, they are identical but they may differ significantly for real systems. An overview of several definitions can be found e.g. in [8]. In the following we will discuss some of them in more details.

- *The average projection of the end-to-end vector on the tangent to the chain contour at a chain end in the limit of infinite chain length.*[25] When the first bond vector \mathbf{r}_1 is selected as the end of chain:

$$l_p^{(1)} = \frac{1}{l} \langle \mathbf{R}_e \cdot \mathbf{r}_1 \rangle = \frac{1}{l} \sum_{i=1}^N \langle \mathbf{r}_1 \cdot \mathbf{r}_i \rangle = l \sum_{i=1}^N \langle \cos \theta_{1,i} \rangle. \quad (2.12)$$

The angular brackets $\langle \dots \rangle$ stand for the average over all possible conformations of the chain with proper statistical weights. This expression was derived for a freely rotating chain [23], but it is also used for calculation of l_p of flexible polymers. It has turned out that due to the end-effects it is better to make a projection of \mathbf{R}_e to direction of some segment in the interior part of the chain.[26]

- *The decay contour length of angular correlations.*[2] It can be shown that correlation from the bond vector \mathbf{r}_j to the bond vector \mathbf{r}_i decays exponentially with the number of bonds j between them:

$$\frac{\langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle}{l^2} = \langle \cos \theta_{i,i+j} \rangle = \exp \left(-\frac{|j \cdot l|}{l_p^{(2)}} \right). \quad (2.13)$$

In the case of a continuous chain, \mathbf{r}_i and \mathbf{r}_{i+j} are the vectors tangent to the chain at positions i and $i+j$. The length of the chain segment between these two positions is denoted as s and angular correlation expressed by eq. 2.13 yields the following

$$\langle \cos \theta(s) \rangle = \exp \left(-\frac{s}{l_p^{(2)}} \right). \quad (2.14)$$

There is no pre-exponential factor, because $\cos \theta(0) = 1$.[7] For a long continuous chain, the first and the second definitions do not differ, because the summation in eq. 2.12 can be replaced by the integration over the contour of continuous chain:

$$l \sum_{i=1}^N \rightarrow \int_0^{R_{\max}} ds$$

$$l_p^{(1)} = \int_0^{R_{\max}} \langle \cos \theta(s) \rangle ds.$$

When we assume that $R_{\max} \gg l_p^{(2)}$ and we substitute $\langle \cos \theta(s) \rangle$ by exponential function from second definition, last equation can be rewritten as:

$$l_p^{(1)} = \int_0^{R_{\max}} \exp \left(-\frac{s}{l_p^{(2)}} \right) ds = l_p^{(2)} \left(1 - \exp \left(-\frac{R_{\max}}{l_p^{(2)}} \right) \right) \cong l_p^{(2)}. \quad (2.15)$$

To find the relation between the persistence length and the bending rigidity of the chain, a model the chain consisting of stiff segments connected with fixed bond

angle is considered. Each segment is approximated by a short elastic rod. The rod with length s bent with radius of curvature θ/s . The elastic bending energy of this rod is proportional to the square of curvature:

$$\Delta E_{\text{bend}} = \frac{1}{2} \kappa_b s \left(\frac{\theta}{s} \right)^2, \quad (2.16)$$

where κ_b is the bending modulus per unit length of polymer.[7] We assume, that the bending of the chain is fully described by the potential 2.16. It can be shown that in the special case for $s \ll l_p^{(2)}$ and small angle θ the persistence length is given by the ratio of bending modulus per unit length and thermal energy $k_B T$

$$l_p^{(2)} = \frac{\kappa_b}{k_B T}. \quad (2.17)$$

This equation is only valid if the dependence of κ_b on temperature is neglected.

- *How to obtain the persistence length experimentally.* In experiment the persistence length can be calculated from expression for end-to-end distance:

$$R_e = 2l_p R_{\text{max}} - 2l_p^2 \left(1 - \exp \left(-\frac{R_{\text{max}}}{l_p} \right) \right) \quad (2.18)$$

or from analogous expression for radius of gyration. The relationship between R_e and l_p has been derived from equation for worm-like chain.[2] The modified form of equation 2.18 is used as a basic relationship to fit the experimental data. Most commonly used methods are light scattering [11], atomic force microscopy [10] and size exclusion chromatography [12].

2.2.2 Persistence length of polyelectrolytes

When extending the concept of the persistence length to polyelectrolytes, the contribution of the electrostatic repulsion to chain rigidity has to be taken into account. The first step towards the understanding of the behaviour of PEs was the introduction of the electrostatic persistence length by Odijk [13] and Skolnick and Fixman (OSF) [14]. It was derived for very stiff chains in a salt solution using the Debye-Hückel model, in which the charged particles interact via screened Coulomb potential. The screening is caused by the presence of salt and means that on the length scales larger than the Debye screening length (see below) the effective interaction potential between charged monomer units decays faster than in the case of salt-free solution. The OSF calculations show that the total persistence length l_p of a polyelectrolyte chain is the sum of the intrinsic, l_p^0 , and electrostatic, l_p^e , persistence length

$$l_p = l_p^0 + l_p^e.$$

The electrostatic persistence length is a function of the Debye screening length, κ^{-1} , which represents the range of screened electrostatic interactions

$$l_p^e = \frac{\alpha l_b}{4\kappa l^2} \quad \kappa^2 = 4\pi l_b I, \quad (2.19)$$

where l_b is the Bjerrum length (see eq. 3.12), α is the degree of ionization of the polymer and I is the ionic strength. The intrinsic persistence length corresponds to the persistence

length of neutral chain and it can be calculated for example in simulations from the second definition [15] and experimentally by the light scattering measurements of PE solutions with high ionic strength.[11] The validity of the OSF predictions was tested by both simulation (e.g. [16, 15, 17]) and theoretical methods (e.g. [27, 28]). Many results indicate that if chain is intrinsically flexible, the exponent of the κ -dependence of l_p^e approaches unity.

The OSF assumption remains valid for stiff chains and there is also a crossover region where the dependence of l_p^e on intrinsic persistence length was predicted. The above mentioned studies lead to agreement that there is no universal way how to describe the persistence length of PEs as a function of ionic strength and/or chain rigidity.

Recently, a new approach toward the persistence length of polyelectrolytes was presented by Manning.[19] His theory is based on the model of null isomer of a polyelectrolyte. It is a hypothetical structure which corresponds to the polyelectrolyte with no ionized groups. The behaviour of the null isomer should be recovered by applying the compression force to the ends of the molecule in order to compensate the stretching force from charge-charge repulsions in chain. The persistence length of a polyelectrolyte l_p is then related to the persistence length of its null isomer, l_p^* :

$$l_p = \left(\frac{\pi}{2}\right)^{2/3} R^{4/3} (l_p^*)^{2/3} z_c^{-2} l_b^{-1} f(\alpha, I), \quad (2.20)$$

where R is the radius of cross section of polymer, z_c is a valence of counterions and $f(\alpha, I)$ denotes the dependence of l_p on the degree of ionization and ionic strength. Manning described the elastic properties of polymers with Hooke's law for rodlike object, so the radius of the polymer cross section in eq. 2.20 corresponds to the radius of the rod. The relationship between the persistence length of a polyelectrolyte and its null isomer is not additive, which is the main difference between OSF and Manning's theory. The derivation of relationship 2.20 is a result of combination of his previous studies about deformation of stiff polymers [20] and condensation of counterions [21].

Manghi and Netz used the variational method to study of persistent length of polyelectrolytes. They came to the conclusion that in general the persistence length of PEs can not be simply described as a summation of the intrinsic and electrostatic persistence length.[29] They argued that at small length scales the persistence length of PEs is mainly given by the intrinsic persistence length and only at larger length scales the contribution of l_p^e becomes important. Manghi and Netz suggested the following expression for the tangent-tangent correlation function for a stiff polymer and/or small screening :

$$\langle \mathbf{r}(\mathbf{s}) \cdot \mathbf{r}(\mathbf{0}) \rangle = B \exp\left(-\frac{s}{l_p^0 + l_p^e}\right) + (1 - B) \exp\left(-s \frac{l_p^e + (1 - B)l_p^0}{l_p^0(l_p^e + l_p^0)(1 - B)}\right), \quad (2.21)$$

where the $\mathbf{r}(\mathbf{s})$ and $\mathbf{r}(\mathbf{0})$ denote the tangent vector to chain in position s and 0 , B is a factor dependent on κ^{-1} . This relationship should also describe the behaviour at small length scales as well as at large ones. In contrast, it seems that OSF theories corresponds to the large-scale limit.

3. Simulation method

3.1 Molecular dynamics

Molecular dynamics is a computer simulation technique used for studying time evolution of a set of interacting particles (which may represent atoms or molecules). The motion of particles is treated within the framework of classical mechanics and it is described by Newton's equations

$$m_i \frac{d^2 \mathbf{R}_i}{dt^2} = \mathbf{F}_i \quad i = 1, 2, 3 \dots n, \quad (3.1)$$

where \mathbf{F}_i is force on a particle i with a mass m_i and is calculated as a negative gradient of potential energy $U(\mathbf{R}^N)$:

$$\mathbf{F}_i = -\frac{\partial U(\mathbf{R}^N)}{\partial \mathbf{R}_i}. \quad (3.2)$$

Potential energy $U(\mathbf{R}^N)$ includes interaction potentials discussed in the next section. These equations are solved numerically. The primary output of the simulation are coordinates of particles as they evolve in time. Macroscopic properties of molecular systems can be obtained from the microscopic properties of the particles using the methods of statistical thermodynamics (for more details, see [30, 31]). In a conventional MD simulation (as was described above) energy E , number of particles N and volume V are constant and system corresponds to a microcanonical ensemble $[NVE]$. The system is prepared by placing N particles into the box with volume V , positions of moving particles are given by position vectors $\mathbf{R}^N = (\mathbf{R}_1, \dots, \mathbf{R}_N)$ and temperature is given by the average of their total kinetic energy [32]:

$$\sum_i^n \frac{m_i |\mathbf{v}_i|^2}{2} = \frac{d}{2} k_B T_k, \quad (3.3)$$

where d denotes the number of degrees of freedom, m_i the mass of particle i , \mathbf{v}_i is its velocity and k_B is the Boltzmann constant. T_k is a time-dependent quantity which is called kinetic temperature. Temperature, as an intensive property, can be calculated as an ensemble average:

$$\langle T_k \rangle = T. \quad (3.4)$$

In this work the properties of polyelectrolyte chain in a solution at constant temperature are studied. Simulations are performed in the canonical ensemble $[NVT]$, characterized by a fixed number of particles N , a fixed volume V and a fixed temperature T . One possibility, how to control the temperature in NVT simulation, is coupling the system to a heat bath.[33] In this work the Langevin thermostat was used. A heat bath is implemented in simulation as an acting of random forces on the particles in the system. They represent also the collisions with the solvent molecules, which are not simulated explicitly.[34] To

incorporated the implicit solvent Newton's equations of motion have been modified by adding two terms on the right side:

$$m_i \frac{d^2 \mathbf{R}_i}{dt^2} = \mathbf{F}_i - \Gamma \frac{d\mathbf{R}_i}{dt} + \mathbf{F}_i^r(t), \quad (3.5)$$

Γ denotes the friction coefficient, $\mathbf{F}_i^r(t)$ is the stochastic force. The term $\Gamma(d\mathbf{R}_i/dt)$ presents drag force and $\mathbf{F}_i^r(t)$ mimics the random collisions of particle i with the surrounding medium. These two forces are coupled through the fluctuation-dissipation theorem [22]:

$$\langle \mathbf{F}_i^r(t) \cdot \mathbf{F}_i^r(t') \rangle = 6k_B T \Gamma \delta_{ij} \delta(t - t'), \quad (3.6)$$

where δ_{ij} is the Kronecker delta and $\delta(t - t')$ the Dirac delta function.

Step-by-step numerical integration is used in order to solve the equations of motion. It is based on finite difference method, where time does not act as a continuous argument but is divided into discrete time intervals - time steps Δt

$$t = t_0 + k\Delta t \quad t \in \langle t_0, t_{\max} \rangle \quad k \in \mathbb{Z}^+.$$

Due to dependence of friction force on velocity, it is useful to combine the Langevin thermostat with velocity Verlet integration method [32].

3.2 Bead-spring model

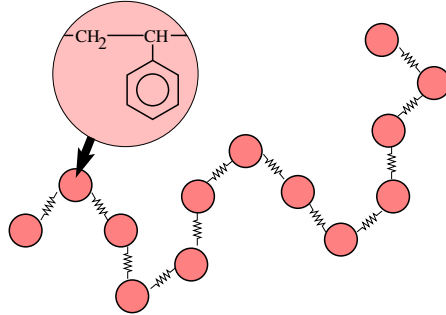


Figure 3.1: Bead-spring model

An efficient computational technique, where the microscopic and mesoscopic approaches are combined is so called "coarse-graining".[35] The coarse-graining means successive reduction of the number of degrees of freedom of molecule, carried out for example by approximating several chemical units (carbon groups) by an effective monomer. The choice of a sufficient coarse-grained model depends on the questions of interest.

The bead-spring models has been often applied in modelling the polymer solutions. In simulations presented in this work, one of the coarse-grained models is used. In our model one or more monomer units of a linear chain are replaced by spherical beads joined by springs, hence, bonds between these beads are flexible.[35] All the particles in simulation (charged and neutral monomers and counterions) are represented by beads of the same size with diameter σ . Charged beads carry the unit electric charge. For modelling the semiflexible polymers the bending potential between beads (see eq. 3.10) can be included, which determines allowed values of the bond angle . Then the bead-spring model becomes a special case of FRC which includes the excluded volume of beads.

3.3 Interaction potentials

3.3.1 Short range potentials

Non-bonding potentials

To model the excluded volume, the soft sphere repulsion of two beads at short distances and van der Waals attractive interactions at slightly longer distances the truncated and shifted Lennard-Jones potential [31] is used

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon_{LJ} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + c_{\text{shift}} \right] & r_{ij} \leq r_{\text{cut}} \\ 0 & r_{ij} > r_{\text{cut}} \end{cases} \quad (3.7)$$

Parameter σ defines the basic unit of length, ϵ_{LJ} controls the strength of the interaction. LJ potential is cut off at a certain point, r_{cut} , and is also shifted upwards to remove the discontinuity in the value of the potential at r_{cut} :

$$c_{\text{shift}} = - \left[\left(\frac{\sigma}{r_{\text{cut}}} \right)^{12} - \left(\frac{\sigma}{r_{\text{cut}}} \right)^6 \right].$$

For interactions between the pairs of beads in the chain the cut-off distance is set to $r_{\text{cut}}=2.5 \sigma$. We set $\epsilon_{LJ}=0.33 k_B T$ in every simulation in this work which corresponds to the Θ solvent (see also sec. 2.1.2). [36] The potential describing the counterion-counterion and counterion-monomer excluded volume interactions is truncated and shifted at the position of its minimum $2^{\frac{1}{6}}\sigma$, so that only the repulsive part of this potential remains. The result is known as the Weeks-Chandler-Andersen potential (WCA):

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon_{LJ} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & r_{ij} \leq 2^{\frac{1}{6}}\sigma \\ 0 & r_{ij} > 2^{\frac{1}{6}}\sigma \end{cases} \quad (3.8)$$

Bonding potentials

The monomer units which are connected by the covalent bond interact via an attractive finitely-extensible non-linear elastic (FENE) potential:

$$U_{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}k_{\text{FENE}}R_{\text{FENE}}^2 \ln \left[1 - \left(\frac{r_{ij}}{R_{\text{FENE}}} \right)^2 \right] & r_{ij} < R_{\text{FENE}} \\ \infty & r_{ij} \geq R_{\text{FENE}} \end{cases} \quad (3.9)$$

with parameters k_{FENE} and R_{FENE} . Parameter R_{FENE} is the maximum stretching at which the elastic energy of the bond becomes infinite. The bond length fluctuations are small (up to 10%), optimum setting of the parameters keeps the bond length at nearly constant value and prevent chain intersection.[36] The chosen values for this work are listed in Table 3.2 in section 3.4.

The FENE potential gives only the attractive part of the bonding potential. In combination with Lennard-Jones potential (eq. 3.7) it produces an asymmetric bonding potential with a single minimum. The obtained potential is shown in Figure 3.2.

Bending potential

In the case of polymer chain which takes a conformation with given bond angles, for instance FRC, the polymer flexibility becomes partially restricted and the three-body interactions contribute to the overall potential energy. The bond-angle potential depends on

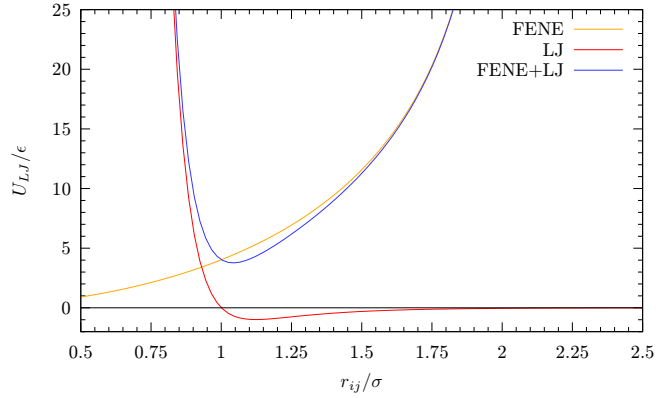


Figure 3.2: FENE and LJ potentials as attractive and repulsive components of the FENE+LJ potential

the variation of the bond angle ϕ (illustrated in figure 2.2), which involves coordinates of three particles. In our simulations it is implemented as a harmonic potential [30] around the equilibrium bonding angle ϕ_0 :

$$U(\theta) = \frac{1}{2}k_{\text{bend}}(\phi - \phi_0)^2, \quad (3.10)$$

where k_{bend} is the bending constant. The greater value of the bending constant k_{bend} , the more stiff is polymer. We chose the value $\phi_0 = \pi$, which corresponds to completely stretched configuration.

3.3.2 Long range potentials

If the polymer is charged, a fraction of monomers f carries the unit charge and an equal number of oppositely charged counterions of the same size as the monomers are added to balance overall charge. The i -th and j -th charges with valency z_i and z_j interact via the unscreened Coulomb potential in a solvent represented by a continuum:

$$U_{\text{Coul}}(r_{ij}) = k_B T l_b \frac{z_i z_j}{r_{ij}}, \quad (3.11)$$

r_{ij} denotes the distance between the charges and l_b is the measure of the strength of the electrostatic interaction called Bjerrum length [3]:

$$l_b = \frac{e^2}{4\pi\epsilon_r\epsilon_0 k_B T} \quad (3.12)$$

It is defined as the distance, at which the interaction energy of two unit charges e equals to thermal energy $k_B T$. The relative dielectric constant of the medium is denoted ϵ_r and ϵ_0 is the vacuum permittivity. For water at room temperature $l_b \approx 7.14\text{\AA}$.

Due to long range nature of electrostatic interactions, the Coulomb potential can not be simply truncated, which poses both mathematical and technical difficulties. Several methods have been developed to treat Coulomb interactions in fully or partially periodic geometries. In this work P³M method of Hockney and Eastwood is used as it is implemented in the simulation software (see [37] and references therein).

3.4 Reduced units

For modelling the molecular system, the standard SI units are not very convenient. They would be either very small or very large at the molecular scale what could lead to rounding errors in computations. To avoid these problems, a more natural set of units is chosen. In this work the energy scale is given by setting $k_B T = 1$. All other values of energy are thus measured in units of $k_B T$. The second basic unit is mass of the bead $m = 1$. The length scale is set by the bead diameter $\sigma = 1$.

Table 3.1: Values of parameters used in the simulations

quantity	symbol	reduced unit	value
number density of particles	ρ	σ^{-3}	2.10^{-5}
bond length	l	σ	≈ 1.0
overall time of simulation	τ_{\max}	$\sigma \sqrt{m/k_B T}$	5×10^5
Bjerrum length	l_b	σ	2.85
friction coefficient	Γ	$\sigma^{-1} \sqrt{k_B T/m}$	1.0

Table 3.2: Interaction parameters of the particles in the simulations

quantity	symbol	reduced unit	value
LJ parameter	ϵ_{LJ}	$k_B T$	0.33
LJ cut-off distance	r_{cut}	σ	2.5
spring constant	k_{FENE}	$k_B T/\sigma$	7.0
maximum bond stretching	R_{FENE}	σ	2.0

3.5 Simulation details

All the simulations were performed using the simulation software ESPResSo - **E**xtensible **S**imulation **P**ackage for **R**esearch on **S**oft **M**atter [37]. It was developed in Max-Planck-Institute for Polymer Research in Mainz in Germany. It is designed to perform Molecular dynamics simulations and analysis of bead-spring models with efficient calculations of the electrostatic interactions. The simulation consists of these three parts.

In the first part, the studied system is defined, i.e., the polymer chain is formed by 200 beads and an appropriate number of counterions (if there were any) is inserted in the simulation box.

The second part is the warm-up. Some particles may overlap in randomly created systems what leads to a very high energy of the system. The warm-up procedure prevents the start-up problems with small separation between beads. During the warm-up loop, all the particles interact by WCA potential, thus there are only repulsive interactions between them. This potential is also modified, that is, below a certain distance the forces are taken constant (it is so called "force cap"). [37] When the given minimum distance between beads is reached, the warm-up loop is stopped and force cap is switched off.

After the warm up the interaction potentials defined in sec. 3.3 are included into the simulation. The third part of the simulation consists of the integration loop and data

analysis. Information about conformations, for which the persistence length is calculated, is stored after the equilibration of the system. Time needed for the equilibration is determined from time evolution of total energy. It is set to $\tau_{\text{equi}}=60000$. After this time, the total energy fluctuates around a constant value. In Figure 3.3 the time evolution of total energy from the beginning of simulation is shown. The equilibration time is marked with the arrow.

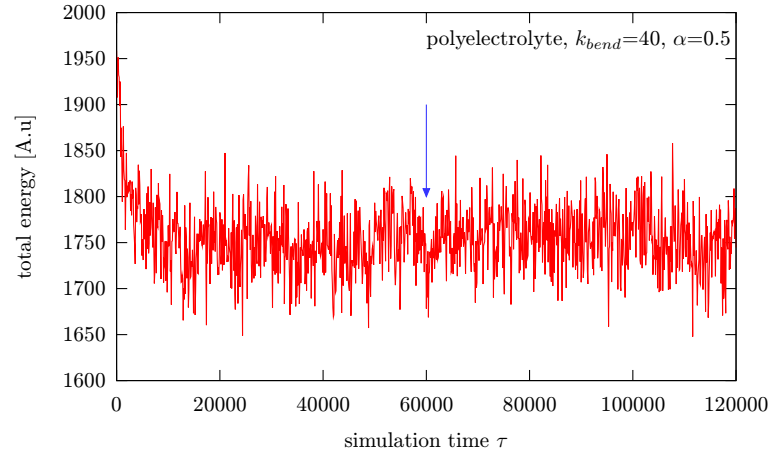


Figure 3.3: The time evolution of total energy in the simulation of polyelectrolyte. Only about 1/4 of the whole simulation run is shown. The equilibration time is marked with the arrow

4. Results and discussion

4.1 Persistence length of neutral polymers

First we took the neutral polymer as a reference system and we analyzed its persistence length l_p^n . The persistence length was calculated from the correlation function:

$$\frac{\langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle}{\langle l^2 \rangle} = \langle \cos(\theta_{(i,i+j)}) \rangle = \exp\left(-\frac{j}{l_p^n}\right). \quad (4.1)$$

The persistence length was obtained by fitting an exponential function (eq. 4.1) to the calculated correlation function.

We studied the relation of l_p^n to the bending constant of the bond-angle potential (eq. 3.10). Because the used bond angle potential 3.10 is the same functional form as the one in eq. 2.16 we can easily obtain using eq. 2.17 that the relation between l_p^n and the bending constant is:

$$l_p^n = \frac{k_{\text{bend}}}{k_B T}. \quad (4.2)$$

The dependence of l_p^n on the bending constant is plotted in Fig. 4.2.

The data points were fitted by function $f(k_{\text{bend}}) = A \cdot k_{\text{bend}}$. Within the accuracy of the fit the resultant slope equals to unity. This result confirms the constant of proportionality between the persistence length of the neutral polymer and the parameter of bond-angle potential.

To illustrate how the value of persistence length affects the conformation of neutral polymers, we show in Figure 4.1 three simulation snapshots of polymers with various bending rigidity ($k_{\text{bend}}=0, 6.4, 48.0$).

Figure 4.1: The neutral polymers with various bending rigidity (from right to left: $k_{\text{bend}}=0, 6.4, 48.0$).

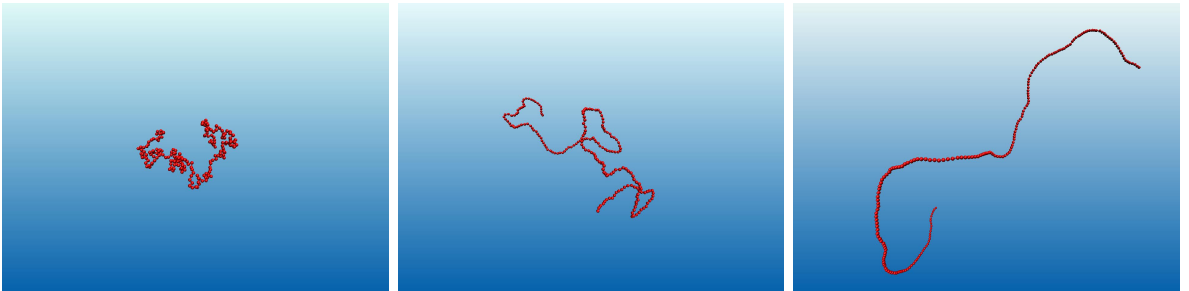
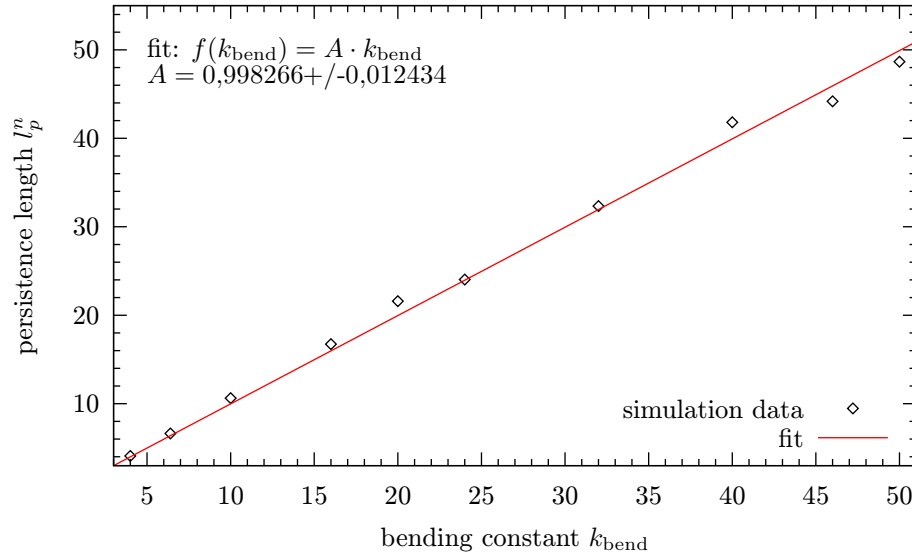


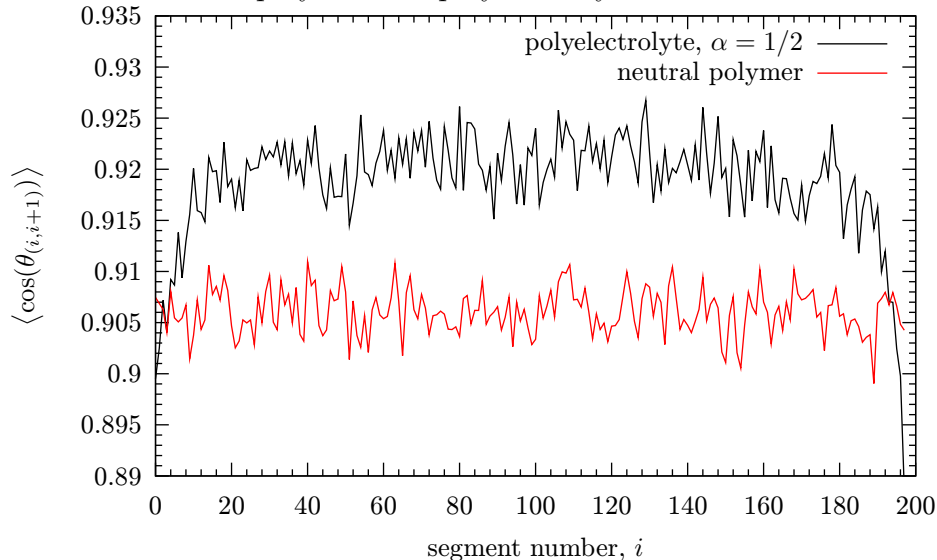
Figure 4.2: The persistence length of neutral polymer as a function of bending constant



4.2 The end-effects of polyelectrolytes

If the bond vectors in eq. 4.1 are adjacent vectors (the distance $j = 1$), from this equation the average cosine of the complementary angle to the bond angle, $\langle \cos(\theta_{(i,i+1)}) \rangle$, is obtained. The average cosine of angle θ as a function of the position in the chain for a neutral polymer and a polyelectrolyte is shown in Fig. 4.3. In simulations of both chains we set the bending constant $k_{\text{bend}} = 10.0$. The degree of ionization of the polyelectrolyte was $\alpha = 0.5$. It can be seen that in the ends of the polyelectrolyte chain the values of

Figure 4.3: The average cosine of the complementary angle as a function of the position in the chain for the neutral polymer and polyelectrolyte



$\langle \cos(\theta_{(i,i+1)}) \rangle$ differ from the values in the internal part of the chain, which does not happen in the case of the neutral polymer. In literature deviations at the ends of the polyelectrolyte chain are referred to as the end-effects. They are caused by the difference of the electrostatic potential along the chain. In the middle of the chain the charged

monomer units interact with all charged species around and the surrounding electric field is symmetrical. The interaction partners for charges placed at the ends of the chain are not distributed uniformly and it leads to different behaviour of the ends of the chain. The simulations show that end-effects increase with increasing degree of ionization of polyelectrolytes (i.e. with increasing linear charge density).

To avoid the influence of the end-effects when determining the persistence length, the scalar product of bond vectors (4.1) was computed only from the middle part of the chain, where the $\langle \cos(\theta_{(i,i+1)}) \rangle$ fluctuates around a constant value (see Fig. 4.3). The computation of $\langle \cos(\theta_{(i,i+1)}) \rangle$ was started at position $i = 20$ and the length of the chain under consideration was 160 monomer units it means the last 20 monomer units in the end were also left out from the calculations. The length of the excluded ends of the chain (20 monomer units) was chosen empirically by analyzing the dependences illustrated in Figure 4.3 for all chains studied in this work.

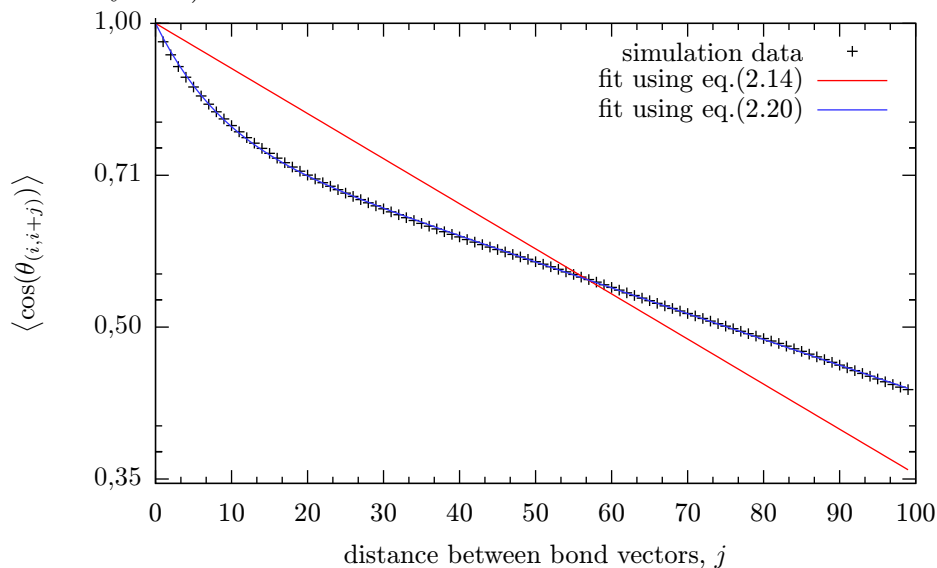
4.3 Persistence length of polyelectrolytes

We studied the polyelectrolytes with degrees of ionization $\alpha = 1/3, 1/4, 1/6$ and various bending rigidities. The orientation correlation function $\langle \cos(\theta_{(i,i+j)}) \rangle$ was calculated for every pair of bond vectors separated by certain distance j (maximum distance was 100).

The orientation correlation function of the polyelectrolyte with the degree of ionization $\alpha = 1/3$ and $k_{\text{bend}} = 28.0$ is plotted in Fig. 4.4. It is apparent, that the $\langle \cos(\theta_{(i,i+j)}) \rangle$ does not follow the single exponential decay (the red line in Fig. 4.4). In contrast to the neutral polymer, the persistence length of the semiflexible polyelectrolyte can not be simply defined as the decay contour length of angular correlations.

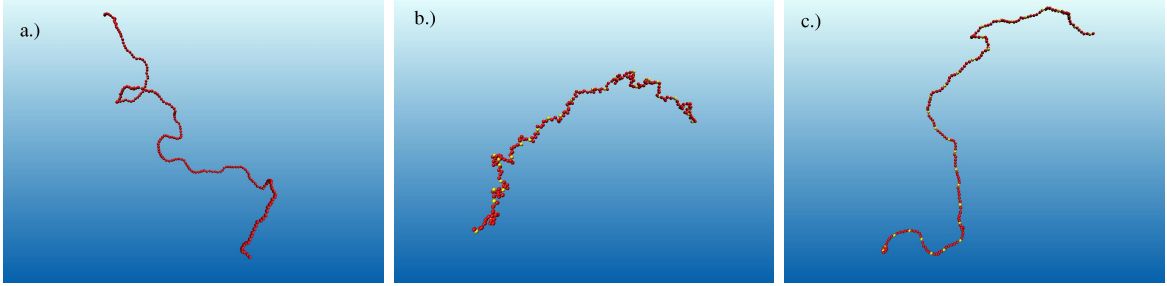
The simulation data can be reasonably well fitted by the model of Manghi and Netz (using equation 2.21).[29] They predicted, that at small length scales the behaviour of semiflexible polyelectrolyte is ruled by the intrinsic persistence length and the effect of long ranged Coulomb interactions appears at larger length scales.

Figure 4.4: The orientation correlation function of polyelectrolyte as a function of distance between the bond vectors (polyelectrolyte: $\alpha = 1/3, k_{\text{bend}} = 28.0$) (semilogarithmic plot with logarithmic y-axis)



The influence of the Coulomb interactions and the intrinsic stiffness of the chain on its rigidity is illustrated by simulation snapshots in Fig. 4.5. The chain in Fig.4.5 a.) and c.) have the same bending constant $k_{\text{bend}}=10.0$, but the first one is the neutral chain and the the other one is the polyelectrolyte. In Fig.4.5b.) and c.) are polyelectrolytes with the same degree of ionization ($\alpha=1/6$), but they differ in the value of k_{bend} (fig. b.): $k_{\text{bend}}=0$, fig. c.): $k_{\text{bend}}=10.0$).

Figure 4.5: The influence of the Coulomb interactions and the intrinsic stiffness of the chain on its rigidity. From the left to the right: neutral polymer ($k_{\text{bend}}=10.0$), polyelectrolyte(FJC, $\alpha=1/6$), polyelectrolyte($k_{\text{bend}}=10.0$, $\alpha=1/6$)



The same two length scale behaviour was found for all the correlation functions of simulated polyelectrolytes. Therefore all the simulation data were fitted using equation 2.21 and the obtained parameters are summarized in Table 4.1. The obtained values of l_p^0 as a function of the bending constant are shown in Fig. 4.6 .

We studied the relation between the intrinsic persistence length and the bending constant. According to the relation 4.2 the expected dependence between l_p^0 and k_{bend} is valid also between l_p^0 of polyelectrolyte and the persistence length of neutral chain. For illustration, there is drawn in Figure 4.6 the guideline with the slope of unity, which represents the predicted ideal case, where the l_p^0 corresponds to k_{bend} (or l_p^n). The values of l_p^0 from simulations increase linearly and the constant of proportionality is unity within the accuracy for every polyelectrolyte.

Table 4.1: The parameters obtained from fitting the simulation data

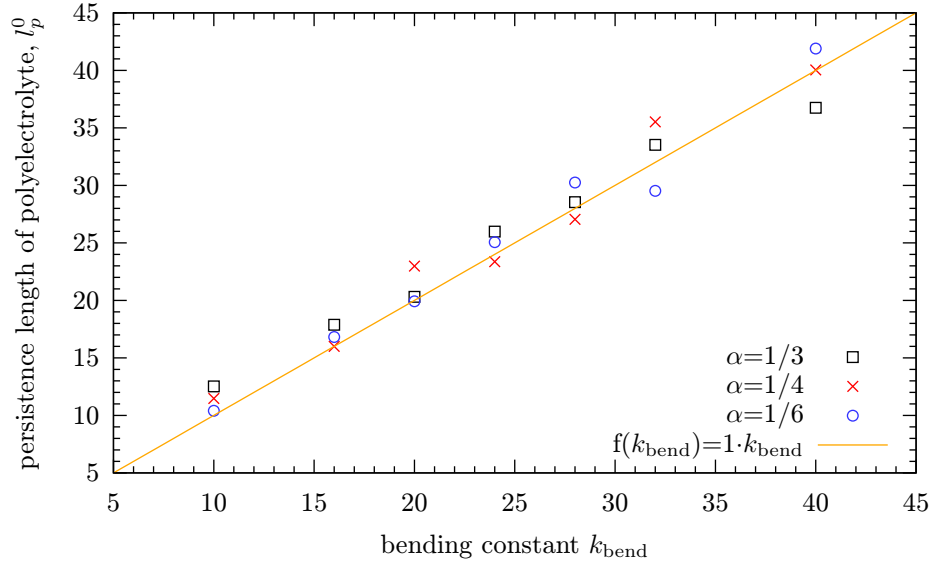
k_{bend}	$\alpha = 1/3$			$\alpha = 1/4$			$\alpha = 1/6$		
	B	l_p^0	l_p^e	B	l_p^0	l_p^e	B	l_p^0	l_p^e
10.0	0.612	12.523	220.188	0.588	11.471	125.976	0.530	10.399	89.105
16.0	0.698	17.883	157.256	0.696	16.002	98.305	0.586	16.816	94.545
20.0	0.756	20.312	116.879	0.649	22.982	166.460	0.645	19.919	89.376
24.0	0.741	25.980	173.954	0.748	23.367	98.184	0.651	25.066	90.998
28.0	0.778	28.544	141.480	0.765	27.047	114.273	0.608	30.245	148.191
32.0	0.779	33.522	140.464	0.665	35.522	262.662	0.770	29.525	73.131
40.0	0.843	36.750	126.193	0.781	40.040	128.438	0.606	41.898	183.301

The values of electrostatic persistence length do not exhibit any trend and we can not say how their values vary with the various bending constants. They are of the same order of magnitude as the length of the part of the chain used for calculation of the scalar product. To analyze the long length scale behavior of the correlation function one needs

either longer polyelectrolyte chain or a polyelectrolyte with smaller degree of ionization, for which l_p^e would be smaller. The simulations of longer polyelectrolytes are in progress and the work will be continued.

Thus, it was verified that the prediction of Manghi and Netz is consistent with the orientational correlation function obtained from simulations.

Figure 4.6: The values of l_p^0 of polyelectrolytes with various degree of ionization as a function of the bending constant.



5. Conclusions

In this thesis the results of simulations of polyelectrolytes and neutral polymers were analyzed in order to study their persistence length as a measure of their stiffness.

The conformation of a neutral polymer can be described by one persistence length which is proportional to the bending modulus of the semiflexible chain. It was verified in simulations that the persistence length of a neutral polymer is given by the ratio of the constant of the bending potential and the thermal energy.

The study of behaviour of polyelectrolytes in salt-free solution has shown that by the determination of their properties one has to take into account the end-effects. We introduced our own method how to avoid the influence of these unfavourable effects.

The orientational correlations of segments of polyelectrolyte chains are ruled by intrinsic stiffness of the chain as well as the electrostatic interactions. The prediction of Manghi and Netz that the orientation correlation function has a double exponential decay was confirmed. At small length scales the conformational behaviour of polyelectrolytes is dominated by the intrinsic persistence length. It is identical with the persistence length of neutral polymer. The value of the electrostatic persistence length which describes the behaviour at larger length scales was found to be comparable to the length of the simulated chains. Further investigation of the electrostatic persistence length will require simulations with longer polyelectrolytes.

The study continues and at the present time the simulations of polyelectrolytes with lower degree of ionization and longer chains than in this thesis are analyzed. The next work will include also the study of polyelectrolytes in salt solutions.

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