Seminar II

The origin of attractive interactions between DNA molecules

Author: Matej Kanduč
Mentor: prof. dr. Rudi Podgornik
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Abstract

In this seminar I present the phenomenon of DNA condensation into packed structures in presence of multivalent counterions. The problem of DNA attractive force cannot be described by standard mean-field approach. The attraction is a consequence of counterion correlations at small DNA-DNA distances. Correlations can be incorporated in the mean-field theory with additional free parameters due to specific geometry of the system. Correlation effect can be introduced also with strong-coupling theory, where counterions are strongly correlated due to strong electrostatic energy.

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1 Introduction

The structure of DNA double helix, with its complementary base-pairing, is one of the greatest discoveries in science in the 20th Century. It was also most dramatic, since, quite unexpectedly, the itself pointed to the way in which a DNA molecule might replicate itself, and hence revealed the ”secret of life” [1].

Deoxyribonucleic acid (DNA) is a nucleic acid that contains the genetic instructions for the development and function of living organisms. All living things contain DNA, with the exception of some viruses with RNA genomes. The main role of DNA in the cell is the long-term storage of information. It is often compared to a blueprint, since it contains the instructions to construct other components of the cell, such as proteins and RNA molecules.

Unlike enzymes, DNA does not act directly on other molecules; rather, various enzymes act on DNA and copy its information into either more DNA, in DNA replication, or transcribe it into protein [2].

Whole length of stretched DNA molecule ranges from several microns in viruses, several millimeters in bacteria and up to meters in higher organisms such as animals and plants.
In eukaryotes such as animals and plants, DNA is stored inside the cell nucleus, while in prokaryotes such as bacteria, the DNA is in the cell’s cytoplasm. The importance of DNA compaction phenomenon is irrefutable, because in living organisms DNA is stored and functions in a compact form of various densities. In the most extreme cases, up to a hundred times higher molecular density compared to the unfolded DNA form is achieved [3]. Two types of DNA compaction can be clearly distinguished in nature: compaction realized in viruses, and compaction of DNA by nanoscale three-dimensional templates such as histones (special proteins). This is not an easy work, because DNA molecules are highly charged (one elementary charge $e_0$ per 0.17 nm). Mechanisms of these compactions are not clearly understood yet, because many different processes are involved. In this seminar we will focus on one important topic of the whole story, namely, how two highly charged DNA molecules can actually attract themselves.

2 Structure of DNA

DNA molecule is a long polymer made from repeating units called nucleotides. Each nucleotide is made of three parts, namely sugar, phosphate, and the base. The sugar in DNA is the pentose (five carbon) sugar 2-deoxyribose. The sugars are joined together by phosphate groups that form phosphodiester bonds between the third and fifth carbon atoms in the sugar rings. The base is attached to the first carbon atom of the sugar.

Each base can be one of four kinds that are found in DNA, namely adenine (abbreviated A), cytosine (C), guanine (G) and thymine (T). Nucleotides connected via phosphate groups are said to form one strand of DNA. The second strand of DNA is held together with the first one by hydrogen bonds between the bases. Here each type of the base on one strand forms a bond with just one type of base on the other strand. This is called complementary base pairing. Adenine bonds with thymine and guanine with cytosine [4]. The sequence of nucleotides represents a genetic code.

![DNA structure](image)

Figure 1: (a) Four nucleotides in the DNA sequence, showing their sugar (S), phosphate (P), and bases (A, T, C, G). (b) Two strands of DNA form a helical structure.

Double stranded DNA is not straight ladder, but is helix-like shaped. The reason that the two DNA strands are twisted in helix is that adjacent base pairs attract themselves.
This attraction is due to van der Waals force and hydrophobic force. Unlike sugars and phosphates, bases are not soluble in water and so tend to avoid water molecules as much as possible in the way that they come closely together, living no room for water molecules between them. The distance between adjacent sugars or phosphates in DNA chain is 0.6 nm and it cannot change much, because the bases are chemically rigid with strong, inflexible bonds between the atoms. If adjacent bases get closer together, they must twist about an imaginary vertical axis into the shape of helix. The twist angle between adjacent nucleotides is approximately 36°.

As the DNA strands wind around each other, they leave gaps between each set of phosphate backbones. There are two of these grooves twisting around the surface of the double helix: one groove is 2.2 nm wide and the other 1.2 nm. The larger groove is called the major groove, while the smaller, narrower groove is called the minor groove (Fig. 1b). These grooves play very important role as binding places for proteins as well as other smaller ions that effect the electrostatics as we will see later.

3 DNA condensation

Under physiological conditions in 0.1 molar solution of NaCl, DNA molecule is highly negative charged because each phosphate group dissociate, leading to charge density of one negative elementary charge, $-e_0$, per 0.17 nm of DNA length. This charge is screened due to mobile positively charged salt counterions and negatively charged coions. A single DNA molecule in such a solution takes on the form of a disordered coil. The reason of disordering are thermal fluctuations that prevent straight form of long molecule. Relatively straight segments of molecule are about 50 nm long (persistence length). If any lengths of the molecule come within 1 nm of one another, they strongly repel. This is seems quite obvious, since DNA molecule is highly charged.

But under different conditions-in a highly dilute aqueous solution that also contains a small concentration of polyvalent cations-the same DNA molecule condenses into tightly packed, circumferentially wound torus [5]. This seems quite unexpectedly. This dramatic decrease in the volume occupied by DNA molecule is called DNA condensation.

![Figure 2: The genome of the λ bacteriophage is wound circumferentially with local hexagonal packing.](image)

Indeed, according to widely used mean-field theory of electrostatic interactions between macro-ions (the Poisson-Boltzmann theory)-two parallel cylinders with the same line
charge always should repel each other [5].

Consider the DNA of bacteriophage T4 (bacterial virus) that is 50 µm long. In dilute solution the disordered coil is about 1 µm large. When packed inside the T4 phage head, the DNA has an outer radius of only 50 nm.

However, a series of experiments on charged biopolymers, including DNA, F-actin fibers, microtubules and aggregating viruses, indicate that in the presence of small amounts of polyvalent salts, the electrostatic interaction is either attractive—in violation of basic Poisson-Boltzmann theory—or so weakly repulsive that attractive forces of a different origin (e.g., hydrophobic or hydration interactions) overwhelm electrostatic repulsion [6]. DNA condensation has been observed by a variety of techniques that detect changes in polymer size or chirality, including various forms of electron microscopy, total intensity and dynamic laser scattering, sedimentation, viscometry, linear optical and circular dichroism, and also fluorescence microscopy with which the condensation of single large T4 DNA molecule was observed [7].

Studies indicated that in aqueous solutions at room temperature, a cation valence of +3 or greater is necessary to cause condensation. Such cations are e.g. the naturally occurring polyamines spermidine(3+) and spermine(4+) and inorganic cation Co(NH$_3$)$_6^{3+}$. Recent results show that divalent Mn$^{2+}$ and Cd$^{2+}$ can also produce toroidal condensates of DNA [7].

4 Mean-field approach

Most investigation of charged soft matter deal with mean-field theory that is related to Poisson-Boltzmann (PB) equation. This theory relies on the following assumptions: (1) the only interactions to be considered are coulombic interactions between charged bodies, (2) permanent and induced dipole-dipole interactions are neglected, (3) the charges are taken as point-like objects (4) the aqueous solution is modelled as a continuous medium with a dielectric constant $\varepsilon$, and (5) the electrostatic potential that each ion sees is a continuous function that depends in a mean-field way on all the other ions [8].

PB equation can be derived from very simple heuristic approach. Consider an ionic solution with two ionic species having positive and negative charge densities of $e_0z_+n_+(r)$ and $e_0z_-n_-(r)$, respectively, where $z_+ > 0$ is the valency of cations and $z_- < 0$ of the anions. The total charge density at each point is then $\rho = e_0(z_+n_+(r) + z_-n_-(r))$.

At any point, the relation between the potential $\phi$ and the charge density $\rho$ is given in terms of the Poisson equation

$$\nabla^2 \phi = -\frac{1}{\varepsilon\varepsilon_0}\rho(r). \quad (1)$$

As each ionic species is in thermodynamic equilibrium, its corresponding density has a Boltzmann distribution, and so we get Poisson-Boltzmann (PB) equation for the potential $\phi$:

$$\nabla^2 \phi = -\frac{e_0}{\varepsilon\varepsilon_0} \sum_i z_i n^0_i e^{-\beta e_0 \varepsilon_0 \phi}, \quad (2)$$

where $n^0_i$ is the reference density of $i^{th}$ species taken at zero potential, $\phi \to 0$. This is a very useful analytical approach with many applications. Because the equation is non-linear, it has closed-form analytical solutions only for a limited number of simple charged boundary conditions. Like any approximation, the PB has its limits of validity; however, in physiological conditions for monovalent salt solution ($z_\pm = \pm 1$), it describes
rather well the ionic distributions. But it misses some important features associated with multivalent counterions [8]. In the case of monovalent salt solution (e.g., Na\(^+\) Cl\(^-\)), where \(z_\pm = \pm 1\) and \(n_+^0 = n_-^0 = n^0\), we get

\[
\nabla^2 \phi = \frac{-2en_0}{\varepsilon\varepsilon_0} \sinh \beta e \phi.
\]

(3)

For weak potential \(e\phi(r)/kT \ll 1\), i.e., for distances \(r\) large enough the PB equation reduces to its linearized form, the Debye-Hückel equation

\[
\nabla^2 \phi = \kappa^2 \phi.
\]

(4)

The Debye screening length is \(\kappa^{-1} = (\beta e^2 n_0 z^2 / \varepsilon\varepsilon_0)^{-1/2}\). In physiological conditions of 0.1 molar NaCl solution, \(\kappa^{-1} \approx 1\) nm. Broadly speaking, this screened potential varies like \(r^{-1} \exp(-\kappa r)\).

### 4.1 Homogenously charged cylinders

Consider a very simplified model of two straight parallel DNA molecules, treated as two parallel homogenously charged cylinders of radius \(a\) and interaxial distance \(R\).

The boundary condition at the surface of both cylinder is

\[
\nabla_r \phi \bigg|_{\partial} = \frac{\sigma}{\varepsilon\varepsilon_0}.
\]

(5)

Simplified equation Debye-Hückel equation (4) can be solved analytically for this case in some limits [9]. The force in this approximation is always repulsive.

We can also solve an exact PB equation (3) for monovalent salt numerically. Results of free energy, shown in Fig. 3, indicate monotonically decreasing function of interaxial distance \(R\). Because the system tends to state with smaller free energy the result is the repulsive force between the cylinders in the case of PB equation.
4.2 Kornyshev-Leikin theory

In 1997 Kornyshev and Leikin extended the theory of interaction between helical macromolecules. They found that details of surface charge pattern may determine the specificity and energetics of DNA aggregation. Their theory explicitly describes fixed, adsorbed, and condensed charges while using the linearized Debye-Hückel model for diffuse cloud of free ions [10].

The theory considers interaction between two long, parallel macromolecules in an aqueous solution. Each molecule has cylindrical water-impermeable inner-core and discrete charged and/or solvated charges located on a coaxial cylindrical surface (Fig. 4). These charges may form a helical or any other pattern.

Figure 4: (a) DNA structure based on crystallographic coordinates. (b) Schematic illustration of DNA surface charge pattern. Negatively charged helical lines of phosphates and positively charged counterions adsorbed in the grooves form stripes of positive and negative charges.

Inside the inner cores, the potential satisfies the Laplace equation,

$$\nabla^2 \phi^{\text{in}}(r) = 0.$$  \hspace{1cm} (6)

Outside the cores, it obeys the linear Poisson-Boltzmann equation,

$$\nabla^2 \phi^{\text{out}}(r) = \kappa^2 \phi^{\text{out}}(r) - \frac{1}{\varepsilon \varepsilon_0} \rho(r).$$  \hspace{1cm} (7)

Here, $\kappa$ is screening parameter and $\rho(r)$ is fixed charged density. The boundary conditions are

$$\phi^{\text{in}}(a) = \phi^{\text{out}}(a),$$  \hspace{1cm} (8)

and

$$\varepsilon' \nabla_r \phi^{\text{in}}(r)_{r=a} = \varepsilon \nabla_r \phi^{\text{out}}(r)_{r=a},$$  \hspace{1cm} (9)

where $\varepsilon$ and $\varepsilon'$ are dielectric constants of water and of the inner cores respectively. Despite its well-known limitations, the linearized Poisson-Boltzmann equation captures the qualitative force features and in many cases yields reasonable quantitative estimates.

Exact solution of above equations for this system is very complicated and therefore, we mention only some results here. Exact expression for the interaction energy has the form

$$\frac{E_{\text{int}}(R)}{L} = u_{\text{cyl}} + u_{\text{self}} + u_{\text{cross}}.$$  \hspace{1cm} (10)
This interaction energy is analogue to free energy $F$, so the force between cylinders can be obtained as its negative derivative with respect to distance $R$. Equation (10) distinguishes three components of the interaction energy: (i) $u_{\text{cyl}}$ corresponds to the energy of interaction of two homogeneously charged cylinders; (ii) $u_{\text{self}}$ is self-correlation energy, which is due to correlated discrete surface charge distributions on each molecule; (iii) $u_{\text{cross}}$ is cross-correlation energy, which is due to nonrandom alignment of discrete charges on the opposing molecules.

The theory of counterion condensation and most models of attraction between polyelectrolytes presume that all counterions are freely mobile. Such an assumption may hold for alkali metal ions. It is doubtful already for divalent alkali-earth ions. It is known, that some counterions possess strong chemical affinity to specific sites on the DNA surface [11]. Based on experimental evidence, the assumption can be brought into the model that DNA-condensing counterions are adsorbed and form a rigid pattern.

In this theory the DNA can be implemented as an ideal double helix with two thin continuous spirals of negative charges (DNA phosphates) and two spirals of positive charges in the middle between the phosphate spirals (cations adsorbed in the grooves). Here an additional parameters can be introduced, namely $\theta > 0$ that represents the fraction of phosphate charges neutralized by the adsorbed cations. Fraction of these counterions $0 \leq f \leq 1$ are adsorbed in minor groove and the rest $(1 - f)$ in major groove.

![Figure 5: Effect of counterion coverage, $\theta$, on DNA condensation at 30% counterion partitioning in the minor groove and 70% in the major groove.](image)

From calculating interaction energy (Fig. 5) one finds that DNA helices may attract each other as a result of counterion binding in DNA grooves that produces axial separation of positive and negative charges. Negatively charged strands may come close to positively charged grooves of the opposing molecules so that the attraction between them keeps the molecules together. This is realised at defined azimuthal orientation of one DNA molecule with respect to the other. This works as an electrostatic zipper running along the whole length DNA-DNA contact. Counterion adsorption onto phosphate strands reduces the attraction due to weaker charge separation, consistent with the observation that $\text{Ca}^{2+}$
and Mg\(^{2+}\), which have high affinity to phosphates, do not induce DNA condensation [11]. The model also suggest that DNA condensation will take place at 70%–30% partitioning of ions between the major and minor grooves. Indeed, most DNA-condensing ions are known to bind preferentially in the major groove. The condensation becomes possible when 0.9 < θ < 1.1, as observed from Fig. 5. This is in agreement with experimental evidence, that condensation appears when more than 90% of DNA charge is compensated [5].

The energy depth at optimal conditions is \(\sim 10k_B T/\text{persistence length}\), close to the estimate based on osmotic stress measurements.

However, Kornyshev-Leikin theory predicts that the adsorption of cations into the major groove strengthens the DNA-DNA attraction. But these calculations were made for the interaction energy between ideal DNA molecules, where attraction was due to register of phosphate strands and grooves on DNA. Real DNAs however are not ideal spirals. Non-ideality of the DNA structure, coming from the sequence-dependent variation of the twist angle between the nearest base-pairs, hampers this strand-groove register. Twist angle between adjacent nucleotides is not exactly 36°, but varies in range from 28° to 42° [16]. This has a profound effect on intermolecular interaction: it appears that for long randomly sequenced torsionally rigid DNA the electrostatic attraction turns into repulsion. But finite twist elasticity of the DNA backbone allows DNA to relax this twist sequence-dependent mismatch and to restore the strand-groove zipper-like register. This makes the DNA-DNA electrostatic interaction attractive again, although reduced as compared to that between the ideal strands [13].

5 Strong counter-ion correlations

Although mean-field approach of Kornyshev and Leikin with additional degrees of freedom for counterions leads to satisfactory results for DNA-DNA attractive interaction, it is known that it could not describe all details of interactions. Thus, the precipitation induced by trivalent or tetravalent ions is not a consequence of the intrinsic structure and flexibility of DNA, but is a common feature of a polyelectrolyte solution [14].

Oosawa was the first to study correlated long-wavelength thermal fluctuations of the condensed counterion density along a pair of rod-like macro-ions [6, 15]. By including correlations between the fluctuations of the two rods, he obtained a nonspecific attractive contribution to the force. But because this fluctuation term was computed as a lowest-order perturbation correction to the mean-field repulsive force, it could not be concluded whether the overall interaction was indeed attractive.

The second mechanism, which has been investigated more recently, focuses on the short-range electrostatic correlations between the counterions of the two clounds. This form of attraction is related to forces explored in earlier work on charged planar surfaces, which suggested that, at low enough temperature, counterions should form a self-ordered two-dimensional Wigner crystal, and that the two mobile surface lattices should attract each other [17, 19]. This is also known as strong-coupling theory of electrostatics and is valid in the opposite limit than mean-field theory.

5.1 Strong-coupling limit

The main idea of strong-coupling theory is that electrostatic interaction between surface with charge density σ and counterions with valency q is much larger than thermal energy.
In this regime counterions essentially form a quasi 2D layer as their separation, $2a_\perp$, at surface is much larger than their distance $\langle z \rangle$ from the surface (Fig.6).

Figure 6: Regime of 2D counterion layer at charged surface where distance between counterions $2a_\perp$ becomes much larger than their distance from the surface.

The structure of such a layer is dominated by mutual repulsion between counterions, which freeze out lateral degrees of freedom [17]. But what is the criterium for such a regime, that $a_\perp \gg \langle z \rangle$? From charge neutrality condition we get

$$\pi a_\perp^2 = \frac{e_0 q}{\sigma}. \quad (11)$$

The average potential energy $E_z e_0 q \langle z \rangle$ of the system is of the order of thermal energy $kT$

$$\frac{\sigma}{2\varepsilon\varepsilon_0} e_0 q \langle z \rangle = kT. \quad (12)$$

We define the square of ratio of $a_\perp$ and $\langle z \rangle$ as

$$\Xi = \frac{1}{2} \frac{a_\perp^2}{\langle z \rangle^2} = \frac{(e_0 q)^3 \sigma}{8\pi(\varepsilon\varepsilon_0 kT)^2}, \quad (13)$$

which is known as coupling parameter [19]. The strong-coupling regime criterium $a_\perp \gg \langle z \rangle$ is analogue to $\Xi \gg 1$.

It can be easy seen that in strong-coupling limit two charged surfaces with counterions between them attract themselves. Because the system is electrically neutral, each surface feels twice as much opposite charge of counterions as the same charge of the other surface. So, the electrostatic component to pressure is attractive

$$p_e = -\frac{\sigma^2}{2\varepsilon\varepsilon_0}. \quad (14)$$

The other component is osmotic, and is due kinetic energy of counterions, and is always repulsive

$$p_{\text{osm}} = \frac{kT\sigma}{ed}. \quad (15)$$

The total pressure between the surfaces is

$$p = p_{\text{osm}} + p_e = \frac{kT\sigma}{ed} - \frac{\sigma^2}{2\varepsilon\varepsilon_0}, \quad (16)$$

and it can be attractive (negative) if separation between the walls $d$ is large enough.

Direct comparisons with experiment are problematic because measurements necessarily include contributions from many nonelectrostatic interactions.
5.2 Strong coupling in DNA-DNA interaction

Now we turn our attention back to DNA molecules again. We want to extract the effect of strong coupling limit on the interaction of two parallel DNA molecules. For simplicity, we assume that DNA molecules are infinitely long and homogenously charged cylinders and have a hard-core excluded-volume interaction. Because strong-coupling is valid only on small distances from charged surface, we suppose only counterions as mobile particles in the system. Here we neglect the presence of oppositely charged coions of the salt because their concentration is much smaller in the vicinity of negatively charged surface. The amount of counterions is defined so that positive counterions compensate negative charge of DNA molecule.

In the table below we see calculated values of coupling parameter $\Xi$ for various types of counterions at the DNA surface.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$\langle z \rangle$ [Å]</th>
<th>$\Xi$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Na$^+$)</td>
<td>2.4</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>2 (Mn$^{2+}$)</td>
<td>1.2</td>
<td>22.4</td>
<td>8.2</td>
</tr>
<tr>
<td>3 (spermidine)</td>
<td>0.8</td>
<td>75.6</td>
<td>12.3</td>
</tr>
<tr>
<td>4 (spermine)</td>
<td>0.6</td>
<td>179</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Monovalent counterions with $\Xi = 2.8$ do not satisfy the criterium $\Xi \gg 1$, and so strong-coupling theory is not relevant for them. This is also a reason, why nothing special happens in monovalent salt. But totally different situation comes in the case of 3- and 4-valent counterions.

Because in strong coupling case counterions do not interact with themeselves we can easily calculate partition function for one counterion

$$e^{-\beta F_1} = \int e^{-\beta W} dV$$

Here, energy $W$ is composed of electrostatic energy between counterion and two cylinders and between cylinders themselves

$$\beta W = -Q \ln R + 2Q (\ln r_1 + \ln r_2),$$

Figure 7: (a) Two identical and parallel cylinders with radius $a$ are considered at axial separation of $R$. The uniform surface charge of cylinders is compensated by the total charge of counterions. (b) Illustrated distances from axis of cylinders.
where we have introduced $Q = \lambda q \varepsilon_0 N / 2\pi \varepsilon \varepsilon_0$, also known as Manning parameter (see above table). Here $r_1$ and $r_2$ are distances from counterion to cylinders (Fig. 7).

$$r_{1,2} = \sqrt{(x \pm R/2)^2 + y^2}$$

(19)

Strong-coupling free energy is then expressed as [17]

$$\frac{\beta F_{SC}}{N} = -Q \ln R - \ln \int_V e^{-2Q(\ln r_1 + \ln r_2)} dx dy$$

(20)

Figure 8: (a) Strong coupling free energy of two-cylinder system as a function of axial distance $R$. Plots are made for four different valencies $q$. (b) Force between the cylinders as calculated from the free energy.

The free energy (Fig. 8) exhibits a long-range attraction and a local minimum at small separations. As mentioned before, the results are not relevant for monovalent counterions ($q = 1$) and for larger separations of cylinders. Here diameters of counterions are not taken into account which can also results on force dependance. But this simple model illustrates how counterion-correlations lead to attractive interaction.

The electrostatic phenomena behind the behaviour of macro-ions in solution are only recently being indentified and understood [5]. We can understand some of this phenomena within the context of mean-field theory, whereas other phenomena require the explicit inclusion of correlations.

These results suggest that shorter-range correlations may provide the key to the attractive interaction of DNA.

6 Some results from MC simulations

The effective DNA-DNA interaction force was also calculated by computer simulations with explicit multivalent counterions and monovalent salt [14]. It was shown, that ionic cloud may not only compensate the macroion charge but even exceed it, resulting in an opposite sign of the electrostatic potential at some distances from DNA surface. Besides this, there is a competition between the multivalent and monovalent counterions to the DNA surface, depending on both species concentration. The multivalent ions tend to replace the monovalent counterions when their concentration is increased. Results on figure 9 show, that there is no attraction between two helices in the case of only monovalent salt. For divalent counterions there appears very small attraction, since for trivalent and tetravalent counterions there exists obvious attraction.
Figure 9: DNA-DNA interaction force $F/F_0$ versus intermolecular separation distance $R$ for 65 mM of tetravalent salt and 25 mM of monovalent salt solution. $F_0 = kT/\text{pitch}$. DNA radius is taken to be 1.1 nm.

for a range of distances $R$ from 0.5 to 2.5 nm. At distances shorter than 0.5 nm a strong repulsion between DNA solvation shells exists. This is in agreement with experimental evidence that in DNA condensates two neighboring molecules never approach each other more closely than 0.5 nm. As seen from Fig. 8, the strong-coupling limit gets attractive forces to much smaller distances $R$. But we must realize that no counterion dimensions were taken into account. Tetravalent ions have diameters of about 0.8 nm [14] and so excluded-volume effect becomes important when distance between cylinders is smaller than counterion diameter. In this case, excess accumulation of counterions in the intervening region between cylinders, which is favored energetically and leads to the strong-coupling attraction, is prohibited [17].

For distances larger than 2.5 nm the ion correlations are diminished and the force is repulsive as predicted by mean-field theory.

7 Conclusion

In this seminar we have tried to describe the phenomenon of DNA-DNA electrostatic attraction.

The forces in charged macromolecular systems are always a balance between repulsive forces of entropic origin and attractive forces of energetic origin. For many systems of chemical interest the repulsive forces dominate and the mean-field description provided by the Poisson-Boltzmann equation is adequate [20].

The main mechanism of attraction is ion-ion correlation effect that cannot be described by simple mean-field theory (PB). These attractive correlations are responsible for DNA condensation and also much more complex processes of compaction of DNA with proteins into chromosomes in higher organisms as well as many biochemical reactions with proteins.

There is no complete theory of counterion correlation effect. Since Kornyshev-Leikin
mean-field approach predicts successful results, it involves an artificial correlations due to included geometrical details with additional free parameters. According to experimental researches on other soft matter systems it became clear that geometry, ion type, details of the surface charges etc. are of secondary importance. The theory of strong coupling on the other hand predicts attraction independent of geometrical details, but it is relevant only for multivalent ions at small interaxial separations. Direct comparisons with experiment are problematic because measurements necessarily include contributions from many nonelectrostatic interactions. Therefore, numerical simulations are usually the main tools to compare analitical theories with them. One would hope that more simple approaches based on different perturbational schemes should suffice to capture the phenomenon at least semi-quantitatively.
References


