Wigner Crystal Model of Counterion Induced Bundle Formation of Rodlike Polyelectrolytes

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(Received 1 October 1998)

A simple electrostatic theory of condensation of rodlike polyelectrolytes under influence of polyvalent counterions is proposed. It is based on the idea that counterions form a Wigner crystal on a background of a bundle of rods. It is shown that, depending on a single dimensionless parameter, this can be a densely packed three-dimensional Wigner crystal or a two-dimensional crystal on the rod surfaces. For DNA the location of charge on the spiral results in a model of the one-dimensional Wigner crystal. It is also argued that the Wigner crystal idea can be applied to self-assembly of other polyelectrolytes, for example, colloids and DNA-lipid complexes. [S0031-9007(99)08957-7]

PACS numbers: 61.20.Qg, 61.25.Hq, 77.84.Jd

Many rodlike polyelectrolytes, such as double helix DNA [1], F-actin, microtubules, and tobacco mosaic virus [2] are known to self-assemble into bundles of parallel densely packed rods. All these macromolecules are negatively charged and their lateral association is induced by Z-valent cations where $Z \geq 2$. For DNA this phenomenon is called condensation and is studied in connection with the dense packing of viral DNA. According to the mean field Poisson-Boltzmann theory, two parallel rods should always repel each other. Two physical phenomena which are not included in this theory were suggested as possible reasons for the puzzling attraction [3–11]. When distance between rods is large their attraction is related to the correlation of thermal fluctuations of screening atmospheres of two rods. At smaller distances one should take into account that the Manning condensation of ions on the surface of rods leads to strong spatial correlations of ions or even to their crystallization. In this situation, two crystals with proper phases attract each other. Below I calculate the binding energy of a dense bundle and therefore talk only about the second mechanism. I also resolve an important contradiction in the literature. Most of the publications deal with two rods and calculate a pairwise force acting between them [3–9]. On the other hand, two recent publications [10,11] claim that bundles are formed by non-pairwise-additive interaction.

The first goal of this paper is to present a theory of attractive interactions of rodlike polyelectrolytes, based solely on electrostatic interactions. It considers formation of densely packed bundles in a very dilute solution of cylindrical rodlike molecules of the radius r and length $L \gg r$. It assumes that the cylindrical surface of a rod is negatively charged with the charge density $-e/b$ per unit length of the rod. Pointlike positive ions with the charge Ze are added to the solution.

The main idea of this paper is that a bundle of parallel rods can be considered as a uniform negative background at which condensed ions form the Wigner crystal (WCR). The cohesive energy of this crystal is the reason for the attraction and the bundle formation. (This idea is similar to the theory of matter in a superstrong magnetic field of a neutron star where electrons behave as negative rods and nuclei form the WCR on the background of electron bundles [12].) For the case in which ions cannot penetrate the rods, the binding energy of the bundle per rod is calculated below as the function of the dimensionless parameter Zb/r. The result is that for $Zb/r \gg 1$, the three-dimensional (3D) densely packed WCR is formed and interaction is not-pairwise-additive. In the opposite case, $Zb/r \ll 1$ the 2D WCR appears on the surface of each rod and the interaction becomes short-range pairwise. My results in the first case qualitatively resemble Ref. [11], while in the second case this paper is close to Ref. [9], where the idea of the surface WCR was originally suggested. None of these papers, however, produced simple analytical dependencies similar to those which I derive below using Zb/r as a large or small parameter of the theory.

The second half of this paper concentrates on the specifics of DNA where surface charges form a spiral. I show that this leads to the appearance of the 1D spiral-like Wigner crystal of ions on the surface of each rod. Interaction of such crystals may determine the DNA condensation. It is also argued that the idea of a WCR can be applied not only to the rods, but also to the self-assembly of many other different polyelectrolytes. I apply this theory to colloids and complexes of DNA with cationic lipid membranes.

Returning to the main problem of rods and pointlike counterions, I argue that for sufficiently large dimensionless parameter $Z\xi$, where $\xi = e^2/b\kappa k_B T$ and κ is the effective dielectric constant of the water-polymer system, rods condense in the maximum density cylindrical bundles of N parallel molecules. At large $Z\xi$ the charge of the bundle is almost completely compensated by the opposite charge of NL/b of positive ions which condense inside the bundle. To find a configuration of condensed ions, one can view the bundle as the uniformly charged cylindrical background. The potential energy of the Coulomb repulsion of ions in these conditions is much larger than their kinetic energy. Therefore, they form the WCR on the negative background. Assume first that N is so large that the radius of the bundle $rN^{1/2}$ is much larger than the lattice constant of the WCR R. In this case ions form a densely packed 3D crystal. One can easily calculate R from the condition that the charge of the Wigner-Seitz cell, R^3/br^2, equals Z. This gives

$$R \sim (Zbr^2)^{1/3}. \tag{1}$$

Comparing R with the bundle radius $rN^{1/2}$ one finds that the 3D case takes place at $N \gg N_c = (Zb/r)^{2/3}$. (In the opposite case $N \ll N_c$ ions form 1D crystal as shown below.) I assume that ions cannot penetrate rods. Then ions can fit in the free space between rods without strong deformation of the 3D crystal only at $R \gg r$. According to Eq. (1) this inequality means that $Zb/r \gg 1$. Now we see how the important parameter Zb/r appears in the theory. Assuming, for the beginning, that rods are narrow and weakly charged so that $Zb/r \gg 1$ one finds that $N_c \gg 1$ so that both situations $N \gg N_c$ and $N \ll N_c$ have to be considered.

The binding energy of a crystal per ion, ε_i, can be estimated as the energy of interaction of an ion with its Wigner-Seitz cell

$$\varepsilon_i \sim \frac{Z^2e^2}{\kappa R}. \tag{2}$$

Substituting R from Eq. (1) one obtains

$$\varepsilon_i \sim \frac{Ze^2}{\kappa b}(Zb/r)^{2/3} \qquad (Zb/r \gg 1; N \gg N_c). \tag{3}$$

If $N \ll N_c$, the bundle is narrow and the ions form a 1D WCR, lattice constant of which, R, is equal to Zb/N. Then, the energy of interaction of an ion with its Wigner-Seitz cell is

$$\varepsilon_i \sim \frac{Ze^2N}{\kappa b}\ln(N_c/N) \qquad (Zb/r \gg 1; N \ll N_c). \tag{4}$$

It is easy to verify that Eq. (2) matches Eq. (3) at $N \sim N_c$. Thus, at $Zb/r \gg 1$, the energy per ion, ε_i, grows linearly at small N and reaches saturation at $N \gg N_c$. This is a clear demonstration of a nonpairwise additive interaction. Of course, the surface correction to the energy of the bundle provides some growth even at $N \gg N_c$ and leads to formation of macroscopic bundles.

In order to obtain the binding energy per molecule, Eqs. (3) and (4) have to be multiplied by the number of ions per molecule, $M = L/bZ$. This transition does not change the dependence on N. Therefore below I will continue to present results in the form of ε_i.

Before switching to the more complicated case $Zb/r \ll 1$, I discuss the condition on the temperature T or, in other words, on the parameter $Z\xi$ at which the theory suggested above is valid. Consider a large almost neutral bundle of 3D densely packed WCR. If $k_BT \ll \varepsilon_i$ the thermal motion can be neglected and my theory is valid. Using Eq. (3) one can rewrite inequality $k_BT \ll \varepsilon_i$ as

$$Z\xi \gg (r/Zb)^{2/3}. \tag{5}$$

At $Zb/r \gg 1$ this inequality is much weaker than the standard condition $Z\xi \gg 1$ of the Manning condensation of ions with charge Z at an isolated molecule, because of the simultaneous interaction of each ion with many rods. Even if one uses $\kappa = 81$ of pure water, $\xi \sim 4$ at room temperature, and the condition of Eq. (5) is easily fulfilled.

One can also argue that at finite T even a large bundle filled by the WCR becomes charged and therefore nonpairwise repulsion energy should be taken into account. To estimate corresponding correction $\Delta\varepsilon_i$ to the binding energy per ion recall that according to Onsager-Manning theory a long cylindrical bundle of N rods has uncompensated charge $\kappa(k_BT)/(Ze)$ per unit length. This charge creates energy $\kappa L(k_BT)^2/(Z^2e^2)$ per unit length of the bundle. Here $L = \ln(r_s/rN^{1/2}) \sim \ln(1/c)$, r_s is the screening radius of the bulk solution, and c is relative concentration of ions in the solution. To calculate $\Delta\varepsilon_i$ this energy should be divided by the number of ions per unit length, $N/(Zb)$. Using then Eq. (3) one obtains

$$\frac{\Delta\varepsilon_i}{\varepsilon_i} = \frac{(r/Zb)^{2/3}}{N(Z\xi)^2}\ln(1/c) \ll 1. \tag{6}$$

The last inequality follows from Eq. (5) and inequality $NZ\xi \gg \ln(1/c)$, which in turn is easy to satisfy for large N at $Z = 3$ ($Z\xi \sim 12$) and for any reasonable c. Thus, net charge of the bundle does not create stronger limitations for this theory than Eq. (5).

It is obvious that when Eq. (5) is valid, the maximum density bundle is more strongly bounded than one with the smaller density. Indeed, the decreasing density results in the increase of the lattice constant R and, according to Eq. (2), substantially diminishes ε_i. At the same time the increase of the entropy term in free energy cannot compensate for this loss in the binding energy.

As stated above, this theory works if $k_BT \ll \varepsilon_i$. Actually the WCR melts when k_BT is yet numerically much smaller than ε_i, so in experimental conditions one deals with strongly correlated liquid, not a crystal. This, however, does not change the estimate for its correlation energy and for ε_i and leaves unchanged the validity criterion of the theory. The fact that it is the short range order of ions which is responsible for the attraction of rods at a finite temperature was emphasized in Ref. [3]. Below, I continue to use the WCR language because it creates a simpler image.

Consider now more strongly charged and thicker rods for which $Zb/r \ll 1$. In this case $N_c \ll 1$ and, therefore, one has to deal only with a 3D problem. However, the rods are so thick that their radius is larger than the lattice constant of the optimal densely packed crystal. If, as we assumed, ions cannot penetrate rods, the optimal densely packed crystal cannot be formed. Under this restriction, ions condense at the surface of each rod forming the 2D WCR [9] with the lattice constant

$$R \sim (Zbr)^{1/2}. \tag{7}$$

An insulated rod has a similar crystal at its surface. The binding energy of the bundle originates in narrow contact stripes where rods pairwise contact each other so that their WCRs overlap. The width W of this stripe will be calculated below. Inside the stripe, densities of both negative background and positive ions are doubled and the local lattice constant R_s becomes smaller ($R_s = R/\sqrt{2}$). As a result, according to Eqs. (2), the cohesive energy of the crystal per ion of the stripe becomes larger than for the case of the two separated rods. Combining Eqs. (2) and (7), one finds that the binding energy of the bundle per one ion of the stripe equals $Z^{3/2}e^2/(br)^{1/2}$. To get ε_i one must multiply this energy by the fraction, $p \sim W/r$, of all ions of the bundle which reside in the contact stripes. The width W can be found from the condition that at the distance W from the line of contact, the surfaces of two contacting rods diverge from each other at the distance of the order of R. Indeed, the interaction between 2D Wigner crystals is exponentially weak if the distance between parallel planes in which they are situated is larger than their lattice constant R. A simple geometrical estimate gives $W \sim (rR)^{1/2}$. Finishing the calculation of ε_i one obtains

$$\varepsilon_i \sim \frac{Ze^2}{\kappa b}(Zb/r)^{3/4} \qquad (Zb/r \ll 1; N \gg 1). \tag{8}$$

Together Eqs. (3) and (8) give binding energy per ion of a 3D crystal at all values Zb/r. At $Zb/r = 1$ they obviously match each other. At $Zb/r \ll 1$ energy given by Eq. (8) is smaller than the one from Eq. (3). This is a natural result of the restriction that ions do not penetrate rods.

Consider now the validity of the main assumption, that an array of negative discrete charges on the rod surface can be effectively replaced by an uniform negative background. This idea works exactly only in the limit $Z \gg 1$. On the other hand, it fails at $Z = 1$ because in the low temperature limit all ions and discrete negative charges form neutral Bjerum pairs and nothing depends on the mutual positions of the rods. Thus, $\varepsilon_i = 0$ at $Z = 1$. What happens at $Z \geq 2$ depends on the spatial distribution of the discreet negative charges. If they are distributed randomly, then at $Z = 2$ Eqs. (3), (4), and (8) overestimate ε_i roughly by a factor of 2, while at $Z \geq 3$ they work well. On the other hand, when negative charges are clustered, ε_i can be much lower even at $Z = 3$. Imagine, for example, that negative charges form compact triplets. Each one would be neutralized by an ion and ε_i would vanish. A more interesting effect of concentration of negative charges in DNA is discussed below.

But first assume that the surface of DNA is uniformly negatively charged. For DNA $b = 0.17$ nm and $r = 1$ nm, so that $Z = 6$ is the border between range of validity of Eqs. (3) and (8). This means that for DNA in this model, attraction is due to the short range pairwise interaction of molecules induced by correlation between their surface WCRs. This conclusion is in agreement with Ref. [9].

Recall now that in DNA, negative charges are located along two spirals which are separated by wide and narrow grooves. For simplicity, assume that the width of the narrow one is zero, which leaves only one spiral of the negative charge with the double density. (This approximation, of course, overestimates the inhomogeniety of the negative charge distribution and can be easily avoided with minor change in the result.) Ions tend to concentrate on the same spiral and form the 1D Wigner crystal along it. When two parallel DNA rods touch each other by these crystaline spirals (for this purpose one rod should be shifted along their direction by the half of the helical period) they create a spot with larger binding energy per ion. Thus, attraction is produced in a way very similar to the case of contacting 2D crystals discussed above. Extending this analogy for two contacting DNA molecules, one can introduce the contact stripe where attraction is generated. The only difference is that the width of this stripe W is smaller for DNA, because the WCR spirals of the two contacting DNA molecules diverge not only in the plain perpendicular to the rods but also along the direction of the rods (spirals cross at a finite angle). One can find that $W \sim Rr/nb \sim R$, where $R = \pi r/n$ is a period of the 1D crystal and $n = 10$ is the number of base pairs in the helix period. Thus, roughly speaking, only one ion per helix period adjusts its position due to the contact and contributes to the binding energy of the two contacting rods. Multiplying Eq. (2) by the fraction of such ions $R/2\pi r$ one obtains

$$\varepsilon_i \sim \frac{Ze^2}{\kappa b}\frac{Zb}{2\pi r}. \tag{9}$$

At $Zb/r \ll 1$, Eq. (9) gives smaller energy than Eq. (8). This is an effect of concentration of negative charges on the spiral. Note that this effect is exactly opposite to the prediction of Ref. [13]. The reason for this difference is that the authors of Ref. [13] assumed that charge of ions is uniformly distributed over DNA surface, so that negative and positive charges are strongly separated. Such a separation of charge costs a large electrostatic energy and can happen only if nonelectrostatic forces dominate. These forces are beyond the scope of this work.

One might wonder whether each contacting pair of DNA molecules in a bundle can gain the energy given by Eq. (9). This can be easily done in a square lattice of rods, with one square sublattice shifted along the rod direction by the half of the helical period. In a densely packed hexagonal lattice one can shift in the same way every second layer, so that each rod is attracted to four of its neighbors. Thus in the approximation of one spiral both lattices have the same energy.

Note that, literally speaking, this theory is applicable only to molecules of DNA which are shorter than its persistent length. It is known that in a weak DNA solution of longer molecules, each molecule self-assembles into a toroidal particle, where locally strands of all turns are parallel to each other. Theory of this paper is applicable to toroidal particles as well.

Although three-dimensional densely packed WCR of ions is not realized in DNA bundles (for $Z < 6$), many other rodlike polyelectrolytes are known. Some of them are narrower or more weakly charged so that $Zb/r \gg 1$ and 3D crystal of ions should appear. PPP3 with $b/r \sim 2$ is a good example [14].

The idea of WCR can be applied also to the attraction of rigid spheres. Thinking about colloids, assume that the surface of sphere is charged negatively and positive ions cannot penetrate it. If spheres are large enough, ions form the 2D WCR at the surface of a sphere. This leads to contact attraction of spheres similar to the one calculated above for two contacting cylinders. The binding energy of two spheres with the radius r and the charge $-Qe$, originates in the contact disc of the radius $(rR)^{1/2}$, where r is the sphere radius, R is the lattice constant of the WCR. (This disc is an analog of the contact stripe for two cylinders. See computer simulation of such a disc in Ref. [15]). The additional energy per ion of the disc is gained, because the disc has a denser background and a larger ion density than the rest of the surfaces of the spheres. Once more ε_i is given by Eq. (2). Multiplying this energy by the number of ions in such a disc, r/R, and substituting $R \sim r(Z/Q)^{1/2}$ one gets a surprisingly simple expression for the binding energy of two spheres

$$\varepsilon \sim \frac{ZQe^2}{\kappa r}, \tag{10}$$

which looks like a Coulomb attraction energy of the spherical colloid particle and a single ion at its surface. Equation (10) fails with the decrease of the ion concentration in the solution, c, when each sphere acquires the net negative charge sufficient to overcome calculated attraction. This happens at $k_B T \ln(1/c) \sim Z^2e^2/\kappa R$. At lower temperature Eq. (10) gives energy which is larger than proportional to T depletion energy of Ref. [15].

There are other applications of the WCR concept. Counterions should not necessarily be small. One can consider condensation of larger and stronger charged counterions, for example, micelles, on a charged rigid surface. Because of strong Coulomb repulsion they should form a 2D WCR. Rodlike counterions also condense on a charged surface. Parallel rods form a periodic array so that their crossections form 1D WCR. In the case of DNA condensed on a supported cationic membrane beautiful images of such a crystal are available [16]. The uniform 3D background for rodlike counterions can be provided by the stack of positive parallel sheets. Complexes of DNA with cationic lipid membranes are good examples of such a system [17]. All the rods orient themselves parallel to each other and to the sheets. At a small enough sheet thickness, the circular cross sections of rods should form the 2D WCR similar to vortex lattice in superconductors, while at larger thicknesses they form parallel 1D crystals in the gaps between sheets.

In conclusion, this paper studies the attraction and self-assembly of rigid polyelectrolytes due to strong correlations in positions of polyvalent counterions. To describe these correlations, I adopt the notion of the WCR. For rods I find that, depending on the value of a single dimensionless combination, Zb/r, optimal cofiguration of ions on the background of a bundle is the 3D densely packed WCR or the 2D crystal on the surface of rods. When applying this theory to DNA condensation I introduce the notion of 1D spiral WCR and estimate the binding energy of two DNA helixes due to the contact of these crystals. I also calculate the binding energy of two colloidal particles created by the contact of WCRs of ions on their surfaces. Future developments of this work should include such factors as behavior of the dielectric constant of water at small distances, the finite size of counterions, and more realistic distributions of polyelectrolyte charges.

I am grateful to V. A. Bloomfield, A. M. Dykhne, M. D. Frank-Kamenetskii, A. Yu. Grosberg, R. Holyst, A. R. Khokhlov, R. Podgornik, and I. Rouzina for valuable discussions. This work was started in the Aspen Center for Physics and was supported by NSF DMR-9616880.

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