Collapse of Flexible Polyelectrolytes in Multivalent Salt Solutions

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The collapse of flexible polyelectrolytes in a solution of multivalent counterions is studied by means of a two state model. The states correspond to rod-like and spherically collapsed conformations respectively. We focus on the very dilute monomer concentration regime where the collapse transition is found to occur when the charge of the multivalent salt is comparable (but smaller) to that of the monomers. The main contribution to the free energy of the collapsed conformation is linear in the number of monomers N, since the internal state of the collapsed polymer approaches that of an amorphous ionic solid. The free energy of the rod-like state grows as N ln N, due to the electrostatic energy associated with that shape. We show that practically all multivalent counterions added to the system are condensed into the polymer chain, even before the collapse.

I. INTRODUCTION

Nucleic acids and many proteins are charged and exhibit self-assembly. For example, DNA with an extended length of the order of centimeters is highly compacted in cells and viruses. The compactness of strongly charged chains in low ionic strength solutions has been a subject of recent great interest [1–12]. Strongly charged chains, though in principle in extended conformations to decrease their electrostatic energy, precipitate into highly compact structures when small amounts of high valence counterions are added to low ionic strength solutions [2–6]. Flexible polymers, including single stranded DNA and many synthetic polymers such as Polyester Sulphonated, precipitate into dense amorphous structures [2]. Semi-flexible polymers, such as long double stranded DNA, and rigid rods, such as short DNA fragments, aggregate into highly compacted ordered structures [13]. Multivalent induced DNA compaction is a promising mechanism to “pack” DNA, a critical problem in gene therapy given that long extended DNA cannot be deliver into cells. Furthermore, the precipitation is correlated with highly accelerated rates of DNA renaturation and cyclization [6], and other important biotechnological processes. Aside from the DNA compaction and its importance in biology and biotechnology, the physics of self-assembly of charged molecules remains an interesting open problem.

The self-assembly of polyelectrolytes is strongly related to the “condensation” of the counterions along the chains. A fraction of the counterions will be condensed, strongly attached to the backbone of the polyelectrolyte to decrease their electrostatic energy. In flexible chains the interaction between the polyelectrolytes and the counterions is non-trivial. The long range electrostatic interaction that leads to ion condensation is strongly dependent on the chain conformation; more ions are condensed when the chain is compacted than when it is extended. The conformation of the chain, reciprocally, depends on the number of condensed counterions, and their distribution along the chain. The correlations between monomers and counterions are such that the higher the number of condensed counterions, the smaller the size of the chain [1]. This mechanism induces a transition between two possible polyelectrolyte conformations: a highly compact shape with nearly zero effective charge (it is neutralized by the condensed counterions) and a rod like shape with a smaller number of condensed counterions.

The above counterion mediated precipitation mechanism is quite general. However, it is non trivial to compute the free energy of the collapsed chains. This paper we use simple physical arguments and known results from related charged systems to construct the free energy of the collapsed state of flexible polyelectrolytes. We aim to describe the multivalent induced precipitation in highly dilute polyelectrolyte solutions at low ionic strength solutions of monovalent ions. It is well documented experimentally [2,6] that in this regime the polyelectrolytes precipitate when the concentration of high valence ions is proportional to the concentration of charged monomers and that the transition is quite universal in this regime as it is independent of the charge density of the chains and on the specific nature of the condensing agents. In this paper we recover this result with a first order transition model from rod-like to collapsed states described below. We find that at the precipitation point all the multivalent ions replace the condensed monovalent ions, as expected, and that the effective charge of the finite size precipitate is nearly zero.

II. MODELING CONSIDERATIONS

In our approach we assume that there are two well defined types of states allowed for the single chain: collapsed and extended. We calculate free energies for each of these types of states and study the conditions under which one of the states is preferred. Ideally, we would like to present a single free energy functional valid for the whole range of conformations of the chain. It is, however, very hard to construct such a functional. On the other
hand, as we aim to show below, there are very distinct characteristics in the two phases so that treating them as different objects is not only possible, but provides a clear view of the reasons behind the transition from extended to collapsed conformations.

It has long been understood how the extended states arise. The bare charge of a polyelectrolyte is always reduced by the condensed counterions, but it is nevertheless sufficient to create repulsions between the segments of the chains that overcome the entropic elasticity of the chain, leading to an almost fully stretched conformation. The collapsed state is, comparatively, much harder to understand. The repulsive interaction between the uncompensated charges is still present, and therefore, a sufficiently strong cohesive energy is necessary to maintain the collapsed state. This cohesive energy has been modeled in previous works by means of virial approximations and other averages over positional fluctuations of the charged particles in the system. We propose here a different approach to the calculation of the cohesive energy for the collapsed state.

In several treatments of the problem of attractions between rod-like polyelectrolytes the attractive energies have been identified as arising from strong correlations between the condensed counterions. These correlations can be so strong as to induce the formation of crystalline order of the condensed counterions. In the same way, we argue that also in the case of flexible polyelectrolytes, purely electrostatic interactions can lead to the collapse of the chains. A second degree of difficulty arises from the fact that even after identifying the origin of the attractive interactions, the calculation of the precise value of the energy of interaction can become a technically difficult problem. In this paper we will adopt the view that in the collapsed state, the monomers and condensed counterions of a sufficiently large polymer approach a homogeneous bulk state inside the collapsed region. There, we can then estimate the interaction energies by considering a similarly composed amorphous ionic solid. One lesson learned from the study of association of rigid polyelectrolytes is that it is possible to estimate interaction energies by simply using low temperature limits plus small corrections. That is, within the collapsed region, the entropic considerations produce only small corrections.

We can indeed consider a thought-experiment in which we cut the polymer bonds so as to have a mixture of single-charge monomers and counterions in solution. In this case we expect to observe the typical behavior of a salt. When the amount of solvent is large, all particles are dissociated, and as the solvent amount decreases, we can observe the formation of salt crystals. This process occurs at common temperatures and concentrations. Rejoining the monomers to form again the polymer chain modifies the previous picture in two ways. First, the dissociation in the presence of large amounts of solvent can never be complete as the counterions can be freed but not the monomeric charges. Second, in the collapsed state, at low solvent concentrations, the crystallization is hindered by the connectivity of the chain, which provides an entropic barrier to full crystallization and imposes a clear, well defined size for the minimum size of the crystal grain (the collapsed radius of gyration).

On the basis of these considerations we obtain a model free energy for both states, and calculate the amount of added multivalent salt required to collapse the chain. While the chain is expected to collapse even without the addition of multivalent salt, such collapse would occur only at very low temperatures, and much of the interest on this process is related to applications at room temperatures. The reason why the multivalent counterions are so effective at collapsing the chain also becomes apparent in the elucidation of the cohesive energy of the collapsed chain. Since this energy is dominated by the electrostatic interaction between particles, the replacement of monovalent by multivalent charges has the effect of highly decreasing the self-energy part of the counterions. This is further helped by the fact that it is entropically much more favorable to free multivalent instead of monovalent counterions. As we will show below, this replacement of charges is almost complete even in the non-collapsed state.

III. FREE ENERGY CALCULATIONS

We describe now the basic parameters of the system. We consider monodisperse polyelectrolyte chains with monomer number \( N \) that we take to coincide with the number of monovalent, positive charges in the chain. We assume that the distance along the chain between charges is a constant \( b \) that is comparable with all other small distances in the system such as the thickness (diameter) of the chain and the non-electrostatic persistence length. The monomer concentration is \( \phi \), and the solution contains several other charged components: a monovalent salt with concentration \( s \), and a multivalent salt with concentration \( m \), and valence \( z \). We assume that the monovalent counterions naturally associated to the chain are identical with the dissociated negative components of the monovalent salt. The concentration of these negative ions is then \( s + \phi \). The size of all the small particles is also taken to be order \( b \). The dimensionless Bjerrum number is the ratio \( Bj = e^2/4\pi\varepsilon \epsilon_B k_B T \), with \( e \) the electron charge, \( \varepsilon \) the permittivity of water, \( k_B \) the Boltzmann constant, and \( T \) the temperature.

A. Energy of free charges

Whether the chain is in a collapsed or in an extended state, the charges that are not condensed to the chain give rise to similar contribution to the free energy mostly
arising form their translational entropy, and we will consider them all at once. A fraction $f$ of the total charge in every chain is compensated by condensed counterions, that remain in close proximity to the chain. This compensating charge is made up from monovalent and multivalent counterions. The respective charge fractions that they compensate are $f_s$, and $f_m$, so that $f = f_s + f_m$. Per chain, we have $f_s N$, and $f_m N/z$, condensed negative monovalent and multivalent ions per chain. The free positve ions per chain of the two different species are simply $sN/\phi$, and $mN/\phi$, since none of the positive ions condense to the chain. Finally, we have $(1 - f_s)N + s/\phi$ free negative monovalent ions and $mN/\phi - f_m N/z$ free negative multivalent ions.

For sufficiently dilute concentrations of polymers the electrostatic contribution of the free charges can be shown to be very small. In a Debye-Huckel approximation, the electrostatic energy (in a per chain basis) is proportional to $\phi^{1/2}$. Instead, the main entropic contribution is proportional to $\ln \phi$. The volume occupied by the chain is considered negligible and we obtain for the translational entropy of the free ions, per monomer, in units of $k_BT$:

$$F_s = \frac{s}{\phi} \ln b^3 s + \left(\frac{m}{\phi} - f_m/\phi\right) \ln b^3 (m - f_m \phi/\phi)$$

$$+ \frac{m}{\phi} \ln b^3 m + (1 - f_s) \ln b^3 (s + (1 - f_s) \phi).$$

(1)

In this expression we have estimated the entropy by counting the number of sites available to the ions in a lattice with sites of size $b$ that are always occupied by ions or solvent molecules. Since the system is dilute we have not included the terms of the form $l(1-s)b^3$ etc.

B. The Extended State

To estimate the electrostatic free energy for the extended state, we assume a simple linear geometry for the chain. We assume that the chain is strongly stretched so that we take the linear size to be simply $L = Nb$. The elastic entropy of the chain plays only a small role, and reduces the effective size only by a small fraction. Assuming a uniform distribution of condensed charges along the chain, the effective charge per monomer is $1 - f_s - f_m$. The main contribution to the electrostatic free energy arises from the interaction of the charges with the logarithmic potential created by the effective charge,

$$F_{ex} = Bj (1 - f_s - f_m)^2 \ln N.$$  

(2)

For the purpose of comparison with the collapsed state, we note that this energy is quadratic in the fraction condensed, and dependent on the size of the system.

C. The collapsed state

We begin with the assumption that the collapsed state is very dense. Taking into account the space needed to accommodate the condensed counterions, we expect the radius of the collapsed polymer to be roughly $R = (2N b^3)^{1/3}$. To calculate the electrostatic free energy of the system we need to determine the distribution of charges within the collapsed polymer. To model this distribution we borrow two arguments from classical electrodynamics and solid state physics.

First, we consider the distribution of uncompensated charges. In the classical (i.e. non-statistical) analog of this problem, whenever there are free mobile charges within a solid of fixed shape, the excess charge resides in the surface of the object. Thus we can argue that the counterions in the collapsed polymer occupy places “deep”, in the collapsed region to cancel the monomeric charge there, while the few uncompensated monomeric charges will appear at the surface of the object. The thermal fluctuations of the system decrease the sharpness of this result, and we expect a broadening of the regions in which there can be detected a non-zero average charge. We separate the collapsed ball into these two regions, the charged surface and the neutral core. Assuming a spherical geometry for the collapsed region, the interaction of the charges at the surface is readily calculated by an application of Gauss’ law, and is simply

$$F_{es} = Bj (1 - f_s - f_m)^2 \frac{N}{(2N)^{1/3} b^3}.$$  

(3)

As we shall see later, the fraction condensed for the collapsed state is very close to unity, and the energetic contribution to this charged shell is very small.

Let us consider now the self-energy of the core, which is, in the average, electrically neutral. When the polymer is collapsed, all charges are very close to each other, and their electrostatic interactions are very strong. For example, for the case of the aggregation of rod-like poly-electrolytes, several model calculations have shown that there are very strong correlations between the condensed counterions leading to the formation of Wigner crystals along the rods. In the present case, however, we cannot argue for such crystallization because of the constraints that the connectivity of the chain imposes. Instead, we propose to view the core as an amorphous ionic solid. Finally, while we do not expect to find a crystalline state, and only observe very strong correlations, the evaluation of the free energy can be carried out in a very similar manner to ionic crystals. This amorphous ionic solid state has also been proposed recently by Lee and Thirumalai that they call Wigner Glass [12].

In the core there is a very strong energetic penalty for conformations in which the charge of a particle is not quickly compensated by its neighbors. This is clearly the case as well in fully crystalline structures, but this
The energy per atom in an ionic crystal is usually presented in the following form:

$$E_{eb} = -e^2 M \frac{z}{r_o},$$

where $r_o$ is the lattice constant and $M$ is the Madelung constant $\Phi$. The Madelung constant depends on the specific lattice structure, but its value is always of order 1. The sum of the interaction of one atom with all other atoms in the crystal is arranged in a convergent series of alternating terms, summing the interaction with a layer of oppositely charged atoms, (nearest neighbors) then with the layer of next-nearest neighbors that are equally charged, etc. Clearly, the final result is dominated by the interaction with the neighbors that compensate the charge of a given particle, and the rest simply modify the prefactor. In the following we sketch a simple estimate for an effective Madelung constant for the collapsed polymer bulk.

We have assumed that all small distances in the system are of order $b$. We cluster one counterion with all the monomers that are required to compensate its charge, 1 for monovalent, and $z$ for multivalent ions. If all the particles in the cluster are at about the same distance from each other, the energy contribution of the cluster is

$$E_{eb} = -Bj \frac{z}{2}(z + 1).$$

This is the first term in the series for the effective Madelung constant, and we will truncate the series at this point. There are $f_m N$ clusters with monovalent counterions, and $f_m N/z$ with multivalent counterions, so that our estimate for the free energy of the bulk of the collapsed state is

$$F_{eb} = -Bj (f_s + \frac{1}{2} f_m (z + 1)).$$

IV. PHASE TRANSITION CONDITIONS.

We can now use the free energy expressions postulated for the collapsed and extended states to calculate the phase diagram of the system which we shall present in $\phi - m$ coordinates. It is useful, however, to carry out further simplifications in the model that lead to some qualitative and quantitative results.

A. Replacement by multivalent counterions

The general expressions for the free energy in the two states, collapsed:

$$F_c = F_{eb} + F_s,$$

and extended:

$$F_x = F_{ex} + F_s,$$

still depend on the fractions condensed $f_s, f_m$. These fractions should be obtained before computing the final free energy. To obtain their values, the free energy is minimized with respect to these variables, which leads to the equations:

$$2 Bj(1 - f_m - f_s) \ln N + \ln b^2(s + (1 - f_s)\phi) = 0,$$

$$2 Bj(1 - f_m - f_s) \ln N + (1/z) \ln b^2(m - f_m\phi/z) = 0.$$ (9)

for the extended state, while for the collapsed state one has:

$$\frac{Bj N}{N^{1/3}}(1 - f_s - f_m) + Bj + \ln b^2(s + (1 - f_s)\phi) = 0,$$

$$Bj N \left(1 - f_s - f_m\right) + Bj \frac{z + 1}{2} + \frac{1}{z} \ln b^2(m - f_m\phi/z) = 0.$$ (10)

The Eqs. (9) imply a particular relation between the fraction condensed of the two species, regardless of the strength of the electrostatic term (measured by $Bj$), given by

$$(b^2(s + (1 - f_s)\phi)^2 = b^2(m - f_m\phi/z).$$ (11)

This relation is essentially a result of the fact the same energy binding $z$ monovalent counterions is what is required to bind one multivalent ion, while the entropy gain of freeing $z$ ions is also $z$ times bigger. For dilute concentrations of monomers and ions, the expressions in Eq. (11) are all small quantities and even for $z = 2$ the exponentiation of the left hand side of the equation leads to an extremely small value for the difference $m - f_m\phi/z$. Thus we conclude that for all practical purposes all multivalent counterions are condensed. At higher concentration of these counterions, there can be a near saturation since the polymer cannot absorb all of them, and it cannot be emptied of monovalent ions (since by Eq. (1) $f_s$ cannot be zero.)

For the second pair of equations Eq. (10) we note that the first terms of the equations, which arise from the electrostatic repulsion of uncompensated charges, present very large prefactors to the effective charge $1 - f_s - f_m$. Clearly, the effective charge must cancel this contribution, and we conclude that, essentially, in the collapsed state all charges are compensated. An analysis similar to the case of the extended conformation implies that the charge compensation must occur first with as many multivalent ions as possible, and then finalize with monovalents so that, roughly, we have $f_m = zm/\phi$, and $f_s = 1 - f_m$. 

$$F_c = F_{eb} + F_s,$$ (7)

and extended:

$$F_x = F_{ex} + F_s,$$ (8)
B. Low Density Limit

Let us now consider the case in which the density of monomers is very low. More precisely we define this regime by the condition that if all chains are extended, they do not overlap. Since the extended size of a chain is $Nb$, the definition is equivalent to $\phi < N/(Nb)^3 = 1/N^2b^3$.

To obtain a simplified formula for the amount of multivalent counterions needed to produce the transition, we need to carry out some simplifications. As the solution becomes more and more dilute, there is a great entropic energy to be gained by freeing the monovalent condensed ions. At the same time, the relation obtained between the amount of condensed ions of the two species still implies that a large number of multivalent counterions are condensed. Thus, a first simplification consist on setting, for the extended state $f_s = 0$, and $f_m = zm/\phi$. Thus, neglecting some other small terms, the energy for the extended state reads:

$$F_x = Bj(1 - \frac{zm}{\phi})^2 \ln N - (1 + \frac{s}{\phi}) \ln b^3(\phi + s). \quad (12)$$

In the collapsed state, we have already discussed that at all concentrations we have almost exactly $f_m = mz/\phi$, and $f_s = 1 - f_m$, which leads to

$$F_c = -Bj(1 - \frac{z(z - 1)m}{2\phi}) - \frac{zm}{\phi} \ln b^3(\phi + s). \quad (13)$$

In the evaluation of the entropic term we have used the fact that the density of required counterions is of the order of the monomer density, so that $\ln b^3f_s(\phi + s) \approx \ln b^3(\phi + s)$.

Equating the previous two approximations for the free energies in the two states leads to a quadratic equation in $zm$ for the density of multivalent counterions required to create the transition. However, from the analysis of these equations, a simpler conclusion can be drawn. By looking to just the entropic terms, of the form $\ln b^3(\phi + s)$, which are the largest contributions to these expressions, it is clear that a transition is only possible when the charge of the multivalent particles approaches that of the monomers:

$$zm \sim \phi. \quad (14)$$

This is the resulting limiting condition for very dilute solutions. We should remark that while this result might appear intuitive, it relies on the specific structure of the extended and collapsed state. Namely, in both states, all multivalent ions are trapped, in the collapses state, the only free monovalent counterions are those that have been replaced by multivalent ones, and in the extended state, all monovalent counterions are free.

C. Dense limit

In the opposite case, for higher concentrations, the model we use cannot give a precise answer as we have neglected the effects of the electrostatic self-energy of the free counterions. Further, as the concentration increases it becomes harder to distinguish the “inside” and “outside” regions of the chain. We can obtain, however, a clear limit for the validity of these approximations, that also signals the onset of new phenomena. In the absence of multivalent counterions, the fraction of monovalent counterions condensed is given to a good approximation by

$$f_s = 1 + \frac{\ln b^3(\phi + s)}{2Bj \ln N}. \quad (15)$$

At the onset of the dilute regime $\phi = b^{-3}N^{-2}$, we recover the Manning formula $1 - f = 1/Bj$. Further increase on the concentration leads to a situation in which the fraction condensed can reach a value very close to 1, so that the effective charge is almost zero and cannot extend the chain. After this point the distinction between the collapsed and non-collapsed states is much less clearly defined. The chain cannot be extended if the electrostatic free energy per monomer smaller than $1k_BT$ (for flexible polymers). This leads then to the following criteria:

$$-\ln b^3(\phi + s) \sim (Bj \ln N)^{1/2}. \quad (16)$$

D. Monovalent Collapse

As mentioned in the introduction, it is expected that monovalent counterions on themselves can collapse the chain even in dilute conditions, if the temperature is sufficiently low. Our model gives a simple criteria for the occurrence of this collapse. The free energy for the extended state can be approximated as

$$F_x = -\frac{(\ln b^3(\phi + s))^2}{4Bj \ln N}, \quad (17)$$

while the energy for the collapsed state is simply approximated by

$$F_c = -Bj. \quad (18)$$

This results in a transition occurring at

$$-\ln b^3(\phi + s) \sim Bj(\ln N)^{1/2}. \quad (19)$$

We remark that this equation differs from Eq. (16), by a $Bj^{1/2}$ factor. This difference implies that the collapse of the chain by its natural monovalent counterions occur within the dilute regime.
V. RESULTS

Solution of the equilibrium equations between the two phases produces a phase diagram that is valid at low concentrations of monomers. We now present results for valences \( z = 2, 3 \), and \( Bj = 2, 3, 4, 5 \). Other parameters take values of \( N = 10^{5}, b^s = 10^{-12}, \) while the data covers monomer concentrations ranging from \( b^s \phi = 10^{-18}, \) to \( 10^{-8} \). These results are presented in Fig. 1-4. Figures 1 and 3 present results for the concentration \( m \), while 2 and 4 show the required ratio \( m/\phi \).

FIG. 1. Plot of \( \log b^s m \), for \( z=2 \) and different values of \( Bj \).

FIG. 2. Plot of the ratio \( m/\phi \), for \( z=2 \) and different values of \( Bj \).

FIG. 3. Plot of \( \log b^s m \), for \( z=3 \) and different values of \( Bj \).

FIG. 4. Plot of the ratio \( m/\phi \), for \( z=3 \) and different values of \( Bj \).

In both cases, \( z = 2 \), and \( z = 3 \), it is clear that as the density of monomer is decreased, the required amount of monovalent counterions required for the collapse falls in the range prescribed by the limiting relation Eq. (14), and the ratio is always somewhat smaller than \( 1/z \).

A. Limits of Applicability

In this subsection we collect the main limitations of our approach. The concentration of multivalent ions at the extended-to-collapse transition \( m^* \) appears to be linear with the concentration of charged monomers \( \phi \) at highly dilute solutions, in agreement with experimental results [6]. As \( \phi \) increases, however, \( m^* \) decreases. Experimental results indicate the opposite behavior [2,5]. This disagreement has two sources: we are neglecting the interchain interactions and also the possibility of other conformations.

In the collapsed state the chains are nearly neutral so one can neglect the chain-chain interactions provided
the concentration is still much lower than the overlap concentration. However, this is not the case of other non-collapsed conformations which have higher effective charge, such as the extended state. Our model takes into account only two states (the stretched and collapsed) of non-interacting chains, so that our results are valid only for highly dilute solution of polyelectrolytes, as has been roughly established in Eq. (16). In a more dense regime the electrostatic free energy of the free counterions becomes relevant while here it has been neglected. Also, our results are only reliable in low ionic strength solutions of monovalent ions and at low concentration of multivalent ions. When the concentration of multivalent ions increases there will be an excess of free multivalent counterions so their electrostatic contribution cannot be neglected. We have also not taken into account the effects of the solvent quality. In poor solvents, for example, it is know that a “necklace” structure might be more favorable than the stretched conformation [17–19].

VI. CONCLUSIONS

A collapsed flexible polyelectrolyte in low ionic strength solutions has a nearly zero effective charge. The charge of the monomers is compensated by condensed counterions. The main contribution to the electrostatic free energy of the collapsed polyelectrolyte is proportional to the number of compensated monomer charges $N$, and the internal state of the collapsed molecule is similar to an amorphous ionic solid. There is a strong electrostatic free energy reduction of the collapsed state when the valence of the condensed counterions increases. Therefore, when multivalent counterions are added at a concentration $m$ less than the concentration of charged monomers $\phi$, all of the multivalent counterions are condensed, replacing the monovalent condensed counterions. Since the multivalent ions reduce the electrostatic free energy, a first order transition occurs from extended to collapsed chain conformations.

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