

# Thermodynamic Properties of a Simple Model of Like-Charged Attracting Rods

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We study the thermodynamic properties of a simple model for the possible mechanism of attraction between like charged rod-like polyions inside a polyelectrolyte solution. We consider two polyions in parallel planes, with  $Z$  charges each, in a solution containing multivalent counterion of valence  $\alpha$ . The model is solved exactly for  $Z \leq 13$  for a general angle  $\theta$  between the rods and supposing that  $n$  counterions are condensed onto each polyion. The free energy has two minima, one at  $\theta = 0$  (parallel rods) and another at  $\theta = \pi/2$  (perpendicular rods). The stability of the parallel and perpendicular configurations is analyzed.

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**KEY WORDS:** Polyelectrolytes; DNA; Manning condensation; like-charge attraction.

## 1. INTRODUCTION

It has been observed that the like charged macromolecules can attract each other in solutions containing multivalent counterions. This attraction manifests itself in *in vitro* formation of toroidal bundles of concentrated DNA,<sup>(1,2)</sup> similar to the one found in bacteriophage heads,<sup>(3)</sup> and the appearance of rod-like bundles of f-actin and tobacco mosaic virus in the presence of multivalent counterions.<sup>(4)</sup> A number of models have been suggested to explain this curious phenomenon. The fundamental ingredient in all of these models is the role played by the condensed counterions.<sup>(5,6)</sup>

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Thus, the attraction has been attributed to the correlations between the condensed counterions on the two polyions.<sup>(7,8)</sup> The mathematical problem of how these correlations can be taken into account is highly non-trivial. Two approaches have been proposed. One relies on field theoretic methodology and uses what can be classified as a high temperature expansion to account for the correlations between the condensed counterions,<sup>(7)</sup> while the second is a zero temperature approximation, in which the counterions are thought to form correlated Wigner crystals on the surfaces of the two polyions.<sup>(8-11)</sup> Neither one of the approaches is exact, however, the zero temperature Wigner crystal approximation is better at capturing the true nature of correlations.<sup>(12,10)</sup>

In earlier work we have introduced a simple model which has allowed us to study *exactly* the force between two parallel charged rods with a layer of condensed counterions.<sup>(9)</sup> In this paper we shall extend this work to allow for a relative inclination between the two rods. This problem is of particular interest in kinetics of the bundle formation, where it has been observed that the bundles of stiff polyions have a characteristic size. This is quite surprising since the correlation induced attraction should favor formation of infinitely thick bundles, after all the ionic crystals can grow to macroscopic sizes. A possible explanation for the bundles not growing beyond some specific size can be found in the kinematics of bundle formation. The condensed counterions do not fully neutralize the charge of a polyion. For a polyion of  $Z$  monomers each with charge  $-q$ , separated by a distance  $b$ , placed in a solvent with dielectric constant  $D$ , in the presence of counterions of charge  $\alpha q$ , the Manning criterion<sup>(13)</sup> states that the number of condensed counterions on a polyion is  $n = (1 - 1/\alpha\xi) Z/\alpha$  where  $\xi = q^2/Dbk_B T$ . Thus, for the case of DNA with divalent counterions, 88% of the DNA's charge is neutralized. It is easy to convince oneself that if the interaction between two rod-like molecules is repulsive, there will be a greater probability that they will be found perpendicular to one another. The correlation induced attraction between the DNA molecules is short ranged. This means that the electrostatic repulsion due to the uncompensated charge is dominant at large distances. Thus, the two polyions will in general repel one another. It is only when the two macromolecules come in a close contact that the thermal fluctuations might be able to overcome the free energy barrier between the perpendicular and the parallel configurations, allowing the correlation induced attraction to take over and the polyions to "bundle up." It has been argued that the size of this free energy barrier scales with the size of the bundle already formed.<sup>(14)</sup> Thus, there comes a point when the thermal fluctuations will not be able to overcome the free energy barrier. Motivated by this discussion we shall now proceed with the study of interactions between rotating like charged rods.

## 2. DEFINITION OF THE MODEL AND ITS SOLUTION

We consider two rod-like polyions, each one with  $Z$  monomers of charge  $-q$  separated by distance  $b$ , Fig. 1. On each polyion,  $n$   $\alpha$ -valent counterions, with charge  $\alpha q$ , are condensed. The sites where the condensed counterions are located are described by occupation variables  $\sigma_{ij}$ , such that  $\sigma_{ij} = 1$  if a counterion is condensed on the  $i$ th monomer ( $i = 1, \dots, Z$ ) of the  $j$ th polyion ( $j = 1, 2$ ) and  $\sigma_{ij} = 0$  otherwise. When a counterion is condensed on a monomer, we assume that the only effect is the renormalization of the local charge, from  $-q$  to  $-q + \alpha q$ . The rods are located on two parallel planes separated by a distance  $d$  and the line joining the centers of the rods is supposed to be perpendicular to these planes. The angle between the directions of the rods is equal to  $\theta$ , so that  $\theta = 0$  corresponds to the case of parallel rods considered<sup>(9)</sup> previously. The definitions above are illustrated in Fig. 1. Notice that, for simplicity, we will consider only odd values of  $Z$ , so that for nonzero values of  $\theta$  the distance between the central charges of each rod vanishes as  $d \rightarrow 0$ . The polyions are placed in a uniform solvent whose dielectric constant is equal to  $D$ . For a given configuration  $\{\sigma\}$  of condensed counterions the Hamiltonian for the pair of polyions may then be written as

$$\mathcal{H} = \frac{q^2}{2D} \sum_{i, i'=1}^Z \sum_{j, j'=1}^2 \frac{(1 - \alpha\sigma_{ij})(1 - \alpha\sigma_{i'j'})}{b\delta(i, j, i', j')}, \quad (1)$$

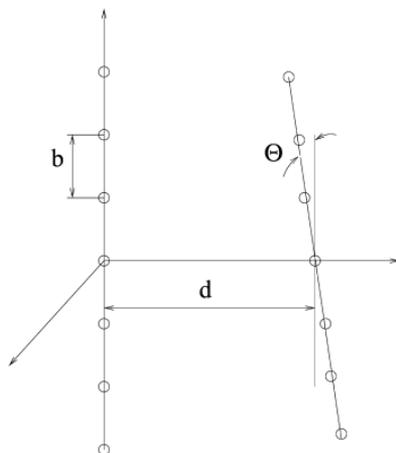


Fig. 1. Two rod-like polyions with  $Z = 7$  charges each.

where the denominator is the distance between the sites  $(i, j)$  and  $(i', j')$ , the sum is restricted to  $(i, j) \neq (i', j')$ , and

$$\delta(i, j, i', j') = \begin{cases} |i - i'|, & \text{if } j = j', \\ \sqrt{x^2 + f_i^2 + f_{i'}^2 - 2f_i f_{i'} \cos \theta}, & \text{if } j \neq j'; \end{cases} \quad (2)$$

with  $x = d/b$  and

$$f_i = \frac{Z + 1 - 2i}{2}. \quad (3)$$

The values of occupation variables obey the constraints  $\sum_{i=1}^Z \sigma_{i1} = \sum_{i=1}^Z \sigma_{i2} = n$ .

The partition function of the model is given by

$$Q = \sum'_{\{\sigma\}} \exp(-\beta \mathcal{H}) = \sum'_{\{\sigma\}} \exp(-\xi H), \quad (4)$$

where the prime denotes the constraint of fixed numbers of condensed counterions on each polyion. The adimensional reduced Hamiltonian  $H$  is given by

$$H = \frac{1}{2} \sum_{(i,j) \neq (i',j')} \frac{(1 - \alpha \sigma_{ij})(1 - \alpha \sigma_{i'j'})}{\delta(i, j, i', j')}, \quad (5)$$

and  $\xi = \beta q^2 / Db$  is the Manning parameter.<sup>(13)</sup> For a given counterion configuration  $\{\sigma\}$ , if a transformation  $\sigma'_{ij} = 1 - \sigma_{ij}$  is performed, the Hamiltonian changes as

$$H(Z, \alpha, n, x, \theta, \{\sigma\}) = (\alpha - 1)^2 H(Z, \alpha', n', x, \theta, \{\sigma'\}), \quad (6)$$

where  $\alpha' = \alpha / (\alpha - 1)$  and  $n' = Z - n$ . This relation leads to the following invariance property of the partition function of the model

$$Q(Z, n, \xi, \alpha, x, \theta) = Q(Z, Z - n, [\alpha - 1]^2 \xi, \alpha / [\alpha - 1], x, \theta), \quad (7)$$

and therefore we may restrict ourselves to  $n < Z/2$  in the calculations. The free energy of the model is  $\phi = -k_B T \ln Q$ , and the force between the rods is  $F = -\frac{\partial \phi}{\partial d}$ . It is then useful to define an adimensional force as

$$f = \frac{Db^2 F}{q^2} = \frac{1}{\xi Q} \frac{\partial Q}{\partial x}. \quad (8)$$

It should be noted that the definition of reduced force  $f$  we use here is different from the one used in ref. 9, since the earlier definition diverges at vanishing temperature. The sign was chosen in such a way that repulsive forces are positive.

To solve the model exactly, one may define activity variables

$$y_i = \exp \left[ -\frac{\xi}{i} \right], \quad i = 1, \dots, Z-1 \quad (9)$$

$$z_{ij} = \exp \left[ -\frac{\xi}{d_{ij}} \right], \quad i, j = 1, \dots, Z, \quad (10)$$

where  $d_{ij} = \sqrt{x^2 + f_i^2 + f_{i'}^2 - 2f_i f_{i'} \cos \theta}$ . It may then be noticed that the partition function may be written as

$$Q = \sum_{i=1}^{N_c} w_i, \quad (11)$$

where

$$N_c = \left[ \frac{Z!}{n! (Z-n)!} \right]^2$$

is the number of condensed counterions configurations and the statistical weight of the  $i$ th configuration is given by

$$w_i = \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{k,l=1}^Z z_{kj}^{v_{ikl}}, \quad (12)$$

$u_{ij}$  and  $v_{ikl}$  being quadratic polynomials in  $\alpha$  with integer coefficients. It is possible to generate these sets of integer numbers with a computer program and thus obtain the partition function of the model exactly. On a conventional personal computer with a rather moderate processing time it is easy to obtain results up to  $Z = 13$ , and simulations<sup>(9)</sup> for larger polyions show that the qualitative behavior of the model does not change much beyond this value, so we will restrict ourselves here to  $Z \leq 13$ .

### 3. RESULTS FOR THE THERMODYNAMIC BEHAVIOR OF THE MODEL

The thermodynamic behavior of the model is determined by the free energy  $\phi$  obtained above. We will start by considering the behavior of  $\phi$

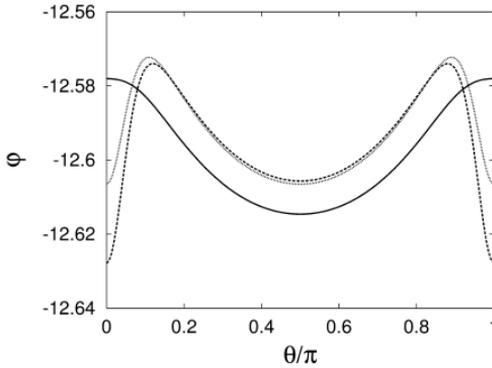


Fig. 2. Free energy  $\varphi$  as a function of the angle  $\theta$ .  $Z = 9$ ,  $n = 4$ ,  $a = 0.8$ ,  $\xi = 2$ . The curves shown are for:  $x = 2$  (—),  $x = 1.3676010335$  (·····), and  $x = 1.3$  (---). Notice that the free energies for  $\theta = 0$  and  $\theta = \pi/2$  are equal in the second case.

as a function of  $\theta$ . For convenience, we define an adimensional free energy

$$\varphi = \frac{Db}{q^2} \phi = -\frac{1}{\xi} \ln Q. \quad (13)$$

The free energy is a function of the parameters  $Z$ ,  $n$ ,  $\xi$ ,  $\alpha$ ,  $x$ , and  $\theta$ . For reasons which will become clear below, we replace the parameter  $\alpha$  by

$$a = \frac{2n\alpha}{Z} - 1, \quad (14)$$

so that we will consider the free energy  $\varphi(Z, n, \xi, a, x, \theta)$ . In all cases we noticed that the global minimum of the free energy is located either at the parallel ( $\theta = 0$ ) or at the perpendicular ( $\theta = \pi/2$ ) configuration of the rods. An example of this is shown in Fig. 2, and one may note that, in general, the parallel configuration is stable for small distance  $x$  and the perpendicular one becomes stable as  $x$  increases. So, in what follows we will concentrate our attention on the parallel and perpendicular rod configurations only.

We will now focus on the regions of the parameter space where the parallel and perpendicular configurations are stable. We will start discussing the behavior of the model at vanishing values of  $x$ . In this limit, the partition sum is dominated by the contributions coming from interactions between charges separated by a distance  $x$ . For the case  $\theta = 0$  we have  $Z$  pairs in this situation. We may then rewrite the partition function as

$$Q_{\parallel} = \sum_{i=1}^{N_c} \prod_{j=1}^{Z-1} y_j^{u_{ij}} Z_0^{\sum_{k=1}^Z v_{ikk}} \prod_{l \neq m} Z_{lm}^{v_{ilm}}, \quad (15)$$

where  $z_0 = z_{kk} = \exp(-\xi/x)$  vanishes as  $x \rightarrow 0$ . Now let us call

$$v = \min_i v_i = \min_i \sum_{k=1}^Z v_{ikk}, \quad (16)$$

and let us suppose that the first  $N_1$  of the  $N_c$  condensed counterion configurations correspond to this value of  $v_i$ . Thus

$$Q_{\parallel} = z_0^v W_{\parallel} (1 + P), \quad (17)$$

where

$$W_{\parallel} = \sum_{i=1}^{N_1} \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{l \neq m} z_{ilm}^{v_{ilm}},$$

and

$$P = \frac{1}{W_{\parallel}} \sum_{i=N_1+1}^{N_c} z_0^{v_i-v} \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{l \neq m} z_{ilm}^{v_{ilm}}$$

vanishes as  $x \rightarrow 0$ , since  $v_i > v$ . The  $N_1$  configurations considered here are the ones that maximize the number of  $(-1, -1 + \alpha)$  pairs separated by a distance  $x$ , and thus  $v = Z - 2n\alpha = -Za$ . For the parallel configuration, we thus have that at small values of  $x$ , the partition function is asymptotically given by

$$Q_{\parallel} \approx W_{\parallel} z_0^{-Za}. \quad (18)$$

A simple combinatorial calculation leads to

$$N_1 = \frac{Z!}{(n!)^2 (Z - 2n)!}. \quad (19)$$

The same line of reasoning may be applied to the perpendicular case, where only the pair of central charges  $([Z+1]/2, 1)$  and  $([Z+1]/2, 2)$  is separated by a distance  $x$ . One, therefore, has in this case

$$Q_{\perp} \approx W_{\perp} z_0^{1-\alpha}, \quad (20)$$

with

$$W_{\perp} = \sum_{i=1}^{N_2} \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{(l,m) \neq ([Z+1]/2, [Z+1]/2)} z_{ilm}^{v_{ilm}}, \quad (21)$$

where the first  $N_2$  configurations are now supposed to be the ones with a central (0, 1) pair, and

$$N_2 = \frac{[(Z-1)!]^2}{(Z-n)! (Z-n-1)! n! (n-1)!}. \quad (22)$$

From Eqs. (18) and (20),  $Q_{\parallel} = Q_{\perp}$  at low distances leads to

$$a = a_0 + a_1 x + \mathcal{O}(x^2), \quad (23)$$

with

$$a_0 = \frac{Z-2n}{Z(2n-1)}, \quad (24)$$

$$a_1 = \frac{2n}{Z\xi(2n-1)} (\ln W_{\perp} - \ln W_{\parallel}). \quad (25)$$

It is thus apparent that the sign of the inclination of the curve  $\varphi_{\parallel} = \varphi_{\perp}$  in the  $(a, x)$  plane at  $x = 0$  is determined by the sign of  $W_{\perp} - W_{\parallel}$ , since  $\ln(x)$  is a monotonically increasing function.

In Fig. 3 the curve of equal free energies in the plane  $(a, x)$ , separating the stable parallel and perpendicular configurations, is shown for the case  $Z = 9$ ,  $n = 2$ . For all temperatures, the curves meet at  $(a_0 = 5/27, x = 0)$ , as expected. For the case of the ground state (vanishing temperature), the curve displays discontinuous derivatives at points where the configurations of the ground state change. Another point which is worth observing is that

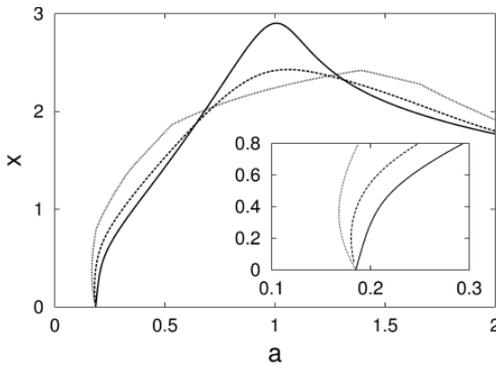


Fig. 3. Curves of equal free energies ( $\varphi_{\parallel} = \varphi_{\perp}$ ) for the model with  $Z = 9$ ,  $n = 2$ , for  $\xi = 1$  (—),  $\xi = 2$  (---) and  $\xi \rightarrow \infty$  (····). The parallel configuration is stable on the right hand side of the curves. Inset shows the reentrant behavior found for some values of  $\xi$  and short distances.

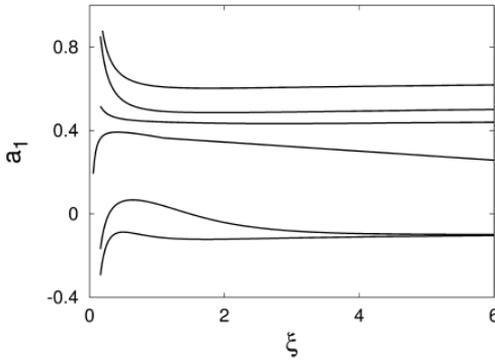


Fig. 4. Inclination of the curves of equal free energies at  $x = 0$ ,  $da/dx = a_1$ , as a function of  $\xi$  for some cases  $(Z, n)$ . From top to bottom:  $(13, 4)$ ,  $(9, 3)$ ,  $(11, 3)$ ,  $(13, 3)$ ,  $(9, 2)$ ,  $(11, 2)$ .

for  $\xi > 1.489528\dots$  or  $\xi < 0.288876\dots$  the curve starts with *negative* inclination at  $(a_0, 0)$ . Thus, for a value of  $a$  somewhat smaller than  $a_0$  the perpendicular configuration is stable at large *and* small distances, while parallel rods are stable at intermediate distances. Thus, in this case we find that the perpendicular phase is reentrant as the distance  $x$  is lowered. Figure 4 shows the initial inclination  $a_1 = (\frac{\partial a}{\partial x})_{x=0}$  as a function of  $\xi$  for some examples. As is apparent in expression 25, these inclinations diverge as  $\xi \rightarrow 0$ , their sign in this limit being determined by  $W_{\perp} - W_{\parallel}$ . As a general rule, one notices that reentrant behavior is found for relatively small values of  $n$  in the examples that we have studied ( $n < 3$  for  $Z = 7, 9, 11$  and  $n < 4$  for  $Z = 13$ ).

Finally, we discuss the behavior of the force defined in E. (8). As a general rule, for sufficiently large values of  $a$ , the force is repulsive at large distances and becomes attractive as the distance is lowered. It is useful to find the value of the distance  $x$  for which the forces  $f_{\parallel}$  and  $f_{\perp}$  vanish. The behavior of these curves at small distances may be found from the asymptotic behavior of the free energies described in Eqs. (18) and (20). We find

$$f_{\parallel} \approx h_{\parallel}x - \frac{Za}{x^2}, \quad (26)$$

where

$$\frac{1}{\xi W_{\parallel}} \frac{\partial W_{\parallel}}{\partial x} = h_{\parallel}x + \mathcal{O}(x^2).$$

Thus, for small values of  $x$ , the curve  $f_{\parallel} = 0$  reads

$$x \approx \left( \frac{Za}{h_{\parallel}} \right)^{1/3}, \quad (27)$$

so that attractive forces in the parallel configuration are possible only if  $a > 0$ , since  $h_{\parallel} > 0$ . This means that a minimum number,  $n = Z/2\alpha$ , of condensed counterions is necessary to produce attraction.<sup>(9)</sup> For the perpendicular configuration, similar considerations lead to

$$f_{\perp} \approx h_{\perp} x - \frac{\alpha - 1}{x^2}, \quad (28)$$

and therefore the curve  $f_{\perp} = 0$  for  $x \ll 1$  is given by

$$x \approx \left( \frac{\alpha - 1}{h_{\perp}} \right)^{1/3}. \quad (29)$$

For small separations between the rods, the curve  $f_{\perp} = 0$ , in the  $(a, x)$  plane, tends to  $a = a_{\perp} = -1 + 2n/Z$ . In Fig. 5 the curves  $f_{\parallel} = 0$ ,  $f_{\perp} = 0$ , and  $\varphi_{\parallel} = \varphi_{\perp}$  are depicted for a particular case. One notices that, for  $a > a_0$ , the force between the rods is attractive for sufficiently small distances  $x$  and the rods are in the parallel configuration. For  $a_{\perp} < a < a_0$  the force is still attractive at small  $x$ , but the rods are in the perpendicular configuration.

The behavior of the force as a function of the distance  $x$ , for  $a = 0.2$ , is shown in Fig. 6. At  $x = 1$  the force is repulsive and the rods are *perpendicular*. As the distance is lowered, the force becomes attractive, with the rods still in the *perpendicular* configuration. At  $x = 0.246924\dots$  the rods change to parallel configuration and the attractive force becomes much larger. At small distances, the force displays an asymptotic behavior of the form  $-Za/x^2$ , according to Eq. (26). A different behavior is found

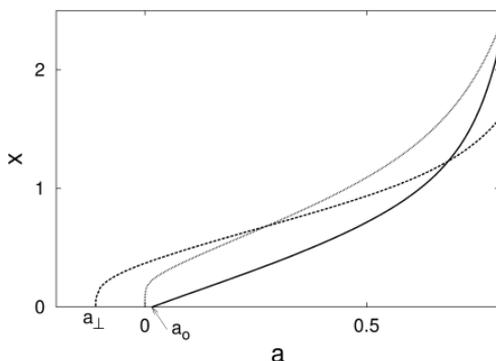


Fig. 5. Curves of equal free energies (—),  $f_{\parallel} = 0$  ( $\cdots$ ), and  $f_{\perp} = 0$  (---), for the model with  $Z = 9$ ,  $n = 4$ , and  $\xi = 1$ . Note that below the solid curve the parallel configuration has the lowest free energy, while above, the perpendicular configuration is energetically favored. The parallel configuration has an attractive force between the polyions below the dotted line. Similarly perpendicular configuration is attractive below the dashed line.

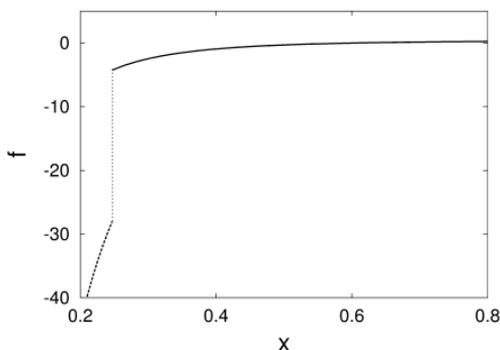


Fig. 6. Force as a function of the distance between rods for  $Z = 9$ ,  $n = 4$ ,  $a = 0.2$  and  $\xi = 1$ . The full line corresponds to perpendicular rods and the dashed line to parallel rods.

for  $a = 0.75$ . In this case the force is *repulsive* at large distances and the rods are perpendicular. As the distance is lowered, the force changes discontinuously to attractive and the rods become *parallel*. Notice that for this value there is no *stable perpendicular* attractive configuration.

Finally, an example of the behavior of the force as a function of the temperature  $1/\xi$  may be seen in Fig. 7. For the values of the parameters used to obtain these data, the parallel configuration is stable. In general, the modulus of the force increases as the temperature is lowered, since the charge correlations grow in this case. However, at relatively low temperatures and short separations between the polyions, this rule may not apply, as is the case in the example shown. The reason for this is that the ground state configuration, which corresponds to the lowest electrostatic energy, is not, in general, the configuration which maximizes the attractive force. For low temperatures and short distances there are configurations which have

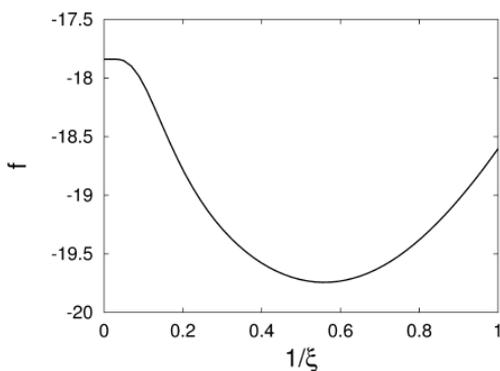


Fig. 7. Force as a function of  $1/\xi$  for  $Z = 9$ ,  $n = 4$ ,  $a = 0.6$ , and  $x = 0.5$  – notice the non-monotonic variation of the force. For  $Z = 9$  and  $n = 2, 3$  a purely monotonic decrease of the modulus of the force as the function temperature is found.

forces more attractive than those found for the ground state. The total force, being a weighted mean of forces associated with all configurations can, therefore, become more attractive than the force at  $T = 0$ .

#### 4. DISCUSSION AND CONCLUSIONS

To get a better understanding of the range of electrostatic correlational forces involved, we study a simple example of two parallel long polyions with  $Z/2$  condensed divalent counterions. In the ground state the counterions are distributed periodically along the polyions. At finite temperature, this periodicity will be destroyed, the correlations between the condensed counterions, however, will persist. Thus, for sufficiently large electrostatic coupling, i.e., Manning parameter, the electrostatic potential at position  $(\rho, s)$  from a polyion can be approximated as,

$$\phi(\rho, s) = q \sum_{n=-\infty}^{\infty} \frac{(-1)^n}{\sqrt{\rho^2 + (s - nb)^2}}. \quad (30)$$

Appealing to Poisson sum rule the asymptotic large distance behavior of this sum can be evaluated yielding

$$\phi(\rho, s) = \frac{4q}{\sqrt{2\rho b}} \exp\left(-\frac{\pi\rho}{b}\right) \cos\left(\frac{\pi s}{b}\right). \quad (31)$$

The electrostatic energy of interaction between two staggered lines of charge is then

$$E = -\frac{4qZ}{\sqrt{2\rho b}} \exp\left(-\frac{\pi\rho}{b}\right) \quad (32)$$

and the force,  $F = -\partial E/\partial\rho$ , is

$$\frac{F}{Z} = -\frac{4q}{\sqrt{2\rho b^3}} \exp\left(-\frac{\pi\rho}{b}\right) \left(\pi + \frac{b}{2\rho}\right) \quad (33)$$

We see that the correlation induced attraction decays exponentially, with the characteristic range of  $l = b/\pi$ .

We have studied the electrostatic interaction between two charged roads with a layer of condensed counterions. This is the simplest model of interaction for like charged polyions in a polyelectrolyte solutions. It is shown that in spite of the equal net charge on the two macromolecules the

correlations between the condensed counterions can produce an effective attraction. We show, however, that this attraction is of extremely short range, comparable to the monomer separation along the macromolecules. Furthermore, it is found that at large distances the monopolar repulsion between the charge densities forces the polyions into a perpendicular configuration. At short distances the correlations between the condensed counterions can become sufficient to produce a macromolecular alignment. The energy barrier associated with the transition from the perpendicular to the parallel configuration might be relevant for the kinematics of bundle formation in solutions of stiff polyelectrolytes.<sup>(14)</sup> We should mention, however, that a line of charge model considered in this work is a strong idealization of real polyions. Thus, the reentrant behavior as well as the non-monotonic variation of force with temperature might be an artifact of not considering the finite radius of the polyions.<sup>(15)</sup> We hope to address these issues in our future work.

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