

Attractive interactions between rodlike polyelectrolytes: Polarization, crystallization, and packing

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We study the attractive interactions between rodlike charged polymers in solution that appear in the presence of multivalence counterions. The counterions condensed to the rods exhibit both a strong transversal polarization and a longitudinal crystalline arrangement. At short distances between the rods, the fraction of condensed counterions increases, and the majority of these occupy the region between the rods, where they minimize their repulsive interactions by arranging themselves into packing structures. The attractive interaction is strongest for multivalent counterions. Our model takes into account the hard-core volume of the condensed counterions, and their angular distribution around the rods. The hard-core constraint strongly suppresses longitudinal charge fluctuations. [S1063-651X(99)13510-4]

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Strongly charged polymers precipitate from a dilute solution into compact structures when high-valence counterions (oppositely charged particles) are added to the solution [1–6]. The counterions experience strong electrostatic attractions to the backbone of the chains, and a finite fraction of them “condense,” i.e., are found within a short distance from the chains [7]. Counterions are more attracted to compact chains or aggregates of rodlike chains. This creates the possibility of a transition from single chains with a small number of condensed counterions to almost neutral aggregates of chains, or even monomolecular collapse in the case of flexible polymers. These aggregates are stable only when the internal arrangement of the counterions within them provides a strong enough cohesive energy.

In this paper we study the attraction between two rodlike polyelectrolytes. We show that it is essential to include the size and angular degrees of freedom (around the rods) of the counterions as well as the discrete nature of the charge along the polyelectrolytes to find the origin and strength of the counterion mediated attraction. Our work suggests that these factors are also crucial in determining the collapse of flexible and semiflexible polyelectrolytes recently studied in Refs. [8–12]. Experimental observations show that the size of the precipitating particles is indeed a relevant parameter in the problem [1,6].

It has been argued that longitudinal charge fluctuations resulting from the thermal motion of point counterions induce attractions between rodlike polyelectrolytes [13,14], and induces “buckling” of semi-flexible polyelectrolytes [11,12]. Here we show that such charge fluctuations are suppressed when the hard-core volume of monomers and counterions are taken into account. Instead, we find that the counterion arrangement around the rods creates a nonzero transversal polarization as the distance between the chains decreases. At very short distances between the rods we find strong longitudinal correlations but only at very short wavelengths, implying a crystalline state along the rod, reinforcing, for the case of multivalent counterions, the attractive interactions due to polarization.

The crystalline structure of the counterions when the rods are at short distance from each other has been suggested in

simulations by Grønbech-Jensen *et al.* [15], and was theoretically proposed by Arenzon *et al.* [16] and Shklovskii [17]. These previous theoretical works retain some of the small size effects of a realistic system, but again use the assumption of negligibly sized counterions. These models do not reveal the polarization effects that appear when the angular degrees of freedom around the rod are considered.

The polymer chains are modeled as rigid rods formed by N repeat units, each with charge $+1$ centered at each of the monomers, as shown in Fig. 1. We label the pair of rods A and B . The diameter of the rods and the spacing between charges are both b . The total length of the chains is $L = Nb$. We will only consider the case in which the chains are parallel and separated by a distance r measured from center to center. The counterions carry a charge $-Z$, and for simplicity we take them to be of diameter b as well. Overall charge neutrality of the system implies that there are N/Z counterions per chain. We assume a concentration of chains c , to be such that the average distance between rods (if noninteracting) is also L , so that $c = 1/L^3$.

A layer of condensed counterions surrounds each chain. The location of a particular counterion is given by its position along the rod z , a radial distance r from the rod, and its angular position θ . We restrict the z coordinate of the con-

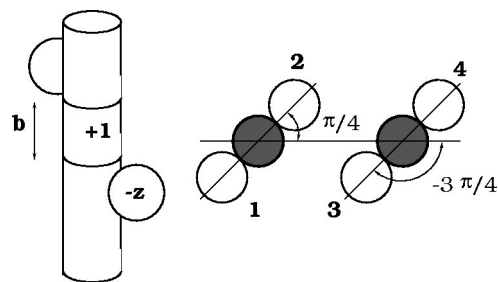


FIG. 1. The diameter of the rod, the size of the counterions, and the basic spacing between charges all have magnitude b . We use two representative states for each monomer in each rod. All occupation is assumed to take place parallel to the centers of the monomers, so that the possible places for occupation form the lattices 1,2,3, and 4, here shown from the top.

densed counterions to take values coinciding with those of the centers of the monomers. The radial distance from the rod for all condensed counterions is assumed always to take the value $r=b$. The angular variable is very important, as it carries information about the local polarization of the rod-counterion system. A suitable simplification that retains this information consists of collapsing the range of angular positions to only two specific locations. These positions are located at angles of $\pi/4$ and $-3\pi/4$ with respect to the plane that contains both rods, and are labeled as shown in Fig. 1. These *ad hoc* positions are meant to represent locations of counterions on one rod that look toward or away from the other rod, and have the convenience of allowing us to consider distances between the centers of rods as small as $\sqrt{2}b$ without worrying about an overlapping of the counterions that would require an explicit introduction of hard-core repulsions. The choice of angles does not significantly change the results. In short, we have modeled the condensed layers as four linear lattices parallel to the rods, whose sites can be occupied by the counterions.

Since our selected geometry takes care of the hard-core interactions between the particles of the system, we can construct a Hamiltonian with only electrostatic interactions. This is given by

$$H_c = l_B \sum_{s \neq t} \frac{1}{2} Z^2 \frac{1}{|\mathbf{r}_s - \mathbf{r}_t|} - l_B \sum_s Z \phi(\mathbf{r}_s). \quad (1)$$

We measure energies in units of $k_B T$, and the prefactor l_B is the dimensionless ratio of the Bjerrum length to the monomer size $e^2/\epsilon b k_B T$, with e being the electron charge, k_B the Boltzmann constant, T the temperature, and ϵ the dielectric constant of water. ϕ is the electrostatic potential created by the charged rods. Ignoring end effects from the rods, this potential is well approximated by $\phi(\mathbf{r}) = 2l_B(\ln(L/r_A) + \ln(L/r_B))$, where r_A and r_B are the distances from the point \mathbf{r} to the axis of the rods A and B , respectively. For the condensed counterions, it is better to change to a local charge representation. Each site of the four lattices can be occupied by one counterion (we neglect multiple occupation), and thus it will carry a charge $q_i(n)$ that can be either $-Z$ or zero. The index i is the (longitudinal) position in the lattice, that can range from 1 to N .

Since the number of monomers is large, we expect that the total number of condensed counterions for a given inter-rod separation will have a narrowly peaked probability distribution. We construct a free energy that assumes that the number of counterions condensed to each of the lattices is fixed, and then we will find the minimum with respect to the occupation numbers. Lattice i carries a fraction f_i of the number of counterions per rod N/Z , and the fraction condensed to rod A is $f_A = f_1 + f_2$, etc.

The free counterions form a dilute charged gas that occupies a volume $V = 2L(L^2 - 4b^2)$. Because of their low density their contribution to the free energy from correlations and screening is negligible. A free counterion at a distance r_c from the center of the system ‘‘feels’’ a potential given approximately by $\phi = 2(l_B/e)(2 - f_A - f_B)(1 - (r_c^2/2L^2))\ln(L/r_c)$, that arises from the effective (uncompensated) charge of the two rods and a cylindrical shell of uniformly distributed free counterions. Averaging this poten-

tial over the volume, and, adding the entropic contribution, we obtain the free energy per monomer due to the free counterions:

$$F_f = \frac{1}{2Z} (2 - f_A - f_B) [\ln((2 - f_A - f_B) N b^3 / V) - 1] + \frac{1}{2} (2 - f_A - f_B)^2 \left(-\frac{3}{2} l_B \right). \quad (2)$$

To obtain the contribution from the condensed counterions, we first consider a high-temperature approach in which we add fluctuations to a uniformly distributed state. Given a condensed fraction f_i at the lattice i , there are $f_i N/Z$ occupied sites. The statistical sum over all states satisfying this restriction can be replaced at high temperatures by Gaussian integrations over a set of continuous local charge variables. The charge $q_i(n)$ is represented by a density $\rho_i(n)$ with mean $-f_i$ and variance $\sigma_i^2 = Z^2(f_i/Z)(1 - f_i/Z)$. This form of the variance is consistent with our assumption of a maximum of one counterion per lattice site, as required by our geometry and hard-core constraints [18]. We can pass to a discrete Fourier representation of the local charge of the form

$$\rho_i(n) = -f_i + \sum_{k \neq 0} \rho_i(k) \exp(ikn), \quad (3)$$

where the only Fourier modes considered are of the form $k = \pm 2\pi m/N$, with m ranging from $-N/2$ to $N/2$. This transformation diagonalizes the part of the Hamiltonian, [Eq. (1)], that corresponds to the condensed counterions, and leads to the free energy per monomer:

$$F_c = \frac{1}{4} \sum_{i,j} f_i V_{ij}^0 f_j + \frac{1}{4N} \sum_{k \neq 0} \ln \det[\mathbf{I} + \mathbf{S}\mathbf{V}(k)] - \frac{1}{2} \sum_i f_i \phi_i + \frac{1}{2} \sum_i \frac{f_i}{Z} \left(\ln \frac{f_i N b^3}{V_c} - 1 \right). \quad (4)$$

The first term is the contribution from the zero modes where the interaction matrix between lattices is $V_{ij}^0 = 2l_B \ln(L/r_{ij})$, with r_{ij} the distance between the axis of the lattices, and the diagonal terms are given by $V_{ii}^0 = 2l_B \ln(L/b)$. The second term is the result of the Gaussian integration over fluctuations, where \mathbf{I} is the identity matrix, \mathbf{S} is a diagonal matrix with entries σ_i^2 , and the interaction terms for the Fourier modes are of the forms $V_{ij}(k) = 2l_B K_0(kr_{ij})$ and $V_{ii}(k) = -2l_B ci(kb)$, with K_0 the modified Bessel function, and ci the cosine integral function. The integrals that define the diagonal expressions are evaluated using the lattice spacing b as a short-distance cutoff so that there is no need for self-energy subtractions. The finite sum over modes also corresponds to distances larger than one lattice spacing. The last term is the entropic contribution of placing $f_i N/Z$ counterions in a volume $V_c = Lb^2$.

A posteriori, we found that at short distances between the rods the condensed counterions are almost fully polarized, occupying the states that face the other rod. The fraction of condensed charge approaches 1 in these sites, while the outward states are almost completely depleted. We can then

look in more detail at the calculation of the free energy for the case of almost full occupation of one of the lattices, $f \rightarrow 1$, so that the variance of the fluctuations becomes $\sigma^2 \approx (Z-1)$. The diagonal interaction term for the highest Fourier modes $k \approx \pm \pi/b$ is negative and of order l_B , corresponding to a decrease in energy from vacating a state next to an occupied one. Since typical values for l_B at room temperature are always larger than 1, these diagonal terms dominate the interaction matrix \mathbf{V} , and therefore the matrix $\mathbf{I} + \mathbf{SV}$ has diagonal elements $1 - (Z-1)l_B$. When the condition

$$(Z-1)l_B > 1 \quad (5)$$

is satisfied, the matrix acquires negative eigenvalues, making the determinant divergent and the high-temperature approximation incorrect. Clearly, this occurs in most cases, except for monovalent counterions ($Z=1$) or for very weakly charged polyelectrolytes for which $l_B \ll 1$. The divergence in the determinant for multivalent counterions signals the onset of crystallization, and thus the free energy should be calculated on the basis of a dominant crystalline ground state. Once we use the correct ground state for both monovalence and multivalence cases, it can be shown that the corrections from fluctuations are very small; that is, the contribution of the determinant in Eq. (4) becomes negligible once the divergent modes are subtracted.

The condition established in Eq. (5) is valid for the geometry considered here, in which all small length scales are comparable to each other. If the rods are considerably thicker, the condition will take the (approximate) form $(Z-1)l_B(2b/(D+b)) > 1$, with D the diameter of the rods.

The proper ground state for each of the inner lattices, when approaching full condensation, is clearly given by an arrangement in which counterions are placed one in every Z sites. (This is the case already for $Z=1$.) As the rods approach each other, the inner lattices interact strongly, but they do not destroy the ground state arrangement. Instead, they can choose a location of the occupied sites, so as to minimize their repulsive interaction. For $Z=2$, for example, one expects one of the internal lattices to be filled in the even sites, while the second is filled in the odd ones.

The calculation of the free energy for the multivalence case can be carried out using the results for the monovalent case, which are given by Eq. (4). We simply renormalize the lattice spacing to Zb , and reduce the available sites by a factor of Z . The elements of the interaction matrix for the

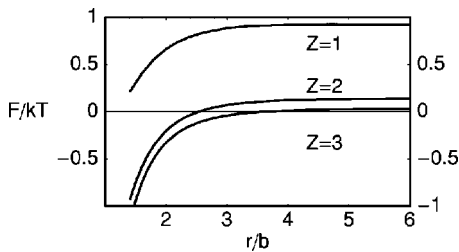


FIG. 2. Results of the minimization of the free energy, for parameters such that $l_B = 4.1$, for valences $Z=1, 2$, and 3 . Energies are shown in units of $k_B T$ and distances in units of b . The zero of the energy in each case is chosen to match the energy at large separations.

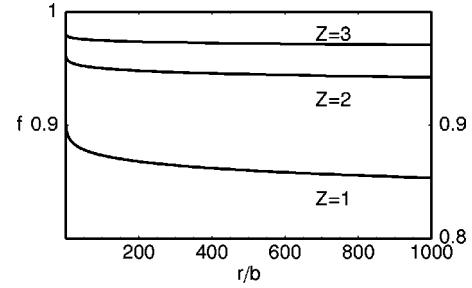


FIG. 3. The total fraction of condensed counterions to each of the rods, as a function of the separation between rods for valences $Z=1, 2$, and 3 . The scale in which the condensed fraction decays to a single rod value is of the order of the size of the rod $L = 10^5 b$. Note the change of scale with respect to Fig. 2.

ground states are now given by $V_{ij}^m = 2l_B \ln(L/r'_{ij})$, with a modified distance between the lattices $r'_{ij} = (r_{ij}^2 + (bZ/2)^2)^{1/2}$ that takes into account the mismatch between the occupied sites in the lattices. The diagonal term is simply $V_{ii}^m = 2l_B \ln(L/Zb)$.

The results presented in Figs. 2–4 are based in this ground-state approximation, but a simple estimate can be made for the size of the corrections to the free energy arising from fluctuations. Consider, for example, the $Z=2$ case. The more important fluctuations around the ground state are the displacements of counterions in a direction longitudinal to the rod. While the full ‘‘phonon’’ spectrum can be calculated for this structure, it is simpler, as a first approximation, to consider independent displacements of the counterions to one site up or down in the rod (a distance b apart). A jump to a neighbor vacant place changes the the energy of interaction with its nearest counterion neighbors by an amount of $\Delta E = \frac{4}{3}l_B$ (given $f \approx 1$). Assuming that a counterion can only occupy its original position and the two empty neighboring sites, we obtain a free energy contribution from these N independent fluctuating modes, per monomer, in units of $k_B T$, of $F_{\text{fluct}} = -\ln(1 + 2e^{-\Delta E}) \approx -2e^{-\Delta E}$. This correction is small for the values of parameters we consider.

In Fig. 2 we present the calculated free energy of the system as a function of the distance between rods. The numerical values for the constants of the system are $T=300$ and $b = 1.8 \text{ \AA}$, so that $l_B = 4.1$ and $N = 10^5$. There is a well of attraction for the mono-valent case of about 0.5 kT , which is

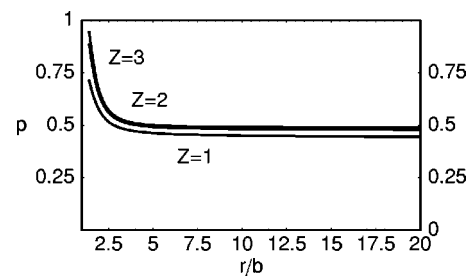


FIG. 4. Polarization of the rods as a function of the separation between rods for valences $Z=1, 2$, and 3 . At very short distances, the polarization is almost complete. Away from the region of strong attraction, the polarization still remains important, and will decay to zero only at distances of order L . The plots for $Z=2$ and 3 overlap almost completely.

not enough to bind the rods, and further, the local minimum at short distances turns out to be of higher energy than the self-energy of two rods separated by a distance L . For $Z = 2$ and 3, the depth of the well is of the order of $k_B T$, and the energy there is lower than their respective reference states.

Figure 3 presents the total amount of condensed counterions for one of the rods, $f_A = f_1 + f_2$. This is always very close to 1 for short distances, and reaches a value near the Manning limit [7], $f = (1 - 1/Zl_B)$ at large separations. We measure the overall polarization p of the rods by the ratio of the difference between the occupation of the inward and outward positions to the total amount of condensed charges; thus, for rod A,

$$p_A = \frac{f_2 - f_1}{f_2 + f_1}. \quad (6)$$

Results for the amount of polarization are shown in Fig. 4. It is clear that the charge will be perfectly balanced when the presence of the second rod is not felt. On the other hand, when the chains are in close contact it is natural for the counterions that occupy the inner sites to be able to interact with the positive charges of both rods, even at the expense of

interacting with other condensed counterions. What it is surprising is that both the polarization and the extra condensation do not decay quickly, and it is necessary to set the distance between the rods to its maximum value L to recover the Manning limit and a symmetric state. A good test of the validity of this theory will be the measurement in simulations and experiments of the transversal polarization of the rods.

In summary, we have shown that the interaction between two charged rodlike polymers generates a strong transversal polarization of their condensed charges, and that at short distances the two rods are strongly driven toward higher counterion condensation. This forces the counterions to crystallize, and then to organize their respective crystals into a packing structure. The final result is an important attraction between the rods when the counterions are multivalent. We found that the finite size of the counterions and their angular degrees of freedom are essential to determine the nature and strength of the counterion-mediated attractions in rigid rods, and we expect this also to be the case in flexible and semi-flexible polyelectrolytes.

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 [18] Our variance differs from the expression used in models that assume point-size counterions (Refs. [14,11]), where the variance is proportional to f_i . A variance proportional to f_i implies, at large condensation fractions, frequent multiple occupation at a monomer site that is inconsistent with the reduced space available to the counterions between the rods.