

## Collapse of Stiff Polyelectrolytes due to Counterion Fluctuations

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The effective elasticity of highly charged stiff polyelectrolytes is studied in the presence of counterions, with and without added salt. The rigid polymer conformations may become unstable due to an effective attraction induced by counterion density fluctuations. Instabilities at the longest (intermediate) length scales may signal a collapse to globule (necklace) states, respectively. In the presence of added salt, a generalized electrostatic persistence length is obtained, which has a nontrivial dependence on the Debye screening length. [S0031-9007(99)09257-1]

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A polyelectrolyte (PE) is an ionic polymer which when dissolved in polar solvents dissociates into a long polymer chain (macroion) and small mobile *counterions*. Because of the electrostatic repulsion of the uncompensated charges on the polymer, the chain is stretched out to rod-like conformations. Naively, one might expect that the more highly charged PEs are the more stiff. However, this tendency is opposed by the stronger attraction to the counterions, which may condense on a highly charged PE, giving it a much lower apparent charge [1,2], and resulting in a lower stiffness. Nonetheless, in a mean-field (Poisson-Boltzmann) treatment of the counterions, the conformation of the PE is stretched.

On the other hand, it is known experimentally that both highly charged flexible PEs (such as polystyrene sulphonate) [3,4] and stiff PEs (such as DNA) [5] can collapse in the presence of multivalent counterions to highly compact states. Rodlike PEs also form bundles under similar conditions [6]. To account for these effects, a relatively long-ranged attractive interaction capable of competing with the residual coulomb repulsion (of the PE backbones with compensated charge densities) is needed.

To understand the origin of the attractive interaction, consider two like-charged substrates on which counterions are condensed. As the two objects approach each other, the counterions may rearrange their positions. Any “correlated separation of charges” now leads to an *attraction* whose range is of the order of the “correlation hole” of the counterions on each substrate. Several different mechanisms may lead to correlated charge separation: At low temperatures, the counterions form a Wigner crystal on the charged substrate, which leads to an attractive interaction with a range set by the lattice spacing [7,8]. Another mechanism for charge separation is a specific binding of counterions to the substrate [9]. In this case, the periodicity, and hence the range of the attraction, is dictated by the underlying structure of the substrate. Thermal fluctuations can also induce instantaneous charge separations which

intercorrelate on the two objects, leading to an attraction similar to the van der Waals interaction. Since dominant contributions come from fluctuations with wavelengths of the order of the separation of the objects, the range of the attraction is set by the distance between them; i.e., the interaction is long ranged [2,10–12].

Recently, there have been a number of studies of the role of counterion condensation in the transition between extended and collapsed states of *flexible* PEs [4,13,14]. The situation is more subtle for *stiff* PEs due to their intrinsic rigidity [15–17]. Here we employ path integral methods [12,18,19] to study the energy cost of deforming a stiff and highly charged PE in the presence of thermally fluctuating counterions. In particular, consider a chain of total charge  $N_c$  and length  $L$ , with a microscopic persistence length  $\ell_p$ , and average separation  $a$  between charges on its backbone, in a neutralizing solution of counterions of valence  $z$ . The PE is highly charged when  $a$  is less than the Bjerrum length  $\ell_B = e^2/\epsilon k_B T$ , where  $\epsilon$  is the dielectric constant of the solvent. (For water at room temperature,  $\ell_B \approx 7.1 \text{ \AA}$ .) We calculate the effective free energy of a fluctuating PE as a perturbative expansion in the deformations around an average rodlike structure. The linear stability of this structure is controlled by a spectrum  $\mathcal{E}(k)$ , as a function of the deformation wave vector  $k$ . A negative value of  $\mathcal{E}(k)$  signals an instability at the corresponding wavelength, leading to phase diagrams as in Figs. 2 and 3 below. In particular, in the absence of salt (see Fig. 2 below), we find that counterion fluctuations *cannot* trigger the collapse of a stiff PE, *unless* it has a microscopic persistence length less than a critical value of

$$\ell_p^c = \Delta \times a \times z^4 \times \left(\frac{\ell_B}{a}\right)^3 \times \left(1 - \frac{a}{z\ell_B}\right)^2, \quad (1)$$

in which  $\Delta$  is a numerical constant given later. For  $\ell_p < \ell_p^c$ , there is a finite domain of intermediate lengths  $L$  of the PE for which a collapsed conformation is favored.

For a low concentration of added salt, we find an effective persistence length of

$$L_p = \ell_p + \frac{a(a/\ell_B)^3}{16z^4(1 - a/z\ell_B)^2(\kappa a)^2 \ln^2(\frac{1}{\kappa a})} - \frac{c_2}{2\kappa \ln(\frac{1}{\kappa a})}, \quad (2)$$

where  $\kappa^{-1}$  is the Debye screening length, related to the salt (number) density  $n$  via  $\kappa^2 = 4\pi\ell_B n$ , and  $c_2$  is a numerical constant given below. The above expression, which is a *nontrivial* generalization of the Odijk-Skolnick-Fixman (OSF) electrostatic persistence length [20], is a sum of repulsive (+) and attractive (-) electrostatic contributions. It can therefore be negative under certain conditions, which we take as an indication of a conformational instability of the rodlike PE (tendency to collapse). This occurs in the regions of the phase diagram indicated in Fig. 3 below, and only for persistence lengths less than a critical value given by an expression similar to Eq. (1). A similar “softening” contribution to the rigidity of charged membranes, and associated conformational instability, is reported in Ref. [21]. There are related instabilities caused by surface fluctuation-induced interactions between stiff polymers on membranes [22].

Without loss of generality, we orient the PE along the  $x$  axis and parametrize its configuration by a 3D vector  $R(x)$ . For small deformations (no overhangs) as in Fig. 1, we can set  $R(x) = [x, \mathbf{r}(x)]$ , where the 2D vector  $\mathbf{r}(x)$  measures transverse deviations from a rod for  $0 \leq x \leq L$ . For each configuration we would like to calculate a constrained partition function  $Z[R]$ , by integrating over all counterion positions in the solution. As this is quite difficult, we instead generalize the approach of Ref. [11] and integrate over a fluctuating counterion charge density along the PE backbone, as [19]

$$Z[R] \equiv e^{-\beta\mathcal{H}_0^{\text{eff}}[R]} = e^{-\beta\mathcal{H}^p[R]} \int \mathcal{D}q(x) \times \exp\left\{-\frac{1}{2} \int \frac{dx}{a} \frac{[q(x) - q_0]^2}{(\delta q)^2} - \frac{\ell_B}{2} \times \int \frac{dx}{a} \frac{dx'}{a} \frac{q(x)q(x')e^{-\kappa|R(x)-R(x')|}}{|R(x)-R(x')|}\right\}. \quad (3)$$

The first term,  $\beta\mathcal{H}^p[R] = \ell_p \int dx (\partial_x^2 R)^2/2$ , is the energy cost of bending the PE, and  $\beta = 1/k_B T$ . In the

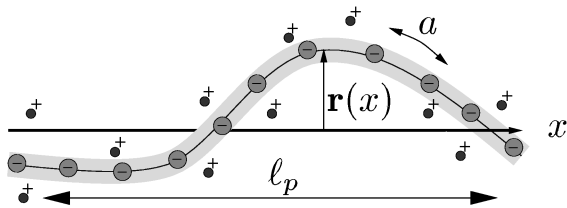


FIG. 1. Transverse deformations of a rodlike PE.

second term, the condensate charge is integrated over a Gaussian distribution of mean  $q_0 = a/z\ell_B$ , and variance  $(\delta q)^2 = z(1 - a/z\ell_B)$  [11,19]. A finite  $\kappa$  anticipates the effect of added salt [23].

Using the methods of Refs. [12,18], the effective Hamiltonian can be calculated perturbatively in the deformation field  $\mathbf{r}(x)$ . In terms of the Fourier modes  $\mathbf{r}(k)$ , the effective free energy cost of deformations is

$$\beta\mathcal{H}_0^{\text{eff}}[\mathbf{r}(x)] = \frac{1}{2} \int \frac{dk}{2\pi} \mathcal{E}(k) |\mathbf{r}(k)|^2 + O(r^4), \quad (4)$$

where, in the absence of salt ( $\kappa = 0$ ),

$$\mathcal{E}(k) = \frac{(q_0^2/a^2)\ell_B k^2 \ln(k/k_0)}{[1 + 2(\delta q)^2(\ell_B/a) \ln(L/a)]^2} - B_1 k^3 + \ell_p k^4. \quad (5)$$

(Despite its appearance, Eq. (5) is *not* a Taylor expansion in  $k$ .) The rigidity term,  $\ell_p k^4$ , ensures stability of the PE at large  $k$  (small length scales). The first term describes the stiffening of the PE due to Coulomb interactions, which is most apparent at long wavelengths, and also involves a cutoff  $k_0 \ll \pi/L$  [24]. Note that the fluctuations in charge reduce the strength of this term considerably, compared to the uniform case with  $(\delta q)^2 = 0$  [25,26]. The new element is the term  $-B_1 k^3$  which is due to the fluctuation-induced attractions [27], and may lead to instabilities at intermediate  $k$ . The coefficient  $B_1$  can be obtained as an integral that depends weakly on  $(\delta q)^2(\ell_B/a)$ , and that for typical values is well approximated as  $B_1 \approx c_1/\ln(L/a)^2$  with  $c_1 \approx 0.101$ .

The rodlike configuration is unstable if any  $\mathcal{E}(k)$  is negative. The onset of instability is thus determined from  $\mathcal{E}(k_m) = 0$ , at the minimum of the spectrum given by  $d\mathcal{E}(k_m)/dk = 0$ . In the limit of  $L \gg a$ , these conditions can be expressed as  $\ell_p = \ell_p^c$ , with the critical persistence length given by Eq. (1) above, with  $\Delta_{sf} \approx c_1^2/\ln^2(L/a) \ln[c_1/2\ell_p k_0 \ln^2(L/a)]$ . For  $\ell_p < \ell_p^c$ , there is a domain of unstable modes for  $k_- < k < k_+$ , where  $k_{\pm} = [c_1/2\ell_p \ln^2(L/a)](1 \pm \sqrt{1 - \ell_p/\ell_p^c})$ . For finite chains, the values of  $k$  are restricted to  $k > \pi/L$ , leading to the following three possibilities: (i) For  $k_+ < \pi/L$ , the unstable modes cannot be accessed and the PE retains its *extended* form. (ii) For  $k_- < \pi/L < k_+$ , the PE is unstable at the longest scales. It will fold in a manner which we interpret as a precursor to collapse into a *globular* state. (iii) For  $\pi/L < k_-$ , the PE is stable at the longest scales, but unstable at intermediate lengths. Although this analysis does not determine the fate of the unstable PE, we guess that this instability signals the formation of a *necklace* structure [28]. These tentative identifications are depicted in the phase diagram of Fig. 2. The boundary of the collapsed phase is obtained from  $k_{\pm} = \pi/L$ , as

$$\frac{\ell_p}{a} \approx \frac{L/a}{\pi \ln^2(L/a)} \left[ c_1 - \frac{(L/a) \ln(\pi/Lk_0)}{4\pi z^4 (\ell_B/a)^3 (1 - a/z\ell_B)^2} \right], \quad (6)$$

and has a nearly parabolic shape.

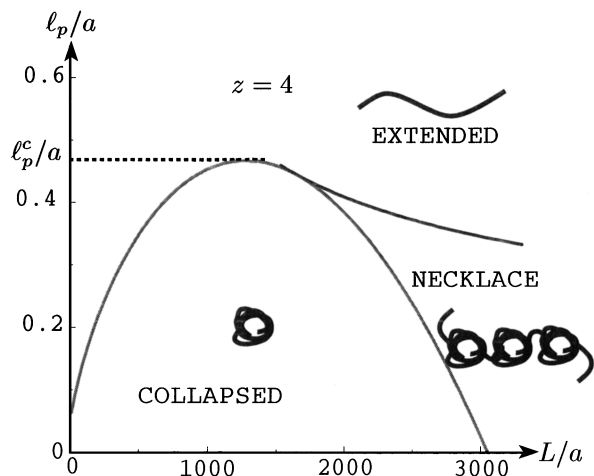


FIG. 2. Phase diagram for the salt-free case, for  $z = 4$ . The parameters  $a = 1.7 \text{ \AA}$  and  $k_0 = 10^{-3} \pi/L$  are used.

For a low concentration of added salt ( $\kappa \neq 0$ ), the energy cost of deformations is again given by Eq. (4), but now the function  $\mathcal{E}(k)$  is analytic, with a well-defined power expansion in  $k$ . The first term in the (properly regularized) expansion is  $L_p k^4$ , from which we can define an effective persistence length given by

$$L_p = \ell_p + \frac{q_0^2 \ell_B}{4[1 + 2(\delta q)^2 (\ell_B/a) \ln(1/\kappa a)]^2 (\kappa a)^2} - \frac{B_2}{2\kappa}. \quad (7)$$

Once again,  $B_2$  is obtained from an integral which has a very slow dependence on  $(\delta q)^2 (\ell_B/a)$  and which, for typical values, can be approximated by  $B_2 \approx c_2 / \ln(1/\kappa a)$  with  $c_2 \approx 0.288$ . This leads to the expression for the persistence length in Eq. (2). It is interesting to note that a similar result has been predicted for stiff polyampholytes [29].

The second term in Eq. (7) reproduces the OSF electrostatic persistence length in the limit  $(\delta q)^2 = 0$  [20], with a reduced charge density  $q_0$ . Upon including the counterion fluctuations,  $(\delta q)^2 \neq 0$ , there is a further reduction in this term. The final term is a negative contribution coming from the fluctuation-induced attractions. The latter reduces the ‘‘rigidity’’ (effective persistence length) of the PE which, if negative, results in conformational instability (collapse). Using this criterion, we obtain the phase diagram of Fig. 3. As in the salt-free case, the phase boundary has a nearly parabolic shape, with a maximum at the critical persistence length given in Eq. (1), with  $\Delta_{as} = c_2^2$ . Note that the maximal persistence length is much larger in the presence of salt, making it much easier to achieve conditions favorable to collapse.

Rather than describing the formal steps of the method and approximations (which will be detailed elsewhere [19]), we conclude with a qualitative summary of the nature of the results and the range of their validity.

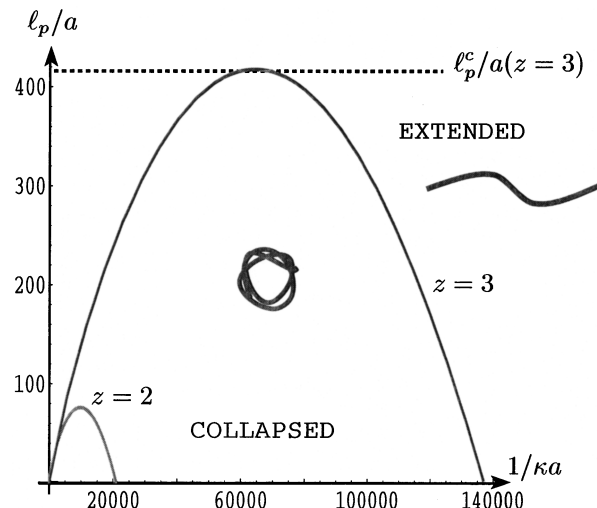


FIG. 3. Phase diagram for the added-salt case, for different values of the counterion valence  $z$ .

From dimensional analysis, it is easy to show that *unscreened* Coulomb interactions make a contribution of  $\ell_B(k/a)^2$  to the rigidity spectrum  $\mathcal{E}(k)$ . In the PB solution, due to charge condensation, the strength of this term is reduced by a factor of  $q_0^2 = (a/z\ell_B)^2$ . If the charge density on the PE is allowed to fluctuate, it is further reduced, and the Coulomb rigidity goes down by a factor of  $(\delta q)^4 (\ell_B/a)^2 \ln^2(L/a)$ , with  $(\delta q)^2 = z(1 - q_0)$ . However, these reductions do not change the overall sign which still prefers a rodlike structure. An attractive (destabilizing) contribution is generated by fluctuation-induced interactions, which are typically independent of microscopic parameters, and hence make a contribution of  $-k^3$  to  $\mathcal{E}(k)$ . Compared to the leading Coulomb contribution, the latter corrections become important at *short scales* of the order of  $a^2/\ell_B$ . We thus may well question the applicability of continuum formulations to describe such a short-distance instability. In hindsight, the phase diagrams of Figs. 2 and 3 indicate that the prefactors involved in the softening of the residual repulsion conspire to make the actual instability lengths quite large ( $\sim z^4 \ell_B^3/a^2$ ), and thus the continuum formulation should hold for a large portion of these phase diagrams [30]. Another potential concern is the relevance of higher order loop corrections when the instability sets in. We are not able to address this issue quantitatively, and it may be best to regard Eq. (3) as a variational approximation to the full problem. Finally, the instability analysis performed here provides us only with information concerning the onset of a conformational change. The final structure of the collapsed chain is naturally beyond this linear stability analysis [5,31].

It is known experimentally that different counterions with the same valence may behave differently as collapsing agents. The difference is usually attributed to modifications in the microscopic structure of the PE that take

place upon binding of the counterions [5]. It is thus plausible that the microscopic features that distinguish between different counterions with the same electrostatic properties can be encoded in a single parameter, the microscopic persistence length, which normally depends only on the local microscopic structure of the PE backbone.

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