Cascade of Transitions of Polyelectrolytes in Poor Solvents

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ABSTRACT: We develop a scaling model for the dilute solution conformation of a uniformly charged polymer in a poor solvent. We find that there is a range of temperatures and charge densities for which the polymer has a necklace-like shape with compact beads joined by narrow strings. The free energy of a polyelectrolyte in this conformation is lower than in a cylindrical globule because the length of the necklace is larger than that of a cylinder and is proportional to the total charge on the chain. With changing charge on the chain or temperature, the polyelectrolyte undergoes a cascade of abrupt transitions between necklaces with different numbers of beads.

I. Introduction

Charged polymers, called polyelectrolytes, have attracted much attention during the past three decades due to their unique properties and their technological importance.[1] One of the main technologically important properties of polyelectrolytes is that they dissolve in water. Water is a poor solvent for many polymers. In poor solvents, chains have negative second virial coefficients, corresponding to an effective attraction between monomers. This attraction causes chains without charged groups to collapse into spherical globules,[2,3] coalesce with each other, and precipitate from solution. The repulsion between charged groups significantly improves polymer solubility in solvents which are poor for uncharged backbones.

In the present paper, we study the configuration of a polyelectrolyte chain in a poor solvent as a function of temperature (solvent quality) and the charge on the chain. The overall shape of a charged polymer in a poor solvent is determined by the balance of the electrostatic repulsion and the surface tension. It was suggested by Khokhlov[4] that, in order to optimize its energy, the polyelectrolyte chain takes the shape of an elongated cylindrical globule. The theory of Khokhlov was extended by Raphael and Joanny[5] to the case of "mobile" charges on the chain and by Higgs and Raphael[6] to the case of screening of electrostatic interactions by added salt.

The cylindrical globule[4−6] is unstable to capillary wave fluctuations similar to the ones that result in the splitting of a charged liquid droplet.[7,8] Kantor and Kardar[9] have recently proposed that a polymer with short-range attraction and long-range repulsion may form a necklace with compact beads joined by narrow strings. Below we extend this idea and develop a scaling theory that describes how, with varying solvent quality or charge on the chain, the polyelectrolyte in a poor solvent undergoes a cascade of abrupt transitions between necklace-like configurations with different numbers of beads. We find that the length of the necklace globule is proportional to the total polymer charge, in agreement with the prediction of Kantor and Kardar,[9] and is larger than the length of the cylindrical globule. Consequently, the free energy of the necklace globule is lower than that of the cylindrical one.

In the next section, we review the main properties of the cylindrical globule[4,5] and present our scaling theory of the necklace state. In section III, we outline the results of a Monte Carlo simulation of a polyelectrolyte chain in a poor solvent. In section IV, we calculate the scattering function for the necklace state of a polyelectrolyte. The results of the paper are discussed in section V.

II. Polyelectrolyte Chain in Poor Solvent

Consider a dilute polyelectrolyte solution of chains with degree of polymerization N, monomer size b, and fraction f of charged monomers in a poor solvent with dielectric constant ϵ. An uncharged chain in a poor solvent forms a globule.[2,3] The monomer density $\rho \approx \tau/b^3$ inside this globule is defined by the balance of the two-body attraction ($BN\rho$) and the three-body repulsion ($b^6N\rho^2$) between the monomers of the chain. Here $B \approx -\tau b^3$ is the second virial coefficient, with the reduced temperature given by $\tau = (\Theta - T)/\Theta$, and b is the bond length. The size R of the globule with density ρ is equal to $R \approx (N/\rho)^{1/3} \approx b\tau^{-1/3}N^{1/3}$.

There is one important length in the globule—the size ξ_T of the density fluctuations (thermal blob size[3]). On length scales smaller than ξ_T, the chain statistics are unperturbed by the volume interactions and are that of a random walk of g_T monomers ($\xi_T \approx bg_T^{1/2}$). On length scales larger than the correlation length ξ_T, the attraction between monomers wins and thermal blobs in the globule are space-filling, $\rho \approx g_T/\xi_T^3$. The number of monomers in a thermal blob is $g_T \approx 1/\tau^2$ and its size is $\xi_T \approx b/\tau$. The surface tension γ of the globule is of the order of kT per thermal blob at the globular surface, $\gamma \approx kT\xi_T^{-2}$ (where k is the Boltzmann constant).

A. Cylindrical Globule.[4−6] If the polymer is charged, the Coulomb repulsion between charged monomers could change the shape of the globule, but would not significantly affect its volume. The volume occupied by the molecule is still defined by the solvent quality, as in the case of the uncharged globule. If the Coulomb repulsion $F_{\mathrm{Coul}} \approx e^2f^2N^2/\epsilon R$ (here e is the elementary charge) becomes comparable to the surface energy $F_{\mathrm{sur}} \approx kTR^2/\xi_T^2$, the total energy of the globule can be lowered either by elongating it into a cylinder or by splitting it into two smaller globules connected by a

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narrow string. This deformation occurs when the total valence of the charge fN becomes larger than $(N\tau/u)^{1/2}$. Here $u \approx l_B/b$ is the ratio of the Bjerrum length $l_B = e^2/\epsilon kT$ to the bond length b.

The elongation of the globule into a cylinder with length L_{cyl} and width D was proposed by Khokhlov[4] and considered in several recent models.[5,6,10] The size of the cylinder can be found by optimizing the sum of the surface energy $F_{sur} \approx kTL_{cyl}D/\xi_T^2$ and Coulomb energy $F_{Coul} \approx e^2f^2N^2/\epsilon L_{cyl}$ at fixed volume $L_{cyl}D^2 \approx b^3N\tau^{-1}$ determined by the solvent quality. This minimization of the free energy $F_{cyl} = F_{sur} + F_{Coul}$ leads to the cylinder length

$$L_{cyl} \approx bN\tau^{-1}(uf^2)^{2/3} \tag{2.1}$$

and width

$$D \approx b(uf^2)^{-1/3} \tag{2.2}$$

It is important to note that the width D of the cylinder is the length scale at which the Coulomb repulsion between charges becomes of the order of the surface energy (electrostatic blob in a poor solvent). The deformation-sensitive part of the free energy of the cylindrical globule of the optimal size L_{cyl} and width D given by eqs 2.1 and 2.2 is

$$\frac{F_{cyl}}{kT} \approx \frac{l_Bf^2N^2}{L_{cyl}} \approx \tau(uf^2)^{1/3}N \tag{2.3}$$

For eqs 2.1–2.3 to be valid, the thermal blob size ξ_T must be smaller than the width of the cylinder D (for $\tau > (uf^2)^{1/3}$). Closer to the Θ-temperature (for $\tau < (uf^2)^{1/3}$), the chain behaves like a charged macromolecule in a Θ-solvent.[3] However, we demonstrate below that the cylindrical globule is not the free energy minimum of a polyelectrolyte chain in a poor solvent (for $\tau > (uf^2)^{1/3}$).

B. Necklace Globule. The problem of the shape of a charged globule is similar to the classical problem of the instability of a charged droplet, considered by Rayleigh.[7] He showed that a spherical droplet with radius R and charge $Q > e(\gamma R^3/kTl_B)^{1/2}$ (where γ is a surface tension) is locally unstable and will spontaneously deform. The equilibrium state of this system is a set of smaller droplets with the charge on each of them lower than the critical one and placed at an infinite distance from each other. This final state is impossible for the charged polymer because it consists of monomers connected into a chain by chemical bonds. In this case, the system can reduce its energy by splitting into a set of smaller charged globules connected by narrow strings—the necklace globule, as it was called by Kantor and Kardar.[9]

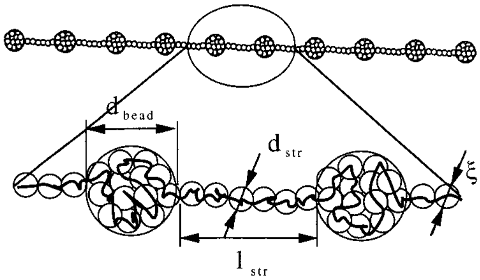

Figure 1. A necklace globule with N_{bead} beads and $N_{bead} - 1$ strings ($N_{bead} = 10$ in the figure). Beads are spherical with diameter d_{bead} and contain m_{bead} monomers each. Strings are cylindrical with length l_{str} and diameter d_{str} and contain m_{str} monomers each. The density of beads and string is the same—dense packing of thermal blobs of size ξ_T.

Consider a necklace globule, as sketched in Figure 1, with N_{bead} beads of size d_{bead} containing m_{bead} monomers in each ($d_{bead} \approx b\tau^{-1/3}m_{bead}^{1/3}$) joined by $N_{bead} - 1$ cylindrical strings of length l_{str} and width d_{str} containing m_{str} monomers each ($m_{str} \approx \rho l_{str}d_{str}^2 \approx \tau l_{str}d_{str}^2/b^3$). The free energy of the necklace is

$$\frac{F_{nec}}{kT} \approx N_{bead}\left\{\frac{l_Bf^2m_{bead}^{\ 2}}{d_{bead}} + \frac{d_{bead}^{\ 2}}{\xi_T^{\ 2}}\right\} + (N_{bead} - 1)\left\{\frac{l_Bf^2m_{str}^{\ 2}}{l_{str}} + \frac{l_{str}d_{str}}{\xi_T^{\ 2}}\right\} + \frac{l_Bf^2N^2}{L_{nec}} \tag{2.4}$$

where $L_{nec} = (N_{bead} - 1)l_{str} + N_{bead}d_{bead}$ is the total length of the necklace. The first pair of terms (the first set of curly brackets) is the electrostatic self-energy and surface energy of the beads. The second pair of terms (the second set of curly brackets) is the electrostatic self-energy and surface energy of the strings. The last term is the electrostatic repulsion between different beads and strings (up to logarithmic corrections). Note that in eq 2.4 and below we have dropped all numerical prefactors. The electrostatic self-energy of a string is $(d_{str}/D)^3$ times smaller than its surface energy, where D is the electrostatic blob size (eq 2.2). Since we are looking for a solution with narrow strings ($d_{str} \ll D$), we can neglect this contribution to the free energy for a weakly charged polyelectrolyte in a poor solvent. The total number of monomers in all strings and beads should be equal to the degree of polymerization N of the chain.

$$N_{bead}m_{bead} + (N_{bead} - 1)m_{str} = N_{bead}m_{bead} + M_{str} = N \tag{2.5}$$

where we have defined a parameter $M_{str} = (N_{bead} - 1)m_{str}$ equal to the total number of monomers in all strings. We rewrite the free energy of the necklace globule in the limit of a string much longer than a bead ($l_{str} \gg d_{bead}$)

$$\frac{F_{nec}}{kT} \approx \left\{uf^2\tau^{1/3}\frac{(N - M_{str})^{5/3}}{N_{bead}^{\ 2/3}} + \tau^{4/3}N_{bead}^{\ 1/3}(N - M_{str})^{2/3}\right\} + \frac{\tau b}{d_{str}}M_{str} + uf^2\tau\frac{N^2d_{str}^{\ 2}}{b^2M_{str}} \tag{2.6}$$

The optimal values of parameters N_{bead}, M_{str}, and d_{str} correspond to the minimum of the free energy. Note that only the first two terms depend on the number of beads N_{bead}. Minimizing the free energy (eq 2.6) with respect to the number of beads leads to the well-known stability condition of a charged droplet[7,8] that gives the number of monomers in a bead

$$\frac{(N - M_{str})}{N_{bead}} = m_{bead} \approx \frac{\tau}{uf^2} \tag{2.7}$$

The derivatives of the first two terms of the free energy (eq 2.6) with respect to M_{str} are d_{str}/D times smaller than the contribution from the surface energy of a string (third term). Therefore we find the total number of monomers in all strings $M_{\text{str}} \approx fN(ud_{\text{str}}^3/b^3)^{1/2}$ and the free energy at this minimum is $F_{\text{nec}}/kT \approx Nf\tau(ud_{\text{str}}/b)^{1/2}$. Note that this free energy decreases with the diameter of the string d_{str}. If d_{str} were to decrease to a value smaller than ξ_T, the largest contribution to the free energy of a string would arise from stretching it as a Gaussian coil. The free energy minimum for $d_{\text{str}} < \xi_T$ increases with decreasing d_{str} as $F_{\text{nec}}/kT \approx Nf(ub/d_{\text{str}})^{1/2}$. Therefore the optimal configuration corresponds to the thickness of a string of the order of the thermal blob size $d_{\text{str}} \approx \xi_T$. The free energy of the necklace in the optimal state is

$$\frac{F_{\text{nec}}}{kT} \approx Nf(\tau u)^{1/2} \qquad (2.8)$$

This free energy is lower than that of a polyelectrolyte in the cylindrical configuration (eq 2.3), $F_{\text{nec}}/F_{\text{cyl}} \approx (\xi_T/D)^{1/2}$, as long as it is in the poor solvent regime ($\tau > (uf^2)^{1/3}$ (corresponding to $\xi_T < D$). This is the condition for the validity of both models. The regime $\xi_T > D$ corresponds to a polyelectrolyte in a Θ-solvent ($\tau < (uf^2)^{1/3}$).

Let us describe the details of the necklace configuration with the free energy minimum F_{nec} (eq 2.8). The total length of the necklace

$$L_{\text{nec}} \approx \frac{M_{\text{str}}}{g_T}\xi_T \approx b\left(\frac{u}{\tau}\right)^{1/2} fN \qquad (2.9)$$

is proportional to the total charge on the chain fN and is longer than that of a cylinder, $L_{\text{nec}}/L_{\text{cyl}} \approx (D/\xi_T)^{1/2}$. This longer length allows the polyelectrolyte to have lower energy because the charges are separated by larger distances. The diameter of the beads is of the order of the electrostatic blob size D—the same as the diameter of the cylinder (eq 2.2)

$$d_{\text{beads}} \approx D \approx b(uf^2)^{-1/3} \qquad (2.10)$$

The length of the string

$$l_{\text{str}} \approx b\left(\frac{\tau}{uf^2}\right)^{1/2} \qquad (2.11)$$

is larger than the diameter of the beads d_{bead} by the factor $(D/\xi_T)^{1/2}$. For $D \gg \xi_T$, most of the mass is concentrated in beads and strings have only $m_{\text{str}}/m_{\text{bead}} \approx (\xi_T/D)^{3/2}$ fraction of the mass. Therefore our optimization of the polyelectrolyte free energy is self-consistent.

The number of beads N_{bead} of the necklace can only be an integer, so the solution of eq 2.7 defines a set of boundaries

$$f \approx \left(\frac{\tau}{u}\frac{N_{\text{bead}}}{N}\right)^{1/2} \quad \text{where } N_{\text{bead}} = 1, 2, 3, \ldots \qquad (2.12)$$

between the states of the necklace globule with different numbers of beads (we have considered the limit $M_{\text{str}}/N \approx (\xi_T/D)^{3/2} \ll 1$). Upon changing the valence f or solvent quality τ, the globule undergoes a cascade of transitions between states with different integer numbers of beads N_{bead} on the necklace.

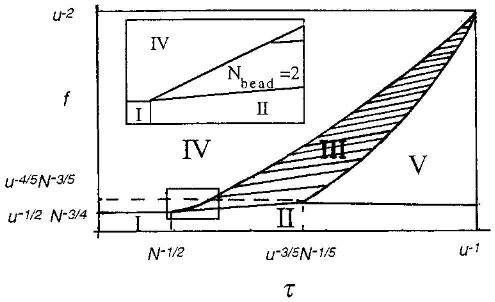

Figure 2. Diagram of states of a polyelectrolyte chain with valence fN containing $N = 100$ monomers in a poor solvent. The effective temperature is $\tau = (\Theta - T)/\Theta$ and the normalized Bjerrum length is $u = l_B/b = 2$. Regime I corresponds to the unperturbed Gaussian coil. In regime II, the chain forms a spherical globule. In regime III, we predict a cascade of abrupt transitions between necklace configurations with different numbers of beads. Regime IV corresponds to a Θ-solvent-like cylindrical configuration. In regime V, we expect counterion condensation.

C. Diagram of States. In Figure 2 we sketch a diagram of states of a polyelectrolyte chain (with $N = 100$ monomers and $u = 2$) in a poor solvent as a function of valence f and solvent quality τ. In region I close to the Θ-temperature ($\tau < N^{-1/2}$) and for lower valence ($f < u^{-1/2}N^{-3/4}$), the short-range attraction between monomers and the electrostatic repulsion between charges are too weak to deform the chain and it behaves like a Gaussian coil. In a poor solvent (further below the Θ-temperature: at effective temperatures $\tau > N^{-1/2}$) and at low charge density f (in region II of the phase diagram), the size of the thermal blob ξ_T is smaller than the Gaussian chain size $R \approx bN^{1/2}$, and the short-range attraction results in a collapse of the chain into a spherical globule. This globule is stable at lower charge density $f < (\tau/uN)^{1/2}$ as long as its surface energy is larger than the electrostatic energy (see eq 2.12 for $N_{\text{bead}} = 1$). At higher valence $f > (\tau/uN)^{1/2}$, the spherical globule is unstable with respect to capillary waves and first splits into a dumbbell with two smaller globules joined by a string of thermal blob width ξ_T ($N_{\text{bead}} = 2$ part of region III—see also insert in Figure 2). As the charge density f increases further, the necklace with two globules (dumbbell) splits into one with three smaller globules connected by two strings of diameter ξ_T. At still higher valence f, it splits again into a necklace with $N_{\text{bead}} = 4$ globules and so on. This cascade of abrupt transitions between the necklaces with different numbers of globules occurs at the boundaries given by eq 2.12 and is shown in region III of the diagram. At the upper boundary $f \approx \tau^{3/2}u^{-1/2}$ of this region, the size of the globules (beads) D is comparable to the width of the strings ξ_T.

Region IV of the diagram above the cascade zone at higher valence f and smaller effective temperature τ corresponds to the Θ-like state of a polyelectrolyte with the chain in the shape of a cylinder. The electrostatic blob in this regime is the length scale at which electrostatic repulsion is of the order of thermal energy kT (but is still given by eq 2.2).[3,11] On length scales smaller than the electrostatic blob size D, the chain is Gaussian. On larger length scales, the electrostatic repulsion forces the polyelectrolyte into a linear array of electrostatic blobs. The length of the polyelectrolyte in this regime (region IV) is $L \approx bN(uf^2)^{1/3}$. Note that at the boundary of regions I and IV (at $f \approx u^{-1/2}N^{-3/4}$), the length L of the chain crosses over to its Gaussian size. At higher valence f we expect Manning condensation[12] to define the upper boundary of region IV. This condensation of counterions occurs at a linear charge density along the cylinder axis higher than l_B^{-1}: $f > u^{-2}$.[12]

In region V of the diagram, the strong electrostatic attraction between counterions and charged groups on the polymer chain also results in counterion condensation. The crossover condition between condensed and free states of counterions can be found by comparing the thermal energy kT with the electrostatic interaction between a bead and a counterion for the necklace globule in regime III ($E_{\mathrm{III}} \approx e^2 m_{\mathrm{bead}} f/\epsilon D$) and between the globule and a counterion for a spherical globule in regime II ($E_{\mathrm{II}} \approx e^2 N f/\epsilon R$). These conditions give the upper, $f \approx \tau^3 u$, and lower, $f \approx \tau^{-1/3} u^{-1} N^{-2/3}$, boundaries of regime V in the diagram of states.

The most striking part of the diagram is region III with the "necklace" cascade of transitions.

III. Monte Carlo Simulations

To check our predictions, we have carried out a Monte Carlo simulation of a polyelectrolyte in a poor solvent. We consider a freely jointed uniformly charged chain consisting of N monomers with charge fe on each.[13,14] The monomers interact with each other through a Coulomb potential

$$\frac{U_{\mathrm{Coul}}(r_{ij})}{kT} = \frac{ubf^2}{r_{ij}}$$

and a Lennard-Jones potential

$$\frac{U_{\mathrm{LJ}}(r_{ij})}{kT} = \epsilon_{\mathrm{LJ}}\left[\left(\frac{r_0}{r_{ij}}\right)^{12} - 2\left(\frac{r_0}{r_{ij}}\right)^{6}\right]$$

where $r_{ij} = |r_i - r_j|$ is the distance between the ith and jth monomers. The Lennard-Jones potential has its minimum value $-kT\epsilon_{\mathrm{LJ}}$ at distance $r_{ij} = r_0$ (in our model, we have chosen r_0 to be equal to the bond length b).

The simulation starts from a random chain configuration $\{r_1, r_2, ..., r_N\}$. An ith monomer is chosen using a random number generator. An attempt is made to rotate it by a random angle around the line connecting monomers $i - 1$ and $i + 1$. The energy of the new configuration is calculated, and this move is either accepted or rejected according to the standard Metropolis algorithm. A single Monte Carlo (MC) step is defined as a simulation run during which attempts were made to rotate N randomly chosen monomers by randomly chosen angles. At each value of u and ϵ_{LJ} (strength of the Lennard-Jones potential), 300 N^2 MC steps were performed for the chain lengths N =16, 32, and 64, 100 N^2 steps for chains with $N = 128$, and 50 N^2 steps for chains with $N = 200$. We have not included the first 20 N^2 MC steps in any of the averages.

The dependence of the reduced mean square radius of gyration R_g^2 of chains with degrees of polymerization $N = 16$, 32, 64, 128, and 200 on the reduced value of the total valence $Q = fN$ of these chains is plotted in Figure 3 for values of the parameters $\epsilon_{\mathrm{LJ}} = 3/2$ and $u = 2$. The square of the radius of gyration R_g^2 is reduced by the factor $N^{2/3}$ to remove the N dependence of the chain size in the compact globular state. The valence Q is normalized by the factor $N^{1/2}$, which is proportional to the value of the critical valence. At lower valence $f < 1.7/N^{1/2}$, the chain forms a spherical globule (see Figure 4a) with a size proportional to $N^{1/3}$ (Figure 3). When the charge density becomes larger than the critical value $f \approx 1.7/N^{1/2}$, the polyelectrolyte takes a dumbbell configuration (Figure4b). At still higher charge density, the polymer can form a necklace configuration of three beads joined by two strings (Figure 4c). These results of the Monte Carlo simulations support our scaling prediction of the "necklace cascade" of transitions of a polyelectrolyte chain in a poor solvent.

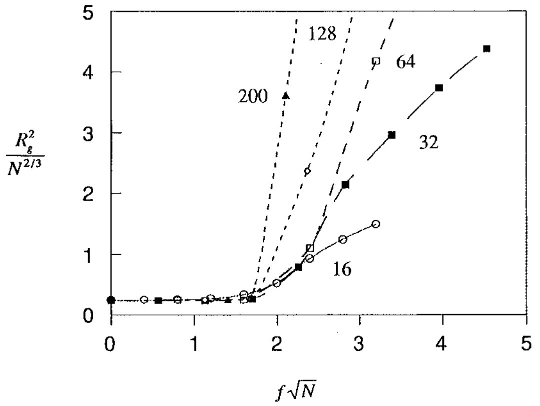

Figure 3. Reduced mean square radius of gyration $R_g^2/N^{2/3}$ as a function of reduced valence $fN^{1/2}$ for chains with degrees of polymerization $N = 16$, 32, 64, 128, and 200.

A structural transition with a sharp increase of chain size at some value of charge density was observed in earlier Monte Carlo simulations of a polyelectrolyte chain in a poor solvent,[15] but the authors did not analyze the corresponding changes of the chain conformation. In a nondynamical Monte Carlo simulation, Higgs and Orland[10] also observed a sharp increase of chain size with increasing coupling constant u, but they interpreted it as confirming Khokhlov's elongated globule picture. The conformation of a polyelectrolyte in a poor solvent regime was not studied in ref 10.

IV. Scattering Function

The predictions of our scaling model can also be tested by small-angle neutron (SANS) or small-angle X-ray (SAXS) scattering experiments. For wavelengths shorter than the chain size in dilute solution or shorter than the correlation length in a semidilute solution, the scattering is dominated by that from a single chain. Therefore on these length scales, the scattering function of the polymer solution containing the necklace globules is

$$S(\mathbf{q}) \approx n_s \langle \sum_{i,j} \exp(-i(\mathbf{r}_i - \mathbf{r}_j)) \rangle_a \tag{4.1}$$

where brackets $\langle\ \rangle_a$ denote averaging over all macromolecular orientations, n_s is the number of macromolecules per unit volume in dilute solutions or the number density of chain sections of the size of the correlation length in semidilute solutions. Summation in eq 4.1 is carried out over all monomers of a given chain (or section of the chain). If the necklace contains N_{bead} beads of size D with m_{bead} monomers in each joined by strings of length l_{str}, then after averaging over all chain orientations, the scattering function (eq 4.1) can be rewritten as

$$S(\mathbf{q}) \approx n_s m_{\mathrm{bead}}^2 \left(N_{\mathrm{bead}} + 2 \sum_{n=1}^{N_{\mathrm{bead}}-1} (N_{\mathrm{bead}} - n) \times \frac{\sin(q l_{\mathrm{str}} n)}{q l_{\mathrm{str}} n} \right) \left(\frac{\sin(qD) - qD\cos(qD)}{(qD)^3} \right)^2 \tag{4.2}$$

Thus we predict an increase of the scattering intensity

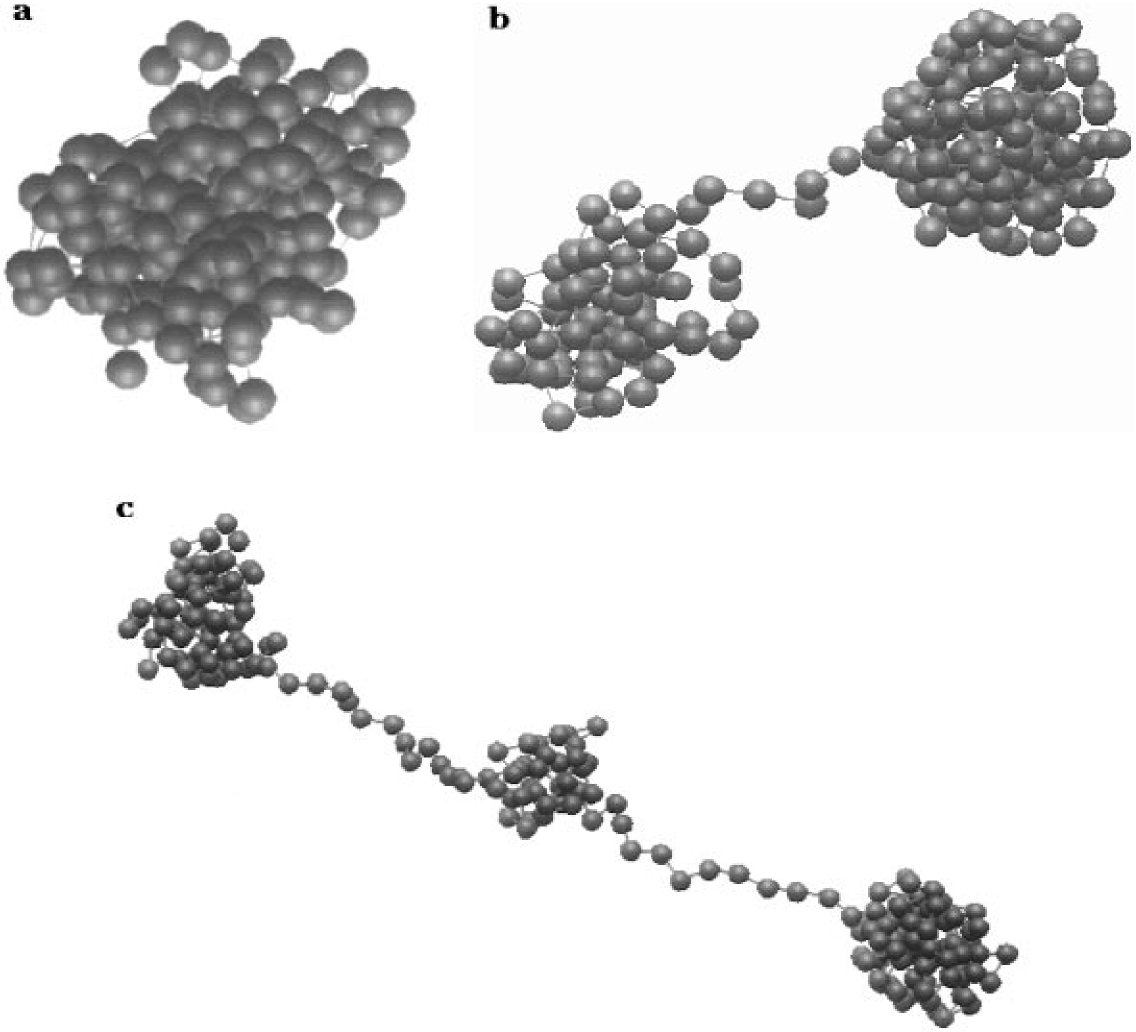

Figure 4. Typical configurations of a freely jointed uniformly charged chain with $N = 200$ monomers interacting via Coulomb and Lennard-Jones potentials (with $\epsilon_{LJ} = 1.5$ and $u = 2$) at three different charge densities: (a) spherical globule for $f = 0$; (b) dumbbell for $f = 0.125$; (c) necklace with three beads for $f = 0.15$.

on length scales of the order of $ql_{str} \approx 2\pi k$, where k is an integer. The second maximum in the scattering function has been recently observed by Williams and Wafa[16] in both SANS and SAXS experiments of poly(styrenesulfonate) (partially sulfonated) in water. This second increase in the scattering was observed at wave vectors higher than the main maximum attributed to the correlation length of the solution. These preliminary data are consistent with our necklace picture, but more detailed experiments are necessary for a more quantitative test of our predictions.

V. Discussion

In the present paper, we have considered a single uniformly charged polyelectrolyte chain in a poor solvent. We have demonstrated that this simple system has a very rich behavior. As a function of the charge on the chain and the solvent quality, a polyelectrolyte chain in a poor solvent undergoes a cascade of abrupt transitions between necklace configurations with different numbers of beads. We have demonstrated that the free energy of these necklace states is much lower (by the factor $(D/\xi_T)^{1/2}$) than that of the cylindrical globule. The length of the necklace L_{nec} is longer than the length L_{cyl} of the cylinder by the same factor. The results of the scaling theory are in agreement with our Monte Carlo simulations and are qualitatively consistent with preliminary results of SANS and SAXS experiments on solutions of poly(styrenesulfonate).[16]

We would like to point out the analogy of the necklace shape of the polyelectrolyte in a poor solvent and the necklace configuration of a polyampholyte (a chain containing both positive and negative charges) discussed by Kantor and Kardar.[9] In the polyampholyte case, both the attractive and repulsive forces are related to the electrostatic interactions. The long-range repulsion is due to the overall charge on the chain. The attraction is due to spatial charge density fluctuations of the Debye−Hückel type. An important difference between the systems is that the polyelectrolyte considered in the present paper is a homogeneous homopolymer. Randomness in the placement of the charges on the chain can be added to the model, leading to a random copolymer of charged and neutral monomers, but it is not essential for the existence of the necklace cascade of transitions (in fact, it may lead to a specific sequence of transitions for each individual chain). Quenched randomness in the position of positive and negative charges along the chain is intrinsic to random polyampholytes. The attraction in random polyampholytes is due to statistical charge fluctuations and is substantially different from that in regular polyampholytes.[17]

We hope that future experiments on charged chains will test the predictions of the necklace model.

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