Stretching necklaces

T.A. Vilgis, A. Johner, J. F. Joanny
Laboratoire Européen Associé, Institut Charles Sadron, 6, rue Boussingault,
F- 67083 Strasbourg, Cedex,
France
(December 11, 2020)

Polyelectrolytes in poor solvents show a necklace structure where collapsed polymer pearls are linked to stretched strings. In the present paper the elasticity of such chains is studied in detail. Different deformation regimes are addressed. The first is the continuous regime, where many pearls are present. A continuous force extension relationship is calculated. The main contribution comes from the tension balance and the electrostatic repulsion of consecutive pearls. The main correction term stems from the finite size of the pearls, which monitors their surface energy. For a finite amount of pearls discontinuous stretching is predicted. Finally counterion effects are discussed qualitatively.

PACS Numbers: 36.20.-r,61.25.Hq,61.41.+e

I. INTRODUCTION

Recently it has become possible to manipulate single polymer chains and to experimentally study their elastic response \[3,4\]. Our aim here is to describe theoretically the single chain elasticity in the specific case of polyelectrolytes in poor solvents, typically in water, a poor solvent for most organic polyelectrolyte backbones. Beside the direct experimental measurements of single chain elasticity, there are at least two other motivations for this study: the possible relation with drag reduction \[3,4\], and the relation to the elastic behavior of more complex structures such as polyelectrolyte gels.

Charged polymers in solution, polyampholytes and polyelectrolytes, are known to reduce drag very efficiently in turbulent flows. This property is shared, to some extent, by neutral polymers. For neutral polymers, drag reduction has sometimes been explained by the dissipation associated to the stretch/ coil transition where the polymer chains undergo a discontinuous elongation. One would also anticipate a large dissipation for a collapsed polymer globule in a poor solvent: even for fairly small variations of the stress there is a significant hysteresis loop in the globule/stretched chain transition. Of course, the concentration of polymer globules in a poor solvent must be extremely low in order to avoid phase separation. It has been suggested recently that polyelectrolytes in poor solvents may exhibit a pearl-necklace structure where collapsed globules, the pearls, are connected by stretched polymer strings. One may look at this system as a way of solubilizing (connected) dense polymer globules at finite concentrations, these structures could then be good candidates to enhance drag reduction.

If the necklaces comprise many pearls (which, we think, might be difficult to achieve for single chains in the accessible experimental range of parameters), thermal fluctuations smear out the single pearl features and the force/elongation curve is continuous. The continuous elasticity of these necklaces may be used as a starting point to model the elasticity of more complex systems: polyelectrolyte gels will be described in a separate paper.

The behavior of polyelectrolyte chains in a Theta solvent has been discussed thoroughly theoretically and it is fairly well understood (we will not need in this paper to consider the bond angle correlations and the persistence length that remain controversial issues). We consider a chain of \( N \) monomers of size \( b \), with a fraction \( f \) of charged monomers. The repulsive Coulombic interaction between charged monomers is written as \( V(r) = k_BT/l_B/r \), with \( l_B = e^2/(4\pi\epsilon k_BT) \) being the Bjerrum length where \( \epsilon \) is the dielectric constant of the solvent and \( e \) the elementary charge. The chain radius can be estimated by a balance between entropy and electrostatic energy that is equivalent to the electrostatic blob model \[5\]: the chain may be viewed as a stretched string of Gaussian isotropic blobs each containing \( (l_B f^2/b)^{-2/3} \) monomers and of radius \( (l_B f^2/b)^{-1/3}b \); the overall chain length is then \( R = bN \left( l_B f^2/b \right)^{1/3} \). The electrostatic interaction is relevant for high enough charge fraction i.e., \( f > N^{-3/4} \), otherwise the chain remains essentially Gaussian isotropic (comprising less than one blob).

If the chain backbone is in a poor solvent (which is often the case in experiments), there is a competition between surface tension effects tending to minimize the polymer/water(solvent) contact area and electrostatics tending to maximize the overall chain size. In the following, the poor solvent conditions are characterized by a negative excluded volume \( v = -\tau b^3 \), where \( \tau = (\theta - T)/\theta \) is the relative distance to the compensation temperature \( \theta \). In the absence of electrostatic interactions, the chain collapses into a dense globule that may be viewed as a small region of dense polymer phase at coexistence with free solvent; the finite size of the globule is associated with an extra energy penalty

\[ 1 - fN f^{-1/3} b^{1/3} - \frac{1}{6} fN f^{-1/3} b^{1/3} \]
due to the polymer-water surface tension. The balance of the osmotic pressure between the dense and dilute phases (of almost vanishing concentration) yields the concentration inside the globule \( c = \tau / b^3 \). Alternatively, the dense phase may be described by a close packing of thermal blobs of size \( \xi = b / \tau \), containing \( g = 1 / \tau^2 \) monomers. A globule of \( N \) monomers has then a radius \( R = b (N / \tau) \). The corresponding surface tension is \( \gamma = k_B T / \xi^2 \propto \tau^2 / b^2 \). For a charged chain, the balance between surface tension and electrostatics was first considered by Khokhlov assuming a cylindrical globular shape \([8]\). This yields a highly elongated globule of length \( L = N b l_B f^2 / (b / \xi)^{2/3} / \tau \) and radius \( R_c = b (l_B f^2 / b)^{-1/3} \) provided that the radius of the chain in the absence of electrostatic interactions, in a spherical globular conformation, is larger than \( R_c \); for smaller chains, the electrostatic interaction is only a perturbation. The elongated cylindrical globule can be looked at as a stretched string of spherical globules of radius \( R_c \).

Recently, it has been proposed by Kantor and Kardar [7,8] that the large spherical globule instability is rather similar to the Rayleigh instability of charged liquid droplets. A large liquid droplet carrying an electrostatic charge, \( \xi \), have a radius equal to \( \xi / \tau \). As shown by Halperin and Zhulina [10], in a first approximation, (discarding finite size corrections) the strings must be far enough apart to connect the pearls with stretched polyelectrolyte strings. This leads to the pearl-necklace model introduced by Dobrynin, Rubinstein and Obukhov [9]. The string monomers are then in equilibrium with the pearl monomers. An equilibrium between a collapsed chain and a globule is also found when an external force is applied on a globule. As shown by Halperin and Zhulina [14], in a first approximation, (discarding finite size corrections) the strings must have a radius equal to \( \xi \) (the thermal correlation length in the pearls), and a tension \( \sigma = k_B l_B T / \xi^2 \). The string tension is qualitatively due to the repulsion between adjacent pearls \( k_B l_B T / \xi^2 \) (a logarithmic factor corresponding to pearls farther apart is omitted), where \( Q \) is the pearl charge and \( l \) the length of a string. The string length is determined by the force balance \( \sigma = k_B l_B T / \xi \) (hence \( \Lambda > 1 \) is required). The function \( f(x) = 2 x^{-1/3} + x^{2/3} \) is plotted in Fig.1.

- It has a minimum at \( x = 1 \), the preferred droplet size contains \( \tilde{m} = \Lambda / 2 \) blobs.
- It changes curvature at \( x = 4 \): an assembly of identical droplets smaller than four times the preferred size is locally stable against polydispersity.
- For a size larger than about 1.4 times the preferred size, it is favorable to split a droplet into two identical droplets.
- The overall free energy \( f(x) \) is rather flat and thermal fluctuations are anticipated to become important for mesosopic systems. For an assembly of 1000 blobs (a rather large number) and a preferred droplet size of 100 blobs, the barrier against splitting all 10 droplets is roughly \( 4 k_B T \) only. The fluctuations become less important with decreasing solvent quality.

![FIG. 1. Free energy per thermal blob of an assembly of isolated droplets comprising \( x \Lambda / 2 \) thermal blobs each. The monodisperse assembly is locally stable for droplet sizes up to four times the preferred size \( \Lambda / 2 \). For droplets larger than \( 1.4x \) it is energetically favorable to split a droplet into two identical smaller droplets (see enhanced figure). Fluctuating between \( x = 0.7 \) and \( x = 1.4 \) only involves a fraction of the thermal energy per droplet for \( \Lambda = 100 \).](image-url)
Though we are discussing here a liquid of disconnected blobs only, we may anticipate that steepest descent calculations where only the most probable necklace conformation is accounted for are not always very accurate.

Let us briefly make a remark on single chain stretching in general. There came up a number of experimental studies. Some of them deal also with DNA stretching and defolding under forces. Theoretical papers describe stretching of DNA molecules. The forces we are going to discuss in the case of polyelectrolytes in poor solvent are much lower than appearing there. In most cases related to the DNA overstretching plays a significant role, in contrast to the problem described here.

The paper is organized as follows: in the next section we first summarize briefly the known results on the pearl-necklace structure; we then discuss the structure of necklaces under an external force; we start with the continuous limit, corresponding to many pearls connected by strings and show that the pearls are "unwinded" by the external force; when the number of pearls becomes small a more detailed treatment is necessary, we study in details the dissolution of a necklace of two pearls. Section III is devoted to a more general discussion of the discreteness of the number of pearls. A somewhat simpler description, that we think still captures the essential physics, is developed to describe individual pearl unwinding for necklaces involving many pearls. Fluctuations progressively smear out force plateaus associated to individual pearls when the number of pearls increases. This whole analysis ignores the role of counterions of the chain. The pearl surface potential however, can be rather high even for moderate charge fractions and some charge regulation due to counterion condensation on the pearls is to be expected. Large pearls inducing counterion condensation and very poor solvents are discussed in section IV where we show that charge regulation can suppress the large globule instability. We also consider very poor solvents for which there is hardly any solvent in the pearl core and the dielectric constant is low; the polyelectrolyte behaves then as an ionomer

II. POLYELECTROLYTES IN POOR SOLVENT UNDER EXTERNAL FORCES

A. Equilibrium necklaces, $\varphi = 0$

Polyelectrolyte chains in a poor solvent show a rich conformational phase behavior because competing interactions are ruling the chain statistics: surface tension drives the globule toward small polymer/water interfaces whilst electrostatics drive it toward large overall extensions. Therefore, the globular structures for large enough charge fractions are no longer spherical as in the case of neutral polymers, but elongated. This was first recognized by Khokhlov who proposed a cylindrical globular shape (assuming that there is only one characteristic length). More precisely he finds that a globule of radius $R$ becomes elongated when $F_{\text{surface}} = \gamma R^2 > F_{\text{el}} = k_B T (l_B f^2 N^2) / R$, i.e., $\tau > (l_B / b)^2 N$. For larger charge fractions the globule elongates to a thickness $D$ and length $L$. This can be seen from a simple free energy balance. The free energy of the cylindrical globule is (remember that the concentration is given by $c = \tau / b^3 = N / (D^2 L)$)

$$F = k_B T \frac{c}{2} \frac{1}{2} \left( \frac{N}{T} \right) \frac{1}{2} + \frac{l_B f^2 N}{L}$$

(2.1)

which yields upon minimization, the length of the cylinder $L = b (N/\tau) (l_B f^2 / b)^{2/3}$ and the diameter comparable to the size $R_c \simeq b (l_B f^2 / b)^{1/3}$ of the marginally stable spherical globule, as already mentioned in the introduction.

Kantor and Kardar have shown that the elongated globule structure is unstable and breaks up into marginally stable pearls by analogy with the Rayleigh instability of charged liquid droplets, as already mentioned in the introduction. The elongated globule breaks up into pearls and strings. The pearls of size $R$, contain $m = c_0 R^3$ monomers, where $c_0 = \tau / b^3$ is the equilibrium concentration of the globule. The elongated strings of length $l$ and diameter $d$, contain $m_s$ monomers. For completeness and later use, we write down the free energy in the following form

$$F = \frac{N}{m} \left\{ \gamma R^2 + \frac{l_B f^2 m^2}{R} + \frac{F_{\text{elastic}}(l)}{k_B T} + \gamma l d + \frac{l_B f^2 m^2}{l} \right\} + \frac{l B f^2 N^2}{L}$$

(2.2)

1 A short account of this work has been presented at the St. Petersburg conference on "Molecular Mobility and Order in Polymer Systems" June 1999.
The terms correspond respectively to the surface energy of the pearls, to the electrostatic self-energy of the pearls, to the elastic free energy of the strings, to their surface energy, to their electrostatic energy and to the entire (smeared out) electrostatic energy of the whole chain. Within the limitations of this model, the necklace structure can be determined by minimization of eq.(2.2). The size of the pearls is \( R \approx R_c = b/(l_B f^2)^{1/3} \) and each pearl contains \( m = (\tau b)/(l_B f^2) \) monomers. The string diameter is \( d = \xi_4 \) and the string length \( l = b(b\tau/l_B f^2)^{1/2} \). The total length of the chain is \( L = bN(l_B f^2/b)^{1/2} \tau^{-1/2} \). This last result shows that the chain is indeed stretched. The physical picture can be summarized as follows: pearls of size \( R_c \) are separated by strings with a tension equal to the critical tension for unwinding pearls \( \sigma \). This tension comes from the long range electrostatic repulsions between pearls. The string length obtained from this argument \( l \) agrees with the minimization of the free energy. It is easily checked that most monomers are packed in pearls and that the stretched strings dominate the total length \( L \).

**B. Necklace stretching in the continuous limit, \( \varphi \neq 0 \)**

We first discuss qualitatively, the effect of an external force \( \varphi \) to the necklace chain. When the polyelectrolyte necklace is stretched under an external force, the pearl size and the string tension are essentially unaffected as they are fixed by the Rayleigh instability and by the equilibrium between pearl and string monomers respectively. The string length \( l \), is given by a force balance on a "half" necklace, relating the tension \( \sigma \), the external force \( \varphi \) and the electrostatic force exerted by the other half necklace, \( \sigma = k_B T \tau/b = \varphi + k_B T l_B Q^2/l^2 \); it increases with the external force and thus some pearls are converted into stretched strings (see Fig.2).

![FIG. 2. The force balance on the half necklace (2) : The tension \( t \) balances the external force \( \varphi \) and the electrostatic force exerted by half necklace 1. Further assuming \( t \sim k_B T \tau/b \) and neglecting the electrostatic interaction between pearls far apart leads to the simple scaling argument for \( l(\varphi) \) and \( L(\varphi) \).](image)

This argument yields the pearl separation length \( l(\varphi) \) as a function of the external force. For moderate external forces where most monomers remain in pearls, we obtain the simple force law

\[
\frac{\varphi}{k_B T} = \frac{\tau}{b} \left( 1 - \left( \frac{L(0)}{L} \right)^2 \right) \tag{2.3}
\]

The corresponding force profile is represented in Fig.3. This equation holds for small enough values of \( L \), i.e., \( L < N b \tau \) and logarithmic factors have been omitted. For larger forces, the hydrophobic forces are not important and the elasticity is the Gaussian elasticity of the strings as for a polyelectrolyte in a Theta solvent. The pearl number is treated here as a continuous variable. At small scales the force curve is expected to show plateaus corresponding to the unwinding of individual pearls, however for a large number of pearls, the curve is rounded by fluctuations. The typical fluctuation of the pearl number must then be larger than one.

To study the deformation behavior of isolated necklaces in more details we use an explicit free energy close to eq.(2.2). A more detailed expression for the interactions between strings and pearls is introduced, and we further account for an imposed external forces \( \varphi \).

\[
\frac{G}{k_B T} = p \left( \frac{\tau}{b} \right)^2 R^2 + (p - 1) \left( \frac{\tau}{b} \right)^2 dl + p \frac{l_B f^2 m^2}{R} + \frac{1}{2} \frac{l_B f^2 M^2}{L} \log(L/d) +
+ 2 \frac{l_B f^2 M M}{L} \log(L/R) + p \frac{l_B f^2 m^2}{l} \log p + \frac{L^2}{2 M b^2} - \varphi L \tag{2.4}
\]
FIG. 3. The force law in the continuous model following the simple scaling argument. The length $L$ is reduced by the equilibrium length $L(0)$ and the plateau value of the force $\sim k_B T \tau/b$ is taken as force unit. The end of this regime is reach when half of the pearls are unwinded, the elasticity is then dominated by the string elasticity and the force increases linearly (for gaussian elasticity), this regime is not shown.

We have used here the geometrical relationships for the necklace structure, the string length between two pearls is $l = L/(p-1)$, where $L$ is the total length of the necklace chain and $p$ the number of pearls; the number of monomers in one pearl is $m = (N-M)/p$, where $N$ is the total number of monomers in the entire chain and $M = (p-1)m_s$ is the total number of monomers in the strings; the diameter of the strings is given by $d^2 = Mb^3/L\tau$; finally the radius of the pearls is $R = ((N-M)/p)^{1/3}b/\tau^{1/3}$. It is useful to note that despite we have written out the logarithmic corrections here, we do not derive with respect to the chain length them in the following. We added them to keep control on the physical origin different terms. Therefore we treat them as constants. Precise numerical factors, however, are omitted as well.

It turns out to be convenient to use again the parameter $\Lambda = b\tau^3/\ell_B f^2$ proportional to the number of thermal blobs in a pearl and the following dimensionless variables, a reduced tension $t = L/(Mb\tau)$ and a reduced external force, $\varphi = \varphi b/\tau$. This amounts to rescale every quantity by the thermal blob. The physically relevant cases correspond to $\Lambda >> 1$, thus $1/\Lambda$ can be used as an expansion parameter. With these definitions we rewrite the free energy as

\[
\frac{G}{k_B T} = p^{1/3}(\tilde{N} - \tilde{M})^{2/3} + \frac{1}{\Lambda p^{2/3}}(\tilde{N} - \tilde{M})^{5/3} + \\
+ \frac{1}{2\tilde{M}} \tilde{M} \log(L/d) + 2\frac{1}{\Lambda t}(\tilde{N} - \tilde{M}) \log(L/R) + \\
+ \frac{1}{\Lambda t} \frac{(\tilde{N} - \tilde{M})^2}{\tilde{M}} \log p \\
+ \tilde{M} t^{1/2} + \tilde{M} t^2 - \varphi \tilde{M} t
\]  

The free energy is expressed only in terms of scaled variables and we introduced $(\tilde{N}, \tilde{M}) = (N, M)\tau^2$. The independent variables for the minimization are \{p, M, t\}. After minimization of the free energy, we obtain

\[
\frac{\tilde{N} - \tilde{M}}{p} = \frac{\Lambda}{2}
\]  

\[
-\frac{2}{3} \left( \frac{\tilde{N} - \tilde{M}}{p} \right)^{-1/3} - \frac{5}{3\Lambda} \left( \frac{\tilde{N} - \tilde{M}}{p} \right)^{2/3} - \left( \frac{\tilde{N} - \tilde{M}}{\tilde{M}} \right)^2 \frac{1}{\Lambda t} \log p - 2\frac{\tilde{N} - \tilde{M}}{\tilde{M}} \frac{1}{\Lambda t} \log p + \\
\sqrt{t} + \frac{1}{2\Lambda t} \log(L/d) - \frac{2}{\Lambda t} \log(L/R) + t^2 - \varphi t = 0
\]  

\[
2t + \frac{1}{2\sqrt{t}} - \frac{1}{\Lambda t^2} \left( 2 \left( \frac{\tilde{N} - \tilde{M}}{\tilde{M}} \right) \log(L/R) + \left( \frac{\tilde{N} - \tilde{M}}{\tilde{M}} \right)^2 \log p \right) - \varphi - \frac{1}{2\Lambda t^2} \log(L/d) = 0
\]

The first equation determines the number of blobs in one pearl, in agreement with our previous arguments. The second derivative with respect to $p$ allows to evaluate the fluctuation of the number of pearls, we find a r.m.s fluctuation...
\[ \delta p = \Lambda^{1/3}/p^{1/2} \] (we neglect here the coupling between the fluctuations of \( p \) and the fluctuations of other variables but this does not qualitatively change the result). The continuous description is consistent for \( p > \Lambda^{2/3} \) when the fluctuation of the pearl number is larger than one. The two other equations determine the effective tension \( t \) and the number of monomers in the strings or equivalently the ratio \( \Delta \) of the number of monomers in the pearls to that in the strings \( \Delta = (\tilde{N} - \tilde{M})/\tilde{M} \).

\[ \begin{align*}
- \frac{3}{2} \left( \frac{2}{\Lambda} \right)^{1/3} - \frac{1}{\Lambda} \Delta (\Delta + 2) \log p + \sqrt{t} + \frac{1}{2\Lambda t} \log (L/d) + \frac{2}{\Lambda t} \log (L/R) + t^2 - \tilde{\varphi}t &= 0 \\
- \frac{1}{\Lambda^2} \Delta \{\Delta \log p + 2 \log (L/R)\} + 2t + \frac{1}{2\sqrt{t}} - \tilde{\varphi} - \frac{1}{2\Lambda t^2} \log (L/d) &= 0
\end{align*} \tag{2.9} \tag{2.10} \]

The external force can be eliminated and

\[ \frac{1}{\Lambda t} \log (L/d) + \frac{2\Delta}{\Lambda t} \log \left( \frac{L}{R p} \right) + \frac{2}{\Lambda t} \log (L/R) - t^2 + \frac{\sqrt{t}}{2} - \frac{3}{2} \left( \frac{2}{\Lambda} \right)^{1/3} = 0 \tag{2.11} \]

For the free necklace, \( \varphi = 0 \), the fraction \( \Delta \) of pearl monomers to string monomers is of order \( \Delta \sim \sqrt{\Lambda/\log p} \). When a finite force is applied, \( \Delta \) decreases. In the limit \( \Lambda \to \infty \), the reduced tension is \( t = t_0 = (1/2)^{2/3} \), which can be used as a basis for an expansion to find approximate solutions. Following eq. (2.11), the leading correction to \( t_0 \) comes from the pearl self-energy; it is negative and proportional to \( \Lambda^{-1/3} \). It is a typical finite pearl size correction proportional to \( \xi_t/R \) and comprising both surface tension and electrostatic contributions of the same order. The next order correction comes from the electrostatic interactions, it is proportional to \( \Delta \) and positive; at small force, it is proportional to \( \Lambda^{-1/2} \log (L/R)/\log p^{1/2} \). At moderate force, the force extension curve to leading order in \( 1/\Lambda \), is given by

\[ \frac{\varphi}{k_B T} = (2t_0 + 1/2\sqrt{t_0}) \frac{\tau}{b} \left( 1 - \alpha \Lambda^{-1/3} \right) - \frac{2Bf^2N^2}{L^2} \log p \tag{2.12} \]

where \( \alpha \) is a positive numerical constant, depending on \( t_0 \) only. This last equation corresponds now to eq. (2.3). Physically it describes the unwinding of pearls by increasing external forces. Two new features appear in comparison with the simple argument above. The first is that a new term which corrects the (bare) line tension \( \sigma = k_B T \pi/\beta \) by a term proportional to \( \Lambda^{-1/3} \). This term has its physical origin in the finite size of the pearls, it is proportional to \( (\xi_t/R)^{1/3} \) as for the unwinding of a neutral globule but has both surface tension and electrostatic contributions of the same order. The other point is the appearance of the logarithmic term, which comes from the interactions between pearls that are dominant. Under the logarithm, the number of pearls can be approximated by \( p = (N \tau^2 - L \tau/\beta) / \Lambda \).

When a finite fraction of the pearls are unwound \( \Delta \) becomes of order unity. The force law eq. (2.12) can no longer be applied when \( L/\tau Nb \sim 1 \). The force is then a second order polynomial in \( \Delta \) and, due to the correction to \( t_0 \) (see eq. 2.11), the linear term in \( \Delta \) is positive; \( \varphi \) is of the form \( \varphi = A - B \Delta^2 + C \Delta \) where all three constants are positive and \( A \) and \( B \) are of the same order. This leads to a spinodal instability when about half of the pearls are unwound. We thus expect the polymer to jump from a metastable necklace to a single string unwinding about half of the pearls at once. Note that our argument relies on small correction terms to the force and tension (as \( \Delta \sim 1 \)); our free energy, involving several approximations, may be too crude in this case. However when half of the pearls are unwound the elasticity is dominated by the string elasticity even in the absence of any transition.

### C. Discrete pearls: two pearl-necklace

When there are only a few pearls in the necklace, the fact that the number of pearls is discrete cannot be ignored. This is of particular importance if the total number of pearls is small as shown by many numerical simulations [21–23]. In this subsection, we discuss the special case of two pearls separated by a string. This is the simplest model which is physically meaningful. For energetic reasons based on the here used free energy, the ends of the necklace chain consist of pearls (a chain with one pearl in the middle and two strings at the end is energetically not favorable). This minimal model has the advantage that the dissolution of the pearls can be computed in details. The number of pearls is fixed, in contrast to the continuous model. If the necklace had more than two pearls, we would have to take into account the fact that the pearls at the chain end, are larger than the central pearls, simply because of smaller electrostatic interactions (one missing neighbor). For a small number of pearls, we expect a discontinuous stretching with force plateaus corresponding to the unwinding of a pearl.
In order to describe the jump from 2 to 0 pearls, we start from a free energy that takes into account the interactions more precisely and includes all the surface and electrostatic free energies:

\[
G = 2\gamma R^2 + \frac{2I_Bf^2m^2}{R} + \gamma Ld + \frac{I_Bf^2M}{L} \log(L/d) + \\
+ 2\frac{I_Bf^2mM}{L} \log(L/R) + \frac{I_Bf^2m^2}{L} + \\
+ \frac{L^2}{2Mb} - \varphi L
\]  

(2.13)

The free energy can be rescaled using dimensionless variables \(\tilde{m} = t^2m\):

\[
\frac{G}{k_BT} = \frac{1}{N} \left(2\tilde{m}^{2/3} + \frac{2}{\Lambda} \tilde{m}^{5/3}\right) + \frac{1}{M} \frac{2\tilde{m}}{N} \log(L/R) + \\
+ \frac{1}{M} \left(1 - \frac{2\tilde{m}}{N}\right) \log(L/d) + \left(1 - \frac{2\tilde{m}}{N}\right) \frac{t}{2} + \\
+ \frac{1}{M} \left(\frac{\tilde{m}}{N}\right)^2 \frac{1}{(1 - 2\tilde{m}/N)} - \tilde{\varphi} \left(1 - \frac{2\tilde{m}}{N}\right)
\]

(2.14)

As the number of pearls is fixed, there are only two variables: the number of thermal blobs in a pearl \(\tilde{m}\) and the reduced tension \(t\). Two simple limits are described by this equation: \(\tilde{m} \to 0\) corresponds to a string with no pearls and the chain is an extended string of thermal blobs in the so-called Pincus regime \[20\]; in the absence of external force, \(\varphi = 0\), we describe a free two-pearl necklace.

The free energy map \(G(t, m)\) eq.\((2.14)\) is shown in Fig.4, for \(\tilde{N} = 2.05\Lambda/2\) with \(\Lambda = 10^3\). The plot is typical for high \(\Lambda\)-values where the description by the most likely necklace (steepest descent) is meaningful.

As the number of pearls is fixed, there are only two variables: the number of thermal blobs in a pearl \(\tilde{m}\) and the reduced tension \(t\). Two simple limits are described by this equation: \(\tilde{m} \to 0\) corresponds to a string with no pearls and the chain is an extended string of thermal blobs in the so-called Pincus regime \[20\]; in the absence of external force, \(\varphi = 0\), we describe a free two-pearl necklace.

The free energy map \(G(t, m)\) eq.\((2.14)\) is shown in Fig.4, for \(\tilde{N} = 2.05\Lambda/2\) with \(\Lambda = 10^3\). The plot is typical for high \(\Lambda\)-values where the description by the most likely necklace (steepest descent) is meaningful.

At low force, there is only one minimum in the \(G\)-map that corresponds to a necklace with roughly the optimal pearl size. For higher applied force the pearls unwind. At some value of the force, situation (a), a second minimum corresponding to a stretched string without pearls appears as a metastable state. With increasing force the free energy \(G\) of the stretched string becomes closer to the necklace free energy, the two minima in the free energy are equal in situation (b): they are separated by a saddle point significantly higher in energy. For even higher forces the necklace becomes metastable; the necklace minimum disappears in situation (b) where roughly half of the pearl content is unwinded. From these simple considerations, we plot an elongation/force diagram in Fig.5 with two branches. The stability exchange (situation (b) in the contour plots) is shown by the dashed line.
FIG. 5. The two pearl necklace branch and the open string branch of the length/force diagram. The values shown correspond to the minima in the previous G-map (Fig.4). The dashed line correspond to the stability exchange (b). The largest hysteresis loop is shown.

Below the dashed line the stretched string branch is metastable whereas above this line, the necklace branch is metastable. In a fast stretch/collapse/stretch cycle we expect a hysteresis loop following most of the metastable branches. In a quasi static extension procedure under imposed increasing force a pseudo-plateau close to the dashed line in the force-extension curve is expected. A better description of the pseudo-plateau requires a more complete theory including thermal fluctuations. A first approximation for the chain partition function is:

$$\Xi = \int dm \, dL \exp\left(-\frac{G(m,t)}{k_B T}\right)$$

where the integral is carried out over the previous t, m map. The average length is obtained as the derivative of the logarithm of the partition function $$\langle L \rangle = \frac{\partial \log \Xi}{\partial \phi}$$. The force-extension curve is plotted in Fig.6.

FIG. 6. Due to fluctuations a force pseudo plateau (rather than a plateau) is found. We plot the force $$\phi$$ against the corresponding average length $$\langle L \rangle$$. The force at the pseudo plateau (say inflection point) is close to the stability exchange value reported in Fig.5, the pseudo plateau extends roughly between the same length as the dashed line in Fig.5. In the pseudo plateau, the length fluctuations are comparable to the average length.

A pseudo-plateau is indeed observed. According to linear response theory, the length fluctuations are obtained from the slope of this curve $$\langle L^2 \rangle - \langle L \rangle^2 = kT \frac{\partial \langle L \rangle}{\partial \phi}$$. The RMS fluctuation of the length is of the order of the average length on the pseudo-plateau and much weaker outside the pseudo-plateau. This description remains crude as we did not allow for unlike pearl sizes. As shown in the simple discussion of the Rayleigh instability for mesoscopic drops, pearl size fluctuations may be important for not too high values of $$\Lambda$$. In the following, we give a simpler description where the tension of the string is kept constant during the pearl unwinding (a reasonable assumption in view of the numerics). It is then possible to get a simple picture also in the case when the necklace has several pearls.
III. DISCRETE PEARL MODEL

So far, we have ignored pearl size fluctuations; in the following we propose a simplified description of the necklace structure that allows to take these fluctuations into account. We describe approximately the necklace by a row of pearls, and we fix the structure of the strings i.e. their tension and their elastic energy per unit length. If the total number of monomers in the strings is \( M \) as above and the total length of the chain (dominated by the strings) is \( L \), \( M/L = \tau/b \) and the total elastic energy of the strings is \( F_{\text{string}} \sim \frac{1}{2} k_B T L \tau/b \).

We then distribute the \( P = N - M \) remaining monomers into \( p \) pearls with masses \( m_i \), which are not necessarily identical. The total free energy includes the pearl self-energy, the string electrostatic energy and the smeared out electrostatic energy \( k_B T l_B \sum f^2 N^2 / L \) between pearls and strings. In this model, all the contributions to the free energy except for the pearl self-energy are identical to those of the continuous model. We do not include here the logarithmic factors in the electrostatic term but they could be included as before. For a fixed length of the chain, the number of monomers in each pearl and the fluctuations of this number are essentially determined by the pearl self-energy, we thus ignore the fluctuations in all the other terms of the free energy. The main approximation of our model is that the length of the chain is only due to the strings and thus that the total number of monomers in the strings and therefore in the pearls are fixed. This approximation may not be quantitative but we expect it to give the correct physical picture and the correct scaling behavior.

In this section, in contrast to previous considerations, we impose the length of the chain and compute the force. In order to discuss this model qualitatively, we further simplify it by assuming that all pearls are identical. In a second step the fluctuations in the number of monomers of the individual pearls are explicitly taken into account.

The free energy of a single pearl is

\[
F_p = \frac{\gamma R^2}{2} + k_B T \frac{f^2 m^2}{R} = k_B T \left( N^{2/3} \tau^{4/3} + \frac{l_B}{b} \tau^{1/3} m^{5/3} \right)
\]  

(3.1)

where \( m \) is the number of monomers in the pearl. The free energy per pearl monomer is then

\[
\tilde{f} = m^{-1/3} \tau^{4/3} + \frac{l_B}{b} \tau^{1/3} m^{2/3}
\]

(3.2)

The free energy per monomer \( \tilde{f} \) plotted as a function of the pearl mass \( m \) has a minimum at \( m_0 = \Lambda/(2\tau^2) \). The second derivative is positive for \( m = m_0 \), it vanishes for \( m = 4m_0 \). In the following, in order to take into account the deviations from the preferred value \( m = m_0 \), we approximate the free energy per monomer by a parabolic form where the parabola has a spring constant \( k = (\partial^2 \tilde{f}/\partial m^2)|_{m_0} = m_0^{-1} (l_B f^2 / b)^{4/3} \). The total free energy of the chain can then be written as

\[
F = F_{\text{cont}}(m_0) + \frac{1}{2} k_B T k m_0 \sum_{i=1}^{p} (m_i - m_0)^2.
\]

(3.3)

where \( F_{\text{cont}} \) is the free energy discussed earlier in the continuous limit with equal numbers of monomers \( m_0 \) in all pearls (\( F_{\text{cont}} \) is in a first approximation given by eq. \( \text{(2.2)} \) or by eq. \( \text{(2.4)} \) where the force term has been omitted) and the sum is over the \( p \) pearls.

As a first step, we consider that all the pearls have the same number of monomers \( m \) that can be different from the preferred value \( m_0 \). When the necklace is stretched, the number of monomers in each pearl decreases. At some point however, it becomes energetically more favorable to have one pearl less. In this crude argument, we assume that the jump from \( p \) to \( p - 1 \) pearls occurs abruptly for a given imposed necklace length, this is equivalent to a large energy scale in the Boltzmann weights and hence to large pearls (\( \Lambda >> 1 \)). The stability exchange from the necklace containing \( p \) pearls to the necklace containing \( p - 1 \) pearls corresponds, in the parabolic potential, to opposite deviations from the preferred pearl size: \( \delta m_p = -\delta m_{p-1} \). On the other hand, due to mass conservation, (the length is imposed), \( p m_p = (p - 1) m_{p-1} \). The necklace thus jumps from \( p \) to \( p - 1 \) pearls for \( \delta m_p = -m_0/(2p - 1) \). For a chain containing \( p \) pearls, we get

\[
\delta m = \frac{1}{p} \left( N - \frac{L}{\tau b} - pm_0 \right)
\]

The force is obtained by derivation of the total free energy, it is equal to

\[
\varphi_p = \varphi_{\text{cont}} - \frac{1}{p} \frac{k m_0}{\tau b} \left( N - \frac{L}{\tau b} - pm_0 \right).
\]

(3.4)
The first term is the force calculated previously in the continuous limit and the second term is the contribution due to the discreteness of the pearls and to the fact that they do not have the preferred size; this "individual pearl" contribution is non-monotonic (see Fig. 7). If the number of pearls in the necklace is small enough, the total force also exhibits downwards jumps.

This occurs if the distance \( l \) between pearls is large enough \(( l > l_0\Lambda^{-2/9}m_0\tau b)\). The branches where the force decreases with length are unstable and the force actually shows a plateau. The plateau is obtained from a Maxwell-like construction on the total force. In practice, for non quasi-static transformations, the system rather follows the metastable branch and, when the applied force increases, the length jumps at the force extrema.

The force jumps obtained upon imposing the chain length are rounded by fluctuations of both the number of monomers in a pearl and the number of pearls. In order to take into account the fluctuations, we compute the partition function of a necklace of \( p \) pearls

\[
Z_p = Z_0 \int \prod_i dm_i \exp \left\{ -\frac{1}{2} k m_0 \left( m_i - m_0 \right)^2 \right\} \delta \left( N - \frac{L}{\tau b} - \sum_{i=1}^p m_i \right).
\] (3.5)

The delta function ensures the mass conservation. The bare partition function is associated to the free energy calculated in the continuous limit \( Z_0 = \exp(-F_{\text{cont}}/k_B T) \). Formally we are looking for the partition function of a row of \( p \) harmonic springs with a fixed total length. The result is

\[
Z = Z_0 \left( \frac{2\pi}{k m_0} \right)^{p/2} \left( \frac{2\pi k m_0}{p} \right)^{1/2} \exp \left\{ -\frac{k m_0}{2p} \left( N - \frac{L}{\tau b} - \sum_{i=1}^p m_i \right)^2 \right\}.
\] (3.6)

The total partition function of the necklace chain is \( Z = \sum_p Z_p \) and the free energy is \( F = -k_B T \log Z \). The force is then obtained by derivation

\[
\varphi = \varphi_{\text{con}} + k_B T \frac{\sum_p \left( \varphi_p \frac{(l_0 f^2 / \tau b)^{-2p/3}}{p^{7/2}} \exp \left( -\frac{\Delta^{2/3}}{p} (N/m_0 - L/(\tau b m_0) - p) \right)^2 \right)}{\sum_p \left( \frac{(l_0 f^2 / \tau b)^{-2p/3}}{p^{7/2}} \exp \left( -\frac{\Delta^{2/3}}{p} (N/m_0 - L/(\tau b m_0) - p) \right)^2 \right)},
\] (3.7)

where \( \varphi_{\text{con}} \) is the force obtained in the continuous approximation 2.12 and

\[
\varphi_p = -2\tau\Lambda^{-1/3} p \frac{\Delta^{2/3} (N/m_0 - L/(\tau b m_0) - p)}{b}.
\] (3.8)

The fluctuations of the pearl number smear out the force oscillations for \( p > \Lambda^{2/3} \) as found previously. The fluctuations of the pearl sizes are reflected by the prefactors \( p^{-1/2} (l_0 f^2 / \tau b)^{-2p/3} \). The sums are evaluated numerically for certain values. The result is displayed on Fig. 8. As in our simple argument where the fluctuations were ignored, the force shows oscillations with unstable decreasing branches that should be replaced by plateaus or pseudo-plateaus using the Maxwell construction. In the limit of very large \( \Lambda \), the decrease of the force becomes very steep and the force on each branch tends to the value given by equation 3.4.
FIG. 8. Same as Fig. 7 but with fluctuations taken into account. We take $\Lambda = 1000$ and $l_B f^2/b = 10^{-4}$. For such high $\Lambda$-values fluctuations have not a dramatic effect when there are only a few pearls, for $\Lambda = 100$ (not shown) the fluctuations almost suppress the first oscillations completely (left of the figure).

IV. LOCALIZED COUNTERIONS: VERY POOR SOLVENT AND COUNTERION CONDENSATION ON THE PEARLS

So far, the counterions of the necklace chain have not been taken into account and have been considered as forming a free ideal solution. There are however cases where this assumption fails.

When the solvent is very poor, the pearls are very dense and the local dielectric constant inside a pearl is lower than that of water by typically one order of magnitude, there are essentially no dissociated charges in the pearl core. Charged systems with low dielectric constants, called ionomers, have been extensively studied \(^{24}\). We follow in this section the lines of a simple model proposed by Dobrynin \(^{25}\).

The electrostatic potential at the surface of a pearl $\sim \tau (l_B/f)^{1/3}$ increases with decreasing solvent quality and decreasing charge fraction. A condensation of the counterions and thus a regulation of the charge of the pearls is expected when this potential becomes of order $k_B T$ i.e. when $\tau^3 > f b/l_B$. The necklace becomes then unstable and collapses to form a compact globule. We now discuss this instability and the effect of an external force.

A. Condensation on the pearls

We assume that the counterions condense to a certain amount on the pearls but that they do not condense on the strings, i.e., the linear charge density along the strings is smaller than the Bjerrum length, which leads to $f < \tau (b/l_B)$. Counterion condensation then only takes place on the pearls. In the simplest description \(^{26}\), the pearls have an effective charge $Q_e$ determined by equilibrating the chemical potential of the counterions to bulk value of the order of the thermal energy $k_B T$.

The pearl-necklace structure is based on a Rayleigh instability. We first discuss the effect of condensation for a “liquid of disconnected blobs”. Let us call $-\alpha k_B T$ the chemical potential of the free counterions and $Q_e$ the net charge of a droplet of radius $R$ and of nominal charge $Q = f \tau R^3/b^3$, the free energy of an assembly of $\tilde{N}$ blobs forming $p$ monodisperse non-interacting droplets of radius $R$ is

$$F = p\gamma R^2 + k_B T p \frac{Q_e^2 l_B}{R} + p\alpha k_B T (Q - Q_e).$$

It includes the surface tension energy, the electrostatic energy of each drop and a chemical potential term for the counterions. After minimization with respect to the effective charge and taking into account the fact that the effective charge must be smaller than the nominal charge we obtain

$$F\tau^3/\tilde{N}k_B T = \frac{\tau^2 b}{R} + \frac{l_B f^2 R^2 \tau^2}{2 b^3} \quad (R < R_{co})$$

$$F\tau^3/\tilde{N}k_B T = \frac{\tau^2 b}{R} - \frac{\alpha^2 b^3}{2 l_B R^2} + f\tau\alpha \quad (R > R_{co})$$

charge regulation takes place for $R > R_{co}$ where $R_{co}^2 = (\alpha b^3)/(f\tau l_B)$. 11
If the fraction of charged monomers is large enough, $a^2 b f / l_b^3 > 1$, in the regime where there is no counterion condensation, the free energy per blob has a minimum at $R_{\text{min}} = b (f b / l_b)^{-1/3}$ (the electrostatic blob size). The associated droplet radius is such that $R_{\text{min}} < R_{\text{co}}$ and the minimum actually exists. In the same range of parameters, in the regime where the counterions condense on the spheres the free energy per blob has a maximum in the charge regulated regime at $R_{\text{max}} = a^2 b^3 / l_b$. The minimum at the preferred pearl size is then stable against the infinite globule. In the opposite limit $a^2 b^3 / l_b > 1$, the free energy per blob decreases monotonically with the radius of the droplets and the largest possible globule is stable. In this case, counterion condensation prevents the Rayleigh instability. The energy per blob is sketched in Fig. 9 for both cases.

![Figure 9](image-url)

FIG. 9. Charge regulation by the pearls. Free energy per blob as the function of droplet radius for an assembly of non interacting droplets, the infinite globule is taken as reference state. The radius is reduced by $R_{\text{co}}$, the crossover radius to charge regulation. The parameter $\beta = \left( ( l_b^3 ) / ( a b^3 ) \right)^{1/2}$ controls regulation by the preferred pearl. The plotted function reads: $f( x, \beta ) = \beta / x + x^2 / 2$ ($x < 1$) and $f( x, \beta ) = \beta / x - x^2 / 2 + 1$ ($\beta > 1$) For $\beta < 1$ there is a preferred pearl located in the non regulated regime, the maximum located in the regulated regime is very shallow (the figure corresponds to $\beta = 1/8$). For $\beta > 1$, there is no finite preferred pearl size, the largest possible globule is stable (the figure corresponds to $\beta = 8$).

The structure of a necklace when there is no counterion condensation on the pearls has been described in the previous sections. The argument on the Rayleigh instability suggests that charge regulation and collapse occur simultaneously, as stated by Dobrynin et al. [25] and Schiessel and Pincus [27] following similar arguments. The situation is also reminiscent of that of cylindrical globules studied by Khokhlov [28] where Manning condensation [29] provokes collapse.

We now turn to the case of a polyelectrolyte chain and consider a necklace structure with condensed counterions on the pearls. The total free energy can be written as

$$
\frac{G}{k_B T} = \rho \gamma R^2 + ( p - 1 ) \alpha / l_d + p \frac{l_B Q^2}{R} + ( p - 1 ) \frac{l_B f^2 m_s^2}{l} + \frac{l_B p^2 Q^2}{L} \log p + \frac{L^2}{M b^2} + \alpha \rho ( Q - Q_c ) - \varphi L
$$

where the first term is the surface contribution of the $p$ pearls, the second term the surface free energy of $p - 1$ strings of length $l$ and thickness $d$, the third term is the electrostatic self-energy of the pearls, followed by the electrostatic self-energy of the strings containing $m_s$ monomers. The fifth term is the total electrostatic interaction between the pearls where the total length of the necklace is $L \simeq ( p - 1 ) l$. The total elastic free energy contribution yields the Gaussian term and finally the next term is the contribution of the free counterions, the last term is the contribution of the external force. The minimization of the free energy eq. (4.2) with respect to $Q_c$ gives the effective charge as a function of the radius $R$ of the pearls and of the distance $l$ between pearls, the onset of charge regulation defined as $Q_c = Q$ is located at $Q = \frac{a R}{l_B ( 1 + \frac{l_B f^2}{l} \log p )}$. Due to the interactions between pearls, the condensation threshold is shifted to a lower pearl charge; the effect depends on the force through $l$ and $p$ and decreases for increasing forces. However this is a small correction for high values of $\Lambda$. Ignoring these corrections, the free energy can be minimized using the same set of variables as in section (II-B). The free energy does not have a minimum at any finite value of $p$ and is minimum for $p = 1$ or $p = 0$. As for the disconnected liquid of blobs, the necklace structure is unstable and as soon as the counterions condense on the pearls, the polyelectrolyte collapses. Within this description there is no regime of necklace stabilized by an external force. We thus conclude that at low charge fraction $f < \tau^3$ where there would be charge regulation by the pearls, the dense globule is stable and stretches discontinuously when the force is equal to $k_B T \tau / b$, the necklace structure is never stable.
B. Very poor solvent

In the preceding sections, we have assumed that the solvent is poor, but that the reduced excluded volume \( \tau \) is smaller than unity, i.e., the correlation length remains much larger than the monomer size. In this case, one can assume that locally the dielectric constant is that of water, that the Bjerrum length has the water value and that the charges are dissociated. Consequently the counterions can be distributed inside the globule, almost freely. In a poorer solvent, the correlation length \( \xi \) is of the order of the monomer size \( b \) and this assumption on the dielectric constant cannot be made. Inside the dense phase, the solution is close to a polymer melt and the Bjerrum length decreases by one order of magnitude. This is also true well inside the pearls; the charges are then not dissociated and a typical ionomer behavior is expected. In the following brief discussion we assume that ion dissociation takes place only at the surface of the globules, and that only those groups localized in a thin shell of the order of the thermal blob size \( \xi \) are dissociated and contribute to the pearl net charge.

The effective charge therefore becomes

\[
Q_e = f R^2 \xi c = f \frac{R^2}{b^2},
\]

where the concentration inside the globule is \( c \propto b^{-3} \). The balance between the electrostatic free energy due to this effective charge and the surface free energy yields the size of the pearls

\[
R = b \left( \frac{\tau}{f} \right)^{1/2},
\]

which enables us to compute the effective pearl charge and pearl electrostatic potential:

\[
Q_e = \left( \frac{b}{l_B} \right)^2 \tau^4 f^{-3},
\]

\[
U_s = (l_B Q_e) / R \sim \frac{\tau^2}{f}.
\]

These expressions are only valid in the range of values of \( \tau \) close to 1 and if part of the dissociated ions do not condense in the outer pearl shell, i.e., \( f > \tau^2 \). On the other hand, the pearl size \( \xi \) must be larger than the string, diameter i.e., the thermal blob size \( \xi \), which yields an upper bound of the form \( f < \tau^{3/2}(b/l_B)^{1/2} \). The charge fraction must thus be in the range

\[
\tau^2 < f < \tau^{3/2}(b/l_B)^{1/2} \tag{4.7}
\]

The number of monomers in the pearl is then \( m = R^3 c \), giving

\[
m = \left( \frac{b}{l_B} \right)^3 \frac{\tau^7}{f^6}.
\]

Again the string length between two pearls can be computed by the force balance. It is given by

\[
l = b \left( \frac{l_B}{b} \right)^{-3/2} \left( \frac{\tau^7}{f^6} \right)^{1/2}
\]

and the calculation of the mass of the strings \( m_s = l d^2 c \) shows that still most charges are indeed in the pearls. If an external force is applied, the force balance has to be modified and the force-extension law is

\[
L = N \left( \frac{b}{\tau/b - \varphi} \right)^{1/2} \left( \frac{l_B}{b} \right)^{3/2} \frac{\tau^6}{f^6}.
\]

This last equation is only valid as long as the pearl mass is much larger than the string mass, i.e., as long as

\[
b \left( \frac{\tau}{b} \right) - \varphi > \left( \frac{l_B}{b} \right)^3 \frac{\tau^6}{f^6}.
\]

For \( f < \tau^2 \) however part of the counterions have to condense onto the outer pearl shell of thickness \( \xi \) in order to decrease the surface potential back to \( k_B T \). In that case the results of the previous section where charge regulation by the pearls was already considered apply. Additionally we remark that the range of parameters is small for the validity of these scaling arguments. Within the presented approach, we cannot guarantee that the necklaces are stable. This remark does not at all affect the regimes discussed, e.g., in [29].
A polyelectrolyte globule in a poor solvent has been shown by Kantor and Kardar [7,8] and Dobrynin and Rubinstein [9] to elongate with increasing charge and to have a necklace structure comprising smaller "pearls" separated by stretched strings quite similarly to the so-called Rayleigh instability of charged liquid droplets. If we neglect the interaction with the charged monomers of the strings and of the other drops, the pearl size is fixed by a Rayleigh criterion, $l_B Q^2 / R \sim \tau R^2 / b^2$. Most monomers are in pearls whereas the strings make most of the chain length. In this paper we discussed theoretically pearl-necklace chain elasticity.

We first developed a continuous picture, valid for a necklace comprising many pearls and where single pearl features are ignored. When the necklace elongates under the action of an external force, the pearls are unwinded and converted into stretched strings. During this process the thermodynamic equilibrium between pearl and string monomers is preserved; this imposes the string tension to $k_B T \tau / b$ and the string diameter, $(b / \tau)$. At equilibrium the tension in a string balances the repulsion between half-necklaces, and the external force. This force balance leads to the simple force/length relation: $\varphi = k_B T (\tau / b - l_B f^2 N^2 / L^2)$. During the unwinding process the length increases by a factor $\Lambda^{1/2}$ where $\Lambda >> 1$ measures the number of thermal blobs in a pearl (or equivalently $\Lambda$ is the inverse of the electrostatic interaction interaction between thermal blobs). This is in contrast with the earlier cylindrical model which predicts that when a force is applied to a spherical globule, the globule becomes unstable when it is elongated by a factor of order two.

In practice, the number of pearls is not always very large (as seen in several numerical simulations) and the discreteness of the pearls becomes an important factor. We have discussed in details a necklace comprising two pearls. When the external force is increased, a well defined metastable single string state appears in addition to the two pearl necklace. For a somewhat higher force, the single string and the two-pearl necklace exchange stability. At this critical force, the pearl size is still close to the pearl size in the absence of external force. When about half of the pearls is unwinded, the metastable two-pearls state disappears and the single string state is the only equilibrium conformation.

For a fast stretch-collapse cycle, a hysteresis loop describing most of the metastable branches is expected. For quasi-static cycles, a force plateau is anticipated at coexistence (due to the one dimensional character of the problem the plateau is not associated to a real phase transition). For necklaces containing more pearls, our description uses a somewhat simpler model, where the intensive string properties, tension etc... are kept constant and where the only variables which are allowed to fluctuate are the number of monomers in a pearl and the number of pearls; this allows a transfer of the monomers from the pearls towards the strings as the applied force is increased. In this model the number of pearls is bound to be an integer. In a first approximation neglecting thermal fluctuations, an abrupt decrease of the pearl number by one unit is predicted for a given length (sequence of lengths). This formally corresponds to an abrupt decrease of the force. There is thus a sequence of Maxwell loops, corresponding to force plateaus in a quasi static transformation, or to a series of spinodal length jumps under increasing applied force. This picture is altered by fluctuations which are usually expected to be important and that smoothen the plateaus.

The pearl-necklace structure of polyelectrolytes relies on a steepest descent description which becomes exact in the thermodynamic limit for macroscopic systems. In the usual Rayleigh instability of small (yet macroscopic) droplets the energy scale, say typically the surface energy of a marginally stable droplet, is large compared to $k_B T$. For mesoscopic systems such as the polyelectrolyte necklace, this is not always the case and thermal fluctuations are often important. In the case of a two pearl necklace we have computed the average length, and the length fluctuation when the necklace is subject to an external force. A pseudo-plateau is indeed found for the force but even for a pearl self-energy as high as $100k_B T$ the plateau is strongly rounded and the length fluctuations in the plateau are roughly as large as the average length. If the necklace contains many pearls, the fluctuations have also been taken into account. The force is the sum of a continuous component that can be calculated from the continuous model and a component arising from the discreteness of the pearl number. This last contribution is non monotonic and can lead to Maxwell loops. However if the self-energy of a pearl is small or if the network comprises many pearls the plateaus are strongly rounded by fluctuations and significant force (pseudo) plateaus are no longer expected.

In the pearl-necklace structure, the electrostatic charge on the pearls is rather high and, even though there is no Manning condensation on the strings or on the smeared out necklace charge, condensation on the pearls (or charge regulation) can occur. In agreement with previous work, charge regulation is found for $f < \tau^3$ and the polyelectrolyte collapses into a large globule whenever counterion condensation becomes important. If an external force is applied, the collapsed globule discontinuously stretches at a critical tension of order $k_B T \tau / b$. The extreme case of a very poor solvent where there is no ion dissociation in the (ionomer-like) dense phase has also been discussed as it is of some experimental relevance. In this case stable necklaces are obtained and the pearls unwind under an external force.

As a remark aside we would like to mention, that we ignored the effect of salt which might be added to the solution. This will be part of a different work. However, we expect that the results presented here are valid as long as the persistence length (including the electrostatic contribution) together with the Debye screening length is larger than...
\( l \) i.e., the distance between two pearls.

Besides direct single chain elasticity measurements and implications for drag reduction in polyelectrolyte solutions and related topics, the single chain elasticity studied in this paper can be used as a basis to investigate more complex systems. In a separate work, we will present results on polyelectrolyte gel elasticity in a poor solvent following Katchalsky’s arguments.

\section*{Acknowledgments}

T.A.V. acknowledges the financial support of the LEA. The hospitality of the Institut Charles Sadron is gratefully appreciated. The authors acknowledge enjoyable and helpful discussions with Phil Pincus. They are also grateful to H. Schiessel, who sent his preprint prior to publication.

\section*{Note added:} After submission of this work, we received a preprint by H. Schiessel In this work the same topic is discussed. The free energies are discussed numerically and the results are complementary to those discussed here.

\begin{thebibliography}{31}

\bibitem{1} X. Châtellier, T. Senden, J.-F. Joanny and J.-M. di Meglio, Europhys. Lett. \textbf{41}, 303, (1998)
\bibitem{2} P. Haronska, J. Wilder and T. A. Vilgis J. Phys. II (France) \textbf{7}, 1273, (1997)
\bibitem{3} P.G. de Gennes, Physica \textbf{140A}, 9 (1986)
\bibitem{4} P. S. Mumick, P. N. Welch, L. Z. Salazin and C. L. Mc Cormick Macromolecules \textbf{27}, 323 (1994)
\bibitem{5} P. G. de Gennes, P. Pincus, R. M. Velasco, and F. Brochard, J. Phys. (France) \textbf{37}, 1461 (1976).
\bibitem{6} A. Khokhlov, J. Phys. A (math. gen.) \textbf{13}, 979 (1980).
\bibitem{7} Y. Kantor and M. Kardar, Europhys. Lett. \textbf{27}, 643 (1994).
\bibitem{8} Y. Kantor and M. Kardar, Phys. Rev. E \textbf{51}, 1299 (1995).
\bibitem{9} A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, Macromolecules \textbf{29}, 2974 (1996).
\bibitem{10} A. Halperin and E. Zhulina, Europhys. Lett. \textbf{15}, 417 (1991).
\bibitem{11} G. U. Lee, L. A. Chrisey, and R. J. Colton Science, \textbf{266}, 771, 1994.
\bibitem{12} M. Rief, F. Oesterhelt, B. Heymann, and H. E. Gaub Science, \textbf{275}, 1295, 1997.
\bibitem{13} T. J. Senden, J. M. di Meglio, and P. Auroy Eur. Phys. J. B, \textbf{3}, 211, 1998.
\bibitem{14} H. B. Li, M. Rief, F. Oesterhelt, and H. E. Gaub Advanced Materials, \textbf{10}, 316, 1998.
\bibitem{15} A. Courvoisier, F. Isel, J. François, and J. Maaloum Langmuir, \textbf{14}, 3727, 1998.
\bibitem{16} P. Cluzel et al., Science, \textbf{271}, 792, 1996
\bibitem{17} C. Bustamente et al., Science, \textbf{265}, 1599, 1994
\bibitem{18} J. F. Marko and E. D. Siggia, Macromolecules \textbf{28}, 8759, 1995
\bibitem{19} A. Johner, T.A. Vilgis, J.-F. Joanny, Polyelectrolyte gel elasticity in poor solvent Macromol. Symp., to appear.
\bibitem{20} P.-G. de Gennes, \textit{Scaling Concepts in Polymer Physics} (Cornell University Press, Ithaca, 1979).
\bibitem{21} P. Chadanowski and S. Stoll, J. Chem. Phys. \textbf{111}, 6534, (1999).
\bibitem{22} U. Micka, C. Holm, and K. Kremer, Langmuir \textbf{15}, 4033 (1999).
\bibitem{23} A. V. Lyulin, B. Dünweg, O. V. Borisov, and A. A. Darinskii, Macromolecules \textbf{32}, 3264 (1999).
\bibitem{24} A. Eisenberg, Polym. J. \textbf{31}, 303 (1999).
\bibitem{25} A. Dobrynin and M. Rubinstein, preprint (1999).
\bibitem{26} F. Oosawa, \textit{Polyelectrolytes} (Marcel Dekker, New York, 1971).
\bibitem{27} H. Schiessel and P. Pincus, Macromolecules \textbf{31}, 7953 (1998).
\bibitem{28} G. Manning, J. Chem. Phys. \textbf{51} 954 (1969).
\bibitem{29} N. Lee and D. Thirumalai, Eur. Phys. J. B \textbf{12}, 599, 1999
\bibitem{30} A. Katchalsky, S. Lifson, and H. Eisenberg, J. Polym. Sci. \textbf{7}, 571 (1951).
\bibitem{31} M. N. Tamashiro, H. Schiessel, preprint.
\end{thebibliography}