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Polyelectrolyte Gel Elasticity in Poor Solvent

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Abstract : Polyelectrolytes in poor solvents are expected to show a necklace structure where collapsed polymer pearls are linked by stretched polymer strands. This prediction by Kantor and Kardar worked out by Dobrynin Rubinstein and Obukhov Macromol.1996,**29**,2974 has mainly be confirmed by computer simulations of Dobrynin ; Darinskii ; Holm and Kremer. We study the unwinding of pearls under an external force. Polyelectrolyte gels in poor solvents are then discussed, mainly on the basis of single chain elasticity following Katchalsky.

The elasticity of neutral polymer gels is fairly well understood and is merely determined by the crosslink density[1]. The shear modulus of unentangled gels is roughly k_BT per crosslink, the simple formula $G \approx k_BTc / N$, where c is the gel density and N the mesh size, is valid under broad conditions. The excluded volume interactions rather determine the compression modulus K. The picture is however complicated by entanglements that may act as effective crosslinks[2] and by heterogeneity[3]. In the case of polyelectrolyte gels we have to account additionally for the counterion pressure and long ranged electrostatic interactions. The swelling equilibrium of θ-gels results from the balance between counterion pressure and gaussian elasticity, the electrostatic interaction being negligible and $G \approx K \approx k_BTcf$, with f the charge fraction[4].

We are considering here polyelectrolytes in poor solvents. The structure of a single chain results from the balance of the interfacial energy F_S between the polymer and water and the electrostatic interaction energy F_{el}.. This was first studied by Khokhlov[5] who proposed an elongated cigar-like shape provided that the electrostatic energy overcomes the surface tension. The relevant surface tension γ is that between the dense polymer phase and water, $\gamma = k_BT\tau^2 / a^2$ with $\tau = -v/a^3$, v being Edwards excluded volume parameter and a the monomer size. The critical globule size for the electrostatic interaction to be relevant is $R_c = a^{4/3}(l_Bf^2)^{-1/3}$. In the Khokhlov picture, the chain is stretched at scales larger than R_C but locally collapsed at scales smaller than R_C, this yields the total length $L = Na(l_Bf^2 / a)^{2/3} / \tau$. Recently it has been proposed by Kantor and Kardar[6] that the elongated globule structure is unstable and splits into

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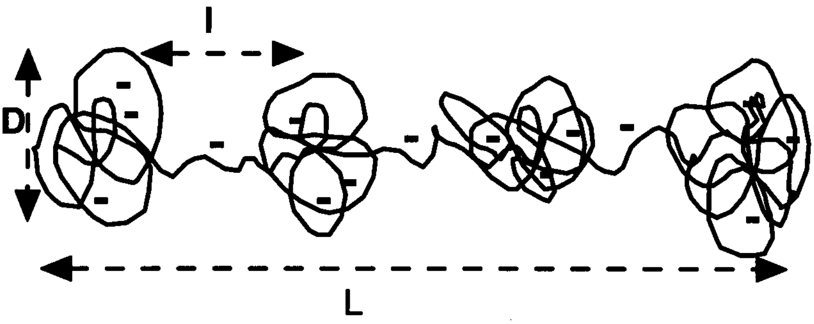
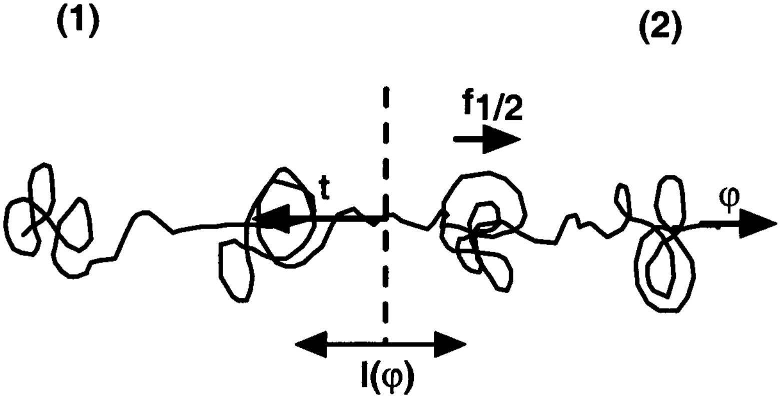
marginally stable globules by analogy with the Rayleigh instability of charged droplets. Due to chain connectivity these globules are separated by stretched strings.



This model known as the necklace model has been developed by Dobrynin et al.[7]. Pearls of size D=R_C are separated by strands at tension $t = k_B T\tau / a$, the critical tension for unwinding pearls, this tension originates in the electrostatic repulsion between pearls, $k_B T l_B Q^2 / l^2$ (up to a logarithmic factor) with Q the charge of a pearl. From this argument, the strand length is found to be $l = (\tau / (l_B f^2 / a))^{1/2} a$. It is easily checked that most monomers are packed in beads and that the stretched strands make most of the total length $L = N(f^2 l_B / a\tau)^{1/2} a$.

When the polyelectrolyte necklace is stretched under an external force φ, the bead size and the strand tension are essentially unaffected. Nonetheless the strand length l, imposed by a force balance increases and thus some pearls are converted into stretched strands.

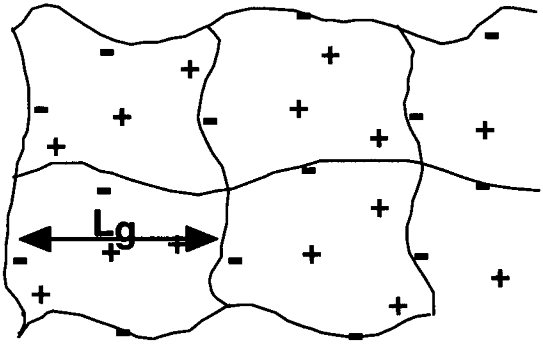


The force balance on the "half" necklace (2), relates the tension t, the external force φ and the electrostatic force $f_{1/2}$ exerted by part (1). This argument yields $l(\varphi)$. For moderate external forces where most monomers remain in pearls, we obtain the simple force law[8]

$$L(\varphi) = L(0)(1 - \frac{\varphi a}{k_B T\tau})^{-1/2}$$

which holds for $L < N\tau a$ and where logarithms have been omitted. At small scales the force curve shows steps corresponding to the unwinding of single pearls, however for a large number of pearls, the curve is rounded by fluctuations (the typical fluctuation of the pearl number is then larger than one).

Following the classical picture by Katchalsky[4], the swelling equilibrium of the gel results from the balance of the counterion pressure $\Pi_{count} = k_B Tfc$ and the elastic stress Π_{elast}.



For the polyelectrolyte gel in poor solvent the elastic energy density is due to the stretched strands:

$$\Pi_{elast} = -k_B T(c/N)(N/m)(l/\xi) = -k_B T\tau/L_g^2 a$$

where L_g is the mesh size, m the monomer content of a bead and $\xi = a/\tau$ the transverse strand size. The last expression assumes a c^* gel[1] where $c = N/L_g^3$. Equating the stresses leads to the equilibrium mesh size and gel concentration:

$$L_g = fNa/\tau \qquad c = \tau^3/N^2 f^3 a^3$$

Both the shear modulus G and the compression modulus K are proportional to

$$\Pi_{count} = k_B Tfc = k_B T\tau^3/N^2 f^2 a^3$$

For non equilibrium gels, the compression modulus is still dominated by the counterion pressure

$$K = k_B Tfc$$

The shear modulus depends on both the preparation state and the swelling state[9,10]. We assume affine gel deformation from the preparation state $\lambda = (c_0/c)^{1/3}$ where c_0 and c are the initial and final gel concentrations. To estimate the elastic energy density stored in the gel we take the semidilute solution at the same concentration c where the chains are stress free as a reference state.

$$G = -(k_B Tc / N)(\lambda R_0 / R)^2$$

For moderate concentrations ($c < c_1 = (l_B / a)^{1/2} f\tau^{-1/2} a^{-3}$), there are several beads in one correlation length $\xi_c = (l_B f^2 / a)^{-1/4} \tau^{1/4} (ca^3)^{-1/2} a$ and the chain makes a random walk of step length ξ_c.

$$R = N^{1/2} (l_B f^2 / a)^{1/8} (ca^3)^{-1/4} \tau^{-1/8} a$$

This leads to the shear modulus

$$G \propto \tau^{1/4} c^{5/6} f^{-1/2}$$

where the dependence upon the preparation state has been dropped.

This could be tested by checking the final pH (or temperature) dependence of the shear modulus for the same preparation state. Similar experiments, where the shear modulus was indeed found to decrease with the charge fraction at fixed final density, were performed in J.S. Candau's group[11].

We studied polyelectrolyte gels in poor solvents at the level of scaling laws. This work may be extended to account for added salt.

Our results are based on single chain elasticity, we expect counterion condensation (or charge regulation by the pearls) to affect the chain elasticity. The dynamics of pearl unwinding/formation could also be considered.

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