

Annealed and Quenched Polyelectrolytes.

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Abstract. – We study theoretically the behaviour of two types of polyelectrolytes in a poor solvent. If the number of charges and their position along the chain is quenched, the collapse is well described by a blob model introduced by Khokhlov. Weak polyacids or polybases have however an annealed structure where the charges are «mobile» along the chain. We show that these polymers undergo a discontinuous charge instability between a small-charge globular state and a high-charge extended state. This could explain several titration and viscometric data. At higher concentration, the electrostatic interaction is more screened for annealed than for quenched polyelectrolytes.

1. Introduction.

The behaviour of charged macromolecules [1-3] does not seem to be well described by the scaling concepts introduced for neutral polymer molecules. This is partly due to the long-range character of the Coulomb electrostatic interactions but also to the presence of the counterions ensuring the overall electroneutrality of the solution.

The strength of the electrostatic interaction can be adjusted by monitoring the charge of the molecules. Experimentally this can be done in two different ways:

One can synthesize copolymers of charged and uncharged monomers and vary the charge fraction. The structure of the molecule is then quenched, the total number of charged groups and their position along the chain being imposed by chemistry. A typical example of these quenched polyelectrolytes would be a polystyrene chain with a few sulfonated monomers.

Annealed polyelectrolytes may be obtained by synthesizing a homopolymer of weak acidic (or basic) monomers and controlling the dissociation of the functional groups through the pH of the solution. Only the average charge of the chain is here fixed: H^+ (or OH^-) ions can recombine and redissociate freely and the charges are «mobile» along the chain. Usually, the average fraction of charged monomers f on the chain is controlled by neutralizing the polyacid solution with a given amount of a strong base (in many cases $f \approx \alpha$, where α is the degree of neutralization).

Titration experiments of annealed polyelectrolytes have been performed rather extensively [4-6]. If the polyelectrolyte is in a reasonably good solvent, the effective pK is a smooth monotonic increasing function of α between 0 and 1 (this is the case for polyacrylic acid in water). If the polymer backbone is more hydrophobic (such as polymetacrylic acid) the effective pK becomes a nonmonotonic function of α . The decreasing part of this curve is often associated to a sharp increase of intrinsic viscosity which seems to indicate a rapid change of the chain conformation from a compact to an extended structure.

Our purpose in this paper is to show how this specific behaviour of annealed polyelectrolytes can be explained by a charge instability of the polyion. Using a blob model first introduced by Khokhlov for quenched polyelectrolytes [7], we predict that in a poor solvent, at a given neutralization degree α , the charge fraction f jumps discontinuously to a higher value. This first-order transition is accompanied by a coil-stretched conformational transition. In the last section we also briefly discuss more concentrated solutions and the ability of annealed polyelectrolytes to form similar mesophases to the one recently predicted for quenched polyelectrolytes [8, 9].

2. Quenched polyelectrolytes: blob model.

We first discuss the behaviour of weakly charged quenched polyelectrolytes in a salt-free poor solvent using Khokhlov blob model [7]. The polymer (made of N monomers of size a) is in a poor solvent at a temperature lower than the Flory compensation temperature θ of the equivalent neutral polymer. In the absence of charges, we measure the attractive interactions between monomers by $\tau = (\theta - T)/\theta$. The conformation of the polyelectrolyte chain results from a competition between these neutral attractive interactions and the Coulombic repulsion. At short-length scales the electrostatic interactions are weak and the chain has the statistics of a collapsed neutral chain [10]. It is then convenient to group the monomers into globular blobs of size D each containing g_D monomers. At larger scales the electrostatic interaction dominates and the chain of blobs is elongated.

Inside the globular blobs, when the blob size D is larger than the thermal correlation length $\xi_t \sim a\tau^{-1}$, the monomer concentration is a constant $c \sim \tau a^{-3}$. (The model is thus meaningful if $\tau < 1$ so that $\xi_t > a$.) The number g_D of monomers per blob is therefore $g_D = \tau(D/a)^3$. A second relation between g_D and D is obtained by balancing the electrostatic energy of a blob by the polymer/solvent interfacial energy $(g_D ef)^2/4\pi\epsilon D \sim \gamma D^2$ (e is the electronic charge, f the fraction of charged monomers and ϵ the solvent dielectric constant). The relevant interfacial tension γ is given by $\gamma \sim kT a^{-2} \tau^2$. This gives the blob size and the number of monomers in a blob

$$D \sim a f^{-2/3} u^{-1/3}, \quad g_D \sim \tau f^{-2} u^{-1}. \quad (1)$$

We have introduced here the dimensionless parameter $u = l/a$, l being the Bjerrum length ($l = e^2/4\pi\epsilon kT$).

At scales larger than D , the chain of blobs has a rodlike structure with an overall radius

$$L = (N/g_D) D \sim a N \tau^{-1} f^{4/3} u^{2/3}. \quad (2)$$

Whenever $f \ll \tau^{1/2} N^{-1/2} u^{-1/2}$, the electrostatic interactions become irrelevant and the chain takes the spherical globular conformation of collapsed neutral chains with a radius $R \sim a N^{1/3} \tau^{-1/3}$.

Another necessary condition for eq. (2) to be valid is that D be larger than the thermal

correlation length $\xi_t = a\tau^{-1}$ which is the width of the interface between the external solvent and the dense blobs: $\tau > f^{2/3} u^{1/3}$. For $\tau < f^{2/3} u^{1/3}$, the chain behaves like a weakly charged macromolecule in a θ -solvent and may be described as a linear chain of Gaussian blobs of size $D \sim af^{-2/3} u^{-1/3}$ within which the electrostatic energy is of order kT . The overall size is then

$$L \sim aNf^{2/3} u^{1/3}. \tag{3}$$

The various regimes for the chain radius are summarized in fig. 1.

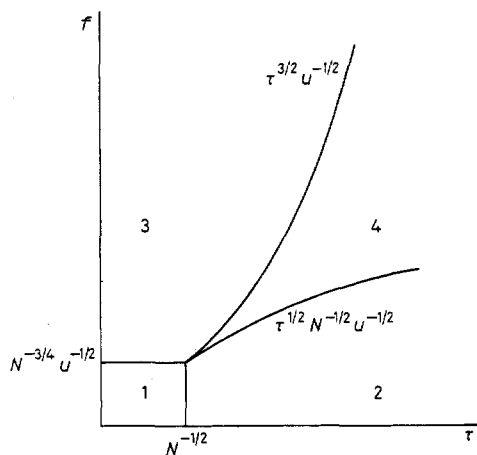


Fig. 1. - Various regimes for the radius of a polyelectrolyte chain in a poor solvent: region 1, Gaussian chain; region 2, collapsed chain; region 3, extended chain of ideal blobs; region 4, extended chain of collapsed blobs.

Another quantity of interest is the electrostatic chemical potential defined by $\mu_{el} = (1/N)(\partial F_{el}/\partial f)$, where $F_{el}(f)$ represents the electrostatic free energy of the chain; it measures the energy that one has to pay to add one extra charge to the chain, at constant number of monomers N .

We consider now only temperatures such that $\tau > N^{-1/2}$. As long as $f < \tau^{1/2} N^{-1/2} u^{-1/2}$, the chain retains a spherical globular conformation and its electrostatic free energy and chemical potential are

$$F_{el} \sim (Nef)^2/4\pi\epsilon R \sim kTf^2 N^{5/3} \tau^{1/3} u, \quad \mu_{el}/kT \sim f\tau^{1/3} N^{2/3} u. \tag{4}$$

For $\tau^{1/2} N^{-1/2} u^{-1/2} < f < \tau^{3/2} u^{-1/2}$, the chain forms a rod of dense collapsed blobs and

$$F_{el} \sim kTN\tau f^{2/3} u^{1/3}, \quad \mu_{el}/kT \sim \tau f^{-1/3} u^{1/3}. \tag{5}$$

Finally, if $f > \tau^{3/2} u^{-1/2}$, the chain behaves like a rod of ideal blobs, whence

$$F_{el} \sim kTNf^{4/3} u^{2/3}, \quad \mu_{el}/kT \sim f^{1/3} u^{2/3}. \tag{6}$$

The crucial point is that the chemical potential μ_{el} has a nonmonotonic variation with the charge density f . In the intermediate range $\tau^{1/2} N^{-1/2} u^{-1/2} < f < \tau^{3/2} u^{-1/2}$, it is a decreasing function of f . This may be understood from the following argument: if charges are added to the chain, the chain stretches rapidly and the charge per unit length is reduced; therefore the electrostatic free energy per charge also decreases. As we shall see in the following

section, the presence of a «kink» in the variation of the electrostatic chemical potential with the fraction of charged monomers is at the origin of the peculiar behaviour of annealed polyelectrolytes.

3. Annealed polyelectrolytes.

3'1. *Equilibrium properties.* – We study now annealed polyelectrolytes in very dilute solutions and focus on the potentiometric titration of a weak polyacid AH by a strong base. The monomer concentration is c and the concentration of the small ions of species i ($i = \text{OH}^-$, H^+ and Na^+) is c_i . The two concentrations c and c_{Na^+} are fixed by the experimental conditions.

The overall neutrality of the solution requires that $\left(\sum_i \varepsilon_i c_i - fc\right) = 0$, where $\varepsilon_i = \pm 1$ is the charge of the ions of species i .

The thermodynamic potential that one has to minimize in order to obtain the equilibrium values of c_{H^+} , c_{OH^-} and f is

$$\frac{\mathfrak{F}}{kT} = \sum_i c_i \left[\log c_i + \frac{\mu_i^0}{kT} - \lambda \varepsilon_i \right] + c \left[f \log f + (1-f) \log(1-f) + f \frac{\mu_{\text{A}}^0}{kT} + (1-f) \frac{\mu_{\text{AH}}^0}{kT} + \lambda f \right] + \frac{c}{N} \left[\log \dot{c} + \frac{F_{\text{el}}(f)}{kT} \right], \quad (7)$$

where $F_{\text{el}}(f)$ is the electrostatic energy of one chain calculated in the previous section and μ_{AH}^0 , μ_{A}^0 and μ_{i}^0 are the standard chemical potential of an undissociated acidic group, of a dissociated acidic group and of an i -ion, respectively. The free energy includes the translational entropy of the various small ions and of the polymer but also the entropy of the charged groups along the chain. The electroneutrality constraint has been taken into account by introducing a Lagrange multiplier λ .

The minimization of \mathfrak{F} with respect to c_{H^+} , c_{OH^-} and f gives the water dissociation equilibrium and the relation between the $p\text{H}$ of the solution and the fraction of charged monomers f

$$p\text{H} = pK_0 + \mu(f), \quad (8)$$

where for convenience we have defined $p\text{H} = -\log c_{\text{H}^+}$ (with a natural logarithm), $pK_0 = (\mu_{\text{H}^+}^0 + \mu_{\text{A}^-}^0 - \mu_{\text{AH}}^0)/kT$ and the total chemical potential of the charges as $\mu(f) = \mu_{\text{el}}(f) + kT \log [f/(1-f)]$.

The fundamental relation (8) shows that by imposing the $p\text{H}$ of the solution, we impose the chemical potential of the charges. The chemical potential $\mu(f)$ is the sum of an entropic contribution which increases with f and of the nonmonotonic electrostatic contribution. If the solvent is not too poor ($\tau < N^{-1/5} u^{-3/5}$) the entropic term dominates and μ increases with f ; the $p\text{H}$ is then a smooth increasing function of the charge density. In a poorer solvent ($\tau > N^{-1/5} u^{-3/5}$) the chemical potential is a nonmonotonic function of f with a minimum value for $f_{\text{min}} = \tau^3 u$ and a maximum value for $f_{\text{max}} = \tau^{1/2} N^{-1/2} u^{-1/2}$. In between these two limits a given value of μ would correspond to three values of f . This result is clearly unphysical, the decreasing part of the curve being thermodynamically unstable. It is the signature of a first-order phase transition between collapsed chains with a charge density f_1 of order f_{max} and extended chains (with a cigar shape) with a charge density f_2 of order f_{min} . The precise values of f_1 and f_2 are given by the classical Maxwell equal-area construction. We directly checked that this construction indeed gives the absolute minimum of the free energy (7). If the $p\text{H}$ is just at the plateau value, we expect an equilibrium between extended and collapsed chains.

This first-order transition could provide an explanation both for the behaviour of the intrinsic viscosity that increases strongly when the chains are stretched and for the titration curve. It also suggests that in a titration experiment one should plot directly the pH which shows a plateau at a conformational transition and not the effective pK (related to μ_{el}) that can be nonmonotonic even if there is no conformational transition (if $N^{-1/2} \ll \tau \ll N^{-1/5} u^{-3/5}$).

3.2. Mesophase formation. – It has been recently shown by Borue and Erukhimovich [8] and Joanny and Leibler [9] that a weakly charged polyelectrolyte in a poor solvent undergoes a mesophase separation transition by lowering the temperature, provided the salt concentration is low enough. These two studies have been concerned with quenched polyelectrolytes.

Following closely the lines of ref. [9] we have investigated the possibility of mesophase formation in annealed polyelectrolyte solutions starting from a Flory-Huggins free energy that includes the entropy of the charges along the chain in the same way as eq. (7).

This free energy allows the calculation of the monomer-monomer structure factor $S(q)$ by considering the free energy associated to fluctuations at a wave vector q of the various concentrations and of the charge density f . We find

$$S(q) = \frac{q^2 + \kappa^2}{[S_0^{-1}(q) + v + w^2 c](q^2 + \kappa^2) + 4\pi f^2}, \quad (9)$$

where v and w are, respectively, the second and the third virial coefficient between monomers ($v = -a^3 \tau$; $w \sim a^6$), $S_0(q)$ is the structure factor of the polyelectrolyte chain in the Gaussian state given by the Debye function and the Debye-Hückel screening length is

$$\text{defined by } \kappa^2 = 4\pi f \left[\sum_i c_i + cf(1-f) \right].$$

This shows that unlike quenched charges, annealed charges do contribute to the Debye-Hückel screening length. Physically, this result is understood as follows: since annealed charges are free to move along the macromolecules, they can be polarized by a test charge and screen the electrostatic interaction without having to carry all the chain with them. The Debye length is thus smaller in the case of annealed polyelectrolytes than in the case of quenched polyelectrolytes.

Apart from this redefinition of κ^2 , eq. (9) is formally identical to the correlation function derived in ref. [8, 9] for quenched polyelectrolytes. As was shown in ref. [9], provided that the salt concentration is small enough, the correlation function $S(q)$ has a peak at a finite wave vector q^* such that $(q^{*2} + \kappa^2)^2 = (48\pi f^2 c)/a^2$. As the temperature is lowered, the peak intensity diverges, indicating the formation of mesophases with a period $2\pi/q^*$. Because of the smaller screening length of annealed polyelectrolytes, the period of the mesophase is slightly larger.

4. Conclusion.

We have emphasized in this paper the difference in behaviour between quenched and annealed polyelectrolytes. In a good or a θ solvent, we do not expect any quantitative difference, more specific effects are found in poor solvents. In extremely dilute solutions, the collapse of quenched polyelectrolytes is continuous and should be well described by the Khokhlov blob model. In the annealed case, we predict a discontinuous first-order collapse transition (in the limit of infinite molecular weights) between an extended state and a globular state. This transition also could provide an at least qualitative explanation for the

variation of the pH observed in titration experiments although no qualitative comparison has been made.

The charge instability leading to the collapse is in a sense rather similar to Manning condensation [11]. If the electrostatic energy per charge is larger than kT the total chemical potential of the charges may be lowered by adjusting the charge distribution. This can be done either by expelling charges and thus diminishing the total charge of the chain but also by increasing the total charge by dissociating some acidic groups: the chain then extends and its elasticity is soft enough that the electrostatic energy per charge decreases. We also note that similar condensation effects occur in ion complexation of polymer solutions [12].

Another important difference between quenched and annealed chains has been shown in more concentrated solutions. In quenched polyelectrolyte solutions only the free ions contribute to the Debye-Hückel screening of the electrostatic interactions. In annealed polyelectrolyte solutions the mobile charges of the polymer also contribute. The screening length is then smaller and annealed polyelectrolytes are less soluble than quenched polyelectrolytes.

In order to test our predictions, it would be interesting to compare systematically the properties of the two types of polyelectrolytes [13]. This however would require that all other physical properties are kept constant (excluded volume, molecular weight, ...) which does not seem to be easily accessible experimentally. A further limitation is that our results were obtained in the asymptotic limit $f \ll 1$, while titration experiments usually show a conformational transition for f of order 0.1.

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