

The swelling of weak polyelectrolytes at low salt concentrations in dilute solution



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ABSTRACT

The possibility of swelling of single polyelectrolyte chains in dilute aqueous solution by free ions in the presence of a small amount of salt is investigated using a mean-field approach. The swelling of chains by free ions is more likely for larger chains in solutions containing only a small amount of salt. The swollen chains are likely to retain a spherical structure.

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1. Introduction

The conformation of single polymer chains is an important basis for understanding wider polymer properties [1–4]; in particular the miscibility of polymers in solution is intimately linked to polymer conformation. Polyelectrolytes are an interesting class of material because their conformation is controlled by solution miscibility and charge [4–6]. Weak polyelectrolytes are those in which solution pH enables control over molecular charge, and thus their conformation. As a consequence, this shape control confers ‘smart’ properties to these materials, due to their capacity for actuation [7–9], which may be used, for example, as a means of controlling adhesion [10–13]. The link between conformational transitions and solubility is already being exploited commercially in drug release applications [14,15].

Weak polyelectrolytes are predicted to have various structures as a function of their size [6]. In dilute aqueous solution the shape of the smallest chains is dominated by their thermal energy, and these form self-avoiding random walks, as predicted by Flory theory for neutral polymers. The size of these is controlled by the degree of ionization but for longer chains the electrostatic energy within the chain becomes significant compared to thermal energy,

and the chain experiences Coulombic repulsion, which is expected to deform it to the shape of a prolate spheroid [6,16]. For larger polyelectrolytes the tension within the chain becomes non-linear and the chain forms rods of connected “electrostatic blobs”, which define the limit below which the conformation is unperturbed by electrostatic effects. Finally, when chains are large enough to bend, such that the Coulombic cost of doing so is comparable to thermal energy (i.e. above their electrostatic persistence length [17,18]) chains can again be considered to be flexible [19].

The addition of salt to the solution complicates the picture due to the effect that salt has in shielding charge. However, for sub-mM quantities of added salt, the Debye length (as a measure of the length scale above which charges are shielded) can be larger than the chain size. In this case, ions close to the polyelectrolyte are not shielded. In this work it is argued that, in solutions with small quantities of salt, polyelectrolytes form a potential well into which ions can fall, and their osmotic pressure causes the polyelectrolyte to have a spherical conformation. In order to describe this, a mean-field argument is used to determine the range of chain sizes and salt concentrations for which an osmotic behaviour occurs.

2. The osmotically swollen chain

The swelling of a neutral polymer chain in a good solvent has long been understood to be a compromise between excluded volume, which stretches the chain, and the entropic elasticity of the

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chain, which limits this deformation. The total energy of this chain is given by

$$E_n = \frac{k_B TR^2}{2a_0^2 N} + \frac{k_B T \nu N^2}{R^3}, \quad (1)$$

where k_B is the Boltzmann constant, T , the absolute temperature, N , the number of monomers in the polymer, ν , the excluded volume, R , the chain size (end-to-end distance), and a_0 , the Kuhn step length. For partially ionized chains in the absence of salt, long-range Coulombic interactions dominate excluded volume and the total energy is given by

$$E_i = \frac{k_B TR^2}{2a_0^2 N} + \frac{3}{5} \left(\frac{f^2 N^2 e^2}{4\pi\epsilon_0\epsilon_r(R/2)} \right), \quad (2)$$

where f is the fraction of monomers containing the elemental charge $\pm e$, ϵ_0 is the vacuum constant, and ϵ_r is the relative permittivity, which for water is $\epsilon_r = 80$. Here the chain is assumed to form a sphere of uniform charge density, which gives rise to the factor $3/5$ in the electrostatic energy term.

A polymer subject only to excluded volume considerations would have a chain length given by the minimization of equation (1), $R \propto N^{3/5}$, and one by electrostatic considerations would have, from the minimization of equation (2), $R \propto N$. For Coulombic interactions to dominate over excluded volume, $R > a_0 N_c^{3/5}$, a requirement which occurs at a critical value of N , given by

$$N_c = \left(\frac{5(4\pi\epsilon_r\epsilon_0)k_B T a_0}{6f^2 e^2} \right)^{5/6} \propto \left(\frac{a_0}{l_B f^2} \right)^{5/6} \quad (3)$$

which is obtained by minimizing equation (2) and substituting $R = R_F = a_0 N^{3/5}$ (the Kuhn step length is used for the Flory radius, R_F and excluded volume corrections are neglected). Here l_B is the Bjerrum length, $e^2/4\pi\epsilon_0\epsilon_r k_B T$, which is 0.7 nm in water. A chain with charge Nfe will attract ions towards it, but only those within a length scale of Nfl_B . Ions located further than this length from the chain will have sufficient thermal energy to escape interactions with the polyelectrolyte. At pH 7 in salt-free solution for example, charges are typically a few microns apart. These are initially attracted into the chain which acts a potential well. In Fig. 1, N_c is plotted as a function of f and it is clear from the calculation that most weak polyelectrolytes are able to absorb free ions into the chain. Here $a_0 = 0.6$ nm, which is typical of many polymers, such as

poly(methacrylic acid) [20] (force spectroscopy measurements were used to obtain a persistence length of 0.3 nm, which is half the Kuhn length).

Chains larger than N_c experience an osmotic pressure from the ions attracted into the chain, which will act to swell the chain. These ions reduce the electrostatic energy in equation (2) to zero or close to zero, so that such osmotically swollen chains are significantly less extended than they would be in the absence of free ions. It is likely that these osmotically swollen chains are equilibrium structures because they use ions from their environment to stabilise the whole chain conformation. The contribution to the free energy due to the osmotic pressure of the ions is proportional to the concentration of the counter-ions [21] and the total free energy is given by

$$E = \frac{k_B TR^2}{2a_0^2 N} + \frac{k_B T f N a_c^3}{R^3} + \frac{k_B T \nu(f) N^2}{R^3}, \quad (4)$$

where a_c is the volume of a free ion and the excluded volume is here dependent upon the degree of ionization. The inclusion of an excluded volume $\nu(f)$ is to prevent the unphysical situation whereby osmotic pressure causes $R \propto N^{2/5}$. The chain size is thus

$$R \propto \left(N^2 a_0^2 (f a_c^3 + \nu(f) N) \right)^{1/5} \quad (5)$$

The ions shield Coulombic repulsion along the chain so that the polymer conformation has only a slightly larger chain-length dependence than the self-avoiding walk, with the osmotic pressure term acting as a perturbation to that of the excluded volume. Excluded volume treatments generally require that neighbouring monomers interact only weakly, which is not a valid approximation in charged systems [22]. However, it can be suggested that because $l_B \approx a_0$, the excluded volume should increase with the degree of ionization and so can as a first approximation be set to $\nu(f) = (1 + f^2) a_0^3$, which uses a weighted average of a_0 and $(1 + f)a_0$. For large Debye lengths, the concentration of charges on the chain can be taken as being fixed (being defined by fN) and the chain persistence length is therefore independent of salt concentration. However, even when the Debye length is significantly larger than the step length (as opposed to chain size) and controls the chain persistence length, the $N^{3/5}$ scaling of chain size is retained [23]. Despite the large Debye length in solution, the Debye length close to the chain will be somewhat shorter due to the larger density of charges within it, so in reality some chain stiffening is likely.

Free ions trapped by the chain may well condense on the chain, reducing f . This has not been considered in the present work, although its effect is only to change the appropriate value of f for a given system rather than change the actual conformational behaviour of the polyelectrolyte.

The usual method of treating the conformational behaviour of polyelectrolytes in dilute solution is due to the Flory arguments of Kuhn, Künzle, and Katchalsky [6,16], which suggest that chains larger than an electrostatic blob form ellipsoid conformations. This model is incompatible with the ideas in the present work, because ions inside the polymer shield the charges on the chain. Nevertheless, for smaller chains ($N \leq 300$) molecular dynamics simulations have shown that Flory arguments are applicable, at least away from chain ends [24]. It will be seen that the arguments presented in the current work are for chains significantly larger than these.

The assumption that the chain is osmotically swollen by a number of counter-ions equal to the number of charges on the chain means that the Coulombic term in equation (2) is discarded from equation (4). However, should there be fewer counter-ions swelling the chain, then the Coulombic term would be required,

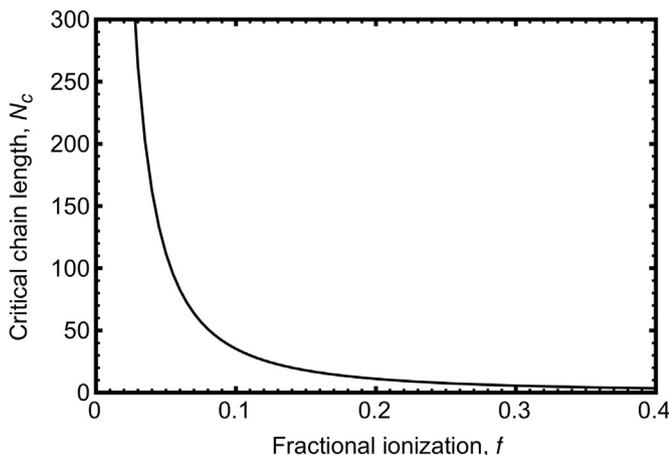


Fig. 1. $N_c(f)$ calculation from equation (3) for $T = 300$ K, $\epsilon_r = 80$, and $a_0 = 0.6$ nm. All but the smallest f will result in ions attracted into the swollen chain.

modified to account for the presence of some counter-ions. Complete osmotic swelling by counter-ions requires the situation whereby, if a fully osmotically swollen chain were considered *a priori*, the number of charges entering the chain would equal those leaving the chain, and this is dependent upon the concentration of ions in the solution. The salt concentration dependence of this swelling is discussed below.

3. Salt concentration

For the theory presented in Section 2 to be valid, the Debye length must be significantly greater than the chain size. Other effects that might affect chain conformation such as stiffening (an increase in persistence length) due to charges on the chain will occur, but are not considered in the treatment described here. Their effect is to decrease the local flexibility of the chain, but is not expected to impact upon the concepts presented here. Charge density fluctuations [6] in the polymer are also neglected.

A Debye length comparable to, or smaller than, the chain size prevents ions in solution from interacting with the chain and therefore the free ion density within the chain resembles that in the surrounding solution. For Debye lengths somewhat greater than the chain size, the chain can act as a potential well, trapping ions within it. The region over which this is appropriate is shown in Fig. 2, where the chain length, N , corresponding to a Debye length of twice the Flory chain size is plotted as a function of molarity of monovalent salt solution. Here, the calculations are for poly(acrylic acid) at pH 7 ($a_0 = 0.63$ nm [25] and $f = 0.3$ [26]) in monovalent salt solution at 300 K.

Although a polyelectrolyte chain can act as a potential well for charges, the barrier to an ion leaving a chain that is swollen by fN ions is easily overcome at room temperature. In order that a detailed balance condition be achieved whereby a chain is swollen by ions, and the number of ions entering the polymer remains the same as the number leaving it, the volume occupied by the chain must be of the same order as that of the average volume in space occupied by one ion, i.e. the inverse of the solution ion density. This requirement means

$$V_{\text{ion}} = \frac{1}{n_{\text{ion}}} = V_{\text{chain}} = \frac{4\pi R_F^3}{3}, \quad (6)$$

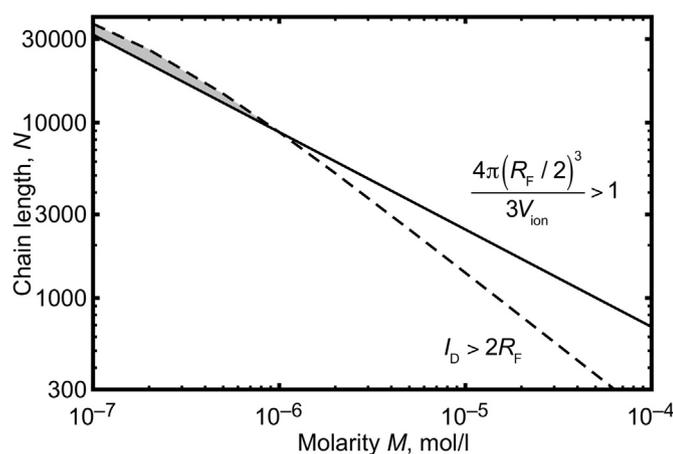


Fig. 2. The broken line shows the polymerization index at which the Debye length, $l_D = 2R_F$. The solid line corresponds to the limit at which sufficient ions are available to the chain, i.e. $V_{\text{chain}} = V_{\text{ion}}$. The shaded area therefore corresponds to the range of chain lengths and molarities for which the theory described herein applies. The molarity includes all ions at pH 7, such that $M = 10^{-7}$ mol/l constitutes no added salt. Here, $f = 0.3$ and $a_0 = 0.63$ nm as is appropriate for poly(acrylic acid) at pH 7.

where n_{ion} is the number of ions of opposite charge to the polyelectrolyte per unit volume and V_{chain} is the volume of a chain. The curve associated with this requirement is also shown in Fig. 2, and limits the region whereby the conditions for osmotic swelling to be fulfilled to relatively large chains at low salt concentrations.

The conclusion that can be drawn from the calculations shown in Fig. 2 is that there is a small window whereby the salt concentration and chain lengths allow for osmotically swollen polyelectrolyte chains in dilute salt solutions. For the largest chains, osmotic swelling is possible even without salt, although ellipsoidal structures predicted by Flory theory [6,16] may have a lower overall energy. However, the calculations are approximate, and it may be that the phenomenon exists over a wider range of chain lengths and ions than predicted here. Molecular dynamics simulations are required to show whether or not this phenomenon exists over a wider range of parameters, whether it is metastable, or even if it exists at all.

In a weak polyelectrolyte in dilute aqueous solution, the charge on the chain is governed by pH, whereby Le Chatelier's principle describes the balance between the ions dissociating from and those associating with the chain. For a salt, it is less clear whether an ion will attach to the chain or not. Salt ions must overcome an activation energy to condense on a polyelectrolyte, because both the ion and the chain are solvated. However, the complexation of polyelectrolytes with ions does reduce the overall energy of the system. Nevertheless, the barriers to complexation are typically large and simulations suggest that ions complexed with a chain are likely to remain bound, but those that are not complexed will remain free over significant time scales [27].

4. Conclusions

A model has been described whereby a polyelectrolyte absorbs ions from a surrounding dilute aqueous solution in which a small amount of added salt is present. The balance between ions entering and leaving the chain and the requirement that the Debye length of the salt solution be large (so that charges in the vicinity of the polymer are not shielded) limits the applicability of the model. The standard model of polymers in dilute solution is based around the theory of Kuhn, Künzle, and Katchalsky [16] and predicts the formation of ellipsoidal structures rather than the spheres that arise from the present considerations. This is significant because smaller chains (which cannot be fully swollen by counter-ions) may still attract some opposite charges within them and this may well have significance for the structures predicted by Kuhn, Künzle, and Katchalsky. Because of this, the possibility that osmotic effects may control polyelectrolyte conformation is worthy of further examination with simulations.

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