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Comment

Interacting rigid polyelectrolytes

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Résumé. — La longueur de persistance des polymères linéaires chargées en solution semi-diluée doit augmenter largement lorsqu'on ajoute du sel. Pour des très longs polymères, la longueur de persistance croît avec la concentration saline à la puissance 5/2, si cette concentration n'est pas trop élevée. En démontrant cette loi d'échelle nous corrigeons notre raisonnement précédent à la lumière de l'article récent de Barrat et Joanny, et en accord avec leur prédiction qualitative.

Abstract. — The persistence length of charged linear polymers in semidilute solution must increase substantially upon addition of salt. For very long polymers the persistence length increases as the salt concentration to the 5/2 power provided this salt concentration is not too large. In deriving this scaling we correct our previous prediction in light of a recent paper by Barrat and Joanny, and in agreement with their qualitative prediction.

In their recent study of the polyelectrolyte persistence length in semidilute solutions, Barrat and Joanny [1] conclude that adding salt increases this persistence length, in accord with our earlier argument [2]. However, Barrat and Joanny disagree with our scaling law for this persistence length; instead, they predict a very strong increase with added salt, without deriving specific scaling properties. Barrat and Joanny's work has led us to revise our earlier argument to accord with their point of view. In so doing, we find a dramatic increase of the length with added salt: the persistence length scales as the salt concentration to the $-5/2$ power. The revised argument gives insight about why the underlying assumption of our original work is suspect. The new persistence length gives added weight to the expectation that for sufficiently high molecular weight, polyelectrolyte solutions must become nematically ordered.

We consider a semidilute polyelectrolyte solution, whose volume fraction $\phi$ is much larger than the overlap concentration $\phi^*$, but much smaller than unity. If the chains are locally straight rods then the typical distance $\lambda$ between chains is of order $\phi^{-1/2}$. All charges are

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monovalent and the charge density is small enough that Manning condensation effects are negligible. With no added salt, Barrat and Joanny (in agreement with Ref. [2]) that the chains are straight rods on length scales smaller than \( \lambda \). Thus the persistence length \( L \) is of order \( \lambda \) in the absence of salt. The electrostatic interactions in this solution are screened out beyond a Debye distance \( \kappa^{-1} \) which is also of the order of \( \lambda \). Since our problem concerns large-scale structure and since Manning effects are presumed unimportant, the role of the free ions is completely accounted for by this screening effect; we may thus ignore the ions as independent degrees of freedom in what follows.

We now add enough salt to decrease this screening length \( \kappa^{-1} \) by a large, finite factor. This reduces the electrostatic interactions between chains and allows the intrinsic rigidity of each chain to play a larger role, thus increasing the persistence length \( L \). Though the increase in \( \kappa \) is presumed large, it is not so large as to compromise the Odijk rigidity of the individual chains. That is, \( \kappa^{-1} \) remains indefinitely larger than the average distance between charges along the chain \( b \) (i.e., the average length per ion on scales of order \( \lambda \)). We now ask how the persistence length \( L \) increases as salt is added.

The persistence length results from the interplay of two competing effects. First, an isolated chain at the given salt concentration has an electrostatic persistence length \( P \) of the order \( (b \kappa^2)^{-1} \), as noted in reference [1]. This length is indefinitely larger than the persistence length \( L \). Thus the chain’s internal electrostatic energy increases much more than \( kT \) upon bending on the scale \( L \). This energy \( B \) for a small length \( \ell \) may be written \( B \approx kT(P/l\ell) \theta^2 \), where \( \theta \) is the bending angle. This rigidity competes with the electrostatic interaction between chains. A fraction \( (\kappa \lambda)^{-2} \) of the volume is unscreened from the chain charges. Without bending or mutual alignment, this fraction of each chain would experience the unscreened interaction, with energy density of order \( kTc_0 \). Here \( c_0 \) is the concentration of chain charges. For a section of straight chain this amounts to an energy per unit length of \( kTc_0 \kappa^{-2} \). The associated interaction energy \( U \) for a length \( \ell \) has the form \( U \approx \ell(\kappa \lambda)^{-2}kTc_0 \kappa^{-2} \approx kT(\ell/b)(\kappa \lambda)^{-4} \).

It is natural to anticipate that the bending energy \( B \) and interaction energy \( U \) are comparable in real solutions. This assumption leads to an estimate of \( \theta \), and thence to the persistence length \( L \). This is the reasoning we used in reference [2]. To probe the validity of this reasoning we examine the individual encounters of a chain with its neighbors. The chain interacts significantly with another if it passes within a distance \( \kappa^{-1} \). Uncorrelated chains make such an encounter in a « collision length » \( \ell = \lambda(\kappa \lambda) \). To reduce the interaction energy from such an encounter, the chain may bend. It may virtually eliminate the interaction energy by bending through an angle \( \theta \approx (\kappa \ell)^{-1} \). Since \( \kappa \lambda \) is large, this angle is small; thus the length \( \ell \) is not sufficient to randomize the direction of the chain. We expect that successive bends are uncorrelated, so that the net angle grows to order unity in a distance \( L = \ell \theta^{-2} \). This \( L \approx \lambda(\kappa \lambda)^5 \). Since \( \kappa^{-2} \) is proportional to the ion concentration \( c_+ \), we find as noted above that \( L \sim c_+^{5/2} \).

This « avoidance-bending » result contradicts the prediction of reference [2], based on the balance of bending and interaction energies. Indeed, there is no such balance implicit in the avoidance-bending picture; in this picture the chains avoid the electrostatic interaction altogether, so its cost is irrelevant. The persistence length is the same as if the chains were strictly mutually avoiding tubes of radius \( \kappa^{-1} \). If one insists that the interaction energy be comparable to the bending energy, one obvious solution is to bend by a substantial angle \( \theta \approx 1 \) on every collision. Such a bending increases the electrostatic energy by a finite factor in the screening volume \( \kappa^{-3} \) where the bend occurs. A strong collision of two chains also increases their electrostatic energy by a finite factor over the same sized volume. We conclude that bending and interaction are comparable if the chains bend through an angle of order unity.
on every collision. In that case the persistence length \( L \) is comparable to the collision length \( \ell \sim \kappa \). This was the conclusion of reference [2].

The « avoidance-bending » scheme clearly has lower total energy than the energy-balance scheme. Thus in the preferred state the energies are not balanced. Normally in a scaling analysis when an energy to be minimized is the sum of two competing pieces, the two are of comparable size when the total is minimized. This is because normally the two pieces have a power-law dependence on the variational parameter. For the electrostatic interactions of the present problem, this is not the case. The interaction energy of two colliding chains falls off sharply with distance-of-closest-approach. It is not a power law. Accordingly, this energy need not be comparable to the bending energy when the total energy is minimized.

We conclude that the avoidance-bending picture is a more correct description of the bending of polyelectrolytes than our previous energy-balance picture. The new picture leads to longer persistent chain segments and lower osmotic compressibility. Now, in contrast with our earlier result, the concentration of these persistent segments may be indefinitely larger than the Onsager concentration. Thus nematic order is expected for sufficiently long chains, as Barrat and Joanny point out. Once nematic order sets in, the reasoning above ceases to be valid. Thus the range of \( \kappa \lambda \) over which the solution remains isotropic cannot be extended arbitrarily with improvements in the experiments. This means there is no rigorous way to test scaling laws for this regime, including the above prediction about the persistence length. The inevitability of nematic order blunts the force of scaling predictions for polyelectrolyte solutions.

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