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COMMENT

On the self-consistent field approach to polyion dimensions in dilute solutions

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Abstract. We present an asymptotic analysis of a model of polyion conformations in dilute solutions which is based on a combination of the Poisson-Boltzmann equation and the self-consistent Gaussian chain model. Logarithmic corrections to power scaling are shown to play an important role in the case of salt-free solutions.

The conformation of polyions in dilute ionic solutions has been considered in the past by several authors. One class of models [1, 2] is based on the worm-like chain concept which is equivalent to an expansion near the limit of a rod-like polyion; the coiled state of the polyion at high salt concentrations is introduced in an *ad hoc* manner via the renormalisation of the persistence length, due to the partially screened electrostatic repulsion between the charged segments of the chain. Another class of models [3-6] is based on the Gaussian chain (GC) notion which underlies the modern treatments of solution behaviour of flexible polymers [7]. The salt-free case has been considered using self-consistent field (SCF) [4] and renormalisation group [5] methods and complete stretching of the polyion was predicted by both. A combination of the SCF approach [8], according to which the electrostatic force on any polymer segment is balanced by the elastic restoring force exerted by its neighbours, and of the Poisson-Boltzmann (PB) equation, which couples the ion charge densities to the electrostatic potential, has been used by Richmond [3] to study the limit of large concentrations of added (1:1) electrolyte. Although Richmond did not explicitly consider the salt-free limit of his model, his asymptotic analysis of the inner region of the polyion, in which the electrostatic screening due to mobile ions is negligible, has been criticised in [4]. While we agree with the criticism of Richmond's analysis [4], we would like to emphasise that the fault lies with the asymptotic analysis of the model. Although the Gaussian model itself can be criticised on the grounds that it does not account for the 'stiffening' of the chain due to electrostatic repulsions at low electrolyte concentrations, it can serve as a useful approximation for coiled polyions at high electrolyte concentrations where calculations based on worm-like models become prohibitively difficult. While this comment does not attempt to carry out a comprehensive analysis of the applicability of this model to polyelectrolytes at arbitrary salt concentrations, we show that the GC-PB model [3] gives the correct results in both the strong and the weak screening limits.

In the following, we present the main model equations; their detailed derivation is given in [3]. Integrating the force balance equation relating the elastic and electrostatic forces on the n th chain segment of length a and charge $-e$, which is located at

a distance r from the origin, we obtain the polyion charge density

$$(1/4\pi r^2) \, dn/dr = (1/4\pi r^2 a)(3/2a^2|\psi|)^{1/2} \quad (1)$$

where ψ is the dimensionless electrostatic potential, in units of $k_b T/e$ (k_b is the Boltzmann constant and T the temperature). Assuming that the electrolyte distribution is determined by the Boltzmann factors $e^{\pm\psi}$ and substituting the charge densities into the Poisson equation, we arrive at the PB equation which can be solved either numerically or by various analytical approximation schemes [9, 10]. Since we are mainly interested in the strong and weak electrolyte limits, we linearise the Boltzmann factors and notice that, although the expansion breaks down in the salt-free limit, the resulting error will not affect our considerations since, in this case, the electrolyte contribution is negligible with respect to that of the polyion (the latter given to all orders in ψ). Scaling the distance (r) in units of Debye screening length κ^{-1} , we write $X = \kappa r$ and use it to define the dimensionless charge, $Q = \psi X$. This gives

$$d^2Q/dX^2 = Q + (l_b/a)|3/2XQ|^{1/2} \quad (2)$$

where $l_b = e^2/k_b T$ is the Bjerrum length. The above equation has to be solved for Q and the resulting expression for the potential should then be substituted into (1). Integration of (1) subject to the boundary condition $r(0) = 0$ gives the scaling of the end-to-end distance R with the degree of polymerisation (proportional to the number of segments, N).

Since we want to derive the scaling laws governing the polyion conformation, the naive approach would be to assume that Q scales like a power of X , substitute it into (2) and obtain the leading exponent in the limits of strong electrolyte screening ($X \gg 1$ for most intrapolyion scales) and that of unscreened Coulomb repulsion ($X \ll 1$). Inspection of (1) and (2) and of the definition of Q leads us to conclude that, since we expect $R \sim N^\nu$, where ν can vary between $\frac{3}{5}$ (coiled polyion) and 1 (stretched polyion), the exponent α ($Q \sim X^\alpha$) has to be in the range $-\frac{1}{3} \leq \alpha \leq 1$. We further observe that in the strong screening limit, $X \gg 1$, the term on the LHS of (2) is small with respect to the other two and the remaining terms have to balance each other. This gives $\alpha = -\frac{1}{3}$ and, upon substitution in (1) and integration, we obtain

$$R \sim N^{3/5} \quad (3)$$

in agreement with [3]. The polyion is thus in a random coil conformation characteristic of the excluded-volume-type behaviour of neutral polymers in good solvents [7].

When naive scaling is applied to the salt-free limit, $X \ll 1$, we notice that the first term on the RHS of (2) is small with respect to the other two. Balancing the dominant terms, we obtain $\alpha = 1$ which leads to the expected stretched polyion exponent, $\nu = 1$. However, a more careful examination reveals that the above argument is wrong since the coefficient of the term on the LHS of (2) vanishes when $\alpha = 1$! Faced with the paradoxical situation in which the exponent both has to be and cannot be equal to unity, we attempt a solution of the form

$$Q \sim X^\alpha \ln(X). \quad (4)$$

Now, there is a non-vanishing contribution on the LHS of (2) coming from the derivative of the $\ln(X)$ term. Equating the powers of X on both sides of (2), we obtain (to logarithmic accuracy!) that $\alpha = 1$ and hence $\nu = 1$ (again, to logarithmic accuracy), in agreement with [4]. Although logarithmic corrections to power scaling are usually neglected in leading power considerations which became commonplace in polymer

science [7], their appearance in (4) has a simple physical meaning. From the relation between the charge Q and the potential ψ , we find that the latter is given by

$$\psi \sim \ln(r) \quad (5)$$

which is the well known expression for the potential of an infinite rod, consistent with our conclusion that the polyion is stretched[†]. Notice that if we were to neglect the logarithmic correction in (4), the electric field, and hence the electrostatic force on the charged segments, would vanish and there would be no stretching force on the polymer. Conversely, using the logarithmic potential of (5), the stretching force on the n th segment scales like $1/r$ which (since $r \sim n$) agrees with the n/r^2 prediction of de Gennes *et al* [4].

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[†] Strictly speaking, we have assumed a spherically symmetric charge distribution and thus (5) can only be taken as an indication that the polyion becomes stretched. Notice, however, that since all rod orientations are equivalent in the absence of a preferred direction, radial symmetry is present even in the stretched state.