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Numerical Evaluation of the Electrostatic Persistence Length of Polyelectrolytes

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ABSTRACT: The electrostatic persistence length of polyelectrolytes is calculated as a function of the ionic strength of the solution. The intramolecular electrostatic interaction energy is numerically evaluated for a wormlike chain model of arbitrary flexibility and is compared to the elastic restoring energy of a stretched random-flight chain of identical chain stiffness. A complicated dependence of the electrostatic persistence length on the contour length of the macroion chain and on the ionic strength of the solution is obtained in qualitative agreement with recent computer simulations.

1. Introduction

Since the early days of polymer science the chain statistics of flexible, charged macromolecules have belonged to the challenging but still unsolved problems in polymer physics. Much theoretical work in this field was published in the middle of this century. Besides the artificial, but nonetheless helpful, "uniformly charged sphere model" by Hermans and Overbeek,[1] also more realistic random chain models for macroions were developed by Kuhn, Künzle, Katchalsky, Lifson, Rice, and Harris.[2-7] The common feature of these theoretical treatments was to balance the increase in the elastic free energy of a random coil by the corresponding decrease of the electrostatic interaction of the charges along the chain as the end-to-end distance is increased. The major source of error in these calculations was probably due to the incorrect evaluation of the electrostatic interaction, because the complete (i.e., higher moments of the) segment distribution of a stretched random-flight chain was not known at the time.

In contrast to this pioneering work, more recent theories independently developed by Skolnick and Fixman[8] and Odijk[9] start from a rigid polyion and calculate the increase in the electrostatic and in the elastic bending energy for a slightly flexing rod (wormlike chain). At equilibrium the total increase in the free energy matches kT, the thermal energy. The corresponding bending force constant leads to the electrostatic contribution, l_{pe}, of the total persistence length, l_{T}, of the macroion

$$l_{\mathrm{T}} = l_{\mathrm{pe}} + l_{\mathrm{p}} \tag{1}$$

with l_{p} being the intrinsic persistence length of the identical molecule without charges. Unfortunately, the elastic bending energy is not known for more flexible chains than slightly flexing rods. Therefore, the "local stiffness" approximation limits the applicability of this approach to only conditions where the intrinsic persistence length is large compared to the Debye screening length, κ^{-1}.

Houwaart and Odijk[10] later extended these calculations to high ionic strength and discussed the excluded-volume problem arising from flexible macroion conformations.

Due to experimental difficulties, a reliable determination of the chain stiffness of macroions at low ionic strength could not yet be performed.[11] However, some experimental investigations have more or less accurately determined the persistence length of macroions in high ionic strength solutions.[12-16] In this regime the Skolnick, Fixman, Odijk (SFO) theory predicts the electrostatic persistence length l_{pe} to vary with the ionic strength I as

$$l_{\mathrm{pe}} \sim I^{-1} \tag{2}$$

whereas most of the experimental data suggest the square-root relation[11]

$$l_{\mathrm{pe}} \sim I^{-1/2}$$

although there is a large scatter of experimental data.

LeBret[17] and Fixman[18] numerically evaluated a more sophisticated model, which takes into account the finite cylinder radius of a charged chain. The resulting electrostatic persistence length merges into the SFO result at low ionic strength but deviates at high ionic strength toward a less pronounced ionic strength dependence. Apparently, the geometric details of the individual macroion determine the shape of the curves. Satisfactory agreement with experimental data on DNA was shown.[17]

In the present paper, we adopt the radial distribution function of a wormlike chain from Koyama[19] for the calculation of the screened Coulomb potential of the macroion. Since an expression for the elastic free energy of a wormlike chain is still missing as discussed above, we calculate the elastic free energy for a stretched random-flight chain according to Kuhn and Grün.[20] The free-energy expression is purely entropic and is known to fail for very large extensions close to the rod limit.[21] This approach is certainly inconsistent in the choice of the different theoretical models but may be nonetheless acceptable because (i) the continuous-chain characteristic function does allow an almost exact calculation of the screened Coulomb potential, (ii) the stretched random-flight chain provides a good approximation for the elastic free energy at least for small chain extensions at high ionic strength, and (iii) the stretched random-flight chain and the wormlike chain model yield equivalent results in the flexible limit. Moreover, a correct and consistent model is currently not available.

2. Calculation of the Free Energy of Semiflexible Macroions

According to Kuhn and Grün the elastic free energy of a stretched flexible chain is given by[20,21]

$$F_{\mathrm{el}} = n_{\mathrm{k}} \ln \left(\frac{\sinh \beta}{\beta}\right) - \left(\frac{\beta x}{l}\right) \tag{3}$$

where β is the inverse Langevin function

$$\beta = L^{*}(x/nl) \tag{4}$$

n_{k} denotes the number of Kuhn segments in the unper-

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turbed state, and the total contour length of the chain is $L = nl$ (n = the number of bonds, l = the effective bond length). In the present approach we approximate the actual extension of the chain, x, by the rms end-to-end distance $\langle R^2\rangle^{1/2}$

$$x \cong \langle R^2\rangle^{1/2} \tag{5}$$

For small extensions eq 3 reduces to the more familiar form

$$F_{\mathrm{el}} = \frac{3}{2}kT\frac{\langle R^2\rangle}{\langle R^2\rangle_0} \tag{6}$$

where the subscript zero denotes the unperturbed flexible limit. The elastic free energies calculated by eqs 3 and 6 differ only slightly (i.e., less than 10%) for $L/l_{\mathrm{T}} > 5$. For smaller values of L/l_{T} the approximation in eq 3 becomes more questionable, which limits the applicability of the present approach to $L/l_{\mathrm{T}} > 5$. The mean-square end-to-end distance of the extended coil is derived for the equivalent wormlike chain as[22,23]

$$\langle R^2\rangle = 2l_{\mathrm{T}}L - 2l_{\mathrm{T}}^2[1 - \exp(-L/l_{\mathrm{T}})] \tag{7}$$

where the total persistence length, l_{T}, is given by eq 1.

For the calculation of the screened Coulomb interaction we utilize the probability density $W(R,s)$ as introduced by Koyama,[19] which is a hybrid of the function for a rod and for a coil

$$4\pi R^2 W(R,s) = R/(2AB\pi^{1/2})\{\exp(-(R - B)^2/4A^2) - \exp(-(R + B)^2/4A^2)\} \tag{8}$$

with

$$A^2 \equiv \langle R^2\rangle(1 - y)/6$$

$$B^2 \equiv y\langle R^2\rangle$$

$$2y^2 = 5 - 3\langle R^4\rangle/\langle R^2\rangle^2$$

Here R is the distance between two points separated by a contour length s. The second and fourth moments $\langle R^2\rangle$ and $\langle R^4\rangle$ are to be evaluated from the exact expressions[23] for a wormlike chain of contour length s; and the parameter y, defined above, varies between the limits zero for a Gaussian chain and unity for a rigid rod.

Equation 8 yields the exact second and fourth moments of the Kratky–Porod wormlike chain model and gives the known even higher moments to within several percent.[19]

The screened electrostatic potential of two charges on the chain separated by the contour distance s is then given as

$$\phi_{\mathrm{cou}}(s) = \int_0^{\infty}\frac{\exp(-\kappa R)}{R}4\pi W(R,s)\,R^2\,\mathrm{d}R \tag{9}$$

with κ^{-1} being the Debye screening length. Integration of eq 9 yields

$$\phi_{\mathrm{cou}}(s) = \frac{\exp(\kappa^2A^2)}{2B}\{\exp(-\kappa B)(1 - \mathrm{erf}\,(\kappa A - B/2A)) - \exp(\kappa B)(1 - \mathrm{erf}(\kappa A + B/2A))\} \tag{10}$$

where erf x is the error function. In the limit of $\kappa = 0$, eq 10 reduces to the result obtained earlier[24] for hydrodynamically interacting segments

$$\phi_{\mathrm{h}}(s) = \frac{\mathrm{erf}\,(B/2A)}{2B} \tag{11}$$

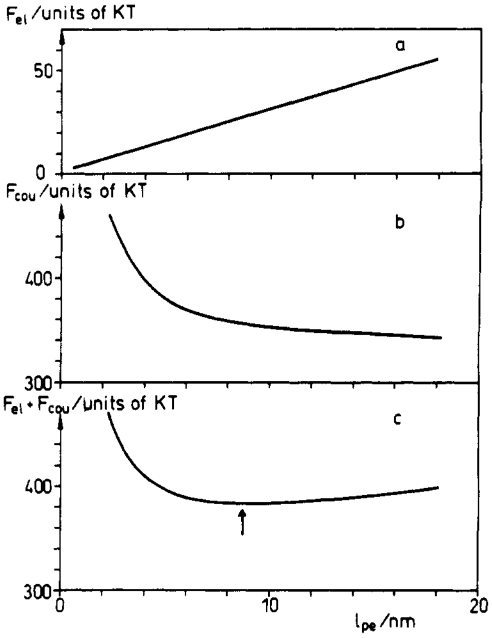

Figure 1. Elastic free energy, F_{el} (a), the screened Coulomb energy, F_{cou} (b), and the sum of F_{el} and F_{cou} (c) plotted vs the electrostatic persistence length, l_{pe}, at constant salt concentration c_{s} = 0.166 mol L^{-1}. The arrow in c indicates the persistence length at the lowest total free energy (l_{pe} = 8.5 nm).

The total electrostatic energy of the chains is now given by

$$F_{\mathrm{cou}}(L) = \int_Q^L (L - s)\phi_{\mathrm{cou}}(s)\,\mathrm{d}s \tag{12}$$

$F_{\mathrm{cou}}(L)$ in eq 12 diverges as the lower integration limit goes to zero. This is well-known from the calculation of the hydrodynamic radius,[23-25] for which a lower integration limit b is introduced as the "hydrodynamically effective cross-section" of the chain.

Upon evaluation of the electrostatic interaction, the lower integration limit is given by the Bjerrum length Q

$$Q = e^2/4\pi\epsilon\epsilon_0 kT \tag{13}$$

where e is the elementary charge, ϵ and ϵ_0 are the relative and in vacuo dielectric permittivities, respectively, and kT is the thermal energy. With the introduction of Q as the lower integration limit, we have implemented counterion condensation[26,27] and do not allow two noncondensed, neighboring charges to be closer than Q. The solution of the integral in eq 12 is performed numerically by using the IMSL-library routine DCADRE in close analogy to earlier work.[24]

Once F_{cou} and F_{el} are obtained for a chain of contour length L and intrinsic persistence length l_{p}, the sum of F_{cou} and F_{el} is minimized at a given ionic strength with respect to l_{pe}, the electrostatic persistence length. Once example of such a minimization is shown in Figure 1 for $L = 10^3$ nm, l_{p} = 0.5 nm, and κ^{-1} = 0.75 nm.

3. Results and Discussion

As a result of the numerical calculation, the electrostatic part of the persistence length, l_{pe}, is plotted in Figure 2 vs the number concentration of a monovalent salt. The intrinsic persistence length is kept constant at l_{p} = 0.5 nm, and the contour length is varied from 10 to 10^4 nm. For comparison, the prediction of the SFO theory is also shown for $L = 10^2$ nm and $L = 10^3$ nm. At high ionic strength the SFO curves are independent of the contour length and yield the frequently discussed I^{-1} dependence of l_{pe}. At low ionic strength the end effects become no-

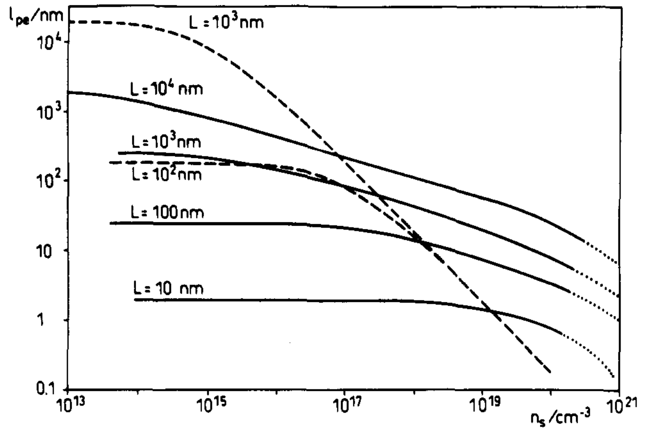

Figure 2. Electrostatic persistence length l_{pe} at the minimum free energy shown as a function of the number concentration of 1-1 salt ions, n_s, for different contour lengths as indicated at the full curves. The intrinsic persistence length is kept constant at $l_p = 0.5$ nm. The dotted curves represent the SFO result for $L = 100$ nm and $L = 1000$ nm, respectively. In the dashed regime the numerical integration (eq 12) is not reliable anymore due to numerical instabilities.

ticeable and eventually an ionic strength independent electrostatic persistence length is observed, whose absolute value varies with L^2. The present calculations yield a much weaker ionic strength dependence of l_{pe}, which does not follow a simple power law. However, at high ionic strength l_{pe} varies approximately as $I^{-1/2}$ as found in several experiments.[11] It is inherent in the present theory that l_{pe} depends on the contour length because the elastic free energy scales with L/l_p, whereas the electrostatic interaction does not. Of course, in the limit of high ionic strength and of long chains l_{pe} should eventually become independent of the chain length. In this regime, the minimum of the free energy as function of l_{pe} is very flat, and accordingly l_{pe} becomes sensitive to small numerical errors and also to small systematic errors that may arise from the approximate character of the model. This chain-length dependence of l_{pe} at finite chain length would not permit an experimental determination of the persistence length from the molecular weight dependence of intrinsic viscosity as often described in the literature.[11-13] Unfortunately, this prohibits the quantitative comparison of the present calculations to the experimental results from viscosity measurements. A plot of l_{pe} vs $I^{-1/2}$ for two different contour lengths and $l_p = 1.5$ nm (Figure 3) demonstrates, however, that the calculated l_{pe} values lie in the upper range of the experimentally reported ones (compare to Figure 2a of ref 11). The light and neutron scattering investigations[13-16] also do not yield precise values for the electrostatic persistence length, most probably caused by the too high polymer concentrations measured. The experimental data, so far, indicate a lower l_{pe} than calculated. Also, these data do not seem to indicate a molecular weight dependence of l_{pe}. To clarify this point, more accurate experimental data are needed.

At low ionic strength our calculated l_{pe} values also become independent of the ionic strength, the plateau value of l_{pe} being proportional to L only. As mentioned earlier, in this regime of high chain extension, the Kuhn and Grün expression underestimates the elastic restoring energy, which consequently leads to smaller calculated electrostatic persistence lengths.

It is also elucidating to discuss results in comparison to some recent computer simulations.[28-31] Carnie et al.[29] report a chain-length-dependent electrostatic persistence length in qualitative agreement with our results except that at high ionic strength l_{pe} seems to become independent of the chain length for long chains. The absolute value for l_{pe} obtained from the simulations, however, is even higher than ours (in contrast to the experimental estimates), most probably because the authors did not introduce counterion condensation and are thus overestimating the electrostatic interaction. In a more recent simulation, Christos and Carnie[28] studied the effect of counterions and of added 1-1 electrolyte on the conformation of short polyelectrolyte chains. An approximate evaluation of these data also leads to a molecular weight dependent electrostatic persistence length even at high ionic strength, which may be due to the small chain length investigated. The absolute value of l_{pe} is significantly smaller compared to the earlier work.[29] Unlike our calculations presented above, the simulations were restricted to short chains ($L \ll 100$ nm), which prohibits a more quantitative comparison as presented here.

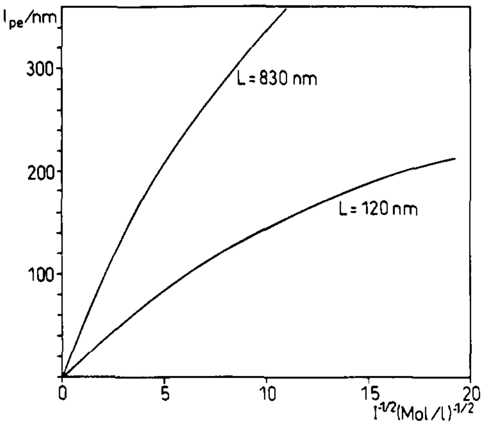

Figure 3. Electrostatic persistence length l_{pe} plotted vs the inverse square root of the ionic strength of the solution for different contour lengths as indicated. The intrinsic persistence length is chosen as $l_p = 1.5$ nm.

4. Conclusion

A numerical computation method for the evaluation of the electrostatic persistence length for infinitely dilute polyelectrolyte solutions has been developed. The calculations are believed to be meaningful at intermediate and high ionic strengths where the Kuhn and Grün expression for the elastic free energy of the chain still holds. As a consequence, a molecular weight dependent electrostatic persistence length is obtained, whose ionic strength dependence qualitatively coincides with experimental investigations in the high ionic strength regime.[11] A quantitative comparison does not currently appear meaningful due to the limited possibility to reevaluate the literature data and due to the apparent shortcomings of the model as discussed above. A precise light scattering investigation of the molecular weight and ionic strength dependence of the electrostatic persistence length is currently underway.[32] Also, it may be possible in future work to avoid the inconsistency in the choice of the model by evaluating the elastic restoring energy from the Koyama probability density function. The continuously charged wormlike chain, which requires the somewhat artificial cutoff at some finite distance (i.e., the lower integration limit Q in eq 12), may also be modified to a discretely charged chain by simply replacing the integral in eq 12 by summation. These changes may be expected to lead to quantitatively different results but will not affect the principal features of the calculations as presented above.

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