Electrostatic Rigidity Considerations for Polymers at Interfaces: Polyelectrolyte Brushes

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1. Introduction

The subject of polymer adsorption over solid substrates has important implications in diverse areas.[1-5] Consequently, over the recent years various theories for polymer adsorption have been put forth and existing theories have been refined. These fall under the category of scaling concepts (of de Gennes and Alexander),[6,7] continuum self-consistent-field (SCF) approach (of Edwards, Freed, Helfand, Muthukumar, Ploehn et al., etc.),[8-16] the lattice version of the SCF approach (of Levine, Roe, Scheutjens, and Fleer, etc.),[17-19] and Monte Carlo simulations (of Cosgrove et al., Theodoreau, etc.).[20,21] Charged polymers at interfaces, called polyions or polyelectrolytes, have also received much attention. The most prominent of these are the theories of Hesselink,[22] Papenhuijzen et al.,[23] and Van der Schee and Lyklema.[24] These theories for polyelectrolytes at interfaces have traditionally focused on extending the SCF and lattice approaches of neutral polymer adsorption by including the effect of charges on the polymer-chain backbone. This was done by including the electrostatic energy in the total internal energy of the system. The stiffness of the chain due to backbone charges (and hence an increased Kuhn length) was not taken into account. We propose that these theories could be improved by taking into account the variation of electrostatic rigidity with backbone charge and ionic strength.

Owing to the intrachain repulsions arising from the backbone charges, the stiffness of the chain increases. This increase in stiffness or electrostatically induced persistence length has been investigated by numerous researchers. From the early works of Hermans and Overbeek[25] and Harris and Rice,[26,27] the theory of *single* polyelectrolyte coils has been refined by various workers like Odijk,[28-30] Fixman and Skolnick,[31,32] Le Bret,[33] Davis and Russel,[34] Kholodenko,[35] etc. While these theories deal with chains in the regime where coil overlap is none or negligible, they nevertheless predict an electrical persistence length as a function of backbone charge density and ionic strength of the solution. We assume that this persistence length would be the same in the presence of highly overlapping coils too. (This assumption may have some limitations, which are discussed at the end of section 2.) In other words, the persistence length is taken to be a property of the chain at a given backbone charge density and ionic strength and is considered independent of the electrical free energy of the segments.

We propose that this changed persistence length changes the statistics applying to a chain in addition to changing the internal energy due to an increased segment size. We restrict ourselves to the mean-field regime where chain and segment concentrations are high and there is complete overlap of coils. This ensures that the potential of any segment (electrostatic or nonelectrostatic) depends only upon the local environment, made up of segments predominantly from other chains. Self-avoidance is therefore not important. (Although this situation truly exists only for polymer melts of uniform composition, as pointed out by de Gennes,[36] it nevertheless is a good approximation for concentrated systems.) Chains are considered to be a sequence of cylindrical, freely hinged segments with a hard-core diameter. The length of the cylindrical segments is subject to change with changing persistence length.

In the next section we present some salient results of recent polyelectrolyte rigidity theories and propose a modification for incorporating the effects of electrostatic rigidity into the framework of existing polyelectrolyte theories. Finally, as an illustration, we investigate the effect of electrostatic rigidity on the recent polyelectrolyte brush theory.[37,38]

2. Electrostatic Rigidity Effects on Polymers at Interfaces

As mentioned earlier, the SCF theories are extended to polyelectrolytes by incorporating charge effects into the existing framework. Invariably the effects are incorporated via an electrical energy, which is added to the total internal energy. The configurational statistics part of the partition function remains unchanged. For example, the canonical partition function is given as[17,23]

$$Q(n,N,V,A) = \frac{\Omega}{\Omega^+} \exp[-\Delta U_t/kT] \tag{1}$$

Here Q is the partition function of n chains of N *statistical* segments each, confined to a volume V and exposed to an adsorbing surface area of A. Ω is the number of ways of arranging these N-mers over the available number of sites while Ω^+ is the number of ways of arranging the same chains over the same volume but without an adsorbing surface (i.e., in bulk). ΔU_t is the total internal energy of the system given as

$$\Delta U_t = \Delta U_{ne} + \Delta U_e \tag{2}$$

Here ΔU_{ne} is the nonelectrostatic part of the total internal energy given by polymer solution theories like Flory–Huggins theory, etc. ΔU_e is the electrostatic part of the internal energy obtained by summing the potential of all charged segments in the system.

We propose that due to increased local stiffness in the chain the configurational part of Q should be altered. This is because the effective number of segments decreases with increasing backbone stiffness. Also, since the effective segment size and its charge change, it is the *effective* potential of each *effective* segment that should be taken into account. Therefore, the effects of changing stiffness are felt through both, the configurational as well as the energy parts of the partition function.

Various researchers have studied the problem of electrostatic stiffness of a charged chain molecule.[28-35] They have demonstrated that increase in stiffness (due to increased electrostatic interaction) leads to increase in the effective length of the segment (or effective Kuhn length). This leads to a decrease in the effective number of segments in the chain, since the total contour length of the chain is a constant. This work proposes that properties of the chain or a system of chains near an interface therefore should be computed taking this into account. As an example, consider a Gaussian N-mer with a Kuhn length, l, in the absence of electrostatic interactions. Its radius of gyration is given as

$$R_g \sim l\sqrt{N} \tag{3}$$

Suppose now that due to local stiffness the effective

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segment length is l_{eff}. Then the effective number of statistical segments is $N_{\text{eff}} = Nl/l_{\text{eff}}$. Therefore, the new radius of gyration, $R_{\text{g,eff}}$ is

$$R_{\text{g,eff}}/R_{\text{g}} = (l_{\text{eff}}/l)^{1/2} \tag{4}$$

The ratio does not equal 1 unless the effective Kuhn length is the same as the original Kuhn length. This simple example serves to illustrate the importance of accounting for electrostatic rigidity in chain statistics.

The above illustrates the change in chain statistics. Now if we take the same chain and subject it to a potential field, its conformation will be perturbed. This will force the chain segments to rearrange into various different conformations possible, each with a certain probability. However, by increasing l_{eff} we also constrain larger parts of the chain to act in coordination, since the whole segment virtually acts as one chemical entity. Thus the interaction potential of the segments also changes. Therefore, the free energy of the chain changes not only through the entropy of conformation but also due to the internal energy of the configuration obtained by summing the interaction potentials of the segments.

We propose that any polyelectrolyte adsorption theory should take these effects into account. In the case of lattice theories it would mean changing the lattice size as a function of both the backbone charge and the ionic strength. This change in the segment size from l to l_{eff} would also be accompanied by the change in the effective charge per segment in order that the total backbone charge remain constant. Of course, the number of segments would change too. Therefore, lattice calculations for different ionic strengths and charges would essentially be performed on lattices of differing sizes with chains of differing N_{eff} and differing effective charge per segment. The electrical energy part of the partition function would be calculated as before since the electrical energy would depend only on the distribution of charges in a potential field computed through the Poisson–Boltzmann equation. This is due to the long-range nature of electrostatic forces, and therefore ΔU_{e} is determined not by the local chain properties but by the collective behavior of all the chains (in the regime where mean-field computations are justified, i.e., high chain densities).[39]

We now present some salient results from some recent theories on electrostatic rigidity. The electrostatic contribution to the effective Kuhn length, l_{e}, is given as[28]

$$l_{\text{e}} = l_{\text{b}}/8\kappa^2 l_{\text{c}}^2 \tag{5}$$

Here l_{b} is the Bjerrum length defined as $(e^2/\epsilon kT)$, ϵ being the dielectric constant for the solvent. If the contour length of the chain is L and it carries Q (stoichiometric) elementary charges, then $l_{\text{c}} = L/Q$, if $L/Q > l_{\text{b}}$; $l_{\text{c}} = l_{\text{b}}$, if $L/Q < l_{\text{b}}$. Note that this definition of l_{c} takes into account counterion condensation; i.e., the effective value of l_{c} never falls below l_{b}. κ^{-1} is the Debye screening length given as $(8\pi Z^2 l_{\text{b}} n_\infty)^{-1}$, n_∞ being the concentration of the Z:Z electrolyte. The effective Kuhn length is, therefore

$$l_{\text{eff}} = l + l_{\text{e}} \tag{6}$$

with l_{e} given by eq 5.

The hard-core volume per segment increases linearly with segment length. If we take the segments to be cylindrical, with a hard-core diameter of δ, then the effective hard-core volume per segment is

$$\nu_{\text{s}} = \frac{\pi}{4} l_{\text{eff}} \delta^2 \tag{7}$$

A note of caution on the limitations of the above equations seems to be in order here. The above results of Odijk and Houwaart (eq 5) are valid for dilute solutions or single coils and also neglect nonlinearities in electrostatics. Russel and Davis[34] and Fixman[31] have obtained more accurate persistence lengths, taking into account a nonlinear Poisson–Boltzmann equation. However, their results are also valid only for single coils or dilute solutions. It is possible that in concentrated solutions the presence of segments from neighboring chains may also affect the electrostatic persistence length. A more important effect could be a position-dependent persistence length near the interface due to the variation of the concentration of co-ions and counterions in that region. For this purpose there is a need to develop theories that address concentrated systems with overlapping coils. In this light eqs 5 and 6 provide an approximate but simple definition of persistence length that suffices to serve the central purpose of this note, viz., to demonstrate the importance of electrostatic persistence length on polyelectrolytes at interfaces.

3. Polyelectrolyte Brush Theory Corrected for l_{e}

Polymer brushes are formed by terminally anchoring the chains in high density. This happens, as pointed out by de Gennes and Alexander,[6,7] when the radius of gyration of the chain, R_{g}, exceeds the spacing between the graft points, D. Milner, Witten, and Cates (MWC)[40] have shown under these conditions that, if the chains are very long and if their lengths are equal, the chemical potential of the segments drops parabolically from the grafting surface. The theory of MWC was recently extended for polyelectrolytes as well by Miklavic and Marcelja[37] and Misra et al.[38] These polyelectrolyte brush theories, like their polymer adsorption counterparts, have not taken into account the corrections due to electrostatically induced persistence length. The concepts alluded to in the previous section are incorporated into these theories quite easily. The χ parameter used is the same as that used earlier. The strength of nonelectrostatic energy density is assumed to depend upon the local segment volume fraction only. With these assumptions in mind, we can write the following three governing equations (detailed discussion on which can be found in ref 38) for the distributions of segment density and electrostatic potential:

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = \frac{rY_3 - 2Bt}{\dfrac{1}{1 - Y_1} - 2\chi} \tag{8}$$

$$\frac{\mathrm{d}Y_2}{\mathrm{d}t} = Y_3 \tag{9}$$

$$\frac{\mathrm{d}Y_3}{\mathrm{d}t} = \sinh(Y_2) + \frac{r}{2n_\infty \nu_{\text{s}}} Y_1 \tag{10}$$

Here Y_1 is the segment density Φ, and Y_2 is the dimensionless electrostatic potential, u, defined as $Ze\psi/kT$, Ψ being the electrostatic potential and Z the valence of the indifferent electrolyte. r is the dimensionless charge per segment given as $r = \pm(l_{\text{eff}}/Zl_{\text{c}})$. Here the value of l_{c} is the *effective value* as defined following eq 5. The positive sign is taken when the backbone charge is negative and vice versa. t is the dimensionless distance from the grafting surface scaled by κ^{-1}. B is a constant that equals $\pi/8N^2 l_{\text{eff}}^2 \kappa^2 = \pi/8L^2\kappa^2$. The above equations are accompanied by the following boundary conditions (see ref 38). Segment density is required to vanish at brush height t^*:

$$t = t^*, \quad Y_1 = 0 \tag{11}$$

The gradient of potential is related to the surface charge,

σ_0, on the grafting surface, giving us

$$t = 0, \quad Y_3 = -\frac{\kappa\sigma_0}{2Zen_\infty} \tag{12}$$

The electrostatic potential and its gradient have to be continuous at t^*; therefore

$$t = t^*, \quad Y_3 = -2\sinh(Y_2/2) \tag{13}$$

Solution of the above governing eqs 8–10 requires the knowledge of t^*, which appears in the boundary conditions (eqs 11 and 13). The value of t^* is determined by requiring it to satisfy the constraint that the number of segments contained in the brush volume per unit area of the wall equals $N_{\text{eff}}\sigma$, σ being the grafting density.

$$\sigma N_{\text{eff}}\nu_s = \frac{1}{\kappa}\int_0^{t^*} \mathrm{d}t\, \Phi(t) \tag{14}$$

In earlier computations the segment length, number of segments, their hard-core volume, and charge were taken to be constant. (In other words, irrespective of backbone charge or ionic strength, the earlier computation took $l_{\text{eff}} = l$ = constant, and the other derived quantities also remained constant.)

In modifying the earlier polyelectrolyte theory, we have left the governing equations intact. The above-mentioned parameters used in these equations have been modified, and the computations are done with effective parameters only. Therefore, l is replaced by l_{eff} and N is replaced by N_{eff} as mentioned in section 2 and so forth for r and ν_s.

4. Results and Discussion

Following the discussion in section 3, computations were performed for chains of total countour length (L) of 10^{-6} m grafted at a density (σ) of 10^{17} m^{-2}. The Kuhn length of the uncharged polymer, i.e., l, was taken to be 1 nm. Therefore, for an uncharged polymer, we have 1000 statistical segments. The hard-core diameter, δ, of the segments is also taken as 1 nm. A χ value of 0.45 was used throughout. Care is taken that the effective number of segments remains large enough to justify the use of continuum theory of MWC and that the height of the brush, while $\gg R_g$, is still low compared to the length of fully stretched chains. The brush height for an uncharged brush $h^* = 3.38 \times 10^{-7}$ m. The scaled distance from the grafting wall, y, is the ratio of actual distance to the height of an uncharged brush (i.e., y = distance/h^*). The scaled brush height y^* is therefore just the ratio of the actual brush height to h^*.

In Figure 1 the segment density distributions are computed by using constant segment length (unadjusted) and effective segment lengths (adjusted) for the same value of ionic strength (0.1 M) and linear charge density of $4 \times 10^8\, e$ m^{-1} ($L = 10^{-6}$ m, $Q = 400$, $l_c = 2.5$ nm, $e = 1.6 \times 10^{-19}$ C). We notice that in the case where the effective length of the segment is larger the segment density distribution spreads farther from the wall. This is because the effective segments have larger potentials due to their larger effective charge and hence try to reduce their potential by moving farther from the wall.

In Figure 2 brush heights are plotted for a constant linear charge density of $4 \times 10^8\, e$ m^{-1} ($l_c = 2.5$ nm) and for varying ionic strengths. Expectedly the brush heights are found to be larger for the case where segment length is adjusted. The deviation from the unadjusted height increases with decreasing ionic strength.

In Figure 3 the effect of linear charge density is studied for a constant ionic strength of 0.1 M.

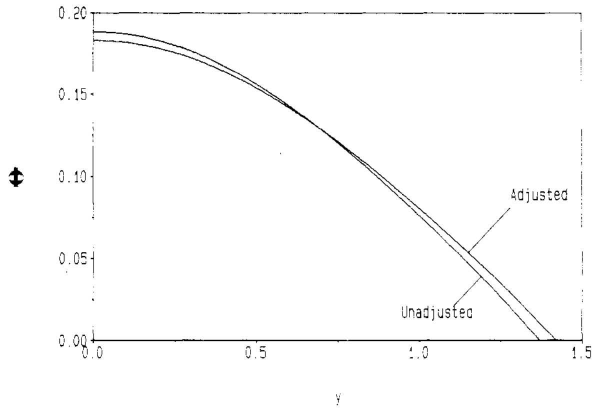

Figure 1. Comparison of segment density profiles (segment volume fraction, Φ, vs scaled distance, y) for constant and corrected segment lengths. The increase in segment length and effective segment potential spreads the segment density outward from the wall. $\sigma = 10^{17}$ m^{-2}, $L = 10^{-6}$ m, $l_c = 2.5 \times 10^{-9}$ m, I = 0.05 M, $\sigma_0 = 0$, and $\chi = 0.45$.

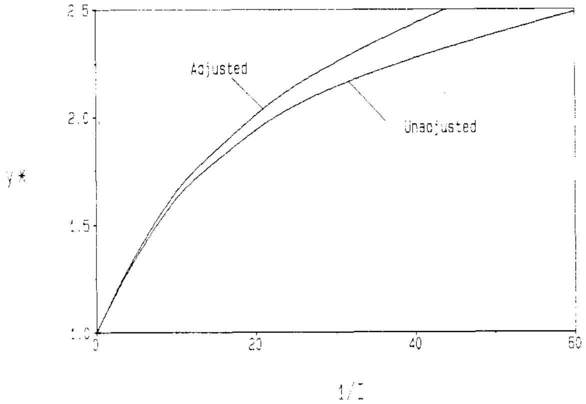

Figure 2. Comparison for the dependence of scaled brush heights, y^*, on ionic strengths. The predicted brush heights are larger when the corrected segment length is used. $\sigma = 10^{17}$ m^{-2}, $L = 10^{-6}$ m, $l_c = 2.5 \times 10^{-9}$ m, $\sigma_0 = 0$, and $\chi = 0.45$.

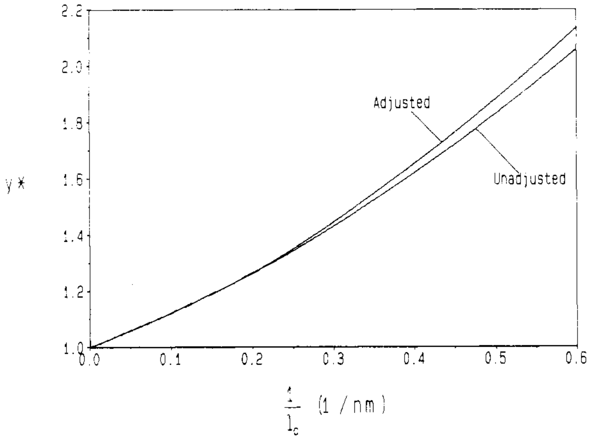

Figure 3. Comparison for the dependence of scaled brush heights, y^*, on backbone charge density. (l_c is the inverse of linear elementary charge density of the chain.) The predicted brush heights are larger when the corrected segment length is used. $\sigma = 10^{17}$ m^{-2}, $L = 10^{-6}$, $I = 0.1$ M, $\sigma_0 = 0$, and $\chi = 0.45$.

Thus, although the total volume displaced by the segments remains the same and the total charge remains constant by increasing l_{eff}, we essentially demand that larger portions of the chain (viz., the segment) have to act in coordination. The increase in l_{eff} also increases the potential of the effective segment since its effective charge is higher and this results in an increase in the brush height as the *effective* segments are forced farther from the wall due to their larger potential.

Polyelectrolyte brush theory is based on the assumption that only the classical paths (or conformations with the minimum action under a given potential) are important and that fluctuations around these paths being small can be neglected. The effect on the free energy part is not felt through the conformational part of the partition function. We, therefore, anticipate an even more pronounced change in polymer conformations where fluctuations are important. The magnitude of these fluctuations will be acutely dependent on the choice of the segment size. It has also been noticed earlier that the choice of the lattice size is quite critical for lattice-based computations.[23] The choice of a lattice size dependent on ionic strength and linear charge density of the chains would probably improve the quantitative agreement between experiment and theory.

5. Conclusions

The computations above show that electrostatically induced persistence length makes a difference in determining the segment density distributions and brush height even in the case of a polyelectrolyte brush, where fluctuations around the classical paths are absent. We conclude that in the case of homopolyelectrolyte adsorption where these fluctuations (or configurations different from the classical paths) are more important, the electrostatic rigidity will also affect the magnitude of these fluctuations by restricting the allowable configurations. This is because the effective number of segments decreases with increased persistence length.

The above treatment is intended to serve as an example of the importance of taking electrostatic rigidity into account. More sophisticated theories for electrostatically induced persistence length and concentrated polyelectrolyte solutions are needed. Another requirement is that there should still be a large enough number of effective segments in order to apply continuum SCF theories as well as lattice theories. This does place a limitation on the range of ionic strengths and linear charge densities in which the earlier polyelectrolyte theories may be corrected. In this light the above treatment seems limited. However it does constitute an important correction to accounting for polyelectrolyte conformations near an interface. Computations for earlier polyelectrolyte theories with a variable lattice size may be performed in order to ascertain the importance of accounting for increased rigidity.

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