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Adsorption of Ionic Block Copolymers: Self-Consistent-Field Analysis and Scaling Predictions

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ABSTRACT: The subject of this paper is the adsorption of ionic diblock copolymers on an uncharged surface. One block, the "anchor", consists of N_A uncharged, adsorbing A segments, whereas the "buoy" block has N_B segments which carry a fixed charge and are nonadsorbing. Upon adsorption these molecules form a layer that resembles a brush of B segments. In contrast with a usual brush, however, the molecules in the adsorbed layer are in equilibrium with those in solution. Consequently, the chain density of the brush is not fixed; its value is determined by the dynamic equilibrium between polymer adsorption and desorption. We interpret the results in terms of the limiting behavior in four regimes, indicated as HU, HC, LU, and LC. The system is classified as either at high (H) or at low (L) anchor density and, irrespective of the anchor density, as either in the charged (C) or in the uncharged (U) regime. We find scaling relations for the adsorbed amount and layer thickness as a function of the block lengths N_A and N_B, the charge $\alpha_B e$ on the B segments, and the salt concentration ϕ_s^b in each of the four regimes. The scaling relations are checked using a self-consistent-field (SCF) lattice theory. The existence of two regimes for uncharged molecules has been reported previously. We argue that those HU and LU regimes are closely related to the two regimes HC and LC we find for charged molecules. Scaling relations can be translated from the uncharged to the corresponding charged regimes by replacing the excluded volume parameter v_B of the buoy segments by an effective electrostatic excluded volume parameter $v_e = \alpha_B^2/\phi_s^b$. In the LC regime the chain density σ scales as $\sigma \propto (N_A/N_B)^{3/2} v_e^{-1}$ and the layer thickness L as $L \propto (N_A N_B)^{1/2}$. The latter scaling is independent of v_e. Using the SCF model, these relations are found to be valid for an adsorbed amount of A segments below 10% of monolayer coverage. In the HC regime the adsorption is dominated by the anchoring block and the scaling relation for the chain density $\sigma \propto 1/N_A$ is identical to that for uncharged molecules. The SCF calculations show that this regime will not be reached in practical situations.

I. Introduction

Polymers are widely used to modify the properties of colloidal systems. They may act as flocculants, stabilizers, or thickeners. Only in recent years has the synthesis of a variety of well-defined (di)block copolymers become feasible. They form a promising class of modifiers, wherein the characteristics of long polymers are combined with the amphiphilic character of surfactants. The length as well as the chemical composition of each of the blocks can be tailored to specific applications. Because of the high cost of developing new kinds of polymers, the ability to predict the behavior of a particular (class of) polymer would be very rewarding.

Several aspects of block copolymer adsorption have been addressed in the past few years. Two of them, although important, will not be dealt with in the present paper. Firstly, we shall consider equilibrium structures only, leaving aside all problems concerning the dynamics of polymer adsorption. Secondly, the formation of micelles in the solution is not taken into account, limiting our treatment to the case of a nonselective solvent or low solution concentrations.

The segment density profile of adsorbed uncharged block copolymers has been investigated theoretically by Evers et al.[1] and Whitmore and Noolandi.[2] When the surface is selective for one of the blocks, this anchor block is adsorbed in a relatively flat conformation. The free "buoy" block, on the other hand, protrudes far into the solution, and its profile is similar to that of a terminally attached chain. The profile has a maximum and extends over a relatively large distance.

The scaling behavior of the adsorbed amount and the layer thickness is interesting from both a theoretical and experimental point of view. This question has been addressed theoretically for uncharged block copolymers with an adsorbing A block (length N_A) and a nonadsorbing B block (length N_B) by Marques and Joanny[3] (MJ). Using a mean-field as well as a scaling approach, they found two regimes. Unless the *A* block is very short, the anchor density is always high, and a regime is found which we denote by HU (high density–uncharged). In this regime the number of chains per surface area, σ, scales as

$$\sigma \propto 1/N_A \qquad \text{(HU)} \tag{1}$$

independent of the value of N_B. The layer thickness L scales as

$$L \propto N_B/N_A^{1/3} \qquad \text{(HU)} \tag{2}$$

On the other hand, for highly asymmetric polymers with a short anchoring block the anchor density is low (LU regime) and the scaling relations are

$$\sigma \propto (N_A/N_B)^{6/5} \qquad \text{(LU)} \tag{3}$$

and

$$L \propto N_A^{2/5} N_B^{3/5} \qquad \text{(LU)} \tag{4}$$

Munch and Gast[4] and, independently, Ligoure and Leibler[5] used a mean-field analysis and obtained expressions that have to be solved numerically. Both groups described the highly asymmetric regime only and found a scaling of L with N_B that agrees roughly with the results of MJ: Ligoure and Leibler find $L \propto N_B^{0.55}$ whereas an exponent of 0.7 was found by Munch and Gast. Several experimental results confirm a scaling behavior with exponents that fall in the same range.[6-9]

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Evers et al.[1] have extended the self-consistent-field (SCF) lattice model, developed originally by Scheutjens and Fleer for the adsorption of homopolymers,[10,11] to the adsorption of block copolymers at solid/liquid interfaces. Their results (interpreted in terms of the adsorbed amount θ, which can be related to the chain density σ through the relation $\theta = \sigma N$, where $N = N_A + N_B$) agree with the qualitative picture of MJ, showing a regime (LU) at low N_A/N_B where σ is an increasing function of N_A and a second regime (HU) at higher N_A/N_B where σ decreases with N_A. For the hydrodynamic layer thickness, an almost linear scaling with N_B was found if N_A is large enough (HU), whereas a clearly less-than-linear scaling with N_B was observed for smaller values of N_A (LU).

To modify systems that contain water as a solvent, polymers must be used that are (at least partly) soluble in water. In most practical cases this means that charged polymers are used. Recently, the first theoretical article on the adsorption of charged block copolymers appeared.[12] The article combines the results of Marques et al.[13] for the adsorption of uncharged copolymers from a selective solvent with those of Pincus[14] for a charged brush. Irrespective of the adsorbed amount, the anchor segments were assumed to form a molten layer of finite thickness. Consequently, only one regime was observed in which the chain density scales as

$$\sigma \propto N_A^{-6/11} N_B^{-3/11} (\phi_s^b)^{1/11} \tag{5}$$

where ϕ_s^b is the salt concentration in the solution. The thickness of the brush scales as $L_B \propto N_A^{-2/11} N_B^{10/11} (\phi_s^b)^{-7/11}$. In the present article we will show that the amount of A segments on the surface is below monolayer coverage for most practical situations, leading to a completely different scaling behavior.

In the past few years, there has been considerable progress on the related case of a charged brush. The papers of Pincus[14] and Zhulina et al.[15] agree on the main points: in the absence of salt the thickness of the brush is proportional to the polymer length N and the square root of the charge density on the chain. It is independent of the anchoring density σ. When the salt concentration in the bulk solution becomes comparable to the counterion concentration in the brush, a different scaling law applies:

$$L \propto N(\alpha_B^2 \sigma / \phi_s^b)^{1/3} \tag{6}$$

where α_B is the valency of brush segments, with $0 \leq \alpha_B \leq 1$.

Our present paper describes an extension of the work of Evers et al.[1] to the case of charged block copolymers. We apply the SCF model to the adsorption of charged block copolymers, where the A segments in the anchor block are still uncharged and adsorbing. The nonadsorbing B segments in the buoy block are charged now and have a valency α_B. For the present paper we restrict ourselves to an uncharged surface. The situation is depicted schematically in Figure 1, where the black parts correspond to *A* segments and the gray sections indicate the buoy (B) blocks. We compare our results to scaling predictions that are obtained by generalizing the charged brush model to the case of adsorbing block copolymers. In section II we present this scaling model, and subsequently we review the basic assumptions of the lattice model in section III. The choice of parameters is discussed in section IV. Then, in section V, we present the results obtained by the lattice theory and compare them with the scaling predictions. These results are discussed in section VI, and finally, the main conclusions are summarized in section VII.

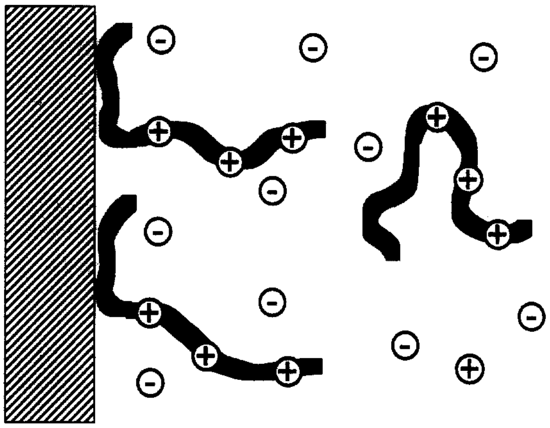

Figure 1. Schematic picture of ionic block copolymers adsorbing to a surface.

II. Scaling Model

We start by briefly reviewing the main arguments of Pincus[14] and Zhulina et al.[15,16] which lead to an expression for the thickness of a charged brush. Subsequently, we extend this model to the adsorption of charged block copolymers, deriving scaling relations for the layer thickness and adsorbed amount.

According to Flory[17] a chain of N_B segments, when stretched over a distance L, stores an amount of elastic energy that is proportional to L^2/N_B. Thus the elastic free energy stored in a (charged) brush containing σ chains per unit area scales as

$$F^{el} \propto \sigma L^2 / N_B \tag{7}$$

The elastic force tends to decrease the layer thickness. Its opposing force is the osmotic pressure of the polymer and counterions, which may be assumed to be trapped in the brush (if $\kappa^{-1} \ll L$). For this osmotic pressure Zhulina et al.[15] derived $P^{osm} \propto (\alpha_B \phi / \kappa)^2$, where ϕ is the average segment volume fraction in the brush, $\kappa \propto (\phi_s^b)^{1/2}$ is the inverse Debye screening length with ϕ_s^b the salt concentration in the bulk solution, and α_B is the valency of the buoy segments. Note that P^{osm} is proportional to ϕ^2, similar to the excluded volume interaction in a dilute *uncharged* brush (good solvent). For the derivation of scaling relations, we may assume a block profile with $\phi \propto \sigma N_B / L$, leading to the following relation for the osmotic pressure in the brush:

$$P^{osm} \propto \alpha_B^2 \sigma^2 N_B^2 / \phi_s^b L^2 \tag{8}$$

A relation for the layer thickness may be obtained from equating the elastic force $\partial F^{el}/\partial L$ to the osmotic force:

$$\partial F^{el} / \partial L = P^{osm} \tag{9}$$

Substitution of relations 7 and 8 into eq 9 leads to eq 6. We write this expression as

$$L \propto N(\sigma \upsilon_e)^{1/3} \tag{10}$$

where we define an effective electrostatic excluded volume parameter

$$\upsilon_e \equiv \alpha_B^2 / \phi_s^b \tag{11}$$

There is an obvious analogy with the classical result $L \propto N(\sigma \upsilon_B)^{1/3}$ for an uncharged brush with excluded volume parameter υ_B.[18] Typical values of α_B and ϕ_s^b lead to values for υ_e of the order of 10 or higher. Consequently, if we wish to compare a neutral brush with an equally stretched charged brush, the brush density has to be lower by a factor ~10 or more for the charged brush.

For the adsorption of ionic diblock copolymers, we have a similar situation. Again, osmotic and elastic forces are balancing each other, but additionally the interaction of anchoring A segments with the surface comes into play. Thus we have one extra degree of freedom, σ, which is fixed in the brush model. For copolymer adsorption it can be determined from the matching equation:

$$\partial F^{\text{ads}}/\partial\sigma = \partial F^{\text{el}}/\partial\sigma \qquad (12)$$

For $\chi_{AS}N_A \gg 1$, the adsorption at any finite polymer concentration may be assumed to be in the plateau region of the adsorption isotherm. The translational entropy of polymer molecules upon adsorption (i.e. the effect of the chemical potential of polymer in solution) may be neglected then. The limited validity of this approximation will be discussed in the Results. Also, the two-dimensional translational entropy of the adsorbed molecule, which is smaller than that of the free molecule, is neglected.

An expression for the energy of the adsorbed anchor layer F^{ads} is not trivial, unless the density of anchor block segments is very low. In this "low anchor density–charged" (LC) regime, anchor blocks (consisting of N_A segments each) are adsorbed in a flat conformation and have no mutual interaction. F^{ads} may then be approximated as consisting of adsorption energy contributions only:

$$F^{\text{ads}} \propto N_A\sigma\chi_{AS} \qquad (13)$$

In this equation χ_{AS} represents the Flory–Huggins interaction parameter between A segments and the adsorbent S. Equation 12 reads now $N_A\chi_{AS} \propto L^2/N_B$ or

$$L \propto (N_AN_B)^{1/2} \quad \text{(LC)} \qquad (14)$$

After substitution of (10) in this expression we find for the chain density

$$\sigma \propto (N_A/N_B)^{3/2}v_e^{-1} \quad \text{(LC)} \qquad (15)$$

There are a few interesting aspects in eqs 14 and 15. Firstly, we note that for uncharged diblock copolymers an analogous reasoning leads to the LU regime where the excluded volume parameter v_B of uncharged B segments is substituted for v_e:

$$L \propto (N_AN_B)^{1/2} \quad \text{(LU)} \qquad (16)$$

$$\sigma \propto (N_A/N_B)^{3/2}v_B^{-1} \quad \text{(LU)} \qquad (17)$$

Secondly, we note that these expressions are in strong contrast with the expressions found by Argillier et al.[12] (eq 5), who assume higher adsorbed amounts and consequently a completely different structure of the anchoring layer.[12]

Thirdly, σ turns out to be proportional to the salt concentration in the bulk (through the dependence $v_e = \alpha_B^2/\phi_s^b$). We can understand this by realizing that, using the approximation of local electroneutrality,[14,15] all electrostatic interactions in the adsorbed layer balance out exactly. Thus the only two opposing forces in the adsorption process are the adsorption energy on the one hand and the translation entropy loss of counterions on the other hand. When looked upon in this way, the process resembles a Henry-type adsorption of counterions, where the adsorbed amount is also linearly proportional to the bulk concentration of these ions.

At higher anchor density no simple relation can be derived, until the "high anchor density" regime (HC) is reached, as described earlier by MJ for uncharged polymers. As indicated already by the name "anchor dominated regime" as used by MJ, it is expected to apply equally well to uncharged (HU) and charged (HC) polymers. Since the chain density σ is given by $\sigma \propto 1/N_A$ for HU and HC regimes alike, it would seem appropriate to merge both regimes into one (H) regime. The stretching of the B block, however, and consequently the thickness of the brush depend on v_e in the HC regime and on v_B in the HU regime.

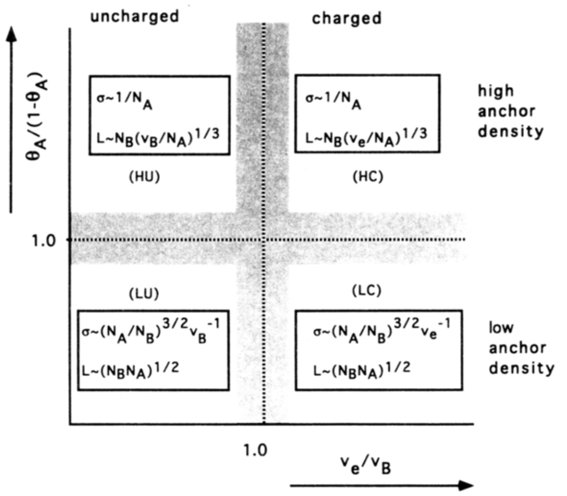

Figure 2. Four regimes for block copolymer adsorption and the scaling relations for the chain density σ and the layer thickness L in each of them. N_A and N_B are the lengths of the anchoring and buoy block, respectively, v_B is the excluded volume parameter of uncharged B segments, and $v_e = \alpha_B^2/\phi_s^b$ is the effective excluded volume parameter of charged B segments, where α_B is the valence of B segments and ϕ_s^b is the salt solution concentration. The adsorbed amount (in equivalent monolayers) of anchoring A segments is given by θ_A, defined as σN_A.

The complete scaling picture is summarized in Figure 2, showing the regimes we expect as a function of $\theta_A/(1-\theta_A)$ and of the ratio v_e/v_B. The quantity θ_A equals $N_A\sigma$; the latter ratio is determined by the buoy segment valency α_B and the salt concentration ϕ_s^b (eq 11). In Figure 2 the boundary between high and low coverage is taken to be located around $\theta_A/(1-\theta_A) = 1$, and the boundary between charged and uncharged to be around $v_e/v_B = 1$. It should be stressed, however, that the transitions are not at all expected to be sharp, which is indicated by the shaded bands in Figure 2. As will be shown in the Results, deviations from the low coverage regime start already at $\theta_A/(1-\theta_A) \simeq 0.1$ (i.e., above 10% of surface coverage for the anchor segments) and the scaling relations for the charged regime are found to apply if $v_e/v_B \gtrsim 10$ (e.g., $\phi_s^b < 10^{-3}$ if $\alpha_B = 0.1$, assuming $v_B \approx 1$).

III. Self-Consistent-Field Lattice Model

We use a self-consistent-field (SCF) lattice model to calculate the distribution of molecules near a surface. The mean-field approximation implies the replacement of the local potential $u(x,y,z,t)$ of a segment at position (x,y,z) and time t by a time-independent potential $u(z)$, of a segment at a distance z from the surface. Hence, a preaveraging over the variables x, y, and t is carried out. The introduction of a lattice is convenient to define and count conformations. A recent comparison between a lattice mean-field and a continuous mean-field model for the structure of an uncharged brush[18] shows that the use of a lattice does not introduce any error when the molecules are large compared to the size of one lattice cell. For the generation of conformations we use a first-order Markov approximation: the position of any segment is determined only by the position of its immediate neighbors. The electrostatic interactions are handled using the multilayer Stern model.[19]

We divide the half-space next to a surface in parallel layers, numbered $z = 1, 2, ..., M$ where M is sufficiently large so that bulk properties are reached at layer M. A conformation of a molecule is defined when for each of its segments the distance to the surface is specified. The (unnormalized) statistical weight G^c of a conformation c is related to its potential energy u^c, which is the summation of the potential energies of its N segments:

$$G^c = \Omega^c e^{-u^c/kT} = \Omega^c \prod_{s=1}^{N} e^{-u(z,s)/kT} = \Omega^c \prod_{s=1}^{N} G(z,s) \quad (18)$$

In this equation Ω^c is the degeneracy of a conformation and depends on the type of lattice. The potential experienced by the sth segment depends both on its position z and on the type of segment s. For example, for a diblock copolymer $A_{100}B_{200}$, $G(z,s) = G_A(z)$ for segments 1–100 and $G(z,s) = G_B(z)$ for segments 101–300. For later use we have defined here the weighting factor $G_A(z)$ for a segment A in layer z as $e^{-u_A(z)/kT}$. For a segment of type A the energy in layer z is given by[1,19]

$$u_A(z) = u'(z) + kT\sum_B \chi_{AB}(\langle \phi_B(z)\rangle - \phi_B^{\,b}) + e\alpha_A\psi(z) \quad (19)$$

where $u'(z)$ is a Lagrange multiplier for layer z, introduced to meet the constraint that the lattice is completely filled:

$$\sum_A \phi_A(z) = 1 \qquad z = 1, ..., M \quad (20)$$

This summation is over all segment types in the system, including the solvent and salt molecules.

The second term in eq 19 takes into account the mixing energy (relative to the bulk solution). In this term χ_{AB} is the well-known Flory–Huggins interaction parameter between segments A and B (with $\chi_{AA} = 0$), and $\langle \phi_B(z)\rangle$ is the volume fraction ϕ_B averaged over the neighbors of a lattice site in layer z. The summation index B runs over all monomer types in the system. In order to account for the adsorption energy in $u_A(z)$, we include in the summation of eq 19 also the surface, considering it as an additional component in the system with (fixed) volume fraction $\phi = 1$ in the layers $z \leq 0$ and $\phi = 0$ in solution ($z > 0$).

The last term of eq 19 represents the electrostatic contribution to the energy of a segment. In this term, e is the elementary charge, α_A is the valence of a segment A, and $\psi(z)$ is the electrostatic potential in layer z, obtained from the set of equations

$$\frac{\partial^2\psi(z)}{\partial z^2} = \frac{\rho(z)}{\epsilon(z)}d^2 \qquad z = 1, ..., M \quad (21)$$

In this equation the lattice spacing d is needed to keep z dimensionless; thus for charged systems the results of the lattice model are no longer invariant to a rescaling of this parameter. In our lattice calculations we use a discrete analogue of eq 21, taking into account the changes in dielectric permittivity between different layers.[19] The space charge density $\rho(z)$ in layer z and the dielectric permittivity $\epsilon(z)$ of layer z are obtained from the following mean-field expressions, in which ϵ_A is the dielectric permittivity of pure A and $V_{\text{cell}} = {}^3/_4(3)^{1/2}d^3$ (hexagonal lattice) is the volume of one lattice cell:

$$\rho(z) = \frac{\sum_A \alpha_A e \phi_A(z)}{V_{\text{cell}}} \quad (22)$$

$$\epsilon(z) = \sum_A \epsilon_A \phi_A(z) \quad (23)$$

The electroneutrality of the system is ensured by setting the field strength at the boundaries to zero:

$$\left.\frac{\partial\psi}{\partial z}\right|_{z=0} = \left.\frac{\partial\psi}{\partial z}\right|_{z=M} = 0 \quad (24)$$

Again, in the lattice model a discrete version of these expressions is used.[19]

In order to calculate the volume fraction profile, we introduce a function $G(z,s|z',s')$, which is the combined statistical weight of all conformations of chain parts starting with segment s' in layer z' and ending with segment s in layer z. Summation of $G(z,s|z',1)$ over all z' leads to the end-point distribution function $G(z,s|1)$ of a sequence 1, 2, ..., s. By definition we have

$$G(z,1|1) = G(z,1) \quad (25)$$

and similarly

$$G(z,N|N) = G(z,N) \quad (26)$$

where N is the number of segments of the molecule.

The first-order Markov approximation allows us to obtain the distribution function $G(z,s+1|1)$ from its predecessor $G(z,s|1)$ by taking into account all possible steps from segment s to $s + 1$, regardless of the positions of all segments 1 to $s - 1$:

$$G(z,s+1|1) = G(z,s+1)\langle G(z,s|1)\rangle \quad (27)$$

where $\langle G(z,s|1)\rangle$ is again a shorthand notation for $G(z,s|1)$ averaged over the neighbors (in layers $z - 1$, z, and $z + 1$) of a lattice site in layer z. Applying expression 27 recursively ($N - 1$) times to starting relation 25 and also ($N - 1$) times to expression 26 generates two sets of N distribution functions. From these sets many characteristics of the adsorbed layer can be calculated. For example, in a system containing a diblock copolymer with block lengths N_A and N_B, respectively, and total length $N = N_A + N_B$, the volume fraction profile of monomer type A is given by

$$\phi_A(z) = \frac{\phi_A^{\,b}}{N_A}\sum_{s=1}^{N_A}\frac{G(z,s|1)G(z,s|N)}{G(z,s)} \quad (28)$$

where $\phi_A^{\,b}/N_A$ is the proper normalization factor if we assume that the interface region is in full equilibrium with the solution far away from the surface (the bulk solution). For large z, where $G(z,s) = 1$, since this weighting factor is defined relative to the bulk solution, eq 28 gives $\phi_A(z) = \phi_A^{\,b}$, the concentration of A segments in the bulk solution.

We now have for any monomer type A in every layer z two unknowns $\phi_A(z)$ and $G_A(z) = e^{-u_A(z)/kT}$ and two corresponding equations: (19) and (28). Additionally, we have for every layer two unknowns $\psi(z)$ and $u'(z)$ with corresponding eqs 20 and 21. This set of equations can be solved numerically.

The excess amount of a monomer type A is defined as

$$\theta_A^{\,\text{ex}} = \sum_{z=1}^{M}(\phi_A(z) - \phi_A^{\,b}) \quad (29)$$

In the remainder of the text we will drop the superscript "ex" and use θ_A instead of $\theta_A^{\,\text{ex}}$.

For the thickness of the adsorbed layer, we will use two measures: the root-mean-square layer thickness δ_{rms} and the hydrodynamic layer thickness δ_h. The RMS layer thickness is given by

$$\delta_{\mathrm{rms}} = \left(\frac{\sum_{z=1}^{M} z^2 \phi_A{}^a(z)}{\sum_{z=1}^{M} \phi_A{}^a(z)} \right)^{1/2} \tag{30}$$

where $\phi_A{}^a(z)$ is the volume fraction profile of adsorbed molecules, defined as the volume fraction of molecules that have at least one segment in direct contact with the surface.[11] It can be obtained in a way similar to that of $\phi_A(z)$; for details we refer to the original papers.[10,11] An expression for the hydrodynamic layer thickness was given by Evers et al.[1]

There is no theoretical limit for the number of different types of molecules that may be included in a system. In the present paper we apply the model to a charged diblock adsorbing onto an uncharged surface from a salt solution. The distributions of salt and solvent molecules are calculated using exactly the same equations as for the polymer. Although in the above theory section we have used A and B to denote general variables, running over all monomer types in the system, in the remainder of the article A and B are specified to be the monomer types in the anchor and buoy block of the polymer, respectively.

IV. Parameters

In this paper we apply the SCF model to the adsorption of a charged diblock copolymer p with an anchoring A block and a buoy B block with block lengths N_A and N_B, respectively, onto an uncharged surface S. The A segments are uncharged and adsorb to the surface ($\chi_{AS} = -4$). The B segments differ from the A segments in only two aspects: they carry a charge $\alpha_B e$ and have no affinity for the surface ($\chi_{BS} = 0$). The effect of four different parameters on the adsorption is studied: the length of the A block N_A, the length of the B block N_B, the segment charge $\alpha_B e$ of the B segments, and the salt concentration in the solution.

The charge of the B block is defined by giving each B segment a valency α_B, where α_B is constant throughout the system (acid–base equilibria are not considered). Different charge densities can be obtained by assigning a value between 0 and 1 to α_B. The charge is thus smeared out: a B block in which 10% of the segments is charged is modeled as a B block where every segment has a charge of 0.1*e*.

The salt concentration in the bulk solution, $\phi_s{}^b$, is defined to be the bulk solution concentration of the coion (Co), the concentration of the counterion (Ct) being $\phi_{Ct}{}^b + \phi_p{}^b \alpha_B N_B/(N_A + N_B)$, where $\phi_p{}^b$ is the polymer volume fraction in the bulk solution. In our computations we choose $\phi_p{}^b = 10^{-6}$. Salt concentrations are also given as volume fractgions. The volume fraction ϕ can be converted to a molarity c through $\phi = cV_m$ where $V_m = N_{Av}V_{cell}$ is the molar volume in liters/mole. The quantity V_{cell} follows from the lattice spacing d and the lattice type; for the hexagonal close-packed lattice[20] used in all our calculations $V_{cell} = {}^3/_4(3)^{1/2}d^3$. We choose $d = 0.6$ nm, giving $V_{cell} = 0.28$ nm^3 and $V_m = 0.17$ L. Hence, the molarity is found from ϕ_s by multiplication by a factor of ~6. A typical value $\phi_s{}^b = 10^{-3}$ of the volume fraction corresponds to a 6 mM salt solution.

All other parameters are kept constant throughout the paper. The solvent, water (W), is assumed to be a Θ-solvent for both segment types ($\chi_{AW} = \chi_{BW} = 0.5$). For the charged B segments, this χ_{WB} parameter represents the nonelectrostatic interaction with the solvent (i.e., if there were no charge on the B segments). The *effective* solvency of charged B segments is much higher due to the electrostatic repulsion, which is automatically accounted for in the SCF model. For predicting the general behavior of classes of polymers, we would have three typical choices for χ_{AW} and χ_{BW}: $\chi = 0$ (good solvent), $\chi = 0.5$ (bad solvent = Θ-solvent), and $\chi > 0.5$ (nonsolvent). In most practical polyelectrolyte/water systems, where the polymer is often insoluble when it is uncharged, the nonelectrostatic interaction is unfavourable ($\chi \geq 0.5$). Therefore a choice $\chi = 0$ seems unrealistic. A very high value $\chi_{BW} \gg 0.5$, however, might lead to a first-order brush-collapse phase transition,[16,21] a phenomenon we do not wish to investigate at present. For simplicity we prefer $\chi_{AW} = \chi_{BW} = 0.5$. We have to realize, however, that the scaling relations in section II were derived for the (unrealistic) case $\chi_{AW} = \chi_{BW} = 0$.

The solvent is modeled as a monomeric component with no charge ($\alpha_W = 0$) and a dielectric permittivity $\epsilon_W = 80\epsilon_0$. The dielectric permittivities of all other substances in the system, of which the precise values are of minor importance, are set equal to $5\epsilon_0$. Salt ions are considered to have only electrostatic interactions; consequently, their χ parameters are set equal to zero. Also χ_{AB} was chosen to be zero.

V. Results

In this section we present the results from calculations with the mean-field lattice model. First we show the volume fraction profiles for one specific set of parameters and then we focus on two more easily measurable quantities, viz. the adsorbed amount and the layer thickness, for a range of parameters.

Profiles. In Figure 3 we show the volume fraction profiles of adsorbing A segments and of nonadsorbing B segments (with $\alpha_B = 0.1$) for a polymer $A_{100}B_{400}$ in a salt concentration of $\phi_s{}^b = 10^{-3}$ ($\phi_{Co}{}^b = 10^{-3}$, $\phi_{Ct}{}^b = 1.02 \times 10^{-3}$), both on a linear scale (Figure 3a, solid curves) and on a logarithmic scale for ϕ (Figure 3b). Like for an uncharged diblock copolymer,[1] the A block adsorbs in a rather flat conformation on the surface, leading to an A profile that drops to a very low value after a few layers. The B profile has a maximum close to the surface and extends far into the solution (in this case ~80 layers): the B block is highly stretched.

In the logarithmic plot (Figure 3b) we notice that at large distances from the surface ($z > 100$) ϕ_A and ϕ_B reach constant values that equal their respective bulk volume fractions. Since the B block is 4 times longer than the *A* block, its bulk volume fraction is also 4 times higher. Another feature of the profiles is the fact that $\phi_A(z)$ in the "brush" region ($5 < z < 80$) is lower than $\phi_A{}^b$. This is due to the fact that free molecules are repelled from this region by the electrostatic potential which is built up by the adsorbing chains. The adsorbed molecules have all their *A* segments close to the surface, and their B segments make up the brush.

The most important difference compared to the profiles of uncharged block copolymers is the density in the brush (and thus the adsorbed amount), which is lower by about a factor of 10 (in this example). Consequently, the average distance between the "anchoring" points is larger than the radius of gyration of the free polymer. In this sense the brush limit, as defined for uncharged terminally anchored chains, is not reached. Still, we will consider the B layer

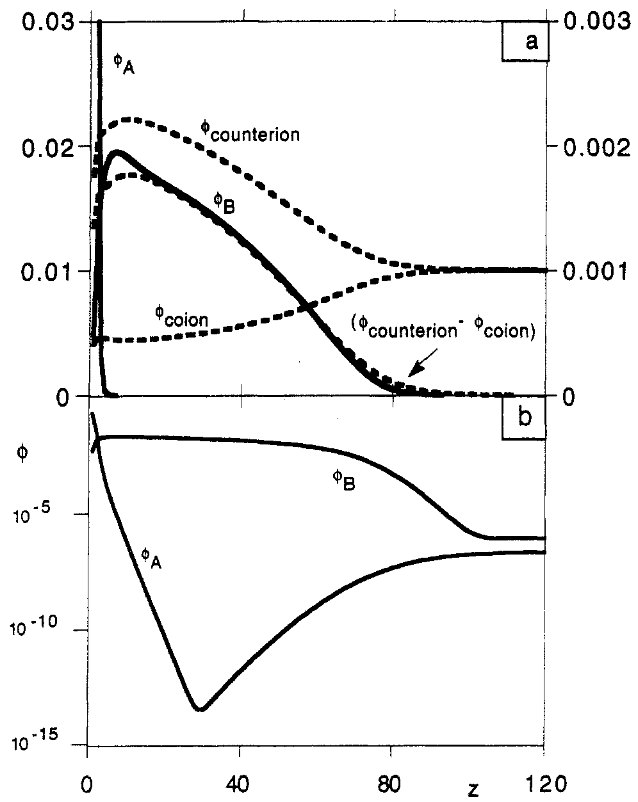

Figure 3. Volume fraction profiles for A segments and B segments (solid curves) and for coions and counterions (dashed curves). Diagram a gives the profiles with a linear scale for ϕ; diagram b, the profiles with a logarithmic scale for ϕ. Parameters: $N_A = 100$, $N_B = 400$, $\alpha_B = 0.1$, $\phi_s^b = 10^{-3}$.

to be a brush since the most important charateristic of a brush, i.e., the strong stretching of the chains, is retained. The stretching of the B block is due to the osmotic pressure of the counterions, which increases the excluded volume interactions considerably.

Furthermore, an irregularity appears at the maximum in the B profile, where (as seen most clearly in the linear plot, Figure 3a) an extra amount of B segments accumulates. For this effect we have the following explanation. Although to a first-order approximation (i.e., the local electroneutrality concept as discussed in section II) the counterion profile is exactly proportional to the B profile, it is clear that it will never decay faster to zero than with the Debye screening length κ^{-1}, which in this case is of the order of 6 lattice layers. Thus, at the solution side of the brush, the counterion profile (or, more precisely, the difference between the profiles of counter- and coions) can almost exactly follow the slowly decaying polymer profile (Figure 3a, dashed curves, right-hand scale). Near the surface, however, $\phi_{Ct} - \phi_{Co}$ cannot follow the much sharper decrease of the B profile. This leads to a surplus of (negative) counterion charge in the depletion layer close to the surface, which slightly deforms the profile of positively charged B segments. A similar phenomenon is observed for nonadsorbing polyelectrolytes for which the profile shows a maximum next to the depletion layer.[19]

Adsorbed Amount. We now turn to the results for the adsorbed amount and discuss them in terms of the four regimes defined in section II. First we consider the dependence on α_B, ϕ_s^b, and N_B. In Figure 4a we show σ as a function of α_B on a log–log plot. All parameters in Figure 4 are the same as those in Figure 3, unless mentioned otherwise. We note that σ is a continuously decreasing function of α_B. Moreover, when $\sigma < 10^{-3}$, corresponding to $\theta_A(=N_A\sigma) < 0.1$, the curve becomes a straight line, indicating a power law behavior $\sigma \propto \alpha_B^{-x}$. The exponent x in this LC region is nearly −2, as predicted in eq 15: $\sigma \propto \upsilon_e^{-1} \propto \alpha_B^{-2}$.

Also in line with eq 15, we see in Figure 4b that σ is a continuously increasing function of ϕ_s^b, and in Figure 4c that it is a continuously decreasing function of N_B (the three curves correspond to an uncharged, an intermediately charged, and a highly charged B block). In all cases shown, we find in the LC regime ($\theta_A < 0.1$) the predicted power law behavior. The slopes corresponding to the exponents of eq 15 are indicated by arrows. In Figure 4d we plot a compilation of Figures 4a,b,c ($\alpha_B = 0.1$), using $N_B^{3/2}\upsilon_e$ as the parameter along the abscissa. The curves fall essentially on one master curve, demonstrating the validity of using an effective excluded volume parameter $\upsilon_e = \alpha_B^2/\phi_s^b$. Moreover, when $\theta_A < 0.1$ the power law equation (15), which was derived for the LC regime in section II, is confirmed. Although in Figure 2 the boundary between the LC and HC regime is taken to be around $\theta_A/(1 - \theta_A) = 1$, Figure 4 clearly shows that deviations from the LC power law start already at a 5 times lower anchor density. Consequently, there must be a rather wide intermediate "regime", obeying neither LC nor HC power laws.

We ascribe the small difference between the dotted curve in Figure 4d (where ϕ_s^b is varied) and the other two curves to the fact that the lattice model incorporates the volume of the salt ions. Because of this volume occupied by the ions, the effect of salt addition is expected to be weaker than on the basis of screening by point charges only.

At high θ_A we would expect to find a "high anchor density" (HC) regime, where σ is independent of N_B, α_B, and ϕ_s^b. We do find a regime where the dependence is much weaker than in the LC regime, but θ_A (proportional to σ) is certainly not constant: with the molecular weights used in this study ($N < 2000$) and with the present choice of χ parameters, the HC regime cannot be reached.

The effect of N_A on the adsorbed amount is somewhat more complicated. In Figure 5 we show σ as a function of N_A for different values of $\upsilon_e = \alpha_B^2/\phi_s^b$, which is a measure for the importance of electrostatic interactions. In the top curve ($\upsilon_e = 0$) we have the uncharged diblock, where electrostatic interactions are absent; in the bottom curve ($\upsilon_e = 10^5$) electrostatic interactions are very strong, and consequently, the adsorbed amount is very low.

The curve for uncharged molecules shows a maximum as discussed earlier by Evers et al.[1] For high N_A the coverage is high and $\sigma \propto N_A^{-1}$, as predicted for the HU regime (eq 1). Left of the maximum σ increases with N_A, but there is no extended region where $\sigma \propto N_A^{3/2}$, as expected according to eq 17 for the LU regime. For small N_A (<20 in this example) the dependence of σ on N_A is very strong and σ becomes too small for the brush regime to be valid. We have here essentially an unsaturated surface and approach the Henry regime where σ depends strongly on N_A because this parameter determines the adsorption energy per molecule. Moreover, in this regime the adsorbed amount (and σ) depends on the polymer solution concentration: it is far below the (pseudo)plateau of the adsorption isotherm.

The curves for the charged molecules in Figure 5 lie entirely below that of uncharged molecules due to the strong electrostatic repulsion. For $\upsilon_e = 10$ ($\alpha_B = 0.1$, $\phi_s^b = 10^{-3}$) the adsorbed amount approaches that of an uncharged polymer in the Henry regime (low N_A) and in the HC regime (high N_A). In the intermediate range of N_A there is still a maximum, and to the left of it the variation of σ with N_A is not too far from the LC prediction $\sigma \propto N_A^{3/2}$ (eq 15), although also here there is no extended

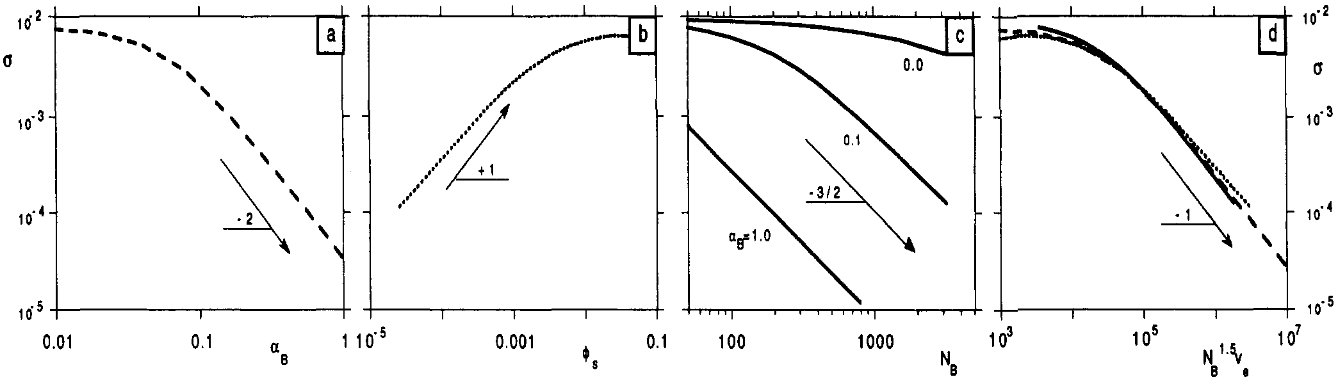

Figure 4. Chain density σ as a function of α_B (a), as a function of $\phi_s{}^b$ (b), and as a function of N_B for three different values of α_B (c). The arrows indicate slopes that correspond to the low anchor density power law behavior (eq 15). Diagram d gives the curves of (a) and (b) and the middle curve of (c) plotted as a function of $N_B{}^{3/2}v_e$. Parameters are the same as in Figure 3, unless indicated otherwise.

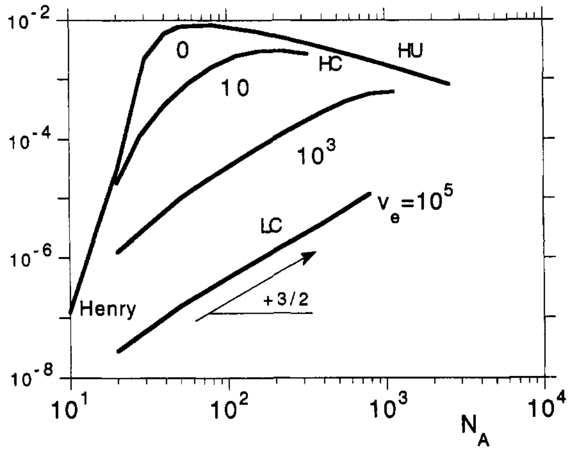

Figure 5. Chain density σ as a function of N_A for various values of the electrostatic excluded volume parameter $v_e = \alpha_B{}^2/\phi_s{}^b$ (indicated). For the curves for $v_e = 10$ and 10^3 the salt concentration is $\phi_s{}^b = 10^{-3}$; for $v_e = 10^5$ this parameter was chosen as $\phi_s{}^b = 10^{-5}$. Other parameters are the same as in Figure 3. The long arrow corresponds to the slope as predicted by eq 15 (LC).

region with a constant exponent. As v_e increases, σ becomes smaller: at $v_e = 10^5$ a nearly straight line is obtained with slope 1.5–1.7, which is very close to the predicted LC power law $\sigma \propto N_A{}^{3/2}$ (eq 15).

We thus find three limiting regimes, where we can understand and predict what is happening: the Henry regime, the high coverage regime (which turns out to be relevant for uncharged molecules only (HU)), and low coverage regime (relevant for charged molecules only (LC)). However, for intermediate values of v_e ($10 \lesssim v_e \lesssim 10^3$) the regimes are not well separated, leading to wide intermediate regions where no simple power law applies.

Layer Thickness. The other interesting quantity of an adsorbed layer is its thickness, for which we use two different definitions. The root-mean-square layer thickness δ_{rms} (which is related to, e.g., the ellipsometric thickness) is weighted by the density of the brush (eq 30). It is therefore rather insensitive to the adsorbed amount and depends mainly on the stretching of individual chains. On the other hand the hydrodynamic layer thickness δ_h (measured by hydrodynamic methods, including dynamic light scattering) is insensitive to the brush density only when the volume fractions are well above 1%.[22] In our calculations, however, we find very low volume fractions and the density has a considerable effect on δ_h.

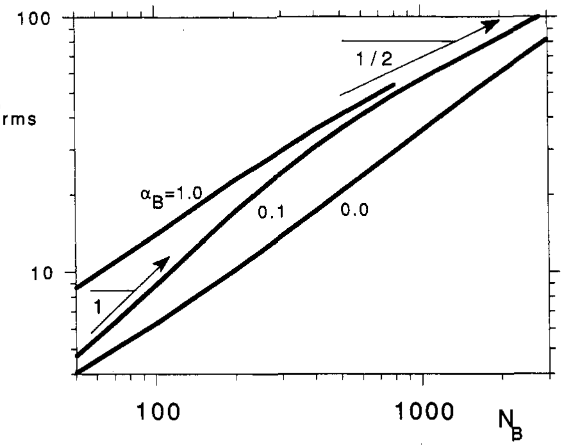

Figure 6. Root-mean-square layer thickness δ_{rms} (in lattice layers) as a function of N_B for three different values of α_B (indicated). Other parameters are the same as in Figure 3; the long arrow corresponds to the slope predicted in eq 14, and the short arrow to the slope in eq 2.

In Figure 6 we show δ_{rms} as a function of N_B for an uncharged diblock ($\alpha_B = 0$) and for two charged diblock copolymers ($\alpha_B = 0.1$, $\alpha_B = 1.0$). If we compare this figure with Figure 4c we see that in all three cases the thickness is an increasing function of the length of the B block, while at the same time the chain density σ decreases with N_B. The charged chains are in the LC regime with $\theta_A(=N_A\sigma) \lesssim 0.1$ (compare Figure 4c) and the layer thickness for long chains more or less follows eq 14, predicting $L \propto N_B{}^{1/2}$ (the corresponding slope is indicated by the long arrow). Two other regimes can be recognized in this figure. For the lowly charged diblock copolymer we find for $N_B < 200$ a regime where δ_{rms} is almost proportional to N_B, corresponding to the HC regime where, according to Figure 2, $L \propto N_B$. At intermediate values for N_B we find a crossover to the LC regime. For the uncharged diblock copolymer at $N_B < 100$ we recognize a "mushroom" regime where B blocks do not interact and $\delta_{rms} \propto N_B{}^{0.5}$. At higher block lengths, chains begin to overlap and this interchain interaction leads to an exponent greater than $^1/_2$. We expect that eventually (at $N_B \gg 10\,000$) the LU regime will be reached and the exponent will decrease again to $^1/_2$.

The effect of increasing the electrostatic interactions on the thickness of the layer is analyzed in Figures 7–9. First we show in Figure 7 that, from inspection of the profiles of B segments, we can distinguish two kinds of behavior. In this figure the B segment volume fraction profiles of an $A_{400}B_{400}$ polymer are plotted for $\alpha_B = 1.0$ at different salt concentrations. At high salt concentrations a decrease in ϕ_s leads to a stretching of the profile and a concomitant decrease in density. For $\phi_s < 10^{-3}$ we still see a decrease in density with decreasing ϕ_s, but now a

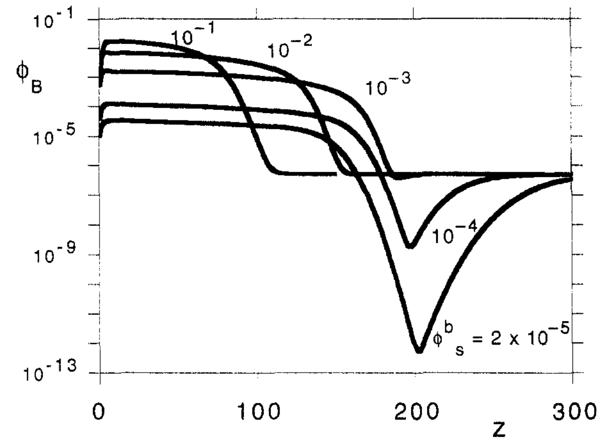

Figure 7. Volume fraction profiles for B segments on a semilogarithmic scale for five salt concentrations (indicated). Other parameters: $N_A = 400$, $N_B = 400$, $\alpha_B = 1$.

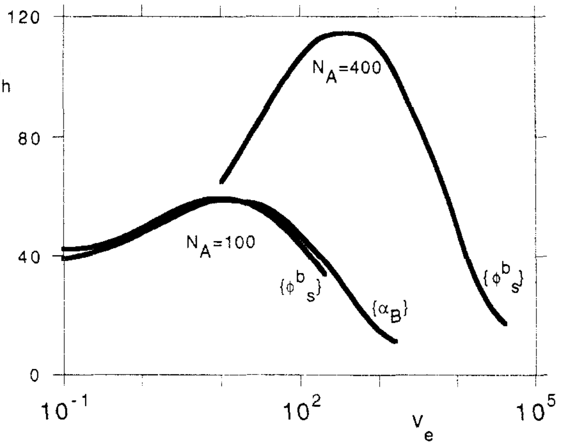

Figure 8. Hydrodynamic layer thickness (in lattice layers) as a function of $v_e = \alpha_B^2/\phi_s^b$ at varying salt concentrations (denoted by $\{\phi_s^b\}$) and at varying segment charges (denoted by $\{\alpha_B\}$). The value of N_A is indicated; N_B equals 400.

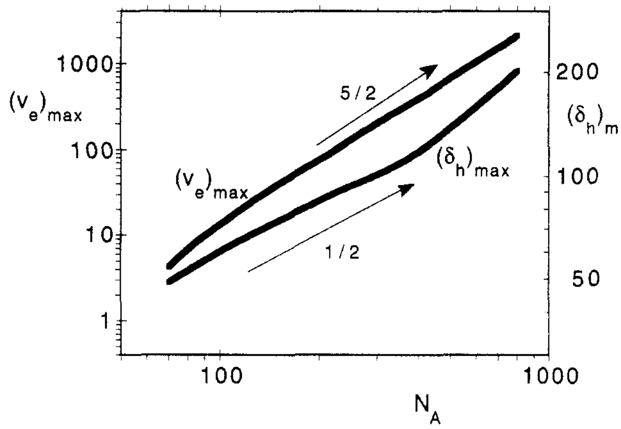

Figure 9. Location (left-hand scale, upper curve) and the height (right-hand scale, lower curve) of the maximum in a curve of δ_h vs v_e (like in Figure 8), as a function of N_A. The upper arrow corresponds to $(v_e)_{max} \propto N_A^{5/2}$; the lower arrow to $(\delta_h)_{max} \propto N_A^{1/2}$. Parameters: $N_B = 400$, $\phi_s^b = 10^{-3}$.

minimum develops at $z \approx 200$ and the stretching of the chains (as measured by the distance between the surface and the minimum) remains constant. These low salt concentrations correspond to the LC power law regime (eq 15). The minimum (not to be confused with the minimum in the A profile shown in Figure 3b) results from the interplay between electrostatic forces acting over a (variable) distance $\sim\kappa^{-1}$ and conformational restrictions (depending on the chain length).

The change in the shape of the profile makes a comparison of RMS layer thicknesses problematic. Instead, we show in Figure 8 the hydrodynamic layer thicknesses corresponding to the profiles in Figure 7. In this figure we plot δ_h as a function of the electrostatic excluded volume v_e, varying either α_B at constant salt concentration (curves marked with $\{\alpha_B\}$) or varying ϕ_s^b at constant charge density (denoted with $\{\phi_s^b\}$). The length of the A block is indicated; N_B equals 400. We find in all three cases a maximum. The increase in δ_h (at low v_e) is a result of the stretching of the chain, the decrease (at high v_e) is caused by chain desorption.

As Figure 8 illustrates, the effects of increasing α_B and decreasing ϕ_s are very similar. Using again the parameter $v_e = \alpha_B^2/\phi_s$ the two curves for $N_A = 100$ overlap nearly completely. The curve for $N_A = 400$, on the other hand, has a distinctly different shape from the curves for $N_A = 100$: it cannot be rescaled in such a way that it overlaps the other two. What we can do, however, is try to predict the location of the maximum $[(v_e)_{max}, (\delta_h)_{max}]$ in the curve. This is shown in Figure 9, where we plot $(v_e)_{max}$ (upper curve) and $(\delta_h)_{max}$ (lower curve) as a function of N_A. Since δ_h is an increasing function of v_e in the HC regime and a decreasing function of v_e in the LC regime, this maximum is located at the upper boundary of the LC regime. Thus the amount of adsorbed A segments at the maximum equals the (constant) boundary value. Using eq 15, which is valid in the LC regime, we find

$$cN_A^{5/2}N_B^{-3/2}/(v_e)_{max} = \text{constant} \qquad (31)$$

This expression leads immediately to $(v_e)_{max} \propto N_A^{5/2}$ and (with eq 14) to $(\delta_h)_{max} \propto N_A^{0.5}$. If we compare the curves to the arrows indicating these theoretical predictions, we find indeed an approximate agreement, although two remarks must be made. Firstly, at low N_A no maximum in δ_h is found and, consequently, the curves end. This is due to the fact that (with the current selection of parameters) for $N_A < 50$ adsorbed amounts never get high enough to leave the LC regime (compare Figure 5). Consequently, the high/low coverage boundary, where the maximum is located, is never reached. Secondly, we find at high N_A deviations that point to the onset of yet another regime. In this regime the A block is no longer flatly adsorbed, leading to an increased total thickness and a stronger dependence on N_A.

VI. Discussion

In this paper we compare a scaling model (section II) describing the adsorption of ionic diblock copolymers with numerical calculations using a SCF model (section III). A first conclusion of our results is that adsorbed amounts are low, typically about a factor of 10 or more lower than for uncharged block copolymers. This has a number of consequences. Firstly, the adsorbing density is lower than the overlapping density. Thus, for this type of polymer, using a reasonable value for the surface affinity, a real brush will never be formed. Still, the adsorbed layer does show brushlike behavior, as a result of the long distance electrostatic repulsion among B segments.

Secondly, the adsorbed amounts are so low that it may be difficult to measure them experimentally. We expect that experiments aimed at measuring the layer thickness will be more successful than those measuring adsorbed amounts only.

Finally, in the SCF calculations the HC regime, where σ should be inversely proportional to N_A and independent of N_B, α_B, and ϕ_s, did not show up. From theoretical considerations[3] such a regime should exists. Possibly, using a longer A block ($N_A \gg 1000$) might lead to this regime. We could not investigate this limit because of our limited computer capacity. What we do reach is a kind of interregime, where σ is still an increasing function of N_A and dependent on the other parameters, even though the dependencies are much weaker than in the low coverage regime.

In the LC regime, the agreement with the simple scaling predictions is surprisingly good, even when $\chi_{BW} = \chi_{AW} = 0.5$, whereas the scaling picture was based upon an athermal solvent. It turns out that the arguments in section II leading to eq 15 offer a good description of the low coverage regime: with the numerical calculations, we do indeed find a power law behavior; the exponents do not differ more than 15% from the predicted values.

For uncharged block copolymers a relation similar to our expression for σ in the low-density regime (eq 17) was also derived by Marquez and Joanny[3] (MJ). For the free energy of a brush (eq 7) they used an alternative expression given by Alexander: $F^B \propto N_B\sigma^{11/6}$ arriving at the slightly different result $\sigma \propto (N_A/N_B)^{6/5}$ instead of $(N_A/N_B)^{3/2}$. Neither of these relations could be confirmed by the SCF calculations (Figures 4c and 5, $\alpha_B = 0$). The assumption that the translational entropy loss of polymers may be neglected is valid only when N_A is sufficiently large ($\chi_{AS}N_A > 100$). Using such a strong anchor block, a low adsorbed amount (typical for the LU regime), can only be found using an extremely long B block, typically of the order ($N_B > 10\,000$). Such chain lengths are beyond our present computer capacity.

From Figure 3 we conclude that the boundary of the low coverage regime is located at an adsorbed amount for the A block around 10% of monolayer coverage. This result can be reformulated using eq 15 and $\theta_A = \sigma N_A$ as

$$(N_B/N_A)^{1/2} > (cN_A\upsilon_e^{-1})^{1/3} \qquad (32)$$

where $c \approx 0.28$ is a numerical constant. The equivalent relation for an uncharged polymer $(N_B/N_A)^{1/2} > (cN_A)^{1/3}$ has already been given by MJ, assuming $\upsilon_B = 1$.

In the numerical calculations we encountered one type of behavior that is not included in the scaling relations depicted in Figure 2. If N_A is smaller than some critical length (in our calculations around 50 segments), the adsorbed amount increases exponentially with N_A. In contrast with the other regimes mentioned so far, calculations show σ to depend on the polymer concentration here. Ultimately (for very short B blocks), the Henry regime will be reached:

$$\sigma \propto \phi_p{}^b e^{aN_A/kT} \qquad (33)$$

where a is a positive numerical constant related to the segmental adsorption energy. The fact that σ depends on $\phi_p{}^b$ for short chains only is in agreement with the results of MJ, who argue that the polymer solution concentration has no effect on the adsorption of diblock copolymers, as long as it is higher than (in their case an extremely low) a critical concentration of the order of e^{-N_A}.

VII. Conclusions

Charged block copolymers with an uncharged anchoring block and a charged buoy block adsorb in low amounts on an uncharged surface, forming a very extended brush of a low density. These charged block copolymers behave qualitatively similar to uncharged block copolymers. In principle, relations valid for uncharged molecules may be applied to the charged ones if an effective excluded volume parameter of charged buoy segments $\upsilon_e = \alpha_B{}^2/\phi_s{}^b$ is substituted for υ_B, the excluded volume parameter of uncharged buoy segments. Here α_B is the valency of the charged segments and $\phi_s{}^b$ is the volume fraction of salt.

If the length of the buoy block is equal to or larger than the length of the anchor and if this block carries a moderate charge, the adsorbed amount decreases even at intermediate salt concentrations ($\upsilon_e > 10$) to extremely low values. This regime can be described very accurately by a simple scaling law: the thickness of the brush (which *is* measurable) is proportional to the geometric mean of the two block lengths and independent of the charge on the buoy block or of the salt concentration.

If the anchor block is much longer than the buoy block, the adsorbed amount can become of the order of one equivalent monolayer, like for adsorbing homopolymers. In this regime no simple scaling law is found. In particular, an inverse proportionality between the chain density and anchor block length N_A, as found for uncharged block copolymers, is not observed: in all relevant cases the chain density is an increasing function of N_A.

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