

On the Monomer Density of Grafted Polyelectrolyte Brushes and Their Interactions

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Most of the modern theories of grafted polyelectrolyte brushes are valid only for moderate stretching of the polyelectrolyte. However, particularly at low ionic strength and high grafting densities, even a moderate charge of the polyelectrolyte can generate a strong stretching. A simple mean field model for strongly stretched grafted polyelectrolyte brushes is suggested, based on an approximate calculation of the partition function of a polyelectrolyte chain. It is shown that the average Boltzmann factor of a possible chain configuration can be approximated by the Boltzmann factor of a configuration with a constant monomer distribution, for which the free energy can be readily obtained. The monomer density in the brush and the interaction between two surfaces with grafted polyelectrolyte brushes could be calculated as a statistical average over all possible configurations. Some simple analytical results are derived, and their accuracy is examined. The dependence of the brush thickness on the electrolyte concentration is investigated, and it is shown that the trapping of a fraction of counterions in the brush influences strongly the thickness of the brush. When two surfaces with grafted polyelectrolyte brushes approach each other more rapidly than the ion diffusion parallel to the surface, the trapping of the counterions between the brushes can affect the interactions by orders of magnitude.

1. Introduction

The grafting of neutral polymers on colloidal surfaces is a well-known method to enhance the stability of colloids, since the steric repulsion between brushes is not highly sensitive to changes in ionic strength or pH, unlike the double layer repulsion induced by surface charges. The predictions of the monomer density distribution and of the thickness of neutral brushes have been challenging problems, the earlier scaling theories assuming a constant density of the monomers within the brush,¹ whereas the most recent ones, originating from a model due to Dolan and Edwards² in which the neutral polymer follows a random walk from the surface in a field generated by the polymer itself, suggested a parabolic density distribution of monomers.³

During the same period, the charged grafted polyelectrolyte chains received considerable less attention than the neutral ones. One of the reasons is that the sufficiently strong charged grafted polyelectrolyte chains are almost completely stretched because of the electrostatic repulsion between their charges, which implies that a step-profile density of the monomers is an accurate approximation.⁴ However, the grafted polyelectrolytes received recently renewed attention because of a plethora of potential applications, such as the possibilities (i) to control the catalytic selectivity of some chemical reactions by varying the thickness of the brush,⁵ (ii) to prevent the adsorption

of proteins on surfaces,⁶ and (iii) to design porous filters for pH-controlled gating.⁷ The recent theories of grafted polyelectrolytes^{8–10} are based on an extension to charged brushes of the approximate solution of the self-consistent field equations obtained for neutral brushes,³ which predicted a parabolic shape for the self-consistent field. However, as pointed out by Shim and Cates,¹¹ the parabolic shape of the self-consistent field is accurate only for a moderate stretching but is not valid for very high and very small stretchings. It should be noted that the Milner–Witten–Cates theory³ leads to the same scaling laws for the thickness of the brush as the step profile (the Alexander model)¹² and that these scaling laws predict vanishing thicknesses for small grafting densities and thicknesses that exceed the length of the grafted polymers at strong stretching.

However, the grafted polyelectrolytes are often strongly stretched, because such stretchings can be sometimes generated by only a moderate charging of the polyelectrolyte. This fact can be understood qualitatively using the following simple analysis. Let us assume that to each grafted chain corresponds an area s^2 on the surface and a parallelepipedic atmosphere with the same bottom area and a length equal to the thickness of the brush. The flux of the electric field through the sides of the parallelepiped is proportional to the inside charge ne . This charge is generated through the dissociation of the polyelectrolyte but also includes the fraction of the polyelectrolyte counterions trapped in the brush and the electrolyte ions.

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The electric field vanishes on the lateral sides of the atmosphere because of the periodicity of the grafting and also on its bottom surface, because of the overall electroneutrality of the system. Therefore, a large electric field is generated at the top of the brush, of the order of $E = ne/\epsilon_0 s^2$, where ϵ is the dielectric constant within the brush and ϵ_0 is the vacuum permittivity. The force required to stretch a polymer is of the order of kT/l , where l is the persistence length.¹³ The force acting on an elementary charge e located at the end of a chain is given by $eE \cong ne^2/\epsilon_0 s^2 \approx kT/l$, which for typical values of the parameters ($\epsilon = 80$, $s^2 = 1000 \text{ \AA}^2$, $l = 10 \text{ \AA}$) leads to a value of the order of unity for n . This result implies that a few charges within the atmosphere are in general sufficient to exert a sensible stretching of the grafted polyelectrolyte. It should be emphasized that the length of the parallelepipedic atmosphere (the thickness of the brush) is in general much larger than its lateral length s , therefore the strong stretching is a result of the confinement of the flux of the electric field to a relatively small area. This strong stretching is in contrast to those of a free polyelectrolyte in a solvent or to a single grafted polyelectrolyte, cases in which much larger charges are required to stretch the polyelectrolyte.

In this paper, a simple modality to calculate the density distribution of the monomers in a grafted polyelectrolyte brush as well as the interaction between surfaces with grafted polyelectrolyte brushes is suggested. The model is an extension to charged polymer brushes of a treatment proposed recently for neutral polymer brushes.¹⁴ It is based on a simplifying assumption applied to a standard Monte Carlo procedure, namely, that the average Boltzmann factor of a possible configuration is dominated by the configuration with the lowest free energy. For a neutral brush immersed in a good solvent, this configuration corresponds to a uniform density of monomers.¹⁴ This constant monomer distribution approximation for each possible configuration was successfully employed by Flory to explain the scaling relation between the length and the gyration radius of a polymer in a good solvent.¹⁵

In polyelectrolytes, the configuration of minimum free energy would be provided by a constant monomer density only if the electrical potential is constant through the brush. Because, as it will be shown in what follows, this condition is almost satisfied, the approximation of a constant monomer distribution is accurate and simplifies considerably the calculations.

2. Monomer Density and Interaction between Polyelectrolyte Brushes

General Framework. The traditional approach to calculate the density distribution of a polyelectrolyte brush consists of generating all the possible configurations of the polyelectrolyte and calculating the total energy corresponding to each configuration. The probability that such a configuration occurs is proportional to its corresponding Boltzmann factor. A simple modality to generate the configurations of a polymer composed of N monomers of length a grafted on a surface is to assume that the polymer is composed of N_l independent pieces of persistence length l , which are connected but can assume any relative orientations. In the absence of any other interactions between monomers (apart from their mutual bonding), the probability that the last monomer of the chain

reaches the distance z is provided by the solution of a random walk¹⁶

$$\Xi_0(z) = 0 \quad (1a)$$

$$z < 0$$

$$\Xi_0(z) = \left(\frac{2}{\pi\sigma^2}\right)^{1/2} \exp\left(-\frac{z^2}{2\sigma^2}\right) \quad (1b)$$

$$z > 0$$

where $\sigma = lN_l^{1/2}$ is the root-mean-square distance of a one-dimensional random walk of N_l steps of length l , if one assumes that the surface represents a perfect reflecting wall for the random walk.¹⁶

In the presence of additional interactions, the probability $\Xi_0(z)$ for a configuration to end up at a distance z must be multiplied by the corresponding Boltzmann factor

$$\Xi(z) = \frac{1}{C_1} \exp\left(-\frac{z^2}{2\sigma^2}\right) \left\langle \exp\left(-\frac{U(z)}{kT}\right) \right\rangle \quad (2a)$$

where $U(z)$ is the total free energy of a configuration and the average $\langle \rangle$ is performed over all possible chain configurations whose last monomer is located at z . The constant C_1 is provided by the normalization

$$\int_0^{Na} \Xi(z) dz = 1 \quad (2b)$$

where $Na = N_l l$ represents the maximum length of the polyelectrolyte.

The main difficulty in eqs 2 is to calculate the Boltzmann factor averaged over all possible configurations. As previously suggested,¹⁴ it will be assumed that the configuration of lowest free energy dominates the partition function (the saddle-point approximation of statistical mechanics) and therefore the average Boltzmann factor of all the configurations which end up at a distance z can be approximated by a Boltzmann factor corresponding to the configuration of lowest free energy. A further approximation is to consider that the configuration of lowest free energy that ends up at the distance z corresponds to a constant density of monomers $\phi(\xi, z)$ distributed between the surface and the distance z

$$\phi(\xi, z) = \frac{N}{s^2 z} \quad (3a)$$

$$0 < \xi < z$$

$$\phi(\xi, z) = 0 \quad (3b)$$

$$\xi > z$$

where N is the number of monomers in a chain and s^2 is the area corresponding to a grafted polyelectrolyte on the surface. The above expressions provide a minimum free energy for neutral chains immersed in good solvents and for charged chains, if the electrical potential would be constant through the brush. Since the calculations show that the potential is almost constant through the brush (see eq 14a and Figure 1), the last condition is almost satisfied and eqs 3 are accurate approximations of the monomer distributions corresponding to the minimum of the free energy.

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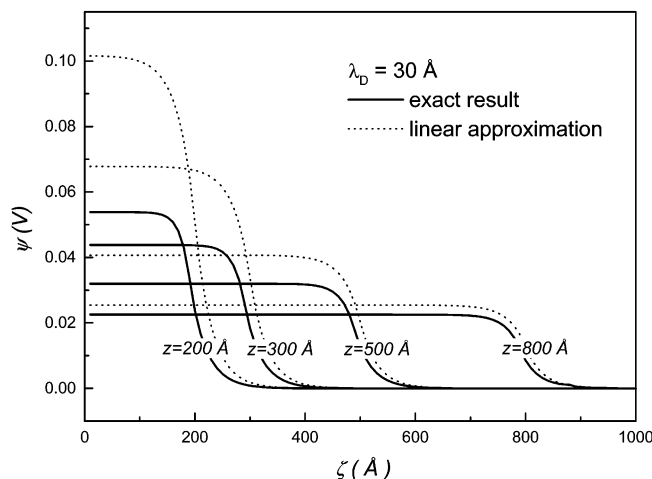


Figure 1. The electric potential as a function of the distance from the surface for various values of z , and $N = 1000$, $a = 1$ Å, $\eta = 0.005$, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$: thick continuous line, exact result; dotted line, linear approximation.

Assuming that each monomer carries an average charge ηe , where η is the degree of dissociation and e is the elementary charge, and that the brush is immersed in an electrolyte solution in contact with an infinite reservoir of concentration c_E , the potential inside the brush obeys the Poisson equation

$$\frac{\partial^2 \psi}{\partial \zeta^2} = \frac{2ec_E}{\epsilon\epsilon_0} \sinh\left(\frac{e\psi}{kT}\right) - \frac{\eta e}{\epsilon\epsilon_0} \frac{N}{s^2 z} \quad (4a)$$

$$0 < \zeta < z$$

$$\frac{\partial^2 \psi}{\partial \zeta^2} = \frac{2ec_E}{\epsilon\epsilon_0} \sinh\left(\frac{e\psi}{kT}\right) \quad (4b)$$

$$\zeta > z$$

where $\psi(\zeta)$ is the electrical potential, ζ the coordinate measured from the surface, ϵ the dielectric constant, ϵ_0 the vacuum permittivity, k the Boltzmann constant, and T the absolute temperature and Boltzmannian distributions were assumed for the electrolyte ions. The solution of eqs 4 is obtained by assuming the continuity of the electric potential and its derivative at $\zeta = z$, and the boundary conditions

$$\frac{\partial \psi}{\partial \zeta} \Big|_{\zeta=0} = -\frac{\sigma_S}{\epsilon\epsilon_0} \quad (5a)$$

and

$$\psi|_{\zeta \rightarrow \infty} = 0 \quad (5b)$$

where σ_S represents the surface charge density. Once the potential has been determined, the total free energy corresponding to a polyelectrolyte configuration that occupies an area s^2 on the surface and whose last monomer is located at the distance z from the surface can be calculated as the sum between a Flory–Huggins free energy, due to the monomer–monomer and monomer–solvent interactions, which does not depend on the charging of the polyelectrolyte and a double layer free energy, due to the charging of the polyelectrolyte and of the grafted surface.

The latter one is composed of the contribution of the electric field¹⁷

$$F_{el}(z) = \frac{s^2}{2} \int_0^\infty \epsilon\epsilon_0 \left(\frac{\partial \psi}{\partial \zeta}\right)^2 d\zeta \quad (6a)$$

and the entropy of electrolyte ions of concentration $c_i(\zeta)$, F_{ent} ¹⁷

$$F_{ent}(z) = kTs^2 \sum_i \int_0^\infty \left(c_i \ln\left(\frac{c_i}{c_E}\right) - c_i + c_E \right) d\zeta \quad (6b)$$

while the Flory–Huggins free energy is given by^{12,18}

$$F_{FH}(z) = s^2 \frac{kT}{a^3} \int_0^z \left(-\frac{1}{2} \tau v^2 \phi^2 + \frac{1}{6} w v^3 \phi^3 \right) d\zeta = \frac{kT}{a^3} \left(-\frac{\tau N^2 v^2}{2s^2 z} + \frac{w N^3 v^3}{6s^4 z^2} \right) \quad (6c)$$

where a is the length of a monomer, v its volume, τ is the dimensionless excluded volume parameter ($\tau < 0$ for a good solvent and $\tau > 0$ for a poor solvent), and w is the third virial coefficient (typically positive and of the order of unity). In this paper it will be assumed that the charges of the surface and polyelectrolyte do not depend on the separation between the two grafted polyelectrolyte brushes and, hence, that the chemical free energy of the double layer is a constant.¹⁷

The probability for a configuration to end up at the distance z is therefore given by

$$\Xi(z) = \frac{1}{C_1} \exp\left(-\frac{z^2}{2\sigma^2}\right) \exp\left(-\frac{F_{el} + F_{ent} + F_{FH}}{kT}\right) \quad (7)$$

The average monomer density $\Phi(z)$ of the brush is the statistical average of the contributions of all configurations that end up at all possible positions between z and Na . The contribution at the location ζ of a configuration which ends up at a distance z equals $\phi(\zeta, z) = N/s^2 z$ when $\zeta < z$ and $\phi(\zeta, z) = 0$ when $\zeta > z$; therefore the statistical average of configurations is given by¹⁴

$$\Phi(z) = \int_z^{Na} \Xi(\zeta) \frac{N}{s^2 \zeta} d\zeta \quad (8)$$

When two surfaces with grafted polyelectrolyte approach each other, the probability for a chain grafted on surface “1” to end up at the distance z_1 from the first surface, whereas a chain which starts on surface “2” to end up at position z_2 from the surface “2” is given by

$$\Xi(z_1, z_2) = \frac{1}{C_2} \exp\left(-\frac{z_1^2}{2\sigma^2}\right) \exp\left(-\frac{z_2^2}{2\sigma^2}\right) \exp\left(-\frac{U(z_1, z_2)}{kT}\right) \Bigg|_{z_1, z_2} \quad (9a)$$

where the average is performed over all possible configurations which end up at z_1 and z_2 , respectively. The normalization constant C_2 is obtained by taking into account that neither chain can be longer than Na and

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both of them should end up somewhere between 0 and $2d$

$$\int_0^\xi \int_0^\xi \Xi(z_1, z_2) dz_1 dz_2 = 1 \quad (9b)$$

where ξ is the shortest of the distances Na and $2d$.

Assuming, as previously, that the partition function is dominated by the configurations with constant monomer density between each of the surfaces and the position z_1 and z_2 , respectively, eq 9a becomes

$$\Xi(z_1, z_2) = \frac{1}{C_2} \exp\left(-\frac{z_1^2}{2\sigma^2}\right) \exp\left(-\frac{z_2^2}{2\sigma^2}\right) \exp\left(-\frac{F_{el} + F_{ent} + F_{FH}}{kT}\right) \quad (10)$$

where the integrals of the electric (6a), entropic (6b), and excluded volume contributions (6c) are this time integrated between 0 and $2d$. The total free energy of the interacting brushes, per unit area, is the statistical average over all possible configurations, given by

$$F_{\text{brushes}} = \frac{1}{s^2} \int_0^\xi \int_0^\xi (F_{el} + F_{ent} + F_{FH}) \Xi(z_1, z_2) dz_1 dz_2 \quad (11a)$$

The force per unit area between surfaces can be obtained from the derivative of the free energy per unit area, eq 11a, with respect to the separation distance $2d$

$$\Pi(2d) = -\frac{\partial F_{\text{brushes}}}{\partial(2d)} \quad (11b)$$

3. Monomer Distribution in a Grafted Polyelectrolyte Brush Immersed in an Infinite Reservoir

A. Linear Approximation. The linear approximation of the Poisson–Boltzmann equation ($\sinh(e\psi/kT) \approx e\psi/kT$) is in general accurate only for small potentials ($\psi < kT/e$). However, it offers insight into the qualitative behavior, even at larger potentials. In the linear approximation, the Poisson–Boltzmann equations (4) become

$$\frac{\partial^2 \psi}{\partial \xi^2} = \frac{\psi}{\lambda_D^2} - \frac{\eta e}{\epsilon \epsilon_0 s^2 z} \quad (12a)$$

$$0 < \xi < z$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = \frac{\psi}{\lambda_D^2} \quad (12b)$$

$$\xi > z$$

where $\lambda_D = (\epsilon \epsilon_0 kT/2e^2 c_E)^{1/2}$ is the Debye–Hückel length, with the solutions

$$\psi(\xi) = \frac{\eta e}{\epsilon \epsilon_0 s^2 z} \lambda_D^2 + A_1 \exp\left(\frac{\xi}{\lambda_D}\right) + A_2 \exp\left(-\frac{\xi}{\lambda_D}\right) \quad (13a)$$

$$0 < \xi < z$$

$$\psi(\xi) = A_3 \exp\left(\frac{\xi}{\lambda_D}\right) + A_4 \exp\left(-\frac{\xi}{\lambda_D}\right) \quad (13b)$$

$$\xi > z$$

Assuming a neutral grafted surface ($\sigma_s = 0$), with the boundary conditions eqs 5a,b, and using the continuity of

the electric potential and its derivative at $\xi = z$, one obtains

$$\psi(\xi) = \frac{\eta e}{\epsilon \epsilon_0 s^2 z} \lambda_D^2 \left[1 - \cosh\left(\frac{\xi}{\lambda_D}\right) \exp\left(-\frac{z}{\lambda_D}\right) \right] \quad (14a)$$

$$\xi < z$$

$$\psi(\xi) = \frac{\eta e}{\epsilon \epsilon_0 s^2 z} \lambda_D^2 \sinh\left(\frac{z}{\lambda_D}\right) \exp\left(-\frac{\xi}{\lambda_D}\right) \quad (14b)$$

$$\xi > z$$

The electrical potential through the brush (eq 14a) is almost constant, since for $(z - \xi)/\lambda_D \gg 1$, $\cosh(\xi/\lambda_D) \exp(-z/\lambda_D) \approx (1/2) \exp(-(z - \xi)/\lambda_D) \ll 1$ and varies notably only when $(z - \xi)/\lambda_D$ is of the order of unity. A typical solution of eqs 14 is compared in Figure 1 to the results obtained from the numerical integration of the Poisson–Boltzmann equations (4a,b) for various values of z (the maximum length of a configuration) and the following values of the parameters: $N = 1000$, $a = 1$ Å, $\eta = 0.005$, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$. The linear approximation is in general not accurate for small values of z , which correspond to large potentials; however, these configurations have also large double layer energies and, therefore, small contributions to the final statistical average.

In the linear approximation, the double layer energy of a configuration of distance z , obtained from the integration of eqs 6a and 6b, is given by

$$F_{DL}(z) = \int_0^z (F_{el} + F_{ent}) d\xi \approx s^2 \frac{\epsilon \epsilon_0}{2} \int_0^z \left(\left(\frac{d\psi(\xi)}{d\xi} \right)^2 + \frac{\psi^2(\xi)}{\lambda_D^2} \right) d\xi = \frac{\lambda_D^2 \eta^2 e^2 N^2}{4 \epsilon \epsilon_0 s^2 z^2} \left(4z + 4\lambda_D \exp\left(-\frac{2z}{\lambda_D}\right) \cosh^2\left(\frac{z}{\lambda_D}\right) - 3\lambda_D - \lambda_D \exp\left(-\frac{4z}{\lambda_D}\right) \right) \quad (15)$$

For a charged polyelectrolyte brush, the double layer energy, eq 15 is in general much larger than the excluded volume interaction, eq 6c. The probability for a brush to end up at a distance z (eq 7) is represented in Figure 2a, for the above values of the parameters and $l = 10$ Å, $\sigma = lN^{1/2} = 100$ Å, $\tau = -1.0$, $w = 0.0$, $v = 1.0$ Å³. Since the selected area corresponding to a grafted chain on a surface is relatively small ($s^2 = 1000$ Å²), low dissociation fractions (of the order of a few percent) are sufficient to generate large electrical potentials and consequently strong stretching of the brush. A qualitative analysis starting from eq 14a shows that the potential at the grafting surface, for a strong stretching ($z \approx Na$), is of the order of

$$\psi(0) \approx \frac{\eta e}{\epsilon \epsilon_0} \frac{N \lambda_D^2}{s^2 z} \approx \frac{\eta e}{\epsilon \epsilon_0} \frac{\lambda_D^2}{s^2 a} \quad (16)$$

This implies that even at moderate electrolyte concentrations ($c_E = 0.01$ M, $\lambda_D = 30$ Å) and small dissociation fractions η , $\psi(0) > kT/e$ and the linear approximation of the Poisson–Boltzmann equations fails. An approximation, which is more accurate at large potentials, is suggested below.

B. Nonlinear Approximation. The numerical solution of the Poisson–Boltzmann system of eqs 4a and b, as well as the analytical solutions (eqs 14) of its linear approximation (eqs 12) indicate that the potential is almost constant through each configuration, until a distance of

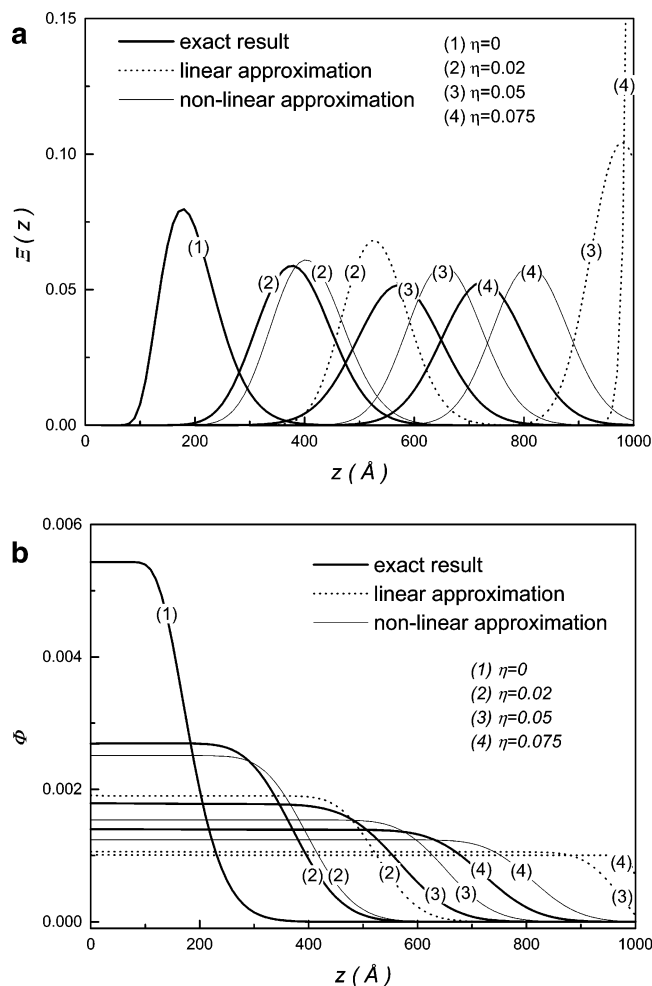


Figure 2. (a) The probability for a chain whose last monomer is located at a distance z for $N = 1000$, $a = 1$ Å, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$, $\sigma = 100$ Å, $\tau = -1.0$, $w = 0.0$, $v = 1$ Å³, and various degrees of dissociation η : thick continuous line, exact result; dotted line, linear approximation; continuous line, nonlinear approximation. (b) The monomer density in brushes with various degrees of dissociation for $N = 1000$, $a = 1$ Å, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$, $\sigma = 100$ Å, $\tau = -1.0$, $w = 0.0$, and $v = 1$ Å³: thick continuous line, exact result; dotted line, linear approximation; continuous line, nonlinear approximation.

the order of λ_D from the maximum length of the configuration (see Figure 1). A simple approximation consists of assuming a constant potential $\bar{\psi}$ between 0 and z . Outside the brush (for $z < \zeta < \infty$), the traditional Poisson–Boltzmann equation is valid and can be integrated to provide¹⁹

$$-\frac{d\psi(\zeta)}{d\zeta}\bigg|_z = \frac{2kT}{\lambda_D e} \sinh\left(\frac{e\psi(z)}{2kT}\right) \quad (17a)$$

where the electric field at z is related to the charge distribution between 0 and z (due to the polyelectrolyte and electrolyte ions), which is given by

$$\int_0^z \left(\frac{\eta e N}{\epsilon \epsilon_0 s^2 z} - \frac{2 e c_E}{\epsilon \epsilon_0} \sinh\left(\frac{e\bar{\psi}}{kT}\right) \right) d\zeta = \frac{\eta e N}{\epsilon \epsilon_0 s^2} - \frac{2 e c_E z}{\epsilon \epsilon_0} \sinh\left(\frac{e\bar{\psi}}{kT}\right) \quad (17b)$$

By combining eqs 17a and b, one obtains

$$\sinh\left(\frac{e\bar{\psi}}{kT}\right) + \frac{2\lambda_D}{z} \sinh\left(\frac{e\bar{\psi}}{2kT}\right) = \frac{\eta N}{2c_E s^2 z} \quad (17c)$$

from which a numerical solution for $\bar{\psi}$ can be readily obtained. When the potential is sufficiently large, $\sinh(e\bar{\psi}/2kT) \ll \sinh(e\bar{\psi}/kT)$ (in many cases λ_D is also much smaller than z), and eq 17c reduces to

$$2c_E \sinh\left(\frac{e\bar{\psi}}{kT}\right) = \frac{\eta N}{s^2 z} \quad (17d)$$

which simply states that the constant potential $\bar{\psi}$ is such that the electrolyte ions compensate exactly the charge of the polyelectrolyte. The solution of eq 17d is provided by

$$\bar{\psi} \approx \frac{kT}{e} \ln\left(\left(\left(\frac{\eta N}{2c_E s^2 z}\right)^2 + 1\right)^{1/2} - \frac{\eta N}{2c_E s^2 z}\right) \quad (18)$$

As a matter of fact, the approximate surface potential predicted by the linear analysis can be derived using the same assumption of a vanishing charge distribution near the grafting surface. Indeed, $\eta N/s^2 z = 2c_E \sinh(e\bar{\psi}(0)/kT) \approx 2ec_E \bar{\psi}(0)/kT = \epsilon \epsilon_0 \bar{\psi}(0)/e\lambda_D^2$, which coincides with eq 16.

In the region of constant potential, the electrostatic energy vanishes (because $d\psi/d\zeta \equiv 0$) while the entropic contribution is given by

$$F_{DL}(z) = kTs^2 \sum_i \int_0^z \left(c_i \ln\left(\frac{c_i}{c_E}\right) - c_i + c_E \right) d\zeta = c_E kTs^2 z \left(\frac{e\bar{\psi}}{kT} \exp\left(\frac{e\bar{\psi}}{kT}\right) - \frac{e\bar{\psi}}{kT} \exp\left(-\frac{e\bar{\psi}}{kT}\right) - \exp\left(\frac{e\bar{\psi}}{kT}\right) - \exp\left(-\frac{e\bar{\psi}}{kT}\right) + 2 \right) \quad (19)$$

The contribution to the double layer free energy from the region between z and infinity can be calculated by solving the corresponding traditional Poisson–Boltzmann equation. However, the value of $\bar{\psi}$ given by eq 18 is an overestimate of the potential inside the brush (since it implies a potential large enough to cancel the charge density in the brush) and consequently eq 19 is also an overestimate of the free energy of the double layer between 0 and z . Therefore, eq 19 can be used as an approximation of the total double layer free energy for the configuration that ends up at the distance z .

In Figure 2a, the probability for a brush to end up at a distance z is calculated using the simple nonlinear approximation based on eqs 18 and 19; this approximation provides in general a much better agreement with the numerical calculations based on the nonlinear equations than the linear approximation at high potentials. The corresponding monomer density distributions, statistically averaged over all possible configurations, are plotted in Figure 2b.

The thickness of the grafted polyelectrolyte brush can be described roughly by the length of the most probable configuration, which is provided by the solution of

$$\frac{d}{dz} \left(\exp\left(-\frac{z^2}{2\sigma^2}\right) \exp\left(-\frac{F_{DL}(z) + F_{FH}(z)}{kT}\right) \right) = 0 \quad (20)$$

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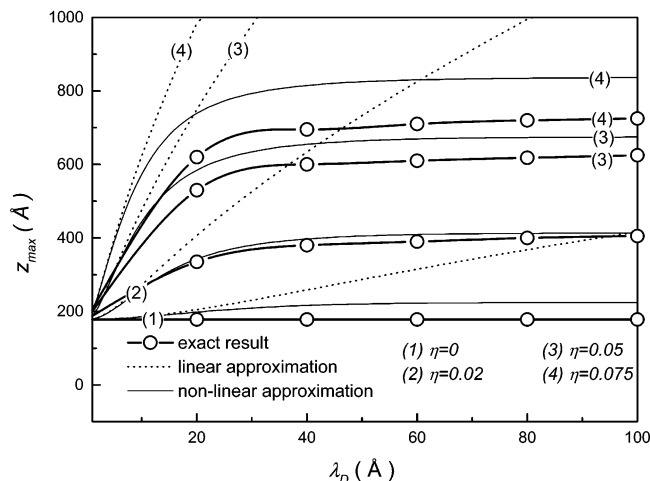


Figure 3. The thickness of the brush (the length of the most probable configuration) vs the Debye–Hückel length for various degrees of dissociation and $N = 1000$, $a = 1$ Å, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$, $\sigma = 100$ Å, $\tau = -1.0$, $w = 0.0$, and $v = 1$ Å³.

The dependence of the length of the most probable configuration on the electrolyte concentration is plotted in Figure 3. The brush is strongly stretched for most ionic strengths. As already noted, this occurs because at lower electrolyte concentrations there are not many electrolyte counterions to screen the polyelectrolyte charges; therefore the potential in the brush is high, even for small degrees of dissociation.

4. Monomer Distribution in a Grafted Polyelectrolyte Brush Immersed in a Finite Reservoir

A. Linear Approximation. As noted in previous sections, even dissociation of the order of a few percent of the grafted polyelectrolyte brushes might be enough to stretch the chains, particularly at low electrolyte concentrations. In an infinite reservoir, the density of the counterions generated by the dissociation of the polyelectrolyte groups vanishes, and only the electrolyte ions are left to compensate the brush charge. An interesting situation occurs when the brush is immersed in a finite reservoir, because a fraction of the counterions of the polyelectrolyte remains trapped inside the brush, neutralizing a part of its charge. In this case, assuming a finite reservoir of length $L > Na$ (see Figure 4), the Poisson–Boltzmann equations become

$$\frac{\partial^2 \psi}{\partial \xi^2} = \frac{e \left(c_1 \exp\left(\frac{e\psi}{kT}\right) - c_2 \exp\left(-\frac{e\psi}{kT}\right) \right)}{\epsilon \epsilon_0} - \frac{\eta e}{\epsilon \epsilon_0} \frac{N}{s^2 z} + \frac{\alpha e N}{\epsilon \epsilon_0 s^2 L} \exp\left(\frac{e\psi}{kT}\right) \quad (21a)$$

$$0 < \xi < z$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = \frac{e \left(c_1 \exp\left(\frac{e\psi}{kT}\right) - c_2 \exp\left(-\frac{e\psi}{kT}\right) \right)}{\epsilon \epsilon_0} + \frac{\alpha e N}{\epsilon \epsilon_0 s^2 L} \exp\left(\frac{e\psi}{kT}\right) \quad (21b)$$

$$z < \xi < L$$

where the constants c_1 , c_2 , and α are related to the concentrations of counterions of the polyelectrolyte and

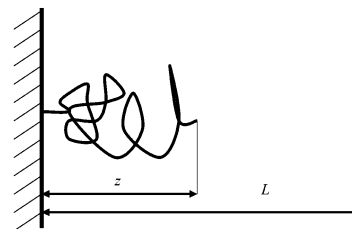


Figure 4. A configuration of a polyelectrolyte molecule, grafted on a surface, whose last monomer is located at the distance z , immersed in a finite reservoir of length L .

of the electrolyte ions through the expressions

$$\int_0^L c_1 \exp\left(\frac{e\psi(\xi)}{kT}\right) d\xi = c_E L \quad (22a)$$

$$\int_0^L c_2 \exp\left(-\frac{e\psi(\xi)}{kT}\right) d\xi = c_E L \quad (22b)$$

$$\int_0^L \alpha \exp\left(\frac{e\psi(\xi)}{kT}\right) d\xi = \eta L \quad (22c)$$

Assuming as above that the grafting surface is not charged ($\sigma_s = 0$), the electroneutrality of the system leads to the boundary conditions

$$\left. \frac{\partial^2 \psi}{\partial \xi^2} \right|_{\xi=0} = 0 \quad (23a)$$

$$\left. \frac{\partial^2 \psi}{\partial \xi^2} \right|_{\xi=L} = 0 \quad (23b)$$

An analytical solution of the above system can be obtained in the linear approximation as follows. The Poisson–Boltzmann equations become

$$\frac{\partial^2 \psi}{\partial \xi^2} = a_1 \psi + a_2 - a_3 \quad (24a)$$

$$0 < \xi < z$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = a_1 \psi + a_2 \quad (24b)$$

$$z < \xi < L$$

where

$$a_1 = \frac{e^2}{\epsilon \epsilon_0 kT} \left(c_1 + c_2 + \alpha \frac{N}{s^2 L} \right) \quad (25a)$$

$$a_2 = \frac{e}{\epsilon \epsilon_0} \left(c_1 - c_2 + \alpha \frac{N}{s^2 L} \right) \quad (25b)$$

$$a_3 = \eta \frac{eN}{\epsilon \epsilon_0 s^2 z} \quad (25c)$$

The solution of the linear system (24), which obeys the boundary conditions (23a,b) and has ψ and $d\psi/d\xi$ continuous at z is determined up to an arbitrary constant potential, which is irrelevant for the problem. It should be, however, noted that eqs 22 imply that the ion concentrations reach the values c_1 , c_2 , and $\alpha N/s^2 L$ at the point where $\psi = 0$. Selecting this point to be at $\xi = L$

(the far side of the reservoir), one obtains the solution

$$\psi(\zeta) = \frac{a_3}{a_1} \left(1 - \frac{\sinh(za_1^{1/2})}{\sinh(La_1^{1/2})} - \frac{\sinh((L-z)a_1^{1/2})}{\sinh(La_1^{1/2})} \cosh(\zeta a_1^{1/2}) \right) \quad (26a)$$

$$0 < \zeta < z$$

$$\psi(\zeta) = \frac{a_3 \sinh(za_1^{1/2})}{a_1 \sinh(La_1^{1/2})} (\cosh((L-\zeta)a_1^{1/2}) - 1) \quad (26b)$$

$$z < \zeta < L$$

Since in the linear approximation

$$\int_0^L \exp\left(\frac{e\psi(\zeta)}{kT}\right) d\zeta = L + \frac{e}{kT} \int_0^L \psi(\zeta) d\zeta = L + \frac{e}{kT} \frac{a_3}{a_1} \left(z - L \frac{\sinh(za_1^{1/2})}{\sinh(La_1^{1/2})} \right) \quad (27)$$

Equations 22 become

$$c_1 = \frac{c_E}{1 + \frac{e}{kT} \frac{a_3}{a_1} \left(\frac{z}{L} - \frac{\sinh(za_1^{1/2})}{\sinh(La_1^{1/2})} \right)} \quad (28a)$$

$$c_2 = \frac{c_E}{1 - \frac{e}{kT} \frac{a_3}{a_1} \left(\frac{z}{L} - \frac{\sinh(za_1^{1/2})}{\sinh(La_1^{1/2})} \right)} \quad (28b)$$

$$\alpha = \frac{\eta}{1 + \frac{e}{kT} \frac{a_3}{a_1} \left(\frac{z}{L} - \frac{\sinh(za_1^{1/2})}{\sinh(La_1^{1/2})} \right)} \quad (28c)$$

It should be again emphasized that the linear approximation is accurate only for $\psi \ll kT/e$. Whereas the solutions for the potential (eqs 26) are qualitatively (but not quantitatively!) valid even for $\psi > kT/e$, eqs 28 fail in this case and might even predict negative concentrations of co-ions.

Equations 28a–c can be solved for the constants c_1 , c_2 , and α as functions of η , c_E , z , and L . Then the double layer free energy of a configuration that ends up at the distance z in a reservoir of finite length L is given by

$$F_{DL}(z) = \frac{s^2 \epsilon \epsilon_0}{2} \int_0^L \left(\frac{d\psi(\zeta)}{d\zeta} \right)^2 d\zeta + kTs^2 \int_0^L \left[\frac{ec_1}{kT} \exp\left(\frac{e\psi}{kT}\right) \ln\left(\frac{c_1}{c_E}\right) - \frac{ec_2}{kT} \exp\left(-\frac{e\psi}{kT}\right) \ln\left(\frac{c_2}{c_E}\right) - c_1 \exp\left(\frac{e\psi}{kT}\right) - c_2 \exp\left(-\frac{e\psi}{kT}\right) + 2c_E + \frac{e}{kT} \frac{\alpha N}{s^2 L} \exp\left(\frac{e\psi}{kT}\right) \ln\left(\frac{\alpha}{\eta}\right) - \frac{\alpha N}{s^2 L} \exp\left(\frac{e\psi}{kT}\right) + \frac{\eta N}{s^2 L} \right] d\zeta \quad (29)$$

where it was taken into account that not only the electrolyte ions but also the counterions of the polyelectrolyte chains contribute to the entropy of the double layer, because, as a result of the double layer formation, their distribution differs from the average density $\eta N/s^2 L$.

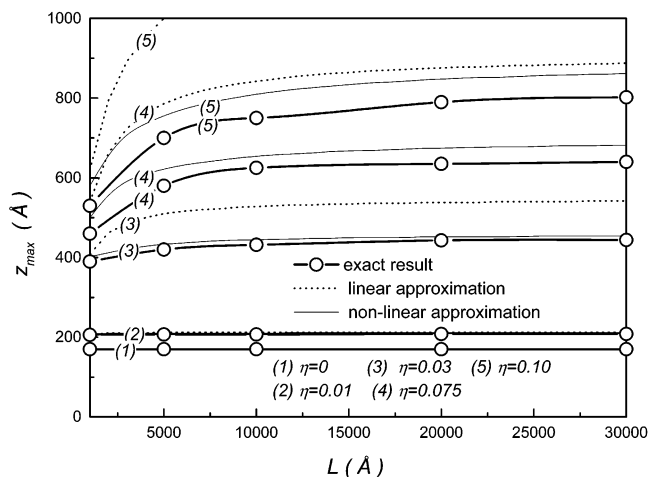


Figure 5. The dependence of the brush thickness (the length of the most probable configuration) on the finite reservoir size L for various degrees of dissociation and $N = 1000$, $a = 1$ Å, $c_E = 0.01$ M, $s^2 = 1000$ Å², $\epsilon = 80$, $\sigma = 100$ Å, $\tau = -1.0$, $w = 0.0$, and $v = 1.0$ Å³.

B. Nonlinear Approximation. The linear approximation in general is not accurate for potentials larger than kT/e . A simple approximation, which is more accurate than the linear one at larger potentials, can be obtained by assuming that the electrical potential is constant along the configuration that ends at the distance z and vanishes in the rest of the reservoir. This average potential can be obtained, as in section 3B, from the condition of vanishing of the total charge density inside the brush

$$\eta \frac{N}{s^2 z} + c_2 \exp\left(-\frac{e\bar{\psi}}{kT}\right) - \left(c_1 + \alpha \frac{N}{s^2 L}\right) \exp\left(\frac{e\bar{\psi}}{kT}\right) = 0 \quad (30a)$$

The conservation of the number of ions in the reservoir (eqs 22) leads to

$$c_1 = \frac{c_E L}{z \exp\left(\frac{e\bar{\psi}}{kT}\right) + L - z} \quad (30b)$$

$$c_2 = \frac{c_E L}{z \exp\left(-\frac{e\bar{\psi}}{kT}\right) + L - z} \quad (30c)$$

$$\alpha = \frac{\eta L}{z \exp\left(\frac{e\bar{\psi}}{kT}\right) + L - z} \quad (30d)$$

The solution of $\bar{\psi}$ from eqs 30a–d can be used to obtain the following approximate expression for the double layer free energy

$$F_{DL}(z) = kTs^2 z \left[\frac{ec_1}{kT} \exp\left(\frac{e\bar{\psi}}{kT}\right) \ln\left(\frac{c_1}{c_E}\right) - \frac{ec_2}{kT} \exp\left(-\frac{e\bar{\psi}}{kT}\right) \ln\left(\frac{c_2}{c_E}\right) - c_1 \exp\left(\frac{e\bar{\psi}}{kT}\right) - c_2 \exp\left(-\frac{e\bar{\psi}}{kT}\right) + 2c_E + \frac{e}{kT} \frac{\alpha N}{s^2 L} \exp\left(\frac{e\bar{\psi}}{kT}\right) \ln\left(\frac{\alpha}{\eta}\right) - \frac{\alpha N}{s^2 L} \exp\left(\frac{e\bar{\psi}}{kT}\right) + \frac{\eta N}{s^2 L} \right] \quad (31)$$

In Figure 5, the length of the most probable configuration is plotted as a function of the reservoir length L for

$N = 1000$, $a = 1 \text{ \AA}$, $l = 10 \text{ \AA}$, $\sigma = lN^{1/2} = 100 \text{ \AA}$, $\eta = 0.01$, $c_E = 0.01 \text{ M}$, $s^2 = 1000 \text{ \AA}^2$, $\epsilon = 80$, $\tau = -1.0$, $w = 0.0$, and $v = 1.0 \text{ \AA}^3$. For small reservoirs, most counterions are not able to leave the brush; hence the overall charging is small. This situation is not unlike some molecular dynamics simulations,²⁰ where the counterions were explicitly taken into account, but the size of the system was limited (because of computational requirements). However, when the brush is embedded in an infinitely large reservoir and chemical equilibrium is reached, there are no counterions left in the brush, and a stronger stretching is achieved.

5. The Interactions between Surfaces with Grafted Polyelectrolyte Brushes: The Role of the Rate of Approach of the Surfaces

A. Thermodynamic Equilibrium (Slow Approach of the Surfaces). The general formalism for the interaction between two surfaces with grafted polyelectrolyte brushes, presented in this paper in section 2, implies that, for each separation distance $2d$, the Poisson–Boltzmann equations have to be solved for every possible configuration of the chains, ending up at z_1 and z_2 , where $0 < z_1 < \xi$, $0 < z_2 < \xi$, ξ being the smallest between the maximum length of a chain, Na , and the distance $2d$ between surfaces. Since such calculations are tedious, here a much simpler analysis is used for the interaction between surfaces. It was shown previously¹⁴ that for neutral brushes and good solvents, the symmetric configurations (for which $z_1 = z_2$) are the most important contributions to the free energy, and (at least at strong repulsion) the contributions of the other configurations can be neglected. Such an approximation is reasonable because for a single brush only the configurations around the most probable one have significant probabilities $\Xi(z)$ (see Figure 2a). For two brushes, $\Xi(z_1, z_2) \approx \Xi(z_1)\Xi(z_2)$ and for the asymmetric configurations ($z_1 \neq z_2$), at least one of the probabilities is small.

For the symmetric configurations with $z < d$, a constant monomer density between surface and z will be considered for each brush, while for $z > d$ (physical overlap of the brushes) it will be assumed that all the monomers are homogeneously distributed between the two surfaces.

In the absence of a surface charge density on the plates ($\sigma_s = 0$), the solution of the Poisson–Boltzmann equations (4a and b) are obtained for the boundary conditions

$$\left. \frac{\partial \psi}{\partial \xi} \right|_{\xi=0} = 0 \quad (32a)$$

$$\left. \frac{\partial \psi}{\partial \xi} \right|_{\xi=d} = 0 \quad (32b)$$

and the requirements of continuity of $\psi(\xi)$ and $d\psi(\xi)/d\xi$ at $\xi = z$. The free energy of each configuration that ends up at the distance z is obtained from eqs 6a–c, while the free energy of the system is obtained from eqs 9–11, by considering only the symmetric configurations

$$F_{\text{brushes}} = \int_0^{2d} (F_{\text{el}}(z) + F_{\text{ent}}(z) + F_{\text{FH}}(z))\Xi(z) dz \quad (33)$$

For small charges of the brush or large ionic strengths, one can employ the linear approximation of the Poisson–Boltzmann equations (eqs 12) with the boundary conditions (eqs 32). The solution that obeys the continuity

conditions at $\xi = z$ is given by

$$\psi(\xi) = \frac{\eta e}{\epsilon \epsilon_0} \frac{N}{s^2 z} \lambda_D^2 \left[1 - \cosh\left(\frac{\xi}{\lambda_D}\right) \frac{\sinh\left(\frac{d-z}{\lambda_D}\right)}{\sinh\left(\frac{d}{\lambda_D}\right)} \right] \quad (34a)$$

$0 < \xi < z$

$$\psi(\xi) = \frac{\eta e}{\epsilon \epsilon_0} \frac{N}{s^2 z} \lambda_D^2 \cosh\left(\frac{d-\xi}{\lambda_D}\right) \frac{\sinh\left(\frac{z}{\lambda_D}\right)}{\sinh\left(\frac{d}{\lambda_D}\right)} \quad (34b)$$

$z < \xi < d$

Consequently the total double layer free energy is given by

$$F_{\text{DL}}(z) = \frac{\eta^2 e^2}{4\epsilon \epsilon_0} \frac{N^2 \lambda_D^2}{s^2 z^2 \sinh^2\left(\frac{d}{\lambda_D}\right)} \left[(2z - \lambda_D) \sinh\left(\frac{2d}{\lambda_D}\right) + \lambda_D \left(\sinh\left(\frac{2d-2z}{\lambda_D}\right) + \sinh\left(\frac{2z}{\lambda_D}\right) - 2z \right) \right] \quad (35)$$

In Figure 6a, the force per unit area between surfaces with grafted polyelectrolyte brushes, plotted as a function of their separation distance $2d$, calculated in the linear approximation, is compared with the numerical solution of the nonlinear Poisson–Boltzmann equations, for a system with $N = 1000$, $a = 1 \text{ \AA}$, $c_E = 0.01 \text{ M}$, $s^2 = 1000 \text{ \AA}^2$, $\epsilon = 80$, $l = 10 \text{ \AA}$, $\sigma = 100 \text{ \AA}$, $\tau = -1.0$, $w = 0.0$, $v = 1.0 \text{ \AA}^3$ and various degrees of dissociation. As expected, even moderate degrees of dissociation of the polyelectrolyte generate large potentials, for which the linear approximation fails.

B. Quasi-Thermodynamical Equilibrium (Rapid Approach of the Surfaces). The motion of the counterions along the distance perpendicular to the surfaces is in general sufficiently rapid to reach the thermal equilibrium along this direction during the interaction. If the approach of the surfaces is slow, the counterions of the polyelectrolyte chains can also reach thermal equilibrium with the infinite reservoir. However, if the surfaces are sufficiently large, and the approaching of the plates sufficiently rapid, the diffusion of the ions in the planes parallel to the surface toward the infinite reservoir might be much slower than the rate of approach of the surfaces. In this case, the ions reach thermal equilibrium along the direction perpendicular to the surfaces but can remain practically trapped between the surfaces. A simple modality to describe such a behavior is to consider a system with infinitely large surfaces, with all the ions (the counterions of the polyelectrolyte chains and the electrolyte ions) located between the surfaces. Each half of the system obeys the same equations as the brush embedded in a finite reservoir treated in the previous paragraph, if the reservoir thickness L is replaced by the (variable) half distance d between surfaces. In the linear approximation, the solution for the potential (up to an arbitrary constant) is provided by eqs 26a,b, while the corresponding double layer free energy is given by eq 29.

In Figure 6b, the force per unit area between surfaces with grafted polyelectrolyte brushes, plotted as a function of their separation distance $2d$, provided by the linear approximation is compared with the numerical result

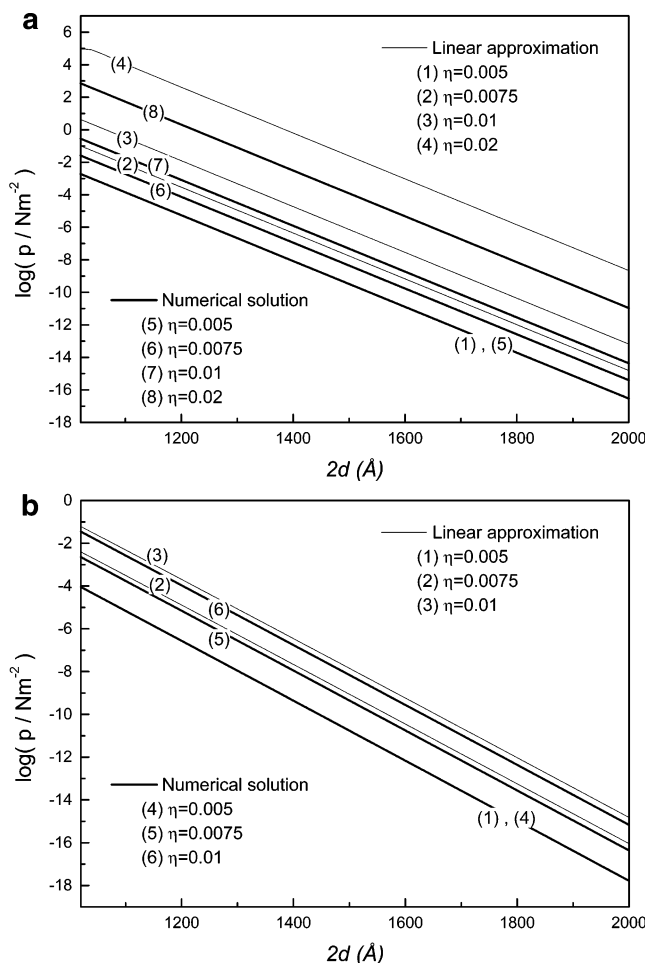


Figure 6. (a) The force per unit area between two identical plates with grafted polyelectrolyte brushes, as a function of the separation distance, for $N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, and $v=1.0$ Å³ calculated in the linear approximation is compared to the numerical result obtained from the nonlinear equations, assuming that the counterions diffuse into an infinite reservoir (slow approach). (b) The force per unit area between two identical plates with grafted polyelectrolyte brushes, as a function of the separation distance, for $N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, and $v=1.0$ Å³ calculated in the linear approximation is compared to the numerical result obtained from the nonlinear equations, assuming that the counterions remained trapped between the plates (rapid approach).

obtained from the integration of a nonlinear system for a system with the same parameter values as above ($N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $l=10$ Å, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, $v=1$ Å³) and various degrees of dissociation. Because of the counterions trapping, the potentials are in general smaller than in the previous case; hence the linear approximation is a better one.

The most interesting results are the changes in the interactions between plates as a function of the rate of approach. The extreme cases, when all the counterions are trapped between plates (rapid approach of the surfaces) and when the counterions diffuse into the infinite reservoir (slow approach of the surfaces) are compared in Figure 7a for a system with the same parameter values as above ($N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $l=10$ Å, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, $v=1$ Å³) and various degrees of dissociation, the force being calculated numeri-

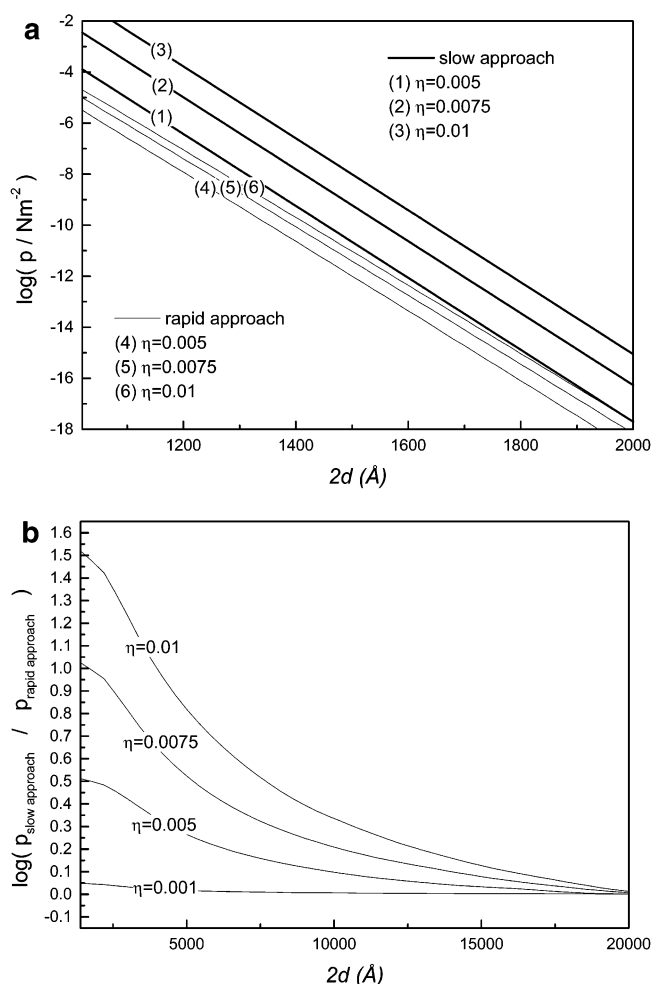


Figure 7. (a) The force per unit area between two identical plates with grafted polyelectrolyte brushes, as a function of the separation distance, for $N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, $v=1.0$ Å³, and various degrees of dissociation, calculated by assuming that the counterions either diffuse into an infinite reservoir (slow approach) or remain trapped between the plates (rapid approach) (b) The ratio between the interactions calculated assuming that the ions reach thermal equilibrium with an infinite reservoir (slow approach of the surfaces) and those calculated assuming that all the ions remain trapped between the surfaces (rapid approach of large surfaces), for $N=1000$, $a=1$ Å, $c_E=0.01$ M, $s^2=1000$ Å², $\epsilon=80$, $\sigma=100$ Å, $\tau=-1.0$, $w=0.0$, $v=1.0$ Å³, and various degrees of dissociation. At small separation distances and even moderate charging, the interactions can differ by orders of magnitude. At large separations, the differences become negligible.

cally in each case, using the nonlinear equations and only the symmetric configurations. Even for moderate degrees of dissociation, there is a difference of orders of magnitude between the two cases. The large difference is due mainly to the strong stretching of the brushes in the absence of the polyelectrolyte counterions. The double layer interaction roughly decays exponentially with a decay length $\lambda_D \cong 30$ Å (for $c_E=0.01$ M), and variations in brush thicknesses of the order of 100 Å lead to changes of orders of magnitude in the interactions. In addition, when the counterions are trapped between plates and compensate a part of the polyelectrolyte charge, a smaller potential is generated. At very large separations between plates, as expected, the difference between the two cases vanishes, because the counterions have sufficient room to leave the brush (see Figure 7b).

6. Conclusion

A simple mean field theory for polyelectrolyte brushes is suggested, based on an approximate Monte Carlo-type calculation. The method can be applied at high polyelectrolyte stretchings, for which the traditional treatments based on the self-consistent-field fail. It is assumed that the Boltzmann factor for the configurations that end up at a distance z from the surface can be approximated by a Boltzmann factor of the configuration that ends at the same distance and has a constant density distribution of monomers. The free energy of the latter can be calculated by solving the appropriate Poisson–Boltzmann equations. Both the density distribution of the monomer in the brush, calculated as the statistical average of all possible configurations, as well as the interactions between surfaces can be provided by this method. Simple expressions for the free energy of a configuration have been obtained, both in the linear approximation (valid at small

potentials) and in a nonlinear approximation, which is more accurate at high potentials. The dependence of the brush thickness (defined as the length of the most probable configuration) on electrolyte concentration was investigated. A simple modality to calculate the interaction between surfaces with grafted polyelectrolyte brushes using only symmetric configurations has been suggested. The possibility for a part of the counterions to remain trapped in the brush was also examined, and it was shown that even at moderate degrees of dissociation of the polyelectrolyte chains, it might reduce the force between brushes by orders of magnitude at small separations. Since for plates approaching rapidly (or having large surfaces) the counterions might not have sufficient time to diffuse into the infinite reservoir, the trapping of counterions can play an important role in colloid coagulation.

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