

Simple Model for Grafted Polymer Brushes

Marian Manciu and Eli Ruckenstein*

Department of Chemical Engineering, State University of New York at Buffalo,
Buffalo, New York 14260

Received January 23, 2004. In Final Form: April 29, 2004

The first theories of grafted polymer brushes assumed a step profile for the monomer density. Later, the real density profile was obtained from Monte Carlo or molecular dynamics simulations and calculated numerically using a self-consistent field theory. The analytical approximations of the solutions of the self-consistent field equations provided a parabolic dependence of the self-consistent field, which in turn led to a parabolic distribution for the monomer density in neutral brushes. As shown by numerical simulations, this model is not accurate for dense polymer brushes, with highly stretched polymers. In addition, the scaling laws obtained from the analytical approximations of the self-consistent field theory are identical to those derived from the earlier step-profile-approximation and predict a vanishing thickness of the brush at low graft densities, and a thickness exceeding the length of the polymer chains at high graft densities. Here a simple model is suggested to calculate the monomer density and the interaction between surfaces with grafted polymer brushes, based on an approximate calculation of the partition function of the polymer chains. The present model can be employed for both good and poor solvents, is compatible with a parabolic-like profile at moderate graft densities, and leads to an almost steplike density for highly stretched brushes. While the thickness of the brush depends strongly on solvent quality, it is a continuous function in the vicinity of the Θ temperature. In good and moderately poor solvents, the interactions between surfaces with grafted polymer brushes are always repulsive, whereas in poor solvents the interactions are repulsive at small separations and become attractive at intermediate separation distances, in agreement with experiment. At large separations, a very weak repulsion is predicted.

1. Introduction

One of the first important applications of polymer brushes was to the stabilization of colloidal dispersions.¹ The brushes were generated through the grafting of polymers on the surface of colloidal particles. When two particles approach each other, the overlap of their polymer brushes generates a steric repulsion, which can prevent their coagulation. A simple theory for polymer brushes was proposed by Alexander,² who assumed that the grafted polymer is composed of a sequence of blobs. The sectional area of each blob was provided by the area occupied by each grafted polymer on the surface, and it was assumed that, inside the blobs, the relation between the chain length and the occupied volume is the same as for a free polymer in a solvent. The repulsion due to the overlap of two polymer brushes was subsequently evaluated by de Gennes³ up to an arbitrary proportionality constant, from scaling considerations.

The simple Alexander–de Gennes theory, which assumed a steplike monomer density in the brush, captured the dependence of the interaction on the physical parameters (length of the polymer, density of grafting, quality of the solvent) and provided a satisfactory approximation for the calculation of the steric repulsion. However, new applications of grafted polymers on surfaces, such as the control of the catalytic selectivities of some chemical reactions by varying the thickness of a brush,⁴ the prevention of the adsorption of proteins on surfaces (a condition required for biocompatibility),⁵ or the control of

a membrane selectivity by changing the pH of the solution⁶ required a more accurate theory of polymer brushes.

The properties of grafted polymer brushes could be determined accurately via the traditional Monte Carlo⁷ or molecular dynamics⁸ simulations. Since one should account not only for the monomer–monomer interactions but also for the interactions with the solvent molecules, in general only calculations for systems of relatively small size could be performed. A modality to increase the calculation efficiency is to employ simplifying assumptions; one of the most successful was proposed by Dolan and Edwards,⁹ who considered that the monomers of the grafted polymer are distributed according to a random walk in an external potential. This potential is generated by monomer–monomer and monomer–solvent interactions and depends on the local monomer concentration. Since the monomer concentration in the brush depends on the potential, which in turn depends on the monomer concentration, the potential can be determined only self-consistently via successive approximations. A convenient modality to implement self-consistent calculations¹⁰ is based on a lattice model due to Scheutjens and Fleer.¹¹ The lattice-based self-consistent field theory was later improved to account for anisotropy, bond correlations, chain stiffness, and intermolecular interactions.^{12–14}

* Corresponding author. E-mail: feaeliru@acsu.buffalo.edu. Telephone: (716) 645 2911/2214. Fax: (716) 645 3822

(1) Napper, D. H. *Polymeric stabilization of colloidal dispersion*; Academic Press: San Diego, CA, 1983.

(2) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.

(3) de Gennes, P. G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.

(4) Ruckenstein, E.; Hong, L. *J. Catal.* **1992**, *136*, 178.

(5) Carignano, M. A.; Szleifer, I. *Colloids Surf. B* **2000**, *18*, 169.

(6) Idol, W. K.; Anderson, J. L. *J. Membr. Sci.* **1986**, *28*, 269.

(7) Muthukumar, M.; Ho, J.-S. *Macromolecules* **1989**, *22*, 965.

(8) Seidel, C. *Macromolecules* **2003**, *36*, 2536.

(9) Dolan, A. K.; Edwards, F. R. S. *Proc. Royal Soc. London A* **1974**, *337*, 509.

(10) Hirz, S. Modeling of Interactions Between Adsorbed Block Copolymers. M.S. Thesis, University of Minnesota, Minneapolis, MN, 1988. Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. *Macromolecules* **1987**, *20*, 1692.

(11) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619 and **1980**, *84*, 178.

(12) Leermakers, F. A. M.; Scheutjens, J. M. H. M. *J. Chem. Phys.* **1988**, *89*, 6912.

(13) Cantor, R. S.; McIlroy, P. M. *J. Chem. Phys.* **1989**, *91*, 416.

Both the Monte Carlo and molecular dynamics simulations, as well as the numerical solutions of the self-consistent field (SCF) equations, are time-expensive and do not offer a clear insight regarding the relations between the parameters of the grafted polymers and the properties of the brushes. A major progress in the analytical approximation of the SCF solution was suggested by Milner et al. (the MWC theory),¹⁵ based on the observation that, at high stretching, the partition function of the brush is dominated by the "classical path" (the most probable distribution). This approach is similar to the semiclassical approach of quantum mechanics, the Wentzel–Kramers–Brillouin (WKB) approximation. Under these assumptions, it turned out that, for equal-length polymer chains, the self-consistent field is parabolic, which leads to a parabolic distribution of the monomer density for neutral brushes. The simplicity of this result became extremely appealing, and most subsequent theories of the polyelectrolyte brushes (such as those of Miklavic and Marcelja,¹⁶ Misra et al.,¹⁷ and Zhulina and Borisov,¹⁸ to name only a few of them) were based on the "parabolic field" approximation. A more intuitive model to describe the parabolic distribution of monomers in grafted polymer brushes was proposed by Pincus,¹⁹ who considered that the profile of the brush is a result of the competition between an excluded-volume free energy and the decrease of the entropy of the polymer in the stretched configuration. Assuming that the excluded volume interactions are proportional to the square of the local monomer concentration and also a Gaussian elasticity of the polymer, this model led also to a parabolic distribution of the monomers in the brush.¹⁹

It should be noted that the "parabolic field" was derived by assuming a high stretching of the polymers; it provides, however, a better description of polymer brushes in the intermediate-stretching regime (good solvents and moderate graft densities). In contrast, the strongly stretched brushes, as obtained from molecular dynamics simulations,⁸ seem to be better described by the Alexander step profile. As a matter of fact, the analytical approximations of the self-consistent field theory provided the same scaling laws for the brush thickness as those derived earlier by Alexander in the framework of the step-profile approximation.¹⁹ These laws clearly fail at both very low graft densities (by predicting a vanishing small thickness of the brush) as well as at very high graft densities (by predicting a brush thickness larger than the length of the grafted polymer).²⁰ The limitation of the parabolic profile description only to brushes with moderate graft densities immersed in good solvents was also recognized by Shim and Cates, who proposed an ad hoc functional form for the free energy of stretching of the chain and consequently obtained a density profile much flatter than a parabola.²¹

Because the neutral polymer brushes are unlikely to be very strongly stretched, the MWC approach usually provides in this case an accurate approximation. The situation is however different for the highly charged grafted polyelectrolytes, which are almost completely

stretched.^{8,22} The purpose of this article is to present a simple method to calculate the thickness of the strongly stretched grafted polymer brushes and the interactions between surfaces covered by strongly stretched brushes. The calculations are based on an approximate Monte Carlo method, involving the assumptions that the configurations of minimum free energy are dominating the partition function and that the probability that the farthest monomer from the surface located at the distance z is approximated by the probability that the last monomer of the chain reaches the same distance. Under this hypothesis, in good solvents, the model predicts a constant density of monomers for each configuration that ends up at distance z , which is similar to the approximation successfully employed by Flory to explain the scaling laws of the free polymers in good solvents.²³

2. The Profile of Neutral Polymer Brushes

The traditional Monte Carlo method implies the generation of all possible configurations of grafted polymers and the calculation of the following partition function for a polymer

$$Z = \sum_i \exp\left(-\frac{U_i}{kT}\right) \quad (1)$$

where k is the Boltzmann constant, T the absolute temperature, " i " runs over all possible configurations and U_i represents the total energy of a configuration, which includes the interactions between the monomers of the same and neighboring polymer chains and the interactions between the monomers and the grafting surface as well as their interactions with the solvent molecules. A usual modality to generate the configurations of a polymer composed of N monomers of length " a " is to assume that the polymer is composed of N_l independent pieces of persistence length " l " (where $lN_l \equiv aN$), that are connected but can assume any relative orientations. This model constitutes the statistical equivalent of a random walk. Since the length of the grafted polymers perpendicular to the surface is much larger than their size parallel to the surface, one can assume that the in-plane monomer concentration is constant. In the absence of any monomer interactions, the probability $\psi'(z)$ for the last monomer of the chain to reach the position z is well approximated (for large N) by the analytical solution of a noninteracting random walk with a perfect-reflecting wall at the origin (see Appendix)²⁴

$$\psi'(z) \cong \sqrt{\frac{2}{\pi\sigma^2}} \exp\left(-\frac{z^2}{2\sigma^2}\right) \quad 0 < z < Na \quad (2a)$$

where $\sigma = l\sqrt{N_l}$ is the root-mean square distance of the random walk of N_l steps of length l . When additional interactions are present, the probability for a configuration to end at a distance z is multiplied by its corresponding Boltzmann factor

$$\psi(z) \propto \exp\left(-\frac{z^2}{2\sigma^2}\right) \sum_i \exp\left(-\frac{U_i(z)}{kT}\right) \quad (2b)$$

where the sum is performed over all possible configurations

(14) Li, B. Q.; Ruckenstein, E. *J. Chem. Phys.* **1997**, *106*, 280.
Ruckenstein, E.; Li, B. Q. *J. Chem. Phys.* **1997**, *107*, 3.

(15) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.

(16) Miklavic, S. J.; Marcelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.

(17) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.

(18) Zhulina, E. B.; Borisov, O. V. *J. Chem. Phys.* **1997**, *107*, 5952.

(19) Pincus, P. *Macromolecules* **1991**, *24*, 2912.

(20) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(21) Shim, D. F. K.; Cates, M. E. *J. Phys. (Paris)* **1989**, *50*, 3535.

(22) Huang, H.; Ruckenstein, E. *J. Colloid Interface Sci.* **2004**, in press.

(23) Flory, P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1971.

(24) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 3.

" f " whose last monomer of the chain is located at z and have the total free energies $U_f(z)$.

The random walk analogy was employed in the derivation of eq 2b only to provide the number of all possible configurations that end up at the distance z . The main difficulty is to calculate the free energies for each of the possible configurations. A first approximation, the mean field approach, consist in assuming that the total free energy density of a configuration (which includes all the interactions between monomers and solvent molecules as well as the chain entropy of mixing) can be described in term of the local monomer volume fraction ϕ by the Flory–Huggins mixing free energy density^{20,23}

$$F_{\text{FH}}(z) = \frac{kT}{a^3} \left(\frac{\phi}{N} \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right) \approx \frac{kT}{a^3} \left((\chi - 1)\phi + \left(\frac{1}{2} - \chi\right)\phi^2 + \frac{1}{6}\phi^3 + \frac{1}{12}\phi^4 \dots \right) \quad (3a)$$

where a is the length of a monomer, χ is the Flory interaction parameter,^{20,23} and the term proportional to $1/N$ was neglected because N is large. The term linear in ϕ , while nonnegligible for the mixing free energy density eq 3a, is not important for the total Flory–Huggins mixing free energy of the configuration, since its integral over the volume of the brush

$$s^2 \int_0^{Na} \left(\frac{kT}{a^3} (\chi - 1) \phi(\zeta) \right) d\zeta = \frac{kTs^2}{a^3} (\chi - 1) \int_0^{Na} \phi(\zeta) d\zeta = \frac{kT}{a^3} (\chi - 1) Nv = \text{const} \quad (3b)$$

provides (see eq 4b) the same constant for each possible configuration, and the same additive constant in the free energy of each configuration does not modify the result. For this reason, a convenient approximation of the Flory–Huggins free energy density is given by^{20,25}

$$F_{\text{FH}}(\phi) \approx \frac{kT}{a^3} \left(-\frac{1}{2} \tau \phi^2 + \frac{1}{6} w \phi^3 \right) \quad (3c)$$

where τ is a dimensionless excluded volume parameter ($\tau = (2\chi - 1)$ with $\tau < 0$ for a good solvent and $\tau > 0$ for a poor solvent) and w is the third virial coefficient, which is positive and typically on the order of unity.²⁵ The latter coefficient should roughly account for the higher order terms in eq 3a (all of them being positive), as well as for the additional interactions between monomers, not included in the traditional Flory–Huggins mixing free energy density eq 3a.

The second approximation employed here is to consider that the configurations of the minimum energy provide most of the contributions to the average Boltzmann factor in eq 2b, the well-known saddle point approximation of statistical mechanics.

For a good solvent, the Flory–Huggins free energy density is minimized by the lowest possible volume fraction of monomers, which is in turn obtained for a completely stretched chain. In the stretched configuration that ends up at the distance $z < Na$ a random walker moves away from the surface until reaches a distance $z' > z$ and then returns to z (such as the length of the path is $z' + (z' - z) = Na$; hence, $z' = (Na + z)/2$). However, there is only one such configuration among the $2C_N^k = 2N!/k!(N - k)!$ configurations that ends up at $z = ka$, where the factor 2 multiplying the binomial coefficient accounts for the

reflecting wall at the origin. While this particular configuration has the highest Boltzmann factor, its contribution to the sum in eq 2b is in most cases not significant, because of its low statistical weight. In what follows, a third approximation will be employed, namely that we will take into account only the configurations for which the last monomer of the chain is also the farthest from the surface. As will be shown below, under these assumptions, the minimum Flory–Huggins free energy in good solvents is provided by the configurations with a constant distribution of monomers. Such a distribution was successfully employed by Flory to derive a relation between the root-mean-square distance between the ends and the number of monomers of a polymer in good solvents,²³ and it provided the correct value for the scaling coefficient in one dimension and values within a percent of the most accurate numerical results in 2 and 3 dimensions.²⁰

The Flory–Huggins free energy of a configuration for which the monomers are confined between 0 and z is given by

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

where the monomer volume fraction ϕ obeys the normalization condition

$$\int_0^z \phi(\zeta) d\zeta = \frac{Nv}{s^2} \quad (4b)$$

where N is the number of monomers of volume v in a chain, s^2 is the area corresponding to a grafted chain on the surface, and Na is the maximum length of a polymer.

The function $\phi(z)$ which minimizes the Flory–Huggins free energy (eq 4a) with the constraint (eq 4b) is provided by the extremum of the functional

$$\int_0^z \mathcal{J}(\phi) d\zeta = \frac{s^2 kT}{a^3} \int_0^z \left(-\frac{\tau}{2} \phi^2(\zeta) + \frac{w}{6} \phi^3(\zeta) + \lambda \phi(\zeta) \right) d\zeta \quad (5a)$$

where λ is a Lagrange multiplier. The corresponding Euler–Lagrange equation

$$\frac{\partial}{\partial \zeta} \frac{\partial \mathcal{J}}{\partial \left(\frac{\partial \phi}{\partial \zeta} \right)} - \frac{\partial \mathcal{J}}{\partial \phi} = 0 \quad (5b)$$

leads to

$$-\tau \phi + \frac{w}{2} \phi^2 + \lambda = 0 \quad (5c)$$

The Euler–Lagrange equation (eq 5c) does not depend on ζ , and the continuous solution is a constant obtained from the constraint (4b):

$$\phi(\zeta, z) = \frac{Nv}{s^2 z} \quad (5d)$$

While (5d) is the only continuous solution that is an extremal of the functional (5a), a discontinuous solution, which corresponds to the separation into two homogeneous phases, might lead to a lower value of the free energy. Therefore, we will consider configurations with volume fraction ϕ_a on a domain (not necessarily connect) of length $z_a < z/2$ and with volume fraction ϕ_b on the remaining

domain of length $z_b = z - z_a$. The restriction that $z_a < z/2$ does not reduce the generality, since the other case is obtained by interchanging the subscripts a and b . The Flory–Huggins free energy of such a configuration is given by

$$U(z, \phi_a, z_a) = \frac{s^2 kT}{a^3} \left(z_a \left(-\frac{\tau}{2} \phi_a^2 + \frac{w}{6} \phi_a^3 \right) + (z - z_a) \times \left(-\frac{\tau}{2} \left(\frac{Nv}{s^2} - \phi_a z_a \right)^2 + \frac{w}{6} \left(\frac{Nv}{s^2} - \phi_a z_a \right)^3 \right) \right) \quad (6)$$

where the normalization eq 4b ($z_a \phi_a + (z - z_a) \phi_b = Nv/s^2$) was taken into account. The extremal of $U(z, \phi_a, z_a)$ with respect to ϕ_a leads to two pair of solutions:

$$(i) \quad \phi_a = \frac{Nv}{s^2 z}, \quad z_a = z, \quad \text{which is equivalent to eq 5d} \quad (7a)$$

$$(ii) \quad \phi_a = \frac{\frac{2\tau}{w} z - \frac{2\tau}{w} z_a - \frac{Nv}{s^2}}{z - 2z_a}, \quad \phi_b = \frac{\frac{Nv}{s^2} - \frac{2\tau}{w} z_a}{z - 2z_a} \quad (7b)$$

Introducing the pair of solutions (eq 7b) in eq 6, the free energy becomes a function of z_a , with its derivative with respect to z_a given by

$$\frac{\partial U(z, z_a)}{\partial z_a} = \frac{2}{3w^2} \left(\frac{Nv}{s^2} w - \tau z \right)^3 \quad (8)$$

For $\tau < 0$ (good solvent), the derivative is always positive; hence, the minimum corresponds to $z_a = 0$, which leads to $z_b = z$ and $\phi_b = Nv/s^2 z$, which is the same as eq 5d.

For $\tau > 0$ (poor solvents), the derivative is positive for z smaller than

$$z_{\min} = \frac{w}{\tau} \frac{Nv}{s^2} \quad (9)$$

and negative for $z > z_{\min}$. In the first case ($z < z_{\min}$, poor solvent), the minimum free energy is obtained again for $z_a = 0$ (a constant distribution of monomers between 0 and z) while in the latter case ($z > z_{\min}$, poor solvent), the Flory–Huggins free energy is a monotonically decreasing function of z_a . However, the volume fraction ϕ_b in eq 7b, which also decreases with increasing z_a , cannot become smaller than that corresponding to a completely stretched chain:

$$\phi_{\min} = \frac{Nv}{s^2 Na} = \frac{v}{s^2 a}$$

The maximum value physically allowed for z_a , obtained from the condition $\phi_b = \phi_{\min}$,

$$\frac{\frac{Nv}{s^2} - \frac{2\tau}{w} z_a}{z - 2z_a} = \frac{v}{s^2 a} \quad (10a)$$

is given by

$$z_{a,\max} = \frac{1}{2} \frac{Na - z}{\frac{\tau}{w} \frac{s^2 a}{v} - 1} \quad (10b)$$

which employed in eq 7b leads to the volume fractions:

$$\phi_a = \phi_{\max} = \frac{2\tau}{w} - \frac{v}{s^2 a} \quad (\text{on a domain of length } z_{a,\max}) \quad (10c)$$

$$\phi_b = \phi_{\min} = \frac{v}{s^2 a} \quad (\text{on a domain of length } z - z_{a,\max}) \quad (10d)$$

Parts c and d of eq 10 simply state that the system separates into two phases, if the solvent is poor ($\tau > 0$) and the confinement is weak ($z > z_{\min} = (w/\tau) Nv/s^2$), but not when the confinement is strong ($z < z_{\min}$). While the diluted polymer in the bulk solvent undergoes a phase separation as soon as τ becomes positive (at the Θ temperature), only the configurations of the grafted polymer that are sufficiently long undergo a phase separation. This occurs because at high volume fractions, the excluded volume interactions (due to the positive third virial coefficient w) dominate the Flory–Huggins free energy and prevent the polymer collapse. If the grafting density is sufficiently high (small s) in eq 9, the minimum length z_{\min} required for phase transition might exceed the maximum length of the polymer Na regardless of the value τ , therefore none of the physically allowed chain configurations undergoes phase separation.

In summary, the configurations of minimum Flory–Huggins free energy for monomers distributed between 0 and z correspond to the following.

(i) Good solvents ($\tau < 0$) and $0 < z < Na$:

$$\phi(\zeta, z) = \frac{Nv}{s^2 z} \quad (5d)$$

(ii) Poor solvents ($\tau > 0$) and $0 < z < z_{\min} = (Nv/s^2)(w/\tau)$:

$$\phi(\zeta, z) = \frac{Nv}{s^2 z} \quad (5d)$$

(iii) Poor solvents ($\tau > 0$) and $z_{\min} = (Nv/s^2)(w/\tau) < z < Na$:

$$\phi(\zeta, z) = \phi_{\max} = \frac{2\tau}{w} - \frac{v}{s^2 a} \quad \text{on an interval of length}$$

$$z_{a,\max} = \frac{1}{2} \frac{Na - z}{\frac{\tau}{w} \frac{s^2 a}{v} - 1} \quad (10c)$$

$$\phi(\zeta, z) = \phi_{\min} = \frac{v}{s^2 a} \quad \text{on an interval of length } z - z_{a,\max} \quad (10d)$$

Therefore, the minimum total Flory–Huggins energy of a chain configuration confined between 0 and z is given by the following.

(i) Good solvent in the range $0 < z < Na$ or poor solvent in the range $0 < z < z_{\min}$:

$$U_{\text{FH}}(z) = s^2 \int_0^z F_{\text{FH}}(\zeta) d\zeta = \frac{kT}{a^3} \left(-\frac{\tau N^2 v^2}{2s^2 z} + \frac{w N^3 v^3}{6s^4 z^2} \right) \quad (11a)$$

(ii) Poor solvent in the range $z_{\min} < z < Na$:

$$U_{FH}(z) = \frac{kTs^2}{a^3} \left(z_{a,\max} \left(-\frac{\tau}{2} \phi_{\max}^2 + \frac{w}{6} \phi_{\max}^3 \right) + (z - z_{a,\max}) \left(-\frac{\tau}{2} \phi_{\min}^2 + \frac{w}{6} \phi_{\min}^3 \right) \right) \quad (11b)$$

The probability for the last monomer of the chain to reach point z is consequently obtained from eq 2b:

$$\psi(z) = \frac{1}{C_1} \exp\left(-\frac{z^2}{2\sigma^2}\right) \exp\left(-\frac{U_{FH}(z)}{kT}\right), \quad 0 < z < Na \quad (12a)$$

where $\sigma = l\sqrt{N_l}$ is the root-mean-square length of the random walk of persistence length l and C_1 is a normalization constant which obeys

$$\int_0^{Na} \psi(z) dz = 1 \quad (12b)$$

The monomer volume fraction in the brush $\Phi(z)$ is the statistical average of the contributions of configurations ending up at different positions. In poor solvents, the configurations with $z > z_{\min}$ that minimize the Flory–Huggins energy do not have a constant monomer density. However, the monomers are equally like to accumulate at a volume fraction ϕ_{\max} in any region between 0 and z ; therefore, an average over all the possible configurations (of the same minimum energy) would lead to a constant monomer density between 0 and z . For $z < z_{\min}$ (in poor solvents) or for good solvents, the configuration of minimum energy corresponds to a constant distribution of monomers between 0 and z , $\phi(\xi, z) = Nv/s^2z$ for $0 < \xi < z$ and $\phi(\xi, z) = 0$ for $\xi > z$. Consequently, the chains that end up at distances smaller than z do not contribute to the volume fraction of the monomers at z , whereas the chains which end up at distances larger than z contribute $\phi(\xi, z) = Nv/s^2z$ with the probability $\psi(z)$ to the total monomer fraction $\Phi(z)$. Therefore, the monomer volume fraction is given by

$$\Phi(z) = \frac{1}{C_1} \int_z^{Na} \psi(\xi) \phi(\xi, z) d\xi = \frac{1}{C_1} \int_z^{Na} \frac{Nv}{s^2\xi} \exp\left(-\frac{\xi^2}{2\sigma^2}\right) \exp\left(-\frac{U_{FH}(\xi)}{kT}\right) d\xi \quad (13)$$

The results will be illustrated through this paper with model calculations for a grafted brush with the following values of the parameters: $s = 10$ Å, $a = 1$ Å, $N = 1000$, $l = 10$, $v = 1$ Å³. In parts a and b of Figure 1, the probability for the last monomer of the chain to be at z (Figure 1a) and the local volume fraction of the monomers in the brush (Figure 1b) are plotted as a function of the distance from the surface for good solvents ($\tau < 0$). In the absence of interactions between monomers $\tau = w = 0$, $\psi(z)$ is Gaussian and the profile of the brush can be roughly approximated by a parabola. The brush is swollen because of the repulsive Flory–Huggins interactions, which increase with increasing volume fraction ϕ . At low graft densities (large values of s , hence low values of ϕ) or for moderately good solvents (small absolute value of τ and w) the brush profile can be still approximated by a parabola. However, by increasing the graft density (small s) or solvent quality (large absolute value of τ) a strongly stretched brush is generated, with an almost constant density profile over most of the brush, but with an exponential-like tail, in agreement with the numerical simulations.⁸ The most likely chain configuration in the brush is obtained from the condition of vanishing of the derivative of $\psi(z)$ with respect to z in eq

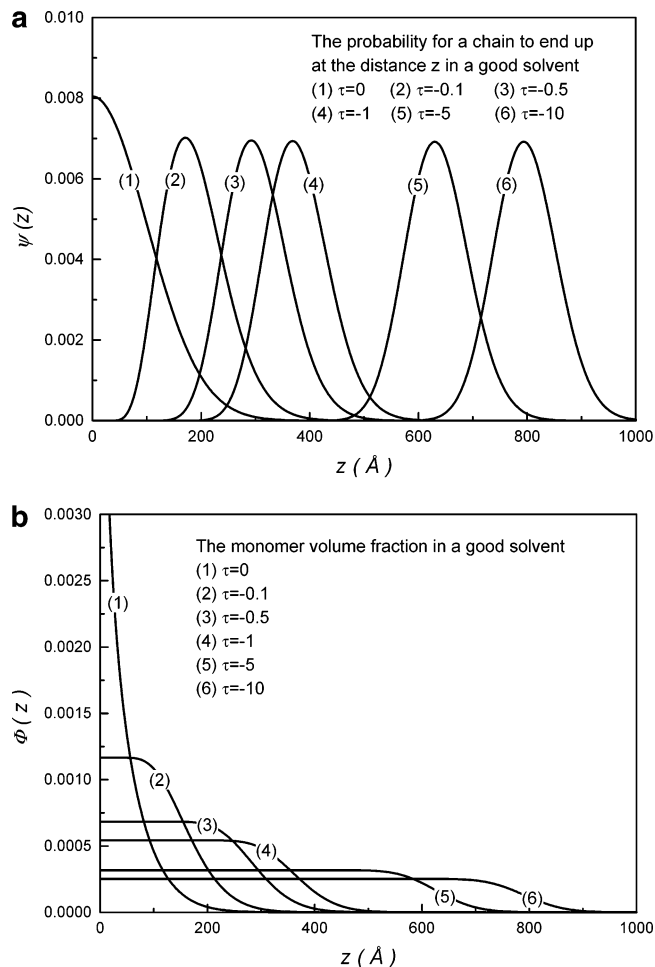


Figure 1. (a) Probability $\psi(z)$ for the last monomer of a grafted chain to be located at the distance z from the surface and (b) the local volume fraction of monomers in a good solvent, for $s = 10$ Å, $a = 1$ Å, $N = 1000$, $l = 10$ Å, $v = 1$ Å³, and various solvent qualities.

12a. Neglecting the second term in the Flory–Huggins interaction ($w = 0$) leads to

$$\bar{z} = \left(-\frac{\tau l^2 N_l N^2 v^2}{2s^2 a^3} \right)^{1/3} \quad (14)$$

If the length of the most probable chain configuration \bar{z} is assumed to be equal to the thickness of the brush L , eq 14 provides the same dependence between the graft density and thickness as the Alexander theory. Whereas eq 14 accounts explicitly for the persistence length of a polymer (its degree of flexibility), with the simplified assumptions that $l \sim a$, $N_l \sim N$, $v \sim a^3$ the Alexander scaling law is completely recovered:

$$L \propto N \left(\frac{\tau v a^2}{2s^2} \right)^{1/3} \quad (15)$$

Here τv represents an “excluded volume” of the interaction.¹⁹

However, as shown in Figure 1a, the approximation of the thickness of the brush by the length of the most probable configuration is in many cases arbitrary, since configurations that end up at different distances can contribute notably to the brush thickness. In addition, the derivation of eq 14 implies that the random walk can be described by a Gaussian extended from $z = 0$ to $z = \infty$,

while the random walk should not exceed the maximum chain length Na . Equations 12 and 13 do account for this inconsistency (by a cutoff in the integral limits) and do not predict a brush thickness that exceeds Na . Another feature of the present model is that whereas at vanishing Flory–Huggins interactions ($\tau = w = 0$) the most probable configuration ends up at $z = 0$, the brush does not collapse on the surface, as suggested by the scaling laws (eqs 14 or 15), because the configurations extended to $z > 0$ have nonvanishing probabilities.

The present model is based on several assumptions: (i) the possible configurations of the grafted chain are described by a random walk; (ii) their free energy densities are expressed as functions of the local monomer volume fraction alone; (iii) the configurations of minimum energy dominate the partition function of the system; (iv) only the configurations with monomers distributed between the surface and the position of the last monomer of the chain, assumed to be the farthest one, are taken into account. The latter assumption basically implies that the probability that the most distant monomer from the surface reaches the distance z is equal to the probability that the last monomer of the chain reaches this distance; this approximation clearly fails when z is in the vicinity of the surface. However, in swollen brushes the behavior of the monomers in the vicinity of the surface is less important than the behavior of the distant monomers, which are primarily responsible for the brush thickness and for the interactions between brushes.

As a matter of fact, in good solvents, the above assumptions predict that only configurations with constant monomer density between 0 and z contribute essentially to the partition function. This is equivalent to the Flory model for polymer swelling in a good solvent, which was remarkably successful, especially for one dimension.^{20,23} It is therefore to be expected that the model is reasonably accurate in good solvents and fails in extremely poor solvents, because the configurations in the vicinity of the surface dominate the collapsed brush. It should be however noted that the sharp distinction between good and poor solvent at the Θ temperature occurs only at high dilutions, whereas for high volume fractions the Flory–Huggins free energy is dominated by the volume-exclusion interaction between monomers and increases with ϕ even for poor solvents. Therefore, at high grafting densities, the brush might be swollen even at temperatures below Θ ; hence, the present model is applicable.

The probability $\psi(z)$ that the last monomer of the chain is located at the distance z , and the volume fraction $\Phi(z)$ of the monomers in the grafted brush immersed in a moderately poor solvent are plotted in Figure 2, parts a and b, using for the parameters the values selected above ($s = 10 \text{ \AA}$, $a = 1 \text{ \AA}$, $N = 1000$, $l = 10$, $v = 1 \text{ \AA}^3$), a fixed value for the third virial coefficient $w = 1$ and various values for the interacting parameter τ . It is of interest to note that the brush thickness is modified continuously when the quality of the solvent changes from good ($\tau < 0$) to poor ($\tau > 0$). This occurs because the Flory–Huggins free energy is minimized by a constant monomer distribution in both good solvents and poor solvent for configurations with $z < z_{\min} = Nv/s^2 w/\tau$. For small values of τ , z_{\min} (for which phase separation occurs) exceeds the maximum length of the chain Na . Therefore, in these cases, the polymer behaves as immersed in a good solvent, even below the Θ temperature. This uniform collapse of the brushes induced by changing the solvent quality is in agreement with the results reported by Ross and Pincus.²⁵

The most probable configurations in Θ solvents ($\chi = 1/2$, $\tau = 0$), obtained from the extremum of eq 12, occurs at a

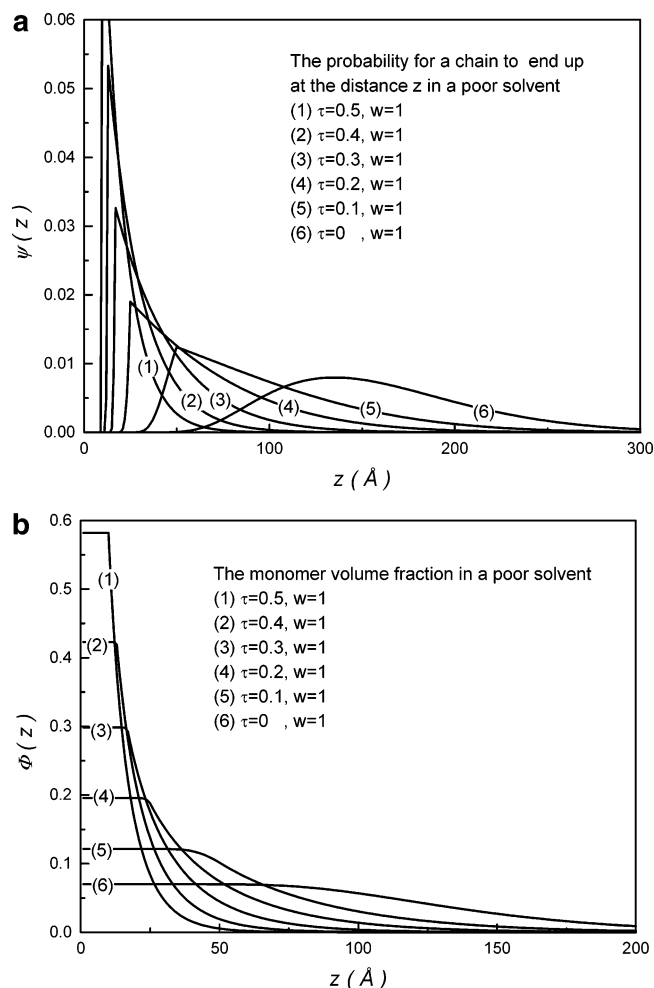


Figure 2. (a) Probability $\psi(z)$ for the last monomer of a grafted chain to be located at the distance z from the surface and (b) the local volume fraction of monomers in a poor solvent, for $s = 10 \text{ \AA}$, $a = 1 \text{ \AA}$, $N = 1000$, $l = 10 \text{ \AA}$, $v = 1 \text{ \AA}^3$, and various solvent qualities.

distance given by

$$\bar{z} = \left(\frac{wN^3N_l v^3 l^3}{3a^3 s^4} \right)^{1/4} \quad (16)$$

which differs from the Alexander scaling law, eq 15.

In Figure 3, the length of the most probable chain configuration (which roughly accounts for the thickness of the brush), is plotted as a function of the quality of the solvent τ for various values of the third virial coefficient w . For small values of the third virial coefficient, there is a large variation in the thickness of the brush (albeit continuous) in the vicinity of the Θ temperature, as observed experimentally.²⁶

3. The Interaction between Grafted Neutral Brushes

A. Good Solvents. When two surfaces with grafted polymer brushes approach each other, the overlap of the neutral brushes generates an interaction between surfaces. In good solvents, the Flory–Huggins mixing free energy density (eq 3c) increases with the monomer concentration; therefore, one expects that the overlap of the brushes would lead always to repulsion. In the present

(26) Kilbey, S. M.; Watanabe, H.; Tirrell, M. *Macromolecules* **2001**, *34*, 5249.

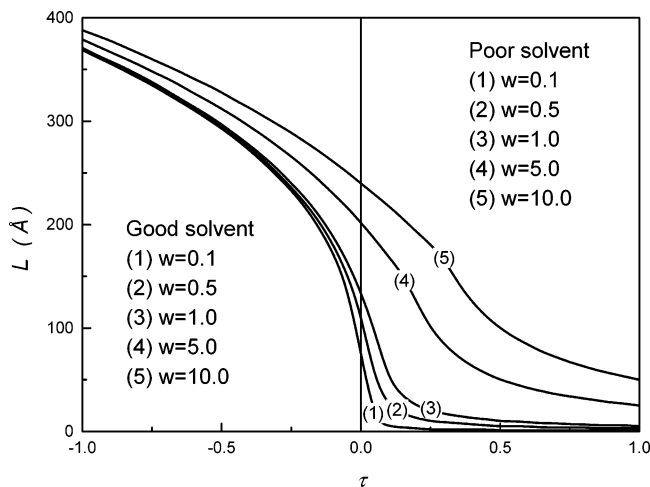


Figure 3. Length $L \equiv \bar{z}$ of the most probable chain configuration as a function of solvent quality for various values of the third virial coefficient w .

model, the profile of each brush depends not only on the physical properties of the individual brushes (number of monomers N , monomer length a , monomer volume v , persistence length l , excluded volume parameter τ , third virial coefficient w , grafting area s^2), but also on the distance $2d$ between surfaces. 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 the position z_2 from the surface “2” is given by (see Appendix):

$$\psi(z_1, z_2) = \frac{1}{C_2} \psi_1'(z_1) \psi_2'(z_2) \sum_{ij} \exp\left(-\frac{U_{FH}^{ij}(z_1, z_2)}{kT}\right) \quad (17a)$$

where the sum is performed over all possible configurations which end up at z_1 and z_2 , respectively, $\psi_k'(z_k)$ ($k = 1, 2$) represents the probability that a random walk, constrained by two reflecting walls at 0 and $2d$, which starts on the surface “ k ” and ends up at the distance z_k from that surface (see Appendix), and the normalization constant C_2 is obtained by taking into account that both chains should end up somewhere between 0 and $2d$:

$$\int_0^{2d} \int_0^{2d} \psi(z_1, z_2) dz_1 dz_2 = 1 \quad (17b)$$

Assuming, as previously, that the Boltzmann factor of a configuration is dominated by the configuration corresponding to a minimum energy $U_{FH}(z_1, z_2)$ with the constraints that all the monomers of the first chain are distributed between the first surface and z_1 while all the monomers of the second chain are distributed between the second surface and z_2 , the total free energy of the overlapping brushes, per unit area, is the statistical average over all possible configurations (see Appendix)

$$F(2d) = \frac{1}{s^2} \int_0^{2d} \int_0^{2d} \psi(z_1, z_2) U_{FH}(z_1, z_2) dz_1 dz_2 \quad (18)$$

and the force per unit area is provided by its derivative with respect to the distance $2d$.

The calculations are considerable simplified if only the symmetric configurations ($z_1 = z_2$) would be taken into account and the paths that reach z after reflections on the opposite walls would be ignored. In this case, eq 17a becomes

$$\psi(z) = \frac{1}{C_2} \exp\left(-\frac{z^2}{\sigma^2}\right) \exp\left(-\frac{U_{FH}(z)}{kT}\right) \quad (19a)$$

The Flory–Huggins free energy for the nonoverlapping configurations ($0 < z < d$) is given by

$$U_{FH}(z) = 2z \frac{kTs^2}{a^3} \left(-\frac{\tau(Nv)^2}{2(s^2z)^2} + \frac{w(Nv)^3}{6(s^2z)^3} \right) \quad 0 < z < d \quad (19b)$$

which is the sum of the energies of the independent configurations that end up at $z_1 = z_2 = z$, while for $z > d$

$$U_{FH}(z) = 2d \frac{kTs^2}{a^3} \left(-\frac{\tau(Nv)^2}{2(s^2d)^2} + \frac{w(Nv)^3}{6(s^2d)^3} \right) \quad d < z < 2d \quad (19c)$$

which implies that, for two overlapping configurations, the minimum Flory–Huggins free energy in good solvents is obtained for a constant distribution of monomers between 0 and $2d$. The free energy per unit area of the system is given by

$$F(2d) = \frac{1}{s^2} \int_0^{2d} \psi(z) U_{FH}(z) dz \quad (19d)$$

and the force per unit area

$$\Pi(2d) = -\frac{\partial F(2d)}{\partial(2d)} \quad (19e)$$

In Figure 4a, the force per unit area between two identical surfaces with grafted polymer brushes immersed in good solvents, with the parameters selected as above ($s = 10$ Å, $a = 1$ Å, $N = 1000$, $l = 10$ Å, $v = 1$ Å³) is calculated for various solvent qualities using all possible configurations (continuous line) as well as the simplified version which accounts only for the symmetric configurations. The ratio between the forces calculated in the two different manners, represented in Figure 4b, shows that the simpler calculation is fairly accurate for high overlaps (strong interactions).

B. Poor Solvents. When the exponential tails of two brushes immersed in a poor solvent overlap, one might expect the local increase in the monomer volume fraction to lead to a more negative Flory–Huggins free energy and therefore to a lower total free energy of the system, which corresponds to an attraction between surfaces. However, as will be shown below, this is not always true.

Earlier experiments on polystyrene adsorbed on mica immersed in cyclohexane showed that below the Θ temperature the force was attractive for large separations between the mica plates, but became repulsive for small separations.²⁷ However, it was found, for the same system, that the attraction persisted even for temperatures higher than Θ . For this reason, its origin was attributed to the formation of polymer bridges between the surfaces.²⁸ Later, another experiment, in which the bridging was essentially eliminated, has shown that at large separations the force was attractive for $T < \Theta$ and repulsive for $T > \Theta$.²⁹

First, let us note that the attractive interaction could not be predicted by theories which did not consider the interpenetration of the chains from opposing surfaces but

(27) Klein, J. *Nature* **1980**, *288*, 248.

(28) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984**, *17*, 204.

(29) Hadzioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

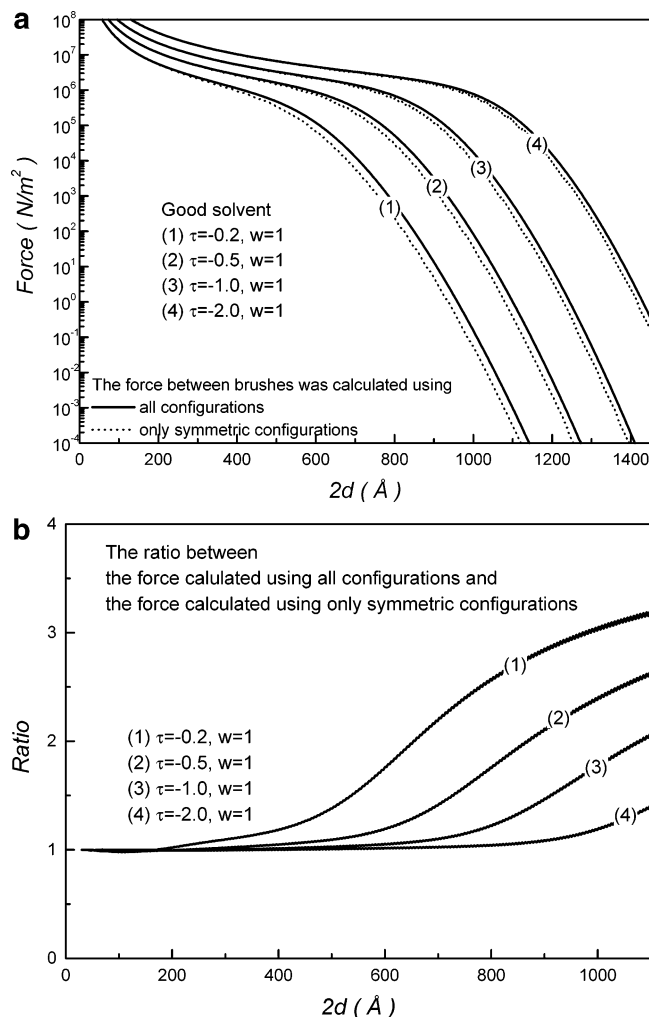


Figure 4. (a) Force per unit area between two identical surfaces with grafted polymers, separated by a distance $2d$ for $s = 10$ Å, $a = 1$ Å, $N = 1000$, $l = 10$ Å, $v = 1$ Å³ in a good solvent, calculated using all possible chain configurations, or using only the symmetric configurations. (b) Ratio between the two forces, showing that the restriction to symmetric configurations is a good approximation, particularly at large interactions.

assumed instead that each brush was distributed between the surface and the middle distance.³ Indeed, in the latter model, the total free energy of the compressed brush should be higher than that of the free brush; otherwise, the brush would have been adopted spontaneously a compressed configuration, even in the absence of the other surface. Therefore, the interactions between surfaces with non-interpenetrating brushes were always repulsive; in those cases, the attraction could be explained only if additional interactions (such as those due to polymer bridging) were taken into account.

Let us now analyze how the interactions between brushes occur in the present model. Our system is described by the statistical average of all possible configurations of chains that start from opposite surfaces and end up at the distances z_1 and z_2 , respectively. For each possible path that is not reflected by the opposite wall, it is assumed that the monomers of the chains grafted on surfaces "1" and "2" are distributed between 0 and z_1 and between z_2 and $2d$, respectively. The paths that are reflected by the opposite walls have the monomers distributed everywhere between 0 and $2d$. Only the configurations that minimize the Flory–Huggins free energy are taken into account. Since a complete evaluation of all possible combinations is quite tedious, we will focus

here only on the symmetric configurations, neglecting also the paths reflected on the opposite walls. As in the previous section, the limitation to symmetric configurations does not affect the results qualitatively.

For the highly confined configurations that end up at distances smaller than $z_{\min} = (w/\tau)(Nv/s^2)$ in a poor solvent, the minimum Flory–Huggins energy is obtained for an uniform (constant) monomer distribution. These configurations behave as immersed in a good solvent even below the Θ temperature (the monomer does not separate from solvent). For the confined configurations, with monomer volume fractions exceeding $\phi_{\max} = 2\tau/w$, corresponding to a separation $2d_{\min} = (w/\tau)(Nv/s^2)$, the increase of the local volume fraction due to the overlap of the brushes leads to an increase of the Flory–Huggins mixing free energy. These unfavorable interactions (dominated by the excluded-volume repulsion) are responsible for the strong, hard-wall-like repulsion, which occurs always at high overlaps ($2d < 2d_{\min}$), regardless of the quality of the solvent.

It is of interest to note that below (but in the vicinity of) the Θ temperature, the minimum confinement distance for which the overlap reduces the free energy might exceed the maximum length of the chains, $2d_{\min} > 2Na$. Because for $2d > 2Na$ there are no interactions between brushes, since the chains cannot overlap, the interactions occur in this case for $2d < 2Na < 2d_{\min}$ and hence are repulsive. Therefore, the brushes repel each other at all separations, as if they would have been immersed in a good solvent. This might explain the repulsion (and no attraction) between brushes observed recently in near- Θ solvents.²⁶

When the separation between surfaces exceeds $2d_{\min}$, the Flory–Huggins mixing free energy decreases for all overlapping ($z > d$) configurations. Using the same procedure as in section 2, one can show that the Flory–Huggins free energy of a configuration whose chains end at z (with $z > d$) is minimized by a constant monomer distribution for $2d < 2z_{\min} = 2(w/\tau)(Nv/s^2)$ and for $2d > 2z_{\min}$ by two constant monomer distributions

$$\phi_a = \frac{\frac{2\tau}{w}2d - \frac{2\tau}{w}z_a - 2\frac{Nv}{s^2}}{z - 2z_a} \quad (\text{over a domain of length } z_a) \quad (20a)$$

$$\phi_b = \frac{2\frac{Nv}{s^2} - \frac{2\tau}{w}z_a}{z - 2z_a} \quad (\text{over a domain of length } z_b = z - z_a) \quad (20b)$$

and the condition $\phi_b = \phi_{\min} = v/s^2a$ leads to the solution

$$z_{2d} = \frac{1}{2} \frac{2Na - 2d}{\frac{\tau}{w} \frac{s^2 a}{v} - 1} > 2z_{a,\max} = \frac{1}{2} \frac{2Na - 2z}{\frac{\tau}{w} \frac{s^2 a}{v} - 1} \quad (20c)$$

The values of ϕ_{\max} and ϕ_{\min} , obtained by introducing eq 20c in eq 20, parts a and b, are the same as those in section 2

$$\phi_a = \phi_{\max} = \frac{2\tau}{w} - \frac{v}{s^2 a} \quad (\text{over a domain of length } z_{2d}) \quad (20d)$$

$$\phi_b = \phi_{\min} = \frac{v}{s^2 a} \quad (\text{over a domain of length } z - z_{2d}) \quad (20e)$$

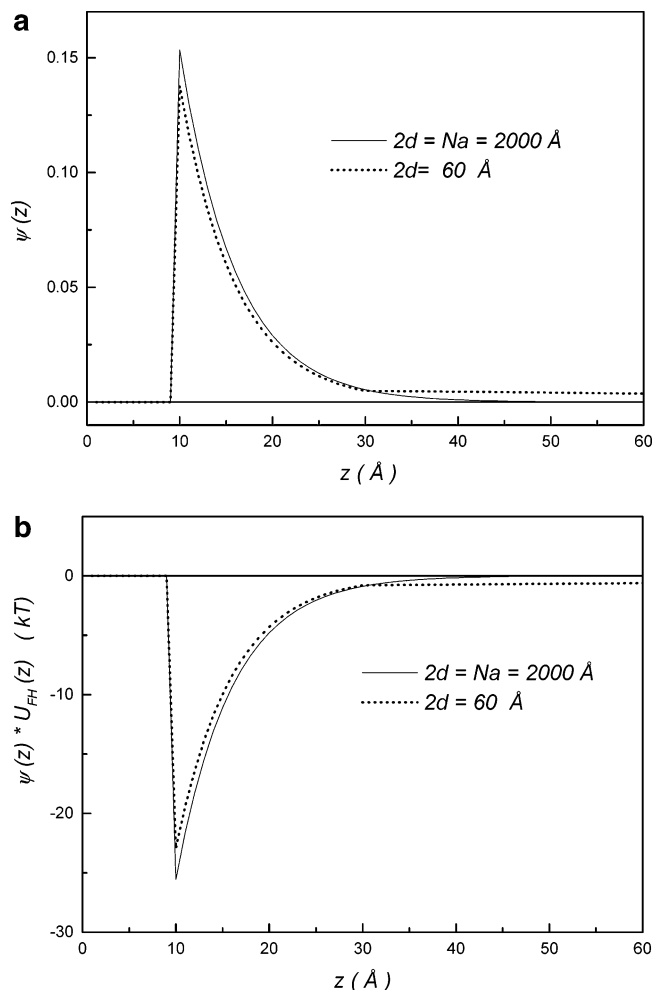


Figure 5. (a) Probability $\psi(z)$ for a chain to end up at distance z in a poor solvent differs in noninteracting brushes ($2d = 2Na = 2000$ Å) and overlapping brushes ($2d = 60$ Å). The swelling of brushes in poor solvents due to overlapping increases $\psi(z)$ at large z on the expense of decreasing $\psi(z)$ at moderate z . Because the former configurations have higher Flory–Huggins mixing free energies, they might increase the total free energy of the system. (b) Function $\psi(z)U_{FH}(z)$, the integral of which provides the total free energy. The balance between its increase (in absolute value) for large values of z and its decrease for small values of z provides the sign of the interactions between surfaces.

In this case, the energy of the overlapping configurations decreases because the length of the interval over which the monomers accumulate to the energetically favorable ϕ_{\max} value increases. The separation of the monomers from the solvent is favored by the presence of the other brush.

Since the overlapping of the stretched configurations lowers their free energy, one expects the overlapping of the brushes to always decrease the total energy of the system at large separations. Surprisingly, this does not happen. In Figure 5a, the probability $\psi(z)$ for a configuration to end at the distance z is compared for large separation distances with the same probability at small separations, when the configurations overlap. The decrease of the energy of the configurations for large values of z leads to an increase in the probability for the chain to reach this distance, at the expense of decreasing $\psi(z)$ for small values of z . However, the “stretched” configurations have higher Flory–Huggins energies than the “collapsed” ones, and the increase of the number of stretched configurations might increase the total free energy of the system. The product $\psi(z)U_{FH}(z)$, whose

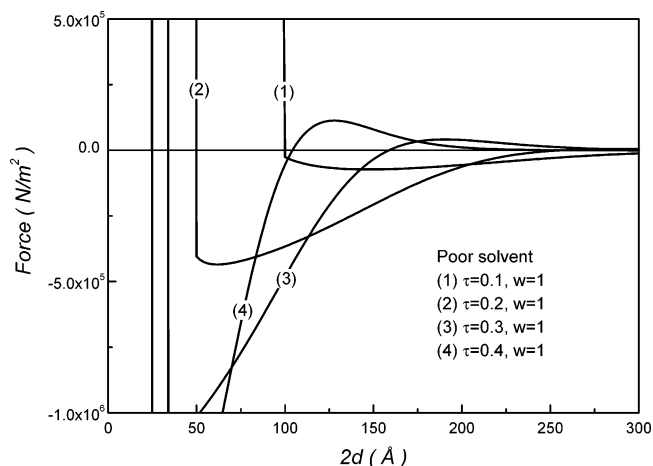


Figure 6. (a) Force per unit area between two identical surfaces with grafted polymers, separated by a distance $2d$ for $s = 10$ Å, $a = 1$ Å, $N = 1000$, $l = 10$ Å, and $v = 1$ Å³ in a poor solvent, calculated using only the symmetric configurations. At small separations, there is a strong repulsion due to excluded-volume interactions (carried by the third virial coefficient). At intermediate separations there is an attractive region due to the decrease of the free energy of configurations due to the chain overlap. At large separations, the swelling of the brush due to chain overlap (the increase of $\psi(z)$ at large z) favors configurations with high Flory–Huggins mixing free energies, thus increasing the total energy of the system and therefore generating a repulsion. The absolute value of this repulsion is, however, smaller by orders of magnitude than the attraction that occurs at intermediate separations and smaller by many orders of magnitude than the strong repulsion that occurs at small separations.

integral with respect to z provides the total free energy, is plotted in Figure 5b.

In Figure 6, the force between brushes is calculated for various solvent qualities. At small overlaps, the decrease of $\psi(z)$ for small z dominates, and the interaction is repulsive. However, at intermediate separations an attraction between brushes occurs, followed by a much stronger repulsion at small separations, in agreement with experiment.²⁷ It should be noted that the very weak repulsion that occurs at large separations, which was not reported experimentally, is by a few orders of magnitude smaller than the attraction and by many orders of magnitude smaller than the strong repulsion at small separations. This weak repulsion is a consequence of the statistical average over possible configurations employed in this article.

4. Conclusions

The traditional analytical treatments of the distribution of monomers in a grafted neutral polymer brush and the interaction between two surfaces with grafted polymer brushes are based either on the assumption of a step profile brush or on a parabolic profile brush. The latter assumption is based on an approximate solution of the self-consistent field equation (MWC).¹⁵ Both approaches predict the same scaling relations between the thickness of the polymer brush and the graft density, which fail at both very low and very high graft densities. In this article an alternate approach was suggested, based on an approximate Monte Carlo procedure. It is assumed that the most contributions to the Boltzmann factor of the configurations that end up at the distance z are provided by the configurations of minimum Flory–Huggins mixing free energy, with a monomer distribution restricted between the surface and the distance z . In a good solvent, these configurations correspond to a constant volume

fraction of monomers, an approach that was successfully employed by Flory to predict the scaling laws of a polymer in a good solvent. The method is particularly valuable for strong-stretched polymers, for which the parabolic approximation is not accurate. Because at high volume fractions of monomers (typical for a high-density polymer graft), the Flory–Huggins free energy increases with the monomer volume fraction and the brushes are swollen even for poor solvent qualities, the method can be applied to high-density brushes immersed in both good and poor quality solvents. When the graft density is not very high, or when the interaction parameters (τ and w) are small, the profile of the brush can be well approximated by a parabola. At higher interactions (either higher graft densities or larger excluded-volumes), the monomer density is almost constant in the vicinity of the surface, but decays exponentially at large distances, in agreement with molecular dynamics simulations and the numerical solutions of the self-consistent field equations. By assuming that the thickness of the brush is equal to the length of the most probable chain configuration (a rather poor approximation), one can recover for good solvents the scaling laws derived by previous analytical treatments; however, the brush thickness obeys a different scaling law at the Θ temperature. The interactions between two surfaces with grafting polymer brushes immersed in good solvents are always repulsive, with a magnitude dependent on the quality of the solvent. For marginally poor solvents, the model predicts also repulsive interactions at any separation. However, for poor solvents, the present theory predicts a very weak repulsion at large separations, followed by a (much stronger) attractive minimum of the free energy at intermediate separation distances, and a strong repulsion at small separations.

Appendix

The probability for an one-dimensional, free and unconstrained random walker, starting from the origin, to reach the distance z after N_l steps of length l is well approximated (at large N_l) by

$$\psi^U(z) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{z^2}{2\sigma^2}\right), \quad 0 < z < N_l l \quad (\text{A1})$$

where $\sigma = l\sqrt{N_l}$ is the root-mean square distance of the random walk.²⁴ The probability for a free random walker that starts at 0 to arrive at the distance z in the presence of a reflecting wall at the distance d_1 is equal to the sum of the probabilities for an unconstrained random walker to arrive at the point z and at its “image” point $2d_1 - z$, in the absence of the reflecting wall.²⁴ When the reflecting wall is located at the origin, the probability for the “reflected” walk to reach a distance $z > 0$ is simply twice the probability to reach the same distance in the absence of the reflecting wall (eq 2a).

The general solution of a random walk on a lattice between perfect reflecting walls was provided by Feller.³⁰ In what follows, a simpler approximate solution will be constructed using the method of images.²⁴ When the walk is confined between two reflecting walls, one at the origin and the other at the distance $2d$, the probability for the constrained walk to reach the distance z , $\psi'(z)$, can be written as a sum of probabilities ψ^U for the unconstrained walk to reach various “image” points, as follows.

$\psi^U(z)$: The possible paths either do not cross the points 0 and $2d$ or cross them an even number of times. The presence of reflecting walls at 0 or $2d$ does not modify the probability to reach z , because after two successive reflections on the same wall the unconstrained path is always recovered.

$\psi^U(-z)$: The possible paths cross an odd number of times the origin. Because of the reflecting wall at 0, the constrained walker arrives at z instead (some paths cross an even number of times $2d$, but inserting a reflecting wall there does not affect the probability, as noted above).

$\psi^U(4d - z)$: The possible paths cross the point $2d$ an odd number of times; because of reflections on that wall, the walker arrives at the point z instead.

$\psi^U(-4d + z)$: The possible paths cross the origin an odd number of times, followed by crossing the point at $-2d$ an odd number of times. Because of the reflection on the walls at origin and at $2d$, the constrained walker reaches the point z instead, and so on. Since the length of the walk cannot exceed $N_l l \equiv Na$, only the image points at shorter distances from origin than Na should be taken into account.

For the monomer distribution, a distinction has to be made between paths of type *a*, which are not reflected by opposite walls, and paths of type *b*, which return to z after reflecting at least once on the opposite wall. In the first case

$$\psi^a(z) = \psi^U(z) + \psi^U(-z) \quad (\text{A2a})$$

and in the calculation of the configuration of minimum energy it will be assumed that the monomers can be distributed between the starting point 0 and the end point z .

For the remaining configurations

$$\psi^b(z) = \psi^U(4d - z) + \psi^U(4d + z) + \psi^U(8d - z) + \psi^U(8d + z) + \dots \quad (\text{A2b})$$

Since the chain reaches both walls at least once, it will be assumed that its monomers are distributed between the walls. The energy of the system of overlapping brushes, per unit area, becomes

$$\begin{aligned} \psi(z_1, z_2) &= \frac{1}{C_2} \psi_1'(z_1) \psi_2'(z_2) \sum_{ij} \exp\left(-\frac{U_{\text{FH}}^{ij}(z_1, z_2)}{kT}\right) \quad (\text{14a}) \\ &\cong \frac{1}{C_2} \left[\psi^a(z_1) \psi^a(z_2) \exp\left(-\frac{U_{\text{FH}}^{aa}(z_1, z_2)}{kT}\right) + \right. \\ &\quad \psi^b(z_1) \psi^b(z_2) \exp\left(-\frac{U_{\text{FH}}^{bb}(z_1, z_2)}{kT}\right) + \psi^a(z_1) \psi^b(z_2) \times \\ &\quad \left. \exp\left(-\frac{U_{\text{FH}}^{ab}(z_1, z_2)}{kT}\right) + \psi^b(z_1) \psi^a(z_2) \exp\left(-\frac{U_{\text{FH}}^{ba}(z_1, z_2)}{kT}\right) \right] \quad (\text{A3}) \end{aligned}$$

where in eq 14a the sum is performed over all possible configurations i, j with chains that start on the surface “1” and “2” and end up at z_1 and z_2 , respectively, while in eq A3 only the configurations of minimum Flory–Huggins free energy are taken into account. In the latter case, the minimum depends on whether the chain reaches the opposite wall (type *b*) or not (type *a*).

For the configurations which do not overlap, the minimum Flory–Huggins energy is obtained for constant monomer distributions between 0 and z_1 , and between the location z_2 and $2d$, respectively. Figure 7 presents the

(30) Feller, W. *An Introduction to Probability Theory and its Application*; John Wiley & Sons: New York, 1968; Vol. 1, Chapter XVI.

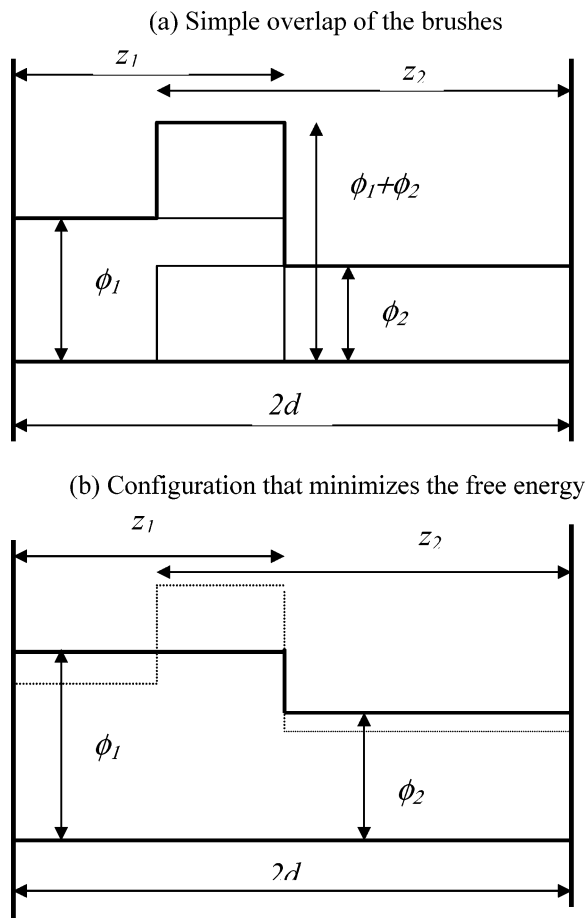


Figure 7. Local volume fractions of the monomers for two configurations of chains which end up at z_1 and z_2 , respectively: (a) simple addition of the volume fractions of the brushes; (b) configuration that minimizes the Flory–Huggins mixing free energy for the conditions mentioned in the text.

monomer distribution obtained from the sum of the volume fractions of two overlapping configurations. This result clearly does not correspond to a minimum Flory–Huggins free energy, because of the high value of ϕ in the overlapping region. A smaller free energy is obtained for the configurations in which the excess volume fraction is redistributed to the nonoverlapping regions. In addition to the requirements that all the monomers of each brush

should be located between 0 and z_1 or z_2 and $2d$, respectively, it will be assumed that in the overlapping region, the number of monomers belonging to each grafted brush is proportional to the volume fraction of those monomers in the nonoverlapping regions. The result is a constant volume fraction ϕ_1 between 0 and z_1 and a constant volume fraction ϕ_2 between z_1 and $2d$, where $\phi_1 > \phi_2$ (see Figure A.1b). The volume fractions in each region obey therefore the conservation equations:

$$(2d - z_2)\phi_1 + \alpha(z_1 + z_2 - 2d)\phi_1 = \frac{Nv}{s^2} \quad (\text{A4a})$$

$$(2d - z_1)\phi_2 + \alpha(z_1 + z_2 - 2d)\phi_2 = \frac{Nv}{s^2} \quad (\text{A4b})$$

$$\alpha\phi_1 + \alpha\phi_2 = \phi_1 \quad (\text{A4c})$$

Equation A4, parts a–c, can be solved for α , ϕ_1 , and ϕ_2 .

For the case *bb*, when both chains undergo reflections on the opposite walls, the Flory–Huggins free energy is minimized by a constant distribution of monomers between walls. In the case *ab*, when the second chain is reflected by the opposite wall, but not the first chain, the proportional redistribution of the excess monomers leads to a configuration with volume density ϕ_1 between 0 and z_1 and ϕ_2 between z_1 and $2d$, which obey the equation_s

$$\alpha z_1 \phi_1 = \frac{Nv}{s^2} \quad (\text{A5a})$$

$$(2d - z_1)\phi_2 + \alpha z_1 \phi_2 = \frac{Nv}{s^2} \quad (\text{A5b})$$

$$\alpha\phi_1 + \alpha\phi_2 = \phi_1 \quad (\text{A5c})$$

and are similar for the *ba* case. The average free energy density is consequently calculated from

$$F(2d) \cong \frac{1}{C_2} \int_0^{2d} \int_0^{2d} \sum_{i=a,b,j=a,b} U_{\text{FH}}^{ij}(z_1, z_2) \psi^i(z_1) \psi^j(z_2) \exp \left(- \frac{U_{\text{FH}}^{ij}(z_1, z_2)}{kT} \right) dz_1 dz_2 \quad (\text{A.6})$$

where the indices i and j run now over the two types of paths, a and b .

LA049781Y