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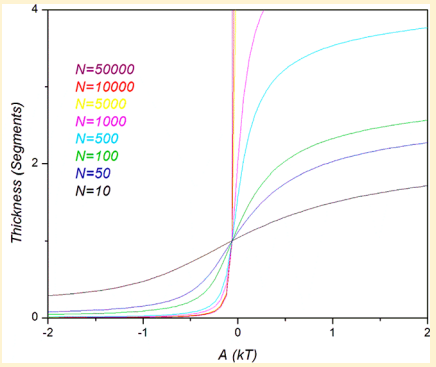
# Size-Dependent Transitions in Grafted Polymer Brushes

Marian Manciu,*[,†] Courtney Bosse,[†] and Eli Ruckenstein[‡]

[†]Physics Department, University of Texas at El Paso, El Paso, Texas 79968, United States

[‡]Chemical and Biological Engineering Department, SUNY at Buffalo, Buffalo, New York 14214, United States

**ABSTRACT:** The partition function of a grafted polymer brush was calculated as a sum over all possible configurations, each of them being an ensemble of $n_1$, $n_2$, ...$n_i$, ... loops having 2, 4, ..., 2$i$, ... segments. A system of equations for the most likely configuration has been obtained, and it was concluded that no solution exists for an infinite chain, with nonvanishing interactions between segments and surface. This implies that an infinite chain is either collapsed on the surface (for attractive interactions) or is forming a stretched brush (for repulsive interactions). However, for finite chains, a solution could be found. When the attractive segment−surface interaction becomes sufficiently strong, the brush collapses on the surface (the "loops" to "trains" transition). When the interaction is repulsive and sufficiently strong, the brush becomes stretched, with most segments belonging to open loops which do not return to the surface (the "loops" to "tails" transition). The critical values of the segment−surface interaction, for which the above transitions occur, depend on the length of the polymer chain as well as on other physical properties of the brush, such as the segment−segment and segment−solvent interactions and the grafting density.




## 1. INTRODUCTION

The interactions between two macromolecular assemblies (such as biological cells or nanoparticles) are sometimes mediated by polymers grafted on their surfaces.[1] Whereas many other water-mediated interactions between macromolecules (such as double layer, hydration[2] or ion hydration[3] forces) can be well described by relatively simple equations, the large number of possible configurations of grafted polymers (which increases exponentially with the number of Kuhn segments) renders impossible the exact solution (via the direct calculation of the partition function) for any polymer longer than about 20 Kuhn segments. An approximate solution for grafted polymer brushes was proposed by de Gennes via a scaling approach.[4] Milner, Witten, and Cates,[5] using a self-consistent field approach, concluded that the monomer density distribution in the brush is not constant (as assumed in the Alexander[6] and de Gennes models[4]) but rather parabolic. Pincus reached the same conclusion, by employing a simple model, in which the parabolic profile of the brush was the result of the competition between an excluded-volume free energy and the entropy of the polymer chains.[7] These models accounted for the monomer−monomer and monomer−solvent interactions but neglected the interactions between monomers and surface, which are expected to strongly affect the profile of the brush. By neglecting the monomer−monomer and monomer−solvent interactions, Rubin concluded that the monomer−surface interaction can lead to the collapse of the polymer brush on the surface.[8]

A simple approximation of the partition function of grafted polymer brushes has been suggested recently,[9] which involves its decomposition in simple configurations (random walks that end at the distance $z$ from the surface), for which the probabilities of occurrence can be calculated without difficulty. The latter probabilities involve an entropic term (the probability for a random walk of $N$ steps to end at a distance $z$ from the surface) and an energy term $\exp(-U/kT)$ due to the segment−segment and segment−solvent interactions. The problem was further simplified by considering, for each random walk that ends at $z$, only the configuration of minimum free energy, $U_{min}$, and neglecting the configurations of higher energies, because they provide negligible contributions to the partition function. This simple model could predict both the steplike (with an exponential tail) monomer density distribution for highly stretched brushes (high grafting densities and/or good solvents) or a parabolic distribution for low grafting densities and poor solvents. Additional approximations led to the well-known scaling laws, and examination of those approximations revealed when the scaling laws are no longer valid.[9]

The approach was extended to grafted adsorbing neutral polymers by decomposing each individual configuration of the chain involved in the partition function in an ensemble of loops of various lengths, whose probabilities of occurrence can be calculated without difficulty.[10] Short loops (in which most monomers are confined to the vicinity of the surface) are called "trains", while open loops are called "tails".[10]

It was shown that for sufficiently high grafting densities and small adsorption energies of the Kuhn segments, the loops unbind from the surface to form tails. In contrast, for sufficiently low grafting densities and large adsorption energies

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of the Kuhn segments, the configurations with many short loops (e.g., trains) are favored (because they provide higher total adsorption energy of the chain).

The increase in the short-range interactions between the Kuhn segments and surface leads to the collapse of the brush on the surface.[10] Whereas in ref 10 the density distribution of monomers in the brush has been calculated via a Monte Carlo procedure, in the present paper an analytical approach is suggested, involving the search for the most likely configuration. It will be shown that for any nonzero interaction between segments and surface, a grafted polymer of infinite length leads either to a collapsed or to a stretched configuration; however, for a grafted polymer of finite length, the collapse or stretching transitions occur when the interactions exceed critical values, which depend on the polymer length.

## 2. THE MOST LIKELY CONFIGURATION FOR SEGMENT−SURFACE INTERACTIONS

In what follows, it will be assumed that the brush is homogeneous in the plane of the surface. Each polymer chain is composed of a number of $N$ Kuhn segments, freely jointed to each other. The density distribution of the Kuhn segments can be approximated by a one-dimensional random walk normal to the surface (which provides an impenetrable barrier to the walk). In the absence of any interactions, a random walk (of infinite length) that leaves the surface has the probability $P_i^\infty$ of first return to the surface after $2i$ steps[11]

$$P_i^\infty = \frac{1}{(2i-1)2^{2i}}\frac{(2i)!}{(i)!(i)!} \tag{1}$$

which, for large values of $i$, can be approximated by[12]

$$P_i^\infty = \frac{1}{2i-1}\sqrt{\frac{2}{(2i-1)\pi}}\exp\left(-\frac{1}{2(2i-1)}\right) \tag{2}$$

an accurate approximation for large $i$ values, for which the use of eq 1 becomes too time-consuming.

Once the walk returns to the surface, it will bind to it, thus forming a closed loop of $2i$ segments, and another random walk, independent of the previous one, will start.

Whereas in three and higher dimensions there is a chance that a random walk will never return to origin, it was demonstrated by Pólya than in one (and two) dimensions a random walk will always return to origin.[11] This implies that any infinite random walk (in one dimension in our case) is composed of closed loops of various lengths that occur with the probabilities given by eq 1, and $\Sigma_i P_i^\infty = 1$.

A finite walk has to finish after $N$ steps, with the last loop open forming a tail. Since large loops cannot be formed if the walk is restricted to $N$ steps (hence $P_i = 0$ for $i > N$), the probabilities of loop formation for finite walks (which should also add to unity) differ from those for an infinite random walk. The probabilities of occurrence of a loop in a finite chain

$$P_i = \frac{n_i}{n_S} \tag{3a}$$

calculated as the fraction of loops of $2i$ segments, $n_i$, divided by the total number of loops $n_S$

$$n_S = \sum_i n_i \tag{3b}$$

are slightly different from the probabilities of loop formation in an infinite chain. Once the walk reaches the maximum number of steps (the number of Kuhn segments of the polymer) it is returned on the surface, and another walk starts. Therefore, for small values of $i$, $P_i$ (for finite chains) are larger than $P_i^\infty$ (for infinite chains), which compensates for large values of $i$, for which $P_i = 0$, whereas $P_i^\infty > 0$ (infinite chains). Still, the probabilities $P_i$ are normalized ($\Sigma_i P_i = 1$) because of eqs 3a and 3b.

However, if the chain is sufficiently long, its finite size does not affect much the relative probabilities of short loops

$$\frac{P_i}{P_{i+1}} \cong \frac{P_i^\infty}{P_{i+1}^\infty} \tag{4a}$$

which implies that

$$P_i = \alpha P_i^\infty \tag{4b}$$

an approximation that will be used through this paper. The value of $\alpha$ for a finite chain of $N$ segments ($1 < i < N$) is determined via normalization condition, eqs 3a and 3b:

$$\alpha = \frac{1}{\sum_{i=1}^{N} P_i^\infty} \tag{4c}$$

The partition function of a grafted polymer chain can be therefore written as a sum over all possible configurations, each configuration involving an ensemble of loops[10]

$$Z = \sum_j \exp\left(-\frac{U_j}{kT}\right) = \sum_{[n_1,n_2,\ldots]} \exp\left(-\frac{U_{[n_1,n_2,\ldots]}}{kT}\right) \tag{5}$$

where $k$ is the Boltzmann constant, $T$ the absolute temperature, and $U$ the total energy of the configuration with $[n_1, n_2, \ldots]$ loops and with the summation performed over all possible configurations. Because any configuration consists of an assembly of $n_1$ , $n_2$, ... loops occurring with probabilities $P_1$, $P_2$, ..., assuming that to each configuration $[n_1, n_2, \ldots]$ corresponds a single value $U(n_1, n_2, \ldots)$, namely the minimum energy of the configuration, the partition function can be simplified to

$$Z = \sum_j \exp\left(-\frac{U_j}{kT}\right) = \sum_{n1,n2,\ldots} \frac{n_S!}{n_1!n_2!\ldots} P_1^{n_1}P_2^{n_2}\ldots P_i^{n_i}\ldots\exp\left(-\frac{U(n_1, n_2\ldots)}{kT}\right) \tag{6}$$

where $n_S = \Sigma_i n_i$ is the total number of loops and $P_i$ is the probability of formation of a loop of $2i$ segments in a finite chain.

Let us first assume that the only interaction in the system is between the Kuhn segments and the surface, with an adsorption energy $A$ per segment adsorbed (negative for attraction and positive for repulsion). Additional interactions, such as the segment−segment and segment−solvent interactions, will be included in calculations in the next section.

When segment−segment and segment−solvent interactions are neglected, the energy associated with each $[n_1, n_2, \ldots]$ configuration depends only on the total number of loops $n_S$, and the partition function becomes


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$$Z = \sum_j \exp\left(-\frac{U_j}{kT}\right) = \sum_{n1,n2,\ldots} \frac{n_S!}{n_1!n_2!\ldots} P_1^{n_1} P_2^{n_2} \ldots \exp\left(-\frac{An_S}{kT}\right) \tag{7}$$

The most likely configuration of the brush is provided by the maximum of

$$\log\left(\frac{n_S!}{n_1!n_2!\ldots} P_1^{n_1} P_2^{n_2} \ldots \exp\left(-\frac{An_S}{kT}\right)\right) \tag{8}$$

with respect to $n_1$, $n_2$, ..., which, after employing Stirling's approximation, $\log(n!) = n\log(n) - n$, reduces for an infinite chain to the system of equations

$$\frac{n_i}{\sum_i n_i} = \frac{n_i}{n_S} \exp\left(\log(P_i) - \frac{A}{kT}\right) \qquad 1 < i < \infty \tag{9}$$

As already mentioned, for an infinite 1D random walk, the random walker will always return to origin; hence, the sum of all probabilities for the formation of loops of $2i$ segments has to be unity:[11]

$$\sum_i P_i = 1 \qquad 1 < i < \infty \tag{10}$$

In the absence of interactions between segments and surface ($A = 0$), the solution of the system of eqs 9 is trivial

$$\frac{n_i}{n_S} = P_i \tag{11}$$

which shows that the number of loops $n_i$ of $2i$ segments in an infinite chain is proportional to their probability of occurrence $P_i$ ($n_i = P_i n_S$). However, when $A$ is nonzero, the system of eqs 9 does not have a physical solution, because for $A > 0$, $n_i/n_S < P_i$ for all $i$ and consequently $\Sigma_i n_i/n_S \equiv 1 < \Sigma_i P_i = 1$. Similarly, for $A < 0$, $n_i/n_S > P_i$ for all $i$, which is also impossible. This implies that the most probable configuration of an infinite chain composed of segments interacting with a surface is either collapsed on the surface (for $A < 0$) or stretched (for $A > 0$).

Let us address now the more realistic case of a finite chain of $N$ segments. The most probable configuration is subject to the constraint

$$2n_1 + 4n_2 + \ldots + 2in_i + \ldots = N \tag{12a}$$

with the additional condition that

$$n_i > 0 \tag{12b}$$

The equations for an extremum in the presence of the constraint 12a

$$\frac{\mathrm{d}}{\mathrm{d}n_i}\left(\log\left(\frac{n_S!}{n_1!n_2!\ldots} P_1^{n_1} P_2^{n_2} \ldots \exp\left(-\frac{An_S}{kT}\right)\right) - \lambda\left(N - \sum_i 2in_i\right)\right) = 0 \tag{13}$$

lead to

$$n_i = n_S \exp\left(\log(P_i) - \frac{A}{kT} - 2i\lambda\right) \qquad 1 < i < i_{max} \tag{14}$$

where $\lambda$ is a Lagrange multiplier and $i_{max}$ is the loop of maximum length compatible with eqs 12a and 12b.

By summing over all values of $n_i$ provided by eqs 14, one obtains

$$\sum_i n_i = \sum_i n_S \exp\left(\log(P_i) - \frac{A}{kT} - 2i\lambda\right) \tag{15}$$

which, because $n_S = \Sigma_i n_i$, reduces to

$$\sum_i \exp\left(\log(P_i) - \frac{A}{kT} - 2i\lambda\right) = 1 \tag{16}$$

which can be solved for $\lambda$. Once $\lambda$ is known, $n_S$ can be determined from the constraint in eq 12a

$$\sum_i 2in_i = 2n_S \sum_i i \exp\left(\log(P_i) - \frac{A}{kT} - 2i\lambda\right) = N \tag{17}$$

In what follows, it will be assumed that any configuration of the grafted chain is composed of closed loops with $1 \le i \le N/2$ and open loops with $N/2 < i \le i_{max} = N$. The small loops with $i = 1$, which correspond to the closest possible approach of the segments to the surface, constitute the trains.

The effect of segment−surface interaction is examined in Figures 1 a and b for $N = 100$ and $N = 1000$, respectively (the segment−segment and segment−solvent interactions are neglected in this section). The probabilities of formation of loops with $2i$ segments, $n_i/n_S$, for various interactions $A$, are plotted as functions of $i$. One can observe that the repulsion between segments and surface affects only slightly the density distribution of segments, whereas the attractive interactions affect much stronger that distribution, particularly for long chains. The reason for this behavior is that, when the segment−surface interaction is attractive, the formation of short loops leads to large $n_S$ values, hence high adsorption energies, $(n_S - 1)A$, associated with these configurations. When the absolute value of $A$ is sufficiently large, the brush collapses on the surface. On the other hand, when the interaction between segments and surface is repulsive, the configurations with large loops (or tails) are favored; hence, $n_S$ is small, and the energy $(n_S - 1)A$ is in this case small; therefore, its effect is less significant than in the former case.

Let us compare the above results to those provided by our previous Monte Carlo simulations. As suggested in ref 10, a trial chain configuration was generated as follows. Successive loops of $j_1$, $j_2$, ... segments have been generated randomly with probabilities $P(i)$ provided by eqs 4 until the total number of segments exceeded $N$ ($j_1 + j_2 + \ldots > N$), the last (incomplete) loop being considered a tail. Once a configuration was obtained, a weighting factor due to the interaction energy, $\exp(-((n_S - 1)A)/(kT))$, was associated with that configuration and another trial was started. Figure 2a shows that, in the absence of surface−segment interactions, a small number of trials ($t = 1000$) was sufficient to obtain good approximations for the probabilities of occurrence of loops in the brush, compared to those provided by the present treatment. When the number of trials was increased ($t = 10^5$), there was almost no difference between the two. However, even for a relatively short chain ($N = 100$) and a small attractive interaction ($A = -0.2\ kT$), $t = 10^5$ Monte Carlo trials fails to reproduce the probability of occurrence of long loops in the brush, overestimating them drastically compared to the present method. The percentage differences between the Monte Carlo simulations and the present calculated probabilities of the loop occurrence in the most likely configuration (eqs


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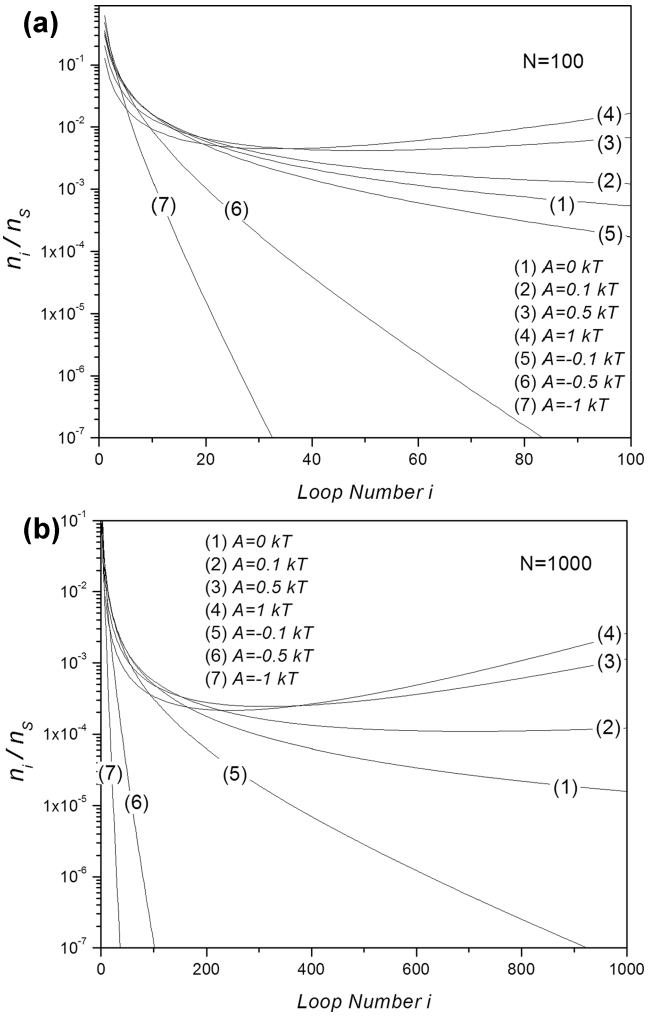


**Figure 1.** (a and b). Probabilities of loops occurrence in brushes of finite chains (a, $N = 100$; b, $N = 1000$) as functions of loop number $i$ for various segment−surface interactions $A$. The change in probabilities (particularly for attractive interactions) is strongly dependent on the length of the polymer chains.

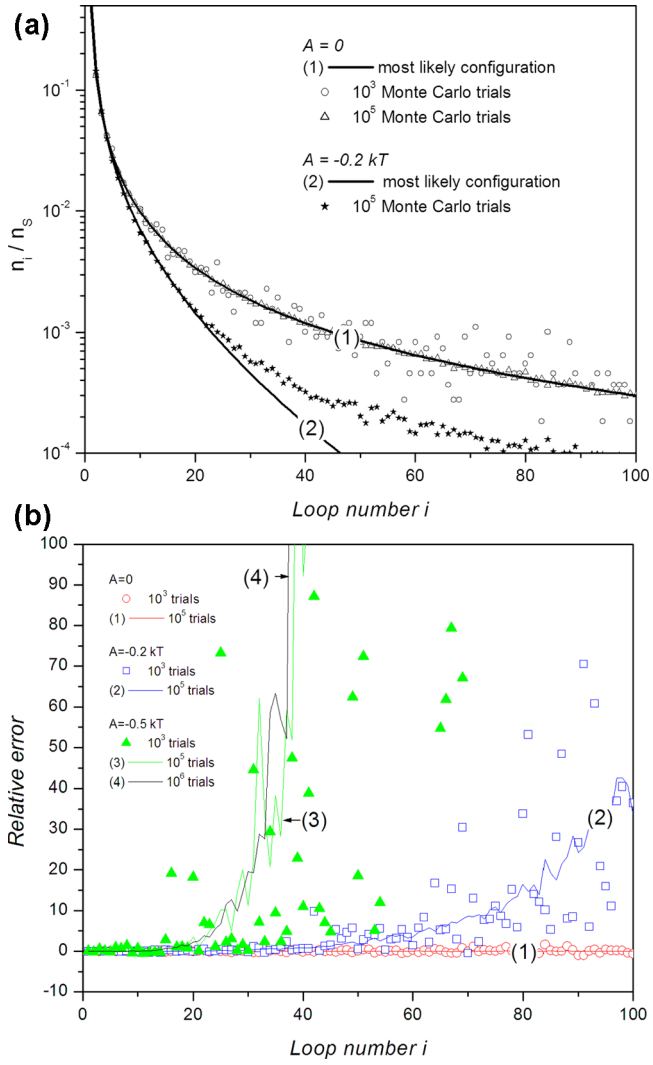


**Figure 2.** (a) Probabilities of loop occurrence in most likely configuration (continuous line) compared to Monte Carlo simulations, for $A = 0$ and $A = -0.2\ kT$, $N = 100$, as functions of loop number $i$. (b) Relative error of the probability of loop occurrence between Monte Carlo simulations and most likely configurations, for various $A$ values.

14−17) are plotted in Figure 2b. For slightly larger adsorption interactions ($A = -0.5\ kT$), even increasing the number of trials to $t = 10^6$ does not improve much the accuracy. The reason for this behavior is that train configurations (with mostly short loops), which possess very large weight factors, are unlikely to be generated in a Monte Carlo trial; for example, a configuration of loops with $i = 2$ has the probability to be generated of only $(1/2)^{N/2}$, and even so it has a large weight factor $\exp(-(NA)/(2kT))$. For $N = 100$ and $A = -0.5\ kT$, the probability is $\sim 10^{-15}$ and the weight factor is $\sim 10^{11}$.

The incapability of Monte Carlo estimations to predict accurately the collapse of the brush was avoided in ref 10 by generating all possible configurations composed of short loops via the Young diagrams; however, the procedure becomes very time-consuming for $N$ larger than about ∼100 segments. The present method can be applied to practically any value of $N$ (it was employed here for up to $N = 50\ 000$).

The dependence of the total number of loops on $A$ is plotted in Figure 3a, for various chain lengths $N$. At large and positive values of $A$, the chains are detached from the surface, forming tails (hence $n_S \rightarrow 1$). At large and negative values of $A$, the chains are collapsed on the surface, forming trains (hence $n_S \rightarrow N/2$).

The profile of the brush (the density of segments as a function of the distance from the surface) is presented in Figure 3b, for $N = 1000$. As in ref 10, it was assumed a uniform density of segments in each loop, which is extended between $z = 0$ (the surface) and $z = ia$ (the maximum possible loop extension). For large repulsive interactions between segments and surface, the distribution of segments is almost steplike, whereas for sufficiently large attractive interactions the distribution becomes exponential-like, with most segments confined to the vicinity of the surface. The profile of a real brush depends also strongly on segment−segment and segment−solvent interactions, which will be taken into account in the next section.

The thickness of the brush, defined as the average distance between segments and surface, is plotted in Figure 4 versus $A$ for various chain lengths. Whereas Figure 2 shows a dramatic increase in the number of loops when $A$ is negative and large in absolute value, Figure 4a shows that the thickness of the brush increases sharply when $A$ becomes positive and large, with


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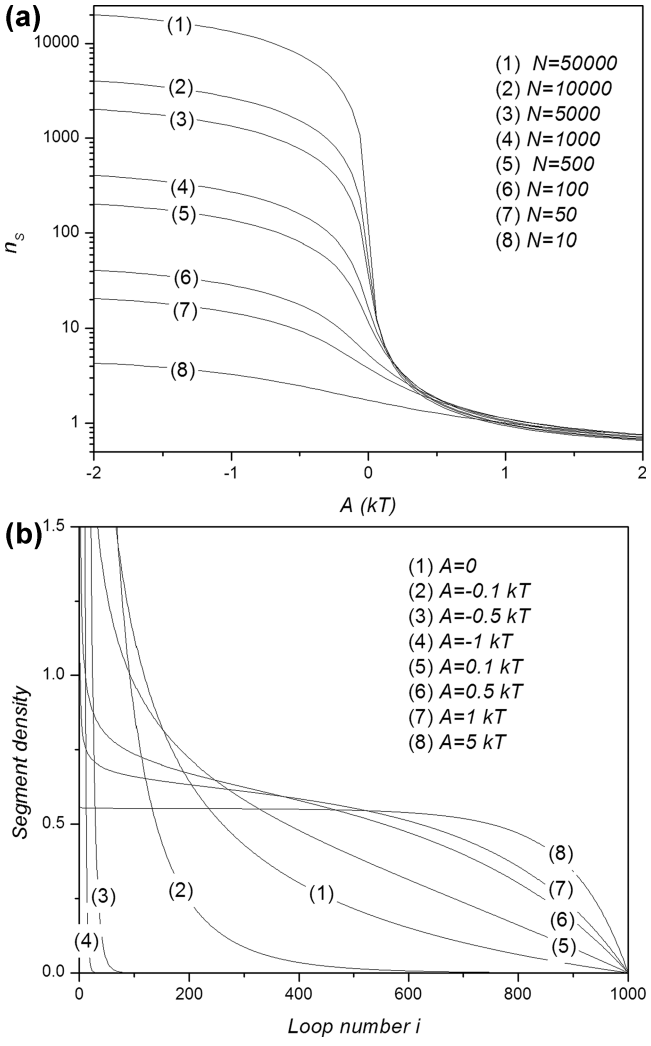


**Figure 3.** (a) Total number of loops, $n_S$, of the most likely configuration, plotted versus $A$ for various polymer chain lengths. (b) Profile of the brush (the density of Kuhn segments as a function of the distance from the surface) for various segment−surface interactions $A$.

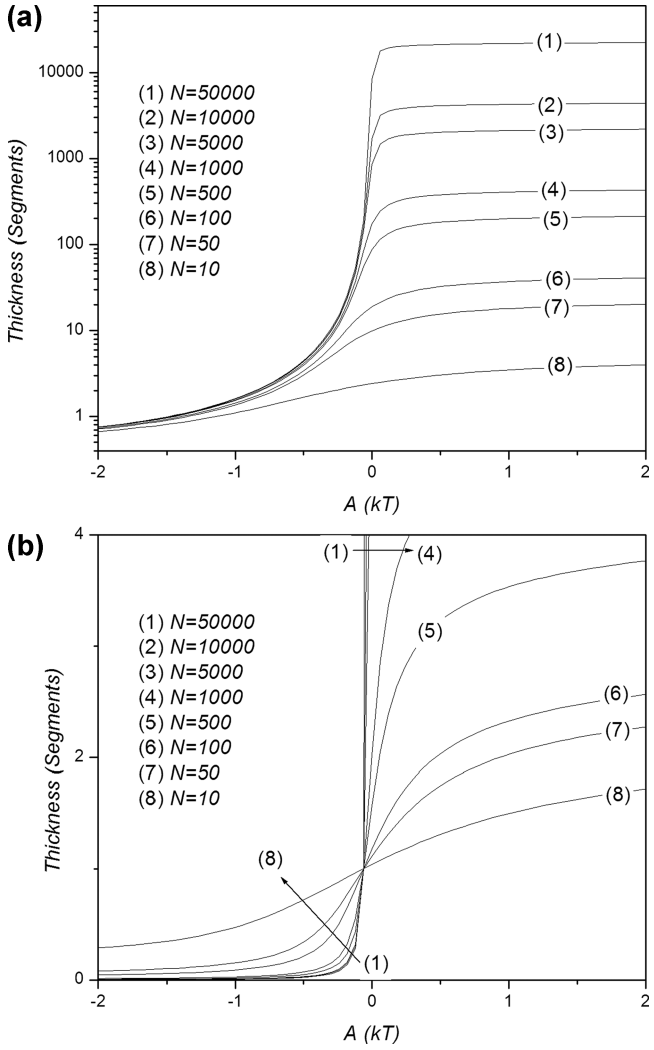


**Figure 4.** (a) Thickness of the brush (calculated as the average distance between a Kuhn segment and the surface) vs $A$, for various chain lengths. (b) Ratio between the thickness of the brush and the thickness of the brush for $A = 0$ shows that the collapse of the brush on the surface is strongly dependent on the length of the polymer.

critical values of A dependent on the length of the chain. In Figure 4b, the ratio between the thickness of the brush and the thickness of the brush for $A = 0$ shows that the critical value of $A$ for the collapse of the brush (which can be defined, e.g., as the value of $A$ at which the brush thickness becomes a few Kuhn segments in length) depends on the length of the polymer.

The probabilities for a segment to belong to a train ($i = 1$), a loop ($1 < i \leq N/2$), or a tail ($N/2 < i \leq N$) are plotted in Figure 5 as functions of $A$, for $N = 100$ and $N = 1000$. Both the collapse of the chain on the surface (loops to trains transition) and the stretching of the polymer (loops to tails transition) as functions of the segment−surface interaction parameter $A$ are strongly dependent on the length of the polymer chain and behave like phase transitions for sufficiently long polymers. In the next section, the role of the segment−segment and segment−solvent interactions on those transitions will be examined.

## 3. THE MOST LIKELY CONFIGURATION FOR SEGMENT−SURFACE, SEGMENT−SEGMENT, AND SEGMENT−SOLVENT INTERACTIONS

Let us now assume that the segment−segment and segment−solvent interactions can be described by the Flory−Huggins free energy density $F_{FH}$[13]

$$F_{FH}(z) = \frac{kT}{a^3}\left(\frac{\phi}{N}\ln(\phi) + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right) \cong \frac{kT}{a^3}((1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)) \quad (18)$$

where $a$ is the length of a Kuhn segment, $\phi$ is the volume fraction of the polymer, $\chi$ is the Flory interaction parameter, and the term containing $N$ is negligible because $N$ is large. Whereas Flory−Huggins free energy is a mean-field approximation for the segment−segment and segment−solvent interactions, any other method that allows one to associate


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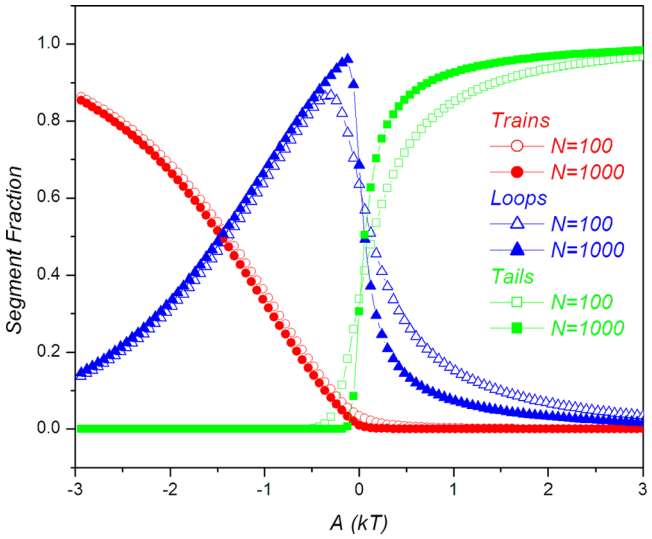


**Figure 5.** Percentages of Kuhn segments belonging to trains, loops, and tails for $N$ = 100 and $N$ = 1000 as functions of the segment–surface interaction $A$.

an energy with a loop can be employed with the method described here.

If a polymer chain consisting of $N$ Kuhn segments of length $a$ and volume $v$ occupies an area $s^2$ on the surface, the grafting density is $D = N/s^2$. For a conformation composed of $N/2i$ loops of $2i$ segments, each loop occupies an area $s^2/(N/(2i)) = (2is^2)/N$. It was shown before[9] that the minimum of the free energy of the configuration is obtained for a stretched loop of length $ia$ with a constant segment density $\phi = (Nv)/(s^2ia)$. The details of the calculations are as follows.

The total free energy associated with a loop (the integral of the free energy density over the volume of the loop) as a functional of $\phi(\zeta)$ is given by

$$U(\phi) = \frac{2is^2}{N}\int_0^{ia} F_{FH}(\phi)\,d\zeta = \frac{2is^2kT}{Na^3}\int_0^{ia}((1-\phi)\ln(1-\phi)+\chi\phi(1-\phi))\,d\zeta \quad (19a)$$

with the condition that the loop contains exactly $2i$ segments:

$$2i = \frac{2is^2}{Nv}\int_0^{ia}\phi(\zeta)\,d\zeta \quad (19b)$$

The function $\phi(\zeta)$ which minimizes the functional 19a with the constraint 19b is provided by the extremum of the functional

$$\boldsymbol{F}(\phi(\zeta)) = \int_0^{ia} F(\phi(\zeta))\,d\zeta = \int_0^{ia}((1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)+\lambda'\phi(\zeta))\,d\zeta \quad (20)$$

where $\lambda'$ is a Lagrange multiplier. The corresponding Euler–Lagrange equation

$$\frac{\partial}{\partial\zeta}\frac{\partial F}{\partial\left(\frac{\partial\phi}{\partial\zeta}\right)} - \frac{\partial F}{\partial\phi} = 0 \quad (21)$$

leads to

$$\ln(1-\phi) - \chi(1-2\phi) = \lambda' - 1 \quad (22)$$

Since the right-hand member is independent of $\zeta$, so should be the left-hand member of eq 22, which implies that $\phi(\zeta)$ = constant. The condition 19b then leads to

$$\phi(\zeta) = \frac{Nv}{s^2ia} \quad (23)$$

Consequently, the minimum Flory–Huggins free energy associated with each loop of $2i$ segments is obtained by integrating over the volume of the loop:

$$U_{FH}(i) = \frac{2is^2}{N}\int_0^{ia} F_{FH}(\zeta)\,d\zeta = \frac{2is^2kT}{Na^3}\int_0^{ia}((1-\phi)\ln(1-\phi)+\chi\phi(1-\phi))\,d\zeta = \frac{2i^2s^2kT}{Na^2}((1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)) \quad (24)$$

The total Flory–Huggins energy of the configuration with $[n_1, n_2, ...]$ loops is the sum

$$U_{FH} = \sum_i n_i U_{FH}(i) \quad (25)$$

and the partition function (eq 6) becomes

$$Z = \sum_j \exp\left(-\frac{U_j}{kT}\right) = \sum_{n1,n2,...}\frac{n_S!}{n_1!n_2!...}P_1^{n_1}P_2^{n_2}...P_i^{n_i}...\exp\left(-\frac{U(n_1,n_2...)}{kT}\right) = \sum_{n1,n2,...}\frac{n_S!}{n_1!n_2!...}P_1^{n_1}P_2^{n_2}...P_i^{n_i}...\exp\left(-\frac{\sum_i n_i U_{FH}(i)}{kT} - \frac{n_S A}{kT}\right) \quad (26)$$

The above expression can be rewritten as

$$Z = \sum_{n1,n2,...}\frac{n_S!}{n_1!n_2!...}\left(P_1\exp\left(\frac{U_{FH}(1)}{kT}\right)\right)^{n_1}...\left(P_i\exp\left(\frac{U_{FH}(i)}{kT}\right)\right)^{n_i}...\exp\left(-\frac{n_S A}{kT}\right) = \sum_{n1,n2,...}\frac{n_S!}{n_1!n_2!...}(P_1')^{n_1}(P_2')^{n_2}...(P_i')^{n_i}...\exp\left(-\frac{n_S A}{kT}\right) \quad (27)$$

which is formally the same as the partition function of a chain in the absence of segment–segment and segment–solvent interactions (eq 7), providing that the probabilities of loop formation for a finite random walk, $P_i$, are replaced by

$$P_i^* = P_i\exp\left(-\frac{U_{FH}(i)}{kT}\right) \quad (28)$$

When $\phi$ is large, the exclusion interactions prevent $\phi$ to reach unity. Whereas the maximum possible value of $\phi$, at close


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packing, depends on the shape of the segments, it will be simply assumed in what follows that $\phi = (Nv)/(s^2ia) < \phi_{max} = 1$ . This implies that the loops with a small number $2i$ of segments cannot be present in the brush, because in this case $U_{FH}(i)$ is divergently large; hence, $P_i^* = 0$ in eq 28, which leads to a lower bound, $i_{min}$, for $i$

$$\phi = \frac{Nv}{s^2ia} < 1 \qquad i > i_{min} = \frac{Nv}{s^2a} \tag{29}$$

Consequently, when segment−segment and segment−solvent interactions are accounted for, the probability of loop formation $P_i^*$ becomes

$$P_i^* \equiv 0 \qquad i < i_{min} \tag{30a}$$

$$P_i^* = P_i \exp\left(-\frac{2i^2s^2}{Na^2}((1-\phi)\ln(1-\phi) + \chi\phi(1-\phi))\right)$$

$$i > i_{min} \tag{30b}$$

where $\phi = (Nv)/(s^2ia)$ and $P_i$ is the probability of loop formation in the absence of segment−segment and segment−solvent interactions.

The effect of segment−segment and segment−solvent interactions on the probabilities of loop formation $n_i/n_S$ is presented in Figure 6a, for a good ($\chi = 0$), neutral ($\chi = 0.5$), and bad ($\chi = 1$) solvent, for $N = 1000$, $A = 0$, and a small grafting density $D = N/s^2 = 0.2$ segments/Å$^2$. Whereas at low grafting densities the effect is negligible, it becomes much stronger for large grafting densities ($D = 1$ in Figure 6b). At very large grafting densities, while the loop with small number of segments are forbidden because of exclusion effects, the probabilities of loops with intermediate values of $i$ are increased, and those of the loops with large values of $i$ are decreased (see Figure 6c).

The thicknesses of the brush, as functions of the interaction between segments and surface ($A$), are shown in Figure 7 for good, neutral, and bad solvents. The dependence of the brush thickness on $A$ is very similar to the one in the absence of segment−segment and segment−solvent interactions, with bad solvents favoring the collapse of the brush on the interface and good solvent favoring the loop to tail transition.

## 4. CONCLUSIONS

The possible grafted chain configurations have been described as ensembles of loops of $2i$ segments, with probabilities equal to those of first return of a random walk (when segment−segment and segment−solvent interaction were neglected), and modified when the latter interactions were taken into account. The most likely configuration with respect to the number of loops of $2i$ segments, $n_i$, provided a system of equations, which does not have solution for an infinite chain with nonvanishing interactions between segments and surface. However, for finite chains the system of equations has solution for any segment−surface interaction $A$. It was concluded that the brush collapses on the surface when the attractive segment−surface interactions are sufficiently large, and the brush stretches when the repulsive segment−surface interactions are strong enough.

The critical values of $A$ at which the loops to trains and the loops to tails transitions start to occur depend strongly on the number of Kuhn segments of the polymer, as well as on the segment−segment and segment−solvent interactions and grafting density. Therefore, for a selected adsorption interaction

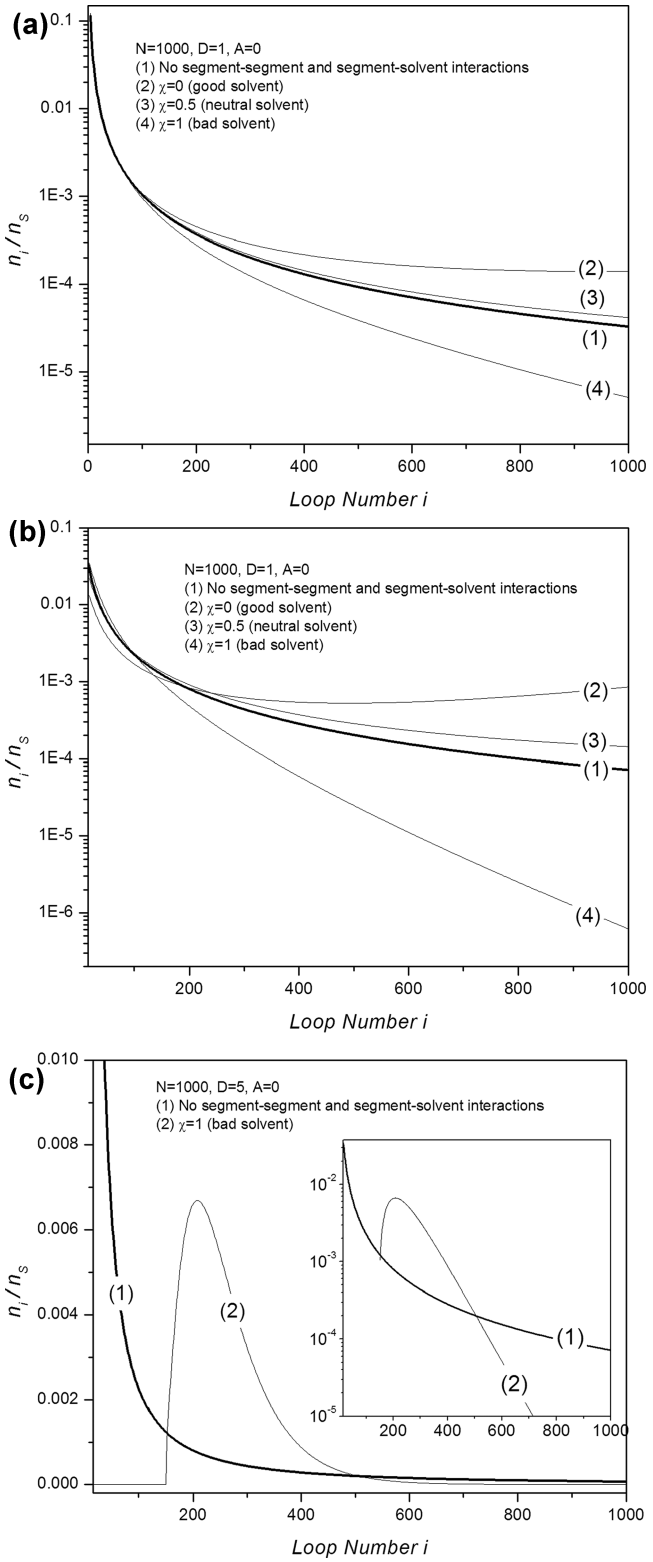


**Figure 6.** (a) Probabilities of occurrence of loops of $2i$ segments in a brush, $n_i/n_S$, for a relatively low grafting density $D = 0.2$ segment/Å$^2$ for a good ($\chi = 0$), neutral ($\chi = 0.5$), and bad ($\chi = 1$) solvent, are compared to the same probabilities in the absence of segment−segment and segment−solvent interactions. The segment−surface interactions have been neglected ($A = 0$). (b) Probabilities of occurrence of loops of $2i$ segments in a brush, $n_i/n_S$, for a relatively large grafting density $D = 1.0$ segment/Å$^2$ for a good ($\chi = 0$), neutral ($\chi = 0.5$), and bad ($\chi = 1$) solvent, compared to the same probabilities in the absence of segment−segment and segment−solvent inter-


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**Figure** 6. continued

actions. The segment−surface interactions have been neglected ($A$ = 0). (c) Probabilities of occurrence of loops of $2i$ segments in a brush, $n_i/n_S$, for a large grafting density $D$ = 5.0 segment/Å$^2$ shows that the bad ($\chi$ = 1) solvent favors the loops of intermediate $i$ values (the inset is the same graph plotted in logarithmic scale).

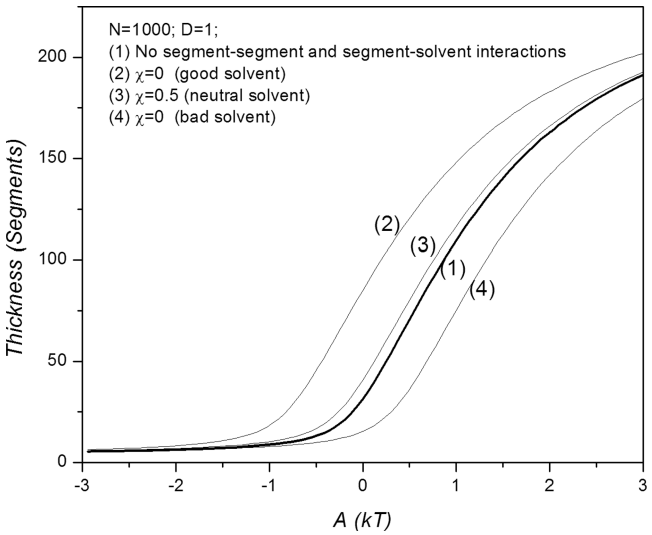


**Figure 7.** Thickness of the brush plotted against $A$, for $N$ = 1000 segments, $D$ = 1 segment/Å$^2$ for a good ($\chi$ = 0), neutral ($\chi$ = 0.5), and bad ($\chi$ = 1) solvent. All curves have behaviors similar to those obtained when segment−segment and segment−solvent interactions have been neglected.

between segments and surface, it is possible to design a polymer brush of certain length and grafting density, whose thickness is strongly dependent om changes in the solvent properties.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: mmanciu@utep.edu.

### Notes

The authors declare no competing financial interest.

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