Excluded volume effects in polymer brushes at moderate chain stretching

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We develop a strong stretching approximation for a polymer brush made of self-avoiding polymer chains. The density profile of the brush and the distribution of the end monomer positions in stretching direction are computed and compared with simulation data. We find that our approach leads to a clearly better approximation than previous approaches based upon Gaussian elasticity at low grafting densities (moderate chain stretching), for which corrections due to finite extensibility can be ignored.

I. INTRODUCTION

Only ideal chain models have been assumed in previous literature for the analytic self-consistent calculation of the polymer brush density profile and the distribution of free ends. Within such an approach, the Gaussian elasticity is typically balanced by repulsive two body interactions, similar to the Flory theory of a polymer in good solvent. This analytic framework is known as the ‘Strong Stretching Approximation’ (SSA), since it also neglects fluctuation effects. It was later extended to account for finite chain extensibility whereby it was shown recently that finite extensibility enhances the surface instability effect in dense brushes.

The SSA predictions for the monomer density profile $\phi(z)$ and the distribution of free ends $P_{N}(z)$ in good solvent have been tested widely with simulation data of brushes made of self-avoiding polymer chains. The ‘standard’ SSA results were found to give a far better agreement to the simulation data as compared to the step-like profile approach suggested by Alexander and de Gennes. Nevertheless, qualitative differences to the SSA approximation were detected. In particular, deviations were found for the distribution of free ends, which were often assigned to finite extensibility effects, even though a rather low grafting density was reached in some of these works. For a better understanding of this point, we focus in the present work on the limit of low grafting densities and moderate chain stretching.

As pointed out by de Gennes, the Flory theory leads to large errors for the individual contributions of elasticity and two body interactions, while the average chain extension is approximated well in most cases. This fact is reflected by the estimate for the chain conformations in a polymer brush, since SSA using ideal chains and scaling models assume Gaussian elasticity at low grafting densities (moderate chain stretching). For large fluctuations towards small chain extensions, the tension blobs increase in size and a continuous but slow cross-over to Gaussian elasticity is expected for the static monomer fluctuations, as for instance, the distribution of the free ends $P_{N}(z)$. Note that this slow cross-over for the static monomer fluctuations was observed previously for unentangled polymer networks.
In the present work, we want to demonstrate that previously observed deviations to the classical SSA approximation extend to very low grafting densities, for which finite extensibility cannot be used as an explanation. We show that the differences between data and theory arise from the approximations used in previous self-consistent calculations. We elaborate this point in the framework of a strong stretching approximation [6] that is extended to incorporate both, the elasticity of self-avoiding chains and the scaling expression for the osmotic pressure (Section III). The theory is written in general form, such that good solvent or Θ-solutions are derived simultaneously. The obtained results are presented in comparison to previous works in section III. Furthermore, in section IV, we put the new predictions to a test with simulation data on polymer brushes at very low grafting densities such that effects of finite extensibility can be ignored. In section V we discuss the scaling of the distribution of free ends and show that simulation data is in agreement with our model but not with the classical SSA. Finally, we discuss our results in section VI.

II. THE STRONG STRETCHING APPROXIMATION FOR A SELF-AVOIDING CHAIN

To simplify notation, we normalize all length units by the length of a Kuhn segment of the chains such that all lengths become dimensionless. Similarly, we make the energy scale dimensionless by putting $k_B T = 1$, with the Boltzman constant $k_B$ and the temperature $T$. Furthermore, we drop all coefficients of order unity, if these do not arise from our computations. Below we consider only the model case of a monodisperse layer of chains with degree of polymerization $N$ that are grafted at a constant grafting density $\sigma$.

Let us first discuss the limits and simplifications of the strong stretching approximation. Due to the assumption that the degree of polymerization tends to infinity, $N \to \infty$, corrections and fluctuations (which are of order $\approx N^{1/2}$) are fully neglected [28]. Hence, the fluctuating tail at the brush surface as observed in simulations and numerical calculations is missing [29]. Also, the depletion effect within the first blob next to the grafting surface is ignored. With increasing $N$, the agreement to SSA is enhanced, as these effects become unimportant.

To apply a SSA, the grafting density $\sigma$ must be large enough to ensure sufficient overlapping of neighbouring chains. Hence, $\sigma \gg \sigma^*$, with $\sigma^* = 1/(\pi R_{g0}^2)$ the overlap density and $R_{g0}$ denoting the radius of gyration of an isolated chain at same solvent conditions. In Ref. [17], this lower bound is estimated as $\sigma \geq 8/(\pi R_{g0}^2)$. Since the ’standard’ SSA [1, 2] neglects finite extensibility of the chains, $\sigma$ must be bound from above to ensure that the chains are not ’overstretched’. This upper bound was roughly estimated as $\sigma \lesssim 0.2$ [3, 6]. In the present work, we also want to neglect finite extensibility effects and conclude for the limits of our approximation:

$$\frac{8}{\pi R_{g0}^2} \leq \sigma \lesssim 0.2 \quad (1)$$

The starting point for our approach is a model equation for the chain deformation. In the limit of weak or moderate chain stretching, all ideal chain models show a linear elongation-force relation

$$\frac{r}{N} \propto e(f) \propto f, \quad (2)$$

where $r/N$ denotes the relative elongation with respect to the contour length (chain length $N$) and the applied force $f$. Let us write the elongation-force relation for a self-avoiding chain in general form [21]

$$e(f) \propto f \frac{1-z}{w}, \quad (3)$$

such that it describes simultaneously a self-avoiding polymer with Flory exponent $\nu \approx 0.588 \approx 3/5$ [22] in good solvents and an ideal chain or a self-avoiding polymer in Θ-solvents with $\nu = 1/2$. As discussed in the introduction, we assume that the elasticity of a chain in a brush at good solvent conditions is well described by an exponent of $\nu \approx 0.588$ in constrast to previous works. Note that the same elongation-force relation was used to describe polyelectrolyte brushes [23], for which the Pincus blob is smaller than the concentration blob due to the osmotic pressure of the counterions. In the following, we only consider the direction perpendicular to the grafting surface (in $z$-direction) and assume that the brush is homogeneous in lateral $xy$-directions.

In the SSA, it is considered that the elongation-force relation of Equation (2), resp. Equation (3), is ‘locally’ valid [6]. Let us introduce $s := i/N$ to denote the normalized chain contour, where $i$ represents the $i$-th segment and discuss the elongation-force relation $e(f)$ under a locally applied force. In this view, the inverse of $e(f)$ gives the amount of ‘segments’ $ds$ being localized in the element $dz$ at position $z$.

Let us choose the boundary conditions such that the first segment is pinned at $z(s = 0) = 0$ and the last segment is elongated to position $z(s = 1) = z_e$. Then, we can write for the contour integral

$$\int_0^1 ds = \int_0^{z_e} dz' \frac{dz'}{e(f)N} = 1. \quad (4)$$

In the following, we describe the chains as a non-harmonic spring in a non-uniform stretching field.
This stretching field along the ‘contour’ s of the chain is generated by a potential field \( \Phi(z) \) in space \( \Theta \):

\[
\frac{\partial f(z(s))}{\partial s} = -\frac{\partial \Phi(z)}{\partial z}.
\]

The following boundary conditions must be fulfilled: 
\( z(s = 0) = 0 \) (grafting condition), \( f(s = 1) = 0 \) (no force on the free chain end in equilibrium) and 
\( z(s = 1) = z_c \) (position of the free chain end). 
Integrating both sides in Equation (5) under these boundary conditions we have:

\[
\int_{f(z_e)=0}^{f(z)} e(f')df' = \Phi(z_e) - \Phi(z).
\] (6)

With Equation (3), we find the following relation between force and potential field

\[
f \propto \left( \frac{\Phi(z_e) - \Phi(z)}{\nu} \right)^\nu.
\] (7)

The self-consistent potential must be that one where the spring is in a state of indifferent equilibrium \( \Theta \). This is the only possibility to provide a continuous distribution \( P_N(z_e) \) of the free ends of monodisperse chains. The self-consistency condition (or the indifferent equilibrium condition) in case of arbitrary \( \nu \) is derived from combining Equation (4) with (3) and (7)

\[
\int_0^{z_e} \frac{dz'}{(\Phi(z_e) - \Phi(z'))^{1-\nu}} = \text{const. \( \forall z_e \).}
\] (8)

Using \( q = z'/z_e \) this transforms to

\[
\int_0^1 \frac{z_e dq}{(\Phi(z_e) - \Phi(z_e q))^{1-\nu}} = \text{const. \( \forall z_e \)},
\] (9)

which can only become independent of \( z_e \), if

\[
\Phi(z) \propto \left( \frac{z}{N} \right)^{1/(1-\nu)}.
\] (10)

In case of a Gaussian chain (or a chain in \( \Theta \)-solvent with \( \nu = 1/2 \)) we recover with \( e(f) = f/3 \), the results of previous works [1, 2, 6, 7]

\[
\Phi(z) = \frac{3\pi^2}{8} \left( \frac{z}{N} \right)^2 \approx 3.71 \left( \frac{z}{N} \right)^2,
\] (11)

while for a swollen chain we find for \( \nu = 3/5 \) and introducing a spring constant \( a \) in Equation (3) that

\[
\Phi(z) = \frac{3}{5} \left( \frac{2 - 2}{\sqrt{5}} \right)^{5/4} \left( \frac{2\pi}{5} \right)^{5/2} a^{-3/2} \left( \frac{z}{N} \right)^{5/2}
\]

\[
\approx \frac{1.2}{a^{3/2}} \left( \frac{z}{N} \right)^{5/2}.
\] (12)

To calculate the profile of the monomer volume fraction \( \phi(z) \) and the free end distribution \( P_N(z) \) we need to define an equation of state relating the monomer chemical potential \( \mu \) to \( \phi(z) \). For the description of polymer brushes originally [1, 2] only the leading order of the virial expansion of the osmotic pressure

\[
\Pi \approx \nu \phi^2
\] (13)

in good solvent was considered. This is similar to the Flory theory, where Gaussian elasticity is combined with repulsive two body interactions. Here, the Parameter \( \nu \) denotes the excluded volume.

In analogy to scaling estimates for the equilibrium degree of swelling of a polymer network [30], we combine the scaling approach for the osmotic pressure of a semi-dilute solution of polymers [30]

\[
\Pi \approx \nu(6\nu-3)/(3\nu-1) \phi^{3/2}/(3\nu-1),
\] (14)

with the scaling of chain elasticity as described by equation (3). Note that the osmotic pressure is \( \propto \phi^3 \) in \( \Theta \)-solutions with \( \nu = 1/2 \) and \( \propto \phi^{2.3} \) with \( \nu \approx 0.588 \) for good solvents.

From Equation (14), the monomer chemical potential \( \mu \) can be obtained from considering the change in free energy

\[
\Delta F = -\int pdV \propto (3\nu - 1)\nu(6\nu-3)/(3\nu-1)M\phi^{1/(3\nu-1)}
\] (15)

using \( \phi = M/V \). Here, \( M \) is the total number of monomers in the system, \( p \) the pressure and \( V \) the volume of the system as measured in unit volumes. The chemical potential is the change in free energy \( F \) upon adding or removing a monomer at constant volume and temperature. Thus,

\[
\mu(\phi) = \left( \frac{\partial F}{\partial M} \right)_{V,T} \propto 3\nu(6\nu-3)/(3\nu-1)\phi^{1/(3\nu-1)}.
\] (16)

Let us use \( H \) to denote the brush height. Since the monomer chemical potential \( \mu(\phi) \) must provide the self-consistent potential profile we have

\[
\mu(z) = \Delta \Phi(z) = \Phi(H) - \Phi(z)
\] (17)

and hence

\[
\phi(z) \propto \nu^{-1}(6\nu-3) \left( \frac{\Phi(H) - \Phi(z)}{3\nu} \right)^{3\nu-1},
\] (18)

where \( \Phi(H) \), and subsequently the brush height \( H \), is fixed by the normalization condition \( \int_0^H \phi(z)dz = N\sigma \). With Equations (18) and (10) we obtain

\[
\int_0^H dz \left( \frac{H}{N} \right)^{\nu} - \left( \frac{z}{N} \right)^{\nu-1} \propto N\sigma.
\] (19)
Using $y := z/H$ this condition becomes

$$\int_0^1 dy \left( 1 - y^{1/(1-\nu)} \right)^{3\nu-1} \left( \frac{H}{N} \right)^{(2\nu)/(1-\nu)} \propto \sigma. \quad (20)$$

As a consequence of this analysis, we recover the scaling relation for the brush height \[13, 19\]

$$H \propto N^{(2\nu-1)/\nu} \sigma^{(1-\nu)/2\nu}. \quad (21)$$

Note, that for Θ-solvents with $\nu = 1/2$ the relations assumed in Equation \[3\] and \[14\] lead to identical results as previous work on a polymer brush in Θ-solution \[2\]. Finally, we have to mention that the ‘standard’ SSA leads to a prediction $H \propto (\sigma)^{1/3} N \[1, 2\]$ that agrees with the scaling result by coincidence, if $\nu = 3/5$, as discussed previously \[31\].

III. THE BRUSH PROFILE AND THE DISTRIBUTION OF END MONOMERS

The brush profile $\phi(z)$ and the free end distribution $P_N(z)$ of the brush chains differ considerably from previous self-consistent models in the ‘standard’ SSA approximation of Refs. \[1, 2\]. The present approach, combining the scaling relations for elongation and osmotic pressure, predicts a clearly different density profile (using Equation \[10\] in Equation \[13\]):

$$\phi(z) = \phi_0 \left( 1 - \left( \frac{z}{H} \right)^{1/(1-\nu)} \right)^{3\nu-1} \quad (22)$$

$$\approx \phi_0 \left( 1 - \left( \frac{z}{H} \right)^{2.43} \right)^{0.76} \quad (23)$$

in contrast to the ‘classical’ parabolic profile

$$\phi(z) = \phi_0 \left( 1 - \left( \frac{z}{H} \right)^2 \right) \quad (24)$$

of Ref. \[1, 2\]. In the case of Θ-solvent, setting $\nu = 1/2$ in eq. \[22\], we obtain the same result

$$\phi(z) = \phi_0 \left( 1 - \left( \frac{z}{H} \right)^2 \right)^{1/2}. \quad (25)$$

as Ref. \[32\] using the ‘standard’ SSA for ideal chains in Θ-solvent.

Note, that the particular brush height $H$ and the maximum monomer density $\phi_0$ depend on $\sigma$ and details of the model as, for instance, the spring constant in Equation \[3\] or the excluded volume parameter $v$ in Equation \[14\]. But the density profile in reduced units $\phi/\phi_0$ and $z/H$ leads to a universal plot for each of the above approximations. In Figure 1 we compare the normalized monomer density profiles of our approach with previous models \[1, 2\]. So far, the ‘Strong Stretching Approach’ in the low to moderate stretching approximation (low to moderate $\sigma$) \[1, 2\] always assumed a Gaussian chain elongation also in good solvent leading to a harmonic density profile ($\phi \sim -z^2$). The $\phi(z)$ in Equation \[23\] leads to a flattened density profile at the grafting surface with a steeper drop at the top of the brush in comparison to ‘standard’ SSA calculations \[1, 2\] making the density profile qualitatively more similar to the Θ-solvent prediction.

In comparison to the changes for the density profile, the differences for the free end distribution $P_N(z)$ are more pronounced. $P_N(z)$ is found \[6\] via an implicit integral equation that becomes

$$\phi(z) \propto \sigma \int_z^H \frac{P_N(z')dz'}{\left( z^{1/(1-\nu)} - z_1^{1/(1-\nu)} \right)^{(1-\nu)}} \quad (26)$$

for swollen chains. With Equation \[23\] and using $y' = z'/H$, resp. $y = z/H$, this leads to

$$\left( 1 - y^{1-\nu} \right)^{3\nu-1} \propto \int_y^1 \frac{P_N(y')dy'}{\left( y_1^{1-\nu} - y^{1-\nu} \right)^{(1-\nu)}}. \quad (27)$$

One can proof by insertion that $P_N$ must be of the following form:

$$P_N(y) \propto y^\nu/(1-\nu) \left( 1 - y^{1/(1-\nu)} \right)^{2\nu-1} \quad (28)$$

$$\approx y^{1.43} \left( 1 - y^{2.43} \right)^{0.176}. \quad (29)$$

The prediction of Equation \[29\] is compared in Figure 2 with the predictions from Refs. \[1, 2\] for the
Gaussian self-consistent field approach in good solvent:

$$P_N(y) \propto y \left( 1 - y^2 \right)^{1/2}$$  \hspace{1cm} (30)

and the solution in Θ-solvent \cite{32} (also obtained within the present approach for \(\nu = 1/2\) in eq. (28)):

$$P_N(y) \propto y.$$  \hspace{1cm} (31)

Note, Equations (29)-31 only hold for 0 \(\leq y = z/H \leq 1\) and are zero otherwise.

The signature of our approximation is the non-linear \(z^{\nu/(1-\nu)}\) dependence at small and intermediate \(z\) and the clear shift of the peak position of \(P_N(z)\) towards the upper free end of the brush in the case of good solvent. The predictions of the above models are now compared with simulation data.

IV. COMPARISON WITH SIMULATION DATA

In a recent work \cite{33}, the cross-linking process of polymer brushes was studied using the Bond Fluctuation Model (BFM) of Ref. \cite{34,35}. The equilibrated and not yet linked brushes of this work were used as starting basis for sampling \(\phi(z)\) and \(P_N(z)\) and we refer the reader to this work for further information on the parameters of the samples, the simulation method and the equilibration of the brushes. Additional samples with large \(N = 256\) and \(N = 512\) at very low grafting density \(\sigma = 1/64 \approx 0.016\) were created in similar manner in order to explore the limit at which finite extensibility can be ignored; further details of these additional simulations courtesy in \cite{36}. To collect data over an extremely long time interval, we use a GPU implementation of the BFM \cite{37} and equilibrated the brushes for more than one decade of relaxation times of the brush polymers.

In Figure 3, we display the resulting density profiles from these simulations in rescaled units. The predicted profile obtained in the present approach for swollen chains fits quite perfectly to the simulation data and provides a clear improvement in comparison with the Gaussian chain approach. In the Figure, we fitted the data only to our model and plotted the Gaussian chain approach for same \(H\) for comparison. The discrepancies between theory and data can be devoted to depletion effects at the (hard) grafting surface and fluctuation effects at the brush surface. For data at largest grafting densities shown in Figure 3, we observe a weak tendency towards a more step-like profile that we devote to the onset of finite extensibility of the chains and the increasing density in the brush, since the limits of our approximation are approached, see eq. 11.

In Figure 4, we test our prediction for the distribution of free chain ends, eqs. (29), with the corresponding simulation data. Also for \(P_N(z)\) our approach fits notably better in comparison to the ‘standard’ SSA result \cite{1,2}, eq. (24). Especially the non-linear slope of \(P_N(z)\) at small \(z\) positions can be explained using our approximation.

The trend of a more flattened density profile \(\phi(z)\) and a rather convex (instead of a concave) slope for the distribution \(P_N(z)\) of free ends is consistent with numerous data presented in previous works \cite{10,17}, where the simulation results were tested against the ‘standard’ SSA predictions. Often such deviations were devoted to finite extensibility effects \cite{13,16}, which is correct for grafting densities larger as in the present study. But for the low grafting densities of our work, finite extensibility cannot be used to explain the discrepancies to the ‘standard’ SSA. The
above results demonstrate that our model is a more accurate approximation for polymer brushes of self-avoiding chains at low grafting densities than previous approaches.

Yet another indication is provided in Refs. 13, 14, where the authors compare simulation results in good and in Θ-solvent. Comparing the chain end distributions for both cases, one can note a clear change in the slope of \( P_N(z) \) at small \( z \), turning from convex in good solvent to a rather linear slope in Θ-solvent, as predicted within our approach (see Figure 1). But the most convincing proof in favor of our approximation is presented in the following section.

V. A TEST OF THE SCALING OF THE DISTRIBUTION OF FREE ENDS

In the following, we use the normalization \( \int_0^H P_N(z)dz = 1 \) to work with a universal \( P_N(z)H = f(z/H) \). At small \( z \), resp. small \( y = z/H \) in eqs. (28) and (30), one can approximate the chain end distribution as \( P_N(z)H \propto y^{\nu/(1-\nu)} \), according to the present approach, or as \( P_N(z)H \propto y \), according to 'standard' SSA. Since \( H \propto N\sigma^{1-\nu}/2\nu \) (resp. \( H \propto N\sigma^{1/3} \)) and \( N^{\nu} \propto R_{g0} \) (the radius of gyration of a single free chain in good solvent), we transform both expressions for the chain end distributions into a universal form as function of \( R_{g0} \). Within the present approach we predict \( P_N(z) \) to show universality at small \( z \) if presented as

\[
P_N(z)\sigma^{1/(2\nu)}R_{g0}^{(1+\nu)/\nu} = f(z/R_{g0}) \propto \left( \frac{z}{R_{g0}} \right)^{\nu/(1-\nu)}.
\]

(32)

For \( \nu \approx 0.588 \) this becomes

\[
P_N(z)\sigma^{0.85}R_{g0}^{2.7} \approx f(z/R_{g0}) \propto \left( \frac{z}{R_{g0}} \right)^{1.43}.
\]

(33)

In contrast the 'standard' SSA expects universality for

\[
P_N(z)\sigma^{2/3}R_{g0}^{7/3} = f(z/R_{g0}) \propto \frac{z}{R_{g0}}.
\]

(34)

In Figures 5 and 6 we present our simulation data in the corresponding scaling forms. The radius of gyration \( R_{g0} \) is measured from the BFM simulations of a single free chain at the corresponding chain lengths. Indeed, at small \( z \) in Figure 5 the curves roughly fall onto each other and deviate as the brush height for the corresponding sample is approached. In contrast, in Figure 6 such a universal behavior cannot be observed at any range of the \( z \) position and the scaling form due to the 'standard' SSA clearly fails. Hence,
the new approach not only accounts for the qualitative difference in form of a changed slope for $P_N(z)$, but it also provides a better scaling of the simulation data.

VI. DISCUSSION

In the present work, we combined the model for the elasticity of self-avoiding chains and the scaling expression for the osmotic pressure in semi-dilute polymer solutions using a generalized 'Strong Stretching Approximation' [6] for the description of polymer brushes. The effect of self-avoidance of the polymer chains in brushes has not been considered in literature so far. Our results are fully consistent with scaling models for the brush height. In the case of good solvent, we predict deviations from the well-known parabolic density profile towards a more step-like form and a rather convex shape of the free end distribution $P_N(z)$ at small height values $z$, which is in contrast to the concave shape obtained previously [1, 2].

Our predictions are supported by simulation data of polymer brushes at very low grafting densities where finite extensibility can be safely ignored. Furthermore, our simulation results and the model predictions are in qualitative agreement with previously observed discrepancies between simulation data at low grafting densities $\sigma$ [11-17] and the classical SSA approximation. Since the valid regime of our approximation - polymer brushes at low to moderate grafting densities and chain stretchings - is often realized in experimental situations, we expect that our contribution is significant for further research. In particular, the predicted changes in the density profile and the free end distribution are fundamental for understanding the compression behaviour of brushes, the interpenetration of two opposing brushes, or the relaxation of chains inside a brush.

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