Fluctuation driven height reduction of crosslinked polymer brushes. A Monte Carlo Study.

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Abstract

We study the changes in the conformations of brushes upon the addition of crosslinks between the chains using the bond fluctuation model. The Flory-Rehner model applied to uni-axially swollen networks predicts a collapse for large degrees of crosslinking $q$ proportional to $q^{-1/3}$ in disagreement with our simulation data. We show that the height reduction of the brushes is driven by monomer fluctuations in direction perpendicular to the grafting plane and not due to network elasticity. We observe that the impact of crosslinking is different for reactions between monomers of the same or on different chains. If the length reduction of the effective chain length due to both types of reactions is accounted for in a function $\beta(q)$, the height of the brush can be derived from a Flory approach for the equilibrium brush height leading to $H(q) \approx H_b \beta(q)^{1/3}$, whereby $H_b$ denotes the height of the non-crosslinked brush.
I. INTRODUCTION

If polymer chains are grafted to a surface densely enough, the chains stretch out due to excluded volume interactions. Alexander and de Gennes developed the first theoretical models for polymer brushes based on mean-field and scaling concepts [1–3]. Later, Semenov [4] introduced a parabolic molecular field to describe the conformations of blocks copolymers in the strong segregation limit. Milner et al. [5] and Skvortsov et al. [47] obtained a similar refined description of the monomer profile inside the brush using self-consistent field approaches. In the scaling approach, the chains are considered as a stretched array of correlation blobs at a grafting density $\sigma$ above the overlap grafting density $\sigma^* \propto R^{-2} \propto b^{-2} N^{-2\nu}$. Here, $b$ is the root mean square bond length, $N$ the degree of polymerization of the chains, $\nu \approx 0.588$ the exponent for chains in athermal solvents [6], and $R$ is the size of a free coil. The correlation length $\xi$ is determined by the grafting density $\xi \approx \sigma^{-1/2}$. Each correlation volume contains

$$g \approx (\xi/b)^{1/\nu} \approx \sigma^{-1/(2\nu)} b^{-1/\nu}$$

(1)

monomers and the equilibrium brush height is given by

$$H_b \approx \xi N/g \approx N\sigma^{(1-\nu)/(2\nu)} b^{1/\nu}.$$  

(2)

Several groups tested these predictions and explored detailed static and dynamic properties of polymer brushes by applying Monte Carlo or Molecular Dynamics simulations [7–16]. On the experimental side, large progress has been made over the years [17] with recent accomplishments allowing very high grafting densities to be examined [18]. Since the polymers in the brush control the net interaction of the surface with its environment, this gave rise to a large variety of different applications. Examples are drug delivery [19], colloid stabilization [20, 21], reduction of friction [22, 24], increasing the bio-compatibility of medical implants [23], and switchable amphiphilic surfaces [26, 27].

For these applications, polymer brushes are often situated on surfaces that are exposed to a harsh environment. This can cause a destruction of the brush and chains may be broken or torn away from the substrate. To reduce degradation, crosslinking the chains is one obvious alternative. In a crosslinked brush, chains form a connected network, which prevents individual chains from leaving the surface layer even if their grafting points are broken. Therefore, crosslinking was used previously for stabilization [28, 29], while it was
also used to freeze a certain state of switchable brushes.

In our preceding publication, we explored the universality of the network structure and the linking statistics parallel to the grafting plane. It was found that a crosslinked brush can be mapped onto a two dimensional percolation problem, whereby the overlap of the chains controls the percolation problem. In the present work, we investigate the changes of the static behavior of polymer brushes upon crosslinking for systems far away from the gel point. In particular, we focus on the experimentally relevant question of the height reduction of the brush due to crosslinking. For a theoretical description of this problem, we derive the uni-axial swelling behavior of a crosslinked grafted layer using two different approaches: the Flory-Rehner Model in section and a new approach considering monomer fluctuations in direction perpendicular to the grafting plane in section. This latter approach predicts that inserting elastically active crosslinks into a brush does not collapse the brush (up to logarithmic corrections as function of the degree of polymerization $q$). This result is in clear contrast to the Flory-Rehner prediction, which leads to a collapse $\propto q^{-1/3}$. In order to directly assess the change of brush height upon crosslinking, we perform a parallel analysis of mono-disperse crosslinked and non-crosslinked brushes with the same degrees of polymerization $N$ and grafting densities $\sigma$ and compare with the predictions of both models. The details of the simulations are described briefly in the following section.

II. SIMULATIONS

We use the Bond-Fluctuation-Model (BFM) as introduced in 1988 by Carmesin and Kremer and extended to three dimensions by Deutsch and Binder. In this model, each monomer is represented by a cube of eight lattice positions on a regular cubic lattice. Excluded volume is modeled by not allowing monomers to overlap. The monomers of one chain are connected by a bond vector out of a predefined vector set. The combination of bond vector set and excluded volume of monomers ensures cut avoidance of strands without an explicit test of the local topology. Solvent is treated implicitly in the athermal limit and hydrodynamics is neglected. The BFM is well suited to capture static and dynamic properties of polymers melts, solutions, and networks.

The present work analyzes the same brushes as our previous work and we refer the reader for details on crosslinking and equilibration to Ref. In brief, we created brushes with...
degrees of polymerization $N = 16, 32,$ and $64$ and grafting densities $\sigma = 1/256, 1/64, 1/25, 1/16, 1/9, 4/25, \text{and } 1/4$. Note that the grafting density $\sigma$ is normalized to the maximum possible grafting density in the BFM model, which is $0.25$ in square lattice units. System sizes varied between approximately $1500$ and $10000$ grafting points arranged regularly on the $xy$-plane. Periodic boundary conditions were applied in $xy$-direction and reflecting boundary conditions in the $z$-direction. After equilibration, crosslinking occurs upon collision of two monomers. We only allow one additional crosslink per monomer. Crosslinking is stopped after a defined number of crosslinks in the sample is established. Note that we varied the crosslinking rate from $1$ to $0.001$ and did not observe a significant modification of the results. Thus, the networks of the present paper were reacted with the maximum possible reaction rate $1$. After crosslinking, brushes are relaxed until no further changes in the brush profile and the average monomer fluctuations were recognized.

III. THE EQUILIBRIUM HEIGHT OF A UNI-AXIALLY SWOLLEN NETWORK

In this section, we assume that a crosslinked brush can be modeled analogous to a uni-axially swollen network. The chains of a polymer brush are concentrated above their overlap concentration. Therefore, introducing additional crosslinks can shrink the brush height only, if the network modulus becomes larger than the osmotic pressure of the grafted chains. On a scaling level, this is equivalent to the condition, that there must be of order one crosslink per blob of the brush. Let us introduce the average number $q$ of crosslinks per chain. We further assume a perfect network structure for simplification. Since any crosslink connects two strands, the average strand length $n$ of a network chain is given by

$$n = N/(2q + 1).$$

Therefore, if this strand length $n$ is larger than the number $g$ of monomers per blob, $n > g$, we expect that the height of the brush remains mainly unmodified. Otherwise, for $n < g$, it is expected that the modulus of the network controls the height of the brush.

For this latter case, we use the Flory-Rehner (FR) approach [39] for network swelling to estimate the shrinking of the brush as function of crosslinking. Here, the mean field estimate for the osmotic pressure

$$\Pi(\phi) = \frac{k_B T}{b^3} \left[ \frac{\phi^2}{2} (1 - 2\chi) + \frac{\phi^3}{3} + ... \right]$$
is balanced by the Gaussian elasticity

\[ G(\phi) = \frac{\nu_2 k_B T (\lambda R)^2}{2 b^2 N} \approx \frac{\phi k_B T (\lambda R)^2}{n 2b^3 b^2 N} \]  

(5)
of the elastic strands as estimated by the phantom network model. \( \nu_2 \) is the number density of elastic strands, \( \chi \) is the Flory interaction parameter, \( \phi \) is the volume fraction of polymer, \( \lambda \) is the deformation ratio of the elastic strands, \( k_B \) is the Boltzmann constant, and we used \( b^3 \) as estimate for the monomeric volume. In order to apply this approach to the equilibrium height of a crosslinked brush we have to consider the particular geometry of the problem and the crosslinking of the chains.

In the Flory-Rehner approach [39], one considers the dry state (no solvent) as reference state for crosslinking. Swelling from the dry state is equivalent to a uni-axial deformation at constant cross-section of the network. This is expressed by introducing deformation ratios \( \lambda_x = \lambda_y = 1 \) parallel to the grafting plane and

\[ \lambda_z = \frac{H}{H_{\text{dry}}} = 1/\phi \]  

(6)
in direction of swelling. Assuming affine deformation of the strands, the change in elastic free energy per strand can be written as

\[ \Delta f_{el} = -T \Delta S_{el} = \frac{k_B T}{2} (\lambda_z^2 - 1) = \frac{k_B T}{2} \left( \frac{1 - \phi^3}{\phi^2} \right). \]  

(7)

Therefore, the density dependence of modulus can be written as

\[ G(\phi) \approx \frac{\phi k_B T}{n 2b^3} \left( \frac{1 - \phi^2}{\phi^2} \right). \]  

(8)

Equilibrium brush height is achieved [49] for \( \Pi(\phi) = G(\phi) \), which leads to

\[ \phi^2 (1 - 2\chi) + \frac{2\phi^3}{3} = \left( \frac{1 - \phi^2}{\phi n} \right). \]  

(9)

For large degrees of swelling, \( \phi \ll 1 \), we drop the third virial and the \( \phi^2 \)-term of the modulus to approximate

\[ \phi \approx \left( \frac{1}{n(1 - 2\chi)} \right)^{1/3}. \]  

(10)

Thus, the Flory-Rehner model predicts for an uni-axially swollen network a continuous shrinking as function of crosslinking:

\[ H \propto n^{1/3} \propto \left( \frac{N}{(2q + 1)} \right)^{1/3}. \]  

(11)
As mentioned above, height reduction due to network elasticity becomes only effective, if $g > n$. Therefore, we have for $g \lesssim n$ the height of the non-crosslinked brush $H_b$ as given in equation (2) and for $g > n$ we expect that

$$H \approx H_b \left( \frac{n}{g} \right)^{1/3}.$$  \hfill (12)

Note that a scaling model for the uni-axial swelling of a network leads to similar results.

We use the z-component of the center of mass of all monomers $z_{CM}$ as indicator for the brush height $H \propto z_{CM}$. It is computed by

$$z_{CM} = \frac{1}{NM} \sum_{m=1}^{M} \sum_{i=1}^{N} z_{m,i},$$  \hfill (13)

where $M$ is the number of chains in the system and $z_{m,i}$ is the z-position of the $i$-th monomer (as counted from the grafting point) of chain $m$. The number of monomers per blob, $g$, is estimated using equation (1).

As reference for the brush size we use the height of the non-crosslinked brush, $H_b$ as determined from the simulation data. In brief, for $H_b$ we found good agreement with the data of previous works [7, 13, 40–42]: the height of the non-crosslinked brushes follows the prediction of equation (2) except of small non-Gaussian corrections due to the overstretching of the chains at large $\sigma$ as discussed previously [13, 43, 44]. Similar observations were made for the parabolic density profile as predicted by self-consistent field (SCF) approaches [4, 5, 45–48] including small deviations to these predictions as discussed in previous work [13, 43, 44].

The height reduction of the brushes is analyzed as function of the degree of crosslinking $q$ using the ratio $g/n$ in Figure 1. For a better comparison, we determine $q$ only from “real crosslinks” that link monomers of different chains and ignore all links between the monomers of the same chain (“self-links”), which do not contribute to elasticity. We observe that most crosslinked brushes remain in the brush dominated regime $n > g$ and no data is clearly in the network regime even though we linked a large fraction of monomers (in some cases up to 1/3 of all monomers). The most important observation is that the data do not collapse as a function of $g/n$. This suggests that there might be a mechanism different to network elasticity that drives the collapse of the brush upon crosslinking. This mechanism is discussed in the following section and we consider it as the main source for height reduction when crosslinking a brush in the swollen state.
FIG. 1: (Color online all Figures) Height reduction of the brush as function of crosslinking. The line indicates the prediction of equation (12) for comparison.

IV. FLUCTUATION DRIVEN HEIGHT REDUCTION OF A BRUSH CROSSLINKED IN THE SWOLLEN STATE

The idea of our approach is that the fluctuations of the monomers in $z$-direction determine an average length reduction of the effective strands of the brush, since monomers with different index $i$ or $j$ as counted from the grafting point are connected as shown in Figure 2a) and b). We aim to show, that this length reduction determines the height reduction of the brushes as function of the degree of crosslinking $q$.

Since the contacts along the same chain and among different chains follow different statistics, we distinguish throughout this section between links that connect monomers of the same chain (“self-links”) from links that connect monomers of different chains (“crosslinks”), see Figure 2a) and b) respectively. In order to demonstrate that the above proposal can be used to understand the height reduction of swollen brushes upon crosslinking, we first analyze the length reduction of the effective chains inside the brush and compare with the simulation data. In a second step, the result for the length reduction is used to compute the height reduction by constructing an appropriate Flory estimate for the brush height.
FIG. 2: Reduction of effective chain length upon crosslinking. Monomer $i$ and $j$ form a “self-link” along chain a). The monomers $i$ and $j$ of the two chains at b) are “crosslinked”. c) and d) describe the two steps for computing the effective elastic chain lengths $N_x$ as discussed in the text.

A. Length reduction of minimal and effective chains inside the brush.

Let us first introduce $N_{\text{min}}$ as the minimum number of bonds along the network structure between a chain end and the grafting plane. We also introduce the effective chain length $N_x$ as the equivalent chain length to describe the modified elasticity of the chain as part of a brush after the crosslinking reactions. Since $N_x$ is difficult to determine from the network data while the determination of $N_{\text{min}}$ is rather trivial, we present here all simulation data as function of $N_{\text{min}}$ and use the mean field relations between the average $N_{\text{min}}$ and $N_x$ as derived below to analyze the height reduction of the brushes in the following subsection.

Self-links lead to dangling loops as shown in Figure 2 a). The length distribution of these loops is dominated by links to the nearest neighbors similar as for linking chains in melts [38]. This is because the return probability decays quicker than $|i - j|^{-1}$ for the self-avoiding walk inside the blob $|i - j| < g$ and for the stretched sections with $|i - j| > g$. The largest contribution to length reduction is thus dominated by the shortest loops. For
the intermediate grafting densities of the present study we conclude, therefore, that the length reduction due to self-links is approximately independent of $\sigma$. Since each self-link roughly leads to the same total change in $N_{\text{min}}$, we expect that the total length reduction $N - \langle N_{\text{min}}(q) \rangle$ due to self-links is proportional to $q$ in first approximation, thus

$$\langle N_{\text{min}}(q) \rangle / N = 1 - \gamma q / N. \quad (14)$$

The brackets denote here the sample average and $\gamma$ is average number of monomers per dangling loop.

The monomer fluctuations in $z$-direction control the average length reduction $N - \langle N_{\text{min}}(q) \rangle$ due to crosslinking different chains. Let us assume a parabolic density profile for the non-crosslinked brush. Then, the fluctuations of monomer $i$ in $z$-direction are roughly $\propto H_i / N$ and thus, depend on the grafting density $\sigma$. In conclusion, the average difference $\langle |i - j| \rangle$ of any two monomers in contact inside an non-crosslinked brush equals the average fluctuation of a strand of $\langle i + j \rangle$ monomers in $z$-direction and thus, $\langle |i - j| \rangle = c N$ using a parameter $c$ to describe the average fluctuations in $z$-direction of a monomer inside the brush.

Let us now consider by $i$ and $j$ the minimum number of bonds between these monomers and the grafting plane. Each crosslink equalizes the minimal distance along the strands to the grafting point at the connected monomers. Each equalization reduces the possible differences $\langle |i - j| \rangle$ of the neighboring connected chains in the same manner as the total average monomer fluctuations in $z$-direction become proportional to the average length of the elastic network strands $n$. Therefore, we conclude that the rate of length reduction during crosslinking is

$$\propto \langle |i - j| \rangle \propto cn \propto cN/(2q + 1). \quad (15)$$

Since the total length reduction is the integral over this rate up to crosslinking degree $q$, the average length reduction $N - \langle N_{\text{min}}(q) \rangle$ is estimated as

$$N - \langle N_{\text{min}}(q) \rangle \approx \int_0^q \frac{cN}{2q' + 1} dq' \approx cN \ln(2q + 1)/2. \quad (16)$$

The relative length reduction $\langle N_{\text{min}}(q) \rangle / N$ is therefore a non-linear function of the degree of crosslinking

$$\frac{\langle N_{\text{min}}(q) \rangle}{N} \approx 1 - c \ln(2q + 1)/2. \quad (17)$$
For testing equation (14) and (17) we separately analyze the length reduction $\langle N_{\text{min}}(q) \rangle / N$ due to self-links and crosslinks. To this end, we virtually remove either all self-links or crosslinks from the sample and determine $N_{\text{min}}$ from the remaining bonds. Also $q$ is computed from the remaining bonds for each particular sample.

Figure 3 shows that the self-link contribution is essentially independent of $\sigma$ and proportional to $q$ as proposed above. The slight deviation between data and linear fit is due to the increased tension along the chains upon crosslinking and the resulting reduced average size of a dangling loops for high degrees of crosslinking. A fit of the data indicates that at the beginning of the reactions, in average about $\gamma \approx 1.9$ monomers are part of a dangling loop, while this drops to about $\gamma \approx 1.5$ monomers for large $q$.

We determined relative distance $\langle |i - j| \rangle / N$ of monomers in contact in the non-crosslinked brush and use these results as parameter $c$. We obtain $c \approx 0.156, 0.168, 0.187, 0.210, \text{and } 0.233$ for the series of samples from $\sigma = 1/4$ to $\sigma = 1/25$. Equation (17) is plotted using these $c$ in Figure 3 without explicitly fitting the data. The qualitative agreement between the data and our simple model is remarkable. Note also the qualitative difference between self- and crosslinks as predicted by our model. For high degrees of crosslinking we observe the same corrections as for the self-loop data, which we attribute again to the increased tension along the chains because of crosslinking. Altogether, the above results are a sound basis to estimate the effective length of the elastic brush chains $N_x$ after crosslinking.

Obviously $N_x = N_{\text{min}}$, if only self-links are present, since the monomers inside a dangling loop do not contribute to elasticity. For the crosslinks, the parts of chains at Figure 2 b) that lie between grafting plane and monomer $i$ or $j$ respectively can be described by a combined chain of length $i + j$ that is grafted at both ends. These chains act in parallel on the crosslink like two independent confining potentials of strength $\propto 1/i$ and $\propto 1/j$. The fluctuations of the crosslink are thus restricted by a confining potential $\propto (1/i + 1/j)$, which is modeled by an elastic chain of

$$n_c = ij / (i + j)$$

segments that connects the grafting plane with the crosslink, see Figure 2 c). In order to project this result back into the brush problem we have to equally split this elastic chain $n_c$ at constant total elasticity of the system. If two chains of $2n_c$ monomers are connected, the combined chain at the connection point equals an elastic chain of $n_c$ monomers, because of $1/n_c = 1/(2n_c) + 1/(2n_c)$. Therefore, the effective chain lengths after splitting as shown in
FIG. 3: Length reduction $\langle N_{\text{min}}(q)\rangle/N$ of chains $N = 64$ due to self-links (full symbols) and crosslinks (hollow symbols) as function of $q/N$.

Figure 2 d) become

$$N_{x,i} = N - i + 2n_c$$  \hspace{1cm} (19)

$$N_{x,j} = N - j + 2n_c.\hspace{1cm} (20)$$

This leads to a net change in the total effective chain length of

$$\Delta N_x = 2N - N_{x,i} - N_{x,j} = \frac{(i-j)^2}{i+j}$$  \hspace{1cm} (21)

per additional crosslink.

There is an average $\langle i + j \rangle = N$ and an average $\langle |i - j| \rangle = cN$ at the beginning of the reaction. Similarly, $\langle i + j \rangle = n$ and $\langle |i - j| \rangle \propto cn \propto cN/(2q + 1)$ at later stages of the reaction. Therefore, we can approximate for the average change in the effective chain length

$$\langle \Delta N_x(q) \rangle = \int_0^q \langle \Delta N_x(q') \rangle \, dq' \approx \int_0^q \left(\frac{c^2N^2(2q'+1)}{N^2(2q'+1)^2}\right) \, dq'$$

$$\approx c^2N\ln(2q+1)/2,$$  \hspace{1cm} (22)

which leads to a relative length reduction of the effective chain length due to crosslinks

$$\frac{\langle \Delta N_x(q) \rangle}{N} \approx 1 - c^2\ln(2q+1)/2.$$  \hspace{1cm} (23)
In our previous work [30] we showed that the number of self-links decays roughly as $\sigma^{-3/2}$ at the gel point, while the number of crosslinks remains constant. Throughout the reactions we do not observe a significant shift from self-links to crosslinks or vice versa. Therefore, we can approximate for the number fraction of self links $f_s \approx 1 / (1 + f_0 \sigma^{3/2})$ and for the fraction of crosslinks $f_c = 1 - f_s$. Note that from the simulation data we obtain $f_0 = 26 \pm 1$.

Assuming no cross-correlations between cross- and self-linking, the relative effective chain length $\beta(q) = \langle N_x(q) \rangle / N$ is computed from the contributions due to self-links and crosslinks

$$\beta(q) = 1 - f_s \gamma q / N - f_c c^2 \ln(2q + 1) / 2,$$

The total average length reduction due to crosslinks and self-links is computed from

$$\frac{\langle N_{\text{min}}(q) \rangle}{N} = 1 - f_s \gamma q / N - f_c c^2 \ln(2q + 1) / 2.$$  

Both are used below to compare with the simulation data.

**B. Height reduction as a result of length reduction**

A simple analytical description of the height reduction of a polymer brush upon crosslinking can be derived by assuming that the chain length resisting the swelling of the brush is homogeneously reduced to $\langle N_x(q) \rangle$, while the excluded volume interactions that drive swelling depend on all monomers and thus remain $\sim N$. This difference can be expressed in a Flory type free energy per chain of form

$$\Delta f \approx k_B T \left[ \frac{3H^2}{2 \langle N_x(q) \rangle b^2} + v N \left( \frac{N \sigma}{H} \right) \right].$$

Here, $v$ is the excluded volume parameter, $k_B$ the Boltzmann constant, and $T$ the absolute temperature. The first term in the square brackets describes the elastic contribution to free energy, while the second term is the mean field estimate for pairwise monomer contacts. Minimization with respect to brush height $H$ leads to

$$H \approx N^{2/3} \left( v \sigma \langle N_x(q) \rangle b^2 \right)^{1/3} \approx H_b \beta(q)^{1/3},$$

which shows that the height reduction $H/H_b$ of the brush depends solely on the average length reduction of the elastic chains in the brush as given by $\beta(q)$.

This prediction is tested against the simulation data in Figure 4. The general trend of the height reduction of the brush is well predicted by our mean field brush model. Note that
FIG. 4: Reduction of brush height upon crosslinking as function of $\langle N_{\min}(q) \rangle / N$ for brushes with $N = 64$ of different grafting densities. The color lines are predictions based upon equation (27) and (25) as computed from the known number fractions $f_c$ and $f_s$ and the separately measured parameters $\gamma$ and $\langle |i-j| \rangle / N \approx c$ for cross- and self-links without additional fit parameter. The black dotted line is the limit of $f_c = 0$.

the deviations between model and data have the same trend as the overestimation of the length reduction $\langle N_{\min}(q) \rangle / N$ at large $q$ in Figure 3. This effect is apparently compensated at high grafting density, since contributions of higher order virial terms are neglected in equation (26).

In order to highlight the main difference between our new model and the uni-axial swelling of a network let us consider the case of crosslinking monomers $i$ and $j$ with $i = j$. According to equation (21), $\Delta N_x = 0$. Thus, if there is $i = j$ for any reaction, the height of the brush is expected to be constant independent of the degree of cross-linking, and therefore, independent of network modulus. In consequence, a brush crosslinked in the swollen state cannot be understood as a uni-axially swollen network. Note that the general trend of the data in Figure 4 clearly supports our hypothesis: For increasing $\sigma$, the samples contains a larger number fraction of cross-links and thus, a larger modulus at same length reduction. But the height reduction becomes smaller for this larger modulus. Nevertheless, if the brush
is linked in the dry state for which the chains are collapsed or near to ideal conformations, we still expect that these samples become equivalent to uni-axially swollen networks upon swelling and that, therefore, the Flory-Rehner model provides a reasonable approximation of experimental data.

The above results show that the relative change in the brush height is rather minor when linking a brush in the swollen state (the cross-link contribution is only a logarithmic correction). This is of particular importance for experimental applications, since the lack of a collapse of the brush upon crosslinking (no different scaling of the brush height) allows to maintain a nearly unmodified function and interaction with the environment, whereby the brush can be stabilized against degradation.

Finally, it is interesting to observe that the frozen-in fluctuations upon crosslinking a brush lead to a measurable height reduction. The height reduction is achieved here by network imperfections and fluctuations in the network structure. This is remarkable, since typically, network defects are associated with a reduction of the network modulus. Similar fluctuations and non-ideality are always present in any crosslinked structure. Therefore, it will be worth investigating in a future work to which extent non-ideal network structures can enhance the elastic modulus of a polymer network or to which extent crosslinking of ordered or stretched networks depends on monomer fluctuations.

V. SUMMARY

In this work, we compare chain conformations of polymer brushes with and without additional crosslinks between the chains. In order to understand the height reduction of a brush upon crosslinking we discuss the Flory-Rehner approach for the uni-axial swelling behavior of a model network. If the grafting density is so high, that the number $g$ of monomers per blob is smaller than the average length $n$ of a network strand, $g < n$, we expect no height reduction of the brush as compared to the non-crosslinked height $H_b = Nσ^{(1−ν)/(2ν)}b^{1/ν}$. For $g > n$ we expect that the brush shrinks with decreasing $n$ (for increasing degree of crosslinking) according to $H ≈ H_b (n/g)^{1/3}$. We observe that it is difficult to reach the strongly crosslinked regime when linking a brush in the swollen state, since in the swollen state, a large portion of reaction connects monomers of the same chain and thus, leads frequently to short dangling loops. Furthermore, the simulation data does not collapse.
as function of $n/g$, which indicates that at least an important correction to scaling is missing in the Flory-Rehner approach.

An alternative model can be obtained by considering the particular statistics of linking the same or neighboring chains. We find that reactions between monomers of the same chain lead to short dangling loops and a length reduction of the effective elastic chains in the brush proportional to the degree of crosslinking $q$. Reactions between different chains lead to a logarithmic correction for the effective elastic chain length. Both corrections depend on local fluctuations of the monomers in direction perpendicular to the grafting plane and can be expressed in terms of a relative length $\beta(q)$ of the effective elastic chain length with respect to $N$. This $\beta(q)$ can be incorporated in a Flory approach for the height of the brush to yield $H(q) \approx H_b \beta(q)^{1/3}$ in good agreement with the simulation data.

The results of the present work have impact on the understanding of previous experimental results. For instance, our results suggest that freezing a certain state of a switchable brush \cite{26} is only effective by linking both components together in a particular switched state, since the collapse due to a selective crosslinking in a co-solvent is rather minor. Furthermore, we expect a different swelling behavior, if the chains are crosslinked in the dry state, whereby the chain conformations are nearly ideal or collapsed. Finally, our results indicate that cross-linking of ordered structures can produce networks with a swelling equilibrium that is not controlled by network modulus. This unexpected result is a challenge for theory and probably a starting point to develop new tailor made materials.

VI. ACKNOWLEDGMENT

M.L. acknowledges funding from the DFG under grant LA 2735/2-1.

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[49] Equilibrium is really attained by minimizing the free energy $\partial F/\partial V = 0$. But since both leading terms for the free energy are power laws in concentration, the present simplified discussion is correct up to a numerical constant [6].

[50] Note that for simplification, we use the geometrical $g = (\xi/b)^{1/\nu} = |2/(b\sigma^{1/2})|^{1/\nu}$ to analyze the simulation data, whereby the factor 2 results from the normalization of $\sigma$ per lattice unit.