Theoretical approaches to starlike polymer brushes in Θ -solvent

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A continuum-space mean-field model for brushes made of starlike polymers in Θ -solvent is developed. The model accounts for the segregation of molecules into two vertical layers and predicts the population fractions of these layers. It reproduces recently reported deviations of the brush heights from scaling theory at moderate and high grafting densities. In the regime of very low monomer densities, the scaling of its brush heights is crossing over to the classical scaling prediction. During our analysis, we modify the elastic properties of the molecules, as well as their volumetric interactions, in order to study the impact of these model parameters on the resulting brush properties. Comparisons with another, recently published mean-field model of brushes on a lattice and with molecular dynamic simulations are carried out. It is demonstrated that most variants of the mean-field models are generating brush heights in reasonable agreement with the simulation data. The partition of molecules into the two populations, however, exhibits a significant model dependence.

I. INTRODUCTION

Polymer brushes consisting of dendritic polymers such as dendrimers have recently moved into the focus of intensive studies, for several reasons: First of all, they can now be made in the laboratory of molecules of low polydispersity [1–4]. Then, scientists are now turning increasingly interested in their vital roles in biological systems [5–7]. Apart from that, branched polymers offer a large number of free ends that may be functionalized, serving in nano-technical applications such as environment-responsive surface layers [8–14], or as anti-fouling barriers [15–17] on sensitive surfaces. When grafted onto colloids, they lead to an improved stability against coagulation, featuring a thinner polymeric layer than colloids decorated with linear chains [18].

On the theoretical side, branched polymer brushes have been approached using mean-field techniques [18–23], which allowed a prediction of the scaling properties of brush heights. Self-consistent-field (SCF) theories have been designed to obtain vertical monomer density profiles of the brushes [22, 24–27]. A common feature of these approaches is that every single molecule of the brush is treated equally, but it has been suspected early on that this might not reflect reality: Inside a dense brush, branched polymers have to segregate into several populations of molecules, each of which featuring different degrees of vertical elongation, in order to assume a homogeneous monomer density [24]. Numerical Scheutjens-Fleer [28] (SF-SCF) simulations on a lattice have verified the existence of such a segregation [21, 22], and in molecular dynamics (MD) simulations, its features have been analyzed in detail [29–32]. It therefore seemed necessary to search for simple mean-field approaches which were able to deal with this multi-population structure of branched brushes, and also to predict the partition of polymers among their different populations [32–35]. An overview about the state of the art of these techniques has recently been compiled [36].

Apart from the dual population model of Polotsky et al. [35], which is based on polymers on a lattice and restricted to brushes of high monomer densities, no formalism is currently able to treat multiple-population brushes in Θ -solvent. This is problematic because recent MD simulations of these brushes have shown significant deviations of the brush heights from predictions of scaling theory [37]. While these deviations have been observed before in brushes made of linear chains [38], it is now of significant interest to verify them and to explain their causes on the level of a simple mean-field theory.

In the present paper, such a dual-population mean-field model, which remains accurate over a wide range of grafting densities and which serves as a tool to understand the properties of branched (starlike) brushes at the Θ -point, is designed. The ingredients to the free energy model are varied, to study the impact of different contributions to the mixing entropy and the elastic properties of the spacers, on the brush heights and the partition of molecules into the two populations. Comparisons with MD simulations and with the recently presented dual population model of Polotsky et al. [35] are included.

The rest of the work is organized as follows: In Sec. II, we briefly introduce our MD simulation model. Section III.1 then derives a dual-population mean-field model for starlike polymer brushes in Θ -solvent, based on the Flory-Huggins approximation of the entropic mixing effects, and a finite-extensible spacer elasticity. The elastic contributions of the retracted star population is included on an approximate level. In Sec. III.2, the lattice-model of Ref. [35] is introduced, and in Sec. IV, an in-depth comparison of the different methods and the MD simulations is carried out. Here, the scaling behavior of the brush heights as a function of the grafting density and of the branching functionality is analyzed. It is shown that deviations from scaling predictions occur as a result of higher order virial contributions to the free entropic mixing energy. It is further shown that the different methods lead to significantly different predictions of the population fractions. Finally, we summarize and discuss our findings in Sec. V.

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II. MD-SIMULATION SETUP

In our MD simulations, the polymers were coarse-grained, freely jointed bead-springs, as first introduced by Kremer and Grest [39]. Details of the simulation procedure have been presented before [29, 32], so that a brief summary of the interaction model has to suffice here:

The beads are spherical monomers which interact via a shifted Lennard-Jones (LJ) potential

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 - \left(\frac{d}{r_c} \right)^{12} + \left(\frac{d}{r_c} \right)^6 \right], \quad (1)$$

where $d = 1$ stands for the bead diameter and ϵ defines the strength of the interaction. The parameter $r_c = 2.5$ is the cutoff distance.

The connectivity between monomers was enforced by a finite extensible nonlinear elastic (fene) potential [39], defined as

$$U_{\text{FENE}}(r) = -0.5KR_0^2 \ln \left[1 - (r/R_0)^2 \right], \quad (2)$$

with a stiff spring constant K and a maximum allowed bond length of $R_0 = 1.5d$. The range of bond lengths has never been exhausted, however: During our simulations, bond lengths varied between $a \approx 0.97$ (relaxed spacers) and $a \approx 1.01$ (in the case of highly tensed spacers at high grafting densities). The simulations were carried out using the open source LAMMPS molecular dynamics package [40], using a Langevin thermostat with fixed temperature T . At $T = 0.75$, the choice of $\epsilon = 0.25$ simulates an implicit Θ -solvent [37, 38], a condition consistently applied throughout this work. A timestep of 0.002τ (LJ-times) was applied.

The brushes were composed of starlike polymers, grafted with one end onto a flat surface to form a 10×10 array. The lateral dimensions of the simulation box were made periodic to avoid boundary effects. The majority of systems contained stars with spacer-lengths of 50 monomers. These brushes were well equilibrated after 10^7 simulation steps (corresponding to $2 \cdot 10^5 \tau$, followed by $5 \cdot 10^7$ steps ($10^6 \tau$) of data acquisition. At low grafting densities, spacer-lengths of 150 monomers were implemented to yield a sufficient overlap between the molecules. Here, the equilibration extended over 10^8 simulation steps, followed by another 10^8 simulation steps for data acquisition.

III. DUAL POPULATION BOX MODELS

Contrary to monodisperse brushes made of linear chains, which contain molecules of qualitatively identical conformations, dendrimer brushes are composed of molecules of qualitatively different conformations. This observation has first been made by Pickett [24], who, with the help of a lattice based numerical SF-SCF method [28] proved that a backfolding of branches into lower regions of the brush is virtually absent. Consequently, in order to keep the monomer density of the brush's lower parts sufficiently high, a certain fraction of

molecules had to retract into a collapsed state. This proposal has been confirmed in subsequent applications of the SF-SCF formalism [21, 22] and in MD simulations of brushes in good solvent [29–31] as well as at the Θ point [37].

FIG. 1. Schematic illustration of a box model with two phases The upper phase is composed of branches of extended molecules, while the lower phase contains their stems and a certain fraction of retracted stars. This fraction is chosen so that the monomer density is uniform and the force-balance at the phase boundary is satisfied.

III.1. Dual phase mean field model in continuum space

In an earlier work, a dual phase mean-field model for starlike polymer brushes in good solvent has been proposed [33]. As sketched in Fig. 1, the box model is made two different layers: The upper layer consists of the q free branches which stem from the extended starlike molecules and which may be treated like an ordinary linear brush. We denote q as the functionality of the grafted star. Each spacer, i.e. the grafted 'stem' and the q free branches, consists of N_S monomers, called 'spacer-length'. Depending on the (initially unknown) fraction λ of extended stars, the upper brush layer is made of a certain number of free branches per unit area, which resembles a linear brush at a certain effective 'grafting density', and a standard mean field model for linear brushes is applied to evaluate its thickness and concentration. In the present work, the formalism is modified to account for brushes in Θ -solvent, and to include an approximate contribution of the elastic free energy to the lower layer of the brush.

If M denotes the total number of molecules grafted onto a substrate of area A , then $\sigma = M/A$ is the definition of the grafting density. The brush may thus contain $\lambda M = \lambda \sigma A$ extended and $(1 - \lambda) \sigma A$ collapsed stars. The effective grafting density of the upper layer is then $\sigma_{\text{up}} = \lambda \sigma q$, and with the stretching ratio $r_{\text{up}} = H_{\text{up}}/N_S$, the compositions of the two phases are identified as

$$c_{\text{up}} = \frac{\sigma_{\text{up}}}{r_{\text{up}}} \quad (3)$$

for the upper phase, and

$$c_{\text{lo}} = \frac{(q+1)\sigma - \sigma_{\text{up}}}{r_{\text{lo}}} \quad (4)$$

for the lower phase. Assuming a uniform monomer density in

the simulation box, $c_{\text{up}} = c_{\text{lo}} = c$, we obtain

$$\frac{r_{\text{lo}}}{r_{\text{up}}} = \frac{q+1}{\lambda q} - 1. \quad (5)$$

The strategy is to first compute r_{up} by minimizing the free energy of that layer, which is treated like an ordinary brush made of linear chains. Applying a Flory-Huggins model for its entropic mixing free energy, we obtain (in units of $k_B T$)

$$F_{\text{FH,up}} = V_{\text{up}} [(1-c) \ln(1-c) + \chi c(1-c)], \quad (6)$$

with the monomer number density $c = c_{\text{up}}$ and the volume $V_{\text{up}} = AH_{\text{up}} = MH_{\text{up}}/\sigma$ of the upper layer. In Θ -solvent, the Flory interaction parameter amounts to $\chi = 1/2$. The elastic free energy of the spacers is taken from the Pade-approximation of the inverse Langevin function, as described in References [33, 41, 42], being the elastic free energy of ideal chains in continuum space and yielding

$$F_{\text{el,up}} = Mq\lambda \left[\frac{H_{\text{up}}^2}{2N_S} - N_S \ln(N_S^2 - H_{\text{up}}^2) \right]. \quad (7)$$

The free branches, vertically stretched out to the stretching ratio r_{up} , generate a total elastic force of

$$k_{\text{branches}} = Mq\lambda r_{\text{up}} \frac{3 - r_{\text{up}}^2}{1 - r_{\text{up}}^2}, \quad (8)$$

which is pulling at the phase boundary that separates the upper from the lower layer. The total free energy $F_{\text{up}} = F_{\text{el,up}} + F_{\text{FH,up}}$ has to be minimized with respect to the stretching ratio r_{up} , leading to

$$\sigma_{\text{up}} r_{\text{up}} \frac{3 - r_{\text{up}}}{1 - r_{\text{up}}} + \ln(1-c) + c + \frac{c^2}{2} = 0, \quad (9)$$

an equation, which is solved numerically for r_{up} .

The next step is the consistence-check of the force-balance at the boundary between the upper and the lower layer. Equation 5 is applied to compute the stretching ratio r_{lo} of the lower layer. This layer contains the stems of the elongated molecules, which are stretched out to the phase boundary, yielding a downward-pull of

$$k_{\text{stem}} = -M\lambda k(r_{\text{lo}}) = -M\lambda r_{\text{lo}} \frac{3 - r_{\text{lo}}^2}{1 - r_{\text{lo}}^2}. \quad (10)$$

Additionally, there exist a total number of $(1 - \lambda)M$ retracted molecules which also contribute to the elasticity of that lower layer. To approximate their contribution, we assume that the free ends of an individual molecule are located at identical vertical heights, and that the total ensemble of retracted molecules is sampling these heights uniformly throughout the lower layer. The finite-extensible character of Eq. 10 prohibits an over-stretching of the lower layer, so that it suffices to use a Gaussian approximation for the elastic forces of the retracted molecules, yielding a contribution of $-3qr/(q+1)$ from each single molecule, stretched out to the stretching ratio r , or

$$k_{\text{all,lo}} = -M(1 - \lambda) \frac{3qr_{\text{lo}}}{2(q+1)} \quad (11)$$

Model	Equations	Ingredients to free energy
MF-CS	9, 12	cont.-space elasticity & all virials
MF-CS(LV)	15, 12	cont.-space elasticity & leading order virial
MF-LS	17, 18	lattice-space elasticity & all virials
MF-DC	Ref. [35]	lattice-space elasticity & all virials

TABLE I. Models and their variations discussed in this work. MF-DC further assumes a dual-concentration density profile, but neglects the tension of the retracted stars.

from the entire ensemble of retracted molecules. The force balance thus yields

$$\lambda \left[qr_{\text{up}} \frac{3 - r_{\text{up}}^2}{1 - r_{\text{up}}^2} - r_{\text{lo}} \frac{3 - r_{\text{lo}}^2}{1 - r_{\text{lo}}^2} \right] - (1 - \lambda) \frac{3qr_{\text{lo}}}{2(q+1)} = 0, \quad (12)$$

where the first term represents the branches of the elongated molecules, the second term their stems, and the third term the retracted molecules. The population fraction λ has to be varied until this balance equation is satisfied. In what follows, we shall refer to this model, i.e. the solution of Eqs. 9 and 12, as our *continuum-space mean-field* (MF-CS) model.

III.2. Box model with two-step density profile

A somewhat modified version of the dual phase boxlike model has recently been presented for starlike brushes by Polotsky et al. [35]. The polymers are described as freely jointed molecules on a lattice. This leads, for a given spacer, to the finite extensible elastic function

$$r(k) = \frac{\sinh k}{2 + \cosh k}, \quad (13)$$

where, as in Eq. 8, r stands for the stretching ratio, and k for the force pulling at the spacer. This equation may be inverted to yield

$$k(r) = \ln \left(\frac{2r + \sqrt{3r^2 + 1}}{1 - r} \right). \quad (14)$$

The monomer's mixing entropy is accounted for by a Flory-Huggins approach as in Eq. 6. The model does not rely on the assumption of $c_{\text{up}} = c_{\text{lo}}$, so that the vertical brush density profile turns into a two-step function. We shall refer to this model as the *dual-concentration mean-field* (MF-DC) model. A disadvantage of this method is the fact that it delivers reliable results only at fairly high brush densities. This is probably a consequence of the absence of any elastic free energy contribution from the lower layer [35]. An extension of the formalism is likely to be possible and it should improve the versatility of this method.

Table III.2 contains a summary of the different models and their abbreviations used in this work.

FIG. 2. Center of mass heights of brushes as a function of grafting density for starlike brushes with functionality $q = 3$. The MD data points display a slope of 0.6 (dashed line), which, at moderate and high densities, is reproduced by the mean-field models (red, blue, green). Using the leading order virial only (MF-CS(LV), orange), the slope reduces to a value of 0.48 (dotted line). Red curve: Solution of Eqs. 9 and 12, blue curve: Eqs. 17 and 18, orange: Eqs. 15 and 12, green: Ref. [35] as discussed in Sec. III.2. Inset: Asymptotic scaling regimes of MF-CS.

IV. RESULTS

Figure 2 displays the center of mass brush heights as a function of grafting density. The heights are scaled by the spacer length N_s , which, at low grafting densities $0.02 \leq \sigma \leq 0.075$ amount to $N_s = 150$, while $N_s = 50$ was applied for the higher density brushes. As has been reported before [37], the brush heights do not scale as $H \sim \sigma^{1/2}$, as predicted by scaling theory, but with a higher exponent close to 0.6. The Mean-field model (red) reproduces this scaling at moderate and high grafting densities, while deviating somewhat at lower densities. In brushes made of linear chains, it has been demonstrated before that the observed deviations from scaling predictions at the Θ -point originate in the influence of the higher order virials [38]. This may be checked by a simple modification of the mean-field model, namely eliminating all but the leading order virial from Eq. 9, leading to the simplified condition

$$\sigma_{\text{up}} r_{\text{up}} \frac{3 - r_{\text{up}}}{1 - r_{\text{up}}} - \frac{c^3}{3} = 0. \quad (15)$$

A solution of this equation, in combination with the force balance Eq. 12, shall be referred to as the *leading-virial continuum-space mean-field* (MF-CS(LV)) model, and this formalism produces the curve as displayed in orange color in Fig. 2. At low grafting densities, the resulting brush heights are close to the simulated brushes. In this regime, the leading order virial suffices to account for the monomer interactions. However, the slope of the curve now exhibits a scaling law of approximately $H \sim \sigma^{0.48}$ (dotted line), close to the universal $\sim \sigma^{1/2}$ scaling as predicted by scaling theory. This result

demonstrates that the observed deviations from scaling theory do in fact originate from the higher order virials that are present in Eq. 9. The inset of Fig. 2 shows how the MF-CS model (red) is gradually crossing over from the universal scaling regime at very low grafting densities, to the non-universal regime in which the curve exhibits a steeper increase. That cross-over takes place at grafting densities about $\sigma \approx 0.01$, which corresponds to monomer concentrations of the order of $c \approx 0.1$.

In this context we note that a recently developed analytical self-consistent field (SCF) model predicts the brush heights of starlike brushes as [23]

$$H = N_s [\sigma(1+q)]^{(1-\nu)/2\nu} \left[\arccos \sqrt{q/(q+1)} \right], \quad (16)$$

with the universal scaling exponent ν . In Θ -solvent, with $\nu = 1/2$, this results into $H \sim \sigma^{1/2}$, and hence it deviates from the simulated MD data, too. Simulations of linear brushes in Θ -solvent have demonstrated that these brushes remained in their universal scaling regimes only at very low grafting densities of $0.01 \gg \sigma$, in which the monomer concentrations were sufficiently low to justify the neglect of the higher order virials [38]. For branched polymer brushes, the grafting densities, at which only the leading order virial suffices, would be even lower, and molecules of very high degrees of polymerization would be required to enter the brush regime – a fact, which makes MD simulations in this sparse brush regime very expensive.

Apart from the influence of the volumetric interactions, it is also interesting to analyze how the elastic properties of the spacers affect the brush heights. Hence, we have replaced the first term in Eq. 9 with the force term of Eq. 14, which leads to

$$\sigma_{\text{up}} \ln \left(\frac{2r_{\text{up}} + \sqrt{3r_{\text{up}}^2 + 1}}{1 - r_{\text{up}}} \right) + \ln(1 - c) + c + \frac{c^2}{2} = 0, \quad (17)$$

the mean-field model of a brush on a lattice. The force balance condition 12 is then modified to

$$q\lambda \ln \left(\frac{2r_{\text{up}} + \sqrt{3r_{\text{up}}^2 + 1}}{1 - r_{\text{up}}} \right) - \lambda \ln \left(\frac{2r_{\text{lo}} + \sqrt{3r_{\text{lo}}^2 + 1}}{1 - r_{\text{lo}}} \right) - (1 - \lambda) \frac{3qr_{\text{lo}}}{2(q+1)} = 0, \quad (18)$$

and we refer to this model as the *lattice-space mean-field* (MF-LS) approach. It differs from the lattice model of Sec. III.2 in two points: First, it assumes a uniform monomer density throughout the brush, and second, an approximate elasticity of the lower brush layer (the third term in Eq. 18) is included. The resulting brush heights (blue curve in Fig. 2) are similar to the results of the continuum-space model (red), and deviate only slightly at high grafting densities. The slope is almost identical to the continuum-space model, which indicates that the scaling behavior of the brush height shows little sensitivity to the choice of the elasticity model of the spacers, at least as long as that model describes spacers of finite extensibility.

FIG. 3. Brush heights as a function of the branching functionality q : The continuum-space (red) and the lattice-space (blue) mean-field models differ mildly. When reduced to the leading order virial (orange), the brush heights are consistently too low. The mean-field theory of Polotsky et al. (green) is restricted to high monomer densities, but accurate. Solid symbols and curves: Grafting density $\sigma = 0.1$, blank symbols and dashed curves: $\sigma = 0.2$. Spacer length: $N_S = 50$.

Figure 3 displays Brush heights as a function of functionality q at two different grafting densities ($\sigma = 0.1$, solid symbols and curves, and $\sigma = 0.2$, shown as blank symbols and dashed lines. Note that we are plotting $H(q)$ as continuous curves, to guide the eye, but that in real systems only integer values for q are possible). The reduction of the mean-field model to the leading order virial (MF-CS(LV), orange) leads to brush heights that are significantly too low. The lattice-space mean-field model computes brush heights (blue) that are slightly above the continuum-space model (red), and the dual-concentration model of Sec. III.2 produces comparable results, though it remains restricted to brushes with sufficiently high monomer densities.

The quantity, of which the restriction to the leading-order virial reduces the brush heights, indicates that these heights depend critically on the particular choice of the volumetric interactions in Eq. 9. These are based on the Flory-Huggins approach of Eq. 6, a mean-field approximation on a lattice. The MD-simulations rely on a bead-spring model in continuum-space, and certain corrections are usually applied to the virial coefficients in order to compensate for these differences [36]. In the present work we have applied all mean-field models without these corrections, since the resulting brush heights are already reasonably close to the simulations. Figure 3 shows that the MF-CS model somewhat underestimates the MD brush heights at high grafting density, $\sigma = 0.2$ (blank symbols and red, dashed curve), which is the consequence of differences between the pair-interactions of the beads (the Lennard-Jones potential of Eq. 1) and their mean-field approximation, Eq. 6, the latter being somewhat softer.

On the other hand, as discussed by Romeis et al. [43], polymers on the lattice (Eq. 14) are stretching almost like Gaussian

chains at low and moderate stretching ratios, while the elasticity in continuum-space (Eq. 8) yields a stiffer spring that contains anharmonic contributions at rather low stretching ratios. This explains why the MF-LS method (blue) yields slightly higher brushes when compared to the MF-CS approach. As a result, the MF-LS method appears to be more accurate at high grafting densities, since here the two opposing tendencies (lower brushes due to softer pair-interactions vs. higher brushes due to softer springs) partially compensate.

It is interesting to note that the brush heights seem to exhibit a power-law scaling of the form $H \sim q^x$. However, the exponents appear to be a function of the grafting density: At $\sigma = 0.1$, the fit results into $x = 0.56$, while at $\sigma = 0.2$, the exponent drops to $x = 0.48$.

FIG. 4. The population fraction λ as a function of the branching functionality q . The MD data are extracted using the vertical distribution of branching points (inset), as described in the text. Upper panel: Grafting density $\sigma = 0.1$, lower panel: $\sigma = 0.2$. Spacer length: $N_S = 50$.

Figure 4 displays the population fraction λ of molecules that reach into the upper layer of the brush (see Fig. 1). The extraction of the population fraction from the MD simulation data is not a straight forward task, because the conformations

of the branched molecules are highly irregular. Consequently, there exist several methods, and these methods lead to results which are compatible – qualitatively – but which may differ quantitatively in certain details [29, 36]. In this work, an analysis of the density distribution $\rho_{bp}(z)$ of the vertical coordinates of the branching points, as shown in the inset of Fig. 4 (upper panel) for the $q = 6$ brush, was used to separate the two molecular populations: The stems of the elongated molecules, which reach into the upper layer of the brush, have to stretch up considerably. As a result, the branching points of these ‘up’-molecules form a well defined peak, the position of which corresponds to the phase boundary between the brush layers. The area below that peak was then used to determine the fraction λ of extended ‘up’ molecules.

At grafting density $\sigma = 0.1$ (upper panel), the fraction λ of extended molecules is initially dropping with the functionality q , passing through a minimum near $q = 5$, and slightly increasing toward higher functionalities. The MF-CS model (Eqs. 9 and 12) shows a semi-quantitative agreement with the MD-data, including a shallow minimum, which, however, is located at higher branching functionalities between about $q = 7$ and $q = 8$. With lattice-space elasticity (MF-LS, Eqs. 17 and 18), λ is lower beyond $q = 5$, but later on, the rise at high functionalities is steeper. The leading-order virial approximation (MF-CS(LV), Eqs. 15 and 12) leads to λ -values which drop monotonously with q . The dual-concentration model (MF-DC, Sec. III.2) predicts population fractions that are far lower, and the curve is monotonously increasing with the branching functionality.

At high grafting density (lower panel of Fig. 4), the deviations between MD-simulation data and mean-field models are rather significant. The MD data display a clear minimum of the ‘up’-population between $3 < q < 4$, and a significant increase at higher functionalities. The MF-CS approach does not account for the latter – it rather produces a mild increase of λ beyond $q = 5$. Its leading virial approximation, MF-CS(LV), drops monotonously. The two methods that are based on the lattice-space elasticity exhibit a notable increase of λ toward high functionalities, but they yield population fractions that are moderately (MF-LS) or significantly lower (MF-DC) than the MD-results.

We note that the deviations between the different approaches, as observed in Fig. 4, are far more significant than any differences found in the predictions of the brush heights. An exception makes the leading virial approximation, MF-CS(LV): Its brush heights are significantly too low, but its population fractions are in close agreement with the competing models at low and moderate branching functionalities, significantly deviating only in the case of brushes with high monomer densities. While the different implementations of the elasticity seem to have little impact on the brush heights, they do make a difference to the resulting population fractions.

The MF-DC model is lacking the elastic free energy contributions of molecules of the lower brush layer. Additionally, it permits a variation of the monomer concentrations of the two layers. The combination of these factors promotes a spurious minimum of the free-energy: The thickness of the lower layer is allowed to increase, while molecules from the

upper layer are retracted, until all molecules occupy a single, expanded layer, which corresponds to the population fraction $\lambda = 0$. Only when the monomer density of that layer exceeds a certain limit, the volumetric interactions are approaching a critical value at which it turns favorable to stretch some of the molecules up into the higher layer. The implementation of an elastic energy for the molecules in the lower layer would help preventing such a collapse into a single layer at moderate monomer densities [35].

V. DISCUSSION AND SUMMARY

Brushes made of starlike polymers display a degree of complexity that is absent in brushes made of linear chains, such as the spontaneous decomposition into two populations with different degrees of vertical elongation. In the present work, a continuum-space mean-field model (MF-CS) for starlike polymer brushes in Θ -solvent is developed. In contrast to a recently presented, lattice-based formalism [35], the model presented here applies to brushes over a wide range of monomer densities.

At very low grafting densities, the brush heights scale with the grafting density as $H \sim \sigma^{1/2}$ (Fig. 2, inset), in accordance with scaling theory and analytical SCF approaches [23], but with increasing grafting density, the scaling exponent increases and reaches values close to 0.6, in agreement with MD simulations. It is shown that the contribution from higher order virials are responsible for that crossover, a phenomenon, which has been reported before with brushes made of linear chains [38].

Several variations of the mean-field model are considered: A replacement of the continuum-space elasticity function with a lattice-space function leads to the MF-LS formalism, i.e. the simultaneous solution of Eqs. 17 and 18, and the restriction of the Flory-Huggins mixing entropy to the leading order virial yields the MF-CS(LV) approach, during which Eqs. 15 and 12 are solved. Compared are the results with the lattice-based mean-field model of Polotsky et al. [35], which allows for a dual step concentration profile of the brush and is thus denoted here as the MF-DC method.

While the brush heights are significantly affected by the choice of the volumetric contributions to the free energy (Fig. 2 and 3), they are only marginally dependent on the elasticity of the chains (note that both, the continuum-space elasticity, Eq. 8, and the lattice-space elasticity, Eq. 13, are finite extensible models, preventing an overstretching of spacers beyond their contour lengths). On the other hand, the population structure of the brushes, i.e. the fraction λ of molecules which reach into the upper layer of the brush, displays a stronger dependence on the elasticity, while the volumetric effects turn important only at high brush densities (Fig. 4). While all models (apart from MF-CS(LV)) are capable of reproducing the brush heights of the MD simulations rather accurately, the population fractions are only in qualitative agreement (MF-CS and MF-LS, MF-CS(LV) at low and moderate monomer densities), or deviating significantly (MF-DS).

During studies of branched polymer brushes in good sol-

vent, it has been speculated whether the different molecular elasticities of both, continuum-space and lattice models, might be responsible for the observed differences in the predicted population fractions [32, 35, 36]. These differences have not only been found in comparisons between various mean-field models, but also in comparisons between MD simulations and numerical lattice-SCF computations. The present work demonstrates that the choice of the elasticity function, even among models which do consider finite extensibility, can

significantly affect the population structure of the brush, but that additional factors are likely to be of importance, too. As a matter of fact, none of the presently available methods is able to reproduce the population fractions of the MD simulations on a fully quantitative level.

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