## Soft Matter

## PAPER

Cite this: Soft Matter, 2015, 11, 2604

Received 23rd December 2014 Accepted 4th February 2015

DOI: 10.1039/c4sm02862g

www.rsc.org/softmatter

## I. Introduction

Polymer brushes are formed when macromolecules are grafted by a chain end on a nonadsorbing substrate surface.<sup>1-3</sup> These soft polymeric layers find numerous applications<sup>2</sup> and have been considered theoretically already for decades,<sup>1,3-5</sup> see a recent review3 for hundreds of references on the subject. However, the overwhelming majority of studies has addressed brushes formed from completely flexible polymers. Grafted stiff or semiflexible chains have only occasionally been considered.6-13 Here we are not concerned with more specialized work considering grafted semiflexible chains in nematic solvents,14-18 or grafted stiff surfactants.<sup>19-21</sup> Recently, there has also been experimental interest in semiflexible polymers grafted to substrates, particularly in a biopolymer context.<sup>22-25</sup> However, the theoretical work often considered the limit of very dense grafting and associated liquid-crystalline orientational order in these brushes, e.g.<sup>10-13</sup>

## Semiflexible polymer brushes and the brushmushroom crossover

Sergei A. Egorov,\*<sup>ab</sup> Hsiao-Ping Hsu,<sup>ac</sup> Andrey Milchev<sup>ad</sup> and Kurt Binder<sup>a</sup>

Semiflexible polymers end-grafted to a repulsive planar substrate under good solvent conditions are studied by scaling arguments, computer simulations, and self-consistent field theory. Varying the chain length N, persistence length  $\ell_{\rm pr}$  and grafting density  $\sigma_{\rm qr}$ , the chain linear dimensions and distribution functions of all monomers and of the free chain ends are studied. Particular attention is paid to the limit of very small  $\sigma_{\alpha}$ , where the grafted chains behave as "mushrooms" no longer interacting with each other. Unlike a flexible mushroom, which has a self-similar structure from the size (a) of an effective monomer up to the mushroom height ( $h/a \propto N^{v}$ ,  $\nu \approx 3/5$ ), a semiflexible mushroom (like a free semiflexible chain) exhibits three different scaling regimes,  $h/a \propto N$  for contour length  $L = Na < \ell_{pr}$ , a Gaussian regime,  $h/a \propto (L\ell_p)^{1/2}/a$  for  $\ell_p \ll L \ll R^* \propto (\ell_p^2/a)$ , and a regime controlled by excluded volume,  $h/a \propto L^2$  $(\ell_p/a)^{1/5}N^{\nu}$ . The semiflexible brush is predicted to scale as  $h/a \propto (\ell_p a \sigma_q)^{1/3} N$  in the excluded volume regime, and  $h/a \propto (\ell_p a^3 \sigma^2)^{1/4} N$  in the Gaussian regime. Since in the volume taken by a semiflexible mushroom excluded-volume interactions are much weaker in comparison to a flexible mushroom, there occurs an additional regime where semiflexible mushrooms overlap without significant chain stretching. Moreover, since the size of a semiflexible mushroom is much larger than the size of a flexible mushroom with the same N, the crossover from mushroom to brush behavior is predicted to take place at much smaller densities than for fully flexible chains. The numerical results, however, confirm the scaling predictions only gualitatively; for chain lengths that are relevant for experiments, often intermediate effective exponents are observed due to extended crossovers.

> Apart from early scaling considerations of a rather qualitative character,6 semiflexible brushes under semidilute concentration conditions and the crossover to the mushroom regime were not considered. We feel, however, that this regime does deserve further study, since the behavior of grafted semiflexible polymers under such conditions presents several interesting complications. Thus, an isolated flexible mushroom under good solvent conditions basically exhibits a self-similar fractal self-avoiding walk like structure, from the length scale of the monomeric unit a up to the coil size, whereby gyration radii components  $R_{gz}$ ,  $R_{gxy}$  in the z-direction perpendicular to the grafting surface, or parallel to it, all scale like a free chain in solution,  $R_{gz} \approx R_{gxy} \propto aN^{\nu}$ . Here N is the number of monomeric repeat units, and  $\nu \approx 3/5$  is the Flory exponent.<sup>26,27</sup> For semiflexible mushrooms, however, the expected behavior is more complicated.

> As is well-known, chain stiffness is characterized by the persistence length  $\ell_p$ , which may be significantly larger than *a* (*e.g.*, for double-stranded DNA  $\ell_p \approx 50$  nm while  $a \approx 3$  nm). When the contour length L = Na (the number of subsequent bonds connecting the units *N* along the chain henceforth will be denoted as chain length) does not exceed  $\ell_p$  much, the macromolecule behaves like a flexible rod. For  $\ell_p/a \gg 1$  even in very good solvents a regime of Gaussian statistics is expected,



View Article Online

View Journal | View Issue

<sup>&</sup>lt;sup>a</sup>Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, D-55128 Mainz, Germany

<sup>&</sup>lt;sup>b</sup>Department of Chemistry, University of Virginia, Charlottesville, VA 22901, USA. E-mail: sae6z@cms.mail.virginia.edu

<sup>&</sup>lt;sup>c</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany <sup>d</sup>Institute for Physical Chemistry, Bulgarian Academia of Sciences, 1113 Sofia, Bulgaria

#### Paper

 $R_g^2 \propto \ell_p L = a^2 (\ell_p/a) N$ . Only when the contour length exceeds a characteristic value  $L^* = \ell_p^{-3}/a^2$  (and the coil radius  $R_g$  exceeds the corresponding coil size  $R^* = \ell_p^{-2}/a$ ), an onset of coil swelling is expected, with ultimately  $R_g \propto (\ell_p/a)^{1/5} a N^{3/5} \cdot 2^{8-30}$  While some evidence for this double crossover has been seen in extensive simulations of free chains,<sup>30</sup> we are not aware of any study of semiflexible mushrooms yet. Such a study will be presented here, and the consequences of this more complicated behavior for the crossover from mushrooms to polymer brushes will be considered. Particular interest will be devoted to the question how the variation of the persistence length affects then the brush height *h* and other structural characteristics of the semiflexible polymer brush.

In Sec. II, we summarize the predictions derivable from Flory theory and other scaling considerations. Sec. III describes numerical results for mushrooms, obtained from Monte Carlo simulations of a self-avoiding walk model on the simple cubic lattice where a bending energy  $\varepsilon_b$  is used to control chain stiffness (applying the pruned-enriched Rosenbluth method {PERM}<sup>31,32</sup>). Sec. IV presents numerical results using the Scheutjens-Fleer lattice version of the self-consistent field theory.<sup>33</sup> This approach allows to address the study of polymer brushes, for the same model of semiflexible chains as considered in the mushroom case by Monte Carlo. In Sec. V, we present results for an alternative model, off-lattice bead-spring chains with a bond bending potential, as used for the study of very dense brushes.12,13 While this model allows to cover the full range of grafting densities, including the mushroom limit, though the range of chain length is restricted to values of N of a few hundred only, it is interesting to compare the physical effects of allowing arbitrarily small bond angles  $\theta$  between subsequent vectors along the chain to the lattice models where only  $\theta = 90^{\circ}$  is possible as a nonzero bond angle. The question for which conditions these rather different coarse-grained models of macromolecules are trustworthy will be briefly discussed. Finally, Sec. VI summarizes our conclusions.

## II. Scaling description

In this section, we summarize predictions on the linear dimensions of the grafted semiflexible chains that are easily derived from the approach well-known as "Flory theory".<sup>26,27</sup> Of course, this approach can only yield power law relations for the chain linear dimensions in the various regimes, apart from prefactors, and it also cannot reliably describe the crossovers between these power laws. In addition, Flory theory requires the exponent  $\nu$  in d = 3 dimensions to be  $\nu = 3/5$ , rather than the more accurate value  $\nu \approx 0.588$ ;<sup>34</sup> also the Flory theory prediction for the chain free energy is unreliable.<sup>26,27,35</sup>

We first consider the dilute limit (grafting density  $\sigma_{\rm g} \rightarrow 0$ , *i.e.* the mushroom regime). In the case when the persistence length  $\ell_{\rm p}$  exceeds by far the size *a* of a (spherical) monomeric unit,  $\ell_{\rm p} \gg a$ , and the chain length *N* is not too large, the excluded volume  $v_{\rm ex}$  between monomeric units can be neglected and the crossover from the rod limit ( $L = Na < \ell_{\rm p}$ ) to the Gaussian limit can be accounted for by the Kratky–Porod model.<sup>36,37</sup> For the mean square end-to-end distance of a free chain this gives

$$\langle R^2 \rangle = 2\ell_{\rm p}L \left\{ 1 - \frac{\ell_{\rm p}}{L} \left[ 1 - \exp(-L/\ell_{\rm p}) \right] \right\},$$
 (1)

which is derived in the continuum limit. On the simple cubic lattice, the analogous expression for a free random walk model of a chain reads<sup>38</sup>

$$\langle R^2 \rangle = Na^2 \left[ \frac{1+t}{1-t} + \frac{2t}{N} \frac{t^N - 1}{(t-1)^2} \right],$$
 (2)

where  $t \equiv \langle \cos \theta \rangle = \exp(-a/\ell_p)$ . Here  $\theta$  denotes the angle between subsequent bond vectors along the chain backbone. While for chains in the bulk eqn (1) and (2) differ very little over the full range  $0 < L/\ell_p < \infty$ , it is clear that for chains grafted at a planar substrate the full cubic symmetry of the lattice model is broken, and strong differences between the continuum model and the lattice model appear in the rod limit. Thus, in the continuum limit, assuming that the orientation of the rod relative to the *z*-axis is random, we have for isolated rods

$$\langle R_z \rangle = \frac{L}{2}, \langle R_z^2 \rangle = \langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R_y^2 \rangle = \langle R^2 \rangle / 3 = L^2 / 3.$$
 (3)

On the lattice, the grafted rod has one direction perpendicular to the grafting surface and four directions parallel to it. Thus,

$$\langle R_z \rangle = L/5,$$
 (4)

$$\langle R_z^2 \rangle = L^2$$
/5,  $\langle R_x^2 \rangle = \langle R_y^2 \rangle = 2L^2$ /5,  $\langle R^2 \rangle = L^2$ 

Therefore, in this hard rod limit the ratio  $\langle R_{xy}^2 \rangle / \langle R_z^2 \rangle$  (with  $\langle R_{xy}^2 \rangle = \langle R_x^2 \rangle + \langle R_y^2 \rangle$ ) takes on the value 2 in the continuum, and 4 on the lattice.

These differences between eqn (3) and (4) will affect the mushroom regime when we consider the rod to coil crossover in the lattice model (Sec. III) and in the off-lattice model (Sec. IV), respectively. Also in the brush regime, for short chains related differences between the lattice (Sec. IV) and continuum (Sec. V) models must be expected.

In the Flory theory, only long chains are considered, so that in the Gaussian regime  $\langle R^2 \rangle = 2\ell_p L$  can be assumed. Flory theory is based on the minimization of the free energy F(R), (which is normalized by  $k_B T$  with  $k_B$  the Boltzmann's constant, and T – the absolute temperature) being hence dimensionless, with respect to the chain linear dimension R. Ignoring prefactors of order unity one sets

$$F(R) = R^2 / (a\ell_{\rm p}N) + v_{\rm ex}N^2 / R^3,$$
(5)

where  $v_{ex}$  represents the excluded volume interaction between effective monomeric units ( $v_{ex}$  has dimension of a volume). Note that Flory theory is too crude to distinguish between a mush-room and a free chain in dilute solution. From  $\partial F(R)/\partial R = 0$  we get, again omitting factors of order unity,

$$R = (a\ell_{\rm p}v_{\rm ex})^{1/5}N^{3/5}, N > N^* = (a\ell_{\rm p})^3/v_{\rm ex}^2.$$
 (6)

From eqn (3)–(5) we note that in the Gaussian regime F(R) =1. Only when  $N > N^*$  is the second term on the right hand side of eqn (5) non-negligible against the first, and the excluded volume effects matter. The chain length  $N^*$  where the crossover from Gaussian mushrooms to swollen mushrooms occurs, corresponds to a coil size

$$R^* = a^{1/2} \ell_{\rm p}^{-1/2} N^{*1/2} = a^2 \ell_{\rm p}^{-2} / v_{\rm ex}.$$
 (7)

Note that for flexible chains,  $\ell_{\rm p} \approx a$  and  $\nu_{\rm ex} \propto a^3$ , so  $N^*$  is of order unity and  $R^*$  of order a. Thus, in the mushroom regime we expect two crossovers, for  $N = \ell_{\rm p}/a$  we have a crossover from grafted rods to Gaussian mushrooms, and for  $N = N^*$ , according to eqn (6), another crossover to mushrooms, swollen by the excluded volume interactions, occur. If we define the height of the mushroom as  $h = \langle R_z \rangle$ , we expect a variation of  $h \propto aN$  for small enough N, followed by  $h \propto (a\ell_{\rm p})^{1/2} \sqrt{N}$ , and finally by  $h \propto (a\ell_{\rm p} v_{\rm ex})^{1/5} N^{3/5}$ . Of course, all these crossovers between the various power laws are expected to be rather smooth, for  $N = \ell_{\rm p}/a$  the flexibility of the rod-like chains comes gradually into play, and similarly the effect of excluded volume sets on gradually.

We now discuss the effect of the two crossovers in the conformational statistics of a single mushroom (from rod to Gaussian coil, when  $L = l_p$ , and from Gaussian to swollen coil, when the mushroom height *h* is of the order of  $R^*$ ) at the mushroom (m) to brush (b) crossover. Of course, one may readily identify the regime of grafting densities where one has isolated mushrooms. For flexible chains under good solvent conditions the lateral linear dimension of a mushroom is given by  $R \propto aN^{3/5}$  and hence the mushroom to brush crossover occurs for  $\sigma_{\rm mb}R^2 \approx 1$ , *i.e.*,  $\sigma_{\rm mb}a^2 \approx N^{-6/5}$ . Here and in the following we denote the grafting density at the 'mushroom to brush' crossover by  $\sigma_{\rm mb}$ . For semiflexible chains, we now have three cases to distinguish:

$$\sigma_{\rm mb}a^2 \approx 1/N^2$$
(rod regime) (8a)

 $\sigma_{\rm mb}a^2 \approx a/(\ell_{\rm p}N)$ (Gaussian chains) (8b)

$$\sigma_{\rm mb}a^2 \approx a^2 (a\ell_{\rm p}v_{\rm ex})^{-2/5} N^{-6/5} (\text{excluded volume regime})$$
 (8c)

Fig. 1 shows a qualitative plot of this mushroom-brush crossover behavior, normalizing *N* by *N*\* and making  $\sigma_g$  dimensionless as  $\sigma_g R^{*2}$ , so that the regime for  $N > \ell_p/a$  is independent of the choice of the persistence length. The three relations (8a) to (8c) then appear as straight lines on the log–logplot. Using *N*/*N*\* as the *Y*-axis, brushes would then be always above, and mushrooms – below these straight lines. The regime  $N \gg \ell_p/a$  is then in these coordinates a universal one, whereby different choices of persistence length superimpose. Of course, if  $\ell_p/a$  is not large, *N*\* is of order unity, and both the regime of grafted Gaussian coils and grafted rods disappears from Fig. 1. Then, for flexible chains, only the topmost mushroom regime (grafted swollen coils) exists. We remark that eqn (8b) and (8c) have already been derived by Birshtein and Zhulina,<sup>6</sup> in a somewhat different context for both flexible and semiflexible



**Fig. 1** Qualitative description of the mushroom to brush crossover for semiflexible polymers, presented as a log–log plot of  $N/N^* \text{ vs. } \sigma_g R^{*2}$ . At  $N/N^* \rightarrow 1$ , a crossover occurs from swollen chains to brushes as described by eqn (8c), while for  $N/N^* < 1$  (but  $N > \ell_p/a$ ) the mushrooms are still Gaussian coils, and eqn (8b) applies. Note that in this qualitative figure, for the sake of better visibility, the choice  $N^* = 10\ell_p/a$  has been made, implying  $\ell_p/a = \sqrt{10}$ : for such a small persistence length a Gaussian regime could not be observed in practice, of course, since the crossovers at  $N = N^*$  and at  $N = \ell_p/a$  are both smooth and spread out over about a decade on the log–log-plot. Therefore, both crossovers would merge, removing any intermediate regime of well-defined power laws.

chains (there the "phase diagram" of polymer brushes was considered as a function of solvent quality, assuming  $v_{\text{ex}} \propto (T - T_{\theta})$  with  $T_{\theta}$  being the  $\Theta$ -temperature of the polymer solution). In ref. 6, however, the regime where the chains behave like grafted rods was disregarded.

We consider now the application of Flory theory to the brush regime. As a variation parameter, the brush height *h* is used, and the Alexander<sup>4</sup>-de Gennes<sup>5</sup> picture of a brush is used, *i.e.*, the volume accessible for the monomeric units of a chain in a brush is assumed essentially as that of a cylinder of height *h* and radius  $1/\sqrt{\sigma_g}$ . In this cylinder the density is then of order  $N\sigma_g/h$ , therefore,

$$\Delta F(h) = \frac{h^2}{a\ell_{\rm p}N} + v_{\rm ex}N^2\sigma_{\rm g}/h,\tag{9}$$

and hence (again ignoring factors of order unity),

$$h = \left(\sigma_{\rm g} a \ell_{\rm p} v_{\rm ex}\right)^{1/3} N. \tag{10}$$

In the regime where the excluded volume interactions described by the second virial coefficient do not matter and due to the large persistence length the chains obey Gaussian statistics, higher order terms in the virial expansion need to be included. The standard assumption is to describe this fact in terms of a factor related to the third virial coefficient. So we take

$$\Delta F(h) = \frac{h^2}{a\ell_{\rm p}N} + w_3 N \left(\frac{N\sigma_{\rm g}}{h}\right)^2,\tag{11}$$

which yields

Paper

$$h = N(a^2 w_3 \sigma_g^2)^{1/4} (\ell_p/a)^{1/4}.$$
 (12)

Eqn (10) and (12) were first proposed by Birshtein and Zhulina,<sup>6</sup> who also discussed the lateral dimensions of the chains in the brush. One may easily verify that the crossover between the result for the brush height, according to eqn (10), and  $h = (a\ell_p v_{ex})^{1/5} N^{3/5}$  in the mushroom regime, {eqn (6)}, occurs for  $\sigma_{mb}$ , as given in eqn (8a)-(c). On the other hand, the crossover defined by h (as given by eqn (12)) becoming equal to Gaussian mushrooms, (eqn (1) and (2)), is not given by eqn (8b) but rather by

$$\sigma'_{\rm mb}a^2 = N^{-1} \left(\frac{\ell_{\rm p}}{a}\right)^{1/2} \left(a^2 w_3\right)^{-1/2} \propto N^{-1} \left(\frac{\ell_{\rm p}}{a}\right)^{1/2}.$$
 (13)

This result shows that the Gaussian mushrooms can interpenetrate to some extent before the monomer density in the brush is high enough so that chain stretching sets in.

# III. Monte Carlo study of semiflexible mushrooms

In this section, we consider self-avoiding walks (SAWs) on the simple cubic lattice, where one chain end is grafted in the plane z = 0, which acts as an impenetrable substrate (*i.e.*, monomerpositions with *z*-coordinates z < 0 are strictly excluded), and a bending potential  $U_{\rm b}(\theta) = \varepsilon_{\rm b}(1 - \cos \theta)$  acts between subsequent bonds of the chain. Unlike the model studied in ref. 39 to clarify the adsorption transition of semiflexible chains, monomers do not experience any binding energy  $\varepsilon$  when they are located in the grafting plane z = 0, so  $\varepsilon \equiv 0$ . Since on the simple cubic lattice the only possible bond angles are  $\theta = 0$ ,  $\theta = \pm 90^{\circ}$  ( $\theta = 180^{\circ}$  which would mean an immediate reversal of the walk is forbidden, of course), the chain partition function  $Z_N$  depends on the single parameter  $q_{\rm b} \equiv \exp(-\varepsilon_{\rm b}/k_{\rm B}T)$  only, which controls the chain persistence length,<sup>30</sup>

$$Z_N(q_b) = \sum_{\text{config}} C_{N,N_{\text{bend}}} q_b^{N_{\text{bend}}}$$
(14)

where  $C_{N,N_{\text{bend}}}$  is the number of configurations of mushrooms with *N* bonds and  $N_{\text{bend}}$  being the number of  $\pm 90^{\circ}$  kinks. Note that the persistence length  $\ell_{\text{p}}$  here is defined in terms of  $\langle \cos \theta \rangle$ as ref. 30

$$a/\ell_{\rm p} = -\ln\langle\cos\,\theta\rangle,\tag{15}$$

where the lattice spacing *a* henceforth will be taken as unit of length a = 1. While for non-reversal random walks on the simple cubic lattice, for which excluded volume interactions are ignored, there is a simple relation between  $l_p$  and  $q_b$ , namely

$$\langle \cos \theta \rangle = 1/(1 + 4q_{\rm b}), \, \ell_{\rm p}(q_{\rm b} \text{ small}) \approx 1/(4q_{\rm b}), \quad (16)$$

now due to excluded volume effects the relation between  $q_{\rm b}$  and  $\ell_{\rm p}$  in general is nontrivial.<sup>30</sup> We also recall that  $\ell_{\rm p}$  should not be associated with the decay of bond orientational correlations with the chemical distance *s* along the chain (as is often

done<sup>27,40</sup>). This decay for large *s* is a power law with an universal exponent<sup>41,42</sup> rather than exponential,<sup>27,40</sup> and hence the asymptotical decay for  $s \rightarrow \infty$  (in the limit of infinite chain length) does not yield any information on the persistence length whatsoever.<sup>42,43</sup> From simulations of unconstrained semiflexible SAW's in the bulk with  $N \leq 50\ 000$  for  $0.005 \leq q_b \leq 1.0$   $\ell_p$  has already been independently obtained and these values are quoted in Fig. 2–5 (ref. 30) and will be used in the present analysis of mushrooms as well.

As in that related work on free nongrafted chains,<sup>30</sup> the pruned-enriched Rosenbluth method (PERM)<sup>31,32</sup> was used, and hence we refer to ref. 30 for all technical details on this algorithm. Fig. 2 shows then the mean squared end-to-end distance components perpendicular ( $\langle R_z^2 \rangle$ ) and parallel ( $\langle R_{xy}^2 \rangle$ ) to the substrate surface, normalized by  $N\ell_p$  and shown as log–log plots  $vs. N/\ell_p$ . Fig. 3 shows analogous data for the mean square gyration radius components,  $\langle R_{gz}^2 \rangle$  and  $\langle R_{gxy}^2 \rangle$ . In all these data we can clearly recognize three regimes: the initial regime for  $N/\ell_p \leq 1$  is almost a straight line with slope one, as expected for the rod regime (of course, only data with large  $\ell_p$  can contribute to this regime). For  $1 < N/\ell_p < 10$  there is a gradual crossover to a



Fig. 2 Log-log plot of the mean square end-to-end distance components parallel-,  $\langle R_z^2 \rangle / (N\ell_p)$  (upper panel), and perpendicular to grafting surface,  $\langle R_{xy}^2 \rangle / (N\ell_p)$  (lower panel), *versus*  $N/\ell_p$ . Monte Carlo data are obtained with the algorithm PERM, including all values of N from N = 30 up to N = 50 000. The choices of  $\ell_p$  included here range from rather flexible chains ( $\ell_p \approx 0.7$ ) to rather stiff chains ( $\ell_p = 52.6$ ), as indicated in the legend. Solid straight line indicates the power law with exponent  $2\nu - 1 = 0.176$ .



**Fig. 3** Log-log plot of the main square gyration radius components parallel-,  $\langle R_{gx}^2 \rangle / (N\ell_p)$  (upper panel), and perpendicular to grafting surface,  $\langle R_{gxy}^2 \rangle / (N\ell_p)$  (lower panel), versus  $N/\ell_p$ . Monte Carlo data are obtained with the algorithm PERM, including all values of N from N = 30 to  $N = 50\ 000$ . The choices of  $\ell_p$  are indicated in the legend. Solid straight line indicates the power law with exponent  $2\nu - 1 = 0.176$ .

horizontal plateau. The presence of this plateau (for  $10 < N/\ell_p < 100$ ) is rather clearly recognizable for the parallel component,  $\langle R_{xy}^2 \rangle / N\ell_p$ , but less so for the component  $\langle R_z^2 \rangle / N\ell_p$ , perpendicular to the grafting surface. Of course, for not so large choices of  $\ell_p$  a plateau (corresponding to Gaussian behavior, *cf.* eqn (1) and (2)) cannot be found. The mushroom conformations crossover from rod-like structures to swollen coils occurs almost immediately, and one observes that  $\langle R^2 \rangle / \ell_p \propto N^{2\nu-1}$  (irrespective of whether *xy* or *z* components and end-to-end distance or gyration radii are considered). Thus, for different choices of  $\ell_p$  and  $N/\ell_p$  large enough, the data are always described by a family of parallel straight lines on the log–log plot.

When we study the data as function of  $N/N^*(\ell_p)$ , rather than  $N/\ell_p$ , however, we see that the data for  $N/N^*(\ell_p) > 10$  settle down on master curves, which exhibit asymptotically simple power laws, as expected from eqn (6). The latter can be rewritten as (recall that  $v_{ex} \approx a^3$  is of order unity here)

$$\langle R^2 \rangle / (\ell_p N) \propto [N/N^*(\ell_p)]^{1/5}$$
 (17)

with a constant of proportionality of order unity, independent of  $\ell_p$ . Fig. 4 confirms the validity of this expectation (note that in Fig. 4 the scaling line has a slope of  $2\nu - 1 = 0.176$ , *i.e.*, we have used a more accurate value  $\nu \approx 0.588$  (ref. 34)).



**Fig. 4** Log-log plot of  $\langle R_z^2 \rangle / (N \ell_p)$  (upper panel) and of  $\langle R_{xy}^2 \rangle / (N \ell_p)$  (lower panel) vs.  $N/N^*(\ell_p)$ , where  $N^*(\ell_p)$  was determined in ref. 30 from the analysis of semiflexible chains in the bulk. Solid straight line indicates the power law with exponent  $2\nu - 1 = 0.176$ .



**Fig. 5** Log-log plot of  $\langle R_{xy}^2 \rangle / \langle R_z^2 \rangle$  vs.  $N/\ell_p$ , including all chain lengths from N = 30 to N = 50 000, and different values of  $\ell_p$  as indicated in the legend. The arrow at the ordinate shows the theoretical value (4) in the rod limit.

#### Paper

Recall that the grafting density  $\sigma_{\rm mb}$  where the crossover from mushroom to brush behavior occurs, can be numerically estimated as  $\sigma_{\rm mb} = 2/(\pi \langle R_{gxy}^2 \rangle)$ . So the curves showing  $\langle R_{gxy}^2 \rangle / N \ell_{\rm p}$ *vs.*  $N/N^*(\ell_{\rm p})$  can be interpreted as  $(2/\pi)/(N \ell_{\rm p} \sigma_{\rm mb})$  as function of  $N/N^*(\ell_{\rm p})$ . These curves should be compared to Fig. 1, where a schematic plot of  $N/N^*(\ell_{\rm p})$  as function of  $\sigma_{\rm g} R^{*2}$  was given (shown in simplified form, for a single choice of  $\ell_{\rm p}$  only, *via* three straight lines on the log–log plot). Indeed, in Fig. 4c we can recognize 3 regimes, but the crossovers between these regimes are smeared out and not sharp.

Finally Fig. 5 presents a plot of  $\langle R_{xy}^{2} \rangle / \langle R_{z}^{2} \rangle$  as function of  $N/\ell_{\rm p}$ . It is seen that for large  $N/\ell_{\rm p}$  (of order 100 or larger) this ratio is close to unity; for  $N/\ell_{\rm p} < 1$  it approaches the value 4, as predicted for the lattice chains in the rod limit (eqn (4)). However, since we know from eqn (3) that the corresponding value of the rod limit for off-lattice chains is 2 rather than 4, we expect that lattice artefacts in this problem are significant for  $N/\ell_{\rm p} < 10$  already, since real macromolecules do not "live" on a lattice.

## IV. Semiflexible brushes studied by SCFT

The Scheutjens–Fleer<sup>33,44–47</sup> lattice version of the self-consistent field theory (SCFT) has been applied to the study of polymer brushes formed from flexible macromolecules extensively, and its technical formulation is well-known. Since the extension to include variable chain stiffness (*via* the parameter  $q_{\rm b} = \exp(-\varepsilon_{\rm b}/k_{\rm B}T)$  used already in the previous section) is straightforward,<sup>48</sup> no details on the implementation of the method are given, and we proceed to a discussion of the results immediately; we only note that due to storage requirements the method becomes impractical for N > 3000; but for the discussion of possible experiments on real polymer brushes that could be produced in the laboratory larger chain lengths would be of little interest anyway. All results presented in this section use the lattice cell size *d* as the length unit and thermal energy  $k_{\rm B}T$  as the energy unit.

In order to make contact with the previous section on mushrooms, we first present plots of  $\langle R_z^2 \rangle / N \ell_p$  vs.  $N / \ell_p$ , for chains in brushes at different grafting densities  $\sigma_{g}$ , (Fig. 6). As for the mushroom, three regimes are again evident: for  $N/\ell_p < 1$ there is the trivial rod regime, then the curves flatten somewhat, before a crossover to the stretched chains in the brushes (where the brush height *h* scales linearly with *N*, and  $\langle R_z^2 \rangle \propto h^2$ , and thus  $\langle R_z^2 \rangle / N \ell_p$  scales again linear with N, but with a smaller prefactor than in the rod regime). Note that for  $\sigma_{\rm g}$  = 0.001 and  $\ell_{\rm p}$ < 10 the data for  $N/\ell_p$  < 10 actually are in the mushroom regime, but in this single-chain regime the SCFT formulation used here does not account for the excluded volume interactions between the monomers properly; therefore data in Fig. 6 describing mushrooms cannot be relied upon, and therefore we do not present a direct comparison with the Monte Carlo data for the mushrooms here.

Taking the average height of the end-monomer length as a measure for the brush height,  $h_e = \langle R_z \rangle$ , we can study the scaling of the brush height with grafting density (Fig. 7a). We see that



**Fig. 6** Log-log plot of  $\langle R_z^2 \rangle / N \ell_p$  for three grafting densities:  $\sigma_g = 0.001$  (upper panel), 0.01 (middle panel) and 0.1 (lower panel). The horizontal straight line (at unity) indicates the trivial behavior for long Gaussian chains, while the straight line with slope unity indicates the rod-like behavior. Several choices of the persistence length  $\ell_p$  (from  $\ell_p = 3.0$  to  $\ell_p = 250.5$ ) are included, as indicated in the key to the figure.

for N = 1000 there is for moderately stiff chains ( $\ell_p \le 10.5$ ) only a single decade in  $\sigma_{g}$  (from 0.01 to 0.1) where the scaling relation for the strong stretching regime ( $h_e \propto \sigma^{1/3}$ , cf. eqn (12)) approximately holds. For smaller  $\sigma_{g}$ , the data still fall in the regime affected by the crossover to mushrooms. On the other hand, when we consider large values of  $\ell_p$  (such as  $\ell_p = 50.5$  or even 250.5), the number of "Kuhn segments" that a chain with N = 1000 can have is simply not large enough to allow a sensible interpretation in terms of scaling relations, power laws, etc. In fact, the height  $h_{\rm e}$  for N = 1000 for  $\sigma_{\rm g} > 0.01$  is clearly rather close to its saturation value,  $h_{\rm e} = 1000$ . This fact that the mushroom to brush crossover and the crossover towards saturation (maximally stretched chains) merge in the variation of  $h_{\rm e}$ with  $\sigma_{\rm g}$ , if  $\ell_{\rm p}$  is rather large, also means that we should not expect that the simple power law  $h_e \propto \ell_p^{1/3} \{\text{eqn (10)}\}$  can work over a broad parameter regime (see Fig. 7b below).

Alternatively, one can define the brush height *h* as the average *z*-coordinate of all monomers, the corresponding results are shown in Fig. 7b. It appears from Fig. 7b that a different value of the exponent in the power law,  $h \propto \ell_p^{0.4}$ , could work better: this could be interpreted as a fundamental flaw in the scaling description. However, when we take the data from



Fig. 7 (a) Log-log plot of the brush height  $h_e/N$  (taken as the average height of the end-monomer and normalized by the chain length N,  $h_e/N = \langle R_z \rangle/N$ ) shown vs. grafting density  $\sigma_g$ , using several choices of  $\ell_p$  from  $\ell_p = 3$  to  $\ell_p = 250.5$ , as indicated in the key to the figure. The solid straight line shows the theoretical power law  $h_e \propto \sigma_g^{1/3}$ . All data refer to N = 1000. (b): log-log plot of the brush height 2h/N (taken as the average z-coordinate of all monomers and normalized by half of the chain length N/2,  $2h/N = 2\langle z \rangle/N$ ) shown vs. persistence length  $\ell_p$ , for four grafting densities  $\sigma_g = 0.1$ , 0.01, 0.001, and 0.0001, as indicated. All data refer to N = 1000. For comparison, the Monte Carlo data for N = 1000 mushrooms (from Sec. III) are included in this plot. The straight lines indicate the theoretical power laws (eqn (10)),  $h \propto \ell_p^{1/3}$  and  $h \propto \ell_p^{1/2}$  (Gaussian mushroom regime), respectively.

the Monte Carlo calculations for mushrooms (also defining  $h = \langle z \rangle$  from the average *z*-coordinate of all monomers), a plot of *h vs.*  $\ell_{\rm p}$  in the regime from  $\ell_{\rm p} \approx 5$  to  $\ell_{\rm p} \approx 50$  and N = 1000 to  $N = 50\ 000$  is also compatible with such an intermediate exponent. In our view, however, this finding is simply an expression of a smooth and slow crossover between different regimes. In fact, Fig. 4 has also demonstrated that these data have not yet reached fully asymptotic power law as function of the chain length,  $\langle R^2 \rangle / (\ell_{\rm p} N) \propto [N/N^*(\ell_{\rm p})]^{2\nu-1} \propto N^{0.176}$ . Therefore, these results clearly demonstrate, that scaling descriptions are by no means the full story, when competition between several different regimes with different power laws occur.

Consider a regime where the mushrooms are not yet in the asymptotic regime described in Sec. II. Then, the relation  $h \propto$  $\ell_p^{2/5}$  may be interpreted in terms of an "effective exponent". As a result, we can find an "effective" crossover scaling description when  $h/(N^{3/5}\ell_p^{2/5})$  is plotted against  $\sigma_g N^{6/5}\ell_p^{-1/5}$  (Fig. 8a). Note that the brush height, scaling like  $h \propto (a\ell_{\rm p}v_{\rm ex})^{1/3}\sigma_{\rm g}^{-1/3}N$ , equals the mushroom height. The latter could be fitted empirically to h  $\propto (a\ell_{\rm p}v_{\rm ex})^{2/5}N^{3/5}$ , as discussed above. This yields a crossover at  $\sigma'_{\rm mb} \propto N^{-6/5} (a\ell_{\rm p}v_{\rm ex})^{1/5}$ . Therefore, in Fig. 8a a plot of  $h/(N^{3/5}\ell_{\rm p}^{-2/5})$ vs.  $\sigma/\sigma'_{\rm mb} \propto \sigma N^{6/5}\ell_{\rm p}^{-1/5}$  was presented. The fact that  $\sigma'_{\rm mb} > \sigma_{\rm mb}$ implies, however, that in between the region of non-interacting mushrooms, ( $\sigma_{\rm g} < \sigma_{\rm mb}$ ), and the region of stretched brushes, (*h*  $\propto N, \sigma_{\rm g} > \sigma_{\rm mb}')$ , a region of strongly interpenetrating mushrooms (or unstretched brushes (with  $h \propto N^{3/5} \ell_p^{2/5}$  as for the isolated mushrooms) should occur for  $\sigma_{\rm mb} < \sigma_{\rm g} < \sigma'_{\rm mb}$ . That would be rather unexpected (although such a behavior is predicted for the intermediate Gaussian regime of stiff chains, see Sec. II).

The quality of the data collapse is quite striking, yet we do not have any sound theoretical argument in favor of a relation  $h \propto \ell_{\rm p}^{2/5} N^{3/5}$  rather than  $h \propto \ell_{\rm p}^{1/5} N^{3/5}$  {eqn (6)} for mushrooms. Thus, we conjecture that this result, (Fig. 8a), is just due to the slow crossover from the  $h \propto \ell_{\rm p}^{1/2}$  relation in the Gaussian regime {eqn (1)} to the relation  $h \propto \ell_{\rm p}^{1/5}$  in the regime dominated by the excluded volume interaction. Therefore, it is plausible that the theoretically predicted crossover scaling works less well in this region (Fig. 8b). On the other hand, we recall that eqn (6) is based on nothing but the Flory description {eqn (5)}, which cannot yield the critical exponent of the *N*dependence correctly ( $\langle R_z^2 \rangle \propto N^{1.176}$  rather than  $N^{6/5} = N^{1.200}$ (ref. 34)), and thus the exponent of the  $\ell_{\rm p}$ -dependence could be seriously in error<sup>30</sup> too. However, chain lengths far exceeding  $N = 50\ 000$  would be needed to clarify this issue.

Finally, we have performed calculations of the brush lateral pressure as a function of persistence length, following the procedure outlined in detail in the earlier SCFT-based study of the lateral pressure of flexible brushes.<sup>49</sup> Our results are presented in Fig. 9, where we show the brush lateral pressure given in units of  $k_{\rm B}T/d^2$ . Fig. 9a gives a log–log plot of the lateral pressure divided by the chain length (N = 1000) shown vs. grafting density, using several choices of  $\ell_{\rm p}$  from  $\ell_{\rm p} = 1$  to  $\ell_{\rm p} = 100.5$ . One sees that for the flexible brush ( $\ell_{\rm p} = 1$ ) the lateral pressure follows the expected power law scaling  $\sigma_{\rm g}^{5/3}$  over the entire range of grafting densities studied. With increasing persistence length, the slope of the curve  $P_{\rm surf}/N vs. \sigma_{\rm g}$  becomes smaller than 5/3 at low grafting densities, while at high  $\sigma_{\rm g}$  it is



**Fig. 8** Upper panel: effective crossover scaling of the brush height *h* as function of grafting density  $\sigma_{\rm g}$ , scaling the ordinate as  $h/(N^{3/5} \ell_{\rm p}^{2/5})$  and the abscissa as  $\sigma_{\rm g}/(N^{-6/5} \ell_{\rm p}^{1/5})$ , for N = 500 and N = 1000 and four choices of  $\ell_{\rm p}$ , as indicated in the key (data points affected by the saturation at the maximum brush height are omitted). Straight line with slope 1/3 on the log–log plot indicates the stretched brush regime. Lower panel: theoretically predicted scaling  $h/(N^{3/5} \ell_{\rm p}^{-1/5})$  vs.  $\sigma_{\rm g}/(N^{-6/5} \ell_{\rm p}^{-2/5})$  for N = 1000.

still close to 5/3. For any value of  $\sigma_{\rm g}$  the lateral pressure decreases with increasing persistence length and appears to approach an asymptotic limiting value for very stiff chains. This trend is further illustrated in Fig. 9b, which gives a linear plot of the brush lateral pressure normalized by its value for very stiff chains  $P_{\rm surf}/P_{\rm surf}(l_{\rm p} = 1000)$  shown *vs.* the inverse persistence length  $l_{\rm p}^{-1}$  for three choices of the chain length N = 100, 250, and 1000 (all data refer to the grafting density  $\sigma_{\rm g} = 0.1$ ). One sees that the lateral pressure grows steadily with decreasing  $l_{\rm p}$ , with the steepness of the increase being independent of the chain length for very stiff chains, but showing a weak *N*-dependence for more flexible chains.

## V. Molecular dynamics results

We consider the standard<sup>12,13</sup> coarse-grained bead-spring model of polymers, augmented by a bond-bending potential. Thus



Fig. 9 (a) Log-log plot of the brush surface pressure divided by the chain length  $P_{\text{surf}}/N$  shown vs. grafting density  $\sigma_{\text{g}}$ , using several choices of  $\ell_{\text{p}}$  from  $\ell_{\text{p}} = 1$  to  $\ell_{\text{p}} = 100.5$ , as indicated in the key to the figure. The solid straight line shows the theoretical power law for the flexible brush  $P_{\text{surf}}/N \propto \sigma_{\text{g}}^{5/3}$ . All data refer to N = 1000. (b) Linear plot of the brush surface pressure normalized by its value for very stiff chains  $P_{\text{surf}}/P_{\text{surf}}(l_{\text{p}} = 1000)$  shown vs. the inverse persistence length  $l_{\text{p}}^{-1}$  for three choices of the chain length N = 100, 250, and 1000. All data refer to  $\sigma_{\text{g}} = 0.1$ .

bonded monomers along the chain interact with the "finite extensible nonlinear elastic" (FENE) potential

$$V^{\text{FENE}}(r) = -0.5kr_0^{2}\ln[(1 - (r/r_0)^2], r < r_0,$$
(18)

 $V^{\text{FENE}}(r > r_0) \equiv 0$ , while for any pair of monomers (both for bonded and nonbonded ones) we assume a purely repulsive Weeks–Chandler–Andersen (WCA)-type interaction,

$$V^{\text{WCA}}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6 + 1/4], r < r_c = \sigma 2^{1/6},$$
(19)

and  $V^{\text{WCA}}(r > r_c) \equiv 0$ . We take  $\sigma \equiv 1$  as the unit length,  $\varepsilon = 1$  as the unit of temperature *T* (which also is put to unity, as well as Boltzmann's constant), and the remaining constants are chosen as  $r_0 = 1.5\sigma$  and  $k = 30\varepsilon/\sigma^2$ . Since the interaction, eqn (19) is purely repulsive, the model corresponds to very good solvent conditions. The bond bending potential is the same as the one used in the MC and SCFT investigations in this work, namely,

$$V_{\text{bend}}(\theta_{ijk}) = \varepsilon_{\text{b}}[1 - \cos(\theta_{ijk})], \qquad (20)$$

where  $\theta_{ijk}$  is the bond angle formed between the two subsequent unit vectors along the bond connecting monomers *i*, *j* and *j*, *k*. The persistence length  $\ell_p$  is properly defined also in the continuum model by the average  $\langle \cos \theta \rangle$ , eqn (15), between subsequent bonds along the chain backbone. However, the relation between  $\ell_p$  and the bending stiffness  $\varepsilon_b$  is no longer given by the lattice model result, eqn (16), of course. In fact, here the bending  $\varepsilon_b$  stiffness is related to the persistence length  $\ell_p$  as  $\ell_p \approx \varepsilon_b/k_BT$ , if we use  $\varepsilon_b \geq 2.^{30}$ 

As usual, the configurations of the chains are generated by the Velocity-Verlet Molecular Dynamics algorithms,<sup>12</sup> applying a Langevin thermostat, *i.e.*, the effective monomer coordinates  $\vec{r}_n(t)$  are propagated using the equation of motion

$$m \frac{\mathrm{d}^2 \vec{r}_n}{\mathrm{d}t^2} = \vec{F}_{\mathrm{tot}}(\vec{r}_n) - \gamma \frac{\mathrm{d}\vec{r}_n}{\mathrm{d}t} + \vec{R}_n(t), \qquad (21)$$

where the mass m = 1 sets the unit of time  $\tau_{\text{MD}} = \sqrt{m\sigma^2/\epsilon} = 1$  as well. The friction coefficient  $\gamma = 0.25$  is chosen, and the random force  $\vec{R}_n(t)$  satisfies a fluctuation–dissipation relation with  $\gamma$  as usual.  $\vec{F}_{\text{tot}}(\vec{r}_n)$  is the force on the effective monomer resulting from the total potential, eqn (18)–(20).

The chains are grafted at a planar impenetrable surface, which repels the monomers with a WCA-potential, using the same parameters as in eqn (19). In x, y-direction parallel to this surface, periodic boundary conditions are used. The grafting sites at this surface form a square array, with a single grafting density  $\sigma_{\rm g} = 64^{-1} = 0.015625$ , while  $\varepsilon$  is varied from  $\varepsilon_{\rm b} = 1$ (flexible chain) up to  $\varepsilon \ge N$ . Since the bond length of the model, defined in eqn (18)–(20), is about<sup>12</sup>  $\ell_b \approx 0.96\sigma$  and the contour length  $L = (N - 1)\ell_b$ , our study encompasses both the range of L >  $\ell_p$  and  $L < \ell_p$ . Equilibration of the structures is monitored by following the decay of the end-to-end vector autocorrelation function of the chains, as usual.<sup>30</sup> Typical snapshot conformations are presented in Fig. 10 for a flexible,  $\ell_p = 1$ , and a semistiff polymer brush,  $\ell_{\rm p} =$  5, indicating the expected larger height and broader lateral spreading of the stiffer chains in the brush, characteristic for the Gaussian regime in Fig. 10b.

In Fig. 11a we present MD data for isolated mushrooms which show how the mean-squared radius of gyration  $R_g^2$  of a semiflexible mushroom varies with growing persistence length  $\ell_p$ . Apart from the rather short polymers with  $N = 50\,100$ , one can readily verify that for  $N \ge 200$  the data partially collapse on a straight line  $R_g^2 \propto \ell_p N$  for an interval of stiffness values  $\ell_p$  whereby this interval becomes broader with growing length of the chains *N*. Therefore, for sufficiently long chains Fig. 11a shows the regime of Gaussian statistics. For very long chains the Gaussian mushrooms go over into swollen coils. A different way



Fig. 10 Snapshots of a polymer brush with N = 200 and grafting density  $\sigma_g = 0.016$  of a flexible,  $\ell_p = 1$ , (a), and a semi-stiff brush,  $\ell_p = 5$ , (b). Typical conformations in the polymer brush are singled out (by showing one chain in yellow) so as to demonstrate the larger 'spreading' of the semi-stiff chains in the Gaussian regime (b) in comparison to the fully flexible ones in the 'excluded volume' regime. For better visibility, despite periodic boundary conditions in lateral directions, all chains are depicted without folding back into the central box whose size is indicated by the green substrate.

to illustrate the same behavior is presented in Fig. 11b, where the scaled lateral,  $R_{gxy}^2$ , and normal,  $R_{gz}^2$ , components of the gyration radius are shown against the chain length *N* measured in units of the persistence length  $\ell_p$ . While initially the stiff chains with  $\ell_p \gg a$  scale with slope one as rigid rods,  $R_{gz}^2 \propto \ell_p^2 N^2$ , at intermediate degrees of stiffness one may observe within some interval nearly horizontal course of the data (*i.e.*, Gaussian coils) which then go over into swollen mushrooms with slope  $2\nu - 1 \approx 0.176$  (dashed-dotted lines), consistent with the MC data shown in Fig. 3. Moreover, Fig. 11b suggests that the Gaussian regime for  $R_{gxy}^2$  extends to somewhat smaller values of  $\ell_p$ , than for  $R_{gz}^2$  as suggested by the horizontal lines. Apparently, the excluded volume interactions are more felt laterally, probably due to the weak repulsion of the mushroom coil by the solid substrate.

Our main result derived from MD data concerns the transition from a very dilute brush, comprised from nearly isolated mushrooms, to a real polymer brush at different degrees of chain stiffness, characterized by  $\ell_{\rm p}$ . In Fig. 12 we plot in log–log coordinates the growth of the brush height,  $h(\sigma_{\rm g}) = \sqrt{\langle R_{\rm gz}^2 \rangle}$ , as



Fig. 11 Variation of the gyration radius  $R_g^2$  normalized by the number of beads, N, with persistence length  $\ell_p$  for single grafted chains of different length,  $50 \le N \le 1000$ . Dashed line with slope unity indicates the growing interval of persistence length values where all curves collapse and follow the scaling  $R_g^2 \propto a \ell_p N$ , typical for the Gaussian regime. (b) Plots of  $R_{gxy}^2$ , (empty symbols), and  $R_{gz}^2$ , full symbols, normalized by  $N\ell_p$ , vs. chain length N rescaled by the persistence length,  $N/\ell_p$ . The Gaussian regime is indicated by horizontal solid lines at intermediate degrees of stiffness  $\ell_p$ . Thick dashed line denotes stiff chain behavior whereas dashed-dotted lines indicate a slope of  $2\nu - 1$  $\approx 0.176$ , typical for the 'mushroom' behavior. Note that  $R_{gxy}^2/R_{gz}^2 = 2$ in the continuum.

dimensionless ratio with respect to the height h(0) of a single mushroom, against polymer length N, divided by the *threshold length*  $N_{\rm mb}$ . Thus,  $N_{\rm mb}$  denotes the chain length when a polymer coating undergoes a crossover from mushroom to brush behavior. For semiflexible chains, as the ones we deal with in this study,  $N_{\rm mb}$  can be determined from the crossover condition,  $\pi \langle R_{\rm gxy}^2 \rangle \sigma_{\rm g} = 1$ , *cf.* Eqn (8b). Taking  $\langle R_{\rm gxy}^2 \rangle = 2\ell_{\rm p}N/18$ ,<sup>30</sup> one obtains thus  $N_{\rm mb} = 9/(\pi \ell_{\rm p} \sigma_{\rm g})$ , which we use as definition in the current investigation. Fig. 12 demonstrates the absence of a Gaussian regime for fully flexible chains where with growing chain length N the polymer coating goes from remotely placed mushrooms to a conventional polymer brush with excludedvolume interactions. In contrast, in the case of semiflexible chains the intersection point of the  $h(\sigma_{\rm g})/h(0)$  curve with 1 occurs at significantly larger values of  $N/N_{\rm mb}$  as  $\ell_{\rm p}$  becomes



**Fig. 12** Variation of the brush height *h*, divided by the height *h*(0) of the corresponding single mushroom, against the ratio *N*/*N*<sub>mb</sub> where *N*<sub>mb</sub> (see text for definition) denotes the chain length, corresponding to the crossover from mushrooms to brush. Here  $\sigma_g = 0.015625$  and *N* = 10, 20, 30, 50, 70, 100, 200, 300, 400, and 500. Both flexible,  $\ell_p = 1$ , and semiflexible,  $\ell_p = 3$ , 5, polymers are shown. Full straight line indicates the expected slope of  $1 - \nu \approx 0.41$  for flexible-, and 0.5 = 1 - 1/2 for Gaussian chains. The inset displays SCFT data for the same parameters.

larger whereby initially  $h(\sigma_g)/h(0) \propto (N/N_{\rm mb})^{0.5}$ . This shift of  $N/N_{\rm mb}$  to large values with increasing stiffness whereby the enhancement of  $h(\sigma_g)/h(0)$  starts to become pronounced means



Fig. 13 Variation of the total monomer density  $\rho(z)$  (filled curves), and the end-monomer density  $\rho_{\rm e}(z)$  (lines), perpendicular to the grafting surface with growing persistence length  $\ell_{\rm p}$  for N = 200. (a) MD data, (b) SCFT results.



Fig. 14 Schematic plot of polymer brush conformations in the 'excluded-volume' regime and in the Gaussian regime subject to different stiffness.

that the individual semiflexible mushrooms can interpenetrate each other strongly. Such behavior does not occur for flexible polymers where the lateral interpenetration is rather avoided owing to chain stretching, typical for standard polymer brushes. Moreover, as the slope of the latter relationship is steeper than that for the flexible brush, one might readily determine from the intersection point of the  $(N/N_{mb})^{0.4}$  line with the different straight lines the particular chain length  $\tilde{N}$  where the Gaussian brush will turn into a brush, governed by excluded-volume interactions again. Since  $\tilde{N}$  changes with persistence length,  $\ell_{p}$ , however,  $\tilde{N}$  might happen to be very large, and thus beyond the scope of experimental verification.

Eventually, we end this section with Fig. 13a and b, demonstrating the consistency of the different methods used in the present study, where a comparison of the profiles of total monomer density,  $\rho(z)$ , and end-monomer density,  $\rho_{\rm e}(z)$ , perpendicular to the grafting plane for polymer brushes with different stiffness is presented. Both the MD data, Fig. 13a, and those from the SCFT study agree well with one another for the given range of persistence lengths  $\ell_{\rm p}$ .

## VI. Summary

In the present study we have considered the effect of varying the chain stiffness of long polymers on the conformation and structure of "mushrooms" (isolated end-grafted macromole-cules on flat planar substrates) and on polymer brushes. We examine in particular the mushroom to brush crossover as the grafting density increases. While for many macromolecules (such as alkanes, polystyrene, *etc.*) a moderate amount of chain stiffness is present, *i.e.*, the persistence length  $\ell_p$  exceeds somewhat the effective bead diameter, very stiff chains (with  $\ell_p \gg a$ ) find increasing interest in the context of biopolymers (*e.g.*, double-stranded DNA).

For free polymers in dilute solutions, as well as for mushrooms, the effect of stiffness is twofold:

(i) the size of the coil (considering contour lengths  $L = Na \gg \ell_p$ ) is considerably larger than for flexible polymers of the same contour length, and

(ii) the effect of the excluded-volume interaction (we consider good solvent conditions throughout) is comparably weaker, since in the volume (of order  $R_g^{3}$ , if  $R_g$  is the coil gyration radius) the density of effective beads is much smaller.

Therefore, for  $L \gg \ell_{\rm p}$  there occurs an intermediate regime of effective Gaussian behavior,  $R_{\rm g}^2 \propto \ell_{\rm p}L$ , before at a characteristic radius  $R^*$  the excluded volume prevails and a scaling  $R_{\rm g}^2 \propto L^{2\nu}$ , with  $\nu \approx 3/5$  being the Flory exponent, takes over.

This weakening of the effective excluded-volume interaction owing to chain stiffness has a significant effect on the mushroom to brush crossover, (Fig. 14). For fully flexible chains, stretching of the chains in the direction perpendicular to the grafting surface sets in whenever the grafting coils start to overlap each other, *i.e.*, for a grafting density  $\sigma_{\rm g} = \sigma_{\rm mb}$  defined by  $\pi R_{\rm g}^2 \sigma_{\rm mb} = 1$ . Mushrooms comprised of semiflexible chains, however, can overlap to a considerable extent, namely for  $\sigma_{\rm mb} < \sigma_{\rm g} < \sigma'_{\rm mb}$  with  $\sigma'_{\rm mb} a^2 N \propto (\ell_{\rm p}/a)^{1/2}$  rather than  $\sigma'_{\rm mb} a^2 N \propto a/\ell_{\rm p}$ .

Note that this behavior differs significantly from the behavior of Gaussian chain near the theta-point, where the excluded-volume interactions are effectively canceled by attractive forces between the monomers. There, the size of the coil is reduced (namely  $R_g^2 \propto a^2 N$ ) in comparison with the swollen coil under good solvent conditions  $(R_g^2 \propto a^2 N^{2\nu})$ . Therefore, the density of effective beads inside the mushroom volume is larger (rather than lower, as for semiflexible polymers). In that case, the mushroom to brush crossover sets in when the mushrooms "touch", so the special regime with two characteristic grafting densities  $\sigma_{\rm mb}$ ,  $\sigma'_{\rm mb}$  is absent. Note, however, that brushes formed from phantom chains would not exhibit stretching of chains at all.

For the brushes formed from semiflexible chains two different scaling regimes are shown to occur. For not too long and rather stiff chains, which (when isolated) behave as Gaussian mushrooms, a variation of the brush height  $h \propto N\sigma_g^{1/2}(\ell_p/a)^{1/4}$  is predicted, that is,  $h(\sigma_g)/h(0) \propto N^{1/2}l_p^{-1/4}$ . However, for very long chains, which when isolated would scale as  $h(0) \propto N^{3/5}(\ell_p/a)^{1/5}$ , the brush height scales as  $h(\sigma_g) \propto N\sigma_g^{1/3}(\ell_p/a)^{1/3}$ . Studying hence the relative brush height  $h(\sigma_g)/h(0)$  at fixed  $\sigma_g$  and fixed  $\ell_p$  as function of *N*, one observes an additional crossover from an  $N^{1/2}$  law to a  $N^{1-\nu} \approx N^{0.4}$  law, (Fig. 12).

Some evidence for these power laws could be obtained both from self-consistent field theory and from Molecular Dynamics simulations. However, for very stiff chains the regime where the brush height is sensitive to excluded-volume effects, (eqn (10)), would require very long chains, which are not accessible by Molecular Dynamics simulations and probably are also not relevant for experiments. Thus, we feel that the regime, where for semiflexible chains in brushes Gaussian statistics still prevails (eqn (12)), is the most relevant one in practice. Of course, since the crossovers between the various regimes are not sharp but rather smooth, one should take the scaling considerations of Sec. II as a qualitative guidance only. This caveat is clearly borne out by our numerical results, both those obtained by lattice Monte Carlo for mushrooms or lattice-based SCFT for brushes, respectively, and by the off-lattice data obtained by Molecular Dynamics. We also stress that lattice artefacts are only identified for the extreme case of rather short stiff rod-like chains, while otherwise the lattice and continuum model results are in very good qualitative agreement. Nevertheless, it

would be interesting to study the double crossover that we predict to occur (Fig. 12 shows data for the first crossover only, but not for the second one that occurs when on the log–log plot the straight lines with slopes 0.4 and 0.5 intersect.) In order to do so, a more efficient simulation technique is needed. An interesting possibility could be the implementation of the Soft Effective Segment (SES) method of Coluzza *et al.*<sup>50–52</sup> For flexible polymers this method has been established as a powerful approach, yet for semiflexible polymers one should carefully test the approach first for bulk polymer solutions. This result is left for future work.

An important application of polymer brushes concerns their use as a lubricant to reduce friction when surfaces are sheared against each other. An intriguing question, that must be left for future work, is the effect of chain stiffness in this context. In previous works,<sup>12,13</sup> we have shown that dense brushes formed from semiflexible chains can be compressed by normal pressure *easier* than comparable brushes formed from flexible chains since the compression is facilitated by a collective tilt of the stretched chains. We expect that a similar effect might contribute to reduce friction during shear deformations but it remains to be demonstrated that such an effect is significant. Thus, our work clearly is only an initial step towards elucidating the rich behavior of semiflexible brushes.

## Acknowledgements

S.A.E. acknowledges financial support from the ACS PRF grant 53934ND6 and from the Deutsche Forschungsgemeinschaft (DFG), grant SFB 625/A3. S.A.E. is grateful to Prof. Frans Leermakers for illuminating discussions and help with using software *sfbox* and his hospitality during S.A.E.'s stay in Wageningen. A.M. thanks DFG for partial support under grants BI314/23 and BI314/24 and also the program "Schwerpunkt für Rechnergestuetzte Forschung in den Naturwissenschaften (SRFN)" for partial support.

## References

- 1 A. Halperin, M. Tirrell and T. P. Lodge, *Adv. Polym. Sci.*, 1992, **100**, 31.
- 2 *Polymer Brushes*, ed. R. C. Advincula, W. J. Brittain, K. C. Caster and J. Rühe, Wiley-VCH, Weinheim, 2004.
- 3 K. Binder and A. Milchev, *J. Polym. Sci., Part B: Polym. Phys.*, 2012, **50**, 1515.
- 4 S. Alexander, J. Phys., 1977, 38, 983.
- 5 P. G. de Gennes, *Macromolecules*, 1980, 13, 1069.
- 6 T. M. Birshtein and Ye. B. Zhulina, *Polym. Sci. U.S.S.R.*, 1983, 25, 2165.
- 7 M. Carignano and I. Szleifer, J. Chem. Phys., 1993, 98, 5006.
- 8 G. G. Kim and K. Char, Bull. Korean Chem. Soc., 1999, 20, 1026.
- 9 C.-M. Chen and Y.-A. Ewa, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **63**, 01506.
- 10 A. Gopinath and I. Mahadevan, *Proc. R. Soc. London, Ser. A*, 2011, **467**, 1665.
- 11 A. Milchev and K. Binder, J. Chem. Phys., 2012, 136, 104901.

- 12 A. Milchev and K. Binder, EPL, 2013, 102, 58003.
- 13 A. Milchev and K. Binder, Soft Matter, 2014, 10, 3783.
- 14 D. R. M. Williams and A. Halperin, *Europhys. Lett.*, 1992, **19**, 963.
- 15 D. R. M. Williams and A. Halperin, *Macromolecules*, 1993, 28, 2025.
- 16 A. Halperin and D. R. M. Williams, *Europhys. Lett.*, 1993, **21**, 575.
- 17 D. R. M. Williams and A. Halperin, *Macromolecules*, 1993, 26, 4208.
- 18 D. R. M. Williams and A. Halperin, Langmuir, 1995, 11, 3636.
- 19 F. M. Haas, R. Hilfer and K. Binder, *J. Phys. Chem.*, 1996, **100**, 15290.
- 20 V. M. Kaganer, H. Möhwald and P. Dutta, *Rev. Mod. Phys.*, 1999, **71**, 779.
- 21 F. Schmid, D. Johannsmann and A. Halperin, *J. Phys. II*, 1996, 6, 1331.
- 22 K. Kegler, M. Salomo and F. Kremer, *Phys. Rev. Lett.*, 2007, **98**, 058304.
- 23 K. Kegler, M. Koniezny, G. Dominquez-Esperinosa,
  C. Gutsche, M. Salomo, F. Kremer and C. N. Likos, *Phys. Rev. Lett.*, 2008, 100(118), 302.
- 24 G. Dominquez-Espinosa, A. Synytska, A. Drechsler, C. Gutsche, K. Kegler, P. Uhlmann, M. Stamm and F. Kremer, *Polymer*, 2008, 49, 4802.
- 25 Y. Higari, R. Okazaki and A. Takahawa, *ACS Marco Lett.*, 2012, **1**, 1124.
- 26 P. G. deGennes *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, 1979.
- 27 A. Yu. Grosberg and A. R. Khokhlov *Statistical Physics of Macromolecules*, AIP Press, New York, 1994.
- 28 D. W. Schäfer, J.-F. Joanny and P. Pincus, *Macromolecules*, 1980, **13**, 1280.
- 29 H. Nakanishi, J. Phys., 1987, 48, 979.
- 30 H.-P. Hsu and K. Binder, J. Chem. Phys., 2012, 136, 024901.
- 31 P. Grassberger, Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top., 1997, 56, 3682.
- 32 H.-P. Hsu and P. Grassberger, J. Stat. Phys., 2011, 144, 597.
- 33 G. Fleer, M. A. Cohen-Stuart, J. M. H. J. Scheutjens, T. Cosgrove and B. Vincent, *Polymers at Interfaces*, Chapman and Hall, London, 1993.
- 34 J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1980, 21, 3976.
- 35 J. Paturej, A. Milchev, S. A. Egorov and K. Binder, *Soft Matter*, 2013, **9**, 10522.
- 36 O. Kratky and G. Porod, J. Colloid Sci., 1949, 4, 35.
- 37 M. Saito, K. Takahashi and Y. Yunoki, J. Phys. Soc. Jpn., 1967, 22, 219.
- 38 P. J. Flory, *Statistical Mechanics of Chain Molecules*, Interscience, New York, 1969.
- 39 H.-P. Hsu and K. Binder, Macromolecules, 2013, 46, 2496.
- 40 M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford Univ. Press, Oxford, 2009.
- 41 L. Schäfer, A. Ostendorf and J. Hager, *J. Phys. A: Math. Gen.*, 1999, **32**, 7875.
- 42 H.-P. Hsu, W. Paul and K. Binder, *Macromolecules*, 2010, 43, 3094.

- 43 H.-P. Hsu, W. Paul and K. Binder, EPL, 2011, 95, 68004.
- 44 F. A. M. Leermakers and J. M. H. M. Scheutjens, J. Chem. Phys., 1988, 89, 2264; F. A. M. Leermakers and J. M. H. M. Scheutjens, J. Chem. Phys., 1988, 89, 6912.
- 45 O. A. Evers, J. M. H. M. Scheutjens and G. J. Fleer, *Macromolecules*, 1990, 23, 5221.
- 46 A. Milchev, S. A. Egorov and K. Binder, *J. Chem. Phys.*, 2010, **132**, 184905.
- 47 A. Milchev, S. A. Egorov and K. Binder, *Soft Matter*, 2014, **10**, 5974.
- 48 C. M. Wijmans, F. A. M. Leermakers and G. J. Fleer, *J. Chem. Phys.*, 1994, **101**, 8214.
- 49 E. P. K. Currie, F. A. M. Leermakers, M. A. C. Stuart and G. J. Fleer, *Macromolecules*, 1999, **32**, 487.
- 50 I. Coluzza, B. Capone and J.-P. Hansen, *Soft Matter*, 2011, 7, 5255.
- 51 I. Coluzza and J.-P. Hansen, *Phys. Rev. Lett.*, 2008, **100**, 016104.
- 52 I. Coluzza, B. Capone and J.-P. Hansen, *J. Chem. Phys.*, 2007, **127**, 171102.