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# Adsorption of branched and dendritic polymers onto flat surfaces: A Monte Carlo study

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Using Monte Carlo simulations based on the bond fluctuation model we study the adsorption of starburst dendrimers with flexible spacers onto a flat surface. The calculations are performed for various generation number  $G$  and spacer length  $S$  in a wide range of the reduced temperature  $\tau$  as the measure of the interaction strength between the monomers and the surface. Our simulations indicate a two-step adsorption scenario. Below the critical point of adsorption,  $\tau_c$ , a weakly adsorbed state of the dendrimer is found. Here, the dendrimer retains its shape but sticks to the surface by adsorbed spacers. By lowering the temperature below a spacer-length dependent value,  $\tau^*(S) < \tau_c$ , a step-like transition into a strongly adsorbed state takes place. In the flatly adsorbed state the shape of the dendrimer is well described by a mean field model of a dendrimer in two dimensions. We also performed simulations of star-polymers which display a simple crossover-behavior in full analogy to linear chains. By analyzing the order parameter of the adsorption transition, we determine the critical point of adsorption of the dendrimers which is located close to the critical point of adsorption for star-polymers. While the order parameter for the adsorbed spacers displays a critical crossover scaling, the overall order parameter, which combines both critical and discontinuous transition effects, does not display simple scaling. The step-like transition from the weak into the strong adsorbed regime is confirmed by analyzing the shape-anisotropy of the dendrimers. We present a mean-field model based on the concept of spacer adsorption which predicts a discontinuous transition of dendrimers due to an excluded volume barrier. The latter results from an increased density of the dendrimer in the flatly adsorbed state which has to be overcome before this state is thermodynamically stable.

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## I. INTRODUCTION

Adsorption of polymers on solid substrates plays an important role in applications and living nature. If all monomers of a polymer molecule interact in the same way with the substrate even weak adsorption energies can lead to strong adsorption of the whole molecule and to full coverage of the substrate even at low concentration of the polymer in solution.<sup>1,2</sup> Strong adsorption effects therefore can frequently not be avoided and lead to changes of physical properties of the adsorbing surface. On the other hand adsorption can be used for controlled surface modification. Adsorption of single molecules on biological surfaces such as cell membranes is important for understanding processes of cell biology such as trans-membrane permeability and translocation of larger molecules.<sup>3</sup> While the adsorption behavior of linear chains is well understood in terms of surface critical phenomena,<sup>4</sup> the influence of polymer architecture on adsorption is an open problem. With respect to topology dendrimers represent the limiting case of the highest degree of branching leading to an exponential growth of the number of monomers with the dendrimer's generation. Thus deviations from the behavior of linear chains are expected to be most pronounced.

In order to understand the adsorption behavior of polymers computer simulations are particularly useful since theo-

retical models such as scaling concepts can be tested on the level of conformation statistics of a single molecule. Coarse grained simulation models can be applied since the universal aspects of polymer adsorption behavior, i.e., order parameters, polymer extensions, and density profiles of flexible molecules should not depend on the atomistic structure, and chemical details only determine local length scales and absolute values of interaction constants.

In previous work various coarse grained simulation techniques were already applied to study principle features of dendrimers and branched polymers close to adsorbing surfaces. Unlike the case of linear polymers qualitatively different states of adsorption were identified already by Mansfield<sup>5</sup> using lattice models for dendrimers up to 8 generations. Here, a weak adsorption region in which the shape of adsorbed dendrimers is only weakly perturbed and several regions in which the adsorbed dendrimers display different conformational features were reported. A similar conclusion was drawn by Ratner *et al.*<sup>6</sup> from Brownian dynamics off-lattice simulations of dendrimers of 3rd generation where three regions of adsorption of dendrimers, referred to as the weak, transition, and strong adsorption, respectively, were described. Using a freely jointed hard-sphere model, Striolo and Prausnitz<sup>7</sup> investigated the adsorption of several types of regularly branched polymers based on the analysis of segment density profiles and potentials of mean force. The authors argued that for strongly

branched polymers such as dendrimers the shape is only weakly perturbed at the adsorption threshold because of the large surface area of the dendrimers' conformations. Halperin and Joanny considered theoretically the adsorption properties of high-functional star-polymers using the blob model.<sup>8</sup> These authors predicted several phases of the star polymer, which were described in the framework of the Daoud-Cotton-model,<sup>9</sup> for surface attractions well above the critical point of the linear chains and which are related to strong excluded volume interactions among the arms of the star. All of these studies agree in the fact that a weak adsorption regime without a shape transition can be distinguished from a strong adsorption regime where a shape transition takes place. This is in strong contrast to linear polymers where the transition is continuous and adsorption is equivalent to a shape transition.

While previous simulation studies revealed many details and peculiarities of dendrimer adsorption a generic physical picture of it is still missing. Considering the fact that adsorption of linear polymers was extensively studied by computer simulation using the guiding concept of crossover-scaling close to a critical point of adsorption, there is no direct linkage of the previously obtained results for branched structures and dendrimers and critical adsorption behavior as discussed in the framework of linear chain adsorption. It is not clear to what extent highly branched structures can be understood using scaling arguments either, and if not, what are the essential differences to linear chains due to branching.

To close this gap in this work we consider the adsorption of dendrimers using scaling concepts of polymer adsorption. Simulations are carried out using the bond fluctuation model (BFM)<sup>10,11</sup> for dendrimers of various generations,  $G$ , and spacer lengths,  $S$ , in a wide range of the interaction strength between the polymers' segments and the surface. Due to high efficiency of the algorithm the calculations can be performed up to large structures. In addition we perform simulations of star-polymers with four arms and various arm-lengths. Star-polymers can be considered as dendrimers of first generation and they reflect the effect of individual branching points on adsorption. Based on extensive Monte Carlo simulation data of dendrimers and star polymers we analyze the influence of regular branching architecture in terms of the scaling approach. Our results reveal that branching has only a minor influence on the critical point of adsorption and star polymers with low degree of functionality can be well described using the concepts developed for linear chains. However, the nature of the adsorption transition differs qualitatively for highly branched polymers. Dendrimers display a two-step adsorption scenario involving a step-like transition from a weakly adsorbed state into a strongly adsorbed state. We propose a simple mean field model which can explain the apparent first-order-like transition scenario below the critical point of adsorption for linear chains.

The remaining part of the paper is organized as follows. In Sec. II we outline the model and the simulation method. The results of our simulations are presented and discussed in Sec. III. Finally, our conclusions and remarks are given in Sec. IV.

## II. MODEL AND SIMULATION DETAILS

We use the BFM<sup>10,11</sup> to simulate dendrimers, see our previous work.<sup>12</sup> The dendrimers form a treelike, hierarchical architecture. A schematic representation of the studied systems is given in the sketch in Fig. 2. In our simulations all monomers are considered of the same kind. In particular with respect to adsorption there is no difference between branching points, linear units, and terminal units.

More specifically, we examine movable, single  $G3$ - $G7$  dendrimers with the core of two bonded monomers, branching functionality  $f = 3$  and spacer length  $S = 1, 2, 4, 8, 16, 32$ . Here, we denote the number of generations by  $G$ . For the simulations a cubic box of the size  $L^3 = 500 \times 500 \times 500u^3$  (where  $u$  is the length unit) is used with periodic boundary conditions in the  $x$ - and  $y$ -directions and with an impenetrable walls at  $z = 0$  and  $z = 500$ . Before simulation runs, the dendrimers were generated by a divergent growth process in the ascending order of the internal generation number  $0 \leq g \leq G$  starting from the core ( $g = 0$ ). Additionally, one of the dendrimers' terminal groups is immobilized and attached at the adsorbing surface. Thus, all monomers except the grafted monomer are movable and the motion of the dendrimers is only constrained by the grafting point via the molecules' connectivity. The largest molecules we simulate consist of  $N \approx 8000$  monomers. The degree of polymerization of the dendrimers of generation  $G$  and spacer length  $S$  studied in this work is given in Table I. For the simulation of star-shaped polymers we use a box size of  $L^3 = 256 \times 256 \times 256u^3$  with the same boundary conditions as for dendrimers and number of arms (functionality)  $f = 4$ . The total number of repeat units varies between  $N = 81$  and 401.

Within the applied Monte Carlo scheme configurations were sampled using the BFM including the standard Metropolis method.<sup>13</sup> We consider the case where each dendrimer bead is subject to a short range attraction exerted on it by the surface. Whenever a bead contacts the surface the system energy decreases by  $\delta$ , which leads to the dimensionless simulation parameter

$$\tau = \frac{k_B T}{\delta}, \quad (1)$$

throughout the paper referred to as the reduced temperature. In Eq. (1)  $k_B$  and  $T$  denote the Boltzmann constant and the absolute temperature, respectively.

In our study, depending on  $G$  and  $S$  the dendrimers were equilibrated for a maximum of  $10^7$  MCS (Monte Carlo Steps; in one MCS on average each monomer is selected to be moved in a randomly chosen, one of the six directions by a single

TABLE I. Degree of polymerization of the studied dendrimers of generation  $G$  and spacer length  $S$ .

$G \backslash S$	$S = 1$	$S = 2$	$S = 4$	$S = 8$	$S = 16$	$S = 32$
$G = 3$	30	58	114	226	450	898
$G = 4$	62	122	242	482	962	1922
$G = 5$	126	250	498	994	1986	3970
$G = 6$	254	506	1010	2018	4034	8066
$G = 7$	510	1018	2034	4066	8130	...

lattice unit), whereas averages were calculated for  $10^3$ – $10^5$  equilibrium configurations stored every  $10^4$ th MCS. The stars were equilibrated for a maximum of  $10^{10}$  MCS and averages were calculated every 5000 MCS in the equilibrated state using up to  $10^7$  configurations. An equilibrium state was considered achieved once the means of various measured quantities characterizing the molecules such as the radius of gyration and the number of adsorbed monomers fluctuated with MCS only. Throughout the paper the errors we calculated using the rebinning method<sup>14</sup> are smaller than the symbols' size. By carrying out two independent runs based on different sequences of random numbers and initiated with two different starting conformations of the *G5* dendrimer with spacers  $S = 8$  and  $S = 32$  at three different temperatures, we also successfully checked the method for its convergence. The results from both calculations agreed with each other within statistical fluctuations. Even at the highest adsorption energy considered monomer movements did not reveal any freezing effect (note that adsorbed monomers are always movable in the direction parallel to the substrate). To avoid kinetic trapping gradual lowering the reduced temperature was applied.

### III. RESULTS

#### A. Adsorption transition

The adsorption of linear chains is well understood as a crossover scenario close to a multi-critical point which can be derived by the formal analogy between statistics of linear polymers and magnetic systems close to the critical point.<sup>4,15,16</sup> More precisely, for formally infinitely long chains there is a critical temperature which separates the bulk state from the surface state. For finite chain length the transition becomes a smooth “crossover” which is controlled by a combination of the distance to the critical point and the chain length, given the fact that the chain length is still sufficiently large. This, in turn leads to simple scaling concepts to rationalize polymer adsorption properties.<sup>2,17</sup> One can expect that these concepts are also valid for more general polymer topologies which lead to self-similar conformational properties.<sup>18,19</sup>

As we showed in our previous work, the conformational properties of dendrimers with flexible spacers up to high generations are well described using Flory-type mean-field arguments and spacer-length scaling. In general, this kind of approach proved useful for describing scaling rules and their limitations of dendronized and linear brushes including brushes grafted to a point, to a line, and to a planar surface, see Ref. 20. It is worth noting that scaling and mean-field arguments for dendrimers can only be valid up to maximum number of generations,  $G_{max}$ , where packing constraints and finite extensibility limit the further growth of perfect dendrimers.<sup>21</sup> This will be discussed in more detail in Secs. III C and IV. For the present model our former studies yield  $G_{max} \simeq 8$  in three spatial dimensions.

For  $G < G_{max}$  dendrimers display a power-law relation between the degree of polymerization and the radius of gyration according to  $R_g \sim N^{1/5}$ .<sup>12</sup> This might suggest that conformational properties of dendrimers are self-similar in this regime with a Flory exponent of  $\nu = 1/5$ . In this case, also

the adsorption behavior of isolated dendrimers may be understood as a crossover scenario close to a critical point of adsorption. On the other hand, the high self-density may lead to more complex adsorption scenarios such as discussed for star polymers with high functionality.<sup>8</sup> Furthermore, the rather good agreement of overall chain size with mean-field arguments does not necessarily imply self-similarity of conformations, which in general require arguments going much beyond the mean-field theory.<sup>22</sup> In order to answer this question we apply scaling concepts to the adsorption of dendrimers and analyze their validity. We have also simulated star polymers in order to investigate the influence of a single branching unit on the adsorption properties.

We first examine the overall order parameter of the adsorption transition defined as  $m = M/N$ ,<sup>4</sup> which is the fraction of monomers in contact with the adsorbing surface, and  $M$  denotes the absolute number of monomers in contact with the surface. In the non-adsorbed case (high temperature)  $m$  goes to zero for  $N \rightarrow \infty$ , while in the adsorbed case (low temperature) the order parameter is finite. We note that the asymptotic limit for dendrimers has to be understood as an appropriate limit of  $S \rightarrow \infty$ . Under the assumption of a critical point of adsorption at  $\tau_c$  the number of adsorbed monomers should scale as

$$M_c = M(\tau_c) \sim N^\phi, \quad (2)$$

where  $\phi$  denotes the crossover exponent which depends on the statistical properties of the polymer.<sup>4</sup> For linear chains the best scaling results are obtained with  $\phi \simeq 0.59$ ,<sup>4,17</sup> while values of  $\phi \simeq 0.5$  were alternatively discussed. Since the crossover exponent is a surface critical exponent it is *a priori* not directly related to the Flory (bulk) exponent for the case of impenetrable surfaces.<sup>23</sup> For penetrable interfaces, however, the relation  $\phi = 1 - \nu$  can be concluded.<sup>24</sup>

In Fig. 1 the order parameter is displayed as a function of the reduced temperature at fixed spacer length,  $S$ . The figures clearly indicate that the dendrimers display an adsorption transition, where the order parameter increases from nearly zero up to some finite value approaching one as the reduced temperature is further decreased. In the low temperature limit adsorption is complete and all monomers are in contact with the surface up to a limiting number of generations  $G_{max}^{2D}$ , which can be directly read-off for the shortest spacers from Fig. 1(a). The issue of complete adsorption is further discussed at the end of Sec. III C.

Based on the overall order parameter we can roughly distinguish between the following regions: The crossover from the non-adsorbed to the adsorbed state is located at around  $\tau \simeq 1$ . A corresponding snapshot is shown in Fig. 2(a). For lower values of  $\tau$  the number of adsorbed monomers increases sharply with lowering temperature, see also the snapshots in Fig. 2(b). For very low values of  $\tau$  almost all of the monomers are on the surface ( $m \simeq 1$ ), see also Fig. 2(c). This corresponds qualitatively to the behavior of linear polymers except for the rather sharp transition into the strongly adsorbed state as will be discussed in more detail below. We note that for the *G7*-dendrimer with the shortest spacer,  $S = 1$ , the fraction of monomers in contact with the surface saturates at about a value of  $m = 0.6$ , which reflects packing constraints in 2D.



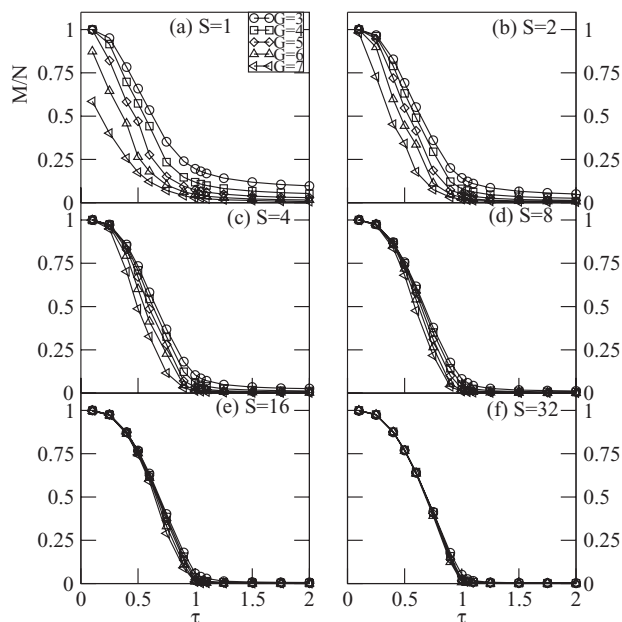


FIG. 1. Fraction of adsorbed monomers  $M/N$  versus the reduced temperature  $\tau$  at fixed spacer length  $S$  and varying generation number  $G$ .

This case illustrates that the limit  $N \rightarrow \infty$  cannot be accessed practically at constant spacer length ( $G \rightarrow \infty$ ), and scaling concepts for dendrimers are limited to finite generations. Alternatively, the simultaneous but rather hypothetical limit of  $N \rightarrow \infty$  and  $S \rightarrow \infty$  might be considered.

In order to find a better estimate of the adsorption transition,  $\tau_c$ , we consider the order parameter as a function of the degree of polymerization at constant temperature.<sup>4,17</sup> Again, under the assumption of criticality and for large values of  $N$  the asymptotic behavior of  $m(N)$  splits into three classes according to three regimes (non-adsorbed, critical, adsorbed):

$$m \sim \begin{cases} N^{-1} & \text{for } \tau > \tau_c \\ N^{\phi-1} & \text{for } \tau = \tau_c \\ N^0 & \text{for } \tau < \tau_c \end{cases} \quad (3)$$

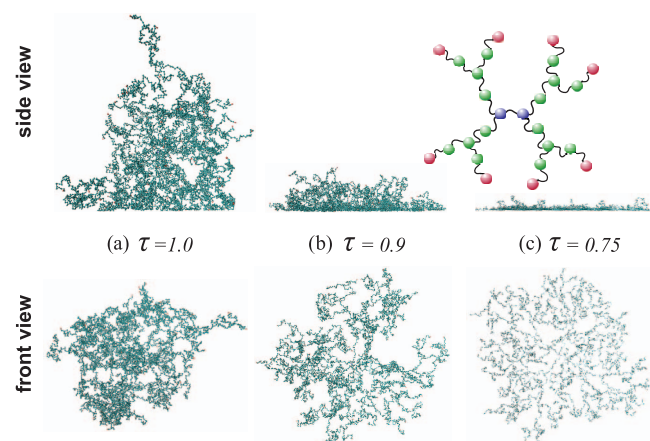


FIG. 2. Snapshots of the  $G_6$  dendrimer with spacer  $S = 32$  at (a)  $\tau = 1.0$ , (b)  $\tau = 0.9$ , and (c)  $\tau = 0.75$ . The architecture for the generation  $G = 2$  and spacer length  $S = 2$  is sketched on the upper right hand side. Red circles represent the terminal groups, blue circles indicate the core. The colors only indicate the different structural units. With respect to adsorption all units behave alike.

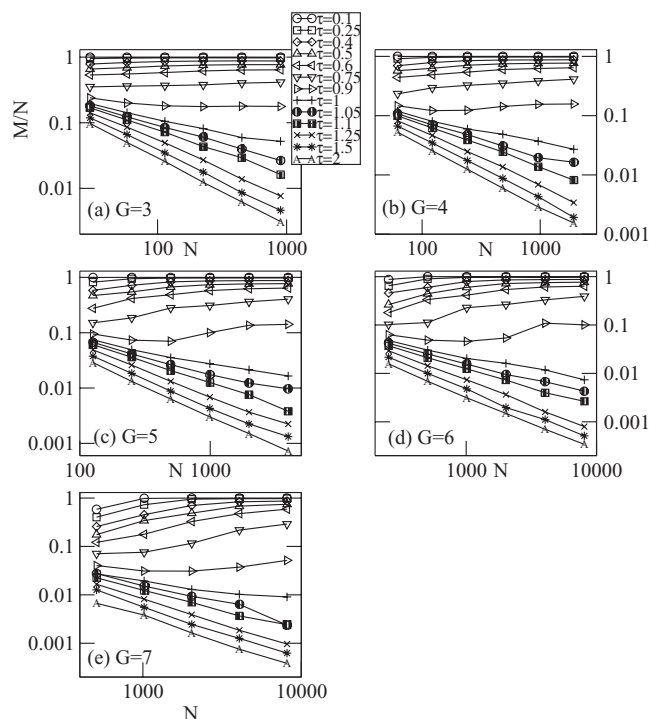


FIG. 3. Isotherms of the order parameter  $M/N$  versus degree of polymerization,  $N$ , at fixed generation number  $G$  and increasing spacer length  $S$ .

In Fig. 3 we display the set  $m(N)$  for fixed generation under the variation of spacer length. The splitting of isotherms into the three asymptotic classes is clearly visible. As the best estimate for the critical point we can take  $\tau_c$  in between  $\tau_c = 1.0$  and  $\tau_c = 1.05$ . The analysis of star-polymers which is based on a much larger data set shows a critical point of adsorption at  $\tau_c = 1.01$ . The best scaling approach for the crossover exponent provides a value of  $\phi = 0.59$  for stars which corresponds to the result for linear chains.<sup>17,25</sup>

It is interesting to note that for higher generations ( $G > 4$ ), see Figs. 3(c)–3(e), the isotherms for  $\tau = 0.9$  change from non-adsorption to adsorption behavior with increasing spacer length. This is an indication that dendrimers of higher generation do not display a smooth adsorption transition. Increasing spacer length reduces excluded volume constraints and increases the strength of adsorption of individual spacers which drives the dendrimer from the non-adsorbed into the adsorbed asymptotics.

The set of critical parameters obtained from Fig. 3 can be tested using the crossover scaling prediction for the order parameter according to

$$M/N^\phi = f_m(N^\phi|\kappa|), \quad (4)$$

with  $\kappa = (\tau_c - \tau)/\tau_c$  being the distance to the critical point and  $y = N^\phi|\kappa|$  is the scaling variable. For the case  $\kappa > 0$  and for  $y \ll 1$  the polymer is non-adsorbed, while for  $y \gg 1$  it is adsorbed. In the adsorbed state according to Eq. (3) we require  $M \sim N$  and thus we obtain

$$M/N^\phi \sim y^{(1-\phi)/\phi}, \quad (5)$$

whereas in the non-adsorbed state we have

$$M/N^\phi \sim y^{-1}. \quad (6)$$

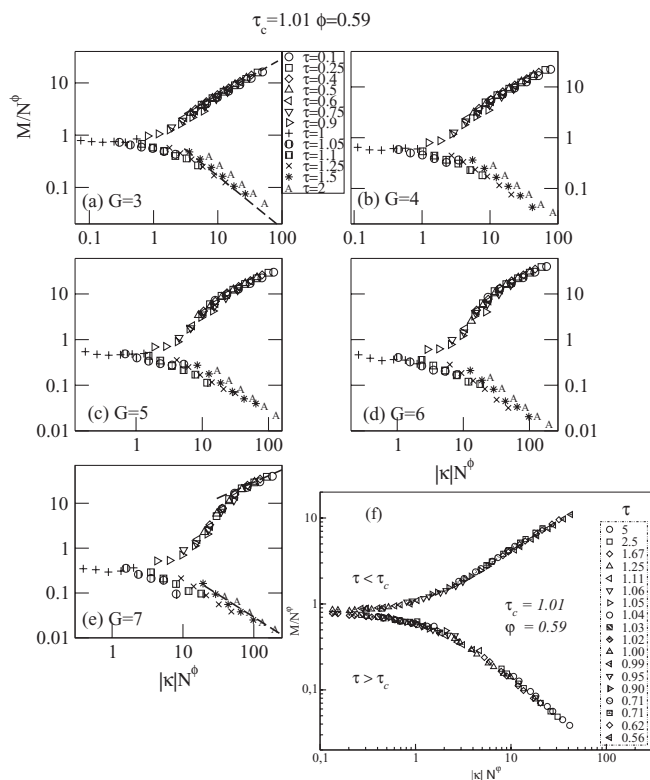


FIG. 4. Scaling plots of the order parameter according to Eq. (4) using  $\phi = 0.59$  and  $\tau_c = 1.01$  at fixed values of  $G$  for dendrimers (a)–(e), and for 4-arm star polymers (f). The predicted asymptotic behavior is indicated by the dashed lines.

In Figs. 4(a)–4(e) we display the scaling plots of the order parameter obtained by applying Eq. (4) for dendrimers with fixed values of  $G$ . The best fit for the critical temperature and crossover-exponent is  $\tau_c = 1.01$  and  $\phi \simeq 0.59$ , respectively. The upper branches of the plots correspond to the adsorbed states (positive values of  $\kappa$ ) while the lower branches correspond to the depleted states (negative values of  $\kappa$ ). The scaling is only moderate but the proper asymptotic behavior is recovered. One notes that a scaling of all plots for different values of  $G$  is not possible. While for  $G = 3$  a gradual adsorption crossover in the adsorbed branch (upper set of curves) is displayed, the results for  $G = 7$  display an unusual crossover with a strong increase for smaller values of  $y$  which changes into the asymptotic slope only for larger values of  $y$ . For comparison we display the results for 4-arm star polymers in Fig. 4(f) which lead to excellent scaling with the set of critical parameter according to  $\phi = 0.59$  and  $\tau_c = 1.01$ .

The deviations from crossover-scaling for dendritic polymers become even more evident in Fig. 5. Here, we display the scaling plot of the order parameter with fixed values of spacer length. Scaling for the adsorbed state is generally not obeyed close to the critical point from small values of  $y$ . We note that using a very low value of the crossover exponent such as  $\phi = 0.3$  gives reasonable results for the limit of small spacer lengths but does not lead to scaling for longer spacers.

From these results we can conclude that effects of finite density (excluded volume) in dendrimers interfere with a critical adsorption behavior. Long spacers facilitate the adsorption and lead to crossover scaling. For dendrimers of high gen-

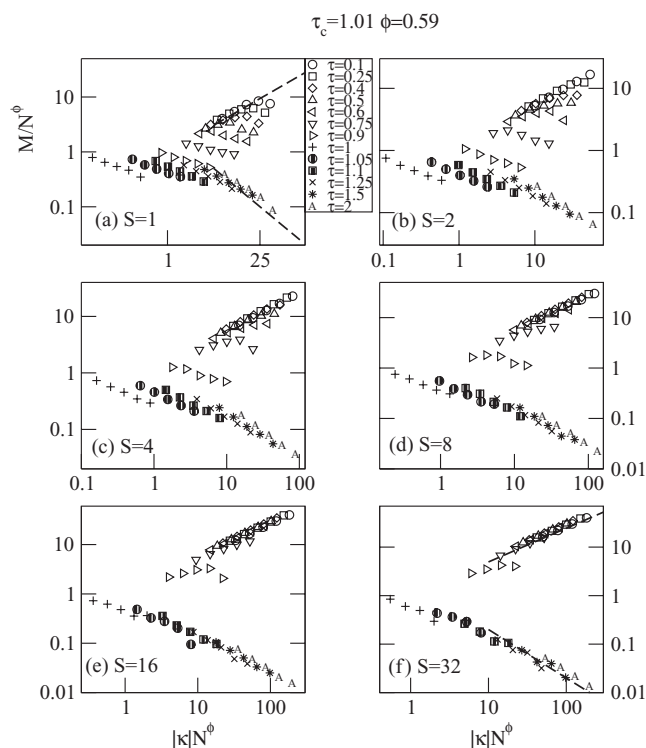


FIG. 5. Scaling plots of the order parameter according to Eq. (4) using  $\phi = 0.59$  and  $\tau_c = 1.01$  at fixed values of  $S$ . The predicted asymptotic behavior is indicated by the dashed lines.

erations a sharp transition is displayed below the estimated critical point of adsorption which is similar to a first-order transition. To analyze this assumption we consider the order parameter for the adsorbed spacers only defined as

$$m_S = \frac{M_S}{S+1}, \quad (7)$$

where  $M_S$  denotes the number of adsorbed monomers within an adsorbed spacer. Because all monomers adsorb on the surface the effective length of a spacer is extended by one bond connecting a branching unit. An adsorbed spacer is defined as a spacer which has at least one monomer in contact with the surface. In Fig. 6 we display the order parameter for the adsorbed spacers,  $m_S$ , as a function of temperature for various generations at a given spacer length. The order parameter displays a smooth crossover independent of the number of generations for values of the spacer length larger than two units. This order parameter monitors the adsorption crossover of nearly independent linear chains.

In Fig. 7 we display the scaling plot for  $m_S$  using the results for the critical set of parameters as for linear chains as obtained in previous work.<sup>17,25</sup> Here, all the data for all generations and spacer lengths larger than two units are collected. The asymptotic slope,  $(1 - \phi)/\phi \simeq 0.7$  is reached. Deviation from scaling is caused by the collapse of the whole molecule at lower temperatures (see discussion below) onto the substrate which leads to saturation effects for spacers adsorption.<sup>2,17</sup> This is indicated by the deviation of the data from the master curve (adsorbed state, upper branch in Fig. 7) which marks the collapse of the dendrimer onto the substrate. For repulsive surfaces,  $\tau > \tau_c$ , lower branch in

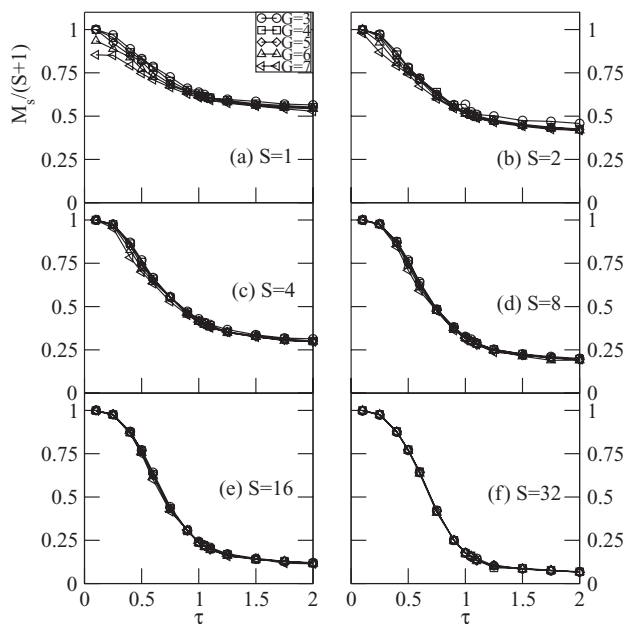


FIG. 6. Fraction of adsorbed monomers per adsorbed spacer,  $m_s$ , as a function of temperature for various generations at a given spacer length. The order parameter is independent of the number of generations for  $S > 2$ .

Fig. 7, the asymptotic scaling is reached for the longest spacers, at high temperatures only. To explain this observation one has to take into account that fixing one end-group to the repulsive surface the excluded volume repulsion within the dendrimer forces monomers to touch the surface around the grafting point, which results in finite concentration of spacers close to the surface. A spacer which is in contact to the surface experiences a certain pressure towards the surface caused by the other spacers which results in a higher order parameter as compared to the single chain grafted to the substrate. We note that this is important for short spacers only, where scaling concepts should not be applied.

In Fig. 8 we display the fraction of adsorbed spacers,  $m_A$ , for the same parameters as shown in Fig. 6. This order param-

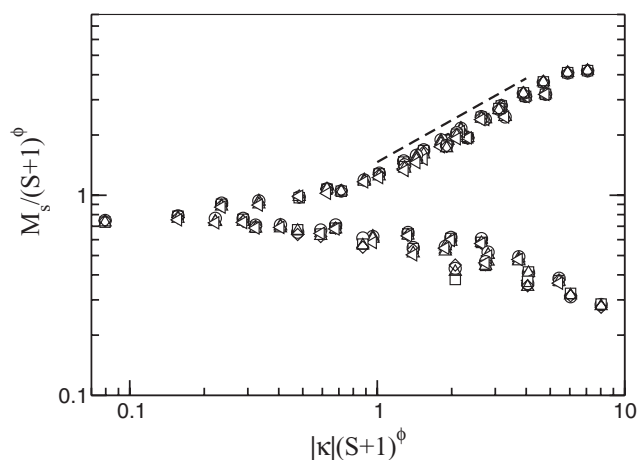


FIG. 7. Scaling plot for the order parameter of adsorbed spacers,  $m_s$ , using the results for the critical set of parameters for linear chains,  $\tau_c = 0.99$ ,  $\phi = 0.59$ . The dashed line indicates the predicted asymptotic slope in the adsorbed state.

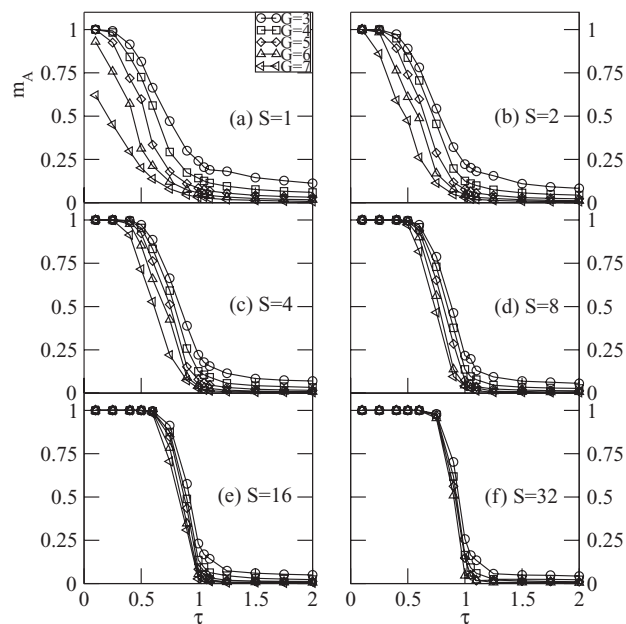


FIG. 8. Fraction of adsorbed spacers,  $m_A$ , as a function of temperature for various generations at a given spacer length.

eter monitors the adsorption transition of the dendrimer as a whole. If the spacer length is increased the transition becomes nearly step-like with the center of the jump shifted to temperatures below the critical point of adsorption. For the longest spacer a first-order like transition independent of the number of generations is displayed, see Fig. 8(f).

From this observations we can conclude the following scenario: Close the critical point of adsorption spacer chains start to adsorb if they are in direct contact to the surface. Because of excluded volume effects the dendrimer as a whole has to overcome a free energy barrier for the transition to the flatly adsorbed state. At lower values of the temperature the effective strength of adsorption of the spacers becomes large enough to favor the flatly adsorbed state of the dendrimer and the molecule shows a collapse-like transition in the direction perpendicular to the substrate. Thus, individual dendrimers display a two-step adsorption scenario which is driven by spacer-adsorption. This explains the poor scaling of the global order parameter,  $m$ , with respect to the number of generations. The latter is given by the product of the two order parameters according to:  $m = m_A \cdot m_s$ , which individually display two types of adsorption transitions. The shape-transition of the dendrimer can be located by the inflection point of the  $m_A(\tau)$ . Depending on the generation for the longest spacers the transition takes place close to  $\tau^*(S = 32) = 0.91 \pm 0.04$  while for smaller spacers the transition is shifted to lower values,  $\tau^*(S = 8) = 0.8 \pm 0.04$ .

The weakly and strongly adsorbed conformations of the dendrimers are also reflected by the shape of the monomer density profiles as functions of the distance from the surface (not shown). In the former states the profiles develop a bimodal shape: At a relatively large distance from the surface the profiles still contain a maximum typical of a desorbed state, whereas directly at the surface enrichment of monomers is seen, which corresponds to adsorbed spacers.



On the other hand, in the strongly adsorbed conformations the profiles change abruptly into a strongly localized distributions at the surface which corresponds to a flat, pancake-like shape of the dendrimers.

## B. Shape functions

In order to analyze the shape changes of the dendrimers we consider the radius of gyration tensor<sup>26–28</sup> defined as

$$R_{\mu\nu} = (1/N) \left[ \sum_i^N (r_{\mu i} - r_{cm,\mu})(r_{\nu i} - r_{cm,\nu}) \right],$$

$$\mu, \nu = x, y, z, \quad (8)$$

where  $r_{\mu i}$  and  $r_{cm,\mu}$  are the coordinates of the  $i$ th monomer and of the center of mass (c.m.) of the dendrimer in the laboratory frame of reference, respectively. From Eq. (8) it follows that  $R_{\mu\nu}$  is real and symmetric and therefore it can be diagonalized by a linear transformation to the principal axis system with the eigenvalues  $\lambda_1, \lambda_2, \lambda_3$  being real and positive. More specifically, the two invariants

$$I_1 = \text{Tr}(R_{\mu\nu}) = \lambda_1 + \lambda_2 + \lambda_3, \quad I_2 = \lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3, \quad (9)$$

are used to define the so-called relative shape anisotropy<sup>26–28</sup>

$$a = 1 - 3(I_2/I_1^2), \quad (10)$$

which takes values between 0 and 1. In particular,  $a = 0$ ,  $a = 1/4$ , and  $a = 1$  for spherical, oblate, and extremely elongated ellipsoids, respectively. The angular brackets denote ensemble averages.<sup>26</sup>

In Fig. 9(a) we display the relative shape anisotropy as a function of the temperature for various spacers at the fixed value of the generation number  $G = 6$ . A step-like transition scenario which corresponds to a collapse of the structure in the direction perpendicular to the surface can be found again for long spacers and high generations. One can observe the shift in the transition with respect to the spacer length. Using the reflection points in Fig. 9(a) to define the collapse-like transition,  $\kappa^* = (\tau_c - \tau^*)/\tau_c$ , we obtain the results displayed in Fig. 10. This is fully consistent with the observation of the transition behavior of the order parameter,  $m_A$ , given in Fig. 8. At low temperature the shape anisotropy reaches the value  $a \approx 0.25$  which signals that the polymers are oblate.

In Fig. 9(b) we display the corresponding result for star polymers. Again, in contrast to dendrimers of higher generation the shape-transition is smooth and starts directly from the critical point of adsorption. We note that in the high temperature limit star polymers display a slightly oblate shape (as dendrimers of low generations, see also Ref. 12), while dendrimers of higher generation are nearly spherical even below  $\tau_c$  in the weak adsorption regime.

## C. Strongly adsorbed state of the dendrimer

Since the adsorbing interface breaks the isotropy of the system, we have to distinguish between the parallel and perpendicular components of the dendrimers' radius of gyration

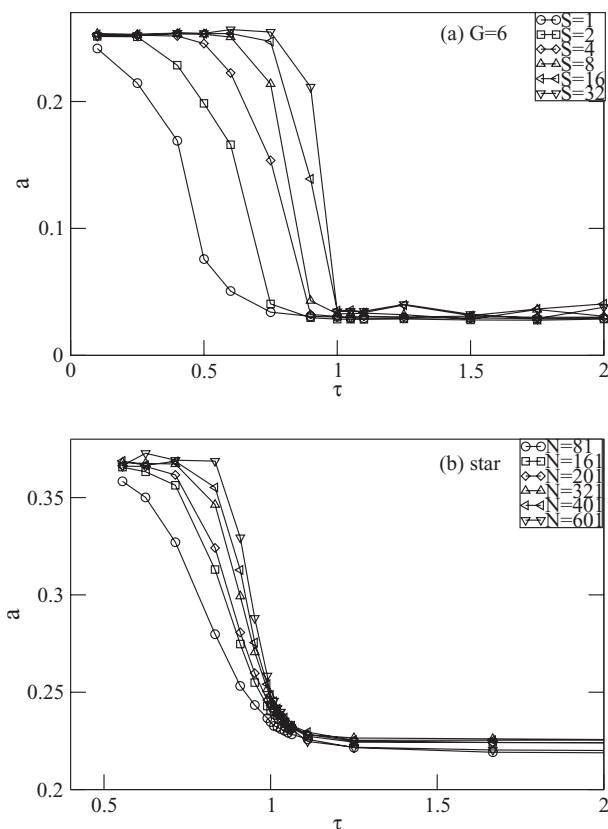


FIG. 9. Shape anisotropy for: (a) G6 dendrimers with different spacer length  $S$  and (b) 4-arm star-shaped polymers with different chain length  $N$ , versus the reduced temperature  $\tau$ .

defined as follows:

$$R_{g\parallel}^2 = \frac{1}{2} \frac{1}{N} \sum_{i=1}^N ((x_i - x_{cm})^2 + (y_i - y_{cm})^2), \quad (11)$$

$$R_{g\perp}^2 = \frac{1}{N} \sum_{i=1}^N ((z_i - z_{cm})^2). \quad (12)$$

In (11) and (12)  $x_i, y_i, z_i$  are the coordinates of the  $i$ th monomer belonging to the dendrimer with the center of mass at  $x_{cm}, y_{cm}, z_{cm}$ , respectively.

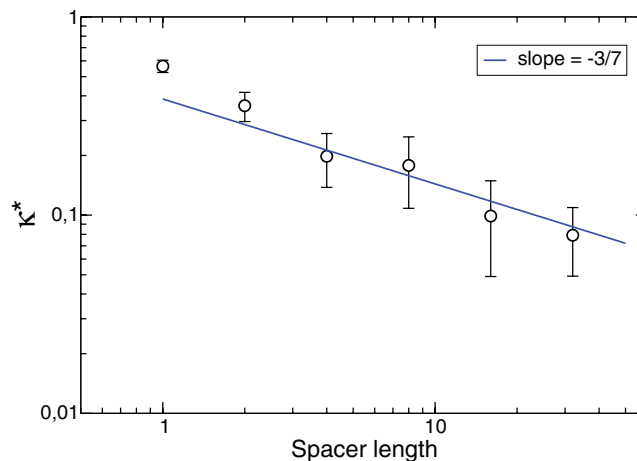


FIG. 10. Apparent point of shape transition obtained from the inflection points in Fig. 9(a) for  $G = 6$ . The solid line indicates the predicted behavior according to Eq. (23).

At high temperatures the dendrimers are nearly isotropic and their extension corresponds to the 3D, or bulk, behavior. In our previous work we showed<sup>12</sup> that the mean field argument<sup>29</sup> is able to describe the scaling of the dendrimer's size in a good solvent according to

$$R_{g\perp} \sim R_{g\parallel} \sim [(GS)^2 N]^{1/5} \text{ for } \tau \gg \tau_c. \quad (13)$$

Here, we focus on the extension of the dendrimer parallel to the surface only.

On the other hand in the limit of low temperatures when the dendrimers are nearly 2D objects we expect the free energy to take the form (with unit-carrying pre-factors omitted, length units are taken in units of a Kuhn segment)

$$\frac{F}{k_B T} = \frac{N}{GS} \frac{R_{g\parallel}^2}{GS} + \frac{N^2}{R_{g\parallel}^2}, \quad (14)$$

leading to

$$R_{g\parallel} \sim [(GS)^2 N]^{1/4} \text{ for } \tau \ll \tau_c. \quad (15)$$

In Figs. 11(a)–11(f) we display  $R_{g\parallel}$  as a function of the scaling variable  $(GS)^2 N$  in various regimes of the temperature. According to Eqs. (13) and (15) we fit the data to a power law according to

$$R_{g\parallel} \sim [(GS)^2 N]^\alpha. \quad (16)$$

It is seen from Fig. 11 that the proposed scaling relation is well obeyed for all generations and spacer lengths  $S > 2$ , except for the intermediate region  $0.75 \leq \tau \leq 0.9$  where some discrepancies occur.

In Fig. 11(g) we plot the apparent exponent  $\alpha$  as a function of the reduced temperature. In the strong adsorption region we obtain  $\alpha \approx 0.254 \pm 0.004$  with a slight tendency to increase as the intermediate region is approached. At higher temperatures around  $\tau = 0.9$  the apparent exponent decreases sharply to  $\alpha \approx 0.202 \pm 0.004$  as the weak adsorption region is entered. Both limiting values correspond to the predicted asymptotic behavior for 2D and 3D, respectively and crossover between both regions is step-like. In the strong adsorbed case (the lowest value of  $\tau$ ) the adsorbed structures are completely flat and all monomers are adsorbed up to a generation of  $G = 7$ . The resulting 2D dendrimers are fully movable and there is no indication for kinetic trapping.

At this point we would like to emphasize again the role of the upper limit for the number of generations. The mean-field concept and the resulting scaling as discussed above are only consistent if the relation  $N \ll (GS)^d$  is fulfilled. This leads to a maximum number of generations  $G_{max}^d(S)$  depending on spatial dimension and spacer length. As we have mentioned above for the isotropic state this results in the empirical estimate of  $G_{max} \simeq 8$  for spacer length  $S = 8$ . For strong adsorption the packing constraints are increased. Our simulations show that dendrimers with very short spacer length of  $S = 1$  cannot be perfectly adsorbed anymore beyond  $G_{max}^{2D}(1) = 6$ , see Fig. 1. For longer spacers, complete adsorption is always possible up to  $G = 7$ . For a recent discussion about the physics of dendrimers with respect to the packing threshold, see the recent work by Kröger *et al.*<sup>21</sup>

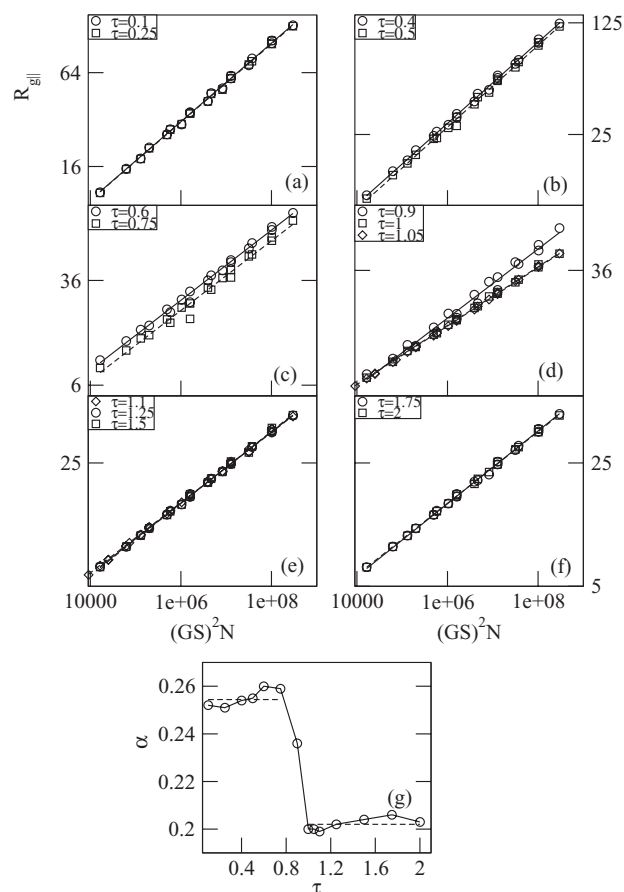


FIG. 11. (a)–(f) Scaling behavior of the parallel component  $R_{\parallel}$  of the radius of gyration of the adsorbed dendrimers at the considered reduced temperatures  $\tau$  for  $S \geq 4$ . The solid and dashed lines are fits to the data points of the form  $R_{\parallel} \sim [(GS)^2 N]^\alpha$ . (g) Exponent  $\alpha$  versus the reduced temperature  $\tau$ . The horizontal dashed lines indicate the effective exponent obtained from averaging the results in the respective asymptotic regions (2D and 3D). The standard deviation of the exponents are of the order of the symbol size.

#### IV. MEAN FIELD SCENARIO FOR THE ADSORPTION OF DENDRIMERS

The previous results reveal two distinct features: Individual spacers display scaling and adsorption behavior analog to isolated linear chains while the dendrimer as a whole collapses at values of the adsorption temperature well below the critical point of adsorption onto the substrate. The threshold for the shape-collapse is apparently shifted closer to the critical point when the spacer length is increased, see Figs. 9 and 10. Let us note at this point that individual threads of the dendrimer are stretched and the only reason for shape persistence of the dendrimer at weak adsorption is excluded volume. Previous work showed that the mean field description of dendrimer conformations shows very good agreement with simulation results under various conditions.<sup>12,30,31</sup> This motivates us to consider a generalization of the mean field model to include the adsorption behavior by using the following free energy:

$$\begin{aligned} F(D, A) &= F_{ad} + F_{EV} + F_{el} \\ &= F_{ad}(D) + v \frac{N^2}{D \cdot A} + \frac{1}{2} \frac{N}{GS} \left( \frac{D^2}{GS} \right) + \frac{N}{GS} \frac{A}{GS}. \end{aligned} \quad (17)$$

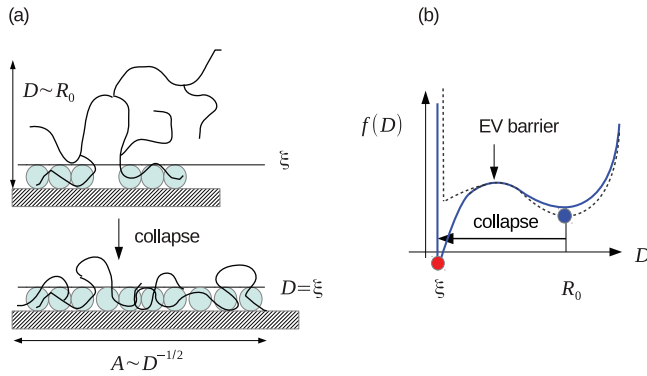


FIG. 12. Collapse-like adsorption transition of a dendrimer according to the mean field model. (a) Sketch of conformations above and below the collapse towards the flatly adsorbed state. (b) Sketch of the mean field free energy as a function of  $D$ . The circles illustrate the stable states at higher temperature (dashed line) and at lower temperatures (solid line).

Here, we used rational units of  $k_B T = 1$  and length scales are given in units of Kuhn segments. The notation for  $GS$  is the same as before. It gives the length of a thread of monomers starting from the core up to a terminal unit. The extension of the dendrimer perpendicular to the surface is denoted by  $D$ , and the squared extension (cross section) of chain parallel to the surface is denoted as  $A = R_{\parallel}^2$ , see Fig. 12(a). We systematically ignore prefactors of order unity.

Both variables,  $A$  and  $D$ , are to be optimized to obtain the smallest value of the total free energy. The strength of the excluded volume interactions is given by  $v$  and it is chosen as a prefactor for the mean field excluded volume interaction given by the second term in the Eq. (17). The third and the fourth terms denote the elastic free energy of stretching in the direction perpendicular and parallel to the substrate, respectively. The first term  $F_{ad}(D)$  does not depend on  $A$  as we will show. Let us now fix the variable  $D$  and optimize the free energy with respect to  $A$ . This gives

$$A = (vN)^{1/2} GS / D^{1/2}. \quad (18)$$

As a consequence the partially optimized free energy reads

$$F(D) = F_{ad}(D) + 2v^{1/2} N \frac{N^{1/2}}{D^{1/2} \cdot GS} + \frac{1}{2} \frac{N}{GS} \left( \frac{D^2}{GS} \right). \quad (19)$$

Note that reduction of extension perpendicular to the surface leads to an *excluded volume barrier* which diverges as

$$F_{EV}(D) \sim 1/D^{1/2}.$$

We note that we obtain the result for the non-adsorbed dendrimer for  $F_{ad} = 0$  after minimization of Eq. (19) with respect to  $D$  with the known result  $D \sim R_{\perp} \sim N^{1/5} (GS)^{2/5}$ , see also Eq. (13). By setting  $D = 1$  we obtain the result for the flatly adsorbed dendrimer simply from, Eq. (18) with  $R_g \sim A^{1/2}$ , see Eqs. (14) and (15).

As we have seen from our simulation results: spacer adsorbs according to the scenario of linear chains below the critical temperature of adsorption. Here, an adsorption unit of the spacer chain consists of  $g$  monomers having the extensions  $\xi \sim g^v$  ( $v \simeq 3/5$  in good solvent) and provide a gain of free energy of the order  $k_B T$ . We call this unit an adsorption blob.

For linear chains the crossover relation determines the blob size:  $g^{\phi} \kappa \sim 1$  (in units of  $k_B T$ ), see also Sec. III A for the discussion of the crossover exponent  $\phi$ . According to the mean field model we assume a homogeneous distribution of spacers within the volume  $V = D \cdot A$ , where we ignore prefactors. Thus, the number of blob-units in contact to the surface determines  $F_{ad}$  according to

$$F_{ad} \sim -\frac{N}{g} \frac{\xi}{D} \sim -N \kappa^{1/\phi} \frac{\xi}{D}, \quad (20)$$

where  $\kappa$  has been defined above Eq. (4). Usage of  $\phi \neq 1/2$  instead of the mean-field result ( $\phi = 1/2$ ) for  $F_{ad}$  reflects the more accurate crossover scaling which is known for linear chains and has also been shown in this work, see Fig. 7, and therefore yields a more appropriate description of the free energy gain of adsorbed spacers. Thus, the overall adsorption of the dendrimer is the result of adsorption of linear spacers put in balance with the excluded volume constraints of the whole molecule which is composed of  $N/S$  spacers. We note that a simple mean-field description of the adsorption free energy does not change the conclusions drawn below. We note further that our description is limited to the crossover temperature of the spacers given by  $S^{\phi} \kappa \simeq 1$ . Even closer to the critical point of adsorption several spacers have to adsorb collectively, a scenario which would be rather speculative at this point.

With this assumption we obtain for the total free energy per monomer unit ( $f = F/N$ )

$$f(D) = -\kappa^{1/\phi} \frac{\xi}{D} + 2v^{1/2} \frac{N^{1/2}}{D^{1/2} GS} + \frac{1}{2} \frac{D^2}{(GS)^2}. \quad (21)$$

One notes that  $f(D)$  diverges for  $D \rightarrow 0$ , which is not outbalanced by the excluded volume barrier. However, this limit is unphysical since the flatly adsorbed state is reached for  $D = \xi$ , and the blob size provides already the minimal length scale. The physical reason behind the blob concept is the competition of entropy reduction due to confinement and gain of adsorption free energy. We do not consider any other confinement effects from the dendrimers conformation (above the scale of a blob). Since the dendrimer is itself in a semi-dilute state of threads (which are also stretched by excluded volume) the confinement of the threads to the size  $D$  should not be relevant. Still, one might discuss a scale of length  $S^v$ , i.e.,  $F_{conf} \sim S/D^{1/v}$ . However, this term is only relevant with respect to  $F_{ad}$  if  $\xi \simeq S^v$ . This is reached at the crossover of the spacers while we are interested in the state well above the adsorption threshold. We note here that formally the confinement energy can be taken into account but does not change the scenario described below. In short, the cut-off at  $\xi = D$  replaces the soft regularization of the free energy using a confinement contribution, see the sketch in Fig. 12(b).

The free energy given by Eq. (21) displays a typical scenario of a discontinuous phase transition: The last two terms define a minimum which corresponds to the non-collapsed state,  $D_b \simeq R_g$  with a free energy given by  $f_b = f(D_b)$ . The first two terms lead to the bending of the free energy function towards negative values for  $D \rightarrow \xi$ . The value of  $f_c = f(\xi)$  gives the free energy in the flatly adsorbed state. This is illustrated in Fig. 12(b). Coexistence is given by  $f_b = f_c$ . By

considering the dominating pairwise contributions of the free energy for the both minima, respectively, we obtain

$$f_b = \alpha \frac{N^{2/5}}{(GS)^{6/5}} = -\kappa^{1/\phi} + 2v \frac{N^{1/2}}{\xi^{1/2}(GS)} = f_c, \quad (22)$$

where  $\alpha$  denotes a numerical constant of order unity which cannot be fixed by the mean field model. We note that also  $v$  and  $\xi$  can only be fixed up to a numerical prefactor. In order to estimate the values of the three contributions in Eq. (22) we start from the bulk contribution,  $f_b$ . The number of monomers in a dendrimer,  $N$ , is limited by the packing constraint, i.e., when the monomer density reaches unity. In accordance with the mean field prediction we obtain the condition  $N \ll (GS)^3$  and thus  $f_b \ll 1$ . On the other hand the adsorption free energy per monomer is given by  $1/g$  which in the case of our simulations is of order unity since the blob size at the collapse-like transition is rather small (shift of  $\tau$  of the order of 0.2...0.5 with respect to the critical point which corresponds to  $\kappa$  in the same range). Thus, we may approach the coexistence condition by  $f_c \simeq 0$  and we obtain for the transition point

$$\kappa^* \sim n^{3/7} G^{-6/7} S^{-3/7} \sim 1/S^{3/7}. \quad (23)$$

Here, we have introduced the number of spacers  $n = N/S$  to obtain the explicit spacer length dependence of the transition temperature. Also, we have used the best estimate for the crossover exponent for linear chains  $\phi \simeq \nu \simeq 3/5$ . This prediction is indicated as a solid line in Fig. 10.

The mean field model thus predicts a discontinuous phase transition from the spherical shape of the dendrimer to the flatly adsorbed state well below the critical temperature of adsorption of the spacer chains. The reason is the densification of the dendrimer upon contraction which is related with an increase of excluded volume interactions. This barrier has to be overcome by the adsorbed spacer before the collapsed conformation in the direction perpendicular to the substrate is thermodynamically preferred.

## V. SUMMARY AND CONCLUSIONS

We have applied the bond fluctuation model to investigate the adsorption behavior of dendrimers in a wide range of their generation, and spacer length near an adsorbing surface. Our results indicate a two-step adsorption scenario for the dendrimers with long spacers: Below a critical temperature of adsorption,  $\tau_c$ , spacers in direct contact to the surface are adsorbed while the dendrimer as a whole is only weakly perturbed and retains a spherical shape. At a characteristic temperature,  $\tau^* < \tau_c$ , the dendrimer undergoes a step-like transition into a flat conformation. This is in contrast to the behavior of star polymers which display a critical crossover-behavior around  $\tau_c$  in analogy to linear chains. Also adsorption of the linear spacers which are in contact with the surface follows crossover-scaling as for linear chains and stars. The estimate for the critical temperature of adsorption,  $\tau_c = 1.01$ , is in good agreement with the behavior of star polymers and previous studies of linear polymers.

The two-step adsorption behavior of dendrimers explains the rather poor crossover-scaling of the overall order parameter which is defined as the fraction of all monomers which

are in contact to the adsorbing surface. While the corresponding order parameter of the adsorbed spacers (spacers which have at least one monomer at the surface) displays crossover-scaling, the fraction of spacers which are adsorbed at the surface displays a step-like transition. Related with this step-like transition the shape of the dendrimer becomes highly anisotropic and the density profile changes from a spherical into a flat shape. In the flatly adsorbed state the lateral extension of the dendrimer follows the scaling behavior for a 2D-object. According to the mean-field prediction we obtain a scaling of  $R_{g\parallel} \sim N^{1/4}$ . Again, this is in contrast to star-polymers which display a smooth crossover-scenario both for the shape and for the density profile.

Our results suggest to discriminate between two states of adsorption for dendrimers with long spacers: A weakly adsorbed regime close to the critical point of adsorption,  $\tau_c$ , which is indistinguishable from the critical point of adsorption of star polymers with low functionality. Here, the dendrimer as a whole retains its shape but sticks to the surface because spacer adsorption provides a decrease in the free energy by several  $k_B T$ . In this state the dendrimer resembles an elastic sphere with a small indentation at the surface. Below a spacer-length-dependent temperature,  $\tau^*(S)$ , the dendrimer collapses in the direction perpendicular to the adsorbing surface. This can be called the strongly adsorbed state of the dendrimer, and  $\tau^*(S)$  corresponds to the temperature of shape-transition. The different regimes are sketched in Fig. 13.

This particular adsorption scenario of dendrimers should be related with strong excluded volume effects. In the bulk repulsion between monomers leads to strong stretching of the individual threads, paths of connected spacers which start in the core of the dendrimer, and lead to the terminal groups.<sup>12</sup> When the dendrimer is flattened these threads have either to extend further in the direction parallel the surface, or the excluded volume interactions are further increased. This gives rise to a free energy barrier for adsorption and can cause a first-order like transition at lower temperatures. Longer spacers increase the effective adsorption per spacer and shift the transition point to higher values of the temperatures, closer to the critical point of adsorption, and thus narrow the range of weak adsorption behavior. Star polymers with only few arms, on the other hand, do not show essential stretching of arms and represent self-similar conformations which display a second-order adsorption crossover. Some of the concepts

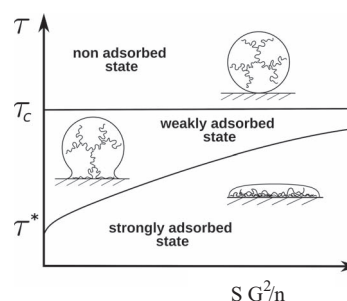


FIG. 13. Sketch of the state diagram of dendrimer adsorption with respect to the spacer length, generation, and number of spacers according to Eq. (23). For a fixed generation this displays the influence of the spacer length on the adsorption behavior.



developed in this work can be transferred to randomly branched polymers with a high branching density or other densely grafted structures such as arborescent grafted polymers.<sup>32</sup>

Our studies show that flexible spacers have a major impact on the adsorption behavior of dendrimers, in particular on the point of shape-transition which correspond to a collapse of the dendrimer from an isotropic into a quasi-2D state. Long spacers lead to a very sharp, well defined collapse of the dendrimer onto adsorbing surfaces, which might have interesting applications for responsible surfaces using grafted dendritic molecules. Many other effects can be used to control the adsorption of dendrimers at surfaces such as functionalization of terminal groups or charge effects which go beyond the scope of the present study.

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<sup>1</sup>G. J. Fleer, M. Cohen Stuart, J. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman and Hall, London, 1993).

<sup>2</sup>E. Bouchaud and M. Daoud, *J. Phys. (Paris)* **48**, 1991 (1987).

<sup>3</sup>J.-U. Sommer, M. Werner, and V. A. Baulin, *Europhys. Lett.* **98**, 18003 (2012).

<sup>4</sup>E. Eisenriegler, K. Kremer, and K. Binder, *J. Chem. Phys.* **77**, 6296 (1982).

<sup>5</sup>M. L. Mansfield, *Polymer* **37**, 3835 (1996).

<sup>6</sup>M. Ratner, I. Neelov, F. Sundholm, and B. Grinyov, *Funct. Mater.* **10**, 273 (2003), <http://www.isc.kharkov.com/journal/contents/10-2/>.

<sup>7</sup>A. Striolo and J. M. Prausnitz, *J. Chem. Phys.* **114**, 8565 (2001).

<sup>8</sup>A. Halperin and J.-F. Joanny, *J. Phys. II* **1**, 623 (1991).

<sup>9</sup>M. Daoud and J. Cotton, *J. Phys.* **43**, 531 (1982).

<sup>10</sup>I. Carmesin and K. Kremer, *Macromolecules* **21**, 2819 (1988).

<sup>11</sup>H. L. Trautenberg, T. Hölzl, and D. Göritz, *Comput. Theor. Polym. Sci.* **6**, 135 (1996).

<sup>12</sup>J. Klos and J.-U. Sommer, *Macromolecules* **42**, 4878 (2009).

<sup>13</sup>N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

<sup>14</sup>V. Ambegaokar and M. Troyer, *Am. J. Phys.* **78**, 150 (2010).

<sup>15</sup>E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, River Edge, NJ, 1993).

<sup>16</sup>H. W. Diehl and S. Dietrich, *Phys. Rev. B* **24**, 2878 (1981).

<sup>17</sup>R. Descas, J.-U. Sommer, and A. Blumen, *Macromol. Theory Simul.* **17**, 429 (2008).

<sup>18</sup>P. M. Lam and K. Binder, *J. Phys. A* **21**, L405 (1988).

<sup>19</sup>E. Bouchaud and J. Vannimeus, *J. Phys. (France)* **50**, 2931 (1989).

<sup>20</sup>M. Kröger, O. Pelag, and A. Halperin, *Macromolecules* **43**, 6213 (2010).

<sup>21</sup>M. Kröger, A. Schlüter, and A. Halperin, *Macromolecules* **46**, 7550 (2013).

<sup>22</sup>P. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

<sup>23</sup>P. G. de Gennes and P. Pincus, *J. Phys. Lett.* **44**, 241 (1983).

<sup>24</sup>P. de Gennes, *J. Phys.* **37**, 1445 (1976).

<sup>25</sup>R. Descas, J.-U. Sommer, and A. Blumen, *J. Chem. Phys.* **120**, 8831 (2004).

<sup>26</sup>D. N. Theodorou and U. Suter, *Macromolecules* **18**, 1206 (1985).

<sup>27</sup>J. Rudnick and G. Gaspari, *J. Phys. A* **19**, L191 (1986).

<sup>28</sup>P. K. Maiti, T. Çağın, G. Wang, and W. Goddard III, *Macromolecules* **37**, 6236 (2004).

<sup>29</sup>D. Boris and M. Rubinstein, *Macromolecules* **29**, 7251 (1996).

<sup>30</sup>J. S. Klos and J.-U. Sommer, *Macromolecules* **43**, 10659 (2010).

<sup>31</sup>J. S. Klos and J.-U. Sommer, *Macromolecules* **46**, 3107 (2013).

<sup>32</sup>M. Gauthier and M. Möller, *Macromolecules* **24**, 4548 (1991).