Pearl-necklace structures of molecular brushes with rigid backbone under poor solvent conditions: A simulation study

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Bottle-brush polymers, where flexible side chains containing \(N\) to 50 effective monomers are grafted to a rigid backbone, are studied by molecular dynamics simulations, varying the grafting density \(\sigma\) and the solvent quality. Whereas for poor solvents and large enough \(\sigma\) the molecular brush is a cylindrical object, homogeneous in axial direction, for intermediate values of \(\sigma\) an axially inhomogeneous structure of “pearl-necklace” type is formed. The “pearls,” however, have a strongly nonspherical ellipsoidal shape, due to the fact that several side chains cluster together in one pearl, qualitatively consistent with predictions of Sheiko et al. [Eur. Phys. J. E 13, 125 (2004)] We analyze the structure of these pearls and study both the transition to the axially uniform cylinder at high \(\sigma\) and to the trivial pearl-necklace structure at small \(\sigma\), where each pearl contains a single collapsed chain only. © 2010 American Institute of Physics. [doi:10.1063/1.3477981]

I. INTRODUCTION

Macromolecules with comblike architecture, where linear or branched side chains are grafted regularly or randomly to a backbone chain have recently found much interest (see the reviews1–4 and references therein). Due to the interplay between steric repulsion between the monomers of the densely grafted side chains and effective attractive interactions that can be controlled by the quality of the solvent, intricate spatial self-organization of these molecular brushes becomes possible. Such bottle-brush polymers can be either flexible or stiff, depending not only on the chemical character of the backbone (which can be anything from a flexible macromolecule up-to a stiff nanorod, e.g., a carbon nanotube),5 but also on the chain length \(N\) and grafting density \(\sigma\) of the side chains. With increasing \(N\) and \(\sigma\) stiffening of intrinsically flexible backbones is induced, see, e.g., Refs. 2, 3, and 6–9. Since the conformations of these complex macromolecular objects in some cases can be sensitive to external stimuli (electric fields, light, or simply changes in \(pH\) value of the solution), various applications have been envisaged,1,3 but this aspect will not be followed up here; rather we focus our interest on the theoretical understanding of structure formation of these molecular brushes exploring the statistical mechanics of a coarse-grained model by computer simulation methods.

Guided by a scaling analysis of the conformations of molecular brushes due to Sheiko et al.,10 we have begun11 a study of molecular brushes with a rigid backbone, varying three parameters, namely, \(N\), \(\sigma\), and the temperature \(T\) (by which we vary solvent quality in our model, focusing on poor solvents, i.e., \(T\) being below the theta temperature \(\theta\)).12 We also note that it is of great interest1–4,13–19 to consider the extension of the model to two chemically different types of side chains,20 but such an extension will be disregarded, as well as effects due to backbone flexibility.21,22 We hope, however, to report on such extensions in future studies. Whereas under good solvent conditions for large grafting density it can be shown that the local structure in a polymer bottle-brush with flexible backbone is almost indistinguishable from a rigid backbone case,23 different properties must be expected under conditions where the “pearl-necklace” structure formation is possible.10

The outline of this paper is as follows. In Sec. II, we briefly summarize the pertinent findings of the scaling theory10 focusing on the regime of parameters where axially inhomogeneous pearl-necklace structures form. Section III describes our model and sketches the analysis needed to characterize size and shape (and other properties) of the “pearls” quantitatively, considering not only average properties, but also fluctuations. Section IV presents our numerical results, while Sec. V summarizes our conclusions.

II. SCALING CONSIDERATIONS

When one discusses the conformation of a free flexible macromolecule in a solution near the theta temperature \(\theta\), scaling theory predicts that the (gyration) radius \(R_c\) of the chain varies as

\[
R_c = N^{1/2} F(N^{1/2} \tau), \quad \tau = 1 - T/\theta.
\]

(1)

where the scaling function \(F(Z)\) has the following limits:

\[
F(Z \to \infty) \propto Z^{-1/3}, \quad R_c \propto \tau^{-1/3} N^{1/3} \text{ as } N \to \infty,
\]

\[
F(Z = 0) = \text{const.}
\]

(2)

\[
F(Z \to -\infty) \propto Z^{2\nu - 1}, \quad R_c \propto (-\tau)^{2\nu - 1} N^{\nu} \text{ as } N \to \infty.
\]

(3)

Here \(\nu=0.588\) (Ref. 24) is the well-known exponent describing the scaling of self-avoiding walks due to excluded-
volume interaction,\textsuperscript{12} and one implies the limits $N \to \infty$ and $\tau \to 0$ taken such that $|Z| \ll \infty$. As usually done, we ignore in our discussion both logarithmic corrections that are expected to occur at the $\theta$-point\textsuperscript{12,28} and corrections to scaling that actually do become important for not very large $N$. In addition, prefactors of order unity are disregarded throughout.

It is useful to interpret scaling theories as a comparison of lengths;\textsuperscript{12} the size of the polymer coil at $T=\theta$ is $R_c = a N^{1/2}$, $a$ being the size of the monomeric unit, and so $Z=\xi/R_c \approx a/\tau$ can also be written as $\xi=\xi/a \approx \tau$ being the size of a “thermal blob.”\textsuperscript{12,27} Being mostly interested in the collapsed globules slightly below the theta point, Eq. (2), we can describe the structure of the coil as a dense packing of blobs with size $\xi=\sqrt{n a}$, where $n$ is the number of monomers per blob. The number of these blobs is $n_b = N/n = N/(\xi/a)^2$.

The density inside this coil should be essentially constant, of order $\rho$ with

$$\rho = n/\xi^3 = 1/(a^2 \xi) = \pi a^3. \tag{4}$$

The surface region of the globule is just the outer “shell” of blobs, of thickness $\xi$, giving rise to a surface free energy (surface tension) $\gamma = n_b^2/R_c^2$, $n_b^2 = n_b^2/\xi^2$ being the number of blobs in this outer shell (remember that the free energy cost of one blob is $k_B T$). Using Eq. (2) one therefore finds (omitting all geometric prefactors)

$$\gamma = \left( \frac{n_b}{R_c^2} \right)^{2/3} = \tau^2 a^{-2}. \tag{5}$$

Equations (4) and (5) not only characterize isolated free chains but also “mushrooms” grafted to the rigid backbone as long as the distance $h=\sigma^{-1}$ between grafting sites is so large that there is no free energy gain when neighboring collapsed globules coalesce. The total surface free energy of a collapsed mushroom then is of order $R_c^2 \gamma = N^{2/3} \tau^{4/3} = (N \tau^2)^{2/3}$.

However, when $\sigma$ is no longer very small, so that the distance $h$ and the radius $R_c$ of the collapsed globular mushroom [as given by Eq. (2)] become comparable, the system can minimize its free energy cost if two or more neighboring globules coalesce. Assuming that the number of thermal blobs remains constant in this process, the bulk free energy does not change and the behavior of the surface free energy decides on the stability of different structures. The object formed by coalescence of two collapsed coils that are grafted a distance $h$ along the backbone apart, given the constraint that one desires to obtain a dense packing of spherical blobs of size $\xi$, clearly will result in an elongated object of length $L$ along the backbone and radius $R$ in the plane perpendicular to the backbone, with $R < L$. Actually, it is conceivable\textsuperscript{10} that a number $m > 2$ of (collapsing) grafted chains join to form an elongated collapsed cluster. However, chains need to stretch in order to connect their parts in the central region of the cluster to the (off-center!) grafting sites. Thus, this chain stretching amounts to some loss in conformational entropy, i.e., there is some free energy penalty due to the “elastic tension” of the stretched strings of blobs necessary to form such elongated clusters. One estimates this elastic tension to be of order $T$.\textsuperscript{10,28} Thus, the free energy cost of a cluster formed by $m$ neighboring chains within a distance $L=nh$ becomes\textsuperscript{10}

$$\Delta F_1(m)/k_B T = (m N \tau^2)^{2/3} - m (N \tau^2)^{2/3} + m^2 (h/\xi) \tau. \tag{6}$$

The total number of monomers in a cluster formed from $m$ chains is $m N$, and hence the total surface free energy cost of such an object is $(m N \tau^2)^{2/3}$, whereas the total surface free energy cost of $m$ separated globules containing $N$ monomers each is $m (N \tau^2)^{2/3}$.

On the average there will be $M/m$ such clusters in our system of $M$ grafted side chains so that the surface free energy cost per grafted side chain is

$$\Delta f(m)/k_B T = \frac{1}{M} \frac{M}{m} \Delta F_1(m)/k_B T \tag{7}$$

Minimizing the free energy cost per chain yields

$$m = N^{1/2} \tau^{1/4} (h/\xi)^{-3/4}. \tag{8}$$

This means that

$$L = mh = a N^{1/2} \tau^{1/4} (h/\xi)^{-3/4}. \tag{9}$$

Sheiko \textit{et al.}\textsuperscript{10} assume that the pearl that is formed is a spherical object. Then the perpendicular (maximal) radius of the cluster $R$ is given by the condition that

$$(m N \tau^2)^{2/3} = \gamma R^2 \tag{10}$$

for the value of $m$ given by Eq. (8), which yields

$$R = a N^{1/2} \tau^{-1/3} (h/\xi)^{-1/2}. \tag{11}$$

A very remarkable feature is the large asymmetry of these two linear dimensions,

$$R/L = (\tau h/\xi)^{-1/2} = (\sigma a/\tau)^{1/2} = (h/\xi)^{-1/2} = (\sigma \xi)^{1/2}, \tag{12}$$

at least in the region $\sigma a \ll \tau$. On the other hand, this asymmetry diminishes with increasing grafting density $\sigma$, and $R = L$ for $\sigma a = \tau$ (apart from prefactors of order unity, of course). It turns out that the condition $\sigma a = \tau$ marks the transition region from the pearl-necklace structure to the regime of the collapsed brush, which lacks spatial nonuniformity in the direction of the cylinder axis.\textsuperscript{10} If we have a uniform cylinder of radius $R$ at density $\rho$ [Eq. (4)], we consider a disk of volume $R^2 h = R^2/\sigma$ in which just one chain of length $N$ is grafted, to conclude that

$$\rho = \pi a^3 = \sigma N/R^2. \tag{13}$$

So we find that

$$R^2/N = \sigma a^3 = (\xi/h)a^2. \tag{14}$$

However, this argument only works if $h$ does not exceed $\xi$, in order to ensure a space-filling packing of blobs in the cylinder. The condition $h = \xi$ (or equivalently, $\sigma a = \tau$) therefore implies that a crossover between the pearl-necklace structure and the uniformly packed cylinder takes place, and for $h/a = 1$ both Eqs. (11) and (14) yield the same result, namely, $R^2/N = a^2$; the chains then have Gaussian character,
tendencies for collapse (due to the fact that $\tau>0$), and for stretching in the direction perpendicular to the cylinder axis (due to the fact that $\sigma>0$) just effectively cancel each other.

The other limit of the pearl-necklace structure, as described by Eqs. (7)–(12), is reached when $m=1$; then we cross over to the regime of individual collapsed mushrooms, as described by Eq. (2), i.e., for

$$N^2\tau = (h/a)^3 = (a\sigma)^{-3}. \quad (15)$$

Note that this boundary does not mean that the individual collapsed chains [of size $R_c=a\sigma^{-1/3}N^{1/3}$, cf., Eq. (2)] just touch: the condition $R_c=a\sigma^{-1/3}N^{1/3}=h$ would yield $(h/a)^3 = N\tau^{-1}$ rather than Eq. (15); due to the gain in surface energy [Eq. (7)] it is predicted that with increasing distance $\tau$ from the theta point the formation of pearls as a collective effect of several stretched mushrooms sets in at smaller grafting densities $\sigma$ already.

At this point, one might question the validity of these scaling arguments, since in each pearl the number $m$ of mushrooms contributing to it is integer, $m=1, 2, 3, \cdots$, whereas the above treatment considers it as a continuous variable. However, whenever one interprets $m$ as an average over many pearls along the backbone, it clearly can be a continuous variable. A more serious criticism, however, perhaps is the fact that the first term on the right hand side of Eq. (7) is appropriate for the surface of a sphere, while actually Eqs. (9) and (11) rather suggest that the pearls are strongly elongated ellipsoids. In that case Eq. (10) would read $(mN^2\tau)^{2/3} = \gamma LR$ leading to $R=\alpha N^{1/2}\tau^{3/4}(h/a)^{3/4}$ giving rise to an even larger asymmetry between $R$ and $L$: $R/L=\alpha \xi$. Clearly, a test of the scaling arguments by simulations seems very desirable.

III. COMMENTS ON THE SIMULATED MODEL AND ITS ANALYSIS

Since the theoretical arguments sketched above do not consider possible end effects at the two ends of the rigid backbone, which is appropriate for very long backbone chains only, of course, which would be hard to deal with in a simulation, we choose periodic boundary conditions in the $z$-direction of the backbone. The number of side chains typically was $M=50$, and therefore the backbone length simply was $L_b=M/\alpha$. The backbone itself simply is taken as a straight line and side chains are grafted at regular intervals $\Delta z=h=1/\alpha$ to it. These side chains are modeled by the standard bead-spring model\textsuperscript{29,30} that has been extensively used in the literature for related work (e.g., polymer brushes grafted to flat walls\textsuperscript{30–34} or cylinders\textsuperscript{35} or spheres,\textsuperscript{36} for instance). Most of this work, however, has been restricted to good solvent conditions; the problem described in Sec. II has not been addressed in any of these early studies.

The side chains are described by effective monomers bound to each other by the finitely extensible nonlinear elastic (FENE)-potential, while all particles interact with a truncated and shifted Lennard-Jones potential ($r=$distance among a pair of beads),

$$U_{FENE} = -\frac{1}{2}k_0\gamma^2 \ln[1 - (r/r_0)^2], \quad 0 < r \leq r_0, \quad (17)$$

acts with the standard\textsuperscript{30,31} choice of parameters $r_0=1.5$ and $k=30$.

In the present paper, we consider only rather short side chain lengths, namely, $N=20, 35$, and 50. It is clear that the interpretation of results for such rather short chains in terms of scaling concepts [which are supposed to be accurate in the limit $N \to \infty$, cf. Eq. (2)] is a delicate matter. However, we emphasize that our range of $N$ corresponds nicely to the range of $N$ available in experiments on bottle-brushes,\textsuperscript{1,3–8} and the scaling theory of Sec. II (Ref. 10) will only be a useful guide for real systems, if it still is qualitatively applicable for such short chain lengths. Still, as an interesting theoretical albeit academic problem, it would be nice to extend our study to chain lengths of several hundreds of effective monomers, but this is prohibitively difficult in the poor solvent regime, where relaxation times of the chains get very long.

In $x, y$-directions, periodic boundary conditions were chosen as well, but the considered linear dimensions of the simulation box were chosen large enough, so that never any interaction of the bottle-brush polymer with its periodic images could occur. Note that no explicit solvent particles are included; solvent quality is simulated indirectly, as is standard practice,\textsuperscript{30} by varying the temperature of the system. For the model defined by Eqs. (16) and (17) the $\theta$ temperature has been estimated roughly as\textsuperscript{31} $\theta = 3.0$, and hence in the present work the range $1.5 \leq T \leq 3.0$ is studied.

Temperature is controlled by the Langevin thermostat in the standard way,\textsuperscript{29,30} i.e., the equation of motion in our molecular dynamics (MD) simulations for the time-dependence of the monomer coordinates $\vec{r}_i(t)$ is

$$m_{ij} \frac{d^2 \vec{r}_{ij}}{dt^2} = -\nabla U_i - m_{ij} \gamma \frac{d\vec{r}_{ij}}{dt} + \vec{f}_i(t), \quad (18)$$

where $t$ is the time, $U_i$ is the total potential acting on the $i$th bead, $\gamma$ is the friction coefficient, and $\vec{f}_i(t)$ is the random force. The latter satisfies the usual fluctuation-dissipation relation

$$\langle \vec{f}_i(t) \cdot \vec{f}_j(t') \rangle = 6k_B T \gamma \delta_{ij} \delta(t-t'). \quad (19)$$

Following previous work,\textsuperscript{29,30} we choose $\gamma=0.5$, choosing also the MD time unit $\tau_{LJ}=(m_1\sigma_{LJ}^2/F_{LJ})^{1/2}=1$. Equation (18) was integrated with the leap frog algorithm,\textsuperscript{37} applying a time step $\Delta t=0.006 \tau_{LJ}$, and utilizing the GROMACS package.\textsuperscript{38}

As is well known, equilibration of collapsed chains via MD methods is very difficult, and thus we briefly describe our equilibration procedures. First the system was equili-
brated at \( T=3.0 \) for a time range of \( 30 \times 10^6 \tau_{LJ} \). To gather statistics, 500 statistically independent configurations at this temperature were used for initial configurations of “slow cooling” runs, where the temperature \( T \) was lowered in steps of 0.1, and running the system at each \( T \) for a time of \( 5 \times 10^5 \tau_{LJ} \). The final configuration of each (higher) \( T \) was used as starting configuration for the next (lower) \( T \). In this way, we generate at low \( T \) and intermediate values of the grafting density \( \sigma \) configurations of clusters (Fig. 1) that are statistically independent of each other. One can see already from the snapshots (Fig. 1) that indeed rather dense clusters containing several side chains occur and the linear dimensions of these clusters (and the number \( m \) of side chains they contain) vary strongly with \( \sigma \).

This spontaneous formation of “clusters” containing several side chains in a cluster is a kind of spontaneous symmetry breaking. Of course, \textit{a priori} there is no reason for the system to “decide,” when one considers the subsequent labels of the grafted chains along the backbone, between which labels of the chains the boundaries between subsequent clusters should occur, since (due to the periodic boundary conditions) we have translational invariance along the \( z \)-axis. So, in principle, we should in a very long MD run observe fluctuations where a chain that was part of a cluster “escapes” from the cluster to become part of the left or right neighboring cluster. In fact, many such fluctuations would amount to effectively causing a random diffusion of the cluster pattern along the \( z \)-axis, together with fluctuations in the characteristic properties (number \( m \) of chains a cluster contains, and its linear dimensions) of each cluster. In this way, the full thermodynamic equilibrium of our quasi-one-dimensional system would be established; note that in quasi-one-dimensional systems with short range forces, a spontaneous symmetry breaking in the sense of well-defined sharp phase transitions cannot occur.\(^{39}\)

Of course, the above discussion is rather hypothetical, for practically accessible MD time scales the escape of any chain from a cluster at \( T=1.8 \) is hardly ever observed, there are huge free energy barriers that one would need to cross. If some chains at \( T=1.5 \) have joined to form a cluster, transitions where a chain leaves a cluster to join a neighboring cluster are prohibitively difficult. So standard MD runs (starting from a single initial configuration) would not sample phase space adequately. This problem is the reason why 500 independent “slow cooling” runs were performed, and we have checked (by variation of the cooling speed and of the number of runs) that this high statistical effort was just enough to obtain meaningful results. Therefore it was not attempted (and not possible) to systematically study much longer chains in this way.

Another difficulty is that for a test of the predictions of Sec. II one needs to identify for each configuration that is analyzed which chains belong to which clusters. We have used the standard Stillinger\(^{40}\) neighborhood criterion for monomers: if two monomers are less than a distance \( r_n \) apart, they are counted as “bound together.” We followed the standard choice \( r_n=1.5\sigma_{LJ} \) and checked that qualitatively very similar results were obtained if one chooses \( r_n \) a bit smaller than this choice (larger values of \( r_n \) are physically hardly significant, since then the particles are too weakly bound, due to the rapid fall-off of the LJ potential).

When the assignment to clusters is achieved, it is

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**Fig. 1.** Examples of snapshot configurations for the pearl-necklace structures of our model, occurring for \( T=1.8, N=50 \), and grafting densities \( \sigma =0.08 \) (a), 0.12 (b), 0.206 (c), and 0.38 (d). Note that in each simulated system we have \( M=50 \) chains, so the total extension of a system along the \( z \)-axis would be \( M/\sigma=50/\sigma \); for clarity only a part of length \( \Delta z=125 \) is shown in all cases. Therefore, the number \( M' \) of chains included in the snapshots in (a) is \( M'=10 \), in (b) \( M'=15 \), in (c) \( M'=25 \), and in (d) \( M'=47 \), respectively.

**Fig. 2.** Probability distribution \( P(N_c) \) of the number of clusters plotted vs \( N_c/M \) for \( T=1.5, M=50 \), and three choices of \( N_c \) : \( N=20 \) (a), 35 (b), and 50 (c). Grafting densities shown are \( \sigma =0.06, 0.08, 0.12, 0.206, 0.38, \) and 0.57.
exhibits rather broad peaks at intermediate values of \( \sigma \). The onset increases strongly with increasing \( N/M \) for several choices of \( N \). The extreme choices would be that every side chain forms a separate globule \( P(N_{cl})=1 \) for \( N_{cl}/M=1 \), which occurs for \( \sigma=0.035 \) in all three cases of Fig. 1, and that there are no separate clusters but all chains belong to a single cluster \( P(N_{cl})=1 \) for \( N_{cl}/M=1/M \), which occurs for \( \sigma \approx 0.76 \) if \( N \geq 35 \) in Fig. 2. For clarity, these extreme cases are not included in Fig. 2. When one studies these distribution functions \( P(N_{cl}) \) at somewhat higher temperatures, e.g., for \( T=2.0 \), one finds a very similar picture: the main difference to \( T=1.5 \) is that the peaks at intermediate values of \( \sigma \) are somewhat broader and correspondingly lower.

For intermediate grafting densities one sees that \( P(N_{cl}) \) exhibits rather broad peaks at intermediate values of \( N_{cl}/M \). It is interesting to note that the widths of these peaks are almost independent of side chain lengths \( N \). Thus we shall consider observables \( \bar{A}(N_{cl}) \) both for the value \( N_{cl}^{\text{max}} \) where \( P(N_{cl}) \) has its maximum, as well as averages

\[
\bar{A} = \sum_{N_{cl}} P(N_{cl}) A(N_{cl}).
\]

\[ (20) \]

IV. RESULTS AND DISCUSSION

Figure 3 presents the average number of clusters per chain \( N_{cl}/M \) plotted versus \( \sigma \). One clearly recognizes for small \( \sigma \) the trivial regime where \( N_{cl}/M=1 \) and every chain collapses in a separate cluster. The onset of the pearl-necklace type regime where neighboring chains join to form larger clusters occurs rather abrupt; the grafting density of this onset decreases with increasing chain length, as expected from Eq. (15). Of course, the available range of chain lengths is too small to make a strong statement whether or not the data confirm the prediction that \( \sigma \approx N^{-2/3} \) at this onset. We also observe that the slope of the decrease of \( \bar{N}_{cl} \) after the onset increases strongly with increasing \( N \). In contrast, the transition to the uniform cylindrical structure near \( \sigma=0.5 \) is rather gradual, and a sharp boundary for this transition presumably does not exist at all. On the other hand, when the clusters contain a large number of grafted chains, the finite value of the total number of grafted chains \( M=50 \) and the periodic boundary condition clearly will cause strong finite-size effects. When we compare the behavior with temperature, we see that the curves for \( T=1.5 \) (full symbols in Fig. 3) are in the upper part always to the left of the corresponding curves for \( T=2.0 \); this means that the transition from the trivial structure (separate collapsed single chains) to the non-trivial pearl-necklace structure (with several chains per pearl) shifts to lower grafting density when \( T \) is lowered, as predicted from the scaling theory!

It also is of interest to consider the information on the average number of chains \( \bar{n}_{ch} \) per cluster (Fig. 4). Now the (rounded) transition to the uniform cylindrical structure (where \( \bar{n}_{ch}=M \)) is more clearly seen. When one considers the
root mean square fluctuation \( \langle R_{g,xy}^2 \rangle \), Fig. 4(b), one finds strong fluctuations (of the order of two to six) in the regime \( 0.3 < \sigma < 0.65 \), where the number of chains per cluster \( n_{ch} \) increases. As expected, the structures that form typically are irregular; one does not expect a periodic “arrangement” of pearls of the same size, but rather strong fluctuations in the “size” of the pearls (as measured by \( n_{ch} \)) do occur.

Whereas for short chains (\( N=20 \)) the behavior at somewhat higher temperatures [e.g., \( T=2.0 \), Fig. 4(c)] is very similar to that of the behavior at \( T=1.5 \) [Fig. 4(a)], for longer chains (e.g., \( N=50 \)) the transition to the axially homogeneous state (where all \( M=50 \) chains are contained in a single cluster) is already completed at \( \sigma=0.48 \).

Figures 5 then give an example how these clusters develop as the temperature is lowered. One sees that in between 2.0 < \( T < 3.0 \) the number of chains per cluster \( n_{ch} \) increases and correspondingly the number of clusters \( \bar{n}_{ch} \) normalized by the number of chains \( M \) decreases when the temperature is lowered (a relation \( \bar{n}_{ch} \sim n_{ch} \approx M \) holds only approximately, due to the strong fluctuations in these quantities relative to their averages). While for \( N=20 \) this monotonic variation continues also at lower temperatures, a pronounced maximum occurs in \( n_{ch} \) around \( T=2.0 \) for the large values of \( N \).

Next we discuss the linear dimensions of the pearls, simply by computing the mean square gyration radius components \( \langle R_{g,xy}^2 \rangle \) of the clusters in axial direction, as well as in transverse direction \( \langle R_{g,xy}^2 \rangle \). Figure 6 shows plots of \( \langle R_{g,xy}^2 \rangle \) versus \( \sigma \) at two temperatures. The horizontal part for small \( \sigma \) shows the region where the clusters just contain individual collapsed chains and there clearly cannot be a dependence on \( \sigma \), of course. Then one observes an almost linear increase with \( \sigma \) in the regime of the pearl-necklace structure, and the data where one takes the full average over the cluster size distribution [Eq. (20)] hardly differ at all from those where one uses the data for the maximum of \( P(N_{ch}) \) only. According to Eq. (11) we would predict that \( \langle R_{g,xy}^2 \rangle \approx \sigma^{1/2} \) in the regime of the pearl-necklace structure, however. Thus, it is gratifying to note that with increasing \( N \) the plot of \( \langle R_{g,xy}^2 \rangle \) versus \( \sigma \) in the relevant regime (0.1 < \( \sigma \) < 0.6) gradually acquires more and more curvature. We interpret this observation in terms of the fact that Eq. (11) can only hold asymptotically in the scaling regime, which clearly cannot be fully reached for the short values of \( N \) that are accessible in our simulations (or in corresponding experiments). It also is interesting to note that at \( T=2.0 \) for large \( \sigma \) and small \( N \) the average values of \( \langle R_{g,xy}^2 \rangle \) decrease again with increasing \( \sigma \), while the values for the maximum of \( P(N_{ch}) \) monotonically increase with \( \sigma \). This does not happen for \( T=1.5 \), however.

The most interesting quantity is the mean square gyration radius \( \langle R_{g,xy}^2 \rangle \) of the clusters, Fig. 7, which we wish to compare to the prediction for the linear dimension \( L \) [Eq. (9)]. The scaling theory in fact predicts that at the onset of the pearl-necklace structure \( \langle R_{g,xy}^2 \rangle \) should exhibit a jump from a small value [of order \( \sigma \sigma^{1/2-2/3} N^{2/3} \) cf. Eq. (2), corresponding to the single collapsed chain] to a much larger
value, namely, of order \( h^2 = \sigma^2 N^{4/3} a^2 \), i.e., increase discontinuously by a factor \( N^{4/3} N^{2/3} \), and with increasing \( \sigma \) (decreasing \( h \)) it should decrease proportional to \( \sigma^{-1/2} \). Of course, for finite chain length the sharp discontinuous transition at the phase boundary \( \tau = (h/a)^2 N^{-2} \) between the regime of single collapsed mushrooms and clusters containing many stretched chains in one pearl of the pearl-necklace structure must be strongly rounded. Due to this rounding, we are not able to see a maximum in \( \langle R^2 \rangle \) after the onset of the pearl-necklace structure at all; rather we see a rapid increase (for \( N=35,50 \)) at small \( \sigma \) (and \( T=1.5 \)), followed by an almost flat region. This flattening is not at all seen for \( N=20 \) and it also is not at all seen for \( T=2.0 \), where rather a broad maximum is reached for \( 0.4 \leq \sigma \leq 0.6 \), which is the region where the axially homogeneous phase starts to take over. These results clearly show that much longer chains (and possibly also temperatures further away from the theta temperature) would be required for a fully convincing test of the scaling theory of Ref. \( 10 \), as it was exposed in Sec. II. However, we emphasize again that our range of side chain lengths does correspond to the range that is achieved in experiment, and furthermore at lower temperatures the collapsed chains would exhibit a glasslike freezing, and then a discussion in terms of equilibrium concepts would be premature.

Of course, it is also of interest to contrast the linear dimensions of the clusters with those of the individual side chains (Figs. 8 and 9). In the regime of very small \( \sigma \), where the clusters contain a single collapsed chain only, the data of Figs. 8 and 9 must agree with the corresponding data of Figs. 6 and 7, of course, and this is readily verified. In the regime of the pearl-necklace structure, where several side chains cluster together in a single pearl, we find that the transverse mean square gyration radii of the clusters typically are about a factor of 2 larger than those of individual chains, which shows that in the transverse direction the clustering of the chains has only a modest effect, as expected. In the longitudinal components (Fig. 9) we see a much more pronounced difference between the behavior of clusters and single chains, however. In the regime where the onset of the clustering occurs \( \langle R^2 \rangle \) for single chain steeply rises to a plateau which is reached at about \( \sigma \approx 0.2 \), while \( \langle R^2 \rangle \) for the clusters continues to grow. While for \( \sigma \approx 0.2 \), we find \( \langle R^2 \rangle \) for clusters to be about twice the value for single chains, the behavior differs dramatically in the region \( \sigma \approx 0.5 \), where the

FIG. 7. Longitudinal mean square gyration radii \( \langle R^2 \rangle \) of the clusters (pearls) for \( T=1.5 \) (a) and \( T=2.0 \) (b) plotted vs grafting density. Two chain lengths \( N=20 \) and 50 are included, as indicated. Full symbols denote properties averaged over the full distribution [Eq. (20)], while open symbols denote the corresponding properties taken for these values of \( N \), only where \( P(N) \) has its maximum values. Note the logarithmic scale of the ordinate in parts (a) and (b) of this figure. Part (c) gives a plot of the ratio \( \langle R^2 \rangle / \langle R^2 \rangle \) vs \( \sigma \) for \( T=1.5 \).

FIG. 8. Transverse mean square gyration radii \( \langle R^2 \rangle \) of individual side chains for \( T=1.5 \) (a) and \( T=2.0 \) (b) plotted vs grafting density. Three chain lengths \( N=20, 35, \) and 50 are included, as indicated.
transition to the axially homogeneous state occurs (where all 50 chains form a single cylindrical cluster, connected into itself through the periodic boundary condition in the $z$ direction). While for single chains $\langle R^2_{g,z}\rangle$ decreases then to a value that is of the same order as $\langle R^2_{g,xy}\rangle$, since there is no longer any reason for the chains to stretch in axial direction, for the clusters very large values ($100 \leq \langle R^2_{g,z}\rangle \leq 1000$) are reached, which simply reflect the finite-size effect due to the finite length of the cylinder, $L=M/\sigma$ (with $M=50$ chains). Assuming a homogeneous density distribution along the $z$-axis and a single cluster, one would obtain $\langle R^2_{g,z}\rangle = (2/L)\int_0^{L/2} z^2 dz = (L/2)^2/3$, and such estimates are consistent with the values seen in Fig. 7(a) for $\sigma > 0.55$, where one uses the data where $P(N_c)$ takes its maximum.

Finally Fig. 10 focuses on the temperature dependence of the mean square cluster radii for $\sigma = 0.38$, i.e., a grafting density where at low temperatures we are in the center of the nontrivial pearl-necklace regime. Note that $\langle R^2_{g,xy}\rangle$ decreases monotonically with decreasing temperature. In contrast, $\langle R^2_{g,z}\rangle$ increases with decreasing temperature, due to the tendency of the chains to join together via stretching in axial direction, such that several chains form a single cluster. This information is consistent with the corresponding decrease in the number of clusters [Fig. 5(a)], demonstrating once more the internal consistency of our analysis.

V. CONCLUSIONS

In the present paper we have presented a detailed simulation study of the pearl-necklace structure that occurs for bottle-brush polymers with rigid backbones and moderately high grafting densities at poor solvent conditions. Particular emphasis has been put to consider the prediction of Sheiko $et$ $al.$,$^{10}$ who suggested that a transition should occur from isolated globules, each containing one collapsed mushroom only, to elongated clusters (with linear dimension $L$ in axial and $R$ in perpendicular direction, with $L/R \gg 1$ at the transition). While the linear dimension of an isolated globule containing a single mushroom is of order $R_c/a = \tau^{-1/3} N^{1/3}$, where $\tau = 1 - T/\Theta$, $T$ is the reduced temperature distance from the theta temperature, the linear dimension $L$ at the transition in the scaling limit is much larger, namely, $L/a = N^{2/3} \rho^{1/3}$, i.e., $L/R_c = N^{1/3} \rho^{2/3} = Z^{2/3} \gg 1$, if the scaling variable $Z = N^{1/2} \tau \gg 1$, which is the limit of interest. Note that rescaling $L$ and $R$ by the ideal (theta point) dimension of a chain ($R_\theta = a N^{1/2}$) we obtain a picture where the $N$-dependence can be absorbed completely (Fig. 11) in the scaling variables $X = N^{1/2} (a/h)$ and $Z$. The transition of the axial linear dimension from the size of an individual collapsed mushroom, $R_c/a N^{1/2} = Z^{-3}$ to the size $Z^{2/3}$ for $X = Z^{-1/3}$ is discontinuous, in the limit where $N \to \infty$, $\tau \to 0$, and $\sigma \to 0$, such that the scaling variables $X,Z$ stay finite and nonzero. In contrast, the perpendicular linear dimension of the cluster is continuous at the transition, $R = R_c$ at $X = Z^{-1/3}$. While the scaling theory predicts that $L/a N^{1/2}$ decreases monotonously with increasing $X$ and $R/a N^{1/2}$ increases monotonously, until $L/a N^{1/2} = R N^{1/2} = 1$ for $X = Z$, where another discontinuous transition from the pearl-necklace chain (many clusters, all have about the same size) to the uniform cylindrical structure (i.e., a
single cluster) is predicted, the simulations show a qualitatively different behavior (dashed-dotted curve in Fig. 11). When the transition from the single collapsed globule structure to the pearl-necklace structure occurs, $L$ rises rapidly and then flattens off, until another smooth gradual rise of $L$ occurs, signifying the transition from many clusters to few clusters and finally a single cluster. The transition from the state with many clusters to one single cluster (to which then all chains belong) rather has the character of a percolation phenomenon in one space dimension; neighboring elongated clusters with increasing grafting density can join to form still more elongated objects.

In view of this qualitative discrepancy between the scaling theory and our numerical data, we have not attempted to construct any scaling function from our data. Obviously, either one would need to reconsider the scaling assumptions or much longer chains need to be simulated in order to reach the scaling limit. The latter task not only would be computationally not at all feasible, but it also is rather irrelevant for the understanding of experimental systems. The length of side chains in experiments would nicely match the range of suitable bottle-brush molecules corresponding to our study. Also, the development of theoretical methods suitable for the study of such nonasymptotic behavior in polymers would seem very desirable.

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11. A brief account of some preliminary results has been published as a letter, P. E. Theodorakis, W. Paul and K. Binder, EPL 88, 63002 (2009).