

# Understanding the Multiple Length Scales Describing the Structure of Bottle-brush Polymers by Monte Carlo Simulation Methods

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Bottle-brush polymers contain a long flexible macromolecule as a backbone to which flexible side chains are grafted. Through the choice of the grafting density and the length of the side chains the local stiffness of this cylindrical molecular brush can be controlled, but a quantitative understanding of these phenomena is lacking. Monte Carlo simulation results are presented and discussed which address this issue, extracting mesoscopic length scales (such as the cross-sectional radius, persistence length, and contour length of these objects). Large-scale

simulations of the bond fluctuation model are combined with simulations of the simple selfavoiding walk (SAW) model with flexibility controlled by a bond-angle potential, using the pruned-enriched Rosenbluth algorithm. It is shown that under good solvent conditions the bottle-brush polymers never display a pre-asymptotic Gaussian regime that would be described by the Kratky–Porod worm-like chain model, unlike the semiflexible SAW model. Implications of these results for the proper interpretation of experiments are discussed.



#### Introduction and Overview

Macromolecules with comb-like chemical architecture, where linear side chains are grafted to a backbone polymer chain have recently found a lot of interest (see reviews<sup>[1-4]</sup>

H.-P. Hsu, K. Binder Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany Fax: (+49) 6131 39 25441; E-mail: hsu@uni-mainz.de, kurt.binder@uni-mainz.de W. Paul Theoretische Physik, Martin Luther-Universität Halle-Wittenberg, von Seckendorff Platz 1, 06120 Halle, Germany E-mail: wolfgang.paul@physik.uni-halle.de and references therein). Due to the interplay of steric repulsion between the monomers of the densely grafted side chains with effective attractive interactions that can be controlled e.g., by solvent quality, intricate spatial self-organization of these molecular brushes becomes possible. With increasing chain length N of the side chains and increasing grafting density already in good solvent conditions a stiffening of an intrinsically flexible backbone can be induced. Since the global conformations of the complex macromolecules are rather sensitive to various external stimuli, various applications have been envisaged (sensors, actuators, building blocks in supramolecular assemblies, etc.<sup>[3,5,6]</sup>). Also in a biological context biopolymers with bottle-brush architecture occur in a variety of

contexts.<sup>[7]</sup> For example, aggrecane molecules that occur in the soft layers of mammalian joints are thought to contribute to the excellent lubricating function of these layers.<sup>[8]</sup> Similar structures occur in neurofilaments.<sup>[9]</sup>

For designing such molecules for possible applications, or for understanding the function of bottle-brush polymers in a biological context, the relation between the properties characterizing the chemical architecture (chemical nature of the backbone and its chain length  $N_h$ ; grafting density  $\sigma$ of the side chains, their chemical nature and their chain length N) and the geometrical structure needs to be understood. This turns out to be a difficult problem, since the conformation of these bottle-brush polymers is characterized by a multitude of length scales. Sometimes one relies on atomic force microscopy observations of bottle-brush polymers adsorbed on substrates, e.g., mica,<sup>[10]</sup> but there is clear simulation evidence<sup>[11]</sup> that the configurational properties of adsorbed (quasi-two-dimensional) bottle-brush polymers differ very much from their (threedimensional) counterparts in dilute solution. This difference is no surprise, of course, since a linear flexible macromolecule with a chain length  $N_b$  (we denote by "chain length" the number of effective subunits of the polymer throughout this paper) exhibits a scaling of its (gyration) radius  $R_g \propto N_b^{\nu}$  where<sup>[12]</sup>  $\nu \approx 0.588$  in d=3dimensions while v = 3/4 for d = 2, in good solvent conditions. Thus, most conclusions about the structure of bottle-brush polymers result from the analysis of small angle neutron scattering (often combined with light scattering) from bottle-brush polymers in solution, e.g., ref.<sup>[13-21]</sup> Such an analysis is difficult for a variety of reasons: (i) in order to have enough scattering intensity, one often does not work in extremely dilute solution, but under conditions where the bottle-brush polymers overlap.<sup>[18,21]</sup> As expected from the behavior of ordinary linear polymers,<sup>[12,22–25]</sup> in semidilute solutions the chain conformations differ substantially from those under very dilute conditions. As is well-known, a description of the concentration dependence is subtle,<sup>[22-25]</sup> simplistic theories like the random phase approximation (RPA)<sup>[12]</sup> cannot be quantitatively relied upon.<sup>[22,23,25]</sup> Thus, the extrapolation of the excess scattering due to the polymers to small volume fraction is difficult. (ii) Real polymers never are strictly monodisperse. For bottle-brush polymers, corrections due to the polydispersity of both the backbone chain and the side chains may be necessary. (iii) The scattering background intensity must be properly subtracted. (iv) While the mean square gyration radius  $\langle R_a^2 \rangle$  of the bottle-brush polymer as a whole can be extracted independent from model assumptions from the behavior at small scattering wave number, q, from a Taylor expansion of the total structure factor  $S(q) = S(0)[1-q^2\langle R_q^2 \rangle/3 + \cdots]$ , all other mesoscopic length scales of interest (Figure 1) such as the cross-sectional radius  $R_{cs}$ , the contour length  $L_{cc}$  and the



Figure 1. Schematic explanation of the multiple length scales for molecular bottle-brush polymers. A coarse-grained continuum description depicts the polymer as a flexible sphero-cylinder with a cross-sectional radius  $R_{cs}$  and a contour length  $L_{cc}$  along the axis of the coarse-grained cylinder. Over a length scale  $\ell_p$ , the persistence length, the cylinder is straight, while over larger length scales it bends. The monomer density distribution in the cylinder is assumed to be uniform. A less coarse-grained view (lower part of the figure) depicts the backbone of the bottle-brush polymer as an SAW of  $N_b$  effective monomeric units connected by effective bonds  $\ell_b$ . Side chains of chain length N (with bond vectors  $\ell_s$ ) are grafted at the effective monomers of the backbone with grafting density  $\sigma$ . Characteristic lengths of interest are the end-to-end distances and gyration radii of both side chains ( $\sqrt{\langle R_e^2 \rangle}$ ,  $\sqrt{\langle R_g^2 \rangle}$ ) and of the backbone ( $\sqrt{\langle R_{e,bb}^2 \rangle}$ ,  $\sqrt{\langle R_{e,bb}^2 \rangle}$ ), respectively.

persistence length  $\ell_p$  can only be extracted via an intricate fitting procedure to a complicated model.<sup>[14–18,21]</sup> This model<sup>[26]</sup> relies on approximations which have been shown to be somewhat inaccurate.<sup>[27]</sup>

In view of all these caveats, it is no surprise that serious disagreements between the findings of various experimental groups on the properties of chemically very similar bottle-brush polymers occur.<sup>[14–16]</sup> Even if one accepts a description in terms of a coarse-grained continuum picture as sketched in Figure 1, the question must be asked what is the quantitative relation between the lengths  $\ell_p$  and  $L_{cc}$  and the chain lengths N,  $N_b$ , and the grafting density  $\sigma$ .







Figure 2. (a) Snapshot of a typical conformation of a simulated bottle-brush polymer [using backbone chain length  $N_b = 1$  027, side chain length N = 24, in the framework of the bond fluctuation model, see The Semiflexible Self-avoiding Walk (SAW) Model section], and three possible corresponding coarse-grained models, a model of freely jointed rods of Kuhn step length  $\ell_k$  and diameter d (b), an SAW model on the simple cubic lattice where 90° bends cost an energy  $\varepsilon_b \gg k_B T$ , so the chain consists of straight pieces of  $n_{\rm str} \gg 1$  steps (c), and a model of tangent hard spheres with radius  $R_{\rm cs}$  (d).

Actually, two scenarios are conceivable (Figure 2): if the coarse-grained length scales satisfy the inequality  $\ell_p \gg R_{cs}$ , the coarse-grained bottle-brush polymer can be described by the Kratky–Porod<sup>[28]</sup> worm-like chain (WLC) model. It can be described by a Hamiltonian<sup>[29,30]</sup>

$$\mathcal{H} = \frac{\kappa}{2} \int_{0}^{L_{cc}} dt \left(\frac{d^2 \vec{r}(t)}{dt^2}\right)^2 \tag{1}$$

where the curve  $\vec{r}(t)$  describes the contour of length  $L_{cc}$ , and the parameter  $\kappa = \ell_p k_{\rm B} T$  describes the bending stiffness. Here, *t* is a coordinate along the (curved) contour of the coarse-grained polymer in Figure 1. Equation (1) neglects excluded volume completely; Pedersen and Schurtenberger<sup>[26]</sup> consider a discrete version of Equation (1) numerically, where cylinders of diameter  $d = 2R_{cs}$  and a Kuhn step length  $\ell_K = 2\ell_p$  are freely jointed [Figure 2(b)], assuming  $\ell_K = 5d$ , and respecting excluded volume. As will be discussed below, this model is equivalent to the original Kratky–Porod model only for not too large  $N_b$  (and  $L_{cc}$ ). The same statement applies to a lattice variant of the Kratky–Porod model with excluded

volume, that will be studied in the present paper, the self-avoiding walk (SAW) on the simple cubic lattice with an energy penalty  $\varepsilon_b/k_{\rm B}T \gg 1$  for 90° bends to the chain [Figure 2(c)]. However, if in the Pedersen–Schurtenberger model<sup>[26]</sup> one would choose  $\ell_K$  and d of the same order, or in the SAW model  $\varepsilon_b$  is of the same order as the thermal energy  $k_{\rm B}T$ even for small  $N_h$  the Kratky–Porod model<sup>[28]</sup> is not a reasonable approximation, as will be shown in the present paper: rather the polymer conformation then resembles a chain of freely jointed spheres of radius  $R_{cs}$  [Figure 2(d)]. Other variants of the Kratky-Porod model, such as the "discrete chain model,"[31] which are used in the context of the stretching response of semiflexible polymers,<sup>[32-40]</sup> are essentially equivalent to the model of jointed cylinders [Figure 2(b)].

Another questionable approximation implicitly inherent in the coarse-grained picture of Figure 1 is that the monomer density inside the effective cylinder stays approximately constant up to the radius  $R_{cs}$  and is zero outside ( $r > R_{cs}$ , see insert of Figure 3). The actual monomer density profile, as it results from simulations of model polymer brushes<sup>[27,41–44]</sup>, differs

very much from a constant (Figure 3), and also the popular assumption<sup>[14]</sup> of a Gaussian density profile,  $\rho_{\rm cs}(r) \propto \exp\left(-r^2/R_{\rm cs}^2\right)$  provides a good fit of the simulation only for  $r \geq 3$  nm, but not close to the backbone. It is clear that a constant density profile  $\rho_{\rm cs}(r)$  may be appropriate for the description of cylindrical micelles, or for bottle-brush polymers in poor solvent conditions, but both the experiments<sup>[13–21]</sup> with which we are concerned here, and the simulations<sup>[27,41–57]</sup> all deal with good solvent conditions, for which excluded volume effects must be considered.<sup>[22,23]</sup>

Experiments<sup>[13–21]</sup> indeed indicate that the length scales of the coarse-grained description (Figure 1) are difficult to understand. For example, Zhang et al.<sup>[16]</sup> present a comparative discussion of the dependence of both  $R_{cs}$ and the Kuhn length  $\ell_K$  (taking the relation  $\ell_K = 2\ell_p$  for granted, as usually done<sup>[58,59]</sup>) on side chain length, for bottle-brush polymers composed from polymethylmethacrylate as a backbone chain and polystyrene side chains. Taking work from several groups in good solvents (cyclohexane, toluene) they report<sup>[16]</sup> exponents  $\nu_{eff}$  in the relation  $R_{cs} \propto N^{\nu_{eff}}$  in the range from 0.56  $\leq \nu_{eff} \leq 0.67$ (we use here the notation  $\nu_{eff}$  instead of the standard







*Figure 3*. Radial density distribution of the monomers  $\rho_{cs}(r)$  in the direction perpendicular to the cylinder axis, for a simulated bottle-brush polymer [using the bond fluctuation model, see The Semiflexible Self-avoiding Walk (SAW) Model section] with a backbone chain of length  $N_b = 259$ , grafting density  $\sigma = 1$ , and side chains of length N = 48 (circles connected by a dotted curve) compared to a Gaussian which results from a fit to an experimental system.<sup>[14,41]</sup> Note that  $R_{cs}$  according to this fit is 6.3 nm while the corresponding value of the simulation (defined from  $R_{cs}^2 = 2\pi \int_0^\infty r^3 dr \rho_{cs}(r)$  with  $2\pi \int_0^\infty r dr \rho_{cs}(r) \equiv 1$ ) is 5 nm. In this comparison, a conversion of lengths from the simulation to the experiment was done requiring that 1 nm = 3.79 lattice spacings, since then a very good agreement between the experimental  $^{[14]}$  and simulated  $^{[41]}$  structure factor is obtained, without any adjustable parameters whatsoever (Figure 4). The insert shows another popular assumption for  $\rho_{cs}(r)$ , namely  $\rho_{cs}(r) = \text{const.}$  for  $o < r < R_{cs}$  and zero else.

notation v for the Flory exponent<sup>[12,22,23,59,60]</sup> since the data refer to a fit in the range 6  $\leq$  N  $\leq$  33). While e.g., for side chain molecular weight  $M_n^{sc} = 3.5. \times 10^3 \,\mathrm{gmol}^{-1}$  these experiments all yield  $R_{\rm cs} \approx$  3 nm, the corresponding estimates for  $\ell_K$  vary from 20 to 65 nm.<sup>[16]</sup> While some of these experiments indicate a rapid increase of  $\ell_K$  with N, other experiments indicate a slow increase, <sup>[16]</sup> and for the system of Rathgeber et al.<sup>[15]</sup> (analyzed in Figure 3, 4) it was suggested that  $\ell_K = 70 \pm 4 \text{ nm}$  for  $N \ge 22 \text{ independent of } N$ , so that  $\ell_K/R_{cs}$  then is a decreasing function of *N*, contrary to theoretical expectations.<sup>[2,46,61-63]</sup> Also the estimated values for the effective contour length L<sub>cc</sub> of the cylindrical brush (Figure 1) seem to be problematic, and our conclusion is that the experiments are not fully understood. We feel that claims in the literature,<sup>[21]</sup> that bottle-brush polymers can be fully accounted for by the WLC model, "flexible cylinders with a circular cross-section and a uniform scattering length density," are overly optimistic (note that this work<sup>[21]</sup> did neither study the variation of the lengths  $R_{cs}$ ,  $\ell_K$ ,  $L_{cc}$  with side chain length N nor with backbone length  $N_{b}$ , unlike<sup>[15]</sup>).

In view of these problems, we wish to clarify by systematic simulation studies whether bottle-brush polymers with both intrinsically flexible backbone and side





Figure 4. log–log plot of the experimental structure factor  $S^{exp}(q)$  of a bottle-brush (with a polyhydroxyethylmethacrylate) [PMMA] backbone of  $N_b^{exp} = 400$  monomers, poly(*n*-butyl acrylate) [PnBA] side chain containing  $N^{exp} = 62$  monomers, grafting density  $\sigma = 1$ ) versus the wavenumber q scaled with the gyration radius ( $R_g^{exp} = 30.5$  nm) of the total bottle-brush polymer (curve). The corresponding simulation result are shown by circles (as discussed in ref.,<sup>[41]</sup> roughly three chemical monomers in the experiment correspond to two effective monomers of the simulation), with  $N_b = 259$  and N = 48. Since in the simulation  $R_g = 115.8$  lattice spacings, a conversion of lengths units such that 1 nm = 3.79 lattice spacings was chosen. Note that both the simulation and the experiment correspond to good solvent conditions (using in the experiment toluene as a solvent, and strictly repulsive excluded volume interactions in the simulation model).

chains under good solvent conditions (as studied experimentally<sup>[13–21]</sup>) on a coarse-grained scale are described by the WLC model [with relatively small excluded volume, i.e., in its discretized version, Figure 2(b), the length  $\ell_K$  of the cylinders is much larger than the diameter] or by a flexible chain of hard spheres [Figure 2(d)], where the sphere radius is of the same order as the cross-sectional radius  $R_{cs}$ , and  $\ell_K = 2R_{cs}$ , in the case of tangent hard spheres. Of course, if one would choose  $\ell_K$  not much larger than d in the model of freely jointed cylinders [Figure 2(b)], there would no longer be an essential difference to the hard sphere chain [Figure 2(d)], but then the WLC model<sup>[28]</sup> no longer is a valid analytical approximation of the model.

In this paper, two models will be studied: (i) the SAW on the simple cubic lattice<sup>[64]</sup> with an energy parameter  $\varepsilon_b$ associated with 90° turns of the SAW, applying the prunedenriched Rosenbluth method (PERM)<sup>[65–67]</sup> and studying single chains up to  $N_b = 50\ 000$ . This model [Figure 2(c)] is well suited to study the crossover between the SAW and WLC models<sup>[44]</sup> [The Semiflexible Self-avoiding Walk (SAW) Model section]. A brief preliminary account of this work was presented in a Letter.<sup>[44]</sup> (ii) The second model (Scaling Analysis of the Bond Fluctuation Model for Bottle-brush Polymers section) that is studied here is the bond fluctuation model of bottle-brush polymers on the simple





cubic lattice, extending work presented earlier.<sup>[41–44]</sup> We shall show that for this model a regime where the WLC model provides an accurate coarse-grained description does not exist, and hence relations such as  $\ell_K = 2\ell_p$  (which are based on ignoring excluded volume interactions, assuming Gaussian chain statistics<sup>[22,58–60]</sup> cannot be found. We rather show that a model such as a flexible chain of tangent hard spheres [Figure 2(d)] is a more appropriate coarse-grained description of such bottle-brush polymers. In this context, we then discuss in which way one can extract a meaningful estimate of the persistence length  $\ell_p$  for bottle-brush polymers, such that it describes their "intrinsic" stiffness, independent of the length  $N_b$  of the backbone. Concluding Remark section summarizes our conclusions.

### The Semiflexible Self-avoiding Walk (SAW) Model

In order to describe local chain stiffness, it is natural to introduce a bond-bending potential, that depends on the angle  $\theta$  between subsequent bond vectors.<sup>[22,58–60]</sup> A simple choice is

$$U_{\text{bend}}(\theta) = \varepsilon_b (1 - \cos\theta). \tag{2}$$

On the simple cubic lattice, the only possible values are  $\theta = 0^{\circ}$  and 90°, of course, and hence  $U_{\text{bend}}(0) = 0$  if the SAW continues straight while  $U_{\text{bend}} = \varepsilon_b$  for  $\theta = 90^{\circ}$ .

However, in order to make contact with the standard theory<sup>[22,58–60]</sup> we remind the reader of a corresponding offlattice model where the angle  $\theta$  is not "quantized" so that for large  $\varepsilon_b$  we expect that the chain typically makes small angles  $\theta$  from one bond to the next one. If one ignores excluded volume, the mean square end-to-end distance then becomes ( $N_b \rightarrow \infty$ ; note  $\langle \cos \theta \rangle \approx 1 - \langle \theta^2 \rangle / 2$ )

$$\langle R_e^2 \rangle = N_b \ell_b^2 \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \approx (4 / \langle \theta^2 \rangle) \ell_b^2 N_b,$$
 (3)

where  $\ell_b$  is the step length. Introducing then the Kuhn step length  $\ell_K$  from a model with *n* steps of an equivalent freely jointed chain,

$$\left\langle R_e^2 \right\rangle = n\ell_K^2, \, n\ell_K = N_b\ell_b \tag{4}$$

immediately yields

$$\ell_K = 4\ell_b / \langle \theta^2 \rangle. \tag{5}$$

On the other hand, the standard definition of a persistence length  $^{[58-60]}\ell_p$  introduces it as the decay length of the orientational correlation of bonds that are s steps



$$\langle \cos\theta(s) \rangle = \exp(-s\ell_b/\ell_p).$$
 (6)

Noting that for Gaussian chains subsequent bond orientations are uncorrelated, hence  $\langle \cos\theta(s) \rangle = \langle \cos\theta \rangle^s = \exp[\sin\langle \cos\theta \rangle] \approx \exp[-s\langle \theta^2 \rangle/2]$ , one finds

$$\ell_p = 2\ell_b / \langle \theta^2 \rangle = \ell_K / 2.$$
 (7a)

and hence

$$\left| R_e^2 \right\rangle = 2\ell_p \ell_b N_b. \tag{7b}$$

These considerations are easily extended to include effects of finite chain length and thus describe the crossover toward the limit of hard rods. For example, introducing the contour length *L* as  $L = N_b \ell_b$ , in the continuum limit (keeping *L* finite,  $\ell_p$  finite, but taking  $N_b \to \infty$  and  $\ell_b \to 0$ ) one finds<sup>[28]</sup>

$$\left\langle R_{e}^{2}\right\rangle = 2\ell_{p}L\left\{1-\frac{\ell_{p}}{L}\left[1-\exp\left(-L/\ell_{p}\right)\right]\right\}.$$
(8)

For  $L \to \infty$  Equation (8) yields the standard Gaussian behavior  $\langle R_e^2 \rangle = 2\ell_p L = \ell_K L = \ell_K \ell_b N_b$  while for  $L \ll \ell_p$  the rod-like behavior occurs,

$$\sqrt{\langle R_e^2 \rangle} = L = \ell_b N_b. \tag{9}$$

Note that in Equation (3)–(9) it makes sense to consider  $N_b$  as the number of bonds rather than the number of monomers (which then is  $N_b + 1$ ) of the chain. An extension of Equation (8) to a discrete WLC (without excluded volume) is<sup>[68]</sup>

$$\left\langle R_{e}^{2}\right\rangle = N_{b}\ell_{b}^{2} \left[\frac{1 + \left\langle\cos\theta\right\rangle}{1 - \left\langle\cos\theta\right\rangle} + \frac{2\left\langle\cos\theta\right\rangle}{N_{b}} \frac{\left\langle\cos\theta\right\rangle^{N_{b}} - 1}{\left(\left\langle\cos\theta\right\rangle - 1\right)^{2}}\right].$$
 (10)

Here  $\langle \cos \theta \rangle = \langle \cos \theta (s = 1) \rangle$ .

However, we stress that real polymer chains never fully behave like Gaussian chains.<sup>[69-74]</sup> Even in dense melts, where Equation (4) still holds asymptotically, Equation (6) fails and one rather encounters a power-law decay of bond orientational correlations<sup>[69-72]</sup>

$$\langle \cos\theta(s) 
angle \propto s^{-3/2}, \quad 1 \ll s \ll N_b.$$
 (11)

The same behavior was found for polymer chains in dilute solution at the  $\theta$  point<sup>[43,74]</sup> (note that there the applicability of the Kuhn length concept is already an approximation, due to the expected logarithmic corrections<sup>[12,22,23]</sup> to the simple power law  $\langle R_e^2 \rangle \propto N_b$  as  $N_b \to \infty$ ).





But Equation (3) and (10) are particularly misleading when one considers polymers under good solvent conditions: since  $\langle R_e^2 \rangle \propto N_b^{2\nu}$  with<sup>[75]</sup>  $\nu \approx 0.588$ , a naive use of  $\langle R_e^2 \rangle = n \ell_K^2$ and  $n = N_b \ell_b / \ell_K$  would require a Kuhn step length  $\ell_K$  that diverges toward infinity as  $\ell_K \propto N_b^{2\nu-1}$  for  $N_b \to \infty$ , which is not a sensible result.

Moreover, Equation (6) fails also, one again encounters a power law decay as well<sup>[76]</sup>

$$(\cos\theta(s))\propto s^{-\beta}, s^* < s \ll N_b; \beta = 2-2\nu = 0.824.$$
 (12)

Here  $s^*$  is of order unity for fully flexible chains, but may be much larger for locally stiff chains [for which Equation (2) holds with  $\varepsilon_b \gg k_{\rm B}T$ , the thermal energy, as discussed below]. For the sake of completeness, we mention that an alternative definition of a "local" persistence length  $\ell_p(k)$ referring to the bond vector  $\vec{a}_k$  connecting monomers at positions  $\vec{r}_k$  and  $\vec{r}_{k-1}(\vec{a}_k = \vec{r}_k - \vec{r}_{k-1})^{[54,58,77]}$ 

$$\ell_p(k) = \ell_b \left\langle \vec{a}_k \cdot \vec{R}_e \middle/ \left| \vec{a}_k \right|^2 \right\rangle \tag{13}$$

is not useful in the case of SAWs either, since<sup>[77]</sup>

$$\ell_p(k) \approx \alpha \ell_b [k(N_b - k)/N_b]^{2\nu - 1}.$$
(14)

As will be discussed below, only the prefactor  $\alpha$  in Equation (14) can be taken as a measure of intrinsic chain stiffness, but not  $\ell_p(k)$  itself, since  $\ell_p(k)$  exhibits a maximum at  $k = N_b/2$  which diverges to infinity proportional to  $N_b^{2\nu-1}$  as  $N_b \to \infty$ .<sup>[43,77]</sup> We recall that this problem is not improved when one considers an average of  $\ell_p(k)$  along the chain,<sup>[58]</sup> while no divergence occurs for<sup>[58]</sup>  $\ell_p(1)$ . However, in simulations the use of  $\ell_p(1)$  is inconvenient, due to the limited statistical accuracy. Note that in the SAW model on the simple cubic lattice we take the lattice spacing as the unit of length and then  $|\vec{a}_k| = \ell_b = 1$ , but for other models (such as the bond-fluctuation model,<sup>[24,78,79]</sup> for instance)  $\ell_b$  may take a different value.

For the SAW model with an energy term as written in Equation (2) the partition function of a walk with  $N_b$  steps and  $N_{\text{bend}}$  90° bends [Figure 2(c)] can be written as

$$Z_{N_b}(q_b) = \sum_{\text{config.}} C_{N_b, N_{\text{bend}}} q_b^{N_{\text{bend}}}$$
(15)

where  $q_b = \exp(-U_{\text{bend}}/k_BT) = \exp(-\varepsilon_b/k_BT)$ . For standard SAW's  $q_b \equiv 1$ , of course. It turns out that the PERM algorithm,<sup>[65–67]</sup> which is a biased chain growth algorithm with resampling, can be applied to the present model for chain lengths up to  $N_b = 50\,000$ . We have explored the range from  $0.005 \leq q_b \leq 1.0$ , covering the full range from very stiff to fully flexible chains.



Figure 5. log–log plot of the rescaled mean square end-to-end distance  $\langle R_e^2 \rangle / (2\ell_b N_b^{2\nu})$  versus  $N_b$ , for chain lengths  $N_b$  up to  $N_b = 50000$ , and many values of the stiffness parameter  $q_b$ , as indicated. The straight line with slope  $2-2\nu$  (for small  $N_b$ ) indicates the limiting slope reached for hard rods, while the slope  $1-2\nu$  (for intermediate values of  $N_b$ ) indicates the behavior expected for Gaussian chains. Solid horizontal plateaus show estimates for  $\ell_{p,R}(q_b)$ , as estimated below (using Figure 11). Adapted from Hsu et al.<sup>[44]</sup>

Since in ref.<sup>[41]</sup> it was suggested that a simple generalization of Equation (7b) to the excluded volume case is

$$\left\langle R_e^2 \right\rangle = 2\ell_{p,R}\ell_b N_b^{2\nu},\tag{16}$$

we plot in Figure 5  $\langle R_e^2 \rangle / (2\ell_b N_b^{2\nu})$  versus  $N_b$ : if for large  $N_b$  a constant plateau is reached, we can estimate the constant  $\ell_{p,R}$  from this plateau value.

We see chains that for not so stiff  $(q_b \gtrsim 0.4, \text{ e.g.}, (\cos\theta) \lesssim 0.413)$ the approach of  $\langle R_e^2 \rangle / (2\ell_b N_h^{2\nu})$  is monotonic, while for stiffer chains  $(q_b < 0.4)$  this ratio develops a maximum, and this maximum shifts to larger and larger chain length as  $q_b$ decreases (and hence the chain stiffness increases). It is clearly seen that for  $q_b \lesssim 0.05$  there is a regime of short chains where the end-to-end distance indeed exhibits rod-like behavior,  $\langle R_e^2 \rangle = \ell_h^2 N_h^2$  and therefore  $\langle R_e^2 \rangle / (2\ell_b N_b^{2\nu}) = (\ell_b/2) N_b^{2-2\nu}$ . Before the data settle down to the asymptotic plateau value described by Equation (16), the data in Figure 5 decreases after the maximum again; and for very small  $q_b$  (such as  $q_b = 0.01$ ) this decrease is consistent with Gaussian behavior of the chains.

A convenient characterization of chain stiffness of the present model is obtained from the distribution  $P(n_{str})$ , Figure 6, where we simply count (using the data for  $N_b = 50\,000$  only, to avoid effects due to the chain ends) how often sequences of  $n_{str}$  bonds without chain bending occur in the chain conformation [see Figure 2(c)]. The straight line fits included in Figure 6 suggest that irrespective of chain stiffness the distribution always is compatible with a







Figure 6. Semi-log plot of the distribution  $P(n_{str})$  versus  $n_{str}$ , for  $q_b$  in the range from  $q_b = 0.1$  to 1.0, i.e., including rather flexible chains (a) and for rather stiff chains  $0.005 \le q_b \le 0.05$  (b). The straight lines indicate fits to simple exponential functions,  $P(n_{str}) = a_p \exp(-n_{str}/n_p)$ . The constants  $a_p$  and  $n_p$  are quoted in Table 1. All data are taken for  $N_b = 50$  000. Adapted from Hsu et al.<sup>[44]</sup>

simple exponential, for large enough  $n_{\rm str}$ 

$$P(n_{\rm str}) = a_p \exp(-n_{\rm str}/n_p). \tag{17}$$

Table 1 lists the constants  $a_p$ ,  $n_p$  and the first moment  $\langle n_{\text{str}} \rangle$  of this distribution as function of  $q_b$ . Note that the length  $\ell_b \langle n_{\text{str}} \rangle$  (with  $\ell_b = 1$  in our model) could be taken as a possible definition of a persistence length characterizing the intrinsic chain stiffness of the model. Of course, only for  $q_b \leq 0.05$  this length is much larger than the bond length, and for  $q_b \rightarrow 0$  the difference between  $\langle n_{\text{str}} \rangle$  and the decay length  $n_p$  disappears.

While the quantities  $n_p$ ,  $\langle n_{str} \rangle$  are well-defined for all values of  $q_b$ , this is not the case for the standard definition of the persistence length  $\ell_p$ , as the decay length of orientational correlations, Equation (6), as Figure 7 shows: in no case one can rely on Equation (6) for the asymptotic decay  $s \rightarrow \infty$  (of course, always  $N_b \gg s$  has to be considered). Equation (6) can be used to describe only the initial decay of  $\langle \cos\theta(s) \rangle$  with s and not the final decay, which always is



*Table 1.* Values of the persistence length  $\ell_p$ , and the constants  $a_p$ ,  $n_p$ , and the first moment  $\langle n_{\rm str} \rangle$  obtained through the curve fitting using Equation (6) and (17), respectively, for semiflexible chains with various values of  $q_b$ .

$q_b$	0.005	0.01	0.02	0.03	0.05	0.10	0.20	0.40	1.0
$\ell_p$	52.61	26.87	13.93	9.54	5.96	3.35	2.05	-	-
$a_p$	0.02	0.04	0.08	0.12	0.19	0.38	0.73	1.42	3.37
$n_p$	51.17	25.95	13.30	9.07	5.68	3.12	1.82	1.13	0.68
$\langle n_{ m str}  angle$	51.72	26.50	13.83	9.60	6.20	3.65	2.36	1.70	1.29



Figure 7. Semi-log plot of  $\langle \cos\theta(s) \rangle$  versus the contour length  $s\ell_b$ , for  $q_b$  in the range from  $q_b = 0.1$  to 1.0 (a) and for rather stiff chains,  $0.005 \le q_b \le 0.05$  (b). All data are taken for  $N_b = 50$  000, and the straight lines indicate fits to Equation (6). The constants  $\ell_p(q_b)$  are also included in Table 1. For rather flexible chains ( $q_b = 1.0$  and 0.4) meaningful fits are not possible. Adapted from Hsu et al.<sup>[44]</sup>

described by the power law, Equation (12), see also Figure 8(a). While for  $q_b = 1.0$  the data rapidly approach the asymptotic power law and also for small *s* the deviations from the power law are rather small and hence it is clear that no region where the exponential law, Equation (6), applies, for  $q_b = 0.1$  (and smaller) the power law only is valid for  $s\ell_b \geq 30$  (or larger), as expected from







Figure 8. (a) log–log plot of  $\langle \cos\theta(s) \rangle$  versus  $s\ell_b$ , for  $q_b = 0.05$ , 0.1, 0.2, 0.4, and 1.0, including only data for  $N_b = 50$  000. The straight line indicates a fit of the power law, Equation (12), to the data for  $q_b = 1.0$ , including only data for  $s\ell_b \ge 10$  in the fit, and requesting the theoretical exponent,  $\beta = 2 - 2\nu = 0.824$ . (b) Local persistence length  $\ell_p(k)$  plotted versus  $k/N_b$ , for  $q_b = 1.0$  (i.e., the standard SAW model), including chain lengths  $N_b = 400-6400$ , as indicated. Curves show fits to Equation (14), with a resulting prefactor  $\alpha = 1.6888$ .

Figure 8(a), since for  $q_b = 0.1$  the exponential decay is a good description for  $s\ell_b < 10$ . Of course, the crossover from the exponential law at small *s* to the power law at larger *s* is rather gradual and in the crossover regime  $(10 \le s\ell_b < 30 \text{ for } q_b = 0.1)$  neither of these laws is accurate.

Qualitatively, the behavior for all smaller values of  $q_b$  is similar [Figure 7(b)]: the exponential decay for  $q_b \leq 0.05$  extends to about  $\langle \cos\theta(s) \rangle \approx 0.05$ , and then a slow crossover to the power law sets in, which is reached when  $\langle \cos\theta(s) \rangle$  has decayed further to about  $\langle \cos\theta(s) \rangle \approx 0.01$ . Since the decay length  $\ell_p$  increases strongly with decreasing  $q_b$ , the range (in the variable  $s\ell_b$ ) over which the exponential decay holds gets larger with decreasing  $q_b$ , of course. However, one must be aware of the condition that s should be at least an order of magnitude smaller than  $N_b$ , otherwise the decay of  $\langle \cos\theta(s) \rangle$  is affected by effects due to the finiteness of the chain length, as demonstrated in our earlier work.<sup>[43]</sup> Thus, one has to be



Figure 9. log–log plot of several estimates for the persistence length  $\ell_p$  versus  $q_b$ . Straight line indicates the asymptotic behavior  $\ell_p \propto q_b^{-1}$ .

very careful with the analysis of the decay of  $\langle \cos\theta(s) \rangle$  to avoid misleading conclusions. For very small  $q_b$  ( $q_b \leq 0.05$ ) the results for  $\ell_p$  from the exponential fits (Table 1) agree roughly with the length  $\langle n_{str} \rangle$ ; for  $q_b = 0.4$  and 1.0 estimates for  $\ell_p$  are not quoted, however, since Figure 7(a) implies that there is no significant range of exponential decay. Also the use of  $\ell_p(k)$  does not help, since the result strongly depends on  $N_b$ , as Figure 8(b) demonstrates, and as is expected from Equation (14). For semiflexible chains, we expect that also  $\ell_p(k)$  will be strongly affected by crossover effects between the various regimes (rod-like versus Gaussian behavior versus excluded volume effects), but these phenomena are left for future studies.

Figure 9 summarizes our results for the standard persistence length  $\ell_p$  and the alternative estimates  $\langle n_{\rm str} \rangle$  and  $n_p$ . It is seen that for  $q_b \ge 0.1$  different methods of estimation give somewhat different answers, and also we do not have the condition  $\ell_p \gg \ell_b$  fulfilled. For  $q_b \le 0.05$  the results based on  $P(n_{\rm str})$  and on  $\langle \cos\theta(s) \rangle$  agree, and furthermore we have the simple relation that  $\ell_p = {\rm const.}/q_b$ .

Thus, it is of interest to what extent Equation (8) or (10) provide accurate descriptions of the data (Figure 10). Since  $L = \ell_b N_b$  holds, and both  $\ell_p$  and  $\langle \cos\theta \rangle$  have been accurately estimated (Table 1), this comparison does not involve any adjustable parameter whatsoever. Indeed, we see that Equation (8 and 10) agree almost perfectly with each other, indicating that the discreteness of our lattice model is irrelevant with respect to our conclusions to what extent the Kratky–Porod WLC model is a valid description of semiflexible polymers under good solvent conditions. Indeed, one can see that this model for small  $q_b \leq 0.1$  describes rather accurately the initial rod-like behavior (where the ratio  $\langle R_e^2 \rangle / N_b$  increases almost linearly), and for still smaller  $q_b (\leq 0.03)$  also the onset of the Gaussian plateau is nicely reproduced. However, in all cases for large







Figure 10. Plot of  $\langle R_e^2 \rangle / (2\ell_b N_b)$  versus  $N_b$ , on linear–linear scales, for  $N_b < 40$  and for  $0.005 \le q_b \le 0.1$  (a) and on log–log scales, up to  $N_b = 50000$  (b), using the data for  $0.005 \le q_b \le 0.2$ . Solid and dotted curves are the predictions of the Kratky–Porod model, Equation (8 and 10), respectively, using the observed results for  $\ell_p$  or  $\langle \cos\theta \rangle$ , respectively [note that on the chosen scales differences between Equation (8 and 10) are almost invisible.] Vertical arrows show our estimates for  $N_b^*$  (see Figure 11 below). Adapted from Hsu et al.<sup>[44]</sup>

enough  $N_b$  systematic deviations due to excluded volume effects occur. While for  $q_b = 0.005$  these deviations are relatively small and occur for extremely long chains only, so the Gaussian plateau extends over more than a decade in  $N_b$ , for  $q_b = 0.05$  the data rise upward from the Gaussian plateau already near  $N_b = 1\,000$ , excluded volume effects clearly being important.

In order to describe the crossover from the Gaussian behavior applicable to semiflexible chains at intermediate values of the chain length to the swollen coil behavior due to excluded volume interactions, we plot in Figure 11  $\langle R_e^2 \rangle / (2\ell_b\ell_p(q_b)N_b)$  versus  $N_b$  and  $N_b/N_b^*(q_b)$ . Here, this crossover chain length  $N_b^*(q_b)$  was found empirically by requiring an optimal fit of the family of curves [Figure 11(a)] on a master curve.

Of course, the scaling shown in Figure 11 is motivated by theoretical arguments, based on a Flory-like treatment.<sup>[80,81]</sup> When we consider a model such as shown in Figure 2(b) where rods of length  $\ell_K$  and diameter *d* are jointed such that the contour length  $L = N_b \ell_b = n \ell_K$ , one can argue that the





Figure 11. log-log plot of  $\langle R_e^2 \rangle / (2\ell_b \ell_p(q_b)N_b)$  versus  $N_b$  (a) and  $N_b/N_b^*(q_b)$  (b), for 0.005  $\leq q_b \leq$  0.2. Here,  $N_b^*(q_b)$  was chosen in order to obtain an optimal fit on a single master curve.

second virial coefficient is proportional to  $v_2 = \ell_K^2 d$  (any prefactors of order unity will be ignored here throughout). Then, the free energy of a chain contains two terms, the elastic energy and the energy due to interactions. Treating the elastic energy as for a free Gaussian chain, and the repulsive interactions in mean-field approximation, one finds

$$\Delta F \approx R_e^2 / (\ell_K L) + \upsilon_2 R_e^3 [(L/\ell_K)/R_e^3]^2,$$
(18)

since the average density of rods in the volume  $R_e^3$  is  $n/R_e^3$ . Minimizing  $\Delta F$  with respect to  $R_e$ , for  $L \to \infty$  one finds the standard Flory-type result

$$R_e \approx (\upsilon_2/\ell_K)^{1/5} L^{3/5} = (\ell_K d)^{1/5} (N_b \ell_b)^{3/5}.$$
 (19)

When one calculates then the free energy cost  $\Delta F$ , one finds that the contribution of the second term in Equation (18) is negligible in comparison with the first one if  $N_b < N_b^*$  with

$$N_b^* = \ell_K^3 / (\ell_b d^2).$$
 (20)

Hence, for  $N_b < N_b^*$  one simply has the scaling of Gaussian coils,  $R_e^2 = \ell_K L = \ell_K \ell_b N_b$ . Comparing this result with Equation (8), which implies rod-like behavior for  $L \le \ell_K$ , i.e.,  $N_b \le \ell_K / \ell_b$ , we recognize that the intermediate



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Gaussian behavior should only exist for

$$\ell_K/\ell_b < N_b < N_b^*. \tag{21}$$

In our SAW model we may take  $d = \ell_b$  and then  $N_b^* = (\ell_K/\ell_b)^3$ , while for a model where  $\ell_K \propto d$  (as we shall see, this case applies to bottle-brush polymers!) one would have  $N_b^* \propto \ell_K/\ell_b$ , i.e., both boundaries of the inequality, Equation (21), are of the same order, and then the intermediate Gaussian regime is absent altogether.

When we consider  $R_e$ , as given by Equation (19), normalized by its Gaussian result, we find that the result can be cast into the form

$$R_e^2/(\ell_K \ell_b N_b) = (N_b/N_b^*)^{1/5}$$
 for  $N_b \gg N_b^*$ . (22)

Since for  $N_b = N_b^*$  the ratio considered in Equation (22) is of order unity, we expect that  $R_e^2/(\ell_K \ell_b N_b)$  is a function of  $N_b/N_b^*$  over the whole range of  $N_b/N_b^*$ , apart from the region of very small values of  $N_b/N_b^*$  [where the crossover to rod-like behavior occurs, which is not described by Equation (18). Beyond the realm of the Flory approximation we expect that the exponent 1/5 in Equation (22) has to be replaced by  $2\nu - 1$ , of course. But it is an interesting question to clarify how the length  $\ell_{p,R}$  [Equation (16)] and the crossover chain length  $N_b^*$  scale with the persistence length  $\ell_p$ . Equation (19) would imply that

$$\ell_{p,R} \propto \left(\ell_p d\right)^{2/5} \ell_b^{1/5}, \quad N_b^* \propto \ell_p^3 / (\ell_b d)^2$$
 (23)

and in order to test these relations, Figure 12 presents loglog plots of  $\ell_{p,R}$  and  $N_h^*$  versus  $\ell_p$ .

A generalization to other scaling exponents would yield  $N_b^* = (\ell_K/\ell_b)^{\zeta}$  instead of Equation (20). Then  $\ell_{p,R} \propto \ell_K^{\mu}$  follows with  $\mu = 1 - \zeta(2\nu - 1)$  by using Equation (22). Figure 12 suggests that  $\zeta \approx 2.5$  and then  $\mu \approx 0.56$  would fit the data better than the corresponding exponents of Equation (23) { $\zeta = 3, \mu = 0.4$ }. We have no explanation for this discrepancy.

We conclude this section by considering the structure factor S(q), since this quantity is experimentally accessible via scattering intensities in dilute solution (Figure 13). The structure factor is defined as

$$S(q) = \frac{1}{(N_b + 1)^2} \left\langle \sum_{j=0}^{N_b} \sum_{k=0}^{N_b} \exp(i\vec{q} \cdot [\vec{r}_j - \vec{r}_k]) \right\rangle$$
 (24)

where  $\{\vec{r}_j\}$  are the positions of the  $(N_b + 1)$  monomers in a conformation that is averaged over. As expected, for  $q \to 0$  we have  $S(q) \approx 1 - q^2 \langle R_g^2 \rangle / 3$ , while for  $q \gg 1/\sqrt{\langle R_g^2 \rangle}$  power laws set in: for the ordinary SAW case  $(q_b = 1)$  we have an extended regime where  $S(q) \propto q^{-1/\nu}$ , as expected, while for very small  $q_b$ , such as  $q_b = 0.005$ , we rather



*Figure 12.* log–log plot of the effective persistence length  $\ell_{p,R}$  and of the crossover chain length  $N_b^*$  as a function of the persistence length  $\ell_p(q_b)$  that describes the initial exponential decay of  $\langle \cos\theta(s) \rangle$  versus *s*, for the semiflexible SAW model. Theoretical predictions and the best fit of our data are shown by solid lines, and thin solid lines, respectively.



*Figure 13.* Structure factor *S*(*q*) normalized such that *S*(*q* = 0) = 1 on a log–log plot versus wavenumber *q* (a) and the corresponding Kratky-plot {*qS*(*q*) vs. *q*} (b). Data for  $N_b$  = 50 000 are shown, including all values of *q*<sub>b</sub>, as indicated. Part (a) shows the slopes predicted theoretically for the standard excluded volume case {*S*(*q*) $\propto q^{-1/\nu}$  with  $\nu$  = 0.588} and for the Gaussian case {*S*(*q*) $\propto q^{-2}$ } as well as for scattering from rigid rods {*S*(*q*) $\propto q^{-1}$ }. Part (b) indicates the estimation of a characteristic wavenumber *q*<sup>\*</sup> from the onset of a flat part ("Holtzer plateau") in the Kratky-plot.





see that S(q) is compatible with  $S(q) \propto q^{-2}$  for small q and then crosses gradually over to  $S(q) \propto q^{-1}$  (as expected for the scattering from rigid rods<sup>[82]</sup>) for larger q.

In order to be able to distinguish the various regimes more clearly, it is customary to analyze the scattering in terms of the so-called Kratky-plot,<sup>[83]</sup> qS(q) is plotted versus q [Figure 13(b)]. Then, for  $q \ll 1/\sqrt{\langle R_q^2 \rangle}$  one has a linear increase, reaches a maximum at  $q_{\rm max} \propto 1/\sqrt{\langle R_a^2 \rangle}$ , followed by a power law decay  $[qS(q) \propto q^{1-1/\nu}$  for the good solvent regime,  $S(q) \propto q^{-1}$  for Gaussian chains, respectively]. While the simulation data for fully flexible chains  $(q_b = 1.0)$ indeed exhibit a straight-line behavior on the log-log plot over almost two decades, 0.01 < q < 1.0, and the slope of this straight line is compatible with the theoretical value  $1-1/\nu \approx -0.70$ , for small  $q_b$  the behavior is less convincing. In principle, for large enough  $N_b$ , where Equation (16) holds, we should see the same exponent from  $q_{\max} < q < q_{ ext{cross}} pprox$  $1/\sqrt{\langle R_g^2 \rangle_{\text{cross}}}$ , with  $\langle R_g^2 \rangle_{\text{cross}}^2 \approx (1/3)\ell_b \ell_p N_b^* = (8/3)\ell_p^4 / \ell_b^2$ , where we have used Equation (20). At  $q = q_{\text{cross}}$  the crossover from excluded-volume dominated behavior to Gaussian-like behavior occurs, i.e., we should see  $qS(q) \propto q^{-1}$ for  $q_{\rm cross} \approx \sqrt{3/8} \ell_b / \ell_p^2 < q < \ell_p^{-1}$ . Since for  $N_b = 50\,000$  we are obviously (Figure 5) too close to  $N_h^*$ , a significant region where  $q_{\text{max}}$  is clearly smaller than  $q_{\text{cross}}$  does not occur, if  $q_b$ is small (such as  $q_b = 0.005$ ). However, since  $\ell_p \approx 53$  for  $q_b = 0.005$ , we would expect two decades in q where the power law  $q^{-1}$  can be observed in Figure 13(b), but actually there is only a single decade (0.002 < q < 0.02) available, due to extended regions of smooth crossover. Figure 13 shows that the onset of the deviation from the law  $qS(q) \propto q^{-1}$  at about q pprox 0.02 yields a reasonable estimate for  $\ell_p^{-1}$  , and not the onset of the so-called "Holtzer plateau"<sup>[84]</sup> at  $q^{*-1}$  where qS(q) becomes strictly independent of q for a (not very extended) region of q. This failure of the method of finding  $\ell_p$ by the onset of the "Holtzer plateau" for the model studied in this section is expected, of course, from the explicit calculation of S(q) for the Kratky–Porod WLC model,<sup>[85]</sup> which shows that the crossover from the  $S(q) \propto q^{-2}$  law to the  $S(q) \propto q^{-1}$  law is very wide, and hence any onset wavevector  $q^*$  for the onset of the "Holtzer plateau" is rather ill-defined. Of course, this problem is not really rectified if one uses  $\ell_p = 3.5/q^*$ , as suggested by Lecommandoux et al.,<sup>[13]</sup> rather than  $\ell_p = 1/q^*$ .

### Scaling Analysis of the Bond Fluctuation Model for Bottle-brush Polymers

In this section, we first summarize the most pertinent findings of our previous Monte Carlo simulations of bottlebrush polymers under very good solvent conditions<sup>[41-43]</sup> and then describe a scaling analysis by which the model [Figure 2(a)] is essentially mapped on a bead-spring type

model [Figure 2(d)]. This analysis (which was briefly mentioned in our Letter<sup>[44]</sup>) implies that bottle-brush polymers are not well-described by concepts based on the Kratky-Porod<sup>[28]</sup> WLC model, even if weak excluded volume interactions [Figure 2(c)] with  $(\ell_K \gg d)$  are included. Of course, if one chooses a model of cylindrical beads with  $\ell_K$ of the same order as d, one does obtain a valid coarsegrained model of bottle-brush polymers, since for such coarse-grained models, the shape of the effective beads (bulky cylinders or spheres) does not really matter. This conclusion, in fact, is already suggested by the snapshot [Figure 2(a)]. Since details on the simulation model and methods have been given elsewhere,<sup>[4–43]</sup> here we give only the salient features. As is well-known, [24,78,79] effective monomers in the bond-fluctuation model block all eight corners of an elementary cube of the simple cubic lattice from further occupation, thus realizing excluded volume interactions. Bond vectors are taken from the set  $\{(\pm 2, 0, 0); (\pm 2, \pm 1, 0); (\pm 2, \pm 1, \pm 1); (\pm 2; \pm 2; \pm 1); (\pm 3, 0, 0); \}$  $(\pm 3, \pm 1, 0)$ ; and permutations thereof}. A combination of local moves (the "L26" move<sup>[72]</sup>) and pivot moves<sup>[86]</sup> provides fast relaxation (see<sup>[87]</sup> for details on the algorithm).

First of all, we demonstrate that the classical formulas for defining a persistence length, such as Equation (6) or (13), do not work.<sup>[43]</sup> As an example, Figure 14 shows  $\ell_p(k)$  for one choice of side chain length N(N = 24). It is seen that Equation (14) provides a reasonable description of the data for all  $N_h$ . The prefactor  $\alpha$  increases with  $N_h$  up to  $N_h \approx 400$ and then settles down at a plateau value  $\alpha \approx$  17 for N = 24. Note that this value increases with N, of course, since increasing the side-chain length causes chain stiffening.<sup>[43]</sup>

When we study the rescaled mean-square end-to-end distance as a function of  $N_b$ , controlling chain stiffness now by varying side chain length N, the resulting picture [Figure 15(a)] differs qualitatively from the SAW model with variable chain stiffness (Figure 5). While in the latter case with increasing stiffness  $q_b^{-1}$  a well-developed rod-like regime followed by a Gaussian behavior resulted, as discussed at length in the previous section, now we encounter a gradual crossover from almost rod-like behavior for relatively short backbone lengths  $N_b$  directly to the SAW limit. Irrespective of the side-chain length N, the data qualitatively resemble the SAW model with  $q_b = 0.4$  or 1.0, respectively (Figure 5). There is one important distinction; however, while for the SAW model in this case the effective persistence length  $\ell_{p,R}$  is very small [in Figure 5, 15(a)] the effective persistence length  $\ell_{p,R}$ can be read off as the plateau value reached for large  $N_{b}$ , which is less than unity for  $q_b > 0.1$ , for bottle-brush polymers  $\ell_{p,R}$  is much larger, and clearly  $\ell_{p,R}$  increases with increasing N.

Figure 15(b) shows that actually the bottle-brush end-toend distances satisfy a simple scaling behavior, if  $\langle R_{e,bb}^2 \rangle$  is







Figure 14. (a) Local persistence length  $\ell_p(k)$  [Equation (13)] plotted vs.  $k/N_b$  for the bond fluctuation model of bottle-brush polymers with grafting density  $\sigma = 1$  and fixed side chain length N = 24, for several values of the backbone length:  $N_b = 131$ , 259, 515, and 963 (from bottom to top). These data can be well fitted by Equation (14), where  $\ell_b = 2.7$  lattice spacings for the bond fluctuation model, if one allows the constant  $\alpha$  to depend on  $N_b$ . (b) Prefactor  $\alpha$  obtained from fitting Equation (14) to the data of part (a), and the data for  $N_b = 195$ , 387, 643, 771, and 1027, plotted versus  $N_b$ . For the range of the fit, only 0.3  $< k/N_b < 0.7$  was used. Note that for  $N_b \ge 400$  a value  $\alpha \approx 17$  independent of  $N_b$  results. Adapted from Hsu et al.<sup>[43]</sup>

also scaled with  $\ell_{p,R}$  (in addition to the factor  $2\ell_b N_b^{2\nu}$ ) and the abscissa variable  $N_b$  is scaled with the appropriate blob chain length  $s_{\text{blob}}$ . This blob size is constructed following the idea of Figure 2 that a bottle-brush polymer can be viewed as a chain of blobs whose radii are chosen such that they reproduce the cross-sectional radius  $R_{cs}(N)$ . Computing the end-to-end distance of subchains of s subsequent monomers taken from the interior of our backbone chains, we get a function  $\Delta r(s)$  shown in Figure 16(a). When we now also record the radial monomer density distribution  $\rho(r)$ , Figure 16(b), we can compute  $R_{cs}$  (cf. Figure 3) and find the number of monomers in a blob from the condition that the blob diameter equals  $2R_{cs}$ ,

$$\Delta r(s_{\rm blob}) = 2R_{\rm cs}(N). \tag{}$$





*Figure 15.* (a) Rescaled mean-square end-to-end distance  $\langle R_{e,bb}^2 \rangle / (2\ell_b N_b^{2\nu})$  of the bottle-brush polymers plotted for grafting density  $\sigma = 1$  and several choices of the side chain length N as function of the backbone chain length  $N_b$ . Adapted from Hsu et al.<sup>[43]</sup> (b) Rescaled mean-square end-to-end distance  $\langle R_{e,bb}^2 \rangle / (2\ell_b \ell_{p,R} N_b^{2\nu})$  plotted versus the rescaled chain length  $N_b$ . Adapted from Hsu et al.<sup>[44]</sup>

The construction is shown in Figure 16(a), and the values  $s_{blob}(N)$  resulting from this approach are then used to rescale  $N_b$  in Figure 15(b). The success of this scaling description shows that we have succeeded to coarse-grain bottle-brush polymers by mapping them to an effective chain model, but this effective model is not the WLC model of Figure 2(b) nor an SAW with high resistance toward bending [Figure 2(c)], but rather the correct picture is a chain of blobs with diameter of the order of the crosssectional diameter of the bottle-brush polymer,  $2R_{cs}(N)$ . Noting that the radio of  $\ell_{p,R}/R_{cs} = 1.11$ , 1.16, 1.23, and 1.28 for N = 6, 12, 18, and 24, respectively, we have verified that the effective persistence length  $\ell_{p,R}$  and the cross-sectional radius are the same, apart from a constant of order unity. This result is consistent with the early predictions by Birshtein et al.<sup>[61]</sup>. At this point, we remind the reader of the criterion for a possible regime of Gaussian behavior of semiflexible chains, Equation (19, 20): if we take  $d = 2R_{cs}$ and  $\ell_K = 2\ell_{p,R} = 2R_{cs}$  as well, we would conclude that  $N_b^* = 2R_{
m cs}/\ell_b = \ell_K/\ell_b$ , i.e., lower and upper limit of the inequality Equation (21) coincide, as we have announced







Figure 16. (a) End-to-end distance  $\Delta r(s)$  of subchains containing s successive backbone monomers for N = 6, 12, 18, and 24. The horizontal solid lines indicate the choices  $\Delta r(s) = 2R_{cs}(N)$ , from which the corresponding values  $s_{blob}$  can be read off (vertical straight lines) (b) radial monomer density profiles  $\rho(r)$  in planes locally perpendicular to the backbones of bottle-brush polymers with backbone lengths  $N_b = 1027$  plotted versus distances r for side chain lengths N = 24, 18, 12, and 6. Adapted from Hsu et al.<sup>[44]</sup>

above. Thus, indeed there is no contradiction with our finding that the WLC model of semiflexible chains is not a faithful description of bottle-brush polymers and no intermediate regime of backbone chain lengths can be found where Gaussian behavior occurs. Thus, Equation (8) must not be used for bottle-brush polymers under good solvent conditions!

In view of the fact that experimental AFM pictures of real bottle-brush polymers (e.g., ref. [3,10]) as well as the snapshot from our own simulation reproduced in Figure 2(a) have sometimes the character of WLCs, the above conclusion may sound surprising at first sight. However, both the snapshot [Figure 2(a)] and the AFM pictures do reveal also some strongly bent regions, where the chains locally have a "horseshoe" or "meander"-like appearance. Thus, we feel that experimental work based on the analysis of AFM pictures via fits to Equation (6) or (8) can yield unreliable results. Of course, it is possible (depending on the chemical structure of both the backbone chain and the side chains and the solvent quality) that one works with chains which are intrinsically stiff, so that the radio  $\ell_{p,R}/R_{cs}$  becomes much larger than unity; then a regime where the WLC model applies indeed could exist. Also, when  $N_b$  is rather short [so that in the scaled plot, Figure 15(b), one works in the regime  $N_b/s_{blob} < 20$ ], it is possible that the WLC model still could be fit to the data, although the resulting values of  $\ell_p$  should not be trusted.

As a final caveat, we draw attention to the fact that the curve  $\Delta r(s)$  versus s in Figure 16(a) for our model is not strictly universal (i.e., independent of N), but there is a slight but systematic increase of  $\Delta r(s)$  at fixed s with increasing N (also there is a related slight but systematic increase of the ratio  $\ell_{p,R}/R_{cs}$  with N, as quoted above.) These observations are the only indications of our results that in fact for very large N a different scaling behavior should emerge, where  $\ell_p/R_{cs} \gg 1$ . The scaling theory of Fredrickson<sup>[62]</sup> predicts that

$$R_{\rm cs} \propto N^{3/4}, \ \ell_p \propto N^{15/8}$$
 (26)

and if the regime where the power laws hold could be reached, Equation (19, 20) would yield (taking  $\ell_K \propto \ell_p, \ d \propto R_{cs}$ )

$$\ell_{p,R} \propto (\ell_K d)^{1/5} \propto N^{21/40}, N_b^* \propto N^{33/8}$$
 (27)

and hence for  $N^{15/8} \ll N_b \ll N^{33/8}$ , a Gaussian behavior could exist also for bottle-brush polymers. However, Monte Carlo studies for bottle-brush polymers with rigid straight backbones, which allow to use side chains of length of several hundred, gave no evidence for the relation  $R_{\rm cs} \propto N^{3/4}$  yet.<sup>[57]</sup> Moreover, numerical self-consistent field calculators of Feuz et al.<sup>[63]</sup> gave compelling evidence that side-chain lengths of  $N \approx 10^3$  or larger are required in order to reach the regime where Equation (26, 27) hold. Such long side chains are not accessible in simulations, but also rather irrelevant for experiment.

## **Concluding Remark**

It has been already discussed in our earlier work<sup>[41–43]</sup> that for bottle-brush polymers formed from flexible chains (both the backbone and the side chains were assumed to behave identical or at least similar) under good solvent conditions the standard approach to introduce a persistence length from the decay of bond-orientational correlations [Equation (6)] fails: on semilog-plots of  $\langle \cos\theta(s) \rangle$  versus the "chemical distance" *s* along the backbone one encounters a systematic curvature, and if one extracts a decay length from a part of such a curve, it is found to





increase systematically with the chain length of the backbone, and is unsuitable as a characteristic of the intrinsic stiffness of the chain.

In the present paper, we have focused upon an alternative approach, namely the use of the Kratky-Porod WLC model [Equation (8)-(10)] to describe the linear dimensions of the chain. While for the SAW model on the simple cubic lattice, where one may introduce an energy parameter penalizing chain bends, one finds a regime of rather stiff chains, where this model provides a reasonable description, before for chain lengths  $N_b > N_b^*$  a crossover to excluded-volume dominated behavior occurs [Equation (18)–(23)], we found that for bottle-brush polymers this model does not hold. Rather we have found that bottle-brush polymers can be mapped on an effective bead-rod or bead-spring model of "blobs" having a diameter equal to the cross-sectional diameter of the bottle-brush polymer. In the regime of side-chain lengths accessible in simulations and experiments, the effective persistence length is of the same order as this cross-sectional diameter, and an additional backbone stiffening predicted by theory is not (yet?) effective. We feel that these findings provide an understanding why experimental studies<sup>[13–21]</sup> have sometimes yielded contradicting results. Most of these studies have taken relations such as Equation (6)-(8) as granted, while our work implies that none of these relations applies for bottle-brush polymers under good solvent conditions, when both backbone and side chains are intrinsically flexible. Note that use of Equation (6) to fit experimental data or simulations over some restricted range of s typically will yield too large values of the persistence length, since the data actually would be described by Equation (12), if  $N_b$ is large enough [if  $N_b/s_{blob} < 20$ , in Figure 15(b) the resulting persistence length depends strongly on  $N_b$ , as demonstrated in ref.<sup>[41–43]</sup>]. Due to the dependence of  $\ell_p(k)$ on  $N_b$ , Equation (14), also the use of  $\ell_p(k)$  leads to an overestimate of the persistence length, in comparison with  $\ell_{p,R}$ . This latter quantity is perfectly well-defined also in the case of strong excluded volume interactions, and for our model varies from about 6.4 (N = 6) to about 17.6 (N = 24) lattice spacings (which would correspond to a variation from about 1.7 nm to about 4.64 nm, if the translation factor of Figure 3, 4 is invoked: these numbers are much smaller than the estimates quoted in the experimental work).

Another length of interest is the contour length  $L_{cc}$  (Figure 1). Taking the mapping of Figure 2(a)–(d) seriously, we would obtain  $L_{cc} = 2R_{cs}N_b/s_{blob}$ , which would yield (for  $N_b = 1\,027$  and N = 6, 12, 18, and 24, respectively) that  $L_{cc} = 1\,989$ , 1824, 1963, and 2016, instead of  $N_b\ell_b \approx 2\,773$  lattice spacings. Thus, the coarse-grained contour length  $L_{cc}$  is about 30% smaller than the "chemical" contour length  $N_b\ell_b$ , in our model.

Our findings imply, however, that for polymers which are locally rather stiff and thin, so that the model of Figure 2(c)

implies, one can find a region of small enough *s* so that Equation (6) can be used for  $s < s^*$ , before a significant deviation from the exponential decay due to crossover to the power law, Equation (12), occurs (Figure 7). Since this crossover is somewhat gradual, a precise choice of  $s^*$  cannot be given. In the range  $0.005 \le q_b \le 0.05$  of our model [The Semiflexible Self-avoiding Walk (SAW) Model section] a choice  $s^* \approx 3\ell_p$  seems reasonable (with  $\ell_p$  varying in between 6 and 53 lattice spacings in this range). In terms of Equation (6) this means that  $\langle R_e^2 \rangle$  has reached about 68% of its (Gaussian) saturation value. Obviously, this is a much smaller value of  $N_b$  rather than the value  $N_b^*$  where crossover to excluded-volume dominated behavior in the mean-square end-to-end distance occurs (Figure 10–12)

#### Nomenclatures

$\vec{a}_k$	bond vector of bond <i>k</i> .
$C_{N_h,N_{\rm bend}}$	number of chain configurations with $N_b$ bonds
	and $N_{ m bend}$ kinks on the sc lattice
d	diameter of a (locally) cylindrical chain
${\cal H}$	Hamiltonian
k	bond index $(k = 1, \ldots, N_b)$
$k_{ m B}$	Boltzmann's constant
L	(actual) contour length of a linear polymer
	$(L = N_b \ell_b)$
$L_{cc}$	effective contour length of a coarse-grained
	chain
$\ell_b$	length of a bond connecting two subsequent
	(effective) monomers
$\ell_K$	Kuhn length of a Gaussian chain
$\ell_p$	persistence length, defined from (initial) expo-
	nential decay of bond orientational correlation
$\ell_{p,R}$	persistence length defined from the chain end-
	to-end distance, in the presence of excluded
	volume.
$\vec{\ell}_s$	bond vector connecting two subsequent (effec-
	tive) side chain monomers
$\overline{M}_n^{\rm sc}$	molecular weight (g∙mol <sup>−1</sup> )
Ν	chain length of the side chain of a bottle-brush
	polymer
$N_b$	"Chain length", i.e., number of bonds in a chain
	(or in the backbone of a bottle-brush polymer,
	respectively)
$N_b^*$	crossover "chain length" above which self-
	avoiding walk statistics holds for stiff chains
n	number of Kuhn steps for a Gaussian chain
$n_{ m str}$	number of straight bonds, withouts kink in
	between
n <sub>p</sub>	decay constant of $p(n_{str})$
$P(n_{\rm str})$	probability that $n_{\rm str}$ consecutive straight bonds
	occur on the sc lattice

wavenumber

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$q_b$	statistical weight of a bond of a semiflexible
	chain $(q_b = \exp(-\varepsilon_b/k_{\rm B}T))$
<i>q<sub>cross</sub></i>	crossover wavenumber
amax.	wavenumber where a maximum in the Kratky-
Alliax	nlot occurs
a*	wave number where Holtzer plateau sets in
9	wave number where Honzer plateau sets in
K <sub>cs</sub> ≓	cross-sectional radius of a bottle-brush polymer
R <sub>e</sub>	end-to-end vector of a side chain of a bottle-
	brush polymer or of a linear chain
$\vec{R}_{e,bb}$	end-to-end vector of the backbone of a bottle-
	brush polymer
$R_a$	gyration radius
$R_{a hh}$	gyration radius of the backbone of a bottle-
9,00	brush polymer
r	radial coordinate (nernendicular to the back-
1	hope of a guindrical chain)
$\vec{z}(t)$	describes the sector of length I
$\vec{r}(t)$	describes the contour of length $L_{cc}$
r <sub>k</sub>	position of effective monomer with label k
S(q)	structure factor
S	monomer index difference along the chain
	contour
<i>s</i> *	crossover index (above which orientational
	correlations display a power law)
S <sub>blob</sub>	number of monomers per blob
Т	absolute temperature
t	coordinate along the (curved) contour of the
	coarse-grained polymer
$U_{\text{bend}}(\theta)$	bending energy
$\nu_2$	second virial coefficient
Z	partition sum
в	exponent which describes the power law decay
<i>P</i> *	of orientational correlations [Equation (2)]
$\Lambda F$	free energy
$\Delta r(s)$	end-to-end distance of s subsequent monomers
$\Delta I(b)$	on the backhone of bottle-brush nolymers
<u> </u>	hending energy
ے ب	overage which describes the networ law
ζ	dependence of N* on (0, (0))
0	dependence of $N_b$ on $(\ell_K/\ell_b)$
θ	bona angle
κ	bending rigidity
$\mu$	exponent which desribes the power law depen-
	dence of $\ell_{p,R}$ on $\ell_K$
ν	"Flory" exponent ( $ u pprox$ 0.588)
$v_{eff}$	effective "Flory" exponent determined for short
	side chain lengths of bottle-brush polymers
$\rho_{\rm cs}(r)$	cross-sectional monomer density
σ	grafting density

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