Modeling of comb polymers with a high branching density

Stefano Elli(*), Fabio Ganazzoli(*), Edward G. Timoshenko(**), Yuri A. Kuznetsov(**)

Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Sez. Chimica, Politecnico di Milano, via L. Mancinelli 7, 20131 Milano, Italy (*)

Theory and Computation Group, Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland (**)

Abstract

I polimeri a pettine altamente ramificati sono attualmente di grande interesse. Costituiti da una catena principale, che lega con una certa frequenza diverse braccia lineari, essi possiedono una notevole rigidità di catena, dalla quale dipendono altre proprietà, come il loro comportamento liotropico sia in soluzione, sia adsorbiti sopra una superficie. Tali macromolecole sono oggetti nanoscopici *(bottle-brush* molecolari) di forma cilindrica le cui dimensioni variano da qualche nanometro (raggio della sezione) a centinaia di nanometri (lunghezza di contorno). Tuttavia ancora oggi sono poco note la loro rigidità e le variabili da cui essa dipende, tra cui il volume escluso dei monomeri e i vincoli stereochimici (connettività, vincoli torsionali). La disponibilità di calcolatori per il calcolo intensivo ha permesso di applicare l'algoritmo Monte Carlo Metropolis a una modellazione "a grana grossa" per descrivere molecole *bottle-brush* in soluzione diluita ed adsorbite su di una superficie. Risultati accurati sono stati ottenuti per il calcolo degli esponenti di Flory, delle lunghezze di persistenza e delle funzioni di distribuzione delle distanze tra monomeri.

Branched macromolecules are currently of great scientific interest. They are formed by a backbone carrying many closely spaced linear arms, and their most important property consists on their backbone stiffness due to the large branching density. From this property, one can reasonably expect lyotropic behaviour of these systems in solution and adsorbed on a surface. These molecules have a cylindrical shape and a characteristic size that ranges from a few nanometers (radius of their circular section) to hundreds of nanometers (contour length). Little is known at present about the nature of the backbone stiffness and its dependence on the monomers excluded volume and on the stereochemical constraints. The availability of high-performance computers allowed us to apply the Metropolis Monte Carlo algorithm to a coarse-grained model to describe bottle-brushes in a diluted solution or adsorbed on a surface.

Accurate results are obtained for the value of the Flory exponent, the persistence length and the distribution functions of the distances between the monomers.

Keywords Monte Carlo simulations; comb polymers; molecular stiffness.

Introduction

Many variables affect the behaviour and performance of polymeric materials, including in particular those related to the detailed chemical structure of the macromolecules, to their molar mass (or chain length) and to their topology. In the last years, much attention has been devoted to the latter issue considering in particular branched polymers. Thus, new synthetic methods have been developed, and the physical properties of these systems have been studied experimentally and, to some extent, also theoretically. In addition to star polymers and to dendrimers, regular comb polymers are currently an important topic. Comb polymers are formed by a molecular backbone carrying many polymeric (or oligomeric) side chains bound to the main chain. Molecular bottle-brushes are comb polymers with a high density of branches. In these molecules, every monomer of the backbone carries a side chain (an arm, or a branch) containing from tens to hundreds of monomers, which may be equal to the backbone monomers, or chemically different. Moreover, the topology of each arm can be linear or dendritic, that is, with a tree-like topology, thus corresponding to a so-called polydendron [1]. Molecular bottle-brushes can be prepared by radical polymerization of a linear or dentritic macromonomer, producing a macromolecule (or better a poly-macromonomer) with a backbone having a polymerization degree of a hundred to a thousand macromonomer units.
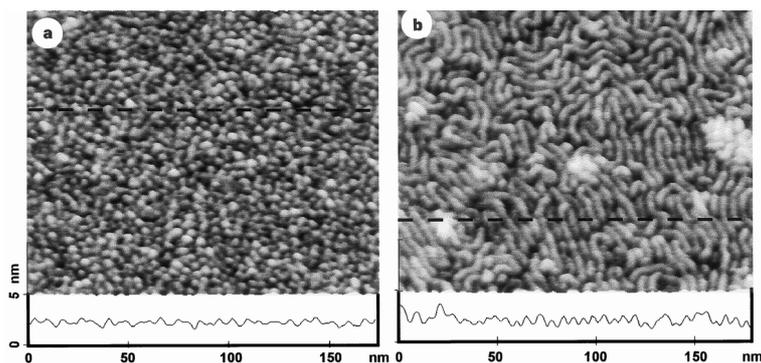

Fig.1 *STM images of polydendron [1] adsorbed on a mica (polar) surface at low molecular weight (a) and at high molecular weight (b). In both cases the sample is obtained by solvent evaporation from a drop of diluted solution deposed on the surface. At the bottom the height profile taken along the dashed line shown in the pictures is reported.*

The conformation of such macromolecules is of paramount interest, because the overall molecular shape depends on the degree of polymerization of the backbone. In fact, if the backbone length roughly matches the length of the arms, the overall

shape is roughly spherical (Fig. 1*a*). Conversely, if the backbone length is much larger than the length of the arms, the whole molecule looks like a cylinder with a peculiar bending stiffness (Fig. 1*b*). This behaviour is observed in different environmental conditions, including both diluted solutions and at the interface with a solid substrate [2-5]. The physical origin and the nature of this stiffness are not fully understood yet and motivated the present study.

These highly branched macromolecules are of great interest both for academic and for technological reasons. In fact, due to the above-mentioned stiffness they show a lyotropic behaviour in a semidiluted solution and adsorbed on a surface (Fig. 2). Moreover, if the side chains are amphiphilic block copolymers containing a polar and a non polar block, the whole molecule can behave like a cylindrical micelle, with a stiff cylindrical core formed for instance by the polar monomers and a coaxial shield of an unlike nature. Such molecules are important from a chemical point of view because they form unimolecular, covalent micelles, which are therefore stable even at infinite dilution, and which may be useful for instance as a nanoreactor [3,4].
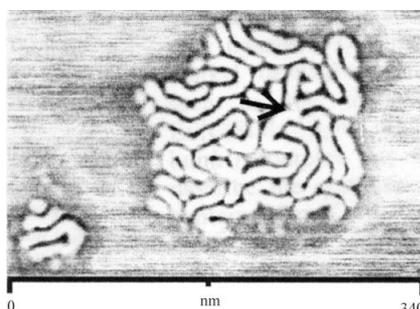
Fig. 2 An AFM image of molecular bottle-brushes adsorbed on mica [5]. It is possible to see highly ordered domains formed by such stiff macromolecules. The sample is prepared after deposition of a solution drop on the mica surface.

High-performance computers and modeling of highly branched comb polymers

The shape and stiffness of bottle-brush polymers in a diluted solution or adsorbed at an interface must obviously be investigated experimentally. However, experimental data often do not provide a full picture and some features of the system behaviour are inaccessible experimentally. For instance, scattering measurements [2] can give information on the average dimensions of the macromolecules through the radius of gyration and its components. Different radiations (light, X-ray, neutrons) may yield complementary results, but usually the true molecular shape is interpreted in terms of "simple" geometries only (rods, disks, ellipsoids, ...). Viscosimetric data yield a different size of the molecule through the hydrodynamic

radius, while osmotic pressure measures the number-average molecular weight but not the molecular size. Microscopic techniques like STM and AFM provide direct images of nanoscopic systems like bottle-brushes, where the molecular size ranges from tens to hundreds of nanometers. Still, the experimental observations cannot provide an exhaustive statistical description of the system. For example, the backbone stiffness in bottle-brushes can be estimated through analysis of the experimental values of the radius of gyration [6] assuming a theoretical model of a stiff chain, namely the popular wormlike model [6,7], even though the latter one is not fully satisfactory. As a result, one may derive an apparent *persistence length*, which provides a quantitative measure of the backbone stiffness in terms of the average length of the segments keeping a given direction. However, it is clear that such measure relies on the assumption that the wormlike model is accurate, which is not true.

A deeper understanding of the system behaviour is provided by a detailed knowledge of its internal energy and entropy. An appropriate balance of these terms in the chosen conditions (solvent, temperature, etc.) yields a full description of the configurational properties of the system, in a statistical mechanical meaning, including parameters like the chain stiffness, the molecular size, various distribution functions, etc. One way to solve this problem is to model the system by computer simulations, and then to calculate average properties of interest, both for a comparison with the experimental data and for a deeper understanding of the system behaviour through more abstract quantities, such as for instance the distribution functions that allow easy calculations of many observable properties. Also, it is possible to fine-tune the model by a comparison with the observed properties so as to sort out the relevant factors and their relative importance.

When building a model of a given system, one needs to find the finest details that are relevant to the problem. For instance, one needs atomistic quantum mechanical models to describe chemical reactions that involve breaking and formation of chemical bonds. However, the overall behaviour of a macromolecule and its dependence from the topology can be studied more usefully adopting less detailed models. If we ignore the most local features, we can choose coarse-grained models. Here, a group of atoms, corresponding to a few monomers, is lumped in a bead, and the beads are connected by segments or springs so as to reproduce the required topology. We then select a bead-bead interaction potential that mimics the solvent effect on the topologically distant beads that come close in space because of molecular flexibility. In Fig. 3 we show the coarse-graining procedure: at left, there is an atomistic drawing of a bottle-brush obtained by polymerization of the macromonomer poly-2-vinylpyridine, and at right a coarse-grained picture of this system. Note that all interactions take place through the beads, whereas the thin cylinders display only the connectivity links.
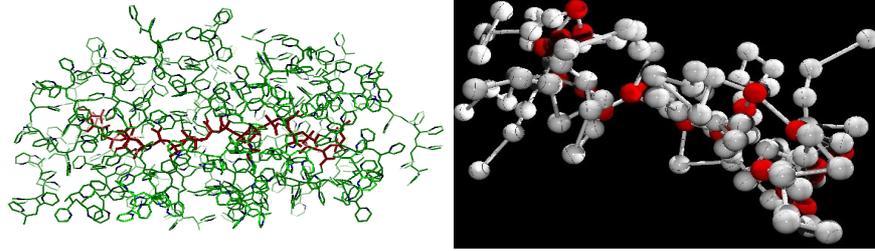
Fig. 3 *A bottle-brush macromolecule described by an atomistic model, at left, and by a coarse-grained one, at right. The atomistic model describe in detail a real system obtained by polymerization of a poly-2-vinylpyridine [5]. In both cases, the molecular backbone is shown in red.*

We adopted a coarse-grained model to study bottle-brush polymers in continuous space. Therefore, the system Hamiltonian H contains two terms, and is reported in eq. 1 in $k_B T$ units, while l, the "bond" length connecting adjacent beads, gives the unit of length:

$$\frac{H}{k_B T} = \frac{1}{2l^2} \sum_{i \sim j} k_{ij} \left(X_i - X_j \right)^2 + \frac{1}{2} \sum_{i,j i \neq j} V^{HS} \left(\left| X_i - X_j \right| \right)$$

$$V^{HS}(r) = \begin{cases} +\infty & r < d_0 \\ 0 & r > d_0 \end{cases}$$

(1)

Here, X_i is the vector position of the i-th bead, and $V^{HS}(r)$ is the two-body non-bonded term, chosen for simplicity as a hard-sphere potential (corresponding to a good-solvent condition), while the symbol ~ indicates the connected beads. Therefore, the first term of the Hamiltonian contains the potential energy of harmonic springs that connect the beads, k_{ij} being the force constant, and accounts for the molecular connectivity and the configurational entropy.

Note that while the coarse-grained model is much simpler than the atomistic model, still the number of variables (the bead coordinates) may become quite large when the backbone length and/or the arm length do increase, in particular for a large branching density. On the other hand, for a polymer chain with N beads the number of pairwise interactions within the potential energy, or at least the number of the distance among all the bead pairs, increases as N^2. The configurational space of the model was sampled with a Monte Carlo algorithm in the Metropolis formulation [8], which is an unbiased procedure that eventually converges to the correct Boltzmann distribution function for any arbitrary starting configuration. The independent configurations are generated by random displacements of a randomly selected bead in continuous space, which provides a fully unbiased procedure. The main practical limitation consists on the relaxation time (or, more precisely, on the number of attempted movements) for equilibrating the system from the initial configuration before beginning the data collection. Moreover, independent configurations are only

found at time intervals of the order of the relaxation time, otherwise significant correlations may be present. In turn, the relaxation time depends on the chosen Hamiltonian, on the number of monomers and on the molecular topology. As a rule of the thumb, for a system with a Hamiltonian like that given in eq. 1 the "relaxation time" τ scales as $\tau \propto N^2$. The trajectory of the model is the ensemble of the independent configurations sequentially obtained from that algorithm, and its length depends on the observables of interest and on the required accuracy of the average quantities.

For an ensemble of Boltzmann-distributed configurations of the system, the average value of a given observable A is obtained from the statistical ensemble as

$$\langle A \rangle \pm \delta A; \qquad \langle A \rangle = \frac{1}{Q} \sum_{j=1}^{Q} A_j \qquad (2)$$

where the angular brackets indicate the average value and δA is the standard error, while Q is the number of independent configurations. δA is obtained from the Central Limit Theorem:

$$\delta A = \sqrt{\frac{\sigma^2 [A]}{Q}}; \qquad \sigma^2 [A] = \frac{1}{Q} \sum_{j=1}^{Q} [A_j - \langle A \rangle]^2 \qquad (3)$$

δA is given by this equation only if the Q configurations of the trajectory are indeed statistically independent. Otherwise, one may correct this expression by introducing the statistical inefficiency s ($s \geq 1$) that quantifies the amount of correlation: $s = 1$ indicates that all the configurations are decorrelated, whereas $s > 1$ indicates that the configurations are not statistically independent. Average values with the least statistical uncertainties are ideally obtained by sampling truly decorrelated configurations, which requires a "distance" in simulation time between two successive samplings in the trajectory that should be of the order of the relaxation time. So the sampling procedures clearly implies very long simulation times.

Results and discussion

1. The average size of bottle brushes

The first results describing the average polymer conformations are given by the overall molecular size through the mean-square radius of gyration $\langle R^2_g \rangle$, or the mean-square end-to-end distance $\langle R^2 \rangle$. These quantities usually increase with the polymer molar mass, or equivalently with the number of beads N *via* simple universal power-law dependence, provided N is large enough:

$$\langle R^2_g \rangle \approx \langle R^2 \rangle \approx N^{2\nu} \qquad (4)$$

where ν is the Flory critical exponent. This power-law relationship turns out to be valid for all linear polymers, independently from the chemical structure of the monomer, while the Flory exponent ν is universal and depends only on the thermodynamic conditions. Accordingly, it can also be efficiently obtained through

coarse-grained models. For the simplest polymer model consisting on the random-walk model where the beads do not interact at all, one finds $\nu = 1/2$. Experimentally, such case is obtained at the so-called Θ temperature, that depends on the given polymer-solvent pair [7]. In a poor solvent, the attractive interactions among the beads lead to a globular state, and the Flory exponent becomes $\nu = 1/3$. In the more common case when the polymer chain is in a good solvent and it is well solvated, the universal Flory exponent is experimentally close to $\nu = 3/5$. This can be theoretically reproduced through the Self-Avoiding Walk model, whereby the beads simply behave as hard spheres. Analytical theories and computer simulations have shown that in this case the best estimate of the Flory exponent is $\nu = 0.5882(11)$ [9]. Because of the excluded-volume among the side chains, we may expect that in bottle-brushes $\langle R^2_g \rangle$ and $\langle R^2 \rangle$ show a faster increase with N than in linear chain. In fact, the steric exclusion among the arms may be efficiently relieved by a significant elongation of the backbone, which corresponds to a large increase of the persistence length compared to linear chains. In fact, we studied bottle-brushes having the following branching density:
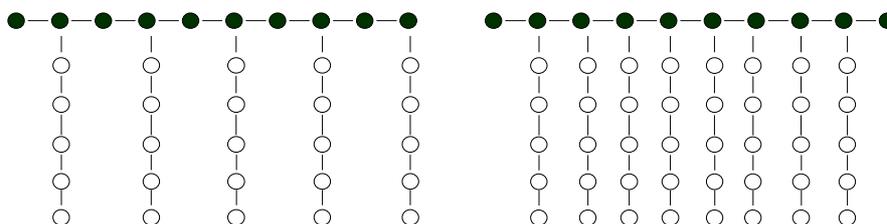
Fig. 4 *Topology of the bottle-brushes. The dark spheres are the backbone beads, and the white spheres are the beads of the side chains. The bottle-brush shown at right (HD) has twice the branching density than the bottle-brush shown at left (LD).*

In both cases the Flory exponent is much larger than in linear chains, as shown in Fig. 5 [10]
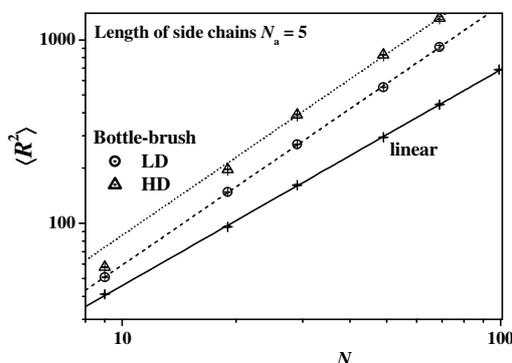
Fig. 5 *The mean-square end-to-end distance as a function of the number of backbone beads N for linear chain and bottle-brushes with a low (LD) and a high*

(HD) branching density (see Fig. 4) plotted in a double logarithmic form. The error bars are smaller than the symbol size. The lines are obtained by fitting the data to the power law of eq. (4).

The data of Fig. 5 were fitted to the power law of eq. (4) and the resulting values of the Flory exponents are reported in Table 1.

Table 1 *The calculated Flory exponent ν of bottle-brushes and linear chains.*

Molecule	Flory exponent ν
Linear	0.588(2)
LD bottle-brush	0.678(2)
HD bottle-brush	0.707(17)

The Flory exponent ν of the linear chain is in perfect agreement with the best theoretical estimates. On the other hand, in bottle-brushes the ν exponent is significantly larger because of the excluded-volume repulsion among the arms that enhance the backbone stiffness. Similar results, not shown for brevity, were found for the mean-square radius of gyration $\langle R^2_g \rangle$.

2. The pair distribution functions

From the theoretical viewpoint, a great amount of information is provided by the pair distribution functions (or p.d.f.) of the distance between monomers i and j of the molecule:

$$g_{ij}(r) = \left\langle \delta(\boldsymbol{r}_{ij} - \boldsymbol{r}) \right\rangle = \frac{1}{4\pi r^2} \left\langle \delta(|\boldsymbol{r}_{ij}| - r) \right\rangle \tag{5}$$

wherefrom a large number of configurational averages can be obtained. These functions can be obtained in a histogram from the instantaneous vector distances $\boldsymbol{r}_{ij}$ between the various bead pairs obtained in the simulation trajectories. While the procedure is very simple in principle, it requires very extensive and lengthy simulations in order to get relatively smooth curves with a small statistical error. Accordingly, such calculations can only be performed on computationally powerful machines, such as a multiprocessor computer. In fact, while the Metropolis algorithm is basically sequential and cannot be easily performed in parallel, using n independent CPUs we can start with n identical initial configurations, and sample their configurational space through n independent runs on the n independent CPUs, provided we choose different initial random seeds for the pseudorandom generator procedures. At the end of n jobs, we simply merge the n statistically independent trajectories. The computer time perfectly scales with the number of CPUs as $1/n$, thus yielding sufficiently long trajectories in a reasonable time. In this way, we could investigate for instance the p.d.f. of the end-to-end distance R for different lengths of the side chains at a fixed backbone length. As an example, we report a typical result in Fig. 6, considering LD bottle brushes with a backbone comprising

20 beads and carrying side chains with a length equal to 0 (a linear chain, actually), 2 or 5 beads.
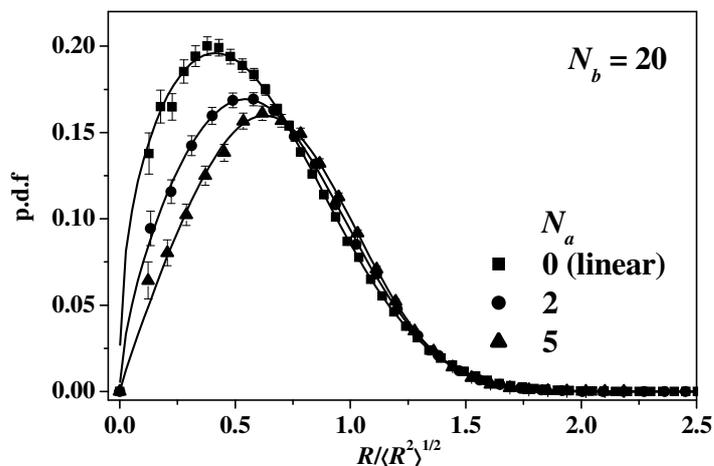
Fig. 6 *The p.d.f. of the end-to-end distance for a bottle-brush with a low density of branching (LD). The number of beads of the backbone, N_b, and of the side chains, N_a, is reported in the figure. The best-fit lines (solid lines) were obtained using the function: $y = A\, x^{\vartheta}\, exp(-B\, x^{\delta})$*

When the length of the side chains increases, then the maximum of the distribution is displaced to a larger abscissa, and its width becomes narrower. In other words, the whole molecule becomes increasingly more elongated with larger backbone stiffness.

3. The persistence length

The stiffness of a polymer chain can be measured by the persistence length, which can be defined through the projection of the end-to-end vector distance $\boldsymbol{R}$ on the generic k-th segment of the backbone:

$$\left\langle l_{pers}^{(k)} \right\rangle = \left\langle \frac{\boldsymbol{r}_{k,k+1}}{\left| \boldsymbol{r}_{k,k+1} \right|} \cdot \boldsymbol{R} \right\rangle \tag{6}$$

Here, $\boldsymbol{r}_{k,k+1}/|\boldsymbol{r}_{k,k+1}|$ is the versor of the k-th segment of the backbone, and the angular brackets indicate the average value, as before. In stiff chains, the segments are correlated in their direction, and the persistence length is significantly larger than 0. Experimentally, the persistence length can only be obtained by fitting some (usually simplified) theoretical model to the data, whereas it can be easily obtained from the simulation trajectories. In Fig. 7 we show the persistence length as a function of the position of the k-th segment along the backbone for two linear chains and two LD bottle-brushes with the same backbone length (30 and 100 beads).

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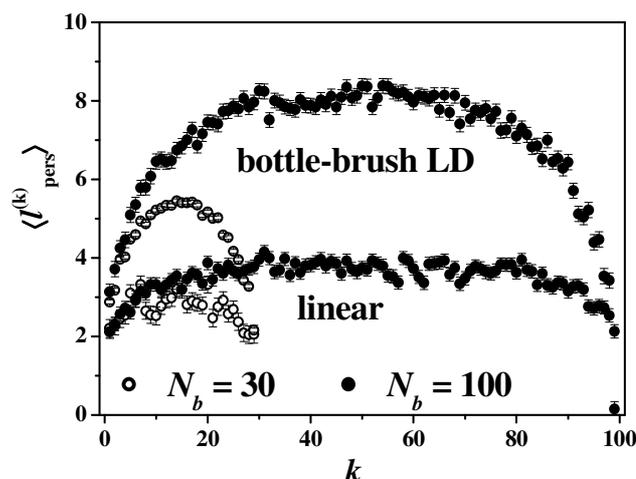
Fig. 7 *The persistence length as a function of the position of the k-th segment for linear chains and bottle-brushes. The number of beads of the backbone, N_b, is indicated in the figure. The bottle-brush molecule contains 5 beads per side chain.*

All these plots have a bell-like shape, indicating that the stiffness is greater at the molecular centre, where a plateau may develop for large enough chains. Conversely, the stiffness becomes significantly smaller close to the backbone ends as an entropic effect due to the larger configurational freedom of the free ends. The stiffness of bottle-brushes shows a large increase with the backbone length, while it quickly achieves an asymptotic, constant value in linear chains. Moreover, Fig. 7 shows that the stiffness of bottle brushes is significantly larger than for linear chains at a given backbone length. As it has already been pointed out before, the persistence length measures the stiffening effect of the backbone, which mainly depends on the excluded-volume interactions among the arms. Therefore, we denoted it as *topological stiffness* [11]. In fact the Hamiltonian of these systems (see eq. 1) does not account for any intrinsic stiffness, usually introduced as a bending stiffness, or through a torsional potential. Such intrinsic stiffness should also contribute to the overall stiffness of bottle-brushes [10,11] because of the chemical constraints on the bond angles and on the torsional potentials. Therefore, the above results provide a simplified model that is however useful to disentangle the relative importance of different contributions to the observed behaviour.

Conclusions

The main purpose of the present contribution is to briefly show how large-scale computational resources may allow to efficiently study highly congested polymer chains. Such systems are of growing interest in nanotechnologies because of the

accurate control on their topology and on the hydrophilic/hydrophobic character that can be experimentally achieved. A coarse-grained model of highly branched polymers can provide important information on the overall molecular size and stiffness in a good solvent. In particular, we can determine the molar-mass dependence of the molecular size, calculate the Flory exponent, determine the pair distribution function and analyze the molecular stiffness through the persistence length. Furthermore, the present model can be easily improved to describe more complicated situations. For instance, we are currently improving the Hamiltonian by adding a one-body potential of a dispersive nature (following the Hamacker approach [12]) to describe the interaction of these systems with an attractive surface. This is precisely the situation shown in Figs. 1 and 2. Unfortunately, the relaxation of an adsorbed molecule turns out to be considerably slower than for the free molecule, with the relaxation time roughly being from two to five times larger than that for the free molecule. For example, in a comb molecule with a backbone of 100 beads, an average branching density and arms of five beads for a total of 350 monomers, the molecular relaxation required about 30 min of CPU time [13] for the isolated molecule, or 87 min for the adsorbed one. Clearly, the calculation of the statistical averages requires much longer simulation times, since the data collection described in the methodological section typically spanned 500 times the relaxation time for the free molecule. As it often happens, these new problems may require an increasingly larger computer power to be thoroughly investigated.

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