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The structure of brushes made of dendrimers: Recent advances

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ABSTRACT

In recent publications, a couple of theoretical models, ranging from simple scaling approaches and box-like mean-field models to self-consistent field techniques, have been proposed to describe the structure of brushes that are composed of dendrimers. In this work, we carry out molecular dynamics simulations in various density regimes, and compare the resulting data with predictions of the latest theoretical models. This study enables us to access the ranges of validity and accuracy of the respective models, as well as their shortcomings. Significant differences in the predicted conformations of the dendrimers are observed and analyzed in the context of their elastic properties in the different models. This work offers guidelines for future research directions, which may lead to further progress regarding the understanding of branched polymer brushes.

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1. Introduction

Brushes made of linear chains have been studied thoroughly during the last decades, and their physical properties and structures are fairly well understood. To the contrary, the detailed structures of brushes made of branched polymers is still a matter of intense research. In the present work, we highlight recent progress in the modeling and simulation of brushes made of grafted dendrimers. These dendrimer brushes are interesting for a couple of reasons: Since they offer an enhanced number of end groups which could be functionalized, they are regarded promising candidates for environment-responsive surface layers [1–6]. They are expected to offer improved anti-inflammatory or anti-fouling properties, i.e. barriers against a penetration by bacteria or proteins [7–9]. If grafted onto colloids, they lead to an improved stability against coagulation, featuring a thinner polymeric layer than colloids decorated with linear chains [10]. Last not least, branched polymer brushes are known to play vital roles in biological materials such as airway epithelia [11], are serving as anti-viral barriers [12] or potential high-efficiency drug-delivery systems [13].

Experimentally, the preparation of polymer brushes follows two approaches, denoted as grafting-from and grafting-to techniques [14]. Dendrimers are synthesized via a step-controlled technique, and a large number of different dendritic polymers of low degree of polydispersity are now being made in the laboratories [15–18].

The present work will focus on advances of the theoretical understanding, the modeling and the simulation of dendrimer brushes. Comparisons of simple, Flory-Huggins based mean field models, both in continuum and on the lattice, with self-consistent field (SCF) techniques and molecular dynamics (MD) simulations will offer insights into basic conformational features and properties of these systems. We will focus on brushes, grafted onto planar substrate, and in good solvent, in which the molecules are highly swollen. In Sec. 2, we will first pay attention to brushes at low grafting densities, for which particularly simple and hence fully analytical formalisms have been derived. In Sec. 3, these models are compared to MD simulation data, and their scaling behavior is evaluated. In Sec. 4, a couple of refined models are presented, which are assuming a dual layer structure of starlike brushes at higher densities and which account for the finite extensibility of the spacers. We will analyze systematic differences between these approaches in Sec. 5, and particularly in Sec. 5.2, in which conformational features of the dendrimers inside the brushes are analyzed. In Sec. 6, we shall critically discuss the progress achieved so far, and then speculate about possible directions which may lead toward future improvements.

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2. Fully analytical brush models

For sparse brushes, in which the monomer densities and the stretching ratios of the spacers remain low, fully analytical models are available. Among these models we may distinguish between single phase box models, in which the monomer density profiles are uniform step-like functions, and SCF models, which usually assume parabolic SCF potentials. Fully analytical solutions for the brush heights and densities seem possible as long as the spacers (i.e. stems or branches of the grafted dendrimers) are inside the weak stretching regime, in which their elastic forces are well approximated by a linear Hooke-law. In the examples considered here, volumetric and entropic mixing effects are approximated by the leading order term of the virial expansion.

2.1. Single phase box models

Simple box models with uniform monomer densities, used to derive scaling laws of the brush height and concentration of dendrimer brushes, are generalizations of the classical Alexander-deGennes model [19,20] and available since quite some time [21]. As has been pointed out by Kröger et al. [22], the validity of the resulting scaling laws is more often than not limited to narrow parameter windows and should therefore be routinely checked with computer simulations. However, recent modifications of boxlike models and SCF theories allow for higher accuracies and hence a superior understanding of the limitations of traditional scaling approaches.

According to the standard mean-field concept of neutral (uncharged) brushes, the total free energy, as a function of the brush height H, is composed of two contributions,

$$F(H) = F_{\mathrm{int}}(H) + F_{\mathrm{el}}(H) \,. \tag{1}$$

The interaction free energy may be taken from a Flory-Huggins type mean-field model [23], or, more generally, approximated as a virial expansion in powers of the number density c,

$$\frac{F_{\mathrm{int}}}{V} = \frac{1}{2}\left(\mathrm{v}c^2 + \mathrm{w}c^3 + \cdots\right) , \tag{2}$$

with the system volume V, the excluded volume coefficient v and the three-body interaction coefficient w. This expansion includes the free energy of mixing of the monomers with the solvent. Within the framework of the Flory-Huggins model, only the coefficient v accounts for enthalpic interactions between the monomers, and thus it depends on the temperature. In good solvent and at low densities, the leading order excluded volume term may suffice, while in Θ-solvent the third order term would define the leading contribution. Here and in all subsequent equations, we express free energies in units of k_BT.

In a box model with uniform density, the number density c and the brush height H are related through

$$c = \frac{MN}{V} = \frac{MN}{AH} = \frac{\sigma N}{H} \,, \tag{3}$$

with the number of monomers N per grafted molecule, the total number M of grafted molecules, the brush area A and the grafting density $\sigma = M/A$, so that *in good solvent*

$$F_{\mathrm{int}}(H) \approx \mathrm{v}\frac{MN^2\sigma}{2H} \,. \tag{4}$$

Under weak stretching conditions of the spacers, the elastic free energy per molecule may be expressed with the help of a simple harmonic potential

$$\frac{F_{\mathrm{el}}}{M} = \frac{1}{2}KH^2 \tag{5}$$

with the molecular spring-constant K (for linear chains, $K = 3/N$; note that we assume a unit bond length or monomer diameter here and in the following equations, unless stated otherwise). The free energy minimum is then obtained from

$$\frac{\partial F}{\partial H} \stackrel{!}{=} 0 = KH - \frac{\mathrm{v}\sigma N^2}{2H^2} \,, \tag{6}$$

yielding

$$H = \left(\frac{\mathrm{v}}{2}\right)^{1/3}\left(\frac{N^2}{K}\right)^{1/3}\sigma^{1/3} \,. \tag{7}$$

The first factor contains the excluded volume coefficient. Since it originates in a Flory theory, being valid on a lattice, it may, during comparisons with other theoretical models in continuum space or with molecular simulations, be used as a free fit parameter. The second factor contains the effective elasticity of the molecule and depends both on its architecture and the mode of stretching, i.e. the conformations of the molecules inside the brush. The third factor contains the scaling of the brush height as a function of the grafting density. More generally, using scaling concepts, the relation $H \sim \sigma^{(1-\nu)/2\nu}$ has been derived for linear brushes [19,20], with the Flory exponent $\nu \approx 0.588 \approx 3/5$. For the monomer concentration inside the box we immediately get

$$c = \left(\frac{2}{\mathrm{v}}\right)^{1/3}(NK)^{1/3}\sigma^{2/3} \,. \tag{8}$$

Note that Eqs. (7) and (8) are fully general and valid for (uncharged) linear brushes as well as dendrimer brushes. Only the elasticity constant K varies, depending on the dendrimer's architecture and also on the assumed stretching scenario, which will be discussed in the following section.

2.2. Stretching scenarios

While the equations derived in the previous section contain the yet unspecified spring constant K, the latter depends on the typical conformations of the molecules and is now to be evaluated for dendrimers in different stretching scenarios.

Fig. 1(a) displays what we shall call the 'all up' conformation of a dendrimer: In this case, all free branches of the dendrimer are stretched up to the same height. Elementary algebra then yields the effective spring constant as

$$K_{\mathrm{au}} = \frac{3q^g}{N} \,, \tag{9}$$

which, with Eq. (7) and the total number of monomers per molecule,

$$N = N_S\,\frac{q^{g+1}-1}{q-1} \,, \tag{10}$$

leads to

$$H_{\mathrm{au}} = \left(\frac{\mathrm{v}\sigma}{6q^g}\right)^{1/3}N = \left(\frac{\mathrm{v}}{6}\right)^{1/3}\sigma^{1/3}N_S\,\frac{q^{g+1}-1}{q-1}q^{-g/3} \,. \tag{11}$$

N_S denotes the number of monomers in each spacer (note that in the present work we focus on symmetric dendrimers, in which N_S is

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