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Dendrimer solutions: a Monte Carlo study

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We study the conformational properties of dendrimers with flexible spacers in solutions over a wide range of concentrations from dilute solutions to melts. By combining large scale computer simulations using the bond fluctuation model with scaling arguments we identify the semi-dilute regime of dendrimers which is controlled by the concentration behavior of the linear spacers. Associated with this observation we find that the decrease in the size of flexible dendrimers is accompanied by increasing interpenetration between the molecules with increasing concentration of the solution. In the melt state we show that the size of individual dendrimers follows the scaling prediction for isolated dendrimers at the θ -point rather than that of collapsed dendrimers. The pair correlation functions between the centers of dendrimers indicate that for short spacers dendrimer solutions retain the morphological characteristics of simple liquids. For long spacers the functions reveal high penetration of neighboring dendrimers in the melt state. Our studies show that flexible dendrimers in solution can be understood with arguments similar to those of linear polymers. The role of generation is to influence the particular form of the crossover-function.

1. Introduction

While the conformational properties of isolated neutral dendrimers are relatively well understood, their behavior and effective interactions in semi-dilute and concentrated solutions are much less explored. It is well known that for linear polymer chains three concentration regions can be distinguished:¹ in the dilute regime at concentration below the overlap concentration, c^* , chains display the scaling behavior $R_g(0) \sim N^\nu$, with the Flory exponent $\nu \approx 3/5$. In the semi-dilute regime, above the overlap concentration, c^* , the size of chains shrinks and follows the relation $R_g(c > c^*) = R_g(0)(c/c^*)^{-1/8}$. In the semi-dilute regime, $c > c^*$, chains display the ideal behavior on large scales due to the screening of the excluded volume interactions according to $R_g(c > c^*) \sim N^{1/2}$. On smaller scales controlled by the correlation length, ξ , which is usually denoted as the blob-size in scaling language, excluded volume correlations persist. For high concentrations where the blob size is of the order of the segment length, c^{**} , ideal chain behavior is expected to dominate the conformation statistics on all scales. Similar scaling laws were shown to be valid for star polymers as well.²

By contrast, it is not clear whether the overlap concentration, c^* , plays a similar role in dendrimer solutions to that for linear

chains and whether similar scaling arguments can be found for dendrimers as they are successfully applied to linear chains. It is not even obvious in which sense a “semi-dilute” regime controlled by scaling laws does exist for dendrimers. More generally, the question is whether there might exist a scaling theory which involves the branching architecture and which of the concepts for linear chains survive in the case of general topology. In this context dendrimers are particularly interesting because of their perfect structure and thorough understanding of the properties of isolated molecules in dilute solutions. This question is of particular importance since existing reports about the concentration effects in dendrimers brought about different results and interpretations that partially contradict each other as we discuss below.

Experimentally the question of the size change of dendrimers in concentrated solutions was investigated with small angle neutron (SANS) scattering over a wide range of dendrimer mass fraction.³ Based on the obtained scattering functions it was suggested that the behavior of dendrimers in solutions is consistent with a model of non-interpenetrating collapse-like behavior of individual dendrimers. In particular, two concentration regimes of dendrimer solutions, referred to as dilute and concentrated solutions, respectively, were postulated. Dendrimers in a dilute solution behave as a dispersion of soft, spherical objects, and their size is not affected by the solution concentration. In highly concentrated solutions the size of the molecules decreases as their number density increases. It was argued that dendrimers collapse to maintain a volume fraction, which corresponds to the volume fraction of random close packing

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of hard spheres. It was further argued that dendrimers are completely non-interpenetrable, and that they have to shrink at high concentrations due to packing effects. Similar conclusions concerning the absence of interpenetration of dendrimers in close proximity were also drawn from other experiments based on Transmission Electron Microscopy,⁴ steady shear rheometry⁵ and small-angle X-ray scattering.⁶ We note that the absence of interpenetration effects does not *a priori* rule out a possible scaling behavior of concentration effects.

By contrast SANS experiments on the $G = 5$ generation poly(propylene imine) dendrimer solutions in D_2O led to the conclusion that the internal structure of these molecules is unaffected by interactions between them. It was pointed out that the poly(propylene imine) dendrimers behave as soft molecules with possible interpenetration at higher concentration but without a substantial impact on the conformational properties of individual dendrimers.⁷ The scattering intensities obtained with other SANS measurements for concentrated solutions of flexible dendrimers of fourth generation in a good solvent also revealed that the shape of dendrimers is practically independent of the solution concentration.⁸ Furthermore, the EPR (electron paramagnetic resonance) spectroscopy and fluorescence depolarization investigations of PAMAM (poly(amidoamine)) dendrimers ($G = 2, 4, 6$) in aqueous solutions indicated that the mobility of the molecules decreases dramatically above a concentration of 30%. This effect is mostly attributed to the viscosity increase at such high concentrations that occurs due to the self-aggregation of dendrimer molecules.⁹

The properties of dendrimers in solutions and the problem of interactions between the individual molecules inspired several theoretical and numerical studies. For instance, by combining the liquid integral equation theory and mean-field arguments an effective interaction potential of a Gaussian form between the dendrimers' centers of mass was derived. By applying this theory to concentrated dendrimer solutions theoretical structure factors were calculated and compared with experiments. The theory resulted in very good agreement with the experiment for concentrations below the overlap concentration by fitting the free parameters of the model.^{10–12} Using Gaussian effective pair potentials along with the mean field density functional theory the structure, phase behavior, and inhomogeneous fluid properties of binary dendrimer mixtures were also studied.¹³ However, the question of interpenetration and possible scaling in the semi-dilute regime cannot be answered by this approach. Moreover, the Gaussian approximation might be limited by excluded volume effects which lead to correlation effects of the dendrimer conformation, in particular for long spacers.^{14,15}

Monte Carlo simulations were employed to examine the role played by many-body effective interactions in concentrated dendrimer solutions made of flexible generation-4 dendrimers.¹⁶ By analyzing the radial distribution functions and the scattering functions between the centers of mass of dendrimers at various concentrations it was found that the effects of the many-body forces are small up to the overlap density and they might be ignored for open dendrimers with long bond lengths.¹⁶ The same simulation technique was used for a comparison between

the structural and thermodynamic properties of linear chains and dendrimers in solution. At low concentrations, due to the more compact architecture of dendrimers, solutions of dendritic polymers have a lower pressure than those of linear chains of the same molecular weight. In the extreme case of concentrated solutions low-generation dendrimers behave similar to linear chains, whereas the pressure of solutions containing high-generation dendrimers increases more rapidly with concentration. A generation dependent shrinking of the dendrimers with increasing concentration was found as well.^{2,17} A rational description of these findings, however, is still missing.

Molecular dynamics simulations addressed the degree of interpenetration of dendrimers, their morphology and organization as well as the dynamic behavior of dendrimers of generations 2 through 5 in the melt, respectively.^{18,19} The analysis of the dependence of the bulk density and molecular packing on the dendrimer molecular weight and intrinsic stiffness was done with this technique too.²⁰ It was found that in the melt of dendrimers as the generation number increases, the molecules assume a more spherical shape, and the degree of interpenetration of individual dendrimers decreases.¹⁸

To conclude, experimental observations contradict about the question of possible interpenetration effects in concentrated dendrimer solutions. Although a couple of simulation studies were carried out and theoretical approaches were presented a unifying model to rationalize the concentration effects in dendrimer solutions, similar to our understanding of linear chains, is missing. Moreover, the role of flexible spacers of various lengths has not been considered in detail and the range of parameters and size in direct monomer-based simulations was very limited. Motivated by these findings, we applied the bond fluctuation model to simulate dendrimer solutions in a wide range of monomer concentrations. In order to clarify the role of both the generation number G and spacer length S in the interactions between the molecules the calculations were done for dendrimers of a few generations and over a large range of spacer-length. Since our previous work indicated spacer-scaling as an essential concept to understand the size and correlation/scattering properties in single dendrimers¹⁵ we used the straightforward generalization of this idea to reflect the concentration effects. The comparison with the simulations shows that concentration dependent spacer scaling is indeed observed, and the generation influences the form of the corresponding crossover functions.

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

II. Model and simulation details

To inspect the dendrimers' behavior we carry out Monte Carlo simulations using the bond fluctuation model (BFM),^{21,22} for details of the implementation see our previous work.¹⁵

More specifically, we examine dendrimer solutions at finite monomer concentrations ranging between $c = 0.01$ and $c = 0.6$ of movable dendrimers with the core of two bonded monomers, branching functionality $f = 3$ in an athermal solvent. We note that a concentration (lattice occupation) of $c = 0.6$ in the BFM corresponds to a dense melt. Dendrimers with such an architecture of their skeleton can be considered as typical in experiments and applications. For example, PAMAM dendrimers can be synthesized up to generation 10 and poly(propylene imine) dendrimers up to generation 5.²³ Spacer length can also be varied in a wide range up to 20.²⁴ Before simulation runs, dendrimers with generation G , spacer length S and branching functionality $f = 3$ are generated by a divergent growth process in the ascending order of the internal generation number $0 \leq g \leq G$ starting from the core ($g = 0$) of two bonded monomers. Thus, the molecules consist of

$$N = 2 + 4S(2^G - 1) \quad (1)$$

monomers,

$$N_t = 2^{G+1} \quad (2)$$

of which are the terminal groups. In Table 1 we display the characteristics of the dendrimers simulated in this work. Within the applied Monte Carlo scheme configurations are sampled using the BFM preserving the bond constraints and the excluded volume, all the results obtained are athermal as far as the solution properties are concerned.²⁵ Thus we are interested in studying the most generic features of dendrimer solutions on the coarse grained level. We leave aside all the peculiarities of real systems and bring out the most fundamental properties characteristic of a broad class of dendrimer solutions.

As aforementioned all dendrimers were generated by a simultaneous growth process where at each step the sample was equilibrated according to the standard BFM algorithm. At the second stage we let the systems reach their equilibrium states by just observing the behavior of various calculated quantities such as the radius of gyration and density profiles. An equilibrium state was considered achieved once these quantities revealed no systematic changes. Only then production runs were performed. We note that the growth algorithm as such produces more compact structures which would underestimate the overlap if not fully relaxed. Typically the dendrimers were equilibrated for about 10^6 MCS (Monte Carlo steps; in one MCS on average each monomer is selected to be moved in a randomly chosen, one of the six directions by a single lattice unit), whereas averages were calculated for about 10^4 equilibrium configurations stored every 10^4 th MCS.

Table 1 Structural parameters (G and S) and the resulting degree of polymerization

G	S				
	4	8	12	16	32
3					898
4	242	482	722	962	
5	498	994	1490	1986	

III. Results

A. Radius of gyration and spacer scaling

In the upper part of Fig. 1 we display the normalized radius of gyration of dendrimers, R_g/R_{g0} , as a function of the rescaled monomer concentration c/c^* . Here, R_{g0} is the radius of gyration of isolated dendrimers ($c = 0$) obtained in our previous work,¹⁵ and c^* is the overlap concentration defined as

$$c^* = \frac{8N}{\frac{4\pi}{3}R_{g0}^3} \quad (3)$$

where N is the number of monomers in the dendrimer. It is well seen that the size of dendrimers decreases monotonously as their concentration in the solution is increased. Our simulations are not in agreement with the segregation (non-interpenetration) hypothesis as clearly seen from Fig. 1(a) (dashed line). Actually, if the dendrimers were segregated in the semidilute regime

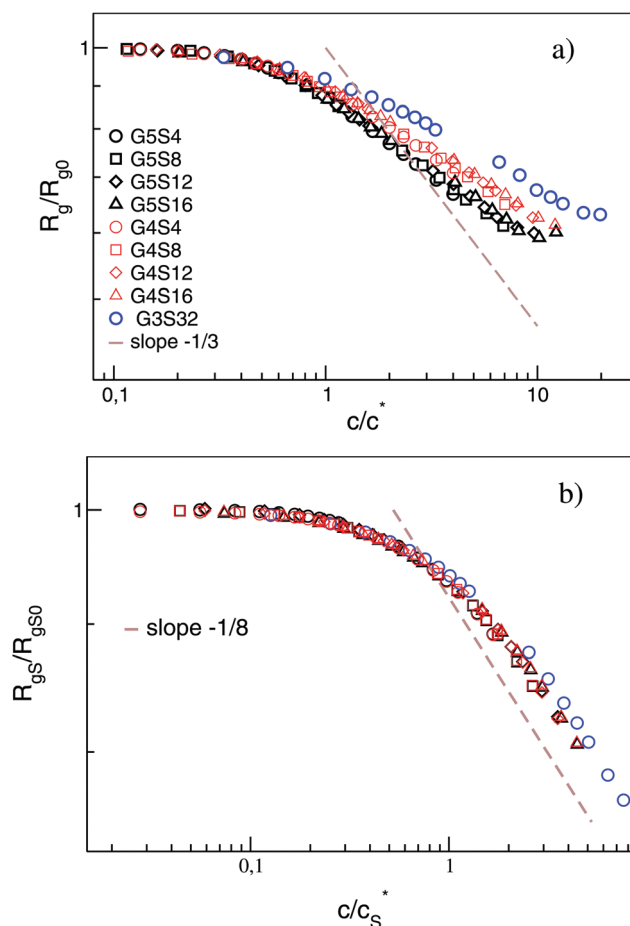


Fig. 1 (a) Rescaled radius of gyration of dendrimers, R_g/R_{g0} , versus the rescaled monomer concentration, c/c^* , where R_{g0} is the radius of gyration of isolated dendrimers and c^* is the overlap concentration of the dendrimers. For dendrimers of the same generation the scaling is appropriate. The dashed line indicates the expected slope if the dendrimer would stay segregated by concentration. (b) Radius of gyration of the spacers for all the dendrimers presented in (a). Very good scaling and the slope predicted for semi-dilute solutions of linear chains indicate that spacer blobs behave like chains in semi-dilute solutions.

their size should decrease with concentration according to $R_g/R_{g0} \sim (c/c^*)^{-1/3}$, which is clearly not the case.

On the other hand, for the given generation numbers G4 and G5 the applied rescaling procedure results in a master curve for all the inspected spacer lengths. In general, Fig. 1 shows that three concentration regions can be distinguished: in the dilute region for concentrations below the overlap concentration, c^* , the dendrimers behave like isolated molecules with their size unaffected by any interactions with the other dendrimers. In the semi-dilute region above the overlap concentration, $c > c^*$, the dendrimers shrink and their size follows the relation for fixed generation G :

$$R_g/R_{g0} = f_G(c/c^*). \quad (4)$$

We note that for fixed generation c^* is proportional to the overlap concentration for spacers as denoted in eqn (5) below. The crossover from dilute to semi-dilute solution behavior takes place at $c \simeq c^*/2$.

In Fig. 1(b) we display the behavior of individual spacer chains with concentration scaling of the corresponding linear polymer solution. In this case

$$c_S^* = \frac{8S}{\frac{4\pi}{3}R_{gS0}^3}. \quad (5)$$

The results indicate that spacer chains behave as in free solution in agreement with the spacer scaling of isolated dendrimers, see ref. 15. The asymptotic slope of the double-logarithmic presentation in Fig. 1(b) corresponds to the well-known scaling prediction for semi-dilute solutions of linear chains: $R_g \sim c^{-1/8}$ (using $\nu \simeq 3/5$).

In the concentrated region typically given by $c > 10c^*$ for our parameters the dendrimers exist in shrunken conformations constituting a melt state. Here, we can distinguish two cases (a) θ -conformation and (b) compact conformations. Note that the θ -state for dendrimers is not ideal and has been investigated for single dendrimers in detail.²⁶ In the θ -state the scaling behavior of the dendrimer size is given by²⁶

$$R_g/S^{1/2} \sim [(N/S)G]^{1/4}. \quad (6)$$

This behavior can be seen in Fig. 2(a), while Fig. 2(b) shows the expected behavior for the compact (poor solvent) state. We can conclude that dendrimers with flexible spacers up to rather high generation do not segregate but intersperse similar to linear polymers in melts. Further we can show that a crossover from the good solvent to the θ -solvent occurs by increasing the concentration.

B. Interpenetration of dendrimers

To quantify the degree of interpenetration between the dendrimers we calculated the mean number, n_0 , of monomers that occupy the volume of a certain molecule, $\frac{4\pi}{3}R_g^3$, and do not belong to it. The results are displayed in Fig. 3. It is clearly seen that as the solution concentration is increased the effect of interpenetration between the molecules is more and more pronounced. Note that this phenomenon is affected considerably by the actual value of

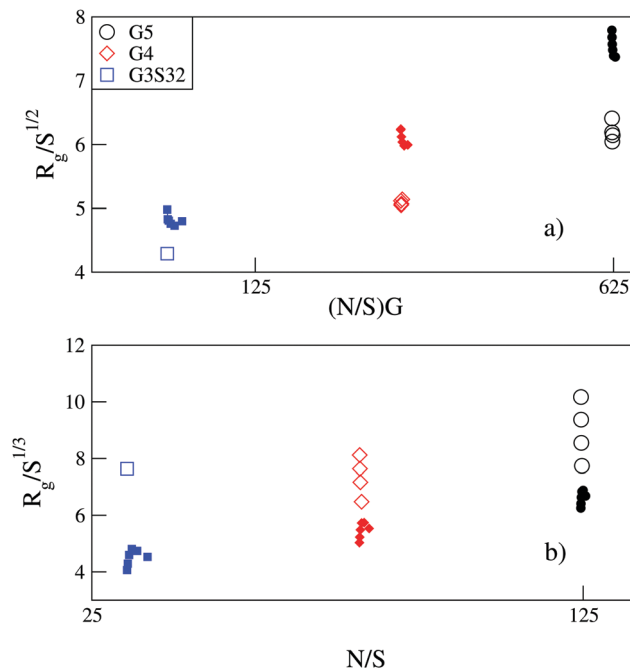


Fig. 2 Rescaled radius of gyration of dendrimers at $c = 0.6$ (open symbols) according to the two different scaling predictions for isolated dendrimers (a) at the θ -point, (b) in a poor solvent.²⁶ For G4 and G5 all spacer length parameters of Fig. 1 are used. More pronounced collapse of the data seen for case (a) indicates that in the limit of high monomer concentrations individual dendrimers in solution follow the behavior at the θ -point rather than in a poor solvent. Filled symbols in (a) were obtained for isolated dendrimers at the θ -point and in (b) in a poor solvent.²⁶

spacer length S . In Fig. 3(b) we display the number of overlapping spacers plotted as a function of the relative concentration in units of spacer-overlap. Again, the results for different spacer length collapse which indicates a self-similar behavior on the scale of spacers as in semi-dilute solutions of linear chains.

The degree of interpenetration between the dendrimers and the morphology of the solutions can also be analyzed using the pair correlation function, $g_{cm,cm}$, between the centers of mass of the dendrimers. As seen in Fig. 4(a) and (e) for dendrimers with short spacers, $S \leq 4$, in a diluted solution the exclusion zone separating the dendrimers is about $2R_g$ wide, and practically the molecules do not overlap. The interpenetration phenomenon occurs as the solution concentration is further increased. However, even in the melt state, $c = 0.6$, the centers of mass of the dendrimers stay apart from each other at the distance R_g . Note that due to the oscillations of the pair correlation function the morphology of the solutions as a whole corresponds to that of isotropic simple liquids.

To some extent our observations can resolve some seemingly contradicting results of the experimental works reporting non-interpenetrating dendrimers in concentrated solutions. In ref. 3, for instance, dendrimers were used with four C–C bonds in the spacer groups²⁷ which is even slightly shorter than the Kuhn-length of polyethylene, and thus corresponds to $S = 1$ in our notation, where spacer-scaling clearly ceases. Our results show that interpenetration can be suppressed by short spacers

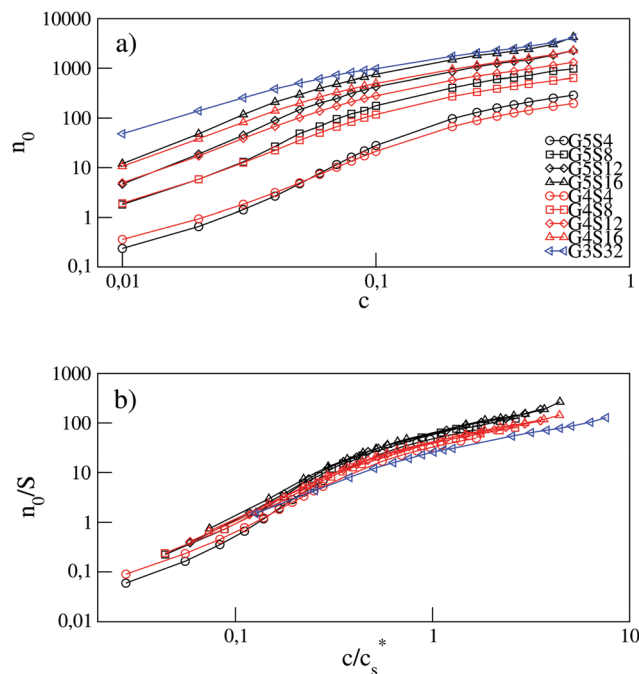


Fig. 3 Interpenetration between dendrimers: (a) mean number of monomers, n_0 , not belonging to the given dendrimer that are localized inside its volume versus the monomer concentration c . (b) n_0/S versus the monomer concentration, c/c_s^* , rescaled by the spacer self-density c_s^* .

at higher generation, which might be additionally related to increased stiffness of the whole dendrimer.

As spacers become longer this picture is retained for the diluted solutions only. In the case of concentrated solutions the exclusion zone as well as the oscillations tend to disappear due to pronounced interpenetration of the dendrimers, see Fig. 4(b)–(d) and (f)–(i). In this case the morphology characteristics of simple liquids is lost. Interestingly, for G5 and G3 dendrimers we observe a peak in the pair correlation function at short distances between the centers of mass, which is most pronounced for $S > 8$. This corresponds to conformations where the centers of two molecules even prefer to be on top of each other.

IV. Summary and conclusions

Unlike linear chains, the concentration behavior of dendrimers has not yet been understood by simple scaling arguments. The behavior of dendrimers, depending on their generation, interpolates between branched polymers and soft colloids. Previous works led to different, partially contradicting results in particular regarding the role of mutual interpenetration of the macromolecules in the concentrated state. In this work we have used extensive Monte Carlo simulations based on the bond fluctuation model to investigate the concentration behavior of dendrimers

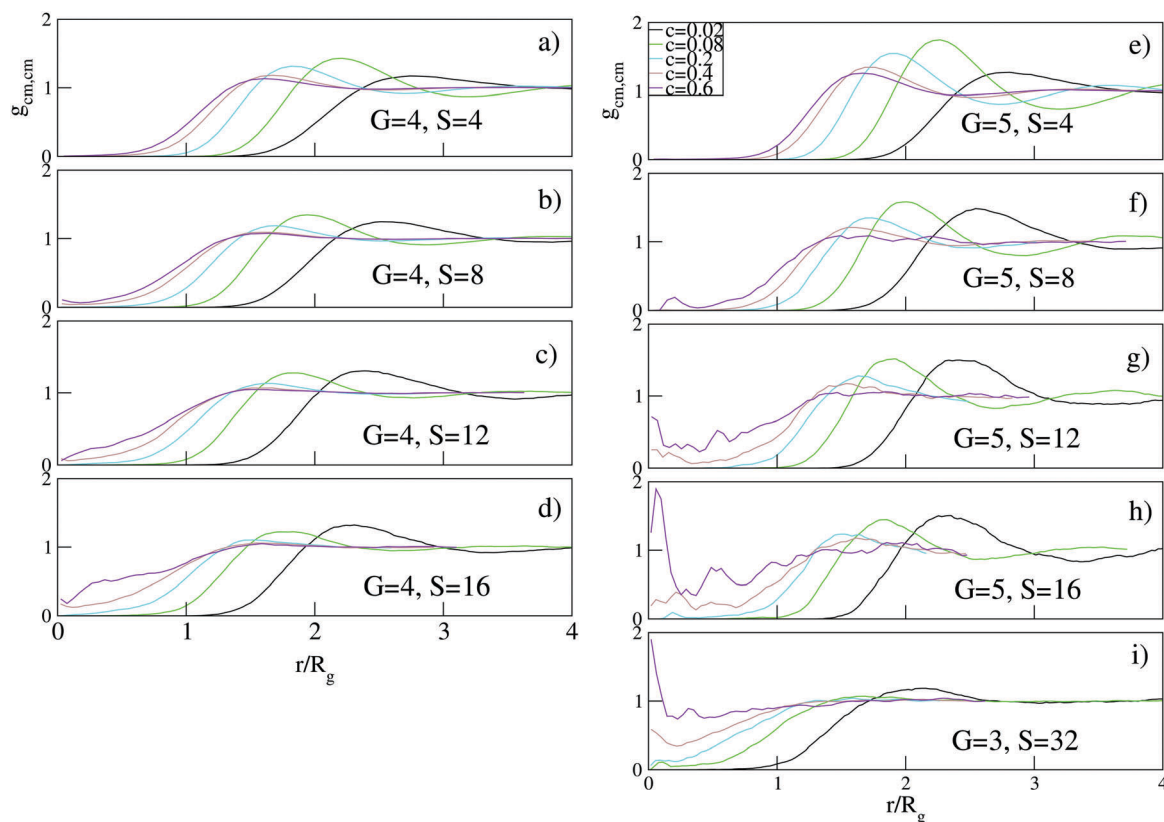


Fig. 4 Pair distribution function, $g_{cm,cm}$, between the centers of mass of two dendrimers in solutions at various concentrations as a function of the distance between the dendrimers. The distance is rescaled by the radius of gyration of dendrimers obtained at the given concentration.

with flexible spacers of various spacer lengths and different generations. We note that the necessity to simulate many dendrimers and a larger range of concentrations makes such studies computationally expensive and here we have concentrated particularly on the spacer-length dependence of dendrimers of generation-5, 4 and a comparison to samples of generation-3 with long spacers. Our studies have addressed the universal behavior of flexible dendrimers, *i.e.*, we have investigated the role of dendritic topology in the concentration behavior of otherwise flexible macromolecules.

We have shown that concentration scaling with respect to spacer length leads to master plots for a given generation for the size of the dendrimer. In particular the radius of gyration of the spacer chains follows the scaling behavior as predicted for solutions of linear chains of the same length. This corresponds to our former results of single dendrimers which showed the dominating role of excluded volume interactions of the spacer chains because of the large conformational freedom of the dendrimer up to high generations.¹⁵ If the overlap density of spacer chains is reached higher concentrations lead to a similar response of the spacers to that as if the dendritic topology between them did not exist.

The influence of the generation is two-fold: first, there exists a range of concentrations between the overlap of the dendrimers and the full overlap of the spacers, *i.e.*, $c^* < c < c_s^*$. This leads to interpenetration and partial screening of the excluded volume interactions of the whole dendrimer. Second, the connectivity within the dendrimer has some influence on the way the spacers interact with each other and between overlapping dendrimers. Both effects shift the crossover values of the concentration and deform the scaling function. As a result there exists no universal scaling function for all generations.

Spacer-scaling could also be achieved without the mutual interpenetration of the dendrimers. In this case the “self-concentration” of each compressed dendrimer would create a semi-dilute solution for its spacers. Several results of our simulations speak against this scenario. Let us start with the melt state. Here, segregation would lead to collapse-like scaling of the size of individual dendrimers. Instead we see rather open conformations which correspond to θ -scaling of isolated dendrimers which we have also studied in detail in previous work.²⁶ Also, the change of the extension of the dendrimers as a function of the concentration is very clearly below the slope of $1/c^{1/3}$ in the full range of concentrations up to the dense state.

The mutual overlap between the dendrimers can be directly measured by calculating the number of monomers of other dendrimers inside the volume of gyration of a tagged dendrimer. This number increases with concentration well beyond the overlap threshold of the dendrimers despite the fact that the radius of gyration shrinks. Strong indication for mutual interpenetration is obtained by inspecting the pair-correlation function between the centers of the dendrimers. While dendrimers of higher generation and short spacers display depletion similar to spheres in simple fluids, larger spacers lead to a peak of the pair-correlation function at high concentrations inside the radius of gyration, even at zero for long spacers. Qualitatively different

behavior for short and long spacers is a possible explanation for the seemingly contradicting experimental results reported in the literature.

To conclude, we have shown that dendrimers with flexible spacers display mutual interpenetration in the concentrated regime which leads to shrinking of the radius of gyration from good solvent scaling to θ -scaling. On the level of the spacers semi-dilute scaling of linear chains can be identified.

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