Colloid–dendrimer complexation†

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We consider amphiphilic dendrimers of the second generation by an appropriate modeling of the intermonomer interactions, introducing suitable attractive microscopic potentials between the inner, solvophobic monomers and repulsive potentials between the outer, solvophilic ones. By employing Monte Carlo simulations, we examine the selective adsorption of such dendrimers onto compact colloidal particles that attract either the core or the shell of the dendrimer, while repelling the rest of the molecule. We measure the effective colloidal–dendrimer interaction and we analyze in detail the conformations of the dendrimer close to the colloid in dependence of the radius of the latter and the microscopic energy parameters. A dendron-by-dendron adsorption of the dendrimer on the colloid under suitable conditions is discovered.

I. Introduction

Dendrimers form a special class of macromolecules, which have an enormous potential due to their regularly branched architecture. Although they were initially considered to be a curiosity, shortly after their first synthesis by Vögtle and coworkers,† they gradually drew vivid interest from various branches of science. The building blocks of an idealized dendrimer consist of identical monomeric units that have a functionality larger than two, i.e., they can chemically bind to three or more of the same type of units. Starting with a single or a pair of these units, one can grow in a controlled fashion successive generations by chemically binding a new unit to all available binding sites. It is, however, by no means necessary that all units are truly identical; for instance, it is possible to tailor a dendrimer by using a different type of unit for each generation and, in fact, even within a generation not all units need be the same.2–4

The enormous flexibility to choose the building units of dendrimers, in combination with a well-defined structure, makes them an interesting object of research in physics, chemistry and medicine, and has lead to applications in gene transduction,5 drug delivery,6,7 bio-sensors8 and contrast agents.9 Most research on such systems to-date has been restricted to their physical and chemical properties, and to their behavior in solution.10,11

The fact that by carefully choosing the different constituents forming the dendrimers the overall behavior can be manipulated, also makes them very interesting from a fundamental point of view, because by tuning the generation number and/or bond stiffness, they can be made to interact with each other as hard, compact-sphere-like objects as well as very soft, blob-like objects.12–14 This last property renders dendrimers into ideal candidates for the study of cluster formation.15–19 Since dendritic macromolecules of lower generation numbers have a rather open structure, they can easily overlap with each other and their centers-of-mass can come arbitrary close to one another. Such a soft interaction potential is required (but not sufficient) for the formation of cluster solids. The crystal lattice of such a solid will not change its lattice constant under compression but will rather incorporate more particles per lattice site. Mladek et al.18 predicted that amphiphilic dendrimers are suitable candidates to exhibit this behavior, which could possibly be enhanced even more by the presence of nearby surfaces.19

In a previous study,20 the effect of planar walls on the behavior of amphiphilic dendrimers of a second generation has been analyzed. Since these molecules are formed by a solvophobic core and a solvophilic shell, they exhibit a “dense-shell” structure,18 rather than the usual “dense core”-forming dendrimers.10,21–23 The presence of an interacting surface evidently affects the conformations of the dendrimers and, depending on whether the core or shell monomers are attracted by the surface, two archetypes of conformations have been found,20 which were named “dead spider” and “living spider” respectively. Here we concentrate on the effect that the curvature of a wall has on the adsorption behavior of these amphiphilic dendrimers by making use of Monte Carlo simulations.24 The rest of the paper is organized as follows. In Section II we highlight the main features of the dendrimer model18 and introduce the curved surface by means of an idealized spherical colloid. By simulating a single dendrimer and a colloidal sphere, we obtain the effective dendrimer–colloid interaction in Section III. In Section IV we analyze the change in conformation of the dendrimers due to the adsorption interaction. Since the adsorption behavior is also affected by the dendrimer concentration, we examine the influence of the latter in Section V and we finish in Section VI with a summary and concluding remarks.

II. Model

To simulate amphiphilic dendrimers, we adopt the model introduced by Mladek et al.18 We consider dendrimers of generation $G = 2$ with two central core particles and functionality $f = 3$. The resulting total of 14 monomers are divided in two classes, which
are required to obtain the amphiphilic property. The two central monomers and the four monomers of the first generation form the solvophobic core particles, which we label by the subscript C. The eight monomers of the second generation form the solvophilic shell of the dendrimer and are labeled by the subscript S.

Interactions between any two monomers (bonded or not), separated by a distance \( r \), are modeled by the Morse potential\(^8\) given by:

\[
\beta \Phi_{\text{Morse}}^{(m)}(r) = \varepsilon_{\text{Morse}} \left( e^{-\sigma_{\text{Morse}} r} - 1 \right)^2 - 1, \quad \mu \nu = \text{CC, CS, SS} \quad (1)
\]

where \( \sigma_{\text{Morse}} \) is the effective diameter between two monomers of species \( \mu \) and \( \nu \) and \( \beta = (k_B T)^{-1} \) the inverse temperature, \( k_B \) denoting Boltzmann’s constant. This potential is characterized by a repulsive short-range behavior and an attractive part at long distances, whose depth and range are parametrized \( \varepsilon_{\text{Morse}} \) and \( \sigma_{\text{Morse}} \), respectively. The diameter \( \sigma \) of the core monomers is chosen to be our unit of length.

Bonding between two neighboring monomers within the dendrimer is modeled by the finite extensible nonlinear elastic (FENE) potential, which is given by:

\[
\beta \Phi_{\mu \nu}^{\text{FENE}}(r) = -K_{\mu \nu} R_{\mu \nu}^2 \log \left[ 1 - \left( \frac{r - l_{\mu \nu}}{R_{\mu \nu}} \right)^2 \right], \quad \mu \nu = \text{CC, CS} \quad (2)
\]

where a spring constant \( K_{\mu \nu} \) restricts the monomer separation to be within a distance \( R_{\mu \nu} \) from the equilibrium bond length \( l_{\mu \nu} \).

In order to achieve the intended amphiphilic behavior of the dendrimers, while staying within the limits of what can be realized in experiments, we use the set of parameters (see Table 1) from the D\(_2\)-model dendrimer,\(^8\) which also enables us to compare the results with those stemming from the simulation of dendrimers in the vicinity of a planar wall.\(^20\)

To model the colloidal particle on which the dendrimers adsorb, we make use of the same ideas as those employed for modeling a planar wall.\(^20\) We assume that the colloidal particle of radius \( R \) consists of a homogeneously distributed collection of Lennard-Jones type particles with diameter \( \sigma_{LJ} \) and, without loss of generality, density \( \rho \sigma_{LJ}^3 = 1 \). Consider first a simple, power-law pair potential acting between a volume element of the colloid and a hypothetical test (monomer) particle:

\[
\beta \Phi_{\nu \nu}^{(t)}(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^n \quad (3)
\]

with some length scale \( \sigma \) and dimensionless energy scale \( \varepsilon \). Then, the total interaction felt by a particle at position \( \mathbf{r} \) outside the spherical colloid is given by

\[
\beta \Phi_{\text{sphere}}^{(t)}(r) = \beta \int d^3r' \varepsilon_{\nu \nu}(r') \Theta(R - |r'|) \quad (4)
\]

where \( r \equiv |\mathbf{r}| \) and \( \Theta(z) \) is the Heaviside step function. This integral can readily be carried out to yield:

\[
\beta \Phi_{\text{sphere}}^{(t)}(r) = \frac{8\pi \rho \varepsilon \sigma^n}{x(n-2)(n-3)(n-4)} \left[ \frac{(n-3)X_s - x}{(x - X_s)^{n-3}} \right] \left[ \frac{(n-3)X_c + x}{(x + X_c)^{n-3}} \right] \quad (5)
\]

where \( x = \rho \sigma^n \) and \( X_c \equiv R/\sigma \). The above potential diverges as the test particle approaches the surface of the sphere from above, \( r \rightarrow R^+ \), so that the colloidal particle is indeed impenetrable to individual monomers. Further, it manifestly depends on the dimensionless energy and density parameters \( \varepsilon \) and \( \rho \sigma^n \) only through their product, so that a change in the internal density of the colloid can be re-adsorbed into a modification of \( \varepsilon \). Thus, we vary here only the latter quantity, fixing the former at the value \( \rho \sigma_{LJ}^3 = 1 \) quoted above.

Since we consider amphiphilic dendrimers, where core and shell particles interact differently, the interactions of the monomers with the colloid will also differ and can either have an attractive range or are purely repulsive. For those monomers that experience an attractive interaction to the colloid, we employ the usual Lennard-Jones interaction between the monomers and the point particles forming our colloid. The resulting interaction with a monomer at a distance \( r \) from the colloid center therefore follows from eqn (5) and is given by

\[
\Phi_{\text{sphere}}^{(\text{att})}(r) = \Phi_{\text{sphere}}^{(t)}(r) - \Phi_{\text{sphere}}^{(s)}(r) \quad (6)
\]

where \( \sigma = (\sigma_{LJ} + \sigma_{\mu})/2 \) and \( \mu \) corresponds to either a core or shell monomer, depending on which of those is attracted to the sphere.

To model the repulsive interaction of the colloid with the remaining species of monomers, we use the same method as for the shifted Lennard-Jones type of interaction, i.e., we determine the distance \( r_\star \), at which the minimum energy in the interaction (6) is found, and apply the appropriate truncation and shift to the attractive potential of eqn (6), rendering the total interaction purely repulsive, viz.:

\[
\Phi_{\text{sphere}}^{(\text{rep})}(r) = \begin{cases} 
\Phi_{\text{sphere}}^{(\text{att})}(r) - \Phi_{\text{sphere}}^{(t)}(r) & r \leq r_\star, \\
0 & r > r_\star. 
\end{cases} \quad (7)
\]

In what follows, we will switch between the case in which the core monomers are attracted to the colloid and the shell ones repelled from it and the complementary one. To simplify the parameters, we chose \( \sigma_{LJ} = \sigma_c \). Note that in the limit \( R \rightarrow \infty \) this reduces to the planar wall interaction.\(^20\)

### III. The effective sphere–dendrimer interaction

In order to investigate the effect colloidal particles have on nearby dendrimers, we measure the effective dendrimer–colloid potentials. Hereto, we perform Monte Carlo simulations in the canonical ensemble, i.e., at constant particle number \( N \), simulation box volume \( V \), and temperature \( T \). In particular, we simulate the interaction of a single dendrimer, represented in a coarse-grained fashion by its center-of-mass, with a single colloidal particle. One method to calculate the effective interaction is by

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Overview of the monomer interaction potential parameters used between core (C) and/or shell (S) monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>( \varepsilon )</td>
</tr>
<tr>
<td>CC</td>
<td>0.714</td>
</tr>
<tr>
<td>CS</td>
<td>0.014</td>
</tr>
<tr>
<td>SS</td>
<td>0.014</td>
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<tr>
<td>FENE</td>
<td>( K / \sigma_c )</td>
</tr>
<tr>
<td>CC</td>
<td>40</td>
</tr>
<tr>
<td>CS</td>
<td>30</td>
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applying the umbrella sampling technique\textsuperscript{24} to constrain the center-of-mass of the dendrimer within a certain range from the spherical particle, measure the probability of finding the dendrimer at a given distance, and combine such probability profiles in order to obtain the full effective interaction potential.\textsuperscript{20}

Here we adopt an alternative but equivalent method, by keeping the center-of-mass of the dendrimer at a fixed distance from the spherical particle. This can easily be achieved by using a Monte Carlo type of move in which a random displacement of one of the monomers is generated and combined with a correcting translation of the full dendrimer in the opposite direction. A summation of the individual forces on each of the monomers by the colloid then yields the effective force of which the ensemble average is calculated. For reasons of symmetry this average will be directed along the vector connecting the centers-of-mass of the sphere and the dendrimer. Finally, the effective dendrimer–colloid potential can be obtained by integrating the force over the distance.

We will distinguish two types of colloidal particles that differ in their interaction with the core and shell monomers of the dendrimers. The first type is characterized by an attractive interaction with the core and a repulsive interaction with the shell (CA-SR).\textsuperscript{20} Fig. 1(a) shows the effective interaction for a colloid with a radius \( R_s = 8\sigma_c \) and several different interaction strengths \( \varepsilon \). In order to facilitate the comparison with results of different sphere diameters and the limiting case of a planar wall, the interaction is plotted as a function of the distance \( h \) between the center-of-mass of the dendrimer and the surface of the spherical colloid. Similar to the case of a planar wall, the interactions remain purely repulsive for relatively weak values of \( \varepsilon \leq 1 \). For intermediate interaction strengths, the dendrimer experiences a repulsive barrier at a distance of roughly \( 4\sigma_c \) and an attractive well at closer distances. For \( \varepsilon \geq 3 \), the barrier disappears almost completely.

The second type of spherical particle we consider, has the opposite properties, \( i.e., \) it repels the core monomers of the dendrimers and attracts the shell monomers (CR-SA). For the same sphere radius \( R_s = 8\sigma_c \) the resulting effective interaction potential is shown in Fig. 1(b). Since in this case the shell monomers that are close to the sphere are already attracted, the dendrimer does not experience a barrier, but only an attractive well, and only at small distances do the short-range repulsive forces become dominant. A striking difference between the two types of colloids can be observed for the large values of \( \varepsilon \).

Whereas in the CA-SR type the effective interaction remains rather smooth, it turns out that for a colloid of the type CR-SA the interaction becomes more irregular. As will be explained in the next section this is not an artifact but it is rather related to structural changes in the dendrimer itself.

It is evident that the curvature of the colloidal sphere has a large influence on the adsorption behavior of the dendrimer. For large radii, the curvature is negligible and one could easily describe the system by using a planar wall. For smaller radii, especially those of the same order of magnitude as the dendrimer itself, the dendrimer will behave very differently. In order to examine this more closely, we compare in Fig. 2 the effective dendrimer–colloid interaction obtained by Monte Carlo simulations for different radii and for both types of spheres.

The fact that the interaction becomes weaker on decreasing the sphere radius is not surprising. This is a direct consequence of the fact that the total interaction of the colloidal particle scales with the size of the sphere as follows from eqn (5). The observation that the interaction strength remains finite at a distance \( h = 0 \) can also easily be explained, by realizing that the center-of-mass of the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Effective interactions between a colloidal particle with radius \( R_s = 8\sigma_c \) and a single dendrimer for different values of interaction strength \( \varepsilon \): (a) the CA-SR case; (b) the CR-SA case. The interaction is plotted against the separation \( h \) between the dendrimer’s center-of-mass and the colloidal surface.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Effective dendrimer–colloid interactions for the two different dendrimer types, varying the energy parameter \( \varepsilon \) and the colloidal radius \( R_s \), as indicated in the legends. (a) CA-SR with \( \varepsilon = 0.5 \), (b) CA-SR with \( \varepsilon = 1.0 \), (c) CR-SA with \( \varepsilon = 0.5 \), and (d) CR-SA with \( \varepsilon = 2.0 \). The interaction is plotted against the distance \( h \) between the colloidal sphere and the center-of-mass of the dendrimer. The insets in panels (b) and (c) show details at zoomed-in regions of \( h \).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Simulation snapshots of the two archetypes of dendrimer conformations near a colloidal sphere of radius \( R_s = 8\sigma_c \). (a) “Dead spider”-conformation for a CA-SR type of sphere. (b) “Living spider”-conformation for a CR-SA type of sphere.}
\end{figure}
dendrimer can actually lie within the sphere, due to the curvature of its surface. Whereas the individual interactions of the monomers at this position would indeed diverge, a dendrimer that lies against the surface will follow the curvature, thus adopting a conformation for which the center-of-mass falls within the colloidal particle. This is illustrated in Fig. 3(b) where a dendrimer in the vicinity of a sphere of the CR-SA type with radius \( R_s = 8\sigma_c \) is shown. Consequently, the effective interaction will still diverge, but at distances \( h < 0 \) provided the sphere is large enough. For small spherical particles the effective interaction remains finite, because the dendrimer can fold itself around it.

For relatively weak interactions, \( \varepsilon \ll 1 \), in the case where the colloidal particle attracts the core monomers (CA-SR–type), the interaction remains purely repulsive for all radii, as can be seen in Fig. 2(a) and (b). The plateaus found for the large spheres, see insets of Fig. 2(b), correspond to structural rearrangements of the dendrimer and disappear for smaller values of the sphere radius.

In the opposite case of a dendrimer of the CR-SA type, shown in Fig. 2(c) and (d), we observe that the depth of the attractive range decreases with decreasing sphere radius and the minimum shifts towards the center, which signals that the center-of-mass of the dendrimer can reach deeper in the interior of the sphere.

**IV. Dendrimer conformations**

The natural conformation for an isolated amphiphilic dendrimer is to have the core monomers, in general, in close proximity to the center-of-mass and that the distance of its monomers from the center increases with the generation number. This is a direct consequence of the bonds within the macromolecule. Although for simple, athermal dendrimers one can observe that for entropic reasons outer monomers can be found close to the center, this is just a relatively small fraction of the overall monomer population. This process of back-folding is easily suppressed by the presence of additional interactions, e.g., in charged dendrimers.\(^{26}\) Also in the present case of amphiphilic dendrimers, the presence of solvophilic end groups in the shell and a solvophobic units in the core will retain the natural dendrimer structure in bulk.

The vicinity of nearby objects, however, will affect the internal structure of the dendrimers. For planar walls, two archetypes of configuration were found.\(^{26}\) In the case of a CA-SR wall, the core monomers are found near the wall and the shell particles are repelled by it. For the other type of wall, the CR-SA case, it is the shell monomers that adsorb to the surface. These two different dendrimer conformations, the “dead spider” and “living spider” respectively, are also found for colloidal spheres as illustrated in Fig. 3. It is clear that the conformations become deformed due to the curvature of the surface, an effect that increases with smaller sphere radii.

To analyze the conformations in more detail, we consider the radial density profiles of the monomers around a colloidal sphere. In Fig. 4 we show radially-averaged monomer densities around a colloid with radius \( R_s = 8\sigma_c \) and interaction strength \( \varepsilon = 1.0 \). Two different, fixed distances \( h \) between the dendrimer’s center-of-mass and the colloidal surface are shown: (a) \( h = 3\sigma_c \) and (b) \( h = 6\sigma_c \). The profiles correspond to core monomers of generation 0 (Z), generation 1 (C), and shell monomers (S).

Similar observations can be made in the case of a sphere of type CR-SA. Results for a sphere with radius \( R_s = 8\sigma_c \) are shown in Fig. 5 for four different distances of the dendrimer to the colloidal surface, where we focus on a rather strong interaction energy, \( \varepsilon = 3.0 \). The reason for this is to examine more closely the irregular behavior in the effective interaction displayed in Fig. 1(b). For a small dendrimer-center to colloid-surface distance, \( h = 1.5\sigma_c \), Fig. 5(a), the center-of-mass of the dendrimer lies deep within the sphere (the individual monomers are always centered on the sphere).
found outside the sphere). The shell monomers are found in a very narrow range close to the surface, which is due to the attraction exerted on them. The core monomers, which are repelled, are found somewhat further away. If the dendrimer distance to the colloidal surface is increased to \( h = 3\sigma_c \), Fig. 5(b), the single peak distribution of the shell monomers has been split in a double peaked structure, whereas the core monomers distribution has become more narrow. It should be noted, however, that the central core monomers (Z) are on average further away from the sphere center than the core monomers of generation 1 (C'). The cumulative profiles shown in the inset, reveal that exactly one of the shell monomers has been detached from the surface of the sphere.

Fig. 5(c) shows the profiles for a distance \( h = 4\sigma_c \). At this distance also the single-peaked distribution of the core monomers of generation 1 has become bimodal. The cumulative profiles indicate that two shell monomers and one core monomer, i.e., one branch of the dendrimer, has been freed from the sphere and extends into the implicit solvent. If the dendrimer-to-colloidal surface distance is increased to \( h = 5\sigma_c \), as can be seen in Fig. 5(d), another shell monomer has left the surface of the sphere. This behavior indicates that the adsorption of the dendrimer on a sphere of the type CR-SA is a gradual process in which on approaching the sphere the natural conformation of the dendrimer is modified in a step-by-step fashion and explains the irregular behavior in the effective interaction shown in Fig. 1(b).

It should be noted that a strong interaction was used to highlight this behavior, but that this scenario also applies to weaker interactions. For the case of a CA-SR sphere, a similar behavior can be observed albeit less pronounced.

Fig. 6 shows the density profiles for the more extreme case of a very small sphere with radius \( R_s = \sigma_c \) of the type CA-SR. Since the total interaction scales proportional to the volume of the sphere, it is rather weak. In fact, although the effective interaction in this case is repulsive, the colloid is small enough to be placed inside the dendrimer. In other words, instead of the dendrimer being adsorbed on the colloid, we find that the colloid gets absorbed by the dendrimer. The density profiles for the shortest distance between the center-of-mass and the colloid indicate that the colloid sticks to typically two of the core monomers, which is energetically the most favorable. If the colloid is moved away from the center-of-mass, such a tight binding to two core particles is no longer possible. For the larger distance, the presence of the colloidal sphere only distorts the natural conformation of the dendrimer to expel the shell monomers from its direct vicinity. This is also illustrated in Fig. 7, where typical configurations of a dendrimer that captures a spherical particle are shown.

V. Dendrimer–colloid mixture

In the preceding sections we analyzed the effective colloid–dendrimer interaction and the change in conformation of a single dendrimer due to the presence of a nearby colloidal sphere. In this section we examine the adsorption behavior of dendrimers with a finite density in the vicinity of a single, isolated colloidal sphere. To this end, we have employed Monte Carlo simulations to study the two types of colloidal spheres for various interaction strengths, radii, and densities, where the position of the sphere is kept fixed. The simulation box, for which periodic boundary conditions are applied, is chosen to be cubic in shape and has a size of \( 40 \times 40 \times 40 \sigma_c^3 \). Given the finite range of the interactions and the maximal extent a dendrimer can have, this guarantees that only the nearest images of dendrimers interact with each other. Two typical snapshots from such simulations are shown in Fig. 8. On the left panel, pertaining to CA-SR
dendrimers, it can be seen that there is a zone around the colloid that is depleted of the monomers. Quite the contrary, on the right panel that refers to CR-SA dendrimers there is strong adsorption of the latter on the colloidal surface.

In Fig. 9 we show the radial density profiles of the dendrimers for a fixed sphere radius $R_s = 8\sigma_c$ and $N = 100$ dendrimers for various interaction strengths $\varepsilon$. In order to have a clearer understanding of their adsorption behavior, not only the density profiles of the centers-of-mass are shown, but also the monomer density profiles of core and shell monomers independently.

In the case in which the core monomers are attracted by the sphere (CA-SR-type) and $\varepsilon = 0.5$, the interaction is still too weak to lead to an effective attraction. Due to the finite density however, dendrimers are pushed against the sphere, leading to an induced ordering. This brings the dendrimers close enough to the sphere, so that their internal conformation is affected and some core monomers attach to the surface, as indicated by the small peak in Fig. 9(a). On increasing the interaction strength to $\varepsilon = 1$, Fig. 9(c), the effective dendrimer–sphere interaction remains still repulsive, but has formed a plateau. This enables the dendrimer to approach the sphere closer and form an initial adsorption layer. The density in this layer further grows for $\varepsilon = 2$, Fig. 9(e), where the effective interaction now has an attractive range, so that almost all dendrimers in the system have been adsorbed. Whereas the core monomers form a clear structure, the shell monomers are only at short ranges repelled by the sphere, but are otherwise more or less homogeneously distributed, only restricted by the internal bonds of the dendrimer.

For the opposite, CR-SA spheres, we always have an attractive range in the effective interaction, which enables the dendrimer to adsorb on the colloidal particle. For the weak interaction $\varepsilon = 0.5$, shown in Fig. 9(b), the dendrimers do not even modify their bulk conformation, and bind with one or more of the shell monomers directly to the sphere. On increasing the interaction strength to $\varepsilon = 1$ and $\varepsilon = 2$, more dendrimers are adsorbed on the sphere. They attach to the sphere with an increasing number of shell monomers per dendrimer, as indicated by the bimodal shell–monomer density profiles, Fig. 9(d) and 9(f).

The effect of the radius of the sphere is examined in Fig. 10, where three different radii are selected. In order to facilitate the comparison between the different profiles, they are grouped in density profiles of the centers-of-mass, the core monomers, and the shell monomers. It can be seen that for all profiles an increasing sphere radius results in a more pronounced structure. This is a direct consequence from the fact that the interaction between the colloidal sphere and a dendrimer, according to eqn (5), scales with its size.

The fact that the same simulation box-size is used for each sphere radius in Fig. 10 also results in a more structured profile, because for the larger spheres an increased effective dendrimer density is obtained. In Fig. 11 this is illustrated by comparing the different radial profiles from a radius $R_s = 8\sigma_c$ sphere at various densities. In the CA-SR case, the increased density, forces a larger fraction of the dendrimers to be near the spherical particle. Due to the repulsive force on the shell monomers, those dendrimers need to adjust their conformations as can be seen from the density profiles for the core monomers. Since in this

![Fig. 9](image-url) Monomer radial density profiles from simulations of $N = 100$ dendrimers around a sphere with radius $R_s = 8\sigma_c$ for the CA-SR case [(a), (c), (e)], and the CR-SA case [(b), (d), (f)]. The interaction strengths are $\varepsilon = 0.5$ [(a), (b)], $\varepsilon = 1.0$ [(c), (d)], and $\varepsilon = 2.0$ [(e), (f)]. The profiles are shown for the center-of-mass, the core monomers, and the shell monomers, as indicated in the legend of panel (a).

![Fig. 10](image-url) Monomer radial density profiles from simulations of $N = 100$ dendrimers around spheres of varying radii, as indicated in the legends of panels (a) and (b). Different panels correspond to the CA-SR case with $\varepsilon = 1.0$ [(a), (c), (e)], and the CR-SA case with $\varepsilon = 0.5$ [(b), (d), (f)]. The profiles are shown for the center-of-mass [(a), (b)], the core monomers [(c), (d)], and the shell monomers [(e), (f)].

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case $\varepsilon = 1.0$, the effective interaction still remains repulsive and the sphere induces a layered structure of dendrimers. In the CR-SA case the shape of the profiles is almost unaffected by the increased density and mainly scales with the density. Only the distance of the adsorbed layer with respect to the sphere is slightly increased, which is necessary in order to create enough space for those dendrimers to bind to the sphere.

VI. Conclusions

We have analyzed the behavior of amphiphilic dendrimers in the vicinity of colloidal spheres. The curvature of the sphere has important consequences for the adsorption behavior of the dendrimers, specifically for the internal structure of the dendrimers. The two archetypes of conformations found in an earlier study,\(^{29}\) the “dead spider” in the case of a CA-SR planar wall and the “living spider” for a CR-SA type of wall, are also present for spherical colloidal particles with the same type of interaction.

It was shown that the adsorption on a sphere or planar wall is a gradual process that depends on the strength of interaction and the nature of the surface. In order to get adsorbed on a CA-SR type of surface, the dendrimers need to overcome an initial barrier due to the repulsive interaction of the shell. Thereafter, the conformation of the dendrimer needs to be inverted in order to bring the core monomers close enough to the surface to get bonded by it, which requires relatively strong interactions. It is much easier for dendrimers to get adsorbed by a surface of the type CR-SA, because the shell monomers that bind to the surface are on average already at the outside of the dendrimer. But also in this case the conformation of the dendrimer is affected in the process. It was shown that in the latter case the adsorption becomes a step-by-step process in which single shell monomers get adsorbed one-by-one.

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