Tunable effective interactions between dendritic macromolecules

I. O. Götzte, H. M. Harreis, and C. N. Likos

Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany

(Received 29 December 2003; accepted 30 January 2004)

We employ extensive Monte Carlo and molecular-dynamics simulations to investigate the effective interactions between the centers of mass of dendritic macromolecules of variable flexibility and generation number. Two different models for the connectivity and steric interactions between the monomers are employed, the first one being purely entropic in nature and the second explicitly involving energetic interactions. We find that the effective potentials have a generic Gaussian shape, whose range and strength can be tuned via modifications in the generation number and flexibility of the spacers. We supplement our simulation analysis by a density-functional approach in which the connectivity between the monomers is approximated by an external confining potential that holds the monomer beads together. Using a simple density functional for the interactions between the monomers, we find semiquantitative agreement between theory and simulation. The implications of our findings for the interpretation of scattering data from concentrated dendrimer solutions are also discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1689292]

I. INTRODUCTION

Dendrimers are synthetically prepared macromolecules with a highly branched structure. Due to their peculiar architecture, the flexibility in modifying it in various ways, and their numerous technological applications, dendrimers have attracted the interest of chemists for a long time. Complementary to their importance in applications is their relevance as model macromolecules that form hybrids between polymeric solutions and colloidal suspensions. Indeed, dendrimers entail internal fluctuations and a large number of possible conformations, a feature akin to that met in polymer chains. At the same time, their highly connected nature restricts the strength of the fluctuations and makes them similar to highly branched polymer microgels. For high generation numbers, dendrimers even behave very similar to compact hard spheres, a property which renders the generation number as a "tuning parameter" to bridge the gap between flexible chains and compact particles. It is customary to denote a dendrimer with \( n \) generations as \( n \)-dendrimer.

Most of the theoretical investigations on the properties of dissolved dendrimers have focused on the questions of their internal conformations and sizes. Despite the original finding of deGennes and Hervet, stating that dendrimers have a dense-shell structure, a number of theoretical and simulational works has shown that this is not the case: Flexible dendrimers display strong backfolding of their terminal groups inside the molecule and the resulting conformation is a dense-core one. Recently, Zook and Pickett revisited the original self-consistent field (SCF)-calculation of de Gennes and Hervet and were able to pinpoint its weak point. The method of de Gennes and Hervet tacitly rests on the reasonable yet incorrect assumption that a single conformation of the dendrimer (called "ground-state" in the language of SCF-methods) dominates all statistical averages in the thermodynamic limit. In reality, though, there are infinitely many degenerate ground states contributing to the self-consistent potential. Accordingly, in the modified calculation, dense-core profiles were obtained, thus the issue of the conformations of isolated dendrimers appears now to be settled.

Much less is known about the effective interaction (to be defined in Sec. II) between two dendrimers. Lue and Prausnitz as well as Lue have carried out simulations based on a tangent-sphere model for the dendrimers, whereas Likos et al. have presented a Flory-type theory yielding a Gaussian interaction potential. Nevertheless, the detailed form of the effective interaction as well as its dependence on generation number and spacer length between the branching points has not been investigated to date. The purpose of this work is to examine in detail this question. The rest of the article is organized as follows: In Sec. II, we present the formalism that introduces the concept of effective interactions and opens the way for their determination in computer simulations. In Sec. III, we introduce two different simulation models and present the methods to obtain the effective interaction and the results. In Sec. IV, we introduce a density-functional theory to deal with the same problem and compare with the findings from the computer simulations. In Sec. V, we discuss the relevance of our findings in analyzing results from scattering experiments and in Sec. VI, we summarize and conclude. Some technical derivations pertinent to the force on the center of mass of interacting dendrimers are presented in the Appendix.

II. THEORETICAL CONCEPTS

When confronted with the very high complexity of the systems typically encountered in soft matter physics, one has to resort to coarse-grained approaches in order to achieve progress in theoretically analyzing their properties. Thereby,
a very useful concept for understanding at least the equilibrium behavior of complex fluids is that of the effective interaction between suitably chosen degrees of freedom. Since the length scales characterizing the solvent and the dissolved particles are vastly different (up to three orders of magnitude), it is reasonable to treat the former as a continuum. Therefore, the solvent is taken into account only as an effective medium and the solubility of the polymers is encapsulated in a small number of parameters, such as the excluded-volume parameter or the form of the monomer–monomer interaction potential. Moreover, since we are not interested in keeping track of all the fluctuating, microscopic degrees of freedom, it is pertinent to choose one effective coordinate that represents somehow the whole macromolecule, integrate out the rest, and envision thereafter the dendrimers as “point particles” interacting by means of an effective potential. The latter includes all the effects of the integrated-out degrees of freedom and the thermodynamics of the system is preserved.

The choice of the effective degrees of freedom is largely a matter of convenience. For star-branched macromolecules, such as star polymers or polyelectrolyte stars, the common anchoring point is the natural choice. For linear polymer chains, both the central monomer and the center of mass have been used as effective coordinates. For dendrimers, the center of mass is a natural choice for two reasons: first, many experimental dendrimers lack a central particle and second because it is precisely the correlations between the centers of mass that are probed in scattering experiments. Since the centers of mass are not real particles of the system, the definition of the effective interaction between those requires some explanation. We present a mathematical definition of this concept below.

Consider two macromolecules consisting of $N$ monomers each. Let $\alpha = 1, 2$ denote the composite molecule and $i = 1, 2, \ldots, N$ be the index characterizing the individual monomer, so that $\mathbf{p}_i$ uniquely denotes the canonical momentum of a particular monomer of mass $m$ and $\mathbf{r}_i$ its position vector. Our starting point is the Hamiltonian of the whole system $\mathcal{H}$, which can be decomposed as follows:

$$\mathcal{H} = \mathcal{H}_{11} + \mathcal{H}_{12} + \mathcal{H}_{22}. \tag{1}$$

Here, $\mathcal{H}_{\alpha \beta}$ includes terms pertaining to interactions between monomers of macromolecules $\alpha$ and $\beta$ only, i.e., $\mathcal{H}_{11}$ and $\mathcal{H}_{22}$ include the interactions between monomers of the same dendrimer (as well as the trivial, kinetic energy terms), whereas in $\mathcal{H}_{12}$ all cross-interactions between monomers belonging to different dendrimers are incorporated. Introducing the pair potential functions $V_c$ and $V_s$ that model the connectivity and the steric interactions between the beads, respectively, we can therefore write

$$\mathcal{H}_{\alpha \beta} = \delta_{\alpha \beta} \frac{N^2}{2m} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \delta_{\alpha \beta} \sum_{i \neq j} V_c(\{\mathbf{r}_i\}) + V_s(\{\mathbf{r}_i\}) + (1 - \delta_{\alpha \beta}) \sum_{i=1}^{N} \sum_{j=1}^{N} V_s(\{\mathbf{r}_i, \mathbf{r}_j\})$$

$$= K + V_{\alpha \beta}, \tag{2}$$

where $\{\mathbf{r}_i\}$ is a shorthand for $(\mathbf{r}_{1a}, \mathbf{r}_{2a}, \ldots, \mathbf{r}_{Na})$, $K$ stands for the kinetic energy and $V_{\alpha \beta}$ for the potential energy. The canonical partition function of the system, $Q$, is defined as

$$Q = \prod_{\alpha = 1}^{2} \int dp_{\alpha}^N \int d\mathbf{r}_{\alpha}^N \exp(-\beta \mathcal{H}), \tag{3}$$

where $\int dp_{\alpha}^N$ is a shorthand for the multiple integral $\int d^3 p_1 d^3 p_2 \cdots d^3 p_{Na}$, similarly for $d\mathbf{r}_{\alpha}^N$. $\beta = (k_B T)^{-1}$, with Boltzmann’s constant $k_B$ and the absolute temperature $T$. Note the absence of the combinatorial factors $N!$ in the definition of the partition function, since the particles are in this case distinguishable due to their connectivity constraints.

In order to define the effective interaction between the centers of mass of the dendrimers, we proceed in a way analogous to that employed for linear polymer chains and introduce the centers-of-mass density operators

$$\hat{\rho}_{cm}^{(a)}(\mathbf{R}_a) = \delta\left[\mathbf{R}_a - \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i\right], \tag{4}$$

where $\mathbf{R}_a$ denotes the position vector of the center of mass of the dendrimer $\alpha$ and $\delta(\cdot)$ is Dirac’s delta function. We keep the centers of mass fixed at the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ and, following Ref. 15, we define the effective interaction $V_{\text{eff}}(\mathbf{R}_1, \mathbf{R}_2)$ as

$$V_{\text{eff}}(\mathbf{R}_1, \mathbf{R}_2) = -k_B T \ln \left[ \frac{\Omega^2}{Q_1} \int d\mathbf{p}_1^N d\mathbf{p}_2^N \int d\mathbf{r}_1^N d\mathbf{r}_2^N \right. \right.$$

$$\left. \times \hat{\rho}_{cm}^{(1)}(\mathbf{R}_1) \hat{\rho}_{cm}^{(2)}(\mathbf{R}_2) \right.$$ 

$$\left. \times \exp[ -\beta (\mathcal{H}_{11} + \mathcal{H}_{12} + \mathcal{H}_{22}) ] \right], \tag{5}$$

where $\Omega$ is the volume of the system and $Q_1$ is the partition function of an isolated dendrimer

$$Q_1 = h^{-3N} \int d\mathbf{p}_1^N \int d\mathbf{r}_1^N \exp(-\beta \mathcal{H}_{11}). \tag{6}$$

The connection of $V_{\text{eff}}$ to the thermodynamics of the system is provided by Eqs. (1), (3), and (5), from which it follows:

$$Q = \frac{Q_1^2}{\Omega^2} \int d^3 R_1 d^3 R_2 \exp[ -\beta V_{\text{eff}}(\mathbf{R}_1, \mathbf{R}_2) ]. \tag{7}$$

The effective potential depends only on the magnitude $R$ of the separation vector $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ between the centers of mass, $V_{\text{eff}} = V_{\text{eff}}(R)$. Its definition in Eq. (5) makes manifest the property $V_{\text{eff}}(R) \to 0$ as $R \to \infty$. Since the effective potential has the form of a restricted partition function, its direct calculation through Eq. (5) in a simulation cannot be achieved through standard simulation techniques. However, it is easy to show from Eq. (5) that the $V_{\text{eff}}(R)$ is related to the correlation function $G(R)$ between the positions of the centers of mass through

$$G(R) = \frac{\exp[ -\beta V_{\text{eff}}(R) ]}{\Omega \int d^3 R \exp[ -\beta V_{\text{eff}}(R) ]} \tag{8}$$
where \(\langle \cdots \rangle\) denotes a canonical average. Since the calculation of expectation values is straightforward in a computer simulation, the last result provides a possibility to measure \(V_{\text{eff}}(R)\) by using standard techniques.

An alternative possibility is offered by considering the force \(\mathbf{F}_a = -\nabla_{\mathbf{R}_a} V_{\text{eff}}(\mathbf{R}_1, \mathbf{R}_2)\) acting on the center of mass of dendrimer \(\alpha\). It can be shown that this force can be calculated as the expectation value of the sum of the forces exerted on the individual monomers, i.e.,

\[
F_a(R) = \left\langle \sum_{i=1}^{N} F_{ia} \right\rangle, \tag{9}
\]

where the subscript on the right-hand side implies that the average has to be evaluated at fixed separation \(R\) between the centers of mass. Since the proof of Eq. (9) above is somewhat technical, we relegate it to the Appendix.

III. SIMULATION

We have applied two different simulation models, so as to obtain independent results and provide a comparison between them. In addition, the application of different simulation models helps to shed light into the question of the sensitivity of the effective interaction on the microscopic details of the system. As will be demonstrated below, the results do depend quantitatively on the numerical values of the microscopic parameters, it is nevertheless possible to make a broad correspondence between different models, so that they yield very similar results for the effective interaction. We present the two models and the simulation techniques in detail below.

A. Simulation models

1. Monte Carlo simulations

A simple model for dendrimers is to treat the monomers as hard spheres of diameter \(\sigma\), which are connected by threads of contour length \(\delta\sigma\). Explicitly, and referring to the notation introduced in Eq. (2), we have

\[
V_s(r) = \begin{cases} 
\infty & \text{for } r/\sigma < 1 \\
0 & \text{otherwise} \end{cases} \tag{10}
\]

for non-bonded monomers and

\[
V_s(r) = \begin{cases} 
\infty & \text{for } r/\sigma < 1 \\
0 & \text{for } 1 < r/\sigma < 1 + \delta \\
\infty & \text{for } r/\sigma > 1 + \delta 
\end{cases} \tag{11}
\]

for connected ones. The properties of isolated dendrimers of this model have been investigated and compared to those of the Lennard-Jones-finite-nonlinear-extensible-elastic (FENE)-model (see below) in Ref. 20. As we are only interested in static properties, we also allow ghost-chains, so the spacer length is not restricted to values smaller than \(\sqrt{2} - 1 \approx 0.414\). We use Monte Carlo (MC) simulations as these are very fast for this model.

Within this model, the most efficient way of measuring the effective interaction is offered by Eq. (8), a technique also applied by Dautenhahn and Hall to measure the potential between two polymer chains.\(^\text{16}\) Indeed, since all forces between monomers identically vanish, Eq. (9) is of no use. The function \(G(R)\) in this case can be obtained by letting two dendrimers freely move within the simulation box (accepting the moves according to the Metropolis criterion), and then making a histogram of the center-of-mass distance \(R\). In order to fulfill the condition \(V_{\text{eff}}(R) \rightarrow 0\) for large separations \(R\), the histogram has to be normalized in such a way that \(G(R) \rightarrow 1\) in the same limit. Then, we can simply set

\[
\beta V_{\text{eff}}(R) = -\ln[G(R)]. \tag{12}
\]

Since the range of the interaction is anticipated to be finite (of the order of the gyration radius \(R_g\) of the dendrimers), we do not need statistics for large distances where the interaction potential vanishes, as this would cost unnecessarily simulation time. In order to prevent this, we accept only moves where the center-of-mass distance is smaller than a cutoff distance \(R_{\text{cut}} \approx 4R_g\). Furthermore, the repulsion between dendrimers at close separations can be very strong, therefore configurations with small \(R\) are extremely unlikely and would not occur in reasonable simulation times. In order to deal with this problem and sample all relevant separations equally, we apply an additional attractive external potential \(\Phi(R)\) acting on the centers of mass. The total interaction potential is then \(\tilde{V}(R) = V_{\text{eff}}(R) + \Phi(R)\), giving rise to the correlation function \(\tilde{G}(R)\). Then, Eq. (12) becomes

\[
\tilde{G}(R) = \exp[-\beta \tilde{V}(R)] = \exp[-\beta(V_{\text{eff}}(R) + \Phi(R))]. \tag{13}
\]

where \(V_{\text{eff}}(R)\), the real effective interaction potential, is then obtained by

\[
\beta V_{\text{eff}}(R) = -\ln[\tilde{G}(R)] - \beta \Phi(R). \tag{14}
\]

The simulation is carried out as follows: we try to move a sphere, and for the new position we check for overlaps and if the maximum bond length condition is fulfilled. If the new position is not allowed, the particle is set back to its old position. This procedure is repeated with all \(2N\) particles. In order to apply the external potential acting on the centers of mass, we use the Metropolis algorithm: Consider a configuration with a center-of-mass distance \(R_{\text{old}}\). After all \(2N\) particles have been moved (or have been tried to move), we calculate the new center-of-mass distance \(R_{\text{new}}\). If \(R_{\text{new}} < R_{\text{old}}, \) the new configuration is accepted, as the external potential is attractive. Otherwise, the new configuration is only accepted with the probability \(\exp[-\beta \Phi(R_{\text{new}}) - \Phi(R_{\text{old}})]\). If it is rejected, all \(2N\) particles are set back to their old positions.

Good statistics can only be achieved if the total potential \(\tilde{V}(R) = V_{\text{eff}}(R) + \Phi(R)\) is smaller than \(-k_BT\) for all distances \(R\); optimally, \(\tilde{V}(R)\) should be independent of \(R\), so that histograms are flat and all \(R\)-regions are sampled equally frequently. As \(\Phi(R)\) has to be chosen in such a way that the real potential and the external potential nearly cancel each other, and \(V_{\text{eff}}(R)\) is not known \textit{a priori}, \(\Phi(R)\) can only be determined within a trial-and-error procedure, where the external potential is improved after each cycle. In contrast to the simulation of the Lennard-Jones-FENE model (see the following subsection), where separate simulations are used for...
discrete values of $R$, this method yields the potential for the whole range $0 < R < R_{\text{cut}}$ in one simulation. Therefore, very long runs are necessary to obtain good statistics. Here we use $10^{10}$ MC steps.

In Fig. 1, simulation snapshots of two G4 dendrimers are shown for a center-of-mass distance $R=0$ and $R=4\sigma$, respectively. When the dendrimers approach each other, they are deformed due to the repulsive interaction. As can be discerned from Fig. 1(b), the dendrimers become almost flat at the midplane between their centers of mass for intermediate separations $R$, whereas they recover their spherical shape for full overlaps, Fig. 1(a). Results for the effective interaction $V_{\text{eff}}(R)$ obtained within this model will be presented in Sec. III B.

2. Molecular-dynamics simulations

To supplement our study, we furthermore carry out molecular-dynamics (MD) simulations of two dendrimers. We adopt the same dendrimer geometry as in the Monte Carlo simulations, whereby all spherical beads representing the atomic groups interact via a purely repulsive Lennard-Jones like potential, $V_s(r)$ (with $r$ denoting the separation between the bead centers) instead of hard-core repulsions. The potential $V_s(r)$ is obtained by truncating the Lennard-Jones potential $V_{\text{LJ}}(r)$ at the minimum position $r_{\text{min}} = 2^{1/6} \sigma_{\text{LJ}}$ and shifting it by the constant $V_{\text{LJ}}(r_{\text{min}})$ to get $V_s(r_{\text{min}}) = 0$,

$$V_s(r) = \begin{cases} 4\epsilon \left( \frac{\sigma_{\text{LJ}}}{r} \right)^{12} - \left( \frac{\sigma_{\text{LJ}}}{r} \right)^{6} + 0.25 \epsilon & ; \; r \leq 2^{1/6} \sigma_{\text{LJ}} \\ 0 & ; \; r > 2^{1/6} \sigma_{\text{LJ}}. \end{cases}$$

The energy scale is set by $\epsilon$, the length scale by the Lennard-Jones diameter $\sigma_{\text{LJ}}$ of the beads. Since no intrinsic stiffness is contained in the model in the form of an orientational bias of the interaction, a bead can be identified as a Kuhn segment. By comparison with experimental data the bead diameter $\sigma_{\text{LJ}}$ can be determined. To model the chemical bonding between neighboring monomers on one dendron, connected beads interact via the attractive finite-nonlinear-extensible-elastic (FENE) potential,$^{22} V_e(r)$, which reads as

$$V_e(r) = \begin{cases} -U_0 \epsilon \left( \frac{R_0}{\sigma_{\text{LJ}}} \right)^2 \ln \left( 1 - \left( \frac{r}{R_0} \right)^2 \right) & ; \; r \leq R_0 \\ \infty & ; \; r > R_0. \end{cases}$$

The location of divergence in the FENE potential, $R_0$, determines the maximum bond length between two monomers. The average bond-length is additionally influenced by the prefactor $U_0$. Both can be varied to account for different experimentally realized dendrimers exhibiting different effective Kuhn lengths. Finally let us note that the temperature of the system is fixed at $T = 1.2k_B$. To determine the effective interaction between two dendrimers at a given center-of-mass separation $R$ we proceed as follows: Two dendrimers are placed at the distance $R$ and standard molecular-dynamics simulation techniques are employed to generate sample configurations. In order to effect the sampling at the given center-of-mass separation, we introduce an external force acting on the two centers of masses after each MD time step in the form of a rigid translational move bringing the two dendrimers back to a center-of-mass separation of $R$. Typically $6 \times 10^7$ MD steps were simulated, with a time-step of $10^{-3} \tau$, yielding a total MD simulation time of $6 \times 10^4 \tau$, whereby $\tau$ is the MD time unit, $\tau = \sqrt{m/\epsilon \sigma_{\text{LJ}}^6}$. Here, $m$ is the mass of one bead. Of the $6 \times 10^7$ MD steps, $10^7$ were used for equilibration. In the remaining simulation time, $5 \times 10^3$ configurations were used to calculate statistical averages of the effective force acting between the two dendrimers centers of masses. Concurrently, statistical averages of the radial density distribution $\rho(r)$ of the dendrimer around its center of mass, the pair distribution function $G(r)$, the form factor $F(q)$, as well as its radius of gyration $R_g$ were measured, yielding results similar to the ones presented in Ref. 23.

B. Results

We start with the model employed for the MC-simulation, which we term bead-thread model. In Figs. 2 and 3 we show the simulation results for G4 and G5 dendrimers with different spacer lengths. Although the repulsion is very strong, the dendrimers are interpenetrable. Increasing the spacer length leads to a softer interaction whose range is also longer. The effective interaction for all spacer lengths considered can be fitted by a sum of two Gaussian functions having the following form:

$$\beta V_{\text{eff}}(R) = \epsilon_1 \exp \left( -\frac{3R^2}{4R_g^2} \right) + \epsilon_2 \exp \left[ -\alpha(R/R_g - \gamma)^2 \right],$$

where $R_g$ is the radius of gyration of the dendrimers, as
obtained by simulation using the same model. The first term in Eq. (17) above is identical in form to the one used previously to describe the interaction in the framework of a Flory-type theory, whereas the second provides a small correction. The quantities $\epsilon_1$, $\epsilon_2$, $\alpha$, and $\gamma$ are fit parameters, whose values are summarized in Table I.

As can be read off from Table I, the effective interaction between dendritic macromolecules has, to an excellent approximation, a Gaussian form centered at the origin, the second term in Eq. (17) providing simply a small correction. Moreover, the strength of the interaction is governed by the spacer length, providing thus a mechanism for tuning the potential experimentally by employing dendrimers of varying flexibility. In particular, in order to achieve an interaction strength of roughly $10 k_B T$, which is the value used to provide an excellent agreement with experimental data for G4-dendrimers, a rather long spacer length, $\delta = 2.0$ must be employed. An additional parameter that allows the tuning of the effective potential is the terminal generation number, $G$ for fixed $\delta$. The effect of the stiffening of the effective interaction with decreasing $G$ and/or increasing $G$ for fixed $\delta$ can be understood by means of the increased crowding of the hard spheres in the interior of the dendritic macromolecule.

<table>
<thead>
<tr>
<th>Generation</th>
<th>$\delta$</th>
<th>$\epsilon_1$</th>
<th>$\epsilon_2$</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4</td>
<td>0.1</td>
<td>55</td>
<td>5.5</td>
<td>6.25</td>
<td>0.950</td>
</tr>
<tr>
<td>G4</td>
<td>0.2</td>
<td>49</td>
<td>5.5</td>
<td>6.50</td>
<td>0.925</td>
</tr>
<tr>
<td>G4</td>
<td>0.3</td>
<td>44</td>
<td>5.0</td>
<td>6.75</td>
<td>0.925</td>
</tr>
<tr>
<td>G4</td>
<td>0.4</td>
<td>39</td>
<td>4.5</td>
<td>5.00</td>
<td>0.900</td>
</tr>
<tr>
<td>G4</td>
<td>2.0</td>
<td>12</td>
<td>0.6</td>
<td>7.00</td>
<td>0.700</td>
</tr>
<tr>
<td>G5</td>
<td>0.1</td>
<td>120</td>
<td>11.0</td>
<td>6.25</td>
<td>0.900</td>
</tr>
<tr>
<td>G5</td>
<td>0.2</td>
<td>104</td>
<td>11.0</td>
<td>6.50</td>
<td>0.875</td>
</tr>
<tr>
<td>G5</td>
<td>0.3</td>
<td>89</td>
<td>10.0</td>
<td>6.75</td>
<td>0.850</td>
</tr>
<tr>
<td>G5</td>
<td>0.4</td>
<td>78</td>
<td>9.5</td>
<td>7.00</td>
<td>0.850</td>
</tr>
</tbody>
</table>

In Fig. 4 we show the results obtained by performing MD simulations employing the Lennard-Jones-FENE model of Eqs. (15) and (16). It can be seen that the specific microscopic model employed does not affect the generic form of the interaction. Once more, the shape of the effective potential is Gaussian and the quantitative details of $V_{eff}(R)$ can be now tuned by changing the microscopic energy parameter $U_0$ and the maximum length $R_0$ of the inelastic springs. In order to attain a value comparable to experiment, $\sim 10 k_B T$, the microscopic energy parameter and the maximum bond length must be tuned to $U_0 = 0.5$ and $R_0 = 10.0$, as can be read off from the inset of Fig. 4. It is worthwhile noting that a simple increase in the value of $R_0$ is not sufficient to bring down the strength of the interaction to $\sim 10 k_B T$, as can be seen from the main plot of Fig. 4. In contrast to the bead-spring model, the maximum extent of the spring is associated with an energetic cost set by the parameter $U_0$. Thus, only a decrease in the value of $U_0$ can bring about the desired strength of the effective interaction and an increase of $R_0$ alone is not sufficient. Otherwise, understanding the influence of these two parameters on the stiffening of the pair potential is quite intuitive: the repulsion that every monomer feels from any monomer of the other dendrimer gets lower the smaller $U_0$ is and, in addition, the larger $R_0$ the more space it has to avoid it.

IV. DENSITY-FUNCTIONAL THEORY

In this section we put forward an attempt to estimate the effective interaction between dendrimers by using techniques from classical density-functional theory (DFT). DFT is a powerful theoretical tool that allows for the calculation of equilibrium density profiles of inhomogeneous fluids and at the same time provides a way for calculating the free energy of the same under the influence of arbitrary external potentials. For simple classical fluids composed of non-bonded molecules, various approximate functionals have been developed in the last two decades. The situation for polymeric fluids, where the bonding between the monomers plays a crucial role, is much less developed. Approximate functionals for polymer chains have been proposed recently, however the complicated, branched connectiv-
ity of dendrimers renders their application to the problem at hand untenable. Hence, we put forward the idea of removing all the bonds from the molecules and formally replacing them with an appropriate external potential \( V_{\text{ext}}(r) \), which is chosen in such a way that the equilibrium profile of an isolated dendrimer coincides with the one that has been obtained from simulation.

Let us consider, therefore, an isolated dendrimer whose one-particle density profile is \( \rho(r) \), where \( r \) measures the distance from its center of mass. The inhomogeneity of this profile is caused by the bonding between the molecules, which, in the spirit of the bead-thread model, we consider as hard spheres of diameter \( \sigma \). In order to achieve the same inhomogeneous profile \( \rho(r) \) in a fluid of hard spheres composed of exactly the same number of particles as those in the dendrimer, one needs to act on the system with an appropriate external potential \( V_{\text{ext}}(r) \). For this system, we thus write down a classical density functional \( \mathcal{F}[\rho] \) of the form

\[
\mathcal{F}[\rho] = k_B T \int d^3 r \rho(r) \left\{ \ln[\rho(r) \sigma^3] - 1 \right\} + \mathcal{F}_{\text{ex}}[\rho] + \int d^3 r V_{\text{ext}}(r) \rho(r),
\]

(18)

where \( \mathcal{F}_{\text{ex}}[\rho] \) is the excess contribution arising from the excluded volume interactions between the monomers. For this term we use the simplest weighted density approximation that was introduced by Nordholm\(^{28} \) and later refined by Tarazona.\(^{29} \)

\[
\mathcal{F}_{\text{ex}}[\rho] = \int d^3 r \rho(r) \psi_{\text{ex}}[\bar{\rho}(r)],
\]

(19)

with the weighted density \( \bar{\rho}(r) \)

\[
\bar{\rho}(r) = \frac{3}{4 \pi \sigma^3} \int d^3 r \Theta(\sigma - r) \rho(r)
\]

(20)

and the excess free energy of the homogeneous hard sphere fluid\(^{30} \)

\[
\beta \psi_{\text{ex}}(\rho) = \eta(4 - 3 \eta)(1 - \eta)^{-2}, \quad \eta = \frac{\pi \rho \sigma^3}{6}.
\]

(21)

In Eq. (20) above, \( \Theta(\sigma - r) \) is the Heaviside step function.

In order to determine the fictitious external potential \( V_{\text{ext}}(r) \), we took the equilibrium density profile \( \rho(r) \) from the MC simulation of an isolated dendrimer of the bead-thread model. Requiring that the functional of Eq. (18) is minimized for this profile, we obtain the equation

\[
\ln[\rho(r) \sigma^3] + \frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} + \beta V_{\text{ext}}(r) = \beta \mu,
\]

(22)

where the second term on the left-hand side denotes the functional derivative with respect to the density and \( \mu \) is a Lagrangian multiplier introduced to guarantee that the number of particles is kept fixed at the number of beads of the dendrimer. Equation (22) can be immediately solved for \( V_{\text{ext}}(r) \).

Due to the approximate character of the excess functional, Eqs. (19)–(21), a technical problem occurs. The high values of \( \rho(r) \) close to the origin, see Fig. 5, cause the external potential \( V_{\text{ext}}(r) \) to develop a deep minimum at \( r = 0 \). The density profile and the external potential are denoted in Fig. 5 and in the inset with the dashed lines. When this potential is reintroduced in Eq. (22) and used to calculate the equilibrium profile, it yields as a stable solution not the original one but another profile, which is similar to the old one away from the origin but has a much higher peak close to \( r = 0 \). This is a combined artifact of the approximate nature of the excess functional and the assumption that all bonds can be removed. In order to remedy this deficiency, we remove the large peak from the simulation density profile, which arises from the two monomers of the zeroth generation and, work with a modified profile that includes the effects of the subsequent generations only. This modified profile is denoted with the solid line in Fig. 5. With this modification, a fictitious external potential is obtained, denoted with the solid line in the inset of Fig. 5, which is now
For every separation $D$, this functional has been minimized with respect to $p_1(r)$ and $p_2(r)$. The equilibrium density profiles serve then to determine also the center-of-mass separation $R$ that corresponds to every $D$ and a relation $D = D(R)$ is established. Clearly, due to the symmetry of the problem, it holds $p_2(r) = p_1(D-r)$, as for the external potentials.

The advantage of this approach compared to the simple Flory-type theory presented in Refs. 7 and 8 is that the resulting density profiles are now deformed with respect to their shape at $R \to \infty$, since the presence of the hard spheres belonging to one dendrimer takes away allowable configurations from those of the other.

The next issue is to identify the effective interaction $V_{\text{eff}}(R)$ between the two dendrimers. At first sight, it would appear that one should state $V_{\text{eff}}(R) = \mathcal{F}[p_1, p_2; D(R)] - \mathcal{F}[p_1, p_2; \infty]$ but this is physically unrealistic. First of all, the true dendrimers are not under the influence of an external potential; the latter has been introduced only as an intermediate step in order to estimate the deformed density profiles. Moreover, the first term in the right-hand side of Eqs. (18) and (23) does not accurately describe the ideal free energy of bonded molecules, which has a much more complicated form that can be read off in Ref. 25. We make here instead the physical assumption that, due to the very high connectivity between the beads, the true ideal term is much smaller in magnitude than the one introduced here. The only term that is realistically reproduced by our hybrid DFT is the excess contribution $\mathcal{F}_{\text{ex}}$, which is also mainly responsible for the reduction of available states for one dendrimer in the presence of the other. Our approach is similar to the Flory idea of removing all connections between monomers and estimating the effective interaction from the overlap of the two undisturbed density profiles. We maintain this spirit but use now the deformed density profiles that arise from the DFT to write

$$V_{\text{eff}}(R) \approx \mathcal{F}_{\text{ex}}[p_1 + p_2; D(R)] - \mathcal{F}_{\text{ex}}[p_1 + p_2; \infty].$$  (24)

Clearly, the last term is just twice the excess free energy of an isolated dendrimer.

The results from the DFT-approach are presented in Figs. 7 and 8 and compared there to simulation. It can be seen that, although the agreement is not spectacular, the approximate DFT introduced here captures the features of the effective interaction semi-quantitatively. The evolution of the strength of $V_{\text{eff}}(R)$ with spacer length and the general shape of the effective potential are reproduced. A general deficiency of the DFT is the systematic overestimation of the width of the effective interaction. This may arise both from the approximate form of the excess density functional and from the fact that we did not allow, in this approach, the fictitious external potentials to vary with $R$. Indeed, in the true dendrimers the bonds bend and yield as $R$ varies, whereas here $V_{\text{ex}}(r)$ maintains its shape for isolated dendrimers for all values of $R$. This constraint causes an overestimation of the effective interaction, however it is not clear at present how it could be lifted in a self-consistent way.

As a quantitative measure of the deformation of the dendrimers with respect to their undisturbed shape, we introduce

---

**FIG. 6.** A sketch showing two confined hard-sphere fluids whose confining potentials are kept a distance $D$ apart. All particles interact with one another but the light (dark) spheres only feel the effect of the light (dark) external potential. Due to the deformation of the density profiles, the distance $D$ does not coincide with the separation $R$ between the centers of mass of the confined fluids.

self-consistent: introducing a $V_{\text{ext}}(r)$ in Eq. (22) and calculating $\rho(r)$ yields as equilibrium profile the input density, denoted with the solid line in Fig. 5. Though this procedure may seem arbitrary at first sight, it carries two additional physical motivations. First, the fact that the bonding between the two innermost monomers cannot be completely removed, hence we replace both of them with a potential barrier into which the monomers of the subsequent generations cannot penetrate. And second, since we are eventually interested in the calculation of the effective interaction, which is caused mainly by the overlap and deformation of the outermost generations, the details in the treatment of the innermost monomers should be not crucial.

In order to calculate the effective interaction $V_{\text{eff}}(R)$, we now extend the treatment to two dendrimers. Consistently with the picture of a single dendrimer, these are modeled as two confined hard-sphere fluids, whose respective external potentials are separated by a distance $D$. All hard spheres interact with each other but the molecules of species $i$ only feel the external potential $V_{\text{ext}}^{(i)}(r)$ that represents the bonding within the macromolecule labeled by $i$ ($i=1,2$). Since the profiles will be distorted, $D$ is not identical to the center-of-mass separation $R$ in general and only in the trivial cases $D=0$ and $D=\infty$ it holds $D=R$. Positioning the first dendrimer at the origin and the second at a distance $D$, it clearly holds $V_{\text{ext}}^{(2)}(r) = V_{\text{ext}}^{(1)}(D-r)$. The physical setup is schematically depicted in Fig. 6. The density functional of Eqs. (18)–(21) is now generalized to two interacting dendrimers and reads as

$$\mathcal{F}[p_1, p_2; D] = k_BT \sum_{i=1}^{2} \int d^3 r \rho_i(r) \left[ \ln \rho_i(r) \sigma^3 - 1 \right]$$

$$+ \mathcal{F}_{\text{ex}}[p_1 + p_2; D]$$

$$+ \sum_{i=1}^{2} \int d^3 r V_{\text{ext}}^{(i)}(r) \rho_i(r),$$  (23)

where the $D$-dependence arises from the separation between the two fictitious external potentials. Since the term $\mathcal{F}_{\text{ex}}$ describes the effect of the interactions between all beads, irrespective of the dendrimer to which they belong, it depends on the total density profile $\rho_1(r) + \rho_2(r)$.
the overlap parameter $O(R)$, defined as follows: consider the midplane between the line connecting the centers of mass of the dendrimers and count the average number of monomers $N(R)$ belonging to the dendrimer whose center of mass lies to the right of this plane, and which lie to the left of the plane. The words “right” and “left” can be interchanged here.

With $N$ being the total number of monomers in the dendrimer, we define

$$O(R) = \frac{2N(R)}{N}. \tag{25}$$

The definition above guarantees that in the limit $R=0$ the overlap parameter attains the value unity. In Fig. 9 we show a representative result, obtained for two G4-dendrimers of spacer length $d=0.1$. Though the DFT still overestimates the overlap between the dendrimers, it provides an improvement upon the result of the undistorted density profiles, which is denoted by the dotted line in Fig. 9.

V. CONNECTION TO EXPERIMENTS

In scattering experiments at vanishing concentration of dendrimers, the form factor $F(q)$ of the macromolecules is measured as a function of the scattering wave vector $q$. The form factor provides information about the size and typical conformation of dendrimers. In two recent publications,\textsuperscript{20,23} it has been demonstrated that both the bead-thread model and the Lennard-Jones-FENE model yield results that can bring about excellent agreement with experimental data on the form factor of G4-dendrimers. Moreover, the bead-thread model correctly predicts the evolution of dendrimers toward compact hard spheres with growing terminal generation number.\textsuperscript{20,31} As it has been argued before,\textsuperscript{20} the broad family of the bead-thread model, parametrized by the value of the spacer length $d$, possesses a degree of universality as far as the form factors are concerned: When plotted against the dimensionless parameter $qR_g$, the form factors arising from different values of $d$ show only minor differences to each other and, when compared to SANS-experiments, all lie within experimental uncertainties. Since in the bead-thread model it holds $R_g = \alpha_s \sigma$, where $\alpha_s$ is a $d$-dependent numerical coefficient of order unity, for every value of $d$ a corresponding length scale $\sigma$ (say, in nanometers) can be chosen, so that the simulation results and the given experimentally measured $F(q)$ agree quantitatively. In other words, on the basis of experimental information on $F(q)$ alone, it cannot be determined which member of the $d$-parametrized family is the best model to describe the real system.

The situation is different when experimental results from concentrated dendrimer solutions are available. In this case, the total scattering intensity contains information about the correlations between the different dendrimers, which is encoded in the static structure factor $S(q)$. The latter quantity is sensitive to the strength of the effective interaction between the centers of mass. As demonstrated in Fig. 10, a soft interaction, such as the one that arises from the bead-thread model for high values of $d$, gives rise to structure factors that are deprived of any significant peaks.\textsuperscript{7,8} On the other hand, stiff dendrimers with short spacer lengths (small $d$) are expected to give rise to scattering profiles exhibiting a strong degree of liquid-like ordering in the system, as can be seen in Fig. 10. The structure factor $S(q)$ does not display the universality of the form factor $F(q)$, even when plotted as a function of $qR_g$. Thus, it provides a suitable tool to deter-
mine which member of the bead-thread family best describes a given solution of flexible dendrimers.

Finally, we note that in view of the fact that the Gaussian interaction between dendrimers can attain values exceeding 100 $k_B T$ at full overlap (see Figs. 2 and 3), the interesting possibility opens up, that one might be able to form crystalline phases in a many-body system of dendrimers. Indeed, as it has been shown recently, the above-mentioned value is the threshold above which particles interacting by means of Gaussian potentials can form stable crystals.

VI. CONCLUSIONS

By carrying out extensive computer simulations with two different models for dendrimers, and for a variety of parameters within those, we have demonstrated that the effective interaction between their centers of mass can be very well approximated by a Gaussian form. The quantitative characteristics of this Gaussian potential, i.e., its strength and range, can be tuned through a variation of the spacer length and the generation number. Thus, dendrimers are one additional physical system in which the family of bounded, ultrasoft, and tunable effective interactions can be materialized. Our study has been supplemented by an approximate density-functional theory in which the connections between the monomers have been replaced by a fictitious external potential. This approach captures the main features of the interaction, although the agreement with the simulation results is still not quantitative.

The possibility to realize Gaussian interactions in physical systems opens up a host of possibilities for exploring the occurrence of phenomena that have been predicted recently for Gaussian mixtures. These systems can be materialized, e.g., by using dendrimer mixtures of different generations and/or flexibility, in order to bring about effective Gaussian repulsions in which the nonadditivity parameter of the cross-interaction can be tuned. In such cases, one may be able to observe a wealth of interesting phenomena, going from demixing to microphase separation and pattern formation under confinement. Moreover, the applicability of the effective potential to describe correlations in concentrated dendrimer solutions should be explicitly investigated via monomer-resolved computer simulations. Going one step further, the relevance of the interaction to the description of the dynamical properties of dendrimers is another question of high topical interest. Work along these lines is currently under way.

ACKNOWLEDGMENTS

We thank Matthias Ballauff for helpful discussions. This work has been supported by the Deutsche Forschungsgemeinschaft.

APPENDIX: PROOF OF EQ. (9)

Let us consider, without loss of generality, the force $F_1 = -\nabla_{R_1} V_{\mathrm{eff}}(R_1, R_2)$ acting on the center of mass of the first macromolecule. First, let us define the variables

$$w_\alpha = \frac{1}{N} \sum_{i=1}^{N} r_{i\alpha},$$

with $\alpha = 1, 2$. Our starting point is Eq. (5) of the main text. Acting with the $\nabla_{R_1}$-operator on both sides and carrying out the trivial integrations over the momenta on the right-hand side, we obtain

$$F_1 = k_B T \int dr_2^N \int dN_1 \delta(R_2 - w_2) \nabla_{R_1} \delta(R_1 - w_1)$$

$$\times \exp[-\beta(V_{11} + V_{12} + V_{22})] \int dr_2^N \delta(R_2 - w_2)$$

$$\times \delta(R_1 - w_1) \exp[-\beta(V_{11} + V_{12} + V_{22})]^{-1}.$$  \(\text{(A2)}\)

Let $Z$ be the denominator in Eq. (A2) above. Writing $\nabla_{R_1} \delta(R_1 - w_1) = -\nabla_{w_1} \delta(R_1 - w_1)$ and taking into account that $V_{22}$ does not depend on the coordinates $\{r_{1i}\}$, $i = 1, 2, \ldots, N$ of the monomers of the first dendrimer, we thus obtain

$$F_1 = -\frac{k_B T}{Z} \int dr_2^N \delta(R_2 - w_2) \exp(-\beta V_{22})$$

$$\times \int dr_1^N [\nabla_{w_1} \delta(R_1 - w_1)] \exp(-\beta(V_{11} + V_{12})).$$  \(\text{(A3)}\)

The potential energy function $V_{11}$ depends only on the relative coordinates of the monomers of dendrimer 1. On the other hand, $V_{12}$ contains all the interactions between monomers of different dendrimers, thus for a fixed conformation $\{r_2^N\}$ of the second dendrimer, it can be considered a function...
of the variables \( \{r_1^j\} \) only. Let us introduce a transformation from the set of variables \( \{r_1^1, r_2^1, \ldots, r_N^1\} \) into the variables \( \{y_1, y_3, \ldots, y_N, w_1\} \), where

\[
y_j = r_j - r_1, \quad j = 2, 3, \ldots, N
\]

and \( w_1 \) is given by Eq. (A1) above. The Jacobian of this transformation is equal to unity and it is straightforward to show that the inverse transformation reads as

\[
r_1^1 = \frac{1}{N} \sum_{j=2}^{N} y_j + w_1, \quad r_j^1 = \frac{1}{N} \sum_{j=2}^{N} y_j - y_1 + w_1, \quad j = 2, 3, \ldots, N.
\]

The potential energy functions transform as follows:

\[
V_{11} \rightarrow \tilde{V}_{11}(y_1, y_3, \ldots, y_N),
\]

i.e., there is no dependence on the variable \( w_1 \), whereas for the cross-interaction term we obtain

\[
V_{12}(r_1, r_2, \ldots, r_N) \rightarrow \tilde{V}_{12}(y_1, y_3, \ldots, y_N, w_1),
\]

where the explicit form of the function \( \tilde{V}_{12} \) is obtained by substituting the transformations (A5) and (A6) in the function \( V_{12} \), explicitly

\[
\tilde{V}_{12} = V_{12} \left( \frac{1}{N} \sum_{j=2}^{N} y_j + w_1, \frac{1}{N} \sum_{j=2}^{N} y_j - y_1 + w_1 \right.
\]

\[
+ w_1, \ldots, \frac{1}{N} \sum_{j=2}^{N} y_j - \left. y_N + w_1 \right).
\]

Under these transformations, Eq. (A3) takes the following form:

\[
F_1 = -\frac{k_b T}{Z} \int dr_2^N \delta(r_2 - w_2) \exp(-\beta V_{22})
\]

\[
\times \int dy_1^{N-1} \exp(-\beta \tilde{V}_{11}) \int d^3w_1
\]

\[
\times [\nabla_{w_1} \delta(r_1 - w_1)] \exp(-\beta \tilde{V}_{12}),
\]

where \( \int dy_1^{N-1} \) is a shorthand for the multiple integral \( \int \cdots \int d^3y_2 d^3y_3 \ldots d^3y_N \). In order to evaluate the last integral in Eq. (A10), we make use of the property of the delta-function

\[
\int d^3x \nabla_x \delta(x - a) f(x) = -\nabla_x f(x) |_{x = a}.
\]

Applying now the above formula for the last integral of Eq. (A10), using the chain rule for Eq. (A9) and the transformations (A5) and (A6), we obtain

\[
\int d^3w_1 [\nabla_{w_1} \delta(r_1 - w_1)] \exp(-\beta \tilde{V}_{12})
\]

\[
= \beta \sum_{i=1}^{N} \left[ \nabla_{r_i} V_{12}(r_1, r_2, \ldots, r_N) \right]
\]

\[
\times \exp(-\beta V_{12}) |_{w_1 = r_1}.
\]

Reverting to the original variables, rearranging terms in Eq. (A10), using Eq. (A12) and reintroducing formally a \( \delta(r_1 - w_1) \)-function to implement the constraint on the center of mass, we have

\[
F_1 = \left\{ \int dr_2^N \int dr_1^N \delta(r_2 - w_2) \delta(r_1 - w_1) \right.
\]

\[
\times \left[ -\sum_{i=1}^{N} \nabla_{r_i} V_{12}(r_1, r_2, \ldots, r_N) \right] \exp(-\beta V_{12})
\]

\[
+ V_{22}) \right\} \left\{ \int dr_2^N \int dr_1^N \delta(r_2 - w_2) \delta(r_1 - w_1)
\]

\[
\times \exp(-\beta (V_{11} + V_{12} + V_{22})) \right\}^{-1}.
\]

The term in the square brackets in the numerator of the right-hand side is the sum of the forces exerted on the monomers of dendrimer 1 from all the monomers of dendrimer 2. There is no contribution to the force from internal forces within the dendrimer, as they cancel in pairs. Moreover, Eq. (A13) makes it manifest that \( F_1 \) is the expectation value of the sum of the individual forces under the constraint of keeping the centers of mass fixed at positions \( R_1 \) and \( R_2 \). This proves Eq. (9) of the main text.