

Comb polymers in dilute solutions: Analytical approach, computer simulations, and experiments

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We analyze the universal conformational properties of comblike polymer topologies in the dilute-solution regime. To this end, we evaluate the effective radii of gyration of polymer structures across a range of parameters, including the number of branching points n , the functionality f (the number of grafted side chains in addition to the backbone), and the relative polymerization degree a , defined as the ratio between the degrees of polymerization of the backbone spacer and the grafted side chains. We combine an analytical approach based on the continuous-chain model and direct polymer renormalization with coarse-grained molecular dynamics simulations and comparison with available experimental data. In particular, we quantitatively estimate the increase in the effective size of comb structures with increasing relative polymerization degree a . Our analytical results show good qualitative agreement with both the simulations and the available experimental data for monodisperse homopolymer combs.

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I. INTRODUCTION

Among the diverse classes of macromolecules, the hyperbranched polymers stand out as a particularly intriguing category that has attracted significant attention in recent years [1–5]. One of the most well-known hyperbranched polymers are dendrimers, which exhibit a highly regular and symmetric branching pattern [6]. Dendritic polymers have demonstrated potential in various fields, including the stabilization of nanocrystals [7], light-emitting materials for optoelectronics [8], and dye loading for advanced imaging applications [5,9]. Additionally, they are widely used in industrial coatings and resins [10], as well as in biomedical applications such as drug delivery systems [1,11], bio-imaging agents [12], tissue engineering scaffolds [13], and bioadhesives [14].

However, in recent decades, researchers have increasingly focused on branched polymers with asymmetric conformations. These polymers offer greater synthetic flexibility, easier scalability, and comparable functionality, making them attractive for a broad range of applications. The versatility and functionality of branched polymers make them a cornerstone of modern material science, and ongoing research continues to unlock new possibilities for their application in advanced technologies and healthcare solutions. Among chemically synthesized branched polymers, a prominent class

is formed by macromolecules featuring branching points distributed along a linear backbone. These are commonly referred to as cylindrical bottlebrush polymers [15], characterized by a high grafting density. The architectural design of these macromolecules—particularly the grafting density and side-chain length—plays a crucial role in determining their structural and rheological behavior [16–19]. The presence of densely packed side chains introduces significant steric interactions, leading to strong spatial correlations among backbone monomers and substantially increased backbone stiffness compared to linear chains [20,21]. As a result, bottlebrush polymers exhibit architecture-dependent rheological properties and can form supersoft materials with elastic moduli comparable to those of gels [18]. The simplest case of bottlebrush topology with only two branching points refers to the pom-pom structure [22,23], which captures key nonlinear-flow features, including lowered zero-shear viscosity and strain hardening in extensional flows [24,25]. The conformational properties of pom-pom polymer structures have been analyzed in Refs. [26–28]. A structurally related class of branched polymers is comb polymers, which feature a lower grafting density [29]. The elongational rheology of a series of polystyrene combs and bottlebrushes has been analyzed in Refs. [25,30,31]. Unlike bottlebrushes, comb polymers in the melt state display pronounced strain hardening under extensional flows. This mechanical response is attributed to the extensibility of the backbone segments between branching points in a semidilute or dilutelike local environment [29].

Branching is central to how polymer architecture governs processing behavior and material properties in both industrial and model systems. A prominent example is low-density polyethylene (LDPE), where long-chain branching enhances melt elasticity and strain hardening, leading to high melt

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strength. These properties are essential for film-blowing and extrusion processes. Owing to these favorable rheological characteristics, LDPE remains one of the highest-volume synthetic polymers, with a global production exceeding 50 Mt/year. Beyond bulk thermoplastics, branched architectures such as comb polymers also find use in advanced functional materials. For instance, they are employed in the surface functionalization of magnetic particles, serving as coating agents that impart steric stability and tunable interfacial properties [32].

The study of conformational properties of macromolecules in dilute solutions represents a foundational aspect of polymer science [33]. At a fundamental level, the behavior and properties of polymeric systems—ranging from mechanical response to transport phenomena—are intimately linked to the conformational characteristics of individual chains. In dilute solutions, the average distance between macromolecules is sufficiently large that intermolecular interactions become negligible. This allows for the investigation of intrinsic single-chain properties such as the radius of gyration and the hydrodynamic radius [34], which are key descriptors of polymer size and shape. These conformational parameters are highly sensitive to both solvent quality and polymer architecture. Importantly, they can be quantitatively predicted using analytical theories [35–37], which have shown strong agreement with experimental observations [37,38] and molecular simulations [26,38–41]. Thus, the dilute solution regime provides a critical testing ground where theoretical models can be directly compared with experiment and simulation, facilitating the development and validation of a fundamental understanding of polymer behavior.

A key strength of analytical approaches to polymers in solutions lies in their ability to describe macromolecular behavior in terms of universal properties—quantities that are largely independent of chemical details and depend primarily on molecular architecture [35,42]. This universality enables comparisons between chemically distinct yet architecturally similar polymers, and allows predictions to be broadly applicable across different systems. Among the most important universal descriptors are scaling exponents, size ratios, and shape characteristics that remain invariant under changes in microscopic chemistry.

Following the pioneering work of Zimm and Stockmayer [36], one widely used metric for quantifying the influence of polymer architecture is the size ratio:

$$g = \frac{\langle R_B^2 \rangle}{\langle R_L^2 \rangle}, \quad (1)$$

which compares the mean-square size $\langle R_B^2 \rangle$ of a branched polymer (such as a comb or bottlebrush) to that $\langle R_L^2 \rangle$ of a linear chain of the same molecular weight. This ratio serves as a sensitive indicator of the conformational impact of branching. The values of size ratio g are influenced by the solvent quality and are found to increase when the excluded volume effect is taken into consideration (good solvent regime) comparing with the Gaussian case (Θ solvent) for different polymer topologies [26–28,43–45].

The size ratio g is used in experimental investigations of high-pressure-processed polyolefins (e.g., LDPE), which are

intrinsically branched because high-pressure radical polymerization promotes both short- and long-chain branching. In this context, size exclusion chromatography – multi-angle laser light scattering (SEC-MALLS) is employed to obtain absolute molar mass M and radius of gyration $R_g(M)$ across the polymer’s molecular-weight distribution, benchmarked against a well-defined linear polyethylene reference to compute $g(M)$. The resulting slice-resolved $g(M)$ serves as an experimental diagnostic of long-chain branching, where values below unity indicate architecture-induced contraction at a given M . Correlating $g(M)$ with extensional rheological metrics (e.g., strain-hardening ratio, melt strength) establishes a direct molecular-to-process linkage that rationalizes and enables prediction of film-blowing stability and overall processing performance.

Theoretical descriptions of the average size R_B and size ratio g of comb polymers in dilute solution often begin with ideal-chain assumptions based on Gaussian statistics [36,46,47]. These models treat the polymer as a collection of freely jointed segments and typically disregard any stiffness or volume exclusion effects. While analytically tractable, such idealized treatments tend to underestimate the actual size of comb polymers observed experimentally. This discrepancy arises primarily because they neglect steric repulsions between densely packed side chains, which can significantly influence the conformation of the backbone. As the side chains become longer or more densely grafted, crowding effects lead to an increase in the effective stiffness of the backbone, manifesting as an extended, rodlike geometry.

To more accurately account for this behavior, researchers have turned to a modified theoretical framework based on the wormlike chain model [48]. In this approach, the backbone is no longer treated as fully flexible, but instead modeled as a semiflexible polymer with a persistence length ℓ that captures the increased rigidity due to side-chain interactions. The side chains themselves are typically assigned a lower persistence length ℓ_s , reflecting their relatively flexible nature, often comparable to that of linear chains in solution. Nakamura *et al.* [48] applied this wormlike comb model to interpret light-scattering measurements of the radius of gyration in dilute solution. By treating ℓ as a fitting parameter, they achieved good agreement with experimental data using $\ell = 5$ nm for the backbone and $\ell_s = 2$ nm for the side chains. These values indicate a significant stiffening of the backbone induced by steric crowding of the side chains, supporting the view that side-chain interactions substantially modify the large-scale conformational properties of the polymer. This perspective has been incorporated into several other theoretical approaches [16,49–51] to combs and bottlebrushes, including scaling theories, free-energy-based models, and self-consistent field calculations, all of which recognize side-chain-induced stiffening as a key factor in determining polymer conformation.

In recent experimental work [52], the degree of compactness of comb polymers in dilute solution was quantified using the ratio $g_H = R_{H,B}^2/R_{H,L}^2$ which compares the square of the hydrodynamic radius $R_{H,B}^2$ of a comb polymer to that $R_{H,L}^2$ of a linear chain with the same molecular weight. The study found that g_H systematically decreases with increasing grafting density, indicating that comb polymers adopt more

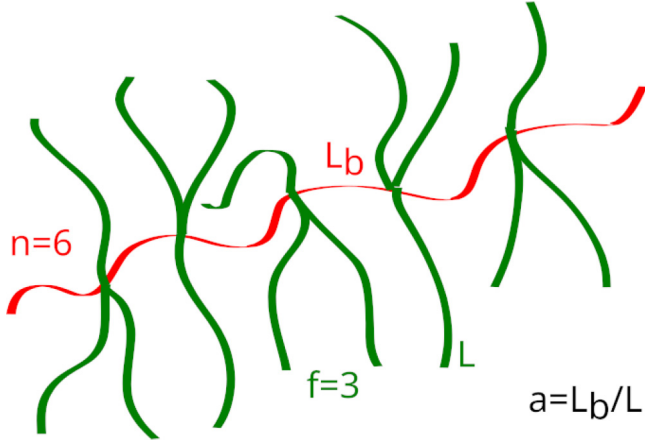


FIG. 1. Schematic illustration of a homopolymer comb polymer consisting of $n = 6$ backbone segments of degree of polymerization L_b (red) with $n - 1 = 5$ branching points, each bearing $f = 3$ side chains (green) of degree of polymerization L . The relative degree of polymerization between the backbone spacer and the side chains is denoted by a . The different colors are used for illustration purposes only, to distinguish the backbone and side chains and to enhance visual clarity.

compact configurations as the number of grafted side chains increases.

In this work, we investigate the conformational properties of comblike polymer architectures (see Fig. 1) using a combination of field-theoretical methods, molecular dynamics (MD) simulations, and experimental data. Our analytical approach is based on a continuous chain model, which provides a microscopic description of the polymer and explicitly incorporates excluded-volume interactions—a key physical feature that is neglected in wormlike chain-based models. Within this framework, we calculate the size ratio of comb polymers relative to linear chains, and compare our theoretical predictions with MD simulation data as well as with available experimental results. This analysis allows us to assess the role of branching and excluded-volume effects on the global conformational behavior of comblike macromolecules.

The paper is organized as follows. In Sec. II, we introduce the analytical model based on a continuous chain formulation that accounts for excluded-volume interactions. Section III describes MD simulations, where comb polymers are modeled as bead-spring chains with tunable architectural parameters. Section IV describes synthesis and characterization of comb polymers. In Sec. V, we present and discuss the results of both analytical calculations and simulations, comparing them with available experimental data. Finally, Sec. VI summarizes our main findings and outlines possible directions for future research.

II. ANALYTICAL APPROACH FOR SIZE RATIO CALCULATION

The continuous chain model represents a polymer as an infinitely thin, continuous trajectory of contour length L , where the spatial position of a point along the chain is described by the radius vector $\vec{r}(s)$, with s denoting the contour coordinate.

For a polymer composed of multiple such trajectories, such as in branched or comblike architectures, the system is described by the following Hamiltonian:

$$H = \frac{1}{2} \sum_{i=1}^F \int_0^{L_i} ds \left(\frac{d\vec{r}_i(s)}{ds} \right)^2 + \frac{u}{2} \sum_{i,j=1}^F \int_0^{L_i} ds' \int_0^{L_j} ds'' \delta[\vec{r}_i(s') - \vec{r}_j(s'')]. \quad (2)$$

Note that the Hamiltonian encodes information about the number of trajectories F , their individual contour lengths L_i , and the type of interaction between points along these trajectories. In the present case, we consider a simple short-range excluded-volume interaction, characterized by a coupling constant u . The connectivity between the trajectories, which defines the overall molecular architecture (e.g., comb structure), is not included directly in the Hamiltonian. Instead, it is imposed through constraints on the end points of the trajectories within the partition function. For the polymer structure considered here, the corresponding partition function is given by the expression

$$Z_{bb} = \frac{1}{Z_0} \int D\vec{r} \prod_{k=1}^{n-1} \delta(\vec{r}_k(L_b) - \vec{r}_{k+1}(0)) \times \prod_{i=1}^f \delta(\vec{r}_k(L_b) - \vec{r}_i(0)) e^{-H}, \quad (3)$$

where n denotes the number of trajectories forming the comb backbone, while f represents the number of side arms radiating from each of the $n - 1$ branching points. This results in a total of $F = n + (n - 1)f$ trajectories. For simplicity in the subsequent analysis, we consider only two distinct contour lengths: L_b for the backbone spacer (distance between two successive grafting points) and L for the side arms. Since, by definition, both L_b and L are treated as infinitely long within the continuous chain model, the final expressions are evaluated in the limit $\lim_{L, L_b \rightarrow \infty} L_b/L = a$, while keeping the ratio $a = L_b/L$ finite.

Within this model the contribution from excluded volume interaction is considered to be much smaller as compared to the Gaussian elasticity term, which allows one to utilize the perturbation theory and consider observables as a series over a dimensionless coupling constant $u_0 = u(2\pi)^{-\frac{d}{2}} L^{2-\frac{d}{2}}$, where u is the bare excluded-volume coupling constant and d is the spatial dimension [35]. As an illustrative example, the partition function can be expressed as a perturbative expansion of the form

$$Z(L, L_b) = Z_0(1 - u_0 Z_1(a, n, f, d) + \dots). \quad (4)$$

Here, Z_0 denotes the Gaussian (nonperturbed) partition function, which is normalized to unity, i.e., $Z_0 = 1$. The term $Z_1(a, F, d)$ represents the first-order correction arising from excluded-volume interactions. Its explicit form is provided in Appendix B. The details of the calculation follow closely the methods presented in our previous works [26–28,38,40,41] and are not repeated here for brevity. Similarly, we can define the radius of gyration. Within the perturbative framework,

R_g^2 can be expressed as a series expansion analogous to the partition function:

$$\langle R_{g|bb}^2 \rangle = \langle R_{g|bb}^2 \rangle^0 \left(1 - u_0 \frac{B(n, a, f, d)}{\langle R_{g|bb}^2 \rangle^0} \right), \quad (5)$$

$$\begin{aligned} \langle R_{g|bb}^2 \rangle^0 &= \frac{dL}{(an + f(n-1))^2} \left(\frac{a^3 n^3}{6} + \frac{n-1}{6} \right. \\ &\quad \times ((an^2 - 2an + 3n - 3)f^2 \\ &\quad \left. + (2a^2 n^2 - a^2 n + 3an - 2)f) \right), \end{aligned} \quad (6)$$

where $\langle R_{g|bb}^2 \rangle^0$ is the Gaussian (unperturbed) contribution discussed in more detail in Ref. [53]. The term $B(n, a, f, d)$ is a nonvanishing contribution from diagram calculation representing the leading-order correction due to excluded-volume interactions. For more details on the derivation, we refer the reader to Ref. [40]. The full expression for the excluded-volume correction to the gyration radius is presented in Appendix B, as it is rather lengthy and technically involved.

Although the model allows for a direct calculation of the gyration radius, the resulting expression cannot be directly compared to simulation or experimental data because it retains an explicit dependence on the chain length L , both directly and indirectly through the dimensionless coupling constant u_0 . While the explicit L dependence can be eliminated by considering universal quantities such as size ratios, the implicit dependence via u_0 must be removed using renormalization group (RG) methods. To achieve this, one introduces RG fixed points such that in the limit $L \rightarrow \infty$, the bare coupling u_0 flows to its renormalized value u_R . In the framework of direct polymer renormalization developed by des Cloizeaux and Jannink [35], the fixed points of the RG flow for the Hamiltonian under consideration are

$$\text{Gaussian : } u_R^* = 0, \text{ for } d \geq 4, \quad (7)$$

$$\text{EV : } u_R^* = \frac{\epsilon}{8}, \text{ for } d < 4, \quad (8)$$

where $\epsilon = 4 - d$ is the deviation from the upper critical dimension and serves as the expansion parameter in the perturbative RG analysis.

In general, the radius of gyration for a polymer with an arbitrary topology can be defined as

$$\langle R_g^2 \rangle = \langle R_{g|0}^2 \rangle \left(\frac{2\pi N}{\Lambda} \right)^{2\nu(\eta)-1} f_p(\eta), \quad (9)$$

where N is the degree of polymerization, Λ is the coarse-graining length scale [54] that sets the resolution of the model, and $f_p(\eta)$ is a topology-dependent crossover function that accounts for solvent quality. The variable η governs the crossover from ideal to swollen conformations: $f_p(\eta) \rightarrow 1$ as $\eta \rightarrow 0$ (corresponding to a Gaussian chain), and $f_p(\eta) \rightarrow 1 + \alpha$ as $\eta \rightarrow \infty$ (corresponding to good solvent), where α is a topology-dependent parameter. The prefactor $(2\pi N/\Lambda)^{2\nu(\eta)-1}$ captures the universal scaling behavior arising from excluded-volume effects and is independent of the molecular topology. Consequently, the influence of polymer architecture is fully contained within the function $f_p(\eta)$, which naturally leads to

defining the size ratio as follows:

$$g_x = \frac{\langle R_{g,1}^2 \rangle_0}{\langle R_{g,2}^2 \rangle_0} \frac{1 + \alpha_1(\epsilon, F, a)}{1 + \alpha_2(\epsilon, F, a)}. \quad (10)$$

Note that the parameters α_1 and α_2 still retain a dependence on the dimensional deviation ϵ and are typically evaluated only to first order in ϵ (i.e., $\propto \epsilon$) within the one-loop approximation. However, achieving quantitative agreement with experimental data requires going beyond this level of approximation—specifically, including terms of order $\propto \epsilon^2$. Unfortunately, such higher-order calculations become extremely challenging, even for relatively simple branched topologies such as star polymers. To overcome the limitations of the standard ϵ expansion, Douglas and Freed (DF) [37] proposed an approximation that provides practical estimates of scaling corrections for complex architectures without requiring full multiloop computations. The DF approach effectively resums the leading excluded-volume contributions. It successfully captures the correct scaling behavior of branched architectures (e.g. stars, combs [37], and pom-poms [26,28]) without invoking higher-order diagrams, a significant advantage given the rapidly increasing number and complexity of Feynman-type diagrams at higher orders. This improvement is especially relevant for comb topologies, where excluded-volume interactions and branching effects are strongly coupled.

The approximation becomes particularly useful when establishing a connection between the RG approach and the two-parameter model in three-dimensional space ($d = 3$). In this context, the topology-dependent correction parameter α can be approximated by the expression

$$\alpha = \frac{3}{4} \frac{\epsilon B(n, a, f, d=3)}{8 \langle R_{g|bb}^2 \rangle^0} - \frac{1}{4}. \quad (11)$$

This approximation has the advantage of retaining valuable structural information encapsulated in $B(n, a, f, d)$ that would otherwise be lost when truncating the full RG expansion at $\mathcal{O}(\epsilon)$. By embedding this structure-specific term into the two-parameter model, it offers a practical route to estimate α beyond one-loop accuracy without explicitly performing a full ϵ^2 calculation, which is often infeasible for complex branched architectures.

Note that for $n = 2$ and $a = 0$, we recover expressions for star polymers, while for $n = 3$ we obtain the expression for a pom-pom polymer [26,28]. For $f = 0$ and in the limit of large n , the expression reduces to that of a linear chain. Due to the complexity and length of the corresponding analytical expressions, we do not reproduce them here but instead refer the interested reader to Refs. [26,28] for the detailed formulas. It is also important to point out that we do not employ the ϵ expansion here, as it has been shown to provide only a qualitative description [38] and, in some cases, such as pom-pom polymers with a large number of side chains, yield to nonphysical results [26].

III. MOLECULAR DYNAMICS SIMULATIONS

The simulations employ a three-dimensional bead-spring coarse-grained model [55], in which each bead has a size σ_L and an equal mass m . The comb polymer architecture is

represented by a backbone of N_b beads, with side chains of N_s beads grafted at a regular spacing characterized by the grafting density z , defined as the fraction of backbone beads bearing side chains. In the present study, $z = 1/3$ corresponds to grafting on every third backbone bead, while $z = 1/9$ corresponds to grafting on every ninth bead. Consistent with the theoretical model, the terminal backbone beads do not carry side chains.

Connectivity between beads is provided by a finitely extensible nonlinear elastic (FENE) spring using the following potential:

$$V^{\text{FENE}}(r) = -0.5kr_0^2 \ln[1 - (r/r_0)^2], \quad (12)$$

with two constants $k = 30\epsilon/\sigma_{\text{LJ}}^2$ and $r_0 = 1.5\sigma_{\text{LJ}}$ with r being a distance between beads. Interaction between nonbonded beads is given by the shifted and truncated repulsive branch of the Lennard-Jones (LJ) potential, also called the Weeks-Chandler-Anderson (WCA) interaction:

$$V^{\text{WCA}}(r) = 4\epsilon_{\text{LJ}}[(\sigma_{\text{LJ}}/r)^{12} - (\sigma_{\text{LJ}}/r)^6 + 1/4]\theta(2^{1/6}\sigma_{\text{LJ}} - r), \quad (13)$$

with ϵ_{LJ} and σ_{LJ} being chosen as units of energy and length, respectively. In Eq. (13), $\theta(x)$ is a Heaviside step function that equals 1 for $x < 0$ and 0 for $x \geq 0$. The choice of the WCA potential corresponds to good solvent conditions, as it models purely repulsive interactions that prevent monomer overlap without inducing attractive forces.

The simulations are carried out using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [56], which integrates Newton's equations of motion via the velocity-Verlet algorithm. A constant temperature T is maintained using a Langevin thermostat with a damping coefficient $\zeta = 0.5 \text{ m}\tau^{-1}$, where $\tau = \sqrt{m\sigma_{\text{LJ}}^2/\epsilon}$ is the LJ time unit. The system consists of 27 molecules placed in a cubic simulation box with periodic boundary conditions. We consider comb polymers with backbones consisting of $N_b = 100, 200$, or 500 beads, and side chains ranging in length N_s from 1 up to 128 beads, grafted onto every ninth or every third bead along the backbone. To model dilute solution conditions, steric interactions between different molecules are turned off. To achieve adequate equilibration of comb polymers, a sufficiently large number of MD steps was used to ensure relaxation of the mean end-to-end distance to its equilibrium value. This criterion resulted in simulation runs ranging from 2×10^6 and 2×10^8 MD steps, depending on the length of the comb backbone, the side chains, and the grafting density. Each simulation runs for at least three autocorrelation times of the radius of gyration to ensure sufficient data collection, using an integration time step of $\Delta t = 0.005\tau$.

The conformational regimes of comblike and bottlebrush polymers can be classified using the dimensionless overlap parameter $N_s z$, which quantifies the combined effect of the side-chain length N_s and the grafting density z [16,17]. For $N_s z \ll 1$, the side chains do not overlap, and the macromolecule adopts the conformation of a loosely grafted comb. When $N_s z \approx 1$, side-chain overlap leads to partial stretching of the backbone, corresponding to a densely grafted comb. At higher values, $N_s z \gtrsim 1$, the polymer enters the bottlebrush regime, initially forming a loosely grafted bottlebrush and, for $N_s z \gg 1$, a densely grafted bottlebrush in which both the side

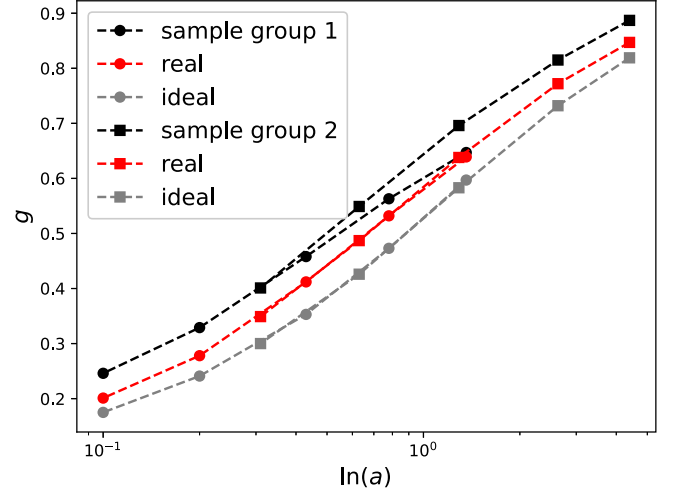


FIG. 2. Size ratios of comb polymers relative to their linear counterparts, obtained from analytical theory for ideal (g_{ideal} in gray) [60] and real conformations (g_{real} in red) and from experiment (g_{exp} in black) [61]. Data for various numbers of backbone segments n between grafting points and for different ratios a . Numerical values corresponding to the data shown are listed in Table III.

chains and the backbone are highly extended. In our simulations, the side-chain length N_s varies over a broad range, from short to very long chains, which allows us to observe a clear crossover from the comblike regimes ($N_s z \lesssim 1$) to the bottlebrush regimes ($N_s z \gg 1$).

IV. SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS

Lightly grafted comb copolymers composed of a polystyrene (PS) backbone and poly(*tert*-butyl methacrylate) [P(*t*BuMA)] side chains were synthesized using a combination of two controlled/“living” radical polymerization techniques: nitroxide-mediated polymerization (NMP) and photoinduced *iniferter* polymerization. The synthetic route and experimental procedures have been described previously and are briefly summarized below [57].

In the first step, random copolymers of styrene (S) and *p*-chloromethylstyrene (CMS) were synthesized via 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)-mediated NMP, yielding P(S-*co*-CMS) precursors with well-defined molecular weights and narrow molecular weight distributions. The reactivity ratios for S ($r_S = 0.72$) and CMS ($r_{\text{CMS}} = 1.08$) ensured a statistical incorporation of CMS units along the PS backbone. In the second step, quantitative nucleophilic substitution of the CMS groups with sodium *N,N*-diethyldithiocarbamate produced macroinitiators bearing covalently attached dithiocarbamate moieties. These served as photoiniferter sites for subsequent side-chain growth under UV irradiation.

The “grafting-from” polymerization of *tert*-butyl methacrylate (P*t*BMA) was initiated photochemically in solution, using a fixed concentration of the macroinitiator and varying [monomer]/[initiator] ratios to achieve precise control over side-chain length. The degree of polymerization of the PS backbone was held constant at $N_b = 95$, with an average

TABLE I. Molecular parameters and absolute sizes of comb copolymers in THF at 25 °. Data are from Ref. [57]. Absolute SAXS R_g values are extracted from the Guinier fits extrapolated to $c \rightarrow 0$.

Sample	M_n (kg/mol)	M_w (kg/mol)	$\bar{D}$	n	N_s	a	R_g (SAXS) (nm)	R_g SEC-MALS (ASTRA) (nm)
M2-DC (macroinitiator)	10.9	11.2	1.03	≈ 11	$N_b = 95$		4.0	3.3
M2-1	28.8	40.3	1.40	≈ 11	14	0.617		
M2-2	63.1	88.9	1.41	≈ 11	42	0.205		
M2-3	80.0	154	1.90	≈ 11	56	0.155	10.8	20.4
M2-4	100	166	1.66	≈ 11	72	0.12	6.8	13.8
M2-5	158	418	2.63	≈ 11	120	0.071	8.0	18.1
M2-6	162	262	1.62	≈ 11	122	0.071	10.3	11.2
M2-7	163	328	2.01	≈ 11	124	0.07	10.3	20.7
M2-8	284	663	2.33	≈ 11	222	0.039	8.0	15.9

of 11 grafting points per chain. The side-chain length, N_s , was varied between 14 and 222 across the M2-1 to M2-8 series.

All polymers were purified by repeated precipitation into methanol and characterized by size exclusion chromatography (SEC) in tetrahydrofuran (THF) using triple detection: multi-angle laser light scattering (MALLS), differential refractometry, and viscometry. The SEC traces were unimodal across the entire series, confirming the absence of crosslinked or multichain species. Absolute values of the number-average molecular weight M_n , weight-average molecular weight M_w , dispersity index $\bar{D}$ (M_w/M_n), intrinsic viscosity η , and radius of gyration R_g were determined for each sample. A detailed summary of the molecular, hydrodynamic, and architectural parameters has been published elsewhere [57]. Here we provide relevant data in Table I.

Small-angle x-ray scattering (SAXS) experiments were performed using a pinhole camera (Molecular Metrology SAXS system) attached to a microfocused x-ray generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector of 20-cm active diameter (Gabriel design). Two experimental setups were used to cover the q range of $0.007\text{--}1.1 \text{ \AA}^{-1}$ ($q = 4\pi \sin(\theta/2)/\lambda$), where λ is the wavelength and θ is the scattering angle. The scattering intensities were placed on an absolute scale using a glassy-carbon standard (NIST SRM 3600). Solvent scattering was measured separately and subtracted prior to data fitting. The radius of gyration R_g was calculated using the Guinier approximation

$$I(q) = I(0) \exp\left(-\frac{q^2 R_g^2}{3}\right), \quad (14)$$

applied to the low- q region of the SAXS curves for the macroinitiator and all graft copolymers in THF solutions at concentrations of 5×10^{-3} , 1×10^{-2} , and $2 \times 10^{-2} \text{ g/cm}^3$. This approach is applicable regardless of the exact particle shape. The values of R_g were subsequently extrapolated to infinite dilution. The typical uncertainty in R_g derived from the Guinier analysis was estimated as $\pm 5\%$, reflecting the statistical error from the low- q region and minor systematic contributions from calibration and background subtraction. The resulting R_g values (with 5% uncertainty) are reported in Table I and represent absolute SAXS measurements, suitable for direct comparison with theoretical and simulation results.

The comb polymers studied here have a PS-type backbone (from functionalized CMS) and PtBMA side chains. Both polymer types are fully soluble in THF at 25 °C and act as good-solvent chains. In particular, dynamic and static light scattering studies of polystyrene in THF [58] demonstrate well-behaved coil and diffusion scaling across molecular weights without aggregation or phase separation [58,59]. Although analogous detailed scattering data for PtBMA in THF are fewer, literature reports of its hydrodynamic and scattering properties under similar conditions support its good solubility and coil behavior. All our SAXS and DLS data (optically clear solutions, no low- q upturn, monomodal DLS) are consistent with these observations. Thus, our combs can legitimately be regarded as homopolymerlike architectures in a good solvent for comparison with theory and simulations.

V. RESULTS AND DISCUSSION

In Fig. 2 we display the size ratio g of comb polymers relative to linear chains of the same molecular weight as a function of the parameter (definitions for different methods are listed in Table II) a , plotting $\ln a$ on the x axis to spread out the data and avoid crowding at small a values. We compare our theoretical predictions with the available experimental data (g_{exp} , shown in black) for the size ratio of homopolymer comb polymers with monodisperse side chains ($\bar{D} \approx 1.05$), as reported in Ref. [61]. For these samples, the parameter a could be reliably estimated. The experimental results g_{exp} are compared with size ratios obtained from our analytical approach for both ideal (Gaussian) conformations (g_{ideal} , shown in gray) and real comb conformations that account for excluded-volume interactions (g_{real} , shown in red). The numerical values corresponding to this plot are summarized in Table III in Appendix C. We observe that the

TABLE II. Connection between the parameters of theory, simulations, and experiments.

Theory	Simulations	Experiments
L	N_s	M_n^{side}
L_b	$1/z$	M_n^{backbone}/n
n	zN_b	n
$a = L_b/L$	$a = 1/(zN_s)$	$a = M_n^{\text{backbone}}/(nM_n^{\text{side}})$

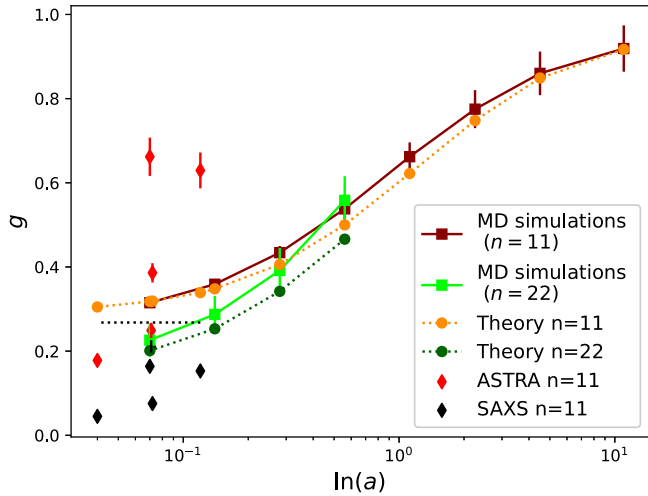


FIG. 3. Size ratio g for comb polymers with grafting density $z = 1/9$ as a function of parameter a , shown on a lin-log scale. Circles represent theoretical predictions from the Douglas-Freed approximation, squares correspond to molecular dynamics simulation data, and diamonds denote experimental results [57]. The horizontal line indicates the limiting value of g as $a \rightarrow 0$, corresponding to a star polymer with 11 arms. Numerical values corresponding to the data shown are listed in Table I (experiments) and Table IV (theory and simulation).

size ratio g increases with increasing a . Large values of a correspond to combs with short side chains relative to the backbone spacers, whereas small values of a indicate comb architectures with long side chains compared to the spacers. As shown in Fig. 2, for small values of a , the discrepancy between the theoretical g_{real} and experimental g_{exp} values remains within approximately 20%. Moreover, this deviation decreases with increasing a , indicating that the theoretical model becomes more accurate for comb polymers with shorter side chains relative to the backbone. Importantly, accounting for excluded-volume effects significantly improves the agreement between theory and experiment, whereas predictions based on ideal conformations systematically underestimate the experimental values across the entire range of a .

In Figs. 3 and 4, the values of the size ratio g obtained from our theoretical model (circles) and molecular dynamics simulations (squares) are compared with the available experimental data for comb copolymers (diamonds). The connections between the parameters used in the theory, simulations, and experiments are provided in Table II. The simulation data correspond to combs with grafting densities $z = 1/9$ and $1/3$. Experimental radii of gyration for the comb copolymers with 11 grafting points were taken from Ref. [57], while the corresponding values for linear chains were estimated using the procedure described in Appendix A.

First, we compare the theoretical predictions with simulation results. The overall theoretical trend of g versus a is well reproduced quantitatively across all MD datasets shown in Figs. 3 and 4. The closest agreement over the entire range of a is observed for loosely grafted combs ($z = 1/9$) with a relatively small number of backbone spacer segments ($n = 11$), corresponding to a backbone degree of polymerization

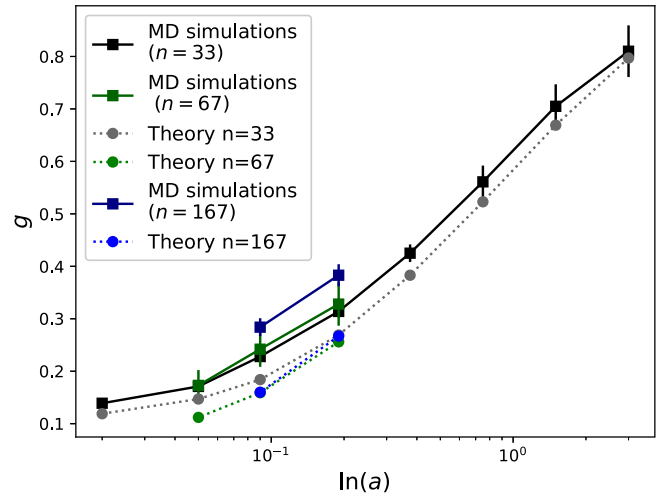


FIG. 4. Size ratio g for comb polymers with grafting density $z = 1/3$ as a function of parameter a , shown on a lin-log scale. Circles represent theoretical predictions from the Douglas-Freed approximation and squares correspond to molecular dynamics simulation data. Numerical values corresponding to the data shown are listed in Table V.

$N_b = 100$ (maroon and orange data points in Fig. 3). For this dataset, simulations accurately reproduce the theoretical predictions for both small and large values of a . For $a > 1$, agreement between theory and simulations is expected. In this regime, the side chains are short and do not interact significantly with each other, and the weak steric effects they impose on the backbone are adequately captured by the perturbative character of our theory. What is less anticipated, however, is the observed agreement at the smallest values of a . In this regime, side chains are sufficiently long to interact and stretch due to mutual excluded-volume effects. The observed agreement can be rationalized by considering the actual segment lengths in the simulations: side chains with $N_s = 64$ or 128 beads are comparable in length to a backbone of 100 beads. This indicates that the contribution of side chains to the overall gyration radius dominates over the backbone, effectively masking the steric effects imposed by the backbone. For comparison, the theoretical size ratio for a 12-arm star polymer relative to a linear chain is 0.249, while for a pom-pom polymer [26–28] (defined as a linear backbone with arms grafted symmetrically at both ends) with six arms on each side and a relative backbone length of 0.78 it is 0.397. The size ratio for comb polymer with 11 side chains lies in between, with 0.315, confirming the dominant role of the side chains in determining the polymer's overall size. Note that MD data for longer backbones with $N_b = 200$ (green squares in Fig. 3) show somewhat reduced agreement with theory, particularly at larger values of a , as the increased backbone length enhances steric interactions and backbone contributions, which are only partially captured by the perturbative approximation. An even greater discrepancy is observed for more densely grafted combs ($z = 1/3$), as shown in Fig. 4, where steric effects become significantly more pronounced.

Next, we compare the predictions of our theoretical model and simulation results with the experimental dataset shown

in Fig. 3, which includes combs with side-chain degrees of polymerization ranging from $N_s = 72$ to 222. These data points correspond to comb copolymers with high polydispersity ($\bar{D} > 1.6$, see Table I) in a solvent that is good for both components. This second dataset pertains to polydisperse copolymers, with both components in a good solvent, and is used to test the applicability of our theory to systems with polydispersity. Among these, three samples share identical architectural parameters but differ in weight-average molecular mass and radius of gyration. We provide results for these samples obtained from two different measurement methods: the red diamonds correspond to SEC-MALS (ASTRA) data, while the black diamonds represent SAXS measurements. Notably, among the red diamonds, only one of the three points shows reasonably good agreement with our theoretical and simulation results. One sample exhibits a substantially lower size ratio, consistent with a starlike polymer architecture featuring 11 arms, while another shows a significantly higher ratio. The latter can likely be attributed to structural heterogeneity, where four or five side chains are substantially longer than the rest, yielding size ratios close to those expected for stars with four [$g(f = 4) = 0.629$] or five arms [$g(f = 5) = 0.527$]. Resolving these discrepancies would require a dedicated theoretical study of the effects of side-chain polydispersity. In contrast, the black points correspond to conformations that are much more compact than an 11-arm star polymer, possibly indicating the presence of loops or, in some cases, even the formation of a highly compact network. However, caution is needed when interpreting these data, since the original papers from which the fitting data in Appendix A were obtained do not specify the measurement methods used. In any case, these situations also call for further theoretical investigation to clarify the influence of polydispersity on g . The two remaining data points correspond to $N_s = 72$ and 222. The $N_s = 72$ sample again behaves more like a star polymer with a smaller number of arms, while the $N_s = 222$ sample exhibits an unusually low size ratio. This small value ($g = 0.1779$) is remarkably close to the theoretical prediction of $g = 0.178$ for a rosette polymer structure [38] containing five chains and six loops, suggesting possible loop formation in this sample. It is worth noting that the monodisperse homopolymer samples in Fig. 2 show a monotonic dependence on a and a reasonably good agreement with the theoretical predictions. In contrast, the copolymer samples in Fig. 3 exhibit an irregular dependence on a , which we attribute to their polydispersity. Although both parts of the copolymer are in a good solvent regime, our current analytical model does not account for the effects of polydispersity.

VI. CONCLUSIONS

In this work, we investigated the conformational behavior of comb polymers with low to moderate grafting densities relative to linear chains of the same molecular mass, using the size ratio as a metric. A comprehensive understanding was achieved by integrating analytical predictions, molecular dynamics simulations, and experimental validation. Our analytical framework, based on the continuous chain model combined with direct renormalization and the Douglas-Freed approximation, successfully captures the key conformational

features of these complex, branched architectures. To test these predictions, molecular dynamics simulations were performed. Overall, the simulations reproduce the general trends predicted analytically. For loosely grafted combs with small and large backbone spacers relative to side-chain length, there is quantitative agreement between theory and simulations, whereas for other cases, the agreement is qualitative. In the analytical approach, we employ a perturbative framework, with calculations carried out to first order beyond ideal chain statistics, which limits the quantitative accuracy in the intermediate backbone spacer regime. Importantly, the analytical predictions show consistent qualitative alignment with available experimental data for homopolymer combs with low side-chain polydispersity [61]. For samples with high polydispersity, only one data point, corresponding to copolymer combs with low grafting density, agrees reasonably with theoretical predictions, while the remaining points indicate a different behavior. Addressing these discrepancies and clarifying the effects of polydispersity will require a dedicated study.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A

One of the experimental samples considered in this study is in fact a copolymer. However, since both components are dissolved under good solvent conditions, it is still meaningful to calculate the corresponding size ratio. A key question arises: which homopolymer data should be used to estimate the radius of gyration of the equivalent linear chain—the backbone (PS) or the side chains [PtBuMA]? While PS has well-established mass-size scaling data available in the literature [63], PtBuMA constitutes a larger fraction of the copolymer's total mass and may therefore provide a more representative estimate. Unfortunately, for PtBuMA, only two data points are available from Polymer Source, with no comprehensive measurements found in the literature to the authors' knowledge.

To address this limitation, we adopt a pragmatic approach: we compile all available data from Ref. [63] and present them in Fig. 5. Notably, the data points (shown in red) cluster along a common black trend line, which is consistent with observations in the original source. This clustering can be attributed to the similarity in both the scaling exponents (as expected for polymers in good solvents) and the prefactors across different polymer types.

TABLE III. Size ratios of comb polymers relative to their linear counterparts are presented as obtained from analytical theory: for ideal (Gaussian) conformations (g_{ideal}) [60], for real conformations including steric interactions (g_{real}) as calculated in this work, and from experimental measurements (g_{exp}) [61]. The data are shown for various values of the number of backbone segments n between grafting points and for different ratios a .

Sample group	n	a	g_{ideal}	g_{real}	g_{exp}
1	31	1.36	0.597	0.649	0.647
1	30	0.78	0.473	0.532	0.563
1	25	0.43	0.353	0.412	0.458
1	29	0.20	0.241	0.278	0.329
1	29	0.10	0.175	0.201	0.246
2	30	4.40	0.819	0.847	0.887
2	28	2.63	0.732	0.772	0.815
2	26	1.29	0.583	0.638	0.696
2	29	0.63	0.426	0.487	0.549
2	28	0.31	0.300	0.349	0.401

By pooling the data, we obtain a sufficiently large dataset that can be split into training and testing subsets using an 80:20 ratio. Linear regression was performed using the *scikit-learn* library [64], resulting in a strong fit with a coefficient of determination $R^2 = 0.98$. Note that the data for PS in THF were included in the fitting procedure, and although the two available points for PtBuMA were not used in the fit, they lie close to the predicted trend line (see green points in Fig. 5). The extracted scaling exponent, $\nu = 0.558(8)$, is

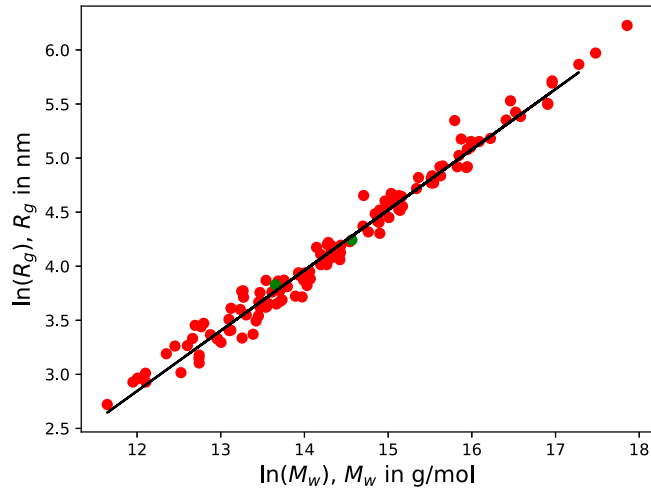


FIG. 5. Experimental data for the radius of gyration for linear chains in good solvents: PS (red circles) [63] and high molecular weight PtBuMA homopolymers were synthesized at Polymer Source Inc. following the procedure described by Varshney *et al.* [66], with molecular characterization data (M_n , M_w , R_g) provided in internal technical datasheets [67] (green circles). Data are plotted in logarithmic scale as a function of molecular weight M . The black solid line represents a fitting line: $\langle R_g^2 \rangle^{1/2} = AM^{\nu_{\text{exp}}}$, with parameters $A = 0.022 \pm 0.002$ and $\nu_{\text{exp}} = 0.558 \pm 0.008$.

TABLE IV. Numerical values for the data presented in Fig. 3.

n	a	g_{MD}	g_{theory}
11	11	0.919	0.917
11	4.5	0.865	0.849
11	2.75	0.775	0.748
11	1.12	0.662	0.622
11	0.56	0.538	0.5
11	0.28	0.434	0.406
11	0.14	0.539	0.348
11	0.07	0.315	0.318
22	0.56	0.558	0.466
22	0.28	0.392	0.342
22	0.14	0.287	0.253
22	0.07	0.226	0.201

slightly lower than theoretical predictions for polymers in good solvents (typically $\nu \approx 0.588$ [65] in three dimensions). The impact of this deviation on the accuracy of the size ratio estimation is difficult to quantify, particularly given the uncertainty in how closely the comb copolymer follows scaling behavior of a linear polymer. Nevertheless, this approximation may introduce some systematic error into the analysis. The resulting fit was then used to estimate the radius of gyration corresponding to a given molecular weight of a comb polymer.

TABLE V. Numerical values for the data presented in Fig. 4.

n	a	g_{MD}	g_{theory}
33	3	0.810	0.797
33	1.5	0.705	0.669
33	0.75	0.561	0.523
33	0.375	0.425	0.383
33	0.19	0.314	0.269
33	0.09	0.228	0.184
33	0.05	0.0.171	0.141
33	0.02	0.139	0.119
67	0.19	0.328	0.256
67	0.09	0.242	0.159
67	0.05	0.173	0.112
167	0.19	0.383	0.267
167	0.09	0.284	0.16

APPENDIX B

The first-order correction Z_1 to the partition function Z of a comb polymer [see Eq. (4)], arising from excluded-volume interactions, is given by

$$\begin{aligned} Z_1(a, n, f) = & \frac{(n-1)f(f-1) - 2a + 2(n-1)f}{\epsilon} - a \ln(n) - a + (n-1)f \\ & - \frac{(n-1)f(f-1)}{2} (\ln(2) - 1) + \sum_{i=1}^{n-1} (2f \ln(ai) - 2f \ln(ai+1)) \\ & - \frac{f^2}{2} \sum_{i=1}^{n-2} (n-i-1)(2 \ln(ai+2) - 4 \ln(ai+1) + 2 \ln(ai)). \end{aligned} \quad (\text{B1})$$

The term $B(n, a, f, d)$ representing a nonvanishing contribution to the leading-order correction from excluded-volume interactions, arising from diagrammatic calculations in the evaluation of the radius of gyration of a comb polymer [see Eq. (5)], is given by

$$\begin{aligned} B(n, a, f, d) = & -\frac{(d^2 - 26d + 136)(an)^{-\frac{d}{2}+5}}{3(d-10)(d-8)(d-4)(d-6)} + 8f^2 \sum_{i=1}^{n-2} \sum_{j=1}^{n-i-1} \left(\frac{(ai)^{-\frac{d}{2}+3}(d-2)(d-4) + 8(aj)^{-\frac{d}{2}+3}}{d(d-6)(d-2)(d-4)} \right) \\ & - \frac{2af(an)^{-\frac{d}{2}+3}(n-1)((d^3 - 18d^2 + 56d - 192)n - (d-8)(d-6)(d-4))}{3((d-8)d(d-6)(d-4)(d-2))} \\ & - \sum_{i=1}^{n-1} \left(\frac{48af(ai)^{-\frac{d}{2}+3}(d^2i - 6di - 4dn + 32n)}{3(d-8)d(d-6)(d-4)(d-2)} \right) - \sum_{i=1}^{n-2} \frac{4(n-i-1)f^2(ai)^{-\frac{d}{2}+3}}{(d-6)(d-4)} \\ & - 8f^2a^2 \sum_{i=1}^{n-2} \sum_{j=1}^{n-i-1} \left(\frac{(a(i+j))^{-\frac{d}{2}+1}(d^2i^2 - 6di^2 + 4dij + 8i^2 - 8ij + 8j^2)}{d(d-6)(d-2)(d-4)} \right) \\ & - 4a^2f^2 \sum_{i=1}^{n-2} \sum_{j=1}^{n-i-1} \left(\frac{i^2(-(-a(j-n))^{-\frac{d}{2}+1} - (a(i+j))^{-\frac{d}{2}+1} + (an)^{-\frac{d}{2}+1} + (ai)^{-\frac{d}{2}+1})}{d(d-2)} \right) \\ & - \frac{f(4(d-10)^2(n-1)^2f + (n-1)(-3d^2 + 54d - 264) + 4n(d-10)^2(n-1)a)}{3(d-4)(d-6)(d-10)(d-8)} \\ & - \frac{f}{3d(d-6)(d-2)(d-4)(d-8)(d-10)} ((n-1)(f-1)(2^{3-\frac{d}{2}}(-3840 + (d-10)(d^3 - 18d^2 + 8d - 192)f) \\ & + 3d^4 - 108d^3 + 1524d^2 - 10320d + 30720 - (4(d-10))(d-12)(d^2 - 6d + 32)f) \\ & + 4n(n-1)(f-1)(d-10)2^{1-\frac{d}{2}}(d^3 - 18d^2 + 8d - 192) - 104d + 384 - d^3 + 18d^2)a \\ & + 2fa^4 \left(\sum_{i=1}^{n-2} (i^2(- (ai)^{1-\frac{d}{2}} - (ai+2)^{1-\frac{d}{2}} + 2(ai+1)^{1-\frac{d}{2}})((i-n)^2 - 1)(i-n)) \right) (d-10)(d-6)(d-8)(d-4) \\ & - f \left(\sum_{i=1}^{n-2} ((-n+1+i)(-2(ai+1)^{1-\frac{d}{2}}((12(f-1))(d-8)(d-10)fi^2a^2(d-4)(d-6) + 12(f-1)(d-8)(d-10) \right. \\ & \times ((d-6)(d-8)(ai+1) - (d^2 - 14d + 32)(ai+1)^2) + 4(d-10)(d^3 - 24d^2 + 140d - 384)(f-1)(ai+1)^3 \\ & + 4(d-10)^2d(d-2)f(ai+1)^3 + d(d-2)(d^2 - 26d + 136)(ai+1)^4) + (ai+2)^{1-\frac{d}{2}}(12(f-1)(d-10)(d-6) \\ & \times (d-8)(d-4)(4f-4 - (2(2f-3))(ai+2) + (f-3)(ai+2)^2) + 8(d-10)(d^3 - 18d^2 + 80d - 192)(f-1) \\ & \times (ai+2)^3 + d(d-2)(d^2 - 26d + 136)(ai+2)^4) + (ai)^{3-\frac{d}{2}}((12(d-8))(d-10) \\ & \times (-8 + (8d-16)f + (d-4)(d-6)f^2) + (8(d-10))i(6d^2 - 60d + 192 + (d^3 - 18d^2 + 80d - 192)f)a \\ & + di^2(d-2)(d^2 - 26d + 136)a^2) + 2^{4-\frac{d}{2}}(d-10)(d^3 - 18d^2 + 8d - 192)(f-1) - 8(d-10)(d-12) \end{aligned}$$

$$\begin{aligned}
& \times (d^2 - 6d + 32)(f - 1))) + 4fa(d - 10) \sum_{i=1}^{n-2} \left(-(ai + 1)^{1-\frac{d}{2}} ((d - 6)(d - 8)(d - 4)(6f - 3 - 12f(ai + 1) \right. \\
& + 6f(ai + 1)^2) + (d - 8)((3(d - 6))(3d - 16)(ai + 1) + (6(-d^2 + 12d - 28))(ai + 1)^2) \\
& + (2(d^3 - 18d^2 + 80d - 192))(ai + 1)^3) + (ai + 2)^{1-\frac{d}{2}} ((d - 6)(d - 8)(d - 4)(12f - 12 - 3(4f - 5)(ai + 2) \\
& + (3(f - 2))(ai + 2)^2) + (d^3 - 18d^2 + 80d - 192)(ai + 2)^3) + (ai)^{3-\frac{d}{2}} (3(d - 8)(d^2f - 10df + 4d + 24f - 8) \\
& + i(d^3 - 18d^2 + 80d - 192)a))(-n + 1 + i)(-n + i)) + f^3 \sum_{i=1}^{n-3} \sum_{j=1}^{n-2-i} \left(\frac{4(n - i - j - 1)}{3d(d - 2)(d - 6)(d - 8)(d - 4)} \right. \\
& \times \left((d^3 - 18d^2 + 80d - 192)(2(aj + 1)^{4-\frac{d}{2}} + 2(ai + 1)^{4-\frac{d}{2}} + (ai + aj + 1)^{1-\frac{d}{2}}(2i + 2j)(i^2 - ij + j^2)a^3 \right. \\
& - (ai + aj)^{1-\frac{d}{2}}(i + j)(i^2 - ij + j^2)a^3 - (aj + 2)^{4-\frac{d}{2}} - (ai + 2)^{4-\frac{d}{2}} - (ai + aj + 2)^{2-\frac{d}{2}}(i^2 - ij + j^2)a^2 \\
& - (ai)^{4-\frac{d}{2}} - (aj)^{4-\frac{d}{2}}) + (aj + 1)^{1-\frac{d}{2}}(d - 8)(3(d - 6)(d - 4) - 3d(d - 6)(aj + 1) + 12(d - 2)(aj + 1)^2) \\
& + (ai + 1)^{1-\frac{d}{2}}(d - 8)(3(d - 6)(d - 4) - 3d(d - 6)(ai + 1) + (12(d - 2))(ai + 1)^2) + (ai + aj + 1)^{1-\frac{d}{2}} \\
& \times (2(d - 12)(d^2 - 6d + 32) + 3(d^3 - 14d^2 + 32d - 256)(i + j)a + (-12(d - 6)(d - 8)(d - 4)ji \\
& + (6d^3 - 96d^2 + 360d - 960)(i + j)^2)a^2 - (144(i + j))dija^3) - (ai + aj)^{1-\frac{d}{2}}((3(d - 8))(i^2 + j^2)(d^2 - 6d + 16) \\
& + 8i(d - 2)j)a^2 - (72(i + j))dija^3) - (ai + aj + 2)^{2-\frac{d}{2}}((d^3 - 18d^2 + 8d - 192)(ai + aj + 1) - 72idja^2) - ((ai)^{3-\frac{d}{2}} \\
& + (aj)^{3-\frac{d}{2}})(3d - 24)(d^2 - 6d + 16) + 3(d - 6)(d - 8)(d - 4)((aj + 2)^{2-\frac{d}{2}}(aj + 1) + (ai + 2)^{2-\frac{d}{2}}(ai + 1))) \\
& + \frac{2(1 - n + i + j)(ai + aj - an - 4f + 4)}{d(d - 2)} \left(-a^2(i^2 + j^2)((ai + aj + 2)^{1-\frac{d}{2}} - 2(ai + aj + 1)^{1-\frac{d}{2}} + (ai + j)^{1-\frac{d}{2}} \right. \\
& + a^2j^2(2(aj + 1)^{1-\frac{d}{2}} - (aj + 2)^{1-\frac{d}{2}} + a^2i^2(2(ai + 1)^{1-\frac{d}{2}} - (ai + 2)^{1-\frac{d}{2}}) - (ai)^{3-\frac{d}{2}} - (aj)^{3-\frac{d}{2}})) \\
& + \sum_{i=1}^{n-1} \frac{1}{3(d - 6)(d - 2)(d - 4)d(d - 8)(d - 10)} \left(2fd(d - 2)((1 + (ai)^{5-\frac{d}{2}} - (ai + 1)^{5-\frac{d}{2}})(d^2 - 26d + 136) \right. \\
& + 4((ai)^{4-\frac{d}{2}} + ai)(d - 10)^2) + 4(d - 10)f((d^3 - 18d^2 + 80d - 192)((2(ai - an - f + 1))((ai + 1)^{2-\frac{d}{2}}(a^2i^2 - ai + 1) \\
& - (ai)^{4-\frac{d}{2}}) + 2f - 2 + an) - (48(3(ai + 1)^{2-\frac{d}{2}}adi + (d - 8)(ai + (ai)^{3-\frac{d}{2}})))(ai - an - f + 1)) \\
& + \sum_{i=1}^{n-2} \frac{8f^2(n - i - 1)}{(d - 6)(d - 2)(d - 4)d(d - 8)} \left(-\frac{d}{3}((ai + 1)^{4-\frac{d}{2}}(d - 2)(d - 10) - (d - 2)(d - 10) \right. \\
& + (ai)^{3-\frac{d}{2}}(adi - 10ai + 3d - 24))) - (d - 8)(f - 1)((ai + 1)^{1-\frac{d}{2}}(8 + (d - 2)(4ai + i^2(d - 4)a^2)) \\
& - (ai)^{3-\frac{d}{2}}(d - 2)(d - 4) - 8)) - \sum_{i=1}^{n-2} \sum_{j=1}^{n-1-i} \frac{8f^2}{3(d - 6)(d - 2)(d - 4)d(d - 8)} ((d^3 - 18d^2 + 80d - 192) \\
& \times ((ai + aj + 1)^{2-\frac{d}{2}}((ai + aj + 1)^2 - 3aj(ai + 1)) - (ai + 1)^{4-\frac{d}{2}} + (aj + 1)^{2-\frac{d}{2}}(a^2j^2 - aj + 1) - (a(i + j))^{2-\frac{d}{2}} \\
& \times a^2(i^2 - ij + j^2) - (aj)^{4-\frac{d}{2}} + (ai)^{4-\frac{d}{2}} - 72adj((ai + aj + 1)^{2-\frac{d}{2}}(ai + 1) + (aj + 1)^{2-\frac{d}{2}} - (a(i + j))^{2-\frac{d}{2}}ai) \\
& + 3(d - 8)((ai + 1)^{1-\frac{d}{2}}a^2ij(d - 6)(adi + 4) - (a(i + j))^{1-\frac{d}{2}}a^2((d - 2)(i^2(d - 4) + 4ij) + 8j^2) - 8(aj)^{3-\frac{d}{2}} \\
& + (ai)^{3-\frac{d}{2}}((d - 2)(d - 4) - d(d - 6)ja) - 16aj)) + \sum_{i=1}^{n-2} \sum_{j=1}^{n-1-i} \frac{4f^2a^2i^2}{d(d - 2)} \left(aj((an - j))^{1-\frac{d}{2}} - (-aj + an + 1)^{1-\frac{d}{2}} \right. \\
& + a(i - n)((ai)^{1-\frac{d}{2}} - (ai + 1)^{1-\frac{d}{2}}) - a(i + j - n)((a(i + j))^{1-\frac{d}{2}} - (ai + aj + 1)^{1-\frac{d}{2}}) + (2(f - 1))((a(i + j))^{1-\frac{d}{2}} \\
& - (ai)^{1-\frac{d}{2}} - (ai + aj + 1)^{1-\frac{d}{2}} + (ai + 1)^{1-\frac{d}{2}})) - \sum_{i=1}^{n-3} \sum_{j=1}^{n-2-i} \frac{4f^3(n - i - j - 1)}{(d - 6)(d - 2)(d - 4)d} ((ai + aj + 1)^{1-\frac{d}{2}} \\
& \times (16 + (4(i + j))(d + 2)a + a^2(i^2 + j^2)(d^2 - 6d + 16) + 8i(d - 2)ja^2) - (ai + aj)^{1-\frac{d}{2}}(a^2(i^2 + j^2)(d^2 - 6d + 16)
\end{aligned}$$

$$\begin{aligned}
 & +8i(d-2)ja^2) + (ai+1)^{1-\frac{d}{2}}ai(d-6)(adi+4) + (aj+1)^{1-\frac{d}{2}}aj(d-6)(adj+4) - ((ai)^{3-\frac{d}{2}} + (aj)^{3-\frac{d}{2}}) \\
 & \times (d^2-6d)-16) - f^3 \sum_{i=1}^{n-3} \sum_{j=1}^{n-2-i} \frac{2a(i+j-n)(i+j-n+1)}{d(d-2)} (a^2(i^2+j^2)((ai+aj+2)^{1-\frac{d}{2}} - 2(ai+aj+1)^{1-\frac{d}{2}} \\
 & +(a(i+j))^{1-\frac{d}{2}} - a^2(i^2(2(ai+1)^{1-\frac{d}{2}} - (ai+2)^{1-\frac{d}{2}} - (ai)^{1-\frac{d}{2}} + j^2(2(aj+1)^{1-\frac{d}{2}} - (aj+2)^{1-\frac{d}{2}} - (aj)^{1-\frac{d}{2}}))) \Big).
 \end{aligned}
 \tag{B2}$$

APPENDIX C

Here we provide the tables with numerical data that were used to build figures in the main text of the paper.

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