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Hierarchical excluded volume screening in solutions of bottlebrush polymers – Electronic Supplementary Information

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MOLECULAR DYNAMICS SIMULATIONS

Simulations of bottlebrush, comb-like, and linear polymer solutions are performed using the coarse-grained bead-spring model of Kremer and Grest [1]. An individual macromolecule is composed of $N_{\rm bb}$ backbone monomers (modeled as excluded volume spheres), which are connected by bonds. To these backbone monomers, we connect side chains with grafting density z. Each side chain contains $N_{\rm sc}$ monomers, which are identical to the monomers of the backbone. The total number of beads in a molecule is $N_{\rm bb}(1 + N_{\rm sc}z)$.

The non-bonded interactions between monomers separated by a distance r are modeled by the truncated and shifted Lennard-Jones (LJ) potential,

$$V^{\rm LJ}(r) = \begin{cases} 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6} + C\right] & r \le r_c \\ 0 & r > r_c, \end{cases} \tag{S1}$$

where the interaction strength, ϵ, is measured in units of thermal energy, $k_{\rm B}T$, σ is the monomer diameter, r_c is the cutoff, and C is the shift of the potential introduced to avoid a discontinuity at $r = r_c$. We use $\epsilon = k_{\rm B}T$, $C = 1/4$, and $r_c = 2^{1/6}\,\sigma$. This choice of parameters results in purely repulsive interactions between monomers, ensuring good solvent conditions at all values of $k_{\rm B}T$. For computational efficiency we do not include attractive interactions which would only be of interests if one wants to vary the solvent quality [2].

The bonded interactions in a molecule are mimicked by the Kremer-Grest potential [1], $V^{\rm KG}(r) = V^{\rm FENE}(r) + V^{\rm LJ}(r)$, with the "finitely extensible nonlinear elastic" (FENE) potential

$$V^{\rm FENE} = -\frac{1}{2}kr_{\rm F}^2 \ln\left[1 - (r/r_{\rm F})^2\right]. \tag{S2}$$

Here, the bond spring-constant is $k = 30\,\epsilon/\sigma^2$, and the maximum bond length is $r_{\rm F} = 1.5\,\sigma$ [1]. All simulations are performed in a cubic box with periodic boundary conditions imposed in all spatial dimensions.

We use the Velocity-Verlet algorithm [3] to solve the Langevin equation of motion for the position $\mathbf{r}_i$ of each monomer with mass m,

$$m\ddot{\mathbf{r}}_i = \mathbf{F}_i^{\rm LJ} + \mathbf{F}_i^{\rm FENE} - \zeta\dot{\mathbf{r}}_i + \mathbf{F}_i^{\rm R}. \tag{S3}$$

The forces $\mathbf{F}_i^{\rm LJ}$ and $\mathbf{F}_i^{\rm FENE}$ respectively follow from the LJ (Eq. S1) and the FENE (Eq. S2) interaction potentials. The third and fourth term on the right hand side of Eq. (S3) are a slowly evolving viscous force, $-\zeta\dot{\mathbf{r}}_i$, and a rapidly fluctuating stochastic force, $\mathbf{F}_i^{\rm R}$. The random force, $\mathbf{F}_i^{\rm R}$, is related to the friction coefficient, ζ, by the fluctuation-dissipation theorem, $\langle \mathbf{F}_i^{\rm R}(t)\mathbf{F}_j^{\rm R}(t')\rangle = k_{\rm B}T\zeta\delta_{ij}\delta(t-t')$. The friction coefficient used in our simulations is

$\zeta = 0.5\, m\tau^{-1}$, where $\tau = \sqrt{m\sigma^2/\epsilon}$ is the LJ time unit. The integration step is taken to be $\Delta\tau = 0.005\tau$, and the thermal energy is constant at $k_\mathrm{B}T = 1$. All simulations are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [4], and the simulation snapshots are rendered using the program Visual Molecular Dynamics (VMD) [5]. Initially, molecules are grown using a self-avoiding random walk technique and placed randomly in the simulation cell. The initial concentration of all systems is small, $c \approx 5 \cdot 10^{-4}\,\sigma^{-3}$. To obtain the desired concentration, the simulation box is gradually decreased in size at constant velocity $10^{-3}\,\sigma/\tau$. Once the target density is reached, simulations are continued for up to at least three relaxation times of the corresponding system. During the equilibration stage, the molecules diffuse on average at least over the root-mean-square end-to-end distance of their backbones.

Simulations of solutions are carried out for linear ($z = 0$), comb-like ($z = 1/3$), and bottlebrush ($z \geq 1$) polymers for a fixed number of backbone monomers, $N_\mathrm{bb} = 100$, in the range of concentration varied from $c = 0.001\,\sigma^{-3}$ (dilute solutions) to $c = 0.85\,\sigma^{-3}$ (melts). The number of monomers per side chain is varied between $N_\mathrm{sc} = 0$ and $N_\mathrm{sc} = 16$ for bottlebrushes with $z = 1$ or $z = 2$ side chains attached to each backbone monomer. For macromolecules with $z = 1/3$, the number of side chains monomers is fixed to $N_\mathrm{sc} = 32$. In addition, for dilute solutions of bottlebrushes ($c = 0.001\,\sigma^{-3}$), the number of backbone monomers is varied (N_bb=50, 100, and 200) as well as the number of side chain monomers (N_sc = 1, 2, 4, 8, 16, 32, and 64) and the grafting density (z = 1, 2, 3, and 4).

SCALING ANALYSIS

Before presenting our scaling analysis for the concentration-dependent properties of bottlebrush conformations, we would like to discuss briefly how our approach compares to the previous models by Birshtein *et al.* [6] and Fredrickson [7], which start out from rod-like backbones, at least, on a local scale. To do so, we revisit our starting point, the free energy of the cylindrical subsegment as given by Eq. (1) in the main text. Instead of minimizing the free energy with respect to l_0 and $R_{\mathrm{sc},0}$, one may assume a stiff backbone inside the cylinder, i.e., $l_0 \propto n_0$. Minimization of F with respect to $R_{\mathrm{sc},0}$ then yields

$$R_{\mathrm{sc},0} \propto N_\mathrm{sc}^{3/4} z^{1/4}. \tag{S4}$$

The above scaling law for the size of side chains is known for bottlebrushes with rod-like backbones, see Refs. [6–8].

The spatial distance between grafting points for bottlebrushes with rod-like backbones, d, may be derived from a simple scaling approach,

$$R_{\mathrm{sc},0} = \tilde{g}(r_0/d) \propto N_\mathrm{sc}^{3/4} z^{1/4}, \tag{S5}$$

where $r_0 \propto N^{3/5}$ denotes the size of a linear (not grafted) chain in dilute solution, and $\tilde{g}(x)$ is a scaling function. This ansatz leads to

$$d \propto z^{-1} \tag{S6}$$

and, thus, to a rigid backbone inside the cylinder. The very same idea can be applied to the side chain scaling derived in the main text for bottlebrushes with semi-flexible backbones [see Eq. (3) in the limit $N_{\mathrm{sc}}z \gg 1$, i.e., $R_{\mathrm{sc}} \propto N_{\mathrm{sc}}^{7/10} z^{1/10}$]. The scaling argument yields

$$d \propto z^{-3/5}, \tag{S7}$$

such that the spatial distance between grafting points resembles a self-avoiding walk statistics [9]. This is the fundamental difference between the scaling law of Eq. (S4) and our result, cf. Eq. (3).

In the following, we present our scaling analysis for concentrations ranging from semi-dilute solutions to melts. The macromolecules start to overlap as the concentration is increased above their overlap concentration, $c > c_1$. With Eq. (6), the overlap concentration reads

$$c_1 \propto \frac{N_{\mathrm{bb}}(1 + N_{\mathrm{sc}}z)}{R_0^3} \propto N_{\mathrm{bb}}^{-4/5}(1 + N_{\mathrm{sc}}z)^{-1/5}. \tag{S8}$$

In the semi-dilute regime, the screening of excluded volume interactions along the backbones is due to the presence of other macromolecules and leads to a random walk of the persistence segments [9]. Therefore, the size of a bottlebrush scales with the number of backbone monomers as

$$R_1 \propto R_0 \tilde{g}_1(c/c_1) \propto N_{\mathrm{bb}}^{1/2}, \tag{S9}$$

where $\tilde{g}_1(x)$ is a scaling function. Together with Eqs. (6) and (S8), we obtain the size of a bottlebrush in concentration regime 1, which reads

$$R_1 \propto (1 + N_{\mathrm{sc}}z)^{3/8} N_{\mathrm{bb}}^{1/2} c^{-1/8}. \tag{S10}$$

Note that for macromolecules with $N_{\mathrm{sc}}z = 0$, Eq. (S10) reproduces the expected power law dependence for linear chains, $R_{\mathrm{linear}} \propto N_{\mathrm{bb}}^{1/2} c^{-1/8}$ [9], which has been confirmed experimentally [10] and by computer simulations [11, 12].

Upon further increase of concentration, $c > c_2$, the persistence segments of neighboring bottlebrushes start to overlap. The corresponding overlap concentration reads

$$c_2 \propto \frac{n_0(1 + N_{\mathrm{sc}}z)}{l_0 R_{\mathrm{sc},0}^2} \propto \left(\frac{N_{\mathrm{sc}}}{z}\right)^{-2/5} (1 + N_{\mathrm{sc}}z)^{-1/5}, \tag{S11}$$

where we have used Eqs. (4) and (5). In concentration regime 2, the self-avoiding walk of monomers inside the cylinder turns into a random walk. Since the excluded volume contribution of the side chains remains unaltered, one may anticipate that the persistence length in this regime is given by

$$l_2 \propto n_2^{1/2}(1 + N_{\mathrm{sc}}z)^{2/5}. \tag{S12}$$

A priori, we do not know how the number of backbone monomers inside the cylinder for regime 2, n_2, depends on N_{sc} and z. However, we may assume that n_2 remains proportional to $z^{-1/2}$, see Eq. (4). Thus, in the limit $N_{\mathrm{sc}}z \gg 1$, Eq. (S12) suggests $l_2 \propto z^{3/20}$. The latter result allows us to perform a crossover scaling,

$$l_2 \propto l_0 \tilde{g}_2(c/c_2) \propto z^{3/20}, \tag{S13}$$

with $\tilde{g}_2(x)$ a scaling function. Together with Eq. (5) and $N_{\rm sc}z \gg 1$, Eq. (S13) leads to

$$l_2 \propto R_{\rm sc,2} \propto N_{\rm sc}^{11/20} z^{3/20} c^{-1/4}, \tag{S14}$$

where $R_{\rm sc,2}$ denotes the size of side chains in regime 2. Within our theoretical picture, both persistence length and size of side chains depend on concentration, but the number of backbone monomers per cylindrical segment in a given concentration regime does not. Thus, Eq. (S14) suggests a decreasing persistence (side chain) length with a constant number of backbone monomers inside the persistence segment.

Equation (S14) can be re-written as $l_2 \propto N_{\rm sc}^{3/20} z^{-1/4} (N_{\rm sc}z)^{2/5} c^{-1/4}$. Together with Eq. (S12) and $N_{\rm sc}z \gg 1$, we obtain

$$n_2 \propto \sqrt{\frac{N_{\rm sc}^{3/5}}{z}}, \tag{S15}$$

which reflects a natural modification of Eq. (4). With Eqs. (S14) and (S15), we obtain the macromolecular size of bottlebrushes in regime 2 ($N_{\rm sc}z \gg 1$),

$$R_2 \propto (1 + N_{\rm sc}z)^{2/5} N_{\rm bb}^{1/2} c^{-1/4}. \tag{S16}$$

Once the concentration is increased even further, $c > c_3$, the macromolecules attain melt concentration and side chains of neighboring macromolecules start to overlap. The corresponding overlap concentration reads

$$c_3 \propto \frac{N_{\rm sc}z}{l_2 R_{\rm sc,2}^2} \propto N_{\rm sc}^{-13/20} z^{11/20}, \tag{S17}$$

where Eq. (S14) in the limit $N_{\rm sc}z \gg 1$ has been used. Due to the screening of excluded volume interactions along the side chains of neighboring macromolecules, one expects that the size of side chains, $R_{\rm sc,3}$, and the corresponding persistence length, l_3, in regime 3 scale as $R_{\rm sc,3} \propto l_3 \propto N_{\rm sc}^{1/2}$. With $\tilde{g}_3(x)$ a scaling function, the crossover scaling

$$l_3 \propto l_0 \tilde{g}_3(c/c_3) \propto N_{\rm sc}^{1/2} \tag{S18}$$

leads to

$$l_3 \propto R_{\rm sc,3} \propto N_{\rm sc}^{1/2} z^{7/26} c^{-4/13}, \tag{S19}$$

where we have used Eqs. (5) and (S17) in the limit $N_{\rm sc}z \gg 1$. In highly concentrated solutions, the persistence length is proportional to the number of side chains within the cylinder, i.e., $l_3 \propto n_3 z$. With Eq. (S19), the number of backbone monomers in the cylinder then is

$$n_3 \propto N_{\rm sc}^{1/2} z^{-19/26}. \tag{S20}$$

The size of bottlebrushes in regime 3, R_3, follows from a random walk of persistence segments with length l_3, where each segment contains n_3 backbone monomers. This yields

$$R_3 \propto l_3 \left(\frac{N_{\rm bb}}{n_3}\right)^{1/2} \propto N_{\rm bb}^{1/2} N_{\rm sc}^{1/4} z^{33/52} c^{-4/13}. \tag{S21}$$

The above scaling result is very close to the one predicted by Borisov *et al.* [13] with respect to all four exponents. However, the underlying assumptions for both models are different. The scaling of bottlebrush size with N_{bb} and N_{sc} has been confirmed recently under melt conditions [14].

With respect to suppressing entanglement effects in order to design super-elastic rubbers, highly grafted bottlebrushes are of particular interest. Here, an additional regime can appear, where compression of the backbone and the side chains can lead to mutual screening of side chains that belong to the same macromolecule. With Eq. (S19), the overlap concentration in regime 4 is

$$c_4 \propto \frac{N_{\text{sc}} z}{R^3_{\text{sc},3}} \propto N_{\text{sc}}^{-1/2} z^{7/26}. \tag{S22}$$

The crossover scaling reads

$$l_4 \propto l_0 \tilde{g}_4(c/c_4) \propto N_{\text{sc}}^{1/2}, \tag{S23}$$

with $\tilde{g}_4(x)$ a scaling function. Using Eq. (5) in the limit $N_{\text{sc}} z \gg 1$, one obtains the concentration dependence of the persistence length in regime 4,

$$l_4 \propto N_{\text{sc}}^{1/2} z^{27/130} c^{-2/5}. \tag{S24}$$

Once more, we assume local stretching of the backbone, i.e., $l_4 \propto n_4 z$, where n_4 denotes the number of backbone monomers per persistent segment for regime 4. With Eq. (S24), this leads to

$$R_4 \propto l_4 \left(\frac{N_{\text{bb}}}{n_4} \right)^{1/2} \propto N_{\text{bb}}^{1/2} N_{\text{sc}}^{1/4} z^{157/260} c^{-2/5}, \tag{S25}$$

for the size of bottlebrushes in regime 4. Together with Eq. (S22), the above equation can be rewritten, such that we obtain Eq. (7) of the main text.

The summary of scaling analysis for different overlap concentrations and predictions for the macromolecular size of bottlebrushes in the corresponding regime of concentrations are listed below in Table S1.

x	c_x	Eq.	R_x^2	Eq.
0	–	–	$N_{\text{bb}}^{6/5} (N_{\text{sc}} z)^{4/5} c^0$	(6)
1	$N_{\text{bb}}^{-4/5} (N_{\text{sc}} z)^{-1/5}$	(S8)	$N_{\text{bb}} (N_{\text{sc}} z)^{3/4} c^{-1/4}$	(S10)
2	$N_{\text{sc}}^{-3/5} z^{1/5}$	(S11)	$N_{\text{bb}} (N_{\text{sc}} z)^{4/5} c^{-1/2}$	(S16)
3	$N_{\text{sc}}^{-13/20} z^{11/20}$	(S17)	$N_{\text{bb}} N_{\text{sc}}^{1/2} z^{33/26} c^{-8/13}$	(S21)
4	$N_{\text{sc}}^{-1/2} z^{7/26}$	(S22)	$N_{\text{bb}} N_{\text{sc}}^{1/2} z^{157/130} c^{-4/5}$	(S25)

TABLE S1: Summary of the theoretically predicted overlap concentrations, c_x ($x = 0, \ldots, 4$), and the corresponding mean-square end-to-end distances, R_x^2, of bottlebrush macromolecules as functions of the degrees of polymerization of the backbone (N_{bb}) and the side chains (N_{sc}), grafting density of the side chains (z), and concentration (c).

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