

Confined Dynamics in Spherical Polymer Brushes

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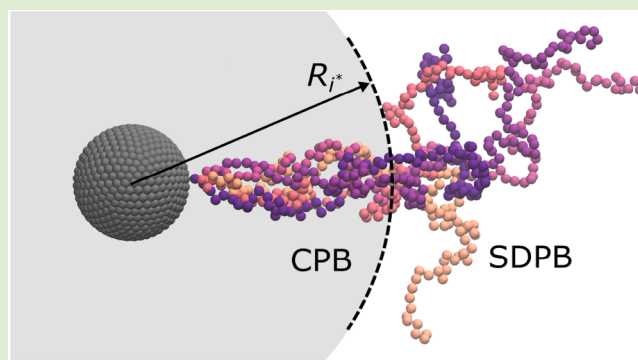


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ABSTRACT: We investigate the dynamics of polymers grafted to spherical nanoparticles in solution using hybrid molecular dynamics simulations with a coarse-grained solvent modeled via the multiparticle collision dynamics algorithm. The mean-square displacements of monomers near the surface of the nanoparticle exhibit a plateau on intermediate time scales, indicating confined dynamics reminiscent of those reported in neutron spin-echo experiments. The confined dynamics vanish beyond a specific radial distance from the nanoparticle surface that depends on the polymer grafting density. We show that this *dynamical* confinement transition follows theoretical predictions for the critical distance associated with the *structural* transition from confined to semidilute brush regimes. These findings suggest the existence of a hitherto unreported dynamic length scale connected with theoretically predicted static fluctuations in spherical polymer brushes and provide new insights into recent experimental observations.



Grafting polymers to the surface of nanoparticles (NPs) can dramatically enhance dispersion in polymer nanocomposites,^{1–5} reduce frictional interactions,^{6,7} and improve the biocompatibility and delivery of drugs^{8–11} and theranostics.^{12–14} Beyond chemically modifying the surface, contributions from the extended structure and dynamic fluctuations of the grafted polymers can enhance their utility.^{15–17} The structure and dynamics of grafted polymers are significantly perturbed from those of free chains for two reasons: the surface tether prevents fluctuations of the grafted end, and the surface localization of the chains increases the local monomer concentration.¹⁸ For planar substrates and sufficiently high grafting density σ , these perturbations lead to extended chain conformations,^{19–23} slower relaxations,^{24,25} and the emergence of collective dynamics.^{26–31}

When polymers are grafted to spherical (or cylindrical) NPs, however, the surface curvature set by the NP radius R_{NP} introduces a radial dependence to the monomer concentration and subsequently to the polymer conformations.^{32–35} Scaling theories predict that the structure of brushes grafted to spherical NPs in a good solvent depends on σ and the radial distance r . At moderate σ , pairwise interactions between monomers lead to a semidilute polymer brush (SDPB) regime in which the brush height h scales with the number of repeat units N as $h \sim (N\sigma^{1/3})^{3/5}$.^{32,36} At larger σ , higher order segmental interactions dominate, leading to a more extended concentrated polymer brush (CPB) regime where $h \sim (N\sigma^{1/2})^\nu$ with excluded volume parameter $3/5 \leq \nu \leq 1$. Because the local monomer concentration decreases with

increasing r , brushes whose length exceeds a critical radius R_{CPB} transition continuously from the CPB regime near the NP surface to the SDPB regime at the periphery.³⁴ These grafted polymer conformations have been confirmed by simulations and experiments.^{37–40}

Similar to structural perturbations, the dynamics of grafted chains deviate from those of free chains. Scaling theory predicts that the relaxation time of brushes scales as $\tau \sim N^3$,^{41,42} slower than for free chains experiencing non-hydrodynamic Rouse ($\tau \sim N^2$) or hydrodynamically coupled Zimm ($\tau \sim N^{3\nu}$) relaxations.¹⁸ The relaxation time of monomers varies non-monotonically with monomer position, with monomers near the chain center exhibiting the slowest relaxations.^{39,43} Additionally, the intrachain relaxations of grafted polymers do not follow simple exponential decays.^{39,44,45} Instead, neutron spin-echo (NSE) measurements find that grafted chains are confined by their neighbors and do not fully relax on observable time scales.^{44,45} By selectively contrast matching the grafted chains, NSE measurements reveal that dynamics are slower in the CPB region than in the SDPB region of a long brush.⁴⁶ This behavior was confirmed in recent molecular dynamics (MD) simulations, which also

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showed that the relaxation time of individual chains increases with increasing confinement (i.e., increasing σ).^{47,48} Although these investigations suggest that the relaxations of grafted polymers are affected by the local brush structure, a direct connection between the brush structure and dynamics has not yet been demonstrated.

Here, we use hybrid MD simulations with a mesoscale solvent model to show that the confined dynamics of polymers grafted to spherical NPs originates from the strong crowding and extended conformation of chains in the CPB regime. In agreement with earlier studies,^{39,43} the relaxation times extracted from the mean-squared displacements (MSDs) are maximal for monomers near the center of the chain and increase with grafting density. For monomers near the particle surface, MSDs exhibit plateaus on intermediate time scales. This intermediate-time plateau is consistent with the confined dynamics observed in NSE experiments,^{44,45} but it has not been scrutinized in previous computational studies of spherical brushes.^{39,48} The plateau value increases with increasing monomer position and finally disappears for monomers sufficiently far from the particle surface, suggesting a continuous transition from confined to unconfined dynamics. To characterize this transition, we determine the monomer position at which the dynamic confinement disappears and show that this position is comparable to that of R_{CPB} , which controls the structural transition between CPB and SDPB regimes. Our findings therefore establish the structural origins underlying the confined, slow relaxations of grafted polymers.

We performed simulations of Kremer–Grest⁴⁹ bead–spring polymers end-grafted to a spherical NP. We included solvent-mediated hydrodynamic interactions (HI) through an explicit, mesoscale solvent modeled using the multiparticle collision dynamics (MPCD) algorithm.^{50–55} For convenience, we define a , m , ϵ , and $\tilde{t} = \sqrt{ma^2/\epsilon}$ as the fundamental units for length, mass, energy, and time, respectively, and report model parameters and physical quantities from the simulations in dimensionless form based on these units. In the following, these units are omitted for brevity. Each polymer chain consisted of 120 monomers with diameter $a_p = 1$. The NP was modeled as a collection of monomer-sized beads positioned at 642 vertices on the surface of a sphere of radius $R_{\text{NP}} = 5$, yielding a surface density of ~ 2 . The positions of the vertices were generated by recursively subdividing the faces of a regular icosahedron into equilateral triangles and then radially scaling the vertices to a distance R_{NP} from the center of the sphere.^{56,57} Spring-like bonds between adjacent monomers on the polymer chains and between the end monomers and grafting sites on the NP surface were modeled using the finite extensible nonlinear elastic (FENE) potential.⁵⁸ Excluded volume interactions between monomer–monomer and monomer–NP beads were implemented using a purely repulsive Weeks–Chandler–Andersen (WCA) potential to mimic good solvent conditions.⁵⁹ A standard MPCD solvent with number density $\rho_s = 5$ was used in conjunction with a momentum-conserving version of the Andersen thermostat,^{60,61} resulting in a fluid with Schmidt number $Sc \approx 12.0$ and dynamic viscosity $\eta_s \approx 4.0$. The MPCD solvent was coupled to the polymer monomers and NP beads using the scheme described in ref 62. Three reduced grafting densities were considered in the hybrid MD–MPCD simulations, $\gamma = \sigma R_{\text{g},0}^2 = \{10, 25, 50\}$, where $R_{\text{g},0} = 8.3$ is the radius of gyration of a free 120-mer chain in an infinitely dilute solution. These values were chosen to fall

within the range probed in recent experiments.⁴⁵ Additional grafting densities ranging from $\gamma = 0.22$ to 50 were considered in a complementary set of implicit-solvent Langevin dynamics (LD) simulations to investigate brush dynamics in the absence of HI. All simulations were performed at a reduced temperature of $T = 1$. Additional details of the models and simulation protocols are presented in the [Supporting Information](#). Chain dynamics were characterized via the time-dependent mean-squared displacements $g_i(t) = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ of individual monomers, where i is the monomer index (1 for the grafted monomer and 120 for the free end); the angle brackets $\langle \dots \rangle$ denote that the average is taken over multiple time origins with the same lag time t for monomers with the same index on different chains. The monomer position vector $\mathbf{r}_i = (x_i, y_i, z_i)$ is defined relative to the reference frame of the NP center of mass. The total MSD was also decomposed in the directions perpendicular and parallel to the NP surface to characterize the anisotropy of the chain dynamics; the perpendicular and parallel components $g_{i,\perp}$ and $g_{i,\parallel}$ were defined to be colinear and orthogonal to the vector $\mathbf{r}_i(0)$, respectively ([Supporting Information, Figure S1](#)).

The resulting MSDs follow the expected behavior for grafted polymer chains ([Figure 1](#)). On short lag times t , the MSDs

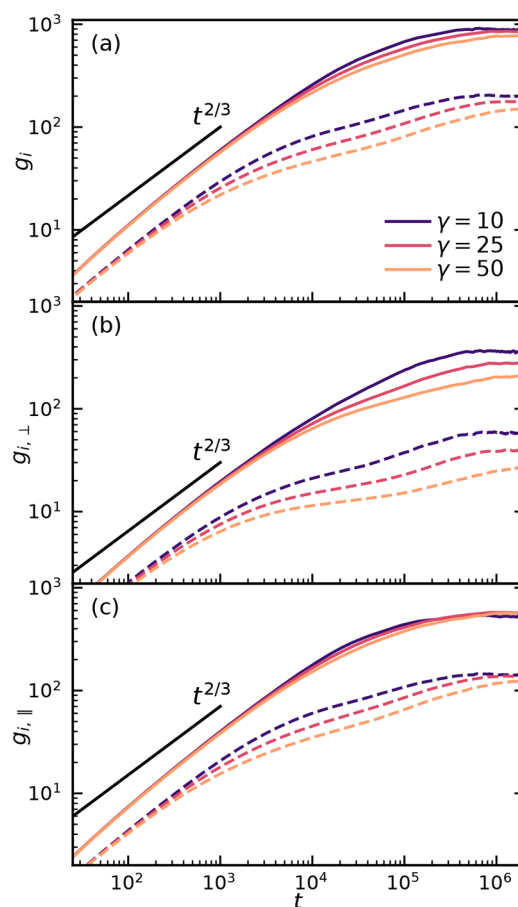


Figure 1. Mean-squared displacements (MSDs) g_i of monomers with indices $i = 40$ (dashed lines) and $i = 120$ (continuous lines) computed from hybrid MD–MPCD simulations for three reduced grafting densities γ . The panels show (a) the total MSD and the components (b) perpendicular and (c) parallel to the NP surface. The black lines show the early time $t^{2/3}$ scaling behavior predicted by the Zimm model for systems with hydrodynamic interactions.

exhibit power-law scaling $g_i(t) \propto t^\alpha$ with $\alpha \approx 2/3$, consistent with experimental observations for NP-grafted polymers in solution.⁴⁵ This power-law behavior emerges because the monomers along the polymer chain are hydrodynamically coupled and follow standard Zimm relaxations.¹⁸ Over long t , g_i saturates at a finite value that increases with the monomer index i . This saturation value is associated with the maximum displacement of the monomers due to the grafting constraint, and it depends on their position along the chain contour, indicated by the index i . Thus, the increase in saturation value with i reflects the increasing magnitude of positional fluctuations accessible to monomers farther from the grafting site on the NP surface.⁶³ Over intermediate time scales, however, we observe the emergence of an intermediate plateau for low monomer indices (i.e., those close to the surface) that gradually disappears as i increases. These intermediate plateaus are consistent with experimental observations, where the plateau was attributed to confinement by neighboring chains.^{44,45} The intermediate slowing of the dynamics is also reminiscent of that observed in supercooled colloidal liquids, where it is attributed to transient caging of a particle by its neighbors.^{64–67} We thus attribute these plateaus to a confinement of grafted chains near the NP surface that weakens farther away. As discussed below, we test this hypothesis by characterizing the range of monomers that exhibit intermediate plateaus as a function of the grafting density.

To examine the (potential) anisotropy of the chain relaxations, we decomposed the total MSD into components perpendicular and parallel to the NP surface (Figure 1b,c). Broadly, the component MSDs exhibit qualitatively similar behavior to the total MSDs, with power-law scalings at short time scales, long-time plateaus, and intermediate plateaus for low-index monomers. Quantitatively, the saturation value for $g_{i,\perp}$ decreases as the grafting density γ increases due to excluded volume interactions that stretch and effectively stiffen the chain, resulting in greater localization of the monomers in the perpendicular direction. By contrast, the saturation value for $g_{i,\parallel}$ is largely insensitive to the grafting density. This insensitivity may reflect the competing effects of decreased positional fluctuations but larger average radial positions (Supporting Information, Figure S2) as the chains extend to accommodate the increased monomer density. These observations are consistent with previous LD simulation studies of semidilute spherical brushes³⁹ as well as scaling theories for planar and cylindrical geometries⁶⁸ that predict that long-time-scale fluctuations normal to the grafting surface are more strongly influenced by γ than those in the lateral direction.

Following the methodology of previous studies,³⁹ we defined an effective relaxation time τ as the time at which the MSD reaches two-thirds of its saturation value $g_i(\tau) = (2/3)g_i(t \rightarrow \infty)$. Although the saturation value of $g_{i,\perp}$ monotonically increases with monomer index, the relaxation time in the perpendicular direction τ_{\perp} is non-monotonic (Figure 2). The relaxation time initially increases with monomer index, as predicted by theory, but then passes through a maximum near the middle of the chain and decreases at higher monomer indices. This decrease in relaxation time occurs because the local monomer concentration decreases with increasing distance from the NP surface, and hence, the motions of the chain segments further from the surface are less hindered by collisions with other chains.³⁹ Relaxation of these segments is also facilitated by their

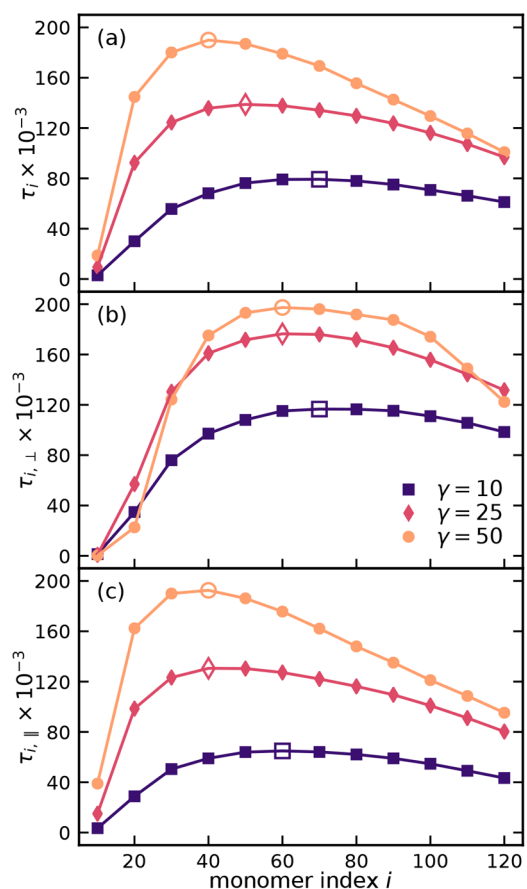


Figure 2. Relaxation times τ from hybrid MD–MPCD simulations as functions of monomer index i computed from (a) the total MSD and the components (b) perpendicular and (c) parallel to the NP surface. Open symbols identify maxima.

proximity to the free chain ends, which are bonded to only one neighbor and hence relax faster. The relaxation time in the lateral direction τ_{\parallel} exhibits similar non-monotonic behavior, but the maximum is shifted to lower monomer indices, suggesting that relaxations in the parallel direction are more sensitive to their proximity to chain ends than those in the perpendicular direction. As expected, both τ_{\perp} and τ_{\parallel} increase with grafting density due to enhanced interactions with neighboring chains. Additionally, the position of the relaxation-time maximum shifts to lower monomer indices with increasing γ and is more pronounced in the parallel direction. This result indicates that the relaxations of monomers near the particle surface are more strongly hindered at higher grafting densities.

While these hindered dynamics are consistent with our hypothesis that grafted chains are confined, we directly tested this confinement picture by analyzing the intermediate plateaus. Specifically, we fitted the logarithm of the MSD to a cubic polynomial near the intermediate plateau, which allowed us to precisely quantify this plateau according to the inflection point of the polynomial. The associated time scale t_c was obtained from the root of the polynomial's second derivative, and the confinement length scale was estimated via $l_c = g_i(t_c)^{1/2}$ (Supporting Information, Figure S3). We focus our analysis on the dynamics in the parallel direction, which directly captures interactions between neighboring chains and removes complicating effects introduced by changes to chain

conformation and the radial distribution of monomers. From this analysis, we find that both l_c and t_c increase monotonically with the monomer index (Figure 3). This increase indicates

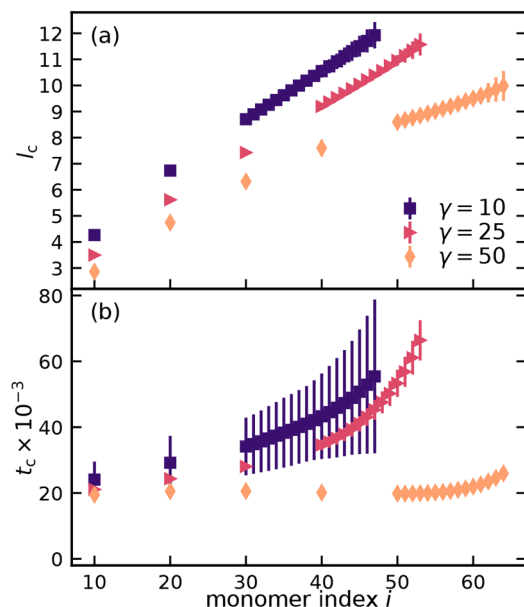


Figure 3. (a) Confinement length scale l_c and (b) associated time scale t_c computed from hybrid MD–MPCD simulations as a function of monomer index i .

that monomers farther from the NP surface can move over longer distances (and, commensurately, need longer times) before becoming confined. Additionally, both l_c and t_c decrease as the grafting density γ increases, consistent with a stronger confinement at higher monomer densities. These trends imply that the chain dynamics are more strongly confined near the NP surface and at higher grafting densities. Comparison of t_c and $\tau_{||}$ reveals that the two time scales are not strongly correlated (Supporting Information, Figure S4), which is expected because they are associated with distinct physical processes and vary differently with monomer index and grafting density.

The inflection point of the fitted polynomial vanishes beyond a critical monomer index i^* that increases with increasing grafting density, suggesting that the intermediate chain dynamics are no longer strongly confined beyond the associated length and time scales l_c and t_c , respectively. According to Ohno et al.'s³⁴ extension of Daoud–Cotton theory,³² the transition between the CPB and SDPB regimes occurs at a critical radius from the NP's center $R_{CPB} = R_{NP} b^2 R_{g,0}^{-2} \tilde{\nu}^{-1} \gamma^{1/2}$, where R_{NP} is the NP radius, b is the (effective) bond length, and $\tilde{\nu} = \nu / \sqrt{4\pi}$ is a rescaled excluded volume parameter. To compare the dynamical confinement to this model, we identified the critical monomer index i^* for each grafting density and computed its average distance from the NP's center R_{i^*} . In qualitative agreement with this theoretical model, we find that R_{i^*} exhibits the predicted dependence on the grafting density and increases as $R_{i^*} \sim \gamma^{1/2}$ (Figure 4). Further, assuming $b = 1.28$ for Kremer–Grest chains,^{35,69} we estimate that $\tilde{\nu} = 0.28$ from the slope of a linear fit to the data. This effective $\tilde{\nu}$ is close to the value $\tilde{\nu} = 0.30$ estimated from experiments³⁴ and simulations,⁴⁸ and it suggests that the chains are strongly stretched on length scales

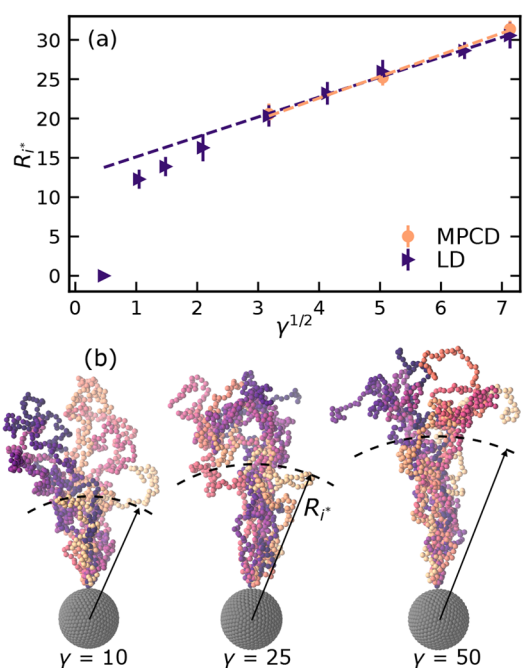


Figure 4. (a) Scaling behavior of R_{i^*} with $\gamma^{1/2}$. R_{i^*} is the average distance of monomer i^* from the NP's center, where i^* denotes the largest monomer index for which an intermediate-time inflection point is observed in the MSD. Symbols show data from the hybrid MD–MPCD and LD simulations (circles and triangles, respectively), and the dashed lines are linear fits indicating $R_{i^*} \sim \gamma^{1/2}$ scaling. (b) Schematic showing the critical radius R_{i^*} below which monomers exhibit confined dynamics at various grafting densities. At each grafting density, 10 different configurations sampled by a single, selected chain over a duration of $\sim t_c$ are rendered. The orange-to-purple (light-to-dark) color scale signifies the chronological order of the sampled chain configurations.

below R_{i^*} due to the confinement imposed by their neighbors. Hence, our results indicate that the observed inflection in the MSDs is indicative of confined chain dynamics near the NP surface, and its presence delineates between the CPB- and SDPB-like regimes predicted by theory.

Complementary LD simulations (without HI) reveal behavior remarkably similar to that of the hybrid MD–MPCD simulations (with HI) performed at the same grafting densities. Indeed, the LD simulations exhibit intermediate time plateaus in the MSDs (Figure 1; Supporting Information, Figure S5) and similar long-time relaxation behavior (Figure 2; Supporting Information, Figure S6). The magnitude of R_{i^*} and its scaling behavior at large grafting densities ($\gamma^{1/2} > 3$) from the two models are nearly indistinguishable (Figure 4). Thus, the confined dynamics in the CPB regime and the transition to SDPB-like behavior do not appear to be strongly influenced by HI, consistent with earlier investigations of free polymers in solution that found that HI are screened at high monomer densities.⁷⁰ Interestingly, extrapolation of a linear fit to R_{i^*} for $\gamma^{1/2} > 3$ yields a positive intercept (i.e., $R_{i^*} > 0$ at $\gamma^{1/2} = 0$), at odds with theoretical expectations. To investigate this possibility, we performed additional LD simulations at lower grafting densities. We observe that R_{i^*} deviates from the $\gamma^{1/2}$ scaling behavior for $\gamma^{1/2} \lesssim 2$ (Figure 4). In the limit of a single polymer chain grafted to the NP, the inflection point in the MSDs vanishes completely for all monomers, and no evidence of confined dynamics is observed (Supporting Information,

Figure S7), suggesting that R_{i^*} is effectively zero (Figure 4). Thus, the LD simulations predict $R_{i^*} \rightarrow 0$ and deviations from $\gamma^{1/2}$ scaling at sufficiently low grafting densities.

In summary, our simulations of spherical polymer brushes in solution demonstrate that chain segments near the grafting surface exhibit an intermediate plateau in their MSDs, consistent with the confined dynamics reported in NSE experiments.^{44,45} By analyzing the intermediate plateaus, we identified the characteristic length scale beyond which the confined dynamics vanish. The variation of this length scale with grafting density is in agreement with that predicted by the extended Daoud–Cotton model³² of Ohno et al.³⁴ for the critical radius associated with the transition from a concentrated to a semidilute polymer brush. While preparing our manuscript, a recent study was published on the dynamics and structure of chains in spherical polymer brushes under melt-like conditions.⁴⁸ Using the theory of Ohno et al.³⁴ for solutions, they estimated the critical radius for the CPB regime and demonstrated that the grafted chains exhibit stretched conformations and slow segmental dynamics below this length scale. Although those observations are consistent with our findings for polymer-grafted NPs in solution, our analysis reveals a hitherto unreported dynamical length scale that behaves similarly to the hypothesized critical radius of the extended Daoud–Cotton model. Thus, we independently validate the extended Daoud–Cotton model and connect dynamical and static fluctuations in spherical polymer brushes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00505>.

Detailed computational methods, additional simulation data, and example analyses (PDF)

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Author Contributions

CRedit: **Shivraj Bhagwatrao Kotkar** conceptualization, data curation, formal analysis, investigation, writing-original draft; **Michael P. Howard** investigation, methodology, writing-original draft, writing-review & editing; **Arash Nikoubashman** investigation, methodology, writing-original draft, writing-review & editing; **Jacinta C. Conrad** conceptualization, funding acquisition, investigation, project administration, writing-original draft; **Ryan Poling-Skutvik** conceptualization, investigation, writing-original draft; **Jeremy C. Palmer** conceptualization, funding acquisition, investigation, project administration, writing-original draft.

Notes

The authors declare no competing financial interest.

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