

Tailoring Nanoparticle Orientation in Polymer Matrices via Nonuniform Grafting: Implications for Nanoparticle Dispersions and Self-Assembled Nanocomposite Morphologies

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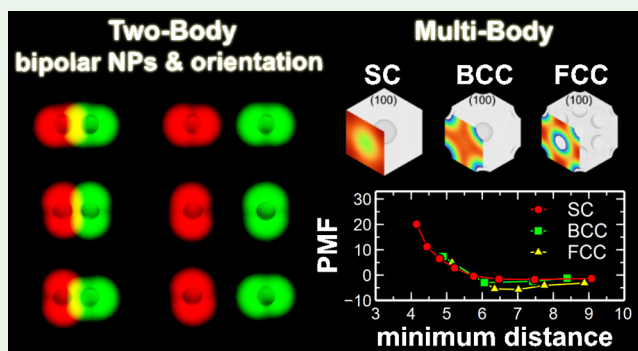
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ABSTRACT: We propose a three-dimensional model implementing a self-consistent field (SCF) mathematical formulation to predict the equilibrium orientation and morphology of grafted nanoparticles (NPs) in a polymer, based on two- and multibody interactions developed among them. First, we investigate the potential of mean force (PMF) between two spherical polystyrene-grafted silica NPs in a polystyrene melt as a function of the matrix-to-grafted chain length ratio and, more importantly, of the distribution of grafting points on their surfaces. While the most common assumption when performing such calculations is an equidistant distribution of grafting points on the surfaces of the NPs, we demonstrate here that the pattern of grafting plays an essential role in the equilibrium orientation and shape assumed by the particles inside the polymer matrix. In equidistant grafting, the role of grafting density is dominant, but, when grafting the chains irregularly, the same number of grafted chains distributed differently can significantly affect the self-assembly tendencies of the particles and the thermodynamic behavior of the composite system. Next, we calculate the free energy of a system of multiple equidistantly grafted nanoparticles exposed to a melt when they are arranged in a simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) lattice as a function of their spatial density. We minimize the free energy with respect to nanoparticle density to impose the condition of thermodynamic equilibrium. Among the three arrangements, the FCC/SC is the most/least stable configuration. The three-dimensional SCF methodology proposed herein addresses all possible degrees of freedom for the molecular-level design of both stable dispersions and self-assembled nanocomposite morphologies with tailor-made properties. It offers a cost-effective approach to creating high-value nanocomposite materials such as polymer-matrix nanocomposites in the rubber industry as well as “particle-solids,” the latter combining toughness with good optical properties.

KEYWORDS: self-consistent field, potential of mean force, grafted nanoparticle, aggregation, dispersion



The ability to predict the morphology of nanoparticles (NPs) inside polymer matrices is essential for the design and manufacture of advanced nanocomposite materials with tailor-made properties.^{1–5} The mechanical and viscoelastic properties of the polymeric materials are enhanced when hosting well-dispersed NPs.^{6–10} There are plenty of experimental studies where the structural, dynamic, and mechanical properties of polymer-grafted nanoparticles (GNPs) are investigated.^{6,11–17} Furthermore, it is imperative to understand the properties of GNPs in the absence of any polymer melt or solvent.^{14,18–21} The latter systems constitute promising candidates for state-of-the-art separation membranes and are also known as “particle solids”.^{22–24}

The chemical grafting of polymer chains on the surface of the NPs is usually performed via the so-called reversible addition–fragmentation chain transfer (RAFT)^{25–27} or ultra-violet (UV) induced reactions,²⁸ while other experimental methodologies to achieve high grafting densities are also

reported.²⁹ According to Bachhar et al.³⁰ the favored equilibrium morphology of hydrophilic GNPs inside an organic matrix is influenced by fluctuations of the particle size and grafting density when preparing the samples, especially at lower grafting densities.^{31–35}

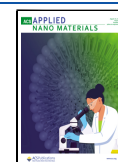
The interactions between two particles, which are embedded in a polymer melt or a solvent are strongly dependent on their size, grafting density, grafted and matrix chain constitution and lengths, and grafting distribution.³⁶ Spherical GNPs with small radius are easier to disperse because their shape and increased

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curvature enhances the penetration tendencies (wetting) of the matrix chains; hence, the GNPs are prevented from collapsing together.^{37,38} Martin et al.³⁹ have performed a detailed investigation of GNP interactions in the case of dissimilar chemistry between the grafted chains and those of the matrix, providing insights into the role of enthalpic interactions on the potential of mean force (PMF) and stabilization of the system. Ghanbari et al.⁴⁰ have studied the dependence of the dynamics of matrix and grafted chains on the grafting density and the molecular weight of matrix chains via coarse-grained molecular dynamics simulations.

Theoretical and simulation methodologies are quite important in predicting equilibrium or dynamical properties of nanocomposite materials based on GNPs and brushes, serving as guides for experimental design.^{21,41–47} Munaò et al.⁴⁸ have implemented a hybrid particle-field methodology to study the interactions of two and three silica GNPs inside a polystyrene matrix and the role of the third NP in shaping chain configurations and stabilizing the system. In their coarse-grained molecular dynamics-self-consistent field (MD-SCF) model, they studied the dispersion state of both bare and grafted silica NPs as a function of the length of matrix and grafted chain lengths and the grafting density. The effect of polydispersity has been investigated recently by Park et al.⁴⁶ The PMF between embedded GNPs has been also studied with molecular dynamics simulations by Meng et al.⁴⁹ and Midya et al.⁴⁵ The effect of thermal fluctuations and aggregation/phase separation mechanisms have been investigated by field-based multiparticle simulations.^{50–52}

An interesting behavior observed both experimentally⁵³ and computationally⁵⁴ is that there is an optimal grafting density for accomplishing a satisfying dispersion of the NPs inside the polymer melt. This phenomenon was demonstrated in the case of two apposed semi-infinite silica plates in previous work by the authors.⁴⁴ Systems of planar geometry have been investigated under various solvent conditions.^{47,55,56} Furthermore, Klushin et al.⁵⁷ and Ivanova et al.^{58,59} have determined the effect of polydispersity of polymer brushes on their structure and the resulting pressure that is exerted on them when they approach each other.

The effect of the solvent on the interactions of two spherical GNPs has been studied by Lovero and Egorov⁶⁰ via MD simulations and SCF theory (SCFT) calculations. The same effect was also addressed by Egorov⁶¹ using density functional theory. Abbas et al.⁶ have published an experimental study where a polychloroprene matrix was reinforced by the addition of silica GNPs at different loadings; reinforcement was achieved at low grafting density and high molecular weight of grafted chains and it was demonstrated that these conditions correspond to successful dispersion of the particles inside the matrix.

In the present study, we investigate the PMF between two GNPs with different grafting patterns/orientations and among multiple GNPs arranged in various lattice configurations, using a SCFT framework, where the free energy is a direct result of the calculation. The silica particles interact via a Hamaker potential with each other and with the polystyrene segments, and entropic factors associated with the conformations of both grafted and matrix polystyrene chains are accounted for explicitly in three dimensions. It is emphasized that deriving the free energy of the system under various geometries and conditions is not trivial when employing particle-based simulation techniques.

Throughout our calculations, we monitor the variation of the free energy of the system as we reduce the distance between the particles. In the case of two-body interactions, the behavior of the free energy is investigated for different grafting distributions on the surfaces of the particles and orientations, whereas for each distribution we vary the matrix-to-grafted chain length ratio. In the case of multibody interactions, the free energy is derived for different particle configurations in the context of periodic boundary conditions on the edges of the box, and we show that the face-centered cubic (FCC) configuration is the most stable, under the conditions of the present study.

We introduce an important aspect missing from the literature, namely, the determination of the free energy of systems with two or multiple nanoparticles of arbitrary particle geometry, relative orientation, and grafting point distribution. Having an accurate model that can take into account all possible molecular degrees of freedom of such complicated systems could serve as a basis for the development of coarse-grained orientation-dependent potentials for particle and particle-field simulations^{62–64} capable of addressing mesoscopic-microscopic regimes; hence, reducing the number (and cost) of experiments needed for molecular design without any a priori knowledge of equilibrium phase behavior and morphology.

Our model invokes an excess free energy density derived from a realistic equation of state in conjunction with a Gaussian thread model for describing the polymer conformations. This approach accurately captures excluded volume effects and cohesive interactions and has been validated extensively against experiments and atomistic simulations in the prediction of thermodynamic properties and structural features of the chains. In particular, the surface tension of various polymer films, its temperature dependence, and the corresponding density profiles are in quantitative agreement with experiments and simulations.⁶⁵ The brush height of grafted chains on nanoparticles in dilute dispersion within polymer melts match SANS experiments,⁶⁶ mesoscopic models⁶⁷ and theory.^{45,68–70} The potential of mean force between large particles in vacuum and embedded in polymer melts⁴⁴ is in accordance with theoretical predictions,^{53,54,71} Moreover, past calculations of solvation-free energies, lead to physically reasonable results.⁷⁰

Our work offers a versatile approach, enabling the design of both stable dispersions and precisely controlled self-assembled nanocomposite morphologies, ultimately presenting a cost-effective route for fabricating high-performance nanocomposites, including polymer-matrix nanocomposites (e.g., the dispersion of surface-grafted silica in polymer matrices) as well as novel particle-solids exhibiting enhanced toughness in conjunction with excellent optical properties.

RESULTS AND DISCUSSION

Our computational framework is based on the solution of the Edwards diffusion equation governing chain statistics inside the domain $\mathcal{R}$, in the context of the Gaussian thread model:^{72–75}

$$\frac{\partial}{\partial N} q_c(\mathbf{r}, N) = \frac{R_{G,c}^2}{N_c} \nabla_{\mathbf{r}}^2 q_c(\mathbf{r}, N) - \beta w'_{ic}(\mathbf{r}) q_c(\mathbf{r}, N),$$

($c = m, g$)

(1)

with the initial condition:

$$q_c(\mathbf{r}, 0) = \begin{cases} 1, & c = m \\ \frac{N_g}{\rho_{\text{seg,bulk}}} \sum_{i_g=1}^{n_g} \frac{\delta(\mathbf{r} - \mathbf{r}_{g,i_g})}{q_m(\mathbf{r}_{g,i_g}, N_g)}, & c = g \end{cases} \quad (2)$$

In eq 1, $q_c(\mathbf{r}, N)$ is the propagator, proportional to the probability that a chain finds itself at position $\mathbf{r}$ at contour length N , with c denoting whether a chain is grafted ($c = g$) or matrix ($c = m$). The variable N ($0 \leq N \leq N_c$) plays the role of time and spans the contour of the Gaussian polymer chains with length N_c . The “diffusion” term $R_{G,c}^2/N_c$ in eq 1 is a measure of conformational stiffness with $R_{G,c}^2 = C_\infty l_{C-C}^2 N_c/6$ being the radius of gyration, where C_∞ is Flory’s characteristic ratio and l_{C-C} the length of a carbon–carbon bond.⁷⁵ The convolution integral in eq 3,

$$\varphi_c(\mathbf{r}) = \frac{1}{N_c} \int_0^{N_c} dN q_c(\mathbf{r}, N) q_m(\mathbf{r}, N_c - N) \quad (3)$$

yields the reduced local density of matrix (m) or grafted (g) segments, which is related with the local number density as $\rho_c = \varphi_c \rho_{\text{seg,bulk}}$, with $\rho_{\text{seg,bulk}}$ being the bulk number density. The interfacial field,

$$w'_{\text{ifc}}(\mathbf{r}) = \left. \frac{\partial f[\rho, \nabla \rho]}{\partial \rho} \right|_{\rho=\rho(\mathbf{r})} - \left. \frac{\partial f[\rho, \nabla \rho]}{\partial \rho} \right|_{\rho=\rho_{\text{seg,bulk}}} + u_s(\mathbf{r}) \quad (4)$$

describes the nonbonded interactions. In detail, the interactions among polymer segments are described by Helfand’s free energy density,

$$f = \frac{1}{2\kappa_T} \left(\frac{\rho}{\rho_{\text{seg,bulk}}} - 1 \right)^2 \quad (5)$$

for prescribed compressibility (κ_T). The segment–nanoparticle interactions, $u_s(\mathbf{r})$ are described with the sphere–sphere Hamaker potential^{76,77} and a hard sphere wall at distance h_{HS} from the NP surface; see Supporting Information Section S1 for more details. To solve the partial differential equation, we use our in-house developed code RuSseL which applies a Finite Element Method^{78–80} in three-dimensional domains of arbitrary geometry.^{81,82} Additional information regarding the convergence scheme, the parameters of the calculations, and the contributions to the grand potential can be found in the methods section.

For the case of two interacting silica NPs in a polymer melt, the geometry and discretization of the considered domain are presented in Figure 1. For calculating the PMF, the two NPs gradually approach each other along the x -axis connecting their centers (see Figure 1). In all cases, the radius of the NPs is $R_S = 2$ nm; the effect of curvature on the stability of the composite system and generally on the configuration of the grafted corona has been studied elsewhere.^{36,69}

While atomic-level faceting becomes increasingly significant for smaller NPs,⁸³ a spherical nanoparticle (NP) geometry was chosen for simplicity and consistency with prior research.^{46,48,82} Nevertheless, incorporating a more realistic polyhedral (faceted) representation into the FEM computations does not introduce substantial difficulties.

The grafting distributions we have addressed are illustrated in Figure 2. The first two rows illustrate systems with two NPs

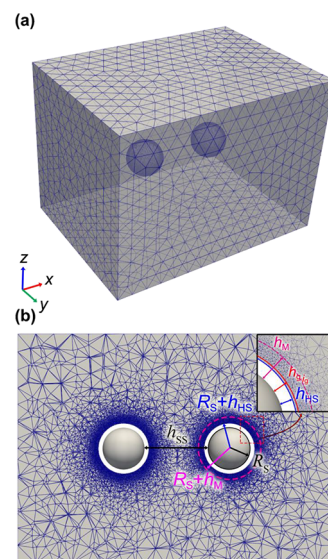


Figure 1. Meshing illustration for two NPs with $R_S = 2$ nm inside a box with dimensions $30 \times 22 \times 22$ nm³. (a) Perspective view showing the mesh at the periodic (box edge) and Dirichlet (solid) boundaries. (b) An xy -slice passing through the centers of the NPs (created with the Slice operation of the Paraview software).^{84,85} The inset depicts an enlarged view of the solid/polymer interface; the solid red line corresponds to the distance of grafting points from the solid surface. The dotted magenta line corresponds to the thickness of the fine-mesh region.

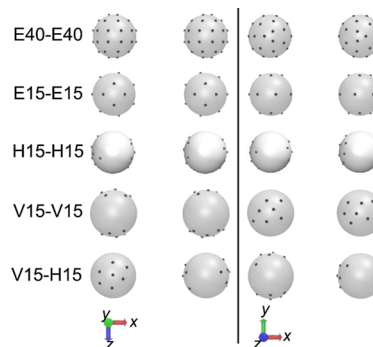


Figure 2. Illustration⁸⁶ of the distributions of grafting points for the PMF calculation between two spherical particles with $R_S = 2$ nm in a melt, in two different projections. The parameters of the equidistant (E40–E40, E15–E15) and nonuniform (H15–H15, V15–V15 and V15–H15) cases are reported in Table 1.

that have been grafted equidistantly using Deserno’s algorithm.⁸⁷ In the case E40–E40, we have grafted 40 chains per NP (mean areal density of grafting points $\sigma_g = 0.8$ nm^{−2}), whereas in the case E15–E15 we have grafted 15 chains per NP ($\sigma_g = 0.3$ nm^{−2}). The last three rows illustrate systems with pairs of nonuniformly grafted NPs created via the Monte Carlo sampling scheme developed in ref 82 (see Methods section Nonuniform Grafting Scheme). Each one of the NPs is grafted with 15 chains that are concentrated near its poles. In the H15–H15 case, the polar axes of the NPs are collinear, aligned along the x -axis; in V15–V15 they are parallel, aligned along the z -axis; and in H15–V15 they are perpendicular to each other. The average grafting density of each system ($\sigma_{\text{g,ave}} = n_g/S_S$ with $S_S = 4\pi R_S^2$ being the surface area of the nanoparticle) and the parameters of the grafting distributions are reported in Table 1. Note that, setting $P_0 = 1$ and $P_i = 0$ in eq 17, renders

Table 1. Parameters for Distributing the Grafting points on the Surfaces of Two Spherical NPs with $R_g = 2 \text{ nm}^a$

system	$\sigma_{g,ave} \text{ (nm}^{-2}\text{)}$	NP ₁		NP ₂	
		pole ₁ (θ)	pole ₂ (θ)	pole ₁ (θ)	pole ₂ (θ)
E40–E40	0.8	Deserno's algorithm ⁸⁷ for generation of 40 grafting points on the surface of each NP			
E15–E15	0.3	Deserno's algorithm ⁸⁷ for generation of 15 grafting points on the surface of each NP			
H15–H15	0.3	0	π	0	π
V15–V15	0.3	$+\pi/2$	$-\pi/2$	$+\pi/2$	$-\pi/2$
H15–V15	0.3	0	π	$+\pi/2$	$-\pi/2$

^aIn the cases E40–E40 and E15–E15, the NPs have been grafted equidistantly with Deserno's algorithm⁸⁷ with $\sigma_g = 0.8$ and 0.3 nm^{-2} , respectively. The cases H15–H15, V15–V15, and H15–V15 refer to nonuniform grafting distributions via a Monte Carlo sampling scheme⁸² with input parameters $P_0 = 0.0$, $P_i = 1.0$, $d_i = 0.5 \text{ nm}$, and the angles θ formed by the radii terminating at the poles with the x -axis connecting the centers illustrated in Table 1.

the insertion probability coordinate (φ , θ) independent, effectively sampling from the uniform probability distribution. Hereafter, nanoparticles with this configuration will be referred to as uniformly grafted.

In this work, we focus on grafting densities that can be obtained using current experimental methods. For instance, Sunday et al.⁸⁸ have demonstrated grafting polystyrene onto silica nanoparticles via atom transfer radical polymerization (ATRP), achieving densities between 0.2 and 0.8 chains/nm^2 . Similarly, RAFT polymers have been grafted onto gold nanoparticles through chemisorption, with grafting densities ranging from 0.8 to 1.1 chains/nm^2 .^{89,90}

In Figure 3, we present the density clouds of grafted chain segments in three-dimensional space for surface-to-surface distance equal to $h_{ss} = \{2.20, 6.12, 12.09\} \text{ nm}$, for the different grafting distributions and orientations of the GNPs shown in

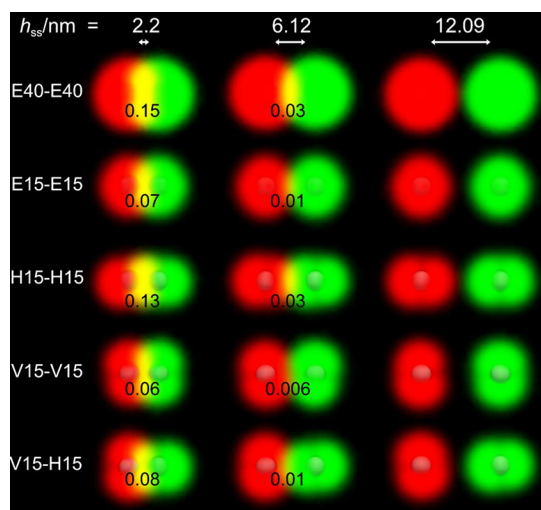


Figure 3. Visualization of the density cloud of polystyrene chains grafted on the surfaces of two silica NPs in a molten polystyrene matrix with varying interparticle distance, h_{ss} . In all cases, $N_m = N_g = 96$ skeletal carbon bonds. The parameters of each system are reported in Table 1. The brush grafted to the left/right GNP is plotted with red/green color, whereas the regions where the brushes interpenetrate are shown with yellow color. The numbers below the yellow regions quantify the chain interpenetration according to eq 6; values below 10^{-3} are not shown.

Table 1. In all cases presented in this figure, the length of matrix chains is equal to that of grafted chains, $N_m = N_g = 96$ skeletal carbon bonds.

We see that, in the irregular grafting cases, the clouds of grafted segments emanating from each particle are distorted as the two particles get closer to each other. This happens because the segments of the grafted chains need to adjust in progressively less space in the interparticle region. To better demonstrate the evolution of the density profiles, we present with different colors the brush corresponding to each particle; red for the left particle, green for the right particle, and yellow for the density profile of segments belonging to the interpenetrating brushes of the two NPs. For more details regarding the 3D visualization of the density profiles and the function of colors, the reader is referred to Section S2 of the Supporting Information. The interpenetration of the grafted chains (numbers below the yellow regions in Figure 3) is quantified via the following equation:

$$\varphi_{g_1 \cap g_2} = \frac{4 \int_D d\mathbf{r} \varphi_{g, NP_1} \varphi_{g, NP_2}}{\int_D d\mathbf{r} (\varphi_{g, NP_1} + \varphi_{g, NP_2})} \quad (6)$$

which takes values between 0 (no interpenetration) and 1 (max interpenetration).

In situations where the (yellow) interpenetration region becomes larger, the entropic repulsion between the chains emanating from the particles is more likely to prevent them from assuming this specific orientation. Furthermore, we can clearly see that in the E40–E40 case, the clouds are so dense that the particle cores are invisible, in contrast to all the rest of the grafting cases.

In Figure 4, we plot the cloud of grafted chain segments for the H15–H15 grafting case (see Table 1) for three different

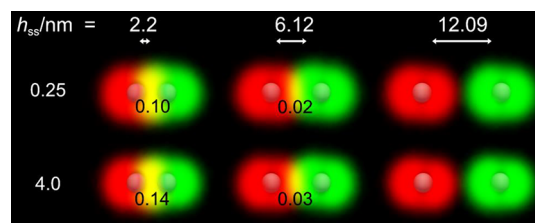


Figure 4. Visualization of the density cloud of polystyrene chains grafted on the surfaces of two NPs in molten polystyrene matrices with varying interparticle distance, h_{ss} and $N_m/N_g = 0.25$ (top) and 4.0 (bottom). In all cases, $N_g = 96$ skeletal carbon bonds. The parameters of the system are reported in Table 1. The brush of the left/right NP is plotted with red/green color, whereas the regions where the brushes interpenetrate are shown in yellow. The numbers below the yellow regions quantify the chain interpenetration according to eq 6; values below 10^{-3} are not shown.

interparticle distances, h_{ss} . In each case, we vary the matrix-to-grafted chain length ratio, N_m/N_g , while keeping the length of the grafted chains constant, $N_g = 96$. According to Figure 4, the cloud of grafted chain segments is slightly suppressed with increasing N_m/N_g . This is because in situations where $N_m/N_g < 1$, the matrix chains more readily penetrate the region occupied by the brush, and, as a result, the grafted chains swell more toward the bulk region.^{69,91} In this 3D view of the density profile, the differences in the grafted clouds with respect to N_m are barely noticeable; in spite of this, the interpenetration according to eq 6 increases considerably (numbers below the

yellow regions) and has a significant impact in the resulting PMF.

We have calculated the PMF between the two NPs for equidistant and nonuniform grafting schemes with varying matrix-to-grafted chain length ratio, as a function of the surface-to-surface distance h_{ss} . The PMF is expressed with reference to the free energy of the two grafted particles at infinite distance; i.e.:

$$\text{PMF}(h_{ss}) = \Delta\Omega(h_{ss}) - \lim_{h_{ss} \rightarrow \infty} \Delta\Omega \quad (7)$$

with $\Delta\Omega$ being the difference of the grand potential with respect to a reference system of matrix chains ($\Omega^{\text{M,bulk}}$) of the same length and at the same temperature and a system of isolated end-pinned unperturbed grafted chains of the same length and at the same temperature ($A^{\text{G,bulk}}$):

$$\Delta\Omega = \Omega - \Omega^{\text{M,bulk}} - A^{\text{G,bulk}} \quad (8)$$

The individual free energy components are reported in the Methods section **Free Energy Terms**.

For $h_{ss} > 12$ nm, the brushes of the two NPs do not interact with each other (e.g., compare the third column of Figure 3), so the free energy of the system at these distances is practically equivalent to the free energy of the two particles when they are at infinite distance from each other.

In our PMF calculations, we considered the Hamaker interaction between silica cores.⁷⁶ However, at relevant distances, this interaction has a negligible effect on the system's total PMF (see Section S1 of the Supporting Information for details on silica–silica and silica–polystyrene interactions). Therefore, the Hamaker interactions are screened and the free energy is dominated by the coating on the nanoparticles.

Our calculations are subject to two main uncertainties: (i) a systematic numerical error due to the vertex distribution in the FEM method, and (ii) a statistical uncertainty from the particular realization of the grafting point distribution employed. To quantify these uncertainties, we conducted benchmarks in Section S3 of the Supporting Information. The analysis reveals that the standard deviation (STD) of free energy due to vertex distribution is ~ 4.5 , 1.2, and 0.6 kJ/mol for moderate, fine, and ultrafine mesh discretization, respectively, whereas the STD due to variations to the grafting point distribution is ~ 1.6 kJ/mol. Based on these findings, the distribution of grafting points appears to be the dominant source of uncertainty for fine and ultrafine meshes.

Figure 5 illustrates the PMF of a pair of two equidistantly grafted GNPs at various distances. The error bars correspond to the standard deviation of the PMF among four calculations at large (“infinite”) separation distances, h_{ss} , between the NPs. When $N_m < N_g$, the PMF increases monotonically with decreasing surface-to-surface NP distance. This is expected, since the shorter matrix chains can penetrate into the brushes and swell them toward the bulk. Shorter matrix chains constitute a better solvent for the grafted corona than longer matrix chains, and thus, at fixed N_g and σ_g , the effective interaction between grafted NPs becomes more repulsive as N_m decreases.

In contrast, increasing N_m/N_g leads to less repulsive PMFs and even to the formation of free energy minima. This is attributed to a phenomenon known as “autophobic dewetting”. Essentially, when matrix chains (N_m) are longer than grafted chains (N_g)—especially at high grafting densities (σ_g)—they

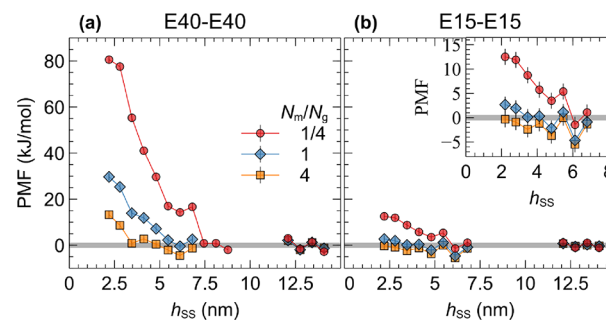


Figure 5. PMF between two silica NPs equidistantly grafted with polystyrene chains as a function of h_{ss} . The two NPs are embedded in a matrix of polystyrene chains and the matrix to grafted chain length ratio assumes the values $N_m/N_g = \{1/4: \text{circle}, 1: \text{diamond}, 4: \text{square}\}$. In all cases, $R_s = 2$ nm and $N_g = 96$ skeletal carbon bonds. Lines are guides to the eye. The parameters for the (a) E40–E40 and (b) E15–E15 systems are reported in Table 1.

experience a greater entropy penalty upon confinement within the interfacial region. This makes it unfavorable for them to penetrate this area, leading to decreased repulsion. A similar behavior has been reported with the one-dimensional counterpart of our model⁴⁴ in the limit of very large nanoparticles (opposing polymer brushes), and also in the literature.^{53,54,71}

We can qualitatively compare the case of $N_m/N_g = 1/4$ in our Figure 5a (circles) with the black line of Figure 6c of ref 48 and see the satisfying agreement between the two plots in the range of distances that we have examined. It would not be of essence to quantitatively compare the two plots, because in the case of Munaò et al.,⁴⁸ a hybrid particle-field methodology is implemented and furthermore, there are certain differences in the parametrization of the system, e.g., in ref 48 the grafting density is 1.0 nm^{-2} , which is considerably higher than the 0.8 nm^{-2} grafting density in our calculations. Furthermore, there is a difference in the representation of the polymer chains themselves: in the case of ref 48, chains are represented by a coarse-grained bead spring model, whereas in our SCFT framework, the polymer chains are Gaussian threads.

Park et al.⁴⁶ have made a detailed analysis of the PMF between two gold NPs as a function of the matrix-to-grafted chain length ratio, comparing their computational model to real systems analyzed via TEM images.⁴⁶ They verified that for lengths of matrix chains equal to or higher than ~ 2 times the length of grafted chains, the latter are not sufficiently wetted by the homopolymer melt; therefore, the system is led to aggregation. Herein we also verify the manifestation of the autophobic dewetting when $N_m/N_g \geq 1$, and we extend the analysis of the system to cases where the inhomogeneous distributions of the grafting points on the particles are an additional parameter of design.

Figure 6 illustrates the PMF of two GNPs with 15 chains that are concentrated near their poles in parallel (H15–H15), perpendicular (H15–V15) and vertical (V15–V15) orientations. It should be stressed here that the aggregation tendencies of two interacting bodies depend on the magnitude of the PMF minima at various orientations and not on the location of the repulsive (positive) part of the PMF; the latter is indicative of the shape of the GNPs and does not convey any information about dispersion.

Similar with the equidistant case (Figure 5), the particles are expected to disperse within the polymer matrix in situations where the matrix chains are short relative to the grafted ones.

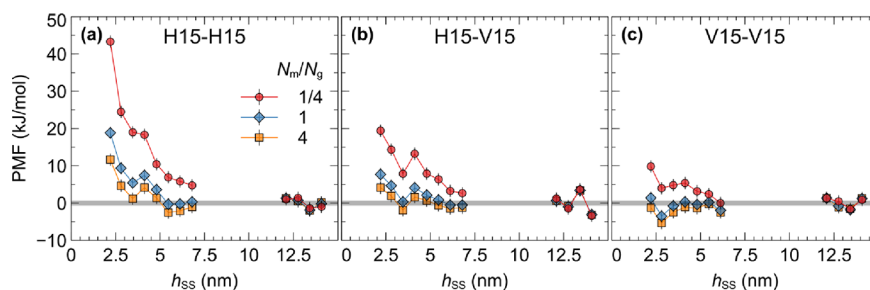


Figure 6. Same as in Figure 5 for the configuration (a) H15–H15, (b) H15–V15, and (c) V15–V15.

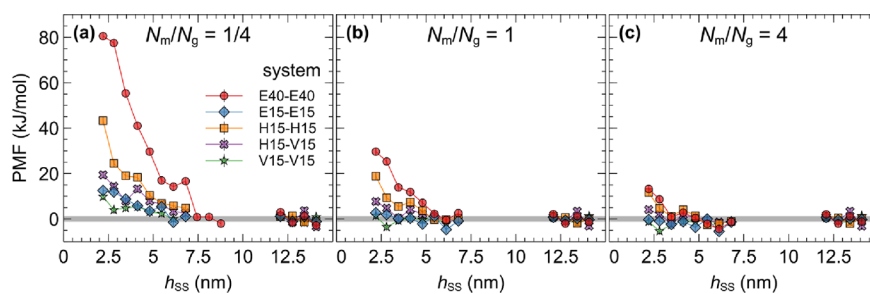


Figure 7. Master plot incorporating data from Figures 5 and 6 rearranged for the same ratio of matrix to grafted chains in each panel: N_m/N_g = (a) 1/4, (b) 1, and (c) 4. The parameters of the different grafting distributions: E40–E40 (circle), E15–E15 (diamond), H15–H15 (square), H15–V15 ($\times$), and V15–V15 (star) systems are reported in Table 1.

For large N_m/N_g ratios, on the other hand, the PMF exhibits minima with orientation-dependent magnitude. The difference in the magnitude of the minima suggests that the relative orientation of the GNPs in the aggregated state can be influenced by the grafting distribution.

In particular, for $N_m/N_g \geq 1$, the V15–V15 case features a pronounced well depth of ca. 5 kJ/mol at 2.8 nm. This depth is well beyond the margin of error associated with our method. In contrast, H15–H15 and H15–V15 feature shallower depths (2–2.5 kJ/mol) on par with the statistical uncertainty. Our findings suggest that the V15–V15 configuration exhibits stronger stability with a tendency to aggregate, with the bare surfaces of nanoparticles facing each other.

This result is not trivial because the relative magnitude of the PMF as a function of the orientation is not known beforehand. For example, supposing that for a different set of parameters, the H15–H15 case featured more pronounced minima than the V15–V15 case, the final aggregated state would be that of GNPs arranged in a chain-like fashion along the horizontal direction. The aforementioned scenario has been shown to be possible for large NPs,⁴⁴ and could be achieved by imposing dense grafting at the poles of the GNPs ($\sigma_g > 0.4 \text{ nm}^{-2}$) and low grafting at the perimeter ($\sigma_g \approx 0.1 \text{ nm}^{-2}$); the former/latter regions feature very strong/no minima (e.g., compare with the third column of Figure 7 in ref 44).

The master plots in Figure 7 display the PMF of the system for all particle orientations. The universal impact of the matrix-to-grafted chain length ratio on the aggregation tendencies is illustrated clearly as the PMF exhibits a minimum with increasing N_m/N_g (from left panel to the right).

In addition, Figure 7 highlights the significant anisotropy (orientation dependence) of effective interactions in inhomogeneous grafting scenarios, as seen in cases H15–H15, H15–V15, and V15–V15. Notably, for the same N_m/N_g , the repulsive strength of the PMF, indicated by the rate of increase

with decreasing distance, follows the trend: H15–H15 (strongest) > H15–V15 (moderate) > V15–V15 (weakest). This behavior directly correlates with the visualizations in Figure 3 and the corresponding interpenetration indices (eq 6) at short distances shown in Figure 3 for $h_{SS} = 2.2 \text{ nm}$; the index values ($0.13 > 0.08 > 0.06$) correlate with the degree of steric repulsion between grafted chains for cases H15–H15, H15–V15, and V15–V15, respectively.

To elaborate, in the H15–H15 case, the PMF is most repulsive because the grafted chains directly oppose each other. As the particles approach, chains on their grafted poles interpenetrate significantly, maximizing the free energy penalty. The H15–V15 case exhibits an intermediate response; only one set of grafted chains is oriented against the other particle, leading to a moderate PMF increase. Finally, the V15–V15 case shows the weakest repulsion. Here, the grafted chains are oriented perpendicular to the interparticle axis, minimizing interpenetration.

Furthermore, when $N_m/N_g = 4$, having 15 chains per particle grafted primarily near the poles in the H15–H15 relative orientation becomes equivalent to having 40 chains of the same length grafted equidistantly on each particle in terms of free energy rise; i.e., compare the squares and circles in the rightmost panel of Figure 7.

For demonstration purposes, we present in Figure 8 the term of the PMF associated with the configurational entropy of grafted chains for all grafting distributions and for $N_m = N_g$. The contributions of the other terms to the PMF are illustrated in Section S4 of the Supporting Information. It is underlined again that the only characteristic that changes between the H15–H15, H15–V15, and V15–V15 cases is the relative orientation of the grafted particles. Note that the free energy term associated with the configurational entropy of grafted chains clearly exhibits a much smaller error; this is the contribution that is mostly affected by bringing the particles closer to each other.

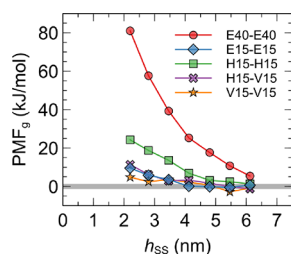


Figure 8. Configurational entropy contribution of grafted chains to the PMF as a function of h_{SS} (eq 16). In all cases, $R_S = 2$ nm and $N_g = N_m = 96$ skeletal carbon bonds. The parameters of the systems: E40–E40 (circle), E15–E15 (diamond), H15–H15 (square), H15–V15 (x) and V15–V15 (star) systems are reported in Table 1.

Extending our calculations beyond two-body interactions, we have also derived the multibody PMF among grafted silica NPs with random grafting (sampled from the uniform probability distribution) which may assume different ordered structures inside the polystyrene melt. The uniformly grafted NPs, were created with the Monte Carlo sampling scheme from ref 82 using a constant insertion probability, i.e., eq 17 with $P_0 = 1$ and $P_i = 0$.

The free energy of the system was studied as a function of the lattice constant for three different NP ordered configurations (Bravais lattices): simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC). In each one of these cases, the distance of the NPs was varied by changing the lattice constant of the periodic cell containing the NPs.

Here we will switch gears and shift our focus to applying these calculations in order to study the configurations of self-assembled nanocomposite morphologies. We will consider cases with $N_m/N_g = 4$, since it is well-known^{44,53,54,71} that for large N_m/N_g , NPs tend to aggregate efficiently within the polymer matrix. For the sake of numerical convenience when running calculations on the multibody interactions, we opted to increase the isothermal compressibility κ_T of the polymer by an order of magnitude.

In Figure 9, we present the contour density profiles of segments belonging to matrix chains within cross sections along the (100) and (111) planes of the respective lattices at low (top) and high (bottom) densities.

A consistent color scheme is used throughout Figure 9 (see color bar) in order to facilitate comparisons for different nanoparticle densities. Regions with low ($\varphi_m = 0$), intermediate ($\varphi_m = 0.5$), and high ($\varphi_m = 1$) concentrations of matrix segments are illustrated with the blue, green, and red colors, respectively. It is important to consider how the distribution of grafted chain segments relates to this visualization; because the total reduced density remains nearly constant, areas depleted of matrix segments (blue) will conversely be enriched with grafted chains, and vice versa.

As the nanoparticle density increases, the available space for matrix chains shrinks. This is reflected by the dominance of the blue color in Figure 9b, indicating a lower overall concentration of matrix segments within the denser lattice.

It becomes clear that the matrix chains are gradually forced to exclusively occupy the decreasing available space that is left beyond the height of the brushes grafted on the NPs. As is better illustrated by the (111) plane, the exclusion of matrix chains from the interfacial region becomes more intense while going from the SC to BCC to FCC lattice, as a result of the closer packing of the NPs. Note that the (111) plane does not

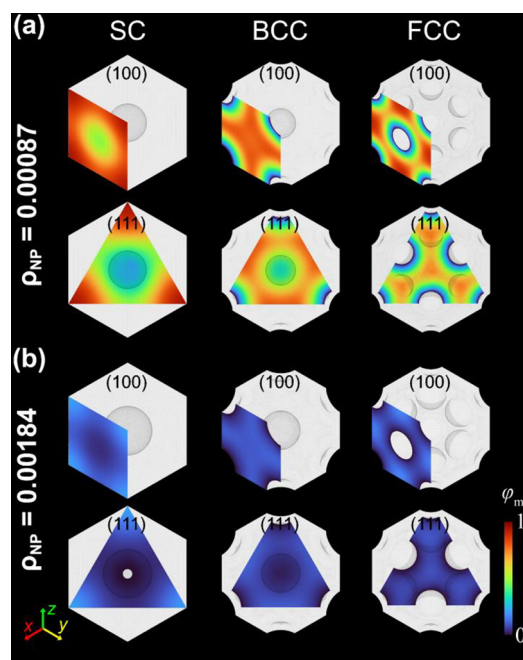


Figure 9. Visualization of contour density profiles of matrix polystyrene chains^{84,85} passing through the (100) and (111) planes of simple-cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) Bravais lattice at NP densities equal to (a) $\rho_{NP} = 0.00087 \text{ nm}^{-3}$ and (b) $\rho_{NP} = 0.00184 \text{ nm}^{-3}$. In all cases, $T = 500 \text{ K}$, $\kappa_T = 3.97 \times 10^{-8} \text{ Pa}^{-1}$, $\sigma_{g,ave} = 1.0 \text{ nm}^{-2}$, $N_g = 96$ skeletal carbon bonds and $N_m/N_g = 4.0$.

pass through the center of the unit cell and that it barely passes through the NP of the SC lattice for $\rho_{NP} = 0.00184 \text{ nm}^{-3}$.

Regarding the effect of the packing on the PMF of the system, we present in Figure 10a the free energy per particle

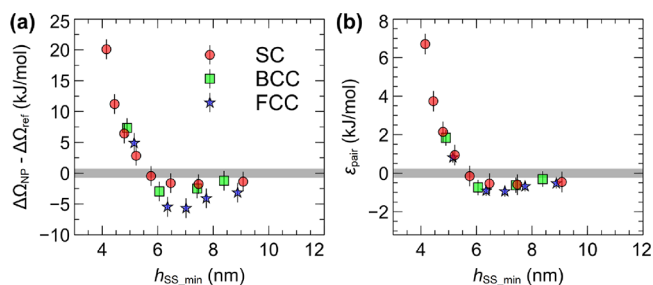


Figure 10. Free energy per NP ($\Delta\Omega_{NP}$), as a function of the minimum surface-to-surface interparticle distance. The SCFT calculation is performed for three different Bravais lattices: simple cubic (SC, circle), body-centered cubic (BCC, square) and face-centered cubic (FCC, star). In all cases, $T = 500 \text{ K}$, $\kappa_T = 3.97 \times 10^{-8} \text{ Pa}^{-1}$, $R_S = 2 \text{ nm}$, $\sigma_{g,ave} = 1.0 \text{ nm}^{-2}$, $N_g = 96$ skeletal carbon atoms and $N_m/N_g = 4$.

$\Delta\Omega_{NP} = \Delta\Omega/n_{NP/cell}$ [where $n_{NP/cell} = 1$ (SC), 2 (BCC) or 4 (FCC); see Table 2] with respect to a reference energy per

Table 2. Parameters of the Multi-Nanoparticle Systems

lattice	$n_{NP/cell}$	n_{neigh}
SC	1	6
BCC	2	8
FCC	4	12

isolated particle $\Delta\Omega_{\text{ref}} = 807.5$ kJ/mol, as a function of the minimum surface-to-surface distance. Figure 10a demonstrates clearly that the most energetically favored configuration is the FCC, followed by the BCC and then the SC. Our results cohere with the experimental and numerical investigations by Midya et al.⁴⁵ on densely-PS-grafted NPs with small grafted chains in relation to the NP radius. Hexagonal-like patterns are illustrated from both experiments and simulations for DP100 in Figure 1b therein,⁴⁵ which are similar to the (111) plane of the stable FCC configurations we identify here.

Supposing (i) perfect pairwise additivity and that (ii) only the first neighbors contribute to the full interaction, the total interaction energy can be related to the (naive) equivalent pairwise interactions as follows:

$$\epsilon_{\text{pair}} = 2 \frac{\Delta\Omega_{\text{NP}} - \Delta\Omega_{\text{ref}}}{n_{\text{neigh}}} \quad (9)$$

with n_{neigh} being the coordination number (number of closest neighbors, see Table 2) for each configuration and ϵ_{pair} being the strength of the equivalent pairwise interactions. The evaluations of ϵ_{pair} for each case are shown in Figure 10b. The values are close to each other, suggesting that the assumption of pairwise additivity is reasonable for the cases considered here. However, a trend emerges, indicating a slight increase in attractive multibody effects with denser packing (SC to BCC to FCC). This effect, however, is relatively weak and could potentially fall within the margin of error associated with our method.

CONCLUSIONS

We have studied the interactions of two and multiple spherical silica GNPs, which are grafted with polystyrene chains and embedded inside a polystyrene melt, in order to provide useful insight into how the particles tend to behave as time drives the system toward thermodynamic equilibrium. We have considered particles with a radius equal to $R_s = 2$ nm, thereby assessing the opposite end of the extreme case where the particles are infinitely large, i.e., solid planar surfaces.⁴⁴

First, we conducted three-dimensional calculations on pairs of equidistant and irregularly grafted NPs, each time varying the distance between the particles systematically at a fixed relative orientation. At each distance, the system free energy was measured, leading to the PMF as a function of the orientation of the NPs and the matrix-to-grafted chain length ratio.

In accordance with earlier works, we find that in situations where the matrix-to-grafted chain length ratio is large (small) the PMF becomes attractive (repulsive) in nature, suggesting that the particles will tend to aggregate (disperse) over time. This effect appears to persist irrespectively of whether the NPs are grafted homogeneously or not, at least for the cases considered here.

The entropy of grafted chains when the two particles get closer to each other decreases, since the available space decreases and so does the number of available conformations. We demonstrated that, when the relative orientation results in extreme crowding of grafted chain segments, then the free energy rises very steeply compared to the case of equidistant grafting. In other words, keeping all other parameters of the system constant, including the number of grafted chains and the grafting distribution, the relative orientation plays a

decisive role in the PMF, and therefore the preferential ordering of the particles.

In the attractive cases where $N_m/N_g \geq 4$, the PMFs of GNPs with bipolar nanopatterning exhibit a fascinating feature in that the potential well across the parallel orientation (V15–V15) is deeper than the potential wells in collinear and perpendicular orientations (H15–H15 and H15–V15). The aforementioned finding suggests that the particles will tend to aggregate assuming preferential orientations that allow the closest approach between the bare parts of the GNP surfaces. This situation cannot be known beforehand, however. By adjusting the molecular parameters of particles that are still preferentially grafted at the poles, it is possible to reverse this effect. It has been shown⁴⁴ that, by adjusting the grafting density and chain length, one can tune the attractive/repulsive nature of the PMF of large NPs; therefore, for a different set of parameters that promote/suppress the attraction along the poles/equators of the NPs, the effect could be reversed. This is a novel finding, especially in the context of a field-based method, since it shows that, by altering the distribution of grafting points on the solid surfaces, one can control effective interactions and self-assembly tendencies of the particles, and therefore generate aggregated microstructures with preferential long-range interactions and desired properties (e.g., enhanced electrical and thermal conductivity).

At high particle concentrations, many-body interactions can affect the equilibrium morphology. In this regard, we investigated the equilibrium interactions of multiple grafted NPs (uniformly grafted sampled from the uniform probability distribution) embedded inside the polymer matrix. More specifically, we have performed three-dimensional calculations on a polystyrene melt containing multiple silica NPs grafted with polystyrene chains in three ordered arrangements: simple cubic (SC), body-centered-cubic (BCC), and face-centered cubic (FCC). At given ambient conditions, and therefore at constant chemical potential of the homopolymer, we have calculated the free energy as a function of the spatial distance of nanoparticles and minimized it to impose equilibrium. At equilibrium, the interparticle distance is very close among the three ordered structures. The stability (depth of the free energy well per nanoparticle), however, increases as we go from the SC to the BCC to the FCC arrangement, which means that the latter is the most probable nanoparticle structure under equilibrium conditions and the parameters of the present calculations. This is in agreement with recent experimental and simulation findings reported by Midya et al.⁴⁵ Furthermore, this multiparticle calculation demonstrated that nearest-neighbor interactions among the particles beyond mere pairwise additivity have a small contribution to the free energy of the system.

The three-dimensional model developed herein and the associated machinery pave the way for the prediction of polymer-NP systems with tailor-made morphologies of theoretical, experimental, and industrial interest, including enhanced rubbers and particle solids. Future directions of this study include the investigation of systems with multiple NPs with irregular grafting distributions, and systems with chemically different grafted and matrix chains or block copolymers,⁹² where the enthalpic interactions among polymer segments of different chemistry and solid surfaces can significantly broaden the spectrum of possible self-assembly behaviors. In addition, the determination of the free energy as a function of the relative orientation among two or more particles can be used

to parametrize orientation-dependent effective potentials for particle-based simulations, hence leading the way to predicting the self-assembly tendencies of systems with thousands of GNPs.

METHODS

Convergence Scheme and Parameters of the Calculations.

The partial differential equations (PDE) are evaluated using the finite element method (FEM)^{78–80} in three dimensions, implemented in our in-house code RuSSEL^{81,82} which is linked with the MUMPS solver.^{93–95} The convergence of eq 1 is realized with a hybrid optimization scheme which relaxes the field by imposing a substitution scheme ($w'_{\text{ifc}} \rightarrow f_{\text{mix}} w'_{\text{ifc, next}} + (1 - f_{\text{mix}}) w'_{\text{ifc, prev}}$) subject to a relaxation parameter $f_{\text{mix}} = \lambda_{\text{mix}} / \max(N_g, N_m)$ and at the same time optimizes the delta function of the grafted chains in order to reduce the error in grafting density below $\varepsilon_g^{\text{tol}}$.

For additional information regarding the spatiotemporal discretization of eq 1 and the convergence of the self-consistent field the reader is referred to Section 2.4 of ref 62. The parameters of the calculations are reported in Table 3.

Table 3. Parameters of the Calculations

parameter	value	source
T	500 K	
$l_{\text{C-C}}$	0.154 nm	
C_∞	9.85	75
M_{monomer}	52.08 g/mol	
$\rho_{\text{mass, bulk}}$	953 kg/m ³	96
κ_T	3.97 GPa ^{−1}	44,81
h_{HS}	0.4 nm	69
σ_{PS}	0.37 nm	96
σ_{SiO_2}	0.30 nm	96
A_{PS}	5.84×10^{-20} J	96
A_{SiO_2}	6.43×10^{-20} J	96
λ_{mix}	0.5	62
$\Delta E^{\text{tol}}/S_g$	10^{-6} (mJ/m ²)	
$\varepsilon_g^{\text{tol}}$	0.5%	

Free Energy Terms. We adopt a grand canonical ensemble formulation to describe the thermodynamics of our system. The free energy of the system is a sum of individual free energy terms, shown in eq 10.

$$\Delta\Omega = \Delta\Omega_{\text{coh}} + \Delta\Omega_{\text{field}} + \Delta\Omega_{\text{m}} + \Delta A_{\text{g}} + \Delta U_{\text{s}} \quad (10)$$

These terms are associated with the cohesive interactions among polymer segments ($\Delta\Omega_{\text{coh}}$),

$$\Delta\Omega_{\text{coh}} = \int_{\mathcal{R}} d\mathbf{r} \{f[\rho(\mathbf{r})] - f[\rho_{\text{seg, bulk}}]\} \quad (11)$$

the energy associated with the self-consistent field ($\Delta\Omega_{\text{field}}$),

$$\Delta\Omega_{\text{field}} = - \int_{\mathcal{R}} d\mathbf{r} \{ \rho(\mathbf{r}) w'(\mathbf{r}) - \rho_{\text{seg, bulk}} w'_{\text{bulk}}(\mathbf{r}) \} \quad (12)$$

the conformational entropy of matrix ($\Delta\Omega_{\text{m}}$) and grafted chains ($\Delta\Omega_{\text{g}}$),

$$\Delta\Omega_{\text{m}} = - \frac{\rho_{\text{seg, bulk}} V}{\beta N_{\text{m}}} (Q_{\text{m}}[w'_{\text{ifc}}] - 1) \quad (13)$$

$$\Delta A_{\text{g}} = - \frac{1}{\beta} \sum_{i_g=1}^{n_g} \ln Q_g[\mathbf{r}_{g, i_g}; w'_{\text{ifc}}] - \frac{1}{\beta} \sum_{i_g=1}^{n_g} \ln \frac{h_{\text{ref}, q=0}}{h_{g, i_g, q=0}} \quad (14)$$

and the interaction energy between the polymer segments and the surfaces of the solid NPs (ΔU_{s}):

$$\Delta U_{\text{s}}^{\text{SGM}} = \int_{\mathcal{R}} d\mathbf{r} \{ \rho(\mathbf{r}) u_{\text{s}}(\mathbf{r}) \} \quad (15)$$

Q_{m} and Q_{g} are the partition functions of the matrix and grafted chains. The second term on the right-hand side of eq 14 renders the configurational entropy independent of the distance of the grafted point from the solid surface.^{36,69} Finally, the contribution of the individual terms to the PMF is denoted as

$$\text{PMF}_a(h_{\text{ss}}) = \Delta\Omega_a(h_{\text{ss}}) - \lim_{h_{\text{ss}} \rightarrow \infty} \Delta\Omega_a \quad (16)$$

with a being coh, field, m, g, or s.

Nonuniform Grafting Scheme. The grafting of NPs with irregular grafting distributions is realized with a Monte Carlo scheme where the probability to accept an insertion of each chain at a certain point $\mathbf{p}(r, \theta, \varphi)$ across the NP surface is given by eq 17:

$$P(\mathbf{p}) = \min \left(1, \max \left(0, P_0 + \sum_{i \in n_{\text{GP}}} P_i \exp \left(- \frac{D(\mathbf{p}, \mathbf{p}_i)^2}{2d_i^2} \right) \right) \right) \quad (17)$$

with P_0 being the background probability, $\mathbf{p}_i = (r, \theta, \varphi_i)$ the coordinate of the Gaussian pulse, P_i a pre-exponential factor, which determines the attraction and repulsion tendencies, and d_i the standard deviation. $D(\mathbf{p}, \mathbf{p}_i)$ indicates the great circle distance between points $\mathbf{p}$ and $\mathbf{p}_i$. For more details, the readers are referred to section 2.6.2 of ref 62.

In conjunction with the algorithm developed in ref 62, we have imposed an additional constraint; we have set a minimum distance r_{min} between two grafting points, so that the maximum local grafting density does not exceed a threshold value $\sigma_{\text{g, max}} = 1.2 \text{ nm}^{-2}$, which is hard to achieve experimentally; assuming hexagonal close packing locally for grafting points, we get $r_{\text{min}}^2 = \frac{2}{\sqrt{3}} \frac{1}{\sigma_{\text{g, max}}} \approx 1 \text{ nm}^2$. In this

manner, we also eliminate discrepancies in the resulting PMF in case two grafting points come too close to each other during the generation process (see Section S5 of the Supporting Information).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.4c03229>.

(S1) Hamaker interactions, (S2) interpreting 3D contour plots, (S3) quantifying uncertainty in free energy calculations: impact of mesh size and grafting point distribution, (S4) components of the PMF, (S5) relationship between grafting point separation and energy (PDF)

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Notes

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ABBREVIATIONS

PDE, partial differential equation; FEM, finite element method; SC, simple cubic; BCC, body centered cubic; FCC, face centered cubic; PMF, potential of mean force; (G)NPs, (polymer-grafted) nanoparticles; SCF(T), self-consistent field (theory); MD, molecular dynamics

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