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Anisotropic aggregation in a simple model of isotropically polymer-coated nanoparticles

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We report a numerical study of a simple, modified Asakura-Oosawa model for nanoparticles that are isotropically grafted with polymer chains. We perform canonical and grand-canonical Monte Carlo simulations to establish a qualitative morphology diagram, as well as quantitative phase diagrams. The morphology diagram qualitatively reproduces experimental observations and theoretical approaches employing more complex models. In addition, we establish the transition lines for a microphase separation and show that the phase behavior saturates for larger polymer sizes. An analytical treatment on the level of the second virial coefficient indicates that this saturation effect is caused by less effective shielding of nanoparticles by longer polymers. Our simple model enables large-scale particle-based simulations of self-assembly of polymer-coated particles.

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I. INTRODUCTION

Polymer nanocomposites (PNCs) are multicomponent materials consisting of a small volume fraction of nanofiller material dispersed in a polymer matrix. The dispersion and nanoscale morphology of the filler have a great influence on macroscopic physical properties such as toughness, stiffness, permeability, electrical conductivity, flammability, and many more [1]. For example, small loadings of carbon nanotubes were shown to provide great mechanical reinforcement and other enhancements such as self-stiffening relative to the single-component material [2–5]. By gaining control over the shape and dispersion of nanostructures in the matrix, one can tailor composites with unique physical features. Such control can be achieved via self-directed nanoparticle self-assembly [6]. For instance, spherical silica nanoparticles (NPs), isotropically grafted with polystyrene chains, were shown to self-assemble into a range of anisotropic structures when immersed in a polystyrene matrix [7]. The formation of these structures, ranging from finite-size clusters or networks of percolating sheets to dispersions of isolated particles, is driven by microphase separation of the grafted polystyrene chains and the inorganic colloids, which in turn is governed by a competition between the short-ranged interparticle attractions (such as dispersion forces, hydrogen bonds, or hydrophobic forces) and grafted chain entropy. Employing a coarse-grained model, computational and theoretical work on such particles correctly predicts the order of formation of nanoparticle superstructures—from spherical, sheetlike, and stringlike to fully isolated particles—as a function of the number (or surface density) and size of grafted chains, which are important parameters controlling morphology and dispersion properties [7,8].

These coarse-grained models do leave out some subtleties of grafted polymer chains. The two main contributions to the polymer chain entropy are (1) the mixing entropy of grafted and matrix chains and (2) a term arising from the elasticity of the brush. Matrix chains smaller than the grafted chains may penetrate or “wet” the brush and increases its average height. Therefore, changing the relative chain size may lead to a wet-to-dry conformational transition of the grafted chains and affects the morphological phase behavior. In addition, changing the NP curvature affects the free volume available to grafted chains, which in turn leads to changes in the entropic loss associated with wetting. Coarse-grained models of functionalized NPs generally combine an implicit polymer solvent with a bead-spring representation for the grafted polymers [7,9,10], thereby ignoring the mixing contribution to the chain entropy. Notwithstanding this simplification, these models are still computationally expensive in large-scale applications. As such, it would be useful to identify an even simpler model that can capture the physical essence of this self-assembly process.

Here we present a Monte Carlo simulation study of a simplified model of these polymer-coated nanoparticle dispersions, where we describe the grafted NPs with a modified Asakura-Oosawa (AO) model [11,12]. While for polymer solutions in a good solvent the polymers behave nonideally, the concept of noninteracting ideal polymers has been used successfully to describe, at least qualitatively, phase separation in colloid polymer mixtures [13,14]. In the standard AO model, the colloids are hard spheres, while the polymers chains are hard spheres that do not interact with other polymers but are impenetrable to the colloids. In our modified AO model, the nanoparticles are represented by attractive hard spheres, while the grafted polymers are viewed as tethered Gaussian chains, represented by Asakura-Oosawa particles in an implicit solvent tethered to the hard sphere. The aim of this work is twofold: (1) show that this very simple model can explain the experimentally observed morphological phase transitions as a function of the two geometrical parameters, the number and size of grafted polymers; and (2) gain insight in the physical mechanism of the self-assembly process and explain qualitatively the observed structures.

The paper is organized as follows. In Sec. II we explain the model, the simulation techniques, and the second virial theory. In Sec. III we first discuss the estimated aggregation transition dependence based on the second virial coefficient analysis. We then discuss the qualitative behavior of the modified AO model in a canonical NVT setup. Next, we quantitatively establish the phase diagram using grand-canonical simulations in combination with histogram reweighting. We end with concluding remarks.
II. METHODS

A. Simulation model

In our modified AO model the nanoparticles are impenetrable hard-spheres of diameter $\sigma$ immersed in a polymer matrix, which is treated as an implicit (monomeric) solvent. The short-ranged attractive forces between the particles (e.g., depletion, van der Waals, hydrogen bond, or hydrophobic interactions) are modeled with an attractive square-well (SW) interaction of depth $\varepsilon$ and range $\lambda \sigma$:

$$\beta U_{cc}(R) = \begin{cases} \infty & R \leq \sigma, \\ -\varepsilon & \sigma < R \leq \lambda \sigma, \\ 0 & R > \lambda \sigma, \end{cases}$$

where $R$ denotes the interparticle distance. The grafted polymers are modeled as interpenetrating spheres with radius $r_g$ that may overlap with each other free of energy cost ($U_{pp} = 0$) but interact as hard spheres with the nanoparticles:

$$\beta U_{cp}(r) = \begin{cases} \infty & r \leq (\sigma + r_g)/2, \\ 0 & r > (\sigma + r_g)/2, \end{cases}$$

where $r$ is the distance between the centers of mass of the nanoparticle and the polymer. These AO spheres are isotropically tethered to the colloidal/nanoparticle with a grafting potential $U_g$ based on the entropic restoring force of a Gaussian chain [15]. The end-to-end probability distribution of the polymer endpoint $r$, is $P(r) \propto \exp[-3r^2/2N_b b^2]$, with $N_b$ the number of segments and $b$ the Kuhn length. This probability translates into an effective potential (free energy) $\beta F(r) = -\ln P(r) = 3r^2/2N_b b^2 + $ constant. If we assume that the center of mass of a grafted chain is halfway between its end-points, i.e., $r \approx r_g/2$ with $r$ the distance between the grafting point and the center of the AO particle, and if the chain is sufficiently long ($N_b \gg 1$), then, using $r^2 \approx N_b b^2/6$, the grafting potential takes the form

$$\beta U_g(r) \equiv (r/\lambda \sigma)^2. \quad (3)$$

Indeed, the Boltzmann distribution $P(r) \propto e^{-\beta U_g(r)}$ of this effective grafting potential results again in the end-to-midpoint distribution of a Gaussian chain. This potential effectively captures the elastic contribution to the chain entropy. We aim to show that this is sufficient in driving the anisotropic aggregation of functionalized NPs.

Denoting the positions of the $N$ nanoparticles by $\vec{R}_i$, each grafted by $f$ polymers with positions $\vec{r}_j^f$, the total energy for the system is thus,

$$U(\vec{R}^N, \vec{r}^N) = \sum_{i \neq j} U_{cc}(\vec{R}_i, \vec{R}_j) + \sum_{i,j}^f \sum_k U_{cp}((\vec{r}_{i,k} - \vec{R}_i \vec{r}_j))$$

$$+ \sum_{i}^{N} \sum_{k} U_g(\vec{R}_i - \vec{R}_i \vec{R}_j), \quad (4)$$

where $\vec{r}_{i,k}$ denotes the position of the $k$th polymer of the $i$th nanoparticle and the grafting points are given by $\vec{u}_{i,k} = M(\vec{R}_i, \lambda_i \vec{u}_k).$ Here, $M(\vec{R}_i)$ denotes the rotation matrix for the orientation $\vec{\Omega}_i$ of the $i$th nanoparticle, and $\vec{u}$ is the unit vector in the reference frame from the center of the nanoparticle to the $k$th grafting point.

In the grand-canonical ($\mu VT$) ensemble we impose the chemical potential $\mu$ of the polymer-coated particles instead of the number $N$. For low values of the functionality $f$ and polymer size $q = 2r_g/\sigma$, a grand-canonical approach will result in a bulk solid of NPs. However, the presence of the polymer matrix was shown to provide stabilization to a cluster phase for isotropic particles in the absence of highly directional interactions [16,17]. The origin of this equilibrium cluster formation was found to be a weak, long-ranged repulsion caused by chain connectivity in the polymer matrix. To prevent complete phase separation into bulk solids, and instead promote a microphase separation into an equilibrium cluster phase, we implement an additional repulsive screening Yukawa potential, mimicking long-ranged repulsive interactions:

$$\beta U_{\gamma}(r) = \begin{cases} 0 & R \leq \lambda \sigma, \\ A \xi \exp(-R/\xi) \equiv \lambda \sigma & R > \lambda \sigma, \end{cases}$$

where $A$ is the strength of repulsion and $\xi$ is its range. The motivation for this exponentially decaying function comes from theoretical work on long-ranged density correlations due to chain connectivity in the matrix [17]. This potential is added to the $U_{cc}(R)$ defined in Eq. (1). The combination of the short-ranged square-well interaction [Eq. (1)] with the long-ranged Yukawa interactions will lead to a finite thermodynamically stable cluster phase [18].

B. Simulation methods

We perform Monte Carlo simulations in the $NVT$ ensemble, employing translation moves for all particles and rotation moves for the combined nanoparticle-polymer molecule. Periodic boundary conditions apply. Due to the strong attraction the system can easily become trapped in a metastable local minimum. To enhance sampling we employ advanced cluster moves. Such cluster moves are based on a modification of the Swendsen-Wang-Wolff algorithm that extends to multiscale, self-assembling systems [19,20].

We sample the system in the $\mu VT$ ensemble using the same set of MC moves as above, to which we add an equal amount of particle insertion and deletion moves. In addition, we employed a configurational-bias algorithm to enhance the efficiency of particle insertion moves [21]. Due to the harmonic nature of the grafting potential, we can significantly speed up the insertion algorithm for growing a polymer-coated NP by drawing random numbers from a Gaussian distribution instead of generating trial positions for each of the $f$ polymers.

To avoid bulk phase separation in the grand-canonical simulations, we employed the modified AO model with the additional long-ranged repulsion. To establish the phase diagram, each system required simulating $M$ state points $(\lambda_i, \mu_i)$ ($i = 1, \ldots, M$), where $\lambda_i = \varepsilon_i / \varepsilon_0$ is a coupling parameter (not to be confused with the square-well width parameter $\lambda$) that couples the interparticle attraction strength of system $i$ to that of a reference system (system 1) through $U_i(r) = U_1(r) + \lambda_i U_{cc,i}(r)$. Here, the reference square-well potential $U_{cc,1}$ has an interaction strength of $\varepsilon_1 = 3 k_B T$. We use a coupling parameter because we do not want to change the repulsive interaction but only change the attractive strength.
Therefore, we do not alter the actual temperature but rather only the attractive part of the potential, $\varepsilon$. We obtain information on the phase boundaries by applying the multiple histogram-reweighting method [22] also known as WHAM. Histograms $f_i(N,U)$ from the $M$ simulations are rescaled using the Ferrenberg-Swendsen iterative procedure [23]:

$$\exp(-\beta F_j) = \sum_N \sum_{U_{cc,1}} \exp(-\beta \lambda_j U_{cc,1} + \beta \mu_j N) \sum_i^M f_i(N,U_{cc,1}),$$

(6)

where $F_j$ is the free energy for state point $j$, characterized by $\mu_j$ and $\lambda_j$, and $K_i$ denotes the number of histogram counts for simulation $i$. Note that due to the introduced coupling parameter, only the square well energy remains in the iterative expression above. The resulting composite probability $P(N,U)$ for arbitrary coupling parameters and chemical potentials can then be used to calculate, e.g., the expectation value $(N)$.

C. Second virial coefficient

We can roughly estimate the strength of interaction $\varepsilon$ at which the transition from monomers to finite aggregates occurs by computing the second virial coefficient for two NPs and solving for $B_2 = 0$ (assuming higher-order terms can be ignored). In Appendix A, we derive the following expression for the second virial coefficient:

$$B_2 = \frac{1}{2} \pi \lambda^3 \sigma^3 - \frac{1}{2} e^{\beta \varepsilon} W_1 + \frac{1}{2} W_2,$$

(7)

with the terms $W_1$ and $W_2$ defined as

$$W_1 = \int_{\sigma}^{\lambda \sigma} dR 4\pi R^2 \chi(R)^2,$$

$$W_2 = \int_{\sigma}^{\lambda \sigma} dR 4\pi R^2 [1 - \chi(R)^2].$$

(8)

Here, the function $\chi(R)$ can be interpreted as the probability that a NP is not shielding a NP at distance $R$ with any of its polymers (see Appendix A for a full expression). Thus, integral $W_1$ is proportional to the probability that two NPs are within interaction range and neither particles are shielding each other, and $W_2$ is proportional to the probability that the NPs are outside their interaction range and at least one is shielding the other. Once these two integrals have been calculated, we may solve $B_2 = 0$ for $\varepsilon$ and obtain an estimate of the interaction strength at which a phase transition occurs. Under the assumption that grafting points can freely move over the surface of the NP, the function $\chi(R)$ reduces to

$$\chi(R) = [\bar{\chi}(R)]^f,$$

(9)

where, setting $d = \frac{1}{2} (q + \sigma)$,

$$\bar{\chi}_1(R) = \begin{cases} 1 + \frac{\int_{d/R}^{x} dx r^2 e^{-\beta^{\varepsilon}(\sigma^2 - r^2)}}{2 \int_{d/R}^{x} dr r^2 e^{-\beta^{\varepsilon}(\sigma^2 - r^2)}} & \text{for } d \leq R < 2d, \\ 1 + \frac{\int_{d/R}^{x} dx r^2 e^{-\beta^{\varepsilon}(\sigma^2 - r^2)}}{2 \int_{d/R}^{x} dr r^2 e^{-\beta^{\varepsilon}(\sigma^2 - r^2)}} & \text{for } 2d \leq R < \infty. \end{cases}$$

(10)

FIG. 1. (Color online) In the top graph, the probability that a NP is not shielding another NP at distance $R$ with any of its $f$ polymers, $[\chi(R)]^f$, is plotted for various $f$ and $q$. In the bottom graph we plotted the interaction strengths $\varepsilon_c$ for which the virial coefficient is zero. The observed trend is that the phase boundaries saturate for large polymer sizes.

III. RESULTS AND DISCUSSION

A. Aggregation transition from $B_2$

Using Eqs. (7) and (10), we can evaluate $B_2$ for arbitrary values of the parameters $q$ and $f$. By solving $B_2 = 0$ for $\varepsilon = \varepsilon_c$, we obtain an estimate of the strength of interaction at which a phase transition occurs. Moreover, we are able to directly observe how this value changes as a function of the functionality and polymer size. In Fig. 1 we plotted $\chi(R)$ and $\varepsilon_c$ for various functionalities and polymer sizes to illustrate the effect of changing these parameters. As the polymer size is increased, the transition values appear to saturate. This effect occurs more strongly for NPs with larger functionalities. Considering that the grafting potential [Eq. (3)] is inversely proportional to $r^2$, we believe this effect is caused by large polymers stretching further from their grafting points leading to less shielding of local interaction volume.

The above analysis yields only an estimate of the transition lines. In the next section we will determine phase transitions in the NVT ensemble by means of the critical self-assembly concentration. In Sec. III C we will turn to a grand-canonical approach for a more accurate quantitative estimate of the phase boundaries.
The fraction for this system is $f$. Grafting with MC simulations in the canonical model, we studied its aggregation properties by employing the square well potential. This is equivalent to decreasing the attraction strength $\varepsilon$. Because the only energetic contribution in the model is from the potential well width, it must be taken that the grafting potential $\beta U_g(r)$ does not scale with the temperature, as it results in a purely entropic force. Experimentally, quenching can, of course, be achieved through decreasing the temperature, but, e.g., also by increasing a depletion force through higher polymer concentration. For each value of $\varepsilon$, the system is allowed to equilibrate for 15 to 25 million MC steps, depending on the functionality $f$, and we perform an additional 30 to 50 million production MC steps for the purpose of collecting data.

During the quenching procedure, the particles aggregate in clusters of different shapes depending on the parameters $q$ and $f$. In order to produce a qualitative morphology diagram, we perform structure analysis on the simulation data. For this purpose, we manually assigned a morphology characterizing the shape of the aggregates for the final output of each quenching series and analyzed the contact order histograms. This qualitative analysis yielded a wide range of morphologies: spherical, cylindrical, (interconnected) sheets/flattened, stringlike/branched, dispersions of short strings and/or small aggregates, and, lastly, fully isolated particles. The results are visualized in a morphological phase diagram (Fig. 2). Despite the highly coarse representation of polymer-coated NPs, we observed the full range of morphologies observed in the experiments in Ref. [7]. The trends in boundaries between morphologies (dashed lines) as a function of $f$ and $q$ are also found to be in qualitative agreement with both experiment and mean-field theory [7,8].

For low values of $q$, polymers are small enough to reside in the interstitial sites of spherical clusters leading to a low ground-state cluster energy with little entropic penalty on the grafted chains. Due to the finite system size, this aggregate is also finite. In principle, this would, thus, represent a bulk phase. Increasing the polymer/colloid size ratio (e.g., for $f = 6$ to $q = 0.35$) leads to the exclusion of polymers from the interstitial space, which is associated with an entropy cost, modeled by the grafting potential. Upon the exclusion, the NPs arrange first into cylindrical and 2D hexagonal sheetlike structures with stabilization energies of around $6 \varepsilon$ per particle. We did not observe a square lattice arrangement in any of our simulations. For large polymer/colloid size ratios, the relatively bulky polymers effectively shield the aggregates leading to either growth in one dimension, i.e., formation of cylindrical (diamonds), (interconnected) sheets or flattened (squares), stringlike/branched (up-pointing triangles), dispersions of short strings and/or small aggregates (empty down-pointing triangles), and fully isolated particles (filled down-pointing triangle). Morphological trends are visualized using dashed lines, and simulation snapshots are provided for all aggregate shapes (polymers are transparent for clarity). Shown at the bottom are contact order histograms for parameter coordinates $(f,q)$ that each assemble into different types of aggregates.
of stringlike structures, or dispersions of short strings and/or fully isolated particles. In Fig. 2, we show histograms of the contact order for several parameter settings, which show the distribution of the number of contacts per particle. A contact is defined as particles interact via the square well interaction. From these distributions it is clear that the stabilization energy per particle changes for each type of morphology.

To track the degree of aggregation as a function of $\varepsilon$, we computed the fraction of particles present in aggregated form $\eta$ averaged over three separate runs. The potential well depth $\varepsilon_c$ for which the critical self-assembly concentration (CSAC) is reached, i.e., $\eta = 0.5$, is shown in Fig. 3 as a function of the polymer size ratio $q$. To illustrate the dependence of the aggregation fraction on $\varepsilon$, we also plotted $\eta$ for various polymer sizes and $f = 6$. From these graphs, we again notice that $\varepsilon_c$ saturates for increasing $q$, and stronger for increasing $f$, in agreement with our theoretical analysis in Sec. II C. We believe two effects may contribute to this behavior. On the one hand, small polymers reside in the interstitial sites of crystalline structures without any substantial entropy cost, and aggregation takes place at relatively low interaction strengths. In fact, if all colloids are at their maximum interaction distance $\lambda \sigma$, for polymers with $q \lesssim 0.35$ in close-packed colloidal crystals there are no many-body interactions of order higher than two. With all colloids at minimum interaction distance, these interactions do not occur below $q \lesssim 0.15$ [24]. Therefore, between these values the many-body nature of polymer-induced interaction rises quickly, forcing the polymers out of the interstitial space. Thus, as observed, for $0.15 < q \lesssim 0.35$, $\varepsilon_c$ rises quickly with $q$. A schematic representation of this effect is shown in Fig. 4. On the other hand, large polymers can deviate further from their grafting points as the grafting potential [Eq. (3)] is inversely proportional to $r_0^2$. This reduces the shielding of the local short-ranged interaction volume and, hence, may lead to saturation of the phase transition point for NPs with bulky grafted polymers. We do note that the observed saturation effect occurs at lower $q$ than predicted in Sec. II C, which we believe is due to the fact that we only account for two-body interactions in the theoretical analysis.

The above results should only be interpreted qualitatively as, notwithstanding the long equilibration times, the actual transition point (of the model) will lie below the measured $\varepsilon_c$ due to hysteresis effects. Moreover, the CSAC is merely an estimate of the phase boundary. As is common for systems with strongly interacting particles, sampling problems and hysteresis manifest themselves around (micro-)phase transitions and impede our ability to accurately locate phase boundaries [25]. We alleviate these problems here by simulating in the grand-canonical ensemble.

C. Grand-canonical ($\mu$VT) ensemble

We performed simulations in the $\mu$VT ensemble for the modified AO model with the additional repulsive Yukawa potential [Eq. (5): $A = 1$, $\zeta = 2.25 \sigma$] for different numbers of grafted polymers $f \in \{4, 6, 8\}$ with various sizes $q \in \{0.20, 0.30, ... , 0.70\}$. Simulations are initiated at $\mu = -13$ $k_B T$ for a small cubic simulation box of size $L \approx 15.2 \sigma$. The chemical potential is slowly increased from $-13$ to $-8.5$ $k_B T$ in steps of 0.25 $k_B T$. To check for hysteresis and obtain sufficient sampling on either side of the phase transition, we subsequently decreased $\mu$ to $-13$ $k_B T$ again. We repeated this procedure for systems with interparticle

FIG. 3. Results (including error bars) from the canonical $NVT$ simulations. The transition interaction strengths $\varepsilon_c$, for which half the NPs are present in aggregates are plotted on the left for all particle types. In most cases, the error bars are smaller than the symbols. NPs with $f = 12$ and $q \gtrsim 0.35$ do not reach a phase transition below $\varepsilon = 10$ $k_B T$ and are, hence, not shown. Plotted on the right is the aggregation fraction $\eta$ as a function of $\varepsilon$ for $f = 6$ and various grafted polymer sizes.

FIG. 4. (Color online) On the left, small polymers (dashed cyan circles) reside in the interstitial space between colloids (red circles). Increasing the polymer size induces interactions that lead to exclusion of polymers from this space and hence decrease their chain entropy. This entropy penalty is captured by the grafting potential and subsequently leads to reorganization of colloids into lower dimensional morphologies to reduce this penalty at the cost of stabilization energy, e.g., from a spherical ($\sim 6 - 12 \sigma$) to hexagonal sheet ($\sim 6 \sigma$) arrangement.
attraction strengths $\epsilon_i \in \{4, 4.25, ..., 9\}$. Thus, the total number of state points sampled per particle type was $M = 720$.

Depending on the particle interaction strength, the number of particles in the simulation box varied from $N = 0$ at the lowest chemical potentials to $N \approx 200$ at the highest. At these high chemical potentials around 5 to 10 clusters usually formed. These clusters assumed a shape in accordance with the morphology diagram in Fig. 2.

To determine the location of the phase transition, we reweighted the histograms collected for all state points using WHAM and then computed the chemical potential $\mu_c$ for which the gas and cluster phases have equal pressures [26]. For this purpose, we defined a particle number $N_c$ that separates each phase and measured the area under the reweighted distribution $P(N, U)$ on either side of the phase boundary. The chemical potential that separates each phase is the one at which integration gives equal areas under the distribution.

Figure 5 depicts the phase transition lines in the $(\mu, \epsilon)$-plane for colloids with six grafted polymers of varying size $q$, as well as cluster size distributions for parameters around the phase transitions. The cluster size distributions in Figs. 5(a) and 5(b) clearly show the phase transition from an ideal gas of monomers to a cluster phase. Beyond the phase transition, we always observe several finite-size clusters in the simulation box, driven by the long-ranged repulsion between particles [18]. In the phase diagram in Fig. 5(c), for NPs with six grafted polymers the transition lines show that the chemical potentials required for inducing this phase transition decreases with the potential well depth, as is expected. Up to $q = 0.50$, increasing the polymer size leads to higher values for $\mu_c$ and $\epsilon_i$. In support of our findings in the previous sections, a saturation effect sets in at $q = 0.50$ and the transition lines are largely unchanged.

From Fig. 5(d), we notice the same effect but to a much lesser extent for $f = 4$, in agreement with the NVT data in Fig. 3 and the results in Sec. II C, that saturation effects are weaker for lower functionalities. Last, we note that the saturation effects occur for slightly lower $q$ compared to the NVT data in Fig. 3, which we can attribute to the presence of the repulsive Yukawa potential.

While one should ensure that these results hold in the limit of infinite system size [27], we have not investigated such finite-size scaling. The box size we employed here allowed shorter equilibration times and more accurate results over a broad range of reduced temperatures.

IV. CONCLUSION

In summary, we have presented a simple model for NPs isotropically grafted with AO particles. The entropy loss of tethered polymers during self-assembly drives the formation of a range of interesting anisotropic aggregates and allows one to tailor nanocomposites with distinct physical features.

We model the elasticity of the polymer brush using a harmonic grafting potential based on the entropic restoring force of a Gaussian chain. In spite of the coarse nature of the model, the resulting morphological phase diagram is in qualitative agreement with previous experimental and theoretical work, as well as trends in the morphological phase transitions. While our simple model cannot account for the effect of the polymer matrix mixing entropy on the wet-to-dry transition in the grafted chain brush, it can qualitatively reproduce the experimentally observed morphological behavior. A more complex model might be devised that includes the mixing entropy effect, but this is outside the scope of this work.
Quantitative analysis of both the canonical and grand-canonical simulations data, as well as the second virial coefficient, point to a saturation effect of the phase transition lines as a function of polymer size $q$. While this could be an artifact of the simple model, we notice that in polymer colloid mixtures the AO model is qualitatively correct for $q \lesssim 0.7$ [13, 14]. For $q \lesssim 0.35$, we attribute this saturation effect to polymer-induced many-body interactions, which lead to exclusion from the interstitial space in a colloid crystal. The associated entropy penalty is then reduced at the cost of stabilization energy, leading to lower-dimensional morphologies as the new equilibrium structure. Large polymers, on the other hand, may lead to reduced shielding of the short-ranged interactions between colloids and further saturation of the phase transition lines.

Our modified AO model reproduces the key qualitative features of anisotropic self-assembly containing only the bare essential physics and should, in principle, also apply to other polymer-coated particle systems. Due to its simplicity and a fast evaluation of the configurational-bias algorithm, it lends itself well to studies of phase behavior on much larger time and length scales.

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**APPENDIX: DERIVATION OF THE SECOND VIRIAL COEFFICIENT**

The second virial coefficient $B_2$ is defined as

$$B_2 = 2\pi \int dRR^2 \left[ 1 - e^{-\beta U_{\text{eff}}(R)} \right],$$

where the isotropic effective interaction $U_{\text{eff}}(R)$ is obtained by integrating over the orientation $\vec{\Omega}_1$ and $\vec{\Omega}_2$ of nanoparticles 1 and 2, respectively, and the coordinates $\vec{r}_1^f$ and $\vec{r}_2^f$ of the $f$ functionalized polymers, yielding:

$$e^{-\beta U_{\text{eff}}(R)} = e^{-\beta U_{\text{eff}}(R)} \int d\vec{\Omega}_1 d\vec{\Omega}_2 d\vec{r}_1^f d\vec{r}_2^f P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_1^f, \vec{r}_2^f ; R) \times e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_i)}.$$  

(A2)

where we have chosen the reference frame such that $\vec{R}_1$ is at the origin and $\vec{R}_2 = \{R, 0, 0\}$. In order to correctly account for the movement of polymers, we weight the integrand in Eq. (A2) with the normalized Boltzmann factor associated with each set of coordinates $\vec{r}_1^f$ and $\vec{r}_2^f$:

$$P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_1^f, \vec{r}_2^f ; R) = \frac{e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_i)+U_{\text{cp}}(\vec{r}_1 - \vec{R}_1)+U_{\text{cp}}(\vec{r}_2 - \vec{R}_2)}}{\int d\vec{\Omega}_1 d\vec{\Omega}_2 d\vec{r}_1^f d\vec{r}_2^f e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_1 - \vec{R}_1)+U_{\text{cp}}(\vec{r}_2 - \vec{R}_2)}}.$$  

(A3)

Because the energies are separable, we can factorize this probability into

$$P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_1^f, \vec{r}_2^f ; R) = P(\vec{\Omega}_2, \vec{r}_2^f ; R) P(\vec{\Omega}_1, \vec{r}_1^f),$$

(A4)

with

$$P(\vec{\Omega}_2, \vec{r}_2^f ; R) = \frac{e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_2)}}{\int d\vec{\Omega}_2 d\vec{r}_2^f e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_2)}}$$

(A5)

and

$$P(\vec{\Omega}_1, \vec{r}_1^f) = \frac{e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_1)}}{\int d\vec{\Omega}_1 d\vec{r}_1^f e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_1)}}.$$  

(A6)

Inserting this into the effective potential yields

$$e^{-\beta U_{\text{eff}}(R)} = e^{-\beta U_{\text{eff}}(R)} \times \int d\vec{\Omega}_1 d\vec{r}_1^f P(\vec{\Omega}_1, \vec{r}_1^f) e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_1)}$$

$$\times \int d\vec{\Omega}_2 d\vec{r}_2^f P(\vec{\Omega}_2, \vec{r}_2^f ; R) e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_2)},$$

(A7)

We can define the integrals

$$\chi_1(R) = \int d\vec{\Omega}_1 d\vec{r}_1^f P(\vec{\Omega}_1, \vec{r}_1^f) e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_1)},$$

(A8)

and

$$\chi_2(R) = \int d\vec{\Omega}_2 d\vec{r}_2^f P(\vec{\Omega}_2, \vec{r}_2^f ; R) e^{-\beta \sum_i U_{\text{cp}}(\vec{r}_i - \vec{R}_2)}.$$  

(A9)

Because of symmetry, the two integrals $\chi_1(R) = \chi_2(R)$ are identical. Note that $U_{\text{cp}}$ may take only one of two values: $e^{-\beta R} = 0$ if a polymer overlaps with the nanoparticle and $e^{-\beta R} = 1$ if there is no overlap. Therefore, $\chi(R)$ can be interpreted as the probability that a NP is not excluding or “shielding” a NP at distance $R$ with any of its polymers.

We can now write the expression for $B_2$ as

$$B_2 = 2\pi \int dRR^2 \left[ 1 - e^{-\beta U_{\text{eff}}(R)} \chi(R)^2 \right].$$

(A10)

Due to the discreteness of the square well potential $U_{\text{sw}}(R)$, the above expression can be evaluated by splitting the integral in Eq. (A10) into three intervals for the center-center distance between the two particles: $0 \leq R < \sigma$, $\sigma \leq R < \lambda \sigma$, and $\lambda \sigma \leq R < \infty$. This results in

$$B_2 = \frac{1}{2} \int_0^\sigma dR 4\pi R^2 \left[ e^{\beta \chi} \right] + \frac{1}{2} \int_\sigma^{\lambda \sigma} dR 4\pi R^2 \left[ 1 - e^{\beta \chi} \right] + \frac{1}{2} \int^{\infty}_{\lambda \sigma} dR 4\pi R^2 \left[ 1 - \chi(R)^2 \right]$$

$$= 2\pi \int_0^\sigma dR R^2 - \frac{1}{2} e^{\beta \chi} \int_\sigma^{\lambda \sigma} dR 4\pi R^2 \chi(R)^2 + \frac{1}{2} \int_{\lambda \sigma}^{\infty} dR 4\pi R^2 \left[ 1 - \chi(R)^2 \right]$$

$$= 2\pi \frac{\lambda \sigma^3}{3} - \frac{1}{2} e^{\beta \chi} W_1 + \frac{1}{2} W_2,$$

(A11)

where the integral $W_1$ is proportional to the probability that two NPs are within interaction range and neither particles are
shielding each other, and $W_2$ is proportional to the probability that the NPs are outside their interaction range and at least one is shielding the other. Once these integrals have been calculated, we may solve for $B_2$ and obtain an estimate of the interaction strength at which a phase transition occurs.

While this expression of $B_2$ is the correct one to evaluate, the integral over all orientations in $\chi(R)$ makes it rather difficult. Therefore, due to the isotropic nature of the nanoparticles, we will assume that the grafting points $\mathbf{u}_{k,i}$ are free to move around on the surface of the NP at a distance $\sigma/2$. The Boltzmann weights are now no longer orientation-dependent and simplify to

$$P(\mathbf{r}_1^f) = \frac{e^{-\beta \sum_1^K U_j(\mathbf{r}_1^f)} \beta U_0^f}{\int d\mathbf{r}_1^f e^{-\beta \sum_1^K U_j(\mathbf{r}_1^f)}} \quad (A12)$$

and

$$P(\mathbf{r}_1^f;R) = \frac{e^{-\beta \sum_1^K U_j(\mathbf{r}_1^f) - \sigma/2}}{\int d\mathbf{r}_1^f e^{-\beta \sum_1^K U_j(\mathbf{r}_1^f) - \sigma/2}}. \quad (A13)$$

Again, due to symmetry, these weights lead to a single expression for $\chi(R)$:

$$\chi(R) = \int d\mathbf{r}_1^f P(\mathbf{r}_1^f) e^{-\beta U_0^f(\mathbf{r}_1^f - \mathbf{R}_1)}$$

$$= \left[ \int d\mathbf{r}_1^f P(\mathbf{r}_1^f) e^{-\beta U_0^f(\mathbf{r}_1^f - \mathbf{R}_1)} \right]^f = \chi_1(R)^f, \quad (A14)$$

where

$$\chi_1(R) = \int d\mathbf{r}_1^f P(\mathbf{r}_1^f) e^{-\beta U_0^f(\mathbf{r}_1^f - \mathbf{R}_1)}.$$

Because the integral in this expression defines a probability, we can generalize the outcome for a system with $f = 1$ to larger functionalities by simply raising to the power $f$. To evaluate this integral, we switch to polar coordinates, i.e., $\mathbf{r}_1 = \{r, \theta, \phi\}$:

$$\chi_1(R) = \frac{\int dr d\phi d\theta r^2 \sin \theta e^{-\beta U_0^f(r - \sigma/2)} \chi_1(R)}{\int dr d\phi d\theta r^2 \sin \theta e^{-\beta U_0^f(r - \sigma/2)}}. \quad (A16)$$

Again, we can make use of $e^{-\beta U_0^f}$ taking one of two values: 0 if there is overlap and 1 if there is none. Therefore, integration over all polymer coordinate angles $\phi$ and $\theta$ in the numerator yields the available surface fraction $p_{av}$ for the polymer at a distance $r$ to the NP. Thus

$$\chi_1(R) = \frac{\int dr d\phi d\theta r^2 e^{-\beta U_0^f(r - \sigma/2)} p_{av}(R,r)}{\int dr d\phi d\theta r^2 e^{-\beta U_0^f(r - \sigma/2)}}. \quad (A17)$$

The available surface fraction for a polymer at distance $r$, while the NP is at a distance $R$, is given by

$$p_{av}(R,r) = \frac{1}{2}(1 + \cos \alpha), \quad \quad (A18)$$

where $\alpha$ is the minimum allowed angle between the position of the polymer and the x axis (see Fig. 6 for a cartoon). For the interval $\{R - d \leq r \leq R + d\}$, where $d = \frac{1}{2}(q + \sigma)$, this angle is given by the straightforward trigonometric relation

$$\cos \alpha = \frac{R^2 + r^2 - d^2}{2rR}. \quad \quad (A19)$$

Outside this interval, $p_{av} = 1$. Note that the distance $r$ is also bounded from below: $r \geq d$. The expression for $\chi_1(R)$ is thus the following piece-wise function:

$$\chi_1(R) = \begin{cases} 
1 + \frac{\int_{d}^{R-d} dr \sin \theta e^{-\beta U_0^f(r - \sigma/2)} \left( \frac{2\beta U_0^f}{2\beta U_0^f + \sigma} - 1 \right)}{2 \int_{d}^{R-d} dr \sin \theta e^{-\beta U_0^f(r - \sigma/2)}} & \text{for} \quad d \leq R < 2d, \\
1 + \frac{\int_{d}^{R-d} dr \sin \theta e^{-\beta U_0^f(r - \sigma/2)} \left( \frac{2\beta U_0^f}{2\beta U_0^f + \sigma} - 1 \right)}{2 \int_{d}^{R-d} dr \sin \theta e^{-\beta U_0^f(r - \sigma/2)}} & \text{for} \quad 2d \leq R < \infty,
\end{cases} \quad (A20)$$

which is Eq. (10) in the main text.