Self-assembly of functionalized colloids and short amyloidogenic peptides: Modelling, theory and simulations
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Chapter 3

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

In this chapter 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, which is described in detail in Section 2.1, enables large-scale particle-based simulations of self-assembly of polymer-coated particles.

3.1 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 impact on the properties of the composite material. The contents of this chapter have been published:
influence on macroscopic physical properties such as toughness, stiffness, permeability, electrical conductivity, flammability and many more [10]. 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 [8, 11–13]. 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 [14]. 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 [9]. The formation of these structures, ranging from finite size clusters or networks of percolating sheets to dispersions of isolated particles, is driven by micro-phase separation of the grafted polystyrene chains and the inorganic colloids, which in turn is governed by a competition between the short-ranged inter-particle 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, 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 [9, 15].

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 [9, 123, 124], 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 [50, 51]. While for polymer solutions in a good solvent the polymers behave non-ideally, the
concept of non-interacting ideal polymers has been used successfully to de-
scribe, at least qualitatively, phase separation in colloid polymer mixtures
[125, 126]. In the standard AO model the colloids are hard spheres, while
the polymers chains are hard spheres that do not interact with other poly-
mers, 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 two fold: 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 poly-
mers, and 2) gain insight in the physical mechanism of the self-assembly
process, and explain qualitatively the observed structures.

The chapter is organized as follows. In the Methods section we explain
the simulation techniques and the second virial theory. In Sec. 3.3 we
first discuss the estimated aggregation transition dependence based on the
second virial coefficient analysis. We refer to Sec. 2.1 for a description of the
model. 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.

3.2 Methods

3.2.1 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 meta-
stable 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 multi-scale, self-assembling systems
[75, 127].

We sample the system in the µVT ensemble using the same set of
MC moves as above, to which we add an equal amount of particle in-
sertion/deletion moves. In addition, we employed a configurational-bias
algorithm to enhance the efficiency of particle insertion moves [71]. 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 $\lambda_i = \varepsilon_i / \varepsilon_1$ 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 $U_i(r) = U_Y(r) + \lambda_i U_{cc,1}(r)$. 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 [89] also known as WHAM. Histograms $f_i(N, U)$ from the $M$ simulations are rescaled using the Ferrenberg-Swendsen iterative procedure [90]:

$$\exp(-\beta F_j) = \sum_N \sum_{U_{cc,1}} \exp(-\beta \lambda_j U_{cc,1} + \beta \mu_j N) \sum_i K_i \exp(-\beta \lambda_i U_{cc,1} + \beta \mu_i N + \beta F_i),$$

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 $\langle N \rangle$.

### 3.2.2 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:

$$B_2 = \frac{2}{3} \pi \lambda^3 \sigma^3 - \frac{1}{2} \varepsilon \lambda \chi(R) R^2 + \frac{1}{2} W_2$$

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

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

$$W_2 = \int_{R_\lambda}^{R_\infty} dR 4 \pi R^2 \left(1 - \chi(R)^2\right).$$
Here, the function $\chi(R)$ can be interpreted as the probability that a NP is \textit{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

$$\chi(R) = [\chi_1(R)]^f$$

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

$$\chi_1(R) = \begin{cases} 
1 + \left( \frac{1}{d} \int_{R-d}^{R+d} dr^2 e^{-\beta U_g(r-\sigma/2)} \left( \frac{R^2 + r^2 - d^2}{2rR} \right) \right) 
\quad \text{for} \quad \sigma \leq R < 2d, \\
1 + \left( \frac{1}{d} \int_{R-d}^{R-d} dr^2 e^{-\beta U_g(r-\sigma/2)} \left( \frac{R^2 + r^2 - d^2}{2rR} \right) \right) 
\quad \text{for} \quad 2d \leq R < \infty.
\end{cases}$$

3.3 Results and Discussion

3.3.1 Aggregation transition from $B_2$

Using equations 3.2 and 3.5, 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. 3.1 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. 2.3) is inversely proportional to $r_g^2$, 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. 3.3.3 we will turn
Figure 3.1: In the top graph the probability that a NP is not shielding another NP at distance $R$ with any of its $f$ polymers, $[\chi_1(R)]^f$, 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.

3.3.2 Canonical (NVT) ensemble

In order to gain insight in the aggregation behavior of our model, we studied its aggregation properties by employing MC simulations in the canonical (NVT) ensemble. The cubic simulation box of length $L \approx 47.1\sigma$ contains 200 NPs, each grafted with $f \in \{4, 6, 8, 12\}$ polymers of size $q = 2r_g/\sigma \in \{0.20, 0.25, ..., 0.70\}$. The overall colloid/nanoparticle packing fraction for this system is $\phi_c = N \pi (\sigma/L)^3 / 6 = 0.001$. We run three separate simulations for each particle type and results will be averaged over these runs.
To investigate the aggregation behavior we increase the attraction strength $\varepsilon$ in steps of 0.5 $k_B T$ from 3 to 10 $k_B T$, while the potential well width is kept constant at $\lambda = 1.15$. Because the only energetic contribution in the model is from the square well potential this is equivalent to decreasing the temperature. (We note that in case the temperature would be changed, care 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 shape 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. 3.2). Despite the highly coarse representation of polymer-coated NPs, we observed the full range of morphologies observed in experiments in Ref. [9]. 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 [9, 15].

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 stringlike structures, or dispersions of short strings and/or fully isolated particles. In Fig. 3.2 we show histograms of the contact order for several
Figure 3.2: Morphological phase diagram of the output structures from the NVT simulations. We identified spherical (circles), cylindrical (diamonds), (interconnected) sheets/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.
Figure 3.3: 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 $q \geq 0.35$ 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.

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 3 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. 3.3 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. 3.2.2. 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 $q \lesssim 0.15$ [128]. 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
Figure 3.4: 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 (\( \sim 6 - 12\varepsilon \)) to hexagonal sheet (\( \sim 6\varepsilon \)) arrangement.

in Fig. 3.4. On the other hand, large polymers can deviate further from their grafting points as the grafting potential (Eq. 2.3) is inversely proportional to \( r_g^2 \). 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. 3.2.2, 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 [105]. We alleviate these problems here by simulating in the grand-canonical ensemble.

### 3.3.3 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. 2.5: \( A = 1, \zeta = 2.25\sigma \)) for different numbers of grafted polymers \( f \in \{4,6,8\} \) with various sizes \( q \in \{0.20,0.30,\ldots,0.70\} \). 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 attraction strengths $\varepsilon_i \in \{4, 4.25, ..., 9\}$. 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 $N \sim 200$ 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. 3.2.

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 [104]. 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.

Fig. 3.5 depicts the phase transition lines in the $(\mu,\varepsilon)$-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 Fig. 3.5a and 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 sized clusters in the simulation box, driven by the long-ranged repulsion between particles [55]. In the phase diagram in Fig. 3.5c 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 $\varepsilon_c$. 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. 3.5d we notice the same effect but to a much lesser extent for $f = 4$, in agreement with the NVT data in Fig. 3.3 and the results in Sec. 3.2.2 that saturation effects are weaker for lower functionalities. Lastly, we also note that the saturation effects occur for slightly lower $q$ compared to the NVT data in Fig. 3.3, 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 [129], 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.
Figure 3.5: Shown at the top are plots of the average number of clusters of size $n$ for NP type $(4, 0.40)$ for $\mu = -8.5 \, k_B T$ and increasing $\epsilon$ (a), and the same plot but then for fixed $\epsilon = 6.75 \, k_B T$ with increasing $\mu$ (b). Here we observe the formation of finite clusters due to the added long-range repulsion, thus preventing the formation of a bulk phase. Phase transition lines for colloids with $f = 6$ and $q \in \{0.2, 0.3, ..., 0.7\}$ (c) and transition points for $\mu = -8.5 \, k_B T$ and $f \in \{4, 6, 8\}$ (d) are shown at the bottom.

3.4 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 \( q \leq 0.7 \) [125, 126]. 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 extend further from their grafting points due to the grafting potential being inversely proportional to \( r_g^2 \). This 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.

A Derivation of the second virial coefficient

The second virial coefficient \( B_2 \) is defined as

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

(3.6)

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 \( \vec{r}_f^1 \) and \( \vec{r}_f^2 \) of the \( f \) functionalized polymers, yielding:

\[
e^{-\beta U_{\text{eff}}(R)} = e^{-\beta U_{\text{cc}}(R)} \int d\vec{\Omega}_1 d\vec{\Omega}_2 d\vec{r}_f^1 d\vec{r}_f^2 \times P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_f^1, \vec{r}_f^2; R) e^{-\beta \sum_i \left[ U_{\text{cp}}(|\vec{r}_1,i - \vec{u}_1,i|) + U_{\text{cp}}(|\vec{r}_2,i - \vec{R}_2 - \vec{u}_2,i|) \right]},
\]

(3.7)

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. 3.7 with the normalized Boltzmann factor associated with each set of coordinates \( \vec{r}_f^1 \) and \( \vec{r}_f^2 \):

\[
P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_f^1, \vec{r}_f^2; R) =
\]

\[
e^{-\beta \sum_i \left( U_g(|\vec{r}_1,i - \vec{u}_1,i|) + U_g(|\vec{r}_2,i - \vec{R}_2 - \vec{u}_2,i|) \right)}
\]

(3.8)

\[
\int d\vec{\Omega}_1 d\vec{\Omega}_2 d\vec{r}_f^1 d\vec{r}_f^2 e^{-\beta \sum_i \left( U_g(|\vec{r}_1,i - \vec{u}_1,i|) + U_g(|\vec{r}_2,i - \vec{R}_2 - \vec{u}_2,i|) \right)}.
\]
Because the energies are separable we can factorize this probability into

\[ P(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}_1^f, \vec{r}_2^f; R) = P(\vec{\Omega}_2, \vec{r}_2^f; R)P(\vec{\Omega}_1, \vec{r}_1^f) \] (3.9)

with

\[ P(\vec{\Omega}_2, \vec{r}_2^f; R) = \frac{e^{-\beta \sum_i^f U_g(|\vec{r}_2, i - \vec{R}_2 - \vec{u}_2, i|)}}{\int d\vec{\Omega}_2 d\vec{r}_2^f e^{-\beta \sum_i^f U_g(|\vec{r}_2, i - \vec{R}_2 - \vec{u}_2, i|)}} \] (3.10)

and

\[ P(\vec{\Omega}_1, \vec{r}_1^f) = \frac{e^{-\beta \sum_i^f U_g(|\vec{r}_1, i - \vec{u}_1, i|)}}{\int d\vec{\Omega}_1 d\vec{r}_1^f e^{-\beta \sum_i^f U_g(|\vec{r}_1, i - \vec{u}_1, i|)}}. \] (3.11)

Inserting this into the effective potential yields

\[ e^{-\beta U_{\text{eff}}(R)} = e^{-\beta U_{\text{cc}}(R)} \times \int d\vec{\Omega}_1 d\vec{r}_1^f P(\vec{\Omega}_1, \vec{r}_1^f) e^{-\beta \sum_i^f U_{\text{cp}}(|\vec{r}_1, i - \vec{R}_2|)} \times \int d\vec{\Omega}_2 d\vec{r}_2^f P(\vec{\Omega}_2, \vec{r}_2^f; R) e^{-\beta \sum_i^f U_{\text{cp}}(|\vec{r}_2, i|)}. \] (3.12)

We can define the integrals

\[ \chi_1(R) = \int d\vec{\Omega}_1 d\vec{r}_1^f P(\vec{\Omega}_1, \vec{r}_1^f) e^{-\beta \sum_i^f U_{\text{cp}}(|\vec{r}_1, i - \vec{R}_2|)} \] (3.13)

and

\[ \chi_2(R) = \int d\vec{\Omega}_2 d\vec{r}_2^f P(\vec{\Omega}_2, \vec{r}_2^f; R) e^{-\beta \sum_i^f U_{\text{cp}}(|\vec{r}_2, i|)}. \] (3.14)

Because of symmetry, the two integrals \( \chi_1(R) = \chi_2(R) \equiv \chi(R) \) are identical. Note that \( U_{\text{cp}} \) may take only one of two values: \( e^{-\beta \infty} = 0 \) if a polymer overlaps with the nanoparticle and \( e^{-\beta 0} = 1 \) 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

\[ B_2 = 2\pi \int dRR^2 \left( 1 - e^{-\beta U_{\text{cc}}(R)} \chi(R) \right)^2. \] (3.15)

Due to the discreteness of the square well potential \( U_{\text{cc}}(R) \), the above expression can be evaluated by splitting the integral in Eq. 3.15 into three intervals for the center-center distance between the two particles:
\{0 \leq R < \sigma\}, \{\sigma \leq R < \lambda \sigma\}, \text{and} \{\lambda \sigma \leq R < \infty\}. \text{This results in}

\[
B_2 = \frac{1}{2} \int_0^\sigma dR 4\pi R^2 + \frac{1}{2} \int_\sigma^{\lambda \sigma} dR 4\pi R^2 \left(1 - e^{\beta \varepsilon} \chi(R)^2\right)
+ \frac{1}{2} \int_{\lambda \sigma}^{\infty} dR 4\pi R^2 \left(1 - \chi(R)^2\right)
= 2\pi \int_0^{\lambda \sigma} dRR^2 - \frac{1}{2} e^{\beta \varepsilon} \int_\sigma^{\lambda \sigma} dR 4\pi R^2 \chi(R)^2 + \frac{1}{2} \int_{\lambda \sigma}^{\infty} dR 4\pi R^2 \left(1 - \chi(R)^2\right)
= \frac{2}{3} \pi \lambda^3 \sigma^3 - \frac{1}{2} e^{\beta \varepsilon} W_1 + \frac{1}{2} W_2
\]  

(3.16)

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 \(B_2 = 0\) for \(\varepsilon\) 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 \(\vec{u}_{k,i}\) 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

![Figure 3.6: Snapshot of two nearby NPs with \(f = 1\). The bottom right polymer is bound to the left NP at a distance \(r\), with the other NP at distance \(R\). Here, the presence of the right NP is excluding a fraction \(1 - p_{av}\) of the surface with radius \(r\) around the left NP, in which the polymer can then not move.](image)
simplify to
\[ P(\vec{r}_f^1) = \frac{e^{-\beta \sum_i U_g(|\vec{r}_{1,i}|-\sigma/2)}}{\int d\vec{r}_f^1 e^{-\beta \sum_i U_g(|\vec{r}_{1,i}|-\sigma/2)}} \]
(3.17)
and
\[ P(\vec{r}_f^2; R) = \frac{e^{-\beta \sum_i U_g(|\vec{r}_{2,i}-\vec{R}_2|-\sigma/2)}}{\int d\vec{r}_f^2 e^{-\beta \sum_i U_g(|\vec{r}_{2,i}-\vec{R}_2|-\sigma/2)}}. \]
(3.18)
Again, due to symmetry these weights lead to a single expression for \( \chi(R) \):
\[ \chi(R) = \int d\vec{r}_f^1 P(\vec{r}_f^1) e^{-\beta U_{cp}(|\vec{r}_f^1| - \vec{R}_2|)} \]
(3.19)
\[ = \left[ \int d\vec{r}_1 P(\vec{r}_1) e^{-\beta U_{cp}(|\vec{r}_1| - \vec{R}_2|)} \right]^f = [\chi_1(R)]^f \]
where
\[ \chi_1(R) = \int d\vec{r}_1 P(\vec{r}_1) e^{-\beta U_{cp}(|\vec{r}_1| - \vec{R}_2|)}. \]
(3.20)
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, \( i.e. \vec{r}_1 = (r,\theta,\phi) \):
\[ \chi_1(R) = \int d\vec{r}_1 P(\vec{r}_1) e^{-\beta U_{cp}(|\vec{r}_1| - \vec{R}_2|)} \]
(3.21)
Again, we can make use of \( e^{-\beta U_{cp}} \) 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
\[ \chi_1(R) = \frac{\int dr d\phi d\theta r^2 \sin \theta e^{-\beta U_g(r|\vec{r}_1| - \vec{R}_2|) - \beta U_{cp}(|\vec{r}_1| - \vec{R}_2|)}}{\int dr d\phi d\theta r^2 \sin \theta e^{-\beta U_g(r|\vec{r}_1| - \vec{R}_2|)}}. \]
(3.22)
The available surface fraction for a polymer at distance \( r \), while the NP is at a distance \( R \), is given by
\[ p_{av}(R,r) = \frac{1}{2} (1 + \cos \alpha) \]
(3.23)
where \( \alpha \) is the minimum allowed angle between the position of the polymer and the \( x \)-axis (see Fig. 3.6 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
\[ \cos \alpha = \frac{R^2 + r^2 - d^2}{2rr}. \]
(3.24)
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:

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

(3.25)

which is Eq. 3.5 in the main text.