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Effect of the Number and Placement of Polymer Tethers on the Structure of Concentrated Solutions and Melts of Hybrid Nanoparticles

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We have generalized and applied the microscopic polymer reference interaction site model theory to study intermolecular pair correlation functions and collective structure factors of concentrated solutions and melts of spherical nanoparticles carrying one, two, or four tethered polymer chains. A complex interplay of entropy (translational, conformational, and packing) and enthalpy (particle−particle attraction) leads to different structural arrangements with distinctive small- and wide-angle scattering signatures. Strong concentration fluctuations indicative of aggregate formation and/or a tendency for microphase separation occur as the total packing fraction or/and particle−particle attraction strength increase. In analogy with block copolymers, the microphase spinodal curve is estimated by extrapolation of the inverse of the amplitude of the small-angle scattering peak. As the number of tethered chains on nanoparticles increases, the microphase separation boundary spinodal occurs at higher particle−particle attraction strength or lower temperature. For nanoparticles with two tethers, increasing the angle between the attached chains shifts the microphase spinodal to lower temperatures. For nanoparticles with four tethers, the structural correlations are insensitive to various symmetric placements. The tendency for microphase transition is enhanced upon asymmetrically placing all four tethers on one side of the particle due to the high anisotropy of steric hindrance.

I. Introduction

Polymer-tethered nanoparticles are a novel class of nanoscale building blocks that can self-assemble into distinct nanostructures such as sheets, wires, and cylinders, with potential applications in photonics and electronics,1 energy storage,2 chemical and biological sensors,3,4 and drug delivery.5,6 Experimentalists have grafted nanometer and micrometer-sized particles with a controlled number of synthetic polymer7−10 or biopolymer11−16 (DNA and proteins) tethers and created hybrid nanoscale materials, such as tethered CdTe quantum dots,8,10 nm gold nanocrystals with grafted oligonucleotides,14 polyethylene oxide (PEO) end-capped with a 1 nm hydrophobic C60 fullerene,9,10 gold nanoparticles with a single tethered PEO chain,15 and PEO-tethered polyhedral oligomeric silsesquioxanes.18 Computer simulations19−30 and coarse-grained theory31,32 have been employed to investigate the assembly of these hybrid tethered particles under a variety of thermal, solvent, and concentration conditions.

We recently33 generalized and applied the microscopic polymer reference interaction site model (PRISM) theory34−37 to study dense solutions and melts of spherical nanoparticles grafted with a single, flexible polymer chain. The role of tether length, particle size, total packing fraction, and particle−particle attraction strength on the real space statistical structure and scattering

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patterns, and the tendency toward microphase separation, was systematically studied. Despite the seeming simplicity of the one tether plus sticky nanoparticle system, a rich physics emerged due to competing entropic and enthalpic effects and asymmetric excluded volume interactions. Strong concentration fluctuations indicative of aggregate formation and/or a tendency for microphase separation occur with increasing total packing fraction and/or particle—particle attraction strength. In analogy with block copolymers, a microphase spinodal curve was deduced by extrapolation of the inverse of the amplitude of the small-angle scattering peak. For nanoparticles with a diameter twice that of the monomer, the microphase spinodal temperature is predicted to grow roughly as a power law function of packing fraction with an exponent much lower than unity. We compared our microphase spinodal calculations with a recent simulation of the phase behavior of single-tethered spherical nanoparticles by Glotzer and co-workers and found the agreement to be surprisingly good. Upon increasing the nanoparticle diameter, the microphase spinodal temperature decreases and its packing fraction dependence qualitatively changes due to the competition between an increased tendency for macrophase separation and a decreased driving force for tether-induced microphase ordering.

In this work, our theory is significantly extended to study multi-tethered spherical nanoparticles. A primary goal is to explore the role of the number of tethers and their variable placement on the nanoparticle spatial organization and aggregation. As the number of tethered chains on nanoparticles increases, the microphase separation spinodal boundary shifts to higher particle—particle attraction strength or lower temperature. For nanoparticles with two tethers, increasing the angle between the chains lowers the microphase spinodal temperatures. For nanoparticles with four tethers, the structure factors and pair correlation functions are insensitive to varying symmetric placement of the chains, although minor changes of the microphase separation temperature do occur for asymmetric placement of the tethers.

In section II, we discuss the model and theory used in this work. Section III briefly considers athermal systems controlled entirely by entropy. Section IV studies the structure of thermal systems of attractive nanoparticles and the tendency for microphase separation as a function of temperature, packing fraction, and number of tethers. In section V, a detailed examination of the effect of placement of two and four tethers on the microphase spinodal temperatures is presented. The paper concludes in section VI with a discussion and future outlook. The Appendix collects mathematical formulas for the intramolecular structure factors of the tethered particles.

II. Model and Theory

A. Model and Interaction Potentials. The polymers are treated as freely jointed chains (FJC) of N spherical interaction sites (monomers) of diameter d connected by a rigid bond of length l = 1.4d (a typical persistence length), where d = 1 is the unit of length used throughout the paper. The FJC tethers are grafted on nanoparticles which are modeled as rigid spheres of diameter D = 2R. A schematic is shown in Figure 1. The total fluid packing fraction is η.

The pair decomposable spherically symmetric interactions between monomers, U_{pp}, and monomers and particles, U_{pc}, are hard core. The potential between hard nanoparticles, U_{cc}, is taken beyond contact to be the attractive branch of the colloid Lennard-Jones (CLJ) potential. The CLJ potential describes the interaction between two nanospheres as a pairwise sum over LJ potentials between elementary units of size b. The inclusion of the repulsive portion of the LJ potential avoids any unphysical divergence of the attractive interactions when the two particles are in contact. An example of the attractive branch of the CLJ potential for D/b = 2 was shown in our previous work, the strength of which is characterized by its absolute value at contact, ε_{cc}. This highly variable attraction is typically of van der Waals origin due to the dielectric constant contrast between the nanoparticle core and the (typically) hydrocarbon tethers and/or solvent. For inorganic or metallic cores, one can have −ε_{cc} much larger than the thermal energy.

B. Polymer Reference Interaction Site Model Theory. PRISM theory describes well the structure of both suspensions and dense melts composed of hard spherical particles and linear chains. The theory consists of a matrix of Ornstein—Zernike-like or Chandler-Anderson integral equations that relate the total site—site intermolecular pair correlation function, g(r) = g_{ij}(r) − 1, to the intermolecular direct correlation function, C_{ij}(r), and intramolecular probability distribution functions, ω_{ij}(r). For a one-component system composed of molecules of an arbitrary number of symmetric inequivalent sites, the matrix PRISM equations in Fourier space are

\[ H(k) = \sum_{\omega} \left( \Omega(k) C(k) \Omega(k) \right) + H(k) \]

\[ H_{ij}(k) = \rho \sum_{\omega} \sum_{\alpha=1}^{N_i} \sum_{\beta=1}^{N_j} \omega_{\alpha\beta}(k) \]

\[ \Omega_{ij}(k) = \rho \sum_{\omega} \sum_{\alpha=1}^{N_i} \sum_{\beta=1}^{N_j} \omega_{\alpha\beta}(k) \]

Here, i and j are two types of interaction sites on the molecule, N_i is the number of interaction sites of type i in a molecule, ρ_i the corresponding total site density, and ρ the molecular number density. We ignore (preaverage) chain end effects as in prior applications of PRISM theory to homopolymers, and block copolymers. Hence, our tethered nanoparticle system contains only two types of sites, monomer (subscript p) and nanoparticles (subscript c). The solvent is considered only implicitly via the interaction potentials associated with the polymers and nanoparticles. Explicit equations for the total intermolecular pair correlation functions, h_{ij}(r), and partial collective structure factors, S_{ij}(k), in Fourier space are given in ref 36.

The intramolecular structure factors for a nanoparticle (1 site of type c) with c/p polymer tethers, each of degree of polymerization N_c, with a total of f_c + 1 sites are

\[ \omega_{cc}(k) = 1 \]

\[ \omega_{pc}(k) = f \sum_{n=1}^{N_c} \frac{\sin(kl)^{n-1}\sin(kR)}{k} \]

condition for the same hybrid particle model. We demonstrated our previous work on single-tethered particles, based on the same simulation which supports the usefulness of the atomic closures the hard core impenetrability conditions are absent, conditions where conformational nonidealities of excluded volume and enthalpic origin are expected to be minimum. In addition, we consider only short tethers, which should also mitigate large nonideal conformational effects, and minimize the unphysical intrachain overlaps present in any ideal chain model. Finally, in our previous work on single-tethered particles, based on the same model and statistical mechanical approximations, we demonstrated a surprisingly good agreement of the predictions of local structure and (estimated) microphase transition with computer simulations for the same hybrid particle model.

To solve the PRISM equations requires approximate closure relations. For polymer nanocomposites, the site-site Percus-Yevick (PY) closure is quite accurate for monomer-monomer and monomer-particle direct correlation functions. A good closure for the particle-particle direct correlation function has been shown to be the hypernetted chain (HNC) approximation, which also ensures that the physical condition \( g_{cc}(r) > 0 \) holds for all \( r \). We have verified that for the ratios \( D/d = 2 \) and 3 studied in this paper the results based on using the HNC and PY closures show little difference. If \( \sigma_{ij} \) is the distance of closest approach between sites of types \( i \) and \( j \), the hard core impenetrability conditions are

\[
g_{ij}(r) = 0 \quad r < \sigma_{ij}
\]

Outside the hard core, the site-site PY approximation for the polymer-polymer and polymer-particle direct correlations is

\[
C_{ij}(r) = (1 - e^{-\beta U_{ij}(r)}) g_{ij}(r) \quad r > \sigma_{ij}
\]

and the HNC closure is

\[
C_{cc}(r) = h_{cc}(r) - \ln g_{cc}(r) - \beta U_{cc}(r) \quad r > \sigma_{ij}
\]

Previous work on polymer nanocomposites and single-tethered nanoparticles has demonstrated that PRISM theory with the above closures accurately captures the polymer-induced interaction of two nanoparticles in concentrated solutions and melts. In addition, our prior work for the single-tether nanoparticle system demonstrated quite good agreement with simulation which supports the usefulness of the atomic closures of eqs 7 and 8. We note that for polymer blends and block copolymers composed of monomers of (nearly) the same size the so-called “molecular closures” have been shown to be most accurate. Whether such closures are preferable for hybrid nanoparticle fluids is unknown, and their investigation is beyond the scope of this work.

To efficiently solve the three coupled nonlinear integral equations, we employ the Kinsol algorithm. This method employs the inexact Newton method which allows much easier solution and rapid numerical convergence of the coupled nonlinear integral equations than the simpler Picard algorithm. The details of the Kinsol program can be found in ref 49.

The dimensionless isothermal compressibility, \( S_0 \), quantifies the amplitude of long-wavelength total density fluctuations and is given by

\[
\frac{1}{S_0} = \rho_c - [\rho_c^2 C_{pp}(k = 0) + 2 \rho_c \rho_s C_{ps}(k = 0)] \rho_\theta
\]

The particle potential of mean force (PMF), \( W_{cc}(r) \), is also of interest

\[
W_{cc}(r)/k_B T = -\ln[g_{cc}(r)]
\]

C. Phase Behavior. PRISM theory describes correlated and spatially segregated, but globally homogeneous, fluid states. It is not a mean field theory and includes concentration fluctuations on all length scales. Hence, literal spinodal instabilities at nonzero wave vectors (structure factor divergences at \( k^* \)) are not predicted. However, in extensive prior applications of the theory to diblock and multiblock copolymers, an analysis of small-angle scattering profiles was proposed which allows a useful estimate of a microphase separation transition in the sense of an extrapolated spinodal instability. In polymer (mean) field theories and experimental scattering analyses, the quantity \( 1/S_0(k^*) \) is taken as the order parameter which would vanish at a literal spinodal instability. The spinodal instability is estimated from PRISM theory via linear extrapolation of \( 1/S_0(k^*) \) as a function of the inverse dimensionless temperature, \( 1/T^* \). When this approach was applied to melts of particles with single tethers, the resulting microphase spinodal curve was in surprisingly good agreement with the order–disorder boundary obtained using simulations by Iacovella et al. This prior work motivates us to analyze the present systems of multilayered particles in an analogous manner. In addition to calculating the microphase spinodal temperatures, we also compare the temperature corresponding to the Verlet-Hansen (empirical) “rule” which correlates a first-order freezing transition of simple liquids with a critical value of the primary ordering peak of \( S_0(k^*) \) vs.

D. System Parameters. The system parameters are polymer tether degree of polymerization, \( N \), number of polymer tethers, \( f \), placement of tethers, ratio of particle-to-tether monomer, \( D/d \), total packing fraction, \( \eta \), and absolute magnitude of the particle–particle attraction strength in units of the thermal energy, \( \epsilon_{cc} \). The persistence length is fixed at 1.4\( d \) and the CLJ

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potential length \( b = d \). Most calculations are for \( N = 8; f = 1, 2, \) and \( 4; \) and \( D/d = 2 \) and 3. The particle–particle attraction strength \( \varepsilon_{cc} \) is varied from 0 (athermal) to 5 K. The total packing fraction, \( \eta \), is varied from 0.05 to 0.6. The typical value of \( 1/S_0 \) for real homopolymer melts is \( \sim 5 \times 10^{-3},53,54,55 \) and by this metric, melt-like conditions for tethered particles are mimicked \( ^{33} \) for \( \eta \geq 0.3 \).

E. Size of the Tethered Nanoparticle. An intuitive measure of the size of a single-tethered nanoparticle is the sum of the particle diameter and twice the radius of gyration of the polymer tether, \( D + 2R_g \). The analogous result for particles with two or four tethers is \( D + 4R_g \). We refer to this global size estimate as method 1. For \( D = 2d \) and a tether of 8 segments, one obtains \( 2.6D \) (5.2d) and \( 4.2D \) (8.4d) as the size of one and two or four tethered particles, respectively. An alternative intuitive measure of a multtethered particle radius (method 2) is to use the analytic formula for the radius of gyration of Gaussian star polymers \( ^{57} \) with \( f \) arms containing \( N \) segments each, and adapt it to a multtethered particle by adding \( D/2 \), due to the nanoparticle core. The result is

\[
R_{g,\text{eff}} = \frac{D}{2} + \frac{d}{\sqrt{6}(N_f + 1)}(2fN + 3f^2N^2 - 2fN^3 + 3f^2N^3)^{1/2}
\]

(11)

A rigorous way (method 3) of quantifying the size follows from total intramolecular structure factor, \( \omega(k) \), which defines the radius of gyration as

\[
\omega(k) = N_{\text{total}} \left[ 1 - \frac{k^2R_{g,\text{eff}}^2}{3} \right] \quad k \to 0
\]

(12)

where \( N_{\text{total}} \) is the total number of sites in the tethered particle (=1 + \( fN \)). The sizes of 1, 2, and 4 tethered particles, with \( D = 2d \) and \( N = 8 \) based on the above three methods, are presented in Table 1.

In the subsequent sections, we first consider entropy-driven assembly of nanoparticles with \( f = 1, 2, \) and \( 4 \) symmetrically placed tethers in the athermal limit, and then at increasing \( \varepsilon_{cc} \) or decreasing temperature. This is followed by studies of the effect of varying tether placements on the assembly of nanoparticles with \( f = 2 \) and 4.

III. Athermal Limit

In the athermal or entropic limit, tether-mediated depletion-like attraction and sterical stabilization effects associated with excluded volume interactions compete in the absence of energetic biases. Here, we focus exclusively on the particle–particle structure factors and real space pair correlation functions.

Figure 1 presents calculations of the collective particle–particle structure factor, \( S_cc(k) \), particle–particle pair correlation function, \( g_{cc}(r) \), and potential of mean force, \( W_{cc}(r) \), (as insets) for nanoparticles of size \( dD = 2 \) with a single tether (\( f = 1 \)), two tethers (\( f = 2 \)), and four tethers (\( f = 4 \)) of length \( N = 8 \), at packing fractions \( \eta = 0.1, 0.2, 0.5, \) and 0.6. For \( f = 2 \), the two tethers are placed at 180° relative to each other. For \( f = 4 \), the grafted chains are placed in a tetrahedral arrangement. Schematics of the tethered particles are also shown in Figure 1.

For the single tether case, \( ^{33} \) a weak small angle “microphase” peak in \( S_cc(k) \) (Figure 1a) emerges at a very high packing fraction of \( \eta = 0.5 \). For two tethers (Figure 1b), a small angle peak is visible only at an even higher packing fraction of \( \eta = 0.6 \) and is much weaker compared to the single tether analogue. For tethers (Figure 1c), there is no small angle peak. Hence, under athermal conditions, the tendency to microphase separate is always very weak and decreases as the number of tethers increases due to reduced steric anisotropy of the particle. The wide angle peak in \( S_cc(k) \) shifts to higher wavevector as packing fraction increases, indicating that the tethered particles are pushed closer together. At fixed \( \eta \), the nanoparticle local cage order, as quantified by the intensity of the wide-angle peak, also decreases strongly with increasing number of tethers.

For all three systems, the real space \( g_{cc}(r) \) displays a growth of the contact value as \( \eta \) increases (Figure 1d,e,f), which decreases as the number of tethers grows due to increased steric repulsion. For the single tether case (Figure 1d), there is no noticeable peak at any other interparticle separation. In contrast, for two tethers (Figure 1e) as packing fraction increases two additional peaks in \( g_{cc}(r) \) develop at \( r/D = 1.5 \) and 2, and for four tethers (Figure 1f), three additional peaks develop at \( r/D = 1.25, 1.65, \) and 2.2. This suggests that under athermal high \( \eta \) conditions, as the number of tethers increases the particles are effectively pushed apart and locally order at larger interparticle separations.

The insets in Figure 1d,e,f show the potential of mean force (PMF) values calculated at \( \eta = 0.2 \) and 0.5. In our previous work \( ^{33} \) on single tethered particles, we found that in the infinitely dilute two-particle limit the PMF is always repulsive. However, as the packing fraction increases from 0.1 to 0.6 the nanoparticle PMF changes from repulsive to strongly attractive at contact, indicating a muted form of entropy-driven depletion attraction of many-body origin. In the case of two-tethered particles (Figure 1d), as the packing fraction increases from 0.2 to 0.5 the potential of mean force changes from repulsive to slightly attractive at contact. Four-tethered particles have a repulsive PMF at both packing fractions. Hence, as the number of tethers increases (or degree of overall particle anisotropy decreases) a higher fraction of the particle surface is covered or shielded by the grafted chains. This enhances the effective steric repulsion between particle cores, which is the expected classic behavior in the high grafting limit. We note that our nanoparticle PMF results are based on a full ensemble-average over all relative orientations. Hence, the interesting question of the vectorial anisotropy of the PMF for nanoparticles with asymmetrically placed tethers cannot be addressed.

IV. Effect of Particle–Particle Attraction Strength

We now consider the same \( f = 1, 2, \) and 4 and \( N = 8 \) tether systems as in section III but in the presence of direct particle–particle attractions of variable contact strength \( \varepsilon_{cc} \) (units of KT). The packing fraction is fixed at the concentrated solution or melt-like value of \( \eta = 0.30 \). The direct attraction between particles can potentially induce macrophase separation or strong aggregate formation and subsequent microphase-type ordering. In analogy with block copolymer assembly in solution and the melt, \( ^{55} \) the latter situation can be viewed as indicating large concentration fluctuations, \( ^{38,59} \) and perhaps a hierarchical assembly where relatively small aggregates or micelles first form, which then organize as a highly correlated liquid. \( ^{36,60} \) As is true for the experimental analysis of scattering curves, the theory is limited in the level of spatial organization that can be deduced on the basis of ensemble-averaged pair correlation functions. However, the theory does provide all three real and Fourier space correlations functions over all length scales.

The prior simulation work and self-consistent field studies of tadpole particles have demonstrated that microphase separation can occur for lightly tethered nanoparticles. However, the general question of whether long-range ordering can be achieved as the nanoparticle size and number and length of tethers are varied, or only finite clusters are formed, or the system remains a correlated fluid of single hybrid particles, is not a priori obvious. The direct particle–particle attraction favors cluster formation and potential microphases, since macroscopic phase separation is frustrated due to intertether excluded volume interactions. In addition, at high volume fractions intertether excluded volume interactions can potentially mediate a weak form of depletion attraction, which favors close nanoparticle contact, since it enhances tether conformational entropy. However, this effect competes with the direct repulsions between tethered chains that tend to push nanoparticles apart (steric stabilization). For lightly tethered particles, the energy-entropy competition can be subtle. Specifically, whether the grafted chains mediate attraction and/or repulsion in the nanoparticle potential of mean force depends on fluid packing fraction, the number and length of tethers, and, in principle, their precise placement. As the number of tethers

### Table 1. Size of Tethered Particles with $D/d = 2$ and Tether Length $N = 8$ Based on the Three Methods Described in Section III

<table>
<thead>
<tr>
<th>number of tethers</th>
<th>method 1 ($d$)</th>
<th>method 2 (eq 10)</th>
<th>method 3 (eq 11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.2d (1.6)</td>
<td>4.43d (1.3)</td>
<td>3.0d (0.9)</td>
</tr>
<tr>
<td>2</td>
<td>8.4d (3.1)</td>
<td>5.36d (2.0)</td>
<td>4.05d (1.5)</td>
</tr>
<tr>
<td>4</td>
<td>8.4d (4.2)</td>
<td>5.8d (2.9)</td>
<td>4.3d (2.15)</td>
</tr>
</tbody>
</table>

*Also presented (in brackets) are the values of $k^*R_{g,eff}$ where $R_{g,eff}$ is half the size of the tethered particle.*
increases, their intermolecular repulsion monotonically suppresses entropy-driven nanoparticle aggregation and increasingly frustrates clustering and microphase separation, resulting in a reduction of the apparent microphase separation temperature. Moreover, we expect that asymmetric placement of multiple tethers reduces the excluded volume induced repulsion between nanoparticle cores.

A. Real and Fourier Space Structure. Figure 2 presents structural results for increasing attraction strengths and nanoparticles of size $D/d = 2$ with a single tether, two tethers (placed at 180°), and four tethers (placed tetrahedrally).

For nanoparticles with a single tether, Figure 2a shows that the particle—particle pair correlation function has a peak at contact and a second smaller peak at $r/D = 2$, as $\varepsilon_{cc}$ increases from zero to 2.5 kT. The corresponding structure factor $S_{cc}(k)$ (Figure 2d) develops a small angle microphase peak, which rapidly intensifies as $\varepsilon_{cc}$ grows. For particles with two tethers, $g_{cc}(r)$ (Figure 2b) exhibits a much lower contact peak, and the small angle microphase peak in the $S_{cc}(k)$ (Figure 2e) grows and sharpens as $\varepsilon_{cc}$ increases. For particles with four tethers, the contact value of $g_{cc}(r)$ and small-angle peak in $S_{cc}(k)$ are even smaller than the corresponding two tether case (Figure 2c,f).

It is interesting to compare the different tether systems at the same $\eta$ and $\varepsilon_{cc}$. As $f$ increases, the small-angle peak in $S_{cc}(k)$ decreases, suggesting more tethers frustrate nanoparticle ordering. This trend is corroborated by the real space $g_{cc}(r)$, where as the number of tethers increases the contact value decreases. In addition, the single tether system has a peak at $r/D = 2$, while there are no additional peaks in $g_{cc}(r)$ for $f = 2$ and 4, and a correlation hole develops that deepens as $f$ and $\varepsilon_{cc}$ increase.

The position of the small angle peak in $S_{cc}(k)$ is related to the microphase-like periodicity. As the number of tethers increases, the location of the small-angle peak nondimensionalized by the nanoparticle diameter, $k_{*}D$, shifts to higher wave vectors (Figure 2).
2d,e,f). Specifically, \( k^0D \sim 1.2, 1.5, \) and 2 for \( f = 1, 2, \) and 4, respectively. The corresponding length scales, \( 2\pi/k^0, \) are 5.2D, 4.2D, and 3.14D, respectively. The schematic of the tethered particles in Figure 1, and results in column 1 of Table 1 indicates that the global tethered particle sizes are \(~2.6D, 4.2D, \) and 4.2D for \( f = 1, 2, \) and 4, respectively. On the basis of this measure of sizes, the periodicity for the single tether system is twice the molecule diameter, and the periodicity for two tethered particles is approximately equal to the molecule diameter. On the basis of the measure of molecule size in columns 2 and 3 in Table 1, the periodicity for single tethered particles is 2.36 and 3.47 times the molecule diameter, respectively, and 1.6 and 2 times the molecule diameter, respectively, for \( f = 2 \) particles.

We note that, for a particle size of \( Dld = 2, \) the positions of the small angle peaks in \( S_{pp}(k) \) (not shown) are very close to the \( k^* \) in \( S_{cc}(k) \). Leibler theory predicts \( k^*R_g \approx 1.95 \) for symmetric diblock copolymers. The values of \( k^*R_g \) for tethered particles (Table 1) based on all three estimates of size are different from the diblock value and dependent on the number of tethers.

We have also performed calculations for \( \eta = 0.5 \) (not shown) and find the same trends as described above for \( \eta = 0.3 \). For both packing fractions, as the number of tethers increases the magnitude of the small angle peak in the \( S_{cc}(k) \) decreases, and \( g_{cc}(r) \) at contact decreases. For constant \( f \) and \( \epsilon_{cc} \), as the packing fraction increases from \( \eta = 0.3 \) to \( \eta = 0.5 \) the contact values of \( g_{cc}(r) \) increase. For example, for two tethers at \( \epsilon_{cc} = 2 \) kT and \( \eta = 0.3 \) and 0.5 we find \( g_{cc}(rD = 1) \sim 3 \) and 7, respectively. Similarly, the intensity of the small-angle peak in \( S_{cc}(k) \) also increases as the packing fraction increases at a constant number of tethers and attraction strength. For example, for \( f = 4 \) and \( \epsilon_{cc} = 5 \) kT, the \( S_{cc}(k^*) \sim 1.6 \) at \( \eta = 0.3 \) compared to \( S_{cc}(k^*) \sim 3.5 \) at \( \eta = 0.5 \).

**B. Aggregation and Mesoscale Ordering.** The coordination number, or number of nearest neighbors, has been computed as a function of \( \epsilon_{cc} \) for \( Dld = 2 \) systems with one, two (placed at 180°), and four (placed tetrahedrally) tethers of length \( D = 1 \) at \( \eta = 0.3 \). This quantity can also be viewed as a measure of molecular aggregation number and is given by

\[
CN = \rho_c \int_{r_1}^{r_2} 4\pi r^2 g_{cc}(r) \, dr
\]

where \( \rho_c \) is the number density of the nanoparticle cores, \( r_1 = D, \) and \( r_2 \) is the location of the first minimum of \( g_{cc}(r) \). As expected, the coordination number increases with \( \epsilon_{cc} \) (Figure 3a), consistent with the enhancement of local cage order and shifting of wave vector of the microphase peak to lower values as attraction strength grows. For fluids of single tethered nanoparticles, \( CN \to 8 \) at \( \epsilon_{cc} = 2.8 \) kT, the highest value of \( \epsilon_{cc} \) for which we could obtain a numerical solution to the theory. Since the system periodicity for the single tether system is roughly twice the molecular size (based on the simple estimates), and given that the coordination number approaches 8, we suspect that the tethered particles form a spherical micelle as shown in the cartoon in Figure 3b. Of course, it is difficult to say if they are in any specific lattice arrangement. Using computer simulations for a similar system, Lacovella et al. found a partial icosahedral arrangement of the particles with the coordination number increasing with the attraction strength.

For two tethers, the coordination numbers at every \( \epsilon_{cc} \) are lower than the corresponding values for the \( f = 1 \) particle. Furthermore, \( CN \to 6 \) at \( \epsilon_{cc} \sim 4 \) kT, the highest value of \( \epsilon_{cc} \) for which we could obtain a solution to the theory. A coordination number of 6 and a periodicity \( (2\pi/k^0) \) of approximately the molecule size suggest that the nanoparticles may arrange in a two-dimensional plane with hexagonal-like packing and tethers above and below the plane (Figure 3c).

For four tethers, the coordination numbers at every \( \epsilon_{cc} \) are significantly lower than for nanoparticles with one or two tethers due to severe steric hindrance for particles to closely approach. The maximum achievable coordination number of \(~7\) and a system periodicity of \( 2\pi/k^0 = 3.14D \) do not suggest any obvious possible type of aggregate packing. However, we note that Lambeth et al. have shown that four-arm star block copolymers with a collapsed \( N \)-isopropylacrylamide (NIPAM) core and dimethylacrylamide (DMA) corona aggregate to form a supramolecular assembly where the cores cluster and the corona chains emanate outward. Perhaps the four tether nanoparticles behave in a similar manner.

**C. Microphase Ordering.** The sharp peak of \( S_{cc}(k) \) and \( S_{pp}(k) \) at a nonzero wave vector \( (k^0 \neq 0) \) that rapidly grows as \( \epsilon_{cc} \) increases suggests the system is approaching a microphase separation transition. Alternatively, a sharp increase at \( k^0 = 0 \) indicates macrophase demixing. In polymer (mean) field theories and experimental scattering analyses, the quantity \( 1/S_{cc}(k^*) \) is taken as the order parameter that would vanish at a literal spinodal instability. In Figure 4, we plot the microphase order parameter, \( 1/S_{cc}(k^*) \), for particles of size \( Dld = 2 \) with one, two, and four tethers at various packing fractions. An apparent spinodal.

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and the corresponding value of $\epsilon_{cc}$, is estimated via linear extrapolation as discussed in section IIC and previously. The determination of the spinodal $\epsilon_{cc}$ is shown at each packing fraction (dotted lines). Note that for all cases the curves show a linear region at high and intermediate temperatures, but “bend up” at high $\epsilon_{cc}$ (low temperatures) due to “fluctuation stabilization” similar to the behavior seen in block copolymers.

At a constant packing fraction, as the number of tethers increase the extrapolated spinodal transition attraction strength, $\epsilon_{cc}$, increases. For example, at $\eta = 0.3$ we find $\epsilon_{cc} = 2.9$, 4.5, and 6.7 for one, two, and four tethers, respectively. In Figure 4d, the spinodal curve, $T^*$ versus $\eta$, is plotted for all three systems. For comparison, the Verlet-Hansen temperatures (dashed lines) are shown along with the macrophase spinodal curve for systems containing bare spheres of size $Dd = 2$ with no tether. As $f$ increases from 1 to 4, the microphase spinodal curve shift to lower temperatures since the tethers sterically frustrate nanoparticle clustering. For all three systems, the Verlet-Hansen curves lie above (higher temperature) the spinodal analogue, qualitatively consistent with the idea that it is an indication of a first-order microphase transition. Prior work for single tethered particles found $T^* \propto \eta^{0.38}$, which is far weaker than the experimental behavior of diblock copolymers in good (athermal) solvents, where $T^{ODT} \propto \eta^{1.6}$. This very different dependence on packing fraction presumably arises from the large excluded volume asymmetry of the tethered nanosphere compared to a diblock copolymer composed of linear chains. For two tethers, the best power law fit of our calculations is $T^* \propto \eta^{0.63}$, while for four tethers, $T^* \propto \eta^{0.54}$. The dependence of $T^*$ on $\eta$ is different for the three cases, and always much weaker than the diblock copolymer in a good solvent analogue.

V. Effect of Tether Placement

The effect of the placement of two and four tethers on the microphase spinodal temperatures and local structure is now addressed. By changing the position of the tethers, the role of entropy and particle anisotropy on aggregate formation at fixed degree of nanoparticle functionalization and chemical composition can be probed.

A. Two Tethers. In the previous sections, the two tethers were placed at 180° from each other. Three additional cases are now considered corresponding to two tethers attached at angles of 60°, 90°, and 120°. The schematics for all four cases are shown on the right-hand side in Figure 5.

Figure 5 presents the particle–particle and monomer–monomer partial collective structure factors, $S_{cc}(k)$ and $S_{pp}(k)$, respectively, and all three real-space site–site pair correlation functions $g_{cc}(r)$, $g_{pp}(r)$ (inset), and $g_{pp}(r)$, for $D/d = 2$, at a packing fraction $\eta = 0.3$ and particle–particle attraction strength of $\epsilon_{cc} = 3$ KT. Figure 5a shows that as the angle between the two tethers increases from 60° to 180° the microphase peak in $S_{cc}(k)$ decreases in amplitude and shifts to higher wave vectors, but there is no change in the local cage (wide angle) peak. The shift in the position of small angle peak, $k^*$, as the angle between the

The partial collective structure factors and real-space site-site pair correlation functions at a constant particle-particle attraction strength but a higher packing fraction $\eta = 0.5$ (not shown here) show the same qualitative trends as demonstrated for $\eta = 0.3$. The minor differences between the two packing fractions, while maintaining all other parameters constant, lie only in the enhanced contact values of the site-site pair correlation functions and the intensity of the small angle peak in the structure factors.

The microphase spinodal curves in the format $T^\ast (\epsilon_c/\eta)$ as a function of packing fraction are presented for the two tether $D/\eta = 2$ system in Figure 6a. Also shown are the Verlet–Hansen criterion analogues, $T_{\text{VH}}$. Both measures of microphase separation temperature decrease monotonically as the tether placement becomes more symmetric. This leads us to the question of whether the position of tethers will continue to affect structure as the nanoparticle size increases. Upon increasing the particle size to $D/\eta = 3$ (Figure 6b), several changes are seen relative to the $D/\eta = 2$ results. The microphase spinodal temperature for $D/\eta = 2$ lies between $T^\ast = 0.2$ and 0.45, compared to $T^\ast = 0.15$ and 0.3 for $D/\eta = 3$. Thus, holding all parameters constant, as particle size increases the spinodal temperatures decrease. The difference between the spinodal temperatures for the two extreme tether placements, 60° and 180°, is larger when $D/\eta = 2$ than for $D/\eta = 3$, especially at high packing fractions. Hence, as nanoparticle size increases the effect of the position of tethers on the microphase transition also decreases. This is likely because of the decreased tether mediated driving force for microphase ordering, and enhanced tendency for macrophase separation, for the larger nanoparticle system.

**B. Four Tethers.** We now study nanoparticles with four tethers placed in a symmetric tetrahedral arrangement on the particle, a symmetric equatorial square planar arrangement, and an asymmetric arc placement. The schematic for these three cases are shown in Figure 7, along with the partial collective structure factors $S_{cc}(k)$ and $S_{pp}(k)$ and three real-space pair correlation

Figure 5. Structure factors (a) $S_{cc}(k)$, (b) $S_{pp}(k)$, and corresponding pair correlation functions (c) $g_{cc}(r)$, and inset $g_{pp}(r)$, and (d) $g_{pp}(r)$ for two tethers placed at 180° (solid line), 120° (dotted line), 90° (dashed line), and 60° (dot-dashed line) on particles of size $D = 2d$ with tether length $N = 8$, total fluid packing fraction of 0.3 and particle–particle attraction strength $\epsilon_c = 3 kT$. Also shown is a schematic of each tethered particle.
functions $g_{cc}(r)$, $g_{pc}(r)$ (inset), and $g_{pp}(r)$ for $N = 8$, $\eta = 0.3$, and $\varepsilon_{cc} = 0, 4, \text{ and } 6 \text{ kT}$. For all $\varepsilon_{cc}$, there are no major differences in $S_{cc}(k)$ (Figure 7a) between the two symmetric placements. Hence, we show only structure factors for the tetrahedral arrangement. There are minor differences in $S_{cc}(k)$ between the symmetric tetrahedral and asymmetric arc (blue lines) placements, mainly at high $\varepsilon_{cc} = 6 \text{ kT}$. The calculations of $S_{pp}(k)$ (Figure 7b) show minor differences between tetrahedral and square planar, especially at low wave vectors, and more significant differences between the symmetric and asymmetric arc placements at all wave vectors. Clearly, grafting all four tethers on one side of the nanoparticle results in a more intense small-angle peak in both structure factors as compared to the symmetric placement. This suggests that upon asymmetrically placing tethers the tendency for microphase transition is enhanced since the steric hindrance is more anisotropic.

Figure 7c,d shows the corresponding pair correlation functions $g_{cc}(r)$, $g_{pc}(r)$ (inset), and $g_{pp}(r)$ for symmetric tetrahedral and asymmetric arc placements. There are only minor differences in the local structure between the different placements. The same
qualitative trends were observed at a higher packing fraction $\eta = 0.5$ (not shown here). The insensitivity of structural correlations to the two symmetric placements, and the insignificant differences in real space pair correlation functions between asymmetric and symmetric placements of the four tethers, raises the question of why the position of two tethers on particles affects their tendency to microphase separate much more than the placement of four tethers. We believe this is because with increasing number of polymer tethers the fraction of the $D/d^2$ particle surface area covered or shielded by the monomer segments also increases. For a higher number of polymer tethers, irrespective of where the polymer tethers are grafted, the surface area coverage is large and the consequences of the precise placement on the local structure are smeared out. However, if the number of monomers decreases (smaller $N$), then surface coverage decreases and the local structure should become more sensitive to the tether placement. We now test this idea by reducing the length of the tether to just one segment.

In Figure 8, the partial structure factors and real-space pair correlation functions are shown for a system of the particles with the four $N = 1$ “tethers” placed tetrahedrally (red lines), in a square planar conformation (black lines), and in an asymmetric arc (blue lines) on the surface of the particles at $\eta = 0.3$ and $\epsilon_{cc} = 0, 1,$ and $2$ kT. The structure factors and pair correlations are clearly different for the various placements. The square planar arrangement displays more local order in $g_{cc}(r)$, while the tetrahedral arrangement results in more local order in $g_{pp}(r)$ (Figure 8c,d). This supports our arguments given above.

**VI. Summary and Discussion**

We have applied the microscopic polymer reference interaction site model theory to study intermolecular pair correlation functions, collective structure factors, and the tendency for microphase separation of dense solutions and melts of spherical nanoparticles carrying multiple polymer tethers. The role of total packing fraction and interparticle attraction strength for particle-to-monomer diameter ratios of 2 and 3, with one ($f = 1$), two ($f = 2$), and four ($f = 4$) tethers of a degree of polymerization of 8, has been studied in depth. A rich interplay of entropic (translational, conformational, and packing) and enthalpic (particle–particle attraction) effects is found that results in different real space structural arrangements with distinctive small- and wide-angle scattering signatures.

Under athermal conditions at high packing fractions (Figure 1), opposing depletion-like and steric stabilization effects compete. For all three tether systems studied, only a very weak precursor of microphase ordering emerges at a very high packing fraction. At a constant packing fraction, as the number of tethers increases the intensity of the small angle peak and the local particle order both decrease. Upon increasing the particle–particle attraction strength at a constant packing fraction, clustering of particles (Figure 2) indicative of aggregate formation is predicted. At constant particle attraction strength and packing fraction, as the number of tethers increases the tendency for cluster formation and number of nearest neighbors decreases. The coordination number grows as the particle attraction strength increases. On the basis of the numerical values of the coordination number and the position of the small-angle peak, a speculative qualitative
picture of the aggregate formed for single-tethered and two-tethered nanoparticles is suggested: a spherical micelle shaped aggregate for f = 1 and a two-dimensional hexagonal-like packing for the two-tethered nanoparticles (Figure 3).

The intensity of the small-angle collective concentration fluctuation scattering peaks was taken as microphase order parameters, and a mean-field inspired analysis was adopted to deduce an extrapolated microphase spinodal temperature, *T*\(^*\) (Figure 4). As expected, *T*\(^*\) increases monotonically with packing fraction. The dependence is roughly a power law with a different exponent for each of the three tethered particle cases. As the number of tethers increases, the microphase spinodal temperature decreases due to packing frustration and reduced global anisotropy of the tethered particle.

For nanoparticles with two and four tethers, the effect of attached chain placement on the structure factors and the microphase transition was presented. For f = 2, increasing the angle between the tethers shifts the microphase spinodal to lower temperatures (Figures 5 and 6). For f = 4, changing the positions of the attached chains from a symmetric square planar arrangement to a symmetric tetrahedral arrangement did not affect the local or mesoscopic structure. However, modifying the position of the four tethers from a symmetric to a highly asymmetric placement on one side of the nanoparticle surface produces modest changes in packing correlations (Figure 7). The tendency for aggregation and microphase-like ordering is enhanced upon asymmetrically placing tethers on one side of the particle. The reason the structure factors are insensitive to the two different symmetric placements of four tethers is because of the higher surface area coverage leading to a smearing out of the chain attachment details.

The theory is based on specific closure approximations and the assumption of tether conformational ideality. In our previous work, we compared the microphase spinodal calculations for single tethered DdI = 2 particles systems with a recent simulation. The agreement is surprisingly good, suggesting that the assumption of chain conformational ideality is reasonably accurate at the melt-like packing fractions, tether lengths, and intermolecular potential cases studied. However, a fully self-consistent PRISM analysis is desirable in order to determine how important nonideal conformational effects are as a function of tether length, number, and placement. Theoretical approach is general and can be applied to systems where the tethers attract each other and/or the nanoparticle. The direction of our ongoing work is applying PRISM theory to study the structure and phase behavior of nanocomposites composed of homopolymers and tethered nanoparticles. Finally, the ability of PRISM theory to compute direct correlation functions and structure factors, especially at large wave vectors, raises the possibility of addressing dynamical phenomena such as glass and gel formation within the framework of mode coupling and beyond statistical dynamical approaches.

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**Appendix: Intramolecular Structure Factors for Tethered Particles**

The intramolecular structure factors for a nanoparticle (1 site of type c) with f polymer tethers each of degree of polymerization N (total of fN +1 sites) are given generally by eqs 3–5 where *T*\(_{ij}(k)\) depends on the number and placement of tethers. For two tethers placed at 180°, 120°, 90°, and 60°, i and j can be 1 or 2, and the *T*\(_{ij}(k)\) are

\[
*T*_{ij}(k) = \frac{\sin(2kr)}{2kr}, *T*_{ij}(k) = \frac{\sin(kR\sqrt{3})}{kR\sqrt{3}},
\]

\[
*T*_{ij}(k) = \frac{\sin(kR\sqrt{2})}{kR\sqrt{2}}, *T*_{ij}(k) = \frac{\sin(kR)}{kR} \quad (A1)
\]

For a spherical particle with four tethers, then i and j can be 1, 2, 3, or 4. If the four tethers are placed in a square planar arrangement (such that the plane passes through the center of the sphere), the elements of *T*\(_{ij}(k)\) are identical

\[
*T*_{ij}(k) = \frac{\sin(kR\sqrt{2})}{kR\sqrt{2}} \quad \text{if } |i-j| = 1 \text{or} 3 \quad (A2a)
\]

\[
*T*_{ij}(k) = \frac{\sin(2kr)}{2kr} \quad \text{if } |i-j| = 2 \quad (A2b)
\]

For four tethers placed in a symmetric tetrahedral arrangement, all *T*\(_{ij}(k)\) are identical

\[
*T*_{ij}(k) = \frac{\sin(kR2\sqrt{\frac{2}{3}})}{kR2\sqrt{\frac{2}{3}}} \quad (A3)
\]

For four tethers placed in an asymmetric arc conformation, where each tether is at an angle of 60° away from each other, the elements of *T*\(_{ij}(k)\) are

\[
*T*_{1,2}(k) = \frac{\sin(kR)}{kR}, *T*_{1,3} = \frac{\sin(kR\sqrt{3})}{kR\sqrt{3}}, *T*_{1,4} = \frac{\sin(2kr)}{2kr} \quad (A4a)
\]

\[
*T*_{2,3}(k) = \frac{\sin(kR)}{kR}, *T*_{2,4} = \frac{\sin(kR\sqrt{3})}{kR\sqrt{3}}, *T*_{3,2} = \frac{\sin(kR)}{kR} \quad (A4b)
\]

Based on symmetry along the arc, *T*\(_{3,1}(k)\) are equal to *T*\(_{2,1}(k)\) and *T*\(_{4,1}(k)\) are equal to *T*\(_{1,1}(k)\).