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Self-Assembly of Polymer-Grafted Nanoparticles in Solvent-free Conditions

Alexandros Chremos^{a)} and Jack F. Douglas^{b)}

Abstract

Grafting of polymer chains onto the surface of spherical nanoparticles leads to a hybrid type of fluid that exhibits properties of both particle suspensions and melts of star polymers—these properties being controlled by the relative dimensions of the grafted polymer chains to the nanoparticle diameter, D , and the number of the number of chains grafted on the nanoparticle surface, f . While polymer-grafted nanoparticles (GNP) of this kind typically have a spherical average shape after grafting even a moderate number of chains, their *instantaneous* molecular shape can fluctuate significantly due to the deformation of the grafted chains. Both simulations and measurements have previously revealed that these “conformationally polarizable” particles can exhibit self-assembly into large scale polymeric structures in both solution and in polymer melts, and we simulate polymer-grafted nanoparticles with D and temperature (T) variations without a dispersing solvent to better understand the nature of this self-assembly process. We observe a reversible self-assembly into linear and branched dynamic GNP structures, where the extent of the assembly and geometry depend on D and T , and we constructed a map capturing the GNP structural behavior with D and T variations. Since the shape of the GNPs appeared to be correlated with the occurrence of the GNP self-assembly, we quantified the average shape and a measure of shape fluctuations to better understand how molecular shape influences their propensity to self-assemble into different structural forms. Based on this framework, we describe the clustering process of the GNPs as an *equilibrium polymerization* phenomenon and we calculate the order parameter governing the dynamic clustering behavior of GNPs, the average mass of the clusters, size distribution, and the apparent fractal dimension of the clusters.

I. INTRODUCTION

Polymer-grafted nanoparticles (GNPs) composed of an inorganic core and a grafted layer of polymer chains possess intriguing properties associated with the propensity of the nanoparticles to associate, influencing electrical conductivity, optical and viscoelastic properties of materials composed of these nanoparticles.^{1–11} GNP-based materials are receiving considerable attention due to the environmental compatibility, light weight, and their relative low vapor pressure.^{6–9} Some notable potential applications with GNPs include lithium-ion and lithium metal batteries,^{12,13} drug-delivery,^{14,15} carbon capture,^{16,17} and water filtration.^{18,19} The rational design of these materials requires a better understanding of the structure-property relationship.

^{a)}alexandros.chremos@nist.gov

^{b)}jack.douglas@nist.gov

The GNPs have been observed, in experiments^{5,6,20,21} and in simulations,^{20,22–25} to associate into dynamic clusters in both solution and in polymer melts, forming string-like and sheet-like aggregates as molecular parameters are varied. The association into large scale clusters can cause significant property changes in the material, making these materials very promising if the clustering can be controlled.^{26,27} Self-assembly, the process by which molecules associate with each other at equilibrium, is observed in many biological systems as the organic scaffold material, e.g., for bones,^{28–30} teeth,²⁹ shells,³¹ and diatoms.³² An understanding of self-assembly in GNP systems becomes essential to determine the molecular parameters that enable the control their structure and stability. However, there are no known governing principles for designing hierarchical organized structures with GNPs. To probe the nature of the association of the GNPs, we choose to study these particles under solvent-free conditions. In this situation, the surrounding environment is composed of other GNPs.^{33–42} Due to the absence of a solvent, glassy physics, rheology, and structure can be studied without the complications from the interactions between the solvent and the GNPs.

GNPs are assumed to be relative spherical, but such a description ignores the impact of average molecular shape and shape fluctuations on the GNP self-assembly process. It has been observed that particles with isotropic interactions tend to form relative spherical clusters,^{43–45} we believe that it is important to consider the deformability of the grafted chain corona, as well the response of the corona to temperature variation. For example, a highly dense corona around a GNP in melt and in solution not only protects the nanoparticle from GNP aggregation, but it can also induce solid-like behavior with temperature increase due to the corona expansion.^{38,46,47} For GNPs having a lower grafting density, the softness and deformability of the corona allows a wide range of molecular shapes, which are transient and change over time. Unfortunately, there has been little systematic investigation regarding the role of the molecular shape of the corona in the GNP self-assembly processes and type of clusters formed.

The objective of our work is to investigate the conditions under which GNP self-assembly occurs in melt and high concentration regimes by characterizing the molecular shape of the particles (nanoparticle and the polymeric corona) and the shape of the GNP aggregates formed. In particular, we use a bead-spring model and molecular dynamics (MD) simulations to study GNP having polymer chains isotropically grafted on the nanoparticle surface. By varying the nanoparticle size relative to the polymer chain, we are able to study distinct materials ranging from star polymer liquids, where the nanoparticle size is negligible small to gel-like structures where the nanoparticles have formed an array of distinct aggregates. We characterize the shape and the distribution of these aggregates with temperature variation and core size. By keeping the nanoparticle-nanoparticle interactions short-ranged and purely repulsive, we study the aggregation phenomenon without interference from the attractive nanoparticle interactions.

This paper is organized as follows. Section II contains details of the coarse-grained model and simulation methods. Results of the shape characterization of the GNP materials and their relation to the self-assembly process are presented in Section III. In Section IV, we conclude our work.

II. MODEL AND METHODOLOGY

The system consists of $N_s = 400$ nanoparticles. An oligomer-grafted nanoparticle is represented as a spherical core particle with f attached chains and each chain is composed of M segments. The nanoparticles have $f = 8$ grafted oligomer chains, where each one has $M = 10$ segments. The first segment of each chain is rigidly attached to the nanoparticle surface. Interactions between polymer segments are described by the cut-and-shifted Lennard-Jones (LJ) potential:

$$V(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - v & r \leq r_c \\ 0 & r > r_c \end{cases}, \quad (1)$$

where v is the value of the (unshifted) Lennard-Jones potential at $r = r_c$. The energy and length reduced units are ϵ and σ and the cutoff distance $r_c = 2.5 \sigma$. The segments along a chain are connected with their neighbors via a stiff harmonic spring, $V_H(r) = k(r - l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 5000 \epsilon/\sigma^2$ is the spring constant.

The core-core and core-segment interactions are modeled as purely repulsive Weeks-Chandler-Andersen potential⁴⁸ with modification taking into account the difference in the particle sizes:⁴⁹

$$V_{\text{WCA}}(r) = \begin{cases} 4\epsilon \left[\left(\left(\frac{\sigma}{r - \Delta_{ij}} \right)^{12} - \left(\left(\frac{\sigma}{r - \Delta_{ij}} \right)^6 + \frac{1}{4} \right) \right] & r \leq r_m \\ 0 & r > r_m \end{cases}, \quad (2)$$

where $r_m = 2^{1/6} \sigma + \Delta_{ij}$. The energy and interaction range parameters are chosen to be the same for interactions between nanoparticle-nanoparticle, nanoparticle-segment, and segment-segment such that $\epsilon_{cc} = \epsilon_{cb} = \epsilon_{bb} = \epsilon$ and $\sigma_{cc} = \sigma_{cb} = \sigma_{bb} = \sigma$. We investigate nanoparticles having a nanoparticle core size $D/\sigma = 1, 2, 3, 4$, and 5 and the shift distance was set to $\Delta_{cc} = D - \sigma$ for the nanoparticle-nanoparticle interactions, and $\Delta_{cb} = (D - \sigma)/2$ for the nanoparticle-segment interactions. The mass of a particle scales linearly with volume, so that m_b and $m_c = D^3 m_b$ for the mass of the polymer bead and core, respectively. Typical molecular configurations are presented in Fig. 1.

Simulations were performed in a cubic box with length L ; periodic boundary conditions was applied in all three directions. The simulations were performed by the large-scale atomic/molecular massively parallel simulator (LAMMPS) developed at Sandia National Laboratories.⁵⁰ Simulations were performed in the NVT ensemble after equilibration in the NPT ensemble at the desired temperature. Time averaging was conducted for $O(10^8)$ time steps after equilibration. The time step was set to $\delta t = 0.005 \tau$, where $\tau = \sigma(m_b/\epsilon)^{1/2}$ is the unit of time. Temperature and pressure are measured in units of ϵ/k_B and σ^3/ϵ , respectively. k_B is Boltzmann's constant. All simulations were performed at $P = 0$ in reduced units, which closely corresponds to atmospheric pressure. The above mentioned approach has been used in the past to probe GNP materials.^{37,51}

III. RESULTS & DISCUSSION

In this section, we begin with a brief description of the general phenomenological behavior of GNP in absence of solvent. The GNP molecular architecture has a large number of molecular parameters, resulting to highly complex structural and dynamical behavior, and thus it is essential to place our work into perspective. The investigation is then extended to the quantification of the GNP's molecular shape and the fluctuation in the molecular shape. We continue our discussion with the quantification of the nanoparticle clustering behavior with variation with the nanoparticle size and temperature.

A. General phenomenology

Fig. 1 provides a schematic of GNP structural behavior seen in our model as D and f are varied. Only a limited number of polymer chains that can be grafted on the surface of a given nanoparticle size, due to excluded volume interactions; we label the molecular parameters above this limit as Regime I in Fig. 1. If the surface of the nanoparticle is large enough to accommodate grafted chains, then there are two types of structural behaviors. In the first regime of structural organization, the polymeric corona shields the GNP and prevents GNP association, resulting in a simple liquid-like structural behavior. The radial distribution between the nanoparticles, $g(r)$, for this type of material is presented in Fig. 1(b), where the size of the GNP is $D/\sigma = 1$; the particular system corresponds to a star polymer melt.^{52,53} If this liquid-like structure is maintained for the whole temperature range while the material is in the liquid state, then the material is called a “star-liquid”; see Fig. 1.³⁸ In the second structural regime, the corona does not provide sufficient protection from aggregation and the formation of clusters starts to occur below a temperature threshold; we label this temperature as T_a . The structural signature of aggregation is observed in $g(r)$ with the emergence of a new peak at short distances. A GNP material that exhibits anisotropic aggregation at lower temperatures is labeled as a gel-forming liquid (G-1),³⁸ see Fig. 1. Representative $g(r)$ curves between star and G-1 liquids are presented in Fig. 1b.

Based on the classification scheme defined above, we aim to gain insight on how the nanoparticle size influences the self-assembly process and the conformational properties. A larger in size nanoparticle in our model has two immediate effects. The first effect is that the surface of the nanoparticle becomes exposed so that nanoparticle-nanoparticle contacts become possible. The second effect is that the segmental density decreases as D increases at fixed T and P (not shown here), even though the nanoparticle volume fraction, $\phi = (\pi D^3/6)/L^3$, increases with D . This additional empty space can be considered as an added “phantom solvent” that reduces the net segment-segment attraction. The aggregation of the GNPs is influenced both by temperature and nanoparticle size and thus we constructed a morphology map with variation of T and ϕ in Fig. 2.

For a small nanoparticle size, $D/\sigma = 1$, no GNP aggregation is observed for all temperatures explored, meaning that the material behaves as a star-liquid. Aggregation starts to occur at relatively small nanoparticle sizes, $D/\sigma \approx 2$, where at relative low temperatures small clusters start to form. Since the GNPs having $D/\sigma \approx 2$ start to associate below $T < T_a \approx 1.1$, then the material is considered as G-1. For $D/\sigma \approx 3$ and even larger D anisotropic aggregation occurs at higher temperatures, i.e., T_a increases with increasing D . We note that

the potential interaction between the nanoparticle cores is purely repulsive and the points of the grafted chains are isotropically distributed meaning that the GNP aggregation mechanism is not driven by the non-isotropic distribution of the grafted chains nor from the attraction of the nanoparticle cores. Evidently, one cannot explain the observed behavior by isotropically averaged two-body interactions alone.

In a previous paper,²⁰ the self-assembly mechanism of GNPs in a polymer matrix was attributed to the strong attractive nanoparticle-nanoparticle interactions bringing the nanoparticles in close proximity by deforming their grafted chains to their side, which in turn prevented other nanoparticles to approach the newly formed aggregate from the sides. Aggregation is balanced by two competing factors: the energy gain when the GNPs approach and the entropy loss of distorting the grafted polymer chains.⁵⁵ The apparent directional nature of the GNPs has been rationalized in the context of a competition between short ranged nanoparticle-nanoparticle attractive interactions versus the long range repulsions from the interacting coronas.^{23,38,45,56–59}

To rationalize the tendency of GNPs to cluster, since in our case the nanoparticle-nanoparticle interactions do not contribute to this behavior, we consider the following thought experiment. Removing in our system the bonds between the chains and the nanoparticles results in a nanocomposite, i.e., nanoparticles in a polymer matrix. We note that the nanoparticle-polymer segment interactions are also purely repulsive, while the interactions between the polymer segments are attractive. With this set of interactions, the nanocomposite system will maximize the number of enthalpic interactions between the polymer segments by minimizing the interface between the nanoparticles and the polymer segments, leading to a phase separation. Thus, the organization of the nanoparticles does not only depend on the interactions between the nanoparticles, but also on their interactions with the polymer segments. In other words, the apparent attractiveness in GNP materials having repulsive nanoparticle interactions, as we observe in this study, is due to the weak (or lack) of attractive interactions between the nanoparticles and polymer-segments. Evidently, the gel-forming behavior of the GNPs, now that the chains are grafted on the surface of the nanoparticles, is a result of the nanoparticles having the tendency to phase separate, but being kinetically and packing frustrated by the grafted polymer layers.

B. Molecular characterization

We next consider the molecular shape characteristics of the GNPs. Although the shape of the nanoparticle itself does not change, the corona composed of polymer chains is “soft”. This means that the overall molecular shape (nanoparticle + corona) in a given environment changes. In our study, the environment is composed by other GNPs and so the average shape is the result of the packing of all the particles and it is expected to influence the molecular conformation of the grafted chains, as well as the average molecular shape of the GNPs. To determine the molecular shape of a GNP, we use the ratio of the hydrodynamic radius over the radius of gyration, R_h/R_g , which is often used descriptor to quantify the shape of arbitrary objects;^{60,61} the calculation of R_h is based on the friction coefficient of an arbitrary shaped Brownian particle. The molecular shape of well defined objects such as sphere, rod, and random coil have been determined by previous studies. For comparison, the values of

R_h/R_g for a smooth sphere is 1.29, for a random walk is 0.79, and for an infinite long rod is 0.^{62,63}

The average molecular shape of GNP particles, $\langle R_h \rangle / \langle R_g \rangle$, is nearly spherical for all values of T and D , as illustrated in Fig. 3a. This should not come as a surprise, even with the expectation that aggregation may affect the GNP average molecular shape. Indeed, GNPs having significant large nanoparticle core size tend to be more spherical, because the size and shape of the nanoparticle core dominates measures of the overall average molecular shape calculation. This is counter-intuitive, because we observe aggregation as D increases and the molecular shape approaches the smooth sphere limit. If the value of the average molecular shape does not provide insights regarding the GNP self-assembly behavior, then is there something else? Looking back at the Fig. 3a, we notice another unexpected behavior. There is a crossover in the temperature dependence of $\langle R_h \rangle / \langle R_g \rangle$. For small in size nanoparticles, a decrease in T results in an increase in the symmetry of the molecular shape, i.e., closer to the smooth sphere limit. This can be rationalized as follows: a decrease in T leads to a decrease of the interparticle distance (increase of density) and by extension to a more compact molecular conformation. For larger in size nanoparticles, a decrease in T results in a decrease in $\langle R_h \rangle / \langle R_g \rangle$, because now the nanoparticles associate with each other causing the deformation of the grafted chains and the molecular shape becomes less spherical. The crossover between these two T -dependent behaviors occurs at $D/\sigma = D_s/\sigma \approx 2.5$, which is near the boundary between star and G-1 liquids, Fig. 2. This also suggests that GNPs having $D = D_s$ have their molecular shape and size (as measured from R_g and R_h) independent of T variation, see Fig. 2. For $D > D_s$, GNPs become less spherical and their size increases with T decreasing, due to stronger tendency of the GNPs to associate compared to GNP systems having $D < D_s$. The nanoparticle size at the crossover between star and G-1 liquids is smaller than D_s , suggesting that D_s characterizes two aspects of G-1 liquids. Here, we consider D_s as a criterion to identify weak and strong associating G-1 type GNPs with $D < D_s$ and $D > D_s$, respectively. Thus, it is not only that shape that matters in the self-assembly process, but also the molecular shape response with the variation of the thermodynamic variables, such as temperature. The crossover in the temperature dependence of the molecular shape is also observed in $\langle R_g \rangle$, as indicated in Fig. 3b. This means that the overall size of the GNP particles is also influenced by their packing.

To better understand this change in molecular shape with temperature, we calculate the size of fluctuations of R_g and R_h with D , see Fig. 3c. Evidently, the size of the fluctuations is large in comparison to the average value of R_g and R_h , indicating that GNP particles are highly “conformationally polarizable”. The degree of this conformational polarizability is influenced by D as follows. For small values of D ($D/\sigma < 2.5$), the standard deviation for R_g remains at the same level, while there is a small increase in the size of the fluctuations for R_h with D increase. For $D/\sigma > 2.5$, R_h continues to increase with D , but the fluctuations of R_g become smaller, Fig. 3c. Curiously, these changes in the fluctuations do not significantly change with temperature, suggesting that the packing and the propensity to self-assemble can be understood from the fluctuations of the molecular shape before self-assembly occurs. This observation warrens further investigation.

To obtain a more detailed understanding of the corona structure and how it is influenced by the GNP packing, we calculate the square-root mean-square end-to-center distance, $\langle R_{ec}^2 \rangle^{1/2}$, and subtract the radius of the nanoparticle:

$$R_{\text{corona}} = \langle R_{ec}^2 \rangle^{1/2} - D/2, \quad (3)$$

where the brackets $\langle \rangle$ represent the time average over all nanoparticles. The effective size of the corona as function of temperature is presented in Fig. 4. When the nanoparticle size is significantly small ($D/\sigma \approx 1$) the corona decreases monotonically with T , which is consistent with our understanding of star polymers. However, for larger in size nanoparticles, a more complex picture arises. As the GNP systems are cooled down, R_{corona} decreases, as in the case of star polymer melts (i.e., $D/\sigma \approx 1$), till it reaches a minimum in the range of $1.25 < T < 1.75$ and at lower temperatures R_{corona} increases. From Fig. 4, we note that at the high T range, an increase in D leads to R_{corona} decrease. This effect arises because a small nanoparticle size implies a high grafting density. For a given number of grafted chains and at high grafting density the grafted-chains become stretched outwards resulting in an increase R_{corona} . Larger in size GNP has lower grafted-chain surface density, since we keep the number of grafted chains fixed, and thus reducing significantly the chain stretching by the chain crowding. For low T values ($T \lesssim 1.5$) and $D/\sigma = 2$, R_{corona} increases significantly and at $T = 0.75$ the size of the corona becomes slightly larger than the corona for $D/\sigma = 1$ at the same temperature. Similar behavior is observed for $D/\sigma = 4$ and 5, but the overall size of the corona was assumed to be smaller, see Fig. 4. The increase of R_{corona} to a large degree is due to the GNPs' aggregation, since the nanoparticles would displace a fraction of their grafted chains so that a neighboring nanoparticle to approach and form an aggregate. While it is tempting to argue that the increase of the size of the corona is solely due to the self-assembly process, a closer investigation is required.

For most cases considered, there is a correlation between the point at which the R_{corona} increases and the point aggregates are formed. Indeed, the minimum in R_{corona} as function of T is closely related to the structural signature of aggregation observed in $g(r)$. For $D/\sigma = 2$ the minimum in R_{corona} occurs at $T \approx 1.25$ even though we do not find evidence of aggregation based on the structural behavior, $g(r)$. Nevertheless, the temperature dependence of R_{corona} is stronger for $D/\sigma = 2$ even though the degree of aggregation, as we discuss in more detail below, is weak. This means that the size of the corona is influenced by the packing even when the nanoparticles are well-dispersed.

C. Equilibrium polymerization model of GNP assembly

We next focus on the formation of anisotropic GNP clusters of different nanoparticle sizes and with temperature variation. First of all, the formation GNP clusters is reversible, meaning that the clusters spontaneously form and break over time. We then expect to describe this clustering as a kind of *equilibrium polymerization*. Equilibrium polymers can form either linear chains or branched polymers whose size depend on temperature, concentration, and the interactions involved.⁶⁴ The attractiveness of equilibrium polymerization from a material synthesis stand point is that the material properties can be

tuned with variation of the thermodynamic parameters^{65,66} and exhibit self-healing properties. Typical examples of equilibrium formation of clusters can be found in: mixtures of star and linear chains,⁶⁷ dendrimers,⁶⁸ ring polymers^{69–71} and microgels.^{72,73,74–78} Equilibrium polymerization was previously observed by GNPs in a solvent, i.e., simulations of grafted poly(ethylene oxide) (PEO) chains in aqueous solutions.^{22,79}

To identify whether a nanoparticle belongs into a cluster, we use a distance criterion, if it is located at a distance $r < D + \sigma/2$ from any nanoparticle of the cluster. We focus only on systems with nanoparticles having $D/\sigma = 3$, since there is little or no aggregation for smaller in size GNPs. Typical examples of clusters formed under these conditions are presented in Fig. 5. We label the probability of finding a nanoparticle cluster of size n_c as $p(n_c)$. The resulting cluster probabilities for GNP having $D/\sigma = 3$ and 4 with temperature variation are presented in Fig. 6. To better quantify the trends of cluster formation, we use the following two metrics. The first metric is the extent of polymerization, Φ , which is the average fraction of GNP in a cluster of $n_c > 1$. Φ is an order parameter, where $\Phi = 0$ corresponds to a dissociated system (i.e., perfect GNP dispersion) and $\Phi = 1$ corresponds to a state where all the nanoparticles are in contact with at least one other nanoparticle. The second metric is the cluster size, which is the average number of nanoparticles in a cluster:

$$\langle n_c \rangle = \int_1^\infty n_c p(n_c) dn_c, \quad (4)$$

which is one the most basic properties for a system under-going equilibrium polymerization. To probe the universal scaling of our results, we rescale the temperature by the temperature at which $\phi = 1/2$ so that the reduced temperature is $T/T_{1/2}$. Indeed, the results for ϕ and $\langle n_c \rangle$ overlap with each other when plotted with this reduced temperature (Fig. 7), thus confirming the universal character of the clustering behavior. At high temperatures ($T/T_{1/2} \approx 1.5$), the nanoparticles are well dispersed, meaning that the majority of nanoparticles are not in a cluster, i.e., $\Phi < 0.1$ as seen in Fig. 7. Moreover, we observe that the cluster distribution decays very quickly and only small size clusters are observed, $n_c \approx 3$ to 5, according to Fig. 6. As temperature is decreased, the probability of finding clusters composed of a large number of nanoparticles increases substantially, which leads to an increase of $\langle n_c \rangle$ as illustrated in Fig. 7.

The study of larger in size clusters becomes challenging because one must be aware of the finite size effects, that is when the size of the clusters becomes comparable to the size of the simulation box. The percolation behavior of our model system is not the primary focus, thus we will only consider non-percolating clusters in our statistics. Additionally, in order to reduce the statistical noise, we exclude cluster sizes that have only been observed in the course of the simulation less than ten times.

In geometric percolation theory, the cluster size increases with the degree of connectivity and above a critical degree of connectivity the cluster size may become infinite, meaning that the system is in a percolating state. The degree of connectivity will depend on the relative positions of the nanoparticles in our case, as well as, other parameters of our system such as temperature. It is known that well below this critical point, the cluster formation by

equilibrium polymerization can be described by an exponential function. Nevertheless, with the growth of larger and larger clusters, the cluster size distribution has a continuous (second order) transition from an exponential form to a power law, at which the percolating clusters dominate the overall behavior. Thus, for non-percolating systems, the probability of finding a cluster of n_c nanoparticles is given by the following relation:

$$p(n_c) = \alpha_0 n_c^{-\tau} \exp(-n_c/\mu), \quad (5)$$

where μ represents a metric of cluster size and τ is an apparent exponent of the power law associated with the probability distribution. The parameter α_0 ensures that the probability distribution is normalized and equal to unity. Within geometrical percolation theory, the probability distribution function is applied up to percolation transition, at which μ diverges and the probability distribution becomes a power law. However, the variation of the parameters τ and μ is not known *a priori* and thus we treat the parameters τ as μ as free parameters. We fit the simulation results to Eq. 5; the quality of the fit is presented in Fig. 6.

As discussed above, the clustering behavior follows universal trends for Φ and $\langle n_c \rangle$ with D variation, *c.f.* Fig. 7. These universal clustering trends are reflected by the overlap between the results for different nanoparticle sizes and having the same reduced temperature dependence. Nevertheless, it is quite clear in Fig. 5 that the shape of nanoparticle clusters formed with the same n_c are quite distinct with D variation. Indeed, the clusters formed by nanoparticles having $D/\sigma = 3$ have only a small number of nanoparticle contacts and the clusters have little flexibility, resulting to clusters to be like stiff polymers. As D increases, the number of nanoparticle contacts increases, and the clusters formed are compact and have more branches. This effect is not captured with the rescaling of temperature with $T_{1/2}$ and a different temperature scale is required. To probe this effect, we note that the apparent exponent τ contains information regarding the topological features of the clusters.

When τ has small positive values $0 < \tau \lesssim 0.3$ then small size clusters are formed, which tend to resemble linear chains. As the system is thermally annealed the cluster size grows and τ increases as well. In geometric percolation theory describing randomly placed non-interacting particles the value of τ is 2.18 and in the prediction from mean field theory is $\tau = 5/2$. For lattice animals $\tau = 3/2$.^{80,81} In essence, the value of the apparent exponent τ reflects how close to the point at which percolating clusters are formed. By rescaling the apparent exponent by the temperature at which $\tau = 1.1$, i.e., $T_{\tau=1.1}$, we find an excellent overlap between the results from nanoparticles having different D , as seen in Fig. 8. The choice of $\tau = 1.1$ is made as this is approximately half way to the exponent for percolating clusters. $T_{1/2}$ and $T_{\tau=1.1}$ as function of D have quite distinct behaviors as illustrated in the inset of Fig. 9, suggesting that $T_{\tau=1.1}$ can be used to define a temperature scale, providing valuable information about the clustering behavior of the system.

The ratio of the two temperature scales, $T_{1/2}/T_{\tau=1.1}$, is close to unity, but monotonically decreases with nanoparticle size, as seen in Fig. 9. $T_{1/2}/T_{\tau=1.1} > 1$ means at $T_{1/2}$ the nanoparticle clusters need to grow more in size to have an apparent exponent half of what is expected at the percolating state. For $T_{1/2}/T_{\tau=1.1} < 1$, the nanoparticles form highly branched

and compact clusters before the system reaches $\Phi = 1/2$, meaning that from the early stages of cluster formation (small values of Φ) the clusters are relatively near the percolating stage. Evidently, this temperature ratio becomes a useful tool for describing how the nanoparticle clusters evolve from linear chain-like to branched percolation clusters. We expect this ratio to be a metric for characterizing cluster branches in many different types of self-assembling materials.

The difference between the two characteristic temperatures is a consequence in part of the molecular architecture and the thermodynamic constraints. To better understand these constraints, we provide the following observations based on Fig. 2. For larger sized nanoparticles, the volume fraction dependence with temperature increases, which means that as the temperature decreases ϕ increases. Typically, self-assembly model systems are operating at constant volume conditions and not at constant pressure as in our model. Moreover, not all volume fractions are accessible with the decrease of temperature and D increase. For nanoparticles with small D , the volume is mostly occupied by the polymeric segments and thus the self-assembly has little room to further develop. For example, the segmental density in the interstitial space between the nanoparticles is approximately, $\rho\sigma^3 \approx 0.88$ and $\Phi \approx 0.06$ for nanoparticles having $D/\sigma = 2$ at $T = 0.5$. Moreover, the particular system is close to the polymer glass transition, meaning that the characteristic temperatures $T_{1/2}$ and $T_{\tau_{1/2}}$ are unreachable even if we reduce T to enhance self-assembly. This fits well with the description of star and G-1 liquids that we discussed at the beginning.

We continue our discussion with the shape characterization of the nanoparticle clusters. In the characterization of the shape for the nanoparticle clusters, we only consider the relevant positions of the nanoparticles belonging to a cluster without taking into account the grafted polymer chains. One way to characterize the shape of a macromolecular structure is by examining the eigenvalues and eigenvectors of the gyration tensor S , which describes the second moments of position for a collection of particles. The label the eigenvalues as λ_1 , λ_2 , and λ_3 and they are related to the square radius of gyration, $R_{g,c}^2$, as follows:

$$\text{Tr } S = \langle R_{g,c}^2 \rangle = \langle \lambda_1 \rangle + \langle \lambda_2 \rangle + \langle \lambda_3 \rangle, \quad (6)$$

where $\langle \lambda_1 \rangle$, $\langle \lambda_2 \rangle$, $\langle \lambda_3 \rangle$ and the $\langle \rangle$ represent time averages. The mass scaling of $R_{g,c}^2$ for the nanoparticle clusters is presented in Fig. 10. At high temperatures, only small size clusters are formed and $R_{g,c}$ scales as $R_{g,c} \propto n_c^\nu$, with $\nu \approx 0.9$; the exponent ν is related to the fractal dimension, $d = 1/\nu$.^{82,83} A fractal dimension of $d \approx 1/0.9 \approx 1.1$ means that clusters are close to one-dimensional objects, e.g., rod-like. Larger in size clusters are formed as the temperature is decreased and above $n_c > 5$ the $R_{g,c}$ mass scaling changes to $\nu \approx 0.5$, which is a result known for lattice animals.⁸⁰ For $D/\sigma = 4$ and 5, thermal annealing leads to even larger in size clusters at which we observe another regime with $\nu \approx 0.33$. We expect a crossover to a smaller exponent for larger clusters, because of screening of the excluded volume interactions as the clusters grow. In particular, we expect a crossover between $\nu = 0.5$, corresponding to the universality class of branched polymers swollen by excluded volume interactions, to the universality class of branched polymers with screened

excluded volume interactions.⁸⁴ Finite size limitations do not permit a definite conclusion regarding such a trend.

We continue our investigation on the nanoparticle cluster shape with the calculation of the ratios of the average values of eigenvalues of the radius of gyration tensor, S . In particular, we focus on the ratios of λ_3/λ_1 and λ_2/λ_1 ; the ratios are plotted in Fig. 11. For nanoparticles having $D/\sigma = 3$, small clusters ($n_c \lesssim 10$) are highly anisotropic, with typical values significantly exceeding values of random walks. For clusters with $n_c > 10$, there is a systematic decrease in the values of the ratios due to the gradual increase of branching. Indeed, a quick inspection of typical clusters for $D/\sigma = 3$ in Fig. 5, the clusters with $n_c > 10$ resemble an assembly of small stiff chains. In contrast, small nanoparticle clusters of larger in size nanoparticles ($D/\sigma > 3$) are anisotropic, but the ratios quickly decay to smaller values since the nanoparticles form more easily highly branched and compact clusters. This is consistent with the idea that the more exposed the surface of the nanoparticle, the higher the probability of neighboring nanoparticles will associate. As a result, the values of the ratios come closer to the expected value for lattice animals, which is consistent with the fractal dimension discussion.⁶³

IV. CONCLUSIONS

We used molecular dynamics simulations of a coarse-grained bead-spring model to investigate the self-assembly process of polymer-grafted nanoparticles (GNPs) in the bulk at solvent-free conditions. GNPs particles exhibit a wide spectrum of structural and clustering behaviors with temperature and nanoparticle size variation. When the nanoparticle size is small then the particles are well dispersed, resembling a star polymer liquid. However, once the nanoparticle size is large enough then a reversible self-assembly is triggered below a critical temperature and GNPs form dynamic branched structures. This is counter-intuitive given that in our model the nanoparticle-nanoparticle interaction is purely repulsive. We constructed a map at which all the self-assembly behaviors are captured. We characterized the molecular shape of GNPs at the different conditions, and we find correlations between the GNP molecular shape and their packing. Additionally, the size of the fluctuations for the molecular size and shape are considerably large, suggesting that these GNPs are highly “conformationally polarizable”. We also quantify the clustering process of the GNPs as an equilibrium polymerization phenomenon and we calculated the order parameter governing the formation of these dynamic clusters, the average mass of the clusters, the apparent fractal dimension of the clusters. We find that small size nanoparticles form highly anisotropic clusters that have a small degree of branching. As the nanoparticle size increases then the clusters become more compact and with more branches. To capture this clustering effect, we have introduced an additional characteristic temperature.

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FIG. 1.

(a) Schematic diagram of the structural regimes of polymer-grafted nanoparticles in the limit of purely repulsive core-core interactions, where f is the number of grafted chains and D is the size of the nanoparticle. The highlighted areas approximately correspond to the different structural behavior regimes, for details see Ref. 38. Regime I corresponds to cases where there are more grafted chains than the surface of the core particle can accommodate. Regime II corresponds to star liquids, which are characterized by a simple liquid-like structure for a wide range of temperatures (see text for details). Regime III corresponds to gel-forming liquids (G-1). The dashed line corresponds to GNPs investigated in the present work. At the bottom, screenshots of typical molecular configurations (nanoparticle + corona) for different nanoparticle sizes are presented. The bare nanoparticle and the grafted segments are also presented. (b) Representative radial distribution functions between nanoparticles, $g(r)$: (top) star liquid; (bottom) G-1. The arrows point to the emergence of ordering, representing the nanoparticle association.

FIG. 2.

Structural behavior diagram of polymer-grafted nanoparticles having $f = 8$ polymer grafted chains with variation of temperature, T , and nanoparticle volume fraction, ϕ . Results for different nanoparticle sizes, D , are also presented; D_s is the critical nanoparticle size at which the average molecular shape is independent of T variation. Symbols represent the different structural behaviors: circles correspond to liquid-like behavior; squares correspond to anisotropic aggregation. The dashed line represents the temperature at which the average fraction of nanoparticles belonging in cluster is equal to $\Phi = 1/2$, i.e., $T_{1/2}$. The dot-dashed line represents the temperature at which the apparent exponent of Eq. 5 is $\tau = 1.1$, i.e., $T_{\tau 1/2}$. The highlighted regions correspond to the materials: star-liquids and gel-forming liquid (G-1). The glass transition temperature is also approximately outlined based on star polymers having $f = 8$.^{53,54}

FIG. 3.

(a) Time average ratio of the hydrodynamic radius over the radius of gyration, $\langle R_h \rangle / \langle R_g \rangle$, as function of the nanoparticle size, D . Results for different temperatures are also presented. The dashed line corresponds to the smooth sphere limit, $R_h/R_g = 1.29$. (b) Time average radius of gyration, $\langle R_g \rangle$, as function of the nanoparticle size, D . (c) Standard deviation of R_g and R_h as function of D at different temperatures: circles ($T = 1.0$), squares ($T = 1.5$), and diamonds ($T = 2.0$).

FIG. 4.

The average size of the corona, R_{corona} , as function of temperature, T . Symbols represent the systems where the nanoparticles are well dispersed (fill symbols) and nanoparticle aggregation is observed (open symbols).

FIG. 5. Screenshots of typical nanoparticle clusters of different nanoparticle populations. Results for different nanoparticle sizes, D , are also presented. The grafted chains are rendered invisible for clarity.

FIG. 6. Probability of finding a nanoparticle cluster of size n_c . The dashed lines are fits to Eq. 5. Results for different nanoparticle size are presented (top) $D/\sigma = 3$ and (bottom) for $D/\sigma = 4$.

FIG. 7. (Top) Average fraction of nanoparticles in a cluster, Φ and (bottom) average number of nanoparticles in a cluster, $\langle n_c \rangle$, as function of a reduced temperature $T/T_{1/2}$, where $T_{1/2}$ is defined as the temperature at which $\Phi = 1/2$. The dashed lines are guides to the eye.

FIG. 8. Parameter τ of Eq. 5 versus the reduced temperature, $T/T_{\tau_{1/2}}$. Results for different nanoparticle diameters, D , are also presented.

FIG. 9.

Characteristic temperatures ratio, $T_{1/2}/T_{\tau_{1/2}}$, as function of the nanoparticle size, D . $T_{1/2}$ is defined as the temperature at which the average fraction nanoparticles belong in a cluster, Φ , equals 1/2 and the temperature at which the apparent exponent τ of Eq. 5 is $\tau = 1.1$. Inset: $T_{1/2}$ and $T_{\tau_{1/2}}$ as function of D .

FIG. 10.

Mean-square radius of gyration of the nanoparticle clusters, $R_{g,c}^2$. Results for different nanoparticle sizes (top) $D/\sigma = 3$ and (bottom) for $D/\sigma = 4$ are also presented. The symbols are the same as in Fig. 6.

FIG. 11. Ratios of average eigenvalues of the radius of gyration tensor for various nanoparticles having a diameter (top) $D/\sigma = 3$ and (bottom) $D/\sigma = 4$. Predictions for ratios for high-mass random walks (RW), lattice animals (LA), and percolation clusters (Perc) are also presented.