ABSTRACT: Molecular dynamics simulations are used to study the effect of passivating ligands of varying lengths grafted to a nanoparticle and placed in various alkane solvents. Average height and density profiles for methyl-terminated alkoxysilane ligands (−O−Si(OH)₂(CH₂)nCH₃ with n = 9, 17, and 35) attached to a 5-nm-diameter amorphous silica nanoparticle with coverages of between 1.0 and 3.0 chains/ nm² are presented for explicitly modeled, short-chain hydrocarbon solvents and for implicit good and poor solvents. Three linear solvents, C₁₀H₂₂ (decane), C₂₄H₅₀ and C₄₈H₉₆, and a branched solvent, squalene, were studied. An implicit poor solvent captured the effect of the longest chain length solvent at lower temperatures, while its temperature dependence was similar to that of the branched solvent squalene. In contrast, an implicit good solvent produced coating structures that were far more extended than those found in any of the explicit solvents tested and showed little dependence on temperature. Coatings equilibrated in explicit solvents were more compact in longer-chain solvents because of autophobic dewetting. Changes in the coating density profiles were more pronounced as the solvent chain length was increased from decane to C₂₄H₅₀ than from C₂₄H₅₀ to C₄₈H₉₆ for all coatings. The response of coatings in squalene was not significantly different from that of the linear chain of equal mass. Significant interpenetration of the solvent chains with the brush coating was observed only for the shortest grafted chains in decane. In all cases, the methyl terminal group tended to the coating edge but was found throughout the entire coating volume, from the core to the outermost shell. Increasing the temperature from 300 to 500 K led to greater average brush heights, but the dependence was weak.

I. INTRODUCTION

Although adding nanoparticles to a polymer matrix can significantly improve the thermal, mechanical, and optical properties of the resulting composite, dispersing nanoparticles in a polymer matrix has proven challenging.¹,² Bare nanoparticles tend strongly toward bulk phase separation and aggregation.¹⁻⁵ One way to overcome this problem is to coat the nanoparticles with chains of the same chemical structure as that of the matrix; then, if the attached ligands are long enough, the nanoparticles can be readily dispersed in the matrix.²,⁴⁻⁹ However, when the chain length of the attached chains is too short, a phenomenon known as “autophobic” dewetting occurs and the nanoparticles again phase separate from the melt. This dewetting occurs because, as first discussed by de Gennes,¹⁰ for end-grafted polymer chains on a flat surface in contact with a polymer melt there is an entropic penalty for the melt chains to mix with short grafted chains.¹¹ The same effect occurs for chains grafted to a nanoparticle.⁶

To obtain a better understanding of the parameters that control the dispersion of nanoparticles in a polymer matrix, a number of experimental studies of phase separation have been carried out.¹⁻⁵,⁷⁻⁹ These studies show that as the chain length of the polymer melt increases, the average height of the attached ligands, commonly referred to as a polymer brush, steadily decreases, reaching a limiting value for long polymer matrix chains. Similar results have been observed in numerical simulations for coarse-grained bead—spring models of grafted chains on a nanoparticle in a matrix of chemically similar chains.¹²⁻¹⁵ However, except for two recent studies of the potential of mean force between grafted nanoparticles in a polymer,¹⁵,¹⁶ these studies do not address the issue of what controls the phase separation. Because of limitations on computer time, most of these previous studies have not modeled grafted nanoparticles in an explicit-atom simulation of a realistic polymer to explore the dependence of the brush density profile on the relative chain length of the grafted and matrix chains and on the grafting density. Here we present explicit-atom simulation results for alkane chains grafted on a nanoparticle in an alkane solvent of increasing chain length. All of our simulations are in the regime where the chain length of the attached ligands and the chain length of the solvents are comparable to the size of the nanoparticles. As a result, the

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standard scaling approaches for either star polymers or flat substrates do not apply.17–19

Since the first reported atomistic simulations of passivated gold nanocrystallites by Luedtke and Landman,20 there have been a number of computational studies of surface-functionalized nanoparticles. Most of these studies have used united atom models20–33 in which the −CH2− and −CH3 groups are treated as individual entities, although recently there have been a few simulations in which all atoms are included explicitly.35–42 In most of these studies, because of computer limitations, the solvent was treated implicitly.20–31 Recent simulations have shown that including the solvent explicitly has a significant effect on the density profile of the ligands, the force between the nanoparticles, and their aggregation.15,16 In most previous simulations that included explicit solvents, only small molecular solvents such as water, ethane, hexane, and decane have been studied.29–39 Most previous studies have been on passivated gold nanoparticles, with the chain length of the ligands varying from butane to octadecane. However, recently Ndroo et al.41,42 have simulated a silica nanoparticle embedded in a melt of 20-monomer atactic polystyrene chains using a fully atomistic model. They have also developed a coarse-grained model based on these simulations and have extended the studies to a range of grafted and melt chain lengths.43 Longer ligand and solvent chains have only been studied using coarse-grained bead-spring models.12,15,16,40,44,45 We have performed explicit-atom simulations of an alkane-coated amorphous silica nanoparticle with ligands varying in length from 10 to 36 carbons in three linear solvents—decane, C12H26, and C16H34—and in a branched solvent—squalene (C30H50). Squalene has a 24-carbon backbone with six methyl side groups and six double bonds and, unlike its linear counterpart n-tetracosane (C24H48), is a liquid at room temperature. As the chain length of the solvent increases, the density profile for the attached ligands smoothly collapses as the solvent chains demix entropically from the attached ligands. We compare our results to simulations in implicit good and poor solvents and show that treating the solvent implicitly does not capture the effect of increasing the length of the solvent chain.

In the next section, details of the model and methodology are presented. In Section III, we compare the density profile for the ligands as a function of ligand chain lengths in the four explicit-atom solvents and compare the results to simulations in a good or poor implicit solvent. We show that the methyl end groups can be found throughout the profile. We then present results for the effect of varying the grafting density. In Section IV, we briefly summarize our main findings. II. MODEL AND METHODOLOGY

We modeled a 5-nm-diameter rigid amorphous silica nanoparticle, coated with methyl-terminated alkoxysilane −O−Si(OH)2(CH3)3CH3 ligands, in hydrocarbon solvents. Chains of length n = 9, 17, and 35 were chemisorbed with trisilanol groups. An example is shown in Figure 1 for the three values of n in the shortest-chain solvent studied, decane. The grafting density was varied between 1.0 and 3.0 chains/nm2, or 80 to 240 ligand chains for a 5-nm-diameter nanoparticle. In what follows, most of the results presented are for a full-coverage density of 3.0 chains/nm2.

All molecular dynamics (MD) simulations were performed using the LAMMPS classical MD code.46 All of the simulations used the all-atom Optimized Potential for Liquid Simulations (OPLS-AA) developed by Jorgensen and co-workers47 for the hydrocarbon interactions. For the ligand—nanoparticle interactions, we followed the model developed by Lorenz et al.48 that combined interaction terms from the OPLS-AA47 and COMPASS force fields.49,50 Nonbonded interactions consisted of a sum of standard 12−6 Lennard-Jones (LJ) and electrostatic potentials, with nearest and next-nearest neighbor pairs excluded, and interactions reduced by a factor of 1/12 for 1−4 neighbor pairs. All LJ interactions were cut off at r = 12 Å; a switching radius of 12 Å was also used as a limit for electrostatic interactions using the particle–particle–particle-mesh (PPPM) algorithm.51 The precision of the PPPM algorithm was set to 1 part in 104. The OPLS-AA potential also includes harmonic bond and angle terms and torsional interactions. A table of all relevant interaction parameters can be found in ref 48. The equations of motion were integrated using a velocity Verlet algorithm with time step of dt = 1 fs. A Langevin thermostat with a 100 fs damping constant was used to regulate the system temperature.52

The nanoparticle core was cut from bulk amorphous silica and then annealed to produce a surface −OH concentration consistent with experimental values.53 The bulk silica was generated from a melt-quench process similar to the method of Lorenz et al.48 The ligands were then attached randomly to the surface oxygens at the desired coverage and equilibrated in an implicit solvent for 1 to 2 ns. The nanoparticle core was treated as a rigid body.

The hydrocarbon solvents were created by equilibrating, at a pressure of 1 atm, four solvents consisting of 12 800 decane (C20H42) chains or 6400 squalene chains at 300 K and 5400 tetracosane (C24H48) chains or 2700 C48H96 chains at 400 K. The higher temperature was necessary for the latter two chain lengths to be above their melting points. Each of these systems was equilibrated by running long enough that the chains moved...
at least their own size. A void in the center of each solvent was created by inserting a soft-repulsive spherical pseudoparticle indenter into the solvent. The indenter was grown slowly from radius zero to a size capable of accommodating each
coated nanoparticle. The overall system dimensions were allowed to expand at constant pressure through the void growth. When the desired size was reached, the pseudoparticle was removed, leaving the void space. The process is illustrated in Figure 2. The system was further equilibrated for 1 ns before the nanoparticle and solvent were merged. Any overlaps were removed using a displacement-limiting integrator (nve/limit in LAMMPS) to prevent large repulsive forces.

The combined systems were equilibrated for 2.5 ns in the isothermal-isobaric (NPT) ensemble. Results for higher temperatures were obtained by raising the temperature for these initial states. All of the results presented here are for \( T = 400 \) K, which were heated from the \( T = 400 \) K systems under constant-volume rather than constant-pressure constraints in order to avoid phase separation.

In a number of previous simulations\(^{20–30}\) the solvent was treated implicitly; to compare our explicit solvent results, we also carried out simulations in both poor and good implicit solvents. Solvents are often handled implicitly by removing all of the solvent atoms and introducing effective interactions that mimic the average effects that would have been produced by explicit interactions with a solvent and/or solvent molecules. For instance, the temperature of a coated nanoparticle is set using a Langevin thermostat to mimic the Brownian motion of a fluid. Furthermore, the effect of the solvation quality of the solvent is often controlled by the strength of attractive interactions between the atoms remaining after solvent removal. To model a good solvent, in which solvent molecules surround and thereby reduce the attractive interactions between the coating chains, the attractive component of the van der Waals force is suppressed artificially. This is accomplished simply by setting the cutoff of the interaction to correspond with the minimum of the LJ potential energy well \( \left( r_c = 2^{1/6} \sigma \right) \) so that the interaction has no attractive region while the repulsive region is unchanged. To model a poor solvent, we treat all of the interactions between atoms the same as in the case when the solvent is included explicitly with \( r_c = 10 \) Å. For the range of temperatures studied here, 300–500 K, this corresponds to a poor solvent in which the solvent molecules do not interpenetrate the coating chains and thus do not significantly reduce the effective interaction between the chains.

### III. RESULTS

The radial density of the ligands coating the nanoparticle is known to depend on the chain length of the solvent, which can lead to autoophobic dewetting as the chain length of the solvent increases. The effect of increasing the chain length of the solvent from 10 to 48 carbons is illustrated by simulation snapshots in Figure 3a,b for \( -O-Si(OH)_3(CH_2)_3CH_3 \) ligands at a coverage of 3.0 chains/nm\(^2\) at 400 K. The radial density of the brush, \( \rho_b(r) \), as function of the distance \( r \) from the center of mass of the nanoparticle is shown in Figure 4 for these two systems as well as for \( C_{24}H_{50} \). For comparison, in Figures 3 and 4, results for an implicit poor and good solvent are also shown. As seen in Figure 4, the coating density profile is more spatially compact and drops more abruptly to zero (indicating phase separation of the coating and solvent) as the chain length of the solvent increases, in agreement with previous work on coarse-grained bead–spring models.\(^{12–16}\) The coating response for the implicit poor solvent is within the range of responses seen in the four explicit solvents and most closely agrees with the response in the longest chain melt \( C_{48}H_{98} \). For the implicit good solvent, the density profile is significantly more extended than for any of the explicit solvents studied.

A quantitative comparison of the difference in brush height as a function of solvent chain length can be directly obtained from the average brush height \( \langle h \rangle \) given by

\[
\langle h \rangle = \frac{\int_R^{\infty} (r - R) \rho_b(r) r^2 \, dr}{\int_R^{\infty} \rho_b(r) r^2 \, dr}
\]

where \( R = 2.5 \) nm is the nanoparticle radius. For the case of grafted chain length \( n = 35 \) at \( T = 400 \) K, \( \langle h \rangle = 18.9, 17.7, \) and 16.3 Å for decane, \( C_{24}H_{50} \), and \( C_{48}H_{98} \), respectively, compared to 16.2 and 20.0 Å for the implicit poor and good solvents. As expected, there is a large decrease in the average height as the chain length of the solvent increases from 10 to 24 to 48.

Density profiles for both the alkoxysilane ligands and solvent chains are shown in Figure 5 for \( n = 17 \) and 35 for the four solvents studied at 400 K. The shape of both profiles changes significantly as the chain length of the solvent is increased from \( C_{24}H_{50} \) (decane) to \( C_{48}H_{98} \) but there is less of a difference between \( C_{24}H_{50} \) and \( C_{48}H_{98} \). The results for squalene and \( C_{24}H_{50} \) are very similar even though squalene, which has the same chain length, has six additional \(-CH_3\) side groups. Only for decane is there any significant interpenetration of the solvent chains into the brush coating. Results for the average brush height \( \langle h \rangle \) for all cases shown in Figure 5 along with those for \( n = 9 \) are given in Table 1.

The effect of varying the temperature in the experimentally accessible range of 300 to 500 K is illustrated in Figure 6. Except for some minimal expansion of the brush at 500 K, which is due largely to the reduction in solvent density, temperature has little effect on the profiles. For example, the average brush height \( \langle h \rangle \) decreases from 19.0 to 18.4 Å for decane and increases from 15.0 to 16.5 Å for squalene as the temperature is increased from 300 to 500 K. Although at low temperatures, the implicit poor solvent behaves like \( C_{48}H_{98} \) at higher temperatures, the trend in the behavior of the poor solvent mimics that of squalene, as the average height increases by about 10 percent between 300 K and 500 K in both solvents. This increase in brush height occurs because the increase in...
temperature improves the quality of the implicit poor solvent by decreasing the relative strength of the van der Waals interaction. For the implicit good solvent the increase in $\langle h \rangle$ from 19.8 Å to 20.0 Å is minimal as the solvent quality is not affected by temperature. In contrast, the real solvent decane shows a slight decrease in brush height.

The density profile for the terminal carbons is shown in Figure 7. The most striking feature of these profiles is that the terminal carbons are not concentrated in the region near the interface but are instead distributed throughout the brush. This is consistent with previous results on polymers attached to a flat substrate. Figure 7a compares the results for the four real solvents: the probabilities of finding terminal carbons near the surface of the silica nanoparticle are comparable and independent of the length of the solvent chains. The broader distribution for the terminal carbon in decane is simply due to the larger extent of the brush in decane. As seen in Figure 7b,c, the effect of temperature on the distribution of the terminal carbons, as for the overall density profiles, is minimal.

The effect of varying the surface coverage is shown in Figure 8 for $-O-Si(OH)_2(CH_2)_nCH_3$ in decane and C$_{24}$H$_{50}$ at 400 K. Near the surface of the silica nanoparticle, the density profiles overlap for both solvents because neither solvent penetrates all the way to the core of the nanoparticle, even for the lowest coverage. This results in density profiles that overlap
near the surface of the nanoparticle, and only for larger radii \( r \) does the local repulsion of the ligands have a strong enough effect to extend the brush for higher coverages. The average brush heights \( \langle h \rangle \) are found to be 16.5, 17.7, and 18.9 \( \text{Å} \) for decane and 13.8, 16.2, and 17.7 \( \text{Å} \) for C\(_{24}\)H\(_{49}\) for coverages of 1.0, 2.0, and 3.0 chains/nm\(^2\), respectively.

**IV. CONCLUSIONS**

We have performed simulations of alkylsilane-coated silica nanoparticles in both real and implicit solvents to observe the effects of the ligand and solvent chain length on the structure of the coating and the solution outside the nanoparticle. Our results show that the brush heights of the ligands attached to the nanoparticle are altered by the solvent length for grafted chains longer than \( n = 9 \). For all coating chain lengths and temperatures, the average brush height is as large as or larger in C\(_{24}\)H\(_{49}\) than in any of the other solvents considered. Of particular interest is the wide distribution of positions for the chain ends relative to the particle surface; conformations ranging from chain ends lying near the particle surface to nearly fully extended chains have been observed under all conditions. In addition, comparison with implicit solvents clearly indicates that the use of an implicit solvent does not capture the changes introduced by solvent length and temperature relative to what is observed for the "real" solvents, although the implicit poor solvent does give results for the density profile in agreement with longer chain solvents (squalene and C\(_{48}\)H\(_{98}\)).

Future work on these systems can proceed on several fronts. The simulation of assemblies of nanoparticles will require the development of coarse-grained potentials of mean force that can efficiently describe the interactions between two (or more) particles in solution. Further research will also be needed to study the "solution" process of nanoparticles in solvents as a function of the chain length of the solvent.

**AUTHOR INFORMATION**

Notes

The authors declare no competing financial interest.

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