

Adsorption and diffusion of colloidal Au nanoparticles at a liquid-vapor interface

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Motivated by recent drop-drying experiments of Au nanoparticle (NP) island self-assembly, we investigate the structure, diffusion, and binding of dodecanethiol-coated Au NPs adsorbed at the toluene-vapor interface using molecular dynamics (MD) simulations as well as analytical calculations. For a 6 nm core diameter NP our results indicate the existence of significant intermixing between the ligands and the solvent. As a result, the NP lies primarily below the interface with only a portion of the ligands sticking out, while the toluene-vapor interface is significantly higher in the region above the NP core than away from the NP. These results are consistent with a competition between the negative free energy of mixing of toluene and the dodecanethiol ligands, which tends to keep the NP below the interface, and the effects of surface tension which keeps the NP near the interface. Consistent with this result, we find that the coefficient for nanoparticle diffusion along the interface is close to the Stokes-Einstein prediction for three-dimensional bulk diffusion. An analysis of the ligand arrangement surrounding the NP also indicates that there is relatively little asymmetry in the ligand-coating. We then consider the effects of van der Waals interactions on the adsorption energy. In particular, we derive an analytical expression for the van der Waals interaction energy between a coated nanoparticle and the surrounding solvent along with a closed-form expression for the van der Waals corrections to the binding energy at the interface due to the long-range core-solvent interaction. Using these results along with the results of our MD simulations, we then estimate the van der Waals corrections to the adsorption energy for dodecanethiol-coated Au nanoparticles at the toluene-vapor interface as well as for decanethiol-coated nanoparticles at the water-vapor interface. In both cases, we find that the long-range core-solvent interaction may significantly reduce the binding energy. Based on these results, we conclude that in many cases, the core-solvent van der Waals interaction is likely to have a significant effect on the binding energy and interface position of Au NPs. Our results also indicate that the competition between the van der Waals interaction and the short-range attraction to the interface leads to the existence of well-defined activation barriers for nanoparticle adsorption from the solvent as well as for interfacial desorption. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4884022>]

I. INTRODUCTION

Colloidal gold nanoparticles (NPs) are of interest in a variety of applications ranging from solar cells to sensors to catalysis and drug delivery.¹⁻³ Recently a drop-drying method to self-assemble a well-ordered monolayer of Au nanoparticles has been developed.⁴⁻⁶ In this method, a droplet of a monodisperse solution of gold nanoparticles, coated with organic ligands to prevent precipitation in solution, is placed on a substrate. As the droplet evaporates, NPs are swept up and adsorbed at the toluene-air interface. The adsorbed NPs then diffuse and nucleate two-dimensional NP islands at the interface. As the droplet continues to evaporate, these islands grow, diffuse, and coalesce as additional nanoparticles are deposited, eventually forming a complete and well-ordered monolayer. The resulting compact film typically exhibits long-range order, is void free, and exhibits very few defects.

While there are a variety of experimental parameters, including nanoparticle size, excess ligand concentration, and droplet evaporation rate which affect the self-assembly process, one of the key quantities controlling the growth is the interfacial adsorption energy or binding energy of a nanoparticle at the interface. Combined with the monomer diffusion rate at the interface, this quantity determines the nanoparticle diffusion length, corresponding to the typical distance a nanoparticle can diffuse (without attaching to another nanoparticle or island) before desorbing from the interface. Accordingly, in order to obtain a fundamental understanding of the drop-drying process it is of interest to obtain a better understanding of the nanoparticle interaction with the interface.

Recently Wi *et al.*⁷ have derived expressions – based on a simplified geometric picture – for the binding energy and position of NPs adsorbed at a solvent-vapor interface as a function of the NP-solvent line-tension as well as the NP-vapor, NP-solvent, and solvent-vapor surface tensions. However, the dependence of these quantities on the density of

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ligands attached to the NP or the excess ligand concentration in solution is in general not known. In a more microscopic approach, Lane and Grest⁸ have carried out molecular dynamics (MD) simulations of alkanethiol-coated Au nanoparticles at a water-vapor interface. Depending on the coating and NP size, the nanoparticle was found to sit either above or below the interface. However, in these simulations the van der Waals interaction energy between the Au core and the ligands and/or solvent was not taken into account.

Here we present the results of MD simulations which we have carried out in order to better understand the adsorption and diffusion of dodecanethiol (DDT)-coated Au NPs at the toluene-vapor interface. We find that in this case the NP adsorbs well below the solvent-vapor interface. In addition, the toluene-vapor interface is somewhat higher in the region above the NP core than away from the NP. These results may be explained by the existence of a competition between the mixing of toluene and dodecanethiol and surface tension effects. Consistent with this result, the coefficient for 2D interface diffusion is also found to be in good agreement with that predicted based on the 3D Stokes-Einstein expression. In good agreement with the findings in Ref. 8 for 8 nm diameter Au NPs coated with decanethiol in decane and water, we also find that for 6 nm dodecanethiol-coated NPs in toluene there is relatively little “asymmetry” or “patchiness” in the ligand-coating either at the interface or in the bulk solvent.

We then consider the effects of the van der Waals core-solvent interaction on the binding energy of Au NPs at a solvent-vapor interface. In particular, we first derive an analytical expression for the van der Waals interaction between a NP in the bulk and the surrounding solvent and show that in general this interaction can be quite significant. We then derive an expression for the van der Waals corrections to the interfacial binding energy which takes into account the difference in the solvent density surrounding a bulk NP and that surrounding a surface NP. Using this expression along with the results of our molecular dynamics simulations, we estimate the van der Waals corrections to the interfacial binding energy for a 6 nm Au NP adsorbed at the toluene-vapor interface. For comparison, we also consider the van der Waals core-solvent interaction for 8 nm diameter Au NPs coated with decanethiol at the water-vapor interface as was studied in Ref. 8. Our results indicate that in this case the van der Waals correction is even larger than for the case of dodecanethiol-coated 6 nm Au NPs in toluene, and as a result significantly reduces both the binding energy as well as the position of the NP above the interface.

Based on these calculations, we conclude that in many cases, the core-solvent van der Waals interaction is likely to have a significant effect on the binding energy and interface position of Au NPs. Our results also lead to a qualitative picture of the interaction between a Au NP and the interface which is somewhat different from that assumed in Ref. 6. In particular, our results indicate the existence of a well-defined activation barrier for NP desorption from an interface along with the existence of a somewhat smaller activation barrier to adsorption from the bulk solvent.

II. SIMULATIONS

In order to better understand the drop-drying experiments carried out in Ref. 6, we have carried out molecular dynamics simulations of 6 nm diameter Au NPs coated with dodecanethiol ligands at the liquid-vapor interface of toluene using the Optimized Potential for Liquid Simulations (OPLS) all-atom potential developed by Jorgensen and co-workers.^{9,10} We note that this potential includes intermolecular and intramolecular Coulomb and Lennard-Jones interactions as well as bond-bending, bond-stretching, and dihedral interactions and has been optimized in order to give good agreement¹⁰ with experimental values for thermodynamic quantities for a wide variety of organic liquids, and has also been shown to be in good agreement with *ab initio* predictions for molecular structures. These results have been recently confirmed in a comparative study¹¹ of the generalized AMBER¹² and OPLS all-atom (AA) force-fields in which it was found that the OPLS/AA potential gave excellent agreement with experimental results for the density, enthalpy of vaporization, heat capacities, isothermal compressibility, and volumetric expansion coefficient for 145 organic liquids including toluene. However, due to the fact that they do not take into account polarization effects, both force-fields were found to underestimate the surface tension for almost all organic liquids including toluene.¹³

As in Ref. 8, both the DDT ligands and the toluene solvent were modeled using an all-atom representation, while the Au core was not included explicitly. Instead, the sulfur head groups of the DDT ligands were attached to the surface of the Au core in a C₅₄₀ spherical fullerene arrangement. We note that this corresponds to a saturated grafting density of 4.77 ligands/nm², in good agreement with experiments.¹⁴ As in Ref. 8, the mass of the Au atoms was distributed equally among the S atoms, which were treated as a rigid body which was allowed to translate and rotate. Our simulations were carried out using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) classical molecular dynamics code.¹⁵

In order to model the solvent-vapor interface, a bulk (cubic) solvent system consisting of 27 000 toluene molecules and periodic boundary conditions was first equilibrated using constant pressure and temperature dynamics with a Nosé-Hoover thermostat^{16–18} at 25° C and a pressure of 1 atm. An interface was then created by doubling the box-height and carrying out simulations with fixed box-size using constant volume and temperature dynamics. In all cases, the ligand-ligand and ligand-solvent van der Waals interactions were cut off at 1.0 nm, while long-range Coulomb interactions were calculated with the fully periodic particle-particle particle-mesh method.¹⁹ However, as in Ref. 8, the van der Waals core-solvent interaction was not included. In order to calculate the corresponding interfacial and bulk radial toluene densities simulations were carried both for a NP at the interface as well as in the bulk.

For the case of a nanoparticle adsorbed at the interface, the NP was introduced just above the toluene-vapor interface and then allowed to be attracted to the interface. Throughout the simulation, the position of the solvent-vapor interface (in

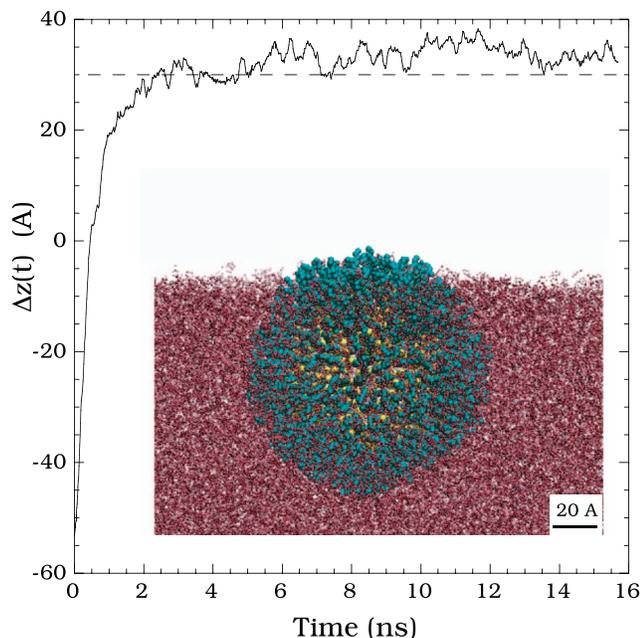


FIG. 1. Distance $\Delta z(t)$ of center of NP below interface as function of time. Dashed line corresponds to position at which the Au core just touches the interface. Inset shows picture of NP at interface at time $t = 8.7$ ns ($\Delta z(t) = 33$ Å).

the portion of the system away from the NP) was calculated by measuring the toluene density as a function of height (in horizontal slabs of width 1 Å in this region) and then assigning the interface height $z_{int}(t)$ to the “midpoint” between the vapor and bulk solvent density. The interfacial radial toluene density $\rho_i(r)$ was then calculated once the NP had equilibrated.

Fig. 1 shows our results for the distance $\Delta z(t)$ of the NP center-of-mass below the interface as a function of time. As can be seen, while the NP starts out above the interface ($\Delta z < 0$) the center-of-mass finally equilibrates at a relatively large distance $\Delta z \simeq 3.4 \pm 0.2$ nm below the interface. As a result, the Au core remains entirely below the interface, with only a portion of the DDT ligands sticking out above (see inset). This behavior may be qualitatively explained by the fact that, due to the relatively small value^{20–23} of the Flory χ parameter for the mixing of toluene and dodecane,²⁴ the free energy of mixing of the ligands and the solvent is negative.²⁵ We note that this is also qualitatively consistent with the fact that both dodecane and toluene are non-polar molecules. On the other hand, since the surface tension of the DDT ligands is smaller than the surface tension of toluene, the DDT-coated Au NP is preferentially adsorbed at the interface, as is observed experimentally.

In order to better understand the binding of the NP at the interface we have also calculated the distribution $P(h)$ (where $h = \Delta z(t) - \bar{\Delta z}$ is the displacement of the NP from its average position with respect to the interface) and have used this to calculate the potential energy $V(h) = -k_B T \ln(P(h))$. Over the range of fluctuations observed in our simulations, we find that the potential energy is well described by the harmonic potential $V(h) = \frac{1}{2}kh^2$ with $k \simeq 0.0076 \pm 0.0008$ eV/Å², while the magnitude of the maximum fluctuation in h (approximately 5 Å) corresponds to a variation of the potential

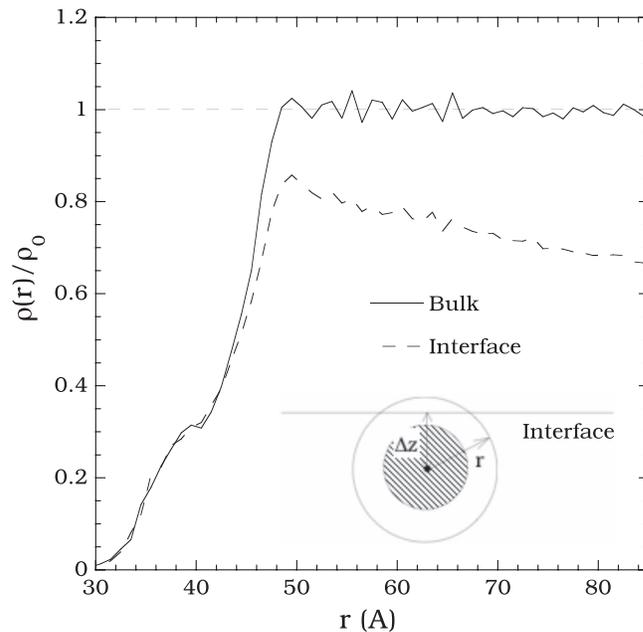


FIG. 2. Calculated radial toluene densities $\rho_i(r)$ and $\rho_b(r)$ relative to bulk toluene density ρ_0 obtained from MD simulations of dodecanethiol-coated 3 nm core radius Au NP in bulk toluene (solid curve) and adsorbed at toluene-vapor interface (dashed curve). Distance of center of NP from interface is $\Delta z = 3.4$ nm.

energy of approximately 0.12 eV. Taking into account the mass m of the NP leads to an estimate of the oscillation period $\tau = 2\pi\sqrt{\frac{m}{k}} \simeq 0.85$ ns which is in good qualitative agreement with our simulation results.

These results can also be used, along with experimental estimates for the NP diffusion length δ , to estimate the activation energy E_a for NP desorption. In particular, assuming transition state theory leads to an expression for the desorption time $\tau_{des} = \tau e^{E_a/k_B T}$. Combining this with experimental estimates⁶ for the thiol-concentration dependent diffusion length ($\delta = \sqrt{2D\tau_{des}}$ where $D \simeq 73 \mu^2/s$ is the estimated NP diffusion coefficient) then leads to estimates for the activation energy ($E_a = k_B T \ln(\delta^2/2D\tau)$) which range from 0.28 eV for low thiol concentration to 0.57 eV at high thiol concentration. It should be noted, however, that since the estimated damping time ($\tau_{damp} = \frac{mD}{k_B T} \simeq 0.04$ ns) due to interaction with the solvent is significantly smaller than the oscillation period τ , the activation barriers are likely to be somewhat lower.

As shown in Fig. 2, we have also calculated the bulk and interfacial radial toluene densities $\rho_b(r)$ and $\rho_i(r)$ (where r is the distance from the center of the NP) surrounding the NP core, corresponding to a NP in the bulk solvent and at the interface respectively. As can be seen, in both cases toluene molecules penetrate close to the NP core. In addition, while the bulk radial density saturates at the bulk toluene density at a distance of approximately 4.9 nm (corresponding to the outer radius of the ligands) the interfacial radial toluene density decreases at large R . However, both the radial bulk and interface density distributions exhibit an inflection point at $r \simeq 4.0$ nm. We speculate that this is due to the fact that at this radius the ligand separation becomes comparable to the lateral size of a

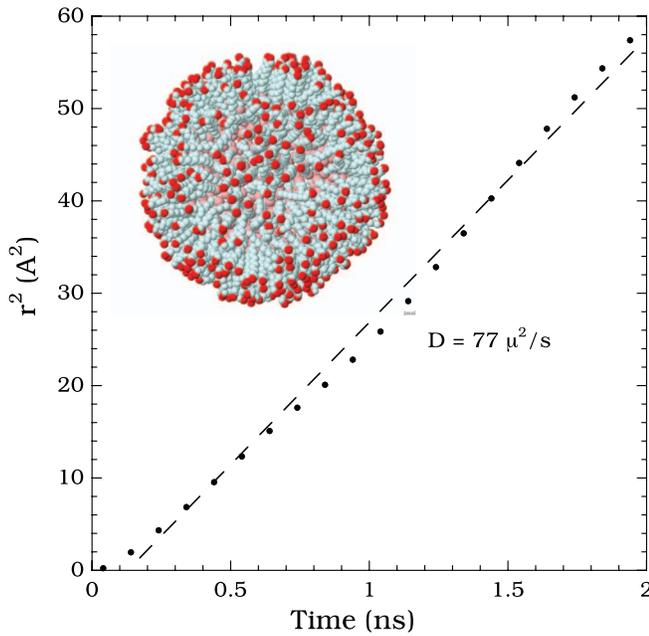


FIG. 3. Mean-square displacement $r^2(t)$ for dodecanethiol-coated 6 nm diameter NP adsorbed at toluene-air interface as function of time. Inset shows structure of ligand-coating (S atoms in pink and CH_3 groups in red).

toluene molecule, thus hindering the diffusion of approaching toluene molecules which are not properly oriented.

One particularly interesting feature of these results is that while the center of the interfacial NP is only 3.4 nm below the interface position (as calculated in the region far away from the NP), the bulk and interface radial densities remain the same up to a radius of approximately 4.2 nm. This may be explained by the fact that – as indicated by a comparison of the toluene density profiles above and away from the NP, and as can also be seen by inspecting the picture shown in Fig. 1 – in the region above the NP the toluene-vapor interface is actually approximately 0.8 nm higher than in the region away from the NP. This result highlights the competition between ligand-solvent mixing (which tends to keep the NP below the interface) and the effects of surface tension.

Since the diffusion of NPs at the interface plays a key role in the island-nucleation process during drop-drying we have also analyzed the NP motion at the interface. Fig. 3 shows our results for the mean-square displacement $r^2(t) = x^2(t) + y^2(t) = 4Dt$ (where D is the diffusion constant) along the interface as a function of time t . From a linear fit, we obtain for the 2D diffusion constant of an adsorbed NP at the interface, $D \simeq 77 \mu\text{m}^2/\text{s}$. We note that this result is in very good agreement with the Stokes-Einstein prediction $D = \frac{kT}{6\pi\eta R} = 73 \mu\text{m}^2/\text{s}$ (where η is the viscosity of liquid toluene) which was calculated in Ref. 6, assuming $R = 5$ nm for the hydrodynamic radius of the NP. The good agreement is most likely due to the fact that the NP remains primarily submerged below the interface, and as a result the diffusion is similar to that of a NP in bulk toluene. We also find no evidence for significant rolling motion. This behavior is in contrast to the “rolling” and anomalous diffusion observed experimentally²⁶ for the case of uncoated NPs in ultrathin (nanometer thick) liquid films.

We have also carried out an analysis of the ligand arrangement surrounding the NP at the interface (see inset of Fig. 3) as well as in the bulk solvent which indicates that the coating shape is only weakly affected by the solvent with relatively little inhomogeneity. This result is consistent with previous results obtained by Lane and Grest⁸ for alkanethiol-coated Au NPs in decane, for which it was found that for small values of the ratio of the coating length to the NP core radius, the distortion of the coating is relatively weak. However, measurement of the aspect ratio of the NP at the interface indicates a slight asymmetry in the overall shape, e.g., the NP is approximately 2% shorter in the vertical direction than in the horizontal direction.

III. VAN DER WAALS INTERACTION

We now consider the effects of the long-range van der Waals interaction between the NP core and the surrounding solvent on the adsorption at an interface.²⁷ As already noted, this interaction has been neglected in our MD simulations as well as in the earlier work by Lane and Grest.⁸ Therefore, it is of interest to determine to what extent the vdW interaction may affect the binding energy and/or adsorption position for a NP at the interface. Using a continuum approach,²⁸ the corresponding interaction may be written as

$$E_{vdW} = -A_{12} \int d^3r_1 \int \frac{d^3r_2}{\pi^2 r_{12}^6}, \quad (1)$$

where 1 corresponds to the NP core and 2 corresponds to the solvent. We note that this expression is expected to be valid for distances r_{12} which are not too small and we assume that the corresponding Hamaker interaction constant A_{12} satisfies $A_{12} = (A_{11}A_{22})^{1/2}$ where A_{11} and A_{22} are the Hamaker constants of the core and solvent, respectively. (For the case of Au NP and toluene solvent we have^{29,30} $A_{11} = 2.8$ eV and $A_{22} = 0.34$ eV which implies $A_{12} = 0.98$ eV.)

For the case of a spherical NP core with radius R_1 , the van der Waals potential energy (per volume of solvent) at a distance R from the center of the sphere is given by²⁸

$$V_{R_1}(R) = -A_{12} \int_{R-R_1}^{R+R_1} dr \frac{R_1^2 - (R-r)^2}{\pi r^5 R}. \quad (2)$$

Carrying out the integral over r one obtains

$$V_{R_1}(R) = -\frac{4A_{12}R_1^3}{3\pi(R^2 - R_1^2)^3}. \quad (3)$$

The van der Waals interaction between a Au NP with core radius R_1 and the surrounding solvent for distances $r > R_2$ from the core center may then be written as

$$E_{out}^{vdW} = \int_{R_2}^{\infty} dR 4\pi R^2 \rho'(R) V_{R_1}(R), \quad (4)$$

where $\rho'(R) = \rho(R)/\rho_0$ is the radial solvent density (relative to the bulk density ρ_0).

If we now assume that the NP is far away from the solvent-vapor interface and that for $r > R_2$ (where R_2 is the radius of the NP coating) the solvent density is equal to the bulk density, which implies $\rho'(r) = 1$, and define the ratio

$\alpha = R_2/R_1$, we obtain for the “outer” interaction between the NP core of radius R_1 and the surrounding solvent for $r > R_2$,

$$E_{out}^{bulk} = -\frac{A_{12}}{3} \left[\frac{2\alpha(\alpha^2 + 1)}{(\alpha^2 - 1)^2} - \ln\left(\frac{\alpha + 1}{\alpha - 1}\right) \right]. \quad (5)$$

As an example, if we consider a 3 nm (core) radius Au NP in bulk toluene, with an outer radius $R_2 = 4.9$ nm (due to the DDT ligands), then the van der Waals interaction energy between the core and this outer solvent region is approximately equal to -1.0 eV.

We now consider the effect of the van der Waals interaction on the interfacial adsorption energy of a Au NP whose center-of-mass is at a distance Δz below the interface. The reduction in the interfacial binding energy due to the van der Waals interaction is

$$\Delta E_{int} = \int_{R_c}^{\infty} [\rho'_b(R) - \rho'_i(R)] 4\pi R^2 |V_{R_1}(R)| dR, \quad (6)$$

where $\rho'_b(R)$ and $\rho'_i(R)$ are the radial toluene densities for a NP in the bulk and at the interface, respectively, R_c is an inner cutoff such that $\rho'_b(R) \simeq \rho'_i(R)$ for $R < R_c$, and $\rho'_b(R) = 1$ for sufficiently large R . For ease of evaluation we may rewrite this in the form

$$\Delta E_{int} = \Delta E_{in} + \Delta E_{out}, \quad (7)$$

where

$$\Delta E_{in} = \int_{R_c}^{R_2} [\rho'_b(R) - \rho'_i(R)] 4\pi R^2 |V_{R_1}(R)| dR \quad (8)$$

corresponds to the contribution near the NP core, which may be calculated using the radial toluene densities $\rho'_b(R)$ and $\rho'_i(R)$ obtained from molecular dynamics simulations, and

$$\Delta E_{out} = \int_{R_2}^{\infty} \cos^{-1}(\Delta z/R) 4R^2 |V_{R_1}(R)| dR \quad (9)$$

corresponds to the contribution far away from the NP where the toluene density below the interface is equal to the bulk toluene density and the toluene density above the interface is equal to zero. As a result, in this region the radial solvent density at a distance R is given by $\rho'_i(R) = 1 - \frac{1}{\pi} \cos^{-1}(\Delta z/R)$.

Using Eq. (8) along with the results for $\rho'_b(R)$ and $\rho'_i(R)$ shown in Fig. 2 and assuming $R_c = 4.05$ nm (corresponding to a value somewhat below the radius at which $\rho'_i(R)$ and $\rho'_b(R)$ begin to diverge) and $R_2 = 8.5$ nm (corresponding to a radius significantly larger than the size of the NP), we find $\Delta E_{in} \simeq 0.26$ eV. Similarly, again taking $R_2 = 8.5$ nm and assuming $\Delta z \simeq 3.4$ nm in Eq. (9), we find $\Delta E_{out} = 0.04$ eV. Combining these results leads to an estimate for the overall reduction of the NP binding energy due to the van der Waals interaction $\Delta E_{int} \simeq 0.30$ eV. We note that this value is comparable to our estimates for the activation energy ($E_a = 0.3$ – 0.6 eV depending on the excess thiol concentration) based on experimental estimates of the diffusion length δ .⁶ Thus, our results indicate that the van der Waals interaction may significantly reduce the binding energy of a NP at the interface and may also increase somewhat the distance Δz of the NP below the interface.

As another example, we consider the case of an 8 nm diameter Au NP coated with decanethiol at the water-vapor

interface which was studied (ignoring the core-solvent interaction) via molecular dynamics simulations in Ref. 8. In this case, due to the hydrophobicity of the decanethiol, the NP sits primarily on top of the interface with only a small portion below the interface. As a result, the outer contribution to the van der Waals correction to the energy in this case may be approximately calculated using the expression

$$\Delta E_{out}^{int} = \int_0^{\pi/2} 2\pi d\theta \sin\theta \int_{R_2}^{R_2/\cos\theta} dR R^2 |V_{R_1}(R)| - \frac{E_{out}^{bulk}(\alpha)}{2}, \quad (10)$$

where the first term corresponds to the missing core-solvent interaction below the center-of-mass of the NP and above the interface in a region between a sphere of radius R_2 touching the interface and the interface, while the second term, given by Eq. (5), corresponds to the missing core-solvent interaction above the center-of-mass of the NP for $R > R_2$. From Ref. 8 we estimate $R_2 \simeq 5.0$ nm (distance from interface to center of NP). Using the Hamaker constant for H₂O, $A_{22} \simeq 0.25$ eV, which implies $A_{12} = \sqrt{A_{11}A_{22}} \simeq 0.7$ eV and $R_1 = 4.0$ nm, we obtain $\alpha = 1.25$ and $\Delta E_{out}^{int} \simeq 2.35$ eV. We note that the dominant contribution here comes from the second term. In addition, due to the large core diameter as well as the fact that the NP is more than halfway out of the water, this outer contribution to the correction to the binding energy is quite large. Thus, in this case it appears that the van der Waals contribution is quite significant. As a result, it is quite possible that the inclusion of the van der Waals interaction in these simulations will significantly reduce the height of the NP above the interface.

The inclusion of the van der Waals interaction also leads to a significant modification to the standard picture of NP adsorption at the solvent-vapor interface. In particular, the competition between the long-range van der Waals attraction between the core and bulk solvent and the short-range attraction between the ligands and the interface leads to the existence of a well-defined activation barrier for interfacial desorption. As an example, we consider the case in which the equilibrium position of the center of the NP is at distance Δz below the interface. As a first approximation, we assume that when $\Delta z = R_{lig}$ (where R_{lig} is the outer radius of the ligands) then the binding energy due to the short-range interaction with the interface decreases to zero. On the other hand, the magnitude of the van der Waals core-solvent interaction increases with Δz , thus decreasing the total energy which leads to the existence of a saddle-point near $\Delta z = R_{lig}$ (see Fig. 4). Thus, the competition between the van der Waals interaction and the short-range interfacial attraction leads to the existence of a well-defined activation barrier for interfacial desorption, as well as a moderate barrier for NP adsorption from the solvent.

While the binding energy of the NP and activation energy E_{des} for desorption are primarily determined by the interaction of the NP with the interface, the activation energy for adsorption from the bulk solvent is primarily due to the loss of core-solvent interaction (compared to bulk) near the

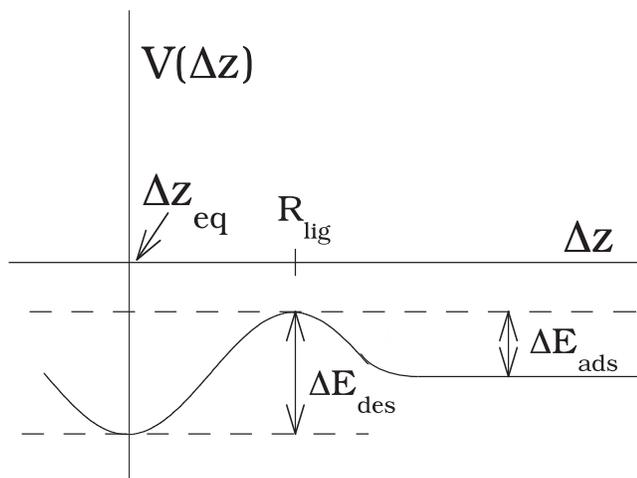


FIG. 4. Diagram showing activation barriers ΔE_{des} and ΔE_{ads} for NP desorption and adsorption.

interface. Accordingly, it may be estimated as

$$\Delta E_{ads} = 2\pi \int_0^{\pi/2} d\theta \sin\theta \int_{R_{lig}/\cos\theta}^{\infty} dR R^2 |V_{R_1}(R)|. \quad (11)$$

Integrating this expression numerically, for the case of a dodecanethiol-coated Au NP with $R_1 = 3.0$ nm (4.0 nm) and $R_{lig} \simeq 4.9$ nm (5.9 nm) with $A_{12} \simeq 1.0$ eV, we obtain $\Delta E_{ads} \simeq 0.09$ eV (0.14 eV). Thus, the core-solvent van der Waals interaction leads to a small but noticeable barrier to nanoparticle adsorption from the solvent. Such a barrier may also play an important role (along with the NP concentration and evaporation rate) in determining the deposition flux in drop-drying experiments.⁶

IV. CONCLUSIONS

We have presented molecular dynamics results, based on the OPLS all-atom potential, for the position, shape, and diffusion of 6 nm core diameter dodecanethiol-coated Au nanoparticles adsorbed at the toluene-vapor interface. Due to the existence of significant intermixing between the ligands and the solvent, we find that the NP lies primarily below the interface with only a portion of the ligands sticking out, while the toluene-vapor interface is somewhat higher in the region above the NP core than away from the NP. These results may be explained by the existence of a competition between the free energy of mixing of toluene and the dodecanethiol ligands, which tends to keep the NP below the interface, and the effects of surface tension, which keeps the NP near the interface. The negative free energy of ligand-solvent mixing is also consistent with the relatively small value of the corresponding Flory parameter as well as the fact that both toluene and dodecane are non-polar molecules. We note that these results lead to a general picture of NP adsorption which is significantly different from the simple geometric picture assumed in Ref. 7, in which the outer ligand shell is treated as a “solid” with no penetration of the solvent inside this shell.

Consistent with our results for NP adsorption, the coefficient for 2D interface diffusion was also found to be in

good agreement with that predicted based on the 3D Stokes-Einstein expression, while no evidence for NP rolling or anomalous diffusion was observed. In addition, we found that, perhaps due to the relatively small ratio of the ligand length to the NP diameter in this case, there is relatively little asymmetry or inhomogeneity in the ligand-coating, either for the NP at the interface or in the bulk solvent. This latter result is consistent with the conclusions in Ref. 8 that the geometric properties dictate when a coating’s spherical symmetry will be unstable and that the chain end group and solvent play a secondary role.

While our MD simulations provide significant insight into the structure and adsorption of Au NPs at the toluene-vapor interface, one issue that should be considered is the accuracy of the OPLS/AA potential. In particular, while the OPLS potential has been shown to give good agreement^{10,11} with experiments for a variety of thermodynamic quantities as well as with *ab initio* predictions for molecular structures – due to the fact that it does not take polarization effects into account – it tends to underestimate the surface tension. This is of particular importance since we expect the primary mechanism for the binding of NPs at the interface to involve surface tension effects. On the other hand, since the binding energy is related to the *difference* in the surface tension of the solvent and ligands, then if the solvent and ligands have similar polarizabilities we might expect that these corrections would cancel out. Such a possibility is supported by the fact that toluene and dodecane have very similar densities and values of the dielectric constant. However, in the future it would be of interest to carry out simulations in which polarization effects are taken into account.

We have also derived general expressions for the strength of the core-solvent van der Waals interaction and its effects on the binding energy of Au NPs at a solvent-vapor interface. In particular, by combining our molecular dynamics results for a dodecanethiol-coated 6 nm diameter Au NP in toluene with analytical results, we have demonstrated that the correction to the binding energy due to the van der Waals interaction can be a significant fraction of the total binding energy. For the case of an 8 nm diameter decanethiol-coated Au NP at the water-vapor interface which was studied via MD simulations in Ref. 8, we have found that the van der Waals correction to the binding energy is even larger. These results also indicate that in the case where the ligands are attracted to the solvent, then for a fixed NP diameter and ligand type, the binding energy of a NP to the interface will increase as the ligand length and distance Δz of the NP core below the interface increase, due to the resulting increase in the long-range core-solvent interaction.

We have also shown that the inclusion of the van der Waals core-solvent interaction leads to a modified picture of NP adsorption at the solvent-vapor interface. In particular, the competition between the long-range van der Waals attraction to the bulk solvent and the short-range attraction to the interface leads to the existence of well-defined activation barriers ΔE_{des} (ΔE_{ads}) for NP desorption (adsorption). For the case of 6 nm (8 nm) core-diameter Au NPs coated with dodecanethiol in toluene, we have estimated ΔE_{ads} and have found that the adsorption barrier is moderately large and increases with

increasing core diameter. In the future, it would be of interest to study the effects of the adsorption barrier on the self-assembly process in drop-drying experiments.

Finally, we note that while it has been previously shown³¹ that the van der Waals interaction can play a significant role in the binding of NPs to form islands, the results presented here indicate that the van der Waals interaction also has a significant effect on the binding energy and position of individual Au NPs at the solvent-vapor interface. Accordingly, we believe that in future simulations of NP adsorption this effect should be explicitly included. One way to do this might be to include an interaction of the form given by Eq. (3) (with some modification for solvent molecules which are very close to the core) between the solvent molecules and the NP core.

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