Critical island-size, scaling and ordering in colloidal nanoparticle self-assembly

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In order to obtain a better understanding of short-range (SR) and long-range (LR) nanoparticle (NP) interactions during the self-assembly of dodecanethiol-coated Au NPs in toluene via drop-drying we have investigated the dependence of the island density, scaled island-size distribution (ISD), and scaled capture-zone distribution (CZD) on coverage, deposition flux, and NP size. Our results indicate that, while the critical island-size is larger than 1 for all NP sizes studied, due to the increase in the strength of the SR attraction between NPs with increasing NP size, both the exponent describing the dependence of the island-density on deposition flux and the critical island-size decrease with increasing NP size. We also find that, despite the existence of significant cluster diffusion and coalescence, the ISD is sharply peaked as in epitaxial growth. In particular, for large NP size, we find good agreement between the scaled ISD and epitaxial growth models as well as good agreement between the scaled CZD and scaled ISD. However, for smaller NPs the scaled ISD is less sharply peaked despite the fact that the critical island-size is larger. This latter result suggests that in this case additional effects such as enhanced island coalescence or NP detachment from large islands may play an important role. Results for the ordering of NP islands are also presented which indicate the existence of LR repulsive interactions. One possible mechanism for such an interaction is the existence of a small dipole moment on each NP which arises as a result of an asymmetry, driven by surface tension, in the thiol distribution for NPs adsorbed at the toluene-air interface. Consistent with this mechanism, we find good agreement between experimental results for the nearest-neighbor island-distance distribution and simulations which include dipole repulsion.

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I. INTRODUCTION

Recently, there has been a lot of interest in the formation of nanostructures via nanoparticle (NP) self-assembly using a variety of non-equilibrium processes ranging from evaporation to dewetting to flows [1–11]. In these studies, the self-assembly process has been found to involve several distinct types of interactions including ligand-ligand [1–3], van der Waals [12–15], magnetic [4] and Coulomb [11] interactions. As a result, a fundamental understanding of NP interactions, in particular at interfaces, is crucial in order to understand the self-assembly process.

One method of particular interest, which has been shown to lead to the formation of highly ordered nanocrystal monolayers [1–3], is the drop-drying of ligand-coated NPs in solution. In particular, in recent drop-drying experiments on 6 nm core-diameter dodecanethiol-coated Au NPs in toluene [3] it was shown that the self-assembly process is controlled by the evaporation kinetics as well as by interactions between the NPs and the solvent-air interface. As a result, the overall island growth rate is determined by a competition between the flux of NPs onto the interface (controlled by the evaporation rate and NP density), NP diffusion due to Brownian motion, and NP desorption from the interface. In particular, it has been found [3] that for sufficiently high NP and excess thiol concentration the diffusion length (corresponding to the typical distance a NP can diffuse before desorbing from the interface) is larger than the typical distance between islands, and as a result all NPs reaching the interface are added to islands.

While these results suggest that in this regime the nucleation and growth of NP islands may be similar to epitaxial growth, it should be noted that there are some major differences. In particular, island diffusion and coalescence are expected to play a much more important role in drop-drying than in epitaxial growth. In addition, long-range (LR) interactions may affect NP island diffusion and ordering at high coverage. In this connection, we note that while the dependence of average quantities such as the diffusion length and average island-growth rate on excess thiol concentration was studied in Ref. [3], the scaling behavior of the island-size distribution and island-density were not studied. An analysis of this scaling behavior provides an important opportunity to obtain a better understanding of the self-assembly process as well as of the short-range and long-range interactions between NPs adsorbed at the toluene-air interface.

Here we present results for the dependence of the island-density on deposition flux and NP size for DDT-coated Au NPs in toluene which we have used to estimate
the critical island-size as well as the strength of the NP interactions at the interface. Our results indicate that, while the critical island-size is larger than 1 for all NP sizes studied, due to the increase in the strength of the short-range (SR) attractive interaction between NPs with increasing NP size, both the exponent $\chi$ describing the dependence of the island-density on deposition flux and the critical island-size decrease with increasing NP size. In addition, we present results for the scaled island-size distribution (ISD) and capture-zone distribution (CZD), and their dependence on NP size. Surprisingly, we find that, despite the existence of significant cluster diffusion and coalescence - which has been previously shown - to dramatically broaden the island-size distribution for the case of a critical island-size of 1 - in our experiments the scaled island-size distribution is sharply peaked as in epitaxial growth. In particular, for large NPs, we find good agreement between the scaled ISD and epitaxial growth models as well as good agreement between the scaled CZD and scaled ISD. However, for smaller NPs the scaled ISD is somewhat broader despite the fact that the critical island-size is larger. This latter result suggests that additional effects such as enhanced island coalescence, NP detachment from large islands, or NP desorption in the early stages of growth may play an important role for smaller NPs.

Finally, we present experimental results for the ordering of NP islands which indicate the existence of a significant LR repulsive interaction. One possible mechanism for such an interaction is the existence of a small net dipole moment $p$ on each NP which occurs as a result of an asymmetry in the distribution of thiols attached to adsorbed NPs. Consistent with this mechanism, we find good agreement between Monte Carlo simulations which take into account dipole repulsion and experimental results for the nearest-neighbor edge-distance distribution between islands. As expected for an interaction which depends on the NP surface area, we also find that the value of $p$ increases with increasing NP size, while for fixed NP size, it decreases with increasing coverage. The corresponding enhancement of island coalescence due to the decrease of the dipole interaction with decreasing NP size also provides a possible explanation for the differences between the experimental ISD and CZD and the predictions of epitaxial growth models for smaller NP sizes.

This paper is organized as follows. In Section II, we provide experimental details for submonolayer dodecanethiol (DDT)-ligated NP island growth. In Sec. III, we first present our results for the dependence of the island density on coverage and for the dependence of the critical island-size on NP size. We then present results for the dependence of the scaled island-size distribution and capture-zone distribution on NP size and compare with epitaxial growth theory. In Sec. III.D and III.E, we discuss the ordering of NP islands and present results for the nearest-neighbor edge-distance distributions obtained from experiment and simulations. Finally, we summarize our results in section IV.

## II. EXPERIMENTAL DETAILS

### Materials

Sodium borohydride (NaBH$_4$) (Alfa Aesar, 98%), gold (III) chloride (AuCl$_3$) (Sigma Aldrich, 99%), dimethyldidodecylammonium bromide (DDAB) (Fisher, 98%), 1-dodecanethiol (Sigma Aldrich, 98%), ethanol (Fisher), and acetone (Fisher) were used without further purification. Toluene (Fisher) was dried using molecular sieves. Single-side polished silicon wafers were obtained from Nova Electronic Materials, Inc.

### Synthesis of nanoparticles

Gold NPs were synthesized according to the Lin et al.[20] protocol. Briefly, 0.156 g of DDAB was added to 15 mL of dry toluene in a 500 mL round-bottomed flask and stirred. Next, 0.052 g of AuCl$_3$ was added into the same flask and sonicated until fully dissolved. While stirring at 800 rpm, 54 $\mu$L of aqueous NaBH$_4$ (9.7 M) solution was added drop-wise to the solution. In about 5 minutes, the yellowish-red AuCl$_3$ solution changed to yellow, then brown-yellow, and finally turned to a purple color after about 10 minutes, indicating formation of polydisperse gold nanoparticles [20]. Once formed, the nanoparticles were ligated by adding 1.2 mL of dodecanethiol (DDT) to the solution and were cleaned by precipitation with ethanol. The precipitate was dried under vacuum.

The broad size and shape distribution was improved by digestive ripening, which produced the spherical and monodisperse nanoparticles required for this study [20, 21]. For digestion, the raw Au NP product was redisolved in 16.2 mL of toluene with 7.4% DDT (v/v) and then heated at 110 °C for 3 hours, which redistributed mass and focused the NP sizes and shapes [1, 20]. After digestion, the solution was kept at 60 °C overnight to allow larger particles to settle [1]. The top half of the solution, containing the most monodisperse NPs, was collected and used for the experiments.

The thiol concentration of the as-synthesized Au NPs was 7.4%. Repeated precipitation with ethanol and redispersion in toluene was used to clean the excess thiol from the solution. This was repeated until the NPs no longer stuck to the air-liquid interface [3]. The excess thiol concentration at this point was assumed to be zero and was then adjusted to suit the needs of the experiment (typically 1 $\times$ 10$^{-3}$ by volume). Before each experiment, the NP solution was centrifuged at 14000 rpm for 7 minutes to remove aggregates and other solids that might be present in the solution.

### Video microscopy

A 50 $\mu$L drop of Au NPs was deposited on a 10 mm × 10 mm Si chip such that the drop was pinned by the edges of the substrate. This was done in an enclosed space to minimize the effect of the surrounding air currents. The drop was then allowed to evaporate under ambient conditions. An Olympus BX-61 microscope was used with an Olympus DP71 digital camera, capable of capturing 1.4 Mpix images at a rate...
of 15 fps. Images were extracted from these videos and analyzed using ImagePro Plus.

We note that due in part to hydrodynamic effects there are surface flows near the edge of the droplet which can lead to inhomogeneities. To minimize these effects, imaging of island formation was done in the center of the droplet. In addition, only regions with relatively uniform island densities and growth rates were studied since this indicated a uniform flux of nanoparticles onto the liquid-air interface.

III. RESULTS

In order to study the dependence of the self-assembly process on NP size, we have carried out experiments for three different NP sizes with Au core diameters $d$ equal to 4.9, 6.0, and 8.0 nm. In most of these experiments the excess thiol concentration was 0.1% by volume fraction while unless otherwise noted the NP concentrations were $3.2 \times 10^{11}/\mu L$, $1.7 \times 10^{11}/\mu L$, and $0.38 \times 10^{11}/\mu L$ for 4.9 nm, 6.0 nm, and 8.0 nm NPs, respectively. Figs. 2(a)-(c) show optical microscopy images of NP islands formed at the toluene-air interface at 3 different coverages ($\theta = 0.1$, 0.28, and 0.44 monolayers or ML) for a NP Au core diameter $d = 6.0$ nm, while Figs. 2(d)-(f) illustrate typical Voronoi cell structures around islands for three different NP sizes at fixed coverage ($\theta = 0.05$ ML). As can be seen, at low coverage the islands are generally compact and circular. On the other hand, at higher coverages the NP islands become somewhat elongated and irregular due to island diffusion, coalescence, and slow relaxation. Such a high island mobility is typically not present in the epitaxial growth of metal/semiconductor islands. This clearly indicates the distinctive difference in submonolayer island growth between the current drop-drying technique and other conventional growth techniques, such as epitaxy, sputtering, and vapor deposition.

A. Dependence of island-density on coverage and NP size

In order to compare with epitaxial growth we have studied the dependence of the island-density on coverage and NP size in the submonolayer regime. As can be seen in Fig. 3(a), for all three NP sizes the coverage increases linearly with time, thus indicating a constant deposition rate or flux as well as the fact [3] that over this coverage range the monomer diffusion length is significantly larger than the typical distance between islands, and as a result, there is minimal monomer desorption.

By analogy with epitaxial growth, we may now define the monomer “hopping rate” $D_h = 4D/a^2$ where $D$ is the monomer diffusion coefficient (which may be approximated using the Stokes-Einstein relation $D = k_B T/6\pi \eta r$ where $\eta$ is the viscosity of toluene and $r$ is the hydrodynamic radius of the NP) and $a$ is the “hopping distance” (assumed to be equal to the nearest-neighbor distance between NPs in a NP island). Assuming $r = 4.45$ nm, 5.0 nm, and 6.0 nm and using the measured values $a = 6.9$ nm, 8.0 nm, and 9.6 nm for 4.9, 6.0 and 8.0 nm diameter NPs respectively, and dividing by the measured flux $F$ in ML/s, leads to values for the dimensionless quantity $R = D_h/F$ corresponding to the ratio of the monomer hopping rate to the deposition flux equal to $5.6 \times 10^8$ for 4.9 nm NPs, $1.5 \times 10^8$ for 6.0 nm NPs, and $4.5 \times 10^8$ for 8.0 nm NPs. We note that these values are roughly consistent with the range of typical values ($R = 10^7 - 10^{11}$) found in epitaxial growth.

Fig. 3(b) shows the corresponding results for the dependence of the island-density $N$ on coverage $\theta$ in ML. As can be seen, the island density decreases with increasing NP size, which is consistent with the increase in the value of $R$ with increasing NP size. In addition, for the largest (8 nm) NP size, the island density remains relatively constant up to a coverage $\theta = 0.3$. On the other hand, for the smaller NP sizes, there is significant coalescence above a coverage of 0.2 ML which leads to a decrease in the island-density with increasing coverage. We note that for both the 4.9 nm and 6.0 nm NPs (see Fig. 3(b)) the dependence of the island-density on coverage can be approximately fit at high coverage using the “percolation-like” form $N(\theta) \sim (\theta_p - \theta)^{0.83}$ where the value of $\theta_p$ ($\theta_p \approx 0.75 - 0.78$) is in good agreement with that obtained for disk percolation ($\theta_p^{\text{disk}} \approx 0.74 - 0.78$) [22].

B. Scaling exponent $\chi$ and critical island size

We now consider the dependence of the island density on deposition flux. One concept which has proved useful in the analysis of epitaxial submonolayer island nucleation and growth [23–29] is that of a critical island size $i$, corresponding to one less than the number of atoms or particles in the smallest stable island (see Fig. 5). In particular, in the case of monomer deposition and diffusion, but in the absence of desorption, cluster diffusion, or a barrier to the attachment of monomers to islands, standard nucleation theory [30] predicts that the island density $N$ in the pre-coalescence regime scales as,

\[ N \sim R^{-\chi} \exp \left[ \frac{E_i}{(i + 2)k_B T} \right] , \tag{1} \]

where $R = D_h/F$ is the ratio of the single-particle (monomer) hopping rate $D_h$ to the (per site) deposition rate or flux $F$, $E_i$ is the binding energy of the critical island of size $i$, $T$ is the substrate temperature and $k_B$ is Boltzmann's constant. For the case of epitaxial growth with isotropic monomer diffusion but no cluster diffusion, standard nucleation theory [30] also predicts $\chi(i) = i/(i + 2)$. We note that at fixed temperature, Eq. 1 also implies that $N(F) \sim F^\chi$.

Fig. 4 shows a log-log plot of our experimental results for the dependence of the island density $N$ on depo-
tion flux $F$ at coverage $\theta = 0.05$ for all three NP sizes. In each case the NP concentration was varied in order to vary the deposition flux [31]. For very small flux ($F < 2 \times 10^{-4}$ ML/s) the island density appears to decrease slightly with increasing deposition flux. However, for larger flux, it exhibits a power-law dependence on flux with an exponent $\chi$ which increases with decreasing NP size. In particular, for 8 nm NPs we find $\chi \approx 0.44$ which is close to the value ($\chi = 1/2$) expected using standard nucleation theory (SNT) for a critical island-size equal to 2, corresponding to a stable trimer in which each NP has at least two nearest-neighbor bonds (see Fig. 5(b)). In contrast, for the 6 nm NP we find $\chi \approx 0.7$ which corresponds using SNT to a significantly larger effective critical island-size ($i \approx 4.7$). This value of $\chi$ is also close to the value ($\chi = 3/4$) expected for a critical island of size 6, which corresponds to one less than the number of NPs in a “magic” [32] island of size 7 (see Fig. 5(c)) in which each NP has at least 3 nearest-neighbor bonds. Finally, for the 4.9 nm NP we find $\chi \approx 1.0$, which corresponds using SNT to a very large (infinite) critical island-size. Table I shows a summary of these results along with the corresponding values of the critical island-size $i$.

We note that these results are consistent with estimates for the dimer binding energy which may be obtained using an effective interaction potential for NPs in toluene which was developed by Khan et al [33], and which takes into account the solubility of dodecanethiol in toluene, the van der Waals attraction [12] between the Au cores, and the ligand-ligand interaction. In particular, applying this potential to the case of 8 nm NPs, a relatively large value of the dimer binding energy ($E_2/k_B T \approx 8.5$ at room temperature) is obtained. This implies that compact islands of size 3 or larger, in which all NPs have at least two nearest-neighbor bonds (corresponding to an activation energy for detachment $E_a/k_B T \simeq 17$ at room temperature) should be relatively stable, thus indicating $i \approx 2$ and $\chi \approx 0.5$. In contrast, the smaller estimated dimer binding energy for 6 nm NPs ($E_2/k_B T \approx 4.7$) is consistent with an effective minimum stable island of size 7 ($i \approx 6$) which implies $\chi \approx 0.75$ in reasonable agreement with experiment. Finally, for 4.9 nm NPs, the estimated dimer binding energy ($E_2/k_B T \approx 3.0$) is sufficiently small that even islands of size 7 are not stable. As a result, the effective critical island size is significantly larger than 6 while the effective value of $\chi$ is close to 1. In this connection we note that the effects of island diffusion and coalescence on the exponent $\chi$ (assuming $D_s \sim s^{-\mu}$ where $D_s$ is the island mobility and $0 < \mu < \infty$) have been studied both for the case of irreversible growth with $i = 1$ [16–18, 34] as well as more recently for higher values of $i$ [35, 36]. In all cases it has been found that, assuming no barrier to island coalescence, the effective value of $\chi$ ranges between a value of 1/2 for small $\mu$ and the standard prediction $i/(i+2)$ for large $\mu$.

For comparison, we consider several other nucleation models which lead to somewhat different expressions for $\chi$ as a function of critical island-size $i$. For example, in the presence of a significant energy barrier for NPs to attach to island edges (corresponding to attachment limited aggregation or ALA) but in the absence of cluster diffusion one has [37, 38] $\chi = 2i/(i+3)$, which implies $i = 1.6$ and 3.0 for 6.0 nm and 4.9 nm NPs respectively (see Table I). However, the ALA value for 4.9 nm NPs is not close to an expected critical island-size, while both values

![Image](image_url)
FIG. 3: (a) Dependence of coverage on time for 3 different NP sizes. For details on growth conditions see text. (b) Corresponding results for the island density $N(\theta)$ as a function of coverage. Solid lines are fits of the form $N(\theta) \sim (\theta - \theta_p)^{0.83}$.

FIG. 4: Island density $N$ as a function of flux $F$ at $\theta = 0.05$ ML for NP sizes of 4.9 nm, 6.0 nm, and 8.0 nm. Solid lines are power-law fits.

are not consistent with our expectation of significant two-bond detachment for these NP sizes. In addition, the ALA value of $i \approx 1$ for 8 nm NPs is not consistent with our expectation, based on estimates [36] of the prefactor and detachment barrier obtained using the Khan et al. potential [33], that dimers are unstable even for 8 nm NPs. Similarly, for the small cluster mobility model [39, 40] or SCM, in which all islands are stable ($i = 1$) but all islands of size $s \leq i^*$ are mobile with the same mobility, while larger islands are immobile, the exponent $\chi_{SCM} = i^*/(2i^* + 1)$. However, this implies a maximum value of $\chi$ ($\chi = 1/2$) which is significantly smaller than that obtained for 6 nm and 4.9 nm NPs.

Finally, in the case of monomer desorption but no cluster diffusion, such that the diffusion length for a monomer is shorter than the typical island separation, Jensen et al. have presented scaling arguments [41] (based on the assumption that the Walton relation [42] holds for $i > 1$ in the presence of desorption) that indicate that $\chi = 2i/3$. However, this implies a minimum value of $2/3$ for $\chi$, along with a value of $4/3$ or higher for larger critical island-size, which is inconsistent with our results for 4.9 nm and 8 nm NPs. Accordingly, we conclude that, while it does not directly take into account the effects of island diffusion and coalescence, standard nucleation theory appears to give reasonable results for the exponent $\chi$.

C. Scaled island and Voronoi cell size distributions

1. Scaling and analytical expressions

We now consider the scaled island-size distribution (ISD) and Voronoi cell or capture-zone distribution (CZD) and their dependence on the NP size. In general we expect that in the pre-coalescence regime, the island-size or area distribution $N_A(\theta)$ (where $N_A(\theta)$ is the density of islands of area $A$ at coverage $\theta$) may be...
written in the scaling form [43, 44],
\[ f(A/A) = N_A(\theta)A^2/\theta, \]
where the scaling function \( f(x) \) is independent of coverage. In the case of epitaxial growth, an expression for the dependence of the scaled ISD on the critical island-size \( i \) proposed by Amar and Family (AF) [45]
\[ f^{AF}(x) = b_ix^i \exp[-ia_ix^{1/a}], \]
(where the constants \( a_i \) and \( b_i \) satisfy the normalization conditions: \( \int [d^{i+1}a] = (ia_i)^{a_i} \) and \( b_i = (\pi a_i)^{i+1}a_i^{i+1} \) has been widely used to compare with epitaxial growth experiments in which cluster diffusion does not play a significant role. We note that this expression implies that the scaled ISD becomes sharper with increasing critical island-size. While more recent work [46–48] (see also Ref. 29) has shown that the scaled ISD also depends on the island morphology, Eq. 3 has been shown to give reasonable agreement with epitaxial growth experiments as well as simulations for critical island-sizes ranging from \( i = 1 \) to \( i = 3 \). However, in some cases (such as organic molecule deposition on semiconductor substrates [49, 50]) in which coalescence due to cluster diffusion is likely to play an important role, it has been found that the scaled ISDs are better described by a Gamma distribution (see Eq. 5) with fitting parameter \( \beta \geq 8 \).–10.

Similarly, the Voronoi cell-size or capture-zone distribution \( n_{A_i}(\theta) \) (where \( n_{A_i}(\theta) \) is the density of islands with Voronoi-cell area \( A_i \) at coverage \( \theta \)) may be written in the scaling form,
\[ C(A_i/A) = \langle A_i \rangle n_{A_i}/N, \]
where \( N \) is the island-density and \( \langle A_i \rangle \) is the average Voronoi area. One form which has been used to fit the scaled CZD in a variety of simulations [51] and experiments [49, 50, 52–55] is the Gamma distribution,
\[ \Gamma_{\beta}(x) = \beta \Gamma(\beta) x^{\beta-1} \exp[-\beta x], \]
where the parameter \( \beta \) satisfies \( \beta = \langle x \rangle^2/\sigma^2 \) where \( \sigma^2 \) is the variance of the size distribution [49]. More recently, Pimpinelli and Einstein [56] have proposed an analytical form based on a generalized Wigner distribution (GWD) [57],
\[ P_{\beta_W}(x) = a_{\beta_W}x^{\beta_W} \exp(-b_{\beta_W}x^2), \]
where the constants \( a_{\beta_W} \) and \( b_{\beta_W} \) are determined by normalization [58] and \( \beta_W = i/\chi \) [59] which implies \( \beta_W = i + 2 \) [60–62] assuming standard nucleation theory.

2. Comparison with experimental results

Figure 6 shows our results for the scaled ISD and CZD for 4.9, 6.0, and 8.0 nm NP sizes, corresponding to the experimental fluxes shown in Fig. 3. As can be seen, in all cases the ISD is sharply peaked despite the existence of significant island diffusion and coalescence. This is in contrast to previous theoretical [16] and simulation [18] results for the case of irreversible island growth \( (i = 1) \) with cluster diffusion and no barrier to island coalescence which indicate the existence of a rapidly decaying distribution with a peak at \( A/A = 0 \) for the case \( D_A \sim A^{-\mu} \) (where \( D_A \) is the mobility of an island of area \( A \)) with \( \mu \leq 1 \). On the other hand, recent simulation results [35, 36] also indicate that for \( i \geq 2 \) the ISD exhibits a well-defined peak near \( A/A = 1 \) even in the presence of significant cluster diffusion and island coalescence. Thus, these results confirm our expectation, based on our analysis in Sec. II.B of the scaling of the island-density with flux, that in all cases the critical island-size is larger than 1.

As shown in Fig. 6(a), there is approximate agreement between the experimental results for the scaled ISD for 8.0 nm NPs and the AF form Eq. 3 for \( i = 2 \). This is consistent with our estimate of the dimer binding energy which indicates that \( i \simeq 2 \), as well as with the experimentally estimated value of \( \chi \simeq 0.44 \) which is close to 1/2. On the other hand, perhaps due to small-island coalescence (which is not taken into account in Eq. 3) the experimental scaled ISD is shifted slightly to the left, with a peak at \( A/A < 1 \) while the tail of the ISD does not decay as rapidly.

Fig. 6(d) shows the corresponding results for the scaled capture-zone or Voronoi-cell area distribution. As can be seen, the scaled CZD is somewhat sharper than the scaled ISD. Accordingly, good agreement is found with a Gamma distribution but with a higher value of \( \beta \) (\( \beta \simeq 8.0 \)). We note that this value is similar to that which has been found for the case of organic molecule deposition on semiconductor substrates [49, 50]. Also shown in Fig. 6(d) are the generalized Wigner distributions (GWDs) with \( \beta_W = i + 2 = 3.6 \) and \( \beta_W = 4 \) (assuming \( i = 2 \)). Both of these distributions give a reasonably good fit to the scaled CZD for 8 nm NPs, although the one for \( i = 2 \) gives a somewhat better fit. On the other hand, the GWD with either \( \beta_W = 1.8 \) (corresponding to \( i = 0.8 \) assuming ALA) or \( \beta_W = 8.4 \) (corresponding to \( i = 3.7 \) assuming SCM) do not give good agreement with the experimental CZD and so are not shown. We thus conclude that for 8.0 nm islands, both the CZD and the ISD are consistent with \( i \simeq 2 \) as expected from standard nucleation theory, but are inconsistent with the values of the critical island-size expected in the case of ALA or SCM. In addition, we note that the relatively good agreement between the scaled ISD and the scaled CZD suggests that for 8.0 nm NPs the CZD plays a key role in determining the ISD and that island-coalescence plays a relatively minor role at low coverage.

In contrast, for 6.0 nm and 4.9 nm NPs, the ISDs are broader and less sharply peaked than for 8.0 nm NPs, and are also broader than the corresponding CZDs. This result is surprising, since in general one expects that for
higher critical island-size both the scaled ISD and the scaled CZD will be significantly sharper. As a result, in this case the AF expression Eq. 3 with the corresponding ALA values \((i = 1.6 \text{ and } 3.0)\) or with the even larger SNT values gives poor agreement with the experimental scaled ISDs. Similarly, the generalized Wigner distribution with \(\beta_W = i + 2\) and the 6.0 nm NP SNT value \(i = 4.7\) as well as the corresponding GWD obtained using the 4.9 nm NP ALA value \(i = 3.0\) or the even larger SNT values also give poor agreement with the experimental CZDs. One possible explanation for this which is also consistent with the discrepancy between the scaled ISD and the scaled CZD, is that, consistent with the results shown in Fig. 3, for 4.0 nm and 6.0 nm NPs, island-diffusion and coalescence play a larger role thus reducing the sharpness of the ISD. Another possible explanation is that due to the weaker binding for 4.9 nm and 6.0 nm NPs, there is significant NP detachment even from large islands, and as a result coarsening effects become important \cite{54}. We note that in this case both the ISD and the CZD are reasonably well described by a Gamma distribution \(\Gamma_\beta(x)\) but with somewhat smaller values of \(\beta\) than for the case of 8.0 nm NPs. Thus, while our results for the scaled ISD and CZD for 8 nm NPs are roughly consistent with standard epitaxial growth theory, there are significant differences for 4.9 nm and 6.0 nm NPs, which indicate that additional processes such as enhanced cluster coalescence or island coarsening may play an important role.
D. Island ordering and nearest-neighbor edge-distance distribution

In order to study the effects of LR interactions, we have also studied the NP island ordering for 6 nm and 8 nm NPs. Fig. 7 shows an optical microscopy image for the case of 6 nm NPs with excess thiol concentration \( f = 0.1\% \) and NP concentration \( c = 7.8 \times 10^{10}/\mu L \) which indicates that at high coverage (\( \theta = 0.51\) ML) the islands tend to order, as can be seen by the fact that each island typically has 6 nearest-neighbors. The corresponding Fast Fourier Transform of the local NP density (see inset) exhibits two well-defined rings, corresponding roughly to the average island distance (inner ring) and average island dimension (outer ring). The six-fold symmetry of the inner ring also indicates the existence of LR orientational ordering.

One possible explanation for this ordering is the existence of island repulsion due to LR interactions, which may also serve to suppress island coalescence. In order to probe the effects of this interaction on the local ordering, we have measured the nearest-neighbor edge-to-edge distance distribution \( P(x) \) surrounding each island during growth. Here \( x \) is the edge-to-edge distance between a central island and its closest neighbor, while \( P(x) \) is the corresponding probability distribution, normalized such that \( \int_0^\infty P(x)dx = 1 \).

As shown in Fig. 8, measurements of \( P(x) \) were carried out for 6 nm NPs at \( \theta = 0.28\) ML and 0.51 ML under the conditions described above as well as for 8 nm NPs at \( \theta = 0.24\) ML with excess thiol concentration \( f = 0.01\% \) and NP concentration \( c = 3.3 \times 10^{10}/\mu L \). We note that in the latter case the island-density \( N = 0.0194 \, \mu m^{-2} \) corresponds to an average island area \( \langle A \rangle = 12.5 \, \mu m^2 \). In contrast, for the 6 nm NPs, the average island area ranged from \( \langle A \rangle = 70.5 \, \mu m^2 \) at \( \theta = 0.28\) ML to \( \langle A \rangle = 104 \, \mu m^2 \) at \( \theta = 0.51\) ML. As shown in Fig. 8(a), the average nearest-neighbor edge distance \( \langle x \rangle \) (corresponding to the peaks in \( P(x) \)) decreases with increasing coverage and is considerably smaller than the expected average edge-to-edge distance \( (3.8 \, \mu m \text{ for } 0.24 \text{ and } 0.51 \, \mu L \text{ data and } 7.6 \, \mu m \text{ for the } 0.28 \, \mu L \text{ data}) \), assuming that the islands are arranged on an ordered triangular lattice. On the other hand, as shown in Fig. 8(b) the scaled distribution \( g(x/\langle x \rangle) = \langle x \rangle P(x) \) is approximately Gaussian and independent of coverage and NP size.

E. Long-range repulsion and comparison with Monte Carlo simulations

One possible mechanism for the LR repulsion between islands is the existence of a small dipole moment on each NP which may arise as a result of an asymmetry in the dodecanethiol distribution surrounding the Au core for NPs at the toluene-air interface. In particular, Hartree-Fock calculations for the case of alkanethiols attached to the Au(111) surface [63], indicate that charge transfer between the S and the Au core will lead to a dipole moment of magnitude \( \sim 0.44 \, eA \) for each dodecanethiol attached to the NP. While the thiol distribution is expected to be symmetric for NPs in solution, thus leading to no net dipole moment, for NPs near the interface we expect that, in order to reduce the surface tension, there will be an excess of dodecanethiols attached to the NP near the interface, thus leading to a net dipole moment per NP which is perpendicular to the interface. The resulting dipole moment leads to a long-range \( 1/r^3 \) repulsion between NPs which, while too weak to significantly affect the NP island binding, leads to a noticeable repulsion between large NP islands.

In order to determine if our experimental results for the nearest-neighbor edge-distance distribution \( P(x) \) may be explained using the assumption of a net dipole moment on each NP, we have carried out Monte Carlo simulations of an idealized system in which for simplicity we have assumed that all islands have the same size and are circular with radius \( R_1 = \sqrt{(A)/\pi} \). We note that the former assumption is a reasonable approximation since the island-size distribution is relatively sharp. Due to the finite-size of the NP core, we expect that an asymmetric thiol distribution may also lead to a small net quadrupole moment. However, for simplicity we have neglected this effect in our simulations.

Using this model we have carried out simulations corresponding to the three different experimental cases shown in Fig. 8 and in each case have adjusted the value of the dipole moment in order to fit the corresponding experimental nearest-neighbor island-distance distribution \( P(x) \). Our simulations were carried out using systems with 25 – 49 islands and periodic boundary conditions, while the system was initialized by placing the islands on a regular triangular lattice with lattice spacing \( a_{lat} = (\langle A \rangle/\sqrt{3} \theta)^{1/2} \) where \( \theta \) is the measured coverage. The island-densities and average island area were the same as in the experiments.

Since for the relatively large island-sizes used in these experiments the time for island growth is much longer than the typical time for ordering and equilibration as well as the typical observation time used to measure the nearest-neighbor edge-to-edge distribution, island-growth was not taken into account in our simulations. Accordingly, in our Monte Carlo simulations, we used the Brownian dynamics method described in Ref. [64] in which the displacement \( \delta r \) of each island after a time \( \delta t \) is given by the Gaussian distribution,

\[
P(\delta r, \delta t) = \frac{1}{4\pi D \delta t} e^{-|\delta r - \mathbf{F}_{ext} \delta t/\gamma|^2/(4D \delta t)}
\]  

where \( D \) is the island diffusion coefficient, \( 1/\gamma = D/(k_B T) \) and \( \mathbf{F}_{ext} \) corresponds to the net force on each island due to the dipole and van der Waals interaction with all of the other islands. Typical values used in our simulations were \( D = 0.01 \, \mu m^2/s \) and \( \delta t = 0.01s \), while averages were typically taken by first equilibrating for \( 10^8 - 10^9 \) Monte Carlo steps (where one Monte
The solid line is a Gaussian fit with the values of $\sigma$ as, interaction energy between two islands may be written $F$ than the NP size, in order to calculate the total force contributions were not affected. Diffusion coefficient and, as expected, the simulated distributions were not affected.

Scaled nearest-neighbor edge-distance distribution $g(x/\langle x\rangle)$ and 0.51 ML data and 7.6 $\mu$m for 0.24 ML data. (b) Scaled nearest-neighbor edge-distance distribution $g(x/\langle x\rangle)$. The solid line is a Gaussian fit with the values of $\sigma(\theta)$ and $\langle x\rangle$ determined from experimental data for $\theta = 0.24$ ML.

FIG. 8: (a) Comparison between experimental results (symbols) for normalized nearest-neighbor edge-distance distribution $P(x)$ with simulation results (solid and dashed curves) based on assumption of a net dipole moment of magnitude $p$ on each NP (see text). Filled symbols correspond to 6 nm NP experiments while open symbols correspond to 8 nm NP experiments. Note that if islands were arranged in an ordered lattice the edge-to-edge distances would be 3.8 $\mu$m for 0.24 and 0.51 ML data and 7.6 $\mu$m for the 0.28 ML data. (b) Simulations were carried out with somewhat higher and/or lower values of the island diffusion coefficient and, as expected, the simulated distributions were not affected.

Since the island-sizes and distances are much bigger than the NP size, in order to calculate the total force $F_{\text{ext}}$ on each island due to dipole repulsion we have used a continuum approach. Using this approach the dipole interaction energy between two islands may be written as,

$$U_{\text{dip}}(l) = \frac{p^2}{4\pi\kappa\epsilon_0} n^2 I(l),$$

where $\kappa = 2.38$ for toluene [65, 66], $p$ is the dipole moment per NP, $n$ is the NP density per unit area in an island [67], and

$$I(l) = \int \int \frac{d^2 r_1 d^2 r_2}{|r_1 - r_2|^3}$$

where the integrals are over each island and $I(l)$ depends on the center-to-center distance $l$ and island radius $R_1$. The net force $F(l)$ may then be obtained by differentiating Eq. 8 with respect to $l$, and numerically evaluating either Eq. 9 or its derivative (for details see Appendix).

FIG. 8(a) shows a comparison between the experimental and simulation results. As can be seen, despite the simplifying assumptions of our model, relatively good agreement between the experimentally measured nearest-neighbor edge-distance distributions and simulations may be obtained by assuming a small net dipole moment $p$ on each NP which is oriented normal to the interface. In addition, the values obtained for $p$ are consistent with the expected value of the dipole moment per thiol (approximately 0.44 e$\cdot$Å) combined with a reasonably small number of “excess” thiols (on the order of 10 – 35) on the “top” of the NP (e.g. at the interface) [68, 69]. However, the magnitude of the dipole moment appears to decrease with decreasing NP radius as well as with increasing coverage for fixed NP radius. The smaller value of $p$ for 6 nm NPs compared to 8 nm NPs is consistent with the expectation that there will be a smaller number of attached thiols per NP, due to the decreased surface area and number of attachment sites in this case. In contrast, the decrease in the dipole moment with increasing coverage for 6 nm NPs may be explained by the fact that as the toluene evaporates the excess thiol concentration increases and as a result there will be more thiols attached to the bottom of the NP, thus reducing the asymmetry. We note that the values of $p$ obtained from our simulations are sufficiently small that they have a negligible effect on the island binding-energies (which are dominated by the attractive van der Waals and ligand-ligand interactions) and also lead to negligible repulsion for small islands. Thus, our simulation results indicate that the observed nearest-neighbor edge-distance distributions are consistent with the existence of a small net dipole moment on each NP which is due to the asymmetry in the attachment of thiols on NPs at the interface.

IV. DISCUSSION

In order to gain a better understanding of the effects of nanoparticle interactions and growth conditions on colloidal Au nanoparticle self-assembly, we have studied the dependence of the island density, island-size distribution, and capture-zone distribution on NP size, excess thiol concentration, coverage, and deposition flux, and have compared our results with existing theoretical results for submonolayer epitaxial growth. We have also studied the ordering of NP islands at high coverages and compared with Monte Carlo simulations.

For the case of 8 nm NP islands we found many similarities with epitaxial growth. In particular, in this case we found that the dependence of the island-density on flux leads to a value for the flux-density scaling expo-
nent which is roughly consistent with a critical island size equal to 2, corresponding to stable trimers. This result is also consistent with the relatively large estimated dimer binding energy for saturated 8 nm DDT-coated Au NPs in toluene ($E_d/k_B T \approx 8.5$ at room temperature) obtained using the potential of Khan et al [33], which indicates a relatively small detachment rate for compact islands with 3 or more NPs.

In addition we have found that for 8 nm NP islands, the island-density stays constant up to a relatively high coverage ($\theta \approx 0.3$ ML) thus indicating that coalescence plays a relatively minor role over this coverage range. Accordingly, the scaled island-size distribution (ISD) is in relatively good agreement with the Amar-Family expression [45] for the case of epitaxial growth with critical island-size $i$ equal to 2. In this case there is also relatively good agreement between the scaled capture-zone distribution and the scaled ISD. The latter behavior is also consistent with experiments [49] on vapor deposition of pentacene on SiO$_2$ at high deposition rate for which there was negligible desorption, as well as with experiments on InAs/GaAs growth [54] at temperatures such that there was relatively little detachment from islands. Due to the high binding energy and activation barrier for desorption, both of these conditions are expected to be the case for 8 nm NP islands. We also find reasonable agreement between the generalized Wigner distribution prediction with $\beta_W = i + 2 = 4$ for the scaled CZD and the experimental distribution, in good agreement with epitaxial growth models. On the other hand, a gamma distribution (with fitting parameter $\beta \approx 8$) appears to give the best fit with the experimental scaled CZD.

In contrast, for 4.9 nm and 6 nm NP islands, we have found that island coalescence becomes important at somewhat lower coverage, and as a result the island-density decreases noticeably over the coverage range $\theta = 0.1 - 0.3$ ML. In addition, due to the smaller binding energy for 4.9 nm and 6 nm NPs, the effective value of the flux-density scaling exponent ($\chi \approx 0.7 - 1.0$) is significantly larger than for 8 nm NPs. These results are consistent with calculations of the dimer binding energy which we have carried out using the potential of Khan et al [33] which indicate that both one-bond and two-bond detachment are significant for 4.9 nm and 6 nm NPs. For 4.9 nm NPs this leads to a significant detachment rate even for islands larger than the “magic” cluster size of 7, thus indicating an effective critical island-size larger than 6.

Somewhat surprisingly, we have found that the scaled ISD for 4.9 nm and 6 nm NP islands is less sharply peaked than for 8 nm NP islands and is also significantly less sharply peaked than expected for such a large critical island-size. As a result, while the scaled CZD is similar to that obtained for 8 nm NP islands, there is a significant difference between the scaled ISD and the scaled CZD in this case. One possible explanation for the relatively broad ISD is that, due to the relatively small NP size (which leads to less dipole repulsion between islands) there is significantly more island coalescence. The increased island coalescence in the nucleation regime tends to smear out the peak near $A/(A) = 1$ in the island-size distribution, in a manner similar to that which was previously found in simulations of irreversible island growth ($i = 1$) with cluster diffusion [18, 19]. In addition, due to the weaker binding in this case, there is significant NP detachment from large islands, and as a result we expect that coarsening effects [70] may also play a role [54].

In addition to the scaling of the island density and island-size and capture-zone distributions, we have also studied the effects of long-range interactions on island ordering. In particular, both the LR orientational ordering observed for 6 nm NP islands at high coverage as well as for our results for the nearest-neighbor edge-distance distributions for 6 nm and 8 nm NP islands, indicate the existence of a repulsive interaction between islands. One possible mechanism for this repulsion is the existence of a small dipole moment on each NP which arises as a result of an asymmetry, driven by surface tension, in the thiol distribution for NPs adsorbed at the toluene-air interface. While such a dipolar interaction leads to a repulsion between NPs which is negligible at short distances compared to the van der Waals and ligand-ligand interaction, due to the fact that it decays more slowly than the van der Waals interaction, for large islands it can lead to significant island repulsion at large distances.

The existence of such a dipolar interaction is supported by the fact that the value needed to obtain good agreement with the experimental nearest-neighbor edge-distance distance distributions corresponds to a relatively small asymmetry (on the order of 10 – 35) between the number of thiols on the “top” of the NP and on the bottom of the NP. The larger dipole moment obtained for 8 nm NPs compared to 6 nm NPs is also consistent with this picture, while the decrease in the dipole moment with increasing coverage is consistent with the expected reduction in thiol asymmetry as the excess thiol concentration increases due to droplet evaporation. The decrease of the strength of the repulsive interaction with decreasing NP size is also consistent with our experimental observations that there is significantly more island coalescence for 4.9 nm and 6.0 nm NP islands than for 8.0 nm NP islands.

Finally, we note that while our analysis of the self-assembly process has focused primarily on NP interactions, some additional factors may also play a role. In particular, as already noted in Sec. II, due to hydrodynamic effects, during the drop-drying process there are interfacial flows along the droplet surface. While we expect that in the early stages of island nucleation and growth the diffusion of small clusters will be dominated by Brownian diffusion, these flows or inhomogeneities may significantly enhance diffusion for larger clusters, and thus contribute to the non-thermal coalescence of large islands. Accordingly, the estimate of the NP dipole moment obtained from our Monte Carlo simulations may actually be a lower bound.

In conclusion, we find that both SR and LR interac-
tions play an important role in NP island self-assembly, while the strength of these interactions increases with NP size. In particular, the short-range attractive ligand-ligand and van der Waals interactions determine the critical island-size, while long-range repulsive interactions affect the later stage island-ordering and coalescence. As a result, the scaling of the island-density, ISD, and CZD as well as the NP island ordering all depend significantly on NP size. In the future, it would be of interest to carry out more detailed simulations of island nucleation and growth which take these interactions into account, in order to understand in more detail the process of NP self-assembly.

Appendix A

While Eq. 9 may be directly evaluated numerically as a function of center-to-center separation \( l \), it is convenient to first reduce it to two one-dimensional integrals using methods similar to those used in Ref. 12. In particular, the \( 1/r^3 \) interaction between a point \( P \) on circular island 2 (which is a distance \( R \) away from the center of circular island 1, see Fig. 9) and all of the points of island 1 which are a distance \( r \) away may be written as \( 2\pi d\theta P \), where \( \theta \) is defined as the half-angle at a point which is a distance \( x \) from the center of a disk of radius \( R \), corresponding to an arc of radius \( y \) passing through the disk. Integrating over all possible values of \( r \) for each \( R \), and then integrating over all possible values of \( R \), we may write,

\[
I(l) = \int_{-l}^{l+R_1} dR \int_{-R}^{R+R_1} dR' \int_{-R}^{R+R_1} dR'' \left( \frac{2r\theta P}{r^3} \right)
\]

which implies \( \theta(l, R) = \cos^{-1} \left( \frac{R^2 + R'^2 - R''^2}{2RR'} \right) \) and \( \theta(R, r) = \cos^{-1} \left( \frac{R^2 + r^2 - R'^2}{2Rr} \right) \). Converting to dimensionless variables \( u = R/R_1, v = r/R_1, \alpha = l/R_1 \) with \( \beta^2 \equiv 1 - u^2 \), we obtain,

\[
I(l) = 4R_1 \int_{-1}^{1} du \int_{-1}^{1} dv \cos^{-1} \left( \frac{\alpha^2 - \beta^2}{2\alpha v} \right) \left( \frac{\alpha^2 - \beta^2}{2\alpha v} \right)
\]

The net radial repulsive force on a disk of radius \( R \) due to another disk of radius \( R_1 \) which is a distance \( l \) away, is then given by,

\[
F(l) = -\frac{p^2}{4\pi\kappa\epsilon_0} \frac{J(\alpha)}{R_1} \frac{\partial I(l)}{\partial \alpha}
\]

which may be rewritten as,

\[
F(l) = \frac{p^2}{4\pi\kappa\epsilon_0} \frac{J(\alpha)}{R_1}
\]

where

\[
J(\alpha) = \int_{-1}^{1} du \int_{-1}^{1} dv \cos^{-1} \left( \frac{\alpha^2 - \beta^2}{2\alpha v} \right)
\]

As noted in the text a similar approach may be used to calculate the van der Waals force between two circular NP islands of radius \( R_1 \) as a function of their center-to-center distance \( l \). However, for the separations of relevance in our simulations this contribution is negligible since the van der Waals attraction decays much more rapidly at large distances than the dipole repulsion.

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[25] NP concentrations ranged from 5.5 × 10^{10} /μL to 3.2 × 10^{13} /μL for 4.9 nm NPs, 1.7 × 10^{10} /μL to 1.8 × 10^{11} /μL for 6.0 nm NPs, and 2.5 × 10^{10} /μL to 7.0 × 10^{10} /μL for 8.0 nm NPs.
[53] a_{βW} = 2Γ(\frac{2w+1}{2})^{\frac{3w+1}{2}}/Γ(\frac{2w+1}{2})^{\frac{3w+2}{2}} and b_{βW} = \frac{\Gamma(\frac{2w+1}{2})}{\Gamma(\frac{2w+1}{2})}^{2}.
Here we have assumed that the NPs are completely submerged in toluene. This is consistent with the results of molecular dynamics simulations [66] which indicate that the Au core remains submerged below the toluene-air interface.