Modeling and Simulating Gold Nanoparticle Interactions on a Liquid-Air Interface

Jennifer Jin[1] and Dr. Jacques Amar[2]

[1]Mary Baldwin College, [2]Department of Physics & Astronomy, University of Toledo

I.   Introduction

Gold nanoparticles suspended in an evaporating toluene droplet move and collect on the surface of the toluene droplet, eventually forming a nanostructure. The ways in which these nanoparticles interact with each other, the air, and the toluene are not known but are crucial for developing self-assembling gold nanostructures [1]. Previous simulations of the gold nanoparticles on the surface of the toluene droplet have not shown agreement with the experimental results [2]. When an energy barrier to nanoparticle coalescence calculated from summing Van der Waals attraction and dipole-dipole repulsion between nanoparticle islands is taken into consideration, the simulation results agree much more strongly with experimental results, thus showing that the effects of attraction and repulsion between gold nanoparticles in an evaporating toluene droplet are not negligible in real-world experiments [1].

II.   Model and Simulations

A code written by Yevgen A. Kryukov utilized Kinetic Monte Carlo simulations to simulate gold nanoparticles on the liquid-air interface of the surface of the toluene droplet. The code uses a model where the gold nanoparticles were perfectly circular particles with a diameter of 6 nm. The quasi-two-dimensional curved surface of the toluene droplet is represented by a two-dimensional triangular lattice upon which monomers, or nanoparticle islands containing only one nanoparticle, are deposited. The deposition of monomers onto the triangular lattice represents gold nanoparticles in the droplet moving to the surface of the droplet as the toluene evaporates. If any of the gold nanoparticle islands' perimeters overlap, those nanoparticle islands then coalesce into a bigger circular nanoparticle island containing the sum of the nanoparticles in

both parent nanoparticle islands. Nanoparticle islands move on the lattice with varying rates depending on the size. The diffusion rate, D_s, is affected by the diffusion exponent µ with the rate $D_s \sim s^{-\mu}$. A µ=1/2 corresponds with uncorrelated evaporation condensation or Brownian (Stokes-Einstein) diffusion of two-dimensional nanoparticle islands, and a µ=1 suggests that the nanoparticle island diffusion is due to correlated evaporation condensation or friction proportional to surface area. In addition, nanoparticle islands smaller than or the same size as the critical island size, i, had monomers detach from the cluster. Islands larger than the critical island size are "stable" with no monomer detachment. Taking into account the fact that gold nanoparticles display triangular ordering, the simulations described in this paper use the parameters i=6 and i=2 (Figure 1) [2].
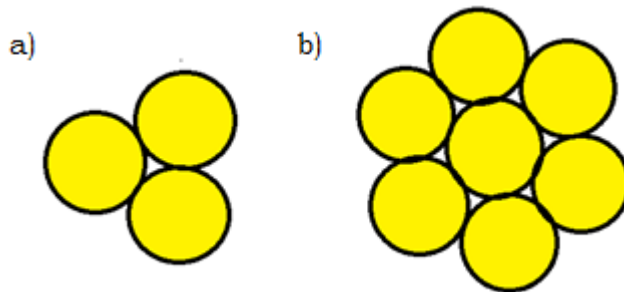

Figure 1. The smallest stable nanoparticle islands for i=2 (cluster a) and i=6 (cluster b).

The changes made to the code added Van der Waals attraction and dipole-dipole repulsion between the nanoparticle islands. Due to the way that the gold nanoparticles in the experiment were synthesized, the gold nanoparticles were covered with dodecanethiol ligands. A dipole bond between gold and sulfur attaches these ligands to the nanoparticle. Normally when the nanoparticle is inside the toluene droplet, it is surrounded on all sides by toluene and is neutral overall due to the dipoles on the nanoparticle cancelling out. On the surface of the toluene droplet, however, asymmetry of the ligands on the nanoparticle causes a net dipole

moment to form on the nanoparticle. Thus, long-range repulsion occurs between two gold

nanoparticle islands [1]. Van der Waals attraction occurs between nanoparticle islands due to

induced temporary dipoles. The Van der Waals attraction's range, $1/r^6$, is much shorter than the

dipole-dipole repulsion force's range, $1/r^3$, so dipole-dipole repulsion acts at longer distances

between nanoparticle islands than Van der Waals attraction. The sum of the total Van der Waals

forces and dipole-dipole repulsion between nanoparticle islands became an energy barrier that

the nanoparticle islands had to overcome before coalescence occurred [3].

Kinetic Monte Carlo simulations determine what action to perform based on random

numbers and probabilities of events calculated from the event's rate. The actions performed by

the simulation are diffusion, deposition, detachment, and coalescence. The rate of diffusion is as

mentioned above related to the size of the nanoparticle island by the diffusion exponent μ with

the rate $D_s \sim s^{-\mu}$. When the nanoparticle island contains fewer or exactly the critical island size i

number of gold nanoparticles, a probability for detachment is calculated [2]. The rate of

coalescence is determined by calculating a probability using an energy barrier equation that

calculated the sum of the dipole-dipole repulsion and Van der Waals attraction between two

nanoparticle islands. Of the two nanoparticle islands, if either are comprised of more than 125

nanoparticles $(s > 125)$, Equation 1 would be used for the energy barrier to coalescence.

$$eb = \frac{s_1(0.0044864s_2{}^{0.45403} - 0.024156)}{s_1 + \frac{s_2{}^{0.75769}}{0.61159}} \quad (1)$$

If both nanoparticle islands' sizes s_1 and s_2 are smaller than 125, Equation 2 would be used

instead.

$$eb = \frac{\frac{0.1231s_2 \cdot s_1}{730.91 + s_2}}{\frac{s_2{}^{0.65526}}{0.44332} + s_1} \quad (2)$$

In both equations, s_2 is the size of the larger nanoparticle island, and s_1 is the smaller

nanoparticle island size. Equations 1 and 2 were found by fitting a line to data from a code that

calculated the Van der Waals attraction and dipole-dipole repulsion between two nanoparticle

clusters of varying size and summed the two forces. The prefactor in the coalescence probability

formula suppresses the likelihood of coalescence. In the simulations performed, four different

coalescence probability formulas were used, shown in equations 3-6.

$$coalprob = 0.1 \cdot e^{\frac{-4 \cdot eb}{k \cdot t}} \qquad (3)$$

$$coalprob = 0.1 \cdot e^{\frac{-8 \cdot eb}{k \cdot t}} \qquad (4)$$

$$coalprob = 0.3 \cdot e^{\frac{-2 \cdot eb}{k \cdot t}} \qquad (5)$$

$$coalprob = 0.3 \cdot e^{\frac{-eb}{k \cdot t}} \qquad (6)$$

A nearest-neighbor table is utilized in the code for tracking nanoparticle islands likely to

trigger a coalescence event, and a coarse-grained binary tree is used to sort and select diffusion

probabilities for different size nanoparticle islands [2].

III.   Results

Island size distributions (ISDs) simulated with Van der Waals attraction and dipole-

dipole repulsion taken into account are closer to the ISDs seen in experiments [1]. The barrier to

coalescence sharpens the ISD peak and shifts the center of the peak to the left to around 1
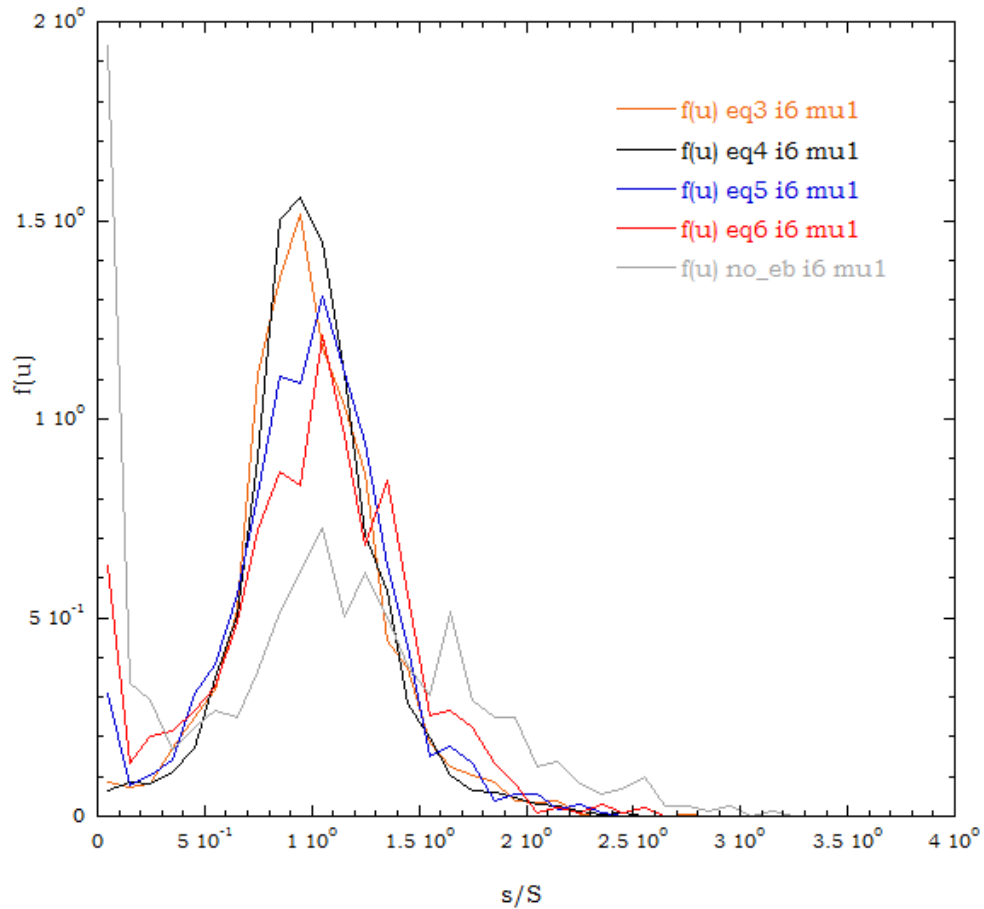
(Figure 2).

Figure 2. Graph comparing the ISDs of the simulations of the four different coalescence

probability formulas (Eq. 3-6) and the ISD of the simulation where the coalescence probability

does not take into account the energy barrier. All simulations were performed on a 2048 by 2048

lattice with a critical island size i of 6 and the diffusion exponent μ equal to 1.

A diffusion exponent μ=½ makes the ISD sharper with a higher peak than μ=1, so the

experimental results, which has a peak of about 0.8, agrees more with μ=1 and diffusion due to

correlated evaporation condensation (Figure 3). The exact difference between the ISD peaks of

simulations with μ=1 and μ=½ cannot be determined from just these simulations because of

fluctuation between different simulations possibly playing a role.

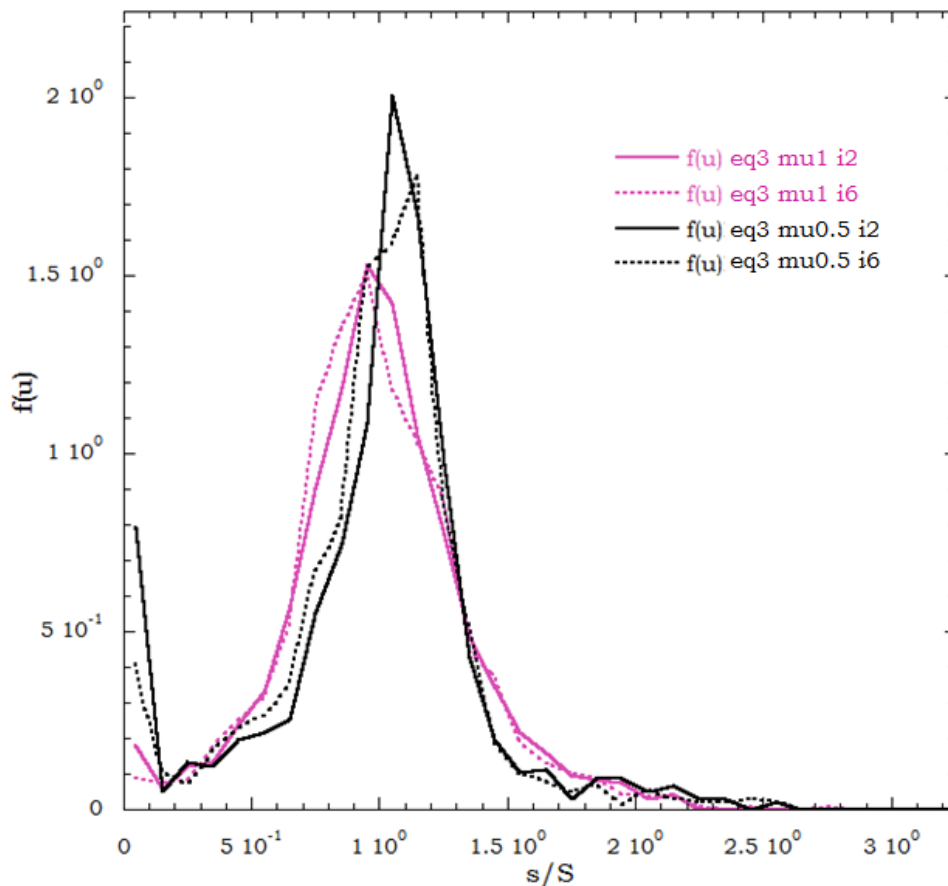Figure 3. Graph comparing ISDs of simulations with differing critical island sizes and either diffusion exponent μ equal to 1 or ½. The dashed lines represent the ISDs of the simulations with $i=6$, whereas the solid lines represent the ISDs of the simulations with $i=2$.

Changing the critical island size from 6 to 2, which would make trimers stable instead of a cluster with seven nanoparticles, does not seem to affect the ISD very much as the variance in ISD between simulations with different i can be attributed to fluctuations due to the kinetic Monte Carlo simulations using random numbers (Figure 4).
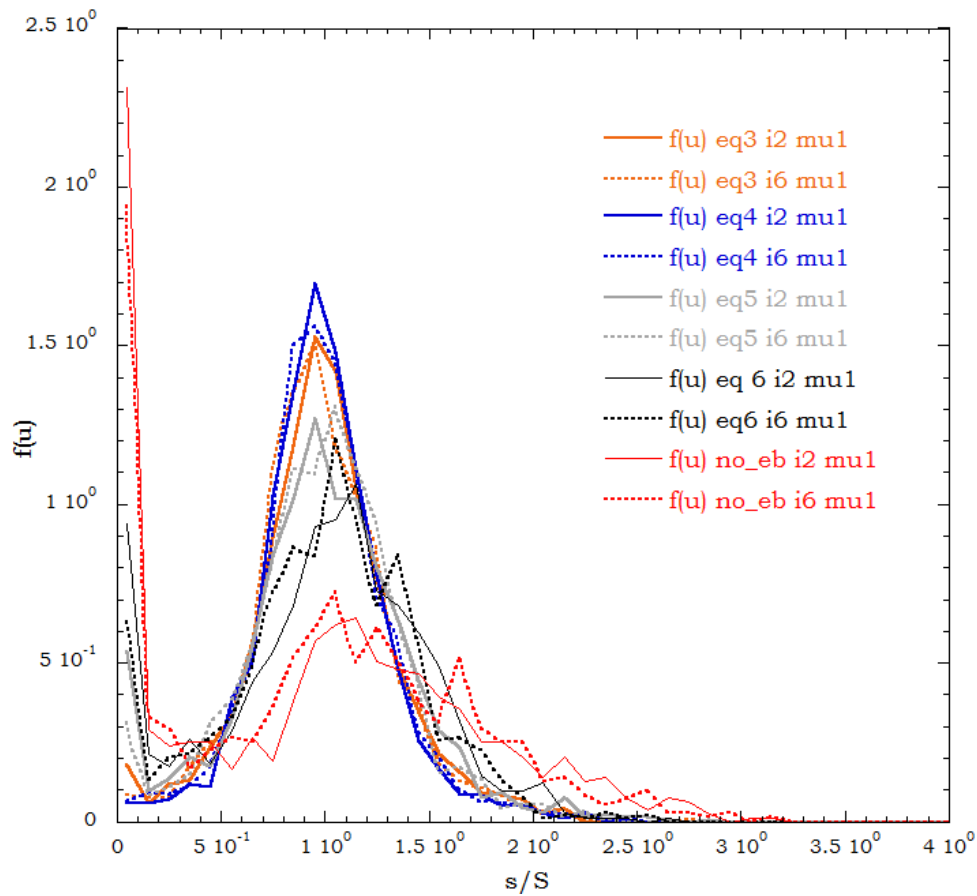
Figure 4. Graph comparing the ISDs of simulations with different coalescence probability formulas and critical island sizes. The dashed lines represent the ISDs of the simulations with i=6, whereas the solid lines represent the ISDs of the simulations with i=2. Dashed and solid lines of the same color have the same coalescence probability.

The ISDs produced by different trials of simulations with the same parameters fluctuate (Figure 5). The fluctuation in ISD between trials are due to the kinetic Monte Carlo code using random numbers to decide if events occur or not in the simulation, meaning that multiple trials should be run and the ISDs averaged to smooth out the ISD and reduce fluctuation.
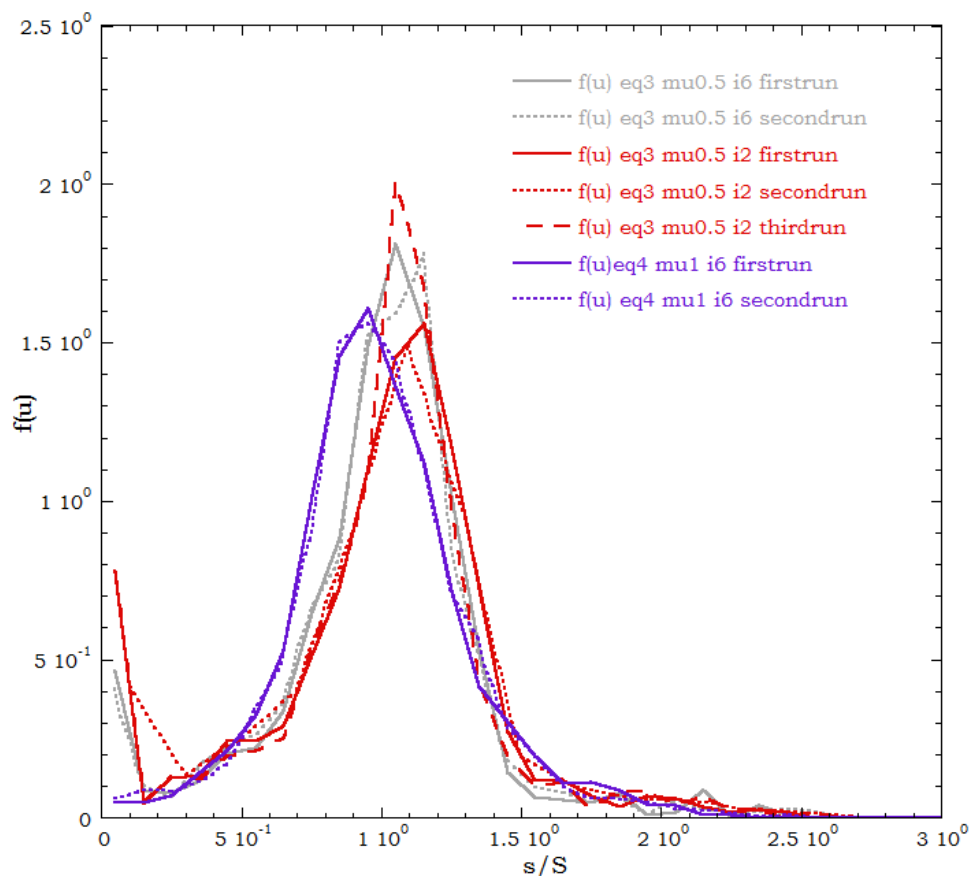
Figure 5. Graph comparing the ISDs for multiple runs of the same simulation parameters for three different parameter sets. The ISDs with the same color have the same parameters applied in the simulation.

IV.   Discussion/Conclusion

Previous simulations of gold nanoparticles on the surface of an evaporating toluene droplet that consider only diffusion, coalescence, and detachment lead to ISDs that do not agree with experimental ISDs. Inclusion of an energy barrier in the probability of nanoparticle island coalescence causes the simulation results to agree much better with the experimental results than previous simulations. In addition, the magnitude of the dipole-dipole repulsion between nanoparticle islands is consistent with observed island-ordering and edge-edge distance distribution. Thus, considering dipole-dipole repulsion and Van der Waals attraction between

nanoparticle islands, as well as anomalous diffusion, will help explain the experimental sharply peaked ISDs. Parameters in the simulation, such as μ and i, also aid in understanding the exact movement of gold nanoparticles. Changing μ from 1 to ½ raises and sharpens the ISD peak, suggesting that gold nanoparticles diffusing with Brownian (Stokes-Einstein) motion or uncorrelated evaporation condensation tend to clump together in relatively more same-size islands than nanoparticles moving due to correlated evaporation condensation or friction proportional to surface area. On the other hand, changing i does not seem to change the ISD in a meaningful manner.

References

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