Simulation of Aggregation of Surfactants in Hydrocarbon-Water Interfaces Utilizing Diffusion Limited Cluster Aggregation (DLCA) Model

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The purpose of this paper is to study the aggregation of surfactants in the interface while observing the structure of these agglomerates. When studying the structure of the agglomerates one has to observe the fractal dimension, center of mass, coordination number for the particles in the final cluster, as well as the correlation function and the radius of gyration. Along with this it has been shown that these clusters are incredibly unstable when they percolate the system, and for that reason one has to study the probability of percolation as the density of particles increases. To study these characteristics and how they evolve as the density of the particles increases in the system a Diffusion Limited Cluster Aggregation (DLCA) simulation has be created to observe the final results of the aggregation of particles in the system. For this we have created an algorithm that, utilizing the characteristics of DLCA, creates a complete cluster, measures the fractal dimension utilizing two methods, calculates the center of mass, the coordination number, as well as calculate the radius of gyration for small clusters. These results have shown that the DLCA simulations give the the expected values of fractal dimensions, they show that the fractal dimension at low densities is constant and as the density increases the agglomerates tend towards the percolating regime. Along with this a cluster with a restriction where the coordination number for any particle cannot be higher than $z = 2$, which gives a 1D cluster that is more similar to the results expected in future simulations with a reversible DLCA system.

1. INTRODUCTION

Surfactans are a unique type of molecule due to the nature of how the molecule is assembled, these particles are amphillic, which means they posses both hydrophilic and lipophilic properties, this makes it an incredibly good chemical compound to reduce in various orders of magnitude of the intefacial tension, as well as other uses. This characteristic makes them of great utility in the industry since they can be used to modify the intefacial properties of various systems.[1] However, it has been observed that for certain surfactans, there exists a relatively long process of equilibration [2] that takes place when the surfactans are placed in and move around the interface, this is due to the fact that these surfactans begin to aggregate as the traverse the interface. This could affect the effectiveness of the surfactants due to the fact that when these percolate across a system it causes a sharp drop in the stability of the formed cluster causing ruptures and therefore, in certain cases, the surfactants would prove inefficient in comparison to a non percolating cluster. Due to this type of reaction it is of great importance to study the structural properties of these agglomerates as well as some microscopic properties, including the fractal dimension, correlation function, coordination number as well as study the densities at which these particles begin to percolate and at what concentrations the fractal passes from the flocculation regime to the percolative regime.

The process of equilibrium in systems of this type has been heavily disputed, but it has been demonstrated that the stabilization of these types of systems are in the range of microseconds, these equilibration times are longer than expected due to the aggregation of surfactants stated previously. [2] This deeply affects previous attempts to study these systems since these simulations have been run utilizing molecular dynamics, since molecular dynamics deals with systems that have an equilibration time of picoseconds. For this reason it is impossible to simulate large systems to study the desired properties utilizing molecular dynamics, for this reason another approach has to be implemented to achieve positive results about the microscopic properties of the agglomerates. To simulate the aggregation of these molecules we have chosen Diffusion Limited Cluster Aggregation (DLCA) as the simulation method.

Along with the previously stated generation of clusters in the interface the Molecular Dynamics simulations also revealed the clusters become increasingly unstable when the aggregate percolates the interface. For this reason it is an important result to observe the evolution of the final clusters when changing the density of particles in the simulated system.

In this paper we establish the starting steps to modify the DLCA model to describe the agglomeration of surfactants in a hydrocarbon-water interface. For that reason in this paper the work is divided into the following parts, section 2 of the paper tackles the theoretical framework required to understand the properties of the analyzed system. Section 3 describes the computational complexities of the created program. In section 4 the results of the simulations are shown, and finally in section 5 the conclusions of the results are displayed.

2. THEORETICAL FRAMEWORK

A. Existing Simulation Methods

The main simulation model for these types of systems is Molecular Dynamics, these simulations calculate the forces acting on every particle and move all of the particles at once, utilizing Newtonian dynamics, for a given time differential. Even though these simulations are extremely precise and simulate diffusion and aggregation of chemical molecules as if they were a real life experiment, these simulations take an enormous amount of computational power and can only simulate extremely small systems due to the fact that the characteristic times of these simulations are in the magnitude of picoseconds, and for that reason can only contain a limited amount of particles. Knowing that the aggregation of surfactans has an incredibly high stabilization time, in the order of magnitude of microseconds, it is impossible to utilize molecular dynamics due to the high stabilization time and the larger size of the system required to calculate the structural properties discussed previously to simulate the aggregation of surfactants in a hydrocarbon-water interface. Knowing this, we have to chose a different simulation type that can handle a large amount of particles in large systems, with high stabilization times, for this we can look for one of the following methods.

There are many methods that can be utilized to simulate the aggregation of clusters to clusters from these the primary examples listed in most articles are the Ballistic model, the Reaction Limited Cluster Aggregation (RLCA) model and the Diffusion Limited Aggregation (DLCA) model (for both irreversible and reversible systems). The Ballistic model consists of a randomly generated set of particles or clusters placed in a grid. Of these, two clusters are chosen at random and utilizing a function called a kernel these two are either joined and moved together or another set of clusters is chosen. In the literature it is stated that a certain kernel function generates clusters very similar to DLCA, however the Ballistic model concentrates more on the kinetics of the system and has certain specifications and limitations to how different clusters can be made. Next is the RLCA model, this process starts out similar to the ballistic model in which N particles are placed in a grid with certain specifications. After this the RLCA method is more similar to DLCA than to the ballistic model due to the fact that clusters are chosen at random and move in a random direction with a constant size of the movement, however where RLCA and DLCA differ is the fact that if two clusters collide a probability is computed for the probability that these clusters will aggregate and if the condition is not met the clusters will push away to their original positions and another will be chosen, on the other hand if the probability is met these clusters will aggregate and move as one larger cluster. This would give good results however there is no limitation on the diffusion for the different clusters, which would result in small variations for the final results, and would less accurately depict the system of surfactants in hydrocarbon-water interfaces that we

want to simulate. Lastly there is DLCA for both the irreversible and reversible cases, in this article we will focus on the former. Irreversible DLCA starts similar to RLCA with N clusters placed in a space, these clusters are chosen and move taking into account their diffusion coefficient until they collide with another cluster, once this happens the clusters aggregate and move as one.[3]

In this particular article we focused on Irreversible DLCA due to the fact that the primary goal of these simulations is to get preliminary results of the aggregation of surfactants in a liquid, as stated in the introduction, and therefore diffusion plays an important part in ensuring that these clusters are as similar as possible to those seen in the literature. DLCA fractals can be seen in many structures in real life including, but not limited to, organic and inorganic aerogels, templated foams and other low porous materials. Until recently DLCA has been utilized in the aggregation of colloidal particles with an interaction potential much greater than k_bT, which implies that the system is invariant under fluctuations in thermic changes, however for this system the interaction potential is not as large as the one expected for this system, for this reason the correct simulation method for these systems would be the DLCA reversible method, which follows the same procedure as the irreversible one, but in this simulation type clusters can break from one and other to form smaller clusters. This would more accurately represent the results of aggregation of surfactans seen in the literature since the DLCA reversible model takes into account the possible thermic fluctuations that can occur in the systems experimentally, as well as take in to account that the interaction potential for these particles is of the order of magnitude of k_bT since the clusters can break apart.

B. Fractal Geometry

Fractal geometry studies the geometric scaling and the symmetries associated with fractal objects. These characteristics are scale invariant which means that at any size of the fractal object they can be studied and are of value. Understanding the fractal geometry of these objects lays a pivotal role in understanding how the resulting fractals interact with fields, as well as their quantum properties, spectroscopy, crystallography, etc. [3] In the case of DLCA the final formed cluster is known as a self-affine cluster, which is not identical in any given area but still has fractal properties.

One of these characteristics is the fractal dimension, the fractal dimension is the best known way to study a disorganized and self-similar system, the fractal dimension can give us an idea of how the structure interacts with wave-particles, fields and can give us other physical properties of the structure.

C. Percolation Theory

Percolation describes under what conditions does the system connects to itself, a common way to describe percolation is in the following manner, if one was to pour a liquid on the top of a porous material, if the liquid reaches the bottom of the material then it is said that it percolates the system, since it can go from one end to another. [4] This is different from the percolation studied in this article but can help to visualize it nonetheless. For the aggregation seen in this model we can view the final cluster as the poured liquid, now if this cluster spans the entire system in one direction, i.e. the x or y direction, then the cluster has gone through the entire system and therefore percolates the system.

From this two states can be obtained, first there is the flocculation state, in which the final cluster can or cannot percolate but particles have to move around the system in order to aggregate. On the other hand there is the percolation state or gelation state, in which the cluster almost certainly percolates the system and the particles in the original system do not have to move much or at all to aggregate to one and other and create the final cluster. The difference between the two states can be easily appreciated due to the fact that the cross between the flocculation state and the percolation state is thought to be an increase in the fractal dimension, which when run form systems of multiple sizes is a distinct point called the gelation point, [5]. At this characteristic density there is a discernible difference between the fractal dimensions of the system, in the case of a 2D lattice the fractal dimension goes from approximately 1.4 to around 1.89. This difference can be observed in the following plot in which the point of gelation has started to be crossed, in this result the curve does not show a discrete point since all of the simulations were performed for a single size of clusters with different densities:

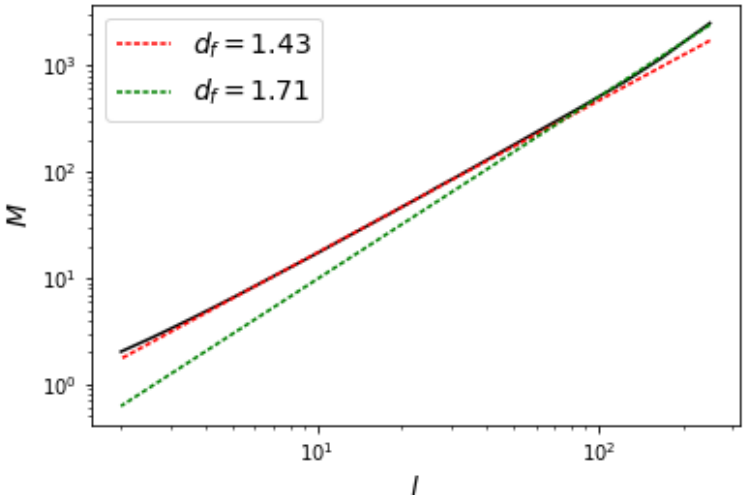

Fig. 1. Fractal dimensions appreciated for a cluster with a density belonging inside of the flocculation regime, and one with a density belonging inside of the percolation regime.

D. Correlation Function

The correlation function is tool utilized, among other applications, to characterize fractals, this function describes the probability that a particle is found at a distance r relative to another particle in the same cluster. This function is incredibly important to observe in the aggregation of clusters due to the fact that its Fourier transformation is exactly its structure factor, this is important since the structure factor is the quantity observed in the experimental results and can therefore rectify the values obtained in these simulations.

E. Periodic Boundary Conditions

The periodic boundary conditions is a common characteristic placed on simulations of this type, they cause the square lattice to act as a continuous torus, which implies that particles that cross the western boarder of the system pass over to the eastern border, along with this particles that cross the southern border of the system navigate to the northern border of the system, this condition also applies in the inverse case in which particles go from east to west and north to south. This condition is placed on the system since the approximation that the system wants to achieve exists in the thermodynamic limits of the simulation, this means that the system expand infinitely in all directions. However, if these conditions were to be implemented in a literal sense one would have to simulate a system of enormous size and number of particles, this is computationally unachievable and for that reason the PBC is extremely helpful.

3. SIMULATION DETAILS

A. Creation of Clusters

The simulation was created with the main idea of DLCA in mind but connected with other elements to cause the clusters to look more like the ones seen in the literature concerning aggregation of surfactants in fluids. For this simulation we take N spheres of diameter $d = 1$ and a distance of interaction (from center to center) of 1 as well. For this particular investigation the primary lattice size studied was L = 500 lattice units (for both on and off lattice simulations), and the particles put into the simulation were 1000, 2000, 4000, 8000, 10000, 120000, 140000, and 150000 for off-lattice simulations and 785, 1570, 3140, 6285, 7855, 9525, 10995, 11780 for on-lattice. The difference in particle amount between off and on lattice simulations for the same density are due to the

next formula [5]:

$$\Phi_{on-lattice} = \frac{N_{on-lattice}}{L^2}$$
$$\Phi_{off-lattice} = \frac{N_{off-lattice}\frac{\pi d^2}{4}}{L^2} \quad \textbf{(1)}$$

This density is the proportion of the entire lattice that is filled, due to the fact that on-lattice particles are made to behave as squares with an area of 1 LU^2 and the off-lattice are circles with an area of $r^2\pi$ it intuitive that the area covered by the two different particles is different, and therefore the density formula for particles on and off-lattice is different. Equating $\Phi_{off-lattice}$ and $\Phi_{on-lattice}$ and simplifying the remaining terms from equation 1 we can get the difference in number of particles between on and off-lattice simulations for a constant lattice size:

$$N_{on-lattice} = N_{off-lattice}\frac{\pi d^2}{4} \quad \textbf{(2)}$$

Once the size of the system and the amount of particles is decided the simulation is started, to do this N particles are initially placed randomly in a 2D space where all particles are at least their distance of interaction, $d_{int} = 1$, or more apart from other particles, this is done to avoid overlapping of these particles; this collocation is similar to diffusing the particles without joining them until a certain specification is achieved, as can be seen in an article published by Rottereau et. al. in 2004 [5]. Now that all the particles are placed we have to simulate diffusion of particles in the interface of a liquid for our system, this is done by utilizing a probability distribution and choosing one cluster at random and roll a dice to see if it moves or not. This is done in the following manner, first a random cluster is chosen, next a probability that this cluster moves is calculated using a formula that will be discussed shortly, and finally a random number from 0 to 1 is chosen and compared to the probability calculated in the previous step, if this probability is greater than the cluster the cluster does not move and a different one is chosen, if the opposite case occurs the cluster moves a step in a random direction of magnitude 1. Since these steps require a probability distribution that mimics the diffusion of particles in a liquid we know that constant of diffusion D is commonly inversely proportional to its diameter of the cluster ($D_{ci} \propto d_{ci}^{-1}$). However, in this case the diffusivity of the cluster is going to be inversely proportional to the mass of the cluster (i.e. the number of particles in the cluster), with this in mind we define a probability distribution utilizing the next form:

$$\sum_{i=1}^{n} \frac{A}{m_{ci}} = 1 \quad \textbf{(3)}$$

Where A is a constant of normalization, m_{ci} is the mass of a cluster in the system and n is the total number of clusters in a system. However since the number of clusters in the system changes over time, since clusters are constantly aggregating, the constant of normalization A has to be variable in time as well, with this in mind we calculate A every time a cluster aggregates to another by isolating it from equation 3, which results in the following formula:

$$A = \frac{1}{\sum_{i=1}^{n} \frac{1}{m_{ci}}} \quad \textbf{(4)}$$

Having A and the probability distribution we can generate a probability that a single cluster will move with the following formula:

$$P(m_{ci}) = (Num.\ Clusters\ Mass\ m_{ci}) * \frac{A}{m_{ci}} \quad \textbf{(5)}$$

This probability will be the one calculated and attributed to every cluster and compared, as stated before, to a random number, which will ensure that we have simulated the diffusion of particles appropriately.

Next, to revise if a particle is within the radius of interaction with another particle we proposed a linked list in which we would have a segmented grid that contains all of the created segmentations of our space and was self referential so that all of the particles in a single spot could be located without having to traverse all of the clusters. This was done with the following procedure. First, we divide our space into $(L/d)^2$ cells, where each square has a length and height of L/d where L is the lattice size and d is the diameter of a particle, then we

"count" in a horizontal manner so that every adjacent square to the right or left is a difference of 1 number away, while adjacent squares above and below are a distance of L numbers away. This is done utilizing the following formula:

$$k = (y//d) * L + (x//d) \tag{6}$$

Where k is the number given to the cell of the grid, x and y are the centers of the particle, d is the size of the diameter of the particles, L is the size of the lattice and $//$ symbolizes the integer division. With this value we can know the relative position of any particle in our grid without traversing through all the particles in the system. With these values the linked list for all the particles in k can be set, for this we have a list that has a length of the total number of cells, i.e. $(L/d)^2$, plus the total number of particles. Now when only one particle is found in a cell it in the kth index of the list with a value of $(L/d)^2 + num.particle$ and points to a negative 1, if another particle is placed in the same box we go to the kth value in the list and then go to the $(L/d)^2 + num.particle$ index in the list and follow this procedure until a negative 1 is found, at this position we change the value from -1 to $(L/d)^2 + num.particle2$. Utilizing this we can place all particles here and know their relative location at all times, and with that we can know their absolute position, their number and what cluster they belong to.

Along with this the system exist inside of periodic border conditions, which in this case means that particles that move past the left border of the system appear on the right side and vice versa, this is the same for the vertical axis in which particles that move past the north border appear on the south border of the system.

Now that we have established the rules for movement in our system we move and revise the adjacent and diagonal cells next to all of the particles in the cluster that was moved. Once revising we check for any particles that are not in the cluster, and the distance from the center of the current particle to the center of the checked particles is less than the distance of interaction. Once the entire cluster has been run through we have all of the particles that could be connected to the cluster, we run through this list of possible particles and keep the one with the smallest distance from center to center. Once this particle is determined we push back the cluster selected to move backwards until the particles are at a distance of exactly 1, this is done to prevent overlapping between particles so our system simulates real life better. The distance pushed back is calculated in the following manner:

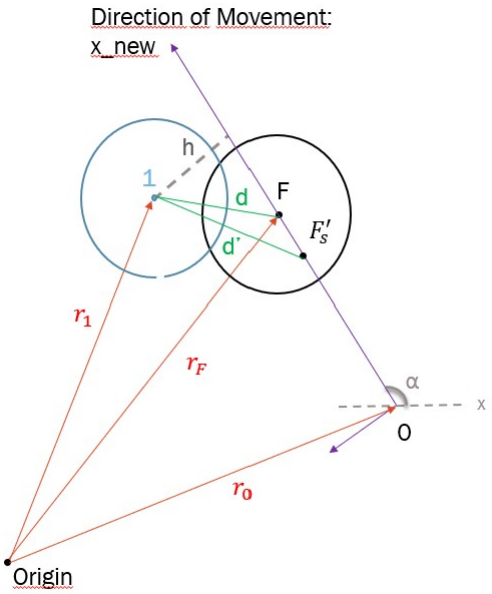

Fig. 2. Calculation of Overlapping distance

Utilizing the figure 2 and the variables displayed in it we can calculate the distance from F to F_s' in the following way:

First we define 2 square triangles utilizing d' and d as the hypotenuse and the distance in the direction of movement from the point F' or F to the projection of the particle 1 on the direction of movement, named x1.

$$\begin{aligned} d^2 &= (x_1 - x_F)^2 + h^2 \text{ Triangle with len } x_F \\ d'^2 &= (x_1 - x_{F'_s})^2 + h^2 \text{ Triangle with len } x_{F'_s} \\ &\text{Isolating the "lengths" of the triangles} \\ (x_1 - x_F)^2 &= d^2 - h^2 \\ (x_1 - x_{F'_s})^2 &= d'^2 - h^2 \end{aligned} \tag{7}$$

and subtracting the first from the second triangle we get:

$$\begin{aligned} (x_1 - x_{F'_s})^2 - (x_1 - x_F)^2 &= d'^2 - d^2 \\ x_1 - x_{F'_s} &= \sqrt{d'^2 - d^2 + (x_1 - x_F)^2} \\ \therefore x_{F'_s} &= \sqrt{d'^2 - d^2 + (x_1 - x_F)^2} - x_1 \end{aligned}$$

Knowing that x_1 is the projection of the collided particle in the direction of movement we can define it as:

$$x_1 = (\vec{r_1} - \vec{r_0}) \cdot (\cos(\alpha) i + \sin(\alpha) j) \tag{8}$$

Substituting the value of x_1 from 8 into 7 we get:

$$x_{F'_s} = \sqrt{d'^2 - d^2 + (x_1 - x_F)^2} - [(\vec{r_1} - \vec{r_0}) \cdot (\cos(\alpha) i + \sin(\alpha) j)] \tag{9}$$

If we subtract $x_{F'_s}$ from the original distance moved, in this case 1, we get the distance that the cluster must be pushed back in order to be in a position where there is no overlap and would have naturally have stopped in experiments.

With all of these components now we can complete clusters that have no overlap and account for diffusion of particles in a liquid.

B. Calculations on Complete Clusters

B.1. Center of Mass

Due to the periodic boundary conditions established in the system one must change the way the center of mass is calculated, since the relative distance, in the system, from one particle to another is not the "real" distance between them in some cases. Therefore the next formula was utilized:

$$\theta_i = \frac{x_i}{x_{max}} * 2\pi$$

Two values can be extracted:

$$\begin{aligned} \xi_i &= \cos(\theta_i) \\ \zeta_i &= \sin(\theta_i) \end{aligned}$$

Adding these values for every particle:

$$\begin{aligned} \bar{\xi} &= \frac{1}{M} \sum_{i=1}^{N} m_i \xi_i \\ \bar{\zeta} &= \frac{1}{M} \sum_{i=1}^{N} m_i \zeta_i \end{aligned} \tag{10}$$

Calculating the average angle:

$$\bar{\theta} = arctan2(-\bar{\zeta}, \bar{\xi})$$

And converting to radians:

$$x_{cm} = x_{max} \frac{\bar{\theta}}{2\pi}$$

Doing this procedure for both x and y generates the center of mass for the system, this method is further demonstrated in [6], where a full mathematical justification is provided.

B.2. Fractal Dimension

To calculate the fractal dimension one of many methods can be utilized, for this simulation specifically we utilize two methods and take the average of the two. The first method consists of dividing the lattice into equal squares and counting the average amount of particles for every square, this is done for various square sizes until a minimum is reached, in this case the minimum is 4 times the diameter of the particles. This results in an exponential relationship in which $avg.\ count \propto \exp d_f$ that when put on a logarithmic scale the slope of the resulting straight line is the fractal dimension. This is done fore real world applications such as finding the coastline of a country due to the fact that when dividing smaller the country into smaller and smaller boxes one can get a more precise location for the coastline without having the precise coordinates for the entire coastline, and this method is also utilized for getting the fractal dimension of a Koch curve, this is similar to the coastline example since when dividing the boxes of the Koch curve into smaller and smaller segments one gets a more clear representation of the Koch curve. These examples can be observed in figure 3.

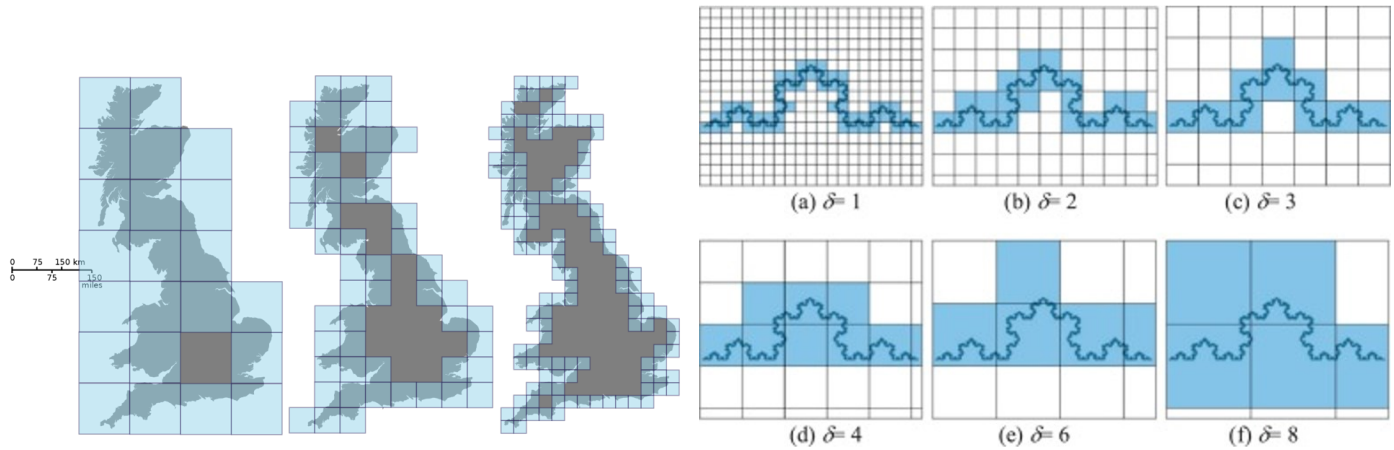

Fig. 3. Examples of where box counting is utilized to determine fractal dimension.

This can be applied to our simulation in the following manner, in figure **??** we can observe how we can divide our system and count the amount of boxes or the average amount of particles for different box sizes. In figure 4 we can observe that boxes that have a particle in the middle of them are counted as one of the boxes of interest, along with that if we count the total amount of boxes and divide the total number of particles between the number of boxes we can obtain the average amount of particles in a cluster.

Therefore applying the method in which the average particles per box is counted and compared vs the length of the boxes created the following graph in figure 6 can be obtained. From this we can extract the the evolution of the system, in a logarithmic scale, represents the fractal dimension i.e. the slope of the resulting straight line is the fractal dimension of the final cluster.

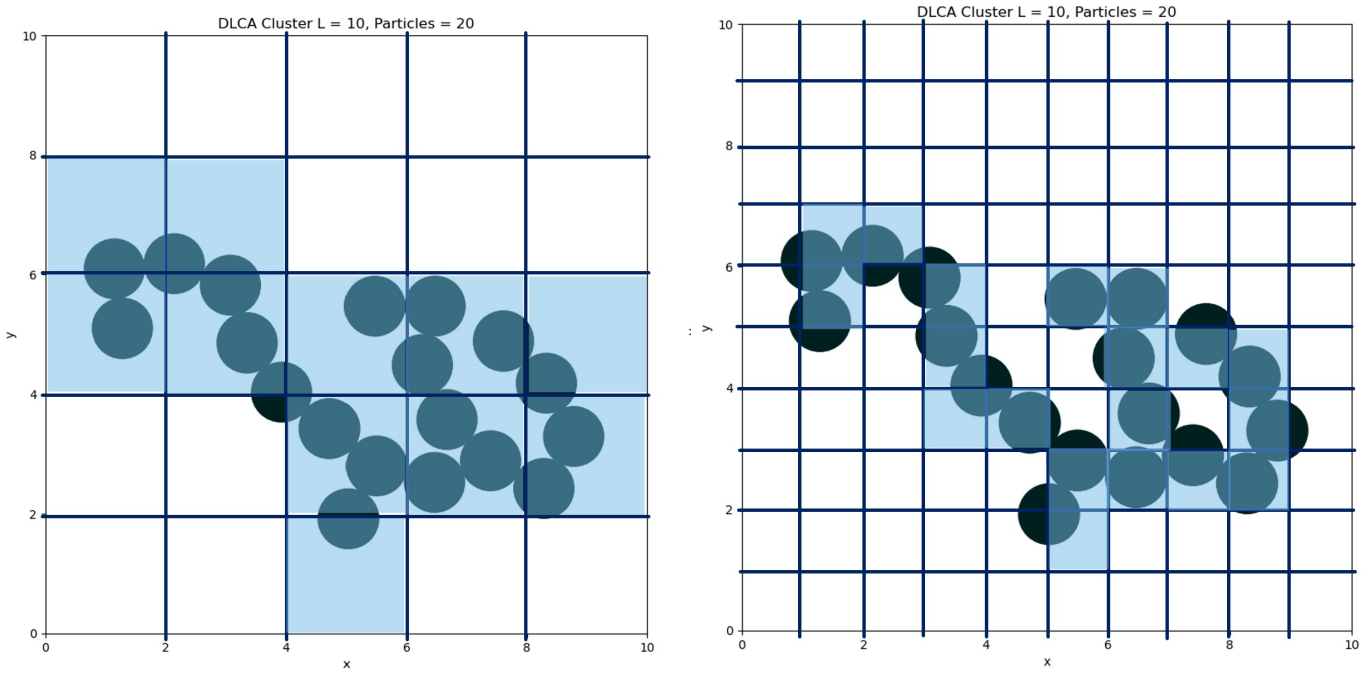

Fig. 4. Example of box counting for cluster of size 10 with 20 particles. The particle is only counted if its center is inside the box, not an edge.

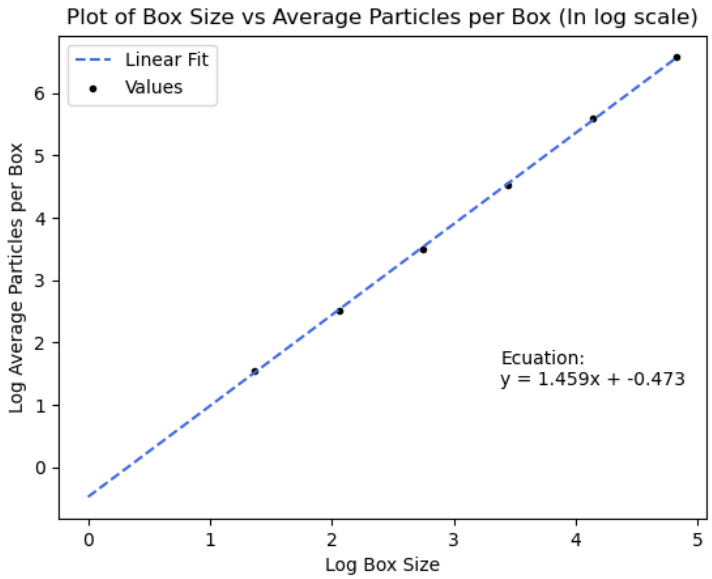

Fig. 5. Calculated fractal dimension utilizing avg. particles per box method of created cluster with 10 thousand particles and a lattice size of 500 lattice units.

The second method consists of dividing the lattice into equal squares and counting the amount of boxes that contain particles. This results in an exponential relationship with the form $num.\ boxes \propto \exp -d_f$ that when put on a logarithmic scale the absolute value of the resulting slope is the fractal dimension.

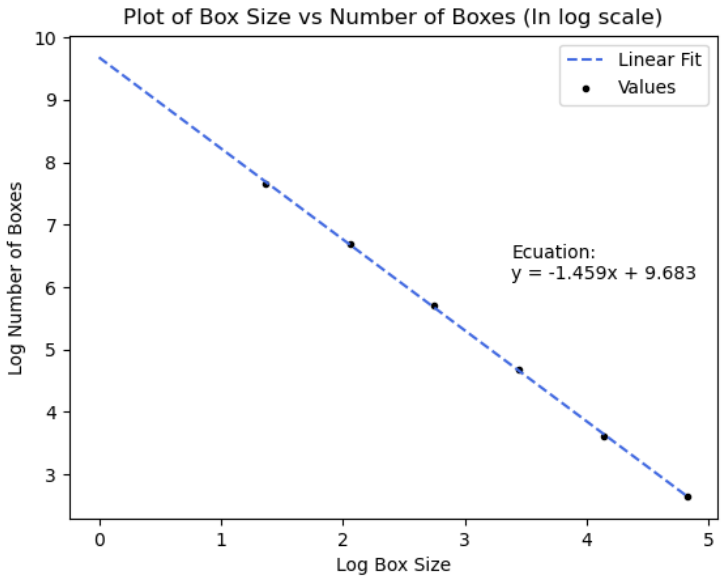

Fig. 6. Calculated fractal dimension utilizing number of boxes method of created cluster with 10 thousand particles and a lattice size of 500 lattice units.

B.3. Percolation

It is known that a system percolates when the entire cluster spans the entire system, this can be easily checked in systems with non periodic border condition by seeing the minimum and maximum value for both x and y to see if one of the two have a size of L. However for systems for periodic boundaries, like this one, the way we utilized to observe if the cluster percolates the system is by dividing the entire grid into cells the size of the diameter of the particles, after this we check if a single particle is found in all of the columns or all of the rows of the system which would mean the system percolates in either x or y respectively. This example can be seen in the figure 7.

C. Additional Properties

An additional restriction can be added so that particles can only aggregate if they are connected to two or less particles, this condition is added to simulate the aggregation of surfactans in a more precise way. Since the surfactants are in reality chemical compounds with a tendency to stick to the edges of chains of these clusters having a restriction that allows this gives the opportunity to study more realistic final aggregates. However the computational restriction did not allow us to complete any of these clusters since the probability that two clusters of this type diminishes drastically during time and is not ensured due to the fact that if an edge is developed inside a cul-de-sac, this particle becomes unreachable since clusters cannot overlap.

Another additional property is the ability for clusters to rotate around their center of mass, this would allow clusters to have an additional type of movement that would also give more realistic results, but since the time of development was limited and the rotation of clusters do not change the results other aspects of the code were prioritized.

4. RESULTS AND DISCUSSION

A. Resulting Clusters

In the following image, applying all of the previously explained elements (excluding the additional properties), three distinct final clusters can be observed. In the top leftmost simulation we have a DLCA off-lattice simulation without any overlapping, in the top rightmost the represented cluster is a DLCA off-lattice simulations with overlap, and finally the bottom middle image represents an on-lattice cluster. For these three results there is an initial density of $\Phi = 0.0341$, which implies 10 thousand particles for the off-lattice

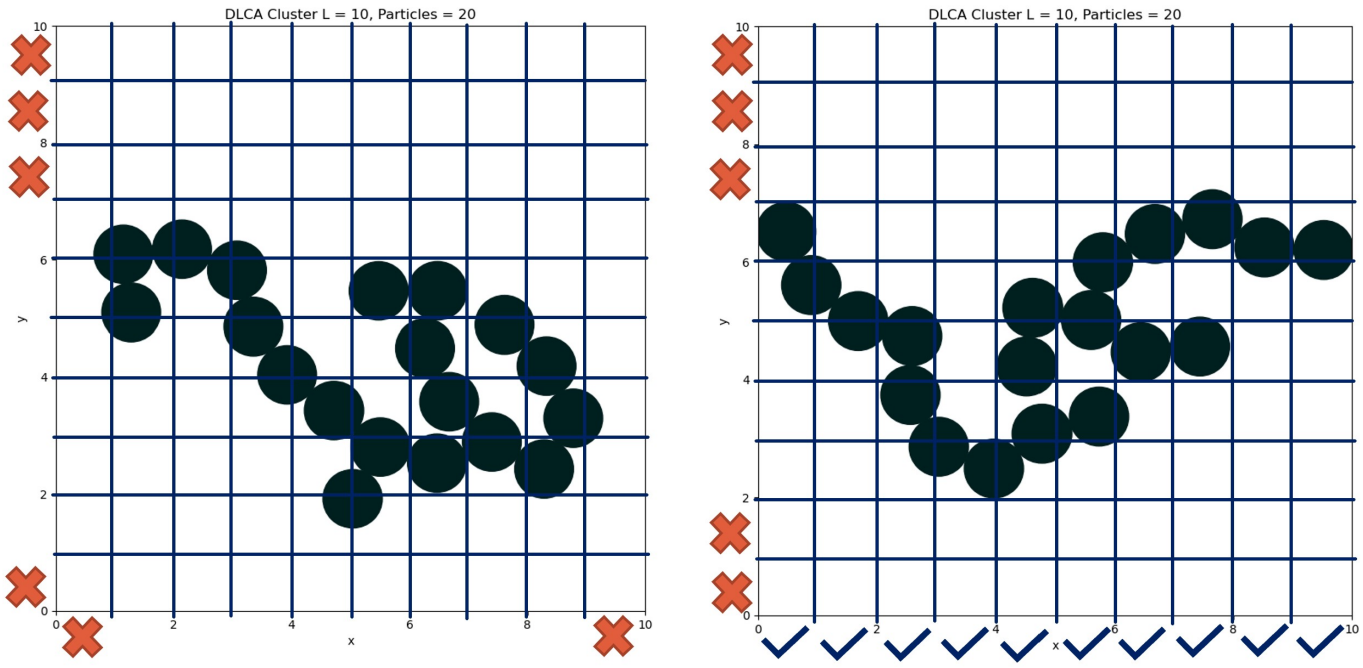

Fig. 7. Example of algorithm to observe if cluster percolates or not. Image on the left does not percolate in neither the x or y direction, and the image of the right percolates in the x direction.

simulations and 7855 particles for the on-lattice simulations. For the on-lattice case and the off-lattice without overlap this density is maintained constant throughout the entire simulations, however for the off-lattice with overlapping the simulation obviously ends with a smaller proportion of covered area. The fractal dimensions for these three simulations should be the same even though the results we compiled show a difference in fractal dimensions for the different simulations, this is due to the low scale effects experienced by the systems.

For these results there are a total over 1000 results for all of the simulations combined, which averages out to around 75 simulations for every density in the three different simulation types.

B. Off-Lattice Without Overlap vs With Overlap

Running multiple runs for the off-lattice simulations with overlap and without overlap for a lattice size of 500 LU and for multiple particle counts we can obtain multiple results to compare the fractal dimensions for different particle counts for both different simulations. To obtain these results we re-calculated the box count for all of the desired clusters, from this the average box count for every box size is obtained, resulting in a 1 dimensional array consisting of the average counted boxes for all runs, after this we apply the methodology discussed previously to obtain the linear fit between the box size and the number of boxes counted (both in logarithmic scale) doing this for multiple densities we can achieve the following linear plot in which we display in figure 10, which shows the number of particles for each line and the corresponding slope of that linear fit.

Repeating the process but recalculating the average number of particles per box for all of the different runs, and once again calculating the linear fit for the average amount of particles vs the size of the box in logarithmic scale and we obtain the fractal dimension for multiple different particle totals for simulations with and without overlap. Which results are seen in figure 10

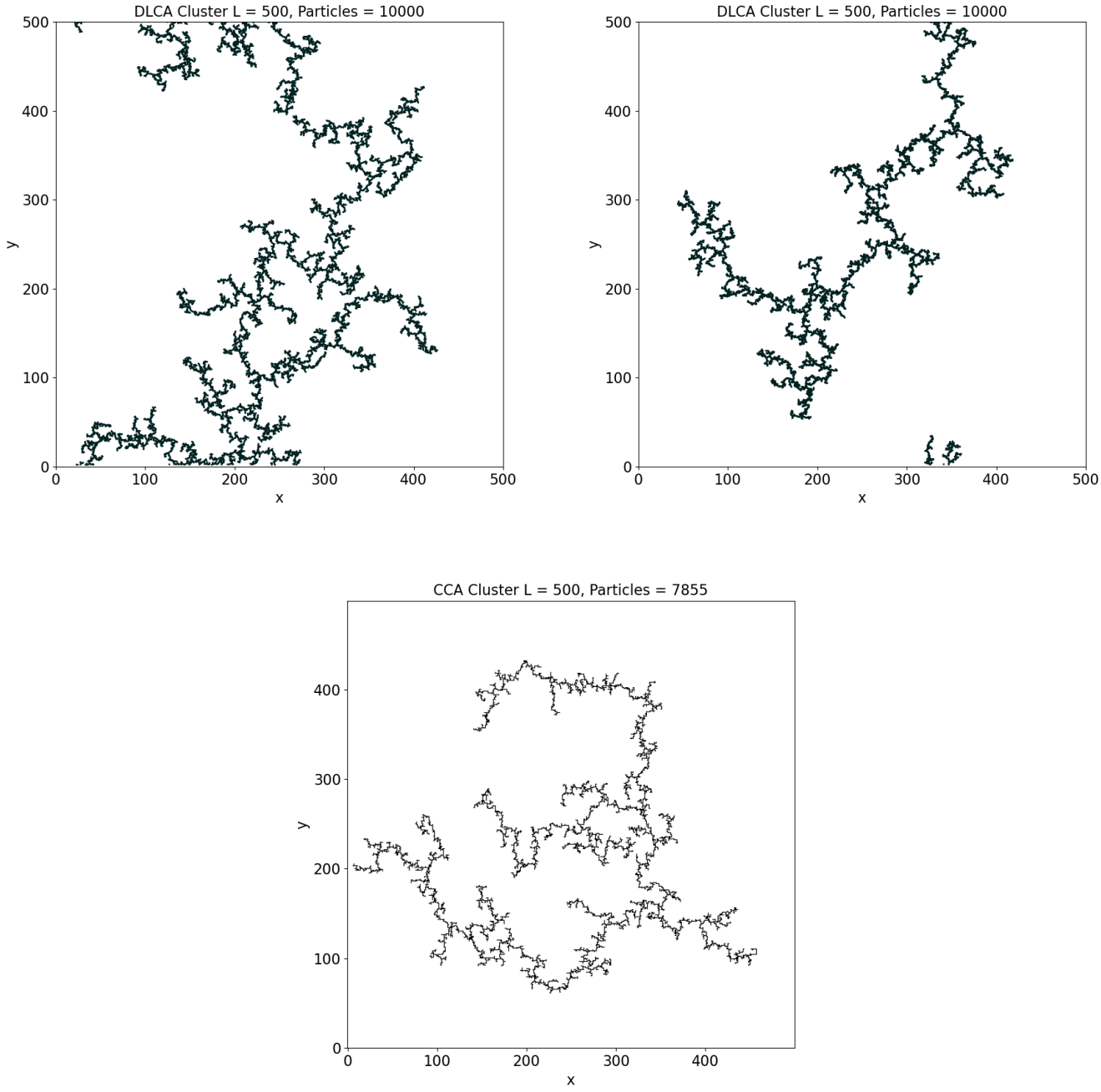

Fig. 8. Final cluster plot for three different clusters with same density. Leftmost image is an off-lattice cluster with no overlap, middle image is an off-lattice cluster with overlap, and rightmost image is an on-lattice cluster.

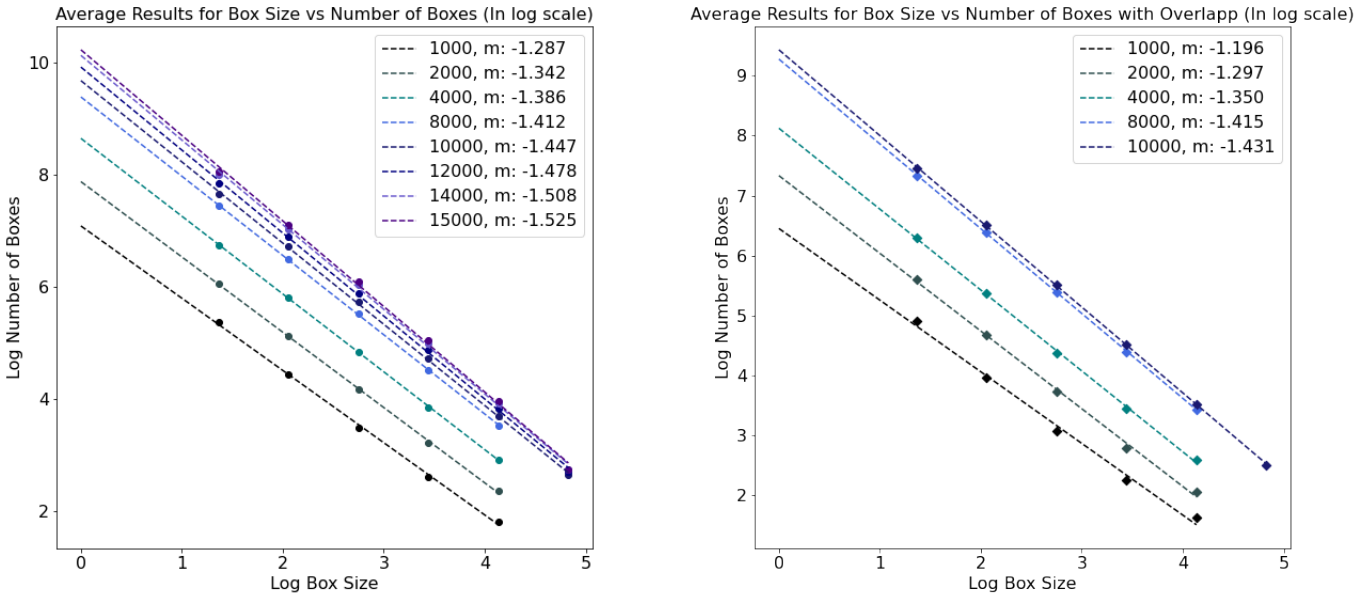

Fig. 9. Average box count and linear fit, with m being fractal dimension, for off-lattice without overlap (left) and off-lattice with overlap (right) simulations.

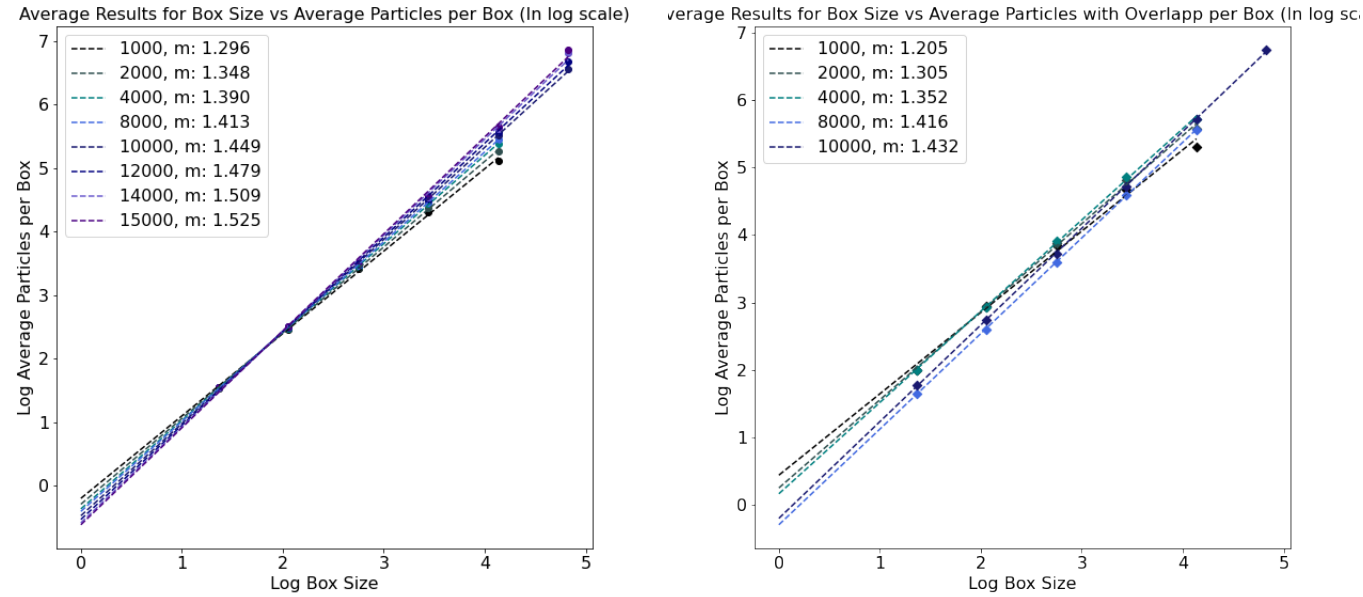

Fig. 10. Average particles per box and linear fit, with m being fractal dimension, for off-lattice without overlap (left) and off-lattice with overlap (right) simulations.

Combining the results from figures 9 and 10 we can obtain the fractal dimension obtained from averaging the absolute value of both the box count and the average particle methods reported for the different total number of particles. Changing these particle counts to densities, which are the same initially but the overlap simulation decreases in density overtime due to the overlap, we can obtain the results in figure 11.

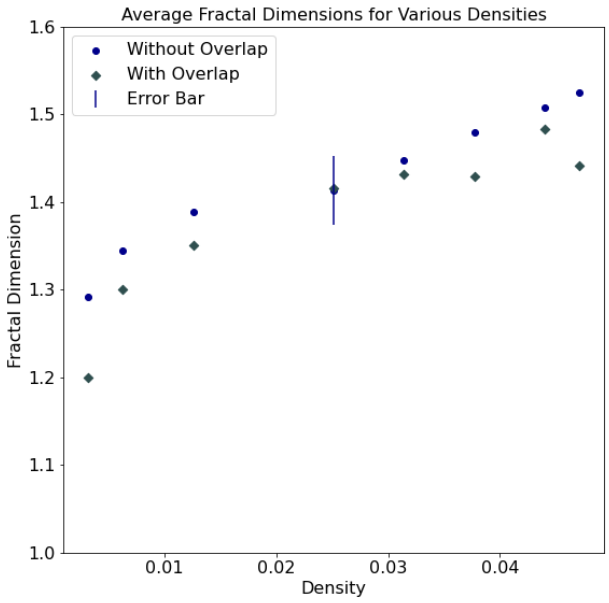

Fig. 11. Fractal Dimensions for different densities for off-lattice simulations with and without overlap.

Observing figure 11 we can observe several differences between the simulations with and without overlap. Clearly there is a difference in the fractal dimension that is not constant, this difference is due to the overlapping causing less "boxes" to be counted and therefore a drop in the fractal dimension is expected. Along with this we can observe that the highest density fractal dimension appears to be off trend with the rest of the results, this can be due to multiple factors, but is primarily due to the fact that when placing the particles initially there is very little left over space for particles to move around without aggregating, this leads to particles overlapping more than usual at the beginning of the simulation since particles are very close together initially and when clusters begin to form the distance between them expands. This can, in turn, be interpreted as the low scaled effects mentioned previously, if one were to expand these systems to be much larger these small overlaps would not affect the fractal dimension and result in the compared simulations having the same fractal dimension. And even including all of the aforementioned errors, if one calculates the standard deviation in the fractal dimensions calculated for most of the given densities the clusters with overlap still fall into a range of one standard deviation.

C. Off-Lattice vs. On-Lattice

Repeating the methodology for the calculation of the on and off lattice fractal dimension comparisons, we can once again obtain the graphs for the linear fits between the average box count and the box size in log scale, along with the average particle count per box vs. the box size in log scale as well for multiple runs of various systems with lattice size L and various densities. In this comparison we cannot run the system for the same number of particles due to the difference in the density formula for off and on lattice systems seen in equation 1, which results in a difference by a factor of $\pi/4$. Therefore observing the average box counts for various densities we can obtain the graphs seen in figure 12.

And repeating the same process for the graphs of average particles per box for the previously discussed systems we can obtain the lines seen in figure 13.

Gathering the results from figures 12 and 13 we can create the average fractal dimension for the simulated densities for both on and off lattice simulations, these results are seen in figure 14.

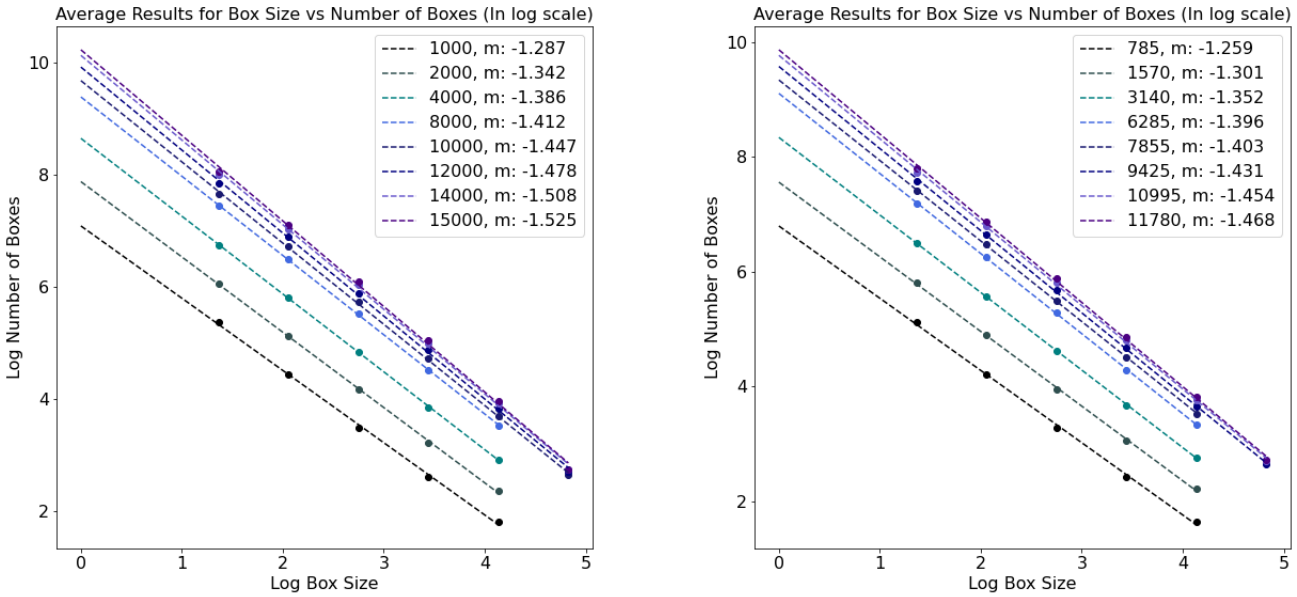

Fig. 12. Average box count and linear fit, with m being fractal dimension, for off-lattice (left) and on-lattice (right) simulations.

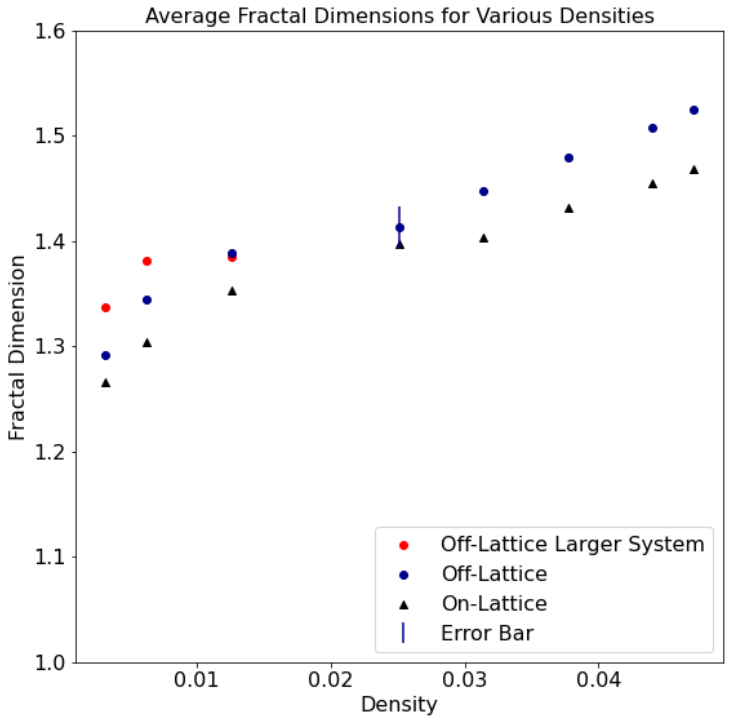

Fig. 14. Fractal Dimensions for different densities (same for on and off-lattice simulations). Note: The lines of z = 5 and z = 6 for off-lattice are completely overlapped since there are no particles with z = 6 and there is an average of 0.0015%.

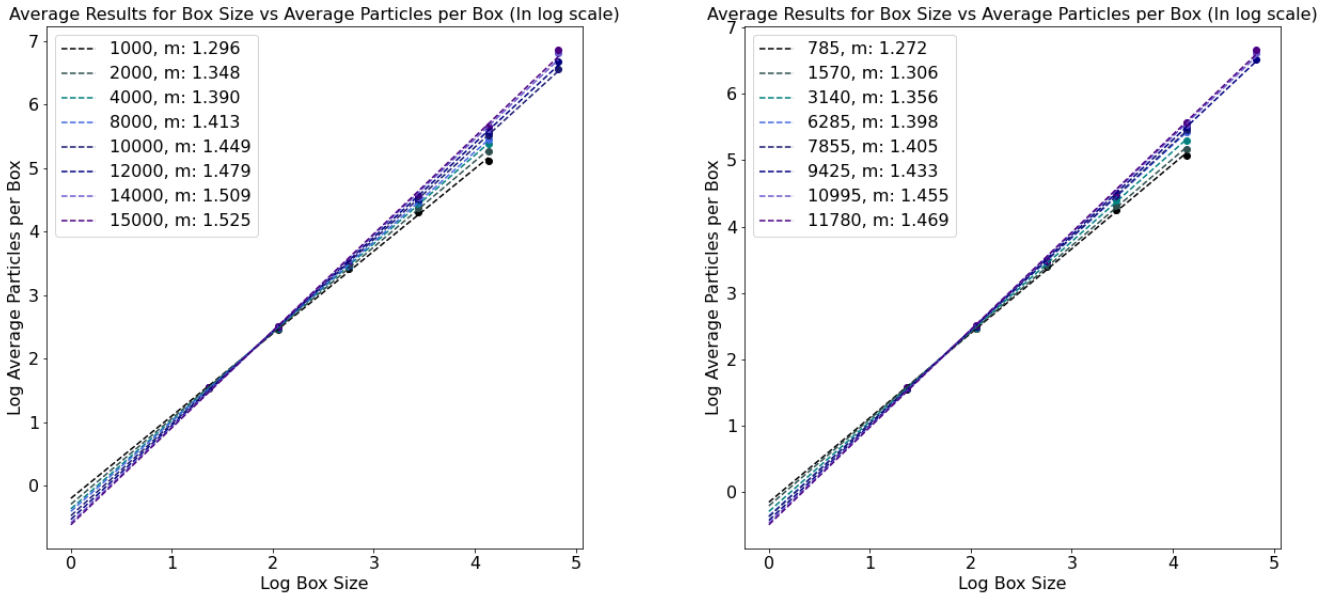

Fig. 13. Average particles per box and linear fit, with m being fractal dimension, for off-lattice (left) and on-lattice (right) simulations.

Observing these results we can see strange behaviour for smaller densities in which the fractal dimension for the system decreases a considerable amount, this can be attributed to size effects that occur due to the reduced size of the system, to correct for this multiple simulations for a lattice size of 707 with double the amount of particles than the original, i.e. for the same three smallest densities. With these corrections, the red dots in figure 14, we can see that the fractal dimension for densities below around 0.3 remains semi-constant and begins to increase at soft rate after this point. This is what is expected from the aggregation of clusters of this type, since at higher densities they begin to transition into a percolation regime (or gel point) instead of staying in the flocculation regime [5], this increment becomes important since it has been shown that when surfactants are in the percolation regime they are extremely unstable and tend to break. Along with this we can observe that off and on-lattice simulations have a similar fractal dimension to each other and even grow at a similar rate when their density increases. This is an important result that supports the statement seen in the literature, which says that on-lattice simulations can accurately represent on-lattice simulations with minor to no differences in fractal dimension. In addition to this, we can calculate a standard deviation for the fractal dimensions of a single total particle count which shows that even though the on-lattice fractal dimensions seem to have a large difference, they are really contained within one standard deviation for the average fractal dimensions for the different densities. This cements the fact that on-lattice simulations can be utilized to approximate off-lattice runs, and with larger systems the differences will diminish until they are completely or almost completely equal to one and other. From this figure we can also observe that we are nearing the point where the system goes from a flocculation regime to a percolation regime, this can be obtained from the plot in figure 1. To further demonstrate that when increasing the size of a system an on-lattice simulation can be utilized to approximate an off-lattice simulation we can plot the average amount of particles each particle of the cluster is connected to for all of the runs and for multiple densities. For off-lattice the maximum number of particles permitted to be connected is z = 6, while the maximum for on-lattice can only be 4 (the four directions of movement), this result can be seen in figure 15.

Examining this graphic we can clearly see that both on and off-lattice simulations have very similar connection between the particles in their final cluster. In this figure we can clearly note that less than 1% of the particles in the off-lattice simulations have a z value of more than 4. This indicates that even though the

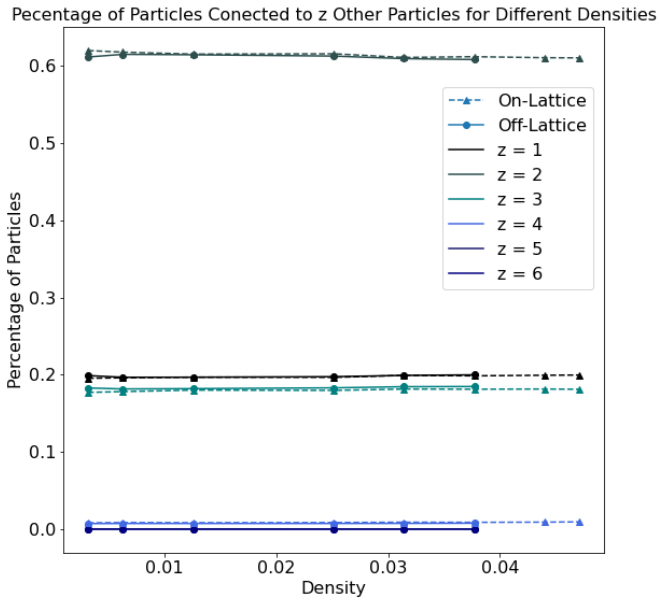

Fig. 15. Percentage of particles that are connected to z other particles in the final cluster.

simulations are different with respect to how the particles are allowed to move, both connect in a similar way. Where most of the particles (slightly more than 60%) connect to only two particles, i.e. are part of a long chain, and around 20% of the particles have only 1 connected particle, i.e. they are an ending point of the cluster, and around 19% of the particles are connected to 3 particles, which indicates they are a point where the cluster branches out further.

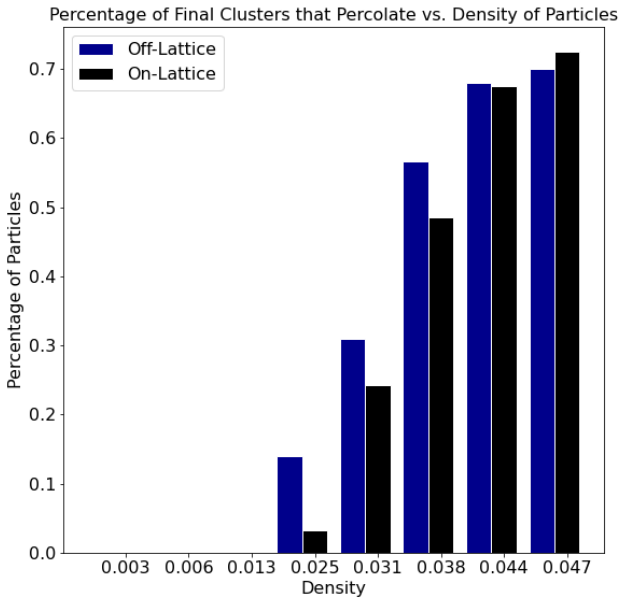

Fig. 16. Percentage of percolation for both on and off- lattice at different densities (same for both on and off-lattice simulations).

C.1. Percolation

The percentages seen in figure 16 are of extreme importance to the analysis of the system, due to the fact that the cluster (for aggregation of surfactans) becomes incredibly unstable when it percolates the system. Along with this the obtained graph shows we do not obtain the threshold where there is a critical point in where the system goes from the flocculation regime to the percolation regime, however we can see that the system does trend towards that threshold.

D. Correlation Function

Due to the complications brought about from the PBC, in which a cluster has to be "unfolded" from the torus to a 2D plane for one to accurately calculate the relative distance from one particle to another, due to this it is better to continue relying on the results for the fractal dimension given by the box-counting methods. However, due to the importance of the correlation function, since the Fourier transformation of the correlation function gives the structure factor for a given structure, one cannot simply discard the calculation of this function. Therefore, choosing a particle center to the center of mass and moving it to the center of the grid, one can achieve an approximation of the correlation function, without including the entire final cluster, with this the following graph can be obtained for a single cluster:

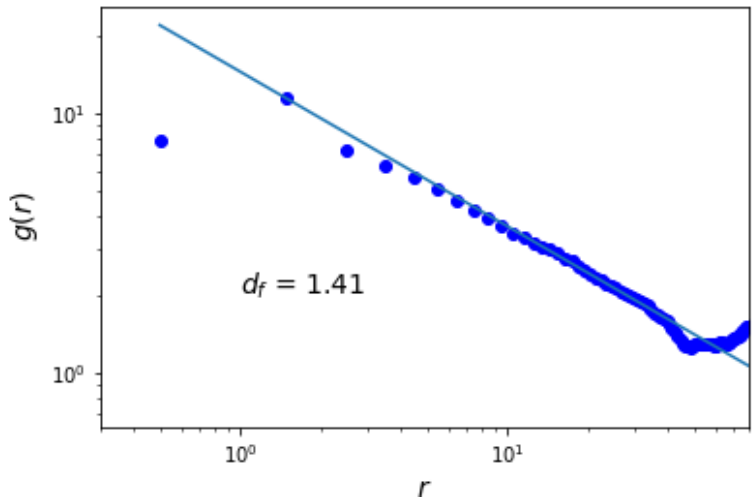

Fig. 17. Correlation function for cluster on lattice size 500 with 10 thousand particles.

Observing figure 17 one can see that a clear limitation to the calculated g(r) is the fact that radius only reaches a magnitude of 20 LU, which is a considerable drop in comparison to the scale seen in the box counting methods, along with this a lot of noise can be seen in the graph and for these reasons it is better to calculate the fractal dimension utilizing the box counting methods.

E. Edge Aggregation Restriction

When adding this restriction there comes a point in the system where, due to the random movements of the clusters, there is no way that the clusters will be able to aggregate to create 1 cluster that exists in the system, however there are clusters that can be analyzed at these points, in the figure 18 we can observe two separate examples of the resulting clusters that exist with this restriction.

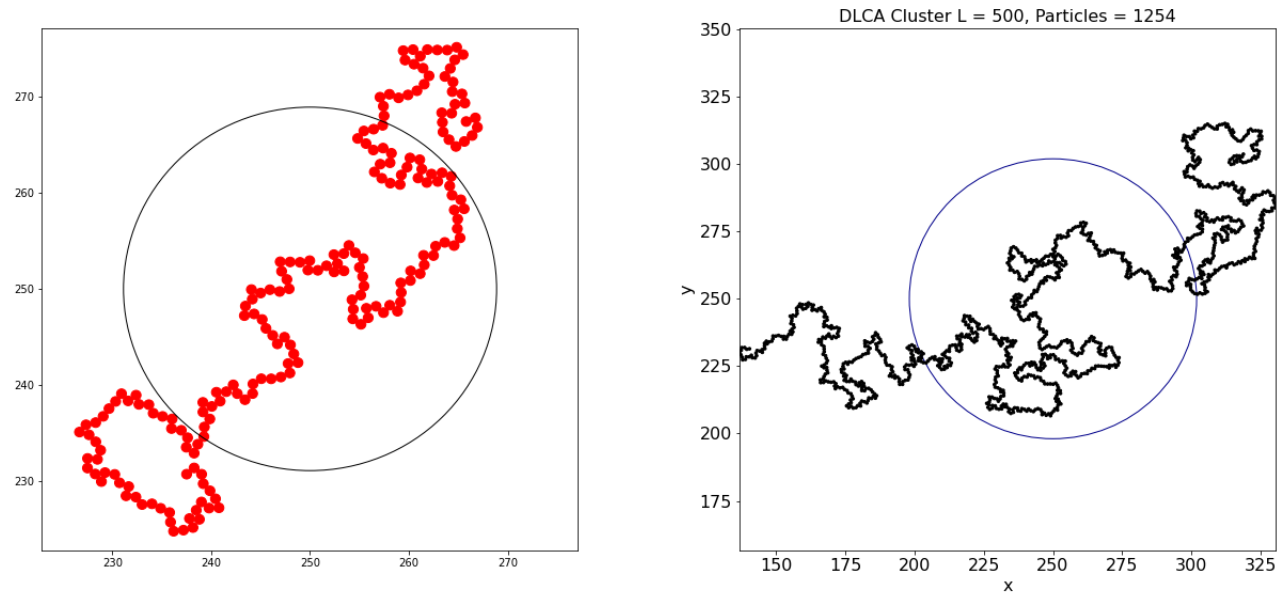

Fig. 18. Clusters created with the edge aggregation restriction. Note although it may seem like it none of the particles in these clusters has more than 2 particles connected to it. The radius of gyration was calculated utilizing the following formula: $R_g^2 = \frac{1}{N}\sum_{i=1}^{N}(|r_i| - |r_{ci}|)^2$.

As can be seen in the left cluster, there is no way another cluster could have entered and connected to neither of the particles at its outer particles since they appear to be inside a cul-de-sac, and since the clusters can never overlap no cluster will be able to enter the cul-de-sac and connect to the particle. Another reason for this type of results is the fact that, since the clusters are unable to rotate, once they get to a certain length it is impossible for them to move in the direction perpendicular to their main length due to the fact that other clusters in the system limit their transnational movement since the clusters can never overlap, and even if the cluster moves vertically the adjacent cluster will cause it to become nearly impossible for the cluster to move to the exact position where it can aggregate, that is if the "cul-de-sac" has not formed.

Having multiple simulations of these clusters and allowing them to evolve during multiple days until they reach a point of "equilibrium", where no more clusters aggregate due to the characteristic shown in 18, we can obtain multiple large clusters that are similar to the two previous clusters shown. Having these clusters we imposed a rule that clusters that have more than 800 particles connected to itself, which nears the lower limit of number of particles seen in previous graphs, are eligible to be analyzed to measure their fractal dimension. Obtaining all of the clusters with the previous specifications and performing both the box counting and the average particles per box methods we can achieve the following graphs seen in figure 19.

From this we can obtain that the fractal dimension is on average 1.244, this is the expected value and can be deduced utilizing the comparison between on and off-lattice simulations. If we analyze figure 14 we can see that the fact that the difference in the possible connections between the on and off-lattice simulations lead to a smaller fractal dimension. Applying to these clusters, if we were to plot the z values for the edge aggregation restricted clusters we would have all of the particles, except for two, with a z value of 2 and the other two particles would have a z value of 1. With those z values we can conclude that the growth of the cluster will be, obviously, different to the ones shown previously and would for these reasons have a lower fractal dimension. Along with this the fractal dimension of the Koch, which is also a one dimensional fractal, curve seen in figure 3 one would utilize the common formula of $d_f = \frac{\log N}{\log \epsilon}$, in the case of the Koch curve the values of N and ϵ are 4 and 3 respectively, giving a value of $d_f = 1.261$. Even though both of these fractals are completely different, however they share the fact that they act as 1D fractals and therefore it is expected that the fractal dimensions

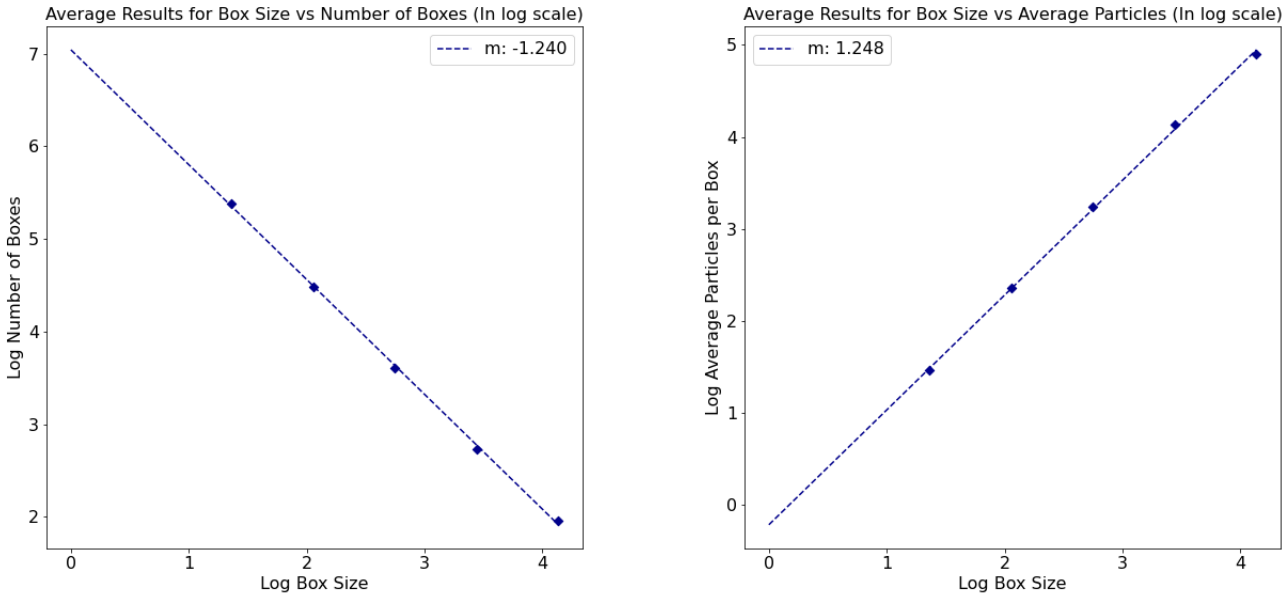

Fig. 19. Box count and average particles per box methods with their respective fractal dimension.

are of similar value, which they are.

5. CONCLUSIONS AND FINAL DISCUSSION

In this paper we developed a computer simulation that successfully emulates the aggregation of clusters for both on-lattice and off-lattice without overlapping, along with the corresponding routines to analyze the fractal dimension, coordination number for all for all of the particles in the cluster, the probability of percolation for multiple results as well as the center of mass and the radius of gyration for small clusters. The obtained results have shown us that the simulations are successful in creating the desired fractals due to the fact that the correlation number between the particles as well as the fractal dimension is the result shown in the literature $d_f = 1.41$.

The results in figure 14 show that the fractal dimension, including the extra simulations of greater size, at low densities are constant and then begin to increase in the form of a soft form at around $\Phi = 0.047$ [5]. Following this the results seen in figure 16 shows us the expected results that at higher density the agglomerates tend to percolate at a higher percentage, meaning that at densities higher than $\Phi = 0.047$ the final clusters of surfactants have a higher probability of being unstable and therefore the surfactants would not have the desired effects if placed at these densities in the interface. Another positive result is that the change between the flocculation regime and the percolative regime can be clearly seen in figures 11, 14, as well as 16, and supports the graphic from 1. This quantity is of extreme importance due to the previously stated fact that aggregates at these densities become incredibly unstable in the percolative state.

An interesting result comes from the restriction clusters, i.e. the ones seen in figure 18, these clusters do not result in the creation of a single final cluster, but of many large clusters that were unable to connect to each other due to multiple factors. This results is due to a combination of DLCA and type of RLCA explained previously which leads to clusters generating properties that prevent them from aggregating further. These results are interesting due to the fact that they completely original and are also more similar to the results that are expected from the DLCA reversible simulations, where no one single cluster can be the final result due to the instability that these clusters show when getting larger.

A. Next Steps

Due to the short time we had to complete this project python was utilized to shorten production time and give more time to investigate and read papers on the subject so that a comprehensive understanding of the physics involved in the problem could be displayed in this paper. However python is not suited for these types of simulations where speed is of the essence since it is not a statically typed language, for this reason the first step for the next part of the project is changing the code to C will provide shorter run times and will allow us to simulate much larger systems and achieve better results. Since the reversible simulations will require much more computation in comparison to the irreversible it is important to generate reduce computational time by a great deal so that there can be a large amount of simulations completed to have a comprehensive and substantial amount of results.

Along with the previous statement it is extremely important to make the system reversible. Since the DLCA model proposed in this system is irreversible it is not taking into account the possible thermal fluctuations that exist in the aggregation of surfactants diffusing in liquids. To account for this we add the reversible restriction, in which clusters can break off one and other at the edges, this will cause the final result of the system to be different to what we are observing in this article, this takes place due to the fact that the final system will not consist of one single cluster, but of multiple clusters of various sizes in a state of equilibrium. Accounting for these differences and calculating their percolation percentage as well as fractal dimension will lead to more realistic results about the aggregation of surfactans diffusing in liquids, and therefore achieve the main goal of both investigations.

Adding to the previous additions it is imperative to create an algorithm to unfold the clusters from the PBC conditions so that quantities such as the radius of gyration and the correlation function can be calculated in larger scales than the one shown in figure 17. Recently the idea of utilizing a tree structure to be able to traverse through the cluster would allow to generate a way in which one can start with a single particle (any particle would do) and from that particle obtain the child nodes, which would represent the neighbours of the particle, and then continue this process for all of the particles until all particles are accounted for. This would be possible due strictly to the fact that neighboring particles are always exactly 1 LU away from each other due to the calculations performed in equation 7 and 8.

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6. ASSOCIATED CONTENT

Original code for off-lattice simulations available in github: https://github.com/DiegoRos/CCA-OffLattice
Original code for on-lattice simulations available in github: https://github.com/DiegoRos/DLCA-OnLattice