Simulating and Visualising Sedimentary Cluster-Cluster Aggregation

K.A. Hawick
Institute of Information and Mathematical Sciences
Massey University – Albany, North Shore 102-904, Auckland, New Zealand
Email: k.a.hawick@massey.ac.nz
Tel: +64 9 414 0800 Fax: +64 9 441 8181
February 2010

Abstract
Recent simulations of diffusion limited cluster-cluster aggregation (DLCA) have shown systematic inhomogeneities in the shape and orientation of clusters formed when a sedimentary force is applied. Using custom simulation and visualisation techniques and programs we have carried out a microscopic study of these sedimentary inhomogeneities and have mapped out the model parameter space. We find various transitional regimes in terms of the sedimentary Peclet number and identifiable time regimes for the growth behaviour of sedimenting clusters. We postulate some explanations based on the microscopic inhomogeneities of typical clusters grown under various conditions and illustrate the effects with visual renderings and systems metrics.

Keywords: DLCA; sedimentary inhomogeneity; visualisation; simulation.

1 Introduction
Cluster aggregation is an important process in material science, chemical engineering and atmospheric science. Well-known material examples include the manner soot particles clump together as well as certain aerosols such as some paint mixtures and other colloids [1–3] and polymers [4]. There is an interesting interplay between the simple particle aggregation effect and the ballistic motion of particles that have a definite weight or preferred diffusive direction such as from a spray or in gravitationally controlled sediments. The “DLCA” model of diffusion limited cluster-cluster aggregation [5] has been studied in two dimensions but until recently has quite computationally expensive to study large systems in 3 dimensions and continues to attract new interest and reported work [6, 7].

The DLCA model is known to have interesting scaling behaviours [8] in terms of its dynamics [9] and also for the morphology of aggregates produced [10] and coagulation properties [11]. The model can be understood only to a limited extent using analytic methods such as mean field theory [12] and therefore numerical simulation methods are required to study the system.

Recent work by Peltomaki [13] and others suggests that sedimenting aggregates do not rotate appreciably but have an anisotropy that is independent of their size. In this paper we explore visual renderings of aggregating clusters in relatively large 2 dimensional model systems and also some small-sized 3 dimensional model systems. We develop some cluster and bulk metrics to compare with visual renderings of the model in different parameter regimes.

In Section 2 we describe how a custom simulation code for the cluster-cluster aggregation code was implemented to support measurements and visualisations of the simulated system. We present some screen-shots and ideas arising from the visualisation of the model in Section 3 and some selected measurements and other results in Section 4. Finally we offer some discussion, conclusions and ideas for further work in Section 5.

2 Custom Simulation Code
As Peltomaki et al. report, typical length scales for sedimenting aggregates in material systems are greater than 1 µm. Our model can be interpreted as having a lattice cell size of approximately this length and we wish to simulate as large a system as possible to capture multiple length scales during sedimentation.
The 3-d model is implemented as a lattice of cells with periodic boundary conditions in two of the dimensions and a preferred or downward direction in the third. The two periodic dimensions can be the same length and it makes most efficient use of memory to make the third downwards direction of the model lattice be as long as possible so that sedimenting clusters have as long an uninterrupted distance to fall as possible. Simulating a 2-d system (which is easier to visualise and easier to study large length scales, we choose the short horizontal direction to have periodic boundaries and the long vertical direction to be the direction of sedimentation.

Diffusion limited aggregation (DLA) is not a particularly difficult simulation to program and can even form a straightforward student programming assignment. Managing multiple clusters diffusing in a system so that clusters can combine and thus the number of separate clusters changes with time, is less trivial. Our diffusion limited cluster-cluster aggregation (DLCA) simulation code is implemented in the C programming language with a set of cluster member lists of references into a d-dimensional space-filling lattice of cells. This approach is memory intensive but makes use of both space-filling and list-oriented algorithms to maximise the speed performance of the simulation.

The system is initially seeded with random individual particles everywhere, and each particle is allowed to diffuse around randomly at each time step. A complete time step being deemed when every cluster has had the opportunity to move once on average. Particles or cluster can move in any of the 4(6) directions for a 2(3) dimensional simulation. If two particles or two clusters encounter each other - become adjacent on the lattice, they are deemed to stick together and become a single rigid cluster for subsequent moves.

The model system is initialised using the d-dimensional space-filling lattice which can have individual cells filled with a volume fraction [14] probability \(v_f\). Individual clusters are then identified, and given separate labels and cluster member pointer data structures can therefore be established. The cluster evolution algorithm can then be implemented by choosing a cluster to make a trial move in a randomly (but biased) direction. If the move leads to two clusters sticking together they are subsequently tracked as a single cluster in the data structure.

Checking whether two clusters are adjacent - and therefore whether they should stick and combine as one - requires an order-\(N \times M\) algorithm to check each \(N^\text{th}\) particle member of each cluster against all the \(M\) particles in the other cluster. This can be slightly speeded up by retaining the full d-dimensional mesh of particle cells in the program data structures, since it means that adjacencies and boundary condition information is available with fewer array/pointer lookups.

The buoyancy force \(\mathbf{F}_b = V \Delta \rho g\) where \(V\) is the volume of the cluster. In the lattice model a cluster of \(s\) particles has a volume of exactly \(s\). The gravitational acceleration is \(g\) in appropriate simulation units and the \(\Delta \rho\) is the difference in particle and background fluid densities. The viscous drag force is given by \(\mathbf{F}_d = -C_v v\) where the constant \(C\) is constant upon the fractal geometry [15] but is of order of magnitude similar to that of a falling ball of radius \(r\) which has \(C = 6 \pi \eta r\), with \(\eta\) being the kinematic viscosity. We assume that although the analytic expression for \(C\) is unknown for our fractal clusters, it is dependent only on an effective hydrodynamic radius. In addition to concentration dependencies [16], we can also assume a relationship such as \(v(s) \approx s^\delta\) for the cluster velocity \(v\) and some scaling exponent \(\delta\).

As Peltonaki reports, a useful measure of the relative strengths or importance of the undirected diffusive properties of a cluster and its sedimentary directed diffusion is the sedimentary Peclet number [17], defined as \(P_s(s) = \frac{v(s)\delta}{\eta}\), where the normal diffusivity is written as \(D\). We thus have a parameter - the Peclet number that lets us investigate different simulation regimes where sedimentation is more (less) important than the normal direction-less diffusion behaviour. Practically this lets us set up the model in terms of very simple biased diffusion probabilities for diffusion downwards (parallel to) and perpendicular to the direction of sedimentation.

\[
p_{\parallel} = \frac{4C_1 s^\gamma + C_1 s^\delta + C_2 s^{2\delta}}{2}
\]
\[
p_{\perp} = 2C_1 s^\gamma
\]

where we follow Peltonaki and take \(\gamma = -0.70\), \(\delta = 0.30\), based on an empirical fractal dimension \(d_f = 1.44\) and the relationships for the diffusion exponent \(\gamma = -1/d_f\) and sedimentary exponent \(\delta = 1 + \gamma\). This yields the following table of practical values:

In practice, this means that quite subtle changes to the relative probabilities for a cluster or particle moving perpendicular to the direction of sedimentation or parallel to it are controlled by the chosen Peclet number. The dependence on the cluster size \(s\) means that larger clusters are heavier and “fall faster” subject to counteracting viscosity and buoyancy effects. This model can readily be implemented as a lookup table and suitable random number generators used to apply the probabilistic diffusion algorithm.
Table 1: For Euclidean dimensions 2 and 3 and corresponding empirical fractal dimensions 1.44 and 1.75, we give calculated values for the directed probability \( p_d \) values for the peak cluster sizes and from which suitable \( C \) values can be calculated.

### 3 Visualisation

In this section we illustrate some of the clusters and cluster-cluster aggregating effects with some 2-dimensional and 3-dimensional rendered screen-shots.

Figure 1: A typical DLA Cluster rendered with 3 separate coloured lights (shades) in each of the x, y and z directions.

A relatively isotropic cluster of particles in shown in Figure 1 giving a shaded 3-d rendering of a typical diffusion limited aggregation (DLA) cluster grown on a cubic mesh lattice structure. This cluster has been in unbiased (ie non-directed) diffusion with no sedimentary effects. Figure 2 shows a 2-d set of such clusters growing together in the DLCA model, again in an unbiased environment. DLCA model clusters grow by absorbing individual particles in their vicinity leaving depletion zones around them, and hence growth slows down accordingly as solute material is used up. Clusters without a biased diffusion direction - as would be caused by realistic gravitational forces - will thus tend to isolate themselves.

Figure 5 shows a dramatic difference when clusters have weight and sedimentary diffusive effects come into play. Now the growing clusters move (in a preferred direction - shown as downwards on the figures) and will collide with other clusters, combining into super-clusters.

Figure 2: A set of clusters aggregating, with unbiased diffusion (zero Peclet number) after 10,000 growth steps with initial fill fraction of 0.01. The red identified cluster (large one at bottom left) was identified as the largest in the system. Statistically these clusters show no isotropic bias in their shape nor orientation.

Figure 3 shows the effect of the critical Peclet number regime. When sedimentary effects are too small compared to normal diffusive effects the system on the extreme right is similar to the non-sedimentary system shown in Figure 2. When the Peclet number is very large, large clusters carve out channels in the system but do not move too far to the right or left and thus cannot find new clusters to aggregate with. They therefore saturate in their growth. Near the critical Peclet number regime, very large clusters can form as they are able to join up with other clusters horizontally, and not just vertically. Note the characteristic “V” or “W” shaped cluster formations formed by clusters aggregating near the critical sedimentary Peclet number regime of approximately \( P_e \approx 5 - 10 \).

Figure 4 shows the shortest path between two leaf nodes in a downwards tree-like aggregate, as typically formed in the system. This typical cluster has been loaded into a graph analysis program and the pathways and other properties investigates. This inverted “V” or “W” shape is quite typical of 2-d clusters and the inverted tree shape appears to shield the inner tendrils from adhering to other clusters, except at the tips, or at the extreme left or right branches.
Figure 3: Snapshots of 1024x512 configuration when $s = 100$ for Peclet number values of 100, 10, 1. Field direction is shown as “down”. Fill fraction is 0.01. The mesh is periodic in both dimensions and a large joined cluster has swept around vertically (middle case). This shows in an exaggerated way the effect of a critical Peclet number of around $5 - 10$.

Figure 4: A single large cluster in a configuration, showing the downwards tree-like structure. The bolded path shows the shortest path between two selected leaf nodes, emphasising the tree-like form of the aggregates.

Figure 5: A set of three-dimensional clusters aggregating, with downward-biased diffusion.
Figure 5 shows a rendered screenshot of a set of aggregating three-dimensional clusters. The model system is 256 × 256 × 1024 cells in size, with sedimentation applied in the longer dimension - shown downwards. Clusters show qualitatively similar effects as those seen in larger 2-dimensional model systems. However it appears that the anisotropic “V” and “W” shapes seen in 2-d are not the same in 3-d models. This raises the question as to whether rotation is in fact an important sub-effect in 3-d systems.

4 Selected Results and Analyses

In this section we present and discuss some quantitative metrics applied to the DLCA model system and the implications for cluster properties. Results are given for numerical on a 2048 × 512 sized model, averaged over 100 random independent model starting configurations. Experimental uncertainties are computed as standard deviations with the error bars typically smaller than the plot symbols shown.

Figure 6: Number of separate clusters in a 2-d model system, averaged over 100 sample runs, with uncertainties smaller than plot symbol sizes.

Figure 6 shows a plot of the number of clusters in a particular system as the simulation progresses. At low Peclet number the straight lines with negative slope on the log-log plots imply that the number of clusters tends to a limiting power law behaviour. In each case the limiting slope appears independent of the Peclet number up to around unity. Thereafter the slope changes, although the precise behaviour is likely strongly influenced by finite systems size effects.

Figure 7 shows a plot of the number of unaggregated particles or monomers in a particular system as the simulation progresses. The number of free monomers decrease...
cays in a non-trivial manner. Solute is effectively used up and the effect is shown to steepen or occur more rapidly at high Péclet numbers when sedimentation effects dominate.

Figure 8 shows a plot of the number of particles in the largest cluster identified in the system. Although the data is only sampled over one representative cluster in each run, it suggest that this characteristic size grows as a power law in simulation time. Figure 9 shows a plot of the mean cluster size and displays a definite crossover in behaviour around a Péclet number of around \( P_e \approx 5 - 10 \).

Another analysis technique (which is faster to compute) involves looking at the individual particles and counts the number of bonds or open surfaces. Figure 10 shows the mean number of bonds and Figure 11 shows the mean number of open surfaces. The ratio of these two is shown in Figure 12. The straight lines on the log-log scale imply that the number of bonds varies as a power of the simulation time. Figure 11 shows the mean number of unbonded particle surfaces \( n_s \) in the system as it varies with simulation time. The straight lines on a log-log scale imply a power-law growth relationship so that \( n_s \approx t^\zeta \) where the growth exponent \( \zeta \) appears to change behaviour above a Péclet number of around \( P_e \approx 1 \).

The peaks in the mean surface to bond rations shown in Figure 12 vary with the applied Péclet number. At small Péclet numbers thes peaks occur quite early in the simulation, whereas for increasing Péclet number - which corresponds to greater influence of the sedimentary diffusion - the peaks occur later in the simulation. Even for very high Péclet number the peak saturation of growth is still seen although the shape of the peak becomes distorted, probably due to finite model system size effects.

5 Discussion and Conclusions

We have described the diffusion-limited cluster-cluster aggregation (DLCA) model and how it can be efficiently simulated and visualised in 2 and 3 dimensional model systems. A visual rendering has been shown to help considerably for models like this where the statistical measurements are difficult to otherwise interpret. These simulations are quite slow and computationally expensive to run but nevertheless configurations and animated movies can still be usefully produced.

The simulation work has shown the effect of the surface to bond ration rising and peaking in simulation time as solute particles are used up, and the position of the
peaks are shown to vary with the Peclet number for sedimentation. The 2-dimensional system shows a clear anisotropy of cluster shape as they sediment, compared to the directionless diffusion case. It is less clear what is happening in a 3-dimensional system and a larger simulated system is really required to properly interpret the clusters visually.

The characteristic “V” and “W” shapes formed by falling clusters and reported for 2-d systems by Peltomaki et al, does however appear to persist in 3-d systems. More work is required to fully characterise this in 3-d system and also to clarify the role or need for rotation of sedimenting clusters. Rotation is not feasible on a lattice cell model, but would be possible with particles and clusters at continuous coordinates in 3-d \( r = (x, y, z) \) space.

We have focussed on a cluster-cluster sticking probability of unity, but it is also possible for clusters to stick with fractional probability and therefore to be able to compactify before they join. Another interesting variation would be to allow large clusters to potentially break at suitably stressed branches and thus to allow the number of clusters in a system to rise as well as fall. There appears scope in this model and its variations to model further materials science properties.

Acknowledgements

It is a pleasure to thank H.A. James for help in coding some of the simulations work reported here.

References