Simulations of colloidal aggregation with short- and medium-range interactions

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Abstract

Extensive numerical simulations are used to simulate the aggregation of colloidal particles confined in a two-dimensional space. The colloidal particles experience short- or medium-range repulsions coming from a potential barrier that inhibits the aggregation of the particles into the primary minimum of the potential. When the potential barrier is short ranged, we find the usual reaction-limited colloidal aggregation (RLCA) or diffusion-limited colloidal aggregation cluster fractal dimensions for a high or low barrier, respectively. However, for medium-ranged, shallow barriers, for which the aggregation takes a long time as in the RLCA case, a very low fractal dimension is obtained, reaching values as low as 1.2 for the longer-ranged potentials considered. Nevertheless, as the aggregation proceeds, the cluster fractal dimension crosses over to a value close to the RLCA one, indicating that the small clusters of low fractal dimensionality act as the aggregating units of an RLCA system, given that they take a long time to react. A correspondence is made between our results and the experimental results by Hurd and Schaefer (Phys. Rev. Lett. 54 (1985) 1043).

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1. Introduction

The colloidal aggregation problem, the prototypical example of a random process that generates highly ramified dendritic structures, has been an active area of research for the past 20 years. Although an approach for the study of the dynamics of colloidal aggregation has been known for a long time [1,2], it was the discovery by Witten and Sander [3] of an aggregation algorithm that proportions similar structures, and the subsequent algorithms by Meakin [4] and by Kolb et al. [5] for cluster–cluster aggregation, that spawned renewed interest in the structure of these fractal colloidal aggregates. Although the two-dimensional aggregation of colloids is a process much less studied than in three dimensions [6], more and more researchers are starting to pay attention to aggregation processes in planar spaces. In 1985 Hurd and Schaefer [7] considered the first two-dimensional, experimental, colloidal aggregation system, consisting of silica microspheres confined to two dimensions at an air–water interface. The charged colloidal particles were trapped at the interface by surface tension and were allowed to aggregate by raising the salt concentration of the water substrate, thereby screening the repulsive electrostatic interactions. In this way, Hurd and Schaefer were able to obtain the fractal dimension of the formed clusters as $1.20 \pm 0.15$. Their explanation for this low value of the fractal dimension as compared to the diffusion-limited colloidal aggregation (DLCA) ($\approx 1.45$) or reaction-limited colloidal aggregation (RLCA) ($\approx 1.55$) values was that the clusters avoided approaching on the sides, which would increase the repulsion felt by both clusters, leading therefore to a sticking by the tips process. The next year a confirmation of the low fractal dimensionality was given by other authors [8] who, unfortunately, were working at a high concentration, for which a crossover from flocculation to gelation was imminent, masking in this way the values of the cluster fractal dimension. They were however able to show that the isolated clusters not belonging to the “infinite”, spanning network, had a fractal dimensionality close to the Hurd and Schaefer value. Shortly after the Hurd and Schaefer paper appeared, a rather artificial aggregation model that emphasises sticking by the tips of the clusters was proposed [9,10], assuming that the clusters were polarizables. That is, it was assumed that opposite charges appeared on their nearest tips and that the electrostatic attraction between them was so strong that it biased the random diffusion of the clusters, allowing them to finally stick on these tips. The value obtained for the fractal dimension with this model [10] was $1.28 \pm 0.03$. Nevertheless, Hurd and Schaefer never considered that each cluster as a whole was polarizable but that, instead, each colloidal particle carried a dipole moment [11] arising from the asymmetry of the counterionic cloud, occurring only in the water subphase of the system, an idea that was originally put forward by Pieranski [12] when considering two-dimensional colloidal crystals. In fact, most modern works [13–15] on the interaction between colloidal particles trapped at the air–liquid interface consistently consider the repulsion between the partially immersed particles as arising from this dipolar repulsion and, additionally, the stronger repulsion of unscreened dipoles on the non-wetted surface of the particles. This unscreened dipole repulsion would lead to strong, longer-ranged interactions, with an algebraic decay.

The purpose of the present work is to perform computer simulations of two-dimensional colloidal aggregation of particles interacting with a repulsive potential
barrier that can be systematically changed in height and range. We preferred to use a potential barrier with no apparent relation to a particular physical system, so that the results could be more universally applicable. A model potential barrier of a Yukawa form: 

\[ V/\kappa = (V_0/\kappa) \exp(-\kappa(r - 1))/r \]

was assumed for this purpose, where the height and range can be systematically varied by varying the parameters \( V_0 \) and \( \kappa \). Here, the distance \( r \) was measured in units of the diameter. The ultimate goal is to get the cluster fractal dimension from the simulations and compare it with known results for the DLCA and RLCA cases, and also with the longer-ranged case of Hurd and Schaefer. In the next section we will sketch the model used to get our results. We will also briefly outline there the parameter values used for each case. In Section 3.1 we will present the results for the fractal dimension obtained for the short-ranged case, with a high value of the \( \kappa \) parameter. We will see how, by varying \( V_0 \) from a low value to a high value, we can crossover from the DLCA fractal dimension of 1.45 to the RLCA value of 1.55. In Section 3.2 we will consider the opposite case of a longer-ranged barrier. We will fix the \( V_0 \) to a given value and vary \( \kappa \) to systematically lower values, in order to consider longer-ranged repulsions. We will see that, in this case, we can recover the low cluster fractal dimension (\( \approx 1.20 \)) of Hurd and Schaefer. Finally, in the last section, we will discuss the results and end with some concluding remarks.

2. The model

This is an off-lattice model in which we consider circular, interacting particles with diameter \( a \), that are initially randomly distributed without particle overlapping in a square box of size \( L \), with periodic boundary conditions. As the aggregation proceeds, we deal with a collection of clusters made of touching disks. The algorithm is as follows:

1. Pick one of the clusters at random.
2. Move it with probability \( D/D_{\text{max}} \) a certain step length \( l \) on a random direction, where \( D(\sim 1/R_g) \) is the diffusion coefficient of the selected cluster and \( D_{\text{max}} \) is the maximum diffusion coefficient of any cluster in the sample. Here \( R_g \) is the radius of gyration of the selected cluster.
3. Calculate the new energy of interaction \( (V_f) \) of the particles of the moving cluster with all the other clusters. If \( V_f \) is smaller than \( V_i \) (the energy of interaction of the particles of the moving cluster with all the other clusters, before the move is performed), the move is accepted; otherwise it is only accepted with probability \( \exp(-|V_f - V_i|)/k_BT) \).
4. If any particle of the moving cluster collides with any other of another cluster, both clusters stick together and are joined.

The concentration was always kept at the low area fraction of 0.001, in order to prevent concentration effects to play a role in the problem [16,17]. In one set of runs, the potential was kept with the relatively short range of \( \kappa = 6 \), while the height
took the values $V_o/k_BT = 0, 1, 2, \ldots, 9$. In another set of runs, the height was fixed at the value $V_o/k_BT = 5/\sqrt{2}$, while the range took the following three values: $\kappa = 2, 1, 1/\sqrt{2}$. For the first set of runs four step lengths were used for each of the cases: $l = a/2.5, a/5.0, a/7.5$ and $a/10.0$. For the second set of runs only the following three step lengths were used: $l = a/2.5, a/5.0$ and $a/7.5$. The number of particles used in each simulation was 20,000, except for the case $V_o/k_BT = 5/\sqrt{2}, \kappa = 1/\sqrt{2}$ and $l = a/7.5$, for which only 3850 particles were considered. It is important to emphasise here that these are highly CPU intensive simulations, particularly for high values of the $V_o$ parameter and/or long ranges. Therefore, when considering decreasing step lengths the simulation time was increasing disproportionately, reaching times of several months in an Origin2000 processor. That is why we could not consider smaller step lengths for the cases mentioned. In Fig. 1 we are showing the potentials used for both sets of runs. A look at these potentials suggests that in order to consider the DLCA and RLCA cases, shorter-ranged potentials (larger values of $\kappa$) than the ones shown should be considered, given that it is generally accepted that a truly RLCA case is obtained with a high barrier of negligible width. However, in that case much shorter step lengths would be needed in order for the particles to be able to thoroughly sample the potential which, as stated, it is for the time being an impossible task to perform.

### 3. Results

#### 3.1. The short-ranged barrier

The fractal dimension $d_f$ was obtained through the radius of gyration method, in which a log–log plot is made of the radius of gyration of all clusters formed during the
Fig. 2. (a) A log–log plot of the average radius of gyration vs. size of all the clusters formed during a simulation for which the parameter values are $V_o/k_BT = 1, \kappa = 6$ and $l = a/7.5$. The arrows limit the region inside which a good straight line is established. (b) Same as in (a) but now for the parameters $V_o/k_BT = 8, \kappa = 6$ and $l = a/10.0$.

aggregation vs. the size of the corresponding cluster. One then obtains a set of points through which a straight line is usually fitted, the $d_f$ is then extracted as the inverse slope of that line. In those cases for which a change in behaviour as a function of size is expected, we have found more advantageous [16] to plot the average radius of gyration, where the average is taken over all clusters lying inside segments of constant length in the logarithmic size scale. In this way one can distinguish the regions for which a straight line is established (something that can not be done when a huge set of scattered points are plotted) and obtain a $d_f$ for each of the regions. In Fig. 2(a) is shown this plot for the $\kappa = 6, V_o/k_BT = 1$ and $l = a/7.5$ case. The portion of the plot between the arrows indicates the region for which a good straight line is established. Before the first arrow we have the usual curvature describing the corrections to scaling for small clusters while, after the second arrow, the points are not considered because they are obtained from averages of very few clusters, having therefore a large uncertainty. The inverse slope proportions the value $d_f = 1.439$ of the fractal dimension for this case, which is close to the accepted value of the DLCA fractal dimension ($d_f \approx 1.45$).

In Fig. 2(b) we are presenting the corresponding plot for the $\kappa = 6, V_o/k_BT = 8$ and $l = a/10.0$ case. The straight line obtained between the two arrows produces the value $d_f = 1.567$, which is now close to the accepted RLCA value ($d_f \approx 1.55$).

In Fig. 3 we are now showing the $d_f$’s obtained for all the short-ranged cases ($\kappa = 6$) as a function of the $V_o/k_BT$ parameter. In Fig. 3(a) we are plotting them for the $l = a/2.5$ case, while in Figs. 3(b)–(d), the plots are for the $l = a/5.0, a/7.5$ and $a/10.0$ cases, respectively. In Fig. 3(a) we can see that the fractal dimension stays at a value around 1.45, no matter the value of the $V_o/k_BT$ parameter. This indicates that, because of the long step length, the clusters can jump over the potential barrier and collide with other clusters, the net effect being that the barrier is not felt and the clusters aggregate as in a DLCA process. However, by decreasing the step length to $l = a/5.0$ (Fig. 3(b)) we can see a noticeable increase of the fractal dimension for the high $V_o/k_BT$ cases, trying to reach values close to those found for RLCA. This indicates that the particles
and clusters are starting to sample the potential more thoroughly, which occurs more abundantly for the $l = a/7.5$ and $a/10.0$ cases (Figs. 3(c) and (d)).

It is interesting to make a plot of the clusters obtained to make a physical visualization of their structure. In Fig. 4(a) we are looking at a portion of a cluster for the $\kappa = 6, V_0/k_BT = 1$ and $l = a/10.0$ case, while in Fig. 4(b) we are considering the same $\kappa$ and $l$, but now with a $V_0/k_BT$ value of 8. We can see that the particles are more crowded in Fig. 4(b) than in Fig. 4(a), as it should be for an RLCA case with a higher fractal dimension. However, by looking at the individual particles with a greater detail we notice in Fig. 4(b), ironically, that the inner structure is a little more open and chainy (with less branching points) than in Fig. 4(a). This reflects the fact that this is not really a true RLCA system, because the potential barrier is not of negligible width. Nevertheless, when looking at the structures in a less detailed manner, the clusters are really RLCA clusters with a fractal dimension around 1.55. That the inner structure is more open and chainy will be magnified when considering the longer-ranged cases, as we will see below.

Fig. 3. (a) A plot of the cluster fractal dimension $d_f$ vs. the parameter $V_0/k_BT$, for the runs with $\kappa = 6$ and $l = a/2.5$. (b) Same as in (a) but now for $l = a/5.0$. (c) As in (a) but now with the value $l = a/7.5$. (d) As in (a) but with the value $l = a/10.0$. 
3.2. The medium-ranged barrier

In Fig. 5 we are considering the log–log plots of the average radius of gyration vs. size for the $V_0/k_BT = 5\sqrt{2}$ and $\kappa = 2$ case. Fig. 5(a) is for $l = a/2.5$, while Figs. 5(b) and (c) are for $l = a/5.0$ and $a/7.5$, respectively. In these new plots we now see that, after the corrections to scaling, the straight line breaks into two straight lines. For the first straight line (small sizes), the cluster fractal dimension takes on the values of 1.385, 1.384 and 1.334, for $l = a/2.5$, $a/5.0$ and $a/7.5$, respectively, which are smaller than the DLCA or RLCA fractal dimensions. For the bigger sizes, however, the new straight line proportions the values of 1.562, 1.638 and 1.558, for $l = a/2.5$, $a/5.0$ and $a/7.5$, respectively. These new values are now closer to the accepted value of the RLCA fractal dimension ($d_f \approx 1.55$), which indicates that the small, open clusters act as the aggregating units of an RLCA system, given that they take a long time to react. The fractal dimension for the small sizes, lower than the DLCA and RLCA fractal dimensions, is however not very close to the 1.20 obtained by Hurd and Schaefer [7]. This prompted us to consider even longer ranges, with the consequent increase in computing time, to see if the $d_f$’s could be diminished further. In Fig. 6 we see the corresponding plots for the $V_0/k_BT = 5\sqrt{2}$ and $\kappa = 1$ case. Again, Figs. 6(a)–(c) are for $l = a/2.5$, $a/5.0$ and $a/7.5$, respectively. Although the fractal dimension for the larger sizes ($d_f = 1.564, 1.627$ and $1.627$, for $l = a/2.5, a/5.0$ and $a/7.5$, respectively) stays at around 1.6, as for the first range considered of $\kappa = 2$, the small-cluster fractal dimensions are now $d_f = 1.281, 1.303$ and 1.351, for $l = a/2.5, a/5.0$ and $a/7.5$. These new values are on average smaller than the corresponding ones for the previous range. The last range we tried, and with only 3850 particles for $l = a/7.5$ as stated, was $\kappa = 1/\sqrt{2}$. In Fig. 7 we see the corresponding plots for this range, again with $V_0/k_BT = 5/\sqrt{2}$. As usual, Figs. 7(a)–(c) are for $l = a/2.5$, $a/5.0$ and $a/7.5$, respectively. In this final case, the large-cluster fractal dimension takes on the values $d_f = 1.573, 1.611$ and 1.527, for $l = a/2.5, a/5.0$ and $a/7.5$, respectively, which are again close to the
corresponding RLCA value. For the small clusters, however, the $d_f$'s are now 1.316, 1.183 and 1.169, which are quite close to the 1.20 of Hurd and Schaefer. All this led us to believe that, indeed, the low value of the experimental fractal dimension is a consequence of a medium-ranged potential barrier. If this were the case, the physical picture proposed by Hurd and Schaefer applies, that is, two colliding clusters could not approach on their sides very easily because that would imply more than a single pair of repelling particles. On the other hand, if the clusters approach by their tips, there is only the potential barrier of a single pair that the Brownian motion has to overcome.

It is instructive to make a plot of the clusters in this medium-ranged case, similar to what we did for the DLCA and RLCA cases. In Fig. 8 we are showing sections of 3 clusters obtained with $V_o/k_B T = 5/\sqrt{2}$, $\kappa = 2$, and with the three different ranges used. Fig. 8(a) is for $\kappa = 2$, while Figs. 8(b) and (c) are for $\kappa = 1$ and $1/\sqrt{2}$, respectively. As we can see very clearly, the longer the range of the potential barrier, the fewer the branching points that the inner structure of the clusters has. In other
words, the inner structure becomes more chainy, leading to a lower fractal dimension for small clusters. The question remains of how is, pictorially, the transition to RLCA for very big clusters. In order to see this, we have to look at the picture of a large cluster with less magnification. In Fig. 9(a) we show a section of a cluster, with half the magnification used in Figs. 8, for the case $V_o/k_B T = 5/\sqrt{2}$, $\kappa = 1/\sqrt{2}$ and $l = a/5.0$. As we can see, the very inner structure remains being chainy while the overall figure looks more crowded (with less open spaces) than a DLCA cluster, shown in Fig. 9(b) for comparison. This means, as stated, that the small, open clusters of low fractal dimensionality act as the aggregating units of an RLCA system, given that they take a long time to react. This is therefore the reason why we have the crossover to RLCA.

4. Discussion and conclusions

We have seen how by introducing a repulsive, thin potential barrier of a sufficient strength (as measured by its height), we can crossover from the usual DLCA regime to a reaction-limited scheme, with the condition that the step length of the walks
performed by the colloidal particles and clusters is sufficiently short compared to the width of the barrier. In this way the particles can sample more effectively the potential felt by them.

On the other hand, by increasing substantially the range of the barrier, even for not very high ones, we can go to a situation for which the mechanism proposed by Hurd and Schaefer applies, namely that the clusters join preferentially at the tips in order to avoid their sides when approaching, which would create a high energy of interaction. However, as the aggregation proceeds, those very stringy and chainy clusters act as the units of an RLCA system, due to the many attempts necessary for two of those clusters to join. An additional required ingredient for this crossover to occur is that when rescaling the small stringy clusters into units of the new system, the interaction potential should not rescale accordingly. Our system complies with this prescription, because the range of the potential continues to be of the order of magnitude of the diameter of the primary colloidal particles. Therefore, this range is now quite small compared to the size of the new units (stringy clusters). In this way we can have a true RLCA system and can expect a change of the fractal dimension from the low values obtained by Hurd and Schaefer to a higher RLCA-type fractal dimension.
Fig. 8. A section of a big cluster obtained during a simulation with $V_o/k_B T = 5/\sqrt{2}$, $l = a/7.5$, and (a) $\kappa = 2$, (b) $\kappa = 1$ and (c) $\kappa = 1/\sqrt{2}$.

Fig. 9. (a) A section of a big cluster obtained during a simulation with $V_o/k_B T = 5/\sqrt{2}$, $\kappa = 1/\sqrt{2}$ and $l = a/5.0$, presented with half the magnification shown in Figs. 4 and 8. (b) A section of a big cluster obtained during a DLCA simulation with $V_o/k_B T = 0$, again presented with half the magnification of Figs. 4 and 8.
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