Colloidal Aggregation in the Presence of Gravity

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ABSTRACT

A computional model for colloidal aggregation is presented that considers the Brownian motion, the sedimentation and the deposition experienced by the colloidal particles and clusters. Among the results, for intermediate strengths of the downward gravitational drift, the aggregation crosses over from diffusion-limited colloidal aggregation (DLCA) to another type of aggregation with a higher cluster fractal dimension, D_f. We also get a critical gelation concentration higher by several orders of magnitude, as compared to the non-drifting case. Although our results are in full accordance with the experimental ones, some interpretations are different.

Keywords: Colloidal Aggregation, Sedimentation, Deposition, Computer Simulations

1 INTRODUCTION

Only a few works [1-6] of the whole lore on colloidal aggregation [7-10] consider the effect of sedimentation and cluster deposition on the resulting cluster formation. However, the combined action of Brownian motion and the external gravitational field may lead to a different behavior on the structural and dynamical quantities describing the aggregates. Experimentalists need to resort to a number of tricks to eliminate the action of the gravitational field, like flipping the sample very often during the aggregation, considering a suspension fluid whose density closely matches that of the colloidal particles, etc., in order to compare their results to the theoretical and simulational ones, for which only the Brownian motion is considered. It is therefore necessary to advance our theoretical and simulational knowledge of colloidal aggregation in the presence of a gravitational field, in order to have a clear knowledge of all the processes occurring in real aggregating systems.

In the most recent experimental studies that consider explicitly the sedimentation of the big clusters and their deposition on the bottom of the sample, Allain *et al* [4, 5] found an increase in the fractal dimension of these settling clusters, attributing this increase to a restructuring mechanism due to the hydrodynamic stresses felt by the different parts of the clusters. Another result found by them was a much higher concentration required to have gelation. In this article we present results of a colloidal aggregation model that takes into account the coupling and interplay between aggregation and sedimentation, and that considers furthermore the subsequent deposition with the consequent mass depletion in the bulk of the sample. Although we are able to obtain the experimentalists results, our interpretation is somewhat different.

2 THE MODEL

The sedimentation velocity experienced by a cluster of N spherical particles of radius a and mass m_o is

$$v_s = \frac{m_o(1-\rho/\rho_o)gN}{f} = \frac{m_o(1-\rho/\rho_o)g}{k_BT} DN \quad , \qquad (1)$$

where ρ_o is the density of the particles, ρ is that of the suspension fluid, f is the friction coefficient of the cluster, D ($\sim N^{-1/D_f}$) its diffusion coefficient and T is the temperature. Let t_o be the time for which the cluster diffuses a particle diameter ($2a$), that is, $t_o = 2a^2/D$. During the same time, the cluster drifts a distance $d_s = v_s t_o = P_e N d$, where $P_e \equiv m_o(1-\rho/\rho_o)ga/k_BT$ is the Peclet number of the colloidal particles in that fluid and d is the diameter of the particles. It is found that P_e is of the order of unity if the particles are 1 μm in diameter, $1-\rho/\rho_o$ is less than but of the order of unity and T is room temperature. However, if the diameter is 0.1 μm such quantity is of the order of 10^{-4}, while if the diameter is 10 μm, P_e goes as high as 10^4. Therefore, 1 μm marks the transition between diffusive and drifting behavior for *individual* particles.

Although we tried to attack this problem computationally a few years ago [6] and were able to show a hint to the crossover to another regime with a higher cluster fractal dimension, the model was uncapable to proportion the much higher critical gelation concentration because there was no deposition built in the model, a necessary ingredient as we will see. At this point we

should recognize that in order to study sedimentation for not very high Peclet numbers, as Allain *et al* did [4, 5], large box sizes have to be used that would allow the growth of clusters big enough capable to start drifting downwards. If in addition the height of the sample has to be about 20 times its lateral dimensions [5], in order to follow the drift of the big clusters, only a huge lattice would permit us to study the sedimentation with deposition. This exceeds by far our available computer memory. Here, a cubic lattice of size L was considered instead, with periodic boundary conditions on the 3 spatial directions, that represents *in an average way* any cubic slice of the prism of height H ($= 20\,L$ in Ref. [5]). Whenever a cluster moves on the z direction a lattice spacing d, a quantity Z_s is updated, that proportions the total distance in units of d that the cluster has moved downwards (taking into account the movement of all its ancestors; i.e., the largest of the two quantities Z_s of the "parent" clusters is inherited to the "child" cluster after a merging). If the movement is downwards, the cluster is taken out of the cubic box (which means that it has been deposited on the bottom) with probability $1/(H - Z_s)$. Thus, the bigger clusters with the larger Z_s are taken out of the sample with higher probability.

Let us define $\Delta t_{dif} \equiv d^2/2D_{max}$ as the time taken by the most mobile cluster to diffuse one lattice spacing. Also, let $\Delta t_{drif} \equiv d/v_s^{max}$ be the time taken by the largest cluster to sediment downwards one lattice spacing. The algorithm is as follows: (a) If $\Delta t_{drif} < \Delta t_{dif}$ then (i) Pick a cluster in a cyclic way. (ii) The time is increased by $\Delta t_{drif}/N_c(t)$, $N_c(t)$ being the number of clusters *in the bulk* at time t. (iii) The quantity $\Delta t_{drif}\ \ v_s/d$ is calculated and the result is added to a variable of that cluster. If the sum is greater than one, the cluster is moved downwards one lattice spacing and the new value of the variable becomes the remainder of the sum modulus one; the variable Z_s is consequently updated to its previous value plus one and the cluster is taken out of the sample with probability $1/(H-Z_s)$. We then go back to the starting situation to calculate Δt_{dif} and Δt_{drif}. (iv) If the cluster is moved but not taken out, we check for overlapping with other clusters, in which case the moving cluster is taken back to its original position and the overlapping clusters are merged. We then go back to the starting situation to calculate Δt_{dif} and Δt_{drif}. (v) The cluster now moves one lattice spacing on a random direction, with probability $(\Delta t_{drif}/\Delta t_{dif})(D/D_{max})$. If it moves along the z direction, Z_s is updated, etc., as in point iii. (vi) If the cluster is moved but not taken out, we check for overlapping, etc., as in point iv. (vii) We go to point i. (b) If, on the other hand, $\Delta t_{dif} \leq \Delta t_{drif}$ we follow the same procedure (a), with the difference that everywhere we find Δt_{drif} it is replaced by Δt_{dif}.

The simulations were stopped just before gelation for the gelling systems; for the non-gelling simulations, they were stopped after all the clusters had been deposited. One volume fraction $\phi = 0.01$ was considered, for which 5 values of P_e were chosen: $P_e = 10^{-8}$ (DLCA simulation), $10^{-3}, 10^{-2}, 10^{-1}$ and 10^{0}. For the first 3 Peclet numbers, the system was gelling, while for the last Peclet number it was non-gelling; for $P_e = 0.1$, some of the simulations percolated the box while the others didn't. For most of the computations, 10 simulations of size $L = 270$ and $H = 10\,L$ were done for each Peclet number, except when trying to calculate the critical concentration to have gelation, in which case L and ϕ were varied also.

3 RESULTS

In Fig. 1a, for $P_e = 10^{-8}$ (DLCA case), is shown a log-log plot of the average radius of gyration of all the clusters formed during the aggregation *vs.* size, the average taken over intervals of constant magnitude on the logaritmic size scale. Although for small cluster sizes we see a curvature that describes the corrections to scaling, after the arrow labeled with the letter a we now see a very good straight line, spanning more than two decades, that ends at the second arrow with the same label. The fractal dimension obtained from this straight line, $D_{fa} = 1.882$, compares well with the reported DLCA value on cubic lattices [11] at the given concentration ($D_f = 1.887$). Beyond the second arrow the big clusters, with a linear size of the order of magnitude of the enclosing box, try to reach the higher percolating clusters fractal dimension. In Fig. 1b, for $P_e = 0.001$, we now clearly see that the straight line breaks into two straight lines, the breaking point occurring at around $N \approx 1000$, signaling two different fractal dimensions, one for the small clusters and another for the big ones. The small clusters fractal dimension, $D_{fa} = 1.872$, is still close to the accepted DLCA value, while the big clusters fractal dimension, $D_{fb} = 2.326$, is now close to the value (2.2 or 2.3) reported by the experimentalists [4, 5] for their big settling clusters. Although Allain *et al* invoked a restructuring mechanism due to the high hydrodynamic stresses felt by the different parts of the big drifting clusters, to account for the increase in the fractal dimension, we are not allowed to do that. Ours is a rigid cluster model that does not permit any restructuring but that, nevertheless, proportions the correct fractal dimension. The explanation proposed here is simpler: *The big settling clusters sweep, on their way downwards, the small clusters and single particles they find below, which in turn get inside the holes of the big clusters, making them more compact.* In Fig. 1c, for $P_e = 0.01$ the breaking point now occurs at around $N \approx 200$, indicating that smaller clusters are now drifting downwards. The small clusters fractal dimension in this case, $D_{fa} = 1.868$, is again close to the accepted

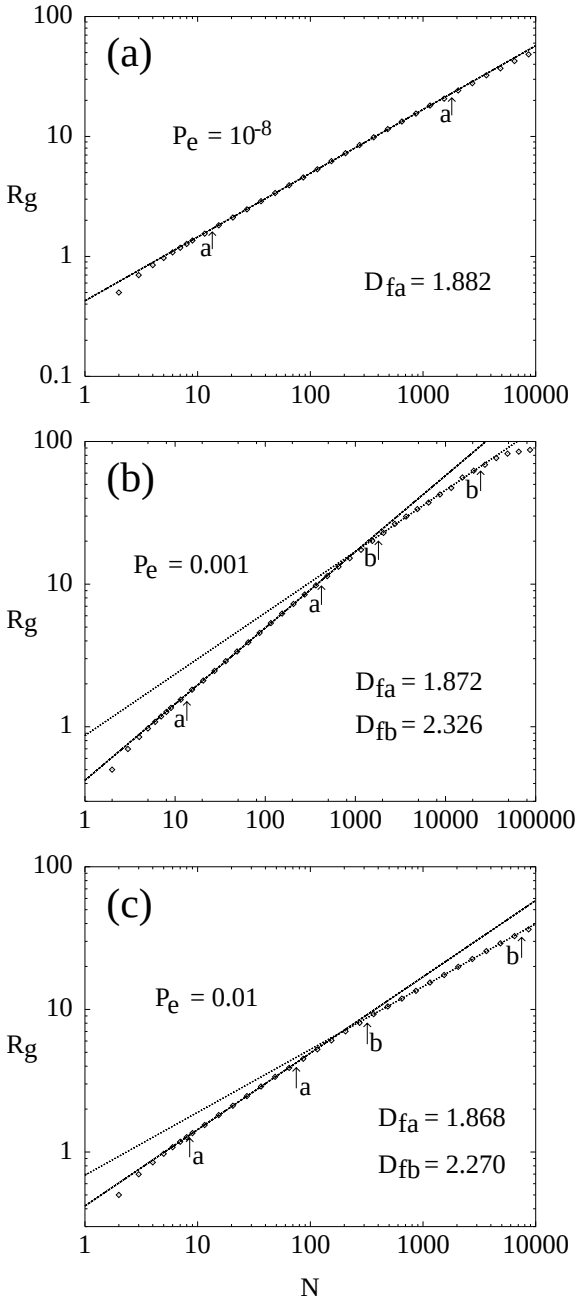

Figure 1: A log-log plot of the average radius of gyration of the clusters *vs.* size for the Peclet numbers: (a) $P_e = 10^{-8}$, (b) $P_e = 0.001$, and (c) $P_e = 0.01$. Between the arrows labeled a and labeled b we can clearly see the appearance of well defined straight lines, defining the small clusters and the big clusters fractal dimension, respectively.

DLCA value, while the big clusters fractal dimension, $D_{fb} = 2.270$, is again close to the Allain *et al* value [4, 5].

The following procedure was used to obtain the critical gelation concentration ϕ^*: For a given Peclet number and a given system size L, about six values of ϕ around (above and below) ϕ^* were considered. For each of those ϕ values 20 (sometimes 40) simulations were run and a record was kept of the number of simulations that percolated the enclosing box. We defined the probability to percolate, P_g, for a given ϕ as the number of simulations that percolated divided by the total number of simulations done for that ϕ. In Fig. 2a are shown the six points for the case $P_e = 0.01$ and $L = 120$, while in Fig. 2b we see the corresponding points for the $P_e = 0.01$ and $L = 210$ case. As it is evident from the figure, the gelation transition becomes sharper the larger the box size we consider. The six points can be fitted very well by the following function:

$$P = (tanh(a(\phi - b)) + tanh(ab))/(1 + tanh(ab)), \quad (2)$$

where a and b are two adjustable parameters. The critical concentration ϕ^* was defined as that ϕ value for which the function P had the value of $1/2$. As it is also evident from the figure, ϕ^* becomes smaller for the larger box sizes.

With the values of ϕ^* as function of P_e and L we are

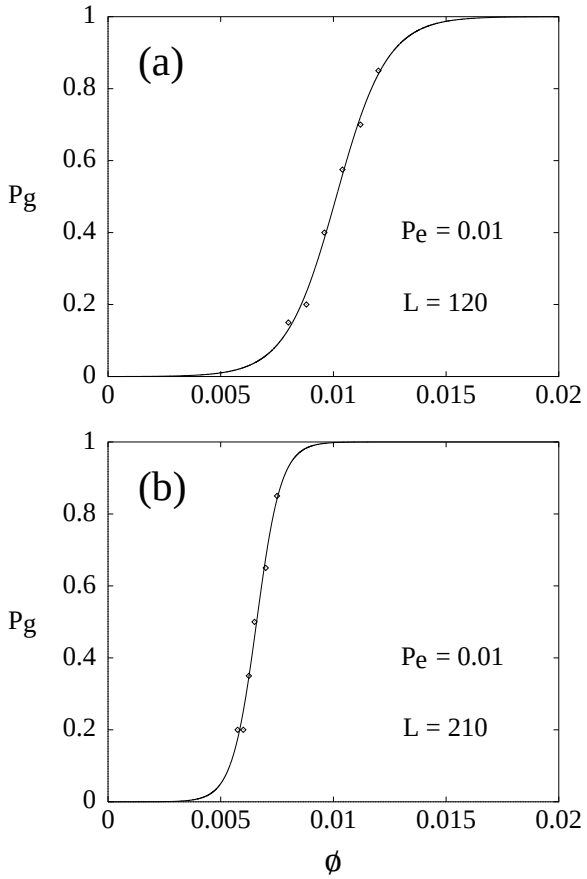

Figure 2: The probability to gel as a function of concentration for: (a) $P_e = 0.01$ and $L = 120$, and (b) $P_e = 0.01$ and $L = 210$.

now able to obtain the phase diagram, shown in Fig. 3. In that figure we are plotting ϕ^* *vs.* $1/L$ for each Peclet number considered. As we can see, the points lie nicely on a straight line whose intercept with the ϕ^* axis gives the critical gelation concentration for the infinite system. Above each of the straight lines we have the gel phase while below we have the sol phase, for the corresponding Peclet number. We note from the figure that the straight line for $P_e = 10^{-8}$ (DLCA case) has a zero intercept with the ϕ^* axis (the small negative value shown in the figure comes from the statistical uncertainties). This should be the case for an aggregating system made of fractal aggregating entities (clusters). The interesting thing is that for the other Peclet numbers the ϕ^* does not extrapolate to zero. The reason for this nonzero value comes from the deposition of the clusters on the bottom, which in turn produces a depletion of mass in the bulk of the sample. This depletion of mass impedes somehow the gelation transition, making it more difficult to occur. This is the ϕ^* change by several orders of magnitude found by Allain *et al* [4], when going from the DLCA case to a Peclet number of about $P_e \approx 10^{-5}$. As a matter of fact, their ϕ^* for the DLCA case is not actually zero because they are not really treating an infinite system: If the width of their sample is of the order of a centimeter while the diameter of the particles is of the order of a tenth of a micron, we estimate that their L is around 10^5. Another proof that the depletion of mass in the bulk causes the high values of the critical gelation concentration comes from the other aggregation model proposed previously by the present author [6], in which only Brownian motion and sedimentation were considered but with no cluster deposition on the bottom of the sample. Although that model proportioned the higher cluster fractal dimension, it was not possible to obtain the much higher (by several orders of magnitude) critical gelation concentration, but only a little bit higher to account for the more compact clusters produced as compared to the DLCA clusters.

In summary, we have shown with a computer aggregation model, that takes into account the sedimentation and deposition experienced by the colloidal particles and clusters, that the system crosses over from DLCA to another aggregation regime with a higher cluster fractal dimension and with a much higher critical gelation concentration. Although these findings are in accord with the experimental results, the interpretation given here for the higher fractal dimension comes from the sweeping mechanism which forces the small clusters and single particles to get into the holes of the big clusters, making them more compact, and not from any restructuring of the clusters as proposed by the experimentalists. We are, however, not saying that there is no restructuring of the big clusters, which looks like a plausible idea. We are only stressing that the main change in D_f comes from the sweeping mechanism.

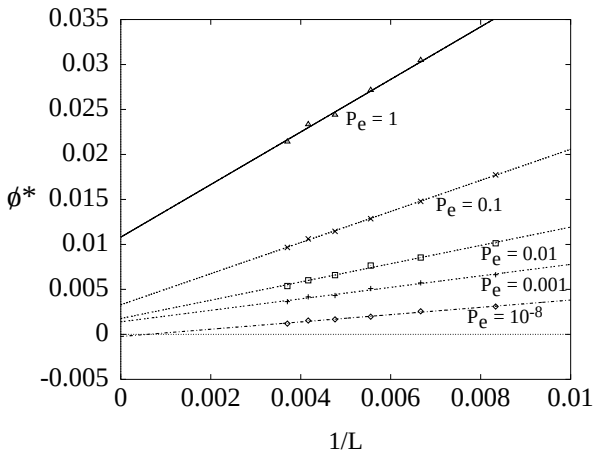

Figure 3: The phase diagram separating the gel phase above the straight lines from the sol phase below, for the different Peclet numbers studied.

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