Aggregation and Sedimentation in Colloidal Suspensions

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We show that the coupling between aggregation and sedimentation in colloidal suspensions gives rise to either cluster deposition or to settling of a gelled suspension, depending on the volume fraction of particles. In the latter case, we report novel settling properties which are interpreted in terms of the specific spatial structuring of the suspensions.

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Recently, many works have been devoted to understanding aggregation phenomena in colloidal suspensions. When the rate of growth is controlled by the Brownian diffusion of clusters, it is now established that the diffusion limited cluster aggregation (DLCA) model provides a fairly good description of simulations and experiments [1–4]. By contrast, investigations of situations where aggregation is due to the combined action of Brownian motion and an imposed external field like gravity are scarce [5,6]. At short times, initially dispersed particles and clusters undergo Brownian motion, and aggregation is still correctly described by the DLCA model. Later on, the clusters may be large enough to settle under gravity, and sedimentation then alters the growth mechanism.

In this Letter, we study a set of novel phenomena arising from the coupling between aggregation and sedimentation in colloidal dispersions. The purpose is twofold. First, we demonstrate that aggregating suspensions may undergo settling in two ways when the volume fraction of particles is varied: by cluster deposition or the collective settling of a gelled suspension. We present the physical origins of these two phenomena using a scaling approach which makes it possible to take into account the competition between cluster diffusion and sedimentation. Second, we show that the settling dynamics of the gelled suspensions can be explained in terms of the existence of a specific spatial structuring.

The experiments reported in the following have been performed with aqueous suspensions of calcium carbonate particles (Socal U1 supplied by Solvay Co.). Calcium carbonate is dense, $\rho = 2.7$ g/cm^3, so that settling takes place rapidly. The particles are 0.07 μm in diameter. Their surface charge is ruled by the concentration of calcium and carbonate ions in the suspending medium [7–9]. In the range of volume fractions investigated ($10^{-4} < \Phi < 3 \times 10^{-2}$), the concentration of calcium ions remains nearly constant, about 2×10^{-4} mol/l, and the pH increases slightly from 8.7 to 9.2. In these conditions, the charge borne by the particles is very small [7–9] and the net colloidal interaction is the van der Waals attraction without electrostatic repulsion. This result is supported by the observation that suspensions are not sensitive to ionic strength variations. The samples are prepared by adding weighed amounts of calcium carbonate powder to deionized water. Before undertaking an experiment, the clusters are fragmented and the colloidal particles dispersed by strong stirring for at least 100 h. We have checked the efficiency and the reproducibility of the dispersion state of the suspension by optical and electronic microscopy. After stirring, the colloidal particles are well dispersed and no cluster with a diameter exceeding 0.2 μm can be found in the suspension. The experimental cells are cylinders which are 12 mm in diameter and 70 mm high; they are completely filled with suspension and sealed carefully to avoid the existence of a meniscus on the top of the suspension. Experimentally, the origin of the time scale is taken when the suspensions are poured into the experimental cells.

We have studied extensively the time evolution of the suspensions as a function of the volume fraction Φ and we have found three distinct behaviors. At low volume fraction, we observe cluster deposition. Just after the suspension has been poured into the experimental cell, it appears uniformly turbid but, after a time, it becomes lumpy and we can discern small aggregates of different sizes which are settling at different velocities. The largest clusters, which fall the fastest, sweep up the small ones underneath and grow the fastest. Gradually, the suspension becomes less and less turbid and, later on, we see perfectly well-defined clusters settling separately in a clear fluid. They deposit at the cell bottom and form a voluminous sediment which compacts slowly. At higher volume fractions, cluster deposition is replaced by collective settling. Aggregates no longer settle separately; instead, they form a gel very quickly, which fills in the whole experimental cell and settles under its own weight afterward. Now, a sharp interface separates the suspension settling underneath from the supernatant clear of particles above. This interface moves downward until it reaches its equilibrium height. Experimentally, we have found that the volume fraction Φ^* separating cluster deposition from collective settling is $\Phi^* \cong 3 \times 10^{-3}$. Finally, there exists a volume fraction, $\Phi^{**} \cong 5 \times 10^{-2}$, above which the colloidal gel does not settle. The existence and the value of Φ^{**} are related to the mechanical properties of the calcium carbonate gel at

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equilibrium; the prediction of Φ^{**} and the study of the regime $\Phi > \Phi^{**}$ are beyond the scope of this Letter, which focuses on the coupling between aggregation and sedimentation, and will not be considered here. In Fig. 1, the different domains of the volume fractions and the corresponding behaviors of the suspension are reported along the vertical axis.

Let us now set out the physical origin of the cluster deposition and collective settling which have just been described. We first consider the suspension in the absence of gravity. Since the interaction between the particles is purely attractive, we expect that the aggregation mechanism in the suspension follows DLCA. In this mode of aggregation [1–4], the cluster size distribution exhibits a well-defined peak; the mean cluster size scales as $s \sim \Phi t/t_p$ and the radius of gyration as $R/a \sim s^{1/D}$, where a is the particle radius, D (=1.78) is the fractal dimension, and $t_p = \pi \eta a^3/k_B T$ is defined from the characteristic time t_0 associated with the Brownian collision rate between single particles [2] as $t_p = t_0 \Phi$ (η is the solvent viscosity, k_B is the Boltzmann constant, and T is the temperature). Now we introduce the effective volume fraction filled by the aggregates, $\Phi_e \sim \Phi(R/a)^{3-D}$, and we distinguish two domains of Φ: For $\Phi < \Phi_g$, the single aggregate grown at infinite time does not fill the whole sample ($\Phi_e < 1$), while for $\Phi > \Phi_g$, a packing of aggregates appears within a finite time [10] t_g ($\Phi_e = 1$ at $t = t_g$). The gel time t_g decreases with Φ as

$$t_g \sim t_p \Phi^{-3/(3-D)}. \tag{1}$$

The volume fraction at which the suspension first gels, Φ_g, is expressed as $\Phi_g \sim (V_p/V)^{(3-D)/3}$, where V_p is the volume of a particle and V is the volume of the sample. Assuming that the prefactor is equal to 1, we find that, in our suspensions, $\Phi_g \cong 5 \times 10^{-7}$, which is clearly much smaller than Φ^*.

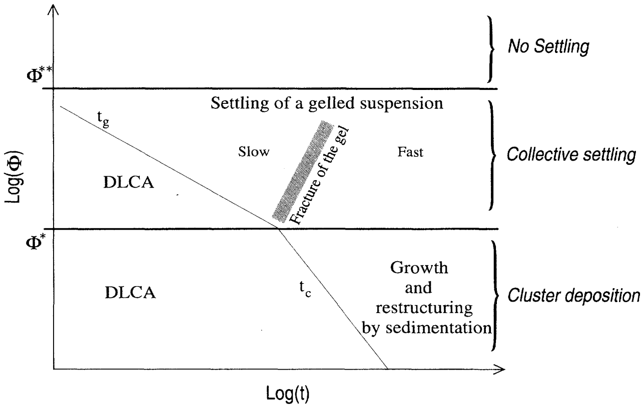

FIG. 1. This diagram depicts the evolution in time of the suspension when the volume fraction of particles is varied and summarizes the leading mechanisms to be considered. The volume fraction at which the suspension first gels in the absence of gravity Φ_g is about 2 orders of magnitude less than Φ^* and it has not been represented.

To investigate how gravity influences the aggregation process, we first consider very dilute suspensions, where Φ_e is always smaller than 1. The relative importance of Brownian motion and of settling can be estimated from the comparison of the time τ_b taken by a cluster to diffuse through the mean distance between the clusters to the time τ_s it takes to settle though the same distance. To obtain τ_b and τ_s, we assume that clusters behave like impenetrable hard spheres for which the radius scales as the radius of gyration R. In the framework of the DLCA model [11],

$$\frac{\tau_s}{\tau_b} \sim \frac{3k_B T}{4\pi \Delta\rho g a^4} \Phi^{-1} \left(\frac{t}{t_p}\right)^{-4/3}. \tag{2}$$

$\Delta\rho$ is the difference between the density of particles and that of the suspending fluid and g is the acceleration of gravity. This ratio becomes equal to 1 at t_c:

$$t_c \sim t_p \left(\frac{3k_B T}{4\pi \Delta\rho g a^4}\right)^{3/4} \Phi^{-3/4}. \tag{3}$$

For $t < t_c$, Brownian motion determines the rate of encounter of the clusters and the growth follows DLCA; for $t > t_c$, the growth rate is ruled instead by sedimentation which prevails over Brownian motion.

In nondilute suspensions ($\Phi > \Phi_g$), two situations can be predicted depending on the relative values of t_c and t_g. When $t_c > t_g$, the growing clusters form a gel which spans all the cell very quickly at time t_g. Gelation is not modified by gravity and the suspension settles under its weight afterward: The suspension undergoes collective settling (see Fig. 1). On the other hand, when $t_c < t_g$, sedimentation begins before gelation takes place; the cluster growth after t_c is modified by the settling motion. The stresses exerted by the surrounding fluid on the clusters give rise to structural rearrangements like loop formation (restructuring) and bondbreakage (fracture) which prevent the aggregates from growing above some maximum size [6,12,13]. Therefore the suspension does not gel, the gel time t_g is no longer defined, and the clusters settle under gravity individually: The suspension undergoes cluster deposition. The value of the volume fraction Φ^* which separates cluster deposition from collective settling is obtained from the condition $t_c = t_g$. Taking for t_c the expression (3) derived in the paragraph above, we get

$$\Phi^* \sim \left(\frac{4\pi \Delta\rho g a^4}{3k_B T}\right)^{(3-D)/(1+D)}. \tag{4}$$

The exponent $(3 - D)/(1 + D)$ is positive; Φ^* increases with the external field amplitude $\Delta\rho g$ and is sensitive to the particle diameter. In our suspensions, we find that $\Phi^* \cong 10^{-2}$, which agrees with the experimental value in order of magnitude. This value is much larger than Φ_g, indicating that the volume fraction required to get gelation under gravity is considerably increased.

The gelled suspensions in the range $\Phi^* < \Phi < \Phi^{**}$ exhibit novel settling properties which are now studied. We have measured the vertical position of the interface that separates the settling suspension from the supernatant

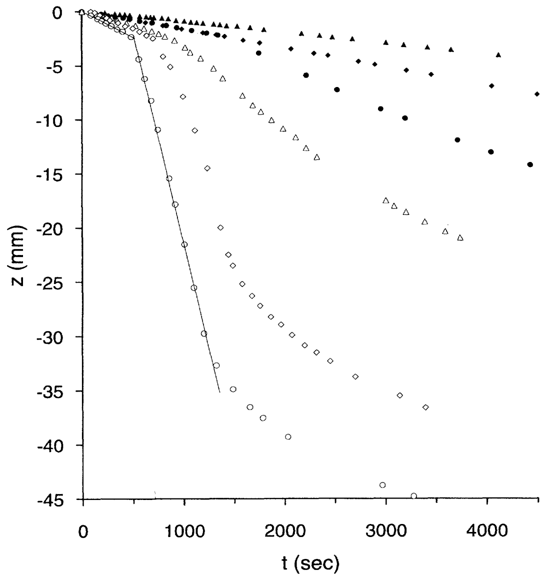

FIG. 2. These plots give the vertical position of the interface that separates the suspension from the clear supernatant versus time. ○: $\Phi = 4 \times 10^{-3}$; ◇: $\Phi = 5 \times 10^{-3}$; △: $\Phi = 6 \times 10^{-3}$; ●: $\Phi = 7 \times 10^{-3}$; ◆: $\Phi = 8 \times 10^{-3}$; ▲: $\Phi = 1 \times 10^{-2}$. For $\Phi = 4 \times 10^{-3}$, we have represented the lines which fit the data in the slow and fast settling regimes.

as a function of time $z(t)$ at different volume fractions. The results are plotted in Fig. 2. In the range $3 \times 10^{-3} < \Phi < 8 \times 10^{-3}$, $z(t)$ decreases slowly first, accelerates suddenly, and continues decreasing quickly, before finally slowing down until it reaches its equilibrium height after about 50 h. We note that the gel time t_g, which can be estimated from (1), is very short in comparison with the time over which settling proceeds ($t_g \cong 15$ s for $\Phi = 5 \times 10^{-3}$). The variations of $z(t)$ in the first and second regimes are linear, thus making it possible to define two settling velocities U_S and U_F which characterize, respectively, the slow and the fast displacements of the interface (slow and fast settling). We have found that the beginning of the fast settling regime corresponds to the appearance within the suspension of a fracture along which water flows upward easily [14]. In the range $\Phi > 8 \times 10^{-3}$, fast settling is not observed. Experimentally, we find that U_S decreases by about a factor of 100 when Φ increases from 3×10^{-3} to 3×10^{-2}; U_F is about 10 times larger than U_S. In Fig. 1, we have indicated schematically the domains where slow and fast settling are observed.

The interpretation of these results calls on the existence of a specific spatial structuralization in the gelled suspension. During the fast settling regime, the gel is broken and the suspending fluid flows upward along preferential paths. In a previous paper [15], we have shown that the variations of U_F are well described by a modified Richardson-Zaki correlation [16] law, $U_F = 0.33(1 - \Phi/\Phi_S)^{5.1 \pm 0.4}$ mm/s, where Φ_S is the particle volume fraction inside the sediment. During the slow settling regime, stress equilibrium in the gel results from the balance between the net weight, the elastic restoring forces, and the hydrodynamic forces that arise from the flow of solvent through the gel. We have studied the influence of the cell dimensions (diameter and height of suspension) on U_S and U_F and we have inferred that the contribution of elasticity can be discarded in our suspensions [14]. Accordingly, we can write the force balance on a slice of suspension at height z as $\Delta\rho g \Phi = \eta f(u - w)$, where f is the hydrodynamic friction and u and w (>0) are the velocity of the particles and that of the solvent in the laboratory frame. From volume conservation, we have $\Phi u + (1 - \Phi)w = 0$. Previous studies have taken the same expression for the hydrodynamic friction as in hard sphere suspensions [17,18]. Here, we describe the settling suspension as a porous medium with a permeability K which is proportional to the square of the characteristic pore radius ξ [19]. In the porous medium frame, f and K are related through $f = (1 - \Phi)/K$. From $\Phi \ll 1$, we deduce $w \ll u$ and $f \cong K^{-1}$. Finally, we find that the settling velocity of the suspension should scale as $U \sim \Phi K$ or $U \sim \Phi \xi^2$.

Let us consider that the gelled suspension is a close packing of aggregates grown by DLCA. In this model, ξ scales as the radius of the aggregates at t_g: $\xi \sim (\Phi t_g/t_p)^{1/D} \sim \Phi^{-1/(3-D)}$, and U varies as

$$U(\Phi) \sim \Phi^{(1-D)/(3-D)}. \tag{5}$$

In Fig. 3 we have plotted the values of U_S measured in our experiments versus Φ, in double logarithmic coordinates. The data collapse onto a straight line indicating that the variations of U_S with Φ follow a power law, as predicted in the close-packing model. This result is related to recent light scattering experiments which have shown that gelation in the DLCA mode is due to the formation of a packing of clusters which have nearly the same size and which are evenly positioned in space [20,21]. It is

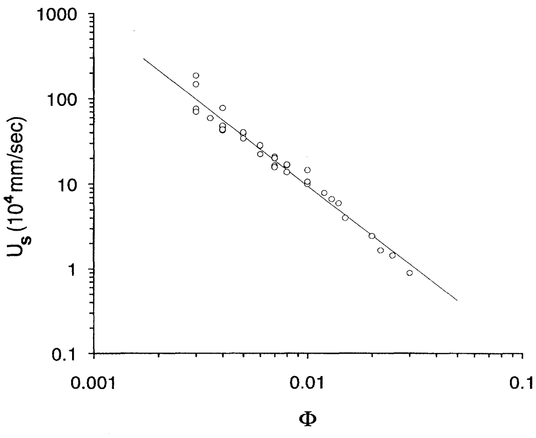

FIG. 3. Log-log plot of the velocity versus the volume fraction in the slow settling regime.

worth noting that predictions based on the percolation model [11] yield a divergence of U_S in the vicinity of Φ^*, which clearly is not observed experimentally. The best fit of the experimental data in Fig. 3 gives the prefactor and the exponent of U_S. The fractal dimension calculated from the exponent is $D = 2.32 \pm 0.05$. This value is equal to the fractal dimension that we have measured for the settling aggregates in the cluster deposition regime [13] within the experimental accuracy. D is larger than in DLCA because, in both regimes, aggregates undergo flow-induced rearrangements which make them more compact than in DLCA. Finally, assuming that the aggregates behave as impermeable spheres and taking for K the Carman-Kozeny expression [19], we can estimate the prefactor of U_S ($\cong 3 \times 10^{-8}$ mm/s), which is in fairly good agreement with the experimental value (1.3×10^{-7} mm/s).

In summary, we have shown that gravity impedes gelation in colloidal suspensions where the volume fraction required to get a gel may by much larger than expected. In turn, the coupling between aggregation and sedimentation gives rise to novel settling properties due to the specific spatial structuring of the suspensions. In gelled suspensions, the early stage of sedimentation corresponds to the settling of a close packing of clusters; the value found for the fractal dimension of the clusters accounts for the existence of flow-induced restructuring. Several interesting questions now arise concerning the late stages of sedimentation (sediment compaction and equilibrium) where the mechanical properties of colloidal gels have to be taken into account. Finally, in the near future, it will be interesting to test the generality of our predictions on other colloidal systems.

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