On Evaluation of Influence of Sedimentation on Colloidal Aggregation

Zhiwei SUN, Shenghua XU and Jie LIU

Abstract

A great deal of effort has been devoted to the influence of gravitational fields on the coagulation process. The Peclet number is commonly used for estimating the importance of the sedimentation influence on the aggregation in comparison to diffusion. González et al.\textsuperscript{1,2} chose a particle diameter as the characteristic length in their Peclet number evaluation and derived $\text{Pe} = m_d (1 - p/p_0) g a_0 / K_B T$, where $m_d$ is mass of the particle, $T$ is room temperature and $K_B$ is Boltzmann constant. They found that $\text{Pe}$ is of the order of unity if the particles are $1 \mu m$ in diameter, $(1 - p/p_0)$ is less than but of the order of unity, see\textsuperscript{1,2}. And then they concluded that “$1 \mu m$ marks the transition between diffusive and drifting for individual particles”. However, we testify that when dealing with the influence of sedimentation on coagulation, taking particle diameter as the characteristic length may be problematic. Our Brownian dynamics simulation shows that the degree of sedimentation influence on the coagulation decreases when the dispersion volume fraction increases. Therefore using a fixed length, such as the diameter of particle, as the characteristic length scale for Peclet number evaluation is not a good choice when dealing with the influence of sedimentation on coagulation. Our simulations demonstrated that several factors in the coagulation process, such as dispersion volume fraction and size distribution, should be taken into account for more reasonable evaluation of the sedimentation influence.

The sedimentation of colloid particles is an important physical phenomenon existing in industrial applications, in the laboratory, and even in daily life. A great deal of effort has been devoted to the influence of gravitational fields on the coagulation process\textsuperscript{1–20}. Basically, it has long been held that gravity is usually of little importance in colloidal coagulation. The magnitude of the sedimentation influence on the coagulation depends on size and shape of particles, as well as the density difference between particle and the liquid phase. The Peclet number is commonly used for estimating the importance of the sedimentation influence on the aggregation in comparison to diffusion. In physics, the Peclet number (Pe) is a dimensionless number, which, in general, represents the ratio of the strength of the convection to the strength of the diffusion: $\text{Pe} = L \nu / D$, where $L$, $\nu$ and $D$ are Characteristic length, velocity and diffusivity, respectively. It can be seen that for approximately zero values of the Peclet number the problem reverts to one of pure diffusion. When $\text{Pe} \gg 1$, diffusive effects are negligible.

Considering a spherical aggregate suspended in the liquid, according to Einstein’s equation the average diffusion length after time $t$ is $L = (2Dt)^{1/2}$. From the balance between gravitational force, buoyancy, and viscous drag, we can obtain the sedimentation velocity of a spherical particle with radius $a_0$, which is given by $v = 2 \Delta \rho g a_0^2 / 9 \eta$ ($\Delta \rho$ is the difference between the density of the particle $\rho_0$ and that of the liquid $\rho$, $g$ is the gravity’s acceleration and $\eta$ is the viscosity of the liquid). Thus the settling length is equal to $vt$. To evaluate the importance of sedimentation influence on aggregation relative to diffusion is to establish a characteristic length and to compare the time in which particles move through this length by diffusion and sedimentation. However, the choice of the characteristic length may make significant difference because of the fact that the “diffusion length increases as the square root of the time whereas the drifting length is linearly related to time.

To estimate the contribution of sedimentation related to the diffusion to the aggregation process, González et al.\textsuperscript{2,3} chose a particle diameter as the characteristic length in their Peclet number evaluation and derived $\text{Pe} = m_d (1 - p/p_0) g a_0 / K_B T$, where $m_d$ is mass of the particle and $K_B$ is Boltzmann constant. They found that $\text{Pe}$ is of the order of unity if the particles are $1 \mu m$ in diameter, $(1 - p/p_0)$ is less than but of the order of unity, and $T$ is room temperature. And then they concluded that “$1 \mu m$ marks the transition between diffusive and drifting for individual particles”. However, choosing small characteristic length scales will be more favorable to the influence of diffusion than that of sedimentation, as the diffusion length is proportional to the square root of time. Thus, not only particle size, but also other environmental factors, such as the dispersion volume fraction and size distribution, has to be taken into account when concerning about the influence of sedimentation on aggregation. When the volume fraction of particles increases the average dis-
tance between particles becomes smaller; the influence degree of sedimentation should go down.

To demonstrate how the degree of sedimentation influence on the aggregation process changes with the volume fraction of particles, a Brownian dynamics simulation was carried out. At the beginning of the coagulation process, all particles with the same radius \(a_0=0.5 \mu m\) are dispersed at volume fraction \(\phi\). The particles' motions are described by the following Langevin equation:

\[
dp/dt = F(t) - \gamma p(t) + R'(t),
\]

where \(p\), \(F(t)\), \(\gamma p(t)\) and \(R'(t)\) are, respectively, momentum of a particle, the conservative force acting on the particle, dissipative and random force terms (\(\gamma\) is the friction coefficient). In the simulation, 80,000 primary spherical particles are used, and the particles are considered as hard spheres. Hydrodynamic and intermolecular forces between particles are ignored, so that \(F(t)\) is only the gravitational force. Since only the changes in the number of collisions caused by gravity were concerned in this study, aggregates are approximated by spheres at all stages of coagulation (the same approximation as in Smoluchowski theory). We further assume that the gyration radius of an aggregate containing \(i\) particles is \(a_0i^{1/3}\), which is correct for coalescing particles (or droplets).

Whenever the distance between two particles with radiiuses \(a_i\) and \(a_j\) was less or equal to \((a_i+a_j)\), they were considered to collide. In the simulation we need to consider only rapid coagulation in a homogeneous medium and particles are assumed to stick together irreversibly whenever they collide.

Considering gravity is the only external force, based on Eq. (1), the updated coordinates of \(i\)-th particle for the time step \(\Delta t\) at time \(t\) were calculated as below:

\[
\begin{align*}
    r_{ik}(t+\Delta t) &= r_{ik}(t) + v_{ik}\Delta t + \Delta r^G_{ik} \\
    k = 1, 2, 3
    \end{align*}
\]

where the subscript \(k\) indicates the three direction in the Cartesian coordinates, and each component of \(\Delta r^G_{ik}\) was taken from a Gaussian distribution with mean zero and variance \(\langle (\Delta r^G_{ik})^2 \rangle = 2D\Delta t\), where the diffusion coefficient, according to the Stokes-Einstein equation, \(D = k_BT/6\pi\eta a\) (\(k_B\) is the Boltzmann constant, \(T\) is temperature and \(\eta\) is the viscosity of the liquid). \(r_{ik}(t)\) is the coordinate of the \(i\)-th particle at time \(t\) and \(v_{ik}\) is the settling velocity of \(i\)-th spherical particle in the \(k\)-th direction. The velocity in the simulation is obtained from the balance between gravitational force, buoyancy, and viscous drag, \(v = 2\Delta pga^2/9\eta\). This Stokes' settling velocity is a good approximation only for the volume fraction of particles is small. With increase of the particle concentration, the settling velocity of individual particle is fluctuating around a mean velocity which is noticeably smaller than that from the above equation, because of the presence of other particles in the fluid, as shown in [2]. However, because the volume fraction of particles concerned in this study is not high (less than \(1 \times 10^{-2}\)) the associated deviations should be negligible.

In order to evaluate the quantitative sedimentation influence, we adopted the "sedimentation influence ratio", described in Ref. [20], which is the ratio of the difference between collision numbers--with and without sedimentation--in a specified interval to the total collision number in this interval. Physically, it is the percentage of collision number caused by sedimentation over the total collision number within the specified interval. The advantage for considering the integral effect is that the sedimentation influence ratio is a more stable quantity than the coagulation rate, and therefore is more suitable for examining small differences in coagulation rate.

If all particles have the same size-monodispersed suspensions, sedimentation will have no direct effect on the coagulation in the early stage of coagulation, which is discussed in Ref. [21]. This is because all particles of the same size have the same settling velocity and therefore should not be additional relative motions compared with Brownian motion. Therefore, the influence of sedimentation depends on particle size distribution but this distribution varies. The sedimentation becomes effective only when different sized particles or aggregates appear. The way of the gravitational influence on the coagulation is reflected by an increase in the number of collisions. Therefore to estimate the accumulated influence of gravity on coagulation for dispersions with initially identical particles, the sedimentation influence ratio can be written as

\[
\theta = (n_{g=1} - n_{g=0})/n_g = 0,
\]

where \(n_{g=1}\) and \(n_{g=0}\) are the accumulated collision number at a special moment during the coagulation process for \(g = 1\) and \(g = 0\) (here \(g = 1\) meaning normal gravity; \(g = 0\) meaning zero gravity), respectively.

For the rapid aggregation, we have

\[
\theta = (\Sigma Z_i|_{g=0} - (\Sigma Z_i|_{g=1}))/(\Sigma Z_i|_{g=0}),
\]

where \(\Sigma Z_i|_{g=0}\) and \(\Sigma Z_i|_{g=1}\) are the total number of particles \((\Sigma Z_i)\) at a special moment, (for instance, the moment when the total number of particles is reduced to half (the coagulation time)), for \(g = 0\) and \(g = 1\), respectively. Since every collision is effective in reducing the total number of particles by one, the increase in the number of collisions at a given moment caused by gravity \((g = 1)\) is strictly equal to the difference between the total number of particles when \(g = 0\) and \(g = 1\). As a matter of fact, \(\theta\) represents the percentage of additional collisions caused by gravity during the period of the coagulation time of \(g = 0\).

In our calculation spherical particles \((\rho_0 = 1.4 \ g/(cm)^3)\) of radius \(a_0 = 0.5 \mu m\) dispersed in water \((1.0 \ g/(cm)^3)\). Temperature \(= 298 K\), \(\eta = 0.1009 \ g/(cm) \cdot s\).
Table 1 Sedimentation influence ratios (θ) vs. volume fraction for initially monodispersed suspensions (a₀ = 0.5 µm) and binary particle mixtures (radius a₀ = 0.5 µm and 1 µm). φ₀ = 1.4 × 10⁻¹

<table>
<thead>
<tr>
<th>Volume fraction</th>
<th>φ₀</th>
<th>10 φ₀</th>
<th>50 φ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ for monodispersed suspensions (%)</td>
<td>3.4</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>θ for binary particle mixtures (%)</td>
<td>201</td>
<td>79</td>
<td>30</td>
</tr>
</tbody>
</table>

and δρ = 0.40 g/(cm)³. We chose the original volume fraction φ₀ = 1.4 × 10⁻⁵. The corresponding number concentration was N₀ = 2.67 × 10⁷/(cm)³. The sedimentation influence ratios were computed for φ = φ₀, φ = 10 φ₀, φ = 50 φ₀ through the Brownian dynamics simulation. The average distances between the particles at the beginning of the coagulation, for φ = φ₀, 10 φ₀ and 50 φ₀, are 33.44 µ, 15.52 µ and 9.078 µ, respectively. The sedimentation influence ratios for φ = φ₀, 10 φ₀ and 50 φ₀ are shown in Table 1. We can see that when increasing the volume fraction, the coagulation processes become much faster, but the differences in collision numbers corresponding to φ = 0 and φ = 1 become smaller. Since 80000 particles were used the calculation the statistical errors are quite small (the relative standard deviation is less than 0.5% over five independent runs). The time step was taken to be 0.0005 s, and therefore 1.4 × 10⁷ steps were needed for a single calculation with t = 7000 s.

According to Smoluchowski theory, which deals only with the rapid coagulation for diluted monodispersed suspensions with φ = 0 case, the change in the total number of particles (ΣZₜ) with time t is given by

\[ ΣZₜ = Z₀/(1 + kₐZ₀t), \]

where Z₀ as the initial number of particles and kₐ = 4 kₐ T/3 δρ is the Smoluchowski coagulation rate constant. Because every collision is effective in reducing the total number of particles by one in the rapid coagulation, we can easily reduce the following expression for the collision number associated with the Smoluchowski theory:

\[ N_{\text{collison}} = kₐZ₀²/(1 + kₐZ₀t). \]

Eq. (3) is also used to estimate the influence of sedimentation on the aggregation for binary particle mixtures (with radius a₀ = 0.5 µm and 1 µm). At the very beginning, the ratio of the number concentration of 0.5 µm and 1 µm particles is 50% to 50%. In this case, the sedimentation affects the aggregation process from its beginning, so we do not need to take long time to check its influence. In Eq. (3), we check the collision number (which is equivalent to the reduction in the total number of particles (ΣZₜ)) at the moment when the total number of particles is reduced to 90% for φ = 0 and φ = 1, respectively. We can see that for φ = φ₀, the sedimentation plays a dominant role in the coagulation: over 200% more collisions are caused by the sedimentation. When the volume fraction decreases, the percentage of the contribution from sedimentation drops further to 79% and 30% corresponding to φ = 10 φ₀ and 50 φ₀, respectively. In addition, obtained from our simulation, the average collision frequencies per particle caused by pure diffusion at the beginning of the coagulation for this binary particle mixtures are 0.0002/s, 0.0026/s and 0.048/s for φ = φ₀, 10 φ₀ and 50 φ₀, respectively whereas those due to the sedimentation are 0.0003/s, 0.0011/s and 0.011/s. The results of our computer simulation show clearly that the effect of sedimentation on the coagulation drops with increasing the volume fraction.

In conclusion, using a fixed length, such as the diameter of particle, as the characteristic length scale for Peclet number evaluation is not a good choice when dealing with the influence of sedimentation on coagulation. Environmental factors in the coagulation process, such as dispersion volume fraction and size distribution, should be taken into account for more reasonable evaluation of the sedimentation influence. The result of our computer simulation has shown clearly that the effect of sedimentation on the coagulation changes with the size distribution and drops with increasing the volume fraction of suspensions. At least for monodisperse suspensions choosing average distance between particles as the characteristic length in Peclet number evaluation is more reasonable than using a fixed length.

Reference

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126.


1634.


Received December 19, 2005
Accepted for publication, December 22, 2006