Towards an Understanding of the Influence of Sedimentation on Colloidal Aggregation by Peclet Number *

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The Peclet number is a useful index to estimate the importance of sedimentation as compared to the Brownian motion. However, how to choose the characteristic length scale for the Peclet number evaluation is rather critical because the diffusion length increases as the square root of the time whereas the drifting length is linearly related to time. 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. The simulations demonstrated that 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.

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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.[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 P_e is a dimensionless number, which in general represents the ratio of the strength of the convection to the strength of the diffusion: $P_e = Lv/D$, where L, v and D are the 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 $P_e \gg 1$, diffusive effects are negligible.

Considering a spherical aggregate suspended in the liquid, we have the diffusion length $L = (2Dt)^{1/2}$ according to Einstein's equation. 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 ρ_0 and that of the liquid ρ, g is the gravity acceleration and η is the viscosity of the liquid). 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 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.*[2,3] chose a particle diameter as the characteristic length in their Peclet number evaluation and derived $P_e = m_0(1-\rho/\rho_0)ga_0/k_BT$, where m_0 is mass of the particle and k_B is Boltzmann's constant. They found that P_e is of the order of unity if the particles are $1\,\mu$m in diameter, $(1-\rho/\rho_0)$ is less than but of the order of unity, and T is room temperature. Then they concluded that $1\,\mu$m marks the transition between diffusive and drifting for individual particles.

However, we think that when dealing with the influence of sedimentation on coagulation, taking particle diameter as the characteristic length may be problematic because the diffusion length is not linearly related to time and shortening characteristic length will be more favourable to diffusion.

As a vivid example, at room temperature a $1\,\mu$m sphere (radius) particle diffuses $1\,\mu$m and needs 2.3 seconds; but to diffuse a distance of 1 mm will require 27 days! Under the same conditions, however, if the sedimentation velocity is $0.2\,\mu$m/s, the time for a particle to drift $1\,\mu$m requires 0.5 s, and drifting 1 mm needs 500 s (a little more than 6 min) only.

Apparently, choosing small characteristic length

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scales will be more favorable to the influence of diffusion than that of sedimentation. The Peclet number is a useful index to estimate the importance of sedimentation as compared to the Brownian motion. However, the method for choosing the characteristic length scale for the Peclet number evaluation is critical. When we are concerned about the influence of sedimentation on aggregation, not only particle size but also environmental factors, such as the dispersion volume fraction and size distribution, have to be taken into account. For one thing, when the volume fraction of particles increases, the average distance 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 (BD) simulation was carried out. The advantage of BD simulation is that, instead of considering the contribution of individual solvent molecules to the suspension dynamics, one considers only their average effect as a random force or Brownian motion on the suspension particles. Therefore, compared with molecular dynamics (MD) simulation, much larger time step can be used in BD simulation.

In the BD simulation, at the beginning of the coagulation process, all particles are dispersed at volume fraction ϕ. Particle motions, driven by the Brownian random force and gravity, and particle collisions lead to coagulation and the formation of larger aggregates. Thus, particles' motions are described by the following Langevin equation:

$$dp/dt = F(t) - \gamma p(t) + R'(t), \tag{1}$$

where $p, F(t), \gamma p(t)$ and $R'(t)$ are, respectively, the momentum of a particle, the conservative force acting on the particle, dissipative and random force terms (γ is the friction coefficient). Here 80000 primary spherical particles with the simplest pair potential, the hard sphere model, were used in the simulation. 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[21]). We further assume that the gyration radius of an aggregate containing i particles is $a_0 i^{1/3}$, which is correct for coalescing particles (or droplets)).

Whenever the distance between two particles with radiuses 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. Particles are assumed to stick together irreversibly whenever they collide. Hydrodynamic and intermolecular forces between particles are ignored.

Considering gravity is the only external force, based on Eq. (1), the updated coordinates of i-th particle for the time step Δt at time t are calculated by

$$r_i(t + \Delta t) = r_i(t) + v_i \Delta t + \Delta r_{ik}^G, \tag{2}$$

where each component of Δr_i^G is taken from a Gaussian distribution with mean zero and variance $\langle (\Delta r_{ik}^G)^2 \rangle = 2D\Delta t$, where the diffusion coefficient, according to the Stokes-Einstein equation, $D = k_B T / 6\pi\eta a$ (k_B is the Boltzmman constant, T is temperature and η is the viscosity of the liquid); $r_i(t)$ is the position of the i-th particle at time t and v_i is the settling velocity of i-th spherical particle, obtained from the balance between gravitational force, buoyancy, and viscous drag, $v = 2\Delta\rho g a^2 / 9\eta$.

Strictly speaking, the above Stokes' settling velocity is a good approximation only for the case that 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 Ref. [12]. However, because the volume fraction of particles concerned in this study is not high (less than 1×10^{-2}), the associated deviations should be negligible.

In order to evaluate the quantitative sedimentation influence, we adopt the sedimentation influence ratio, described in Ref. [20], which is the ratio of the difference in 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. 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 of 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

$$\theta = (n_{g=1} - n_{g=0}) / n_{g=0}, \tag{3}$$

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 $g = 0$, respectively.

For the rapid aggregation, we have

$$\theta = ((\Sigma Z_i|_{g=0}) - (\Sigma Z_i|_{g=1}))/(\Sigma Z_i|_{g=0}), \quad (4)$$

where $(\Sigma Z_i|_{g=0})$ and $(\Sigma Z_i|_{g=1})$ are the total number of particles (ΣZ_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 the difference in the total number of particles when $g = 0$ and $g = 1$. As a matter of fact, θ represents the percentage of additional collisions caused by gravity during the period of the coagulation time of $g = 0$.

In our calculation, spherical particles ($\rho_0 = 1.4\,\mathrm{g/(cm)^3}$) of radius $a_0 = 0.5\,\mu\mathrm{m}$ are dispersed in water ($1.0\,\mathrm{g/cm^3}$). Temperature=298 K, $\eta = 0.1009\,\mathrm{g\,cm^{-1}s^{-1}}$, and $\Delta\rho = 0.40\,\mathrm{g/cm^3}$. We choose the original volume fraction $\phi_0 = 1.4 \times 10^{-5}$. The corresponding number concentration was $N_0 \approx 2.67 \times 10^7/\mathrm{cm}^3$. The sedimentation influence ratios are computed for $\phi = \phi_0$, $\phi = 10\phi_0$, $\phi = 50\phi_0$ by the Brownian dynamics simulation. The average distances between the particles at the beginning of the coagulation, for $\phi = \phi_0$, $10\phi_0$ and $50\phi_0$, are $33.44\,\mu$m, $15.52\,\mu$m and $9.078\,\mu$m, respectively. The sedimentation influence ratios for $\phi = \phi_0$, $10\phi_0$ and $50\phi_0$ are listed in Table 1.

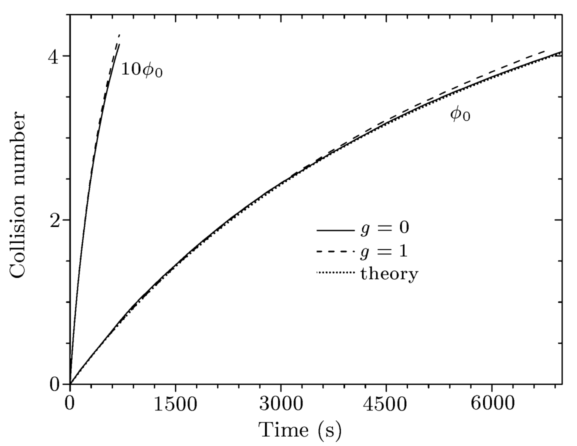

Fig. 1. The collision numbers versus time for initial monodispersed suspensions ($a_0 = 0.5\,\mu$m) of $\phi = \phi_0$ and $\phi = 10\phi_0$, in the $g = 0$ and $g = 1$ cases, respectively (the total particle number at $t = 0$ is 80000). The theoretical collision number calculated from Eq. (6) is represented by the dotted line, which is almost overlapped with the solid line.

Typical curves of time evolution of the collision numbers for $\phi = \phi_0$ and $\phi = 10\phi_0$, under $g = 0$ and $g = 1$ cases, respectively, are shown in Fig. 1. We can see that at the early stage of the coagulation, there is no difference between the curves with $g = 0$ and $g = 1$ and the difference increases with time when large particles form. Compared the curves associated with $\phi = \phi_0$ and $\phi = 10\phi_0$, when the volume fraction increases, the coagulation processes become much faster, but the differences in collision numbers corresponding to $g = 0$ and $g = 1$ become smaller. Since 80000 particles are used in the calculation, the statistical errors are quite small (the relative standard deviation is less than 0.5% over five independent runs). The time step is taken to be 0.0005 s, and therefore 1.4×10^7 steps are needed for a single calculation with $t = 7000$ s).

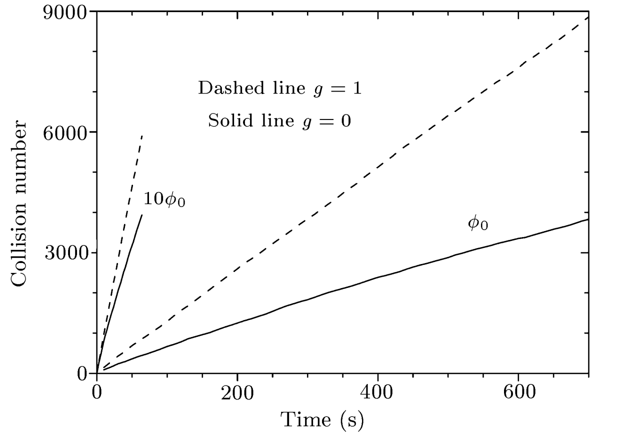

Fig. 2. The collision numbers versus time for binary particle mixtures (radius $a_0 = 0.5\,\mu$m and $1\,\mu$m) of $\phi = \phi_0$ and $\phi = 10\phi_0$, in the $g = 0$ and $g = 1$ cases, respectively (the total particle number at $t = 0$ is 40000).

According to the Smoluchowski theory,[21] which deals with only the rapid coagulation for diluted monodispersed suspensions with the $g = 0$ case, the change in the total number of particles (ΣZ_i) with time t is given by

$$\Sigma Z_i = Z_0/(1 + k_s Z_0 t), \quad (5)$$

where Z_0 as the initial number of particles and $k_s = 4k_B T/3\eta$ 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:

$$N_{\text{collision}} = k_s Z_0^2 t/(1 + k_s Z_0 t). \quad (6)$$

Figure 1 shows that the theoretical collision number from Eq. (6) is very close to that from our simulation with the $g = 0$ case.

When the suspension is composed of particles with different sizes, the influence of sedimentation will be more easily observed. In the simulation, Eq. (3) is also used to estimate the influence of sedimentation on the aggregation for binary particle mixtures (with radius $a_0 = 0.5\,\mu$m and $1\,\mu$m). At the very beginning, the ratio of the number concentration of $0.5\,\mu$m and $1\,\mu$m 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 (ΣZ_i)) at the moment when the total number of particles is reduced to 90% for $g = 0$ and $g = 1$, respectively. We can see that for $\phi = \phi_0$, the sedimentation plays a dominant role in the coagulation: over 200% more collisions are caused by the sedimentation. When the volume fraction increases, the percentage of the contribution from sedimentation drops further to 79% and 30% corresponding to $\phi = 10\phi_0$ and $50\phi_0$, 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 $\phi = \phi_0$, $10\phi_0$ and $50\phi_0$, 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 the increasing volume fraction. The typical plot of collision numbers versus time for the binary particle mixtures (radius $a_0 = 0.5\,\mu$m and $1\,\mu$m) of $\phi = \phi_0$ and $\phi = 10\phi_0$, in the $g = 0$ and $g = 1$ cases, respectively (the total particle number at $t = 0$ is 40000). Obviously, the gravitational influence on the coagulation becomes much more significant for the binary particle mixtures, yet the influence becomes smaller when ϕ increases.

Table 1. Sedimentation influence ratios θ versus volume fraction for initially monodispersed suspensions ($a_0 = 0.5\,\mu$m) and binary particle mixtures (radius $a_0 = 0.5\,\mu$m and $1\,\mu$m) ($\phi_0 = 1.4 \times 10^{-5}$).

Volume fraction	ϕ_0	$10\phi_0$	$50\phi_0$
θ for monodispersed suspensions (%)	3.4(±0.2)	2.3(±0.1)	1.5(±0.1)
θ for binary particle mixtures (%)	201(±2)	79(±1)	30(±1)

In conclusion, using a fixed length (e.g. the diameter of particle) as the characteristic length scale for the 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 the increasing volume fraction of suspensions.

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