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New models and predictions for Brownian coagulation of non-interacting spheres

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ABSTRACT

The classical steady-state Smoluchowski model for Brownian coagulation is evaluated using Brownian Dynamics Simulations (BDS) as a benchmark. The predictions of this approach compare favorably with the results of BDS only in the dilute limit, *that is*, for volume fractions of $\phi \leqslant 5 \times 10^{-4}$. From the solution of the more general unsteady-state diffusion equation, a new model for coagulation is developed. The resulting coagulation rate constant is time-dependent and approaches the steady-state limit only at large times. Moreover, in contrast to the Smoluchowski model, this rate constant depends on the particle size, with the transient effects becoming more significant at larger sizes. The predictions of the unsteady-state model agree well with the BDS results up to volume fractions of about $\phi = 0.1$, at which the aggregation half-time predicted by the Smoluchowski model is five times that of the BDS. A new procedure to extract the aggregation rate constant from simulation results based on this model is presented. The choice of the rate constant kernel used in the population balance equations for complete aggregation is also evaluated. Extension of the new model to a variable rate constant kernel leads to increased accuracy of the predictions, especially for $\phi \geqslant 5 \times 10^{-3}$. This size-dependence of the rate constant kernel affects particularly the predictions for initially polydisperse sphere systems. In addition, the model is extended to account in a novel way for both short-range viscous two-particle interactions and long-range many-particle Hydrodynamic Interactions (HI). Predictions including HI agree best with the BDS results. The new models presented here offer accurate and computationally less-intensive predictions of the coagulation dynamics while also accounting for hydrodynamic coupling.

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1. Introduction

Dispersion stability is an important problem for many applications of colloidal and nanoparticle systems including drug delivery [1], inkjet printing [2–4], and flow assurance [5]. Colloidal particles with sizes smaller than about 5 μm are subjected to significant Brownian motion in a liquid dispersion medium. As a result, the particles will eventually collide with each other. These collisions can cause the particles to "stick" together, *that is*, irreversibly aggregate or coagulate. Additional collisions lead to the formation of ever larger aggregates, which either settle or float when they become sufficiently large [6–8]. Fluid particles can also coalesce after coagulation, forming a larger spherical particle. This equivalent-sphere model is sometimes used even for non-coalescing aggregates. A dispersion is considered "colloidally" stable if the primary particles retain their individual and kinetic independence, and unstable if the particles coagulate or coalesce. The rate at which collisions lead to an aggregation event, or the aggregation rate, is also dependent upon the thermodynamic and hydrodynamic interactions between the particles.

The classical approach for describing "perikinetic" coagulation rates was first developed by Smoluchowski [6,8,9], who considered the limit of "rapid" coagulation, whereby every collision leads to irreversible aggregation. In this model, the particles are transported toward each other by a steady-state diffusive flux in the absence of any interacting forces other than a very short-range interaction that leads to particle capture. In other words, the coagulation of "hard-spheres" is modeled via a diffusion-limited aggregation process. The Smoluchowski analysis applies to quite dilute dispersions because of the use of the following two simplifying assumptions: (1) only collisions of primary particles that form dimers are considered, and (2) a particle's diffusion coefficient is set equal to the "infinitely-dilute" Stokes–Einstein value.

The steady-state flux approach was extended by Fuchs [10] to coagulation in the presence of any attractive or repulsive interparticle forces. This is the Fuchs–Smoluchowski model. These two models have been used extensively to describe coagulation rates and to aid in the interpretation of experiments and simulations. Discrepancies between experimental data and the Fuchs–Smoluchowski model predictions were attributed to (1) model approximations, as will be shown here, (2) incomplete knowledge of interparticle forces, (3) particle shape effects, and (4) no accounting for Hydrodynamic Interactions (HI) that develop between

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particles. Several methods for including HI into the Fuchs–Smoluchowski model have been reported [11–15].

One of the most powerful and commonly used tools to study coagulation in colloidal dispersions is numerical simulations. A popular method, highly suited for the study of aggregation dynamics, is Brownian Dynamics Simulations (BDS) [12,16]. By employing a stochastic-dynamics approach, BDS enables a direct simulation of the coagulation dynamics over a limited range of experimentally relevant timescales. Spatial correlations in the particles' relative motion due to HI can also be included in BDS. Given a known interparticle force, BDS yields the dynamics of a "real system" without the need of the simplifying assumptions used in the Smoluchowski and Fuchs–Smoluchowski models.

In these two classical models, the initial transient state dynamics are ignored. One of the goals of this article is to evaluate the implications of this assumption. BDS results are therefore compared to the coagulation dynamics predicted by the Smoluchowski steady-state model (SS model) and a new model that utilizes the more general unsteady-state diffusion equation (USS model). Analytical solutions for the complete population-balance equations with the USS model are reported here for the first time, which compare quite favorably to BDS results at low volume fractions. The unsteady-state equation has been used previously to obtain only an unsteady-state flux in the numerical analysis of Roebersen and Wiersema [17], while a brief analytical treatment of a subset of the full population balance equations has been reported previously [18]. Overall, the USS model predicts significantly smaller half-times of aggregation for a given dispersion especially for large-diameter particles, indicating that transient effects are very important.

In the general population balance equations used for obtaining the aggregation dynamics, one often uses the simplifying assumptions that only binary collisions occur and that the kinetic rate constant k_{ij} for particles of size i and j (i and j being the number of primary particles per aggregate) is the same as k_{11} (the rate constant for two primary particle collisions). These simplifications should only be valid in the early stages of aggregation of initially monodisperse spheres. In this article, we also evaluate the effect of using a variable versus a fixed k_{ij} on the aggregation dynamics. This is done by comparing the predictions of the analytical USS model with a fixed k_{ij} (equal to k_{11}) and a new numerical USS model with variable k_{ij}. Previous numerical analyses [19,20] were limited to the SS model and encumbered with some computational difficulties that restricted the size of the aggregates that could be considered. The effect of the initial polydispersity of the system is also studied.

Furthermore, new semi-analytical SS and numerical USS models are reported that include the effect of many-body hydrodynamics [21,22] and viscous interactions [23]. Similar to the computational scheme introduced by Urbina-Villalba et al. [15], these models account for the volume fraction dependence of the diffusion coefficient and the large HI that develop at close interparticle distances due to lubrication effects. A comparison of the predictions of these models with the BDS results accounting for HI is also presented.

Finally, we determine the volume fraction (ϕ) limits of the SS and USS models. The predicted half-times of aggregation for different volume fractions obtained from the SS and USS models are compared to the BDS results. For the hard-sphere interactions considered here, the maximum ϕ value for the dilute dispersion approximation of the SS model is about 0.0005. Beyond such small values, the USS models or the BDS simulations should be used.

Having accurate predictions of the coagulation dynamics allows for more reliable comparisons to experimental data. In turn, this enables the improved extraction of kinetic constants from such data. The USS models described in this article provide plausible predictions, at least with respect to the results of BDS. Models that account for non-steady-state effects should therefore be applicable to describing coagulation dynamics at much longer times and for larger aggregate sizes than can be described using BDS.

2. Steady-state and unsteady-state diffusion models

2.1. Models without hydrodynamic interactions

The models discussed in this section are primarily applicable to initially monodisperse spheres of radius R when the dominant particle aggregation mechanism is "perikinetic", or via diffusive or Brownian motion (toward the end of this section and in Section 4.5, we discuss certain cases of initially polydisperse spheres). The particles coagulate as hard-spheres in the absence of any medium or long-range attractive or repulsive forces. It is assumed that there is a short-range attractive force between the particles of sufficient strength to form an irreversible bond once they come into contact with each other. This force does not affect the diffusion of the particles toward each other. In the early stages of aggregation, monomer particles coagulate to form dimers. Trimer and higher aggregate cluster formation is ignored. For the later stages of the aggregation process, population balance equations are employed for obtaining the general cluster dynamics.

Some key steps in the derivation of the steady-state flux (Smoluchowski model) and the unsteady-state flux diffusion models are presented here. Even though the derivation of the classical Smoluchowski model for the early stages of aggregation can be found in the literature, it is briefly reviewed in order to highlight some points regarding the assumptions involved. As in Smoluchowski's original analysis, a spherical coordinate system is chosen with the origin fixed at the center of one particle, which is assumed to be "fixed" or stationary. Another particle diffuses toward the fixed particle. This particle moves until it "touches" the fixed particle, thereby instantaneously forming a dimer. Thus, the process is divided in to two steps: (1) a diffusion step and (2) an instantaneous reaction step when the particles collide. In the diffusive step, a diffusive flux toward the fixed particles is obtained, which is taken to be spherically symmetric. The flux J_1 of the monomer particles crossing a unit area toward the fixed particle per unit time, for quite dilute dispersions, is given by Fick's law

$$J_1 = -D_1 \frac{\partial \rho_1}{\partial r} \tag{1}$$

where r is the radial distance from the center of the fixed particle, D_1 is the monomer particle self diffusion coefficient, and $\rho_1(r,t)$ is the spherically symmetric number density of monomer particles, which is also a function of time t. The number density of the particles in the bulk dispersion far away from the fixed particle, N_1, is uniform and constant during the particle diffusion step. The number density of the particles at $r = 2R$, where the two particles collide, is zero. The bulk dispersion is a "source" for particles, while the fixed particle acts as a particle "sink". A differential number balance across a spherical shell of an inner radius $r \geqslant 2R$ and thickness dr yields the unsteady-state diffusion equation for $\rho_1(r,t)$.

$$\frac{\partial \rho_1}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_1 \frac{\partial \rho_1}{\partial r}\right) \tag{2}$$

For infinitely dilute dispersions, the diffusion coefficient D_1 is given by the Stokes–Einstein equation:

$$D_1 = \frac{k_B T}{6\pi\eta a} \tag{3}$$

where a is the hydrodynamic radius of the particles ($a = R$ here), T is the absolute temperature, k_B is Boltzmann's constant, and η is the solution Newtonian viscosity. The boundary conditions are

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