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NUMERICAL SIMULATION OF RESTRUCTURING BEHAVIOR OF NON-FRACTAL AGGREGATE IN SIMPLE SHEAR FLOW

A dissertation submitted in partial fulfillment of the requirements
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by
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Abstract

Understanding the behavior of colloidal aggregates in fluid flow is one of the fundamental issues for the prediction and control of the dispersion state of colloidal suspension, which is widely encountered in several engineering fields. The structure of the aggregate has a significant role for both the microstructure and macroproperties of the dispersion. An aggregate may vary its structure by three aspects: aggregation with the other to form a larger one, breakup into several smaller pieces, and restructuring *i.e.* the particles composing aggregate changes their position relatively but still connect to the others. It has been found out that the restructuring not only changes structure of the aggregate itself, but also has a crucial impact on the aggregation and breakup. Therefore, the restructuring of aggregate contributes important role on the overall performance of the dispersion. Recent studies have suggested that in simple shear flow, a widely used model flow system, the aggregate is apt to have high fractal dimension, and the behavior of such aggregates is complicatedly diverse. Consequently, the restructuring behavior of aggregate having high fractal dimension in simple shear flow is important for either understanding the mechanism of restructuring, or developing highly accurate model predicting the properties of dispersion.

In this study, the restructuring behavior of non-fractal aggregate in simple shear flow is investigated. Numerical simulation is conducted to examine the effect of aggregate structure and shear flow condition on the restructuring of aggregate, and the underlying mechanism. The aggregate is composed of a number of monosized, spherical, and hard primary particles. The attraction between particles is calculated by the retarded van der Waals potential. For a system of many particles in fluid medium, the hydrodynamic interaction is very important for a dynamical system, yet very complicated. Stokesian dynamics is a simulation technique which is capable of capturing the complex many-body hydrodynamic interaction. Therefore, Stokesian dynamics approach is employed in the study.

The dissertation consists of six chapters.

Chapter 1 presents the background and the statement of the study. The gap between the recent studies and this work is also given.

Chapter 2 gives details of the numerical simulation, including the construction of the mathematical formulation, the way it is applied to the study, verification of the method, and the simulation conditions of the study.

In Chapter 3, the restructuring behavior of a non-fractal aggregate in simple shear flow is explored. The effect of initial coordination number and the intensity of shear flow on the restructuring of aggregate is investigated. The temporal change in internal structure of the non-fractal aggregate, in terms of coordination number, is examined. It shows that after subjected to shear flow, the aggregate rotates around the vorticity axis and deforms along the streamline. The deformation progresses with time: from spherical shape to ellipsoidal one; finally followed by recovering to almost spherical shape. Simultaneously, the coordination number of aggregate alters and reaches a stable value. The restructuring

of aggregate originates from the superimposition of rotational and extensional component of simple shear flow. The aggregate restructures so that a stable structure corresponding to the applied shear flow is obtained. At the same fluid shear stress condition, despite of the significant difference in the initial packing properties, the stable structure of aggregate likely exist at quite compact state, and the stable structure reveals slight difference. The dependence of stable structure on shear flow condition shows similar manner for all aggregates. The stable aggregate in weaker flow is more dense than that in the stronger flow. However there is a limit for such compact structure. A kinetic model based on simultaneous formation and disintegration of links between primary particles is proposed. The model results seem suitable to explain the restructuring of non-fractal aggregate within the scope of the study. The kinetic model furthermore exhibits the dynamic characteristic of the aggregate when the aggregate obtains its stable state.

Chapter 4 focuses on a systematic approach for predicting the restructuring of non-fractal aggregate and interprets the physical meaning of restructuring. At first, the transition among stable aggregates reveals to have some reversibility. Further analysis on the volume fraction of the aggregate obtained at the weak flow condition indicates that such aggregate expresses kind of inherent characteristic which is suitable to employ in the general relation of restructuring. By considering these inherit structure into a parameter representing the ability of primary particles to form connection with the others, defined as connection capability, a specific relation between the temporal change in connection capability and the tensile strength of aggregate, calculated by Rumpf's theory, during the restructuring of aggregate is established. Regarding the stable structure of aggregate in simple shear flow, when the inherit structure of aggregate is taken into account, it shows that the prediction of stable structure and the progress toward stable structure are possible to obtain.

In chapter 5, the criteria for restructuring of non-fractal aggregate are analyzed by determination of the strength of aggregate and the hydrodynamic stress acting on the aggregate by fluid. As for the condition of the non-fractal aggregate in this study, the effect of penetration of fluid flow on the restructuring of the aggregate is examined. It shows that the penetration of fluid flow on the aggregate is weekly dependent on porosity of the non-fractal aggregate in the study. Based on the contribution of structure of aggregate on the restructuring and the tensile strength of aggregate, criteria for restructuring of non-fractal aggregate are found out.

Chapter 6 is the general conclusion of the dissertation.

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Table of Contents

1	Introduction.....	1
1.1	Colloidal suspension is everywhere!	1
1.2	Basic requirements for colloidal suspension	2
1.3	The role of restructuring of aggregate	3
1.4	Statement of problem	4
	References.....	4
2	Theoretical background & Simulation method	8
2.1	Hydrodynamic interaction of multi-particle system: Stokesian Dynamics	8
2.1.1	Governing equations for fluid flow	8
2.1.2	Integral representation solution of Stokes equation	9
2.1.3	Multipole expansion	10
2.1.4	Mobility matrix.....	12
2.1.5	Lubrication correction	14
2.2	Stokesian Dynamics simulation model	14
2.3	Structure of aggregate	16
2.3.1	Background	16
2.3.2	Simulation of non-fractal aggregate	17
2.3.3	Characterization of aggregate.....	19
2.4	Simulation condition	19
2.5	Discussion on assumption and verification	21
2.5.1	Discussion on assumption	21
2.5.2	Verification of simulation method.....	22
	References.....	25
3	Stability of restructured non-fractal aggregate in simple shear flow.....	28
3.1	Effect of initial structure on shape and coordination number of aggregate.....	28
3.2	Effect of fluid shear stress on shape and coordination number of aggregate	31

3.3	Stability of restructured non-fractal aggregate	33
3.4	Kinetic model	35
3.5	Conclusion.....	36
	References.....	36
4	Restructuring capability of non-fractal aggregate in simple shear flow.....	38
4.1	Reversibility of stable aggregate	38
4.2	Characteristics of limit aggregate.....	39
4.2.1	Local volume fraction by Voronoi tessellation	39
4.2.2	Effective volume fraction.....	41
4.3	Physical relation of connection capability and strength of aggregate in restructuring.....	44
4.4	Scaling law for the stable structure of aggregate.....	46
4.5	Conclusion.....	48
	References.....	48
5	Criteria for the restructuring of non-fractal aggregate in simple shear flow	50
5.1	Introduction	50
5.2	Theory	50
5.3	Evaluation of the penetration of fluid flow for the restructuring of non-fractal aggregate	52
5.4	Conclusion.....	54
	References.....	54
6	Conclusions.....	55
	Appendices	56
	Appendix A. Calculation of the mobility matrix (Durlafsky <i>et al.</i>, 1987).....	56
	Appendix B. The effect of particle surface separation on the coordination number	58
	Appendix C. Calculation of effective volume fraction of aggregate by equivalent ellipsoid	59
	Appendix D. Porous sphere model by Adler and Mills (1979)	60

List of Figures

Figure 2.1	The symmetric component and antisymmetric component of force dipole [6].	11
Figure 2.2	Illustration of simple shear flow in Cartesian coordinate	15
Figure 2.3	The rotational component and deformation component of simple shear flow and its equivalent streamline.	16
Figure 2.4	A three-dimensional fractal aggregate formed by primary spherical particle with diameter d . Seven particles have been joined to form crosses. Then seven of these crosses have been joined to form a larger crosses and so on. Such structure is called Vicsek fractal and its fractal dimension is 1.77.	17
Figure 2.5	Actual structure of colloidal aggregate. (a) Diffusion limit aggregate [11], (b) Reaction limit aggregate [11], (c) Shear induced aggregate [12], (d) Aggregate is formed by drying a microdroplet $d_f \approx 3$ [13].	17
Figure 2.6	The making of aggregate by centripetal force. The images from left to right is the evolution of the assemblage with time.	18
Figure 2.7	The non-fractal aggregate with different connectivity	18
Figure 2.8	The number of particle along the nondimensional radius R/a from the center of the aggregate.	18
Figure 2.9	Retarded van der Waals force for a couple of particles	20
Figure 2.10	Instantaneous motion of three spheres located at unequal distance. $\tilde{t}$: nondimensional time ($=U_t t / a$, U_t : terminal velocity), $\tilde{d}$: nondimensional settling distance ($=d / a$, d : settling distance), C : ratio of initial distance between sphere 1 and 2 to sphere 2 and 3. The initial distance between sphere 1 and 3 is $12a$ (a the radius of sphere). The lines connecting the particles are only for illustration and play no role in the simulation. The image is adapted from Harada <i>et al.</i> (2006) [16].	23
Figure 2.11	The relation between fluid shear stress $\mu\dot{\gamma}$ and the weight average number of particle per fragment at steady state. The fractal dimension of the aggregate before subjected to fluid flow is $d_f \approx 1.8$ (Figure is modified from [21]).	24
Figure 2.12	Comparison of the rotation and deformation of an aggregate in simple shear flow for one cycle between simulation and Blaser's experimental study [23].	25
Figure 3.1	Instantaneous structure of aggregate in (a) shape and (b) coordination number k of various aggregates in fluid shear stress condition $\mu\dot{\gamma} = 26.9$ Pa. The arrow is to indicate the position of $\dot{\gamma}t$ in (b). The dotted box has a width equal to the nondimensional time of one rotation of shear flow. The coordination number within the box shows a periodic fluctuation in approximately one rotation of the aggregate.	29

Figure 3.2	The identity between the rotation of dense aggregate $k_0 = 5.54$ and the shear flow in condition $\mu\dot{\gamma} = 26.9$ Pa. The nondimensional time of one cycle of fluid shear flow is 4π . The pink and cyan colored particles are to indicate the rotation of the aggregate in clockwise direction.	30
Figure 3.3	Coordination number of aggregate at different shear stress conditions for aggregate with initial coordination number (a) $k_0 = 5.54$, (b) $k_0 = 3.02$.	32
Figure 3.4	Stable coordination number k_s of aggregates at various shear flow conditions $\mu\dot{\gamma}$. The black lines along the points are to guide the eye. The dash-horizontal lines show some values of initial coordination number of aggregate before subjected to the flow $\mu\dot{\gamma}$.	34
Figure 3.5	Change in coordination number with nondimensional time by simulation results and model results for the initial aggregate of $k_0 = 2.00$ and $k_0 = 5.54$ at different fluid shear rate.	36
Figure 4.1	Coordination number profile for restructuring of initial aggregate k_0 and limit aggregate $k_{\max}$ at the same shear flow condition $\mu\dot{\gamma} = 26.9$ Pa.	38
Figure 4.2	Radial distribution of particle volume fraction at initial structure and stable structure of aggregates at condition $\mu\dot{\gamma} = 12.0$ Pa.	41
Figure 4.3	Change in (a) coordination number k and (b) volume fraction ϕ at various shear flow conditions for the aggregate with $k_0 = 3.02$. The horizontal line shows the value of $k_{\max}$ and $\phi_{\max}$ for this aggregate. The blurred profile shows the irregular change of aggregate toward breakup. The irregular aggregate and its equivalent ellipsoid when the aggregate is toward breakup are also given. Legends in (a) and (b) have the same meaning.	43
Figure 4.4	Relation of the saturation degree $(k_{\max} - k)/k$ and inversed strength of aggregate $(k\phi)^{-1}$ during the restructuring from initial structure toward stable structure in various shear conditions.	46
Figure 4.5	Relation of stable structure of aggregate with fluid shear stress $\mu\dot{\gamma}$ and the limit structure $k_{\max}\phi_{\max}$.	47
Figure 5.1	Spherical coordinate system for porous sphere model [1].	51
Figure 5.2	Restructuring regime of aggregate as a function of screened radius of aggregate. $f_{\min}$ is determined by porous sphere model [1]. The gray area shows the restructuring regime for the investigated conditions in this study.	53

List of Tables

Table 2.1	Summarization of simulation parameters for particle and fluid properties.	21
Table 4.1	Typical properties of limit aggregate obtain at weak flow condition $\mu\dot{\gamma} = 12.0$ Pa.	44
Table 5.1	Properties of initial aggregate and limit aggregate obtained at weak flow condition using porous sphere model. The assumed Poision ratio is $p = 0$, the value of $\mu\dot{\gamma}^*$ is determined from Figure 3.4.	54

Chapter 1 Introduction

1.1 Colloidal suspension is everywhere!

Colloidal suspension (*i.e.* solid particles with the size of 1-1000 nm dispersed in fluid) is regarded as one of fluids called complex fluid [1,2,3,4]. Such a name implies that the microstructure of the fluid and the consequent physical properties behave complexly and differently depending on the applied conditions such as concentration, size of solid particles, the interaction among particles, and the type, intensity of fluid flow. Diversity in structure of suspension basically originates from the arrangement and properties of the particles. The particles are able to gather to form larger aggregates or cluster (aggregation process), and reversely the aggregates can be disaggregated into smaller fragments (breakup).

The appearance of colloidal suspension flow has become ubiquitous not only in several fields in industry, such as pharmaceutical, cosmetics, plastics, food processing, paint, ink, environmental engineering, civil engineering, material engineering, but also in unit operation, for example, mixing, sedimentation, transportation. Here, some noticeable applications are introduced.

One of important issue of colloidal suspension in environmental engineering is solid-liquid separation processes, e.g. filtration [5,6], sedimentation [7,8], gravity thickening [9,10] and dewatering [11]. Sedimentation of small particles (the size of 1-1000 nm) in fluid medium can be very problematical and difficult to control because the effect of gravity is dominated by other interactions at colloidal scale and molecular scale. It has been known that changes in properties of the cluster of particles, such as size, structure, density eventually alter the settling velocity [7,8,9,10]. The removal of particles is accelerated when enlarging the size and compacting the structure of cluster of particles by using flocculant coupled with mixing aggregation.

In opposite to the solid-liquid separation where the aggregation of particle is preferable, generating and maintain the dispersion state of nano-and micro-particle is usually the main target in modern trend applications such as ceramic coating, biomaterials, electronic and semiconductor materials, especially when advanced materials are searched for [12,13,14,15,16]. For instance, the development of dispersion technique of ceramic suspension has brought about the significant improvement in properties of basic electronic components such as capacitor (condenser), semi-conductor integrated circuit, eventually

leading to minimizing size and enhancing the performance of electronic devices such as smart-phone, USB, etc.

When dealing with transporting the suspension flow, it is important to know the rheological properties of the suspension such as viscosity [17]. Notable industries relate to this issue are paint, ink industry. Recently, the shear-thickening behavior of suspension has been applied to develop the making of body armour or healthcare equipments [18,19,20].

Furthermore, the movement of colloids in water-body is vital for risk assessment of water quality, transport of contaminant in ocean, lake, river, and groundwater [21,22,23,24].

Knowledge on the structure of suspension in static fluid is extensively investigated. However, when the solid particles and the fluid are in motion, difficulty arises due to the nature of hydrodynamic interaction which has many-body and long-range characteristics. Understanding the behavior of colloidal suspension in this case is a fundamental issue to predict, control, and improve several industrial processes.

1.2 Basic requirements for colloidal suspension

Population balance concept is important to numerous applications of engineering fields. In particulate system where the clusters of particles are simultaneously created and destroyed by the aggregation and breakup process, respectively, the dynamic evolution of the cluster mass distribution can be described by population balance model. For clusters with mass k at time t , the change rate in its number density $N_k(t)$ is conventionally composed of two terms: aggregation term and breakup term as follows [15]:

$$\frac{dN_k(t)}{dt} = \underbrace{\frac{1}{2} \sum_{i+j=k} K_{ij}^A N_i(t) N_j(t) - N_k(t) \sum_{i=1}^{\infty} K_{ki}^A N_i(t)}_{\text{Aggregation}} + \underbrace{\sum_{m=k+1}^{\infty} K_m^B \Theta_{m,k} N_m(t) - K_k^B N_k(t)}_{\text{Breakup}} \quad (1.1)$$

The aggregation term in Eq.(1.1), from left to right, represents: (i) the formation of cluster of mass k from smaller cluster i and j with aggregation rate constant K_{ij}^A , and (ii) the aggregation of cluster of mass k and the other cluster of mass i to form a larger cluster with aggregation rate constant K_{ki}^A . As for the breakup term, it composes of two components: (i) the breakup of cluster of mass m larger than k with breakup rate constant K_m^B to produce cluster of mass k which is characterized with a probability expressed by the fragment mass distribution function $\Theta_{m,k}$, and (ii) the breakup of cluster of mass k into smaller fragments with breakup rate constant K_k^B . Those rate constants for aggregation term and breakup term, and fragment mass distribution function above play a crucial role in population balance model. As a result, both the aggregation and breakup of aggregate have attracted intense interest since they are considered as the key events for fully understanding the distribution of aggregate mass. Several studies, via experiments, theory, numerical simulation, have been conducted in order to find those important parameters and the mechanism controlling them [25,26]. Recently, it has been found that the restructuring of the aggregate, i.e the change in relative position of particles composing aggregate but the particles still

attach together, may significantly affect the overall property of aggregate by population balance model [27]. The restructuring effect of the aggregate should be taken into account for the prediction of suspension behavior, especially where stringent specification is required.

1.3 The role of restructuring of aggregate

In general, the behaviors of an aggregate in flow field, such as rigid-like motion, restructuring and breakup, depend on the hydrodynamic stress acting on the aggregate, and the strength of aggregate itself [28,29,30,31,32,33]. The task of determination of such hydrodynamic stress and strength of aggregate is very complicated since the colloidal aggregate has a wide variety of structure which greatly affects those properties. The restructuring of aggregate, where the primary particles of the aggregate are relatively in motion but still attach together, can be considered as an intermediate stage between the rigid-like motion and breakup. While understanding about the breakup of aggregate is well established by extensive studies [28,29,30,32,33,34,35,36,37], that of the restructuring is not completely understood. It is because when the restructuring occurs, the structure of aggregate alters dynamically, which complicatedly affect the hydrodynamic interaction and the strength of aggregate. Even the case of one isolated aggregate, in other words, the case of dilute suspension, the phenomena is still complicated and lack of understanding. The restructuring of aggregate has significant impact on the breakup and aggregation of aggregate [38,39], because it possibly occurs either before [32,36] or after the breakup event [34,37]. As a result, the structure of aggregate and the rheological properties of the colloidal suspension are completely affected, and severe error may emerge if the restructuring is not taken into account.

The behavior of aggregate in simple shear flow has attracted a lot of interest due to its ubiquity in engineering fields. In non-sheared system, the aggregate often has fractal structures. In sheared system, the aggregate loses its fractal property and the aggregate is apt to exist in the form of high fractal dimension proved by experiment [29], simulation [34,37,40], and analytical model [41]. It is because when the restructuring of the aggregate has occurred, the branches of the aggregate bends and reconnects, leading to a more compact structure [32,33,42]. Furthermore, the breakup behavior of low fractal aggregate is predictable, whereas the high fractal aggregate behaves diversely [32,35,43]. The explanation for the later can be analyzed from two perspectives. From the static point of view, the complex connectivity inside the high fractal aggregate influences the way of distribution and propagation of force, therefore the resulting stress differs within parts of the aggregate [35,44]. From the dynamic point of view, the restructuring of aggregate takes place, leading to significant change in structure compared to its initial one, and eventually determines the way that the aggregate breaks [32,45,46]. Therefore, understanding the restructuring behavior of high fractal dimension aggregate contributes important information for kinetics of aggregation model and breakup model. Experimental study for two-dimensional non-fractal aggregate shows that there is a significant change in the internal structure of aggregate: under shear flow, the

particles of the aggregate rearrange into a more ordered structure: the hexagonal packing [47]. For three-dimensional aggregate [29,48], the change of internal structure of aggregate is unknown due to lack of proper observing devices.

Numerical simulation is extensively employed to investigate the behavior of aggregate in fluid flow. The notable issue in simulation of colloidal system is dealing with hydrodynamic interaction of many-particle system. In particular, neglecting hydrodynamic interaction leads to overestimation of growth rate of aggregate [49], and the force that the fluid acts on particle [33]. Insight description of the many-body nature of hydrodynamic interaction is therefore important to understand the mechanism governing the behavior of the aggregate.

1.4 Statement of problem

The restructuring of high fractal dimension aggregate significantly affects the overall performance of colloidal suspension. In this study, the restructuring behavior of an isolated non-fractal aggregate in simple shear flow is investigated by numerical simulation. The attraction between particles is calculated by retarded van der Waals force. The many-body hydrodynamic interaction is estimated by Stokesian dynamics approach. The dynamics of the aggregate whose initial structure varies from loose to dense in fluid shear conditions is studied. The main purposes of this study are to find the extent of the restructuring [50], and how to predict the restructuring of the aggregate. The results from this simulation study can be transferred to formulations involving population balance models or dynamics, to improve the design and controlling of colloidal systems.

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Chapter 2 Theoretical background & Simulation method

In this section, the required information to perform the simulation of this study is presented. Important features of Stokesian dynamics for the many-body nature of hydrodynamic interaction for finite number of particles in unbounded flow are summarized. The making of the non-fractal aggregate composing of many primary particles, the basic governing equations describe the motion of multi-particle aggregate in fluid flow field, discussion on simulation conditions and verification of simulation method will be given.

2.1 Hydrodynamic interaction of multi-particle system: Stokesian Dynamics

Stokesian dynamics, proposed by Brady *et al.* [1,2], is a simulation technique for dynamical behavior of many spherical particles dispersed in a fluid medium. Stokesian dynamics is able to capture both the extremely complex long-range many-body hydrodynamic interaction, and the lubrication forces for the nearly touching particles. The method is found suitable to simulate the dynamic behavior of colloidal system compared to other method such as Lattice Boltzmann Method or Finite Element Method [3].

Stokesian dynamic method starts with solution of Stokes flow induced by a point force. The flow disturbed by many particles is treated as a superposition of point forces located on the surface of rigid and spherical particles. The integral representation of the velocity field is employed to make use of the linearity of the Stokes equations. Then a multipole expansion is applied so that linear relations between the force moments and the velocity moments are obtained. The external force acting on the particle and the flow field is related by a mobility matrix which is a purely geometric quantity. The effect of lubrication can be further estimated by special treatment technique to mobility matrix.

2.1.1 Governing equations for fluid flow

For incompressible Newtonian fluid of viscosity μ and density ρ in zero-Reynolds number limit, the motion of the fluid is governed by equation of continuity Eq.(2.1) and Stokes equation Eq.(2.2).

$$\nabla \cdot \mathbf{u} = 0 \quad (2.1)$$

$$\nabla \cdot \boldsymbol{\tau} = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (2.2)$$

where $\mathbf{u}$ is velocity field, $\mathbf{u} = \mathbf{u}(\mathbf{x})$ at arbitrary position $\mathbf{x}$, $\boldsymbol{\tau}$ fluid stress tensor, p pressure.

The theory for the relation of fluid stress and the rate of deformation is Newtonian constitutive equation as in Eq.(2.3), which is based on the hypothesis that the stress is linear with respect to the rate of strain tensor $\mathbf{e}$

$$\boldsymbol{\tau} = -p\boldsymbol{\delta} + 2\mu \left(\mathbf{e} - \frac{1}{3} \boldsymbol{\delta} (\nabla \cdot \mathbf{u}) \right) \quad (2.3)$$

$$\mathbf{e} = \frac{1}{2} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (2.4)$$

where $\boldsymbol{\delta}$ is Kronecker delta tensor [4].

2.1.2 Integral representation solution of Stokes equation

The problem of flow field induced by a point force which is located at $\mathbf{y}$, with direction k , at zero-limit Reynolds number regime can be described as

$$\nabla p^k(\mathbf{x}, \mathbf{y}) - \mu \nabla^2 \mathbf{u}^k(\mathbf{x}, \mathbf{y}) = \boldsymbol{\delta}(\mathbf{x} - \mathbf{y}) \mathbf{e}^k \quad (2.5)$$

$$\nabla \cdot \mathbf{u}^k(\mathbf{x}, \mathbf{y}) = 0 \quad (2.6)$$

where $\mathbf{u}^k(\mathbf{x}, \mathbf{y})$, $p^k(\mathbf{x}, \mathbf{y})$ is the velocity and pressure at arbitrary position $\mathbf{x}$ caused by a point force place at $\mathbf{y}$, $\boldsymbol{\delta}(\mathbf{x} - \mathbf{y})$ Dirac delta function, $\mathbf{e}^k$ unit vector at direction k .

The solution of above problem is

$$\mathbf{u}^k(\mathbf{x}, \mathbf{y}) = \frac{1}{8\pi\mu} \left(\frac{\boldsymbol{\delta}}{r} + \frac{\mathbf{r}\mathbf{r}}{r^3} \right) = \frac{1}{8\pi\mu} \mathbf{J}(\mathbf{x} - \mathbf{y}) \quad (2.7)$$

$$p^k(\mathbf{x}, \mathbf{y}) = \frac{1}{4\pi} \frac{\mathbf{r}}{r^3} \quad (2.8)$$

where $\mathbf{r} = \mathbf{x} - \mathbf{y}$ and $r = |\mathbf{x} - \mathbf{y}|$. The Oseen tensor is a geometric quantity, *i.e.* independent of fluid properties. Oseen tensor in the form using Einstein notation [5] is

$$J_{ij}(\mathbf{x} - \mathbf{y}) = \frac{\delta_{ij}}{r} + \frac{r_i r_j}{r^3} \quad (2.9)$$

Then, for the problem of disturbed flow caused by arbitrary force field located at the surface of a rigid particle, the integral representation of velocity field around a particle of surface S

$$\mathbf{u}(\mathbf{x}) = -\frac{1}{8\pi\mu} \int_S \mathbf{J}(\mathbf{x} - \mathbf{y}) \cdot \boldsymbol{\tau}(\mathbf{y}) \cdot \mathbf{n}(\mathbf{y}) dS \quad (2.10)$$

where $\boldsymbol{\tau}(\mathbf{y})$ the fluid stress tensor at $\mathbf{y}$, $\mathbf{n}(\mathbf{y})$ is normal vector at $\mathbf{y}$ outward the surface.

Finally, for a system of multiple particles of radius a in unbounded fluid, the velocity field is formulated as summation of velocity induced by each particle

$$\mathbf{u}(\mathbf{x}) = -\frac{1}{8\pi\mu} \sum \int_{S_\alpha} \mathbf{J}(\mathbf{x} - \mathbf{y}) \cdot \boldsymbol{\tau}(\mathbf{y}) \cdot \mathbf{n}(\mathbf{y}) dS \quad (2.11)$$

where S_α is surface of particle α .

2.1.3 Multipole expansion

The case that flow induced by particle α whose center is at $\mathbf{x}_\alpha$ is examined. Formally, the size of the particle is set much smaller than the distance between point outside the particle and center of particle, i.e. $|\mathbf{y} - \mathbf{x}_\alpha| \ll |\mathbf{x} - \mathbf{x}_\alpha|$. Applying Taylor expansion for Oseen tensor at $\mathbf{y}$ about $\mathbf{y} = \mathbf{0}$ will give

$$J_{ij}(\mathbf{x} - \mathbf{y}) = J_{ij}(\mathbf{x} - \mathbf{x}_\alpha) - (\mathbf{y} - \mathbf{x}_\alpha)_l \frac{\partial}{\partial x_l} J_{ij}(\mathbf{x} - \mathbf{x}_\alpha) + \frac{1}{2} (\mathbf{y} - \mathbf{x}_\alpha)_l (\mathbf{y} - \mathbf{x}_\alpha)_m \frac{\partial}{\partial x_l} \frac{\partial}{\partial x_m} J_{ij}(\mathbf{x} - \mathbf{x}_\alpha) - \dots \quad (2.12)$$

When multiple particles of radius a exist in unbounded fluid, the velocity field as in Eq.(2.11) after substituted the expansion of Oseen tensor, and set $\mathbf{y}^\alpha = \mathbf{y} - \mathbf{x}_\alpha$, $\mathbf{f}(\mathbf{y}) = \boldsymbol{\tau}(\mathbf{y}) \cdot \mathbf{n}(\mathbf{y})$ is

$$u_i(\mathbf{x}) = -\frac{1}{8\pi\mu} \sum \left[\underbrace{J_{ij} \int_{S_\alpha} f_j dS}_{\text{zeroth-order moment}} - \underbrace{(\partial_l J_{ij}) \int_{S_\alpha} y_l^\alpha f_j dS}_{\text{first-order moment}} + \underbrace{\frac{1}{2} (\partial_l \partial_m J_{ij}) \int_{S_\alpha} y_l^\alpha y_m^\alpha f_j dS}_{\text{second-order moment}} + \dots \right] \quad (2.13)$$

The velocity field by using multipole expansion can often be truncated; it means that only the first few terms need to be retained for a good approximation to the original function. In Stokesian dynamics, the zeroth-order, first-order, and trace of second-order moment is maintained. The mathematical relation of resulted force and the torque exerting on fluid by particle is as following

$$F_i^\alpha = -\int_{S_\alpha} \tau_{ik} n_k dS = -\int_{S_\alpha} f_i dS \quad (2.14)$$

$$T_i^\alpha = -\int_{S_\alpha} (\mathbf{y}^\alpha \times \mathbf{f})_i dS = \varepsilon_{ijk} \int_{S_\alpha} f_j y_k^\alpha dS \quad (2.15)$$

The zero-moment of force is the resulted force acting on the particle. The first-moment of force, or force dipole, is mathematically described as

$$D_{jk}^\alpha = \int_{S_\alpha} f_j y_k^\alpha dS \quad (2.16)$$

The force dipole composes of two tensors: a mean normal stress tensor tending to change the volume of the fluid, and a deviatoric tensor tending to distort the fluid. The deviatoric tensor $\tilde{D}_{jk}^\alpha$ is calculated as follows:

$$\tilde{D}_{jk}^\alpha = D_{jk}^\alpha - \frac{1}{3} D_{ii}^\alpha \delta_{jk} \quad (2.17)$$

$\tilde{D}_{jk}^\alpha$ can be decomposed into the symmetric tensor S_{jk}^α and antisymmetric tensor T_{jk}^α as

$$\tilde{D}_{jk}^\alpha = S_{jk}^\alpha + T_{jk}^\alpha \quad (2.18)$$

$$S_{jk}^\alpha = \frac{1}{2} (D_{jk}^\alpha + D_{kj}^\alpha) - \frac{1}{3} D_{ii}^\alpha \delta_{jk} \quad (2.19)$$

$$T_{jk}^\alpha = \frac{1}{2} (D_{jk}^\alpha - D_{kj}^\alpha) \quad (2.20)$$

The physical image of symmetric tensor S_{jk}^α and antisymmetric tensor T_{jk}^α is given in Figure 2.1.

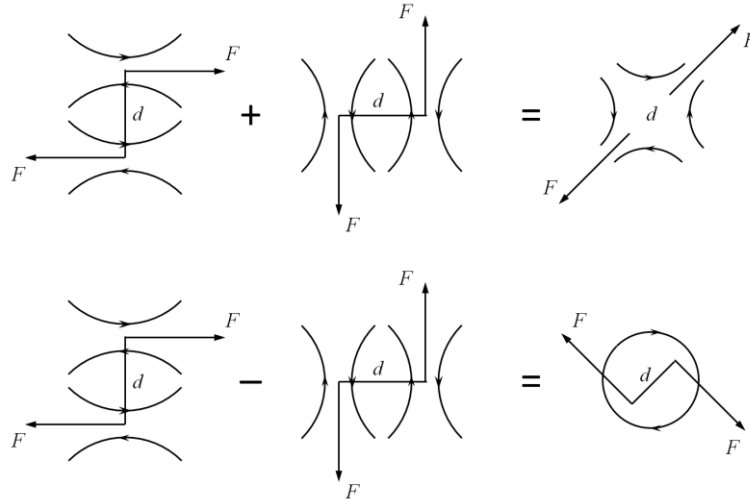


Figure 2.1 The symmetric component and antisymmetric component of force dipole [6].

The mutual relation of the antisymmetric tensor T_{jk}^α and the torque in Eq.(2.15) is given as

$$\varepsilon_{ijk} T_{jk}^\alpha = -T_i^\alpha \quad (2.21)$$

$$\frac{1}{2} \varepsilon_{jkl} T_l^\alpha = -T_{jk}^\alpha \quad (2.22)$$

where $\varepsilon = \varepsilon_{ijk}$ is Levi-Civita symbol [4].

In Eq.(2.13), as for the second-order moment component, only the mean normal contribution is considered.

$$\frac{1}{3} \left(\frac{1}{2} \partial_m \partial_m J_{ij} \int_{S_\alpha} y_m^\alpha y_m^\alpha f_j dS \right) = \frac{1}{6} a^2 \nabla^2 J_{ij} F_j^\alpha \quad (2.23)$$

The velocity field as in Eq.(2.13) is obtained as follows

$$\begin{aligned} u_i(\mathbf{x}) &= \frac{1}{8\pi\mu} \sum \left[\underbrace{J_{ij} F_j^\alpha}_{\text{zeroth-order moment}} + \underbrace{R_{ij}^\alpha T_j^\alpha - K_{ijk}^\alpha S_{jk}^\alpha}_{\text{first-order moment}} + \underbrace{\frac{1}{6} a^2 \nabla^2 J_{ij} F_j^\alpha}_{\text{second-order moment}} + \dots \right] \\ u_i(\mathbf{x}) &= \frac{1}{8\pi\mu} \sum \left[\left(1 + \frac{1}{6} a^2 \nabla^2 \right) J_{ij} F_j^\alpha + R_{ij}^\alpha T_j^\alpha - K_{ijk}^\alpha S_{jk}^\alpha + \dots \right] \\ \mathbf{u}(\mathbf{x}) &= \frac{1}{8\pi\mu} \sum \left[\left(1 + \frac{1}{6} a^2 \nabla^2 \right) \mathbf{J} \cdot \mathbf{F}^\alpha + \mathbf{R}^\alpha \cdot \mathbf{T}^\alpha - \mathbf{K}^\alpha : \mathbf{S}^\alpha + \dots \right] \end{aligned} \quad (2.24)$$

where R_{ij}^α , K_{ijk}^α are dependent on the position of the particle, defined as

$$R_{ij}^\alpha = \varepsilon_{ijk} \frac{r_k}{r^3} \quad (2.25)$$

$$K_{ijk}^\alpha = -3 \frac{r_i r_j r_k}{r^5} \quad (2.26)$$

For a system of finite particles in fluid, the velocity field can be expressed by the force $\mathbf{F}$, torque $\mathbf{T}$ and stresslet $\mathbf{S}$ exerting on fluid by each particle and the position of each particle in the system.

2.1.4 Mobility matrix

The flow field as given in Eq.(2.24) is the flow induced by the existence of many particles. Considering that N particles are put in a flow field characterized by $\mathbf{u}^\infty(\mathbf{x})$, i.e. the undisturbed flow field, the particles will affect the velocity field, which is a superimposition of the undisturbed flow $\mathbf{u}^\infty(\mathbf{x})$ and the velocity induced by the N particles $\mathbf{v}'(\mathbf{x})$ determined as Eq.(2.24).

$$\begin{aligned} \mathbf{v}(\mathbf{x}) &= \mathbf{u}^\infty(\mathbf{x}) + \mathbf{v}'(\mathbf{x}) \\ \mathbf{v}(\mathbf{x}) &= \mathbf{u}^\infty(\mathbf{x}) + \frac{1}{8\pi\mu} \sum_{\beta=1}^N \left[\left(1 + \frac{1}{6} a^2 \nabla^2 \right) \mathbf{J}(\mathbf{x} - \mathbf{x}^\beta) \cdot \mathbf{F}^\beta + \mathbf{R}(\mathbf{x} - \mathbf{x}^\beta) \cdot \mathbf{T}^\alpha - \mathbf{K}(\mathbf{x} - \mathbf{x}^\beta) : \mathbf{S}^\beta + \dots \right] \end{aligned} \quad (2.27)$$

The above equation means that if the undisturbed flow, the position of particle, the force, torque, stresslet acting on fluid by particles are known, the velocity field of many-particle system can be determined. The next part shows the calculation method for the force, torque, stresslet acting on fluid by particles.

The undisturbed flow can be decomposed into translational velocity, rotational velocity and rate of strain tensor as following

$$\mathbf{u}^\infty(\mathbf{x}) = \mathbf{U}^\infty + \boldsymbol{\Omega}^\infty \times \mathbf{x} + \mathbf{E}^\infty \cdot \mathbf{x} \quad (2.28)$$

According to Faxen's law [6,7], for a particle α put in a flow field $\mathbf{v}(\mathbf{x})$, the fluid exerts force $\mathbf{F}_f$, torque $\mathbf{T}_f$, and stresslet $\mathbf{S}_f$ on particle.

$$\mathbf{F}_f = 6\pi\mu a \left(1 + \frac{1}{6} a^2 \nabla^2\right) \mathbf{v}(\mathbf{x}^\alpha) - 6\pi\mu a \mathbf{U}^\alpha \quad (2.29)$$

$$\mathbf{T}_f = 4\pi\mu a^3 \nabla \times \mathbf{v}(\mathbf{x}^\alpha) - 8\pi\mu a^3 \boldsymbol{\Omega}^\alpha \quad (2.30)$$

$$-\mathbf{S}_f = \frac{20}{3} \pi\mu a^3 \left(1 + \frac{1}{10} a^2 \nabla^2\right) \mathbf{e}'(\mathbf{x}^\alpha) + \frac{20}{3} \pi\mu a^3 \mathbf{E}^\infty \quad (2.31)$$

where $\mathbf{U}^\alpha$, $\boldsymbol{\Omega}^\alpha$ are the translational velocity and rotational velocity of the particle α . The deformation of the particle is not considered due to the rigid particle assumption.

If the inertia of the both particle is neglected, the force acting on particle by fluid counterbalances with any external force $\mathbf{F}^\alpha$ $\mathbf{T}^\alpha$ acting on the particle, e.g. gravity, as a result of the third law of motion.

$$\mathbf{F}^\alpha = -6\pi\mu a \left(1 + \frac{1}{6} a^2 \nabla^2\right) \mathbf{v}(\mathbf{x}^\alpha) + 6\pi\mu a \mathbf{U}^\alpha \quad (2.32)$$

$$\mathbf{T}^\alpha = -4\pi\mu a^3 \nabla \times \mathbf{v}(\mathbf{x}^\alpha) + 8\pi\mu a^3 \boldsymbol{\Omega}^\alpha \quad (2.33)$$

$$-\mathbf{S}^\alpha = \frac{20}{3} \pi\mu a^3 \left(1 + \frac{1}{10} a^2 \nabla^2\right) \mathbf{e}'(\mathbf{x}^\alpha) + \frac{20}{3} \pi\mu a^3 \mathbf{E}^\infty \quad (2.34)$$

Substituting Eq.(2.27) into Eq.(2.32), (2.33), it gives the relation of motion of a particle α with external force $\mathbf{F}^\alpha$ and torque $\mathbf{T}^\alpha$ in a flow field disturbed by N particles $\mathbf{v}(\mathbf{x})$ as given in Eq.(2.27).

$$\mathbf{U}^\alpha - \mathbf{u}^\infty(\mathbf{x}^\alpha) = \frac{\mathbf{F}^\alpha}{6\pi\mu a} + \left(1 + \frac{1}{6} a^2 \nabla^2\right) \mathbf{v}'(\mathbf{x}^\alpha) \quad (2.35)$$

$$\boldsymbol{\Omega}^\alpha - \boldsymbol{\Omega}^\infty = \frac{\mathbf{T}^\alpha}{8\pi\mu a^3} + \frac{1}{2} \nabla \times \mathbf{v}'(\mathbf{x}^\alpha) \quad (2.36)$$

$$-\mathbf{E}^\infty = \frac{\mathbf{S}^\alpha}{\frac{20}{3} \pi\mu a^3} + \left(1 + \frac{1}{10} a^2 \nabla^2\right) \mathbf{e}'(\mathbf{x}^\alpha) \quad (2.37)$$

It is reminded that $\mathbf{v}'(\mathbf{x})$ is the disturbed field caused by the particle β except for particle α , and $\mathbf{e}'(\mathbf{x})$ is the deformation rate tensor of flow field $\mathbf{v}'(\mathbf{x})$. Substituting $\mathbf{v}'(\mathbf{x})$ from Eq.(2.27) into the set of three equations above, and rewriting in the form of matrix leads to

$$\begin{pmatrix} \mathbf{U}_\alpha - \mathbf{u}^\infty(\mathbf{x}^\alpha) \\ \mathbf{U}_\beta - \mathbf{u}^\infty(\mathbf{x}^\beta) \\ \vdots \\ \boldsymbol{\Omega}_\alpha - \boldsymbol{\Omega}^\infty \\ \boldsymbol{\Omega}_\beta - \boldsymbol{\Omega}^\infty \\ \vdots \\ -\mathbf{E}^\infty \\ -\mathbf{E}^\infty \\ \vdots \end{pmatrix} = \mathbf{M} \cdot \begin{pmatrix} \mathbf{F}_\alpha \\ \mathbf{F}_\beta \\ \vdots \\ \mathbf{T}_\alpha \\ \mathbf{T}_\beta \\ \vdots \\ \mathbf{S}_\alpha \\ \mathbf{S}_\beta \\ \vdots \end{pmatrix} \quad (2.38)$$

Eq.(2.38) shows the relation of relative motion of particle to fluid to external force exerting on particles. The mobility matrix $\mathbf{M}$ is dependent only on the position of the particles. Details of mobility matrix $\mathbf{M}$ are given in Appendix A.

2.1.5 Lubrication correction

The lubrication force is significant when the distance of particle surface reaches very small value. Lubrication in Stokesian dynamics is taken into account by special treatment to the mobility matrix, which will be given in the next section.

2.2 Stokesian Dynamics simulation model

The backbone of the simulation method for the hydrodynamic interaction of multiple particles in fluid flow is Stokesian dynamics [1,2]. The explanation on Stokesian dynamics is given in Chapter 2.1. Here, only the concept and the basic equations for simulation procedure are given. The particles are assumed hard and spherical. For a finite number of particles in fluid flow, the relation between the force exerting on particles and the relative motion of particles to the fluid flow is shown as following

$$\begin{pmatrix} \mathbf{F} \\ \mathbf{T} \\ \mathbf{S} \end{pmatrix} = \mathbf{M}^{-1} \cdot \begin{pmatrix} \mathbf{U} - \mathbf{u}^\infty \\ \boldsymbol{\Omega} - \boldsymbol{\Omega}^\infty \\ -\mathbf{E}^\infty \end{pmatrix} \quad (2.39)$$

where

$$\mathbf{M}^{-1} = \begin{pmatrix} \mathbf{R}_{FU} & \mathbf{R}_{F\Omega} & \mathbf{R}_{FE} \\ \mathbf{R}_{TU} & \mathbf{R}_{T\Omega} & \mathbf{R}_{TE} \\ \mathbf{R}_{SU} & \mathbf{R}_{S\Omega} & \mathbf{R}_{SE} \end{pmatrix} \quad (2.40)$$

where $\mathbf{F}, \mathbf{T}, \mathbf{S}$ are the external force, torque and stresslet acting on particles; $\mathbf{U}, \boldsymbol{\Omega}$ the particle velocity and rotational velocity; $\mathbf{u}^\infty, \boldsymbol{\Omega}^\infty, \mathbf{E}^\infty$ the velocity, rotational velocity and rate of strain tensor of the

undisturbed flow; $\mathbf{R}_{FU}$, $\mathbf{R}_{TU}$, etc. the components of the resistance matrix which are determined from the mobility matrix $\mathbf{M}$ and dependent only on the position of the particles. The calculation method of the mobility matrix $\mathbf{M}$ can be found in [8] or Appendix A. According to Eq.(2.39), the translational and rotational velocity of particles is calculated as below

$$\begin{pmatrix} \mathbf{U} \\ \boldsymbol{\Omega} \end{pmatrix} = \begin{pmatrix} \mathbf{u}^\infty \\ \boldsymbol{\Omega}^\infty \end{pmatrix} + \begin{pmatrix} \bar{\mathbf{R}}_{FU} & \bar{\mathbf{R}}_{F\Omega} \\ \bar{\mathbf{R}}_{TU} & \bar{\mathbf{R}}_{T\Omega} \end{pmatrix}^{-1} \cdot \left[\begin{pmatrix} \mathbf{F} \\ \mathbf{T} \end{pmatrix} + \begin{pmatrix} \bar{\mathbf{R}}_{FE} \\ \bar{\mathbf{R}}_{TE} \end{pmatrix} : \mathbf{E}^\infty \right] \quad (2.41)$$

where $\bar{\mathbf{R}}_{FU}$, $\bar{\mathbf{R}}_{F\Omega}$, etc. are the components of the grand resistance matrix $\bar{\mathbf{R}}$ in which the lubrication correction is included.

$$\bar{\mathbf{R}} = \mathbf{M}^{-1} - \mathbf{M}_{2B}^{-1} + \mathbf{R}_{2B} \quad (2.42)$$

where $\mathbf{M}_{2B}$ is the two-body mobility matrix calculated in a similar way with $\mathbf{M}$, $\mathbf{R}_{2B}$ the two-body resistance matrix [2-6]. The dynamic behavior of all particles is performed by numerical integration of Eq.(2.41) while the matrices are continuously updated with each time step.

The behavior of an isolated aggregate is investigated in simple shear flow. Simple shear flow, as illustrated in Figure 2.2, is characterized by shear rate $\dot{\gamma}$, which expresses the gradient velocity u_x^∞ along the y direction. The undisturbed flow $\mathbf{u}^\infty = (\dot{\gamma}y, 0, 0)^T$ in Cartesian coordinate, in order to be viably used in Eq.(2.41), is decomposed into rotational component and deformation component, characterized by $\boldsymbol{\Omega}^\infty$ and $\mathbf{E}^\infty$ respectively, and shown in Eq.(2.43)-(2.45). The representation of such components, and its equivalent streamline is described in Figure 2.3.

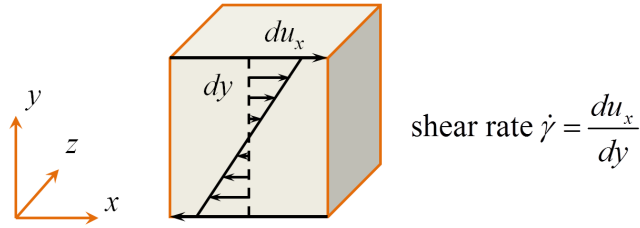


Figure 2.2 Illustration of simple shear flow in Cartesian coordinate

$$\mathbf{u}^\infty(\mathbf{r}) = \boldsymbol{\Omega}^\infty \times \mathbf{r} + \mathbf{E}^\infty \cdot \mathbf{r} \quad (2.43)$$

$$\boldsymbol{\Omega}^\infty = -\frac{\dot{\gamma}}{2} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (2.44)$$

$$\mathbf{E}^\infty = \frac{\dot{\gamma}}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.45)$$

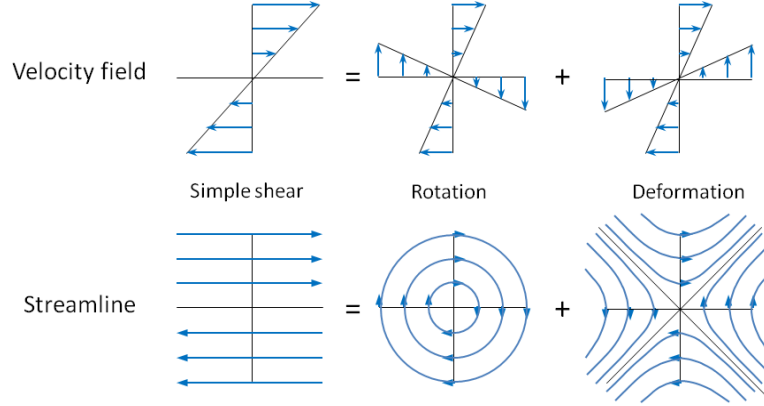


Figure 2.3 The rotational component and deformation component of simple shear flow and its equivalent streamline.

2.3 Structure of aggregate

2.3.1 Background

The dispersed colloidal particles, under the influence of forces such as attractive van der Waals force, may induce the aggregation of particles. As a result, the particles are not in the dispersed state but assemble together, which is usually called aggregate.

The aggregate exhibits a particular geometrical characteristic which can be expressed by fractal geometry [9]. The number of particles of such aggregate can be scaled as a power of its size as follows:

$$N(r) = f_p r^{d_f} \quad (2.46)$$

where f_p is the prefactor. The exponent is called fractal dimension d_f , which quantitatively describes the space-filling property and self-similarity property, is an important parameter to characterize the aggregate [10]. An example of the ideal self-similar fractal aggregate formed by crossed pattern of particle, also known as Vicsek fractal, is illustrated in Figure 2.4. Fractal dimension of a three-dimensional aggregate is in the range of $1 \leq d_f \leq 3$. Higher values of d_f mean that the particles fill the space more. The structure of the aggregate is diverse because it is dependent on the nature of the driving force leading to assembling and the kinetics underlying. Figure 2.5 shows the actual aggregates formed under different mechanism and its fractal dimension. One can see that the low fractal aggregate has many branches and occupies large space, whereas the high fractal aggregate has more particles filling up inside.

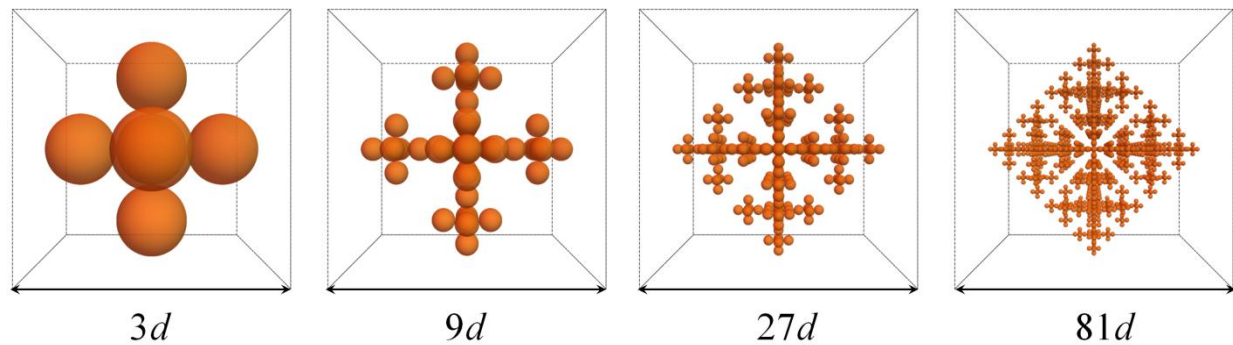


Figure 2.4 A three-dimensional fractal aggregate formed by primary spherical particle with diameter d . Seven particles have been joined to form crosses. Then seven of these crosses have been joined to form a larger crosses and so on. Such structure is called Vicsek fractal and its fractal dimension is 1.77.

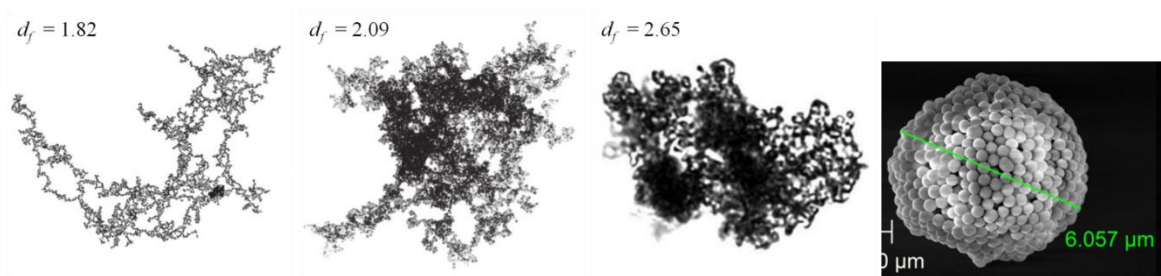


Figure 2.5 Actual structure of colloidal aggregate. (a) Diffusion limit aggregate [11], (b) Reaction limit aggregate [11], (c) Shear induced aggregate [12], (d) Aggregate is formed by drying a microdroplet $d_f \approx 3$ [13].

2.3.2 Simulation of non-fractal aggregate

The 3-dimensional non-fractal aggregate has fractal dimension $d_f = 3$. The particles composing the aggregate well fill the space. The aggregate is homogeneous. The number of particles of the aggregate is 100 particles. In order to construct the non-fractal aggregate as illustrated in Figure 2.7, the particle-cluster aggregation model is employed while applying centripetal force to a given number of particle randomly distributed [14]. Figure 2.6 illustrates the process of making the aggregate. It should be noted that the simulation procedure for assembling the aggregate before subjected to fluid flow is independently carried out. By varying some parameters in the procedure such as friction coefficient or damping coefficient, an aggregate with different connectivity is created. Coordination number, a common parameter describing the packing property of granular material at a local scale, is used to evaluate the internal connectivity of the aggregate.

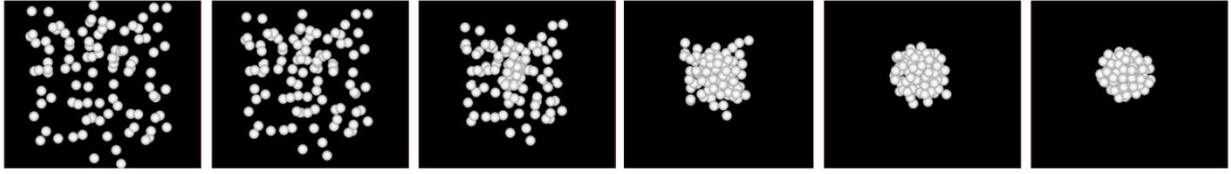


Figure 2.6 The making of aggregate by centripetal force. The images from left to right is the evolution of the assemblage with time.

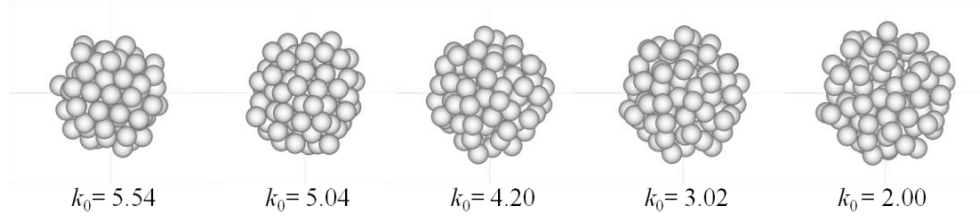


Figure 2.7 The non-fractal aggregate with different connectivity

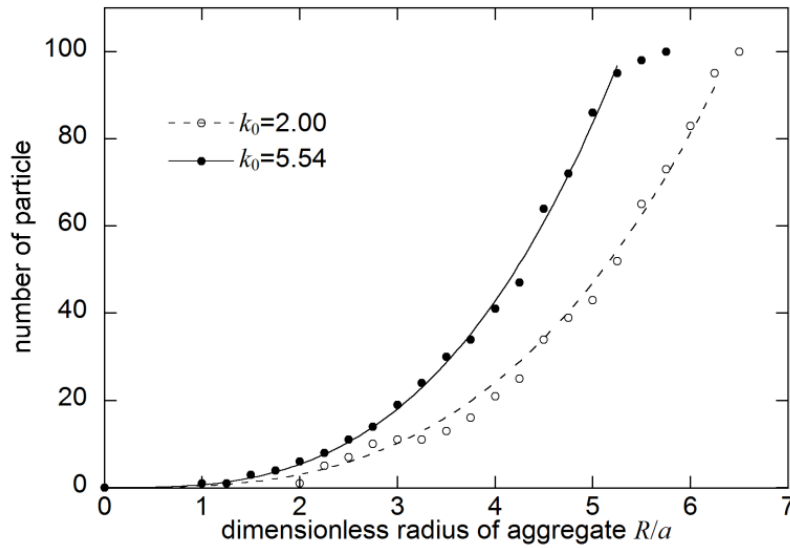


Figure 2.8 The number of particle along the nondimensional radius R/a from the center of the aggregate.

The coordination number for an identified particle is defined as the number of its surrounding particles within a designated separation. In this study, the coordination number of an aggregate is an average value, and the designated separation of particle's surface is set at 2 nm. The value of 2 nm is able to represent the connection among the particles when considering the van der Waals interaction. Readers may refer to Appendix B for more detail. The initial configuration of the aggregate ranges from a very loose structure,

whose coordination number is low at $k_0 = 2.00$ to a very dense structure, $k_0 = 5.54$, as shown in Figure 2.7. Furthermore, Figure 2.8 illustrates the accumulated number of particles along the radius of aggregate from the center. The continuous curve following the third power of the nondimensional radius of aggregate is depicted, which validates the non-fractal and isotropic characteristics of the aggregate used in the study.

2.3.3 Characterization of aggregate

The direct output properties of aggregate in the study are the connectivity of aggregate and the volume fraction. The former is presented by average coordination number. The volume fraction of aggregate in local scale and global scale is calculated by Voronoi tessalation and equivalent ellipsoid, respectively. Detail of each characterization will be given in the later sections.

2.4 Simulation condition

It is assumed that the primary particles of the aggregate are hard, smooth, and spherical. The size of particle is $2a = 650$ nm in diameter. The properties of particles and fluid are those of polystyrene and ethanol. The particle density, the fluid density and the fluid viscosity are $\rho_p = 1056$ kg/m³, $\rho_f = 790$ kg/m³ and $\mu = 1.2 \times 10^{-3}$ Pa·s, respectively. The aggregate is composed of 100 primary particles. Due to its colloidal size, the retarded van der Waals is employed as the main interaction between the particles. However, when the distance between the surface of particle is very small around a few Angstroms, simply applying such attractive interaction is quite impractical because the other complex phenomena at molecular scale are dominant [15]. Therefore, when the surface distance of particle is less than 1 nm, the attractive force is set to be zero and none of molecular-scale interaction is taken into account. The non-dimensional attraction force for a couple of particles used in this study is given in Figure 2.9. One of the important parameters in van der Waals force is the maximum attractive force, which is fundamental to estimate the cohesive strength of particles. Due to small distance of $\delta = 1$ nm, the maximum attractive force F_M is approximately equal to the non-retarded condition, which is

$$F_M = \frac{A_H a}{12\delta^2} \quad (2.47)$$

where A_H is non-retarded Hamaker constant, for polystyrene-ethanol system $A_H = 9.68 \times 10^{-21}$ J; thus $F_M = 2.62 \times 10^{-10}$ N.

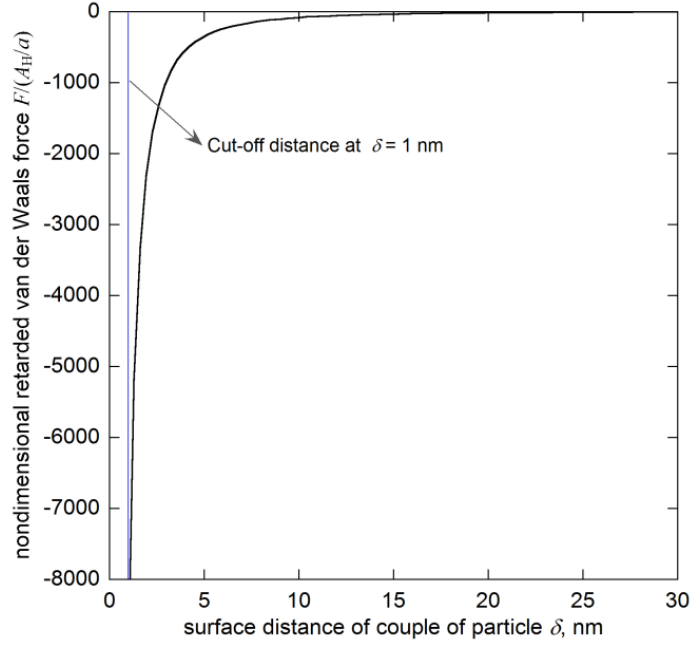


Figure 2.9 Retarded van der Waals force for a couple of particles

The discrete nature of the simulation method leads to two following problems:

- The overlap of particles possibly occurs even when the lubrication correction is included in the grand resistance matrix as given in Eq.(2.42).
- The required force to separate a pair of particle, for example, when they attracts the most at F_M , is underestimated.

In order to solve the above issues, the time step must be small enough, but not very small so that the computational time required for the dynamics of aggregate is reasonable. The time step t , is chosen so that the nondimensional time for one time step is $\dot{\gamma}t = 0.007$. The error for separating a pair of particle is approximately 8% of F_M for such time step. Moreover, in case fluid shear stress condition $\mu\dot{\gamma} \leq 10.5$ Pa, the smaller time step is set.

In summary, the parameters of the simulation condition when an aggregate is subjected in simple shear flow are given in Table 2.1. The variables are the initial coordination number and the intensity of shear flow. This is the pioneer study examining the restructuring of non-fractal aggregate considering different initial packing property. The effect of fluid shear flow is important because it affects the hydrodynamic interaction. The value of shear rate is in the range of $\dot{\gamma} = 5000\text{--}75000 \text{ s}^{-1}$, which is usually encountered in processes such as pipe flow, mixing and stirring, injection, extrusion.

Table 2.1 Summarization of simulation parameters for particle and fluid properties.

Parameter	Value
Fixed parameters	
Radius of particle	$a = 325 \text{ nm}$
Density of particle (polystyrene)	$\rho_p = 1056 \text{ kg/m}^3$
Number of particle of aggregate	$N = 100$
Hamaker constant (non-retarded)	$A_H = 9.68 \times 10^{-21} \text{ J}$
Cut-off distance for van der Waals force	$\delta = 1 \text{ nm}$
Density of fluid (ethanol)	$\rho_f = 790 \text{ kg/m}^3$
Viscosity of fluid	$\mu = 1.2 \times 10^{-3} \text{ Pa}\cdot\text{s}$
Variables	
Coordination number of aggregate	$k_0 = 2.00, 3.02, 4.20, 5.04, 5.54$
Fluid shear stress	$\mu\dot{\gamma} = 6\text{Pa} - 90\text{Pa}$

2.5 Discussion on assumption and verification

2.5.1 Discussion on assumption

On particle and fluid inertia:

Stokesian dynamics is viable when the inertia of fluid and particle is neglected, *i.e.* $Re \ll 1$ and $St \ll 1$ correspondingly. The formula of Re and St are given again for convenience:

$$Re = \frac{\rho_f a U}{\mu} \ll 1 \quad (2.48)$$

$$St = \frac{\rho_p a U}{\mu} \ll 1 \quad (2.49)$$

where U is the characteristic velocity. The properties of the particle and fluid (Table 2.1) lead to $U < O(10^0) \text{ m/s}$. There are two kinds of characteristic velocity in the study

- Based on the balance of inter-particle force (characterized by A_H/a) and drag force $6\pi\mu aU$, it is derived that $U = A_H/6\pi\mu a^2$. Straightforwardly, $U < O(10^{-5})$ and satisfies the above condition.
- Based on particle radius and shear rate, then $U = a\dot{\gamma}$. In order to satisfy $U < O(10^0) \text{ m/s}$, it requires that the shear rate $\dot{\gamma} < O(10^7) \text{ s}^{-1}$ or fluid shear stress $\mu\dot{\gamma} < O(10^4) \text{ Pa}$. The range of $\mu\dot{\gamma}$ investigated in the simulation is set $\mu\dot{\gamma} < 90 \text{ Pa}$.

On Brownian motion:

The Brownian motion is negligible if the work of drag force is much larger than the thermal fluctuation energy of particle, *i.e.* $Pe \gg 1$.

$$Pe = \frac{6\pi\mu a^3 \dot{\gamma}}{k_B T} \quad (2.50)$$

where Boltzmann constant is $k_B = 1.38 \times 10^{-23}$ J/K, and temperature $T = 300$ K. The constrain of Pe leads to $\mu\dot{\gamma} > 6$ Pa ($Pe \approx 1000$).

On gravity effect

As can be seen in Table 2.1, the density of particle is larger than that of fluid, which may affect the dynamics of particles. The Bond number Bo , which describes the ratio of cohesive force to buoyancy, is define as

$$Bo = \frac{F_M}{F_{\text{buoyancy}}} = \frac{\frac{A_H a}{12\delta_{\min}^2}}{(\rho_p - \rho_f) \frac{4}{3} \pi a^3 g} = \frac{A_H}{16\pi(\rho_p - \rho_f) a^2 g \delta_{\min}^2} \quad (2.51)$$

where g is gravitational acceleration, $g = 9.81$ m/s². The value of Bo in the study is $Bo > O(10^5)$, meaning that the attraction between particle is dominant over gravity. Therefore, the effect of gravity is negligible.

2.5.2 Verification of simulation method

Verification 1: settling of three spheres

Firstly, Stokesian dynamics is verified via the settling of three spheres as illustrated in Figure 2.10 [16]. The dynamics of the three spheres in vertical plane is calculated by Stokesian dynamics approach, and compared with the results obtained from collocation method by Ganatos *et al.* (1978) [17], which is considered as the exact solutions. The numerical results by Stokesian dynamics, both settling distance and the position of the three particles, are almost similar to that by Ganatos *et al.* In other words, Stokesian dynamics approach is capable of capturing the many-body hydrodynamic nature among the particles.

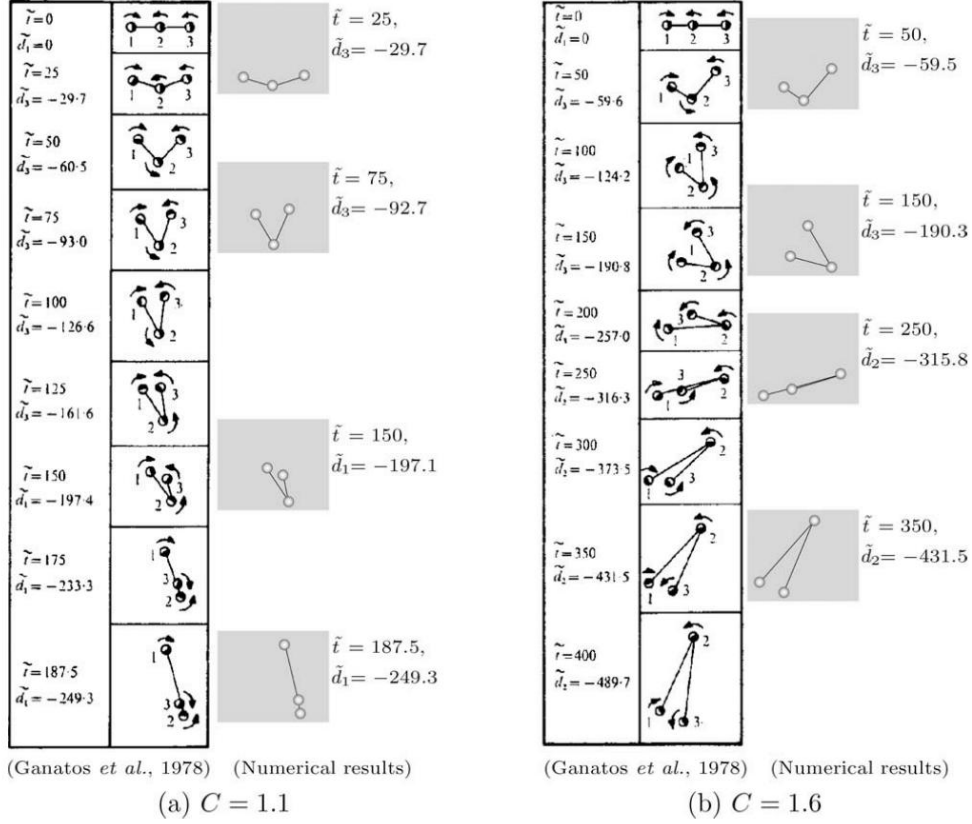


Figure 2.10 Instantaneous motion of three spheres located at unequal distance. $\tilde{t}$: nondimensional time ($=U_t t/a$, U_t : terminal velocity), $\tilde{d}$: nondimensional settling distance ($=d/a$, d : settling distance), C : ratio of initial distance between sphere 1 and 2 to sphere 2 and 3. The initial distance between sphere 1 and 3 is $12a$ (a the radius of sphere). The lines connecting the particles are only for illustration and play no role in the simulation. The image is adapted from Harada *et al.* (2006) [16].

Verification 2: Breakup of fractal aggregate

The low fractal dimension aggregate (*i.e.* the aggregate with a very ramified structure) easily undergoes breakup into several fragments in shear flow. Experimental [18,19] and simulation studies [16,20,21] suggest that the weight average number of particles per fragment $\langle N_p \rangle$ follows power-law with the fluid shear stress $\mu\dot{\gamma}$ as following

$$\langle N_p \rangle = \text{constant}(\mu\dot{\gamma})^{-q} \quad (2.52)$$

where the constant is proportional to the bond strength between particles, q is the fracture component which is mainly dependent on the fractal dimension of the aggregate. The breakup of fractal aggregate whose fractal dimension is $d_f \approx 1.8$ in shear flow is investigated and compared with other works. In

detailed, an isolated aggregate undergoes breakup when subjected to shear flow characterized by $\mu\dot{\gamma}$. After breakup, the weight average number of particle per fragment is determined according to Eq.(2.53)

$$\langle N_p \rangle = \frac{\sum_i i n_i}{\sum_i n_i} \quad (2.53)$$

where n_i is the number of fragment that has i particle. Figure 2.11 exhibits the weight average number of particle per fragment with fluid shear stress conditions. The fracture component q , which is the slope, of this study [16] is comparable with other works [21,22]. The offset can be attributed to different parameter of simulation, such as, initial number of particle of aggregate, particle size, the particle-particle interaction between particles, and particle-fluid interaction model. The good agreement of fracture component shows that Stokesian dynamics is capable of simulating the dynamic behavior of fracture aggregate.

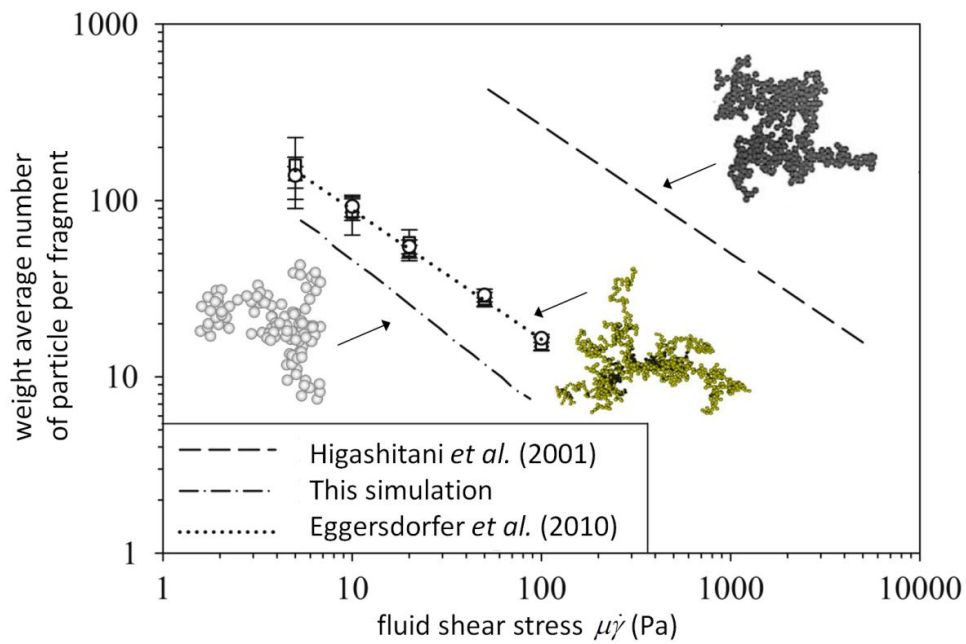


Figure 2.11 The relation between fluid shear stress $\mu\dot{\gamma}$ and the weight average number of particle per fragment at steady state. The fractal dimension of the aggregate before subjected to fluid flow is $d_f \approx 1.8$ (Figure is modified from [21]).

Verification 3: Restructuring of aggregate

Specifically for the simulation condition of this study, the behavior of an aggregate in shear flow is numerically simulated by Stokesian dynamics method, then compared with experimental result by Blaser 2000 [23], as displayed in Figure 2.12. It should be noted that the conditions of simulation and

experiment are not exactly the same; however, the figure shows the rotation and deformation of the aggregate in approximately one cycle of aggregate. Figure 2.12 reveals qualitative agreement as the aggregate stretches and bends continuously.

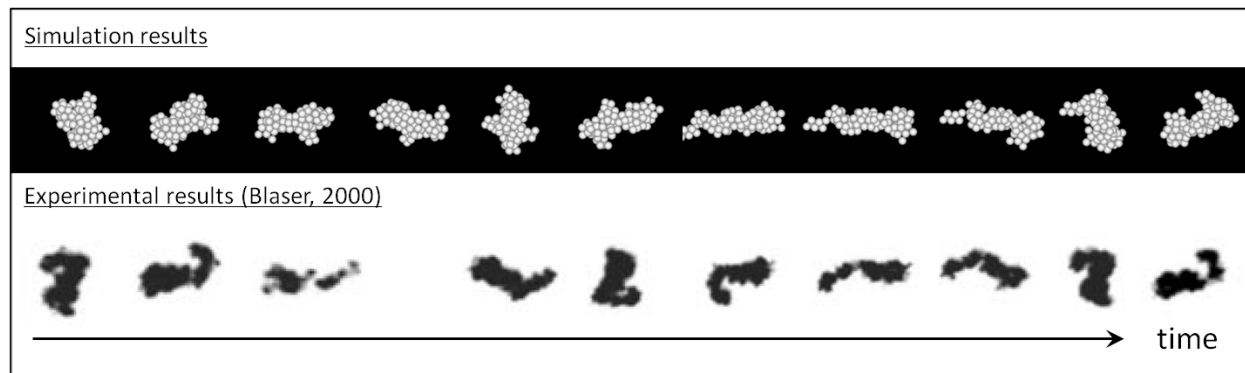


Figure 2.12 Comparison of the rotation and deformation of an aggregate in simple shear flow for one cycle between simulation and Blaser's experimental study [23].

Recently, researches on the behavior of aggregate sometimes involve more complicated inter-particle interaction, e.g. tangential force, due to its significant effect on the restructuring fractal aggregate [22,24, 25]. In particular, it is reported that the branches of the fractal aggregate is more invulnerable to bending moment [22,24,26]. However, a systematic understanding on such tangential force has not well established, leading to difficulties in the construction of a represent model. Another uncertainty is the effect of tangential force on non-fractal aggregate, which has not been investigated so far. In addition, the scope of this study is to examine the effect of hydrodynamics of many-body rather than the effect of interparticle interaction on the aggregate. Due to these reasons, the tangential force is neglected in the simulation. It is found that although the force model in this study is simple, some properties expressing the dynamic behavior of aggregate in fluid flow is reasonably comparable with experiment results [23,27] and simulation results [22,28] where more complex force model is applied.

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Chapter 3 **Stability of restructured non-fractal aggregate in simple shear flow**

In this chapter, the dynamics of restructuring of non-fractal aggregate is analyzed in terms of internal connectivity of the primary particles, expressed by the average coordination number. The effect of initial configuration of aggregate and fluid shear flow condition on the restructuring of aggregate is investigated. A kinetic model describing the change in connectivity is proposed. The content of the chapter is presented in article [1].

3.1 Effect of initial structure on shape and coordination number of aggregate

The distribution of primary particles of non-fractal aggregate is quite homogeneous. However, the aggregate may have either loose or dense structure. The effect of initial non-fractal aggregate on the restructuring in the same fluid flow condition is studied. Figure 3.1a shows the instantaneous structures of various aggregates at the same fluid shear condition $\mu\dot{\gamma} = 26.9$ Pa. The loose aggregate with the initial coordination number $k_0 = 2.00$ deforms immediately while it keeps rotating around the vorticity axis, which is the z axis perpendicular to the page. The deformation is complicated including stretching, compressing and bending; then the deformation gradually decreases after several rotations and the shape of the aggregate is eventually maintained. In comparison, the more dense aggregate $k_0 = 3.02, 4.20$ slightly deforms to an ellipsoid and quickly recovers to a spherical structure quite similar to the initial one. The most dense aggregate $k_0 = 5.54$ retains its outer shape and rotates almost identically with the flow whose nondimensional time per rotation is $\dot{\gamma}t = 4\pi$, as illustrated in Figure 3.2. Preliminary observation on the change in shape of aggregates reveals that although the aggregates are non-fractal, the restructuring behaves differently depending on the connectivity of the primary particles. The degree of deformation of aggregate further suggests that the dense aggregate has higher resistance to shear flow than the loose aggregate does.

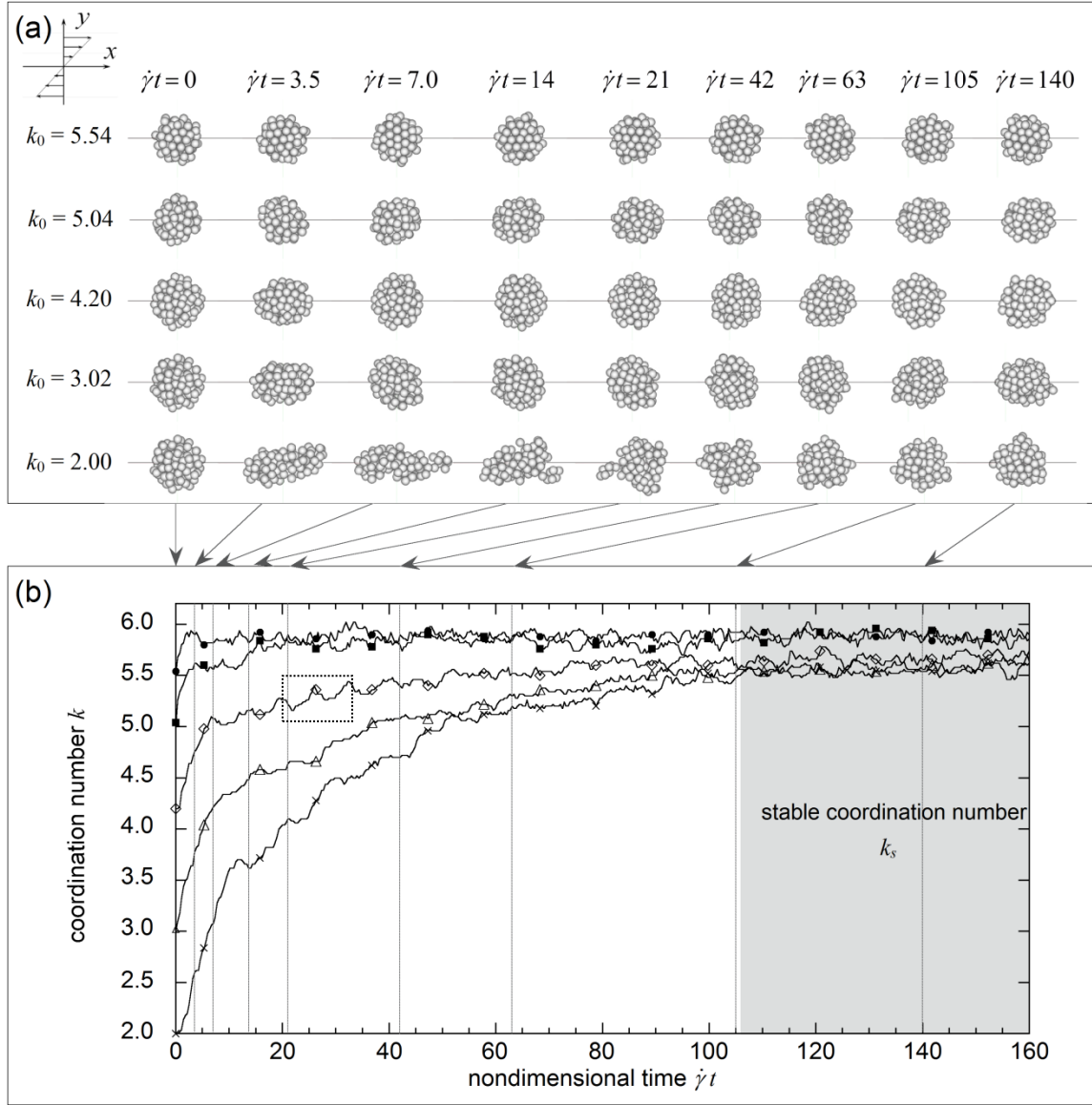


Figure 3.1 Instantaneous structure of aggregate in (a) shape and (b) coordination number k of various aggregates in fluid shear stress condition $\mu\dot{\gamma} = 26.9$ Pa. The arrow is to indicate the position of $\dot{\gamma}t$ in (b). The dotted box has a width equal to the nondimensional time of one rotation of shear flow. The coordination number within the box shows a periodic fluctuation in approximately one rotation of the aggregate.

In order to evaluate the change in the internal structure of the aggregate, the coordination number of aggregate is determined. Figure 3.1b shows the change in coordination number of the aggregate with nondimensional time $\dot{\gamma}t$ at the same condition as Figure 3.1a. The evolution of coordination number shows that the aggregate restructures according to two time scales. The short-term deformation, exhibited

by the periodic fluctuation of coordination number, is possibly explained by the passage of aggregate through the principal axes of stress tensor of simple shear flow twice per rotation (see Figure 2.3 for the decomposition of simple shear flow in to rotation component and deformation component). It can also be seen in the dotted box in Figure 3.1b that the coordination number fluctuates approximately twice in the nondimensional time of one rotation. Via such short-term deformation and in longer time scale, the coordination number levels off and approaches stable value k_s as identified in Figure 3.1b. The existence of stable coordination number coupling with the periodic fluctuation at the investigated condition $\mu\dot{\gamma} = 26.9$ Pa indicates that perhaps the stable state of aggregate is dynamic equilibrium in nature, resulting from the short-term deformation.

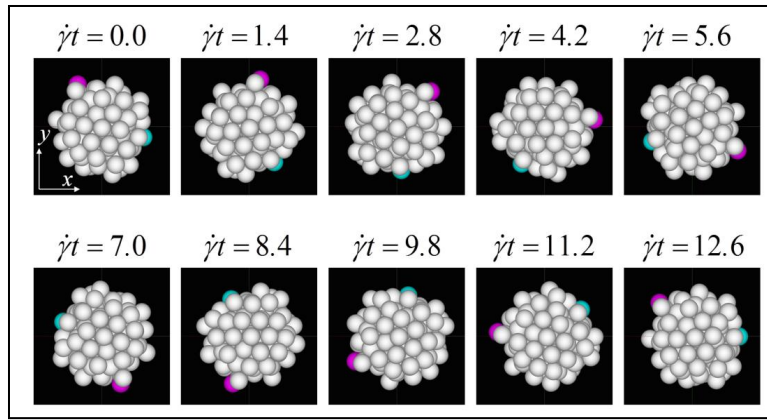


Figure 3.2 The identity between the rotation of dense aggregate $k_0 = 5.54$ and the shear flow in condition $\mu\dot{\gamma} = 26.9$ Pa. The nondimensional time of one cycle of fluid shear flow is 4π . The pink and cyan colored particles are to indicate the rotation of the aggregate in clockwise direction.

As presented in Figure 3.1, whether the deformation of shape is significant or not, changes in coordination number for all aggregates are observed until leveled-off values are reached, which are defined as the stable coordination number k_s . The stable coordination number k_s of the aggregate is distinguished from the initial one. In this condition of fluid shear stress $\mu\dot{\gamma} = 26.9$ Pa, all of the aggregate becomes more dense than its initial structure. Moreover, the coordination numbers of the five aggregates are very different at initial states, but almost similar at the stable states under the same shear flow condition, as shown in the grey area. At this stage, the reasons causing the slight difference of stable coordination number k_s is still unknown. Discussion about this issue will be given in later parts after more results are obtained. However, possible explanation is as follows:

- (i) The first reason may cause from the systematic error of k_s .
- (ii) The other reason possibly originates from the shape of the stable structure. The stable structure of loose aggregate is less spherical, thus it has more particles exposing to the fluid

flow than that of dense aggregate. As a result, k_s of loose aggregate is less than that of dense aggregate.

- (iii) The aggregate has some inherent characteristics. In this case, the difference in stable coordination number is not caused by the error like case (i) and (ii), but by the ability of the aggregate during restructuring.

3.2 Effect of fluid shear stress on shape and coordination number of aggregate

This section examines the influence of fluid shear condition on the restructuring of an aggregate. Figure 3.3 shows the effect of fluid shear stress $\mu\dot{\gamma}$ on temporal change in coordination number for some representative aggregates: dense aggregate $k_0 = 5.54$ and loose aggregate $k_0 = 3.02$. The figure shows that the applied fluid shear stress affects the restructuring of aggregate in two aspects: the shape of coordination number profile and the value of stable coordination number k_s . According to Harada *et al.* (2007) [2], the change in coordination number profile of the very dense aggregate (at the limit of random closed packing in their study) is divided into three stages:

- Stage [I]: the cluster quickly gains a stable structure equivalent to the stable coordination number,
- Stage [II]: the coordination number linearly decreases due to formation of cracks,
- Stage [III]: the coordination number rapidly decreases before the breakup of cluster.

The profiles of k in Figure 3.3a for $k_0 = 5.54$ are in good agreement with the description of the three-stage above. The coordination number shifts from k_0 to k_s in a short time within one rotation (stage I). The slopes in stage II depends on the shear condition, when $\mu\dot{\gamma} = 26.9$ Pa, stage II is very long and the profile almost maintains at the value of k_s . For higher shear stress $\mu\dot{\gamma} = 44.9$ Pa, the constant region of k_s is followed by a decreasing trend. As increasing $\mu\dot{\gamma}$ from 44.9 Pa to 59.8 Pa, the decreasing trend is steeper than the previous one. For this dense aggregate, the stable coordination number in such cases are easily recognized because stage II is much longer than stage I, and the region of constant k_s is explicitly given. The change in k_s with $\mu\dot{\gamma}$ while the aggregate keeps its spherical shape, as given in the figure, may indicate that the applied shear flow strongly affects the inner connectivity of the aggregate even if the change in shape is not visibly observed.

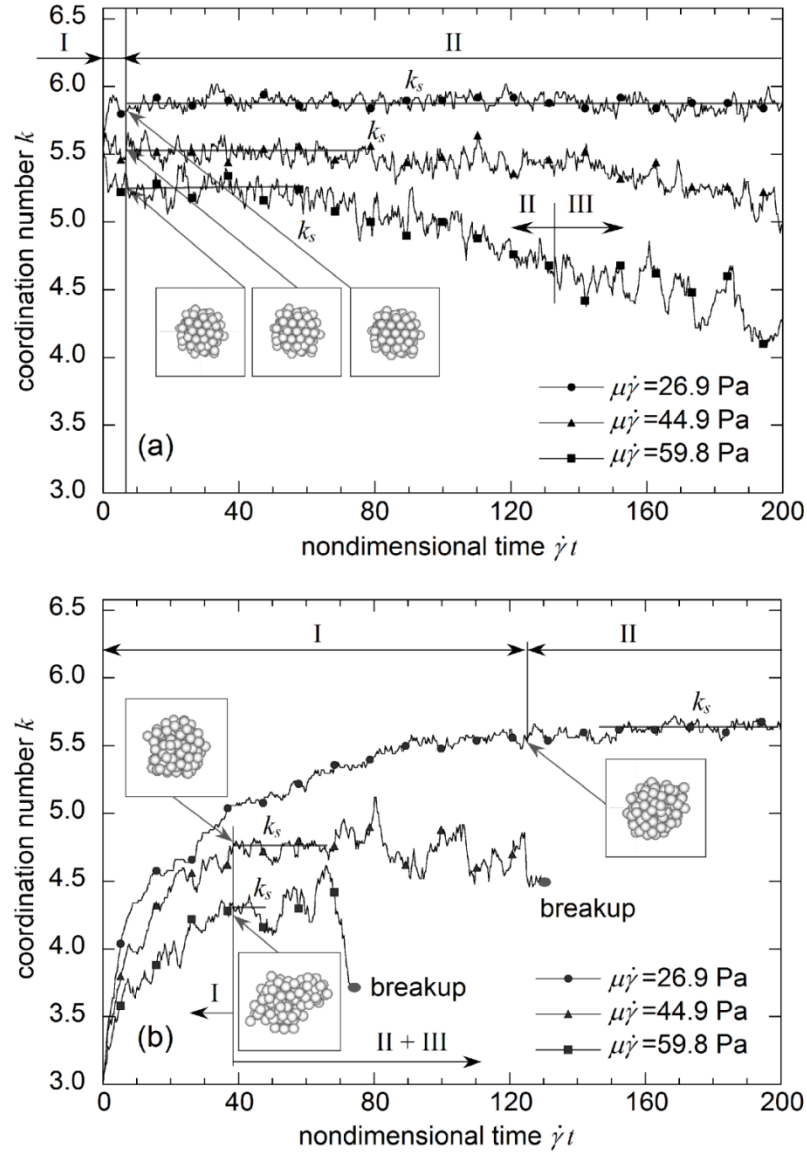


Figure 3.3 Coordination number of aggregate at different shear stress conditions for aggregate with initial coordination number (a) $k_0 = 5.54$, (b) $k_0 = 3.02$.

The results of loose aggregate ($k_0 = 3.02$) from Figure 3.3b also shows that the fluid flow condition influence the restructuring. At fluid shear condition $\mu\dot{\gamma} = 26.9$ Pa, the coordination number k varies then approaches stable value, which is considered as stage I and stage II respectively. Different from dense aggregate, here the stage I prolongs while the deformation of the outer shape of this loose aggregate takes place. However, toward the end of stage I, little or no deformation is observed, and the shape of the aggregate at the end of stage I is almost spherical (see also Figure 3.1). At higher shear stress $\mu\dot{\gamma} = 44.9$ Pa, the profile expresses that stage II lasts for a short time compared to stage I, and there is a rapid change

of coordination number to the breakup (stage III). For $\mu\dot{\gamma} = 59.8$ Pa, stage II and stage III are not clearly distinguished. Moreover, it is observed that in the two later cases of shear stress, the aggregate at the end of stage I has an irregular shape instead of a spherical one. The findings suggest that the restructuring of loose aggregate toward stable state is disrupted by the breakup process when the shear stress is higher than a critical one, which is somewhere between 26.9 Pa and 44.9 Pa in the condition of Figure 3.3b for example. Therefore, the stable coordination number is also affected and difficult to determine in these cases. Since the aim of this research is about the restructuring of aggregate, the study focuses on the case that a stable structure can be clearly obtained, *i.e.* stage II is longer than stage I and a spherical shape at the end of stage I is accomplished. For such behavior, the restructuring is dominant over breakup.

Focusing on the stable coordination number k_s , the data in Figure 3.3 show that the applied fluid shear stress $\mu\dot{\gamma}$ is able to make the dense aggregate $k_0 = 5.54$ become more or less compact compared to initial structure (as k_s is greater or smaller than k_0 Figure 3.3a). On the other hand, the loose aggregate $k_0 = 3.02$ becomes more compact regardless the value of $\mu\dot{\gamma}$. The fluid flow condition seems to have different influence on the restructuring of dense or loose aggregate. However, the final states of the aggregates are quite compact with stable coordination numbers above 4.0.

3.3 Stability of restructured non-fractal aggregate

In this section, the final state, *i.e.* the stable coordination number k_s of aggregate is investigated. Figure 3.4 exhibits the dependence of stable coordination number k_s on the external fluid shear stress $\mu\dot{\gamma}$ and initial coordination number k_0 when the restructuring is dominant over breakup. The initial coordination number varies from very loose ($k_0 = 2.0$) to very dense ($k_0 = 5.54$). The range of fluid shear stress is in the range of $6 \text{ Pa} \leq \mu\dot{\gamma} \leq 75 \text{ Pa}$. The results in Figure 3.4 show that

- The stable coordination number of aggregate k_s is significantly different from the initial one k_0 for most of the cases
- At the same $\mu\dot{\gamma}$ condition, little difference of k_s is observed among aggregates.
- As the flow is weak below a certain value $\mu\dot{\gamma}^*$, k_s is a constant which is independent of fluid flow but still slightly dependent on initial coordination number k_0 . Otherwise, k_s linearly decreases with fluid shear stress $\mu\dot{\gamma}$. Such linearity suggests that there are similar pattern for the restructuring of either dense aggregate or loose aggregate.

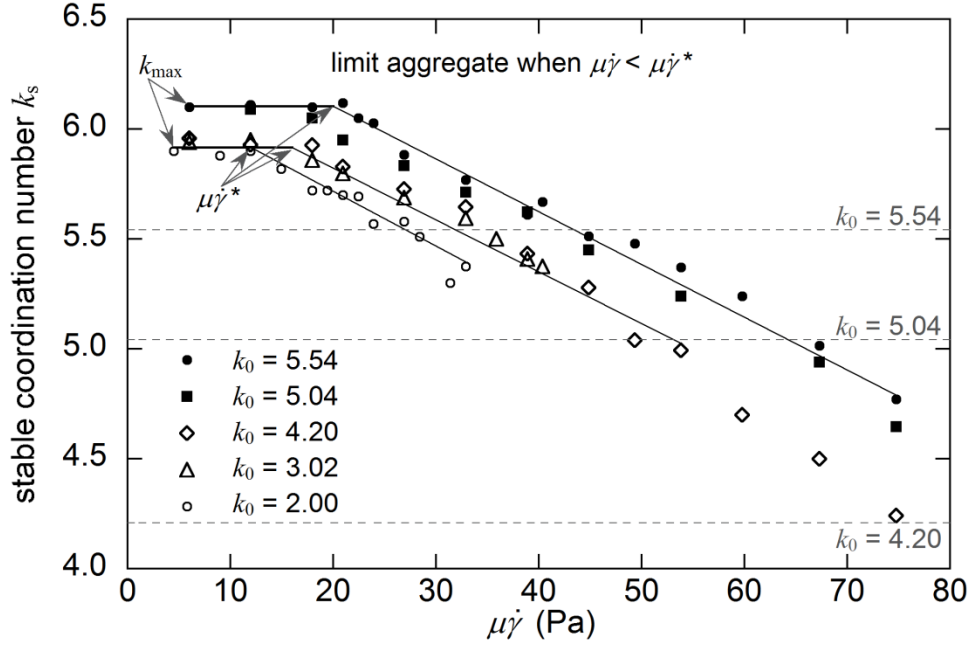


Figure 3.4 Stable coordination number k_s of aggregates at various shear flow conditions $\mu\dot{\gamma}$. The black lines along the points are to guide the eye. The dash-horizontal lines show some values of initial coordination number of aggregate before subjected to the flow $\mu\dot{\gamma}$.

Regarding the stable structure of aggregate at weak shear flow condition $\mu\dot{\gamma} \leq \mu\dot{\gamma}^*$, the coordination number of such stable structures obtains highest and constant value, which is called as limit aggregate whose coordination number is $k_{\max}$. The existence of $k_{\max}$ implies the limit of the restructuring for non-fractal aggregate, *i.e.*, the simple shear flow is capable of compacting the non-fractal aggregate until a limit is reached. Slightly difference in the value of $k_{\max}$ is observed for the loose aggregate group ($k_0 = 2.00, 3.02, 4.20$) whose $k_{\max} \approx 5.95$ and the dense group ($k_0 = 5.04, 5.54$) whose $k_{\max} \approx 6.10$. Such value of $k_{\max}$ is similar to the coordination number of random closed packed mono-spheres whose value is about 6.0 [3-6]. As mentioned in the end of Section 3.1 about three possible reasons for the slight difference of stable coordination number k_s of five different initial aggregate in the same shear flow $\mu\dot{\gamma} = 26.9$ Pa, the slight difference of $k_{\max}$ makes it hard to conclude whether it is caused by systematic error, or the particles at the outer layer, or the inherent structure of aggregate. However, the offset of the solid lines in Figure 3.4 suggest that the gap of k_s and $k_{\max}$ maybe originate from inherent structure of aggregate. The analysis of limit aggregate at $k_{\max}$ will be performed in the later part of this dissertation (Section 4.2).

3.4 Kinetic model

A model based on micromechanics is proposed to elucidate the restructuring of aggregate, *i.e.*, the change in coordination number with time [7]. The net rate of change in coordination number is considered as the sum of the formation rate and the disintegration rate of links connecting a particle to its surrounding ones. Assuming that all particles in the aggregate obey the same rule and then the temporal change of the coordination number is described as the following differential equation:

$$\frac{dk}{d(\dot{\gamma}t)} = \frac{dk^+}{d(\dot{\gamma}t)} + \frac{dk^-}{d(\dot{\gamma}t)} \quad (3.1)$$

According to Eq.(3.2) and Eq.(3.3), the rate of the formation and the disintegration of links are assumed proportional to the number of vacancy and the number of bond, respectively

$$\frac{dk^+}{d(\dot{\gamma}t)} = C^+(k_{max} - k) \quad (3.2)$$

$$\frac{dk^-}{d(\dot{\gamma}t)} = -C^-k \quad (3.3)$$

where C^+ and C^- are coefficients of proportionality and k_{max} is the maximum coordination number at which the aggregate is able to obtain by restructuring, *i.e.* the k_{max} at weak flow condition as shown in Figure 3.4. Integrating Eq(3.1) from $\dot{\gamma}t = 0$ to arbitrary $\dot{\gamma}t$ gives the analytical solution as following

$$k = \frac{C^+k_{max}}{C^+ + C^-} - \left(\frac{C^+k_{max}}{C^+ + C^-} - k_0 \right) e^{-(C^+ + C^-)\dot{\gamma}t} \quad (3.4)$$

where k_0 is the initial coordination number of aggregate. Figure 3.5 shows the model results obtained from Eq.(3.4) by least-squares fitting method. The data employed in the fitting are limit from the initial value to the constant region. The model is able to describe the simulation results for all aggregate whose initial structure varies from loose to dense and even in the case that the restructuring is partially affected by breakup. Therefore, the restructuring of non-fractal aggregates can be explained by the proposed mechanism. Furthermore, the stable state of aggregate is considered dynamic equilibrium obtained when the formation rate and the disintegration rate are equal.

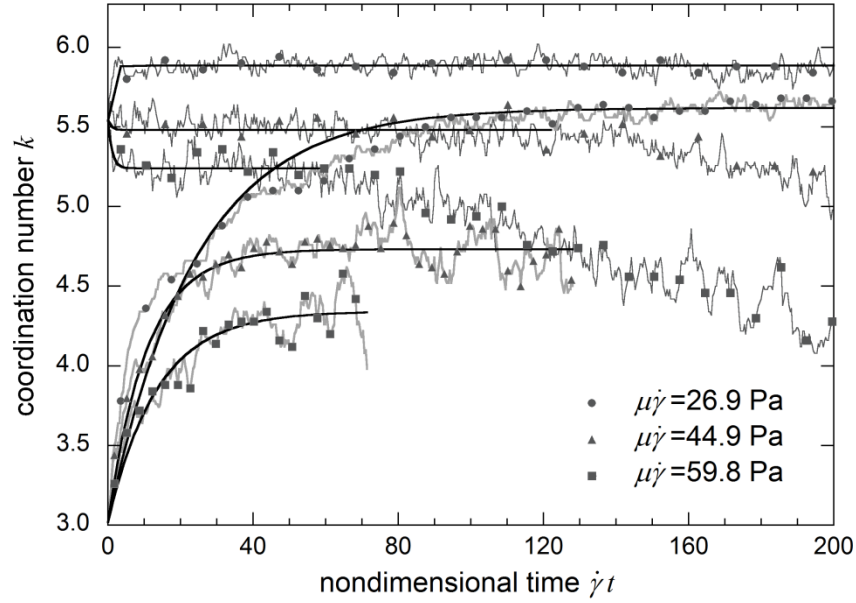


Figure 3.5 Change in coordination number with nondimensional time by simulation results and model results for the initial aggregate of $k_0 = 2.00$ and $k_0 = 5.54$ at different fluid shear rate.

3.5 Conclusion

Numerical simulation on the dynamics of non-fractal aggregate shows that the restructuring has occurred due to the nature of simple shear flow. The connectivity of the aggregate changes until a stable structure is obtained. In most of the case, the aggregate is apt to have a more compact structure, excepting for the case of very dense aggregate in high fluid shear condition. Both the fluid shear stress and initial configuration of aggregate affects the restructuring behavior. The restructuring of aggregate can be explained by a kinetic model based on the formation and disintegration of the links between particles.

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Chapter 4 Restructuring capability of non-fractal aggregate in simple shear flow

The content of this chapter focuses on establishing a comprehensive approach to predict the corresponding structure of a given aggregate in simple shear flow. In order to obtain a general relation for restructuring, several considerations on the uniqueness of stable aggregates, the limit of restructuring, and the physical meaning of the restructuring are analyzed.

4.1 Reversibility of stable aggregate

The limit aggregate (*i.e.* the stable structure of aggregate obtained in weak flow) perhaps is a special case because it is not dependent on the condition of flow. In this part, how the initial aggregate and limit aggregate affecting the restructuring is put into consideration. Figure 4.1 shows how the initial aggregate (for the case $k_0 = 2.00, 5.54$) and its limit aggregate affect the stable structure at $\mu\dot{\gamma} = 26.9$ Pa.

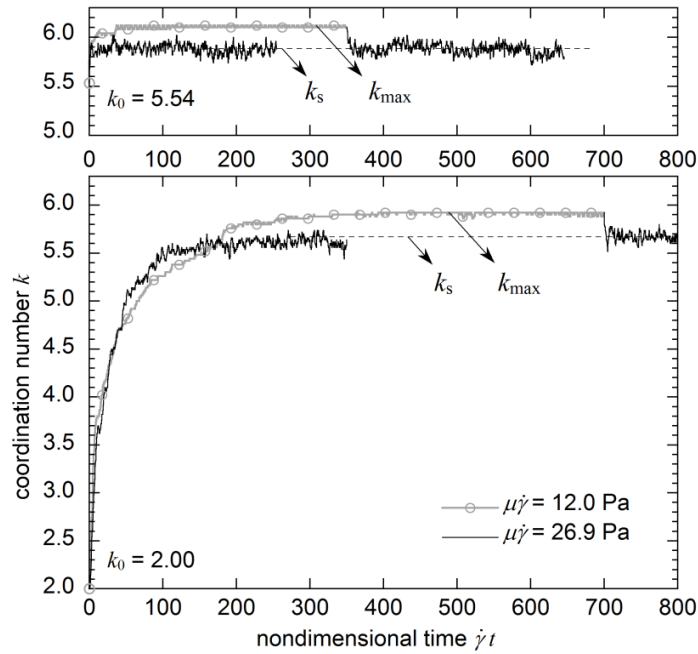


Figure 4.1 Coordination number profile for restructuring of initial aggregate k_0 and limit aggregate $k_{\max}$ at the same shear flow condition $\mu\dot{\gamma} = 26.9$ Pa.

As given in Figure 4.1, for fluid shear condition $\mu\dot{\gamma} = 26.9$ Pa, the initial aggregate k_0 restructures to its stable state k_s . Additionally, in the case of weak flow $\mu\dot{\gamma} = 12.0$ Pa, the aggregate with k_0 gradually obtains the limit structure $k_{\max}$. Such corresponding $k_{\max}$ aggregate is then subjected to a stronger flow condition $\mu\dot{\gamma} = 26.9$ Pa, and the new stable structure is observed. It reveals that the limit aggregates at $k_{\max}$ restructures again to a new stable coordination number similar to the value k_s at which the initial aggregate k_0 directly achieves in strong fluid flow condition $\mu\dot{\gamma} = 26.9$ Pa. This kind of behavior is met for both the very loose aggregate $k_0 = 2.00$ and the very dense aggregate $k_0 = 5.54$. The results indicate that maybe there is a mutual relation between the initial aggregate and the limit aggregate obtained in weak flow, and the limit aggregate possibly plays a role in the restructuring of aggregate. Therefore, study on the properties of limit aggregate can provide important information for the prediction of restructuring of aggregate.

4.2 Characteristics of limit aggregate

As mentioned in Chapter 3 (see Figure 3.4), under the low regime of fluid shear stress $\mu\dot{\gamma}$, the limit aggregate is obtained, and the stable coordination number shows constant values $k_{\max}$. In detail, for the dense aggregates with $k_0 = 5.54$ and $k_0 = 5.04$, the coordination numbers of limit structure is $k_{\max} \approx 6.10$ which is the highest value in all investigated conditions, whereas the aggregates with $k_0 = 4.20, 3.02, 2.00$ obtain the slightly lower value at $k_{\max} \approx 5.95$. However there is still uncertainties about the small difference of $k_{\max}$. In this section, analysis on the properties of the limit aggregate obtained in the condition of weak flow is performed in terms of volume fraction. Two different scales on the volume fraction are considered. The local volume fraction of each particle composing the aggregate is determined by Voronoi tessellation. The other approach is from the point of view of a global scale.

4.2.1 Local volume fraction by Voronoi tessellation

In order to explain such a difference of stable coordination number in low shear stress, the volume fraction of aggregate is investigated from a local viewpoint of each particle. The particle volume fraction is defined as the ratio of the particle's volume to its Voronoi cell [1]. Figure 4.2 presents the volume fraction of particles along the distance from the aggregate's centroid, for initial aggregate and limit aggregate.

The trend of the data along the radius of aggregate is similar in all cases, which is illustrated by the relatively uniform volume fraction at the inner part, and the dramatic decrease values at the outer part that more exposes to the surrounding fluid. Here only the data from the inner part of the aggregate are taken into account. The dense aggregates with $k_0 = 5.54$ and $k_0 = 5.04$ exhibit that the volume fraction is almost identical between the stable state and initial state whose volume fraction is around the value of random close packed structure. On the other hand, the aggregates in the case $k_0 \leq 4.20$ show that, the stable state is

more compact than the initial one, but not as compact as the aforementioned dense aggregate. These results may cast some light on the restructuring mechanism. In particular, for the dense aggregates, the particles are trapped among their neighbors, and move restrictively within the existed void during restructuring. Therefore, the structure of the dense aggregate can be considered static equilibrium . In opposite, the initial volume fraction of the loose aggregates with $k_0 \leq 4.20$ suggests kind of unstable structure. Under the external shear stress, the particles restructure, form more connections, and the aggregate eventually becomes more compact with time. As the volume fraction increases, the void among the particle also reduces, leading to the inability of particles to explore the space around them. The state that the particles are no more capable of occupying their surrounding space is regarded as quasi-stable whose volume fraction is lower than that of random close packing [2]. In conclusion, the results of Figure 4.2 reveal that the dependence of stable structure on initial coordination number originated from the irreversible transition from quasi-stable structure to static-equilibrium, which also explains the small gap of k_s shown in Figure 3.4 when shear stress is low (see Section 3.3).

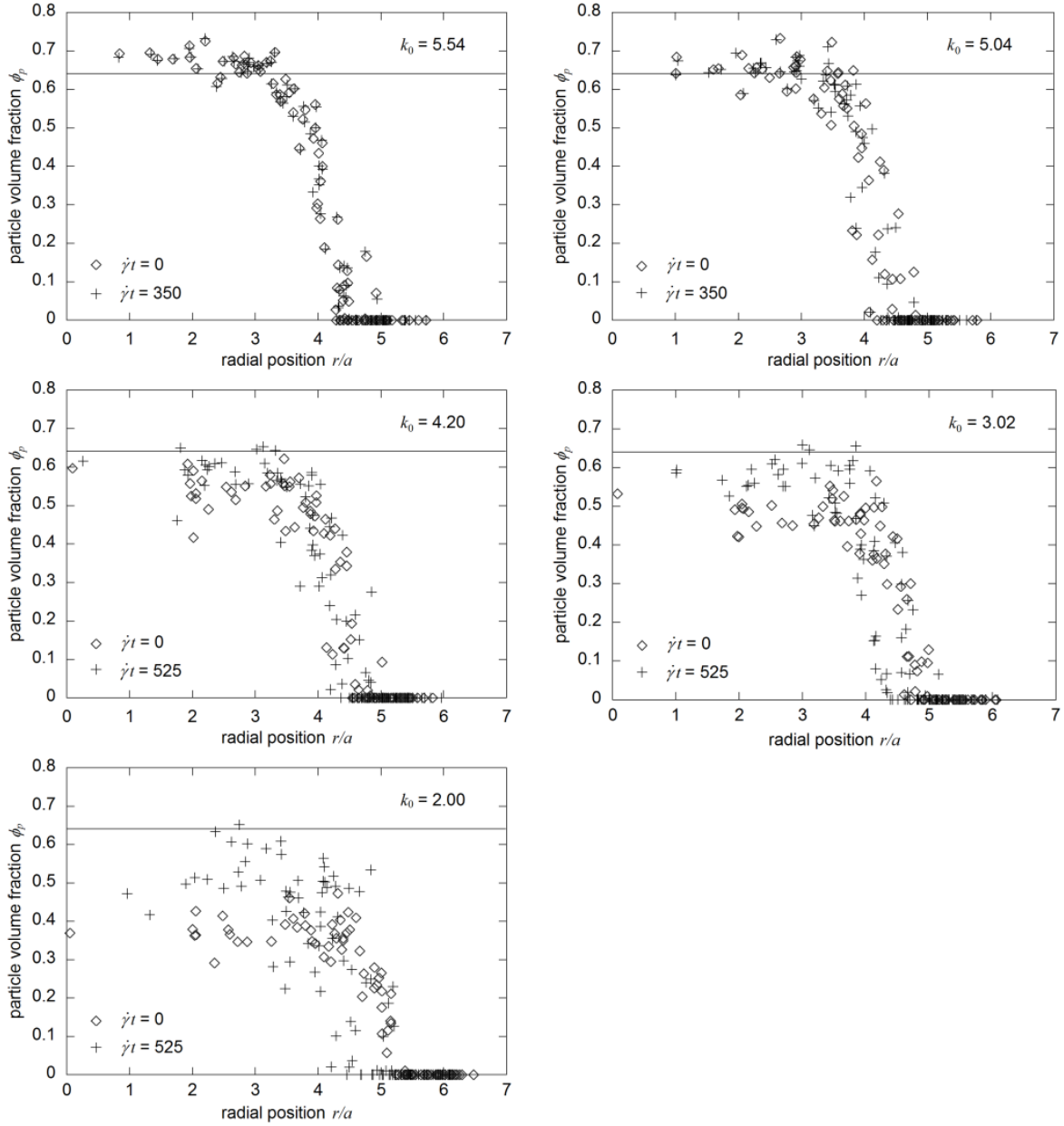


Figure 4.2 Radial distribution of particle volume fraction at initial structure and stable structure of aggregates at condition $\mu\dot{\gamma} = 12.0$ Pa.

4.2.2 Effective volume fraction

The use of local volume fraction by Voronoi tessellation provides very detail information. However, the calculation program of Voronoi tessellation in this study has two main restrictions: (i) it is unable to correctly calculate for the outside particles, and (ii) it is not suitable to calculate for dynamic data. Therefore, the other approach which is free from such restrictions considered. The effective volume fraction, which is averagely calculated for the whole aggregate, is employed. The effective volume

fraction ϕ of aggregate is the ratio of volume of all particles to the volume occupied by aggregate, which is considered as an ellipsoid having the same principal moment of inertia [3]. Readers may refer to Appendix C for the detailed calculation.

Figure 4.3 shows the temporal change in coordination number and volume fraction for the aggregate $k_0 = 3.02$ at some fluid shear stress values. The inset shows the data for weak flow $\mu\dot{\gamma} = 12.0$ Pa. The horizontal line indicates the properties of the limit aggregate obtained at $\mu\dot{\gamma} = 12.0$ Pa: coordination number $k_{\max}$ and volume fraction $\phi_{\max}$. The coordination number and volume fraction of aggregate are determined when the aggregate still keeps a spherical or ellipsoidal shape, because when the shape of aggregate is irregular and toward breakup, the fitting ellipsoid is no longer suitable to describe the occupied space of the aggregate, which can be observed in Figure 4.3. It is worth to note that the volume fraction is determined at each time step totally similar to the coordination number. The volume fraction profile is quite smooth, whereas the coordination number one is sharply fluctuated. This is because the later is directly determined from each particle of the aggregate, which reflects the connectivity at a local scale. On the other hand, fitting the aggregate by the equivalent ellipsoid involves the global characteristic. Consequently, the temporal change in volume fraction is more gradual and less abrupt than that of coordination number.

As can be seen in Figure 4.3, during the restructuring of aggregate, the behavior of volume fraction is quite similar to coordination number in two aspects: the approach to a stable value, and the dependence on fluid flow. The result suggests that there is a correlation between the coordination number and the volume fraction during the restructuring of the non-fractal aggregates. However, this correlation, as shown in Figure 4.3, seems complicated because there are many affecting factors such as fluid shear rate and initial configuration of the aggregate. From the well-known relation between coordination number and the porosity of packing of uniform lead spheres determined by Smith [4] in Eq.(4.1), such approach is applied for the case of restructuring of aggregate. However, the value of $k(1-\phi)$ during restructuring of aggregate is not a constant value (the results are not shown here). Maybe different packing technique, and the sample size are the main reason causing the complex relation between k and ϕ [5,6]. On that account, another perspective should be examined (section 4.3).

$$k(1-\phi) \cong 3.1 \cong \pi \quad (4.1)$$

It is found out that the limit structure of aggregate in weak flow also has highest volume fraction $\phi_{\max}$. Table 4.1 gives the properties of aggregate at the weak flow condition $\mu\dot{\gamma} = 12.0$ Pa. The data shows that for the limit structure of the aggregate, the difference of volume fraction $\phi_{\max}$ ($\phi_{\max} \approx 0.50-0.66$) is more significant than that of coordination number $k_{\max}$ ($k_{\max} \approx 5.90-6.10$). In other words, the effect of initial aggregate on limit aggregate is clearly expresses by $\phi_{\max}$ rather than $k_{\max}$. The reason explaining such the case that the aggregate has quite similar coordination number ($k_{\max} \approx 5.90-6.10$) but different volume fraction ($\phi_{\max} \approx 0.50-0.66$) possibly originates from the spatial arrangement of the particles. The

coordination number describes the connectivity of particles quantitatively, yet the distribution of such connectivity cannot be expressed. It is possible that the volume fraction partly reflects how the particles arrange.

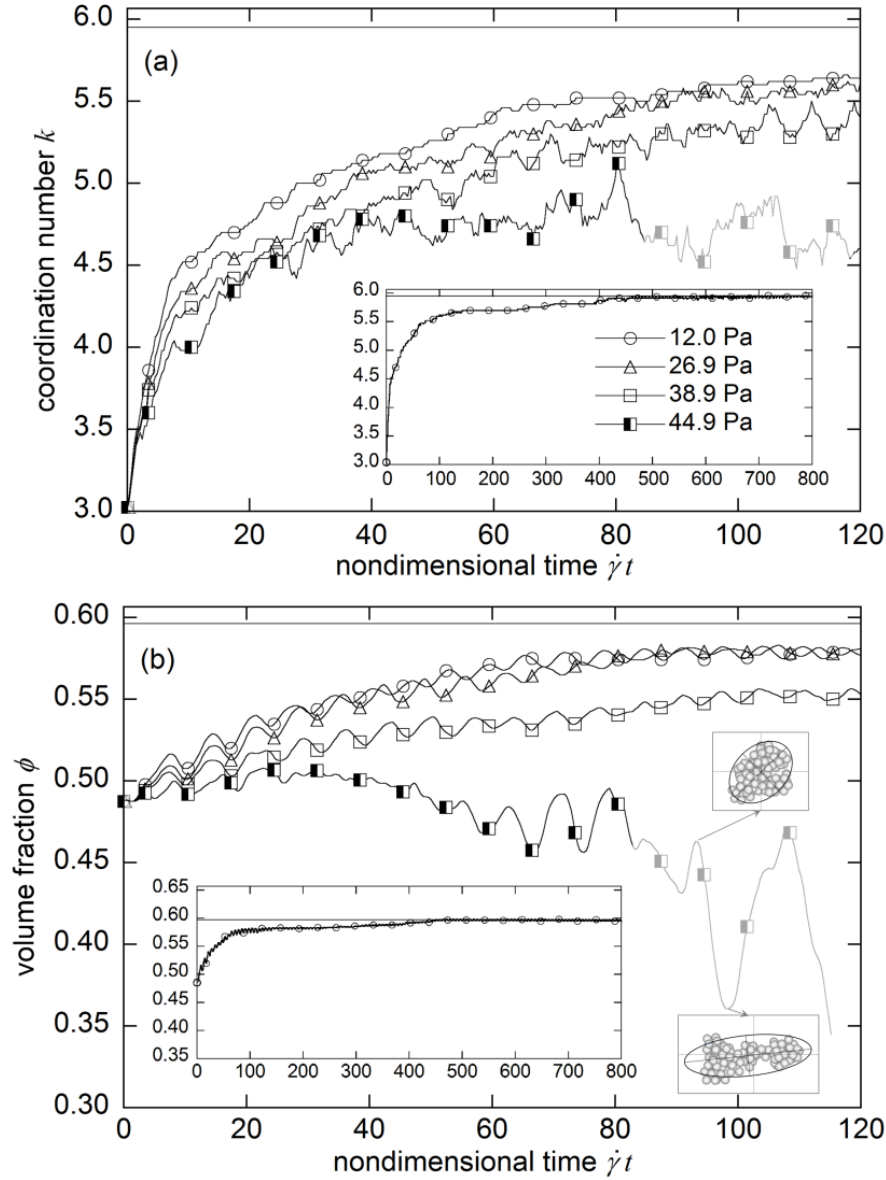


Figure 4.3 Change in (a) coordination number k and (b) volume fraction ϕ at various shear flow conditions for the aggregate with $k_0 = 3.02$. The horizontal line shows the value of $k_{\max}$ and $\phi_{\max}$ for this aggregate. The blurred profile shows the irregular change of aggregate toward breakup. The irregular aggregate and its equivalent ellipsoid when the aggregate is toward breakup are also given. Legends in (a) and (b) have the same meaning.

Table 4.1 Typical properties of limit aggregate obtain at weak flow condition $\mu\dot{\gamma} = 12.0$ Pa.

k_0	ϕ_0	$k_{\max}$	$\phi_{\max}$
2.00, fractal	0.054	5.90	0.500
2.00	0.371	5.92	0.516
2.50	0.438	5.94	0.570
3.02	0.488	5.96	0.596
3.98	0.534	5.90	0.590
4.20	0.559	5.92	0.602
4.80	0.618	5.95	0.628
5.04	0.654	6.09	0.658
5.54	0.665	6.10	0.666

The other issue is the dependence of $\phi_{\max}$ on the initial configuration of aggregate. As can be seen in Table 4.1, aggregate of smaller ϕ_0 results in smaller $\phi_{\max}$. Moreover, by conducting similar simulation for the other non-fractal aggregates (number of particle $N = 100$), the $\phi_{\max}$ is somewhat typical value depending on the initial one. Such typical $\phi_{\max}$ is about $\phi_{\max} \approx 0.52$ for initial aggregate of very loose structure (even including the fractal aggregate with number of particles $N = 100$ particles and fractal dimension $d_f = 1.8$), $\phi_{\max} \approx 0.59$ for moderate loose one. The dense aggregate does not vary $\phi_{\max}$ so much compared to ϕ_0 . Limit structure of the fractal aggregate is in agreement with Seto *et al.* (2012) [7], where they reports that the fractal aggregate restructures to a more compact spherical or rod structure whose volume fraction is about 0.48-0.54, similar to $\phi_{\max} \approx 0.50$ in the study. The dependence of $\phi_{\max}$ on ϕ_0 is unclear. It may relate to the mobility of the particle during the restructuring of aggregate. Interestingly, the range of $\phi_{\max}$ in this study ($\phi_{\max} \approx 0.50$ -0.66) is similar to the volume fraction of jammed packing of identical hard spheres, which is in the range of 0.52-0.74 [8]. In conclusion, the properties of the limit aggregate, $k_{\max}$ and $\phi_{\max}$ show some inherent characteristics related to the restructuring of aggregate within the investigated conditions of this study.

4.3 Physical relation of connection capability and strength of aggregate in restructuring

As mentioned elsewhere, the temporal coordination number and volume fraction of aggregate are dependent on the shear flow condition (see Figure 3.1, Figure 3.3, Figure 4.3). Moreover, the limit aggregates obtained in weak shear condition have kind of inherent characteristics for the restructuring of the aggregate. In order to find a physical interpretation of restructuring of aggregate, two parameters are introduced. Firstly, the ratio of the number of unlinked particle to linked particle, defined as $(k_{\max} - k)/k$, where $k_{\max}$ are taken from Table 4.1, is considered. This ratio roughly indicates the saturation degree of the internal connectivity, or the capability of forming connection among particles. As the non-negative

value $(k_{\max} - k)/k$ approaches zero, k more approaches $k_{\max}$, *i.e.* the particles are more saturated and less capable of rearranging their relative position. Secondly, according the famous Rumpf's theory [9], the value $(k\phi)^{-1}$ representing the inversed strength of aggregate is given as the following equation

$$\sigma_{\text{Rumpf}} = \frac{9F}{8\pi d^2} k\phi \propto k\phi \quad (4.2)$$

where σ_{Rumpf} is the tensile strength of aggregate, F the maximal attractive force between two particle, d the diameter of particle, ϕ the volume fraction of aggregate. The value of the proportional factor $9F/(8\pi d^2)$ is approximately 220 Pa according to the conditions of this study. Since k and ϕ change during the restructuring of aggregate, $(k_{\max} - k)/k$ and $1/k\phi$ are also functions of nondimensional time. Then instead of observing the temporal change in k and ϕ , and the dependence on fluid flow field $\mu\dot{\gamma}$, the saturation degree of internal connectivity $(k_{\max} - k)/k$ and the inversed strength of aggregate $(k\phi)^{-1}$ during the restructuring of aggregate are calculated. Figure 4.4 shows the relation of $(k_{\max} - k)/k$ and $(k\phi)^{-1}$ during the restructuring of aggregate at various shear stress $\mu\dot{\gamma}$ for different initial aggregate from loose ($k_0 = 2.00$) to dense ($k_0 = 5.54$).

In detail, Figure 4.4 presents the result for aggregate $k_0 = 3.02$. Such data in Figure 4.4b are calculated from the data in Figure 4.3. While Figure 4.3 shows that the dependence of k and ϕ on nondimensional time $\dot{\gamma}t$ and fluid shear stress $\mu\dot{\gamma}$ is complicated and unpredictable, Figure 4.4b reveals a very simple representation of restructuring process from the initial structure toward the stable one in terms of $(k_{\max} - k)/k$ and $(k\phi)^{-1}$: a linear trend. Such a linear trend is observed for all investigated aggregates in the study. For the case of loose aggregate ($k_0 = 2.00, 3.02, 4.20$), Figure 4.4a-c indicates that there is a shift from the initial value toward smaller ones when the restructuring of aggregate occurs, *i.e.* the aggregate gradually develops more internal connection and increases its strength until a stable structure is reached. The position of stable point depends on the flow field and is not clearly shown. The discussion about the stable states will be examined later. As for the very dense aggregate ($k_0 = 5.04, 5.54$), Figure 4.4d-e reveals that aside from the aforementioned behavior, the aggregate is able to shift from initial position outward the origin of the graph when the flow is strong enough. It means that the dense aggregate can becomes loose, but still maintain a specific relation between the internal connection and strength of aggregate. Generally, during the restructuring of given aggregate, the parameter $(k_{\max} - k)/k$ and $(k\phi)^{-1}$ show a trend of linear relation related regardless the condition of shear flow. It further suggests that if the limit structure (*i.e.* the aggregate in weak flow, whose position in Figure 4.4 is the intersection with horizontal axis) of a given aggregate is known, the restructuring behavior in terms of saturation degree and inversed strength of aggregate is possible to be determined.

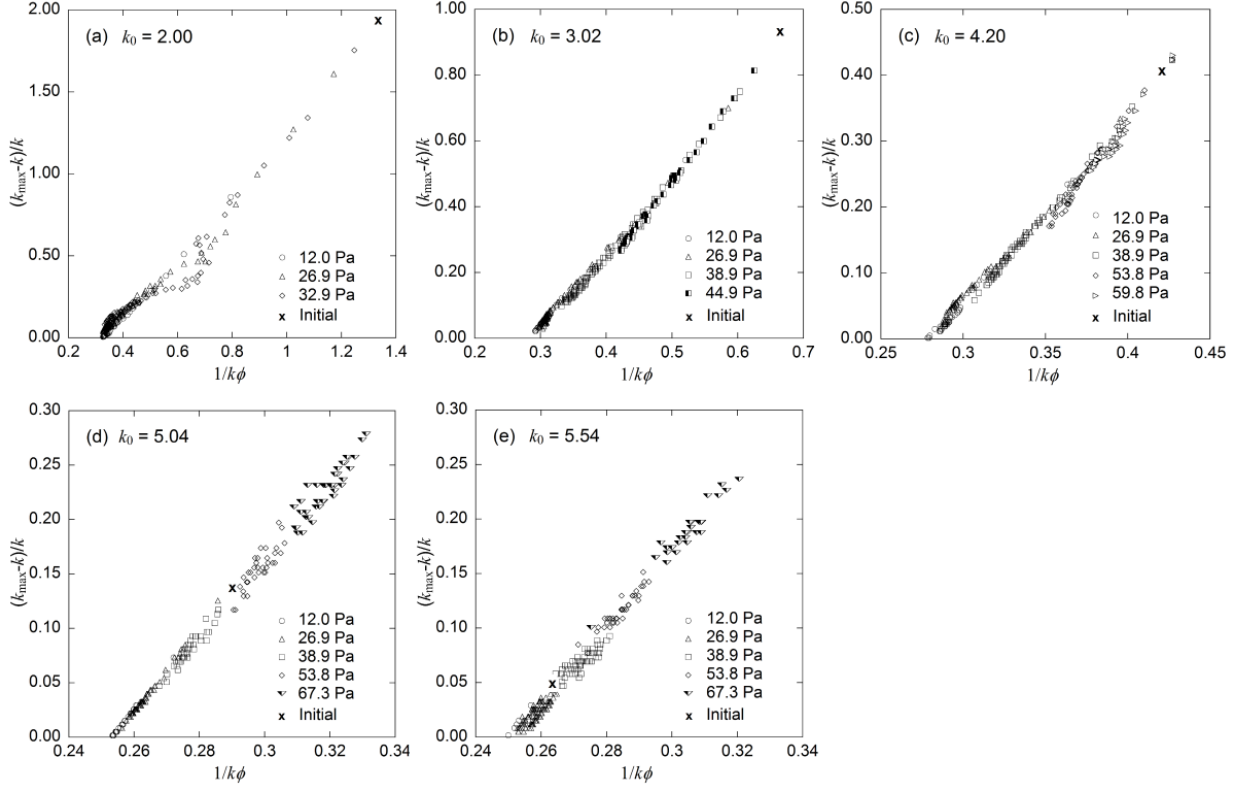


Figure 4.4 Relation of the saturation degree $(k_{\max} - k)/k$ and inversed strength of aggregate $(k\phi)^{-1}$ during the restructuring from initial structure toward stable structure in various shear conditions.

4.4 Scaling law for the stable structure of aggregate

The aim of this section is to investigate the final structure of an aggregate corresponding to a given fluid flow condition. About the restructuring of a given aggregate characterized by initial coordination number k_0 , it has been previously shown in Chapter 3 that the aggregate restructure to a stable state k_s corresponding to the applied fluid flow condition $\mu\dot{\gamma}$; especially in low shear rate region, k_s reaches its maximal value defined as $k_{\max}$. Figure 4.4, which relates the saturation degree of connection among particles $(k_{\max} - k)/k$ to the inversed strength of aggregate $(k\phi)^{-1}$, expresses how these properties change when the aggregate restructures from the initial configuration to the stable one, is insufficient to provide the corresponding stable structure for fluid shear stress $\mu\dot{\gamma}$. It is noted that in Figure 4.4, the represented position of stable structure, whose coordinates for horizontal axis and vertical axis are $1/k_s\phi_s$ and $(k_{\max} - k_s)/k_s$, respectively, belongs to the linear trend. By similar approach to Figure 4.4, scaling for the final state of a restructured aggregate is performed.

The properties of aggregate at stable structures corresponding to flow conditions is analyzed based on the simulation results of the restructuring of aggregates in simple shear flow. At each applied shear stress $\mu\dot{\gamma}$, the saturation degree of stable aggregate regarding the ratio of unlinked particle to linked particle

$(k_{\max} - k_s)/k_s$ is determined. In other words, for each given aggregate k_0 , the saturation degree at stable state $(k_{\max} - k_s)/k_s$ is dependent on $\mu\dot{\gamma}$. As for the fluid shear stress condition $\mu\dot{\gamma}$, it is rescaled with the strength of aggregate at limit structure, *i.e.* $\mu\dot{\gamma}/k_{\max}\phi_{\max}$. Physical image of such scaling is that, instead of applying $\mu\dot{\gamma}$ directly to the initial aggregate, the aggregate is firstly put in weak flow condition so that a limit structure is achieved, then the weak flow is switched to $\mu\dot{\gamma}$. As a result, $\mu\dot{\gamma}/k_{\max}\phi_{\max}$ inherently indicates the restructuring of the limit aggregate $k_{\max}$, rather than k_0 , in the fluid flow $\mu\dot{\gamma}$. Readers may refer to Figure 4.1 for a clearer illustration. Figure 4.5 expresses the relation of $(k_{\max} - k_s)/k_s$ and $\mu\dot{\gamma}/k_{\max}\phi_{\max}$ for many aggregates.

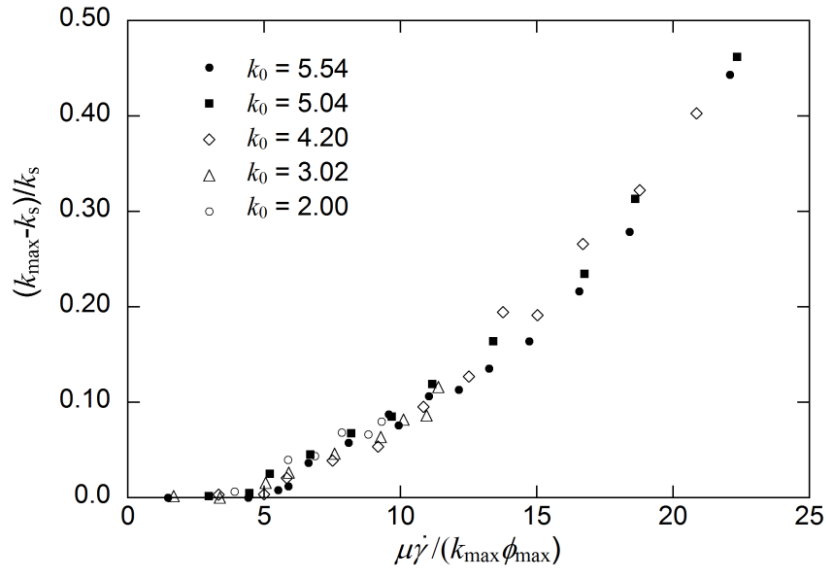


Figure 4.5 Relation of stable structure of aggregate with fluid shear stress $\mu\dot{\gamma}$ and the limit structure $k_{\max}\phi_{\max}$.

It reveals that when the fluid shear stress is scaled with the strength of the limit aggregate, the saturation degree $(k_{\max} - k_s)/k_s$ seems to collapse to one curve and independent of the initial structure of aggregate. Figure 4.5 also shows that $(k_{\max} - k_s)/k_s$ increases with $\mu\dot{\gamma}/k_{\max}\phi_{\max}$, meaning that if shear flow is stronger, the aggregate is more loose and weaker compared to the limit structure. In conclusion, if the limit structure of the aggregate is taken into account, the properties of stable aggregate in simple shear flow is possible to be predicted.

Furthermore, it is found out that the value of $(k_{\max} - k_s)/k_s$ in Figure 4.5 has some relation to kinetics of restructuring. The proposed kinetic model of the restructuring and its verification can be found in Section 3.4. The model describes the temporal change in coordination number during the restructuring of aggregate. The core of the model is analogous to micromechanics of granular material. The change rate of

coordination number $dk/d(\dot{\gamma}t)$ comprises of two parallel components: (i) forming rate which is proportional to the number of unlinked particles, *i.e.* the available space around particle, defined as $C^+(k_{\max} - k)$, and (ii) cut rate which is proportional to the number of linked particles, defined as C^-k . In the model, C^+ and C^- are proportional coefficients, determined by least-square method from the simulation data, represent the likeliness of forming and cutting of a link, respectively. From the model, when the stable structure of aggregate is obtained, the formation rate and the cut rate of particle is equal, leading to $C^-/C^+ = (k_{\max} - k_s)/k_s$. By considering the proposed kinetic model, the relation of kinetic coefficients and the dynamic property of the aggregate is able to be established. Figure 4.5 which exhibits the saturation degree of stable aggregate $(k_{\max} - k_s)/k_s$ not only helps to predict the properties of stable aggregate in the corresponding fluid condition, but also provides information for the kinetics. In detail, the value of $(k_{\max} - k_s)/k_s$ can be classified into two parts: $(k_{\max} - k_s)/k_s \rightarrow 0$ and $(k_{\max} - k_s)/k_s > 0$. When $\mu\dot{\gamma}/k_{\max}\phi_{\max} \leq 5$, Figure 4.5 shows $(k_{\max} - k_s)/k_s \rightarrow 0$, or $C^-/C^+ \rightarrow 0$, which can be interpreted as $C^- \rightarrow 0$ while $C^+ \neq 0$. It means that when the aggregate restructure from k_0 to $k_{\max}$ in weak flow, the weak flow induces the connection of particles but is not strong enough to break the link once it is made. When limit aggregate $k_{\max}$ is obtained in weak flow, the flow has no effect on aggregate except for the rotation. Otherwise, when the flow is strong enough $\mu\dot{\gamma}/k_{\max}\phi_{\max} > 5$, then C^-/C^+ increases, the cutting of links between particle starts to dominate, consequently, the stable aggregate at this region has less connection than the limit aggregate ($k_s < k_{\max}$).

4.5 Conclusion

The capability of restructuring of non-fractal aggregate in simple shear flow is numerically performed. At low fluid shear conditions, the restructuring of aggregate is no longer dependent on the fluid shear stress. The stable structure in such cases, which is called limit structure, seems to be typically determined based on the initial configuration and have kind of inherent characteristic for the restructuring of aggregate. When the limit structure of the aggregate is taken into account, a linear relation between the saturation degree and the inverse strength of aggregate during restructuring can be determined. Moreover, the corresponding structure of aggregate in fluid shear flow is established by scaling law.

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Chapter 5 Criteria for the restructuring of non-fractal aggregate in simple shear flow

In this chapter, criteria for restructuring of non-fractal aggregate in simple shear flow are investigated by considering the hydrodynamic stress acting on aggregate by fluid, and the cohesive strength of the aggregate. The method proposed by Adler and Mills (1979) [1] for breakup of aggregate is modified then applied for the restructuring. In detail, the effect of aggregate structure on the penetration of fluid flow is examined.

5.1 Introduction

The behavior of aggregate suspending in a fluid medium is mainly based on the information of the hydrodynamic stress acting on aggregate by fluid and the strength of aggregate. There have been several studies attempting to establish the criteria for breakup of aggregate, usually as a function of aggregate size and fluid shear stress [bagster, adler, Sonntag, vanni]. They determine the distribution of hydrodynamic stress of aggregate and then compared with the cohesive strength of aggregate to decide the breakup occurs or not. Several kinds of assumption on aggregate structure have been made, for example, aggregate is an impermeable sphere [2], uniformly porous sphere [3], non-uniformly porous sphere [4]. Recently, numerical simulation method is possible to calculate the distribution of hydrodynamic stress of an aggregate composing of several primary particles without any assumption on the aggregate structure [5]. Compared to breakup criteria, the restructuring criteria are still lacking of understanding because the dynamics of restructuring is much more complex. In this study, the criteria for the restructuring of non-fractal aggregate is conducted in a similar manner with the breakup of porous sphere proposed by Adler and Mills [1]

5.2 Theory

The aggregate is analyzed in a similar manner with the analytical method for predicting the breakup of aggregate proposed by Adler and Mills [1]. They consider that the aggregate is a uniformly porous sphere, the breakup of aggregate is fast, and deformation of aggregate is negligibly small. The hydrodynamics inside and outside the sphere is governed by continuity, Stokes equation and Brinkman

equation. The velocity field induces effect on the internal stress of the porous sphere. Because the porous medium does not deform, the relation of velocity field and the solid stress tensor $\boldsymbol{\sigma}$ of the porous sphere can be analytically obtained. Then the breakup of the porous sphere is predicted by the solid stress tensor $\boldsymbol{\sigma}$ and the strength of the porous medium S . As the Mises yield condition is applied, the criterion for the sphere not to breakup is defined as Eq.(5.1).

$$\boldsymbol{\sigma}_D : \boldsymbol{\sigma}_D \leq 2S^2 \quad (5.1)$$

where $\boldsymbol{\sigma}_D$ is the deviatoric part of the solid stress tensor $\boldsymbol{\sigma}$. In the case of simple shear flow, the equivalent form of Eq.(5.1) can be rewritten as

$$\left(\frac{\mu \dot{\gamma}}{S} \right)_{\text{Break}} \leq f_{\min}(R, \kappa, p, \mathbf{r}) \quad (5.2)$$

In Eq.(5.2), f depends only on the properties of the porous sphere, including the radius R of the sphere, the permeability κ , Poisson ratio p of the porous medium, and the position $\mathbf{r}$ inside the sphere in the spherical coordinate (Figure 5.1). For a given porous sphere, f varies with the position $\mathbf{r}$ inside the sphere. Choosing the position $\mathbf{r}$ to minimize f is required for the use of the breakup criterion in Eq.(5.2). Details of the calculation are given in Appendix D. The function $f(R, \kappa, p, \mathbf{r})$ can be roughly interpreted as the penetration effect of flow field on the resulting stress acting on the porous sphere, and it directly related to the hydrodynamic stress acting by fluid on the porous sphere. The above relation means that for a porous sphere whose properties are known, a critical fluid shear stress for the breakup can be specified. The breakup event in the model is assumed instant, *i.e.*, parts of sphere detach without changing their structure.

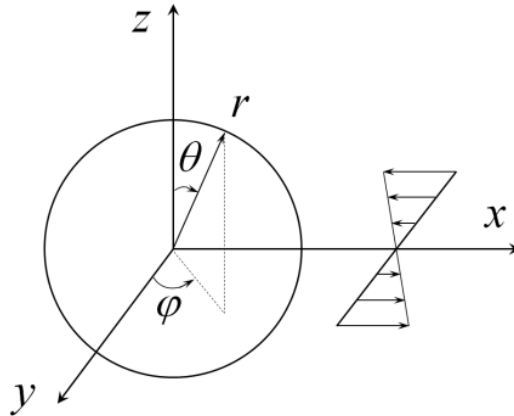


Figure 5.1 Spherical coordinate system for porous sphere model [1].

5.3 Evaluation of the penetration of fluid flow for the restructuring of non-fractal aggregate

In this study, it has been shown that at weak flow condition the aggregate exist in the form of limit structures (shown by the constant region $k_{\max}$ of Figure 3.4, or $(k_{\max} - k_s)/k_s \approx 0$ region in Figure 4.5). Such limit aggregate are spherical, and rotate like a rigid body, therefore it is suitable to consider the aggregate as a porous sphere. If the flow is stronger, the aggregate restructures from the limit structure toward another one whose connectivity is less connected than $k_{\max}$. Differ from Adler and Mills [1] where the criterion are used between the rigid-like behavior and breakup, here the model for the rigid-like behavior and restructuring is applied. The criterion is similar to Eq.(5.2) and given as

$$\frac{\mu\dot{\gamma}}{\sigma_{\text{Res}}} \leq f_{\min}(R, \kappa, p, r) \quad (5.3)$$

where σ_{Res} is characteristic restructuring strength of aggregate, the value of $f_{\min}$ shows the influence of aggregate properties, e.g. size, permeability, on the resulting hydrodynamic stress acting on the aggregate as mentioned above. Assuming that the limit aggregate is a porous sphere whose permeability is based on Happel's formula [5]:

$$\kappa = \frac{2}{9} \frac{a^2}{\phi} \frac{3 - \frac{9}{2}\phi^{\frac{1}{3}} + \frac{9}{2}\phi^{\frac{5}{3}} - 3\phi^2}{3 + 2\phi^{\frac{5}{3}}} \quad (5.4)$$

where a is the radius of particle, ϕ is the volume fraction of aggregate. Then $f_{\min}$ is numerically calculated for various values of $R/\sqrt{\kappa}$ which physically represent the screened radius of the aggregate or, in other words, the size of aggregate compared to the size of the pore (Appendix D). Figure 5.2 shows the dependence of $f_{\min}$ on $R/\sqrt{\kappa}$ for $p = 0$. It is reported that there is no significant difference for $0 \leq p \leq 0.25$.

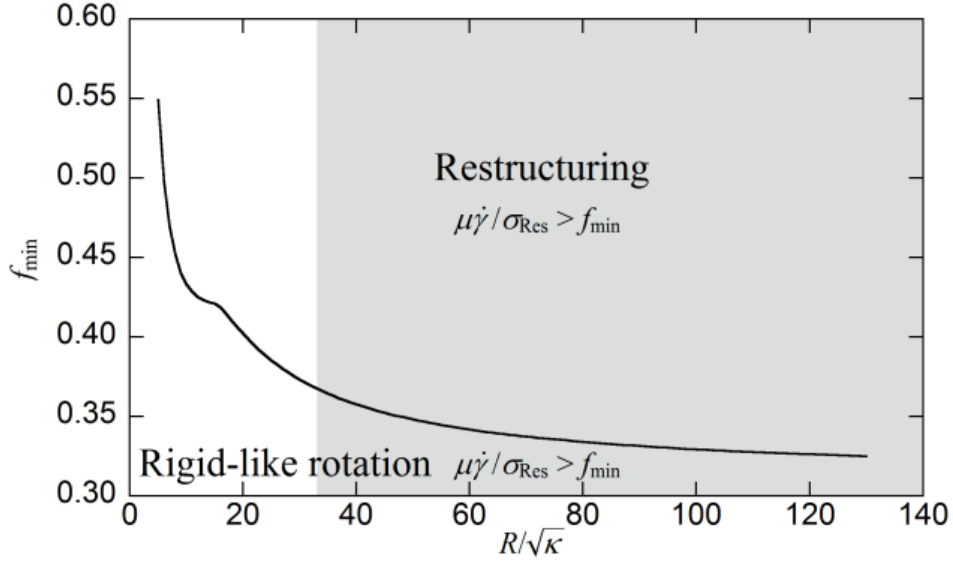


Figure 5.2 Restructuring regime of aggregate as a function of screened radius of aggregate. $f_{\min}$ is determined by porous sphere model [1]. The gray area shows the restructuring regime for the investigated conditions in this study.

In general, the decrease in $f_{\min}$ with $R/\sqrt{\kappa}$ means that the fluid flow is more difficult to penetrate the more dense aggregate. As a result, the resulting hydrodynamic stress acting on the dense aggregate is higher than that on loose aggregate. Moreover, according to Eq.(5.3), two regions are determined in Figure 5.2: above and below the curve. The region below the curve indicates the conditions that when the applied fluid shear stress $\mu\dot{\gamma}$ and the restructuring strength of aggregate σ_{Res} satisfy $\mu\dot{\gamma}/\sigma_{\text{Res}} \leq f_{\min}$, then the aggregate behaves like a rigid body. The region above the curve denotes the case $\mu\dot{\gamma}/\sigma_{\text{Res}} > f_{\min}$ where the aggregate undergoes restructuring. As for the investigated condition in this study, the restructuring regime falls in the gray area. Table 5.1 provides the data for the initial aggregate and the limit aggregate obtained in weak flow $\mu\dot{\gamma} = 12.0$ Pa. In this gray part, $f_{\min}$ does not significantly vary, *i.e.*, the effect of structure of aggregate on the penetration of fluid flow plays a minor role. It is suggested that when construct a model describing the restructuring of non-fractal aggregate based on the hydrodynamic stress and strength of aggregate, the parameter describing the influence of structure on hydrodynamic stress can be considered to be simplified, the model should focus on the effect of the strength of aggregate.

Based on the above result, the criteria for restructuring of aggregate are put into consideration. The so-called restructuring strength σ_{Res} for the limit aggregate is calculated. Assuming that the restructuring strength is proportional to tensile strength of aggregate $\sigma_{\text{Res}} = \alpha\sigma_{\text{Rumpf}}$, then the ratio of restructuring strength to tensile strength, is determined in the range of $\alpha \approx 1/14$ - $1/20$ (Table 5.1). It is reasonable when the restructuring strength is smaller than the tensile strength [4]. The result can be used for developing a restructuring model for non-fractal aggregate. Moreover, the relation of restructuring strength and tensile

strength may further reveal a way to couple the restructuring and breakup of aggregate in particulate suspension.

Table 5.1 Properties of initial aggregate and limit aggregate obtained at weak flow condition using porous sphere model. The assumed Poisson ratio is $p = 0$, the value of $\mu\dot{\gamma}^*$ is determined from Figure 3.4.

Initial structure						Limit structure at weak flow condition							
k_0	ϕ_0	R_0/a	$\kappa_0/a^2 \times 10^3$	$R_0/\sqrt{\kappa_0}$	$f_{\min}$	$\mu\dot{\gamma}^*$	$k_{\max}$	$\phi_{\max}$	R/a	$\kappa/a^2 \times 10^3$	$R/\sqrt{\kappa}$	$f_{\min}$	α
2.00	0.371	6.46	38.2	33.1	0.368	12	5.92	0.516	5.79	10.1	57.7	0.343	19.4
3.02	0.488	5.90	13.1	51.5	0.347	16	5.96	0.596	5.52	4.54	81.9	0.334	16.4
4.20	0.559	5.63	6.62	69.2	0.338	16	5.92	0.602	5.50	4.26	84.2	0.333	16.5
5.04	0.654	5.35	2.40	109.1	0.328	20	6.09	0.658	5.34	2.30	111.4	0.328	14.6
5.54	0.665	5.32	2.11	115.7	0.327	20	6.10	0.666	5.32	2.09	116.3	0.327	14.8

5.4 Conclusion

The effect of penetration of fluid on non-fractal aggregate is analytically examined based on the porous sphere model [1]. The structure of the aggregate shows minor influence to the resulted fluid stress acting on it. In other words, at the same condition of shear flow, the restructuring of non-fractal aggregate is mostly contributed from the strength of aggregate.

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Chapter 6 Conclusions

The restructuring behavior of non-fractal aggregate is numerically studied by Stokesian dynamics approach. The effect of initial structure of aggregate and intensity of simple shear flow is investigated.

Under the effect of rotation component and deformation component of simple shear flow, the aggregate rotates and deforms. The restructuring of aggregate exhibits via the change in either shape or coordination number which represents the internal connectivity of the particles. The stability of the aggregate is revealed by evolution of coordination number toward a stable value corresponding to fluid shear condition. Especially in the weak flow, the restructuring of aggregate reaches its limit in compacting the aggregate to highly randomly connected structure. Comparing to effect of shear flow, the initial configuration of aggregate has slight influence on the stable coordination number. Kinetic model based on the instantaneous formation and cut of the link between aggregate is able to describe the restructuring of aggregate.

Although the restructuring with time is an irreversible process, the transition among stable aggregate shows certain degree of reversibility. The structure of the limit aggregate, which is stable aggregate obtained at weak flow condition, seems to have inherent characteristics for the restructuring of aggregate in various conditions of shear flow. When the strength of aggregate at the limit structure is taken into account, the behavior of the non-fractal aggregate in shear flow is possible to obtain. Moreover, a linear relation between the saturation degree of connectivity and the inversed strength of aggregate is established. Such relation is able to provide insight information for the final state of aggregate and how the final state is acquired.

The structure of non-fractal aggregate affects the hydrodynamic stress and the strength of aggregate, which are the two factors deciding how the aggregate responds in flow. By employing the porous sphere model, it reveals that within the range of investigation conditions, the structure of aggregate has little influence on the penetration of fluid flow on aggregate, while the strength of aggregate is more prominent to be affected by aggregate structure. Criteria for restructuring of aggregate based on tensile strength are examined.

Appendices

Appendix A. Calculation of the mobility matrix (Durlafsky *et al.*, 1987)

For a system of monosized, finite spherical particles in unbounded fluid field, the grand mobility matrix, which relates the relative velocity of the particle to fluid, to the external force acting on the particle $\alpha, \beta, \dots$ is shown in the following equation

$$\begin{pmatrix} U_\alpha - u^\infty(x^\alpha) \\ U_\beta - u^\infty(x^\beta) \\ \vdots \\ \Omega_\alpha - \Omega^\infty \\ \Omega_\beta - \Omega^\infty \\ \vdots \\ -E^\infty \\ -E^\infty \\ \vdots \end{pmatrix} = \begin{pmatrix} \mathbf{a}_{\alpha\alpha} \mathbf{a}_{\alpha\beta} \dots & \tilde{\mathbf{b}}_{\alpha\alpha} \tilde{\mathbf{b}}_{\alpha\beta} \dots & \tilde{\mathbf{g}}_{\alpha\alpha} \tilde{\mathbf{g}}_{\alpha\beta} \dots \\ \mathbf{a}_{\beta\alpha} \mathbf{a}_{\beta\beta} \dots & \tilde{\mathbf{b}}_{\beta\alpha} \tilde{\mathbf{b}}_{\beta\beta} \dots & \tilde{\mathbf{g}}_{\beta\alpha} \tilde{\mathbf{g}}_{\beta\beta} \dots \\ \vdots & \vdots & \vdots \\ \mathbf{b}_{\alpha\alpha} \mathbf{b}_{\alpha\beta} \dots & \mathbf{c}_{\alpha\alpha} \mathbf{c}_{\alpha\beta} \dots & \tilde{\mathbf{h}}_{\alpha\alpha} \tilde{\mathbf{h}}_{\alpha\beta} \dots \\ \mathbf{b}_{\beta\alpha} \mathbf{b}_{\beta\beta} \dots & \mathbf{c}_{\beta\alpha} \mathbf{c}_{\beta\beta} \dots & \tilde{\mathbf{h}}_{\beta\alpha} \tilde{\mathbf{h}}_{\beta\beta} \dots \\ \vdots & \vdots & \vdots \\ \mathbf{g}_{\alpha\alpha} \mathbf{g}_{\alpha\beta} \dots & \mathbf{h}_{\alpha\alpha} \mathbf{h}_{\alpha\beta} \dots & \mathbf{m}_{\alpha\alpha} \mathbf{m}_{\alpha\beta} \dots \\ \mathbf{g}_{\beta\alpha} \mathbf{g}_{\beta\beta} \dots & \mathbf{h}_{\beta\alpha} \mathbf{h}_{\beta\beta} \dots & \mathbf{m}_{\beta\alpha} \mathbf{m}_{\beta\beta} \dots \\ \vdots & \vdots & \vdots \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}_\alpha \\ \mathbf{F}_\beta \\ \vdots \\ \mathbf{T}_\alpha \\ \mathbf{T}_\beta \\ \vdots \\ \mathbf{S}_\alpha \\ \mathbf{S}_\beta \\ \vdots \end{pmatrix} \quad (\text{A1})$$

Each term $\mathbf{a}, \mathbf{b}, \dots$ in mobility matrix is dependent only on the location of the center of particle. The set of (A2) and (A3) shows the details of the calculation for each term. Einstein notation is employed for convenience.

$$\left. \begin{aligned} \mathbf{a}_{ij}^{\alpha\beta} &= x_{\alpha\beta}^a e_i e_j + y_{\alpha\beta}^a (\delta_{ij} - e_i e_j) \\ \mathbf{b}_{ij}^{\alpha\beta} &= y_{\alpha\beta}^b \varepsilon_{ijk} e_k \\ \mathbf{c}_{ij}^{\alpha\beta} &= x_{\alpha\beta}^c e_i e_j + y_{\alpha\beta}^c (\delta_{ij} - e_i e_j) \\ \mathbf{g}_{ijk}^{\alpha\beta} &= x_{\alpha\beta}^g (e_i e_j - \frac{1}{3} \delta_{ij}) e_k + y_{\alpha\beta}^g (e_i \delta_{jk} + e_j \delta_{ik} - 2e_i e_j e_k) \\ \mathbf{h}_{ijk}^{\alpha\beta} &= y_{\alpha\beta}^h (e_i \varepsilon_{ijk} e_l + e_j \varepsilon_{ikl} e_l) \\ \mathbf{m}_{ijkl}^{\alpha\beta} &= \frac{3}{2} x_{\alpha\beta}^m (e_i e_j - \frac{1}{3} \delta_{ij}) (e_k e_l - \frac{1}{3} \delta_{kl}) \\ &\quad + \frac{1}{2} y_{\alpha\beta}^m (e_i \delta_{jl} e_k + e_j \delta_{il} e_k + e_i \delta_{jk} e_l + e_j \delta_{ik} e_l - 4e_i e_j e_k e_l) \\ &\quad + \frac{1}{2} z_{\alpha\beta}^m (\delta_{ik} \delta_{jl} + \delta_{jk} \delta_{il} - \delta_{ij} \delta_{kl} + e_i e_j \delta_{kl} + \delta_{ij} e_k e_l \\ &\quad + e_i e_j e_k e_l - e_i \delta_{jl} e_k - e_j \delta_{il} e_k - e_i \delta_{jk} e_l - e_j \delta_{ik} e_l) \end{aligned} \right\} \quad (\text{A2})$$

$$\left. \begin{aligned}
x_{11}^a &= x_{22}^a = 1, & x_{12}^a &= x_{21}^a = \frac{3}{2}r^{-1} - r^{-3}, \\
y_{11}^a &= y_{22}^a = 1, & y_{12}^a &= y_{21}^a = \frac{3}{4}r^{-1} - \frac{1}{2}r^{-3}, \\
y_{11}^b &= -y_{22}^b = 0, & y_{12}^b &= -y_{21}^b = -\frac{3}{4}r^{-2}, \\
x_{11}^c &= x_{22}^c = \frac{3}{4}, & x_{12}^c &= x_{21}^c = \frac{3}{4}r^{-3}, \\
y_{11}^c &= y_{22}^c = \frac{3}{4}, & y_{12}^c &= y_{21}^c = -\frac{3}{8}r^{-3}, \\
x_{11}^g &= -x_{22}^g = 0, & x_{12}^g &= -x_{21}^g = \frac{9}{4}r^{-2} - \frac{18}{5}r^{-4}, \\
y_{11}^g &= -y_{22}^g = 0, & y_{12}^g &= -y_{21}^g = \frac{6}{5}r^{-4}, \\
y_{11}^h &= y_{22}^h = 0, & y_{12}^h &= y_{21}^h = -\frac{9}{8}r^{-3}, \\
x_{11}^m &= x_{22}^m = \frac{9}{10}, & x_{12}^m &= x_{21}^m = \frac{9}{2}r^{-3} - \frac{54}{5}r^{-5}, \\
y_{11}^m &= y_{22}^m = \frac{9}{10}, & y_{12}^m &= y_{21}^m = \frac{9}{4}r^{-3} - \frac{36}{5}r^{-5}, \\
z_{11}^m &= z_{22}^m = \frac{9}{10}, & z_{12}^m &= z_{21}^m = \frac{9}{5}r^{-5}.
\end{aligned} \right\} \quad (\text{A3})$$

Appendix B. The effect of particle surface separation on the coordination number

The restructuring of a very loose aggregate in a fluid shear stress of $\mu\dot{\gamma} = 26.9$ Pa is considered. The temporal change in coordination number of the aggregate is determined. The condition for the designated particle surface distance for particle connection varies from 1 nm to 10 nm. As shown in Figure B1, the coordination number profile is almost similar when the distance is 1.5-10 nm. In the case of 1nm, the result is different because the van der Waals interaction is cut off if the surface distance is less than 1 nm. Therefore, except for the value less than or equal 1.0 nm, the other choice of surface distance of a few nm is possible to represent the connection between the particles.

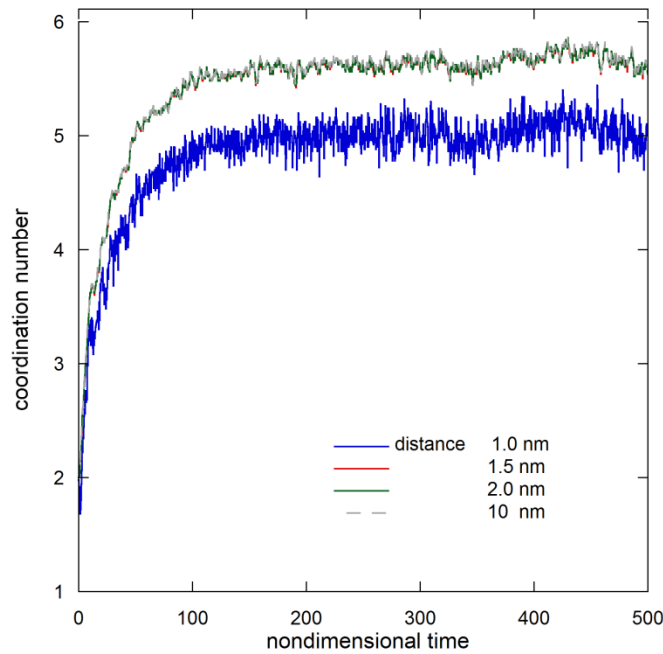


Figure B1 Average coordination of an aggregate ($k_0 = 2.0$ when the surface distance is 2 nm) in fluid shear stress $\mu\dot{\gamma} = 26.9$ Pa for different condition of particle surface distance.

Appendix C. Calculation of effective volume fraction of aggregate by equivalent ellipsoid

The aggregate is considered to be equivalent of an ellipsoid which has the same principal of moment of inertia. The inertia tensor $\mathbf{I}$ of the aggregate is calculated as follows

$$\mathbf{I} = \begin{bmatrix} \sum_{i=1}^N [(y_i - y_c)^2 + (z_i - z_c)^2] & -\sum_{i=1}^N (x_i - x_c)(y_i - y_c) & -\sum_{i=1}^N (x_i - x_c)(z_i - z_c) \\ -\sum_{i=1}^N (x_i - x_c)(y_i - y_c) & \sum_{i=1}^N [(x_i - x_c)^2 + (z_i - z_c)^2] & -\sum_{i=1}^N (y_i - y_c)(z_i - z_c) \\ -\sum_{i=1}^N (x_i - x_c)(z_i - z_c) & -\sum_{i=1}^N (y_i - y_c)(z_i - z_c) & \sum_{i=1}^N [(x_i - x_c)^2 + (y_i - y_c)^2] \end{bmatrix} \quad (\text{C1})$$

where x_c, y_c, z_c are the coordinates of the center of mass of aggregate composed of N particle, x_i, y_i, z_i the coordinates of the i th particle in the aggregate. The eigenvalues I_1, I_2, I_3 of the eigenvectors determined from the inertia tensor $\mathbf{I}$ are the three principal moment of inertia. The length of the semi-principal axis of the equivalent ellipsoid is given by the followed equations.

$$a_1 = \sqrt{\frac{5}{2} \frac{I_2 + I_3 - I_1}{N}}, \quad a_2 = \sqrt{\frac{5}{2} \frac{I_1 + I_3 - I_2}{N}}, \quad a_3 = \sqrt{\frac{5}{2} \frac{I_1 + I_2 - I_3}{N}} \quad (\text{C2})$$

The volume fraction of the aggregate, which is the ratio of the total volume of particles to the volume of the equivalent ellipsoid, is straightforwardly given as

$$\phi = \frac{N}{a_1 a_2 a_3} \quad (\text{C3})$$

Appendix D. Porous sphere model by Adler and Mills (1979)

The porous sphere model proposed by Adler and Mills (1979) is able to calculate the hydrodynamic stress acting on a position inside the non-deformable porous sphere. The calculation is performed in spherical coordinates for an arbitrary position $\mathbf{r}(r, \theta, \varphi)$ inside the porous sphere of radius R . The nondimensional radius is employed, defined as

$$\xi = \frac{r}{\sqrt{\kappa}} \quad (\text{D1})$$

$$\xi_1 = \frac{R}{\sqrt{\kappa}} \quad (\text{D2})$$

The value of the right hand side of Eq.(5.2) is calculated as following

$$f = \frac{\sqrt{2}}{5} \frac{10\hat{\psi}_2 + \hat{\psi}_0}{\sqrt{A}} \quad (\text{D3})$$

The ξ -dependent function ψ_n and the ξ_1 -dependent function $\hat{\psi}_n$ are denoted as

$$\psi_n = \psi_n(\xi) = \left(\frac{1}{\xi} \cdot \frac{d}{d\xi} \right)^n \frac{\sinh \xi}{\xi} \quad (\text{D4})$$

$$\hat{\psi}_n = \psi_n(\xi_1) \quad (\text{D5})$$

The value of A is determined as follows

$$\begin{aligned} A = & 2 \left[I + \frac{1}{2} U \hat{\psi}_2 (\xi_1^2 - 3\xi^2) - F \hat{\psi}_2 \right]^2 + \xi^2 \sin^2 \theta \left[J \left(\frac{J}{2} + \frac{2I}{\xi} \right) \right. \\ & \left. + U \hat{\psi}_2 \left(4I + J \frac{\xi_1^2 - \xi^2}{\xi} \right) + 2U^2 \hat{\psi}_2 (\xi_1^2 - 2\xi^2) - 4F \hat{\psi}_2 \left(\frac{J}{2\xi} + U \hat{\psi}_2 \right) \right] \\ & + 4\xi^4 \sin^4 \theta \cos^2 \varphi \sin^2 \varphi \times \left\{ (\psi_2 - 7\psi_3)^2 + \psi_3^2 + \frac{K^2}{2\xi^2} \right. \\ & \left. - \psi_4 (2I + J\xi + K\xi) + U \hat{\psi}_2 [2\psi_3 - 4\psi_4 U \hat{\psi}_2 (\xi_1^2 - \xi^2)] + \frac{2}{3} U_2 \hat{\psi}_2^2 + 2\psi_4 F \hat{\psi} \right\} \end{aligned} \quad (\text{D6})$$

The function I, J, K in the above equation is dependent on ξ and ξ_1

$$I = 2\hat{\psi}_2 - 2\psi_2 + \psi_1 \quad (\text{D7})$$

$$J = \xi(\psi_2 - 4\psi_3) \quad (\text{D8})$$

$$K = \xi(\psi_2 - 6\psi_3) \quad (\text{D9})$$

The parameters b , U , V and W express the property of the porous sphere via the screened radius ξ_1 and the Poisson's ratio p , denoted as

$$b = 1 - 8 \frac{\hat{\psi}_3}{\hat{\psi}_2} \quad (\text{D10})$$

$$U = \frac{1 + p - 3bp}{7 + 5p} \quad (\text{D11})$$

$$V = \frac{4 + 2p - b(7 - 4p)}{2(7 + 5p)} \quad (\text{D12})$$

$$W = \frac{6 + 4p - b(7 + 2p)}{2(7 + 5p)} - \frac{1}{\xi_1^2} \cdot \frac{5\hat{\psi}_1 - \hat{\psi}_0 - 20\hat{\psi}_2}{2\hat{\psi}_2} \quad (\text{D13})$$

Finally, F is defined as

$$F = \xi_1^2 \left(W + \frac{U}{2} \right) - \xi^2 \left(\frac{3U}{2} + V \right) \quad (\text{D14})$$

In general, for a given porous sphere whose properties are fixed, the value of f is only dependent on the position of the porous sphere. The extremes of f are numerically obtained by searching thorough the porous sphere.