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Geometrical Analysis of Particle System Dispersed in Liquid

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Abstract—It is well known the settling behavior of fine particles in liquid changes at a certain particle concentration. Particles, which settle independently, coagulate each other and make a clear interface over a certain concentration. The particle concentration affects the settling behavior as the gap between particles, which is a very important factor of particle-particle interaction. In this paper the average particle interval, distance to the closest particle and contact particle number on a specified particle is discussed geometrically in cases of a mono-size and multi-size particle system. And the collision free path of multi-size particles settling under the gravity is also discussed. The calculated results can interpret experimental results.

Key Words : Slurry, Suspension, Gelation, Particle concentration, Network structure

INTRODUCTION

The settling or sedimentation behavior of fine particles in liquid is strongly influenced of particle concentration. In dilute suspension particles settle independently, however, over certain concentration particle make a clear interface between suspension and supernatant during sedimentation. It is called zone settling. The making an interface is mainly controlled by particle size and density, particle interaction and concentration.

The particle interaction including particle size has been discussed in mainly colloid science field for a long time and it is now possible to analyze simple system quantitatively. In spite of that the particle interaction is a function of the gap between particles, the discussion about the gap seems to be few so far.

In general the particle distance is estimated from the cell volume which is calculated from the following equation.

$$\text{cell volume} = \frac{\text{volume of particle system}}{\text{particle number in the system}} . \quad (1)$$

If the cell is supposed as a sphere, the sphere diameter corresponds to the particle distance and if cubic, the side does. This approach is popular for example Tsubaki and Tien applied this approach to analyze granular moving bed filtration process. Suzuki *et al.*, discussed this approach for analysis of yielding phenomena of powder bed. The particle distance can be estimated easily from this approach, however, particles are separated at the same distance and never contact each other. This will be a disadvantage to analyze coagulation or gelation phenomena.

Chandrasekhar proposed the following equation to calculate the distance to the closest particle from the specified particle.

$$f(r^*)\,\mathrm{d}r^* = \left[1 - \int_1^{r^*} f(r^*)\,\mathrm{d}r^*\right] \cdot f_0(r^*)\,\mathrm{d}r^* , \quad (2)$$

where $f(r^*)\,\mathrm{d}r^*$ is the probability that the closest particle is in the spherical shell between r^* and $r^* + \mathrm{d}r^*$. The first term of the right side is the probability that only the specified particle is in the sphere of radius r^*. The second term is the probability that the closest particle is in the sphere of radius r^* and calculated from particle concentration and radial distribution function. As the radial distribution function is introduced, the particle distance has distribution. The problem of this approach is that particles can not exist in the spherical shell between $r^* = 1/2$ and 1. It is obvious geometrically that particle can not exist in the shell, however, particle can exist in the shell mathematically as many as the product of particle volume fraction and the shell volume.

In this paper it is supposed that particle can exist in the spherical shell between $r^* = 1/2$ and 1 as particles contacting on a specified particle. And the distance to the closest particle and contact particle number on a specified one is discussed geometrically in cases of a mono-size and multi-size particle system. And the collision free path of multi-size particles settling under the gravity is also discussed.

MODELING

In this paper the particle distance and interval are defined as shown in Fig. 1. The particle distance is the distance from the center to the center of two particles. The particle interval is the particle distance projected on a line, which runs through the particles. Every valuable having dimension of length is divided by particle size or the valuable is divided by the median particle size of a cumulative volume distribution if particles have size distribution.

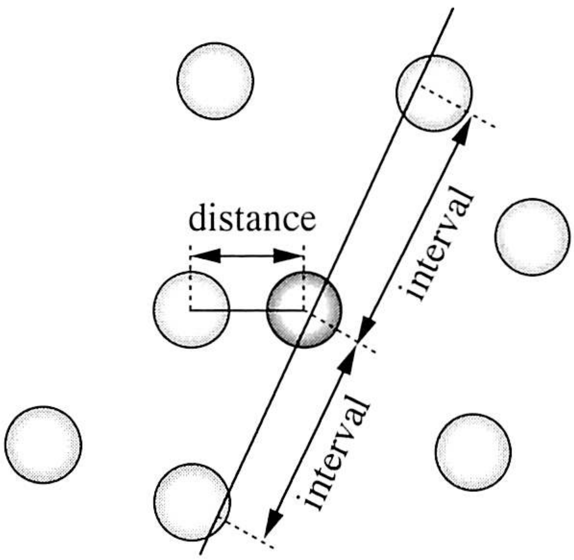

Fig. 1. Definition of particle distance and interval.

Mono-size particle system

The size of every particle is x and $x^* = 1$.

Particle interval

The average particle interval can be estimated from the fact that the length fraction on a line that runs through a particle system equal to the volume fraction of the particle system. If the average chord length $\overline{a^*}$ from a sphere of unit diameter is determined, the length fraction on a line can be calculated. The chord length a^* at radius r^* is the following equation as shown in Fig. 2.

$$a^* = \sin\theta . \tag{3}$$

The probability that a radius is between r^* and $r^* + \mathrm{d}r^*$ is

$$\frac{2\pi\, r^* \mathrm{d}r^*}{\pi\left(\frac{1}{2}\right)^2} = 8r^*\, \mathrm{d}r^* . \tag{4}$$

From Eqs. (3), (4) the average chord length $\overline{a^*}$ is

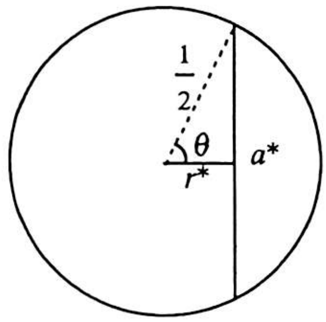

Fig. 2. A chord from a unit diameter sphere.

$$\overline{a^*} = \int_0^{1/2} \sin\theta \cdot 8r^*\, \mathrm{d}r^* . \tag{5}$$

Equation (5) can be calculated easily using $r^* = (\cos\theta)/2$. Finally $\overline{a^*}$ is

$$\overline{a^*} = \frac{2}{3} . \tag{6}$$

$\bar{a} = \frac{2}{3}x$

The average particle number N on a line of 1 m in a particle system is correlated to the volume fraction ϕ by the following equation.

$$\frac{\phi}{x} = \frac{2}{3} N . \tag{7}$$

And then the average particle interval is given by the following equation.

$$\overline{L^*} = \frac{1}{Nx} = \frac{2}{3\phi} . \tag{8}$$

Distance to the closest particle

Supposing a virtual shell consisted of a virtual sphere of radius r^* and a specified particle, the number m of particles in the shell can be calculated by the following equation.

$$\frac{4}{3}\pi\left(r^{*3} - \frac{1}{8}\right)\phi = m\frac{\pi}{6} . \tag{9}$$

If the radius where $m = 1$ is defined as the distance to the closest particle R_c^*, R_c^* is calculated from the Eq. (10).

$$R_c^* = \frac{1}{2}\left(\frac{1}{\phi} + 1\right)^{1/3} . \tag{10}$$

For comparison the distance to the closest particle of regular packing structures is calculated by the following equations. In case of cubic system the distance to the closest particle R_{cub}^* is

$$R^{\bullet}_{cub} = \left(\frac{\pi}{6\phi}\right)^{1/3}. \tag{11}$$

In case of body centered cubic system the distance to the closest particle $R^{\bullet}_{bcc}$ is half of the diagonal length of the unit cubic in [111] direction.

$$R^{\bullet}_{bcc} = \frac{\sqrt{3}}{2}\left(\frac{\pi}{3\phi}\right)^{1/3}. \tag{12}$$

In case of face centered cubic system the distance to the closest particle $R^{\bullet}_{fcc}$ is half of the diagonal length of the unit cubic in [110] direction.

$$R^{\bullet}_{fcc} = \frac{1}{\sqrt{2}}\left(\frac{2\pi}{3\phi}\right)^{1/3}. \tag{13}$$

Number of particles contacting on a specified particle

Supposing a virtual shell consisted of a specified particle and a sphere of $r^{\bullet} = 1$ as shown Fig. 3. And the number M_1 of first layer particles contacting on the specified particle can be presumed to be the particle number existing in the virtual shell. Substituting $r^{\bullet} = 1$ into Eq. (9),

$$M_1 = 7\phi \tag{14}$$

The number M_2 of the second layer particles contacting on the first layer particles is also calculated by the same way. Supposing a virtual shell consisted of a sphere of radius 1 and a first layer particle, the number M_2 of particles in the virtual shell could be calculated. Since the volume of the cross part formed by the two virtual shells in Fig. 3 is already considered for the first layer particle, the cross part volume should be subtracted for considering the second layer particles. In general the volume of a spherical crown of radius r is

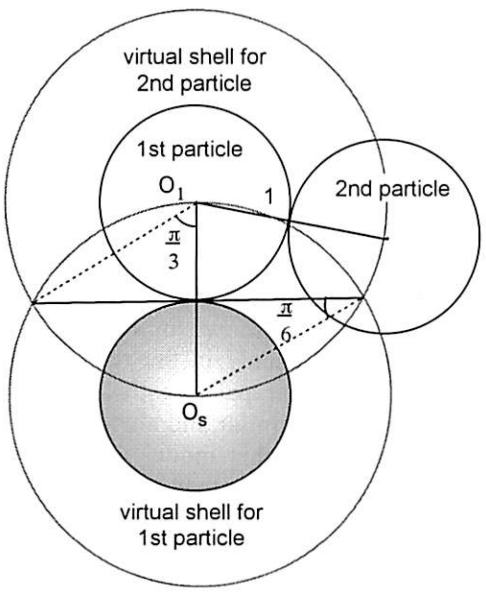

Fig. 3. Virtual spheres containing contact particles.

$$v = \frac{s}{4\pi r^2}\frac{4\pi r^3}{3} - \frac{\pi}{3}(r\sin\theta)^2 r\cos\theta, \tag{15}$$

where s is the surface area of the crown, and

$$s = \int_0^{\theta} 2\pi\, r\sin\theta \cdot r\mathrm{d}\theta = 2\pi\, r^2(1-\cos\theta). \tag{16}$$

Substituting Eq. (16) into Eq. (15),

$$v = \frac{\pi r^3}{3}\{2(1-\cos\theta) - \sin^2\theta\cos\theta\}. \tag{17}$$

Substituting $r = 1$, $\theta = \pi/3$ into Eq. (17), the space volume V_2 existing the second layer particles is

$$V_2 = \frac{4}{3}\pi - 2v = \frac{5}{4}\pi. \tag{18}$$

If the interaction between contacted particles can be neglected M_2 is given by the following equation.

$$M_2 = M_1\frac{V_2\phi}{\pi/6} = \frac{105}{2}\phi^2. \tag{19}$$

Multi-size particle system

Particle interval

The average chord length $\bar{a}$ from a sphere of diameter x is

$$\bar{a} = \frac{2}{3}x. \tag{20}$$

The number $\mathrm{d}N_m$ of spheres of diameter x on a 1 m line in a particle system is determined by the following equation.

$$\phi \cdot q_3(x)\,\mathrm{d}x = \bar{a}\cdot \mathrm{d}N_m. \tag{21}$$

The average particle interval is given by Eq. (22).

$$\overline{L_m} = \frac{1}{N_m} = \frac{2}{3\phi}\frac{1}{\int_0^{\infty}\frac{q_3(x)}{x}\mathrm{d}x}. \tag{22}$$

Equation (22) is divided by $x_{3,50}$ for reducing length dimension.

$$\overline{L^{\bullet}_m}\cdot\phi = \frac{2}{3}\frac{1}{\int_0^{\infty}\frac{q_3(x^{\bullet})\,\mathrm{d}x^{\bullet}}{x^{\bullet}}}. \tag{23}$$

Distance to the closest particle

Supposing a virtual shell in which one particle exists, the radius R_c is determined by Eq. (24) like the case of mono-size particle system.

$$\frac{4\pi}{3}\left(R_c^{\bullet 3} - \frac{d^{\bullet 3}}{8}\right)\int_0^\infty \frac{q_3(x^\bullet)\,\phi}{\frac{\pi}{6}x^{\bullet 3}}\,\mathrm{d}x^\bullet = 1. \tag{24}$$

The definite integral in Eq. (24) is the particle number in unit volume.

$$R_c^\bullet = \frac{1}{2}\left\{\frac{1}{\phi\int_0^\infty \frac{q_3(x^\bullet)}{x^{\bullet 3}}\,\mathrm{d}x^\bullet} + d^{\bullet 3}\right\}^{\frac{1}{3}}. \tag{25}$$

The average value of $R_c^\bullet$ is

$$\overline{R_c^\bullet} = \int_0^\infty R_c^\bullet q_0(d^\bullet)\,\mathrm{d}d^\bullet, \tag{26}$$

where $q_0(x)$ is a particle number density distribution.

Number of particles contacting on a specified particle

The contact number $\mathrm{d}M_{m1}$ of particle X on a specified particle D is given by Eq. (27).

$$\frac{\pi}{6}\left\{(x^\bullet + d^\bullet)^3 - d^{\bullet 3}\right\}\phi\, q_3(x^\bullet)\,\mathrm{d}x^\bullet = \frac{\pi}{6}x^{\bullet 3}\cdot \mathrm{d}M_{m1}. \tag{27}$$

The total number of particles contacting on a specified particle D is

$$M_{m1} = \phi\int_0^\infty \frac{(x^\bullet + d^\bullet)^3 - d^{\bullet 3}}{x^{\bullet 3}}\, q_3(x^\bullet)\,\mathrm{d}x^\bullet. \tag{28}$$

The average contact number $\overline{M}_{m1}$ is

$$\overline{M}_{m1} = \int_0^\infty M_{m1}\, q_0(d^\bullet)\,\mathrm{d}d^\bullet. \tag{29}$$

Collision free path

In multi-size particle system collision of particles due to the difference of settling velocity influences coagulation phenomena as much as particle distance. It is supposed that a specified particle D collides to particle X. The particle diameters and settling velocities are d, x and u_d, u_x, respectively. It is assumed that the settling velocity of particle X is zero and a specified particle D collides to particle X with velocity $|u_d - u_x|$. If a particle X exists in a cylinder of diameter $d + x$ of which center is the center of the particle D, the particle D can collide to the particle X. The height of the cylinder is $|u_d - u_x|t$, therefore the dimensions of the cylinder are depend on particle size x. The number $\mathrm{d}m$ of particle X existing in the cylinder in sedimentation time t is determined by the following equation.

$$\mathrm{d}m = |u_d - u_x|\, t\frac{\pi}{4}(d+x)^2 \frac{\phi\, q_3(x)\,\mathrm{d}x}{\frac{\pi}{6}x^3}. \tag{30}$$

The collision time t_c is determined as the time when the particle number becomes 1 in the cylinders.

$$\int_0^1 \mathrm{d}m = \phi\, t_c \int_0^\infty |u_d - u_x| \frac{3(d+x)^2}{2x^3} q_3(x)\,\mathrm{d}x. \tag{31}$$

The collision free path z of particle D is given by

$$z = u_d\, t_c. \tag{32}$$

The particle settling velocity is expressed by the following Richardson-Zaki's equation.

$$u_x = \frac{(\rho_p - \rho_f)\, g(1-\phi)^k}{18\mu} x^2. \tag{33}$$

Combining Eqs. (31), (32), and (33), the collision free path z of a particle having size d is

$$z = \frac{2d^2}{3\phi\int_0^\infty \frac{|d-x|(x+d)^3}{x^3} q_3(x)\,\mathrm{d}x}. \tag{34}$$

Consequently, the average collision free path in a multi-size particle system is calculated by the following equation.

$$\overline{z^\bullet} = \int_0^\infty z^\bullet q_0(d^\bullet)\,\mathrm{d}d^\bullet. \tag{35}$$

CALCULATION AND DISCUSSION

Mono-size particle system

Particle interval and distance to the closest particle

The particle interval and the distances to the closest particle calculated by Eq. (8) and Eqs. (10) - (13) respectively are shown in Fig. 4. The particle interval decreases keenly in the region of low concentration. In regular packing the distances to the closest particle are similar and always greater than 1. On the contrary, in this model the distance to the closest particle is shorter than those of regular packing and can be smaller than 1. That the distance to the closest particle is smaller than particle size means one or more particles contact on a specified particle in this model.

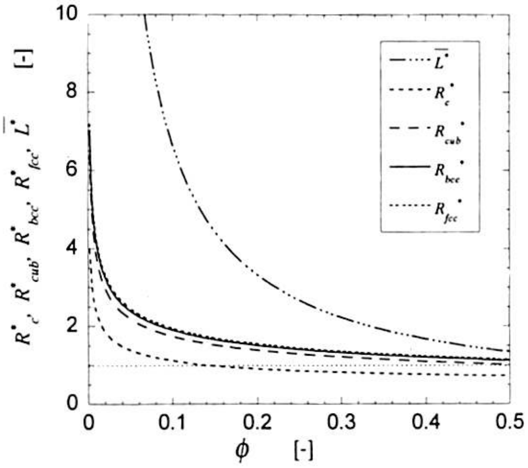

Fig. 4. Particle interval and distance to the closest particle in a mono-size particle system.

Number of particles contacting on a specified particle

The number of the first and second layer particles is calculated from Eqs. (14), (19) and the results are shown in Fig. 5 with the sum of them. If the average coordination number of a particle is bigger than 2, particles could make a three dimensional network structure. Figure 5 suggests that suspension have a possibility to make a network structure if the volume concentration exceeds about 10%.

Tsubaki *et al.* (1998), dispersing 0.48 μm alpha-alumina powder in aqueous solution of polyacrylic ammonium, measured the packing fraction of sediment settled in a centrifugal field by changing suspension concentration. The suspension of 5 vol% did not make a clear supernatant zone, on the contrary the 10 vol% suspension made a clear interface between supernatant and suspension. Making a network structure is determined by not only geometrical factor but also other factors, such as inter-particle interaction and particle collision due to settling velocity difference, however, this model could be strong tool to analyze coagulation phenomena.

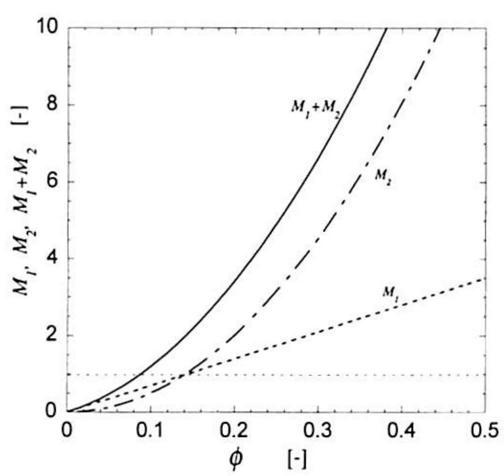

Fig. 5. Number of particles contacting on a specified particle in a mono-size particle system.

Multi-size particle system

A logarithmic normal distribution is supposed as the particle size distribution of a multi-size particle system. If a particle size is normalized by the median particle size of a cumulative volume distribution $x_{3,50}$, the distribution function is

$$q_3(\ln x^*) = \frac{1}{\sqrt{2\pi}\ln\sigma_g}\exp\left(-\frac{\ln^2 x^*}{2\ln^2\sigma_g}\right). \tag{36}$$

The calculation parameter is geometric standard deviation σ_g.

Particle interval

The particle interval and number on a 1 m-length line are calculated by Eqs. (21), (23) and shown in Fig. 6. The particle number increases and the particle interval decreases with σ_g.

Supposing 1 m^3 mono-size particle system of which particle size, volume concentration and particle number are $x_{3,50}$, ϕ, and n_0 respectively, the particle number ratio n/n_0 is given by

$$\frac{n}{n_0} = \int_0^\infty \frac{q_3(\ln x^*)}{x^{*3}}\,\mathrm{d}\ln x^*. \tag{37}$$

The particle number density distribution is determined by

$$q_0(x^*) = \frac{\dfrac{q_3(\ln x^*)}{x^{*3}}\,\mathrm{d}\ln x^*}{\displaystyle\int_0^\infty \frac{q_3(\ln x^*)}{x^{*3}}\,\mathrm{d}\ln x^*}. \tag{38}$$

The particle number distribution $n\,q_0(x^*)/n_0$ is shown in Fig. 7.

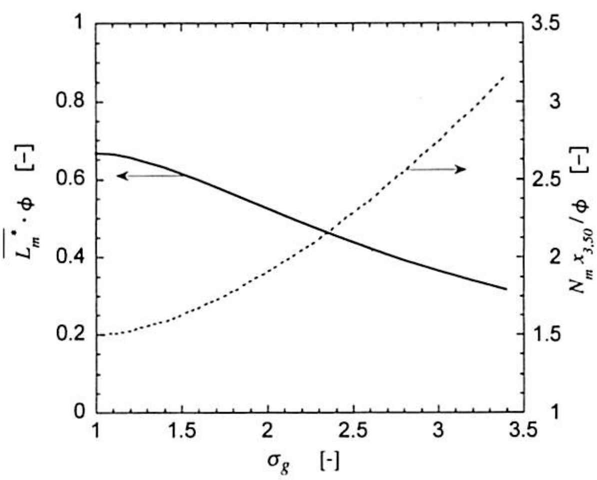

Fig. 6. Particle interval and number on a unit length line in a multi-size particle system.

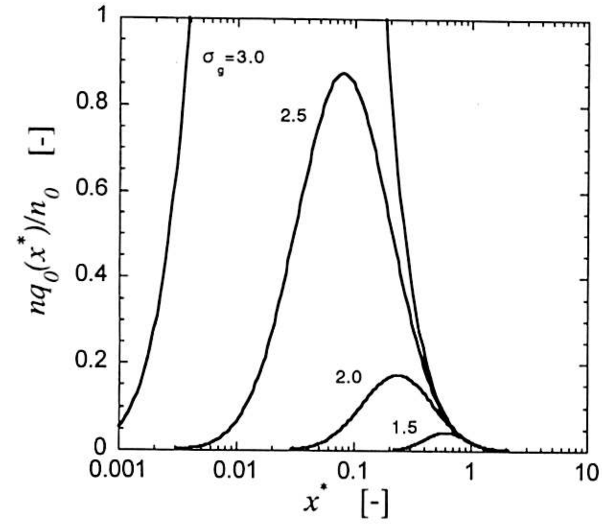

Fig. 7. Particle number distribution.

As shown Fig. 7 smaller particles increase with σ_g extremely. The increase of smaller particles decreases the particle interval and increases the particle number in Fig. 6.

Distance to the closest particle

The average distance to the closest particle is decreases with σ_g as shown Fig. 8(a). However, if the distance is reduced by $x_{0,50}$, the distance increases with σ_g because of the decreasing of $x_{0,50}$ as shown in Fig. 8(b). As the most particles are near $x_{0,50}$ in multi-size particle system, particles are relatively dispersed with σ_g.

Number of particles contacting on a specified particle

In case of $\sigma_g = 2.0$ the number of contacting particles on a specified particle M_{m1} is calculated by Eq. (28) as shown Fig. 9. The value of M_{m1} increases exponentially with specified particle diameter d^*, however, the number of particles bigger than 0.5 is negligible small as shown Fig. 9. From this reason the average contact number $\overline{M}_{m1}$ decreases with σ_g as shown Fig. 10.

It can be said from Fig. 8(b) and Fig. 10 that particles are more dispersed and few contacting to the other particles in a multi-size particle system having a wider distribution.

Collision free path

The collision free path z^* of a specified particle having diameter d^* was calculated by Eq. (34) and the examples are shown in Fig. 11. As σ_g increases, z^* decreases and the peaks of the z^* distributions sift to fine size in Fig. 11. The average collision free path $\overline{z^*}$ in a multi-size particle system calculated by Eq. (35) is shown in Fig. 12. The value of $\overline{z^*}$ decreases keenly and then semi-logarithmically with σ_g.

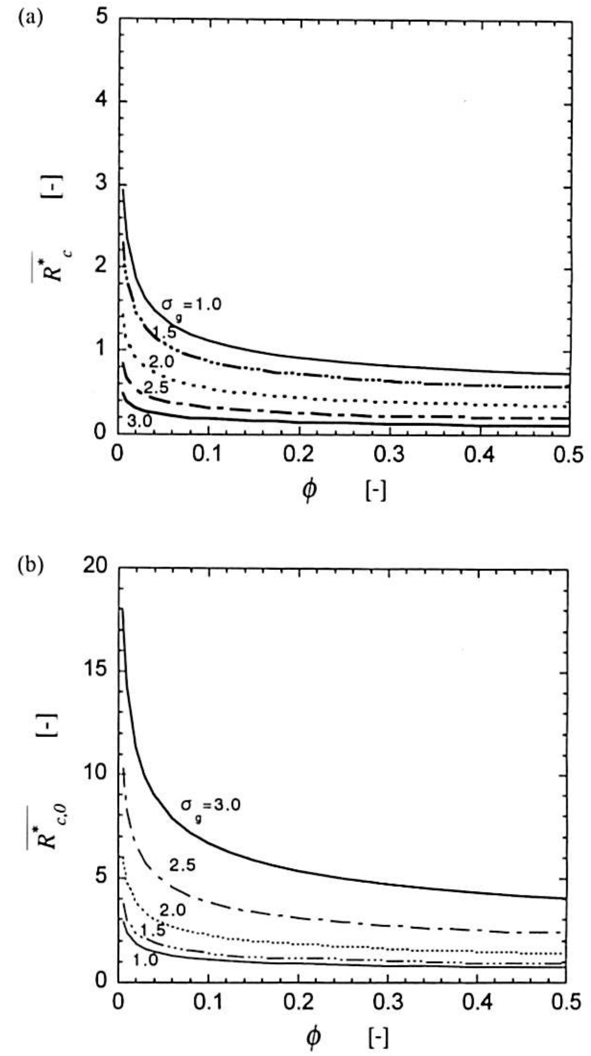

Fig. 8. (a) Average distance to the closest particle in a multi-size particle system; (b) average distance to the closest particle in a multi-size particle system (particle size is reduced by $x_{0,50}$).

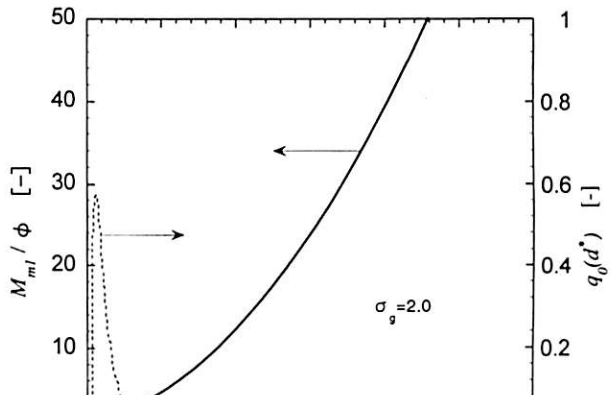

Fig. 9. Number of particles contacting on a specified particle of diameter d in a mono-size particle system.

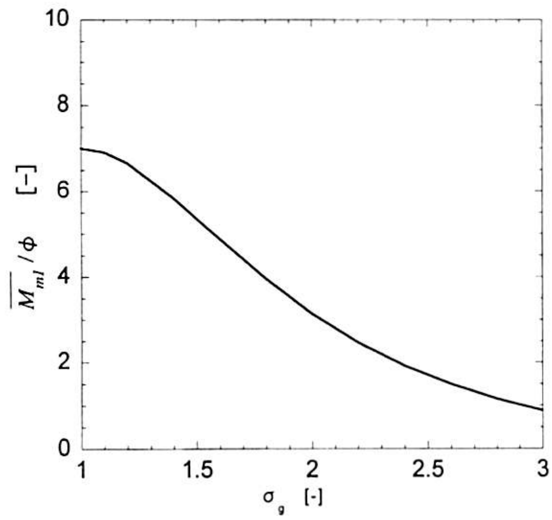

Fig. 10. Average contact number on a particle in a multi-size particle system.

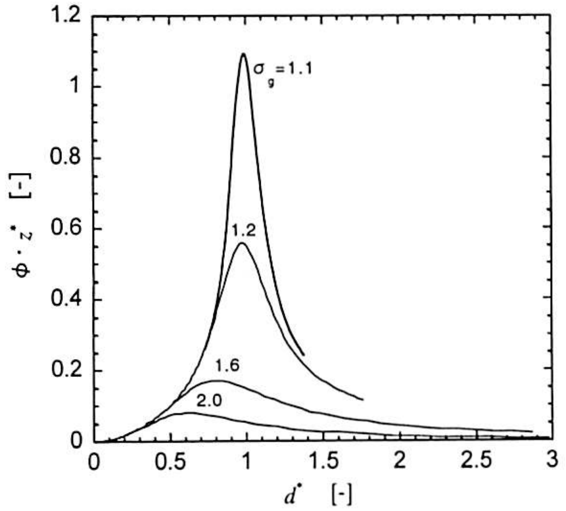

Fig. 11. Collision free path of a specified particle of diameter d in a mono-size particle system.

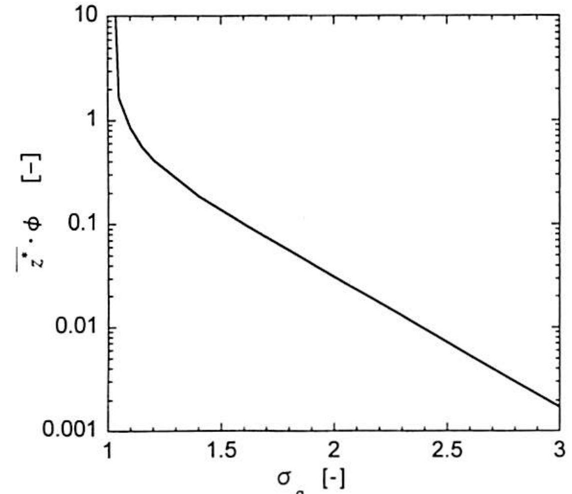

Fig. 12. Average collision free path of a particle in a multi-size particle system.

Figure 12 shows that particles having size distribution colloids in a short distance. As mentioned above, increasing of σ_g acts on coagulation of particles negative geometrically, however it promotes coagulation due to particle collision.

CONCLUSION

In this paper the average particle interval, distance to the closest particle and contact particle number on a specified one were calculated geometrically in cases of mono-size and multi-size particles. From the calculation and discussion it was clarified how the particle concentration and size distribution affect particle coagulation as the following.

In mono-size particle system particles have possibility to make a network structure over about 10 vol% because the particle contact number (coordination number) can be bigger than 2.

Although wide size distributions having the same volume mean diameter make particles dispersed geometrically and act on coagulation negative, the particle collision frequency during sedimentation increase with the width of size distribution and promote coagulation.

NOMENCLATURE

a	chord length, m
d	size of a specified particle, m
$f(r)$	existing probability density of the nearest particle, m^{-1}
$f_0(r)$	particle existing probability density, m^{-1}
g	gravitational acceleration, m · s^{-2}
k	constant
L	particle interval on a line in mono-size particle system, m
M_1	number of first layer particles contacting on a specified particle
M_2	number of second layer particles on a specified particle
m	particle number in a virtual sphere
N	particle number on a line of 1 m, m^{-1}
n	particle number in 1 m^3 multi-size particle system, m^{-3}
n_0	particle number in 1 m^3 mono-size particle system, m^{-3}
$q_0(x)$	particle number density distribution, m^{-1}
$q_3(x)$	particle volume density distribution, m^{-1}
R_{bcc}	R_c of bcc structure, m
R_c	distance to the closest particle, m
R_{cub}	R_c of cubic structure, m

R_{fcc}	R_c of fcc structure, m
r	radius, m
s	surface area of a spherical crown, m^2
t_c	collision time, s
u_d	settling velocity of a specified particle, $m \cdot s^{-1}$
u_x	settling velocity of a particle, $m \cdot s^{-1}$
V_2	volume existing second layer particles, m^3
v	volume of a spherical crown, m^3
x	particle size, m
$x_{0,50}$	median particle size of a cumulative number distribution, m
$x_{3,50}$	median particle size of a cumulative volume distribution, m
Z	average collision free path in a multi-size particle system, m
z	collision free path of a specified particle, m

Greek symbols

θ	angle
μ	liquid viscosity, $Pa \cdot s$
ρ_f	liquid density, $kg \cdot m^{-3}$
ρ_p	particle density, $kg \cdot m^{-3}$
σ_g	geometric standard deviation of particle size distribution
ϕ	particle volume fraction

Superscripts

*	reduced length by $x_{3,50}$
–	average value

Subscript

m	multi-size particle system

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