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The collision efficiency of spherical dioctyl phthalate aerosol particles in the Brownian coagulation*

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The collision efficiency in the Brownian coagulation is investigated. A new mechanical model of collision between two identical spherical particles is proposed, and a set of corresponding collision equations is established. The equations are solved numerically, thereby obtaining the collision efficiency for the monodisperse dioctyl phthalate spherical aerosols with diameters ranging from 100 to 760 nm in the presence of van der Waals force and the elastic deformation force. The calculated collision efficiency, in agreement with the experimental data qualitatively, decreases with the increase of particle diameter except a small peak appearing in the particles with a diameter of 510 nm. The results show that the interparticle elastic deformation force cannot be neglected in the computation of particle Brownian coagulation. Finally, a set of new expressions relating collision efficiency to particle diameter is established.

Keywords: aerosol particle, Brownian coagulation, collision efficiency, Van Der Waals force

PACC: 4755K, 9260M, 9265V

1. Introduction

The investigation of particle transport and coagulation has attracted much attention due to its all-pervading presence.[1,2] For example, aerosol particles in diameters ranging from 100 to 1000 nm are the major unstable suspended substances whose suspension lasts nearly a week in the polluted air of urban areas. The aerosol particles can also be sucked into deeper parts of the lung. If those aerosol particles are toxic, they will be very harmful to human health. The predominant driving force leading particle–particle encounters to coagulate is the Brownian motion of particles with radii less than 1000 nm.[3−5] Thus, Brownian coagulation plays a significant role in the growth of aerosol particles.

During the early stage of the coagulation of initially monodisperse aerosol particles, only collisions between the original particles play an important role in the evolution of the particle size distribution. Thus, the rate of change in the number of singlet particles per unit volume, n, is governed by[6]

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = k_{\mathrm{c}} n^2 = k_0 \alpha n^2, \tag{1}$$

where k_{c}, the rate constant for singlet–singlet collisions, is typically factored into an ideal rate k_0 that would occur in the absence of interparticle hydrodynamic and colloidal interactions and a collision efficiency α that denotes the probability of coagulation in a collision process of two particles of some size and a certain kind of material in a particular circumstance. Smoluchowski has determined the value of k_0 for Brownian coagulation. Therefore, it is important and essential to find the accurate collision efficiency α.

Derjaguin and Landau[7] and Verwey and Overbeek[8] determined the collision efficiency in the presence of van der Waals and electrical double layer forces. Spielman[9] and Hoing *et al*[10] calculated the collision efficiency of Brownian coagulation by considering colloidal forces under a continuum assumption. Hocking[11] gave initial consideration of the non-continuum effect on a lubrication flow between two spheres. Russel *et al*[12] calculated the rate of Brownian coagulation of aerosol particles by taking the van der Waals force into account. Chun and Koch[6] considered the effects of non-continuum lubrication force and van der Waals force in the coagulation process of monodisperse aerosol particles for predicting the initial coagulation rate. However, the elastic force arising

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from particle deformation in the process of collision between particles is one of factors affecting the collision efficiency, but it was not taken into account in the above investigations. The collision efficiency in the presence of van der Waals force and elastic force appears to be an unexplored research topic up to now because the elastic force is somewhat complicated. Therefore, this study aims at presenting the collision efficiency in the presence of van der Waals force and elastic force, and exploring whether the elastic force can be neglected.

2. Expression of basic forces

2.1. Van der Waals force between particles

The interparticle attraction force, i.e. van der Waals force, is generated because of the electropolar effect when particles approach each other. Van der Waals force cannot be neglected in a range of $10^{-2} \geq Kn \geq O(10)$ where Kn is the Knudsen number representing the ratio of the mean-free path to the particle radius. Based on the Hamaker theory, the expression of van der Waals potential energy is given by

$$\phi_{\mathrm{v}} = -\frac{A}{12h}\frac{d_{\mathrm{p1}}d_{\mathrm{p2}}}{d_{\mathrm{p1}}+d_{\mathrm{p2}}}, \tag{2}$$

where d_{p1} and d_{p2} are the diameters of the two particles, separately, h is the interparticle distance, and A is the Hamaker constant. Assuming $d_{\mathrm{p1}} = d_{\mathrm{p2}} = d_{\mathrm{p}}$, the Hamaker constant for two identical particles in a medium can be obtained from the following relation:[13]

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)^2 + \frac{3P_{\mathrm{l}}v_{\mathrm{e}}}{16\sqrt{2}}\frac{(n_1^2-n_3^2)^2}{(n_1^2+n_3^2)^{3/2}}, \tag{3}$$

where k is the Boltzmann's constant, T is the absolute temperature, P_{l} is the Planck's constant, v_{e} is the plasma frequency of the free electron gas, which is typically taken as $3.0\times10^{15}\mathrm{s}^{-1}$, n_1 and ε_1 are the index of refraction and dielectric constant for the particles, respectively, n_3 and ε_3 are the index of refraction and dielectric constant for the suspending medium, respectively. Based on expression (2), the van der Waals force is given as

$$F_{\mathrm{vdw}} = \frac{\partial\phi_{\mathrm{v}}}{\partial h} = -\frac{A}{12h^2}\frac{d_{\mathrm{p1}}d_{\mathrm{p2}}}{d_{\mathrm{p1}}+d_{\mathrm{p2}}}. \tag{4}$$

Expression (4) is valid only on condition that the aerosol particles are considered as volumeless particles. In the present study the particles experience a certain deformation in the process of collision, therefore, the modified expression of van der Waals force is given as[14]

$$F_{\mathrm{vdw}} = \frac{Ad_{\mathrm{p}}}{24Z_0^2} + S(d_{\mathrm{p}}-S)\frac{A}{6Z_0^3}, \tag{5}$$

where S is the displacement of deformed particle, Z_0 is the action distance of the van der Waals force, which is typically taken as 16.5–40 nm.

2.2. Interparticle elastic deformation force

Two identical spherical particles experience a central collision as shown in Fig.1. S is the displacement of linear deformation along the axis for particle A. The collision process of two particles can be divided into two stages, i.e. compression and spring-back. When deformation of particle A comes to the maximum value $S_{\max}$, the relative velocity between two particles is 0. According to the elastic impedance of the particle material, the spring-back of particle takes place while the process of compression ends.

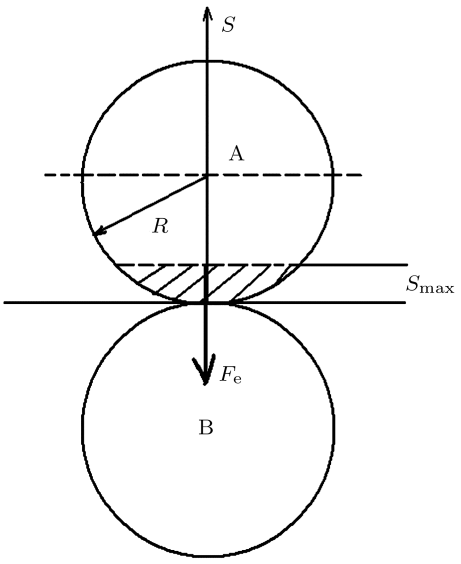


Fig.1. Schematic diagram of the collision between two particles.

In order to calculate the elastic deformation force, the coordinate system is established as shown in Fig.2, in which the circle represents the cross section of particle while the oblique line part refers to the deformation

area during the collision. The equation describing the particle surface is

$$x^2 + [y - (R - S_{\max})]^2 = R^2 \quad (y < 0), \tag{6}$$

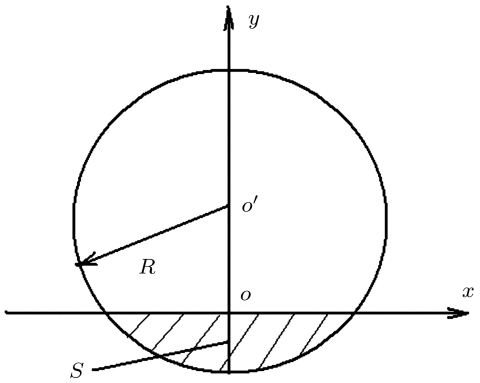


Fig.2. Coordinate system for the calculation of deformation force.

The elastic deformation force F_e that is induced by the deformation of particle A in Fig.1 and exerted on particle B is given by

$$\mathrm{d}F_e = k_s(-y) \cdot \mathrm{d}x \cdot 2\pi x, \tag{7}$$

where k_s is the stiffness of material. The value of k_s depends on material characteristic and can be expressed as a function of particle diameter, i.e. $k_s = f(d_p)$.

Integrating Eq.(7) yields

$$\begin{aligned} F_e &= \int \mathrm{d}F_e = \int_{y=0}^{y=-s} \pi k_s(-y)\mathrm{d}x^2 \\ &= \pi k_s \int_0^s (-y)\mathrm{d}(-y^2 + 2(R-S)y + 2RS - S^2) \\ &= \pi k_s \left[y^3 - 2(R-S)y^2 + (S^2 - 2RS)y\right]|_0^{-s} \\ &\quad -\pi k_s \int_0^{-s} (y^2 - 2(R-S)y + S^2 - 2RS)\mathrm{d}y \\ &= \pi k_s \left(\frac{S^3}{3} - \frac{d_p}{2}S^2\right) \end{aligned} \tag{8}$$

3. The double-particle collision model

3.1. Basic assumptions

Several assumptions are introduced for building the collision model.

(1) Since the diameter of particle varies in a range that is several times the mean free path of gas, there are a great number of random collisions between particles and gas molecules. Therefore, the particles are in random thermal motion, and the system composed of particles can be considered as a type of ideal gas.

(2) The system composed of particles obeys the laws of conservation of mass and volume in the process of coagulation.

(3) In the process of coagulation, the particles remain spherical in shape though particle size varies.

(4) The collision between two particles is a central collision, i.e. the tangential force induced by a non central collision can be neglected.

3.2. Stage of particle compression

Consider two identical spherical particles in contact with each other at one point. One particle has an initial velocity v_0 while the other is at rest. In the process of central impact, van der Waals force F_{vdw} and the elastic deformation force F_e are taken into account. In the coordinate system as shown in Fig.3 the governing equation in the process of particle compression is

$$\begin{aligned} &m\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} = (F_e - F_{vdw}) + (F_e - F_{vdw}), \\ &v|_{t=0} = -v_0, S|_{t=0} = 0. \end{aligned} \tag{9}$$

where m is the mass of particle, S represents the linear deformation length of the particle surface, v is the relative velocity between two particles. Defining $x(1) = S = (d_p - x)/2$, $x(2) = v$ with d_p being the particle diameter, Eq.(9) can be changed into

$$\begin{aligned} &\frac{\mathrm{d}(x(1))}{\mathrm{d}t} = -\frac{1}{2}x(2), \\ &\frac{\mathrm{d}(x(2))}{\mathrm{d}t} = \frac{2}{m}(F_e - F_{vdw}), \\ &x(1)|_{t=0} = 0, \\ &x(2)|_{t=0} = -v_0, \end{aligned} \tag{10}$$

in which F_{vdw} and F_e can be calculated from expressions (5) and (8).

Equation (10) is solved to give a maximum deformation $S_{\max}$ that is essential for judging whether the two particles will coagulate. Moreover, $S_{\max}$ is the bridge between the compression stage and the spring-back stage. Based on $S_{\max}$, the governing equations for the spring-back stage can be established.

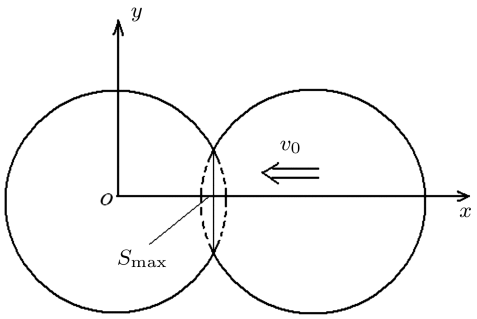


Fig.3. Relative coordinate system for collision model.

3.3. Stage of spring-back

Since the collision is considered as an imperfect elastic collision here, the elastic deformation forces in the stages of compression and spring-back are different, which results in the loss of mechanical energy in the process of collision. The coagulation will occur when the loss is large enough.

The expression of elastic deformation force F_{e_1} in the stage of spring-back for the imperfect elastic collision process is

$$F_{e1} = \begin{cases} \pi k_s \left(\dfrac{d_p}{2} \left(S_{\max} - \dfrac{1}{e}(S_{\max} - S) \right)^2 - \dfrac{1}{3} \left(S_{\max} - \dfrac{1}{e}(S_{\max} - S) \right)^3 \right) & S \in [0, (1-e)S_{\max}] \\ 0 \quad S \in ((1-e)S_{\max}, S_{\max}] \end{cases}, \tag{11}$$

where e is the coefficient of restitution. Based on expression (11), the governing equation in the stage of spring-back can be given as:

$$\begin{aligned} &\frac{\mathrm{d}(x(1))}{\mathrm{d}t} = -\frac{1}{2}x(2), \\ &\frac{\mathrm{d}(x(2))}{\mathrm{d}t} = \frac{2}{m}(F_{e1} - F_{vdw}), \\ &x(1)|_{t=0} = S_{\max}, \\ &x(2)|_{t=0} = 0. \end{aligned} \tag{12}$$

4. Determination of collision efficiency

Particles experience the processes of collision, deformation, spring-back and separation or coagulation. In the process of collision, mechanical energy will lose due to the characteristics of imperfect elastic collision. Therefore, two particles will coagulate if the relative velocity between the two particles is reduced to zero before spring back. Otherwise, the two particles will be separated from each other. By determining the critical velocity at which the coagulation occurs, we can refer ourselves to Maxwell velocity distribution to find a corresponding probability. This probability is the collision efficiency of Brownian coagulation.

According to Eqs.(10) and (12), the relationship between S, v and t can be obtained. In the function of $v(t)$, we can obtain non-zero root t_{10} for which $v(t)$ has a minimum value, and then we search for the value of $S(t_{10})$. $S(t_{10}) \geq 0$ means that the two particles have not been separated from each other when relative velocity declines declined to zero, i.e. the coagulation occurs. Otherwise, i.e. for $S(t_{10}) < 0$, no coagulation happens. Then, we can have a critical velocity v_{cr} at which the coagulation occurs. Substituting v_{cr} into the Maxwell velocity distribution, we can obtain the collision efficiency α

$$\begin{aligned} \alpha &= \int_0^{v_{cr}} f(v)\mathrm{d}v \\ &= \int_0^{v_{cr}} 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \mathrm{e}^{-\frac{mv^2}{2kT}} v^2 \mathrm{d}v. \end{aligned} \tag{13}$$

5. Results and discussion

5.1. Calculation method and condition

Equations (10)–(13) are solved numerically by using the fourth-order Runge–Kutta method. The dioctyl phthalate aerosols are chosen as the particles. Some parameters of the dioctyl phthalate aerosols are listed in Table 1.

Table 1. Values of relevant parameters of dioctyl phthalate aerosols.

A	μ/Pa·S	k_s	d_p/nm	$\rho/(\mathrm{kg/m^3})$	λ/nm	e
6.8×10^{-20}	17.8×10^{-6}	$f(d_p)$	$100 - 760$	0.982	65	0.7

In Table 1, A is the Hamaker constant, μ is the viscosity of the gas, ρ is the density of the gas, λ is the mean-free path of the molecule, e is the coefficient of restitution, k_s is the stiffness of particle, and $f(d_p)$ is given by the experimental data[15,16]

$$\ln\left(\frac{k_s}{10^7}\right) = -15d_p^3 - 33d_p^2 - 29d_p + 6 \quad d_p \in [0.1\mu m, 0.8\mu m]. \tag{14}$$

5.2. Relationship between S_{max} and v in the stage of compression

Figure 4 shows the relationship between S_{max} and v in the stage of compression with $d_p = 300\,nm$ and, correspondingly, $k_s = 1 \times 10^7$. It can be seen that the maximum deformation S_{max} is directly proportional to the relative velocity v between two particles. The curve in Fig.4 can be expressed as a polynomial as follows:

$$S_{max}(v) = (0.0147v^3 + 0.0500v^2 - 0.0107v + 0.1060) \times 10^{-6}. \tag{15}$$

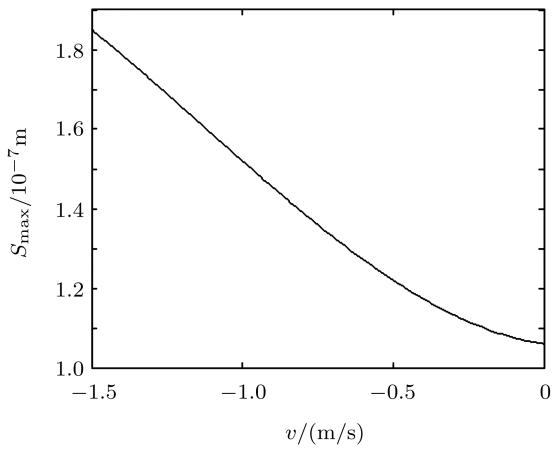


Fig.4. Relationship between S_{max} and v in the stage of compression ($d_p = 300\,nm$).

5.3. Relationship between S_{max} and S_f in the stage of spring-back

The relationship between S_{max} and S_f is shown in Fig.5, in which S_f is the particle deformation corresponding to the case where the relative velocity of two particles reduces to zero. The curve in Fig.5 can be expressed as a polynomial as follows:

$$S_f(S_{max}) = -5.7333 \times 10^{14} S_{max}^3 + 1.674 \times 10^8 S_{max}^2 - 12.6598.7 S_{max} + 10^{-8}. \tag{16}$$

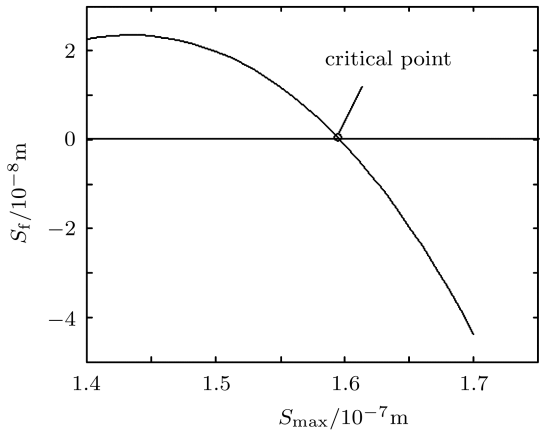


Fig.5. Relationship between S_{max} and S_f in the stage of spring-back ($d_p = 300\,nm$).

5.4. Collision efficiency of particles with a diameter of 300 nm

From Figs.(4) and (5), we can obtain the critical value $(S_f)_{cr}$ of S_f. $(S_f)_{cr}$ is the particle deformation corresponding to the case where the coagulation of particles takes place. Substituting $(S_f)_{cr}$ into expression (16) yields $(S_{max})_{cr} = 1.59 \times 10^{-7}\,m$. Substituting $(S_{max})_{cr}$ into expression (15), we finally obtain the critical velocity $v_{cr} = 1.1\,m/s$ for the two identical particles to coagulate. According to expression (13), the collision efficiency α is obtained as

$$\alpha_{300nm} = \int_0^{1.1} f(v)dv = \int_0^{1.1} 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 dv = 0.7447. \tag{17}$$

5.5. Collision efficiency of particles with diameters ranging from 100 to 760 nm

Formula (17) is obtained in the case of particles with a diameter of 300 nm. With the same procedure we calculate the collision efficiencies for the particles with diameters ranging from 100 to 760 nm. The calculated results are shown in Fig.6 in which Devir's experimental data[15,16] are also given. Devir used a modified Sinclair-LaMer generator to produce aerosols composed of dioctyl phthalate drops with a mean size in a range of 500–800 nm and standard deviation of the radius, less than 10%. A Dergaguin counter is

used to determine the number density of droplets as a function of time during the initial stages of coagulation. We can see that the calculated results are in agreement with the experimental data qualitatively for the particles with a mean size in a range of 500–760 nm. The collision efficiency decreases with the increase of particle diameter in a range of 100–500 nm. There is a small peak of collision efficiency around $d_{\mathrm{p}} = 510\,\mathrm{nm}$ after which the collision efficiency decreases again. Generally speaking, the effect of van der Waals force on the particle coagulation becomes weak with the increase of particle diameter. If the elastic deformation force is not taken into consideration, the collision efficiency will decrease monotonically with the increase of particle diameter under the action of van der Waals force. Therefore, the appearance of a small peak of collision efficiency around $d_{\mathrm{p}} = 510\,\mathrm{nm}$ is related to the interparticle elastic deformation force. For the cases of particles with small diameters, e.g. $d_{\mathrm{p}} \leq 500\,\mathrm{nm}$, van der Waals force is predominant, so collision efficiency decreases with particle diameter increasing. When the particle diameter increases further, the function of interparticle elastic deformation force becomes stronger. However, the elastic deformation force does not change with particle diameter monotonically according to expressions (8) and (14), and there exists a maximum occurring around $d_{\mathrm{p}} = 510\,\mathrm{nm}$ as shown in Fig.6. It is evident that collision efficiencies obtained separately with and without taking the interparticle elastic deformation force into account are different. Therefore, the interparticle elastic deformation force cannot be neglected in the computation of particle Brownian coagulation. From Fig.6 we can built a polynomial of α with respect to d_{p} as shown below:

$$\begin{aligned} &\alpha(d_{\mathrm{p}}) = 69d_{\mathrm{p}}^4 - 72.8d_{\mathrm{p}}^3 + 26d_{\mathrm{p}}^2 - 4.6d_{\mathrm{p}} + 1.1957 \\ &d_{\mathrm{p}} \in [100\,\mathrm{nm}, 500\,\mathrm{nm}], \\ &\alpha(d_{\mathrm{p}}) = 0.4791d_{\mathrm{p}}^2 - 1.0209d_{\mathrm{p}} + 1.0468 \end{aligned} \tag{18}$$

$$d_{\mathrm{p}} \in [500\,\mathrm{nm}, 760\,\mathrm{nm}]. \tag{19}$$

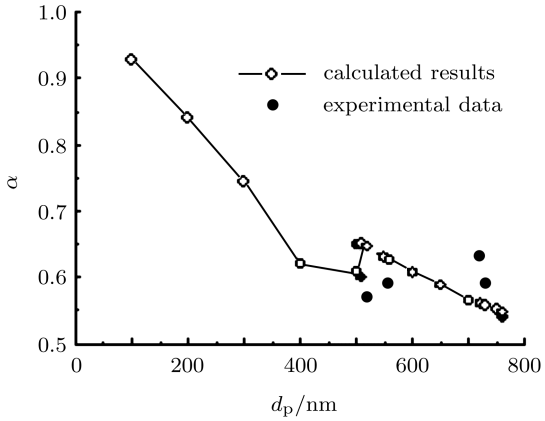


Fig.6. Collision efficiencies with particle diameter varying.

6. Conclusions

Brownian coagulation plays a significant role in the growth of aerosol particles. Whether the two particles coagulate is related to the particle collision efficiency that depends on the collision model of particles and elastic force arising from particle deformation. The collision efficiency is studied in this paper by building and solving numerically the collision equation for monodisperse dioctyl phthalate spherical aerosols with diameters ranging from 100 to 760 nm in the presence of van der Waals force and elastic deformation force. The calculated results are in agreement with the experimental data qualitatively. The results show that the collision efficiency decreases with the increase of particle diameter except there appears a small peak around $d_{\mathrm{p}} = 510\,\mathrm{nm}$. The interparticle elastic deformation force may not be neglected in the computation of particle Brownian coagulation. Finally, a set of new expressions relating collision efficiency to particle diameter is established.

References

[1] Wang W B, Lin F, Liu H J, Yue X, Chen J H, Li H, Ren L H and Tang D G 2007 *Chin. Phys.* **16** 2818

[2] Lin J Z, Li J, Zhu L and Olson J A 2005 *Chin. Phys.* **14** 1185

[3] Yu M Z, Lin J Z, Chen L H and Chan T L 2006 *Acta Mech. Sin.* **22** 293

[4] Chan T L, Lin J Z, Zhou K and Chan C K 2006 *Journal of Aerosol Science* **37** 1545

[5] Lin J Z, Chan T L, Liu S, Zhou K, Zhou Y and Lee S C 2007 *Int. J. Nonlinear Sciences and Numerical Simulation* **8** 45

[6] Chun J and Koch D L 2006 *Journal of Aerosol Science* **37** 471

[7] Derjaguin B V and Landau L 1941 *Acta Physicochim URSS* **14** 633

[8] Verwey E J W and Overbeek J TH G 1948 *Theory of the Stability Lyophobic Colloids* (New York: Elsevier) p636

[9] Spielman L A 1970 *Journal of Colloid and Interface Science* **33** 562

[10] Hoing E P, Roebersen G J and Wiersema P H 1971 *Journal of Colloid and Interface Science* **36** 97

[11] Hocking L M 1973 *Journal of Engineering Mathematics* **7** 207

[12] Russel W B, Saville D A and Schowalter W R 1989 *Colloidal Dispersions* (Cambridge: Cambridge University Press) p95

[13] Israelachvili J 1992 *Intermolecular and surface forces*(New York: Academic) p106

[14] Zhang W B, Qi H Y, You C F and Xu X C 2002 *Journal of Tsinghua University* (Science and Technology) **42** 1639

[15] Devir S E 1963 *Journal of Colloid and Interface Science* **18** 744

[16] Devir S E 1967 *Journal of Colloid and Interface Science* **21** 80