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# The effect of weak gravitational force on Brownian coagulation of small particles

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The coagulation rate of a dilute polydisperse suspension of particles is considered for small Péclet number, which provides a measure of the ratio of the relative gravity-induced motion to Brownian motion between two rigid spheres. In particular, a four-term expansion for the dimensionless coagulation rate (Nusselt number) as function of the Péclet number is developed by making use of a singular perturbation method. In the limit of the radius of one of the two spheres becoming small, the result agrees with Acrivos & Taylor's (1962) work on mass transfer to spheres at small Péclet number.

## 1. Introduction

In this paper we consider the coagulation rate of a dilute, polydisperse, statistically homogeneous suspension of small rigid spherical particles. The particles are settling under gravity through Newtonian fluid with speeds which vary with their size and their density. They are also in random motion due to Brownian thermodynamics. The particles exert attractive van der Waals forces on each other, and two particles which come into contact through the action of this force form a permanent doublet. The rate at which the suspension becomes coagulated is in large part determined by the rate of doublet formation, and it is this quantity that we seek to determine. The effect of weak gravitational force on Brownian coagulation is found by means of a four-term expansion for the dimensionless coagulation rate (Nusselt number).

The method of calculation involves use of the pair-distribution function $p_{ij}(\boldsymbol{r})$, and a singular perturbation technique. Near the test sphere $i$ (the inner region) Brownian motion balances the interparticle force – van der Waals force – and the relative gravity-induced motion between the test sphere $i$ and a sphere $j$ is negligible when the Péclet number is small. However, far from the test sphere $i$ (the outer region) the relative gravitational motion is no longer small and must be taken into account. Then in the outer region Brownian motion balances the relative gravity-induced motion, and the influence of interparticle force is negligible owing to its rapid decay. Thus, an expansion in terms of Péclet number, $\mathscr{P}_{ij}$, for $p_{ij}(\boldsymbol{r})$ is not valid for large distances of sphere $j$ from sphere $i$ (inner expansion). It has therefore to be matched with a separate expansion which is calculated in the outer region (outer expansion). The method of matched asymptotic expansions is then used. Using this method, van de Ven & Mason (1977) calculated the case of weak shear-induced/strong Brownian motion coagulation rate as far as the second term of order $\mathscr{P}_{ij}^{\frac{1}{2}}$, and Melik & Foglor (1984*a*) calculated the case of weak gravity-induced/strong Brownian motion coagulation rate as far as the second term of order $\mathscr{P}_{ij}$. The purpose of this paper is

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simply to continue the analysis of Melik & Fogler (1984*a*) as far as the fourth term of order $\mathscr{P}_{ij}^2$, thus improving representation of the coagulation rate.

The basic procedure of the method of matched asymptotic expansions used in this paper is very similar to the one used in Acrivos & Taylor's (1962) work on mass/heat transfer to or from a sphere at small Péclet number. For a detailed description of the method, the reader is referred to Acrivos & Taylor (1962). It is of interest to note that the two problems have some connection. The result of this paper agrees with Acrivos & Taylor's (1962) result, when the radius of sphere $j$ approaches zero.

## 2. Basic equation for the pair-distribution function

The first step for calculating the coagulation rate in a dilute polydisperse suspension is to determine the pair-distribution function $p_{ij}(\boldsymbol{r})$, defined as the probability that the centre of sphere $j$ (with radius $a_j$, density $\rho_j$ and number density $n_j$) lies within unit volume at position $\boldsymbol{r}$ relative to the centre of the test sphere $i$ (with radius $a_i$, density $\rho_i$ and number density $n_i$). Having determined the pair-distribution function, the coagulation rate can be calculated, since the flux of sphere $j$ across the contact surface $r = a_i + a_j$ ($r = |\boldsymbol{r}|$) enclosing each sphere $i$ can then be calculated.

Because the spheres are small, the inertia forces of both the spheres and the fluid may be neglected. The relative velocity of the two spheres can be decomposed into linearly independent contributions from gravity, interparticle force, and Brownian thermodynamic force. The equation for $p_{ij}(\boldsymbol{r})$ and the corresponding boundary conditions are then as follows (Wen & Batchelor 1985):

$$\frac{\partial p_{ij}}{\partial t} + \nabla_r \cdot \left\{ p_{ij}\, \boldsymbol{V}_{ij} - p_{ij}\, \boldsymbol{D}_{ij} \cdot \nabla_r \left( \frac{\Phi_{ij}}{kT} \right) - \boldsymbol{D}_{ij} \cdot \nabla_r p_{ij} \right\} = 0, \tag{2.1}$$

and

$$p_{ij} = 0 \quad \text{at} \quad r = a_i + a_j, \quad p_{ij} \to 1 \quad \text{as} \quad r \to \infty, \tag{2.2}$$

where $\boldsymbol{V}_{ij}$ is the relative gravitational velocity of the two spheres, $\Phi_{ij}$ is the interparticle potential, $k$ the Boltzmann constant, $T$ the absolute temperature, $\boldsymbol{D}_{ij}$ is the relative Brownian diffusive tensor of the two spheres.

Provided the suspension is dilute, the rate of conversion of singlets into doublets is not too rapid, and the interparticle potential satisfies the requirements pointed out by van de Ven & Mason (1977), and Melik & Fogler (1984*a*), a steady state can be approximately reached in the initial stage of the coagulation process. The divergence term of the relative velocity of the two spheres in (2.1) is thus equal to zero. Choosing the relative gravitational velocity $V_{ij}^{(0)}$ of the two spheres when they are far apart as the representative magnitude of $\boldsymbol{V}_{ij}$, and the relative Brownian diffusivity $D_{ij}^{(0)}$ of the two spheres when they are far apart as the representative magnitude of $\boldsymbol{D}_{ij}$, (2.1) and (2.2) reduce to the following dimensionless forms:

$$\mathscr{P}_{ij} \nabla_s \cdot \left\{ \frac{\boldsymbol{V}_{ij}}{V_{ij}^{(0)}} p_{ij} \right\} - \nabla_s \cdot \left\{ p_{ij} \frac{\boldsymbol{D}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_s \left( \frac{\Phi_{ij}}{kT} \right) \right\} - \nabla_s \cdot \left\{ \frac{\boldsymbol{D}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_s p_{ij} \right\} = 0, \tag{2.3}$$

and

$$p_{ij} = 0 \quad \text{at} \quad s = 2, \quad p_{ij} \to 1 \quad \text{as} \quad s \to \infty, \tag{2.4}$$

where $s$ is the dimensionless distance between the centres of the two spheres scaled on the average radius, namely $\boldsymbol{s} = 2\boldsymbol{r}/(a_i + a_j)$, and $s = |\boldsymbol{s}|$. The Péclet number $\mathscr{P}_{ij}$ now is defined as $(a_i + a_j)\, V_{ij}^{(0)}/2D_{ij}^{(0)}$, and is assumed to be small.

In the case of sedimenting spheres of non-uniform size, the relative velocity of two spheres which are far apart from other spheres has the form (Batchelor 1982):

$$\boldsymbol{V}_{ij}(\boldsymbol{r}) = \boldsymbol{V}_{ij}^{(0)} \cdot \left\{ \frac{\boldsymbol{rr}}{r^2} L(s) + \left( \boldsymbol{I} - \frac{\boldsymbol{rr}}{r^2} \right) M(s) \right\}, \tag{2.5}$$

and the relative Brownian diffusivity tensor has the form (Batchelor 1982),

$$\boldsymbol{D}_{ij}(\boldsymbol{r}) = D_{ij}^{(0)} \left\{ \frac{\boldsymbol{rr}}{r^2} G(s) + \left( \boldsymbol{I} - \frac{\boldsymbol{rr}}{r^2} \right) H(s) \right\}. \tag{2.6}$$

The scalar functions $L$, $M$, $G$, $H$ can be obtained from the low-Reynolds-number hydrodynamics (Jeffrey & Onishi 1984), and have been calculated by Batchelor & Wen (1982) for rigid spheres. Because of the decomposition of the solution into an inner and an outer expansion, the necessity of which has been mentioned in the above section, only the far-field asymptotic forms for them are needed.

We substitute the far-field asymptotic expression for the mobility functions (Jeffrey & Onishi 1984) in the scalar functions $L, M, G, H$ given by Batchelor (1982). The following far-field asymptotic forms are obtained:

$$L(s) = 1 + \frac{L_1}{s} + O(s^{-3}), \tag{2.7}$$

$$M(s) = 1 + \frac{M_1}{s} + O(s^{-3}), \tag{2.8}$$

$$G(s) = 1 + \frac{G_1}{s} + O(s^{-3}), \tag{2.9}$$

$$H(s) = 1 + \frac{H_1}{s} + O(s^{-3}), \tag{2.10}$$

where

$$L_1 = \frac{3(1-\lambda^3\gamma)}{(\lambda^2\gamma - 1)(1+\lambda)} \quad \text{and} \quad M_1 = \tfrac{1}{2}L_1, \tag{2.11}$$

$$G_1 = \frac{-6\lambda}{(1+\lambda)^2} \quad \text{and} \quad H_1 = \tfrac{1}{2}G_1. \tag{2.12}$$

The two parameters $\lambda$ and $\gamma$ in the above expressions are the size ratio and the reduced density ratio of the two spheres:

$$\lambda = \frac{a_j}{a_i}, \quad \gamma = \frac{\rho_j - \rho_0}{\rho_i - \rho_0}, \tag{2.13}$$

where $\rho_0$ is the density of the fluid. The divergence term of $\boldsymbol{V}_{ij}/\boldsymbol{V}_{ij}^{(0)}$ is given by (Batchelor 1982)

$$\nabla_s \cdot \left( \frac{\boldsymbol{V}_{ij}}{V_{ij}^{(0)}} \right) = \frac{\boldsymbol{V}_{ij}}{V_{ij}^{(0)}} \cdot \frac{\boldsymbol{s}}{s} W(s). \tag{2.14}$$

The far-field asymptotic form for the scalar function $W(s)$ is as follows (Batchelor 1982):

$$W(s) = \frac{120\lambda^3(\gamma-1)}{(\lambda^2\gamma-1)(1+\lambda)^4}\frac{1}{s^5} + O(s^{-7}). \tag{2.15}$$

We now turn to the problem of the interparticle potential $\Phi_{ij}$. Only the case of rapid flocculation is considered in this paper. The interparticle potential is thus dominated by the attractive van der Waals potential. The expression for $\Phi_{ij}$ is given by (Hamaker 1937)

$$\Phi_{ij} = -\tfrac{1}{6}A\left\{\frac{8\lambda}{(s^2-4)(1+\lambda)^2}+\frac{8\lambda}{s^2(1+\lambda)^2-4(1-A)^2}+\ln\frac{(s^2-4)(1+\lambda)^2}{s^2(1+\lambda)^2-4(1-\lambda)^2}\right\}, \tag{2.16}$$

where $A$ is the composite Hamaker constant. From (2.16), it is easy to show that the far-field asymptotic form for the attractive van der Waals potential is

$$\Phi_{ij} = -\frac{1024}{9}\frac{A\lambda^3}{(1+\lambda)^6}\frac{1}{s^6}+O(s^{-8}). \tag{2.17}$$

Of course, (2.16) and (2.17) describe the unretarded van der Waals potential. In 1977, van de Ven & Mason said, '...the interaction energy at large particle separation is determined by van der Waals attraction. At such separations the forces are retarded and $V_{\text{int}}$ (i.e. $\Phi_{ij}$ in the present work) is proportional to $s^{-2}$...'. To include the retardation effects in the outer region is certainly necessary. However, the fairly slow $s^{-2}$ decay of the van der Waals potential proposed by van de Ven & Mason (1977), and then by Melik & Fogler (1984*a*) in their outer region analysis cannot be correct, since the retardation effects are to weaken not to strengthen the van der Waals force. The decay of the retarded van der Waals potential must be more rapid than $s^{-6}$. For the case of an equal-size system, Feke & Schowalter (1983) cited a far-field asymptotic expression for the retarded van der Waals potential as follows:

$$\Phi_{ij} = -\frac{16A}{9s^6}\left(\frac{2.45}{p}-\frac{2.04}{p^2}\right), \quad s \gg 1. \tag{2.18}$$

In this expression $p = 2\pi(s-2)/\lambda_{\text{L}}$, where $\lambda_{\text{L}}$ is the dimensionless London wavelength scaled on the radius of the spheres. Just as we expect, (2.18) does show a more rapid $s^{-7}$ decay as $s \to \infty$.

Although decay as $s^{-2}$ is not correct, in §4 we shall see that it does not affect Melik & Fogler's (1984*a*) two-term expansion result. However, it will certainly affect the third- and the fourth-term expansion results, which are calculated in this paper.

In the case of rapid flocculation, the repulsive potential $V_{\text{R}}$ is approximated by a thin double layer potential. For an unequal-size system Melik & Fogler (1984*a*) gave the following form:

$$V_{\text{R}} = \pm\tfrac{1}{2}\epsilon_0 a_i \psi_0^2\frac{\lambda}{1+\lambda}\ln\left[1\pm\exp\left(-\tau(s-2)\right)\right], \tag{2.19}$$

where $\epsilon_0$ is the dielectric strength, $\psi_0$ the surface potential, and the parameter $\tau$ is the dimensionless reciprocal of the Debye–Hückel double layer thickness scaled on the reciprocal of the average radius $\frac{1}{2}(a_i+a_j)$. Since (2.19) is valid only for thin double layers, $\tau \gg 1$.

From (2.19) we may see that the far-field asymptotic form for the thin double layer repulsive potential is

$$V_{\text{R}} = O(\mathrm{e}^{-\tau s}) \quad \text{as} \quad s \to \infty. \tag{2.20}$$

Obviously the decay of this type of repulsive potential is much more rapid than the negative-power decay of the attractive van der Waals potential.

## 3. Inner expansion and outer expansion for $p_{ij}$

In this section we shall calculate a four-term inner expansion and a three-term outer expansion for $p_{ij}$. The technical aspects of this section are presented in a concise manner since the analysis closely follows the analysis of mass/heat transfer from a sphere at low Péclet number (Acrivos & Taylor 1962). We choose a spherical polar coordinate system such that its origin is at the centre of the test sphere $i$, and the direction of the polar axis coincides with $V_{ij}^{(0)}$. Thus the problem is axisymmetric about the polar axis, and $\theta$ is the polar angle.

According to the method of matched asymptotic expansions, we construct an 'inner' and an 'outer' expansion. The inner expansion is assumed to be of the form

$$p_{ij} = \sum_{n=1}^{\infty} p_{ij}^{(n)}(s,\theta)\, t_n(\epsilon) \quad \text{with} \quad t_1(\epsilon) = 1, \tag{3.1}$$

where the perturbation parameter $\epsilon = \mathscr{P}_{ij}$, and $t_n(\epsilon)$ $(n = 1,2,\ldots)$ and also $\hat{t}_n(\epsilon)$ $(n = 1,2,\ldots)$ in the outer expansion (3.3) are gauge functions (Van Dyke 1975), which are not necessarily simple powers of $\epsilon$, and for the moment are restricted only by the requirements

$$\lim_{\epsilon\to 0} \frac{t_{n+1}(\epsilon)}{t_n(\epsilon)} = 0 \quad \text{and} \quad \lim_{\epsilon\to 0} \frac{\hat{t}_{n+1}(\epsilon)}{\hat{t}_n(\epsilon)} = 0.$$

The inner equation is the same as (2.3). The set of equations for $p_{ij}^{(n)}$ $(n = 1,2,\ldots)$ can be obtained by substitution of the expansion (3.1) in (2.3). The boundary conditions imposed on $p_{ij}^{(n)}$ are

$$p_{ij}^{(n)} = 0 \quad (n \geqslant 1) \quad \text{at} \quad s = 2. \tag{3.2}$$

These boundary conditions are insufficient to uniquely determine $p_{ij}^{(n)}$. However, additional conditions at $s \to \infty$ are furnished by matching the inner and outer expansions in their common domains of validity.

The outer expansion for $p_{ij}$ is assumed to be of the form

$$\hat{p}_{ij} = \sum_{n=1}^{\infty} \hat{p}_{ij}^{(n)}(\rho,\theta)\, \hat{t}_n(\epsilon) \quad \text{with} \quad \hat{t}_1(\epsilon) = 1. \tag{3.3}$$

The contracted radial coordinate $\rho$, where $\rho = \epsilon s$, is introduced in the outer region so that the perturbation parameter $\epsilon$ can be scaled out in the outer equation; then we have

$$\nabla_\rho \cdot \left\{ \hat{p}_{ij} \frac{\boldsymbol{D}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_\rho \left( \frac{\Phi_{ij}}{kT} \right) + \frac{\boldsymbol{D}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_\rho \hat{p}_{ij} - \frac{\boldsymbol{V}_{ij}}{V_{ij}^{(0)}} \hat{p}_{ij} \right\} = 0. \tag{3.4}$$

The set of equations for $\hat{p}_{ij}^{(n)}$ $(n = 1,2,\ldots)$ can also be obtained by substitution of the expansion (3.3) in (3.4). The boundary conditions are

$$\hat{p}_{ij}^{(1)} \to 1, \quad \hat{p}_{ij}^{(n)} = 0 \quad (n \geqslant 2) \quad \text{as} \quad \rho \to \infty. \tag{3.5}$$

These boundary conditions are also insufficient. However, additional conditions at $\rho \to 0$ are imposed by the requirements that the outer and inner expansion be matched.

To see the similarity of the problem to the mass/heat transfer problem, we now find the equation for the first outer expansion term $\hat{p}_{ij}^{(1)}$.

Substituting (3.3) in (3.4) and taking the leading term yields the equation for the first outer expansion term. Putting the far-field asymptotic forms for $V_{ij}$, $\boldsymbol{D}_{ij}$, and $\Phi_{ij}$, (2.7), (2.8), (2.9), (2.10) and (2.17) in the resulting equation, and again taking the leading term yields

$$\nabla_\rho^2 \hat{p}_{ij}^{(1)} - \frac{V_{ij}^{(o)}}{V_{ij}^{(0)}} \cdot \nabla_\rho \hat{p}_{ij}^{(1)} = 0. \tag{3.6}$$

The van der Waals attractive potential term disappears in the outer expansion term equation owing to its rapid $s^{-6}$ decay. The outer region equation (3.6) with constant diffusivity and a uniform stream field is very similar to the convective–diffusion equation in the mass/heat transfer problem. Hence it is not surprising that the problem of coagulation at small Péclet number can be tackled by the method used in the mass/heat transfer problem at small Péclet number. The method of Acrivos & Taylor (1962) is thus used in this paper.

Following the procedure of Acrivos & Taylor (1962), it can be shown that for the inner expansion the solutions are

$$t_2(\epsilon) = \epsilon, \quad t_3(\epsilon) = \epsilon^2 \ln \epsilon, \quad t_4(\epsilon) = \epsilon^2, \tag{3.7}$$

and

$$p_{ij}^{(1)} = \mathrm{e}^{-\Phi_{ij}/kT} \left\{ 1 - 2C_\varphi \int_s^\infty \frac{\mathrm{e}^{\Phi_{ij}/kT}}{s^2 G(s)} \mathrm{d}s \right\}, \tag{3.8}$$

$$p_{ij}^{(2)} = C_\varphi p_{ij}^{(1)} + Q(s) P_1(\cos\theta), \tag{3.9}$$

$$p_{ij}^{(3)} = \tfrac{1}{3}(5H_1 - 4M_1) C_\varphi p_{ij}^{(1)}, \tag{3.10}$$

$$p_{ij}^{(4)} = R_0^{(4)} + R_1^{(4)} P_1(\cos\theta) + R_2^{(4)} P_2(\cos\theta), \tag{3.11}$$

where $P_l(\cos\theta)$ $(l = 0, 1, 2)$ are the Legendre polynomials of order $l$. The solution $p_{ij}^{(1)}$ given by (3.8) was first derived by Derjaguin & Muller (1967), and is a pure diffusion result. The integral constant $C_\varphi$ is given by

$$C_\varphi = \left\{ 2 \int_2^\infty \frac{\mathrm{e}^{\Phi_{ij}/kT}}{s^2 G(s)} \mathrm{d}s \right\}^{-1}. \tag{3.12}$$

The scalar function $Q(s)$ in the particular solution for the second inner expansion terms $p_{ij}^{(2)}$ (see (3.9)) satisfies the following ordinary differential equation:

$$\frac{\mathrm{d}}{\mathrm{d}s}\left\{ s^2 G \left[ Q \frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\Phi_{ij}}{kT}\right) + \frac{\mathrm{d}Q}{\mathrm{d}s} \right] \right\} - 2HQ = \frac{2C_\varphi L}{G} + s^2 p_{ij}^{(1)} \left[ W - L \frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\Phi_{ij}}{kT}\right) \right]. \tag{3.13}$$

with the boundary conditions

$$Q = 0 \quad \text{at} \quad s = 2, \quad Q \rightarrow -C_\varphi \quad \text{as} \quad s \rightarrow \infty. \tag{3.14}$$

The complementary solution $R_0^{(4)}$ for the fourth inner expansion term $p_{ij}^{(4)}$ (see (3.11)) is given by

$$R_0^{(4)} = A_0^{(4)} p_{ij}^{(1)} + \tfrac{1}{3} \mathrm{e}^{-\Phi_{ij}/kT} \int_2^s \mathrm{e}^{\Phi_{ij}/kT} \left\{ \frac{LQ}{G} + C_\varphi[(s-2) + (4M_1 - 5H_1) \ln \tfrac{1}{2}s] \frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\Phi_{ij}}{kT}\right) + C_\varphi \left[ 1 + \frac{4M_1 - 5H_1}{s} \right] \right\} \mathrm{d}s - \tfrac{1}{3} C_\varphi [(s-2) + (4M_1 - 5H_1) \ln \tfrac{1}{2}s], \tag{3.15}$$

where the coefficient $A_0^{(4)}$ is of the form

$$A_0^{(4)} = C_\varphi\left(\frac{2M_1-3H_1}{2}+\frac{5H_1-4M_1}{3}C_E-\frac{4M_1-3H_1}{3}\ln 2+C_\varphi-\tfrac{2}{3}\right)$$
$$-\frac{1}{3}\int_2^\infty e^{\Phi_{ij}/kT}\left\{\frac{LQ}{G}+C_\varphi[(s-2)+(4M_1-5H_1)\ln\tfrac{1}{2}s]\frac{d}{ds}\left(\frac{\Phi_{ij}}{kT}\right)\right.$$
$$\left.+C_\varphi\left[1+\frac{4M_1-5H_1}{s}\right]\right\}ds. \tag{3.16}$$

Here $C_E = 0.577216$ is the Euler constant. The precise forms of the scalar functions $R_1^{(4)}$ and $R_2^{(4)}$ in the particular solutions of the fourth inner expansion term $p_{ij}^{(4)}$ are not required in the present work, since only the coagulation rate is considered in this paper (see next section).

In outer region, the solutions of outer expansion are found to be

$$\hat{t}_2(\epsilon) = \epsilon, \quad \hat{t}_3(\epsilon) = \epsilon^2, \tag{3.17}$$

and $$\hat{p}_{ij}^{(1)} = 1, \tag{3.18}$$

$$\hat{p}_{ij}^{(2)} = -\frac{2C_\varphi}{\rho}e^{-\frac{1}{2}\rho(1-\cos\theta)}, \tag{3.19}$$

$$\hat{p}_{ij}^{(3)} = e^{\frac{1}{2}\rho\cos\theta}\left\{e^{-\frac{1}{2}\rho}\sum_{l=0}^{2}\pi B_l^{(3)}P_l(\cos\theta)\sum_{m=0}^{l}\frac{(l+m)!}{(l-m)!\,m!}\frac{1}{\rho^{m+1}}+\sum_{l=0}^{2}u_l^{(3)}\right\}, \tag{3.20}$$

where the integral constants $B_l^{(3)}$ $(l = 0,1,2)$ are as follows:

$$B_0^{(3)} = \frac{C_\varphi}{\pi}\left(H_1-2C_\varphi-\frac{5H_1-4M_1}{3}C_E\right), \tag{3.21}$$

$$B_1^{(3)} = -\frac{2C_\varphi}{\pi}(M_1-H_1)(C_E-1), \tag{3.22}$$

$$B_2^{(3)} = \frac{C_\varphi}{3\pi}(H_1-3M_1)(3-C_E), \tag{3.23}$$

and the particular solutions $u_l^{(3)}$ $(l = 0,1,2)$ are

$$u_0^{(3)} = C_\varphi P_0(\cos\theta)\left\{\frac{2H_1}{\rho^2}e^{-\frac{1}{2}\rho}-\frac{5H_1-4M_1}{3}\left[\frac{e^{\frac{1}{2}\rho}}{\rho}\int_\rho^\infty\frac{e^{-x}}{x}dx+\frac{\ln\rho}{\rho}e^{-\frac{1}{2}\rho}\right]\right\}, \tag{3.24}$$

$$u_1^{(3)} = 2C_\varphi(M_1-H_1)P_1(\cos\theta)\left[\frac{1}{\rho}\left(1-\frac{2}{\rho}\right)e^{\frac{1}{2}\rho}\int_\rho^\infty\frac{e^{-x}}{x}dx\right.$$
$$\left.-\frac{1}{\rho}\left(1+\frac{2}{\rho}\right)e^{-\frac{1}{2}\rho}\ln\rho-\frac{2}{\rho^2}e^{-\frac{1}{2}\rho}\right], \tag{3.25}$$

$$u_2^{(3)} = -\tfrac{1}{3}C_\varphi(H_1-2M_1)P_2(\cos\theta)\left[\frac{1}{\rho}\left(1-\frac{6}{\rho}+\frac{12}{\rho^2}\right)e^{\frac{1}{2}\rho}\int_\rho^\infty\frac{e^{-x}}{x}dx\right.$$
$$\left.+\frac{1}{\rho}\left(1+\frac{6}{\rho}+\frac{12}{\rho}\right)e^{-\frac{1}{2}\rho}\ln\rho+\frac{6}{\rho^2}\left(1+\frac{6}{\rho}\right)e^{-\frac{1}{2}\rho}\right]. \tag{3.26}$$

## 4. The calculation of the coagulation rate

The coagulation rate $F_{ij}$ is actually the net flux of sphere $j$ across the contact surface enclosing the test sphere $i$, viz.

$$F_{ij} = n_j \int_{r=a_i+a_j} \left\{ -\boldsymbol{V}_{ij} p_{ij} + p_{ij} \boldsymbol{D}_{ij} \cdot \nabla_r \left( \frac{\Phi_{ij}}{kT} \right) + \boldsymbol{D}_{ij} \cdot \nabla_r p_{ij} \right\} \cdot \boldsymbol{n} \, \mathrm{d}A. \tag{4.1}$$

We define the dimensionless coagulation rate Nusselt number $\mathscr{N}_{ij}$ as the dimensionless net flux of sphere $j$ scaled on the zero-Péclet-number net flux, then

$$\mathscr{N}_{ij} = \frac{F_{ij}}{4\pi (a_i + a_j) C_\varphi D_{ij}^{(0)} n_j} = \frac{1}{C_\varphi} \int_0^\pi \left\{ G \left[ p_{ij} \frac{\mathrm{d}}{\mathrm{d}s} \left( \frac{\Phi_{ij}}{kT} \right) + \frac{\partial p_{ij}}{\partial s} \right] \right\}_{s=2} \sin\theta \, \mathrm{d}\theta. \tag{4.2}$$

Expanding $p_{ij}$ in terms of Legendre polynomials $P_l(\cos\theta)$, it is evident that by virtue of the orthogonality of $P_l(\cos\theta)$, only those $P_0(\cos\theta)$ terms in $p_{ij}$ – say $p_{ij}^0$ – contribute to the flux integral in (4.2). Thus we have

$$\mathscr{N}_{ij} = \frac{2}{C_\varphi} \lim_{s\to 2} \left\{ G \left[ p_{ij}^0 \frac{\mathrm{d}}{\mathrm{d}s} \left( \frac{\Phi_{ij}}{kT} \right) + \frac{\mathrm{d} p_{ij}^0}{\mathrm{d}s} \right] \right\}. \tag{4.3}$$

Substituting the inner expansion (3.1) with (3.7), (3.8), (3.9), (3.10), (3.11) in (4.3) yields the four-term expansion for $\mathscr{N}_{ij}$ namely

$$\mathscr{N}_{ij} = 1 + C_\varphi \mathscr{P}_{ij} + \frac{2\lambda^4\gamma - 3\lambda^3\gamma + 3\lambda - 2}{(\lambda^2\gamma - 1)(1+\lambda)^2} C_\varphi \mathscr{P}_{ij}^2 \ln \mathscr{P}_{ij} + A_0^{(4)} \mathscr{P}_{ij}^2 + o(\mathscr{P}_{ij}^2), \tag{4.4}$$

where the coefficient of the fourth term $A_0^{(4)}$ is given by (3.16). The first two terms of the expansion (4.4) agree with the result of Melik & Fogler (1984*a*). Their incorrect $s^{-2}$ decay of the van der Waals potential does not affect their two-term expansion, since $s^{-2}$ decay makes the interparticle potential term in the first two outer expansion term equations disappear. The second inner expansion term $p_{ij}^{(2)}$ given by (3.9) is thus the same as Melik & Fogler's solution (63) in their 1984*a* paper. However, the $s^{-2}$ decay will certainly affect the third and the fourth term, since in that case there will be an interparticle potential term appearing as a non-homogeneous term in the corresponding outer expansion equations, whereas the more rapid $s^{-6}$ decay will still make them disappear.

In order to gain a better understanding of the coupled Brownian and and gravity-induced coagulation process, the dimensionless coagulation rate $\mathscr{N}_{ij}$ as function of the Péclet number has been calculated for a typical hydrosol dispersion in which $\gamma = 1, \lambda = 0.5, A = 5 \times 10^{-21}$ J and $kT = 4 \times 10^{-21}$ J (then $A/kT = 1.25$) (Davis 1984). Figure 1 gives the computed results for $0 \leqslant \mathscr{P}_{ij} \leqslant 1$. (From (3.12), (3.16), it can be shown that $C_\varphi = 0.570$, and $A_0^{(4)} = -0.0976$. The size ratio 0.5 has been chosen since this case might show a more clear effect of the gravity-induced motion.)

Curve 1 in figure 1 corresponds to the result of Melik & Fogler. The term $C_\varphi \mathscr{P}_{ij}$ is the leading term of the effects of gravity-induced motion on the Brownian coagulation rate. It is always positive. In the outer region, the leading term of the gravitational relative velocity of the two spheres is $V_{ij}^{(0)}$, which is a uniform stream field. The uniform stream field transfers sphere $j$ from infinity to $s \sim O(\mathscr{P}_{ij}^{-1})$ without changing the concentration of sphere $j$. It thus increases the overall concentration difference of sphere $j$ in the inner region. The increase of the overall concentration difference enhances the Brownian diffusive flux of sphere $j$, then enhances the

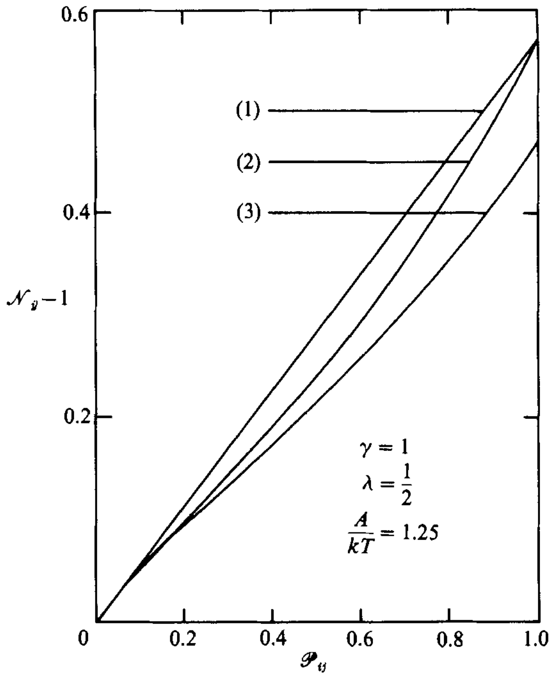


FIGURE 1. The dimensionless coagulation rate at small Péclet number: (1) $\mathcal{N}_{ij} = 1 + C_{\varphi}\mathscr{P}_{ij}$; (2) the first three terms of expansion (4.4); (3) the four-term expansion (4.4).

Brownian coagulation rate. Curves 2 and 3 show the effects of successive addition of further terms in the Nusselt number expansion. Actually they show the effects of the hydrodynamic interactions between the two spheres on the uniform stream field $V_{ij}^{(0)}$ and the constant diffusivity $D_{ij}^{(0)}$ in the outer region, and then on the Brownian coagulation rate. The effects can either be positive or negative. For the case shown in figure 1, the effects of the third and the fourth term are both negative. However, the modifications made by these terms must be small as indicated by curve 2 and curve 3, since they are terms of an asymptotic expansion. Therefore, the gravity-induced motion always increases the Brownian coagulation rate.

## 5. The connection between the problems of coagulation and mass transfer

Acrivos & Taylor (1962) obtained the asymptotic expansion of the dimensionless mass transfer rate $N$ for a sphere with radius $a$ immersed in a uniform external flow in terms of the Péclet number $P$ for $P \ll 1$, which truncated to order $O(P^2)$ is given by

$$N = \frac{F}{4\pi a K(C_1 - C_0)} = 1 + P + 2P^2 \ln P + [\tfrac{121}{240} + 2(C_E + \ln 2)]P^2 + o(P^2). \qquad (5.1)$$

Here $F$ is the dimensional mass transfer rate, $4\pi a K(C_1 - C_0)$ is the zero-Péclet-number mass transfer rate, $K$ the molecular diffusivity, $C_1$ and $C_0$ the concentration at the surface of the sphere and that at infinity. $P$ is defined as $aU_\infty/2k$, where $U_\infty$ is the velocity of the external uniform flow.

On the other hand, as $\lambda \to 0$, and $a_j \to 0$, we have

$$L(s) \to 1 - \frac{3}{s} + \frac{4}{s^3}, \tag{5.2a}$$

$$M(s) \to 1 - \frac{3}{2s} - \frac{4}{s^3}, \quad W(s) \to 0, \tag{5.2b}$$

$$G(s) \to 1, \quad H(s) \to 1, \tag{5.2c}$$

$$\Phi_{ij} \to 1, \quad C_\varphi \to 1, \tag{5.2d}$$

$$M_1 \to -\tfrac{3}{2}, \quad H_1 \to 0. \tag{5.2e}$$

Substituting (5.2*a–e*) in (3.13), the solution for $Q(s)$ satisfying the boundary condition (3.14) can be found to be

$$Q(s) = -1 + \frac{3}{s} - \frac{3}{s^2} + \frac{2}{s^3}. \tag{5.3}$$

Then substitution of (5.2*a–c*) and (5.3) in (3.16) yields

$$A_0^{(4)} = \tfrac{121}{240} + 2(C_E + \ln 2). \tag{5.4}$$

With the results (5.2*d*) and (5.4). The four-term expansion for the dimensionless coagulation rate (4.4) reduces to

$$\mathscr{N}_{ij} = \frac{F_{ij}}{4\pi a_i D_{ij}^{(0)} n_j} = 1 + \mathscr{P}_{ij} + 2\mathscr{P}_{ij}^2 \ln \mathscr{P}_{ij} + [\tfrac{121}{240} + 2(C_E + \ln 2)]\mathscr{P}_{ij}^2 + o(\mathscr{P}_{ij}^2). \tag{5.5}$$

The Péclet number $\mathscr{P}_{ij}$ now reduces to $a_i V_i^{(0)}/2D_{ij}^{(0)}$, where $V_i^{(0)}$ is the Stokes terminal velocity of the test sphere $i$ under gravity. Comparing (5.1) with (5.5), it appears that (5.5) agrees with (5.1), if we make the assumptions that as $\lambda \to 0$, $a_j \to 0$, then $a_i \to a$, $D_{ij}^{(0)} \to K$, $n_j \to (C_1 - C_0)$, $V_i^{(0)} \to U_\infty$.

The fact that the coagulation rate in the limit of the radius of sphere $j$ becoming small agrees with the mass transfer rate is remarkable, but is not a surprise. In fact, it is easy to understand from the viewpoint of a physical model for coagulation. When $\lambda \to 0$, $a_j \to 0$, the effect of sphere $j$ on the flow field due to the settling of sphere $i$ disappears, and sphere $j$ moves in the same way as a fluid point. Thus the flow field tends to that produced by a sphere immersed in a given uniform flow. As $\lambda \to 0$, $\boldsymbol{D}_{ij}$ tends to $D_{ij}^{(0)}\boldsymbol{I}$, $\Phi_{ij} \to 0$ ($A \neq 0$ is required). Thus the coagulation model formally reduces to the mass transfer model.

## 6. Discussion

In §3, we have used the far-field asymptotic form for the van der Waals potential, (2.17), without considering the retardation effects and the repulsive potential. However, it is not difficult to see that the form of the four-term expansion for Nusselt number (4.4) would be unchanged even when we include the effects of retardation and the repulsive potential.

According to DLVO theory (Derjaguin & Landay 1941; Verwey & Overbeek 1948), the total interparticle potential $\Phi_{ij}$ can be obtained by summing the attractive and repulsive potential. Form (2.20) we have seen that, for the case of rapid flocculation, the decay of the thin double layer potential is much more rapid than $s^{-6}$ as $s \to \infty$.

Hence the repulsive potential term cannot appear in the outer expansion term equations, and the form of the resulting expansion for $\mathcal{N}_{ij}$ should be the same as before. Of course, the values of $C_\varphi$ and $A_0^{(4)}$ should be changed when the repulsive potential is considered.

The far-field asymptotic form of the retarded van der Waals potential for an unequal-size system seems to be not available. The expression (2.18) is valid only for an equal-size system. Perhaps the right-hand side of (2.18) should be multiplied by a numerical coefficient which depends on $\lambda$, and the dimensionless London wavelength $\lambda_L$ should be scaled on the average radius $\frac{1}{2}(a_i+a_j)$ when the unequal-size system is considered. In the case of the near-field asymptotic expansion, the numerical coefficient is $4\lambda/(1+\lambda)^2$ (Davis 1984), and the dimensionless London wavelength is just scaled on $\frac{1}{2}(a_i+a_j)$ (Melik & Fogler 1984*b*). If the above supposition is right, then the decay of the retarded attractive potential would still be $s^{-7}$ as $s \to \infty$, and would still make it disappear in the outer expansion term equation. The same is true even if the above supposition is not right. Anyway, the decay of the retarded van der Waals potential should be more rapid than $s^{-6}$, since the effect of retardation is to weaken the van der Waals attractive potential. Thus the form of the four-term expansion for $\mathcal{N}_{ij}$ (4.4) would be unchanged even if we include retardation effects. The only things changed are the values of $C_\varphi$ and $A_0^{(4)}$. They should be smaller than those obtained from (2.16) and (2.17), since both retardation and repulsive potential contribute negative effects on the van der Waals attractive potential. Incidentally, the incorrect $s^{-2}$ decay used by Melik & Fogler (1984*a*) should also affect the value of $C_\varphi$ (i.e. $W_{Br}$ in their paper). The values of their $C_\varphi$ would possibly be larger than the actual values of $C_\varphi$ owing to the fairly slow $s^{-2}$ decay of the retarded attractive potential.

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