# The Effect of Weak Shear–induced Motion on Brownian Coagulation of Aerosol Particles①

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ABSTRACT

The coagulation rate of a dilute polydisperse aerosol dispersion of particles is considered for small Peclet number, which provides a measure of the ratio of the relative shear–induced motion to Brownian motion between two rigid spherical aerosol particles. The asymptotic form of the relative velocity of two unequal particles immersed in a simple shear flow when they are far apart is obtained. Using a singular perturbation method, a two term expansion for the dimensionless coagulation rate (Nusselt number) as function of the Peclet number is developed. In the limit of the radius of one of the two spheres becoming small, the result agrees with the dimensionless mass transfer rate to an aerosol particle at small Peclet number.

**Key words**: Aerosol dynamics, Coagulation, Peclet number

## I. INTRODUCTION

We consider in this paper the coagulation rate of a dilute polydisperse, statistically homogeneous aerosol dispersion of small rigid spherical particles. The particles have relative bulk convection due to simple shear ambient flow. 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 aerosol 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 shear–induced motion on Brownian coagulation is found by means of a two–term expansion for the dimensionless coagulation rate (Nusselt number).

The method of calculation involves use of the pair–distribution function $p_{ij}(\vec{r})$, 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 shear–induced motion between the test sphere $i$ and a sphere $j$ is negligible when the Peclet number is small. However, far from the test sphere $i$ (the outer region) the relative shear–induced motion is no longer small and must be taken into account. Then in the outer region Brownian motion balances the relative shear–induced motion, and the influence of interparticle force is negligible owing to its rapid decay. Thus, an expansion in terms of Peclet number, $P_{ij}$, for $p_{ij}(\vec{r})$ is not valid for large distances of sphere $j$ from sphere $i$ (inner expansion). It has therefore to be

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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 and Mason (1977) calculated the case of weak shear–induced / strong Brownian motion coagulation rate of a monodisperse dispersion as far as the second term of order $P_{ij}^{1/2}$, and Melik and Fogler (1984) calculated the case of weak gravity–induced / strong Brownian motion coagulation rate as far as the second term of order $P_{ij}$. Wang and Wen (1990) calculated the same case as Melik and Fogler as far as the fourth term of order $P_{ij}^2$. The prupose of this paper is simply to generalize the analysis of van de Ven and Mason (1977) from the case of a monodisperse dispersion to the case of a polydisperse dispersion.

The basic procedure of the method of matched asymptotic expansions used in this paper is the same as the one described by van Dyke (1975). For a detailed description of the method, the reader is referred to van Dyke (1975). It is of interest to note that the problem of coagulation has some connection with the problem of mass transfer. The result of this paper agrees with the mass transfer result, when the radius of sphere j approaches zero.

## II. THE STATEMENT OF THE PROBLEM

For a dilute dispersion of small spherical particles in a fluid subjected to Brownian motion, interparticle force potential and forced convection, the governing equation for the pair–distribution function $p_{ij}(\vec{r})$ which represents the probability in a unit volume of finding the centre of particle $j$ at the position $\vec{r}$ relative to the centre of the test particle $i$ is (Wen and Batchelor 1985)

$$\frac{\partial p_{ij}}{\partial t} + \nabla \cdot \left\{ \vec{V}_{ij}^{*} - \vec{\mathbf{D}}_{ij} \cdot \nabla \left(\frac{\Phi_{ij}}{kT}\right) p_{ij} - \vec{\mathbf{D}}_{ij} \cdot \nabla p_{ij} \right\} = 0, \tag{1}$$

where $\vec{V}_{ij}^{*}$ is the relative shear–induced velocity, $\vec{\mathbf{D}}_{ij}$ is the relative Brownian diffusivity tensor, $\Phi_{ij}$ is the interparticle force potential (here is the van der Waals attractive potential for the case of rapid coagulation), $k$ the Boltzmann constant and $T$ the absolute temperature of the fluid.

Since the dispersion is assumed to be 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 and Mason (1977) and by Melik and Fogler (1984), (note that the van der Waals potential just satisfies these requirements), a steady state can be approximately reached in the initial stage of the coagulation process. Thus, Eq. (1) reduces to

$$\nabla \cdot \left( \vec{V}_{ij}^{*} p_{ij} - \vec{\mathbf{D}}_{ij} \cdot \nabla \left(\frac{\Phi_{ij}}{kT}\right) p_{ij} - \vec{\mathbf{D}}_{ij} \cdot p_{ij} \right) = 0, \tag{2}$$

and the boundary conditions are (Wen and Batchelor, 1985)

$$p_{ij} = 0 \qquad \text{at} \qquad r = a_i + a_j, \tag{3}$$

$$p_{ij} \to 0 \qquad \text{as} \qquad r \to \infty, \tag{4}$$

where $a_i$ and $a_j$ are the radius of the sphere $i$ and sphere $j$ respectively.

We consider a set of Cartesian coordinates, the axis $Ox^{*}$ is in the direction parallel to the ambient simple shear flow velocity $\vec{U}^{*}$, $Oy^{*}$ is perpendicular to the zero velocity plane of the ambient flow, so that the ambient flow velocity $\vec{U}^{*}$ is expressed as

$$\vec{U}^{*} = \Gamma y^{*} \vec{e}_{x^{*}}, \tag{5}$$

where $\Gamma$ is the shearing rate of the ambient flow. We now nondimensionalize Eq. (2) and the boundary conditions (3), (4) by choosing $(a_i + a_j)/2$ as the representative magnitude of $r$, $D_{ij}^{(0)}$ as the representative magnitude of $\overline{\mathbf{D}}_{ij}$ which is the value of the relative Brownian diffusivity as $r \to \infty$, and $\Gamma(a_i + a_j)/2$ as the representative magnitude of $\vec{V}_{ij}^*$. Then Eqs. (2), (3), (4) and (5) are given in dimensionless form by

$$\nabla_s \left\{ \frac{\overline{\mathbf{D}}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_s p_{ij} \right\} + \nabla_s \left\{ \frac{\overline{\mathbf{D}}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_s \left( \frac{\Phi_{ij}}{kt} \right) p_{ij} \right\} = P_{ij} \nabla_s \cdot \{ \vec{V}_{ij} p_{ij} \}, \tag{6}$$

$$p_{ij} = 0 \quad \text{at} \quad s = 2, \tag{7}$$

$$p_{ij} \to 0 \quad \text{as} \quad s \to \infty, \tag{8}$$

$$\vec{U} = y \vec{e}_x, \tag{9}$$

where $\vec{s} = 2\vec{r} / (a_i + a_j)$ and $s = |\vec{s}|$, $P_{ij}$ is the Peclet number and $P_{ij} = \Gamma(a_i + a_j)^2 / 4D_{ij}^{(0)}$, $\vec{V}_{ij} = 2\vec{V}_{ij}^* / \Gamma(a_i + a_j)$, $\vec{U}$, $y$, $x$ are the dimensionless ambient velocity and the dimensionless coordinates.

The dimensionless relative Brownian diffusivity tensor is given by (Batchelor, 1982)

$$\frac{\overline{\mathbf{D}}_{ij}}{D_{ij}^{(0)}} = G(s) \frac{\vec{s}\vec{s}}{s^2} + H(s) \left( \overline{\mathbf{I}} - \frac{\vec{s}\vec{s}}{s^2} \right), \tag{10}$$

where the longitudinal scalar function $G(s)$ and the transverse scalar function $H(s)$ are known functions of $s$ from low–Reynolds–number hydrodynamics (Jeffrey and Onishi, 1984), and have been calculated for two unequal rigid spheres by Batchelor and Wen (1982). In this paper only the far field asymptotic forms of G and $H$ are needed to be known explicitly. Substituting the far field asymptotic expression of the mobility function (Jeffrey and Onishi, 1984) into the expression of $G$ and $H$ given by Batchelor (1982), we have

$$G(s) = 1 + \frac{G_1}{s} + O(s^{-3}), \tag{11}$$

$$H(s) = 1 + \frac{H_1}{s} + O(s^{-3}), \tag{12}$$

where

$$G_1 = 2H_1 = -\frac{6\lambda}{(1+\lambda)^2}. \tag{13}$$

Here $\lambda$ is the size ratio of the two spheres, $\lambda = a_j / a_i$. Only the case of rapid flocculation is considered in this paper. The interparticle force potential is thus dominated by the attractive van der Waals potential and the retardation effects are neglected temporally in this section. Then, $\Phi_{ij}$ is given by (Hamaker, 1937)

$$\Phi_{ij} = -\frac{A}{6} \left[ \frac{8\lambda}{(s^2 - 4)(1+\lambda)^2} + \frac{8\lambda}{s^2(1+\lambda)^2 - 4(1-\lambda)^2} + \ln \frac{(s^2 - 4)(1+\lambda)^2}{s^2(1+\lambda)^2 - 4(1-\lambda)^2} \right], \tag{14}$$

where $A$ is the composite Hamaker constant. From (14) it can be easily shown that the far field asymptotic form for $\Phi_{ij}$ is (Wang and Wen, 1990)

$$\Phi_{ij} = -\frac{1024}{9}\frac{A\lambda^3}{(1+\lambda)^6}\frac{1}{s^6} + O(s^{-8}). \tag{15}$$

III. THE ASYMPTOTIC FORM OF $\vec{V}_{ij}$ AS $s \to \infty$

At first, the particle $j$ is assumed to be so far away from particle $i$ that they move separately in the ambient flow with no hydrodynamic interaction. Then the velocity of sphere $j$ is the same as its local flow. The velocity of sphere $j$ relative to sphere $i$ is then

$$\vec{V}_{ij}^{*(0)} = \Gamma y^* \vec{e}_{x^*}. \tag{16}$$

In the second place, we consider the leading term of the hydrodynamic interaction between the two particles. Suppose that only particle $i$ exists in the ambient flow. From Eq. (12) of Wen, Zeng and Wang (1994), the leading term of the modification of the existence of particle i is of order $r^{*-2}$:

$$\overline{\Delta\vec{V}}_i^{*(1)} = -\frac{5a_i\Gamma}{(1+\lambda)^2}\frac{1}{s^2}\sin^2\theta\sin2\varphi\vec{e}_s + O(s^{-4}). \tag{17}$$

If particle $j$ is at the position $\overrightarrow{r^*}$, its velocity relative to the space point which coincides with the centre of the particle $i$ is $\vec{V}_{ij}^{*(0)} + \overline{\Delta\vec{V}}_i^{*(1)}$. Furthermore, particle $i$ itself is moving relative to the space point due to the existence of particle $j$ in the flow. Similar to (17) its velocity is

$$\overline{\Delta\vec{V}}_j^{*(1)} = -\frac{5a_i\Gamma\lambda^2}{(1+\lambda)^2}\frac{1}{s^2}\sin^2\theta\sin2\varphi\vec{e}_s + O(s^{-4}). \tag{18}$$

Thus, as $s \to \infty$ the velocity of particle j relative to particle $i$ is

$$\vec{V}_{ij} = y\vec{e}_x - \frac{10(1-\lambda+\lambda^2)}{(1+\lambda)^2}\frac{1}{s^2}\sin^2\theta\sin2\varphi\vec{e}_s + O(s^{-4}). \tag{19}$$

This result agrees with a recent more detailed deduction given by Wang (1992). Similarly, further terms can be found out. However, in this paper it is sufficient to know that the second term of the asymptotic expansion of $\vec{V}_{ij}$ as $s \to \infty$ is of order $s^{-2}$ and its divergence is of order $s^{-4}$, i.e.

$$\nabla \cdot \vec{V}_{ij} = O(s^{-4}). \tag{20}$$

IV. THE CONSTRUCTION OF THE ASYMPTOTIC SOLUTION

It can be shown that the perturbation problem of Eq. (6) with the boundary conditions (7) and (8) is a singular perturbation problem. The non-uniformity region is $s \sim s_c = O(P_{ij}^{-1/2})$. To handle the problem in this region, we choose the following contracted variable

$$\rho = P_{ij}^{1/2} s \tag{21}$$

as the outer variable and we denote $p_{ij}$ by $\hat{p}_{ij}$ in the outer region. Then, the outer equation is given by

$$\nabla \cdot \left\{ \frac{\vec{\mathbf{D}}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_\rho \hat{p}_{ij} - \frac{\vec{\mathbf{D}}_{ij}}{D_{ij}^{(0)}} \cdot \nabla_\rho \left(\frac{\Phi_{ij}}{kT}\right)\hat{p}_{ij} - \vec{V}_{ij}\hat{p}_{ij} \right\} = 0. \tag{22}$$

The inner equation is (6). The inner region and outer region solutions are assumed to be of the forms

$$p_{ij}(\bar{s}) = \sum_{n=1}^{\infty} t^{(n)}(\varepsilon) p_{ij}^{(n)}(\bar{s}), \tag{23}$$

$$\hat{p}_{ij}(\bar{\rho}) = \sum_{n=1}^{\infty} \hat{t}^{(n)}(\varepsilon) \hat{p}_{ij}^{(n)}(\bar{\rho}), \tag{24}$$

respectively, where $\varepsilon$ is the perturbation parameter, $\varepsilon = P_{ij}$, and $t^{(n)}(\varepsilon)$ and $\hat{t}^{(n)}(\varepsilon)$ are asymptotic sequences with

$$t^{(1)}(\varepsilon) = 1. \tag{25}$$

The boundary conditions for $p_{ij}^{(n)}(\bar{s})$ and $\hat{p}_{ij}{}^{(n)}(\bar{\rho})$ are

$$p_{ij}^{(n)} = 0 \quad \text{at} \quad s = 2, \tag{26}$$

$$\hat{p}_{ij}^{(1)} \to 1 \quad \text{as} \quad \rho \to \infty, \tag{27a}$$

$$\hat{p}_{ij}^{(1)} \to 0 \quad \text{as} \quad \rho \to \infty \quad \text{for} \quad n \geqslant 2. \tag{27b}$$

These boundary conditions are insufficient to uniquely determined $p_{ij}^{(n)}$ and $\hat{p}_{ij}^{(n)}$. However, additional conditions at $s \to \infty$ and $\rho \to 0$ are furnished by matching the inner and outer expansions in their common domains of validity.

Following a procedure similar to that used in Wang and Wen (1990), the first two terms of the inner and outer expansions are found to be

$$p_{ij}^{(1)} = e^{-\Phi_{ij}/kT}\left[1 - 2C_\Phi \int_s^\infty \frac{e^{-\Phi_{ij}/kT}}{s^2 G(s)} \mathrm{d}s\right], \tag{28}$$

$$p_{ij}^{(2)} = 2C_\Phi \beta_0 p_{ij}^{(1)}, \tag{29}$$

$$\hat{p}_{ij}^{(1)} = 1, \tag{30}$$

$$\hat{p}_{ij}^{(2)} = 2\hat{C}^{(1)}, \tag{31}$$

and

$$t^{(2)} = P_{ij}^{1/2}, \qquad \hat{t}^{(1)} = 1, \qquad \hat{t}^{(2)} = P_{ij}^{1/2}, \tag{32}$$

where $C_\Phi$ is given by

$$C_\Phi = \left\{ 2\int_s^\infty \frac{e^{-\Phi_{ij}/kT}}{s^2 G(s)} \mathrm{d}s \right\}^{-1}, \tag{33}$$

$\beta_0$ is given by

$$\beta_0 = \frac{1}{2\pi^{1/2}} \int_0^\infty \frac{\mathrm{d}s}{s^{3/2}} \left[1 - \frac{1}{(1 + \frac{1}{12}s^2)^3}\right] = \frac{0.914}{2\pi^{1/2}}, \tag{34}$$

$\hat{C}^{(1)}$ is given by

$$\hat{C}^{(1)} = \frac{1}{2\pi^{1/2}} \int_0^{\infty} \frac{ds}{s^{3/2}(1+\frac{1}{12}s^2)^{1/2}} \exp\left\{ -\left[ \frac{(\hat{x}-\frac{1}{2}\hat{y}s)^2}{4(1+\frac{1}{12}s^2)s} + \frac{\hat{y}^2+\hat{z}^2}{4s} \right] \right\}. \tag{35}$$

Solution (28) was first derived by Derjaguin and Muller(1967) for zero–Peclet–number problem and the corresponding coagulation rate $F_{ij}^{(0)}$ was

$$F_{ij}^{(0)} = 4\pi(a_i + a_j) C_{\Phi} D_{ij}^{(0)} n_j, \tag{36}$$

where $n_j$ is the number density of particle $j$. We use $F_{ij}^{(0)}$ to define the dimensionless coagulation rate $N_{ij}$. i.e.

$$N_{ij} = \frac{F_{ij}}{F_{ij}^{(0)}}, \tag{37}$$

where the dimensional coagulation rate is actually the net flux of sphere $j$ across the contact surface $r = a_i + a_j$ enclosing the test sphere $i$, viz.

$$F_{ij} = n_j \int_{r=a_i+a_j} \{ -\vec{V}_{ij} p_{ij} + p_{ij} \vec{\mathbf{D}} \cdot \nabla_r (\frac{\Phi_{ij}}{kT}) + \vec{\mathbf{D}} \cdot \nabla_r p_{ij} \} \cdot \vec{n} dA. \tag{38}$$

Then,

$$N_{ij} = \frac{2}{C_{\Phi}} \lim_{s \to 2} \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \{ G[p_{ij} \frac{d}{ds}(\Phi_{ij} / kT \quad ) + \frac{dp_{ij}}{ds}] \} \sin\theta d\theta d\varphi. \tag{39}$$

From (39), (23), (25), (28)–(32), the asymptotic expansion for $N_{ij}$ is found to be

$$\begin{aligned} N_{ij} &= 1 + 2C_{\Phi}\beta_0 P_{ij}^{1/2} + O(P_{ij}^{1/2}) \\ &= 1 + 2C_{\Phi}\beta_0 \left[ \frac{\Gamma a_i^2 (1+\lambda)^2}{4D_{ij}^{(0)}} \right]^{1/2} + O\left( \left[ \frac{\Gamma a_i^2 (1+\lambda)^2}{4D_{ij}^{(0)}} \right]^{1/2} \right). \end{aligned} \tag{40}$$

The first term in Eq. (40) is of course the pure Brownian diffusion result. the second term represents the leading term of the effect of the weak shear flow on Brownian coagulation. It is always positive. The effect of weak shear is always to increase the coagulation rate. Similar to the case of mass transfer, the increase is due to the increase of the overall concentration difference of particle $j$ within the region $s \sim s_c$ caused by the simple shear flow.

## V. THE RELATION BETWEEN THE COAGULATION RATE AND MASS TRANSFER RATE

As $a_j \to 0$, $\lambda \to 0$, then $C_{\Phi} \to 1$, Eq. (40) reduces to

$$F_{ij} \big|_{\lambda \to \infty} = 4\pi a_i D_{ij}^{(0)} n_j [1 + \beta_0 (\frac{\Gamma a_i^2}{D_{ij}^{(0)}})^{1/2}] + O([\frac{\Gamma a_i^2}{D_{ij}^{(0)}}]^{1/2}). \tag{41}$$

If we consider $a_i$ as the radius a of a spherical particle in the mass transfer problem, $D_{ij}^{(0)}$ as the diffusivity of the diffusivible quantity, $n_j$ as the concentration difference of the diffusivible quantity between the surface of the particle and infinity, (41) agrees with the mass transfer rate (see the first two terms of the expansion (49) in Wen, Zeng and Wang, 1994).

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 view point 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 test sphere $i$ immersed in a simple shear flow 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 shear flow. As $\lambda \to 0$, $\vec{\mathbf{D}}_{ij}$ tends to $D_{ij}^{(0)}\vec{\mathbf{I}}$, ($A \neq 0$ is required). Thus the coagulation model formally reduces to the mass transfer model.

## VI. COMPARISON WITH VAN DE VEN AND MASON'S WORK

van de Ven and Mason (1977) calculated the leading term of the effect of a weak shear ambient flow on the coagulation rate of a monodisperse dispersion ($\lambda = 1$), and gave the expansion for the coagulation rate $j$ as

$$J = 16\pi C_{\Phi} N_0 D_0 b[1 + 2C_{\Phi}\beta_0(\frac{\Gamma b^2}{D_0})^{1/2}] + O(\frac{\Gamma b^2}{D_0}), \tag{42}$$

where $N_0$ is the number density of the spherical particle, $D_0$ is the Brownian diffusivity for a single particle. This is exactly the case with $\lambda = 1$ studied in this paper. However, the result is different from that given by (40) with $\lambda = 1$ by a factor $1/\sqrt{2}$ in the correction term.

In van de Ven and Mason (1977), the Brownian diffusivity tensor in the governing equation for the pair–distribution function is taken as half of the mutual Brownian diffusivity tensor. To account for the mutual diffusivity, a factor 2 is added in the formulae by which the coagulation rate is derived from the inner expansion of the pair–distribution function. This assumes that the coagulation rate is proportional to $D_0$. It is true for the first term in (42). However, the second term is in fact proportional to $\sqrt{D_0}$. Thus, the coagulation rate is overestimated by a factor $\sqrt{2}$.

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