

## **Analytical Investigation in Brownian Diffusion of Airborne Particles with Slip/No-slip Interfaces**

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### **Abstract**

The Brownian motion for an aerosol dispersion stating that suspending particles are rigid and the surrounding fluid may slip and/or not slip at the solid-fluid interface was investigated analytically. Particles were assumed to be close enough to interact hydrodynamically. Based on Einstein's prescription of Brownian motion, the Brownian diffusivities in two different types of situation were deduced. The first concerned a homogeneous dilute suspension, and the relative diffusivity of two rigid slip/no-slip spheres with a given separation was derived. The second concerned a suspension in which there was a gradient in concentration of particles. The thermodynamic force on each particle in this case was shown to be equal to the gradient of the physical potential of particles, which brings considerations of the multiparticle-excluded volume into the problem. Determination of the sedimentation velocity of particles falling through fluid under gravity, for which a theoretical result corrected to the first order in volume fraction of the particles, was available. The diffusivity of the particles was found to increase slowly as the concentration rose from zero. These results were generalized to the case of an (dilute) inhomogeneous suspension of several different species of particle with slip/no-slip surfaces, and expressions were obtained for the diagonal and off-diagonal elements of the diffusivity matrix. Our results, presented in simple closed forms, agreed very well with the existing solutions for the limiting cases of no-slip at the particles' surfaces. Also, the limiting diffusion situations of perfect-slip particles in gas or spherical gas bubbles in liquid were considered in this article.

**Keywords:** Diffusion; Particle interactions, Concentration gradient; Polydispersed aerosol.

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## INTRODUCTION

The unpredictable motion of small particles suspended in a fluid is known as Brownian motion, which is ascribed to the impact of molecules of the suspending medium (more actually, raised from the random fluctuations in the density of the fluid molecules). This phenomenon is named for Robert Brown, British botanist, who first observed the effect with pollen grain in 1827 (Ross and Morrison, 1988). In 1905, Einstein noticed the resemblance between Brownian motion and the hypothetical motion of gas molecules according to the kinetic theory of gases. After introducing the Stokes resistance law, Einstein derived that the diffusivity due to Brownian motion has the uniform value:

$$\mathbf{D} = kT \mathbf{b} = \frac{kT}{6\pi\eta a} \mathbf{I} \quad (1)$$

where  $k$  is the Boltzmann constant;  $T$  is the absolute temperature;  $\mathbf{I}$  is the unit dyadic;  $\eta$  is the viscosity of the surrounding fluid; and the second-rank tensor  $\mathbf{b}$  is the particle mobility, which the particle velocity impacted by a steady force  $\mathbf{F}$  can be represented by  $\mathbf{b} \cdot \mathbf{F}$ . Eq. (1) is the well-known Stokes-Einstein equation, which is applied to an extremely dilute dispersion of no-slip solid spheres and/or a colloidal dispersion without consideration of particle interactions. In practical applications, one would be able to calculate the particle sizes by means of Eq. (1) from the measurements of the diffusion coefficients of particles in suspension. In addition, the equation can be applied to obtain the Avogadro's number if the diffusion of the molecules in solution is measured. Nowadays diffusion coefficients are used to determine particle sizes and effective viscosity of a colloidal suspension, or polymer molecular weights (Ross and Morrison, 1980; Chen *et al.*, 2002).

On the other hand, the Stokes-Einstein equation can be extended to the liquid drops situation when the modified Stokes resistance law of fluid drops (Hadamard, 1911; Rybczynski, 1911) is introduced; i.e.,

$$\mathbf{D} = \frac{kT(1 + \eta^*)}{2\pi\eta a(2 + 3\eta^*)} \mathbf{I} \quad (2)$$

where  $\eta^*$  is the internal-to-external viscosity ratio of the droplet. Since the fluid viscosities are arbitrary, Eq. (2) degenerates to Eq. (1) for the cases of diffusion of a solid sphere (Stokes particle) when  $\eta^* \rightarrow \infty$  and to the same cases for a gas bubble with spherical shape in the limit  $\eta^* = 0$ . So, the diffusivity of an isolated gas bubble is larger than a solid sphere at the same particle size

and environment.

The classical theory of Brownian diffusion developed by Einstein and many later workers is concerning with random migration of isolated colloidal particles or large solute molecules due to interaction with molecules of the suspending fluid. The results of this theory are applicable to very dilute solution or suspensions in which the particles on average are far apart from each other. In most practical applications, multiparticle systems are more important than the single particle situation; the latter condition can represent only the limiting case at low dispersed phase hold-up. In dispersions, particle interactions could be of primary importance and were related to the concentration dependence of the ensemble-averaged settling velocities of the particles (Batchelor, 1972, 1982; Reed and Anderson, 1980; Keh and Chen, 1997) and of the effective transport properties (Batchelor, 1976, 1977, 1983; Chen, 1999; Chen *et al.*, 2002). Problems concerning the hydrodynamic interactions between two or more no-slip solid particles and/or fluid droplets have been treated extensively in the past (Happel and Brenner, 1983; Kim and Karrila, 1991; Keh and Tseng, 1992; Keh and Chen, 1997).

When one tries to solve the Navier-Stokes equations, it is usually assumed that no slippage arises at the solid-fluid interfaces. Actually, this is an idealization of the transport processes occurring. That the adjacent fluid (especially if the fluid is a rarefied gas) can slip over a solid surface has been confirmed, both experimentally and theoretically (Kennard, 1938; Loyalka, 1990; Ying and Peters, 1991; Hutchins *et al.*, 1995). Presumably any such slipping would be proportional to the local velocity gradient next to the solid surface (Basset, 1961; Happel and Brenner, 1983; Chen, 2002), at least so long as this gradient is small. The constant of proportionality,  $C_m l / \eta$ , may be called a “slip coefficient.” Here,  $l$  is the average mean free path of gas molecules, and  $C_m$  is a dimensionless constant related to the momentum accommodation coefficient at solid surface. Although  $C_m$  surely depends upon the nature of the surface, examination of the experimental data suggests that it will be in the range 1.0-1.5 (Davis, 1972; Talbot *et al.*, 1980; Loyalka, 1990). Note that the slip-flow boundary condition is not only applicable for a gas-solid surface in the continuum regime (Knudsen number  $l/a \ll 1$ ), but also appears to be valid for some cases even into the molecular flow regime ( $l/a \geq 1$ ). Considering Stokes law modified by Basset (1961), the Stokes-Einstein equation of diffusivity of aerosol particle was formulated as:

$$\mathbf{D} = \frac{kT(1 + 3C_m Kn)}{6\pi\eta a(1 + 2C_m Kn)} \mathbf{I} \quad (3)$$

where  $Kn = l/a$  denotes the Knudsen number of the aerosol system. In the limiting situation of  $C_m = 0$ , Eq. (3) reduces to the Stokes-Einstein formula (1). On the other hand, Eq. (3) can be

simplified to the diffusion of a perfect slip sphere  $C_m \rightarrow \infty$  (the particle acts like a spherical gas bubble in a liquid phase) and be consistent with Eq. (2) by taking  $\eta^* = 0$ . Note that, as a comparison between Eqs. (2) and (3), the flow field and corresponding diffusivity of a slip solid sphere was the same as the flow pattern and Brownian diffusivity of a fluid drop with a value of  $\eta^*$  equal to  $1/(3C_m Kn)$  (Chen *et al.*, 1999; Chen and Yang, 2000). However, the hydrodynamic interactions between two aerosol particles with finite values of  $C_m Kn$  were, both physically and mathematically, different from those between two no-slip particles and/or fluid droplets (Reed and Morrison, 1974; Chen and Keh, 1995; Keh and Chen, 1997).

The objective of the present work is to analytically study the Brownian diffusion of aerosol under consideration of particle hydrodynamic interactions in a general situation. Particles may differ in radius and in physical properties, while there are slip velocities existing at the particle surface. Both the particles and suspending fluid are assumed to be incompressible, so that there is no change of volume accompanying diffusion. In addition, the particles are assumed to be large enough with respect to the molecular sizes of the suspending fluid, thus the surrounding fluid can be regarded as a continuum. The interaction results between two aerosol particles, which were derived analytically by using a method of twin multipole expansions (Keh and Chen, 1997), are applied to solve these problems. The analytical formulations are analogue to the related articles studied for no-slip solid spheres (Batchelor, 1976) and for liquid drops (Chen, 1999). The result is an indirect but general prescription of multiparticle Brownian diffusive flux which is the same as if certain steady forces were acting on the particles.

### ***Interactions between two aerosol particles***

The slow motion of two spherical airborne particles in an unbounded gas medium, which is Newtonian and incompressible, is considered. The particles can differ in radius, and there exists the hydrodynamic slip at the surfaces of particles. For the quasi-steady situation, the velocity field  $\mathbf{v}$  and dynamic pressure field  $p$  satisfy the Stokes equations:

$$\eta \nabla^2 \mathbf{v} - \nabla p = \mathbf{0} \tag{4a}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{4b}$$

where  $\eta$  is the fluid viscosity. The boundary conditions require that there be no relative normal flow at the surface of each sphere and that the tangential velocity of the fluid relative to the sphere at a point on its surfaces be proportional to the tangential stress prevailing at the point (Kennard, 1938); that means a tangential slip boundary. That is,

$$r_i = a_i: \quad \mathbf{v} = \mathbf{U}_i + a_i \boldsymbol{\Omega}_i \times \mathbf{e}_{r_i} + \frac{C_{mi} l}{\eta} (\mathbf{I} - \mathbf{e}_{r_i} \mathbf{e}_{r_i}^T) \mathbf{e}_{r_i} : \boldsymbol{\tau} \quad (i = 1 \text{ or } 2) \quad (5)$$

where  $\boldsymbol{\tau}$  ( $= \eta[\nabla \mathbf{v} + (\nabla \mathbf{v})^T]$ ) is the viscous stress tensor,  $\mathbf{e}_{r_i}$  is the unit vector in the direction  $r_i$  of the spherical coordinates,  $C_{mi}$  is the frictional slip coefficient about the surface of particle  $i$ , and  $l$  is the mean free path of the surrounding gas medium. In Eq. (5),  $\mathbf{U}_i$  and  $\boldsymbol{\Omega}_i$  are the instantaneous translational and angular velocities, respectively, of the particle  $i$ .

Discussion of the slow motion problem can be described using either resistance problem or mobility problem. The resistance problems are ascribed as those in which the forces acting on the particles have to be determined for the particles' motion in the surrounding fluid. Here the particle velocities are settled, and the problem can be solved straightforwardly. While the mobility problem is defined as that in which the forces and torques acting on the particles are prescribed and the velocities of particles in the ambient fluid are to be determined. The presentation of the mobility problem is rather awkward since the boundary conditions involve the unknowns, but in many physical problems the force and torque are the prescribed quantities, so the particles move accordingly. The result of motion of two interacting particles can be expressed as:

$$\mathbf{U}_1 = \mathbf{M}_{11} \cdot \mathbf{U}_1^{(0)} + \mathbf{M}_{12} \cdot \mathbf{U}_2^{(0)} \quad (6a)$$

$$\mathbf{U}_2 = \mathbf{M}_{21} \cdot \mathbf{U}_1^{(0)} + \mathbf{M}_{22} \cdot \mathbf{U}_2^{(0)} \quad (6b)$$

With

$$\mathbf{U}_i^{(0)} = \frac{1 + 3C_{mi} Kn}{6\pi\eta a_i (1 + 2C_{mi} Kn)} \mathbf{F}_i \quad (i = 1 \text{ or } 2) \quad (7)$$

which is the translational velocity of particle  $i$  subject to an applied force  $\mathbf{F}_i$  in the absence of the other particle (Basset, 1961). The dimensionless mobility tensor  $\mathbf{M}_{ij}$  is a function of the slip coefficients, orientations, sizes and separation distances of the particles. When one sphere is separated far away from the other particle, it is evident that:

$$\mathbf{M}_{11} = \mathbf{M}_{22} = \mathbf{I}, \quad (8a)$$

and

$$\mathbf{M}_{12} = \mathbf{M}_{21} = \mathbf{0}. \quad (8b)$$

The dimensionless mobility tensors can be further written as:

$$\mathbf{M}_{ij} = M_{ij}^{(p)} \mathbf{e}\mathbf{e} + M_{ij}^{(n)} (\mathbf{I} - \mathbf{e}\mathbf{e}), \quad (9)$$

where  $i$  and  $j$  equal 1 or 2 and  $\mathbf{e}$  is the unit vector directing from center of sphere 1 toward the center of sphere 2.

In the following discussion,  $C_{mi}^* = C_{mi}l/a_i$  is defined and  $C_{m1}^* = C_{m2}^* = C_m^*$  is assumed for simplification (if not, the problem is much more complicated and hard to formulate analytically). Using an analytical formulation of a method of twin multipole expansions, the scalar mobility functions  $M_{11}^{(p)}$ ,  $M_{12}^{(p)}$ ,  $M_{11}^{(n)}$  and  $M_{12}^{(n)}$  were obtained (Keh and Chen, 1997):

$$M_{11}^{(p)} = 1 - \frac{15}{4} C_{23} C_{25} \frac{a_1 a_2^3}{r_{12}^4} + \frac{15}{2} C_{23} C_{05} \frac{a_1^3 a_2^3}{r_{12}^6} - \frac{1}{10} C_{23} (2C_{(-3)2} - 45C_{05} + 63C_{27}) \frac{a_1 a_2^5}{r_{12}^6} + O(r_{12}^{-8}) \quad (10a)$$

$$M_{12}^{(p)} = \frac{3}{2} C_{23} \frac{a_2}{r_{12}} - \frac{1}{2} C_{03} \left( \frac{a_1^2 a_2}{r_{12}^3} + \frac{a_2^3}{r_{12}^3} \right) + \frac{75}{4} C_{23} C_{25} \frac{a_1^3 a_2^4}{r_{12}^7} + O(r_{12}^{-9}) \quad (10b)$$

$$M_{11}^{(n)} = 1 - \frac{1}{80} C_{23} (4C_{(-3)2} C_{03} + 60C_{(-1)4} + 21C_{27}) \frac{a_1 a_2^5}{r_{12}^6} + O(r_{12}^{-8}) \quad (10c)$$

$$M_{12}^{(n)} = \frac{3}{4} C_{23} \frac{a_2}{r_{12}} + \frac{1}{4} C_{03} \left( \frac{a_1^2 a_2}{r_{12}^3} + \frac{a_2^3}{r_{12}^3} \right) + O(r_{12}^{-9}) \quad (10d)$$

where  $C_{ij} = (1 + iC_m^*) / (1 + jC_m^*)$ ,  $a_i$  is the radius of particle  $i$  and  $r_{12}$  is the center-to-center distance of the pair. The other mobility functions  $M_{21}^{(p)}$ ,  $M_{22}^{(p)}$ ,  $M_{21}^{(n)}$  and  $M_{22}^{(n)}$  can be obtained from the above equations by replacing  $a_1$  by  $a_2$  and  $a_2$  by  $a_1$ . In the limit of  $C_m^* = 0$  (no-slip particles), a set of more accurate mobility functions was derived by Jeffrey and Onishi (1984).

$$M_{11}^{(p)} = 1 - \frac{15}{4} \frac{a_1 a_2^3}{r_{12}^4} + \frac{1}{2} \left( 15 \frac{a_1^3 a_2^3}{r_{12}^6} - 4 \frac{a_1 a_2^5}{r_{12}^6} \right) - \frac{3}{4} \left( 5 \frac{a_1^5 a_2^3}{r_{12}^8} - 22 \frac{a_1^3 a_2^5}{r_{12}^8} + 3 \frac{a_1 a_2^7}{r_{12}^8} \right)$$

$$-\frac{1}{4} \left( 70 \frac{a_1^5 a_2^5}{r_{12}^{10}} + 375 \frac{a_1^4 a_2^6}{r_{12}^{10}} - 120 \frac{a_1^3 a_2^7}{r_{12}^{10}} + 9 \frac{a_1 a_2^9}{r_{12}^{10}} \right) + O(r_{12}^{-12}) \quad (11a)$$

$$M_{12}^{(p)} = \frac{3}{2} \frac{a_2}{r_{12}} - \frac{1}{2} \left( \frac{a_1^2 a_2}{r_{12}^3} + \frac{a_2^3}{r_{12}^3} \right) + \frac{75}{4} \frac{a_1^3 a_2^4}{r_{12}^7} - \frac{15}{4} \left( \frac{a_1^5 a_2^4}{r_{12}^9} + \frac{a_1^3 a_2^6}{r_{12}^9} \right) + \frac{3}{4} \left( 10 \frac{a_1^7 a_2^4}{r_{12}^{11}} - 151 \frac{a_1^5 a_2^6}{r_{12}^{11}} + 10 \frac{a_1^3 a_2^8}{r_{12}^{11}} \right) + O(r_{12}^{-13}) \quad (11b)$$

$$M_{11}^{(n)} = 1 - \frac{17}{16} \frac{a_1 a_2^5}{r_{12}^6} - \frac{1}{8} \left( 10 \frac{a_1^5 a_2^3}{r_{12}^8} - 9 \frac{a_1^3 a_2^5}{r_{12}^8} + 9 \frac{a_1 a_2^7}{r_{12}^8} \right) - \frac{3}{16} \left( 35 \frac{a_1^5 a_2^5}{r_{12}^{10}} - 54 \frac{a_1^3 a_2^7}{r_{12}^{10}} + 18 \frac{a_1 a_2^9}{r_{12}^{10}} \right) + O(r_{12}^{-12}) \quad (11c)$$

$$M_{12}^{(n)} = \frac{3}{4} \frac{a_2}{r_{12}} + \frac{1}{4} \left( \frac{a_1^2 a_2}{r_{12}^3} + \frac{a_2^3}{r_{12}^3} \right) + \frac{7}{64} \left( 80 \frac{a_1^7 a_2^4}{r_{12}^{11}} - 79 \frac{a_1^5 a_2^6}{r_{12}^{11}} + 80 \frac{a_1^3 a_2^8}{r_{12}^{11}} \right) + O(r_{12}^{-13}) \quad (11d)$$

When  $C_m^* \rightarrow \infty$  (perfect-slip spheres), these mobility functions with higher order of  $r_{12}^{-1}$  than those in Eq. (10) were (Keh and Chen, 1997).

$$M_{11}^{(p)} = 1 - \frac{a_1 a_2^3}{r_{12}^4} - \frac{a_1 a_2^5}{r_{12}^6} - \frac{a_1 a_2^7}{r_{12}^8} - \left( 4 \frac{a_1^4 a_2^6}{r_{12}^{10}} + \frac{a_1 a_2^9}{r_{12}^{10}} \right) + O(r_{12}^{-12}) \quad (12a)$$

$$M_{12}^{(p)} = \frac{a_2}{r_{12}} + 2 \frac{a_1^3 a_2^4}{r_{12}^7} + 3 \left( \frac{a_1^5 a_2^4}{r_{12}^9} + \frac{a_1^3 a_2^6}{r_{12}^9} \right) + \left( 4 \frac{a_1^7 a_2^4}{r_{12}^{11}} + 6 \frac{a_1^5 a_2^6}{r_{12}^{11}} + 4 \frac{a_1^3 a_2^8}{r_{12}^{11}} \right) + O(r_{12}^{-13}) \quad (12b)$$

$$M_{11}^{(n)} = 1 + \frac{1}{8} \frac{a_1 a_2^5}{r_{12}^6} + \frac{1}{5} \frac{a_1 a_2^7}{r_{12}^8} + \frac{1}{4} \frac{a_1 a_2^9}{r_{12}^{10}} + O(r_{12}^{-12}) \quad (12c)$$

$$M_{12}^{(n)} = \frac{1}{2} \frac{a_2}{r_{12}} + \frac{3}{16} \frac{a_1^5 a_2^6}{r_{12}^{11}} + O(r_{12}^{-13}) \quad (12d)$$

Using the so-called connector algebra, Geigenmuller and Mazur (1986) obtained the explicit formulas for the mobility functions  $M_{11}^{(p)}$ ,  $M_{12}^{(p)}$ ,  $M_{11}^{(n)}$  and  $M_{12}^{(n)}$  in power series of  $1/r_{12}$  up to  $O(r_{12}^{-7})$  for the case of identical fluid drops. The above expressions agreed with (and were more

accurate than) their results (by taking the relative viscosity of the drops  $\eta^*$  as zero) for the case when  $C_m^* \rightarrow \infty$ . It also found that the interaction between two slip spheres with finite value of  $C_m^*$  were different from that between two fluid drops with a value of  $3\eta^*$  equal to  $1/C_m^*$ , although the flow field induced by an isolated aerosol sphere was equivalent to the external flow field caused by an isolated fluid drop under this condition (Chen *et al.*, 1999; Chen and Yang, 2000).

The exact solution of the mobility functions  $M_{11}^{(p)}$  and  $M_{12}^{(p)}$  for two slip spheres was also obtained using bipolar coordinates (Chen and Keh, 1995). As comparison of the asymptotic results with the exact solution for the case of two identical spheres ( $a_1 = a_2 = a$ ,  $C_{m1} = C_{m2} = C_m^*$ ) experiencing equal applied forces ( $\mathbf{F}_1 = \mathbf{F}_2 = F\mathbf{e}$ ), one had  $M_{11}^{(p)} = M_{22}^{(p)}$ ,  $M_{12}^{(p)} = M_{21}^{(p)}$  and  $\mathbf{U}_1 = \mathbf{U}_2 = U\mathbf{e}$  (with  $U/U^{(0)} = M_{11}^{(p)} + M_{12}^{(p)}$ ), and the asymptotic approximation for various values of  $C_m^*$  were in good agreement with those of the exact solution. For example, the errors in velocities are less than 1.7% for cases  $2a/r \leq 0.9$  or 4.7% for cases  $2a/r \leq 0.9999$  if the asymptotic formula is accurate to  $O(r_{12}^{-7})$ .

## DIFFUSION IN A HOMOGENEOUS AEROSOL

In this section we consider the relative diffusion of spherical aerosol particles in a dilute homogeneous suspension. Also, the particles may differ in radius and are close enough to interact hydrodynamically. The pair is regarded to be isolated from the other particles, or the possibility of another particle being close to the group in a dilute suspension is small. A steady external interactive force with mutual potential energy  $\Phi(\mathbf{r}_{12})$ , which depends only on the relative position vectors  $\mathbf{r}_{12}$  ( $= r_{12}\mathbf{e}$ ) and not on the location of the pair in space, is assumed to be applied to the particles of the group in an equilibrium situation. In addition, there is another interactive force with mutual potential energy  $\Psi(\mathbf{r})$ , which in the case of our rigid spheres is infinite if the two particles overlap and zero otherwise. Since the pair of particles is independent of other particles in the suspension, the joint probability distribution of the position vectors of the pair particles satisfied the Boltzmann distribution (Batchelor, 1976):

$$P(\mathbf{r}_{12}) = P_0 \exp\left(-\frac{\Phi + \Psi}{kT}\right) \quad (13)$$

where  $P_0$  is a constant determined by the normalization condition  $\int P(\mathbf{x}_i) d\mathbf{x}_i = 1$  ( $\mathbf{x}_i$  is the position vector of the center of particle  $i$ ).

The diffusive flux of one particle relative to the other in a thermodynamic equilibrium situation is equal and opposite to the convective flux produced by a steady applied force. On condition that the two fluxes are independent, one can view that the relative diffusion of the pair as if each



particle were acted on by a steady force equal and opposite to that derived from  $\Phi$ . This fictitious steady force acting on particle  $i$  is:

$$\mathbf{F}_i = -kT \frac{\partial \ln P}{\partial \mathbf{x}_i} \quad (i = 1 \text{ or } 2) \quad (14)$$

Thus, when the probability density function  $P$  for the particle configuration is known, the relative diffusive flux can be calculated. Such a calculation involves a consideration of the hydrodynamic interaction of two relatively moving particles under the action of the forces represented by Eq. (14).

After introducing the particle mobility defined in Eq. (6) into the relation of local flux balance in equilibrium state (Batchelor, 1976; Chen, 1999), the diffusive flux of particle 2 relative to particle 1 is:

$$(\mathbf{U}_2 - \mathbf{U}_1)P(\mathbf{x}_1, \mathbf{x}_2) = -\mathbf{D}_{21} \cdot \nabla P(\mathbf{x}_1, \mathbf{x}_2) \quad (15)$$

where the relative diffusivity of two slip spheres with separation vector  $\mathbf{r}_{12}$  is:

$$\mathbf{D}_{21} = \frac{kT}{6\pi\eta a_1 C_{23}} \left( \mathbf{M}_{11} + \frac{a_1}{a_2} \mathbf{M}_{22} - \frac{a_1}{a_2} \mathbf{M}_{12} - \mathbf{M}_{21} \right) \quad (16)$$

This is the diffusivity that is needed in an investigation of pair-distribution function of mobility tensor in a dilute homogeneous suspension of spheres subjected to a bulk deforming motion, which has been described in the previous section. The corresponding diffusivity  $\mathbf{D}_{12}$  (also concerning parameters in following) can be easily derived from the above formula by changing the subscripts.

On substituting the expressions for the mobility tensors defined by Eq. (9) we find:

$$\mathbf{D}_{21} = D_0 \left[ N^{(p)} \mathbf{e}\mathbf{e} + N^{(n)} (\mathbf{I} - \mathbf{e}\mathbf{e}) \right] \quad (17)$$

where

$$D_0 = \frac{kT}{6\pi\eta a_1 C_{23}} \left( 1 + \frac{a_1}{a_2} \right) \quad (18a)$$

$$N^{(p)} = \frac{a_2 M_{11}^{(p)} + a_1 M_{22}^{(p)} - 2a_1 M_{12}^{(p)}}{a_1 + a_2} \quad (18b)$$

$$N^{(n)} = \frac{a_2 M_{11}^{(n)} + a_1 M_{22}^{(n)} - 2a_1 M_{12}^{(n)}}{a_1 + a_2} \quad (18c)$$

In the limiting case of  $C_m^* = 0$  (i.e.  $C_{23} = 1$ ), Eqs. (17) and (18a) describe the relative pair diffusion of no-slip particles and are coincident with the work derived by Batchelor (1976), which the mobility coefficients were in power series of  $1/r_{12}$  up to  $O(r_{12}^{-7})$ . When  $C_m^* \rightarrow \infty$  (resulting to  $C_{23} = \frac{2}{3}$ ), there is a pair diffusion system of perfect-slip spheres. Consideration of the two spheres are separated by an infinite distance, the mobility coefficients satisfy  $M_{11}^{(p)} = M_{11}^{(n)} = 1$ ,  $M_{12}^{(p)} = M_{12}^{(n)} = 0$ , and it easily results that  $N^{(p)} = 1$ ,  $N^{(n)} = 1$  and  $\mathbf{D}_{21} = D_0 \mathbf{I}$ .

In this situation, the diffusivity tensor  $\mathbf{D}_{21}$  will approach the form of Eq. (3) if the radii of the particles are different significantly. That means that the relative diffusivity of two particles is dominated by the diffusion behavior of the small particle.

For two identical spheres ( $a_1 = a_2 = a$ ,  $C_{m1} = C_{m2} = C_m$ ,  $M_{11}^{(p,n)} = M_{22}^{(p,n)}$ ,  $M_{12}^{(p,n)} = M_{21}^{(p,n)}$ ), Eq. (18) results that:

$$D_0 = \frac{kT}{3\pi\eta a C_{23}} \quad (19a)$$

$$N^{(p)} = M_{11}^{(p)} - M_{12}^{(p)} \quad (19b)$$

$$N^{(n)} = M_{11}^{(n)} - M_{12}^{(n)} \quad (19c)$$

### ***Diffusion of an aerosol down a concentration gradient***

Here we consider a polydispersed aerosol, which the suspending particles are with different particle sizes and physical properties, diffusing down a prescribed concentration gradient. This usually happens in nature and manufacturing processes. All the suspending particles are rigid and have  $N$  different types, which are denoted by the suffix  $i$ , and the slippage characteristics at the gas-particle interfaces are introduced simultaneously. Based on a thermodynamic analysis and

riding on a reference frame in which fluid molecules are force free, the diffusive flux of particle and fluid with respect to the fluid molecules is the same as if each particle of type  $i$  is acted on by a modified  $\mathbf{F}_i^*$  (Batchelor, 1976):

$$\mathbf{F}_i^* = -\sum_{j=1}^N \left( \frac{\partial \mu_i}{\partial n_j} \right)_{p,T} \nabla n_j - \frac{\phi_i}{1-\varphi} \sum_{j=1}^N n_j \left[ \sum_{k=1}^j \left( \frac{\partial \mu_k}{\partial n_k} \right)_{p,T} \nabla n_k \right] \quad (i = 1, 2, \dots, s) \quad (20)$$

where  $a_i$  and  $n_i$  are the radius and number density of the  $i$ -type particle,  $\phi_i = \frac{4}{3}\pi a_i^3$  denotes the volume of a single particle, and  $\varphi (= \sum \phi_i n_i)$  is the total volume fraction of the particles in suspension. The chemical potential of particle  $i$  denoted by  $\mu_i$  depends on  $n_1, n_2, \dots$ , and not on  $n_i$  alone. We shall assume that the total volume fraction of the particles  $\varphi$  is small, and seek expressions for the fluxes of the different kinds of particles which take into account pair interactions only. Application of statistical thermodynamics, Eq. (20) can be found with approximation that (Batchelor, 1976):

$$\mathbf{F}_i^* = -kT \nabla (\ln n_i) - kT \phi_i \sum_j \left( 1 + \frac{a_j}{a_i} \right)^3 \nabla n_j \quad (21)$$

Because of the particle interactions influencing the movement of particles, the velocities of the particles in the suspension moving under the acting steady forces will not all be the same, and will depend on the geometrical configuration and the physicochemical properties at the particle-fluid interfaces. We are interested in the mean velocity of particles of type  $i$  relative to axes such that there is zero mean flux of material volume in the suspension, given that a particle of type  $j$  are acted on by the external force  $\mathbf{F}_j^*$ . Let  $\langle \mathbf{U}_i \rangle$  denote this average particle velocity of type  $i$  resulting from the fictitious applied force (or termed a thermodynamic force), and should be calculated for a reference frame in which the net particle and fluid flux is zero. This is of course the average particle velocity of each type relative to the walls of a vessel containing a statistically homogeneous suspension. One can also describe  $\langle \mathbf{U}_i \rangle$  as the average velocity of type  $i$  particle relative to the velocity that they will have if they were acted on by zero force. Based on a microscopic model of particle interactions in a dilute dispersion, which comprises both statistical and low Reynolds number hydrodynamic concepts (Batchelor, 1972; Reed and Anderson, 1980; Keh and Chen, 1997), the mean  $\langle \mathbf{U}_i \rangle$  velocity is given by:

$$\begin{aligned}
 \langle \mathbf{U}_i \rangle &= \mathbf{U}_{i0} + \mathbf{U}_{i0} \sum_j \varphi_j \left( 1 + \frac{a_i}{a_j} \right)^3 \int_0^1 [M_{11}^{(p)} + 2M_{11}^{(n)} - 3] \lambda \, d\lambda \\
 &+ \sum_j \mathbf{U}_{j0} \varphi_j \left\{ -1 - 3 \frac{a_i}{a_j} C_{23} - \left( \frac{a_i}{a_j} \right)^2 \right. \\
 &\left. + \left( 1 + \frac{a_i}{a_j} \right)^3 \int_0^1 \left[ M_{12}^{(p)} + 2M_{12}^{(n)} - \frac{3a_j}{a_i + a_j} C_{23} \lambda \right] / \lambda^4 \, d\lambda \right\} \quad (22)
 \end{aligned}$$

where  $\varphi_j = \frac{4}{3} \pi a_j n_j$ ,  $\mathbf{U}_{i0} = \mathbf{F}_i^* / 6\pi\eta a_i C_{23}$  and  $\lambda = (a_1 + a_2) / r_{12}$ . After introducing the mobility functions of pair-wise interactions formulated in Eq. (10), the average velocity of type  $i$  aerosol spheres can be derived by recalling that  $\mathbf{U}_{i0} / \mathbf{U}_{j0} = (a_i / a_j)^2$  for the assumption of  $C_{mi}^* = C_{mj}^* = C_m^*$  as (Keh and Chen, 1997):

$$\frac{\langle \mathbf{U}_i \rangle}{\mathbf{U}_{i0}} = 1 + \sum_j \alpha_{ij} \varphi_j + O(\varphi^2) \quad (23)$$

where  $\alpha_{ij}$  was formulated in Eq. (93) by Keh and Chen (1997). For a suspension of no-slip particles ( $C_m^* = 0$ ) and of perfect-slip particles or spherical gas bubbles ( $C_m^* \rightarrow \infty$ ), the mobility functions in Eqs. (11) and (12), respectively, can be calculated to the order of  $r^{-11}$ ; thus a more accurate expression for  $\alpha_{ij}$  was obtained in Eqs. (94) and (95) by Keh and Chen (1997).

The number flux of type  $i$  airborne particles relative to zero-volume-flux axes is then (Batchelor, 1983):

$$n_i \langle \mathbf{U}_i \rangle = \frac{n_i \mathbf{F}_i^*}{6\pi\eta a_i C_{23}} \left[ 1 + \sum_j \alpha_{ij} \varphi_j + O(\varphi^2) \right] \quad (24)$$

Following from Eqs. (21) and (23), this flux can be presented by:

$$n_i \langle \mathbf{U}_i \rangle = -\mathbf{D}_{i0} \left[ \nabla n_i + \varphi_i \sum_j \left( 1 + \frac{a_j}{a_i} \right)^3 \nabla n_j \right] \left[ 1 + \sum_j \alpha_{ij} \varphi_j + O(\varphi^2) \right] \quad (25)$$

where the isotropic diffusivity tensor  $\mathbf{D}_{i0}$  of an extremely dilute dispersion of independent slip sphere is defined by Eq. (3) with replacing  $a$  by  $a_i$ . This expression for the flux of  $i$ -type particles may also be written as  $-\Sigma \mathbf{D}_{ij} \cdot \nabla n_j$ . The diagonal element of the diffusivity matrix is:

$$\frac{\mathbf{D}_{ii}}{\mathbf{D}_{i0}} = 1 + (\alpha + \xi)\varphi_i + \sum_{j(j \neq i)} \varphi_j C_{23} \left[ -\frac{15}{4} C_{25} \frac{a_i}{a_i + a_j} + \frac{5}{2} C_{05} \frac{a_i^3}{(a_i + a_j)^3} - \frac{1}{40} (4C_{(-3)2} + 20C_{(-1)4} - 60C_{05} + 91C_{27}) \frac{a_i a_j^2}{(a_i + a_j)^3} \right] \quad (26)$$

where the interaction coefficient  $\alpha$  is (Keh and Chen, 1997):

$$\alpha = -(2 + 3C_{23}) - \frac{15}{8} C_{23} C_{25} + \frac{5}{16} C_{03} C_{25} - \frac{1}{320} C_{23} (4C_{(-3)2} + 20C_{(-1)4} - 160C_{05} + 91C_{27}) + \frac{75}{256} C_{23} C_{25}^2 \quad (27)$$

In the limiting case for a suspension of no-slip spheres ( $C_m^* = 0$ ), the mobility function can be calculated more accurately to the order of  $r^{-11}$  by Eq. (11) (Jeffrey and Onishi, 1984) which obtains  $\alpha = -6.553$ . On the other hand, for a suspension of perfect-slip spheres ( $C_m^* \rightarrow \infty$ ), the mobility function can be evaluated from Eq. (12) of the same accuracy and results  $\alpha = -4.486$  (Keh and Chen, 1997). The other coefficient  $\xi$  on the right hand side of Eq. (26), which is related to the second virial coefficient for the osmotic pressure of the dispersion, depends on the interaction between pairs of particles. Using a standard method of evaluating the configuration integral for dispersion in equilibrium, Hill (1960) resulted with  $\xi = 8$  for the hard-sphere model of our assumption.

On the other hand, the off-diagonal element is:

$$\frac{\mathbf{D}_{ij}}{\mathbf{D}_{i0}} = \varphi_i \left[ \left( \frac{a_j}{a_i} \right)^3 + 2 \left( \frac{a_j}{a_i} \right)^2 + 3(1 - C_{23}) \left( \frac{a_j}{a_i} \right) + \frac{75}{16} C_{23} C_{25}^2 \frac{a_i^3 a_j}{(a_i + a_j)^4} \right] \quad (i \neq j) \quad (28)$$

The off-diagonal contribution to the particles of type  $i$  due to a gradient of concentration of particles of type  $j$  is essentially a consequence of: (a) the movement of  $i$ -type particles to regions of lower  $j$ -type concentration where more sites are available, and (b) the back-flow in the medium which is needed to compensate for the volume flux associated with the movement of  $j$ -type

particles down their concentration gradient. In the limited situations of no-slip particles ( $C_m^* = 0$ ) and perfect-slip particles ( $C_m^* \rightarrow \infty$ ), the results of Eqs. (26) and (28) can be formulated to more accurate forms by introducing the mobility functions of Eqs. (11) and (12). They are:

$$\frac{D_{ii}}{D_{i0}} = 1 + 1.447\varphi_i + \sum_{j(j \neq i)} \varphi_j \left[ -\frac{15a_i}{4(a_i + a_j)} + \frac{20a_i^3 - 11a_i a_j^2}{8(a_i + a_j)^3} - \frac{25a_i^5 - 75a_i^3 a_j^2 + 18a_i a_j^4}{20(a_i + a_j)^5} - \frac{245a_i^5 a_j^2 + 750a_i^4 a_j^3 - 294a_i^3 a_j^4 + 36a_i a_j^6}{56(a_i + a_j)^7} \right] \quad (29a)$$

$$\frac{D_{ij}}{D_{i0}} = \varphi_i \left[ \left( \frac{a_j}{a_i} \right)^3 + 2 \left( \frac{a_j}{a_i} \right)^2 + \frac{75a_i^3 a_j}{16(a_i + a_j)^4} - \frac{5a_i^5 a_j + 5a_i^3 a_j^3}{8(a_i + a_j)^6} + \frac{800a_i^7 a_j - 4177a_i^5 a_j^3 + 800a_i^3 a_j^5}{256(a_i + a_j)^8} \right] \quad (i \neq j) \quad (29b)$$

for the dispersed particles with no-slip boundary, and

$$\frac{D_{ii}}{D_{i0}} = 1 + 3.514\varphi_i - \sum_{j(j \neq i)} \varphi_j \left[ \frac{a_i}{(a_i + a_j)} + \frac{a_i a_j^2}{4(a_i + a_j)^3} + \frac{3a_i a_j^4}{25(a_i + a_j)^5} + \frac{8a_i^4 a_j^3 + a_i a_j^6}{14(a_i + a_j)^7} \right] \quad (30a)$$

$$\frac{D_{ij}}{D_{i0}} = \varphi_i \left[ \left( \frac{a_j}{a_i} \right)^3 + 2 \left( \frac{a_j}{a_i} \right)^2 + \left( \frac{a_j}{a_i} \right) + \frac{a_i^3 a_j}{2(a_i + a_j)^4} + \frac{a_i^5 a_j + a_i^3 a_j^3}{2(a_i + a_j)^6} + \frac{32a_i^7 a_j + 51a_i^5 a_j^3 + 32a_i^3 a_j^5}{64(a_i + a_j)^8} \right] \quad (i \neq j) \quad (30b)$$

for the perfect-slip particles situation.

When one considers the diffusion of a monodispersed aerosol down a concentration gradient of particles, the analysis can be simplified straightforwardly by the above derivation of the polydispersed situation with setting  $i = j$ , and the result is:

$$\frac{D}{D_0} = 1 + (\alpha + \xi)\varphi + O(\varphi^2)_0 \quad (31)$$

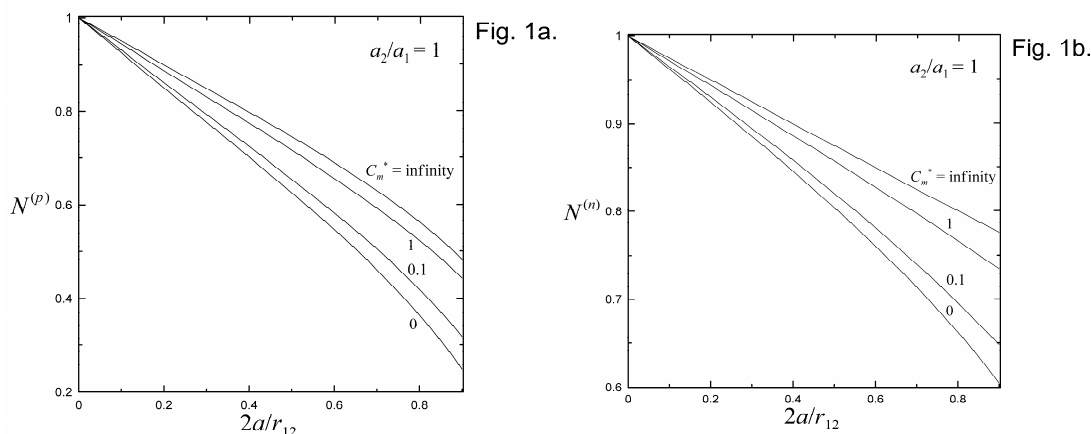
where  $\mathbf{D}_0$  is the diffusivity tensor of a particle without consideration of the effect of particle interaction defined by Eq. (3);  $\varphi(\mathbf{x})$  is the volume fraction of particles ( $=\frac{4}{3}\pi a^3 n$ , where  $a$  is the radius of a particle and  $n(\mathbf{x})$  denotes the particle concentration at position  $\mathbf{x}$ ). It appears that the enhancement of the diffusivity due to the greater availability of particle sites in regions of lower concentration is greater than the reduction due to hydrodynamic hindrance to the movement of particles.

## RESULTS AND DISCUSSION

In Fig. 1, the dimensionless functions of  $N^{(p)}$  and  $N^{(n)}$  in Eqs. (18b) and (18c) for the relative diffusion of two identical spheres at various values of  $C_m^*$  are plotted versus the separation parameter  $2a/r_{12}$ . It indicates that both the values of  $N^{(p)}$  and  $N^{(n)}$  are decreasing monotonically during the increase of separation parameter  $2a/r_{12}$ , which denotes the hydrodynamic interaction becomes significant as the two particles move closer and this influence of particle configuration retards the diffusion of particles. The existence of the neighboring particle acting as an obstacle of particle motion makes the diffusivity small, and this hindrance effectively increases with decreasing distances between particles. The decreasing rate of relative diffusivity becomes remarkable as the slip coefficient becomes small, since the decrease in slip at the particle surface increases the energy dissipation in particle motion. The energy consumption is more significant in the axisymmetric motion of the pair than that in asymmetric movement in each specified situation, and it results in the value of  $N^{(p)}$  always being less than that of  $N^{(n)}$ . This also describes that the interacting effect due to the axisymmetric motion of particles dominates the relative diffusivity of the pair.

For the relative diffusion of two particles with different radii the values of  $N^{(p)}$  and  $N^{(n)}$  at various  $a_2/a_1$  and  $(a_1+a_2)/r_{12}$  for  $C_m^* = 0.1$  are displayed in Fig. 2. Again, both the values of  $N^{(p)}$  and  $N^{(n)}$  decrease when the separation parameter  $(a_1+a_2)/r_{12}$  is increasing, and the value of the axisymmetric function  $N^{(p)}$  is always less than the values of asymmetric function  $N^{(n)}$  for all cases of the specified variables. Note that  $M_{12}^{(p,n)} / M_{21}^{(p,n)} = a_2 / a_1$  is sustained under our consideration of  $C_{m1}^* = C_{m2}^* = C_m^*$ , the values of  $N^{(p)}$  and  $N^{(n)}$  for  $a_2/a_1 = 0.1, 0.2$  and  $0.5$  are equal to that for the situations of  $a_2/a_1 = 10, 5$  and  $2$ , respectively. The plots show that the relative diffusivity reaches the minimum value when the particle sizes of the pair are equal ( $a_1 = a_2$ ); that is, the increase of particle size difference ( $= |a_1 - a_2|$ ) would increase the relative diffusivity of the pair. When the size of particle 1 is relatively larger than that of particle 2 ( $a_1 \gg a_2$ ), the motion of particle 1 is the same as if it is isolated. Here, the influence of the existence of particle 2 on the motion of particle 1 can be ignored ( $M_{12}^{(p,n)} \approx 0$ ), thus

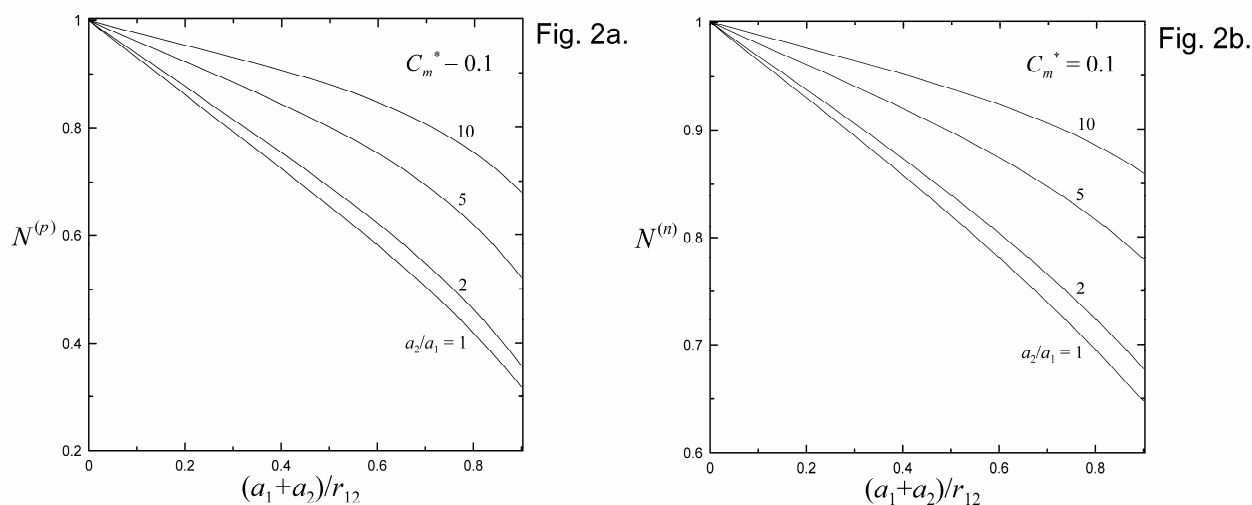
$N^{(p)} = M_{22}^{(p)} = 1$  and  $N^{(n)} = M_{22}^{(n)} = 1$ . On the contrary as  $a_1 \ll a_2$  is approached, the relations  $N^{(p)} = M_{11}^{(p)} = 1$  and  $N^{(n)} = M_{11}^{(n)} = 1$  result. In these two limiting situations, the largest value of diffusivity is reached and equal to the independent diffusivity of the small particle. Again, it explains that the behaviors of diffusion are dominated by the small particles. General speaking, the interaction effect of particles will decrease the relative diffusion coefficient in all configurations of the pair.



**Fig. 1.** Dimensionless coefficients (a)  $N^{(p)}$ , and (b)  $N^{(n)}$  versus the separation parameter  $2a/r_{12}$  with  $C_m^*$  as a parameter for the relative diffusion of two identical particles.

Considering the Brownian motion of an aerosol down a concentration gradient of particles, the diffusion coefficients are influenced significantly by the mobility function (23), as shown by Eqs. (26) and (28). Here, the values of  $\alpha_{ij}$  are notably negative (Keh and Chen, 1997). This means that the hydrodynamic interactions of airborne particle always hinder particle motions under an applied force, and the average velocity of the particles in a suspension of zero-volume-flux is smaller than the velocity of an isolated aerosol sphere. This hindrance effect on the bulk behavior of particle motion is enhanced with the increase of particle concentration. In the particular situation of a monodispersed aerosol, the magnitude of  $\alpha$  is in the range between 4.486 and 6.553, and it increases monotonically with the decrease of  $C_m^*$ . Here, the combination of the hydrodynamic and thermodynamic effects deduces that the value of  $(\alpha + \xi)$  is always positive, and it increases monotonically with the increase of  $C_m^*$ . So, the isotropic diffusivity of a monodispersed aerosol is larger than that evaluated from the modified Stokes-Einstein formula (3) for extremely dilute situations. This effect drives the particles to move in the opposite direction of the concentration gradient, where there are more free sites for particles. It also explains that the effect of bulk diffusion of particles tends to unify the inhomogeneous distribution of particles.





**Fig. 2.** Dimensionless coefficients (a)  $N^{(p)}$ , and (b)  $N^{(n)}$  versus the separation parameter  $(a_1 + a_2)/r_{12}$  with  $a_2/a_1$  as a parameter for the relative diffusion of two particles with different radii ( $C_m^* = 0.1$ ).

Fig. 3 illustrates the normalized diffusivities of a monodispersed aerosol with respect to the variations of  $C_m^*$  and/or volume fraction of particles. Obviously, if the slippage phenomenon occurring at the particle-fluid interface becomes significant (i.e., a larger value of  $C_m^*$ ), the Brownian diffusion of the suspension will be increased accordingly at constant volume fraction of suspending particles. Owing to the viscous drag of the surrounding fluid nearby, the particles are insignificant at large values of  $C_m^*$ , which makes the energy dissipation of particle motions decrease, the diffusion of particles is improved. In Fig. 3(a) the dimensionless diffusivity  $\mathbf{D}/\mathbf{D}_0$  is linearly proportional to the volume fraction of dispersed particles because of the neglect of the higher terms of  $O(\phi^2)$ , which should be important in a concentrated aerosol suspension. It is practical in most aerosol systems. The plots of dimensionless diffusivity  $\mathbf{D}/\mathbf{D}_0$  relative to the marked variation of  $C_m^*$  with  $\phi$  as a parameter are displayed in Fig. 3(b). Here, the dimensionless diffusivity  $\mathbf{D}/\mathbf{D}_0$  increases monotonically and nonlinearly with the increase of  $C_m^*$ . In addition, the increase of particle concentration will increase the diffusivity of the monodispersed aerosol and drive the Brownian diffusion to be remarkable. It denotes that the increase of volume fraction of particles makes the thermodynamic effect much more important than the effect of hydrodynamic retardation on the diffusion of particles.

When one considers the movement of a polydispersed aerosol down a concentration gradient, the diffusivity is more complicated as shown in Eqs. (26) and (28). The value of the mobility parameter  $\alpha_{ij}$  is always negative and increases monotonically with the increase of  $C_m^*$  (Keh

and Chen, 1997). The values of  $|\alpha_{ij}|$  can be larger than the thermodynamic parameter  $\xi$  ( $= 8$ ) for the situations of  $a_j/a_i \geq 2$ . Here, the hindrance effect of hydrodynamic interactions will suppress the thermodynamic effect, and thus the combination effect will retard the diffusion of particles. However, this influence should be noted only in a concentrated suspension of airborne particles, such as the total volume fraction of particles larger than 0.2, and it is not considered in our results of Eqs. (26) and (28) owing to the neglect of  $O(\varphi^2)$ . Generally, the particle concentration drives the suspended particles to diffuse from the region of more particles to that of fewer particles.

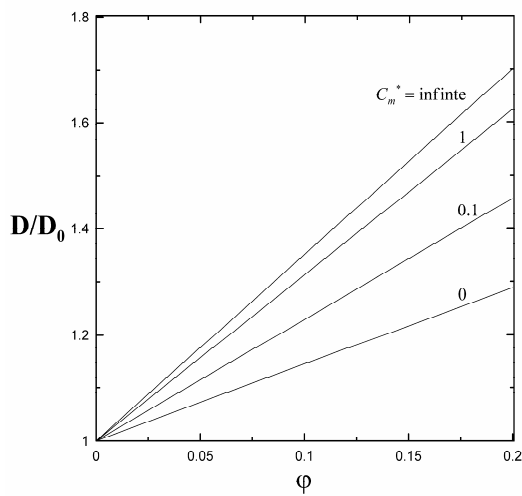


Fig. 3a.

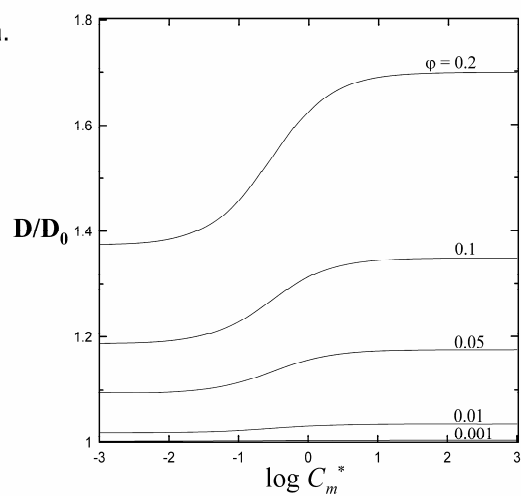


Fig. 3b.

**Fig. 3.** Diffusivities of a monodispersed aerosol down a concentration gradient: (a) versus the particle volume fraction  $\varphi$  with  $C_m^*$  as a parameter; (b) versus  $C_m^*$  with the particle volume fraction  $\varphi$  as a parameter.

Several interesting cases can be approached from examining polydispersed aerosol. First, we consider few particles of radius  $a_1$  in a suspension containing many particles of radius  $a_2$ . It is common in many experiments to view the particle 1 as tracer particles. This situation can be simplified by setting  $i = 1$ ,  $j = 2$  and  $\varphi_1 \ll \varphi_2$ , and thus the diffusivities of this system are:

$$\frac{D_{11}}{D_{10}} = 1 - \varphi_2 C_{23} \left[ \frac{15}{4} C_{25} \frac{a_1}{a_1 + a_2} - \frac{5}{2} C_{05} \frac{a_1^3}{(a_1 + a_2)^3} + \frac{1}{40} (4C_{(-3)2} + 20C_{(-1)4} - 60C_{05} + 91C_{27}) \frac{a_1 a_2^2}{(a_1 + a_2)^3} \right] \quad (32a)$$

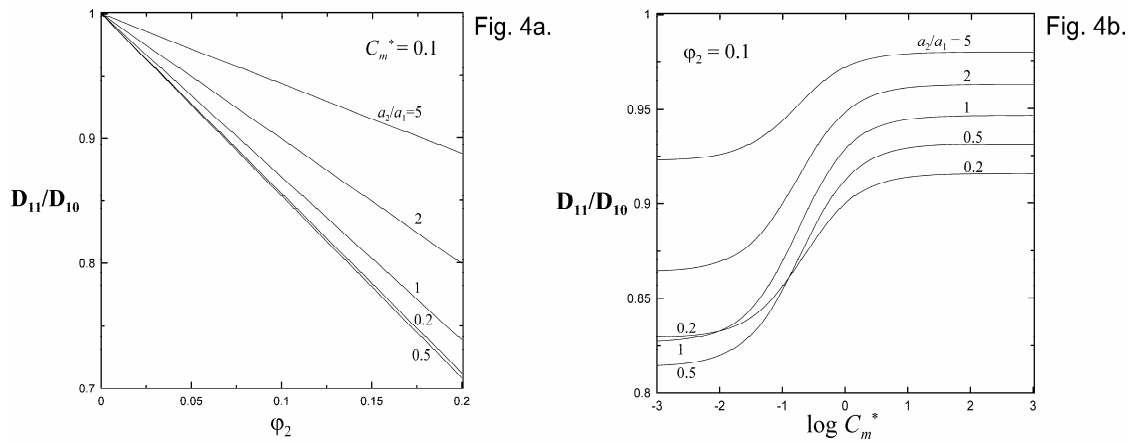
$$\mathbf{D}_{12} \approx 0 \tag{32b}$$

In addition if  $a_1 = a_2$ , the numerous particles of type 2 are acting as passive obstacles to migration of particles of type 1, and:

$$\frac{\mathbf{D}_{11}}{\mathbf{D}_{10}} = 1 - \varphi_2 C_{23} \left( \frac{91}{320} C_{27} + \frac{15}{8} C_{25} - \frac{1}{2} C_{05} + \frac{1}{16} C_{(-1)4} + \frac{1}{80} C_{(-3)2} \right) \tag{33}$$

which represents the reduction in the rate of change of mean square displacement of type 1 particles due to the presence of type 2 particles. Fig. 4. displays the normalized diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$  predicted by Eqs. (32a) and (33) with respect to the volume fraction of particle 2 ( $\varphi_2$ ) and slip coefficient  $C_m^*$  for several radius ratios ( $a_2/a_1$ ). It shows that the increase of the volume fraction of particle 2 decreases the diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$ . This is because the increase of the volume fraction of particle 2 is the same as the increase of passive obstacles, and this makes the movement of the tracer particles (type 1) more difficult. The retardation effects on the diffusion of tracer particles (type 1) would be significant if the radius of the tracers were larger than that of the obstacles (type 2 particles); however, it is not a monotonic function of  $a_2/a_1$ . In this situation the surface property of the obstacle particle (particle 2) plays an influential role in diffusivity, which can be easily understood by setting the limitation of  $a_1 \gg a_2$  in Eq. (32a), so the reduced diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$  is not a monotonic function of  $a_2/a_1$ . On the contrary, the influence of the presence of type 2 particles, which obstructs the diffusion of type 1 particles, on the diffusion of the tracers is insignificant, since the size of particle 2 is much larger than that of particle 1 at the same volume fraction of the obstacles, and this hindrance effect decreases monotonically with the increase of  $a_2/a_1$  for  $a_2 > a_1$ . This denotes that a target particle is easier to diffuse down a concentration gradient in a dispersion of larger obstacle particles than to diffuse in the situation as the obstacle particles are smaller under the consideration of a same volume fraction.  $\mathbf{D}_{11}/\mathbf{D}_{10}$  approaches 1, which is independent of the interfacial properties of particles, as  $a_1 \ll a_2$ . Again, it explains that small particles dominate the diffusion behavior.

In Fig. 4(b) the diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$  is illustrated versus  $C_m^*$  with  $a_2/a_1$  as a parameter when the volume fraction of type 2 particles is 10 percent. The increase of the slippage property at the particle surfaces decreases the hindrance effect of their diffusion, and the diffusivity increases monotonically with the increase of  $C_m^*$ . In addition, the diffusivity,  $\mathbf{D}_{11}/\mathbf{D}_{10}$ , increases monotonically with the increase of  $a_2/a_1$  when the slip coefficient is not too small (say,  $C_m^* > 0.2$ ).



**Fig. 4.** Diffusivities  $D_{11}/D_{10}$  of few particles of type 1 (tracer) in a dispersion of many type 2 particles down a concentration gradient: (a) versus particle volume fraction  $\varphi$  for  $C_m^* = 0.1$ , and: (b) versus  $C_m^*$  for  $\varphi = 0.1$ , with  $a_2/a_1$  as a parameter.

The second special case of Eqs. (26) and (28) considers that there are only two types of particles in dispersion and their number densities in the local controlled volume are equal to each other. Thus, the volume fractions of each type of particles can be related to the total volume fraction ( $\varphi$ ) in dispersion by:

$$\varphi_1 = \frac{a_1^3}{a_1^3 + a_2^3} \varphi \tag{34a}$$

$$\varphi_2 = \varphi - \varphi_1 = \frac{a_2^3}{a_1^3 + a_2^3} \varphi \tag{34b}$$

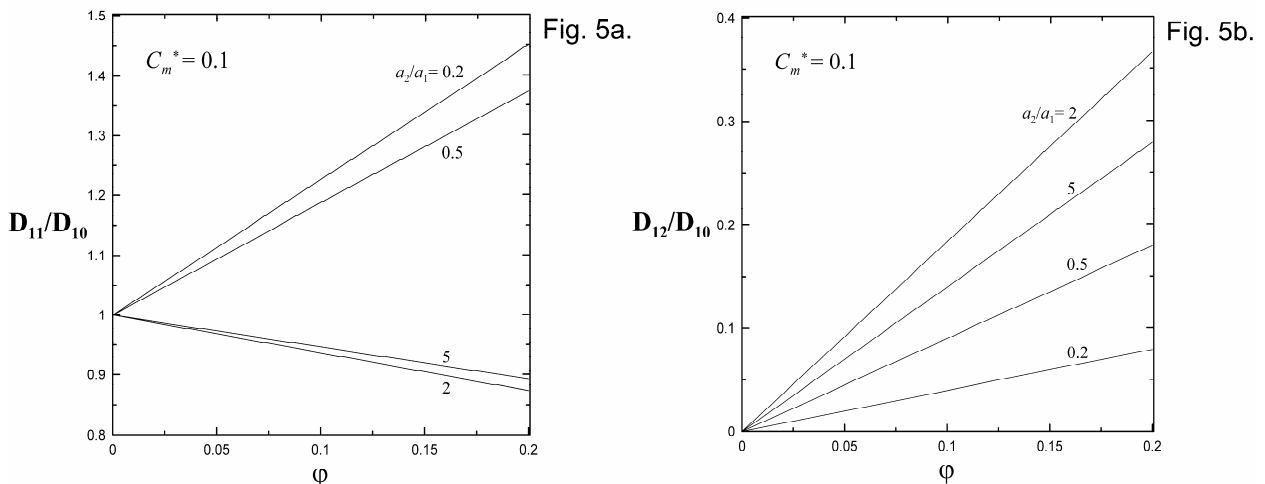
Substitution of Eq. (34) into Eqs. (26) and (28) results in:

$$\frac{D_{11}}{D_{10}} = 1 + \frac{a_1^3 \varphi}{a_1^3 + a_2^3} \left\{ \alpha + \xi - C_{23} \left( \frac{a_2}{a_1} \right)^3 \left[ \frac{15}{4} C_{25} \frac{a_1}{a_1 + a_2} - \frac{5}{2} C_{05} \frac{a_1^3}{(a_1 + a_2)^3} \right. \right. \\ \left. \left. + \frac{1}{40} (4C_{(-3)2} + 20C_{(-1)4} - 60C_{05} + 91C_{27}) \frac{a_1 a_2^2}{(a_1 + a_2)^3} \right] \right\} \tag{35a}$$

$$\frac{D_{12}}{D_{10}} = \frac{a_1^3 \varphi}{a_1^3 + a_2^3} \left[ \left( \frac{a_2}{a_1} \right)^3 + 2 \left( \frac{a_2}{a_1} \right)^2 + 3(1 - C_{23}) \left( \frac{a_2}{a_1} \right) + \frac{75}{16} C_{23} C_{25} \frac{a_1^3 a_2}{(a_1 + a_2)^4} \right] \tag{35b}$$

The corresponding diffusivities  $\mathbf{D}_{22}$  and  $\mathbf{D}_{21}$  can be easily obtained by changing the subscripts.

Results of  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and  $\mathbf{D}_{12}/\mathbf{D}_{10}$  calculated from Eq. (35) at various values of  $a_2/a_1$  are plotted versus total volume fraction of suspending particles in Fig. 5. It can be seen that the values of  $\mathbf{D}_{11}/\mathbf{D}_{10}$  increase with the increase of total volume fraction as  $a_1 > a_2$ , and in contrast, they decrease with the increase of  $\varphi$  when  $a_1 < a_2$ . Note that the particle size strongly influences the diagonal element of diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$  in the situation of equal-number-density of bi-dispersed systems;  $\mathbf{D}_{11}/\mathbf{D}_{10} > 1$  for  $a_1 > a_2$  and  $\mathbf{D}_{11}/\mathbf{D}_{10} < 1$  for  $a_1 < a_2$ . When the off-diagonal element of diffusivity is considered, relations of dependence of the diffusivity  $\mathbf{D}_{12}/\mathbf{D}_{10}$  on the volume fraction  $\varphi$  are much simpler than those of  $\mathbf{D}_{11}/\mathbf{D}_{10}$ , as illustrated in Fig. 5(b). The values of  $\mathbf{D}_{12}/\mathbf{D}_{10}$  are always increasing as  $\varphi$  increases. Generally speaking,  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and  $\mathbf{D}_{12}/\mathbf{D}_{10}$  are not a monotonic function of  $a_2/a_1$ . The curves in Fig. 5 are all straight, due to the fact that diffusivity is a linear function of  $\varphi$ .



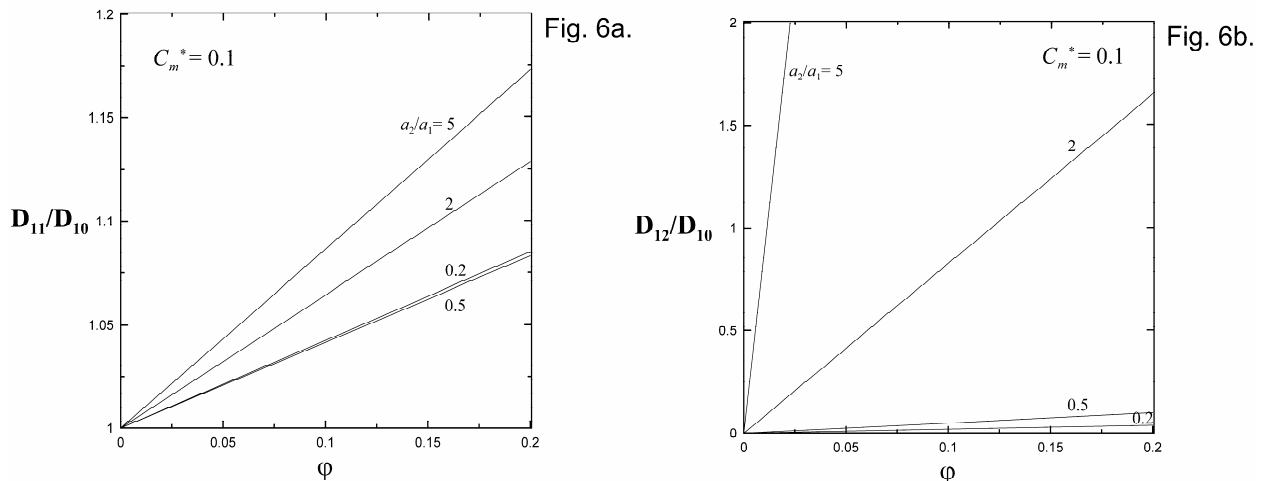
**Fig. 5.** Diffusivities (a)  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and (b)  $\mathbf{D}_{12}/\mathbf{D}_{10}$  of an aerosol of two types of particles for equal number densities down a concentration gradient versus the total volume fraction of particles  $\varphi$  for  $C_m^* = 0.1$  with  $a_2/a_1$  as a parameter.

Another particular case of a polydispersed aerosol with two types of particles can be approached by the consideration of equal volume fractions of each type of particles ( $\varphi_1 = \varphi_2 = \frac{1}{2}\varphi$ ), in comparison with the above case. Here, the diffusivities are:

$$\frac{\mathbf{D}_{11}}{\mathbf{D}_{10}} = 1 + \varphi \left\{ \frac{1}{2}(\alpha + \xi) - C_{23} \left[ \frac{15}{8} C_{25} \frac{a_1}{a_1 + a_2} - \frac{5}{4} C_{05} \frac{a_1^3}{(a_1 + a_2)^3} + \frac{1}{80} (4C_{(-3)2} + 20C_{(-1)4} - 60C_{05} + 91C_{27}) \frac{a_1 a_2^2}{(a_1 + a_2)^3} \right] \right\} \quad (36a)$$

$$\frac{\mathbf{D}_{12}}{\mathbf{D}_{10}} = \varphi \left[ \frac{1}{2} \left( \frac{a_2}{a_1} \right)^3 + \left( \frac{a_2}{a_1} \right)^2 + \frac{3}{2} (1 - C_{23}) \left( \frac{a_2}{a_1} \right) + \frac{75}{32} C_{23} C_{25}^2 \frac{a_1^3 a_2}{(a_1 + a_2)^4} \right] \quad (36b)$$

In Fig. 6, the diffusivities  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and  $\mathbf{D}_{12}/\mathbf{D}_{10}$  are drawn versus the total volume fraction with  $a_2/a_1$  as a parameter. The variations of the diagonal diffusivity  $\mathbf{D}_{11}/\mathbf{D}_{10}$ , due to the changes of volume fraction  $\varphi$  illustrated in Fig. 6(a), are quite different from the previous situation of equal number densities. Here, the diffusivities, both diagonal and off-diagonal elements, are always increasing with the increase of total volume fraction of particles, based on the assumption of equal volume fraction of the two type particles. In addition, the bulk diffusivity of each type of particles is larger than that predicted by modified Stokes-Einstein equation, Eq. (3). In general,  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and  $\mathbf{D}_{12}/\mathbf{D}_{10}$  increase with the increase of  $a_2/a_1$  as  $a_2/a_1 > 1$ , and the variations of  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and  $\mathbf{D}_{12}/\mathbf{D}_{10}$  are insensitive at different values of  $a_2/a_1$  for cases of  $a_2/a_1 < 1$ .



**Fig. 6.** Diffusivities (a)  $\mathbf{D}_{11}/\mathbf{D}_{10}$  and (b)  $\mathbf{D}_{12}/\mathbf{D}_{10}$  of an aerosol of two types of particles for equal volume fraction down a concentration gradient versus the total volume fraction of particles  $\varphi$  for  $C_m^* = 0.1$  with  $a_2/a_1$  as a parameter.

## CONCLUSIONS

In this article, an analytical investigation of Brownian diffusion of a homogeneous and/or non-homogeneous aerosol was developed for the consideration of particle interactions. The particles could be different in particle size, and there was a slippage feature occurring at the gas-particle interfaces. The original argument of Einstein's was generalized to show that the particle flux in probability space due to Brownian was the same as that which would be produced by the application of a certain thermodynamic force to each particle. This prescription was then applied to deduce the Brownian diffusivities in two different types of situations: (a) a homogeneous dispersion which was being deformed; (b) a suspension in which there was a gradient of concentration of particles. In the previous situation, the relatively translational diffusivity of two slippage particles was formulated from the properties of the low-Reynolds number flow due to the two-particle interactions. While the latter addressed the diffusivity, expressed by the diagonal and off-diagonal elements of the diffusivity matrix, in a concentration gradient which brought considerations of the multi-particle-excluded volume into the problem. The diffusivity of the particles was found to increase slowly as the concentration rose from zero. In addition, if the slippage characteristic at the particle surface becomes significant, the energy dissipation due to particle interactions will decrease, making the bulk diffusivity large. Generally, the particles with a small radius dominated the Brownian diffusion.

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## NOTATION

- $a$  = particle radius, m  
 $C_{ij}$  =  $(1 + iC_m Kn)/(1 + jC_m Kn)$   
 $C_m$  = slip coefficient at the particle surface  
 $C_m^*$  =  $C_m Kn$   
 $\mathbf{D}$  = diffusivity tensor,  $m^2/s$   
 $D_0$  = relative diffusivity defined by Eq. 18a,  $m^2/s$   
 $\mathbf{e}$  = unit vector pointing from particle one to particle 2  
 $\mathbf{F}$  = force exerted on a particle by the fluid, N

- I** = unit dyadic  
**k** = Boltzmann constant, m N 1/K  
**Kn** = Knudsen number ( =  $l/a$  )  
**l** = mean free path of the gas molecules, m  
**M<sub>ij</sub>** = dimensionless mobility tensors defined by Eq. 6  
**M<sub>ij</sub><sup>(p,n)</sup>** = dimensionless mobility coefficient defined by Eq. 9  
**n** = particle number density, 1/m<sup>3</sup>  
**p** = dynamic pressure, N 1/m<sup>2</sup>  
**P** = probability density function  
**T** = absolute temperature, K  
**U** = translational velocity of a particle, m 1/s  
**v** = fluid velocity field, m 1/s  
**r** = vector pointing from particle 1 to particle 2, m  
**r** = equal to  $|\mathbf{r}|$ , m  
**r<sub>12</sub>** = center-to-center distance between particle 1 and particle 2, m  
**x** = position vector, m

*Greek letters*

- α** = particle interaction coefficient of  $O(\varphi)$  in suspension  
**μ** = chemical potential, m N  
**φ** = volume fraction of particles in suspension  
**Φ** = energy potential, m N  
**Ψ** = mutual potential, m N  
**Ω** = angular velocity of a particle, 1/s

*Subscripts*

- 0** = particle center  
**1** = particle 1  
**2** = particle 2  
**i** = *i*-type particle  
**j** = *j*-type particle

*Superscripts*

- (0)** = infinite dilution



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