BROWNIAN COAGULATION OF AEROSOLS IN TRANSITION REGIME

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Short paper
DOI: 10.2298/TSCI1205362C

The collision efficiency of Brownian coagulation for monodisperse aerosol particles in the transition regime is considered. A new expression for collision efficiency is proposed taking into account the influence of tangential relative motion when two particles get close enough during the diffusion process. The breakaway point from which the theory of near continuum regime no longer applies can thus be obtained easily. A comparison with experimental measurements shows the accuracy of the results predicted by the new theory.

Key words: *collision efficiency, tangential motion, breakaway point*

Introduction

Brownian coagulation is a process whereby particles collide with one another due to their relative Brownian motion, and adhere to form larger particles [1, 2]. Many properties of aerosol systems, such as light scattering [3], toxicity as well as physical processes including diffusion, condensation and thermophoresis depend strongly on their size distribution [4, 5]. Therefore, Brownian coagulation is of great importance in many areas of science and technology [6, 7]. The aerosol particle dynamics depends upon the Knudsen number, which is defined by $\mathrm{Kn} = \lambda/a$, where λ is the molecular mean free path in the gas and a is the radius of the aerosol particles.There are two limiting regimes corresponding to large and to small values of Kn for which the theory is well characterized. In the continuum regime where $\mathrm{Kn} < 0.1$, coagulation rate was given by Smoluchowski [8]:

$$K_S = \frac{2kT}{3\mu}(a_1 + a_2)\left(\frac{1}{a_1} + \frac{1}{a_2}\right) \tag{1}$$

where k is the Boltzmann constant, T – the absolute temperature, μ – the gas viscosity, and a_1 and a_2 are the radii of two sizes of particles. When the Cunningham correction factor is used to the diffusivity of particles, the Smoluchowski coagulation rate can be extended into the range $0.1 < \mathrm{Kn} < 1$:

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$$K_S = \frac{2kT}{3\mu}(a_1 + a_2)\left[\frac{C(\mathrm{Kn}_1)}{a_1} + \frac{C(\mathrm{Kn}_2)}{a_2}\right] \tag{2}$$

The Cunningham correction factor is: $C(\mathrm{Kn}) = 1 + \mathrm{Kn}[1.257 + 0.40 \exp(-1.10/\mathrm{Kn})]$ [9]. In the free molecule regime, the coagulation rate is given by [10]:

$$K_m = \sqrt{\frac{8\pi kT(m_1 + m_2)}{m_1 m_2}}(a_1 + a_2)^2 \tag{3}$$

where m_1 and m_2 are the particle masses.

The transition regime is characterized in the range of 1 < Kn < 50. In the transition regime the coagulation rate is described neither by the continuum theory nor by kinetic theory. Wang and Lin [11] studied evolution of number concentration of nanoparticles undergoing Brownian coagulation in transition regime. Yu *et al*. [12] studied Taylor-expansion moment method for nanoparticle coagulation

In the entire size regime due to Brownian motion, Fuchs [13] found a semi-empirical solution of the coagulation coefficient by assuming that outside of a certain distance, namely an average mean free path of an aerosol particle, the transport of particles is controlled by the continuum diffusion theory with the slip correction and that inside the distance the particles move like in a vacuum which can be described by simple kinetic theory. Dahneke [14] treated the diffusion process as a mean free path phenomenon. Otto *et al*. [15] summarized these different theories as well as the harmonic mean method and other Fuchs-like methods [16]. Davies [17] reviewed experimental data and pointed out that the coagulation rate of aerosol particles was a unique function of the Knudsen number up to Kn = 15 and is equal to K_o, the product of the Smoluchowski coagulation rate and the Cunningham correction factor.

New expression of coagulation rate

In Fuchs' theory the diffusing particles within the distance $\varDelta_F$ of the sphere surface are regarded as being in a vacuum. This model is somewhat reasonable since $\varDelta_F$ is of the order of the particle mean free path. In present study, we followed Fuchs' approach and divided the whole space around the particle into two regions by a certain distance $\varDelta$. The diffusing particles beyond $\varDelta$ obeyed classical Smoluchowski diffusion behavior while the ones within this distance would be affected by tangential relative motion of two particles. Outside the distance of $\varDelta$, the transport of particles obeys the continuum diffusion theory and is described by Smoluchowski equation [18]:

$$\frac{\partial n_2}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{12}\frac{\partial n_2}{\partial r}\right) \tag{4}$$

where n_2 represents the number density distribution of the particles with radius a_2. The co--ordinate r has its origin at the center of particle with radius a_1. With boundary conditions $n_2 = n_2^{\varDelta}$ when $r = \varDelta$ and $n_2 = n_2^{\infty}$ when $r = \infty$, the solution can be expressed as $n_2 = \Delta(n_2^{\varDelta} - n_2^{\infty})/r + n_2^{\infty}$. Inside the distance of $\varDelta$, the transport of particles is described by diffusion process but is affected by tangential relative motion of two particles. Mean radial velocity of sphere 2 can be derived as $\bar{v}_r = 2D_{12}/r$.

The equation that describes the transport of particles inside Δ thus should be given by:

$$\frac{\partial n_2}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_{12}\frac{\partial n_2}{\partial r}-\frac{2D_{12}}{r}n_2\right)\right] \tag{5}$$

which can also be solved with boundary conditions $n_2 = 0$ when $r = a_1 + a_2$ and $n_2 = n_2^{\Delta}$ when $r = \Delta$. The fluxes at the distance of Δ, which is the interface of two regions, should be matched and finally the coagulation rate can be derived and is given by $K = 3\delta K_c/(\delta^3 + 2)$ in which $\delta = \Delta/a_{12}$ and $\delta \geq 1$. By matching the solution of free-molecule regime, the dimensionless distance can be expressed as $\delta = (3K_C/K_m)^{1/2}$.

Results and discussion

Figure 1 shows the Brownian collision efficiency [19], which is the ratio of actual coagulation rate to ideal rate K_S, in the transition regime predicted by different theories. All of the collision efficiencies are calculated based on ρ = 1.00 g/cm^3, T = 300 K, $\mu = 1.83 \cdot 10^{-5}$ kg/m·s and the mean free path of gas molecule $\lambda = 65 \cdot 10^{-9}$ m. Kim *et al.* [20] studied the Brownian coagulation of aerosols in the transition regime for 0.8 < Kn < 5.5. Figure 2 shows the experimentally determined collision efficiencies of Brownian coagulation, together with predictions given by present work, Fuchs [14] and Davies [18]. The theoretical predictions in fig. 2 were obtained based on T = 293 K, $\mu = 1.83 \cdot 10^{-5}$ kg/m·s, $\lambda = 66 \cdot 10^{-9}$ m, and ρ = 0.887 g/cm^3 for oleic acid, and ρ = 2.16 g/cm^3 for sodium chloride.

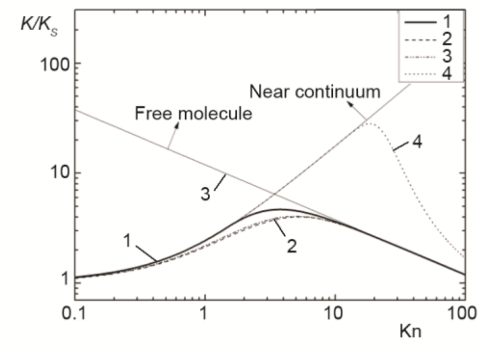

Figure 1. Brownian collision efficiency in the transition regime. 1 – Present theory, 2 – Fuchs' formula, 3 – Dahnekes' formula, 4 – Davies' formula

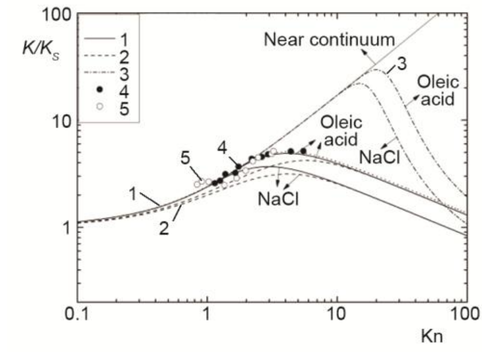

Figure 2. Comparison between various theoretical predictions and experiments. 1 – Present theory, 2 – Fuchs' formula, 3 – Davies' formula, 4 – NaCl, 5 – oleic acid

The collision efficiency calculated by present theory can predict the experimental results accurately, while the Fuchs' formula underestimates the collision efficiencies in almost all range of Knudsen number of experiments and Davies' formula can predict the results when Kn is small enough and overestimate the breakaway point from which the near continuum formula can not provide the actual collision efficiency. None of the three theoretical expressions can predict the collision efficiencies of Brownian coagulation for the solid particles of sodium chloride properly. But when the equivalent density of solid polymer is introduced in present theory, the collision efficiencies predicted by present theory could fit experimental data well. The empirical formula for this equivalent density is given by $\rho_e = N \rho r_o^3/r_c^3$ in which N is the number of original particles in polymer, ρ and r_o are the density and radius of original particles respectively and r_c is the circumscribed sphere radius of the polymer. When $N = 4$ and the centers of these original particles are at four corners of a tetrahedron, the circumscribed sphere radius can be expressed as $r_c = [(3/2)^{1/2} + 1]r_o$.

Conclusions

By matching the fluxes at this certain length and making use of the coagulation rate in the free molecule regime, where the Knudsen number Kn > 50, a new expression for Brownian coagulation rate is raised. Four theoretical predictions of collision efficiencies including the one of present theory are compared in the range of 0.1 < Kn < 100 and the result shows the present expression can give the collision efficiency in the transition regime properly. A comparison with the experimental results shows the accuracy of the theoretical predictions of present work and the importance of accounting for the influence of tangential relative motion when Kn is large enough for monodisperse aerosols. The present theory can also predict the breakaway point of monodisperse liquid aerosols from which the formula of near continuum regime no longer applies and the influence of tangential motion appears. For the aerosols of solid particles, none of the theories could predict the collision efficiency accurately. But if the new concept of equivalent density is introduced, the present expression of collision efficiency can predict experimental results of sodium chloride aerosols accurately.

Acknowledgments

This work was supported by the National Natural Science Foundation of China.

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Paper submitted: August 1, 2012
Paper revised: September 6, 2012
Paper accepted: September 12, 2012