Some Problems in Size Measurement of Submicron Particles

Yasuo Kousaka
Department of Chemical Engineering
University of Osaka Prefecture

Abstract

Some problems that the author has encountered in size measurement of submicron particles in air and in water have been outlined. When particle size is smaller than around 0.5 μm, the mean velocity caused by Brownian motion of a particle, which cannot be repressed by any usual means, becomes comparable with the gravitational settling velocity in air and exceeds the velocity in water. When the number concentration of particles is higher than about $10^8$ particles/cm$^3$, Brownian coagulation, which cannot be repressed in air and in water unless the use of appropriate dispersion agents becomes significant. Size measurement by sedimentation methods in one or both of these cases gives an erroneous result. Another difficulty arises in size measurement of aggregate particles composed of submicron primary particles. When one may want to know the size distribution of aggregates as they are, sedimentation in air is effective. For measurement of primary particle size composing aggregates, on the other hand, sedimentation in water is effective since deaggregation in water is much easier than in air. As to submicron liquid droplets there is a problem of stability. Even if they have low vapor pressure such as oil, they can easily evaporate to decrease in size by the Kelvin effect which becomes significant as the droplet size decreases.

1. Introduction

Particles in submicron range undergo the Brownian motion which results from the collision of surrounding gas or liquid molecules with the particles. Consequently such a motion causes deposition of particles on the wall of a size analyzer and Brownian coagulation under the condition of high number concentration, which have undesirable effects on size measurement.

Particle deposition is practically unavoidable in air or in water. Coagulation, on the other hand, can be prevented in water, although it is also unavoidable in air except under a sufficiently reduced number concentration. When an appropriate dispersion agent is added in suspension, electrical repulsion resulted from it would take place among the particles and prevent coagulation.

Other phenomena causing problems in size measurement of small particles are evaporation and condensation. Evaporation takes place on the surface of liquid droplets suspended in air due to a vapor pressure rise on their surfaces having curvature by the Kelvin effect. A temperature drop within the system, on the other hand, causes condensation of a vapor on the particle surfaces, also producing problems in size measurement especially when very fine hygroscopic particles are kept suspended in air.

This paper summarizes some problems, such as not only those above stated but deaggregation and particle shape, which the author has encountered in size measurement for recent several years.

2. Brownian coagulation and deposition

The particle behavior in a small sedimentation cell as illustrated in Fig. 1 is discussed here so as to easily obtain an experimental verification. In this cell, a fluid is stationary and an ex-
ternal force acting on particles is limited to the gravitational force. In addition horizontal particle diffusion is negligible because the cell width B is sufficiently large compared with the cell depth H. When particles of radius \( r \) exist in such a cell, the particle number concentration \( n \) at the point below the suspension surface \( y \) at the lapse of time \( t \) is given by the following population balance equation.

\[
\frac{\partial n(r, t)}{\partial t} = D(r) \frac{\partial^2 n(r, t)}{\partial y^2} - u_t(r) \frac{\partial n(r, t)}{\partial y} + \frac{1}{2} \int_{\rho=0}^{\rho=\infty} K_B(\sqrt{r^3 - \rho^3}, \rho) n(\sqrt{r^3 - \rho^3}, t) \times n(\rho, t) \left( \frac{r}{\sqrt{r^3 - \rho^3}} \right)^2 d\rho - \int_{\rho=0}^{\rho=\infty} K_B(r, \rho) n(r, t) n(\rho, t) d\rho
\]

where \( D(r) \) and \( u_t(r) \) denote the diffusion coefficient and the terminal settling velocity of a particle having radius \( r \) respectively. The first term in the right hand side accounts for the Brownian diffusion, the second for the gravitational sedimentation, the third represents the number of newly formed particles with radius \( r \) by collision of two particles, while the last term represents the decrease in number of particles with radius \( r \) and density \( \rho \) by collision with other particles. In collision, it is assumed that two particles collided with each other form a new spherical particle whose mass is the same as the combined mass of two smaller particles. In addition, \( K_B \) is estimated by the following coagulation function.

\[
K_B(r, \rho) = \frac{2kT}{3\mu} (r + \rho) \left\{ \frac{C_m(r)}{r} + \frac{C_m(\rho)}{\rho} \right\}
\]

where \( C_m(r) \) is the slip coefficient, \( K \) the Boltzmann's constant, \( \mu \) the viscosity, and \( T \) the temperature. The numerical calculation of Eq. (1) in dimensionless form under various conditions provides changes in the number concentration of particles of the radius \( r \) at the depth \( y \) with the time \( t \). It is assumed that the initial size distribution of the particles introduced into the cell shown in Fig. 1 is regarded as a log-normal one in the calculation. This result estimates the effect of coagulation on a sedimentational size analysis, using the ratio of the coagulation rate to the gravitational settling velocity \( CG \), as shown in the following equation.

\[
CG = K_0 n_0 C_m(r_{go}) H/\mu u_t(r_{go}) Z, \quad K_0 = \frac{2kT}{3\mu}
\]

In the similar manner it also estimates an effect of the diffusion on the analysis, using the ratio of the diffusion rate to the gravitational settling velocity \( DG \), as given by the following equation.

\[
DG = D(r_{go})/Hz u_t(r_{go}) Z
\]

where \( n_0, r_{go}, H, \) and \( Z \) are an initial particle number concentration, an initial geometric mean radius, a sedimentation cell depth, and a centrifugal effect (centrifugal acceleration divided by gravitational acceleration) respectively. \( Z \) is unity in the gravitational field.

2.1 Brownian coagulation

The sedimentational size analysis is discussed here to determine cumulative size distributions by observing time-dependent changes in the particle number concentration at the depth \( y \) shown in Fig. 1. Fig. 2 indicates a calculated result obtained from Eq. (1) when the first term due to diffusion is negligible.\(^{11} \) The abscissa represents a dimensionless radius \( \tilde{r} \) (\( r \) divided by \( r_{go} \)) modified by the slip coefficient, and the ordinate indicates a cumulative under-size. The broken line in this figure shows either a true particle size distribution when the number concentration is sufficiently low (\( CG \cdot y \approx 0 \)), \( \bar{y} = y/H \) or the initial size distribution of the particles introduced into the cell illustrated in Fig. 1 when the concentration is high (\( CG \cdot \bar{y} \neq 0 \)). In the case of high concentration, the change in number concentration of the particles in the cell depends on the Brownian coagulation as well as the gravitational settling. Accordingly these two effects cause faster decrease in the number concentration at the depth \( y \) in Fig. 1 than that of the gravitational
settling alone, and provide the same result as would be obtained from the analysis of larger particles. Hence the particle size distribution shown in Fig. 2 shifts to the larger side as \( C G \cdot \bar{y} \) increases. The author experimentally verified that such phenomena could actually happen as follows.

A microscopic sedimentation analyzer (Shimadzu SA-MID) was used for the experiment, which converts the time-dependent changes of the particle number at the depth \( y \) in Fig. 1 into the particle size distribution by observing from the top using a TV camera and an ultramicroscope. In order to calibrate this analyzer, standard particles of polystyrene latex whose size was known (geometric mean radius \( r_{go} = 2.85 \mu m \), geometric standard deviation \( a_g = 1.16 \)), were used being sufficiently diluted and dispersed in water. Consequently the good result could be obtained as shown in Fig. 3.

Fig. 4, (1) indicates an experimental result of cigarette smoke which was diluted 100 times in clean air just after smoke generation. Fig. 4, (3) represents one under the highly concentrated condition without dilution. These results show the Brownian coagulation would cause remarkable changes in particle sizes of cigarette smoke. Fig. 4, (2) shows, on the other hand, the case where the smoke was diluted by small amounts of clean air before its introduction into the cell so as not to cause coagulation in the cell. The comparison between the result of (2) and that of (3), therefore, estimates the
effect of coagulation in the cell. The solid line in Fig. 4, which is theoretically obtained, shows good agreement with experimental results.

In general, particle sizes of a highly concentrated aerosol vary remarkably by Brownian coagulation, as shown in Fig. 4. It may be roughly calculated, for instance, that an aerosol of $10^{12}$ particles/cm³ in number concentration and 0.1 μm in diameter will change to that of 10⁹ particles/cm³ and 1 μm in one second. Therefore it must be careful in not only sedimentational size analysis but other size analyses when particle number concentration is high.

2.2 Deposition by Brownian diffusion

Fig. 5 shows a calculated result of monodisperse particles where the third and the fourth term of the right hand side in Eq. (1) are negligible or the effect of coagulation is unnecessary to be taken into account. This figure suggests how the dimensionless number concentration $\bar{n} (\bar{n} = n/n_0, n_0$ is initial number concentration) will depend on the lapse of time $t$ at the dimensionless depth $\bar{y} (\bar{y} = y/H)$ in the sedimentation cell. Weak diffusion ($DG$ is small) causes a sharp boundary in the concentration toward the sedimentational direction or $y$ direction, whereas strong one ($DG$ is large) extends a broad concentration distribution toward $y$ direction. Accordingly monodisperse particles would be pretendedly observed as polydisperse when $DG$ is large.

Fig. 6 shows a result experimentally obtained using the above stated analyzer to identify how such a diffusion could have effects on size measurement. The broken line represents a true particle size distribution, when the sedimentation cell is set in the centrifugal field with large $Z$ or $DG$ is small in Eq. (4). The solid circles in the right side, on the other hand, which were experimentally obtained, show approximate agreement with the solid line resulted from the solution of Eq. (1).

Since the diffusion coefficient $D$ in Eq. (4) increases with the decrease in particle size, an average particle displacement in one second would become comparable to the gravitational settling velocity. A simple calculation will provide the approximate accordance between these two values under the condition of 3 g/cm³ in particle density and about 0.4 μm in radius in water (1 g/cm³ and 0.25 μm in air). Therefore the gravitational sedimentation in water might cause large errors in size measurement when particles are smaller than 0.4 μm in radius. The
settling velocity of the above stated particles is to be estimated as $0.7 \mu m/sec$, hence such a small convective flow arising in the sedimentation cell would provide a distrustful result in size measurement. Since diffusional deposition on the vertical wall is not taken into account in the analysis of this paper, an increase in $H$ will not necessarily provide a successful conclusion in the analyzer where such an effect should be taken into account.

2.3 Simultaneous effect of Brownian coagulation and deposition

It is possible to prevent Brownian coagulation in water by adding an appropriate dispersion agent which permits particles to repulse electrically each other. However both Brownian coagulation and deposition may have effects on particle size measurement simultaneously if a dispersion agent is unappropriate or measurement is to be conducted in air. Fig. 7 shows the particle size distributions of needlelike iron oxide particles (length-to-diameter ratio is about 6) measured in water containing no dispersion agent. The open circles illustrated in the left side represent experimental results obtained by a centrifugal sedimentation. Solid circles illustrated in the right side, on the other hand, offer those by the gravitational sedimentation method under the influence of coagulation and deposition, and the solid line shows the corresponding result calculated by Eq. (1).

3. Evaporation and condensation

Behavior of aerosols is discussed in this section. When liquid droplets suspended in a gas is small, evaporation causes their size reduction or extinction even if a vapor pressure of the liquid is rather low. When supersaturation of a vapor is formed in a gas due to a temperature drop, the vapor condenses around the particles in the gas to increase their sizes. Such a size change will become remarkable when particles are small.

Evaporation and Condensation discussed here are based on the following equations.

$$P_0 = \exp \left( \frac{-2\gamma}{rK} \right)$$  \hspace{1cm} (5)
$$\frac{dr}{dt} = \frac{D(r)M}{r \rho_d R} \left( S \frac{P_s(T_B)}{T_B} - \frac{P_0(T_0)}{T_0} \right) (1 + \frac{P_0(T_0) + S P_s(T_B)}{2P_t} \left( \frac{K_n + 1}{1.333 K_n + 1} \right) \times (1 - \frac{r}{r_B})^{-1})$$  \hspace{1cm} (6)
$$T_0 = \frac{\lambda D(r)M}{KR} \left( S \frac{P_s(T_B)}{T_B} - \frac{P_0(T_0)}{T_0} \right) \times \left( 1 + \frac{P_0(T_0) + S P_s(T_B)}{2P_t} \right) + T_B$$  \hspace{1cm} (7)

Eq. (5) shows a vapor pressure rise at the particle surface by the Kelvin effect. $P_0$ and $P_s$ are vapor pressures at the particle surface and at the flat surface respectively, $\gamma$ is a molar volume, $\sigma$ a surface tension, $K$ the Boltzmann’s constant, and $T$ a temperature.

Eq. (6) indicates either the evaporation rate of liquid droplets, or the growth rate of particles by condensation when a vapor reaches supersaturation. $M$ is a molecular weight, $\rho_d$ a density of condensed liquid, $R$ the gas constant, $S$ a degree of saturation, $T_B$ a temperature at the radius $r_B$ distant form the particle center. $P_t$ a total vapor pressure, $K_n$ the Knudsen number, and $T_0$ a particle surface temperature which can be obtained from Eq. (7). In Eq. (7), $\lambda$ and $K$ are a latent heat and a thermal conductivity of a gas respectively. The radius $r_B$ in Eq. (6), which is based on the cellular model, corresponds to that of a sphere having an average amount of gas distributed to each particle.
3. 1 Evaporation

The stability of water droplets suspending in air is discussed here as the most familiar instance. Fig. 8 shows a calculated result of the time-dependent change in water droplet radii obtained from Eq. (5), Eq. (6), and Eq. (7). This figure, where $r_0$ denotes the initial water droplet radius, $n$ the droplet number concentration, and $S_0$ the degree of initial saturation, suggests that water droplets would evaporate and vanish in a short time when $r_0$ and $n$ are small. When the concentration $n$ is high, droplets are comparably stable, because the evaporated vapor contributes to the increase in the degree of saturation. Although the droplet clouds were assumed to exist in an infinite space in Fig. 8, the droplet size will decrease in a small cell faster than in the case of Fig. 8 due to vapor condensation on the wall. It was assumed in this figure that $S_0 = 1$ (initial relative humidity = 100%); but when $S$ is smaller than a unity, for instance $S = 0.5$ (relative humidity = 50%), water droplets of $r_0 = 1\mu m$ and $n = 10^4$ droplets/cm$^3$ will vanish in $5 \times 10^{-3}$ seconds.

Liquid droplets with lower vapor pressure than that of water such as DOP or DBP have been often applied to experiments because these droplets of more than $r_0 = 0.5\mu m$ are relatively stable. Even such droplets, which are regarded as stable in general, however, might be subject to the influence of evaporation since the Kelvin effect increases with the decrease in particle size. This is recognized in Fig. 9 which shows droplet size distributions of DOP and silicone oil obtained by a size analyzer based on the Kelvin effect. These droplets were generated by an aerosol generator of an evaporation-condensation type and then classified by a differential mobility analyzer (DMA). Since DOP and silicone oil droplets classified by DMA are possibly estimated to be of the same size, the difference of the distributions in Fig. 9 will depend on the evaporation which takes place in approximately 10 seconds after the DMA to the size analyzer. In other words, DOP droplets evaporates faster than silicone oil droplets. The author has been practically unable to generate ultrafine droplets with a radius of less than 0.005\mu m, because such particles might vanish by the time when the measurement begins even if they could be generated. Therefore measurement of submicron liquid droplets should require sufficient care.

3. 2 Condensation

When adiabatic expansion or heat removal from the outside cools an aerosol containing the vapor such as water vapor under the nearly saturated condition, size enlargement will take place which results from condensation of the supersaturated vapor on the particle surface. Although this size enlargement is relatively slight in general if the particle size is large, it becomes remarkable when particle sizes are smaller than 0.1\mu m. The size enlargement of hygroscopic particles due to condensation resulted from temperature drop could take place in unsaturated conditions, hence much care must be required in measurement of such particles. The size enlargement of NaCl particles experimentally obtained under the increased humid conditions is shown in Fig. 10 as an example.
4. Deaggregation

Size measurement is often conducted in water to determine size distributions of primary particles. In such a case, preliminary treatments are practically performed preceding the size measurement; at first the disintegration of aggregates by a mechanical force (deaggregation), then the addition of dispersion agent to prevent reaggregation of once deaggregated particles. When particles suspended in air are to be measured, on the other hand, differently conditioned particle sizes are desired; the size of aggregated particles and that of deaggregated or primary ones.

Fig. 11 shows an experimental result obtained from the size analysis of aggregates deaggregated in air and in water by the microscopic sedimentation analyzer as previously stated. The deaggregation was achieved in water suspension containing 0.2% (weight basis) NaHMP with a repetition of strong suction and discharge using a syringe. The measured values have a good concord with Feret diameters determined by an electron microscope. The iron oxide particles used in the experiment were shaped like spheres derived from rounded cubes. The agreement of these two results suggests that particles could be completely deaggregated into primary particles in water. The solid circles in this figure, on the other hand, represent the particle size distribution of iron oxide powders which were deaggregated in air by a high speed rotating blade disperser. This result shows how difficult it is to deaggregate fine aggregates in air.

In general aggregated particles may be effectively deaggregated by;
- velocity gradient of a fluid
- acceleration or retardation of particles in a fluid
- particle collision with obstacles in a flow field

The formers might be effective in a liquid, whereas the latter has been experimentally verified to be the most effective in air. In each case, stronger mechanical forces would be required with the decrease in particle size.

The method to prevent reaggregation of once aggregated particles depends on the condition around them; the low concentration of less than $10^7$ particles/cm$^3$ is effective in air, while an addition of an appropriate dispersion agent is so in water. Fig. 12 shows the $\xi$-potential measured for the determination of the most suitable amount of a dispersion agent that can provide a successfully deaggregated or reaggregation-free condition. $\xi$-potentials in this figure were determined by observing horizontal velocity of particles using a cell with platinum electrodes instead of the cell of the analyzer previously stated. They could suggest the most suitable concentration, having a good accord-
Fig. 12 Relation among NaHMP concentration, geometric particle radius and ζ-potential

correlation with geometric particle radius \( r_{go} \), as shown in this figure.

5. Particle shape, charging and thermal convective flow

The effects of particle shape on size measurement are also important, not limited solely to submicron particles. It should be natural that a size distribution of non-spherical particles depend on the principle of the sizing method used. Fig. 13 shows Stokes diameters, Feret diameters (2-dimensional), and major axis lengths of needlelike particles with an aspect ratio (length-to-diameter ratio) of approximately 12 as an extreme example.

With respect to aggregated particles, sizing would become more difficult because of the difficulty in the estimation of the density taken porosity into account as well as the shape.

Fig. 14 shows the electrical charge of aggregated CaCO₃ dispersed in air which is represented in terms of electrical mobility. This figure suggests that aggregated particles are highly charged positive or negative. Size measurement of highly charged particles in air sometimes leads to a wrong result because of the electrical precipitation of particles in a sizing instrument. Furthermore in a sedimentation method, thermal convective flow of a fluid in the cell would cause a problem. Since a particle of 0.4μm in radius and 3g/cm³ in density sedimentates in water at approximately 0.7μm/sec as stated in 2.2, such a velocity induced by a convective flow in the cell could be unavoidable unless the severe temperature control throughout the cell. \( G_r \) (Grashof) number will provide an approximate criteria to estimate the degree of the convective flow, but can scarcely offer a general quantitative criteria to evaluate as to various shapes of cells. Accordingly size measurement which is subject to an influence of slight convection as above stated should be avoided.

6. Conclusion

Several problems in size measurement of submicron particles were discussed through our experiences and observations. The obtained results are as follows:

(1) The effect of Brownian diffusion of particles on sedimentational size measurement becomes important, when particle size is smaller than about 0.8μm (0.5μm in air).

(2) Addition of an appropriate dispersion agent in water or reduced particle number con-
Concentration less than $10^7$ particles/cm$^3$ in air is effective to prevent aggregation in size measurement.

(3) Centrifugal sedimentation can minimize the effects of a convective flow in the cell as well as two above-mentioned phenomena.

(4) Small liquid droplets are likely to vanish due to evaporation even if vapor pressure of a liquid is low.

(5) Deaggregation of aggregated particles requires stronger mechanical forces with the decrease in particle size. Great difficulty would be encountered especially in deaggregation of particles in air.

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