1. Introduction

Submicron particles or ultrafine particles have been paid increasing attention in various fields, and attention seems to be shifted to smaller and smaller particles with the times. In fact, detection, characterization and control of particles of 0.1 μm or smaller in size have become important in clean rooms for semiconductor production processes, in fine ceramics industries, in combustion processes, and in atmospheric or indoor environmental problems, and so on.

Some topics on submicron particles suspending in a gaseous or liquid medium will be briefly introduced in this paper. In the former section of this paper, typical size-dependent properties of a particle are looked through, and topics on coagulation and deposition which may play an important roll in a particle dispersed system in industrial processes are introduced in the following sections.

2. Size-dependent properties of submicron particles

Typical size-dependent properties of particles suspending in air and in water are shown in Fig. 1 together with the corresponding equations. The solid lines in the figure are those in air, while the dashed lines in water and the one-point dashed line are in low-pressure air. The curves appearing in the figure are briefly explained in the following.

Terminal settling velocity in the gravity field, \( u_t \), decreases both in air and in water with the decrease in particle size, as is expressed by Eq. (1). The distortion in the small size range of the solid line of \( u_t \) is caused by the slip coefficient \( C_e \), which is size-dependent as shown in Eq. (2). The slip coefficient \( C_e \) increases with the decrease in size of particles suspending in a gaseous medium, but it is always unity for particles suspending in a liquid medium. It increases with the decrease of gas pressure \( p \) as shown in Eq. (3), an example of which is shown in Fig. 1 (\( C_e^* \)).

When a particle is small, Brownian motion which is caused by random variations in the incessant bombardment of molecules against the particle occurs. The average absolute value of Brownian displacement in one second, \( l \), is shown in Fig. 1, which is obtained as \( t = 1 \) sec in Eq. (4). The intersections of the curves of \( l \) and \( u_t \) lie in around 0.5 μm in air and 1 μm in water. If one may observe the settling velocity of such a small particle in a short time, it will be a resultant velocity caused by both gravitational settling and Brownian motion. \( D \) in Eq. (4) is the particle diffusion coefficient which is given by Eq. (5). The larger values of \( D \) indicate that more vigorous Brownian motion and more rapid particle transfer in a particle concentration gradient occur. As is seen in Fig. 1, the particle diffusion coefficient in water is much smaller than that in air.

\( \tau_g \) in Fig. 1 is called relaxation time and is given by Eq. (6). It has a unit of time and it characterizes the time required for a particle to relax its velocity to a new condition of forces. When a particle is projected into a stationary fluid with a velocity \( u_0 \), it will travel a finite distance before it stops. Such a distance is called stop-distance and is given by \( u_0 \tau_g \). So \( \tau_g \) can be a measure of inertial motion of a particle in a fluid.

\( B_e \) in Fig. 1 is the electrical mobility which expresses the velocity of a charged particle in an electric field of unit strength. The steady particle velocity in an electric field \( E \) is given by \( EB_e \). Since \( B_e \) depends upon the number of elementary charge which a particle carries,
Fig. 1  Size-dependent properties of a particle suspending in air and in water.
$n_p$, as seen in Eq. (7), $n_p$ should be made clear to determine $B_n$. $n_p$ is predictable with aerosol particles in most cases, where particles are charged by diffusion of ions. An example where particles are charged in a large number of bipolar ions by diffusion is shown in Fig. 2. In a liquid, on the other hand, it is difficult to predict $n_p$ in general because of the complex interaction between a particle and surrounding ions. Figure 3 shows the particle trajectories in air in a vertical parallel plate electrodes. The zigzag movement in the figure is caused by Brownian motion and the trajectories in the vertical direction indicate that the particles are electrically neutral, say, uncharged.

$p_d/p_w$ in Fig. 1 is the ratio of the vapor pressure on a droplet surface to that on a flat surface of the same liquid. Vapor pressure on a droplet surface increases with the decrease of droplet diameter. This phenomenon is called Kelvin effect and is given by Eq. (8). If the supersaturation of water vapor $S$ surrounding a single isolated water droplet is larger than $p_d/p_w$, the droplet grows by condensation of surrounding water vapor. If $S < p_d/p_w$, that is, the surrounding supersaturation lies in below the curve $p_d/p_w$ in Fig. 1, the water droplet disappears by evaporation. Thus the curve $p_d/p_w$ in Fig. 1 indicates the critical relationship between droplet diameter and the surrounding vapor pressure that the droplet can be stable. In the liquid phase, however, it is not clear that Eq. (8) can be applicable.

When a temperature gradient is established in a gas, the aerosol particles in that gas are driven from high to low temperature regions. This effect is called thermophoresis. The curve $u_{th}$ in Fig. 1 is an example (NaCl particle in air) of thermophoretic velocity at a unit temperature gradient, that is, $1^\circ C/cm$. If the temperature gradient is $10^\circ C/cm$, $u_{th}$ becomes ten times higher than that shown in the figure.

The curve denoted as pulse height illustrates a typical photomultiplier response of scattered light from a particle. The intensity of scattered light is proportional to six power of the particle diameter when particle size is smaller than the wave length of incident light. The curve demonstrates the steep decrease in intensity of scattered light from a particle.

3. Coagulation

Figure 4 illustrates the change in the number concentration of cigarette smoke particles with time by Brownian and turbulent coagulation. Initial particles (at $t = 0$ sec) have about $0.9 \mu m$ in geometric mean diameter, 1.4 in geometric standard deviation and $10^7$ particles per cubic centimeter in concentration. Figure 4-(a) shows the number change due to Brownian coagulation in a closed chamber (vertical cylinder: 19 cm in diam. and 20 cm in height). Figures 4-(b) and (c) show the number change due to turbulent coagulation in the chamber with buffer plates stirred by six flat-bladed turbine (diameter is 9 cm). The intensity of turbulence of Fig. 4-(c) is higher (average energy dissipation rate $\epsilon_o \approx 4 \times 10^7 \text{ cm}^2/\text{s}^3$) than that of Fig. 4-(b) ($\epsilon_o \approx 7 \times 10^6 \text{ cm}^2/\text{s}^3$). It is seen
Fig. 4 Number change due to Brownian and turbulent coagulation of cigarette smoke particles.
that number change with time is significantly enhanced by turbulence.

Change in particle number concentration $n$ with time $t$ for monodisperse particles is expressed as follows,

$$\frac{dn}{dt} = -Kn^2 \quad (9)$$

where $K$ is coagulation rate constant. The values of $K$ for Brownian and turbulent coagulation in a gaseous and a liquid-phase are shown in Fig. 5. The time to reach half of the initial particle number concentration are illustrated in Table 1. The value of $K$ for turbulent coagulation, on the other hand, is proportional to $d_p^3 \sqrt{\epsilon}$: this means that turbulent coagulation plays an important role when particle size becomes large, which is illustrated in Fig. 5 for monodisperse particles and the given intensities of turbulence.

Coagulation in a liquid, mainly in water, is somewhat different from that in a gas because particles are highly charged in water in most cases. When particles are charged in the same polarity in water, the electrostatic repulsion between two particles, which is shown as the energy barrier in Fig. 6(b), prevents coagulation. The energy barrier as high as $20kT$ ($k$: Boltzmann constant, $T$: absolute temperature) is enough to prevent coagulation, which can be easily attained by adding appropriate dispersion agents in water. Submicron particles in a gaseous medium, on the other hand, can not be highly charged since ion concentration in a gaseous medium is generally low compared with that in water, and then electrical repulsion may hardly be expected, which is shown in Fig. 6-(a). This means that submicron particles in a gas can not be held stable in a state of high concentration, which is one of the disadvantages of industrial particle production processes in a gaseous medium.

4. Deposition

Deposition of submicron particles suspending in a fluid onto surfaces exposed to that fluid is caused by particle diffusion, inertial motion and additional external forces such as gravitational, thermophoretic and electrostatic forces. Particle deposition caused by diffusion and electrostatic force becomes important in a submicron size range, whereas deposition by inertial and gravitational forces is less important in that range, which is obvious in Fig. 1 (see $D$, $B_e$, $\tau_g$ and $u_e$).

Decrease in particle number concentration of an aerosol flowing through a horizontal pipe in a laminar state, for an example, is shown in Fig. 7, where $R$ is the pipe radius, $u_{xav}$ the mean velocity of the flowing aerosol, $x$ the tube length, and $n_0$ and $\bar{n}$ are, respectively, the particle number concentration at the pipe inlet.

![Fig. 5 Brownian and turbulent coagulation rate constants for monodisperse particles](image-url)
Fig. 6 Interaction energy vs. separation for combined London van der Waals attraction, double layer repulsion and Born repulsion

Fig. 7 Decrease in number concentration of an aerosol flowing through a horizontal pipe in a laminar state

and the pipe outlet. The curve of \( \sigma = 0 \) in the figure indicates the number decrease due to Brownian diffusion alone, and the other curves indicate those accompanied by gravitational sedimentation.

Another example which may be important for particle production processes in gaseous media is shown in Fig. 8. The plots are the experimental results obtained in a closed, cylindrical vessel similar to the former section. The abscissa \( \beta \) in the figure is deposition rate constant which is a measure of particle deposition rate, and is defined as follows,

\[
\frac{\bar{n}}{n_0} = e^{\beta t}
\]

where \( n_0 \) and \( \bar{n} \) in this case are the number concentration of aerosol particles at time \( t = 0 \) and at time \( t \), respectively. The dashed line and the corresponding plots are the particle deposition rate constant where a natural convective flow exists throughout the vessel. The other solid lines are for those turbulent flow existence.

\( N_s \) in the figure is the revolution of stirrer and \( \epsilon_0 \) the corresponding average energy dissipation rate. It is seen in the figure that turbulence clearly enhances particle deposition on walls and that Brownian deposition is predominant in the smaller size range whereas deposition due to gravitational settling is predominant in the larger size range. The plots in the figure are obtained by the present author and his co-workers, and the lines are those calculated from the theory proposed by Crump and Seinfeld.

If there exists a temperature gradient in the vicinity of a wall which has lower temperature than a fluid, thermophoresis shown in Fig. 1 enhances particle deposition on the wall.

Particle deposition is also enhanced if particles are charged in opposite polarity to a wall. If aerosol particles are charged in bipolarity, a wall charged in either polarity can enhance deposition of particles charged in opposite polarity to that wall.

The deposition mechanism of particles suspending in a liquid is essentially the same as that in a gas if the electrical repulsion
shown in Fig. 6-(b) is not strong. However, particle deposition in a liquid medium is thought to be less important than in a gaseous medium, because, in a liquid medium, electric double layer repulsion is not neglected in most cases, particle diffusion coefficient, gravitational settling velocity and inertial effect are small, and because re-entrainment of particles once caught at walls takes place rather easily compared with that in a gaseous medium.

5 Conclusion

Size-dependent behavior, mainly dynamic behavior, of submicron particles suspending in a fluid has been summarized. And then the topics on coagulation and particle deposition on walls have been outlined. Another interesting topics on submicron particles from an industrial point of view will be gas- or liquid-to-particle conversion, that is, particle production process, but unfortunately it is too complicated and has not well been understood for the time being.

References

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