

We saw in Section 9.3 that for $t \gg \tau$, the particle velocity relaxes to a pseudo-steady-state value. We assume that to be the case here, namely, that the Brownian motion of the particle is sufficiently slow, that the particle has time to “relax” after each fluctuating impulse. Under this assumption, we drop the exponential in (9.63) to obtain

$$\frac{1}{2} \frac{d}{dt} \langle r^2 \rangle = \frac{3kT\tau}{m_p} \quad (9.64)$$

which, on integration, becomes

$$\langle r^2 \rangle = \frac{6kT\tau}{m_p} t = \frac{2kTC_c t}{\pi\mu D_p} \quad (9.65)$$

The Brownian motion can be assumed to be isotropic so $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle$. Thus

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{2kTC_c}{3\pi\mu D_p} t \quad (9.66)$$

This result, first derived by Einstein by a different route, has been confirmed experimentally. It indicates that the mean square distance traversed by a Brownian particle is proportional to the length of time it has experienced such motion.

We should note that we have obtained the foregoing results in a more or less formal manner without attempting to justify from a rigorous mathematical point of view the validity of the Langevin equation as the basic description of the particle motion. The theoretical results we have presented can be rigorously justified. A good starting point for the reader wishing to go deeply into its theory is the classic article by Chandrasekhar (1943), which is reprinted in Wax (1954).

9.5.1 Particle Diffusion

The movement of particles due to Brownian motion can also be viewed as a macroscopic diffusion process. Let us discuss the connection between these two different perspectives on the same process. If $N(x, y, z, t)$ is the number concentration of particles undergoing Brownian motion, then we can define a Brownian diffusivity D , such that

$$\frac{\partial N(x, y, z, t)}{\partial t} = D\nabla^2 N(x, y, z, t) \quad (9.67)$$

If we relate the Brownian diffusivity D to the mean square displacements given by (9.66), then (9.67) can provide a convenient framework for describing aerosol diffusion. To do so, let us repeat the experiment above, namely, let us follow the Brownian diffusion of N_0 particles placed at $t = 0$ at the $y - z$ plane. To simplify our discussion we assume that N does not depend on y or z . Multiplying (9.67) by x^2 and integrating the resulting

equation over x from $-\infty$ to ∞ , we get

$$\int_{-\infty}^{+\infty} x^2 \frac{\partial N}{\partial t} dx = \int_{-\infty}^{+\infty} x^2 D \frac{\partial^2 N}{\partial x^2} dx \quad (9.68)$$

The LHS can also be written as

$$\int_{-\infty}^{+\infty} x^2 \frac{\partial N}{\partial t} dx = N_0 \frac{\partial \langle x^2 \rangle}{\partial t} \quad (9.69)$$

and the RHS of (9.68) as

$$\int_{-\infty}^{+\infty} x^2 D \frac{\partial^2 N}{\partial x^2} dx = 2DN_0 \quad (9.70)$$

Combining (9.68), (9.69), and (9.70) results in

$$\frac{\partial \langle x^2 \rangle}{\partial t} = 2D \quad (9.71)$$

or after integration

$$\langle x^2 \rangle = 2Dt \quad (9.72)$$

We can now equate this result for $\langle x^2 \rangle$ with that of (9.66) to obtain an explicit relation for D

$$D = \frac{kTC_c}{3\pi\mu D_p} \quad (9.73)$$

which, without the correction factor C_c , is the *Stokes–Einstein–Sutherland relation*. Note that for particles that are larger than the mean free path of air, $C_c \simeq 1$ and their diffusivity varies as D_p^{-1} . As expected, larger particles diffuse more slowly. In the other extreme, when $D_p \ll \lambda$, $C_c = 1 + 1.657(2\lambda/D_p)$ and D can be approximated by $2(1.657)\lambda kT/3\pi\mu D_p^2$. Therefore, in the free molecule regime, D varies as D_p^{-2} .

Diffusion coefficients for particles ranging from 0.001 to 10.0 μm diameter in air at 20°C are shown in Figure 9.8. The change from D_p^{-2} dependence is indicated by the change of slope of the line of D versus D_p .

The importance of Brownian diffusion as compared to gravitational settling can be judged by comparing the distances a particle travels as a result of each process (Twomey 1977). Over a time of 1 s a 1- μm -radius particle diffuses a distance of about 4 μm , while it falls about 200 μm under gravity. A 0.1 μm radius particle, on the other hand, in 1 s, diffuses a distance of about 20 μm compared to a fall distance of 4 μm . Even though a 1 μm particle's motion is dominated by inertia and gravity, it still diffuses several times its own radius in 1 s. The motion of the 0.1 μm particle is dominated by Brownian

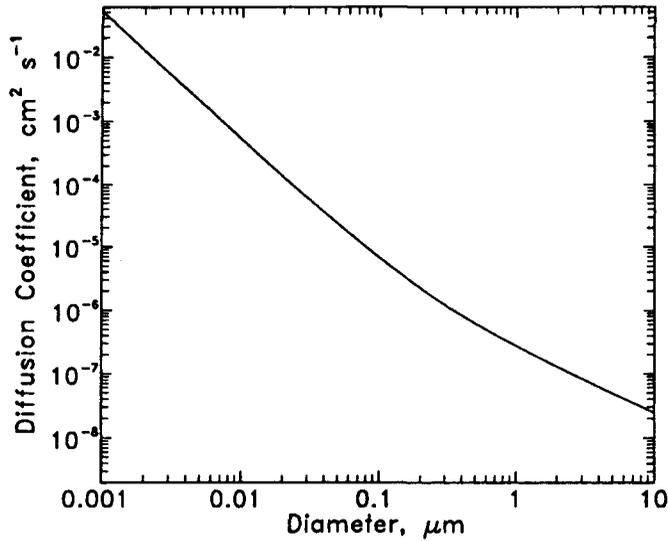


FIGURE 9.8 Aerosol diffusion coefficients in air at 20°C as a function of diameter.

diffusion. For a 0.01- μm -radius particle, Brownian diffusion further outweighs gravity; its diffusive displacement in 1 second is almost 1000 times its displacement because of gravity.

Note that the magnitude of diffusion coefficients of gases is on the order of $0.1 \text{ cm}^2 \text{ s}^{-1}$. Therefore a $0.1 \mu\text{m}$ particle diffuses in a quiescent gas roughly 10,000 times more slowly than a gas molecule, and Brownian diffusion is not expected to be an efficient transport mechanism for aerosols in the atmosphere.

9.5.2 Aerosol Mobility and Drift Velocity

In the development of Brownian motion up to this point, we have assumed that the only external force acting on the particle is the fluctuating Brownian force $m_p \mathbf{a}$. If we generalize (9.52) to include an external force \mathbf{F}_{ext} , we get

$$m_p \frac{d\mathbf{v}}{dt} = \mathbf{F}_{\text{ext}} - \frac{m_p}{\tau} \mathbf{v} + m_p \mathbf{a} \quad (9.74)$$

As before, assuming that we are interested in times for which $t \gg \tau$, and taking mean values, the approximate force balance is at steady state:

$$0 = \mathbf{F}_{\text{ext}} - \frac{m_p}{\tau} \langle \mathbf{v} \rangle \quad (9.75)$$

The ensemble mean velocity $\langle \mathbf{v} \rangle$ is identified as the *drift velocity* $\mathbf{v}_{\text{drift}}$, where

$$\mathbf{v}_{\text{drift}} = \frac{\mathbf{F}_{\text{ext}} \tau}{m_p} \quad (9.76)$$

The drift velocity is the mean velocity experienced by the particle population due to the presence of the external force \mathbf{F}_{ext} . For example, in the case where the external force is simply gravity, $\mathbf{F}_{\text{ext}} = m_p \mathbf{g}$, and the drift velocity (or settling velocity) will simply be $\mathbf{v}_{\text{drift}} = \mathbf{g}\tau$ [see also (9.41)]. When the external force is electrical, the drift velocity is the electrical migration velocity [see also (9.49)]. Therefore our analysis presented in the previous sections is still valid even after the introduction of Brownian motion.

It is customary to define the generalized particle *mobility* B by

$$\mathbf{v}_{\text{drift}} = B\mathbf{F}_{\text{ext}} \quad (9.77)$$

Therefore the particle mobility is given by

$$B = \frac{\tau}{m_p} = \frac{C_c}{3\pi\mu D_p} \quad (9.78)$$

The mobility can also be viewed as the drift velocity that would be attained by the particles under unit external force. Recall (9.50), which is the mobility in the special case of an electrical force. By definition, the electrical mobility is related to the particle mobility by $B_e = qB$, where q is the particle charge. A particle with zero charge, has a mobility given by (9.78) and zero electrical mobility.

Finally, the Brownian diffusivity can be written in terms of the mobility [see also (9.73)] by

$$D = BkT \quad (9.79)$$

a result known as the *Einstein relation*.

Gravitational Settling and the Vertical Distribution of Aerosol Particles Let us consider the simultaneous Brownian diffusion and gravitational settling of particles above a surface at $z = 0$. At $t = 0$, a uniform concentration $N_0 = 1000 \text{ cm}^{-3}$ of particles is assumed to exist for $z > 0$ and at all times the concentration of particles right at the surface is zero as a result of their removal at the surface.

1. What is the particle concentration as a function of height and time, $N(z, t)$?
2. What is the removal rate of particles at the surface?

The concentration distribution of aerosol particles in a stagnant fluid in which the particles are subject to Brownian motion and in which there is a velocity v_t in the $-z$ direction is described by

$$\frac{\partial N}{\partial t} - v_t \frac{\partial N}{\partial z} = D \frac{\partial^2 N}{\partial z^2} \quad (9.80)$$

subject to the conditions

$$\begin{aligned} N(z, 0) &= N_0 \\ N(0, t) &= 0 \\ N(z, t) &= N_0 \quad z \rightarrow \infty \end{aligned} \quad (9.81)$$

where the z coordinate is taken as vertically upward.

The solution of (9.80) and (9.81) for the vertical profile of the number distribution $N(z, t)$ is

$$N(z, t) = \frac{N_0}{2} \left[1 + \operatorname{erf} \left(\frac{z + v_t t}{2\sqrt{Dt}} \right) - \exp \left(-\frac{v_t z}{D} \right) \operatorname{erfc} \left(\frac{z - v_t t}{2\sqrt{Dt}} \right) \right] \quad (9.82)$$

We can calculate the deposition rate of particles on the $z = 0$ surface from the expression for the flux of particles at $z = 0$,

$$J = D \left(\frac{\partial N}{\partial z} \right)_{z=0} + v_t N(0, t) \quad (9.83)$$

Recall that $N(0, t) = 0$ in (9.83). Combining (9.82) and (9.83) we obtain

$$J = N_0 \left\{ \frac{v_t}{2} \left[1 - \operatorname{erf} \left(-\frac{v_t t}{2\sqrt{Dt}} \right) \right] + \left(\frac{D}{\pi t} \right)^{1/2} \exp \left(-\frac{v_t^2 t}{4D} \right) \right\} \quad (9.84)$$

According to (9.84), there is an infinite removal flux at $t = 0$, because of our artificial specification of an infinite concentration gradient at $z = t = 0$. We can identify a characteristic time τ_{ds} for the system

$$\tau_{ds} = \frac{4D}{v_t^2} \quad (9.85)$$

and observe the following limiting behavior for the particle flux at short and long times:

$$\begin{aligned} J(t) &= N_0 \left[\left(\frac{D}{\pi t} \right)^{1/2} + \frac{v_t}{2} \right] & t \ll \tau_{ds} \\ J(t) &= N_0 v_t & t \gg \tau_{ds} \end{aligned} \quad (9.86)$$

Thus, at very short times, the deposition flux is that resulting from diffusion plus one-half that due to settling, whereas for long times the deposition flux becomes solely the settling flux. For particles of radii $0.1 \mu\text{m}$ and $1 \mu\text{m}$ in air (at 1 atm, 298 K), τ_{ds} is about 80 s and 0.008 s, respectively, assuming a density of 1 g cm^{-3} . For times longer than that, Brownian motion does not have any effect on the particle motion. The aerosol number concentration and removal flux are shown in Figures 9.9 and 9.10. The system reaches a steady state after roughly 100 s and at this state 0.23 particles are deposited per second on each cm^2 of the surface (Figure 9.10). Note that the concentration profile changes only over a shallow layer of approximately 1 mm above the surface (Figure 9.9). The depth of this layer is proportional to D/v_t . Note that the example above is not representative of the ambient atmosphere, where there is turbulence and possibly also sources of particles at the ground.

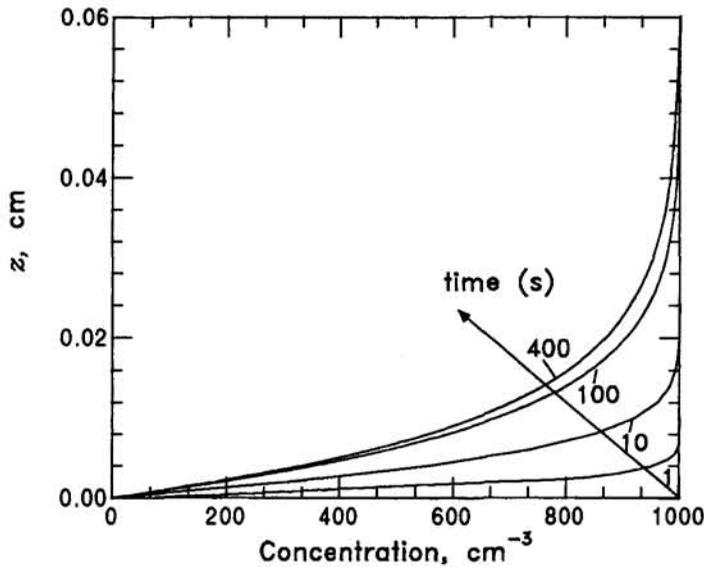


FIGURE 9.9 Evolution of the concentration profile (times 1, 10, 100, and 400 s) of an aerosol population settling and diffusing in stationary air over a flat perfectly absorbing surface. The particles are assumed to be monodisperse with $D_p = 0.2 \mu\text{m}$ and have an initial concentration of 1000 cm^{-3} .

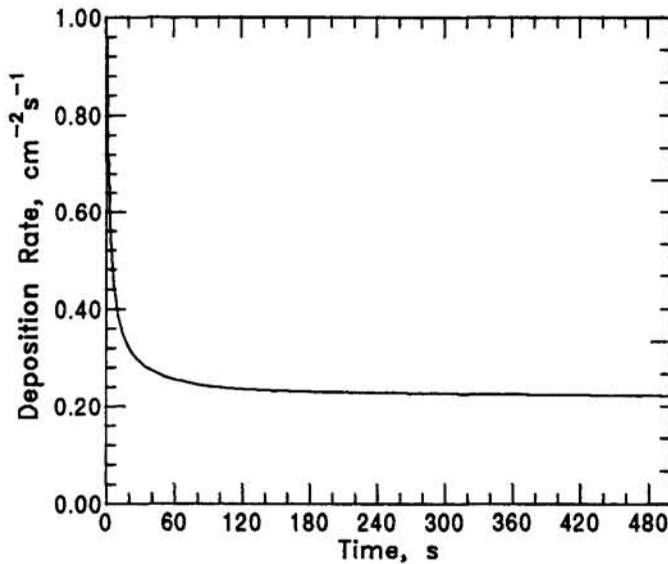


FIGURE 9.10 Removal rate of particles as a function of time for the conditions of Figure 9.9.

9.5.3 Mean Free Path of an Aerosol Particle

The concept of mean free path is an obvious one for gas molecules. In the Brownian motion of an aerosol particle there is not an obvious length that can be identified as a mean free path. This is depicted in Figure 9.11 showing plane projections of the paths followed by an air molecule and an aerosol particle of radius roughly equal to $1 \mu\text{m}$. The trajectories

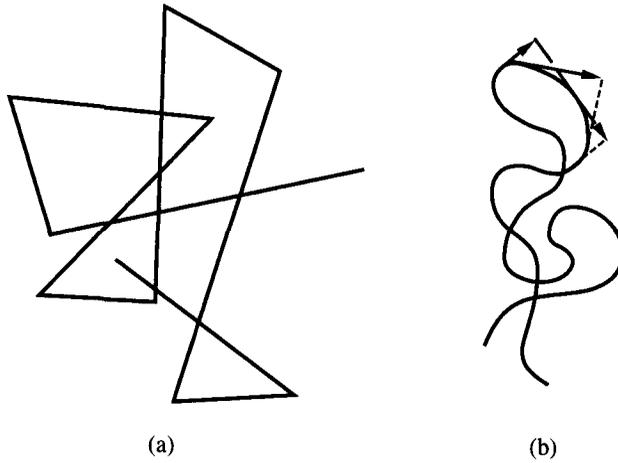


FIGURE 9.11 A two-dimensional projection of the path of (a) an air molecule and (b) the center of a 1- μm particle. Also shown is the apparent mean free path of the particle.

of the gas molecules consist of straight segments, each of which represents the path of the molecule between collisions. At each collision the direction and speed of the molecule are changed abruptly. With aerosol particles the mass of the particle is so much greater than that of the gas molecules with which it collides that the velocity of the particle changes negligibly in a single collision. Appreciable changes in speed and direction occur only after a large number of collisions with molecules, resulting in an almost smooth particle trajectory.

The particle motion can be characterized by a mean thermal speed \bar{c}_p :

$$\bar{c}_p = \left(\frac{8kT}{\pi m_p} \right)^{1/2} \tag{9.87}$$

To obtain the mean free path λ_p , we recall that in Section 9.1, using kinetic theory, we connected the mean free path of a gas to measured macroscopic transport properties of the gas such as its binary diffusivity. A similar procedure can be used to obtain a particle mean free path λ_p from the Brownian diffusion coefficient and an appropriate kinetic theory expression for the diffusion flux. Following an argument identical to that in Section 9.1, diffusion of aerosol particles can be viewed as a mean free path phenomenon so that

$$D = \frac{1}{2} \bar{c}_p \lambda_p \tag{9.88}$$

and the mean free path λ_p combining (9.73), (9.87), and (9.88) is then

$$\lambda_p = \frac{C_c}{6\mu} \sqrt{\frac{\rho k T D_p}{3}} \tag{9.89}$$

TABLE 9.5 Characteristic Quantities in Aerosol Brownian Motion

$D_p, \mu\text{m}$	$D, \text{cm}^2 \text{s}^{-1}$	$\bar{c}_p, \text{cm s}^{-1}$	τ, s	$\lambda_p (\mu\text{m})$
0.002	1.28×10^{-2}	4965	1.33×10^{-9}	6.59×10^{-2}
0.004	3.23×10^{-3}	1760	2.67×10^{-9}	4.68×10^{-2}
0.01	5.24×10^{-4}	444	6.76×10^{-9}	3.00×10^{-2}
0.02	1.30×10^{-4}	157	1.40×10^{-8}	2.20×10^{-2}
0.04	3.59×10^{-5}	55.5	2.98×10^{-8}	1.64×10^{-2}
0.1	6.82×10^{-6}	14.0	9.20×10^{-8}	1.24×10^{-2}
0.2	2.21×10^{-6}	4.96	2.28×10^{-7}	1.13×10^{-2}
0.4	8.32×10^{-7}	1.76	6.87×10^{-7}	1.21×10^{-2}
1.0	2.74×10^{-7}	0.444	3.60×10^{-6}	1.53×10^{-2}
2.0	1.27×10^{-7}	0.157	1.31×10^{-5}	2.06×10^{-2}
4.0	6.1×10^{-8}	5.55×10^{-2}	5.03×10^{-5}	2.8×10^{-2}
10.0	2.38×10^{-8}	1.40×10^{-2}	3.14×10^{-4}	4.32×10^{-2}
20.0	1.38×10^{-8}	4.96×10^{-3}	1.23×10^{-3}	6.08×10^{-2}

Certain quantities associated with the Brownian motion and the dynamics of single aerosol particles are shown as a function of particle size in Table 9.5. All tabulated quantities in Table 9.5 depend strongly on particle size with the exception of the apparent mean free path λ_p , which is of the same order of magnitude right down to molecular sizes, with atmospheric values $\lambda_p \simeq 10-60 \text{ nm}$.

9.6 AEROSOL AND FLUID MOTION

In our discussion so far, we have assumed that the aerosol particles are suspended in a stagnant fluid. In most atmospheric applications, the air is in motion and one needs to describe simultaneously the air and particle motion. Equation (9.36) will be the starting point of our analysis.

Actually (9.36) is a simplified form of the full equation of motion, which is (Hinze 1959)

$$\begin{aligned}
 m_p \frac{d\mathbf{v}}{dt} = & \frac{3\pi\mu D_p}{C_c} (\mathbf{u} - \mathbf{v}) + V_p \rho \frac{d\mathbf{u}}{dt} + \frac{V_p}{2} \rho \left(\frac{d\mathbf{u}}{dt} - \frac{d\mathbf{v}}{dt} \right) \\
 & + \frac{3D_p^2}{2} (\pi\rho\mu)^{1/2} \int_0^t \frac{(d\mathbf{u}/dt') - (d\mathbf{v}/dt')}{(t-t')^{1/2}} dt' + \sum_i \mathbf{F}_{ei}
 \end{aligned} \tag{9.90}$$

where V_p is the particle volume. The second term on the RHS is due to the pressure gradient in the fluid surrounding the particle, caused by acceleration of the gas by the particle. The third term is the force required to accelerate the apparent mass of the particle relative to the fluid. Finally, the fourth term, the Basset history integral, accounts for the force arising as a result of the deviation of fluid velocity from steady state. In most situations of interest for aerosol particle in air, the second, third, and fourth terms on the RHS of (9.90) are neglected. Assuming that gravity is the only external force exerted on the particle, we again obtain (9.36).

Neglecting the gravitational force and particle inertia leads to the zero-order approximation that $\mathbf{v} \simeq \mathbf{u}$; that is, the particle follows the streamlines of the airflow. This approximation is often sufficient for most atmospheric applications, such as turbulent

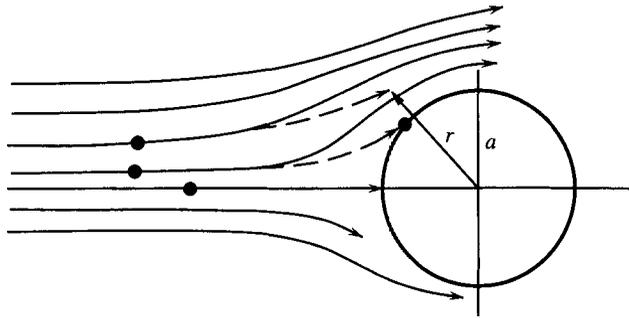


FIGURE 9.12 Schematic diagram of particles and fluid motion around a cylinder. Streamlines are shown as solid lines, while the dashed lines are aerosol paths.

dispersion. However, it is often necessary to quantify the deviation of the particle trajectories from the fluid streamlines (Figure 9.12).

A detailed treatment of particle flow around objects, in channels of various geometries, and so on, is beyond the scope of this book. Treatments are provided by Fuchs (1964), Hinds (1999), and Flagan and Seinfeld (1988). We will focus our analysis on a few simple examples demonstrating the important concepts.

9.6.1 Motion of a Particle in an Idealized Flow (90° Corner)

Let us consider an idealized flow, shown in Figure 9.13, in which an airflow makes an abrupt 90° turn in a corner maintaining the same velocity (Crawford 1976). We would like to determine the trajectory of an aerosol particle originally on the streamline $y = 0$, which turns at the origin $x = 0$.

The trajectory of the particle is governed by (9.37). Neglecting gravity, the x and y components of the equation of motion are after the turning point

$$\begin{aligned} \tau \frac{dv_x}{dt} + v_x &= 0 \\ \tau \frac{dv_y}{dt} + v_y &= U \end{aligned} \tag{9.91}$$

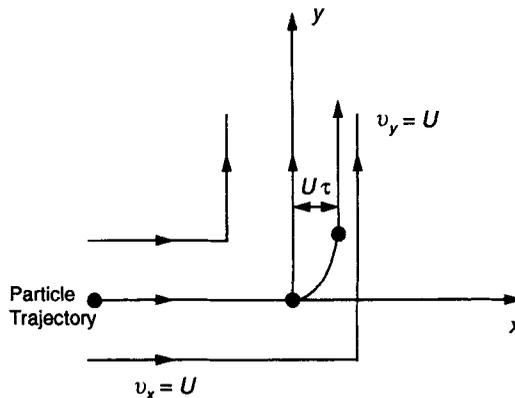


FIGURE 9.13 Motion of an air particle in a flow making a 90° turn with no change in velocity.

and as $v_x = dx/dt$ and $v_y = dy/dt$, we get

$$\begin{aligned}\tau \frac{d^2x}{dt^2} + \frac{dx}{dt} &= 0 \\ \tau \frac{d^2y}{dt^2} + \frac{dy}{dt} &= U\end{aligned}\quad (9.92)$$

subject to

$$x(0) = 0, \quad y(0) = 0, \quad \left(\frac{dx}{dt}\right)_{t=0} = U, \quad \left(\frac{dy}{dt}\right)_{t=0} = 0 \quad (9.93)$$

Solving (9.92) subject to (9.93) gives the particle coordinates as a function of time:

$$x(t) = U\tau[1 - \exp(-t/\tau)] \quad (9.94)$$

$$y(t) = -U\tau[1 - \exp(-t/\tau)] + Ut \quad (9.95)$$

We see that for $t \gg \tau$, the particle trajectory is described by $x(t) = U\tau$ and $y(t) = Ut$. Thus the particle eventually ends up at a distance $U\tau$ to the right of its original fluid streamline. Larger particles with high relaxation times will move, because of their inertia, significantly to the right, while small particles, with $\tau \rightarrow 0$, will follow closely their original streamline. For example, for a 2- μm -diameter particle moving with a speed $U = 20 \text{ m s}^{-1}$ and having density $\rho_p = 2 \text{ g cm}^{-3}$, we find that the displacement is 0.48 mm, while for a 20- μm -diameter particle $U\tau = 4.83 \text{ cm}$.

The flow depicted in Figure 9.13 is the most idealized one representing the stagnation flow of a fluid toward a flat plane (see also Figure 9.14). If we imagine that in Figure 9.14 there is a flat plate at $x = 0$ and that $y = 0$ is the line of symmetry, then all the particles that initially are a distance smaller than $x_0 = U\tau$ from the line of symmetry will collide with

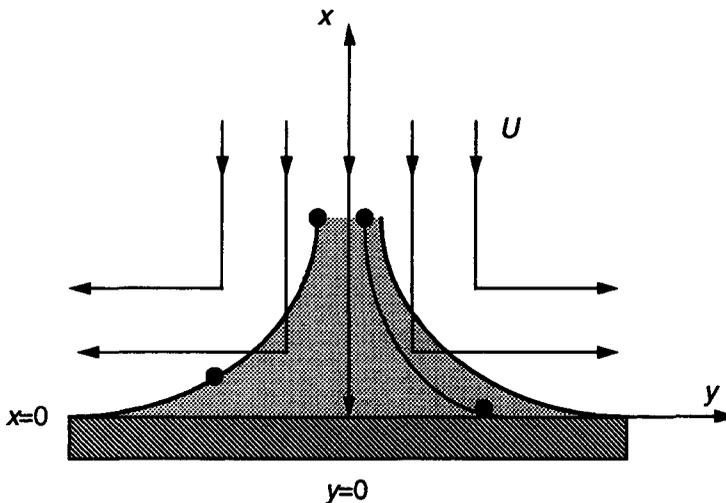


FIGURE 9.14 Idealized flow toward a plate.

the flat plate. On the other hand, particles outside this area will be able to turn and, avoiding the plane, continue flowing parallel to it.

A more detailed treatment of the flow in such situations is presented by Flagan and Seinfeld (1988) considering more realistic fluid streamlines.

9.6.2 Stop Distance and Stokes Number

Let us consider a particle moving with a speed U in a stagnant fluid with no forces acting on it. The particle will slow down because of the drag force exerted on it by the fluid and eventually stop after moving a distance s_p . We can calculate this *stop distance* of the particle employing (9.39), neglecting gravity, and noting that $v = ds/dt$. The motion of the particle is described by

$$\tau \frac{ds^2}{dt^2} + \frac{ds}{dt} = 0, \quad s(0) = 0, \quad \left(\frac{ds}{dt} \right)_{t=0} = U \quad (9.96)$$

with solution

$$s(t) = \tau U \left(1 - \exp\left(-\frac{t}{\tau}\right) \right) \quad (9.97)$$

Note that as $t \gg \tau$, $s(t) \rightarrow s_p$, where

$$s_p = \tau U \quad (9.98)$$

is the particle stop distance. For a 1- μm -diameter particle, with an initial speed of 10 m s^{-1} , for example, the stop distance is $36 \mu\text{m}$.

Let us write the equation of motion (9.37) without the gravitational term, in dimensionless form. To do so we introduce a characteristic fluid velocity u_0 and a characteristic length L both associated with the flow of interest. We define dimensionless time t^* , distance x^* , and velocity v^* by

$$t^* = \frac{t u_0}{L}, \quad x^* = \frac{x}{L}, \quad u_x^* = \frac{u_x}{u_0} \quad (9.99)$$

Placing (9.37) in dimensionless form gives

$$\frac{\tau u_0}{L} \frac{d^2 x^*}{dt^{*2}} + \frac{dx^*}{dt^*} = u_x^* \quad (9.100)$$

Note that all the variables of the system have been combined in the dimensionless group $\tau u_0/L$, which is called the *Stokes number* (St):

$$\text{St} = \frac{\tau u_0}{L} = \frac{D_p^2 \rho_p C_c u_0}{18 \mu L} \quad (9.101)$$

Note that the Stokes number is the ratio of the particle stop distance s_p to the characteristic length of the flow L . As particle mass decreases, the Stokes number also decreases. A small Stokes number implies that the particle is able to adopt the fluid velocity very quickly. Since the dimensionless equation of motion depends only on the Stokes number, equality between two geometrically similar flows indicates similarity of the particle trajectories.

9.7 EQUIVALENT PARTICLE DIAMETERS

Up to this point we have considered spherical particles of a known diameter D_p and density ρ_p . Atmospheric particles are sometimes nonspherical and we seldom have information about their density. Also a number of techniques used for atmospheric aerosol size measurement actually measure the particle's terminal velocity or its electrical mobility. In these cases we need to define an equivalent diameter for the nonspherical particles or even for the spherical particles of unknown density or charge. These equivalent diameters are defined as the diameter of a sphere, which, for a given instrument, would yield the same size measurement as the particle under consideration. A series of diameters have been defined and are used for such particles.

9.7.1 Volume Equivalent Diameter

The volume equivalent diameter D_{ve} is the diameter of a sphere having the same volume as the given nonspherical particle. If the volume V_p of the nonspherical particle is known then:

$$D_{ve} = \frac{6}{\pi} V_p^{1/3} \quad (9.102)$$

For a spherical particle the volume equivalent diameter is equal to its physical diameter, $D_{ve} = D_p$.

To account for the shape effects during the flow of nonspherical particles, Fuchs (1964) defined the shape factor χ as the ratio of the actual drag force on the particle F_D to the drag force F_D^{ve} on a sphere with diameter equal to the volume equivalent diameter of the particle:

$$\chi = \frac{F_D}{F_D^{ve}} \quad (9.103)$$

The dynamic shape factor is almost always greater than 1.0 for irregular particles and flows at small Reynolds numbers and is equal to 1.0 for spheres. For a nonspherical particle of a given shape χ is not a constant but changes with pressure, particle size, and as a result of particle orientation in electric or aerodynamic flow fields.

The dynamic shape factor for flow in the continuum regime is equal to 1.08 for a cube, 1.12 for a 2-sphere cluster, 1.15 for a compact 3-sphere cluster, and 1.17 for a

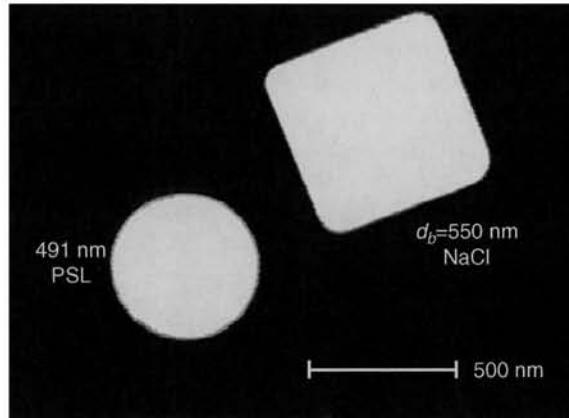


FIGURE 9.15 A micrograph of a single NaCl particle with electrical mobility equivalent diameter of 550 nm. The dry NaCl is almost cubic with rounded edges. Also shown is a polystyrene latex (PSL) particle with diameter of 491 nm (Zelenyuk et al. 2006).

compact 4-sphere cluster (Hinds 1999). These values are averaged over all orientations of the particle, which is the usual situation for atmospheric aerosol flows ($Re < 0.1$) because of the Brownian motion of the particles. Liquid and organic atmospheric particles are spherical for all practical purposes. Dry NaCl crystals have cubic shape (Figure 9.15), while dry $(\text{NH}_4)_2\text{SO}_4$ is approximately but not exactly spherical (Figure 9.16). Dynamic shape factors ranging from 1.03 to 1.07 have been measured in the laboratory (Zelenyuk et al. 2005) with the higher values observed for larger particles with diameters of ~ 500 nm.

Nonspherical particles are subjected to a larger drag force compared to their volume equivalent spheres because $\chi > 1$ and therefore settle more slowly. The terminal settling velocity of a nonspherical particle is then [following the same approach as in the derivation of (9.42)]

$$v_t = \frac{1}{18} \frac{D_{ve}^2 \rho_p g C_c(D_{ve})}{\chi \mu} \quad (9.104)$$

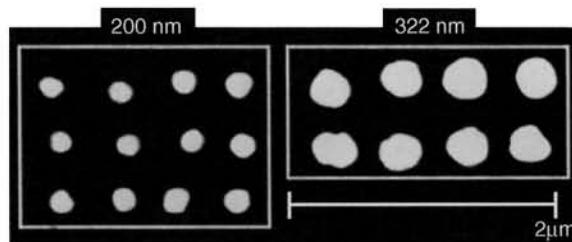


FIGURE 9.16 Ammonium sulfate particles with electrical mobility diameters of 200 and 322 nm (Zelenyuk et al. 2006).

Volume Equivalent Diameter An approximately cubic NaCl particle with density 2.2 g cm^{-3} has a terminal settling velocity of 1 mm s^{-1} in air at ambient conditions. Calculate its volume equivalent diameter and its physical size using the continuum regime shape factor.

The terminal settling velocity is given by (9.104), so after some rearrangement; we obtain

$$D_{ve}^2 C_c(D_{ve}) = (18 v_t \mu \chi) / (\rho_p g) \quad (9.105)$$

and substituting $v_t = 10^{-3} \text{ m s}^{-1}$, $\mu = 1.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$, $\chi = 1.08$ for a cube, $\rho_p = 2200 \text{ kg m}^{-3}$ for NaCl we find that

$$D_{ve}^2 C_c(D_{ve}) = 1.62 \times 10^{-11} \text{ m}^2 = 0.162 \mu\text{m}^2$$

This equation needs to be solved numerically using (9.34) for calculation of the slip correction, $C_c(D_{ve})$, to obtain $D_{ve} = 0.328 \mu\text{m}$. One can also estimate the value iteratively assuming as a first guess that $C_c = 1$ and then $D_{ve} = 0.402 \mu\text{m}$. This suggests that for this particle $D_{ve} \gg 2\lambda$ and the exponential term in (9.34) will be much smaller than the 1.257 term. With this simplification we are left with the following quadratic equation for D_{ve}

$$D_{ve}^2 + 0.163 D_{ve} - 0.162 = 0$$

with $D_{ve} = 0.329 \mu\text{m}$ as the positive solution. Our simplification of the slip correction expression resulted in an error of only 1 nm.

To calculate the physical size L of the particle, we only need to equate the volume of the cube to the volume of the sphere:

$$L^3 = (\pi/6) D_{ve}^3 \text{ and } L = 0.264 \mu\text{m}$$

This calculation requires knowledge about the shape of the particle and its density.

9.7.2 Stokes Diameter

The diameter of a sphere having the same terminal settling velocity and density as the particle is defined as its *Stokes diameter* D_{St} . For irregularly shaped particles D_{St} is the diameter of a sphere that would have the same terminal velocity. The Stokes diameter for $Re < 0.1$ can then be calculated using (9.42) as

$$D_{St} = \left(\frac{18 v_t \mu}{\rho_p g C_c(D_{St})} \right)^{1/2} \quad (9.106)$$

where v_t is the terminal velocity of the particle, μ is viscosity of air, and ρ_p is the density of the particle that needs to be known. Evaluation of (9.106) because of the dependence of C_c on D_{St} requires in general the solution of a nonlinear algebraic equation with one unknown. For spherical particles by its definition $D_{St} = D_p$ and the Stokes diameter is equal to the physical diameter.

Stokes Diameter What is the relationship connecting the volume equivalent diameter and the Stokes diameter of a nonspherical particle with dynamic shape factor χ for $Re < 0.1$?

Calculate the Stokes diameter of the NaCl particle of the previous example. The two approaches (dynamic shape factor combined with the volume equivalent diameter and the Stokes diameter) are different ways to describe the drag force and terminal settling velocity of a nonspherical particle. The terminal velocity of a nonspherical particle with a volume equivalent diameter D_{ve} is given by (9.104),

$$v_t = \frac{1}{18} \frac{D_{ve}^2 \rho_p g C_c(D_{ve})}{\chi \mu}$$

By definition this settling velocity can be also written as a function of its Stokes diameter as

$$v_t = \frac{1}{18} \frac{D_{St}^2 \rho_p g C_c(D_{St})}{\mu}$$

Combining these two and simplifying we find that

$$D_{St} = D_{ve} \left(\frac{C_c(D_{ve})}{\chi C_c(D_{St})} \right)^{1/2} \quad (9.107)$$

The Stokes diameter of the NaCl particle can be calculated from (9.106):

$$D_{St}^2 C_c(D_{St}) = 0.150 \mu\text{m}^2$$

and solving numerically $D_{St} = 0.313 \mu\text{m}$. This value corresponds to the volume equivalent diameter that we would calculate based on the terminal velocity of the particle if we did not know that the particle was nonspherical.

For most atmospheric aerosol measurements the density of the particles is not known and the Stokes diameter cannot be calculated from the measured particle terminal velocity. This makes the use of the Stokes diameter more difficult and requires the introduction of other equivalent diameters that do not require knowledge of the particle density.

9.7.3 Classical Aerodynamic Diameter

The diameter of a unit density sphere, $\rho_p^\circ = 1 \text{ g cm}^{-3}$, having the same terminal velocity as the particle is defined as its classical aerodynamic diameter, D_{ca} . The classical aerodynamic diameter is then given by

$$D_{ca} = \left(\frac{18 v_t \mu}{\rho_p^\circ g C_c(D_{ca})} \right)^{1/2} \quad (9.108)$$

Dividing (9.108) by (9.106), one can then find the relationship between the classical aerodynamic and the Stokes diameter as

$$D_{ca} = D_{St}(\rho_p/\rho_p^o)^{1/2} [C_c(D_{St})/C_c(D_{ca})]^{1/2} \quad (9.109)$$

For spherical particles we replace D_{St} with D_p in this equation to find that

$$D_{ca} = D_p \left(\frac{\rho_p}{\rho_p^o} \right)^{1/2} \left(\frac{C_c(D_p)}{C_c(D_{ca})} \right)^{1/2} \quad (9.110)$$

For a spherical particle of nonunit density the classical aerodynamic diameter is different from its physical diameter and it depends on its density. Aerosol instruments like the cascade impactor and aerodynamic particle sizer measure the classical aerodynamic diameter of atmospheric particles, which is in general different from the physical diameter of the particles even if they are spherical.

Aerodynamic Diameter Calculate the aerodynamic diameter of spherical particles of diameters equal to 0.01, 0.1, and 1 μm . Assume that their density is 1.5 g cm^{-3} , which is a typical average density for multicomponent atmospheric particles.

Using (9.110), we obtain

$$D_{ca}^2 C_c(D_{ca}) = 1.5 D_p^2 C_c(D_p)$$

for $D_p = 0.01 \mu\text{m}$, $C_c = 22.2$, and $D_{ca}^2 C_c(D_{ca}) = 3.33 \times 10^{-3} \mu\text{m}^2$ with solution $D_{ca} = 0.015 \mu\text{m}$. Repeating the same calculation we find that for $D_p = 0.1 \mu\text{m}$, $C_c = 2.85$, and $D_{ca}^2 C_c(D_{ca}) = 0.043 \mu\text{m}^2$, resulting in $D_{ca} = 0.135 \mu\text{m}$. Finally, for $D_p = 1 \mu\text{m}$ we find that $D_{ca} = 1.242 \mu\text{m}$. For typical atmospheric particles the aerodynamic and physical diameters are quite different (more than 20% in this case) with the discrepancy increasing for smaller particles.

Vacuum Aerodynamic Diameter Calculate the ratio of the aerodynamic to the physical diameter of a spherical particle of density ρ_p in the continuum and the free molecular regimes.

Using equation (9.110) yields

$$D_{ca}/D_p = (\rho_p/\rho_p^o)^{1/2} [C_c(D_p)/C_c(D_{ca})]^{1/2} \quad (9.111)$$

For conditions in the continuum regime the slip correction factor is practically unity and

$$D_{ca}/D_p = (\rho_p/\rho_p^o)^{1/2} \quad (9.112)$$

If the particle is in the free molecular regime, then $2\lambda \gg D_p$ and the second term dominates the RHS of (9.34), which simplifies to

$$C_c(D_p) = 2.514 \lambda/D_p$$

Combining this and simplifying, we find that in the free molecular regime:

$$D_{ca}/D_p = (\rho_p/\rho_p^\circ) \tag{9.113}$$

The aerodynamic diameter of a spherical particle with diameter D_p and nonunit density will therefore depend on the mean free path of the air molecules around it and thus also on pressure [see (9.6)]. For low pressures resulting in high Knudsen numbers, the particle will be in the free molecular regime and the aerodynamic diameter will be proportional to the density of the particle and given by (9.113). This diameter is often called the *vacuum aerodynamic diameter* or the *free molecular regime aerodynamic diameter* of the particle. A number of aerosol instruments that operate at low pressures such as the aerosol mass spectrometer measure the vacuum aerodynamic diameter of particles. In the other extreme, for high pressures resulting in low Knudsen numbers the particle will be in the continuum regime and its aerodynamic diameter will be proportional to the square root of its density (9.112). This is known as the *continuum regime aerodynamic diameter*.

The aerodynamic diameter of the particle changes smoothly from its vacuum to its continuum value as the Knudsen number decreases.

9.7.4 Electrical Mobility Equivalent Diameter

Electrical mobility analyzers, like the differential mobility analyzer, classify particles according to their electrical mobility B_e given by (9.50). The electrical mobility equivalent diameter D_{em} is defined as the diameter of a particle of unit density having the same electrical mobility as the given particle. Particles with the same D_{em} have the same migration velocity in an electric field. Particles with equal Stokes diameters that carry the same electrical charge will have the same electrical mobility.

For spherical particles assuming that the particle and its mobility equivalent sphere have the same charge then $D_{em} = D_p = D_{ve}$. For nonspherical particles one can show that

$$D_{em} = D_{ve} \chi \frac{C_c(D_{em})}{C_c(D_{ve})} \tag{9.114}$$

Instruments such as the differential mobility analyzer (DMA) (Liu et al. 1979) size particles according to their electrical mobility equivalent diameter.

PROBLEMS

- 9.1_A (a) Knowing a particle's density ρ_p and its settling velocity v_t , show how to determine its diameter. Consider both the non-Stokes and the Stokes law regions. (b) Determine the size of water droplet that has $v_t = 1 \text{ cm s}^{-1}$ at $T = 20^\circ\text{C}$, 1 atm.
- 9.2_A (a) A unit density sphere of diameter $100 \mu\text{m}$ moves through air with a velocity of 25 cm s^{-1} . Compute the drag force offered by the air. (b) A unit density sphere of diameter $1 \mu\text{m}$ moves through air with a velocity of 25 cm s^{-1} . Compute the drag force offered by the air.

- 9.3_A Calculate the terminal settling velocities of silica particles ($\rho_p = 2.65 \text{ g cm}^{-3}$) of 0.05 μm , 0.1 μm , and 0.5 μm , and 1.0 μm diameters.
- 9.4_A Calculate the terminal settling velocities of 0.001, 0.1, 1, 10, and 100 μm diameter water droplets in air at a pressure of 0.1 atm.
- 9.5_A Develop a table of terminal settling velocities of water drops in still air at $T = 20^\circ\text{C}$, 1 atm. Consider drop diameters ranging from 1.0 to 1000 μm . (Note that for drop diameters exceeding about 1 mm the drops can no longer be considered spherical as they fall. In this case one must resort to empirical correlations. We do not consider that complication here.)
- 9.6_A What is the stop distance of a spherical particle of 1 μm diameter and density 1.5 g cm^{-3} moving in still air at 298 K with a velocity of 1 m s^{-1} ?
- 9.7_B A 0.2- μm -diameter particle of density 1 g cm^{-3} is being carried by an airstream at 1 atm and 298 K in the y direction with a velocity of 100 cm s^{-1} . The particle enters a charging device and acquires a charge of two electrons (the charge of a single electron is $1.6 \times 10^{-19} \text{ C}$) and moves into an electric field of constant potential gradient $E_x = 1000 \text{ V cm}^{-1}$ perpendicular to the direction of flow.
- Determine the characteristic relaxation time of the particle.
 - Determine the particle trajectory assuming that it starts at the origin at time zero.
 - Repeat the calculation for a 50-nm-diameter particle.
- 9.8_C At $t = 0$ a uniform concentration N_0 of monodisperse particles exists between two horizontal plates separated by a distance h . Assuming that both plates are perfect absorbers of particles and the particles settle with a settling velocity v_t , determine the number concentration of particles as a function of time and position. The Brownian diffusivity of the particles is D .
- 9.9_B The dynamic shape factor of a chain that consists of 4 spheres is 1.32. The diameter of each sphere is 0.1 μm . Calculate the terminal settling velocity of the particle in air at 298 K and 1 atm. What is the error if the shape factor is neglected? Assume the density of the spheres is 2 g cm^{-3} .
- 9.10_B Derive (9.110) using the appropriate force balance for the motion of a charged particle in an electric field.
- 9.11_B Spherical particles with different diameters can have the same electrical mobility if they have a different number of elementary charges. Calculate the diameters of particles that have an electrical mobility equal to that of a singly charged particle with $D_p = 100 \text{ nm}$ assuming that they have 2, 3, or 4 charges. Assume $T = 298 \text{ K}$ and 1 atm.

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