

# 9 Dynamics of Single Aerosol Particles

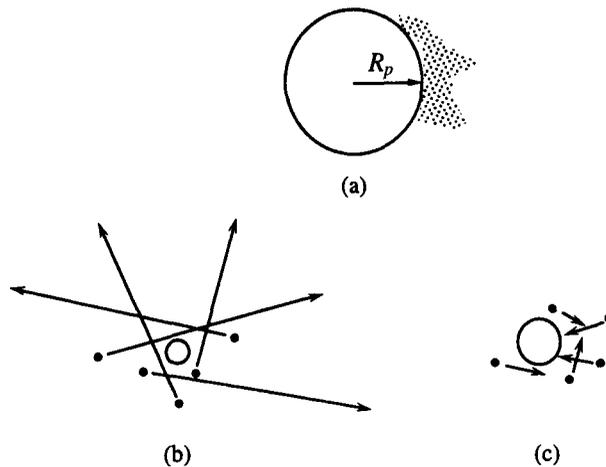
In this chapter, we focus on the processes involving a single aerosol particle in a suspending fluid and the interaction of the particle with the suspending fluid itself. We begin by considering how to characterize the size of the particle in an appropriate way in order to describe transport processes involving momentum, mass, and energy. We then treat the drag force exerted by the fluid on the particle, the motion of a particle through a fluid due to an imposed external force and resulting from the bombardment of the particle by the molecules of the fluid. Because of its importance in atmospheric aerosol processes and aqueousphase chemistry, mass transfer to single particles will be treated separately in Chapter 12.

## 9.1 CONTINUUM AND NONCONTINUUM DYNAMICS: THE MEAN FREE PATH

As we begin our study of the dynamics of aerosols in a fluid (e.g., air), we would like to determine, from the perspective of transport processes, how the fluid “views” the particle or equivalently how the particle “views” the fluid that surrounds it. On the microscopic scale fluid molecules move in a straight line until they collide with another molecule. After collision, the molecule changes direction, moves for a while until it collides with another molecule, and so on. The average distance traveled by a molecule between collisions with other molecules is defined as its *mean free path*. Depending on the relative size of a particle suspended in a gas and the mean free path of the gas molecules around it, we can distinguish two cases. If the particle size is much larger than the mean free path of the surrounding gas molecules, the gas behaves, as far as the particle is concerned, as a continuous fluid. The particle is so large and the characteristic lengthscale of the motion of the gas molecules so small that an observer of the system sees a particle in a continuous fluid. At the other extreme, if the particle is much smaller than the mean free path of the surrounding fluid, an outside observer of the system (Figure 9.1) sees a small particle and gas molecule moving discretely around it. The particle is small enough that it resembles another gas molecule.

As usual in transport phenomena, one seeks an appropriate dimensionless group that reflects the relative lengthscales outlined above. The key dimensionless group that defines the nature of the suspending fluid relative to the particle is the *Knudsen number* (Kn)

$$\text{Kn} = \frac{2\lambda}{D_p} = \frac{\lambda}{R_p} \quad (9.1)$$



**FIGURE 9.1** Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ( $\text{Kn} \rightarrow 0$ ), (b) free molecule (kinetic) regime ( $\text{Kn} \rightarrow \infty$ ), and (c) transition regime ( $\text{Kn} \sim 1$ ).

where  $\lambda$  is the mean free path of the fluid,  $D_p$  the particle diameter, and  $R_p$  its radius. Thus the Knudsen number is the ratio of two lengthscales, a length characterizing the “graininess” of the fluid with respect to the transport of momentum, mass, or heat, and a length scale characterizing the particle size, its radius.

Before we discuss the role of the Knudsen number, we need to consider the calculation of the mean free path for a vapor. It will soon be necessary to calculate the mean free path both for a pure gas and for gases composed of mixtures of several components. Note that even though air consists of molecules of  $\text{N}_2$  and  $\text{O}_2$ , it is customary to talk about the mean free path of air,  $\lambda_{\text{air}}$ , as if air were a single chemical species.

**Mean Free Path of a Pure Gas** Let us start with the simplest case, a particle suspended in a pure gas B. If we are interested in characterizing the nature of the suspending gas relative to the particle, the mean free path that appears in the definition of the Knudsen number is  $\lambda_{\text{BB}}$ . The subscript denotes that we are interested in collisions of molecules of B with other molecules of B. Ordinarily, air will be the predominant vapor species in such a situation. The mean free path  $\lambda_{\text{BB}}$  has been defined as the average distance traveled by a B molecule between collisions with other B molecules. The mean speed of gas molecules of B,  $\bar{c}_B$  is (Moore 1962, p. 238)

$$\bar{c}_B = \left( \frac{8RT}{\pi M_B} \right)^{1/2} \quad (9.2)$$

where  $M_B$  is the molecular weight of B. Note that larger molecules move more slowly, while the overall mean speed of a gas increases with temperature. The mean speed of  $\text{N}_2$  at 298 K is, according to (9.2),  $\bar{c}_{\text{N}_2} = 474 \text{ m s}^{-1}$  and for oxygen  $\bar{c}_{\text{O}_2} = 444 \text{ m s}^{-1}$ . Molecular velocities of other atmospheric gases at 298 K are shown in Table 9.1.

Let us estimate what happens to a B molecule during a unit of time, say, a second. During this second the molecule travels on average  $(\bar{c}_B \times 1 \text{ s}) \text{ m}$ . If during the same

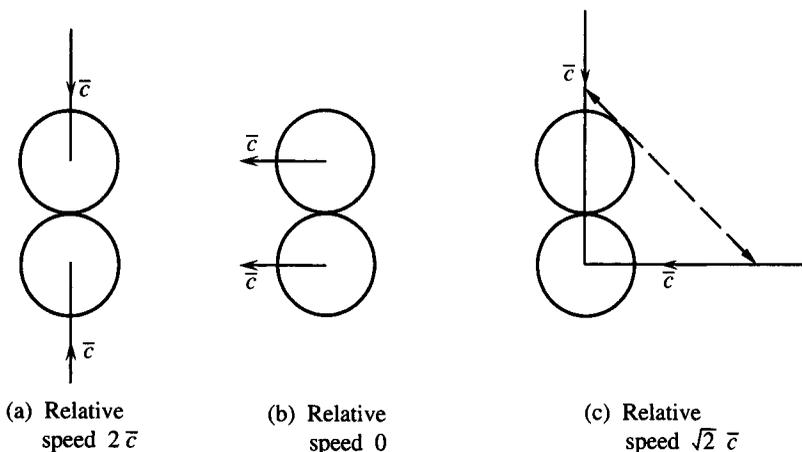
**TABLE 9.1 Molecular Velocities of Some Atmospheric Gases at 298 K**

Gas	Molecular Weight	Mean Velocity, m s <sup>-1</sup>
NH <sub>3</sub>	17	609
Air	28.8	468
HCl	36.5	416
HNO <sub>3</sub>	63	316
H <sub>2</sub> SO <sub>4</sub>	98	254
(CH <sub>2</sub> ) <sub>3</sub> (COOH) <sub>2</sub>	132	219

second it undergoes  $Z_{BB}$  collisions, then its mean free path will be by definition

$$\lambda_{BB} = \frac{\bar{c}_B}{Z_{BB}} \tag{9.3}$$

Thus to calculate  $\lambda_{BB}$  we need to first calculate the collision rate of B molecules,  $Z_{BB}$ . Let  $\sigma_B$  be the diameter of a B molecule. In 1 s a molecule travels a distance  $\bar{c}_B$  and collides with all molecules whose centers are in the cylinder of radius  $\sigma_B$  and height  $\bar{c}_B$ . Note that two molecules of diameter  $\sigma_B$  collide when the distance between their centers is  $\sigma_B$ . If  $N_B$  is the number of B molecules per unit volume, then the number of molecules in the cylinder is  $\pi\sigma_B^2\bar{c}_BN_B$ . Above we have calculated the number of collisions assuming that one molecule of B is moving while the rest are immobile and in the process we have underestimated the frequency of collisions. In general, all particles are moving in random directions and we need to account for this motion by estimating their relative speed. If two particles move in opposite directions, their relative speed is  $2\bar{c}_B$  (Figure 9.2). If they move in the same direction, their relative speed is zero, while for a 90° angle their relative



**FIGURE 9.2** Relative speeds (RSs) of molecules for (a) head-on collision ( $RS = 2\bar{c}$ ), (b) grazing collision ( $RS = 0$ ), and (c) right-angle collision ( $RS = \sqrt{2}\bar{c}$ ). For molecules moving in the same direction with the same velocity, the relative velocity of approach is zero. If they approach head-on, the relative velocity of approach is  $2\bar{c}$ . If they approach at 90°, the relative velocity of approach is the sum of the velocity components along the line.

velocity of approach is  $\sqrt{2} \bar{c}_B$  (Figure 9.2). One can prove that the latter situation represents the average, so we can write

$$Z_{BB} = \sqrt{2} \pi \sigma_B^2 \bar{c}_B N_B \quad (9.4)$$

and the mean free path  $\lambda_{BB}$  is given by

$$\lambda_{BB} = \frac{1}{\sqrt{2} \pi \sigma_B^2 N_B} \quad (9.5)$$

Note that the larger the molecule size,  $\sigma_B$ , and the higher the gas concentration, the smaller the mean free path.

Unfortunately, even though (9.5) provides valuable insights into the dependence of  $\lambda_{BB}$  on the gas concentration and molecular size, it is not convenient for the estimation of the mean free path of a pure gas, because one needs to know the diameter of the molecule  $\sigma_B$ , a rather ill-defined quantity as most molecules are not spherical. To make things even worse, the mean free path of a gas cannot be measured directly. However, the mean free path can be theoretically related to measurable gas microscopic properties, such as viscosity, thermal conductivity, or molecular diffusivity. One therefore can use measurements of the above gas properties to estimate theoretically the gas mean free path. For example, the mean free path of a pure gas can be related to the gas viscosity using the kinetic theory of gases

$$\lambda_{BB} = \frac{2\mu_B}{p(8M_B/\pi RT)^{1/2}} \quad (9.6)$$

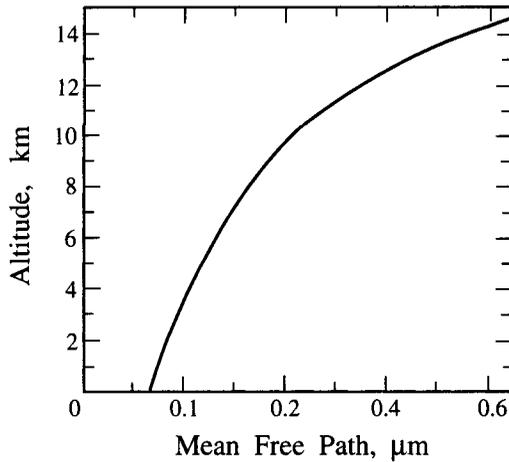
where  $\mu_B$  is the gas viscosity (in  $\text{kg m}^{-1} \text{s}^{-1}$ ),  $p$  is the gas pressure (in Pa), and  $M_B$  is the molecular weight of B.

**Calculation of the Air Mean Free Path** The air viscosity at  $T = 298 \text{ K}$  and  $p = 1 \text{ atm}$  is  $\mu_{\text{air}} = 1.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ . The air mean free path at  $T = 298 \text{ K}$  and  $p = 1 \text{ atm}$  is then found using (9.6) to be

$$\lambda_{\text{air}}(298 \text{ K}, 1 \text{ atm}) = 0.0651 \text{ } \mu\text{m} \quad (9.7)$$

Thus for standard atmospheric conditions, if the particle diameter exceeds  $0.2 \text{ } \mu\text{m}$  or so,  $\text{Kn} < 1$ , and with respect to atmospheric properties, the particle is in the *continuum regime*. In that case, the equations of continuum mechanics are applicable. When the particle diameter is smaller than  $0.01 \text{ } \mu\text{m}$ , the particle exists in more or less a rarified medium and its transport properties must be obtained from the kinetic theory of gases. This  $\text{Kn} \gg 1$  limit is called the *free molecule* or *kinetic regime*. The particle size range intermediate between these two extremes ( $0.01\text{--}0.2 \text{ } \mu\text{m}$ ) is called the *transition regime*, and there the particle transport properties result from combination of the two other regimes.

The mean free path of air varies with height above the Earth's surface as a result of pressure and temperature changes (Chapter 1). This change for standard atmospheric



**FIGURE 9.3** Mean free path of air as a function of altitude for the standard U.S. atmosphere (Hinds 1999).

conditions (see Table A.7) is shown in Figure 9.3. The net result is an increase of the air mean free path with altitude, to roughly  $0.2\ \mu\text{m}$  at 10 km.

**Mean Free Path of a Gas in a Binary Mixture** If we are interested in the diffusion of a vapor molecule A toward a particle, both of which are contained in a background gas B (e.g., air), then the description of the diffusion process depends on the value of the Knudsen number defined on the basis of the mean free path  $\lambda_{AB}$ . The mean free path  $\lambda_{AB}$  is defined as the average distance traveled by a molecule of A before it encounters another molecule of A or B. Note that because ordinarily the concentration of A molecules is several orders of magnitude lower than that of the background gas B (air), collisions between A molecules can be neglected, and the collisions between A and B are practically equal to the total number of collisions for an A molecule. The Knudsen number in the case of interest is given by

$$\text{Kn} = \frac{2\lambda_{AB}}{D_p} \quad (9.8)$$

and we need to estimate  $\lambda_{AB}$ . Jeans showed that the effective mean free path of molecules of A,  $\lambda_{AB}$ , in a binary mixture of A and B is (Davis 1983)

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi N_A \sigma_A^2 + \pi(1+z)^{1/2} N_B \sigma_{AB}^2} \quad (9.9)$$

where  $N_A$  and  $N_B$  are the molecular number concentrations of A and B,  $\sigma_A$  and  $\sigma_{AB}$  are the collision diameters for binary collisions between molecules of A and molecules of A and B, respectively, where

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (9.10)$$

and  $z = m_A/m_B = M_A/M_B$  is the ratio of molecular masses (or molecular weights) of A and B. The first term in the denominator of (9.9) accounts for the collisions between A molecules, while the second for the collisions between A and B molecules. If the concentration of species A is very low (a good assumption for almost all atmospheric situations),  $N_A \ll N_B$  and (9.9) can be simplified by neglecting the collisions between A molecules as

$$\lambda_{AB} = \frac{1}{\pi(1+z)^{1/2} N_B \sigma_{AB}^2} \quad (9.11)$$

Note that the molecular concentration  $N_B$  can be calculated from the ideal-gas law  $N_B = p/kT$ , where  $p$  is the pressure of the system. The mean free path of the trace gas A in the background gas does not depend on the concentration of A itself. This is not a surprise, as we have assumed that the concentration of A is so low that A molecules never get to interact with each other. However, the mean free path of A depends on the sizes of the A and B molecules, and on the temperature and pressure of the mixture.

The mean free path once more is usually calculated not by (9.11) because of the difficulty of directly measuring  $\sigma_{AB}$ , but from the binary diffusivity of A in B,  $D_{AB}$ . This diffusivity can be either measured directly or calculated theoretically from the Chapman–Enskog theory for binary diffusivity (Chapman and Cowling 1970) by

$$D_{AB} = \frac{3}{8\pi} \frac{[\pi k^3 T^3 (1+z)/(2m_A)]^{1/2}}{\rho \sigma_{AB}^2 \Omega_{AB}^{(1,1)}} \quad (9.12)$$

where  $\Omega_{AB}^{(1,1)}$  is the collision integral, which has been tabulated by Hirschfelder et al. (1954) as a function of the reduced temperature  $T^* = kT/\varepsilon_{AB}$ , where  $\varepsilon_{AB}$  is the Lennard-Jones molecular interaction parameter. For hard spheres  $\Omega_{AB}^{(1,1)} = 1$ , and for this case the following relationship connects the mean free path  $\lambda_{AB}$ , and the binary diffusivity  $D_{AB}$

$$\lambda_{AB} = \frac{32}{3\pi(1+z)} \frac{D_{AB}}{\bar{c}_A} \quad (9.13)$$

Note the appearance of the molecular mass ratio  $z = M_A/M_B$  in (9.13). Many investigators have assumed  $z \ll 1$  either explicitly or implicitly and this has been the source of some confusion. We can identify certain limiting cases for (9.13):

$$\begin{aligned} \lambda_{AB} &= 3.397 \frac{D_{AB}}{\bar{c}_A} & z \ll 1 \\ &= 1.7 \frac{D_{AB}}{\bar{c}_A} & z = 1 \\ &= \frac{3.397 D_{AB}}{z \bar{c}_A} & z \gg 1 \end{aligned} \quad (9.14)$$

Additional relationships have been proposed to determine the mean free path in terms of  $D_{AB}$ . From zero-order kinetic theory, Fuchs and Sutugin (1971) showed that

$$\lambda_{AB} = 3 \frac{D_{AB}}{\bar{c}_A} \quad (9.15)$$

while Loyalka et al. (1989) used

$$\lambda_{AB} = \frac{4}{\sqrt{\pi}} \frac{D_{AB}}{\bar{c}_A} = 2.257 \frac{D_{AB}}{\bar{c}_A} \tag{9.16}$$

An additional relationship between the mean free path and the binary diffusivity can be derived using the kinetic theory of gases. The derivation relies on a simple argument involving the flux of gas molecules across planes separated by a distance  $\lambda$ . Consider the simplest case, only a single gas, some of the molecules of which are painted red. Assume that the number  $N'$  of red molecules is greater in one direction along the  $x$  axis, and consequently, if the total pressure is uniform throughout the gas, the number  $N''$  of unpainted molecules must also vary along the  $x$  direction. Let us define the “mean free path” for diffusion as  $\lambda$ , so that  $\lambda$  is the distance both left and right of the plane at  $x$  where the molecules (both painted and unpainted) experienced their last collisions. We are purposely not defining  $\lambda$  precisely at this point. Figure 9.4 depicts planes at  $x^* + \lambda$  and  $x^* - \lambda$ .

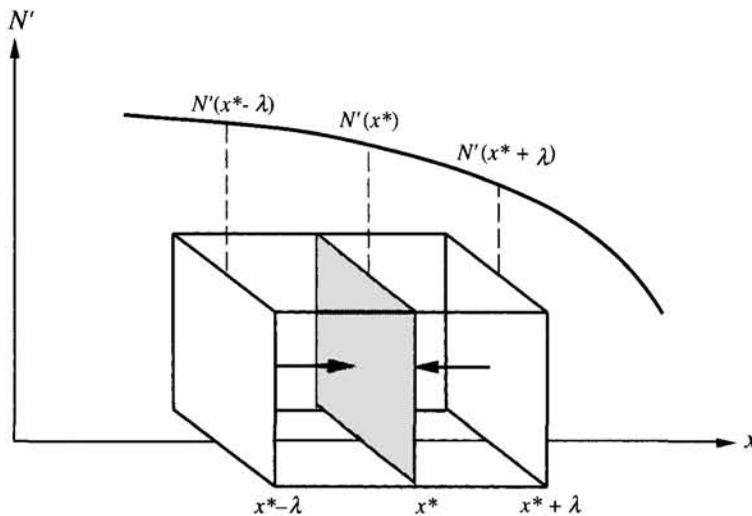
For molecules in three-dimensional random motion, the number of molecules striking a unit area per unit time is  $\frac{1}{4}N\bar{c}$ . If  $\lambda$  is the average distance from the control surface at which the molecules crossing the  $x^*$  surface originated, then the left-to-right flux of painted molecules is  $\frac{1}{4}\bar{c}N'(x^* - \lambda)$ , while the right-to-left is  $\frac{1}{4}\bar{c}N'(x^* + \lambda)$ .

The net left-to-right flux of painted molecules through the plane of  $x^*$  is (in molecules  $\text{cm}^{-2} \text{s}^{-1}$ )

$$J = \frac{1}{4}\bar{c}[N'(x^* - \lambda) - N'(x^* + \lambda)] \tag{9.17}$$

Expanding both  $N'(x^* - \lambda)$  and  $N'(x^* + \lambda)$  in Taylor series about  $x^*$ , we obtain

$$J = -\frac{1}{2}\bar{c}\lambda\left(\frac{\partial N'}{\partial x}\right)_{x=x^*} \tag{9.18}$$



**FIGURE 9.4** Control surfaces for molecular diffusion as envisioned in the elementary kinetic theory of gases.

Comparing (9.18) with the continuum expression  $J = -D(\partial N'/\partial x)$  results in  $D = 0.5\bar{c}\lambda$  or, equivalently

$$\lambda = 2\frac{D}{\bar{c}} \quad (9.19)$$

Since the red molecules differ from the others only by a coat of paint,  $\lambda$  and  $D$  apply to all molecules of the gas. Thus the diffusional mean free path  $\lambda$  is defined as a function of the molecular diffusivity of the vapor and its mean speed by (9.19).

Expressions (9.13), (9.15), (9.16), and (9.19) have different numerical constants and their use leads to mean free paths  $\lambda_{AB}$  that differ by as much as a factor of 2 for typical atmospheric gases. The consequences of using these different expressions are discussed in Chapter 12. In the remaining sections of this chapter we focus on the interactions of particles with a single gas, air, with a mean free path given by (9.6) and (9.7).

## 9.2 THE DRAG ON A SINGLE PARTICLE: STOKES' LAW

We start our discussion of the dynamical behavior of aerosol particles by considering the motion of a particle in a viscous fluid. As the particle is moving with a velocity  $u_\infty$ , there is a drag force exerted by the fluid on the particle equal to  $F_{\text{drag}}$ . This drag force will always be present as long as the particle is not moving in a vacuum. To calculate  $F_{\text{drag}}$ , one must solve the equations of fluid motion to determine the velocity and pressure fields around the particle.

The velocity and pressure in an incompressible Newtonian fluid are governed by the equation of continuity (a mass balance)

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \quad (9.20)$$

and the Navier–Stokes equations (a momentum balance) (Bird et al. 1960), the  $x$  component of which is

$$\rho \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} \right) = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) + \rho g_x \quad (9.21)$$

where  $\mathbf{u} = (u_x, u_y, u_z)$  is the velocity field,  $p(x, y, z)$  is the pressure field,  $\mu$  is the viscosity of the fluid, and  $g_x$  is the component of the gravity force in the  $x$  direction. To simplify our discussion let us assume without loss of generality that  $g_x = 0$ . The  $y$  and  $z$  components of the Navier–Stokes equations are similar to (9.21).

Let us nondimensionalize the Navier–Stokes equations by introducing a characteristic velocity  $u_0$  and characteristic length  $L$  and defining the dimensionless variables

$$U_x = \frac{u_x}{u_0}, \quad U_y = \frac{u_y}{u_0}, \quad U_z = \frac{u_z}{u_0}, \quad \xi_x = \frac{x}{L}, \quad \xi_y = \frac{y}{L}, \quad \xi_z = \frac{z}{L} \quad (9.22)$$

and the dimensionless time and pressure:

$$\tau = \frac{t u_0}{L} \quad \text{and} \quad \phi = \frac{\rho L}{\rho U_0^2}$$

Then (9.20) and (9.21) can be rewritten using the definitions presented above

$$\frac{\partial U_x}{\partial \xi_x} + \frac{\partial U_y}{\partial \xi_y} + \frac{\partial U_z}{\partial \xi_z} = 0 \quad (9.23)$$

and

$$\frac{\partial U_x}{\partial \tau} + U_x \frac{\partial U_x}{\partial \xi_x} + U_y \frac{\partial U_x}{\partial \xi_y} + U_z \frac{\partial U_x}{\partial \xi_z} = -\frac{\partial \phi}{\partial \xi_x} + \frac{1}{\text{Re}} \left( \frac{\partial^2 U_x}{\partial \xi_x^2} + \frac{\partial^2 U_x}{\partial \xi_y^2} + \frac{\partial^2 U_x}{\partial \xi_z^2} \right) \quad (9.24)$$

where  $\text{Re} = u_0 L \rho / \mu$  is the *Reynolds number*, representing the ratio of inertial to viscous forces in the flow. Note that all the parameters of the problem have been neatly combined into one dimensionless number,  $\text{Re}$ . The above nondimensionalization provides us with considerable insight, namely, that the nature of the flow will depend exclusively on the Reynolds number.

For flow around a particle submerged in a fluid, the characteristic lengthscale  $L$  is the diameter of the particle  $D_p$ , and  $u_0$  can be chosen as the speed of the undisturbed fluid upstream of the body,  $u_\infty$ . Therefore

$$\text{Re} = \frac{\rho u_\infty D_p}{\mu}$$

One could also use the radius  $R_p$  of the particle as  $L$  and then define  $\text{Re}$  as  $\rho u_\infty R_p / \mu$ . Clearly, these differ only by a factor of 2. We will use the Reynolds number  $\text{Re}$  defined on the basis of the particle diameter in our subsequent discussion.

When viscous forces dominate inertial forces,  $\text{Re} \ll 1$ , and the type of flow that results is called a low-Reynolds-number flow or creeping flow. In this case the Navier–Stokes equations can be simplified as one can neglect the left-hand-side (LHS) terms of (9.24) (note that  $1/\text{Re}$  then is a large number) to obtain at steady state:

$$\frac{\partial \phi}{\partial \xi_x} = \frac{1}{\text{Re}} \left( \frac{\partial^2 U_x}{\partial \xi_x^2} + \frac{\partial^2 U_x}{\partial \xi_y^2} + \frac{\partial^2 U_x}{\partial \xi_z^2} \right) \quad (9.25)$$

The solution of (9.23) and (9.25) to obtain the velocity and pressure distribution around a sphere was first obtained by Stokes. The assumptions invoked to obtain the solution are (1) an infinite medium, (2) a rigid sphere, and (3) no slip at the surface of the sphere. For the solution details, we refer the reader to Bird et al. (1960, p. 132).

Using the spherical coordinate system defined in Figure 9.5, the pressure field around the particle is given by (Bird et al. 1960)

$$p = p_0 - \frac{3}{2} \frac{\mu u_\infty R_p}{r^2} \cos \theta \quad (9.26)$$

where  $R_p$  is the particle radius,  $p_0$  is the pressure in the plane  $z = 0$  far from the sphere,  $u_\infty$  is the approach velocity far from the sphere, and gravity has been neglected.

Our objective is to calculate the net force exerted by the fluid on the sphere in the direction of the flow. This force consists of two contributions. At each point on the surface of the sphere there is a force acting perpendicularly to the surface. This is the normal force.

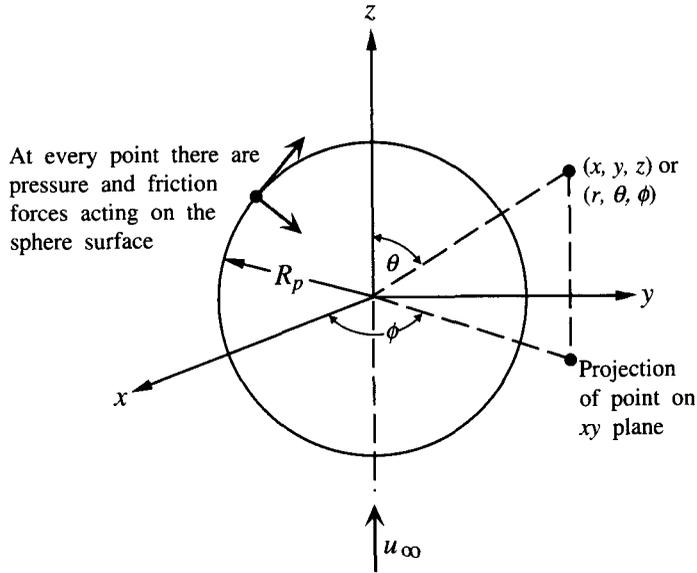


FIGURE 9.5 Coordinate system used in describing the flow of a fluid about a rigid sphere.

At each point there is also a tangential force exerted by the fluid due to the shear stress caused by the velocity gradients in the vicinity of the surface.

To obtain the normal force on the sphere, one integrates the component of the pressure acting perpendicularly to the surface. Then the normal force  $F_n$  is found to be

$$F_n = 2\pi \mu R_p u_\infty \tag{9.27}$$

The calculation of the tangential force requires the calculation of the shear stress  $\tau_{r\theta}$  and then its integration over the particle surface to find the tangential force  $F_t$

$$F_t = 4\pi \mu R_p u_\infty \tag{9.28}$$

Both forces act in the  $z$  direction (Figure 9.5) and the total drag exerted by the fluid on the sphere is

$$F_{\text{drag}} = F_n + F_t = 6\pi \mu R_p u_\infty \tag{9.29}$$

which is known as *Stokes' law*. Note that the case of a stationary sphere in a fluid moving with velocity  $u_\infty$  is entirely equivalent to that of a sphere moving with a velocity  $u_\infty$  through a stagnant fluid. In both cases the force exerted by the fluid on the particle is given by (9.29).

### 9.2.1 Corrections to Stokes' Law: The Drag Coefficient

Stokes' law has been derived for  $Re \ll 1$ , neglecting the inertial terms in the equation of motion. If  $Re = 1$ , the drag predicted by Stokes' law is 13% low, due to the errors

introduced by the assumption that inertial terms are negligible. To account for these terms, the drag force is usually expressed in terms of an empirical *drag coefficient*  $C_D$  as

$$F_{\text{drag}} = \frac{1}{2} C_D A_p \rho u_\infty^2 \quad (9.30)$$

where  $A_p$  is the projected area of the body normal to the flow. Thus for a spherical particle of diameter  $D_p$

$$F_{\text{drag}} = \frac{1}{8} \pi C_D \rho D_p^2 u_\infty^2 \quad (9.31)$$

where the following correlations are available for the drag coefficient as a function of the Reynolds number:

$$\begin{aligned} C_D &= \frac{24}{\text{Re}} & \text{Re} \lesssim 1 & \text{ (Stokes' law)} \\ C_D &= 18.5 \text{Re}^{-0.6} & \text{Re} \gtrsim 1 & \end{aligned} \quad (9.32)$$

Note for  $C_D = 24/\text{Re}$ , the drag force calculated by (9.31) is  $F_{\text{drag}} = 3\pi \mu D_p u_\infty$ , equivalent to Stokes' law.

To gain a feeling for the order of magnitude of  $\text{Re}$  for typical aerosol particles, the Reynolds numbers of spherical particles falling at their terminal velocities in air at 298 K and 1 atm are shown in Table 9.2. Thus for particles smaller than 20  $\mu\text{m}$  (virtually all atmospheric aerosols) Stokes' law is an accurate formula for the drag exerted by the air. For larger particles (rain and large cloud droplets) or for particles in rapid motion one needs to use the drag coefficient correlations presented above.

### 9.2.2 Stokes' Law and Noncontinuum Effects: Slip Correction Factor

Stokes' law is based on the solution of equations of continuum fluid mechanics and therefore is applicable to the limit  $\text{Kn} \rightarrow 0$ . The nonslip condition used as a boundary condition is not applicable for high  $\text{Kn}$  values. When the particle diameter  $D_p$  approaches the same magnitude as the mean free path  $\lambda$  of the suspending fluid (e.g., air), the drag force exerted by the fluid is smaller than that predicted by Stokes' law. To account for

**TABLE 9.2 Reynolds Number for Particles in Air Falling at Their Terminal Velocities at 298 K**

Diameter, $\mu\text{m}$	Re
0.1	$7 \times 10^{-9}$
1	$2.8 \times 10^{-6}$
10	$2.5 \times 10^{-3}$
20	0.02
60	0.4
100	2
300	20

**TABLE 9.3 Slip Correction Factor  $C_c$  for Spherical Particles in Air at 298 K and 1 atm**

$D_p, \mu\text{m}$	$C_c$
0.001	216
0.002	108
0.005	43.6
0.01	22.2
0.02	11.4
0.05	4.95
0.1	2.85
0.2	1.865
0.5	1.326
1.0	1.164
2.0	1.082
5.0	1.032
10.0	1.016
20.0	1.008
50.0	1.003
100.0	1.0016

noncontinuum effects that become important as  $D_p$  becomes smaller and smaller, the *slip correction factor*  $C_c$  is introduced into Stokes' law, written now in terms of particle diameter  $D_p$  as

$$F_{\text{drag}} = \frac{3\pi\mu u_{\infty} D_p}{C_c} \quad (9.33)$$

where

$$C_c = 1 + \frac{2\lambda}{D_p} \left[ 1.257 + 0.4 \exp\left(-\frac{1.1D_p}{2\lambda}\right) \right] \quad (9.34)$$

A number of investigators over the years have determined the values for the numerical coefficients used in the expression above. Allen and Raabe (1982) have reanalyzed Millikan's data (based on experiments performed between 1909 and 1923) to produce the updated set of parameters shown above.

Values of  $C_c$  as a function of the particle diameter  $D_p$  in air at 25°C are given in Table 9.3. The slip correction factor is generally neglected for particles exceeding 10  $\mu\text{m}$  in diameter, as the correction is less than 2%. On the other hand, the drag force for a 0.1  $\mu\text{m}$  in diameter particle is reduced by almost a factor of 3 as a result of this slip correction.

### 9.3 GRAVITATIONAL SETTLING OF AN AEROSOL PARTICLE

Up to this point, we have considered the drag force on a particle moving at a steady velocity  $u_{\infty}$  through a quiescent fluid. Recall that this case is equivalent to the flow of a

fluid at velocity  $u_\infty$  past the stationary particle. The motion of the particle, however, arises in the first place because of the action of some external force on the particle such as gravity. The drag force arises as soon as there is a difference between the velocity of the particle and that of the fluid. The basis of the description of the behavior of a particle in a fluid is an equation of motion. To derive the equation of motion for a particle of mass  $m_p$ , let us begin with a force balance on the particle, which we write in vector form as

$$m_p \frac{d\mathbf{v}}{dt} = \sum_i \mathbf{F}_i \quad (9.35)$$

where  $\mathbf{v}$  is the velocity of the particle and  $\mathbf{F}_i$  is the  $i$ th force acting on the particle.

For a particle falling in a fluid there are two forces acting on it, the gravitational force  $m_p \mathbf{g}$  and the drag force  $\mathbf{F}_{\text{drag}}$ . Therefore, for  $\text{Re} < 0.1$ , the equation of motion becomes

$$m_p \frac{d\mathbf{v}}{dt} = m_p \mathbf{g} + \frac{3\pi\mu D_p}{C_c} (\mathbf{u} - \mathbf{v}) \quad (9.36)$$

where the second term of (9.36) is the corrected Stokes drag force on a particle moving with velocity  $\mathbf{v}$  in a fluid having velocity  $\mathbf{u}$ . Equation (9.36) implicitly assumes that even though the particle motion is unsteady, this acceleration is slow enough that Stokes' law applies at any instant. This equation can be rewritten as

$$\tau \frac{d\mathbf{v}}{dt} = \tau \mathbf{g} + \mathbf{u} - \mathbf{v} \quad (9.37)$$

where

$$\tau = \frac{m_p C_c}{3\pi\mu D_p} \quad (9.38)$$

is the characteristic *relaxation time* of the particle.

Let us consider the case of a particle in a quiescent fluid ( $\mathbf{u} = \mathbf{0}$ ) starting with zero velocity and let us take the  $z$  axis as positive downward. Then the equation of motion becomes

$$\tau \frac{dv_z}{dt} = \tau g - v_z \quad v_z(0) = 0 \quad (9.39)$$

and its solution is

$$v_z(t) = \tau g [1 - \exp(-t/\tau)] \quad (9.40)$$

For  $t \gg \tau$ , the particle attains a characteristic velocity, called its *terminal settling velocity*  $v_t = \tau g$  or

$$v_t = \frac{m_p C_c g}{3\pi\mu D_p} \quad (9.41)$$

**TABLE 9.4 Characteristic Time Required for Reaching Terminal Settling Velocity**

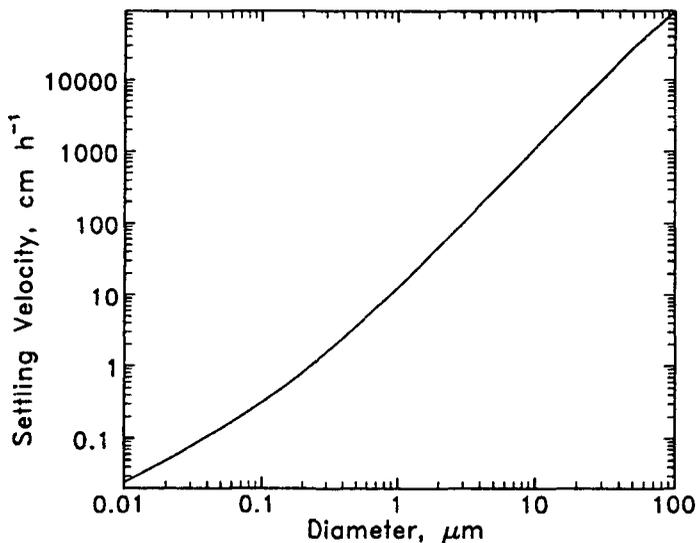
$D_p, \mu\text{m}$	$\tau, \text{s}$
0.05	$4 \times 10^{-8}$
0.1	$9.2 \times 10^{-8}$
0.5	$1 \times 10^{-6}$
1.0	$3.6 \times 10^{-6}$
5.0	$7.9 \times 10^{-5}$
10.0	$3.14 \times 10^{-4}$
50.0	$7.7 \times 10^{-3}$

For a spherical particle of density  $\rho_p$  in a fluid of density  $\rho$ ,  $m_p = (\pi/6)D_p^3(\rho_p - \rho)$ , where the factor  $(\rho_p - \rho)$  is needed to account for both gravity and buoyancy. However, since generally  $\rho_p \gg \rho$ ,  $m_p = (\pi/6)D_p^3\rho_p$  and (9.41) can be rewritten in the more convenient form:

$$v_t = \frac{1}{18} \frac{D_p^2 \rho_p g C_c}{\mu} \quad (9.42)$$

The timescale  $\tau$  indicates the time required by the particle to reach this terminal settling velocity and is given in Table 9.4. The relaxation time  $\tau$  also describes the time required by a particle entering a fluid stream, to approach the velocity of the stream. Thus the characteristic time of most particles of interest to achieve steady motion in air is extremely short.

Settling velocities of unit density spheres in air at 1 atm and 298 K as computed from (9.42) are given in Figure 9.6. Submicrometer particles settle extremely slowly, only a few

**FIGURE 9.6** Settling velocity of particles in air at 298 K as a function of their diameter.

centimeters per hour. Particles larger than 10  $\mu\text{m}$  settle with speeds exceeding 10  $\text{m h}^{-1}$  and therefore are expected to have short atmospheric lifetimes.

Our analysis so far is applicable to  $\text{Re} < 0.1$  or particles smaller than about 20  $\mu\text{m}$  (Table 9.2). For larger particles, one needs to use the drag coefficient as an empirical means of representing the drag force for higher Reynolds numbers. The equation along the direction of motion of the particle in scalar form, assuming no gas velocity, is then

$$m_p \frac{dv_z}{dt} = m_p g - \frac{1}{8} \pi \frac{C_D}{C_c} \rho D_p^2 v_z^2 \quad (9.43)$$

At steady-state  $v_z = v_t$ , the particle reaches its terminal velocity given by

$$v_t = \left( \frac{4gD_p C_c \rho_p}{3C_D \rho} \right)^{1/2} \quad (9.44)$$

However, as  $C_D$  is a function of  $\text{Re}$  and therefore  $v_t$ , we have only an implicit expression for  $v_t$  in (9.44). One needs then to solve (9.44) numerically with  $C_D$  calculated by (9.32) or one can use the following technique (Flagan and Seinfeld 1988).

If we form the product

$$C_D \text{Re}^2 = \frac{C_D v_t^2 D_p^2 \rho^2}{\mu^2} \quad (9.45)$$

and substitute into this the  $v_t$  given by (9.44), we obtain

$$C_D \text{Re}^2 = \frac{4D_p^3 \rho_p \rho g C_c}{3\mu^2} \quad (9.46)$$

$C_D \text{Re}^2$  can be calculated from (9.32) and one can prepare the plot of  $C_D \text{Re}^2$  versus  $\text{Re}$  shown in Figure 9.7. The terminal velocity can now be calculated as follows. First, we calculate  $C_D \text{Re}^2$  using (9.46). Then using Figure 9.7, we calculate  $\text{Re}$ . Then

$$v_t = \frac{\mu \text{Re}}{\rho D_p}$$

and there is no need to solve the system of nonlinear algebraic equations.

**Settling Velocity** Calculate the settling velocity of a 200- $\mu\text{m}$ -diameter droplet with density  $\rho_p = 1 \text{ g cm}^{-3}$ . What would be the value if one uses Stokes' law?

For a drop with  $D_p = 200 \mu\text{m}$  using (9.34),  $C_c = 1$  and therefore from (9.46)  $C_D \text{Re}^2 = 385$ . Using Figure 9.7, we find that the corresponding Reynolds number is roughly 10. Now the terminal velocity can be calculated from the definition of  $\text{Re}$  and it is approximately  $75 \text{ cm s}^{-1}$ .

Using Stokes' law given by (9.42) we calculate  $v_t = 120 \text{ cm s}^{-1}$ . Stokes' law overestimates the settling speed of such a droplet by 60%.

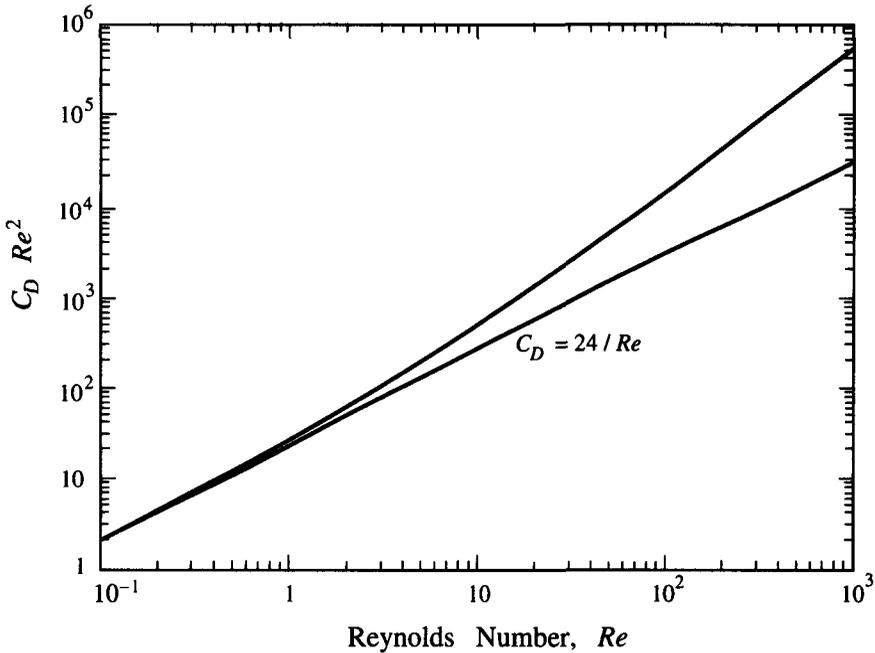


FIGURE 9.7  $C_D Re^2$  as a function of  $Re$  for a sphere.

#### 9.4 MOTION OF AN AEROSOL PARTICLE IN AN EXTERNAL FORCE FIELD

The force balance presented in (9.35) describes the motion of a particle in a force field. As long as the particle is not moving in a vacuum, the drag force will always be present, so let us remove the drag force from the summation of forces

$$m_p \frac{d\mathbf{v}}{dt} = \frac{3\pi\mu D_p}{C_c} (\mathbf{u} - \mathbf{v}) + \sum_i \mathbf{F}_{ei} \quad (9.47)$$

where  $\mathbf{F}_{ei}$  denotes external force  $i$  (those forces arising from external potential fields, such as gravity and electrical forces).

Situations in which a charged particle moves in an electric field are important in several gas-cleaning devices and aerosol measurements. If a particle has an electric charge  $q$  in an electric field of strength  $\mathbf{E}$ , an electrostatic force

$$\mathbf{F}_{ee} = q\mathbf{E}$$

acts on the particle. The equation of motion for a particle of charge  $q$  moving at velocity  $\mathbf{v}$  in a fluid with velocity  $\mathbf{u}$  in the presence of an electric field of strength  $\mathbf{E}$  is

$$m_p \frac{d\mathbf{v}}{dt} = \frac{3\pi\mu D_p}{C_c} (\mathbf{u} - \mathbf{v}) + q\mathbf{E} \quad (9.48)$$

At steady state in the absence of a background fluid velocity, the particle velocity is such that the electrical force is balanced by the drag force and

$$\mathbf{v}_e = \frac{qC_c}{3\pi\mu D_p} \mathbf{E} \quad (9.49)$$

where  $\mathbf{v}_e$  is termed the *electrical migration velocity*. Note that the characteristic time for relaxation of the particle velocity to its steady-state value is still given by  $\tau = m_p C_c / 3\pi\mu D_p$  regardless of the external force influencing the particle. Thus, as long as  $\tau$  is small compared to the characteristic time of change in the electric force, the particle velocity is given by (9.49). Defining the *electrical mobility* of a charged particle  $B_e$  as

$$B_e = \frac{qC_c}{3\pi\mu D_p} \quad (9.50)$$

then the electrical migration velocity is given by

$$\mathbf{v}_e = B_e \mathbf{E} \quad (9.51)$$

## 9.5 BROWNIAN MOTION OF AEROSOL PARTICLES

Particles suspended in a fluid are continuously bombarded by the surrounding fluid molecules. This constant bombardment results in a random motion of the particles known as *Brownian motion*. A satisfactory description of this irregular motion (“random walk”) can be obtained ignoring the detailed structure of the particle–fluid molecule interaction if we assume that what happens to the aerosol fluid system at a given time  $t$  depends only on the system state at time  $t$ . Stochastic processes with this property are known as *Markov processes*.

In an effort to understand quantitatively Brownian motion, let us consider a particle that is settling in air owing to the action of gravity. As we have seen, the particle eventually reaches a terminal velocity that depends on the size of the particle and the viscosity of the air. A drag force is generated, depending on the velocity of the particle, that acts in a direction opposite to the direction of motion of the particle. If our particle is sufficiently large, say, 1  $\mu\text{m}$  or larger, then the individual bombardment by microscopic gas molecules will have little effect on its motion that will be determined more or less solely by the continuum fluid drag force and gravity. However, if we consider a particle that is only a few nanometers, a size comparable to that of the gas molecules, then its motion will exhibit fluctuations from the random collisions that it experiences with gas molecules.

Let us consider a particle that is initially at the origin of our coordinate system. Assuming that the only force acting on the particles is that resulting from molecular

bombardment by fluid molecules, the particle will start moving randomly from its original position and after time  $t$  will be at location  $\mathbf{r}_1 = (x_1, y_1, z_1)$ . If we repeat the same experiment with a second particle, we will find it at  $\mathbf{r}_2 = (x_2, y_2, z_2)$  after the same period. Let us continue this experiment with an entire population or an ensemble of particles. If we average the displacements  $\langle \mathbf{r} \rangle$  of all these particles, we expect the average  $\langle \mathbf{r} \rangle$  to be zero since there is no preferred direction in Brownian motion. Can we then say anything quantitative about Brownian motion? We know that the average mean displacements  $\langle x \rangle$ ,  $\langle y \rangle$ ,  $\langle z \rangle$  of a particle ensemble will be zero, but this is not enough. We need a measure of the intensity of Brownian motion, something that will allow us to distinguish between particles moving slowly and randomly and particles moving rapidly and randomly. The traditional measure of such intensity is the mean square displacement of all particles  $\langle r^2 \rangle$ , or for the three directions  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ , and  $\langle z^2 \rangle$ . Note that these means cannot be zero, as averages of positive quantities. We expect that the higher the intensity of the motion, the larger the mean square displacements. Since the mean square displacement is an important descriptor of the Brownian motion process, let us see what we can learn about this quantity.

Equations (9.35) and (9.47) provide a convenient framework for the analysis of forces acting on particles. These equations simply state that the acceleration experienced by the particle is proportional to the sum of forces acting on the particle. We have used this equation so far for “deterministic” forces, namely, the gravity, drag, and electrical forces. We now need to use the stochastic Brownian force, which is simply the product of the particle mass  $m_p$  and the random acceleration  $\mathbf{a}$  caused by the bombardment by the fluid molecules. Then the equation of motion is

$$m_p \frac{d\mathbf{v}}{dt} = -\frac{3\pi\mu D_p}{C_c} \mathbf{v} + m_p \mathbf{a} \quad (9.52)$$

Dividing by  $m_p$ , (9.52) becomes

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau} \mathbf{v} + \mathbf{a} \quad (9.53)$$

where  $\tau$  is the relaxation time of the particle. The random acceleration  $\mathbf{a}$  is a discontinuous term, since it represents the random force exerted by the suspending fluid molecules that imparts an irregular, jerky motion to the particle. The equation of motion written to include the Brownian motion has its roots in two worlds: the macroscopic world represented by the drag force and the microscopic world presented by the Brownian force. The decomposition of the equation of motion into continuous and discontinuous pieces in (9.53) is an ad hoc assumption that is intuitively appealing and more important leads to successful predictions of particle behavior. Equation (9.53) was first formulated by the French physicist, Paul Langevin, in 1908 and is referred to as the *Langevin equation*. This equation will be the starting point in our effort to calculate the mean square displacement  $\langle r^2 \rangle$ .

Let us begin by taking the dot product of  $\mathbf{r}$  and (9.53):

$$\mathbf{r} \cdot \frac{d\mathbf{v}}{dt} = -\frac{1}{\tau} \mathbf{r} \cdot \mathbf{v} + \mathbf{r} \cdot \mathbf{a} \quad (9.54)$$

Then ensemble averaging this equation (over many particles) gives

$$\left\langle \mathbf{r} \cdot \frac{d\mathbf{v}}{dt} \right\rangle = -\frac{1}{\tau} \langle \mathbf{r} \cdot \mathbf{v} \rangle + \langle \mathbf{r} \cdot \mathbf{a} \rangle \quad (9.55)$$

Since we assume that there is no preferred direction in  $\mathbf{a}$  (directional isotropy of collisions),  $\langle \mathbf{r} \cdot \mathbf{a} \rangle$  will be equal to zero, giving

$$\left\langle \mathbf{r} \cdot \frac{d\mathbf{v}}{dt} \right\rangle = -\frac{1}{\tau} \langle \mathbf{r} \cdot \mathbf{v} \rangle \quad (9.56)$$

Now since

$$\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{v} \rangle = \left\langle \mathbf{r} \cdot \frac{d\mathbf{v}}{dt} \right\rangle + \left\langle \frac{d\mathbf{r}}{dt} \cdot \mathbf{v} \right\rangle \quad (9.57)$$

or, equivalently

$$\left\langle \mathbf{r} \cdot \frac{d\mathbf{v}}{dt} \right\rangle = \frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{v} \rangle - \langle v^2 \rangle \quad (9.58)$$

(9.56) becomes

$$\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{v} \rangle = -\frac{1}{\tau} \langle \mathbf{r} \cdot \mathbf{v} \rangle + \langle v^2 \rangle \quad (9.59)$$

The term  $\frac{1}{2} m_p \langle v^2 \rangle$  is the kinetic energy of the system and as energy is partitioned equally in all three directions, each with an energy of  $\frac{1}{2} kT$  for a total of  $\frac{3}{2} kT$ , we obtain that  $\langle v^2 \rangle = 3kT/m_p$ . Thus (9.59) becomes

$$\frac{d}{dt} \langle \mathbf{r} \cdot \mathbf{v} \rangle = -\frac{1}{\tau} \langle \mathbf{r} \cdot \mathbf{v} \rangle + \frac{3kT}{m_p} \quad (9.60)$$

Integrating this ordinary differential equation for  $\langle \mathbf{r} \cdot \mathbf{v} \rangle$  we find

$$\langle \mathbf{r} \cdot \mathbf{v} \rangle = \frac{3kT\tau}{m_p} + c \exp(-t/\tau) \quad (9.61)$$

Now we note that

$$\langle \mathbf{r} \cdot \mathbf{v} \rangle = \left\langle \mathbf{r} \cdot \frac{d\mathbf{r}}{dt} \right\rangle = \frac{1}{2} \frac{d}{dt} \langle r^2 \rangle \quad (9.62)$$

so that (9.61) becomes

$$\frac{1}{2} \frac{d}{dt} \langle r^2 \rangle = \frac{3kT\tau}{m_p} + c \exp(-t/\tau) \quad (9.63)$$