3 Aerosol Fundamentals

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INTRODUCTION

The term *aerosol* refers to an assembly of liquid or solid particles suspended in a gaseous medium long enough to be observed or measured. The term originated as the gas phase equivalent to the term *hydrosol*, which refers to a suspension of particles in a liquid (from the Greek word combination "water particle"). Manufactured and naturally produced particles, found in ambient and industrial air environments or in industrial process gas streams, may have a great diversity in size, shape, density, and chemical composition. The diversity of microscopic particles, includes what we might think are ideal shapes, such as spheres (droplets of water or oil) or cylinders (glass fibers). However, it also includes more complex shapes such as crystalline particles, which have some regular and some fractured surfaces; asbestos fibers, which are often bundles of finer fibrils but may be matted clumps of fibrils; and carbon black particles, which often consist of an extended framework of very small spheroids. All these have a different chemical constitution. Even if all these particles have the same microscopically observed diameter, the mass, surface area, and other properties of each particle are likely to be quite different. Part III, the Applications Section of this book, discusses a wide range of particulate types in many different environmental and industrial settings.

A variety of techniques are available for obtaining useful information about these particles. One way to detect the particles is by scattering light from them. The scattering pattern produced by spheres is quite predictable, while that from glass fibers is predictable only if their orientation relative to the light beam is known. The light pattern from asbestos fibers might be similar to that from glass fibers in some cases, but may be much more complex when the fibers are splayed bundles or matted clumps. Much less light might be scattered by carbon black due to its light-absorbing properties.

To characterize the size of spherical droplets, a single parameter, such as the droplet diameter, may suffice. With fibers, two dimensions may be sufficient, although often two may not be enough for less regular shapes. Clearly, for more complex particles we have to choose the particle properties that are important for our purposes in order to make a meaningful measurement. We can characterize particles by shape parameters observed under a microscope; light-scattering properties using an optical particle counter or a nephelometer; elemental or

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chemical properties with X-ray fluorescence or infrared spectroscopy; surface properties with a pycnometer or by an adsorption measurement; or dynamic behavior from measurement of settling velocity or diffusion. Note that one characteristic (e.g., physical size) may not correlate well with another characteristic (e.g., chemical composition). However, any or all of these types of characterization may be important for the scientist. For example, to estimate the toxicity of an aerosol entering the lung, one needs to know the size-dependent diffusion, gravitational settling, impaction, and interception properties of the particles to determine the deposition rate within the lung. In addition, the chemistry, surface area, and fibrosity of the particles may indicate their interactions with the lung tissues once they are deposited.

Sand found on a beach also comes in many different sizes, but here the shapes tend to be closer to those of spheres because the material has been subjected to erosive forces of wind and water motion. When measuring these macroscopic materials as to their physical, chemical, and biological composition, we must use different methods and techniques. Similarly, when measuring microscopic materials, a diversity of methods and techniques is used. In this chapter, common aerosol characteristics are introduced in preparation for more detailed discussions of specific measurement techniques that are discussed in later chapters.

DESIRABLE VERSUS UNDESIRABLE AEROSOLS

The development of many aerosol sampling and analysis techniques has been stimulated by a variety of applications. Since approximately the 1950s, advances in aerosol measurement have been motivated by investigations into the health effects of radioactive aerosols and industrial aerosols in the workplace and the environment. More recently, a great deal of effort has gone into trying to understand the effect of various natural and manmade aerosols on global warming. The production of high-speed integrated circuits has required increasingly cleaner environments to reduce contamination by aerosol particles. These efforts not only have resulted in more refined and sensitive instruments but also have increased understanding of particle generation and transport mechanisms. All these efforts have largely been aimed at reducing contaminants. In contrast, a great deal of knowledge is gained today by researchers working with "desirable" aerosols used to produce high technology materials such as ceramic powders, superconducting materials, and optical fibers.

UNITS AND USE OF EQUATIONS

All equations and calculations in this book are in Système Internationale (SI) units. Whenever deemed appropriate, calculations in centimeter–gram–second (cgs) units are shown subsequently in brackets. Because aerosol particles range in diameter from about 10^{-9} m to about 10^{-4} m, the unit of *micrometer* ($1\,\mu\mathrm{m} = 10^{-6}\,\mathrm{m}$) is generally used in discussions of particle dimensions. For instance, a particle most hazardous to the human respiratory system is on the order of 10^{-6} m in diameter and is conveniently described as a $1\,\mu\mathrm{m}$ particle. The term *micron* has been used in the past as a colloquial version of micrometer, but it is no longer accepted in technical writing. Researchers manufacturing aerosols through evaporation and subsequent condensation processes may deal with particles in the 0.01 to $0.1\,\mu\mathrm{m}$ range or even smaller and therefore prefer to express the particle sizes in nanometers ($1\,\mathrm{nm} = 10^{-9}\,\mathrm{m}$). In calculations requiring the use of SI units, micrometer is converted to meter by multiplying by 10^{-6}. If calculations are performed in cgs units, micrometer is converted to centimeter by multiplying by 10^{-4}. In this book, *particle size* always refers to particle diameter. In some publications, particle radius is used instead.

The SI unit for aerosol mass concentration, that is, the mass of particulate matter in a unit volume of gas, is expressed in $\mathrm{kg/m^3}$. Because the amount of aerosol mass is generally very low, the aerosol mass concentration is usually expressed in g/m^3, mg/m^3, μg/m^3, or ng/m^3. Particle velocity (e.g., under the influence of gravity or an electric field) is expressed in m/s [shown also in cm/s in brackets]. Volume is frequently indicated in liters (L = 10^{-3} m^3) because sampling volumes are often on the order of liters.

Aerosol number concentrations are expressed in number/m^3 [number/cm^3]. The older unit of millions of particles per cubic foot (mppcf) is given in parentheses when dealing with engineering systems and applications regulated by the U.S. Environmental Protection Agency. Tables in Appendix B give the conversion factors for the major units used by the practioner or researcher dealing with aerosols.

The SI unit for pressure is expressed in Pascal (1 Pa = 1 N/m^2). Atmospheric pressure (101 kPa = 1.01×10^6 dyne/cm^3) may also be referred to as 1 atm (= 14.7 psig = 760 mm Hg = 1040 cm H_2O = 408 inch H_2O). Gas and particle properties are listed at normal temperature and pressure (NTP), which refers to 101 kPa and 293 K [1 atm and 20°C = 68°F]. Many handbooks list values at 101 kPa and 273 K [1 atm and 0°C] (standard temperature and pressure = STP), which are less useful because most aerosol measurements in the environment are at temperatures close to 293 K [20°C].

EXAMPLE 3–1

A miner drilling into a rock face during his work shift hits a seam of quartz (a form of crystalline silica extremely hazardous to the lungs). The X-ray diffraction analysis on the personal sample taken over a period of 240 min at 1.7 L/min indicates 240 μg of respirable crystalline silica. Assume that this represents pure silica particles and that they are 2.8 μm diameter spherical particles with a density of 2660 kg/m^3 [2.66 g/cm^3]. What was the airborne exposure concentration in particles/m^3, particles/cm^3, mppcf (million particles per cubic foot), kg/m^3, g/m^3, mg/m^3, and μg/m^3?

Answer: The volume, v_p, of a single silica particle of physical diameter, d_p, is

$$\begin{aligned} v_p &= \frac{\pi}{6} d_p^3 = \frac{\pi}{6}(2.80 \mu\text{m})^3 = 11.5 \mu\text{m}^3 \\ &= 1.15 \times 10^{-17} m^3 \left[1.15 \times 10^{-11} cm^3\right] \end{aligned}$$

The mass, m_p, of a particle with density, ρ_p, is

$$\begin{aligned} m_p &= \rho_p v_p = (2.66 \times 10^3 \,\text{kg/m}^3)(1.15 \times 10^{-17} \text{m}^3) = 3.06 \times 10^{-14} \,\text{kg} = 3.06 \times 10^{-11} \text{g} \\ &= 3.06 \times 10^{-8} \,\text{mg} = 3.06 \times 10^{-5} \mu\text{g} \end{aligned}$$

The number of particles, n_p, in 240 μg of silica mass is

$$n_p = \frac{\text{silica mass}}{\text{single particle mass}} = \frac{240 \mu\text{g}}{3.06 \times 10^{-5} \mu\text{g}} = 7.84 \times 10^6 \text{ particles}$$

At flow rate, Q, and sampling time, t, the volume of sampled air, v_a, is

$$\begin{aligned} v_a &= Qt = \left(1.7 \frac{\text{L}}{\text{min}}\right)(240 \text{min}) = 408 \text{L} \\ &= 0.408 \text{m}^3 \left[4.08 \times 10^{-5} \text{cm}^3\right] \end{aligned}$$

The number concentration, c_n, of silica particles is, therefore,

Continued

$$c_n = \frac{n_p}{v_a} = \frac{7.84 \times 10^6 \text{particles}}{0.408 \text{m}^3} = 1.92 \times 10^7 \frac{\text{particles}}{\text{m}^3}$$

$$= 19.2 \frac{\text{particles}}{\text{cm}^3} = 0.545 \text{mppcf}$$

The particle mass concentration, c_m, is

$$c_m = m_p c_n = (3.06 \times 10^{-11} \text{g})\left(1.92 \times 10^7 \frac{\text{particles}}{\text{m}^3}\right)$$

$$\doteq 5.88 \times 10^{-4} \frac{\text{g}}{\text{m}^3} = 0.588 \frac{\text{mg}}{\text{m}^3} = 588 \frac{\mu\text{g}}{\text{m}^3}$$

Silica is one of the most toxic dusts encountered in the workplace. The current exposure standard in the United States is 50 μg/m³. Thus, this measurement indicates excessive exposure. In comparison, the workplace standard for the least toxic materials is 10 mg/m³. The environmental air quality standard in the United States is 80 μg/m³. The units of mppcf are no longer in common use for air measurements. They were popular for the measurement of dust concentrations by light microscopy.

Calculations occasionally will also be performed in both these systems to facilitate conversion because each system has its advantages. Electrostatic calculations in the SI system has an advantage in that it uses the familiar units of volts and amperes. The elementary unit of charge, e, is equal to 1.6×10^{-19} coulomb. However, there is some convenience in using the cgs units because the proportionality constant in Coulomb's Law is unity. In this system, all electrical units are defined having the prefix "stat." The elementary unit of charge, e, is equal to 4.8×10^{-10} statcoulomb. The electric field is expressed in statvolts/cm. One statvolt equals 300 volts in SI units. Also, particle motions expressed in cm/s reflect convenient magnitudes of particle velocity in an electric field.

It is assumed that the reader has available a computer to perform calculations. The reader is encouraged to experiment with the equations given in this book by calculating the results with a variety of input parameters to gain a feeling for the resulting values and how they behave. Spreadsheet programs are particularly useful for this purpose, and most of the equations given in this book have been set up in the Aerosol Calculator spreadsheets described in Chapter 2.

COMMON TECHNICAL AND DESCRIPTIVE TERMS

Various names are used to describe airborne particulate matter. The name *particle* refers to a single unit of matter, generally having a density approaching the intrinsic density of the bulk material. Individual particles may be chemically homogeneous or contain a variety of chemical species as well as consist of solid or liquid materials or both. Particle shapes may be simple, as in spherical liquid droplets, or complex, as in fiber bundles or agglomerated smoke. Many of the following terms do not have strict scientific definitions but rather are in common use as merely descriptive terms, often indicating the appearance or source of the particles.

Aerosol: An assembly of liquid or solid particles suspended in a gaseous medium long enough to be observed or measured. Generally, the sizes of aerosol particles are in the range of 0.001 to 100 μm. If the particle concentration is large enough that the density of the aerosol is more than about 1% greater than the gas alone, the assembly is considered a cloud and has bulk properties that differ from a more dilute aerosol. Note: The technical use of the term *aerosol* is much broader than the every-day usage referring to droplets emitted from a spray can

Bioaerosol: An aerosol of biological origin, including airborne suspensions of viruses, pollen, bacteria, and fungal spores and their fragments

Cloud: A high-density suspension of particles in air, often with a well-defined boundary

Dust: Solid particles formed by crushing or other mechanical breakage of a parent material. These particles generally have irregular shapes and are larger than about 0.5 µm

Fog or Mist: Liquid particle aerosol. These can be formed by condensation of supersaturated vapors or by physical shearing of liquids, such as in nebulization, spraying, or bubbling

Fume: Particles that are usually the result of condensed vapor with subsequent agglomeration. Solid fume particles typically consist of complex chains of submicrometer-sized particles (usually < 0.05 µm) of similar dimension. Fumes are often the result of combustion and other high temperature processes. Note that the common usage of *fume* also refers to noxious vapor components

Haze: A visiblity-reducing aerosol

Nanoparticle: A particle in the size range of 1 to 100 nm

Particle: A small, discrete object

Particulate: An adjective indicating that the material in question has particle-like properties. Less properly used as a term for particle

Smog: An aerosol consisting of solid and liquid particles, created, at least in part, by the action of sunlight on vapors. The term smog is a combination of the words smoke and fog and often refers to the entire range of such pollutants, including the gaseous constituents

Smoke: A solid or liquid aerosol, the result of incomplete combustion or condensation of supersaturated vapor. Most smoke particles are submicrometer in size

Spray: Droplet aerosol formed by mechanical or electrostatic breakup of a liquid

A number of terms describe the shape and origin of particles in an aerosol. These include

Agglomerate: A group of particles held together by van der Waals forces or surface tension

Aggregate: A heterogeneous particle in which the various components are not easily broken apart. The term *heterogeneous* indicates that the individual components may differ from each other in size, shape, and chemical composition

Flocculate: A group of particles very loosely held together, usually by electrostatic forces. Flocculates can easily be broken apart by shear forces within the air

Primary particle: A particle introduced into the air in solid or liquid form. A primary particle is often contrasted to a secondary particle

Secondary particle: Usually a particle formed in the air by gas to particle conversion. This term is sometimes used to describe agglomerated or redispersed particles

Appendix A gives additional definitions of aerosol terms.

PARTICLE SIZE AND SHAPE

Particle size is important because it largely determines the behavior of the particle in gas suspension. Particles behave differently in different size ranges and are even governed by different physical laws. For example, on the earth's surface, particles only slightly larger than gas molecules are governed primarily by Brownian motion, while large, visible particles are affected primarily by gravitational and inertial forces.

Particle size and shape can be quite complex and are often defined only to the extent that one can measure or calculate them. Therefore, there are numerous definitions of particle size and shape that depend on the measurement technique or on the use to which the parameter will be put. For instance, an electron microscope is a common means for measuring the size and shape of a particle. To accomplish this type of measurement, a particle is collected on a substrate, a process that may place the particle on the surface in some preferred orientation. The analyst measures the particle by comparison with standard-sized objects within the observation area. Except for ideally shaped spherical particles, the analyst usually reduces a complex shape to one or two measured parameters, for example, width, or diameter and length. With an image analysis system, one may be able to extract more features of a particle's shape. The usual aim in collecting this type of information is to reduce the data collected from each particle to the fewest numbers that can adequately characterize the particle.

Size Parameters

A commonly used term in aerosol science and technology is that of *equivalent diameter*. This refers to a diameter that is a measurable index of a particle. When a particle is reported by a technique, the measurement usually corresponds to a specific physical property. Thus, an equivalent diameter is reported as the diameter of a sphere having the same value of a specific physical property as the irregularly shaped particle being measured (Fig. 3–1). When the motion of a particle is of concern, the *mobility equivalent diameter*, d_B, is the diameter of a sphere with the same mobility as the particle in question.

For instance, *aerodynamic (equivalent) diameter* (equivalent is sometimes left out or implied) is the diameter of a standard-density (1000 kg/m^3 or 1 g/cm^3) sphere having the same

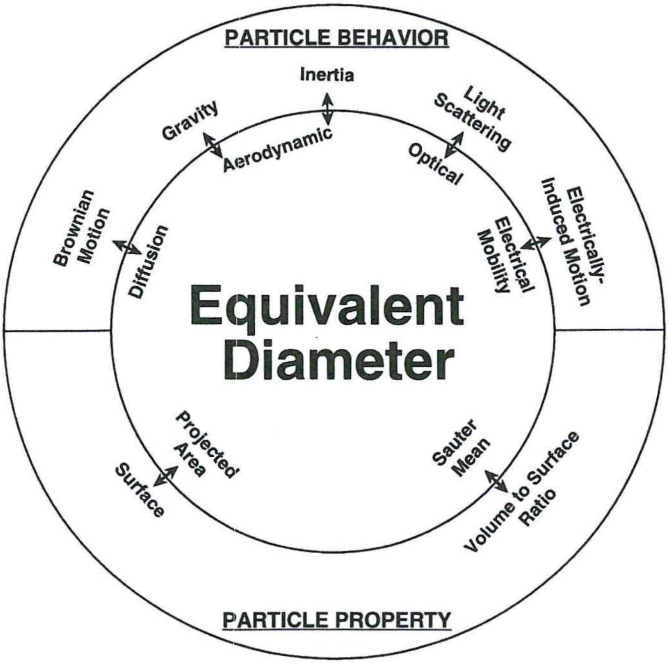

Fig. 3–1. Particle size definitions that depend on observations of particle properties or behavior.

gravitational settling velocity as the particle being measured. This definition is often used for characterizing particles that move primarily by settling as opposed to diffusion in still air (i.e., diameters larger than about 0.3 μm at normal atmospheric temperature and pressure). Reference to the aerodynamic diameter of a particle is useful for describing particle settling and inertial behavior in the respiratory tract, one of the body organs most at risk upon exposure to toxic aerosols. The behavior of particles in other devices such as filters, cyclones, and impactors is also often governed by the aerodynamic flows around the particles, and the sizes are therefore reported in terms of the particles' aerodynamic diameter. As will be seen in the next chapter, a solid, spherical particle's gravitational settling velocity is proportional to the *particle density*, ρ_p, the square of the *physical particle diameter*, d_p, and the *Cunningham slip correction factor*, C_c. The latter is introduced because the suspending gas is not a continuous fluid, but consists of discrete molecules. The slip correction factor, described in more detail in the next chapter, is a function of particle diameter, that is, $C_c = C_c(d_p) = C_{c,d_p}$. Thus

$$\rho_p C_{c,d_p} d_p^2 = \rho_0 C_{c,d_a} d_a^2 \tag{3–1}$$

One of the conditions chosen here is that of a sphere with standard particle density $\rho_0 = 1000\,\text{kg/m}^3$ [$1\,\text{g/cm}^3$], which defines the particle diameter as the aerodynamic diameter, d_a

$$d_a = d_p \left(\frac{C_{c,d_p}}{C_{c,d_a}} \right)^{1/2} \left(\frac{\rho_p}{\rho_0} \right)^{1/2} \tag{3–2}$$

When the particle density is close to standard density, C_{c,d_p} differs little from C_{c,d_a}, and the ratio of the two slip correction factors can be approximated by one. For particles above about 1 μm, the slip correction factor is close to unity, so this ratio can be approximated by one even for particle densities very different from unity. Therefore, for many applications, Eq. 3–2 reduces to

$$d_a = d_p \left(\frac{\rho_p}{\rho_0} \right)^{1/2} \tag{3–3}$$

EXAMPLE 3–2

What is the aerodynamic (equivalent) diameter of a spherical particle that is 3 μm in diameter and has a particle density of $4000\,\text{kg/m}^3$ [$4\,\text{g/cm}^3$]? Ignore the slip correction factors. *Answer*: From Eq. 3–3:

$$d_a = d_p \left(\frac{\rho_p}{\rho_0} \right)^{1/2} = 3\,\mu\text{m} \left(\frac{4000}{1000} \right)^{1/2} = 6\,\mu\text{m}$$

This indicates that a 6 μm standard-density particle gravitationally settles at the same velocity as the 3 μm particle with the higher density.

A particle may be extremely complex in shape, such as an agglomerate. In this case, a significant part of the internal volume of the particle is made up of voids. When describing the properties or behavior of such a particle, two additional definitions are available: the *mass equivalent diameter*, for which the particle is compressed into a spherical particle without voids; and the *envelope equivalent diameter*, for which the particle voids are included in the sphere. The mass equivalent diameter is convenient because it uses the bulk density of the material, a parameter often available in the literature (e.g., Lide, 1994) or easily measured. Further discussions of nonspherical particles are presented in Chapters 4 and 23.

Microscopes and other particle imaging systems are often used to measure particles. For instance, observing a particle's silhouette and calculating the diameter of a circle that has the same area gives the *projected area (equivalent) diameter*. Collecting an aerosol particle for measurement in a microscope can cause a number of biases to occur in the assessment of the original aerosol. For instance, the collected particle may be oriented by the surface. A fiber usually settles onto a surface with its long axis parallel to the surface. An agglomerate may collapse onto the surface from gravity or from surface tension of adsorbed water and appear more spread out than in its original form. The continued air flow over the particle may desiccate it, thus reducing it in size and mass. The collected particle may also react with the collection substrate, which may change the particle's size and chemical composition. The analyst needs to consider these possibilities when using data from methods involving sample collection (see Chapter 12)

We note here a dichotomy in measurement technique, namely, that of collection of an aerosol particle for laboratory measurement versus direct, in situ measurement of the particle. Traditionally, collection followed by measurement was often the most readily available. This approach still has its advantages because it brings to bear the many powerful analytical techniques available in the laboratory. However, this approach has the disadvantages that the particles may be modified by the transport and collection processes and that the analytical result is not immediately available. In situ techniques, on the other hand, provide a more limited degree of particle characterization.

In situ techniques can be subdivided further into extractive and external sensing techniques. Extractive techniques require the aerosol to be brought to the instrument sensor, while external sensing techniques measure the aerosol in its undisturbed state. For example, Chapter 15 describes mainly instruments that detect light scattered from particles brought into an instrument,while Chapter 16 describes light-based systems that detect particles some distance from the instrument.

A common in situ technique is the measurement of light scattered from the particles. The amount of light scattered from individual particles is a complex function of particle parameters of size, shape, and refractive index as well as instrumental parameters such as the wavelength of light and the scattering angle. The usual approach is to define an optical equivalent diameter that is the diameter of a calibration particle that scatters as much light in a specific instrument as the particle being measured. For simple particle shapes, such as spheres, ellipsoids, and rods of known chemical composition, the amount of light scattered may be calculated exactly. For most particles with more complex shapes, the association between optical equivalent diameter and a physically useful property is often difficult to establish precisely. Despite this, light scattering as an instrumental technique has a number of distinct advantages. These advantages include rapid, continuous, and sensitive detection of particles, often at relatively low cost.

Spray aerosol droplets used as fuels in combustion processes burn or react at their surfaces. Therefore, a useful measurement parameter is the *Sauter mean diameter*, the diameter of a droplet whose surface-to-volume ratio is equal to that of all the droplets in the spray distribution.

Because submicrometer particles move primarily by Brownian diffusion, it is natural to define their size by a *diffusion equivalent diameter*, that is, the diameter of a standard-density spherical particle with the same rate of diffusion as the particle being measured. For compact particles, the diffusion equivalent diameter is very close to the physical diameter, as might be measured with an electron microscope.

The measurement of small particles by diffusion-based techniques is often relatively slow and has poor resolution (see Chapter 19). In an electric field, a particle of known charge moves along a predictable trajectory. Therefore, the electrical mobility of a charged particle in an electric field is the basis for defining the *electrical mobility equivalent diameter*. Particle motion in an electric field can yield high-resolution measurements as well as separation of desired particle sizes (see Chapter 18).

In addition to the various equivalent diameters mentioned above, any other physical property, such as mobility in a magnetic field, external surface area, radioactivity, and chemical or elemental concentration, can be used to determine an equivalent diameter.

Size Ranges

Although it is customary to discuss particulate clouds in terms of particle size, rarely is such cloud composed of single-diameter particles—only in the laboratory and then only with great care can single-sized aerosols be produced. Such single-sized particulate aerosols are referred to as *monodisperse*. These aerosols are useful for studying their size-dependent properties or for calibrating instruments. Whether dust, mist, or fume, virtually all naturally occurring aerosols are a mixture of a wide variety of particle sizes, that is, they are *polydisperse*.

A large airborne molecule can be considered a very small aerosol particle. Although air consists of nitrogen, oxygen, and other gases, air molecules can be considered for most calculations as having an average diameter of 0.37 nm (0.00037 µm). In comparison, aerosol particles are generally 1 nm (0.001 µm) in diameter or larger. Fume particles of this size can be seen only immediately upon condensation from the vapor state. A short time later, the high concentration of these very small particles causes coagulation into larger entities, ultimately reaching sizes near 1 µm.

Conversely, dust particles result from size reduction of larger materials. Generally, one considers particles less than 100 µm (0.1 mm) in diameter to stay airborne long enough to be observed and measured as aerosols. For example, human hairs range from about 50 to about 100 µm in diameter. If they were cut into small pieces and released into the air, they would be near the upper limit of the aerosol size range. Size reduction of bulk material by mechanical forces, be they natural or induced by human action, can occur only for sizes where the externally applied forces are greater than the internal cohesion forces. Particles smaller than about 0.5 µm are relatively rare in dust distributions for this reason.

PARTICLE SUSPENSIONS

Because an aerosol is a system of airborne particles suspended in a gas medium, one generally considers the gas properties and flow dynamics first and then evaluates how individual particles follow or deviate from the gas motion. The difference in trajectories between particles and gas molecules is the basis for many aerosol particle size measurement techniques. It is also the basis for many devices controlling aerosol contaminants and for techniques manipulating aerosol particles for manufacturing purposes. Changes in gas properties generally affect the particle trajectories.

As an example, one may appreciate the need for dealing with air flow characteristics first by asking how much aerosol deposition will occur 50 km from an aerosol-emitting power plant. The wind velocity determines the speed with which the aerosol is transported away from the power plant. Large particles gravitationally settling in a shorter time than is available for transport to the 50 km distant site will not be found at the receptor site. The mechanism of settling and dispersion is determined by the degree and mode of turbulence. Returning to aerosol measurement principles, a commonly used instrument, the horizontal elutriator, size-selectively removes particles in a horizontal flow channel. Here, the gas flow is generally "well behaved" by the careful avoidance of air turbulence.

INSTRUMENT CONSIDERATIONS

In general, one cannot obtain particle size information on the entire 5 decade size range of 0.001 to 100 µm with a single instrument. On a macroscopic scale, this would be equivalent to measuring a 1 mm distance with a small scale and then using the same scale for measuring a 1 km distance (which is six orders of magnitude larger than 1 mm). When sensing with optical techniques utilizing white light, the wavelength of visible light from about 0.4 to 0.7 µm limits the observation of particles to about this size range and larger. Inertial techniques become inefficient below about 0.5 µm at normal temperature and pressure. In an electron microscope, the observational tool is electromagnetic radiation (electrons) with a much smaller wavelength that can "see" much smaller particles. Therefore, one expects to apply different instrumental techniques, measuring different size parameters, for submicrometer- versus supermicrometer-sized aerosols.

Most aerosol sizing instruments effectively measure over a size range no larger than $1^1/_2$ orders of magnitude. Thus, the largest measurable size may be about 50 times the smallest measurable size for a given instrument. Because most of the size parameters measured relate to the particle surface, volume, or mass, this size range corresponds to a surface range of 2500 and a volume or mass range of 125,000. Instruments measuring a cumulative value (e.g., total mass or number) can cover a wider size range. Preferably, each aerosol sizing instrument should give a monotonically increasing response to increases in particle size. Unfortunately, some optical devices may detect the same amount of scattered light for more than one particle size, resulting in significant loss of size resolution.

When a single-source aerosol is measured by any of the above-mentioned size parameters, the representative particle size is usually quoted as the *mean size* (average of all sizes), *median size* (equal number of particles above and below this size), or the *mode* (size with the maximum number of particles). The spread of the particle size distribution is characterized by an *arithmetic* or *geometric* (logarithmic) *standard deviation*. Typically, the particle size distribution is *lognormal*, that is, the particle concentration versus particle size curve looks *normal* (also referred to as *bell-shaped* or *Gaussian*) when the particle size is plotted on a logarithmic scale (see Chapters 6 and 22).

The reason for the use of this logarithmic or geometric size scale can be conceptualized by breaking a piece of blackboard chalk. For example, a 64 mm long piece of chalk would break up into two pieces of 32 mm length each. Subsequent breakup yields pieces of 16, 8, 4, 2, and 1 mm, and so forth, length until the internal forces resist further breakage. The ratio of adjacent sizes is always two, thus appearing at the same linear distance on a logarithmic or geometric size scale. Because with each breakage step more and more particles are produced, the distribution is skewed so that there are many more small particles than large ones. This exercise of breaking up a piece of chalk mimics the way many natural and manmade forces generate aerosols. Generally, aerosol particle sizes therefore are plotted on a logarithmic size scale.

Many aerosols measured in ambient or industrial air environments or in industrial process streams are a mixture of aerosols, resulting in more than one particle mode and covering a wide size range. This may make the measurement and analysis of the aerosols considerably more complex. In general, one should attempt to first identify all aerosol sources and decide what information is needed and for what purpose. This decision will then point the way to the best available instrument to reach the desired objective.

Aerosol instruments not only differ by the size parameter that they measure, but each size parameter may "weigh" the particle size differently. A grocery store analogy can help elucidate this concept. If 10 large apples and 100 small raisins are purchased, the median size by *number count* is somewhat larger than the size of the raisins. The median is close to that of the raisins because the median size divides the "population" in two, but in this case most of the "population" consists of small raisins. If each piece of fruit is weighed on a scale, the weight of the apples dominates, and the median size "by mass" is considerably larger. Thus, aerosol measurement "by mass" results in a larger median size than aerosol measurement "by count," although the same particle size distribution is measured. Therefore, any size result should be accompanied by a description of the *weighing factor*, or the *weighting* as it is commonly called.

If many particles in an aerosol are measured and the particles are grouped into discrete, contiguous, size bins, the size distribution can be represented by plotting particle number versus size. The lower and upper particle diameter limits, d_l and d_u, of each size bin need to be chosen with some care in order to get a useful description of the overall size distribution. The number of particles in each bin will depend on the size of the bin, that is $d_u - d_l$. To remove this bin width dependence, the number of particles in each bin is usually normalized by dividing the number of particles in the bin by the bin width. Size distribution properties are discussed further in Chapters 6, 7, and 22.

PARTICLE SHAPE MEASUREMENT

Traditionally, particle shape has been acknowledged by including a *shape factor* in the particle motion equations. For a nonspherical particle, inclusion of this factor in the equation allows one to calculate the desired parameter while characterizing complex particle shapes by a single dimension. Although this provides an indication of the particle's behavior under certain conditions, it does not provide sufficient detail to fully characterize the particle. For instance, the particle's reactivity is a sensitive function of the particle's surface, and often the shape and texture provide clues as to the particle's formation and history. Because powerful computers are now available, image analysis methods will be described that characterize the shape more directly. It is generally difficult to measure the shape of all particles in an aerosol; therefore, careful measurements on a few particles are often assumed representative of the entire aerosol.

A variety of schemes have been developed to measure the outline shape and detailed texture of particles. Simple shapes, such as spheres (droplets) and rods (simple fibers), can be completely described by one or two dimensions, respectively. More complex shapes are difficult to characterize. For instance, measuring the distance of the particle perimeter from the particle centroid and analyzing this distance as a function of angle using Fourier analysis has been proposed as a classification scheme for particle shapes (Beddow et al., 1977). A number of similar shape description techniques have also been described (Kaye, 1981). However such techniques are generally limited to the outline profile of a particle and cannot characterize all the surface complexities and convolutions of many particles.

If a particle were a long, straight chain, it might be characterized as a one-dimensional object having primarily length. Complex branching, however, causes the particle to take up more space than a linear object while not meeting the criteria for a sheet-like (two-dimensional) or a spheroidal (three-dimensional) object. It can, however, be characterized by assigning it a fractional, or *fractal*, dimension. The term *fractal* was coined by Mandelbrot (1983) and has found use in a wide range of applications, including particle shape, turbulence, lung structure, and fibrous filter structure (Kaye, 1989). The principal characteristic of a fractal object is that a measure of complexity is similar on several measurement scales. For instance, if one looks at a fume particle at several different magnifications, the variation, or complexity, may appear very similar. This property of similar complexity at several scales, or scale invariance, is described by the mathematical concept of self-similarity. In Figure 3–2, an agglomerate is presented at several

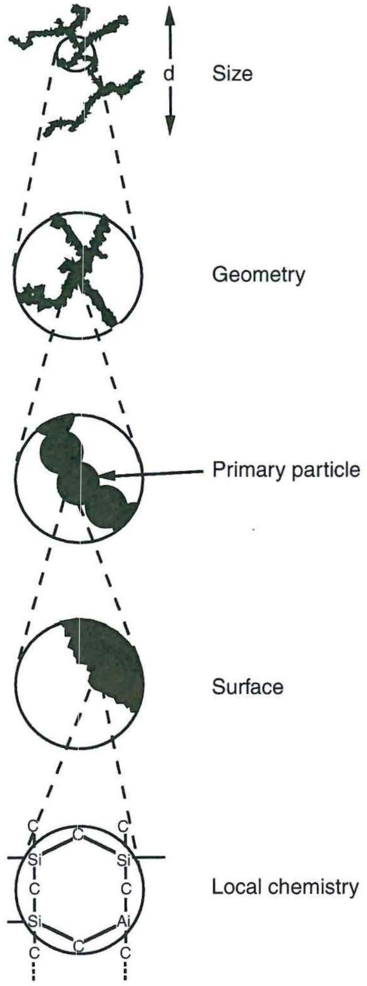

Fig. 3–2. Schematic structure of an agglomerate in two-dimensional space. Scanning down the figure corresponds to viewing the particle at ever higher magnification. (Adapted from Schaefer and Hurd, 1990.)

scales. Generally, self-similarity only occurs between the first and third scales from the top.

The observed shape of a particle is the result of its history. The fume particle, for instance, begins as a vapor condensing into spherules. The spherules, being very small, diffuse rapidly and coagulate into branched chains, as, for example, the zinc oxide fume particle in Figure 3–3. As the chains increase in size and the number of individual spherules in the neighborhood decreases, the chains may intercept one another and form larger agglomerates. Such an agglomerate might be observed at several magnifications, ranging from the structure of the entire particle down to the chemical structure of the surface. Thus, at lowest magnifications, the complex structure can be represented by a fractal dimension; at an intermediate magnification, the spherules have nearly integral dimension; at higher magnification still, the spherule surface may be rough and characterized by another fractal dimension. Fractal and other nonspherical particles are discussed further in Chapter 23.

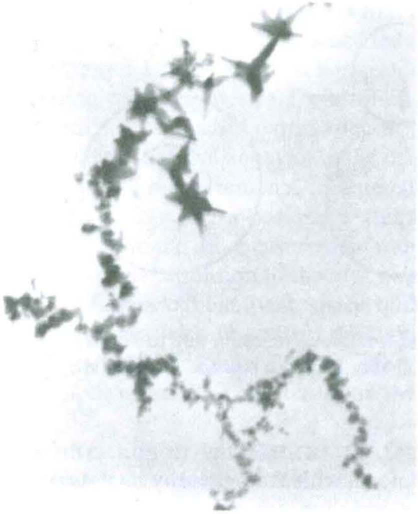

Fig. 3–3. A typical fume particle is an agglomerate of smaller particles formed from condensed vapor. This is a zinc oxide fume particle indicating condensation components with different levels of crystallization.

PARTICLE FORCES

The intra- and interparticle forces that hold particles together or to a surface, and the forces that detach particles from each other or from a surface, are difficult to quantitate for use by the practitioner. These forces may depend on particle bulk and surface parameters (size, shape, roughness, chemistry), the properties of the surrounding gas (temperature, humidity) and the mechanics of the contacting particles (relative particle velocity, contact time). These forces will, therefore, be described qualitatively.

When particles are subjected to an external force, such as gravity or an electrical force, the particles will move in the force field. The migration velocity in the force field is particle-size dependent, a fact that is exploited by most aerosol-sized spectrometers for particle size discrimination.

Adhesion Forces

In contrast to gas molecules, aerosol particles that contact one another generally adhere to each other and form agglomerates. If they contact a surface, such as a filter or any other particle collection device, they are assumed to adhere to the surface (i.e., particle adhesion is the working hypothesis of these devices).

The London–van der Waals forces, which are attractive in nature, act over very short distances relative to particle dimensions (Friedlander, 1977: 44). According to the theory of their origin, random motion of the electrons in an electrically neutral material creates instantaneous dipoles that may induce complementary dipoles in neighboring material and thus attract the surfaces to each other.

Most particles 0.1 µm or larger carry some small net charge that exerts an attractive force in the presence of a particle with an opposite charge (Hinds, 1999: 143). For two charged particles (point charges), this force is inversely proportional to the square of the separation distance. After two surfaces have made contact with each other by either or both of the above

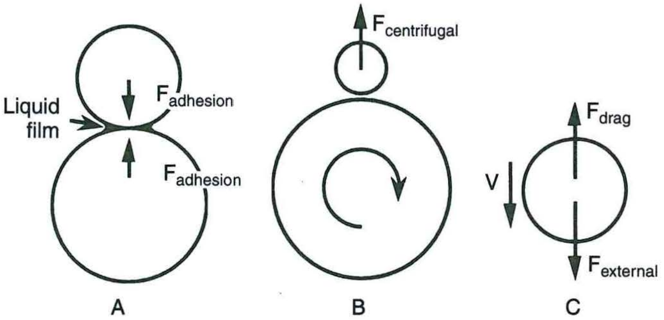

Fig. 3–4. Examples of particle forces. **A**, Adhesion due to liquid film. **B**, Detachment due to centrifugal force. **C**, Particle motion at velocity *V* due to balance between drag force and an external force.

forces, the surfaces may deform with time, thereby increasing the contact area and decreasing the separation distance and thus increasing the force of adhesion.

Figure 3–4A exemplifies how air humidity may affect particle adhesion. At high humidity, liquid molecules are adsorbed on the particle surface and fill the capillary spaces at and near the point of contact. The surface tension of this liquid layer increases the adhesion between the two surfaces.

Detachment Forces and Particle Bounce

Figure 3–4B exemplifies the detachment of a particle from a rotating body. The centrifugal force is proportional to the particle's mass or volume, that is, particle diameter cubed (d^3). Detachment by other types of motion, such as vibration, is similarly proportional to d^3, while detachment by air currents is proportional to the exposed surface area, that is, d^2. In contrast, most adhesion forces are linearly dependent on particle diameter. Thus, large particles are more readily detached than small ones. While individual particles less than 10 µm are not likely to be easily removed (e.g., by vibration), a thick layer of such particles may be easily dislodged in large (0.1 to 10 mm) chunks (Hinds 1999: 144). Re-entrainment of particles from a surface into an aerosol flow may, therefore, create measurement problems after a significant number of particles has been deposited from the aerosol.

If an aerosol flow is directed toward a surface (e.g., in filters and impactors), particles with sufficient inertia will deviate from the air stream lines and move toward the surface. Liquid and sticky small particles will deposit on the surface. Upon contact, a solid particle and the surface may deform. If the rebound energy is greater than the adhesion energy, a condition that may occur for sufficiently high-impact velocity, a solid particle will "bounce," that is, move away after contact with the surface. On contact with the surface, some or all of the particle's kinetic energy is converted to thermal energy, resulting in reduced kinetic energy on rebound or heating of the particle–surface interface on sticking, respectively. Grease or oil on the surface will generally increase the likelihood of adhesion, but, after a layer of particles has been deposited, the incoming particles may bounce from the top surface of the previously deposited particles. Particle adhesion on impact is an especially critical factor in inertial collection devices, as indicated in Chapter 10.

Externally Applied Forces

When an airborne particle is subjected to an externally applied force (e.g., gravity), it will be moved by that force. Opposing this external force is the aerodynamic drag force, as shown in Figure 3–4C. When the two forces are in equilibrium, which happens almost instantaneously (there is a very short relaxation time, having consequences that are discussed later), the particle moves in the force field with migration velocity V. Knowledge of the two opposing forces allows determination of this velocity. Particle velocity is important for estimating collection on surfaces as well as for separating particles by size. Quite often, aerosol measurements are designed to simulate some natural process, such as particle deposition in the respiratory system. Thus, it is important to understand the aerosol behavior in the original system as well as in the instrument in order to make accurate measurements. Instrumental techniques based on the forces involved in the original process (e.g., gravitational settling and diffusion as in particle deposition in the respiratory system) make the measurement more useful and relevant.

In space, astronauts must pay special attention to the dust generated by their clothing and the activities they engage in. Otherwise, their living space quickly becomes polluted with aerosols. On earth, gravity has a major cleaning effect on ambient and industrial aerosols. Larger particles tend to settle out more rapidly. Because the gravitational force is readily accessible for measurement applications, it is the basis for the definition of aerodynamic diameter.

We are familiar with the attraction of lint particles to clothing. This is due to charge differences between the lint and the clothing. Similarly, charged aerosol particles can be attracted to or repelled from charged surfaces or other particles. Few particles carry no charge, although the magnitude of charge can vary greatly. Particles that are freshly aerosolized tend to carry greater charge levels than particles that have been airborne for hours or longer. This aging effect is due to the attraction of oppositely charged airborne ions produced by natural radiation. For aerosol particles that are highly charged, the electric force may exceed the gravitational force by several orders of magnitude. This readily generated force can be used for air cleaning as well as particle separation and measurement, for example, with electrical mobility analyzers (see Chapter 18).

If there is a gradient in the number of particles present in the air, a diffusion force can be defined that moves the particles from the high concentration to the low concentration environment. It is often the dominant motive force for particles smaller than about 0.2 μm diameter. The diffusion battery, for example, is commonly used for measuring submicrometer particles. Diffusion is also important for understanding the particle and gas deposition properties of the human lung. If the suspending gas is a nonuniform mixture of gases, the particles also may be moved by diffusiophoretic forces caused by the concentration gradient of the gas components (see Chapter 19).

Inertial forces can be applied to particles by forcing the suspending air to change direction. Size-dependent inertial effects are used for particle separation, collection, and measurement in such devices as impactors, cyclones, and acceleration nozzles (see Chapters 10, 13, and 17). Impaction is an important mechanism for particle deposition in the respiratory system (see Chapter 25).

If there is a temperature gradient in the aerosol-containing space between two surfaces, the higher activity of the air molecules near the hot surface pushes the particles toward the colder surface (thermophoretic force). This property is exploited in the thermal precipitator, which is used to collect particles onto a desired surface (see Chapter 10). A special case of thermophoresis, but generally not very useful as a measurement tool, is produced by light. Illumination of a particle heats up one side of the particle as well as gas molecules nearby that push the particle toward the colder side. Illumination can also produce radiation pressure whereby the stream of photons exerts a force on the particle (photophoresis). A focused laser beam can been used as optical "tweezers" to move small particles (e.g., bacteria) in a liquid.

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