

## SEVEN

### Properties of Aerosols

With this chapter we begin the study of aerosols. An aerosol consists, roughly speaking, of a dilute suspension of relatively immobile, relative massive particles in air. Table 7.1 presents a comparison of the relative size, mass, and concentration of gas molecules (e.g.,  $N_2$ ) and aerosols. This chapter is devoted to ways of characterizing aerosol size distributions and to typical atmospheric size distributions. Its object is to gain familiarity with aerosol size distribution data and their manipulation. Subsequent chapters will deal with the mechanics of single aerosol particles, the formation of aerosols by nucleation, and the behavior of aerosol populations.

#### 7.1. THE SIZE DISTRIBUTION FUNCTION

An aerosol can be envisioned as a population of particles each consisting of an integral number of molecules or monomers. The smallest aerosol particle could be defined in principle as that containing two molecules or two monomers. The population can then be characterized by the concentrations of each cluster; that is,  $N_k$  = concentration (per  $cm^3$  of air) of particles containing  $k$  molecules. While rigorously correct, this "discrete" way of characterizing the distribution quickly becomes unwieldy because of the very large number of molecules that go to make up even the smallest of aerosol particles. For example, a sulfuric acid/water particle at equilibrium at 30 percent relative humidity of  $0.01 \mu m$  diameter consists of approximately  $10^4$  molecules of sulfuric acid.

Beyond a relatively small number of molecules, say about 100, an aerosol population can be treated as if its size variation is essentially continuous. In doing so, we replace the discrete size index  $k$  by the particle diameter  $D_p$  and the discrete number concentration  $N_k$  by the size distribution function  $n(D_p)$ , defined as follows:

$$n(D_p) dD_p = \text{number of particles per } cm^3 \text{ of air having diameters in the range } D_p \text{ to } D_p + dD_p$$

TABLE 7.1. Size, Mass, and Concentration of Aerosol Particles Relative to Gas Molecules

	Diameter	Mass	Concentration
Gas molecules (e.g., N <sub>2</sub> )	0.00038 μm (= 3.8 Å)	4.6 × 10 <sup>-23</sup> g	≈ 10 <sup>19</sup> cm <sup>-3</sup>
Aerosols	0.01 to 10 μm	10 <sup>-18</sup> g to 10 <sup>-9</sup> g	< 10 <sup>8</sup> cm <sup>-3</sup>

The total number of particles per cm<sup>3</sup> of air of all sizes is then just

$$N = \int_0^{\infty} n(D_p) dD_p \quad (7.1)$$

From the viewpoint of probability theory,  $n(D_p)$  is the probability density function for particle size. Thus, a more precise term for  $n(D_p)$  is a size distribution density function, although the word "density" is usually omitted in describing  $n(D_p)$ . The units of  $n(D_p)$  are  $\mu\text{m}^{-1} \text{cm}^{-3}$ , and those of  $N$  are  $\text{cm}^{-3}$ . If the aerosol population is changing with time then we may write  $n(D_p, t)$  and  $N(t)$ . Similarly, if there is a spatial variation,  $n$  can be expressed as  $n(D_p; x, y, z, t)$  and  $N$  as  $N(x, y, z, t)$ .

We can define a normalized size distribution function  $\tilde{n}(D_p)$  by  $\tilde{n}(D_p) = n(D_p)/N$ , such that  $\tilde{n}(D_p) dD_p =$  the fraction of the total number of particles per cm<sup>3</sup> of air having diameters in the range  $D_p$  to  $D_p + dD_p$ . The units of  $\tilde{n}(D_p)$  are  $\mu\text{m}^{-1}$ .

It is often of interest to know the distributions of both particle surface area and volume with respect to particle size. Considering all particles as spheres, we define the surface area distribution function as

$$n_s(D_p) = \pi D_p^2 n(D_p) \quad (\mu\text{m}^2 \mu\text{m}^{-1} \text{cm}^{-3}) \quad (7.2)$$

and the volume distribution function as

$$n_v(D_p) = \frac{\pi}{6} D_p^3 n(D_p) \quad (\mu\text{m}^3 \mu\text{m}^{-1} \text{cm}^{-3}) \quad (7.3)$$

The total particle surface area and volume per cm<sup>3</sup> of air are

$$S = \pi \int_0^{\infty} D_p^2 n(D_p) dD_p = \int_0^{\infty} n_s(D_p) dD_p \quad (\mu\text{m}^2 \text{cm}^{-3}) \quad (7.4)$$

$$V = \frac{\pi}{6} \int_0^{\infty} D_p^3 n(D_p) dD_p = \int_0^{\infty} n_v(D_p) dD_p \quad (\mu\text{m}^3 \text{cm}^{-3}) \quad (7.5)$$

Normalized surface area and volume distributions can then be defined by  $\tilde{n}_s(D_p) = n_s(D_p)/S$  ( $\mu\text{m}^{-1}$ ) and  $\tilde{n}_v(D_p) = n_v(D_p)/V$  ( $\mu\text{m}^{-1}$ ).

If the particles all have density  $\rho_p$  ( $\text{g cm}^{-3}$ ) then the distribution of particle mass with respect to particle size is

$$n_m(D_p) = \left(\frac{\rho_p}{10^6}\right) \left(\frac{\pi}{6}\right) D_p^3 n(D_p) = \frac{\rho_p}{10^6} n_v(D_p) (\mu\text{g } \mu\text{m}^{-1} \text{cm}^{-3}) \quad (7.6)$$

where the factor of  $10^6$  is needed to convert  $\rho_p$  from  $\text{g cm}^{-3}$  to  $\mu\text{g } \mu\text{m}^{-3}$ , to maintain the units of  $n_m(D_p)$  as  $\mu\text{g } \mu\text{m}^{-1} \text{cm}^{-3}$ .

Because particle diameters in an aerosol population typically vary over several orders of magnitude, it is often convenient to express the size distribution in terms of the logarithm of the diameter, either  $\ln D_p$  or  $\log D_p$ .

### 7.1.1. Distributions Based on $\log D_p$

Let us define  $n(\log D_p) d \log D_p =$  number of particles per  $\text{cm}^3$  of air in the size range  $\log D_p$  to  $\log D_p + d \log D_p$ . Note that  $n(\log D_p)$  is *not* the same function as  $n(D_p)$ . Rather than introduce new notation for  $n(\log D_p)$  to differentiate it from  $n(D_p)$ , we will always indicate the independent variable, either  $D_p$  or  $\log D_p$ . Formally we cannot take the logarithm of a dimensional quantity. Thus, when we write  $\log D_p$  we must think of it as  $\log(D_p/1)$ , where the "reference" particle diameter is  $1 \mu\text{m}$  and is thus not explicitly indicated. The units of  $n(\log D_p)$  are  $\text{cm}^{-3}$  since  $\log D_p$  is dimensionless. The total number concentration of particles is

$$N = \int_{-\infty}^{\infty} n(\log D_p) d \log D_p (\text{cm}^{-3}) \quad (7.7)$$

and the normalized size distribution function with respect to  $\log D_p$  is  $\tilde{n}(\log D_p) = n(\log D_p)/N$ , which is dimensionless. Note that the limits of integration in Eq. (7.7) are now  $-\infty$  to  $\infty$ .

Just as we defined surface area and volume distributions with respect to  $D_p$  we can do so with respect to  $\log D_p$ ,

$$n_s(\log D_p) = \pi D_p^2 n(\log D_p) (\mu\text{m}^2 \text{cm}^{-3}) \quad (7.8)$$

$$n_v(\log D_p) = \frac{\pi}{6} D_p^3 n(\log D_p) (\mu\text{m}^3 \text{cm}^{-3}) \quad (7.9)$$

with

$$S = \int_{-\infty}^{\infty} \pi D_p^2 n(\log D_p) d \log D_p = \int_{-\infty}^{\infty} n_s(\log D_p) d \log D_p \quad (7.10)$$

$$V = \int_{-\infty}^{\infty} \frac{\pi}{6} D_p^3 n(\log D_p) d \log D_p = \int_{-\infty}^{\infty} n_v(\log D_p) d \log D_p \quad (7.11)$$

Since  $n(D_p) dD_p$  = the differential number of particles in the size range  $D_p$  to  $D_p + dD_p$ , this quantity is sometimes expressed as  $dN$ , with similar notation for the other distributions. Thus, using this notation we have:

$$dN = n(D_p) dD_p = n(\log D_p) d \log D_p \quad (7.12)$$

$$dS = n_s(D_p) dD_p = n_s(\log D_p) d \log D_p \quad (7.13)$$

$$dV = n_v(D_p) dD_p = n_v(\log D_p) d \log D_p \quad (7.14)$$

Based on this notation, the various size distribution functions are often written as

$$n(D_p) = \frac{dN}{dD_p} \quad \tilde{n}(D_p) = \frac{dN}{N dD_p}$$

$$n(\log D_p) = \frac{dN}{d \log D_p} \quad \tilde{n}(\log D_p) = \frac{dN}{N d \log D_p}$$

$$n_s(D_p) = \frac{dS}{dD_p} \quad \tilde{n}_s(D_p) = \frac{dS}{S dD_p}$$

$$n_s(\log D_p) = \frac{dS}{d \log D_p} \quad \tilde{n}_s(\log D_p) = \frac{dS}{S d \log D_p}$$

$$n_v(D_p) = \frac{dV}{dD_p} \quad \tilde{n}_v(D_p) = \frac{dV}{V dD_p}$$

$$n_v(\log D_p) = \frac{dV}{d \log D_p} \quad \tilde{n}_v(\log D_p) = \frac{dV}{V d \log D_p}$$

To conform with the common notation we will often express the distributions in this manner.

### 7.1.2. Relating Size Distributions Based on Different Independent Variables

It is important for us to be able to relate a size distribution based on one independent variable, say  $D_p$ , to one based on another independent variable, say  $\log D_p$ . The basis for such relationship is Eq. (7.12). In a particular incremental particle size range  $D_p$  to  $D_p + dD_p$  the number of particles  $dN$  is a certain quantity, and that quantity is the same regardless of how the size distribution function is expressed. Thus, in the particular case of  $n(D_p)$  and  $n(\log D_p)$  we have that

$$n(D_p) dD_p = n(\log D_p) d \log D_p \quad (7.15)$$

Say we have  $n(D_p)$  and wish to calculate  $n(\log D_p)$  from it. Thus,

$$n(\log D_p) = n(D_p) \frac{dD_p}{d \log D_p} \quad (7.16)$$

Now, since  $d \log D_p = d \ln D_p / 2.303 = dD_p / 2.303 D_p$ , Eq. (7.16) becomes

$$n(\log D_p) = 2.303 D_p n(D_p) \quad (7.17)$$

which is the desired relationship between  $n(D_p)$  and  $n(\log D_p)$ .

This procedure can be generalized to relate any two size distribution functions  $n(u)$  and  $n(v)$  where  $u$  and  $v$  are both related to diameter  $D_p$ . The generalization of Eq. (7.15) is

$$n(u) du = n(v) dv \quad (7.18)$$

and if we seek to calculate  $n(u)$  in terms of  $n(v)$ , we write

$$n(u) = n(v) \frac{dv/dD_p}{du/dD_p} \quad (7.19)$$

## 7.2. PROPERTIES OF SIZE DISTRIBUTIONS

Given an aerosol size distribution, represented either in discrete form as  $N_k$ , or in continuous form as  $n(D_p)$ , it is of interest to be able to compute certain properties of the distribution. Those properties of interest are the so-called *moments* of the distribution, and the two moments of most interest are the mean and the variance.

To define these moments in terms of size distributions, let us assume first that we have a discrete distribution given as  $N_k$ ,  $k = 1, 2, \dots, M$ . We recall that  $N_k$  is the number concentration ( $\text{cm}^{-3}$ ) of particles containing  $k$  mole-

cules. The mean number of molecules in the population  $\bar{k}$  is given by

$$\bar{k} = \frac{\sum_{k=1}^M k N_k}{\sum_{k=1}^M N_k} \quad (7.20)$$

and the variance, a measure of the spread of the distribution around the mean size  $\bar{k}$ , is given by

$$\sigma^2 = \frac{\sum_{k=1}^M (k - \bar{k})^2 N_k}{\sum_{k=1}^M N_k} \quad (7.21)$$

A value of  $\sigma^2$  equal to zero would mean that every one of the particles in the distribution is precisely of size  $\bar{k}$ . An increasing  $\sigma^2$  indicates that the spread of the distribution about  $\bar{k}$  is increasing.

We will deal most frequently with aerosol size distributions expressed in continuous form. Given the size distribution  $n(D_p)$ , the mean particle diameter of the distribution is defined by

$$\begin{aligned} \bar{D}_p &= \frac{\int_0^\infty D_p n(D_p) dD_p}{\int_0^\infty n(D_p) dD_p} \\ &= \frac{1}{N} \int_0^\infty D_p n(D_p) dD_p \end{aligned} \quad (7.22)$$

The variance of the distribution is

$$\begin{aligned} \sigma^2 &= \frac{\int_0^\infty (D_p - \bar{D}_p)^2 n(D_p) dD_p}{\int_0^\infty n(D_p) dD_p} \\ &= \frac{1}{N} \int_0^\infty (D_p - \bar{D}_p)^2 n(D_p) dD_p \end{aligned} \quad (7.23)$$

Some other properties of a distribution that might be of interest are the mean surface area and mean volume,

$$\bar{S} = \frac{1}{N} \int_0^\infty \pi D_p^2 n(D_p) dD_p = \frac{1}{N} \int_0^\infty n_s(D_p) dD_p \quad (7.24)$$

$$\bar{V} = \frac{1}{N} \int_0^\infty \frac{\pi}{6} D_p^3 n(D_p) dD_p = \frac{1}{N} \int_0^\infty n_v(D_p) dD_p \quad (7.25)$$

Table 7.2 presents a number of other mean values of importance in characterizing an aerosol size distribution.

TABLE 7.2. Mean Values of Importance in Characterizing an Aerosol Size Distribution

Property	Defining Relation	Description
Number mean diameter	$\bar{D}_p = \frac{1}{N} \int_0^{\infty} D_p n(D_p) dD_p$	Average diameter of the population
Median diameter	$F(D_p, \text{median}) = \frac{N}{2}$	Diameter below which one-half the particles lie and above which one-half the particles lie
Mode	$\left[ \frac{dn(D_p)}{dD_p} \right]_{D_p, \text{mode}} = 0$	The diameter at which the largest number of particles lie, i.e. the most frequently occurring diameter
Surface area mean diameter	$\begin{aligned} \pi D_{p, \text{avg. surface area}}^2 \\ = \frac{1}{N} \int_0^{\infty} n_s(D_p) dD_p \end{aligned}$	Diameter of that particle whose surface area equals the mean surface area of the population
Volume mean diameter	$\begin{aligned} \frac{\pi}{6} D_{p, \text{avg. volume}}^3 \\ = \frac{1}{N} \int_0^{\infty} n_v(D_p) dD_p \end{aligned}$	Diameter of that particle whose volume equals the mean volume of the population
Surface area median diameter	$\begin{aligned} \int_0^{D_{p, \text{surf. area median}}} n_s(D_p) dD_p \\ = \frac{1}{2} \int_0^{\infty} n_s(D_p) dD_p \end{aligned}$	The diameter below which one-half the particle surface area lies and above which one-half the particle surface area lies
Volume median diameter	$\begin{aligned} \int_0^{D_{p, \text{vol. median}}} n_v(D_p) dD_p \\ = \frac{1}{2} \int_0^{\infty} n_v(D_p) dD_p \end{aligned}$	The diameter below which one-half the particle volume lies and above which one-half the particle volume lies

### 7.3. THE LOG-NORMAL DISTRIBUTION

The next question that arises in our study of aerosol size distributions is: what functions are commonly used to represent aerosol size distributions? To represent particle size distributions  $n(D_p)$  we need a function that is defined only for  $D_p \geq 0$  and which is zero for  $D_p = 0$  (clearly no particles can exist of size zero) and approaches zero as  $D_p \rightarrow \infty$  (no particles can exist with infinite

size). While many distributions with such properties exist, several of which will be given in Chapter 17, a popular one for representing aerosol size distributions, and one with a host of desirable properties is the *log-normal distribution*.

If a quantity  $u$  is normally distributed, the probability density function for  $u$  obeys the Gaussian distribution,

$$n(u) = \frac{N}{(2\pi)^{1/2}\sigma_u} \exp\left[-\frac{(u - \bar{u})^2}{2\sigma_u^2}\right] \quad (7.26)$$

where  $n(u)$  is defined for  $-\infty < u < \infty$ ,  $\bar{u}$  is the mean of the distribution,  $\sigma_u^2$  is its variance, and

$$N = \int_{-\infty}^{\infty} n(u) du \quad (7.27)$$

A quantity that is log-normally distributed has its logarithm governed by a normal distribution. If the quantity of interest is particle diameter  $D_p$ , then saying that an aerosol population is log-normally distributed means that  $u = \ln D_p$  satisfies Eq. (7.26). For now we will use the natural logarithm  $\ln D_p$ ; later we will also express our result in terms of  $\log D_p$ .

Letting  $u = \ln D_p$ , we express Eq. (7.26) as

$$n(\ln D_p) = \frac{N}{(2\pi)^{1/2} \ln \sigma_g} \exp\left[-\frac{(\ln D_p - \ln \bar{D}_{pg})^2}{2 \ln^2 \sigma_g}\right] \quad (7.28)$$

where we have let  $\bar{u} = \ln \bar{D}_{pg}$  and  $\sigma_u = \ln \sigma_g$ . For the moment we will consider  $\bar{D}_{pg}$  and  $\sigma_g$  to be merely the two parameters of the distribution. Shortly we will discuss the physical significance of these parameters. It is more convenient to have the size distribution function expressed in terms of  $D_p$  rather than  $\ln D_p$ . The form of Eq. (7.17) appropriate to this transformation is  $n(\ln D_p) = D_p n(D_p)$ , so that Eq. (7.28) becomes

$$n(D_p) = \frac{N}{(2\pi)^{1/2} D_p \ln \sigma_g} \exp\left[-\frac{(\ln D_p - \ln \bar{D}_{pg})^2}{2 \ln^2 \sigma_g}\right] \quad (7.29)$$

This is the conventional form of the log-normal distribution used in describing aerosol size distributions.

We now wish to examine the physical significance of the two parameters  $\bar{D}_{pg}$  and  $\sigma_g$ . To do so let us examine for the moment some properties of the normal distribution Eq. (7.26). The cumulative distribution function  $F(u)$  is the probability that  $u$  will lie in the range  $-\infty$  to  $u$ ,

$$F(u) = \int_{-\infty}^u n(u') du' \quad (7.30)$$



Let us calculate the mean diameter  $\bar{D}_p$  of a log-normally distributed aerosol. By definition, the mean diameter is found from

$$\bar{D}_p = \frac{1}{N} \int_0^\infty D_p n(D_p) dD_p \quad (7.37)$$

which we wish to evaluate in the case of  $n(D_p)$  given by Eq. (7.29). In evaluating the integral it is useful to let  $u = \ln D_p$ , in which case Eq. (7.37) becomes

$$\bar{D}_p = \frac{1}{\sqrt{2\pi}\sigma_u} \int_{-\infty}^{\infty} \exp(u) \exp\left[-\frac{(u - \bar{u})^2}{2\sigma_u^2}\right] du \quad (7.38)$$

By expanding the exponent in the integral and completing the square, we obtain

$$\bar{D}_p = \frac{1}{\sqrt{2\pi}} e^{\bar{u}} e^{\sigma_u^2/2} \int_{-\infty}^{\infty} \exp\left[-\frac{(u - (\bar{u} + \sigma_u^2))^2}{2\sigma_u^2}\right] \frac{du}{\sigma_u} \quad (7.39)$$

To evaluate the integral we let  $t = (u - (\bar{u} + \sigma_u^2))/\sqrt{2}\sigma_u$  and we get

$$\bar{D}_p = \frac{1}{\sqrt{\pi}} e^{\bar{u}} e^{\sigma_u^2/2} \int_{-\infty}^{\infty} e^{-t^2} dt \quad (7.40)$$

and since the integral equals  $\sqrt{\pi}$ , the final result is

$$\begin{aligned} \bar{D}_p &= e^{\bar{u}} e^{\sigma_u^2/2} \\ &= \bar{D}_{pg} \exp(\ln^2 \sigma_g / 2) \end{aligned} \quad (7.41)$$

We see that the mean diameter of a log-normal distribution depends on both  $\bar{D}_{pg}$  and  $\sigma_g$ .

### 7.3.1. Plotting the Log-Normal Distribution

The log-normal distribution has the useful property that when the cumulative distribution function is plotted against the logarithm of particle diameter on special graph paper with one axis scaled according to the error function of Eq. (7.35), so-called log-probability paper, a straight line results. The point at which  $F(D_p) = 0.5$  occurs when  $\ln D_p = \ln \bar{D}_{pg}$ . The point at  $F(D_p) = 0.84$  occurs for  $\ln D_p = \ln \bar{D}_{pg} + \ln \sigma_g$  or  $D_p = \bar{D}_{pg} \sigma_g$ . The geometric mean or median is the value of  $D_p$  where the straight line plot of  $F$  crosses the 50th percentile. The slope of the line is related to the geometric standard deviation  $\sigma_g$  which

By letting  $D_p^\gamma = \exp(\gamma \ln D_p)$ , expanding the exponential and completing the square in the exponent, Eq. (7.43) becomes

$$n_\gamma(D_p) = \frac{N}{(2\pi)^{1/2} D_p \ln \sigma_g} \exp \left[ \gamma \ln \bar{D}_{pg} + \frac{\gamma^2}{2} \ln^2 \sigma_g \right] \\ \times \exp \left[ - \frac{(\ln D_p - (\ln \bar{D}_{pg} + \gamma \ln^2 \sigma_g))^2}{2 \ln^2 \sigma_g} \right] \quad (7.44)$$

Thus, we see that if  $n(D_p)$  is log-normal,  $n_\gamma(D_p) = D_p^\gamma n(D_p)$  is also log-normal with the same geometric standard deviation of  $\sigma_g$  as the parent distribution and with the logarithm of the medium diameter given by

$$\ln \bar{D}_{pg\gamma} = \ln \bar{D}_{pg} + \gamma \ln^2 \sigma_g \quad (7.45)$$

Now if we return to Figure 7.1, we note that the surface area and volume distributions are also log-normal (i.e., represented as straight lines), with the same slope (i.e., the same  $\sigma_g$ ) but with median values that are shifted to larger particle sizes in accordance with Eq. (7.45). For the particular distribution shown in Figure 7.1,  $\bar{D}_{pg} = 1.0 \mu\text{m}$  and  $\sigma_g = 2.0$ , the resulting surface area and volume median diameters are approximately  $2.6 \mu\text{m}$  and  $4.2 \mu\text{m}$ , respectively.