

#### 4. CONTINUITY EQUATION FOR AEROSOLS

An aerosol particle is characterized by its shape, size, and chemical composition. Models generally assume that particles are spherical; this is strictly correct only for liquid particles, but for solid particles it can be viewed as an operational approximation (that is, we view the irregularly shaped particle as behaving as a sphere of equivalent radius). One can then characterize the aerosol size distribution by the *number size distribution function*  $n_N(r)$  (particles  $\mu\text{m}^{-1} \text{cm}^{-3}$ ) such that  $n_N(r)dr$  represents the number of particles per  $\text{cm}^3$  of air in the radius size range  $[r, r+dr]$ . Other related measures of the aerosol size distribution are the *surface area size distribution function*  $n_S(r) = 4\pi r^2 n_N(r)$  and the *volume size distribution function*  $n_V(r) = (4/3)\pi r^3 n_N(r)$ . Plots of the aerosol size distribution generally show  $n_N(\log r) = \ln(10) r n_N(r)$ , representing the number of particles in the size range  $[\log r, \log r + d\log r]$ . Similar expressions apply for  $n_S(\log r)$  and  $n_V(\log r)$ . Use of the log scale is convenient to account for the variation of particle sizes over typically 5 orders of magnitude, from  $10^{-3}$  to  $10^2 \mu\text{m}$ . An aerosol composed of particles of a single size is called *monodisperse*, while an aerosol composed of particles of multiple sizes is called *polydisperse*. Aerosols produced in the lab under carefully controlled conditions can approach the monodisperse limit. Aerosols in the atmosphere are polydisperse.

The number size distribution function can be integrated to determine the total number concentration, total mass concentration, and other features of the aerosol over selected size ranges or over the entire size distribution [Seinfeld and Pandis, chapter 7.1]. The chemical composition of the aerosol can be characterized by constructing separate size distribution functions, one for each chemical component of aerosol, and by making assumptions about the mixing of chemical components within individual aerosol particles. Here a “chemical component” refers for example to sulfate, soot, organic, soil dust, or sea salt aerosol. An *external aerosol mixture* is one where there is no mixing between particles of different chemical components, that is, where each individual particle is made up of a single component. An *internal aerosol mixture* is one where there is complete mixing between particles of different chemical components so that all aerosol particles of a given size have the same chemical composition. The true mixing state of the aerosol lies between these two extremes. For computational convenience, models often assume external or internal aerosol mixtures as limiting cases for describing aerosol evolution.

The continuity equation introduced in chapter 1 can be applied to different size classes and chemical components of aerosols in the same way as for gases. The transport operator (chapter 2) is exactly the same, since the particles are sufficiently small that they are advected by the wind in the same way as gases, except that one should add a sink term from gravitational settling in the case of very large particles ( $> 10 \mu\text{m}$  in the troposphere,  $> 1 \mu\text{m}$  in the stratosphere). The chemical operator (chapter 3) is exactly the same if we are only interested in the total mass concentrations of different aerosol chemical components (without regard to their size distributions).

If we are interested in describing the evolution of the aerosol size distribution, however, then we need to introduce specific terms in the continuity equation to account for condensational growth and for coagulation between aerosol particles. For mass accounting purposes it is more convenient to use volume rather than radius as the independent variable to characterize the aerosol size distribution. We thus define a *volume distribution function*  $n_N(v)$  such that  $n_N(v)dv$  represents the number of particles in the volume range  $[v, v+dv]$ . The relationship between  $n_N(v)$  and  $n_N(r)$  can be derived by equating the number of particles in the volume range  $[v, v+dv]$  with that in the equivalent size range  $[r, r+dr]$ :

$$n_N(v)dv = n_N(r)dr \Rightarrow n_N(v) = \frac{dr}{dv} n_N(r) = \frac{1}{4\pi r^2} n_N(r) \quad (4.1)$$

The local evolution of the aerosol size distribution (that is, the equivalent of the chemical operator) can be written as

$$\frac{\partial n_N(v)}{\partial t} = \left[ \frac{\partial n_N(v)}{\partial t} \right]_{\text{condensation/evaporation}} + \left[ \frac{\partial n_N(v)}{\partial t} \right]_{\text{coagulation}} + P - L \quad (4.2)$$

where  $P$  and  $L$  include terms from emissions, deposition, chemical production and loss, and *nucleation* (formation of new particles from the gas phase). The first two terms on the right-hand side describe the evolution of the aerosol size distribution, while the other terms describe sources and sinks of particles.

The condensation/evaporation term can be calculated from knowledge of the *condensation growth rate*  $I(v) = dv/dt$  representing the growth rate ( $\text{cm}^3 \text{s}^{-1}$ ) of particles of volume  $v$ . Consider a volume element  $[v, v+dv]$ . The particles growing into that volume element over time  $dt$  are those that were in the volume element  $[v, v-I(v)dt]$ ; their number concentration  $n_N(v)I(v)dt$ . Similarly, the number concentration of particles growing out of the volume element is  $n(v+dv)I(v+dv)dt$ . Thus the change in the volume distribution function is

$$\left[ \frac{\partial n_N(v)}{\partial t} \right]_{\text{condensation/evaporation}} = -\frac{\partial I(v)n_N(v)}{\partial v} \quad (4.3)$$

The coagulation term is defined by the frequency of collisions between particles (collision usually results in coagulation). We characterize the collision frequency by a *coagulation coefficient*  $\beta(v, v')$  ( $\text{cm}^3 \text{particle}^{-1} \text{s}^{-1}$ ) representing the rate constant at which particles of volume  $v$  collide with particles of volume  $v'$ . In this manner, the rate of production of particles of volume  $(v+v')$  by collision of particles of volume  $v$  and  $v'$  is given by  $\beta(v, v')n_N(v)n_N(v')(dv)^2$ . To determine the change with time in the number concentration of particles in the volume element  $[v, v+dv]$  due to coagulation processes we consider collisions with particles over the entire range of the size distribution and account for both production and loss of particles out of the volume element:

$$\left[ \frac{\partial n_N(v)}{\partial t} \right]_{\text{coagulation}} = \frac{1}{2} \int_0^v \beta(v', v-v') n_N(v') n_N(v-v') dv' - n_N(v) \int_0^\infty \beta(v, v') n_N(v') dv' \quad (4.4)$$

where the  $\frac{1}{2}$  coefficient on the first term of the right-hand side is to avoid double-counting. Replacement of (3.4) and (3.3) into (3.2) yields the continuity equation for aerosols, also called the *general dynamic equation* for aerosols. Physical formulations for  $I(v)$ ,  $\beta(v, v')$ , and for the aerosol nucleation and deposition terms are presented in detail in Seinfeld and Pandis (chapter 12).

The numerical solution to the general dynamic equation for aerosols in atmospheric models is done by either of two approaches, the *sectional method* or the *moments method*. In the sectional method one divides the aerosol size distribution into discrete size bins and discretizes (3.2) over each size bin. This approach can be made as accurate as one likes, but a drawback is that a large number of size bins (of the order of 100) is needed to provide an acceptable resolution of the size distribution extending from  $10^{-3}$  to  $10^{-2}$   $\mu\text{m}$ . An alternate approach is the *moments method*, where one decomposes the size distribution in terms of its *normalized moments*  $M_i$  such that

$$M_i = \frac{\int_0^\infty r^i n_N(r) dr}{\int_0^\infty n_N(r) dr} \quad (4.5)$$

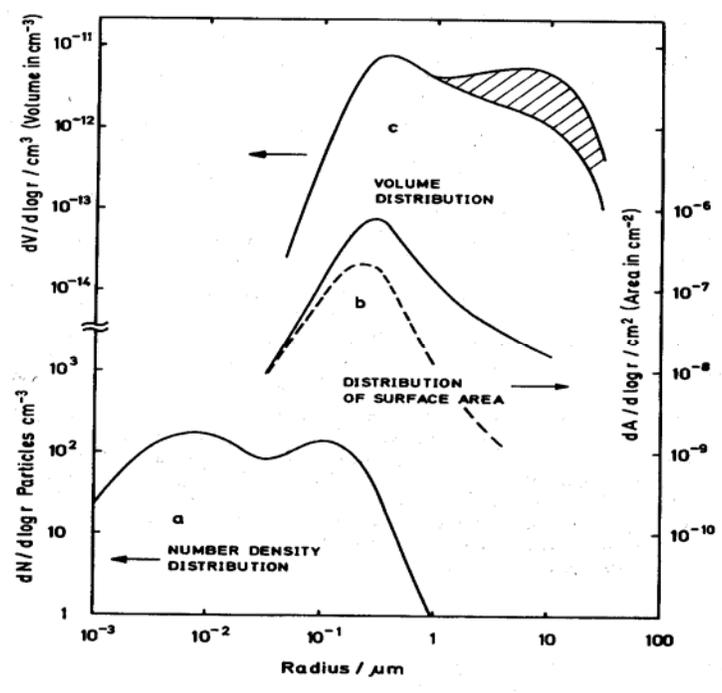
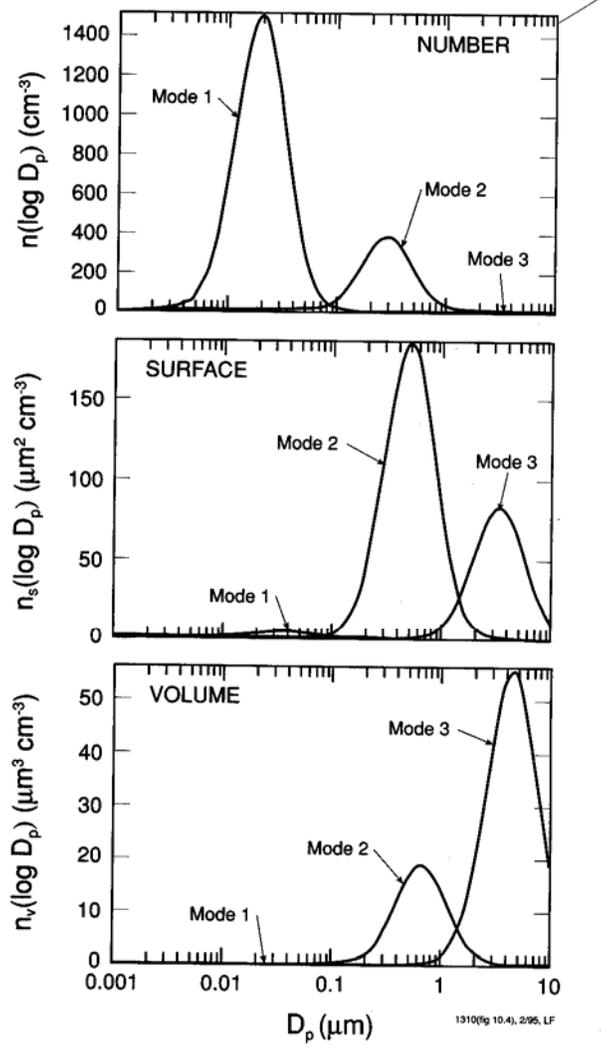
Any size distribution can be decomposed in terms of these normalized moments:

$$n_N(r) = \sum_{i=0}^{\infty} \alpha_i M_i \quad (4.6)$$

where the coefficients  $\alpha_i$  are in units of  $\text{cm}^{-i}$ . For aerosol size distribution functions, which are relatively smooth, one can capture most of the detail with just a few moments. Thus the moments offer a computationally economical representation of the aerosol size distribution in terms of only a few variables. A difficulty, however, is expressing the different terms in equation (3.2) in terms of their moment equivalents. This requires some assumption about the shape of the aerosol size distribution. One generally assumes a *log-normal distribution*, representing the normal distribution of the logarithm of  $(n(r))$ :

$$n_N(\ln(r)) = \frac{N}{(2\pi)^{1/2} \ln \sigma_g} \exp\left[ \frac{-\ln(r/r_g)}{2 \ln^2 \sigma_g} \right] \quad (4.7)$$

where  $N$  is the total number concentration of particles,  $r_g$  is the median radius of the aerosol population, and  $\sigma_g$  is the *geometric standard deviation* of the distribution (such that 67% of the particles lie in the size range  $r_g/\sigma_g$  to  $r_g\sigma_g$ ). For a monodisperse aerosol,  $\sigma_g = 1$ ; for typical log-normal approximations of the atmospheric aerosol,  $\sigma_g$  is in the range 1.5-2. Observed aerosol size distributions can in general be represented fairly well as a sum of lognormal distributions.



**Figure 4.9.** Number, surface area, and volume distributions for a trimodal aerosol; each mode is lognormal with a geometric standard deviation of 1.7. Geometric mean diameters used: Mode 1:  $\overline{D_{pg}} = 0.02 \mu\text{m}$ ; Mode 2:  $\overline{D_{pg}} = 0.3 \mu\text{m}$ ; Mode 3:  $\overline{D_{pg}} = 2 \mu\text{m}$ .

Typical size distribution of marine aerosol, from Warneck [1999]. The contribution from the sea salt component is hatched.