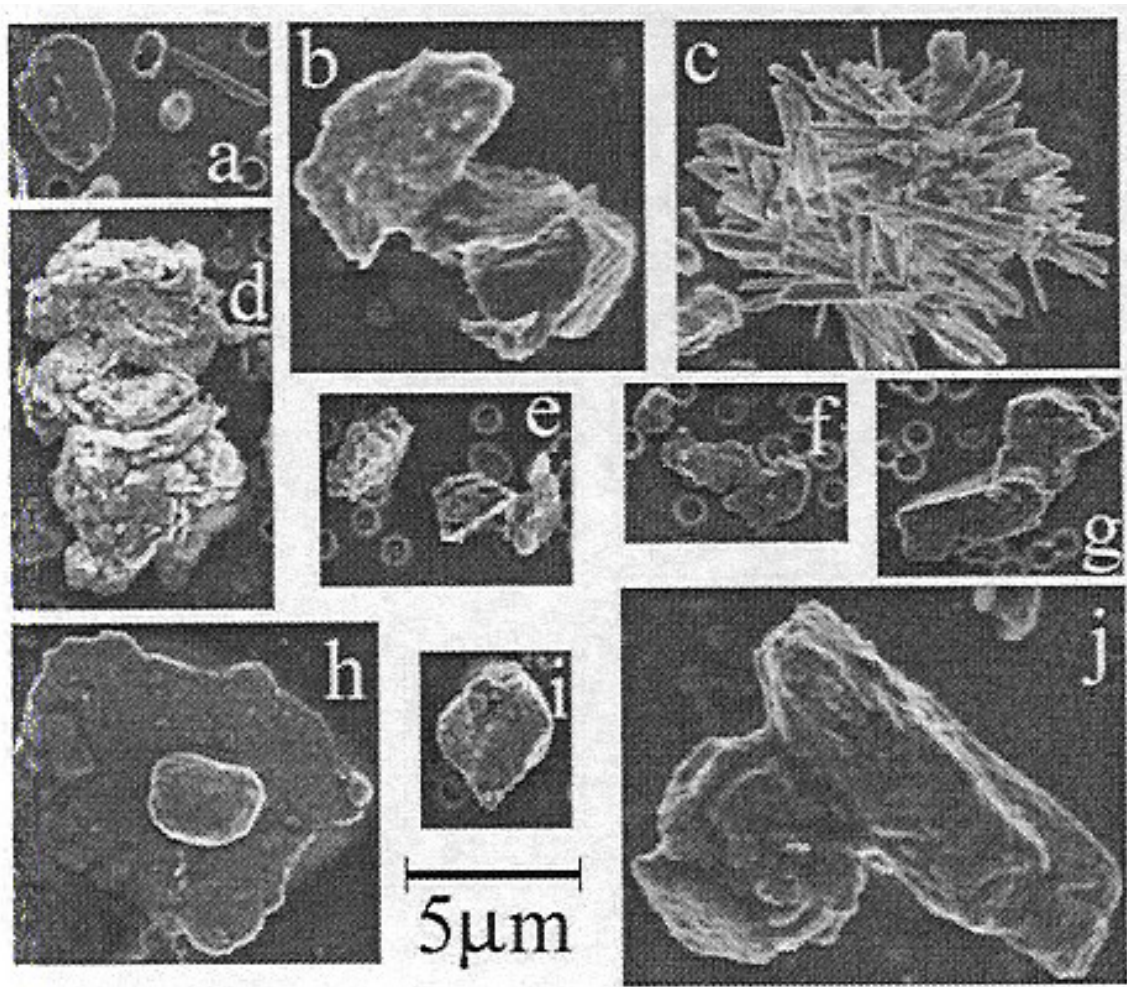


Lecture 2. Physical properties

1. Aerosol Size Distribution

Radius or diameter characterize size of one particles, but the particles may have complex shapes + radii vary by orders of magnitude => NOT one size but size distribution covering full spectrum of radius.

Figure2.1. Detailed electron micrographs of individual dust particles collected in Puerto Rico (Reid et al., 2003).



If particle is non-spherical, its equivalent radius is introduced. There are several ways to define particle equivalent radius (for instance, aerodynamic equivalent radius, which is

radius of a sphere that experience the same resistance to motion as the nonspherical particle).

How to calculate aerodynamic radius

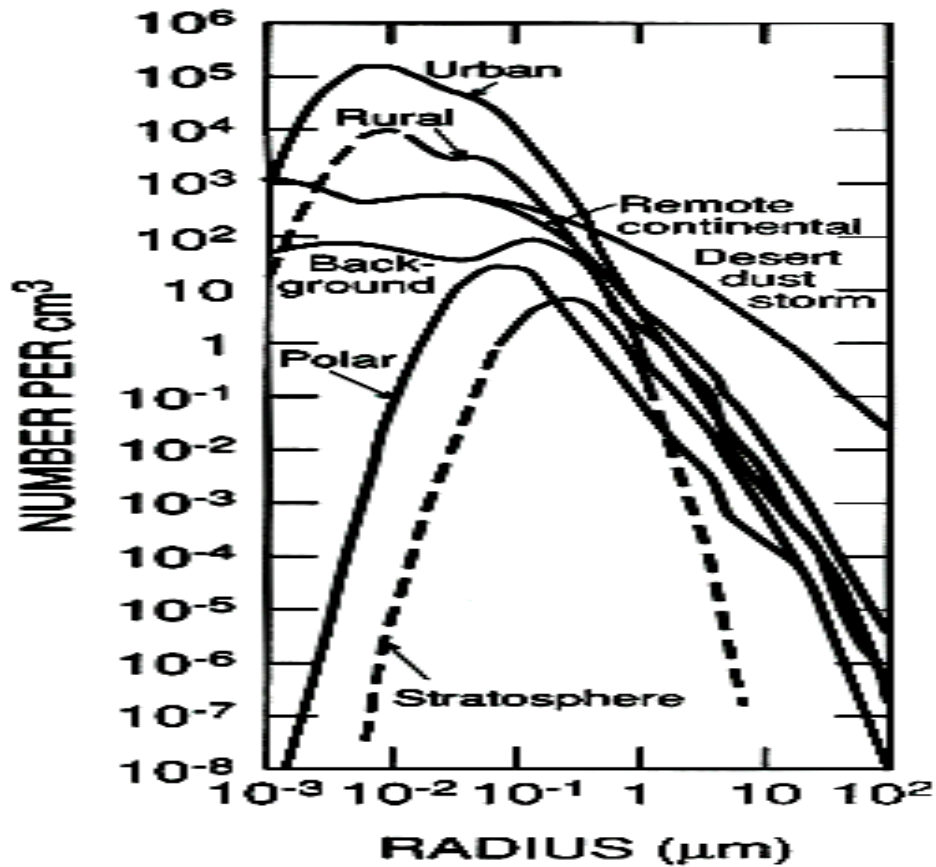
The Stokes law gives the force (drag) acting on a smooth particle due to laminar flow of air. $F_{\text{drag}}=6\pi\mu r_p u_t$ where μ is the dynamic viscosity [kg/m/s], r_p the radius of the spherical particle, and u_t is the speed of the fluid. For a particle falling freely $mg=4/3g\pi\rho_p r_p^2=F_{\text{drag}}$, and the settling velocity is given by:

$v_t = \frac{2 r_p^2 \rho_p g C_c}{9 \mu}$ where $C_c = 1 + \frac{\lambda}{r_p} [1.257 + 0.4 \exp(-\frac{1.1 r_p}{\lambda})]$ is the slip correction factor to take into account that the drag force is smaller than predicted for particles of the order of the mean free path λ . The values of C_c is around 1 for $r_p=1 \mu\text{m}$ and $C_c=2$ for $r_p=0.1\mu\text{m}$. As λ increases with decreasing atmospheric pressure C_c increases with altitude in the troposphere and should not be neglected in modeling aerosol removal.

The Stokes radius r_{st} is the radius of a sphere having the same terminal settling velocity and density as the particle. The aerodynamic radius for a sphere of unit density is then given by:

$$r_a = r_{st} \sqrt{\frac{\rho_p C_c(r_{st})}{C_c(r_a)}}$$

Figure 2.2 Typical aerosol number distributions in different environments.



Number distributions are important for microphysical processes but for air quality volume size distribution is more important as the mass concentration is monitored, while for optical properties the surface area or volume size distribution is responsible for light attenuation.

Clean Air Act requires EPA to set the National Ambient Air Quality Standards NAAQS.

Table 2.1 EPA standards for particulates

Particulate Matter with diameter less than 2.5 or 10 μm	Primary Standards (Maximum concentration)	Averaging Period
PM2.5	15 μg/m ³	1 year
PM2.5	35 μg/m ³	24 hours
PM10	150 μg/m ³	24 hours

By assuming spherical particle it is easy to evaluate from figure 2.2 the mass concentration of particles in a size range and compare the values with EPA standards of Table 2.1

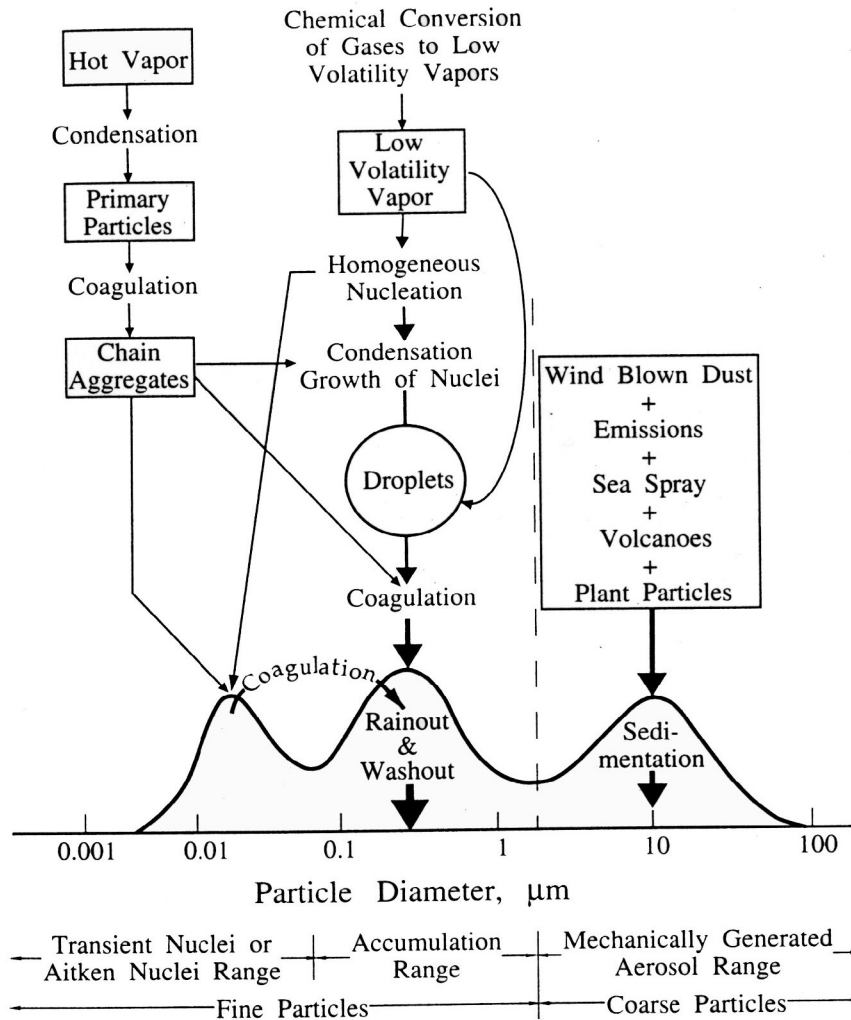


Figure 2.1 Distribution of surface area of ambient aerosols (from Whitby and Cantrell, 1976).

Aerosol distribution characterized by 3 modes:

fine mode ($d < 2.5 \mu\text{m}$) and **coarse mode** ($d > 2.5 \mu\text{m}$);

fine mode is divided on the **nuclei mode** (about $0.005 \mu\text{m} < d < 0.1 \mu\text{m}$) and

accumulation mode ($0.1 \mu\text{m} < d < 2.5 \mu\text{m}$).

NOTE: The distinction between fine and coarse particles is a fundamental because, in general, the fine and coarse particles mode originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, have different chemical composition, have different optical properties, etc.

Once in the atmosphere, atmospheric aerosols evolve in time and space:

1. may be transported in the atmosphere;
2. may be removed from the atmosphere (by dry deposition, wet removal, and gravitational sedimentation);
3. can change their size and composition due to microphysical transformation processes;
4. can undergo chemical transformation.

2. Mathematical formulation of aerosol distribution.

- The diameters of atmospheric aerosol particles span over four orders of magnitude, from a few nanometers to around 100 μm . Particle number concentrations may be as high as 10^7 to 10^8 cm^{-3} . Thus, a complete description of the aerosol size distribution may be a challenging problem. Therefore, several mathematical approaches are used to characterize the aerosol size distribution.

Discrete approximation: particle size range is divided into discrete intervals (or size bins) and the number of particles is calculated in each size bin.

Continuous approximation: particle size distribution is represented by analytical function vs. radius.

Let's consider first **discrete approximation** of aerosol size distribution.

Table 25.2. Example of segregated aerosol size information.

Size range (diameter, μm)	Concentration (cm^{-3})	Cumulative concentration (cm^{-3})	Normalized concentration ($\mu\text{m}^{-1}\text{cm}^{-3}$)
0.001 - 0.01	100	100	11111
0.01-0.02	200	300	20000
0.02-0.03	30	330	3000
0.03-0.04	20	350	2000

0.04-0.08	40	390	1000
0.08-0.16	60	450	750
0.16-0.32	200	650	1250
0.32-0.64	180	830	563
0.64-1.25	60	890	98
1.25-2.5	20	910	16
2.5-5.0	5	915	2
5.0-10.0	1	916	0.2

Cumulative concentration is defined as the concentration of particles that are smaller than or equal to a given size range.

Normalized concentration is defined as the concentration of particles in a size bin divided by the width of this bin.

If the i -bin has N_i particle concentration, thus normalized concentration in the i -bin is

$$n_{Ni} = N_i / \Delta D_i$$

where ΔD_i is the width of the i -bin.

- Discrete size distribution is typically presented in the form of histogram.

Figure 25.3 Histogram of aerosol particle number concentrations vs. the size range for the distribution of Table 25.2.

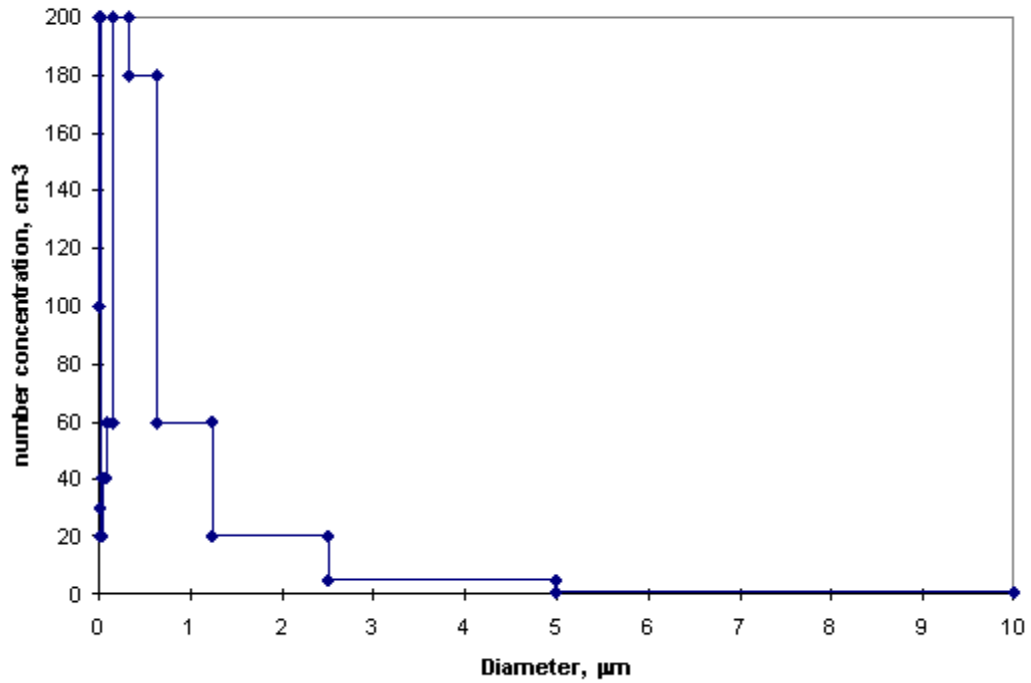


Figure 25.4 Histogram of aerosol particle number concentration normalized by the width of the size range for the distribution of Table 25.2.

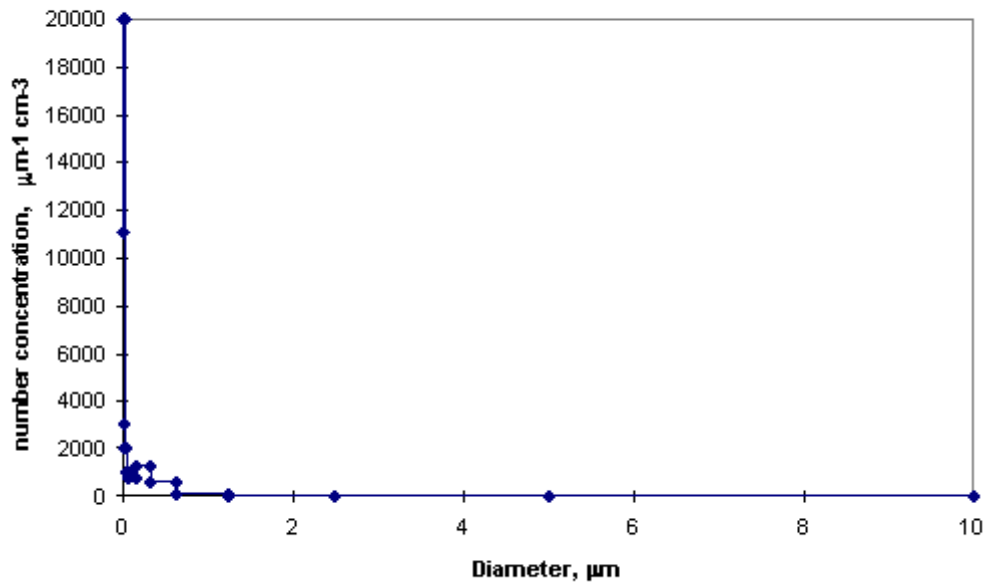
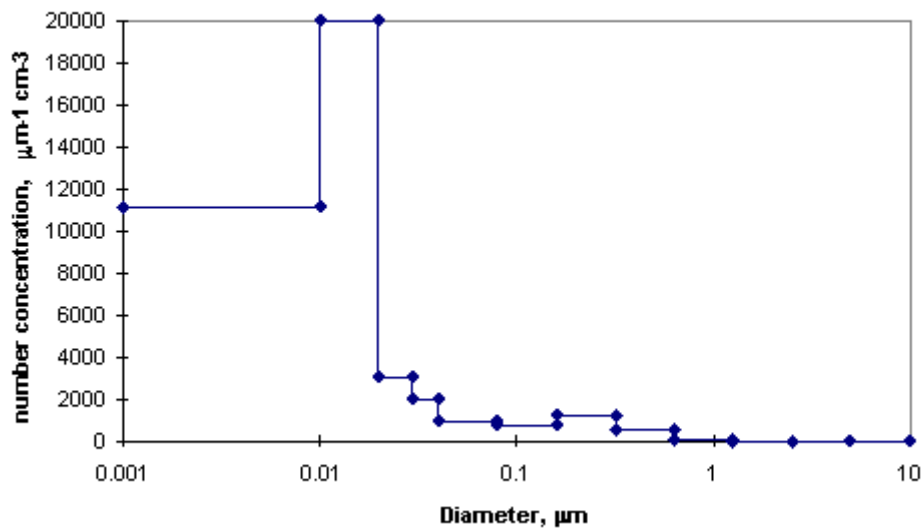


Figure 25.5 Same as Figure 25.4 but plotted vs. the logarithm of the diameter.



NOTE: That in Figures 25.3-25.4 smaller particles are hardly seen, but if a logarithmic scale is used for the diameter (Figure 25.5) both the large- and small-particles regions are depicted.

Major limitation of discrete approximation:

loss of information about the distribution structure inside each bin.

Let's consider **continuous approximation**.

We can define the size distribution function $n_N(D)$ as follows:

$n_N(D) dD$ = the number of particles per cm^3 of air having diameters in the range D and

$D + dD$ (here dD is an infinitesimally small increase in diameter).

If units of $n_N(D)$ are $\mu\text{m}^{-1}\text{cm}^{-3}$ and the total number of particles per cm^3 , N , is then just

$$N = \int n_N(D) dD$$

On the other hand

$$n_N(D) = dN/dD$$

NOTE: both sides of the equation above represent the same aerosol distribution, and both notations are widely used.

Several aerosol properties depend on the particle surface area and volume distributions with respect to particle size.

Let's define aerosol surface area distribution $n_S(D)$ as

$n_S(D) dD$ = the surface area of particles per cm^3 of air having diameters in the range D and $D + dD$ (here dD is an infinitesimally small increase in diameter).

If all particles are spherical and have the same diameter D in this infinitesimally narrow size range that each of them has surface area πD^2 , we have

$$n_S(D) = \pi D^2 n_N(D)$$

Here $n_S(D)$ is in $\mu\text{m cm}^{-3}$.

Thus the total surface area S of the aerosol particles per cm^3 of air is

$$S = \pi \int D^2 n_N(D) dD = \int n_S(D) dD$$

Here S is in $\mu\text{m}^2 \text{cm}^{-3}$.

Let's define aerosol volume distribution $n_V(D)$ as

$n_V(D) dD$ = the volume of particles per cm^3 of air having diameters in the range D and $D + dD$ (here dD is an infinitesimally small increase in diameter),

and therefore

$$n_V(D) = \pi D^3 n_N(D) / 6$$

Here $n_V(D)$ is in $\mu\text{m}^3 \text{cm}^{-3}$.

Thus the total aerosol volume V per cm^3 of air is

$$V = \pi/6 \int D^3 n_N(D) dD = \int n_V(D) dD$$

Here V is in $\mu\text{m}^3 \text{cm}^{-3}$.

- The aerosol distribution is more convenient to express as functions of $\ln(D)$ or $\log(D)$, because particle sizes span several orders of magnitude.

Let's define the number distribution function $n_N^e(\ln(D))$ in cm^{-3} as

$n_N^e(\ln(D)) d \ln(D)$ = the number of particles per cm^3 of air having diameters in the range $\ln(D)$ and $\ln(D) + d \ln(D)$.

NOTE: We cannot take the logarithm of a dimensional quantity. Thus, when we write $\ln(D)$ we really mean $\ln(D/1)$, where the "reference" particle diameter is $1 \mu\text{m}$ is not explicitly indicated.

The total number of particles per cm^3 , N , is then just

$$N = \int n_N^e(\ln(D)) d \ln(D)$$

The surface area and volume distributions as functions of $\ln(D)$ can be defined similarly to those with respect to D , as

$$n_S^e(\ln(D)) = \pi D^2 n_N^e(\ln(D))$$

$$n_V^e(\ln(D)) = \pi D^3 n_N^e(\ln(D)) / 6$$

Here $n_S^e(\ln(D))$ is in $\mu\text{m}^2 \text{cm}^{-3}$, and $n_V^e(\ln(D))$ is in $\mu\text{m}^3 \text{cm}^{-3}$.

Thus for S and V we have

$$S = \pi \int D^2 n_N^e(\ln(D)) d \ln(D) = \int n_S^e(\ln(D)) d \ln(D)$$

$$V = \pi/6 \int D^3 n_N^e(\ln(D)) d \ln(D) = \int n_V^e(\ln(D)) d \ln(D)$$

NOTE: The above aerosol distributions can be also expressed as functions of the base 10 logarithm $\log(D)$, defining $n_N^o(\log(D))$, $n_S^o(\log(D))$, and $n_V^o(\log(D))$.

Thus we have

$$dN = n_N(D) dD = n_N^e(\ln(D)) d \ln(D) = n_N^o(\log(D)) d \log(D)$$

$$dS = n_S(D) dD = n_S^e(\ln(D)) d \ln(D) = n_S^o(\log(D)) d \log(D)$$

$$dV = n_V(D) dD = n_V^e(\ln(D)) d \ln(D) = n_V^o(\log(D)) d \log(D)$$

Since $d \log(D) = d \ln(D) / 2.303 = dD / 2.303 D$, we can relate the distributions above as:

$$n_N^e(\ln(D)) = D n_N(D)$$

$$n_S^e(\ln(D)) = D n_S(D)$$

$$n_V^e(\ln(D)) = D n_V(D)$$

$$n_N^o(\log(D)) = 2.303 D n_N(D)$$

$$n_S^o(\log(D)) = 2.303 D n_S(D)$$

$$n_V^o(\log(D)) = 2.303 D n_V(D)$$

- Several mathematical functions are used to describe the atmospheric aerosol distribution (lognormal function, power-law function, etc.)

Log-normal function:

$$n_N(D) = dN / dD = \frac{N}{\sqrt{2\pi} D \ln(\sigma_g)} \exp\left[-\frac{\ln^2(D/D_g)}{\ln^2(\sigma_g)}\right]$$

Or

$$n_N(\ln(D)) = dN / d \ln(D) = \frac{N}{\sqrt{2\pi} \ln(\sigma_g)} \exp\left[-\frac{\ln^2(D/D_g)}{\ln^2(\sigma_g)}\right]$$

Where **N** is the total aerosol number concentration, **D_g** and **σ_g** are the parameters of a log-normal distribution: **D_g** is the **median diameter**, that is, the diameter for which exactly one-half of the particles are smaller and one-half are larger; and **σ_g** is termed **geometric standard deviation**, which is a ratio of the diameter below which 84.1% of the particles lie to the median diameter.

NOTE: A lognormal function is very often used to represent aerosol size distribution because of its properties.

Some properties of the log-normal distribution:

- If the number distribution **n_N(D)** is log-normal, the surface distribution **n_S(D)** is also log-normal with the same geometric standard deviation **σ_g** and with the surface median diameter, **D_{gS}**, given by

$$\ln(D_{gS}) = \ln(D_g) + 2 \ln^2(\sigma_g)$$

- If the number distribution **n_N(D)** is log-normal, the volume distribution **n_V(D)** is also log-normal with the same geometric standard deviation **σ_g** and with the volume median diameter, **D_{gV}**, given by

$$\ln(D_{gV}) = \ln(D_g) + 3 \ln^2(\sigma_g)$$

Volume size distribution

$$n_v(\ln(D)) = dV / d \ln(D) = \frac{C_v}{\sqrt{2\pi \ln(\sigma_g)}} \exp\left[-\frac{\ln^2(D/D_v)}{\ln^2(\sigma_g)}\right]$$

Where D_v is the volume median diameter (mean logarithm of diameter)

$$\ln D_v = \frac{\int \ln D \frac{dV}{d \ln D} d \ln D}{\int \frac{dV}{d \ln D} d \ln D}$$

σ_v is the standard deviation from the volume median diameter

$$\sigma_v = \sqrt{\frac{\int (\ln D - \ln D_v)^2 \frac{dV}{d \ln D} d \ln D}{\int \frac{dV}{d \ln D} d \ln D}}$$

C_v is the volume concentration

$$C_v = \int \frac{dV}{d \ln D} d \ln D$$

Figure 25.6 Particle number log-normal distribution with $D_g = 0.8 \mu\text{m}$ and $\sigma_g = 1.5$, for $N = 1000 \text{ cm}^{-3}$

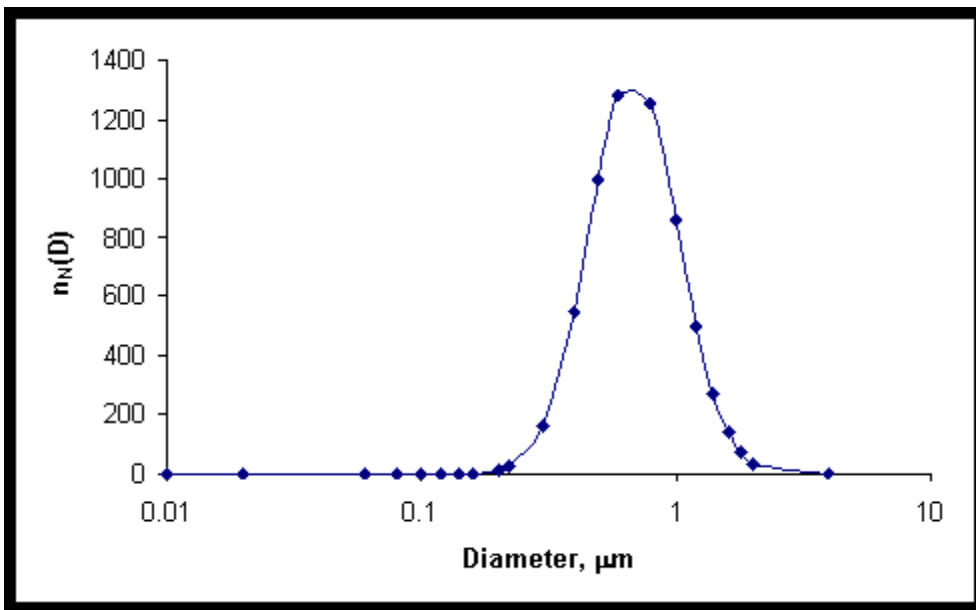
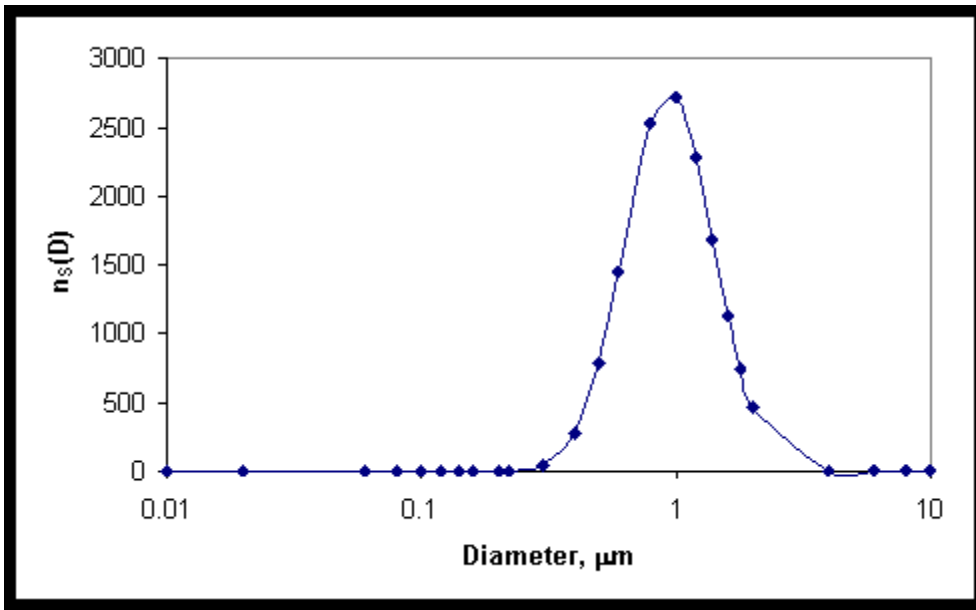


Figure 25.7 Particle surface log-normal distribution for number distribution from Figure 25.6



NOTE: $n_N(D) = dN/dD$ and $n_S(D) = dS/dD$

NOTE: For multiple modes, lognormal functions are summed. For m modes, the volume size distribution is given by

$$n_v(\ln(D)) = dV / d \ln(D) = \sum_{i=1}^m \frac{C_V^i}{\sqrt{2\pi \ln(\sigma_g^i)}} \exp\left[-\frac{\ln^2(D/D_V^i)}{\ln^2(\sigma_g^i)}\right]$$

Table 2.2 Selected values of r_g (median radius) and σ_g standard deviation for different aerosol types

Aerosol type	Density [g/cm ³]	r_g [μm]	σ_g
Sulfate	1.7	0.07	2
Organic carbon	1.8	0.02	2.2
Black carbon	1	0.01	2
Dust	2.6	0.04	2
	2.6	0.07	2
	2.6	0.14	2
	2.6	0.24	2
	2.6	0.42	2
	2.6	0.72	2
	2.6	1.4	2

Sea Salt	2.2	0.2	2
	2.2	1.64	2

Power-law function (or Junge distribution):

$$n_N^o(\log(D)) = C / (D)^\alpha$$

where **C** and **α** are constants.

Plotting of the power-law distribution on log-log coordinates results in a straight line with slope **-α** and for **D = 1 μm**, **n_N^o = C**.

- This distribution function assumes that the aerosol number concentration decreases monotonically with increasing particle size. This is not generally true for atmospheric aerosols so the power-law can be used for particles of **D > 0.1 μm**.
- The main advantage of power-law distribution is its simplicity.
- For spherical particles, the volume distribution **n_v^o(logD)** is given by

$$\frac{dV}{d \log D} = \frac{1}{6} \pi C D^{3-\alpha} \quad \text{and if } \alpha=3 \text{ then } n_v^o(\log D)=C$$