Equivalent particle sizes

The terms *particle size* and *diameter* are unambiguous only for spheres. For non-spherical particles some form of *equivalent diameter* is used. It is important to realise that the commercial instruments available for particle sizing measure *different* equivalent diameters, so that *one would expect them to give different answers when measuring the same sample*. With some knowledge of the particle shape, however, it is often possible to convert from one equivalent diameter to another. The following definitions are in common use.

(i) *equivalent-volume sphere diameter, d_v*

This is the diameter of the sphere with the same volume, v, as the particle

$$d_v = \left(\frac{6v}{\pi} \right)^{1/3} \tag{1.21}$$

The value of d_v is *not* dependent on the orientation of the particle.

(ii) *equivalent-surface sphere diameter, d_s*

This is the diameter of a sphere with the same surface area, S, as the particle

$$d_s = \left(\frac{S}{\pi} \right)^{1/2} \tag{1.22}$$

Again, d_s is independent of orientation.

(iii) *equivalent-projected-area circle diameter, d_A*

This is the diameter of a circle with the same area, A, as the projected area of the particle.

$$d_A = \left(\frac{4A}{\pi} \right)^{1/2} \tag{1.23}$$

The value of d_A *is* dependent on orientation.

(iv) *Stokes' diameter, d_{st}*

This is the diameter of a sphere with the same density and terminal velocity as the particle (in the Stokes regime).

$$d_{st} = [18 \, \mu V_t / (\varrho_p - \varrho)g]^{1/2}$$

where V_t is the particle terminal velocity, ϱ_p is the particle density, ϱ is the fluid density, g is the gravity constant.

The Stokes diameter and the equivalent- volume sphere diameter are simply related,

$$d_{st} = \left[\frac{3\pi d_v^3}{c} \right]^{1/2} \tag{1.27}$$

where c is the hydrodynamic resistance of the particle ($3\pi d$ for a sphere). c can be calculated exactly for various model shapes in preferred or random orientations.

(v) *aerodynamic diameter, d_a*

This is the diameter of a sphere of density 1000 kg/m^3 and the same settling velocity as the particle (in the Stokes regime).

$$d_a = [18 \, \mu V_t / C_a (\varrho_0 - \varrho)g]^{1/2} \qquad (1.28)$$

where $\varrho_0 = 1000$ kg/m^3 and C_a is the appropriate Cunningham slip-correction factor for d_a. From (1.26) and (1.28),

$$d_a = d_{st} \left[\frac{C_{st} \, (\varrho_p - \varrho)}{C_a \, (\varrho_0 - \varrho)} \right]^{1/2} \qquad (1.29)$$

The choice of equivalent diameter depends on the use to which the data are put. For example, if the efficiency of an inertial separating device such as a cyclone is required, it is appropriate to use the Stokes diameter, since this best describes the behaviour of particles suspended in a fluid when inertial effects are dominant.

Averages

To define a particle size distribution completely requires a large amount of information, such as Table 1.1, for example. It is obviously advantageous to be able to approximate the distribution by some form of mathematical function, and many such functions are available. Each requires at least two calculated parameters: one to define the location of the distribution and one to define its width. The first of these parameters is usually some form of 'average', such as the *mean* (strictly *arithmetic mean*), *geometric mean*, *median* or *mode*.

The *arithmetic mean*, $\bar{d}_p$, is given by the sum of all the particle diameters, divided by the total number:

$$\bar{d}_p = \frac{\Sigma d}{N} = \frac{\Sigma n_i d_i}{\Sigma n_i} \tag{1.5}$$

$$= \int_0^\infty d_p f(d_p) \mathrm{d}d_p \tag{1.6}$$

The *geometric mean*, d_g, is defined as

$$d_g = [d_i^{n1} d_2^{n2} d_3^{n3} \ldots d_i^{ni}]^{1/N} \tag{1.7}$$

The *median* is the diameter for which one half of the total number of particles are larger, and one half smaller. It divides the frequency distribution into equal areas and is the diameter which corresponds to $F = 0.5$ on the cumulative distribution curve. The advantage of the median is that it is less affected by skewness (lack of symmetry) of the distribution than the mean.

The *mode* is the most frequent size, i.e. the highest point on the frequency curve. For monodisperse distributions all four of these averages are equal. For distributions which are skewed towards larger sizes as in Figure 1.4, which is frequently the case for particles,

mode < median < mean.

The *mass mean diameter*, d_{mm}, is given by

$$d_{mm} = \Sigma \left[\frac{m_i}{M} d_i \right] \tag{1.12}$$

where m_i is the mass of particles in the ith interval and M is the total mass. The ratio (m_i/M) is a form of weighting factor in the averaging process. If *particle shape is not a function of particle size* for the distribution, i.e. we can write

$$m_i = k d_i^3 \tag{1.13}$$

where k is a constant for all values of d_i, then

$$d_{mm} = \frac{\Sigma m_i d_i}{M} = \frac{\Sigma n_i d_i^4}{\Sigma n_i d_i^3} \tag{1.14}$$

(The *mass mean diameter* should not be confused with the *diameter of average mass*.) In a similar way, the *surface mean diameter* (also known as the 'volume-surface mean' or the 'Sauter mean') is given by

$$d_{sm} = \frac{\Sigma s_i d_i}{S} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} \tag{1.15}$$

where s_i is the surface area of particles in the ith interval and S is the total surface area. The surface mean diameter is the appropriate diameter to use when calculating the pressure drop through a packed bed of particles at low Reynolds numbers .
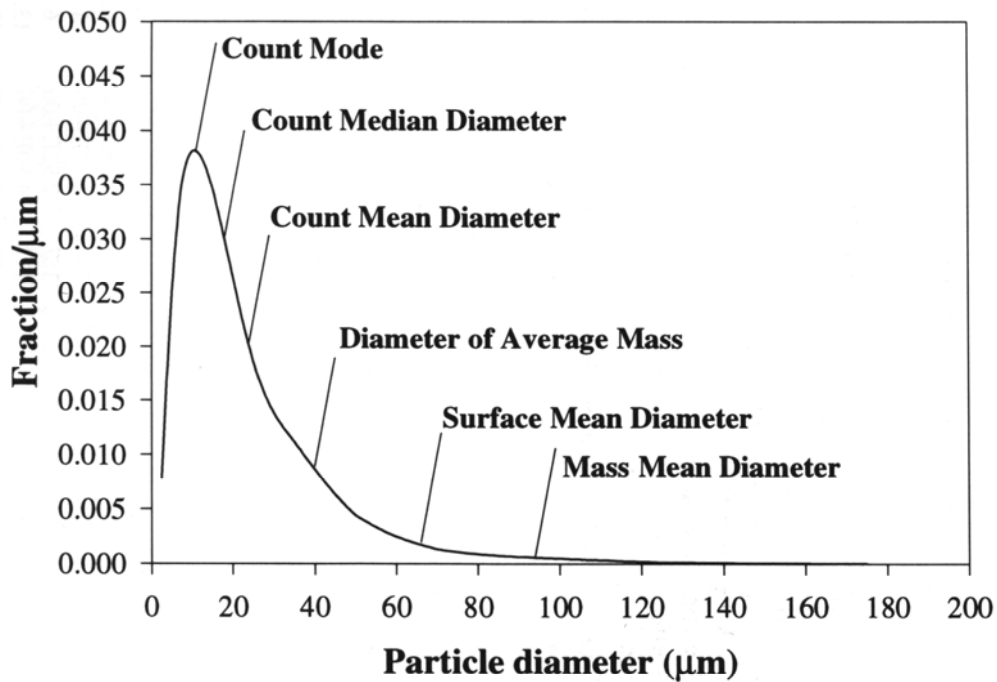

Figure 1.6 Averages of the distribution.

The averages marked on the frequency distribution curve.

Methods of presenting data of particle size distribution measurements

Table 1.1   Example of a particle size distribution

Diameter range (μm)		Count frequency	Fraction per μm	Percent	Cumulative percent
Lower	Upper				
0	5	39	0.00780	3.9	3.9
5	10	175	0.03500	17.5	21.4
10	20	348	0.03480	34.8	56.2
20	30	187	0.01870	18.7	74.9
30	40	112	0.01120	11.2	86.1
40	60	89	0.00445	8.9	95.0
60	80	27	0.00135	2.7	97.7
80	100	13	0.00065	1.3	99.0
100	150	8	0.00016	0.8	99.8
150	200	2	0.00004	0.2	100.0
		1000		100.0	

Table 1.1 is a set of particle size data for 1000 particles, the size being measured by some unspecified method. It consists of particle counts within a number of discrete size intervals and is therefore an example of a *number distribution*. Some size measuring devices allow the limits of the sizing intervals to be defined by the user, in which case it is preferable to keep the *resolution* (the interval width divided by the mean interval size) approximately constant, for example by using a geometric progression of interval limits: x, x^2, x^3 . . . x^n. Frequently, the limits of the intervals are not user-defined, but this does not prevent an accurate representation of the particle size distribution from being obtained.

The data of Table 1.1 are most simply
represented as a *frequency histogram* (Figure 1.2). The problem with this
representation is that the heights of the rectangles must depend to some
extent on the width of the interval, which makes comparison difficult. It is
preferable, therefore, to divide each interval count by the total number of
counts, to obtain the fractional count in each size class, and then to divide this
fraction by the interval width (usually in micrometres). If fraction/μm is now
plotted as a histogram against particle size (Figure 1.3) the resulting
representation has the important property that the area under each rectangle
represents the fraction of particles in that size interval. The total area is thus
equal to one.
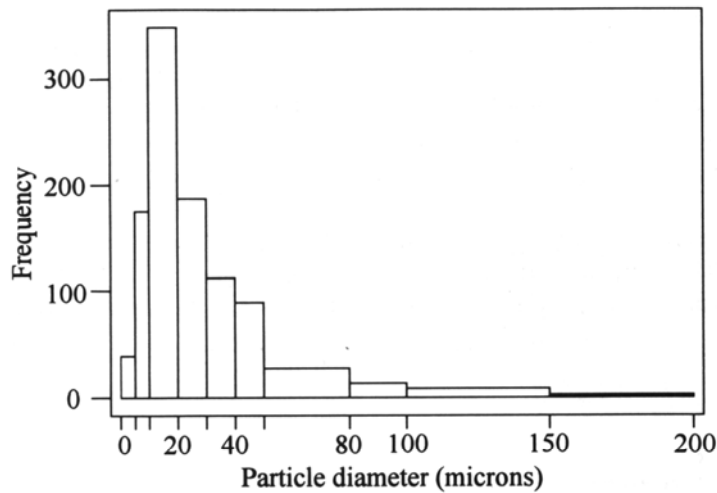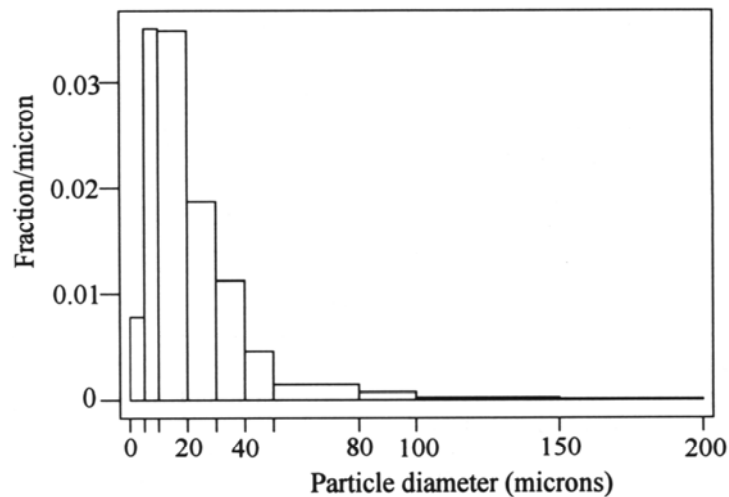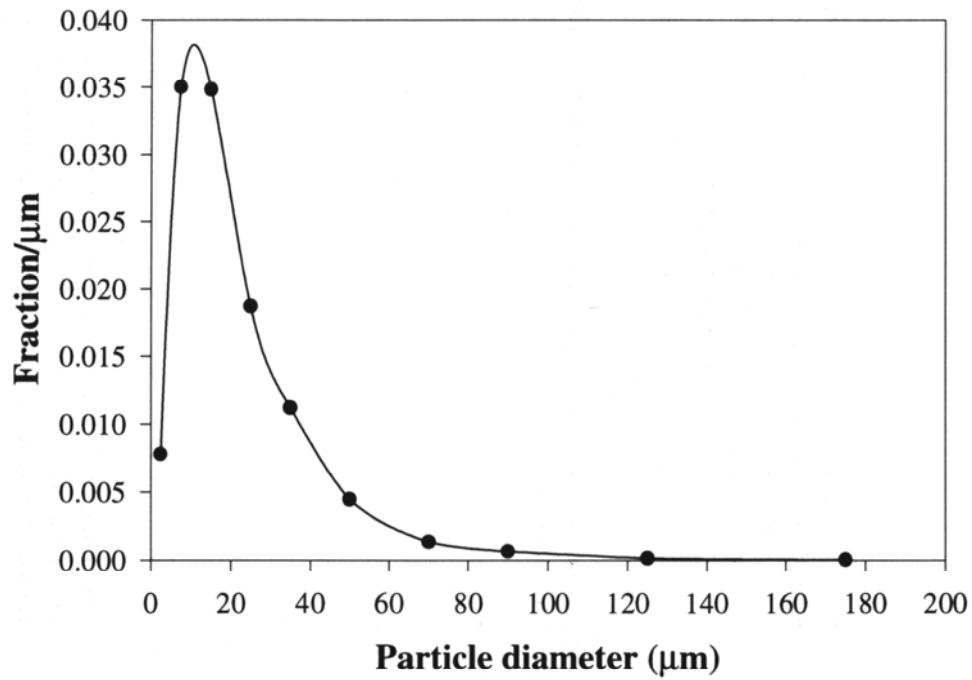

Figure 1.2 Number frequency distribution.

Figure 1.3 Fraction per μm versus particle size, discrete number distribution.

The frequency distribution may be *discrete*, as in Figure 1.3, or a smooth line may be drawn through the tops of the frequency rectangles at the mean point of each interval to form a *continuous* distribution, as in Figure 1.4.

Figure 1.4 Fraction per μm versus particle size, continuous number distribution.

For a continuous distribution, the fraction of the total number of particles having diameters between *a* and *b* is the integral under the distribution curve between these limits

$$f_{ab} = \int_a^b f(d_p)\mathrm{d}d_p \tag{1.1b}$$

where $f(d_p)$ is the continuous frequency distribution function. The total area is again unity:

$$\int_0^\infty f(d_p)\mathrm{d}d_p = 1 \tag{1.2b}$$

An alternative representation of particle size distributions is the *cumulative* distribution, shown in Figure 1.5 for the same data as in Table 1.1. For a continuous distribution, the cumulative distribution function, $F(a)$, is defined as the fraction of the total number of particles with diameters less than a,

$$F(a) = \int_0^a f(d_p)\mathrm{d}d_p \tag{1.3}$$

or

$$f(d_p) = \frac{\mathrm{d}F(d_p)}{\mathrm{d}d_p} \tag{1.4}$$
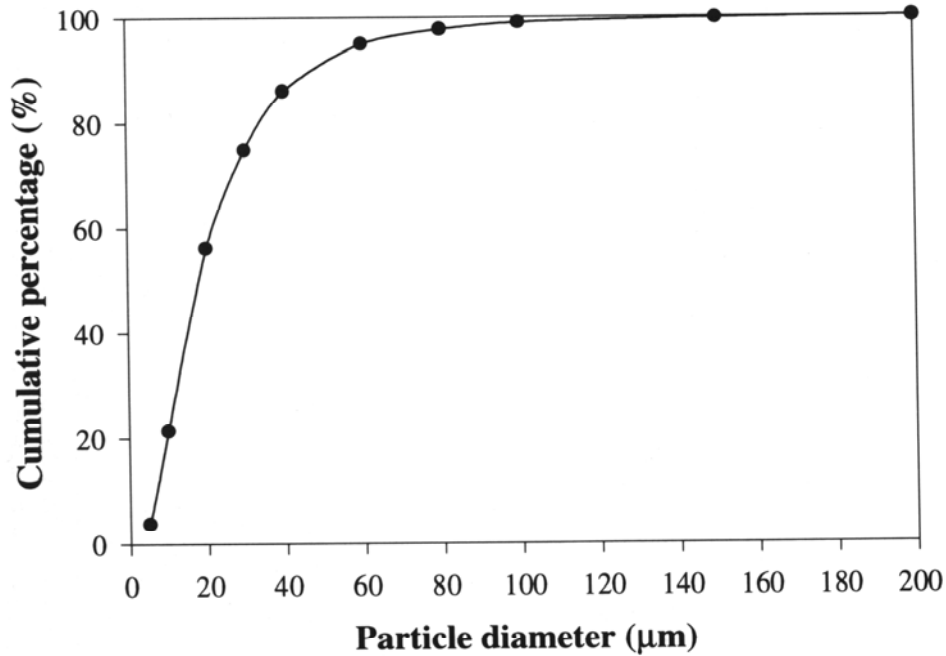

**Figure 1.5** Cumulative number distribution.

Thus the frequency function at any point can be obtained from the slope of the cumulative distribution function.

Because the cumulative distribution is the integral of the frequency function, it is less sensitive to 'scatter' in the data. 'Smoothing' of measurements and interpolation between measured points on the distribution are therefore simple and reliable. For these reasons, it is common practice to work with the cumulative distribution function rather than the frequency function.
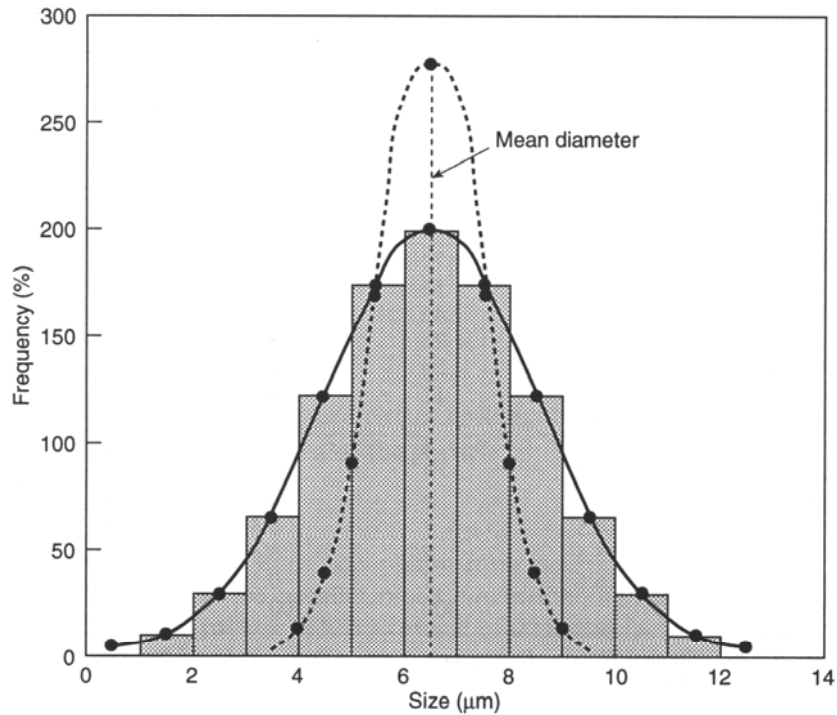
Histogram of normal particle size distribution. (From N. G. Stanley-Wood, *Enlargement and Compaction of Particulate Solids*, Butterworths, p. 12 (1983).)
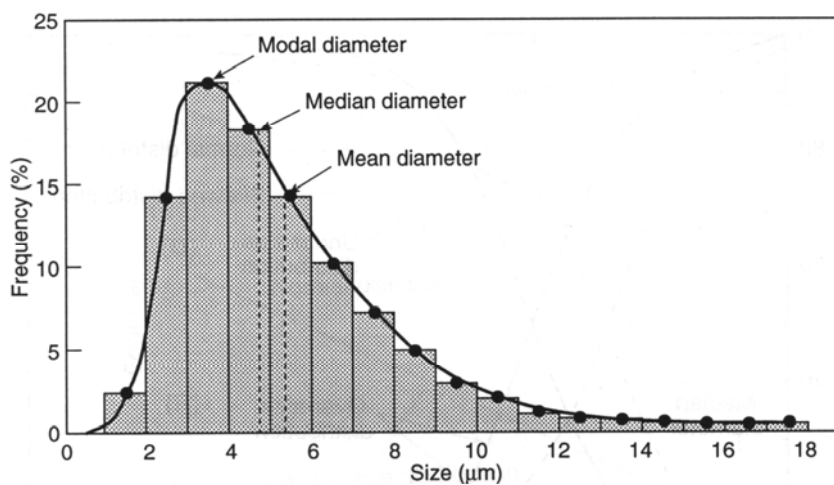

Histogram of skewed particle size distribution. (From N. G. Stanley-Wood, *Enlargement and Compaction of Particulate Solids*, Butterworths, p. 12 (1983).)

The powder consisting of particles of relatively homogeneous size is usually known as a monodispersion; the powder consisting of particles of heterogeneous size covering a wide size range is known as a polydispersion. In general a curve of size distribution is often steeply sided towards the smaller sizes , and consequently found to be an asymmetric curve with a tail that extends far towards the large sizes.
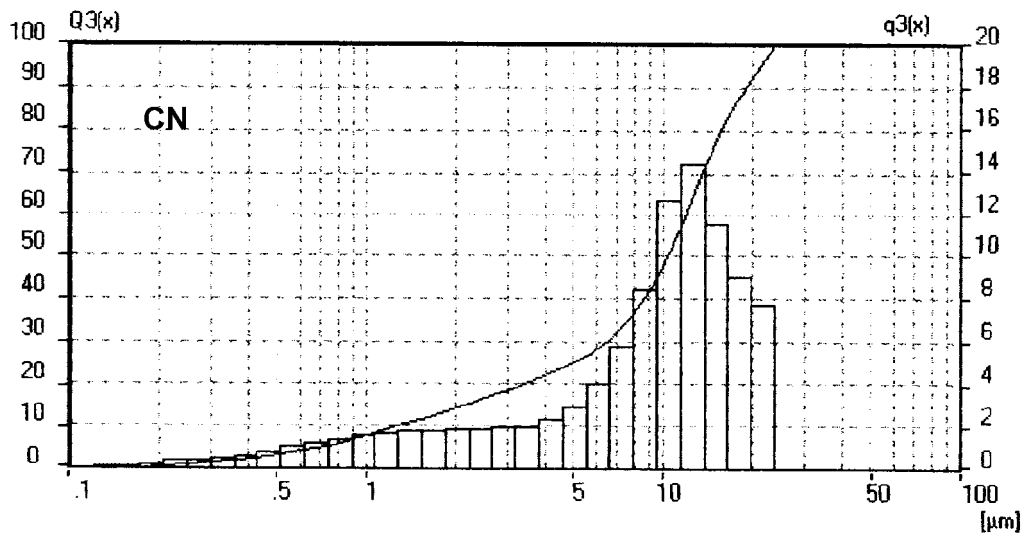
Particle size distribution of an unmilled zirconia-yttria powder.
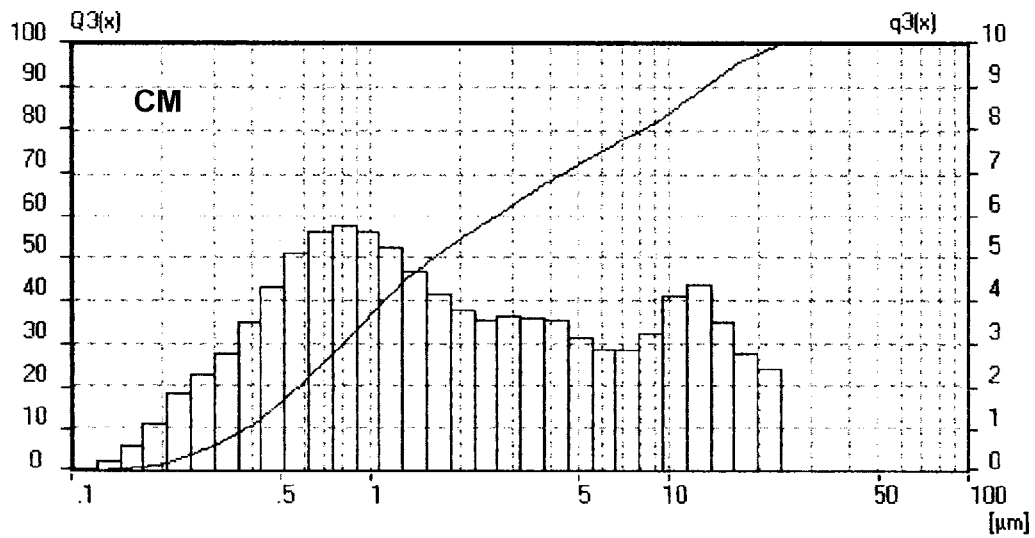
Particle size distribution of the powder after attrition milling.

Based on the ratio of the number of particles more (or less) than a given particle size to the total number of all the particles, a cumulative distribution curve is derived as shown in Fig. 5.8. This is also the fraction of the particles remaining on or passing through a screen of a given size and is
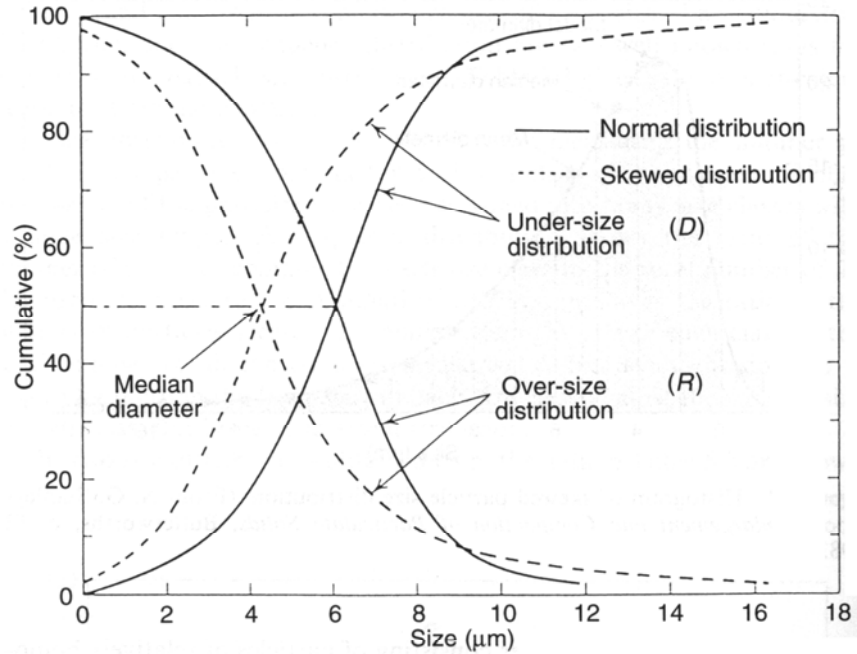
Cumulative particle size distributions.

called the 'over-size distribution' (curve descending to the right) or the 'under-size distribution' (curve descending to the left). The relation between the two curves is shown by

$$D = (100 - R) \tag{5.6}$$

where D is the cumulative amount (%) under screen size and R is the amount (%) above screen size.

As mentioned above, various size distributions may be derived based on different variables, and consequently different information may be obtained from each distribution. However, there remains the question of how many particles are needed in order to obtain the size distribution of all the particles with high precision. The answer is given in Fig. 5.9. To reduce measuring error, it is necessary to take as large a number of particles to be measured as possible, and the number to be measured becomes greater as the width of the size distribution increases.

Model Distribution Functions

Cumulative distributions can be fitted by a linear function if the data fit a suitable mathematical function. This curve fitting gives no insight into the fundamental physics by which the particle size distribution was produced. Three common functions are used to linearize the cumulative distribution: the normal distribution function, the log-normal distribution function, and the Rosin–Rammler distribution function. By far athe most commonly used is the log-normal distribution function.

Normal Distribution

This type of distribution occurs when the measured value of the size is determined by a large number of small additive effects, each of which may or may not operate. This distribution gives the well-known bell-shaped curve. It might be expected that many distributions follow this function but only narrow size ranges of classified material follow this distribution. Real distributions are skewed to larger sizes.

The equation representing a normal distribution is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{-(x - \bar{x})^2}{2\sigma^2}\right]$$

where σ is the standard deviation with units of length and $\bar{x}$ is the arithmetic mean size giving $f(x)$ units of length^{-1}. The distribution is normalized so that

$$\int_{-\infty}^{\infty} f(x)\,dx = 1.$$

The cumulative distribution is the integral of the distribution function.

$$F(x) = \int_{-\infty}^{x} f(x)\,dx.$$

A size distribution that fits the normal distribution equation can be represented by two parameters, the arithmetic mean size, $\bar{x}$, and the standard deviation, σ. The mean size, $\bar{x}$, is the size at 50% of the distribution, also written as x_{50}. The standard deviation is easily obtained from the cumulative distribution as

$$\sigma = x_{84\cdot13} - x_{50} = x_{50} - x_{15\cdot87}.$$

The normal distribution has the disadvantage that finite fractions of the distribution occur at sizes less than zero, which is physically unrealistic.

A plot of the cumulative normal distribution is linear on normal probability paper.

Log-Normal Distribution

The log-normal distribution is frequently observed in ceramic powder processing. The log-normal distribution is skewed to larger sizes compared to the normal distribution and has no finite probability for sizes less than zero as seen with the normal distribution. It is obtained by replacing x with $z = \ln d$ in the normal distribution, which gives the following distribution function :

$$f(z) = \frac{1}{\sigma_z \sqrt{2\pi}} \exp\left[\frac{-(z - \bar{z})^2}{2\sigma_z^2}\right]$$

where σ_z is the standard deviation of z and $\bar{z}$ is the mean value of z. The cumulative distribution is again simply the integral of the distribution function:
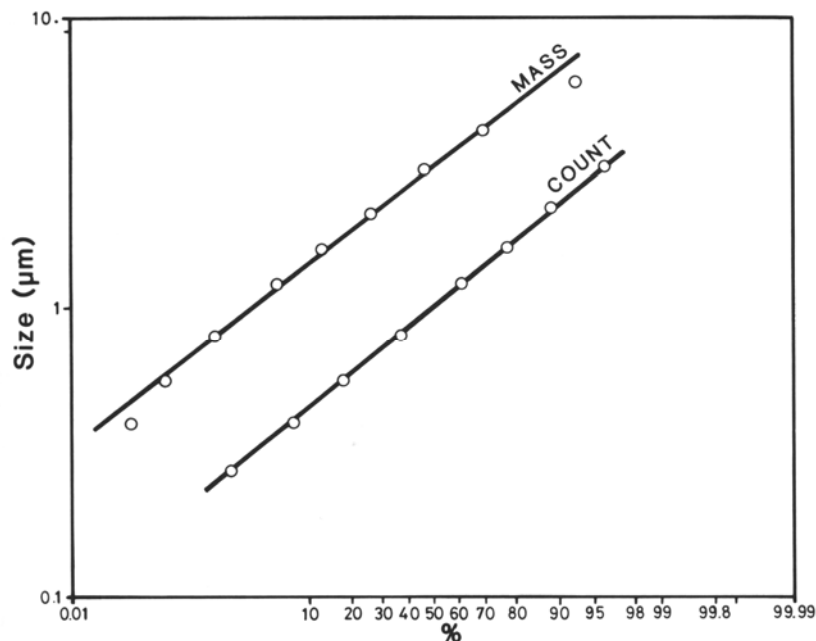
$$F(z) = \int_{-\infty}^{z} f(z)\, dz$$

This distribution can be rewritten in terms of size, d, as follows:

$$f(d) = \frac{1}{\ln \sigma_g \sqrt{2\pi}} \exp\left[\frac{-\left(\ln\left(\frac{d}{\bar{d}_g}\right)\right)^2}{2(\ln \sigma_g)^2}\right]$$

where $\bar{d}_g$ is the geometric mean size and σ_g is the geometric standard deviation.

A plot of the cumulative log-normal distribution is linear on log-normal probability paper.

Linearized log-normal distribution plot: Cumulative % less than versus size.

A size distribution that fits the log-normal distribution equation can be represented by two numbers, the geometric mean size, $\bar{d}_g$, and the geometric standard deviation, σ_g. The geometric mean size is the size at 50% of the distribution, d_{50}. The geometric standard deviation is easily obtained from the following ratios:

$$\sigma_g = \frac{d_{84\cdot13}}{d_{50}} = \frac{d_{50}}{d_{15\cdot87}} \geq 1.0.$$

If the number distribution follows a log-normal distribution then the surface area and the weight distributions also follow log-normal distributions with the same geometric standard deviation. Conversion from one log-normal distribution to another is easy.

Rosin-Rammler Distribution

For materials that have undergone comminution, the Rosin–Rammler distribution is frequently applicable. The Rosin–Rammler weight distribution is given by

$$f(x) = nbx^{n-1} \exp(-bx^n)$$

where n is a characteristic of the material and b is a measure of the range of particle size, x, being analyzed. Integration of this distribution gives the cumulative weight distribution

$$F(x) = \exp(-bx^n)$$

which gives a straight line when the double log of $F(x)$ is plotted versus log x. The ratio of $\tan^{-1}(n)$ to $x_{36.8}$ is a form of variance of the size distribution.

$F(x)$ is a mass percent of the particles larger than a given size. The mean size is the size at 36.8% of the distribution, written as $x_{36.8}$ or d_0. The measure of width of the distribution is n. The value of n can be read from linearized Rosin-Rammler distribution as a slope of the straight line.
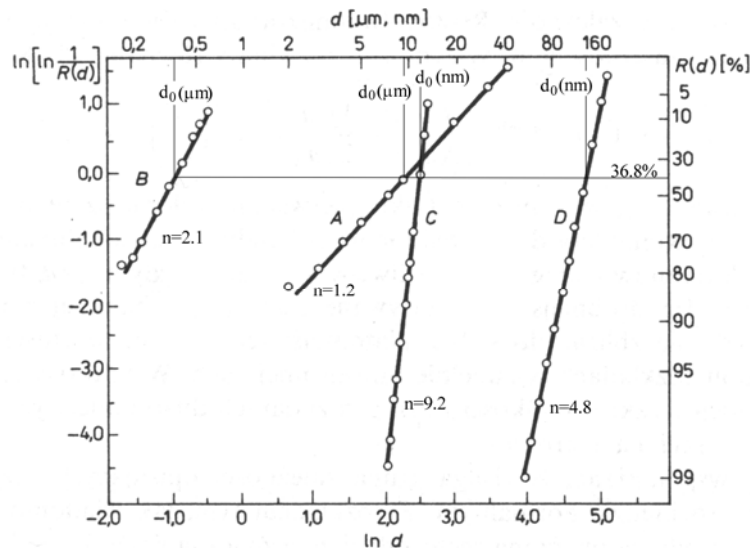
A – powdered glass in the CaO-B_2O_3-SiO_2 system, ball-milled, B - α-Al_2O_3 powder, milled in a ring-mill, C – 6.5 mol % Y_2O_3-ZrO_2 s.s. powder calcined at 800°C, D – hydrothermally crystallized powder of $NiFe_2O_4$.

In general, particles prepared by the solution techniques, especially precipitation methods, are found to have a size distribution that fits a log-normal distribution.

Powders prepared by comminution are frequently described by the Gaudin, Schuhmann and Rosin-Rammler laws.

Powder characterization

Weighted distributions

So far we have considered only *number* or *count* distributions. Frequently we are more interested in some *weighted distribution*, such as the *mass* or *surface distribution*. For example, the commonly used method for obtaining the size distribution of coarse particles is sieving, in which the test sample is placed on the top of a stack or nest of sieves, with mesh sizes decreasing with height in the stack, and the apparatus is shaken. Each sieve is then weighed, so that the result is a distribution of the *mass* of particles with diameters between each sieve size. While the *number* distribution gives the fraction of the total *number* of particles in any size range, the *mass* distribution gives the fraction of the total *mass* contributed by particles in any size range. It is important to realise that the graphical representations and the values of the averages for these two commonly used distributions are *different*. A product which is 90% by number within the required size range may contain only 10% by weight of saleable material!
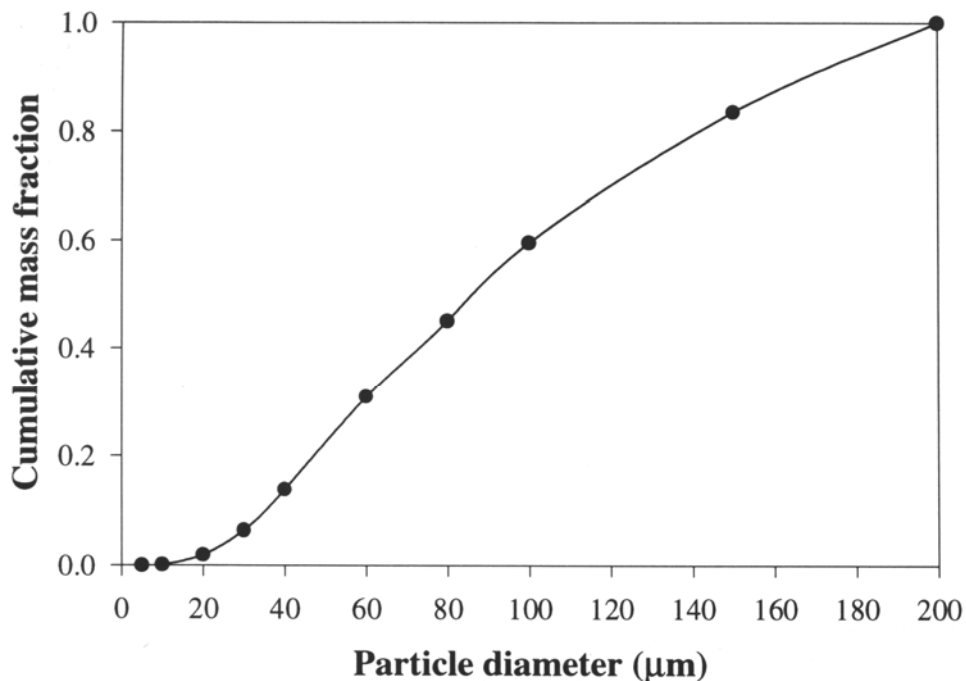

Figure 1.7   Cumulative mass distribution.

In converting from a number distribution to a mass distribution, or vice versa, it is important to consider the accuracy of the extremes of the distributions. A 10 μm particle has 1000 times the mass of a 1 μm particle. Thus a small error in the upper size classes of a number distribution will have a significant effect on the resulting mass distribution. Since the number of particles in any upper size class is usually small it is essential to repeat the count several times to avoid the usual problems of small-number statistics. Conversely, when converting from a mass distribution to a number distribution, small errors in the lower size classes of the mass distribution are magnified by the conversion, producing large errors in the number distribution.

Particle size and shape

It is difficult to express the shape and size of powder particles because the powder is generally composed of inhomogeneous particles of differing shapes and sizes. Various terms for expressing different shapes verbally are given in a table below. However, these terms for describing different shapes seem not to be well enough defined.

Various descriptive terms for particle shape

Spherical	Rod-like	Dendritic
Cubical	Porous	Spongy
Prismoidal	Acicular	Angular
Platy	Needle-like	Sharp-edged
Flake-like	Fibrous	Sharp-cornered
Granular	Blocky	Rounded

Sources: K. Yamaguchi, *Bull. Ceram. Soc. Jpn.*, **19**, 962 (1984); and S. Miwa, *Introduction to Powder Engineering*, Nikan Kogyo Press, p. 23 (1981)

If the particles in a powder are of approximately the same size and geometrical shape such as spherical, cubical or rod-like, a representative size of the particles can be given as the diameter or the length of a side. But if the particles are of heterogeneous shape, then it may be difficult to decide on the representative size.

Figure 5.1 shows how to express the size of a particle of irregular shape by using lengths b, l and h. Here, b is the short-axis diameter, l is the long-axis diameter and h is the height or thickness, lying in the directions of three mutually perpendicular axes when the particle to be measured is placed in a stable position on a horizontal plane.
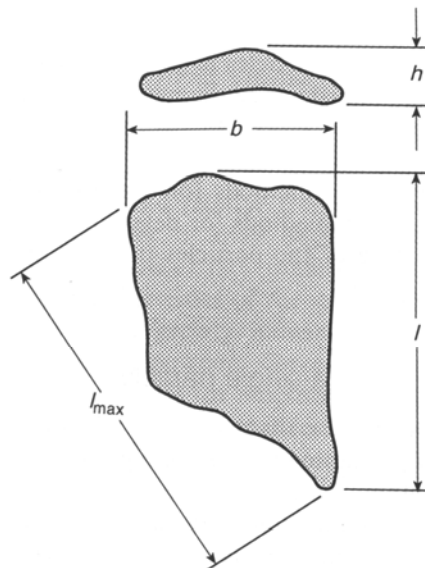

Figure 5.1 Meaning of h, b, l and l_{max} in the Heywood method. (From N. G. Stanley-Wood, *Enlargement and Compaction of Particulate Solids*, Butterworths (1983).)

In Fig. 5.3 the method of determining projected particle sizes is shown for a particle lying on a flat plane and viewed from above through a microscope. The Feret diameter is determined by the distance between two tangents of the particle drawn in the same direction. The Martin diameter is the length of the line (drawn in a constant direction) that divides the projected area of the particle into two equal areas. The Krumbein diameter is the longest line that can be drawn on the projected area in a constant direction. Finally, the Heywood diameter is the equivalent diameter of the circle that has the same area as the projected area. The Feret and Krumbein diameters are frequently used as simple measurement methods. It has also been found that the relationship between these representative diameters is that Feret diameter > Heywood diameter > Martin diameter, as shown in Fig. 5.4.

(a) Feret diameter

(c) Krumbein diameter

(b) Martin diameter
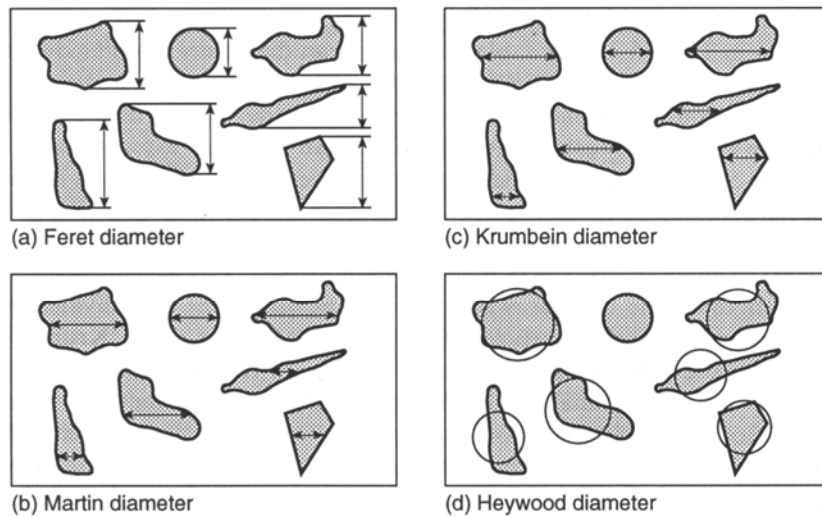
(d) Heywood diameter

Figure 5.3 Measurements of particle diameter from projected particle shape. (From S. Miwa, *Powder Sci. Eng.*, **11** (3) 50 (1979).)

Heywood diameter

Martin diameter

Feret diameter

Frequency (cm^{-1})

Particle size (mm)
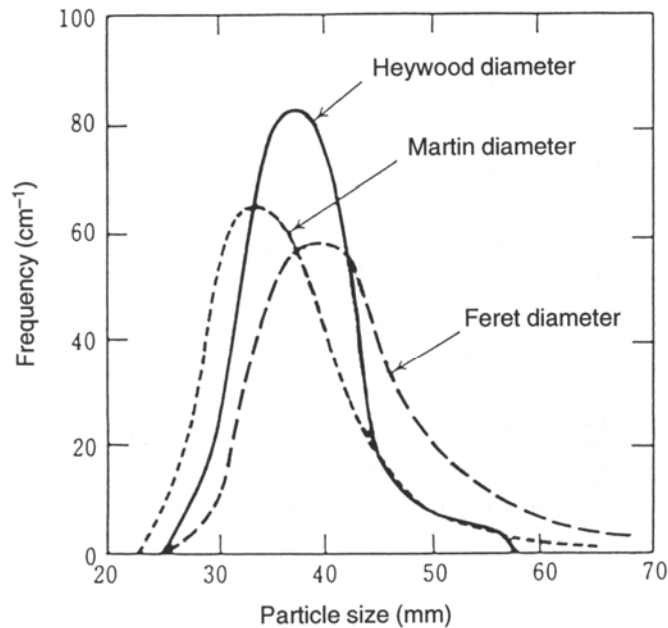
Figure 5.4 Comparison of different particle diameters obtained from projected particle shape. (From H. Heywood, *Chem. Ind.*, **56**, 149 (1937).)

Shape indices

A shape index and a shape coefficient are generally used to express particle shape in numerical terms; the index indicates a shape itself by the numerical value, whereas the coefficient relates to a particle shape factor found through the behaviour of the powder. The calculation of a shape index may be carried out by reference to a related object for the measurement, which is then applied to the expression for the shape index. For example, a length degree (length ratio), flatness and Zingg index are often used as shape indices. These indices are calculated from the following equations by using the width b, length l and thickness h:

$$\text{length degree (ratio)} = \frac{\text{long} - \text{axis diameter}}{\text{short} - \text{axis diameter}} = \frac{l}{b}$$

$$\text{flatness} = \frac{\text{short} - \text{axis diameter}}{\text{thickness}} = \frac{b}{h}$$

$$\text{Zingg index} = \frac{\text{length degree}}{\text{flatness}} = \frac{lh}{b^2}$$

One of the simplest definition of particle shape is that due to Wadell (1932), who defined sphericity, ψ, as

$$\psi = \frac{\text{surface area of sphere having same volume as particle}}{\text{surface area of particle}}$$

$$= (d_v/d_s)^2$$

Clearly, $\psi \leqslant 1$.

Sampling

Only very rarely is it possible to perform a size analysis on the entirety of the powder of interest. The aim of sampling is to obtain a fraction which is representative of the whole.

Allen (1996) states the 'golden rules' of sampling as

(a) a powder should always be sampled while in motion;
(b) it is better to take the whole of the powder for a short time than some of the powder for a longer time.

The enemy of good sampling is *segregation* (see Williams, 1990) which is the word used to describe the separation of particles due to differences in physical properties such as shape and density. One of the most common forms of segregation occurs when particles are tipped onto surfaces or into bins and the coarser particles tend to roll down the sloping sides of the tip, leaving a greater concentration of fine particles near the centre. Methods and devices for reliable sampling in these and other circumstances are given by Allen (1996). When obtaining a small sample for analysis, it is advisable to use a device such as a 'riffler' to divide the bulk into many smaller samples, and to further subdivide these samples by the same technique until a sufficiently small sample is obtained.

An interesting method for describing the roughness of a particle profile relies on the use of *fractal geometry*, and is entertainingly explained by Kaye (1989), who is largely responsible for popularising the technique. One might imagine 'stepping' around a particle profile using a pair of dividers, as shown in Figure 1.12, in order to measure the length, P, of its perimeter. If the 'step length', λ, is now decreased and the operation repeated, P will, in general, be larger, as smaller details of the profile can now be detected. In fact, as λ decreases, $P(\lambda)$ increases without limit, which is sometimes called the 'coastline of Britain problem', reflecting the geographical origins of the subject. It is sometimes the case that

$$P(\lambda) = k\lambda^{(1 - \delta)}$$

where δ is the so-called 'fractal dimension', which takes a value between 1 for a perfectly smooth line and 2 for an infinitely re-entrant (or 'space-filling') line. A plot of log P versus log λ enables δ to be obtained. In practice, the utility of this approach is limited by the fact that for real particle profiles δ is not often constant,
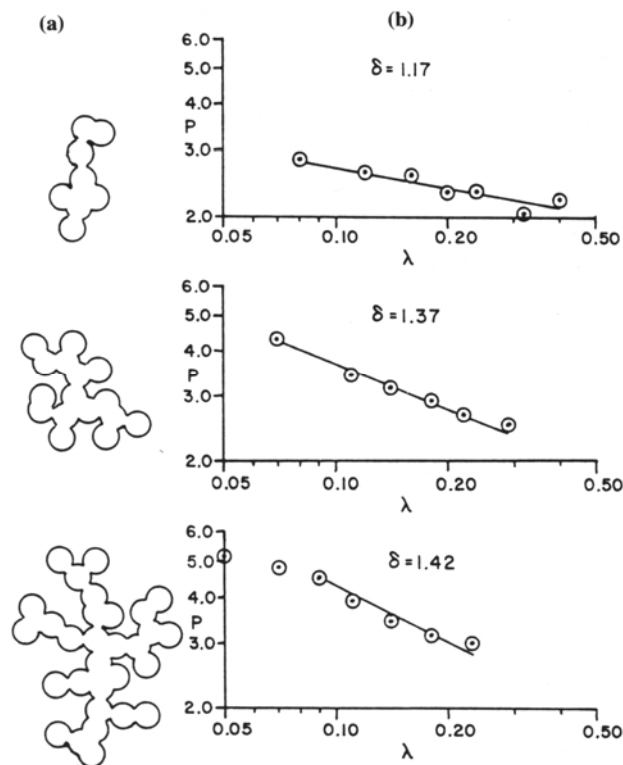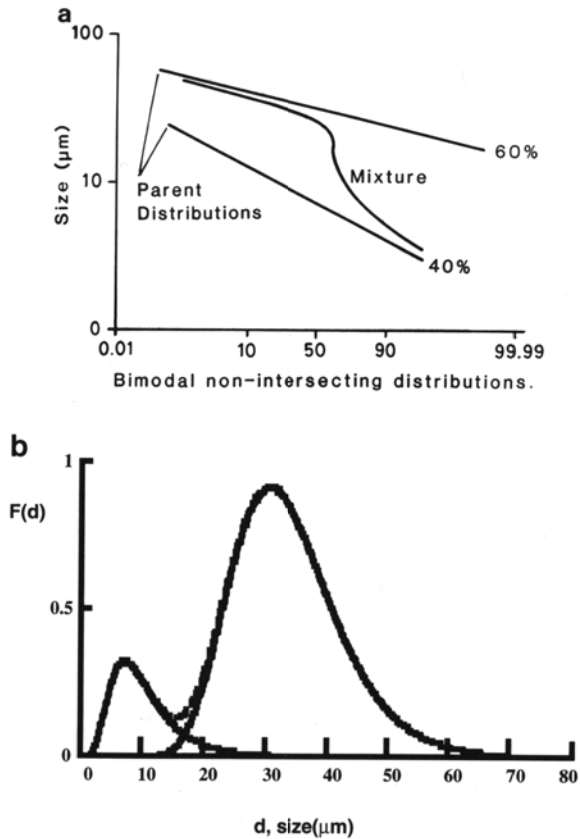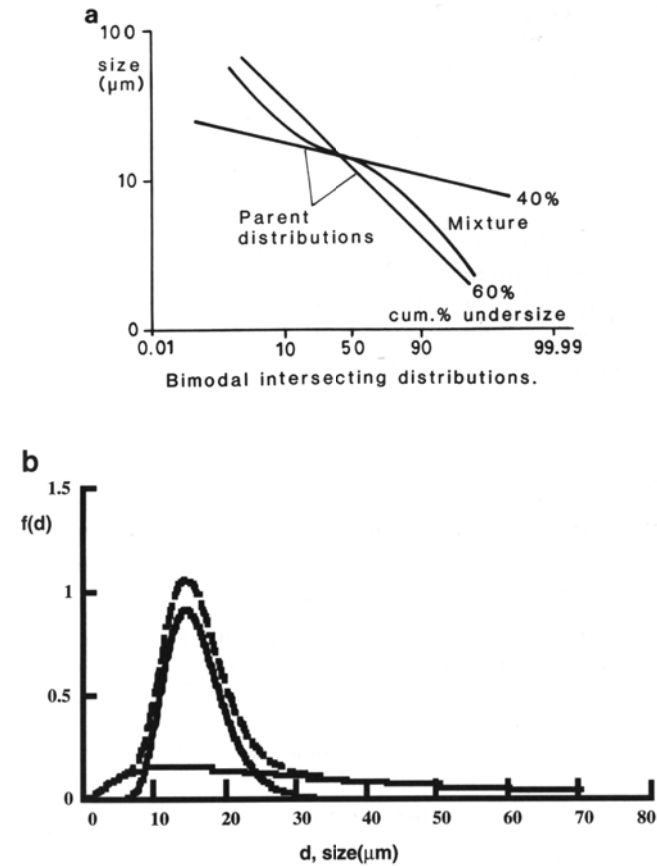

Figure 1.12 Examples of fractal plots (Kaye, 1989).

FIGURE 2.13 Mixing two size distributions, bimodal nonintersecting distributions: (a) linearized log-normal plot, (b) relative % versus size. Taken from Figures 4.14 and 4.15 in Allen [1].

FIGURE 2.14 Mixing of two size distribution–mono modal intersecting distributions: (a) linearized log-normal plot, (b) relative % versus size. Taken from Figures 4.16 and 4.17 in Allen [1].

Blending powder samples