6
Determination of Physical Properties of Fine Particles, Nanoparticles and Particle Beds

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6.1 Introduction to Common Particle Properties

Process design in particle technology is closely connected to the physical behavior of disperse systems. Knowledge of the physical properties is of vital importance for understanding and optimization of processes and operations. A disperse system consists of individual particles whose physical properties have to be characterized as precisely as necessary. In process engineering such properties are called granometric properties. Considering particulate solids as the material most commonly produced in particle technology, there is in many cases a very complex influence of the individual particle characteristics on the behavior of the population as a whole, for example flow, compression and permeation behavior of particle beds.

In this context, particle size analysis is an important issue in particle processing and product handling of fine (d < 100 μm), ultrafine (d < 10 μm) and nanosized (d < 0.1 μm) particles. Experimental determination appears to be easy, but especially for ultrafine- and nanosized dispersed systems one should take into account critical aspects arising, for example from shape, surface interactions, concentration, and homogeneity of the particles. Likewise, experimental techniques available for particle sizing, for example image analysis, electron microscopy, light scattering, laser diffraction, and ultrasonic methods, use different physical theories as their basis (see Section 6.2).

Assemblies of individual particles with a diameter d (spherical shape is often the basic assumption of the measurement method) can be described mathematically with the help of cumulative particle size distributions as the particle size frequency distribution, and the index r denotes the quantity measured (e.g. number- or mass-based distributions).

\[
Q_r(d) = \frac{d_{\text{max}}}{d_{\text{min}}} \int_{d_{\text{min}}}^{d_{\text{max}}} q_r(d) d(d)
\]  

(6.1)
Herein,

\[ q_r(d) = \frac{dQ_r(d)}{d(d)} \]  

(6.2)

The cumulative particle size distribution \( Q_r(d) \) is normalized to a maximum value of 1, but the particle size frequency distribution has to be determined in the unit per length, for example \( \mu m^{-1} \).

Physical properties, such as specific surface area, internal particle porosity, and pore size distributions of particles and agglomerates, are closely related to the particle size. The most commonly used experimental technique is the gas (nitrogen, helium) adsorption method (BET method). There is a series of other physical properties which depend on particle size, for example probability of particle breakage, strength and the elastic-plastic contact behavior. Here, impact tests are used to determine the particle restitution coefficient. Other properties result from the interaction between the surface and volume forces, for example adhesion and dispersion or the tendencies to agglomerate and to disperse. Related experimental techniques are the centrifuge method or atomic force microscopy (AFM). Granulometric properties also include the determination of different particle densities, for example solid particle density measured by helium pycnometry, as well as pore size distributions by porosimetry (Section 6.3).

The physical properties of packed and moving beds of particulate solids are not only connected to the characteristics of the individual particles, but also to the properties of the particle assembly as a whole. In practice, the behavior of particle beds can be very complex, that is there is a variety of interactions, and complicated because of the extremely large particle number of fine powders. The main features of particle beds are, for example bulk and tapping density, rheological behavior of suspensions, flow and compression behavior of powders. These “properties” should be understood as material or “constitutive” functions, which depend on other material properties, such as particle size, surface interactions, fluid properties within voids, and ambient conditions like pressure. Examples are the elasticity, yield stress, internal friction, flowability, compressibility and fluidizability of powders, but also the viscosity of suspensions and pastes, and the mechanical flow behavior of filter cakes. The main experimental techniques to investigate these “constitutive functions” are various shear tests presented in Sections 6.4 and 6.5.

6.2
Analysis of Particle Size Distribution

6.2.1
Image Analysis by Optical and Scanning Electron Microscopy

The most important feature of particulate systems is the particle size. Obvious tools to measure size are optical, electron and scanning probe microscopes. In optical and electron microscopy the principles of diffraction, reflection and refraction of radiation
are used; the goal is to produce a magnified visual image of an object too small to be seen with the naked eye. Concerning optical microscopy there are many modifications in addition to the ordinary light microscope, for example fluorescence microscopy, polarized light microscopy, near-field optical microscopy, and so on.

6.2.1.1 Optical Microscopy
The ability to resolve fine sample details is most relevant for the performance of a microscope. In this connection, the physical properties of light and the materials used for lenses are important. The resolution ability is the minimum distance at which two features of an object can be separated optically. According to Eq. 6.3 the minimal distance \( l_s \) depends on the wavelength of the incident light \( \lambda \) and the numerical aperture \( A \) of the optical system.

\[
l_s = \frac{0.61 \lambda}{A} = \frac{0.61 \lambda}{n \sin \varphi}
\]  

Resolution is usually evaluated for the wavelength of green light, \( \lambda = 550 \text{ nm} \), that corresponds to the maximum sensitivity of the human eye. Thus, due to diffraction, an optical microscope is limited physically to a resolution of around 0.2 \( \mu \text{m} \). Generally, the technique of optical microscopy is applied down to a resolution of about 1.0 \( \mu \text{m} \). Visual methods offer major advantages for users since the particles can actually be seen. However, sample preparation is one of the critical steps involved. The samples must be dispersed to create clear images of the particles. Visual techniques are often more convenient for particle shape analysis than for particle size determination (Davidson and Abramowitz, 1999).

6.2.1.2 Electron Microscopy
If nanoscaled particles need to be visualized (size is about from 1 to 100 nm), transmission electron microscopy (TEM) can be used effectively. In general, the conventional TEM is quite similar to a light microscope. A beam of electrons is transmitted through the sample; an image is formed, magnified, and directed to a screen, or is detected by a sensor such as a CCD camera. As the de Broglie wavelength of an electron is much smaller than the wavelength of visible light, the resolution limit of TEM is much smaller than 1 nm. In scanning transmission electron microscopy (STEM), an electron beam is focused on a small spot and is scanned over the sample surface. At each spot, the transmitted signal is recorded to build up an image. Problems with TEM microscopy arise from difficulties in getting a sample into a highly evacuated chamber, and from changes in the sample structure caused by interactions with the electrons and the vacuum.

In scanning electron microscopy (SEM), an electron beam is also passed point-by-point across the sample surface. In contrast to conventional TEM, scanning electron microscopy produces images by detecting secondary electrons which are emitted from the surface due to excitation by the primary electron beam (Amelinckx et al., 1997).
6.2.1.3 Image Analysis

Image analysis offers the possibility to measure both the size and the shape of particles using their two-dimensional projections. This approach is often considered as an ideal reference technique to validate other particle size distribution characterization methods, however, one should pay attention to practical limitations due to sample preparation and theoretical problems concerning the definition of particle size and shape.

Image analyzing systems capture a two-dimensional image of three-dimensional particles. The digital process requires the definition of gray tone limits to detect particles electronically in an 8-bit gray tone image, followed by conversion of the gray tone into a binary image (binarization). In this way, a value is assigned to every pixel of the original image between 0 (black) and 255 (white). The last step is particle sizing.

For simplicity, often only one single length is used to describe the particle size. However, there are many methods to define this length, unless the particle is a perfect sphere.

To represent particles that are not perfect spheres, the following geometrical characteristics are commonly used (compare with Section 5.2.2):

1. main dimensions of the particle,
2. statistical lengths, for example Feret, Martin and maximum chord length,
3. other geometrical features, for example equivalent circle diameter, projected areas, shape factors.

To get the statistical lengths, Fig. 6.1, the outline of the projection area of randomly orientated particles, is analyzed. Due to the variable particle orientation, it is necessary to define a direction of measurement. The Feret chord length $d_F$ is the distance between two parallel tangents to the particle outline perpendicular to the measurement direction. The Martin chord length $d_M$ is defined as the length of the line which bisects the projection area; the maximum chord length $d_S$ is the greatest distance inside the particle projection area in the measurement direction.

Further frequently used geometrical characteristics are the equivalent circle diameter $d$ and the sphericity $s_U$. The equivalent circle diameter is the diameter of a circle with an area that is equal to the projected area $A$ of the particle in a stable position. The sphericity compares the projection area $A$ of the real particle relative to the projection area of an ideally spherical particle; $U$ is the circumference of the real
particle. Equation 6.5 is the transformation of a more general, three-dimensional shape factor according to Wadell (1932) to planar, two-dimensional particle images.

\[ d = 2 \cdot \sqrt{A/\pi} \quad (6.4) \]

\[ \psi_u = 4 \cdot \pi \cdot \frac{A}{U^2} \quad (6.5) \]

More and more, particle structures are characterized by using the concept of the fractal structure to describe the contour as a characteristic of the shape and the roughness of particle. The particle outline can be reshaped by a polygon. The total length of the polygon \( L \) correlates with the length of a single polygon element \( \lambda \) according to the relationship

\[ L = k \lambda^{1-D} \quad (6.6) \]

For two-dimensional images, the fractal dimension \( D \) is a non-integer number with \( 1 \leq D \leq 2 \). In this context, a line has the fractal dimension \( D = 1 \), a square the fractal dimension \( D = 2 \).

Finally, the particle shape can be specified in terms of a Fourier series. In the relationship the distance \( r \) from particle edge points to the center of the area can be described in dependence on the angle \( \varphi \), running from \( 0^\circ \) to \( 360^\circ \). \( R \) is the radius of a circle with an area equal to the projected area. \( A_k \) are Fourier series coefficients that have to be calculated (Rumpf, 1990).

\[ \frac{r(\varphi)}{R} = \lim_{N \to \infty} \sum_{k=0}^{N} A_k \sin(k \varphi + \delta_k) \quad (6.7) \]

6.2.2 Laser Light Scattering and Diffraction for Dilute Particle Dispersions

The scattering phenomenon is based on the fact that electromagnetic radiation interacts with matter. This effect appears when a light ray hits an atom, molecule or particle. Different mechanisms of interaction are possible, dependent on size, wavelength of the incident light as well as other physical particle properties. Generally, the term scattering covers reflection and refraction as well as diffraction.

A well known example of light scattering is the Tyndall effect occurring when white polychromatic light passes through a solution of colloidal particles. Here, light scattering is observed at a right angle to the incident light as a blue shining light. Another example in nature is the blue color of the sky.

An exact theoretical treatment of the light scattering phenomenon is not simple (compare with Section 5.4.3). Only the Mie theory (Mie, 1908) gives a complete analytical solution of the Maxwell equations for spherical particles. Consequently, the Mie theory is widely used when dealing with scattering problems on the basis of the exact Maxwell equations. It embraces all possible ratios of particle size to the wavelength of incident light.
Several approximate approaches are described in the literature (Van de Hulst, 1981; Kerker, 1988), which are applicable, in contrast to the Mie theory, only for certain ranges of particle size in relation to the wavelength $\lambda$ of incident light.

1. The Rayleigh theory (Rayleigh, 1871) is valid for particle sizes ranging from about 0.5 nm to $\lambda/20$. It is assumed that an isotropic particle has only one scattering center; the scattered light is independent of this center. Electromagnetic waves polarize the scattering center thus inducing a Hertz dipole moment inside the particle. These oscillating electrons cause a secondary light emission.

2. The Rayleigh–Gans–Debye theory (Gans, 1925) is an extension of the Rayleigh approximation. Here, the electromagnetic wave of the scattered light is a superposition of single contributions resulting from infinitesimal volume elements of scattering centers inside the particle. The Rayleigh–Gans–Debye theory can be used for larger particles with sizes up to $\lambda/6$.

3. If the particle size is from about $4\lambda$ up to several mm, the application of the Fraunhofer theory is possible. Here, the interaction of the particle with light can be explained with the help of the classical laws of optics.

The scattering of light in gases was first treated quantitatively by Rayleigh (Rayleigh, 1871) to explain the blue color of the sky and the red color of the sunset. He observed that the intensity $I$ of the scattered light correlates with the wavelength $\lambda$ ($I$ proportional to $\lambda^{-4}$). A shorter wavelength – blue light – gives a more intense scattered light. The intensity $I$ of the scattered light depends on the scattering angle $\theta$, the interaction between particles, and the possibility to polarize them.

For one small isotropic particle that scatters light of incident intensity $I_0$ and wavelength $\lambda$, the scattering intensity $I$ at a distance $l$ from the scattering source and the angle $\theta$ between the incident and detected intensity will be given for polarized light by

$$\frac{I}{I_0} = \frac{\sin^2 \theta}{l^2} \cdot \frac{16\pi^4}{\lambda^4} \alpha^2,$$

and for non-polarized light by

$$\frac{I}{I_0} = \frac{1 + \cos^2 \theta}{l^2} \cdot \frac{8\pi^4}{\lambda^4} \alpha^2 \quad (6.9)$$

Here, $\alpha$ is the polarizability of the particle; it is assumed that $\alpha$ is proportional to the particle volume, with the consequence that the intensity $I$ of scattered light is proportional to $d^6$, $d$ being the particle size. Note, that every particle generates scattered light.

Strictly speaking, Eqs. 6.8 and 6.9 are only valid for ideal gases. However, it is possible to modify both equations in a way that scattering in dilute suspensions of particles can be specified in detail. Here, it is not the polarizability $\alpha$ of the particle that is important for the scattering phenomenon, but local and temporal density fluctuations of the polarizability $\alpha$ in a volume element of the suspension, caused by
fluctuations in the particle concentration $C_s$ (theory of Einstein and Smoluchowski about density fluctuations; Smoluchowski, 1908; Einstein, 1910).

In the static light scattering experiment, the physical framework is represented by the Rayleigh–Debye equation (Einstein, 1910; Rayleigh, 1910)

$$\frac{KC_s}{R_0} = \left( \frac{1}{M_W} + 2BC_s + \ldots \right) \frac{1}{P(\theta)}$$  \hspace{1cm} (6.10)

Here, $M_W$ denotes the weight averaged or apparent molecular mass of the particles that characterizes their sizes, $C_s$ the particle mass concentration, and $B$ the so-called second virial coefficient reflecting the particle–particle interactions for non-ideal systems. $R_0$ is the so-called Rayleigh ratio (from Eq. 6.9 for non-polarized light)

$$R_0 = \frac{I}{I_0} \frac{1}{V} \frac{l^2}{1 + \cos^2 \theta}$$  \hspace{1cm} (6.11)

The Rayleigh ratio includes the scattered light intensity of the suspension $I$, the incident light intensity $I_0$ (here, both intensities are excess intensities reduced by the background scattering of the suspension medium) as well as the scattering geometry (distance from scattering source to detector $l$, scattering volume $V$ for the instrument). The optical constant $K$ embeds the scattering ability of the particle suspension; $K$ includes the wavelength of the incident light $\lambda$, the refractive index of the suspension medium $n_0$ as well as the differential refractive index increment $\left( \frac{dn}{dc_s} \right)$ – the change in the refractive index $n$ of the suspension as a function of the change in particle concentration $C_s$. $N_A$ is Avogadro’s number. For many systems the differential refractive index increment is available in the literature (Brandrup and Immergut, 1999); while for new combinations it can be measured by the use of a differential refractometer. Note that a difference in the refractive indices of the suspension medium and the particle is a prerequisite for scattering.

$$K = \frac{2\pi^2 n_0^2}{N_A \lambda^2} \left( \frac{dn}{dc_s} \right)^2$$  \hspace{1cm} (6.12)

Small particles ($d < \lambda/20$) have an isotropic scattering behavior, the form factor is $P(\theta) = 1$. The graphical plot of Eq. 6.10 is $KC_s/R_0$ vs. $C_s$, the so-called Debye plot. Here, the $y$-axis intercept is the reciprocal apparent molecular mass $M_W$; the slope of the graph, $2B$, gives the second virial coefficient $B$.

For larger particles ($d > \lambda/20$) having an anisotropic scattering behavior, the form factor or intraparticle structure factor $P(\theta)$ has to be used to correct the angular scattering dependence of the scattering intensity of the sample. Thus, Eq. 6.10 represents a function of the particle mass concentration $C_s$ and the scattering angle $\theta$. In Fig. 6.2, a commonly used evaluation approach – the so-called Zimm plot – is shown, plotting $KC_s/R_0$ against $\sin^2(\theta/2) + kC_s$, where $k$ is an arbitrary constant chosen to spread the experimental data and make graphical extrapolations easier (Zimm, 1948). The reciprocal apparent molecular mass $M_W$ can be determined from the intercept point on the $y$-axis. From the grid in Fig. 6.2, two types of curves are obtained, one by connecting the experimental points with the same scattering angle $\theta$.
by extrapolating to $C_s \to 0$, and the other by connecting the experimental points at the same concentration and by extrapolating to $u \to 0$. Extrapolation at the scattering angle $u = 0$ to $C_s \to 0$ generates a line with a slope $2B$ yielding the second virial coefficient $B$; extrapolation at the particle concentration $C_s = 0$ to $u \to 0$ generates a line with a slope yielding the form factor $P(u)$ (Guinier, 1939) with

$$P(u) = 1 + \frac{4\pi n^2 d_g^2}{\lambda^2} \sin^2 \left( \frac{\theta}{2} \right)$$

(6.13)

$P(u)$ is connected to the square of the diameter of gyration, $d_g$, where $d_g$ is defined as twice the radius of gyration $r_g$.

Thus, the following set of parameters is accessible through static light scattering: (i) the apparent molecular mass $M_W$, (ii) the radius of gyration $r_g$ and (iii) the second virial coefficient $B$.

The prerequisite of the scattering processes already considered here is that the frequencies of the incident and the scattered light are the same (elastic scattering process). However, when observing scattering particles in liquids, it is found that there is a remarkable frequency broadening of the scattered light compared to the incident monochromatic laser beam. The mean frequency has been unchanged. These are so-called quasi-elastic scattering processes; line broadening results from Brownian diffusion of the scattering particles due to collisions with liquid molecules.

Quasi-elastic light scattering (QELS) is a commercially well established laser light scattering method, widely used in the single particle scattering regime to observe the dynamic behavior of nanoscaled systems (Pecora, 1985). Synonyms used are photon correlation spectroscopy (PCS) or dynamic light scattering (DLS).

The quasi-elastic frequency line broadening results, as mentioned above, from thermal fluctuations of the nanoparticles. Simply considered, this corresponds to a so-called Doppler shift. On the one hand, it is possible to measure the frequency

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**Fig. 6.2** Zimm plot to determine (i) the apparent molecular mass $M_W$; (ii) the diameter of gyration $d_g$ and (iii) the second virial coefficient $B$ from static light scattering experiments.
broadening by interferometry. The quasi-elastic scattering signal matches a Lorentz curve; the width of the curve correlates with the self-diffusion coefficient of the particles. The experimentally possible frequency resolution is about $10^{11}$ Hz, compared with a smaller line broadening for slower diffusion processes in pure liquids of about $10^6$ Hz. On the other hand, modern instruments measure intensity fluctuations of the scattered light. These intensity fluctuations are the result of interferences of scattered light coming from the particle diffusion; fluctuation time ranges from about microseconds to milliseconds. The applied measurement procedure first aims to gain the intensity of fluctuations quantitatively and secondly for result interpretation, to calculate the particle size. One option is to use an autocorrelation function.

The autocorrelation function correlates the scattered light intensity $I(t)$ with the intensity $I(t)$:

$$G^2(t, t + \tau) = \left< I(t) \cdot I(t + \tau) \right> = \lim_{\tau \to \infty} \int_0^\tau I(t) \cdot I(t + \tau) dt$$

(6.14)

Simply speaking, the correlation of the local particle arrangement at a starting time $t$ is compared with that arrangement at a later time $t + \tau$. Here, the brackets $\left< \right>$ mean a summation (integral) of the intensity products measured at different times; $\tau$ is the correlation or sample time. As dynamic light scattering has a stochastic nature $G^2(\tau)$ represents an exponential decay. For interpretation, $G^2(\tau)$ has to be normalized to $g^2(\tau)$

$$g^2(t, t + \tau) = \frac{\left< I(t) \cdot I(t + \tau) \right>}{\left< I(t) \right>^2}$$

(6.15)

and converted into the autocorrelation function of the electrical field, $g^2(\tau)$

$$g^2(t, t + \tau) = 1 + |g^1(t, t + \tau)|^2$$

(6.16)
Assuming an idealized monodisperse particle size, $g^1(\tau)$ is a simple e-function,

$$g^1(t, t + \tau) = \exp(-\Gamma \tau) \quad (6.17)$$

where $\Gamma$ represents the characteristic decay rate; $\Gamma$ is related to the translational diffusion coefficient $D$ and scattering vector $q$,

$$\Gamma = D \cdot q^2 \quad (6.18)$$

$$q = \frac{4\pi n_0}{\lambda} \sin \left(\frac{\theta}{2}\right) \quad (6.19)$$

The reciprocal value of $\Gamma$ is the characteristic decay time $\tau_C$. The scattering vector $q$ is the difference between the wave vectors of the scattered and the incident light. The value of $q$ is constant for a given system, depending only on scattering angle $\theta$, the wavelength of the incident light $\lambda$, and the refractive index $n_0$ of the liquid.

The hydrodynamic particle diameter $d_{\text{H}}$ can be obtained by applying the Stokes–Einstein equation to

$$d_{\text{H}} = \frac{k_B T}{3 \pi \mu D} \quad (6.20)$$

where $k_B$ is the Boltzmann constant, $T$ is the Kelvin temperature and $\mu$ is the dynamic viscosity of the liquid. Note, that the particle size $d_{\text{H}}$ is assumed as sphere equivalent.

For practically relevant products, particle sizes are distributed. Since every particle size has its own characteristic decay rate, the auto correlation function $g^1(\tau)$ represents an integral function

$$g^1(t, t + \tau) = \int_0^\infty \exp(-\Gamma \tau) G(\Gamma) d\Gamma \quad (6.21)$$

Here, $G(\Gamma)$ is a normalized distribution function of the decay rates. The term $G(\Gamma)d\Gamma$ is proportional to the fraction of the light intensity scattered by particles with decay rates in the range $\Gamma$ to $\Gamma + d\Gamma$. Consequently, $G(\Gamma)d\Gamma$ is related to the particle size frequency distribution $q_0(d)$.

A problem arising here is to calculate the correct particle size distribution. A small change in the autocorrelation data leads to a dramatic change in the particle size distribution. Several mathematical approaches have been developed to solve this ill-posed numerical problem:

1. A simple algorithm is the cumulant method (Koppel, 1972). Here, a cumulant generating function has to be calculated in terms of the logarithmic autocorrelation function for a monodisperse particle size, leading to a linear graph. For a particle size distribution experimental data are fitted to a polynomial function. This leads to an average particle diameter (first moment of light intensity correlated particle size distribution) and to a polydispersity index, assuming a Gauss distribution.
2. In the multiexponential sampling analysis the autocorrelation function represents a sum of discrete exponential functions in a logarithmic distance with related amplitudes that can be fitted, for example by a non-linear least-square (NLLS) algorithm (Lawson and Hansen, 1974).

3. Likewise, the Contin analysis (Provencher, 1982) is an iterative method to solve the inverse Laplace transform. Here, the best particle size distribution is selected from a set of solutions assuming the best fit as well the simplest distribution.

   The dynamic light scattering is an excellent method for spherical particles with narrow distributions. Difficulties arise when both conditions are not fulfilled. Sample preparation is most important, because nanoparticles, liquid convection and coarse particle sedimentation may disturb the measuring procedure.

   For concentrated suspensions that show a multi-scattering behavior, an alternative approach is the NIBS (non-invasive back scattering) technology. The scattering volume of the sample is near the wall of the test cell to shorten the laser path through the suspension and to avoid multi-scattering behavior.

   Laser diffraction spectroscopy is a widely used technique in scientific and industrial applications to determine particle sizes from about 4 \( \lambda \) to several millimeters. The investigation of suspensions as well as of dry powders is of interest, sampling is possible off-line as well as on-line. Here, application of the Fraunhofer theory is possible, explaining the particle interaction with light by classical laws of optics. That means, diffraction occurs at the interphase of the particle and leads to interferences of the diffracted waves (see the principle of Huygens).

   For Fraunhofer diffraction on a spherical, absolutely opaque single particle, the relationships can be deduced: \( I \) is the intensity of the diffracted laser light, \( I_0 \) the intensity of the incident light, \( l_s \) the distance of the diffracting particle from the screen, \( \lambda \) the projection surface area of the particle, \( \lambda \) the wavelength of the incident light, \( J_1(\xi) \) the first order Bessel function, \( \theta \) the diffraction angle, and \( d \) the particle size.

   \[
   \frac{I}{I_0} \propto \frac{A}{\lambda^2} \left( \frac{2J_1(\xi)}{\xi} \right)^2
   \]

   \[
   \xi \approx \frac{\pi d}{\lambda} \cdot \sin \theta
   \]

   Due to the Bessel function in Eq. 6.22, about 84\% of the intensity of the diffracted light is found at the interference maximum of zeroth order (\( \theta \rightarrow 0 \)) of the diffraction pattern; the intensity \( I \) is proportional to \( d^4/l_s^2 \). Otherwise, at interference maxima of higher order intensities \( I \) is proportional to \( d^2/l_s^2 \).

   By analogy to diffraction at an optical slit, a diffraction pattern is generated behind particles. If diffraction occurs at spherical particles, concentric circles are observed. Near the particle, Fresnel diffraction occurs. The interference pattern is distance dependent, but far from the particle (\( l_s \gg d^2/\lambda \)) application of the Fraunhofer approximation is possible; these interference patterns become distance independent (for a particle of 1 mm this distance from the particle is about 1.6 m). For an assembly
of particles there is a superposition of diffraction light from each particle. This leads to uncertainty in the diffraction pattern.

To overcome these problems, in the instrumental implementation the diffracted as well the transmitted light is focused on a plane. Using a lens with a focal width \( f \) it is possible to transform the angle-dependent Fraunhofer diffraction of each particle into a local distance on the screen by the relationship

\[
D = \theta \cdot f
\]  

(6.24)

Here, \( D \) is the distance from the light axis on the screen and \( \theta \) the diffraction angle. This means that the image of the diffraction pattern of all particles is radially symmetric. Inserting Eqs. 6.23 and 6.24 into Eq. 6.22, with \( \sin \theta \approx \theta \) for small diffraction angles, the intensity of the diffracted light \( I(D,d) \) is obtained as

\[
I(D,d) \approx \frac{\pi d^2}{4 \lambda f} \left( \frac{2j_1(\xi)}{\xi} \right)^2
\]  

(6.25)

with

\[
\xi \approx \frac{\pi d D}{\lambda f}
\]  

(6.26)

Considering now an assembly of \( N \) particles, there is a superposition of the Fraunhofer diffraction pattern \( I(D,d) \) of each particle; intensity \( I(N,D,d) \) is proportional to \( N \), where \( q_0(d) \) is the particle size frequency distribution.

\[
I(N,D,d) = N \int_{d_{\text{min}}}^{d_{\text{max}}} I(D,d) \cdot q_0(d) \, d(d)
\]  

(6.27)

In the instrumental implementation, the experimental intensity distribution \( I(N, D,d) \) has to be transformed into a particle size frequency distribution \( q_0(d) \).

For particle systems not meeting the Fraunhofer approximation \( (d > 4 \lambda) \), Mie theory is implemented in modern laser diffraction instruments. Mie theory can predict scattering intensities for all particles, small or large, transparent or opaque. It allows phenomena of primary scattering from the surface of the particle and secondary scattering caused by light refraction within the particle to be included. However, extra data of material properties are needed, for example light absorption coefficient, difference of refractive indices of particle and fluid. According to ISO 13320, Mie theory offers the best general solution for particles smaller than 50 \( \mu \)m (Born and Wolf, 1993).

For very fine particles the forward diffraction is quite low, with the consequence that it is impossible to detect the diffracted light by ring detectors. Modern instruments, for example Mastersizer 2000 (Malvern Instruments Inc.), have additional detectors, see Fig. 6.4. Thus, diffracted light can be measured by so-called forward and large angle detectors. In addition, the back-scattered light intensity is used to determine particle size distributions. A further improvement of resolution for very fine particles is possible by using lasers with a blue light source \( (\lambda = 466 \text{ nm}) \) instead of a red light source \( (\lambda = 633 \text{ nm}) \).
6.2.3 Ultrasonic Methods for Dense Particle Dispersions

Ultrasonic techniques give an extraordinary tool to characterize concentrated particle dispersions. An acoustic spectrometer measures the attenuation of ultrasound, the propagation velocity of this sound and/or acoustic impedance, depending on the instrument. The acoustic signal contains information about the particle size distributions, volume fraction and structural and thermodynamic particle properties.

6.2.3.1 Acoustic Attenuation Spectroscopy

Acoustic spectroscopy uses sound wavelengths in the range from 15 μm to 1.5 mm, corresponding to frequencies from 1 to 100 MHz. The acoustic behavior of dispersions is based on several attenuation phenomena. Besides material-specific contributions of the particles and the liquid (inner absorption loss), interactions between liquid and solid phases have to be taken into account.

An important reason for attenuation is scattering; this phenomenon includes diffraction and reflection on particles that disturb the straight propagation of sonic waves. Other reasons for attenuation are thermal and viscous effects caused by pulsation and oscillation of particles. The pulsation effect is due to local pressure fluctuations in the fluid leading to local dispersion density and particle concentration changes. Viscous losses are due to relative movement between oscillating particles and fluid. Additionally, at high particle concentration there are structural losses as a result of interactions of the dispersed particles (adhesion and electrostatic double layer repulsion), water dipoles and directional hydrogen bonds (cluster formation). Viscous attenuation is dominant.

For the experimental determination of particle sizes, the main input parameters needed are the density of the suspension and the volume fractions of each phase. For systems which have a low density difference between particles and fluid, thermophysical properties, for example thermal conductivity, specific heat capacity, thermal expansion coefficient, are required additionally. Usually, attenuation is more sensitive to particle size than the propagation velocity of sound. Currently approximations used for calculating the particle size from attenuation data are based on scattering or
coupled phase approaches. A comparison of these theories is quite complex, the validity of different models depends on the investigated system. Generally, the determination of the attenuation spectrum as well as the calculation of particle size distributions is quite sophisticated, however, today it can be conducted with a high precision and accuracy. In many cases, it is now possible to determine particle sizes in suspensions experimentally for particle volume fractions $\varphi_s \leq 50\%$ (Dukhin and Goetz, 2004).

6.2.3.2 Electrokinetic Sonic Amplitude Spectroscopy

Electro-acoustics is another ultrasound-based technique, applied for colloidal particles having, normally, electrochemical double layers. Here, it is possible to obtain information about the particle size as well as about the zeta-potential. In electro-acoustics, acoustic and electric field effects are coupled. There are two ways to generate this phenomenon, depending on which field is the driving force and what the response is. In the electrokinetic sonic amplitude (ESA) technique, the electrical field is the driving force, followed by an acoustic response; in the colloid vibration potential (CVP) or colloid vibration current (CVI) techniques the acoustic field is the driving force, followed by an electric response.

The ESA effect arises because the colloidal particles are driven away from or towards the electrodes, causing a local compression wave of the liquid around them. The strength of the resulting ESA signal is influenced by the density difference between the particle and the fluid and by the volume fractions. It also depends on the zeta-potential, since this affects the particle velocity in the electrical field. The particle velocity has a time lag to the electrical signal, indicating the inertia or mobility of the particle and thus the size of the particle. Consequently, determination of the particle size and the zeta-potential from the ESA signal requires the calculation of the dynamic mobility spectrum,

$$\text{ESA} = A(\omega) \cdot \varphi_s \cdot \frac{\Delta \rho}{\rho} \cdot Z \cdot \mu_D$$ (6.28)

Here, ESA denotes the measured ESA signal, $\mu_D$ the dynamic particle mobility. $A(\omega)$ is the calibration function depending on the frequency $\omega$ of the electrical field; $\varphi_s$ is the particle volume fraction, $\Delta \rho$ the density difference between particle and fluid, $\rho$ the fluid density and $Z$ the acoustic resistance. According to O’Brien et al. (1995) the dynamic mobility $\mu_D$ is related to the zeta-potential and the particle size,

$$\mu_D = \frac{2 \varepsilon \xi}{3 \mu} G(d, \omega) \cdot (1 + f)$$ (6.29)

This correlation is valid for a spherical particle with a thin double layer. In Eq. 6.29, $\varepsilon$ refers to the permittivity of the fluid; $\mu$ is the dynamic viscosity and $\xi$ the zeta-potential. The $G(d, \omega)$ factor represents the effect of the inertia on the dynamic mobility. The $(1 + f)$ factor in Eq. 6.29 is proportional to the tangential electrical field at the particle surface. It depends on, for example the permittivity of the particle and the surface conductance of the double layer.
For a particulate system with \(N\) particles the experimental dynamic mobility represents an averaged or mean value of all particles (first statistical moment), herein referred to as \(\langle \mu_D \rangle\). It can be written formally in an integral equation

\[
\langle \mu_D \rangle = \frac{1}{d_{\text{min}}} \int_{d_{\text{max}}} \mu_D(d, \xi, \varphi) \cdot q_0(d) \, d(d)
\]

(6.30)

\(q_0(d)\) being the particle size frequency distribution. Here, again, the problem is the numerically poorly conditioned equation. A small error in the measurements leads to a substantial error in the particle size frequency distribution. But, nevertheless, in our opinion, it seems that the ESA technique gives more accurate results for higher concentrations than ultrasonic attenuation spectroscopy.

### 6.3 Measurement of the Physical Properties of Particles

#### 6.3.1 Solid Density Analysis by He-Pycnometry

**6.3.1.1 Introduction**

In technical processes the density of the material provides not only a feature of quality that keeps a process under control but also reveals important information about the nature and structure of the final product.

The true or solid density of a powder equals the mass of a quantity of the solid material divided by the volume that this material occupies

\[
\rho_s = \frac{m_s}{V_s}
\]

(6.31)

Thus, the density can be determined by measuring both the mass and the volume of the particles (Webb and Orr, 1997). The mass can be measured by using a balance with suitable accuracy.

However, the measurement of the volume is the actual problem because shapes and geometrical structures of particles frequently differ. According to both surface shape and internal structure, there are different definitions of the solid volume of a powder. Only for a non-porous and perfect sphere can the volume be calculated easily and directly after measuring its diameter.

In many cases, coarse and fine particles have both manifold irregularities of the surface and their internal structure like slits, fissures and pores. The solid density (also termed true, absolute or skeletal density) is then characterized by the mass and the volume of the solid after exclusion of all pores. This means that all internal voids (pores, cracks, slits etc.) connected to the surface should be excluded to fulfill the typical volume definition as “the space occupied by an object”. In the case of pores enclosed by solid matter that have no access to the surface, the pore volume is
included because there is no realistic chance to detect it. The accuracy and precision of the volume determination depend strongly on the sample preparation. Especially, the sample should be free of moisture and volatile substances. This can be ensured by intensive desorption, for example by heating under vacuum.

6.3.1.2 Volume Determination Using Gas Pycnometry

There are several methods to detect the volume of irregularly shaped particles. In this section the most common method, namely gas pycnometry, is explained.

In gas pycnometry, no open pores or other open internal cavities will count towards the volume of solids, so that the experimental volume determination leads to the true or solid density, which is a property of the material of the particles. There is no influence of the structure of the particles. The method is based on the fact that the used gas is displaced by the solid object. In a gas pycnometer the displacement is detected by a pressure change. As already pointed out, the volume of solid matter can be determined independently of the surface structure and the existence of open pores of any size or shape.

A pycnometer has a chamber of precisely known volume that is used to determine an unknown volume of matter. Though pycnometers can operate using different media, the gas pycnometer is the most commonly applied instrument. If using helium, the gas penetrates into open pores larger than 0.1 nm. Thus, almost all pores will be detected. If a liquid is used it can happen that only a fraction of the pores will be filled by penetration of the liquid, depending on the particle and liquid properties (Fig. 6.6).
Incomplete wetting leads to a wrong skeletal volume determination. Hence, in order to find the true value of the solid volume helium is preferred. The principle of gas pycnometry (Micromeritics Instrument Corporation, 1992) is based on volume measurement by using the ideal gas law, so that the displacement of gas by a solid matter can be detected by the pressure change. Sample and reference chambers (Fig. 6.7) are pre-calibrated to quantitatively determine the volume of an unknown sample. The volumes of the sample and reference chambers must be known.

The measurement procedure of the unknown sample volume is performed in the following way. After weighing, the sample is placed into the sample chamber. Then:

1. A helium atmosphere is created inside the instrument to rinse the sample intensively.
2. After pressurizing the sample chamber, the attained stabilized pressure $P_1$ is measured.
3. Subsequently, by expansion of this gas into a precisely calibrated volume (reference chamber) the pressure drops to pressure $P_2$.

Both pressure $P_1$ and pressure $P_2$ have to be monitored in an equilibrated state. Assuming a constant temperature, the calculation of the sample volume is performed by

$$P_1 \cdot (V_{S-Ch} - V_{Sample}) = P_2 \cdot (V_{S-Ch} + V_{Ref} - V_{Sample}), \quad (6.32)$$

(S-Ch: sample chamber, Ref: Reference chamber) which leads to calculation of the volume of the sample, as

$$V_{Sample} = V_{S-Ch} - \frac{V_{Ref}}{P_2^2} \left( \frac{P_1}{P_2} - 1 \right) \quad (6.33)$$

The accuracy of gas pycnometry in the determination of solid volume is at least $\pm 0.2\%$ of the respective sample chamber volume. Moisture and volatile substances in the sample can contribute to pressure change and, thus, cause errors and instabilities. Pressure instabilities lead to a wrong determination.
6.3.2 Specific Surface Area by Gas Adsorption Method

6.3.2.1 Physical Principles
Gas adsorption on the outer surface and the pore walls of solids is a common phenomenon (Webb and Orr, 1997; Lowell and Shields, 1991). Adsorption on the outer surface is influenced by surface imperfections and irregularities. In the case of porous particles, these effects are superposed by effects of their internal structure, that is the shape and dimensions of the pores. Surface molecules interact with gas molecules by molecular interaction forces (Van der Waals forces), resulting in adhesion of gas molecules onto the solid surface. This is called physical adsorption. Physical adsorption is influenced by the interaction potential $U$ between the gas (adsorbate) and the surface (adsorbent), absolute temperature $T$ and pressure $P$ (see Fig. 6.8). Pressure means total pressure in a pure gas atmosphere and the partial pressure of the considered component in the case of a gas mixture.

The number or amount of adsorbed gas molecules can be expressed as

$$N_{ads} = f(P, T, U) \quad (6.34)$$

which reduces to

$$N_{ads} = f(P, U) \quad (6.35)$$

at constant temperature, and to

$$N_{ads} = f(P) \quad (6.36)$$

with a particular vapor at constant temperature ($U = \text{const.}, T = \text{const.}$).

Equation 6.36 is a general representation of the so-called sorption isotherm. Frequently, the amount of adsorbed species is expressed as a mass content related to the mass of the adsorbent, and it is plotted as a function of the relative pressure $P/P^*$ of the vapor phase. The adsorbate equilibrium pressure $P$ is normally related to the saturation pressure $P^*$. The gas is considered to be below its critical temperature and,

Fig. 6.8 Phases involved in gas adsorption.
therefore, condensable. Alternatively, the volume of adsorbed gas under standard conditions $V_{\text{STP}} \left(0^\circ\text{C}, 1.013 \text{ bar}\right)$, can be plotted on the ordinate (Fig. 6.9).

It has been found that measured adsorption isotherms can usually be divided into five different types (Fig. 6.10). Each of them reflects a typical adsorption behavior of the solid that may be correlated with the size of the pores (see Section 6.3.3).

- The type 1 curve is encountered with particles that are microporous (see Section 6.3.3). Their pore sizes are of the order of magnitude of the adsorbate molecule diameter (smaller than 2 nm). Overlapping potential forces in the pores result in condensation of the adsorbate that will fill up the pores. The adsorbed gas is essentially influenced by the geometrical shapes of the pores, especially at very low relative pressures.

- Type 2 isotherms are encountered for mesoporous particles with pore sizes from 2 to 50 nm. The adsorption of gas molecules takes place on the pore surfaces in
multiple layers. The number of adsorbed layers can increase at higher relative pressures and tend ultimately to apparent infinity.

- Type 3 curves indicate a behavior when the adsorbate interaction with an already adsorbed layer is stronger than the interaction between the solid surface and the adsorbate. The isotherm shape is convex with increasing relative pressure.

- Type 4 isotherms reflect in their upper part adsorption that occurs on particles with meso- or macro-pores (Section 6.3.3). With increasing relative pressure the elevated adsorbate uptake is caused by capillary condensation in such pores.

- Type 5 curves are encountered for particles that exhibit a small adsorbate–adsorbent interaction like in type 3 isotherms. Furthermore, the particles possess meso- or macro-pores that result in similar adsorption behavior to type 4 isotherms.

The well-established and standardized method of gas adsorption can contribute to the detection of surface irregularities and internal pore structures: In this way, it represents a powerful tool to characterize any powders. Especially, techniques have been developed that enable generation of important information about surface area, total pore volume and pore size distribution.

### 6.3.2.2 Surface Area Determination using the BET-Model

The BET-theory was developed by Brunauer, Emmett and Teller (Brunauer et al., 1938; Lowell and Shields, 1991). It provides the basis for a well-established method to calculate the surface area of powdered particles from measured adsorption data by using nitrogen gas at a temperature of 77 K. BET theory describes the adsorption of molecules on surfaces in multiple layers as a function of the relative pressures of the adsorbate in the gas phase. A major model parameter is the amount of molecules needed to cover the surface completely by a monomolecular layer, corresponding to the gas volume $V_{\text{mono}}$. The second parameter $C$ describes the adsorption behavior of the first layer of molecules; it increases exponentially with their adsorption enthalpy (bond energy of adsorbate molecules) and may be considered as constant for constant temperature. The model uses the strong assumption that subsequent molecular layers do not interact with the solid surface. With increasing relative pressure, more and more of these layers will form (typically, none of them will be fully occupied). For an infinite number of possible layers, the relationship between relative pressure $P/P^*$ and adsorbed amount of gas can be given in a linear form (Brunauer et al., 1938)

$$\frac{P}{V_{\text{ads}} \cdot (P^* - P)} = \frac{1}{V_{\text{mono}} \cdot C} + \frac{(C-1) \cdot P}{V_{\text{mono}} \cdot C \cdot P^*}$$  \hspace{1cm} (6.37)

which is typically valid for moderate relative pressures from 0.05 to 0.30. (For higher values of $P/P^*$ the theory needs to be extended to account for the finite size of the pores.)

The straight line corresponding to Eq. 6.37 is plotted in Fig. 6.11.
From this plot, the axis intercept
\[ a = \frac{1}{V_{\text{mono}} \cdot C} \]  
and slope
\[ b = \frac{C-1}{V_{\text{mono}} \cdot C} \]
can be determined to calculate the monolayer capacity.

Equations 6.38 and 6.39 lead to:
\[ V_{\text{mono}} = \frac{1}{a+b} \]  
\[ C = \frac{b}{a} + 1 \]

Based on the known cross-sectional area of nitrogen molecules \((A_{\text{N}_2} = 0.162 \text{ nm}^2)\),
the so-called BET-surface area,
\[ A_{\text{BET}} = \frac{V_{\text{mono}} \cdot N_A \cdot A_{\text{N}_2}}{V_{\text{mol}}} \]
can be calculated from the monolayer volume \(V_{\text{mono}}\), Avogadro’s constant \((N_A = 6.022 \times 10^{23} \text{ mol}^{-1})\) and the molar volume \((V_{\text{mol}} = 22.41 \text{ mol}^{-1})\).

For calculation of the BET surface area the adsorption isotherm needs to be measured as described above (multipoint BET method) to determine the quantity of nitrogen adsorbed in the monolayer. In some cases if the adsorption constant \(C\) exceeds 100, and therefore \(b \neq f(C) \gg a\), the experimental effort can be reduced by measuring the adsorbed amount only at a \(P/P^*\) value of 0.3 (single-point method) to get the monolayer volume.

Based on Eq. 6.41 for relatively high values of \(C\) the intercept \(a\) may be neglected as compared to the slope
\[ a = \frac{b}{C-1} \]
It is \((C - 1)/C \approx 1\) so that Eq. 6.37 becomes
\[
\frac{P}{V_{\text{ads}} \cdot (P^* - P)} \approx \frac{P}{V_{\text{mono}} \cdot P^*}
\] (6.44)
which leads to the following equation for calculation of the monolayer volume
\[
V_{\text{mono}} \approx V_{\text{ads}} \left(1 - \frac{P}{P^*}\right)
\] (6.45)

By using the single-point method the surface area is calculated again by Eq. 6.42.

Strictly speaking, the BET method is best applicable to particles whose adsorption isotherm is of type 2. Nevertheless, the approach can provide useful orientation and a basis for comparison between different products, even if the prerequisites of the BET theory are not fulfilled completely, that means also for other isotherm types.

6.3.3
Pore Size Distribution by Gas Adsorption Method

6.3.3.1 Introduction
In general, porosity is defined as the ratio of the volume of cavities to the total volume (that means the volume plus pore volume). According to the IUPAC convention (International Union of Pure and Applied Chemistry) pores of solids are classified depending on their diameter into micropores (< 2 nm), mesopores (from 2 to 50 nm) and macropores (> 50 nm), see Rouquerol et al. (1994).

Porous materials can also be distinguished by the structure of their pores. Various types of often encountered pores are illustrated in Fig. 6.12 (Rouquerol et al., 1994), namely:

1. Closed pores, totally isolated in the solid, without connection to the surface,
2. shallow pores resulting from irregularities of the outer surface of the particle,
3. open, bottle neck pores that may cause hysteresis of the adsorption curve,
4. open pores with only one end, described as blind,
5. funnel-shaped pores,
6. open pores that go through from one side of the particle to the other.

Fig. 6.12 Different types of pores in a solid particle.
The condensation of adsorbed gas molecules in pores is thermodynamically preferred. This effect is based on the overlap of attractive interaction potentials of the pores that leads to a stronger adsorbate bonding and gas condensation compared to the adsorption on plane surfaces. Specifically, condensation occurs first in small pores and proceeds in the larger pores as the amount of gas molecules in the environment increases or, in other words, as the gas pressure increases. Vice versa, desorption starts at large pores down to small pores which have a high bond capacity for condensed gas molecules.

6.3.3.2 Assessment of Microporosity

Generally it is observed that the adsorption behavior of gases is modified in micropores as compared to adsorption on a plane surface since the closeness of the pore walls is associated with an increase in the strength of the adsorbent–adsorbate interaction, especially at very low \( \frac{P}{P^*} \). Additionally, condensation effects are encountered which lead to complete filling of the pores at somewhat higher \( \frac{P}{P^*} \). This results in an adsorption according to the classical Langmuir isotherm (type I). For calculation of the micropore volume it is hence assumed that the micropores are completely filled with liquid adsorbate.

A frequently used method for calculation of the micropore volume was developed by Dubinin and Radushkevich (Webb and Orr, 1997). Their approach is based on the potential theory of Polanyi that describes the adsorption of pure gases in microporous materials. According to Polanyi theory each adsorbent possesses a characteristic adsorption potential \( E \) or adsorption enthalpy, that is bond energy of the adsorbate molecules. Consequently, the micropore volume filled by liquid adsorbate at the relative pressure \( \frac{P}{P^*} \) is a function of the molar adsorption potential \( E \), which is equivalent to the energy needed to transfer the molecules from the adsorbed to the gaseous state. In the case of \( T < T_{\text{critical}} \), Dubinin uses for the adsorption potential the expression

\[
E = R \cdot T \ln \left( \frac{P}{P^*} \right) \tag{6.46}
\]

that represents the characteristic property of the adsorbate and the adsorbent and reflects the so-called bond strength or affinity behavior of the particle surface–condensed gas interactions. Further, an affinity coefficient

\[
\beta = \frac{E}{E_0} \tag{6.47}
\]

is introduced that is a measure of adsorbability of different adsorbates to the adsorbent. Here, \( E_0 \) is the characteristic molar adsorption bond potential of standard vapor.

Dubinin and Radushkevich assumed that the dependence of the adsorbed volume on the adsorption potential can be expressed by the characteristic function

\[
V_{\text{ads}} = V_{\text{micro}} \cdot \exp \left[ -\frac{RT}{\beta E_0} \cdot \ln \left( \frac{P^*}{P} \right) \right]^2 \tag{6.48}
\]
which can be transformed into

\[ \ln V_{\text{ads}} = \ln V_{\text{micro}} - \frac{RT}{\beta E_0} \ln^2 \left( \frac{P^*}{P} \right) \]  

(6.49)

When plotting measured values of the adsorbed volume as \( \ln V_{\text{ads}} \) versus \( \ln^2 \left( \frac{P^*}{P} \right) \), as in Fig. 6.13, often a linear segment of the curve with slope \( \frac{RT}{\beta E_0} \) can be observed. From this segment the micropore volume \( V_{\text{micro}} \) can be estimated by extrapolation. For evaluation of \( V_{\text{micro}} \), adsorption data in the relative pressure range \( 10^{-4} < \frac{P}{P^*} < 0.1 \) should be used.

6.3.3.3 Assessment of Mesoporosity

Capillary condensation is observed especially in so-called meso- and macro-pores (Fig. 6.14). By steadily increasing the relative pressure capillary condensation takes place first in relatively small pores and then proceeds to larger ones. If the adsorbent contains no macropores, it is observed that the isotherm comes to a plateau at high relative pressure \( P/P^* \). This state corresponds to a completely filled state of the mesopores. Thus, the calculation of the total meso-pore volume is based on the fact that the

Fig. 6.13 Evaluation of adsorption data by the method of Dubinin–Radushkevich.

Fig. 6.14 Scheme of capillary condensation.
vapor adsorbed at the plateau (at \( P/P^* \approx 1 \)) has filled the meso-pores in the normal liquid state. Mesopore volume calculation is usually performed by means of the Kelvin equation in its general form

\[
r_c = -\frac{2 \cdot \sigma_{lg} \cdot \tilde{V}_{mol} \cdot \cos\delta}{RT \cdot \ln(\frac{P}{P^*})}
\]  

(6.50)

where \( r_c \) is the radius of the meniscus, \( \sigma_{lg} \) is surface tension (i.e. bond potential per unit surface), \( \delta \) is the contact angle and \( \tilde{V}_{mol} \) is the molar volume of the liquid condensate.

When using nitrogen, Eq. 6.50 can be transformed to

\[
r_c = -\frac{0.9573 \text{ nm}}{\ln(\frac{P}{P^*})}
\]  

(6.51)

If we assume that the surface of the pore is covered by a layer of adsorbed molecules before capillary condensation proceeds, the radii from Eqs. 6.50 and 6.51 have to be corrected by the thickness \( t \) of the adsorbed layer in order to obtain the pore radius, with the assumption that the contact angle \( \delta \) is set to zero:

\[
r_{pore} = r_c + t.
\]  

(6.52)

This postulates that an adsorbed film with thickness \( t \) remains on the pore wall when desorption occurs. When using nitrogen as adsorbate, de Boer et al. (1965) developed for \( t \) the expression

\[
t = 0.1 \text{ nm} \sqrt{\frac{13.99}{0.034 - 0.4343 \cdot \ln(\frac{P}{P^*})}}
\]  

(6.53)

Barrett, Joyner and Halenda (BJH) have implemented the above described model into a procedure for the assessment of pore size distribution by stepwise calculation on the basis of measured adsorption data (Webb and Orr, 1997). This method is strictly valid only for the determination of cylindrical pores within the mesopore range (>2 nm); it assumes a sorption isotherm of type 4. Condensation occurs in the pores, with a relative pressure corresponding to the Kelvin radius \( r_c \). Furthermore, it is assumed that a multilayer with surface area \( A_{pore} \) and thickness \( t \) exists and is changing by evaporation or condensation. The method is applicable on either desorption or adsorption isotherms.

\[
\Delta V_{pore,i} = \left( \frac{r_{pore}}{r_c} \right)^2 \cdot \left[ \Delta V_{i,i} - \Delta t_i \cdot \sum A_{pore,i} \right]
\]  

(6.54)

The relationship between the mean pore radius \( r_{pore,i} \), mean Kelvin radius and the corresponding pore volume \( \Delta V_{pore,i} \) is based on a relative pressure change \( \Delta P_i/P^* \) which has to be performed stepwise downwards in the relative pressure range from 0.99 to 0.3 (Lowell and Shields, 1991).
The liquid volume $\Delta V_{li}$ can be calculated using the standard volume $\Delta V_{STP}$ obtained directly from the isotherm by

$$\Delta V_{li} = \frac{\Delta V_{STP} \cdot M}{\rho_1 \cdot V_{mol}} = 1.545 \cdot 10^{-3} \cdot \Delta V_{STP} \quad (6.55)$$

Here, $M$ is the molar mass and $\rho_1$ is the density of the liquid; (for nitrogen: $M = 28$ g mol$^{-1}$, $\rho_1 = 809$ kg m$^{-3}$).

In Eq. 6.54 the pore volume $\Delta V_{pore,i}$ is calculated from the evaporated part of the liquid volume plus the volume remaining adsorbed on the walls of the pores. This volume can be determined from the surface area $A_{pore,i}$ (surface area previously created by desorption, see Fig. 6.14) multiplied by the change in film depth $\Delta t$. In the case of assumed cylindrical pores with the radius $r_{pore,i}$ the fraction area can be calculated with

$$A_{pore,i} = 2 \frac{V_{pore,i}}{r_{pore,i}} \quad (6.56)$$

By summation of the incremental $\Delta V_{pore,i}$ depending on the pore radius $r_{pore}$ the cumulative pore volume plot can be obtained (see Fig. 6.15).

6.3.3.4 Simplified Assessment of Pore Volume

The total pore volume of particles $V_{total}$ can be estimated approximately in a very simple way by measuring the adsorbed volume in a relative pressure range from a minimum of $10^{-3}$ up to a value near to unity and assuming that the adsorbed amount fills up all pores completely in the form of liquid condensate. In the first part of the curve at relative pressures $p/p^*$ smaller than 0.3, the measured isotherm has a relatively steep slope. This behavior is caused by the presence of micropores. In the second part, at relative pressures greater than 0.3, further slopes are encountered. This region can be attributed to the existence of meso- and macro-pores with a volume of $(V_{total} - V_{micro})$. In Fig. 6.18 a simple tangent method is used to find characteristic points of the isotherm and the volumes $V_{micro}$ and $V_{total}$. 

![Cumulative pore volume plot](image)
To convert the adsorbed volume $V_{STP}$ estimated from the isotherm curve at standard conditions to liquid volumes corresponding to pore volumes such as $V_{total}$ and $V_{micro}$, Eq. 6.55 can be used. However, it should be noted that measured adsorption isotherms of different materials may have similar characteristics to those presented in Fig. 6.16. Especially for fine compact powders, for example materials with large surface area without any presence of pores, adsorption isotherms show, in the relative pressure range below 0.3, comparable trends to isotherms of porous materials. Thus, the above-described method should be considered with care and applied only to materials which are known to be microporous.

6.3.3.5 Measurement Set-Up and Test Method

There are different methods for determining adsorption data. Both, the volumetric and gravimetric methods aim to measure the quantity of gas condensed on a solid surface at equilibrated vapor pressure. Depending on the measurement set-up, the amount of adsorbed gas is determined as a volume or mass (weight). When using the gravimetric method, the accuracy of measurement depends essentially on the sensitivity of the balance. Usually, the sample mass has to be confined to very small amounts that must be representative. The accuracy of volumetric instruments depends on the quality of pressure gauges. It has to be noted that the equilibration of gas pressure is achieved after numerous cycles. In the following, a volumetric measurement set-up of Porous Materials Inc., Ithaca, is exemplarily presented (Fig. 6.17).

The principle of operation is comparable with that of pycnometry. The sequential steps are as follows:

1. Placement of a known sample mass in the sample chamber,
2. pre-treatment of the sample at elevated temperature under vacuum to remove adsorbed gases and moisture,
3. immersion of the sample chamber in a Dewar vessel containing liquid nitrogen,
4. stepwise pressurization of the reference chamber, gas expansion to sample chamber until the relative pressure point is reached,
5. calculation of the adsorbed gas amount using the ideal gas law.

The reference volume is pressurized with adsorbate gas and is then isolated, so that the resulting gas pressure \(P_i\) can be measured. This gas is then allowed to expand into the sample chamber where adsorption at the sample takes place. When the pressure has equilibrated, the final gas pressure \(P_f\) is measured. The molar amount of gas adsorbed at the sample can be calculated stepwise (subscript \(n\) corresponds to one step) by:

\[
N_{ads} = \sum_{n=1}^{N} (N_{ads,n} - N_{ads,n-1})
\]

with incremental steps

\[
N_{ads,n} - N_{ads,n-1} = (P_{f,n} - P_{f,n-1}) \cdot \frac{V_{Ref}}{R \cdot T_{inst}}
\]

\[
-(P_{f,n} - P_{f,n-1}) \cdot \left( \frac{V_{inst}}{R \cdot T_{inst}} + \frac{V_{test} - V_{sample}}{R \cdot T_{test}} \right)
\]

The volumes of the instrument (reference volume \(V_{Ref}\), instrument volume at instrument temperature \(V_{inst}\), test volume \(V_{test}\) at liquid nitrogen temperature) are determined by a calibration test, while \(V_{sample}\) can be calculated from the mass of the sample via gas pycnometry.
6.3.4 Measurement of Particle Adhesion

6.3.4.1 Particle Adhesion Effects
Particle adhesion can occur by one or more of the following bonding effects, Fig. 6.18 (Rumpf, 1958, 1974, 1975; Schubert, 1979, 2003; Borho et al., 1991; Tomas, 1991, 2007a, b):

- Surface and field forces at direct contact:
  - Van der Waals forces (all dry powders consisting of polar, induced polar and non-polar molecules, for example minerals, chemicals, plastics, pharmaceuticals, food),
  - Electrostatic forces,
    - electric conductor (metal powders),
    - electric non-conductor (polymer powders, plastics),
  - Magnetic force (iron powder);

- Material bridges between particle surfaces:
  - Hydrogen bonds of adsorbed surface layers of condensed water (powders),
  - Organic macromolecules as flocculants in suspensions (in waste water);
  - Liquid bridges of

---

(a) Surface and field forces at direct contact
- Van der Waals forces
- Electrostatic forces
  * Conductor
  - surface charge
  * Non-conductor
- Magnetic force
  magnetic dipole

(b) Material bridge between contacts
- Organic macromolecules (flocculants)
- Liquid bridge bonds
  * Low viscosity
  * High viscosity
- Solid bridge bonds
  * Recrystallisation of liquid bridges
  * Contact fusion by sintering
  * Chemical solid-solid reaction

(c) Interlocking by hook-like bonds

Fig. 6.18 Particle adhesion and micro-processes of bonding of particles in contact.
6.3.4.2 Comparison between Different Adhesion Forces

The strengths of different adhesion effects are compared in Fig. 6.19. Disregarding the solid bridge bonds, the liquid bridge is the dominant adhesion force (Rumpf, 1974), as

\[ F_{\text{ad}}(d) = \frac{8 \pi \eta d \sin \theta}{3} \left( \frac{1 + \cos \alpha}{1 - \cos \alpha} \right)^{1/2} \]

where \( F_{\text{ad}} \) is the adhesion force, \( d \) is the particle size, \( \eta \) is the viscosity, \( \theta \) is the wetting angle, and \( \alpha \) is the bridge angle. The contact potential \( U \) is given by

\[ U = \frac{1}{2} q_{\text{max}} \frac{q_{\text{max}}}{C_{H,sw} \frac{q_{\text{max}}}{2}} \]

where \( q_{\text{max}} \) is the surface charge density, \( C_{H,sw} \) is the Hamaker constant for particle-water-particle interaction. Instead of the plate one can also consider a coarse particle with a large radius of surface curvature.
long as a liquid bridge is formed, see for example Tomas (1991); Schubert (1982); Emnis et al. (1990).

In the absence of a liquid bridge, the van der Waals force of a dry contact dominates. The van der Waals force decreases considerably in a wet environment because of the reduction of the Hamaker constant by the interstitial water. This effect is widely used in washing processes. For charged particles such as toner particles the Coulomb force becomes important. The surface-charge density is assumed to be \( q_{\text{max}} = 16 \times 10^{-18} \text{ A s } \mu\text{m}^{-2} \), which is the maximum value decided by the electric field limit for discharge. Sometimes the Coulomb force may be larger than the van der Waals force because the maximum surface-charge density is determined by the voltage limit rather than the field limit (Masuda and Gotoh, 1997).

In the above discussion, the effects of the atmospheric conditions are not taken into consideration. Because of the humidity of the ambient air water is adsorbed at particle surfaces. These surface layers of condensed water markedly increase the effective contact zone. By molecular bonds between these condensed liquid molecules (known as surface tension), these surface layers may additionally form small liquid bridges, which results in the alternation of the adhesive force (Rumpf, 1958; Chigazawa et al., 1981). The humidity also changes the adsorbed water layer thickness (Chigazawa et al., 1981; Tomas, 1983), and hence also affects the adhesion force. Thus, the adhesion is influenced by mobile adsorption layers due to molecular rearrangement and development of additional hydrogen bonds (Schubert, 2003).

As long as the liquid bridge is stable, the critical separation for rupture is about \( a_{\text{crit}} = \sqrt[3]{V} \), where \( V \) is the volume of the bridge (Lian et al., 1993). The separation hardly influences the bond force. Van der Waals forces and Coulomb forces (for a conductor) have similar long-range force-separation (distance) curves \( F_{\text{a,10}}(a) \), Fig. 6.19b. The Coulomb forces of a non-conductor do not depend on separation. This principle is widely used to precipitate dust particles in an electric field.

The effect of van der Waals forces depends strongly on the roughness of a surface, Fig. 6.19c. A minimum van der Waals force is seen versus roughness height \( h_r \) for different particle sizes \( d \). The influence of roughness for liquid bridge bonds and adsorption layers (humidity) is comparatively small. The adhesion will also be affected by temperature (Masuda and Gotoh, 1997). It is worth noting here that the particle weight for \( d < 100 \mu\text{m} \) is very small compared to the adhesion forces, which dominate particle interaction in the gravitational field.

Recently, the force–displacement behavior of elastic, elastic–adhesion, plastic–adhesion, elastic–plastic, elastic–dissipative, and plastic–dissipative contacts has been discussed in detail in a review paper by Tomas (2007a,b).

### 6.3.4.3 Survey of Adhesion Force Test Methods

The principles of various methods used to measure the adhesion force are shown in Fig. 6.20. All these methods involve application of an external force on the particles. The interacting force between two microscopic bodies is measured by the spring balance method as a function of the elongation of the spring when the bodies are separated. In the centrifugal method, the plate on which particles are deposited is put on a centrifuge to press particles on the surface by a compressive force \( F_C \) and, after
this so-called contact preconsolidation, to detach the particles (Krupp, 1967). The centrifugal force that is necessary to remove half of the deposited particles is measured to evaluate the average adhesion force (Graichen et al., 1974; Schütz and Schubert, 1976, 1980; Schmidt, 1998). When the plate is turned perpendicularly to the axis of revolution, the tangential or shear force distribution of the contacts can be measured by the cumulative mass fraction of detaching particles.

The vibration method, first described by Derjaguin and Zimon (1961), is based on particle detachment from a vibrating surface caused by its inertia at a certain acceleration. Thus, the vibration not only yields a detachment or pull-off force to compensate the adhesion force, but also causes compressive normal forces between particles and surface of the same order. For example, these alternating contact compression and detachment forces are frequently used during the dynamic stressing of cohesive powders as flow promotion in the practice of process engineering (Kollmann and Tomas, 2002).

The impact separation method uses an acceleration generated by the bullet (Derjaguin et al., 1968) or hammer impact (Otsuka et al., 1983). When a fluid flow field is applied to particles adhered on a plate, the particles suffer a force caused by the flow. At a certain flow velocity, particles start to detach from the plate. Then, the adhesion force can be obtained as a function of flow velocity and/or stress (Matsusaka et al., 1994).

Vibration and the hydrodynamic method were recently combined. Particle detachment events are continuously recorded and correlated with acting acceleration, particle mass and flow conditions, which allows calculation of the pull-off force (Hucke et al., 2002).

6.3.4.4 Particle Interaction Apparatus According to Butt

In a direct force–separation measurement the atomic force microscope (AFM) can be used. The particle is stuck at a cantilever in the so-called “colloid probe technique” (Butt et al., 1995), Fig. 6.21. The sample is moved up and down against the fixed
cantilever by applying a voltage to the piezoelectric translator. The cantilever deflection $\Delta a_C$ is measured versus the position of the piezo $\Delta a_p$, normal to the surface. To obtain a force distance curve, $\Delta a_C$ and $\Delta a_p$ have to be converted into normal force and separation (distance). The normal force $F_N = k_C \times \Delta a_C$ is obtained by multiplying the deflection of the cantilever by its spring constant $k_C$, and the tip–sample separation $a = \Delta a_C + \Delta a_p$ is calculated by adding the deflection $\Delta a_C$ to position $\Delta a_p$.

The deflection of the cantilever is normally measured using the optical lever technique. A beam from a laser diode is focused onto the end of the cantilever and the position of the reflected beam is monitored by a position sensitive detector array (photodetector). The backside of the cantilever is usually covered with a thin gold layer to enhance its reflectivity. When a force is applied to the probe, the cantilever bends and the reflected light beam move through a certain angle.

The resolution of the optical lever technique is roughly $10^{-13} \Delta w / \sqrt{\Delta t}$ ($\Delta w$ pixel width at the photosensor, $\Delta t$ the time for measuring a pixel of the force curve). With, typically, $\Delta t = 0.1$ ms the height-position resolution is 0.01 nm. But, in practice, the position sensitivity is often limited by thermal cantilever vibrations, which are $\sqrt{4 \cdot k_B T / 3 \cdot k_C}$ ($k_B$ Boltzmann constant, $T$ temperature and $k_C$ spring constant of the cantilever). With typical spring constants between 0.01–1 N m$^{-1}$ the amplitude of thermal noise is 0.7–0.07 nm at room temperature.

The primary result of AFM measurements is a plot of the deflection of the cantilever $\Delta a_C$ versus the height position of the sample, $\Delta a_p$. A cycle in the force

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**Fig. 6.21** Measurements of adhesion force – separation function by particle interaction apparatus (PIA) according to Butt et al. (1995).
measurement starts at a large tip–surface separation. At large distances no force acts between tip and sample; the cantilever is not deflected. In the scheme of Fig. 6.22 it was assumed that at smaller distances a repulsive force acts between tip and sample. Hence, when the sample approaches the tip the cantilever bends upwards. Since tip and sample are not in contact, this region is often referred to as the non-contact region. At a certain point the tip often jumps onto the sample surface. This “jump-in” occurs when the gradient of attractive force exceeds the spring constant plus the gradient of repulsive forces. Further sample movement generates a deflection of the cantilever by the same amount as the deflection of the sample. The nearly vertical force–separation curve represents this “contact region”, which includes contact loading. Then the sample is withdrawn at point U and moves to the detachment point A. Finally, its starting position is reached. During retraction the tip often sticks to the surface up to large distances due to adhesion. To obtain force–separation curves the original deflection-position curves have to be converted (Butt et al., 1995).

Cantilevers for AFMs are usually V-shaped to increase their lateral stiffness. They are typically 100–200 μm long, each arm is about 20 μm wide and 0.5 μm thick. The spring constant of V-shaped cantilevers is often approximated by that of a rectangular bar of twice the width of each arm, for details see Butt et al. (1995). Friction forces as a function of normal forces can also be measured by AFM equipment (Schwarz et al., 1997; Carpick et al., 1996; Ecke and Butt, 2001; Jones, 2003).

6.3.5 Measurement of Particle Restitution Coefficient

Particles (raw materials, intermediate and final products) are subjected to a lot of mechanical stressing during their processing sequence. During testing of the particles (compare with Section 5.5), stressing methods (impact) and their frequencies must be set equivalent to the conditions occurring in processing equipment such as dryers, conveyors, granulators or mixers. The restitution coefficient is a very important material parameter to describe the particle dynamics in particle and particle–fluid flows. The restitution coefficient is needed to describe the damping force and energy
in numerical discrete modeling of particles, see for example Kruggel-Emden et al. (2006), and depends on many parameters, such as impact velocity, material behavior of impact bodies, their particle size, shape, roughness, moisture content, adhesion properties and process conditions, for example temperature.

An impact between solid bodies (particle–particle or particle–wall) occurs in a very brief period of time. The impact period can be divided into two phases, compression and restitution. The contact force versus time and displacement during the impact between a soft spherical particle and a stiff wall by different types of deformation behavior is shown in Fig. 6.23. During the initial period of impact the contact partners are compressed and their kinetic energy is transformed into internal energy of deformation, friction and adhesion. The reaction force deforms the particle contact, which leads to the contact displacement or overlap as response. With increasing indentation the contact force increases and the relative velocity of contact partners decreases. If the deformation is rate-independent (elastic and plastic behavior), the maximum indentation and maximum contact force occur when the normal component of relative velocity vanishes (Stronge, 2000).

The elastic part of the impact energy absorbed during the compression is released during restitution and leads to the elastic force that separates the contact partners during the restitution phase of impact. The dissipation of the kinetic energy of the partners during the impact can be described by the restitution coefficient. The coefficient of restitution is a ratio of impulse during the restitution phase of impact \((t_C \leq t \leq t_R)\) to that during the compression phase \((0 \leq t \leq t_C)\)

\[
e = \frac{\int_{t_C}^{t_R} F \, dt}{\int_{0}^{t_C} F \, dt} = \sqrt{\frac{E_{\text{kin,R}}}{E_{\text{kin}}} - 1 + \frac{E_{\text{diss}}}{E_{\text{kin}}}} = \frac{v_R}{v} \tag{6.59}
\]
Moreover, the impulse ratio in Eq. 6.59 gives the square root of the ratio of elastic strain energy $E_{\text{kin},R}$ released during the restitution to the impact energy that is initial kinetic energy $E_{\text{kin}}$. Both contributions of impact energy can be obtained from the force–displacement curve, Fig. 6.23b. Hence, the restitution coefficient is the square root of the ratio of the area below the curve during unloading (restitution) to that during loading (compression).

In the case of elastic impact the impact energy absorbed during compression is fully restored during the rebound and so the relative velocity of contact partners before impact is equal to that after the impact, $e = 1$ in Eq. 6.59 (Hagedorn, 1995). In the case of full dissipation of initial kinetic energy due to plastic deformation, adhesion, friction in the contact as well as propagation of the stress waves, the impact bodies are not separated after the unloading (restitution), $e = 0$ in Eq. 6.59. The force–displacement curve of perfectly plastic contact partners does not show elastic restitution as illustrated in Fig. 6.23b. For elastic–plastic behavior during the impact, the restitution coefficient is in the range $0 < e < 1$, see examples in Hunter (1957); Goldsmith (1960); Walton and Braun (1986); Foerster et al. (1994); Hagedorn (1995); Labous et al. (1997); Lorenz et al. (1997); Iveson and Litster (1998); Huang et al. (1998); Stronge (2000); Kharaz et al. (2001); Louge and Adams (2002); Fu et al. (2004); Coaplen et al. (2004); Chandramohan and Powell (2005); Stevens and Hrenya (2005); Seifried et al. (2005); Weir and Tallon (2005); Dong and Moys (2006); Antonyuk (2006); Kantak and Davis (2006); Mangwandi et al. (2007).

Different types of equipment have been developed to measure the restitution coefficient. These can be divided into free-fall, particle–particle and pendulum tests. The typical experimental set-up for the free-fall experiments used by many authors, for example Goldsmith (1960); Walton and Braun (1986); Kharaz et al. (2001); Louge and Adams (2002); Fu et al. (2004); Dong and Moys (2006); Antonyuk (2006); Mangwandi et al. (2007), is shown in Fig. 6.24. Before the fall, a particle is held at a height $h$ from the target with the help of vacuum tweezers. The particle falls freely onto a target and reaches a rebound height $h_R$ after the impact. The movement of the particle near the contact point, before and after the impact, is recorded by a high-speed video camera. From video analysis the impact and rebound velocities of the particle can be obtained to calculate the restitution coefficient. From the ratio of energies in Eq. 6.59, it follows that the coefficient of restitution is a ratio of rebound relative velocity $v_R$ (by $t = t_R$) to that before impact $v$ (by $t = 0$).

Two different types of impact, that is normal and oblique, are described by normal and tangential restitution coefficients. The vectors of the velocity before and after the impact can be decomposed into normal $v_N$ and tangential $v_T$ components as shown in Fig. 6.24. The ratio of the normal component before and after the impact determines the normal restitution coefficient:

$$e_N = \frac{v_{N,R}}{v_N} = \sqrt{\frac{h_R}{h}} \quad (6.60)$$

Similarly, the tangential restitution coefficient is obtained by:

$$e_T = \frac{v_{T,R}}{v_T} \quad (6.61)$$
To describe the oblique impact the measurements are carried out at different angles of incidence ($\theta$ in Fig. 6.24) in the range $0^\circ$ to $90^\circ$. Additional information about the impact behavior can be obtained from the measured angle $\theta_R$ and the angular speed of rotation $\omega_R$ created during rebound (Kharaz et al., 2001; Dong and Moys, 2006).

Neglecting the fluid drag force acting upon the particle during free fall and rebound, the normal coefficient of restitution can also be determined as a ratio of heights after and before impact, Eq. 6.60. In this case, only the rebound height of the particle $h_R$ needs to be measured during the fall experiments.

In several publications (Goldsmith, 1960; Walton and Braun, 1986; Kharaz et al., 2001; Louge and Adams, 2002; Fu et al., 2004) the restitution coefficient was measured without any initial spin of particles. In fact, the vacuum nozzle prevents initial rotation. To release the particle with a predefined initial spin, the particle can be wrapped with a strip of paper that unwraps during the fall under gravity (Dong and Moys, 2006). The angular velocity of the particle can be varied using strips with different unwrapping length. A disadvantage of this method is the possible slip of the particle during the unwrapping.

In many cases, the same material is chosen for the target of fall experiments as the material of the walls of the apparatus that is going to be used in the investigated process. However, some authors have investigated the impact of particles on targets covered with a specific layer. The knowledge of respective impact characteristics is necessary for the description of particle-collisions in the presence of solid or liquid layers that occur in some processes such as wet comminution, fluidized bed spray granulation, filtration and so on. Kantak and Davis (2006) performed impact tests of steel and Teflon balls with wet or dry porous layers placed on the quartz wall. In the
work of Huang et al. (1998) the influence of milling conditions, including impact velocity, ball size and powder thickness was studied by fall tests. During these experiments a steel ball fell onto steel powder particles located in a shallow recess in the hardened steel plate.

The elastic stress waves arising in the contact area can have significant effects on the restitution coefficient. At the beginning of contact deformation, the spherical elastic wave expands away from the contact region into the target. After reflection from the target borders, the wave comes back towards the contact area. If the contact time is longer than the period of wave propagation in the wall, then the wave front will reach the contact partners and lead to loss of kinetic energy, which was first calculated by Hunter (1957). Thus, the thickness of the wall to be used must be sufficiently large to exclude the energy dissipation due to reflected elastic waves, according to the condition

\[ \delta > \frac{v_l t_R}{2} \]  

(6.62)

The speed \( v_l \) of the longitudinal wave propagating through the target (wall) can be calculated from the modulus of elasticity \( E \), Poisson’s ratio \( v \) and the density \( \rho \) of the target (Landau and Lifschitz, 2001):

\[ v_l = \left[ \frac{E \cdot (1-v)}{\rho \cdot (1-v) \cdot (1-2v)} \right]^{\frac{1}{2}} \]  

(6.63)

The duration of the impact \( t_R \) in Eq. 6.62 can be estimated using Hertz’s theory of elastic impact:

\[ t_{R,el} = 2.87 \left[ \frac{m^2 (1-v^2)^2}{v \cdot r \cdot E^2} \right]^{\frac{1}{2}} \]  

(6.64)

where \( m \) is the mass and \( r \) the radius of the particle.

For particle–particle impact experiments, in contrast to the above category of devices, two particles are bought to collision with each other without any rigid tool involved (Foerster et al., 1994; Labous et al., 1997; Lorenz et al., 1997; Chandramohan and Powell, 2005). This type of stressing occurs in fluidized bed granulation and comminution. The experimental device consists of two vacuum tweezers that are placed on top of each other to release the particles. The top particle is dropped first and reaches, in a definite time, the bottom particle, which is released second. After the release of the top particle, the bottom vacuum nozzle must be quickly taken out of the way of the top particle. A high-speed camera records the collision. To achieve a central impact, the release mechanisms of these devices must be accurately centered.

Pendulum-based experiments are also performed to measure the restitution coefficient of particle–wall, particle–particle and particle–beam impacts. The pendulum experiments are shown schematically in Fig. 6.25. The two particles are attached with fine wires to a horizontal overhead plate at a certain distance from each other. During the experiment the particles are simultaneously released and collide in the
normal direction. The relative impact velocity can be calculated from the distance between the overhead plane and the impact point. The velocity of the particles after the impact can be calculated by measuring the time between two points on the path of the particles using high-speed video recording or photodiodes (Iveson and Lister, 1998; Coaplen et al., 2004; Stevens and Hrenya, 2005; Weir and Tallon, 2005; Seifried et al., 2005).

The coefficient of restitution can decrease with increasing impact velocity, as was shown in many experimental studies (Goldsmith, 1960; Kharaz et al., 2001; Fu et al., 2004; Stevens and Hrenya, 2005; Kantak and Davis, 2006; Mangwandi et al., 2007). If the behavior of the particles during impact is not viscous or if the impact force value is below the yield point, the restitution coefficient can be constant. This behavior is illustrated in Fig. 6.26 for some granules examined by Antonyuk (2006). It is evident that all three granules produce an elastic–plastic impact. The increase in the impact velocity in the examined range did not change the coefficient of restitution. As revealed by repeated compression tests of these granules, the loading force level does not affect the ratio of plastic strain energy to the elastic strain energy. Under the
assumption that the force–displacement behavior during slow stressing is approximately the same as during dynamic stressing, this fact can give a rational explanation for the constant restitution coefficient.

An increase in material temperature can change the contact behavior of particles from predominantly elastic to elastic–plastic or viscoplastic. In this case the restitution coefficient is decreased. The results of impact tests between carbide and PVC at different temperatures are shown in Fig. 6.27. For a given impact velocity the decrease of the restitution coefficient with temperature is relatively small from −20 to 70 °C (in the glassy state) while a severe decrease can be observed at a temperature of approximately 70 °C and above, as PVC begins to behave as a viscoplastic material (Pouyet and Lataille, 1975).

6.3.6 Particle Abrasion and Breakage Tests

6.3.6.1 Survey of Test Methods and Principles

During production, transportation and handling particles are mechanically stressed due to particle–particle and particle–apparatus wall impacts (Fig. 6.28). These can lead to the breakage and attrition of particles.

Attrition is defined here as the partial breakage of particles resulting in the formation of fine fragments due to friction or low normal forces. Repeated interparticle and particle–wall interactions lead to breakage of sharp edges, roughness and defects on the surface of the particles. Attrition tests in fluidized beds (see Section 5.4) show that the surface of the particles becomes smoother (Fig. 6.29). The formed fragments are much smaller than the initial particles. The mass and size of the fragments depend on the intensity (stress level, velocity, configuration of impact partners) and the frequency of the impact events (Pouyet and Lataille, 1975; Joost and Schwedes, 1996; Rangelova, 2002; Dück et al., 2003; Seifried et al., 2005). The particle size and morphology (shape and texture) also have significant effects on the

![Fig. 6.27 Coefficient of restitution of cylindrical tungsten carbide impacted on a PVC target versus the carbide temperature for four different impact velocities (Pouyet and Lataille, 1975).](image-url)
amount of fines, since these factors determine the coordination number (mean number of contact points) and so the force transfer between colliding partners.

High normal forces during compression or impact loading lead to breakage when the particle is crushed into several big fragments. Factors affecting the breakage mechanism are intensity and frequency as well as material behavior and the microstructure of the particles. The basis of breakage phenomena has been studied using spherical particles, see for example Rumpf (1965); Schönert (1966); Kiss (1979); Beekman et al. (2003); Sheng et al. (2004); Samimi et al. (2005); Antonyuk et al. (2006).

In general, particulate products should not form dust and fragments during transportation, storage and handling. For example, particle attrition and breakage during spray granulation in a fluidized bed affect granule growth, nucleus formation and, therefore, residence time distribution and product quality. The strength of

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**Fig. 6.28** Typical stressing of particles during (a) rotation in a drying drum; (b) granulation in fluidized bed; (c) transportation and (d) discharge.

**Fig. 6.29** SEM of surface of sodium benzoate granule (a) before and (b) after abrasion test in the fluidized bed: 1 – visible roughness, 2 – defects (Heinrich and Mörl, 1999).
particles defines the maximal stress conditions to which they can be subjected without damage. On the other hand, the particles should be soft enough in order to retain their solvability, dispersibility, moisturizing properties and to avoid complications during further processing. For example in the production of high performance ceramics, powders that have been granulated first so that they do not break during transport, may fail during further press agglomeration (Agniel, 1992).

In order to optimize production processes and minimize the product quality losses during transportation and handling, the mechanical behavior and breakage mechanisms of particles are investigated by different testing methods (Fig. 6.30, see also Section 5.5). The necessary method is chosen depending on the stressing conditions of particles in the investigated industrial process and the probable failure mechanisms, that is attrition or breakage.

![Fig. 6.30 Testing methods for investigation of deformation and breakage behavior of particles according to Antonyuk (2006).](image)
All testing methods can be categorized into two groups: stressing of particles in a bed (Fig. 6.30a–f) and single particle tests (Fig. 6.30g–n). The behavior of particles in the bed regarding their attrition resistance, compression and impact strengths is studied using the stressing in rotating drums, fluidized beds, shear and press cells, vibration chamber and air gun.

The rotating drum is a standard device for measurement of particle attrition in the chemical and pharmaceutical industries (Grant and Kalman, 2001). In this test, the particle size distribution of the examined sample is analyzed after a predefined time of rotation and compared with an initial distribution to obtain the attrition mass fraction. The rotation speed, duration of operation, weight and temperature of the sample can be varied.

The behavior of a single particle can be tested by compression, tension, bending and impact tests (Fig. 6.30g–n). With these experiments the influence of single particle properties such as size, porosity and roughness on the mean behavior in the bed can be determined. One of the most important tests, the simple uniaxial compression of a single particle, will be introduced in the following section.

### 6.3.6.2 Compression Test

The compression test of a single particle up to the point of primary breakage determines the minimum energy requirement for the breakage, as shown first by Carey and Bosanquet (1933). The losses of stressing energy are much higher in particle bed crushing than in compression of a single particle, because of friction and plastic deformation of the particles at the contacts. Due to the comparatively low deformation rate (from μm min⁻¹ to cm min⁻¹) the secondary breakages that take place after the primary breakage can be separately observed in the compression test.

In a pioneering publication of Rumpf (1965) the deformation and breakage behavior of solid particles was described by force–displacement curves measured by compression tests. In recent works, various granules have been investigated using the compression test, namely: Al₂O₃ produced by fluidized bed-spray granulation (Agniel, 1992), enzyme (Beekman et al., 2003), polymer-bound Al₂O₃ granules (Sheng et al., 2004), detergents (Samimi et al., 2005), calcium carbonate (Mangwandi et al., 2007).

The principle of the uniaxial compression test is shown in Fig. 6.31. During the movement of the punch towards the fixed upper plate, a contact between the particle and the fixed plate is created. During the stressing period, displacement and force values are measured. Compression tests are carried out either with strain control (constant stressing velocities) or stress control (fixed stress or load rate).

#### Force–Displacement Behavior

The typical force–displacement curve of a spherical zeolite granule with elastic–plastic properties is presented in Fig. 6.32 (Antonyuk et al., 2005).

At the beginning of punch–particle contact the micro-asperities on the particle surface are deformed due to micro-plastic yielding. On further stressing, elastic contact deformation of the granule takes place. The contact force $F_{N,el}$ in the normal
direction during the elastic deformation $s$ of the granule with diameter $d$ compressed between two walls can be described by the Hertz contact theory (Hertz, 1882) as

$$F_{N,el} = \frac{1}{6} E' \sqrt{d \cdot s^3}$$  \hspace{1cm} (6.65)

**Fig. 6.31** Principle of single particle compression test (Antonyuk et al., 2005).

**Fig. 6.32** Typical force-displacement curve for a zeolite 13X granule ($d = 1.2$ mm) during compression test at the stressing velocity of 0.02 mm s$^{-1}$.
The effective modulus of elasticity $E^*$ of both granule (without index) and punch (index w) is given by:

$$E^* = 2 \left[ \frac{1-\nu}{E} + \frac{1-\nu_w^2}{E_w} \right]^{-1},$$  \hspace{1cm} (6.66)

where $\nu$ and $\nu_w$ are the Poisson ratios of the granule and the punch (wall).

The contact stiffness measured by the compression test can be evaluated from part II of the curve in Fig. 6.32. Due to the parabolic curvature of the function $F_{N,el}(s)$, the contact stiffness in the normal direction increases with increasing deformation and particle diameter:

$$k_{el} = \left( \frac{2}{k} - \frac{2}{k_w} \right)^{-1} \approx \frac{k_N}{2} = \frac{dF_{N,el}}{ds} = \frac{1}{4} E^* \sqrt{d \cdot s}.$$  \hspace{1cm} (6.67)

Based on Eqs. 6.66 and 6.67, Young's modulus and the stiffness of the particle during elastic deformation can be obtained. For the case of zeolite 13X granules it is: $E = 2.3$ GPa, $k_N = 295$ N mm$^{-1}$ (at the yield point F that marks the beginning of plastic deformation).

When the yield point F in Fig. 6.32 is reached, plastic deformation begins. This is confirmed by the increasing deviation of the experimental curve F–B from the theoretical Hertz curve. The breakage of the particle follows at point B, then the multiple stressing leads to failure of the fragments.

**Cyclic Stressing Tests** Because of fatigue of particles during cyclic loading, their breakage can occur at stress levels that are substantially lower than the failure stress during static loading. The reduction of fracture strength occurs because of the formation and propagation of shear zones and micro-cracks during each cycle. This effect can be described with the Wöhler curve (Riehle and Simmchen, 2002). Investigations of solid particles and agglomerates demonstrate the considerable effect of repeated loading on the breakage point. Tavares and King (2002) described a decreasing elastic–plastic stiffness of solids during repeated impact and explained the breakage behavior by the formation and propagation of damages. On the contrary, the stiffness of spherical granules was found to increase with increasing number of loading/unloading compression cycles as long as the saturation of the plastic deformation is not reached (Antonyuk, 2006). The intensity and the frequency of stressing, the particle size and the microstructure have an influence on the resistance of the material against the cyclic loading. Beekman et al. (2003); Pitchumani et al. (2004) have also confirmed this effect for granules.

During a repeated compression test, the punch moves towards the upper plate and presses the particle up to a defined force. Then, the punch moves downwards, thus the unloading of the particle takes place. A typical force–displacement diagram for the repeated compression of zeolite granule (Antonyuk, 2006) is shown in Fig. 6.33. During the measurement, a zeolite granule was repeatedly loaded and unloaded with a velocity of 0.02 mm s$^{-1}$ up to the force $F_{cyc} \approx 0.7F_B$, which is called the stressing amplitude. At this load a large displacement due to plastic deformation (O–E1 in Figure 6.33) is observed. The area between unloading (U1–E1) and reloading curves...
(E₁–U₂) characterizes the energy dissipation or the damping behavior of the particle during one compression cycle. This inelastic deformation work is reduced with each cycle. During the first cycle, the maximum plastic deformation and the highest breakage limit can be observed.

The number of cycles to breakage depends on the stressing intensity and material properties. The cyclic stiffening or hardening generates changes in the structure of the material at the contact points, where the internal stresses are very high. Material density and contact stiffness are increased. With the increase in cycle number, micro-cracks propagate inside the specimen. The granule stores cyclic loading energy during every elastic–plastic deformation, so that fatigue develops and a lower breakage force than for single loading is obtained.

The fracture stress (first breakage point) is not constant for a given size of granule. The mechanical characteristics of the primary particles and the bonding agents are randomly distributed within the granule volume. The porosity and shape of the particles and the orientation and size distribution of defects have a large effect on the breakage behavior. The pores can be regarded as crack-release zones. The pores and structural defects in granulated particles are similar to imperfections, inhomogeneities or micro-cracks in compact solid materials. The highest local tensile stress is generated at these defective zones in the granules, so that the fracture starts from these zones.

**Breakage Probability** The probability that a particle will fracture depends on the applied stressing intensity and frequency, material properties and particle size. May (1975); Klotz and Schubert (1982) describe fragment size distribution and
breakage probability for glass particles, clay pellets and cement clinkers by three and four parametric log-normal distributions; they also calculate the specific surface of fragments. During compression-shear tests of various materials Hess (1980) observed a reduction of breakage force and energy because of the additional shear stress. Kerber (1984) showed that there is a strong influence of shape and roughness of the stressing tools on the mass-related breakage energy for gypsum, limestone and quartz bulk materials.

Traditionally, the breakage probability is measured versus the mass-related breakage energy, which can be obtained from the area below the force–displacement curve up to the primary breakage point B in Fig. 6.32. The results for zeolite 13X granules are shown in Fig. 6.34. For increasing particle size the curve is shifted to the left. That means, to initiate the fracture at the same probability level a higher mass-related energy is required for smaller granules than for larger granules.

An overview of models to describe the breakage probability of granules and to calculate functions such as those of Fig. 6.34 can be found in Antonyuk (2006).

6.3.6.3 Impact Test

Different experimental equipment has been developed to conduct single particle impact tests. Based on the impact geometry, this equipment can be categorized into three groups:

1. Particle–wall impact;
2. double impact between two rigid plates;
3. particle–particle impact.

In air guns, particles are accelerated in a long tube towards a target by means of air pressure. This type of device enables one to realize single particle–wall impacts at different velocities, impact angles and target materials. The test conditions can be set equivalent to the stressing conditions of particles during pneumatic conveying, drying or mixing. Therefore, important information about the breakage processes during

![Fig. 6.34 Breakage probability P for zeolite 13X granules of different size versus mass-related breakage energy Wm.](image-url)
impacts with, for example bends of a pneumatic conveyor or flash dryer tube, can be obtained by this testing method. Air guns have been used for impact experiments with single particles and agglomerates – press agglomerates of cement matrix and quartz particles, brown coal, concrete ball, alumina, glass, polystyrene, wood, carbide, calcium carbonates powder, acrylic resin and polymethyl methacrylates (Tschorbajisjki, 1969; Kiss, 1979; Tomas et al., 1999; Salman et al., 2002, 2004; Chaudhri, 2004).

During the double plate stressing experiment, a particle is loaded between two rigid plates. The impact velocity can be adjusted, and the impact force and deformation can be measured in these devices. This type of equipment has been used to study the breakage behavior of quartz, apatite, limestone, cement clinker, marble, acrylic resin, polymethyl methacrylate, plaster spheres, concrete ball and sodium benzoate granules (Tavares and King, 2002; Chaudhri, 2004; Pitchumani et al., 2004; Wu et al., 2004; Khanal, 2005; Antonyuk et al., 2006).

In contrast to the above two categories of devices, two particles are mutually stressed without use of any rigid tool in particle–particle impact tests (Labous et al., 1997; Weir and Tallon, 2005). This type of stressing occurs in fluidized bed granulation and comminution.

A typical device for particle–wall impact tests is shown in Fig. 6.35 (Antonyuk et al., 2006). The particles are fed with the help of a vibrating feeder (1) into the hopper of the injector (2). The vibrating feeder is installed in a sealed chamber, connected to the feed hopper of the injector, in order to avoid false air entrainment from the environment and reverse flow from the injector.

![Fig. 6.35 Impact test rig according to Antonyuk et al. (2006).](image-url)
The particles are further fed into an air stream of defined velocity in the acceleration tube (3). Air pressure is generated in the compressed air tank (5) by means of a compressor (4). The control valve (6) is installed between two nozzles, which are connected by means of two check valves, so that air velocity in the acceleration tube can be adjusted. The air velocity can be measured at the attached Pitot tube (7).

The particles collide horizontally with a hardened steel target (8) in the impact chamber (9). After the impact, fragments and unbroken particles fall into a filter (12). The velocity of this fall is increased by means of two aspirators (13) placed in parallel at the outlet of the test rig. The removal of the fragments from the impact chamber in vertical directions at high velocity helps to avoid additional impacts of the particles with internal walls and other fragments. The particle size distribution of the fragments is measured on-line with a laser diffraction spectrometer (11) before entering the filter. Video recording can be performed through the glass window of the impact chamber by means of a high-speed digital video camera (10).

For example, the images from the high-speed video recording in Fig. 6.36 show the impact breakage of three different granules: \(\gamma\)-Al\(_2\)O\(_3\), zeolite 13X and sodium benzoate at an impact velocity of 23 m s\(^{-1}\) (Antonyuk, 2006). The \(\gamma\)-Al\(_2\)O\(_3\) granules behave in an elastic–brittle way during impacts. The granule is separated into several meridian fragments due to meridian cracks. The zeolite and sodium benzoate deform plastically during the contact. At high granule velocity, secondary cracks are formed in a direction perpendicular to the direction of impact. Many fine particles are produced during crack propagation and crack branching.

Because of the various mechanical properties of the particles, their microstructures and different stressing conditions, the deformation and breakage behavior of

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**Fig. 6.36 Images from high-speed video recording of the impact of granules at 23 m s\(^{-1}\) (13 600 frames per second):**

(a) \(\gamma\)-Al\(_2\)O\(_3\); (b) zeolite 13X; (c) sodium benzoate.
solid particles and granules during impact and compression is still not completely understood, but is an area of continuing research.

6.4 Testing of Particle Bed Properties

In particle processing and product handling, the well-known flow problems of dry cohesive powders in process apparatuses or storage and transportation containers include bridging, channeling, widely spread residence time distribution associated with time consolidation or caking effects, chemical conversions and deterioration of bioparticles. Avalanching effects and oscillating mass flow rates in conveyors lead to feeding and dosing problems. Finally, insufficient apparatus and system reliability of powder processing plants are also related to these flow problems of particle beds. Thus, it is essential to understand the fundamentals of particle adhesion with respect to product quality assessment and process performance in particle technology.

Generally, compressible and cohesive powders are considered here. However, only the non-rapid frictional flow with shear rates \( v_S \ll 1 \text{ ms}^{-1} \) and, consequently, a small shear stress contribution of \( \tau \ll \rho_b v_S^2 \approx 1 \text{ kPa} \) is described. The shear stress contribution by particle–particle collisions or a turbulent-equivalent momentum transfer is negligible. Thus, the shear resistance of a cohesive powder is dominated by Coulomb friction between the adhering particles. In terms of fluid dynamics, this frictional powder flow is characterized by the independence of shear rate.

6.4.1 Bulk Density and Tapping Density

In contrast to liquids, particle beds such as powders and bulk solids are more or less compressible, like gases. Thus, the density of bulk solids depends strongly on the effect of external forces in the form of stresses, impacts or vibrations. Therefore, one can distinguish between different types of bulk density depending on the strains occurring during the corresponding process. The density is measured using a vessel of known total volume, \( V \), by weighing the solid mass, \( m_s \), that exactly fills this vessel:

\[
\rho_b = \frac{m_s}{V}
\]  

(6.68)

The vessel is provided with a cap in order to be able to fill in a larger volume first, which will then be reduced accurately with a stripper to the real measuring volume after removal of the cap. For the determination of the bulk density, \( \rho_{b,0} \), of a loosely packed bulk solid the vessel is filled as carefully as possible without any pre-consolidation. A shear cell can also be used as the reference vessel.

To measure the tapping density, \( \rho_{b,t} \), the loosely filled measuring tank with the cap is placed on an eccentric driven desk and exposed to vertical drop impacts of low frequency (DIN-EN ISO 787-11, 1995). During this process the bulk solid will be compressed to the tapping density, which is also determined by weighing after
stripping. The degree of compression depends on the elasticity of the vessel and the height of fall (drop delay) as well as the number of drop impacts.

### 6.4.2 Angle of Repose of a Moving Particle Bed

Several empirical methods are commonly used to assess the flow properties of free-flowing bulk solids or granular materials, for example to determine the angle of repose, $\phi_r$ (Fig. 6.37). However, these simple test methods result in different angles of repose. A conical heap, Fig. 6.37a, will yield a different angle of repose, $\phi_r$, compared to a wedge-shaped heap. For a hopper that is discharged from a central outlet, Fig. 6.37b, the angle of repose is higher, but in a rotating drum still another (smaller) angle of repose will prevail. To measure the angle of repose correctly, the DIN ISO 4324 1983 should be used. The determination of the angle of repose of a bulk solid takes place by outflow of a given bulk volume through a hopper with a certain geometry on an even plate at a given gap between the hopper and the plate. The discussed methods can be applied with acceptable scattering and errors only for cohesionless and free-flowing bulk solids.

### 6.4.3 Flow Behavior of Cohesive and Compressible Bulk Solids

A bulk solid represents either an inactive and stable or an unstable and moving (“flowing”) particle packing whose pores are filled with gas and/or liquid. Despite inhomogeneities, bulk solids can be treated as a continuum over a length scale of $D > 25 d$ (Tomas, 1991). A fluidized bulk solid behaves like a Newtonian liquid (like a dilute suspension). With an increase in the bulk density, the bulk solid behaves more and more like an elastic–plastic frictional material. After time consolidation, a comparatively rigid solid state of the powder bed is often obtained (Tomas and

---

![Fig. 6.37 Methods to measure the angle of repose for free-flowing bulk solids.](image)
Schubert, 1981, 1982; Tomas, 1983, 1991, 1997). However, a cohesive powder can also show compressibility like a gas (Tomas, 2004a, b; Grossmann et al., 2004; Grossmann and Tomas, 2006).

To describe the stress states of the non-rapid frictional flow of cohesive and compressible bulk solids a couple of different material characteristics are needed, Tab. 6.1.

An essential problem in powder mechanics is to measure that stress state at which flow (breakage or failure) of the bulk solid is initiated within a processing apparatus. Consequently, a flow criterion should give a statement about the stress which leads to flow connected with irreversible plastic deformation or to yield. This failure limit, called yield locus, cannot be crossed. The yield locus shows the dependence of the shear stress $\tau$ on the normal stress $\sigma$, whereby the slope of the yield locus line is a measure of the internal friction of the bulk solid. Table 6.1 gives an overview of different friction angles of the yield loci. In Fig. 6.38 the flow characteristics of cohesive bulk solids are shown.

The yield locus is characterized by its slope $\tan \varphi_i$ and the intersection with the $\tau$-axis, the so-called cohesion $\tau_c$. It ends on the Mohr-circle of cohesionless steady-state flow.

**Tab. 6.1** Survey of different frictional failure limits (yield loci) in powder mechanics.

<table>
<thead>
<tr>
<th>Yield locus</th>
<th>Characteristic friction angle</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>yield locus, $t = 0$</td>
<td>angle of internal friction $\varphi_i$</td>
<td>incipient flow, internal friction flow</td>
</tr>
<tr>
<td>time yield locus, $t &gt; 0$</td>
<td>angle of internal friction $\varphi_{it}$</td>
<td>flow after a storage time</td>
</tr>
<tr>
<td>stationary yield locus</td>
<td>stationary angle of internal friction $\varphi_{st}$</td>
<td>cohesive steady-state flow</td>
</tr>
<tr>
<td>effective yield locus</td>
<td>effective angle of internal friction $\varphi_e$</td>
<td>cohesionless steady-state flow</td>
</tr>
<tr>
<td>wall yield locus</td>
<td>wall friction angle $\varphi_w$</td>
<td>powder wall friction</td>
</tr>
</tbody>
</table>

Fig. 6.38 Flow characteristics of bulk solids on a phenomenological basis (Jenike, 1964).
that is determined by the minor and major principle stresses $s_2$ and $s_1$. The position of the yield locus depends on the bulk density, $\rho_b$, so that it is shifted upwards with increasing bulk density. This results in a family of yield loci (not shown in Fig. 6.38).

To determine the strength properties of cohesive powders the uniaxial compressive strength $s_c$ is significant; this applies to a powder that has been exposed to the major consolidation stress $s_1$. The uniaxial compressive strength is the stress that leads to a failure or breakage of a bulk solid cylinder consolidated with the stress $s_1$ by uniaxial pressure. This means that a powder can flow more easily with a smaller $s_c$ at a given $s_1$. To characterize the flowability of cohesive powders the ratio of the major principle stress $s_1$ to the uniaxial compressive strength $s_c$ is used. According to Jenike (1964) this ratio is denoted here by “flow function” (in the sense of a dimensionless number), Tab. 6.2. A scheme to better understand the meaning of the flow function is shown in Fig. 6.39.

$$ff_c = \frac{s_1}{s_c}$$  \hspace{1cm} (6.69)

Free-flowing powders have practically no uniaxial compressive strength ($s_c = 0$), so that the flow function tends to infinite. The category “hardened” is defined by the fact that the major principle stress $s_1$ is smaller than the uniaxial compressive strength $s_c$.

**Tab. 6.2** Classification of powders according to Jenike (1964); Tomas (1983).

<table>
<thead>
<tr>
<th>Flow function $ff_c$</th>
<th>Characteristic behavior</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10 &lt; ff_c$</td>
<td>free flowing</td>
<td>dry sand</td>
</tr>
<tr>
<td>$4 &lt; ff_c &lt; 10$</td>
<td>easy flowing</td>
<td>moist sand</td>
</tr>
<tr>
<td>$2 &lt; ff_c &lt; 4$</td>
<td>cohesive</td>
<td>dry cement</td>
</tr>
<tr>
<td>$1 &lt; ff_c &lt; 2$</td>
<td>very cohesive</td>
<td>moist powders</td>
</tr>
<tr>
<td>$ff_c &lt; 1$</td>
<td>non-flowing hardened</td>
<td>aged cement</td>
</tr>
</tbody>
</table>

**Fig. 6.39** A scheme to explain the flow function $ff_c$: (a) Generation of a bulk solid cylinder by applying the major principal stress $s_1$, (b) measurement of the uniaxial compressive strength $s_c$ of the preconsolidated cylinder until failure.
6.4.4 Flow Criteria of Preconsolidated Cohesive Powders on a Physical Basis

The microscopic failure conditions of particle contacts can be formulated using the elastic–plastic and frictional particle contact model (Tomas, 2000a, b, 2001a, b, 2004a, b, 2007a). Macroscopically, it is worth noting here that the stressing pre-history of a cohesive powder flow is in most practical cases stationary (steady-state) and results significantly in a cohesive stationary yield locus in the \(\tau - \sigma\) diagram of Fig. 6.40, according to the equation

\[
\tau = \tan\varphi_{st} \cdot (\sigma + \sigma_0).
\]  

This steady-state flow is characterized by a dynamic equilibrium of simultaneous contact shearing, unloading and failing, followed by the creation of new contacts, loading, reloading, unloading and shearing again.

The isostatic tensile strength \(\sigma_0 = (1 - \varepsilon_0)/\varepsilon_0 F_{110}/d^2\) of an unconsolidated powder without any particle contact deformation is microscopically referred to the adhesion force \(F_{110}\) and to the initial porosity \(\varepsilon_0\) of a very loose packing, see Section 6.4.1. The stationary angle of internal friction \(\varphi_{st}\) determines the slope of the stationary yield locus (SYL) for elastic–plastic frictional contacts and is related to the angle of internal friction \(\varphi_i\) for incipient contact failure (slope of yield locus) as (Tomas, 2001b):

\[
\tan\varphi_{st} = (1 + \kappa) \cdot \tan\varphi_i
\]

The dimensionless, elastic–plastic contact consolidation coefficient \(\kappa\) determines the slope of the adhesion force \(F_{11}\) influenced by predominant plastic contact failure:

\[
\kappa = \frac{\kappa_p}{\kappa_A} - \frac{P_{VdW}}{P_f} \cdot \frac{1}{\frac{2}{5} + \frac{1}{5} \frac{\Delta p}{\Delta e} - \frac{P_{VdW}}{P_f}}
\]

![Fig. 6.40 Yield characteristics of a cohesive powder in the \(\tau - \sigma\) diagram on a physical basis. In general, the steady-state flow of a powder is cohesive. Hence, the total normal stress consists of an external contribution, \(\sigma\), plus (by absolute value) an internal contribution by the preconsolidation dependent isostatic tensile stress \(\sigma_Z\), Eq. 6.77. The diagram ends with the consolidation locus and its isostatic pressure \(\sigma_{iso}\).](image-url)
Thus, the softer the particle contacts, the larger the differences between these friction angles and, consequently, the more cohesive is the macroscopic powder response after preconsolidation.

For these poorly flowing cohesive and compressible powders, Tomas (2000a, b, 2001a, 2003a, b, 2004a, b) has developed a constitutive equation to describe the linear increase in adhesion force $F_{\text{H}}$ for elastic–plastic contact deformation by the model “stiff particles with soft contacts”:

$$F_{\text{H}} = \frac{\kappa_A}{\kappa_A - \kappa_p} \cdot F_{\text{H}0} + \frac{\kappa_p}{\kappa_A - \kappa_p} \cdot F_N = (1 + \kappa) \cdot F_{\text{H}0} + \kappa \cdot F_N$$  \hspace{1cm} (6.73)

The adhesion force $F_{\text{H}0}$ without additional consolidation ($F_N = 0$) can be approached as a single rigid sphere–sphere contact. However, if this particle contact is soft enough the contact is microscopically flattened by an external normal force $F_N$ to a plate–plate contact. The elastic–plastic contact area coefficient $\kappa_A$ represents the ratio of plastic particle contact deformation area $A_{\text{pl}}$ to total contact deformation area $A_K = A_{\text{pl}} + A_{\text{el}}$ and includes a certain elastic displacement (Tomas, 2000a, b):

$$\kappa_A = \frac{2}{3} + \frac{1}{3} \cdot \frac{A_{\text{pl}}}{A_K}$$  \hspace{1cm} (6.74)

The solely elastic contact deformation $A_{\text{pl}} = 0$, $\kappa_A = 2/3$, has only minor relevance for cohesive powders in loading, but for the completely plastic contact deformation ($A_{\text{pl}} = A_K$) the coefficient $\kappa_A = 1$ is obtained. For the plate–plate model of the flattened contact, the plastic repulsion coefficient $\kappa_p$ describes a dimensionless ratio

$$\kappa_p = \frac{P_{\text{vdW}}}{P_f} = \frac{C_{\text{H,sls}}}{6 \cdot \pi \cdot a_0^2} \cdot \frac{P_f}{6 \cdot \pi \cdot a_0^2} = \frac{4 \cdot \sigma_{\text{sls}}}{a_0 \cdot P_f}$$  \hspace{1cm} (6.75)

of the attractive van der Waals pressure

$$P_{\text{vdW}} = \frac{C_{\text{H,sls}}}{6 \cdot \pi \cdot a_0^2} = \frac{4 \cdot \sigma_{\text{sls}}}{a_0}$$  \hspace{1cm} (6.76)

to a constant repulsive particle micro-hardness $P_f$ (or micro-yield strength) as response. The surface tension solid–liquid–solid amounts to $\sigma_{\text{sls}} \approx 0.25–50$ mN m$^{-2}$ and, consequently, $P_{\text{vdW}} \approx 3–600$ MPa. For rigid (ideally hard) contact this plastic repulsion coefficient is infinitely small, that is $\kappa_p \approx 0$ and for a soft or compliant contact $\kappa_p \rightarrow 1$.

The Hamaker constant (Hamaker, 1937) $C_{\text{H,sls}} = (0.2–40) \times 10^{-20}$ J for solid–liquid–solid interaction (subscript sls) according to the continuum theory of Lifshitz (1955, 1956) is related to continuous media and depends on their permittivities (dielectric constants) and refractive indices, for details see Krupp (1967); Israelachvili and Tabor (1973) or Israelachvili (1992). The characteristic adhesion separation for the direct contact of spheres is of a molecular scale (atomic center-to-center distance) and can be estimated for the total force equilibrium $F = -dU/da = 0$ of molecular attraction and repulsion potentials. This separation of the interaction potential minimum amounts to about $a_0 = 0.3–0.4$ nm. With respect to large specific surfaces of ultrafine particles, this separation $a_0$ depends on the properties of liquid-equivalent packed adsorbed water layers (Tomas, 2007a).
The linear yield locus, Fig. 6.40, is obtained from resolution of a general square function and Taylor expansion series (Tomas, 2001b, 2004b) to

\[
\tau = \tan \varphi_1 \cdot (\sigma + \sigma_z) = \tan \varphi_1 \cdot \left(\sigma + \frac{\sigma_{R,\text{st}} - \sigma_{M,\text{st}}}{\sin \varphi_1}\right)
\] (6.77)

and is quite simple to use \((\sigma_{M,\text{st}}, \sigma_{R,\text{st}})\): center and radius stresses of cohesive steady-state flow, respectively). Using the mentioned radius and center stresses, the essential flow parameters can be calculated as one set of linear constitutive equations (Tomas, 2004a, b). They describe for instantaneous consolidation the so-called consolidation locus (CL)

\[
\sigma_R = \sin \varphi_1 \cdot (-\sigma_{M,\text{st}} - \sigma_{M,\text{st}}) + \sigma_{R,\text{st}},
\] (6.78)

for incipient yield the yield locus (YL)

\[
\sigma_R = \sin \varphi_1 \cdot (\sigma_{M,\text{st}} - \sigma_{M,\text{st}}) + \sigma_{R,\text{st}},
\] (6.79)

and for the cohesive steady-state flow the stationary yield locus (SYL)

\[
\sigma_{R,\text{st}} = \sin \varphi_{\text{st}} \cdot (\sigma_{M,\text{st}} - \sigma_0).
\] (6.80)

The consolidation locus and the instantaneous yield locus describe the limits of incipient plastic deformation during consolidation and flow. The stationary yield locus is the envelope of all stress states (Mohr circles) for steady-state flow with a certain negative intersection of the abscissa \(\sigma_0\). From the cohesionless steady-state flow, that is \(\sigma_0 \approx 0\), the effective yield locus can be obtained (Tomas, 2004a, b), see Fig. 6.38. The effective angle of internal friction is the slope of the effective yield locus. This depends on the average pressure \(\sigma_{M,\text{st}}\):

\[
\sin \varphi_c = \sin \varphi_{\text{st}} \left(1 + \frac{\sigma_0}{\sigma_{M,\text{st}}}\right)
\] (6.81)

With the derivation of the linear yield locus, Eq. 6.77 and Fig. 6.40, the uniaxial compressive strength or unconfined yield stress, \(\sigma_c\), results in a linear function of the major principal stress, \(\sigma_1\), for details see Tomas (2004a, b), Fig. 6.41:

\[
\sigma_c = \frac{2 \cdot (\sin \varphi_{\text{st}} - \sin \varphi_c)}{(1 + \sin \varphi_{\text{st}}) \cdot (1 - \sin \varphi_c)} \cdot \sigma_1 = \frac{2 \cdot (\sin \varphi_{\text{st}} - \sin \varphi_c)}{(1 + \sin \varphi_{\text{st}}) \cdot (1 - \sin \varphi_c)} \cdot \sigma_0
\] (6.82)

Equivalent to this linear function of the major principal stress, \(\sigma_1\), the absolute value of the uniaxial tensile strength, \(\sigma_{Z,1}\), also results in a linear function of the major principal stress, \(\sigma_1\):

\[
\sigma_{Z,1} = \frac{2 \cdot (\sin \varphi_{\text{st}} - \sin \varphi_c)}{(1 + \sin \varphi_{\text{st}}) \cdot (1 + \sin \varphi_c)} \cdot \sigma_1 + \frac{2 \cdot \sin \varphi_{\text{st}} + \sigma_0}{1 + \sin \varphi_{\text{st}}}
\] (6.83)

Again, it should be noted that both \(\sigma_c\) and \(\sigma_{Z,1}\) depend on the preconsolidation level of the shear zone which is expressed by the consolidation stress, \(\sigma_1\), applied during steady-state flow. After one day of storage under this major principal stress, \(\sigma_1\), a considerable time consolidation occurs, as shown in Fig. 6.41. Equivalent linear functions can be used to describe these very problematic time consolidation effects in powder processing and handling (Tomas, 1991, 1997, 2000a, 2001b, 2003a).
6.4.5 Translational Shear Cell according to Jenike

The most common device to determine the flow behavior and flow properties of cohesive bulk solids is the translational shear cell according to Jenike. In 1964 Jenike published his fundamental work on silo and bulk solids technology and introduced a translational shear tester. This tester was the first one designed for the purposes of powder technology (e.g. measurement at small stresses $\sigma < 50$ kPa).
The shear cell of the Jenike shear tester consists of a bottom ring (also called mold ring), an upper ring of the same diameter lying above the bottom ring, and a shear lid (Fig. 6.42). At the shear lid the normal force $F_N$ is centrally applied. The upper ring is displaced horizontally against the fixed bottom ring by a motor driven stem. In a modern arrangement of the translational cell, the shear force $F_S$ is applied by pulling the stem instead of pushing (Jenike, 1964) to improve the homogeneity of the normal stress distribution within the cell (to avoid a bending moment of the lid). This shear force is recorded versus time or shear displacement. Due to the displacement of the upper ring and the shear lid against the bottom ring, the bulk solid incurs a shear deformation. The normal stress $\sigma$ and shear stress $\tau$ acting in a horizontal plane between bottom and upper ring are determined by dividing the normal force $F_N$ and the shear force $F_S$ by the cross-sectional area of the shear cell $A$.

To measure one point of a yield locus, the shear cell is loosely filled with a sample of the bulk solid. A manual preconsolidation (The Institution of Chemical Engineers, 1989) of the powder follows and afterwards the sample is presheared. Finally, the sample is sheared to failure, as explained in the previous paragraph. For the next point of the yield locus, a new bulk solid sample has to be prepared and sheared again.

Although the Jenike shear tester is widely accepted, a disadvantage might be the time needed for one test (1–2 h per yield locus, depending on the powder and the skills of the operator). During this time the operator must be present. In addition, the manual preconsolidation of each material sample can be a source of measurement errors. Due to the limited shear displacement (maximum: twice the thickness of the wall of the upper ring), very elastic bulk solids can hardly be tested, because these powders need too much shear displacement to reach steady-state flow.

The Jenike shear tester in the laboratory of the present authors has been supplemented with a system to determine accurately the vertical movement of the shear lid, Fig. 6.43. Four laser sensors were mounted to measure the distance between shear lid and sensor position. From the vertical movement of the shear lid the dilatancy in the shear zone can be determined. The dilatancy reflects an expansion in the bulk volume and, consequently, a decrease in the bulk density in the shear zone during shear flow.

The vertical movement of the shear lid is measured by the single point optical triangulation method. This method uses a laser light source, a lens and a linear light-sensitive sensor. The light source (typically a laser or LED) illuminates a point on the object. An image of this light spot is then formed on the sensor surface. When the object is moved, the image moves along the sensor area. By measuring the location of
the light spot image, the distance of the object from the instrument can be determined, provided that the baseline length and the angles are known. In Magdeburg the sensor is a position sensitive detector (PSD). Such detectors are often chosen for devices measuring over a small range. They provide an analog output, which is ideal for use with pass–fail applications.

6.4.5.1 The Shear Testing Technique SSTT according to ICE

The determination of the yield locus with a Jenike shear tester is standardized in the translational shear test according to SSTT (The Institution of Chemical Engineers: European Federation of Chemical Engineering, 1989). The technique involves three steps: preconsolidation, preshear and shear. With the first two steps a reproducible initial state with a stress and strain history corresponding to the conditions of “steady-state flow” is created. This means that flow under a constant shear force is reached at a normal stress, \( \sigma_{\text{pre}} \), during the preshear, Fig. 6.45. Because of the limited shear displacement of the Jenike shear cell, this initial stress state can be reached only with a preconsolidation of the powder. The conditions of preconsolidation must be varied until a critical consolidation level is reached at about \( s_{\text{crit}} = 3 \text{ mm} \) (Fig. 6.44a).

At the beginning of the preshear, the bulk solid is deformed elastically (point A in Fig. 6.44b). This is also the beginning of frictional plastic deformation of the sheared powder. In the further process the sample is consolidated (point B in Fig. 6.44b) until a constant shear force value is reached. Here the stationary flow starts. During this shearing a shear force–displacement curve corresponding to the behavior of an overconsolidated bulk solid can be seen in Fig. 6.44b. Such a curve has a shear force maximum (point C). The material volume inside the shear zone expands (dilates) depending on the applied normal load and the shear velocity.

Measurements with the translational shear cell according to Jenike provide during preshearing the maximal value of the shear stress \( \tau \) corresponding to the applied normal stress \( \sigma \), Fig. 6.45. Because of the unknown dimensions of the shear zone, the
deformation and the change in volume cannot be determined exactly. The bulk solid starts to flow if the acting shear stress is sufficient to destroy the interparticle adhesion force. Then, the yield limit is reached. The acting shear and normal stresses correspond to the maximum stresses that the bulk solid can endure.

After the preshear, the procedure is continued with reduced normal load $\sigma$ in order to obtain one shear point. This is repeated at least two times for each of four different values of $\sigma$ with fresh samples. For cohesive powders, a shear force maximum can be obtained during the shear, Fig. 6.45a. For cohesionless powders the material sample starts to flow stationary at a lower shear force level. One point of the yield locus results directly from the shear stress $\tau$ and the normal stress during shear $\sigma$, Fig. 6.45b. Several shear points are combined to a yield locus that can be approximated by a straight line in the stress range $\sigma = (0.25 \sim 0.8) \sigma_{\text{pre}}$. By variation of the normal stress during preshear, $\sigma_{\text{pre}}$, a family of yield loci is obtained with the parameters preshear stress $\sigma_{\text{pre}}$, center stress during steady-state flow $\sigma_{\text{M, st}}$, bulk density $\rho_b$ or porosity $\varepsilon$.

**Fig. 6.45** (a) Results of translational shear test and (b) evaluation of the yield locus. The shear displacement, $s$, is directly related to the recorded time, $s = \nu_c \cdot t$, at a constant shear rate $\nu_c$. 

**Fig. 6.44** (a) Possible shear force–displacement curves during preshear; (b) Shear force–displacement curves for preshear and shear.
The discussed test method is used to calibrate the simulations of shear dynamics by the discrete element method (DEM) with physically realistic material data, Tykhoniuk et al. (2007).

6.4.6
Ring Shear Tester according to Schulze for Dry Powder

Ring shear testers (rotational shear testers) have been used in soil mechanics since the 1930s (Hvorslev, 1939). In the 1960s Walker designed a ring shear tester for bulk solids (Carr and Walker, 1967, p. 68), where lower stresses than those used in soil mechanics are of interest. In the following decades different ring shear testers have been built and investigated (e.g. Münz, 1976; Gebhard, 1982). In 1992 a ring shear tester (type RST-01.01) was developed by Schulze (Schulze, 1994), followed by a computer-controlled version in 1997 (type RST-01.pc). With the control software yield loci, wall yield loci, time consolidation, and so on, can be measured automatically. The principle of the shear cell of a ring shear tester is shown in Fig. 6.46. The ring-shaped (annular) bottom of the shear cell contains the bulk solid sample. The (annular) lid is placed on top of the bulk solid specimen. The lid is fixed at a crossbeam.

A normal force $F_N$ is exerted on the crossbeam in the rotational axis of the shear cell and transmitted through the lid to the bulk solid specimen. Thus, a normal stress $\sigma$ is applied to the bulk solid sample. The counterbalance force $F_A$ also acts in the center of the crossbeam. $F_A$ is directed upwards and is created by counterweights. It counteracts the gravity forces of the lid, the hanger, and the crossbeam.

To shear the bulk solid, the lid and the bottom ring of the shear cell must rotate relative to each other. This is accomplished by rotating the bottom ring in the
direction of the arrow $\omega$ ($\omega$ is the angular velocity), whereas the lid and the crossbeam
are prevented from rotation by two tie-rods connected to the crossbeam. Each of the
tie-rods is fixed at a load beam, so that the forces, $F_1$ and $F_2$, acting in the tie rods can
be measured. Both forces ensure that the lid is self-centered during the measure-
ment, which is necessary for correct results.

The bottom of the shear cell and the lower side of the lid are rough in order to
prevent the bulk solid from sliding relative to these surfaces. Therefore, rotation of
the bottom ring relative to the lid creates a shear deformation within the bulk solid.
Through this shearing the bulk solid is deformed and, thus, a shear stress $\tau$ prevails.
The forces acting in the tie rods ($F_1$ and $F_2$) are directly proportional to the shear stress
$\tau$ acting in the bulk solid.

The test procedure is quite similar to the test procedure recommended for the
Jenike tester (preshare and shear, see Section 6.4.5). However, the test procedure for
the ring shear tester is less time-consuming, easier to perform, and, hence, less
influenced by the operator who accomplishes the test. This, in combination with the
principle of the ring shear tester, results in a good reproducibility compared to other
testers (Verlinden, 2000).

With the ring shear tester a complete set of yield loci is usually measured with only
one bulk solid sample. In order to measure another point of the yield locus with the
same sample, after every shear period the normal stress is increased to the preshear
stress $\sigma_{\text{pre}}$ (the normal stress applied during the first preshear period), and the bulk
solid is presheared again until steady-state flow is reached. Thus, the bulk solid is
again critically consolidated. Afterwards, the same sample can be sheared again
under another normal stress $\sigma$ to obtain the next point of the yield limit in the $\sigma$–$\tau$
diagram. This succession of shear and preshear at $\sigma_{\text{pre}}$ continues until a sufficient
number of points of the yield limit are known.

6.4.7
Press Shear Cell according to Reichmann for Wet Filter Cake

The increasing amount of nanodisperse ($d < 100$ nm) to ultrafine ($d < 10 \ \mu m$) particles
from sol–gel, crystallization or precipitation processes and the increasing amount of
finest sludges in waste water treatment, mineral and chemical processing lead to
problems in dewatering processes.

The particulate solids of these suspensions form very compressible cakes with
extremely low permeability in filtration processes. However, the mechanical expres-
sion of as much liquid as possible out of compressible cakes can reduce the water
content significantly and, thus, minimize the energy demand of subsequent thermal
drying. For applied pressures of $\Delta P = 0.5$ to $5$ MPa the filtrate-related specific energy
consumption of mechanical dewatering amounts only to $W_{m,l} = \Delta P/\rho_1 = (0.5–5)$ kJ
kg$^{-1}$. This is very favorable in comparison with the specific energy consumption of
thermal drying, which follows in the processing sequence. On the other hand, the
flow and storage behavior of these finest particulate solids has a large influence on the
reliability of handling and storing equipment. Cohesion, shear strength and uniaxial
compressive strength are important parameters for design purposes (Reichmann and Tomas, 2001).

The mentioned nanoparticle dispersions are not easy to handle, because their flow behavior is at the transition between concentrated particle suspension, paste rheology dominated by viscous flow, and powder mechanics of compressed, liquid saturated particle packings. For the latter, contact deformations with interparticle Coulomb friction ($\varphi_I > 0$) are dominant (Fig. 6.47).

Generally, in a volume element of wet paste with closed boundaries, a closed system, no fluid is able to penetrate through the boundary walls. An external total pressure $P$ loads both, the liquid (with pressure $P_l$) and also the particle phase (with pressure $P_s$), where

$$P = P_l + P_s \tag{6.84}$$

and both pressure increments are

$$dP = dP_l + dP_s \tag{6.85}$$

The compressibility of the liquid phase

$$-dV_l / (V_l \cdot dP_l) = k_l \tag{6.86}$$
increases if gas is dissolved or gas bubbles are dispersed in the liquid (softening effect). In contrast, capillary pressure within the fine pores causes a stiffening of the liquid. Long-range ionic liquid–particle and van der Waals particle–particle interactions enhance additionally the stiffening and shear-thickening effects. Shear-thinning can be observed as well (Tomas and Reichmann, 2002).

However, if the walls of the volume element are semi-permeable membranes the liquid can leave the process chamber and the dispersion is compressed to form a particle packing (filter cake) that is drained to the equilibrium of capillary pressure in the pores. The attractive capillary pore pressure can only be compensated by a large overpressure to drain the packing. This gives rise to a capillary pressure distribution due to the pore size distribution in a random packing.

During short-term expression, the permeability of the packing is not sufficiently high and the liquid remains in the fine pores. The behavior of the packing is equivalent to that of a closed system. But if the liquid in the porous packing is given enough time to penetrate and drain, then the pressure drop, \(-dP_i\), of the pores creates simultaneously an increasing loading of the particle contacts of the packing, \(dP_s\); (if \(P = \text{const}\) then \(dP = 0\) and \(dP_i + dP_s = 0\)). Now, the particles are able to approach each other. Direct contacts are formed and deformed by normal forces. The shear strength depends on normal stress, friction angles and particle contact deformation characteristics. Additionally, liquid permeation kinetics, packing density, pore size distribution and pressure drop influence the shear and normal stress level.

The expression process can be distinguished into filtration and consolidation subprocesses, Fig. 6.48. In the filtration stage (index F) a filter cake builds up. The compressible cake consists of fine particles, which are more or less compressible, mainly dependent on particle contact stiffness. Thus, the cake may be consolidated after filtration by applying a mechanical pressure. This second stage of the process is the consolidation stage (subscript c). The decreasing volume of the cake leads to a

![Diagram](image.png)

**Fig. 6.48** Two-stage expression characteristics (filtration and consolidation) of a suspension with particle volume concentration \(\varphi_s\) (Reichmann and Tomas, 2001).
minimal amount of water in the pores. A dense particle packing saturated with liquid is obtained. During the expression process the liquid flows through a compressed packing and there, the flow rate difference between solid and liquid has to be taken into account. The dynamic cake formation (Fig. 6.48), with cake height first increasing to $h(t_F)$ and then decreasing to $h(t_c)$, causes a liquid drag force acting on the particles. This leads to an axial particle stress, $P_s$, transmitted to the particle contacts.

To obtain material properties such as packing porosity, permeability, wall friction angle and lateral stress ratio a test apparatus that can imitate in situ the expression process and measure the parameters of constitutive models has been developed by Reichmann. This apparatus is a combination of laboratory filter, compression-permeability-cell and high pressure ring shear cell, Fig. 6.49 (Reichmann and Tomas, 2001).

To determine the material properties of a compressed cake, the feed suspension is filled into the ring chamber. The ring piston above the ring chamber is moved towards the suspension. An open valve removes the air between the piston and the suspension until the piston touches the upper suspension level. After this touch the valve is closed. Then a constant piston pressure is applied to drain the suspension. A sensor built in the piston surface indicates this isostatic pressure. Filtrate flows through the supported filter medium; the piston velocity is equal to the filtrate volume flow rate per unit filter area. To prevent suspension losses, Teflon double-lip seals are fixed at the inner and outer circumference of the ring piston. As the filtrate runs dry the cake is consolidated, $dV < 0$, with a nearly isostatic stress. The packing porosity or density can be easily determined from the cake height $h(t_c)$ obtained from the piston position and the initial solid mass per filter surface area in the suspension. The solid density $\rho_s$ is obtained with a helium pycnometer (see Section 6.3.1). The permeability can be calculated by applying Darcy’s law. The filtrate mass flow rate is recorded by means of a balance.

To measure the flow behavior of the cake, the ring cell rotates, driven by a motor, with a variable number of revolutions. The two lever arms fix the piston. They are connected with force sensors to determine the required force to fix the piston, which is the shear force. To avoid a sliding of the material at the wall, the bottoms of the
piston and ring chamber are covered with small flight plates. Applying additionally a
preshear stress at a certain normal pressure between the plates, the particle packing
structure is destroyed, so that the cake is either compressed and drained \( (dV < 0) \) or
flows with expanding shear zone \( (dV > 0) \) (Tomas and Reichmann, 2002).
This compression and flow behavior can be determined with the shear procedure
according to Schulze (1994), as already described in Section 6.4.6.

6.4.8
Survey of Selected Direct and Indirect Shear Testers

6.4.8.1 The Biaxial Shear Tester according to Schwedes
Another device to determine the flow behavior of bulk solids is the biaxial shear tester
(Schwedes, 2002). In the biaxial shear tester the bulk solid sample is confined in
lateral \( x \)- and \( y \)-directions by four steel plates. Vertical deformations of the sample are
avoided by stiff top and bottom plates. The material sample can be loaded by the four
lateral plates, which are linked by guides so that the horizontal cross-section of the
sample may take rectangular shapes. In deforming the sample, the stresses \( \sigma_x \) and \( \sigma_y \)
can be applied independently of each other in both the \( x \)- and \( y \)-directions. To avoid
friction between the material sample and the steel plates, the plates are covered with
thin rubber membranes. Silicon grease is placed between the steel plates and the
rubber membranes. Thus, it is ensured that no wall shear stresses can occur on the
\( x \)-, \( y \)- and \( z \)-planes, and that \( \sigma_x \) and \( \sigma_y \) are the principal stresses.

The biaxial shear tester can also be used to obtain a yield locus corresponding to
Figs. 6.38 and 6.45. The minor principal stress \( \sigma_2 \), for example acting in the
\( y \)-direction, is kept constant during a test (Fig. 6.50). In the \( x \)-direction, a positive
strain rate \( \dot{\varepsilon}_1 \) is applied, resulting in an increasing major principal stress \( \sigma_1 \). The value
of \( \sigma_1 \) increases continuously up to the point of steady-state flow. After this “preshear”,
the stress state is reduced to a smaller \( \sigma_2 \) value and the second step of the shear
process is performed by applying again a positive strain rate \( \dot{\varepsilon}_1 \) in the \( x \)-direction.

6.4.8.2 The Uniaxial Tester according to Enstad
The uniaxial tester is an indirect shear tester, where the compressive failure strength
can be determined immediately as a function of the previous consolidation. The
powder sample is uniaxially consolidated in a die by pressing down a piston
(Fig. 6.51). The boundary between the sample and the die is made nearly frictionless
by means of a lubricated flexible rubber membrane. After consolidation to a

Fig. 6.50 Shear at constant \( \sigma_2 \) in the biaxial shear tester (Schwedes, 2002).
pre-decided consolidation stress, the axial stress is removed and the die taken away. Then, the unconfined sample is loaded again until it fails and the compressive strength is measured (Nysæter and Enstad, 2006).

Several features of the uniaxial tester are shown in Figs. 6.51 and 6.52. A flexible membrane is stretched between the outer periphery of the piston and the inner periphery of the lower part of the confining die (see Fig. 6.51). A ring is mounted on the lower part of the die to protect and keep the membrane in a locked position. This concept will ensure that the membrane and the powder sample always have a matching strain. To minimize the friction that develops on the interface between the membrane and the die wall, the die wall is highly polished and lubricated.

As the sample is deformed by the vertically moving piston, the membrane will come into full contact with the die wall. Air confined in the sample leaks out of a filter.

Fig. 6.51 Consolidation and failure test by the uniaxial tester (Nysæter and Enstad, 2006).

Fig. 6.52 (a) Consolidation and (b) failure measurement (Nysæter and Enstad, 2006), see also Fig. 6.39.
in the cup covering the bottom part of the sample. The die is mounted on a lower bearing, while the piston is mounted on a rod that is placed on an upper bearing. Mounted correctly, this will ensure coaxiality of the piston and the die.

When filling the sample into the die, the die is turned upside down, the bottom cup is removed, and the die is fixed in a special frame, which can vibrate the die during filling with adjustable frequency and amplitude. A suction system in the frame sucks air from the space between the membrane and the die wall, which is formed because of the stretching of the membrane. By use of the suction the membrane is brought back towards the die wall. The powder is then filled into the die either with a spoon or with a vibration feeder.

In the uniaxial tester (see Fig. 6.52) a cylindrical sample is compressed by an axial consolidation stress, \( \sigma_1 \), that causes a deformation, \( \varepsilon_1 \). A cylindrical die encloses the sample and hinders radial expansion \( (\varepsilon_3 = 0) \). The sample will, therefore, be compacted. The axial consolidation stress will cause a radial consolidation stress, \( \sigma_3 \), against the die wall. The radial consolidation stress will be smaller than the axial consolidation stress \( (\sigma_1 < \sigma_3) \). This type of consolidation is called uniaxial consolidation. When the sample has been consolidated at the chosen consolidation stress \( \sigma_1 \) for a certain time, the axial consolidation stress is reduced to zero. The strength of the powder is measured by removing the cylindrical die, so that the sample can expand in a radial direction, before the axial stress is increased again until the sample collapses (at \( \sigma_c \)).

6.4.8.3 Couette Device by Tardos

In a Couette device (Tardos et al., 2003) the powder is sheared between two vertical cylinders by rotating the inner cylinder at different rotational rates.

The instrument is similar to devices used to characterize fluids, except that the walls of the device are covered with sandpaper of a coarseness similar to the particle diameter of the powder. A schematic representation of the device is shown in Fig. 6.53. Inner and outer cylinders of different sizes are used to obtain different sizes of the shear gap as well as different overall heights. The device is equipped with sensors to measure normal stresses in both horizontal and vertical directions at a given height in the powder bed. The advantage of this unit is that coarse and fine powders from millimeter down to micron size can be tested. The torque on the rotating inner cylinder can be checked from the current drawn by the electric motor. The unit is equipped with a small observation window on the outer wall, at a piston not covered by sandpaper.

Both stress sensors and the torque measurement are connected to a data acquisition system that enables the measurement of stresses and their fluctuations at high sampling rates.

The experimental Couette device can be mounted on a bench with feeding systems for filling and emptying the instrument. A computer-controlled camera can be used to image the flow.

6.4.8.4 Powder Flow Analyzer ShearScan TS12 by AnaTec

The ShearScan TS12 (AnaTec, 2001) measures automatically the flow characteristics of powders and granular materials. The shear tests are accomplished similarly to the
Jenike (1964) method. All samples are automatically consolidated to the same point. This improves the reproducibility of analysis, as compared to traditional tests, by eliminating operator errors due to over-twisting or under-twisting.

At the beginning of the experiment, the material sample is placed inside the shear cell. After the start of the measurement the upper piston drives automatically downwards and consolidates with a certain number of twistings the material sample at a given pressure. During the measurement the lower ring of the shear cell moves. The shear force is measured by a pressure sensor. After reaching stationary flow, the normal load is reduced stepwise, then the material sample is sheared again.

**6.4.8.5 Survey of Different Shear Testers**

Normally, the flow behavior of cohesive bulk solids is determined with the translational shear cell according to Jenike in a low pressure range (1–50 kPa), with a small shear velocity (1–2 mm min⁻¹), and a shear displacement of about 6 mm.
Li and Puri (2003) carried out experiments in the middle pressure range (< 690 kPa) and in the high pressure range (< 21 MPa). They found a relationship between loose bulk density and compressibility of bulk solids. If the initial bulk density is low, then the bulk solid is highly compressible, and vice versa.

The press shear cell of Tomas and Reichmann (2002) can determine the flow behavior of wet cohesive bulk solids after press filtration (Section 6.4.7). This press shear cell can also be used to determine yield loci of dry cohesive powders in the medium pressure range at shear velocities of up to 0.042 m s$^{-1}$ (2520 mm min$^{-1}$) which are much higher than those attainable with the Jenike shear tester (Grossmann et al., 2004).

To investigate the flow properties of bulk solids several devices are available, for example Jenike shear tester, ring shear tester and biaxial box. These shear testers have been evaluated and compared with each other by Schwedes (2000); Kamath et al. (1993). Tab. 6.3 summarizes the comparison between different shear testers.

<table>
<thead>
<tr>
<th>Measuring of</th>
<th>Jenike shear tester</th>
<th>Ring shear tester</th>
<th>Press shear cell</th>
<th>Biaxial box</th>
<th>Couette device</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield loci</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Wall friction</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Time yield loci</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Compressibility</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Abrasion</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Pressure range</td>
<td>low</td>
<td>low</td>
<td>middle</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td></td>
<td>(&lt;50 kPa)</td>
<td>(&lt;50 kPa)</td>
<td>(50–1 MPa)</td>
<td>(&lt;50 kPa)</td>
<td>(&lt;50 kPa)</td>
</tr>
<tr>
<td>new sample needed?</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

6.5 Measurement of Particle Bed Movement in Rotary Drums by High-Speed Camera

Various processes, such as grinding, sieving, mixing and drying, are conducted in rotary drums. Usually, particles move in a more or less diluted bed that is characterized by a collisional flow regime with shear rates $\nu_S > 1$ m s$^{-1}$. They contact each other and transfer impact forces, momentum or heat over their contacts. The shear stress contribution by particle–particle collisions or a turbulent-equivalent momentum transfer, see Section 6.3.5, is no longer negligible. During their motion in these drums, particles change their physical properties, especially their size, mixing state and moisture content. The following factors control the motion of a particle bed in a rotating drum (Schöner, 2003):

- Diameter and circumferential velocity of the drum,
- type, size and flow properties of the particles,
- number of particles in the drum,
material, profile and geometry of the interior coating of the drum.

Depending on the process, the drum is partially filled with a definite number of particles. This filling can be characterized by the particle load or particle charge, which is the ratio of the volume of the particle bed filling the drum, $V_b$, to the net volume of the drum, $V$:

$$
\varphi = \frac{V_b}{V} = \frac{m_s}{\rho_p (1 - e_b) V}
$$

(6.87)

Special motion patterns appear when the drum rotates at different circumferential velocities. This velocity determines the height to which particles can be lifted by the rotary motion of the drum before they start moving down. At lower circumferential velocities, particles roll and slide from the top to the bottom of the heap, not losing contact with their neighbors. This pattern is called cascading (Fig. 6.55a). At higher speeds, particles lose their contacts and fall in a parabolic curve to the toe of the heap, producing a pattern named cataracting (Fig. 6.55b). Centrifuging occurs above a critical speed and lets the particles permanently stick on the inner wall of the drum (Fig. 6.55c). Naturally, every transition from one state to another goes smoothly.

The speed of a rotating drum can be given as a percentage of its critical speed. This concept assumes that at the highest point of the drum, at a distance $R$ from the center of rotation, two forces, the radial force and weight, act on a particle of mass $m_p$ and are
in balance when the particle starts to centrifuge:

\[
\frac{m_p \cdot v^2}{R} = m_p \cdot g \tag{6.88}
\]

Provided that the drum is much larger than the particle, which is normally the case, and provided that the particle is in direct contact with the drum wall and follows its rotation without any slip, the speed of this particle meets that of the drum. This speed is called theoretical critical circumferential speed,

\[
v_{\text{crit}} = \sqrt{R \cdot g} \tag{6.89}
\]

\(R\) and \(g\) are the radius of the drum and the gravitational acceleration, respectively. This speed can be converted into revolutions per second by dividing by \(2\pi R\). To compare drums of varying sizes, it is customary to give a percentage of the critical speed (Schönert, 2003; Perry and Green, 1999; Bernotat and Schönert, 2005).

\[
\psi = \frac{v}{v_{\text{crit}}} \tag{6.90}
\]

Motion patterns can also be characterized by the angle between the vertical and the radius drawn to the point of change from circular to parabolic motion, shown in Fig. 6.56a. The measurement of the angle of repose of granular materials in rotating drums is described in detail by Lina et al. (2005a, b).

During uniform rotation, a particle bed develops typical velocity zones characterized by particles that move in the same direction at similar speeds. Four zones can be distinguished (Fig. 6.56, Schönert, 2003): the climbing zone, where the drum lifts the particles to a higher position; the falling zone, where particles lose contact with the drum, falling down fast; the rolling zone, where layers of particles slide on each other; and the placing zone, representing the tail of the particle bed, where particles, hit by other falling particles, take positions from which they are lifted. Common ranges of drum speeds are given in Tab. 6.4. In drums used in industry, particles do not normally reach the centrifugal state.

![Fig. 6.56 A particle bed in a drum rotating at 70% of critical speed, shown schematically (a) (Schönert, 2003) and photographically (b). On the left, the zone labels mean: a, climbing, b, falling, c, rolling, and d, placing.](image-url)
Tab. 6.4 Industrial applications of rotary drums and their typical operating speeds.

<table>
<thead>
<tr>
<th>Process</th>
<th>Equipment</th>
<th>Percentage of critical speed</th>
<th>Dominant motion pattern</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>rotary dryer</td>
<td>5–20</td>
<td>cascading</td>
<td>Perry and Green (1999)</td>
</tr>
<tr>
<td>Grinding</td>
<td>ball mill</td>
<td>60–80</td>
<td>cascading–cataracting</td>
<td>Schürrer (2003); Perry and Green (1999);</td>
</tr>
<tr>
<td></td>
<td>autogenous mill</td>
<td>70–90</td>
<td>cataracting</td>
<td>Bernotat and Schönert (2005)</td>
</tr>
<tr>
<td></td>
<td>disc granulator</td>
<td>60–75</td>
<td>cataracting</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6.57 (a) Photographs taken at a shutter speed of 1/1000 s; (b) photographs taken at a shutter speed of 1/12 s; and (c) DEM simulations showing a particle bed of 10-mm glass spheres moving at different drum speeds.
The inner wall of rotary drums is often lined by replaceable liners, which are usually made of steel or rubber. These lifters help to raise the particles and minimize the slip between wall and particles. The effect of bar lifters is shown in Fig. 6.57. A drum of 300 mm in diameter, packed with 10-mm glass spheres at \( \varphi = 30\% \), rotates at different circumferential velocities, producing different motion patterns. Flashlight reflections mark the path of the balls, especially at a shutter speed of 1/12 s. Different lengths of the luminous trails indicate here different ball velocities.

Computer simulations using the discrete element method (DEM) (Cundall and Strack, 1979; Cundall et al., 2005) are capable of producing realistic motion patterns (Fig. 6.57). In Fig. 6.58, they give additional information about the velocity distribution of the balls, whose graytones change with their velocity, and about the mass center of the particle bed, marked by the black cross, whose position alters with drum speed.

Centrifuging does not necessarily start at exactly 100\% of critical speed. Projecting liners as well as large particle loads cause particles to centrifuge at lower speeds, whereas slippery liners and small particle loads inhibit the onset of centrifuging (Perry and Green, 1999; Bernotat and Schönert, 2005). No example given above refers to wet operation. However, wet operation is similar in principle to dry operation. In wet operation, the motion patterns occur at higher drum speeds because liquid reduces the friction between drum and particles, and enlarges forces that resist particle motion.

![Fig. 6.58 DEM simulation of a ball mill rotating at 72% of critical speed.](image-url)
6.6 Conclusions

The experimental methods and the physical models shown in this chapter can be used for the determination of the properties of powder products of different particle size (nanoparticles to granules), moisture content (dry, moist and wet) and material (minerals, chemicals, pigments, waste, plastics, food etc.). For example, data from compression and impact tests of granules have been evaluated. The presented methods are powerful in describing the frictional shear flow of cohesive and compressible powders.

By modelling the single particle adhesion and by suitable micro–macro interaction rules, constitutive equations were shown to describe the preconsolidation-dependent mechanical behavior of cohesive powders and to simulate the dynamics of packed particle beds in powder processing, that is agglomeration, disintegration, size reduction, powder storage and flow. With this knowledge and the respective tools, improved apparatus design (process chambers, feed hoppers, silos and conveyors) can be accomplished for process industries.

Additional Notation Used in Chapter 6

\begin{align*}
A & \quad \text{aperture} \quad \text{m} \\
A & \quad \text{area (surface, cross-sectional)} \quad \text{m}^2 \\
A & \quad \text{calibration function} \\
a & \quad \text{molecular separation distance} \quad \text{m} \\
B & \quad \text{second virial coefficient} \quad \text{mol m}^3 \text{kg}^{-2} \\
C_s & \quad \text{particle mass concentration} \quad \text{kg m}^{-3} \\
D & \quad \text{fractal dimension} \\
D & \quad \text{distance from the light axis on the screen} \quad \text{m} \\
d_s & \quad \text{maximum chord length} \quad \text{m} \\
E & \quad \text{modulus of elasticity} \quad \text{N m}^{-2} \\
E & \quad \text{molar adsorption potential} \quad \text{J mol}^{-1} \\
ESA & \quad \text{ESA (electrokinetic sonic amplitude) signal} \quad \text{Pa m} \text{V}^{-1} \\
e & \quad \text{restitution coefficient} \\
F & \quad \text{force} \quad \text{N} \\
f & \quad \text{focal width} \quad \text{m} \\
f & \quad \text{factor} \\
f_{c} & \quad \text{flow function} (f_{c} = \sigma_{c}/\sigma_{a}) \\
G^2 & \quad \text{autocorrelation function of the scattered light intensity} \quad \text{W}^2 \text{m}^{-4} \\
g^1 & \quad \text{normalized autocorrelation function of the electrical field} \\
g^2 & \quad \text{normalized autocorrelation function of the scattered light intensity} \\
h & \quad \text{height} \quad \text{m} \\
l & \quad \text{intensity of light} \quad \text{W m}^{-2} \\
J_1 & \quad \text{first order Bessel function}
\end{align*}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>optical constant</td>
<td>mol m$^2$kg$^{-2}$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>J kg$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>spring constant, stiffness</td>
<td>N m$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>compressibility</td>
<td>Pa$^{-1}$</td>
</tr>
<tr>
<td>$l_s$</td>
<td>distance between macroscopic objects</td>
<td>m</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight averaged or apparent molecular mass</td>
<td>kg mol$^{-1}$</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
<td>mol$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index</td>
<td>—</td>
</tr>
<tr>
<td>$n_0$</td>
<td>refractive index of suspension medium</td>
<td>—</td>
</tr>
<tr>
<td>$P$</td>
<td>breakage probability</td>
<td>—</td>
</tr>
<tr>
<td>$P(\theta)$</td>
<td>form factor</td>
<td>—</td>
</tr>
<tr>
<td>$Q$</td>
<td>cumulative sum distribution function</td>
<td>—</td>
</tr>
<tr>
<td>$q$</td>
<td>scattering vector</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$q$</td>
<td>surface charge density</td>
<td>As m$^{-2}$</td>
</tr>
<tr>
<td>$q$</td>
<td>frequency distribution function</td>
<td>various</td>
</tr>
<tr>
<td>$R_d$</td>
<td>Rayleigh ratio</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$r, R$</td>
<td>radial coordinate, radius</td>
<td>m</td>
</tr>
<tr>
<td>$S$</td>
<td>saturation</td>
<td>—</td>
</tr>
<tr>
<td>$s$</td>
<td>displacement</td>
<td>m</td>
</tr>
<tr>
<td>$t$</td>
<td>adsorbed film thickness</td>
<td>m</td>
</tr>
<tr>
<td>$U$</td>
<td>contact potential</td>
<td>V</td>
</tr>
<tr>
<td>$U$</td>
<td>circumference</td>
<td>m</td>
</tr>
<tr>
<td>$U$</td>
<td>interaction potential</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$V_{mol}$</td>
<td>molar volume</td>
<td>m$^3$mol$^{-1}$</td>
</tr>
<tr>
<td>$W$</td>
<td>work</td>
<td>J</td>
</tr>
<tr>
<td>$W_m$</td>
<td>mass-related energy consumption</td>
<td>J kg$^{-1}$</td>
</tr>
<tr>
<td>$w$</td>
<td>width</td>
<td>m</td>
</tr>
<tr>
<td>$Z$</td>
<td>acoustic resistance</td>
<td>kg m$^{-2}$s$^{-1}$</td>
</tr>
</tbody>
</table>

**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>bridge angle</td>
<td>rad</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>polarizability of particle</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>affinity coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>decay rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>contact angle</td>
<td>rad</td>
</tr>
<tr>
<td>$\delta$</td>
<td>wall (target) thickness</td>
<td>m</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>strain</td>
<td>—</td>
</tr>
<tr>
<td>$\dot{\varepsilon}$</td>
<td>strain rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>zeta-potential</td>
<td>V</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle (scattering, wetting, diffraction, impact, rebound)</td>
<td>rad</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>elastic–plastic contact consolidation coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$\kappa_A$</td>
<td>elastic–plastic contact area coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$\kappa_p$</td>
<td>plastic repulsion coefficient</td>
<td>—</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>length of a single polygon element</td>
<td>m</td>
</tr>
<tr>
<td>$\mu_D$</td>
<td>dynamic particle mobility</td>
<td>m² V⁻¹ s⁻¹</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>normal stress</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_c$</td>
<td>uniaxial compressive strength</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_{M,st}$</td>
<td>center stress of the Mohr circle for steady-state flow</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_{pre}$</td>
<td>preshear normal stress</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_{R,st}$</td>
<td>radius stress of the Mohr circle for steady-state flow</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_Z$</td>
<td>isostatic tensile strength</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_{Z,1}$</td>
<td>uniaxial tensile strength</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>isostatic tensile strength of the unconsolidated powder</td>
<td>Pa</td>
</tr>
<tr>
<td>$\sigma_{1,2}$</td>
<td>principle stresses (major, minor)</td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>correlation or sample time</td>
<td>s</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>cohesion</td>
<td>Pa</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>volumetric particle load</td>
<td>—</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>friction angle in powder mechanics</td>
<td>rad</td>
</tr>
<tr>
<td>$\varphi_s$</td>
<td>particle volume fraction</td>
<td>—</td>
</tr>
<tr>
<td>$\psi$</td>
<td>ratio of actual to critical speed</td>
<td>—</td>
</tr>
<tr>
<td>$\psi$</td>
<td>sphericity</td>
<td>—</td>
</tr>
<tr>
<td>$\omega$</td>
<td>frequency of the electrical field</td>
<td>s⁻¹</td>
</tr>
</tbody>
</table>

**Additional Notation Used in Chapter 6**

**Subscripts and superscripts**

- A: area related
- ads: adsorbed
- B: breakage
- b: bulk, bed
- C: cantilever
- c: compressive
- crit: critical
- ct: compressive for time consolidation
- cyc: cyclic
- diss: dissipation
- e: effective
- el: elastic
- F: Feret chord length
- F: filtration
- f: final
- g: gyration
- H: hydrodynamic
- H: Hamaker adhesion
- H0: single rigid contact without deformation
- i: internal friction
it  internal friction for time consolidation
inst  instrument
K  contact, sum of plastic and elastic deformations
K  piston
kin  kinetic
l  longitudinal
M  Martin chord length
micro  micropores
mono  monolayer
N  in normal direction
p  piezo
pl  plastic
R  rebound (restitution)
R  impact duration
Ref  reference
r  distributed quantity index
rep  repose
r  roughness
S  shear
S-Ch  sample chamber
STP  standard conditions (273.15 K, 1.013 bar)
s  maximum chord length
s  solids (particle), solid matter
st  steady-state, stationary
T  tangential
t  tapping
U  circumferential
VdW  van der Waals
0  reference (incident, loosely packed, molecular etc.)
effective, combined

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Determination of Physical Properties of Fine Particles, Nanoparticles and Particle Beds

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Determination of Physical Properties of Fine Particles, Nanoparticles and Particle Beds


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