Particle Technology Laboratory
Prof. S. E. Pratsinis

pratsinis@ptl.mavt.ethz.ch
http://www.ptl.ethz.ch

ETH

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

MILLING & ANALYSIS

OF PARTICLES

Assistants:

Gian Nutal Schädli, Room ML F24, e-mail: schaedli@ptl.mavt.ethz.ch

(Substitute) Rajesh Koirala, Room ML F25.2 e-mail: rkoirala@ptl.mavt.ethz.ch

Contents

1 Introduction

Many technically interesting materials are solids. These solids have to be transported, stored, precisely mixed with other materials or separated from them. In most cases, the solids are machined into granules, dust or more general "particles" with a size between 1 μm and 1 mm, because in this form the materials are easy to handle.

Beside the material properties, which are mainly determined from chemical composition of the solids, the geometrical properties of the particles are of special importance. For example the flow behavior of the particles in a moving fluid is determined by the size and shape of the particles. Also the chemical conversions of the solids is determined by the mass and energy transport to the surface, and is thus dependent on size and shape of the particulate material.

Determined by the fabrication or exploitation process of the solid particles, not all the geometric properties of all particles are the same. Besides the description of the single particles, also the description and knowledge about variance and distribution of properties are of importance.

Because solid particles are mostly processed in large quantities, properties of the bulk particulate material (or a particle collective) have to be known as well. These properties can only be derived from single particle properties to a small degree and have to be determined separately.

2   Milling

The state of dispersion of a particulate material determines its properties in many different ways (e.g. solubility, dispersibility in fluids, flow behavior, color). For this reason, milling plays an important role in many industrial fields (construction materials, mining industry, chemical industry, food industry). About 4% of the electric energy production worldwide is used for milling processes and about 1% of the industrial production is produced using milling processes.

2.1   Break-up scenarios in milling

If a solid body has to be divided, internal tensions have to overcome the binding forces of the atoms in the body. This normally happens via external forces, which are applied via the contact points of the particles leading to deformation and tensions.

Deformation and tension are bound to physical laws and can be divided into three limits: elastic, plastic or viscous behavior.

The theoretical fracture tension σ_{th} required to overcome atomic binding forces may be derived with assumption of an ideal atomic lattice and uniform tension:

$$\sigma_{th} = \frac{E\gamma_A}{a_0}.$$

a_0:lattice constant

E:elastic modulus

γ_A: specific free boundary surface

The difficulty in calculation of the above mentioned equation is due to the fact that the specific free surface γ_A is not accessible offhand. An estimation gives :

$$\frac{E}{5} > \sigma_{th} > \frac{E}{15}.$$

The real toughness is lower for some orders of magnitude than the theoretical fracture stress. The reason for this is explained by the fact that real crystal lattices are never perfect. Errors in crystal lattices lead to local tensions that are larger than the average tension in the body. Fracture starts though from such weak spots and will spread.

The fracture may be described as a crack growing process in submicroscopic, microscopic and macroscopic dimensions.

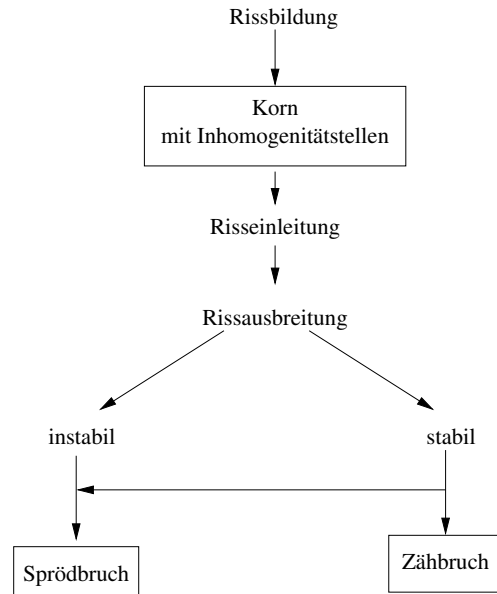Fig. 1 shows the possibilities in growth of the cracks.

Figure 1: *possibilities of crack formation (schematic)*

Crack initiation is the transition from a static into an dynamic crack. Right after that, growth of the crack follows. The crack grows larger and in the end the body fractures. Stable growth of the cracks is enabled by constant energy supply from outside and leads to macroscopic ductile fracture. An instable spreading of the cracks is due to internally stored energy in form of tension that is converted into the energy required for growth of the cracks. The growth of the cracks happens at very fast velocities ($>$ 1000 m/s) and leads to macroscopic brittle fracture.

The crack growth may be initiated by pressure, sheer or impact as Fig.2 shows.
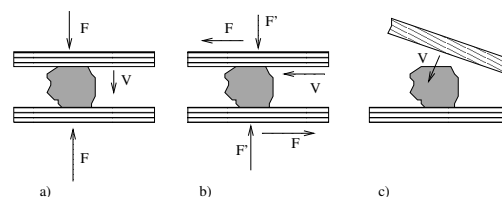

Figure 2: *strain between two surfaces: a) Pressure b) shear c) impact*

2.2 Milling kinetics

The changing particle size distribution of the milled good as a function of time is most easy to characterize qualitatively if the material has initially only one particle size. At the start of milling the first size class is continually diminished, (Curve A Fig. 3) first faster and then slower. An average particle size class is initially built up. With further milling time this size class reaches a maximum percentage (Curve B Fig. 3) since this class is milled to a smaller particle size class. Very small particle size classes evolve with time during the milling process. (Curve C Fig. 3)
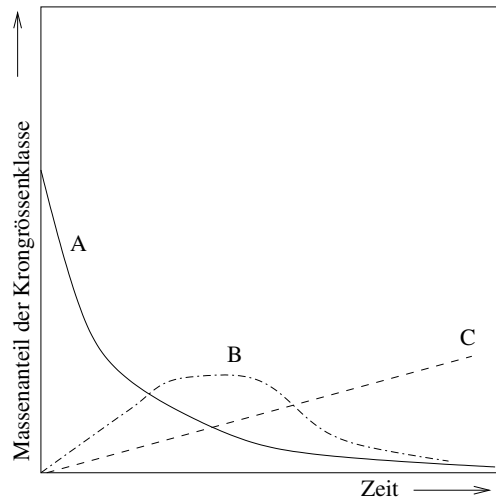

Figure 3: *milling kinetic of a discontinuous milling process*

In modeling of a discontinuous milling process, it may be assumed that particle size distribution is not a function of position in the milling good (due to good mixing in the milling process) and is homogeneous over the whole good.

The following integral equation describes a discontinuous milling process:

$$\underbrace{D(y,\tau)}_{\substack{\text{massfraction} <y \\ \text{after t } t=\tau}} = \underbrace{D(y,0)}_{\substack{\text{massfraction} < y \\ \text{at } t=0}} + \underbrace{\int_0^\tau \int_{x=y}^{x_0} \frac{\partial D(x,t)}{\partial x} S(x) B(y,x) dx dt}_{\text{massfraction} < \text{y generated from x} < \text{y during } \tau} \quad .$$

The mass-based milling speed $S(x)$ describes the selective disaggregative events. It is the mass fraction of the differential particle size class $x \ldots x+dx$ which is fractured per unit time. (When implementing such a model one has to distinguish between particle size before and after the fracture event). The breakup event is characterized by the

fragments size distribution $B(x,y)$. This describes the mass fraction $< y$ that results from selected mass of $x \ldots x + dx$ per unit time due to a fracture.

2.3 Milling laws

The connection between milling work and milling events is subject to research for more than 100 years. Rittinger investigated the decomposition of a cube into smaller cubes and postulated that the required energy W_R is proportional to the new generated surface ΔA:

$$\frac{\Delta A}{W_R} = const.,$$

$$S_M = \frac{S}{M} \propto \frac{d_p^2}{\rho_p d_p^3} = \frac{1}{\rho_p d_p}.$$

S_M is the mass specific surface.

Therefore the specific milling work may be described as follows:

$$W_{M,R} = C_R \left(\frac{1}{d_{p,\omega}} - \frac{1}{d_{p,\alpha}} \right),$$

Where $d_{p,\alpha}$ is the particle size of the initial milling goods, $d_{p,\omega}$ is the particle size of the milled good and C_R is a constant depending on the properties of the milling good and the mill and has to be determined experimentally. Rittinger's law applies best at small particle sizes ($d_{p,\omega}$ in the order of μm)

Kick postulated in 1885, that milling work is proportional to the deformed volume:

$$W \propto V,$$

$$W_M = \frac{W_{M,K}}{S_M} \propto \frac{d_p^3}{d_p^2} = d_p,$$

$$dW_{M,K} \propto d_p dS_M,$$

$$dS_M \propto -\frac{d(d_p)}{d_p^2}.$$

When the two last equations are put together the specific milling work according to Kick is:

$$W_{M,K} = c_K \ln \frac{d_{p,\alpha}}{d_{p,\omega}}.$$

c_K is a constant of proportionality.

If the particle end size is small, calculations are done following Rittinger. When the size difference between initial and end particle size is small and end particle size is large (crushing of rocks), then the correlation of Kick is more suitable (See Fig.4).

In the 50s Bond came up with an empirical relation covering the range between Rittinger and Kick's law, correlating the mass specific comminution work $W_{M,K}$ with the 80 %–particle size $d_{80,\alpha}$ and $d_{80,\omega}$ respectively:

$$W_{M,B} = c_B \left(\frac{1}{\sqrt{d_{p,\omega}}} - \frac{1}{\sqrt{d_{p,\alpha}}} \right).$$

also written in the following form:

$$W_{M,B} = 10 W_{i,m} \left(\frac{1}{\sqrt{d_{80,\omega}}} - \frac{1}{\sqrt{d_{80,\alpha}}} \right).$$

$W_{i,m}$ is the work needed for comminution a large (infinitely large) particle to 100 μm. (Bond work index)

$$W_{i,m} = \frac{P}{\dot{m}} \quad \left[\frac{Wh}{kg} \right]$$

These indexes can be looked up in literature or be determined experimentally.

For quartz sand: $W_{i,m} \cong 16 \frac{kWh}{t}$

P: Comminution power (acting on particles) $[W]$

$\dot{m}$: Throughput $[\frac{kg}{h}]$

The work needed for technical milling is a manifold of the newly generated surface energy. The growth in surface energy is not a good value for definition of the theoretical efficiency η_{th}. The efficiency is better described by the resistance to cracks R.

$$\eta_{th} = \frac{\Delta A \; R}{2 \; W_{M,B}}$$

ΔA: growth in surface

R: resistance to crack formation in minerals $R = 30 - 60 \frac{J}{m^2}$ (take $45 \frac{J}{m^2}$)
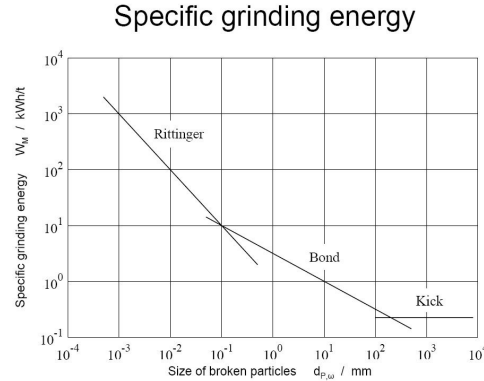
Specific grinding energy

Figure 4: *Specific comminution energy according to Rittinger, Bond and Kick*

3 Mills

3.1 Mills with loose milling tools

This is a big group of mill designs with freely moving tools such as spheres, sticks or short cylinders or also coarse grains of the milling good themselves (autogenous milling). The milling tools (also called grinding media) are located in a closed vessel and are accelerated by the movements of the vessel or by a stirring mechanism. The relative movement of the milling tools strains the milling good in between.

3.2 Ball mills

Ball mills are the most important group of such machines. Different sizes of such machines exist from laboratory scale to full industrial scale. The vessel is cylindrical shaped and filled with 25 to 45% balls with same or different sizes. The fill-degree (also filling factor) is defined as the quotient of the volume of the milling tools and volume of the vessel. Depending on the rotation speed and the fill-degree, three different movement states of the balls may be distinguished: Crawling (cascade movement), falling (cataractous movement) and centrifuging (Fig. 5). The change between these states is a smooth transition. Centrifuging starts at a critical rotation speed n_c, that can be calculated with centrifugal force $\omega^2 R = 2\pi^2 n^2 D$ is equal to gravitational force g:

$$n_c = \left(\frac{g}{2\pi^2 D}\right)^{\frac{1}{2}},$$

with D in meters and n_c in rotations per second. In practical applications, 75% of critical speed has proven to be a good value.
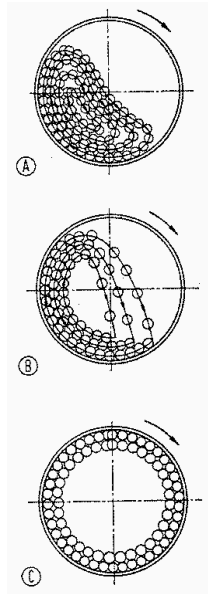

Figure 5: *Movement states of the filling*

In our lab course, we will work with a centrifugal ball mill. The feedstock can be filled up to 10 mm and will be milled to particles of about 1 μm. The mill consumes a maximum power of 100 W. (Do not assume the mill produces 100W of comminution power)

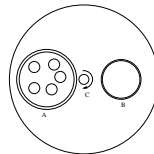In Fig. 6 the parts of the mill are described.

Figure 6: *Centrifugal ball mill*

A: milling room with balls

B: counterweight to milling room and content

C: shaft

The mill is able to turn up to 500 rpm and mill 200 ml of feedstock.

4   Sieving (Screening)

Sieving or screening is the separation process of a particulate good according to its grain sizes, where a perforated area lets small particle sizes pass through and keeps back larger sizes.

In practice the meshes of a sieve never select a sharp particle size class. Not every mesh has the exact same size, and the size distribution is enlarged even further due to wear. Fig. 7 shows the geometry of a mesh. The weaving process shapes the mesh trapezoidal. The effective size of a mesh is for a spherical particle the width m.
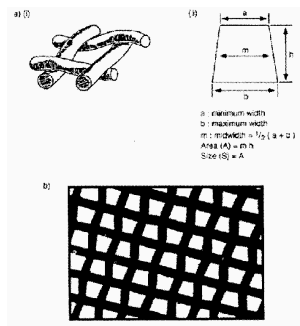

Figure 7: *a) Meshes of a woven sieve. b) Sieve under a microscope.*

To determine the size of the meshes and the mesh-size distribution, analysis can be done with a microscope. The meshes will not be uniform in size, there is a cerain distribution of mesh sizes due to manufacturing tolerances.

Sieving analysis of a particle collective can thus not produce a sharp cut between particle size classes. (undersizes: between particle with average size smaller than average mesh size and oversizes: particles larger in size than average mesh-size) In Fig. 8 the analysis of spherical shaped copper particles is shown. One can observe that some larger particles may have passed through the meshes. On the other hand some smaller particles that should have passed the meshes remain in the oversizes. A small spectrum of sphere sizes even got caught in the sieve meshes.

The sieve analysis is a cheap and uncomplicated measurement to determine the particle size distribution. For this, a stack of several sieves is used with decreasing mesh size from top to bottom (see Fig. 9).

The material is placed on the topmost sieve and the whole stack is set to swing. After
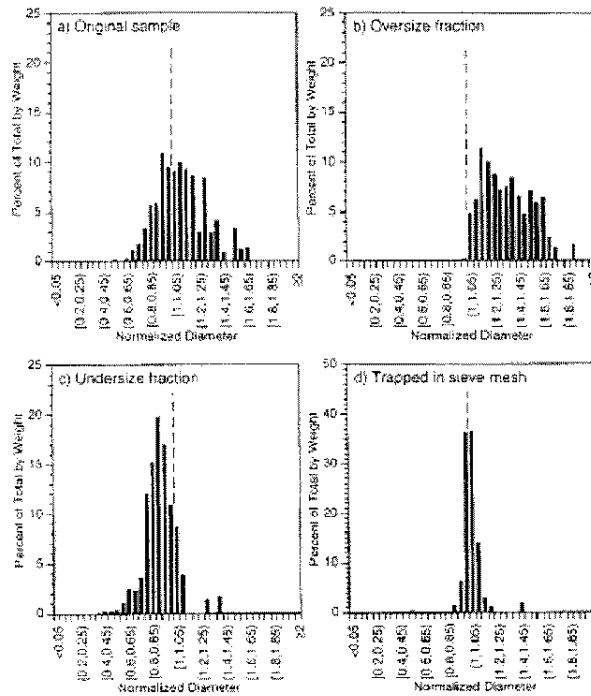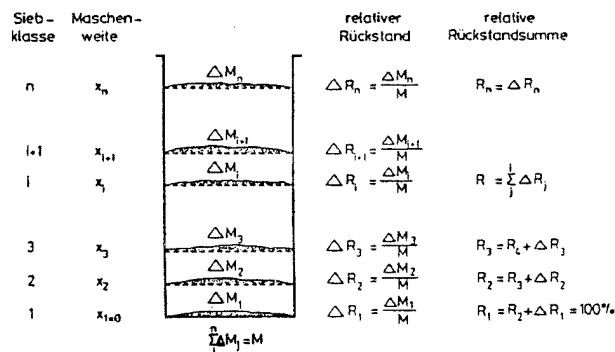
Figure 8: *Analysis of a sieve with copper spheres*

Figure 9: *Scematic of sieve analysis*

a certain time the residues on the different stages are weighted.

The analyzed material is divided into several size ranges called **classes**. The mass remaining ΔM_i on the sieve i is called **residue**. The equivalent diameter of the particles of class i is between the upper **class boundary** and the lower boundary, thus between the mesh size of the sieves above and below the particles. The difference is called the **class width**.
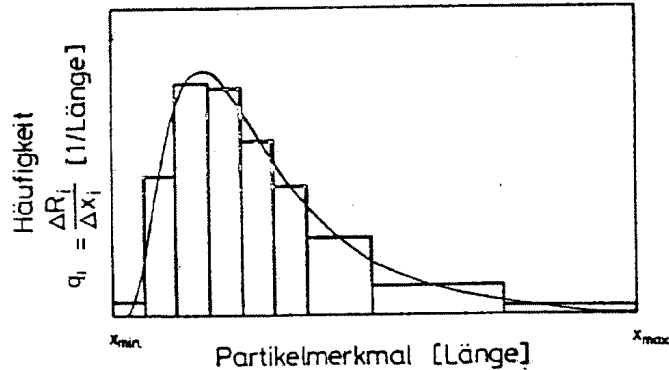
Figure 10: *Histogram*

A common graphic representation of the results of a screening analysis is the **histogram**. (Fig. 10)

q_i is the residue that is related to the total mass M and the class width $\Delta x_i = (x_{i+1} - x_i)$.

$$q_i = \frac{\Delta M_i}{M \Delta x_i} = \frac{\Delta R_i}{\Delta x_i},$$

which can also be defined from **relative residues**

$$\Delta R_i = \frac{\Delta M_i}{M}$$

is plotted over the class boundaries from x_i to x_{i+1} in form of columns (pillars) The change from discrete to differential representation of the data is the **distribution density function** (Fig. 10):

$$q(x) = \frac{1}{M} \frac{dM}{dx} = \frac{dR}{dx}.$$

The sum of the relative residues leads to (starting from the top sieve) the cumulative relative residues R_i. If R_i is plotted against the mesh size x_i the residues characteristic line $R_i = R(x)$ is obtained. On the other hand $D_i = 1 - R_i = D(x)$ is the throughput characteristic line or cumulative distribution. (Fig.11 top)

The residues are weighted in screening analysis. This way a **mass distribution** is obtained ($Q_3(x) = D(x)$). Likewise the particles on each sieve could be counted, what would lead to a **number (or count) distribution** (Q_0). It is a big effort to count particles though and thus the count distribution is normally not used in practical applications.
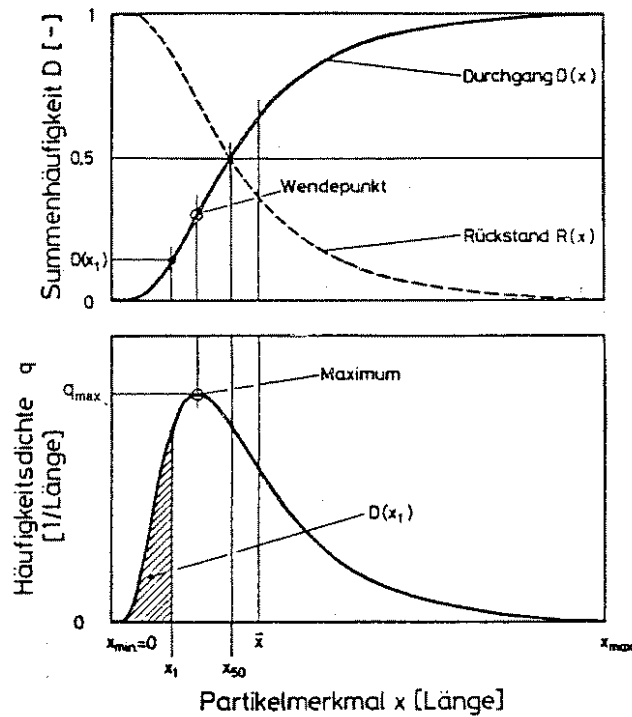
Figure 11: *Cumulative distribution and distribution density function of a lognormal distribution*

Mass and count distributions can be calculated from each other by **moments**. The distributions differ from each other in the way that the maximum of the mass distribution is at larger sizes than the maximum of the count distribution. This is the case, because smaller particles have a smaller mass than an equal number of larger particles.

Figure 12: *Mass and count-distribution of the same particle sample*

Moments

General representation of a moment of a distribution $q_r(x)$ is

$$M_{k,r} = \sum x_i^k q_r(x_i) = \int_{x_{min}}^{x_{max}} x^k q_r(x) dx.$$

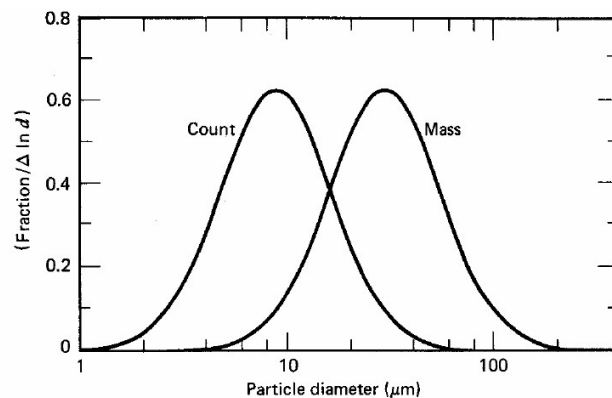$r = 0, 1, 2, 3$ is number, length, surface, volume.

k is the corresponding moment.

x is the particle characteristic.

i is the size class i

Example

The third moment of a count distribution is the total volume V of all particles:

$$M_{3,0} = V = \int_0^\infty x^3 q_0(x) dx.$$

The particle characteristic x is the particle size (diameter).

Moments are used to convert an arbitrary distribution into an other (for example the mass distribution into a number distribution)

General:

$$q_r(x) = \frac{x^{r-j} q_j(x)}{M_{r-j,j}}.$$

Example: Conversion of a count distribution into a volume distribution:

$$q_3(x) = \frac{x^3 q_0(x)}{M_{3,0}} = \frac{x^3 q_0(x)}{V}.$$

Averages There are a couple of averages which characterize a distribution:

Arithmetic average: $\overline{x} = \frac{\sum x}{N}$ x: diameter of a particle, N: number of particles.

Median : $\overline{x}_{me}$ or $x_{50,r}$: The diameter dividing the distribution into two parts with equal numbers of particles above and below this size. r= 0,1,2,3 stands for count, length, sufrace and volume.

Mode: $\overline{x}_{mo}$: The most frequent diameter in the distribution. The diameter at the maximum of the distribution density function.

diameter of average mass: $\overline{x}_g = \left(\frac{\sum n_i x_i^3}{N} \right)^{\frac{1}{3}}$.

mass mean diameter: $\overline{x}_m = \frac{\sum n_i x_i^4}{\sum n_i x_i^3} = \frac{\sum m_i x_i}{\sum m_i}$

Sauter mean diameter: $\overline{x}_s = \frac{\sum n_i x_i^3}{\sum n_i x_i^2} = \left(\frac{6}{\rho} \right) \frac{M}{A}$ for spherical particles.

M: total mass, A: Total surface.

Logarithmic normal distribution

The primary result of a particle size analysis is a distribution in graphical or tabular form. These data are though unhandy and not very useful for comparisons. That is the reason why discrete experimental data is often fitted with continuous distribution functions. This way the distribution is reduced to a few characteristic numbers. Mostly those distribution functions have two parameters: one describing the position of the distribution and the other describing the scattering or spread. These parameter are determined mostly by plotting the cumulative distribution in a diagram whose axes are scaled in a way that the cumulative distributions is linear. (only works if the real particle size distribution is described well enough by the chosen function to modify the chart axis) Note: This is not a log-log plot!

One distribution function that works for a lot of cases is the log-normal distribution. (DIN 66 144). There is no physical reason for this, it is just a empirical observation. In this distribution function $\ln(x)$ is normally distributed and the geometric standard deviation σ_g describes the spread around $\ln(x_{50,r})$ (median). The density function of the log-normal count distribution is the following:

$$q_0(x) = \frac{1}{\ln\sigma_g\sqrt{2\pi}\cdot x}\exp\left(-\frac{1}{2}\left(\frac{\ln(x/x_{50,0})}{\ln\sigma_g}\right)^2\right)$$

$$\ln\sigma_g = \sqrt{\frac{1}{1-N}\sum_i n_i\left(\ln x_i - \ln(x_{50,0})\right)^2}.$$

The cumulative distribution is:

$$Q_0(x) = \int_0^x q_0(\xi)d\xi.$$

where ξ is an integration variable.

As visible in the density function, the parameters describing the distribution are:

Postion of distribution:	$x_{50,r}$	Median; $(Q_r(x_{50,r}) = 50\%)$
Spread/Width of distribution:	σ_g	Geometric standard deviation

The **advantages** of the log-normal distribution are the **good representation of the fine particles** in most fabrication processes. Any weighted (count, mass, etc.) distribution

of a log-norm distribution is again a log-norm distribution with the same geometric standard deviation. **Calculation of important characteristic numbers** is rather **easy for log-norm distributions:**

Volume specific surface:

$$S_v = \frac{6}{x_{50,3}} \exp\left(\frac{\sigma_g^2}{2}\right)$$

Sauter mean diameter:

$$x_s = \frac{M_{3,0}}{M_{2,0}} = x_{50,3} \exp\left(-\frac{\sigma_g^2}{2}\right)$$

Moments:

$$M_{k,r} = x_{50,r}^k \exp\left(\frac{k^2 \sigma_g^2}{2}\right),$$

Differently weighted distributions:

$$q_k(x) = \frac{\exp\left(\left(-\frac{1}{2}\frac{\ln(x/x_{50,r})}{\sigma_g} - (k-r)\sigma_g\right)^2\right)}{\sigma_g \sqrt{2\pi} \cdot x}.$$

Medians of differently weighted distributions:

$$x_{50,r} = x_{50,s} \exp\left((r-s)\sigma_g^2\right)$$

A **disadvantage** of the log-normal distribution is the large size fraction is not limited and the fraction of large sizes is (theoretically) always overestimated. In practical application this is not a problem, because $q_r(x)$ is never zero for large x but is very small, so that differences compared to measured distributions are negligible.

For evaluation, the residues m_i shall be collected and subsequently normalized by the total mass M. The cumulative distribution function $(D(x) = Q_3(x))$ shall be calculated and plotted in the log-normalprobability chart (last page) on the y-axis (in %) versus particle size (corresponding to intermediate sizes between sieve mesh width).

If the measurements plot in this chart is approximately a straight line, the distribution is log-normal. The median $x_{50,3}$ at $Q_3(x_{50,3}) = 50\%$ can be directly read from the graph, regardeless whether the plot is linear or not. The geometric standard deviation σ_g can be estimated by the following equation:

$$\sigma_g = \left(\frac{x_{84,3}}{x_{50,3}} \right).$$

If both the parameters of the log-normal distribution are known, the histogram can be compared with the approximated frequency distribution curve. For this the frequency distribution curve should be placed through the averages of each size interval defined by the mesh sizes.

This is a graph paper / chart template for particle size distribution analysis.

Axes:
- Horizontal axis (bottom): Particle Size x — logarithmic scale from 1.0E-1 to 1.0E+3 (1.0E-1, 1.0E+0, 1.0E+1, 1.0E+2, 1.0E+3)
- Vertical axis (left): Durchgang % — with values 99.9, 99.5, 99.0, 98.0, 95.0, 90.0, 80.0, 70.0, 60.0, 50.0, 40.0, 30.0, 20.0, 10.0, 5.0, 2.0, 1.0, 0.5, 0.1
- Second vertical scale: 3.0, 2.0, 1.0, 0.0, -1.0, -2.0, -3.0

Label at bottom right: c