The EU FP7 NanoDefine Project

Development of an integrated approach based on validated and standardized methods to support the implementation of the EC recommendation for a definition of nanomaterial

Report of the potentials of the transformation of non-counting methods size distributions into number weighted size distributions of the constituent particles based on instrument manufacturers algorithms

NanoDefine Technical Report D3.6

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NanoDefine in a nutshell

The EU FP7 NanoDefine project was launched in November 2013 and will run until October 2017. The project is dedicated to support the implementation of the EU Recommendation on the Definition of Nanomaterial by the provision of the required analytical tools and respective guidance. Main goal is to develop a novel tiered approach consisting of (i) rapid and cost-efficient screening methods and (ii) confirmatory measurement methods. The "NanoDefiner" eTool will guide potential end-users, such as concerned industries and regulatory bodies as well as enforcement and contract laboratories, to reliably classify if a material is nano or not. To achieve this objective, a comprehensive inter-laboratory evaluation of the performance of current characterisation techniques, instruments and software is performed. Instruments, software and methods are further developed. Their capacity to reliably measure the size of particulates in the size range 1-100 nm and above (according to the EU definition) is validated. Technical reports on project results are published to reach out to relevant stakeholders, such as policy makers, regulators, industries and the wider scientific community, to present and discuss our goals and results, to ensure a continuous exchange of views, needs and experiences obtained from different fields of expertise and application, and to finally integrate the resulting feedback into our onoing work on the size-related classification of nanomaterials.

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III. Glossary

Terms and definitions in this report are in accordance with ISO 9276-1 -2 -3 and classical text-books of particle sizing and mathematics.

size x

equivalent diameter or characteristic length

equivalent diameter x_Z

diameter of a sphere being equivalent to particle with respect to property Z

characteristic length

any length describing the outer dimensions of a particle (mostly in imaging), e. g. Feret diameter, rod diameter, cord length

type of quantity (TOQ) A

cumulable property of particle system (or single particle) used to quantify the relative amount of particles in the individual size classes, e. g. number, mass, light scattering, X-ray extinction

index of TOQ r

employed when TOQ refers to geometric properties, equals the exponent of this property with respect to Metre; e. g. $r = 0$ for number, $r = 2$ for surface, $r = 3$ for volume

sum function $Q(x)$

cumulated relative amount of particles with size $\leq x$; where amount refers to the TOQ – indicated by index: $Q_r(x)$ or $Q_A(x)$, e. g. sum function of number weighted distribution $Q_0(x)$

density function $q(x)$:

first derivative of $Q(x)$ with respect to x;
for a 50%-50%-bimodal distribution with distinct modes: when $q(x)$ is plotted on x-axis, the area below the two modes is identical

transformed density function $q^*(x)$

first derivative of $Q(x)$ with respect to $\ln x$;
for a 50%-50%-bimodal distribution with distinct modes: when $q(x)$ is plotted on $\log x$-axis, the area below the two modes is identical

median (size) $x_{50,r}$

halves the particle population with respect to the TOQ when particles are sorted according to size; $Q_r(x_{50,r}) = 0.5$

modal size of the density function $x_{\mathrm{mod},r}$

position of local maximum of $q_r(x)$

modal size of the transformed density function $x_{\mathrm{mod}*,r}$

position of local maximum of $q^*_r(x)$

(raw) moment of the size distribution $M_{k,r}$ or $M_{k,A}$

expectation value of x^k of the (x^r or quantity A weighted) size distribution,
$$M_{k,r} = \left\langle x^k \right\rangle_r = \int x^k \, dQ_r$$

<u>(power) mean</u> $\overline{x}_{k,r}$

"integral average"/"effective size", $\overline{x}_{k,r} = \left[\int x^k \mathrm{d}Q_r\right]^{1/k}$; $\overline{x}_{0,r} = \exp\left[\int \ln x \mathrm{d}Q_r\right]$

k = -1,0,1,2 → harmonic, geometric, arithmetic, quadratic mean

<u>integral size</u>

few techniques allow for the immediate derivation of a mean size from the detected signals, e. g. BET yields S_V and x_{BET}, SAXS yields S_V (via Porod's invariant) and x_{SAXS}, DLS yields D_{eff} (via initial slope of ACF) and x_{cum}, photometric turbidity yields $C_{\mathrm{ext,eff}}$ (knowing volume concentration) and thus x_{photo}, XRD yields peak broadening b and thus x_{XRD}

<u>constituent particle (cp)</u>

individual particles that can be identified within an agglomerate; frequently identical to or identified with the primary particles.

<u>primary particle</u>

particles from which an agglomerate is formed; frequently identical to or identified with the constituent particles of the agglomerate (or aggregate).

<u>agglomerate</u>

generic term for a contiguous cluster of particles which are held together by physical adhesion forces, chemical bonds, and/or form closure; the individual particles from which an agglomerate is formed are called primary particles, particles that can be identified within an agglomerate are called constituent particles, the agglomerate itself is sometimes called a secondary particle; note that agglomerates may possess a multiscale structure due to consecutive agglomeration processes (e.g. aggregation of primary particles in a flame, agglomeration of aggregates in the gas phase, compaction of agglomerates in powder bulk phase); agglomerates can be classified by the kind and strength of the particle bonds (e.g. aggregates for strong adhesion forces and flocs for weak ones).

<u>aggregate</u>

agglomerate with relatively strong interparticle adhesion, commonly applied to agglomerates of colloidal particles that are closely touched or even sintered; sometimes referred to agglomerates "that cannot be dispersed further" or to agglomerates, in which particles are attached via faces rather than via contact points – the former "definition" reveals a poor understanding of deagglomeration processes, whereas the latter is particularly meaningful for pigment characterisation.

<u>measurement principle</u>

(physical) effect that is employed for the quantification of the measurand (e.g. particle size, zeta-potential); the dependency of the effect on the measurand has to be well-defined; examples: i) settling velocity grows with particle size, ii) diffusion coefficient is inversely proportional to size, iii) 2D-images obtained by orthogonal projection allow the direct quantification of characteristic lengths and areas.

<u>measurement technique MT</u>

specific way of employing a measurement principle for the quantification of a measurand (e.g. particle size); similar measurement techniques are sometimes grouped as one measurement method; examples: i) the settling velocity as a measure of size (= measurement principle) can be measured by gravitational sedimentation with an X-ray transmission detector (= measurement technique) or by centrifugal sedimentation in homogenously filled cuvettes with an optical transmission detector, ii) the diffusion coefficient can be measured with dynamic light scattering by means of a self-beating autocorrelation detector or by means of homodyne light detection and frequency analysis, iii) sphere diameters can be derived from images of a scanning electron microscope, which were obtained with or without using the emitted secondary electrons.

characterisation method CM

specific procedure for the characterisation of a material which includes the steps of sample preparation, sample analysis with (a) certain measurement technique(s) and subsequent data interpretation

IV. Abbreviations and acronyms

AC	analytical (disk- and cuvette) centrifugation
ALS	angular light scattering
BET	Brunauer–Emmett–Teller method of analysing gas adsorption data
CM	characterisation method
DLS	dynamic light scattering
DEMS	differential electrical mobility spectroscopy
EC	European Commission
EMS	electroacoustic mobility spectroscopy
FFF	field flow fractionation
LD	laser diffraction (spectroscopy)
MT	measurement technique
OCA	optical centrifugation analysis
OS	optical spectroscopy
PTA	particle tracking analysis
SAXS	small-angle X-ray scattering
SEM	scanning electron microscopy
SFM	scanning force microscopy
TEM	transmission electron microscopy
TOQ	type of quantity
TRPS	tuneable resistive pulse sensing
USSP	ultrasonic spectroscopy

V. Summary

This deliverable briefly reviews the mathematical basics and the practical problems for transforming size distributions into number weighted distributions of (constituent) particles. It further describes and discusses various strategies employed in commercial instruments and in academic research that can enhance the performance of transformation procedures. It closes with a discussion on the possibilities and limits of transformations in the case of fractal aggregates.

1 Introduction

Each particle sizing technique can be attributed a characteristic type of size distribution, which is defined by the probed particle property (equivalent diameter x_Z) and by the type of quantity (TOQ), in which the size classes are intrinsically weighted. For instance, dynamic light scattering (DLS) intrinsically yields (scattered light) intensity weighted distributions of the (apparent) hydrodynamic diameter $Q_{int}(x_{hd})$, while analytical centrifugation with an X-ray detector measures the volume weighted distribution of the Stokes diameter $Q_3(x_{Stokes})$. The differences among the numerous kinds of size distributions are considerable and should be adequately accounted for when interpreting or comparing particle sizing results (cf. Figure 1).
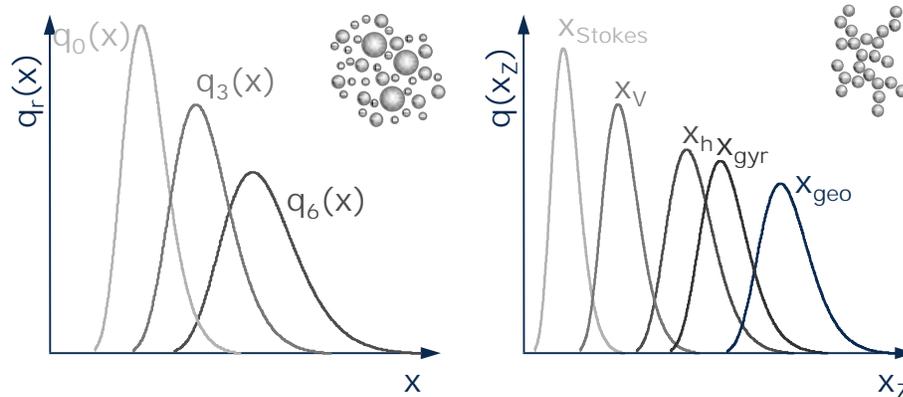
Figure 1: illustration of the impact of TOQ on the size distribution of polydisperse samples (left) and schematic plot of the distributions of different equivalent diameters for fractal aggregates (right)

A common way to cope with this situation is the conversion of size distributions (i. e. from $Q_A^{(Z)}(x_Z)$ to $Q_B^{(Y)}(x_Y)$). Conversion is of general relevance in particle sizing; it is e. g. employed

- when testing the conformity to product specification (e. g. if specification defines $Q_3(x)$, yet the analytical techniques just provides $Q_0(x)$),

- when monitoring industrial processes, e. g. if number weighted median $x_{50,0}$ is to be controlled, whereas online-MTs deliver $Q_3(x)$,

- for the validation of (new) measurement techniques,

- for the combination of different MTs when analysing very polydisperse systems.

Within NanoDefine conversion becomes a crucial point when using rapid screening methods (also: *tier 1 methods*) for the evaluation of substances and products with respect to their identification as nanomaterials or not. As the current EC recommendation for a definition of nanomaterial is based on the number weighted median size of constituent particles, any screening method should be able to approximately measure this parameter. However, only few techniques yield number weighted size distributions of the constituent particles ($Q_0(x_{cp})$), whereas most MTs do neither probe the constituent particles nor do they deliver number weighted size distributions. NanoDefine then requires a transformation of size distribution $Q_A(x_Z)$ into $Q_0(x_{cp})$, which means a twofold conversion of i) TOQ and ii) equivalent size. The latter can be even described more precisely, since the definition of nanomaterials refers to the smallest dimension of particulate objects. Hence, if the constituent particles are non-spherical, then "size of the constituent particles" means the smallest outer dimension (e. g. the diameter of rod-like particles).

It is obvious that the required transformation is a serious challenge for the general case. However, the degree of sophistication related with this way of data processing depends on the specific characterisation method (CM). It is possible to distinguish CMs, which …

- rely on imaging techniques (e. g. TEM, SFM) and which immediately yields $Q_0(x_{cp})$;

- are based on MTs that provide $Q_0(x_Z)$ (e. g. DEMS, PTA, TRPS); for them, transformation becomes necessary in case particles are non-spherical or aggregates;

- are based on MTs that provide $Q_{A\neq0}(x_{cp})$ (e. g. SAXS); transformation then just refers to the conversion of the TOQ;

- are based on MTs that provide $Q_{A\neq0}(x_{Z\neq cp})$ (e. g. FFF, AC; DLS, ALS, OS, USSP); transformation then refers to both, conversion of the TOQ and conversion of the equivalent diameter.

The list implies that for the majority of MTs there is no simple way of eliciting $Q_0(x_{cp})$ – if any. Even more, it is evident that any reliable transformation of size distributions requires prior knowledge on the morphology of the particle system (e. g. deviation from spherical shape, structural parameters of aggregates).

2 Transformation of size distributions

2.1 Mathematical route

Consider the general case of the distribution of a parameter x_Z (e. g. disc thickness or any equivalent diameter) weighted by the quantity A (e. g. volume or scattering intensity), which is to be transformed in the distribution of parameter x_Y weighted by quantity B. This can be described in terms of the density functions as

$$q_A^{(Z)}(x_Z) \rightarrow q_B^{(Y)}(x_Y) \tag{1}$$

$$\text{with } q_A^{(Z)}(x_Z) = \frac{dQ_A}{dx_Z} \text{ and } q_B^{(Y)}(x_Y) = \frac{dQ_B}{dx_Y}. \tag{2}$$

Typical particle systems are not only polydisperse, but also polymorphic. As a result, there is no unambiguous relation between the different size parameters x_Z and x_Y (e. g. spheres and cubes of same volume differ in surface area). Yet in practice it is convenient to assume a strict correlation, which can be expressed as shape function

$$x_Z = {}_{YZ}(x_Y) \tag{3}$$

with the special case of x_Y being the volume equivalent diameter

$$x_Z = \{_Z(x_V). \tag{4}$$

The strict correlation also means that the distribution function obeys the following relationship:

$$dQ_A(x_Y) = dQ_A(x_Z) \tag{5}$$

(note however that $q_A^{(Y)}(x_Y) \neq q_A^{(Z)}(x_Z)$).

For instance, the transformation of the volume equivalent diameter x_V into the surface equivalent diameter x_S can be expressed as $\{_S(x_V) = {}^{-1/2} \cdot x_V$, where j denotes Wadell's sphericity. If the particles are rod-like with an aspect ratio $_{...} = L/D$ the transformation of the surface equivalent diameter x_S diameter into the smallest particle dimension (i. e. D) is described as $_{SD}(x_S) = x_S / \sqrt{\frac{1}{2} + ...}$.

While eqs. (3)-(5) describe the transformation of size parameters an additional step is required for the conversion with respect to TOQ. For this purpose the relationships between quantities A and B and particle size have to be known:

$$A = f_{A,Z}(x_Z) = f_{A,Y}(x_Y) \text{ and } B = f_{B,Z}(x_Z) = f_{B,Y}(x_Y). \tag{6}$$

Together with the shape function (eq. (3)) it is then possible to conduct the transformation of size distribution for continuous size distributions

$$q_B^{(Y)}(x_Y) = \frac{f_{B,Y}(x_Y)}{f_{A,Y}(x_Y)} \cdot \frac{\partial_{YZ}}{\partial x_Y} \cdot q_A^{(Z)}(_{YZ}(x_Y)) \bigg/ \int \frac{f_B(x)}{f_A(x)} \cdot dQ_A \tag{7}$$

and for discrete size distributions

$$\Delta Q_{B,i} = \frac{f_{B,i}}{f_{A,i}} \cdot \Delta Q_{A,i} \left/ \sum \frac{f_{B,k}}{f_{A,k}} \cdot \Delta Q_{A,k} \right. . \tag{8}$$

The TOQ functions f_A and f_B may concern physical quantities like scattering intensity or turbidity, which can be referred to the particles individual contribution (e. g. scattering or extinction cross section C_{sca} and C_{ext}, respectively). Or they concern geometric properties like number, projection area or volume. Sometimes it is possible to relate physical quantities to geometric properties (e. g. weight to volume if mass density is uniform, scattering intensity to the squared volume for nanoparticles, or light extinction to the projected area if particles are much larger than 1 µm).

When the TOQs A and B can be considered as geometric properties, which are proportional to x^r and x^s, respectively, the integral in eq. (7) becomes a raw moment of the size distribution. For spherical particles the conversion of size distributions is then achieved by

$$q_s(x) = x^{s-r} q_r(x) \left/ \int x^{s-r} dQ_r = x^{s-r} q_r(x) \right/ M_{s-r,r} . \tag{9}$$

Number weighted size distributions are thus obtained by

$$q_0(x) = x^{-r} q_r(x) \left/ \int x^{-r} dQ_r = x^{-r} q_r(x) \right/ M_{-r,r} . \tag{10}$$

The introduction of the moments of the size distribution is particularly useful, when analytical distribution functions (e. g. log-normal distribution) are employed because their moments can be easily computed from the distribution parameters (Rumpf & Ebert 1964).

2.2 Problems encountered when transforming size distributions

While the mathematical concept for transforming size distributions is fairly clear, the problems encountered in practice are not. In general, these problems are hardly related to mathematical / numerical issues, but predominantly result from the physics of the measurement principle and the limitations of real measurement systems. The measurement principle defines the probed particle property and the intrinsic TOQ. It thereby sets fundamental limits on the degree to which the transformation can be performed. In addition we have to acknowledge that each analytical technique, even each instrument type has specific detection and measurement limits. The former refer to limits, beyond which any sensitivity to particles is lost (e. g. in OCA when optical extinction is too low). Whereas the latter refer to such limits, beyond which size distribution cannot be resolved (e. g. in ALS when particles are too small or in AC when particles are too coarse).

Several issues may arise when transforming size distributions:

- The particle morphology (shape, structure) is not known or just in terms of qualitative descriptors.

- The particle morphology can be only quantified by few (often one) population averaged parameters (e. g. aspect ratio of rods, fractal dimension of aggregates).

- The measurement results of non-spherical particles depend on the particle orientation (e. g. when analysing images of platelets).

- The measurement range does not cover the complete size range of the particle system.

- The sensitivity of the analytical instrument is not uniformly distributed along the measurement range; the level of uncertainty varies with particle size.

- Error propagation amplifies measurement uncertainties during conversion (e. g. those at the lower end of $Q_3(x)$ when converted to $Q_0(x)$).

- The information content of the measurement data is limited, thus leaves a principal uncertainty on the shape of the distribution functions which propagates at conversion.

- The information content of the measurement data may significantly vary for the different kinds of distribution functions (i. e. the capability to distinguish separate modes of a size distributions may depend on whether $Q_0(x)$ or $Q_3(x)$ is requested).

- The interval width of discrete size distributions adversely affects the conversion (typical problem when converting $Q_3(x)$ results of sieve analyses to $Q_0(x)$).

The severity of these problems does not only depend on the employed MTs, but also on the material system. In general, the problems are reduced (i. e. the reliability of conversion is increased), when particles are virtually spherical, polydispersity is low and particle sizes are well within the measurement range.

3 Strategies for enhancing the quality of transformation

In order to cope with the various problems that are encountered during transformation several strategies are used in research as well as in commercial instruments. They address different issues and can be regarded supplementary. However, in particular for spectroscopic ensemble techniques different strategies may fuse into one approach. For this reason the conversion for ensemble methods is separately commented on in section 3.3.

It should be noticed that for analytical tasks in research fields the problems related to particle sizing and transforming size distribution are much better known than for instrument manufacturers supplying their MTs for a preferably wide field of products and applications. For this reason, it is possible to find more sophisticated solutions by researchers than by instrument manufacturers.

3.1 Strategies of coping with non-spherical particles

Non-spherical particles considerably complicate the analysis of measurement data and the transformation of size distributions. This is due to several reasons. Mathematical models for the probed particle property and the detected TOQ i) have to be established and ii) require quantitative morphological parameters. Moreover, frequently it is not possible to distinguish between polydispersity and variation in shape (aggregate structure), which introduces an additional polydispersity to the measured results. Yet, even for monomorphic particle systems a shape-related polydispersity can be observed, when particle orientation affects the measurement results (e. g. in ALS). Effects of particle shape and orientation are differently tackled.

S1 – ¡ignore shape, assume spherical particles!

This is fairly typical for any commercial particle sizing technique (e. g. in DEMS – SMPS manual, AC – CPS operating manual, DLS – ZetaSizer® manual, Windox® manual, ALS – Mastersizer manual, USSP – DT-1200 user handbook). Measurement results are then interpreted in terms of "equivalent diameters", which is a well-accepted concept in particle sizing. Consequently, conversion of particle size distributions then just concerns the TOQ, i. e. only the step $Q_A(x_Z) \rightarrow Q_B(x_Z)$ is regarded. Since all particles are considered spherical, the TOQ functions f_A and f_B (eqs. (6)) are computed for spheres, which may introduce a systematic error to the distribution $Q_B(x_Z)$. This error is the more significant the larger the deviation from spherical shape is.

For instance, it can be shown that the Stokes diameter x_{Stokes} of fractal aggregates is much smaller than their hydrodynamic diameter x_{hd} or the diameter of gyration x_{gyr}. This may lead to a situation, in which $x_{Stokes} < 100$ nm, while the optically relevant size $x_{gyr} > 100$ nm (Babick et al. 2012b). An optical model based on the Stokes diameter (i. e. Rayleigh scattering with $I_{sca} \sim x^6$) would be therefore inadequate for the conversion step.

However, if the deviations from spherical shape are of minor degree the TOQ conversion is hardly affected by shape (Fernlund et al. 2007).

S2 – ¡assume a uniform, regular shape for all particles!

Such shapes may be spherical core-shell structures, spheroids and cylindrical particles (including thin discs and long rods), which can be quantified by one (few) parameter(s) (e. g. relative shell thickness, and aspect ratio). If the MT provides enough details in its measurement data it may be even possible to adjust these shape parameters in addition to the size distribution. Such a procedure can be found in commercial SAXS instrumentation (Nano-Solver® manual). Yet, usually the shape parameters cannot be derived from the measurement (e. g. in standard DLS) and have to be provided as further model parameter in the data analysis (Hallet et al. 1991, Patty & Frisken 2006).

S3 – ¡assume random orientation for non-spherical particles!

This assumption is frequently justified when single particles are observed over long periods or when the measurement is conducted of a huge number of particles simultaneously. In quiescent fluids particles randomly align due to Brownian rotation, while in turbulent flow particles rotate by eddy motion. The assumption of random alignment is not only relevant for converting size distribution, but rather fundamental for data interpretation (e. g. in SAXS or ALS measurements).

S4 – ¡conduct the analysis for a defined alignment of non-spherical particles!

A defined alignment is mostly achieved, when particles are collected on substrate for imaging techniques (e. g. SEM). For coarse, micrometre-sized non-spherical particles a defined alignment can be achieved in laminar flow (aero- or hydrodynamic focussing). In the context of nanomaterial characterisation this has to be considered when analysing nanorods / nanofibres with extremely high aspect ratios.

3.2 Strategies aiming to minimise effects of error propagation

A fundamental quality of measurement results is their uncertainty, which may be of various origins. In particle sizing the uncertainty refers to both, the particle size x and the relative amount associated with it (i. e. $q(x)$). It is rather obvious that these uncertainties also affect the outcome of particle size transformation. However, only few papers directly address this issue (e. g. Besançon et al. 1990, Witt et al. 2007, Hogg 2008). Figure 2 illustrates this effect for the conversion of simulated number weighted size distributions $q_0(x)$ into $q_3(x)$, when the uncertainty solely results from the limited sample size (i. e. number of particles counted) and thus obeys the Poisson statistics.
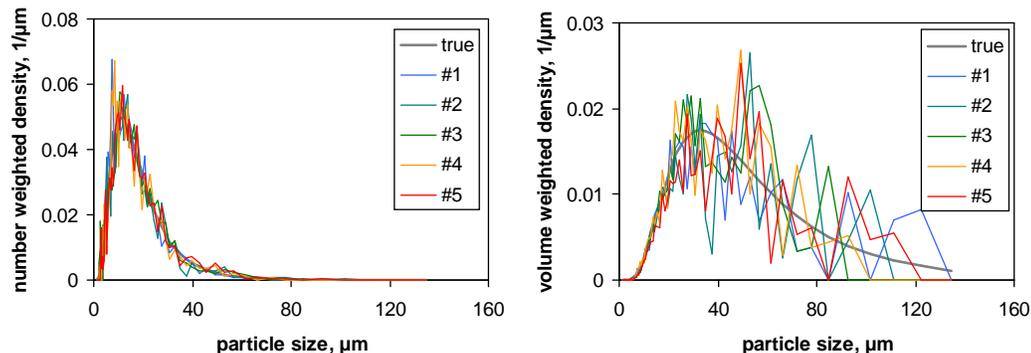
Figure 2: simulated density functions of a disperse system with log-normal size distribution ($x_{50,0}$ = 16 µm, †$_{ln}$ = 0.6) when a total number of 1000 particles is examined; left: number weighted (given), right: volume weighted (after conversion)

The example shows that slight uncertainties at the upper edge of the number weighted density functions $q_0(x)$ are disproportionatey magnified after the conversion in $q_3(x)$. In general one can state that conversion from $o_r(x)$ into $a_{s>r}(x)$, amplifies uncertainties at the upper edge of the size distribution, whereas conversion from $o_r(x)$ into $a_{s<r}(x)$ amplifies the errors at the lower edge of the size distribution. The problem is frequently aggravated by the fact that the uncertainty at the edges of a size distribution is particularly high. This results from the rare occurrence of very fine or very coarse particles and/or from a reduced sensitivity of the MT at the boundaries of its measurement range.

Error propagation does not only concern the edges of a size distribution, but also its complete shape, which is – inter alias – described by polydispersity parameters or the occurrence of several modes. It is thus related to other critical issues in particle sizing, such as the accurate measurement of monodisperse samples (usually an artificial polydispersity is introduced by the measurement principle or by the practical limitations of sensor technique) or the distinction of separate size modes. The problem of resolving the shape of the size distribution refers to any kind of sizing technique yet is highlighted for spectroscopic ensemble techniques.

### 3.2.1   Uncertainty at the edges of the size distribution

Uncertainties at the edges of size distributions originate from statistical effects when detecting few very coarse or very fine particles, from reduced sensitivity, from crossing the measurement limits or even from MT-specific problems (e. g. baseline drift in disc centrifugation). As a result the density function may appear noisy at the edges or the minimum and maximum size values are not accurately measured. There are several strategies to cope with this.

S5 – ¡ignore the uncertainty at the edges of the distribution function!

In default of reliable data on the uncertainty it is rather common to not particularly treat the measurement data at the edges of the size distribution. Noise in the density function is deliberately left as an indication of uncertainty. The advantage of this approach is not to feign accuracy, where it is not, and not to introduce bias to the size distribution. However, it usually impedes the reliable conversion of size distributions. For this reason, some commercial instruments facilitate a subsequent data treatment by users.

S6 - ¡make assumption on the edges of the size distribution!

In order to enhance the conversion of size distributions it is possible to smooth out the density functions at the lower and upper edges or to set values for minimum and maximum particle size (m_{an} and m_{axi}). This strategy is particularly applied for counting and fractionating Mats (e. g. DEMS, AC). When converting into number weighted size distribution, one should note that any data treatment at the lower edge of the size distribution has a considerable impact on the outcome (Figure 3). Hence any smoothing should be well-reasoned and any value of x_{min} should be well-justified by additional measurements.
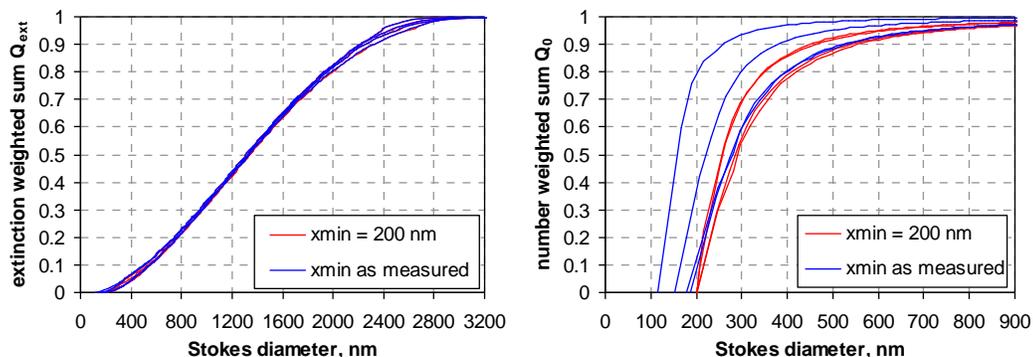
Figure 3:   impact of pre-setting the minimum particle size on the conversion of extinction weighted (left) to number weighted (right) size distribution; polydisperse silica particles measured with an optical curette centrifuge (4 repeated measurements)

S7 – ¡give notice, if measurement limit is crossed!

When size distributions touch the limits of the measurement range of a given MT one is faced with two questions: Are the amounts of the finest (or coarsest) particles accurately determined? And does the size distribution extend beyond the measurement limits of the MT? Therefore, some commercial instruments provide a data quality assessment based on the knowledge of the theoretical range (or functional space) of the measurement signals (e. g. exponential decay in DLS) or on the calculated distribution function. This assessment indicates if size range is exceeded and / or if further data treatment (like conversion) is meaningful. Such assessments are frequently encountered for spectroscopic ensemble techniques (e. g. DLS – Easier® manual, ALS – Window® manual, USSP – DT-1200 user handbook).

3.2.2   Uncertainty on the details of the size distribution

Interlaboratory comparisons of particle sizing techniques typically show a good agreement with regard to the location (I. e. median, modal or mean values) but rather significant deviations with regard to the details of the size distribution (e. g. variance, skew ness, and number of modes).

This is partly due to specific limitations of the employed instrumentation and to the incompleteness of the models (e. g. with respect to particle morphology or model parameters). Additionally, the deviations originate in the limited capability of any measurement principle to resolve details of the size distribution – which is especially relevant for spectroscopic ensemble techniques (cf. section 3.3). As the uncertainty on details of the size distribution also influences the quality of transforming size distribution the according approaches to cope with it are considered below.

<u>S8 – ¡do not introduce any bias (a priori knowledge) to data analysis!</u>

This means that the existence of uncertainty may be acknowledged, yet it is not tackled. Positively seen, the measurement results are not manipulated. Such kind of data treatment is very common for counting and fractionating techniques (e g. DEMS or AC). Users would reduce the uncertainty of their results by increasing the sample size and / or number of measurements. However, in this way only the repeatability uncertainty is addressed, whereas fundamental limitations of the measurement principle and instrumentation remain.

<u>S9 – ¡define the shape of the size distribution by supposing a mathematical distribution function!</u>

Mathematical distribution functions are fairly popular in particle sizing for several reasons:

- few parameters suffice to describe the whole size distribution;

- usually, moments and characteristic parameters of the size distribution (e. g. mean, modal or median values) can be quickly computed by means of simple equations

- accordingly, the conversion of size distributions with respect to geometric TOQ are rather fast

- the stochastic nature of particle generation processes (e. g. precipitation, grinding) corresponds to a specific kind of size distribution, I. e. if chosen properly, mathematical distribution functions are the best representation of the disperse system (Techno & Yawned 1986, Limpet et al. 2001).

Frequently, gamma distribution and Waybill distribution are used for approximating the real size distribution. However, the most popular kind is the log-normal distribution (with various extensions and modifications) because of its favourable mathematical properties, which simplify the calculation of power means and the conversion to other Toss. Such distribution functions are either presupposed in data analysis (concerns spectroscopic ensemble techniques) or applied posterior to the measured size distribution (mainly for results of fractionating and counting Mats). Commercially, the strategy is typically used for USSP (e. g. DT-1200 user handbook, UltraSizer® manual), EMS (e. g. Acoustosizer® manual) and SAXS (e. g. Nano-Solver® manual). Sometimes it is also employed as an alternative analysis route to DLS (e. g. Window® manual) and for the fitting of directly measured size distribution in AC (e. g. LUMiSizer® manual). It should be emphasised that the choice of the distribution function exerts a crucial influence on the performance of conversion (Figure 4).
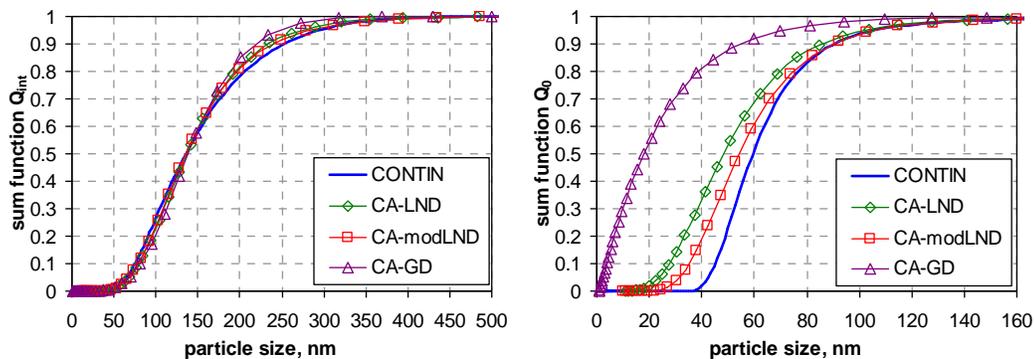
Figure 4: DLS results of a colloidal alumina when derived with standard inversion algorithm (CONTIN) and by fitting the raw data via cumulant analysis (CA) to analytical distribution functions: log-normal distribution (LND), modified log-normal (modLND) with minimum size set to 10 nm, and gamma distribution (GD); plotted as intensity weighted (left) and number weighted (right) size distribution

<u>S10 – ¡restrict the shape of the size distribution without mathematical distribution functions!</u>

This means that the shape of the size distribution is implicitly constrained by certain assumptions that refer to the value of the density function (non-negative constraint), to the correlation among the individual size classes (e. g. expressed as "uniformity", smoothness", "entropy") or to the spectral range of the density function (e. g. quantified via singular value decomposition – e.g Finsy et al. 1989). This kind of approach is standard in commercial instruments for ALS (e. g. Heuer & Leschonski 1985, Riefler & Wriedt 2008) and DLS (e. g. often CONTIN-based, Finsy et al. 1993, Maier et al. 1999). A major criticism to this way of data analysis is that the outcome depends on the parameterisation of analysis algorithms. Indeed, several commercial instruments allow the users to select the parameter settings (e. g. as "general purpose" or "multiple narrow modes"). One measurement analysed with different parameter settings typically yield different results – in particular with respect to the distribution width. The impact on the converted size is then rather serious (Figure 5).
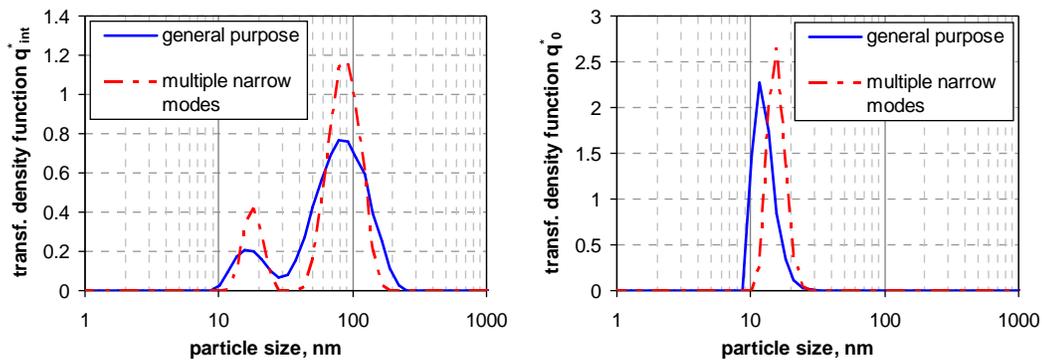

Figure 5: DLS results of a colloidal silica when calculated with two different settings of the inversion algorithm ("general purpose" and "multiple narrow modes"); plotted as intensity weighted (left) and number weighted (right) size distribution

It may be further noted that constrained numerical inversion procedures may produce artefact modes in the size distribution for compensating insufficiencies of the model (e. g. with regard to particle shape) which can be highly emphasised at the transformation of size distribution (cf. discussion by Andrés et al. 1998).

3.2.3 Uncertainty regarding the interval width

If the measurement results of particle sizing are not expressed in terms of an analytical distribution function they consist of a vector with relative amounts $\Delta Q_{r,i}$ per size class i (and the corresponding values for the density and sum function). The number of size classes and their interval width are either defined by the technical specification of the MT or can be freely adjusted by the user. For spectroscopic ensemble techniques it is only important to avoid too broad interval widths, whereas for fractionating or counting methods the principal minimum to the interval size is defined by the resolution of the MT and a practical lower limit exists by the request to gather sufficiently strong signals (or counts) within each size class. With respect to the transformation of size distributions it is usually sufficient to provide ≥ 10 size classes per decade (Figure 6).
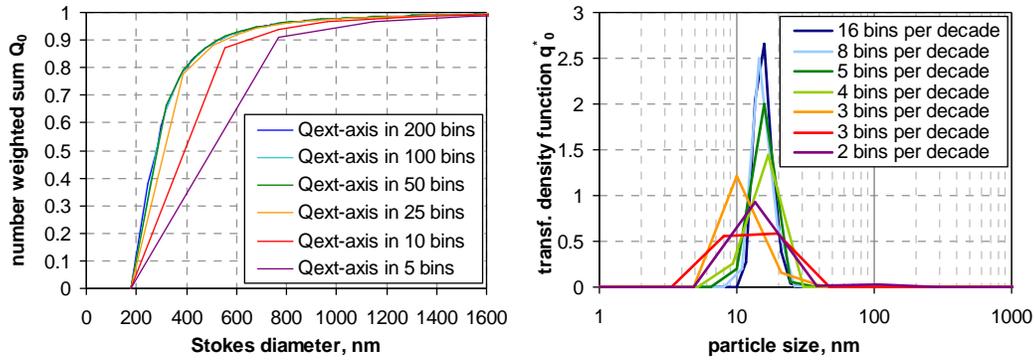
Figure 6: impact of the interval width (expressed as number of intervals per decade) on the eventually obtained number weighted size distribution for AC measurements (mono-modal silica system) and for DLS measurements (bimodal colloidal silica)

3.3 Special remarks on conversion for spectroscopic MTs

The immediate result of spectroscopic ensemble techniques are signal spectra, i.e. the variation of the measured signal g over the spectral parameter s (time, space or frequency). Each size fraction x possesses a characteristic spectrum $k_r(s,x)$, which in general covers the whole spectral range. Assuming that each size fraction contributes independently and linearly to the measured signal spectrum, the determination of the size distribution requires the inversion of a linear integral equation (Fredholm type):

$$g(s) = b(s, c_r) + c_r \cdot \int k_r(s, x) q_r(x) \mathrm{d}x \,, \tag{11}$$

where c_r is the particle concentration for the TOQ r and $b(s,c_r)$ is a size-independent baseline signal. When s is varied over a sufficiently wide range, the spectrum can be normalised, which eliminates the concentration influence[1]. In contrast to counting or fractionating techniques, the *intrinsic type of quantity* is not necessarily obvious. Indeed, eq. (11) can be expressed and solved for any type of quantity r. Yet, the intrinsic type of quantity of spectroscopic techniques refers to the impact of a single particle to the integrated signal spectrum. For instance, if the integral over the signal spectrum of one particle is proportional to the particle volume, the intrinsic type of property is the volume ($r = 3$).

The intrinsic TOQs of DLS is the scattering intensity, which converges to the squared particle volume (i. e. $r = 6$) for nanoparticles. In USSP and EMS the intrinsic TOQ is identified as the particle volume (i. e. $r = 6$), whereas for a classical LD instrumentation it is the particle surface (i. e. $r = 2$).

The calculation of the size distribution $q_r(x)$ out of a signal spectrum $g(s)$ is called *inversion*. There is a vast literature on mathematical inversion algorithms, but none of them is free of bias, which is either introduced by defining the kind of the distribution function (strategy 9) or by quantifying certain features of the distribution function (e. g. smoothness or spectral range – strategy 10). This is necessary, because the *information content* of signal spectra with respect to the details of size distributions is limited. The degree to which polydispersity, the occurrence of separate size modes etc. can be accurately resolved depends on the physics behind the measurement as well as on the specific instrumentation employed. Quantitative assessments of the information content have been published only for few MTs (e. g. DLS – Finsy et al. 1992, ALS – de Vos et al. 1996, EMS – Knösche 2001, USSP – Babick & Ripperger 2002).

With regard to conversion different strategies are employed in research and in commercial instruments.

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[1] Note that the impact of concentration c_r is lost if $g(s)$ refers to the phase shift rather than to the magnitude of a measured quantity.

S11 – ¡solve the Fredholm equation only for the intrinsic TOQ, convert afterwards!

This strategy is usually employed in commercial USSP and EMS instruments, because their main field of application is the characterisation of dense suspensions and emulsions for the purpose of process monitoring, where typically volume weighted size distributions are required. Also in most DLS instruments the results are preferentially presented within the intrinsic TOQ and – if needed – subsequently converted to volume or number weighted size distributions. This procedure is meaningful because the information content of spectral signals is at maximum for size distributions at the intrinsic TOQ (cf. de Vos et al 1996, Figure 7, and Figure 8).
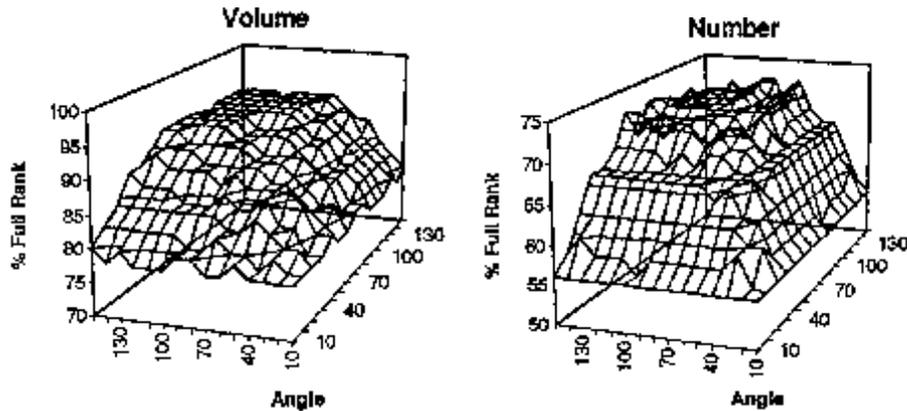
Figure 7:   rank of kernel matrices of ALS data when inversion aims at volume weighted size distributions (left) and number weighted size distributions (right); the lower the rank the lower is the information content of the data (de Vos et al. 1996)
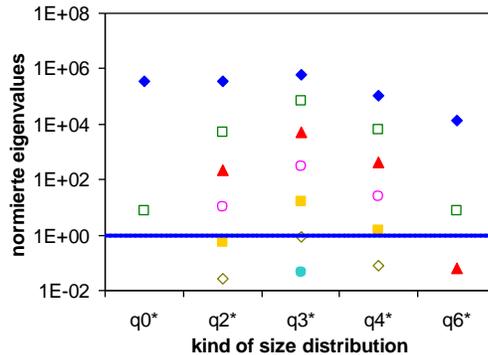
Figure 8:   normalised eigenvalues of the covariance matrix of the kernel function for USSP when signal spectra are evaluated to different kinds of distribution functions; the number of normalised eigenvalues > 1 indicates the pieces of information that can be extracted from the ultrasonic spectra (data for SiO_2 in water measured from 3 MHz to 100 MHz)

S12 – ¡solve the Fredholm equation only for either $Q_3(x)$ or $Q_0(x)$!

For the sake of comparison with other particle sizing results it is often preferred to compute the results of spectroscopic ensemble techniques as either number or volume weighted size distributions. This is, for instance, the classical approach of LD instruments ($Q_3(x)$ is calculated; Heuer & Leschonski 1985, de Boer et al. 1987, Neumann & Kramer 2002). It is also found for SAXS instruments ($Q_3(x)$, NanoSolver® manual). There are also commercial DLS instruments, which primarily solve the inversion problem for $Q_3(x)$ instead for $Q_{int}(x)$ (Geers et al. 2008). This is particularly meaningful for disperse systems with spherical particles above 100 nm, when the scattering properties may considerably vary along the size axis. Direct calculation of number weighted size distribution is mainly a topic in research (e. g. Martelli et al. 2002 for SAXS; Mazumder et al. 1995, and Riefler & Wriedt 2008 for ALS; Hallet et al. 1991, Hanus & Ploehn 1999, and Patty & Frisken 2006 for DLS).

4 Transformation for fractal aggregates

Fractal aggregates differ from regularly packed aggregates or homogeneous particles by several properties:

- the distribution of mass is not uniform,
- the density (alternatively: porosity) changes with size,
- the deviations among the various equivalent diameters are enormous,
- physical properties like diffusion coefficient or scattering intensity are less determined by the outer dimensions, but rather by the internal structure.

Ignoring these points when characterising systems of fractal aggregates may considerably mislead the particle size range. Moreover, it will adversely affect the transformation of measured size distributions.
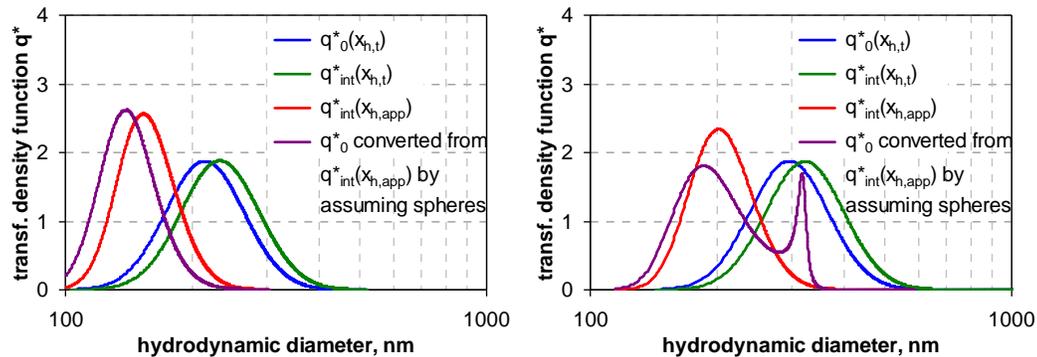
Figure 9: calculated distributions of the hydrodynamic diameter of fractal aggregates with uniform constituent particles and a log-normal distribution in the aggregation number; the figures show the number and intensity weighted distribution of the translational hydrodynamic diameter $x_{h,t}$, the intensity weighted distribution of the apparent hydrodynamic diameter (i. e. the immediate DLS result) and the corresponding number weighted distribution, when the conversion assumes homogenous spheres; left: $x_{cp} = 10$ nm, $N_{50} = 400$, right: $x_{cp} = 20$ nm, $N_{50} = 200$

In Figure 9 this problem is illustrated for DLS measurements. The situation refers to particle systems, which consist of fractal aggregates of uniformly sized constituent particles with a log-normal distribution of the aggregation number (i. e. number of constituents the aggregate is made of). DLS results of such systems can be predicted by a stepwise calculation of the number weighted and intensity weighted distributions of the aggregates hydrodynamic properties (cf. Babick et al. 2012a). The scattering properties of the aggregates can be computed by means of the Rayleigh-Debye-Gans approximation, which usually holds true for nanosized constituent particles (e. g. Sorensen 2001). Additionally, the impact of aggregate rotation needs to be regarded, since it diminishes the apparent diffusion coefficient (e. g. Lindsay et al. 1988, Babick et. al. 2012c). It appears that intensity weighted size distribution delivered by DLS instruments (i. e. $q_{int}(x_{h,app})$) would be considerably finer than the number weighted size distribution of the translational hydrodynamic diameter $q_0(x_{h,t})$), which, e. g., can be measured with PTA. Conversion of the measured intensity weighted size distribution into number weighted size distribution under the assumption of homogeneous spheres results in a shift to even finer particles and may sometimes yield artificial modes.

The example clearly demonstrated the extent of potential errors in particle sizing and transforming size distributions, when the morphology of the particles is wrongly described. In contrast, meaningful data analysis can be performed if the fractal nature of the particle is identified and the average size of the constituent particles is known (e. g. by BET measurements). An according analysis scheme has been described by Babick et al. (2012b) for DLS and for AC measurement results. The authors were able to approximate the number weighted distributions of aggregate size for suspensions of fumed silica. The aggregate size was either expressed as aggregation number, as diameter of gyration or as translational hydrodynamic diameter.

In a similar manner, Lall & Friedlander (2006) (cf. also Lall et al. 2006) proposed a procedure to characterise fractal aerosol particles by means of DEMS measurements, which intrinsically yields number weighted size distributions of the aerodynamic mobility. Again, the size of the constituent particles was required as input parameter.

In summary, the transformation of size distributions with respect to TOQ and aggregate size can be considerably enhanced by employing adequate models. Nonetheless, it is not possible to derive size distributions of the constituent particles out of MT that are based on particle mobility (concerns e. g. DEMS; PTA, FFF, AC, DLS, USSP, EMS). This task remains the domain of imaging techniques and special field perturbations techniques like SAXS.

5   Conclusion

In general, the transformation of particle size distribution refers to both, re-scaling of size axis (i. e. transforming the probed particle property) and conversion with respect to the type of quantity (TOQ). The principal mathematical scheme for such a procedure is clear, yet there are considerable obstacles when it is to be applied in practice. These obstacles can be assigned to issues regarding the particle morphology and to "technical" limitations like signal noise, non-uniform sensitivity, limited measurement range or limited information content. Researchers and instrument manufacturers are aware of such problems and thus have developed several strategies to cope with them. However, such strategies are rarely universally used, but specifically employed for certain (types of) MTs (or even instruments) and material systems. A major difficulty in particle sizing (incl. the transformation of size distributions) consists in the data analysis of non-spherical particles. Most often, morphology remains unknown or cannot be easily quantified. Most (commercial) MTs therefore stick to the assumption of spheres. This may result in considerable mis-evaluation of size distributions – as has been illustrated for fractal aggregates. Only in few cases, commercial instruments allow for non-spherical (yet regular) particle morphology.

The special analytical task of transforming size distributions to number weighted distributions of the constituent particle size ($Q_0(x_{cp})$) can – in a strict sense – be only fulfilled with MTs that probe the properties of the constituent particles inside aggregates. Only few particle sizing techniques are capable to this. The vast majority of MTs, in particular those that in some way probe the particles' mobility, cannot reveal the individual properties of constituent particles. This underlines the necessity to develop new characterisation methods that – e. g. by combining different CTs – facilitate a likewise fast and reliable evaluation of substances and products as regards NMs identification.

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<u>AC</u>

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<u>EMS</u>

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7 Symbols

symbol	description	SI-unit
a	particle radius	m
c_r	concentration of quantity x^r	m^r/m
D	diameter	m
f	TOQ function	n.d.
$g(s)$	spectral function (on spectral parameter s)	n.d.
$k_r(s,x)$	kernel function	n.d.
I_{sca}	scattering intensity	W/srad
L	length	m
$M_{k,r}$	k-th raw moment of size distribution weighted in x^r	m^r
x	particle size, equivalent diameter	m
x_{gyr}	diameter of gyration	m
$x_{h,app}$	apparent hydrodynamic equivalent diameter	m
$x_{h,t}$	translational hydrodynamic equivalent diameter	m
$\bar{x}_{k,r}$	k-th power mean of size distribution weighted in x^r	m
x_{Stokes}	Stokes diameter (settling velocity equivalent diameter)	m
x_V	volume equivalent diameter	m
$Q_{A/B}(x)$	sum function weighted in quantity A / B	1/m
$q_{A/B}(x)$	density function weighted in quantity A / B	1/m
$q^*(x)$	transformed density function	-
W_{YZ}	shape function relating x_Y to x_Z	m
$\{_Z$	shape function relating x_V to x_Z	m
...	aspect ratio	-
j	Wadell's sphericity	-