NORMAL VS. LOGNORMAL DISTRIBUTIONS IN AEROSOL SYNTHESIS

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***Summary**: The aim of this paper is to clarify the use of terminology and notation used in the analysis of aerosol particle sizing, nanoparticle suspensions and nanoparticle powder on the basis of the log-normal distribution. The connection between the log-noma1 distribution and the normal distribution is shown; the mathematical basis for the both distributions is presented.*

***Key words**: normal distribution, lognormal distribution, aerosol statistics, nanoparticles*

1. NORMAL DISTRIBUTION

A continuous random variable X is a variable which can take any real value within a certain range. Individual measurements of this variable are usually denoted by the corresponding lower case letter x. For a continuous variable X, the probability that X is exactly equal to a particular value is zero, i.e. $(\forall a)\ P(X=a)=0$. For a continuous variable we can only talk about the probability that an event lies in an interval, and:

$$P(a \le X \le b) = P(a \le X < b) = P(a < X \le b) = P(a < X < b). \text{ [21]}$$

The Normal distribution is a continuous theoretical probability distribution and, probably, the most important distribution in Statistics. Normal Distribution is a descriptive model that describes many real world situations and is widely used in the all fields of science. They are the most important probability distributions in statistics and can be used to approximate other distributions, such as discrete binomial distributions. The most important application of the normal distribution lies in the Central Limit Theorem. This theorem states that no matter what type of distribution a population may have, as long as the sample size is at least 30, the distribution of sample means will be normal. If the population is itself normal, then the distribution of sample means will be normal no matter how small the sample is. This phenomenon is best understood when observing the probability density function (PDF) of the Normal distribution.
A random variable X is said to have a normal (or Gaussian) distribution with parameters μ and σ,

where $-\infty < \mu < \infty$ and $\sigma > 0$, with probability density function $f(x)=\dfrac{1}{\sigma\sqrt{2\pi}}\cdot e^{-\frac{1}{2\sigma^2}(x-\mu)^2}$ for $-\infty < x < +\infty$,

where $\pi = 3.14159\ldots$ and $e = 2.7183\ldots$ (see figure 1).
The PDF is in fact the equation of a curve that represents the relative frequency or frequency density of occurrence of values of a random variable between given limits. A PDF encloses a total area of 1 so that it can be used to calculate probabilities by mere integration. The Normal distribution is completely characterized by its two parameters μ and σ^2 its mean and variance respectively, hence the notation $X \approx N(\mu,\sigma^2)$.
The mean of the distribution determines the location of the center of the graph, and the standard deviation determines the height and width of the graph. When the standard deviation is large, the curve is short and wide; when the standard deviation is small, the curve is tall and narrow. All normal distributions look like a symmetric, bell-shaped curve, as shown below. The Normal curve is symmetrical about the line x = μ and bell-shaped. Since a normal variable assumes values ranging from $-\infty$ to ∞, its curve is asymptotic to the x-axis, that is, the normal curve keeps on approaching the x-axis without touching it at its ends, known as the lower and upper tails. The diagram below is a representation of the normal curve:[22]

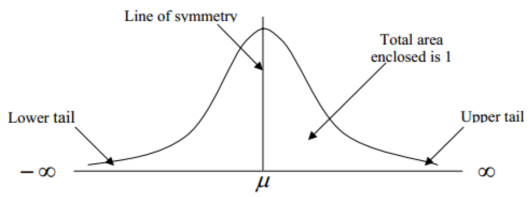


Figure 1: Graph of density function for normal distribution

Properties of the Normal Model with effects of μ and σ are shown on the following figures (Figure 2.a. Identical means but different standard deviations, Figure 2.b. Different means but identical standard deviations, Figure 2.c. Different means and different standard deviations)

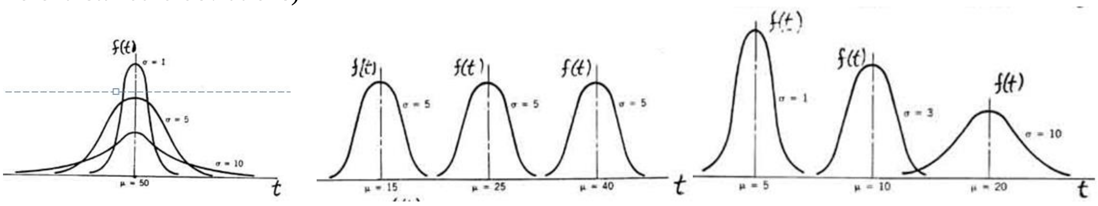


Figure 2.a Figure 2.b Figure 2.c

Additionally, every normal curve (regardless of its mean or standard deviation) conforms to the following "rule 68-95-99.7 ".

- About 68% of the area under the curve falls within 1 standard deviation of the mean, $P[\mu - \sigma < X \leq \mu + \sigma] = 0.6826 = 68.26\%$.
- About 95% of the area under the curve falls within 2 standard deviations of the mean, $P[\mu - 2\sigma < X \leq \mu + 2\sigma] = 0.9544 = 95.44\%$
- About 99.7% of the area under the curve falls within 3 standard deviations of the mean, $P[\mu - 3\sigma < X \leq \mu + 3\sigma] = 0.9974 = 99.74\%$.

Clearly, given a normal distribution, most outcomes will be within 3 standard deviations of the mean.
Because every normal distribution can be transformed to the standard normal distribution, you can use z-scores and the standard normal curve to find areas (and therefore probability) under any normal curve. There are infinitely many normal distributions, each with its own mean and standard deviation. The normal distribution with a mean of 0 and a standard deviation of 1 is called the standard normal distribution. The horizontal scale of the graph of the standard normal distribution corresponds to scores.

If $X \approx N(\mu,\sigma)$ and if $Z = \dfrac{X-\mu}{\sigma}$ then $Z \approx N(0,1)$.

A normal distribution with μ = 0 and σ = 1, is called the standard normal distribution (see figure 3). $P(X < x') = P(Z < z')$

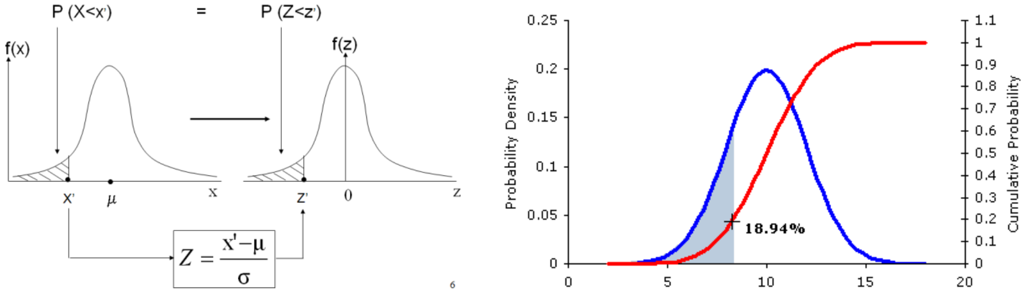


Figure 3. Standard and Cumulative normal distribution [22]

A probability is a number expressing the chances that a specific event will occur. This number can take on any value from 0 to 1. A probability of 0 means that there is zero chance that the event will occur; a probability of 1 means that the event is certain to occur. Numbers between 0 and 1 quantify the uncertainty associated with the event. Its probability density function is $f(z) = \dfrac{1}{\sqrt{2\pi}} e^{-\frac{z^2}{2}}, -\infty < z < \infty$.

A cumulative probability is a sum of probabilities. In connection with the normal distribution, a cumulative probability refers to the probability that a randomly selected score will be less than or equal to a specified value, referred to as the normal random variable (see figure 3).

2. LOGNORMAL DISTRIBUTION

A lognormal distribution has two distinct properties: it is always positive (bounded on the left by zero), and it is skewed to the right (see figure 4). The lognormal and normal distributions are related: if a random variable X is lognormally distributed, then its natural log, ln(X) is normally distributed. (Thus the term "lognormal" - the log is normal.)

The log-normal distribution is a function distributing a dependent variable in a normal or Gaussian fashion on a logarithmic scale of the independent variable. This function has been used for a long time to describe size distributions of particle properties in atmospheric aerosols. A distribution that is log-normal in one of its moments will be log-normal in any of its moments with the same geometric standard deviation, describing the spread of the dependent variable. The median diameter of the distribution of any moment is equal to the corresponding geometric mean diameter, and is related to the integral of that moment by a simple factor. [17]

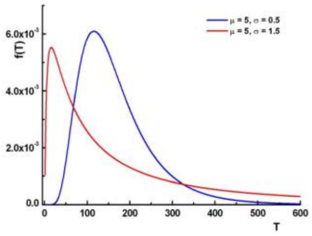


Figure 4. Typical lognormal distribution

For a monodisperse aerosol, a single number—the particle diameter—suffices to describe the size of the particles. The frequency function is:[19]

$$df = f(d_p)dd_p$$

Where d_p is the physical (or geometric) diameter of the particles - if the particle is spherical the meaning of this parameter is obvious, otherwise it does not have a precise meaning-,

df is the fraction of particles having diameters between d_p and $d_p + dd_p$.

Therefore, the area under the frequency curve between two sizes a and b represents the total fraction of the particles in that size range: $f_{ab} = \int_a^b f(d_p)dd_p$

The normal distribution usually does not suitably describe particle size distributions in aerosols because of the skewness associated a long tail of larger particles.
A more widely chosen log-normal distribution gives the number frequency as:

$$df = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(d_p - \overline{d_p})^2}{2\sigma^2}} dd_p ,$$

where: σ is the standard deviation of the size distribution and $\overline{d_p}$ is the arithmetic mean diameter.

The log-normal distribution has no negative values, can cover a wide range of values, and fits many observed size distributions reasonably well.

2.1. Aerosol and nanoparticle lognormal distributions

Because the properties of particles with respect to each of these issues are strongly affected by particle size, many instruments have been developed to measure the concentration of particles (e.g., number, mass, or chemical species concentration) as a function of particle size.[20]
Many properties of aerosol particles and nanoparticles depend on their size and most aerosols have log-normal size distributions. Common types of size distributions

- Number (number of particles of given size)
- Mass (or Volume)
- Surface Area.

On the figure below (see figure 5) is shown the normal distribution of atmospheric aerosols which are not very common (see figure 5 on the left), and lognormal distribution which appears as a normal distribution when x-axis is plotted on log scale(see figure 5 on the right):

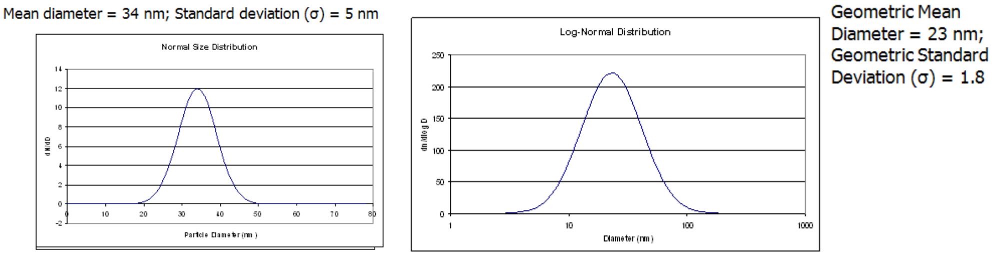


Figure 5. Aerosols normal and lognormal distribution

Atmospheric aerosol size distributions show modal structure and can be represented best by a lognormal size distribution function.

The aerosol lognormal number size distribution, expressed as the number of particles per logarithmic size interval, can be represented as

$$\frac{dn}{d\ln d_p} = \frac{F_{m0}}{\sqrt{2\pi}\ln\sigma_g}\cdot\exp\left(-\frac{(\ln d_p - \ln d_{g0})^2}{2(\ln\sigma_g)^2}\right)$$

where d_p being particle diameter, σ_g being the geometric standard deviation of distribution, σ_{gN} being the number-median diameter, and F_{m0} being the number concentration at the diameter σ_{gN}.

The geometric mean a_g of a number, n, of quantities a_i is defined by the relation:

$$a_g = (a_1 \cdot a_2 \cdot \ldots a_n)^{1/n}.$$

The log normal distributions for aerosol population can be given in terms of the number concentration, surface distribution or volume distribution.

Assuming spherical particles, the total particle surface S, can be written as a function of parameters of number-size distribution

$$S = 4\pi\left(\frac{d_{gN}\cdot\exp(2(\ln\sigma_g)^2)}{2}\right)^2 N\cdot\exp\left[-\frac{(\ln\{d_{gN}\cdot\exp(2(\ln\sigma_g)^2\} - \ln d_{gN})^2}{2(\ln\sigma_g)^2}\right]$$

The total particle volume V, can be written as a function of parameters of number-size distribution on the following way

$$V = \frac{4}{3}\pi\left(\frac{d_{gN}\cdot\exp(3(\ln\sigma_g)^2)}{2}\right)^2 N\cdot\exp\left[-\frac{(\ln\{d_{gN}\cdot\exp(3(\ln\sigma_g)^2\} - \ln d_{gN})^2}{2(\ln\sigma_g)^2}\right].$$

However, the total number, N, and the geometric number mean radius, d_p, are very poor indicators of mass and light scattering properties of a given size distribution. At the same time, the total volume, V, and the geometric volume mean radius, are very good indicators of mass and light scattering.

The log normal distributions are best suited to describe the aerosol population and nanoparticle size distribution and hence it is widely used for aerosol and nanoparticle studies. Many investigators, [18] have used cumulative plots on log probability paper for presenting atmospheric size distributions of aerosol mass measured by cascade impactors. A straight line is then drawn through the points (usually only four to six in number) and a geometric mean and standard deviation obtained for characterizing the distribution.

Figure 6 is a plot on log probability, and it is apparent that the distribution is not log normal. If it were log normal, the number, surface, and volume weightings would be parallel straight lines.

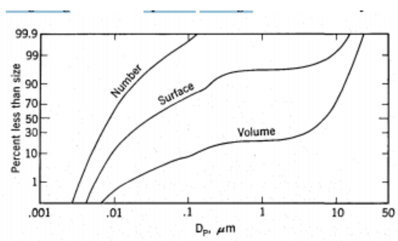


Figure 6. Cumulative number, surface, and volume distributions which are definitely not log-normal [18]

In the research connected to nanoparticle synthesis, characterization and application, determination of aerosol and particle size is always one of the main topics. There are various instruments for measurement of nanoparticles in aerosol, suspension or dry powder form. All of them have certain advantages and specific limitations. Those instruments are usually equipped with various software for processing of measured data and are offering several presentation of particle size distribution. As explained in this paper, the optimal particle size distribution for real systems is lognormal distribution. Here are presented results of measurments of droplet size distribution in one aerosol and nanoparticle size distribution in one suspension. For the aerosol based synthesis methods are both, droplet and particle size important since particle size is directly proportional to droplet size [21]:

$$D_p = D \cdot \left(\frac{c_{pr} \cdot M_p}{\rho_p \cdot M_{pr}} \right)^{1/3}$$

(c_{pr}: precursor concentration, M_p: powder molecular weight, ρ_p: powder density, M_{pr}: precursor molar mass, D: droplet size)

Droplet size distributions were measured without dilution of the aerosol and at same atomization and carrier gas parameters like in the synthesizing process parameters. For those investigations a laser diffraction system (Malvern Spraytec) equipped with a 300 mm focusing lens was used. Size measurement by laser diffraction is based on the size dependent scattering angle of light at a droplet or particle and therefore the scattering signal from the aerosol is detected in order to determine the droplet size distribution. All experiments were conducted with using ultrasonic atomizers (GAPUSOL 9001, RBI; France), one with 0,8 MHz and another with 2,5 MHz operating frequency. Solutions were prepared in different concentrations; carrier gas (N2) flow rate was changed to test the influence of flow rate. In some experiments surface active additives were added to precursor solutions to test influence of physical properties of solution (surface tension and density) on droplet size distribution. Some of the experimental results are presented (see Fig. 7).

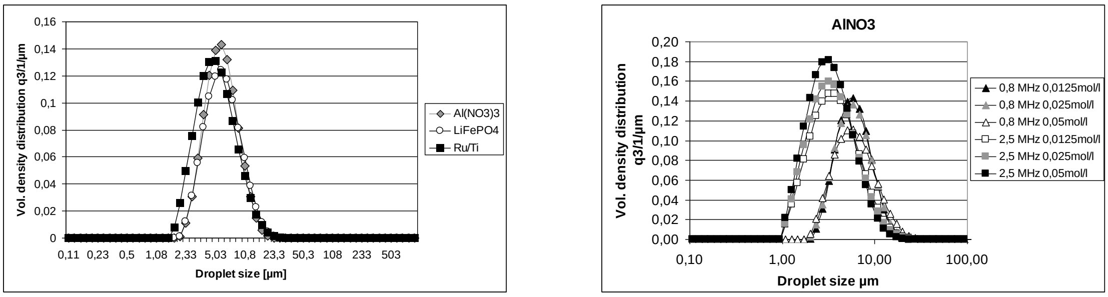
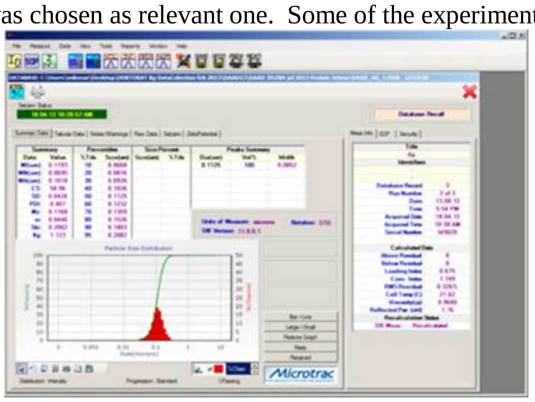


Figure 7: Influence of physical properties of solution on particle size (right) and Influence of ultrasonic frequency and concentration of solution od droplet size distribution [22]

Second example for lognormal application is one of actual research of this study group related to modeling of synthesis process of silver nanoparticles. In the scope of this project the Microtrac Wave device was used for measuring a particle size distribution for suspension of silver nanoparticles. The measurement principle of Microtrac Wave is based on DLS (Dynamic Light Scattering) and it is using heterodyne set-up (mixing the original laser light into the scattered light is like amplifying the scatter signal). For processing of measured data the software package for particle size distribution Flex 11.0 was used. In the scope of the research, over sixty experiment of synthesis of silver nanopowder was conducted, under different experimental parameters. For all nanopowder the size distribution was determined, since it is one of the main characteristic of nanoproduct (next to morphology and chemical composition). Number, volume and area lognormal size distribution was determined for all samples. In order to have optimal compare with SEM/TEM image analysis, number distribution was chosen as relevant one. Some of the experimental results are presented (see Fig. 8 and Fig. 9).



Summary

Data	Value
MV (µm)	0,689
MN (µm)	0,0451
MA (µm)	0,1757
CS	34,15
SD	0,01174
PDI	2,543
Mz	0,692
si	0,677
Ski	0,454
Kg	1,313

Figure 8. Flex 11.0 software and tabulation of part of experimental results

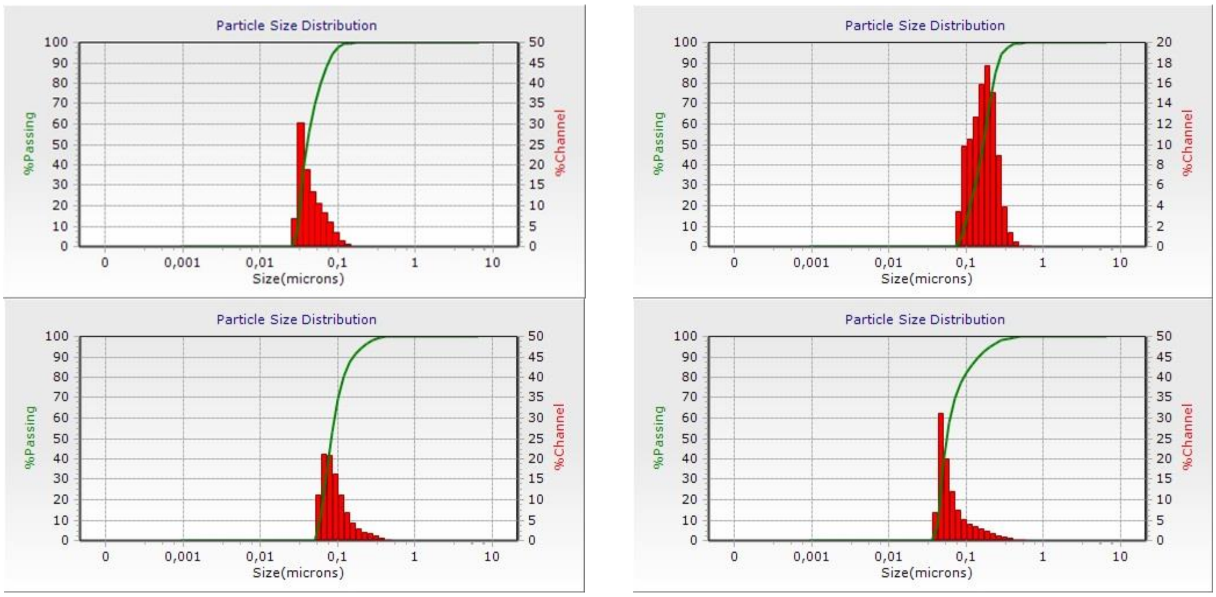


Figure 9. Nanotrac Analysis Option: Lognormal size number distribution for an aerosol model

For each of over sixty samples, seven measurement repetitions were done. Each measurement last 30 seconds and all measurements are saved separately. At the end it is possible to compare all plots or to use the average values of those seven measurements. In Fig. 9 it is to see that each of the samples has specific shape of the particle size distribution. In conducted research the main criteria for description of particle size distribution were taken median number diameter and standard deviation. Those two values were used in further research for validation of the process and produced powder.

CONCLUSION

The purpose of this paper is to clarify math terminology used in the analysis aerosol and nanoparticles size data in the research projects connected to synthesis, characterization and application of nanoparticles. In this purpose were used the measurements of the series of experiments which are realized on the device Microtrac Wave based on DLS (Dynamic Light Scattering) supported with software Flex 11.0 and measurements of droplet size distribution measured by the laser diffraction system (Malvern Spraytec). Examples of the approximation of the aerosol and nanoparticles size distributions are given here by using data from a set of more of 60 aerosol size distribution profiles measured during the experiment that took place at the Institute for Process Metallurgy and Metal Recycling (IME), RWTH Aachen University, Germany, during 2013. In most of the nanoparticles and aerosol research projects droplet and particle size distribution is one of the crucial criteria for characterization and valuation, and from this reason right understanding of measuring data has very high importance.

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