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Higher order statistics in signal processing and nanometric size analysis

N. CRETU*, I. M. POP
Physics Department, Transilvania University, Brasov, Romania

A method for the characterisation of the distribution of nanoparticles is proposed, by using the skewness and kurtosis of experimental values. The method is analysed on several examples and the different properties it presents are extracted. Further, the method is applied on nanoparticle data in order to better characterise its distribution and to eliminate noise.

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1. Introduction

Certain computer applications in simulation, analysis and processing of experimental data allow the use of algorithms able to involve real time observation and analysis. For this reason in particular, the introduction of statistical analysis of signals in physical measurements is considered opportune. Also, better computing capacity allows the real time use of higher order statistics based on the estimation of the higher moments in data acquisition , for example in the detection of stationary or transient phenomena . The most used statistical features are kurtosis and skewness.

The kurtosis is the ratio between the fourth central moment of a distribution and the fourth power of the distribution's standard deviation. Skewness is given by the ratio of the third moment about the mean and the third power of the standard deviation. If we analyze a time signal $x(t)$ with a Gaussian distribution of the amplitude, the value of kurtosis is 3. Because many signals we meet in practice tend to have such a distribution of the amplitude, excess kurtosis is used as well, computed by subtracting the constant 3 from the value of kurtosis, so we obtain an estimate of kurtosis, equal to zero in the case of Gaussian distributions of experimental data and non-zero for other distributions. This ensures a criterion to recognize and separate Gaussian and non-Gaussian signals.

Kurtosis can be applied in the time domain or in the frequency domain. If the kurtosis is estimated with the amplitude of the Power Spectral Domain (PSD) components, it is named spectral kurtosis. Time domain kurtosis is mostly used in industrial diagnosis of some phenomena which can produce damage to a system. In [1] a fatigue analysis under Gaussian and non-Gaussian loading is obtained by using kurtosis analysis. Kurtosis was also used for blind deconvolution separation of multiple sources mixed by mechanical systems [2]. In [3], a mixed method is examined through kurtosis analysis and non-Gaussian projections, to explore the clustering structure of the experimental data. Using supplementary computer simulations and kurtosis estimation in [4], the crack detection of thin isotropic rectangular plates and the effect of the added noise are examined.

More applications are reported in the spectral kurtosis domain. The first important application reported in the field is the paper of Dwyer, which computed spectral kurtosis to separate underwater acoustic signals [5]. In [6] spectral kurtosis was used to detect transient signals from mechanical systems.

A very important topic consists in the application of the spectral kurtosis to the study of nonlinear effects. It is reported that the nonlinear effects are correlated with strong non-Gaussian behavior of external action and structural response [7]. A very comprehensive analysis and a kurtosis estimator is proposed by Vrabie and collaborators [8], by applying spectral kurtosis for bearing fault detection in induction motors. For the high frequency domain, spectral kurtosis analysis is reported in exploring the RF noise in microwave low-noise devices [9].

In signal processing spectral kurtosis is a complementary method close to PSD signal analysis. Using dynamic PSD spectrum, Nita and collaborators [10] proposed a method for the radio frequency interferences (RFI) excision, by using an algorithm based on the spectral kurtosis, which was applied to the microwave spectrum of solar radiation. In fact, it is possible by using the dynamic PSD, to detect and analyze the short transient signals which appear in the system's evolution, by continuous data acquisition, sequential PSD evaluation and a kurtosis analysis of each point of the Fourier transformation of PSD sequential spectrum. For example, in Figure 1 we plotted such an analysis, obtained by simulation of a continuous white noise signal with two transient stationary sinusoidal signals corresponding to 10 and 20 KHz superposed at three different time moments. The graph confirms the method of analysis based on spectral kurtosis as apt to distinguish the transient signals in physical systems.

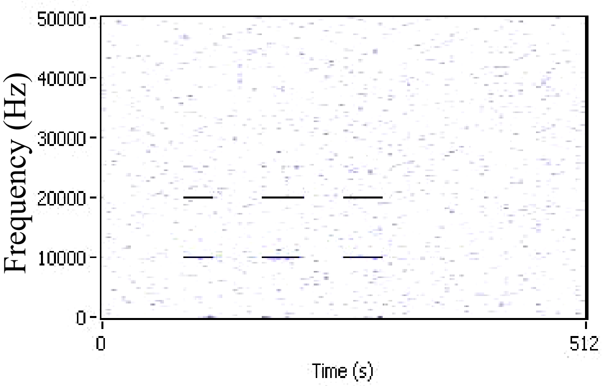

Fig. 1 Transient signals detected by dynamic spectral kurtosis

Important applications of higher order statistics have been reported in the field of image analysis. In this area, kurtosis and skewness are used to analyze the shape of nanometric materials [11,12,13]. The present paper proposes an analysis referring to the use of kurtosis vs. skewness as size estimator and to predict the existence of single or multiple Weibull distribution, together with an experimental application of the method on some nanometric materials used as electrodes in fuel cell batteries.

2. Skewness and kurtosis for different distributions

The most common distributions which affect the experimental data in physics are:

1) The uniform distribution:

$$f(x) = \frac{1}{b-a},\ x \in [a;b] \tag{2}$$

2) The Gaussian distribution:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-m)^2}{2\sigma^2}\right] \tag{3}$$

3) The exponential distribution:

$$f(x) = \lambda \exp(-\lambda x),\ x \ge 0, \lambda > 0 \tag{4}$$

and particularly for size distribution in powders,

4) The Weibull distribution:

$$f(x) = weib(x, r, \theta) = \frac{r}{\theta}\left(\frac{x}{\theta}\right)^{r-1} \exp\left[-\left(\frac{x}{\theta}\right)^{r}\right], \quad x \ge 0, r > 0, \theta > 0 \tag{5}$$

and, related to it:

5) The double Weibull distribution:

$$f(x) = a \cdot weib(x, r_1, \theta_1) + b \cdot weib(x - c, r_2, \theta_2), \quad a + b = 1, c > 0 \tag{6}$$

Skewness (Skew), kurtosis (Kurt), and kurtosis vs. skewness (Kurt-Skew) for the first three kinds of distributions are illustrated in Figure 2. The corresponding values were computed on subsets of the ordered set of initial values. The subsets are indicated in the graphs by their count.

For the uniform distribution, both skewness and kurtosis present small variations, these variations consisting in statistical fluctuations due to the finite number of values in each subset, as seen on the Kurt-Skew diagram.

For the case of the normal distribution a characteristic symmetrical U-shaped Kurt-Skew diagram is obtained.

It has a left branch which decreases where the skewness is negative and a right branch which increases where the skewness is positive. Its minimum corresponds to the point of zero skewness and kurtosis. This is due to the fact that, the normal distribution has zero skewness and kurtosis and it is best represented by the middle subset. Its symmetrical shape also occurs for different values of the distribution's parameters and thus it can be used to recognize the normal distribution.

The exponential distribution gives a raising Kurt-Skew diagram which is almost linear. Its increasing tendency seems to be a characteristic of many distributions with positive skewness.

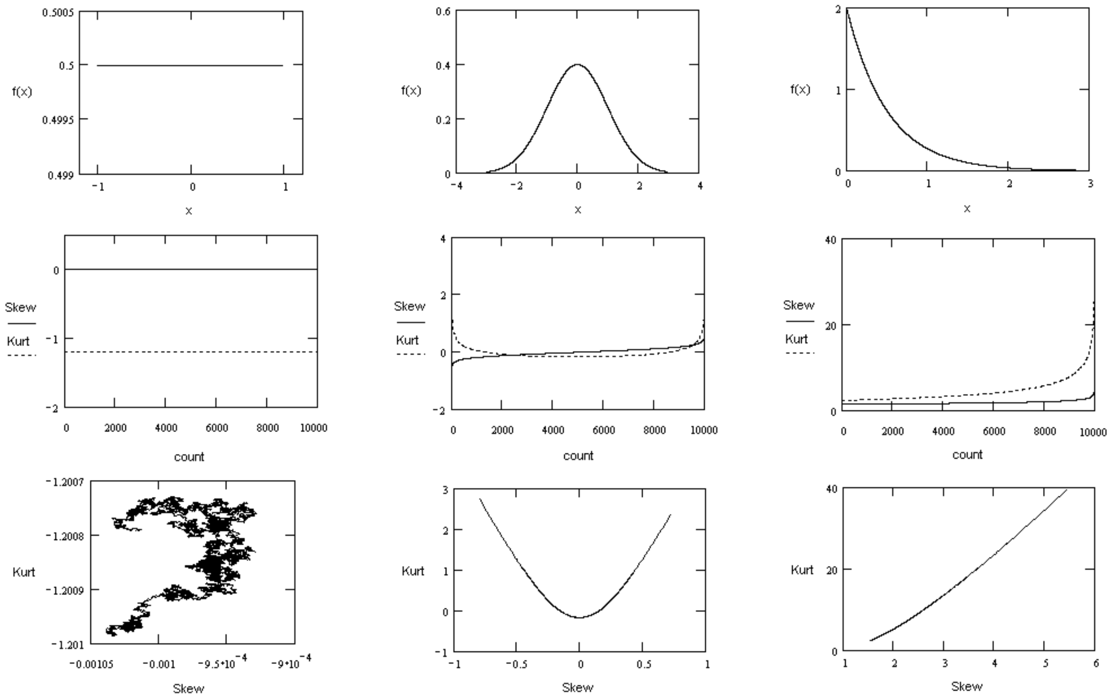

Fig. 2 Uniform distribution on interval (left); normal distribution with parameters, $m = 0$*,* $\sigma = 1$ *(center); exponential distribution with parameter* $\lambda = 2$ *(right)*

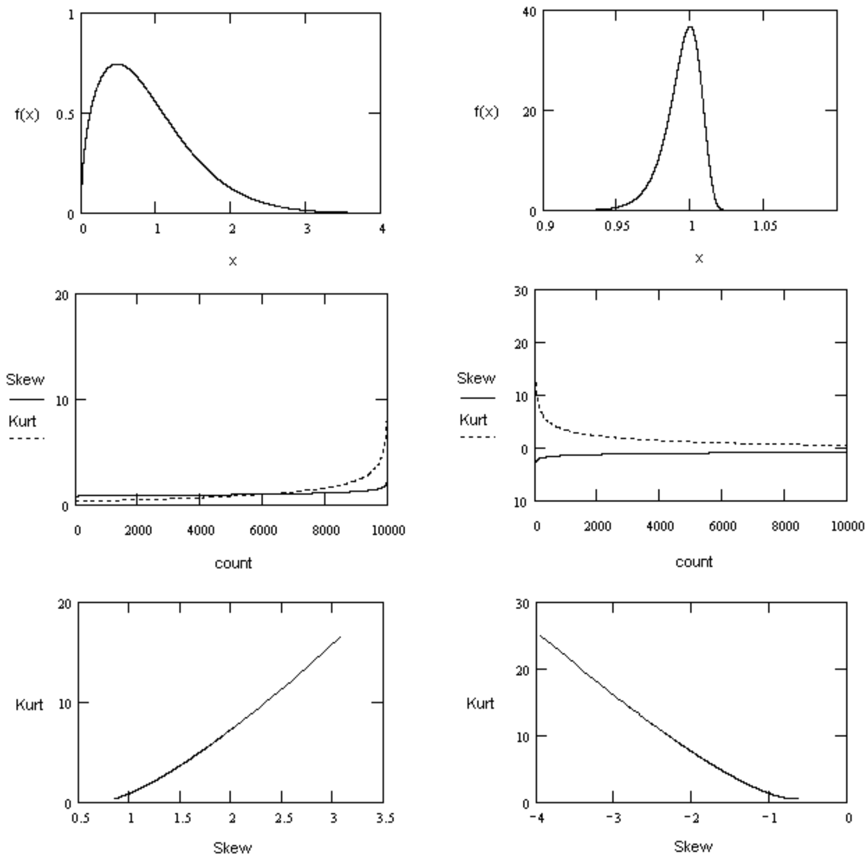

Fig. 3 Weibull distributions with parameters $r = 1.5$*,* $\theta = 1$ *(left);* $r = 100$*,* $\theta = 1$ *(right)*

Figure 3 shows the case of two Weibull distributions. The first one is positively skewed and has an increasing Kurt-Skew diagram, while the second is negatively skewed and its Kurt-Skew decreases.

For both cases, the Kurt-Skew diagrams are almost linear. In the case of the second diagram, the Kurt-Skew diagram ends in a short “tail” to the lower end, towards zero on the skewness axis. The tail diverges from the linearity of the diagram and it is reminiscent of the right branch in the Kurt-Skew diagram of the normal distribution.

An interesting case is the double Weibull distribution. This distribution is composed of two Weibull distributions placed at different positions with two maxima for well-chosen parameter values. Its estimators are presented in Figure 4.

The magnitude of the left Weibull compared to the right Weibull increases from left to right in the figure, while their positions are fixed. The right Weibull has parameter $r_2 = 3.4$ in order to approach a normal distribution, so the right Weibull has zero overall skewness and kurtosis. The left Weibull is positively skewed.

The Kurt-Skew diagram is almost linear, especially in the last two cases (center and right) in the figure. It is decreasing in the first case, where the skewness is negative, and increasing in the last two cases, where the skewness is positive; this monotonicity seems to be independent of the sign of the kurtosis. In the first case, the Kurt-Skew diagram presents a short tail towards zero skewness.

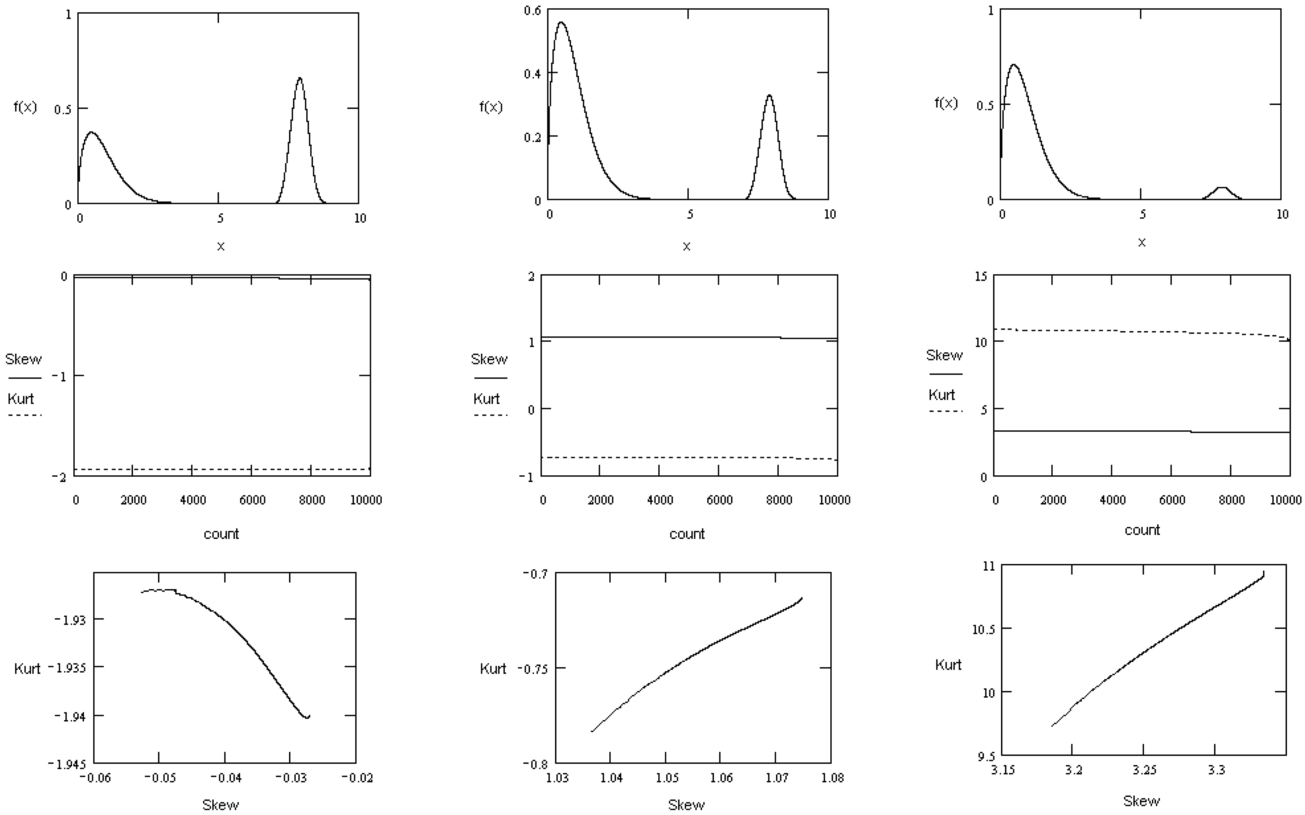

Fig. 4 Double Weibull distributions with parameters $r_1 = 1.5$, $r_2 = 3.4$, $\theta_1 = \theta_2 = 1$, $c = 7$ *and* $a = b = 1/2$ *(left);* $a = 3/4$, $b = 1/4$ *(center);* $a = 19/20$, $b = 1/20$ *(right)*

Fig. 5 shows the same graphs for double Weibull distributions having two Weibulls in different positions.

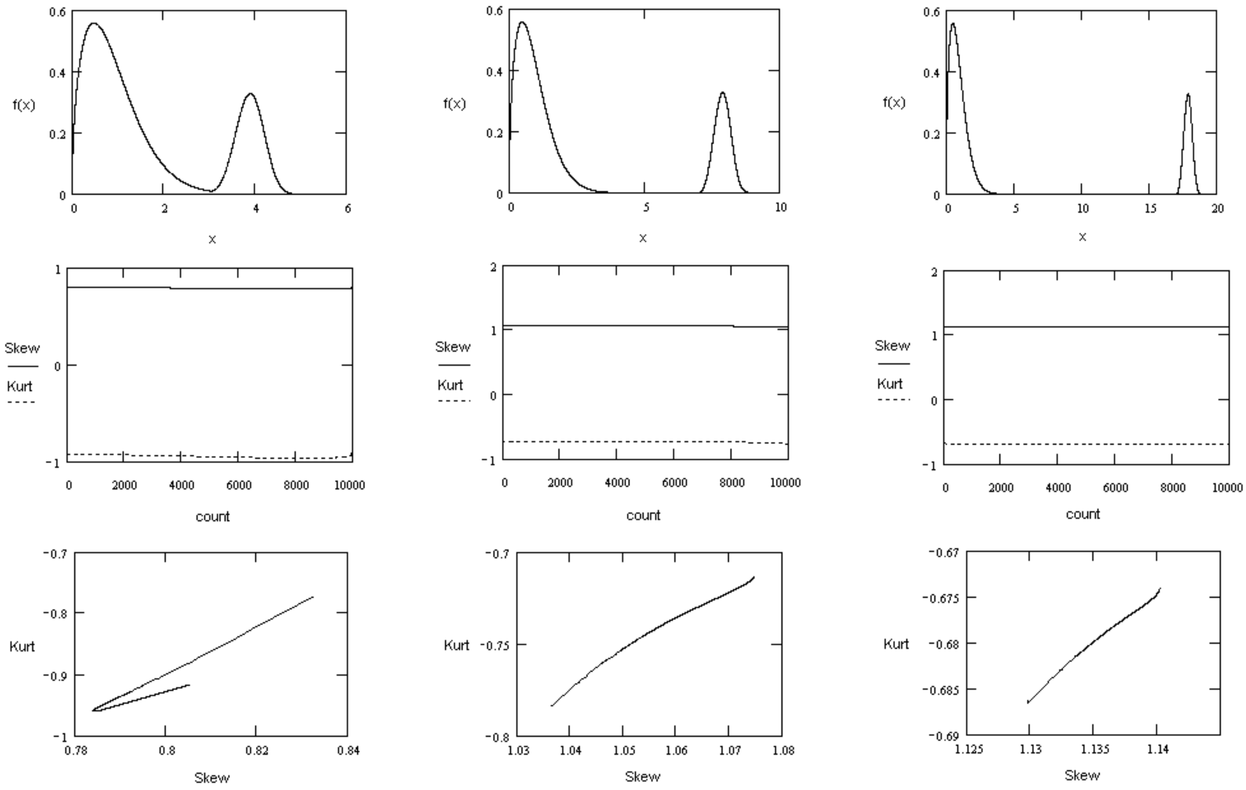

Fig. 5 Double Weibull distributions with parameters $r_1 = 1.5$, $r_2 = 3.4$, $\theta_1 = \theta_2 = 1$, $a = 3/4$, $b = 1/4$ *and* $c = 3$ *(left);* $c = 7$ *(center);* $c = 17$ *(right)*

The slope of the Kurt-Skew diagram increases from the left case (close maxima) to the right case (far away maxima). This is due mostly to the fact that the kurtosis of subsets varies less for far away maxima than it varies for close maxima, while the skewness of subsets has about the same variation in all three cases.

The development of the tail in the lower end of the Kurt-Skew diagram is seen better in Figs. 6 and 7.

The considered parameters are given in the figure's caption. One can see that the tail appears below the main branch of the Kurt-Skew diagram and, as the importance of the left Weibull increases (i.e. a increases), it rotates towards the main branch, passes over it and then goes down to acquire the same slope as the main branch, thus fusing with it.

The tail doesn't always appear towards zero skewness (see the right case in Fig. 6).

The slope of the linear approximation of the Kurt-Skew diagram (with the tail included) does not have precise monotonicity.

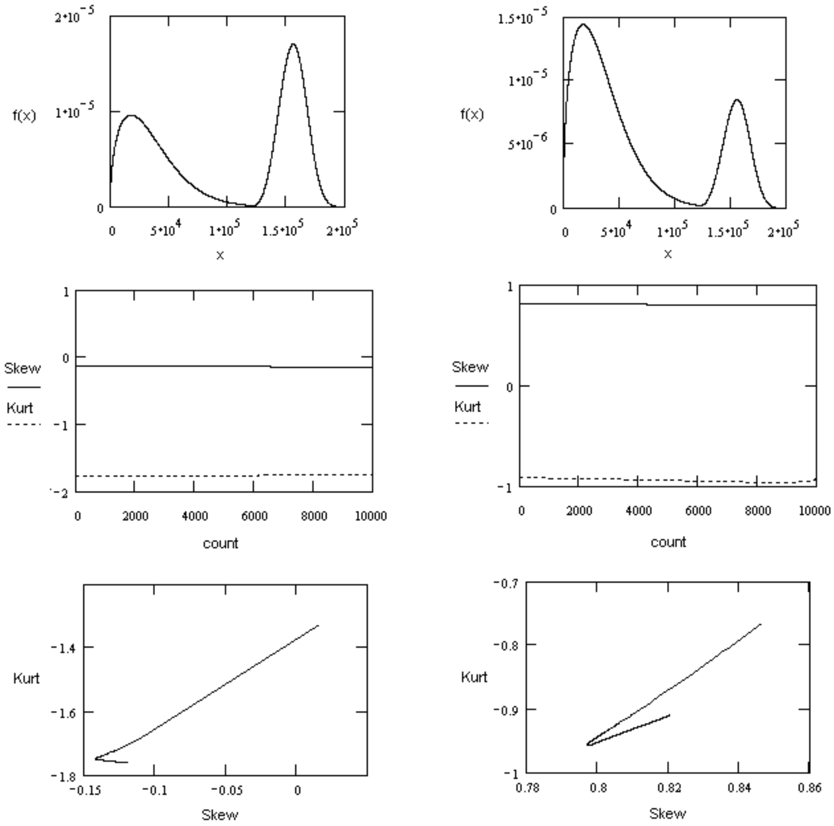

Fig. 6 Double Weibull distributions with parameters $r_1 = 1.471$, $r_2 = 3.4$, $\theta_1 = 38\,479.515$, $\theta_2 = 1$, $c = 121\,426.477$ *and* $a = b = 1/2$ *(left);* $a = 3/4$, $b = 1/4$ *(right)*

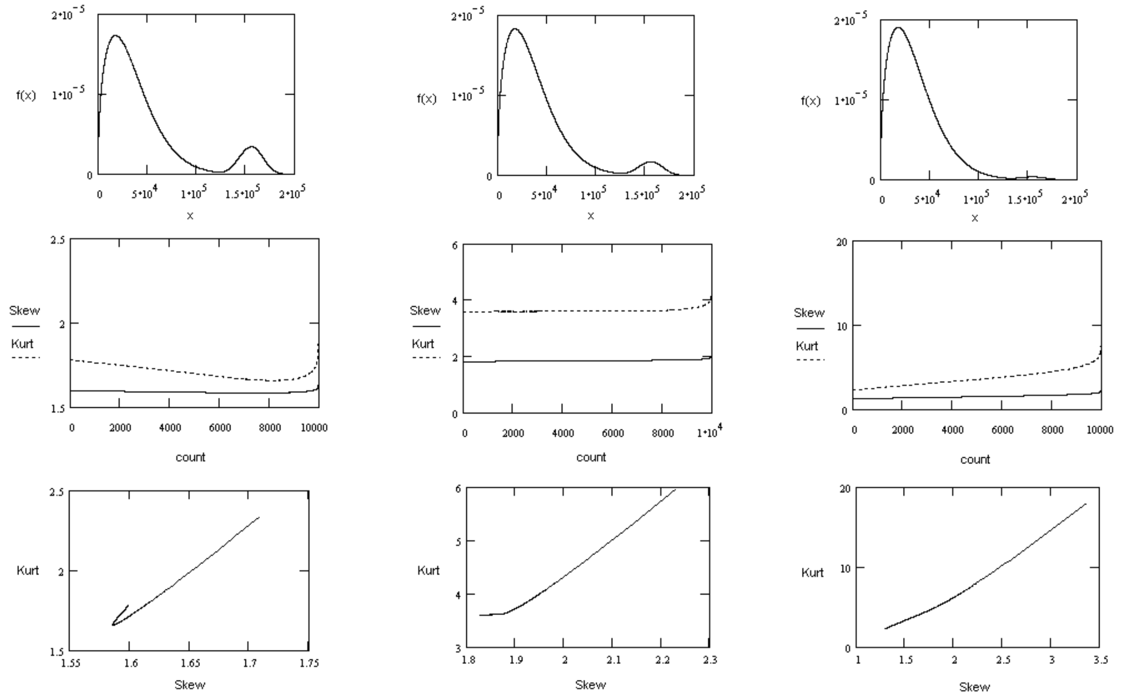

Fig. 7 Double Weibull distributions with parameters $r_1 = 1.471$, $r_2 = 3.4$, $\theta_1 = 38\,479.515$, $\theta_2 = 1$, $c = 121\,426.477$ *and* $a = 9/10$, $b = 1/10$ *(left);* $a = 19/20$, $b = 1/20$ *(center);* $a = 99/100$, $b = 1/100$ *(right)*

3. Experimental estimations

We applied the higher order statistical analysis based on kurtosis and skewness to study the volume distribution of a 10YSZ nanometric 10% stabilized zyrconia powder sample. The experimental values were obtained by image analysis, obtained by TEM with a microscope JEM-200CX. Fig. 8 gives the histogram of particle volumes.

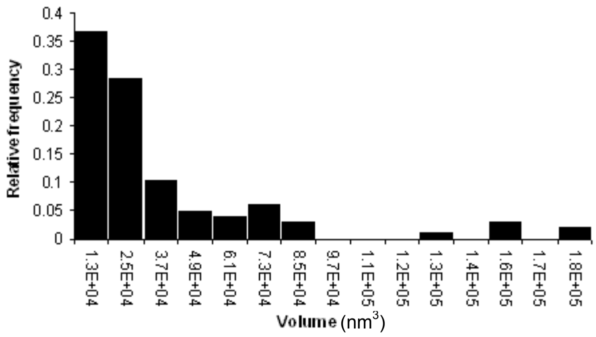

Fig. 8 The histogram of the particle volumes of the alumina-zyrkonia sample

The particle volumes seem to have a Weibull distribution, moreover there seems to be a second lower maximum around $156\ 000\ nm^3$.

By considering the Weibull distribution, the theoretical probability $P(v)$ that particles have a volume V higher than v is:

$$P(v) = \Pr ob(V > v) = \exp\left[-\left(\frac{v}{v_0}\right)^r\right] \qquad (7)$$

where r and v_0 are parameters which were determined by fitting this function to the experimental values. To confirm our supposition according to a Weibull distribution of the particle size, we computed the experimental probabilities as the relative number of the particle population with volume greater than a given volume:

$$P_i = \frac{N(V > v_i)}{N_t} \qquad (8)$$

where v_i is the $i-th$ volume in ascending order, $i = 1,2,...,N_t$. The results are presented in Fig. 9 .

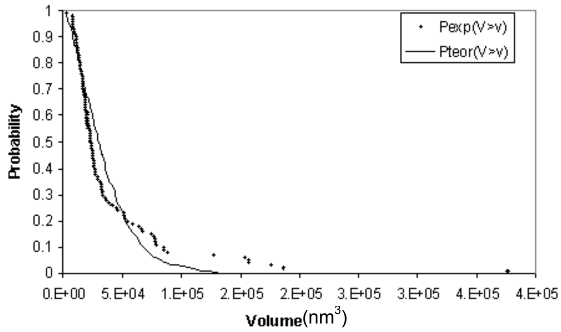

Fig. 9 The fit of the experimental distribution probability with the theoretical Weibull distribution

One feature makes a difference between the experimental and the theoretical values: the experimental probability P_i is smaller than the theoretical one for small volumes and it exceeds the theoretical one for bigger volumes; the dividing limit between the two trends is set at about $50\ 000\ nm^3$. This means that more particles are concentrated at higher volumes. This is a real feature and not just noise and it is a consequence of the particle growth during the sol-gel process.

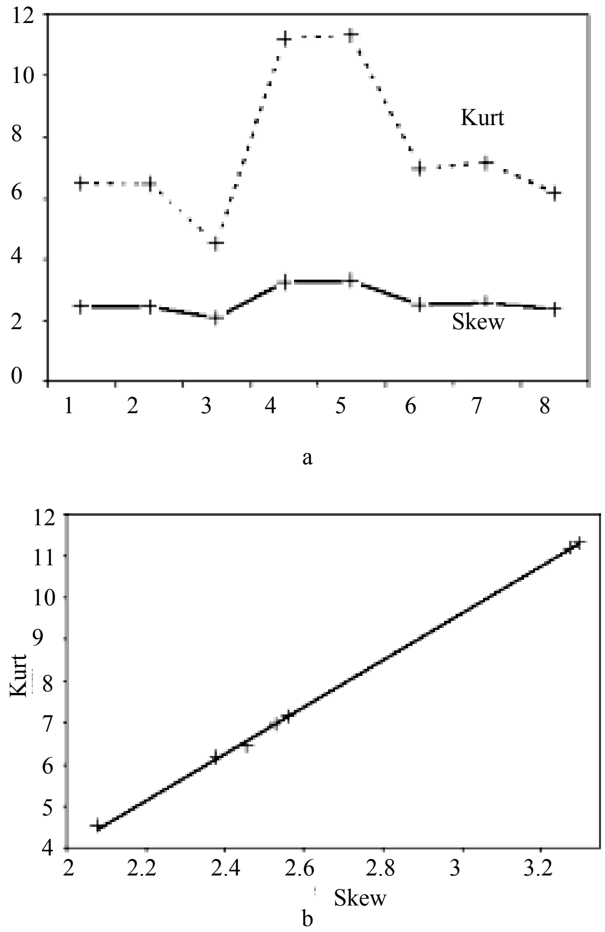

Fig. 10 Indicators for the experimental values: the subset Skewness and Kurtosis graph (a); the Skew-Kurt diagram with linear fit (b)

To test the probability that the second maximum is a real feature we used the double Weibull distribution with the theoretical graph illustrated in the middle of Figure 7. The comparison between theoretical and the experimental case given in Figure 10, reveals some differences. Firstly, the spectrum of values for kurtosis is different for the experimental and the theoretical case. Indeed, the average experimental kurtosis is 7.54, while the theoretical kurtosis is about 3.67. The skewness values are closer in the two cases, i.e. 2.63 experimentally and 1.87 theoretically. These differences may be due to the roughness of the experimental selection, compared to the one used theoretically. Then, the Kurt-Skew diagram does have a very short tail, much shorter than the theoretical one because the tail is due to the second maximum. Further investigations reveal that the experimental linear approximation slope for the Kurt-Skew diagram is 5.612 experimentally and just 2.586 theoretically. These considerations lead us to the conclusion that the experimental data may be affected by a lot of noise, thus the particle volume distribution is given only by the first Weibull.

4. Conclusions

Higher order statistics can be applied in the study of the particle size distribution in nanometric powder characterization. By using the graph of kurtosis vs skewness as size estimator it is possible to predict the existence of single or multiple Weibull distribution of particle size in a powder sample. This method is apt to improve the existing statistical methods.

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*Corresponding author: cretu.c@unitbv.ro