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An alternative method for obtaining distributions of submicrometric particles: analysis using virtual samples

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Sumario. Algunos métodos conocidos permiten encontrar los momentos y las funciones de distribución de probabilidades correspondientes. Nosotros mostramos una manera alternativa de generar una función densidad, usando una función transformadora (la T-función) y la correspondiente ecuación diferencial de transformación (la T-ecuación). Esta T-función puede definirse en un proceso experimental, y se obtendría en las mediciones de laboratorio. Se obtiene la equivalencia matemática de la conocida ecuación de Svedberg-Oden, normalmente usada en procesos de sedimentación gravimétricos, y la T-ecuación diferencial. Se muestra algunas T- funciones y las correspondientes funciones densidad, así como sus gráficos para los procesos de segundo orden. Usando una muestra virtual de partículas de parámetros conocidos, y basado en un método óptico de medición, es simulado el proceso de determinación experimental de distribuciones de partículas pequeñas suspendidas en un líquido. Las funciones de densidad obtenidas usando este método alternativo presentan una concordancia satisfactoria, comparadas con las funciones de la muestra virtual correspondiente.

Abstract. Some known methods allow to find the moments and the corresponding probabilities distribution functions. We show an alternative way to generate density funtions, using a transforming function (T-function) and the corresponding differential transforming equation (T-equation). This T-function can be defined from an experimental process, and would be obtained in laboratory measuring. It is obtained the mathematical equivalence of the known and usually used in gravimetric sedimentation process Svedberg-Oden´s equation and the differential T- equation. Some T-functions and the corresponding density functions, as well as their graphics for processes of second order, it is shown. Using a virtual sample of particles of well-known parameters and based on an optical measuring method, the experimental determination process of suspended in a liquid small particle distributions, is simulated. The density functions obtained using this alternative method show a satisfactory agreement in comparison with the functions of the corresponding virtual sample.

keywords. particle characterization 02.70.Ns; particle suspensions 82.70.Kj; probability theory 02.50.Cw

1 Introduction

Some known methods allow to find the moments and the corresponding distribution functions of probabilities. Unlike to named generating functions, or characteristic functions[1], we show an alternative way[2] to generate density functions, by means a transforming function (T-function) $G(t)$, and the corresponding differential transforming equation (T-equation).

The cumulative or integral distribution function, and the corresponding density function, also called differential distribution function, for the random variable t, are usually defined respectively as[1]

$$P = P(\tau < t) \quad (0.1)$$

$$F(t) = \frac{dP(t)}{dt} \quad (0.2)$$

We consider a transforming T- function *G(t)* as a function that expresses a certain process behavior.

The integral function *P(t)* defined in (1.1) is always a non-decreasing function of *t*. For this cumulative distribution and for the corresponding density function (1.2), the T-function *G(t)* will be a non-increasing function of *t*. Next we considered only this type of functions *G(t)*, which not subtract generality to results.

Functions equivalent to (1.1) and (1.2), for characterizing distributions of temperature, mass, size or other parameters, corresponding to different types of physical systems, would be defined from appropriate T- functions.

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2 A transforming function for obtaining the distribution density

The transforming T-function in second order processes. Among all the possible processes, here we considered a second order process, defined when the density function *F (t)* is related with the corresponding T- function *G(t)* through the differential T- equation,

$$F(t) = -\frac{t}{\tau_0}\frac{dG(t)}{dt} \quad (0.3)$$

$$G(0) = 1 \quad (0.4)$$

where τ_0 is a time parameter.

Some more general cases could be analyzed.

When the T-function can be defined from an experimental process, it would be obtained in laboratory measurings. By means of a known T- function *G(t)*, and using the T-equation (2.1), we obtain in a direct way the corresponding density function *F (t)*.

We will consider here the case of physics conditions for the existence of *G(t)*, according to (2.1).

For a differential equation (2.1), with corresponding initial condition, the uniqueness theorem states that there is a one-to-one correspondence between distribution functions and T- functions. Table I gives some examples of transforming T- function, the corresponding density functions, and their graphics for second order processes.

By integrating the differential equation (2.1), with initial condition *G(0) = 1*, we obtain formally the T-function as:

$$G(x) = 1 - \tau_0 \int_0^x \frac{F(t)}{t}\, dt \quad (2.3)$$

The integral distribution *P (t)* is in this case obtained according to density function from (2.1) by means the formula;

$$P(x) = \int_0^x F(t)\, dt \quad (2.4)$$

where x represent here the process time values.

The Svedbeg-Oden´s equation. Among the most elementary methods using the process of centrifugal or gravimetric sedimentation to obtain the integral distribution function $P = P(t)$ of a sample of particles in suspension, we consider the known Svedberg-Oden´s method[3] of tangential intercepts, corresponding to equation (2.5).

According to this method, the particles integral distribution function for size can be obtained as:

$$P(t) = H(t) - t\frac{d}{dt}H(t) \quad (2.5)$$

Where $H = H(t)$ is a function characterizing the variation of sedimented mass or fraction settled in time *t*.

Next we show the equivalence of known Svedberg-Oden´s equation (2.5), for gravimetric sedimentation, and the T- equation (2.1).

The T-function for particle distributions. The methods of gravimetric sedimentation use the deposited mass, and how it is increasing with time. However, instead of deposited mass, it is possible to obtain the in time mass variation inside a small suspension volume, using an optical method, [3] finding also the functions of particles distribution.

For this we take, instead of *H(t)*, a measure of the time change of this function in a small region. Thus, we choose the T-function *G(t)* as,

$$G(t) = \tau_0 \frac{d}{dt} H(t) \quad (2.6)$$

Deriving the Svedberg-Oden´s equation (2.5) in both members and substituting, according to equation (2.6), if one keeps in mind (1.2), it is obtained in direct way the T-equation (2.1). The density *F(t)* is then defined from the corresponding T- function *G (t)*.

For characterizing the time mass variation of particles in a small measuring region, we choose the T-function *G (t)* as proportional to decreasing law of particle mean mass in the small volume,

$$G(t) = \frac{M(t)}{M_0} \quad (2.7)$$

Where *M (t)* is the mean mass of a particle in time *t*, and M_0 its value in $t = 0$.

3 Obtaining the density functions from virtual samples

To show the feasibility of method we considered a particles virtual sample. Here a particles virtual sample is the distribution functions and the parameters whose well-known numeric values corresponds with the attainable parameters from experimental measurements using samples of real particles.

These virtual samples were previously prepared with chosen parameters. The calculation of the samples was carried out by independent way. A watery suspension was supposed, and the water density was considered *1,00*. Symmetrical and asymmetrical forms for the virtual particles sample density functions were considered. Next we choose a very simple mathematical structure for describing these density functions.

The asymmetric density function. As asymmetric density function we take,

$$f(t) = \frac{t}{\tau^2} e^{-\frac{t}{\tau}} \tag{0.5}$$

Where the time parameter τ corresponds to the value where it happens the maximum of the function. For this function, τ is also a mean time in that a particle crosses the measuring region.

As parametric model for the distribution density function, the Euler´s Beta function with two form parameters, p, q , was selected.

The density function is represented as;

$$F(t) = A\, t^{p-1}\,(1-t)^{q-1} \tag{0.6}$$

Where A is a normalization constant.

The T-function $G(t)$ is then obtained from (2.3) as;

$$G(x) = 1 - \tau_0 A \int_0^x t^{p-2}(1-t)^{q-1} dt \tag{0.7}$$

Next, in Table II we considered for the case of asymmetric virtual sample five mass values, equivalent to five measurements .

To obtain the solutions, it is solved the following system of non- linear equations, using the minimum error routine of the MathCad 2000 Professional software.

In the equation system the time values from Table II appear in the superior limit of integrals, normalized in relation to a time parameter T, as x_1, x_2, x_3, x_4, x_5. In this example $T = 1500$ minutes.

$$x_i = \frac{t_i}{T} \cdots i = 1, 2, ..., 5 \tag{0.8}$$

The simulated measured masses appear to the left of the equations, in the numerators, as M_1, M_2, M_3, M_4 and M_5. We take five parameters in the equations, with the conditions;

$$p > 0\,;\, q > 0\,;\, A > 0;\, M_0 > 0$$

The system of equations is:

$$\begin{aligned}
\frac{1}{A} &= \int_0^1 t^{p-1}(1-t)^{q-1} dt \\
\frac{M_1}{M_0} &= 1 - \tau_0 A \int_0^{x_1} t^{p-2}(1-t)^{q-1} dt \\
\frac{M_2}{M_0} &= 1 - \tau_0 A \int_0^{x_2} t^{p-2}(1-t)^{q-1} dt \\
\frac{M_3}{M_0} &= 1 - \tau_0 A \int_0^{x_3} t^{p-2}(1-t)^{q-1} dt \\
\frac{M_4}{M_0} &= 1 - \tau_0 A \int_0^{x_4} t^{p-2}(1-t)^{q-1} dt \\
\frac{M_5}{M_0} &= 1 - \tau_0 A \int_0^{x_5} t^{p-2}(1-t)^{q-1} dt
\end{aligned} \tag{0.9}$$

Where A is the normalization parameter, p, q are the form parameters of Beta function, τ_0 is a time parameter, and M_0 is the mean particle mass for $t = 0$.

Table II
The simulated experimental values from the asymmetric virtual sample.

Number	Time (minutes)	Mean mass (grams)
1	1	3,210 x 10^{-12}
2	25	2,842 x 10^{-12}
3	50	2,123 x 10^{-12}
4	25	1,581 x 10^{-12}
5	100	1,185 x 10^{-12}

Table III
The simulated measured values of M_i / M_0, and the corresponding values evaluated for the T-function $G(t)$ from (3.3) and (3.5) using the obtained parameters.

Number	M_i / M_0	$G(t_i)$
1	0,98812	0,98812
2	0,24191	0,24189
3	0,55295	0,55802
4	0,41182	0,41125
5	0,31143	0,31141

Table IV
Simulated experimental values from the symmetric virtual sample.

Number	Time (minutes)	Mean mass (grams)
1	1	3,499 x 10^{-12}
2	4	3,424 x 10^{-12}
3	8	3,141 x 10^{-12}
4	12	2,290 x 10^{-12}
5	30	1,250 x 10^{-12}

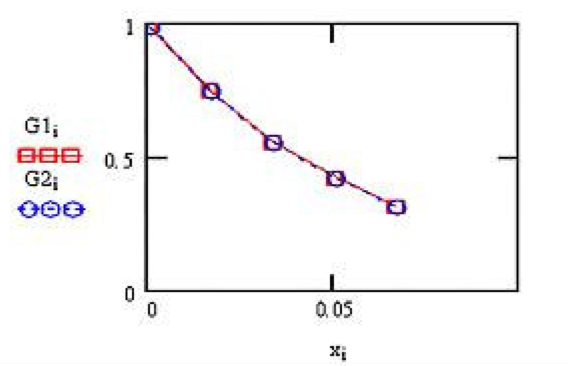
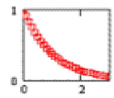
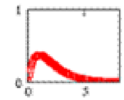
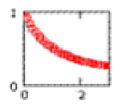
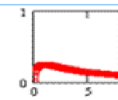
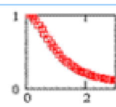
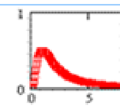
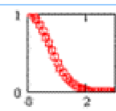
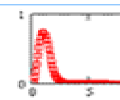
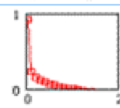
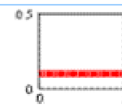
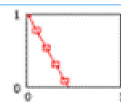
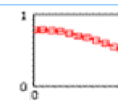
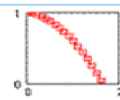
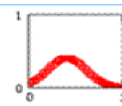


Figure 1. Results of Table III for the values of transforming T- function $G(t)$, where: $G1 = Mi /Mo$ are the simulated experimental values, and $G2 = G(ti)$ the corresponding values evaluated from (3.5) and (3.3).

Table I

Some transforming T- functions, the corresponding density functions, and their graphics for second order processes. Here the parameter $\tau_0 = s$

G(t)		*F(t)*	
$e^{\frac{-t}{s}}$		$\frac{t}{s^2}\cdot\exp\left(\frac{-t}{s}\right)$	
$\frac{1}{\left(1+\frac{t}{s}\right)}$		$\frac{t}{\left[s^2\cdot\left(1+\frac{t}{s}\right)^2\right]}$	
$\frac{1}{\left[1+\left(\frac{t}{s}\right)^2\right]}$		$2\cdot\frac{t^2}{\left[s^3\cdot\left(1+\frac{t^2}{s^2}\right)^2\right]}$	
$e^{\frac{-t^2}{s}}$		$2\cdot\frac{t^2}{s^2}\cdot\exp\left(\frac{-t^2}{s}\right)$	
$-s\cdot\frac{(\ln(t))}{\Delta t}$		$\frac{1}{\Delta t}$	
$1-\frac{3}{2}\cdot\mathrm{atan}(\exp(t))\cdot\pi+\frac{3}{8}\cdot\pi^2$		$\left(\frac{\pi}{2}\right)\cdot\frac{1}{\left(e^{-t}+e^{t}\right)}$	
$1-\frac{3}{2}\cdot\mathrm{erf}\left(\frac{1}{2}\cdot t\sqrt{2}-\frac{1}{2}\cdot v\sqrt{2}\right)-\frac{3}{2}\cdot\mathrm{erf}\left(\frac{1}{2}\cdot v\sqrt{2}\right)$ (*)		$\left(\frac{1}{s\sqrt{2\cdot\pi}}\right)\cdot e^{\frac{-(t-v)^2}{2\cdot s^2}}$	

(*) We consider the real error function erf(x), defined as; $erf(x) = \frac{2}{\pi}\int_0^x \exp(-t^2)dt$

The solutions are, with five decimals, $M_0 = 3{,}80501\text{x}10^{-12}$ g; p = 1,99209; q = 12,10108; τ_0 = 0,05201; A = 321,09398.

Comparison of simulated measured and evaluated values for T-function are shown in Table III.

The results from Table III are shown in the graph of Figure 1, describing *G(t)* as decrease in time of the particles mean mass in measuring region. The comparation of density function obtained with the simulated data is shown in Figure 2, where f(t) is the virtual sample curve and F(t) is the curve obtained from (3.2), according to proposed method. In this example, for virtual sample curve, the distribution maximum is reached at 85,235 minutes, and for the curve obtained from (3.2) at 84,522 minutes.

The symmetric density function. We take this function as a Gaussian virtual sample.

$$f(t) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(t-\mu)^2}{2\sigma^2}} \qquad (0.10)$$

Table IV gives the corresponding simulated mean mass values in time for this Gaussian sample.

By solving the non- linear equations system gives the following values; $M_0 = 3{,}49902 \text{ x } 10^{-12}$ g, $A = 1{,}13215 \text{ x } 10^{-5}$, p = 1,93944, q = 10,84923, τ_0 = 0,18541.

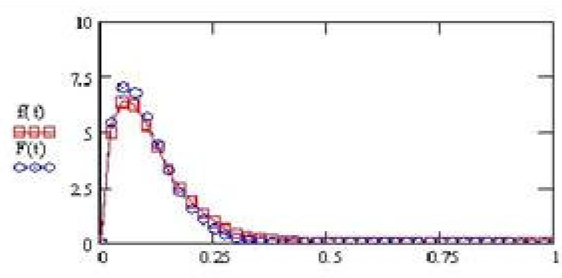


Figure 2. Representation of both curves for the asymmetric case. Here *f(t)* is the simulated experimental curve, given by (3.1) and *F(t)* is the corresponding curve obtained using the proposed method, according to (3.2). The abscissas axis is adimensional and is normalized with regard to an arbitrary time value T, taken in the present example like 1500 minutes.

The result can be observed in Figure 3, where distribution maximum is reached now for simulated experimental curve at 10,5 minutes, and for the proposed method curve at 11,281 minutes. The abscissas axis is here normalized to 30 minutes.

From figures 2 and 3 we can observe satisfactory results when the virtual sample distributions is recovered from the proposed method. It could be proven that using the Euler´s Beta function, with two form parameters, *p, q*, the result is satisfactory so much for symmetrical as asymmetrical distributions.

The corresponding integral function of particle distribution *P(t)* would be calculated in these cases from (2.4),

$$P(t) = \frac{1}{A}\int_0^x t^{p-1}(1-t)^{q-1}dt \ . \tag{0.11}$$

3 Conclusions

An alternative way to generate a density function was shown. It was defined a transforming function (T-function) like a function expressing a certain process behavior. By means of this function and using the differential transforming equation (T-equation), the corresponding density function is obtained in a direct way. A group of T- functions, and the corresponding density functions obtained using the T-equation, were shown.

It was obtained the equivalence of the known Svedberg-Oden´s equation and the T- equation, for finding the distribution functions of particles in suspension. The T- function depends in this case on the time decrease law of particle mean mass inside a small suspension region.

Using the proposed method virtual samples of small particle distributions were investigated, choosing like parametric model the Euler´s Beta function, with two form parameters, *p, q*. The obtained results were satisfactory so much for symmetrical as asymmetrical distributions. It was supposed that parameters of the investigated virtual samples are equivalent to those attainable from measurements, by using an optical system.[3]

In the frame of this work, different particle virtual samples with mean diameters from 1 micrometer until less than 50 nanometer were processed. Different particle density- from 1,05 (latex) up 4,20 (titanium dioxide) were considered, with satisfactory results.

In real samples the results would depend strongly on the quality of *G(t)* measurings.

A wide summary of optical techniques for characterizing particles can be consulted in the specialized literature.[4] The proposed alternative method shown in this work would be extended to others applications.

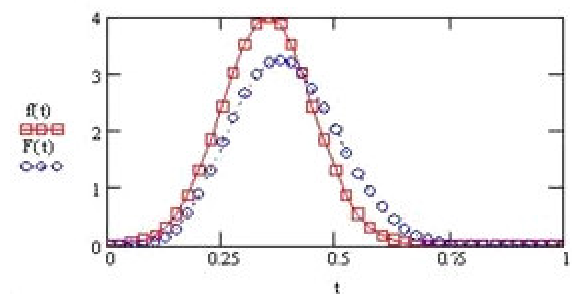


Figure 3. Comparison of curves for the Gaussian case, where *f(t)* is again the simulated experimental curve and *F(t)* is the curve obtained by this alternative method. The time parameter T normalizing the abscissas axis is in this case 30 minutes.

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