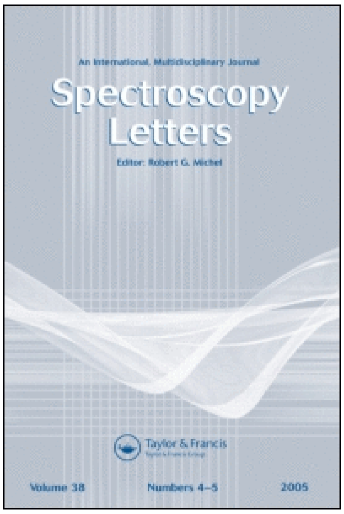

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APPLICATION OF A LAPLACE TRANSFORM METHOD TO THE STUDY OF BINARY MIXTURES OF SPHERICAL AND ROD-LIKE PARTICLES FOR LOW INTENSITY LEVELS.

KEY WORDS: Rayleigh Scattering. Macromolecules.

Photon counting.

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ABSTRACT

A Laplace Transform (LT) method is used to improve the results obtained in a quasi-elastic

scattering (QELS) experiment. This is designed to determine the characteristic parameters of a bimodal solution of spherical and rod-like macromolecules. The theoretical study and the experimental simulation are carried out for low light levels, and the results show that the LT technique provides a real alternative to the second order correlation function, $g^{(2)}(\tau)$, in QELS measurements for these particularly difficult experimental conditions.

1.- INTRODUCTION

QELS, and particularly the measurement of $g^{(2)}(\tau)$, has been a successful method[1] in the analysis of hydrodynamic properties of macromolecules in monomodal solutions: spherical, rod-like, once-broken rod, and spheroid shaped particles[2,3]. The analysis was extended to binary mixtures of two sized spherical particles[4,5], and also to mixtures of spherical and rod-like particles[6]. [The term 'solutions' may not be as accurate as 'suspensions' but, because of its broad use in the literature, we will attach to it].

When the intensity of light is very low (less than one photocount per coherence time) the estimation of $g^{(2)}(\tau)$ becomes less efficient, and the measurement of the time interval between successive photoelectrons (or, more precisely, the measurement of the LT of the time interval probability between successive photoelectrons, Q(s)) gives us a better signal to noise ratio and a better fitting of the characteristic parameters, as has been shown in previous works[4,7].

This analysis tries to set the theoretical expressions for the errors involved in the calculation of the characteristic parameters of binary mixtures of spherical and rod-like particles, comparing $g^{(2)}(\tau)$ and Q(s) methods. The behaviour of these errors will be shown as a function of the spherical solute, the scattering angle, and relative scattering intensity ratio between rods and spheres, α.

In the last part of the work, an experimental simulation is carried out to check the previous theoretical model, in such a way that one can cover a great number of experimental situations. A computer simulation like this has already been used for characterizing binary mixtures by means of the second order factorial moment of the number of photopulses[8], $n^{(2)}(T)$, and by means of the $g^{(2)}(\tau)$ function, for low light levels.

[In this work, particles will be considered "pure", which is quite a realistic approximation. We will not be taking into account the individual polydispersity (size variation) and other experimental corrections, such as the aggregation level, the flexibility of rods, and other small effects.]

2.- THEORY

2.1 Measurement of $g^{(2)}(\tau)$.

Let us consider a laser light beam of wavelength λ incident on a dilute solution of a binary mixture of spherical and rod-like particles. If the size of the illuminated volume is enough so that the number of scatterers is large, then the emerging light field is Gaussian, and Siegert's equation is fulfilled. Therefore, we can obtain the value of $g^{(2)}(\tau)$ (second order correlation function) from the measurement of $g^{(1)}(\tau)$ (first order correlation function), substituting[9]:

$$g^{(2)}(\tau) = 1 + C\left[\frac{|g_s^{(1)}(\tau)|^2}{(1+\alpha)^2} + \frac{|g_r^{(1)}(\tau)|^2}{(1+\alpha^{-1})^2} + \frac{|g_s^{(1)}(\tau)||g_r^{(1)}(\tau)|}{(1+\alpha)(1+\alpha^{-1})}\right] \quad (1)$$

where $g_r^{(1)}(\tau)$ and $g_s^{(1)}(\tau)$ are the first order correlation functions of the light scattered by the rods and the spheres respectively, C is the spatial coherence factor, and α is the ratio of the intensities scattered by the two fractions of the solute, $\alpha = I_r/I_s$, as previously stated.

For the individual $g^{(1)}(\tau)$ functions we have:

$$|g_s^{(1)}(\tau)| = \exp\{-\Gamma_s \tau\} \quad (2.a)$$

$$|g_r^{(1)}(\tau)| = b_o \exp\{-\Gamma_{or} \tau\} + b_1 \exp\{-\Gamma_{1r} \tau\} \quad (2.b)$$

being: $\Gamma_s=(D_T)_s K^2$ $\qquad b_i = B_i / B$

$\Gamma_{or}=(D_T)_r K^2$ $\qquad B = \Sigma Bi$

$\Gamma_{1r}=(D_T)_r K^2 + 6D_r$

where: $K=(1/\lambda)4\pi n \sin(\theta/2)$; $\theta \equiv$ scattering angle.

$n \equiv$ refractive index of solvent.

$\lambda \equiv$ laser wavelength.

B_i are the Pecora Coefficients[10], which are a function of the product KL (L being the length of the rods).

The Translational Diffusion Coefficient of the sphere, $(D_T)_s$, characterizes the dynamic behaviour of that particle in the solution, and is related to the diameter of the spheres[11].

The Translational and Rotational diffusion coefficients of the cylindrical particles, $(D_T)_r$ and D_R respectively, are also related to the geometrical parameters (diameter and length) via Broersma's empirical model[12].

An overview of these relations (Eq.1 and 2) shows that a good characterization of the mixture can be achieved just by calculating the values of Γ_s, Γ_{0r} and Γ_{1r}. This, in principle, can be done by means of a fitting procedure after the measurement of the $g^{(2)}(\tau)$ function of the bimodal solution.

The measurement of $g^{(2)}(\tau)$ is made through the experimental estimator:

$$\hat{g}^{(2)}(lT) = \frac{\frac{1}{N-l}\sum_{j=0}^{N-l+1} n(jT)\, n((j+l)T)}{\frac{1}{N}\left[\sum_{j=0}^{N-1} n(jT)\right]^2} \; ; \; (l=1,2,...M) \quad (3)$$

where T is the sample time, N is the total number of samples, M is the number of channels of the correlator, and n(jT) is the number of photocounts from the instant t=jT to the instant t=jT+T.

If the intensity of the detected light is very low (such that $m\tau_c<1$, m being the mean count rate (s^{-1}) which means less than 1 photocount per coherence time), then the theoretical expression for the fluctuations of $g^{(2)}(\tau)$ is given by[1]:

$$\mathrm{Var}\left[g^{(2)}(lT)\right] = \frac{g^{(2)}(lT)}{N\bar{n}^2} \quad (4)$$

where n is the mean number of photons per sample time.

Expressions Eq.3 and Eq.4 lead us to corresponding expressions for the error involved in the determination of parameters from the estimated $g^{(2)}(\tau)$.

$$\mathrm{Var}\,\Gamma_i = \left\{\sum_{l=1}^{M} \frac{\left(\frac{\partial}{\partial \Gamma_i} g^{(2)}(lT)\right)^2}{\mathrm{Var}\left(g^{(2)}(lT)\right)}\right\}^{-1} \quad (5)$$

where Γ_i may be Γ_s, Γ_{0r}, or Γ_{1r}.

2.2 Measurement of Q(s)

When the intensity of light is very low, the estimate of $g^{(2)}(\tau)$ loses its accuracy and the time interval probability between successive photoelectrons, P(t) becomes an alternative technique. In particular we have applied a method[13] based on the LT of the time interval probability, Q(s):

$$Q(s) = \int_0^\infty P(t)\, e^{-st}\, dt \qquad (6)$$

The experimental estimate of which is given by:

$$\hat{Q}(s) = \frac{1}{N_Q} \sum e^{-st_i} \qquad (7)$$

N_Q being the number of intervals t_i considered.

When $m\tau_c \ll 1$ we have[13] :

$$Q(s) = \frac{L(s)}{1 + L(s)} \qquad (8)$$

where L(s) is the LT of the time interval probability between a given photoelectron and any other arriving afterwards.

For stationary Gaussian light, L(s) verifies :

$$L(s) = \overline{m}\, TL\left[g^{(2)}(\tau) \right] \qquad \textbf{(9)}$$

Hence, substituting Eq.1 and Eq.2 in Eq.9, and then in Eq.8, we have an expression for Q(s) as a function of coefficients Γ_s, Γ_{0r}, and Γ_{1r}.

Then we can find again the expressions for variances of Γ_i when measured through a Q(s) estimator:

$$Var\left[\Gamma_i \right] = \left(\frac{\partial Q(s)}{\partial \Gamma_s} \right)^{-2} Var\left[Q(s) \right] \qquad \textbf{(10)}$$

where, in case of low light levels, Var[Q(s)] is:

$$Var\left[Q(s) \right] = \frac{1}{N_Q}\left[Q(2s) - Q^2(s) \right] \qquad \textbf{(11)}$$

The expressions found for e_{Γ_i}, when making the derivatives, aren't simple, and non-trivial dependencies appear. That induces us to make several plots of the errors involved in Γ_i measurements.

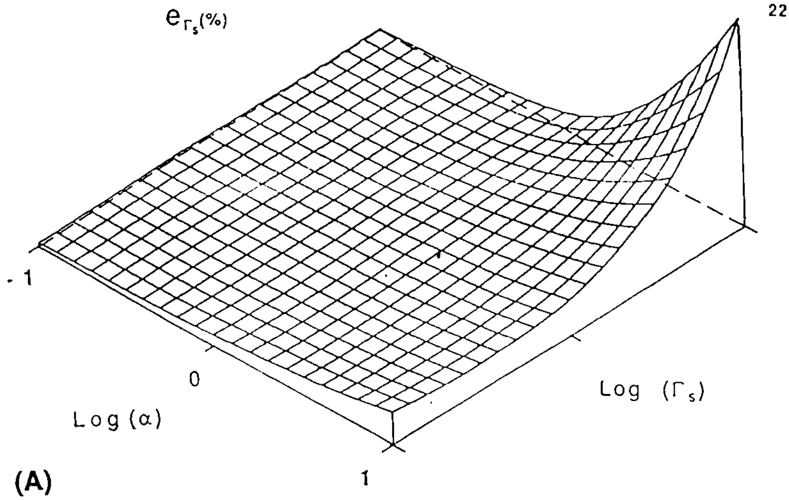
3.- THEORETICAL RESULTS.

Among all the dependence plots that Eq.5 and Eq.10 may lead to, we will show only the most interesting ones: Fig.1 to 4.

Figs. 1.a and 1.b show the similarity of error dependencies, as obtained both by means of Q(s) or $g^{(2)}(\tau)$, with two parameters: α and Γ_s. Error $[e_{\Gamma_s}]_{Q(s)}$ keeps under $[e_{\Gamma_s}]_{g^{(2)}(\tau)}$ (see maximum value in the figure), which proves the quality of the Q(s) estimator in these conditions. It is also clear that the determination of Γ_s, the characteristic parameter of the sphere, improves as α gets lower, as was expected, since a small α (remember $\alpha=I_r/I_s$) means that most of the light is being scattered by the spheres. Error also shows a slight minimum with respect to Γ_s, which corresponds to sphere particles sized similar to the rod length.

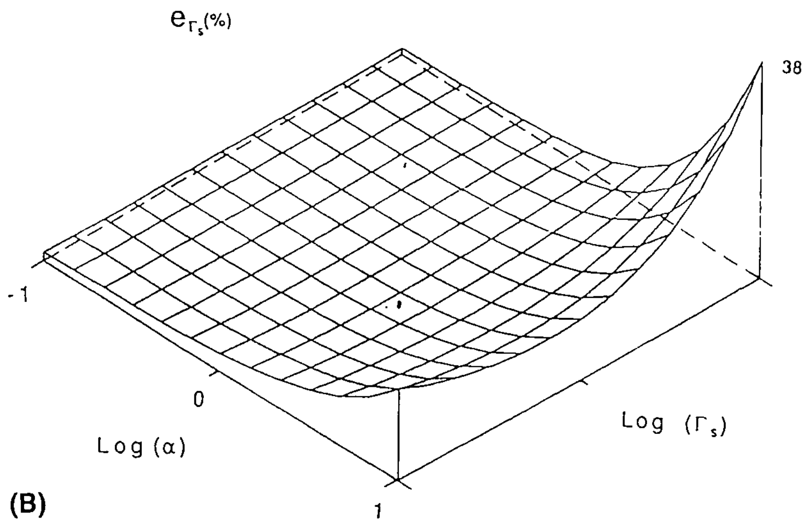
Fig.2, 3 and 4 show the error in determining Γ_s, Γ_{0r} and Γ_{1r} as a function of α and the scattering angle θ. The suspended solutes are latex spheres of radius 100nm. and Tobacco Mosaic Virus (TMV) as rod-like particles. TMV has many references in QELS (see for example Refs.14 and 15) and its dimensions may be taken as: length L≡300nm., section diameter, d≡18nm.

The three figures show an evident dependence on α. As a increases, the error in the estimate of Γ_{0r} and Γ_{1r} decreases, and the same happens with Γ_s for lower values of α. Fig.2 shows no important dependence on the scattering angle θ, while Fig.3 presents a slight minimum. Fig.4 shows that the determination of parameter Γ_{1r} depends dramatically on scattering angle, which induces us to take this dependence as the criterium



(A)

FIG.1.a Theoretical error (expressed in %) in obtaining Γ_S through the measurement of Q(s), as a function of the intensity ratio α and the magnitude of Γ_S for an angle $\theta=90°$ and a value of $sT_C=1$.



(B)

FIG.1.b Same as Fig.1.a when the function originally evaluated is $g^{(2)}(\tau)$.

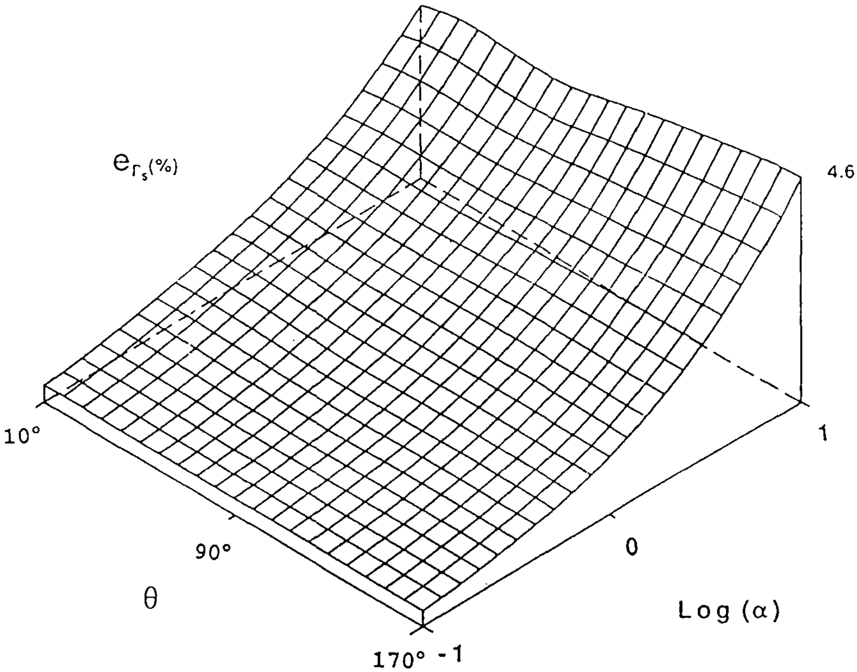


FIG.2 Behaviour of the error (expressed in %) in obtaining Γ_s through the measurement of Q(s), as a function of the angle θ and the intensity ratio α for a mixture of TMV + 1000 Å spheres and a value of $sT_c = 1$.

on which to choose the observation angle in further measurements. This behaviour of error is due to the relationship between the Pecora coefficient b_1 and θ.

In all cases, the corresponding plots of the error when using $g^{(2)}(\tau)$ are very similar, errors keeping over those found for Q(s) by a factor of 3 or more.

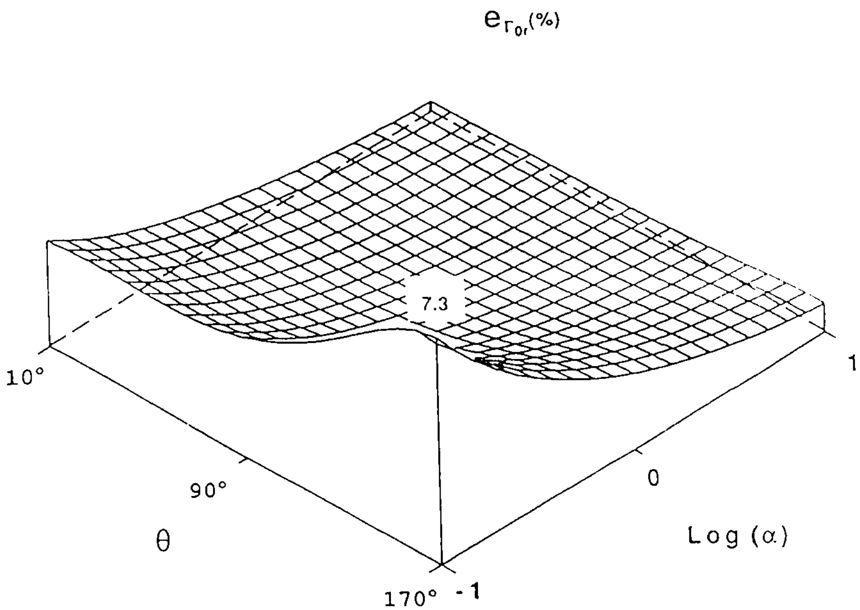


FIG.3 Same as Fig.2, when obtaining the parameter Γ_{or}.

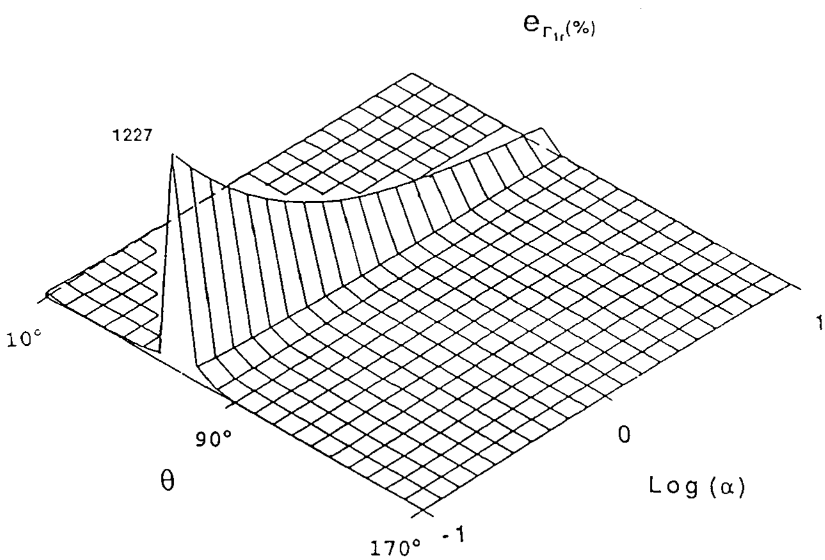


FIG.4 Same as Fig.2, when obtaining the parameter Γ_{1r}.

4.- EXPERIMENTAL SIMULATION

In order to study the value of the relative errors involved in the experimental determination of parameters Γ_s, Γ_{0r} and Γ_{1r}, we have simulated the values of Q(s) and $g^{(2)}(\tau)$ (taking into account Eq.4 and Eq.11 and a well known simulation method[16,17]) for a bimodal solution of TMV with either 10 or 100 nm. diameter latex spheres. The mean parameters of the experiment were fixed as follows: 0.1 photocounts per coherence time. Total time of measurement=1000s. Number of series for each situation: 10. For $g^{(2)}(\tau)$ a 64 channels correlator was simulated and the coherence factor was taken as C=1. For Q(s), ten values of s were chosen around the value that minimizes the error. (For the sake of brevity, we don't include the study as a function of the product $s \cdot T_c$.)

Table 1 shows the error in the determination of Γ_s, e_{Γ_s}, through the fitting of $g^{(2)}(\tau)$ and Q(s), for α=0.1,1 and 10. The results obtained for the errors in the determination of Γ_{0r} and Γ_{1r}, that is, $e_{\Gamma_{0r}}$ and $e_{\Gamma_{1r}}$ are shown in Table 2 and Table 3 respectively, also for α=0.1,1 and 10.

5.- CONCLUSIONS

The theoretical model has shown that the scattering angle must be carefully chosen when

TABLE 1

e_{Γ_s}(%)	$g^{(2)}(\tau)$		Q(s)	
	TMV+10	TMV+100	TMV+10	TMV+100
α=0.1	1.3	2.5	1.5	4.6
α=1	5.5	5.5	2.1	1.9
α=10	22.4	14.4	7.0	7.7

TABLE 2

$e_{\Gamma_{0r}}$(%)	$g^{(2)}(\tau)$		Q(s)	
	TMV+10	TMV+100	TMV+10	TMV+100
α=0.1	27.3	17.9	5.8	5.0
α=1	8.1	6.3	3.2	2.2
α=10	4.6	5.1	1.8	1.5

TABLE 3

$e_{\Gamma_{1r}}$(%)	$g^{(2)}(\tau)$		Q(s)	
	TMV+10	TMV+100	TMV+10	TMV+100
α=0.1	27.0	19.1	4.6	4.2
α=1	11.9	12.8	2.7	3.1
α=10	10.6	8.0	1.6	1.6

parameters related to rod-like particles are to be determined.

The simulation process shows that the lowest error is found for small values of α when determining Γ_s, and for high values of α when determining Γ_{0r} and Γ_{1r}. This is in accordance with the theoretical model.

Values of a close to 1 will produce the best simultaneous measurement of parameters Γ_s, Γ_{0r} and Γ_{1r}, according to tables 1, 2 and 3. When values of a separate from 1, some errors will increase rapidly, while others will only decrease slowly.

What is more remarkable is the behaviour of Q(s) compared with $g^{(2)}(\tau)$. The errors obtained through this last method behave in the same manner as those found from Q(s) but are always larger.

The same conclusion can be obtained from the simulation process; $g^{(2)}(\tau)$ errors are always higher than those corresponding to Q(s) measurements.

The above comments lead us to the conclusion that, when analyzing binary mixtures of spherical and rodlike particles for low intensity levels, Q(s) estimation proves more effective in determining the mean parameters, and constitutes an alternative to the measurement of $g^{(2)}(\tau)$. Moreover, experimental measurement of Q(s) is simpler and cheaper, since we don't need a correlator, but only a time interval counter and a computer to keep values of t_i and evaluate Q(s).

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