Implementation and comparison of dynamic and static light scattering techniques for polidisperse particle sizing using a CCD camera

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Abstract. Laser techniques for particle sizing are used in industrial as well as in scientific applications due to the direct connection between the measured quantities in light dispersion processes and particle properties. We have successfully implemented two light scattering techniques, adapted to function with a CCD camera as detector: the dynamic technique, studies the temporal correlation of the scattered light in a fixed direction (known as DLS for “Dynamic Light Scattering”); the static technique, retrieves the mean intensity distribution as a function of the scattering direction. We present experimental results on monodisperse and polidisperse solutions of latex spheres diffusing in water and compare the performance of these techniques. The statistical averaging over the CCD pixels allows significant reduction of measurement times.

1. Introduction

The scattering of light may be thought of as the redirection that takes place when an electromagnetic wave encounters an inhomogeneity or change in the optical properties of the medium. Light scattering is the result of the complex interaction between light and matter. In this interaction, the electron cloud of the molecular structure of the scattering object is perturbed periodically with the same frequency as the electric field of the incident wave, resulting in an oscillating induced dipole moment that radiates energy. The majority of the light scattered is emitted at the frequency of the incident light. This process is referred to as elastic light scattering.

There are several frameworks that deal with the problem of elastic light scattering. A simplified model applicable in the case of dielectric particles much smaller than the wavelength of the incident radiation, is known as the theory of Rayleigh scattering. But it is also possible to solve the strict problem of a plane wave incident on a homogeneous sphere (absorbing or non-absorbing) without a particular bound on particle size. This is the theory of Mie scattering.

In this work, we illuminate a sample composed of latex spheres diffusing in water. Due to the stochastic interference associated with the scattering waves, the intensity profile has a speckled appearance which fluctuates in time, as the particles undergo Brownian motion. We present two techniques that use the information contained in the speckle pattern to retrieve the particle size distribution in the sample.
In the dynamic technique, we register the intensity fluctuations from independent speckle grains in the far field at a fixed scattering angle and by means of the inversion of the intensity autocorrelation function it is possible to extract the particle size distribution.

In the static technique, we register independent speckle patterns in the near field of the sample, as proposed by F. Ferri et al. [1], so that each pixel of the detector is reached by light scattered in all the directions that the system can scatter at. Then, the angular scattered intensity distribution can be calculated by analyzing the statistical properties of the recorded images. The particle size distribution can be retrieved from the angular scattered intensity distribution.

Both inversion problems are ill posed and regularization techniques need to be introduced in order to successfully solve them.

2. The dynamic technique

When monochromatic light is scattered by a medium with random fluctuations of the refractive index, a speckled field emerges, due to the random interference of the scattered elementary waves. In our case, the intensity fluctuations of the scattered light arise from the fact that the scattering particles are undergoing diffusive Brownian motion. The diffusion coefficient $D$ which characterizes the Brownian motion of a particle with radius $r$ in a fluid with viscosity coefficient $\eta$ has been extensively investigated [2] and can be approximated by the well known Einstein relation given by:

$$D = \frac{k_B T}{6\pi \eta r} \quad (1)$$

where we can see that $D$ is inversely proportional to the particle size. That is, the smaller the particles are, the faster their motion or diffusion.

If we place a detector in the far field, in a position forming an angle $\theta$ with respect to the incident direction, we can define the transferred wave vector $q = k_s - k_o$, where $k_o$ is the incident wave vector and $k_s$ is the scattered wave vector. As shown in Figure 1, in the case of elastic scattering ($|k_o| = |k_s|$), $q = 2k_o \sin(\theta/2)$.

**Figure 1.** Wave vectors involved in an event of elastic scattering. $k_o$ is the incident wave vector, $k_s$ is the scattered wave vector, $q$ is the transferred wave vector, $q_F$ is the Fourier vector and $\theta$ is the scattering angle.

The intensity fluctuations registered by the sensor can be characterized by the autocorrelation function (ACF) which quantifies the degree to which the intensity fluctuations remain correlated over time.

It is useful to normalize the intensity fluctuations registered by a single pixel over time $I(t)$ as:
\[ i(t) = \frac{I(t) - \langle I(t) \rangle}{\sqrt{\langle I(t)^2 \rangle - \langle I(t) \rangle^2}} \]  

(2)

Then, the normalized intensity autocorrelation function \( C_2(t) \) given by:

\[ C_2(t) = \langle i(0)i(t) \rangle \]

(3)

and the normalized electric field autocorrelation function \( C_1(t) \):

\[ C_1(t) = \frac{\langle E(0)E(t) \rangle}{\langle I(t) \rangle} \]

(4)

satisfy the following relation, as is shown in [2, 3]:

\[ C_2(t) = \beta |C_1(t)|^2 + \alpha \]

(5)

where \( \alpha \) and \( \beta \) are parameters that depend on the experimental set up. \( \beta \) is determined by the ratio between the size of the speckle grains and the pixel or detector size. In the optimal situation, when both are comparable, \( \beta \to 1 \). \( \alpha \) corresponds to the baseline of the intensity autocorrelation function and ideally \( \alpha \to 0 \). When non-zero, it may contain information about long-time fluctuations which are comparable to the total time of measurement, originated by instabilities in the system, presence of dust in the sample, etc.

In the case of a monodisperse sample of particles undergoing Brownian motion, the autocorrelation functions take the following form:

\[ C_1(t) = e^{-q^2D(r)t} \]

(6)

\[ C_2(t) = \beta e^{-2q^2D(r)t} + \alpha \]

(7)

In the case of a polidisperse sample of particles, with a size distribution given by \( n(r) \), the autocorrelation functions can be described by:

\[ C_1(t) = \int_0^\infty n(r)I_{MIE}(q,r)e^{-q^2D(r)t}dr \]

(8)

\[ C_2(t) = \beta \left( \int_0^\infty n(r)I_{MIE}(q,r)e^{-q^2D(r)t}dr \right)^2 + \alpha \]

(9)

where the factor \( I_{MIE}(q,r) \) stands for the solutions of the Mie scattering, and correspond to the mean scattered intensity in the far field for a particle of radius \( r \), collected with a transferred wave vector \( q \), or equivalently, in a direction \( \theta \). A complete derivation of these solutions can be found in the books of H. C. van de Hulst [4] and M. Kerker [5]. It is important to note that retrieving \( n(r) \) using the integral equation 8 is a linear problem.

The experimental set-up involved in this technique is presented in Figure 2. A thin flat sample cell is illuminated by an expanded and filtered He-Ne laser beam (\( \lambda = 632.8nm \)). The CCD camera is positioned in the far field, forming an angle \( \theta_o = 5.6^\circ \) with respect to the optical axis of the system.

The experimental procedure consists of registering highly correlated speckle images with the CCD camera during 45 seconds, with a frame rate of 20 fps and a resolution of 320 \( \times \) 240 pixels. For each pixel of the CCD sensor, we obtain a vector of intensities indexed by the sampled times \( I_t \), which can be normalized using eq. 2 to obtain \( i_t \).
The Brownian motion of the particles is a wide-sense stationary process, that is, these two conditions are met: \( \langle i(t) \rangle \) is independent of \( t \) and \( \langle i(t_1) i(t_2) \rangle \) depends only on the time difference \( \tau = t_2 - t_1 \). For this kind of processes, it has been shown that the power spectrum: \( S(\omega) = \left\langle \left| FT \{ i(t) \} \right|^2 \right\rangle \) and the intensity autocorrelation function \( C_2(t) \) form a Fourier transform pair, that is: \( S(\omega) = FT \{ C_2(t) \} \). This relationship is known as the Wiener-Khinchin theorem, and its full demonstration can be found in the book of J. Goodman [6]. By means of this theorem, we can calculate the autocorrelation function as: \( C_2(t) = FT^{-1} \left\{ \left\langle \left| FT \{ i(t) \} \right|^2 \right\rangle \right\} \).

In Figure 3 we show an experimental example of the registered intensity fluctuations and the mean intensity autocorrelation functions obtained.

In order to obtain the particle size distribution, we calculate \( C_1(t) \) by means of eq. 5 and we use the inversion algorithm known as Non-negative Least Squares (NNLSQ) proposed by Lawson and Hanson [7].

3. The static technique
Suppose we illuminate a scattering sample with an expanded beam and register the intensity distribution at an observation plane (OP) located at a close distance \( d \) from the sample cell, as schematically shown in Figure 4.
Given a low concentration of particles, the scattered field \( e_s(r, t) \) (which fluctuates over time) interferes with the transmitted field \( e_o(r) \) (constant in time), with:

\[
|e_s| \ll |e_o|
\]  

As a result, a fluctuating speckle pattern emerges in an observation plane close to the sample. Ferri et al. [1] show that there is a region close to the sample, denominated near field, in which the speckle grain size depends only on the size of the scatterers and not on the sample-detector distance \( d \) or the incident wavelength \( \lambda \). The condition of near field is related to the existence of a maximum dispersion angle at which particles scatter light, so the effective area of the sample that contributes to a single point on the observation plane (\( D^* \) in Fig. 3) is smaller than the total illuminated area of the sample (\( D \)), if the distance \( d \) is sufficiently small. This allows for a constant speckle grain size in a range of distances \( d \).

The experimental procedure consists of registering \( N \approx 30 \) independent speckle images with the CCD camera, usually taken with a temporal interval \( \Delta t = 5s \). The intensity distribution \( I(r, t) \) in a given image will be:

\[
I(r, t) = |e_o(r)|^2 + |e_s(r, t)|^2 + e_o^\ast(r)e_s(r, t) + e_o(r)e_s^\ast(r, t)
\]

Subtracting pairs of successive images \( I_1(r, t) \) and \( I_2(r, t+\Delta t) \), and using eq. 10 we obtain the interference terms:

\[
\delta I(r, t, \Delta t) = e_o(r)e_s^\ast(r, t+\Delta t) - e_o(r)e_s^\ast(r, t) + e_o^\ast(r)e_s(r, t+\Delta t) - e_o^\ast(r)e_s(r, t)
\]

Calculating the Fourier components (in 2 dimensions), expressed in capital letters, of the eq. 12 and applying the convolution theorem for \( e_o(r) \) a plane wave, we obtain:

\[
FT[\delta I(q_F, t, \Delta t)] = E_s^\ast(-q_F, t+\Delta t) - E_s^\ast(-q_F, t) + E_s(q_F, t+\Delta t) - E_s(q_F, t)
\]

where \( q_F \) is the Fourier vector associated to the spatial frequencies defined in Figure 1. Then, \n
\[
|FT[\delta I(q_F, t, \Delta t)]|^2 = |\alpha_1|^2 + |\alpha_2|^2 + \alpha_1^\ast\alpha_2 + \alpha_1\alpha_2^\ast
\]

where \( \alpha_1 = E_s^\ast(-q_F, t) + E_s(q_F, t) \) and \( \alpha_2 = E_s^\ast(-q_F, t+\Delta t) + E_s(q_F, t+\Delta t) \).

The mean value of the first two terms in 14 is the same and is directly related to the angular scattered intensity distribution. The last two terms contain information about the correlation between the images and their mean value vanishes when \( \Delta t \) is greater than the correlation time.
of the speckle pattern. The angular scattered intensity distribution \( I(\theta) \) can be finally obtained from:

\[
I(\theta) \approx \left| \langle FT[\delta I(\mathbf{q}_F, t, \Delta t)] \rangle_{t, \mathbf{q}_F} \right|^2
\]

(15)

where the mean value over \( \mathbf{q}_F \) requires averaging over the directions given by all azimuthal angles \( \phi \), as shown in Figure 5.d.

The angular scattered intensity distribution for a polidisperse sample of particles with a size distribution \( n(r) \), takes the form of a Fredholm equation of the first kind:

\[
I(\theta) = \int I_{MIE}(r, \theta) n(r)dr
\]

(16)

In order to retrieve \( n(r) \) from eq. 16, we used the modified Chahine algorithm proposed by F. Ferri et al. [8]. In Figure 5 we show an experimental example of the registered speckle patterns and the angular scattered intensity distribution obtained with this technique.

![Figure 5](image)

**Figure 5.** (a) Speckle pattern at time \( t \). (b) Speckle pattern at time \( t + \Delta t \). (c) Difference between speckle patterns (a) and (b). (d) Power spectrum of (c). (e) Angular scattered intensity distribution obtained by adding all pixels in concentric rings in (d).

4. Experimental results and comparison

In this section we present a summary of the results obtained with both techniques for monodisperse and polidisperse samples. In Figure 6 we show the results obtained with the dynamic technique and in Figure 7, the results obtained with the static technique are presented.
Figure 6. Summary of samples analyzed and results obtained with the dynamic technique. Each pair of bars corresponds to a different sample. In each pair, the bar in the left represents the composition of the sample prepared, and the bar in the right is the composition retrieved experimentally with the technique.

Figure 7. Summary of samples analyzed and results obtained with the static technique. Each pair of bars corresponds to a different sample. In each pair, the bar in the left represents the composition of the sample prepared, and the bar in the right is the composition retrieved experimentally with the technique.
We have shown that both techniques were successfully applied to the problem of micro-particle sizing. From the Figures 6 and 7, it becomes evident that the static technique is limited by diffraction when characterizing particles smaller than the wavelength. The dynamic technique is not affected by this phenomenon, being limited only by the maximum frame rate of the CCD sensor, which allows the characterization of particles down to approximately 0.02\(\mu m\).

In relation to the retrieved compositions of the samples prepared, in the case of the static technique, the uncertainties found in the relative concentrations of the components were lower than 10%. The dynamic technique presented relative uncertainties of approximately 15%.

One of the main advantages of the static technique is the short measurement times involved. It requires at most 100 seconds to obtain satisfactory results, that is, 20 images with an interval of 5 seconds. In contrast, the dynamic technique needs at least 15 minutes to reach a good experimental record, which corresponds to 20 independent measurements of 45 seconds each.

The static technique is a differential technique, which greatly relaxes the requirements on the optical/mechanical stability of the setup. Nevertheless, the use of a highly coherent light source is crucial, because it involves interference with optical path differences in the order of centimeters. It is not viable to implement the static technique with more affordable and portable light sources such as laser diodes. The dynamic technique is not affected by low coherence because it only depends on the activity of the speckle pattern, and not its spatial structure.

5. Conclusions
We have implemented and validated a dynamic and a static light scattering technique to characterize particle size distributions. We satisfactorily characterized monodisperse and polidisperse samples of latex particles in the radius range 0.22\(\mu m\) - 1.50\(\mu m\), with uncertainties lower than 0.06\(\mu m\) in sizes and lower than 15\% in concentrations.

The presented dynamic technique with CCD camera is advantageous with respect to the traditional DLS technique which uses a monolithic detector, because the statistical averaging provided by the CCD sensor allows the reduction of measurement times. Traditional DLS involves measurement times of approximately 1 hour, and the stability of the system is required during the whole procedure. On the other hand, the dynamic technique with CCD camera involves successive independent measurements of 45 seconds each, so the stability of the system is reduced drastically, and the total measurement time is reduced 4 times.

In relation to the performance of the static and dynamic techniques, we have found important advantages and limitations on both sides. It is worth noticing that, since the set-ups of both techniques are very similar (the detection lens is the only difference), it is not difficult to use both techniques complementarily to analyze the same sample.

Acknowledgments
This work was supported by CONICET, research grants UBACYT 2008-2010 I004 and 418, UBACYT 2010-2012 20020090100136 of the Universidad de Buenos Aires and research grant PICT2004 - 26037 of the Agencia Nacional de Promoción Científica y Tecnológica.

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