Investigation on the Possibility of Designing an Educational Dynamic Light Scattering Device for Sizing Particles Suspended in Air

Dan CHICEA  
Research Center for the Physics of Complex Systems, Lucian Blaga University of Sibiu, Dr. Ion Ratiu str., no. 5-7, Sibiu, 550012, ROMANIA  
dan.chicea@ulbsibiu.ro

Cristian LECA  
Research Center for the Physics of Complex Systems, Lucian Blaga University of Sibiu, Dr. Ion Ratiu str., no. 5-7, Sibiu, 550012, ROMANIA  
cristian.leca@continental-corporation.com

ABSTRACT

If a light beam meets a fluid that contains scattering centers randomly distributed in suspension, light is scattered by each of them. If the light source is coherent, the scattered waves will be also coherent, therefore they will interfere. The fluctuations of the far-field interference signal, once recorded and digitized, become a time series that can be later on analyzed to produce the average size of the suspended particles or the size distribution. The technique wears the name of Dynamic Light Scattering. We present the results of our investigation on the possibility of using an educational model, made of low-cost, conventional electronics, for recording the time signal of light scattered by particles suspended in the air as the carrier fluid. The device can be used in measuring the particle size in exhaust gases of conventional power plants or automobile engines.

Keywords: Dynamic Light Scattering (DLS), Particle sizing, Exhaust gas, Educational Model.

INTRODUCTION

When a light beam is targeted on particles suspended in a carrier solvent, each particle in the beam area scatters light, thus becoming a secondary light source. The particles act like scattering centers (hereafter SCs). If the incident light beam is coherent, so are the scattered waves, and, consequently, they will interfere. The consequence of the Brownian motion of the suspended particles that scatter light is the restless moving aspect of the interference field, having the aspect of “boiling speckles”. There have been published articles describing the variation of the moments of the digitized image, as the speckle contrast, average intensity and speckle with some parameters of the SCs as the diameter and the number per volume unit, and references (Piederriere & all, 2004a, Piederriere & all, 2004b, Chicea, 2007) are just some of them, but they are not optimal for particle sizing in dynamic processes where both the number of SCs and the SCs diameter can change in time (Chicea, 2007). The procedure that makes use of the dependence between the speckle dynamics and chaotic motion of the particles is called Dynamic Light Scattering (DLS) and the fundamental theory of the procedure is presented in many works, out of which we mention just a few (Clark & all, 1970, Goodman, 1984, Van de Hulst, 1981 and Xu, 2002).
DLS is widely used to analyze the size and dimension distributions of nano-particles, colloids, and proteins in the suspension of various solvents (Bhattacharjee, 2016). The DLS technique turned to be appealing (Stetefeld & all, 2016) as it has certain advantages over other experimental methods. The DLS technique can be used for investigating suspensions on a wide range of sample buffer, over a relatively big range of temperatures and of concentrations, as well. Moreover, DLS requires small amounts of sample. Above many other techniques, DLS has the advantage of providing absolute rather than relative results, therefore it does not require calibration.

The DLS technique has been established for quite some time (Clark & all, 1970). In the pioneering stage of DLS, photomultiplier tubes were the only choice for detectors, as they have a fast response with good amplification (Berne and Pecora, 2000). Later on, photomultiplier tubes were replaced with photo-diodes, which were replaced by the next stage in performance, which were the avalanche photo-diodes (Berne and Pecora, 2000). Better in performance were the P-I-N diodes, which replaced them (Berne and Pecora, 2000). Autocorrelator was the name of the hardware part used to compute the autocorrelation function of the DLS time series. As time passed Laser diodes proved that can replace the gas Lasers. A PC started to be used to record the DLS time series. It can also replace the autocorrelator in processing the DLS time series. All these technological improvements made possible a considerable simplification of the experimental setup, as can be found in many papers, (Chicea & all, 2012) and (Chicea, 2012) being just some of them.

This paper presents the results of the work carried on to investigate the possibility of performing DLS measurements on samples that have air as a carrier fluid, aiming to perform particle sizing in exhaust gases of industrial furnaces, as a power plant heating source, or the in exhaust gases of an automobile engine. Moreover, we investigated the possibility of designing an educational model of a DLS device, with low cost, conventional electronics, and a PC for both data acquisition and time series processing.

**THE DLS DATA PROCESSING PROCEDURE**

A schematic of a simple DLS setup is depicted in Fig. 1. The coherent light source can be either a He-Ne laser or a Laser diode. The wavelength is a typical 633 nm and the scattering angle $\theta$ is variable, as will be presented in the next section. The DLS experiment is intended to be carried on at 20 °C. The samples consist of particles with the size in the range $10 – 1510$ nm, suspended in the air. The cuvette-detector distance $D$ is assumed to be 0.1 m.

If we use a detector at angle $\theta$ and if we digitize the signal with a data acquisition system (DAS hereafter), we record a DLS time series. It consists of a set of values recorded in a digital format at equally spaced time intervals $\Delta t = \frac{1}{f}$, where $f$ is the DAS sampling rate. As stated in (Goodman, 1984, Tschurnuter, 2000 and Weiner, 1990) the width of the autocorrelation function of the time series is proportional to the diffusion coefficient. The diffusion coefficient is directly related to the SC diameter. An alternative version, which allows us to perform a straight analysis of the possibility of performing DLS on suspensions in air, is described below.
The pioneering works (Clark & all, 1970, Dubin & all, 1967) and the following theoretical refinement (Berne and Pecora, 2000, Goodman, 2000, Hect, 2001), revealed that the frequency spectrum of the intensity is related to the probability density function (hereafter PDF). The frequency spectrum is linked to the autocorrelation of a process, as stated by the Wiener-Khintchine-Theorem. The Fourier transform of the intensity time series is the power spectrum, or the intensity frequency spectrum, FS hereafter. The spectrum calculated from the experimental data can be described using the Lorentzian line $S(f)$ (1).

$$S(f) = a_0 \cdot \frac{a_1}{(2\pi f)^2 + a_1^2} \quad (1)$$

The Lorentzian line $S(f)$ has two parameters $a_0$ and $a_1$. The optimum values of the parameters can be determined using a least squares fit minimization procedure to match $S(f)$ to the frequency spectrum (Chicea & all, 2012 and Chicea, 2012) The radius can be calculated using equations (2) and (3):

$$R = \frac{2k_BT^2}{6\pi\eta a_1} \quad (2)$$

where:

$$K = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \quad (3)$$

In (2) and (3) $R$ is the average radius of the suspended particles, $\eta$ is the dynamic viscosity of the solvent, $k_B$ is Boltzmann's constant, $\theta$ is the scattering angle, $T$ is the suspension absolute temperature, $n$ is the refractive index of the solvent and $\lambda$ is the wavelength of the laser radiation (Chicea & all, 2012 and Chicea, 2012).

**THE DLS FOR SCATTERING CENTERS IN AIR AS SOLVENT**

Equation (1) with $a_1$ computed as in equation (2), with $K$ replaced from equation (3) can be used to predict the shape of the FS of the DLS time series of the scattered light from particles in a certain solvent, at a certain temperature and a particular scattering angle.

If SCs are suspended in water at 20°C, $n=1.33$ and $\eta=1.02*10^{-3}$ daP. If the solvent the particles are suspended into is air, $\eta=1.81*10^{-5}$ daP, which is two orders of magnitude smaller, and this affects the $a_1$ parameter for the same radius of the particles. By reverting the first part of equation (2) we notice that for the same radius R of the particles, $a_1$ is inversely proportional to $\eta$, therefore a decrease in $\eta$ will increase the $a_1$ parameter, therefore the turnover point in the plot of the frequency spectrum versus frequency, as in Figures starting with 2, will be shifted toward bigger frequencies. This feature requires higher data acquisition sampling rates $f$, therefore more expensive data acquisition systems, thus leaving the area of the intended device, which is a low cost using conventional rather than custom design electronics.

Firstly, a simulation of the frequency spectrum of a time series acquired using a sampling rate of 100 KHz was carried on, for diameters in the set: 10.00, 176.67, 343.33, 510.00, 676.67, 843.33, 1010.00, 1176.67, 1343.33, 1510.00 nm. The simulation for these diameters was carried on at each angle in this set: 10, 20, 30, 40, 50, 60, 70, 80, 90°. The typical angle for DLS scattering is 90° and the simulated frequency spectrum for the diameters in the set mentioned above, hereafter the diameter set, are illustrated in Figure 2.

Examining Figure 2 we notice that the turnover point in the lowest curve is not within the frequency range in the plot, therefore a least square fit will not identify $a_1$ in equation (1), hence the correct radius of the particles, but might work for bigger particles, like the second in the set, having a diameter of 176.67 nm.
Figure 2: The simulated FS for the set of diameters at a scattering angle of 90°. The lower curve is the FS for the lowest diameter, 10 nm, while the upper curve is for the biggest diameter, 1510 nm.

Figure 3 depicts the simulated frequency spectrum for the diameters in the diameter set for the same sampling of 100 KHz, recorded at a scattering angle of 50°. We notice that the turnover point in the lowest curve is at the edge of the frequency range in the plot, therefore the least square fit will not be precise in identifying a₁ in equation (1), hence the correct radius of the particles.

If we run the simulation for smaller scattering angles, like 50°, we get the lines in Figure 4, for the same sampling rate, of 100 KHz. Figure 4 suggests that DLS is possible in the air, for such relatively low sampling rates. Even so, low as they might appear, such sampling rates are not easy to be achieved with relatively low-cost electronics. We include in this category the audio class of preamplifiers and amplifiers, which have a reasonably lower cost as they are produced in very big numbers.

If we move to the class of low cost electronics, we have in mind sampling rates of up to 44 KHz. Moreover, we can imagine using the sound card of the PC or laptop, which is a low cost and good quality DAS. It turned to be so as it has been constantly been improved for decades and keeps a low price as it is produced in very big numbers and can be found in any desktop or laptop. The sound cards can record data with 16 bits resolution, with a certain caution, provided that there is no spectral attenuation from the detector to the input.

The simulations were run again for the diameters in the same set and for the same scattering angles, aiming to find the conditions where DLS FSs can be processed by fitting the Lorentzian line to them, but for a sampling rate of 44 KHz. The first choice would be to use the FSs for time series recorded at 90°, as the turnover points for different diameters are maximally distanced from each other, and this increases the precision in assessing the diameter. The plot of the FS versus frequency is not depicted in this paper, because it would simply present the curves in Figure 2, but for the frequency range 0 – 22 KHz, as the output of the fast Fourier algorithm is.
Figure 3: The simulated FS for the set of diameters at a scattering angle of 50°. The lower curve is the FS for the lowest diameter, 10 nm, while the upper curve is for the biggest diameter, 1510 nm.

Figure 4: The simulated FS for the set of diameters at a scattering angle of 10°. The lower curve is the FS for the lowest diameter, 10 nm, while the upper curve is for the biggest diameter, 1510 nm.

We notice that the conclusion is the same, which is that a least square fit will not identify $a_1$ in equation (1), hence the correct radius of the particles, but might work for bigger particles, like the
second in the set, having a diameter of 176.67 nm. But particles of such a big diameter can hardly be considered to be nanoparticles. The purpose of this simulations, as stated in the introduction section, is to investigate the possibility to detect nanoparticles in air, therefore recording time series at 90° with such a small sampling rate cannot work.

The plots were computed and examined for different angles, starting from 1°, and we can conclude that the time series recorded at 10° can possibly be processed by fitting the Lorentzian line to the computed FS and finding a1 and here from the diameter of the particles. Figure 5 depicts the simulated frequency spectrum for the diameters in the diameter set for the sampling rate of 44 KHz, recorded at a scattering angle of 10°.

**Figure 5:** The simulated FS for the set of diameters at a scattering angle of 10°. The lower curve is the FS for the lowest diameter, 10 nm, while the upper curve is for the biggest diameter, 1510 nm. The sampling rate was 44 KHz.

**CONCLUSIONS**

This manuscript presents briefly the DLS technique, with a very simple, educational experimental setup and one of the procedures that are currently used in processing the DLS time series, which consists of computing the FS and fitting an analytical function to it. The parameters determined from the fit are directly linked to the average diameter of the particle suspended in the solvent.

We performed a computer simulation of the FS produced by particles which have air as the solvent, which is a modeling of the particles in the exhaust gases of a power plant or of a Diesel or Otto engine. We maintained the goal of keeping the experimental setup at the educational level, with using a low-cost DAS, even the sound card of the PC or laptop and a low-cost audio preamplifier. For this purpose, we investigated the possibility of using a sampling rate of 44 KHz, which is the upper limit of the sampling range for a conventional PC sound card.

The results of the computer simulation reveal that theoretically, DLS in the air as the solvent is possible for particles with the size in the range of 10 – 1500 nm, with a sampling rate as low as 44 KHz, if the recording is carried on at low scattering angles, as 10°. There does remain an
experimental problem to be addressed, which is related to the minimum intensity that can be detected with a reasonably good signal to noise ratio. It is related firstly to the decreasing of the scattered light intensity with the scattering angle, as described in the Monte Carlo simulation reported in (Chicea & Turcu, 2007 and Chicea, 2008). The minimum intensity required for a precise output of the procedure is also related to the design of the preamplifier, but this is experimental work on this subject, in progress for the time being.

As the title of the paper suggests, this paper presents not the device but the results of the theoretical investigation on the possibility of designing and using a low cost, educational model for performing particle sizing in air. The theoretical investigations narrowed the range of the setup parameters to the region where DLS is possible in air, as pointed out above. Moreover, the model is educational, primarily because it can be assembled from low cost parts during a laboratory session by students. The setup parameters can be easily modified by desire and the parameters of the data acquisition can be adjusted to any values. The length of the time series can be decided according to the desired precision. Writing a simple code for processing the time series, as explained in this manuscript, by fitting an analytical function to the power spectrum, is again one of the goals to be achieved by students during a laboratory session and these steps will help them understand in detail the DLS technique.

With these particularities in mind, we can conclude that the model we propose can be functional and can be used for teaching students the DLS technique during one or more laboratory sessions at the master and doctoral levels.

ACKNOWLEDGMENT

The work presented here was partially supported by the ULBS internal research grants LBUS-IRG-2017-03 and LBUS-IRG-2018-04.

REFERENCES

Bhattacharjee, S. (2016). DLS and zeta potential – What they are and what they are not?, Journal of Controlled Release, 235, 337–351.

Berne B.J. & Pecora R. (2000). Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics, Mineola, Dover Publications.

Chicea D. (2007). Speckle size, intensity and contrast measurement application in micron-size particle concentration assessment, European Physical Journal Applied Physics, 40, 305-310, doi: 10.1051/epjap:2007163

Chicea, D. & Turcu, I. (2007). RWMCS - An alternative random walk Monte Carlo code to simulate light scattering in biological suspensions, OPTIK, 118(5), 232-236.

Chicea D. (2008). Coherent light scattering on nanofluids: computer simulation results, Applied Optics, 47(10), 1434-1442.

Chicea D. (2012) A Study of Nanoparticle Aggregation by Coherent Light Scattering, Current Nanoscience 8(2), 259-265.

Chicea D., Indrea E. & Cretu C.M. (2012). Assessing Fe3O4 nanoparticle size by DLS, XRD and AFM, Journal of Optoelectronics and Advanced Materials, 14(5-6), 460-466.
Clark N.A., Lunacek J.H. & Benedek G.B. (1970). A study of Brownian motion using light scattering, *American Journal of Physics*, 38(5), 575-585.

Dubin S.B., Lunacek J.H. & Benedek G.B. (1967). Observation of the spectrum of light scattered by solutions of biological macromolecules, *Proceedings of the National Academy of Sciences*, 57(5), 1164-1171, [https://doi.org/10.1073/pnas.57.5.1164](https://doi.org/10.1073/pnas.57.5.1164).

Goodman J.W. (1984). *Laser speckle and related phenomena*, J.C. Dainty, (Ed.), Berlin, Heidelberg, New York, Tokyo, Springer-Verlag.

Goodman J.W. (2000). *Statistical Optics*, Wiley Classics Library Edition, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, John Wiley & Sons, Inc.

Hecht E. (2001). *Optics*, New York, Addison-Wesley.

Piederriere Y., Cariou J., Guern Y, Le Jeune B., Le Brun G. & Lotrian J. (2004). Scattering through fluids: speckle size measurement and Monte Carlo simulations close to and into the multiple scattering, *Optics Express* 12, 176-188.

Piederriere Y., Le Meur J., Cariou J., Abgrall J.F. & Blouch M.T. (2004). Particle aggregation monitoring by speckle size measurement; application to blood platelets aggregation, *Optics Express*, 12, 4596-4601.

Stetefeld, J., McKenna, S.A. & Patel, T.R. (2016). Dynamic light scattering: a practical guide and applications in biomedical sciences, *Biophysical Reviews*, 8, 409–427.

Tscharnuter W. (2000). Photon Correlation Spectroscopy in Particle Sizing, in *Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), Chichester, John Wiley & Sons Ltd, 5469-5485.

Van de Hulst H.C. (1981). *Light Scattering by Small Particles*, New York, Dover Publications.

Weiner, B.B. (1996). Chapter 5: Particle sizing using ensemble averaging techniques, in: *Liquid-and Surface-Borne Particle Measurement Handbook*, J.Z. Knapp, T.A. Barber and A. Liebermann (Eds.), New York, 55–172, Marcel Dekker Inc.

Xu R. (2002). *Particle Characterization: Light Scattering Methods*, New York, Boston, Dordrecht, London, Moscow, Kluwer Academic Publishers.