

**SIMULATION MODELS FOR AEROSOL  
CHARACTERIZATION BY ELASTIC LIGHT  
SCATTERING WITH SPECIAL EMPHASIS ON PHOTON  
CORRELATION EXPERIMENTS IN THE NANO-  
PARTICLE SIZE RANGE**

**The summary of Ph.D. dissertation**

LÉNÁRD VÁMOS

SUPERVISOR: Dr. PÉTER JANI

Research Institute of Solid State Physics and Optics of HAS  
Budapest  
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## Introduction

*The subject of aerosols<sup>1</sup> goes back to many years and enters into many aspects of science and technology. Optics, heat transfer, biology, meteorology and pollution are just a few areas where the behavior of small particles suspended in gas is of vital importance. Aerosol particles can be characterized by their size, composition, shape, mass, density, charge, color, number, gas/particle phase equilibrium etc. No technology exists to measure every aspect of these properties simultaneously. Depending on the application of interest, a number of techniques can be used to analyze and characterize the particles. The elastic light scattering measurements and the theoretical interpretation of such data yield precise determination of size, refractive index, shape, orientation or concentration, for example. Very often the optical methods are the only way to study aerosol properties (astronomic observation, solar photometry, satellite remote sensing, real-time non intrusive flow or combustion analysis etc.).*

*Particle characterization techniques based on light scattering also have a wide family; each of them is specialized for some measurement parameters beside different circumstances. However the expanding research fields of the aerosol science requires further developments of the applied techniques (real time techniques for environmental/process monitoring, analysis of biological and chemical reactions, refinement in sensing for nanoparticle characterization).*

*Exotic mechanical, optical, biochemical and catalytic properties make nanoparticles (particles smaller than 100 nanometers) of special interest. Novel experimental and theoretical methods are under development and/or needed to characterize their formation and behavior. Nanoparticle aerosols play an important role in the environment, in global climate, in human health (especially occupational health), in materials processing (semiconductor industry), in military and homeland security and certainly in nanotechnology. The widening application fields require high precision characterization beside the particle generation.*

*On the other hand the reduction in size of modern electromechanical systems – from micro (MEMS) to nano (NEMS) – brings with it decreasing dimensions to be tested and characterized. Thus, the sensitivity requirements of the testing device and methodology are increased. The direct measurement capability that interferometric techniques offer also makes this*

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<sup>1</sup> In general the systems constituted by microscopic solid or liquid particles dispersed in gaseous phase are known **aerosol**. Examples are smoke, oceanic haze, fog, air pollution, smog and CS gas.

Outlines in conference proceedings:

- OUTL.1. Jani P, Vámos L, *Improved algorithm for the particle size measurement in photon correlation measurements*; In: *Proceedings of the European Aerosol Conference EAC2005 (Ghent, Belgium, 28 Aug.-2 Sept., 2005)*; Ed.: W. Maenhaut, 83, 2005
- OUTL.2. Jani P, Vámos L, *Scattering properties of coated nanoparticles compared to water droplets*, 7th International Aerosol Conference IAC2006 (St. Paul, Minnesota, USA, 10-15 Sept., 2006, 490p.)
- OUTL.3. Vámos L, Jani P, *Wavelength and refractive index independent number concentration determination algorithm for ensemble of aerosol particles*, European Aerosol Conference EAC 2007, Salzburg, Austria, 9-14. Sept. 2007, T02A043

Other publications:

- OUTL.4. Jani P, Vámos L, *Accuracy of light propagation direction measurement by scattered intensities*; *Journal of Aerosol Sciences*; 35, 273-275, 2004
- OUTL.5. Vámos L, Jani P, *Monitoring of growth of cloud droplets ensembles with soot and salt condensation nuclei*, European Aerosol Conference EAC 2009, Karlsruhe, Germany, 6-11. Sept. 2009, T091A30

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- [Koukoulas et al. 2008] Koukoulas T., Theobald P.D., *Optical Interferometry Measures the Deflection of Carbon-Based Nanosensors*, EUROPhotonics, June 2008
- [Naqwi Amir A. 1996] Naqwi Amir A, Menon Rajan, Fingerson Leroy M, *An adaptive phase/Doppler system and its applications including particle sizing in submicron and nanometer ranges* *Experiments in Fluids*. Vol. 20, no. 5, pp. 328-334. Mar. 1996
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- [Vámos L., 2003] Vámos L., *Nanorészecskék méretének és sebességének szimultán meghatározása rugalmas fényszórás módszerével*, BME, 2003

Laser Doppler anemometry/velocimetry (LDA/LDV) offers a non-intrusive in-situ single particle characterization solution among the several particle characterization methods, that's why it is commonly used both in scientific and industrial environments, especially in extreme conditions. Such are for instance combustion research, wave dynamics, coastal engineering, tidal modeling, river hydrology, experimental verification of CFD models, wind tunnels etc. Although the standard LDA was developed to flow velocimetry, the particle size measurement was also solved by further construction in phase Doppler anemometry (PDA) with lower size measurement limit commonly acknowledged to be 500nm.

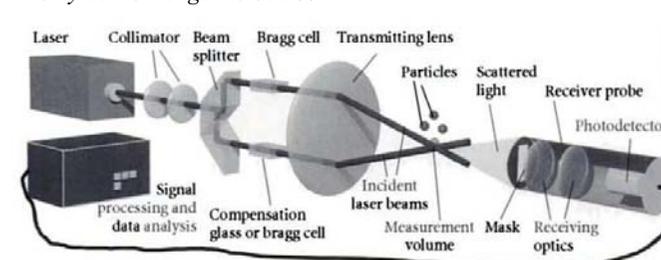


Fig. 1. Dual-beam laser Doppler anemometer ©H.E. Albrecht et al. 2002

The sizing of nanoparticles by LDA is a challenging task. Although the theoretical possibility of sizing 20nm metal particles by a modified planar PDA was shown in [Naqwi Amir A. 1996], the realization of the advised method is reduced by the particle damage threshold at high intensities. Several other methods exist for more or less similar optical arrangements like LDA using analog detector signal (time-shift technique, rainbow refractometry and shadow Doppler technique, techniques based on signal amplitude or visibility measurements) but none of them can be applied below 500nm. From the light scattering non-intrusive techniques the photon correlation and reference beam method can be used for nanoparticles. Another sensitive technique is the low angle laser light scattering, which measures the particle size distribution from 20nm. (Mastersizer of MALVERN) using several detectors. However this technique is specialized for particle ensembles, consequently information on single particle size and velocity is not obtained.

Particle sizing sensitivity can be influenced by the illumination beam power and detection sensitivity. The upper limit of the illumination beam power is determined by the breakdown threshold of the aerosol. However the really high detection sensitivity can be reached by photon counting mode. It requires a special data acquisition and photon correlation processing method [Cummins and Pike, 1976]. Parallel to the clipped and scaled photon correlators Chopra and Mandel [Chopra and Mandel, 1973]

developed an autocorrelation computing process for low count rates eliminating the unnecessary computing with zeros following from lap tag multiplication and summation in. By this way the computing process become faster and applicable for real time measurements. In earlier works of P. Jani [P. Jani et al. 1998] the cumulated autocorrelation function (ACF) were generated by the same way down to 300nm particle sizes. However the progress in the semiconductor devices during the years and also in the quantum efficiency and maximum count rate of the avalanche photon counting detectors (APD) opened the way to the nanometer size range down to ca. 50nm particle size according to our previous approximation [REF.3.]. In my diploma work [Vámos L., 2003] a refined method was developed for the so called R parameter method of particle sizing. This method bases on the monotonic increase of the detected signal visibility with the particle size in a given range. The above method works also in the nanometer size range, as it is shown in this thesis, the dominant physical effect is not the change of the visibility but the high rapid increase of the scattering intensity and the saturation of the detectors with the size.

## Research Objectives

The central theme of this thesis is the real-time characterization of aerosols especially in the submicron/nanometer size range (below 500nm) which is extremely required for both the research area and the industry. The dual-beam LDA working in photon correlation mode can detect the nanoparticles, but the size measurement has been unsolved yet. The main purpose of my work is to develop a robust sizing method for LDA systems especially in the nanoparticle size range. The previously developed sizing method for visibility is studied and compared by simulations to scattered intensity measurements in case of nanoparticles. The scattered intensity is found to be a more robust and sensitive technique. To reduce the calibration cost and increase the accuracy a model-based signal processing method was developed for the particle sizing.

Although the standard signal processing methods for photon correlation LDA build up the cumulative autocorrelation function from several particles transits and result the mean velocity, only 100 photons are enough for velocity measurements better than 1%. It is not possible to gather such an amount of counts from a single particle transit (burst) and using the system in single operation mode.

Following an introduction the second chapter gives the theoretical and computational background for the elastic light scattering according to the Mie theory. However beyond the discussion of the grounds this part consist of two thesis points connecting to the ambiguities in sizing of coated

## Publications

Referred papers:

- REF.1. Jani P, Vámos L, Photon correlation experiments for simultaneous velocity and size measurement of submicron particles; APH B) *Quantum Electronics*, 20, 177-184, 2004 imp. fact.: 1.397  
 REF.2. Jani P, Vámos L, Nemes T, Timing resolution (FWHM) of some photon counting detectors and electronic circuitry, *Meas. Sci. Technol.* 18 155-60 2007 doi:10.1088/0957-0233/18/1/019, imp. fact: 1.493  
 REF.3. Vámos L, Jani P, Nanoparticle sizing algorithm for photon correlation LDA, *Optical Engineering*, 49, 1, 2010, imp. fact: 0.722

Papers in conference proceedings:

- PROC.1. Vámos L, Jani P, Simulation of LDA and PDA measuring techniques in the nanometer particle size range, In: *Proc. SPIE Int. Soc. Opt. Eng.* 5948, 59481Q (2005), (9 pages)  
 PROC.2. Vámos L, Jani P, Optimization algorithm of LDA signal processing for nanoparticles, In: *Proc. SPIE Int. Soc. Opt. Eng.* 6293, 629303 (2006), (8 pages)  
 PROC.3. Vámos L, Jani P, Törésmutató és hullámhossz független részecskeszám meghatározási algoritmus, *Magyar Aeroszol Konferencia, Siófok-Szabadifürdő*, 57-58, 2006. 05. 25-26.  
 PROC.4. Vámos L, Jani P, Lee filtered burst selecting in the photon correlation LDA signal processing, In: *Proc. SPIE Int. Soc. Opt. Eng.* 7003A-41 (2008), (8 pages)  
 PROC.5. Vámos L, Jani P, Dynamic range of submicron/nanoparticle sizing with photon correlation LDA, In: *Proc. SPIE* 7355, 73550P (2009), (12 pages)  
 PROC.6. Vámos L, Jani P, Só és korom kondenzációs maggal rendelkező felhőcsepp sokaság képződésének monitorozása, *Magyar Aeroszol Konferencia, Balatonfüred*, 48-49, 2009.04.27-28.  
 PROC.7. Vámos L, Jani P, Scattering properties of water coated carbon nanoparticles, In: *Proc. 18th International Conference, Nucleation and Atmospheric Aerosols*, P1.53, pp. 828-831, 2009.08.10-14., Prague

6. I have developed a complex particle characterization method for dual-beam photon correlation LDA system with simultaneous number counting, burst selecting, velocity measurement and sizing. By adapting the methods of the TCSPC technique for burst selecting the method gives opportunity to detect individual particles even from 5 photons at high SNR levels, when the detected bursts originate from real particle transits. The individual velocities can be estimated with  $\pm 10\%$  uncertainty at 70% confidence level already from 20 photons. Ensemble and single particle sizing methods were developed and studied by mono- and polydisperse ensembles. For low photon rates (below 20 photons) and low SNR levels (down to 2dB/burst) the background compensated burst size analysis was the most robust technique. [PROC.4.]

## Applications

By this way the developed simulation software package provide an effective tool for nanoparticle sizing by the dual-beam photon correlation LDA technique. The development of such a single particle counter for non-invasive simultaneous size and velocity measurement in the particle range is supported by a grant from the Central Hungary Operational Programme (project number: KMOP-1.1.1-07/1-2008-0056, short name: NANO-LDA). The first prototype is planned to be constructed until 2011. The fields of applications range from optimizing nanoparticle synthesis with high spatial and temporal resolution over the controlled formation of nanostructured films by nanoparticle deposition to contamination control in low pressure CVD processes and to work place exposure studies. In the nanoparticle production and processing area several high-ranking companies (such as Degussa AG, Heraeus Quartz Glass company) show interest in the NANO-LDA project.

In general, gas phase synthesis and handling of nanoparticles is indicated when extremely high purities are required such as in the production of optical fibers (impurity levels of ppb) or in a fabrication of components for nanoelectronics. The proposed measuring technique will contribute to substantial reduction of deficient products by the on-line monitoring of the contamination level during the production process.

nanospheres and particle concentration measurements of monodisperse ensembles.

The fundamentals of the LDA technique appear in Appendix 3. It has been previously studied in detail and it does not constitute a part of my research but it is required for the understanding. Then the signal processing of the photon-correlation LDA system is shown and a short summary is given about the sizing techniques based on LDA systems.

In the third chapter the complete simulation model of a dual beam planar photon correlation LDA system is described based on Appendix 3., including models for laminar flow, elastic light scattering, single particle detection, photon detection and noise effects.

In the fourth chapter my developments and results are shown about nanoparticle sizing with photon-correlation dual-beam LDA. Firstly the problem of burst finding is discussed. Then a model-based optimization method is proposed for submicron/nanometer particle sizing based on scattered intensity. A detailed error discussion is given about the sizing method and the burst selecting further techniques are proposed to reduce the trajectory error. A calibration measurement is shown by the present optical setup in RISSPO and the lower size limit of the particle detecting and sizing is estimated. Finally a discussion of the complete signal processing (burst selecting, velocimetry and single particle sizing) is given for monodisperse and polydisperse ensembles using the simulation results.

## Methodology

The general theory of elastic light scattering for homogenous spheres developed by Mie and others gives an infinite series for the field vectors and so this research field is a typical example of the computational physics.

Another main reason for resorting to simulated data is because the exact statistics of the input data are known, hence the bias and variance of the size estimator being investigated can be determined exactly. Data simulation is therefore essential for development of algorithms. Furthermore the sizing estimator uses the whole simulation of the particulate LDA system.

Among the several numerical approaches the Lorenz-Mie theory was used for the problem of homogenous spheres, single layered spheres and cylinders. Certainly the complete simulation of the photon correlation LDA system requires several other numerical methods. Simpson's formula was used in the integration of the scattered intensity over the detector surface. The stochastic processes (such as photon detection, particle detection, noise effects) were generated by Monte Carlo method using the theoretical probability density functions (PSD). The burst finding process including the Lee-filter was adapted from the Time Correlated Single Photon Counting

(TCSPC) technique and developed to the particulate requirements of the photon-correlation LDA. As a detector calibration an accurate new method was proposed and applied for timing jitter measurements of single photon counting detectors. Estimations for the velocity were given by the custom direct way using the first peak of the power spectral density function (PSD), which was generated from the autocorrelation function of the detected signal (time series of the photon count signals) by Fourier transform (FFT). Maximum search algorithm was used to get the velocity from the Doppler frequency after a parabolic interpolation for the first peak.

An iterative parametric method was developed for the sizing in which a zero searching algorithm and the least square method were combined to get a robust method for low photon rates i.e. low SNR.

## New scientific results

1. In the study of unpolarized visible elastic light scattering by Mie computation on water ( $n=1.33$ ) coated carbon ( $n=1.95+i0.66$ ) spheres in the size range below 600nm. I have shown the decreasing impact of the core on the scattering properties (scattering cross sections and amplitude of the forward scattering lobe) when the layer thickness becomes larger than the core radius. However below 200nm core size the scattered intensity ratio of the coated particle to the pure water particle with the same size in a particulate direction has a one order of magnitude dynamic range with a monotonic, sharp decrease depending very weakly on the core size until the layer thickness grows up to the core radius. Hence I have demonstrated that the relative scattered intensity measurements on one-layered single particles of known size or their monodisperse ensemble make possible the rough estimation (within 10% uncertainty) of the layer thickness smaller than the core radius. [OUTL.2.][PROC.6.]

2. I have shown for monodisperse ensemble that the average of the scattered intensity relative to its standard deviation for a quasi-static particle ensemble illuminated by an incident pulse train is equal to the square root of the particle number in the measurement volume. As an application a simple and robust measurement method of the particle number concentration was proposed for monodisperse ensembles. I have studied the validity of the wavelength and refractive index independence of the method by numerical computations for non-absorbing (water) ensembles with different log-normal distributions and shown that the practical limit chosen for monodispersity (i.e.  $\delta < 5\%$ ) is coincident with the validity criterion. [PROC.3.][PROC.6.][OUTL.3.]

3. I have proposed an improved measurement scheme for the timing resolution of some commercially available photon detecting and counting APD-s. The statistics of the time intervals corresponding to time of flight through passive media was recorded while the effect of the timing jitter of the laser source and detector electronics was avoided. Consequences of intrinsic photon arrival time ambiguity are taken into account. This improved scheme leads to better timing resolutions than claimed by the manufacturers. In one exemplary case the mean value is 31.2 ps instead of 40 ps. [REF.2.]
4. I have developed a simulation model for planar PDA and LDA systems and studied the particle sizing methods below 0.5 $\mu$ m particle diameter, where the planar PDA technique was found to be useless. In signal processing of the photon correlation dual beam LDA I have shown that the size dependence of the R parameter in the submicron range is dominated by the high power increase of the scattering amplitude for visible wavelengths and the simultaneous decrease of the modulation depth of the detected signal instead of the visibility changes in the scattered intensity. As a consequence it was established that the scattered intensity has more than one magnitude wider dynamic range than the R parameter (up to 600nm) [REF.1.][PROC.1.][OUTL.1.]
5. I have developed a model-based optimization process for single particle sizing by dual-beam photon correlation LDA from low photon rates (down to ca. 20 counts/burst) in the submicron/nanometer range below 600nm. To construct a robust algorithm an iterative parametric method in the correlation domain combines a L1 norm based on zero search algorithm and a L2 norm based on minimum search algorithm (LSQM). A calibration measurement was presented to estimate the system parameter (intensity scale factor) of the particular laboratory LDA system. As a numerical example it was shown that the experimental system used in our laboratory requires  $1.23 \cdot 10^5$  W/cm<sup>2</sup> power density of the illumination laser at 350nm wavelength for detecting 20 photons from a single 50nm polystyrene latex particle passing through the measurement volume with 5m/s. The corresponding 95% confidence interval ranges from 42.9nm to 58.1nm for axial transits. [REF.3.][PROC.2.][PROC.5.]