Universitatea "Lucian Blaga" din Sibiu

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DESIGNING A DEVICE FOR MEASURING THE SIZE OF PARTICLES IN GAS USING DYNAMIC LIGHT SCATTERING

- Abstract -

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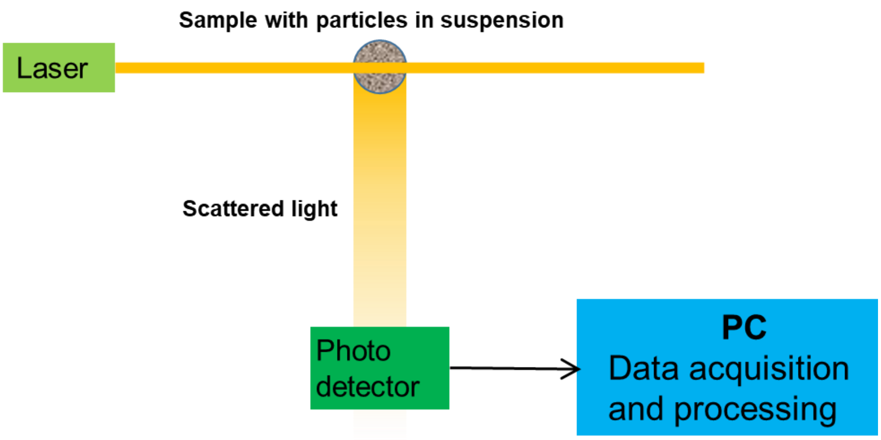
1. Short description of Dynamic Light Scattering

The idea of Dynamic Light Scattering, in short DLS, is one century old, but the available technology in that time did not allow a practical device. The equipment for DLS includes an intense monochromatic light source and a computer for complex data analyze. After 1965 lasers and computers became available and the first DLS experiments were possible.

Until now, DLS was applied exclusively to liquid samples with particles in suspension. The purpose of this work is to prove the possibility of DLS in air and to describe the experimental device for DLS in air realized by the author.

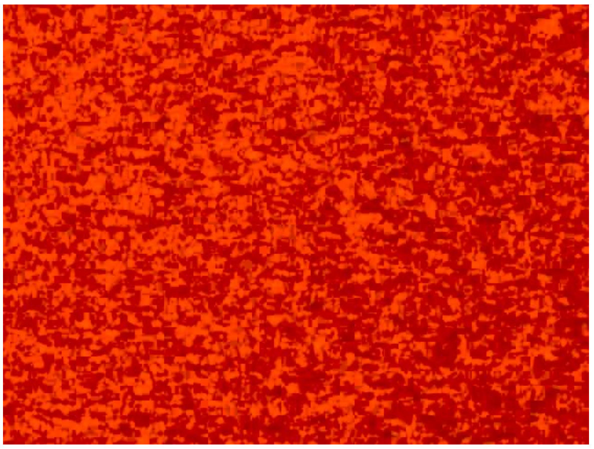
In the first chapters, a very simplified and intuitive description of classical DLS method is presented. A few important equations are included. Only the most important physical issues are explained which are necessary for a basic understanding of DLS. A detailed analyze and description of DLS is in the complete thesis.

Any experimental device for DLS must have a monochromatic light source, a sample with particles in suspension, a photodetector, an amplifier, a data acquisition system and a computer for data processing.



The monochromatic light from laser is scattered by particles. Light from all illuminated particles arrives at photodetector. The intensity of light in each point, including on photodetector, is the sum of the intensity from all particles. The light from each particle has a certain phase depending on the travelled distance and the position of particle. Therefore, the resulting phase on photodetector has a value between 0 and π depending on the position of particles. An interference image is created on photodetector (and in any other point).

The distribution of light on the area near detector is like this:



Picture taken with a TTL camera without lens.

Speckles are directly on the CCD image sensor 23mm wide.

Red-orange light is from a He-Ne laser.

Bright spots are for constructive interference, dark spots are for destructive interference.

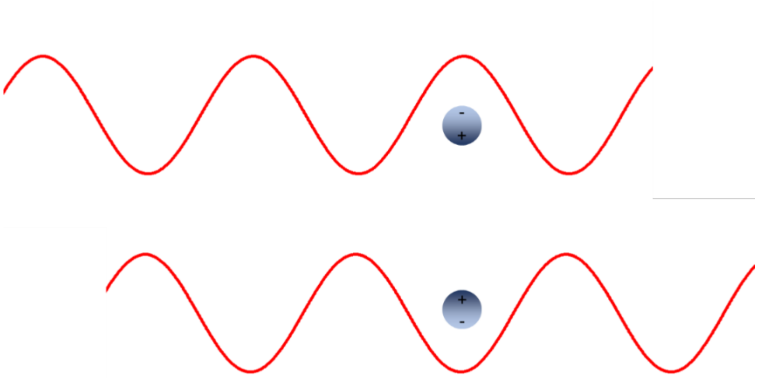
Speckles is the established term in Light Scattering for these spots on image.

The particles scattering the light are moving continuously due to thermal agitation (Brownian motion) mainly. As a result, the distance from particles to detector is changing continuously and the phase is changing as well. Therefore, the phase is time dependent. The change of phase $\varphi(t)$ is random. The instantaneous intensity of light on detector is as random as the Brownian motion itself. Therefore, one instantaneous value of the light intensity gives no information about scattering process or about particles. A large amount of data must be collected from the photodetector and processed by a computer to get the desired information about particles.

Basically, the Brownian motion of particles suspended in a liquid is slower if they are large and is faster if they are small. The motion of speckles is alike and, consequently, the signal generated by photodetector has high frequency for small particles and lower frequency for large particles. The frequency of the signal from photodetector is processed and analyzed by a computer and the size of particles is calculated.

2. Light Scattering on Particles

The electric field in light interacts with the particle. The oscillation of electric field is perpendicular on the direction of propagation and has the frequency ν. The electric field of the light moves the charges in the particle and creates a dipole. The charges move with the same frequency ν as the electric field of light. If the particle is small compared to the wavelength, then the electric field is quasi homogenous in the particle. The assembly of charges in the particle will move simultaneously and synchronously with the electric field of light. The particle becomes an oscillating dipole, as can be seen in the picture.



The Dipole Momentum μ is:

$$\mu = \alpha E = \alpha E_0 \cos(2\pi\nu t - kx) = \mu_0 \cos(2\pi\nu t - kx)$$

$$(\mu_0 = \alpha E_0)$$

The movement is sinusoidal and an electromagnetic field is generated by the moving particles. Scattered light has the same wavelength as the incoming light.

This kind of scattering, on particles much smaller than the wavelength, is called Rayleigh scattering and is characterized by being isotropic; it is equally intense in all directions relative to the direction of the incoming light (it is independent of the scattering angle θ).

A large particle, with size comparable to the wavelength, has a different behavior. The constituent parts of a large particle scatter light with different phase. The resulting intensity in one direction is the interference of light waves scattered by each constituent part. The resulting intensity in one direction depends on the size and the shape of particle and is quite complex. In general, the highest intensity is for low scattering angle and the intensity decreases when the angle increases.

The total scattered light from a large particle is anisotropic and is a function of the scattering angle θ. This function, named the **Form Factor**, has the obvious definition:

$$P(\theta) = \frac{I_s(q)}{I_s(0)}$$

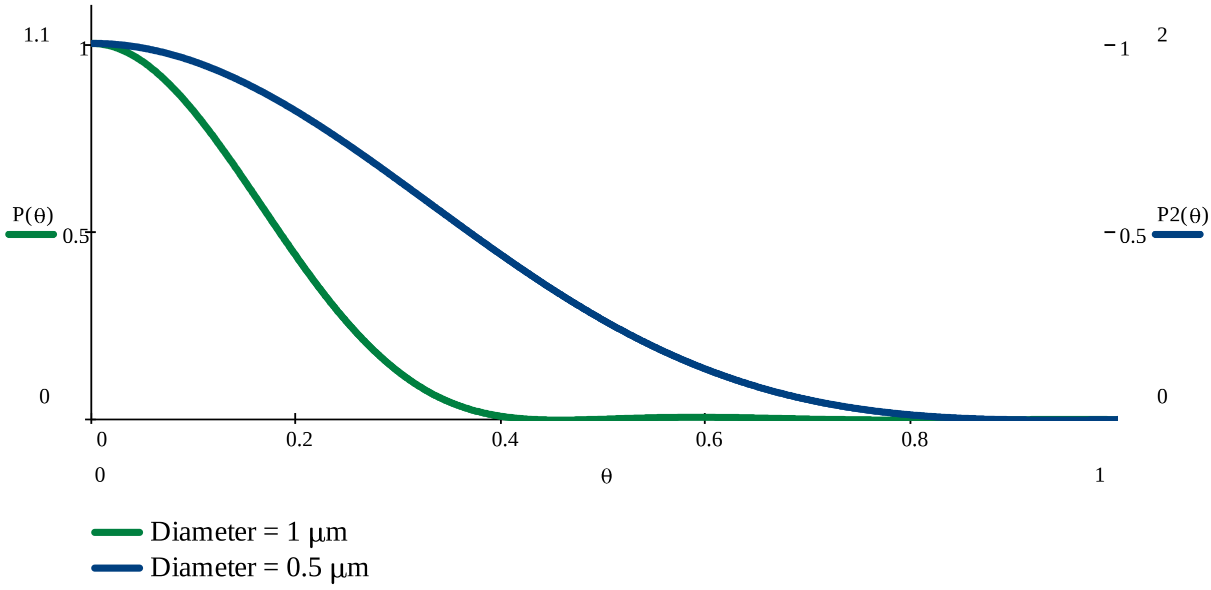
$I_s(q)$ is the scattered light in the direction given by the scattering vector q and $I_s(0)$ is the scattered light in the forward direction for $\theta = 0$. The Form Factor depends on a few parameters and is difficult to be calculated for a general case. The particular case of a large, spherical, homogenous particle was calculated:

$$P(q) = \left(\frac{3 \cdot (\sin(qR) - qRcos(qR))}{q^3R^3}\right)^2$$

The scattering vector q is defined as the change of direction of scattered light:

$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$$

A graph of the Form Factor is created in Mathcad for λ=633nm (HeNe laser) and for particles of 500nm and 1000nm.



The form factor is very important in Static Light Scattering. In SLS the size of particles is calculated from the experimental measurement of form factor.

Form factor is not directly involved in Dynamic Light Scattering. But the relation between light intensity and scattered angle is very important when the experimental device is designed.

3. Analyze of the motion of particles

The principle of DLS is quite simple. Particles suspended in a fluid have a Brownian motion. The motion depends on several parameters: viscosity of fluid, temperature and, very important, the size of particles. Obviously, the larger the particles the slower the motion. DLS is an optical method to acquire information about the speed of suspended particles and, after a quite complex analyze, to get the size of particles. The viscosity must be known to calculate the size, or the viscosity can be calculated if the size is known.

The viscosity η and the radius R of a spherical particle are related in the Stokes equation:

$$F = 6\pi\eta R v$$

F is the friction force, η is the viscosity, R is the radius of particle and v is the velocity.

Stokes-Einstein equation for diffusion coefficient is:

$$D = \frac{k_B T}{6\pi\eta R}$$

D is the diffusion coefficient, k_B is Boltzmann's constant and T is the temperature in K.

The main purpose of DLS is to determine the diffusion coefficient. Then the radius of particles in suspension can be calculated, knowing the viscosity:

$$R_h = \frac{k_B T}{6\pi\eta D}$$

R_h is the hydrodynamic radius, meaning the radius obtained from viscosity and diffusion. The hydrodynamic radius R_h is the real radius of the particle for a spherical shape. If the particle is not spherical, the friction force is the same as for a spherical particle with an equivalent hydrodynamic radius R_h.

The constituent particles of a fluid, the molecules, have a continuous, random motion called Thermal motion. The large number of collisions and particles with different velocities are involved in a macroscopic system. Because this large number, the precise move of each particle can not be predicted or calculated. But the macroscopic parameters can be predicted and calculated with high accuracy. It is the physical statistics which calculates the macroscopic parameters based on the microscopic parameters of particles.

DLS analyzes the motion of particles suspended in a fluid. The particles are usually smaller than 1µm but roughly 1000 times larger than a molecule. The particle in suspension collides continuously with surrounding molecules. Impulse is exchanged in these collisions and the particle has a random motion, similar to the motion of molecules, but with a corresponding lower velocity. The instantaneous velocity or position of a suspended particle in fluid can not be predicted or calculated. Instead, the physical statistics can calculate the probability that a particle is in a certain volume. One can imagine a particle in the origin of a coordinate system at moment $t = 0$. The initial position is $\vec{r} = 0$. After several collisions with molecules the particle will be in the position $\vec{r}$ at time t. The particle has moved randomly during the time t and the new position can not be calculated. Instead, the probability to be located in a volume centered on origin can be calculated:

$$P(\vec{r}, t|0,0) = (4\pi Dt)^{-\frac{3}{2}} \cdot e^{-\frac{r^2}{4Dt}}$$

D is the diffusion coefficient.

r is the distance between the final position at time t and the initial position at time 0. The travel of the particle is longer than r because several collisions and changes of direction occur in the time t.

The distance r is longer for a higher diffusion coefficient D. This means that the particle has a higher probability to be found in a larger volume after the time t for a higher diffusion coefficient and lower viscosity η.

The average squared distance which a particle is moving in the time t is:

$$\langle x^2 \rangle = 2Dt$$

A particle should move a distance of λ/2 to produce a destructive interference and thus a variation in the intensity of light on photodetector. This distance must be in the direction of the photodetector, or else the direction of scattering must be considered. The phase difference is $\Delta\varphi = \vec{r} \cdot \vec{q}$. For a a destructive interference, phase difference is π and $\Delta\varphi = \pi = \vec{r} \cdot \vec{q}$. A characteristic time τ_0 can be defined as the time which is necessary for a particle to travel a distance of λ/2:

$$\left(\frac{\pi}{q}\right)^2 = 2D\tau_0$$

$$\tau_0 = \frac{\pi^2}{2Dq^2}$$

This characteristic time τ_0 is the link between the movement of particles and the light on photodetector.

4. Statistical Analyze of the Ensemble of Particles

The autocorrelation function $R_E(t)$ was introduced to analyze the scattered light and to get a quantitative measure of the fluctuations. In principle, the *field autocorrelation function* can be obtained by measuring the electric field of the scattered light Es(t) in the moment t and after a time lapse τ and calculating their product. This pair of measurements must be repeated many times. The autocorrelation function is calculated as the average of the products: $R_E(t) = \langle E(t)\cdot E(t+\tau)\rangle$. Or, the equivalent detailed definition for a continuous aquisition is:

$$R_E(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T E_s(t)\cdot E_s(t+\tau)dt$$

The integral contains the electric field of scattered light recorded in the t moment and after a time difference τ. This is the *field autocorrelation function* for the scattered light.

A similar function is defined for the intensity of the scattered light Is(t). The intensity of light is the power of light per area unity. The intensity is proportional with the square of electric field. The *intensity autocorrelation function* is:

$$R_I(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T I_s(t)\cdot I_s(t+\tau)dt$$

Both functions can be used, in principle, to calculate the diffusion coefficient but only the second one, intensity autocorrelation, is practically usable.

For a “stationary” system, the autocorrelation function do not depend on the beginning moment t, nor on the number of measurements or total duration. But it depend on time difference τ.

The autocorrelation function is very important for DLC due to its relationship with the spectrum of the scattered light fluctuations. The relation between the spectrum of scattered light and autocorrelation function is provided by the Wiener-Khinchin (Хинчин) theorem:

$$S_I(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} R_I(\tau)\, d\tau$$

$S_I(\omega)$ is the frequency spectrum of the intensity and $\omega = 2\pi\nu$ is the angular frequency.

The demonstration of the Wiener-Khinchin theorem is quite elaborate and is not subject of this work.

The intensity of light is $I(t) = \beta|E(t)|^2$ and $E(t) = E_0 \cdot e^{i(\vec{k}_0\cdot\vec{r}-\omega_0 t)}$ is the electric field.

The autocorrelation function for intensity is:

$$R_I(\tau) = \langle I(t) \cdot I(t+\tau) \rangle = \beta^2 \langle \left|\vec{E}(t)\right|^2 \cdot \left|\vec{E}(t+\tau)\right|^2 \rangle =$$

$$= |E_0'|^4 \beta^2 \cdot \langle \sum_i \sum_j \sum_k \sum_l e^{i[\Phi_i(t)-\Phi_j(t)]} \cdot e^{i[\Phi_k(t+\tau)-\Phi_l(t+\tau)]} \rangle$$

After a series of calculations and physical considerations, the intensity autocorrelation function is:

$$R_I(\tau) = N^2 |E_0'|^4 \beta^2 \cdot \left(1 + e^{-2Dq^2|\tau|}\right)$$

The Wiener-Hinchin theorem can be applied for the intensity of light:

$$S_I(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\tau} R_I(\tau)\, d\tau = N^2 |E_0'|^4 \beta^2 \int_{-\infty}^{\infty} e^{-i\omega\tau} \left(1 + e^{-2Dq^2|\tau|}\right) d\tau$$

After calculating the integral and considering the symmetry of $R_I(\tau)$ around $\tau=0$, the spectrum of the intensity results:

$$S_I(\omega) = N^2 |E_0'|^4 \beta^2 \left[2\pi\delta(\omega) + \frac{2(2Dq^2)}{\omega^2 + (2Dq^2)^2}\right]$$

Some terms can be grouped in a_0 and a_1. The additive constant can be simply eliminated.

$$\boxed{S_I(\omega) = a_0 \cdot \frac{a_1}{\omega^2 + (a_1)^2}}$$

This last equation can be directly used in practice to analyze the data delivered by an experimental device.

$S_I(\omega)$ is the spectrum of scattered light. (The frequency dependency of amplitude.)

a_0 is the amplitude (constant) which is not involved in calculations for DLS.

The radius of particles is calculated from constant a_1:

$$R = \frac{2k_B T}{6\pi\eta a_1} \left(\frac{4\pi}{\lambda} \sin\frac{\theta}{2}\right)^2$$

$\omega = 2\pi\nu$ is the angular velocity and ν is the frequency (measured), λ is the wavelength of light, θ is the scattering angle, $D = \frac{k_B T}{6\pi\eta R}$ is the diffusion coefficient, k_B is Boltzmann's constant, T is the temperature in Kelvin, η is the viscosity.

An important remark: DLS method can determine the size of particles from known constants and parameters of experimental device. No calibration is necessary!

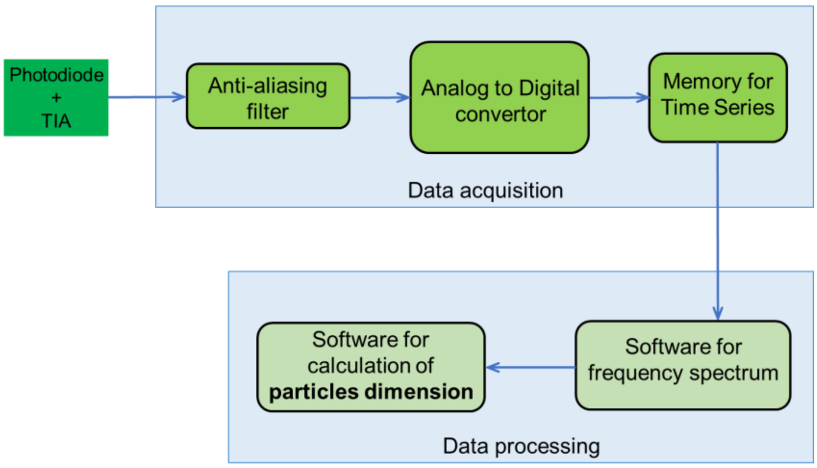
The analyzed situation, when all particles in suspension have the same size and the same diffusion coefficient, is a *monodisperse solution*.

In the general situation, the particles in suspension are not identical. They have different size and thus different diffusion coefficient. A solution with particles of different diffusion coefficient is a *polydisperse solution*. Finding the dimension of particles, or rather the distribution of size for polydisperse solutions, is not an easy task. Several attempts were done by researchers but none of them is fully accurate, nor easy applicable. For information only, some of these methods are listed here.

- Inverse Laplace transformation
- Exponential Sampling Method
- Contin method
- Multiexponential analysis
- Cumulant analysis

5. Data analyze in a DLS experiment

An overview of electronic equipment for data processing is in the block diagram:

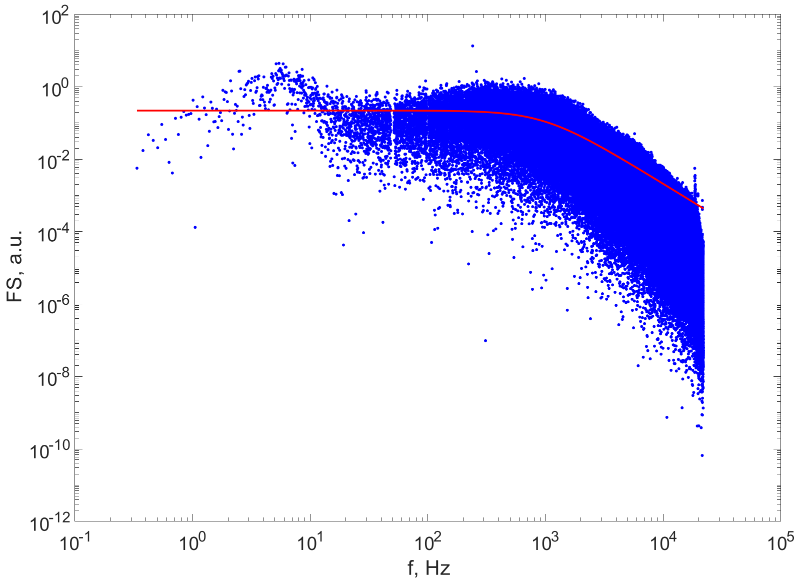


The main steps in data acquisition and processing are:

- A photodetector generates an electric signal proportional with the intensity of light.
- The signal is properly amplified.
- After low-pass filter, an analog to digital convertor digitizes the signal and generates a Time Series which is stored in memory.
- A computer analyzes the Time Series and generates the frequency spectrum (by Fast Fourier Transform or Artificial Neural Network).

- Parameters a_0 and a_1 are found so that the analytical function S(ω) (Lorentzian Line) best matches the experimental frequency spectrum.
- The average radius of particles in suspension R is calculated from a_1.

The image is an example of matching Lorentzian Line, calculated by least squares fit minimization procedure, superimposed on a set of experimental results (blue dots) with high noise.



6. DLS in Air – Problems and Solutions

The primary aim of this research is to perform, for the first time, Dynamic Light Scattering in air as solvent. A few difficulties must be overcame to accomplish the aim.

Intensity of scattered light

The intensity of scattered light is much lower in air for 2 reasons. One reason can be observed in the graphs of the frequency spectrum. The area under the line is the same for both water and air (in linear scale). In other words, the same power of the scattered light is spread in a wider spectrum of frequency.

The second reason is the concentration of particles in suspension. In general, particles suspended in air are in low concentration compared with particles in liquid. The liquid probes are more turbid than gaseous probes. The direct result for DLS in air is that a smaller amount of light is scattered. The photodetector and the amplifier must be more sensitive.

Frequency

The frequency spectrum which is analyzed in a DLS experiment is

$$S_I(\omega) = a_0 \cdot \frac{a_1}{\omega^2 + (a_1)^2}$$

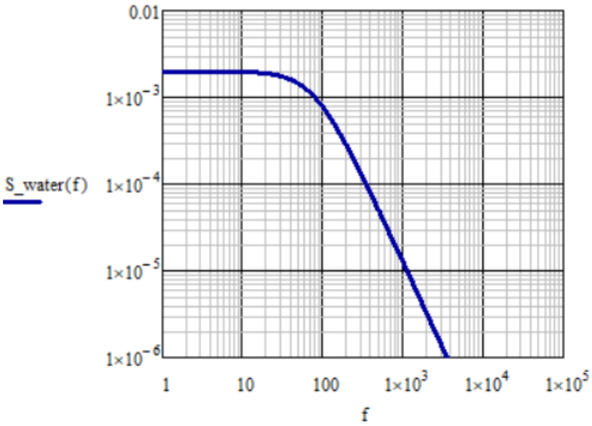
The parameter a_1 is:

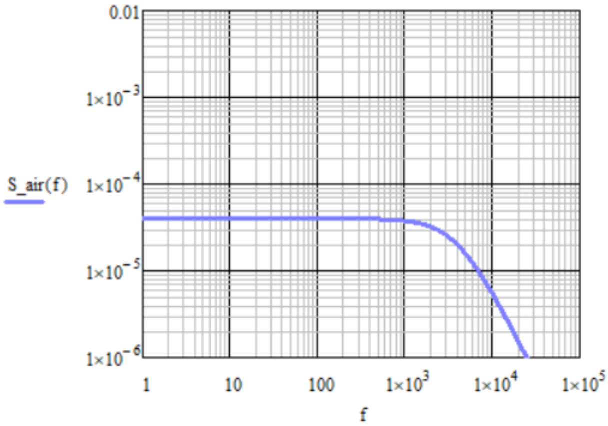
$$a_1 = 2\frac{k_B T}{6\pi\eta R}\left(\frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)^2$$

The viscosity η of water is roughly 50 times higher than the viscosity of air at 20°C.

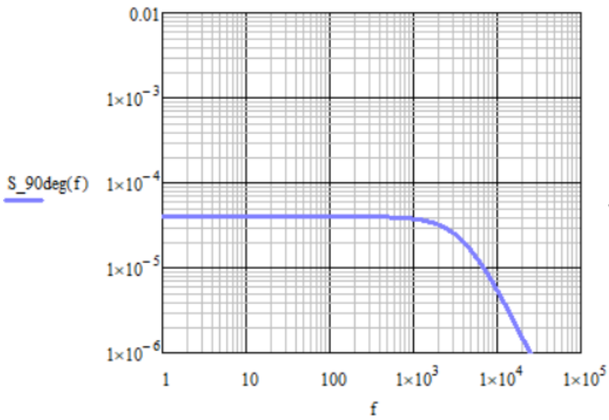
η water = 1000µPa·s and η air = 18.5µPa·s

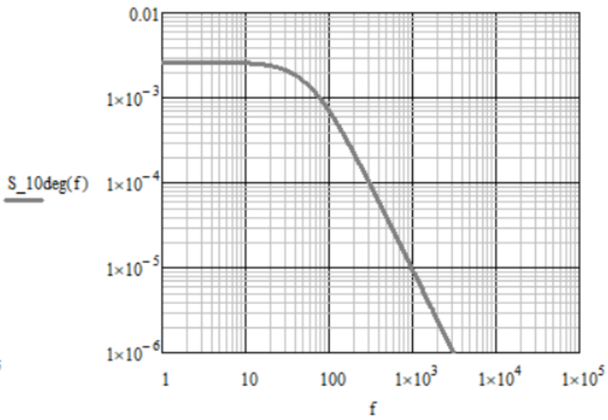
A simulation in MathCad was done for frequency spectrum for a typical DLS in water and in air. In the graphs below, all parameters are identical except the viscosity.





The above graphs show that if the viscosity decreases 50 times, the roll-off (corner) frequency increases accordingly, from 100Hz in water to 5kHz in air. An experimental device for performing DLS in air must be designed for higher frequency. Though, the experimental device designed by the authors has some improvements which reduce partially the maximum frequency. We can observe in the above equation for a_1 parameter that a decrease of the scattering angle θ can compensate partially the decrease of viscosity η. DLS in air was performed with θ = 10° while classical DLS in liquid is performed with θ = 90°. The improvement of reducing scattering angle from 90° to 10° is obvious in the following MathCad graphs. Higher amplitude and lower frequency can be achieved.





Sample preparation

The liquid samples which are analyzed by DLS can be prepared easily. The solvent with suspended particles is simply poured in a glass cuvette which is placed in front of the laser. The gaseous samples are more difficult to prepare and handle. The particles in air are usually not stable because suspended particles tend to settle and to adhere to the cuvette walls. Moreover, a sample of gaseous suspension should be collected or prepared somehow in a sealed glass cuvette. In our experiments, a continuous flow of air with particles was maintained during experiment.

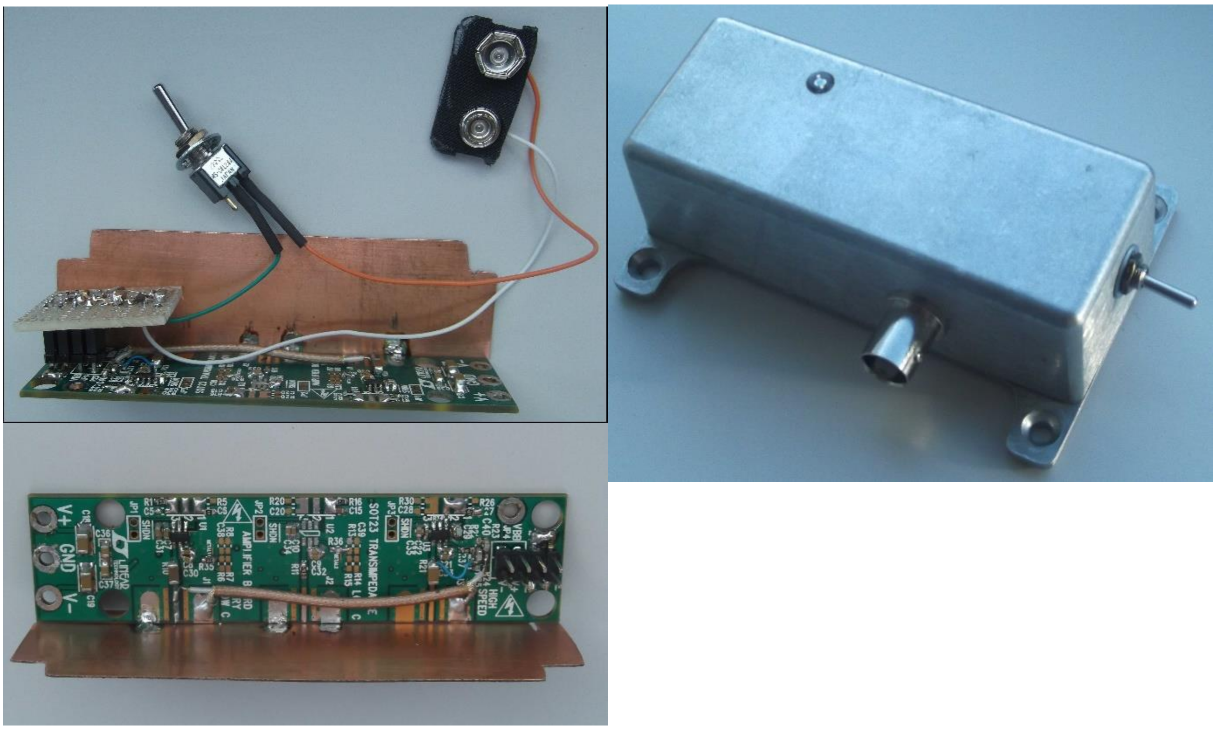
7. Experimental Equipment for DLS in Air

Before designing the experimental device, all parameters for DLS in air were calculated (intensity of scattered light, speckle dimension, level of electric signal, frequency bandwidth, errors, noise, etc.). These calculated parameters are requirements for the experimental device. The electronic device was tested with calibrated light source to verify the design.

The equipment used for DLS in air consists of the following components:

- Mechanical setup to support all components
- He-Ne laser, $\lambda = 633$nm
- Sample with particles in suspension in air. The sample is described in the next chapter.
- PIN photodiode which must detect light intensity of 1nW/mm^2.
- Transimpedance amplifier with gain = $10^7\Omega$
- Voltage amplifier and low-pass filter with gain = 100V/V
- Analog to Digital convertor consists of a high performance sound card for computer. A frequency bandwidth of 20kHz is enough for the improved setup with low scattering angle.
- Computer with MatLab for data analyze. Algorithms in MatLab were developed for matching Lorentzian Line on experimental frequency spectrum, finding parameters a_0 and a_1 and calculating the size of particles.

A metal housing 90mm x 40mm x 30mm accommodated the photodiode, transimpedance amplifier, voltage amplifier, 9V battery and voltage regulator. This arrangement provides the lowest noise and external perturbations.



8. Experimental Results

DLS experiments were performed on a few samples of particles in air. The results are summarized in the following table.

Sample	a_1 Hz	Average diameter nm	Alternative measurement nm	Error nm	Kn (Knudsen)
Smoke from paper burning, with flame	244.2	565	200-3000 Burning wood	45	0.14
Wick of a wax candle, smoldering	1771.4	78	30-1000 Oil smoke	6.2	0.83
Nebuliser	410.0	336	(not conclusive)	27	0.19
Cigarette smoke	6166.0	22	10-4000 Tobaco smoke	1.8	3
Smoke from paper, smoldering	9393.1	15	10-200 Soot	1.2	4.4

The size of similar particles, measured by alternative methods for confirmation and validation of DLS in air (non DLS), can be found in column Alternative measurement. The average dimension of particles measured by DLS in air are validated by the values from Alternative measurements. Nevertheless, these experimental results must be regarded with caution.

- As explained earlier in this abstract, the data analyze is for monodisperse solutions and can produce only the average size of particles. All types of particles in air and all measured samples are polydisperse solutions and consist of particles with a wide range of dimensions.
- Some experiments of DLS in air were done with low volumetric concentration of particles. This leads to a low intensity of scattered light, noisy signal and increased errors when parameters a_0 and a_1 are fitted. For example, particles generated by a nebulizer have a low volumetric concentration, the signal is very noisy and the result is not conclusive.
- The calculated error in the table includes the errors of scattering angle and temperature. It do not include the noise which can not be estimated accurately.

9. Importance of DLS in air

A number of methods and techniques are available for measuring the dimension of particles suspended in air (optical methods, mechanical methods, gravimetric methods, with ionization, microscopy, etc.). Dynamic light scattering is a new method with certain advantages compared with existing methods. Although the DLS in air experiments performed by the author have not a high precision, this is an issue for all methods for measurement of small particles. Optical microscopy is limited by the wavelength of light, that is about 1μm. More sophisticate methods, like Atomic Force Microscopy have also limited precision. Other methods are either slow and difficult or very inaccurate.

An important particularity of DLS is the fact that it can calculate the size of particles based only on constants. No calibration is necessary.

Considering the specific advantages and disadvantages of DLS in air, some applications and practical uses of this method can be proposed.

Exhaust particles

The exhaust gas (smoke) from combustion engines is analyzed only for the amount of particles. The size of particles would be very useful but can not be analyzed currently. DLS can be applied for frequent analyze of particles size in the exhaust gas.

Smoke and fire detectors

Smoke detectors can detect only the presence of particles in air. No other information about particles or smoke. A detector based on DLS would provide valuable information about the size of particles. This would distinguish smoke from dust or other false alarms. The firefighters would be happy to have additional information about a fire from the beginning of alarm. A smoke detector based on DLS can tell the difference between an active fire and a smoldering fire because the smoke particles have different size.

Powder

Industrial domains which use or produce powder are very numerous. Pigment for paint, toner for printers, flour and many other powders. The size of particles can be estimated quickly by DLS in air.

Particulate matter

Particulate matter means particles suspended in atmosphere. It is analyzed as part of environment monitoring. An alternate method for monitoring the size of particles could be DLS. Though, DLS can be applied with difficulty for particulate matter because the density of particles is very low.

Dust in air

There are industrial domains where dust in air must be monitored for human safety. For example, the dust of coal in mines, cement or dust powder in constructions, powder in mills, etc. DLS would provide additional useful information about the size of particles.

Aerosols

Aerosols are often used in medical cure. For best results, the size of generated particles must have an optimal size. The size can be measured by DLS in air and then the generator can be adjusted accordingly.

Fog

Fog is composed of water *droplets* suspended in air. The size of droplets is important for estimating, for example, the visibility or the risk of glazed frost. DLS could be a suitable method for measuring the size of droplets in fog or clouds.

Other applications

DLS in air can replace other classical methods due to low price and ease of used, compared to more sophisticated methods. Or can replace simple, cheap devices due to additional information available about the size of particles.

10. Conclusion

To our knowledge, DLS method was never applied to particles in gas. This research work proves the possibility of measuring the size of particles in suspension in air by DLS method. Moreover, this is possible by a small, portable, automated, calibration free, low cost device.

This work is a proof of concept for Dynamic Light Scattering in air. Improvement of precision and versatility are subject of future research.

Maybe the most important limitation of actual DLS is the limitation to monodisperse solutions. The particular case of monodisperse solutions is only a low fraction of cases where particles in suspension must be analyzed, therefore the applicability of DLS is quite limited for the moment. Future research will extend the applicability of DLS method to polydisperse solutions.

The first step in DLS in air was done. Many other directions of research are open for improvement, solving remaining issues and widening its field of application.

Cristian Leca

Sibiu, September 2021