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USING DYNAMIC LIGHT SCATTERING EXPERIMENTAL SETUP AND NEURAL NETWORKS FOR PARTICLE SIZING

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Abstract: *Using a Lorentzian function fit as reference, a basic experiment was designed for processing Dynamic Light Scattering time series, allowing to estimate the average particle size of a suspension. For fitting the averaged power spectrum of the time series, several neural network configurations were tested in order to compare the results with the reference. The results of this comparison revealed a good match, serving as a proof of concept for using neural networks as an alternative for DLS time series processing.*

Key words: Dynamic Light Scattering, Suspensions, Particles, Neural Networks, Time Series

1. Introduction

The study of nanoparticles is a topic of major interest in the last decades due to the wide array of applications, especially in the area of biology and medicine. As a consequence of their small size, one order of magnitude smaller than the living cells, they can be used to deliver various substances to living cells, producing, in general, only minor perturbations. The applications of these nanomaterials were presented in several papers, such as [1]. During development of these applications, there were concerns about the toxicity of these methods. As a result, techniques for monitoring the nanoparticles concentration were also developed [2].

The properties of the systems of nanoparticles are in direct relation to the size distribution of the particles in the fluid. For this reason, the size characterization of these systems is one relevant aspect for further development of the nanotechnology applications. There are various techniques used for this. One modern technique is the Transmission Electron Microscopy (TEM) which evaluates particles in the range from nanometers to micrometers. This method has a good resolution but is in general expensive, time consuming and does not work in-situ. Another method is the X-Ray powder diffraction which can offer the size distribution of the particles [3]. For metal oxides, for which the assumption used is that the crystallite size is the same as the particle size, the Scherrer equation [4] can offer the mean particle size. For colloidal particles, the Guinier formula [5] can be used in a similar way. However, also these two methods are slow and do not work in-situ. The particle size for nano-systems can also be assessed by the method called "Atomic Force Microscopy" (AFM) [6], [7]. Paper [7] shows a comparison of AFM with TEM. Results show that AFM sizing requires very thin samples over several layers. The samples are scanned line by line and this takes a lot of time. Comparisons and reviews of other techniques used for nanoparticle size characterization are presented in many papers, such as [8]. As in [9], the properties of the nanofluid change very fast during nanoparticle aggregation, and as a consequence, a fast procedure for monitoring the size is needed. A valid option for this are the optical procedures, which use coherent light scattering.

The optical methods make use of an incident coherent beam of light which illuminates an active sample volume containing the nanoparticles. Each particle represents a scattering center and becomes a secondary light source. The intensity of the scattered light is anisotropic and depends on the size and shape of the scattering centers. This is described by the phase function, for which there are several models used to represent it [10],[11],[12].

If the incident beam is coherent, so are the secondary waves emitted by each scattering center. If a screen or a detector is present, all the wavelets emitted by all the scattering centers in the beam area will interfere on each location of the screen, producing an interference field having maxima and minima randomly distributed. This field is named speckled far field. The intensity on each location carries

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information on the phases of all the scattering centers in the active volume of the sample.

The scattering centers are moving in a complex manner, as a result of sedimentation and stochastic Brownian motion [13]. As it has been shown in [9], the scattering centers velocity associated with the sedimentation is few orders of magnitude smaller than the velocity associated with Brownian motion for the size ranges corresponding to nanoparticles. The motion of the scattering centers generate a dynamic optical behavior of the far interference field, which appears like “boiling speckles”. The size of the scattering centers influence parameters like average intensity, speckle size or speckle contrast in the interference image. The same parameters are affected by the concentration of the scattering centers [14], [15], [16], [17], [18]. As a consequence, a process where both the concentration and the size of the particles change with time, such as particles aggregation, cannot be monitored using the basic, first order, speckle statistics.

The speckle dynamics is however correlated with the Brownian motion, and this correlation is used by the method called Dynamic Light Scattering (DLS) or Photon Correlation Spectroscopy (PCS). The theoretical foundation for this method is explained in many papers, such as [13], [16], and [17].
This paper presents an innovative alternative approach for extracting the size information from the time series recorded in a Dynamic Light Scattering experiment, using a specialized Neural Network. The Neural Network concept is not new, there are many papers and books available [19], [20], which explain the key concepts in high detail.

There are several papers showing the usage of Neural Networks in Physics, and in particular, in Optics. Paper [21] shows a method for measuring the size of soft particles of spherical type by analyzing the angular distribution of scattered light with a three layer Neural Network. Another paper, [22] presents a Neural Network implementation for pattern recognition used in a flow cytometer for identifying the presence of dangerous fibers, like asbestos, in air. Papers [23] and [24] present results on evaluating the size and refractive index for particles in suspension using measurement of angle-dependent light scattered and analyzing the radial basis function with a Neural Network. Another paper [25] presents results for a Neural Network which was fed with data from the polarized light signature in the shape of Mueller matrix for detecting amino acids and other organic compounds of solid type.

The task we are interested in is to compute the output of a function that has an unknown analytic form, based on the training of the Neural Network with sets of input data with known output. The work presented here uses a Neural Network approach for DLS time series data processing and should be viewed as a proof of concept and as a step toward designing a miniature device for Dynamic Light Scattering particle sizing, able to evaluate the average particle size for a suspension of nanoparticles with a precision similar to the classical procedure.

2. Methods and Procedures

2.1 The Dynamic Light Scattering Procedure

The experimental setup used is presented in Fig. 1. It consists of a LASER diode emitting a continuous beam, a sample placed in a transparent glass cuvette and a detector which forwards the electrical signal to a data acquisition connected to a PC USB port.

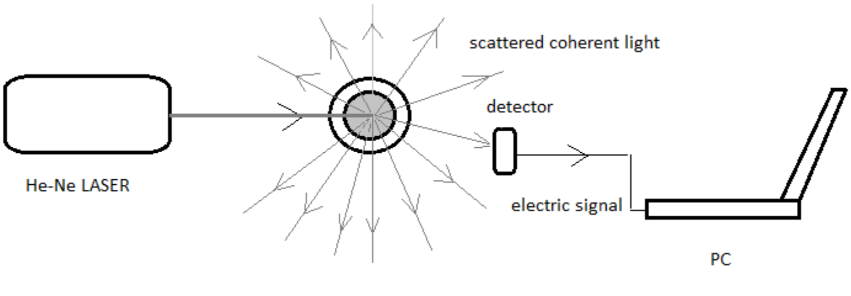

Fig. 1 The schematic of a Dynamic Light Scattering experiment

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When the incident light meets the particles from the active volume, anisotropic elastic light scattering takes place. The anisotropy is described by the coefficient g, which averages the cosine of the polar scattering angle. This anisotropy coefficient depends on the scattering center diameter. Using Mie calculations, a simple phase function is describing the functional dependence of the g parameter to the nanoparticles diameter [26]. This result can be tested using Monte Carlo methods [11]. As described in [11], [27], in a simplified Static Light Scattering experiment, the mentioned function can be used to evaluate the nanoparticles diameters by measuring the anisotropy parameter.

The coherent secondary waves interfere, with phases carrying information on the motion of each scattering center. The pattern obtained on a screen has time variation. Monitoring this time variation in a particular point generates a time series which contains the useful information about the particles. This information is extracted by using the Dynamic Light Scattering method, described and developed since decades [28], [29], [30]. We will not repeat this description in detail, but will briefly summarize the key points below.

In a first step, the time series is recorded using the above or similar experimental setup. The frequency spectrum is calculated using the Fourier Transform. The theoretical spectrum can be represented by a Lorentzian function S(f), which has two parameters, a_0 and a_1:

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

In equation (1), f is the frequency and a_0, a_1 are the mentioned parameters. The parameter a_0 affects the equation in a linear way, scaling up the function to reach an initial plateau. The parameter a_1 affects the equation in a non-linear way, having the effect of shifting the values along the frequency axis, in a logarithmic scale. This theoretical function can be used to fit the measured frequency spectrum using a method like the least square minimization. This method is described in [28], [29], [30]. Experiments showing results with this method are described in [27], and [31].

The fitting procedure offers as output the two parameters, which can then be used to evaluate the particle radius R:

$$K = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \qquad (2)$$

$$R = \frac{2 k_B T K^2}{6\pi\eta a_1} \qquad (3)$$

In equation (3), T is the absolute temperature of the sample, k_B is Boltzman's constant, η is the dynamic viscosity of the solvent, θ is the scattering angle, n is the refractive index of the solvent and λ is the wavelength of the laser radiation in vacuum.

As the purpose of this paper is to present a proof of concept for using Neural Networks in Dynamic Light Scattering particle sizing, a basic experimental setup design has been used in simulated time series, and this assumes a low frequency data acquisition system. As the data acquisition was 100 Hz, the frequency spectrum covers the range 0-50 Hz, which is a very narrow range. In order to use the setup for smaller particles sizing, a small angle was chosen, more precisely 2.7927^o and this makes the rolling point in the Lorentzian line to be shifted in the above mentioned frequency range.

With this basic experimental setup, recording at low scattering angle and with very low frequency, one cannot expect to assess diameters bigger than 150 nm, in a reasonably precise manner, as the frequency spectrums overlap for bigger diameters. Therefore this limit was set as the upper bound in the Neural Network section.

This simplified Dynamic Light Scattering procedure was presented in this subsection because we used it as a reference method in particle sizing. For this purpose the procedure as described here, including the computer codes previously written and used [27], [31] were tested again. The whole set of data that was used to train the Neural Network, the clean input, as described in the next section, was used as input for the Dynamic Light Scattering procedure. The predicted diameters were identical with the diameters used in generating the frequency spectrums used as input, and such a figure with a line f(x)=x is not presented here. Therefore, the classical procedure, of fitting the Lorentzian line using a nonlinear

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minimization procedure, finding the two parameters, a_0 and a_1 and further on assessing the particles diameter using eq. (2) and (3) was used in the work reported in this article and considered as reference.

2.2. The Neural Network approach

2.2.1. The Neural Network Design

For the work presented in this paper we have used a predefined tool named "nftool" in MATLAB. This function creates a standard Neural Network with configurable number of neurons in the layers and with randomized values for the biases and weights. We configured a neural network with three layers. In the initial configuration, the first layer or the input layer had 50 neurons, corresponding to the input data of 50 values. The second layer or the hidden layer had a fixed amount of neurons and the third layer, the output layer, had only one neuron, corresponding to the one output, the average diameter of the particles evaluated.

In order to have a standard input for the Neural Network, the frequency spectrum is normalized. This normalization procedure requires two steps. In a first step, the values of the frequency spectrum, both the frequency and the spectrum, are averaged over a number of fixed intervals. We have used 50 fixed intervals. In a second step the average values are scaled so that the maximum value correspond to 1. The same normalization procedure was used for the frequency spectrum computed on the time series recorded during experiments, making sure that the averaging intervals are exactly the same as those used for training the Neural Network.

2.2.2 The Neural Network Training Procedure

The training was done using the Levenberg-Marquard algorithm [32]. The duration of the training was 60 seconds using an Intel Core I3 4160 CPU at 3.6 GHz. Two different training procedures were used to train a ready to use Neural Network. For the first training procedure a set of time series was generated as a sum of sine functions generated with a number of 1301 frequencies in the range 0-50 Hz. The frequencies f_k were generated using a random number generator with an uniform distribution in the above mentioned range. The initial phases of each component (sinus function) φ_k were generated randomly as well, and uniformly in 0-2π range. The amplitude of each component was calculated using the square root of S(f) in eq. (1).

The sum of all the components was computed for each time value t_i of the time series and each value was squared, to produce a time series $x(t_i)$ of positive values, as the experimental time series is. Time series were generated using frequencies equally spaced in the interval.

The next step in preparing the input data for Neural Network training consisted in computing the frequency spectrum using a fast Fourier transform routine. The third step consisted in computing the averages on 50 intervals and to normalize the simulated frequency spectrum. The fourth step consisted in putting together the set of input data, each set as a column for one diameter, in an array.

3. Results and discussion

After several attempts of training the Neural Networks, we realized that we need to use a big array of input data and the array consisted of 2250 sets, covering the diameter range from 1 to 150 nm, with a step of 1 nm, having 15 sets of normalized frequency spectrums for each diameter value. We called this type of Neural Network a "noisy input trained Neural Network", hereafter niNN. The niNN had 26 neurons in the hidden layer.

The second training procedure used clean inputs, meaning that the input was an array having each set in a column, as in the first training procedure. Each column had 50 values, which are the values of the ideal frequency spectrum, normalized as described before and computed for exactly the same 50 frequencies as for the first procedure and as for the frequency spectrum computed from experimentally recorded time series for the same scattering angle. We named this second type of input sets a clean input and the Neural Networks produced in this manner "clean input trained Neural Network", hereafter

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"ciNN". We tried several Neural Networks of this type and realized that large set of input data is required in training in order to get good results, as in the first type of Neural Networks. One of them was trained with an array of 150 sets of frequency spectrums, each corresponding to a diameter. The diameters were chosen from 1 nm to 150 nm, with a step of one nm. After several trial and error attempts we chose 20 neurons for the hidden layer. The overall fit after the training procedure was 0.999999 which is a very good value and named this "ciNN1".

Fig. 2 illustrates the values of the diameters computed using the Neural Network after training, having the same set as input.

We notice that the ciNN1 predicts accurate values for all the diameters in the range while niNN1 predicts bigger values for smaller diameters and reaches a plateau for diameters bigger than 70 nm. The niNN predicts a diameter far away from the one used in generating the input data if d<100nm. A possible explanation lays in the input data used to train both niNN and ciNN. In the diameter range bigger than 100 nm, for the small angle used in generating the input data and for the small data acquisition rate used in generating the input data and in simulating the time series, the frequency spectrums are almost overlapped.

4. Conclusion

We can conclude that ciNN, trained using an array of clean input sets, is the best choice, as it can reproduce without any error the input set of data if the array that was used to train the Neural Network is served as input and this procedure. Training the Neural Network with clean input is better than training it with very noisy input, no matter how big the number of input sets is.

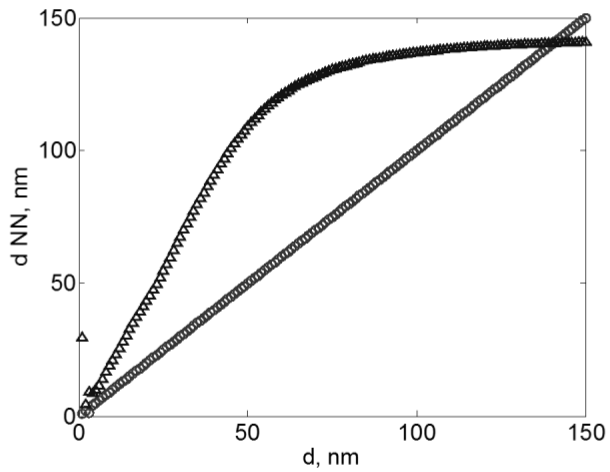

Fig. 2 The values of the diameters computed with ciNN1, circles, and with niNN1, triangles The abscissa is the diameter used for generating the set of clean frequency spectrum for both sets.

The newly proposed approach implies training a Neural Network with a big set of data, either simulated or experimental. The training itself requires also a big number of floating point operations, maybe even bigger than the least square minimization procedure. As soon as the Neural Network is trained, the network parameters can be exported and imported after that on another, much weaker, computational platform. For evaluating the average diameter from the frequency spectrum, the NN approach requires much smaller number of floating point operations than the classical method. This is a key point in being able to design and implement a compact, portable optical device used for particle sizing based on a very modest computing platform.

The results on simulated time series, prove that Neural Networks can be used with success in processing Dynamic Light Scattering time series for particle size estimation. At the moment of writing this paper, the authors are working on improving the proposed procedure, making it more robust and efficient in terms of computational cost. In addition, a prototype for the palm-sized computational device

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is under construction. The results of this subsequent work will be presented in future papers.

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