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Direct Optical Particle Tracking - a technique for size distribution assessment

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Abstract
Nanotechnology, an emerging discipline within material science, has ushered in a new era of engineering by creating nanostructured materials with distinctive properties suitable for a wide range of bioengineering applications. The shape and size of these materials constitute critical variables, determined by the chosen synthesis method and chemical precursors. Silver nanoparticles, synthesized through chemical processes, exhibit antibacterial properties when their size falls within a specific range. However, measuring the size of such nanoparticles, typically in the nanometer to tens of nanometers range, necessitates specialized techniques like Dynamic Light Scattering and Transmission Electron Microscopy. These methods are often limited by assumptions, high costs and longer measurement times. This paper introduces a novel approach utilizing Direct Particle Tracking for assessing particle size distribution in the early stages of nanoparticle synthesis. The study used realistic computer simulations of nanoparticle diffusion, employing the CHODIN code and a specific code for Direct Particle Tracking written for this purpose. The Brownian motion of each particle is recorded, the mean square displacement is computed and the diffusion coefficient, as well. The diameter of each particle is assessed and here from the particle distribution. The results on simulated particle diffusion demonstrate the feasibility of using Direct Particle Tracking as an effective method for size distribution assessment in the initial phases of nanoparticle synthesis. This innovation opens the door to real-time monitoring and control of nanoparticle size in bioengineering applications, promising significant advancements in the field of nanotechnology.

Keywords: Nanoparticles, Size distribution, Diffusion Simulation, Direct Particle Tracking

1. INTRODUCTION

Nanotechnology has developed lately as an innovative area of science for the high need of various practical and ingenious applications. This science area has a huge potential in applications with different purposes offering ingenious solutions to problems from medicine, agriculture, electronics, environment, food additives or cosmetics [1, 2].

Nanomaterials are produced and designed in many forms and types. One of the most interesting classes of materials are nanoparticles, which are defined as 0D structures with dimensions less than 100 nm [3]. The size is the most important aspect regarding nanoparticles, together with their shape and surface since in medical applications a nanometric level is the main factor to be considered. Besides their small sizes, the large surface area to volume ratio compared to bulk sizes exhibits stronger effect [4] since the number of interactions is increased. The size can influence the final physical-chemical characteristics and their medical purpose.

Nanomaterials, including the nanoparticles, present a different behavior comparing to bulk materials due to their distribution and diffusion in different media. Their large surface to volume ratio allows the exposure of a higher number of particles per unit while their reactivity is increased. A different dispersion of atoms in their structure and at their surface allows them to be captivated easier

in biological liquids by multiple interactions with charged molecules. Besides, in case of nanoparticles, the atoms are dispersed differently, so their binding energy is also modified comparing to microparticles [5, 6]. These observations lead to different physical-chemical properties of nanoparticles comparing to other sizes. Their diffusion is the main aspect to be studied since once their sizes decrease, their tendency is to flow faster to the targeted systems.

The nanoparticles sizes influence led us to the desire of a deeper investigation of their behavior in suspensions. For instance, silver nanoparticles show a better antibacterial activity once their dimension decreases, observation proven by multiple research studies [7-9]. Silver nanoparticles are versatile materials, able to be synthesized in different shapes or sizes. In biomedical applications, they are considered strong antimicrobial agents due to their ability of altering bacteria species and to their ability to inhibit bacteria replication. This phenomenon is correlated with their nanometric dimensions since based on their multiple interactions with internal structures of bacteria, the production of reactive species of oxygen begins and the bacterial biofilm formation is stopped.

The importance of obtaining particles at nanometric level through various physical or chemical processes sustains the development of an innovative characterization technique called *Direct Particle Tracking (DPT)*. This tracking analysis technique is able to determine the diameter of each particle from a suspension based on their diffusion in the media desired.

DPT is an optical pathway of detecting nanoparticles trajectories in real-time based on their dynamics in a fluid. Since DPT represents an electronic and optical setup, this biophysical technique observes and analyzes the trajectory of each particle from a suspension based on its Brownian motion and reconstructs its path using the software developed in the laboratory. Particle motion depends on its diffusion, therefore the media properties and the chemical composition of the suspension targeted are factors to be considered once the sample is observed in the microscope field. Besides nanoparticles, DPT can be applied to various molecules or cells, including bacteria, for a better understanding of their motions in liquids. This versatility of the method allows us to consider it an important tool in the characterization steps once a suspension need to be tested.

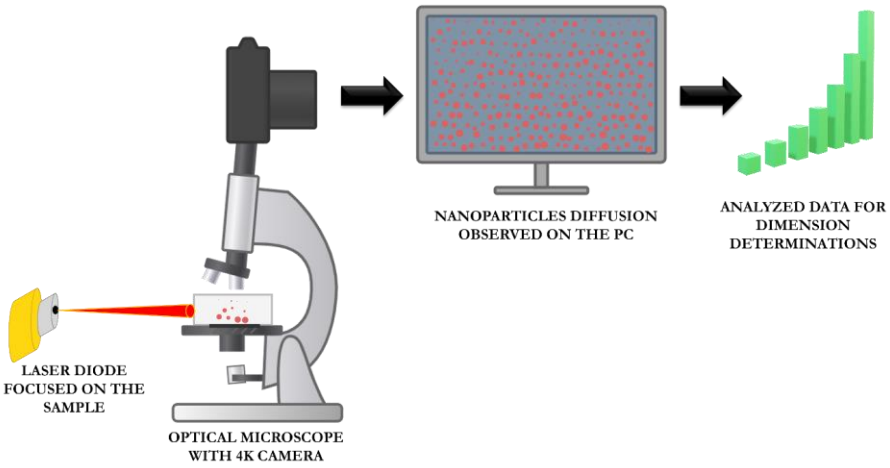

Fig. 1. Illustration of DPT technique

Figure 1 presents the setup proposed for DPT for a real-time visualization of nanoparticles. The sample, a small quantity of the suspension, is introduced in the cavity which is placed on an optical microscope. The cavity is illuminated using a laser diode based on a red light, wavelength 650 nm, powered at 5V. Once the light beam is focused on the sample, each particle from the suspension captures and scatters light in a different amount, therefore they will be observed in different forms on the computer screen. On top of the microscope is placed a 4k CCD camera which allows a real-time analysis of each single particle from a frame. The camera records a video based on the diffusion of each particle. Further, the software analysis will determine the particle size distribution in a 2D system

depending on the diffusion time identified. The final analysis will release the diameter of each particle from the suspension based only on the diffusion of each structure identified, therefore the possible assumptions used in other characterization techniques will be eliminated and by using DPT precise and accurate results will be obtained.

2. MATHEMATICAL CONSIDERATIONS OF DPT

The principle behind DPT is based on the Brownian motion of particles, more precisely on their free diffusion in the suspension. The particles possess a free motion, as it can be observed in Figure 2, which can be explained by multiple mathematical equations presented further. The trajectories of diffused particles posses a random movement in the cavity due to multiples interactions between molecules. Depending on the media studied, their properties can influence these trajectories. For instance, the composition of a biological fluid or its viscosity are factors which can decrease the diffusion rate and time of particles.

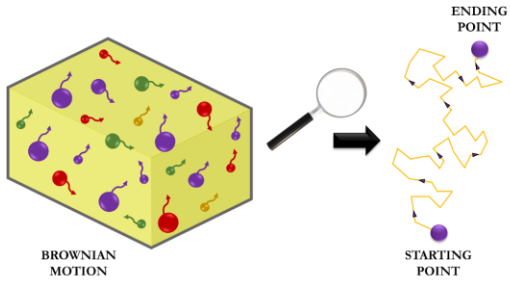

Fig. 2. Brownian motion of nanoparticles in a fluid

The diffusion coefficient for each particle is analyzed in a 2D system in which the particles move. Each trajectory is determined in a (x,y) system considering a specific framerate. This analysis of random movement is represented by a parameter called mean square displacement (MSD) [10, 11] which is determined using the further equations and which is used for the calculation of the diffusion coefficient:

$$MSD_x(\Delta t) = 2D_x\Delta t; MSD_y(\Delta t) = 2D_y\Delta t \tag{1}$$

$$4D = 2D_x + 2D_y \tag{2}$$

$$MSD(\Delta t_n) = 4D\Delta t \tag{3}$$

where D is the diffusion coefficient, D_x is the diffusion coefficient on the x axis and D_y is the diffusion coefficient on the y axis.

Once the D is extracted, each nanoparticle's diameter is determined using the Stokes-Einstein equation where d is the hydrodynamic diameter, k is the Boltzmann constant, T is the temperature, D is the diffusion coefficient and η is the viscosity of the medium:

$$D = \frac{kT}{3d\pi\eta} \tag{4}$$

Even if there are still a number of classical techniques which are based on this equation, DPT has the advantages of precise results in short time since their dimensions are determined based only on their size distribution depending on the diffusion in the suspension. Furthermore, DPT does not depend on the quantity of the scattered light comparing big particles with the smaller ones, so more accurate results comparing to other techniques are provided.

3. SIMULATIONS RESULTS AND DISCUSSIONS

The results presented in this paper are related to the simulations performed using the software developed for this method on silver nanoparticles suspensions. The simulations show a prototype in the particles movement and can reveal if the method worth to be implemented in the laboratory. Using the conditions similar to these from the real experiments, the software programs is tested and the method can be validated.

The diffusion was simulated using a CHODIN code in three dimensions, yet the results are presented in 2D since the microscope field is the projection of motion in two dimensions. The conditions simulations of these experiments include a number of 100 particles, with various diameters, 20 nm, 90 nm and 190 nm, water at 20°C as solvent, a dynamic viscosity of 10^{-3} daP and a framerate of 20 frames/second. The particles were assumed to be silver nanoparticles (Ag NPs) with a density of 10.5 g/cm^3. At the beginning of each simulation the particles were set at (0,0,0).

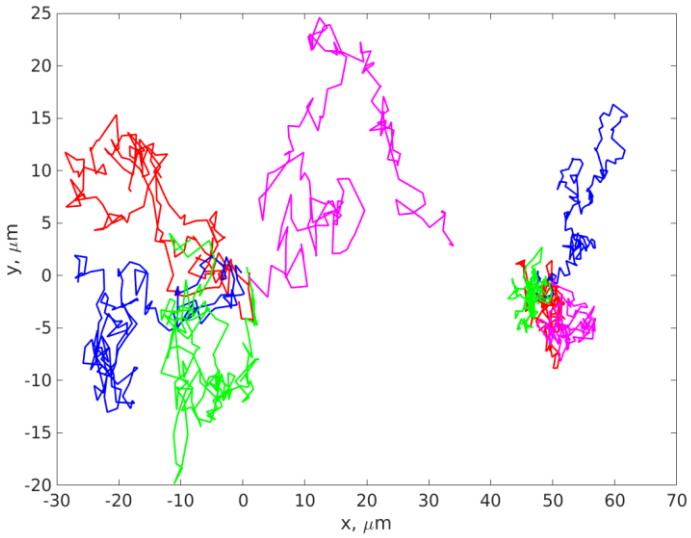

Fig. 3. Trajectories in 2D system of two random populations of diffused particles during simulations

Figure 3 shows the trajectories of two populations of diffused particles, at 20 nm and at 90 nm. It can be observed a random distribution of particles for each group, therefore the Brownian movement identification is proved. The trajectories show different diffusion rates comparing both populations, therefore a diversity in particles sizes in this suspension is suggested.

The recorded data was analyzed for each individual particle at each frame and the MSD parameter was obtained. The next step in the analysis was the calculation of diffusion coefficient using eq. (4) for the final diameter determination. Figure 4 presents the simulated diameters which are found mostly in the range 17-24 nm consistent with the value of 20 nm introduced in simulation. The peaks observed confirms the diversity of particles dimensions observed also in the Figure 3. The next diameter tested was 90 nm and the results of the size distribution are presented in Figure 5. The gaussian shape of the curve confirms the diversity of particles, while the maximum of the diameters is centered at around 90 nm, the value used for the simulation. The last simulation performed was for 190 nm and the results are presented in Figure 6. It can be observed that the diameters are found in the range 160-220 nm, results which are also consistent with the value introduced which was 190 nm in this case. All three histograms suggest nanometric dimensions for the particles tested, so DPT method proved to be valid for further laboratory experiments.

The spread observed in all three results is caused by the small number of particles analyzed since a Monte Carlo type simulation is performed. However, for a more objective view, a bigger number of particles can be tracked for a longer time.

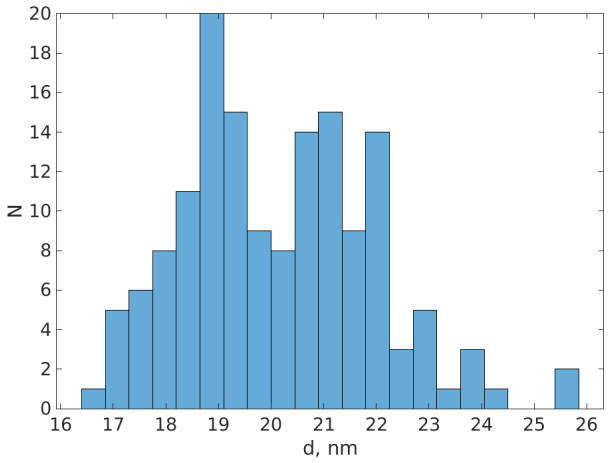

Fig. 4. Histogram of simulated particles diameters with 20 nm

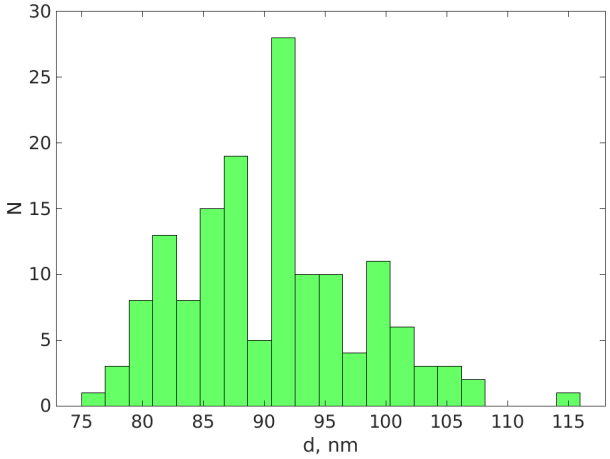

Fig. 5. Histogram of simulated particles diameters with 90 nm

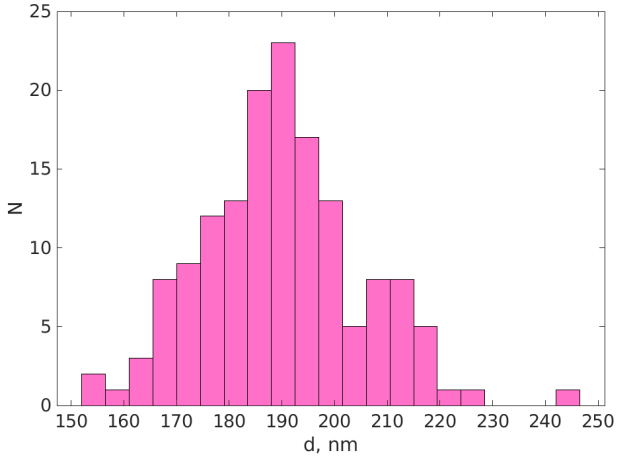

Fig.6. Histogram of simulated particles diameters with 190 nm

The results presented in Figure 7 show the histogram regarding the diameters of three different populations of nanoparticles simulated in the same time. The results show that the diameters were found in the ranges used for simulation, so the previous results are sustained and the method seems to offer accurate results.

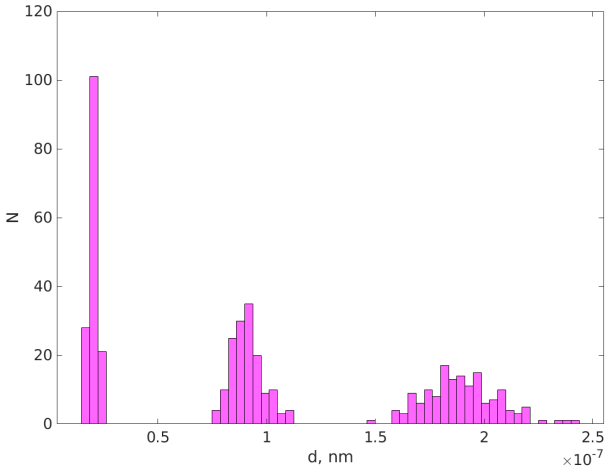

Fig. 7. Histogram of three simulated populations of particles diameters with 20 nm, 90 nm and 190 nm

4. CONCLUSIONS

The results presented regarding the DPT simulations validated the method proposed for size determinations of nanoparticles by proving that the software proposed works properly. The trajectories showed the recording of Brownian motions by identifying randomly movements of particles with different dimensions. Furthermore, the histograms regarding the size distribution of three different particles of 20 nm, 90 nm and 190 nm showed a nanometric diameter for the particles investigated, so further experiments are encouraged to be performed in the laboratory.

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