Particle Size Measurements of Dark and Concentrated Dispersions by Dynamic Light Scattering

In this paper, we introduce an innovative device for nanoparticle sizes measurement in dark and concentrated media based on dynamic light scattering (DLS). Conventional DLS is a powerful technique to characterisedilute and transparent dispersions of nanoparticles. However, it becomes ineffective in dark media, since the laser beam is absorbed by the sample and can induce an interfering effect. In the case of concentrated samples, the artefact of multiple scattering also biases the measurement. To circumvent these problems, we propose an original optical configuration that combines back-scattered light detection and the capability to control the sample thickness. The benefits of these improvements are discussed through experimental results obtained from measurement on model latex dispersions.

> *"Dynamic light scattering is a well-suited technique for nanoparticles size measurement in dilute and transparent dispersions"*

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INTRODUCTION

Research on nanoparticles covers a wide range of interests in the fields of physics, chemistry and material science. In particular, the characterisation of particle sizes and aggregates formation is a key issue in some processes of mesoporous materials preparation since they will affect the final network and micropore structures.

In this proceeding, we introduce an innovative device for nanoparticle size measurement in dark and concentrated media. The 'Vasco' is issued from a mature and patented technology [6] transferred from the Institut Français du Pétrole (IFP) to Cordouan Technologies and was initially developed to study the kinetics of asphaltene aggregation in toluene–heptane mixtures [1].

We first present the principle of conventional dynamic light scattering with dilute state before reviewing the main limitations of this technique. We especially focus on the case of dark and concentrated samples that traditionally present some major difficulties for such an analysis and which are typically the case for many research and industrial applications. Then, we show how the original optical configuration of 'Vasco' can overcome these kinds of experimental problems.

PRINCIPLE AND LIMITATIONS OF TRADITIONAL DYNAMIC LIGHT SCATTERING

Principle

Dynamic Light Scattering (DLS) is a powerful technique to characterise dilute and transparent dispersions of particles. Based on the analysis of scattered light fluctuations caused by the Brownian motion of particles, it provides sizes measurements from the nanometer up to a few microns.

Its principle consists in analysing the light scattered by a suspension as a function of time at a given angle (Figure 1). The correlation function calculated from the scattered light intensity fluctuations allows, then, to determine the diffusion coefficient D of Brownian particle [4,5].

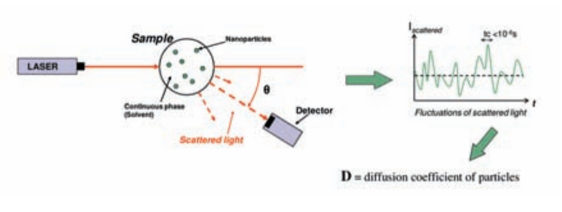

Figure 1. Illustration of the dynamic light scattering principle.

Knowing the viscosity of the continuous phase, the hydrodynamic radius of objects can then be evaluated through the Stokes-Einstein law (equation 1).

Where D is the diffusion coefficient of particles, Kb the Boltzmann constant, T the temperature, η the dynamic viscosity of the continuous phase and Rh the hydrodynamic radius. This law applies only to homogeneous and dense objects that are assumed to be spherical and without interactions. It reflects the fact that at a constant viscosity and temperature of the continuous phase, the larger the particles are, the slower they move in the solution. Note also that the hydrodynamic radius of an object corresponds to the radius of its dense core, plus the thickness of any layer of adsorbed molecules on its surface (e.g, polymers, surfactants), plus the thickness of its solvation layer (counter-ions moving with the particle) *(Figure 2)*. The hydrodynamic radius can, then, provide additional information compared with radius measured by others techniques, as Transmission Electron Microscopy (TEM).

Nevertheless, conventional DLS techniques have to deal with significant limitations, especially when analysing dark and concentrated dispersions.

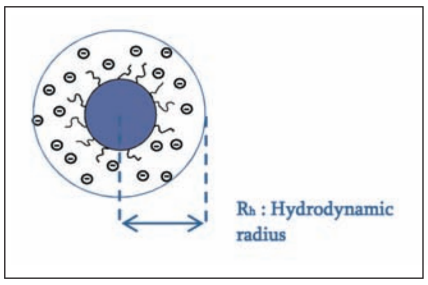

Figure 2. Selection of dispensers available on the market.

Measurement in dark and opaque media

Actually, traditional DLS becomes ineffective in opaque media, since no light is transmitted through the sample. Moreover, low heat capacity solvents or organic components can be extremely sensitive to the thermal effects induced by the absorption of the incident laser beam [2]. This phenomenon is usually underestimated but we show, for instance, that simply adding black ink to a latex dispersion can significantly affects the size measurement.

Figure 3 displays experimental results for a polystyrene latex dispersed in water, stabilised by ionic surfactants and having an average diameter of 30nm by TEM (latex synthesised in the EPCP laboratory, IPREM-CNRS, Pau, France). This sample was previously diluted to 0.001wt% to avoid concentration effects on the measurement. A direct DLS analysis of this transparent dispersion indicates that the average hydrodynamic diameter is 32nm (blue bars on the graph). However, after adding 10wt% of black and soluble organic ink to the sample *(see picture on Figure 4)*, we measure a diameter of 24nm (red bars on the graph), i.e. a decreased of 25% of the size value.

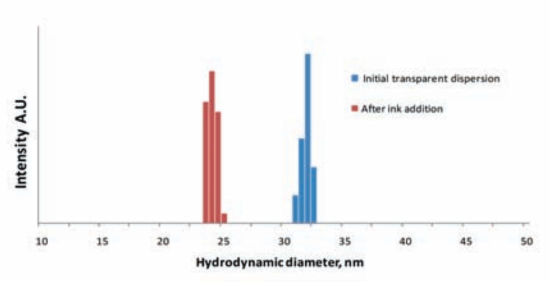

Figure 3. Selection of dispensers available on the market.

Note that the macroscopic change of sample viscosity and refractive index induced by the ink addition is taken into account for this diameter calculation and does not explain the variation. On the other hand, the local heating caused by laser absorption can strongly bias the measurement since it leads to a local change of the sample temperature and viscosity. It is also possible that a thermal effect induces a convective movement of particles in addition to the Brownian motion [3].

Figure 4. Selection of dispensers available on the market.

The multiple-scattering artifact

Results obtained on concentrated samples with conventional DLS are also highly affected by a phenomenon called multiple scattering artefact. Whereas, a photon is scattered one time in the volume of a diluted sample before being detected by the photo-detector, several scattering events occur in concentrated samples since particles are closer to each other *(Figure 5)*. This phenomenon interferes with the correlation calculations and leads usually to underestimate the hydrodynamic radius of particles.

Multiple scattering can quickly occurs with the increasing of concentration, and can be observed as soon as the sample becomes turbid.

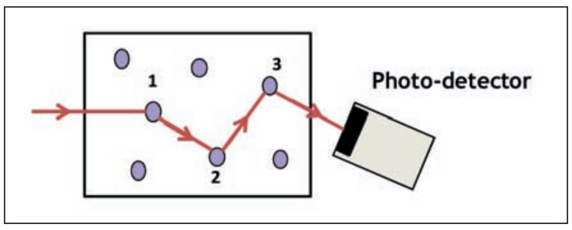

Figure 5. Selection of dispensers available on the market.

To illustrate this phenomenon a commercial standard latex (Merck Estapor® K010 microsphere having a diameter of 98nm by TEM) is analysed at two different concentration, 0.001wt% and 0.1wt%. *Figure 6* shows that a conventional DLS analysis of the more concentrated sample (red bars on the graph) gives an effective diameter of 84nm.

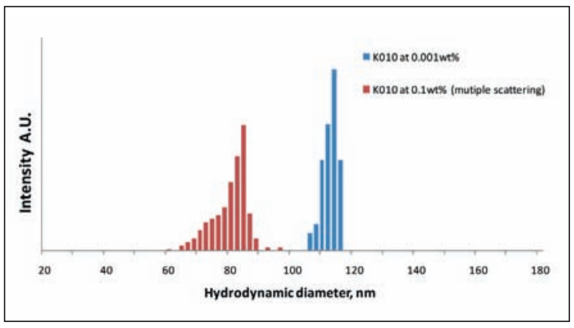

Figure 6. Selection of dispensers available on the market.

This value is quite lower than the hydrodynamic diameter measured in the diluted state (blue bars on the graph), i.e. 115nm and even lower than the dense core diameter of particles measured by TEM. This significant error on the measurement (27%) is a typical consequence of multiple scattering and is one of the reasons why DLS technique was traditionally devoted only to the very diluted samples.

SOLUTIONS PROVIDED BY THE SAMPLE CELL DESIGN

In order to circumvent these problems, we propose an original design of the sample cell to enhance the DLS instrument with back-scattered light detection and the capability to control the sample thickness. As presented in *Figure 8*, the bottom of the measuring cell is formed by the upper surface of a glass prism guiding the incident laser beam to the sample. This configuration allows also the photo-detector to collect the back-scattered light signal at an angle of 135°. In addition, the cell is hermetically closed by a mechanical system that includes a mobile glass rod with a photon trap. This rod can both control the sample thickness (down to few tens of microns) and absorb the excess of transmitted light.

Figure 7. Selection of dispensers available on the market.

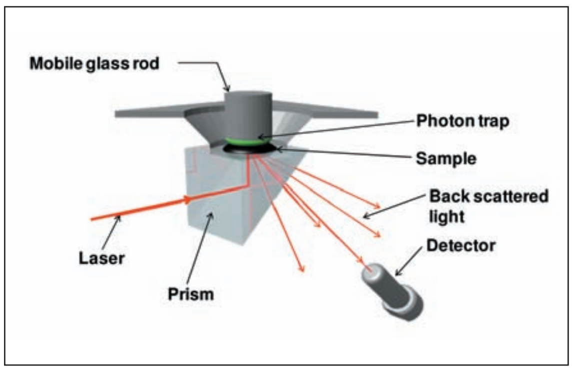

Figure 8. Selection of dispensers available on the market.

Back-scattered light detection presents two main benefits. In opaque media, it provides much higher detection efficiency than conventional transmission arrangement since scattered light does not have to cross the whole sample to be collected. Second, it decreases the multiple-scattering effect since it is less probable for a photon to be scattered several times backward than forward in the sample volume. However, this detection is usually insufficient to settle the problem with very concentrated systems. Moreover, it does not prevent the local thermal effect induced by the laser beam.

The measurement can then be strongly improved by the capability to control the sample thickness. Actually, for concentrated dispersions, it appears that lowering the volume of analysis reduces significantly the probability for a photon to be scattered several times.

Thus, the multiple-scattering artefact, observed with the 0.1wt% standard latex introduced in part 2.3 *(Figure 6)*, is well corrected by adjusting the sample thickness to 20 microns. Using the thin layer analysis mode, we actually measure a hydrodynamic diameter of 115nm (Figure 9.a), which is the expected value (same diameter than in the dilute state). This specific configuration also prevents the sample from being locally heated by the laser. It is well known, that light absorption is depending on the distance it travels through the material. This phenomenon is expressed in the Beer Lambert law (equation 2).

Where I and I0 are, respectively, the intensity of transmitted and incident light, α the material absorption coefficient and ℓ, the path length. Thus, the thinner is the sample layer, the lower is the laser absorption effect. Finally, the 'photon trap' in the cell mobile rod absorbs the excess of transmitted light.

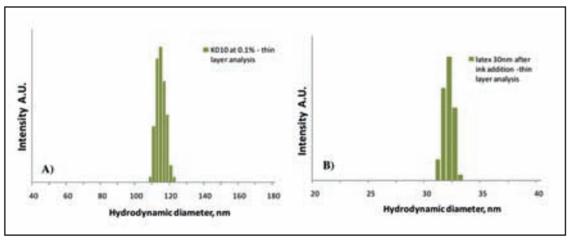

Figure 9. Selection of dispensers available on the market.

Figure 9.b presents a new measurement of the dark sample introduced in part 2.2. We observe that adjusting the sample thickness to 20 microns allows measuring the same hydrodynamic diameter than without adding black ink in the sample, i.e. 32nm. The thin layer analysis actually provides a significant improvement for such a dark sample.

CONCLUSION

Dynamic light scattering is a well-suited technique for nanoparticles size measurement in dilute and transparent dispersions. Nevertheless, conventional DLS techniques become ineffective in opaque media, since no light is transmitted through the sample. Moreover, low heat capacity solvents or organic components can be extremely sensitive to the thermal effects induced by the absorption of the incident laser beam. We show, for instance, that simply adding black ink to a latex dispersion can bias the measurement by 25%.

In the case of concentrated sample results obtained by conventional DLS are also affected by the artefact of multiple scattering. In comparison with the hydrodynamic diameter measured in the dilute state, we actually observe an error of 27% on a latex standard measurement when its concentration is raised to 0.1wt%.

In order to circumvent this problem, we propose an original design of the sample cell and the optics arrangement to combine two improvements of the DLS instrument: Back-scattered light detection which provides a much higher detection efficiency for opaque sample and decreases the instrument sensitivity to multiple scattering. The capability to control the sample thickness, down to few ten microns, which limits further this artefact and strongly reduces the laser thermal effect. These innovations make the instrument perfectly suitable for ink, paint or concentrated emulsion analysis, for example.

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