Measuring multi-modal particle sizes using DLScat

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Introduction

Simultaneous Multi-Angle Dynamic Light Scattering (DLS) is an advanced analytical technique designed to enhance the precision and reliability of particle size characterization in liquid suspensions. By simultaneously collecting scattered light at multiple detection angles, this method provides a more comprehensive scattering profile compared to conventional single-angle DLS [1-3]. This multi-angular approach mitigates angle-dependent measurement artifacts and significantly improves resolution, particularly for polydisperse or complex samples.

In the present study, Simultaneous Multi-Angle DLS was employed to characterize a bimodal particle mixture comprising 40 nm gold colloids and 600 nm polystyrene spheres. The technique enabled accurate differentiation of the two distinct particle populations within a single measurement, demonstrating its efficacy in resolving wide size distributions. The enhanced data quality and improved interpretability offered by Simultaneous Multi-Angle DLS with a combination of CONTIN algorithm make it a highly suitable tool for detailed analysis of nanoparticle systems, supporting more confident assessments of sample properties and overall quality.

Theory

Dynamic Light Scattering (DLS) analyses fluctuations in scattered light intensity to quantify the Brownian motion of particles in suspension. These fluctuations are rooted in thermal motion and can be translated into correlation functions, which provide access to diffusion behaviour and, ultimately, particle size. Please refer to the application note SI-0012 for detailed light scattering theory.

Size distribution analysis from DLS data typically employs either the Cumulant method for monomodal samples or the CONTIN algorithm for broader or polymodal distributions [4,5]. In this study, the bimodal sample was analyzed using CONTIN, a regularization technique well-suited for polydisperse systems. It provides stable, high-resolution size distributions without requiring assumptions about the number of particle populations. Combined with Simultaneous Multi-Angle DLS, CONTIN analysis enhances data resolution and interpretability, making this approach a robust and reliable solution for characterizing complex nanoparticle systems and assessing sample quality.

Sample Preparation

A standard and nearly monodispersed polystyrene particle suspension with a diameter of 600 nm (polydispersity index ≈ 0.05) and a concentration of 10 % w/v in water was procured from Sigma-Aldrich (Schnelldorf, Germany). Gold (Au) nanoparticle solution of 40 nm diameter (polydispersity index ≈ 0.08) and a concentration of 0.01 % is purchased from BBI Solutions (Freiburg, Germany). Milli-Q water was obtained from Sigma-Aldrich (Taufkirchen, Germany) and used as the dispersing medium. All measurements were conducted using a glass cuvette with an internal path length of 10 mm.

To prepare the sample for DLS measurements, 1 µL of the stock polystyrene solution and 100 µL of Au colloids were mixed with 25 mL of Milli-Q water. From this diluted suspension, 1 mL was transferred into the cuvette for measurement.

Results

The DLScat system characterizes particles by detecting scattered light simultaneously at multiple angles: forward (14.9°), side (74.4°, 90.0°, and 105.6°), and backward (163.0°). The particle size distribution of the 40 nm Au nanoparticles and 600 nm PS nanoparticles mixture is presented in Figure 1.

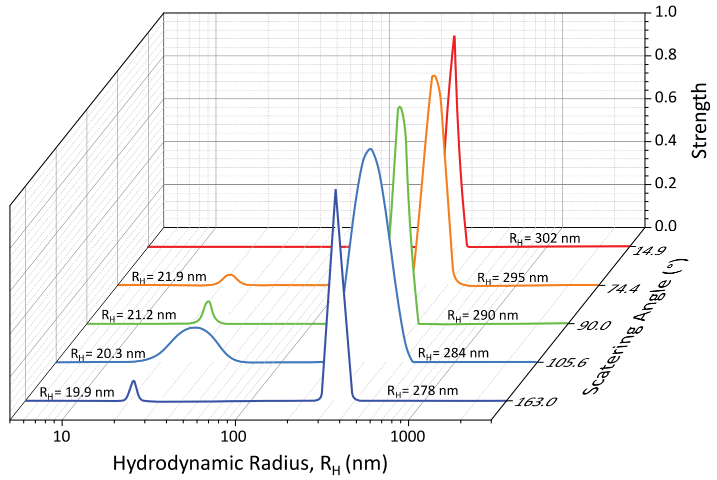

Fig. 1: Particle size distribution of a mixture of 40 nm gold colloids and 600 nm polystyrene spheres at multiple scattering angles

For particles smaller than ≈ 60 nm, backscattering alone is generally sufficient to estimate size accurately, as the scattering is nearly isotropic. However, for larger particles, scattering becomes angle-dependent (anisotropic), and relying on a single detection angle can lead to incomplete or misleading size estimations. Each angle effectively samples a slightly different distribution, especially in the presence of multimodal particles.

In such cases, single-angle autocorrelation functions can be significantly distorted, potentially yielding incorrect hydrodynamic radius (R_H) values. This limitation is illustrated in Figure 1, where forward angle detects only one dominant size mode, potentially masking subtle polydispersity or minor populations. To improve sizing accuracy and resolve any angle-dependent scattering effects, the decay rate Γ is measured across different angles (using CONTIN fitting) and plotted as a function of the squared scattering vector q^2, which is directly related to the scattering angle. Two different Γ values were obtained at all the scattering angles except forward scattering. The larger PS nanoparticles of 600 nm dominate in the forward scattering.

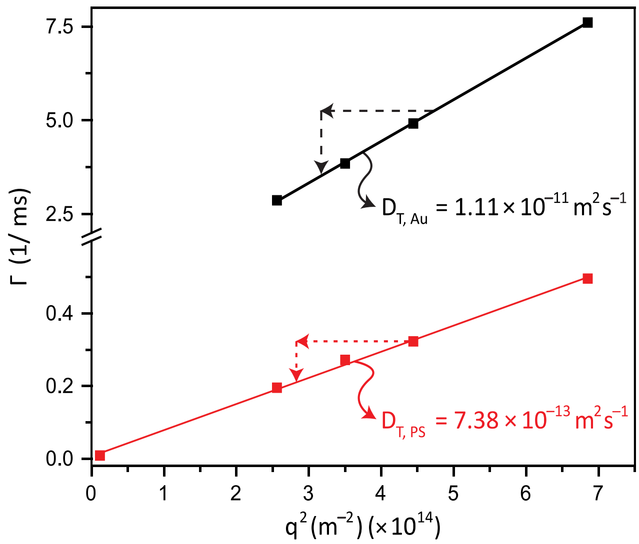

Fig. 2: Calculation of both the translational diffusion coefficients ($D_{T,Au}$ and $D_{T,PS}$).

By performing a linear fit to this data and extrapolating to q^2 = 0, two angle-independent diffusion coefficients D_0 is obtained. Using the Stokes–Einstein equation, D_T is then converted to the hydrodynamic radius R_H. In this experiment, the calculated $R_{H,0}$ were **20.4 nm** and **307.7 nm**.

Table 1: DLS parameters of the mixture of Au and PS nanoparticles to calculate the hydrodynamic radius

		Peak-1		Peak-2	
Scattering Angle (Θ)	q^2 (m^{-2})	Γ (s^{-1})	R_H (nm)	Γ (s^{-1})	R_H (nm)
14.9	1.17×10^{13}			8.8	302
74.4	2.56×10^{13}	2865.7	21.9	195.2	295
90.0	3.50×10^{13}	3846.9	21.2	271.8	290
105.6	4.44×10^{13}	4912.2	20.3	322.8	310
163.0	6.85×10^{13}	7599.5	19.9	495.8	311
D_T $(m^2 s^{-1})$		1.11×10^{-12}		7.38×10^{-13}	
$R_{H,0}$ (nm)		20.4		307.7	

It is important to note that the DLS determines the hydrodynamic size, which accounts for the particle core plus any surface-bound solvent molecules or stabilizing layers (e.g., surfactants, adsorbed ions). In the case of gold colloids and polystyrene spheres dispersed in water, a thin hydration shell forms around each particle, slightly increasing its effective size in solution.

DLScat offers two fitting methods CONTIN and cumulant for size characterization. For samples exhibiting low polydispersity (polydispersity index ≈ 0.05) and a single particle population, multi-order cumulant fitting is appropriate. For more complex, multimodal distributions, the CONTIN algorithm provides superior resolution and more accurate size estimations.

DISCUSSION

To gain insight in the sample's behaviour, the D_{app} vs q^2 plot (D_{app} is the diffusion coefficient calculated from each scattering angle) can be plotted and studied in detail. The negative slope suggests that the particles are either unstable or still growing. The positive slope refers to the stabilized particles with a certain amount of polydispersity but if the slope is close to 0, the particles are either monodispersed or nearly monodisperse, or the particles are too small to be angle-dependent and do not show any changes in the diffusion coefficient upon changing the scattering angle.

DLScat based on our powerful Time-Tagger 20 technology makes it possible to use Simultaneous Multi-Angle DLS technique that helps in determining the particle size information with much higher resolution compared to the single scattering angle DLS instruments. The more accurate size measurements can add significant value to the user understanding on the sample measured while performing other techniques such as TEM and SANS/SAXS etc. DLScat covers the limitations of goniometer-based DLS systems especially in the time-sensitive sample.

CONCLUSION

The DLScat system, powered by our proprietary Time Tagger 20 technology, enables Simultaneous Multi-Angle DLS with unmatched temporal resolution and sensitivity. By capturing scattering data across a wide range of angles in a single acquisition, DLScat offers an outstanding resolution and reliability.

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