Dynamic light scattering (DLS)

Lecture by

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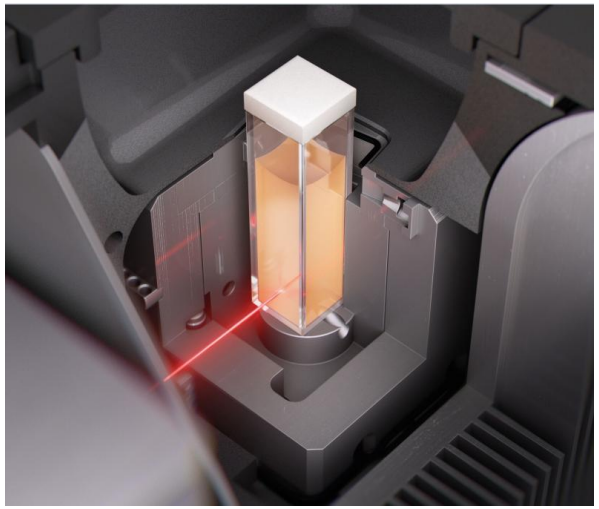


The principles of dynamic light scattering

Dynamic light scattering (DLS) definition

Is the most common measurement technique for particle size analysis in the nanometer range up to several micrometers (average size and size distribution of particles in a suspension).

Advantages of this technique:

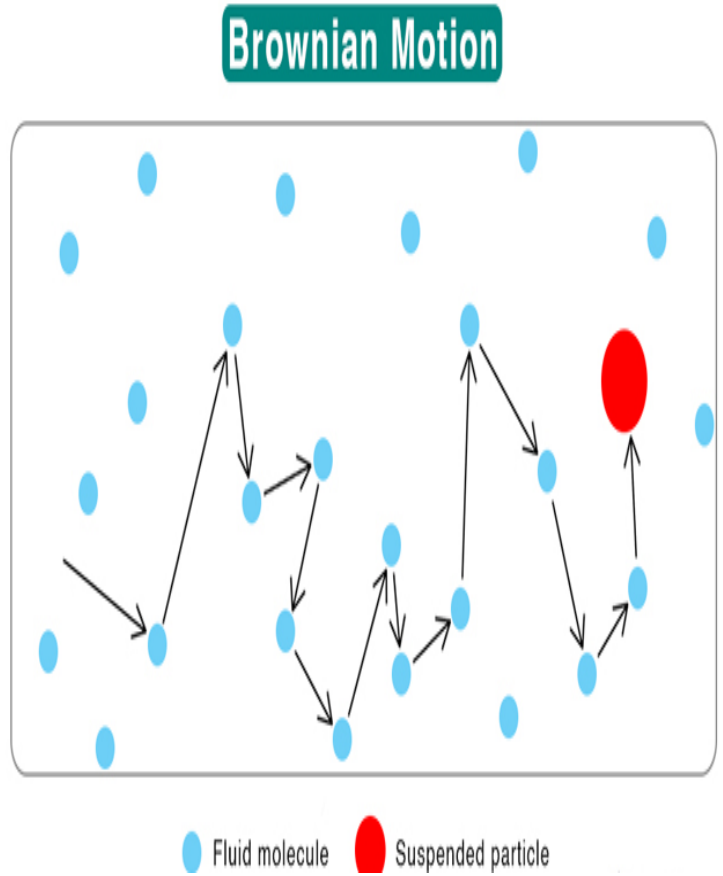
1. Relatively fast
2. Non-invasive
3. Requires minimal sample preparation and can be re-used after the measurement. But it does require low particle concentration.

Outlines

- DLS theory
- DLS setup
- Determining particle size.
- Typical outcome of a DLS analysis
- Practical tips on measurement settings and data verification.

Theoretical background of dynamic light scattering

- **Dynamic light scattering (DLS) is based on the Brownian motion of dispersed particles.**
- When particles are dispersed in a liquid they move randomly in all directions.



Principle of Brownian motion:

Particles are constantly colliding with solvent molecules. These collisions cause a certain amount of energy to be transferred, which induces particle movement.

The energy transfer is more or less constant and therefore has a greater effect on smaller particles.

As a result, smaller particles are moving at higher speeds than larger particles.

If you know all other parameters which have an influence on particle movement, you can determine the hydrodynamic diameter by measuring the speed of the particles.

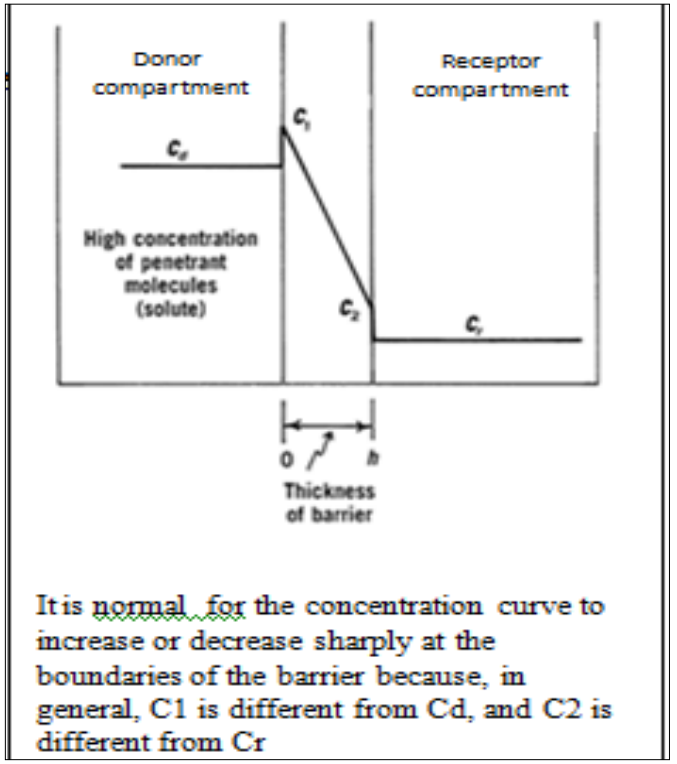
- The relation between the **speed of the particles and the particle size** is given by the Stokes-Einstein equation (Equation 1). The **Stokes-Einstein equation** is a formula that relates the **diffusion coefficient** of a particle in a fluid to **temperature, viscosity**, and the **particle's size**. It bridges **statistical mechanics** (Einstein) with **fluid dynamics** (Stokes).

- The **speed of the particles** is given by the translational diffusion coefficient D.

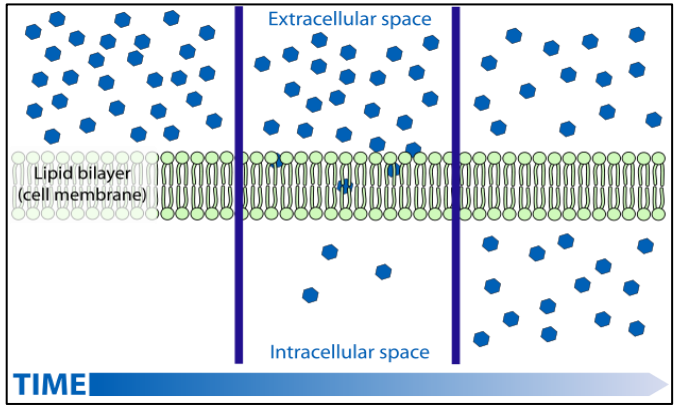
- Further, the equation includes the **viscosity of the dispersant and the temperature because both parameters directly influence particle movement.**

- Higher temperature → faster diffusion (since thermal energy increases).
- Larger particle or more viscous fluid → slower diffusion.

- A basic requirement for the Stokes-Einstein equation is that the **movement of the particles needs to be solely based on Brownian motion.**



It is normal for the concentration curve to increase or decrease sharply at the boundaries of the barrier because, in general, C1 is different from Cd, and C2 is different from Cr



- If there is sedimentation (Large particles), there is no random movement, which would lead to inaccurate results.

- Therefore, the onset of sedimentation indicates the upper size limit **(USL)** for DLS measurements. In contrast, the lower size limit **(LSL)** is defined by the signal-to-noise ratio. Small particles do not scatter much light, which leads to an insufficient measurement signal.

Note: Signal-to-Noise Ratio (SNR) in DLS refers to the ratio of the intensity of the **scattered light signal** (from particles) to the **background noise** (from detector noise, ambient light, or electronic interference).

$$\text{SNR} = \frac{\text{Signal (scattered intensity)}}{\text{Noise (background fluctuations)}}$$

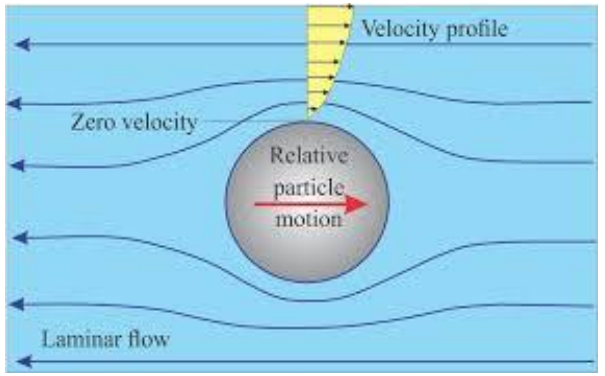
- **DLS measures Brownian motion of particles by analyzing fluctuations in scattered light intensity** — so **accurate fluctuation data** is critical. If noise dominates:

The **autocorrelation function** becomes distorted, **particle size distributions** may be incorrect, and hard to distinguish **real signal** from **random variations**.

Equation 1:

The Stokes-Einstein equation

$$\mathbf{D} = \frac{K_B \mathbf{T}}{6\pi\eta R_H}$$



D Translational diffusion coefficient of particles [m²/sec] – "represent speed of the particles"

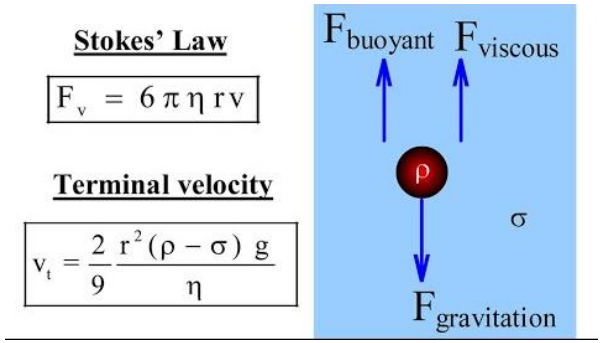
k_B Boltzmann constant [m².kg/K.s²]= 1.38 X 10^{-3} (J/K)

T Temperature [K]

η Dynamic viscosity of the fluid [Pa.s]

R_H Hydrodynamic spherical radius [m]

π (pi) approximately = 3.1416



The basic DLS setup

The basic setup of a DLS instrument:

- A single frequency laser is directed to the sample contained in a cuvette.
- If there are particles in the sample, the incident laser light gets scattered in all directions.
- The scattered light is detected at a certain angle over time and this signal is used to determine (**diffusion coefficient and the particle size**) by the Stokes-Einstein equation.

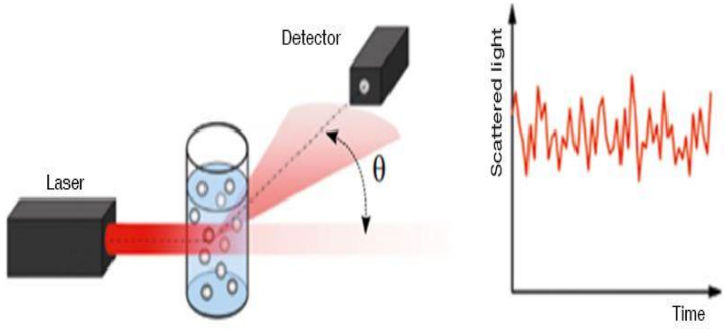


Figure 1: Basic setup of a DLS measurement system. The sample is contained in a cuvette. The scattered light of the incident laser can be detected at different angles.

Note:

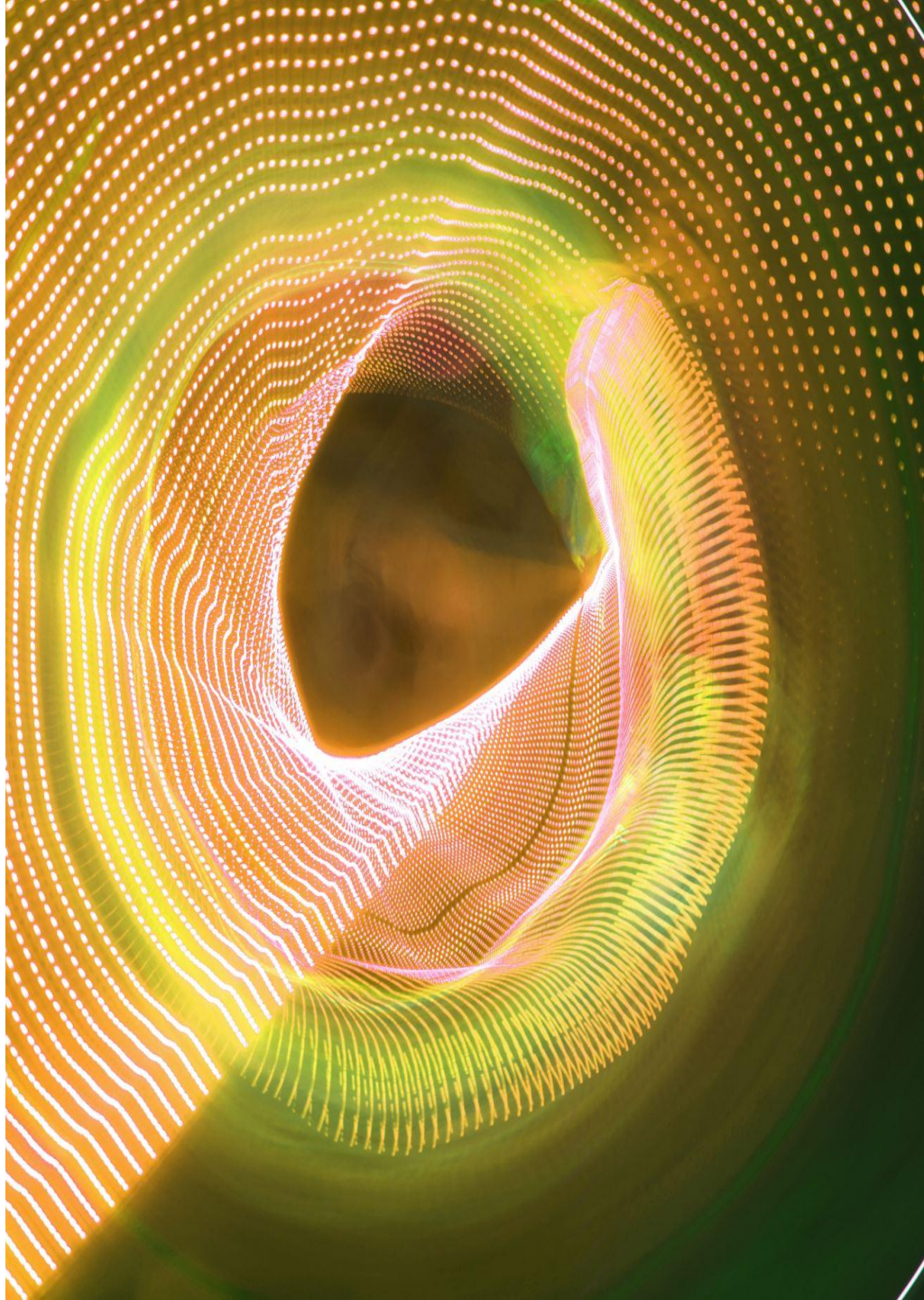
1. The incident **laser light** is usually **attenuated by a gray filter** which is placed between the laser and the cuvette (filter settings are either automatically adjusted by the instrument or manually).

2. When **turbid samples** are measured the detector would **not be able to process the amount of photons** (laser light is attenuated to receive a sufficient but processable signal at the detector).

3. Modern DLS instruments include two, or in the case of Litesizer™ 500 (3 detection angles) for particle size measurements. Depending on the turbidity of the sample, side scattering (90°) or back scattering (175°) is more suitable. A forward angle (15°) can be used to monitor aggregation.

Intensity trace and correlation function

- The **scattered light** is detected over a certain time period to (**monitor the movement of the particles**).
- The intensity of the scattered light is not constant but will fluctuate over time.
- **Smaller particles,** which are moving at higher speeds, **show faster fluctuations** than larger particles.
- **Larger particles,** result in **higher amplitudes** between the maximum and minimum scattering intensities, as shown in Figure 2 (upper panels).
- This initial intensity trace is further used to generate a correlation function (Fig. 2, lower panels).



The **correlation function** describes (**how long a particle is located at the same spot within the sample**).

- **Small particles** move quickly so the decay is fast.
- **Larger particles** move slowly so the decay of the correlation function is delayed.

At the beginning the correlation function is linear and almost constant (particle is still at the same position as it was the moment before).

Later, exponential decay of the correlation function (the particle is moving).

Notes:

- The **baseline** (indicate there is no similarity to the initial spot, and the correlation function shows a linear behavior again).
- The **decay of the correlation function** (gives information of the size-dependent movement).
- The **decay** (indirect measure of the time the particles need to change their positions).

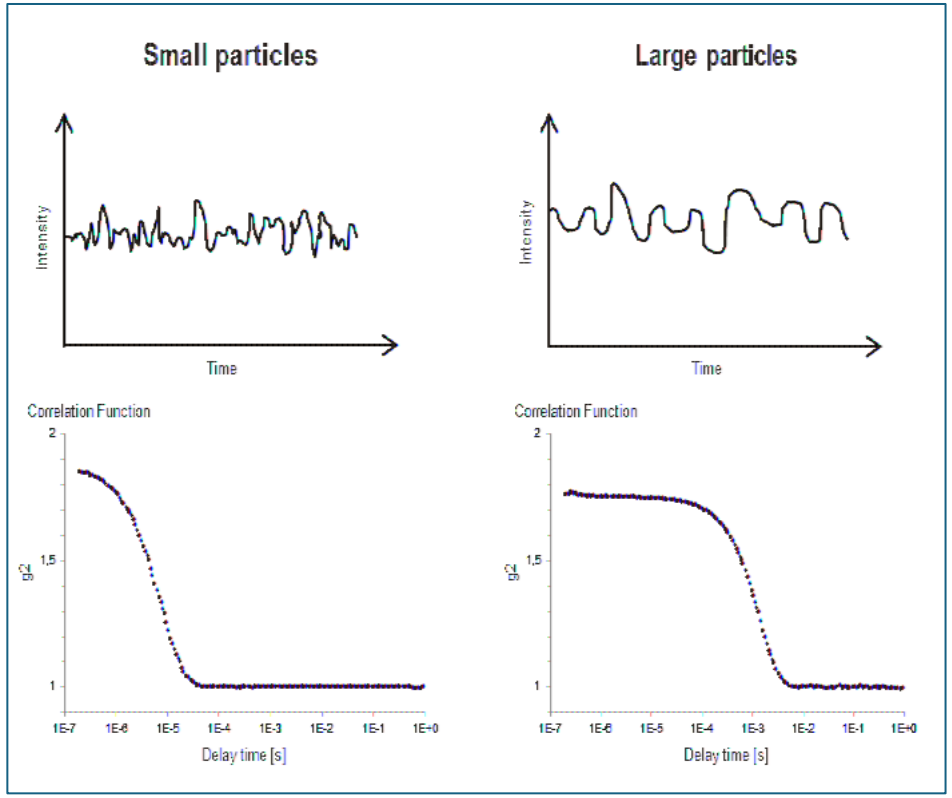


Figure 2: Differences in the intensity trace and correlation function of large and small particles. Smaller particles show faster fluctuations of the scattered light and a faster decay of the correlation function.

- **Correlation function** is a mathematical description of the fluctuations of the scattered light (determine the translational diffusion coefficient).
- The **diffusion coefficient** is determined from the cumulant algorithm to fit the correlation function (ISO-standardized procedure).
- The hydrodynamic diameter (i.e. particle size) is obtained by Stokes-Einstein equation.

- The **intensity of the scattered light at a time t** is compared with the intensity of the same intensity trace shifted by the delay time τ (tau) as visualized in Figure 3. (Different delay times are marked by a different color).

- **Single value of G2** is obtained by (adding the product of two values at the same time of two intensity traces), which is indicated by the colored connection for one position per delay time.

Different delay times results in the desired correlation function.

- These calculations are done in real time and plotted over a logarithmic time axis.

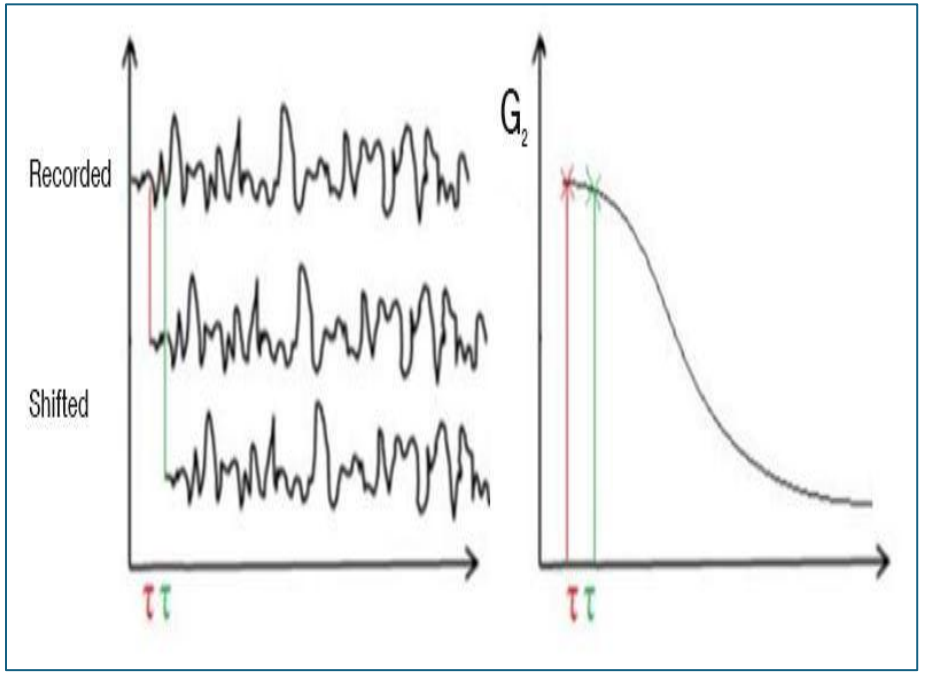


Figure 3: Translating the intensity trace (left panel) into a correlation function (right panel)

Measurement results

- The term **hydrodynamic diameter** (refers to the particle size of smooth, spherical particles which diffuse at the same speed as the particles of the sample).
- **Polydispersity index (PDI)** is describing the broadness of the particle size distribution (PDI calculated by the cumulant method). A value below 10 % reflects a monodisperse sample and indicates that all of the measured particles have almost the same size.

Note:

- The particle size of the sample is not measured directly but is based on the movement of the particles.
- PDI does not provide any information about the shape of the size distribution or the ratio between two particle fractions.
- This information is given by the particle size distribution chart, which is part of the one-page workflow of the Litesizer™ 100/500 software (see Figure 4).

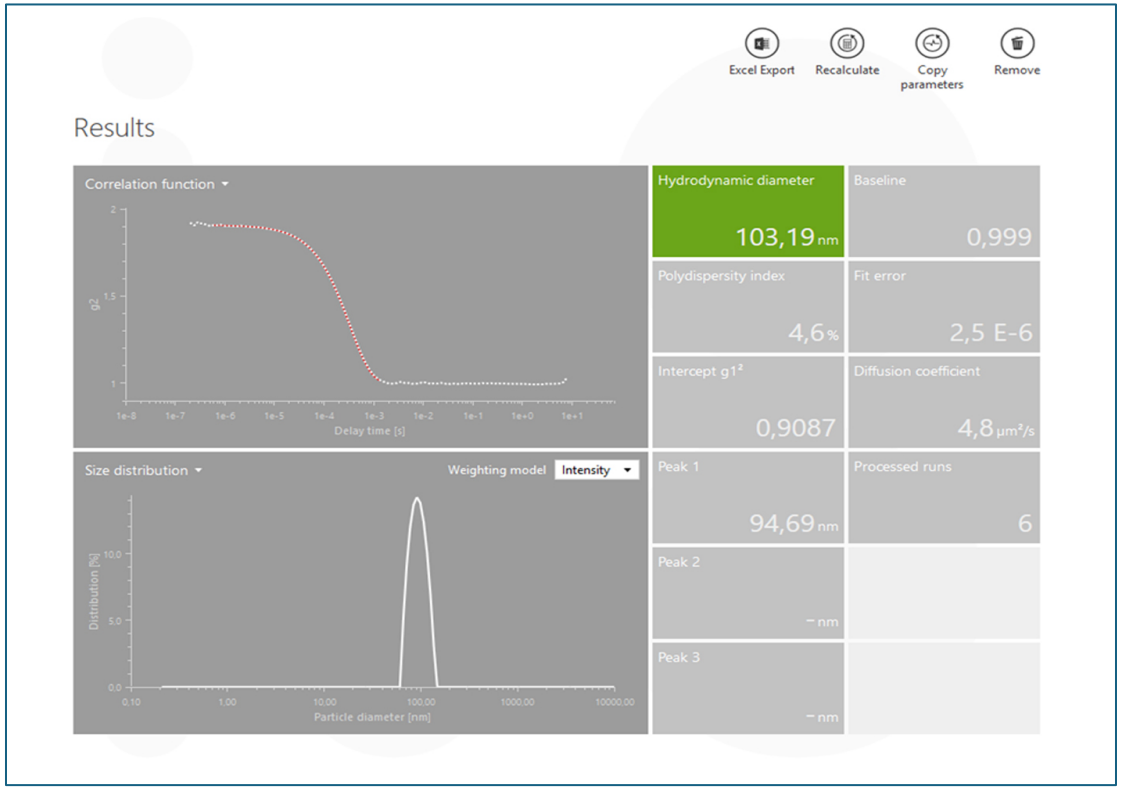
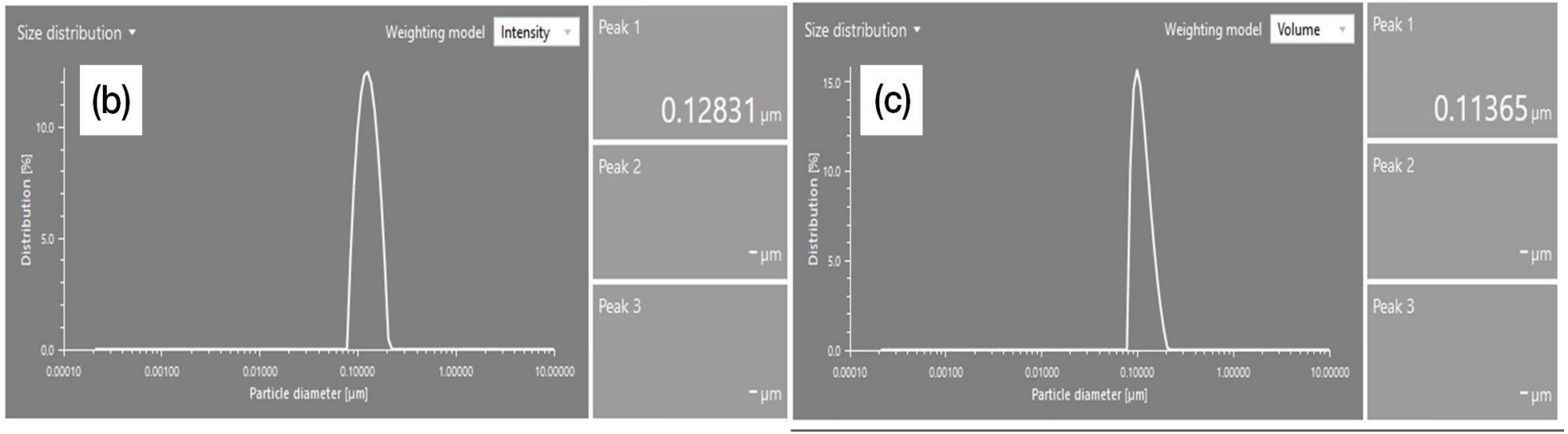


Figure 4: Typical result overview of a DLS measurement. The initial results (hydrodynamic diameter, polydispersity index) are displayed as well as information about the correlation function (baseline, intercept, etc.). The particle size distribution chart gives further information about different size populations within the measured sample.

- As the results of DLS measurements are intensity-based technique (the intensity fluctuations over time are detected) this is the primary weighting model displayed in a DLS software.

Its emphasis on **larger particles** (they scatter more light than smaller particles).

- The intensity-based distribution can be re-calculated to a volume- and number-based distribution that show a tendency to **smaller particle fractions** (the material refractive index and the absorbance of the measured sample at the wavelength of the laser need to be known).



Verifying the data quality of DLS measurements

- During a measurement, **DLS software shows live signals of the intensity trace and the generated correlation function**. These signals provide a lot of information on the data quality:

1. The **intensity trace** show regular fluctuations of the scattered light, if **monodisperse samples** are measured (when sharp spikes are observed, the sample is contaminated by dust particles or aggregates).

2. The **intensity trace** ramps up or down (A steady increase or decrease in intensity trace shows a thermal gradient during the measurement time). Further, a **steady increase can indicate aggregation**, and a **steady decrease may be due to sedimentation**.

3. The **correlation function** gives information about (**signal-to-noise ratio** and **presence of dust particles or aggregates**). The **signal-to-noise ratio of the correlation function at small delay times, called intercept.** If there is not enough signal collected, difference will be low and no meaningful correlation function can be generated (if very small particles are measured or the particle concentration is too low).

4. The **correlation function** for monomodal dispersion (smooth with a single exponential decay).

5. A **non-linear baseline** (several bumps) **indicates the presence of dust particles or aggregates**.

Choosing the right measurement angle

- Modern DLS instruments provide different detection angles for particle size measurements (**typically at 15°, 90°, and 175°**). Litesizer™ 500 uses the included transmittance measurement for automatic angle selection (Side- or back scattering is automatically selected by the instrument depending on which is the most suitable angle for the measured sample).

- **If the measurement is performed at 175°, this is back scattering**. At this angle the scattering volume (the volume where there is overlap between incident laser beam and the detected light) is near the front cuvette wall (i.e. path length of the laser within the sample is very short).

Uses: for highly concentrated and turbid samples (minimizes the effect of multiple scattering).

- Multiple scattering means that the light is scattered at more than one particle, which can interfere with the measurement signal.

- In order to further minimize the path length of the laser the focus position can also be adjusted (Figure 5).

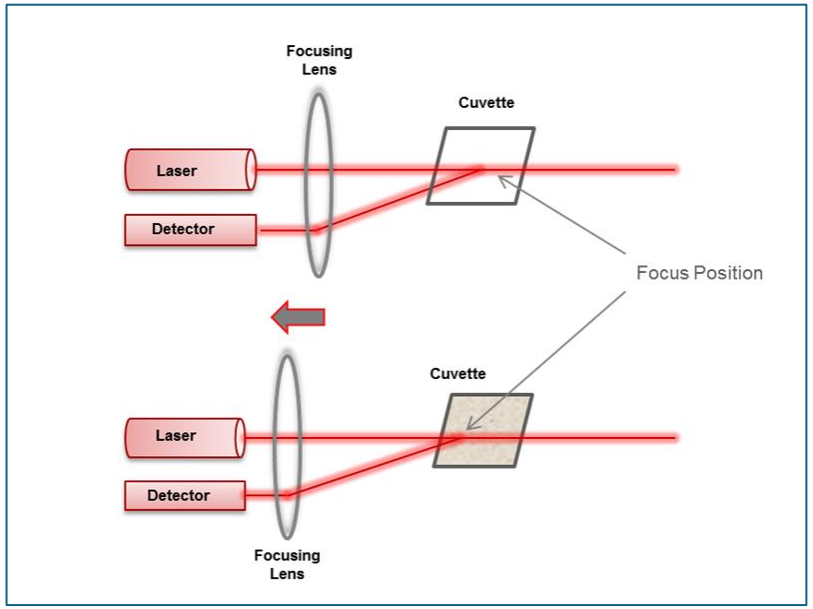


Figure 5: DLS instruments can adjust the focus position by moving a focusing lens. If the focus position is near the front cuvette wall, multiple scattering events can be minimized. The overlap of the incident laser beam and the scattered light is called scattering volume.

- Side scattering at 90° (angle of choice for weakly scattering samples of small particles) (Because the flare created by the laser at the cuvette wall is blocked from entering the detection optics and this leads to a cleaner result).

Measurements done using the side angle are less sensitive to dirt and scratches on the cuvette wall.

- The forward angle at 15° is used to (monitor aggregation or if a sample of smaller particles contains a few large particles). As larger particles scatter more light in the forward direction than in other directions these particles are emphasized at this angle.

By comparing the results with other measurement angles the presence of aggregates can be monitored.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