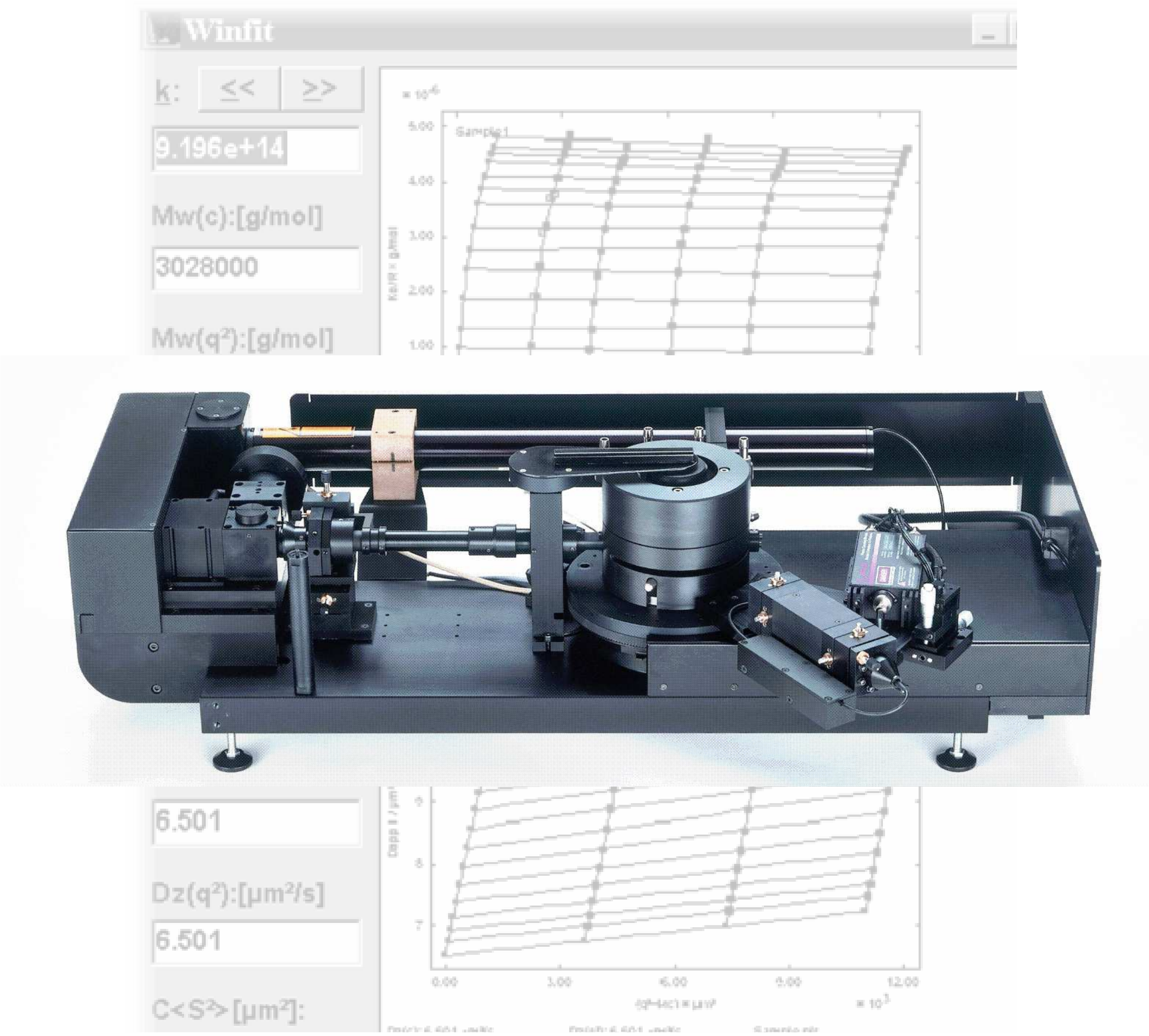
# *ALV / CGS-3 Super Compact Goniometer System*

## A Guide to perform
## Simultaneous Dynamic & Static Light Scattering Measurements
## using the ALV-5000 & 60X0 Software



Winfit

k: 9.196e+14

Mw(c):[g/mol] 3028000

Mw(q²):[g/mol]

6.501

Dz(q²):[µm²/s] 6.501

C<S²>[µm²]:

# Content

# 1. General Notes about Simultaneous Static and Dynamic Light Scattering Measurements

## *1.1 Introduction*

The ALV / CGS-3 Compact Goniometer System is designed to perform Dynamic (DLS) and Static Light Scattering (SLS) data simultaneously.
Two different data file systems are used in the ALV-5000 & 60X0 software. The correlation function and count rate trace data together with all relevant sample parameters can be stored as TAB separated ASCII values, and, the angular and concentration dependent normalized mean values of the scattering intensity as well as diffusion coefficients derived by a Cumulant analysis (up to third order) of the correlation functions are stored in a file with a special binary record format (DILS file format).
An analysis of SLS/DLS data stored in DILS file format can easily be performed using the ALV/Static & Dynamic Fit and Plot program by creating ZIMM, BERRY and GUINIER plots, plots of diffusion coefficients versus $q^2$ and form factor plots.

## *1.2 Measurement of Laser Beam Intensity and Sample Temperature*

The ALV / CGS-3 System Compact Goniometer System provides with the possibility to measure the laser beam intensity using a monitor diode and the sample temperature using a Pt-100 temperature probe inserted in the index matching fluid.
Both information is vital for high quality Static Light Scattering measurements and once the appropriate settings are performed in the "Option Setup" after each restart of the ALV-5000 & 60X0 Correlator software the measurements are initialized automatically.
Performing Static Light Scattering without monitoring of the laser beam intensity results in a limitation of the precision of these measurements due to the laser intensity fluctuation, which can be as high as +/- 3% for long time measurements.
Temperature measurement is necessary for correcting the Rayleigh Ratios for the STANDARD, but usually the absolute influence is significantly smaller than that of laser intensity fluctuation. Please remember, that the ALV/Pt-100 probes used for temperature measurement have an absolute precision of +/- 0.2 K within the range of 263.17 ... 373.17 K and higher absolute precision requires special calibration by the user. The relative precision of the temperature measurement is about +/- 0.01 K.

## *1.3 Measurement of the standard sample (STANDARD Mode)*

The measurement of a STANDARD sample with known Rayleigh Ratio is the most critical point in Static Light Scattering, which defines the limit of accuracy for estimation of the absolute value of the scattering ratio of an unknown sample.
All goniometer systems are in general not adjusted to give absolute values of measured scattering intensities, but relative only. To perform measurements of absolute values of static light scattering intensities the optical efficiency of a measuring system is calibrated by measurement of a STANDARD sample with a-priori known Rayleigh Ratio.
A common STANDARD used is toluene, due to its very well tabulated values of the Rayleigh Ratios and existing interpolation formula to correct the Rayleigh Ratios for different wavelengths of the laser and the actual sample temperature.
But, about 30% of the light scattered by toluene is due to depolarised light scattering. This fact has to be considered because the ALV Compact Goniometer System offers for SLS/DLS measurements the following two set-up's of detection systems:

1. **Standard set-up (VU set-up):** vertical polarised laser light and non-polarised detection, and
2. **Optional set-up (VV set-up):** vertical polarised laser light and vertical polarised detection (e.g., using a Glan-Thompson prism).

The values of the Rayleigh Ratio for toluene differ in both cases by about 30% and depending on the actual set-up the correct value has to be selected for calculation (see chapter 2.2.3).

If the count rate is very low, an usual situation for the STANDARD measurement (since no scattering particles are within the sample, but scattering is just due density fluctuations within the fluid), the precision of the measurement is shot noise limited, that is the finite number of photons detected with the total measurement time is the major noise source for this measurement.

A good approximation to this noise contribution is the standard Gaussian approximation, i.e.,

$$3\sigma = \pm 3\,\frac{\sqrt{N}}{N}$$

with $N$ being the total number of photons detected. That means, a 1 kHz count rate requires about 30 s of total measurement time for a 1% precision and the three sigma approximation (99,5 % of all measurements are within this error region).

The STANDARD measurement should be performed with highest possible precision, and, in order to check the current mechanical and optical alignment conditions with very small angular steps (use 1° steps if possible). The precision machined mechanics of ALV-goniometer systems ensures that these measured STANDARD values remain within the limits measured for very long times, usually more than 6 months, provided the ambient temperature of the room is kept at the set temperature within ± 1°C. However, to perform SLS measurements with highest precision it is recommended to perform a STANDARD measurement prior to the measurement of a sample series at those angles, where the sample series will be measured.

### *1.4 Measurement of the solvent sample* (SOLVENT Mode)

SLS measurements are often performed on dilute solutions, where the excess scattering ratio is used to estimate molecular weights, radius of gyration and other relevant physical parameters. Therefore, the knowledge of the scattering ratio of the solvent is required to obtain the excess scattering ratio.
If the STANDARD and SOLVENT sample are identical (both toluene, for example), the file obtained from the STANDARD measurement can also be used as the SOLVENT file. Otherwise a measurement of the scattering intensities of the solvent is required, and the same remarks regarding measurement conditions as for the STANDARD measurement apply.

For further data evaluation using the SOLVENT data, only the scattering ratio and refractive index of the solvent are of interest, all other parameters (Rayleigh Ratio etc.) stored in the file are ignored in further calculations.

### *1.5 Measurement of the solution samples* (SOLUTION Mode)

In SOLUTION mode angular dependent values of the scattering intensity of a solution are measured and absolute scattering ratios or excess scattering ratios are calculated based on the STANDARD and SOLVENT measurement. Furthermore, apparent diffusion coefficients can be obtained from Cumulant analysis up to third order and stored together with the scattering ratios of the solution.
Results of successive measurement of sample series with different concentrations can be appended to one file.

In general, the measurement conditions in SOLUTION mode are similar to that of the STANDARD or SOLVENT mode, but one must be take care of the following:

- Depending on the size of the scattering particles the scattering intensities may vary with the scattering angle and the intensity is increasing with smaller angles, thus a dynamics of more than a factor of $10^4$ in the intensity can be detected over the entire angular range (e.g., Mie scattering regime).
  Adjustment of the laser beam intensity at the lowest measurement angle to such a scattering intensity not exceeding the safe intensity level of the actually used photon detector ensures proper operation and avoids possible damage of the detector due to intensity overload. Furthermore, the adjustment has to be made so that a level of laser beam intensity is chosen that still guarantees a linear relation between photon density and count rate.
- AutoScaling should be switched on (see chapter 2.1).
- The measurement duration of a single run depends on the observed largest correlation time $t_c$ and is in most cases defined by diffusion noise (or whatever process responsible for the observed correlation) rather than photon noise. Typically, the fluctuation of the light scattered due to the particle diffusion becomes as large as several 10 ms at low angles and measurement precision may require total measurement times of several 10 s, even if shot noise considerations only may lead to much smaller measurement times. A rough estimation of the diffusion noise can be obtained from the following relation:

$$3\sigma_D \cong \pm 12\,\sqrt{\frac{t_c}{duration}}$$

# 2. Performing Simultaneous SLS and DLS Measurements

## *2.1 Setting of General Parameters*

Prior to start a measurement in STANDARD, SOLVENT or SOLUTION mode using the QuickSet "General DLS and SLS" the following parameters should be checked for correct setting (for more information please refer to the on-line help of the ALV-5000 & 60X0 Correlator software:

1. Option Setup (Menu Setup):
   communication port for communication with the LSE-unit,
   temperature and monitor diode measurement,
   Pseudo-cross mode selected, if Dual-APD used for detection,
   count rate alert (5000 kHz)

2. ALV-Correlator Setup (Menu Setup):
   correlation mode, (AUTO, SINGLE or CROSS)
   Autoscaling (off in STANDARD and SOLVENT mode, on in SOLUTION mode),

3. Sample Description (Menu Sample):
   sample name,
   refractive index and viscosity of solvent or sample res.,
   laser wavelength,

4. AutoSave Option (Menu File)
   to store the individual correlation functions for further data analysis if required (only in SOLUTION mode).

## *2.2 The QuickSet "General DLS and SLS" (Menu QuickSet, Dynamic / Static Light Scattering*

### 2.2.1 General remarks

The QuickSet "General DLS and SLS" has to be used to perform any angular dependent SLS and/or DLS measurements.
All parameters necessary to perform a measurement are set in 3 steps, the first is to set *Measurement Control parameters*, the second to check the *Static & Dynamic LS Options* and the third to define the *Measurement Type* and to enter the appropriate filename to store data. Once the parameters are set a measurement can be started by clicking the *Start Measurement* button.
If the check box "Generate measurement protocol" is set the window *Static/Dynamic Light Scattering Data* containing a table of the measured quantities and a plot of the calculated scattering ratio vs. angle is automatically opened to display the results of the measurement. Clicking the *Stop Measurement* button at the bottom of this window interrupts the actual measurement after finishing the actual run.

After completion of a particular measurement or in case of interrupting a measurement a new measurement can only be started using the QuickSet "General DLS and SLS" again. After starting a new measurement the user is asked either to clear all previous results in the protocol table of the window *Static/Dynamic Light Scattering Data* or to append the new data. Up to 500 measurements can be displayed in the table, this corresponds, e.g., to a measurement of 10 different samples or concentrations at 50 scattering angles. In STANDARD and SOLVENT mode data are **not** appended to the files, instead old data in the files are overwritten. Therefore, to proceed with a STANDARD or SOLVENT measurement after interrupting the measurement a new filename must be entered and the data can only be merged into one file after completion of the measurement using the MS-WINDOWS® Editor.

### 2.2.2 Step 1: Measurement Control

Up to 6 ranges with particular settings for minimum and maximum angle, angular step increase, number of runs per angle and duration of a single run can be defined. At least 1 range must be entered into the table using the button *Accept this Set* to enable starting a measurement via the button *Start Measurement*.

For further data treatment it is recommended to use the same settings of minimum, maximum angle and angular step increase for corresponding measurement in STANDARD, SOLVENT and SOLUTION mode, although it is not strictly required.
A Dust Filter can be enabled to repeat a measurement at a particular angle if the standard deviation of the measured mean count rates of all runs at this particular angle exceeds the value set.

### 2.2.3 Step 2: Static & Dynamic LS Options

The following options can be enabled:

- *Measure and correct for detector dark counts*:
  Measurement and correction of detector dark counts should be performed if the count rate of the sample at 90° scattering angle (usually in STANDARD or SOLVENT mode) is not larger than a factor of 100 compared to the dark count rate of the photon detection unit. If the option is enabled, a 30 s measurement of the dark count is performed prior to start the angular dependent measurement and the measured mean dark count rate is then subtracted from the measured mean count rate of each single run.

  The default setting of this option is disabled.

- *Use Toluene Rayleigh Ratios as standard:*
  If this option is enabled the program assumes toluene be used as standard sample and the Rayleigh Ratio $RR_{VU}$ of toluene is extrapolated for the laser wavelength set and temperature measured assuming a non-polarized detection (VU set-up). Furthermore, the refractive index set in the corresponding input line is used as refractive index of the standard, independent on the refractive index set in the *Menu Sample*.
  Provided a polarized detection (VV set-up) is used the sub-option *Compute Rayleigh Ratio for VV-Scattering* must be enabled to use the correct Rayleigh Ratio $RR_{VV}$ instead of $RR_{VU}$.
  If the option is disabled the Rayleigh Ratio of the standard must be entered in the corresponding input line. In this case the refractive index specified in the *Menu Sample* is used as refractive index of the standard sample.

  The default setting of this option is enabled and use of $RR_{VU}$ for non-polarized detection. This option affects only measurements in STANDARD mode.

- *Compute and store Cumulant Analysis:*
  If this option is enabled a Cumulant analysis up to third order is performed with the correlation function of each single run. The mean apparent diffusion coefficient and their standard deviations are stored and the mean apparent hydrodynamic radius calculated from the Cumulant analysis of first order is displayed in the measurement protocol. The last channel that is included in the Cumulant analysis is selected using a data cut off defined in percentage of the intercept of the correlation function (default value is 10% which is a reasonable value for a narrow unimodal distribution of correlation times).

  The default setting is to enable this option. Calculations are only performed for measurements in SOLUTION mode, i.e., it is not necessary to disable this option in STANDARD and SOLVENT mode explicitly.

- Generate a measurement protocol:

If this option is enabled the window *Static/Dynamic Light Scattering Data* is opened after the measurement is started using the *Start Measurement* button.

The default setting is to enable the option.

### 2.2.4 Step 3: Measurement Type

In this step the measurement mode is selected and the appropriate file names are entered. Filenames can either be entered via keyboard after selecting the appropriate input using the mouse cursor or selected from the standard file dialog after clicking on the folder icon positioned right from the input line.
If STANDARD or SOLVENT mode is selected only the filename for the standard or solvent file has to be entered. Default filenames are *Standard.tol* and *Solvent.tol*, but any other filenames and extensions are accepted by the program.
In SOLUTION mode a standard file name must be entered that contains valid data of a STANDARD measurement. If either no solvent file name is entered or the option *Measure without solvent information/file* is enabled the calculations are performed without subtracting the scattering ratio of the solvent from the scattering ratio of the solution. A valid file name must be entered prior starting the measurement, no default file name is given but in order to be able to import the file into the ALV/Static & Dynamic Fit and Plot program the file extension *.sta should always be used. Furthermore, the values for the concentration and the refractive index increment have to be entered. In SOLUTION mode only data may be appended to an existing file.

### 2.2.5 Measurement Protocol and further data analysis

Depending on the measurement mode different entries are displayed in the table of the measurement protocol. For a detailed description please refer to the on-line help of the ALV-5000 & 60X0 Correlator software. All data displayed in the table can be exported via the clipboard into other worksheet oriented programs for further data evaluation and plotting.
Using the ALV/Static & Dynamic Fit and Plot program all data stored in standard, solvent and solution files can be plotted and further analyzed. For more details please refer to the on-line help of this program.

## *2.3 Data Processing*

The following calculations are performed during execution of the QuickSet "General DLS and SLS":

1. *in STANDARD, SOLVENT and SOLUTION mode:*
   - calculation of the scattering vector
     ($\lambda$ is the laser wavelength, n is the refractive index of standard or solvent/solution sample)

$$q = \frac{4\pi n}{\lambda} \mathrm{Sine}\left(\frac{\Theta}{2}\right)$$

   - normalization of the measured mean count rate for the scattering volume (Sine($\Theta$)) and the laser beam intensity measured using the monitor diode ($I_{mon}$)

$$\mathrm{Ratio}_{\mathrm{Standard/Solvent}} = \frac{\mathrm{CR}_{\mathrm{Standard/Solvent}}\ \mathrm{Sine}(\Theta)}{I_{\mathrm{mon}}}$$

$$\mathrm{Ratio}_{\mathrm{Solution}} = \frac{\mathrm{CR}_{\mathrm{Solution}}\ \mathrm{Sine}(\Theta)}{I_{\mathrm{mon}}}$$

1. *in SOLUTION mode:*
   - calculation of the optical constant K (dn/dc is the refractive index increment of the solution, NA is the Avogadro number)

$$K = \frac{4\,\pi^2 \left(\frac{dn}{dc}\ n_{\mathrm{Solvent}}\right)^2}{N_A\ \lambda^4}$$

   - calculation of the scattering ratio R taking into account the Herman & Levinson correction factor for the scattering volume due to refraction effects for samples with refractive index different to the refractive index of the standard sample (J.J. Hermans, S. Levinson, J.Opt.Soc.Am., **41**, 1033 (1951)),
     ($RR_{\mathrm{Standard}}$ is the Rayleigh Ratio of the standard sample)

$$R = \frac{R_{\mathrm{Solution}} - R_{\mathrm{Solvent}}}{R_{\mathrm{Standard}}}\ RR_{\mathrm{Standard}} \left(\frac{n_{\mathrm{Solvent}}}{n_{\mathrm{Standard}}}\right)^2$$

   - calculation of Kc/R (c is the concentration of the solution)
   - calculation of the apparent hydrodynamic radius according to the Stokes/Einstein relation (if Cumulant analysis is enabled), (T is the absolute temperature, k is Boltzmann' constant, $\eta$ is the viscosity of the solvent and $\Gamma$ the correlation rate obtained from the Cumulant analysis of first order)

$$\mathrm{Rad} = \frac{kT}{6\,\pi\,\eta\,\overline{\Gamma}}\ q^2$$

# Appendix

## *A: Reflection Correction of the Measured Scattering Ratio*

### **Correction of reflection effects on the measurement of absolute scattering ratios using cylindrical cuvettes**

Light passing through an transition between two dielectric materials having different dielectric constants, i.e., refractive indices, is partially reflected. For perpendicular incident light and isotropic dielectric materials the reflection coefficient $r = I_{refl.}/I_0$ is independent on polarisation and can be obtained from the Fresnel equation for perpendicular incidence of light:

$$r = (n_1 - n_2)^2 / (n_1 + n_2)^2 \qquad (1)$$

with $n_1$ and $n_2$ being the refractive index of each material. Equation (1) is valid within the required precision even for deviation from perpendicular incidence up to 10° which allows for separation of reflection and refraction effects. Refraction effects are in general considered by the Herman & Levinson correction.

Samples of reflection coefficients for various refractive index differences are given below.

| approx. value of sample refractive index | sample fluid | reflection coefficient at transition of fluid to SUPRASIL cuvette (n = 1.47) | reflection coefficient at transition of fluid to borosilicate glass (n = 1.52) |
|---|---|---|---|
| 1.5 | toluene | 0.01 % | < 0.01 % |
| 1.4 | THF | 0.06 % | 0.17 % |
| 1.33 | water | 0.25 % | 0.44 % |
| 1.0 | air | 3.6 % | 4.25 % |

Due to the non-linear dependence of the reflection coefficient from the refractive index difference a remarkable amount of reflected light is only observed for refractive index differences larger 5-10 %.

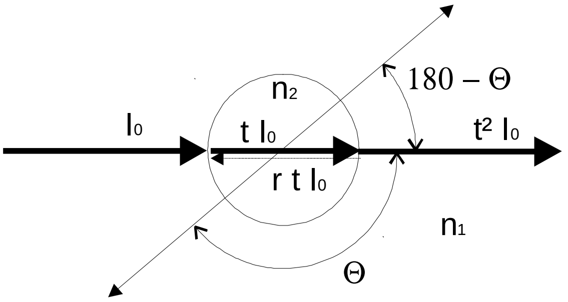
In order to minimise the effects of cuvette curvature (refraction) on the laser beam the standard procedure for SLS measurement is to transform the stronger curvature of the sample cuvette into an appropriately reduced curvature by using an Index Matching Vat (IMV) of an increased wider diameter, filled with a fluid of a refractive index as close as possible to refractive index of the cuvette. Additionally the use of the IMV almost completely reduces the reflection effects at the outer surface of the cuvette.

ALV Goniometer Systems include a precisely machined IMV made from SUPRASIL quartz glass having two plan parallel windows at 0° and 180° position to allow non-refracted passing of the laser beam through the IMV. Additionally the entrance and exit window for the illuminating laser beam are broadband multi-layer antireflection coated at the outer surfaces to minimise reflection of the laser beam below 0.2 % per surface.

Furthermore, the upper part of the heat exchanger holds the sample cuvette in position and blocks mechanically the rear side of the cylindrical wall of the IMV and, therefore, no reflection of scattered light at this glass/air transition occurs. In this case there is only the glass/air transition in the detection path that lowers the transmission of scattered light by a factor of 0.96 due to reflection, but independent of the type of sample and sample cell inserted into the IMV. This transition loss must not be included into the reflection correction, because it is already included in the STANDARD measurement used to calculate absolute scattering ratios.

In the following we restrict ourselves to use of an index matching fluid with a refractive index differing no more than 0.03 from refractive index of the cuvette used, which is a mandatory condition to perform SLS measurements over a wide angular range. In this case only the sample/cuvette interface may produce reflected light. All other interfaces have negligible reflection coefficients. Furthermore, we consider only first order reflections because higher order reflections have intensities below the noise level.

The following drawing shows an idealised ray tracing of a laser beam through a cuvette with refractive index $n_1$ that contains a liquid with refractive index $n_2$.



$I_0$ is the primary laser beam intensity (monitored using the ALV / Monitor Diode) and each time either the laser beam or the scattered light passes the interface between fluid and cuvette reflection occurs reducing the transmitted beam intensity by the factor $t = 1 - r$ (assuming no measurable energy loss due to absorption and scattering at the transition and in the fluid).

The detected intensity of the scattered light at the angle Θ consists of 4 contributions:

I. light scattered from the primary laser beam at a scattering angle Θ,

II. light scattered from the primary laser beam at a scattering angle 180°- Θ and then reflected to the observation angle Θ,

III. light scattered from the reflected part of the primary laser beam at a scattering angle 180°- Θ,

IV. light scattered from the reflected part of the primary laser beam at a scattering angle Θ and then reflected to the observation angle Θ; this will be neglected as being a second order reflection that is in any case by orders of magnitude lower than contribution I.

The contribution II cannot be neglected due to the cylinder lens effect of the cuvette, resulting in collection of scattered light from a similar or even larger size of the scattering volume compared to contribution III.

The contributions to the measured intensity of scattered light can be calculated according to the following formulas:

I. $$I_1 = \left( \frac{R_\Theta}{\sin(\Theta)} \quad tI_0 \right) \quad t$$

II. $$I_2 = r \left( \frac{R_{180^\circ - \Theta}}{\sin(180^\circ \ - \ \Theta)/k'} \quad tI_0 \right) \quad t$$

III. $$I_3 = \left( \frac{R_{180^\circ - \Theta}}{\sin(180^\circ \ - \ \Theta)} \quad r\,(tI_0) \right) \quad t$$

where $R_\Theta$ resp. $R_{180°-\Theta}$ is the normalised scattering ratio of the fluid at the angle Θ resp. 180°- Θ. The factor k' accounts for the change of the scattering volume actually contributing to the detected light due to the reflection at the rare side of the cuvette. In general k' depends on the diameter of the cuvette, the refractive index of the sample and the geometrical parameter of the detected volume and, therefore, on the scattering angle Θ,. Although, this factor is difficult to calculate one can show, that using a cuvette with 20 mm diameter, a sample with $n_2 = 1.33$ and an optical detection system with an cylindrical geometry of the detection volume having a diameter of 0.8 mm, $k' \cong 1$ at 90° and at maximum $k' \cong 1.2$ at 150° assuming homogeneous illumination and even less assuming Gaussian intensity distribution of the laser beam and the detected light. Therefore, $k' = 1$ is assumed for further calculations

Summing and sorting equations I.-III. using the identity sin(Θ) = sin(180°- Θ) results in the following equation for the normalised measured intensity of scattered light:

$$R_\Theta^{meas} = \frac{I_\Theta^{meas}}{I_0} \sin(\Theta) \ = R_\Theta \ t^2 \ + R_{180^\circ - \Theta} \ 2\,t^2\,r \tag{2}$$

For a Rayleigh scattering sample $R_\Theta = R_{180°-\Theta}$ yields and equation (2) reduces to

$$R_\Theta^{meas} = \ R_\Theta \ t^2 \ (1+2\,r) \cong R_\Theta \tag{3}$$

where the relation $t^2(1+2\,r) \cong 1$ yields within much better than 1 % even for r = 4 %.

In general a correction of the measured scattering ratio at the angle Θ for contributions of reflected light can be performed based on the measurement of the scattering ratio at the counter angle 180° - Θ according to the following formula:

$$R_\Theta = R_\Theta^{meas} \left( \frac{1-2\,r\ R_{180°-\Theta}^{meas} / R_\Theta^{meas}}{t^2} \right) \qquad (4)$$

It is evident from equation (4) that only for $R_\Theta << R_{180\,-\,\Theta}$ a remarkable contribution of reflected light is observed that requires a correction of the measured scattering ratio. Therefore, a correction of reflection effects is only necessary for samples that show large angular dependencies for the values of the scattering ratio (depending on the value of r a variation of more than 1 order of magnitude should be obtained), and, furthermore, the correction is only required for angles where the lower scattering ratio is detected compared to the detected value at the counter angle. The restriction that a correction of reflection effects is only possible at angles where the scattered intensity at the counter angle can be measured is usually not a limit, because in most cases the correction has to be performed at large angles where a measurement at the counter angle is no problem.

## Conclusion:

A reflection correction is not required for systems showing Rayleigh Scattering behaviour, i.e., STANDARD and SOLVENT measurements are not affected by reflection effects.

A correction is only required for systems showing a strong angular dependence of the scattering ratio and an appropriate routine to correct the reflection effect using equation (4) is included in the ALV / Static & Dynamic Fit and Plot program.

## *B: ALV / STATIC and DYNAMIC Enhancer*

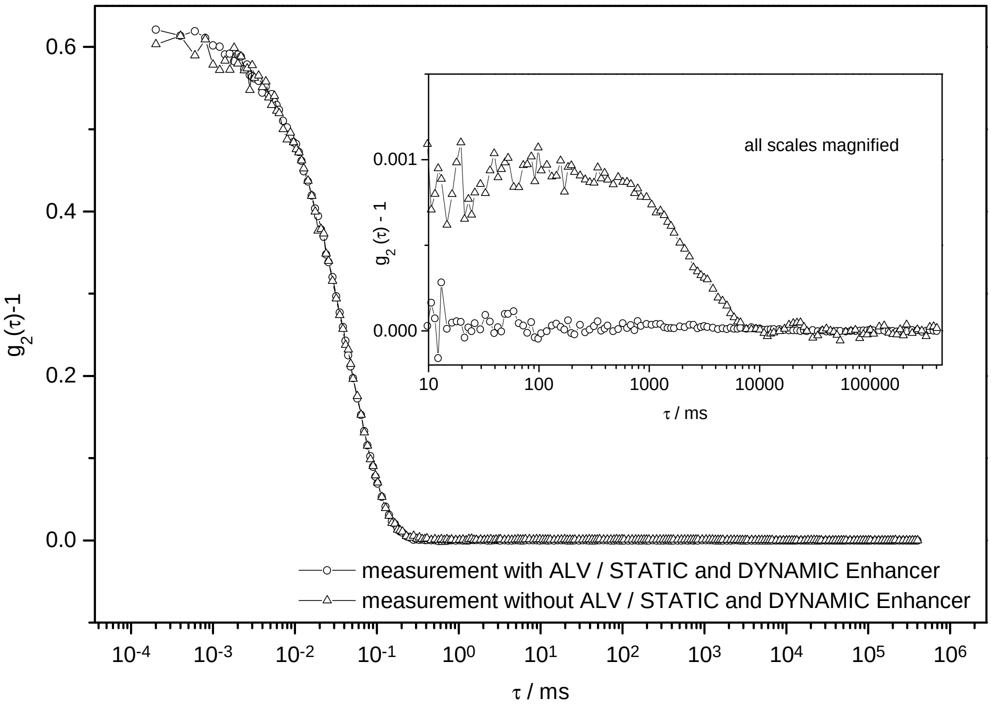
### What is the ALV / STATIC and DYNAMIC Enhancer?

The ALV / STATIC and DYNAMIC Enhancer was developed by ALV company to optimize GRIN lens fiber optical detection of scattered light for SLS and DLS measurements. Use of the ALV / STATIC and DYNAMIC Enhancer for SLS and DLS measurements results in optimum performance of GRIN lens fiber optical detection with no additional slow term fluctuations of the transmitted light intensity due to physical fiber properties. The following measurements demonstrate the superior performance of the ALV / STATIC and DYNAMIC Enhancer.

**Laser:** frequency doubled Nd:YAG laser, Single Longitudinal Mode ($TEM_{00}$) $\lambda = 532$ nm, P = 50 mW,

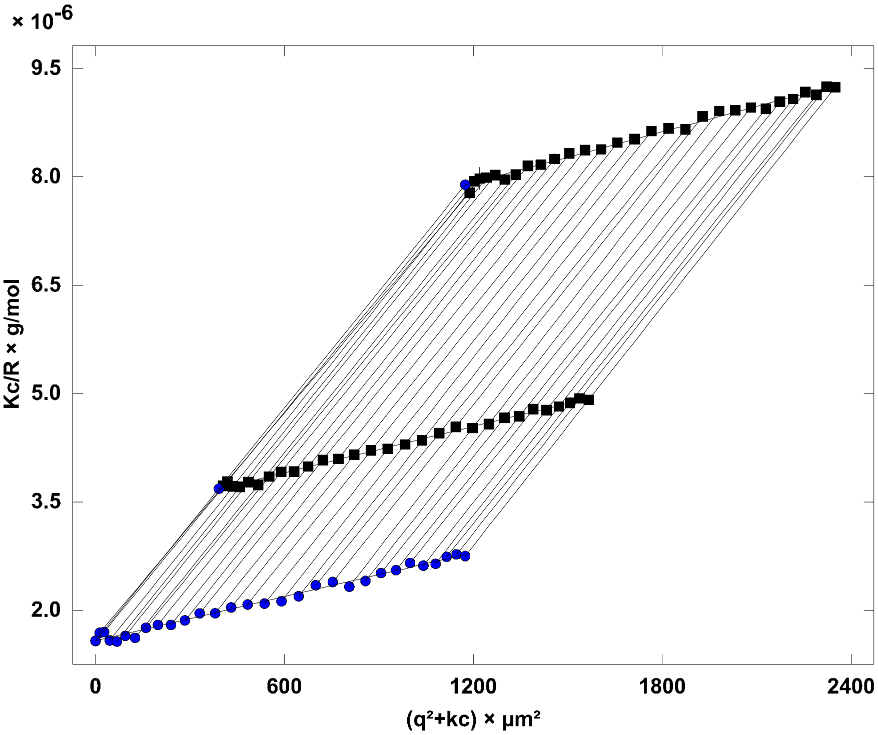
**Detection:** ALV/SO-SIPD DUAL photomultiplier / Pseudo-Cross correlation

**DLS measurement conditions:** Polystyrene in toluene, c = 1 g/l, 1 run a 1200 s, $\Theta = 90°$

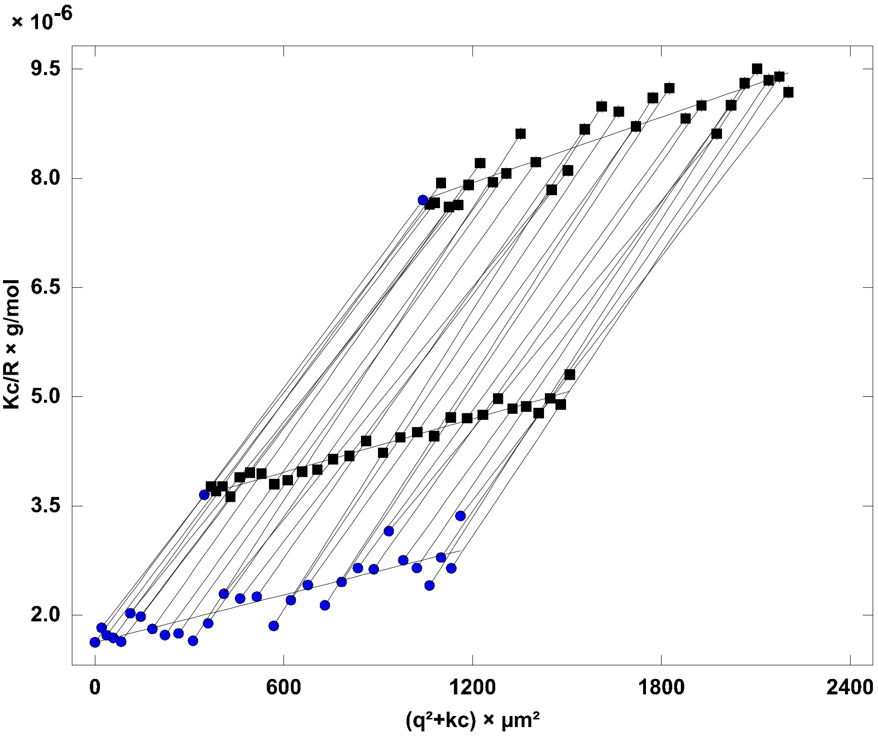


**SLS measurement conditions:** 3 runs a 20 s, Θ starting from 15° to 150°, step 5°,

detection with optical fiber with ALV / STATIC and DYNAMIC Enhancer:



detection with optical fiber without ALV / STATIC and DYNAMIC Enhancer:



**Zimm analysis of the measured data:**

without use of ALV / STATIC and DYNAMIC Enhancer:

| File | Conc/(g/dm³) | Mw(app)/(g/mol) | <S²>(app)/µm² | Rg(app)/nm |
|---|---|---|---|---|
| Conc.=0 | 0.0000 | 614600 | 2.000e-3 | 44 |
| PS1.dat | 1.0000 | 273800 | 1.005e-3 | 31 |
| PS1.dat | 3.0000 | 129800 | 5.850e-4 | 24 |

Mw(c): 614600 g/mol (± 0 %) Mw(q²): 614600 g/mol (± 4.72 %)
Rg: 44.72 nm (± 5.76 %) A2: 1.01e-6 mol dm³/g² (± 0 %)

with use of ALV / STATIC and DYNAMIC Enhancer:

| File | Conc/(g/dm³) | Mw(app)/(g/mol) | <S²>(app)/µm² | Rg(app)/nm |
|---|---|---|---|---|
| Conc.=0 | 0.0000 | 633800 | 1.933e-3 | 43 |
| PS2.sta | 1.0000 | 271600 | 8.701e-4 | 29 |
| PS2.sta | 3.0000 | 126700 | 4.449e-4 | 21 |

Mw(c): 633800 g/mol (± 0 %) Mw(q²): 633800 g/mol (± 1.01 %)
Rg: 43.97 nm (± 1.26 %) A2: 1.05e-6 mol dm³/g² (± 0 %)

## Conclusion:

From the plots shown and the results of the Zimm analysis it is evident, that the use of the ALV / STATIC and DYNAMIC Enhancer decreases drastically the statistical variance of the measured mean intensity of the scattered light, which in turn reduces the error of estimation of physically relevant quantities as e.g., molecular mass, radius of gyration etc.. Furthermore, a reduction of correlated noise distribution to the baseline of the correlation function of more than one order of magnitude is achieved.