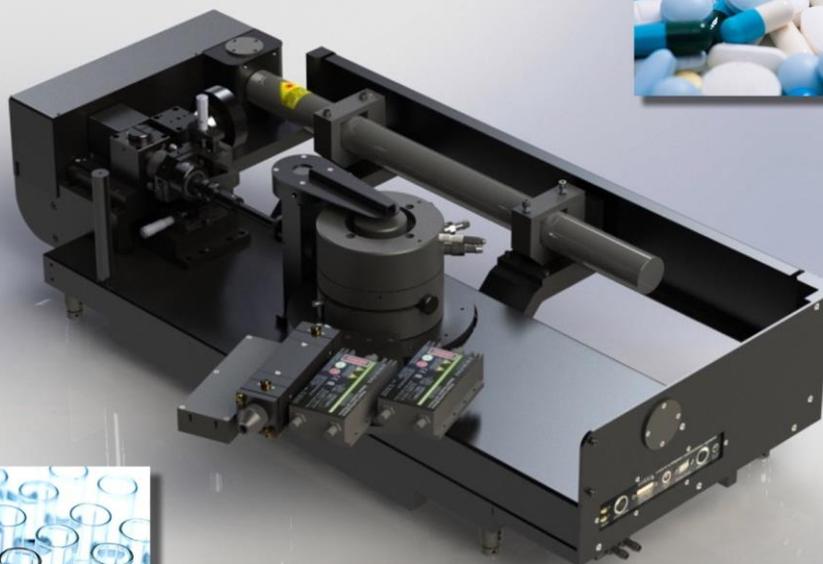


**Document :** Technical Data,  
ALV / CGS-3 Compact Goniometer System

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## ALV / CGS-3, General Data

<b>Size and Weight</b>	
Instrument size <i>An additional Anti-Vibration Table is not required !</i>	450 mm (w) x 980 mm (l) x 350 mm (h) (650 mm width with safety cover mounted)
Total Weight of Goniometer	approx. 45 kg
<b>Adjustment Tools and Recommendations <sup>(1)</sup></b>	
Double Needle Unit	part of the delivery.
<b>Software <sup>(1)</sup></b>	
ALV-700X Correlator Software V.3.X	Standard Delivery
ALV-Fit & Plot Software	Standard Delivery
<b>Computer Requirements</b>	
Computer (not part of delivery, unless otherwise stated )	AMD® or INTEL® processor, Dual or Quad-Core CPU recommended USB 2.0 or USB 3.0 connection (USB 3.0 needs to be fully compatible to USB 2.0) ≥ 2 GByte RAM or more ≥ min. 20 Mbyte free hard disk memory 1024 x 768 graphics resolution (Full-HD recommended) DVD or CD-ROM drive Printer
Monitor (not part of the delivery, unless otherwise stated)	ALV recommends the use of 21" or larger CRTs
Operating System (not part of the delivery, unless otherwise stated)	WINDOWS®-XP/7/8/8.1/10 (32-bit or 64-bit Version)
<b>Room Requirements <sup>(2)</sup></b>	
Room Light Level	any standard room can be used, however, for eventual re-alignments the light level in the room should be reducible (e.g. via blinds)
Thermal Requirements	the room temperature should be stable to +/- 1.5°C within 24 h. Direct air blow onto the goniometer system must be avoided.
Clean Room Requirements	the goniometer system can be operated in a standard room, however, care must be taken to avoid dust contamination of the to be measured samples.

- (1) The ALV-Correlator Software for WINDOWS Software includes full support of the ALV-Goniometer Systems. This software is used for experiment control, graphic visualisation of the measured data (correlation function, count rate traces, temperature traces ...) and for Dynamic Light Scattering data reduction. The ALV-Fit&Plot software allows the generation of several plots for Static Light Scattering (Zimm, Berry ..., Diffusion Coefficient plots, Form Factors ...), working on the data files generated by the ALV-Correlator Software for WINDOWS.

- (2) The room conditions are very important to optimally operate the goniometer system. The temperature stability of the room should be within +/- 1.5°C, since the goniometer system will **not show any noticeable adjustment variation** for temperature fluctuations within this limit. For larger temperature fluctuation, the alignment can no longer be guaranteed to stay constant. There is no need to operate the goniometer system under clean room condition, however, since dust is the number one enemy of light scattering, care has to be taken not to contaminate neither the sample, nor the cuvette nor the index matching fluid with dust. If long measurement times are required for whatever reason and dust is a critical issue for the particular sample, ALV recommends the use of a laminar flow box for sample preparation. Likewise, extremely clean solvents must be used in such situations.

## General Measurement Range

<b>General Measurement Range for DLS/SLS</b>	
Particle Size Range (hydrodynamic radius)	0.5 nm – 5µm radius depending on the sample properties and concentration, even smaller sizes can be measured
Radius of Gyration Range	min. Radius of Gyration approx. 5 nm smaller radius of gyration down to 0.5nm radius can be calculated from obtained hydrodynamic radius using specific shape information
Molecular Weight Range	See chapter 1.5 « Minimum Determinable Molecular Weight”

## Goniometer Mechanics, Technical Data

<b>Angular Range of Goniometer <sup>(1)</sup></b>	
Goniometer Angular Range	effective : 12° ... 152° scattering angle recommended : 17° ... 150° scattering angle
Goniometer Angular Resolution	0.0125°
Goniometer Angular Travel Speed	up to 20° / s, user selectable
Limit Switches	two optical limit switches
<b>Cell Housing <sup>(2)</sup></b>	
Accuracy of Centricity	typ. better than +/- 5 µm in plane of rotation
Accuracy of Orthogonality	typ. better than +/- 10 µm residual tilt
<b>Index Matching Vat <sup>(3)</sup></b>	
Index Matching Vat Size and Material	quartz glass, 85 mm outer diameter with two parallel quartz glass windows at 0° and 180°, anti-reflection coated
Accuracy of Centricity	typ. better than +/- 5 µm in centre of rotation
Accuracy of Orthogonality	typ. better than +/- 10 µm residual tilt

(1) The angular resolution is an absolute value. A special „homing“ mechanics / electro-optics combination ensures „home“ positioning to absolutely precise to approx. +/-0.003°.

(2) These two parameters determine the accuracy of the cell housing and with this the sample cuvette are positioned in both, the centre of rotation in the angular direction and the plane of rotation (which corresponds to the remaining tilt error). While the values given above are remarkably low, they are required at such precision to perform high accuracy Static Light Scattering measurements. Both parameters are part of the alignment

procedure and are, using the special ALV-Alignment Tools, measurable and reproducible by the user. The special ALV-Cuvette holder ensures that cuvettes of a certain outer dimension range (e.g. 9.8 mm ... 10.2 mm for the 10 mm cuvette holder) are automatically centred to the above precision, provided the cuvette itself show less centricity errors, of course.

- (3) The two plan-parallel windows ensure undistorted laser beam entry, travel and exit through the index matching vat. Both windows are anti-reflection coated which ensures minimum back-reflection. Centricity and orthogonality determine the accuracy of the index matching vat in both, the centre of rotation in the angular direction and the plane of rotation (which corresponds to the remaining tilt error). As with the cell housing, both parameters are part of the alignment procedure and are, using the special ALV-Alignment Tools, measurable and reproducible by the user.

## Laser Illumination, Technical Data

<b>Laser Type and Output Power</b>	
Laser DPSS Type 660nm or Laser DPSS Type 523nm or Laser DPSS Type 660nm	single frequency CW diode pumped laser @ $\lambda = 660 \text{ nm}$ (single longitudinal mode), output power 50 mW before optical isolator, power stability better +/- 0.5% over 24 h, ~15 min. warm-up time required  Frequency-doubled Nd-YAG @ $\lambda = 532 \text{ nm}$ (single longitudinal mode), output power 50 mW before optical isolator, power stability better +/- 0.5% over 24 h, ~15 min. warm-up time required  single frequency CW diode pumped laser @ $\lambda = 660 \text{ nm}$ (single longitudinal mode), output power 100 mW before optical isolator, power stability better +/- 0.5% over 24 h, ~15 min. warm-up time required
Laser Beam Folding Unit	two fully shielded Ag-mirrors (coated) with > 95% reflection. Both mounted in fully orthogonal mirror adjuster (X/Y and tilt/turn).
<b>Laser Beam Attenuation</b>	
Optical Attenuator	stepper motor driven optical attenuator with 100%, 30%, 10%, 3%, 1%, 0.3%, 0.1% and „SHUT“ transmission steps
<b>Laser Beam Monitorisation</b>	
Monitor Diode Unit	very high linearity 4-quadrant optical diode, allows beam stability & intensity monitorisation, used to compensate for the actual laser beam attenuation.
<b>Laser Focusing</b>	
Laser Focusing Optics	achromatic lens system mounted in X-Y & tilt/turn

	adjustable holder with focal length = 300 mm
<b>Laser Safety Class <sup>(1)</sup></b>	
Laser Safety Measures	fully tubed laser beam, beam trap at 0° scattering angle, additional cover, mechanical „beam block - cuvette release“ mechanism.
Applicable Laser Safety Class in operation mode	<b>Laser Class 1, EN 60825-1/11.01</b>
Applicable Laser Safety Class in adjustment mode	<b>Laser Class 3B, EN 60825-1/11.01</b>

- (1) Please note : The ALV/CGS-3 is a Class 1 Laser Products in operation and maintenance mode. However, during an eventual alignment procedure, the laser must be aligned to the goniometer, which requires the removal of all of the several laser beam tubings etc. While being aligned, the goniometer system does no longer correspond to a Class 1 Laser product, but must be treated as corresponding to a Class 3B Laser Product.  
**Special regulations may apply in your country for handling Class 3B Laser Products.**



## Optical Detection, Technical Data

<b>Optical Detection Unit</b>	
Optical Detection Unit	special optical fiber based detector, type ALV-Static & Dynamic Enhancer - 1 for either Laser Type 1/3 (660nm) or Laser Type 2 (532 nm)
<b>Optical Detection Details <sup>(1)</sup></b>	
Number of Modes Detected	~1 mode detection characteristics, not susceptible to „interferometer effects“
Detection Volume	approximately 0.3 mm <sup>3</sup> (1 x 1 x 0.3 mm) at 90° scattering angle
q <sup>2</sup> -Range Laser Type 1 (632.8 nm)	7.62 x 10 <sup>12</sup> ... 6.56 x 10 <sup>14</sup> [1/m <sup>2</sup> ] (water as solvent)
q <sup>2</sup> -Range Laser Type 2 (532 nm)	1.25 x 10 <sup>13</sup> ... 1.34 x 10 <sup>15</sup> [1/m <sup>2</sup> ] (water as solvent)
<b>Depolarized Light Scattering <sup>(2)</sup></b>	
Detection Beam Analyzer (optional)	Analyzer prism (Glan Thompson) with better 10 <sup>5</sup> extinction ratio in a fully compensated rotatable holder.

- (1) The detection volume must not be mixed with the sample volume. While the sample volume is cuvette dependent, the detection volume is an optical parameter. For 10 mm outer diameter cuvettes and approx. 5 mm filling height, the actual sample volume required for these cuvettes is approx. 250 µl. Smaller inner diameter cuvettes are principally usable as well, but may show reduced performance for SLS measurements.
- (2) Depolarized light scattering requires that the light is analysed for the depolarized light amount at highest accuracy (and thus again polarization ratio). The ALV/CGS-3 has provision to insert a Glan-Thompson Prism in front of the optical detector as analyser in a fully compensated rotation holder. This allows depolarization as well as polarized light scattering being performed.

## Single Photon Detection, Technical Data

<b>ALV-High Q.E. Avalanche Photo Diode</b>	
Max. Quantum Efficiency Max. Count Rate for 1% Linearity Max. Peak Count Rate Max. Dark Counts	> 50% Q.E. at 633 nm, > 35% Q.E. at 532 nm > 500 kCps > 10 MCps (protected at 8 MCps) < 300 Cps (typically)
Overload Protection Min. Accessible Correlation Lagtime	ALV-Overload Protection Unit and/or ALV-LSE-III approx. 1 $\mu$ s at 20 kCps or more
<b>PseudoCross Correlation Setup with ALV-High Q.E. APD DUAL</b>	Consists of two ALV-High Q.E. APDs in Pseudo-Cross-Correlation Mode with 50:50 fiber-optical beam splitter
Min. Accessible Correlation Lagtime	less than 50 ns at < 1% distortion in $g^{(2)}(t)$

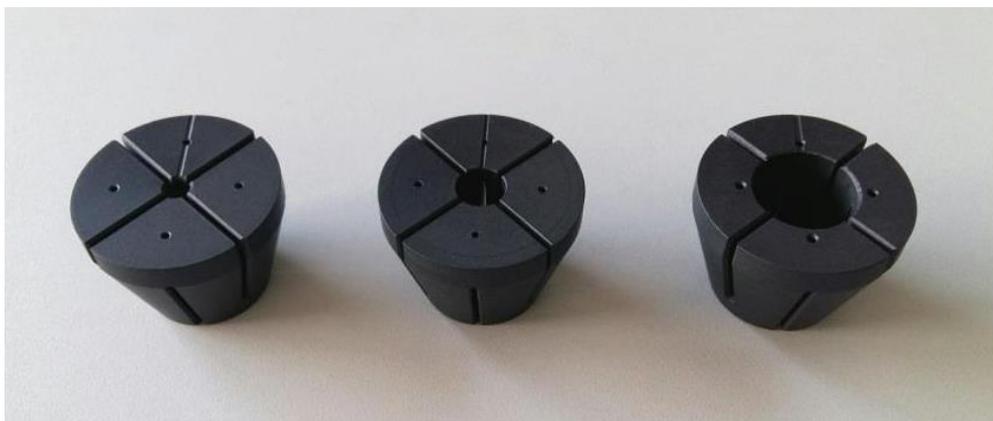


Detection unit with PseudoCross Correlation Setup consisting of two ALV-High Q.E. APD units

## Thermal Control, Technical Data

<b>Standard Cell Housing</b>	
Cell Housing Material	cell housing with aluminium or black stainless steel (optional) heat exchanger ensuring min. thermal gradient in the sample cuvette, black PTEP outer insulation
Cuvette holders	precision cuvette holder made of "black" Teflon for most gentle handling of cuvettes; using conical bore in the upper heat exchanger to accept cuvette holders; cuvette holder for cylindrical cuvettes with outer diameter of 10.0mm and 20.0mm (5.0mm optional)
Thermostatisation	via external waterbath circulator, control via secondary Pt-100 probe (optional)
Max. Operation Temperature Range <sup>(1)</sup>	-6°C ... +90°C
<b>Temperature Measurement / Control</b>	
Primary Temperature Probe	Pt-100 based probe measures in index matching fluid, -20°C ... +175°C measurement range
Temperature Measurement Accuracy	+/- 0.1 °C absolute (not certified, but by design) +/- 0.01 °C relative
Temperature Control Accuracy	depending on the waterbath circulator used, typ. +/- 0.05°C.
Measurements Below Dew Point	cell housing has provision to blow dry air/nitrogen against the index matching vat, fully avoiding condensation problems.

(1) The temperature range given above is the absolute max. allowed temperature range for which the ALV / CGS-3 will keep its alignment to the required precision. For measurements at high temperatures, special fluids for the waterbath circulator must be used (e.g. glycol or mineral oils). Silicone oils must never be used as circulator fluid any time ! Likewise, special fluids must be used as index matching fluid for temperatures larger than approx. 45°C. Silicone oils must never be used as index matching fluid any time !



Cuvette holders for cylindrical cuvettes with outer diameter of 5.0mm, 10mm and 20mm.

### ALV / CGS-3 Heat Exchanger Options

Material	IMF Toluol	IMF cis- Decalin	IMF Water*	Temperature range**
Aluminium Black anodized, standard delivery	+++	-	+	-6°C ... 60°C
Stainless steel blackened, optional	+++	++	++	-6°C ... 80°/90°C

\* Water as index matching fluid (IMF) is only barely suitable as the low refractive index of water does not provide an appropriate optical transition to the used glass materials of the cuvette / IMV (quartz glass/ BSG glass)

\*\* For a temperature range above 50°C the use of toluene as index matching fluid (IMF) is no longer recommended.

At temperatures below 15°C cis-decaline gets highly viscous/wax like and therefore only limited suitable for working temperatures below typical room temperature. Additionally, due to its corrosive properties, cis-decalin should not be used with the aluminium made heat exchanger.

For working temperatures above 80°C up to 90°C an additional heat exchanger must be integrated in the base plate of the ALV/CGS-3 System.



Heat exchanger unit made of aluminum



Heat exchanger unit made of stainless steel

## Digital Correlator, Technical Data

	ALV/LSE-5004 Light Scattering Electronics including ALV-7004/USB Correlator *
<b>Auto/Cross Correlation Modes</b>	Yes
<b>SINGLE Mode, 100% Real Time Efficiency</b>	Yes, 25 ns Initial Sampling Time <sup>(1)</sup> [Optional 3.125 ns Initial Sampling Time] <sup>(2)</sup>
<b>DUAL and QUAD Mode, 100% Real Time Efficiency</b>	Yes, 25 ns Initial Sampling Time <sup>(1)</sup> [Optional 3.125 ns Initial Sampling Time] <sup>(2)</sup>
<b>Max Number of Channels</b>	312
<b>Max. Number of Parallel Sampling Times</b>	38 [41] <sup>(2)</sup>
<b>Max. Sampling Time Range</b>	25 ns ... 3435,9 s [3.125 ns ... 3435,9 s] <sup>(2)</sup>
<b>Max. Lag Time Range</b>	1 : 2,2 x 10 <sup>12</sup>
<b>Correlation Channel Structure</b>	ALV-16 / 8 Channel Multiple Tau Structure
<b>Input data width</b>	Increasing with sampling time
<b>Max. Input Count Rate SINGLE / DUAL / QUAD Mode</b>	up to 80 MHz per input sustained, 160 MHz peak

\* The ALV-7004/FAST Multiple Tau Digital Correlator is available as option.

(1) Both Cross Correlation functions, namely IN0 / IN1 and IN1 / IN0 can be computed simultaneously. This mode can be used to slightly decrease the shot noise on the cross correlation function by computing the average of the IN0 / IN1 and the IN1 / IN0 correlation function for shorter lag times when used with the (optional) ALV - High QE APD DUAL detector. While the shot noise reduction usually is very small only in comparison to the total noise on the correlation function (namely shot noise and signal noise), care must be taken to use this scheme for input signals with Gaussian or at least very near Gaussian statistics only.

(2) When using the optional available ALV-7004/FAST Multiple Tau Digital Correlator

## Measurement & Sensitivity

### How is this chapter organized ?

In this section, the sensitivity and the measurement's ranges in terms of Molecular Weight, Diffusion Coefficients, Hydrodynamic Radius etc. are addressed. Instead of simply stating a couple of numbers, for each parameter a short theoretical section is given, followed by the effective capability of the ALV-goniometer system.

### Why is this chapter organized in such a way ?

This approach, while a bit less compact than a list of „Technical Data“ shall allow the potential user of an ALV-goniometer system to, in advance, judge if the sample system he/she is aiming at is within the range of „measurable sample systems“ for the specific ALV-goniometer system.

***ALV does not believe that the complex interplay of sample characteristics and sample parameters to be extracted from the light scattering measurement can be expressed in a simple „Technical Data Table“ with just a few entries, unless a clear specification of how these parameters are derived is given.***

# Static Light Scattering

## 1.0 Brief Theory, Static Light Scattering

To determine the capability of a light scattering apparatus in terms of Static Light Scattering, three major parameters must be precisely analysed :

- ***the accuracy of the to be expected  $1/\sin(\Theta)$  dependence of the „detection volume“ versus the scattering angle***
- ***the overall sensitivity of the illumination/detection system***
- ***the angular resolution of the detection system***

To determine the angular dependence of the light scattered by the sample, obviously a measurement of the light scattered by the sample at a certain number of different scattering angles is required. Still, for any given scattering angle, the „equivalent detection volume“ is depending on the actual scattering angle used. While the „detection volume“ is smallest at 90° scattering angle (the intersection of detection and illumination is minimum at this angle), angles different from 90° will show increased „detection volumes“. Effectively, this „detection volume“ scales with

$$1.0.0 \quad V_{Det} \cong \frac{1}{\sin(\Theta)}$$

and thus, each measured scattered intensity value requires a „ $\sin(\Theta)$  correction“ to be comparable to the intensities measured at any other angle. For a sample not showing any angular dependence in the scattering intensity, applying this correction should lead to a straight line for the corrected scattering intensities versus the scattering angle. Any deviation from this straight line must be addressed to systematic errors in the light scattering apparatus. The importance of this systematic deviation to be as small as possible is the determination of the **Radius of Gyration** and **Form Factors**. Both lead to certain angular dependencies of the light scattered by the sample and small angular dependencies can only be reproducibly measured, if the systematic error of the apparatus is significantly smaller than the to be expected angular dependency of the scattered light for this sample.

Still, care must be taken to judge the „residual deviation“ precisely. Using a large detector aperture and thus sacrificing both, angular resolution of the detection and the ability to perform Dynamic Light Scattering measurements as well, the „residual deviation“ can be made quite small - however at the cost of decreased overall accuracy. ALV never used and will never use such „tricks“ and all ALV-goniometer systems use high angular definition detection systems which allow near to perfect coherent detection, a must for high quality simultaneous Static and Dynamic Light Scattering measurements.

The second parameter is the overall sensitivity of the illumination/detection system. This parameter defines to some extent „the number of counts/s“ the apparatus will detect for a given sample system. Two general routes to a high sensitivity exist, the use of high power lasers (several 100 mW, Ar-Ion lasers, for example) or the used of highly optimized detection systems at moderate laser powers (a few 10 mW, HeNe laser, for example).

While the first approach (the traditional approach) has disadvantages only, namely, high laser cost, enormous light density in the sample with all the photo-chemical and thermal problems involved etc., the second approach requires much higher overall detection sensitivity than any traditional approach. In fact, using the ALV-Static & Dynamic Enhancer techniques coupled with most modern single photon detectors, such high increase of the detection sensitivity is very well possible.

## 1.1 Measuring the Standard

All Static Light Scattering measurements rely on the measurement of a **Standard**. The typical Standard used for Static Light Scattering Measurements is Toluene, for the simple reason that the **Rayleigh Ratios** of Toluene are rather high and precisely known for a vast range of illumination wavelengths and temperatures. These Rayleigh Ratios are required for the determination of the „absolute scattering“ of the sample (which, without a measurement of a Standard, would be very tedious to obtain) and with that for Molecular Weight determination.

In the measurement, the **Excess Scattering** is determined, which links the scattering of the sample measured by the apparatus to the absolute scattering by:

$$1.1.0 \quad I_{Excess}^{Sample} = \frac{I_{rel.}^{Sample} - I_{rel.}^{Solvent}}{I_{rel.}^{Standard}}$$

$$I_{abs.}^{Sample} = RR \cdot I_{Excess}^{Sample} = RR \cdot \frac{I_{rel.}^{Sample} - I_{rel.}^{Solvent}}{I_{rel.}^{Standard}}$$

Clearly, a precise measurement of the Standard is the single most important key to a precise determination of the absolute scattering of the sample, since the error can be expressed as :

$$1.1.1 \quad \partial_{abs.} I_{Excess}^{Sample} = \frac{1}{I_{rel.}^{Standard}} (\partial_{abs.} I_{rel.}^{Sample} + \partial_{abs.} I_{rel.}^{Solvent} + \partial_{abs.} I_{rel.}^{Standard} I_{Excess}^{Sample})$$

$$\partial_{rel.} I_{Excess}^{Sample} = \partial_{rel.} I_{rel.}^{Standard} + \left( \frac{\partial_{abs.} I_{rel.}^{Sample} + \partial_{abs.} I_{rel.}^{Solvent}}{I_{Excess}^{Sample}} \right)$$

which clearly indicates that for any sample showing a reasonable Excess Scattering, the error in the measurement is dominated by the Standard's error.

Two sources of errors are dominating the Standard's error, the counting error due to the statistical nature of the detection process which introduces an error in the determination of the actual scattering intensity and the systematic error, due to the imperfection of the light scattering apparatus.

Assuming Gaussian statistics for the counting process, the absolute error of a counted number of counts is proportional to the square root of the counted number. Likewise, the relative error is inversely proportional to the square root of the counted number, ensuring that the relative counting error converges to zero for larger and larger counted numbers (while the absolute error does not, obviously).

Both error contributions are independent to each other, thus the classical Gaussian error summation formula applies. In detail, the total error can be expressed as :

$$\partial_{abs.} I_{rel.}^{Standard} = \sqrt{(\partial_{Counting} I_{rel.}^{Standard})^2 + (\partial_{Systematic} I_{rel.}^{Standard})^2}$$

$$\partial_{rel.} I_{rel.}^{Standard} = \sqrt{\frac{(\partial_{Counting} I_{rel.}^{Standard})^2 + (\partial_{Systematic} I_{rel.}^{Standard})^2}{(I_{rel.}^{Standard})^2}}$$

### 1.1.2

$$\partial_{Counting} I_{rel.}^{Standard} = \sqrt{I_{rel.}^{Standard}} \quad (\text{as follows from counting statistics})$$

$$\partial_{rel.} I_{rel.}^{Standard} = \sqrt{\frac{1 + I_{rel.}^{Standard} (\partial_{Systematic} I_{rel.}^{Standard})^2}{I_{rel.}^{Standard}}}$$

To obtain a total error less than +/- 1%, say 0.3% error in the Standard measurement, one has to count at least 100.000 counts (1  $\sigma$ ) or 300.000 counts (3  $\sigma$ ) for the Standard (assuming the systematic error is significantly smaller than the +/- 1 %).

From this it follows, that to ensure reasonable measurement times, the count rate (or counts/s) for the Standard (here Toluene) should be larger than 10.000 counts/s at 90° - with this, a certain +/- 1% (3  $\sigma$ ) accuracy for the Standard's counting error can be reached within 30 s measurement time per angle already.

***The counting error in the Standard measurement is the dominating error as long as it is larger than the systematic error of the light scattering apparatus. To ensure the relative counting error drops in a reasonable short measurement time, a high number of counts/s from the Standard scattering must be detected.***

***Under these circumstances, the accuracy of the measurement is limited solely by the residual systematic error of the light scattering apparatus, which, by design, must be kept as small as possible as well.***

## 1.2 Resulting Illumination/Detection Efficiency

Count Rates for a Toluene Standard at 90° Scattering Angle using the ALV-Static & Dynamic Enhancer allowing simultaneous SLS and DLS with Laser Type 1 (HeNe, 22 mW, 632.8 nm)

Illumination/Detection Efficiency	Toluene at 90° Scattering Angle
ALV / CGS-3 (HeNe 632.8 nm)	> 20.000 Counts/s

or the ALV-Static & Dynamic Enhancer allowing simultaneous SLS and DLS with Laser Type 2 (frequency-doubled NdYAG, ~45 mW after after optical isolator, 532 nm)

Illumination/Detection Efficiency	Toluene at 90° Scattering Angle
ALV / CGS-3 (Nd-YAG, 532 nm)	> 45.000 Counts/s

Residual Systematic Errors over the entire Scattering Angle Range (17° ... 150°) for a Toluene Standard using the ALV-Static & Dynamic Enhancer allowing simultaneous Static and Dynamic Light Scattering in a 10 mm o.d. quartz glass cuvette

Residual Systematic Errors	Over Scattering Range of 17° ... 150°
ALV / CGS-3 Goniometer System	+/-0.5% absolute (+/-1 % absolute guaranteed)

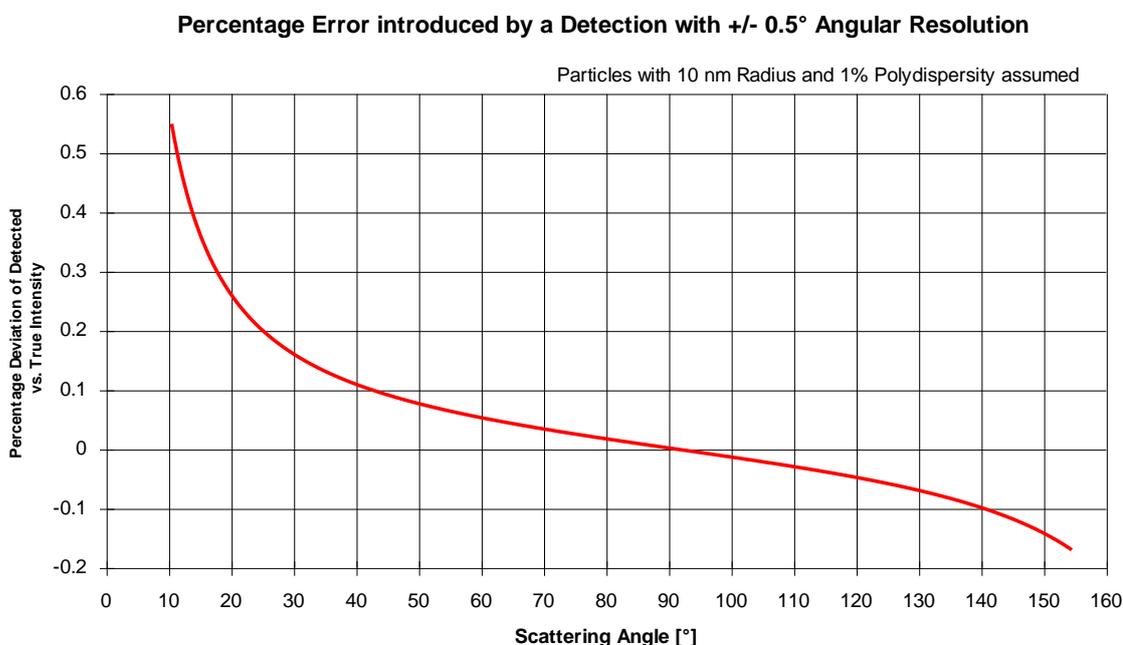
Achieving such little systematic errors requires proper alignment of the goniometer system and even more important, proper preparation of „clean and dust-free“ Toluene. Values as low as +/- 0.3% have been achieved, but these require additional effort in system alignment and advanced sample preparation procedures. **The guaranteed value for the residual systematic error is +/- 1% peak-to-peak for 20° ... 150° measured for toluene in a 20 mm quartz cuvette)**

### 1.3 Angular Resolution of the Detection System

Every detection used within a light scattering apparatus will not just detect light from a single angle or scattering vector, but over a certain range of scattering angle / vectors instead.

While this fact is sometimes used to „enhance“ the detection sensitivity of the apparatus by increasing the angular range being detected (and thus decreasing the angular resolution as well as increasing the count rate), several drawbacks from doing so must be expected.

The major problem of course is, that with such a poor angular resolution, no Dynamic Light Scattering can be performed at all (see below for details). But even for Static Light Scattering, the difference of using a „near diffraction limited“ fiber optics (ALV-Static & Dynamic Enhancer), which has an angular resolution in the order of  $0.02^\circ$  or using a rather large pinhole optics (say  $800\ \mu\text{m}$ ,  $2F/2f$  optical system with  $50\ \text{mm}$  focal length), which has approx.  $1^\circ$  angular resolution only, can be quite dramatic. See the below graph for the percentage error introduced using such a poor angular resolution optics.



While the errors are still small enough to allow Molecular Weight Determination, exact determination of the Radius of Gyration becomes difficult to impossible for smaller particles - the systematic distortions due to the poor angular resolution can easily be of the same order as the slope of the intensity versus scattering angle for small particles !

Since the errors introduced roughly scale linearly with the angular resolution of the optics, a high angular resolution optics, such as the ALV-Static & Dynamic Enhancer, can be shown to introduce absolutely negligible amounts of systematic error ( $< 0.02\ \%$ ) only and such a small amount will never become visible in a measurement.

## 1.4 Molecular Weight Determination

The determination of the Molecular Weight of a sample requires the knowledge of a few more parameters, in particular sample parameters. The relation of sample's scattering absolute intensity at sample concentration  $c$  and scattering angle  $\Theta$ , it's Molecular Weight, (small) Radius of Gyration and 2<sup>nd</sup> Virial Coefficient is given as :

$$1.4.1 \quad \frac{Kc}{R_\theta} = \left( \frac{1}{M_w} + 2A_2c \right) \left( 1 + \frac{1}{3} \left( \frac{4\pi n R_g \sin\left(\frac{\Theta}{2}\right)}{\lambda} \right)^2 \right)$$

$$1.4.2 \quad \frac{Kc}{R_\theta} = \left( \frac{1}{M_w} + 2A_2c \right) \left( 1 + \frac{1}{3} q^2 R_g^2 \right)$$

for  $q = 0$  and  $c = 0$  on the r.h.s. this simplifies to

$$1.4.3 \quad \frac{1}{M_w} = \frac{Kc}{RR I_{Excess}^{Sample}}, \text{ with } RR \text{ being the Standard's Rayleigh Ratio}$$

and

$$1.4.4 \quad K = \frac{(2\pi \frac{dn}{dc} n_{Standard})^2}{\lambda^4 N_A}$$

$K$  is the „optical constant“, adjusting for the samples optical contrast in the solvent ( $dn/dc$ ), and the standard's refractive index.  $N_A$  is the Avogadro Constant.

As seen above, the Molecular Weight is proportional to the sample's scattering intensity and inversely proportional to the samples' concentration and could directly be computed if the scattering intensity measured at  $q = 0$  and  $c = 0$  was known.

Neither of these limits is reachable in practice obviously, and thus an extrapolation must be used for the absolute scattering intensity at  $\Theta \rightarrow 0$  and  $c \rightarrow 0$ . This is performed by measuring several sets of sample concentrations (3 ... 5) at different scattering angles (20 ... 30).

The optical constant  $K$  is depending on two sample parameters,  $dn/dc$  and  $n_{Standard}$ . For the expert reader, the above formula is already corrected for cylindrical cuvettes using the Herman & Levinson corrections.

$dn/dc$  is a very subtle parameter - it reflects the sample' visibility in the solvent. A sample with higher  $dn/dc$  will scatter more light than a sampler with lower  $dn/dc$ , but equal Molecular Weight. Roughly speaking, for a low  $dn/dc$  sample, the same scattering requires higher concentration than for a high  $dn/dc$  sample of equal  $M_w$ . If the  $dn/dc$  is near to zero, the sample is practically invisible in the solvent and no scattering will appear, no matter of the  $M_w$  or concentration.

***This again shows, that a single parameter definition, like „min.  $M_w = 10.000$  dalton“ does not make much sense, unless the  $dn/dc$  and concentration is specified as well. It is much better practice, to define a minimum scattering the sample should show, best in terms of the Standard scattering !***

In fact, the sample should not scatter less than 10% of the Toluene Standard scattering - most real-world samples do in fact scatter much more. Measurements with less sample scattering is principally possible, but very difficult in terms of sample preparation, since very long measurement times are required and within these measurement times, a „clean“ measurement must be ensured, which practically means no dust must be present in the detection volume for the entire measurement time. At 10% Toluene scattering, the measurement times required to achieve a 1% counting accuracy for the sample scattering are (per measurement at 90° scattering angle) :

<b>Measurement Time for 1% Counting Error</b> 10% Excess Scattering, 90° Scattering Angle	
ALV / CGS-3 (HeNe, 632.8 nm)	approx. 60 s
ALV / CGS-3 (Nd-YAG, 532 nm)	approx. 27 s

## 1.5 Minimum Determinable Molecular Weight

Please note, that the minimum determinable Molecular Weight is principally independent of the detection/illumination used, but solely defined by the allowed Excess Scattering, the sample's  $dn/dc$  and the sample concentration. Still, the measurement time required to achieve the necessary counting error is very dependent on the detection/illumination used and this is why the illumination/detection efficiency is so important - if a measurement has to be performed ten times longer because of too little illumination/detection efficiency, the sample has to be clean enough to allow such a long time measurement !

<b>Excess Scattering = 10%, <math>dn/dc = 0.1</math> ml/g</b>	
<b>Sample Concentration</b>	<b>Min. Molecular Weight</b>
0.01 mg/ml	1400000 dalton
0.1 mg/ml	140000 dalton
1 mg/ml	14000 dalton
10 mg/ml	1400 dalton

<b>Excess Scattering = 10%, dn/dc = 0.2 ml/g</b>	
<b>Sample Concentration</b>	<b>Min. Molecular Weight</b>
0.01 mg/ml	360000 dalton
0.1 mg/ml	36000 dalton
1 mg/ml	3600 dalton
10 mg/ml	360 dalton

If a more relaxed sample preparation procedure must be sufficient or a short total measurement time is of importance, the Excess Scattering should be much higher (as it is usually anyway) and below are the minimum Molecular Weights for a sample scattering as much as the Standard scattering. The required measurement times per scattering angle for 1% accuracy dramatically drop to (per angle, 90° values shown):

<b>Measurement Time for 1% Counting Error</b> 100% Excess Scattering, 90° Scattering Angle	
ALV / CGS-3 (HeNe, 632.8 nm)	approx. 6 s
ALV / CGS-3 (Nd-YAG, 532 nm)	approx. 2.7 s

with the minimum measurable Molecular Weight increasing accordingly.

<b>Excess Scattering = 100%, dn/dc = 0.2 ml/g</b>	
<b>Sample Concentration</b>	<b>Min. Molecular Weight</b>
0.01 mg/ml	3600000 dalton
0.1 mg/ml	360000 dalton
1 mg/ml	36000 dalton
10 mg/ml	3600 dalton

## 1.6. Minimum Measurable Radius of Gyration

To extract the Radius of Gyration, the slope of the angular dependent scattering intensities must be calculated for the extrapolation  $c \rightarrow 0$ . This is possible only, if the slope is significantly larger than the residual counting errors and systematic errors of the absolute scattering intensities. If we assume that these errors are within 1% in total and measurements at 20 different angles are taken, an overall slope of approximately 0.3% over the measured angular range (17° ... 150°) is still significant. In this case, this slope is equivalent to a Radius of Gyration of approx. 5 nm.

<p><b>Min. Measurable Radius of Gyration</b> 0.3% slope over Scattering Range of 17° ... 150°</p>	
<p>ALV / CGS-3</p>	<p>min. Radius of Gyration approx. 5 nm  smaller radius of gyration down to 0.5nm radius can be calculated from obtained hydrodynamic radius using specific shape information</p>

## 1.7. Minimum Measurable 2<sup>nd</sup> Virial Coefficient

<p><b>Min. Measurable 2<sup>nd</sup> Virial Coefficient</b> depending on actual sample concentrations used</p>	
<p>ALV / CGS -3</p>	<p>min. Virial Coefficient approx. <math>10^{-7} \text{ mol dm}^3 / \text{g}^2</math></p>

# Dynamic Light Scattering

## 2.0. Brief Theory

In contrast to the Static Light Scattering, not the time integrated intensity at a given scattering angle is important for Dynamic Light Scattering, but the temporal fluctuation of this intensity due to the **Brownian Motion** of the particles in the sample.

To determine this (short time) temporal fluctuation of the intensity, both, a very coherent illumination as well as a very coherent detection is required, since this intensity fluctuation is solely caused by phase changes in the light fields scattered by each particle onto the detector. Phase changes due to position changes of the particles (the Brownian Motion) will cause the measured intensity to change as well.

In fact, this requires coherent light for illumination, since with decreasing coherence, the phase changes will average more and more to zero and no fluctuation will become visible anymore. Likewise, an incoherent detection will lead to the same general problem. The fluctuation, especially in its temporal behaviour, contains the required information for Dynamic Light Scattering - the faster the fluctuation is, the faster the particles move within the solvent and obviously, this is directly linked to a larger **Diffusion Coefficient** and thus smaller **Hydrodynamic Radius** and vice versa. Still the fluctuation itself is by no means deterministic - as the particles position change in a completely random way, the intensity fluctuations will do accordingly.

Large position changes in a given time are less probable than small position changes and thus large intensity fluctuations are less probable than small ones. Using a **Digital Correlator**, these probabilities can be transformed into a **Correlation Function**, which, after applying a bit of math, reveals the desired target parameters, namely Fluctuation Rates or Diffusion Coefficients. Still any process within the sample leading to position fluctuations of the light scattering centres (which is more relaxed than talking about „particles“) is measurable via Dynamic Light Scattering and not all of these are necessarily caused by Diffusion in the strict sense, but might be due to particle interaction, particle flexibility etc.

To determine the capability of a light scattering apparatus in terms of Dynamic Light Scattering, the following parameters must be precisely analysed :

- ***the detection efficiency in terms of Count Rate x Coherence Factor***
- ***the temporal resolution of the entire chain of optical detection, single photon detection and digital correlator***
- ***the long-time Count Rate stability of the entire system***

The detection efficiency is a crucial point for Dynamic Light Scattering, but different from Static Light Scattering not only a problem of the Count Rate itself, but as well a problem of the ratio of fluctuating and non-fluctuating part of the detector signal. A high Count Rate is totally useless, if there is no more fluctuation visible in the signal.

It can be shown, that the statistical accuracy of the Correlation Function is for a given measurement time and a certain sample is constant, as long as the relative fluctuating part of the Correlation Function (also called relative intercept) and the Count Rate satisfies :

$$Intercept_{rel} \text{ Count Rate} = const.$$

This simple relation however is difficult to fulfil for all geometrical optics based detectors (thus such detectors using pinholes or slits), for such a type of detector and assuming near Gaussian field fluctuation (which is generally true for light scattering, besides non-ergodic systems), the relative intercepts and the Count Rate scale as :

**Geometrical Optics :**

2.0.0 
$$Intercept_{rel.} = \frac{1}{1+N_{Mode}}, \text{ Count Rate} \cong N_{Mode}$$

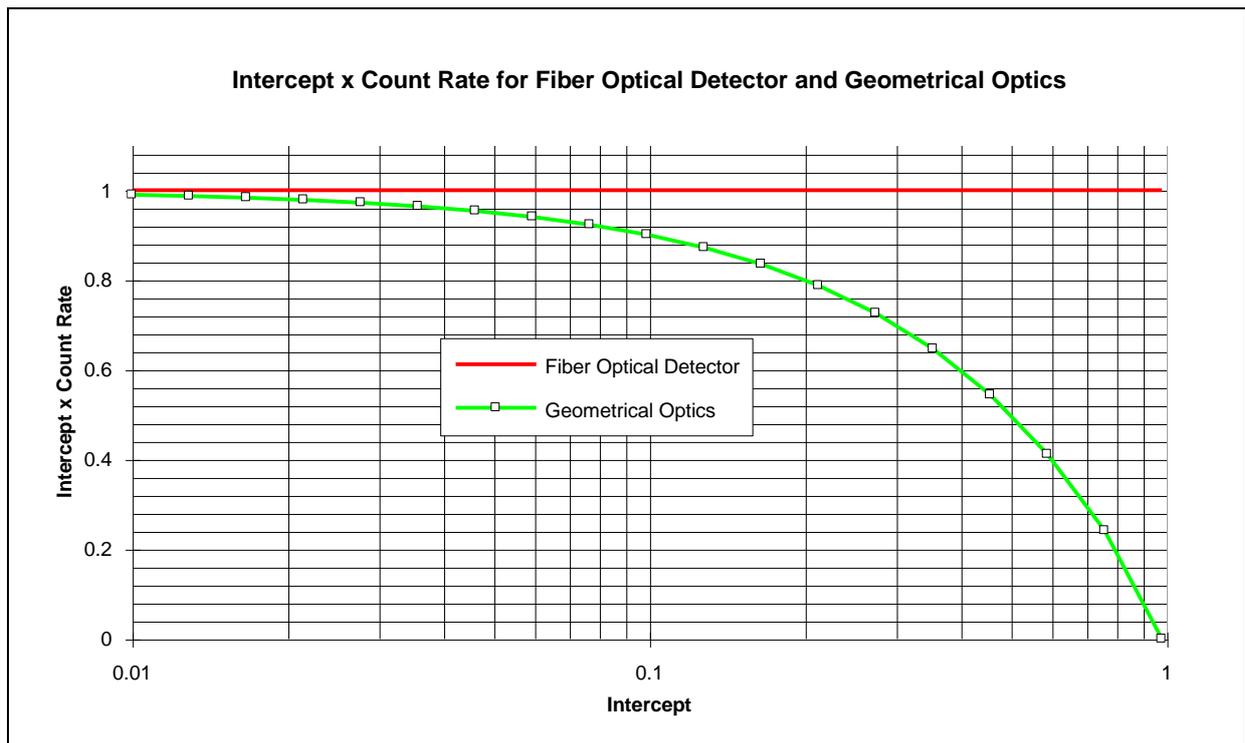
$$Intercept_{rel.} \text{ CountRate} = \frac{N_{Mode}}{1+N_{Mode}} \neq const.$$

while the relations for Fiber Optical Detectors can be shown to satisfy :

**Fiber Optical Detection :**

2.0.1 
$$Intercept_{rel.} = \frac{1}{N_{Mode}}, \text{ Count Rate} \cong N_{Mode}$$

$$Intercept_{rel.} \text{ CountRate} = \frac{N_{Mode}}{N_{Mode}} = 1 = const.$$



The above figure clearly shows the major disadvantage of using Geometrical Optics for detection - for high relative intercepts, which require a small number of modes ( $N_{Mode}$ ) or coherence areas to be detected only (-> **Coherent Detection**), the product of Intercept x Count Rate will drop dramatically, while it stays completely constant for the Fiber Optical Detection.

Another important fact is, that a relative intercept larger 1 is not possible for Geometrical Optics explicitly and is not possible for Fiber Optical Detectors as well (an optical fiber must at least propagate a single mode, thus  $N_{Mode} \geq 1$ ).

The enormous light loss of the Geometrical Optics over the Fiber Optical Detector is easy to explain - these are simply diffraction losses which increase dramatically for higher and higher angular definition (and thus smaller and smaller pinhole size).

Only in the limit of very large area detectors (***incoherent detection***) and thus small intercepts, both detection methods will show similar efficiency, for the simple reason that the diffraction loss of the Geometrical Optics becomes negligible in this limit. But this limit is of no further interest, since a high relative intercept is absolutely desirable for two reasons :

- ***because it is equivalent to a high angular resolution***
- ***because all residual „instabilities“ and „distortions“ of the detection and illumination, such as laser power instabilities, thermal drifts of the detectors quantum efficiency, afterpulsing of the single photon detector etc. will be linearly added to the correlation function and thus will have relative minimum at maximum relative intercept only.***

For a still reasonable efficiency, Geometrical Optics cannot be used with high intercepts and the Fiber Optical Detection is the much better choice. In addition, it is by far more easy to align and allows for certain additional „optimizations“ (which in detail are out for scope of this brief theoretical discussion) which will even further enhance the detection efficiency over Geometrical Optics.

## 2.1. Selecting the „best“ Number of Modes

One property of Fiber Optical Detectors however is, that they cannot propagate an arbitrary number of modes, but a discrete number only (and even here, not 1, 2, 3, but 1 mode, 3 modes, 6 modes etc.). This behaviour seems to give the engineer of a light scattering system not much choice at all :

Number of Modes propagated by a simple Optical Fiber System	Relative Intercept
either 1	1
or 3	0.333
or 6	0.166
or 10	0.1
...	...

While seemingly the best choice, the use of a strictly single mode fiber might not be the best choice for simultaneous DLS & SLS at very low scattering intensities (however, as we see below, it normally is the best choice for DLS). The next best choice would thus be to use a 3 mode fiber, which however would already drop the intercept to „just“ 0.333 - a 3 times increase in the „residual instabilities“ would be the result.

However, with some additional technology involved (which again in detail is out for scope of this theoretical discussion), such „residual instabilities“ can be ensured to be small enough to make full use of the 3-fold increase in detected light of a 3 mode fiber over a single mode fiber. ALV thus decided to make use of this technology in the ALV-Static & Dynamic Enhancer - 3 Detection System.

Depending on the users choice, either approximately 3 modes are propagated (ALV-Static & Dynamic Enhancer - 3) or approximately 1 mode is propagated (ALV-Static & Dynamic Enhancer, default configuration) such, that the below described „interferometer problem“ is fully avoided.

## 2.2 Solving the „Interferometer Problem“

The question still open is, whether the use of just a single mode does really minimize the relative contribution of the „residual instabilities“ ? **The answer is a clear NO !**

One particular problem of coherent light propagation systems (with the single mode fiber being a famous member) is that they as well act as interferometer. Photons, once coupled into such a fiber, will not lose their mutual phase condition and if mixed at a certain point (namely the reflection points at the in-coupling / out-coupling zones) will coherently interfere.

At the outcoupling point for example (which in fact is just the end of the fiber), a high difference of refractive index exists, namely that of the fiber (near to 1,5) and that of the air (near to 1). As usual for refractive index changes, light is reflected and in this case reflected back to the fiber. This effect will happen every time light crosses such a refractive index change point (input / output of the fiber) and effectively this is equivalent to an interferometer - not a very good one, since the Q value is very little - only a few % of the light is reflected, but still a notable amount of light is reflected and mixed with the unreflected light etc.

This effect in itself would not really disturb the measurement - as long as the mixing stayed constant and did not change in time. Indeed, the mixing condition does change dramatically in time for two simple reasons - thermal drifts and vibration.

Per 1 m fiber length, the phase change of 632,8 nm light propagating through the fiber can be shown to be with approx. 90 rad / °C, leading to a complete phase change per 0.06°C already. Thus a thermal drift of just 0.03°C (half phase) will be sufficient to cause more than 8% (assuming 4% reflection at the fiber output) intensity fluctuation at the fiber output.

Reducing the fiber length helps - with using just 10 cm of fiber length, the effect would show up with the same magnitude at a thermal drift of 0.3° C. Keeping in mind that standard laboratory conditions allow a temperature change in the order of 1°C total per hour easily, even a 10 mm fiber length would not really solve the problem, but just reduce it to roughly +/- 2 % intensity fluctuation - however, this „fiber“ would not be long enough to ensure reasonable mode characteristics at all and would even be too short to make use of it as being a fiber. Even worse, thermal drifts are just one reason for this effect, another is pressure change within the fiber, which can very well be caused by vibration or simply „movements“ of the fiber as well.

Another simple to understand insight is, that this effect very much depends on the coherence of the coupled photons and the coherence of the fiber propagation - the better the coherence, the better the mixing, the larger the instabilities.

**Maximum instability must be expected using a single mode fiber as is, because it fully conserves the coherence of the incoupled light. Using very reduced fiber length will somewhat decrease the fluctuation magnitude, but will as well reduce it's filtering properties in terms of propagating just a single mode.**

In addition, an approximately linear decreasing instability with the number of modes propagated can be expected - approx. 1/3 of the intensity instability for a three mode fiber and approx. 1/6 of the intensity instability for a 6 mode fiber. It is this interferometer effect which limits the relative „residual instabilities“ of the fiber optics ! However, with some additional ALV technology involved, there is a complete solution to this problem.

The ALV-technique used ensures that the interferometer effect vanishes to much less than 0.05% instead of the 8 % intensity instability single mode fibers can easily show and the ALV-Static&Dynamic Enhancers make of course full use of this advanced technique as well.

***Fiber Optical Detection Systems are superior over classical Geometrical Optics for DLS measurements in terms of detection efficiency. However, Fiber Optical Detection Systems show, specially if high coherence detection is used, additional intensity instabilities due to the „interferometer effect“, specially for single mode fibers. Additional measures have to be taken to avoid this effect as much as possible. The ALV-Static & Dynamic Enhancer Detection Systems features near to single mode detection at even higher efficiency than using a single mode fiber while almost completely suppressing the „interferometer effect“.***

### 3.0. The Digital Correlator

Having a highly efficient light detector is one key to a successful DLS measurement. Still, a few more ingredients are required to actually perform the DLS measurement and furthermore to extract the desired target parameters, such as the **Diffusion Coefficient** or **Hydrodynamic Radius**.

Dynamic Light Scattering measures the fluctuation of the light caused by the position changes of scattering centres in the sample due to **Brownian Motion**, for example. As noted above, such position change is fully random and likewise the resulting intensity fluctuation of the light scattered is random as well. Simply recording the intensity will thus not give further insight about the diffusion process at all and instead, special **Signal Processing** must be used. Typically, a **Correlation Function** is computed, which for DLS scales the relative probability of fast to slow fluctuation of the light intensity to each other. In there, the complete information about the diffusion process is buried, since small position changes leading to small phase changes and thus small intensity changes are more probable within a given **Sampling Time** than large changes obviously. The actual phase change a scattering centre produces for a given position change depends on two, the actual position change and the angle of detection. While this phase change is larger for back scattering (thus detection against the propagation of the primary laser light), it vanishes for a detection angle going to 0°. At detection angle 0°, no phase change will ever occur, the fluctuation time becomes infinite

Furthermore, the phase change depends on the wavelength of the primary laser light used, the larger the wavelength, the smaller the phase change per position change. Generally, a scattering vector is computed which includes all these parameters in a single value, namely (and again, as with SLS ):

$$3.0.0 \quad q^2 = \left( \frac{4\pi n \sin\left(\frac{\Theta}{2}\right)}{\lambda} \right)^2$$

and for a single species of diffusing particles (all of equal size), the correlation function can be computed to be :

$$3.0.1 \quad g_2(t) = e^{-2tDq^2}$$

with  $D$  being the Diffusion Coefficient of the scattering centres in the solvent. The above correlation function is called the „Intensity Correlation Function“ since it is computed from the light intensity at the detector.

The **Diffusion Coefficient** is (assuming the Einstein-Stokes relation applies) linked to the **Hydrodynamic Radius** via :

$$3.0.2 \quad D = \frac{kT}{6\pi \eta R}$$

with  $k$  being the Boltzmann Constant,  $T$  the temperature in Kelvin, and  $\eta$  the solvent viscosity at this temperature and  $R$  is the **Hydrodynamic Radius**. The sample temperature measurement is part of the ALV-Goniometer System and is precise to approx. +/- 0.1°C absolute and +/- 0.01°C relative.

As can be seen from the above formulae, the „decay“ of the exponential function with  $t$  (the lag time) depends on the Diffusion Coefficient as well as the  $q^2$  used (which, for a given system, solely depends on the solvent's refractive index as well as the scattering angle). To further exploit the required performance of the Digital Correlator, a few „real world“ parameters must now be used to compute effective decay rates. We therefore transform the above formula to

$$3.0.3 \quad g_2(t) = e^{-2\Gamma t} \quad 2\Gamma = 2Dq^2$$

Typical Diffusion Coefficients for particles in water are between **5000  $\mu\text{m}^2/\text{s}$  (< 0.1 nm particle size) to 0.1  $\mu\text{m}^2/\text{s}$  (> 5  $\mu\text{m}$  particle size)**, for less viscous solvents (toluene, THF ...) linearly higher, for high viscosity media linearly lower. Thus, a max/min range of 10000  $\mu\text{m}^2/\text{s}$  down to 0.01  $\mu\text{m}^2/\text{s}$  shall be considered for the Diffusion Coefficient in the following, along high/low refractive index solvents ( $n = 1.6$  resp. 1.33), min/max obtainable scattering angle ( $12^\circ$  and  $152^\circ$ ) and the use of the two possible wavelength laser (532 nm and 632.8 nm)

Diffusion Coefficient $D$	Scattering Vector $q^2$ (HeNe, 632.8 nm)	Decay Rate $2\Gamma$
10000 $\mu\text{m}^2/\text{s}$	$1.34 \times 10^{15} \text{ 1/m}^2$	13.400.000 1/s
0.01 $\mu\text{m}^2/\text{s}$	$7.62 \times 10^{12} \text{ 1/m}^2$	0.0762 1/s

Clearly, the digital correlator must be able to process signals with an average fluctuation times in the order of 0.07  $\mu\text{s}$  (the inverse of the Decay Rate) as well as signals with an average fluctuation time of about 13 s and all of these at optimum statistical accuracy.

It is known from information theory, that to reasonably sample a certain signal, the sampling frequency must be higher than the maximum frequency of the signal to be sampled. For the special case of periodic signals, a factor of two faster sampling is sufficient, in the case of DLS, there is no maximum frequency in principal (the frequency spectrum is continuous). Theoretical considerations as well as practical experience shows, that a, compared to the periodic signal case, significantly faster sampling is required and 4 ... 10 times „oversampling“ proved to be sufficient to avoid „aliasing distortions“. This leads to a minimum/maximum sampling times of the digital correlator as follows :

Decay Rate $2\Gamma$	Required Sampling Time
minimum 0.07 $\mu\text{s}$	7 ns ... 17.5 ns
maximum 13 s	1.3 s ... 3.25 s

For certain, the above sampling time range will cover all diffusive processes within a given sample and as well covers all scattering angles usable within the ALV-Goniometer Systems. At best, all these sampling times should be available within a single measurement and without user interaction in terms of sampling time adjustment etc. Another important aspect of the digital correlator is that it should work as real time electronics, thus every incoming pulse (generated by a photon) must be processed.

Both requirements are totally fulfilled by the ALV-7004/FAST Multiple Tau Digital Correlators. They process up to 42 parallel sampling times (from 3.125 ns ... > 3400 s) into up to 344 correlation channels, fully real time and without any user interaction required in terms of sampling / lag time adjustment.

Sometimes, however, much faster processes may be present in the sample which are no longer related to translational diffusion, but to other effects, such as rotational diffusion, for example.

*For diffusive processes, a fastest sampling time in the range of 100 ns ... 200 ns is normally sufficient even for very small particles (fast diffusion), largest possible  $q^2$  and solvents with rather small viscosity. Still, full real time operation is a must for the entire sampling / lag time regime. Both of these requirements are totally fulfilled by the ALV-7004 Multiple Tau Digital Correlator Series. Faster sampling times are required only, if special experiments must be conducted, such as depolarized light scattering at very small particles aiming at the rotational diffusion coefficient. For these cases, the ALV-7004/FAST Multiple Tau Digital Correlator Series can be used instead of the ALV-7004*

#### 4.0 Single Photon Detectors used in the ALV / CGS-3

Principally, any single photon detector can be used for SLS/DLS measurements as long as they transform a single photon into a countable electrical pulse. However, since a correlation function of the incoming electrical pulses is to be computed, the undistorted translation of the incoming photon into outgoing electrical pulses is of major importance. If there is a certain detector inherent „correlation“ in this pulse generation process, it will distort the resulting correlation accordingly. Such inherent „correlations“ usually are :

- dead time effects, which decrease the probability of detecting a photon if another photon was detected a certain (small) time before
- afterpulsing, which increases the probability of a secondary electrical pulse following the first pulse without an additional photon being detected.

While the first effect decorrelates (thus decreases the correlation function), the second effect adds a significant correlation to the correlation function of the light signal. Both processes are in quite different time scales, while dead times usually show up in the sub 100 ns regime, afterpulsing usually shows up in the 100 ns ... 1  $\mu$ s regime.

Clearly, without special selection of the single photon detector and pulse amplification/generation electronics, the entire lag time range below 1 ... 2  $\mu$ s is usually unusable due to detector correlations. But even selection of the single photon detectors (were selection here is not pointing to the dark counts, which have little to no effect on the correlation function's quality) will not solve this problem completely - **single photon detectors which fulfill all requirements to allow high quality correlation function accumulation at below 10 ns sampling time simply do not exist !**

For this reason, a special setup consisting of two independent ALV-High Q.E. APDs plus an fiber-optical beam splitter can be used. While both detectors see half of the same light (that is, both see the same light fluctuation caused by the diffusion process), their actual photon detection remains independent from each other and with that the effects of afterpulsing and dead-times. While the later simply vanishes as first order effect (higher order effects are still present as a non-linear count rate / illumination behaviour), afterpulses get „distributed“ over the entire lag time range and show up as marginal additional noise (this, however, is not true for very small lag times in the sub 50 ns regime. Small additional distortions may be present at such small lag times for various reasons out of scope of this technical data sheet. Nevertheless it should be noted, that this lag time regime is usually not even accessible with a single detector due to dead time effects )

## 5.0 The Long Time Count Rate Stability of the Entire System

Using the ALV-Static & Dynamic Enhancer and the ALV-High Q.E APD, the ALV / CGS-3 Goniometer Systems long time count rate stability (24 hours and longer) can be shown to be solely limited by the long-time stability of the laser source (which is approx. +/- 1% or better over 24 h for the HeNe laser, and approx. +/-0.5% for the NdYAG laser). The laser source intensity changes are fully compensated for in Static Light Scattering measurements via the Monitor Diode Unit.

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