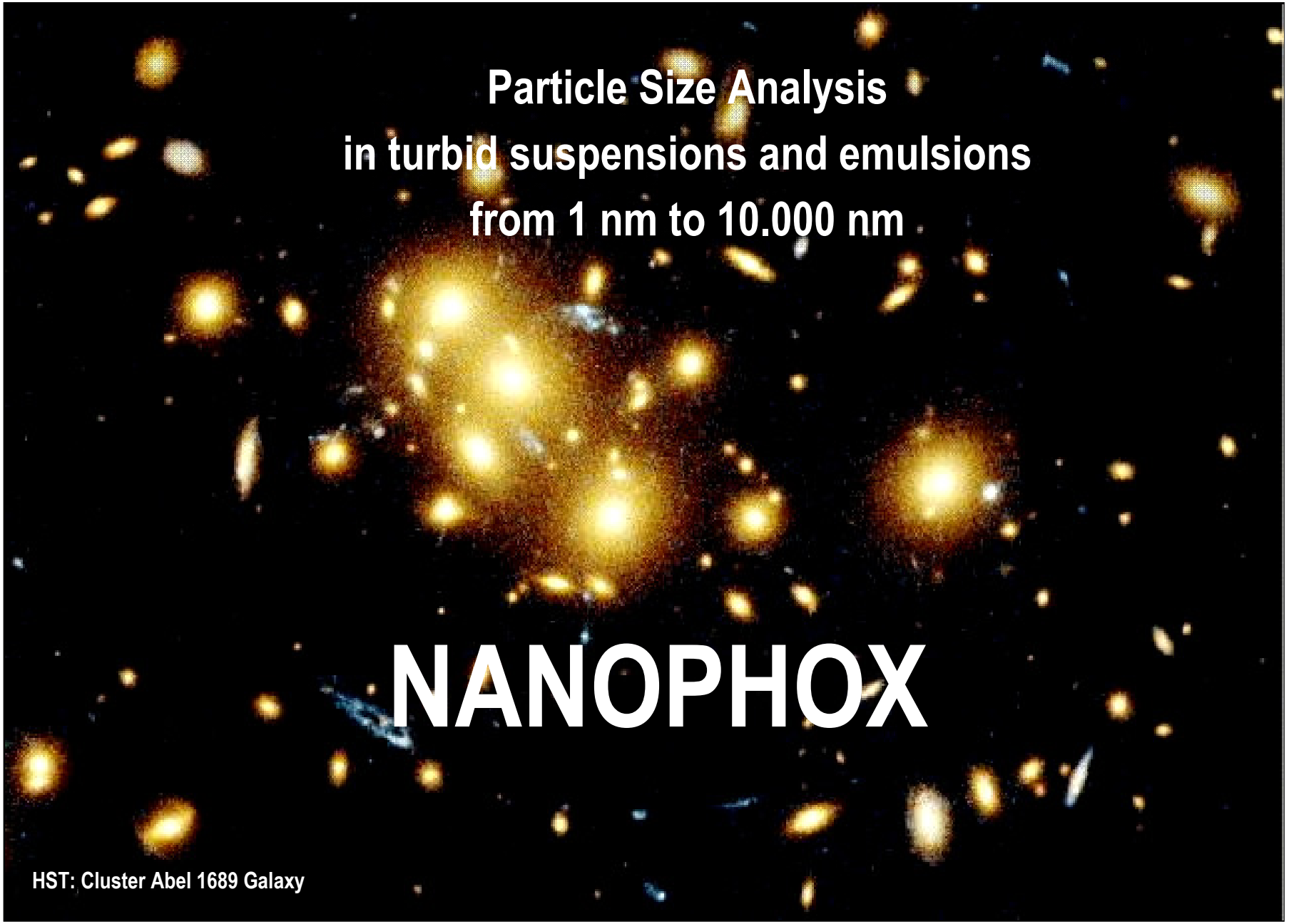
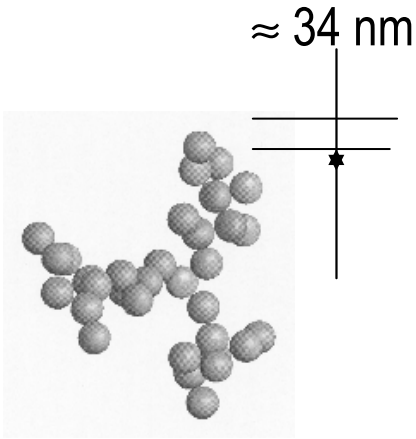


Introduction

★ Particles in the nanometre range offer numerous new properties:

- ✔ Scratchproof surfaces and coatings
- ✔ Conductive glass
- ✔ Non corrosive steel
- ✔ Optical storage capacity of plastics
- ✔ Bullet proof synthetic fibres

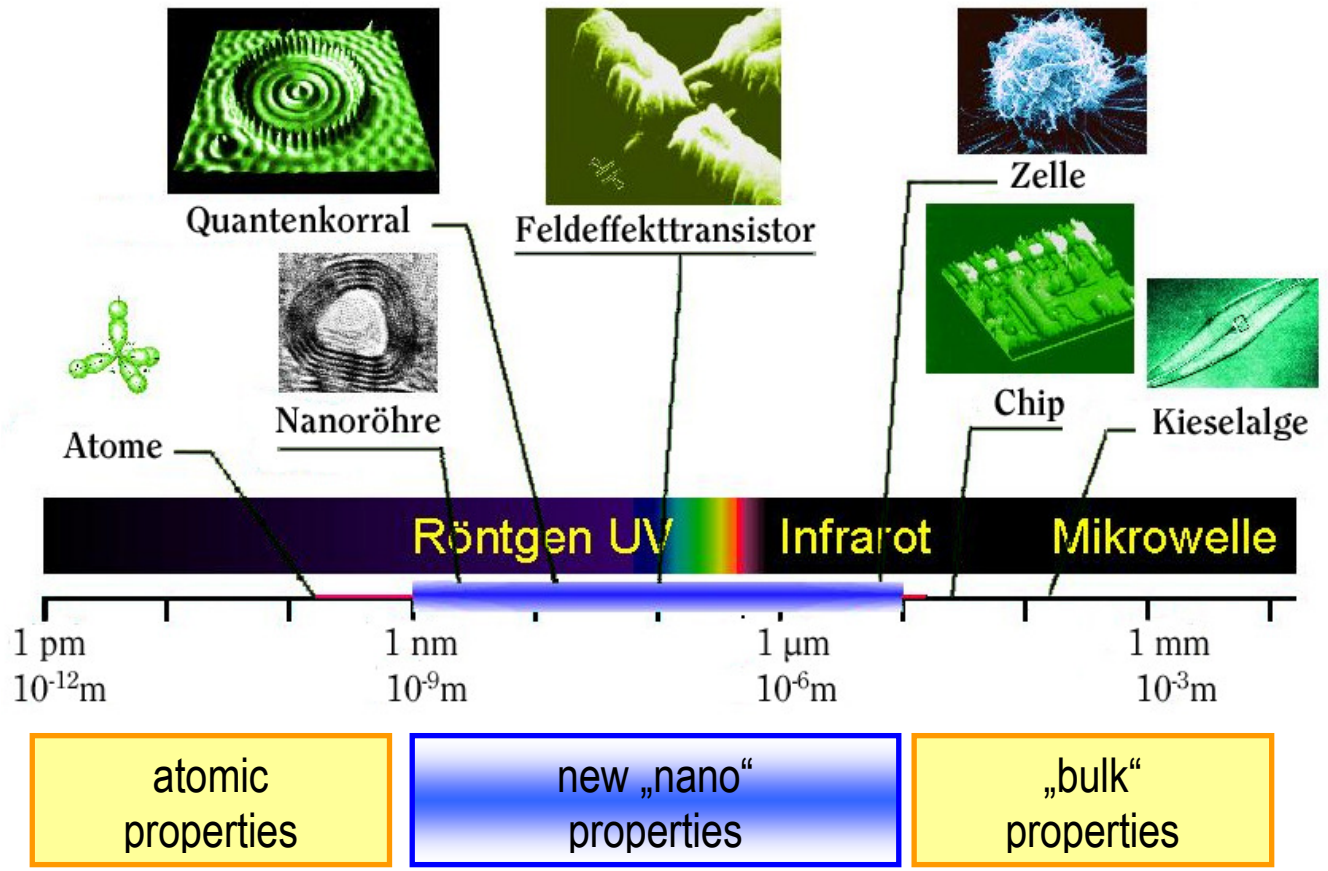
★ Can be designed e.g. in composite products, which contain large amounts of transparent fumed silica in the nanometre range as filler in a plastic matrix



Example Aerosil Typ „0.2 – 2 µm“
about. 50 Weight. %

Size Scales

★ The new properties of these fillers are related to their particle size



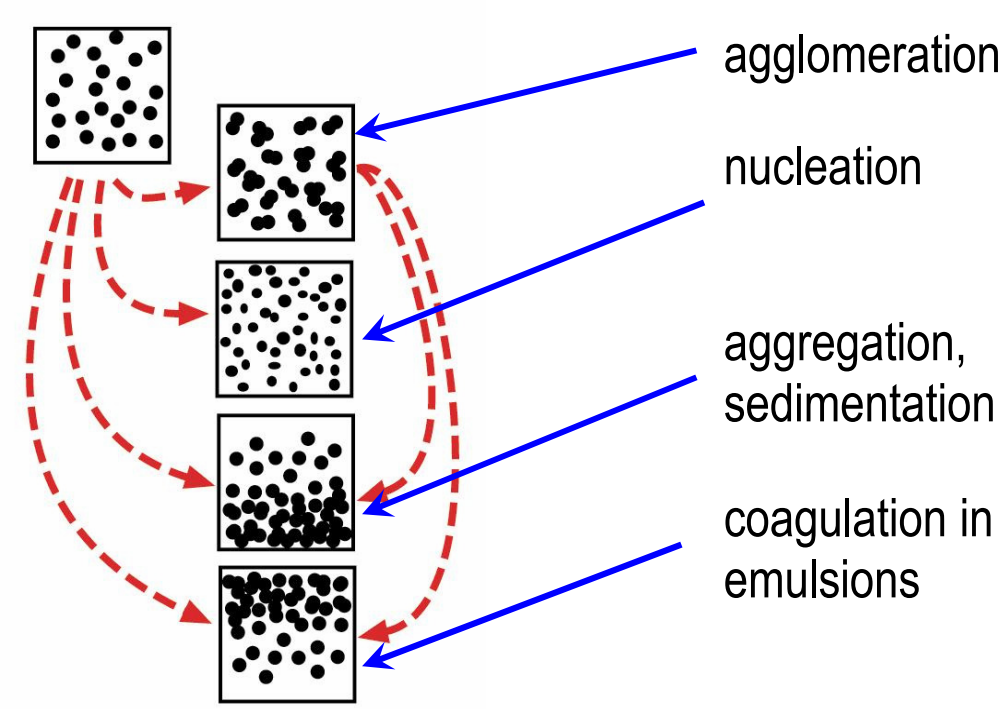
atomic properties	new „nano“ properties	„bulk“ properties

Material Characteristics

★ Material characteristics depend on

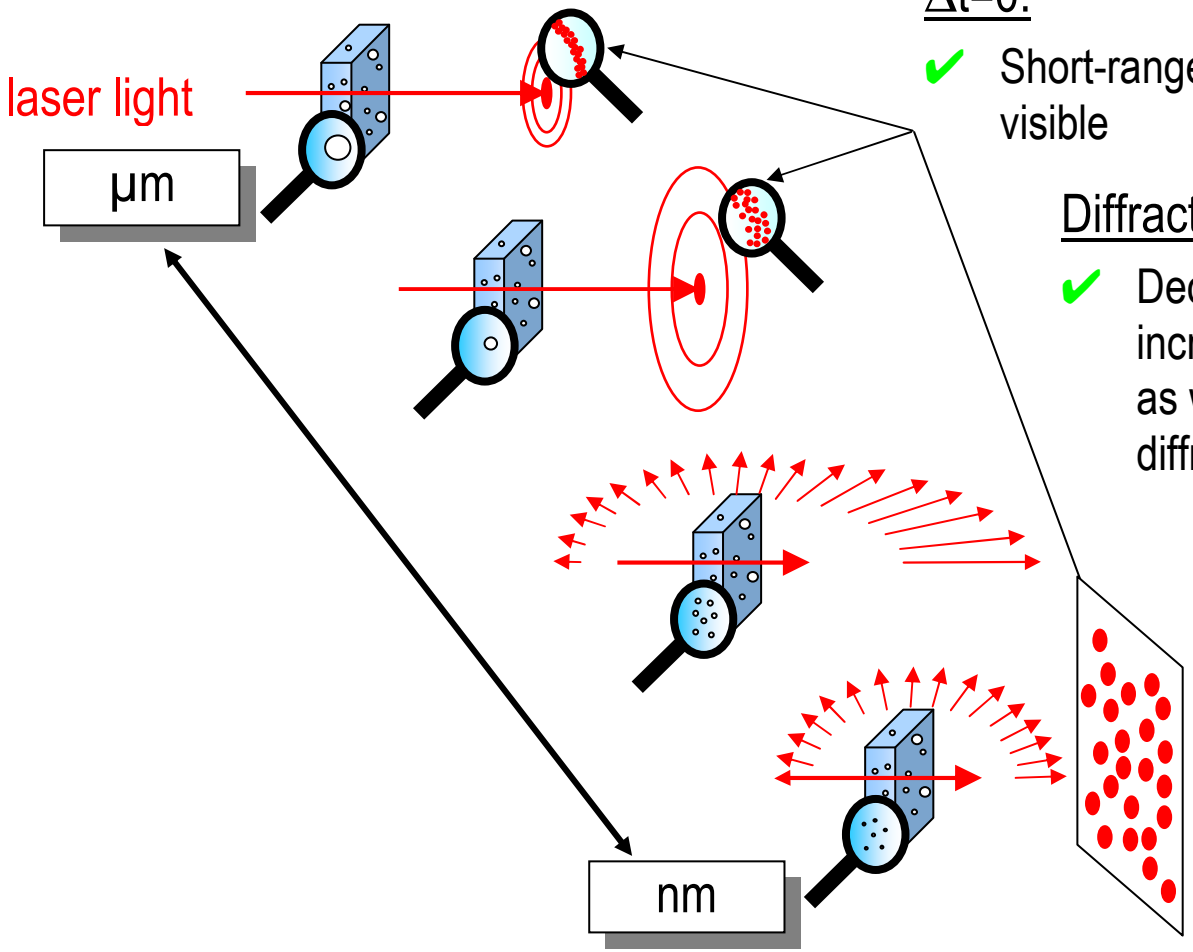
- ✔ The particle size distributions
- ✔ The stability of such distributions

★ Nano particles having extremely large surfaces tend to



Photon Correlation Spectroscopy (PCS)

Interaction of laser light and particles



Δt=0:

✔ Short-range order of particles is visible

Diffraction:

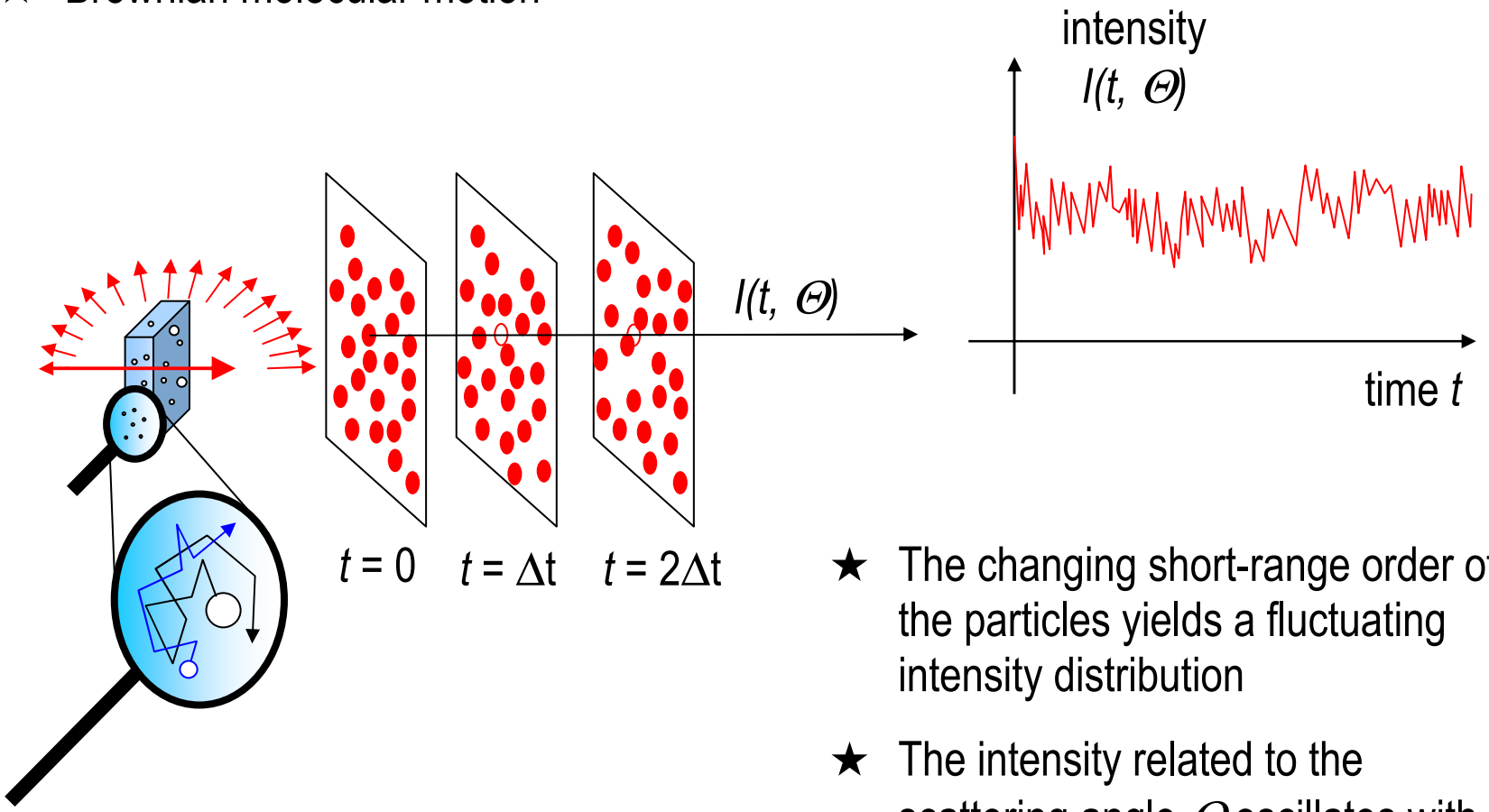
✔ Decreasing particle size increases the diffraction-angles as well as the blurring of the diffraction pattern

Scattering:

✔ Outside low angle light scattering (LALS) particle diameters, only light scattered at wide angles is available for size measurement

Interaction of laser light and particles in the nanometre range

★ Brownian molecular motion



★ The changing short-range order of the particles yields a fluctuating intensity distribution

★ The intensity related to the scattering angle Θ oscillates with time t

★ Brownian molecular motion

✔ The phenomenon was correctly assumed by W. Ramsay in 1876 and proven by A. Einstein and M. von Smoluchowskiin in 1905/06

✔ „Stokes Einstein“ relation applies:

$$D(x) = k_B T / 3\pi\mu x$$

D	diffusion constant
k_B	Boltzmann-constant
T	absolute temperature
η	dynamic viscosity of surrounding medium
x	particle diameter

applying the auto-correlation function $G(\tau)$

$$G(\tau) = \langle I^s(\theta,0)\, I^s(\theta,\tau)\rangle = \langle I\rangle^2 (1 + \exp(-2\, D(x)\, q^2\, \tau)) = \langle I\rangle^2 (1 + \exp(-2\, q^2\, k_B T\, \tau/3\pi\eta x))$$

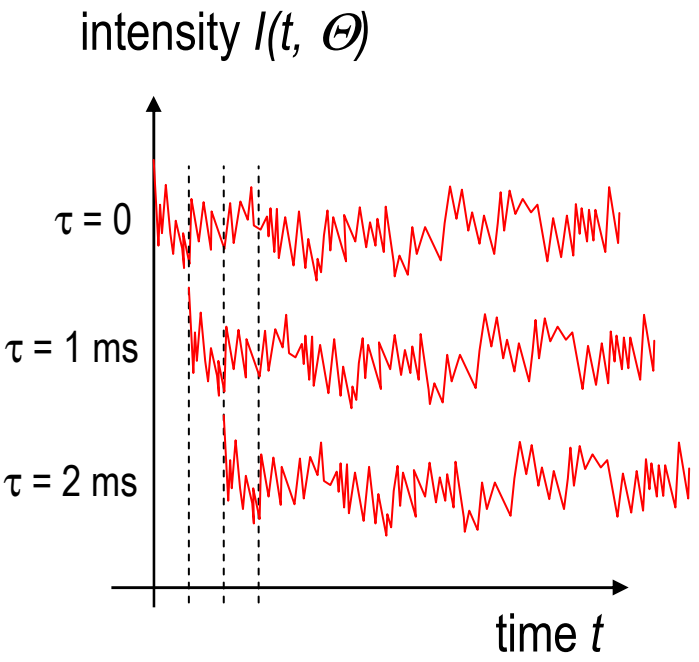
↳ decay constant $\propto$ diffusion D(x) = $\dfrac{k_B T}{3\pi\eta x}$

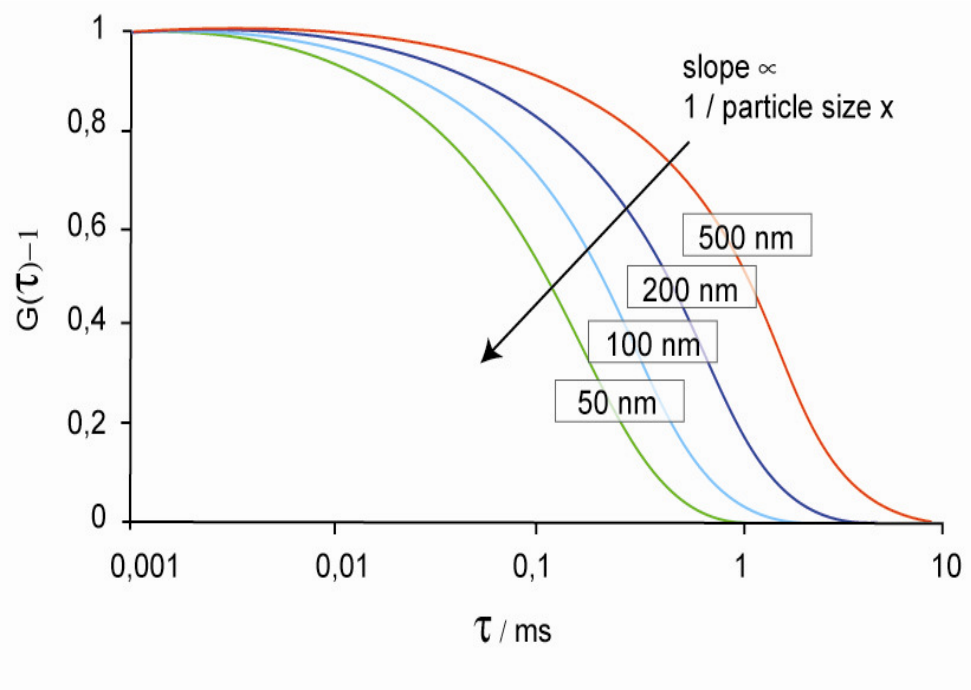
↳ decay constant $\propto$ 1/particle size x

★ Determination of particle size

☆ Calculation of auto correlation function $G(\tau)$

☆ Evaluation of particle size from slope $\ln(G(\tau)-1)$





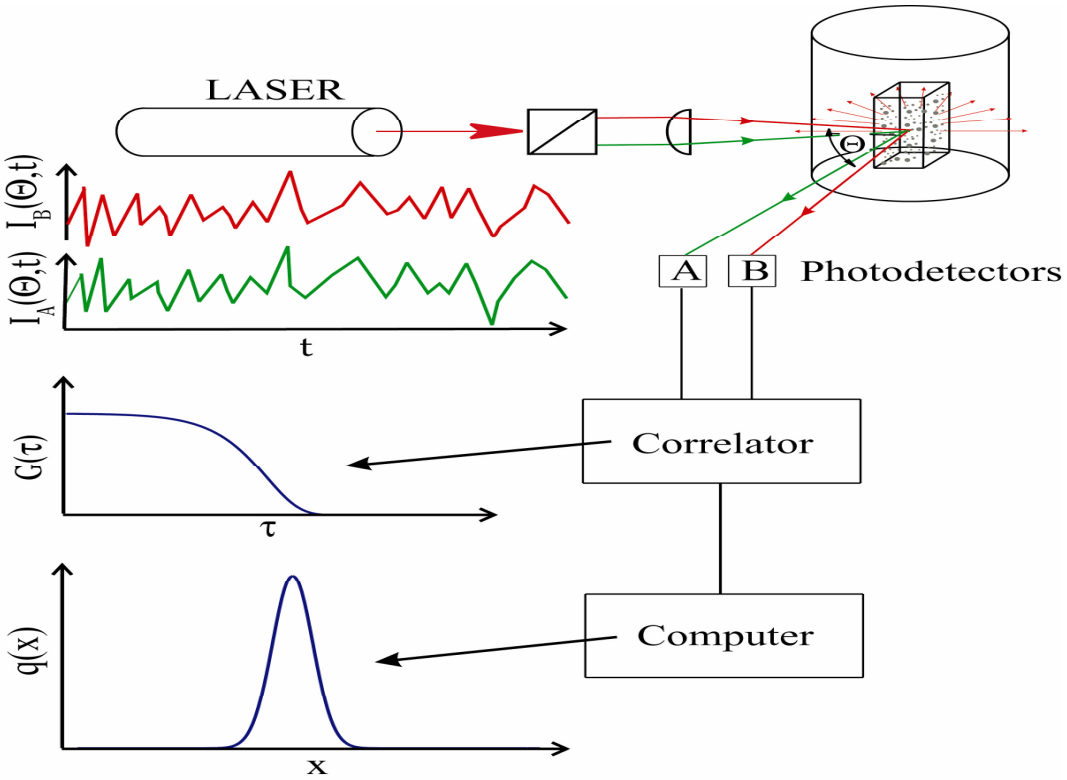
Limitations of PCS

- ★ Valid only for non-interacting, spherical particles
- ★ Singularly scattered laser light
- ★ Multiple scattering in turbid suspensions of high concentrations distorts the result
  - ✘ Depends on concentration
  - ✘ And cuvette position
- ★ To avoid multiple scattering PCS has to be operated at extremely low concentrations:
  - ✘ Low scattering intensities
    - ↳ Poor signal-/noise ratio
    - ↳ Long analysis times
  - ✘ Dilution not only delicate → often even non-permissible
  - ✘ Contaminations → dust bastardises the result
  - ✘ Stability of sample ?

↳ Improvement of principle: Elimination of influence of multiple scattering

Photon Cross Correlation Spectroscopy (PCCS)

Principle

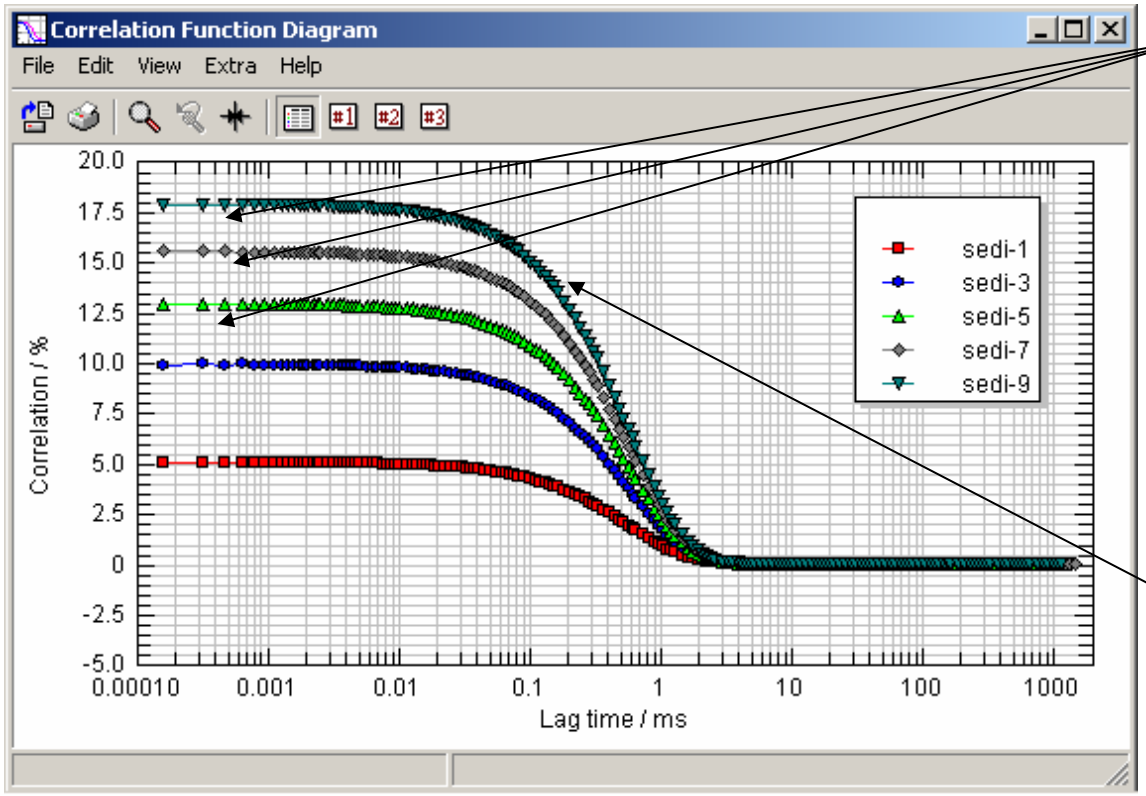


- ✔ Two laser beams cross over in the sample container and generate two similar signal patterns (speckles)
- ✔ Identical parts can be selected by correlation of the intensities of two equivalent signal spots

Result

★ Key principle: 3D-cross correlation

✔ Selection of singularly scattered light



2 measured variables:

1. Amplitude ∝ singularly scattered part

✔ Mutation of sample → change of amplitude

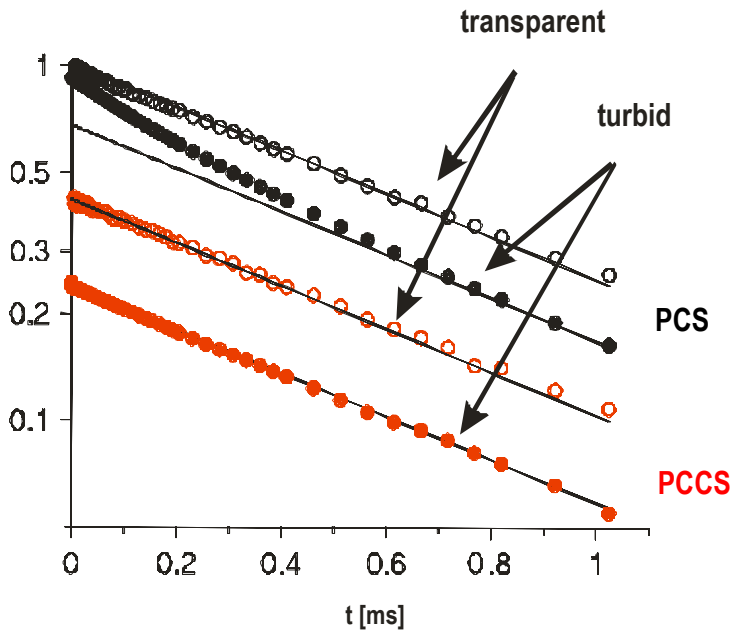
↳ Potential for stability analysis

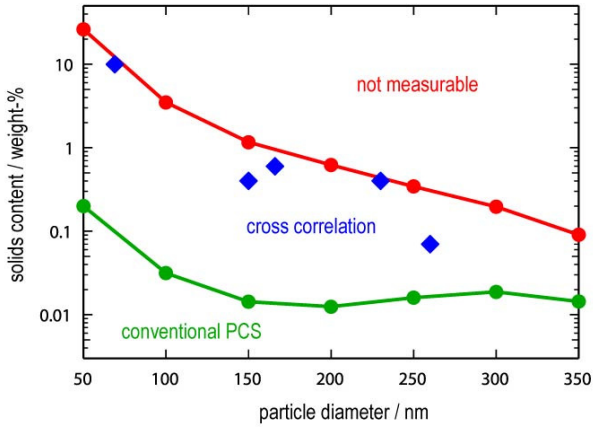
2. Slope ∝ 1/particle size *x*

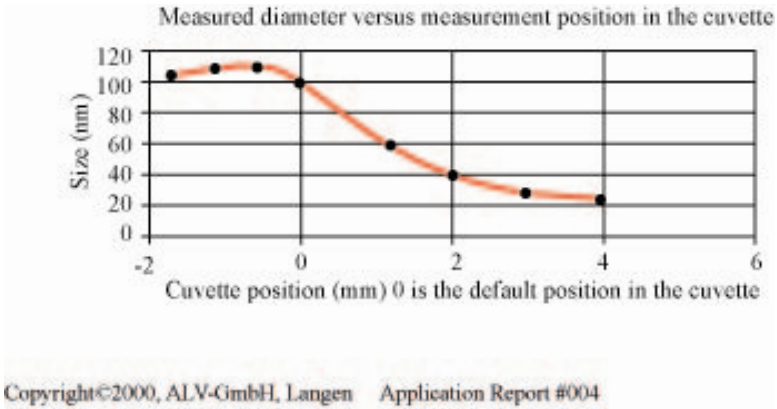
✔ PCCS provides exact information for turbid samples

Elimination of multiple scattering portion:

★ Latex in H_2O, 107 ± 10 nm (TEM)

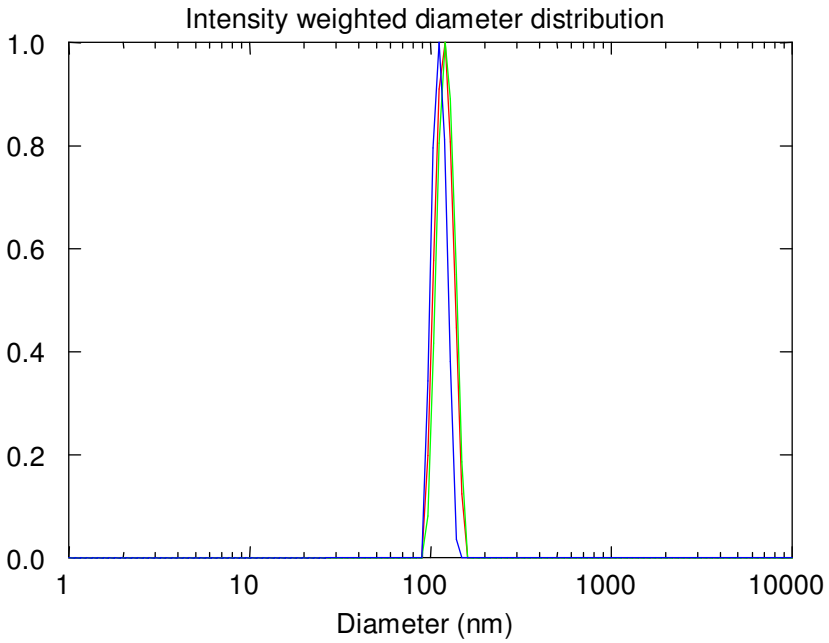




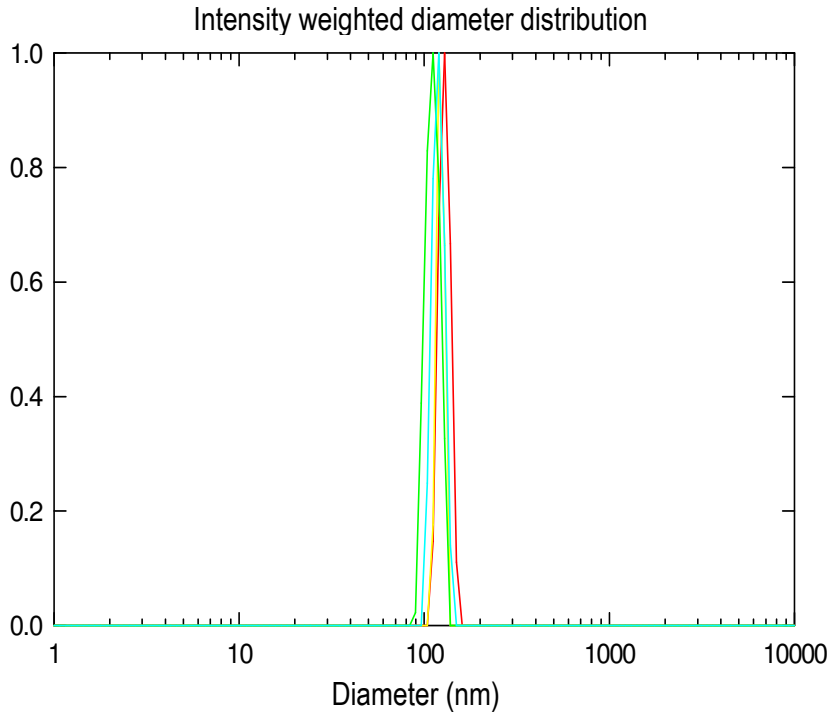


Transparent: Transmission 99.7 %
Turbid: Transmission 0.7 %
Both: (1x1 cm^2-cuvette)

Independence on Cuvette Position and Concentration:

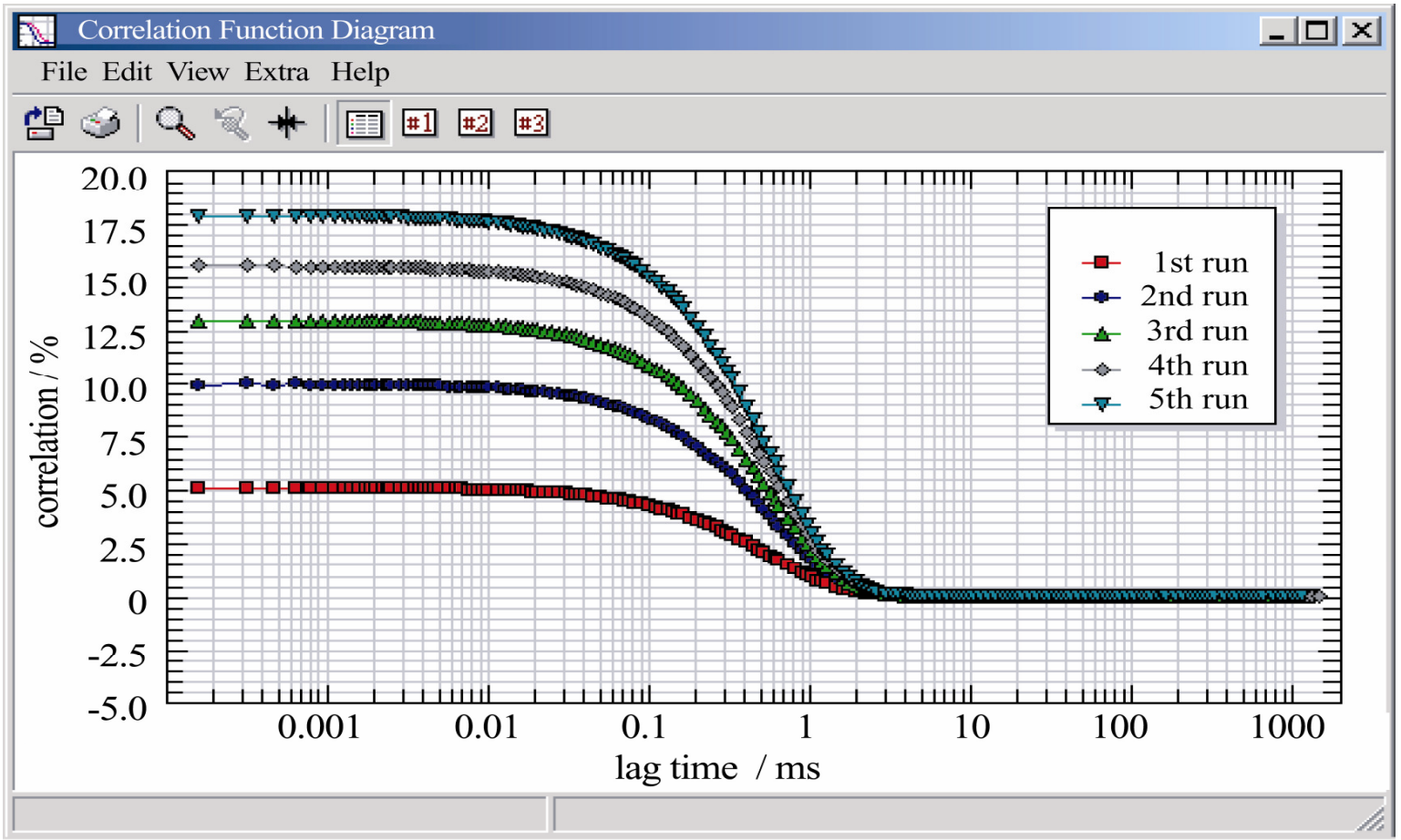


Latex 120 nm,
0.2 weight %, 3 different cuvette positions



Latex 120 nm,
4 concentrations: 2; 0.4; 0.2; 0.1 weight %

Concurrent Analysis of Stability and Particle Size



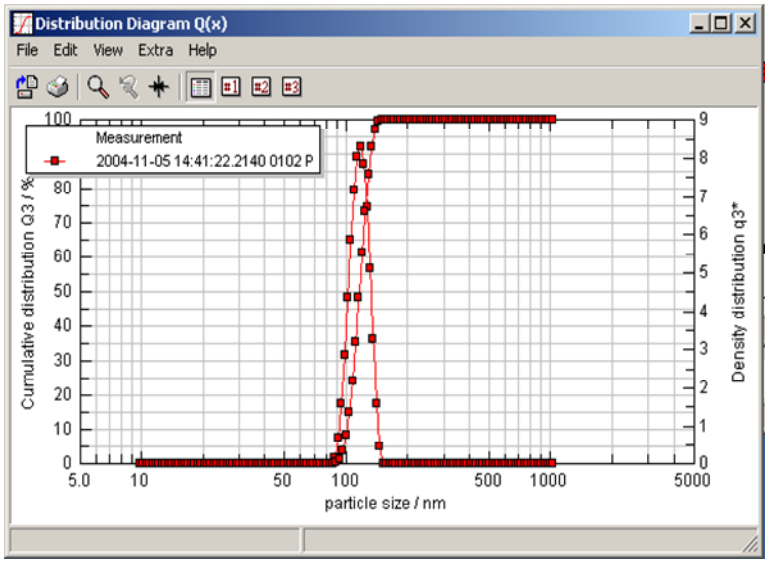
Sedimentation of a turbid quartz suspension over many hours

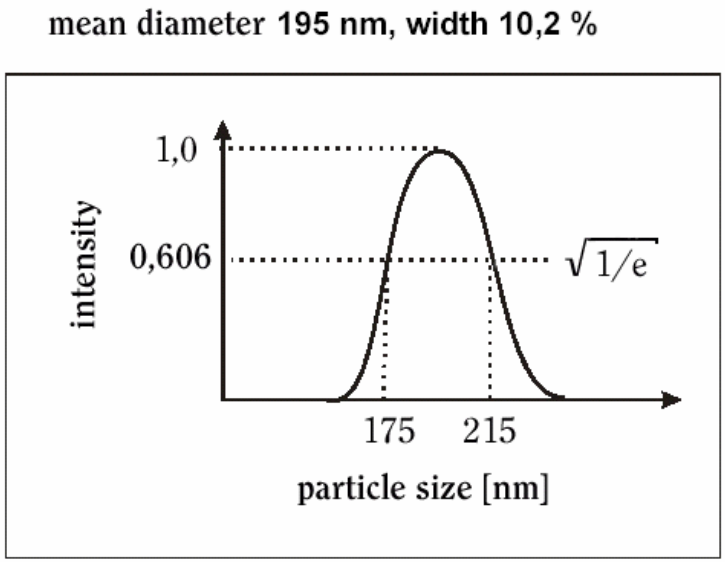
Evaluation

Standard evaluation (2nd Cumulant)

★ Presumes and requires mono modularity and yields:

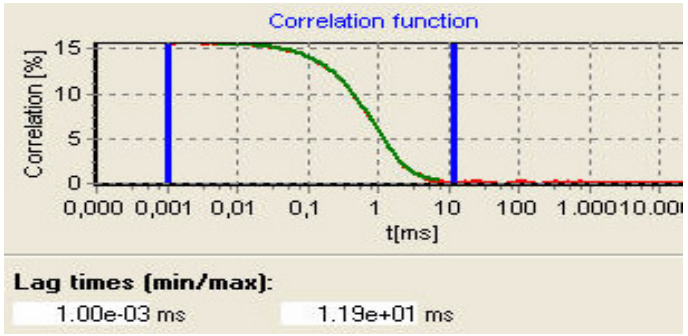
- ✔ Median diameter of the distribution
- ✔ Indication as to the width of distribution (width ± %)
- ✘ No information regarding the internal structure of the total distribution





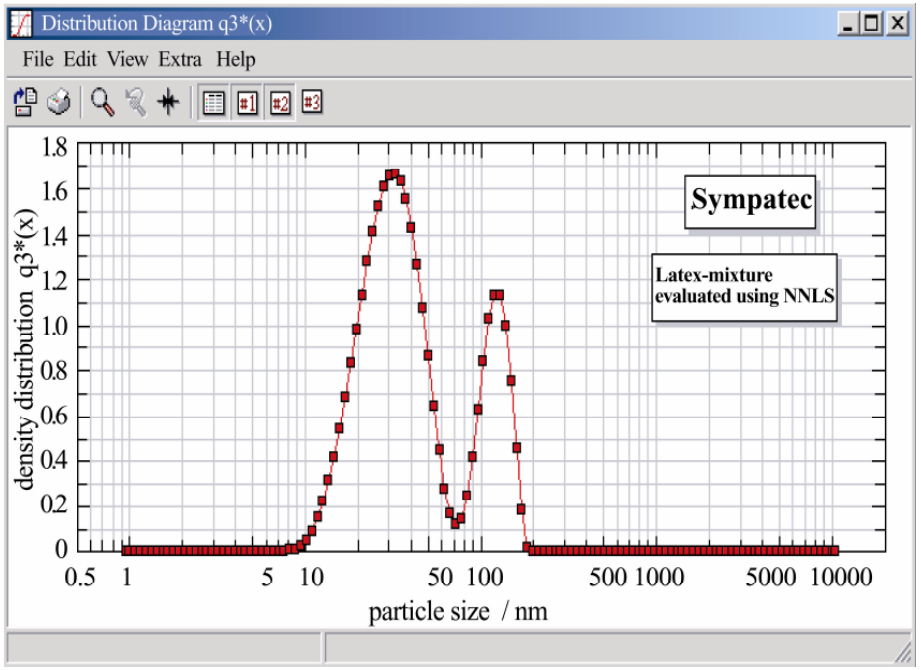
mean diameter: 195 nm
width: ± 10.2 %

NNLS (Non Negative Least Square):

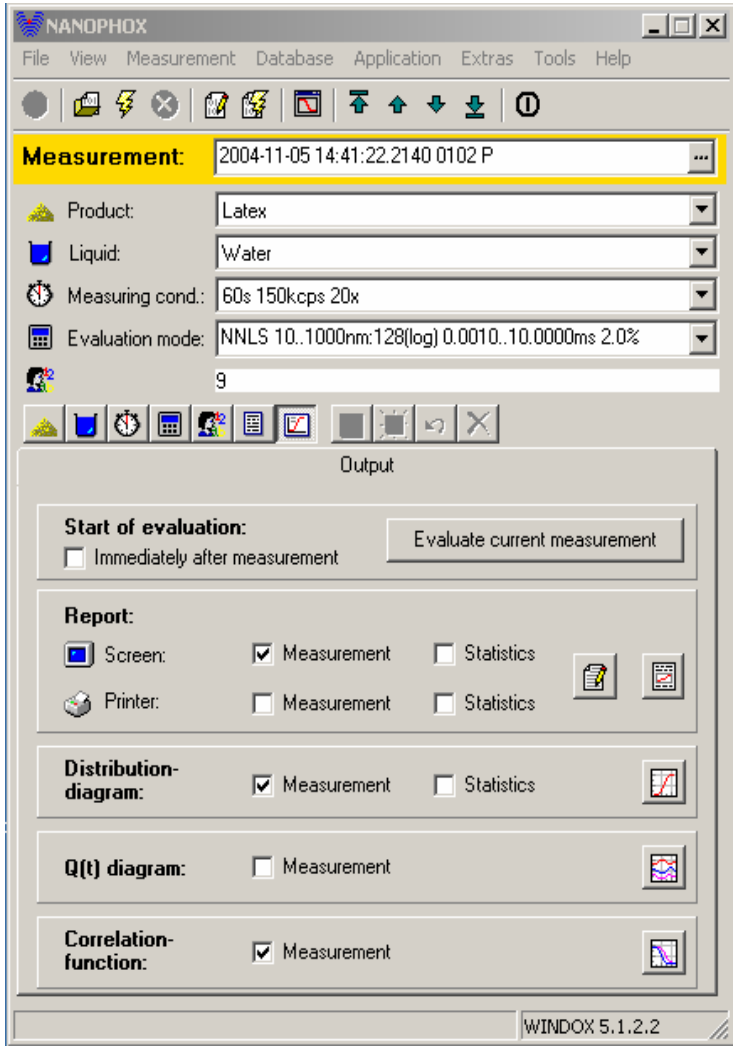


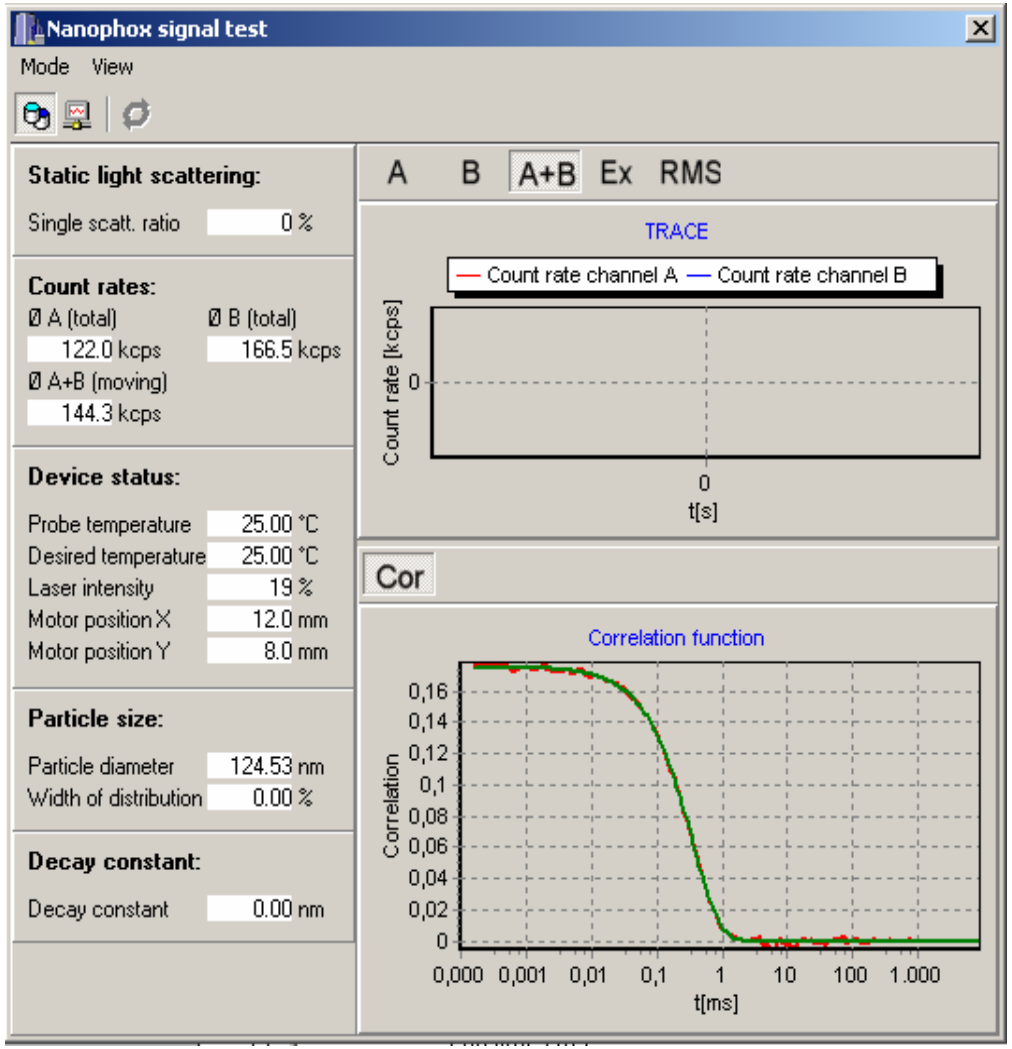
- ✔ Selection of the best fitting window determines the quality of the evaluation

- ✔ Indication of structure of the distribution possible
- ✔ For selection of the properly detected area (best fit) reliable information for the single modes



WINDOX 5 Operation Control and Evaluation Software





NANOPHOX™

PCCS – technology made by Sympatec GmbH

Technical Data NANOPHOX™

Measuring range:	1 nm – 10.000 nm
Principle:	Dynamic light scattering
Scattering angle:	90 degree
Evaluation:	3-D cross correlation
Analysis volume:	ca. 0.3 ml
Sample container:	Cuvette 10x10 mm^2
Cuvette position:	Automatic or manual
Light source:	HeNe-laser, 10 mW max.
Wave length:	632.8 nm
Class of laser:	3B
Class of instrument:	1
Optics:	No adjustment requested
Temperature range:	15 – 40°C , typ. 22 – 25°C recommended, via software
Temperature stability:	0.05°C (≅ 0.1 % precision during evaluation of particle size)
Precision of temperature control:	0.1°C ≅ 0.2 % precision of particle size

NANOPHOX Conclusions

★ Photon Cross Correlation Spectroscopy (PCCS) provides:

- ✔ Concurrent analysis of particle size from 1 nm to 10 µm and stability of sample
- ✔ For T=const. only η (dynamic viscosity of liquid) requested (refractive index n for mass and volume proportions only)
- ✔ Cross correlation completely eliminates the multiple scattering allotment
  - Analysis with turbid and coloured samples
  - Independence of results on concentration and cuvette position
  - No adaptation of evaluation to multiple scattering necessary
- ✔ Analysis for high concentrations
  - Normally no dilution required
  - No special request for cleanliness (as for PCS)
  - No special glass cuvette necessary)
  - Rapid, statistically secure analysis due to high counting rate
  - Easiest handling