A multi-angle DLS, SLS and D-DLS instrument **THETIS™** :

the most advanced solution for nanoparticles characterization from Cordouan Technologies

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LABOREXPO
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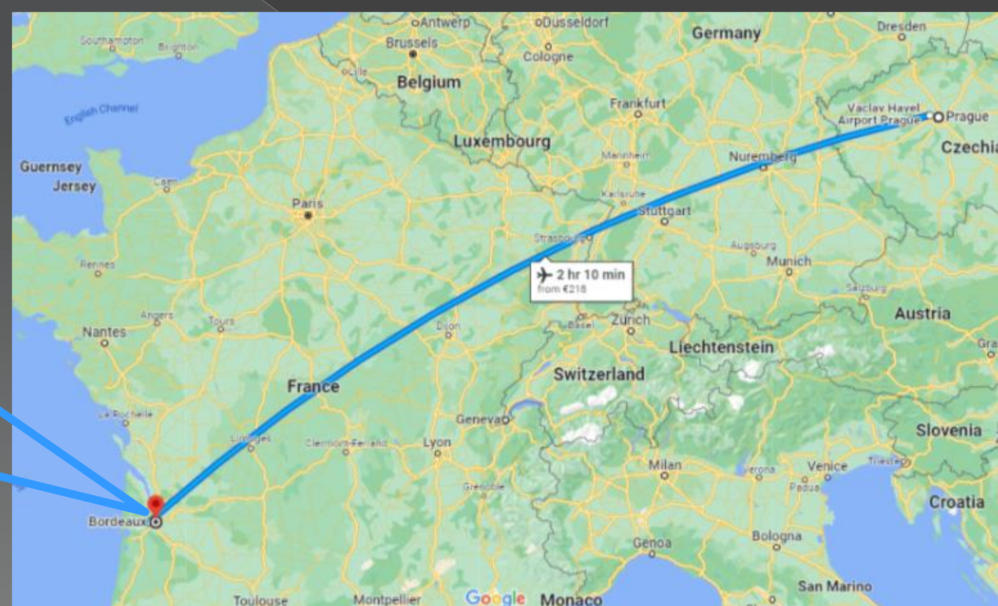
Cordouan Technologies in brief

- Founded: September 2007, ~15 years of expertise and experience
- Location : «Route des lasers» Bordeaux, France
- Team: 12 highly skilled employees (PhDs, Engineers in physics & chemistry)
- Our activity: development, Industrialization, manufacturing of innovative and advanced solutions to research lab and industry for nanoparticles and nanomaterial characterization



Cordouan Technologies in brief

NEW PRODUCT

VASCO

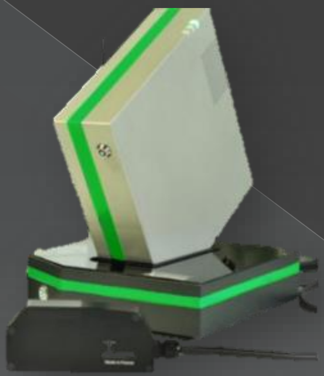
DLS for high concentration and absorbing samples

WALLIS

Zeta potential

VASCO KIN

In situ time resolved DLS



AMERIGO

Standard cell, *In situ* Time resolved DLS & Zeta potential

THETIS

Continuous Multi angle Time resolved DLS, SLS and DDLS

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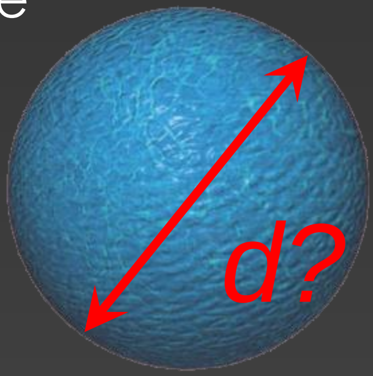
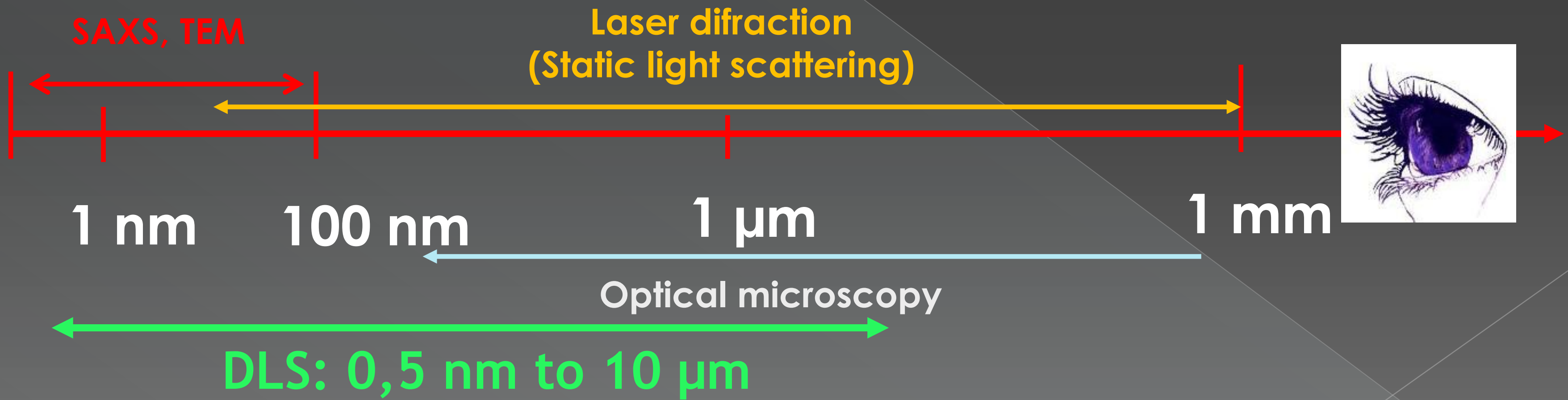
Why Nanoparticles size matters ?

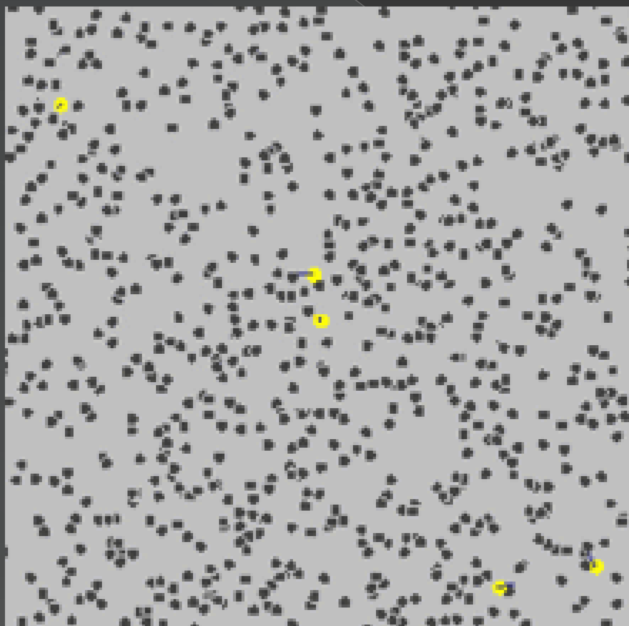
- Related to the specific surface of the particles
- Ability to penetrate membranes or interact with surface
- Functionalization and self assembly capabilities
- Optical, mechanical and electrical properties
- Etc.

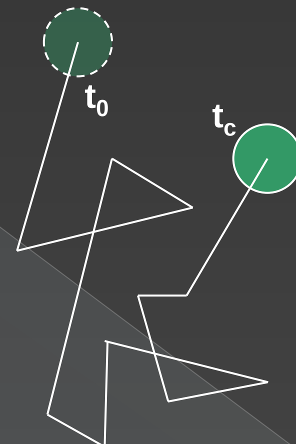




Brownian motion: a signature of NP size

Brownian motion= Random "walk"





Diffusion coefficient   time

$$< X^2(\tau) > \sim 2\, D\, \tau$$

L. BACHELIER (1901)

viscosity   Boltzman   temperature

NPs:
Hard spheres

$$D = \frac{KT}{3\pi\eta\emptyset_H} \quad \Rightarrow \quad \emptyset_H = \frac{KT}{3\pi\eta D}$$

EINSTEIN & STOKES (1905)

Hydrodynamic diameter

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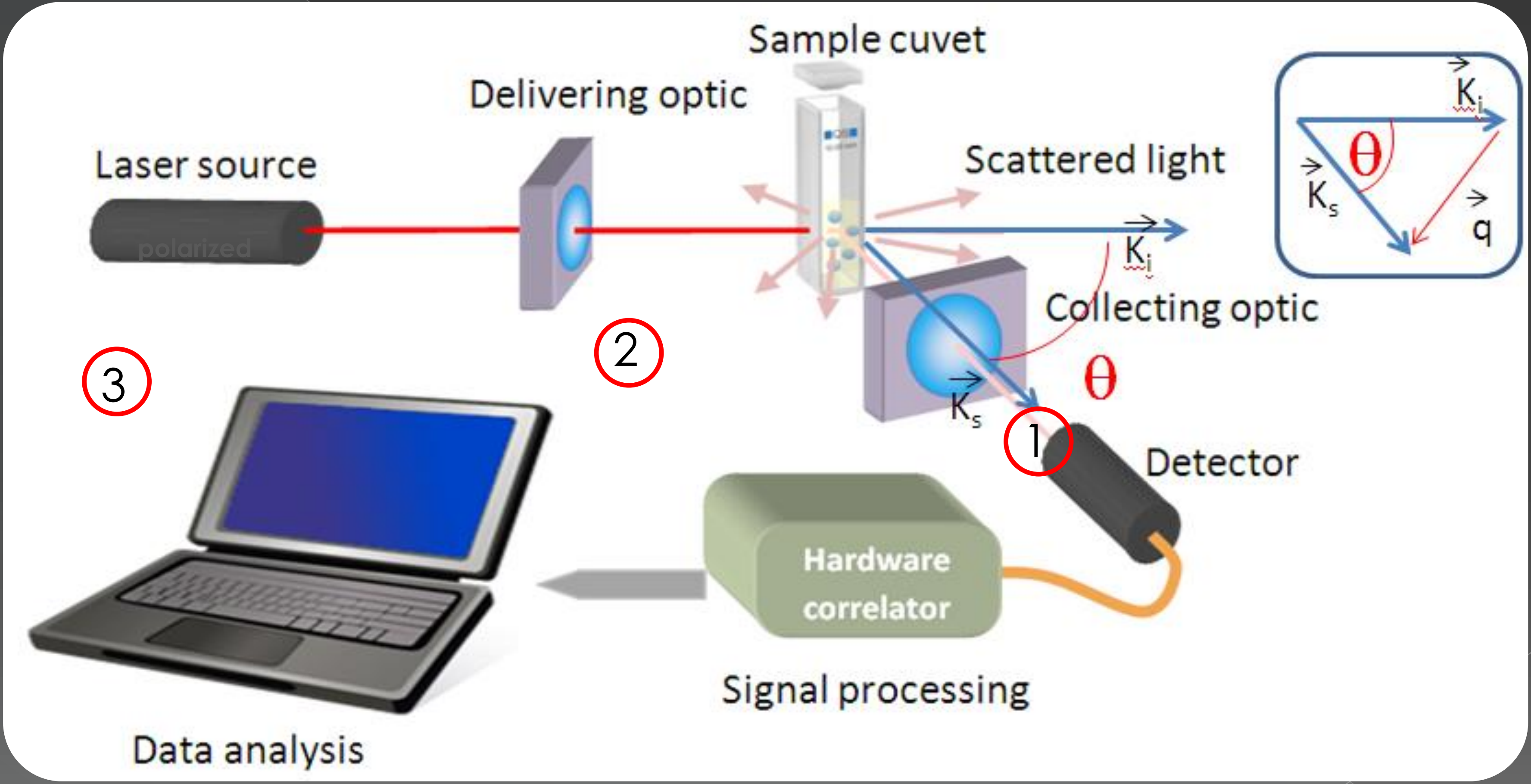
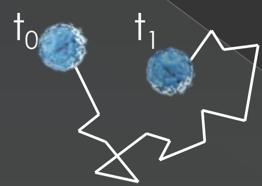
DLS measurement Principle (1)

- Measure light scattering fluctuation to probe the Brownian motion of NPs



DLS measurement Principle (2)

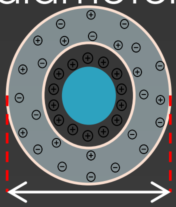
Brownian motion



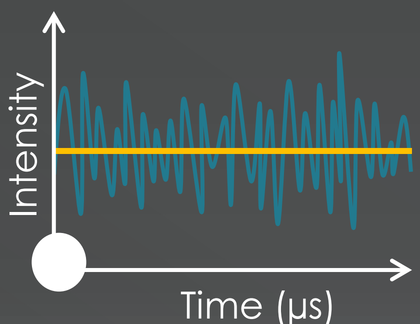
Translational Diffusion coefficient

Stokes-Einstein equations

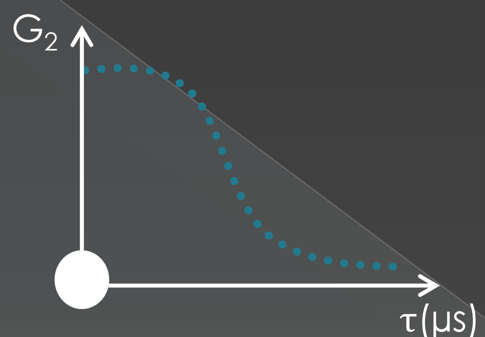
Hydrodynamic diameter



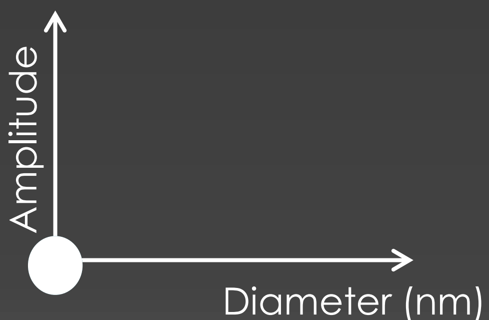
Light intensity



Autocorrelation



Size Distribution



EM field:

$E(\omega\tau) = \sum E_i e^{-i(\boldsymbol{kr} - \omega\tau)}$

Intensity:

$I(\tau) = E(\tau)\, E^*(\tau)$

$G_2 = A + \beta \exp(-2\Gamma\tau)$

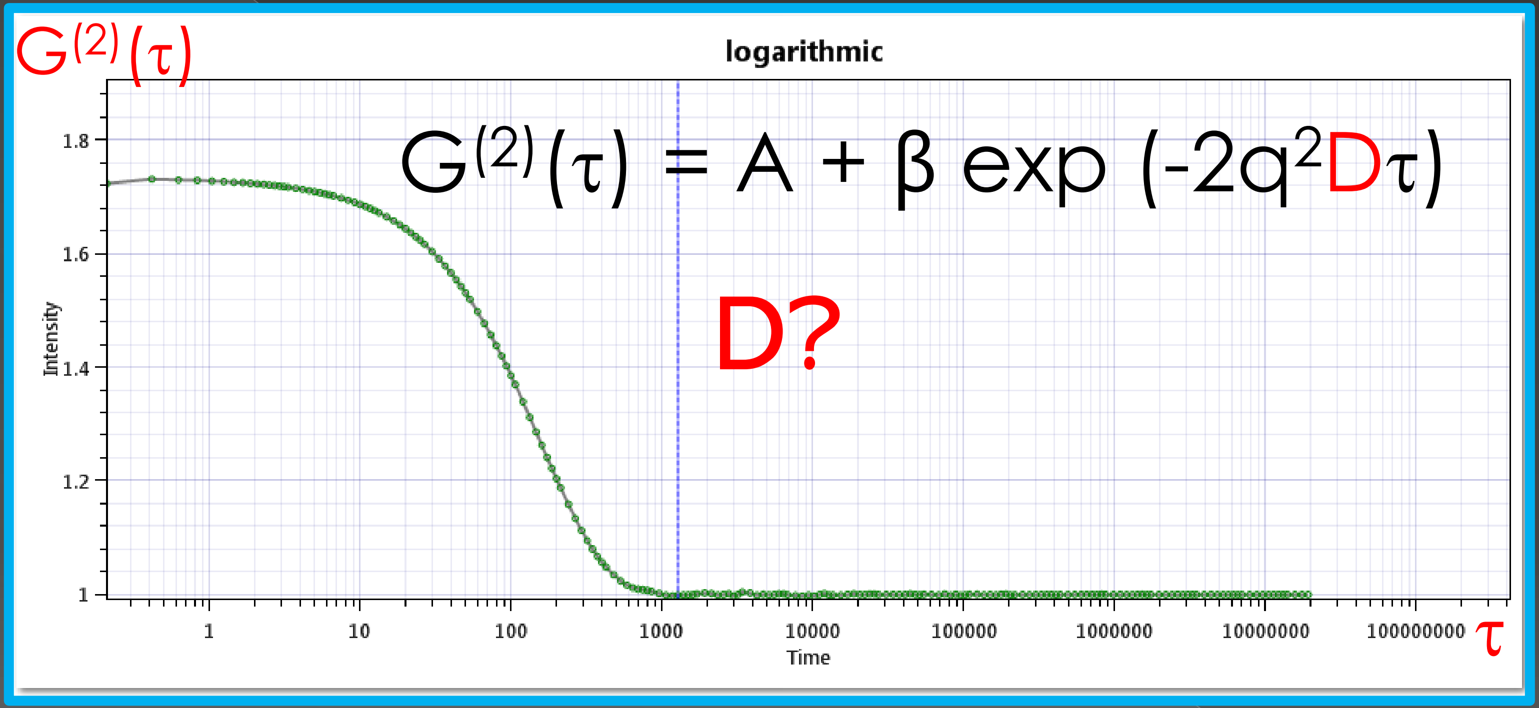
$q = \frac{4\pi n_0}{\lambda} \sin {}^{\theta}/_{2}$

$\Gamma = q^2 D$

$$\emptyset_H = \frac{KT}{3\pi\rho\, D}$$

Correlogram & Data processing

Inversion problem : How to find the optimum exponential curve fitting the experimental correlogram?

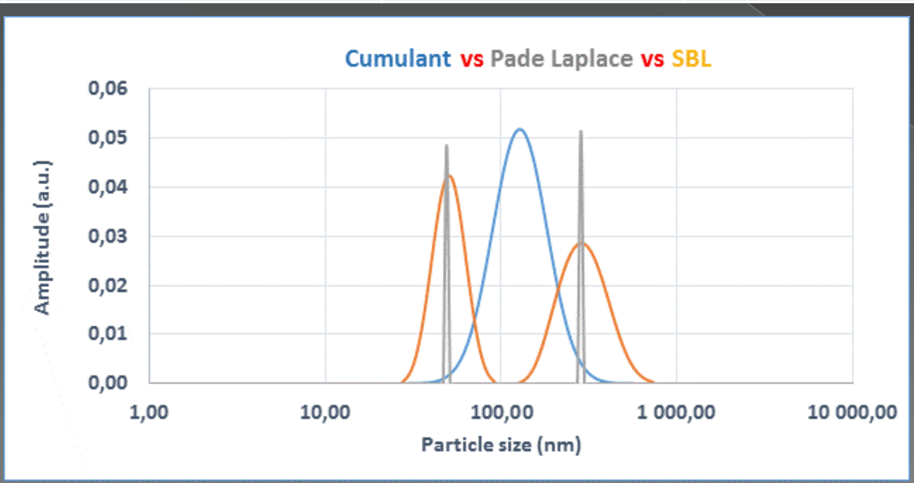


Fit leads to D, and D to the diameter of NPs $\emptyset_H$.

$$\emptyset_H = \frac{KT}{3\pi\eta D}$$

Inversion algorithms for NP size analysis

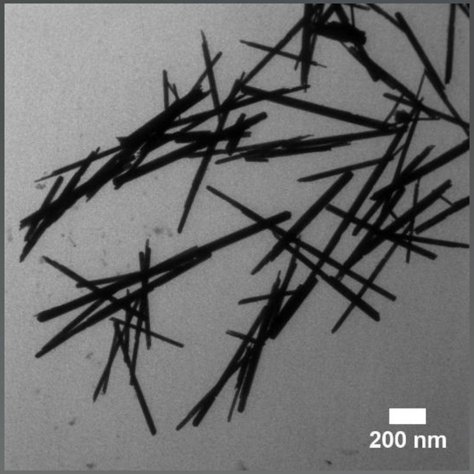
Algorithm	Number of populations	Distribution	Model
Cumulants	Monomodal Continuous	Yes	$G(\tau)=A+B\,e^{-\Gamma\tau}$; Gaussian with Zavg & PDI
Pade Laplace	Multi modal discrete	No	$G(\tau)=A+\sum_{i=1}^{250} B_i\,e^{-\Gamma_i\tau}$
SBL (**S**pace **B**asel **L**earning)	Multimodal continuous	Yes	$G(\tau)=A+\int_0^{10\mu m} B(z)\,e^{-\Gamma(z)\tau}dz$

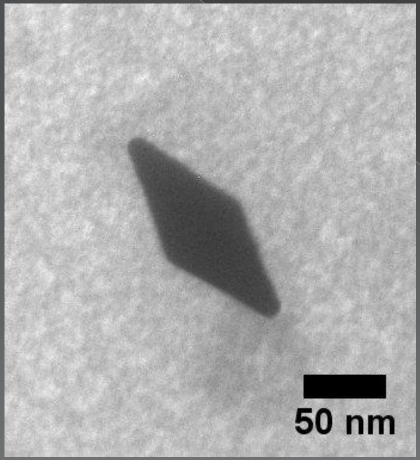


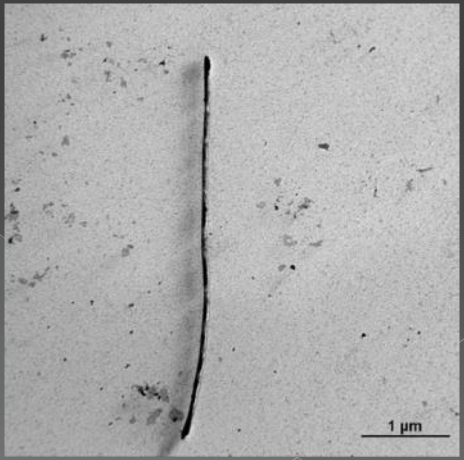
DLS measurement

Why Nanoparticle shape matters ?

1. Advanced materials needs more sophisticated NPs
2. Graphene, Carbon nanotube, Silver nanotube are the next generation electrical transmitters
3. New shapes for NPs available now







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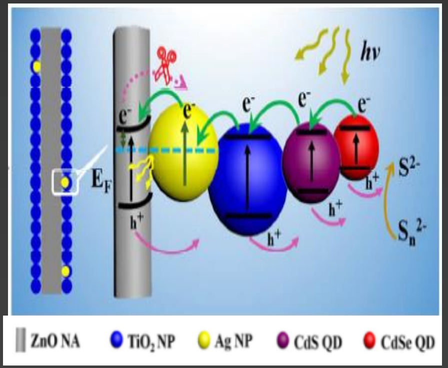
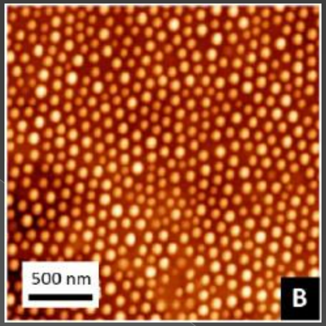
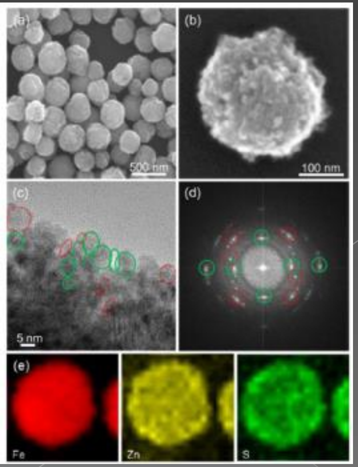
Examples of anisotropic NPs

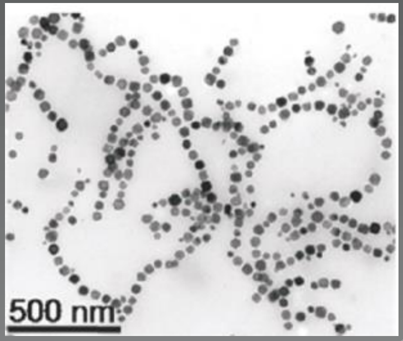
Hybrid nanomaterials :

- ✓ ***Combination*** of various material properties into one
- ✓ ***Rise of*** new ***properties***,
- ✓ Examples :
  - Efficient solar cell materials
  - New optical materials
  - Nanocrystals for structural improvement
  - Magnetic NPs for imaging









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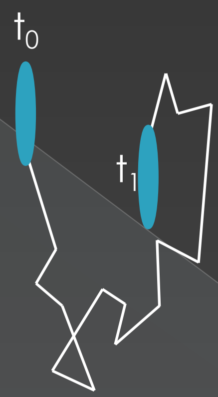
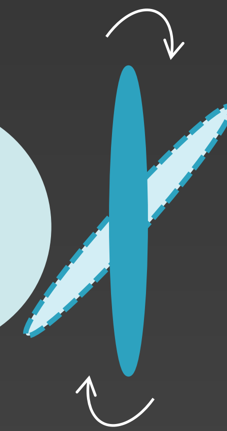
Behaviour of anisotropic particles

Translational
Diffusion coefficient
D_t



Rotational
Diffusion coefficient
D_r



2 different movements : translational and rotational

2 different Diffusion coefficients

Anisotropic Diffusion Coefficients

$$D_t = \frac{k_B T}{3\pi\eta L} \times \left[\ln\left(\frac{L}{w}\right) + \gamma\right]$$

$$D_r = \frac{k_B T}{3\pi\eta L^3} \times \left[\ln\left(\frac{L}{w}\right) + \varepsilon\right]$$

- Calculation can be performed
- **L, w and L/w can be obtained**

- L **length**
- w **width**
- $^{L}/_{w}$ **aspect ratio**

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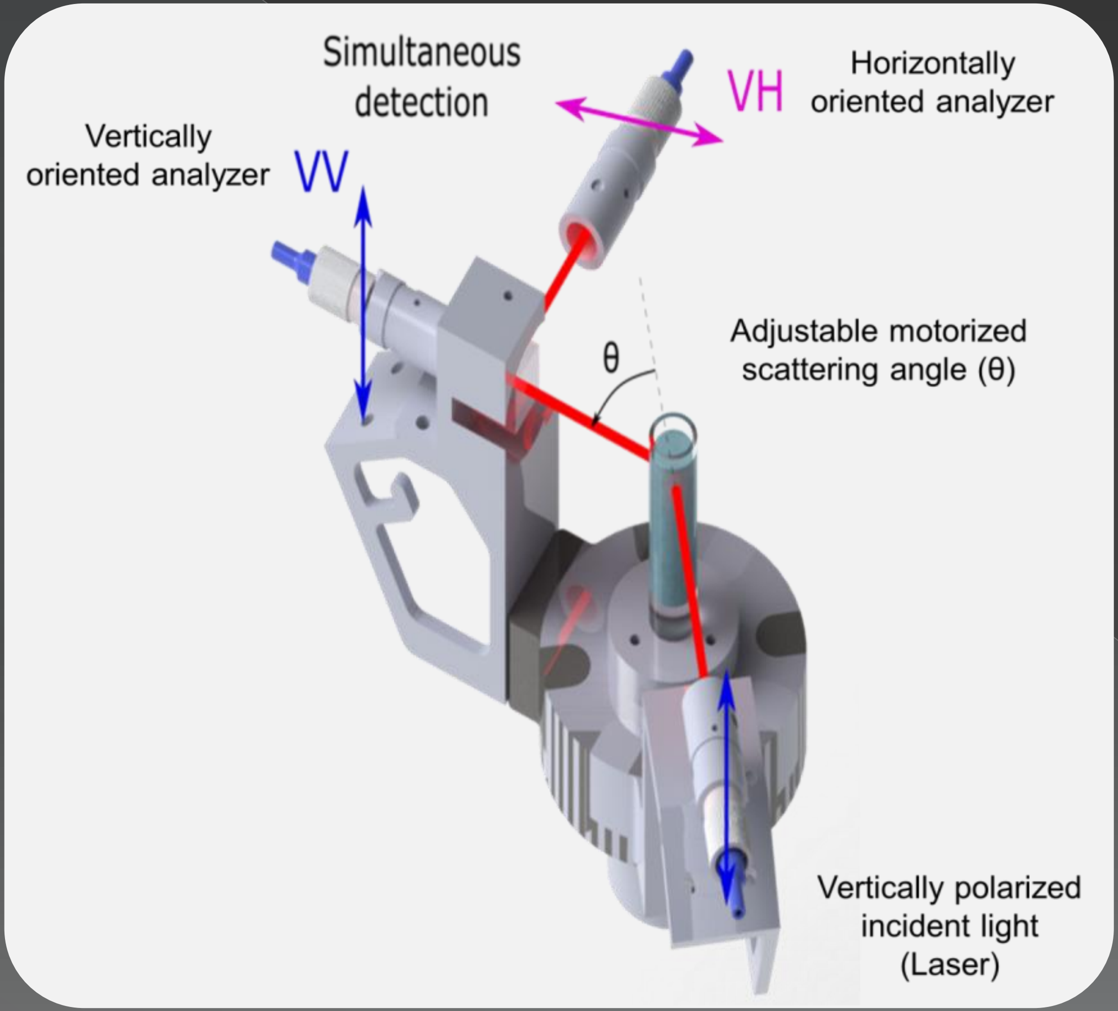
D-DLS Principle



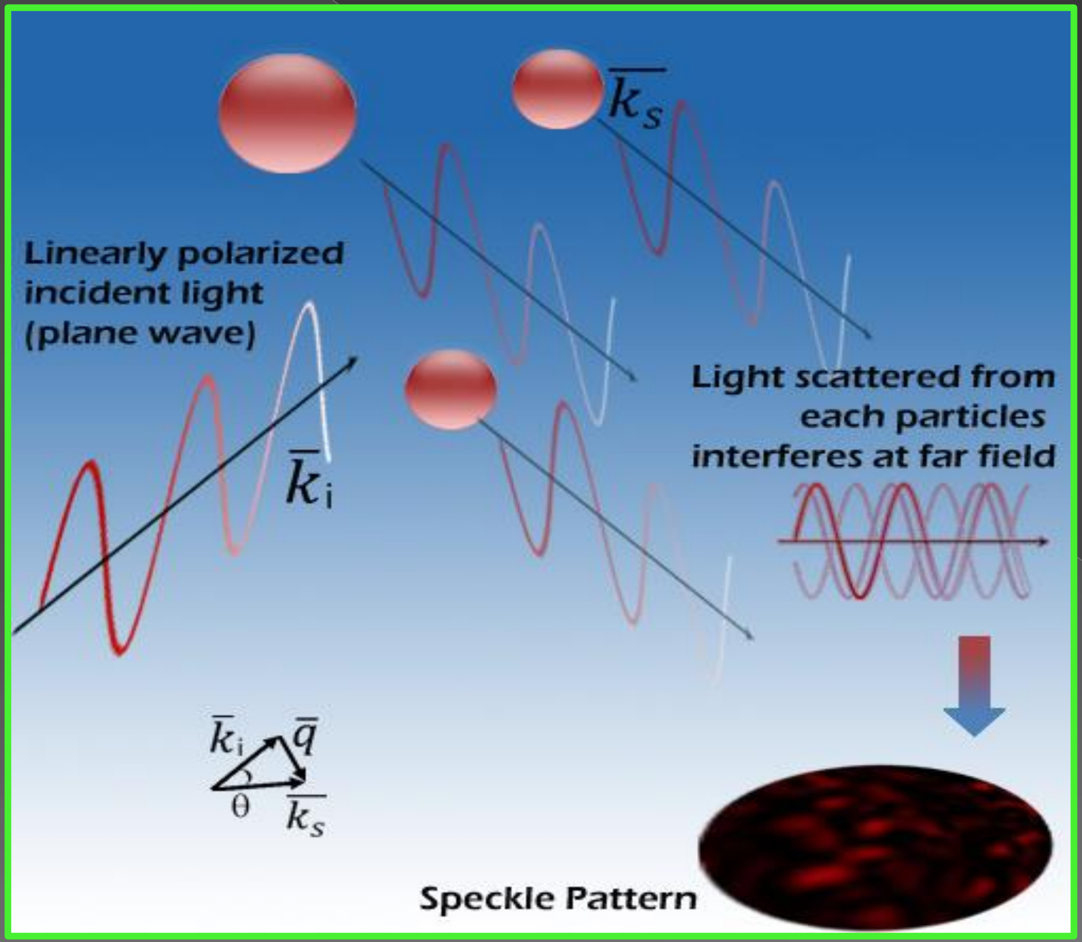
Step1:

Detecting intensity on **VV**

Step 2:

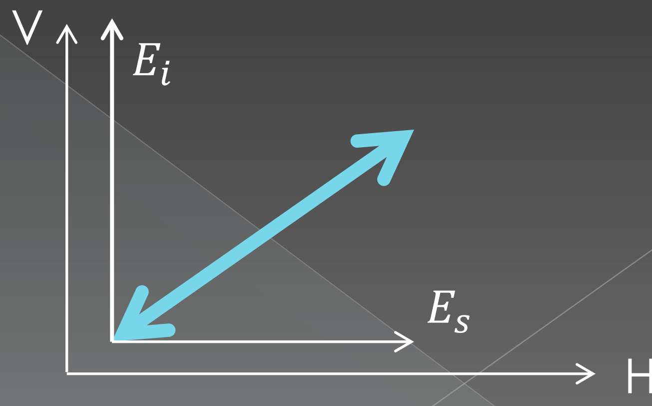
Detecting intensity on **VH**

D-DLS Principle



For spherical particles no photons on VH

Particles anisotropy leads to photons on VH



Analytical method

① $$G_{VV}(\tau) = A_1 exp^{-(\Gamma_t+\Gamma_r)\tau} + A_2 exp^{-(\Gamma_t)\tau} + B$$

$$G_{VH}(\tau) = A_3 exp^{-(\Gamma_t+\Gamma_r)\tau} + B$$

VV and VH autocorrelation functions

$$\Gamma_t = D_t q^2$$

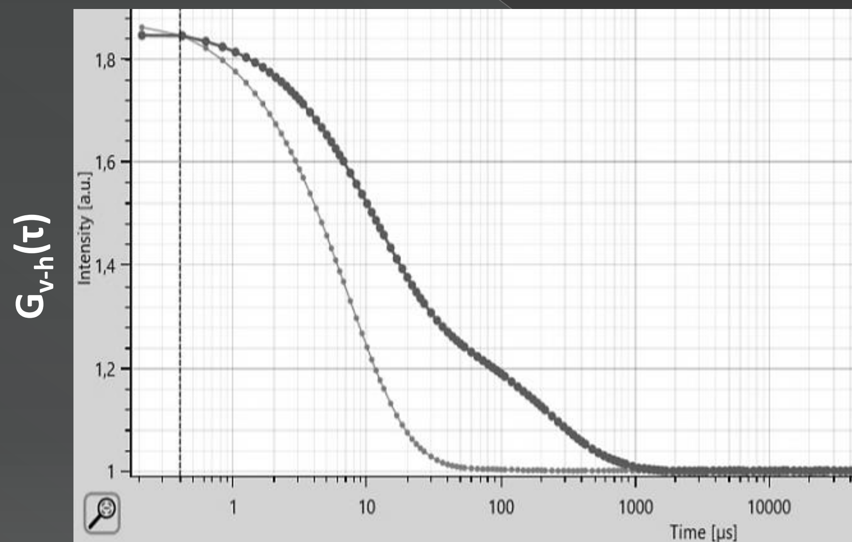
$$\Gamma_r = 6D_r$$

For isotropic particles : A_3 & $A_1 \ll A_2$

Analytical method

① $$G_{VV}(\tau) = A_1 exp^{-(\Gamma_t+\Gamma_r)\tau} + A_2 exp^{-(\Gamma_t)\tau} + B$$

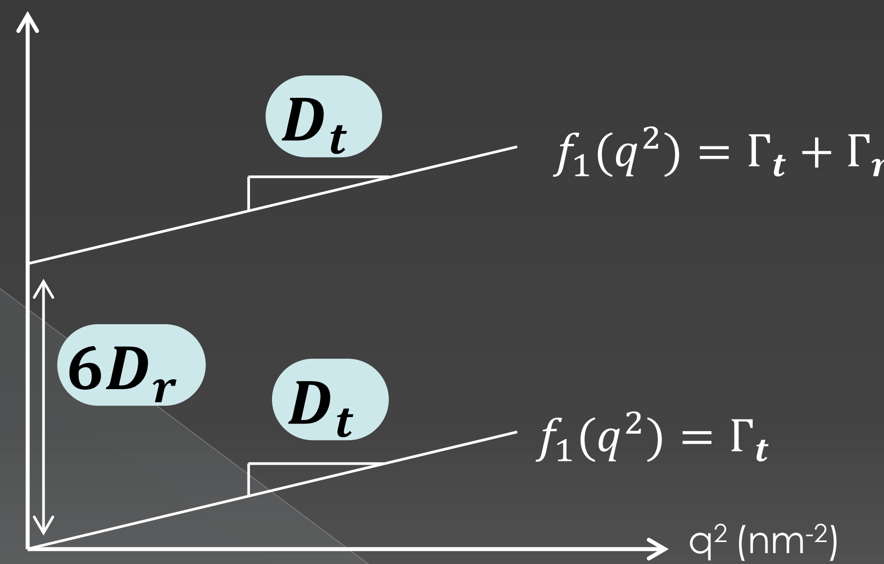
$$G_{VH}(\tau) = A_3 exp^{-(\Gamma_t+\Gamma_r)\tau} + B$$



② $$\Gamma_t + \Gamma_r = D_t q^2 + 6D_r$$

$$\Gamma_t = D_t q^2$$

③ coefficients D_t and D_r



④ Calculation

Length L, Aspect Ratio L/w and width w

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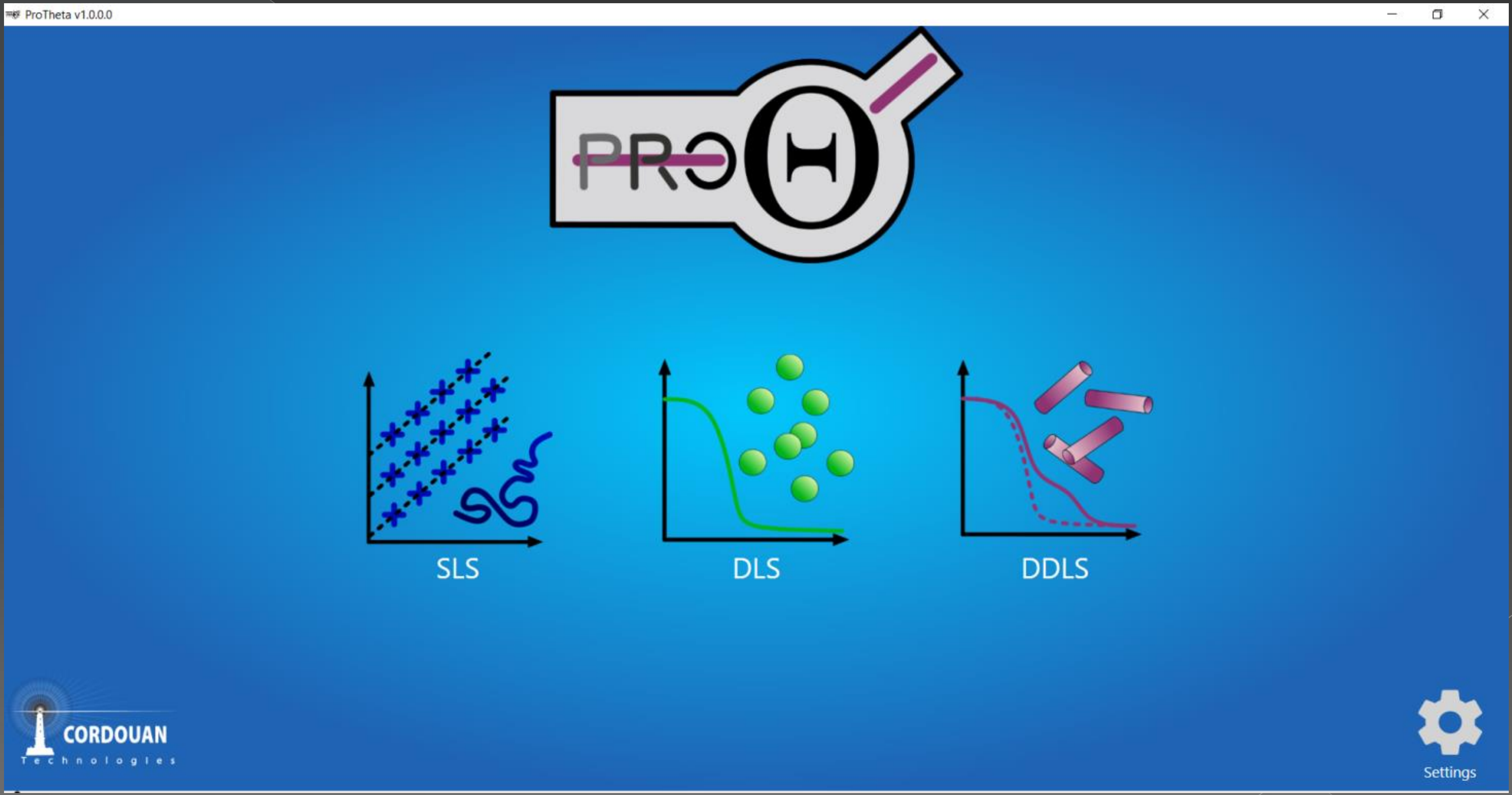
THETIS: A multi-angle DLS, SLS & D-DLS

- **DLS, D-DLS** and **SLS** in one instrument
- **Multi-angle** scattering measurement system : from **30° to 160°**
- **Real time** and Time resolved Software correlator
- High Power single mode laser λ=635 nm
- Scattered Intensity measurements on **2 perpendicular polarizations**
- **Temperature** controlled **from 1° C to 70 ° C**
- **Molecular weight, concentration** and replay modes for DLS and DDLS data
- **3 different algorithms** for particle size measurements

ProTheta software



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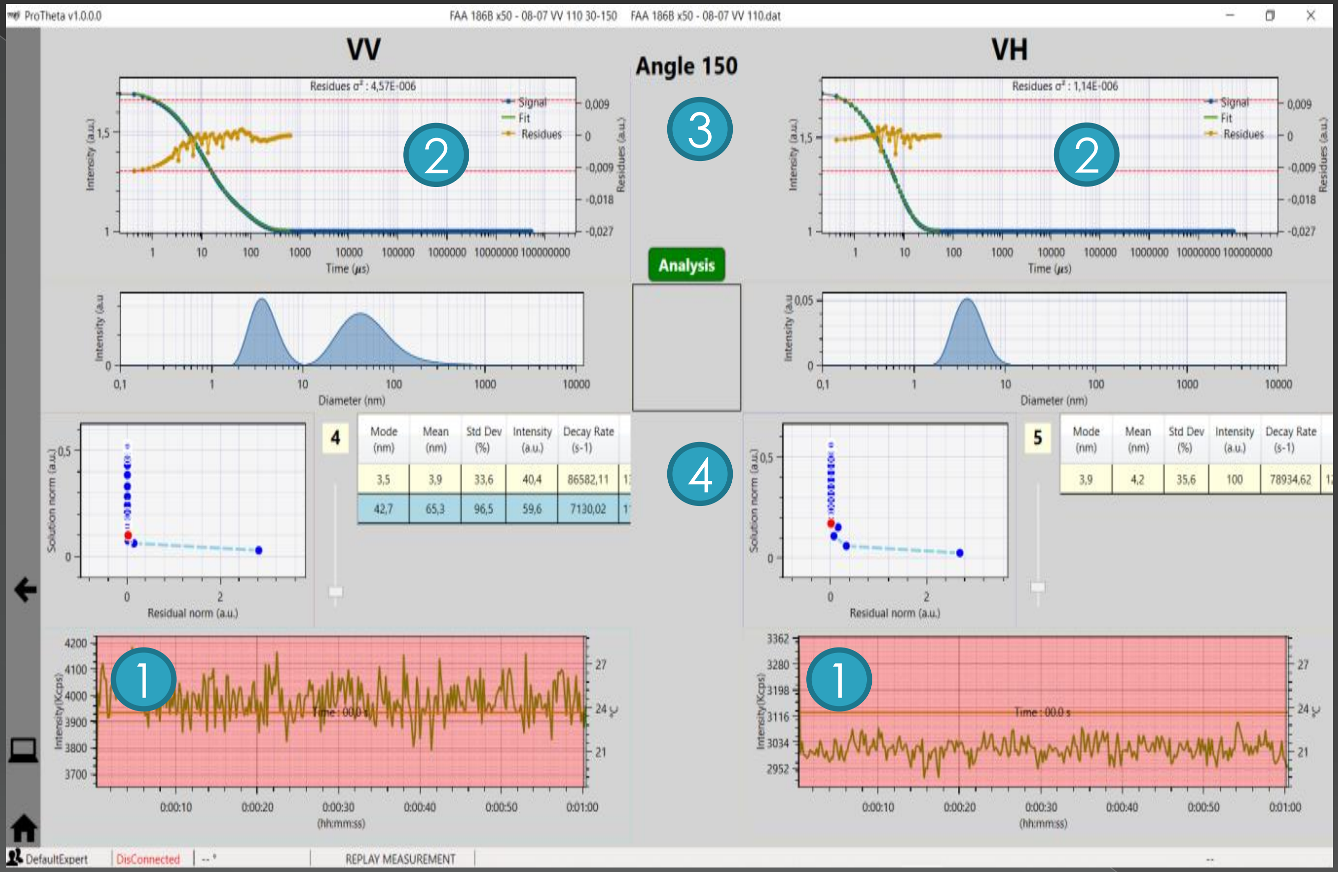
Advanced functionalities & intuitive menus



1. 2 Channels (VV, VH) Time resolved D-DLS
2. Both VV and VH correlogram
3. User selected/automatic scattering angle setting
4. Automatic calculation of length, width & Aspect ratio / Rotational & Translational Diffusion Coefficient measurements

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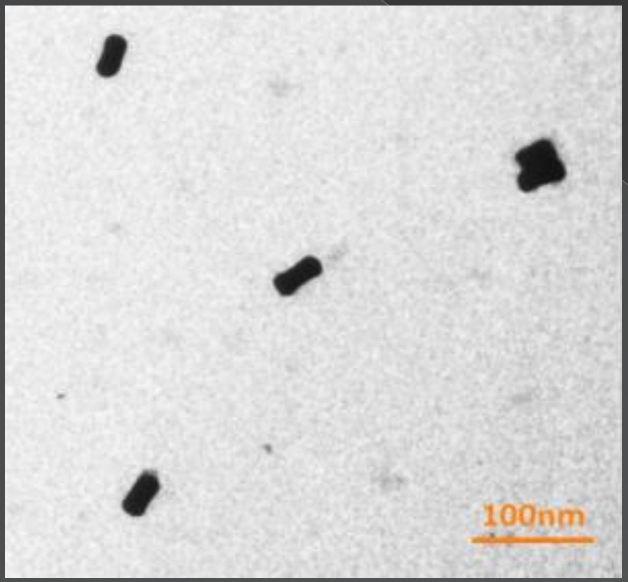
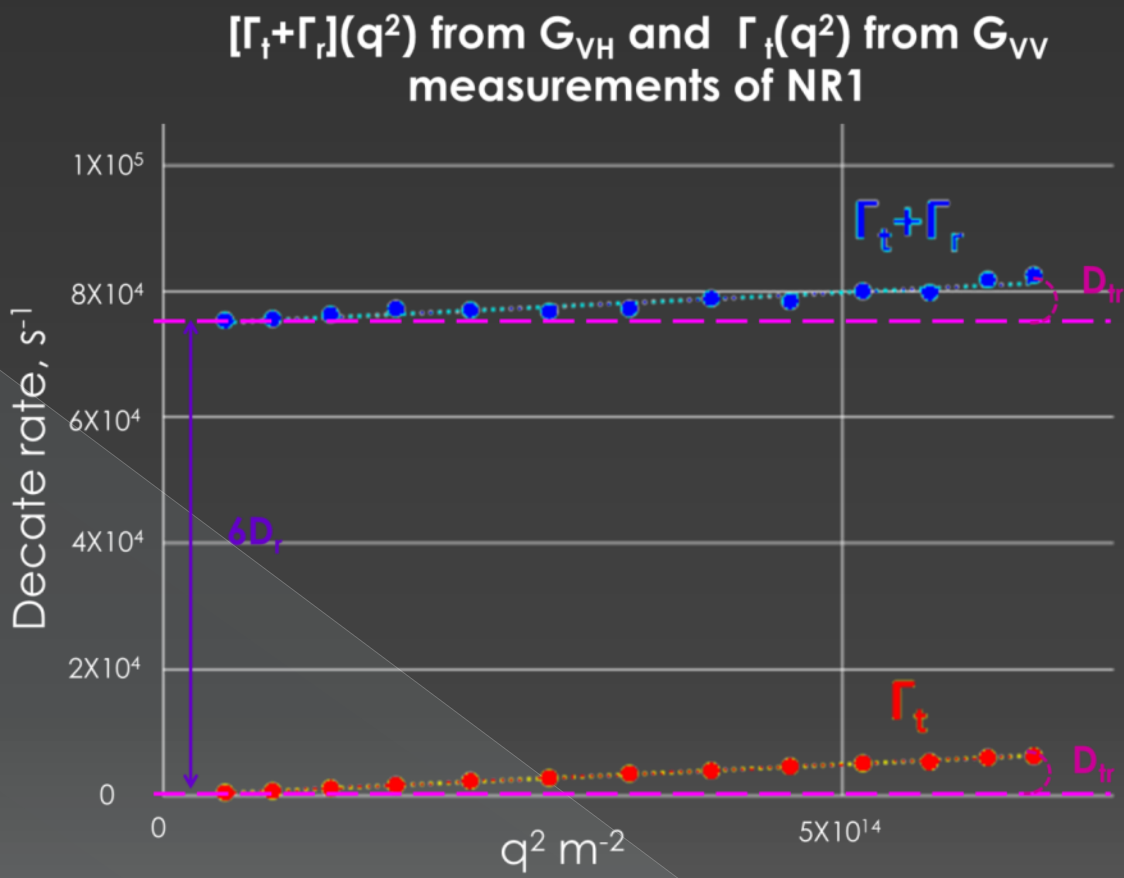
Experimental results on nanorods





Parameter	D-DLS THETIS	TEM
L (nm)	46	**47**
L/w	1.4	**1,8**
w (nm)	34,8	**26**

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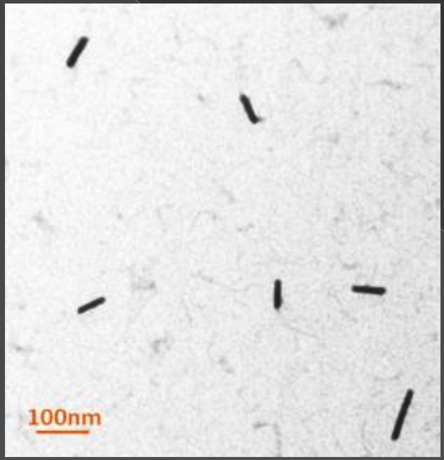
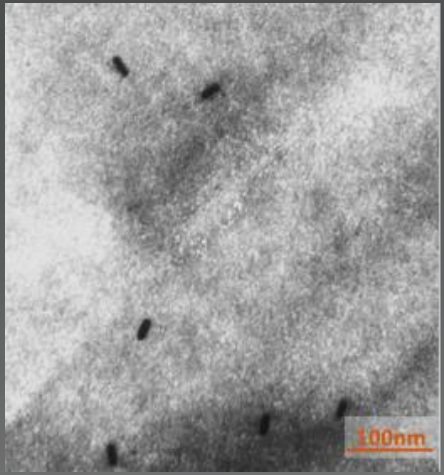
Experimental results on nanorods



Parameter	D-DLS THETIS	TEM
L (nm)	70,7	**66,4**
L/w	5	**4**
w (nm)	14,2	**16,5**



Parameter	D-DLS THETIS	TEM
L (nm)	28,5	**28,3**
L/w	1,7	**2**
w (nm)	16,8	**14,5**

Thank you for your attention

Děkuji za pozornost

Дякую за увагу

Merci pour votre attention

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