An introduction to Nano-particle characterization using light scattering: Principle & Applications

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Definition (Europe): “A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm”; But more generally for colloid size ranges from 1 nm to 10 µm!

http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm

• Promise of major technologic, economic, societal & environmental impacts
• Already in the field ….. And it is just the beginning!

food  Pharma  Cosmetic  Environment

Petrol  Battery  Automotive

https://www.understandingnano.com/nanoparticles.html
Part I: Nano particle size measurement

Size matters!!

- Related to the specific surface of the particles
- Ability to penetrate membranes or interact with surface
- Aggregation and stability of suspensions
- Functionnalisation and self assembly capabilities
- Optical, mechanical and electrical properties
Nano Material size scale: some examples

- Water
- Glucose
- DNA diameter
- Virus
- Bacteria
- Cell
- Sugar grain
- Ping pong ball
- Tennis ball

10^{-1} 1 10 10^2 10^3 10^4 10^5 10^6 10^7 10^8

Nanometers

- Liposome
- Micelle
- Dendrimer
- Polymer
- Gold
- Quantum dot
- Carbon nanotube
Many mature characterization techniques for particle size

- Classical Optical microscopy
- SAXS, TEM
- Laser Diffraction (Static light scattering)
- DLS: 1 nm to 10 µm

4 decades of size range!!!
DLS uses Brownian motion as a signature of particle size

Brownian motion = Random “walk”

\[ \langle X^2(t) \rangle \sim 2D \ t \]

\[ D = \frac{KT}{3\pi \eta \phi_H} \]

\[ \phi_H = \frac{KT}{3\pi \eta D} \]

NPs: hard spheres without interactions

EINSTEIN & Stokes (1905)

L. BACHELIER (1901)
DLS measurement principle: 3 steps process

➢ Measure light scattering fluctuation to probe the Brownian motion
Fit leads to $D$, and $D$ to the diameter of NPs $\phi_H$.

$$G^{(2)}(\tau) = A + \beta \exp(-2q^2D\tau)$$

with $q = \frac{4\pi n_0}{\lambda}\sin(\theta/2)$

$$\phi_H = \frac{KT}{3\pi\eta D}$$
Correlogram representation: Linear vs Logarithmic

**Linear correlator**

**Multi-tau/Log correlator**

**Linear** time scale

**Logarithmic** time scale

30 nm

300 nm

30 nm + 300 nm
## Inversion algorithms for monomodal and polymodal analysis

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Number of populations</th>
<th>Distribution</th>
<th>Model</th>
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| **Cumulants** | 1 Continuous Gaussian with Zavg & PDI | Yes | \( G(\tau) = A + B e^{-\Gamma \tau} \)  
\( Z_{avg} = \frac{k_B T q^2}{3\pi \Gamma} \);  
*Distribution width = Z_{avg} * \sqrt{PDI}* |
| **Pade Laplace** | Multi (up to 3) discrete | No | \( G(\tau) = A + \sum_{i=1}^{250} B_i e^{-\Gamma_i \tau} \) |
| **SBL**       | Multi continuous      | Yes | \( G(\tau) = A + \int_0^{10 \mu m} B(z) e^{-\Gamma(z) \tau} dz \) |
Monomodal sample (one population) 100 nm Latex NPs

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<td>SBL</td>
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Bi-modal sample (two populations) 30 nm +100 nm Latex NPs mixture

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Importance of powerful algorithms for high resolution measurement

30 nm + 100 nm Polystyrene latex (PSL) - unknown ratio, blindfolded sample test

Efficient algorithms make a clear difference for high resolution particle size measurement on complex samples.
Light Scattering: some useful rules of thumb:

MIE/ Rayleigh Theory

\[ I_{\text{Scatt}} \sim K \cdot I_0 \left( \frac{(n^2-1)}{(n^2+2)} \right)^2 \cdot \frac{\phi_H^6}{\lambda^4} \]

Particle refractive index

Laser Wavelength

**Rule of thumb #1:** the scattering efficiency (cross section) of the particles is 2.3 times higher for a laser wavelength @532 nm than that of a laser @656 nm

**Rule of thumb #2:** light intensity scattered by 10nm spherical particles is $10^6$ (one million!) times lower than for 100 nm particles,
Light Scattering: some useful rules of thumb:

Scattering cross section angular dependance with particle size

Backscattering detection prevents from multiple scattering (concentrated samples) and allows to detect small particles in presence of bigger ones.
SLS/DLS bench with goniometer multi angle measurements

- Adjustable scattering angle
- Several detectors
- Static and Dynamic Light Scattering
- Cross correlation
- Particle size and Molecular weight measurements
- Mainly for diluted samples
- Expensive and large dimensions
DLS bench top equipments

- Disposable cell
- Embedded cell

### Disposable cell
- Size range: from 1 nm up to 10 µm
- Bench top configuration: solutions dedicated to laboratory analysis
- Fast and relatively cheap compared to TEM and SAXS!
- **Batch Measurements**
- But not fitted for process and in situ measurement!!!
• Innovation in the sample cell configuration: Dual Thickness Control (DTC- patented)
• Thin layer analysis: prevents the sample from local heating and multiple-scattering.
• Backscattering detection (135°): low multiple scattering, better contrast for small particles
• Higher detection efficiency in opaque media.
• Solvent-proof cell measurement without consumables
• Proprietary inversion algorithm allowing efficient size distribution analysis
• Technology transfer from the French Institute of Petroleum
Common DLS artefacts and DTC benefits:

- **Measurement of dark/opaque media**

  A standard polystyrene latex (Ø=30nm by TEM) is mixed with black soluble ink (10wt%).

  **Without DTC**
  - 24nm
  - 32nm

  ➢ 25% error caused by the laser absorption!!

  **With DTC**
  - 32nm

- **Measurement of concentrated samples**

  A standard polystyrene latex (Ø=100nm by TEM) measured at 0.1 wt%.

  **Without DTC**
  - 85 nm
  - 115 nm

  ➢ Decrease of the measured hydrodynamic radius

  **With DTC**
  - 115 nm

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**DTC reduces impact of multiple scattering and light absorption**
In situ head concept: the power of DLS, the flexibility of Optical fiber

- Non invasive, no need to batch the sample
- Adjustable working distance /scattering angle
- Alignment laser for easy installation
- High accuracy remote temperature sensor
- Easy maintenance
- Ideal for measurements in glass capillaries, or in situ

A change of paradigm: “bring your measurement to your process!”
VASCO KIN: In Situ Time Resolved Nanoparticle Size Analyzer

Optical unit
- Fast acquisition electronics
- APD detector
- Laser source

Control unit
- computer
- power supply

Dedicated software

Optical fiber umbilical

In situ remote probe
Application Examples
Example of kinetic study: Gelification of colloidal silica

- "Ludox-TM 50" 5wt% pH=3 + 10wt%NaCl

Detected intensity vs time

Z-average vs time
Example 1

Combined Remote DLS & High flux SAXS for NPs synthesis monitoring

SNOW CONTROL FP7 Project
Combined Remote DLS & High flux SAXS for NPs synthesis monitoring

SAXS sample chamber

Micro reactor

X-rays

DLS Laser

Flow-through capillary

Used for ZP measurements

Precursors

Syringe pumps

F1

F2

reactor chip inside the climate controller

flasks for stock solutions, water and ethanol

vacuum tight feed-through

syringe pumps

outlet pipe/bend protection

plastic framework

laser beam

capillary

inlet pipe

VascoFlex

X-ray beam
On line SiO2 NPs synthesis monitoring

Hydrolysis – condensation method: TEOS in Ethanol (F1) + NH3 in H2O (F2)

Impact of flow rate (F1+F2)

Impact on precursors mixing ratio (F1/F2)

- Consistent results between SAXS and DLS measurements
- Allow to track and tune synthesis process in an accurate way
Example 2

In situ kinetics monitoring of Microwave assisted NPs synthesis
In situ kinetics monitoring of Microwave assisted NPs synthesis

- In situ DLS successfully integrated into a commercial microwave reactor
- Under test and qualification at the College de France-Paris
Validation tests done on SiO2 slurries

<table>
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<th>True temperature</th>
<th>Corresponding Viscosity (cP)</th>
<th>Corrected Averaged size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>0.55</td>
<td>76</td>
</tr>
<tr>
<td>90°C</td>
<td>0.3</td>
<td>72</td>
</tr>
<tr>
<td>140°C</td>
<td>0.196*</td>
<td>68</td>
</tr>
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- Very consistent and reproducible results
- 1st demonstration ever done opening up new possibility on NP synthesis monitoring
Example 3

Particle Size Measurement inside supercritical CO$_2$ synthesis reactor
Particle Size Measurement inside supercritical CO$_2$ synthesis reactor

Reactor (100 bars, 40°C)

DLS probe
Particle Size Measurement in supercritical CO$_2$ synthesis reactor

- 10 wt% styrene rel. to system, 10 wt% Dowfax 8390 (surfactant) rel. to monomer, 8 wt% Hexa Decane rel. to styrene
- Sonicated for 10 min, 65% input intensity
- CO$_2$ is used to control the size of nano-emulsion droplets

- Use DLS measurements to correlate turbidity variation with particle size
- Implement accurate control of the size of monomer droplets/NP
Example 4

Environmental application: Nano Plastic detection in Ocean water
Environmental study: Evidence of Plastic NPs in Ocean

Lab study of Plastic NPs formation under oceanic like UV insolation conditions

Floating particles

More small particles but big ones also (>2μm)
Example 5

Measurement in Bio pharma injectable
Preliminary measurements on Flew injectable vaccines
Other examples...
Examples of instrumental coupling

with SAXS instrument

with crystalization reactors

With SANS/SAXS Lines
to µfluidics chips
Bibliography

Generality and theory on nanoparticle characterisation using light scattering:


• Tharwat Tadros ; General Principles of Colloid Stability; Colloids and Interface Science Series, Vol. 1

• Hunter R, Zeta potential in colloidal science; Academic press, New York, 198

• ISO13099B1,Colloidal systems—Methods for Zeta potential determination Part 1: Electroacoustic and electrokinetic phenomena

Some publications with our instruments

• Polymer-grafted iron oxide nanoparticles as thermosensitive MRI contrast agents and magnetic nano-heaters, Gauvin Hemery & al, Journal of Physics D: Applied Physics


• Structure and Dynamic Properties of Colloidal Asphaltene Aggregates; Joëlle Eyssautier & al; Langmuir, 2012, 28 (33), pp 11997–12004 - American Chemical Society

• Marine plastic litters: the unanalyzed nano-fraction, Julien Gigault & al; The Royal Society of Chemistry, Env. Sci. Nano, 2016, 00, 1-3
Thank you for your attention!

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