



pragolab

Velikost (nano)částic a stabilita koncentrovaných disperzí včetně popisu tuhnutí tenkých vrstev

Mgr. Anna Kolouchová, Ph.D.



Na velikosti záleží...

Souvisí se **specifickým povrchem** částic

Schopnost proniknout membránami

Schopnost povrchových interakcí

Agregace a **stabilita** suspenzí

Funkční chování (self assembly)

Optické, mechanické a elektrické vlastnosti

Atd.

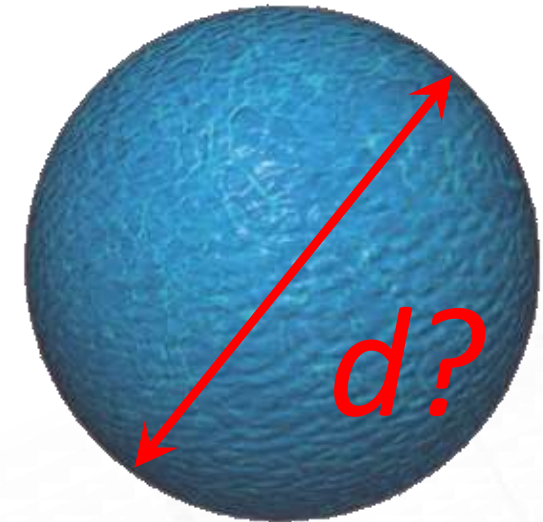
Elektronová mikroskopie: **TEM**

Impedance: Coulterův princip

Sedimentace: **Diferenciální centrifugace**

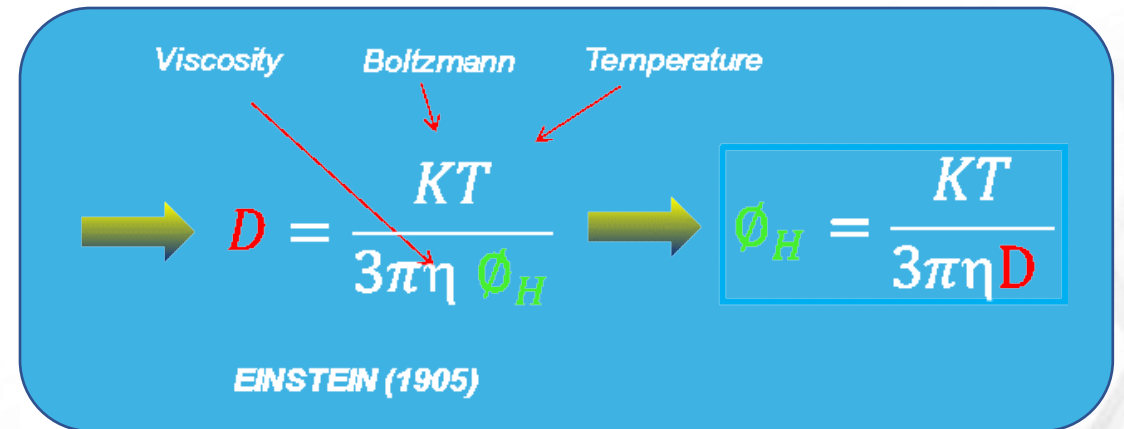
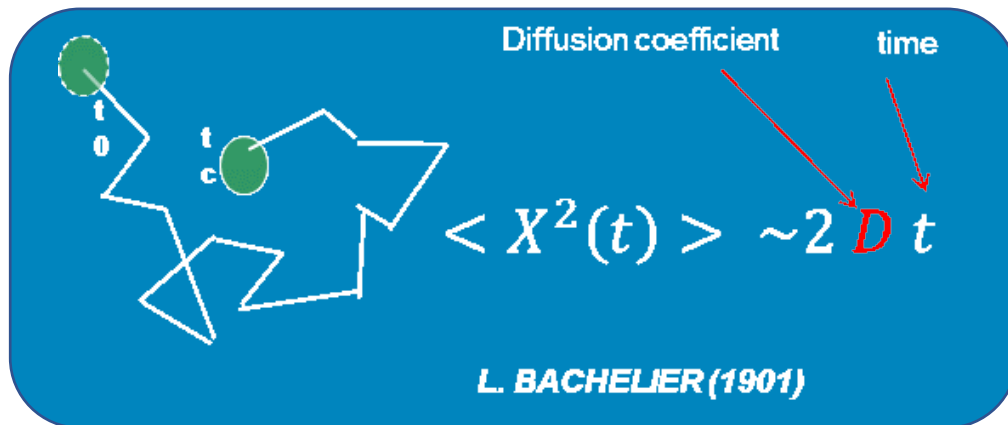
Rezonance: resonant mass detection

Optické: particle tracking, laserová difrakce, **dynamický rozptyl světla (DLS)**

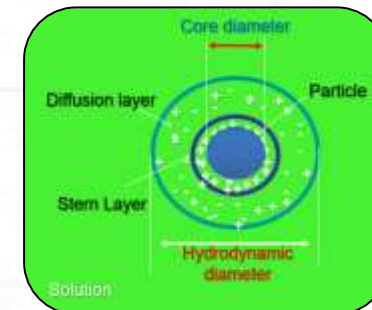
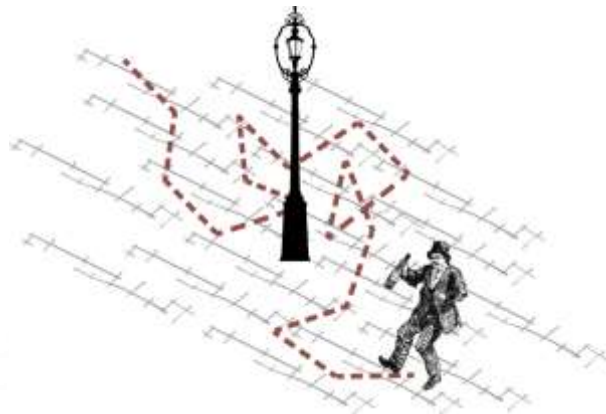


Velikost se podepisuje i na stylu chůze...

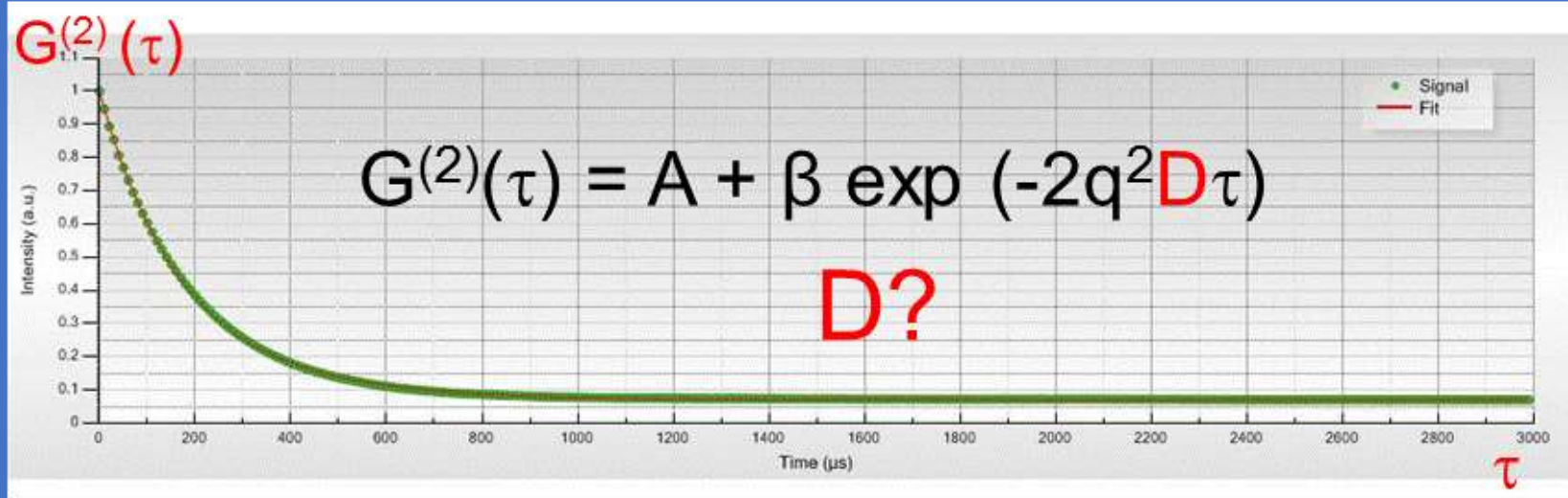
Brownův pohyb... náhodný pohyb v plynném nebo kapalném médiu, tepelný pohyb, *jehož důsledkem je difúze*



HYDRODYNAMICKÝ PRŮMĚR ČÁSTICE



Autokorelační funkce:



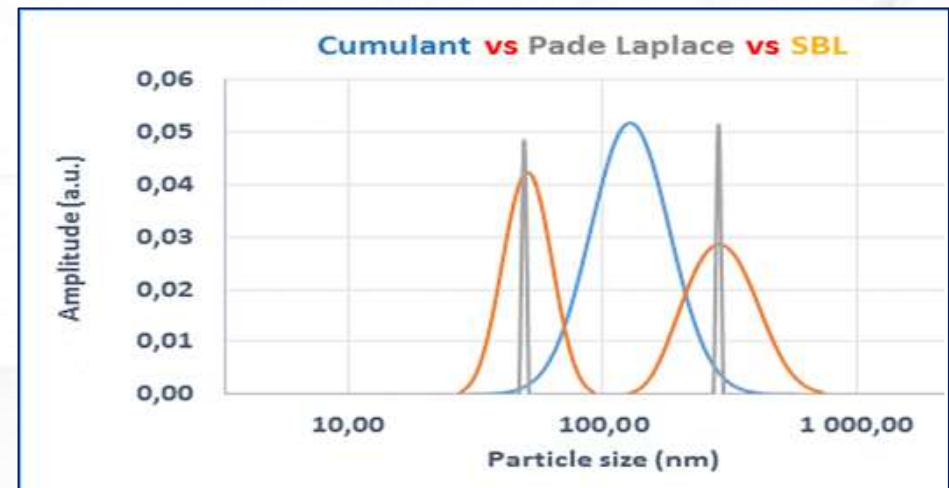
Fit leads to D , and D to the diameter of NPs ϕ_H .

$$D \longrightarrow \phi_H = \frac{KT}{3\pi\eta D}$$

Monomodální vs. polymodální analýza:

Designation	Equation	Distribution type	Authors ref
Cumulant	$G_2(\tau) = A + \beta e^{-2\Gamma\tau}$	Gaussian	B Frisken & al
Pade Laplace	$G_2(\tau) = A + \sum_{i=1}^{250} B_i e^{-2\Gamma_i\tau}$	Discrete	Yeremian & al.
Sparse Bayesian Learning	$G_2(\tau) = A + \int_0^{10\mu m} B(\Gamma) e^{-2\Gamma\tau} d\Gamma$	Continuous	R Ansari & al

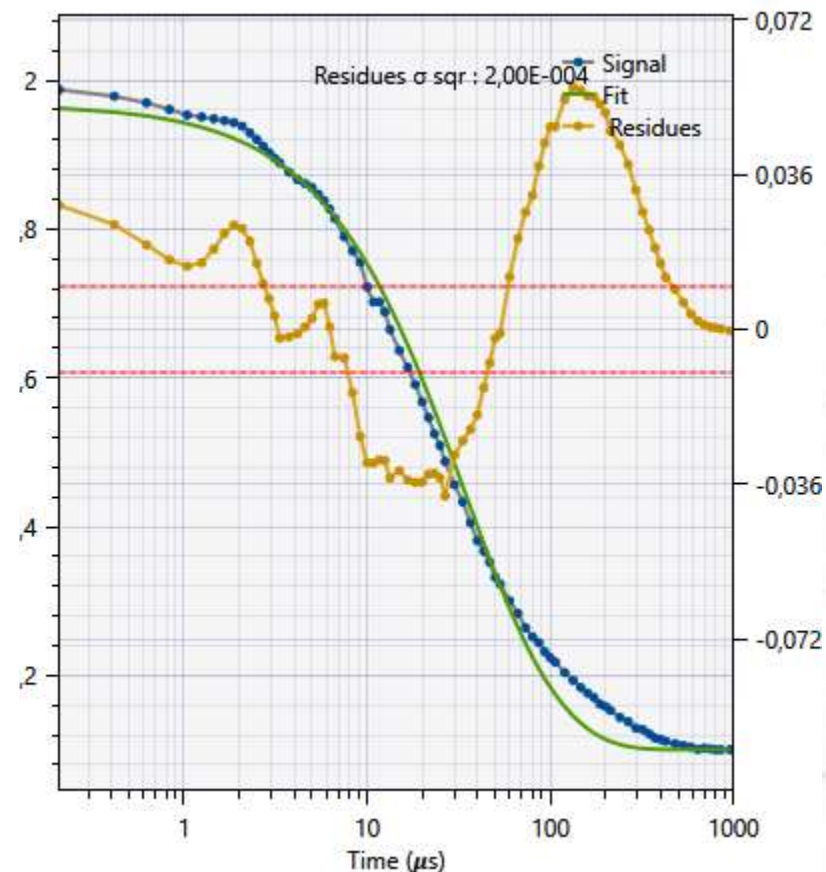
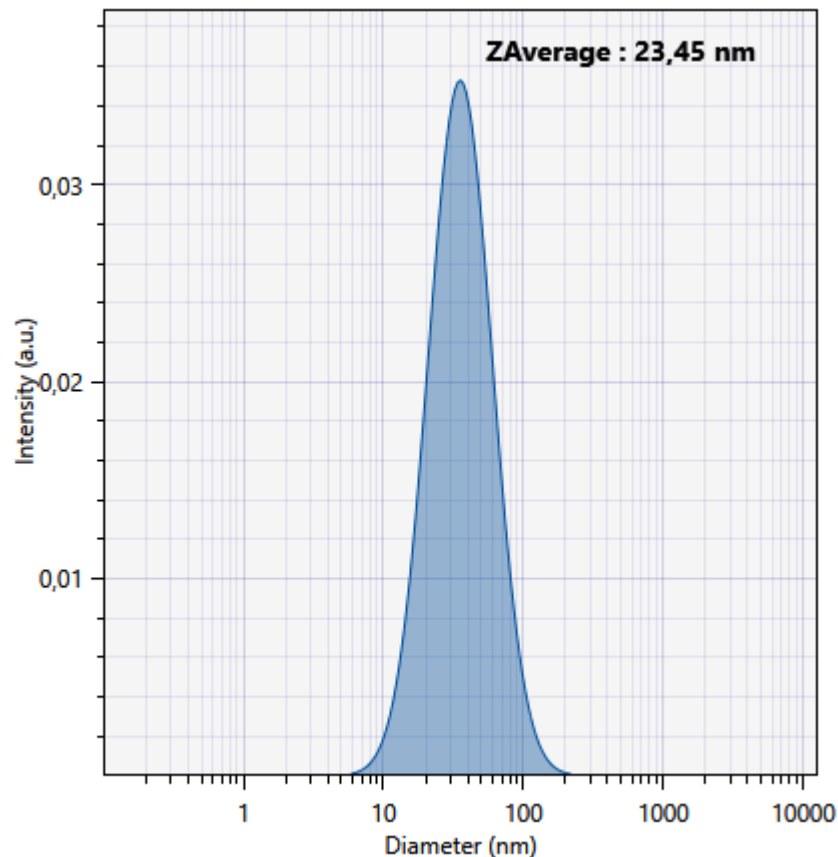
Z-average + PDI (polydispersity index)



Co když vzorek obsahuje víc než jednu populaci částic?



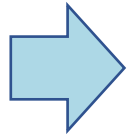
Law	LogNormal	LogNormal
Size (nm)	100	10
Std Dev (%)	1	1
Ratio Relative	1	1



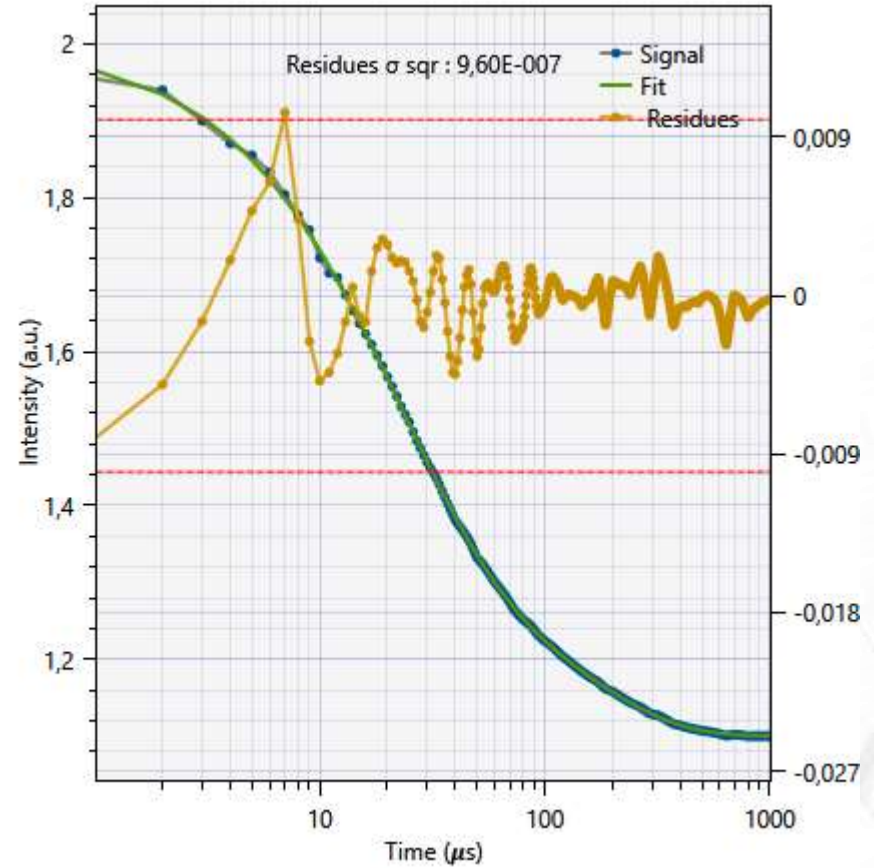
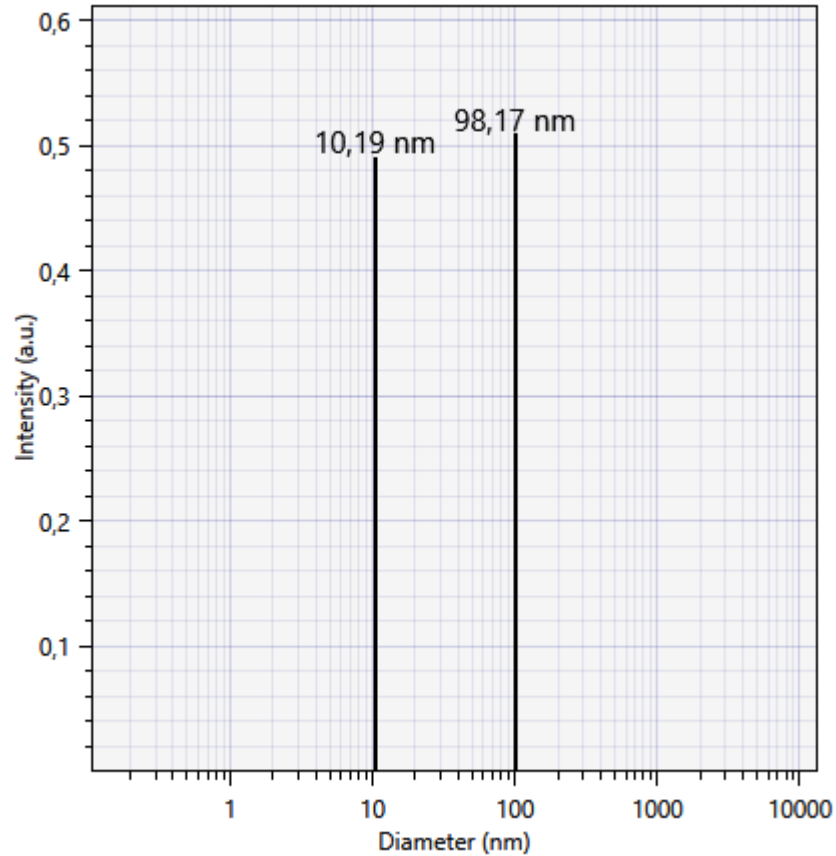
± 1,0 %

Cumulant	$G_2(\tau) = A + \beta e^{-2\Gamma\tau}$	Gaussian	B Frisken & al
----------	--	----------	----------------

Co když vzorek obsahuje víc než jednu populaci částic?



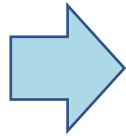
Law	Size (nm)	Std Dev (%)	Ratio Relative
LogNormal	100	1	1
LogNormal	10	1	1



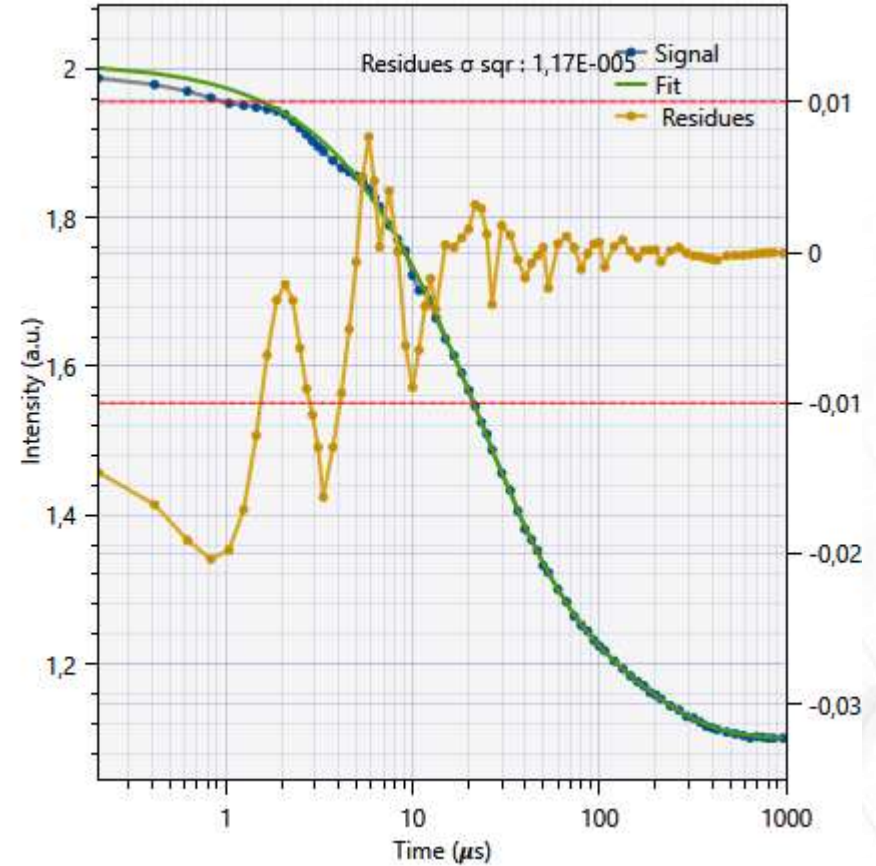
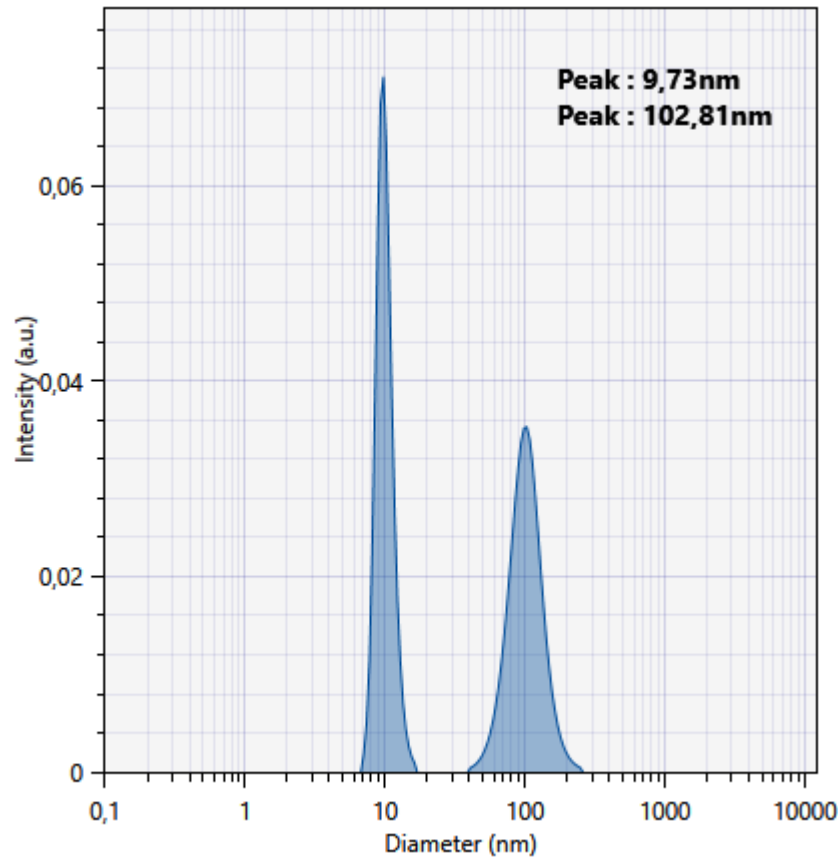
± 1,0 %

Pade Laplace	$G_2(\tau) = A + \sum_{i=1}^{250} B_i e^{-2\Gamma_i \tau}$	<u>Discrete</u>	Yeremian & al.
--------------	--	-----------------	----------------

Co když vzorek obsahuje víc než jednu populaci částic?



Law	Size (nm)	Std Dev (%)	Ratio Relative
LogNormal	100	1	1
LogNormal	10	1	1



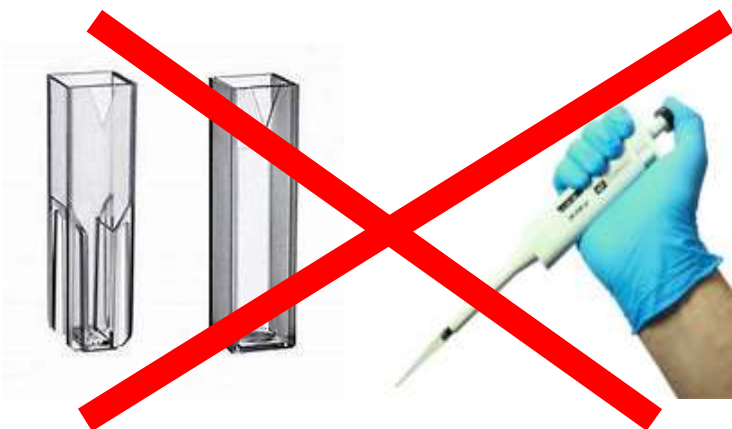
± 1,0 %

Sparse Bayesian Learning	$G_2(\tau) = A + \int_0^{10\mu m} B(\Gamma) e^{-2\Gamma\tau} d\Gamma$	Continuous	R Ansari & al
--------------------------	---	------------	---------------

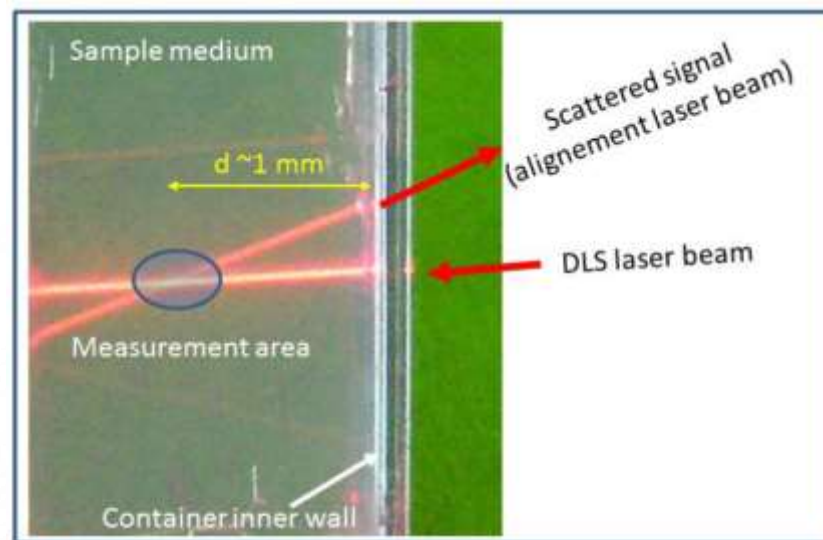
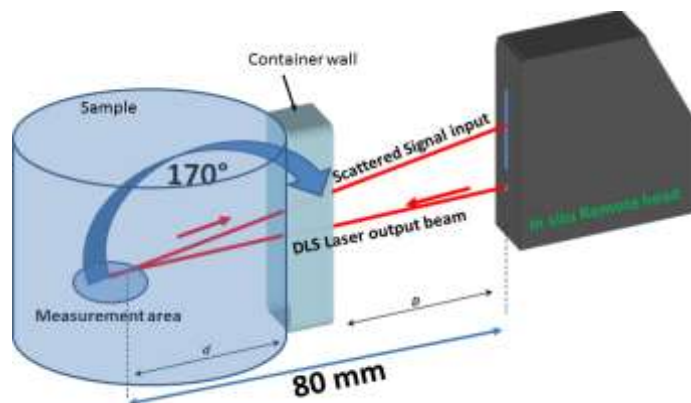
Vasco Kin



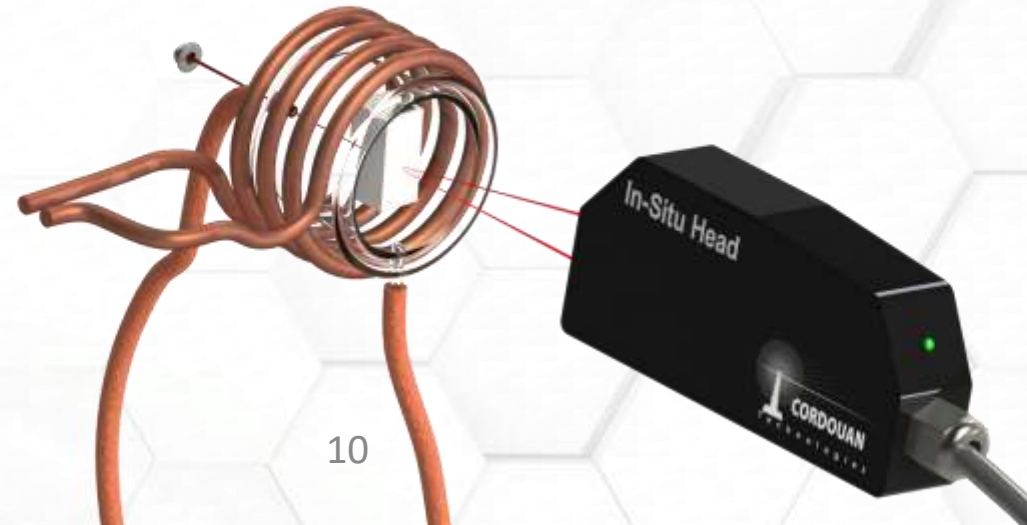
In situ měření:



- Odpadá manipulace se vzorkem
- Snižuje riziko kontaminace
- Ochrana operátora
- Šetří čas!

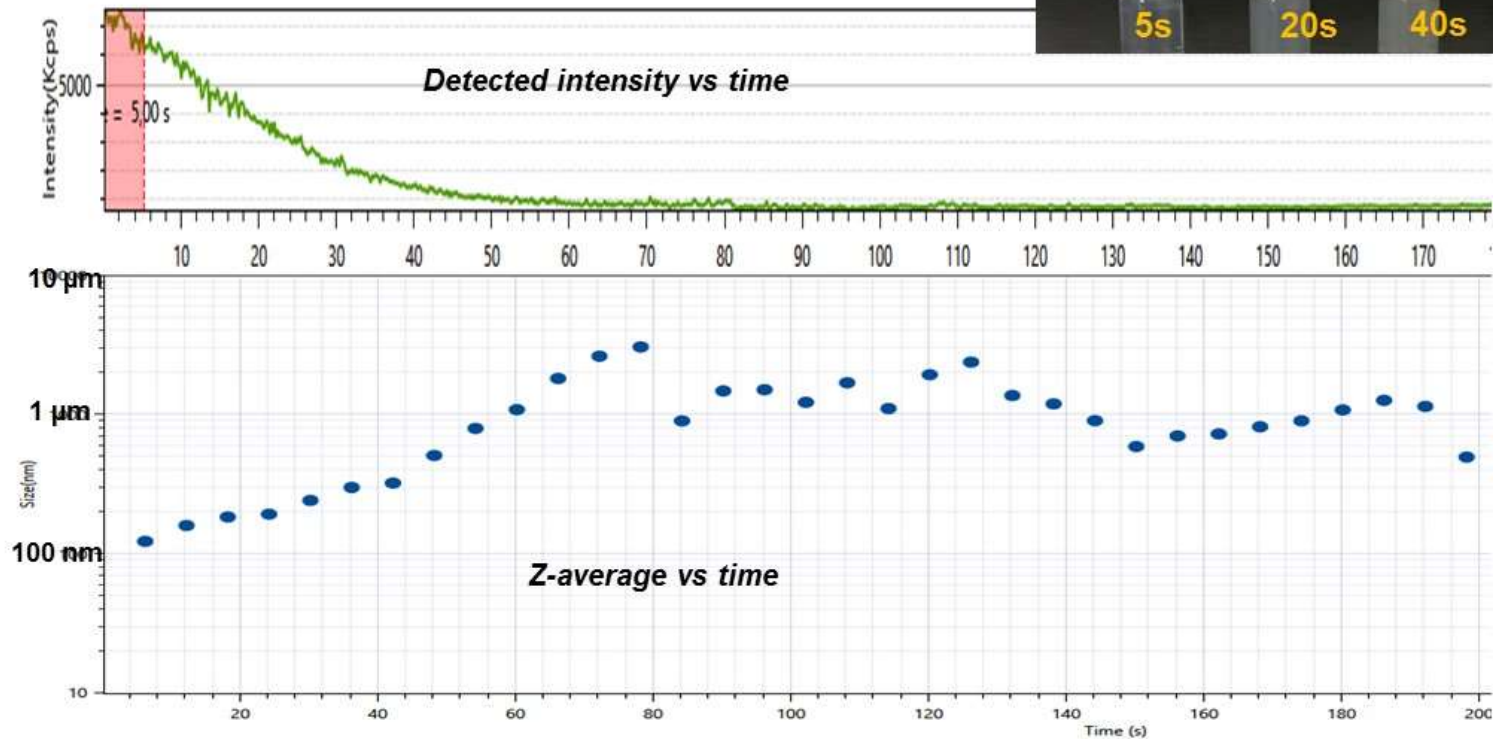
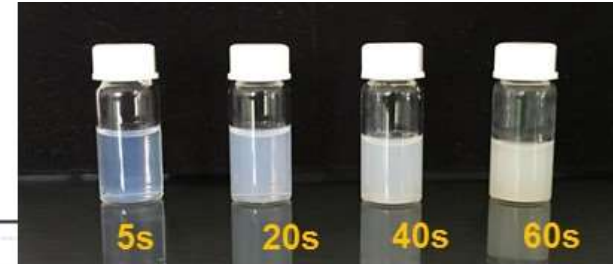


Výhody:



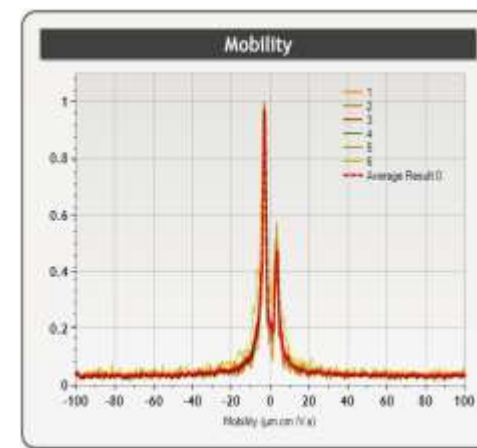
Proč měřit kineticky?

➤ « Ludox-TM 50 » 5wt% pH=3 + 10wt%NaCl



Wallis

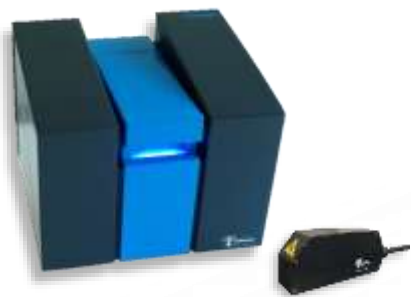
Analyzátor *zeta-potenciálu* využívající principu Laser Doppler Electrophoresis (LDE)



Resolution < 0.5 mV

Amerigo

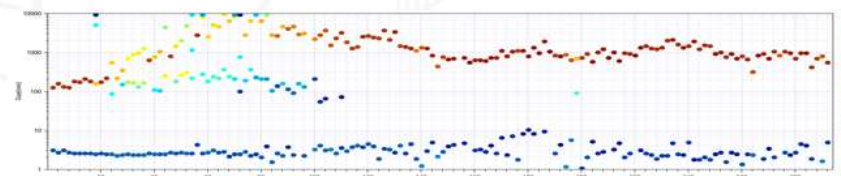
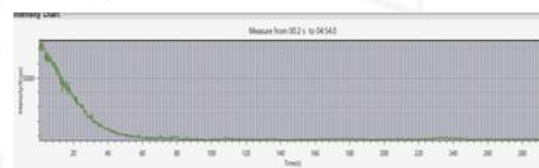
Analyzátor 2v1 *nanoparticle size & zeta potential*



Možnost připojení externí hlavy!
Kinetická analýza

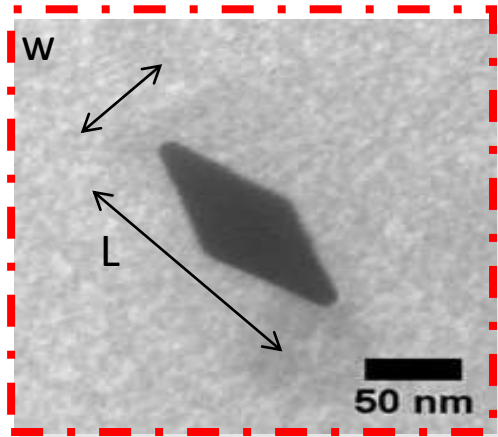


Integration: 2s / resolution: 2s

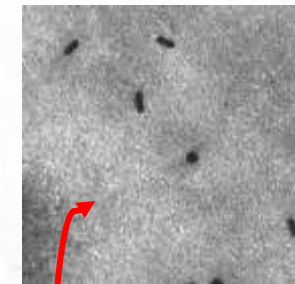
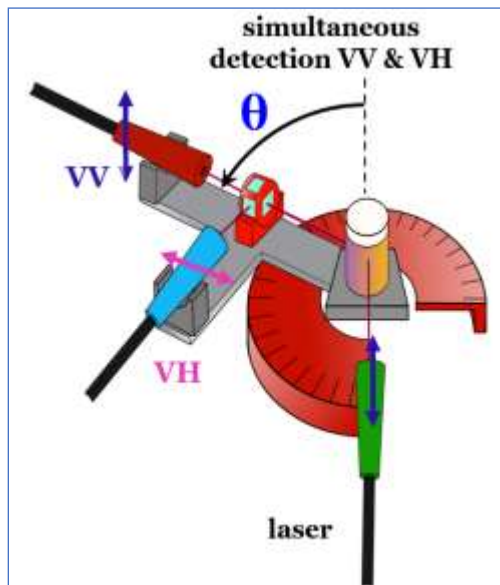
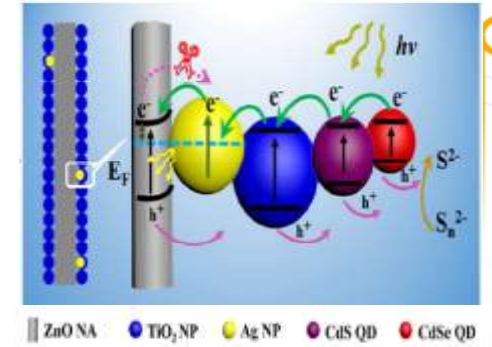


THETIS: A multi-angle DLS, SLS & D-DLS

Depolarized DLS



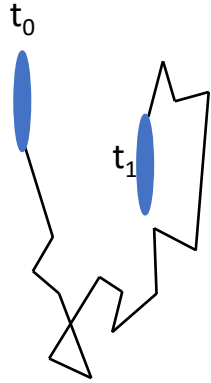
- DLS, DDLS and SLS in one instrument
- Multi-angle scattering measurement system: 30 to 160 degrees
- Real time and Time resolved Software correlator
- High Power single mode laser @ 635 nm
- Scattered Intensity measurements on 2 perpendicular polarizations
- Temperature controlled from 1 to 70 degrees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



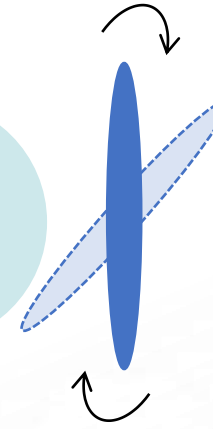
Parameter	D-DLS THETIS	TEM
L (nm)	28,5	28,3
L/w	1,7	2
w (nm)	16,8	14,5

Chování anizotropních částic

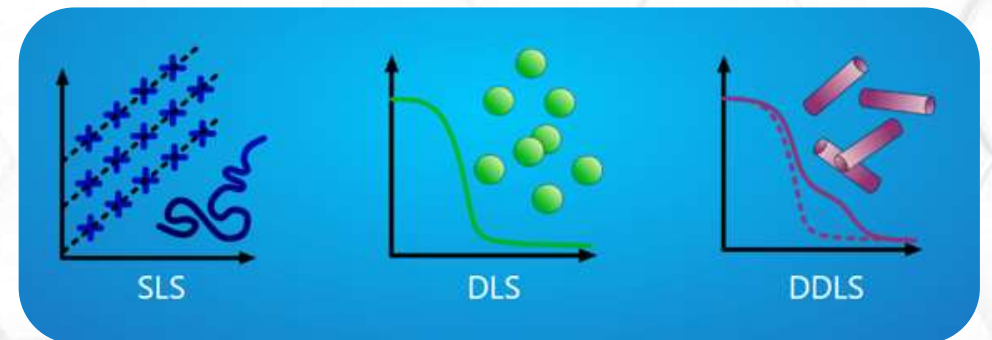
Translational Diffusion
coefficient
 D_t



Rotational
Diffusion coefficient
 D_r



1. 2 rozdílné pohyby: translační a rotační
2. Vedou ke 2 rozdílným difúzním koeficientům!
3. Vyžaduje polarizaci dopadajícího světla



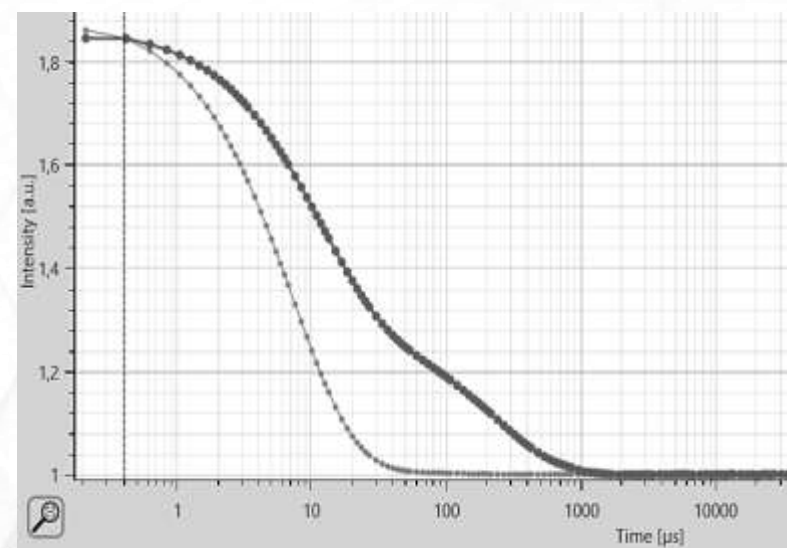
Anizotropní difúzní koeficienty:

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

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

- **L**: length
- **w**: width
- **L/w**: aspect ratio

1. Výpočet je proveditelný
2. Získáme parametry L a W



Chytrá charakterizace materiálů



MORE THAN
2000
R&D LABS
EQUIPPED

Our technologies are in the heart
of the world scientific community



MORE THAN
20%
OF ANNUAL TURNOVER
INVESTED IN R&D

Our core value
is innovation



MORE THAN
3000
SCIENTIFIC PUBLICATIONS
AND PATENTS

The TURBISCAN is the reference
in stability characterization



Nástroje charakterizace koncentrovaných disperzí:

- *V nativní formě, bez denaturace*
- *Snadné ovládání*
- *Od formulace po aplikaci*

ISO TR 13097 / ISO TR 18811 / ISO 13014
ASTM D 7061

TURBISCAN

STABILITY & SIZE

DISPERSION STABILITY & SIZE
BY MULTIPLE LIGHT SCATTERING

DISPERSION STATE

SIZE

Dispersibility, aggregation..

STABILITY

Size variation, migration...

FLUIDICAM

RHEOLOGY ON CHIP

FLOW RHEOLOGY
BY MICROFLUIDICS

RHEOLOGY

FLOW BEHAVIOR

Injectability, sprayability...

STRUCTURE AT REST

Gelling, stability...

RHEOLASER

MICRORHEOLOGY

ZERO SHEAR
MICRORHEOLOGY

THERMAL ANALYSIS
BY MICRORHEOLOGY

THERMAL ANALYSIS

PHASE TRANSITION

Crystallization, melting...

FROM FORMULATION TO APPLICATION

Rychlé stanovení stability koncentrovaných disperzí

- Turbiscan

TURBISCAN

STABILITY & SIZE

DISPERSION STABILITY & SIZE
BY MULTIPLE LIGHT SCATTERING

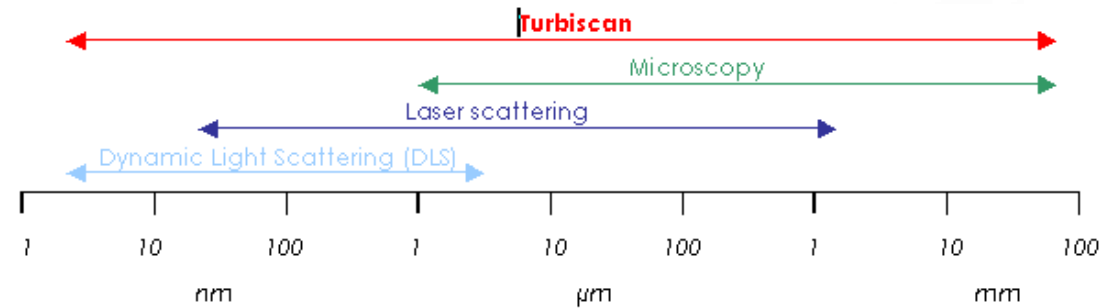
DISPERSION STATE

SIZE

Dispersibility, aggregation...

STABILITY

Size variation, migration...



FROM FORMULATION TO APPLICATION

Turbiscan

Jak dobře je produkt **dispergovaný**?

Jaká je **velikost částic** při plné koncentraci?

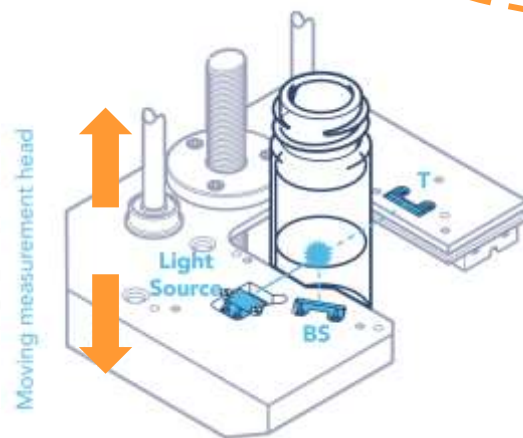
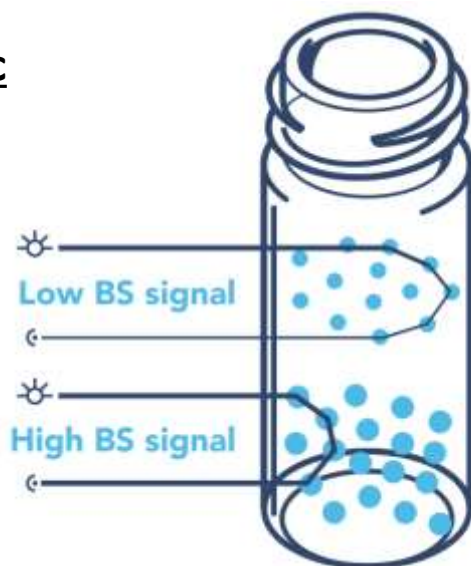
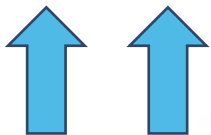
Může být produkt resuspendován?

Jaká je skladovatelnost produktu?



d : velikost částic

Φ : koncentrace



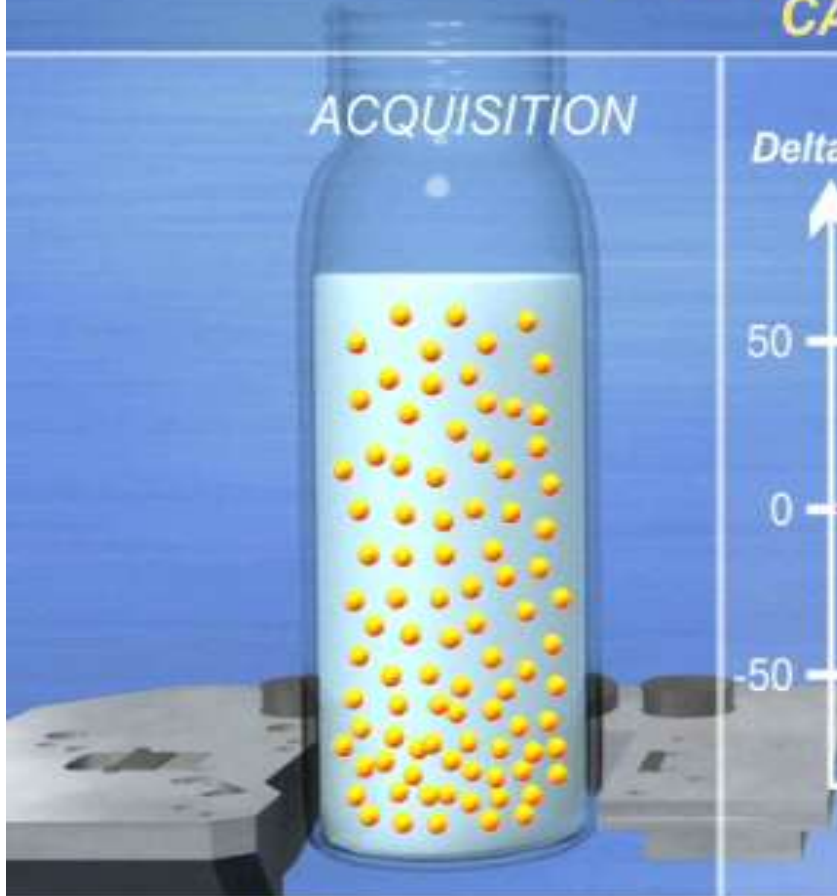
Skenování probíhá v **celé výšce vzorku** v čase:

Změna signálu ➡ Změna vzorku ➡ Sledování stability

TURBISCAN TECHNOLOGY

CASE 2 : Sedimentation

ACQUISITION



DATA

Delta BS

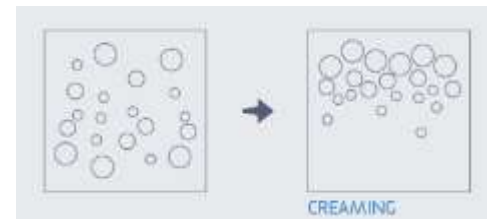
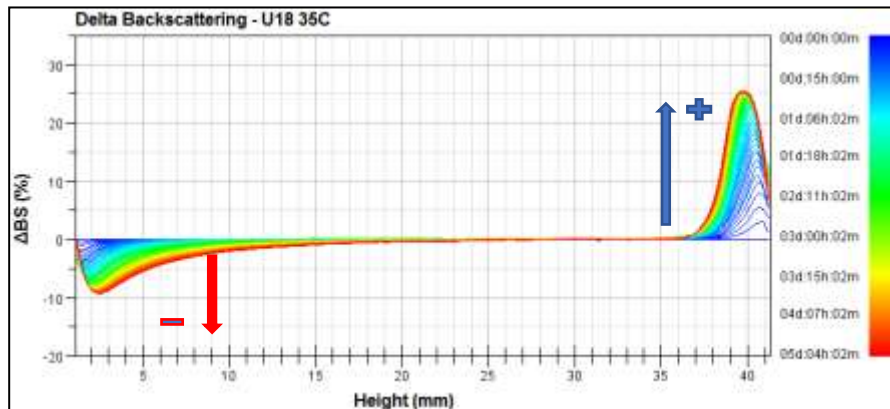
50

0

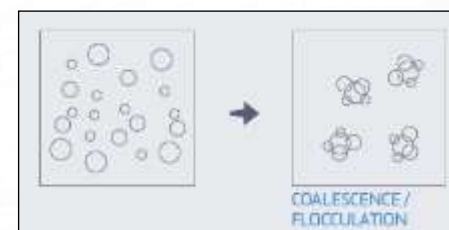
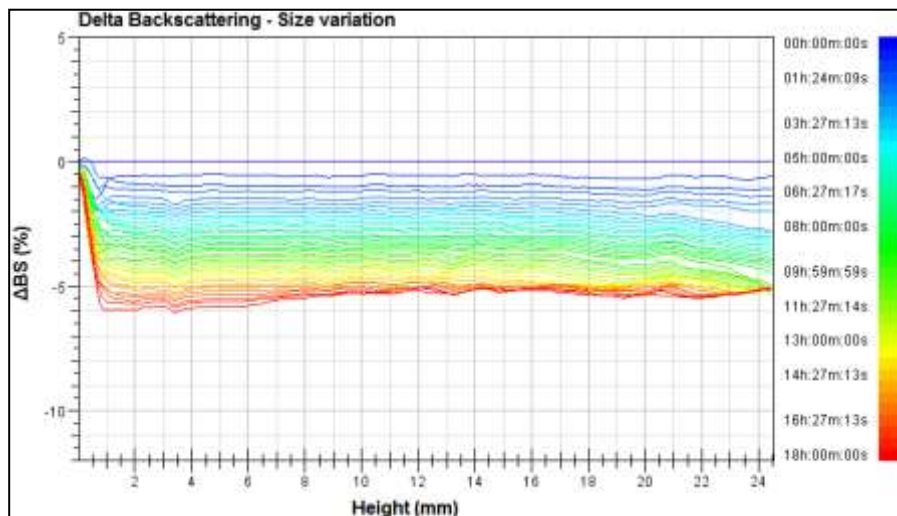
-50

$t = 0 \text{ min}$

Height (mm)



Pěnění

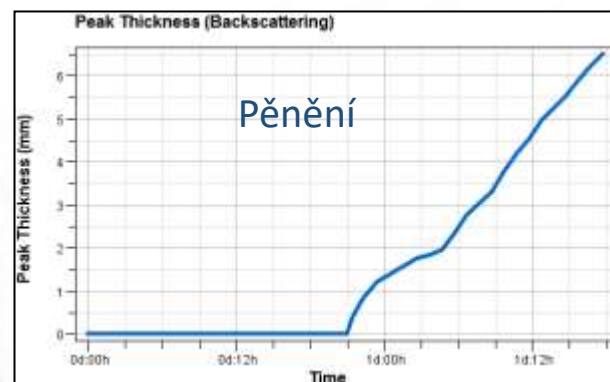
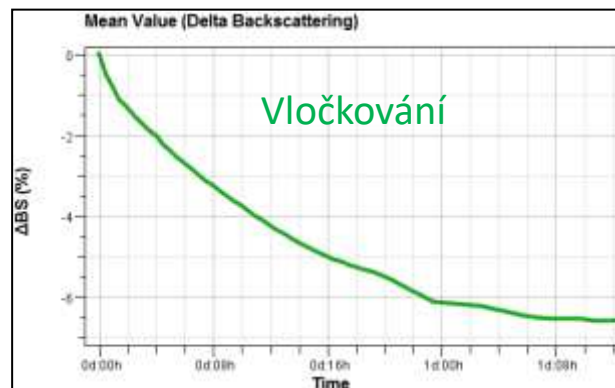
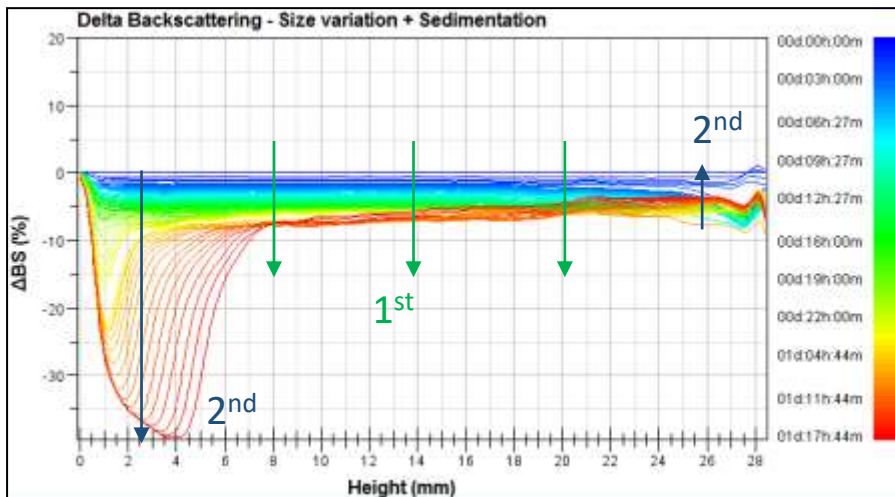


Změna velikosti

Celý vzorek: snížení / zvýšení signálu

TURBISCAN DATA

Komplexní destabilizační jevy



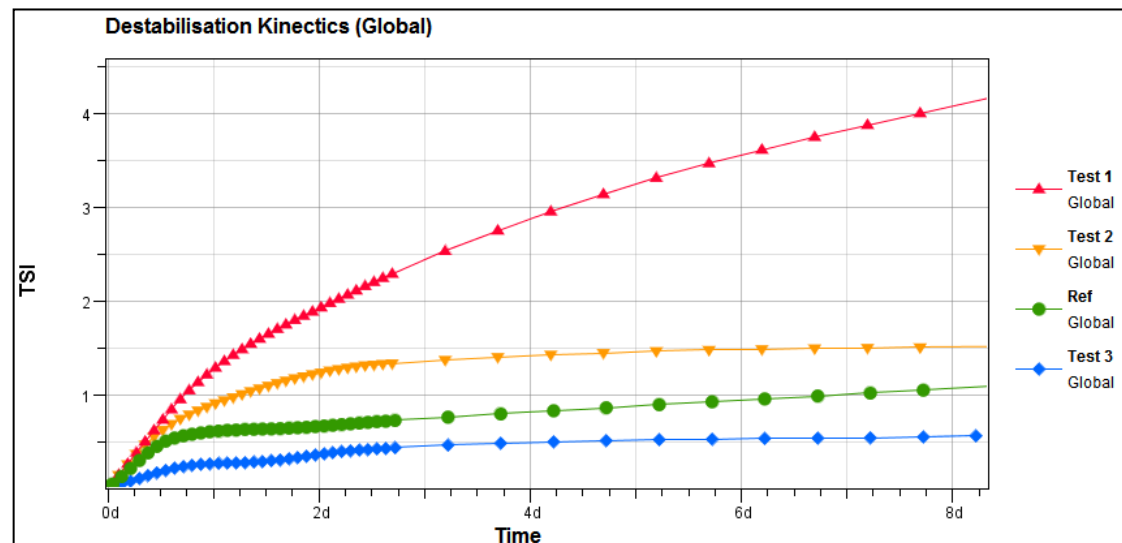
Komplexní pochopení destabilizace a kinetiky každého jevu

TURBISCAN DATA

TSI – Turbiscan stability index

$$TSI = \sum_i \frac{\sum_h |scan_i(h) - scan_{i-1}(h)|}{H}$$

Kritéria stability jedním kliknutím: Turbiscan Stability Index



Málo stab.



Více stabilní

Název vzorku	TSI (8 dnů)
Test 1	4.1
Test 2	1.5
Ref	1.1
Test 3	0.6

- ✓ Parametr stanovený jedním kliknutím
- ✓ Nejsou vyžadovány žádné další informace o vzorku
- ✓ Zohledňuje VŠECHNY TYPY DESTABILIZAČNÍCH PROCESŮ
- ✓ Unikátní číslo umožňující porovnání a poměření komplexních vzorků

TURBISCAN DATA


Shrnutí

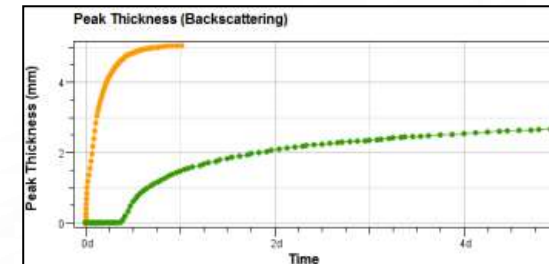
Výhoda 1 : Úspora času

- ✓ Vysoké optické rozlišení ($40\mu\text{m}$) = až 50krát rychlejší
- ✓ Urychlení vlivem teploty = až 200krát rychlejší analýza



Výhoda 2 : Identifikace jevu a kvantifikace

- ✓ Jev: Migrace a/nebo změna velikosti
- ✓ Jak rychle:  a expertní režim



Výhoda 3 : Objektivita a sledovatelnost

- ✓ Dokumentace stabilních studií
- ✓ Nástroj pro správu a prodej



TURBISCAN DNS (Dispersibility and Stability)

Funkce Turbiscan Mix a Turbiscan Loop

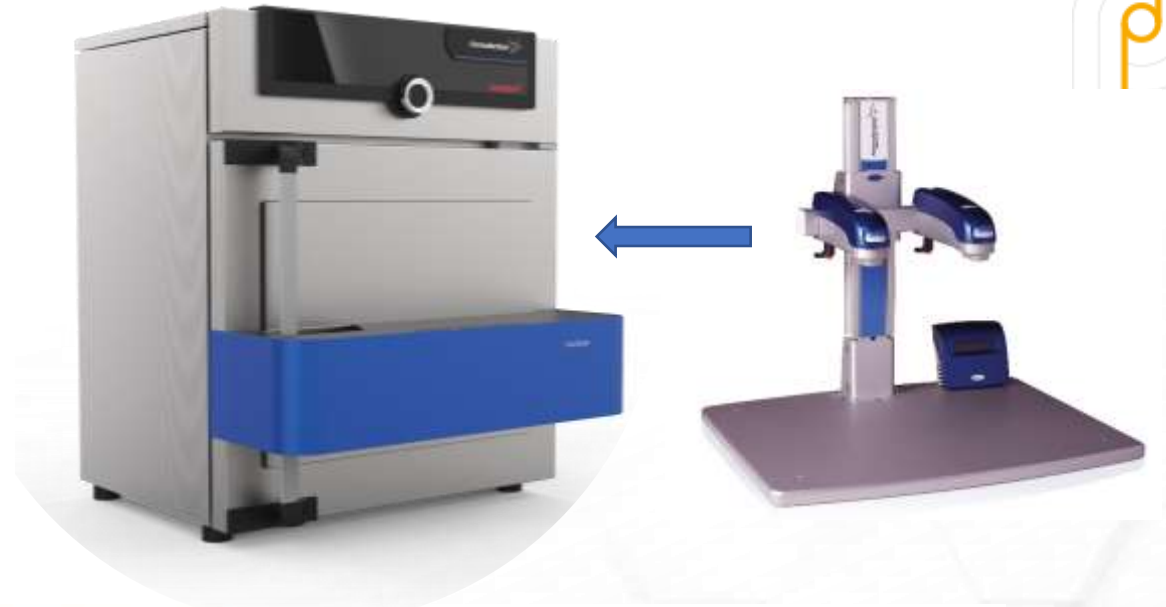
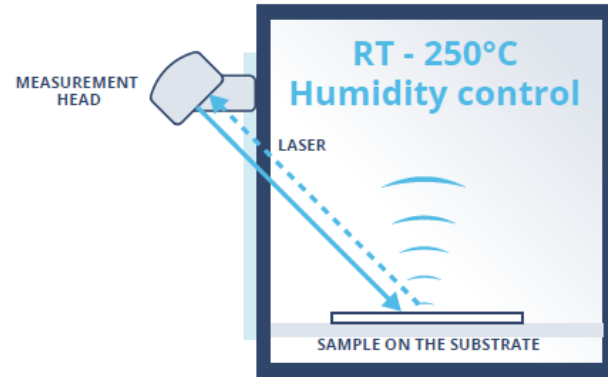


- Měření za současného míchání (funkce T-MIX) nebo přivádění roztoku do měřicí nádoby pomocí peristaltické pumpy (funkce T-LOOP, cirkulace).
- Optimalizace složení, stanovení (re)dispergovatelnosti a stability probíhá v rámci jednoho přístroje.

Nátěry a tenké vrstvy

CurinScan

MEASUREMENT PRINCIPLE



Technical
paints & inks



Powder
coatings



Adhesives



Cosmetics



Batteries
slurries



Elastomers

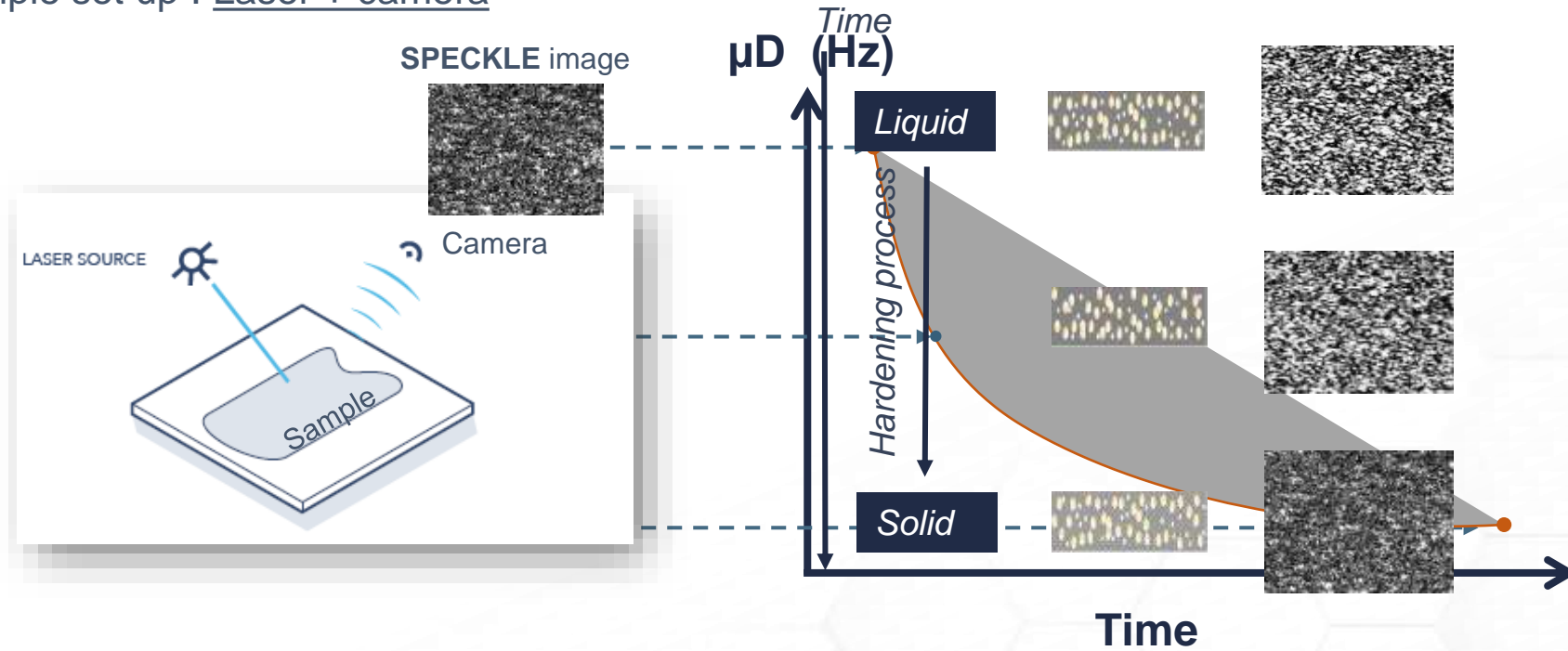
❑ Multispeckle – Diffusive wave Spectroscopy:

❑ Principle of measurement : Set- up



⇒ How the speckle image probes drying/curing kinetics ?

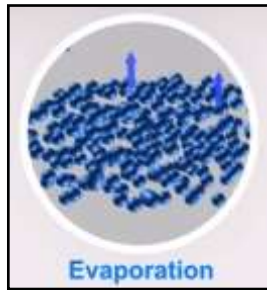
⇒ Simple set up : Laser + camera



μD evolution allows to monitor the drying & curing kinetics

RHEOLASER COATING

Valuable information



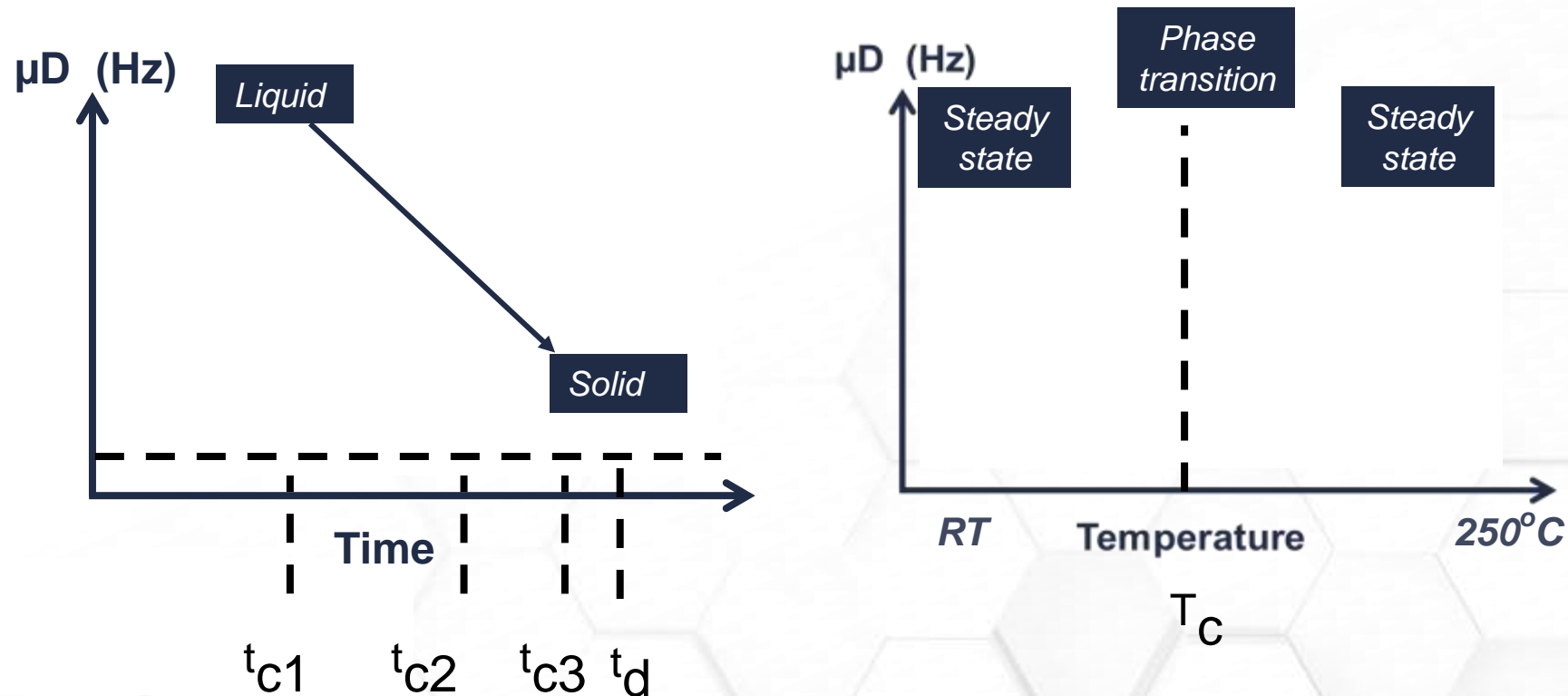
t_c at XX°C XX μ m thick	
t_{c1}	X min
t_{c2}	X min
t_{c3}	X min

1- *Drying time: Temperature, humidity, substrate, thickness...*

2- *Drying steps & characteristic times*

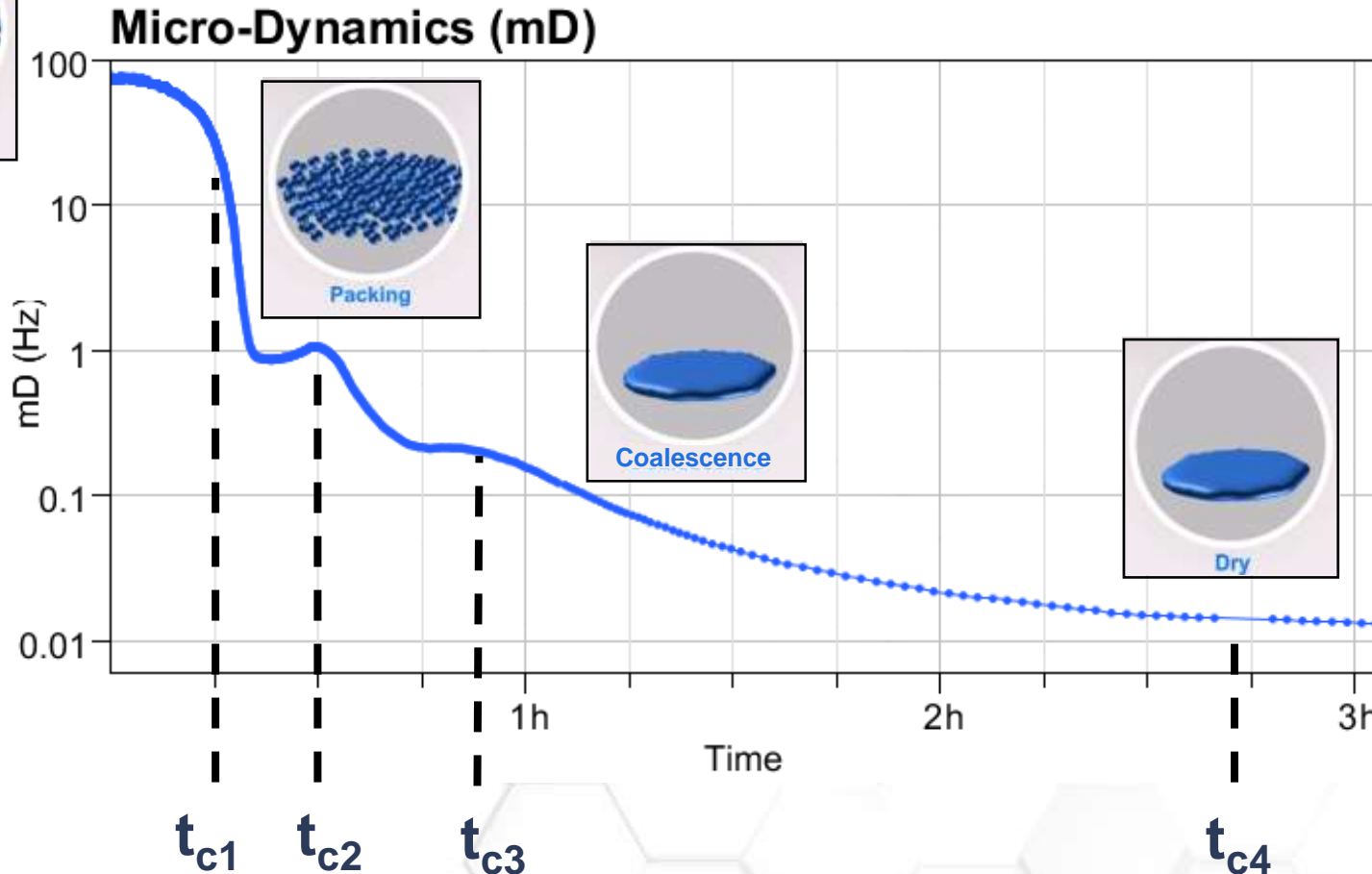
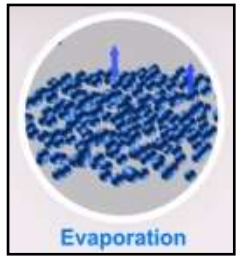
3- *Transition temperature*

→ *Optimization curing/drying protocol*



Paint & Inks example

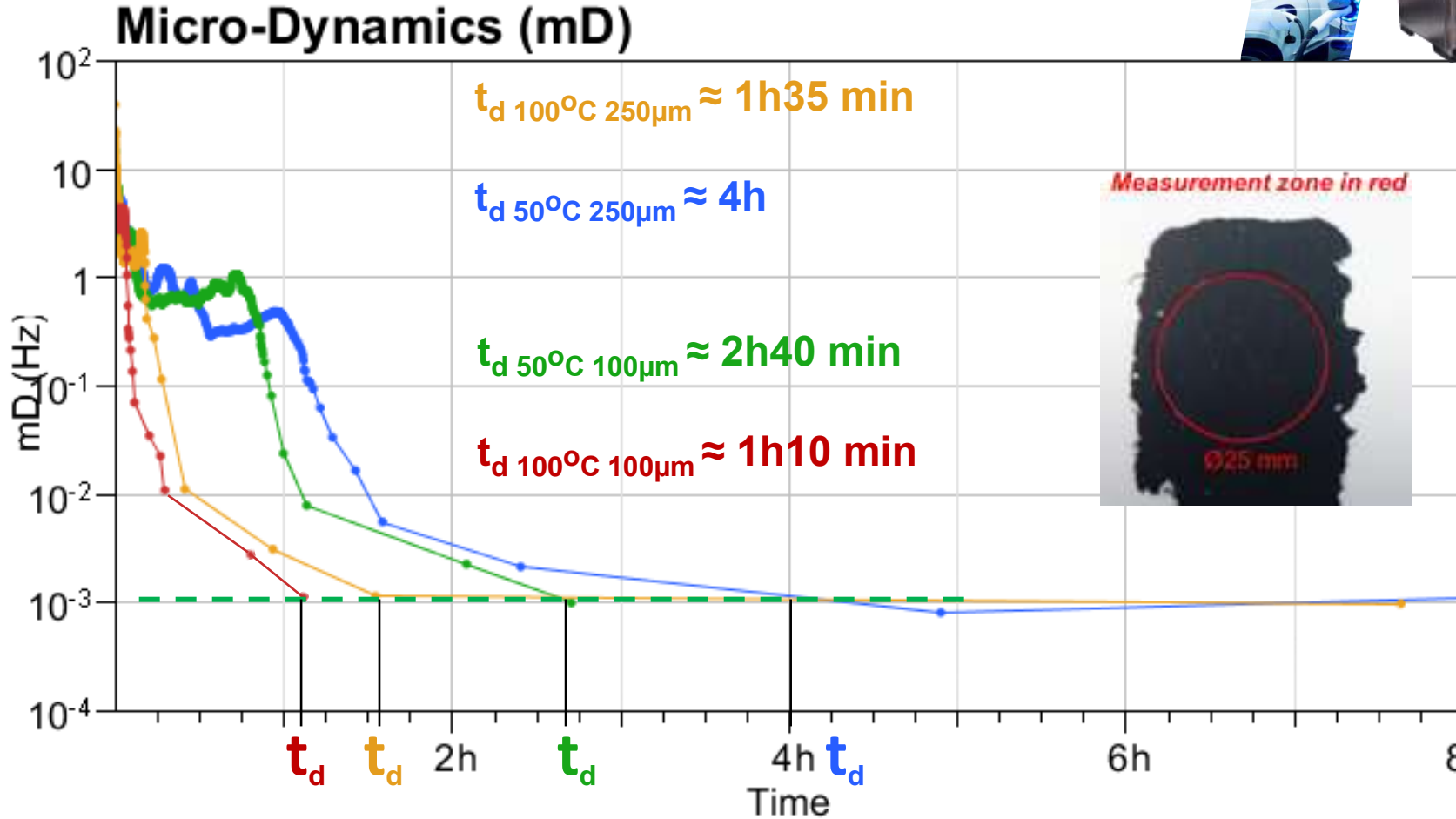
Monitoring the drying/curing kinetics
Determine the characteristic steps & times



t_c at 25°C	
t_{c1}	15 min
t_{c2}	30 min
t_{c3}	50 min
t_{c4}	2h30

RHEOLASER COATING

Cathode Slurry – different T & thickness



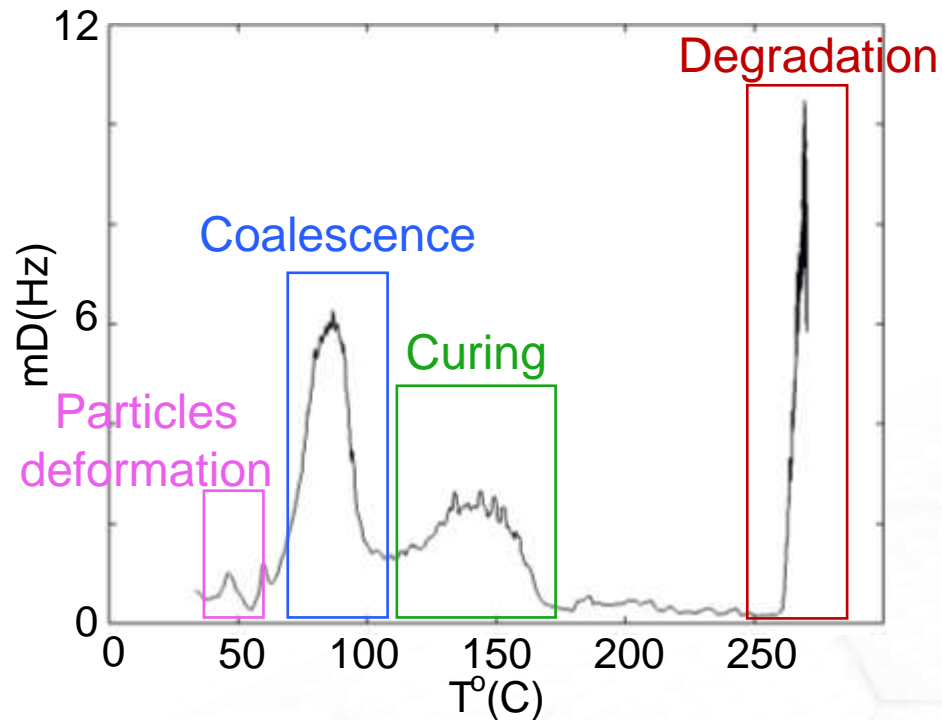
Detection of characteristic times ' t_d '
Clear Thickness & T influence on the drying process!

RHEOLASER COATING

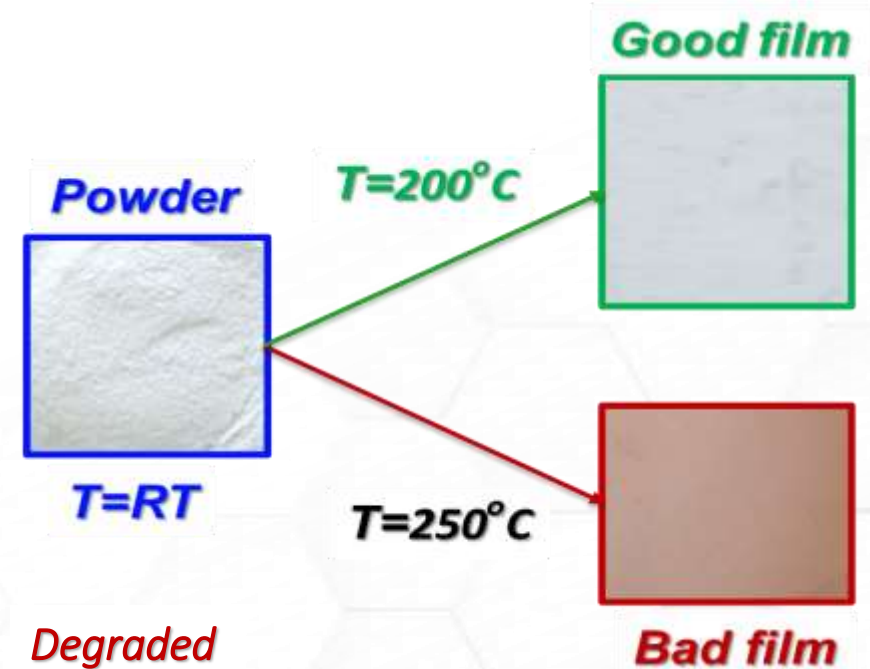
Powder Coatings – T increase

$RT \rightarrow 250^{\circ}C$

- The finish is **harder** and **tougher** than conventional paint
- Very **good mechanical** and **chemical resistance**
- **Eco-friendly** and **sustainable** systems

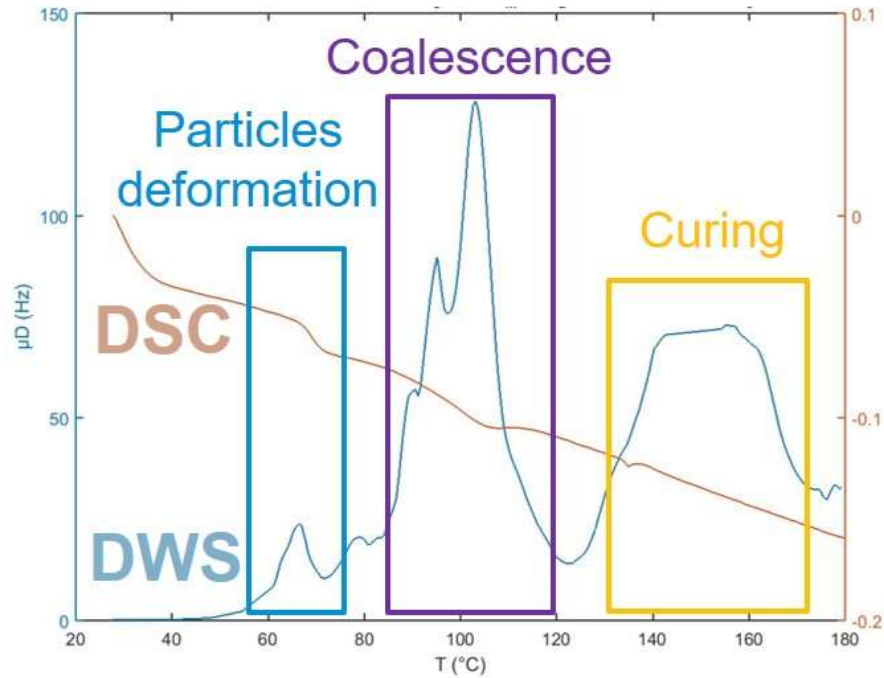


Clear identification of the different curing steps



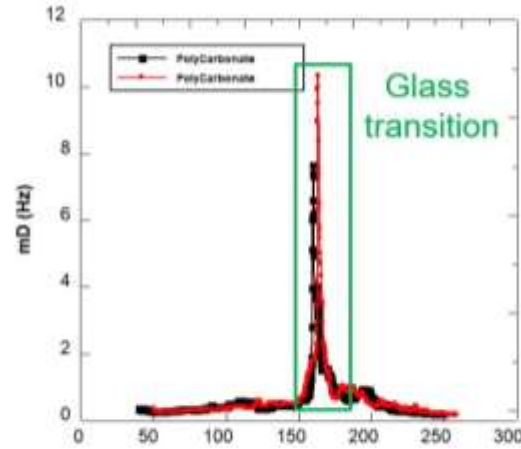
Determination of the degradation temperature !!!

μ D & Heat flow Vs T



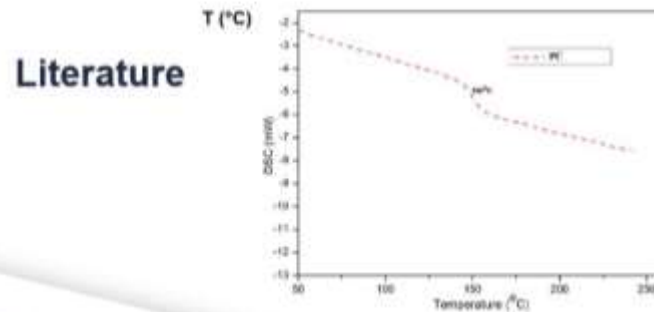
μ D pics are clearer

→ DWS is more sensitive than the DSC for **this type of reactions**, not very energetic



DWS pic is in agreement with the DSC T_g but clearer

→ DWS is more sensitive than the Chip DSC for **this type of reactions**, not very energetic



Charde, S. J., Sonawane, S. S., Sonawane, S. H., & Shimpi, N. G. (2018). Degradation Kinetics of Polycarbonate Composites: Kinetic Parameters and Artificial Neural Network. *Chemical and biochemical engineering quarterly*, 32(2), 151-165.

Příklad nátěrů a inkoustů

- Sledování kineticky vytvrzování/sušení a stanovení charakteristických kroků a časů

→ **Optimalizace formulace & vytvrzovacího protokolu**

- Pochopení vlivu vlhkosti a teploty nebo substrátu

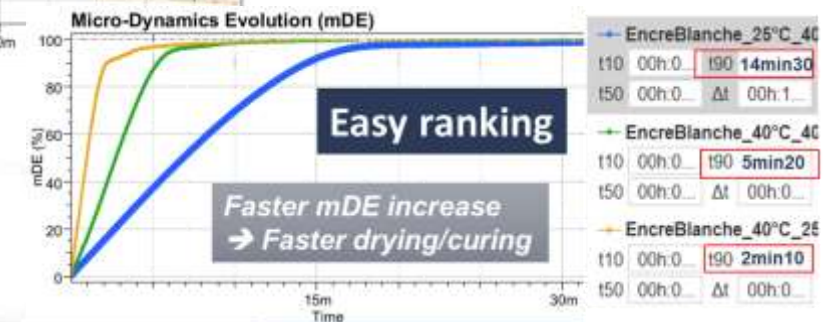
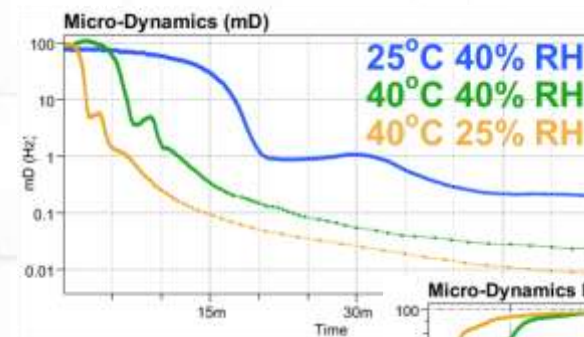
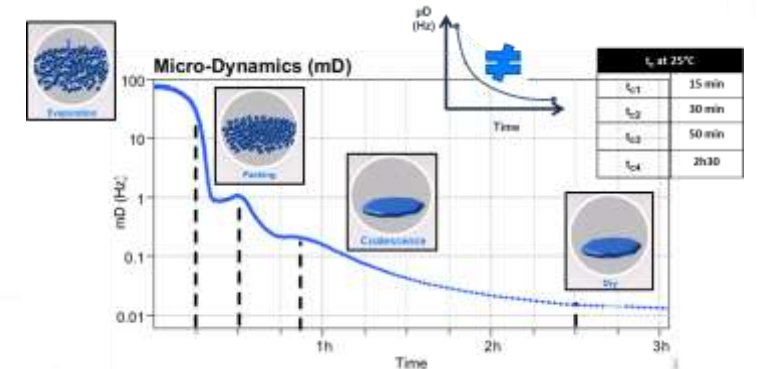
→ **Realistické podmínky**

- Porovnání různých formulací a podmínek

→ **Kvantitativní informace**

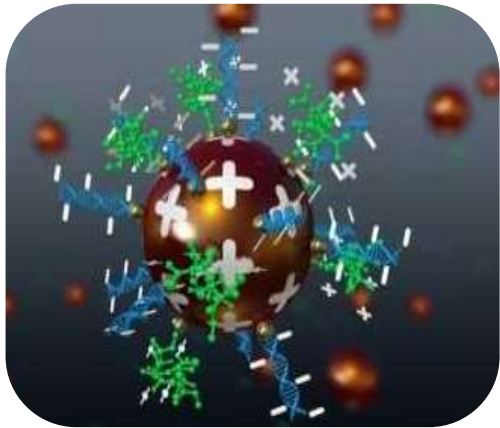
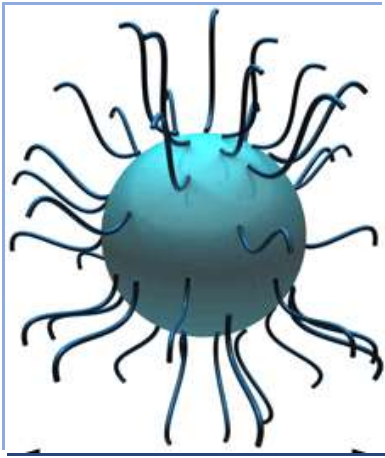
- Libovolný substrát možnost navrstvení více vrstev

→ **Reálné vzorky**



Quantitative information

t90 ≈ Open time



Děkuji!

