MICRORHEOLOGY FOR SOFT MATERIALS

« Non contact measurement of viscoelastic properties of biopolymers »

- Pascal BRU -

AGENDA

1. Soft materials
2. What is MicroRheology?
3. Rheolaser: The instrument
4. Application examples

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INTRODUCTION

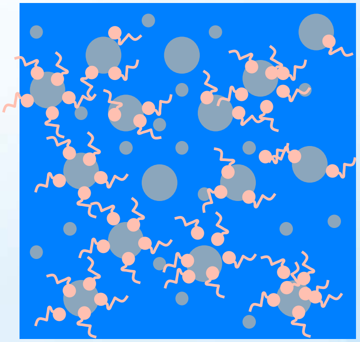
Why Rheology is important?

⇨ Because it allows to characterise end use properties like:

- Flowability 
- Spreadability 
- Shape stability 
- Gelation 
- Recovery after a stress 
- Stability 
- ….

SOFT MATERIALS

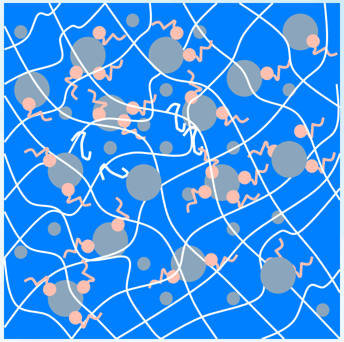
Characteristics



❑ Formulation in 1980's
⇨Surfactants

Fluid like systems

Goal:
⇨ Good dispersion



❑ Formulation : Today
⇨Surfactants + polymers

Gel like systems

Goal:
⇨ End use properties management / visco-elastic control

Decrease of the fat contents in food industry
Improvement of spreadability of creams …
Environmental / health issues
Better properties for drilling fluids

SOFT MATERIALS

Properties

Most of the soft materials are visco-elastic (non newtonian)

→ Visco-elastic behavior depends on time scale observation

→ time

Solid	Liquid
↓	↓
Elasticity	Viscosity

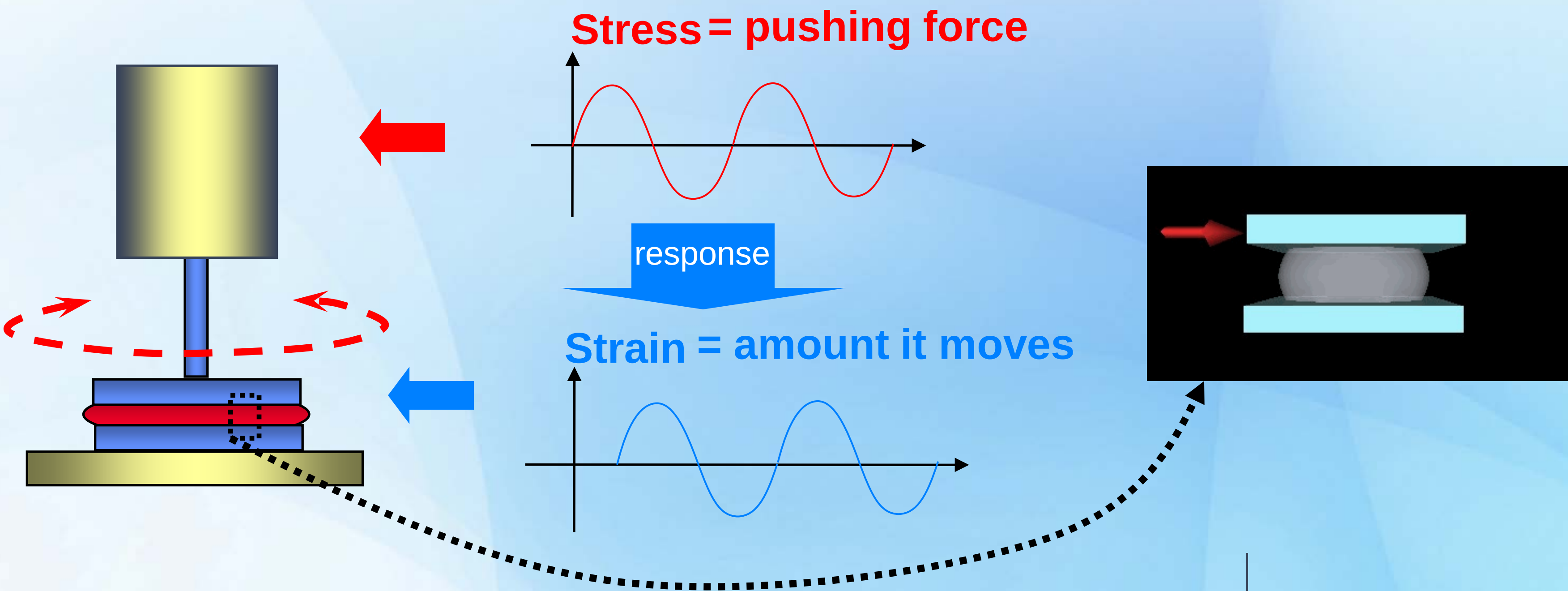
High ← Low

Frequency $= \frac{1}{\text{time}}$

Properties

How to measure visco-elasticity?

⇨Oscillation analysis : Rheometer



Relation Stress / Strain depends on the visco-elastic properties

Elastic modulus G'
Viscous modulus G''

Rheology

Oscillation analysis

⇨ Experiments are complex to perform:

- Find the right geometry
- Sampling is critical : volume, evaporation, drying…
- Risk of sample denaturation
- Intrusive measurement => no evolution (Rheolgy versus ageing time)

Formulaction
Smart scientific analysis

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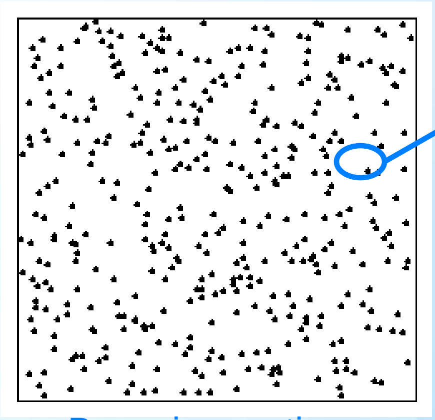
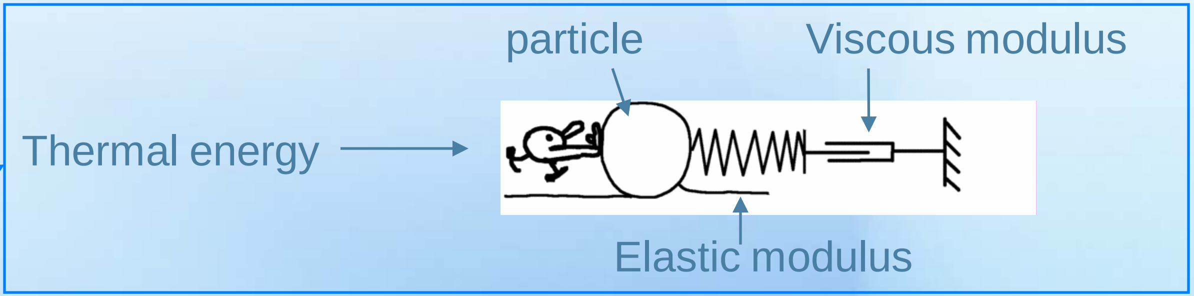
THE CONCEPT OF MICRORHEOLOGY

⇨ Thanks to Brownian motion the particle feels the viscoelastic structure:



Brownian motion

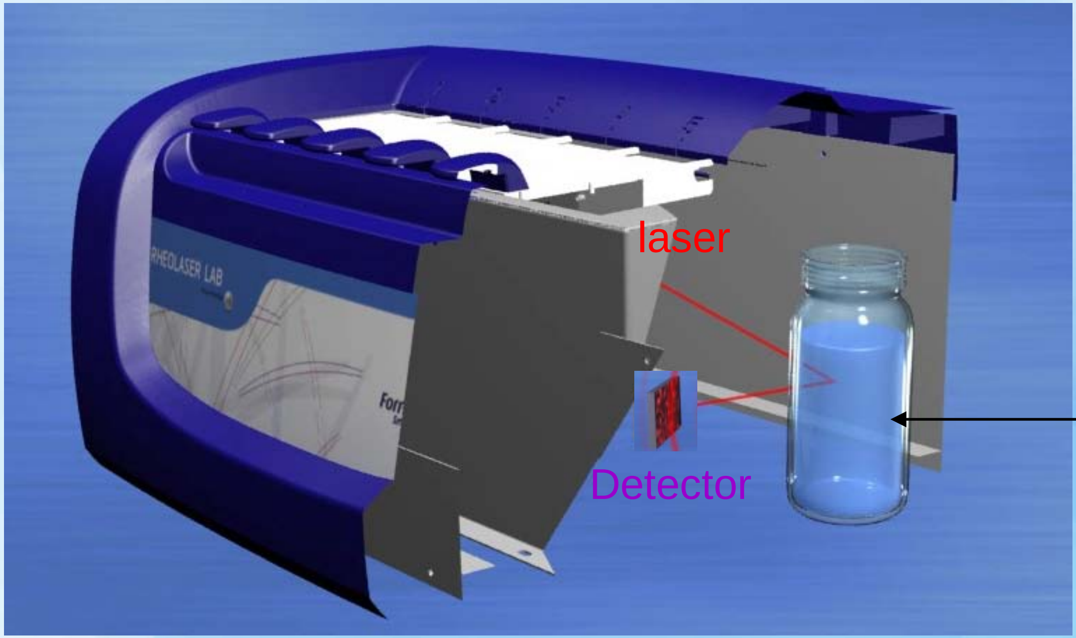


Stress → Thermal Energy k_bT
Strain → Particle Displacement

- ❑ Particle motion speed = Viscosity
  - Fast motion => low viscosity
  - Slow motion => high viscosity
- ❑ Particle displacement = Elasticity
  - Long displacement => low elasticity
  - Short displacement => high elasticity

⇨ MS-DWS records the particles mobility & displacement

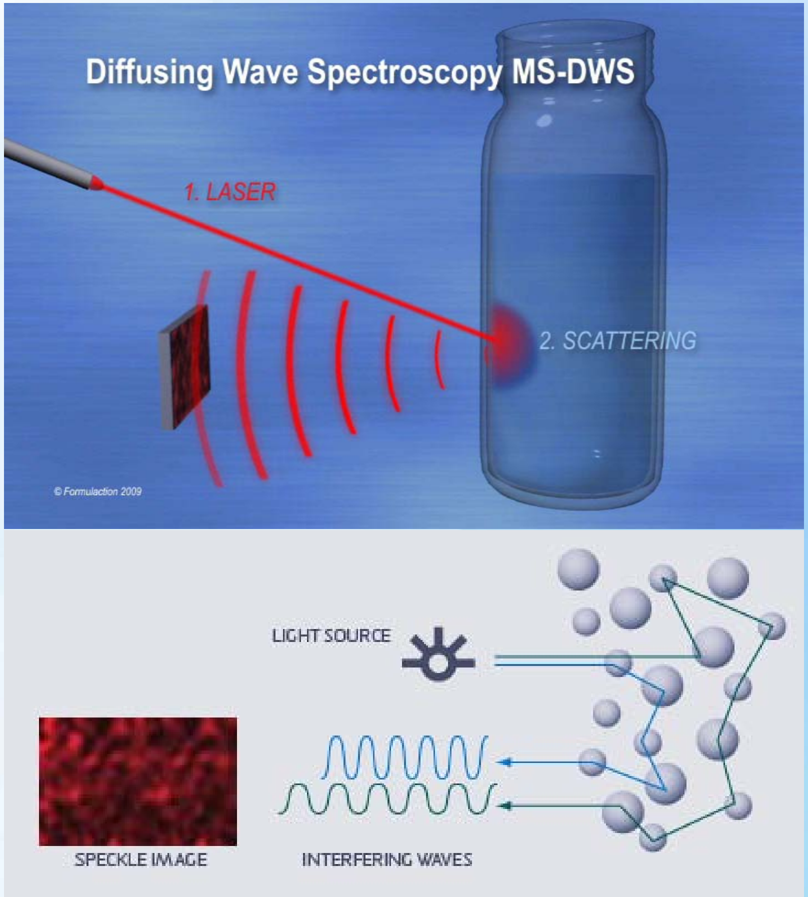
Experimental set up

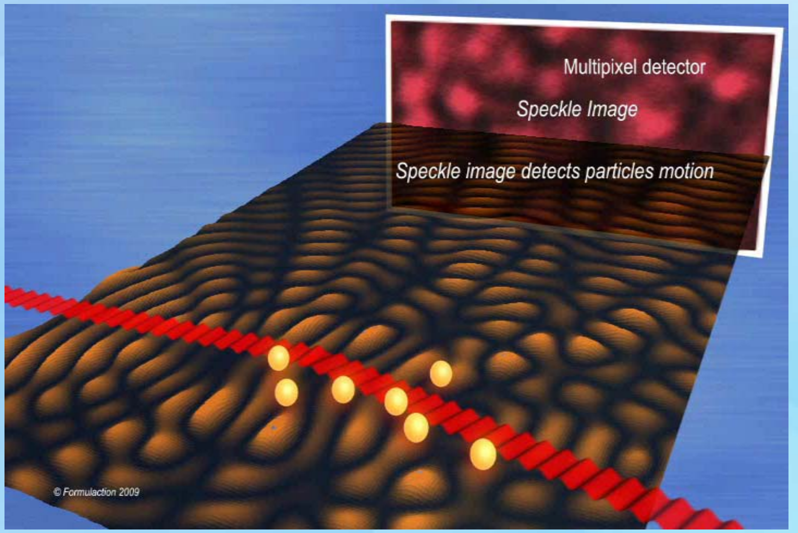


⇨ MS-DWS principle of measurement

MS-DWS

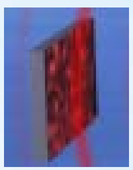
⇨Measurement of particles mobility in opaque media



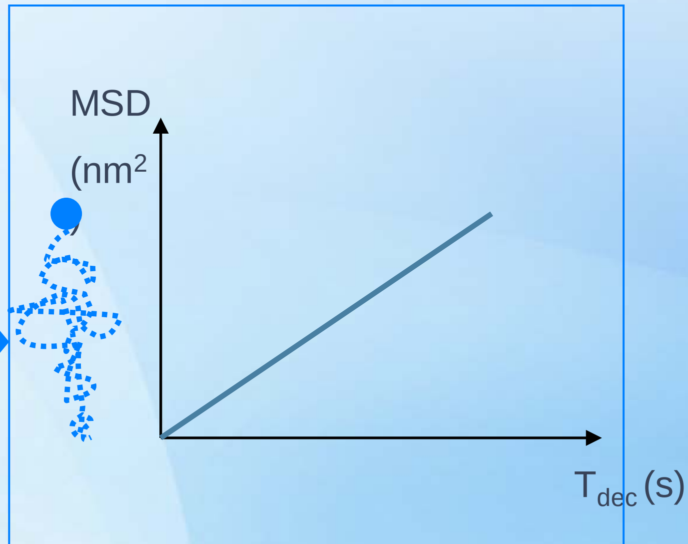


MS-DWS

⇨Particle Mean Square Displacement (MSD)

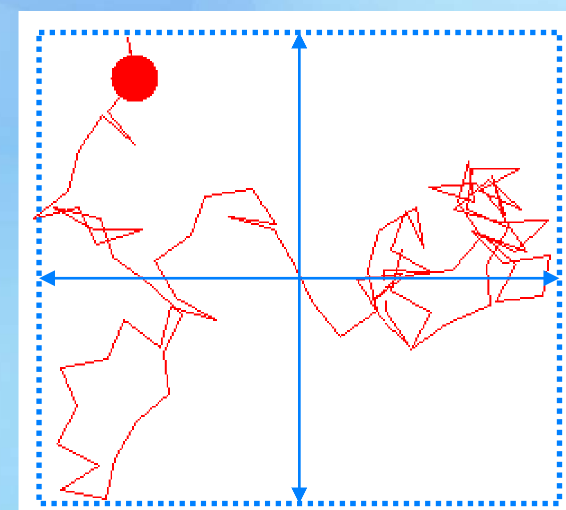


Patented algorithm



Particle Mean Square Displacement

Mean Square Displacement

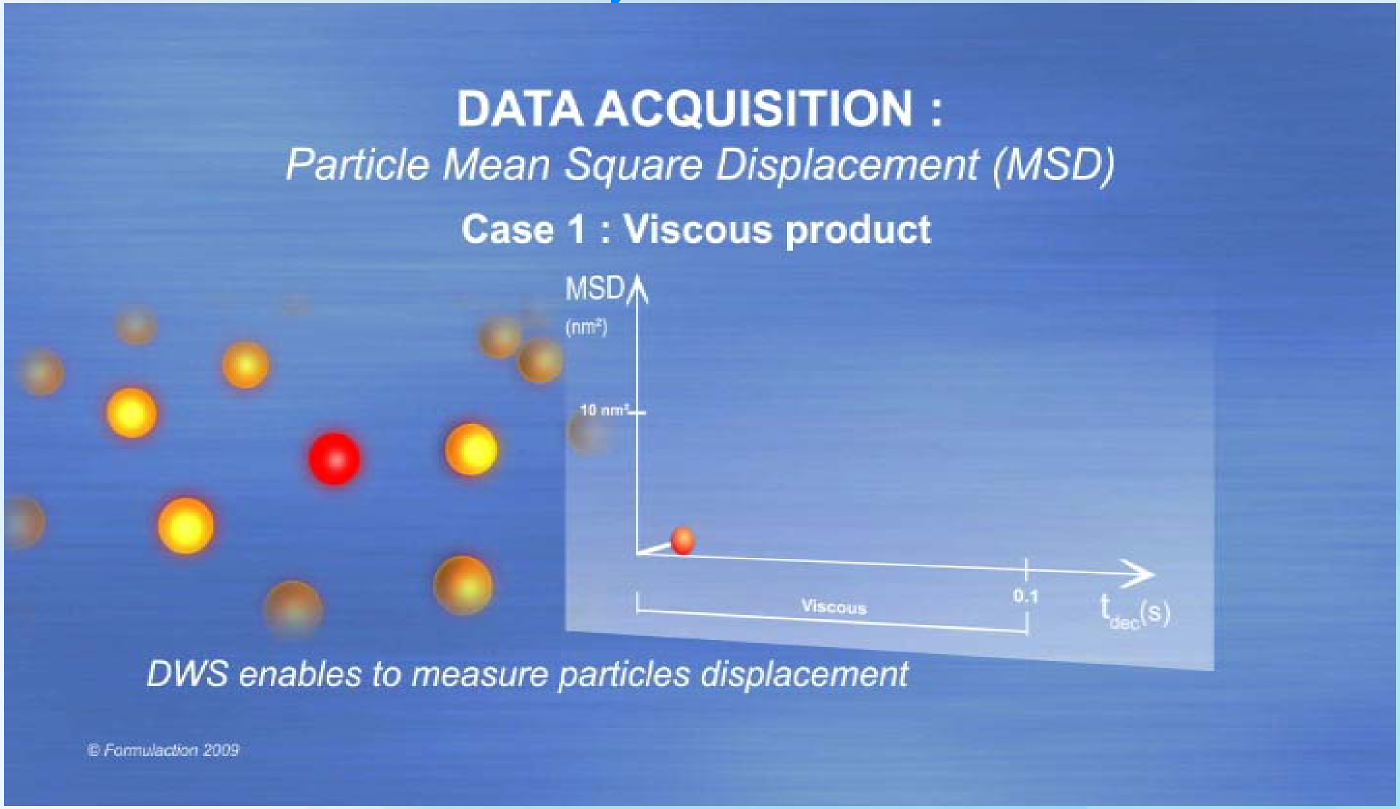


RHEOLASER

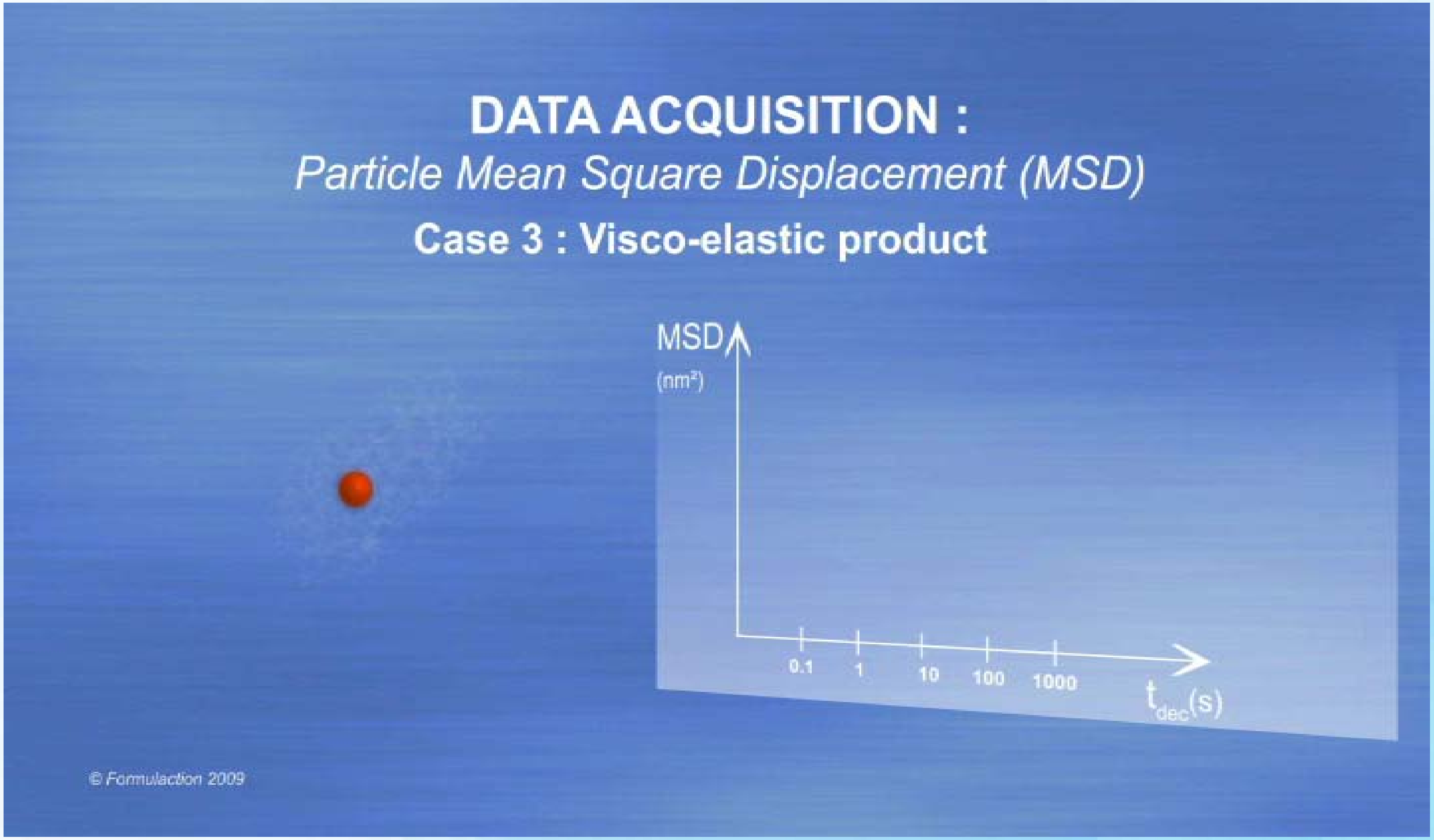
Particle Mean Square Displacement

Soft material properties affect the MSD of the particles

Purely Viscous → Particle is free to move



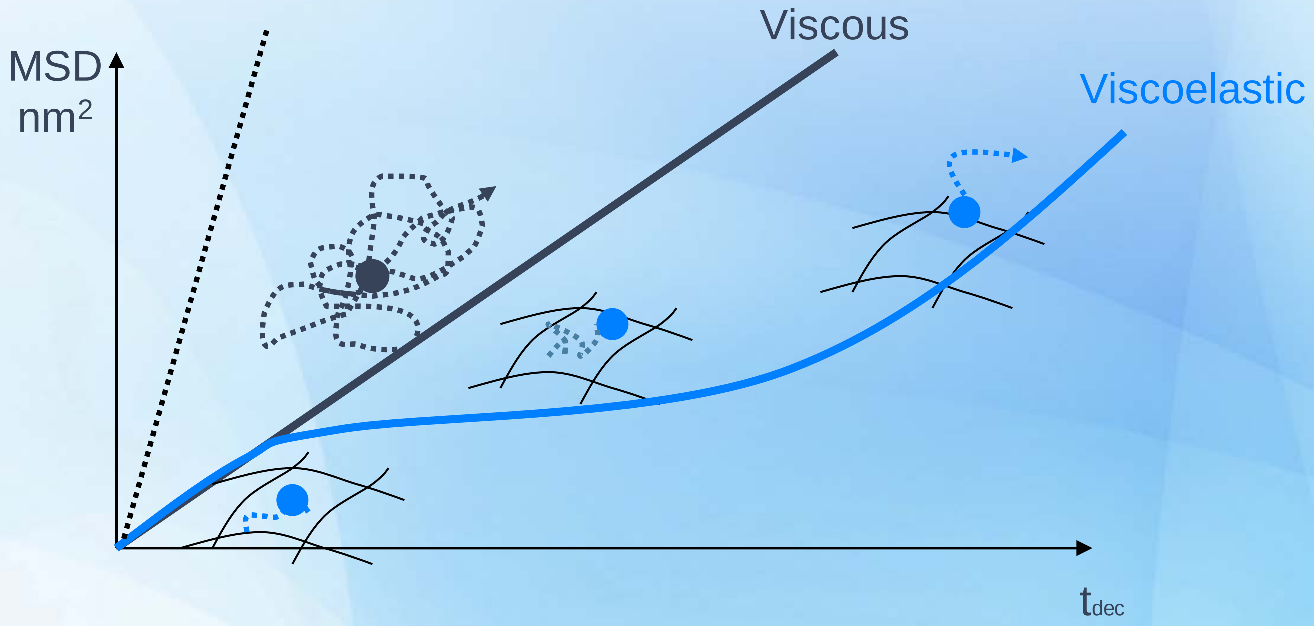
DWS measures displacement of many particle



DWS measures displacement of many particle

MEAN SQUARE DISPLACEMENT

⇨ MSD is the viscoelastic signature



⇨ Type of motion:

- Slope ≤ 1 => Brownian
- Slope > 1 => Ballistic (sedimentation…)

Formulaction
Smart scientific analysis

RHEOLASER

⇨3 parameters to monitor end use properties

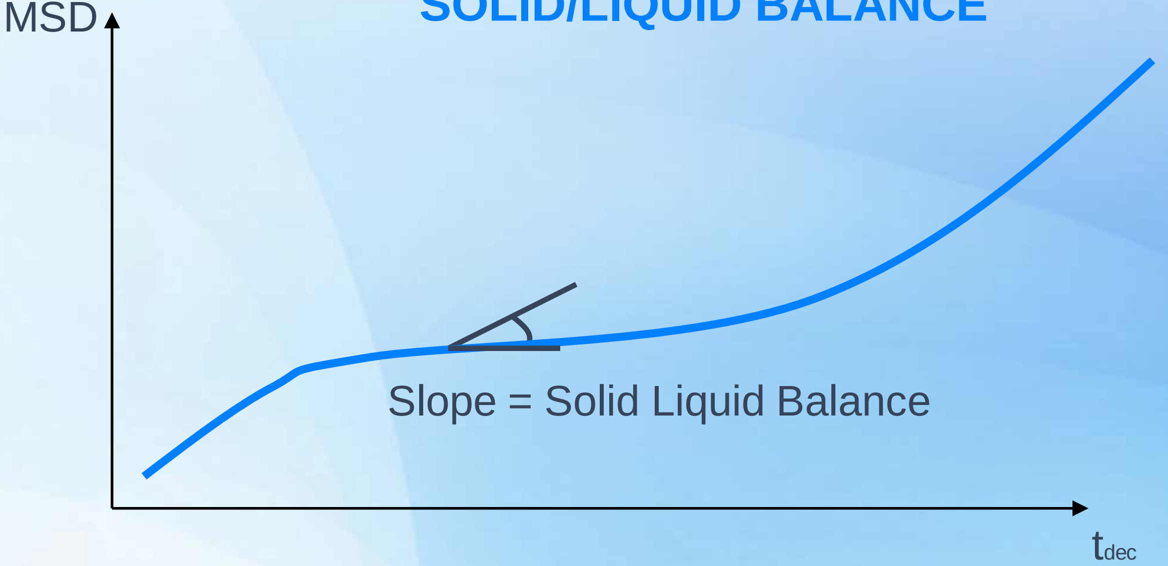
- Solid/Liquid balance SLB
- Elasticity Index EI
- Macroscopic Viscosity Index MVI

⇨ FOR EASY SAMPLES COMPARISON

DATA TREATMENT

⇨ 3 key parameters

SOLID/LIQUID BALANCE



- Slope < 0.5 => Solid behavior dominates (=> gel)
- Slope =0.5 => Solid = Liquid (=> Viscoelastic)
- Slope > 0,5 => Liquid behavior dominates

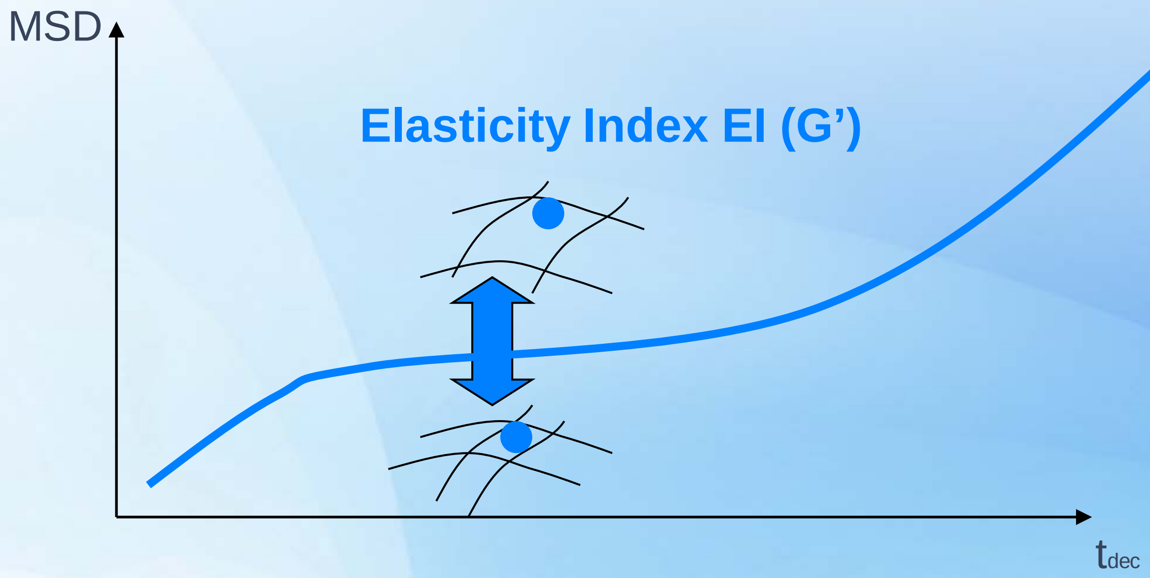
RHEOLASER

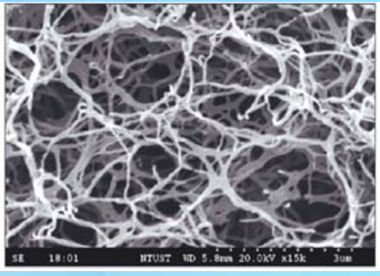
⇨ Is my sample more solid than liquid?

⇨ SAMPLES CAN BE RANKED EASILY

DATA TREATMENT

⇨ 3 key parameters



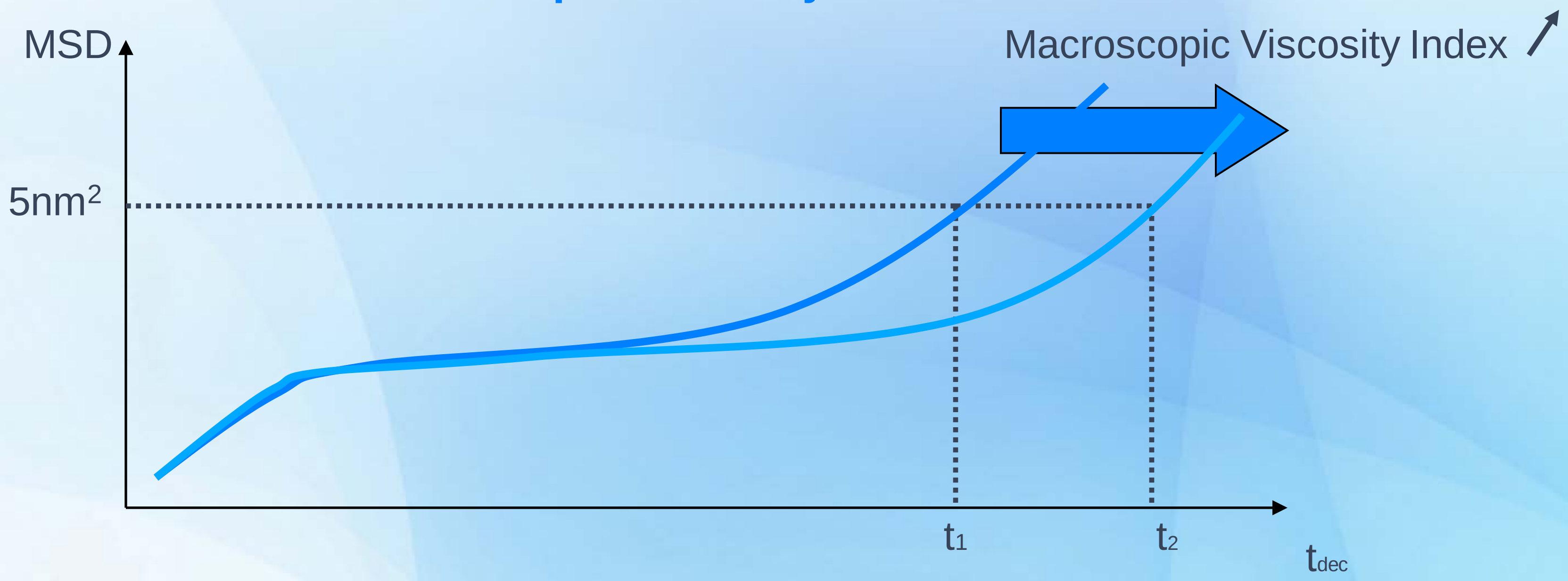


- Elasticity Index: How is the polymer matrix?
  ⇨ gelation, structure recovery, cross linking…

DATA TREATMENT

⇨ 3 key parameters

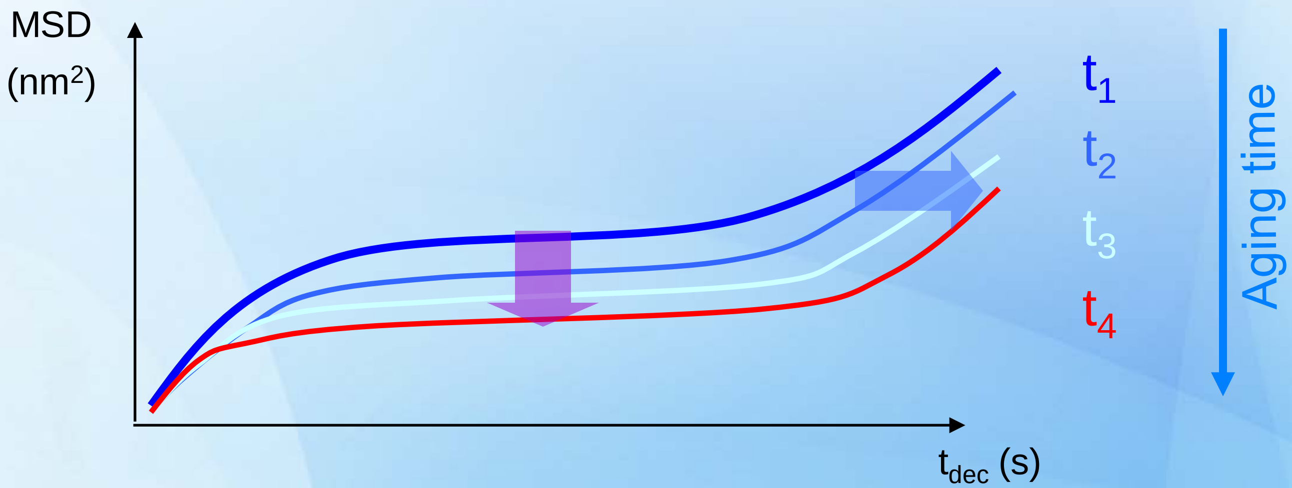
Macroscopic Viscosity Index

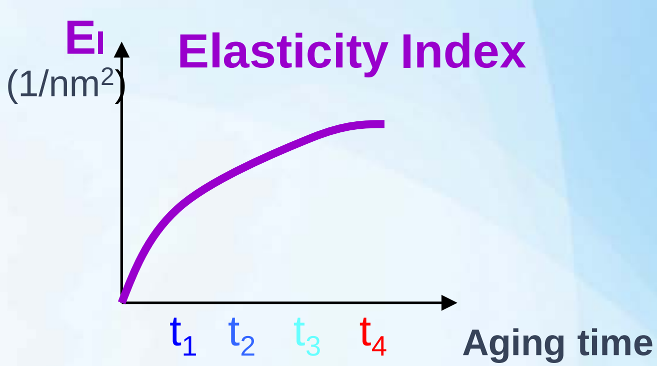


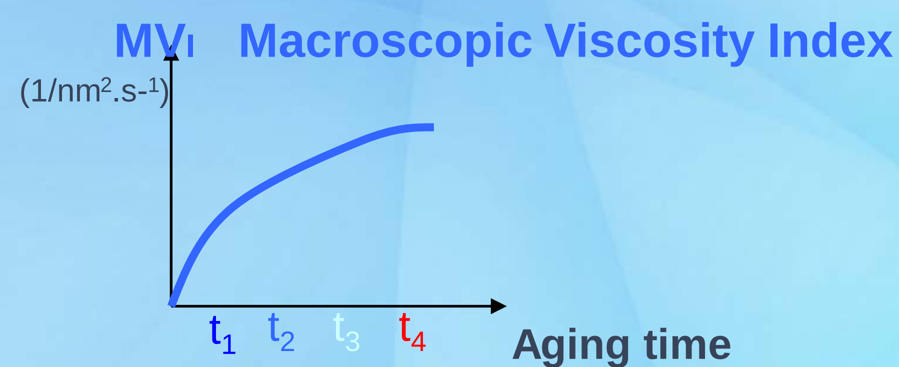
- Macroscopic viscosity: How does the sample flow?
  ⇨ flowability, stability, thickening power (texture) ….

DATA TREATMENT

⇨ Kinetic analysis



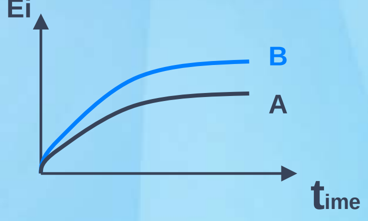




SPECIFICATIONS

- A unique tool to measure viscoelastic properties
  - Easily : 1 tube (4-20 ml) / 1 click
  - 6 measuring positions
  - Viscoelastic analysis
    - ⇨ Non contact
    - ⇨ No denaturation
    - ⇨ No stress
  - Simple parameters vs aging time
    - ⇨ Elasticity Index
    - ⇨ Viscoelastic balance
    - ⇨ Macroscopic Viscosity Index

⇨Easy **samples comparison**



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GELATION PROCESS
Experiment

R6+

⇨2 gelatins were prepared, using 2 grades of gelatin

- ✓Gelatin A (LOW level of gel)
- ✓Gelatin B (HIGH level of gel)

⇨Gelation process:

- ✓Products are first heated → homogenous liquid

(gelatin and water + introduction of TiO_2 in order to have scatterers)

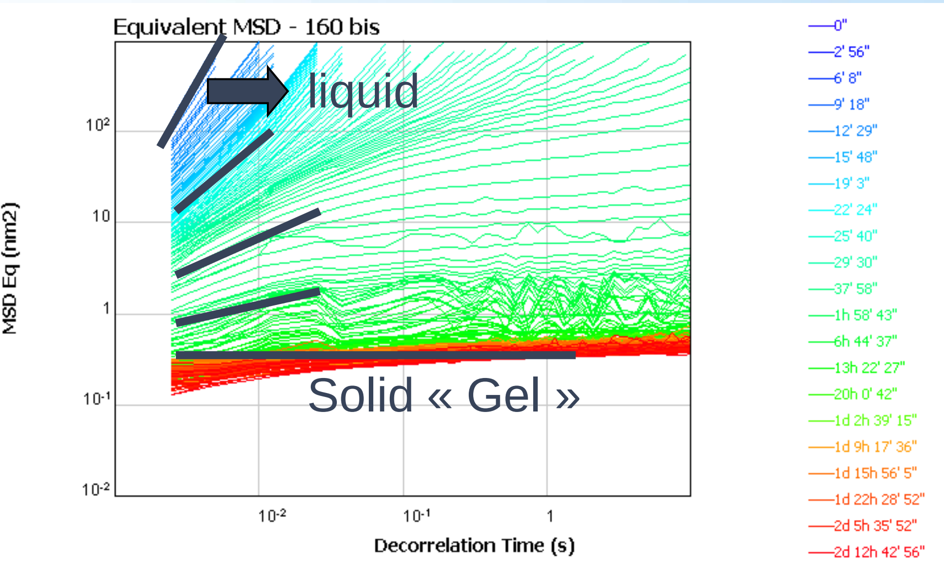
- ✓Sample is then cooled down → solidification

(liquid warm sample is introduced in RheoLaser, following the gelation process)

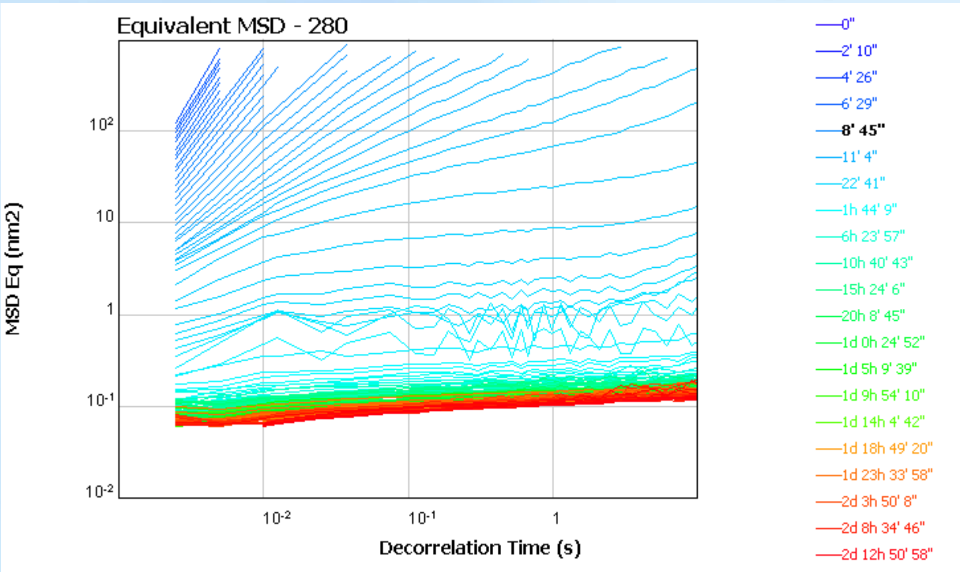
GELATION PROCESS

Study of 2 gelatins

Gelatin A

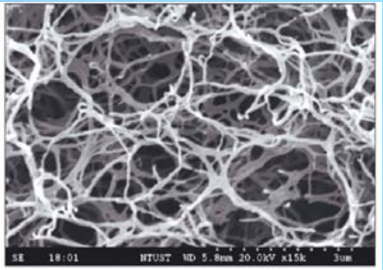


Gelatin B



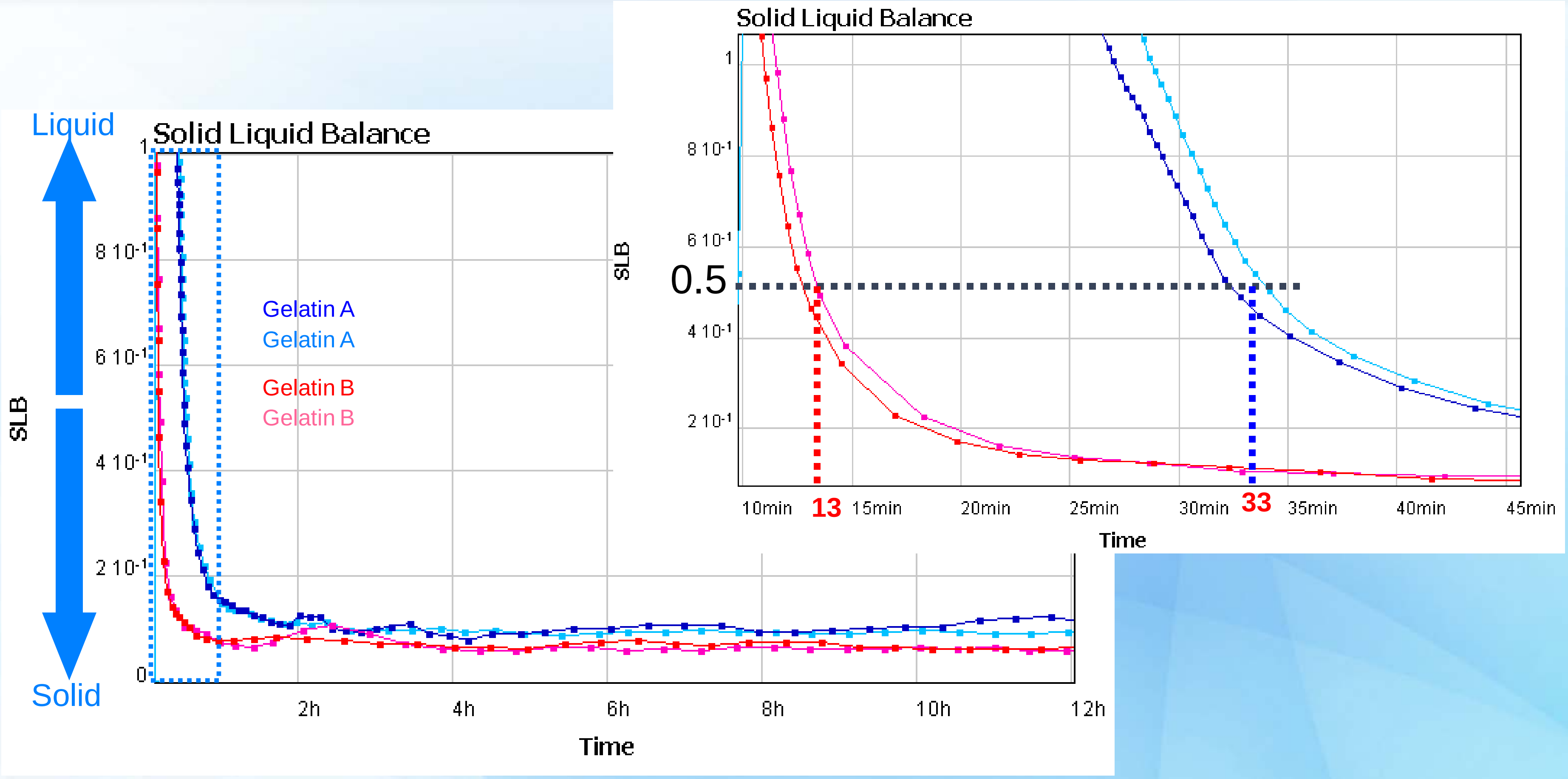
- At short time : liquid behavior
- At longer time: Solid behavior => Gel

Polymer network



GELATION PROCESS

Study of 2 gelatins

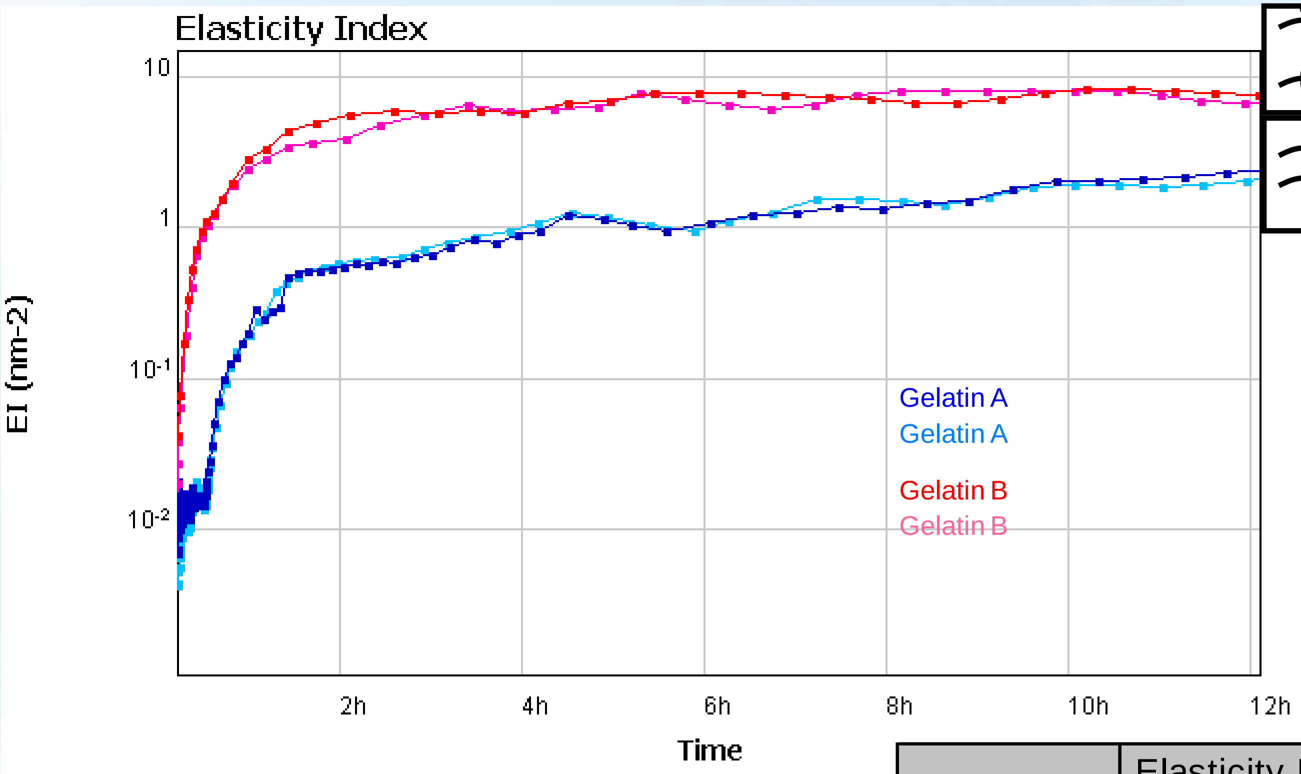


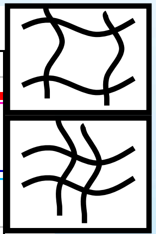
⇨ Gelatin B forms faster than A (at SLB = 0,5)

- Gel time B = 13 min
- Gel time A = 33 min

GELATION PROCESS

Study of 2 gelatins



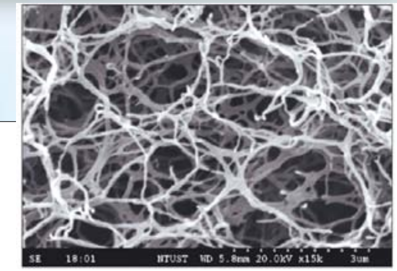


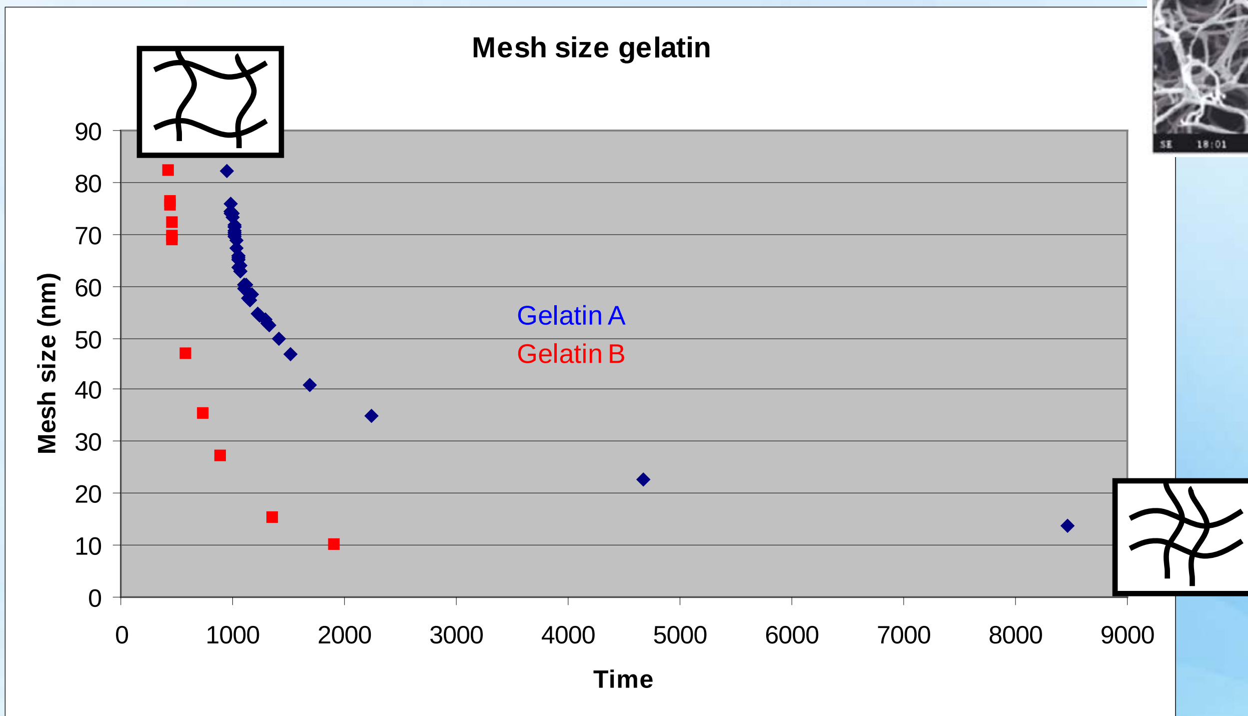
- ⇨ Gelatin B forms faster than A
- ⇨ Gelatin B forms a stronger gel than A

	Elasticity Index (nm-2)	Gel formation 80%
gelatin A	2,0	7h00
gelatin B	8,1	4h30

GELATION PROCESS
Study of 2 gelatins

Computation of Network Size





$G'^{p}_{\mu R} = k_B T/(\text{mesh size})^3$ ➡ G' ↗ → Mesh size ↘

⇨Mesh size decreases faster with a stronger gelatin (B stronger than A)

→ Stronger gel structure

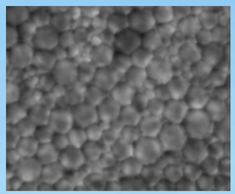
Emulsion and polymer :

Polymers are more and more added in emulsions in many industries like : Food, cosmetic, Pharmaceutical, bitumen, paint ……

WHY ?

2 mains reasons : end-use properties and cost

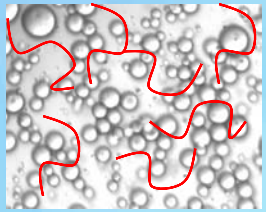
- Thickening effect
- Replace oil by water → light products , lower components cost
- Changing flow properties
- Modifying thixotropy
- Stabilizing effect…..



Concentrated emulsion (ϕ = 75%)

dilution →

Addition of polymer

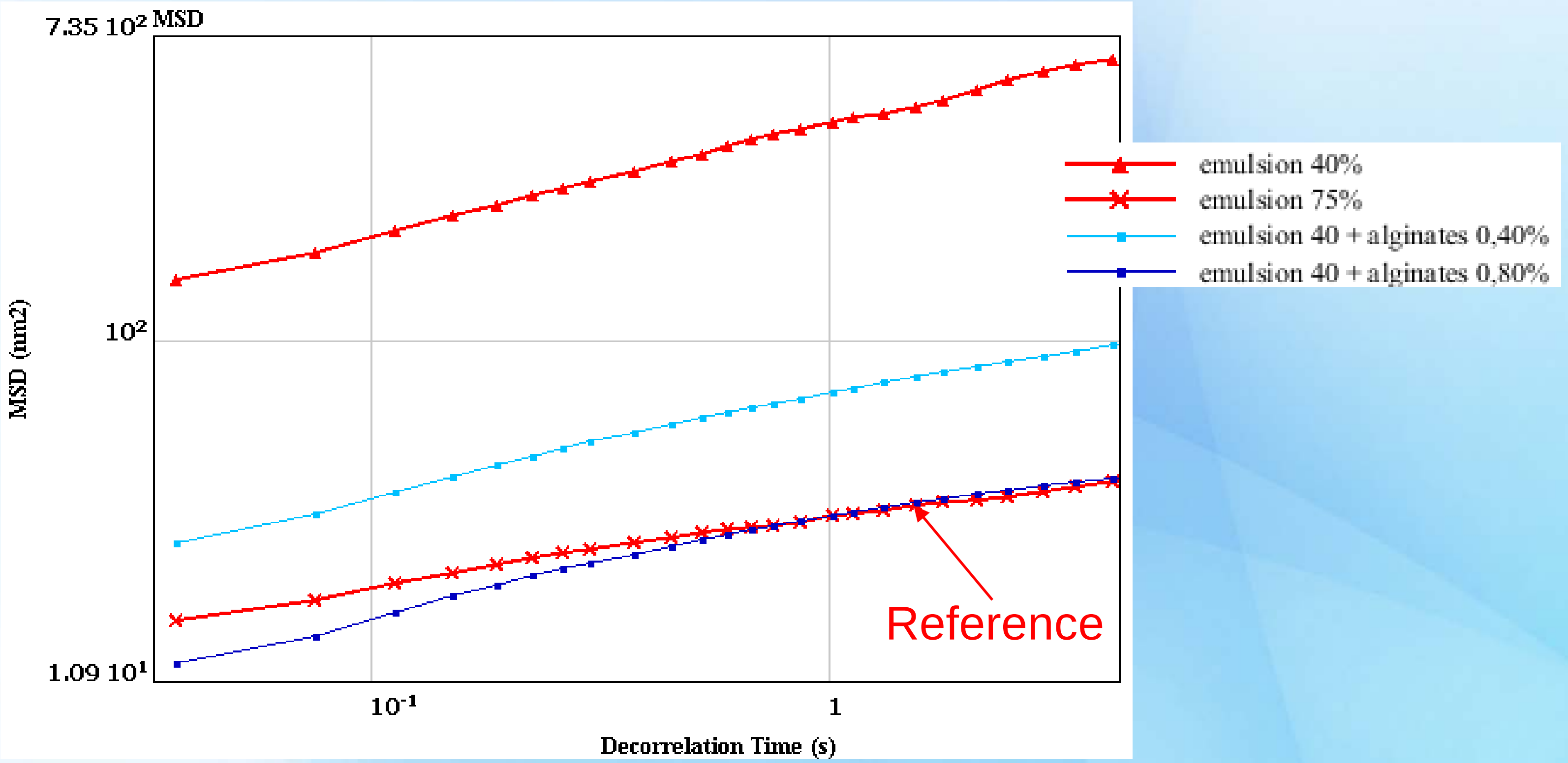


Diluted emulsion (ϕ = 40%)

EMULSION AND POLYMERS

Polymer concentration effect

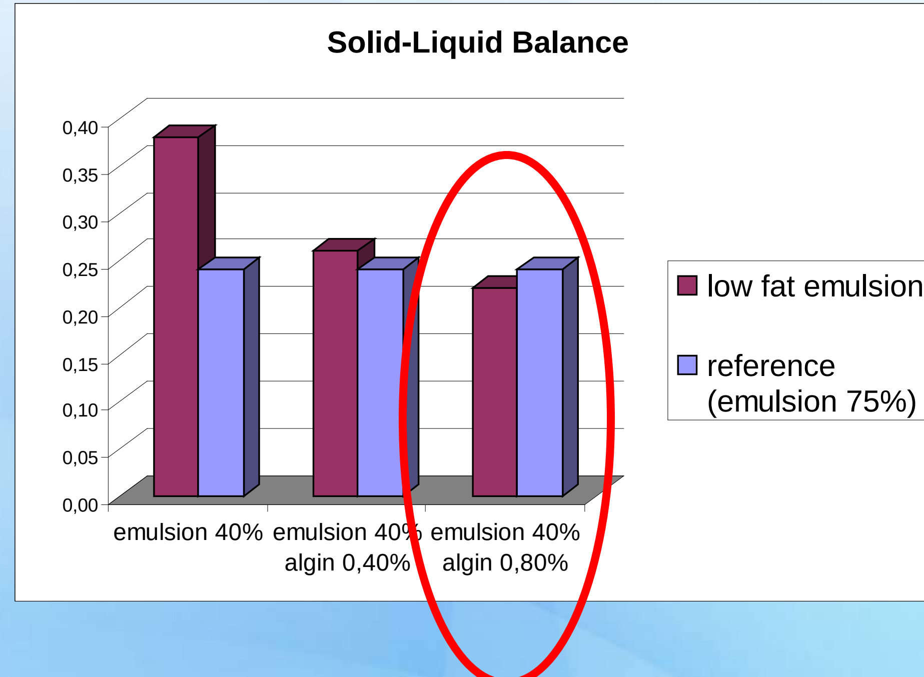
I work on emulsions, I want to add alginates to decrease oil concentration, which concentration I choose to keep similar end-use properties?



⇨ MSD curves evolve versus polymer concentration

EMULSION AND POLYMERS

Polymer concentration effect



⇨ Increase of polymer concentration → properties closer to reference emulsion (fat emulsion 75%)

I can dilute my emulsion from 75% to 40% and add 0,8% of alginates, my final product will have **same thickiness**, **same stiffness**, **same shape stability!!!**

CONCLUSIONS

- Rheolaser **compares** end use properties related to visco-elasticity
    - Easily
    - Results do not depend on the operator
        - ⇨ sampling in glass cell
- **At rest** thanks to a non contact optical measurement
- **Versus aging time** on the very same sample
- By monitoring the **evolution of simple parameters** like:
    - - Elasticity Index
    - - Macroscopic Viscosity index
    - - Solid/liquid balance