# Libération de solvant à partir de microgels sous sollicitations mécaniques

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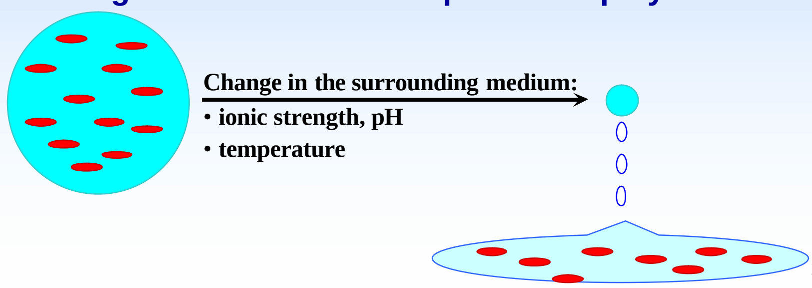
## Introduction

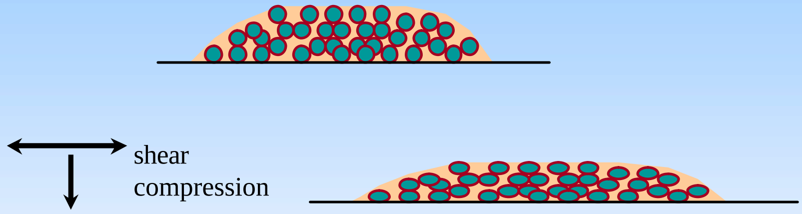
**Controlled release :**
- fixed quantity released
- regular in time
- enough long duration

« intelligent » or « stimuli-responsive » polymers



## Introduction

**Micro-particles (gels, capsules) in cosmetic, pharmacological and food applications, painting, etc:**




**Particle deformation**: influence the flow properties

**Solvent release**:
- positive if active compounds have to be released
- negative for processing

**Influence of mechanical stresses on a micro-particle: very important, but not well studied**

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## Introduction

### Objectives:

- **to study the behaviour (deformation) of a micro-particle (micro-gel, micro-capsule) under flow**
- **to investigate the ways of solvent release induced by shear**
- **to understand the phenomena observed**

***in situ* study using rheo-optical tools**

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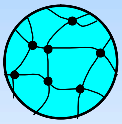
**Materials**
**gels**

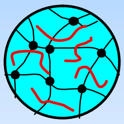
**Synthetic gel « Aqua Keep »:**
0.75 sodium polyacrylate/0.25 polyacrylic acide

Swollen in:

- water



- a linear polymer solution
(hydroxypropyl cellulose, polyvinylpyrrolidone, modified glucose, etc)



$d_0$ = 50 - 150 µm, swelling degree Q = 50 - 280 g/g

**Natural gel 1** (ENITIAA, Nantes):

k-carrageenan:
gelation of micro-droplets of 1.5% k-carrageenan+water+0.01 M $CaCl_2$

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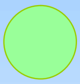
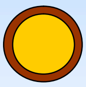
**Materials**
**gels**

**Natural gel 2** (Inotech, Suisse):



Alginate:
Obtained from 1% alginate+water solution

**Natural capsule** (DELSI, St.-Petersbourg, Russia):



Shell: chitosan+sodium alginate in the presence of $CaCl_2$ ,
Core: 2% sodium alginate solution

**Micro-particles were dispersed in a silicon oil and studied by rheo-optics**

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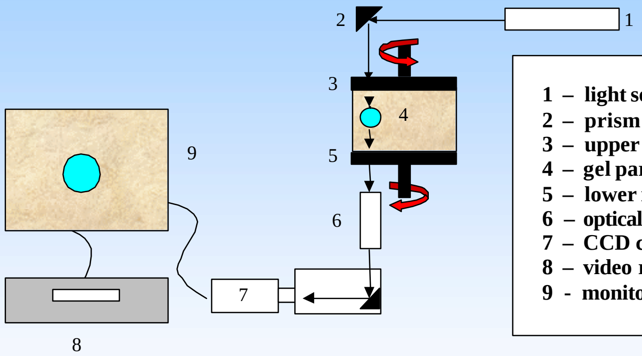
## Method
### rheo-optics

**Rheo-optical counter-rotating system**




1 – light source
2 – prism
3 – upper rotating plate
4 – gel particle in silicone oil
5 – lower rotating plate
6 – optical microscope
7 – CCD camera
8 – video recorder
9 - monitor

**We measure :**

- particle deformation L/D
- solvent release

} f (time, stress)

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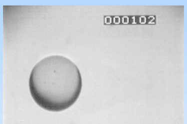
## Results
### visual observations

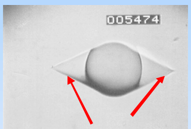
**Micro-gel deformation and solvent release:**

**reversible phenomena**

**a) synthetic gel swollen in water :**

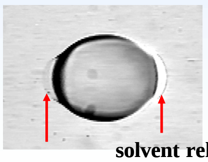



gel at rest




released water
shear stress 750 Pa

**b) synthetic gel swollen in a linear polymer solution** (1% aqueous hydroxypropyl cellulose)**:**



solvent released
shear stress ~1000 Pa

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## Results
### visual observations

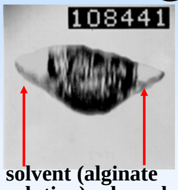
**c) natural gel 1 (k-carrageenan):**

gel at rest

**solvent released,**
shear stress 1300 Pa

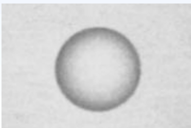
**d) chitosan-alginate capsule:**


capsule at rest

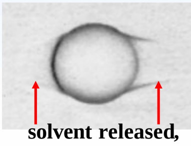



solvent (alginate solution) released,
stress ~ 600 Pa

**e) natural gel 2 (alginate):**



gel at rest



**solvent released,**
shear stress 1000 Pa



## Results
### visual observations

**Solvent detachment and dispersion in the matrix (silicon oil): irreversible phenomena**

**a) dispersion in the flow direction:**

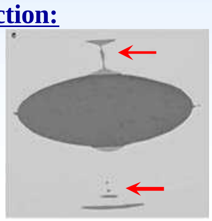
Synthetic gel swollen in a linear polymer solution (1% aqueous hydroxypropyl celulose):

**dispersion of solvent droplets in the silicon oil**

flow direction

**b) dispersion in the vorticity direction:**

Synthetic gel swollen in a linear polymer solution (10% aqueous hydroxypropyl cellulose):

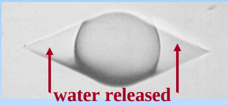


vorticity

flow direction

## Results
### gel deformation and solvent release in the flow direction

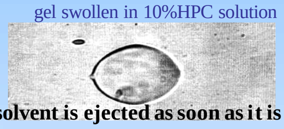
**a) gel swollen in water:**




- gel is *weakly* deformed
- large amount of solvent (water) stays around the gel
- solvent (water) is *never detached*

**b) gel swollen in a polymer solution:**

gel swollen in 10%HPC solution



**solvent is ejected as soon as it is released**

- gel is *strongly* deformed
- very small amount of solvent (polymer solution) stays around the gel
- solvent (polymer solution) is *detached* as soon as it is released and dispersed

**WHY ?**

**The interfacial tension solvent-matrix plays an important role**

**High interfacial tension –> solvent stays around the gel –> energy is dissipated in the solvent cones –> gel is not deformed**

**Lower interfacial tension –> solvent is easily detached and dispersed in the matrix–> gel is deformed**

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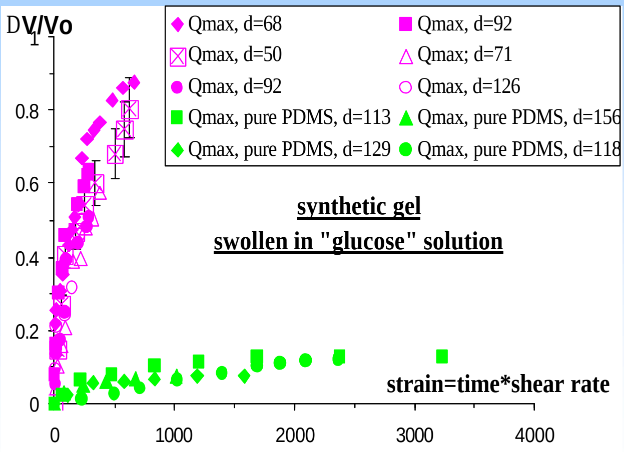
## Results and discussion
### solvent release and volume loss: influence of the interfacial tension

- a surfactant is added to the silicone oil
- fixed gel swelling degree
- fixed solvent




**The lower is the interfacial tension => the easier are the interfacial instabilities generated, leading to the break-up of the released solvent => a faster gel volume loss**

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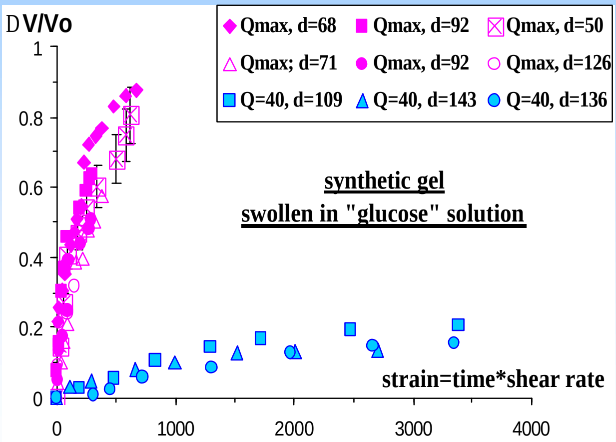
## Results and discussion
**solvent release and volume loss: influence of gel degree of swelling**

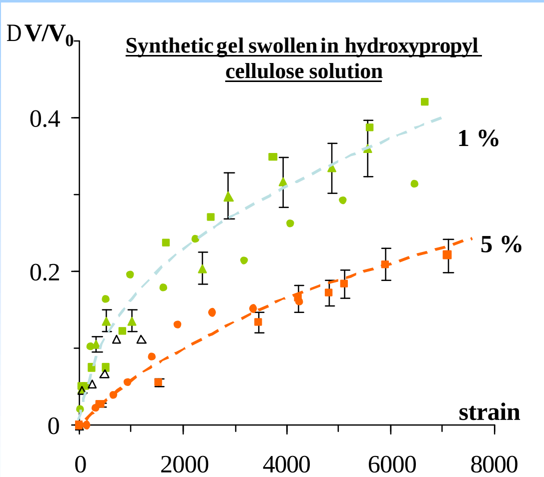
- gels swollen at maximum and < max
- fixed interfacial tension
- fixed solvent




The less gel is initially swollen, the higher is its elastic modulus => larger stresses are needed to release the same amount of solvent as compared with the gel swollen at equilibrium. 13

## Results and discussion
**solvent release and volume loss: influence of solvent viscosity**

- fixed solvent but of different concentrations
- fixed interfacial tension
- fixed degree of swelling




The higher is solvent viscosity, the higher stresses are requested to release the same amount of solvent. 14

## Results and discussion
### analysis of gel volume loss

**How to analyse gel volume loss?**

In drug release/controlled release:
- Fickian diffusion
- other diffusion-based approaches
- models for swellable carriers (Peppas, etc)

} not applicable

Weibull formula: $$m = 1 - exp\left( \frac{-(t - T_0)^b}{a} \right)$$

In the first approximation:

**Kinetics of volume loss:** **DV/Vo = 1 – exp(-k * strain)**

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## Results and discussion
### gel deformation in the flow direction

| | Solvent of synthetic gel; gel swollen at equilibrium except mentioned "40 g/g" | | | | | | | | | | Alginate gel |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | PVP | | HPC | | Modified glucose | | | | Water | | |
| | 1 % | 1 % Q = 40 g/g | 1 % | 5 % | 1 % | 1 % Q = 40 g/g | 1 % without surfactant | 5 % | $Q_{eq}$ | $Q_{eq}$ without surfactant | |
| Interfacial tension oil/solvent, mN/m | 2 | 2 | 3 | 3 | 2 | 2 | 9 | 2 | 2 | 17 | 17 |
| Solvent viscosity, Pa s | 1.4 $10^{-3}$ | 1.4 $10^{-3}$ | 1.8 $10^{-3}$ | 7 $10^{-3}$ | 1.5 $10^{-3}$ | 1.5 $10^{-3}$ | 1.5 $10^{-3}$ | 1.9 $10^{-3}$ | 1.0 $10^{-3}$ | 1.0 $10^{-3}$ | 1.0 $10^{-3}$ |
| k $10^{-5}$ | 120 | 14 | 15 | 7 | 320 | 11.5 | 8.5 | 110 | 14 | 0 | 6 |

**Quick release - high *k* values:**
- low interfacial tension
- low solvent viscosity
- high gel swelling degree

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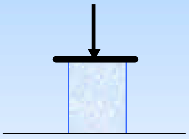
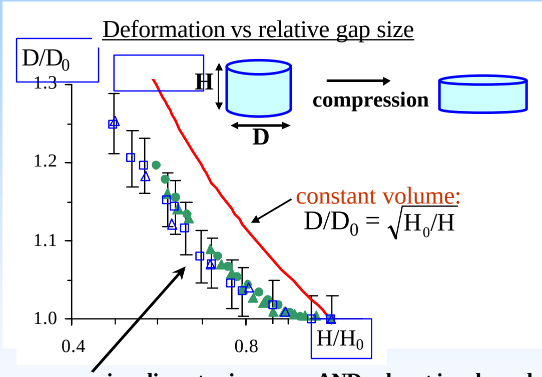
## Results and discussion
### gel behaviour under compression

**Solvent release: is it a general reaction to a mechanical stress?**

<u>A gel block under compression:</u>



- gel in block in the air;
- large deformations




**under compression diameter increases AND solvent is released**

- **loss of volume**
- **no pressure threshold**

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## Conclusions

**Under shear**:

a) *gel deforms*;
b) *solvent can be released* from the gel in the *flow* and *vorticity* directions
c) *solvent can be permanently detached* from the gel and dispersed in the matrix;
d) gel volume loss (amount of solvent dispersed in the matrix) depends on the interfacial tension, gel swelling degree and solvent viscosity

These phenomena have a general character (different types of micro-gels and capsules

Prospective for controlled release applications

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