



**HAL**  
open science

## Multiscale investigation of viscoelastic properties of biopolymer matrices

Alberto Varela Feijoo, Philippe Djemia, Tetsuharu Narita, Frédéric Pignon,  
Alain Ponton

► **To cite this version:**

Alberto Varela Feijoo, Philippe Djemia, Tetsuharu Narita, Frédéric Pignon, Alain Ponton. Multiscale investigation of viscoelastic properties of biopolymer matrices. 54<sup>ème</sup> congrès annuel du Groupe Français de Rhéologie, Oct 2019, Montpellier, France. hal-03049037

**HAL Id: hal-03049037**

**<https://hal.science/hal-03049037v1>**

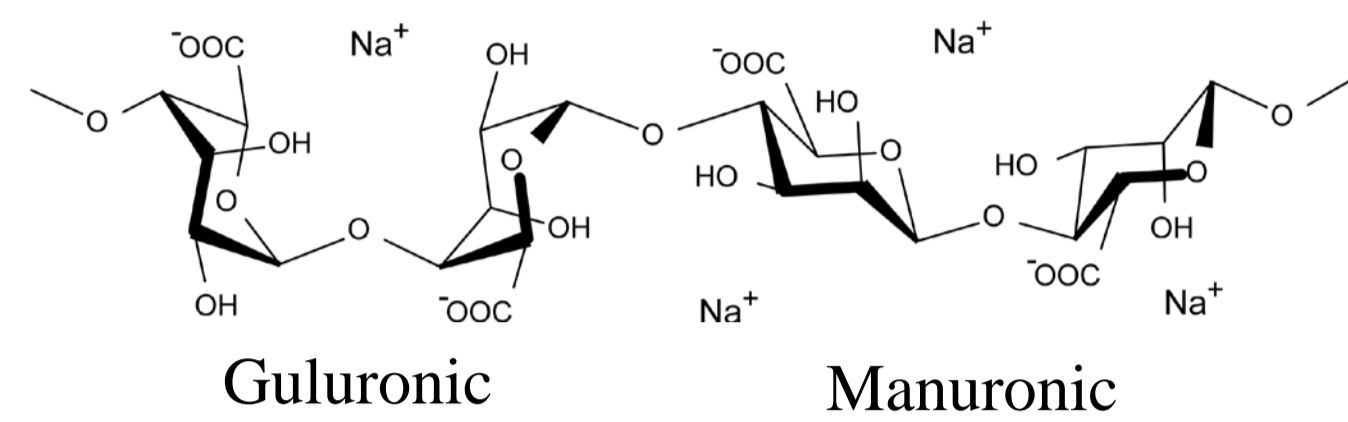
Submitted on 9 Dec 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

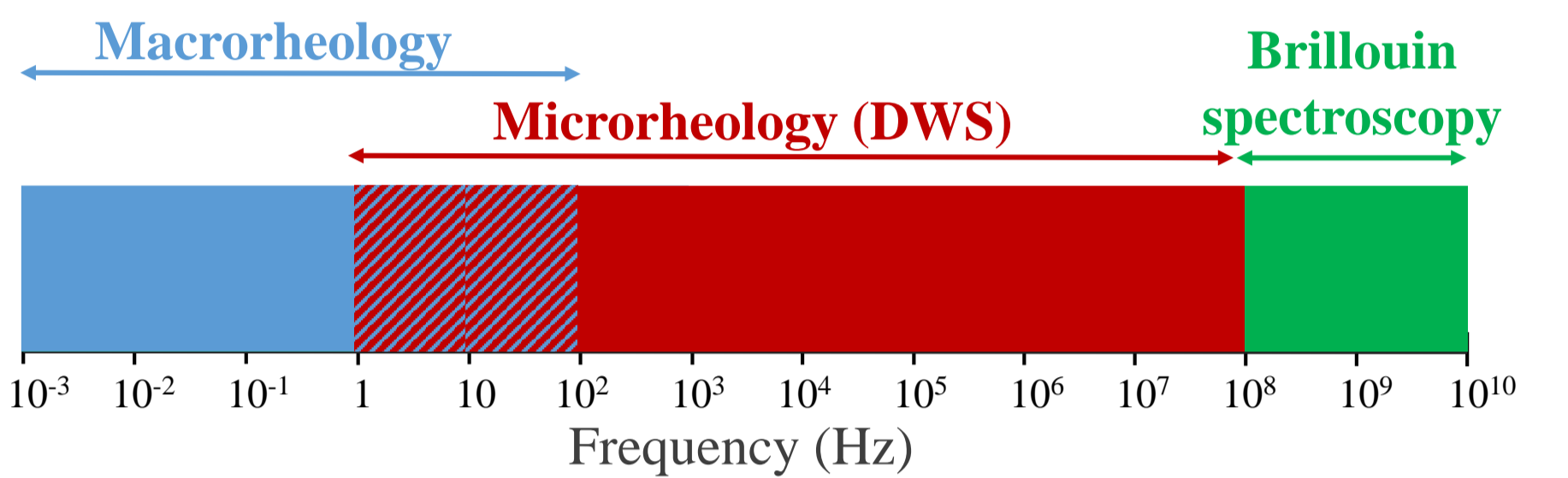
## Objectives

- How to study at different scales the viscoelastic and structural properties of biopolymer networks to be used as matrix for biocompatible nanocomposites?

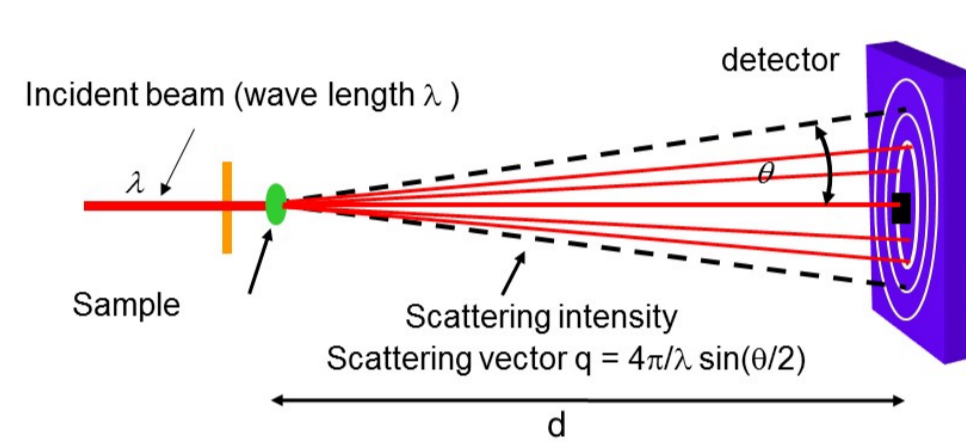


Entangled aqueous solutions of sodium alginate

Combining four complementary experimental methods



Structural characterization



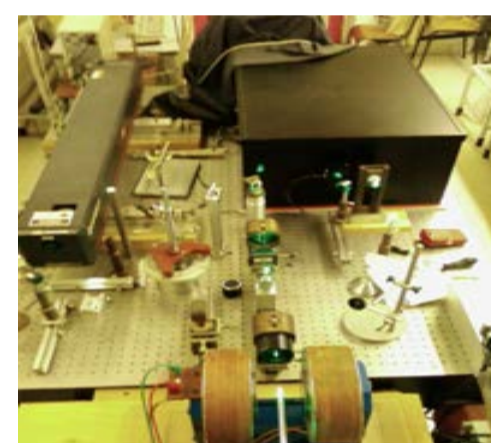
Small angle X-ray scattering



Macro-rheology



Diffusing-wave spectroscopy



Brillouin spectroscopy

## Material and methods

### Macro-rheology (0,01Hz-100Hz)

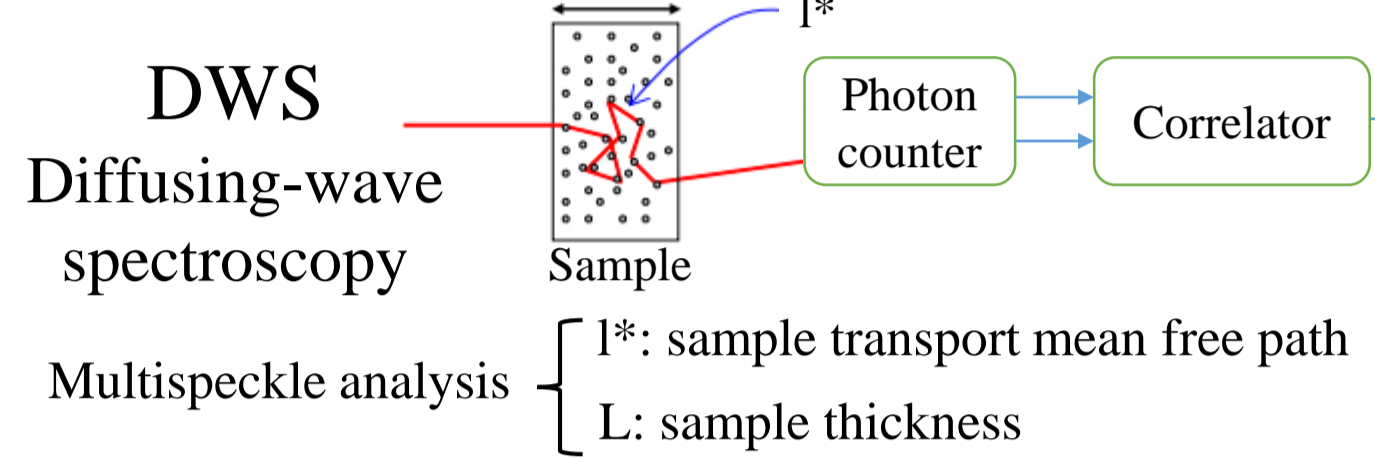
Cone-and-plate  
Material: titanium  
 $\varnothing = 60$  mm  
 $\theta = 1^\circ$   
Gap = 51.2  $\mu$ m

### Small angle X-ray scattering (SAXS)

European Synchrotron Radiation Facility (ESRF, Grenoble, France)  
 $\lambda_{RX} = 0.1$  nm, sample-to-detector distances between 2 m and 31 m.  
 $2.10^{-3} \text{ nm}^{-1} \leq q \leq 3.5 \text{ nm}^{-1}$ ,  $1.8 \text{ nm} \leq \lambda \leq 3141 \text{ nm}$

### Microrheology – Diffusing-wave spectroscopy (DWS) (1Hz-1MHz)

- Determination of the mean square displacement of microparticles undergoing a Brownian motion in viscoelastic media.



- Multispeckle analysis:  $l^*$ : sample transport mean free path,  $L$ : sample thickness
- Polystyrene spherical microparticles Alkyl-OH surface ( $\phi = 500$  nm, conc. = 1%)

### Determination of viscoelastic properties

$$\alpha = \frac{\partial \ln(\Delta r^2(t))}{\partial \ln t}$$

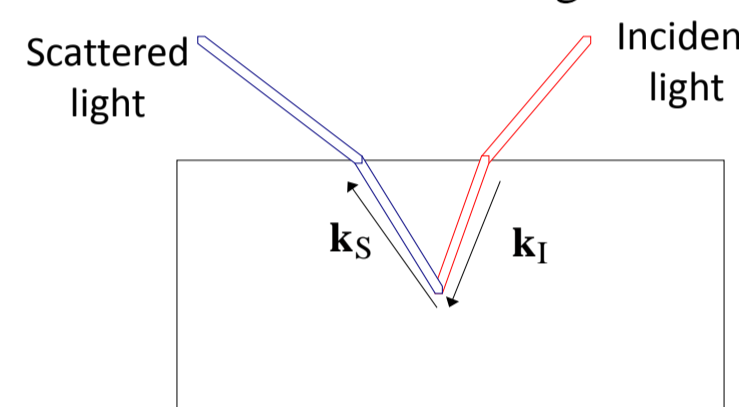
$$G^*(\omega) = \frac{k_B T}{\pi R(\Delta r^2(1/\omega))\Gamma[1 + \alpha(\omega)]}$$

Elastic moduli:  $G'(\omega) = G^*(\omega) \cdot \cos\left(\frac{\pi\alpha(\omega)}{2}\right)$

Viscous moduli:  $G''(\omega) = G^*(\omega) \cdot \sin\left(\frac{\pi\alpha(\omega)}{2}\right)$

### Brillouin spectroscopy (GHz)

- Brillouin scattering: exchange of energy with thermally driven acoustic waves, leading to a frequency shift between incident and scattered light.



### Determination of viscoelastic properties

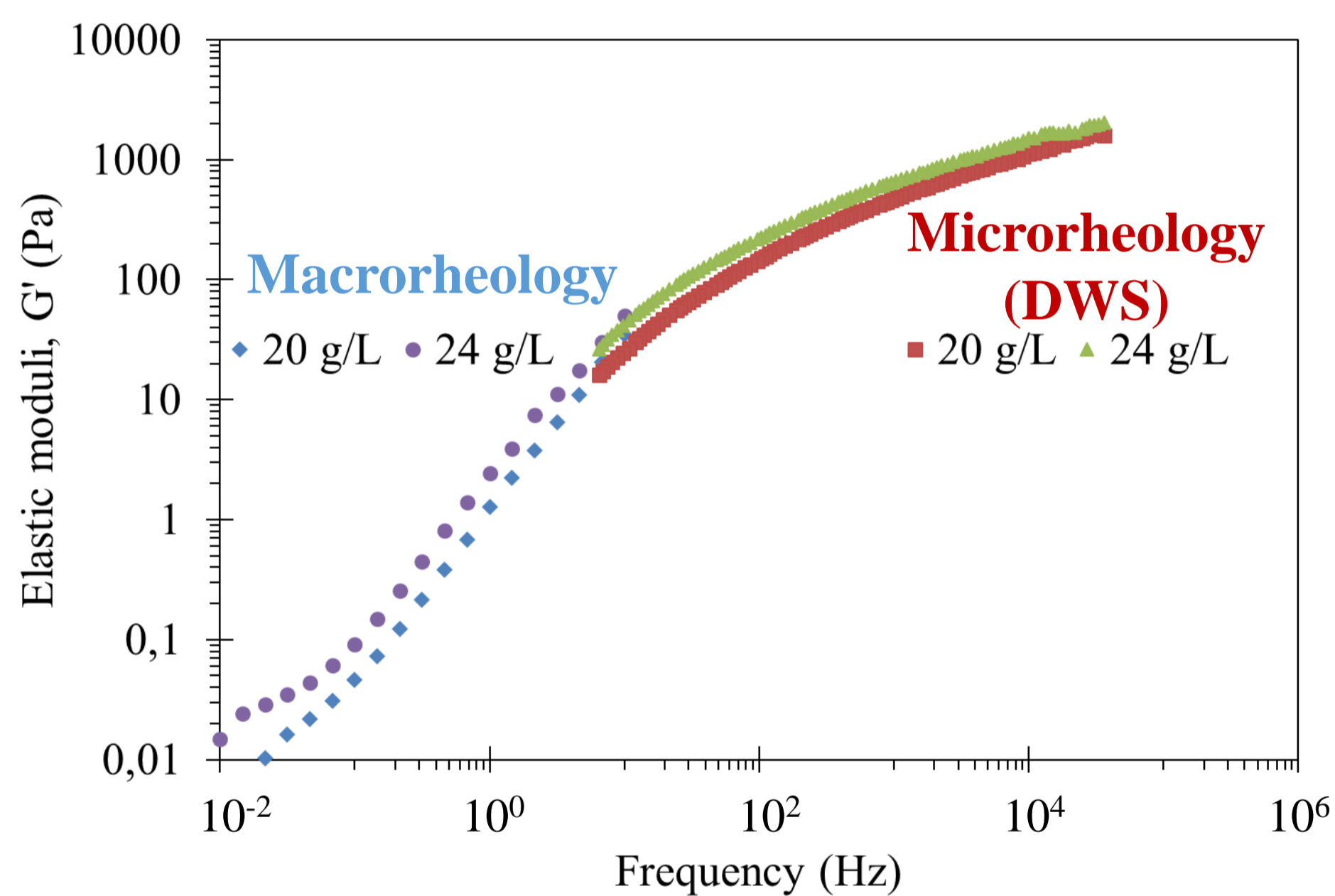
- Elastic constant:  $C_{11}$  (GPa)

$$v_L = \frac{2 \cdot \pi \cdot f_L}{k} \quad k = \frac{4 \cdot \pi \cdot n}{\lambda_L} \quad C_{11} = \rho \cdot v_L^2$$

Stokes ( $W_0 - W \cdot K_0 \cdot K$ )  
Anti-Stokes ( $W_0 + W \cdot K_0 \cdot K$ )  
Viscosity:  $\eta$  (Pa.s)

$$\eta = \frac{\rho \cdot \Gamma}{k^2}$$

### Macro/micro rheology



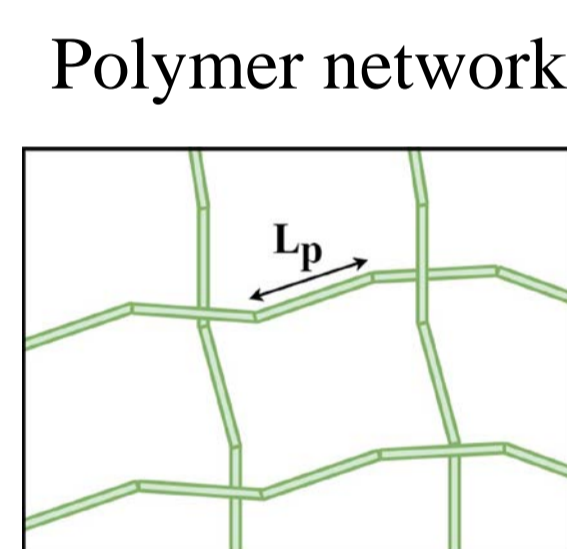
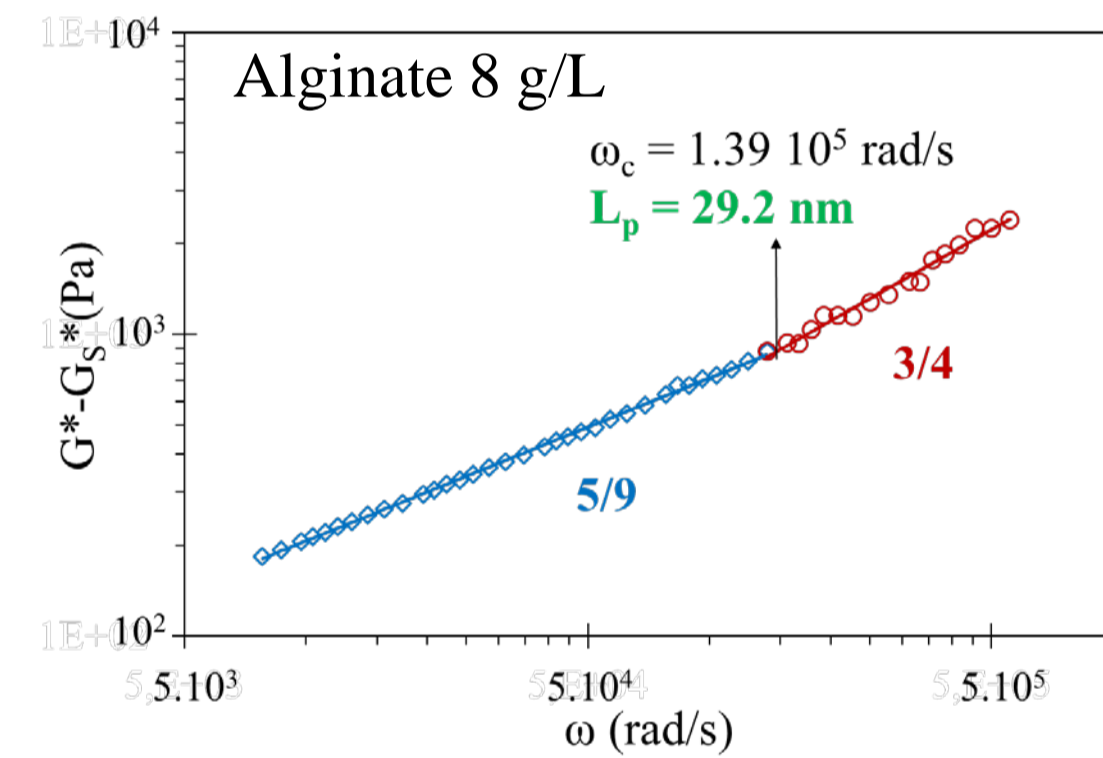
- Good agreement between the results of macro and micro rheology.
- Continuous study of the viscoelastic properties between  $10^{-2}$ - $10^5$  Hz.

### Bending mode and Zimm-Rouse mode (DWS)

#### High frequency single chain dynamics

$$G^* \sim \omega^{3/4} \text{ Bending mode (high } \omega) \quad (\omega = 2 \pi f)$$

$$G^* \sim \omega^{5/9} \text{ Zimm-Rouse mode (lower } \omega)$$



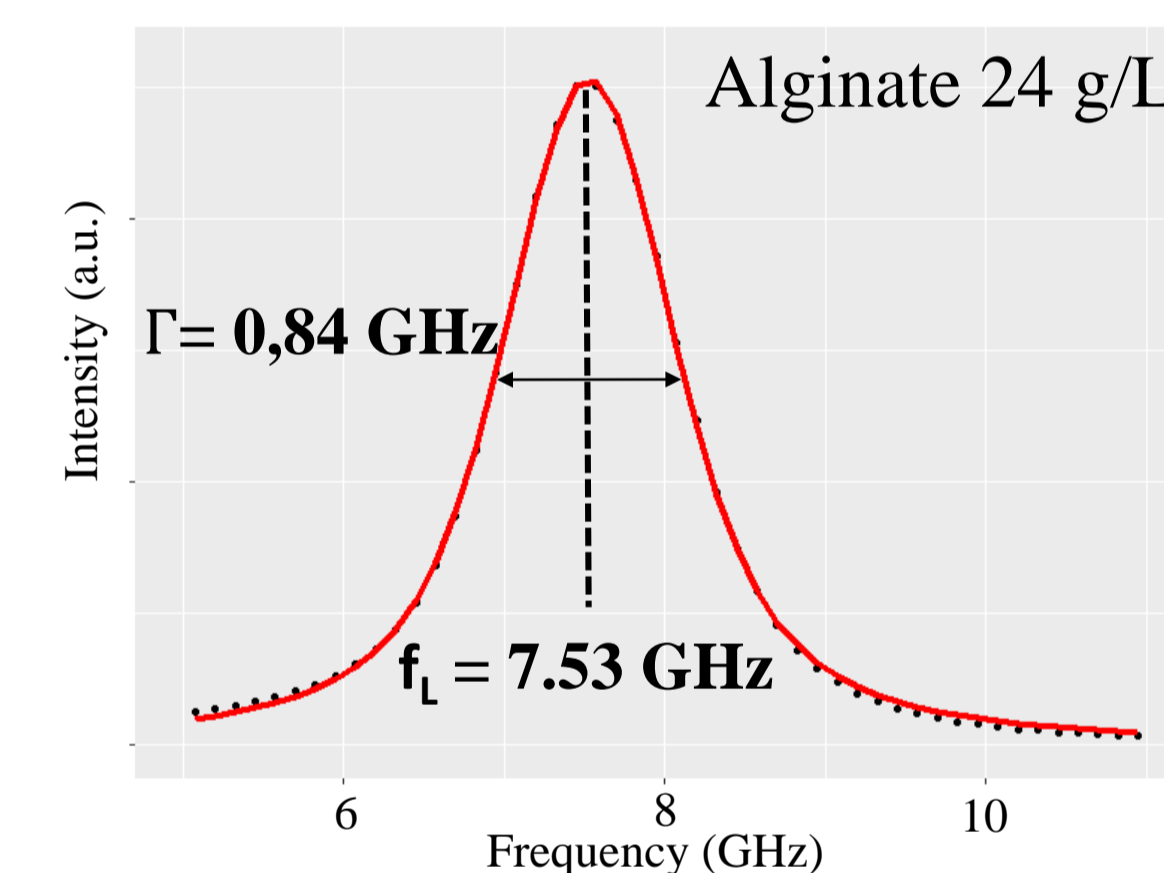
C alginate (g/L)	$\omega_c$ (rad/s)	$L_p$ (nm)
2	$6.25 \cdot 10^4$	38.1
4	$8.93 \cdot 10^4$	33.8
8	$1.39 \cdot 10^5$	29.2
14	$1.92 \cdot 10^5$	26.2

Persistence length,  $L_p$

$$\omega_c = \frac{k_B T}{8 \eta_s L_p^3}$$

### Brillouin spectroscopy (GHz)

- Obtention of Brillouin spectra of scattered light (Stokes and anti-Stokes peaks)
- Fitting of the peaks with a Voigt function to  $f_L$  (and  $C_{11}$ ) and  $\Gamma$  (and  $\eta$ )
- Subtraction of device linewidth: Gaussian  $\sigma = 0.314$  GHz



$$C_{11} = x_w \cdot M_w + (1 - x_w) M_{alg}$$

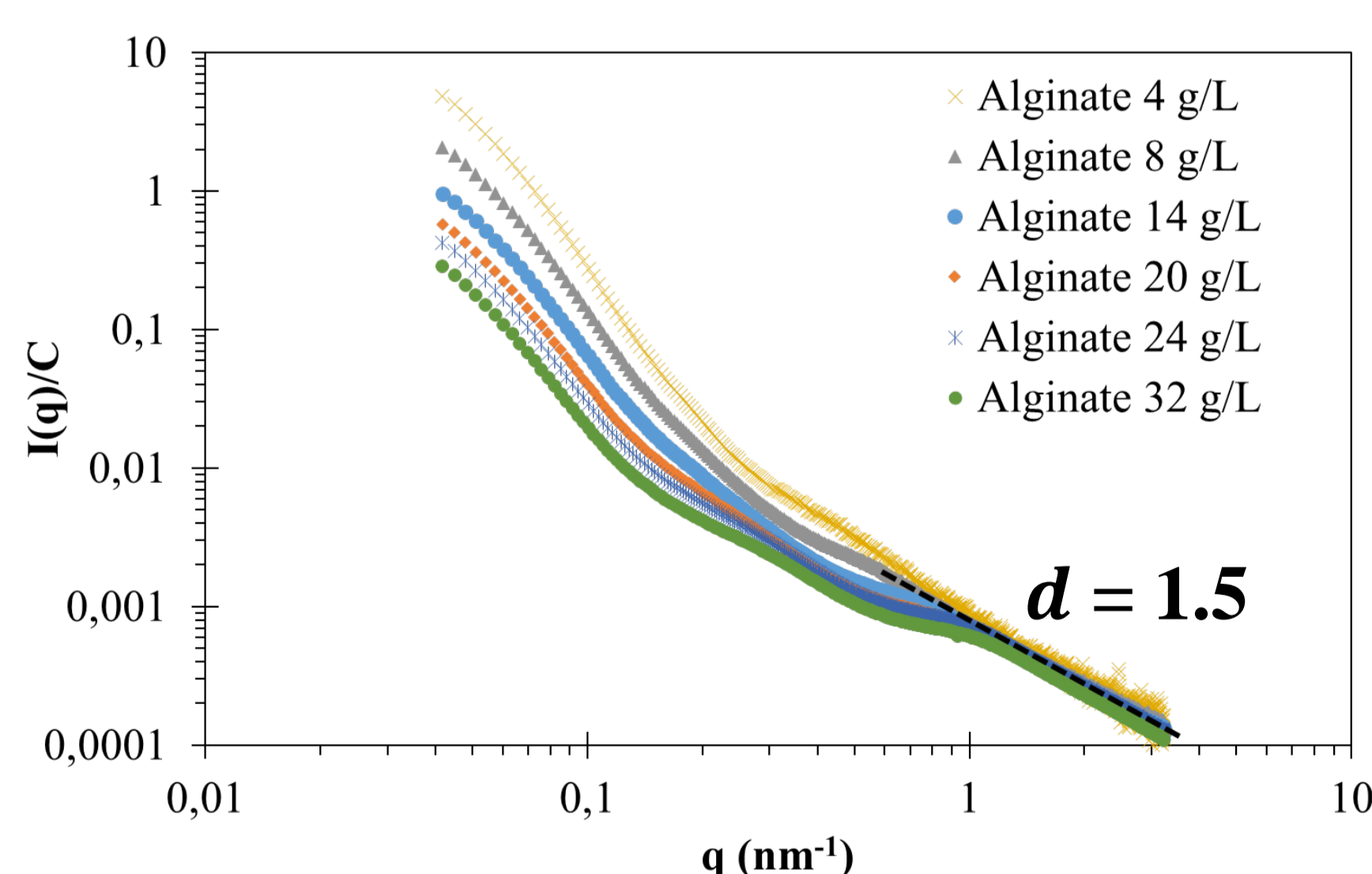
- $x_w$ : mass fraction of water
- $C_{11}$ : elastic constant determined for alginate solution at different concentrations
- $M_w$ : elastic constant determined for water
- $M_{alg}$ : "intrinsic" elastic constant of alginate

$$M_{alg} = 4.95 \text{ Pa}$$

C alginate (g/L)	$f_L$ (GHz)	$\Gamma$ (GHz)	Volumic mass (kg/m <sup>3</sup> )	Refractive index	$v_L$ (m/s)	K (nm <sup>-1</sup> )	$C_{11}$ (GPa)	$\eta$ (mPa.s)
24	7.527	0.842	1011	1.335	3000	0.0315	2.275	0.857

## Structure (SAXS)

### Scattered intensity per monomer unit



$$\frac{I}{C} \propto q^{-d} \text{ at high } q \text{ values}$$

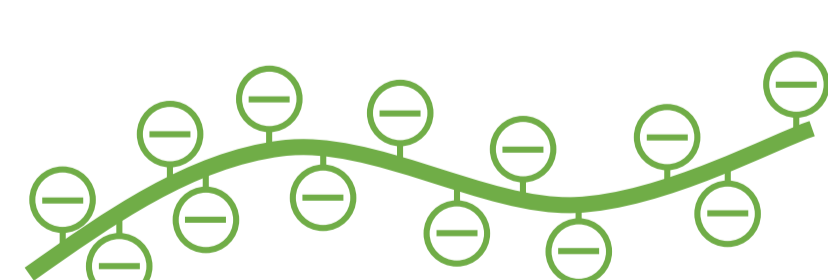
d: fractal dimension

$d = 5/3$



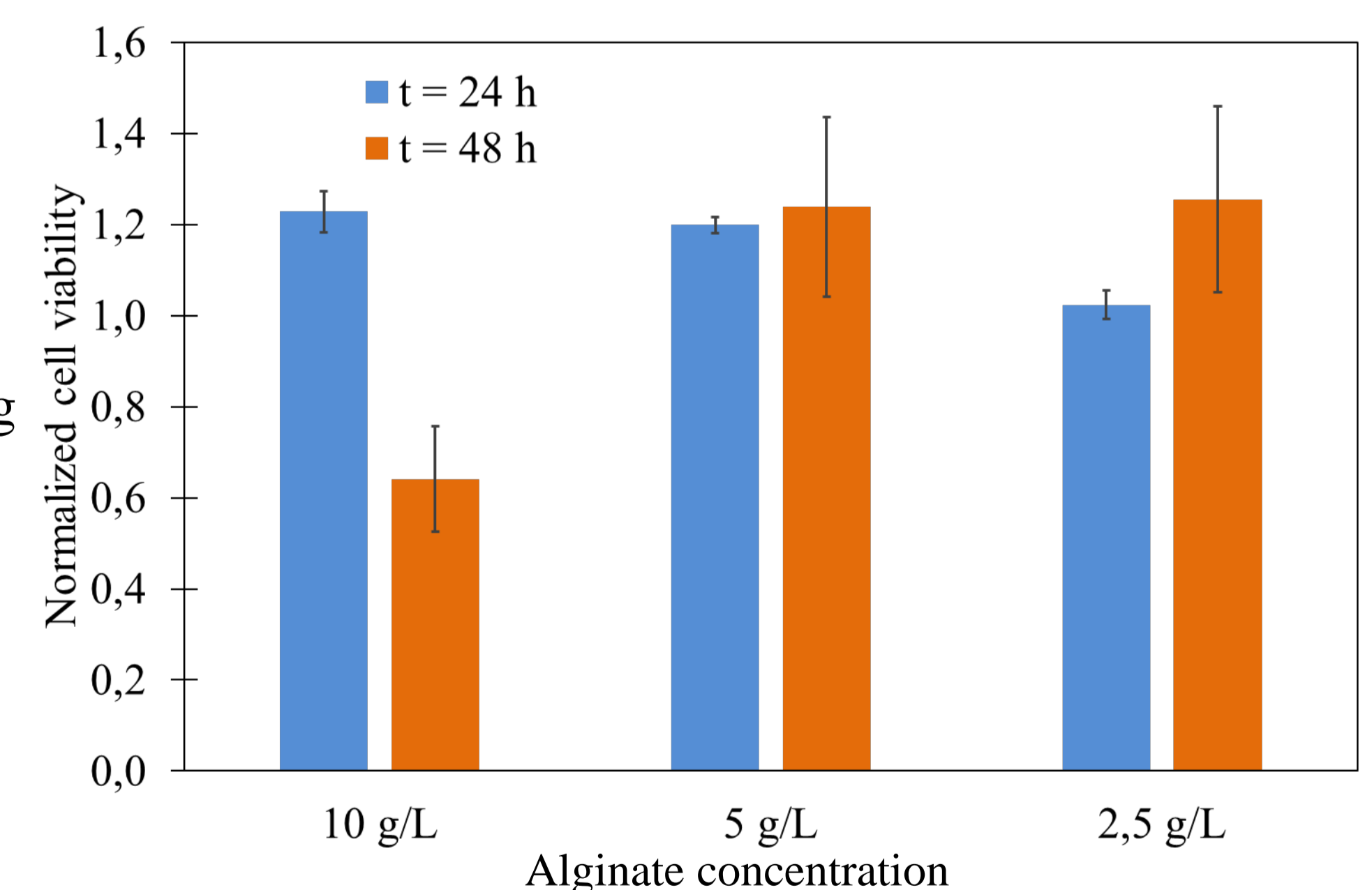
Random coil conformation  
Neutral polymer at good solvent

$d = 1$



Rodlike chains  
Electrostatic repulsion

- Type of cells: fibroblast NIH 3T3
  - Concentration: 25.000 cells/well
- Colorimetric assay for cell viability using Tetrazolium salt (WST-1) reduced by living cells to form formazan
- Number of metabolically active cells  $\propto$  Formed formazan dye determined by absorbance



- No cytotoxicity for concentrations of alginate 5 and 2.5 g/L at 24 or 48 h.
- No cytotoxicity for concentrations of alginate of 10 g/L at 24 h.
- Low cytotoxicity for alginate concentration of 10 g/L at 48 h.

## Conclusions

- Results obtained by macro-rheology and Diffusing-Wave Spectroscopy (DWS) in a reasonably good agreement to investigate viscoelastic properties of aqueous solutions of sodium alginate over 7 frequency decades ( $10^{-2}$ - $10^5$  Hz) with a transition from viscous to elastic behavior as the frequency is increased.
- The complementary results of Brillouin spectroscopy confirms a viscoelastic behaviour at  $10^9$  Hz range dominated by an elastic behavior.
- Estimation of a fractal dimension from SAXS measurements
- Aqueous solutions of sodium alginate present a good biocompatibility as confirmed by cell viability assay