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Multiscale investigation of viscoelastic properties of biopolymer matrices

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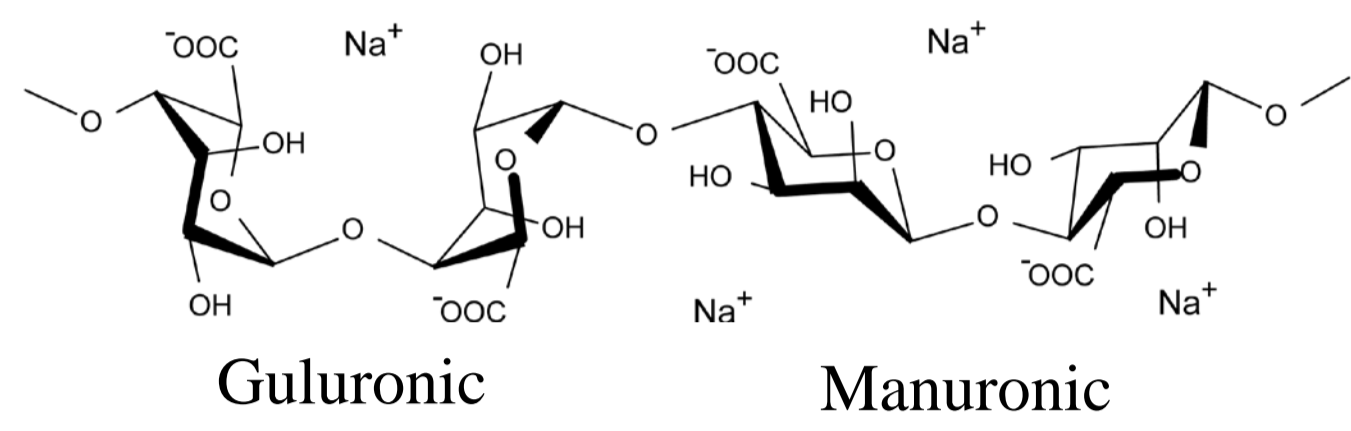
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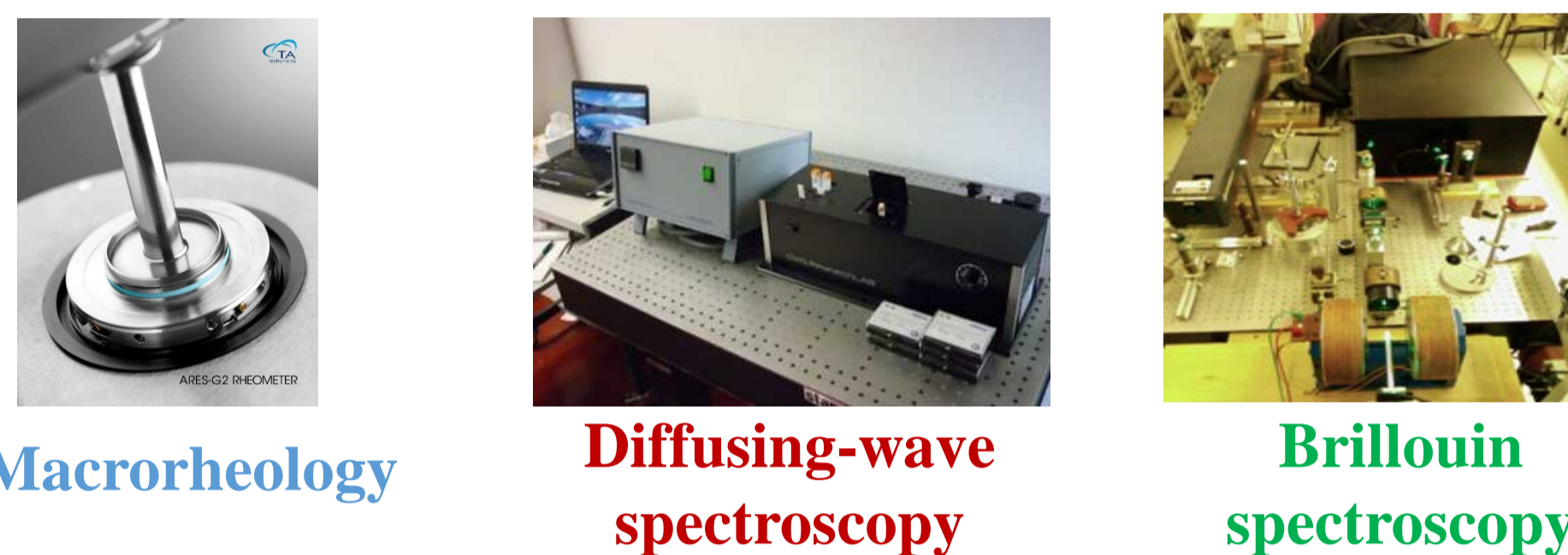
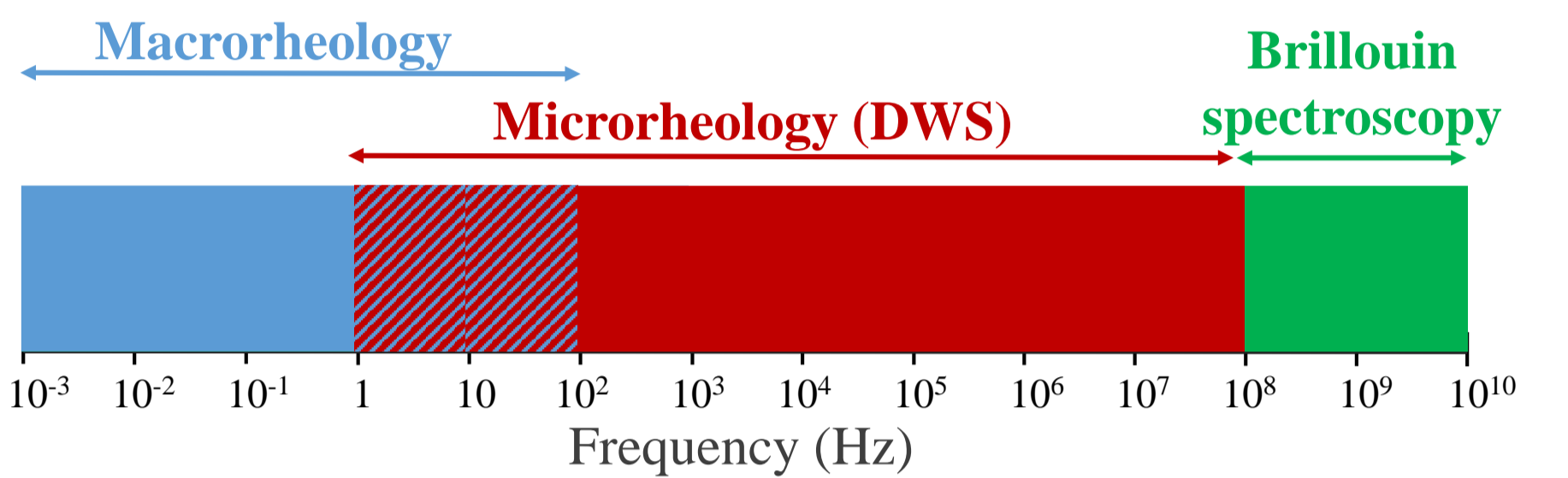
Objectives

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

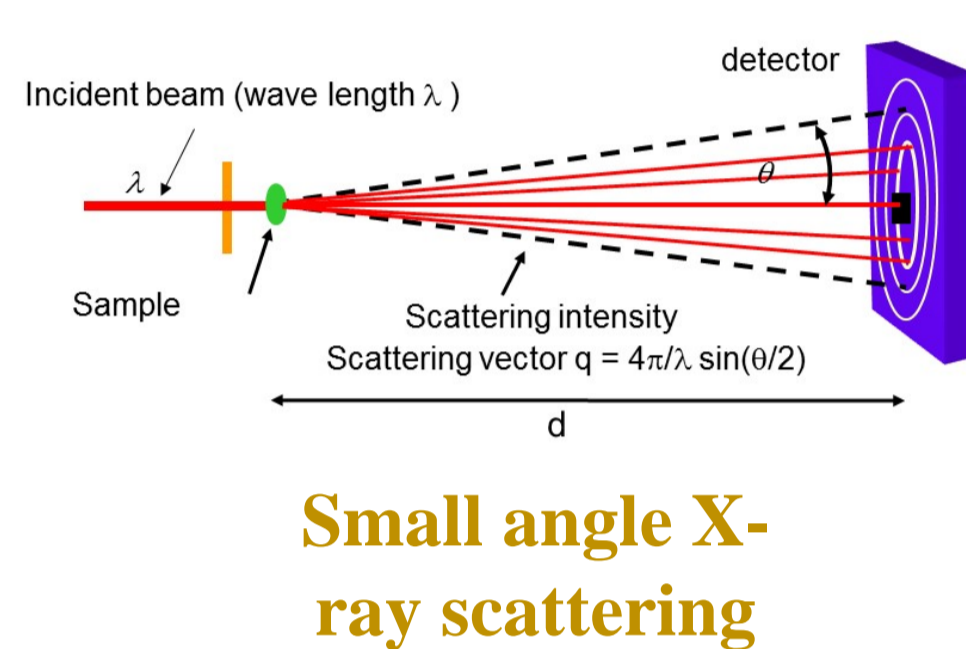


Entangled aqueous solutions of sodium alginate

Combining four complementary experimental methods



Structural characterization



Material and methods

Macrorheology (0,01Hz-100Hz)

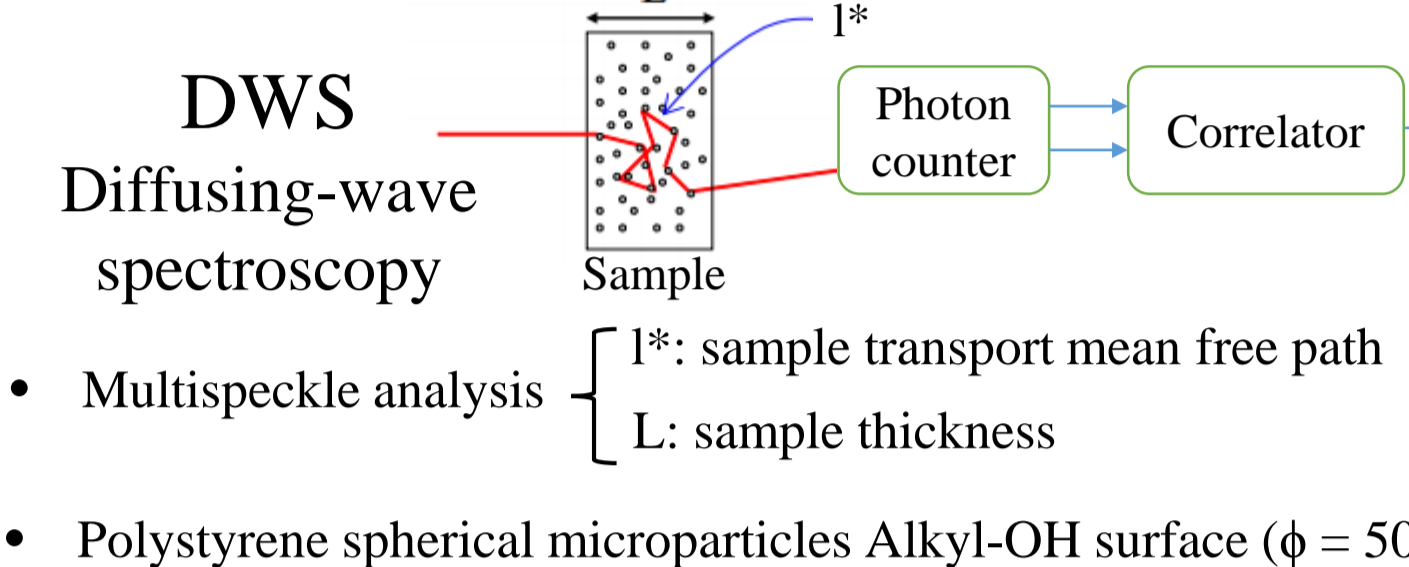
Cone-and-plate
Material: titanium
 $\varnothing = 60$ mm
 $\theta = 1^\circ$
Gap = 51.2 μ m

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.



Determination of viscoelastic properties

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

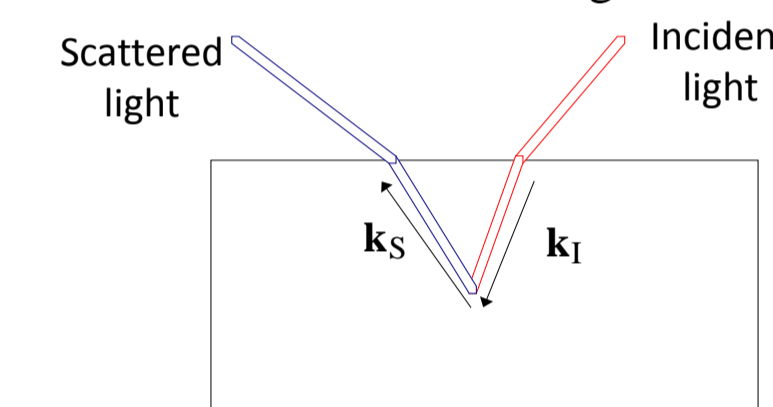
$$G^*(\omega) = \frac{k_B T}{\pi R(\Delta r^2(1/\omega))\Gamma[1 + \alpha(\omega)]}$$

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.



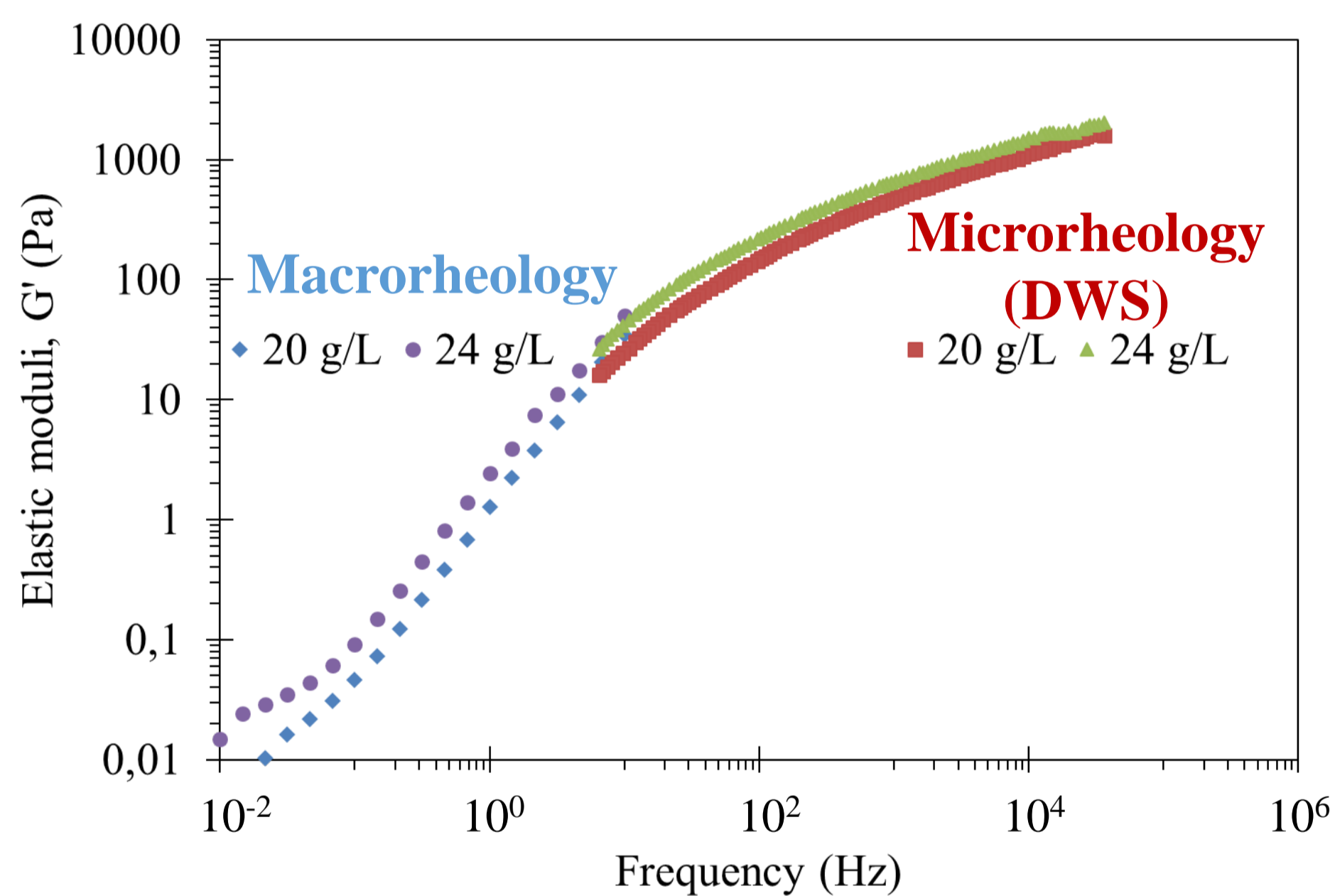
Determination of viscoelastic properties

- 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 ($W_0 - W_s \cdot K$)
Anti-Stokes ($W_0 + W_s \cdot K$)

Macro/micro rheology



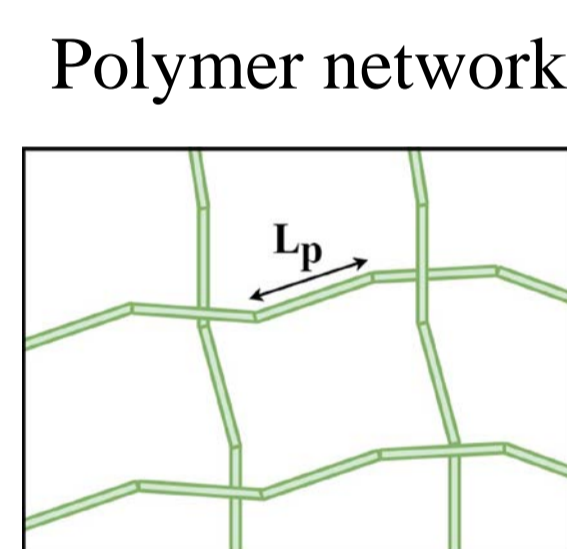
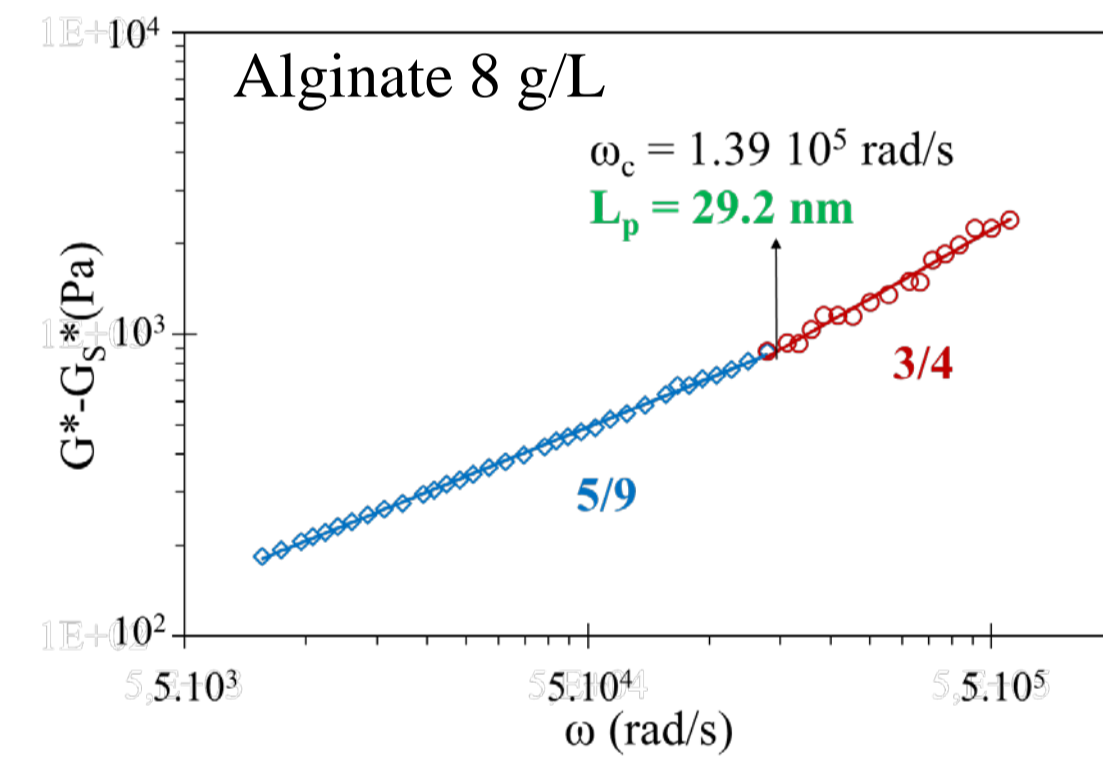
- Good agreement between the results of macro and micro rheology.
- Continuous study of the viscoelastic properties between 10^{-2} - 10^5 Hz.

Bending mode and Zimm-Rouse mode (DWS)

High frequency single chain dynamics

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

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



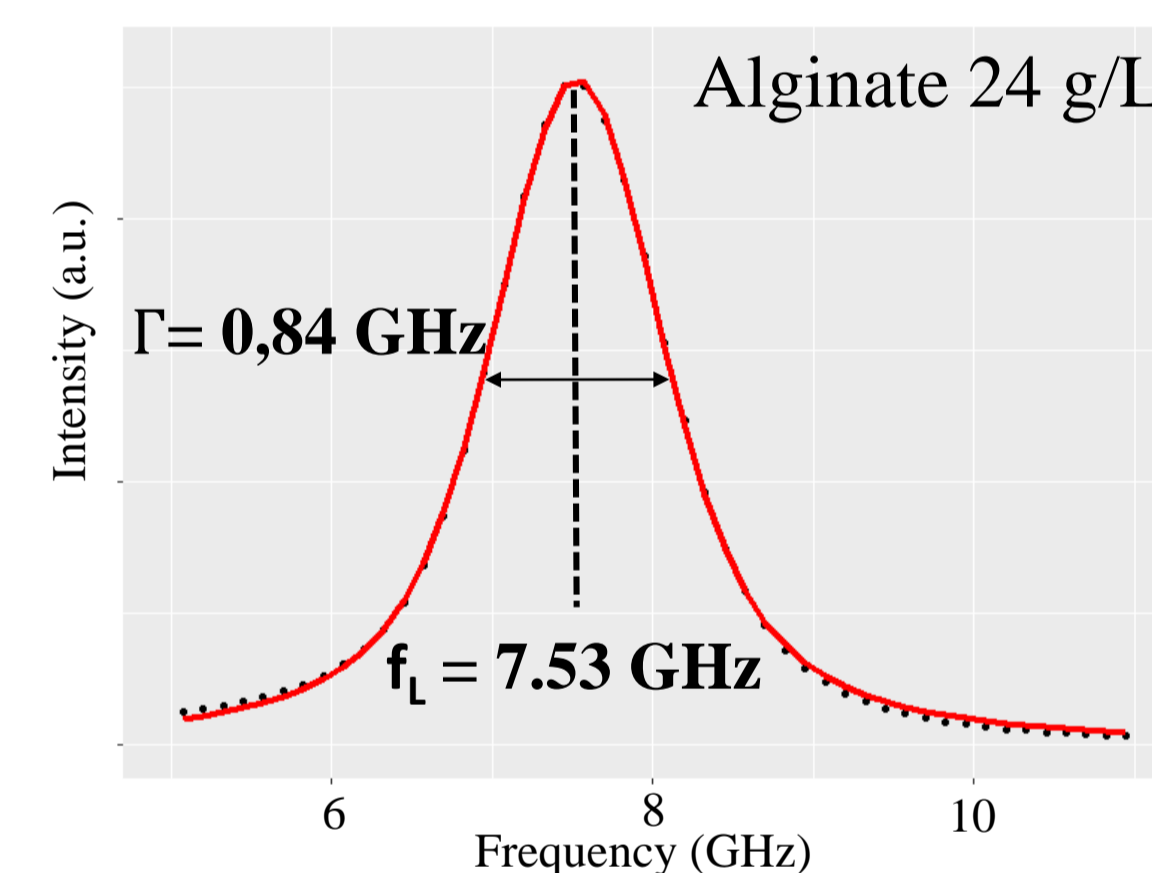
C alginate (g/L)	ω_c (rad/s)	L_p (nm)
2	$6.25 \cdot 10^4$	38.1
4	$8.93 \cdot 10^4$	33.8
8	$1.39 \cdot 10^5$	29.2
14	$1.92 \cdot 10^5$	26.2

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 Γ (and η)
- Subtraction of device linewidth: Gaussian $\sigma = 0.314$ GHz



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

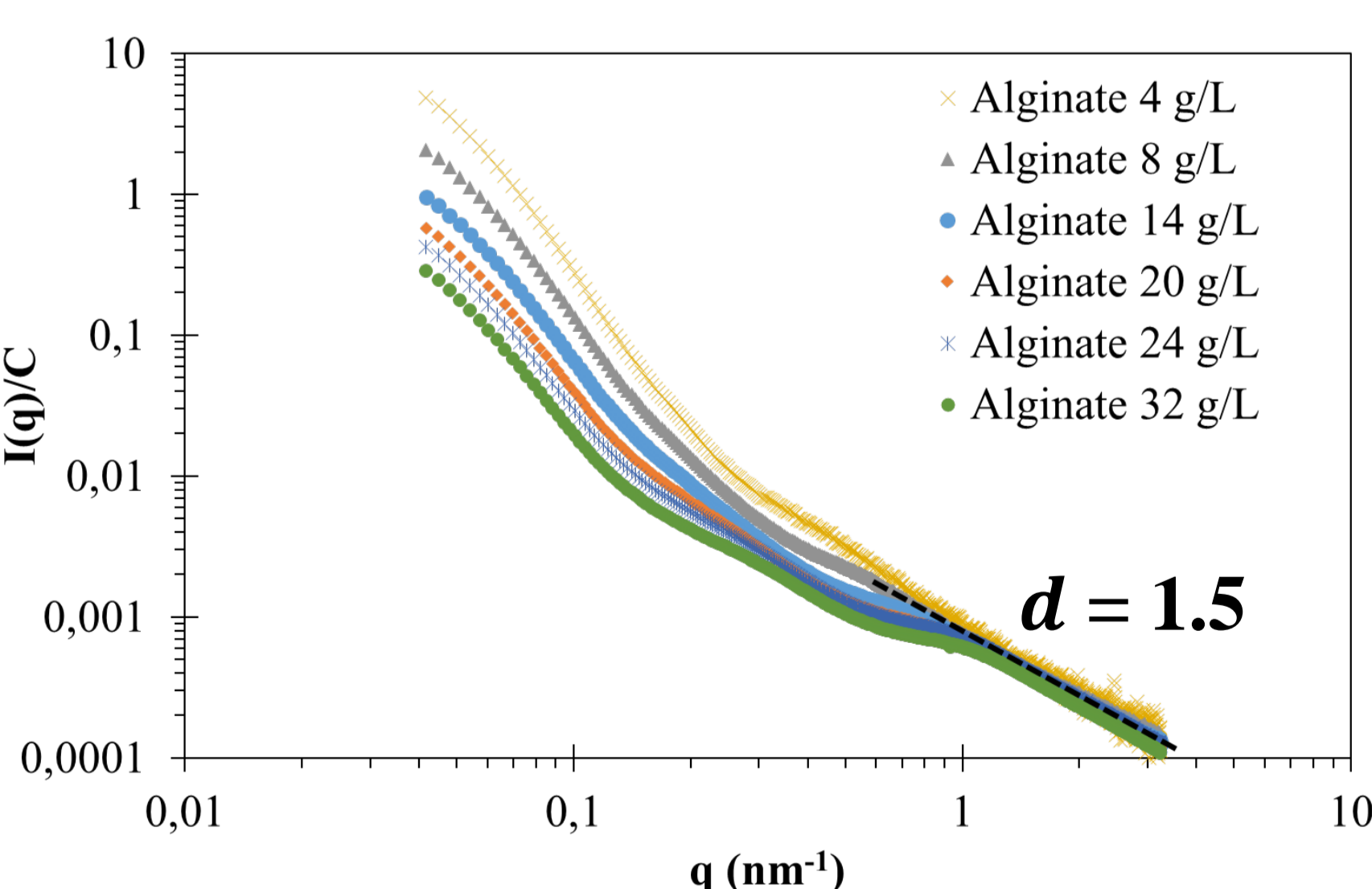
- x_w : mass fraction of water
- C_{11} : elastic constant determined for alginate solution at different concentrations
- M_w : elastic constant determined for water
- M_{alg} : "intrinsic" elastic constant of alginate

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

C alginate (g/L)	f_L (GHz)	Γ (GHz)	Volumic mass (kg/m ³)	Refractive index	v_L (m/s)	K (nm ⁻¹)	C_{11} (GPa)	η (mPa.s)
24	7.527	0.842	1011	1.335	3000	0.0315	2.275	0.857

Structure (SAXS)

Scattered intensity per monomer unit



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

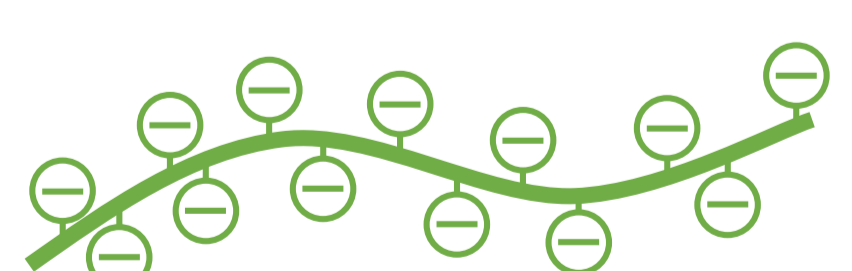
d: fractal dimension

$d = 5/3$



Random coil conformation
Neutral polymer at good solvent

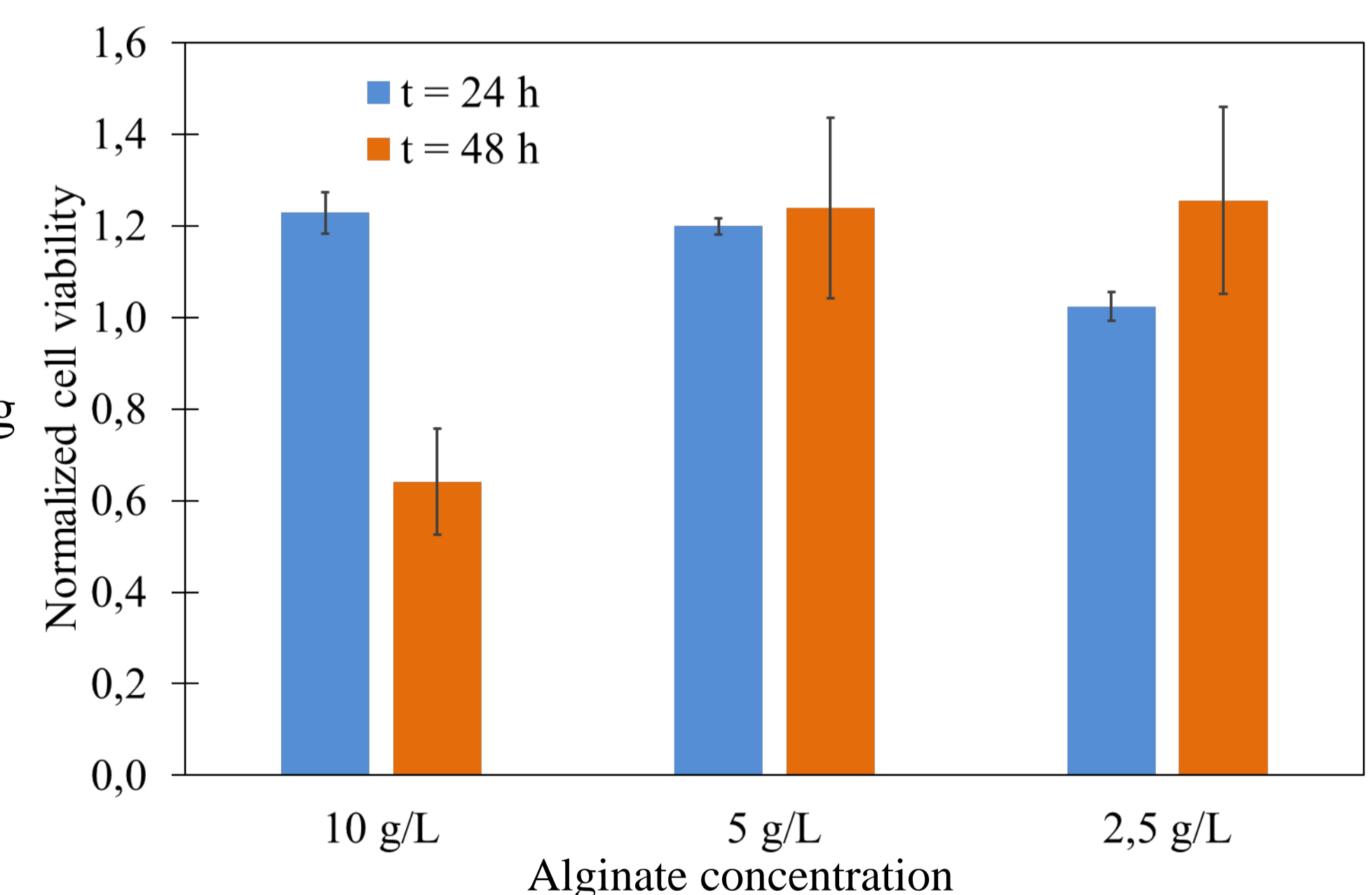
$d = 1$



Rodlike chains
Electrostatic repulsion

Biocompatibility

- 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 colored 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