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Alexandre Cordinier, Nicolas Hucher, Michel Grisel

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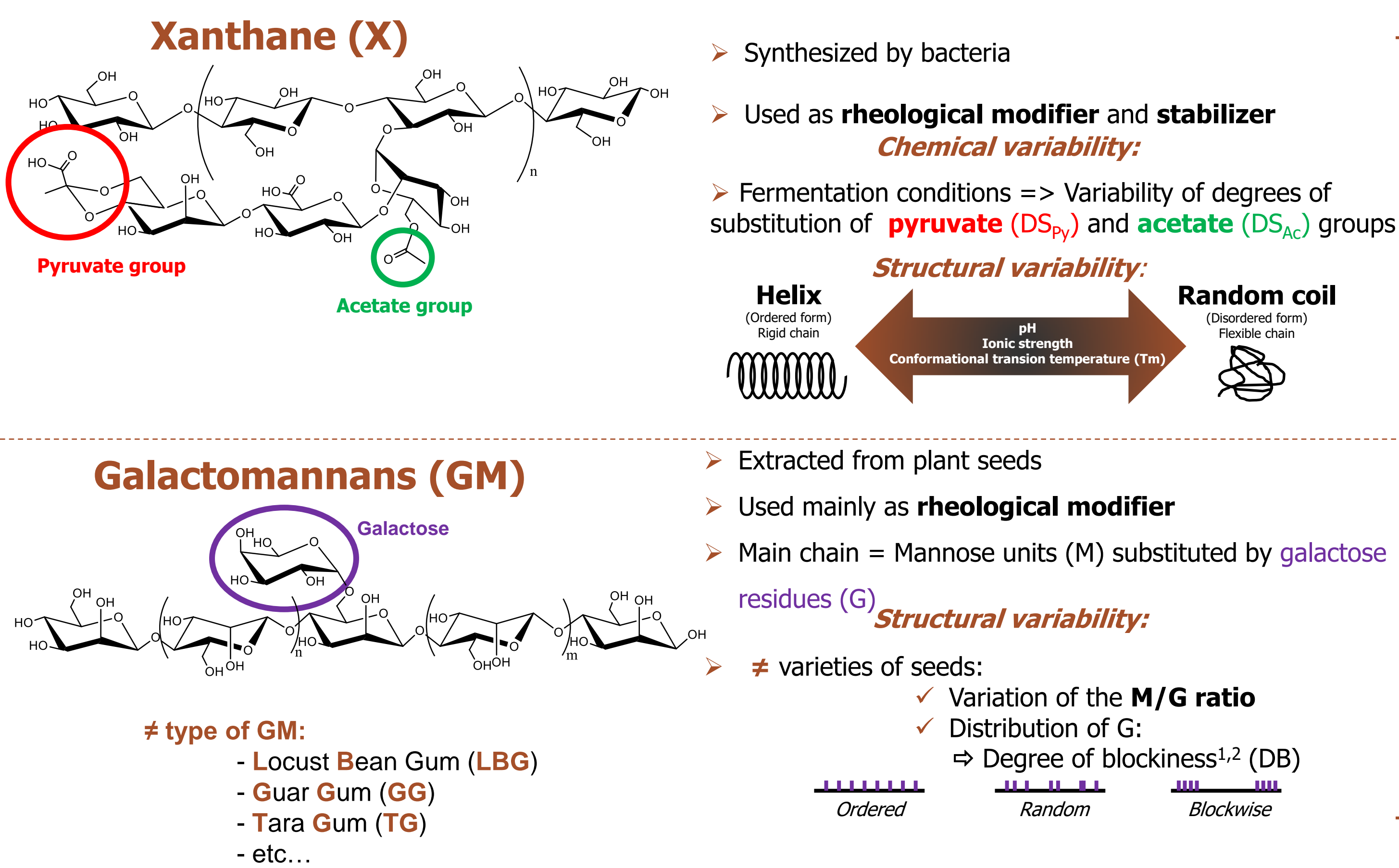
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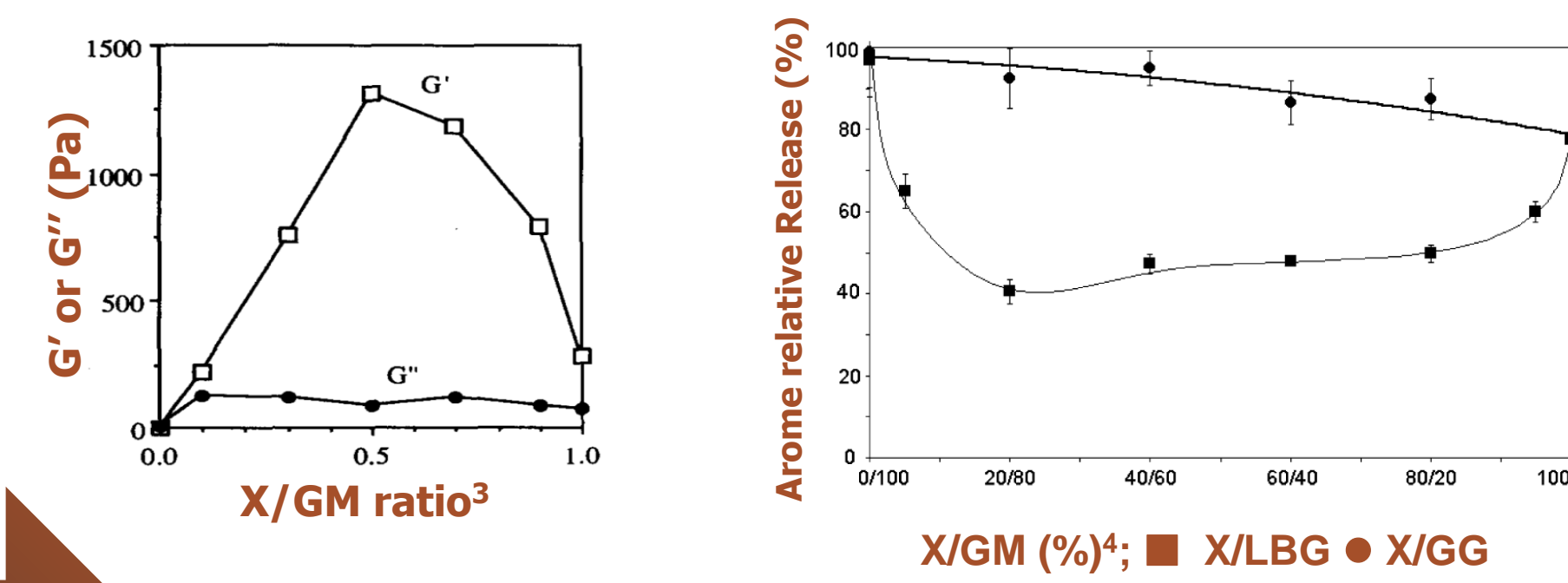
Exploring the nature and kinetic of establishment of molecular interactions in aqueous solution: the example of polysaccharide systems

Unité de Recherche en Chimie Organique et Macromoléculaire
Normandie Univ, UNIHAVRE, FR 3038 CNRS, URCOM, 76600 Le Havre, France

Alexandre Cordinier^a, Nicolas Hucher^a and Michel Grisel^a
Alexandre.cordinier@univ-lehavre.fr

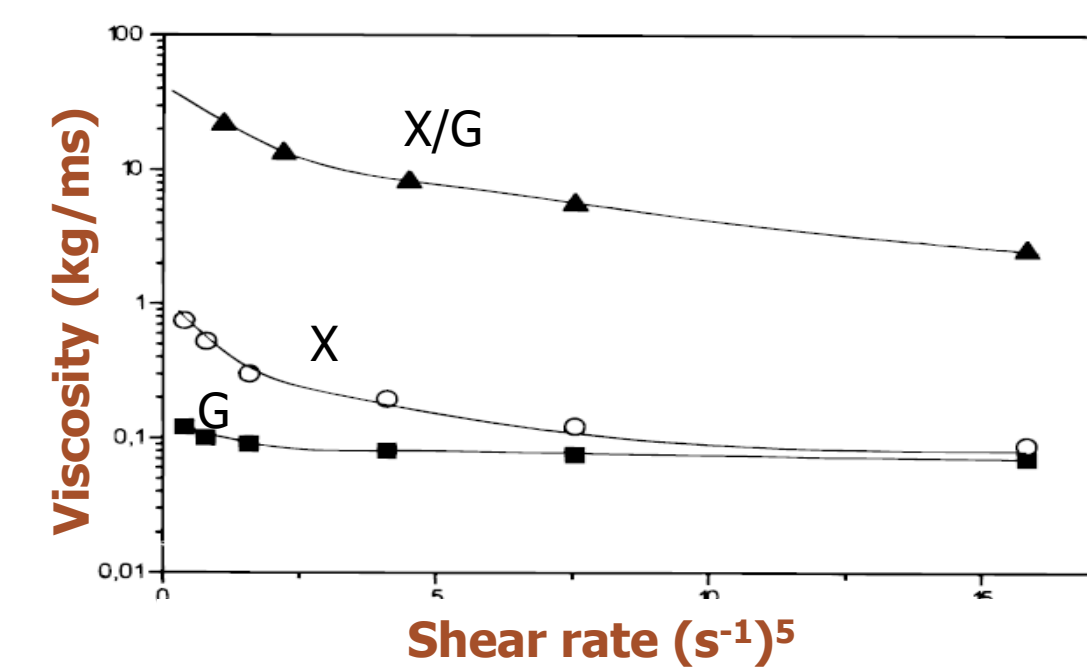


Context



- Mixed in **specific conditions** ⇒ **POSITIVE SYNERGY** between X and GM
- Over the past 50 years, several interaction models have been proposed:
 - ✓ Dea & Morris' model⁶ based on **polarimetric measurements**
 - ✓ Tako's model⁷ based on **rheological measurements**
 - ✓ Cairns' model⁸ based on **X-ray diffraction measurements**

Synergy X/GM



3 ≠ models based on 3 ≠ techniques
≠ Conformations or ≠ chemical structures of X

On the ground of the observations done at the macroscopic scale, why one model would be more accurate than another ?

⇒ Check what happen at microscopic scale !

Objectives

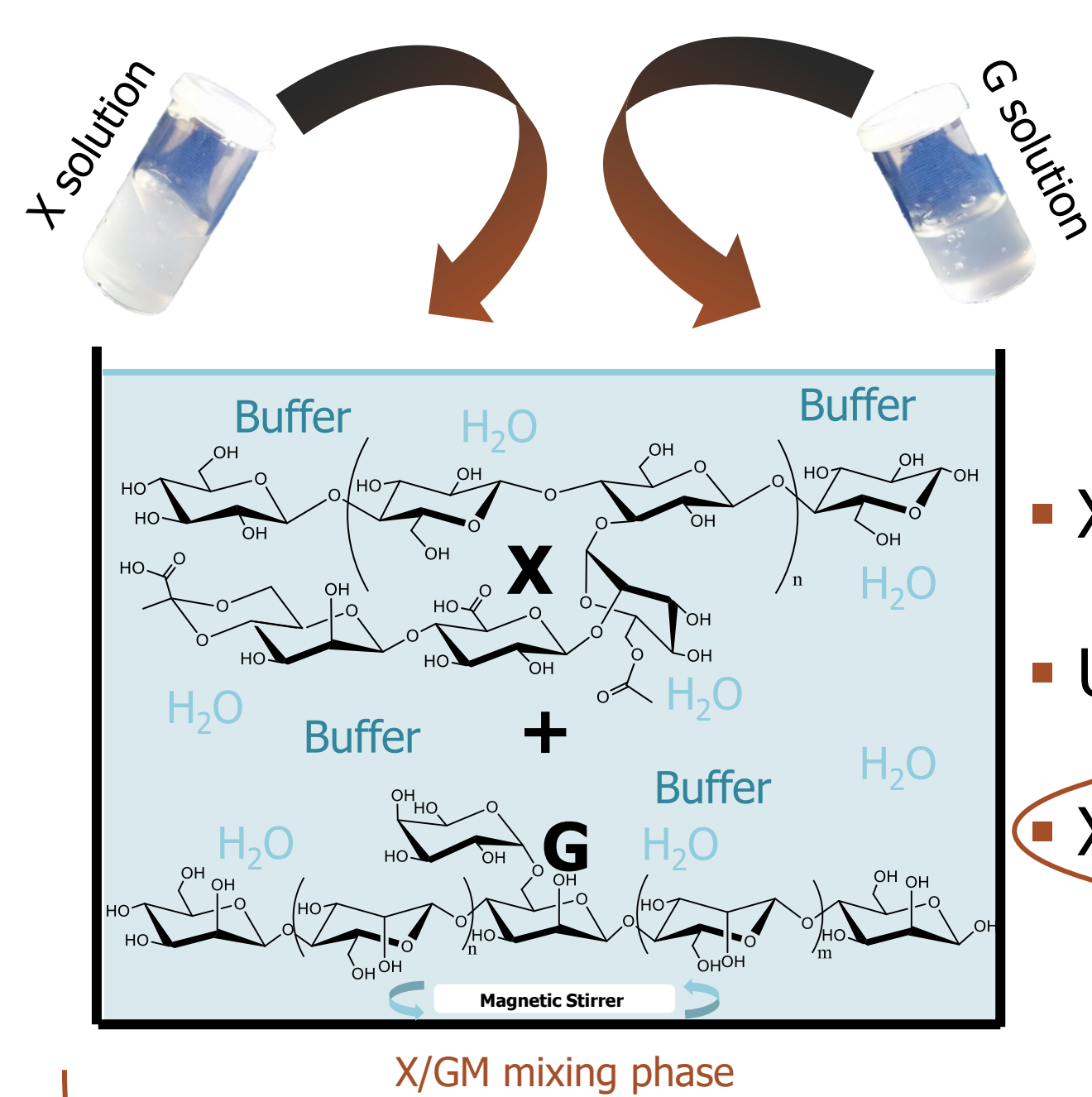
⇒ Develop an universal analytical tool to study the interactions at the molecular level

The aim of this project is to characterize the interactions at the molecular scale between polymers in solution

Characterization of interactions at the molecular scale ?

FLUORESCENCE SPECTROSCOPY

At the macroscopic scale



X/GM mixtures preparation

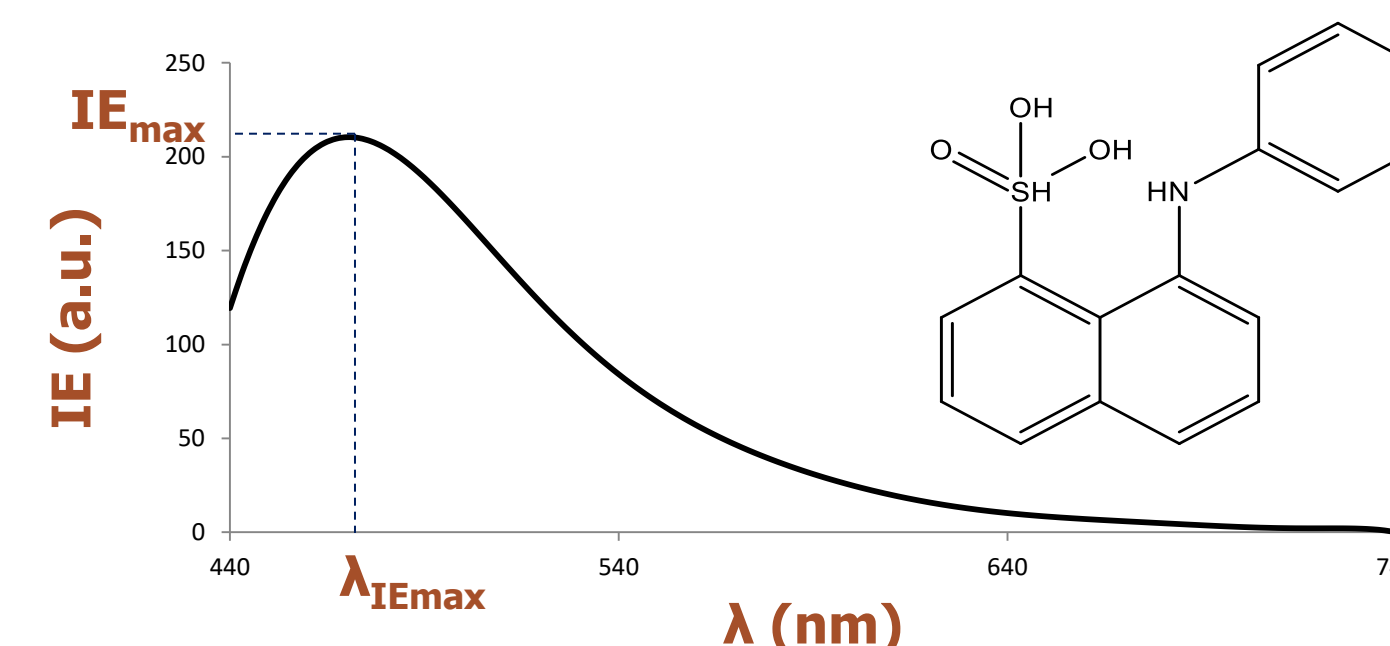
- X/GM mixtures at 0.2% (w/w)
- Use of a phosphate buffer at pH 7.4
- X/GM mixture stirred during ~ 1/2 h

High shear rates !

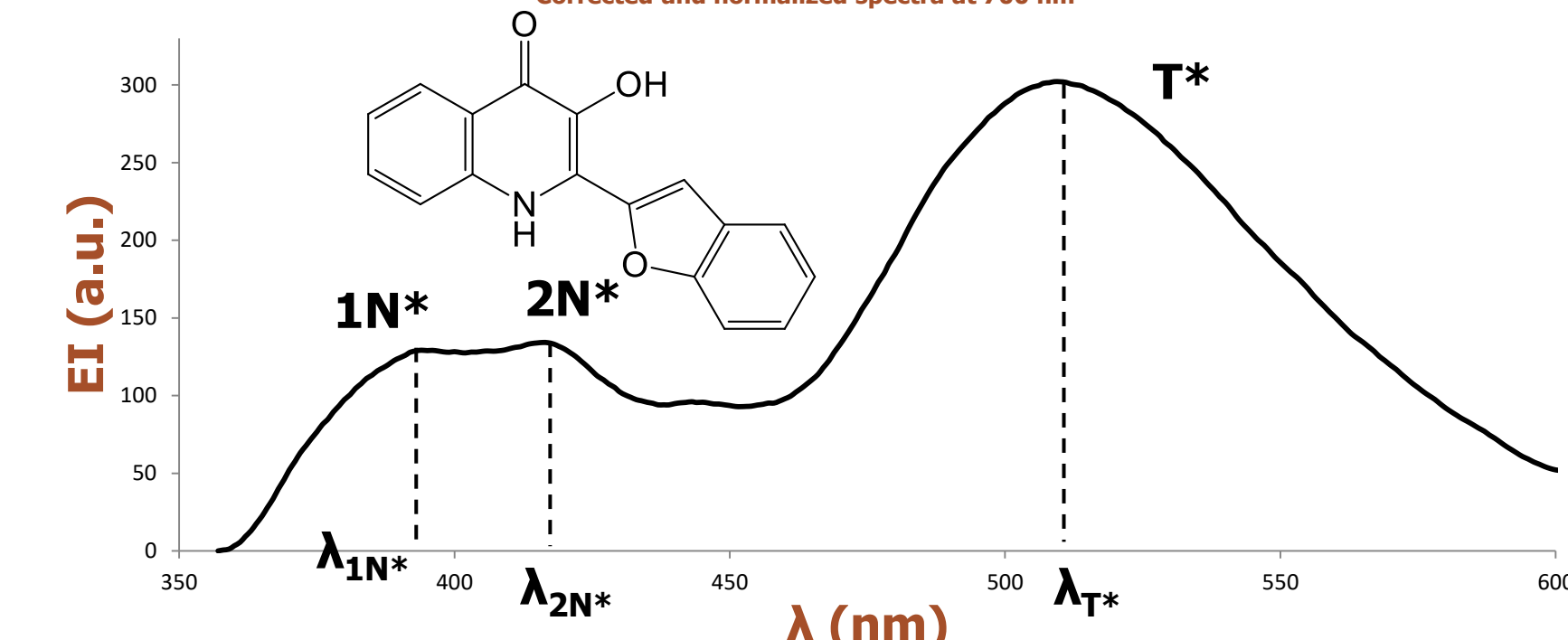
At the molecular scale

- ⇒ Use of 2 molecular specific probes
- ⇒ Same mixing process between X and GM as at the macroscopic scale
- ⇒ Injection of 1 of the 2 selected **fluorescence probes**: 8-anilino-1-naphtalen sulfonic acid (**ANS**) or 2-benzofuryl-3-hydroxy-4(1H)-quinolone (**3HQ-Bf**) in small quantities

ANS spectra in X/LBG mixture (1:1; 0.2% w/w)



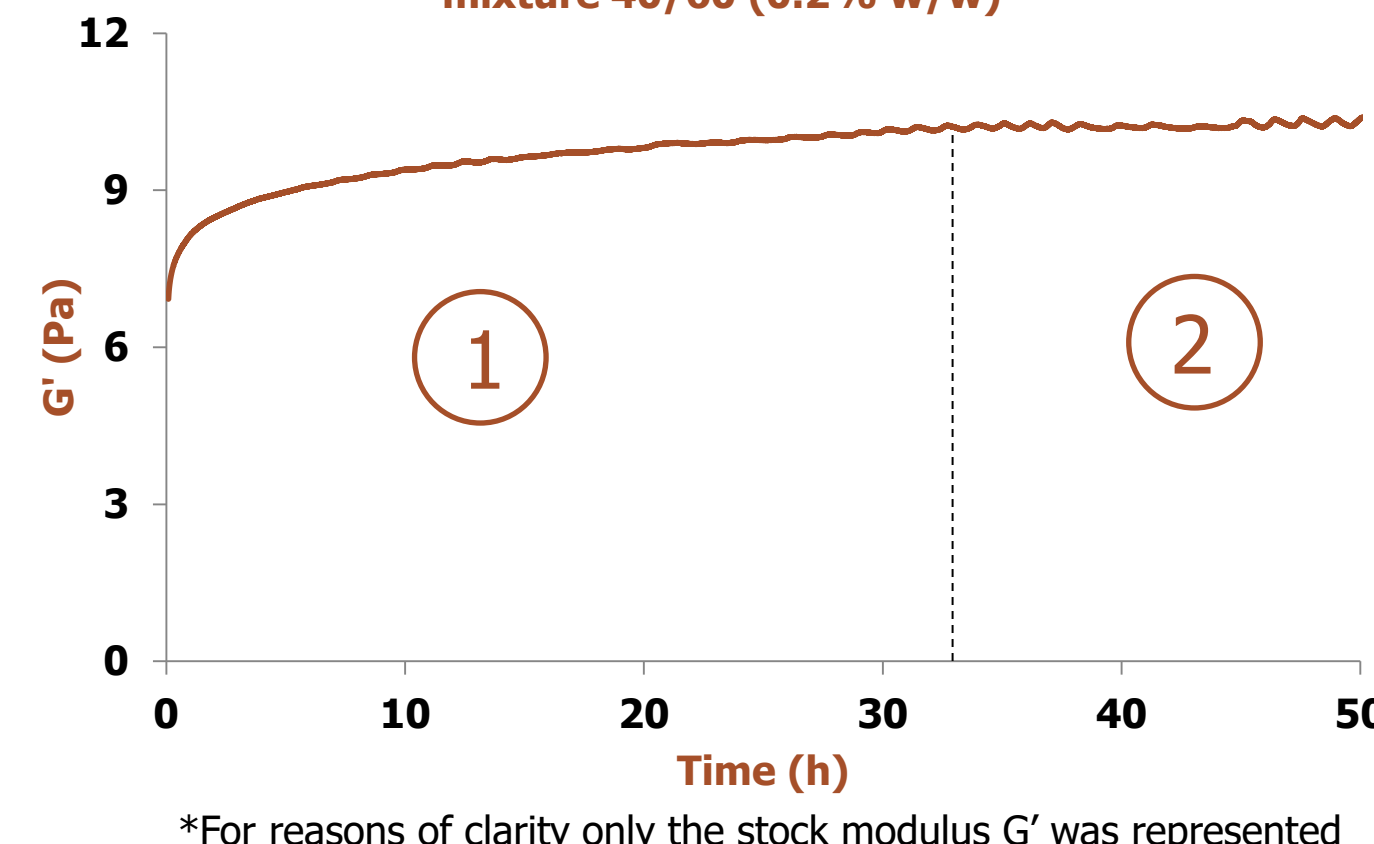
3HQ-Bf spectra in X/LBG mixture (1:1; 0.2% w/w)



- The ANS probe is **sensitive to Hydrophobic interactions**⁹ (EI)
- H₂O is a **quencher** to the fluorescence of ANS probe
- The ANS probe is also sensitive to the **polarity** of the medium (λ)
- ANS is not available commercially
- The 3HQ-Bf probe is **sensitive to H-Bonds**¹⁰ in its close environment
- 3HQ-Bf is not available commercially, it has to be **synthesized**
- 3HQ-Bf is a **ratiometric** probe
- Ratio EI_{N*}/EI_{T*} ≈ **Strength of the H-bond network**

Use of a Discovery Hybrid Rheometer to follow viscoelastic properties of our X/GM mixtures with time

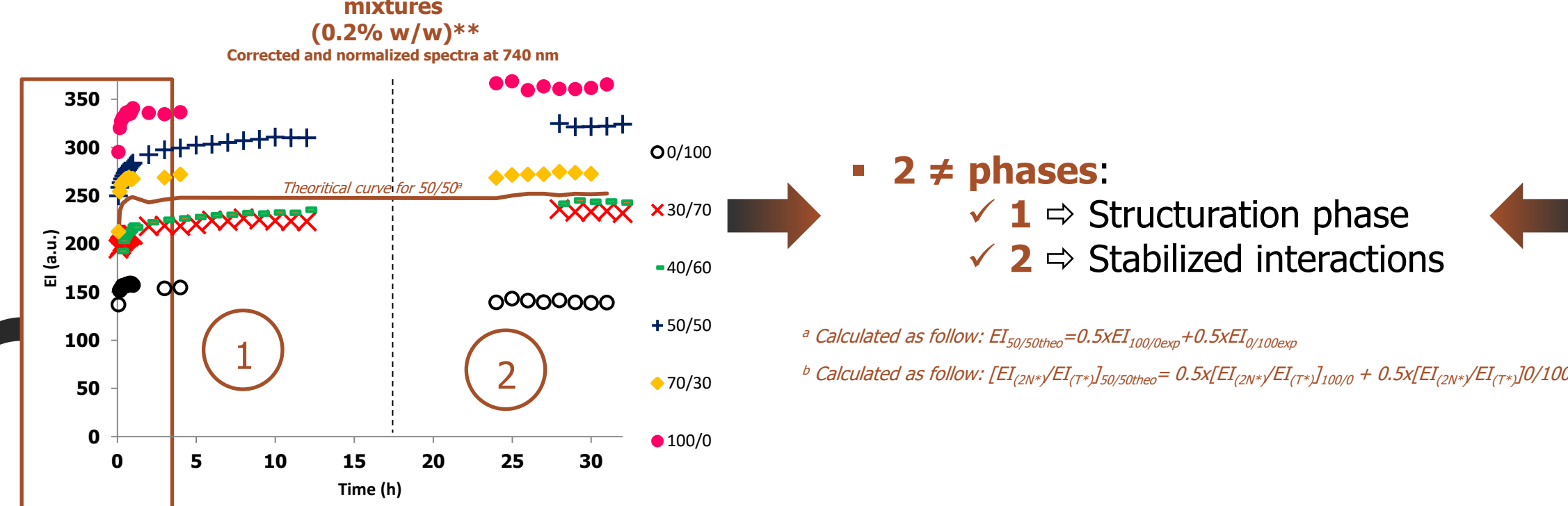
Evolution of the viscoelastic properties of a X/LBG mixture 40/60 (0.2% w/w)*



- Stabilization of viscoelastic properties is not happening suddenly
- 2 ≠ phases:
 - ✓ 1 ⇒ Structuration phase
 - ✓ 2 ⇒ Stabilized system
- The period of the structuration phase is depending on the composition of X/GM mixture
- The period of the structuration phase is depending also of the mixture preparation conditions
- Few studies have been made about this structuration step^{11,5}

*For reasons of clarity only the stock modulus G' was represented

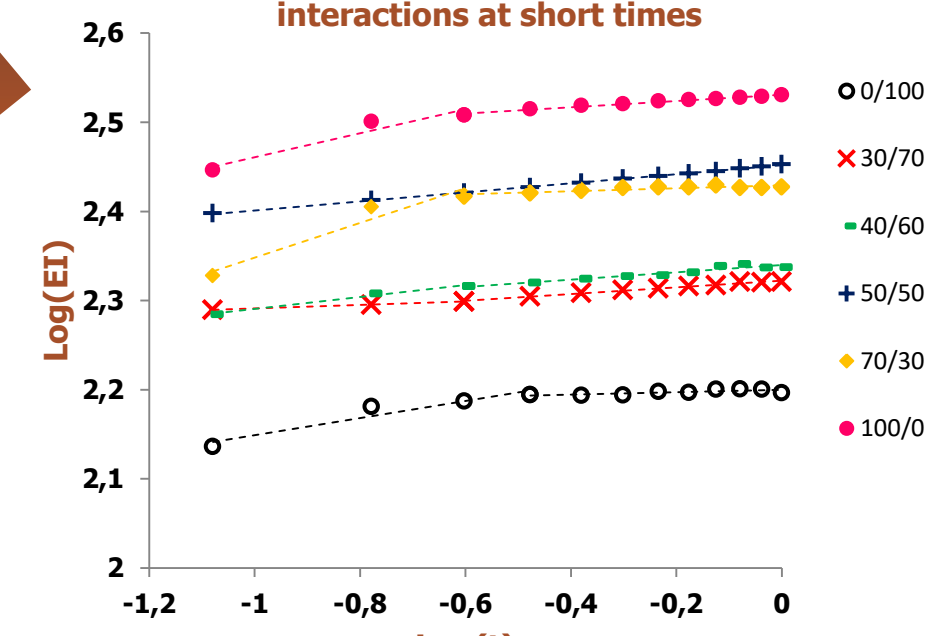
Evolution of hydrophobic interactions in X/LBG mixtures (0.2% w/w)**



- 2 ≠ phases:
 - ✓ 1 ⇒ Structuration phase
 - ✓ 2 ⇒ Stabilized interactions

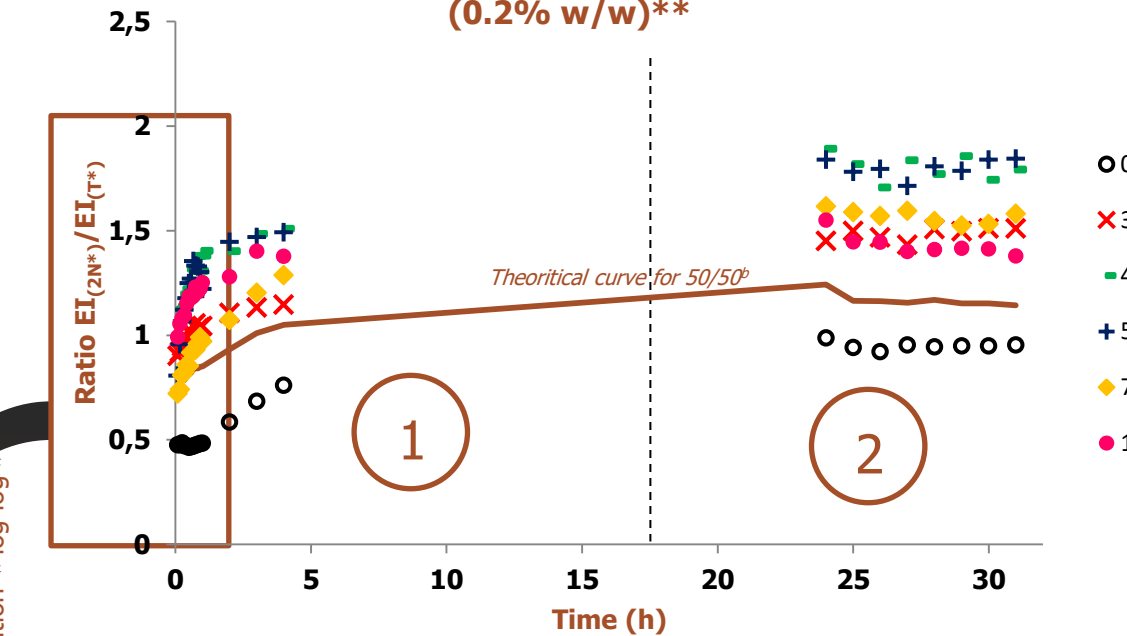
* Calculated as follow: EI_{max} = 0.5EI_{max} + 0.5EI_{min}
 ** Calculated as follow: EI_{N*}/EI_{T*} = 0.5EI_{N*}/EI_{T*} + 0.5EI_{N*}/EI_{T*}

Kinetic of structuration of hydrophobic interactions at short times

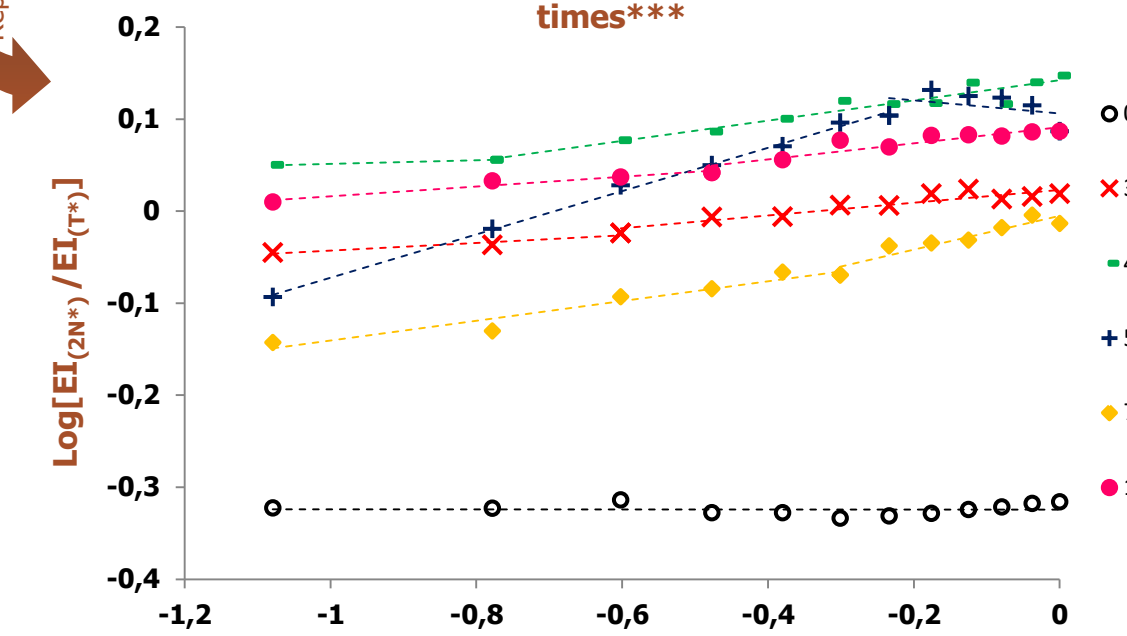


- Interaction structuration depends on the **composition** of X/GM mixture

Evolution of the H-Bond network with time in X/LBG mixtures (0.2% w/w)**



Kinetic of structuration of the H-bond network at short times***



**For reasons of clarity standard deviations were not represented
 ***Dotted lines only help to read the graphs

Conclusions

References

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