DYNAMIC LIGHT SCATTERING STUDY OF TEMPERATURE AND pH-SENSITIVE COLLOIDAL MICROGELS

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Outline

1. Soft Matter & Colloidal Suspensions

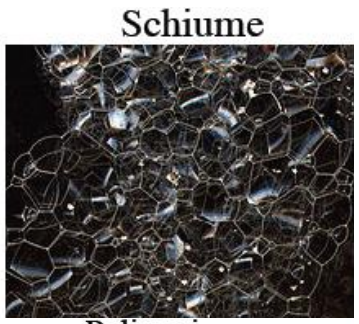
2. IPN microgels of PNIPAM and PAAC

3. *Dynamic Light Scattering (DLS): Thermo and pH-sensitive behavior*

Soft Matter & Colloidal Suspensions

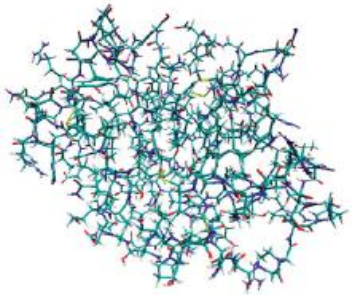
Soft Matter

- Foams, emulsions, polymer solutions, etc…



Colloidal Suspensions

- Colloidal particles suspended in a continuous medium (size ~1 nm- 1 μm)
- **Interparticle Potential easily tunable**
- **Exotic phase diagram with different arrested states**

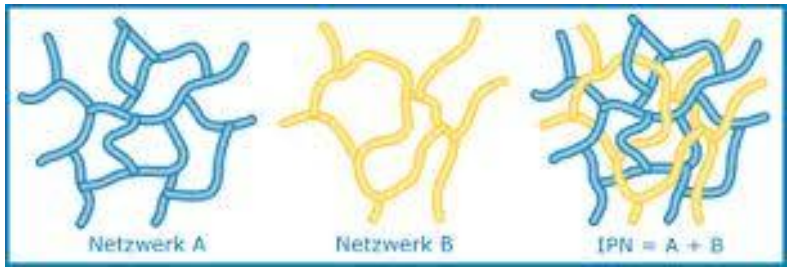


IPN Microgel of PNIPAM and PAAC

Colloidal suspensions of microgels:

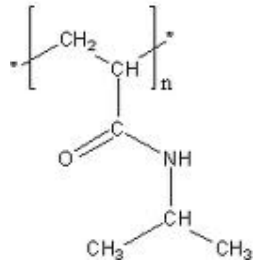
- Tunability of the Interaction Potential
- Sensitiveness to external parameters (temperature, pH) ➡ *Smart Material*

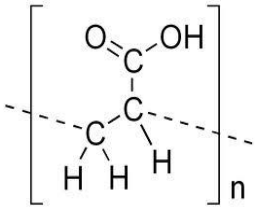
Intepenetrated Polymer Network microgel



PNIPAM Thermo-sensitive + *PAAc pH-sensitive* ➡ *Independent responsivness to T and pH*

$(C_6H_{11}NO)_n$

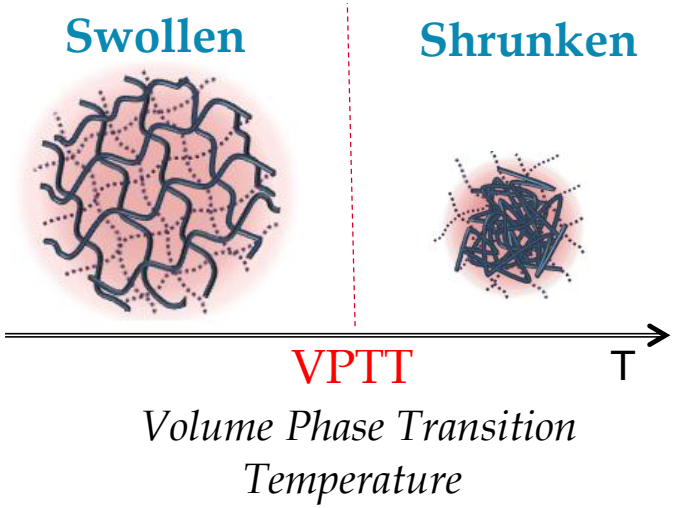




$(C_3H_4O_2)_n$

IPN Microgel of PNIPAM and PAAC

Phase behavior as a function of T, **pH** and C_w

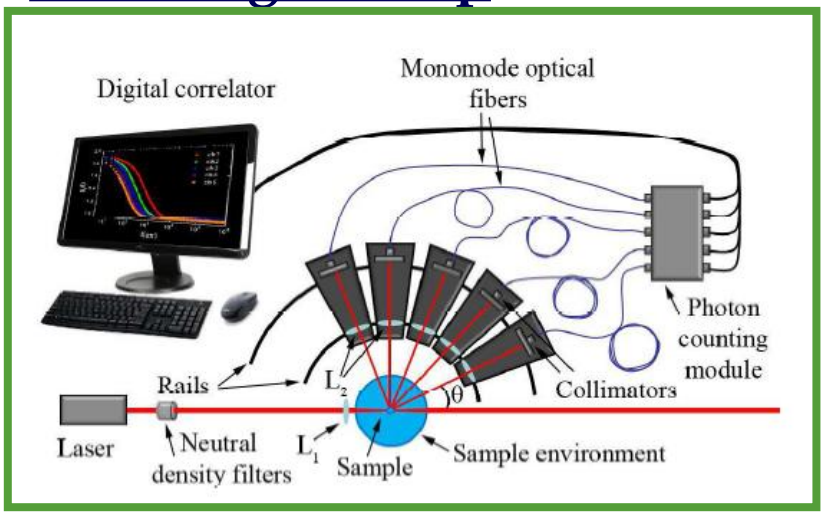


➡ ***Dynamics*** ⟶ **DLS** — *Dynamic Light Scattering*

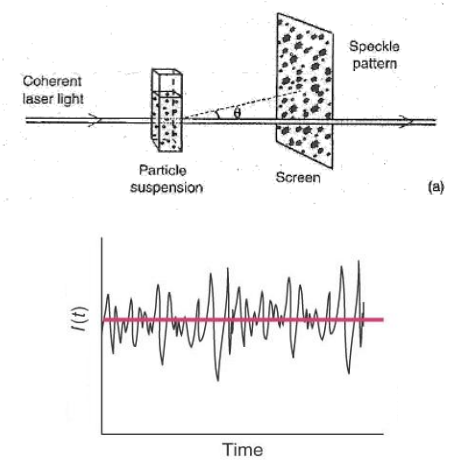
➡ ***Local Structure*** ⟶ **SANS** — *Small Angle Neutron Scattering*

Dynamic Light Scattering (DLS)

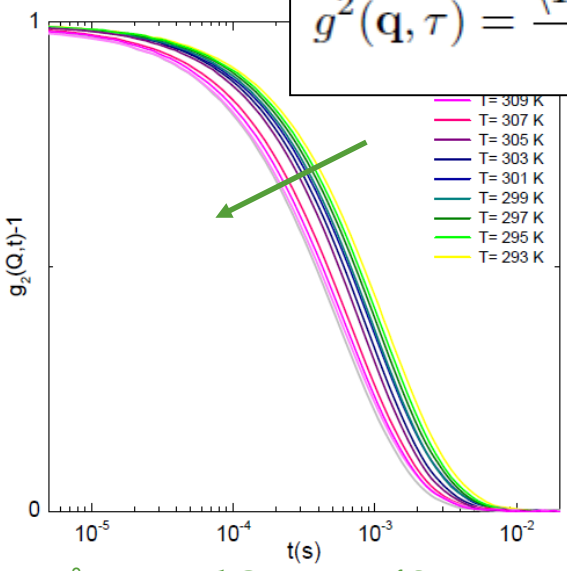
Multiangle setup



Temperature dependent behavior



$$g^2(\mathbf{q},\tau) = \frac{\langle I(\mathbf{q},t)I(\mathbf{q},t+\tau)\rangle}{\langle I(\mathbf{q},t)\rangle^2}$$



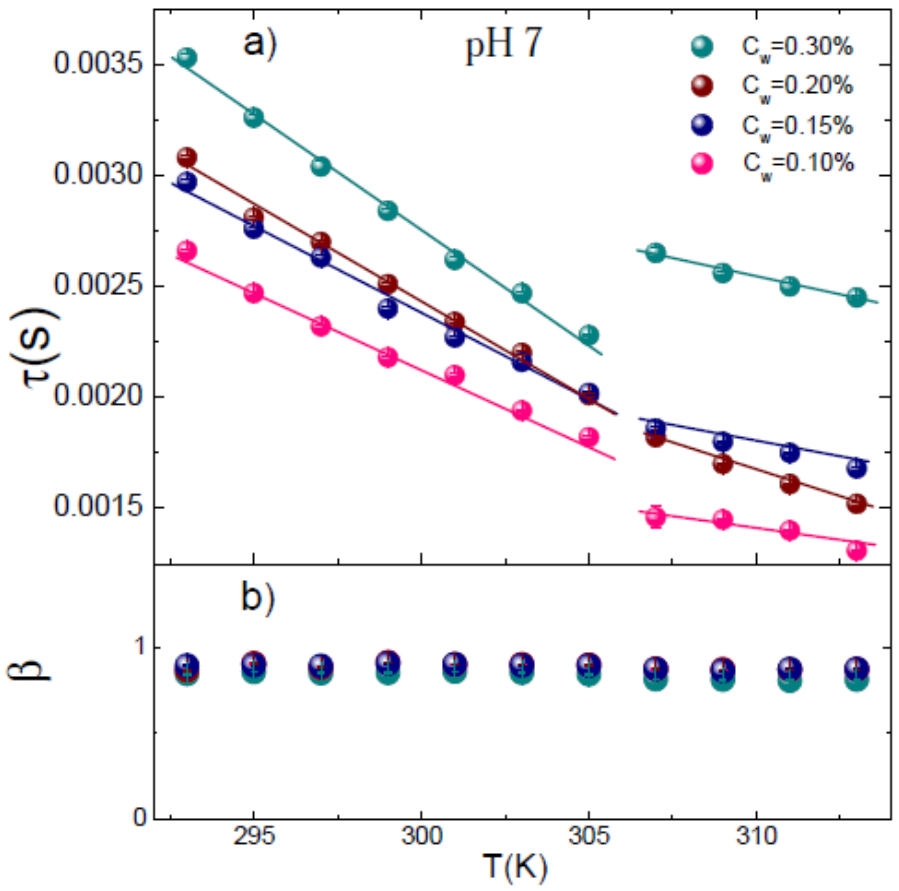
➡ ***Colloidal suspensions***

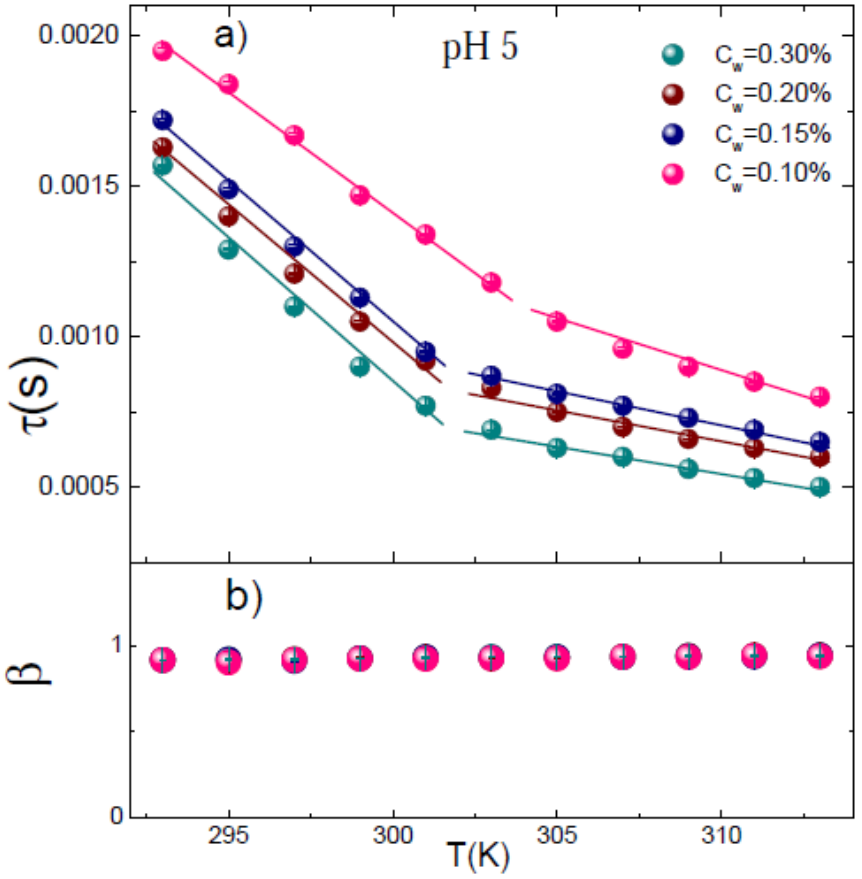
$$g^2(\boldsymbol{q},\tau) = 1 + b[(e^{-t/\tau})^{\beta}]^2$$

Kohlrausch-Williams-Watts expression

Dynamic Light Scattering: Thermo and pH-sensitive behavior

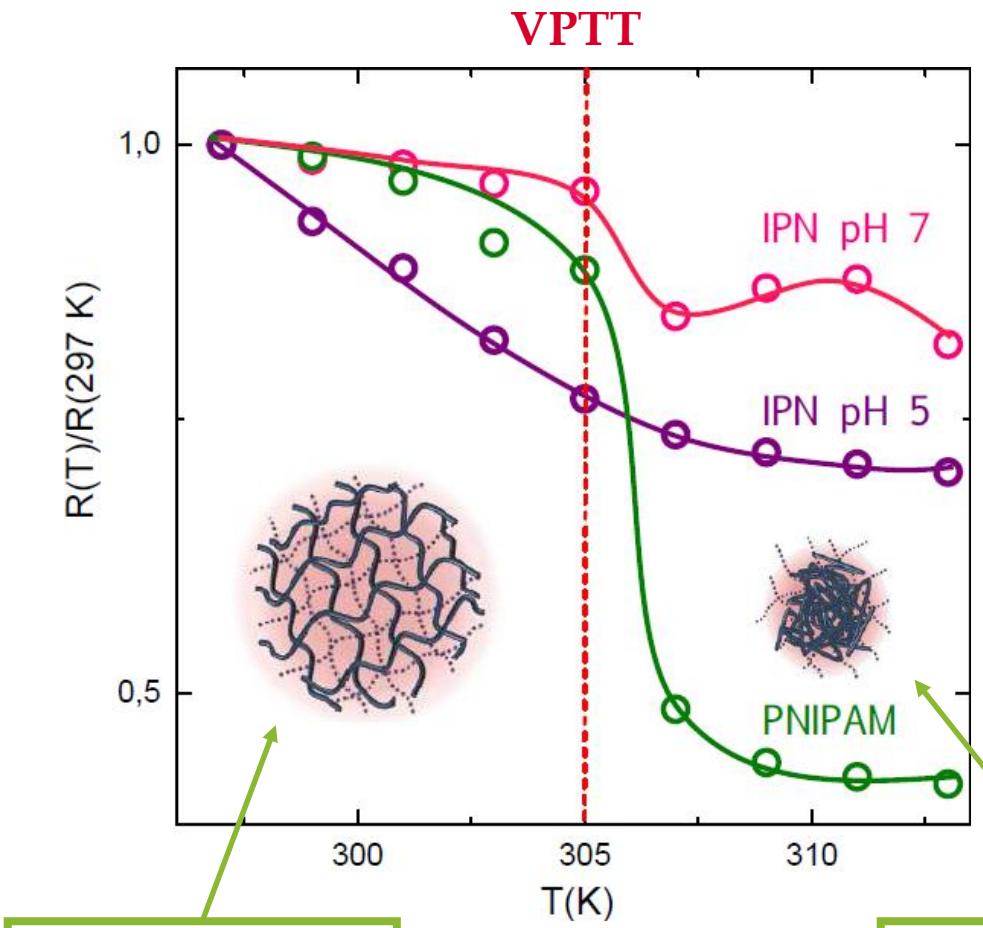
IPN microgels in H_2O solutions





V. Nigro et al., J. Non-Cryst. Solids **407**, 361-366 (2015)

Dynamic Light Scattering: Thermo and pH-sensitive behavior



- T < VPTT : Swollen phase
  Polymer-solvent interactions
- T > VPTT : Shrunken phase
  Polymer-polymer interactions
- Functionalization by introducing the poly-acrylic acid

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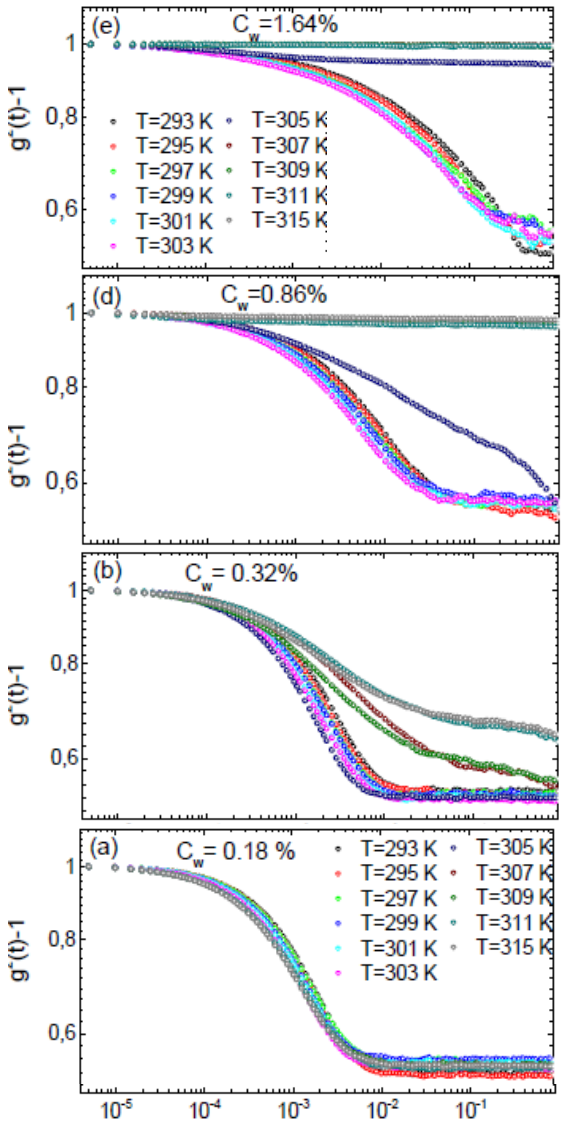
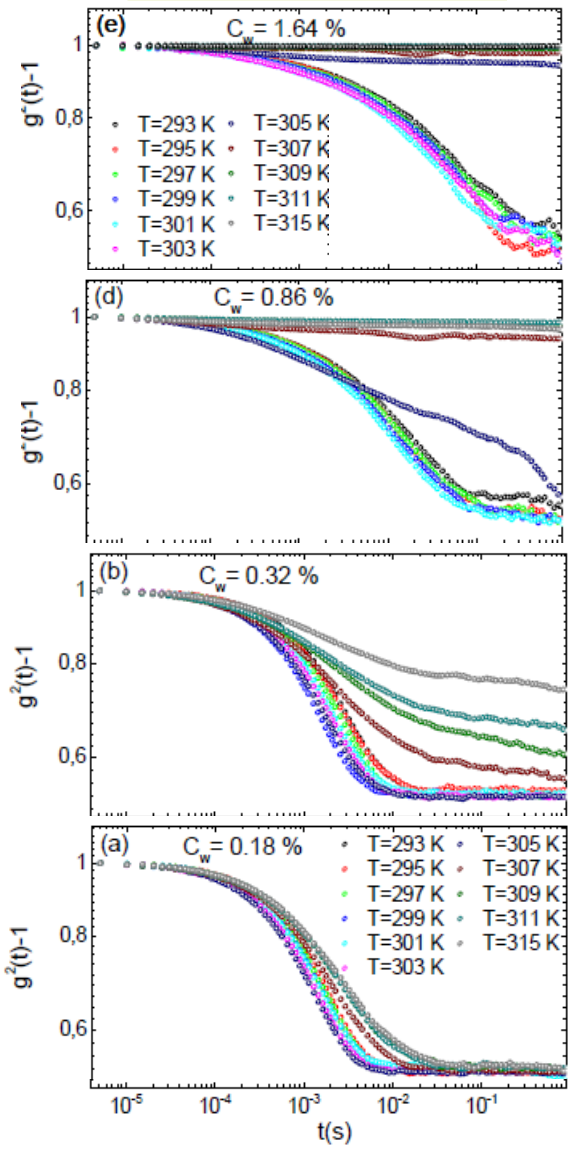
Dynamic Light Scattering: Thermo and pH-sensitive behavior

High concentration behavior

Acidic pH

Neutral pH

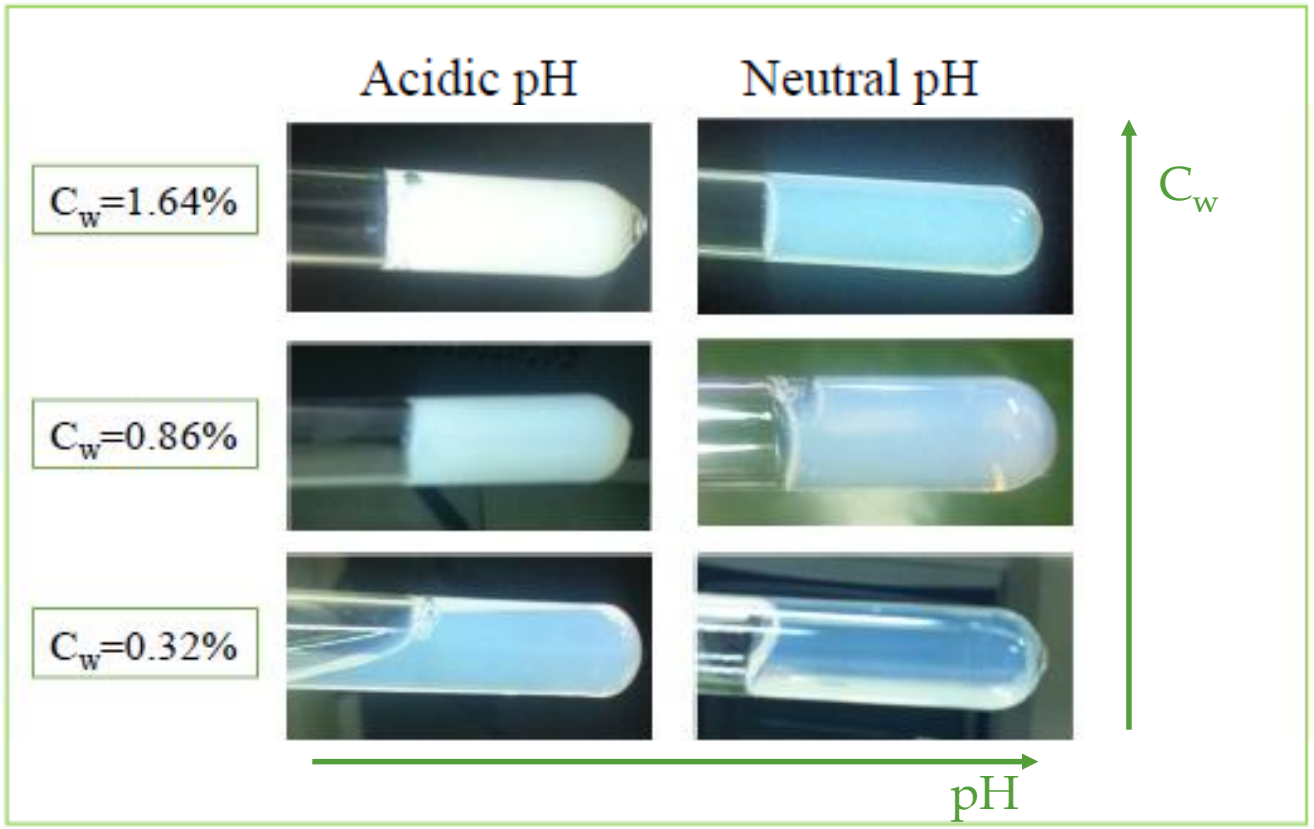




Transition from ergodic to non-ergodic dynamics

C_w

Dynamic Light Scattering: Thermo and pH-sensitive behavior

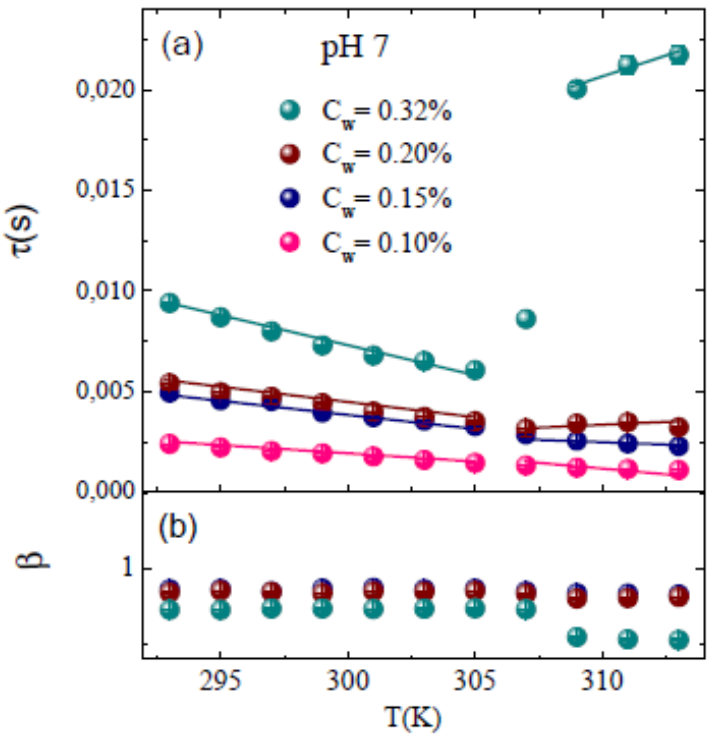


Non-ergodic transition controlled by C_w and pH:

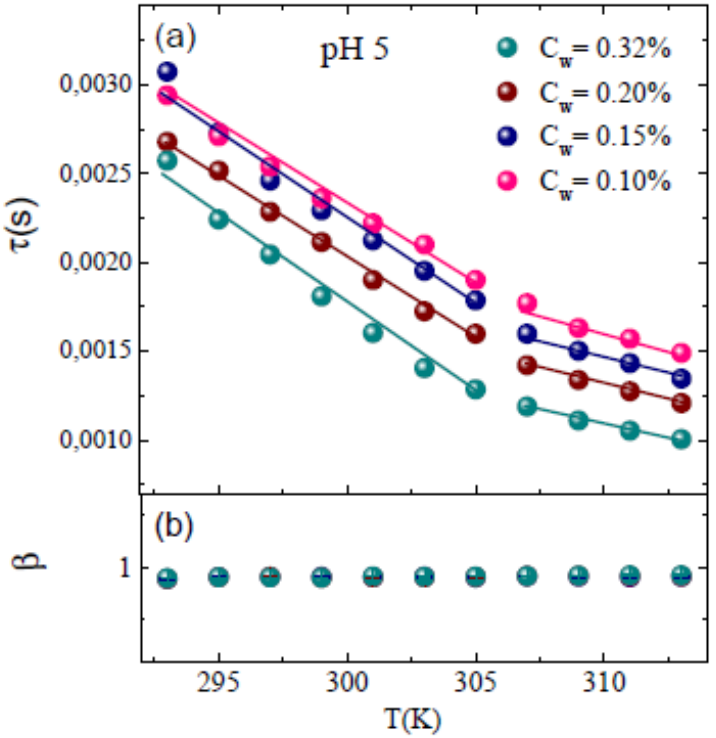
- Non-ergodic state at high C_w
- Increasing viscosity at neutral pH

Dynamic Light Scattering: Thermo and pH-sensitive behavior

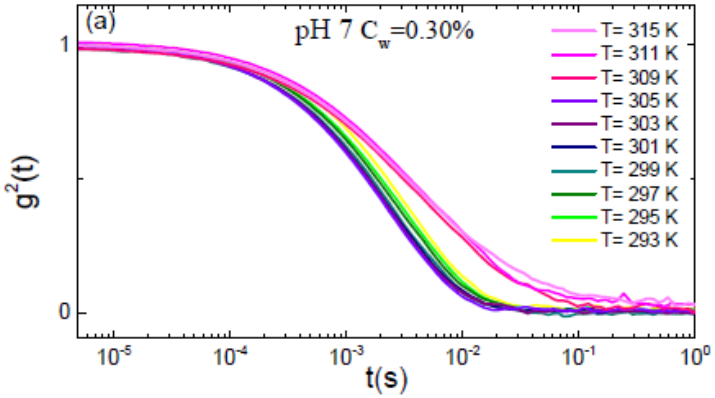
IPN microgels in D_2O solutions



Similar swelling behavior and C_w dependence as H_2O samples



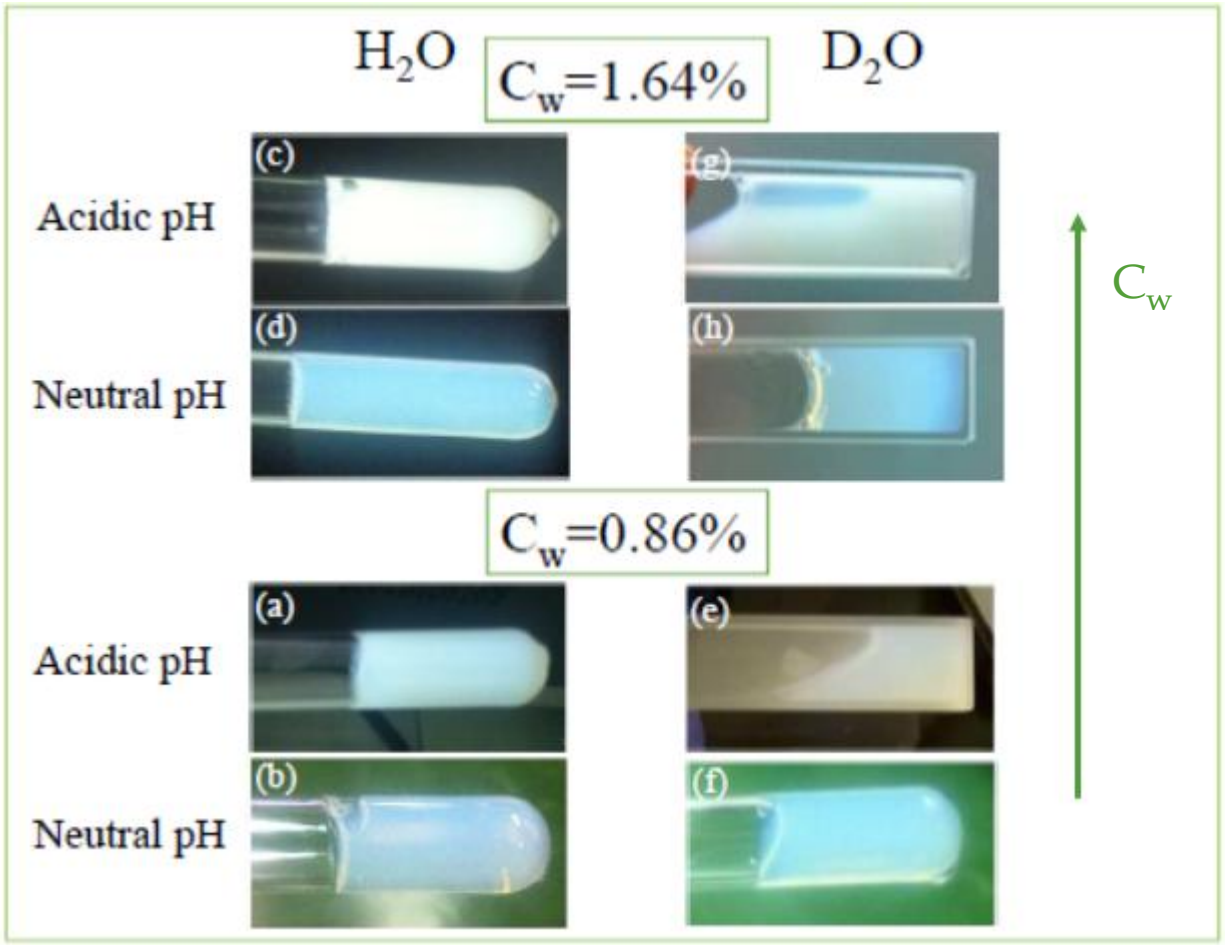
Stretched behavior at C_w = 0.30% and pH 7



Shift of the VPT

Dynamic Light Scattering: Thermo and pH-sensitive behavior

High concentration behavior



Non-ergodic transition controlled by C_w, pH and solvent:

- Non-ergodic state at high C_w and neutral pH
- Slower transition in D_2O

Conclusions….

T < LCST:

- Swollen state
- Liquid phase at high C_w

T > LCST:

- Shrunken state
- Arrested state at high C_w

Acidic pH:

- Reduced swelling capability
- Arrested state at high C_w

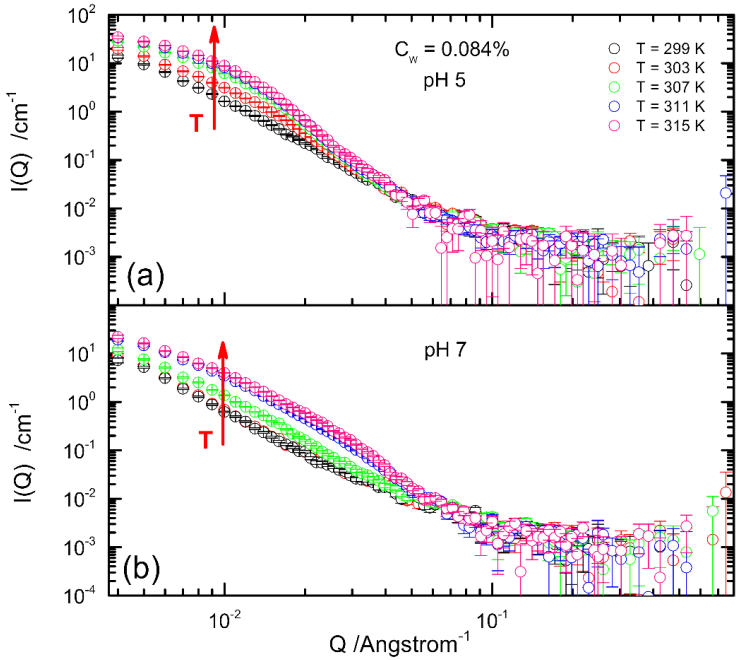
Neutral pH:

- Sharp transition
- Non-ergodic transition at low C_w

Non-ergodic transition at the VPT tuned by C_w, pH and solvent

Small-Angle Neutron Scattering: Intra-Particle Structure

Temperature, pH and C_w behaviors



T -dependence:

Inhomogeneous local structure — VPT — **Porous solid-like structure**

T

pH -dependence:

Acidic pH

H-bonds between PAAc and PNIPAM

Neutral pH

Independent networks

V. Nigro et al., J. Chem. Phys. **143**, 114904 (2015)

For further details:

Struttura locale e transizione di volume in microgel colloidali: un'indagine SANS

M.A.Ricci

24/09 h 16:50 - Fisica applicata, beni culturali e acceleratori

Acknowledgement

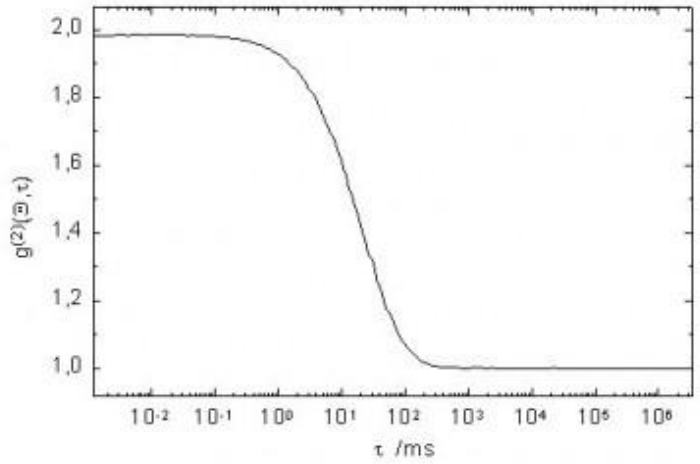
- *Barbara Ruzicka*
- *Roberta Angelini*
- *Monica Bertoldo*
- *Maria Antonietta Ricci*
- *Fabio Bruni*

Dynamic Light Scattering (DLS)

Monodisperse system

$$g^2(q,\tau) = 1 + b[e^{-t/\tau}]^2$$

relaxation time



Colloidal suspensions

$$g^2(q,\tau) = 1 + b[(e^{-t/\tau})^{\boldsymbol{\beta}}]^2$$

Stretching coefficient

Kohlrausch-Williams-Watts expression

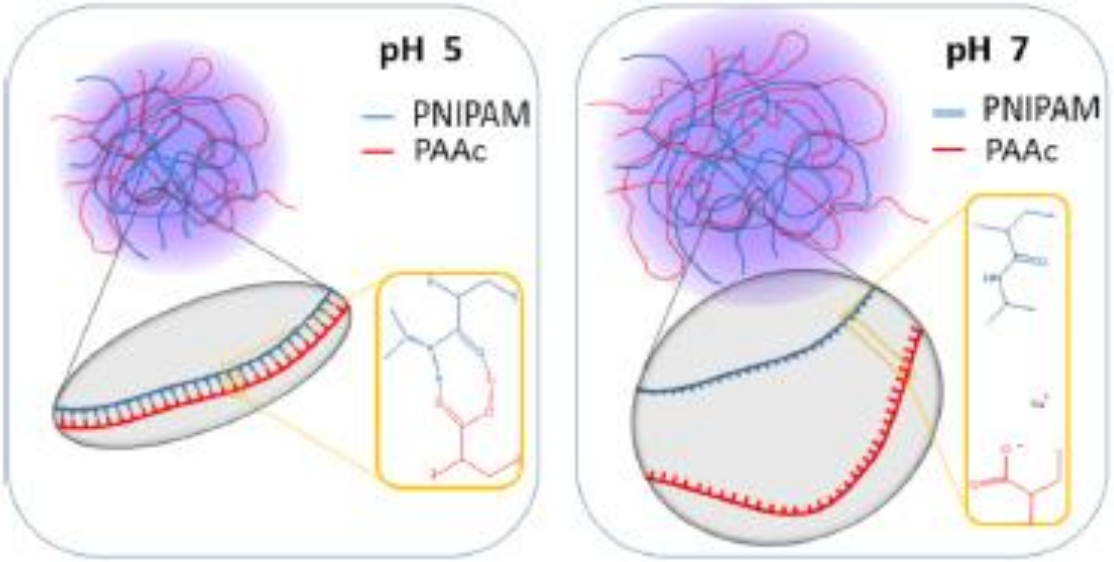
Brownian motion

$$\tau = {}^{1}/_{q^2 D_t} \quad \Rightarrow \quad D = \frac{k_B T}{6\pi\eta r}$$

STOKES-EINSTEIN

non-interacting spherical particles

Intra-Particle Structure

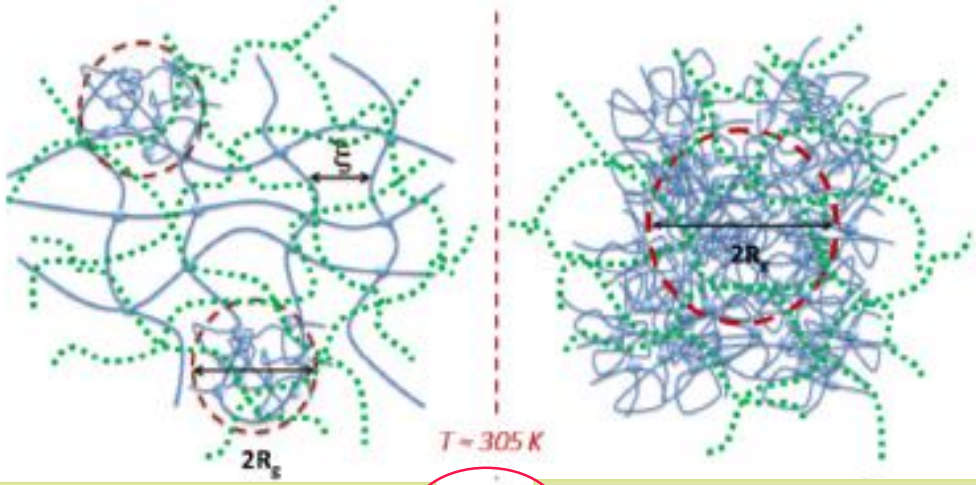


- Acidic pH :

H-bonds between PAAc and PNIPAM

- Neutral pH :

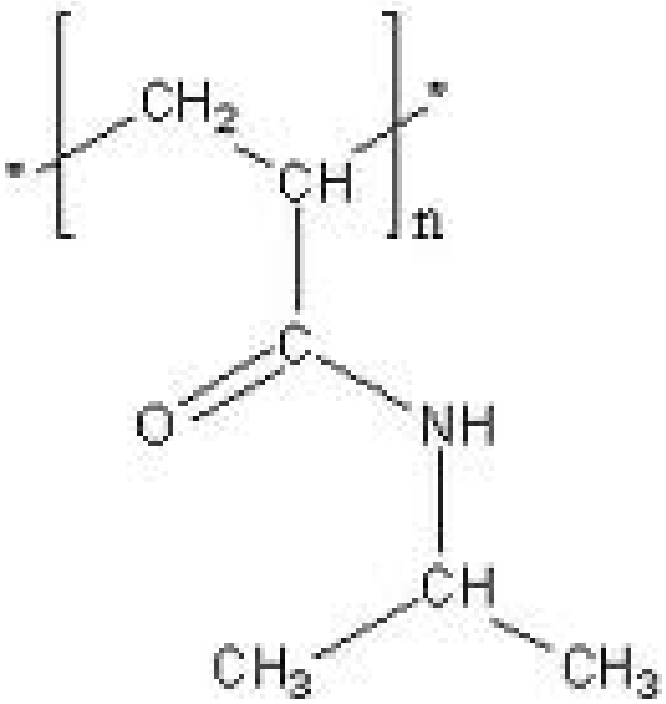
Independent networks



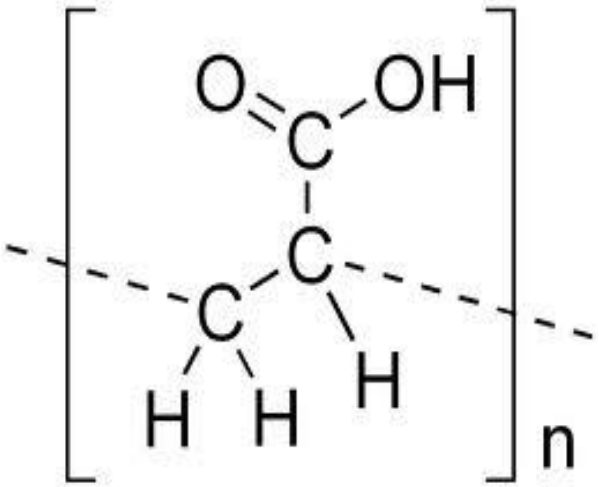
Struttura locale disomogenea LCST **Porous solid-like structure**

T

PNIPAM



PAAc



IPN Microgel of PNIPAM and PAAC

PNIPAM microgel:

- Thermo-sensitive

➡ Phase behavior

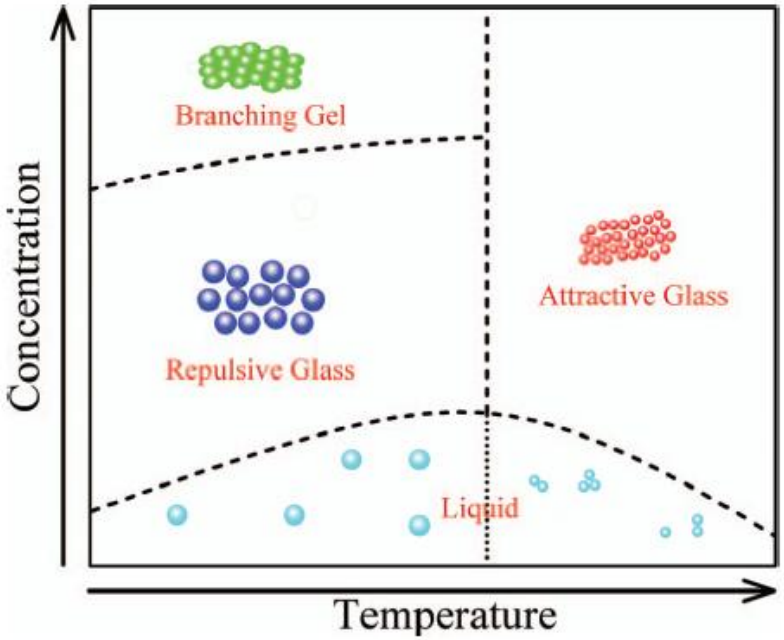
T-dependent

- T<LCST : solvent-polymer interactions
- T>LCST : polymer-polymer interactions

+ affected by C_w

Transizione vetro-gel

- Low C_w: *liquid phase*
- Intermediate C_w : *glass phase*
- High C_w alte: *gel transition*



Wang et al.,
J. Chem. Phys. 140
(2014)