Rheology of gels

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Rheology can be used to detect phase transition phenomena

- Polymeric materials relax with a broad spectrum of relaxation modes
- Extra long relaxation modes arise from large scale, supermolecular structures which are formed due to phase transitions
- Examples:

  Flow-induced crystallization

  Liquid crystals

  Electrorheological fluids

  Gelation → Classification

  Microstructure

  Rheological characterization

Classification - 1

- There is no simple and unique definition of the *gel* state
  - Gels are mainly constitued by a fluid, yet they retain their shape (solid-like behavior)
  - As opposed to ordinary solids, gels can support large strains to a high elastic limit in response to small stresses
  - Retention of shape implies some connectedness throught the system

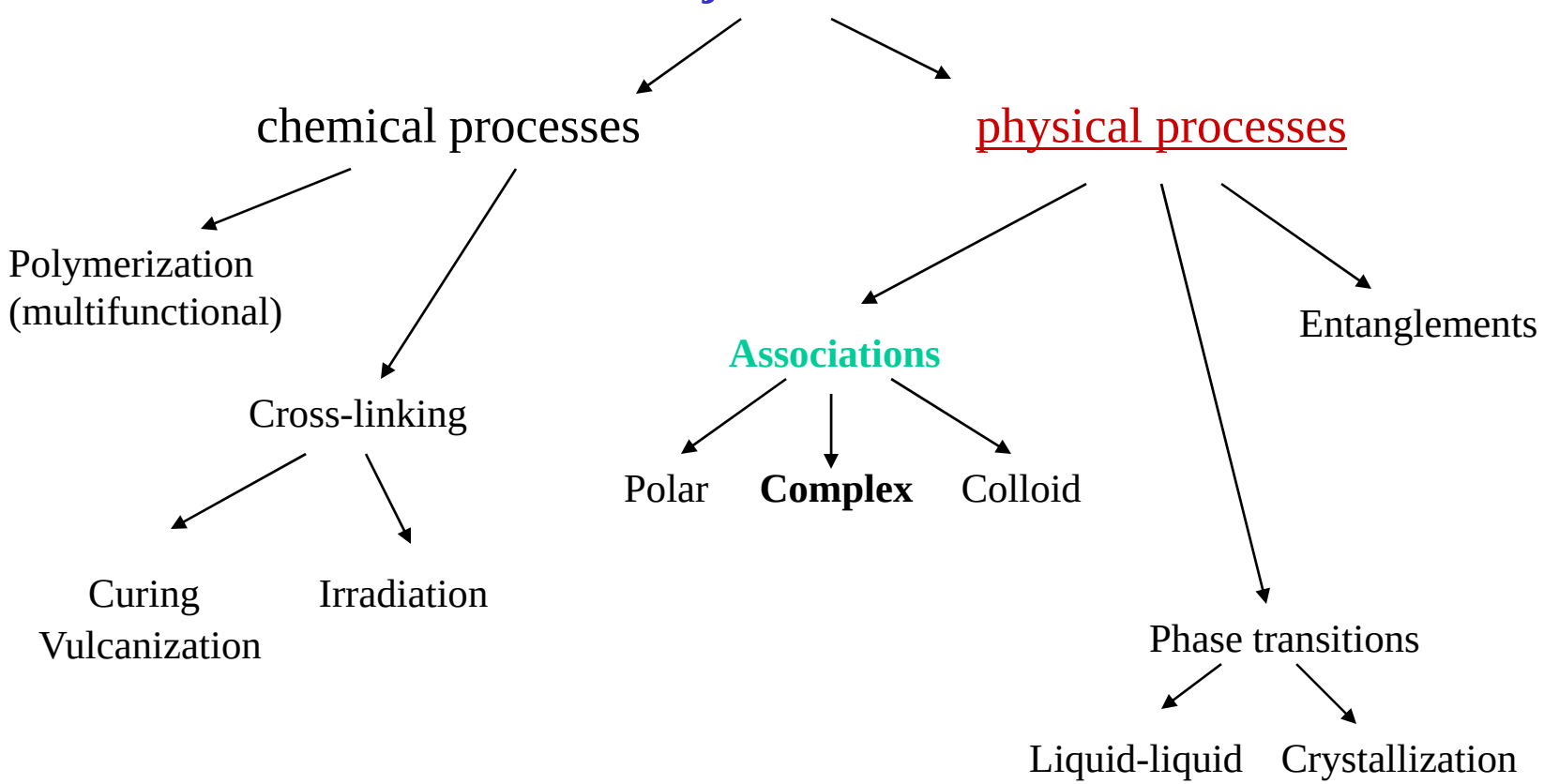
Existence of a **network**

- The connecting elements of the network can be individual chain molecules (polymer gels) or larger assemblies of molecules (colloidal gels)

- Wide range of applications: lubricants, cosmetics, food products...

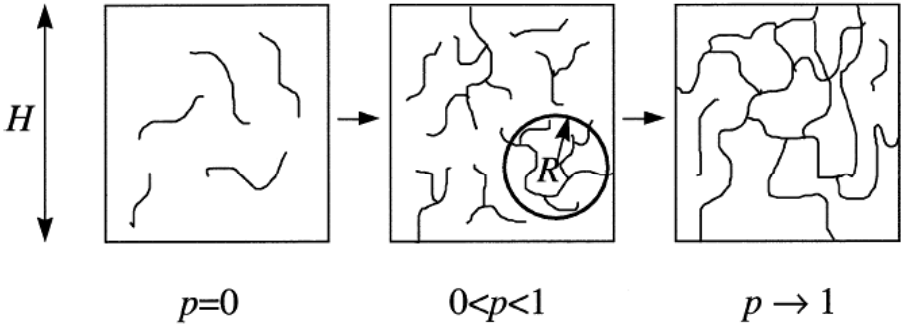
Classification - 2

Gels can be classified according to the processes creating **junctions**



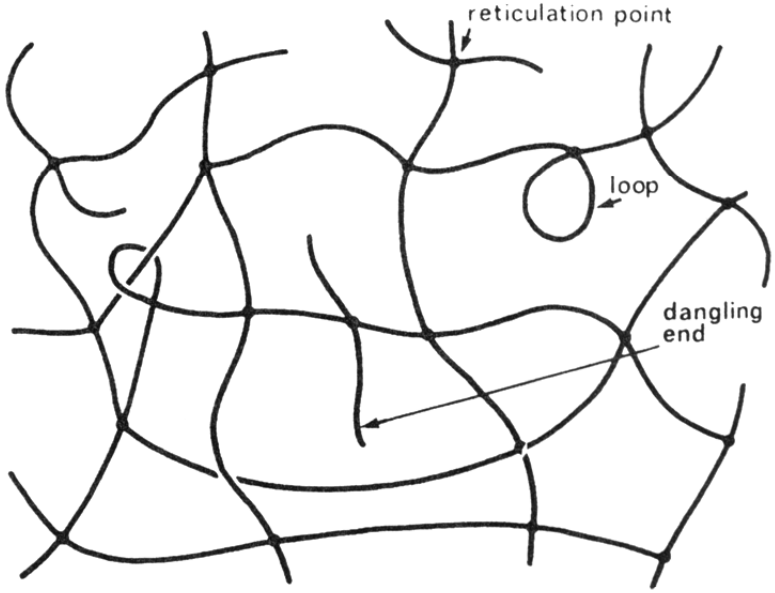
Structure

Cluster growth during crosslinking



Critical gel

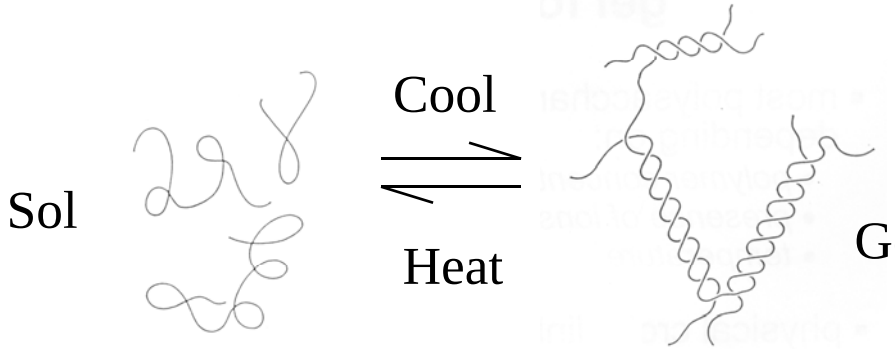
Polymer gel network



Branching or multifunctionality

Example of physical gelation by complex associations:

Coil-to-helix transition



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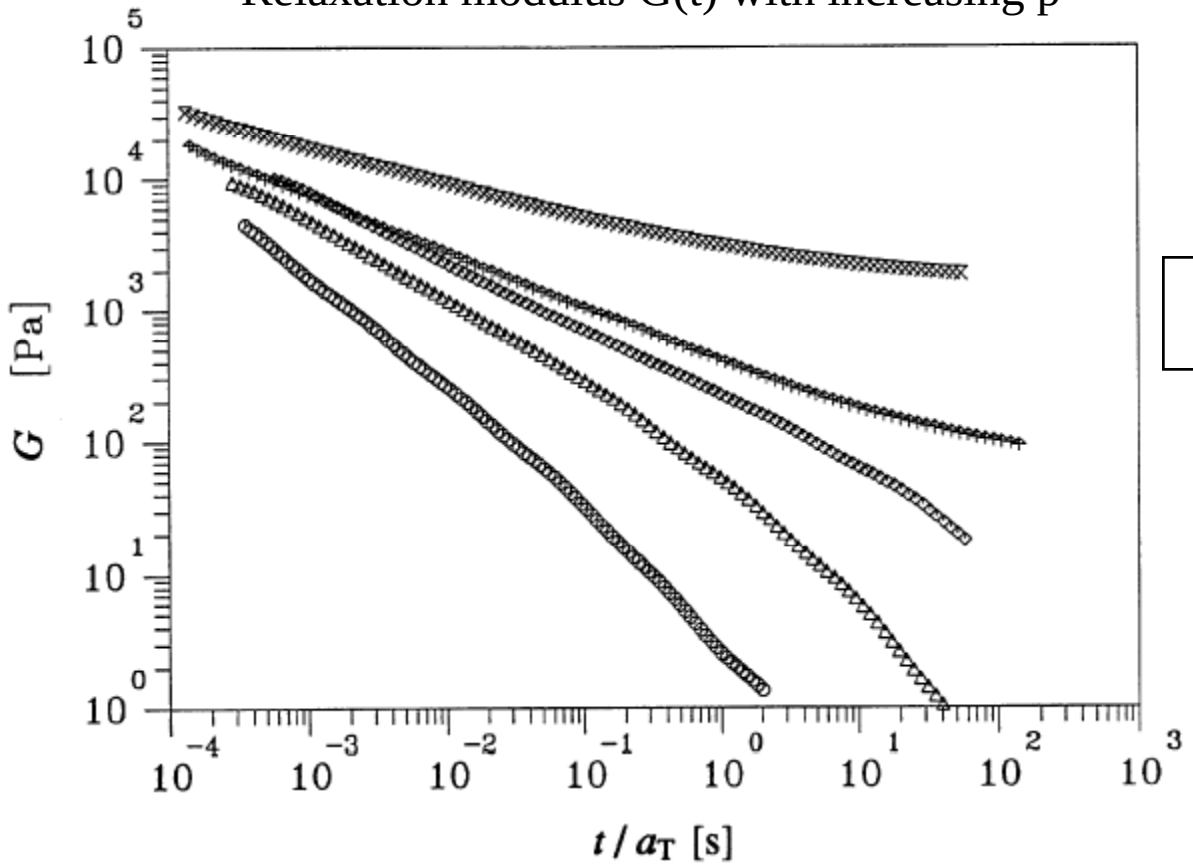
Rheological observations of the sol-gel transition

Relaxation modulus G(t) with increasing p



Step shear strain experiment

PDMS sample (Chambon and Winter, 1986)

At the gel point

$$G(t) = St^{-n} \qquad \text{for} \qquad \lambda_0 < t < \infty$$

Power law behavior (rheology probes self-similar regions of the critical gel)

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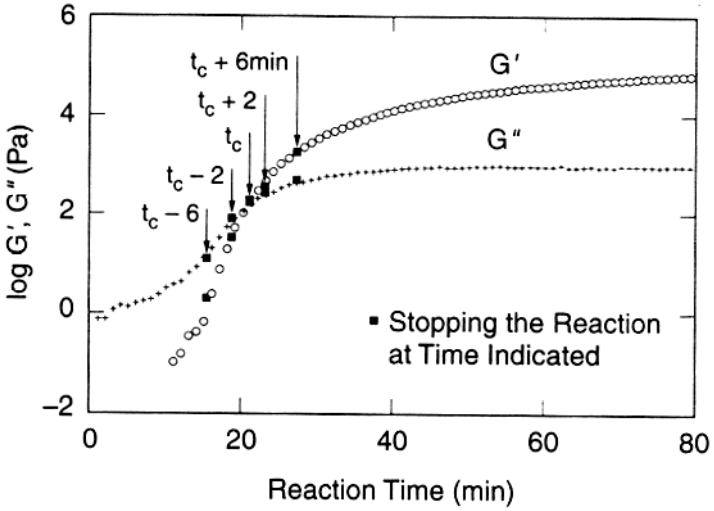
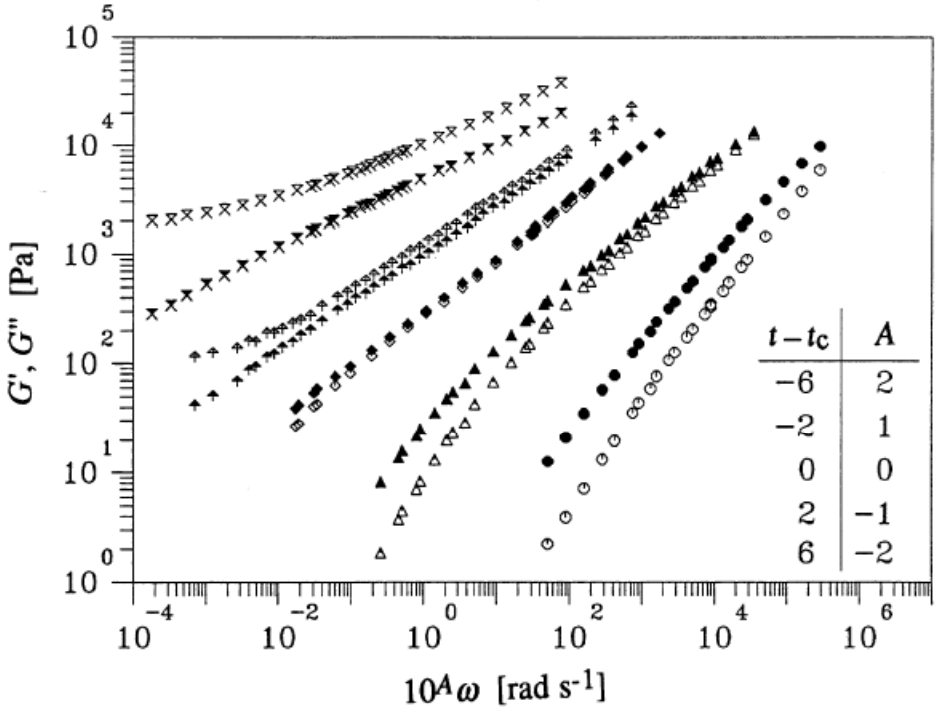
Rheometry near the gel point

Crosslinking stopped at intermediate states with a catalyst poison



t_c = gel point

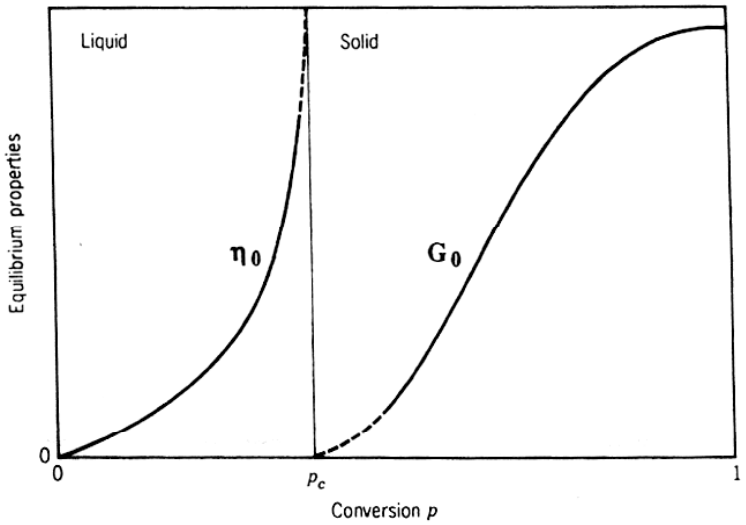
Dynamic tests on partially crosslinked samples



Detection of the critical point - 1

- Diverging rheological properties

  Data extrapolation is needed

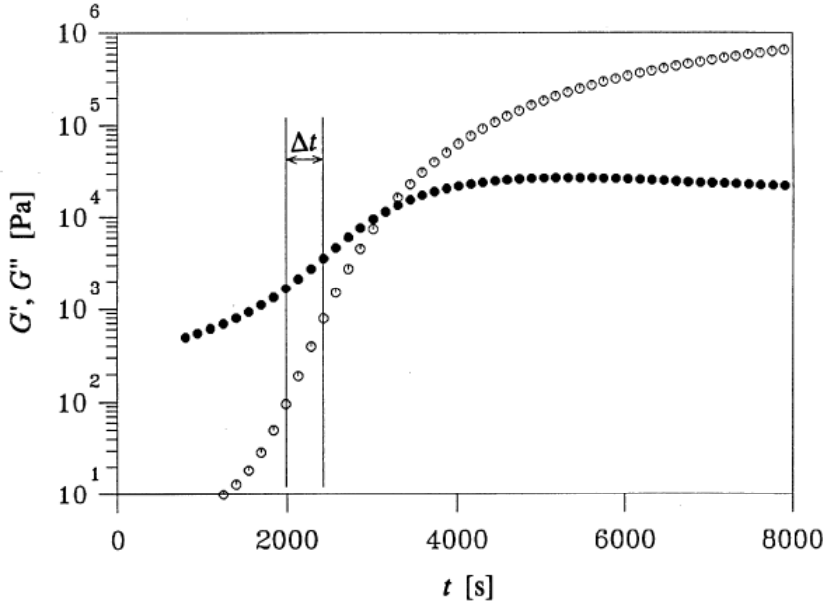


$$G_0 = \nu kT$$

Modulus of fully cured elastic solid

- Cross-over of G' and G''

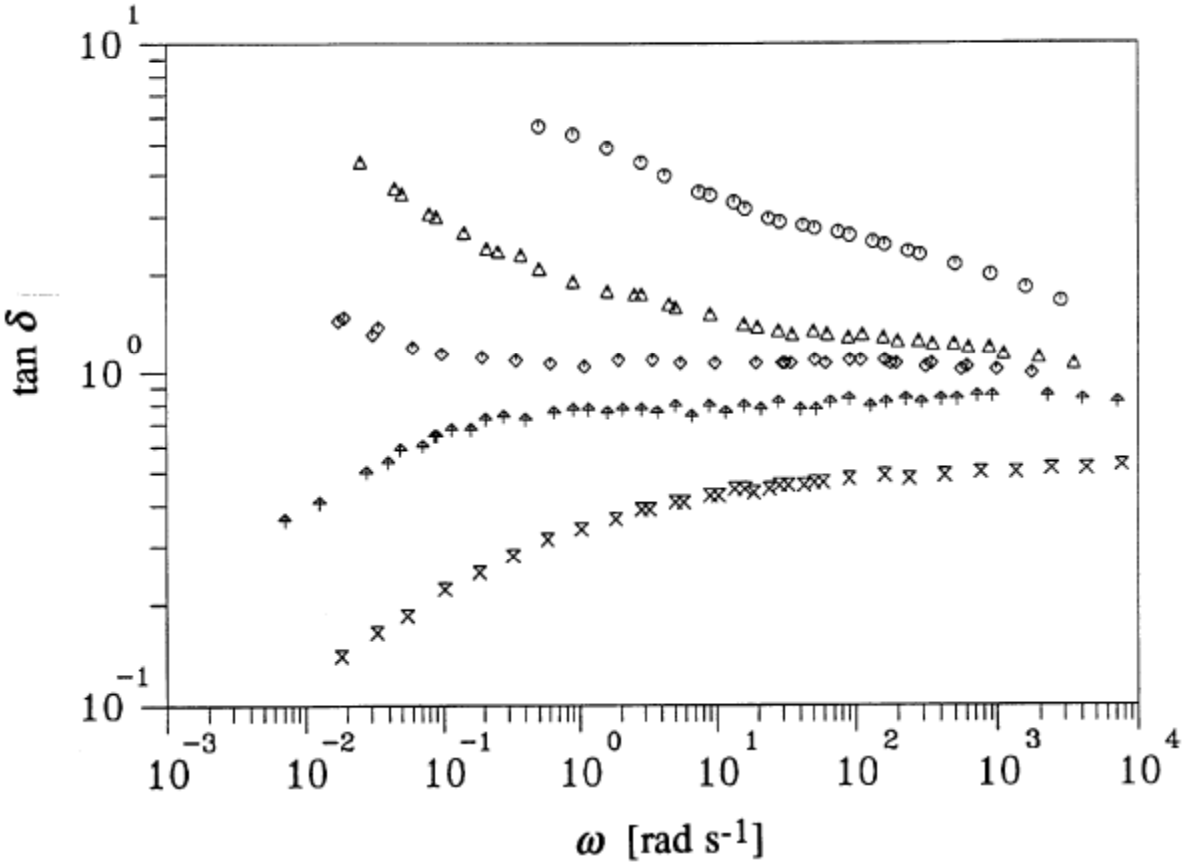
  Results are dependent on the probing frequency



Detection of the critical point - 2

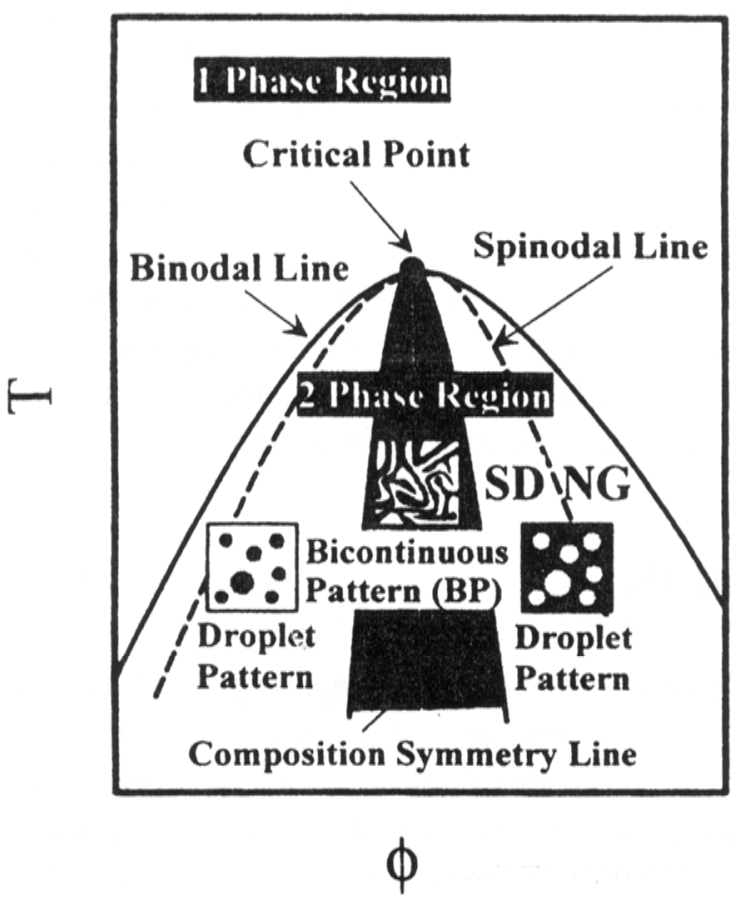
- Winter and Chambon method

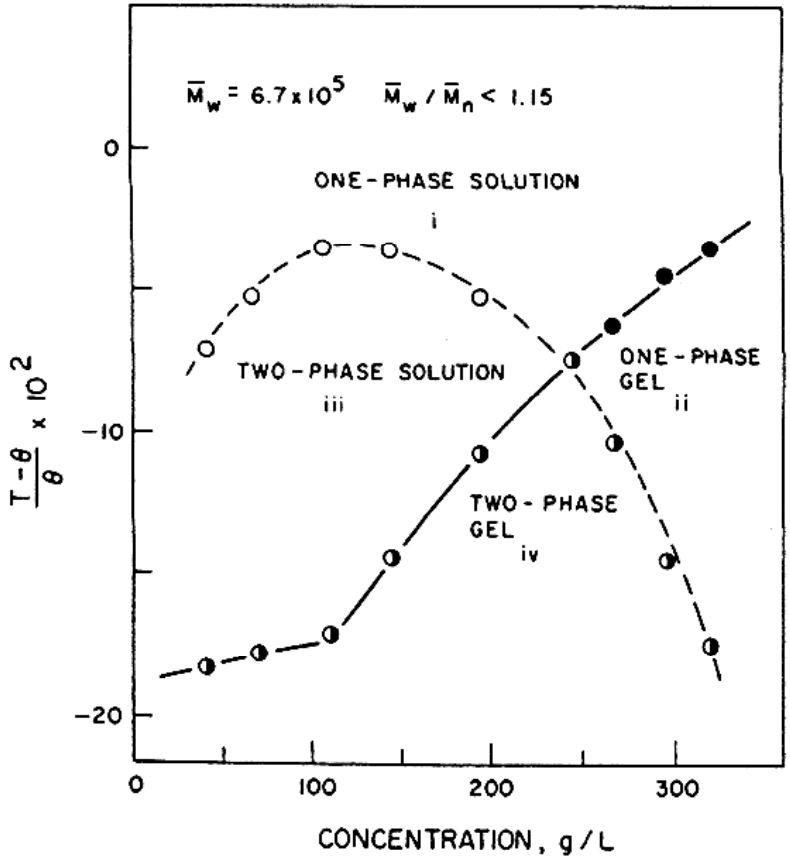
At the gel point tan δ is independent of frequency



Physical gels

Gelation and phase separation





Rheological characterization - 1

Case study: **gelatin gels**

- Gelatin is obtained from hydrolitic degradation of collagen (rupture of triple-helix structure)

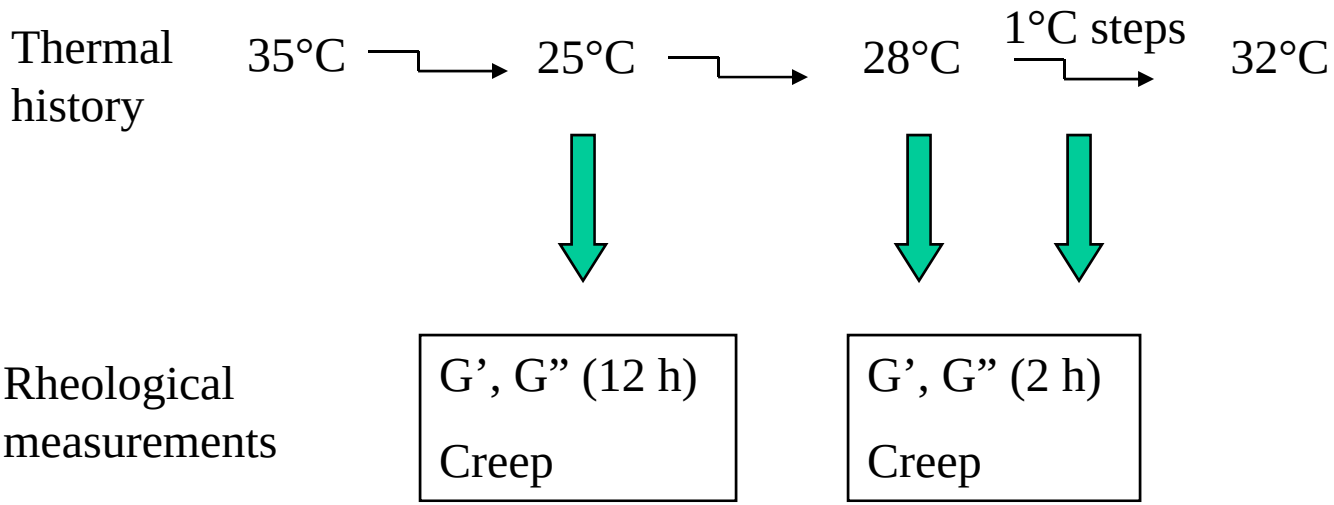
- Gelation mechanism: helix binding (thermoreversible)

- Melting point of gelatin gels depends on concentration, pH, ionic strenght

Rheological characterization - 2

Description of experimental protocol

- Sample: 3 wt% gelatin solution in H_2O
- Sample sealed with silicone oil



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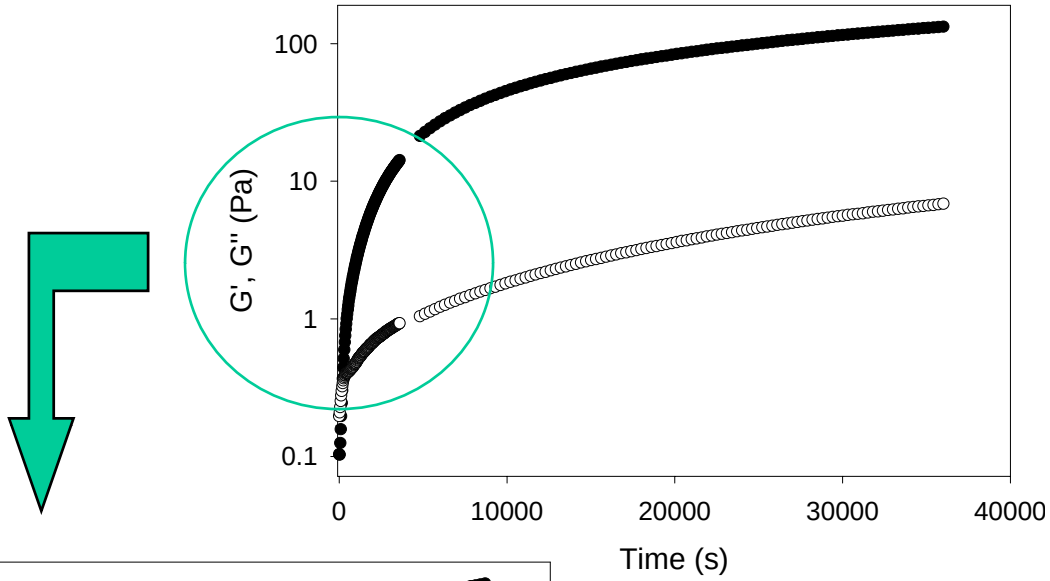
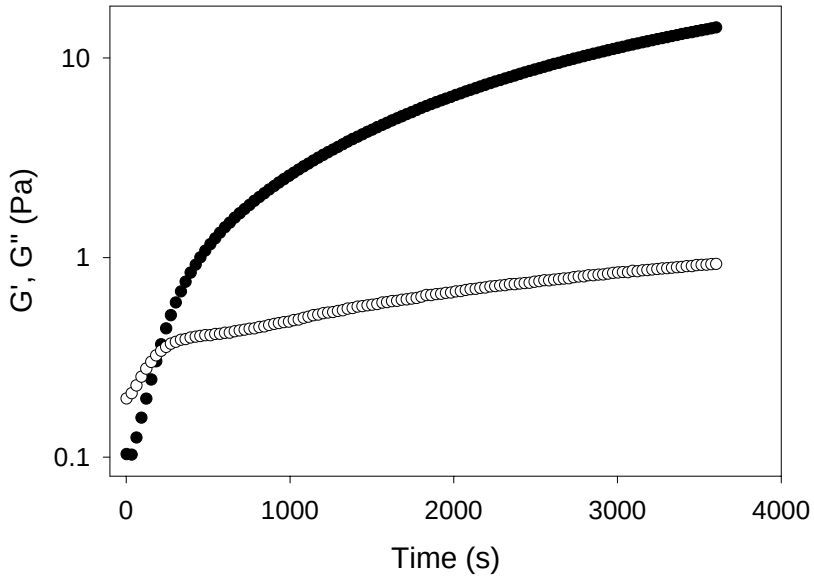
Rheological characterization - 3





3 wt% gelatin solution in H_2O

T = 25°C

Time	1st h	subsequent 11 h
Stress	2 Pa	10 Pa

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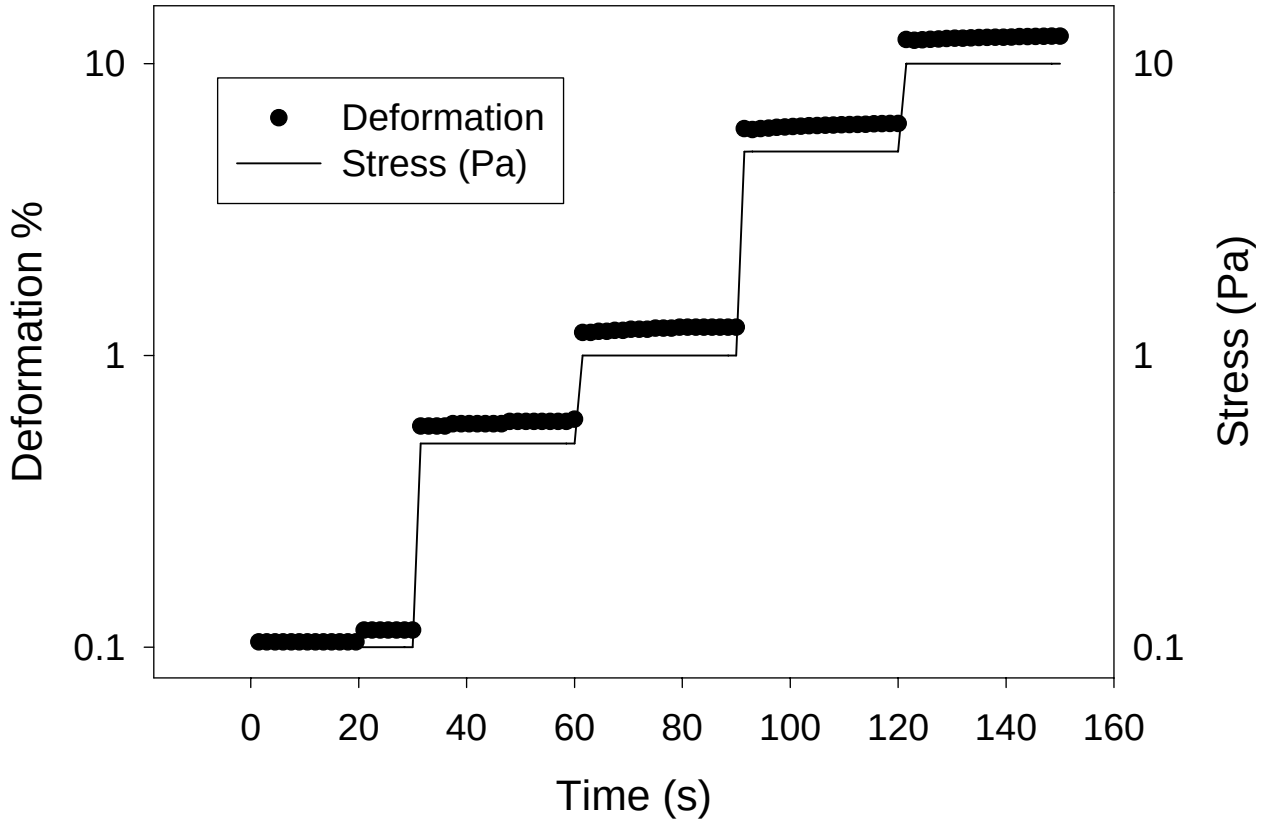
Rheological characterization - 4

3 wt% gelatin solution in H_2O

Creep 0.1 - 10 Pa T = 25°C



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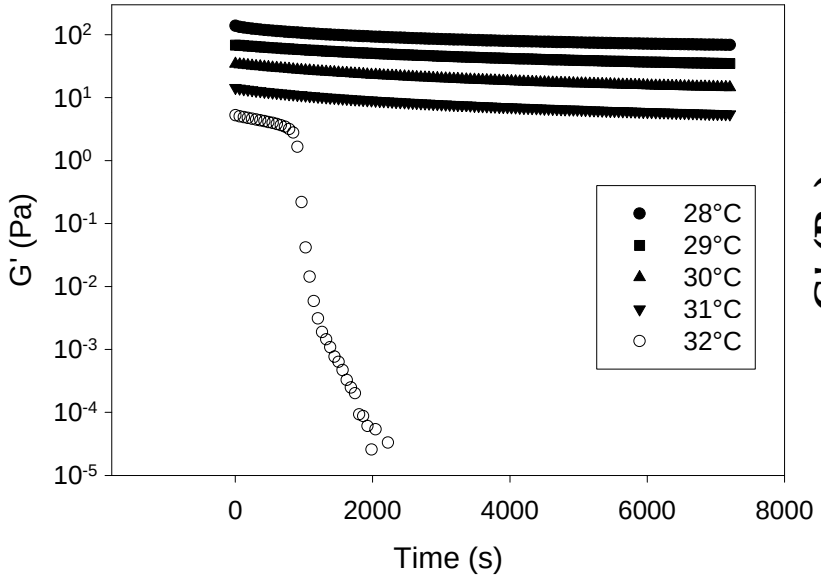
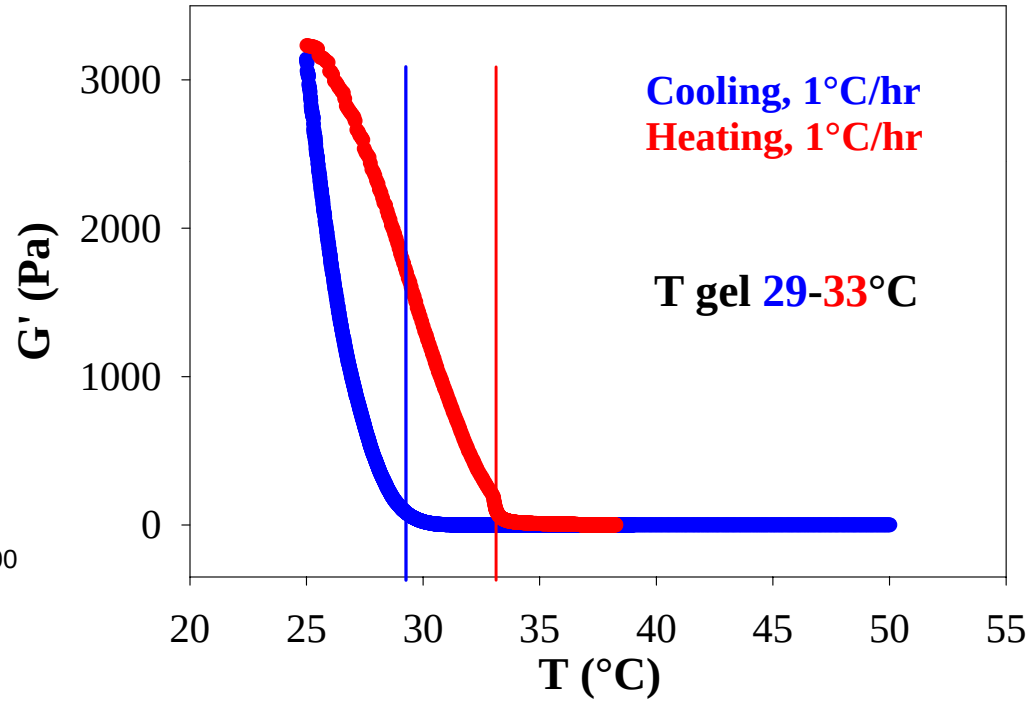
Rheological characterization - 5

3 wt% gelatin solution in H_2O

G' vs time at 5 temperatures from 28°C to 32°C

Determination of gel point





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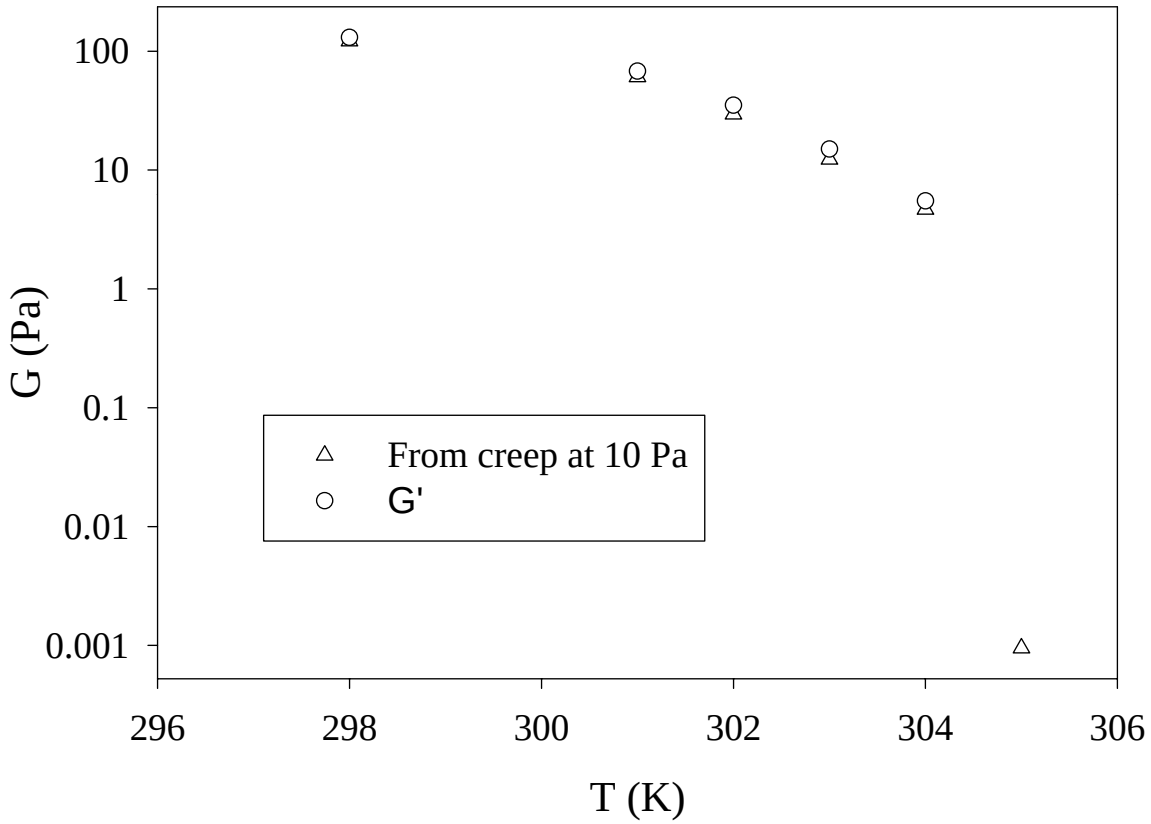
Rheological characterization - 6

3 wt% gelatin solution in H_2O

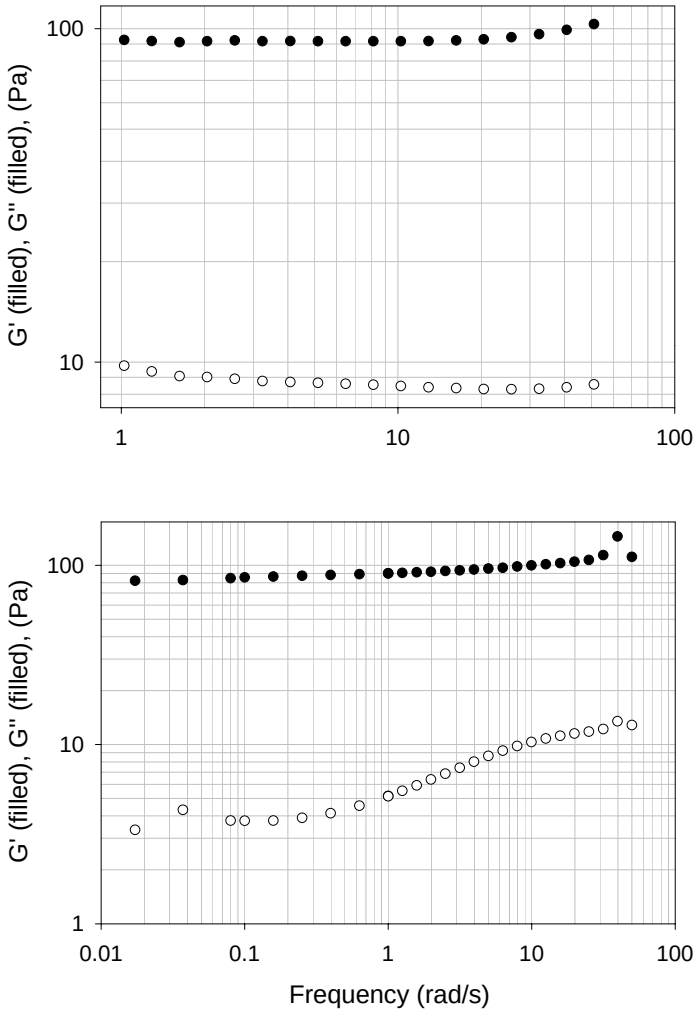
Comparison of G from oscillatory and creep data



Rheological characterization - 7

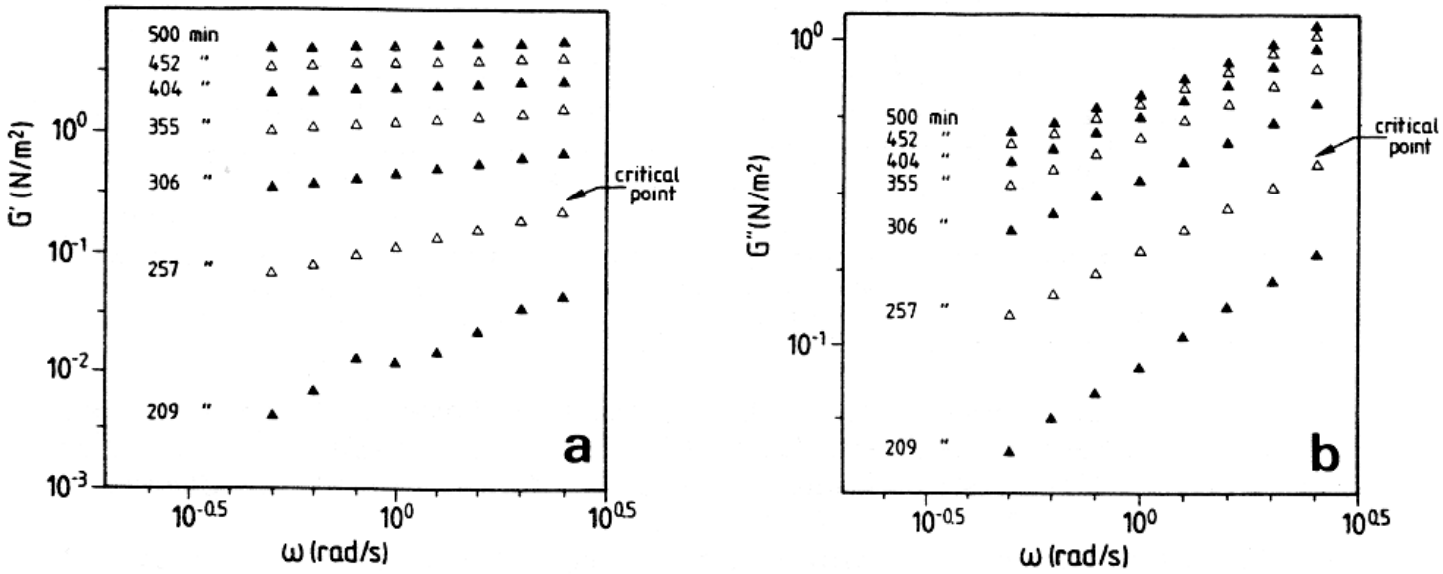
3 wt% gelatin solution in H_2O

G’ and G” *vs* frequency



Rheological characterization - 8

Determination of gel point: application of the Winter and Chabon method

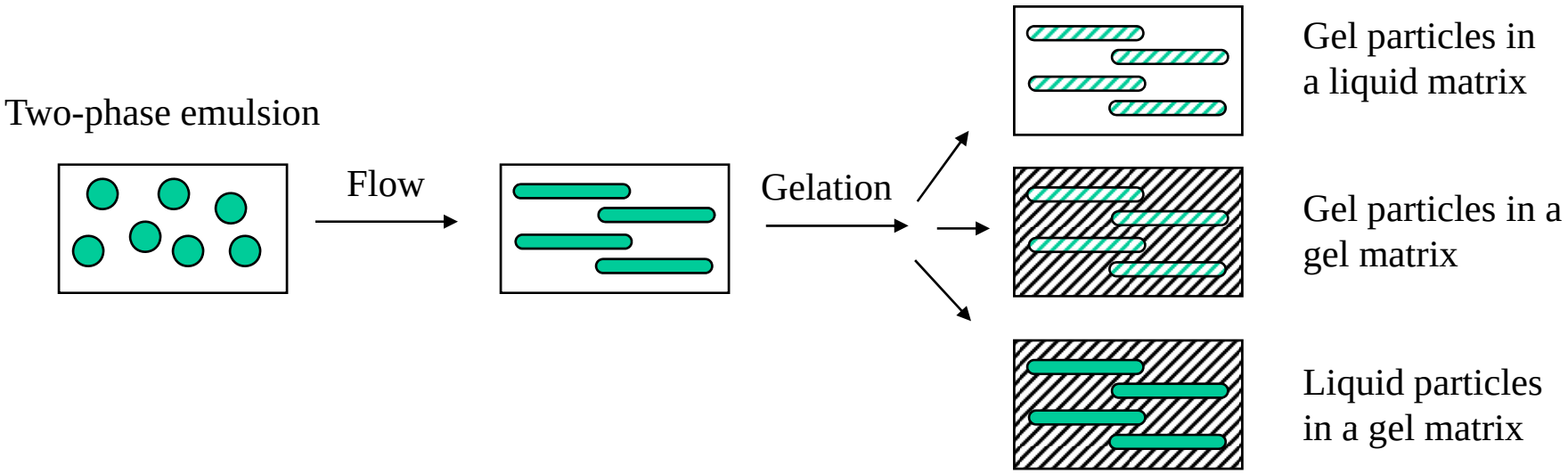


5% wt aqueous gelatin (Mw = 151 kg/mole) at 26°C

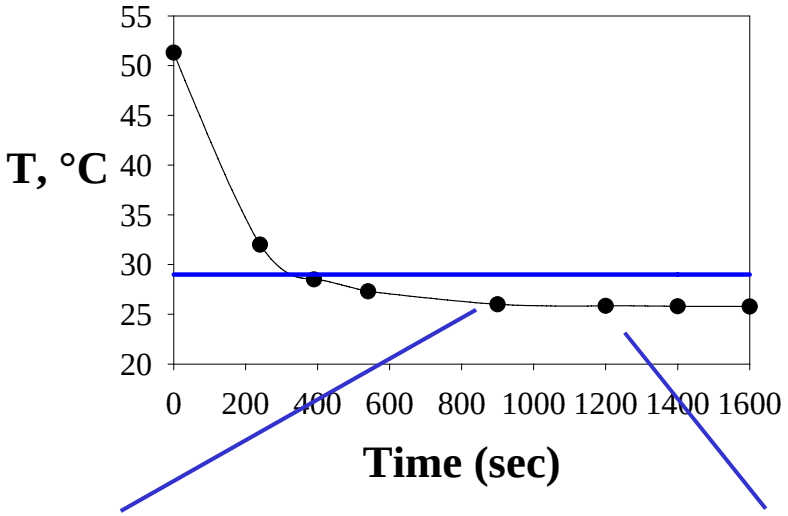
Emulsions with a gelled phase - 1

- Water-in-water emulsions
  - Biphasic aqueous mixtures of protein and polysaccharide
  - Used in low-fat food products as fat substitutes
  - Examples: Gelatin/maltodextrin, Gelatin/dextran, Na-caseinate/Na-alginate

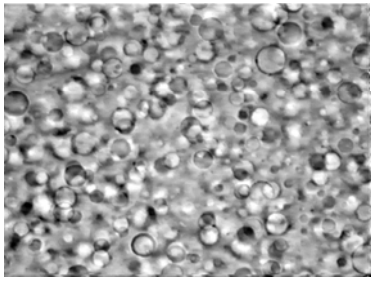
- Flow-induced microstructure can be “freezed” by gelation

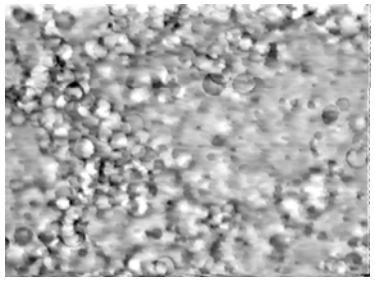


Emulsions with a gelled phase - 2

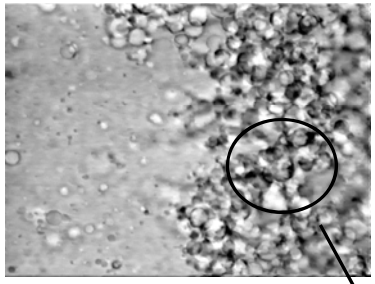


Aqueous mixture of gelatin and dextran
Quench experiment during shear flow
T gel = 29 °C

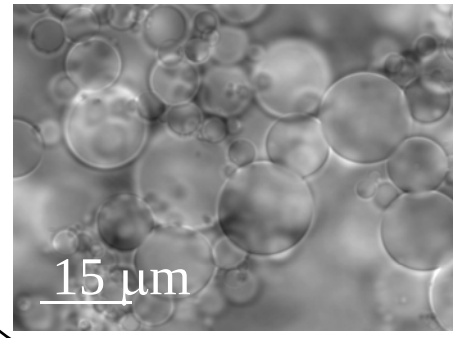




Partial coalescence

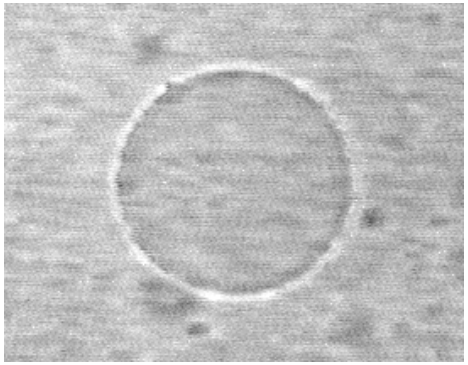


Clusters

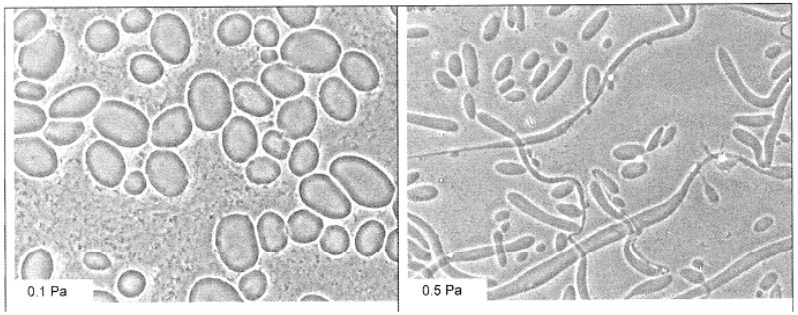


Emulsions with a gelled phase - 3

- Final morphology depends both on material properties and flow conditions



Gellan/ K-carrageenan (video)



Gellan/Na-alginate
(Wolf et al, 2000)