Computer simulations of gel-formation via catalytic reaction

Walter Kob

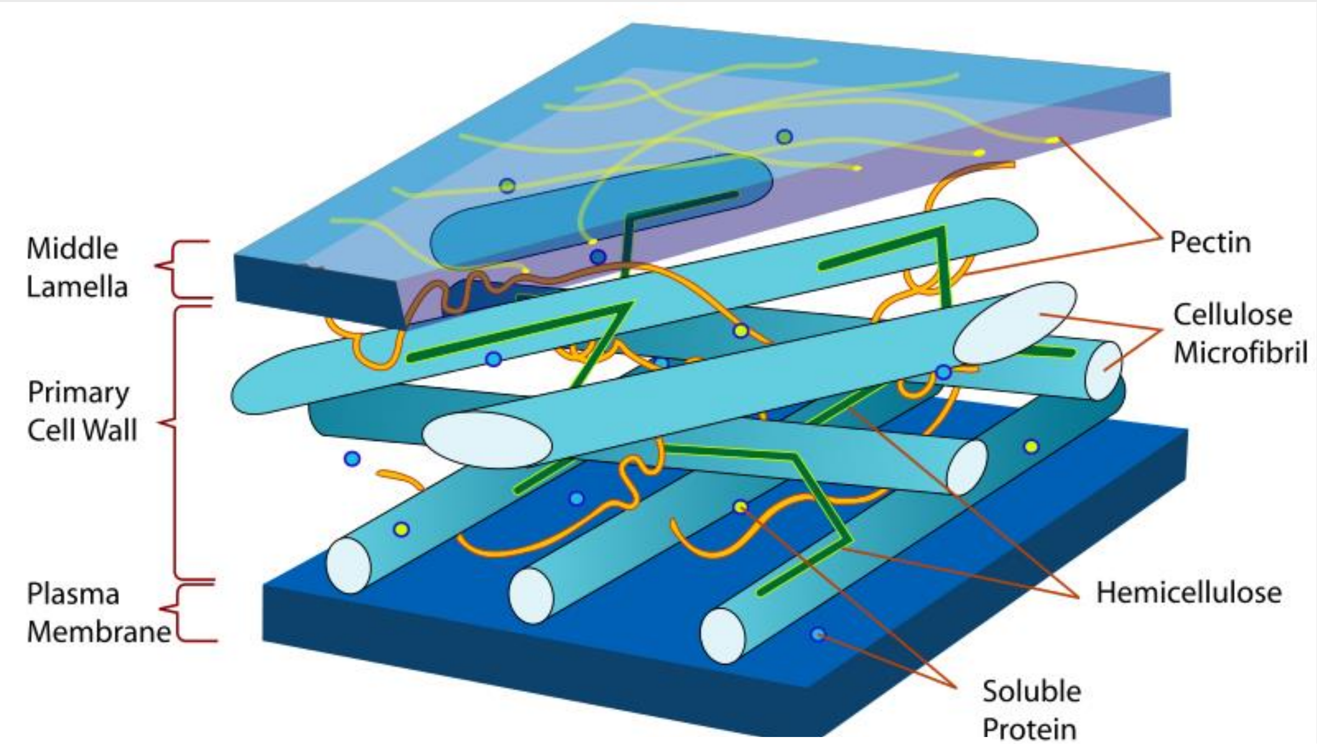
In collaboration with: Virginie Hugouvieux (INRA)

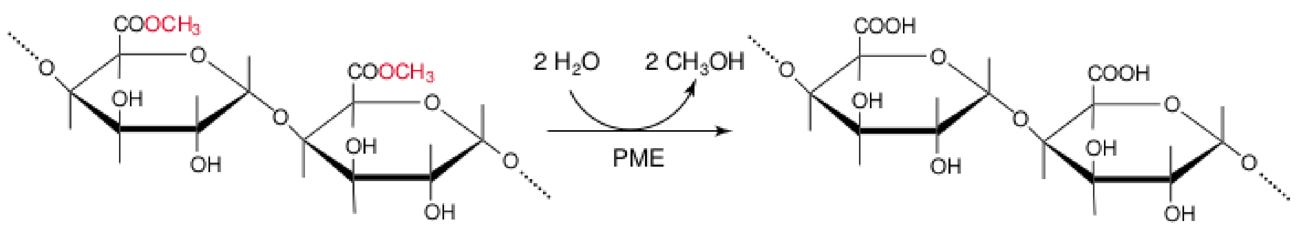
University of Montpellier
France

Correlation and Disorder
ICTS, Bangalore
29 May – 2 June, 2017

Motivation: Rigidity of Plant Cells

- Pectin: Longish polymer that is an important building block of the wall of plant cells

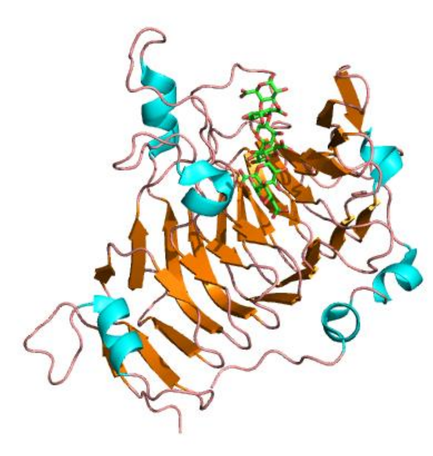




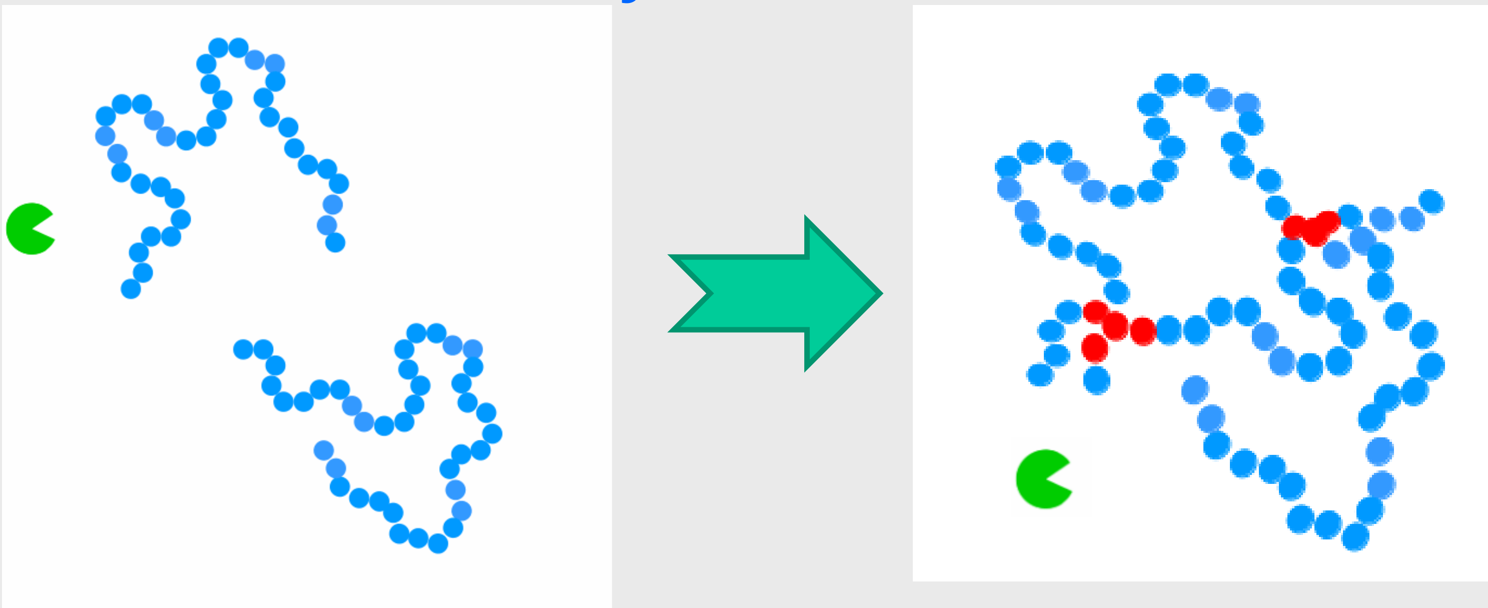
TRENDS in Plant Science

Pectin methylesterase (enzyme)

Makes that the groups of the polymer become attractive
⇒ Formation of a gel ⇒ stability of the cell



The Physicists Cartoon



Model

- Polymers: Chains of soft-spheres , $V(r)=r^{-12}$, (A particles) + FENE potential
- Colloids: Soft spheres with diameter 2 times the one of monomers
- Reaction: If a colloid comes sufficiently close to a monomer, it transforms the monomer from a soft sphere to a Lennard-Jones particle (B particles) $\Rightarrow$ attraction
- Length of chains=100; 408 chains; molecular dynamics

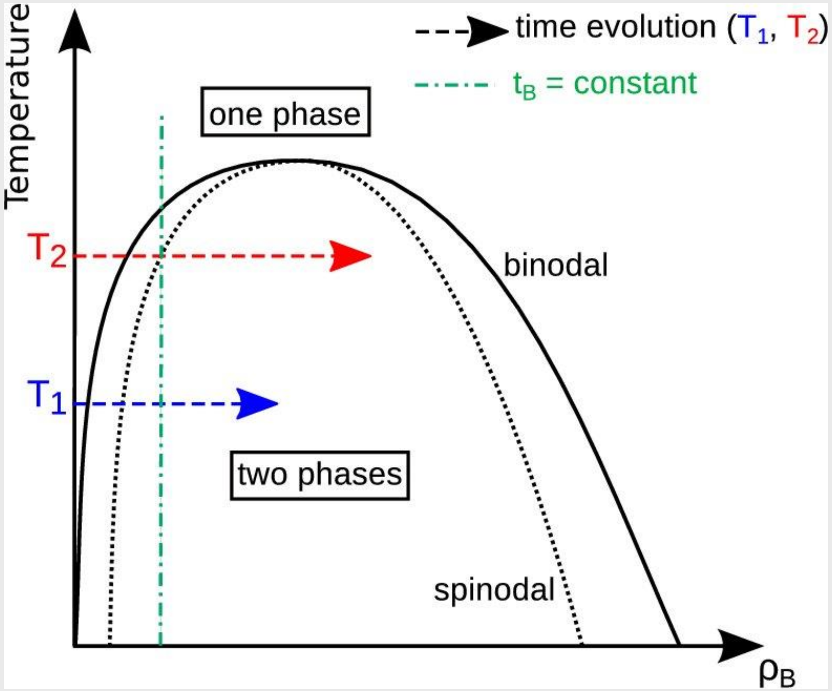
What to expect

- Due to the conversion of A particles (purely repulsive) into B particles (have mutal attraction), the effective attractive interaction between the polymers increases with time:

- Short times: Very few B particles $\Rightarrow$ gas of B particles (in a sea of A particles); homogeneous

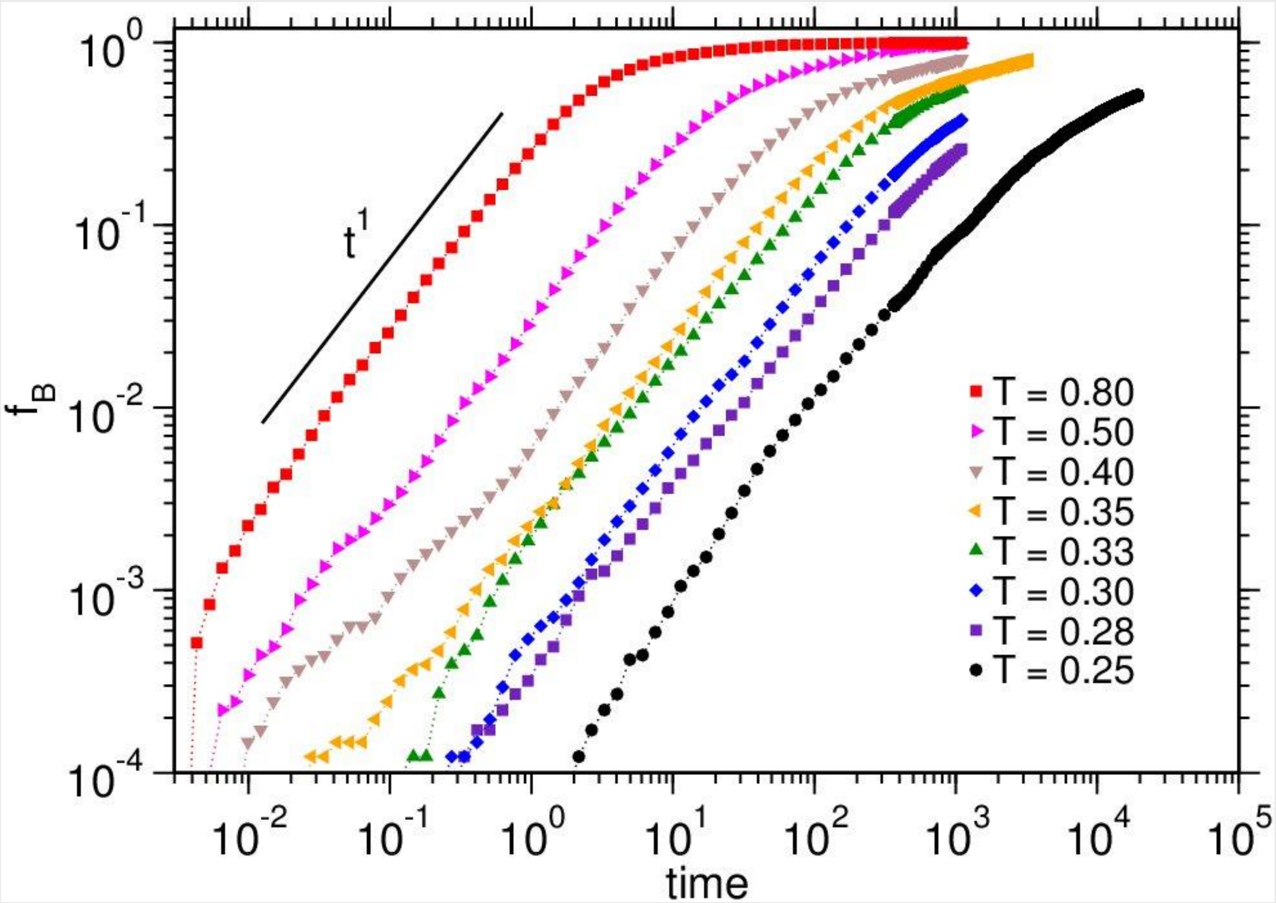
- Increasing time: Number of B particles increases and system enters in coexistence region $\Rightarrow$ will start to phase separate into B rich and B poor phase

- Large times: System wants to phase separate completely but might be hindered because of slow dynamics, i.e. it will form a gel (=disordered structure)



Number of B particles ⇒ Attraction

- f_B = fraction of B particles in the system = N_B/(number of monomers)

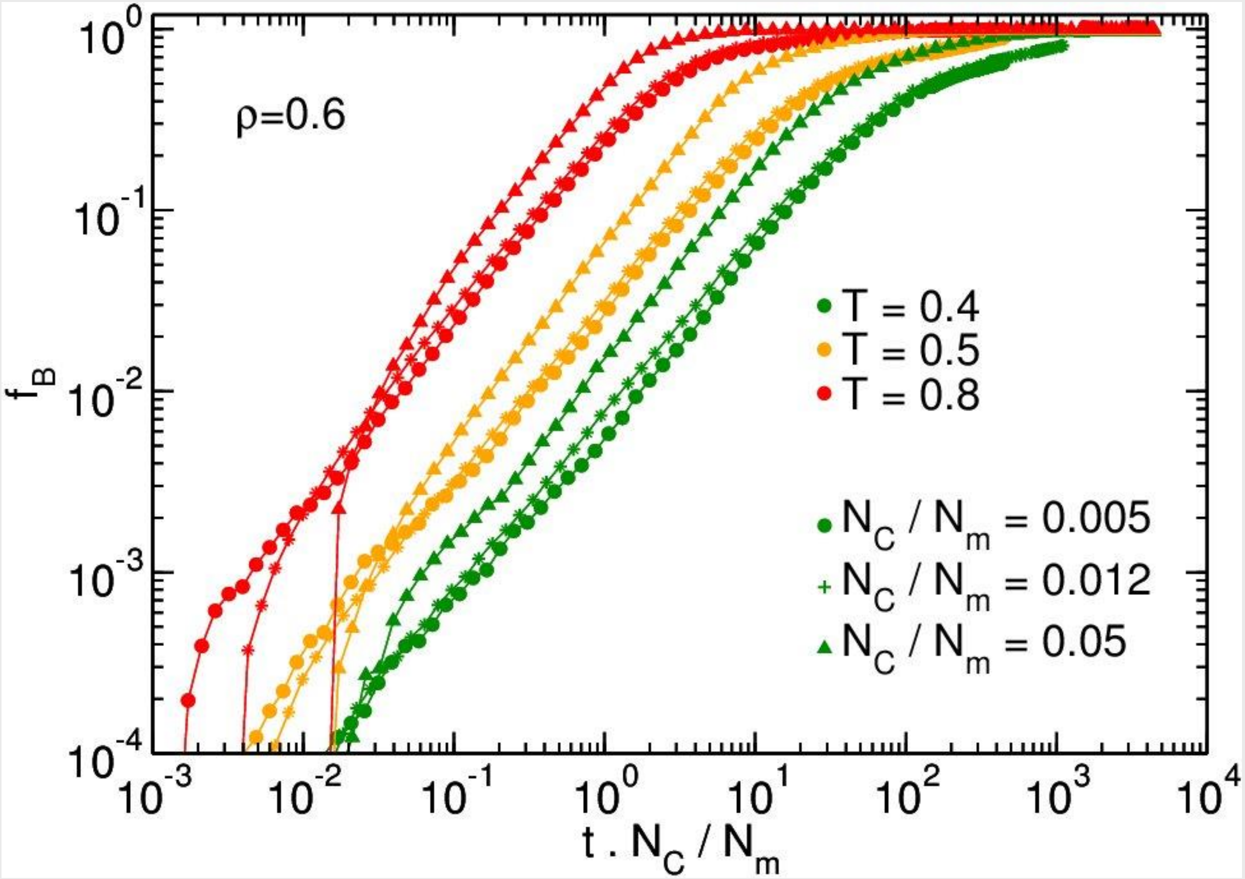


- Short and intermediate times: Linear time dependence
  ⇒ Colloids always find new A monomers that can be converted into B monomers
- Long times: Saturation: All A monomers have been converted into B particles
- Dynamics quickly slows down if T is decreased

Dependence on concentration of colloids

- How does the conversion speed depend on the concentration of colloids? If the colloids act independently, the relevant time scale is

  time · N_c / N_m

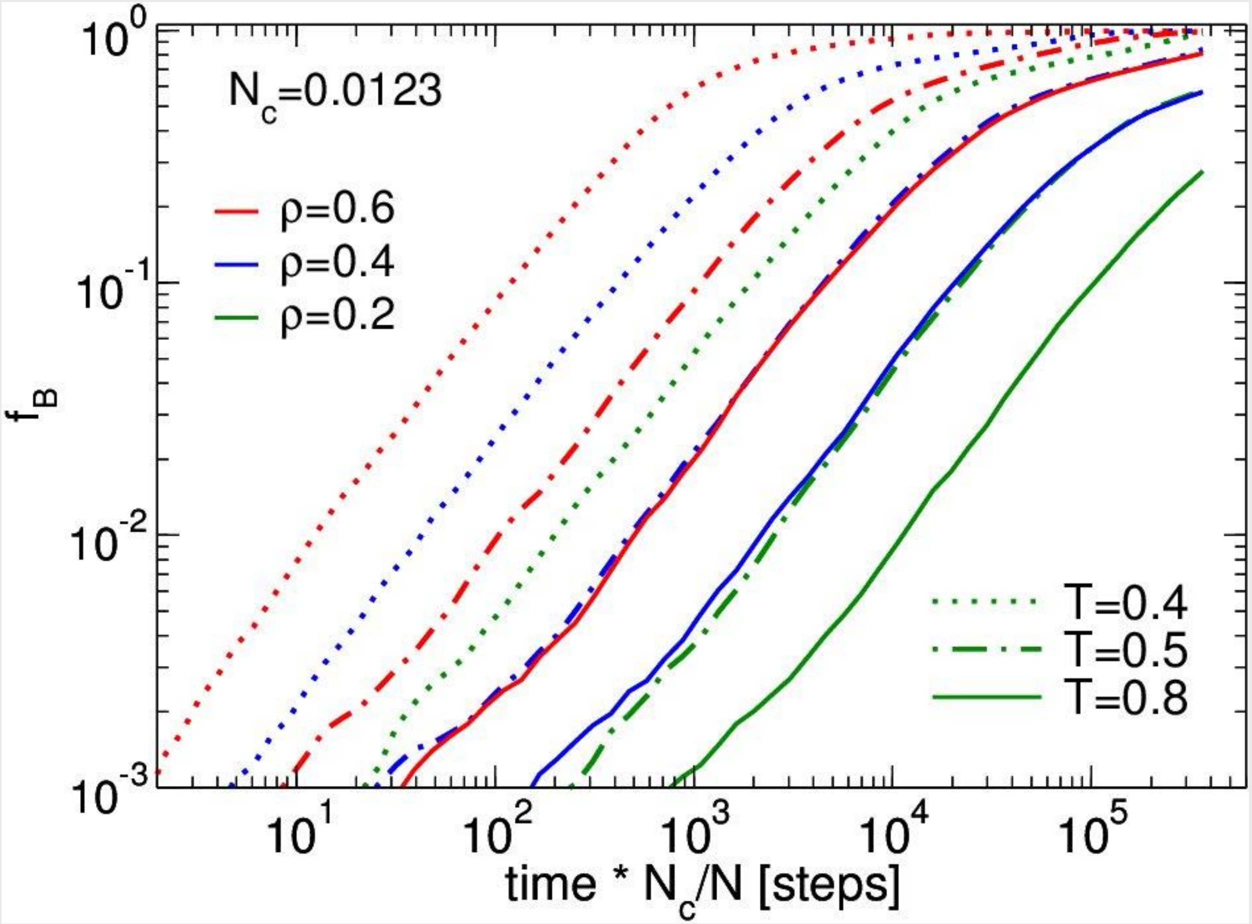


Master curve
⇒No strong dependence on concentration if conversion speed is measured in N_c / N_m and if concentration is small

In the following:
$N_c/N_m=0.01$

Different densities of the polymer melt

- How does the conversion speed depend on the density of the polymers?

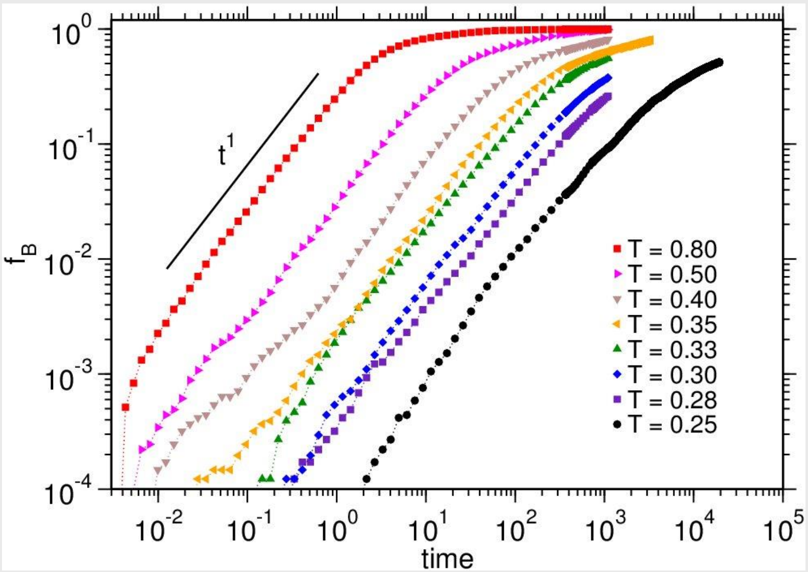


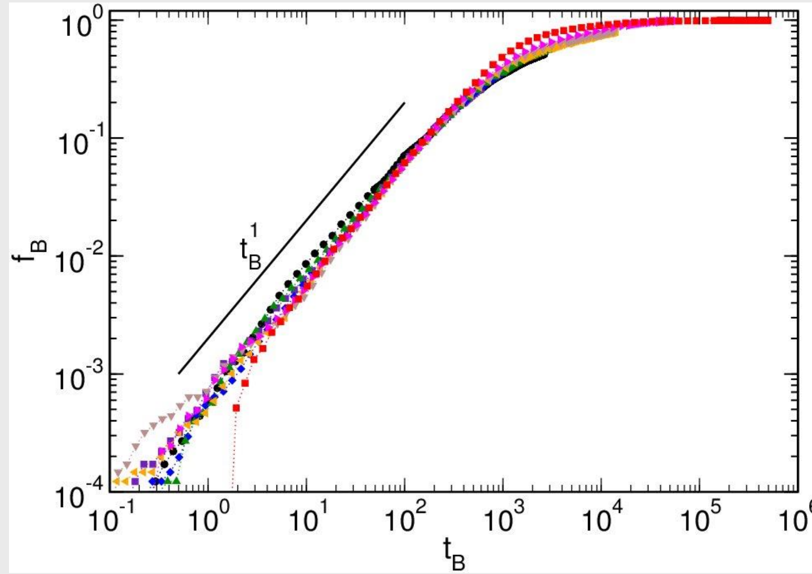
⇒ The higher ρ, the faster is the conversion (approx. exponential ρ-dependence)

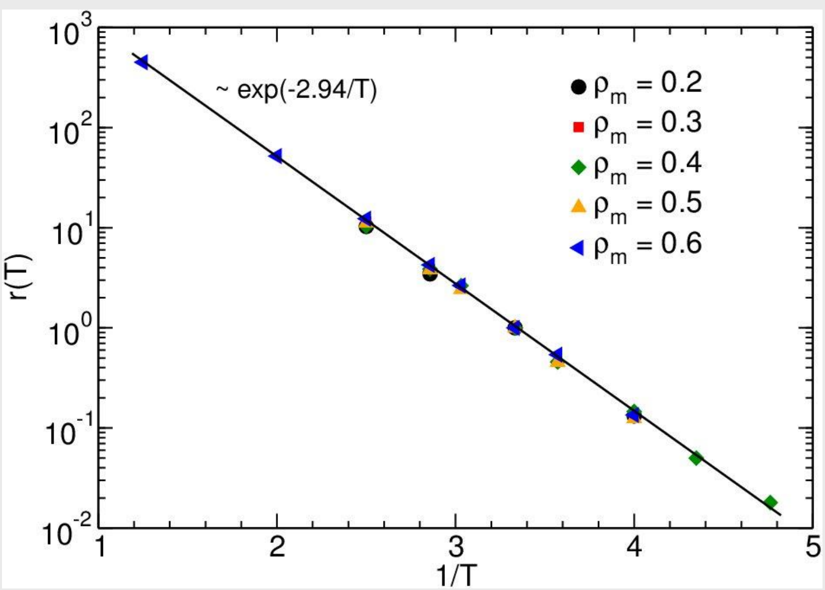
Influence of temperature

- Time dependence of f_B seems to be independent of temperature

  $\Rightarrow$ build master curve by introducing scaled time $t_b = r(T) \cdot t \cdot N_c / N_m$



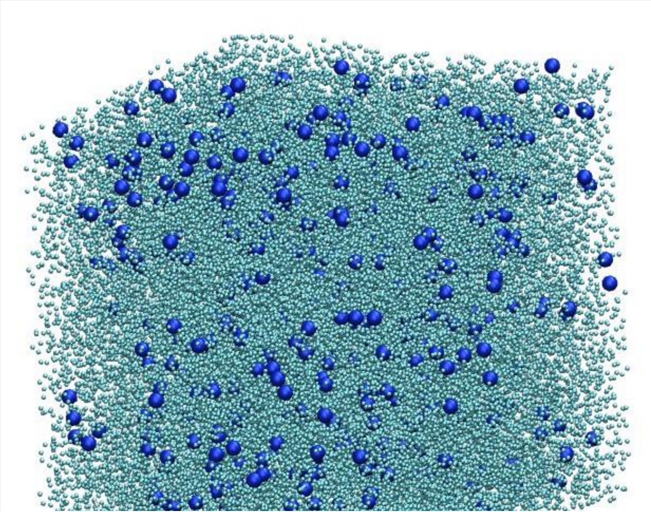




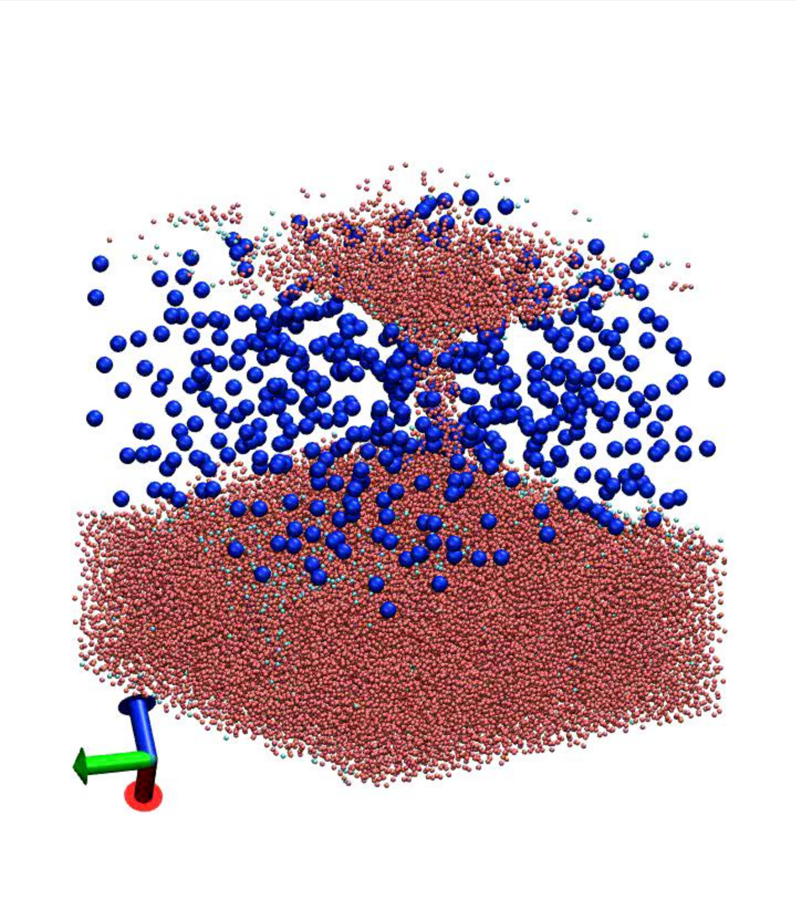
- Same $t_B \Leftrightarrow$ same number of B $\Leftrightarrow$ same thermodynamic driving force to make phase separation
- Scaling factor r(T) shows Arrhenius dependence on T
- Activation energy is just the barrier a colloid has to surmount to approach a A monomer to convert it into a B monomer (=2.77)

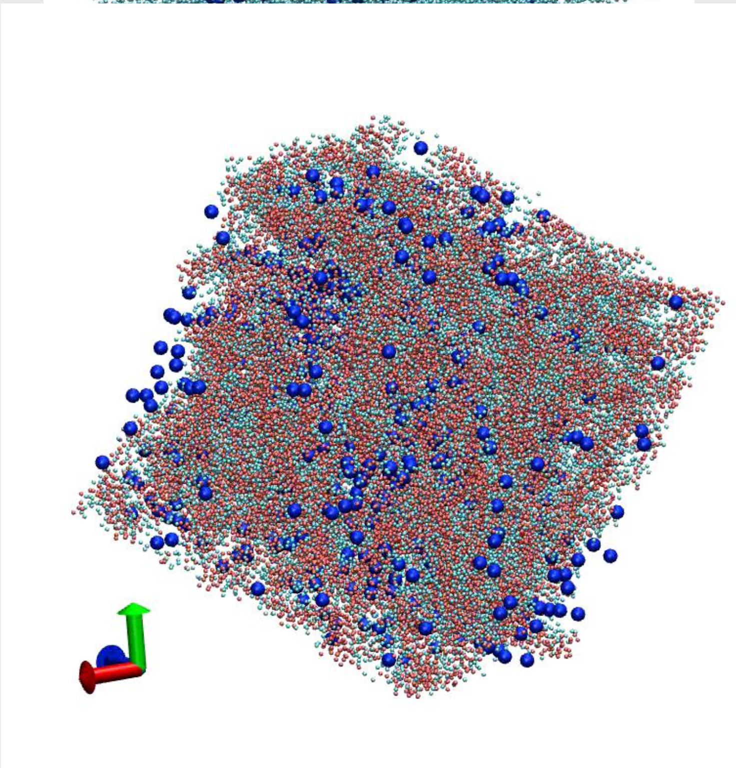
Snapshots

- Time evolution of the structure



- t=0; system made of on spheres) (li

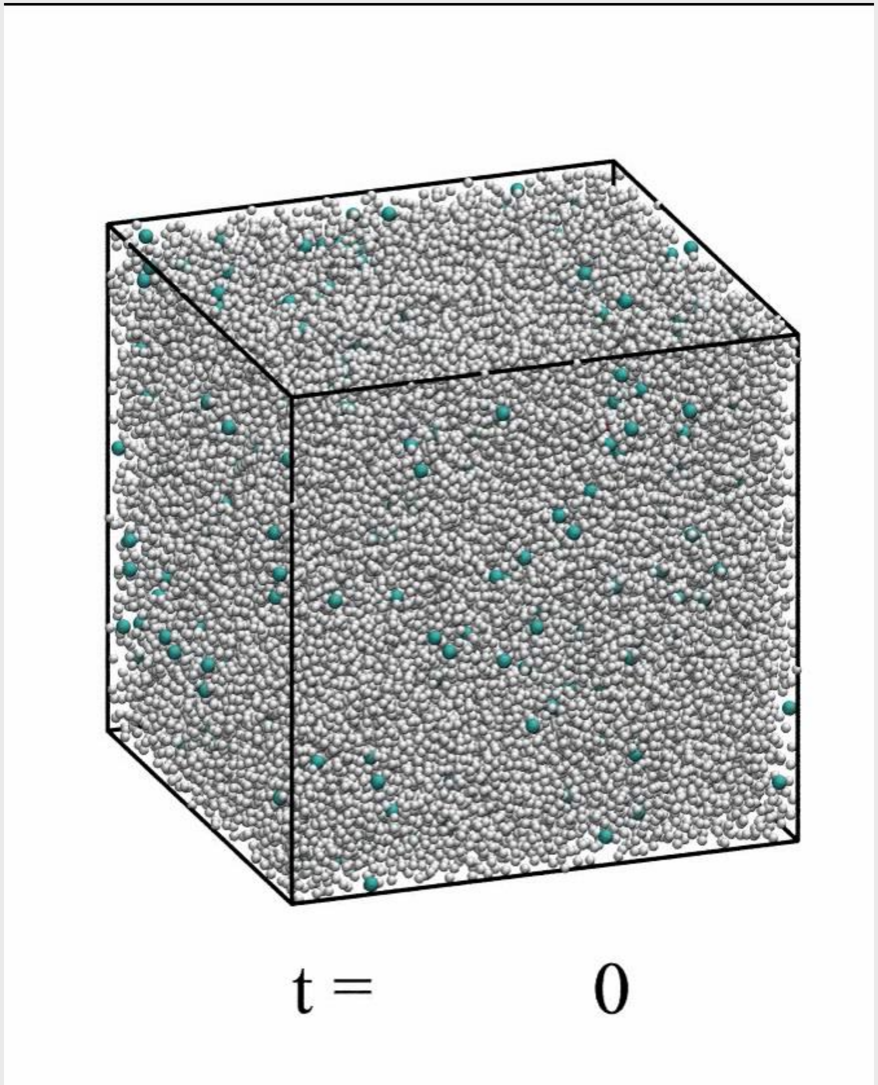


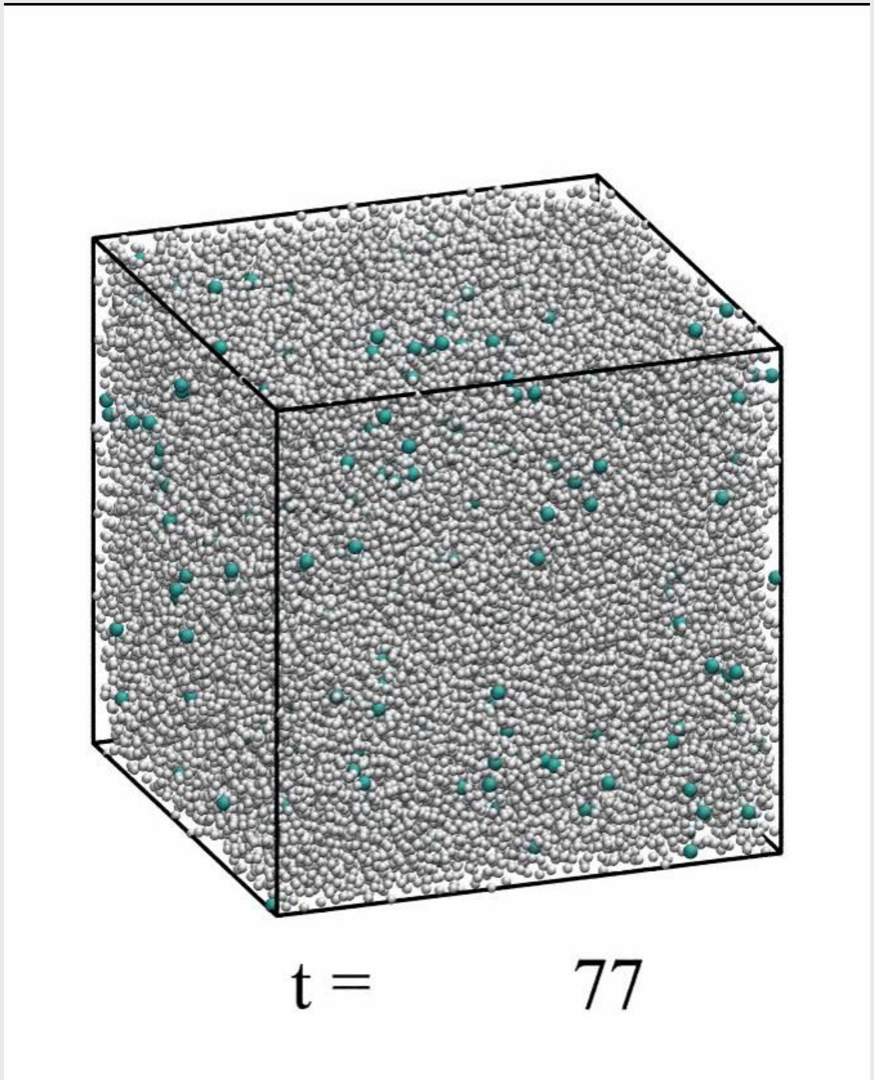


- High T: At large times the system undergoes a complete phase separation

- t large; system starts to become heterogeneous; chains are made of repulsive A particles and attractive B particles (red); presence of clusters of B monomers

Time dependence of the transformation

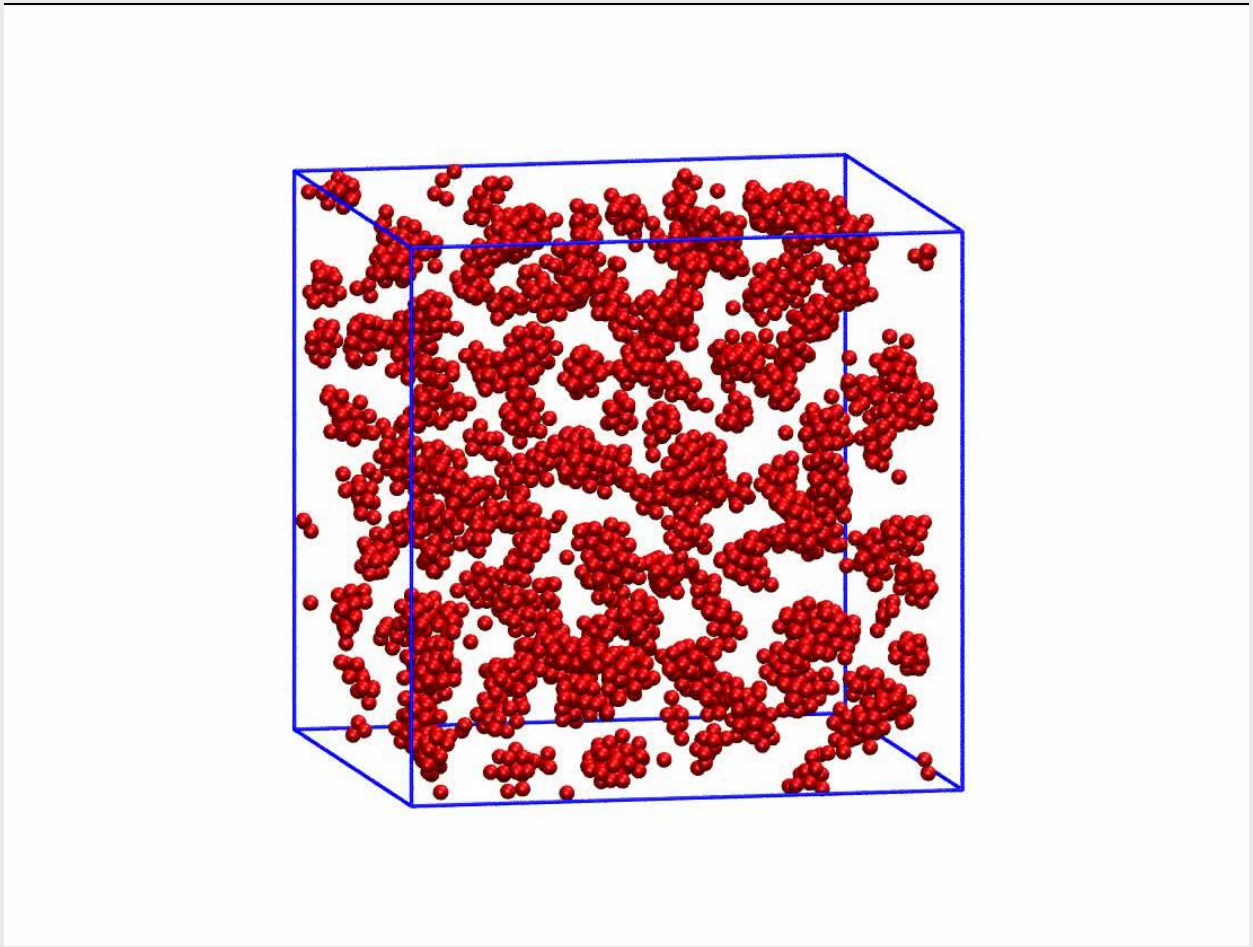




- T=0.4

- T=0.25

Cluster phase of attractive particles



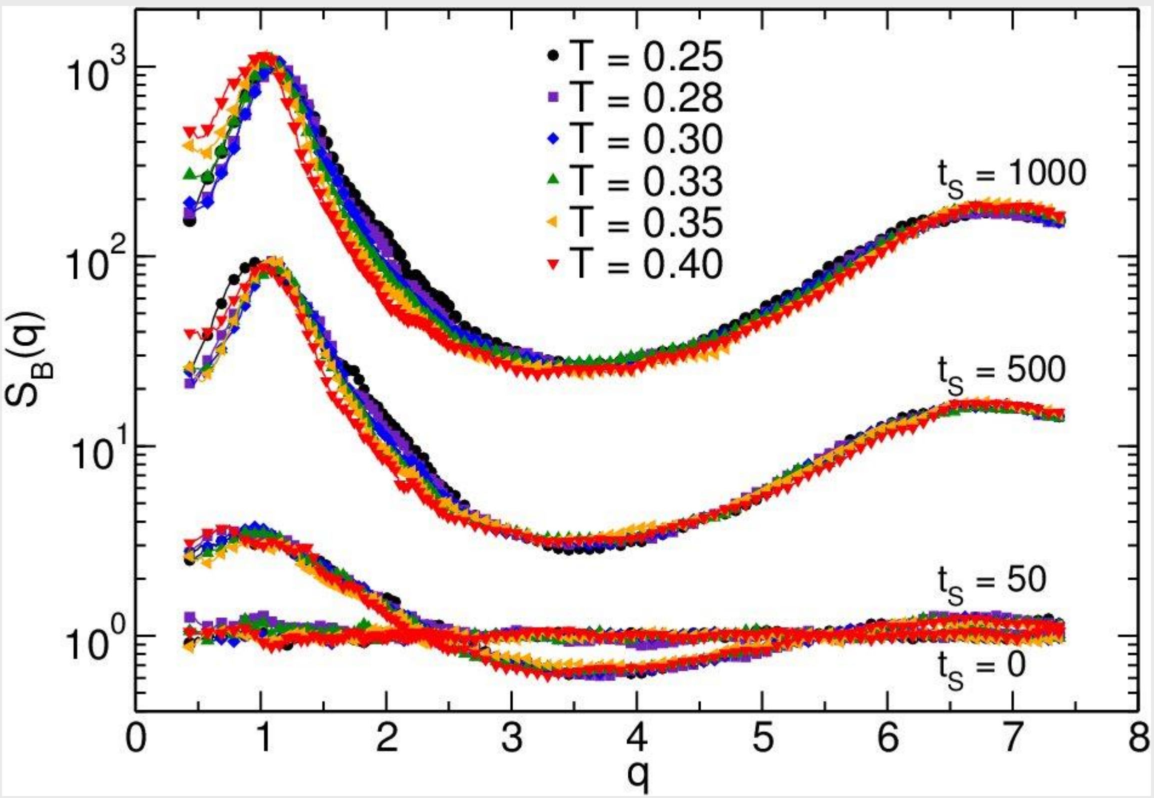
$\Rightarrow$ Presence of clusters of B particles $\Rightarrow$ ordered meso-phase inside the disordered gel

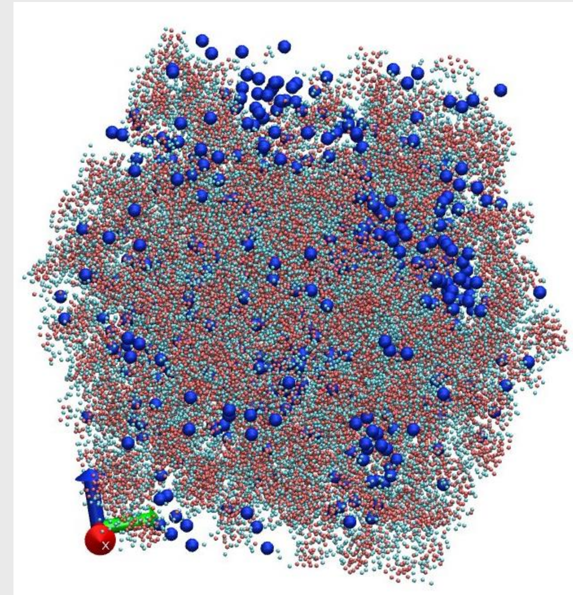
Time dependence of structure

- Structure of the gel is inhomogeneous but seems to be similar at all (low) temperatures. Is it possible to define a iso-structural time scale t_s at which the structure is the same?

$$t_s(T,t) = t_B \cdot s(T) = r(T) \cdot t \cdot N_c / N_m \cdot s(T)$$

$r(T) \Leftrightarrow$ driving force; $s(T) \Leftrightarrow$ reaction of system





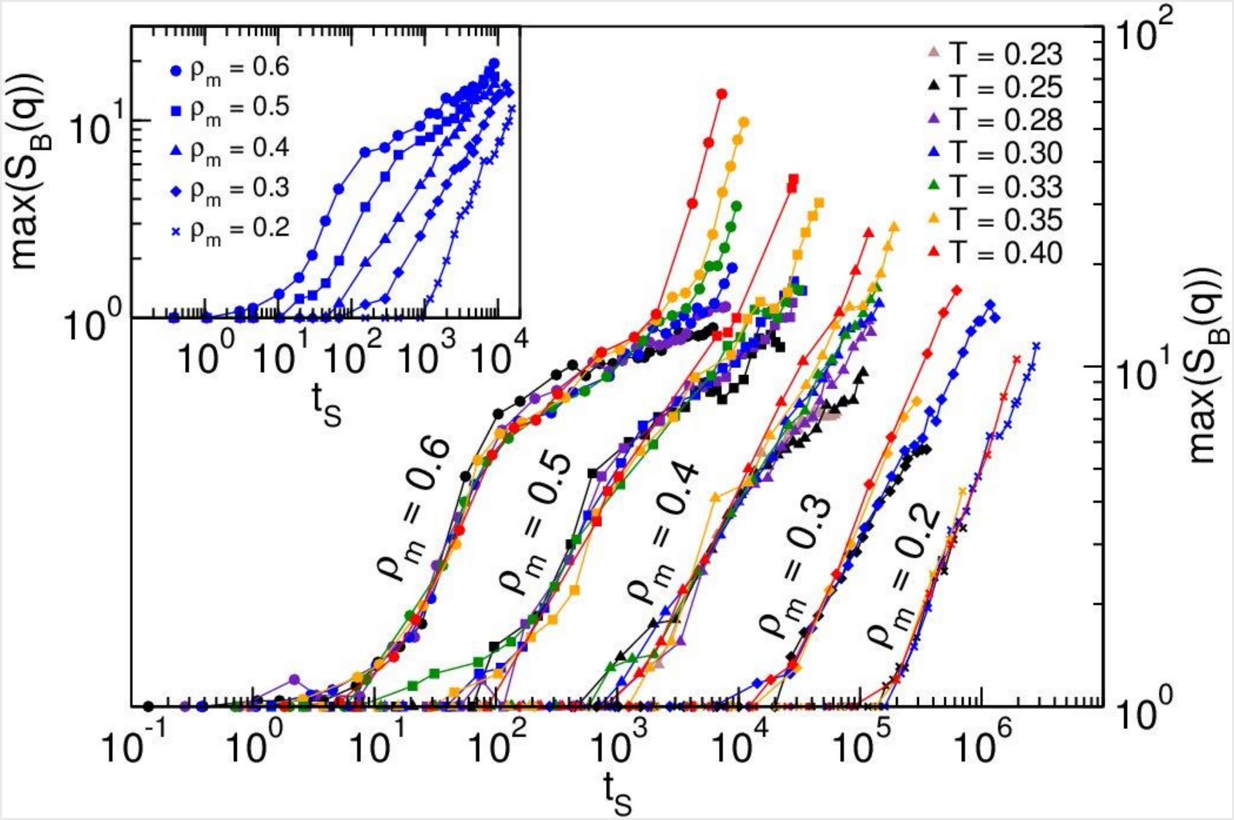
- Iso-structural time t_s does indeed exist!

$\Rightarrow$ During the gelation dynamics the system visits the same points in configuration space but the time depends on T

- Pronounced peak at small wave-vector because of clusters

Time dependence of structure: 2

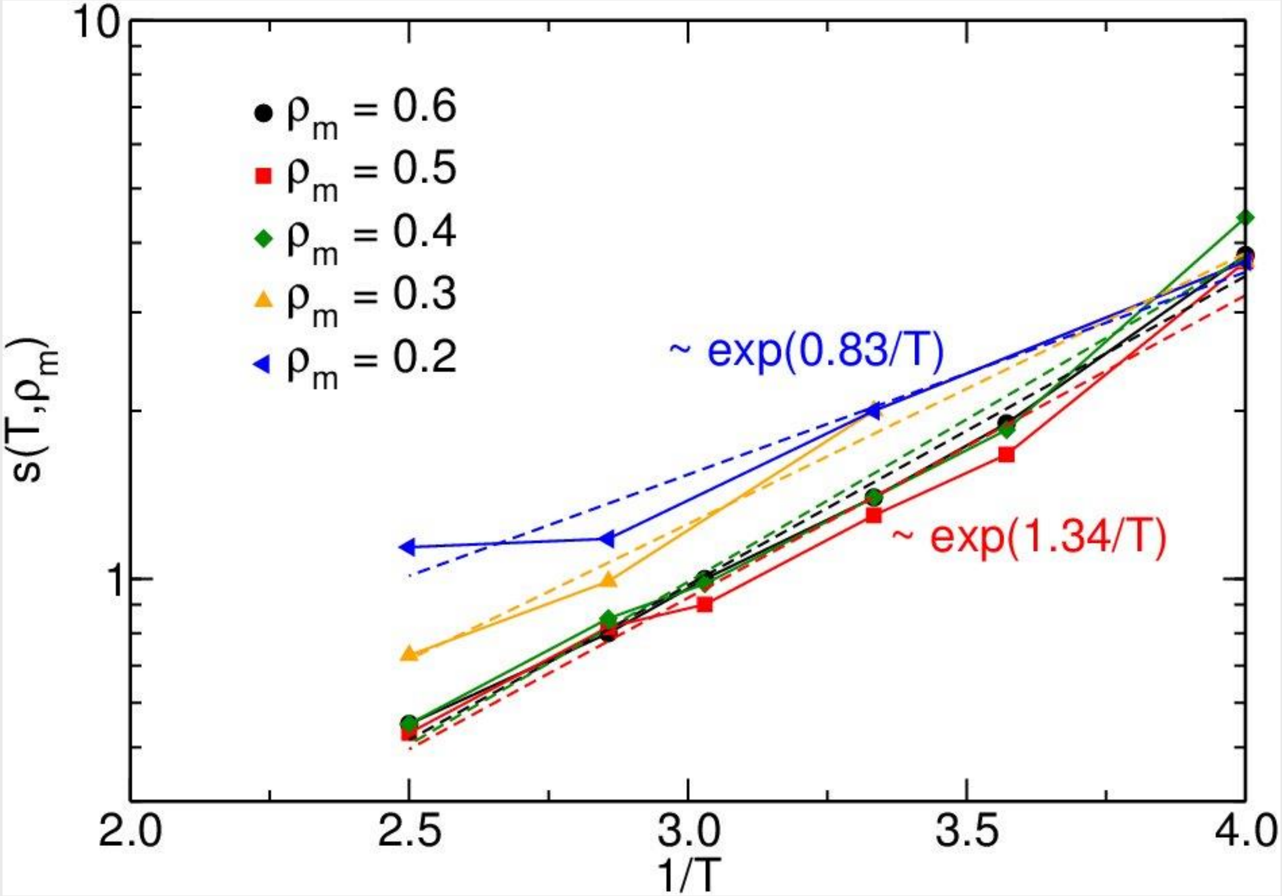
- Consider time dependence of height of peak (=clusters)



- Fast growth of peak at intermediate times, then plateau before final growth
- Length of plateau increases with T decreases $\Rightarrow$ meso-structure can be stabilized for very long times
- Growth of peak is faster if density is high

Temperature dependence s(T)

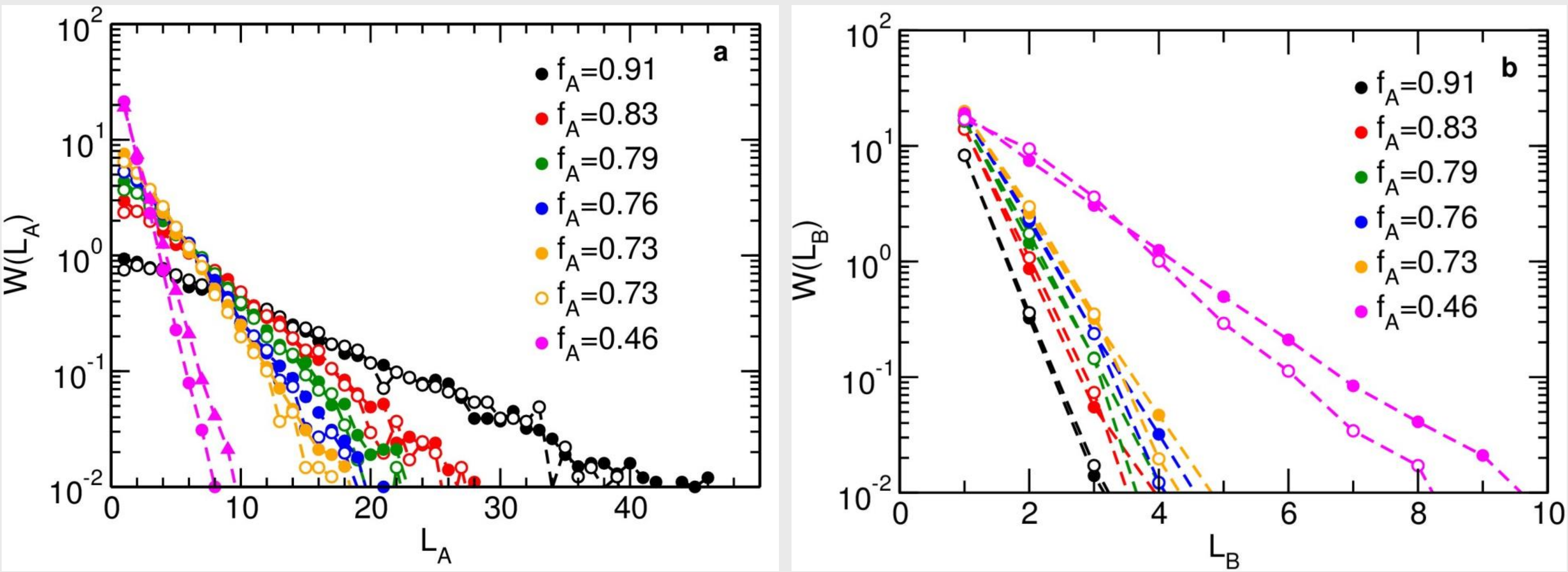
- Recall: $t_s(T,t) = t_B \cdot s(T) = r(T) \cdot t \cdot N_c / N_m \cdot s(T)$



- Time scaling factor s(T) shows an Arrhenius dependence with an activation energy that is close to the depth of the potential well between two B particles (=1.0)

Random Block Copolymers

- Previous theoretical studies on random block copolymers: Fredrickson, Milner (PRL 1991); Sung, Yethiraj (Macromol. 2005)
- Polymer is given by A monomers (probability f_A) and B monomers (probability f_B=1-f_A); Also define probability p_{AA}= probability that an A monomer is neighbor of another B monomer; likewise p_{AB} and p_{BB}
- Depending on T, f_A, p_{AA}, p_{BB} such a polymer mixture can be homogeneous or demix

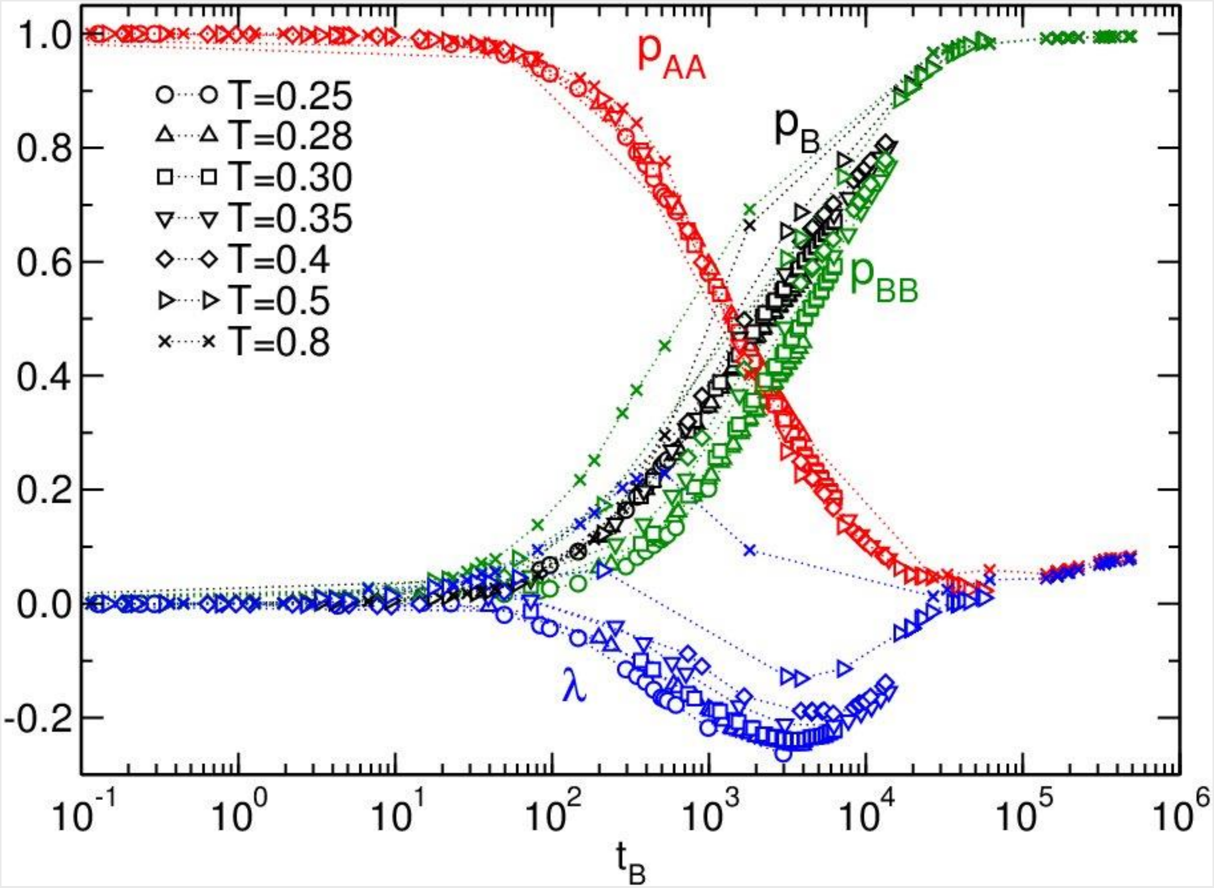


- LA : Probability to find in the polymer L_A consecutive monomers of type A
- Our polymer system is a realization of a random block copolymer!

Random Block Copolymers: 2

- Time dependence of the parameters that are relevant to make a mapping to random block copolymers

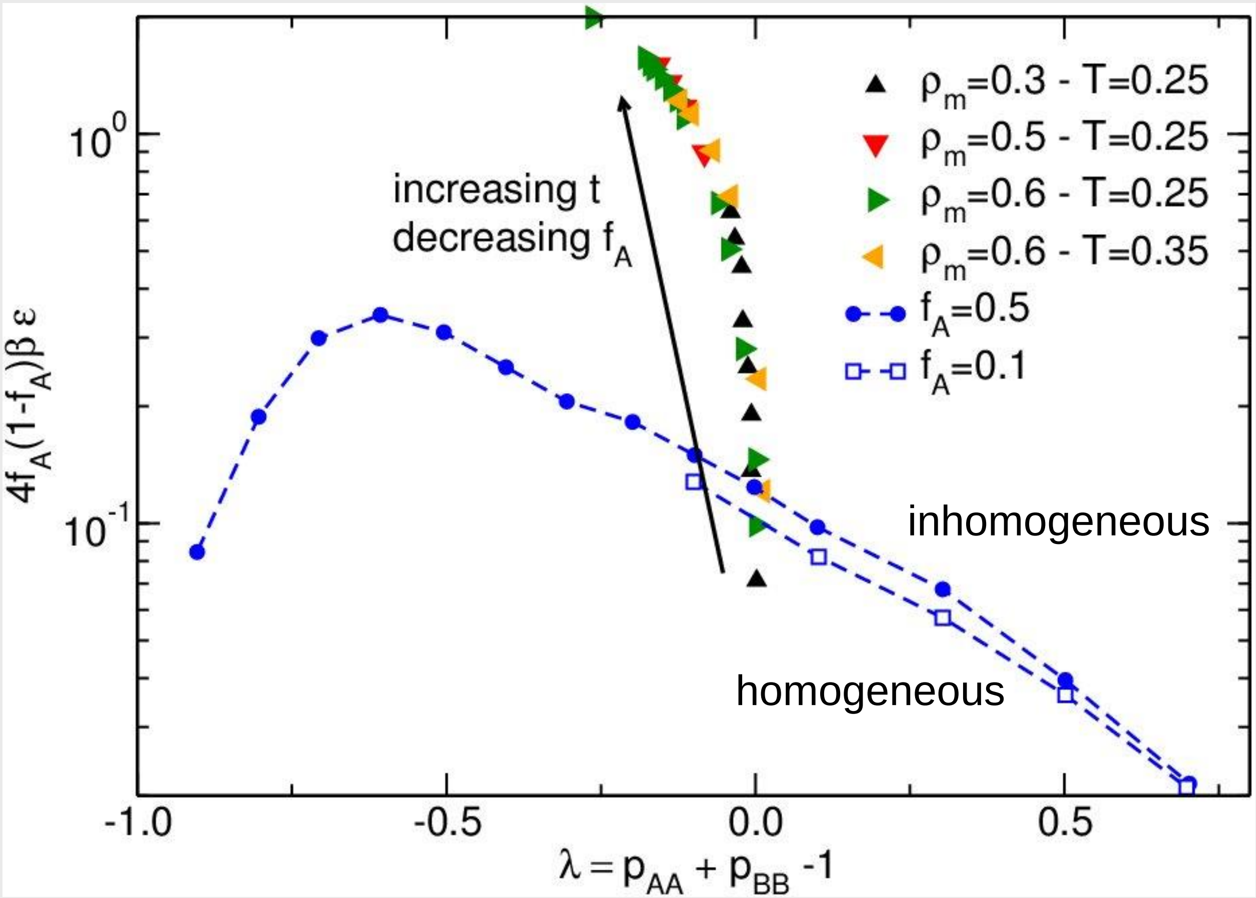
NB: Relevant time scale is t_B, the concentration of the B monomers (and hence of the A monomers)

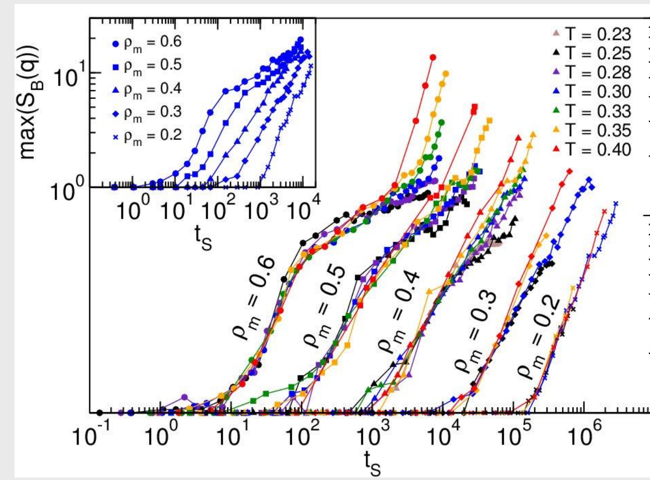


- $\lambda = p_{AA}+p_{BB} -1$
- The relevant parameters of the model fall onto a master curve $\Rightarrow$ mapping to random block copolymer is also independent of T

Random Block Copolymers: 3

- Sung and Yethiraj (Macromol. 2005) have determined the stability limit of the homogeneous phase for random block copolymers





- We find that in our system the cluster peak shoots up when the system crosses the predicted phase boundary

$\Rightarrow$ evidence that the creation of the cluster phase can be described by the theory of random block copolymers

Summary

- Simulations of a polymeric system for which a catalytic reaction (colloids) leads to increasing attraction between the polymers ⇒ "Phase diagram" becomes time dependent ⇒ phase separation or formation of gel

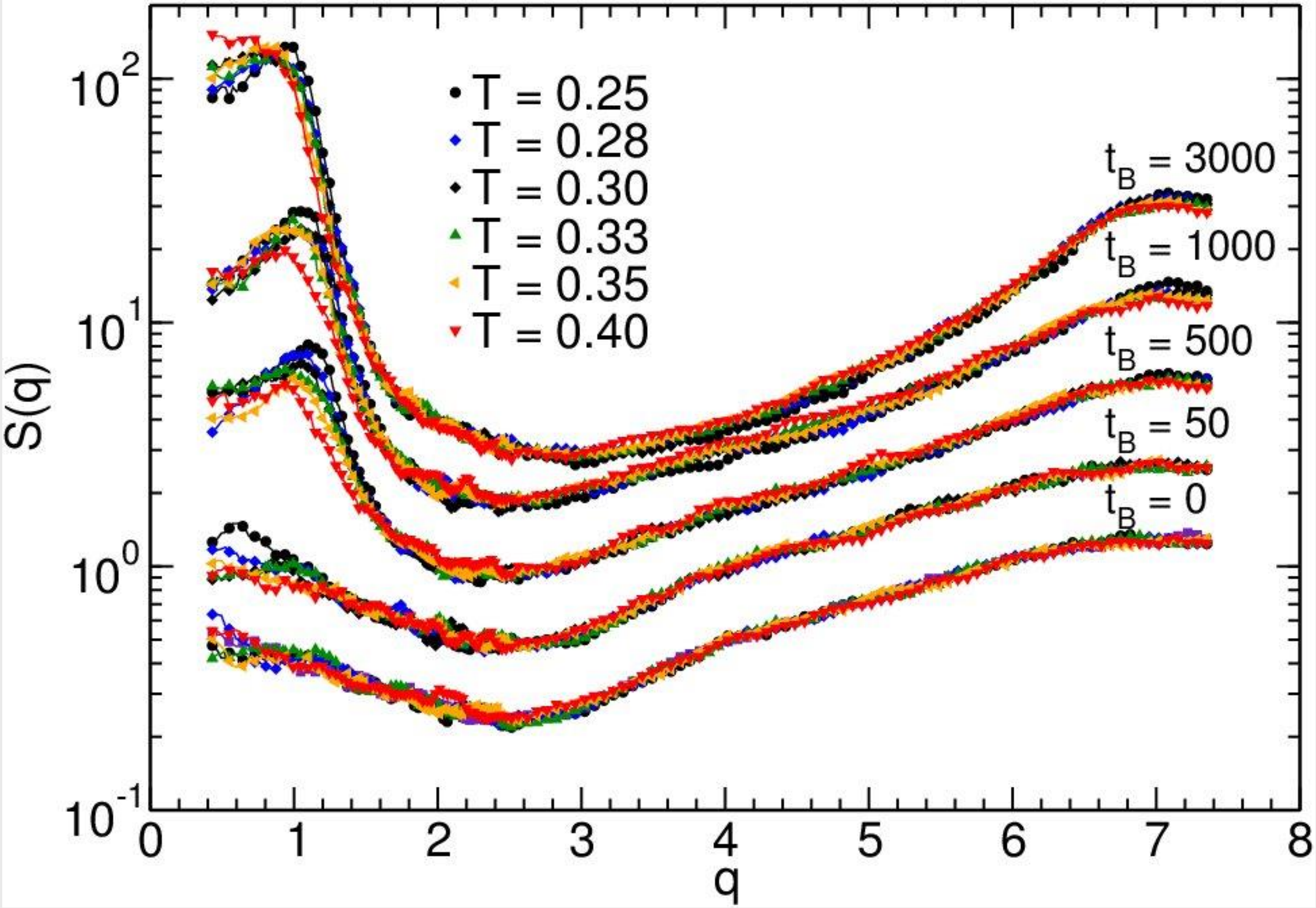
- At intermediate time scales, system forms a meso-phase of clusters imbedded in an amorphous polymer matrix

- Short and intermediate times: Up to a T-dependent scaling factor, the non-equilibrium dynamics is independent of temperature

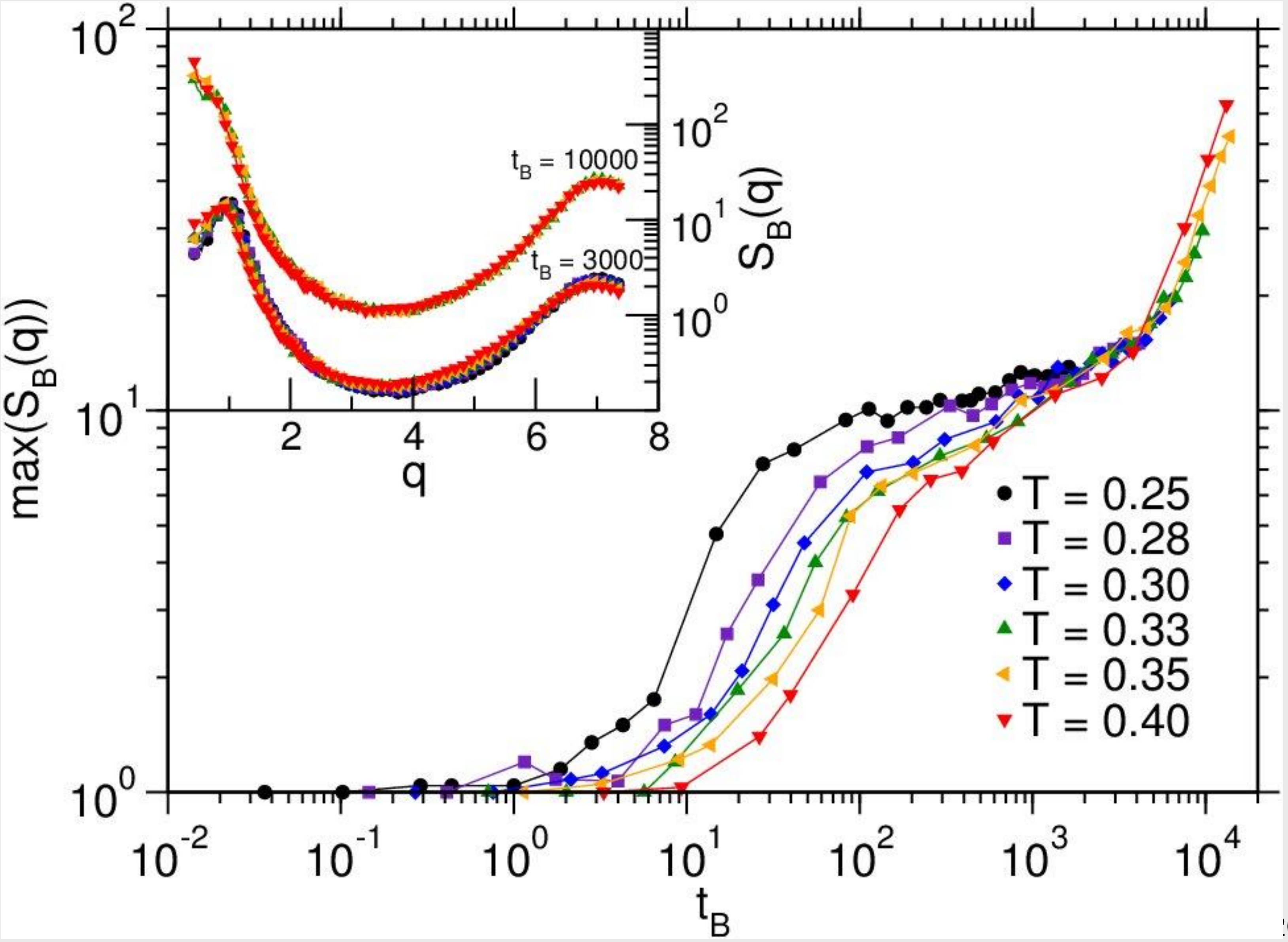
- Transformation dynamics can be understood quantitatively from the parameters of the model.

- Internal "chemical" structure of the polymers is very similar to the one of a random block copolymer. Theory of random block copolymers seems to be able to give a semi-quantitative prediction of the stability limit of the homogeneous phase.

- Many open questions: BD instead of ND; can colloids be trapped in the gel phase? Can the cluster phase be completely stabilized? Connect back to the biological system, …



T = 0.25
T = 0.28
T = 0.30
T = 0.33
T = 0.35
T = 0.40
t_B = 3000
t_B = 1000
t_B = 500
t_B = 50
t_B = 0
S(q)
q



10^2
10^1
10^0
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
10^4
t_B
$\max(S_B(q))$
2
4
6
8
q
$S_B(q)$
$t_B = 10000$
$t_B = 3000$
T = 0.25
T = 0.28
T = 0.30
T = 0.33
T = 0.35
T = 0.40