Strings, droplets and tubes
How does phase separation take place in a gel?

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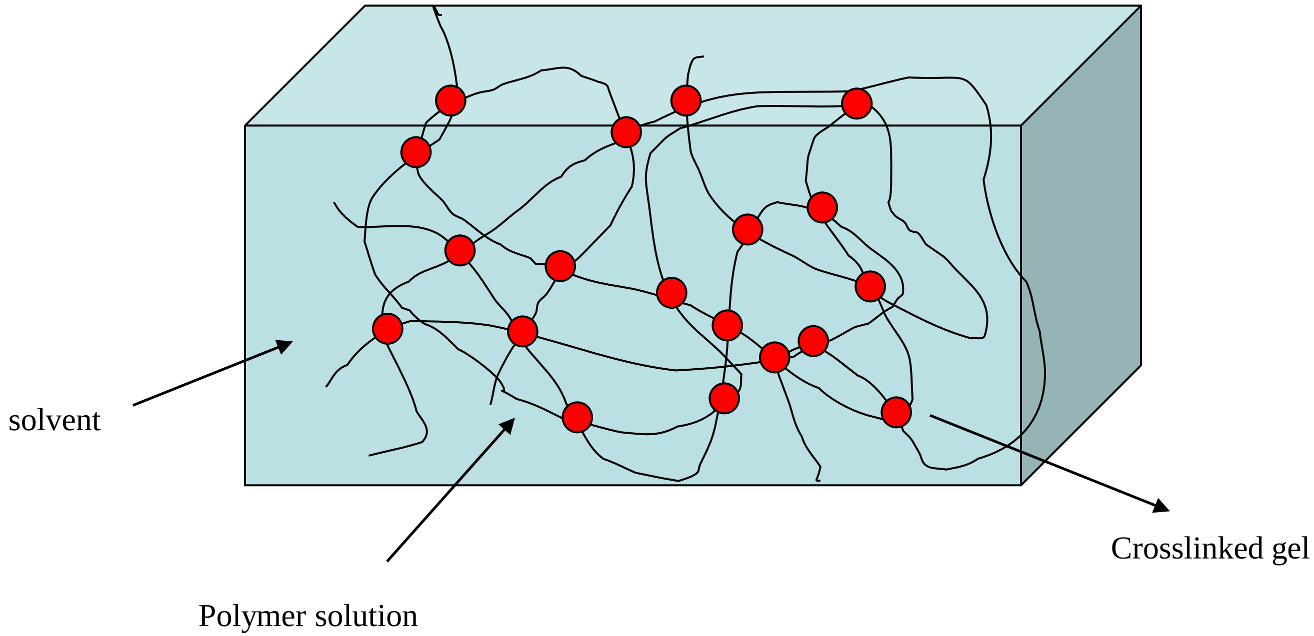
Europhys. Lett. **77,** 58007 (2007)
Macromolecules **41**, 3267 (2008)
Soft Matter **4**, 18 (2008)
Phys. Rev. E **79**, 040401 (2009)

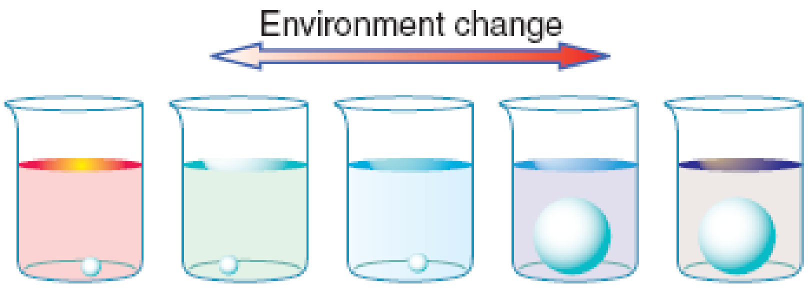
O. Peleg (BIU, ETH)
M. Kröger (ETH)

Gel: Giant 3d polymer network permeated by solvent



Last 30 years: light, neutron and x-ray scattering – gels are random inhomogeneous solids

Phase transitions in gels:



Thousand-fold change of volume –
diapers !

How fast is the transition for a gel of size L?

Simple estimate: $T = L^2 / D$

$D = 10^{-6}$ cm^2/sec

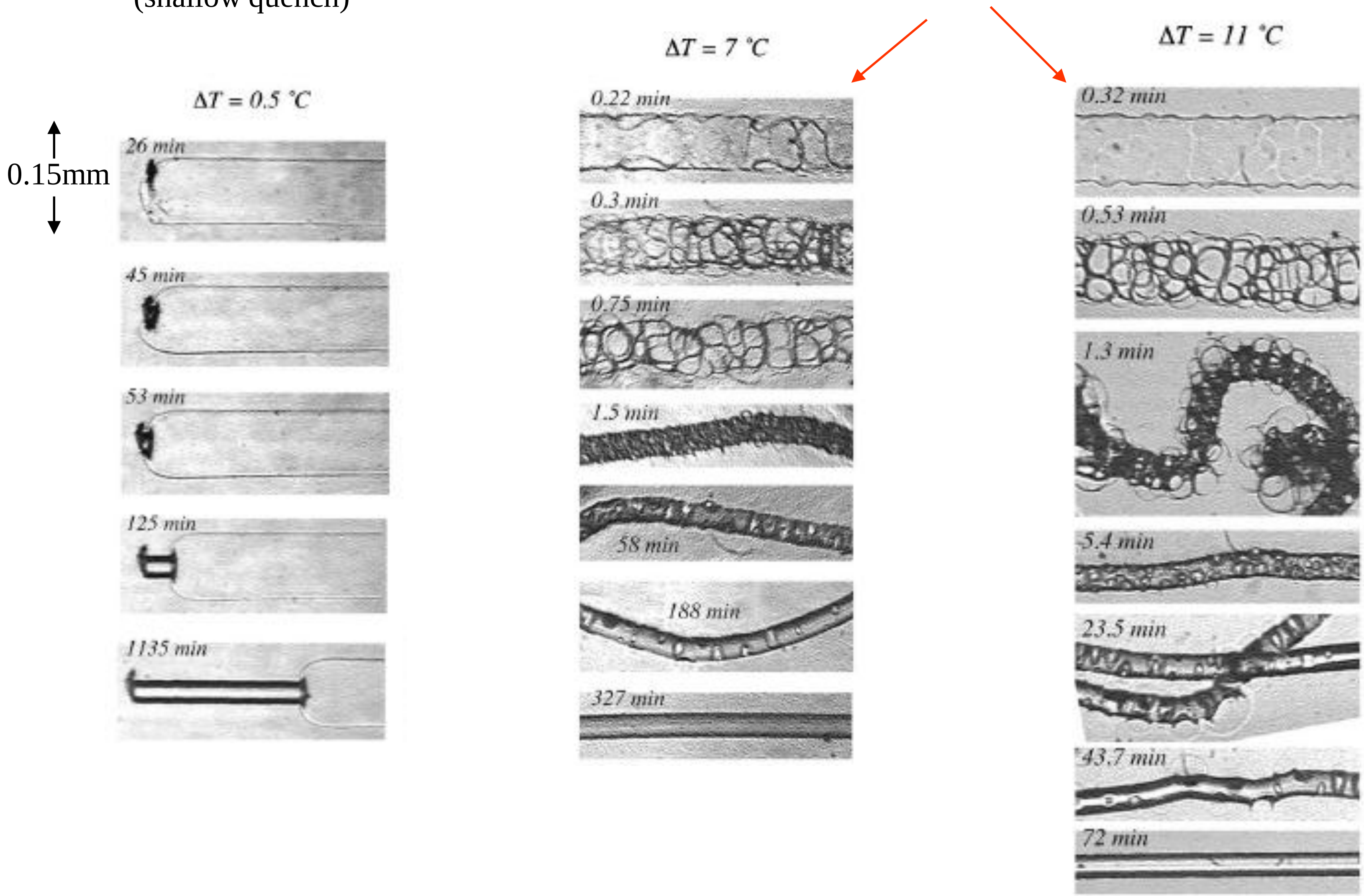
For L=1 cm, $T=10^6$ sec

For L=10 micron, T=1 sec

Phase transitions in NIPA-AA gels

Volume transition
(shallow quench)

Initial microphase separation
followed by volume transition
(deep quench)



Decoupling microphase separation (MS) and volume transition (VT):

1. By using large gels – fast MS vs. slow VT

2. By fixing the total volume (boundaries): only MS is possible!

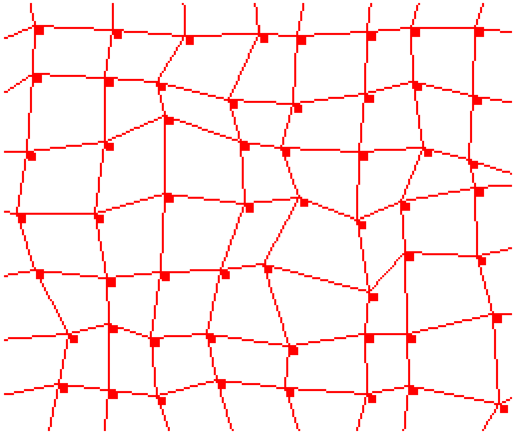
Questions:

What sets the length scale of microphase separation?

What are the characteristic patterns?

MD simulation of a two dimensional "gel"

Network: point particles connected by harmonic springs (no solvent!)



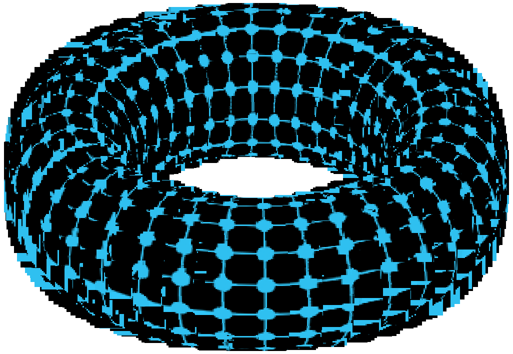
Each particle is connected to 4 (square lattice) or 6 (hexagonal lattice) neighbors

Network topology is fixed throughout!

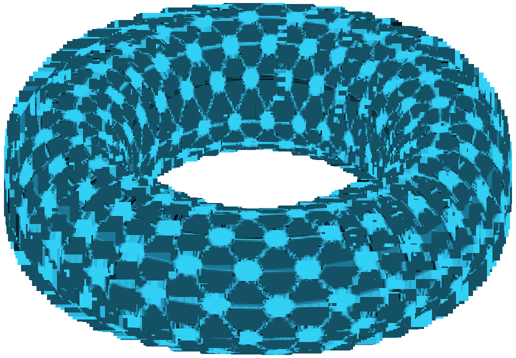
N=10,000 and 250,000 particles

Instead of fixing the gel to the walls – periodic boundary conditions:

Square lattice



Hexagonal lattice

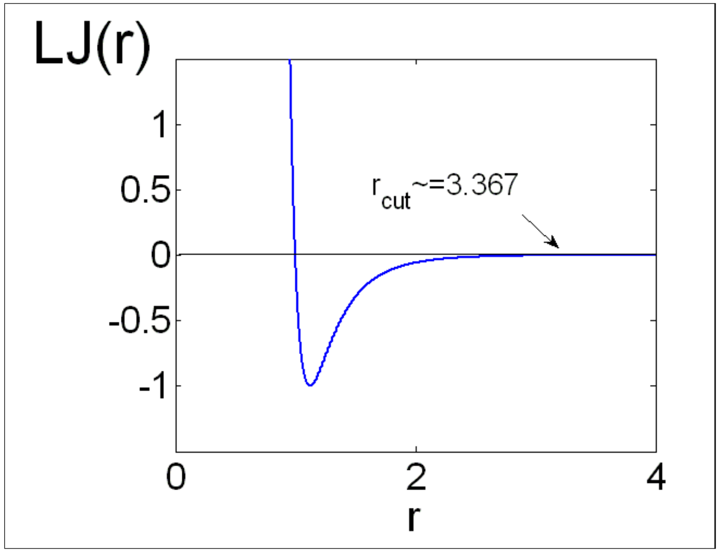


Start from perfect lattice of stretched springs of length l_0 (zero equilibrium length)

Driving force for phase separation – short-range attraction between particles

Lennard-Jones potential

$$U_{LJ}(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$$



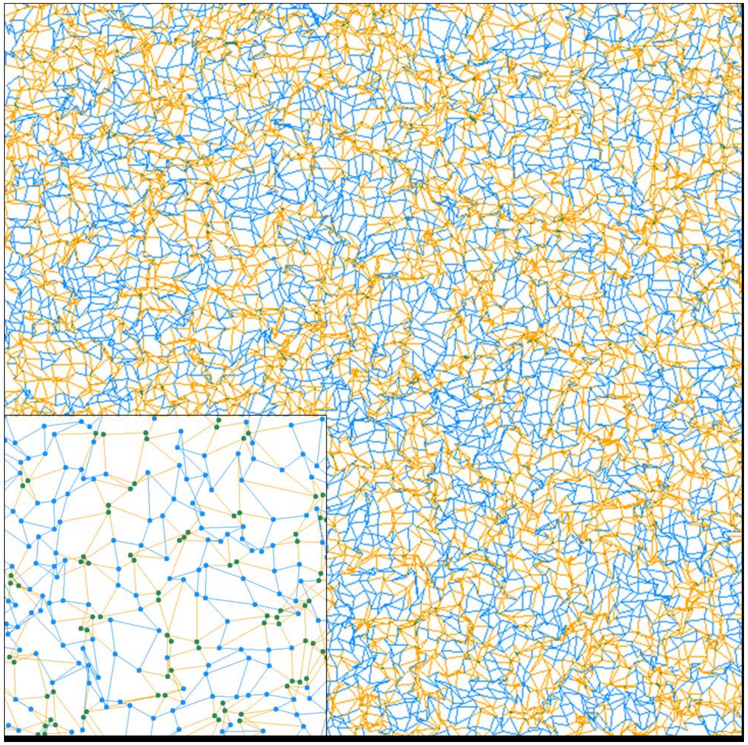
Opposing force – elasticity of stretched springs

$$U_{spring}(r) = \frac{1}{2}kl^{2}$$

Thermal bath fixes temperature T (average kinetic energy)

Start at high temperature (homogeneous) phase and quench to desired temperature

k=0.1
T=0.9



$$r_{\min} = 2^{1/6} < r_{cl} = 1.5 < r_{cut} = 3 \times 2^{1/6}$$

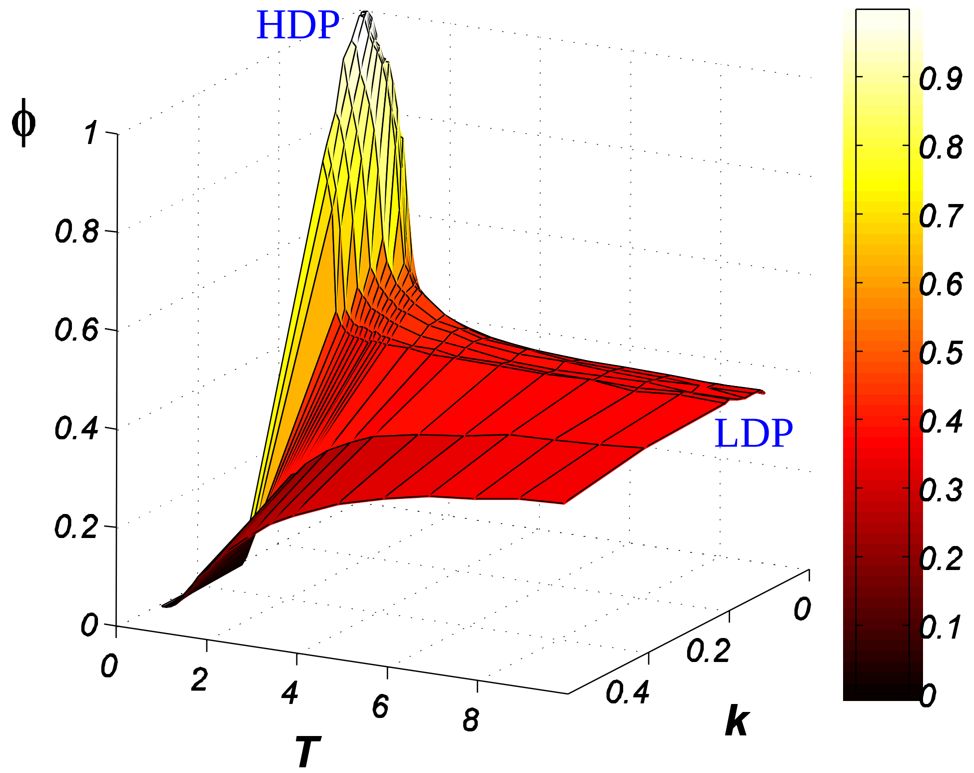
Isolated particles and springs connecting isolated particles - blue

Particles in clusters and springs connecting particles in clusters - green

Springs connecting clusters and isolated particles - orange

Phase diagram:

Fraction of particles in clusters (ϕ) vs temperature (T) and spring constant (k)



Microphase separation for $k_{min} < k < k_{max}$

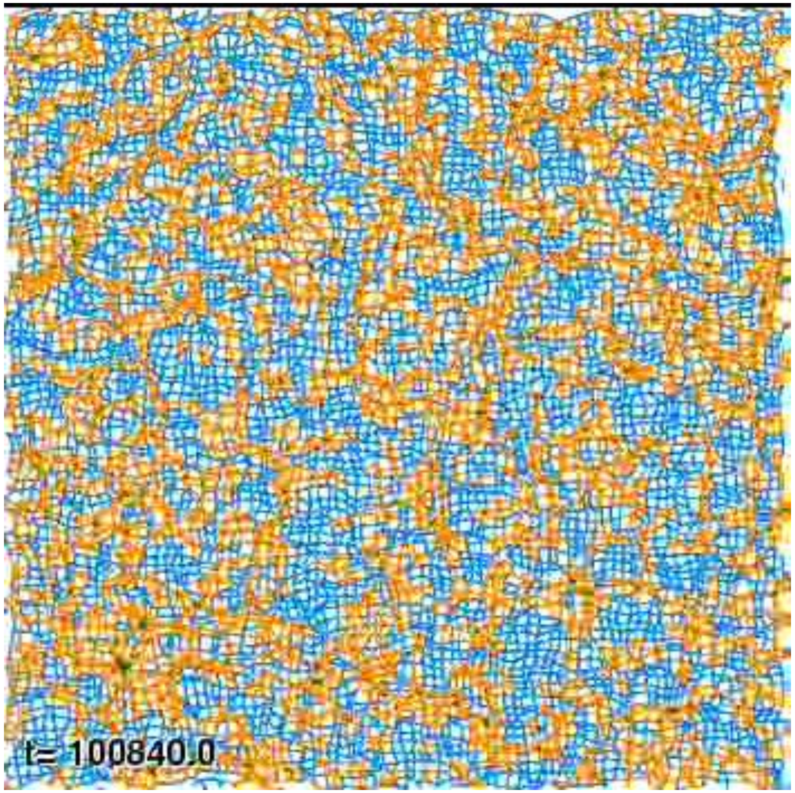
Liquid-like behavior (macrophase separation) for $k < k_{min}$ – elasticity negligible

No transition for $k > k_{max}$ – attraction suppressed by stretching

A percolating high density cluster (PHDC) appears at T=T*

Initial square grid; N=10,000; k=0.1, T*=0.43

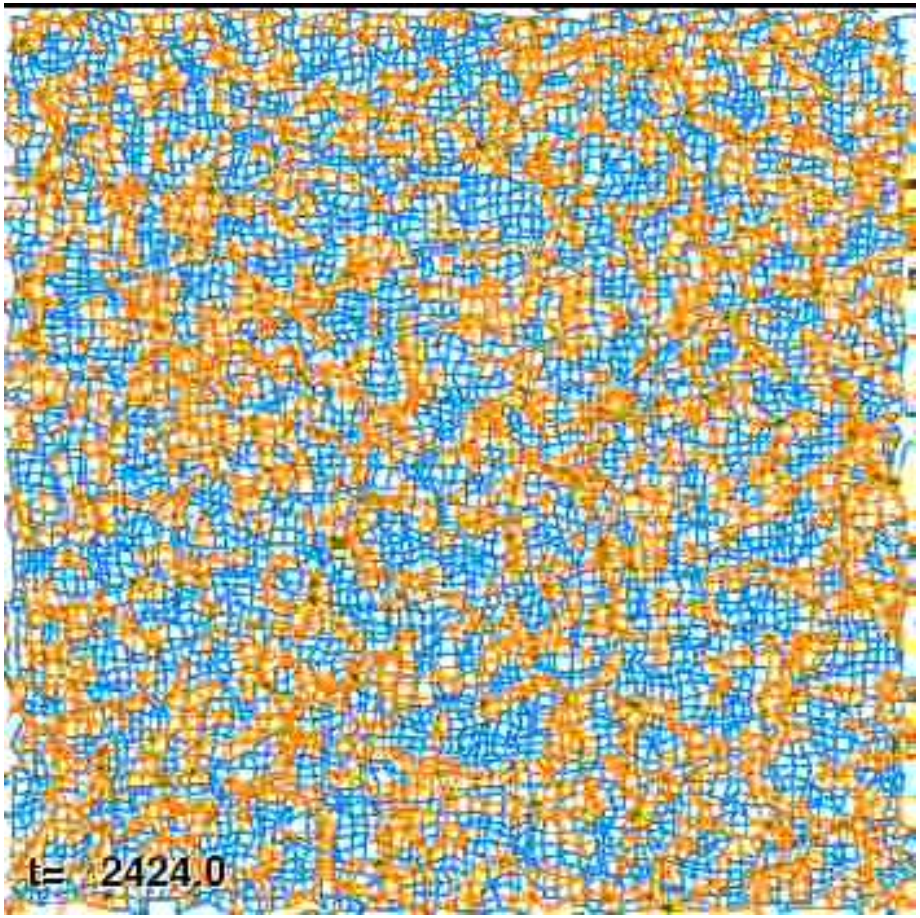
Nucleation of a PHDC:



This mechanism leads to the formation of a network of strings connected by 3-fold vertices!

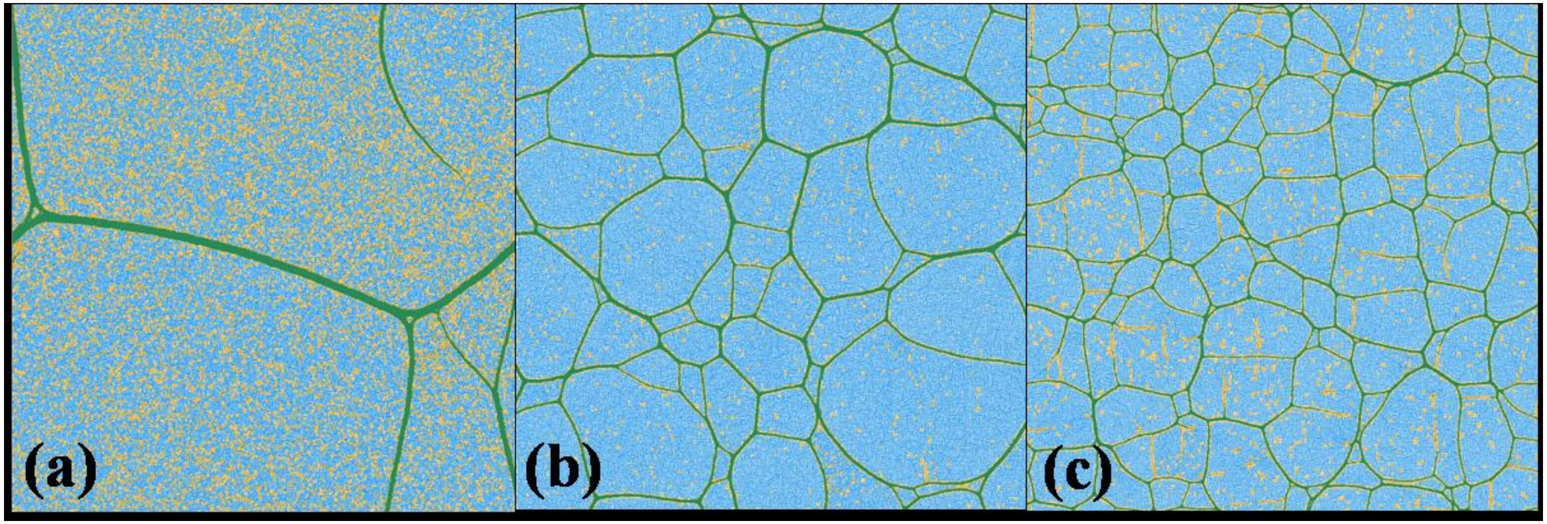
Another run – different initial conditions

Initial square grid; N=10,000; k=0.1, T*=0.432



Typical patterns:

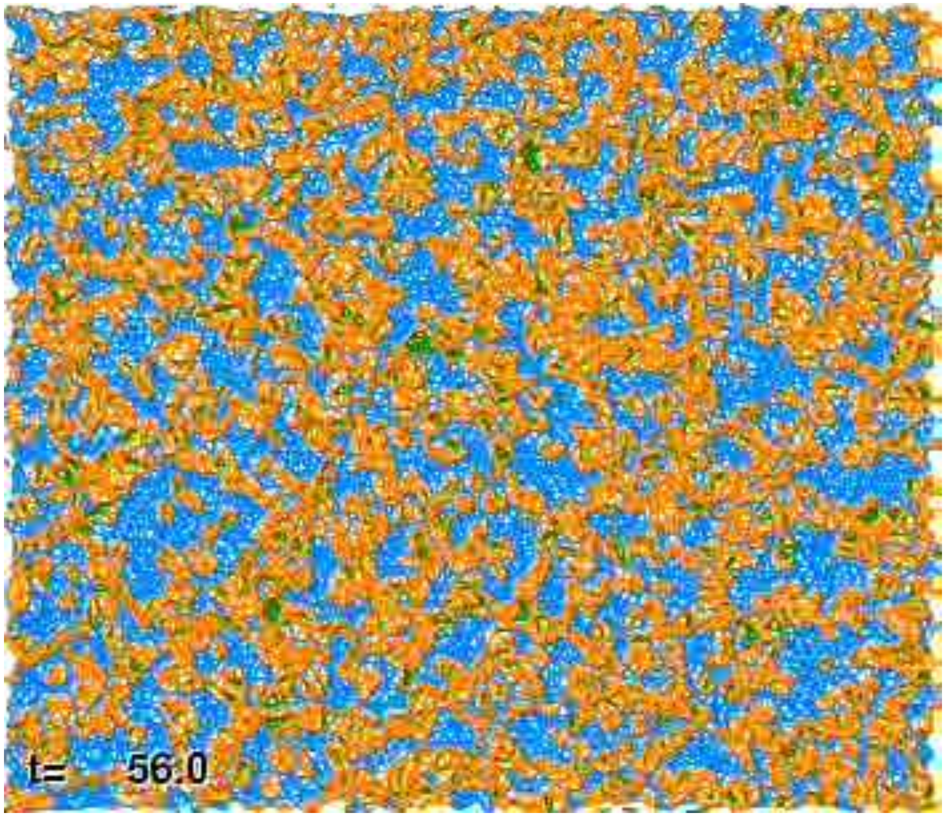
Initial square grid; N=250,000; k=0.1



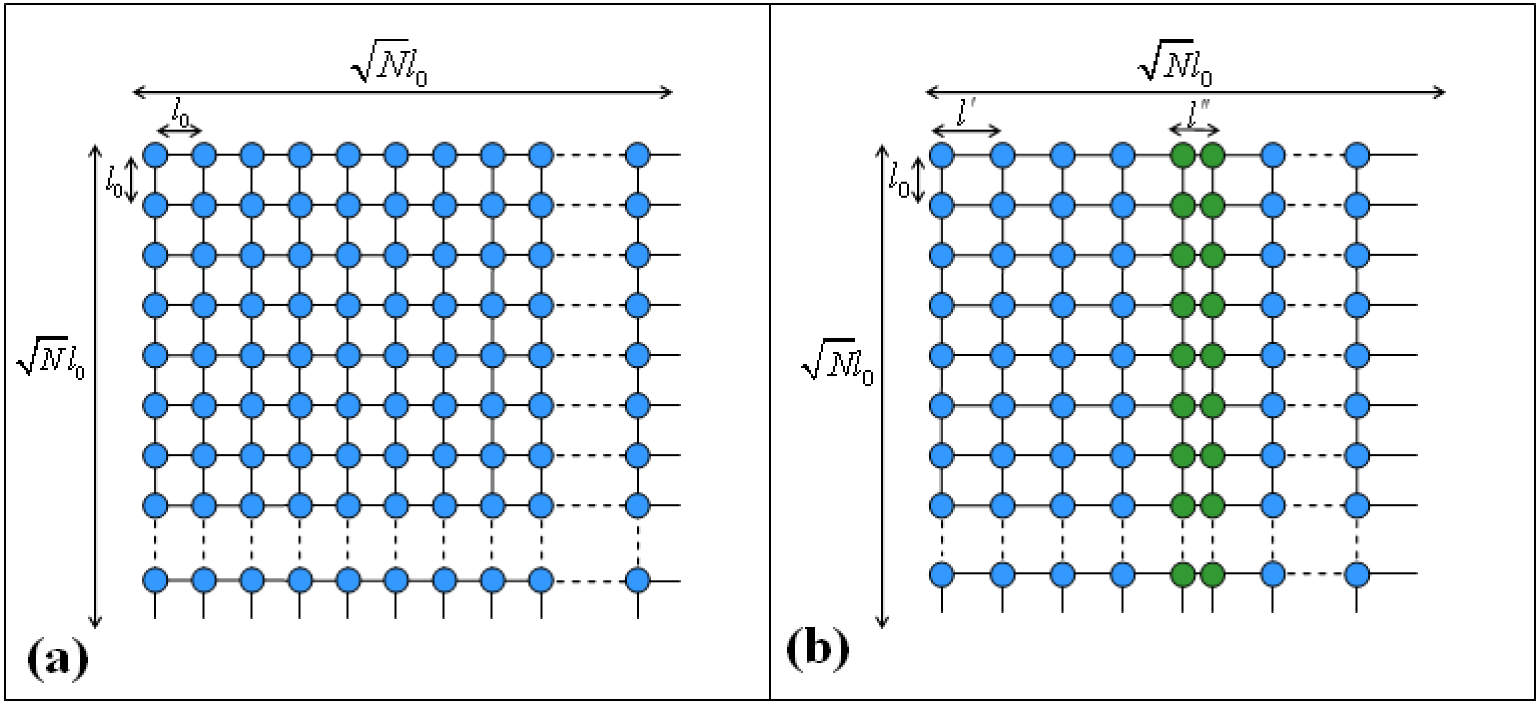
T=T*=0.432 T=0.35 T=0.25

Glassy behavior at lower temperatures – relaxation slows down with quench depth

Initial hexagonal grid; N=10,000; k=0.0667, **T=0.3**

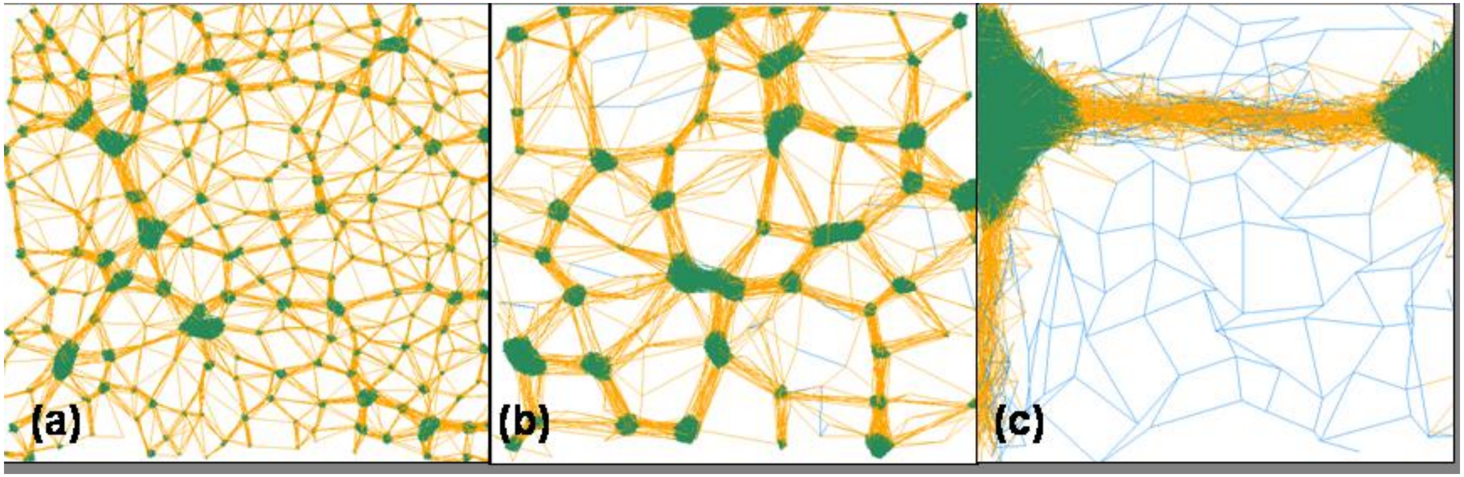


Physical mechanism: phonon-assisted condensation (lowest energy modes)?



What happens for weaker spring constants?

Initial square grid; N=10,000; k=0.001



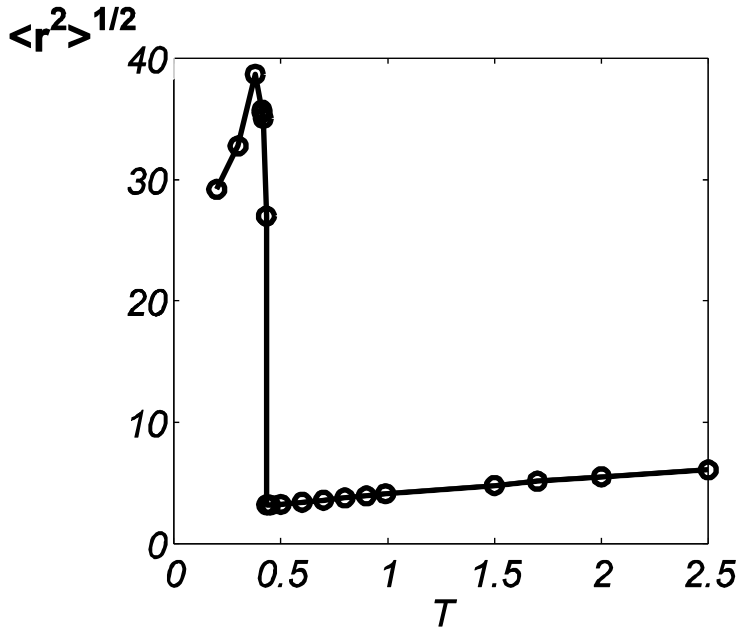
T=0.2 T=0.3 T=0.5

Network of droplets

Mesoscopic reorganization of the network below T*

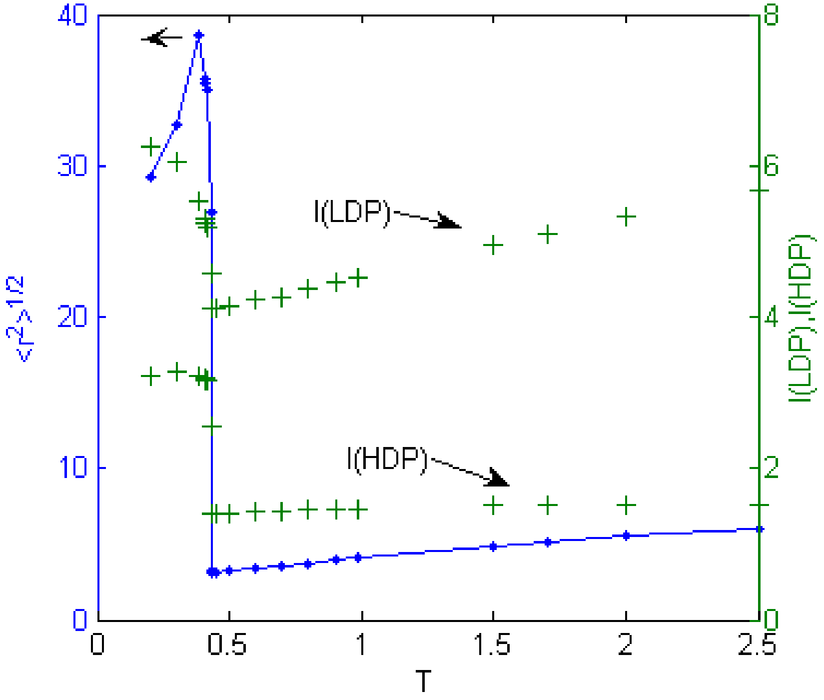
Initial square grid; N=10,000; k=0.1

RMS displacement
of a point in the network



$$l_0\,(3.5) \ll \left\langle r^2 \right\rangle^{1/2} \ll L\,(350)$$

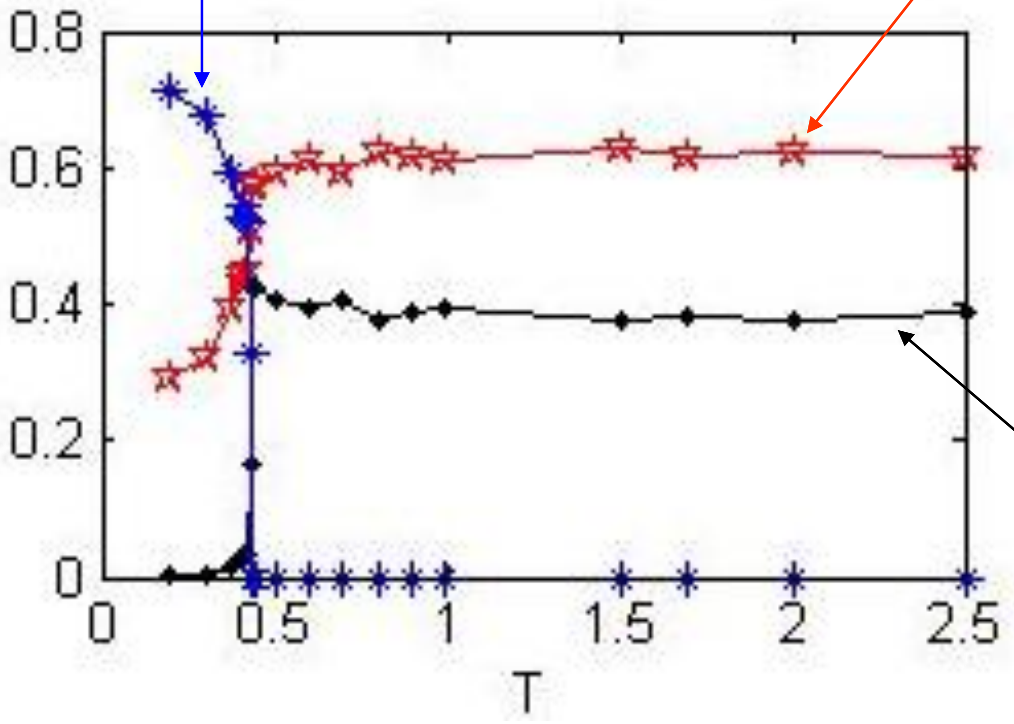
Spring lengths in high and low density phases



Springs are stretched in **both** phases below T*

Fraction of particles in PHDC

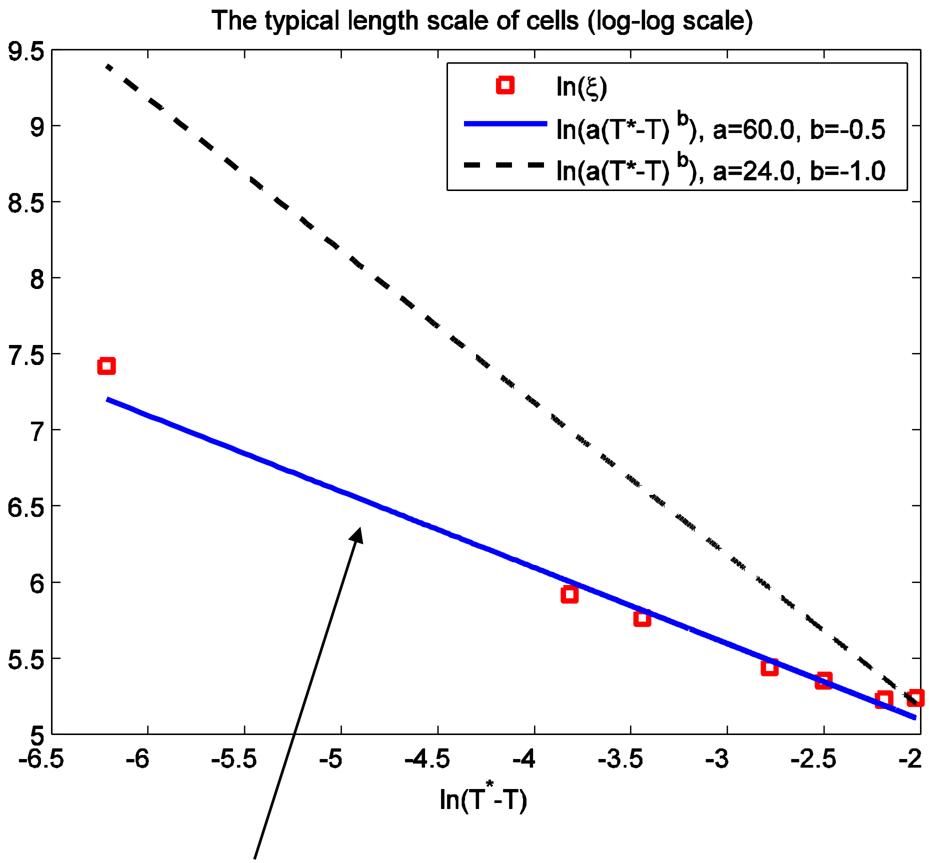
Fraction of isolated particles



Fraction of particles in small clusters

Formation of percolating high density cluster (PHDC) – at the expense of small clusters

How does the characteristic size of domains change with temperature?

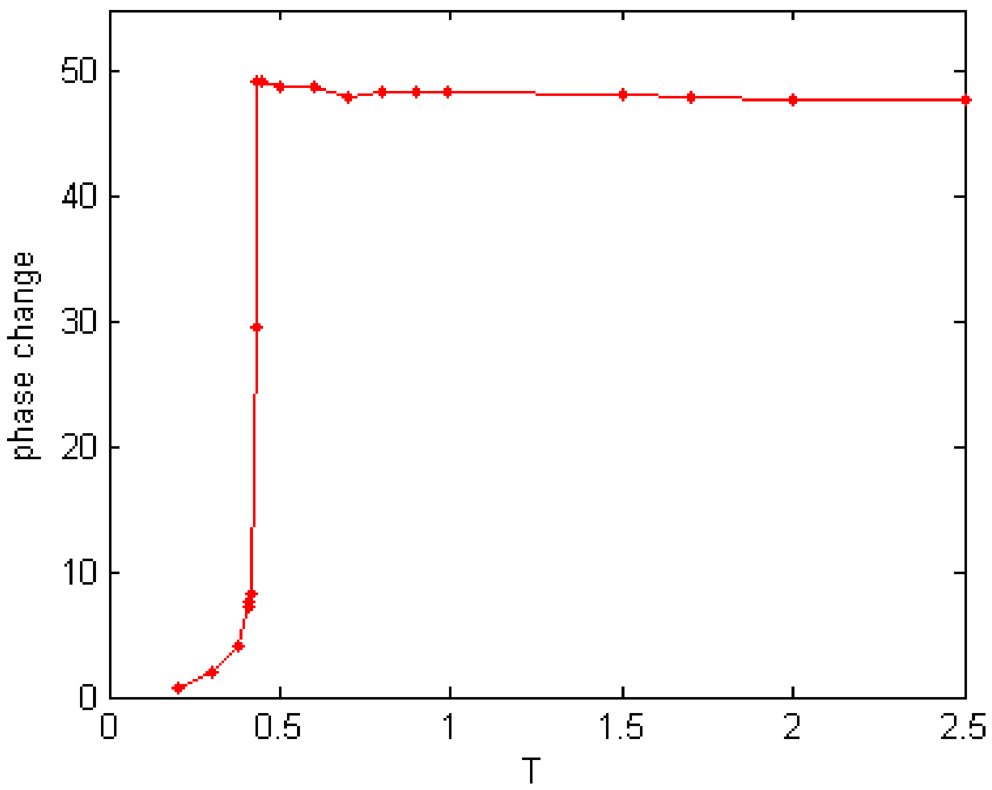


Ising mean field exponent - 0.5 !

Elasticity = long range interactions: fluctuations suppressed?

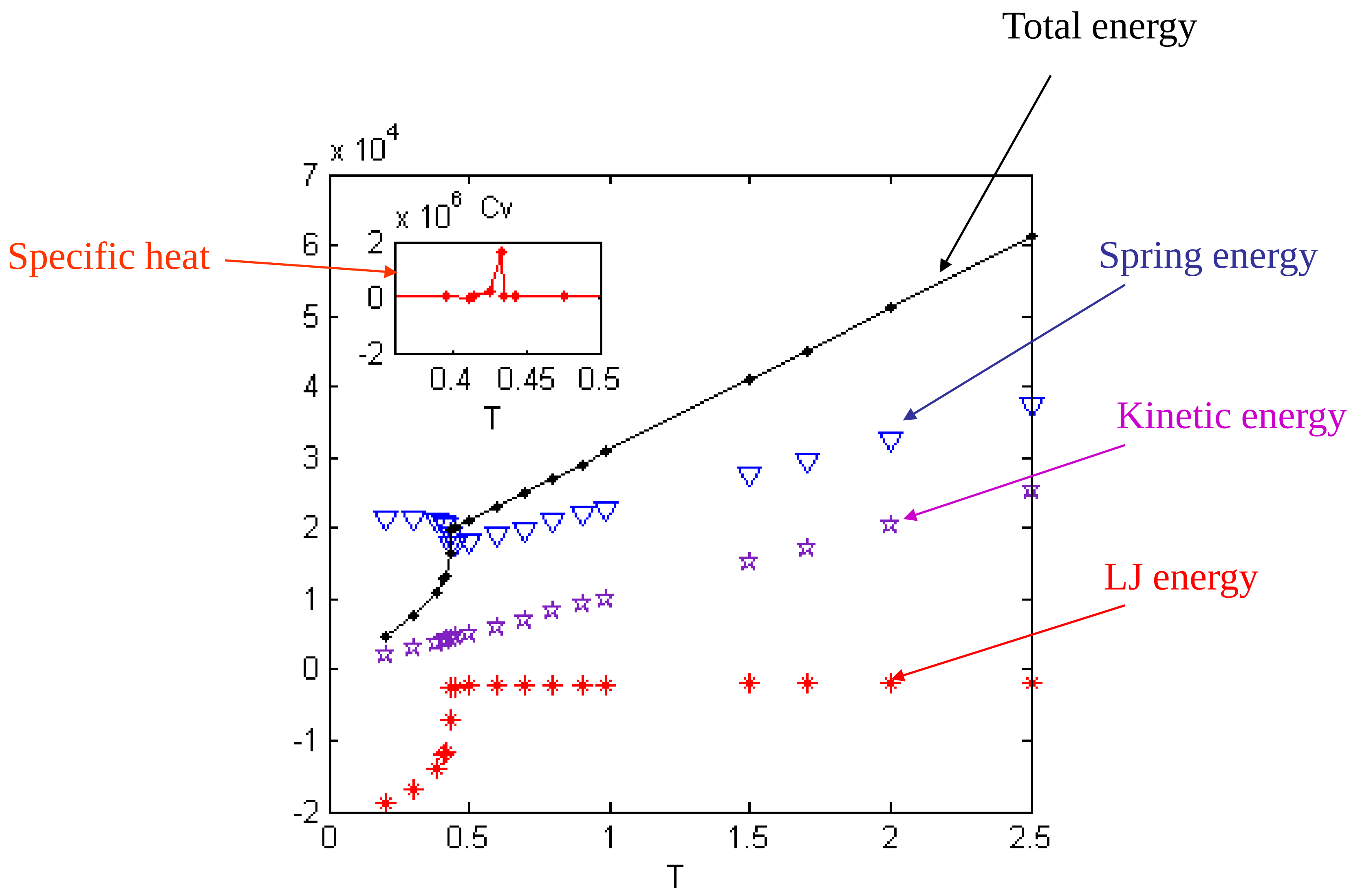
Is equilibrium reached?

Fraction of particles that change phase between HDP and LDP in 500,000 steps:



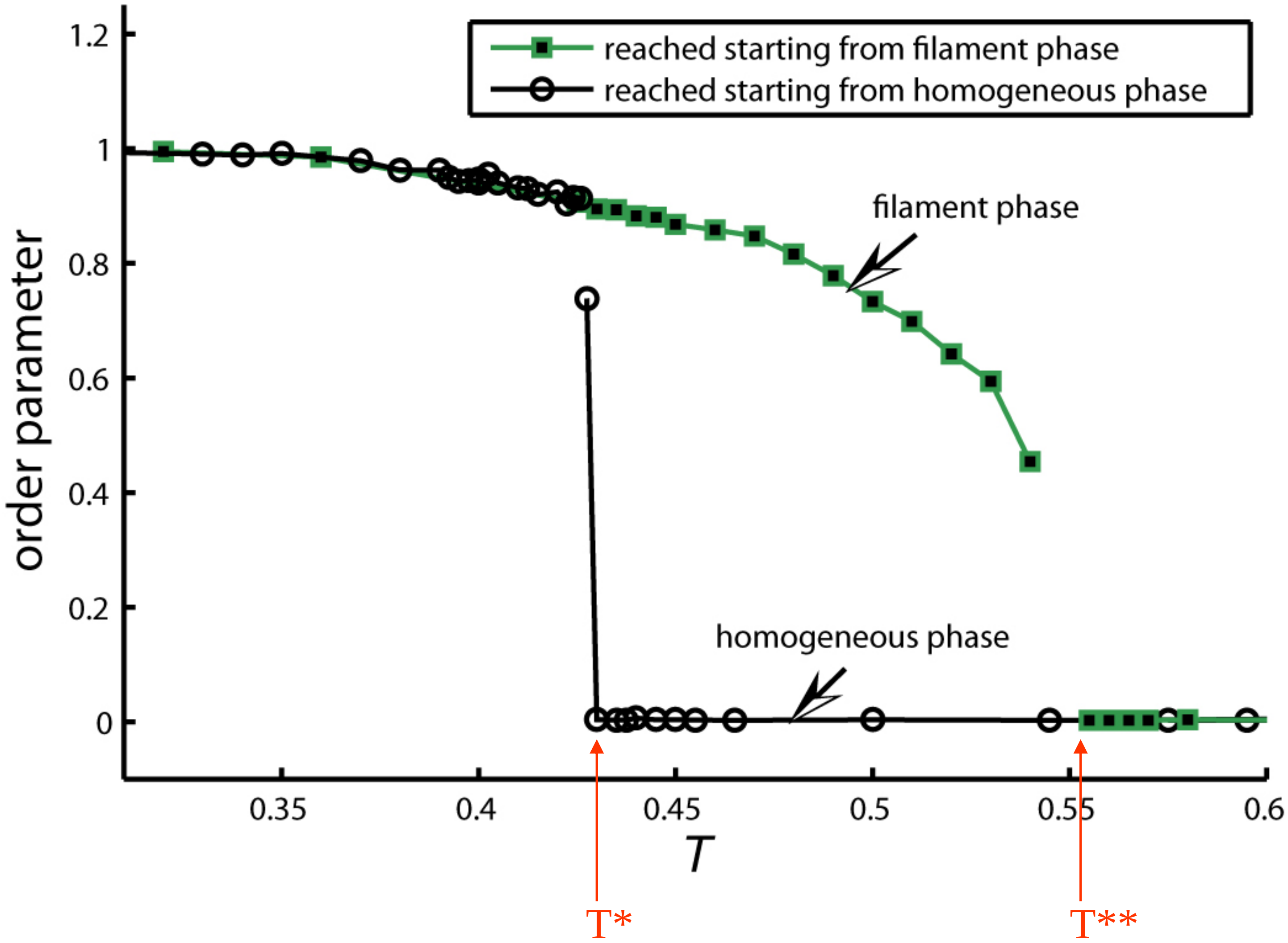
Yes, in an “experimental” sense!

“Thermodynamics”?



1st order transition?

Hysteresis:



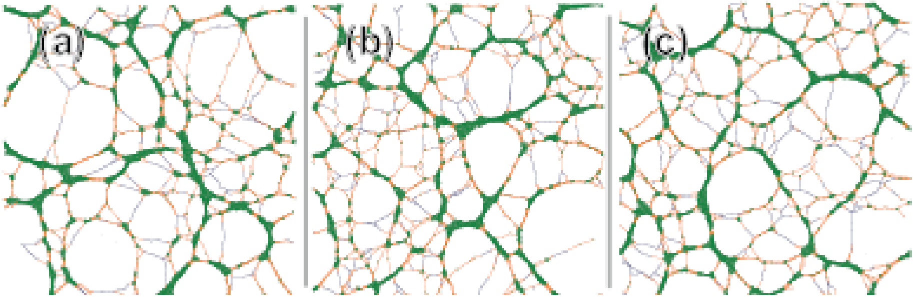
reached starting from filament phase
reached starting from homogeneous phase
filament phase
homogeneous phase
order parameter
1.2
1
0.8
0.6
0.4
0.2
0
0.35
0.4
0.45
0.5
0.55
0.6
T
T*
T**

How robust are our results?

We assumed perfect topology – real networks are randomly connected!

Start from a perfect 4-functional network and disconnect springs at random

30% disconnected
springs

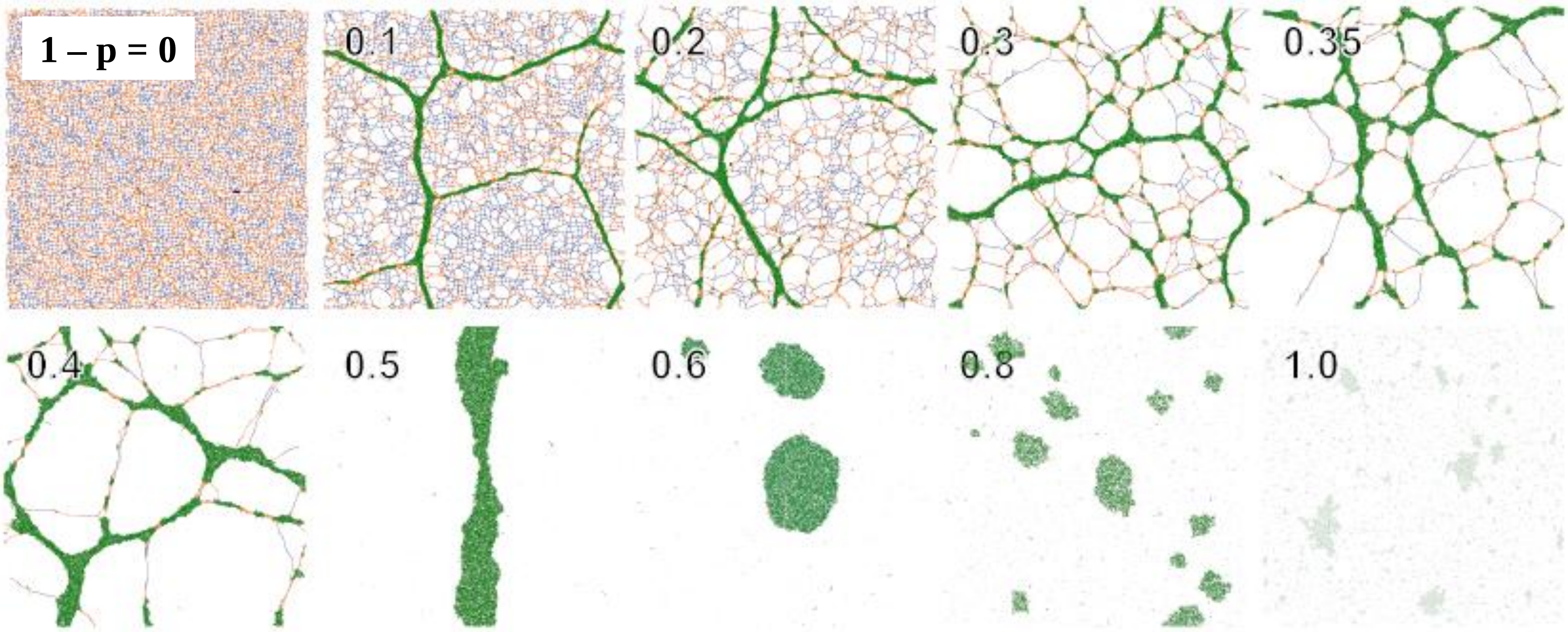


Snapshots of networks generated with different random number generator
T=0.3

Different realizations are statistically equivalent

1-p – fraction of disconnected springs

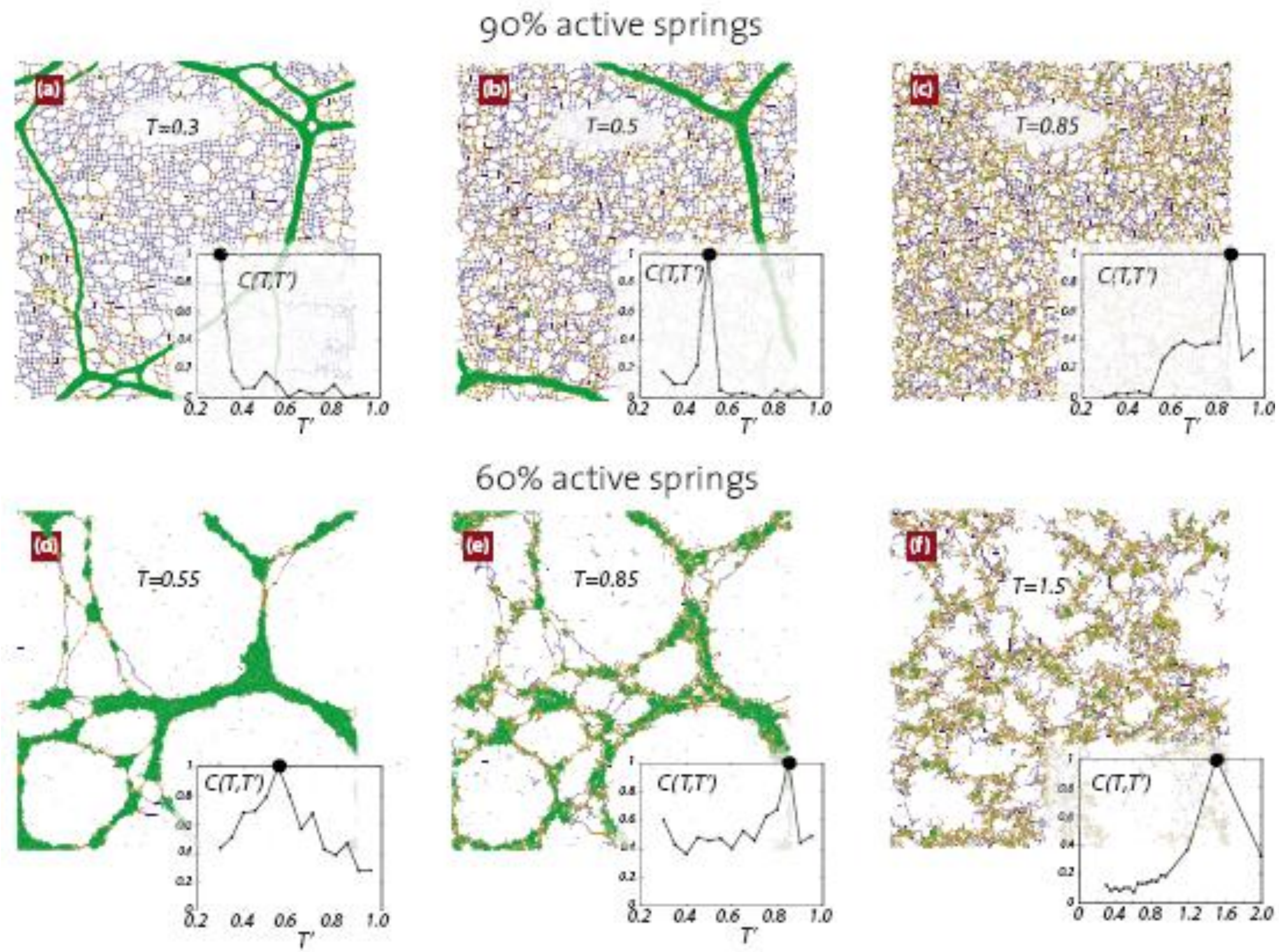
T=0.45



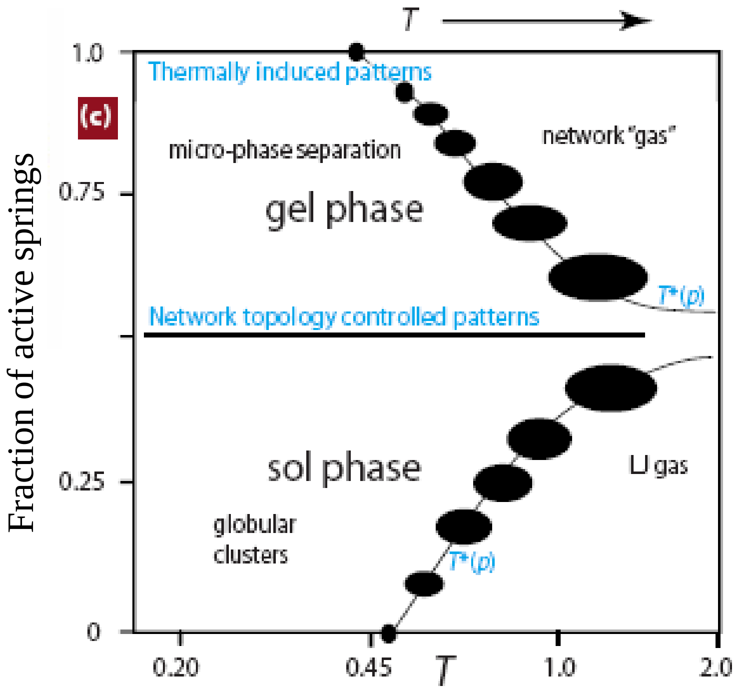
Sol-gel transition at p=0.5

Do gels remember their structure?

100% active springs - Shape and location of patterns determined by thermal fluctuations
no memory of network structure!



Memory of structure – heterogeneous nucleation about high temperature density profile



T
1.0
0.75
0.25
0
(c)
Thermally induced patterns
micro-phase separation
network "gas"
gel phase
T*(p)
Network topology controlled patterns
sol phase
LJ gas
globular
clusters
T*(p)
0.20
0.45
T
1.0
2.0
Fraction of active springs

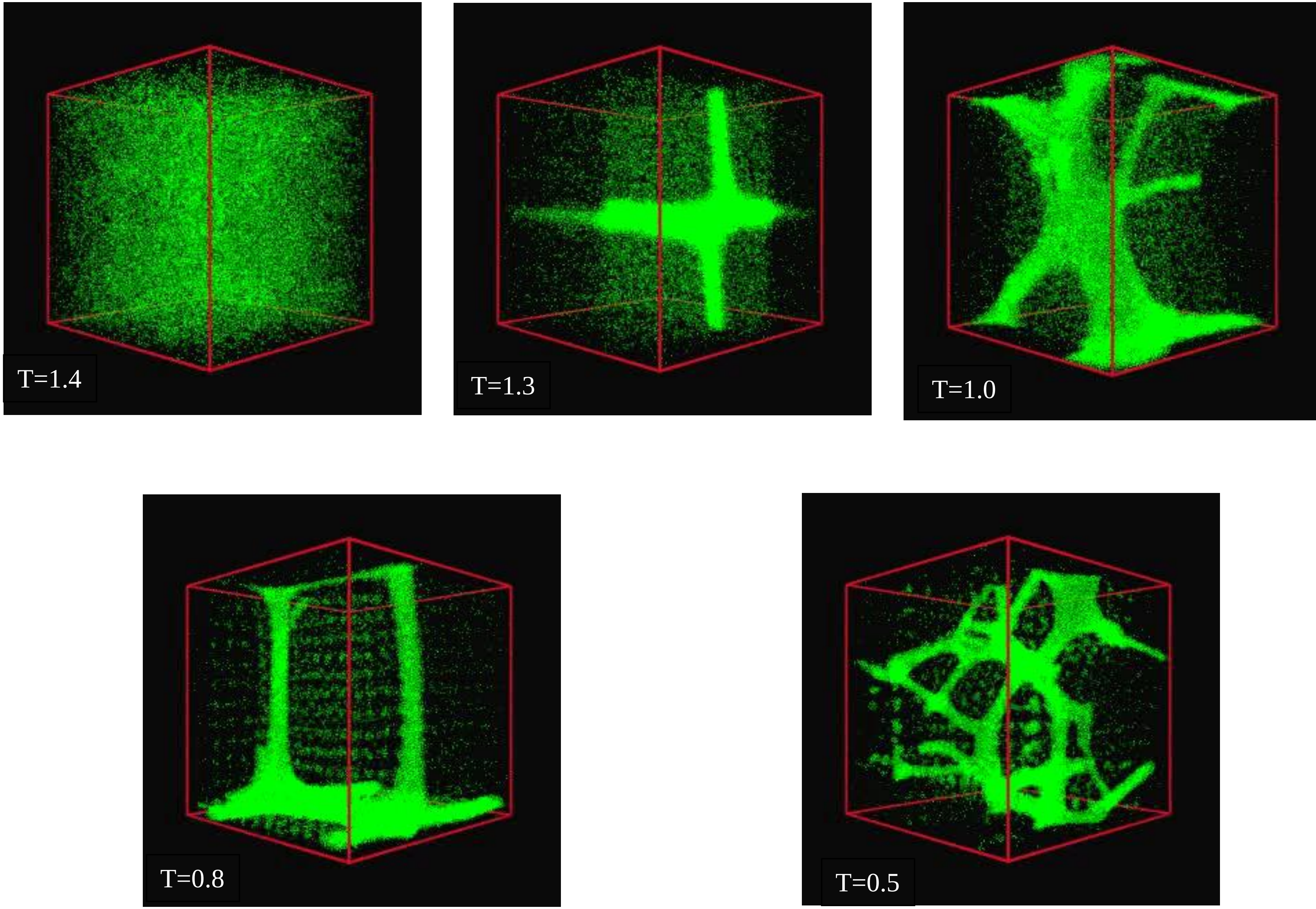
Partial summary:

Microphase separation in a broad range of parameters, in 2d

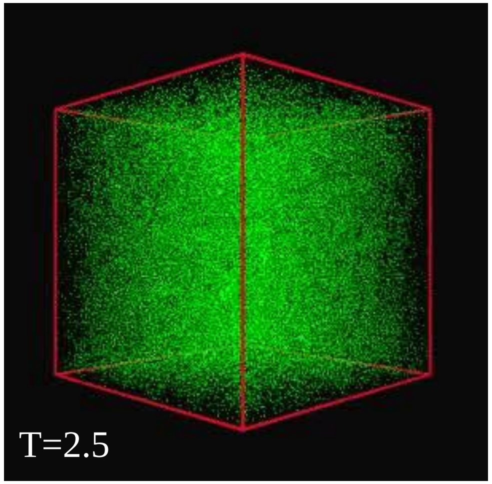
What happens in 3d – droplets, strings or surfaces?

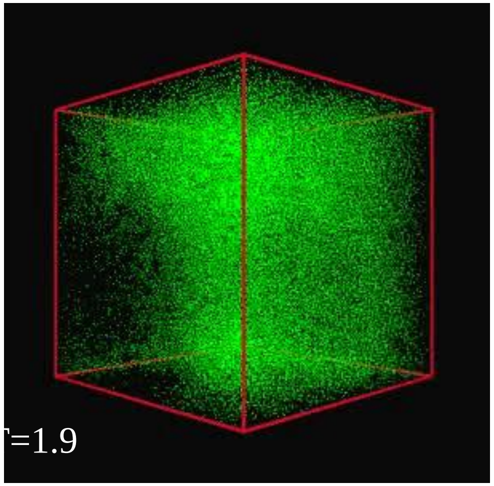
Square lattice, 40x40x40 particles

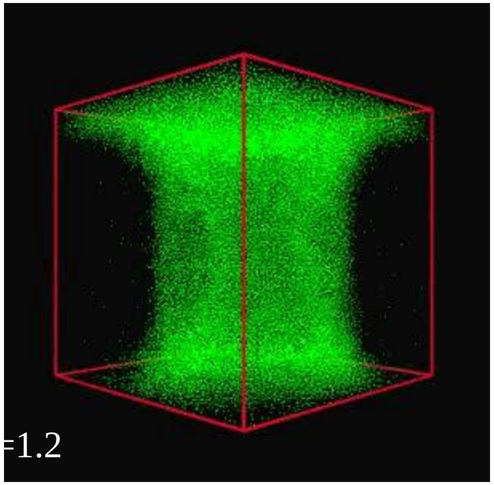
Dilute network **K=0.05, g=3**

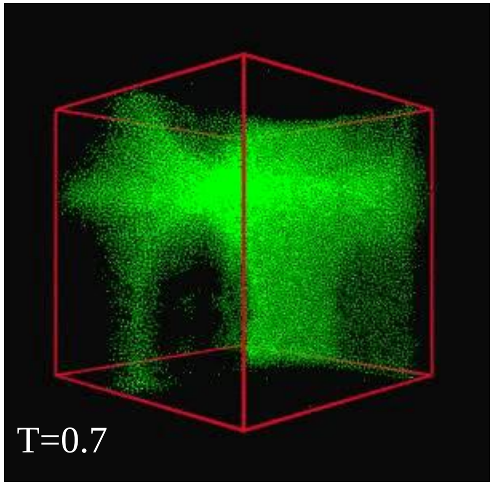


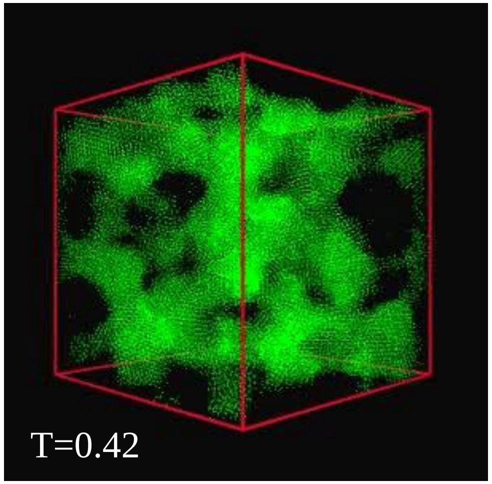
Dense network **K=0.05, g=1.5**











Dilute gels: coexistence of ordered droplet phase with 3d network

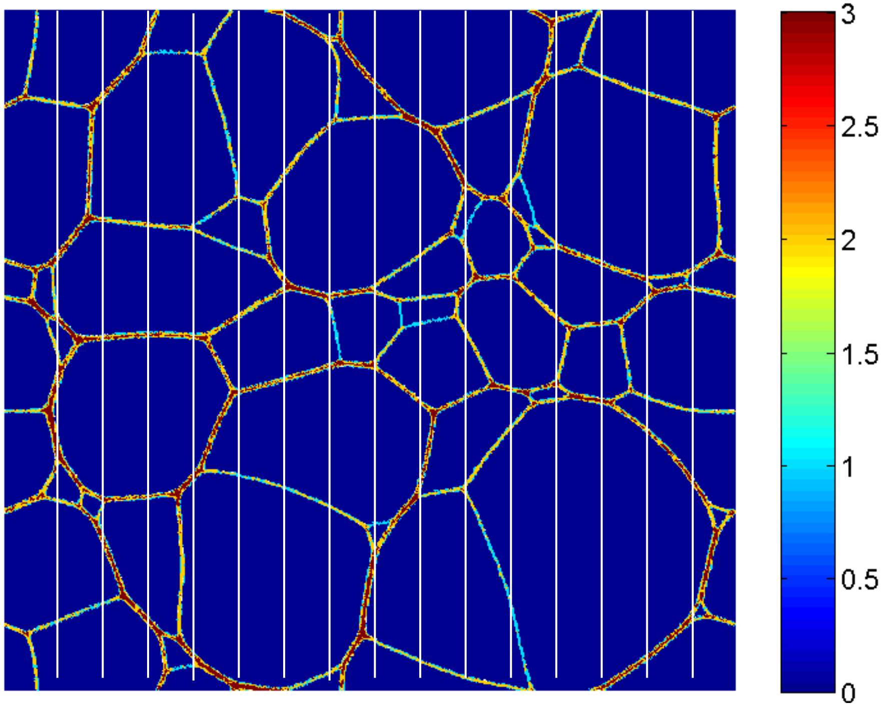
Dense gels: “Plumber’s nightmare” (diffuse bicontinuous structures)

Question: usually the scale of microphase separation is set by molecular size (micelles, vesicles and bilayers of amphiphilic molecules)

How does the interplay between long range elastic forces and short range attractions determine the scale of the patterns?

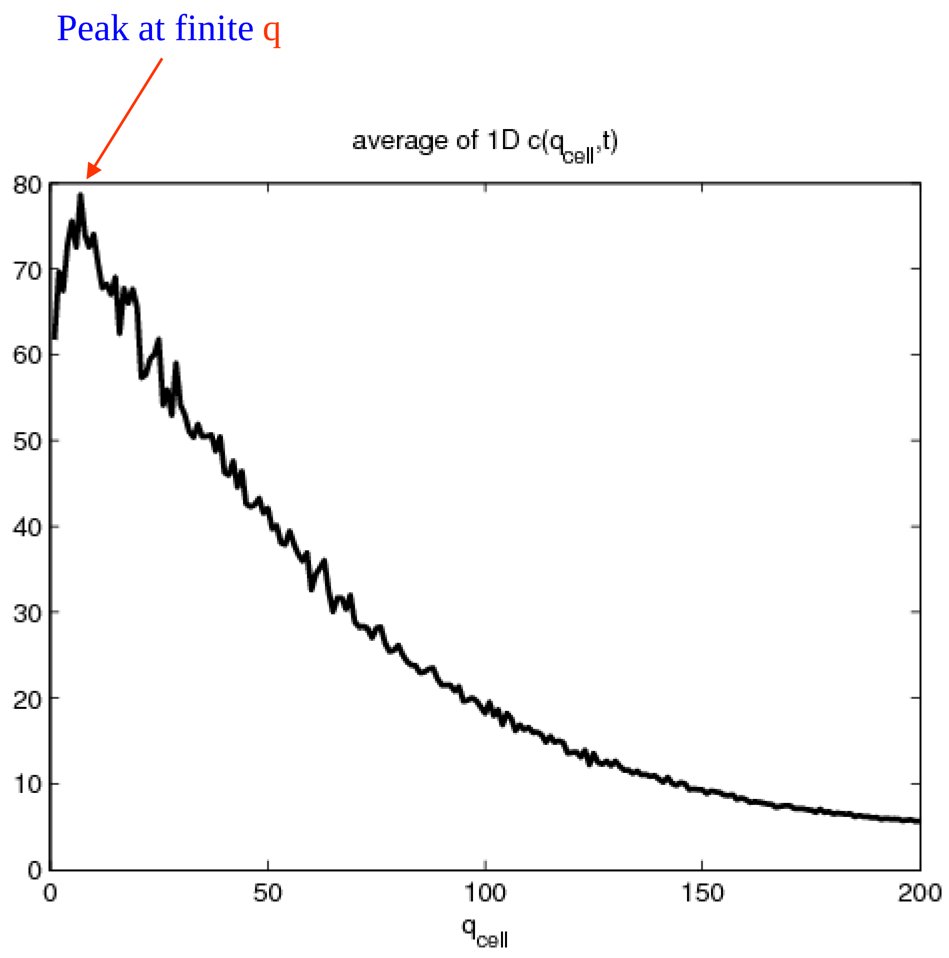
How does the characteristic size of domains change with temperature?

1. Coarse grain the density pattern:



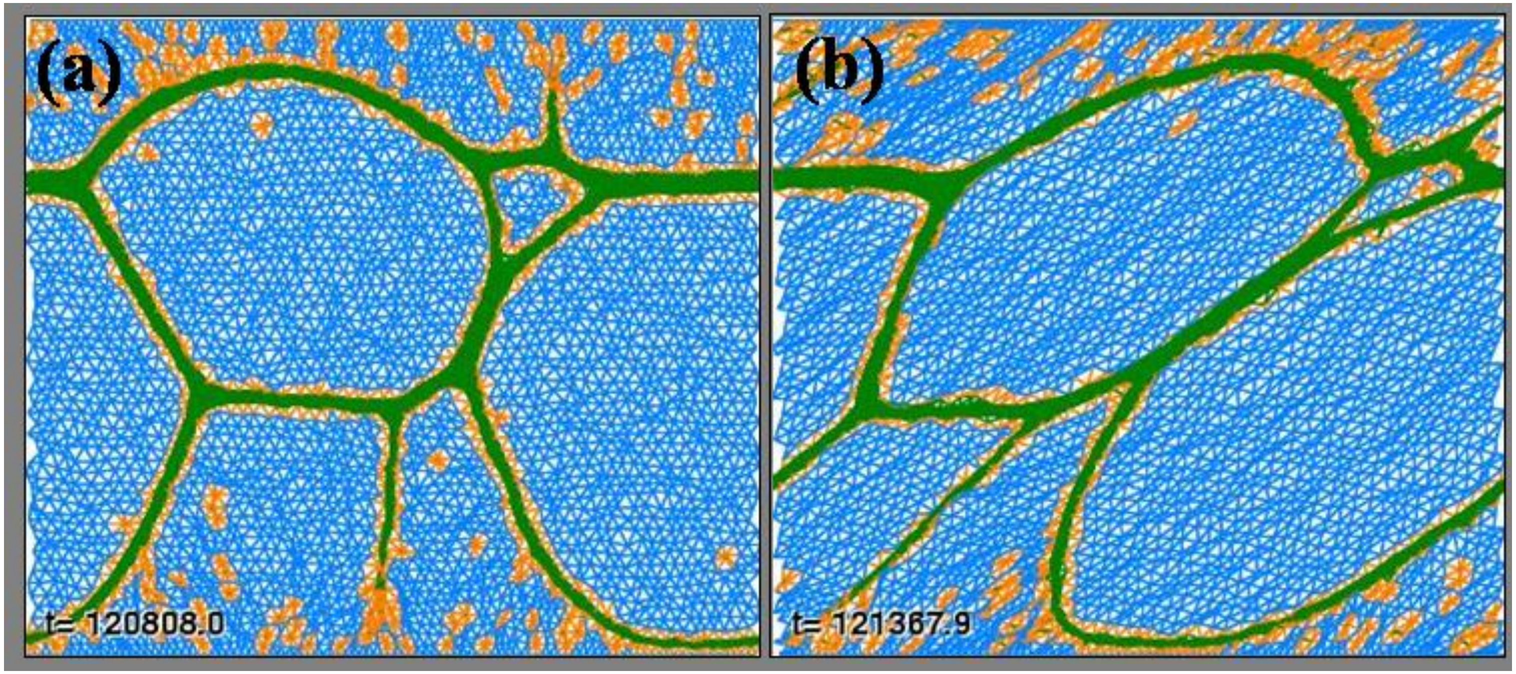
2. Divide the pattern into thin slices along some direction and Fourier transform the density in each slice

3. Average over the slices

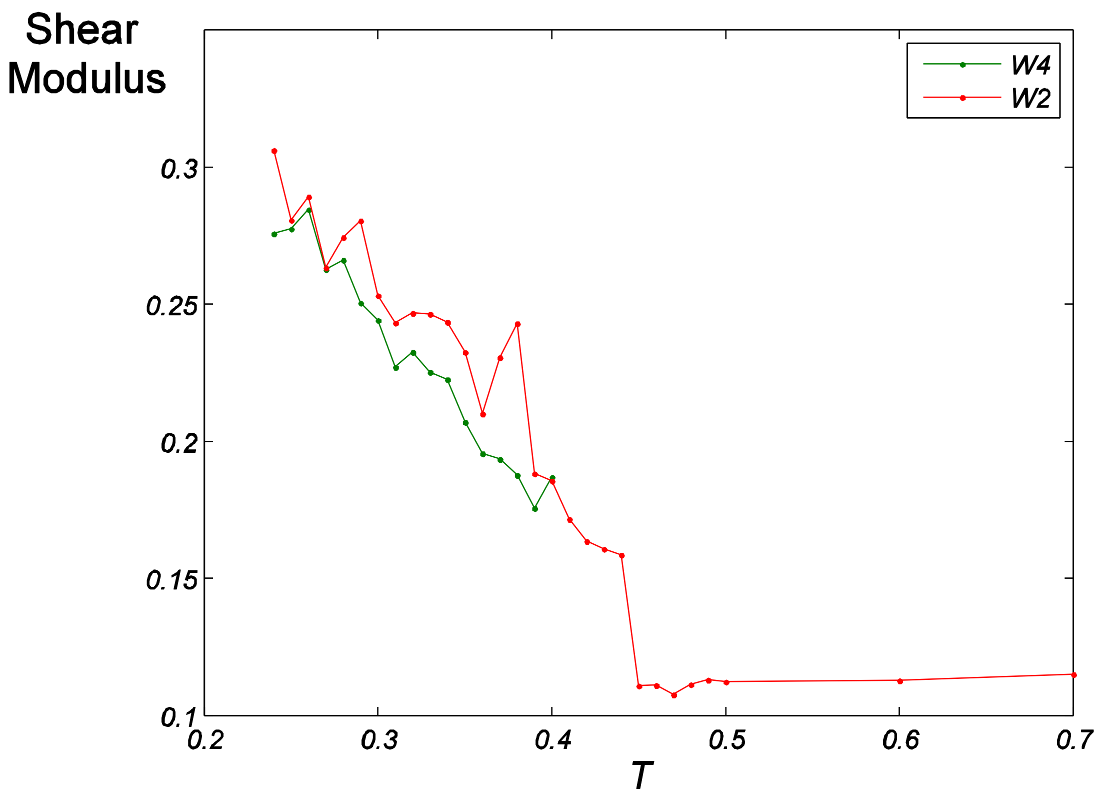

Peak at finite q
average of 1D c(q_cell,t)
80
70
60
50
40
30
20
10
0
0
50
100
150
200
q_cell

Response to shear:

2 walls in the Y-direction, periodic along X



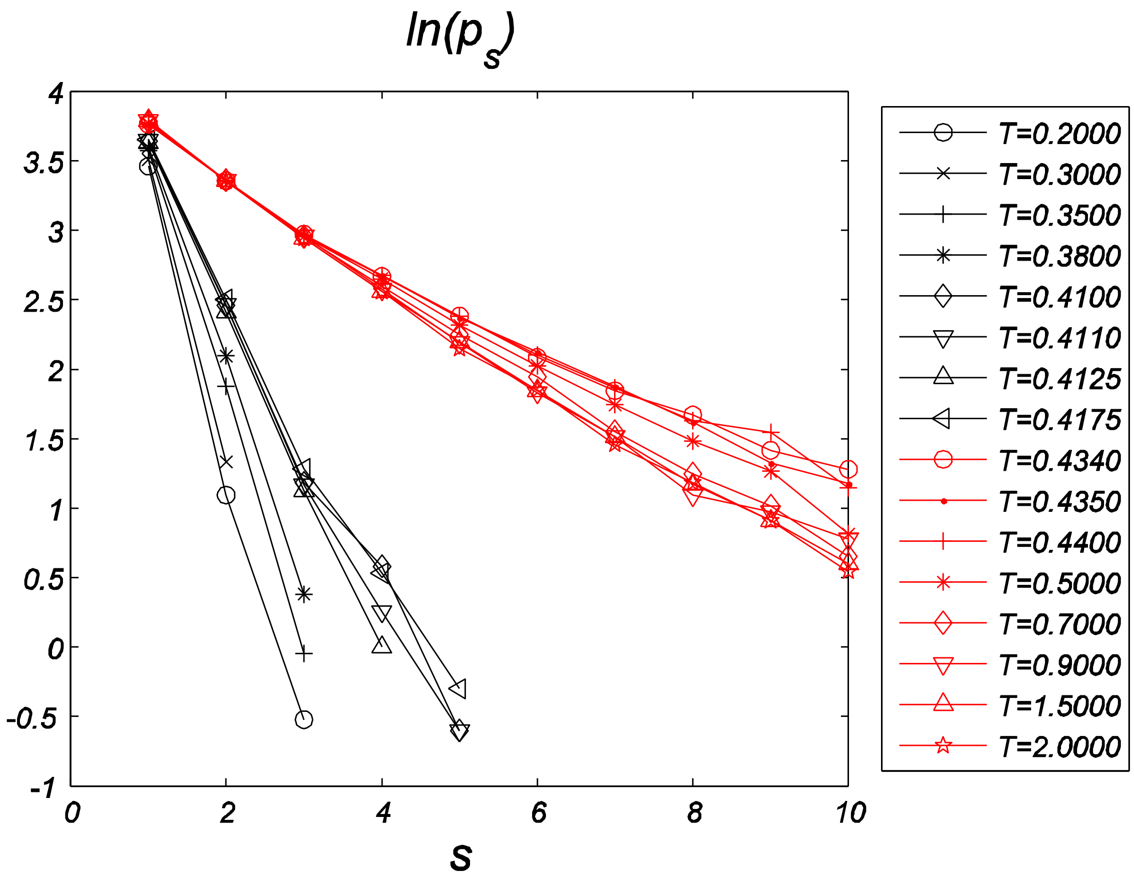
Start from hexagonal lattice; N=10,000; k=0.0667; T=0.3



Shear rigidity enhanced by formation of “super-network”

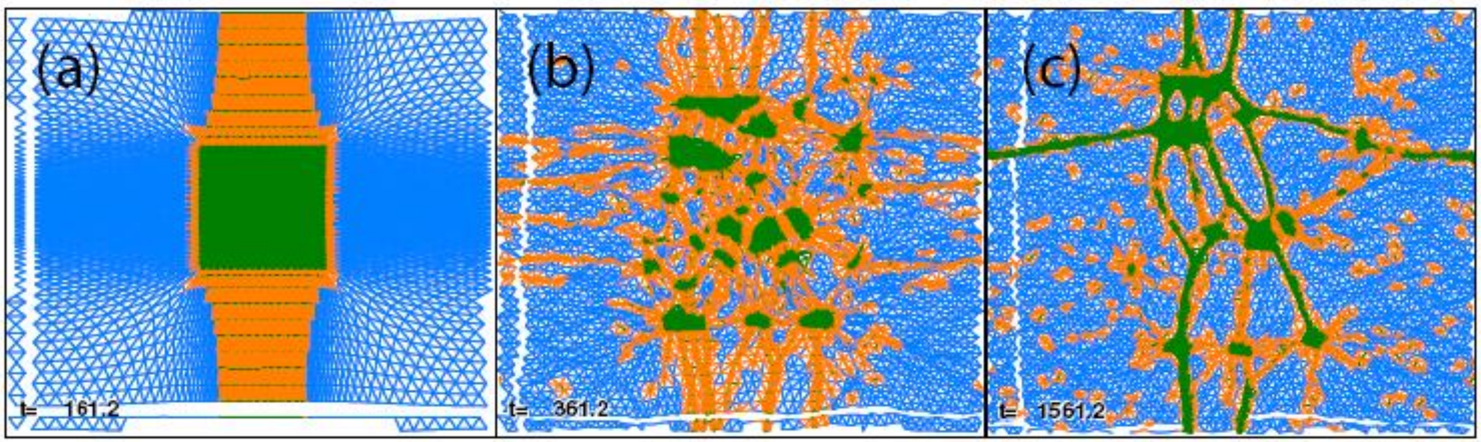
Distribution of clusters

Probability of a cluster of s particles: $p_s \propto e^{-ms}$

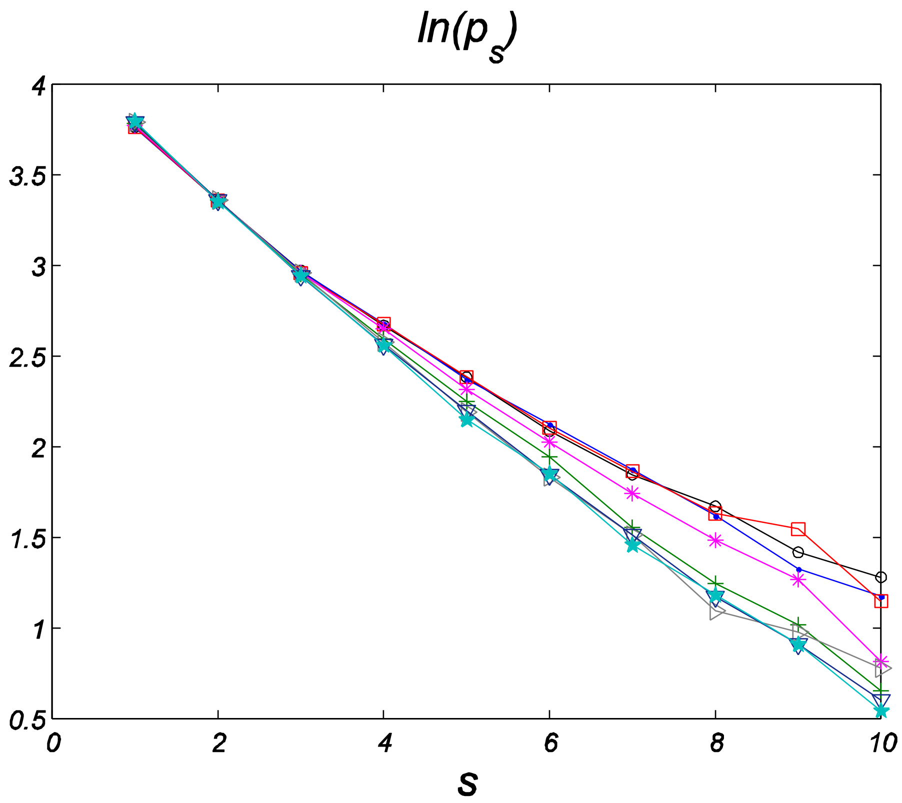


Is the steady state stable under large perturbation of initial conditions?

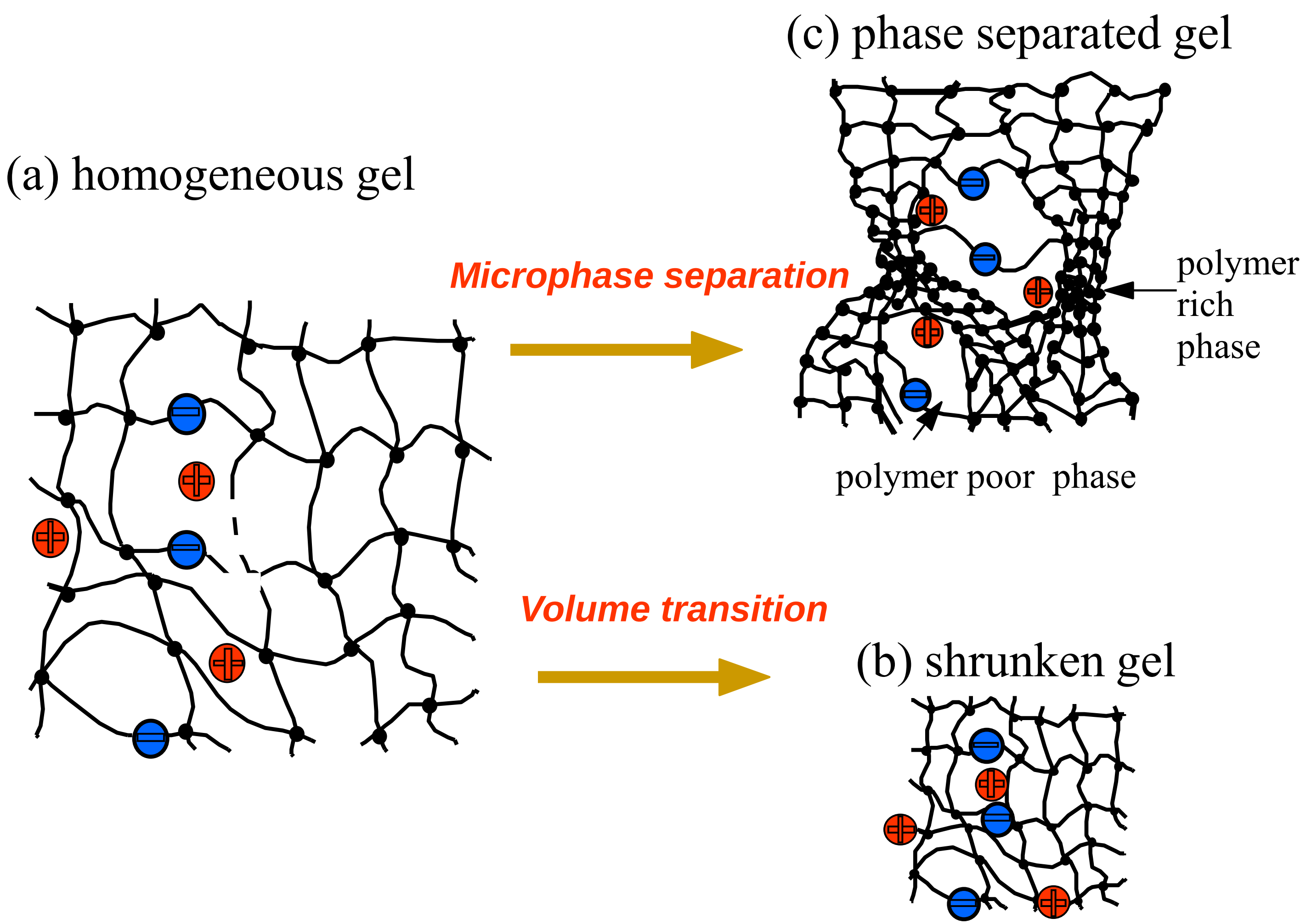
Start from a compact cluster



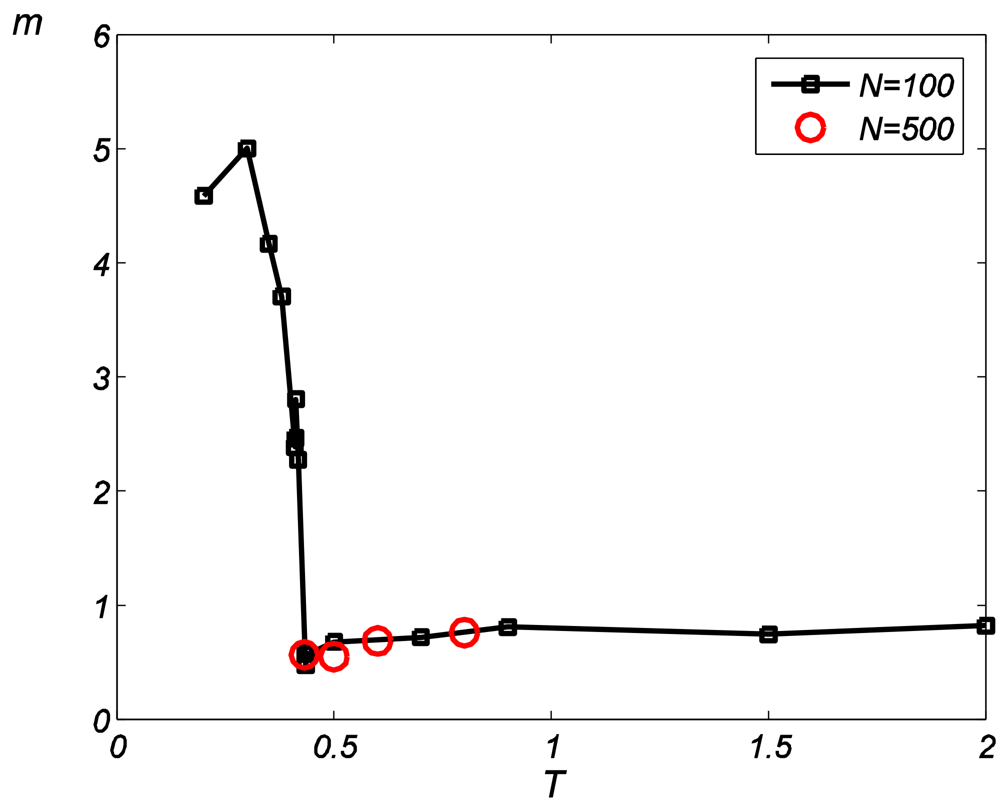
Yes – linear filaments develop!


ln(p_s)
4
3.5
3
2.5
2
1.5
1
0.5
0
2
4
6
8
10
s

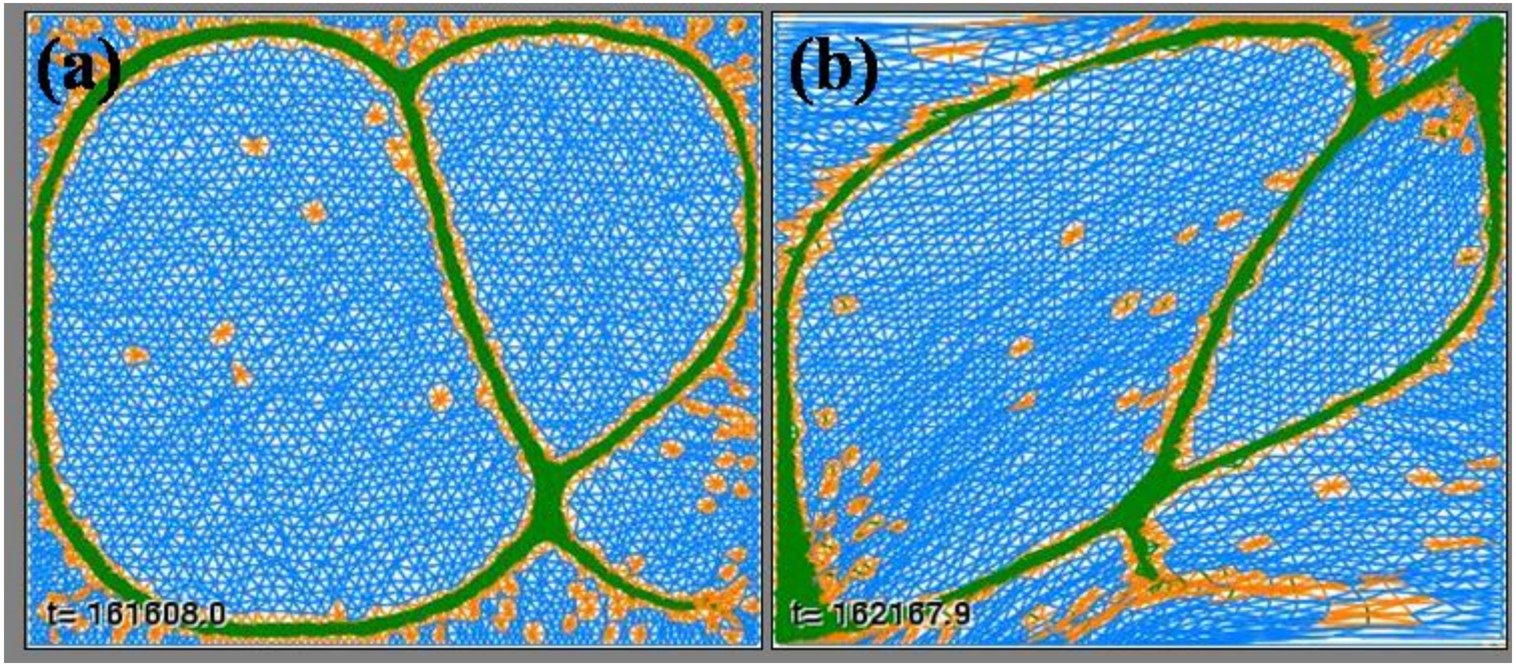
Phase separation vs Volume transition in charged gels

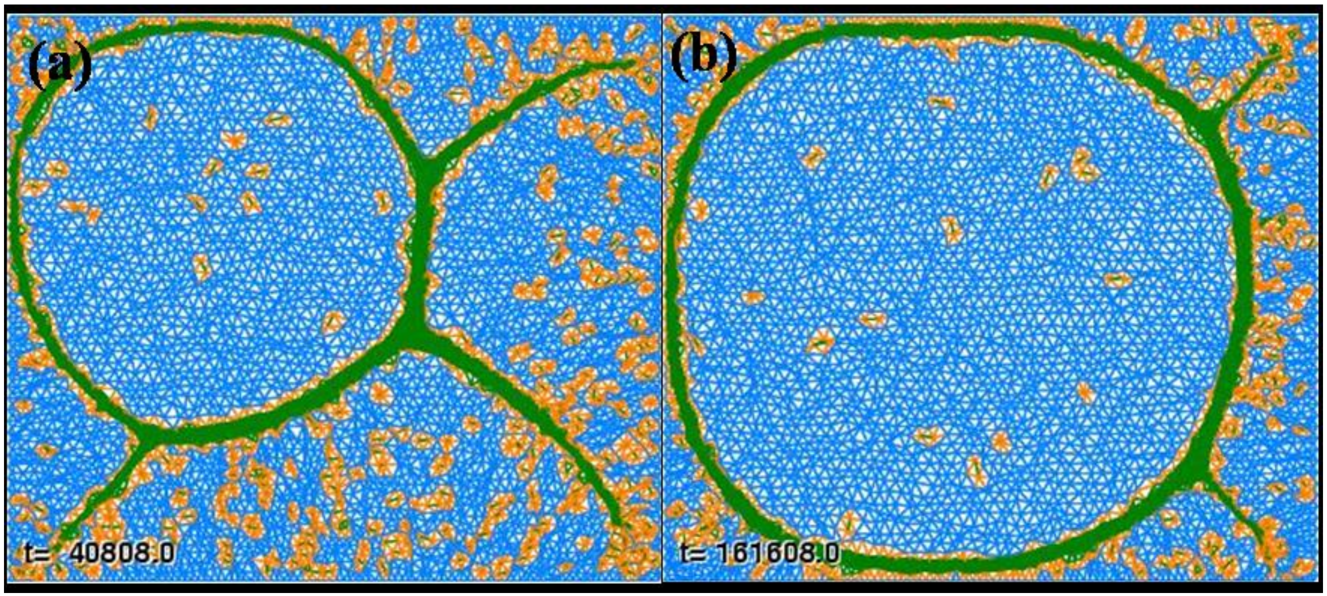


Shibayama, *Macromol. Chem. Phys.* **199**, 1-30 (1998)

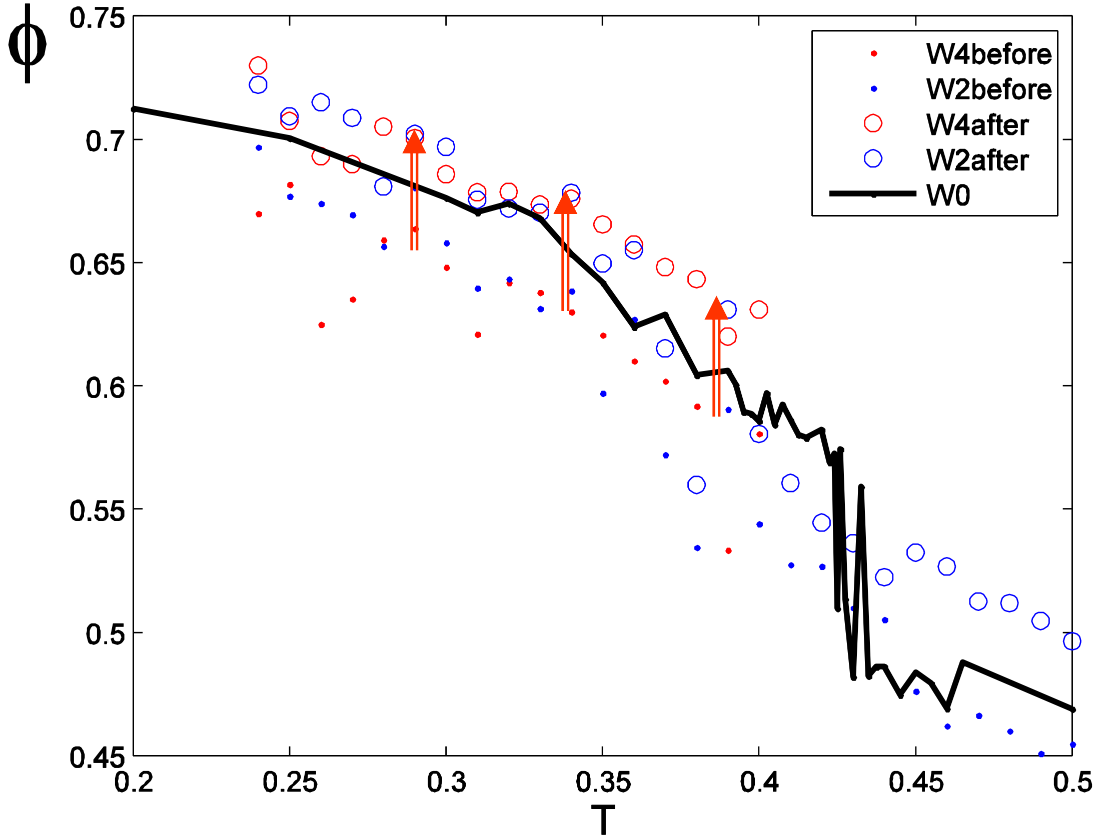


Larger (finite) clusters strongly suppressed below T*!


(a)
t= 161608.0
(b)
t= 162167.9


(a)
t= 40808.0
(b)
t= 161608.0

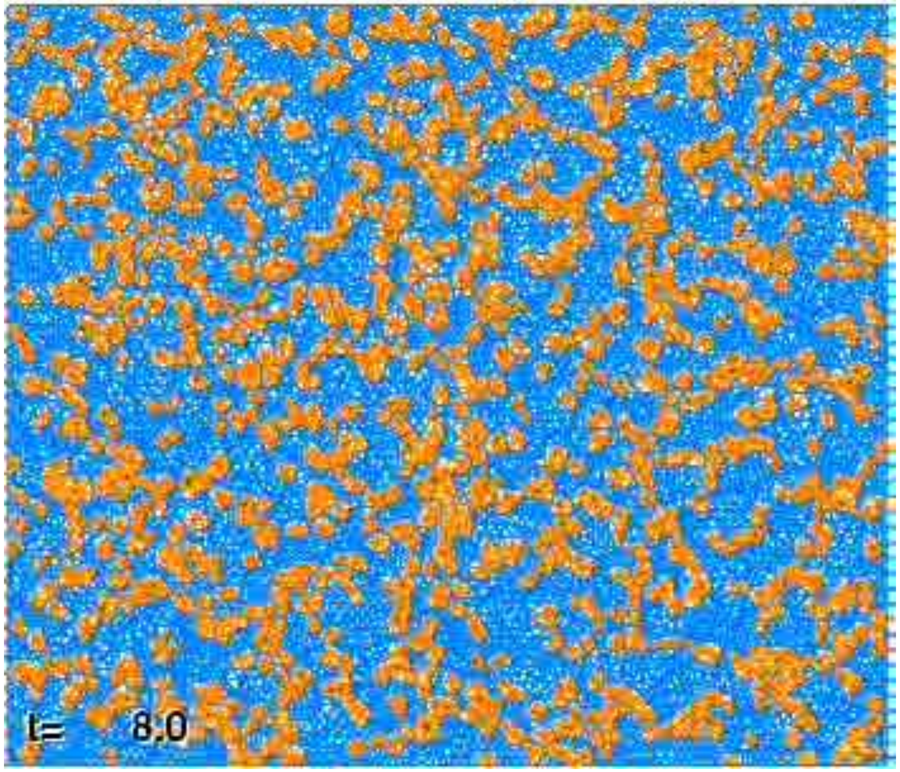
Effect of walls and of shear on order parameter:



1. Walls smoothen the transition – finite size effect?

2. Phase separation enhanced by shear

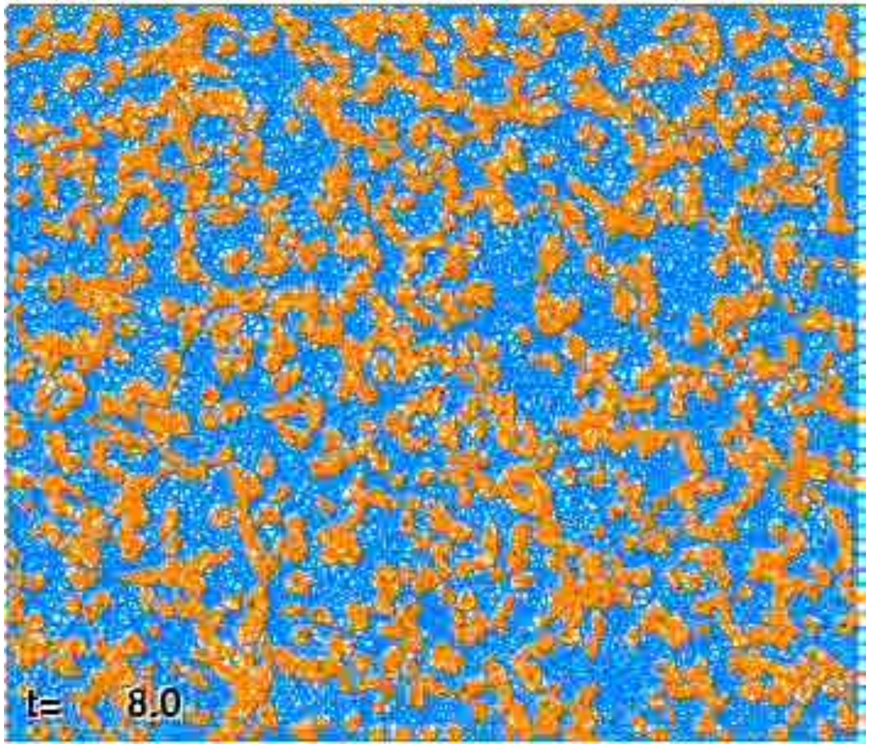
Hexagonal lattice, N=10,000, k=0.0667; **T=0.3**; 4 walls



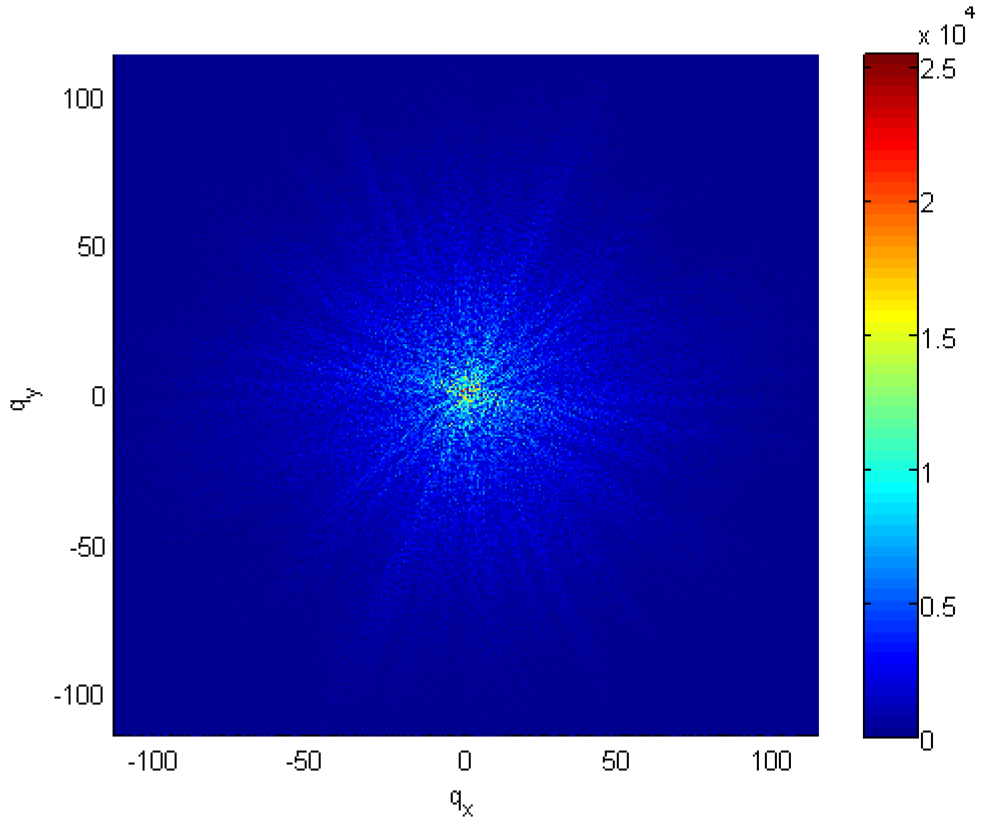
At lower temperatures – filamentous cells

The effect of walls

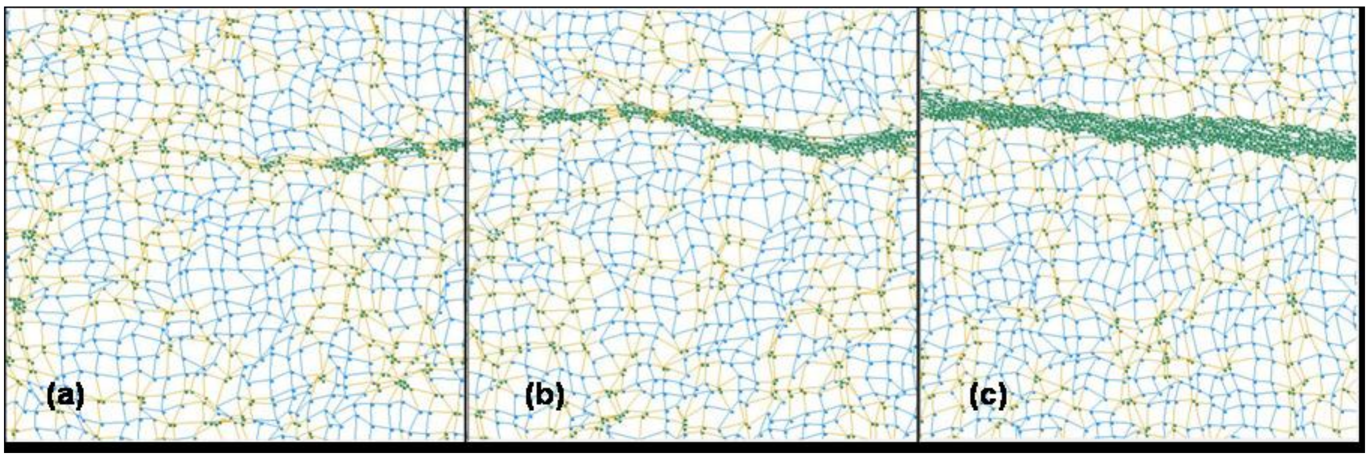
Hexagonal lattice, N=10,000, k=0.0667; **T=0.4**; 4 walls

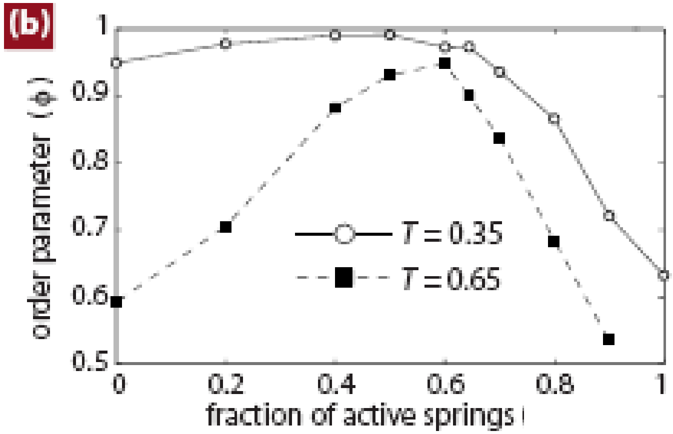


Near the transition – a single closed filament



x 10^4
2.5
2
1.5
1
0.5
0
100
50
0
-50
-100
q_y
-100
-50
0
50
100
q_x


(a)
(b)
(c)


(b)
order parameter (ϕ)
fraction of active springs
T = 0.35
T = 0.65
0.5
0.6
0.7
0.8
0.9
1
0
0.2
0.4
0.6
0.8
1