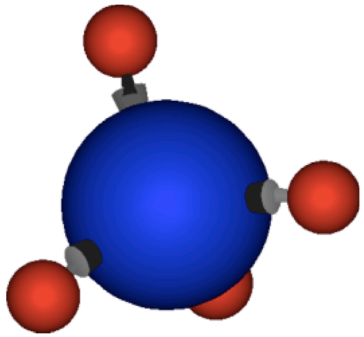
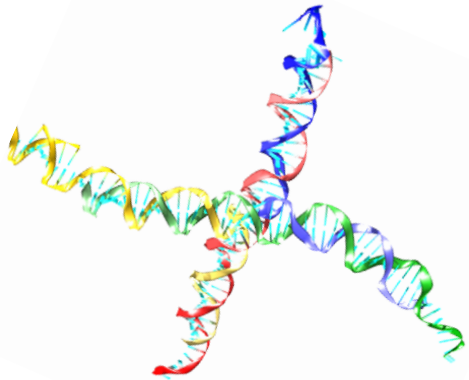
15th International Conference on Magnetic Fluids ICMF-15
July 4-8 2016 Ekaterinburg.

Competing interactions: from dipolar particles to DNA gels

Francesco Sciortino

http://glass.phys.uniroma1.it/sciortino/

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COLLDENSE
COLLOIDS with DESIGNED RESPONSE

Outline:

A review of our last years work on the dipolar hard-sphere model

Is there a "gas-liquid" critical point ?
Monte Carlo simulations at low T(Albert's question)

Patchy models with similar behavior
Competitive interactions

From in-silico to the real world: a designed example of competitive interactions: a re-entrant DNA hydrogel

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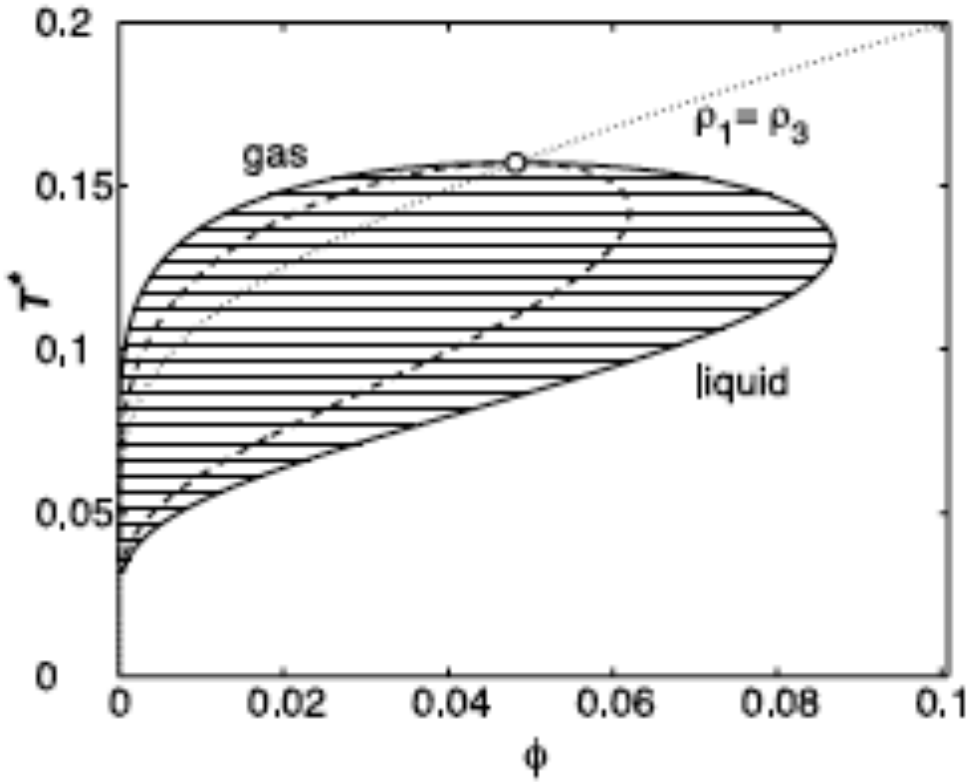
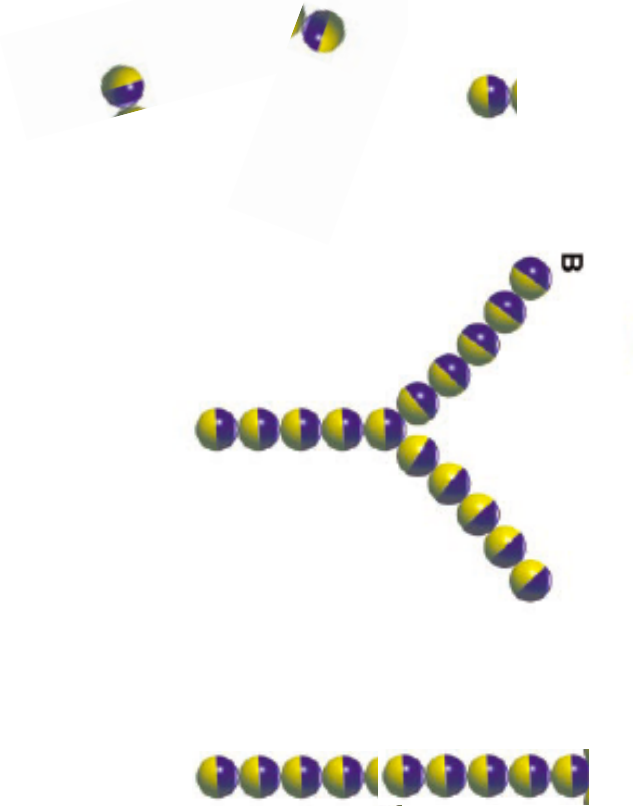


Fig. 2. The phase diagram of the dipolar network calculated for defect energies of $\varepsilon_1 = 0.67$ and $\varepsilon_3 = 0.12$. At the critical point (circle), the coexistence curve (thick solid line), the phase stability boundary (dashed line), and the connectivity transition (dotted line) meet. The lines denote the coexistence of the end-rich "gas" with the junction-rich "liquid." At low temperatures, the coexistence region narrows to very low densities.



Tlusty-Safran, Science (2000)

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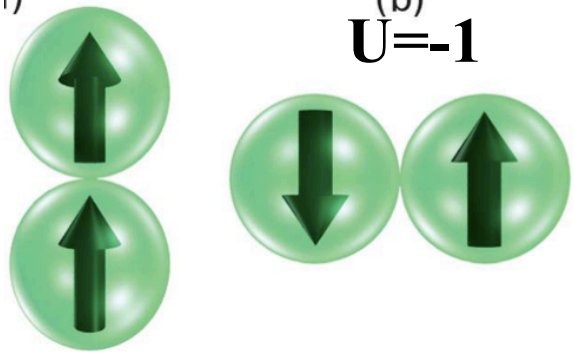
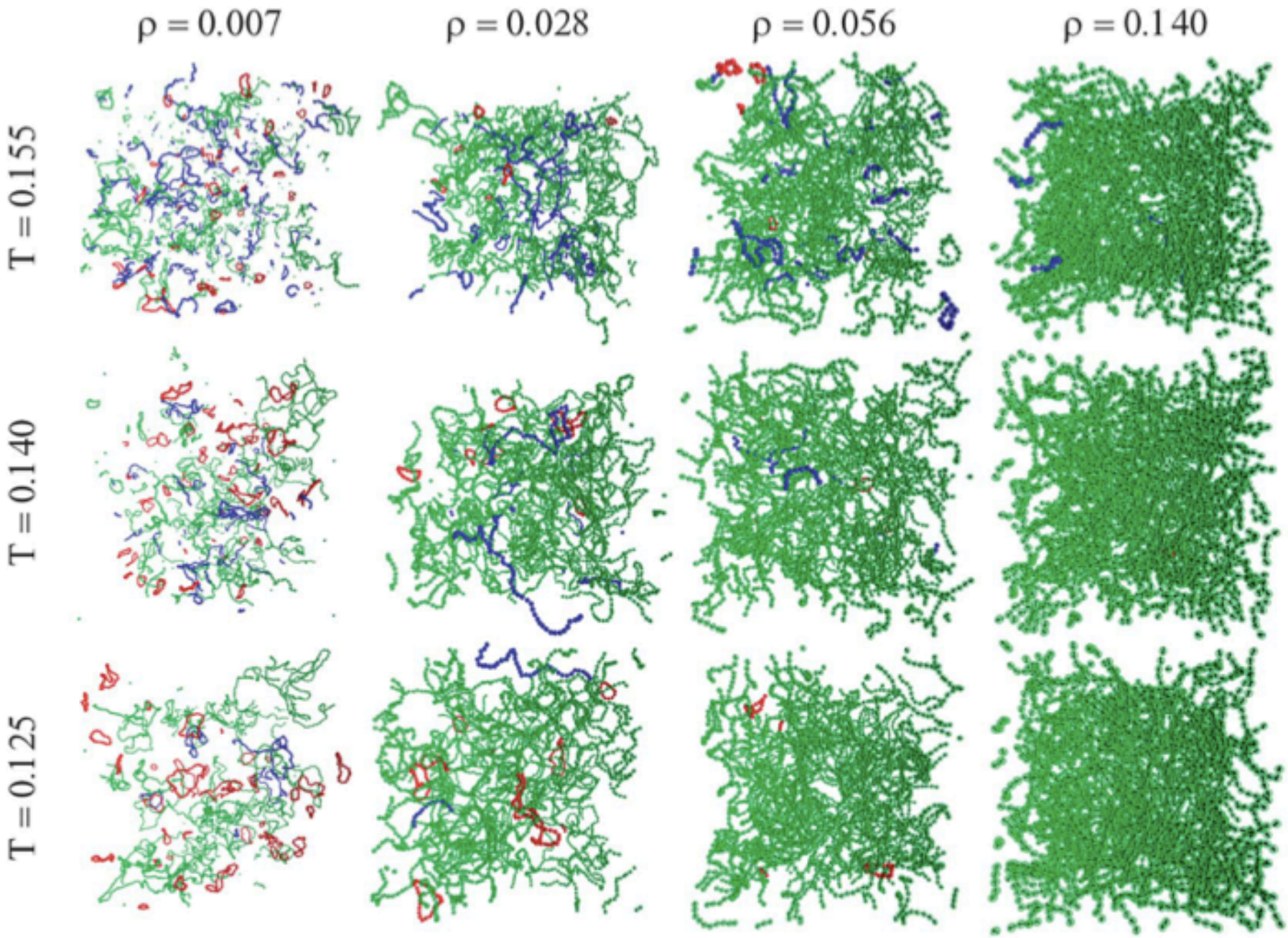
Simulation Methods

- Grand Canonical Monte Carlo (Ewald Sums)
- Advance Volume Biasing (100x). Biased insertion
- Successive Umbrella Sampling (100x)

Wide region of densities, down to T*=0.125





Typical snapshots of equilibrium configurations of DHS at $T = 0.125, 0.140, 0.155$ and $\rho = 0.007, 0.028, 0.056, 0.140$. The

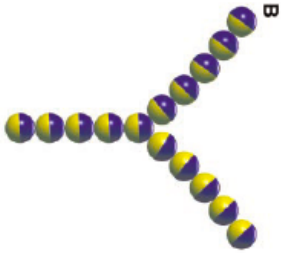
PRL 107, 237801 (2011) PHYSICAL REVIEW LETTERS week ending 2 DECEMBER 2011

No Evidence of Gas-Liquid Coexistence in Dipolar Hard Spheres

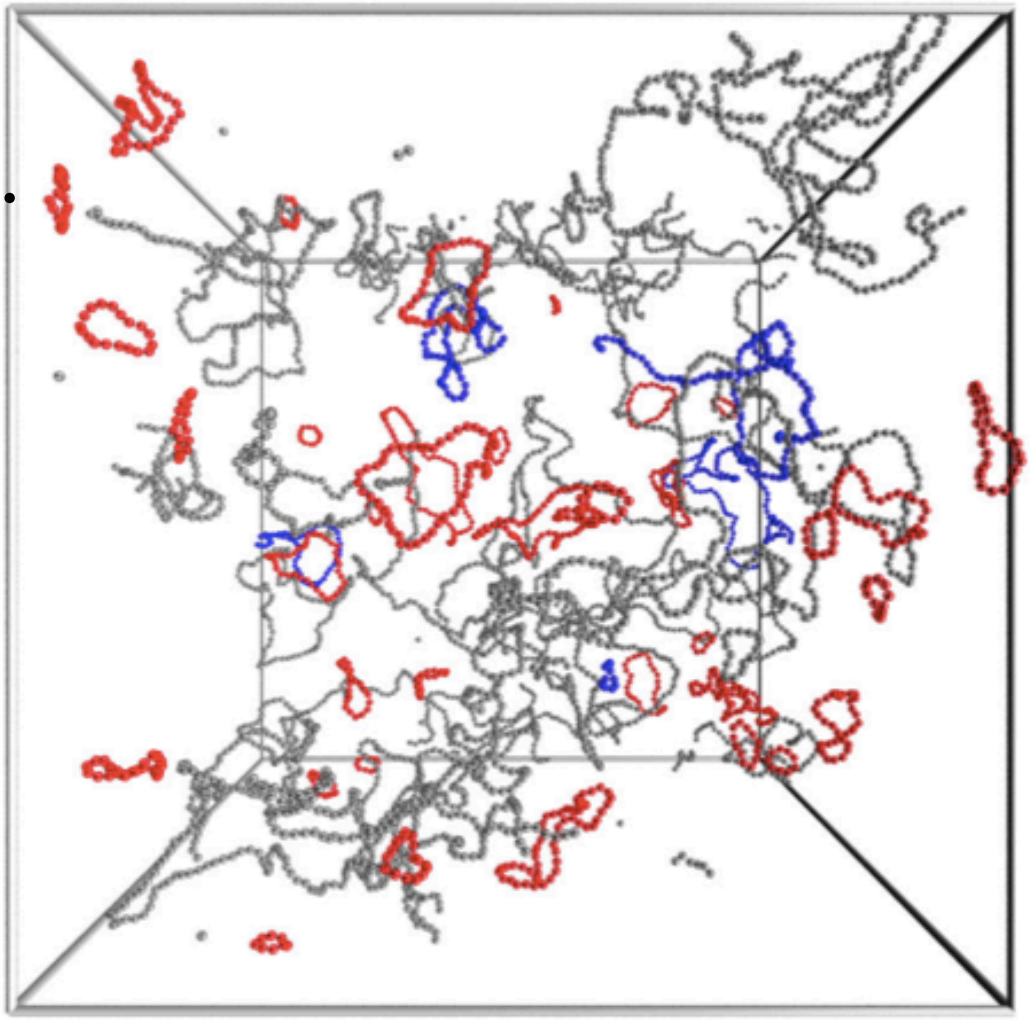
Lorenzo Rovigatti and John Russo
Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00185 Roma, Italy

Francesco Sciortino
Dipartimento di Fisica and CNR-ISC, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00185 Roma, Italy

In the competition between branching and linear chains….



a new actor: The Ring



Nonmonotonic Magnetic Susceptibility of Dipolar Hard-Spheres at Low Temperature and Density

Sofia Kantorovich,[1,2] Alexey O. Ivanov,[1] Lorenzo Rovigatti,[2] José Maria Tavares,[3,4] and Francesco Sciortino[2,5]

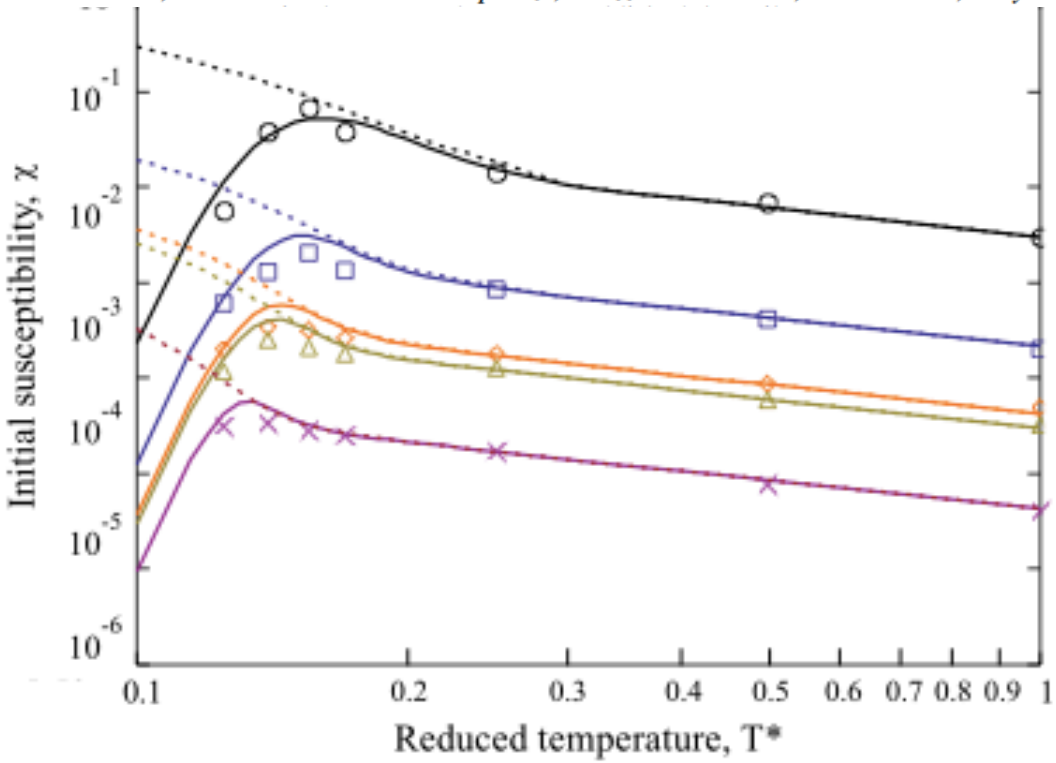
[1]*Ural Federal University, Lenin Avenue 51, 620083, Ekaterinburg, Russia*

[2]*Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 2, 00185 Roma, Italy*

[3]*Instituto Superior de Engenharia de Lisboa-ISEL, Rua Conselheiro Emídio Navarro 1, P-1950-062 Lisbon, Portugal*

[4]*Centro de Física Teórica e Computacional, Avenida Professor Gama Pinto 2, P-1649-003 Lisbon, Portugal*

[5]*CNR-ISC, Università di Roma La Sapienza, Piazzale A. Moro 2, 00185 Roma, Italy*



The effect of the rings on the initial magnetic susceptibility

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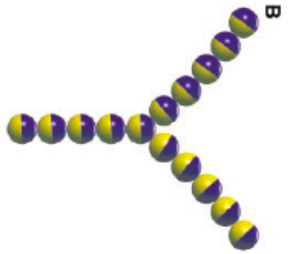
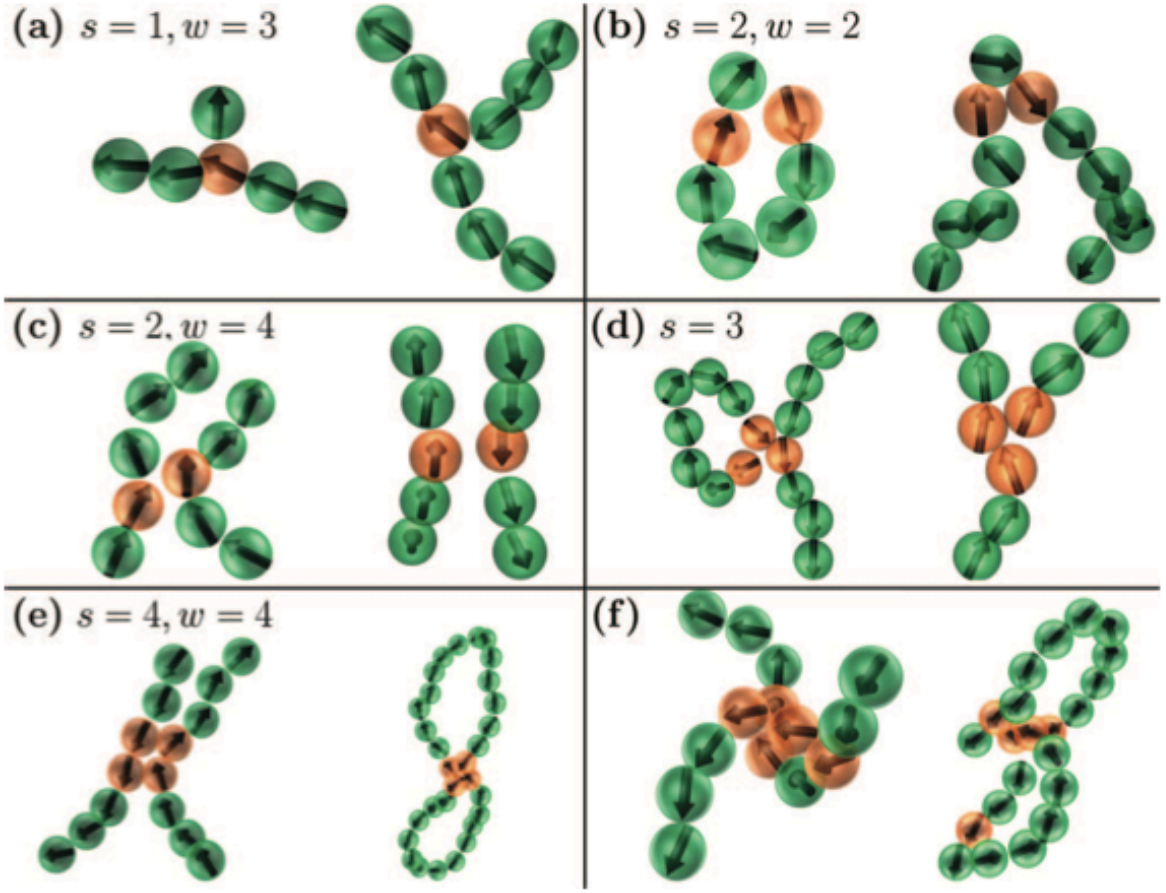
Should we add other ingredients to Safran's approach beside the ring ?



Yes ! Other defects are becoming important at low T



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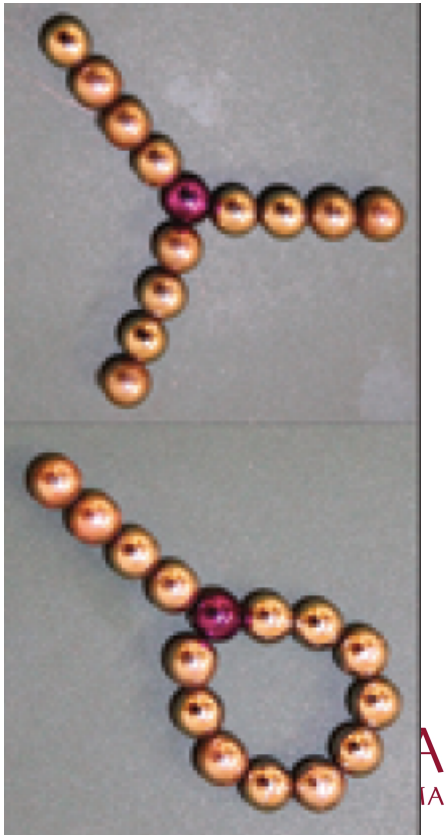
The primary clusters: chain and ring

Interaction
chain-chain

Interaction
chain-ring



Branching
chain-chain

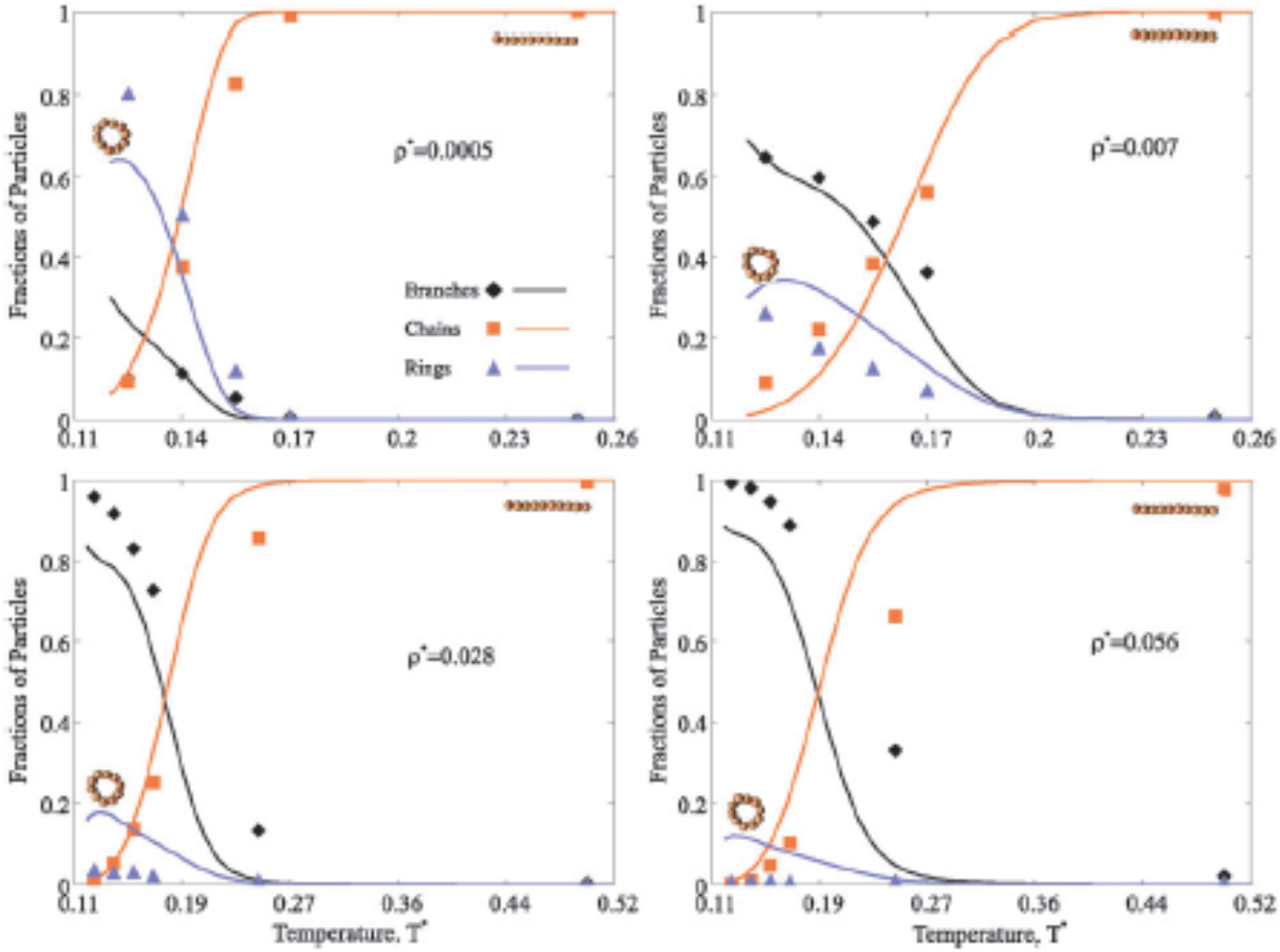
Branching
chain-ring

Interaction
ring-ring

Cite this: *Phys. Chem. Chem. Phys.*, 2015, **17**, 16601

Temperature-induced structural transitions in self-assembling magnetic nanocolloids

Sofia S. Kantorovich,*[ab] Alexey O. Ivanov,[b] Lorenzo Rovigatti,[a] Jose M. Tavares[cd] and Francesco Sciortino[e]



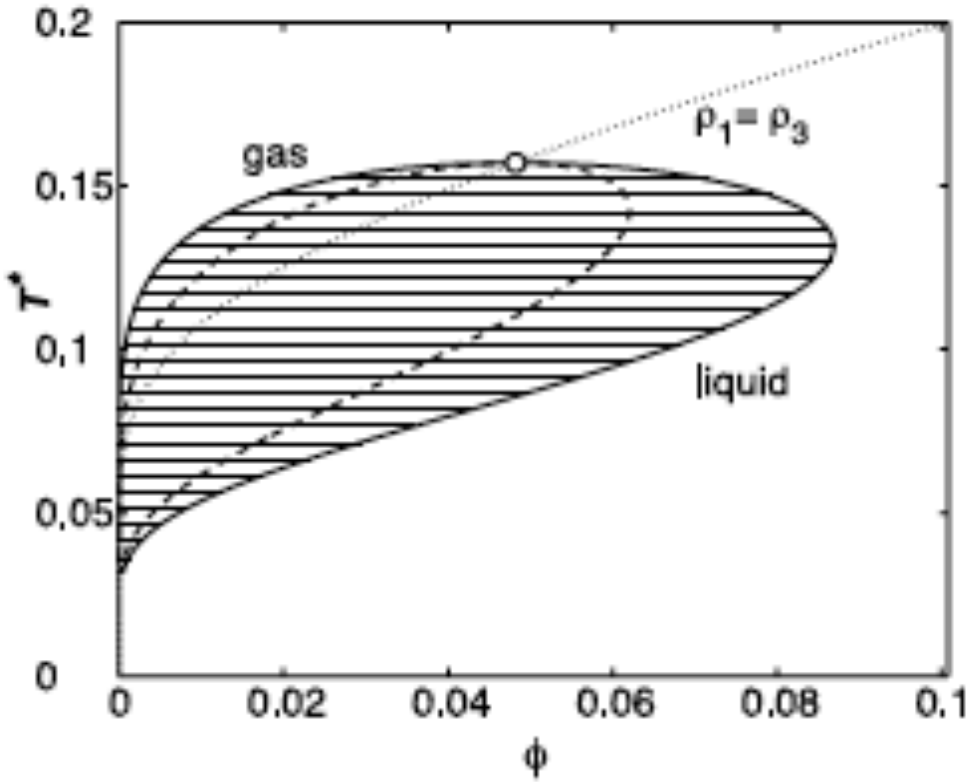
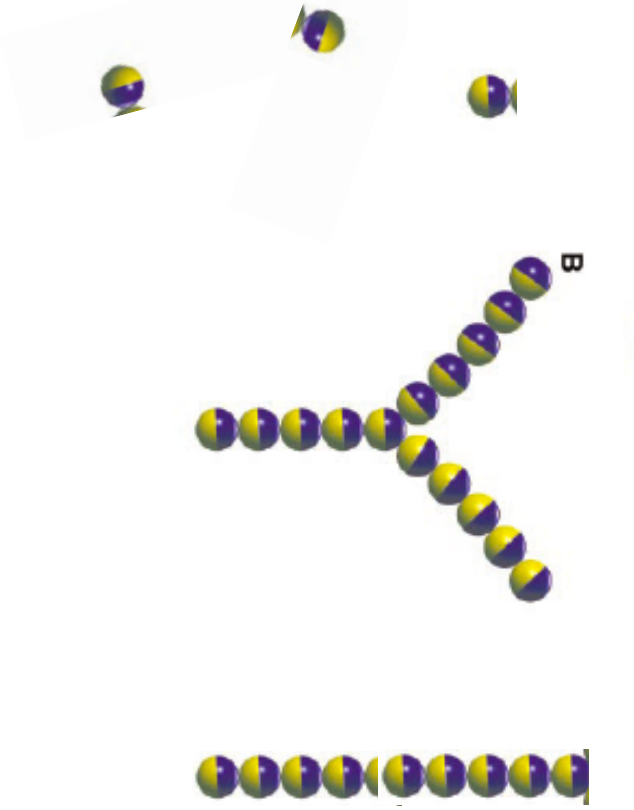


Fig. 2. The phase diagram of the dipolar network calculated for defect energies of $\varepsilon_1 = 0.67$ and $\varepsilon_3 = 0.12$. At the critical point (circle), the coexistence curve (thick solid line), the phase stability boundary (dashed line), and the connectivity transition (dotted line) meet. The lines denote the coexistence of the end-rich "gas" with the junction-rich "liquid." At low temperatures, the coexistence region narrows to very low densities.



Tlusty-Safran, Science (2000)

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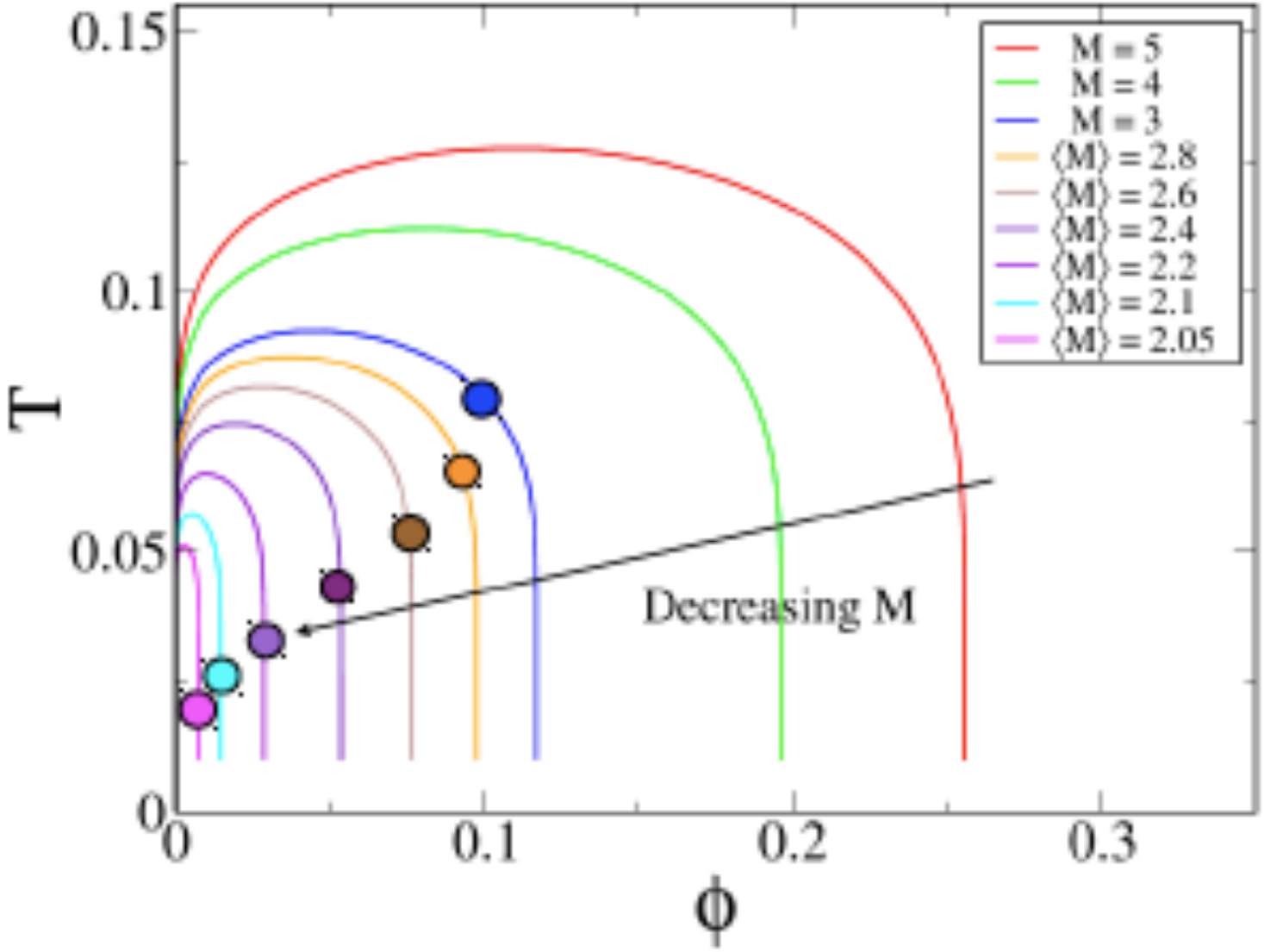
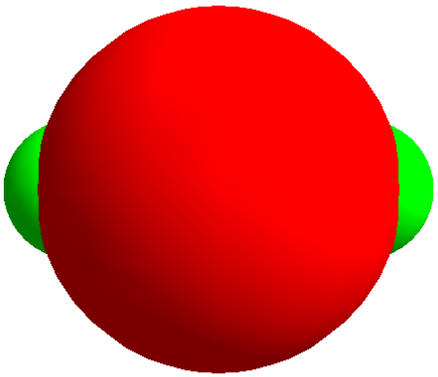
Effective temperature valence



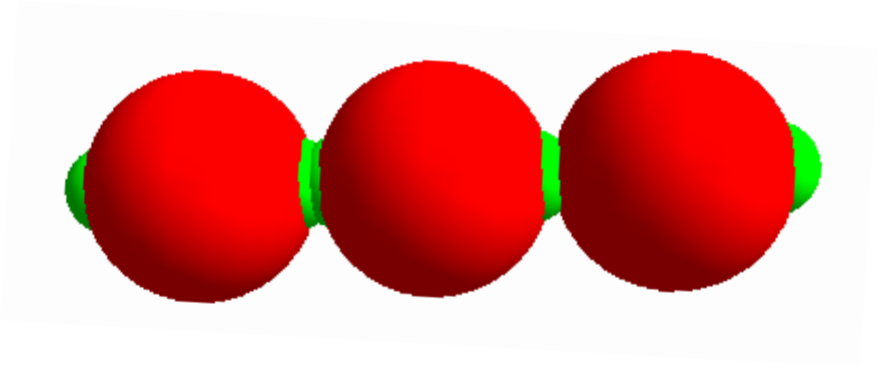
E. Bianchi et al., PRL **97**, 168301 (2006)

A patchy particle models that behaves as Safran's DHS

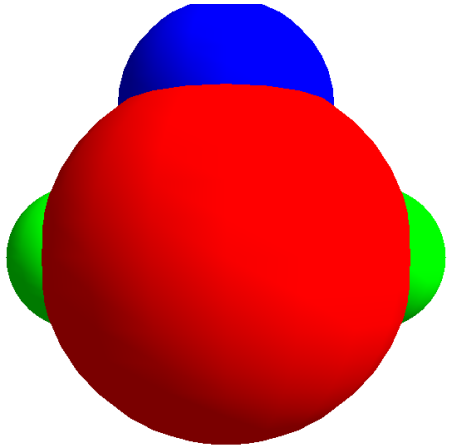
PATCHY PARTICLES THAT FORM CHAINS:



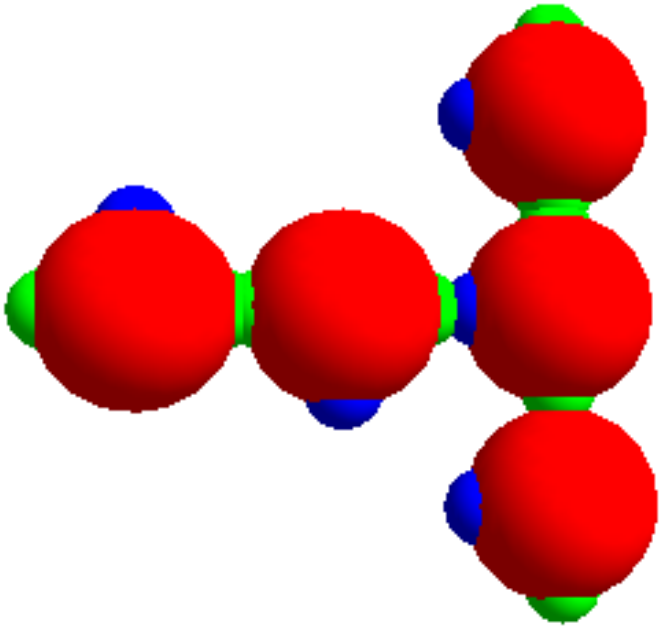
ε_{AA}



ADD BRANCHING POSSIBILITIES

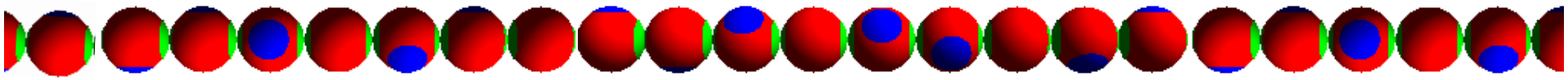


ε_{AB}



How the ground state looks like ?

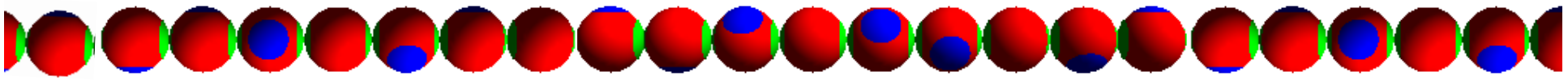
Start from an infinite chain of AA bonds



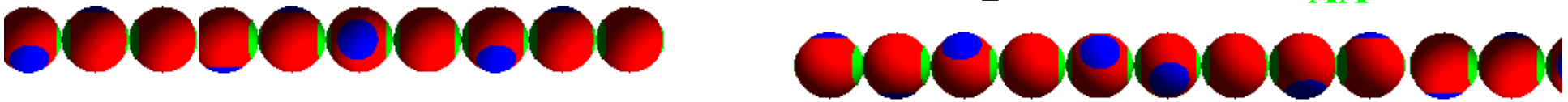
Splitting the chain in two parts costs ε_{AA}

How the ground state looks like ?

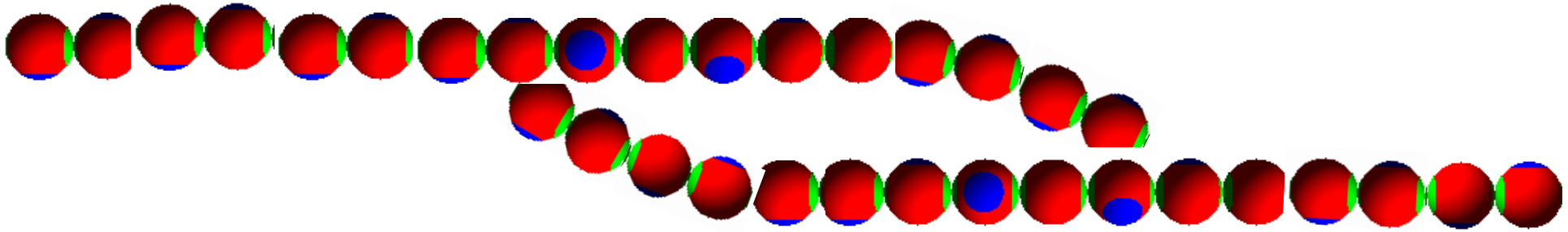
Start from an infinite chain of AA bonds



Splitting the chain in two parts costs ε_{AA}



Joining the two newly created ends provides a gain of $-2\varepsilon_{AB}$



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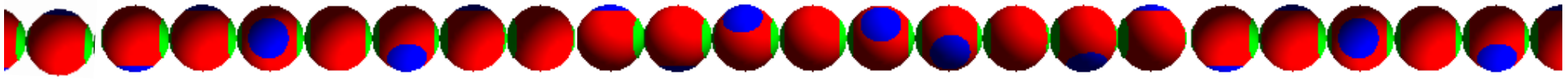

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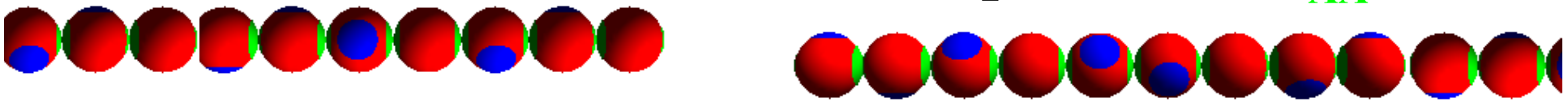

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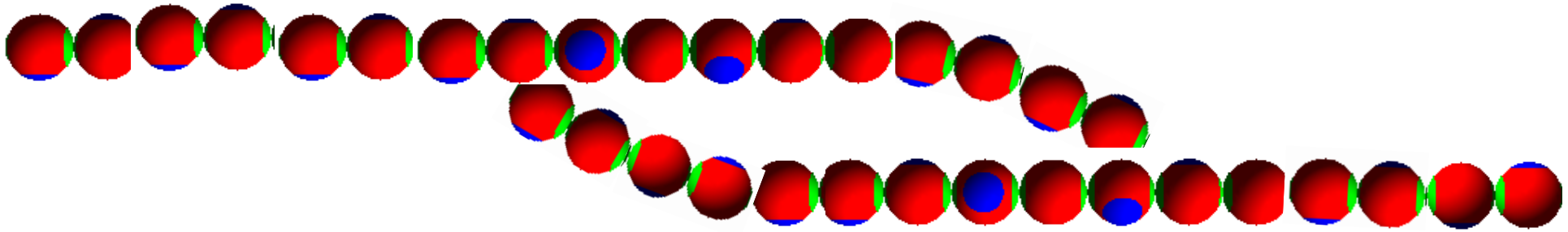

$$\Delta E=\varepsilon_{AA}-2\varepsilon_{AB} > 0$$

$\varepsilon_{AB}/\varepsilon_{AA}=0.5$

Chaining wins at low T

Branching wins even at low T

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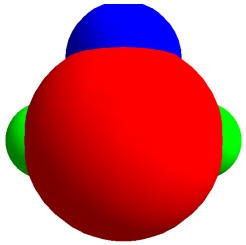
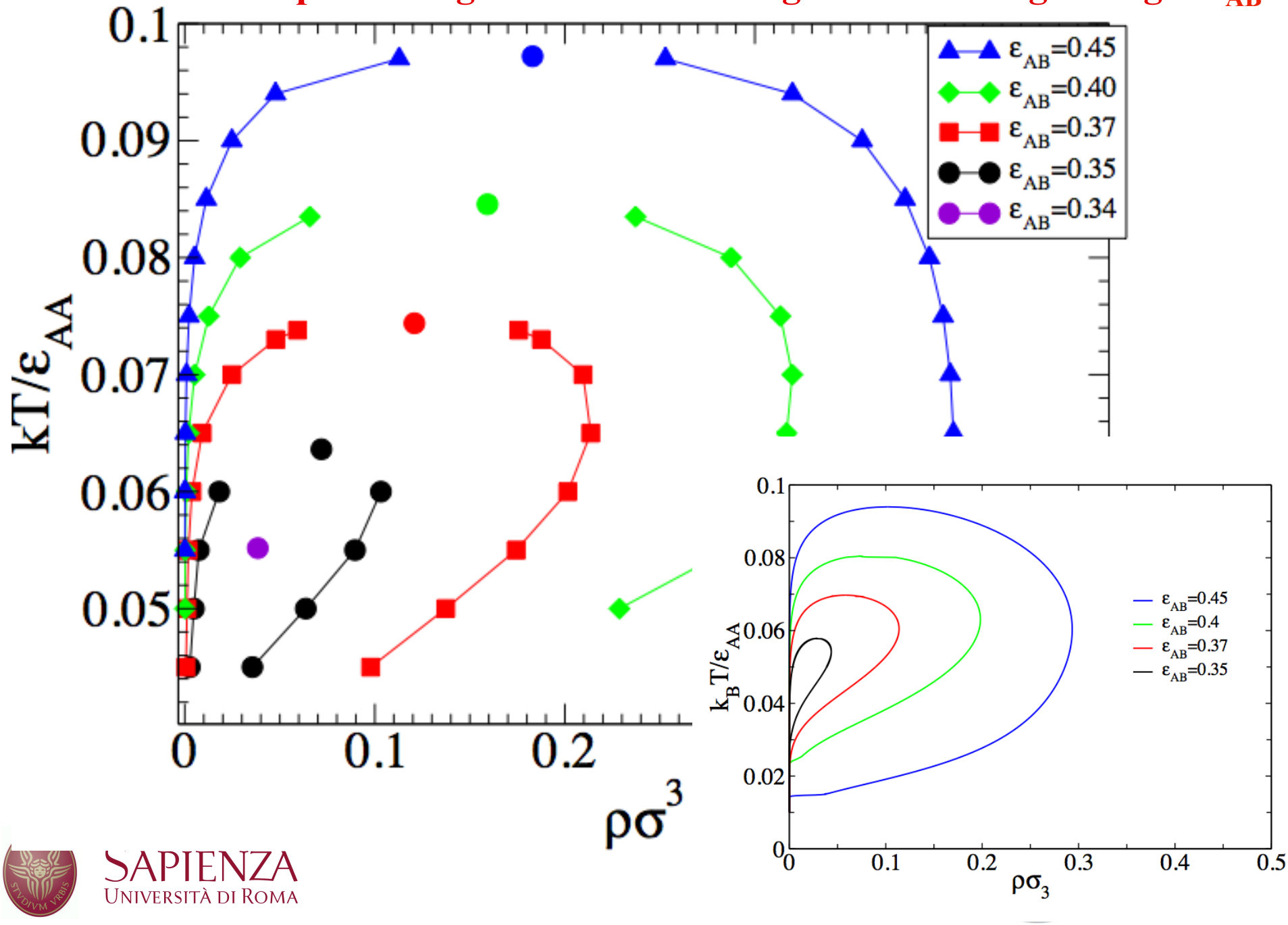
A patchy model with a “pinched” phase diagram



Russo et al PRL 106, 085703 (2011);

Evolution of the phase diagram on modulating the branching strength ε_{AB}



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Re-entrant Phases: What is the physics of competitive interactions ?

the emergence of a structure controlled by energy (stable at low T) which competes with a structure stabilized by entropy at intermediate T.

entropy-energy balance to stabilize different local structures:

Our goal: to design (and to experimentally realize) a patchy-particle gel that forms both on cooling AND on heating

Gelling by Heating

Sándalo Roldán-Vargas[1], Frank Smallenburg[1], Walter Kob[2] & Francesco Sciortino[1]

SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

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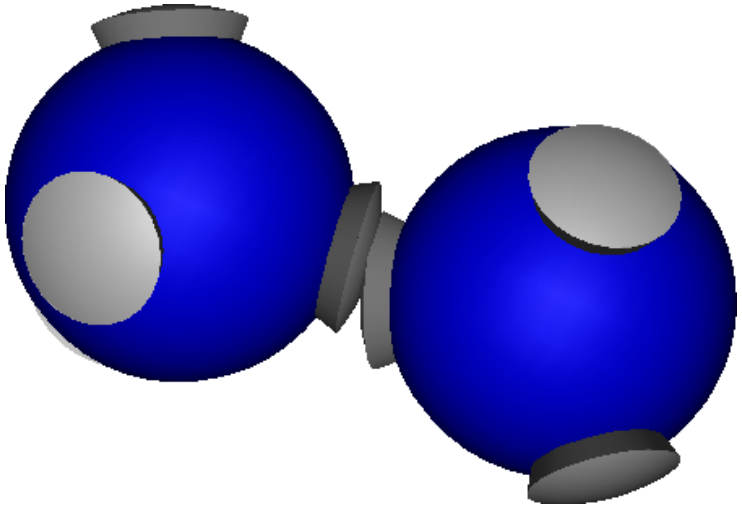
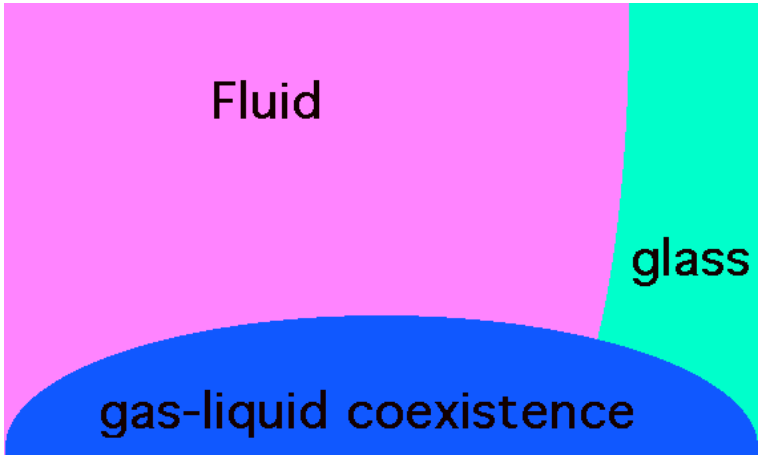
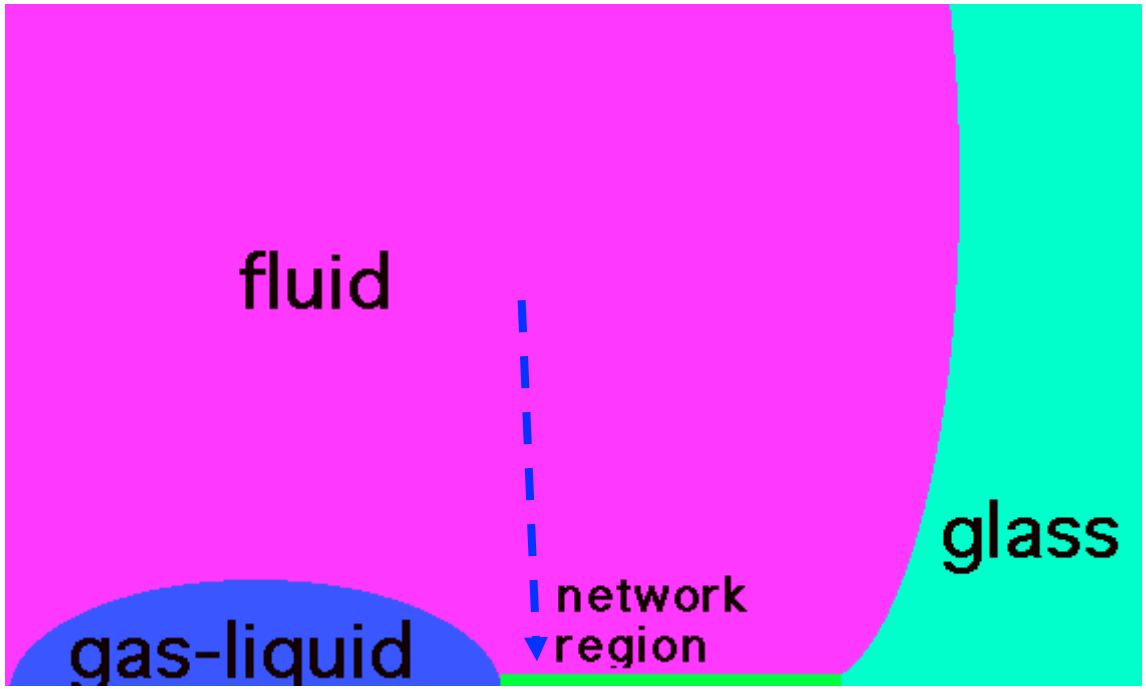
How do we form an equilibrium gel ?



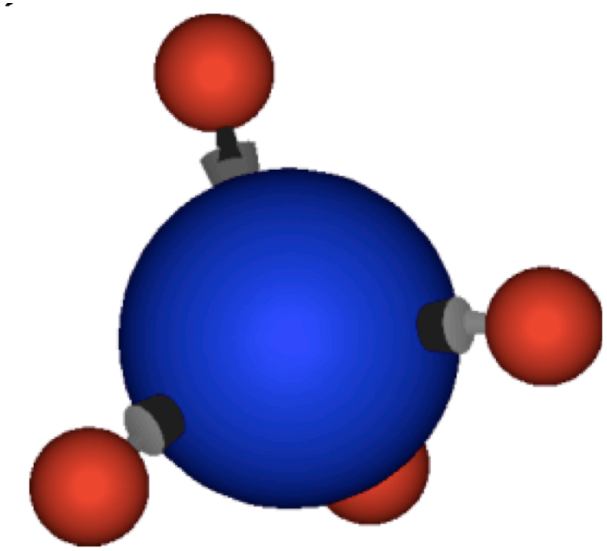


Small Valence

The essence of the gel state of matter



How do we break a gel ?



Network

$2\varepsilon_{AA}$

Blocked particle

$4\varepsilon_{AB}$

$\varepsilon_{AB} < \varepsilon_{AA}/2$

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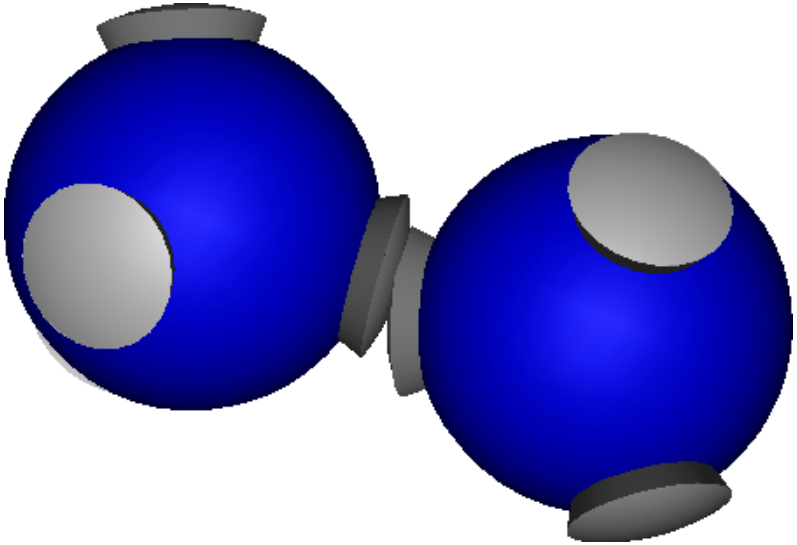
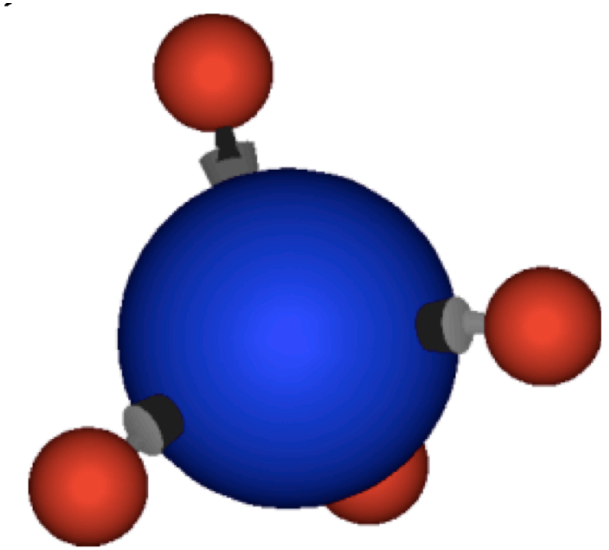
How to stabilize the network: Entropy

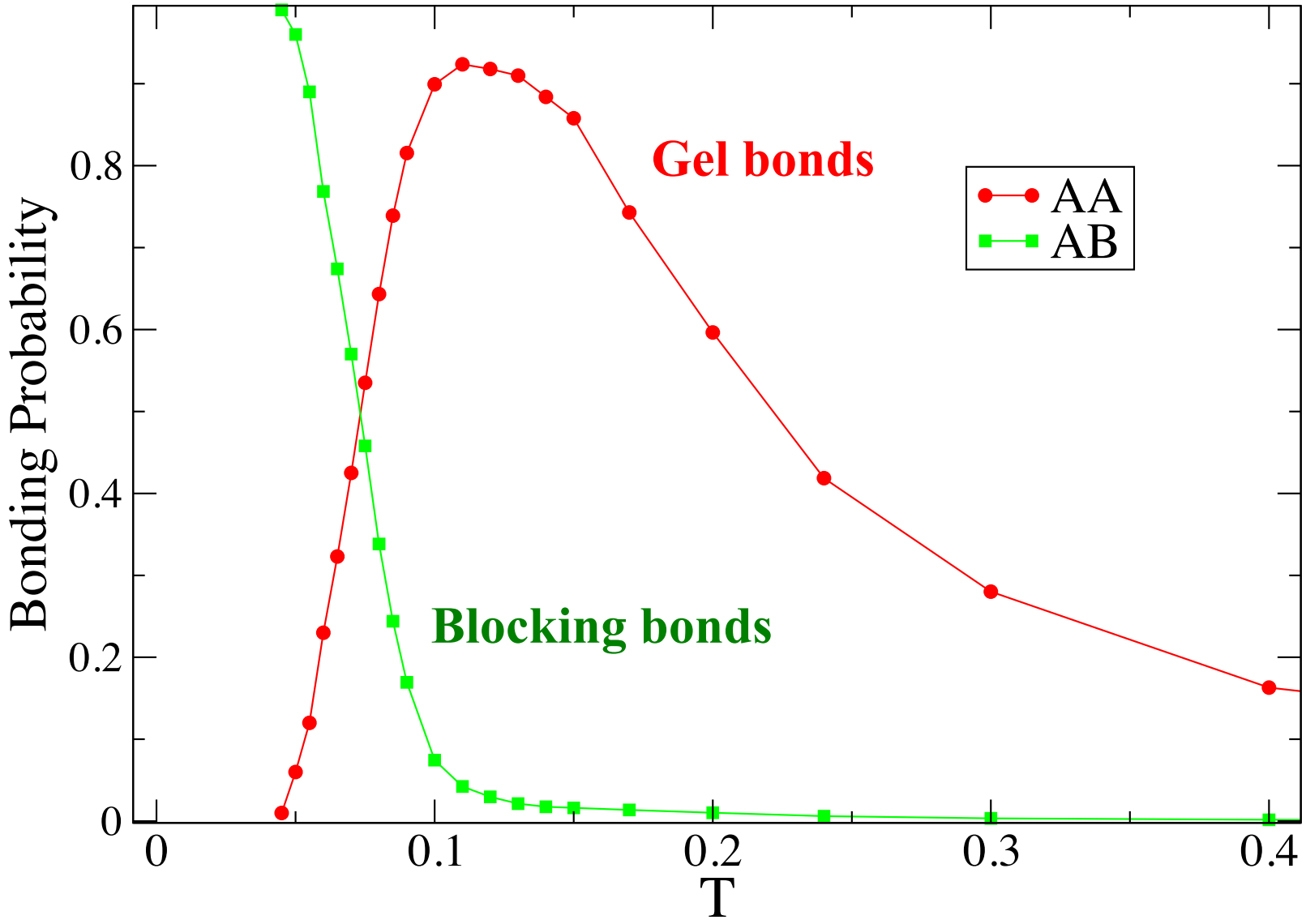
Bonding volume AA >> Bonding volume AB



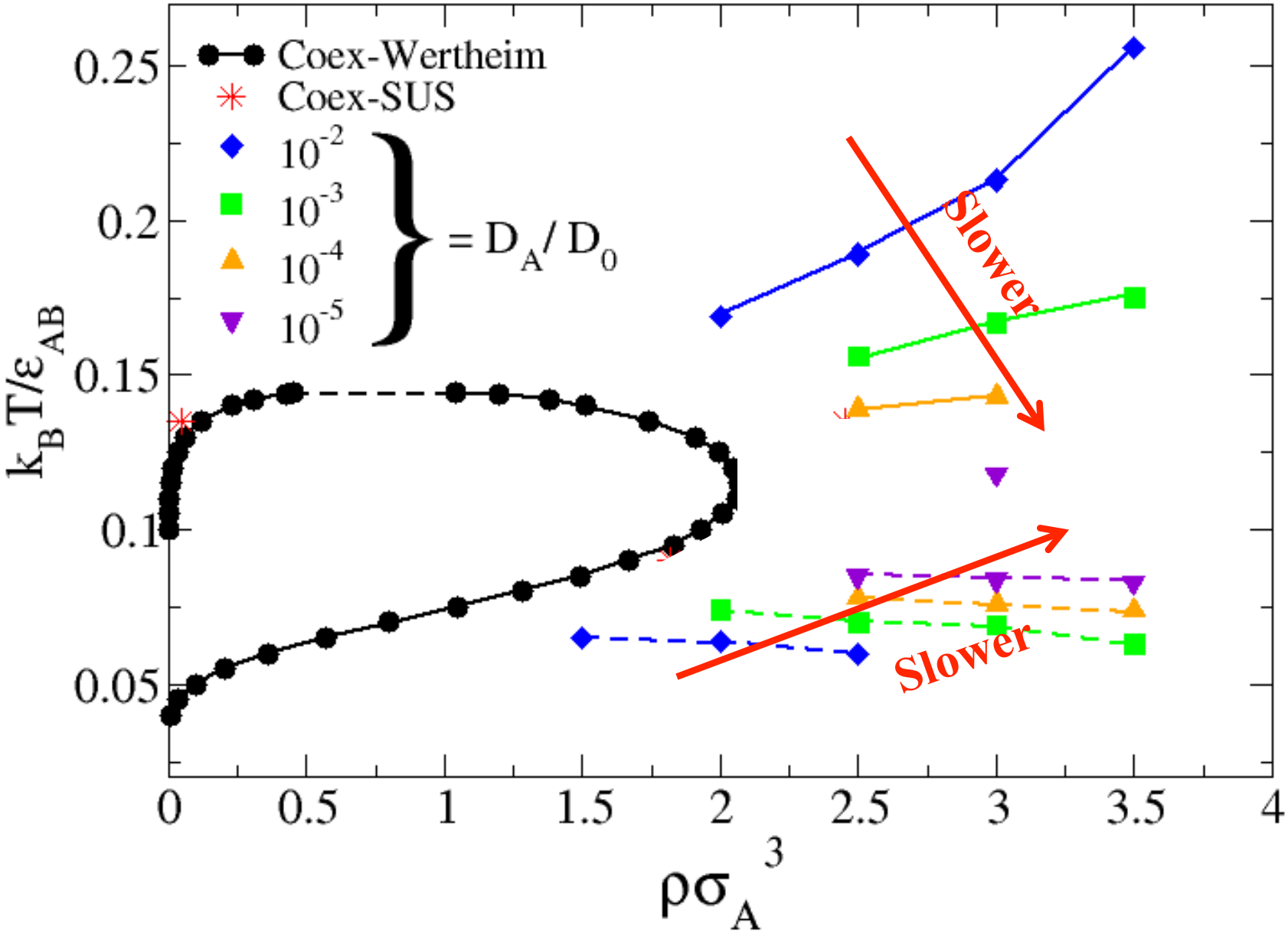


Forming and melting the gel

Wertheim theory



Simulations



Can we design a system that does it in the laboratory ?

Bulk quantities of patchy particles !

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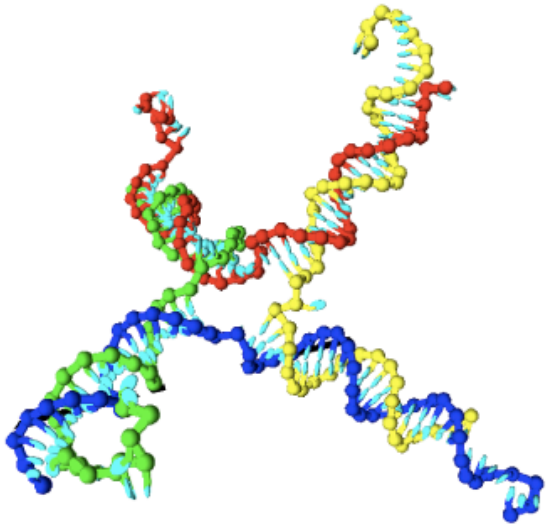
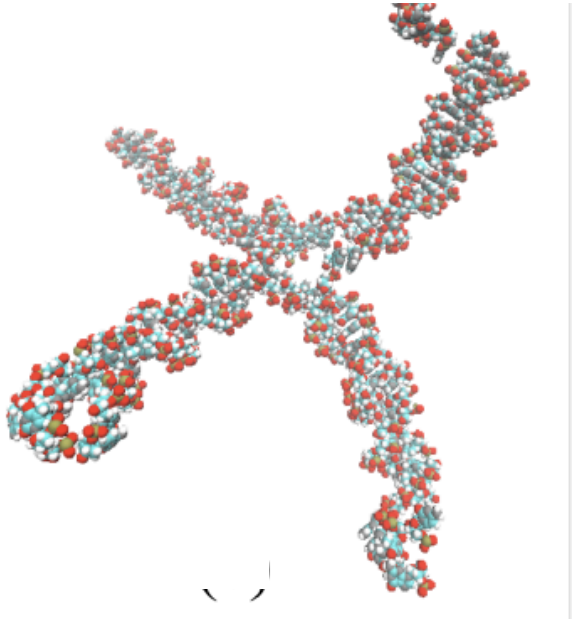
Experiments: DNA constructs: The patchy particles





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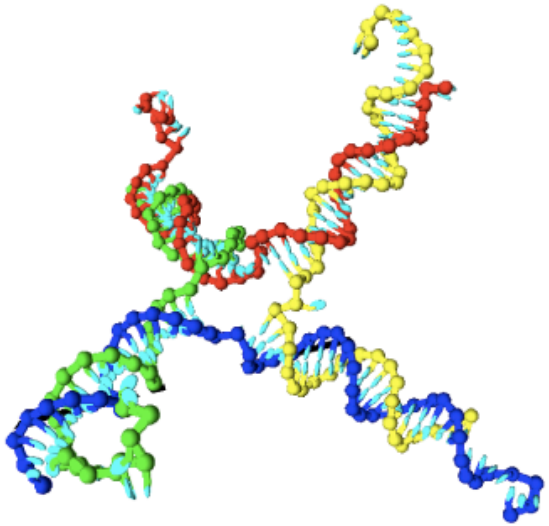
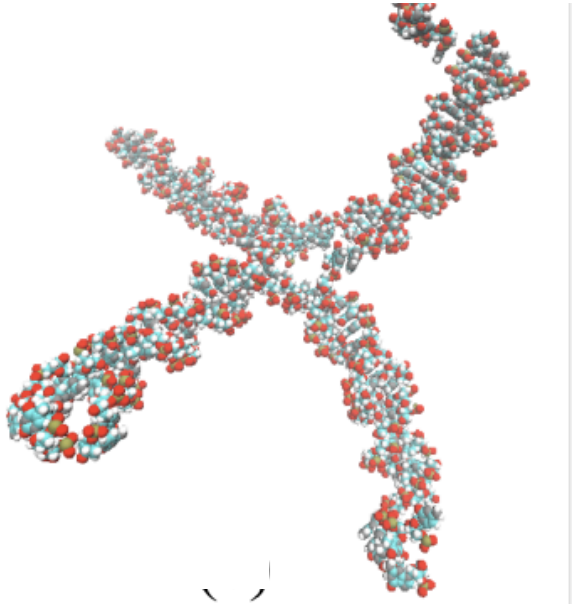
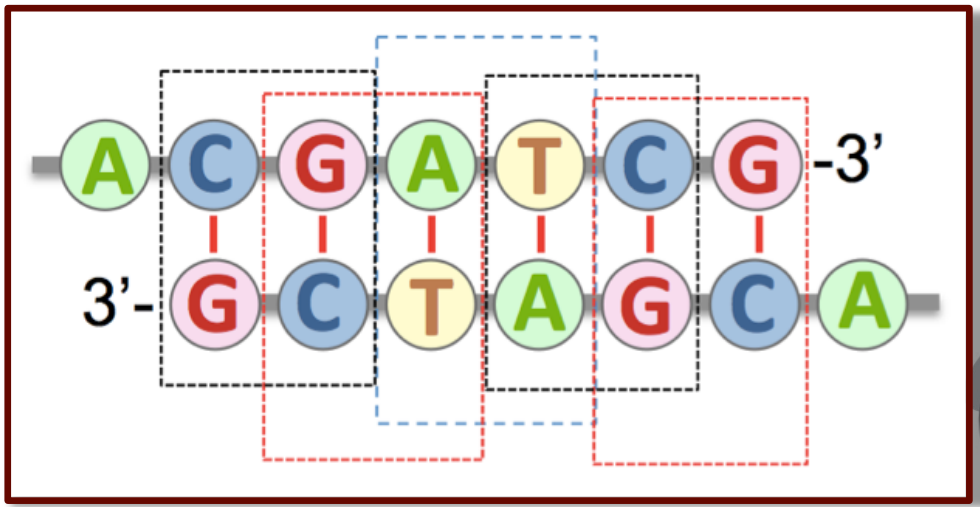
Experiments: DNA constructs: The patchy particles







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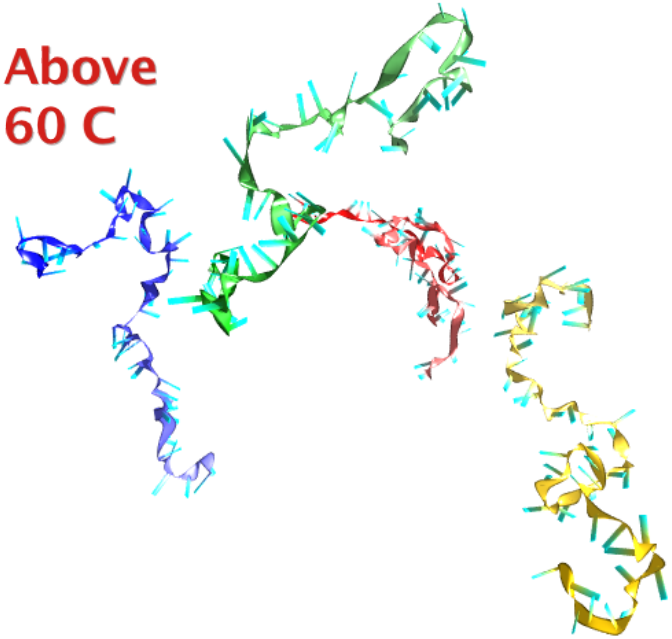
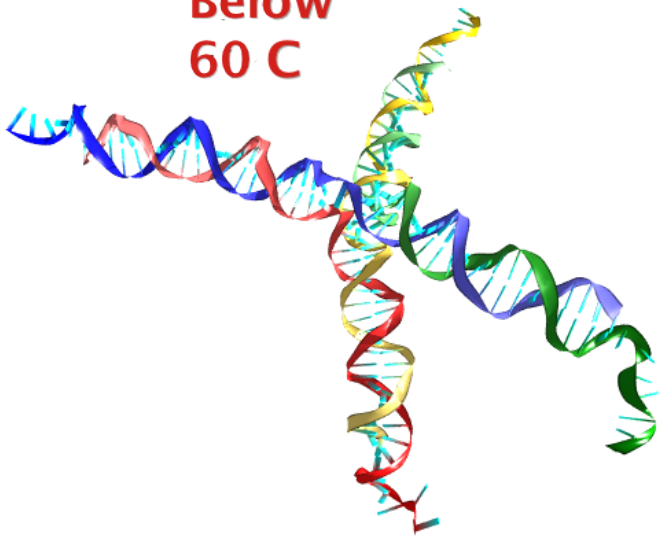
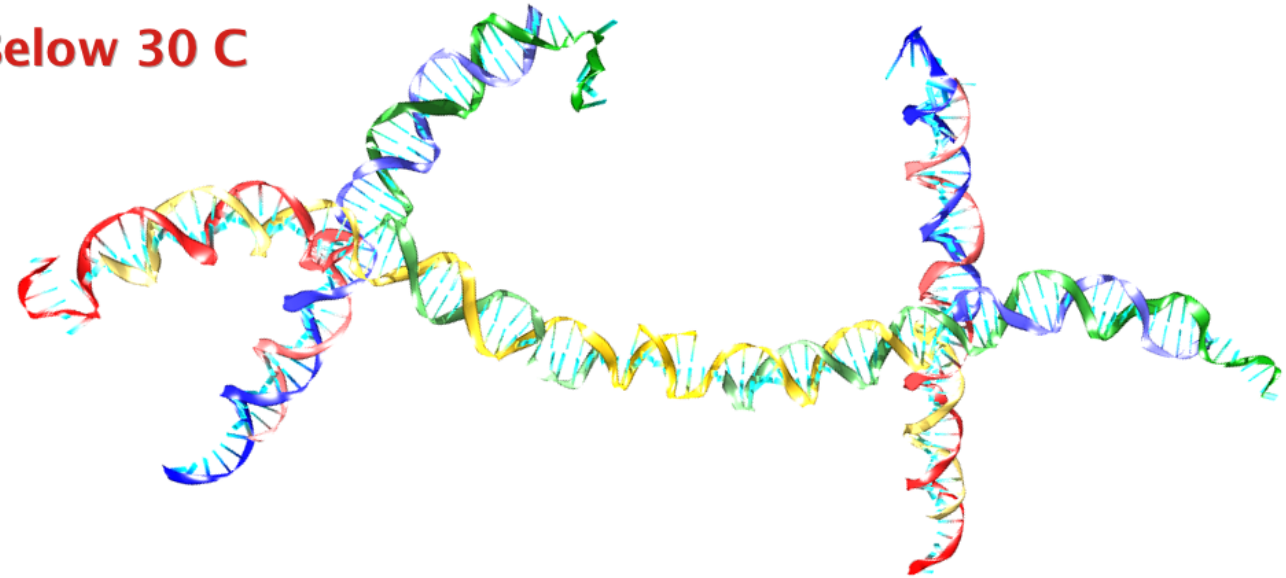
Above
60 C



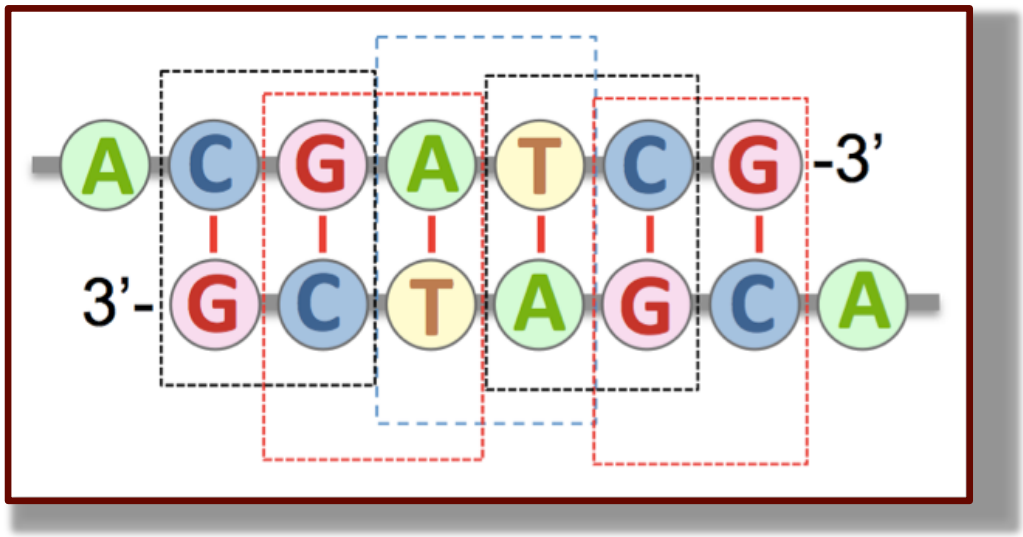
Below
60 C



Below 30 C



The competitor….. (B particle)



("palindromic")

Two serious problems to solve:

1) How to avoid BB pairing ?
2) How to increase the entropy cost of bonding ?

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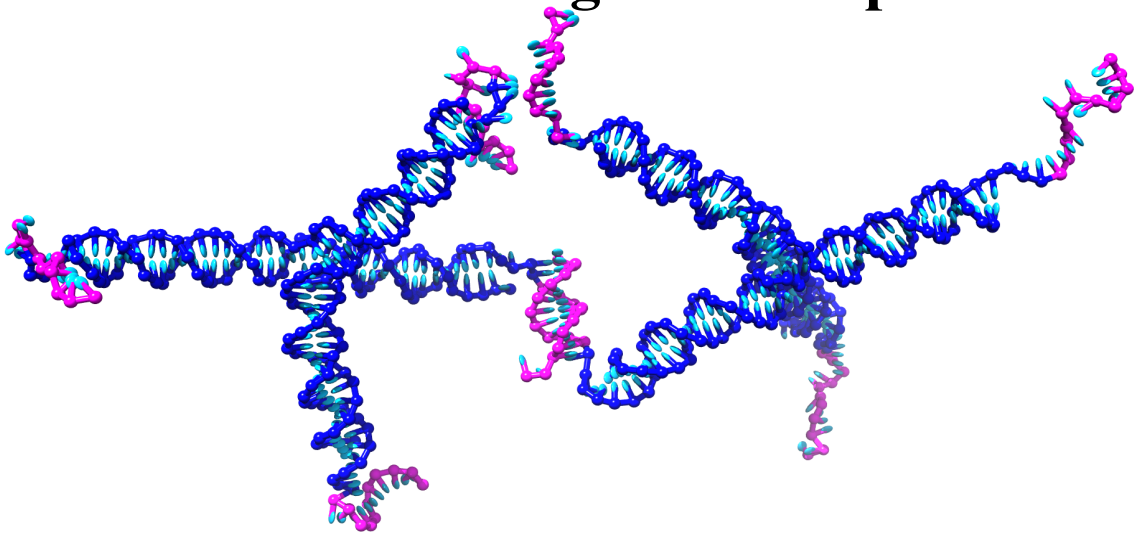
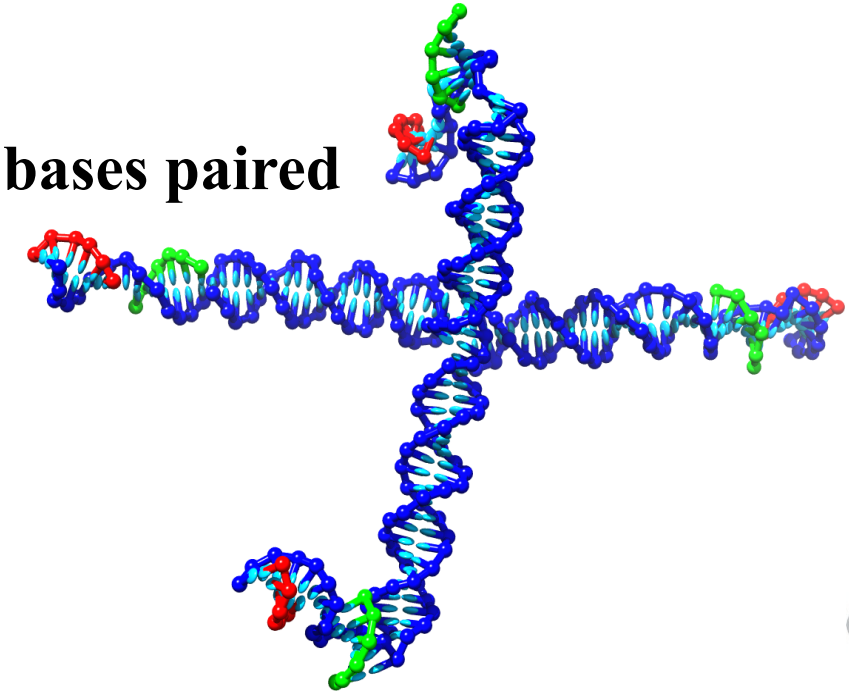
AA-bonding: 8 bases paired



AB-bonding: 12 bases paired



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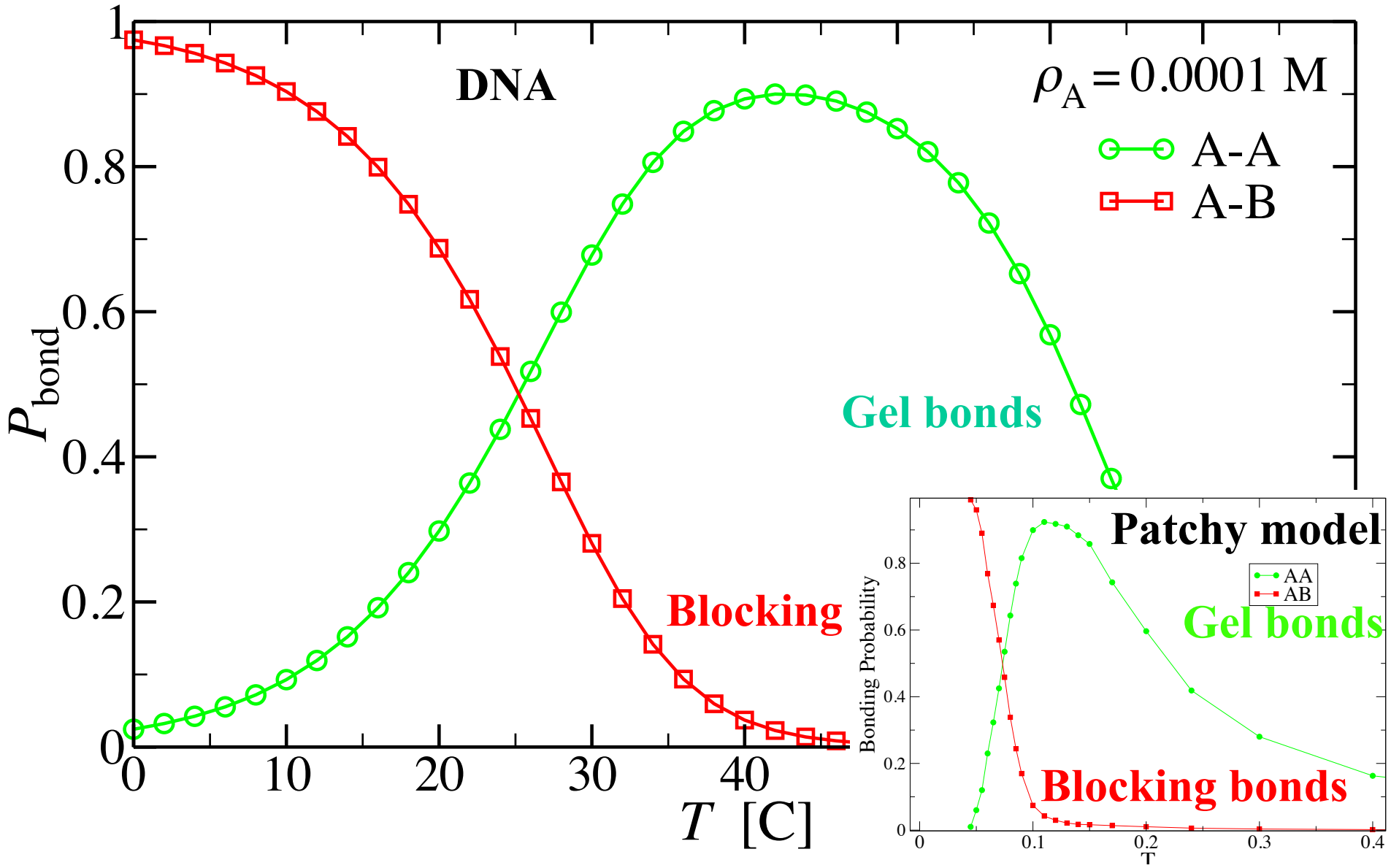
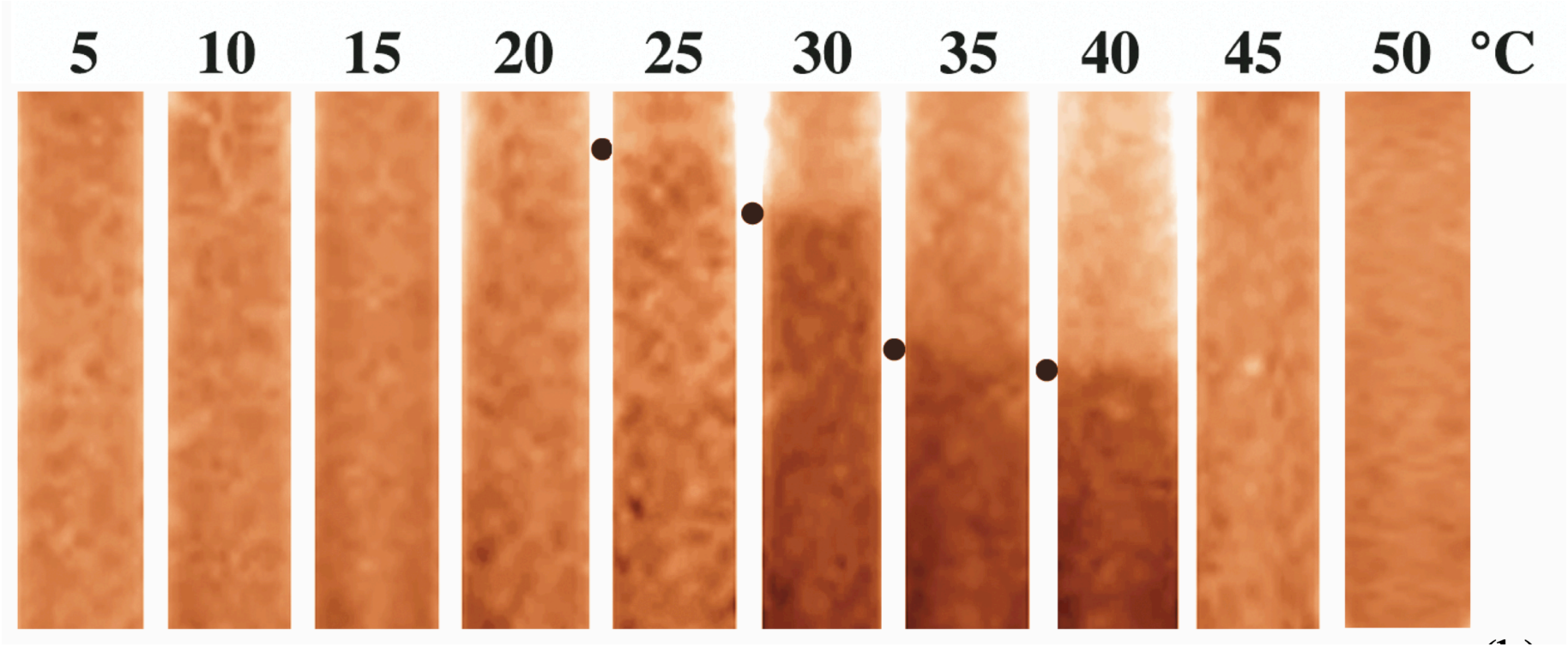
Nupack Evaluations: www.nupack.org



Now… experiments:
The phase diagram



(ethidium bromide)

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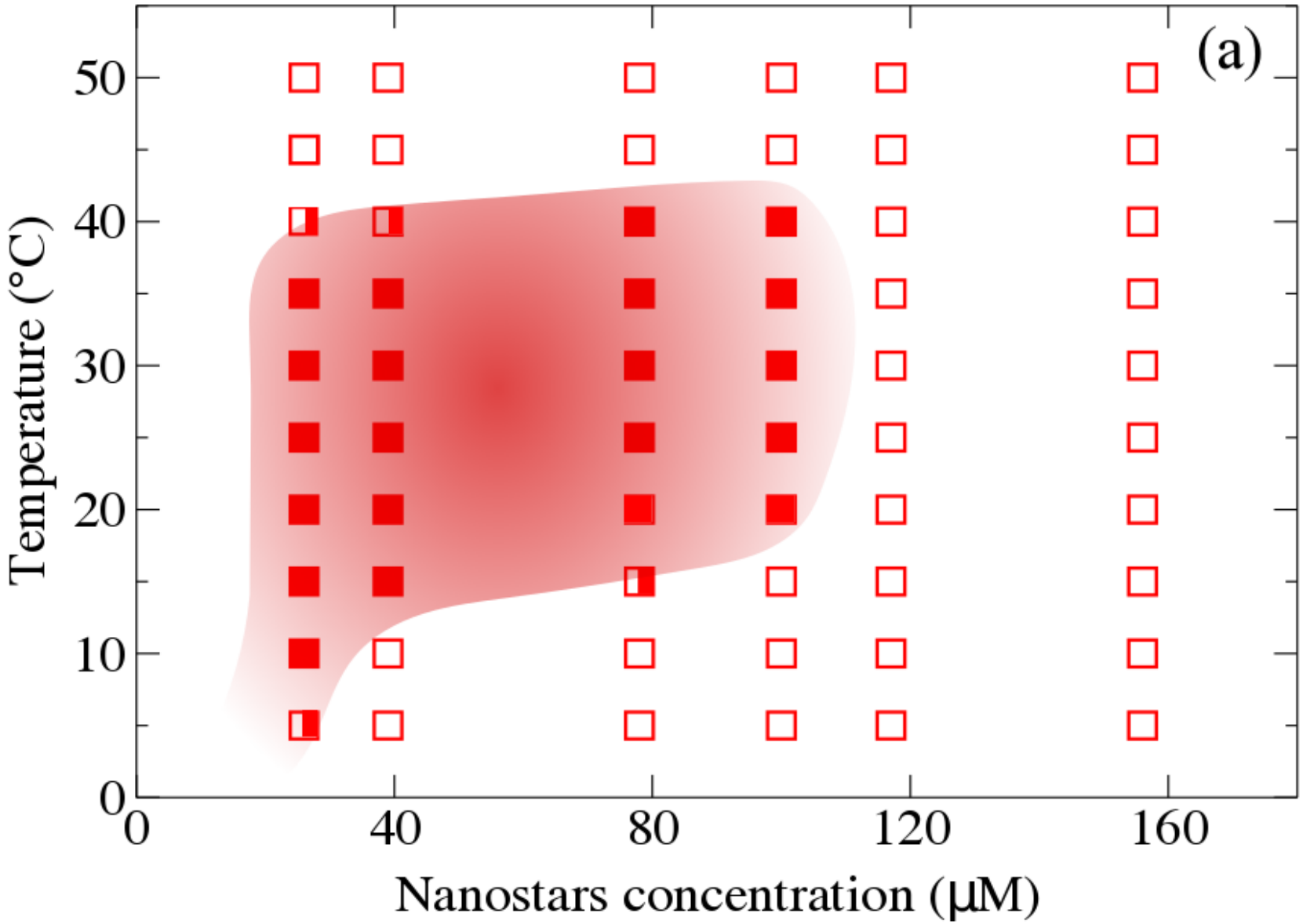
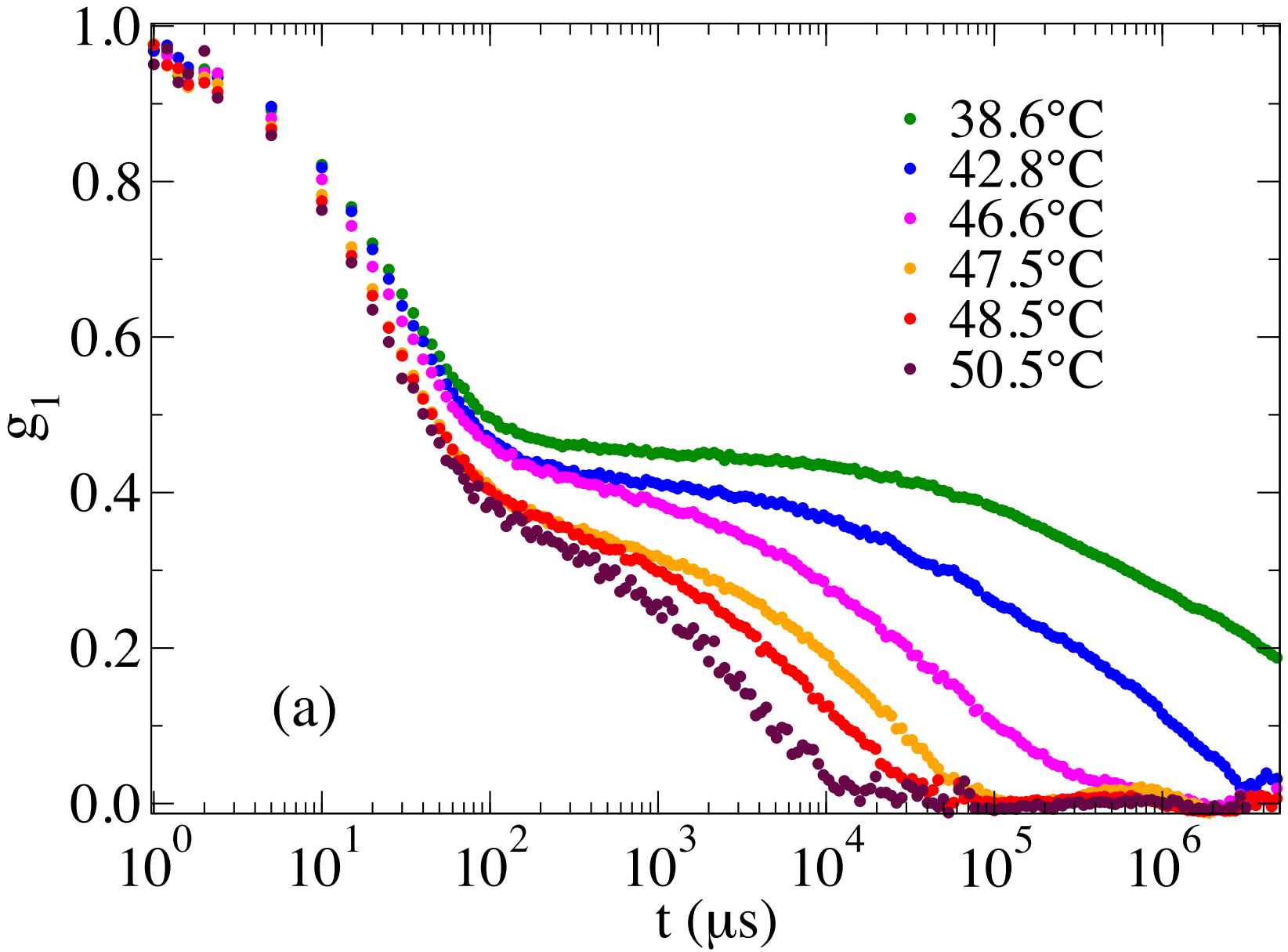
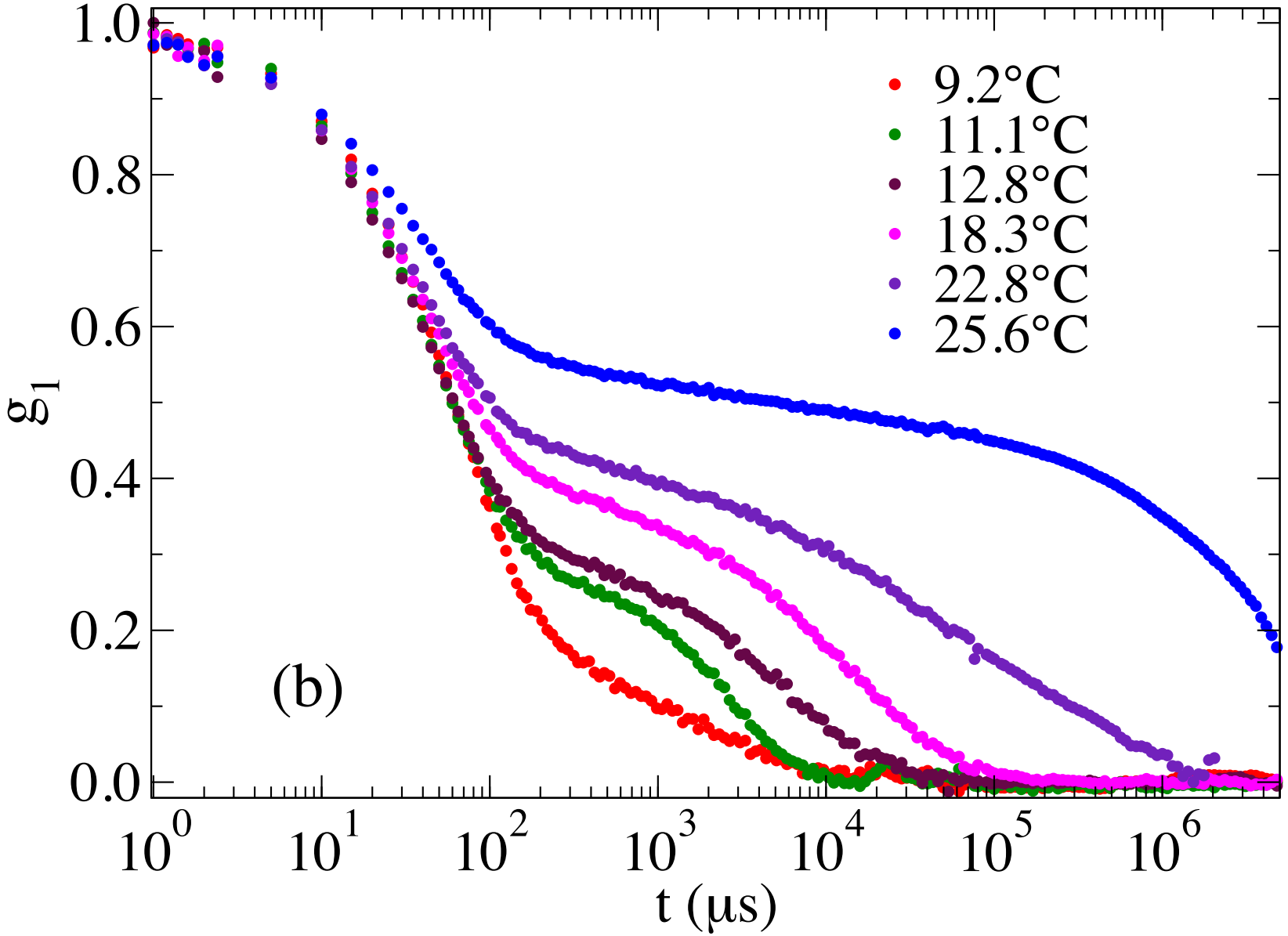
The phase diagram:



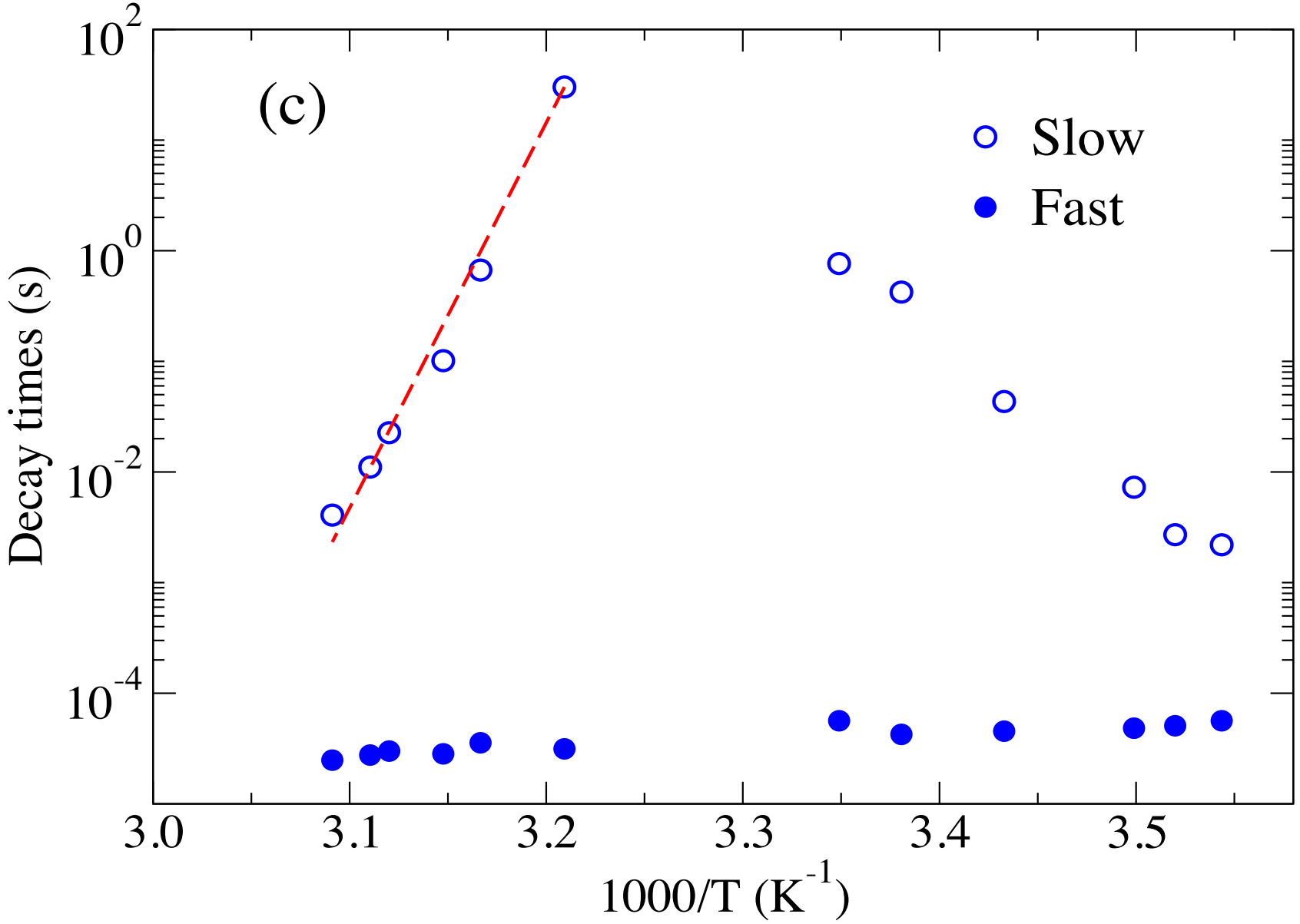
The T-region where the gel forms

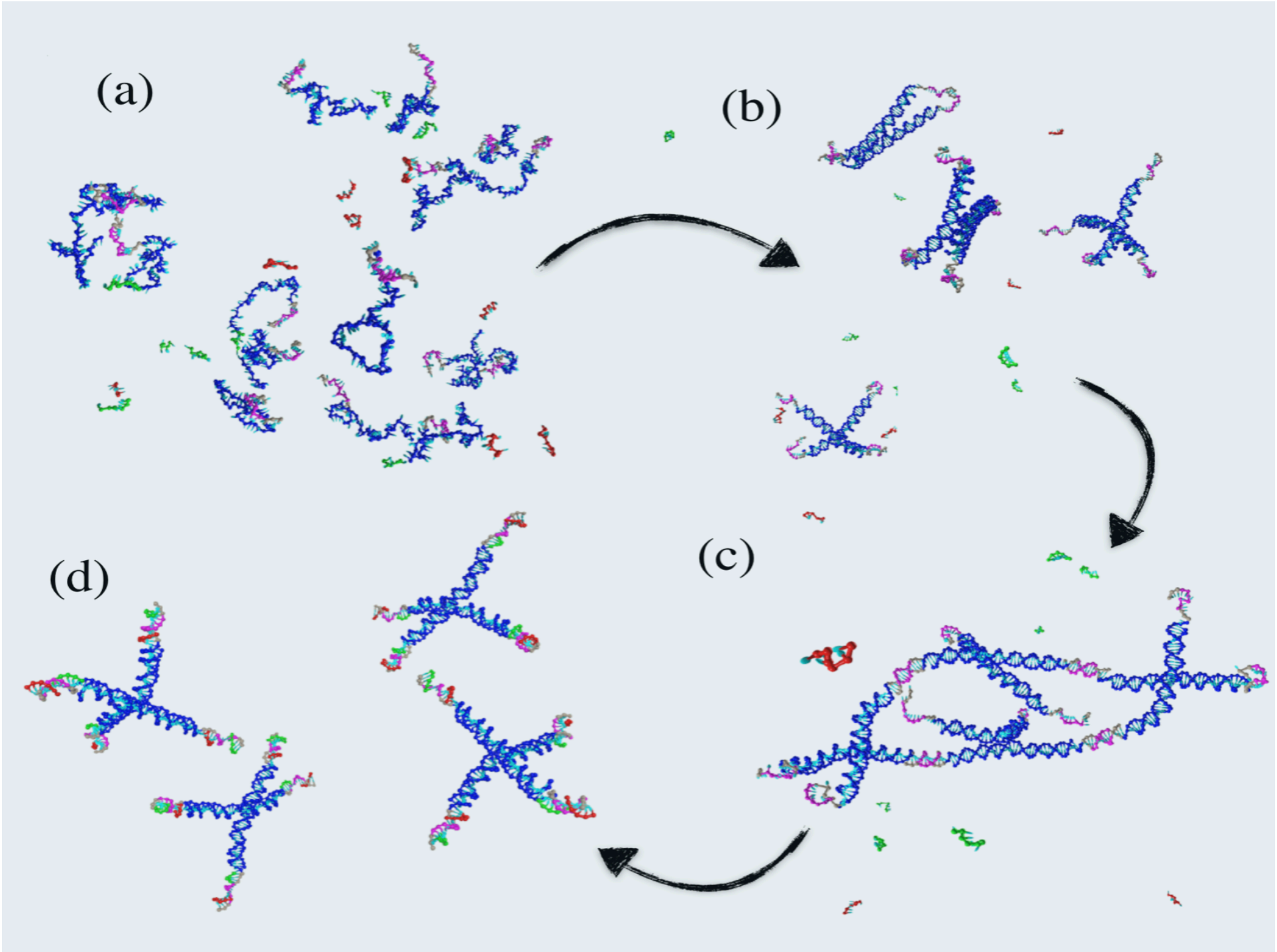


The T-region where the gel breaks



The characteristic time




(a)
(b)
(c)
(d)

Conclusions

DHS.. Attempt to write a "expanded" Free-energy accounting for rings and ring-ring interactions

Competitive interactions: very powerful concept for designing sensitive structured materials

DNA constructs: tuning the material properties by design (including non-monotonic T dependence)

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Thanks to…

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Walter Kob, Sandalo Roldan, Frank Smallenburg - Gel on heating (in silico)

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Flavio Romano - Gel on heating (design)

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