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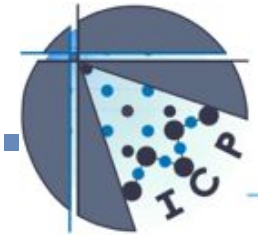

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Two Simple Microscopic Models for Ferrogels: A Simulation Approach

R. Weeber[1], S.S. Kantorovich[1,2], C. Holm[1]

1) Institut für Computerphysik, Universität Stuttgart, Germany
2) Sapienza Univ. of Rome, Piazzale A. Moro 2, 00185, Rome, Italy

Overview: Talk has 2 Parts

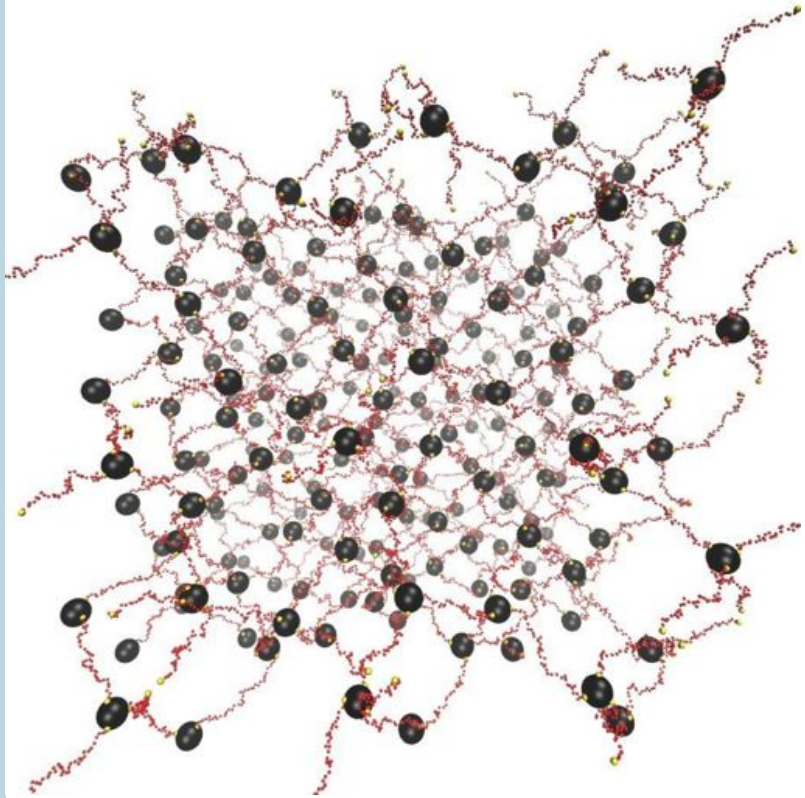
R. Weeber, S. Kantorovich, C.H.

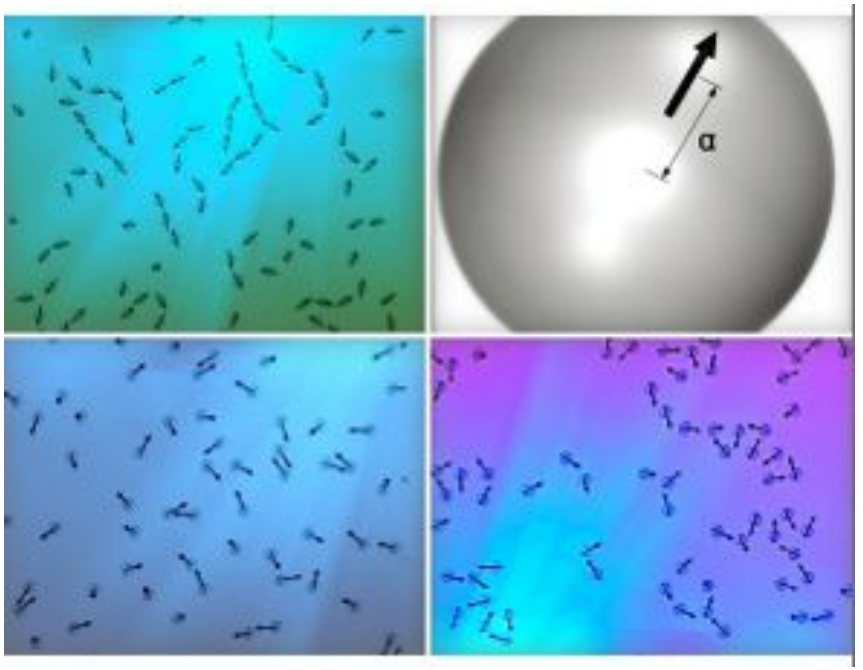
- Magnetic Gels

M. Klingikt, R. Weeber, S. Kantorovich, J.Cerda, C.H.

- Shifted Dipolar Particles

How to Tune Soft Magnetic Matter?





We can make the carrier fluid more complex
=> Magnetic gels

We can make the magnetic nanoparticles more complex
=> Shifted Dipolar colloids

Outline 1: Magnetic Gels

- What are ferrogels
- How can they deform in a magnetic field
- Model building (trying to follow reality):
- Some simulational details
- Model 1: deformation due to chaining
- Model 2: deformation due to torque transmission
- Summary

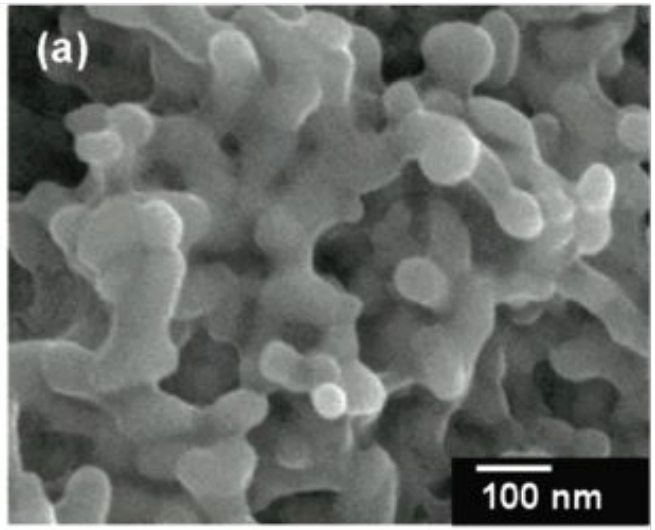
What are magnetic gels

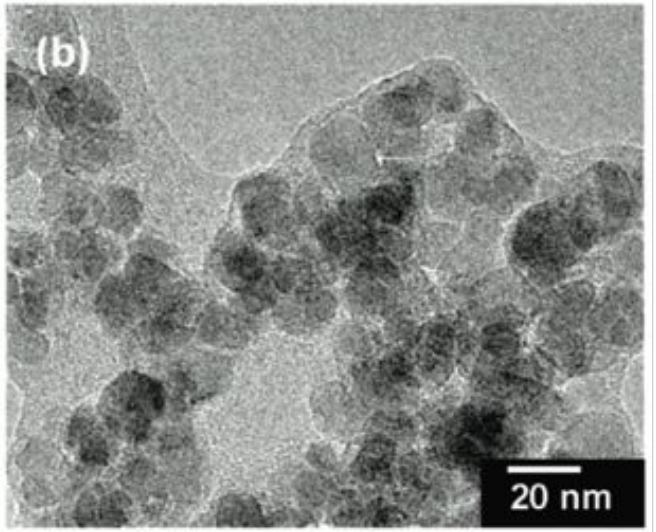
- Magnetic nanoparticles embedded in a hydrogel
- Combination of elastic

and magnetic properties

Applications:

- Drug delivery systems
- Actuators
- Artificial muscels





Shang-Hsiu Hu et al.

Hydrogels

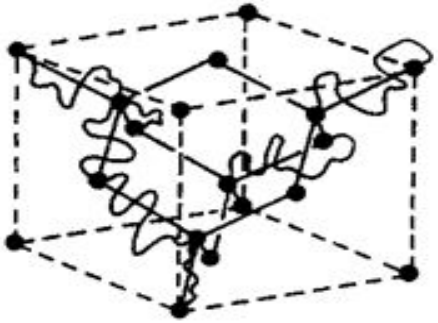
- A polymer network immersed in water
- Can react to chemical and physical environment
- Used in contact lenses, diapers, drug delivery systems

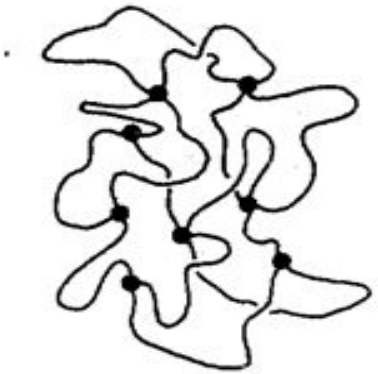
Water cleanage,

Templating via

microgels

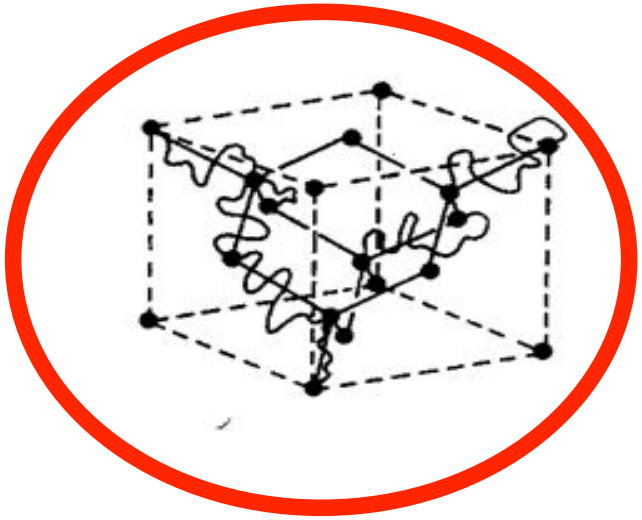
Model Networks

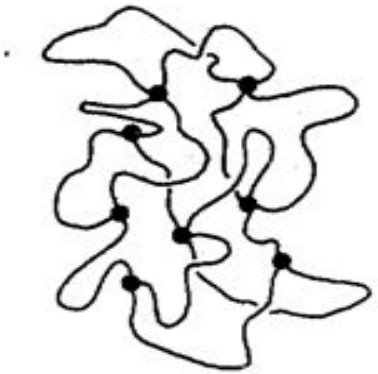




- Olympic gels
- Lattice Networks
- Endlinked melts
- Crosslinked melts

Model Networks





- Olympic gels
- Lattice Networks
- Endlinked melts
- Crosslinked melts

Control over network architecture

Ferrogel Model Network

Model 1:

An f^{th} fraction of bead carries a magnetic moment

Model 2:

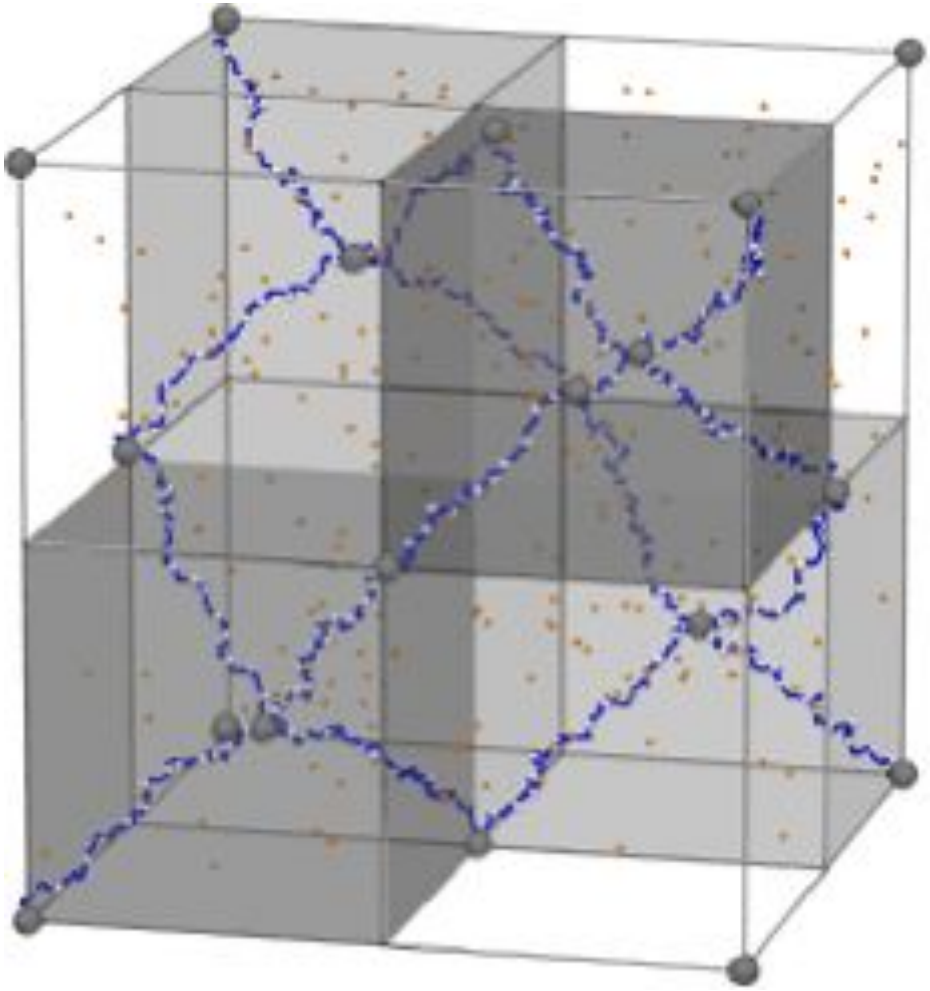
Only the network nodes carry a magnetic moment

Parameters:

dipolar interaction strength
Chain lengths
Number of magnetic particles

Observables:

- chain's end-to-end distance $\langle R_E^2 \rangle$
- dipole alignment
- magnetization in a field
- elastic constants



diamond-like topology
Coarse grained representation of a gel

How can Ferrogels deform?

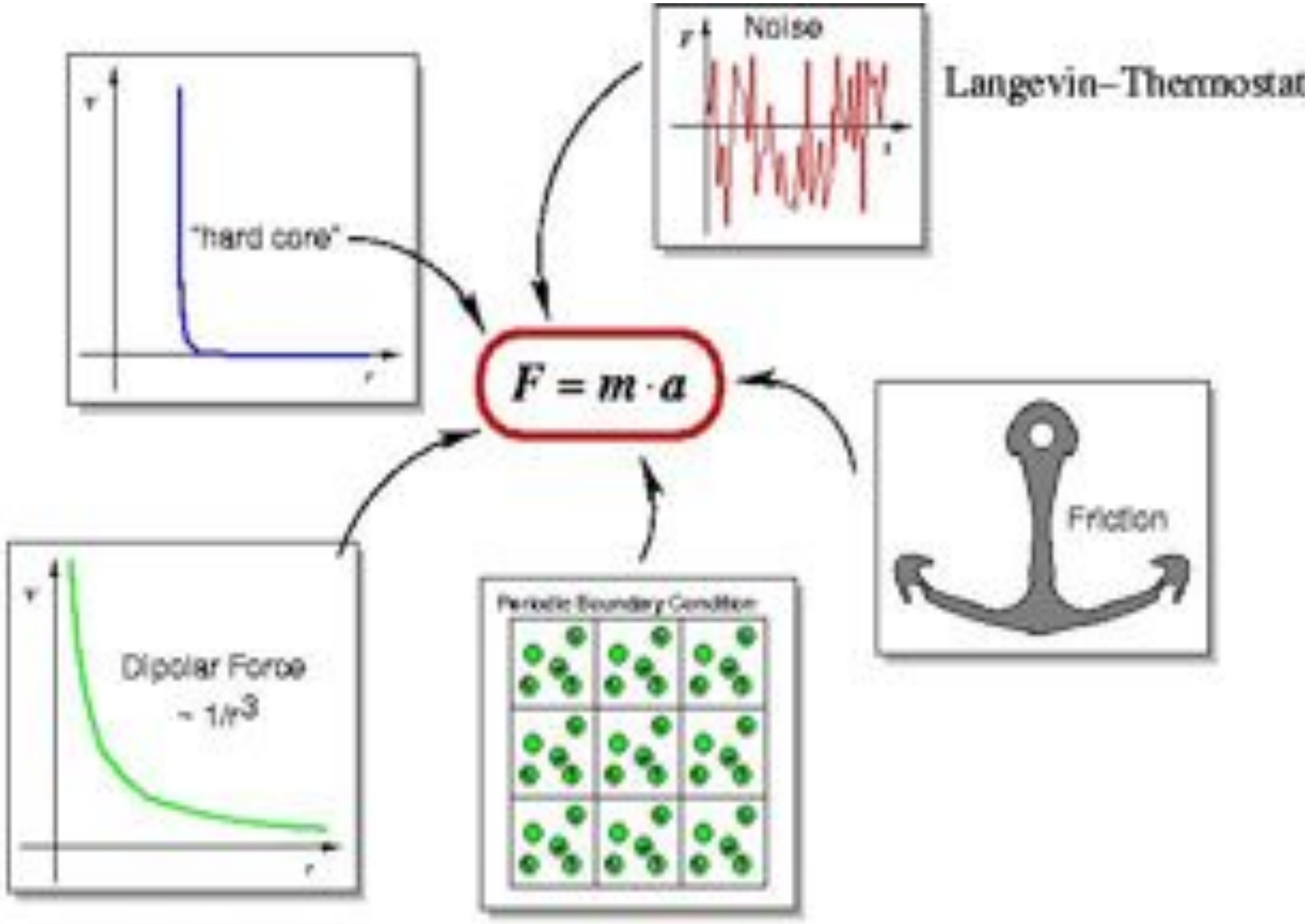
- In a field gradient:

magnetic particles move and deform the matrix

- In a homogeneous field:

1) (Model 1) particles align to form clusters (chains)
2) (Model 2) The rotation of the dipolar particle (Brownian relaxation) transmits torques onto the matrix

Principle of Molecular Dynamics



Dipolar P3M plus DLC

Langevin Dynamics Equ. of Motion

$$\mathcal{M}_i \dot{\mathbf{v}}_i = \mathbf{F}_i - \Gamma_T \mathbf{v}_i + \boldsymbol{\xi}_i^T ,$$

$$\mathbf{I}_i \cdot \dot{\boldsymbol{\omega}}_i = \boldsymbol{\tau}_i - \Gamma_R \boldsymbol{\omega}_i + \boldsymbol{\xi}_i^R ,$$

Random forces with zero first moment

$$\langle \xi_{i\alpha}^T(t) \rangle = 0,$$

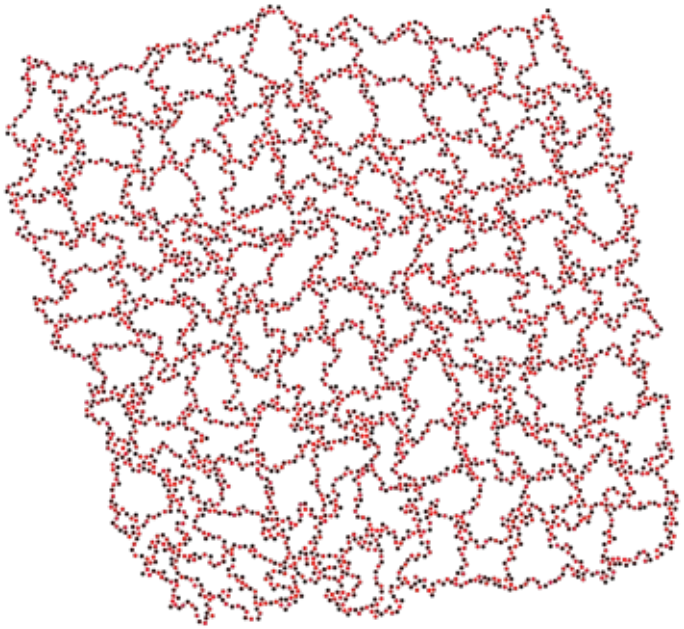
$$\langle \xi_{i\alpha}^R(t) \rangle = 0,$$

Dissipation-Fluctuation theorem

$$\langle \boldsymbol{\xi}_{i\alpha}^T(t) \cdot \boldsymbol{\xi}_{j\beta}^T(t') \rangle = 6kT\Gamma_T \delta_{ij}\delta_{\alpha\beta}\delta(t-t'),$$

$$\langle \boldsymbol{\xi}_{i\alpha}^R(t) \cdot \boldsymbol{\xi}_{j\beta}^R(t') \rangle = 6kT\Gamma_R \delta_{ij}\delta_{\alpha\beta}\delta(t-t')$$

Model 1 (2D)

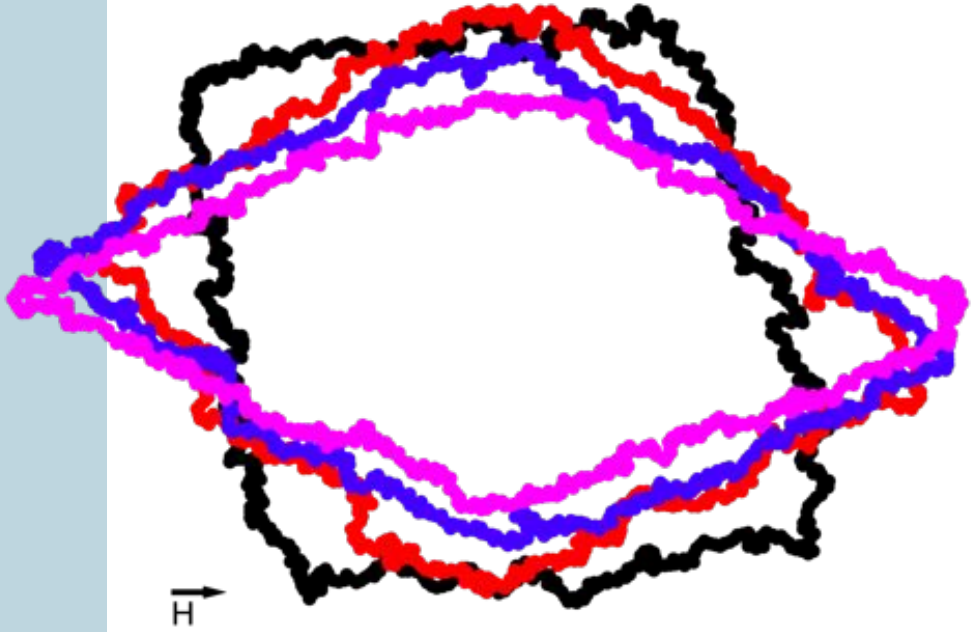


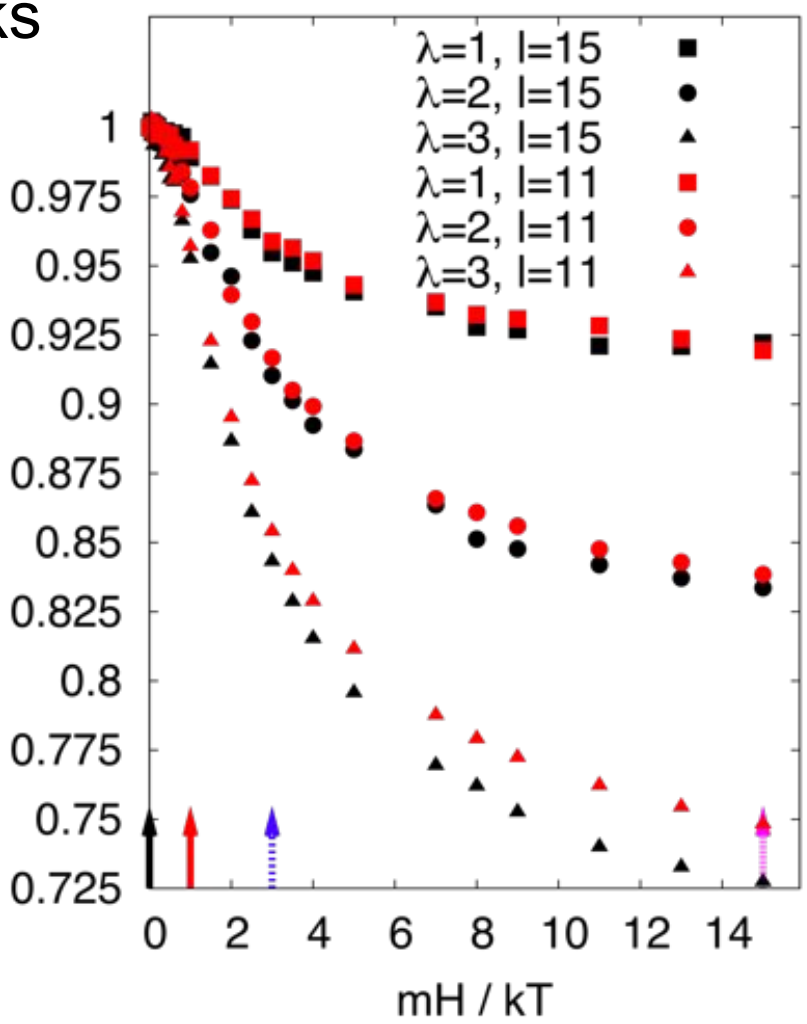
- magnetic particles
- non-magnetic particles

Diamond lattice, 15 particles per chain, f=1/2
Harmonic bonds between beads
Simulated with MD, using direct sum for dipolar interaction
Open boundary, area not fixed

Model 1 in Magnetic Field

In a magnetic field the gel shrinks

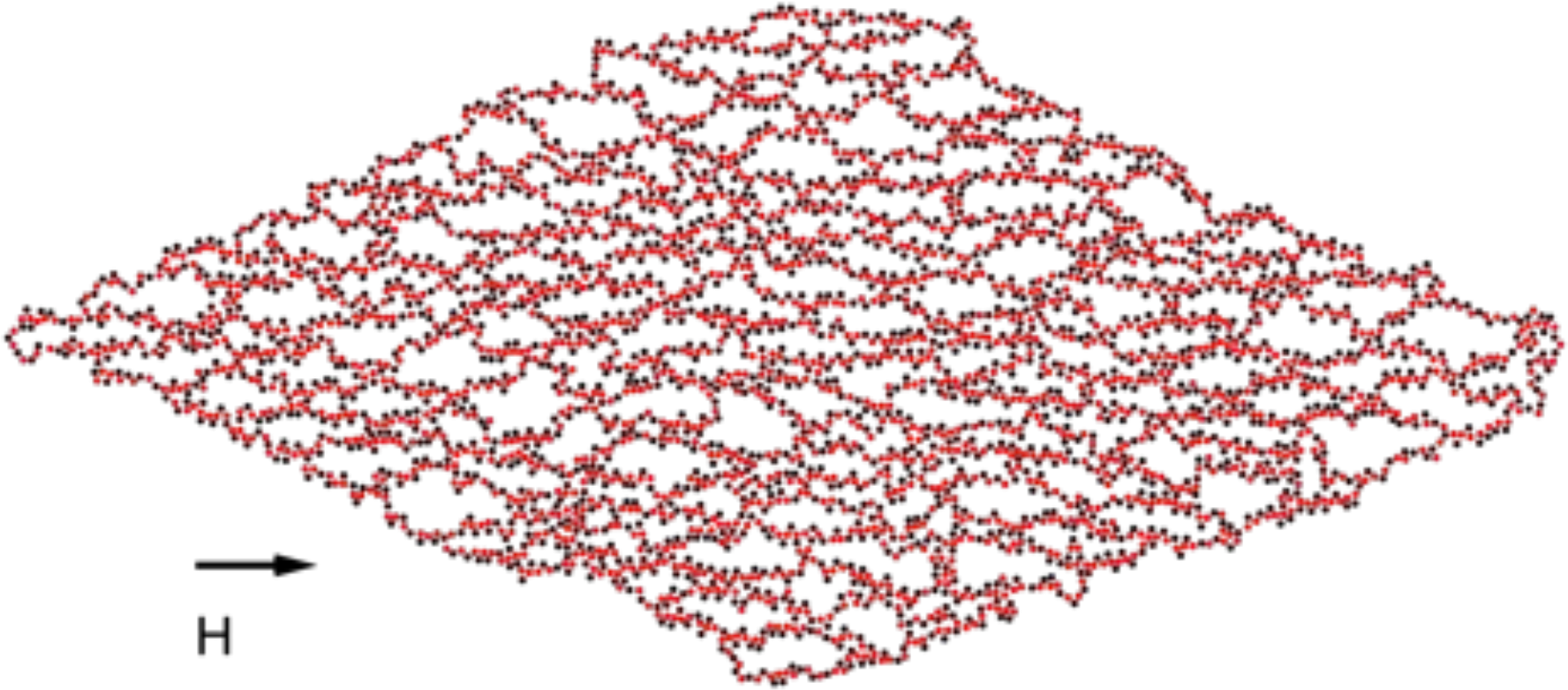




- Elongation parallel to **H**
- Shrinking perpendicular to **H**

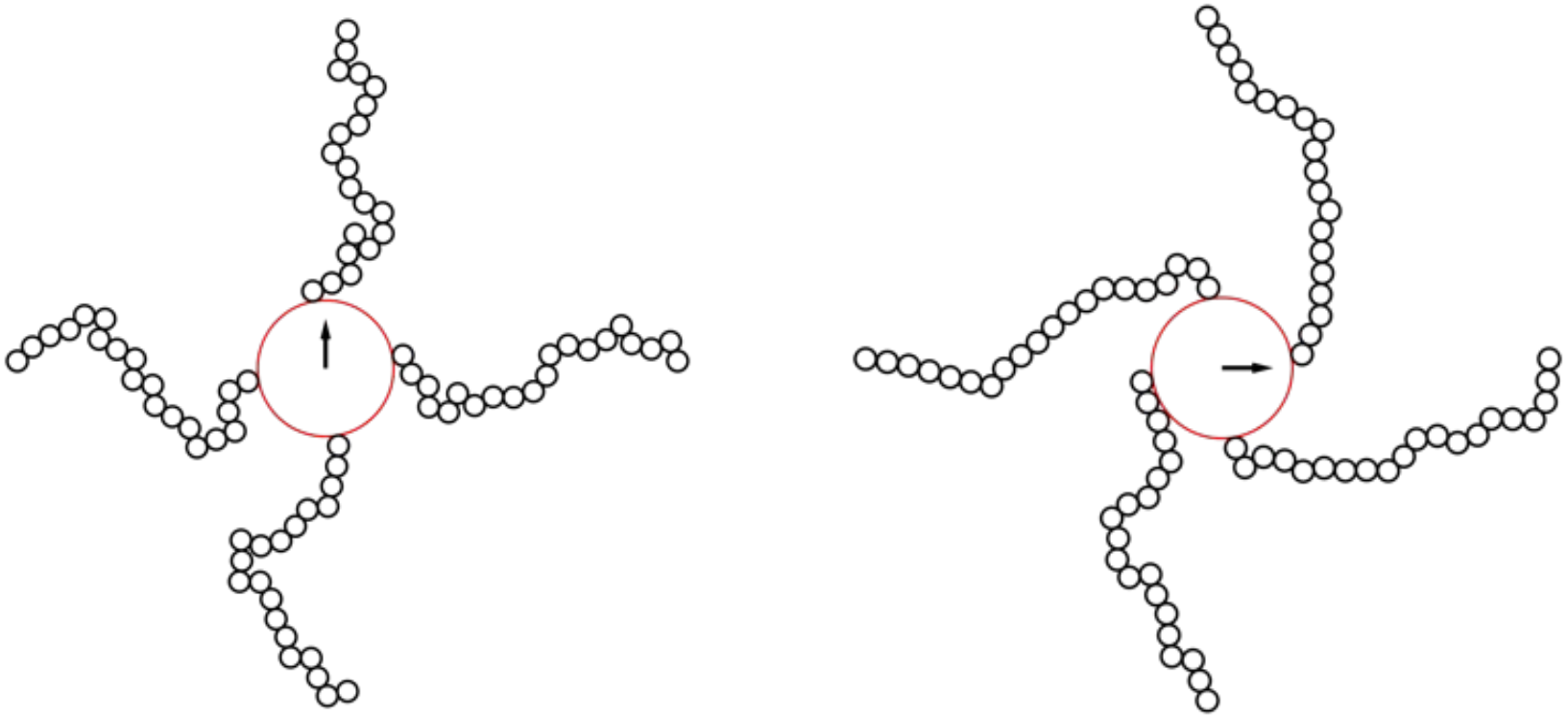
The longer the chain, the more the gel shrinks

Reason for Shrinkage



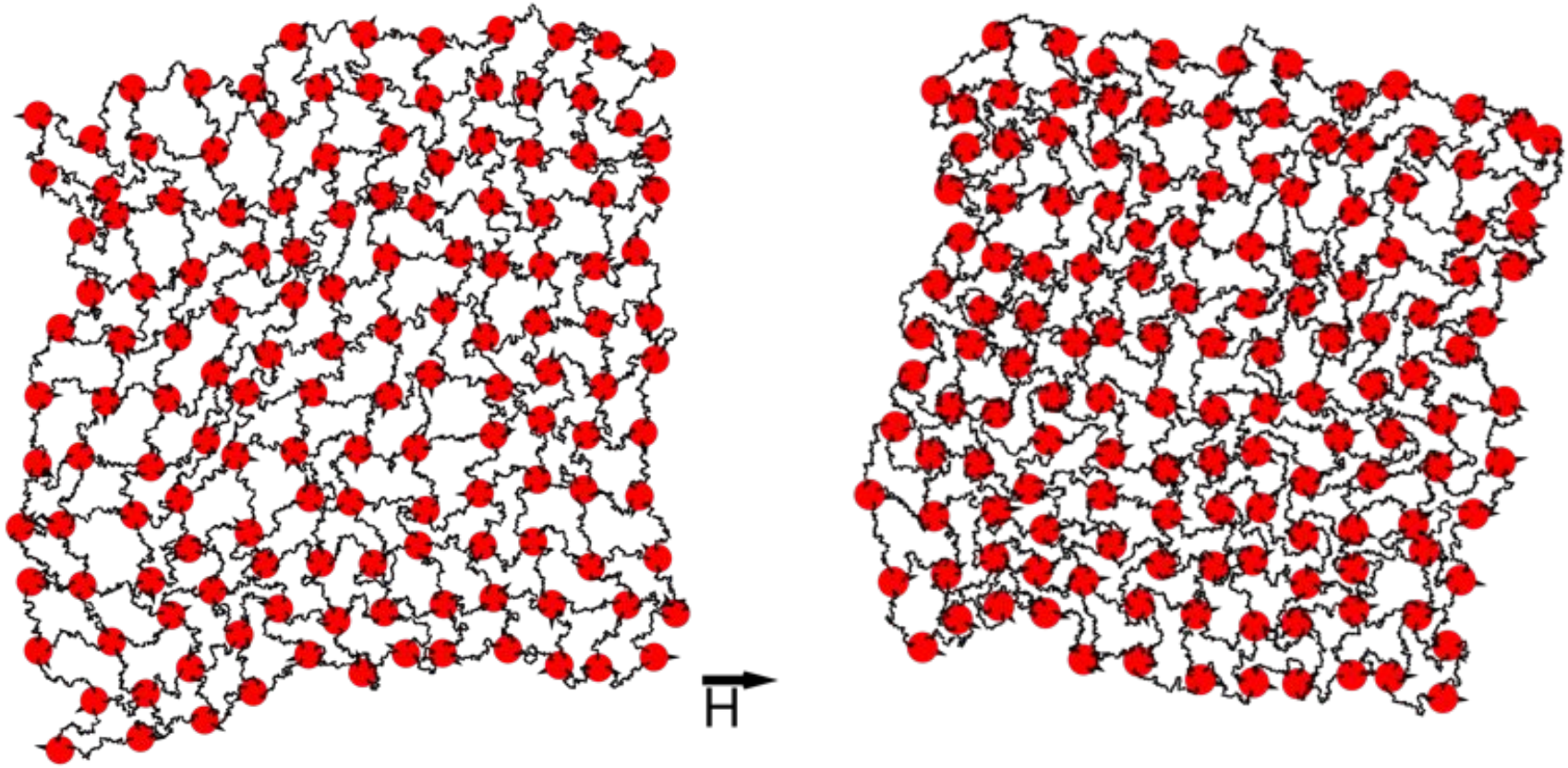
- Non-magnetic particles are pushed out of the chain
- Chains bend to align along the magnetic field lines

Model 2: Magnetic Crosslinkers



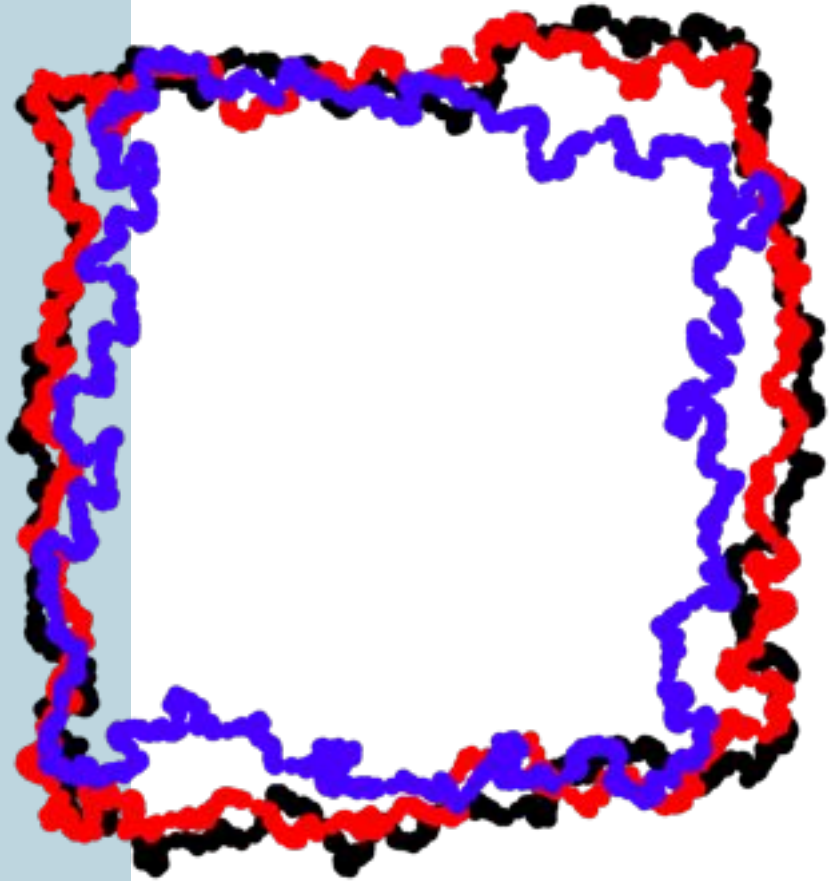
- Polymer network cross-linked with magnetic particles
- Polymers are attached to specific binding sites on the magnetic nanoparticle
- Only the node particle reacts to the field, no internode DD
- inspired by work of A. Schmidt (Köln)

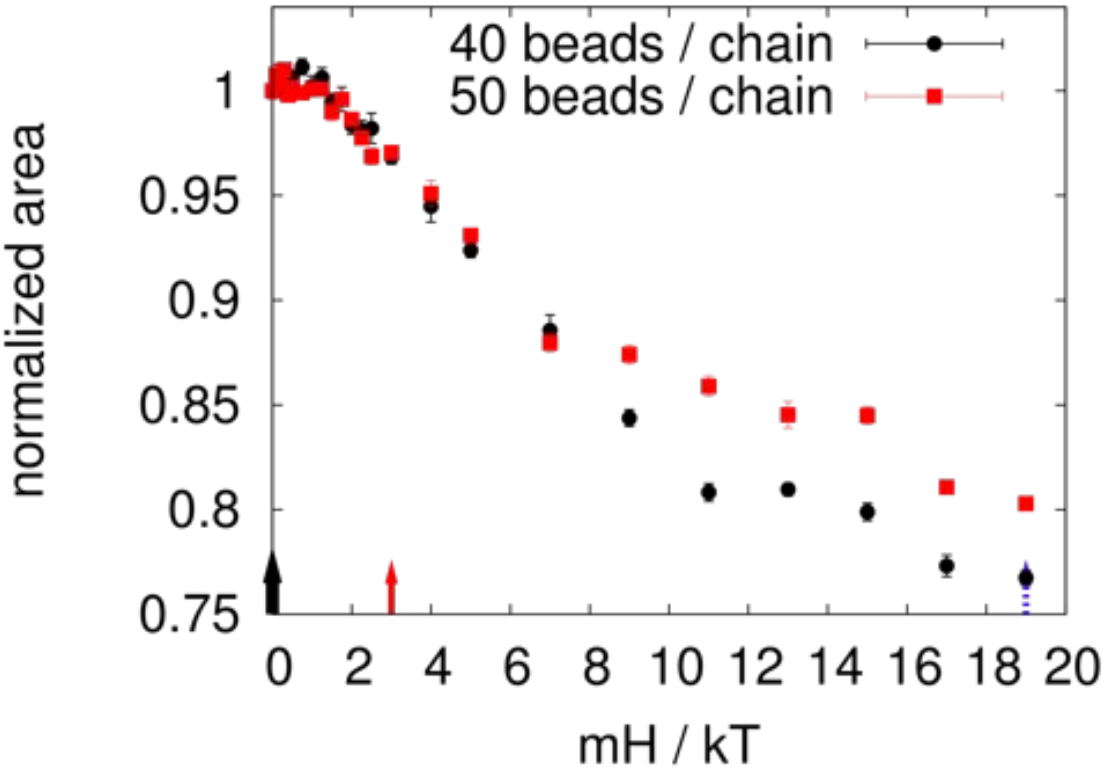
Model 2 in 2D



In a magnetic field te chains rolls up around the aligning magnetic particles
=> The gel shrinks

Shrinking Mechanism

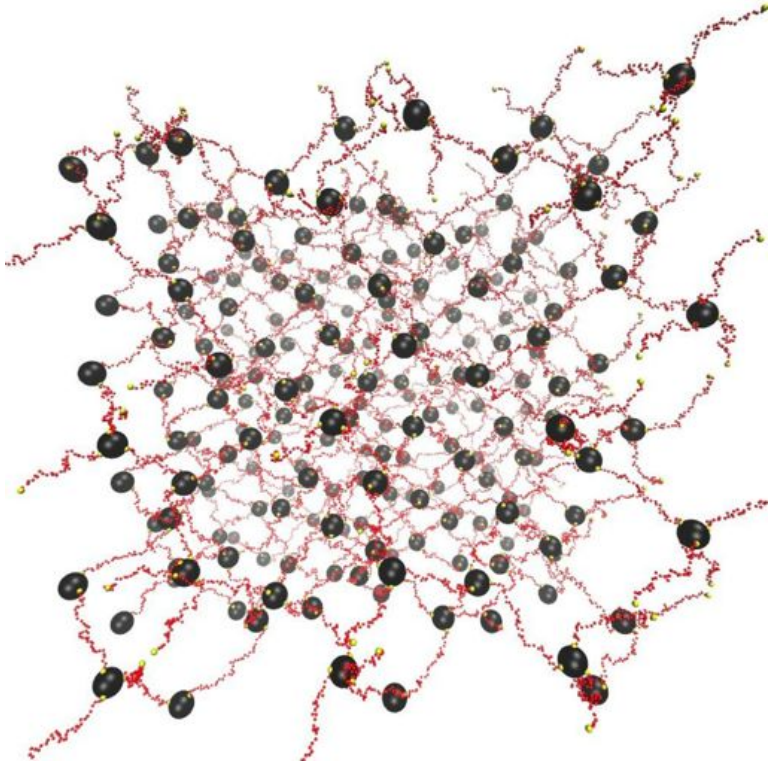




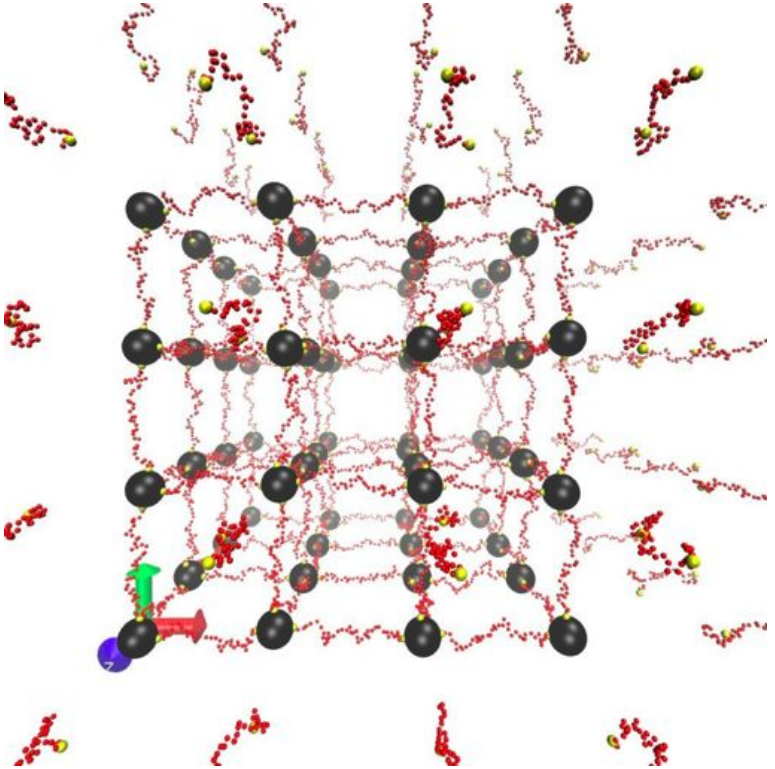
The shorter the chain, the more the gel shrinks

The stress on all chains attached to a magnetic partice is the same
=> The gel shrinks isotropically

Model 2 in 3D



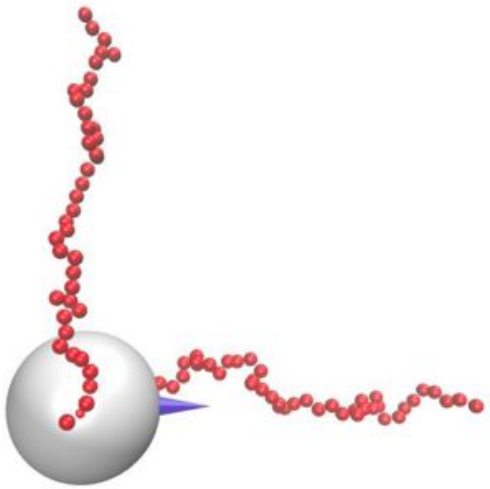
Diamond N_c=4

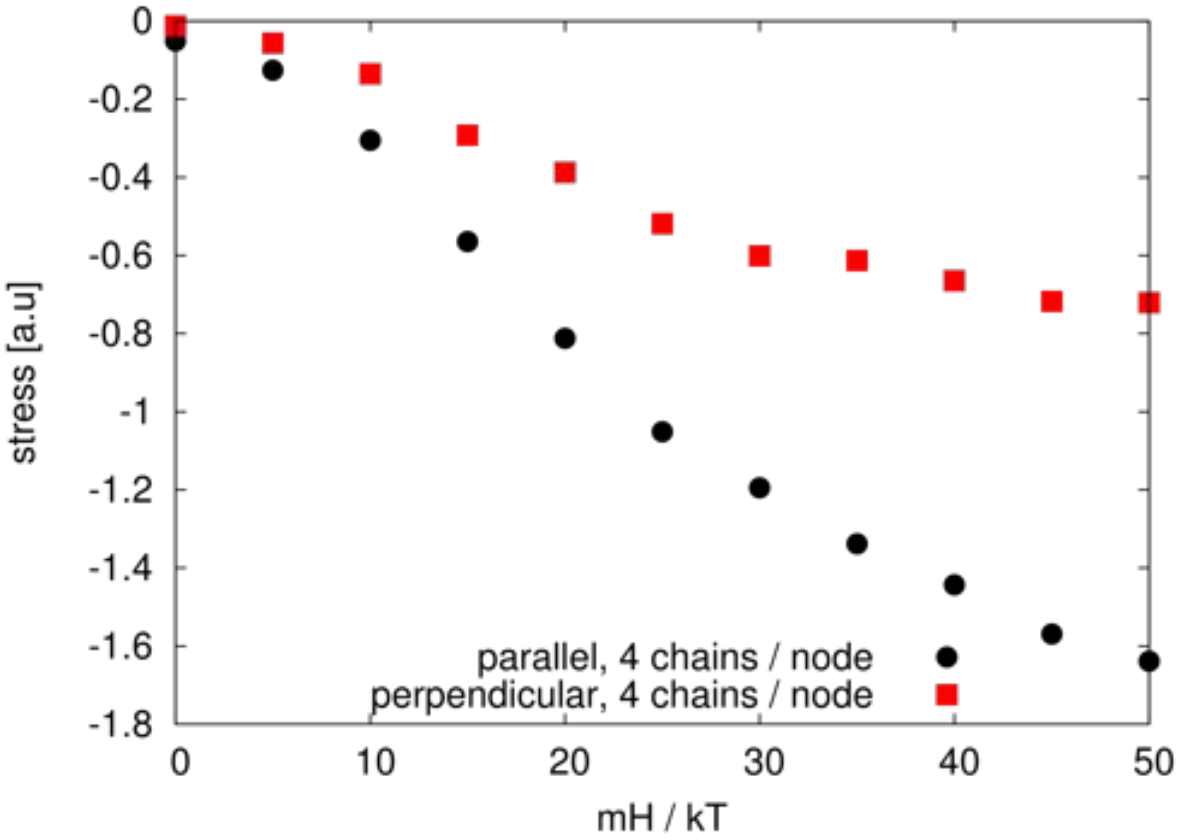


Simple cubic N_c=6

- Chains attached to surface of magnetic nanoparticle
- Simulation initially in NVT ensemble
- Volume iteratively changed to reach P=0 equilibrium state

Influence of Magnetic Field

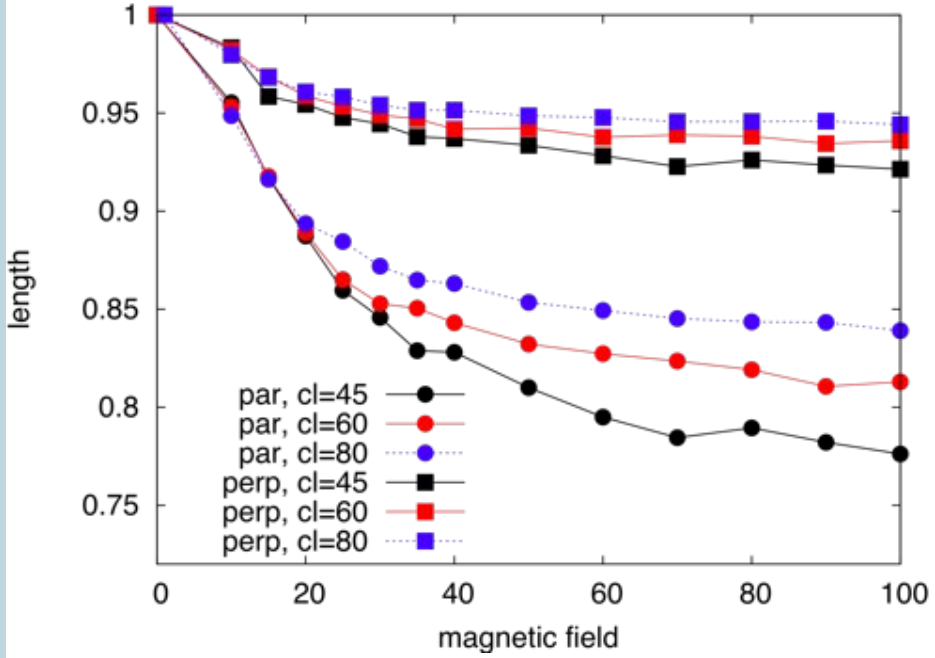


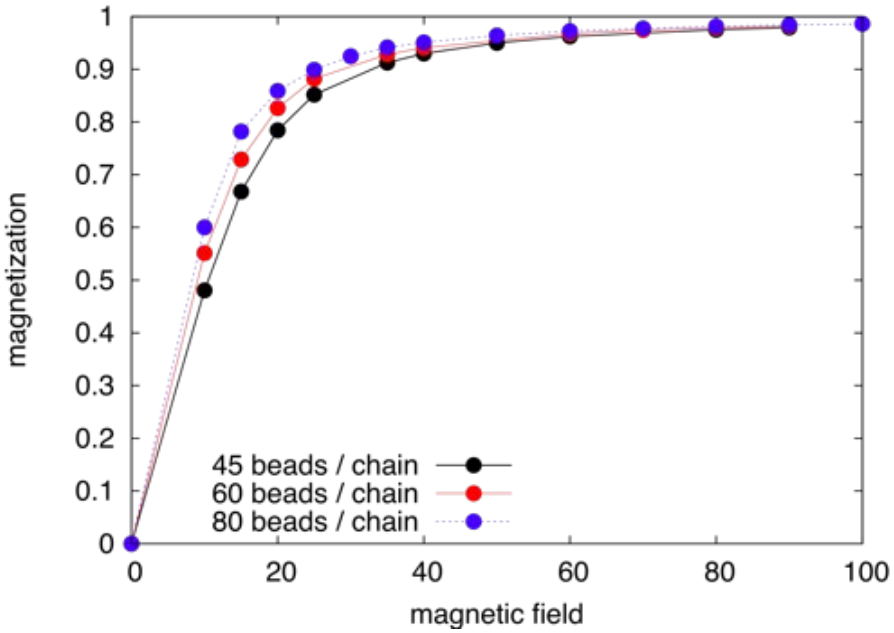


- Rotation around the field axis is possible
- Rotation around the other axis is hindered by the field

- Volume kept constant
- Higher stress in field direction, more contraction along this direction

Shape Change and Magnetization





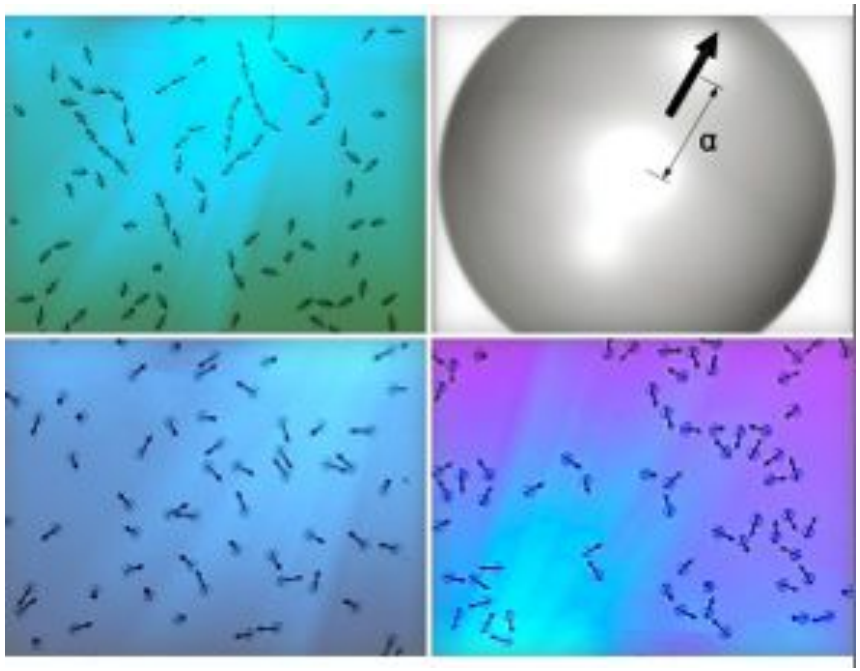
The gel shrinks stronger in field direction
A very strong field is required to magnetize the sample
Again shorter chains show stronger contraction

Summary Magnetic Gels

- Gels can contract in homogeneous fields due to 2 mechanisms
  - Chaining of dipolar particles in close distance
  - Transmitting the induced torque due to induced field alignments of the magnetic nodal particles that act as crosslinkers for the polymer strands
  - Differences in 2 and 3 dimensions (more d.o.f)

R Weeber S. Kantorovich and C. Holm, Soft Matter in press (2012)

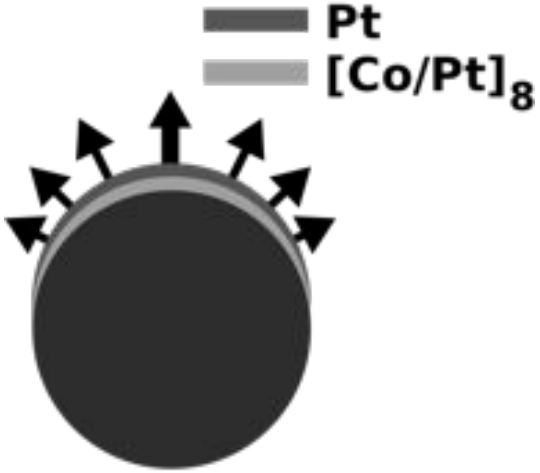
Part 2: Shifted Dipolar Particles



Use of Novel MNP for increasing Complexity

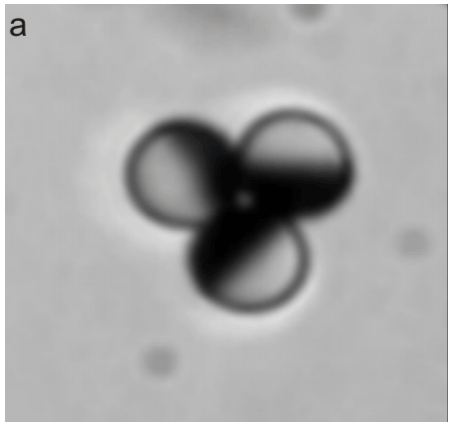
First we discuss only q2D geometries!

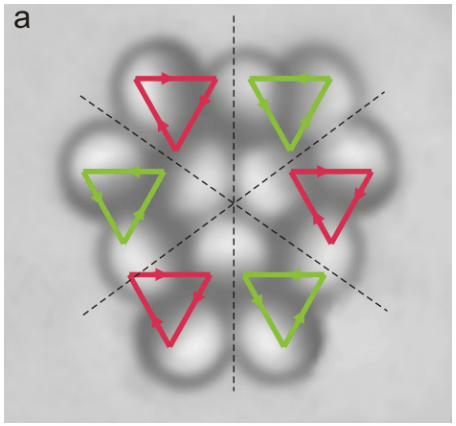
Inspiration from Experiments

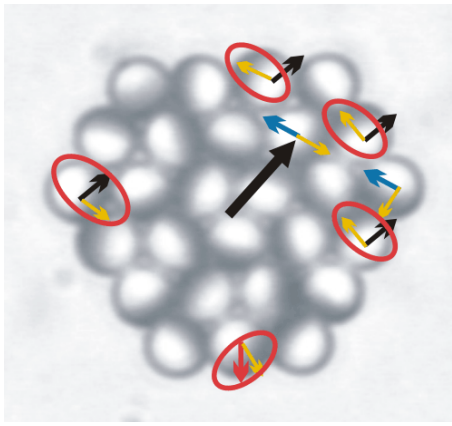


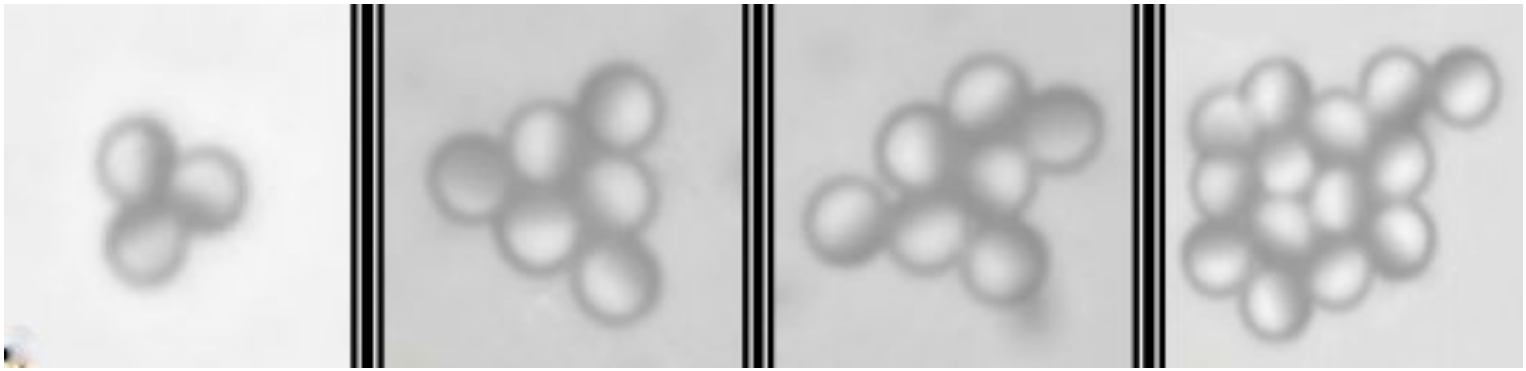
L. Baraban et al., *PRE* **77,** 031407 (2008)

Barabaran et al. observe very stable „magic clusters“ with 3, 12, (27) particles





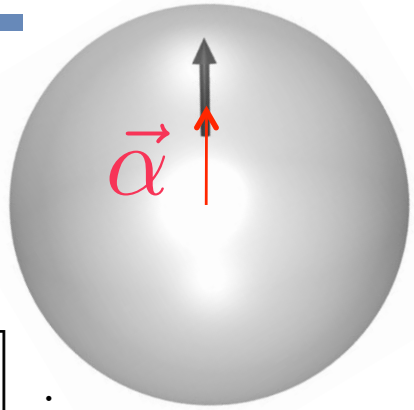




Shifted Dipol Model

Steric Interaction (WCA)
plus dipolar

$$\alpha = \frac{|\vec{\alpha}|}{R}$$



$$U_{dd}(\mathbf{m_i}, \mathbf{m_j}, \mathbf{r_{ij}}) = -\frac{\mu_0}{4\pi}\left[3\frac{(\mathbf{m_i}\cdot\mathbf{r_{ij}})(\mathbf{m_j}\cdot\mathbf{r_{ij}})}{r^5} - \frac{(\mathbf{m_i}\cdot\mathbf{m_j})}{r^3}\right] .$$

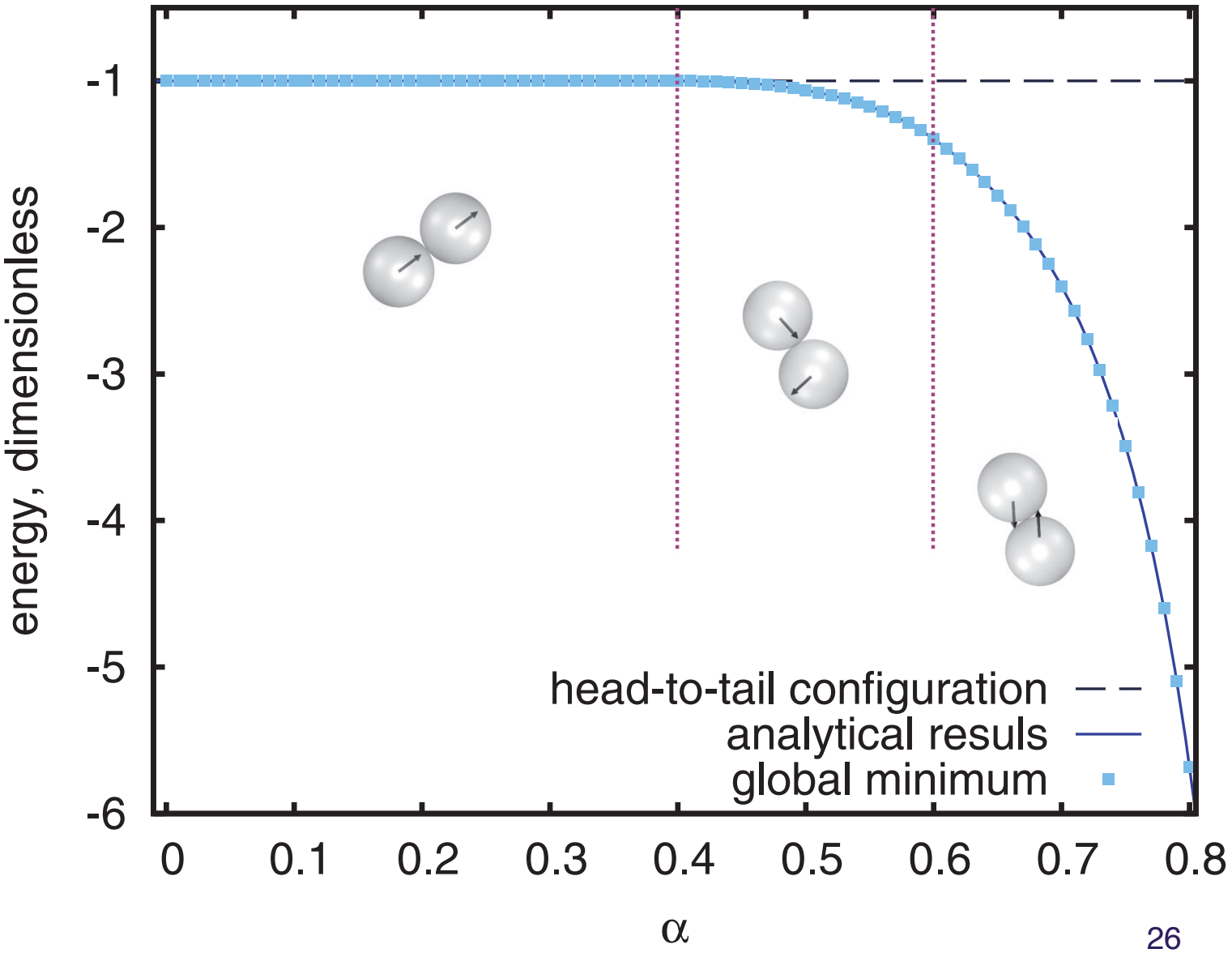
$$\mathbf{r_{ij}} = \mathbf{r_i} - \mathbf{r_j} \quad , \quad r = |\mathbf{r_{ij}}|$$

$$\lambda = \frac{\mu_0|\mathbf{m}|^2}{4\pi k_B T d^3} \qquad \lambda^* = \gamma(\alpha)\cdot\lambda$$

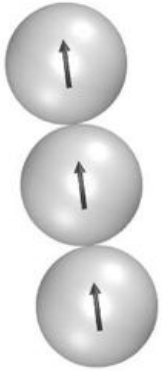
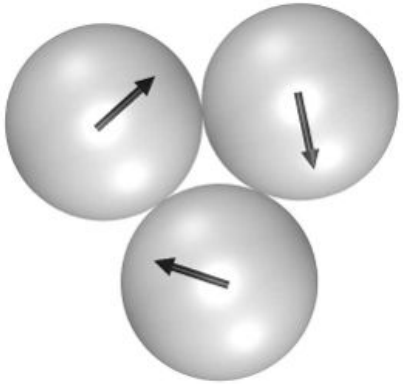
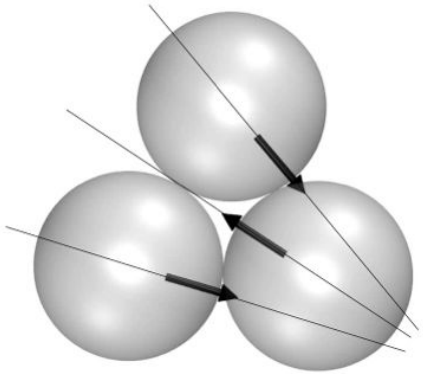
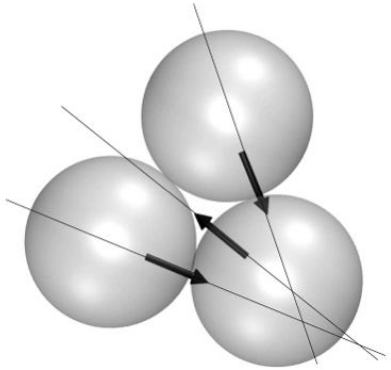
$$\gamma(\alpha) = \frac{U_{gs}(0)}{U_{gs}(\alpha)}$$

α	$\gamma(\alpha)$
0	1
0.4	0.9999
0.5	0.9396
0.6	0.7163
0.7	0.4164
0.8	0.1761

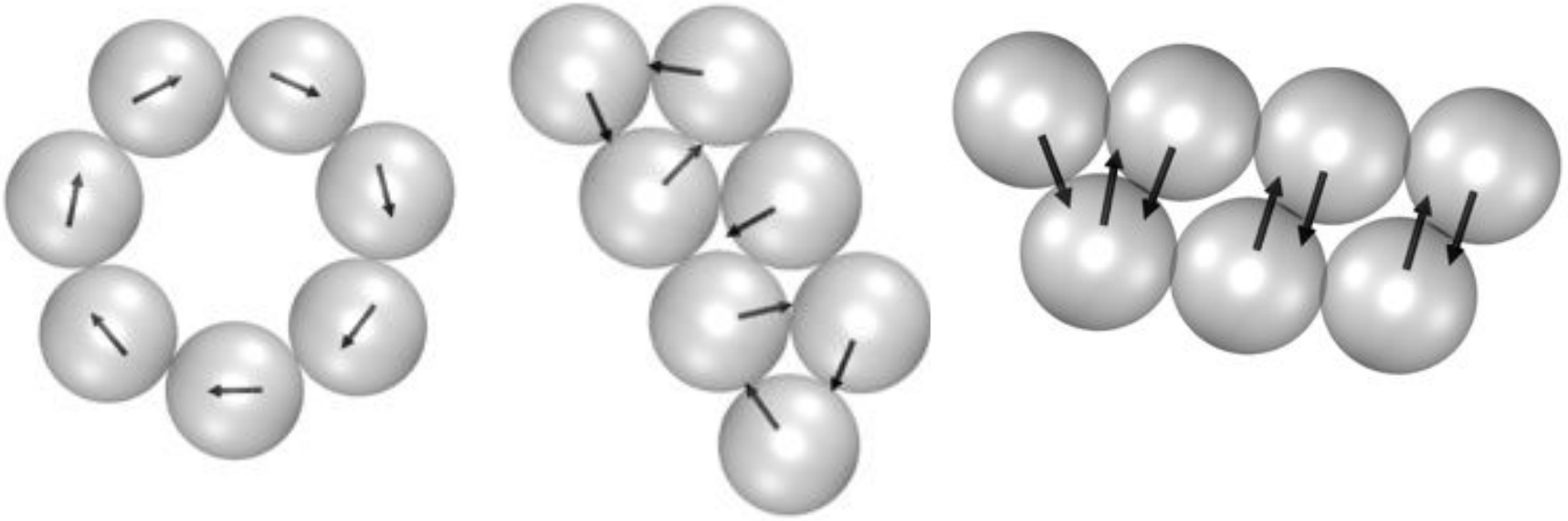
Two-particle ground states



3-Particle Clusters

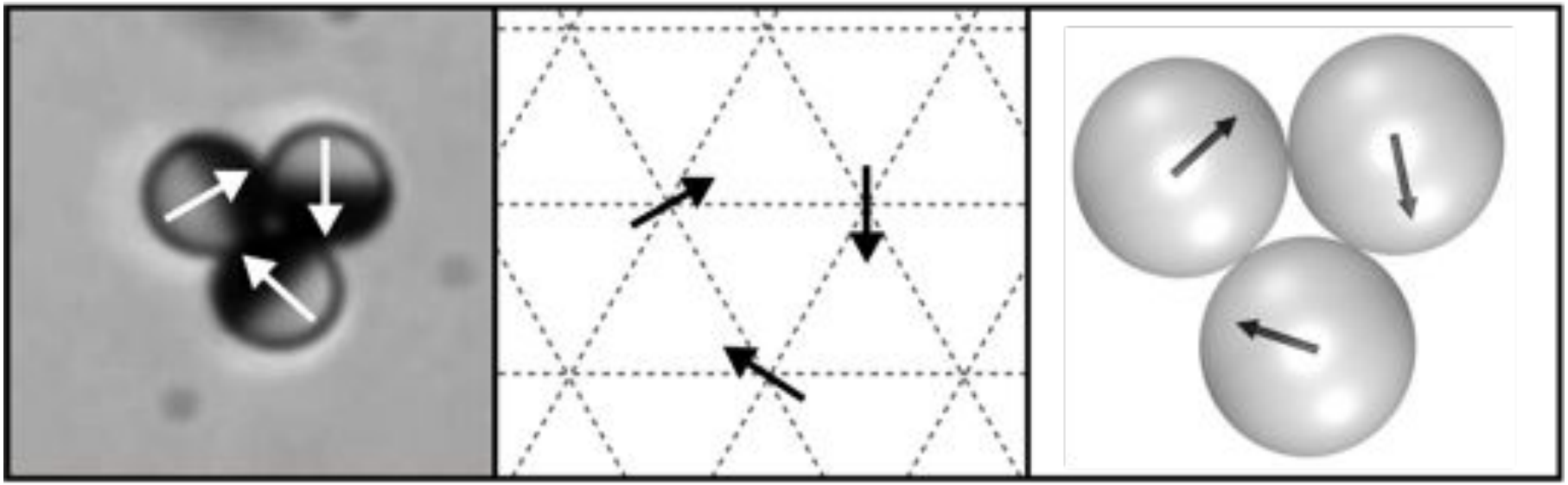
C3-I	C3-II	C3-III	C3-IV
			
$\alpha = 0$	$\alpha = 0.3$	$\alpha = 0.81$	$\alpha = 0.85$
$0 < \alpha$	$0.258 < \alpha$	$0.799 < \alpha$	$0.83 < \alpha$
< 0.258	< 0.799	< 0.83	< 1

Higher Order Clusters



$\alpha = 0.0$ $\alpha = 0.67$ $\alpha = 0.85$

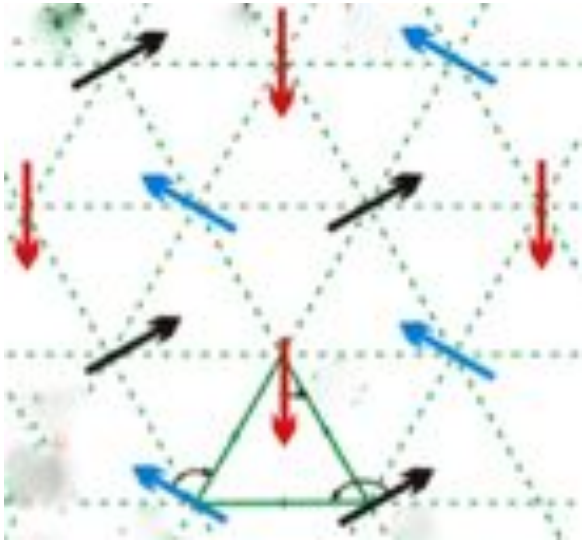
Baraban 3-Particle Cluster



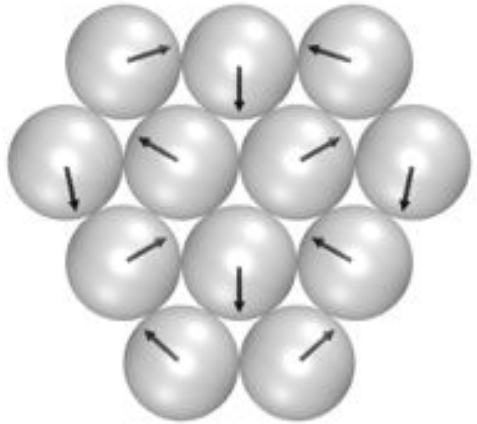
$$\alpha \approx 0.5$$

Triangular configuration obsered for wide range of $0.258 < \alpha < 0.799$

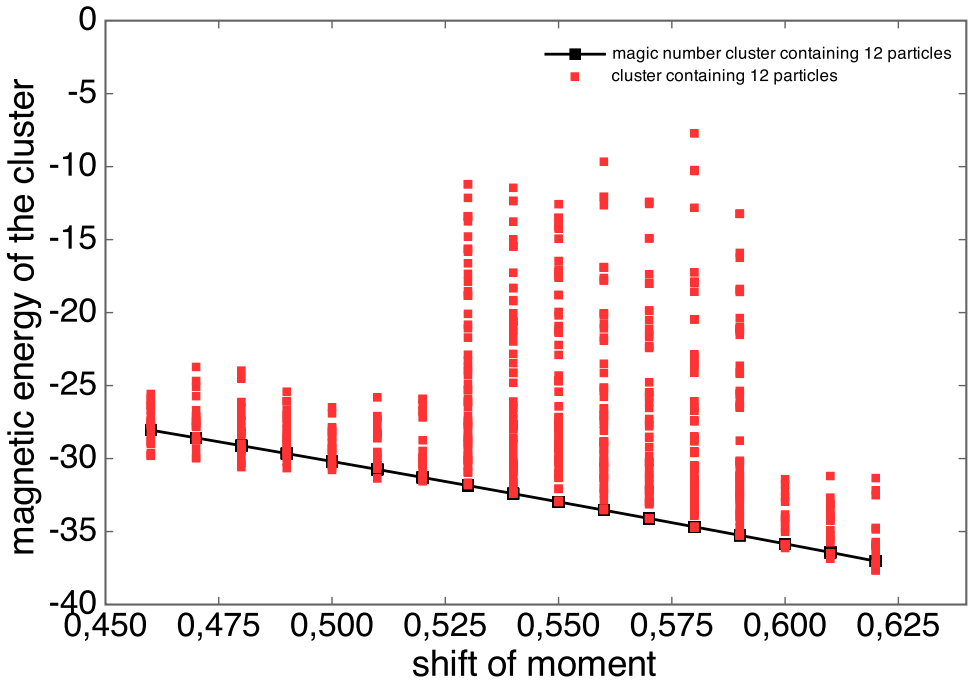
12-Particle „Magic Cluster“

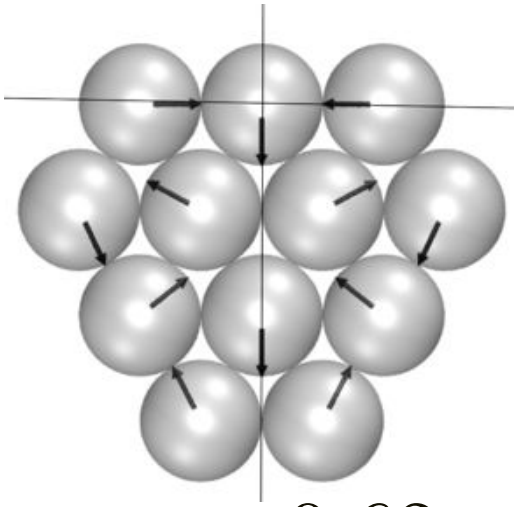


Best „match“



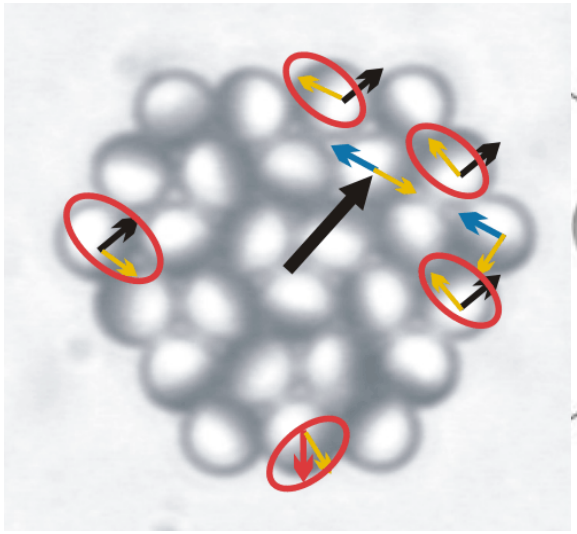
$\alpha = 0.47$

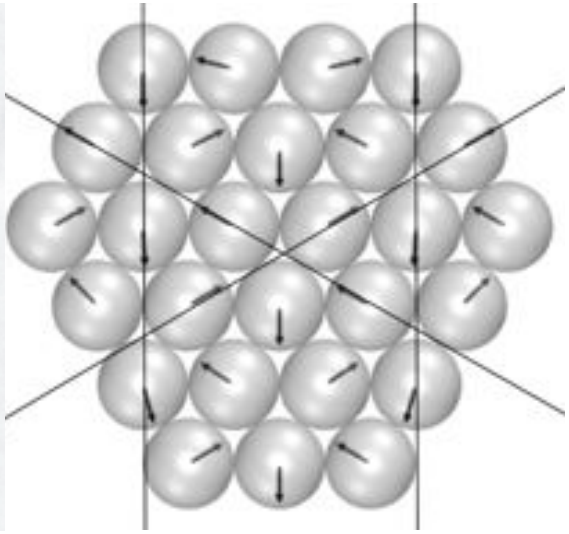




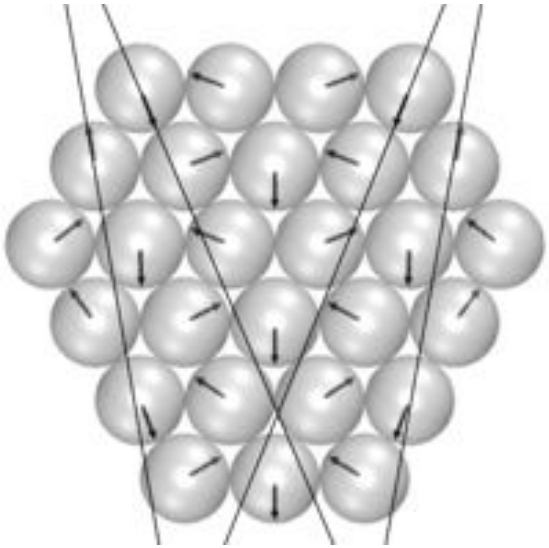
$\alpha = 0.62$

27-Particle „Magic Cluster“

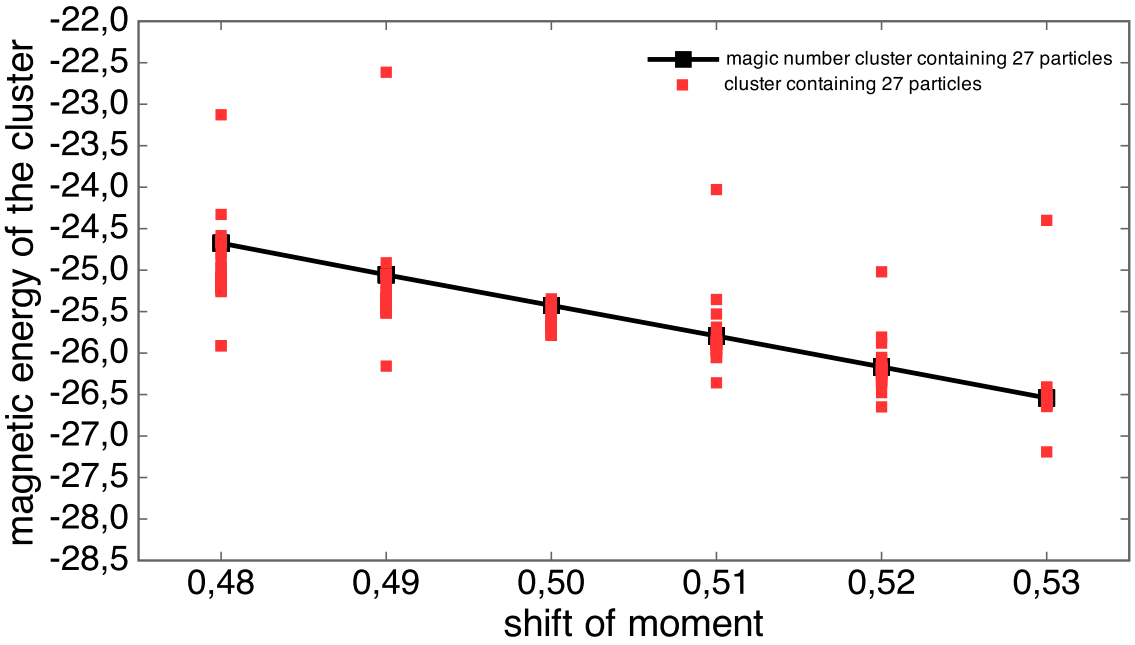




$\alpha = 0.68$



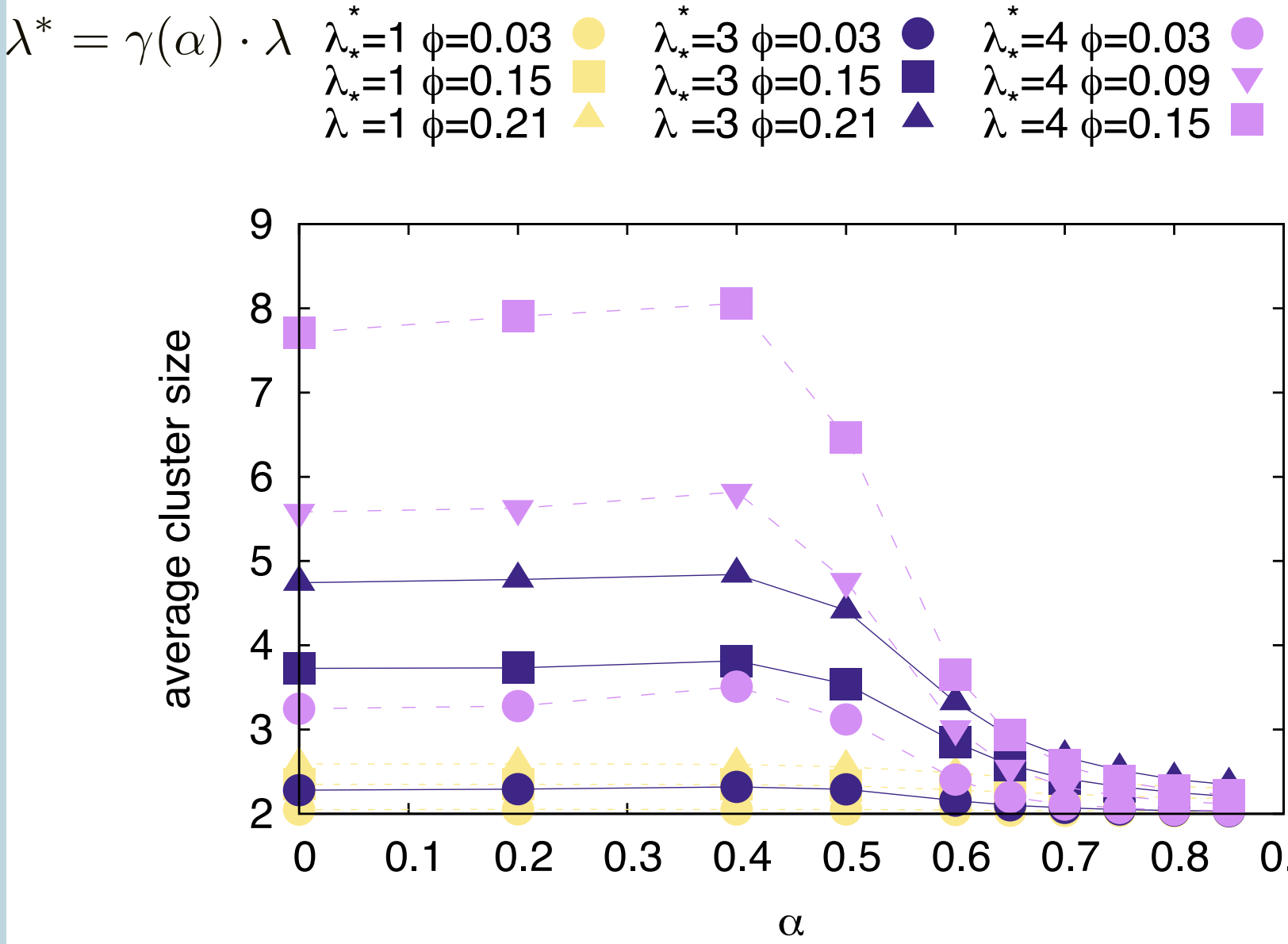
$\alpha = 0.53$



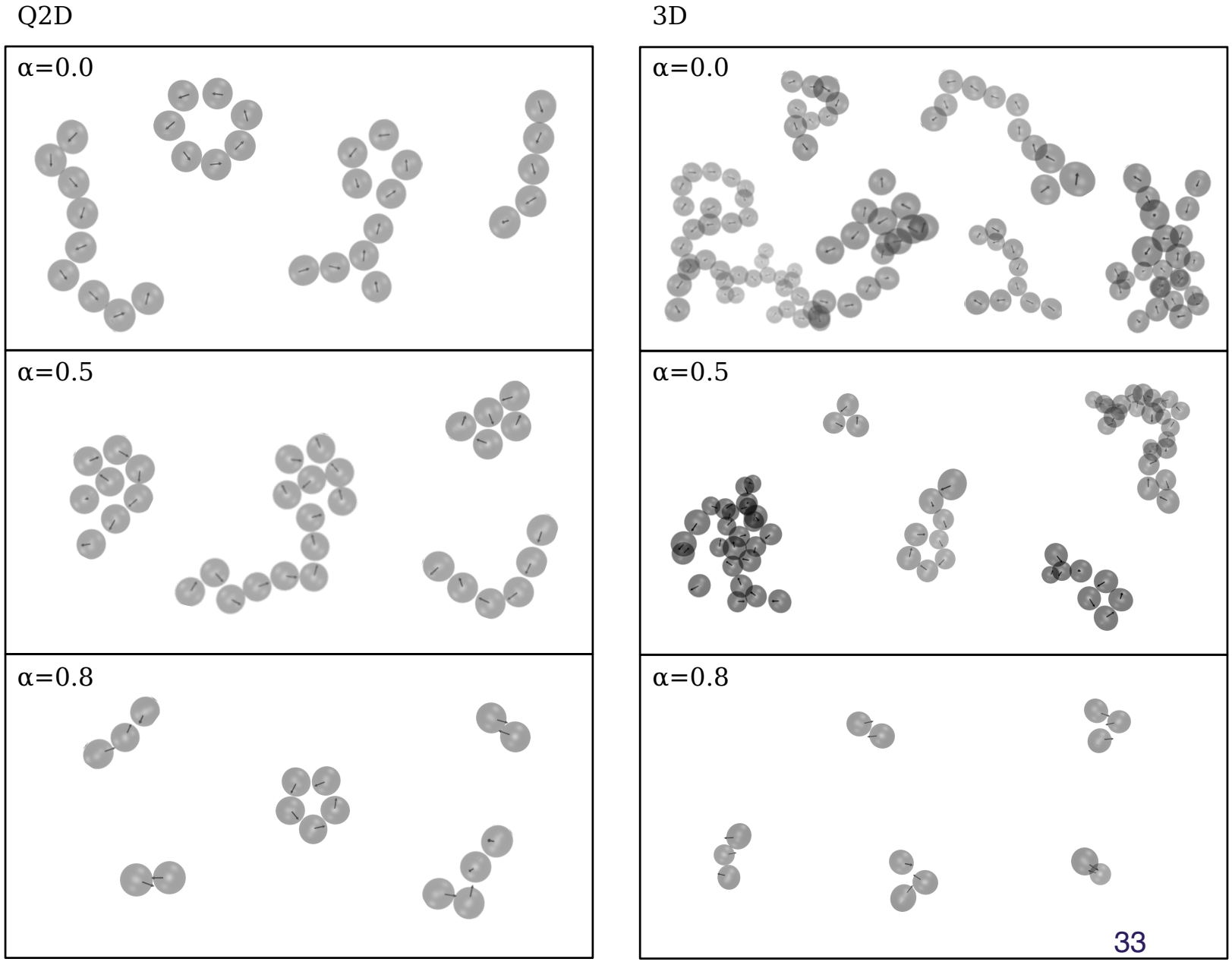
Magic cluster does not corresspond to the ground state

Cluster Size at Room Temperature

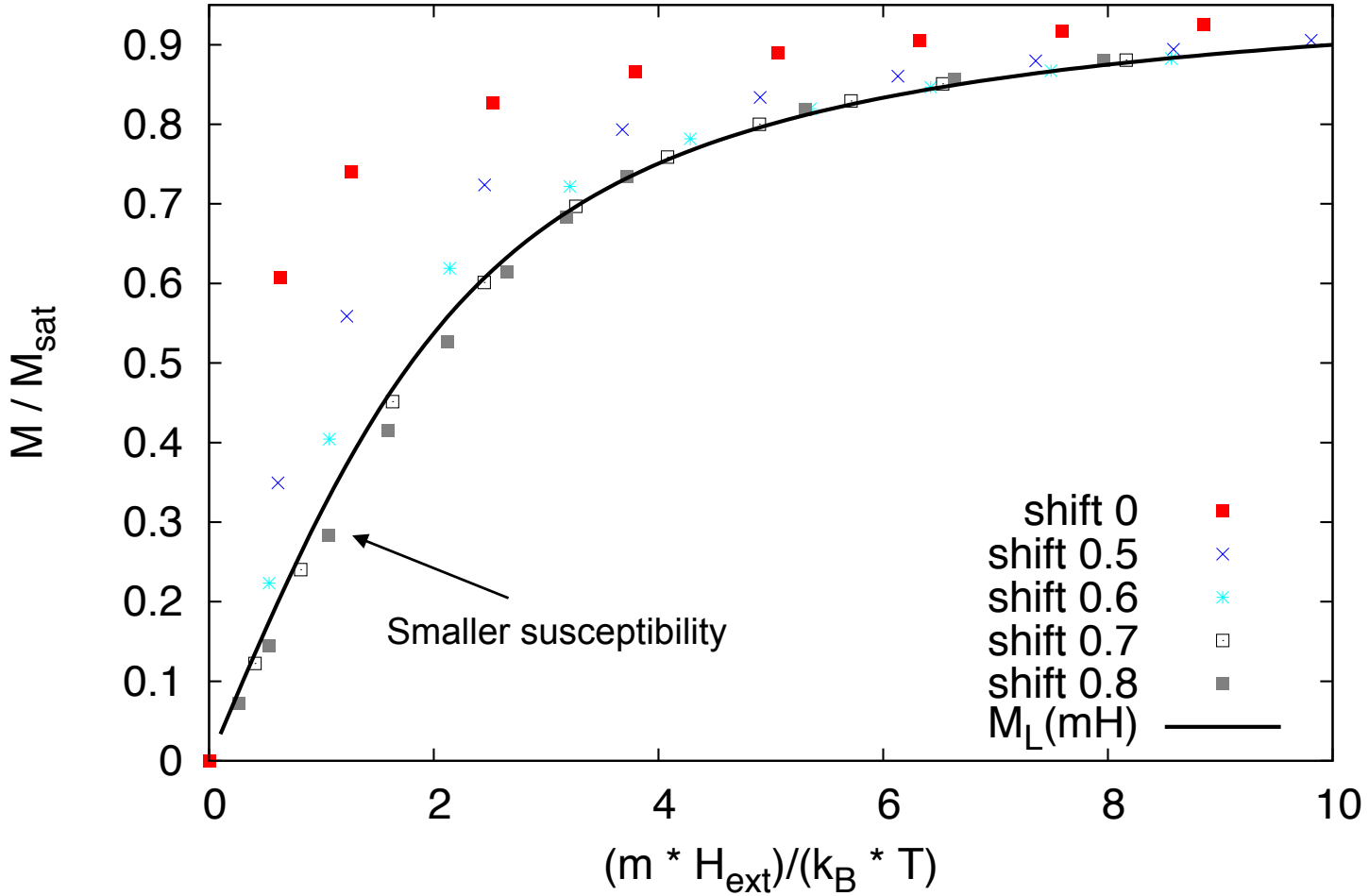
$\lambda^* = \gamma(\alpha) \cdot \lambda$



Cluster at finite Temperature



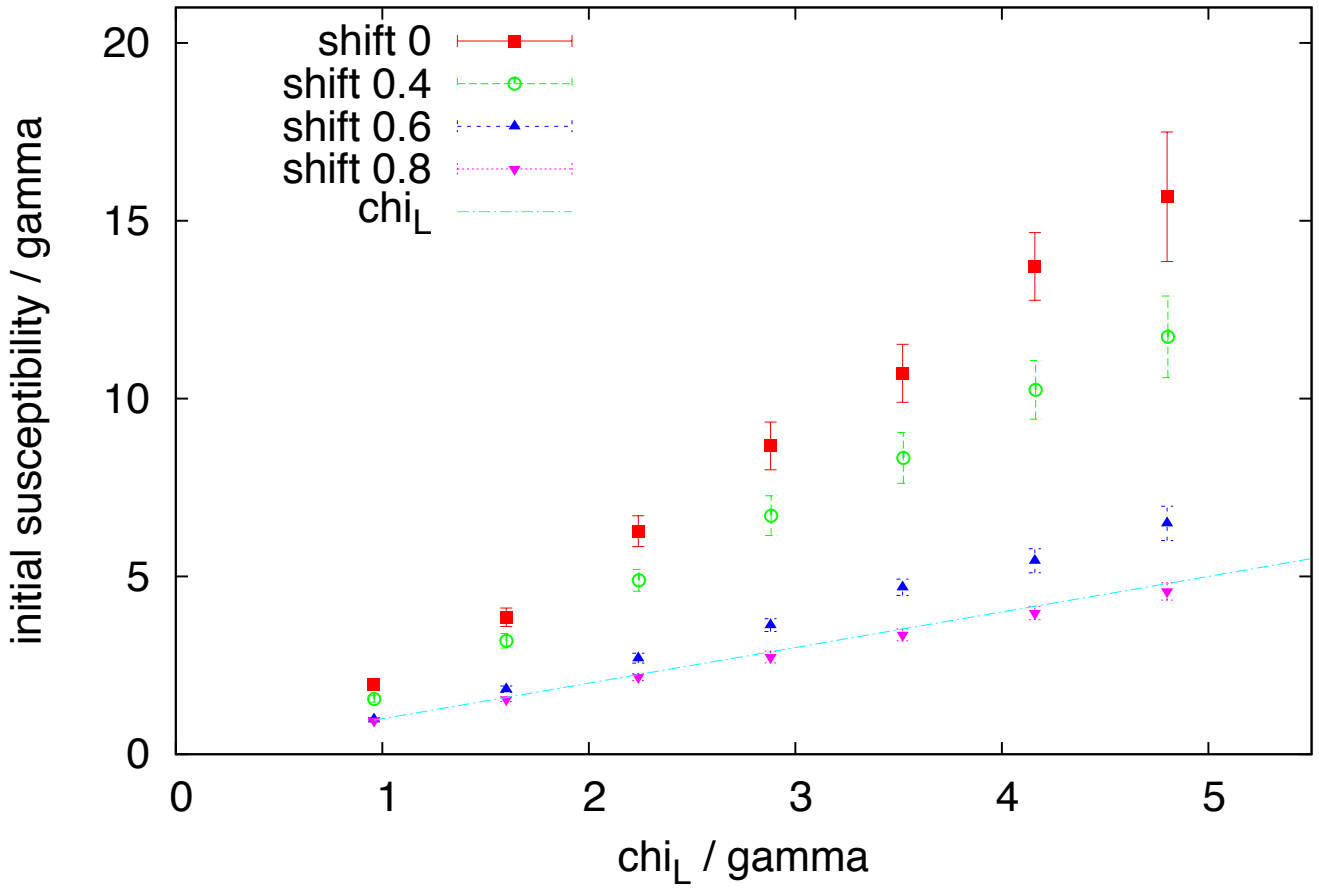
Magnetization Behavior of SD



At large field values and large shifts, the clusters of anti-parallel dipoles break up under the influence of strong fields=> reversable self-assembly !

Susceptibility for λ*=4

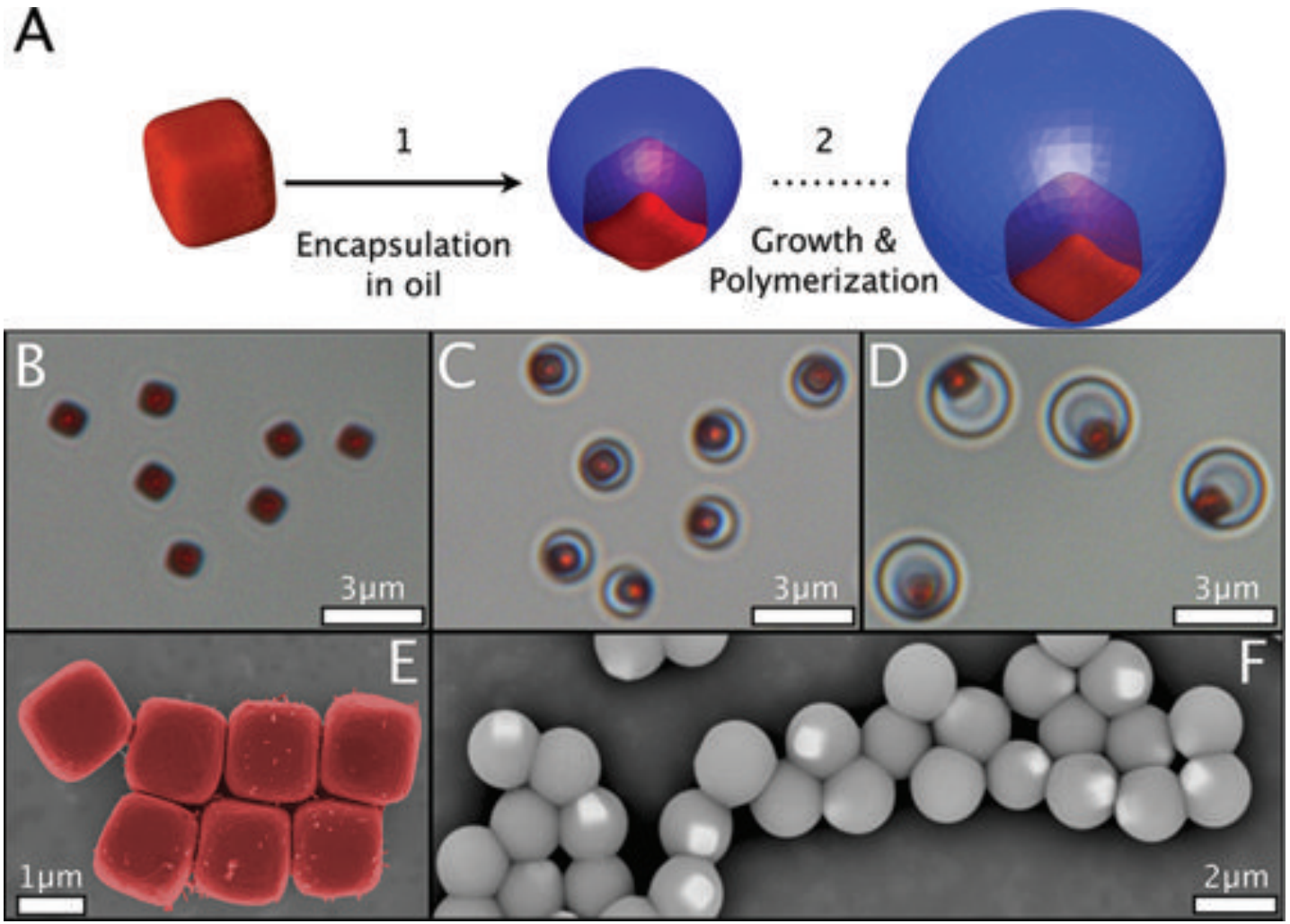
$$\chi_L = \rho \frac{m^2}{3\mu_0 kT}$$



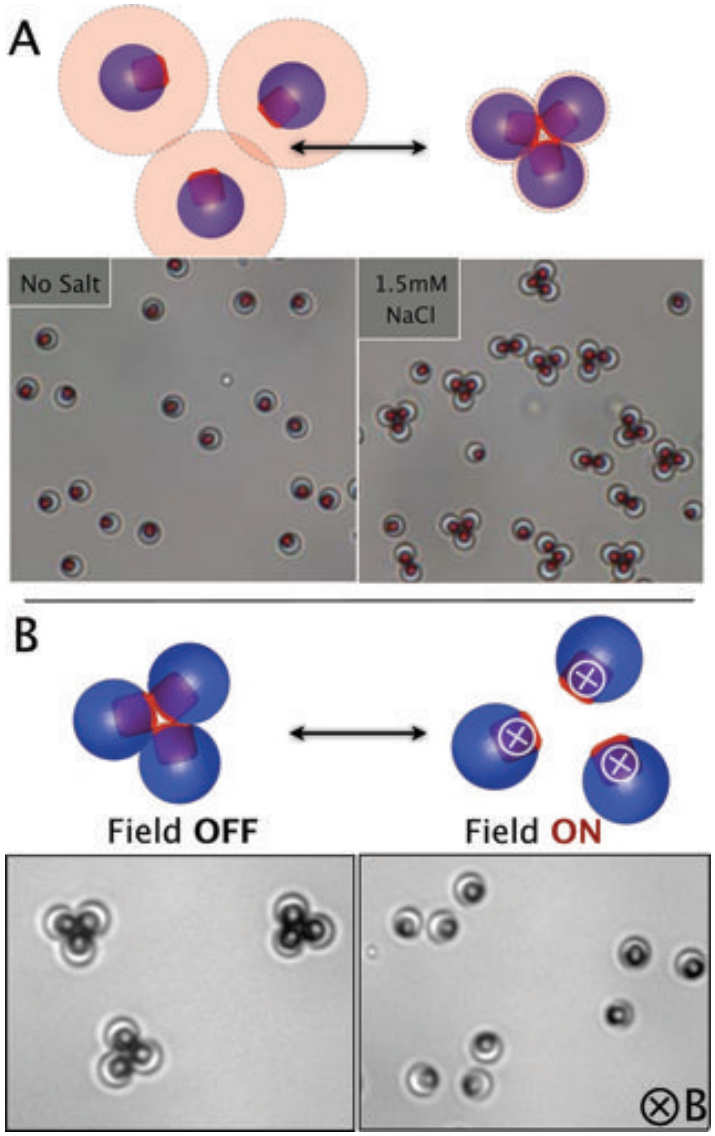
Initial susceptibility can be smaller than Langevin law!
Due to occurance of many clusters with zero magnetic moment

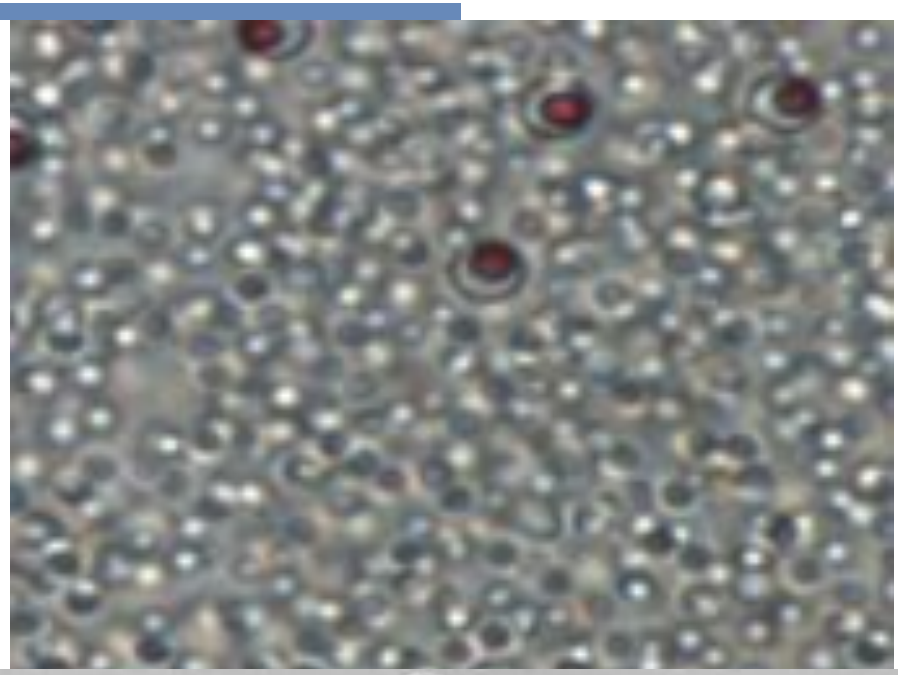
New Experimental Realisation

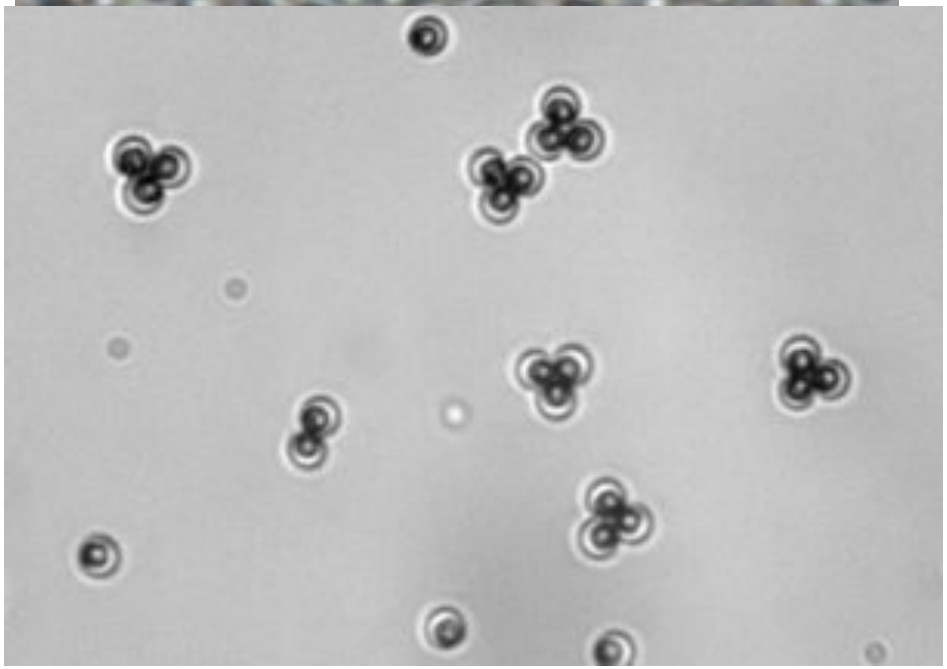
D. Pine group, *Magnetic Click Colloidal Assembly* J. Am. Chem. Soc. **134**, 6112-6115 (2012)



Pine‘s Patchy Colloids







Summary Part 2

•the form of ground state clusters changes from chains and rings over triangles to structures with antiparallel orientation of magnetic moments with increasing shift α

•the size of clusters is controlled by α, λ^*, and ϕ, whereas its structure is dominated by α

•for large shifts initial susceptibility is lower than the initial susceptibility of a Langevin ideal superparamagnetic gas

•A strong applied field at high shifts can reversibly unbind anti-parallel pairs

S. Kantorovich, R. Weeber, J.J. Cerdà, C. H., "Ferrofluids with shifted dipoles: ground state structures“ Soft Matter **7**, 5217, (2011).
S. Kantorovich, R. Weeber, J.J. Cerdà, C. H, "Magnetic particles with shifted dipoles“, JMMM **323,** 1269 (2011),
M. Klinkigt, R. Weeber, S. Kantorovich, C. Holm, in preparation (2012).

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- All simulations were

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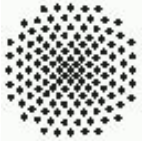
Thank you for listening

Chance to visit Stuttgart



University of Stuttgar
Germany

- CECAM Tutorial:

”Simulating Soft Matter with ESPResSo, ESPResSo++ and VOTCA“

It takes place at the Institute for Computational Physics, Stuttgart University, **08 - 12 October, 2012**

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