The Influence of Self-assembly on the Magnetic Response of Dipolar Soft Systems

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Varenna, July 2015

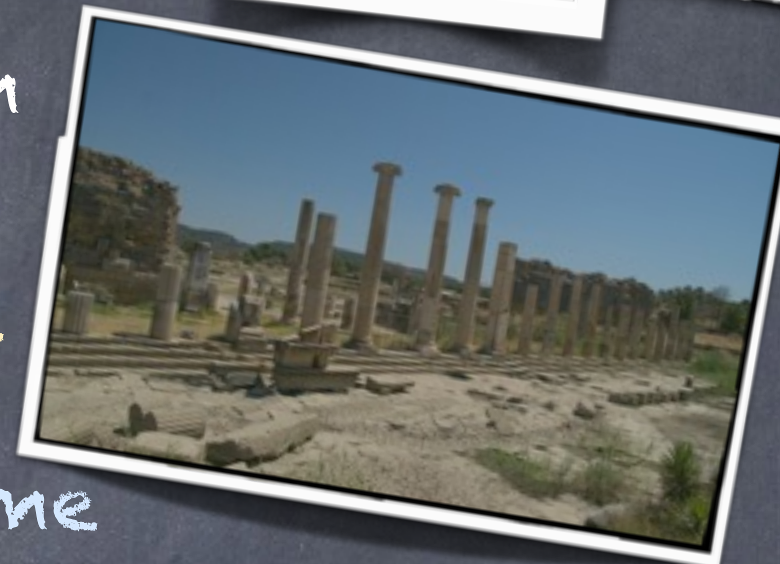
Plan

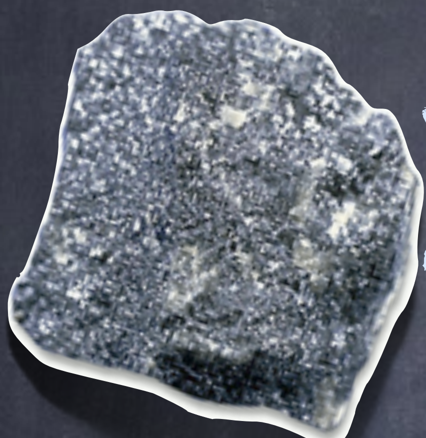
- Magnetism in SM, basic ideas
- Interactions/Models
- Magnetic response
  - from Langevin
  - to Self-Assembly
- Away from spheres
- Conclusions

Magnetism

1st "scientific discussion" on magnetism (Thales of Miletus, around 600 BC).

Magnesia, Greece





"The lodestone makes iron come or it attracts it." (Ancient China)

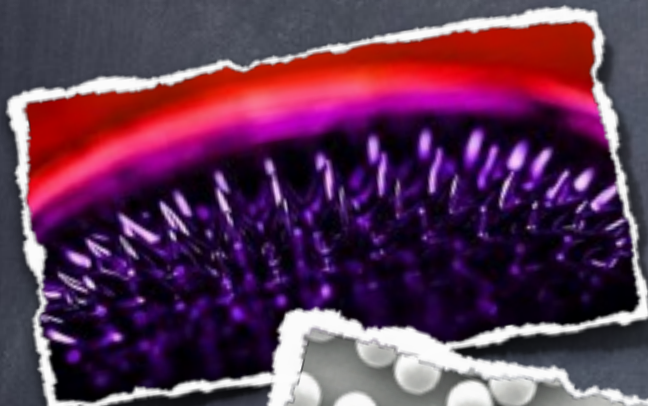
1st Compass
Shen Kuo
11th century

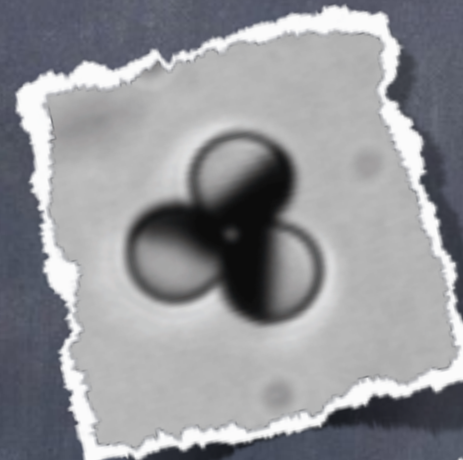
William Gilbert: "On the Magnet and Magnetic Bodies..." (1600)

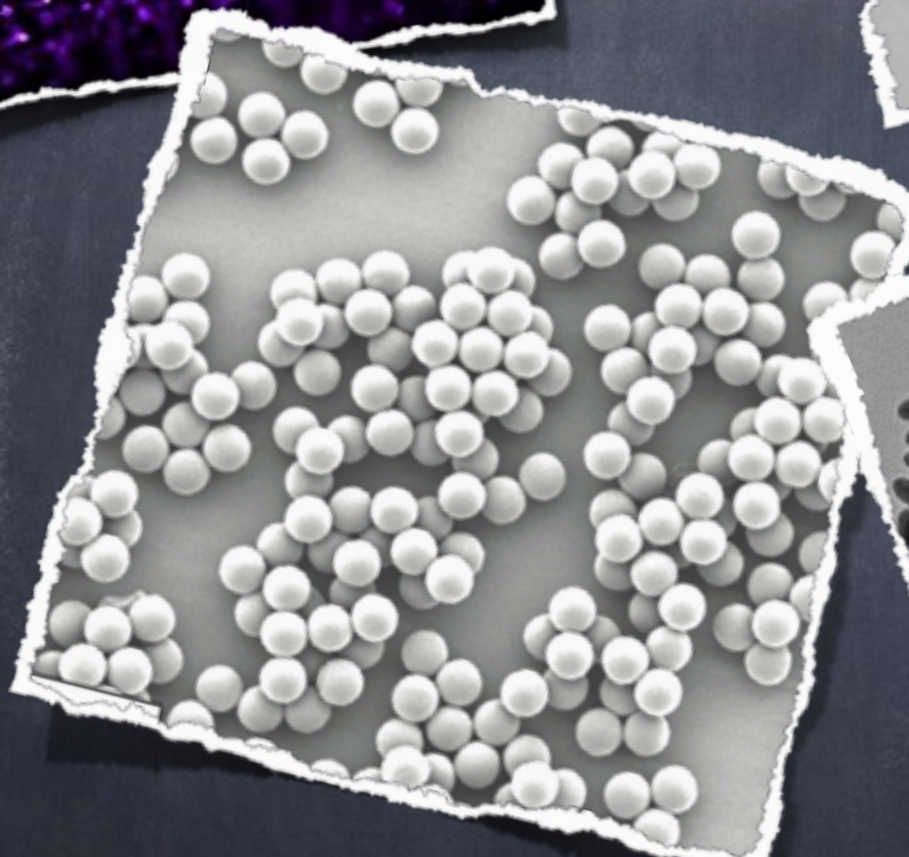
19th Century:
Oersted, Maxwell, Faraday, Gauss...
(Electromagnetism)

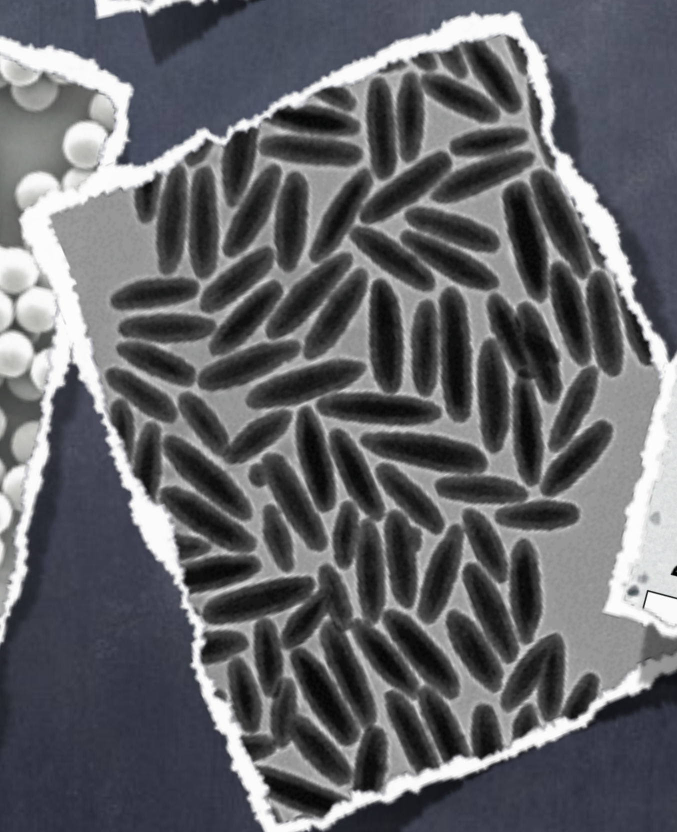
20th Century:
QUANTUM

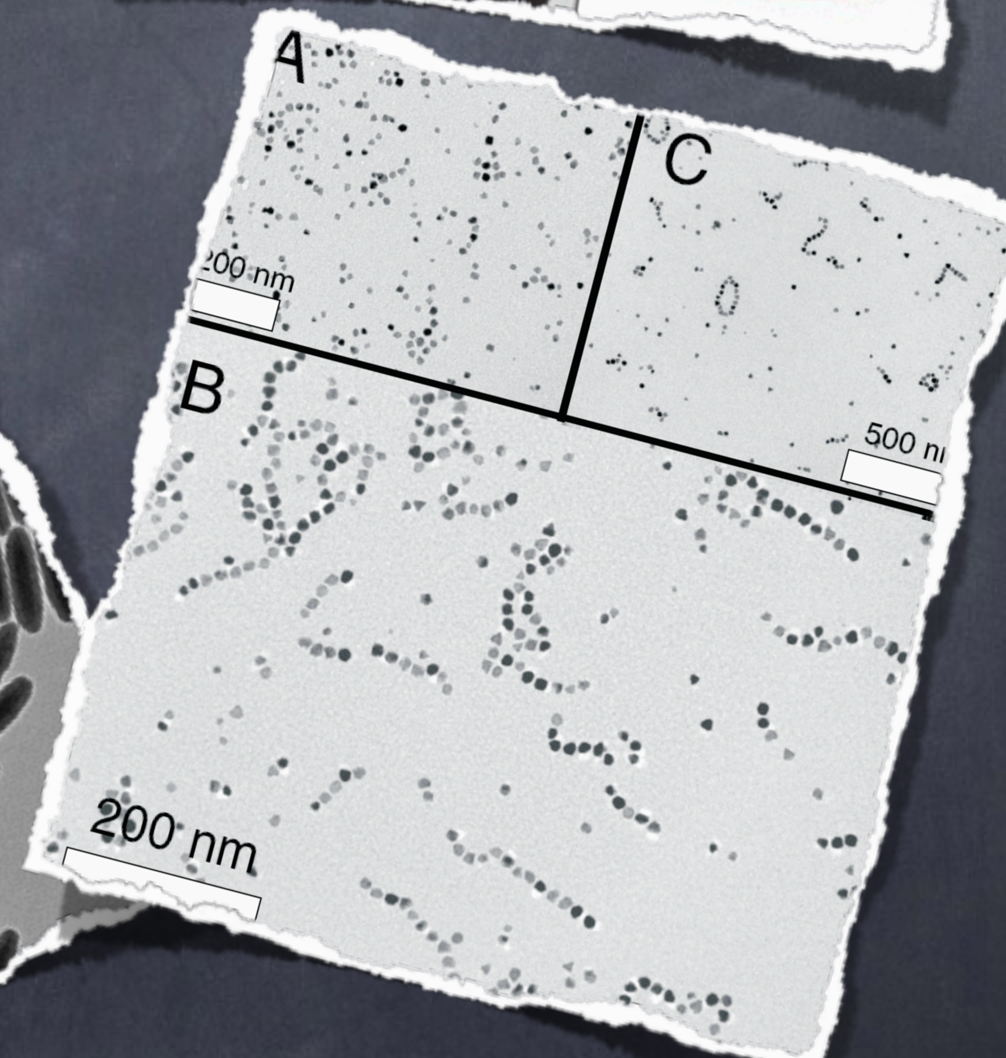
Magnetic soft matter











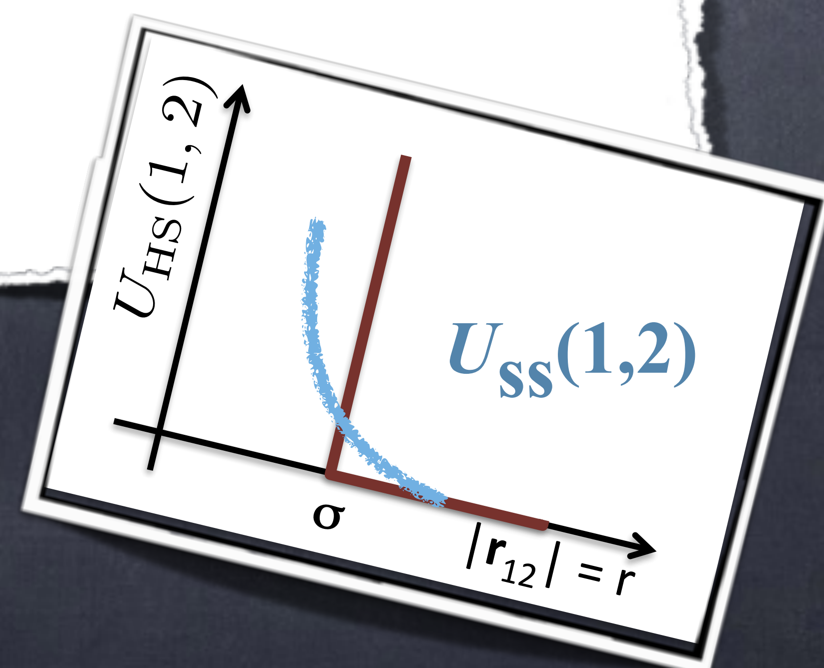
From works of:
Philipse's, Erbe's, Kretchmar's and Tschöpe's groups

Interactions/Models

- hard or soft spheres
- point dipole in the centre
- they can be described with few parameters:

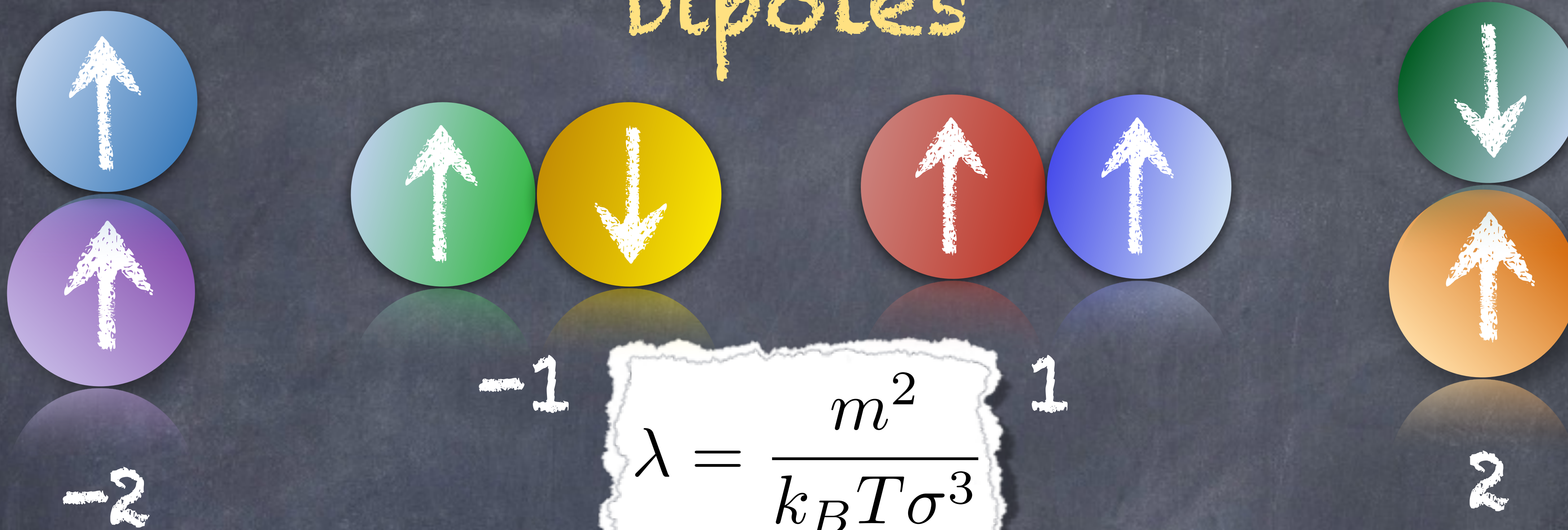
$$U_{\mathrm{DD}}(1,2) = \frac{m^2}{r^3}\left[(\hat{m}_1 \cdot \hat{m}_2) - 3(\hat{m}_1 \cdot \hat{r}_{12})(\hat{m}_2 \cdot \hat{r}_{12})\right]$$

$$\lambda = \frac{m^2}{k_B T \sigma^3} \qquad \rho = \frac{N\hat{\sigma}^3}{\hat{V}}$$



Interactions/Models

Dipoles



$$\lambda = \frac{m^2}{k_B T \sigma^3}$$

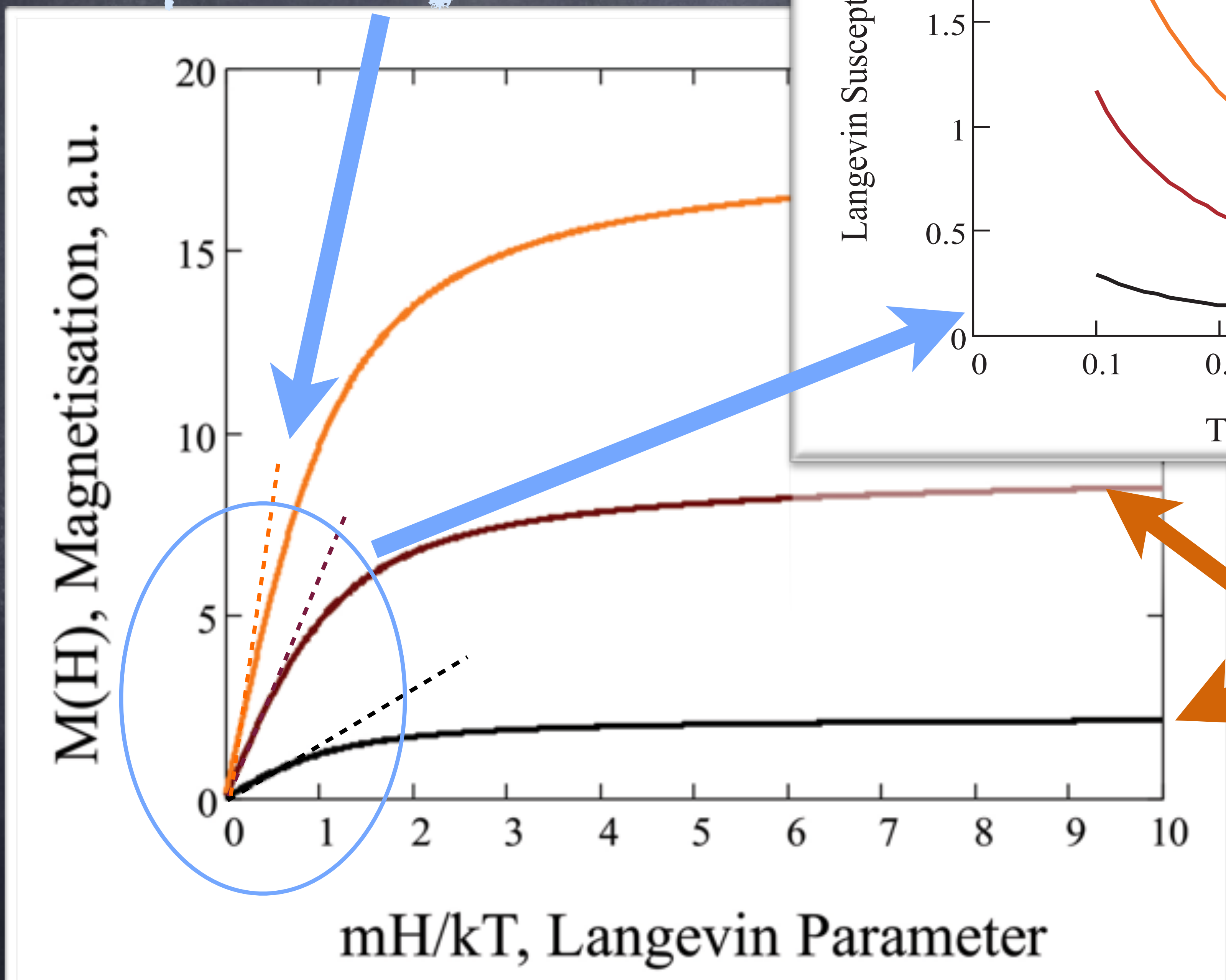
Zeeman

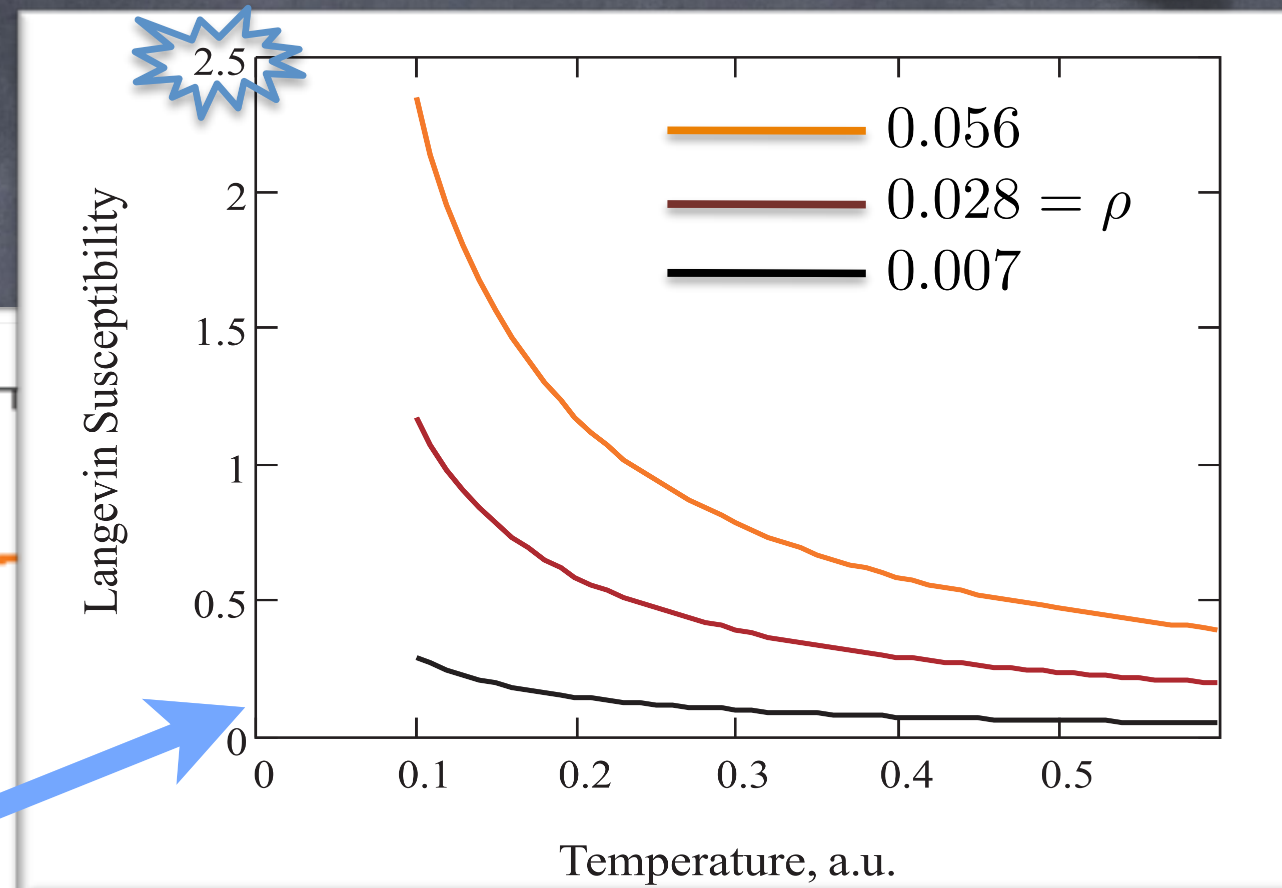
Peter Zeeman

$$E = -(\mathbf{m} \cdot \mathbf{H})$$

Magnetic response

Initial Susceptibility, ~<m²>

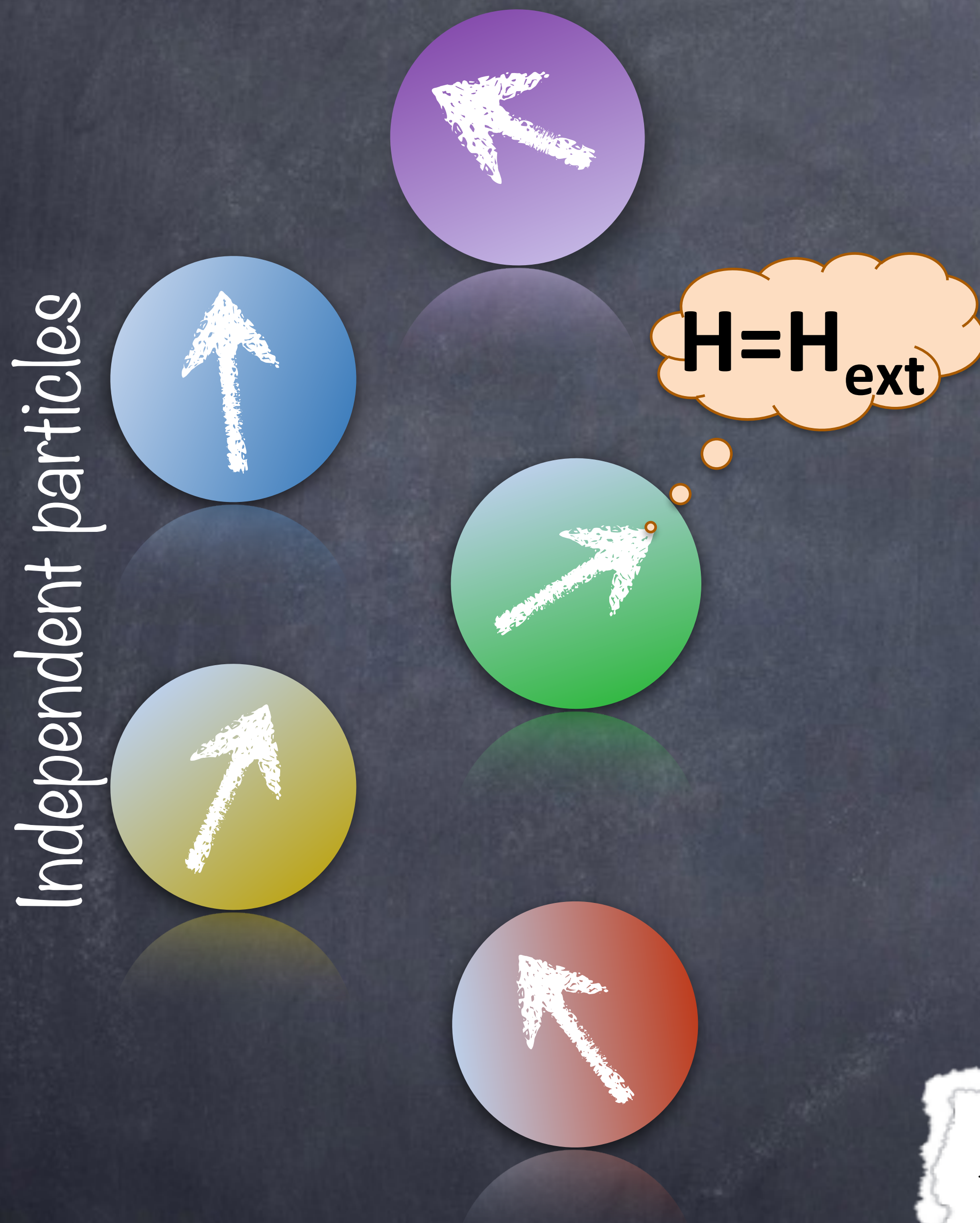


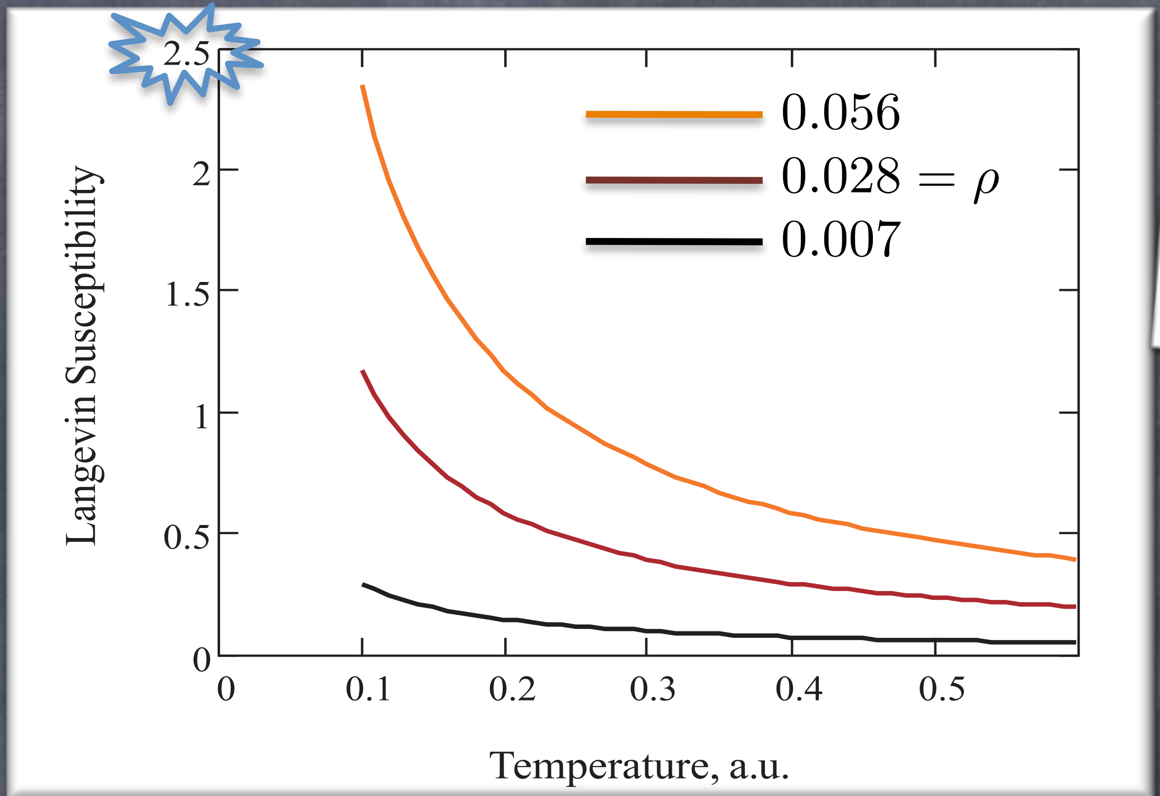


Saturation magnetisation, ~<m>

Susceptibility

...From Langevin

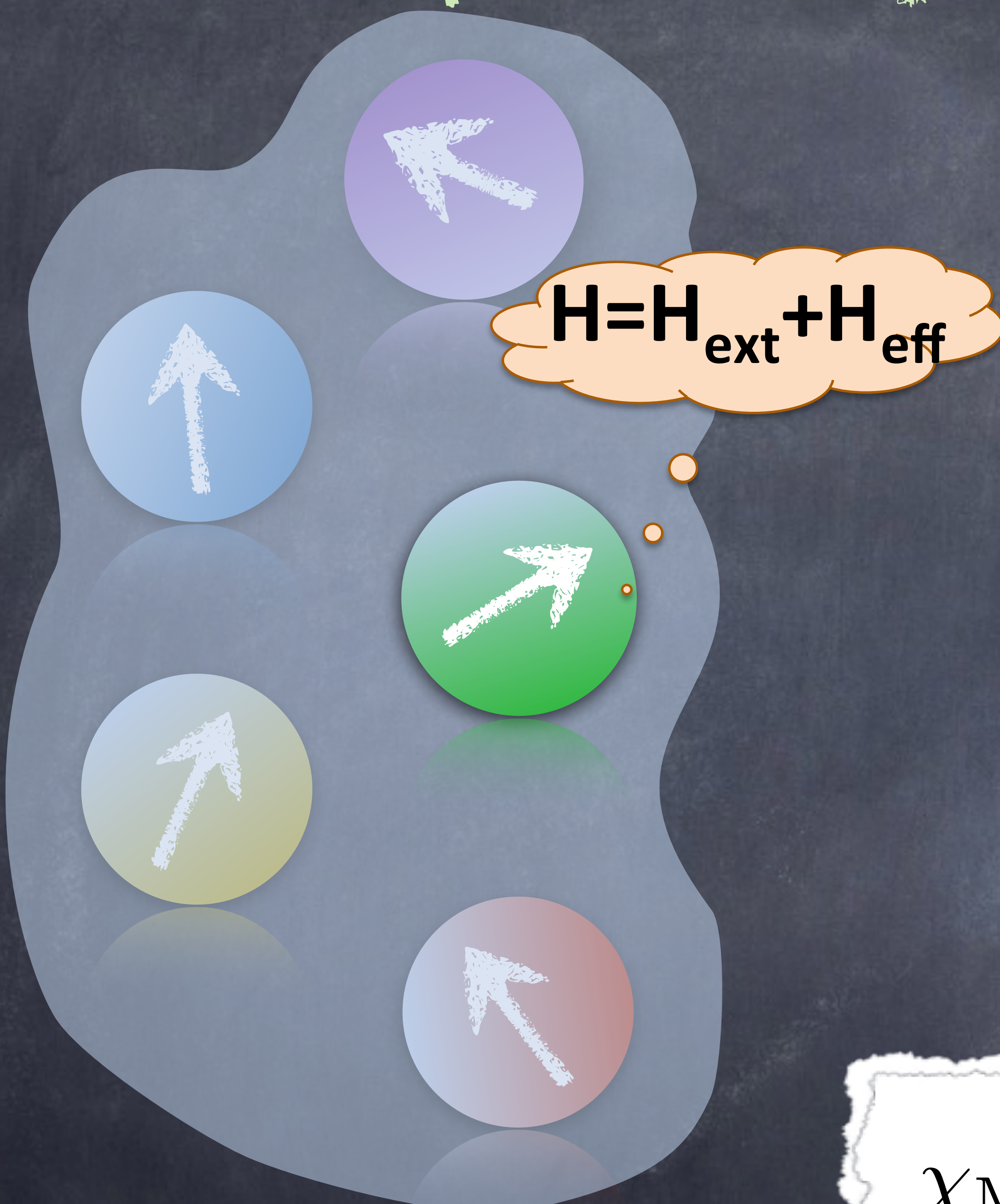




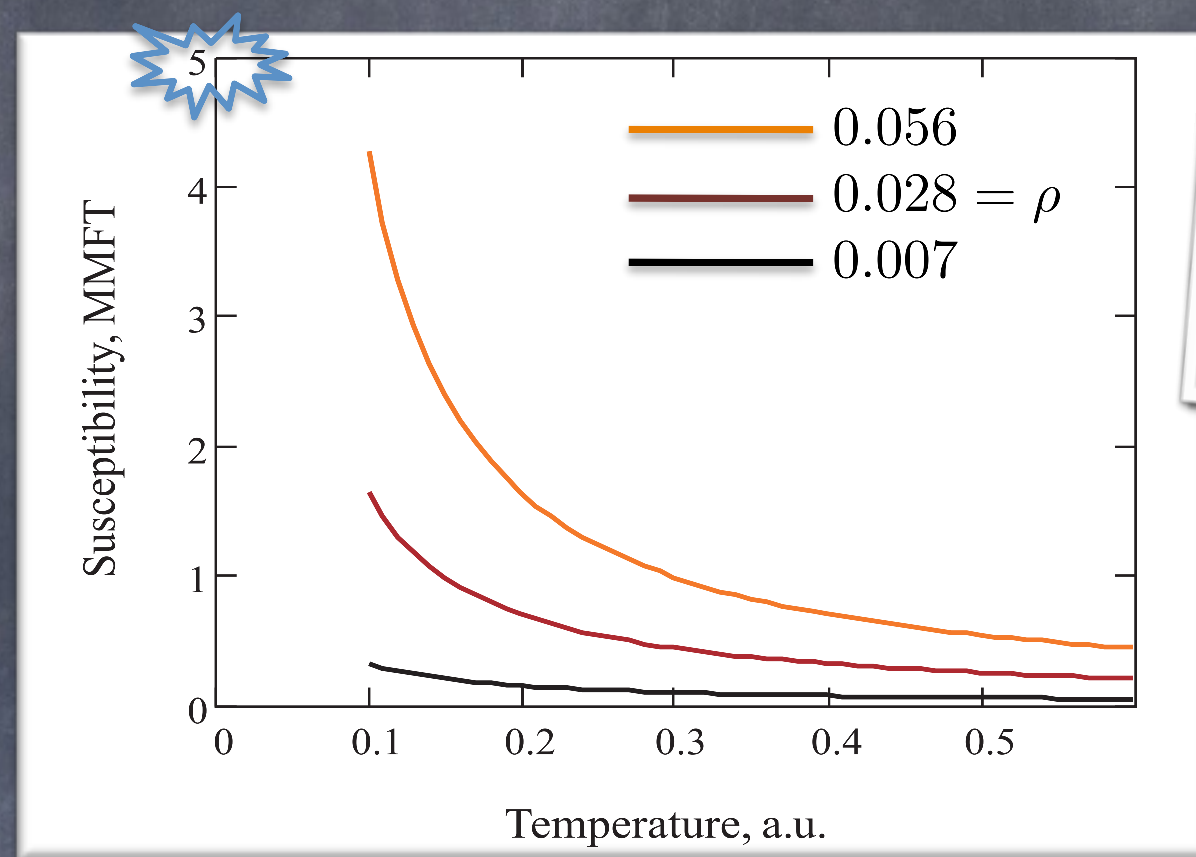
$$\lambda \sim \frac{1}{T} \quad \chi_{\mathrm{L}} = \frac{4\pi}{3}\sigma^3\rho\lambda$$

P. Langevin, Ann. de chim. et phys. 1905.

Susceptibility



...to the Mean-Field



$$\chi_{\mathrm{M}} = \chi_L \left(1 + \frac{\chi_L}{3} + \frac{\chi_L^2}{144}\right)$$

A. Ivanov et al., PRE, 2001.

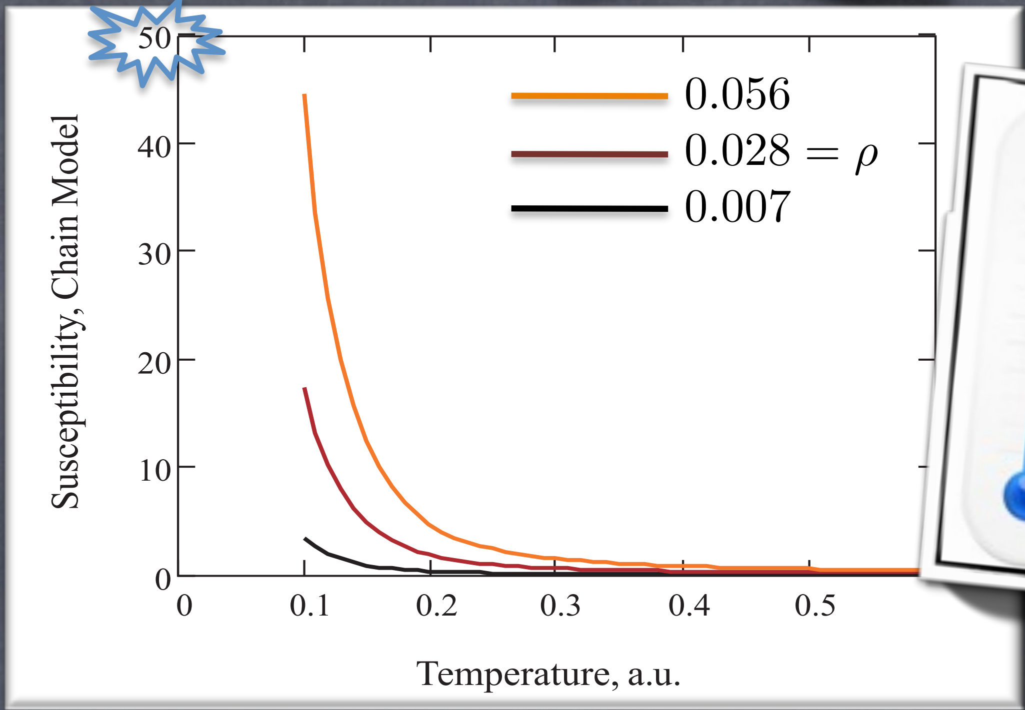
...CHAINS

Let us do some maths!

Susceptibility

...CHAINS!!!!

$H = H_{ext} + H_{eff} + Chains$



Difficult to deal with!

$$p(T,\phi) = \frac{1 + 2q(T)\phi - \sqrt{1 + 4q(T)\phi}}{2q(T)\phi}$$ Probability of forming a dimer (from DFT)

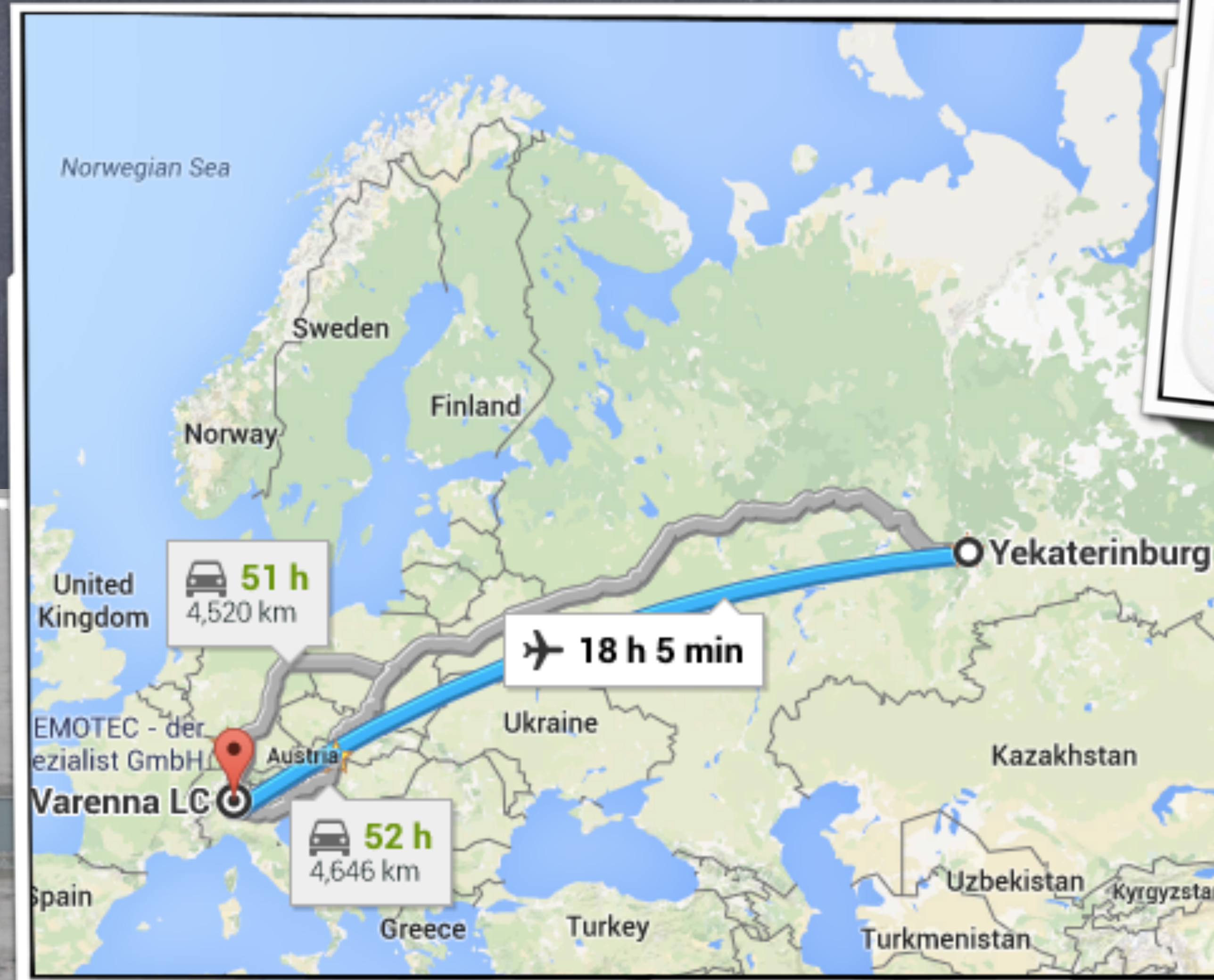
Dimer partition function $$q(T) = \int_{\text{Chains}} d\mathbf{\Omega} d\mathbf{r} \exp\left(-\frac{U_{\text{DD}}(1,2) + U_{\text{HS}}(1,2)}{k_B T}\right)$$

$$K(T) = \frac{1}{q(T)} \int_{\text{Chain}} d\mathbf{\Omega} d\mathbf{r} \cos\omega \exp\left(-\frac{U_{\text{DD}}(1,2) + U_{\text{HS}}(1,2)}{k_B T}\right)$$ Correlation coefficient

Susceptibility $$\chi_{\text{C}} = \chi_{\text{L}} \frac{1 + p(T,\rho)K(T)}{1 - p(T,\rho)K(T)} \left(1 + \frac{\chi_{\text{L}}}{3}\right)$$

M Klokkenburg et al., J.Phys: Cond. Matter, 2008.

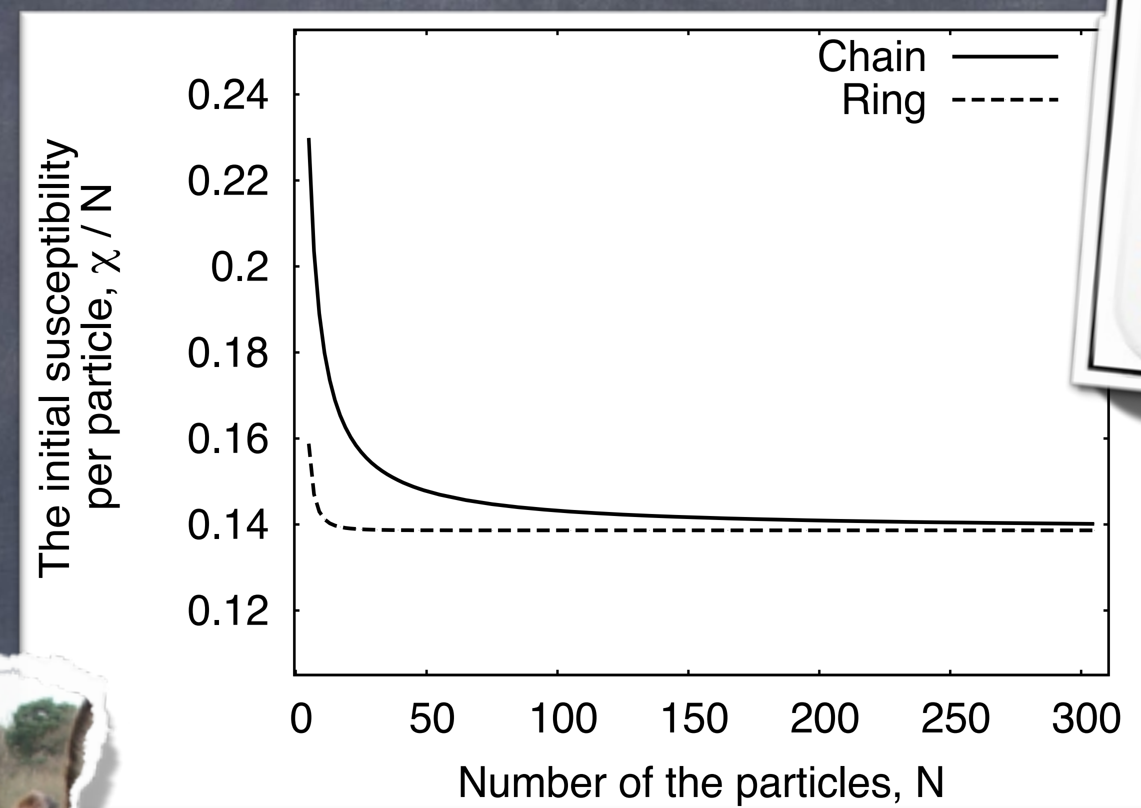
...Let us go colder!



Rings

Ground State

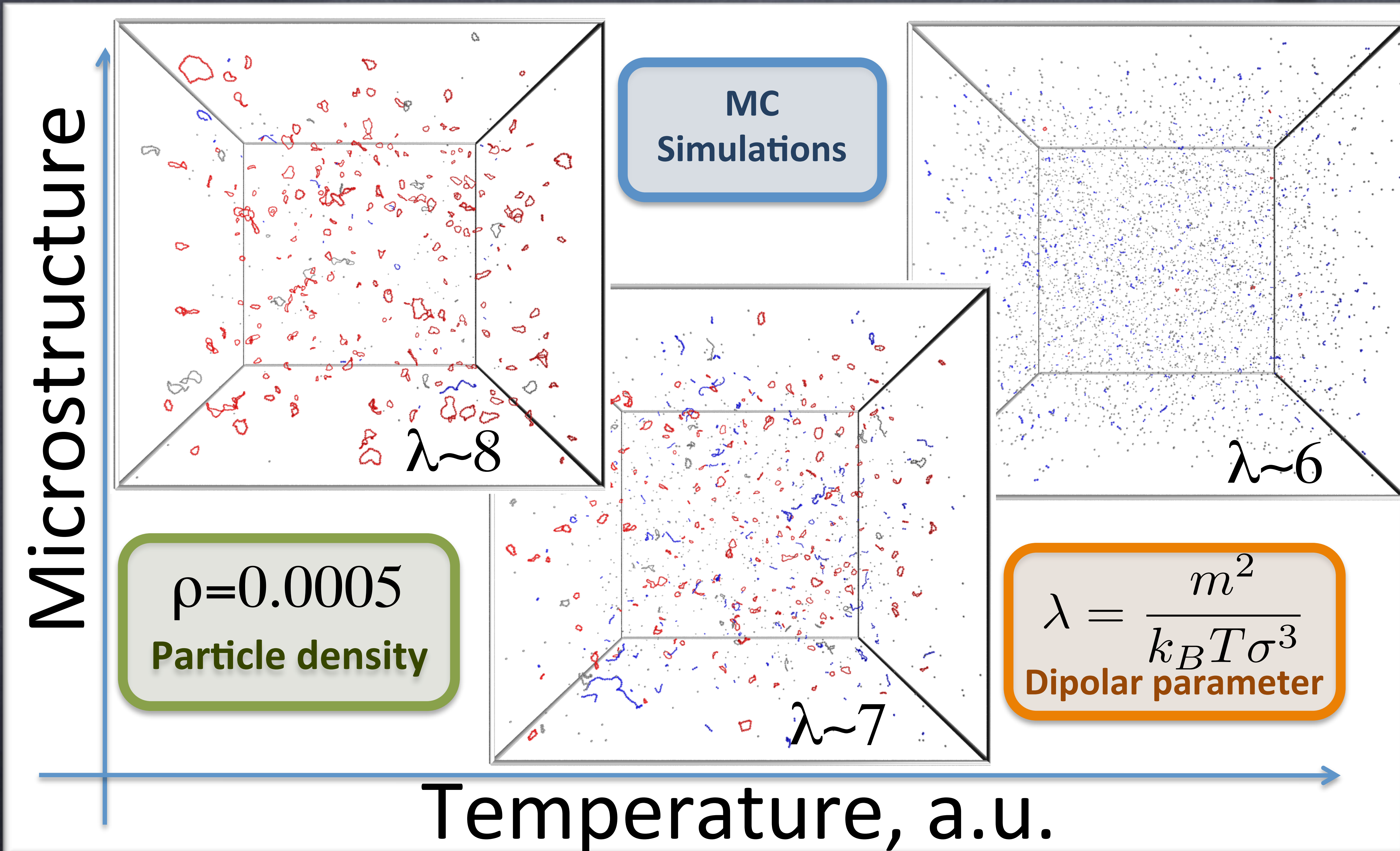
T=0



Also difficult to deal with!

T. Prokopyeva et al., PRE, 2012.

Gas Case



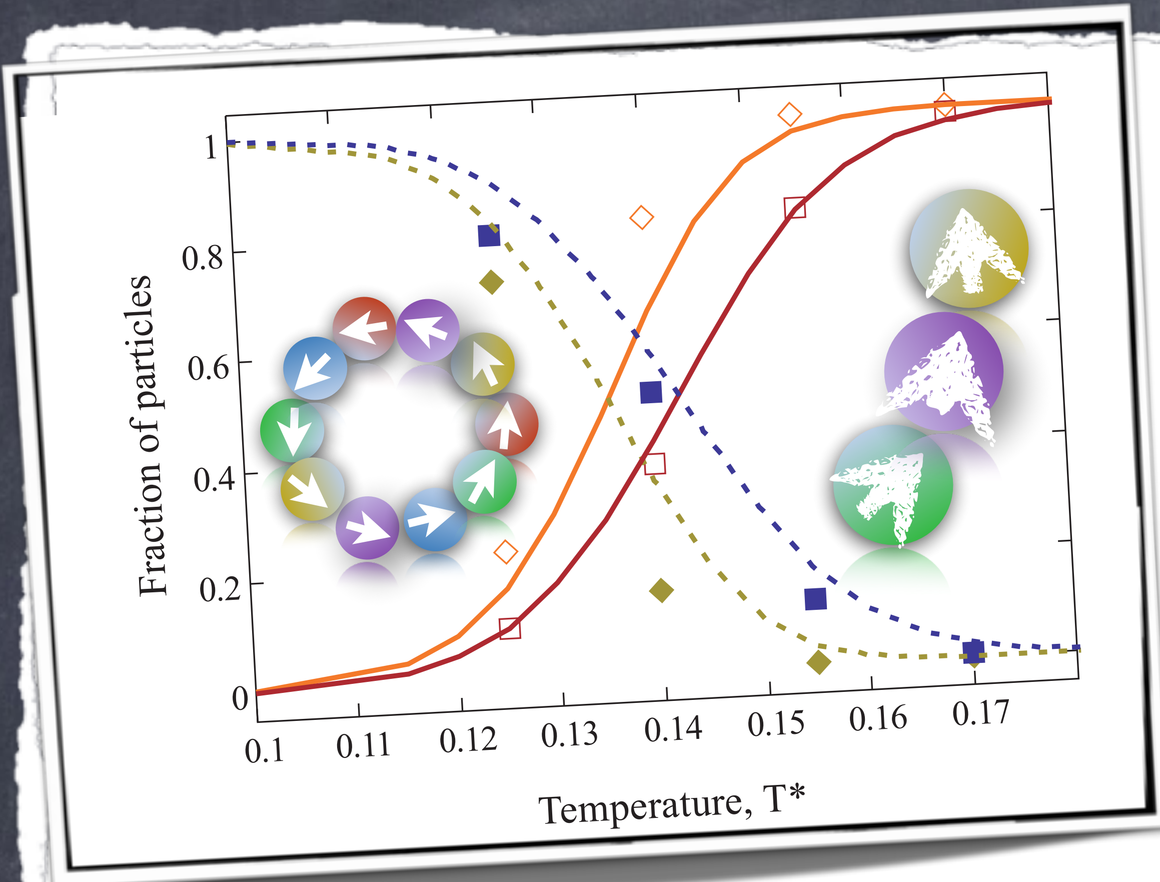
Snapshots provided by L. Rovigatti and F. Sciortino

Gas Case

Chains and Rings!

Really difficult to deal with!

Gas Case



$$\frac{F[\{g_n\},\{f_n\}]}{Vk_BT} = \sum_{n=1}^{\infty} g_n \ln\frac{g_n v}{eQ_n} + \sum_{n=5}^{\infty} f_n \ln\frac{f_n v}{eW_n}, \quad (1)$$

where g_n and f_n are the equilibrium volume fractions of chains and rings, respectively; Q_n and W_n denote the corresponding (normalized by V/v) partition functions of an n-particle chain and ring. The free-energy functional [Eq. (1)] has to be minimized with respect to the distributions $\{g_n\}$ and $\{f_n\}$ preserving φ,

$$\sum_{n=1}^{\infty} g_n n + \sum_{n=5}^{\infty} f_n n = \frac{\varphi}{v}. \quad (2)$$

$$Q_n(T^*) = q^{C(n)}; \qquad W_n(T^*) = Q_n(T^*)\frac{q^{R(n)-C(n)}}{n^{3\nu+1}}, \quad (3)$$

where

$$R(n) = \frac{n}{2}\sin^3\frac{\pi}{n}\left(\sum_{k=1}^{[(n-1)/2]}\frac{\cos^2(\frac{\pi k}{n})+1}{\sin^3(\frac{\pi k}{n})} + \mathrm{R}_{(n+1)/2}\right);$$
$$C(n) = \sum_{k=1}^{n}\frac{n-k}{k^3} \sim n\zeta(3) - \frac{\pi^2}{6}, \qquad (n \geq 4), \quad (4)$$

with $\zeta(3)$ denoting the Riemann zeta function of three; $\mathrm{R}_{(n+1)/2}$ stands for the residual of division, and $[\cdot]$ has the meaning of the integer part of the expression in the brackets. The low-T dimer partition function q (note that $C(2) = 1$ and hence $Q_2(T^*) = q$), derived first by de Gennes and Pincus, is

$$q(T^*) = \frac{T^{*3}}{3}\exp\left(\frac{2}{T^*}\right). \quad (5)$$

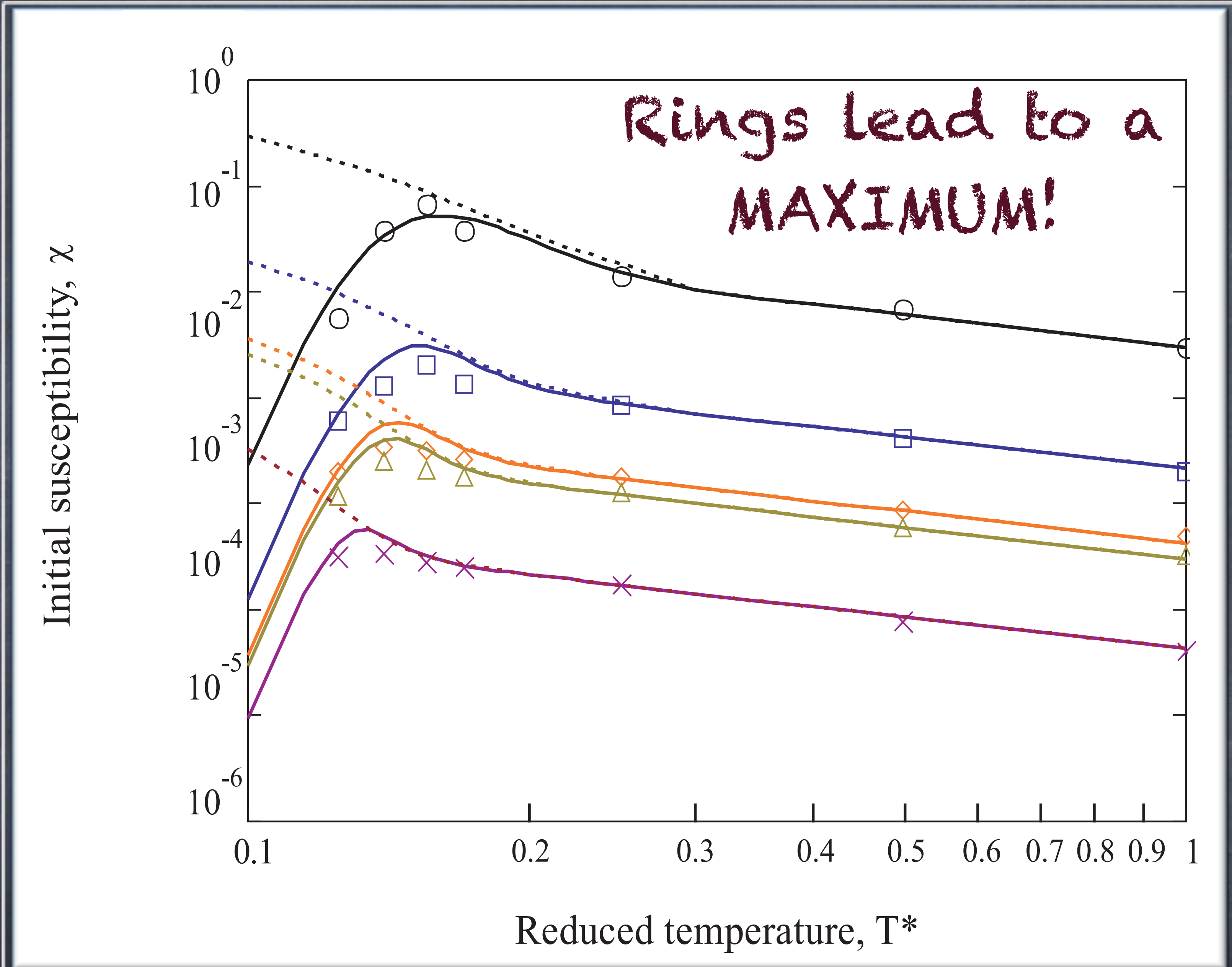
In Eq. (3), $\nu = 0.588$ is the self-avoiding random walk exponent. The term $1/n^{3\nu+1}$ in $W_n(T^*)$ captures the difference in entropy between chains and rings arising from the n ways of opening a ring to form a chain; the difference between the numbers of self-avoiding paths of chains and rings is proportional to $n^{3\nu}$. Finally, minimizing Eq. (1), one obtains compact expressions for g_n and f_n,

$$g_n = \frac{1}{v}Q_n p^n, \qquad f_n = \frac{1}{v}W_n p^n. \quad (6)$$

Here, p, the Lagrange multiplier to be found from Eq. (2), has the meaning of activity.

S.K. , A. Ivanov, L. Rovigatti, J.M. Tavares, F. Sciortino, PRL 2013

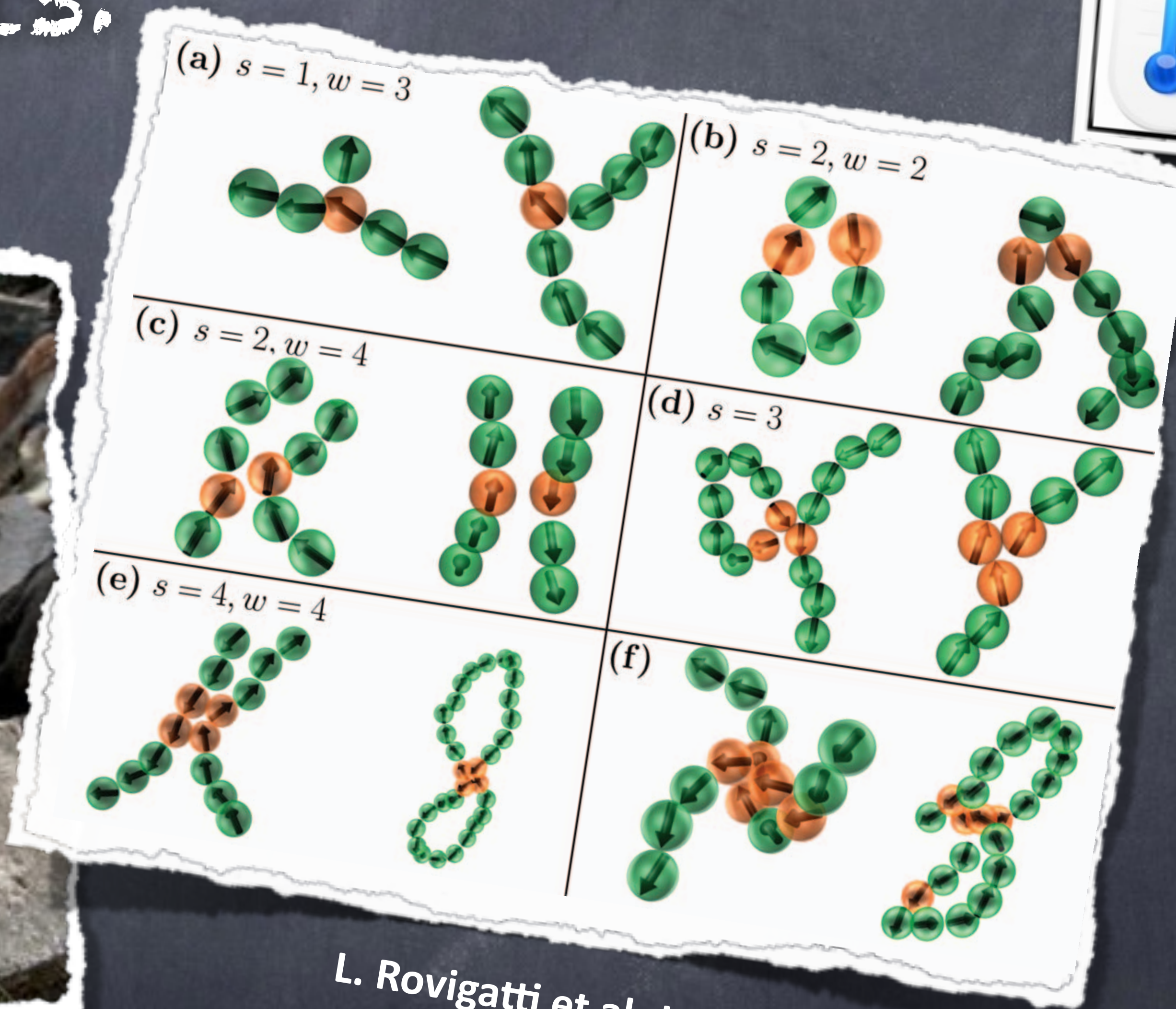
Gas Phase



S.K. , A. Ivanov, L. Rovigatti, J.M. Tavares, F. Sciortino, PRL 2013

Getting denser

Chains, Rings and various defects!

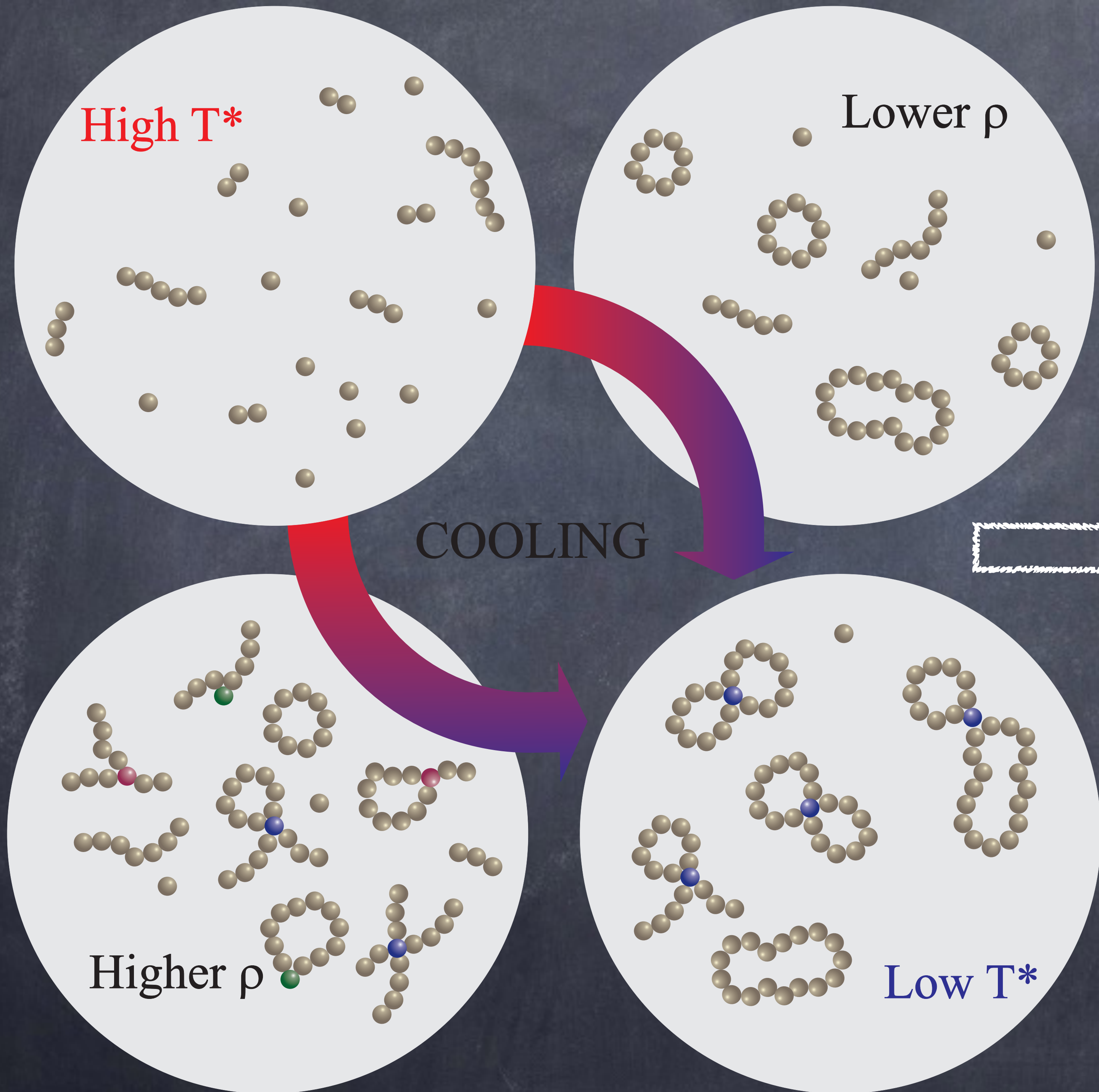


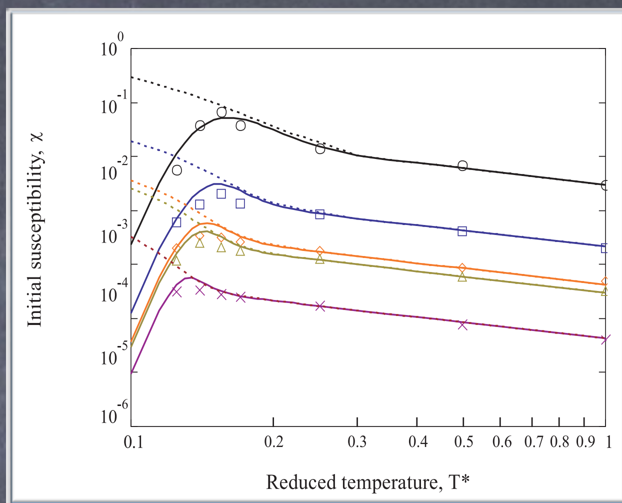
L. Rovigatti et al. J.Chem. Phys. 2013

(...)* difficult to deal with!

*Really-really, for instance

Summary: DHS as we know them



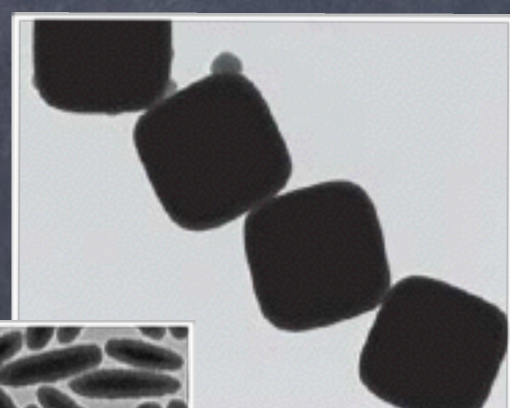


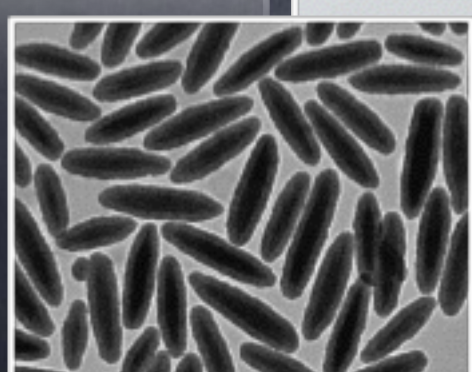
SK, L. Rovigatti, J.M. Tavares, A. Ivanov, F. Sciortino, PCCP, 2015

Away from dipolar hard spheres!

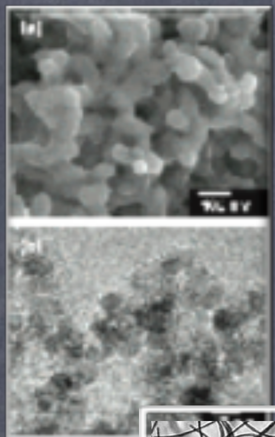
Particle

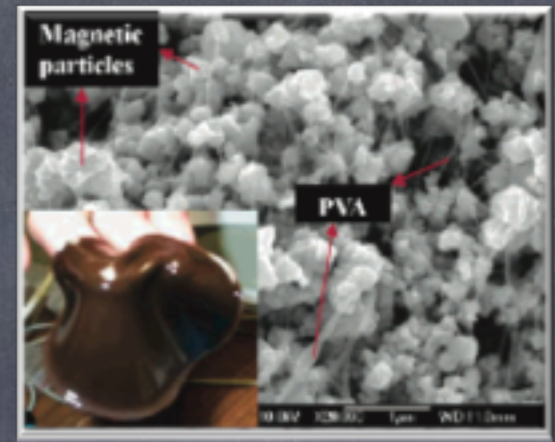
Carrier

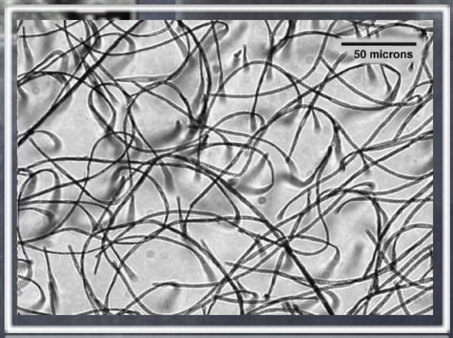




L. Baraban et al.
L. Rossi et al.
P. Binder et al.







Shang-Hsiu Hu et al.
C. Goubault et al.

How to model the change of the carrier?

Common:

$$U_{dd}(\vec{r}_{ij};\vec{\mu}_i,\vec{\mu}_j) = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r^3} - \frac{3\,[\vec{\mu}_i \cdot \vec{r}_{ij}]\,[\vec{\mu}_j \cdot \vec{r}_{ij}]}{r^5}, \quad U_{\mathrm{LJ}}(r) = 4\epsilon_s[(\sigma/r)^{12} - (\sigma/r)^6],$$

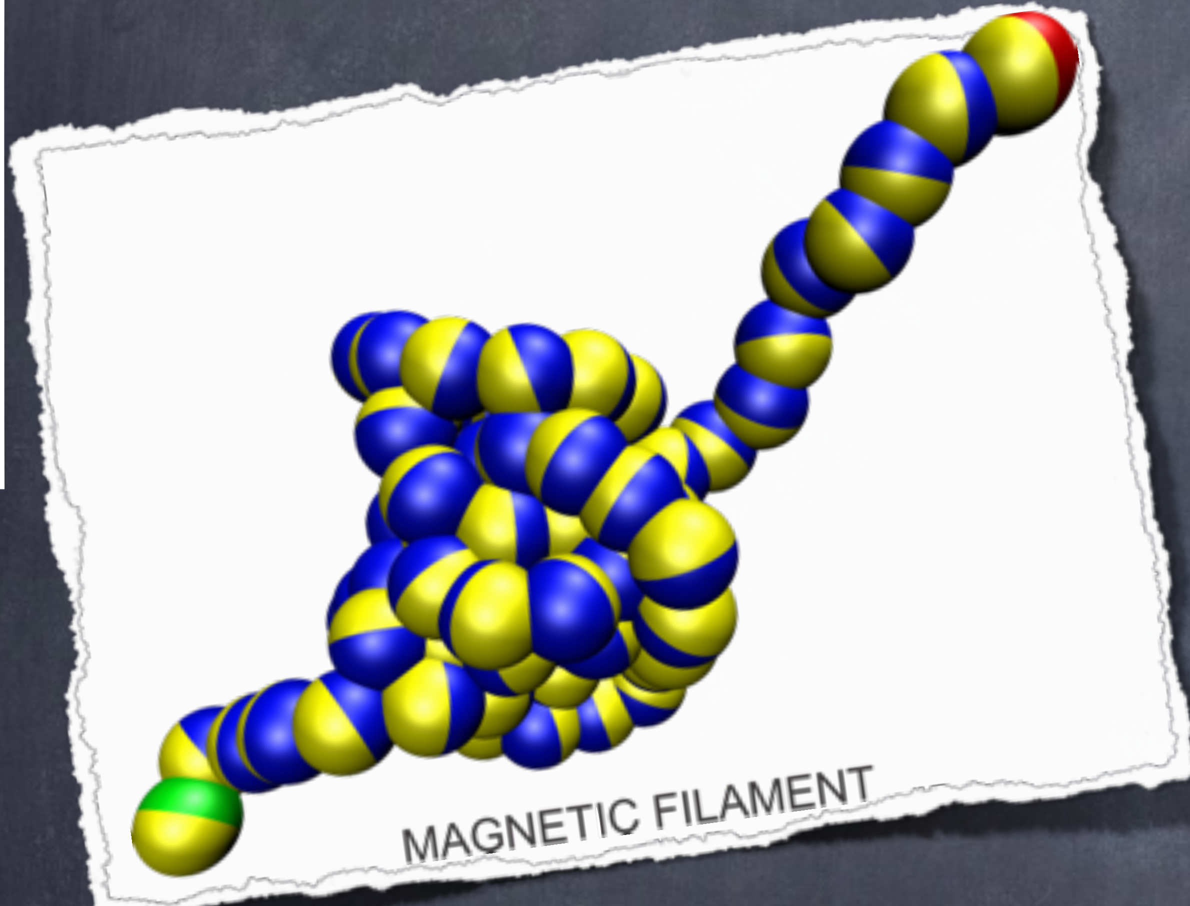
$$U_{\mathrm{WCA}}(r) = \begin{cases} U_{\mathrm{LJ}}(r) - U_{\mathrm{LJ}}(r_{cut}), & r < r_{\mathrm{cut}} \\ 0, & r \geq r_{\mathrm{cut}} \end{cases}$$

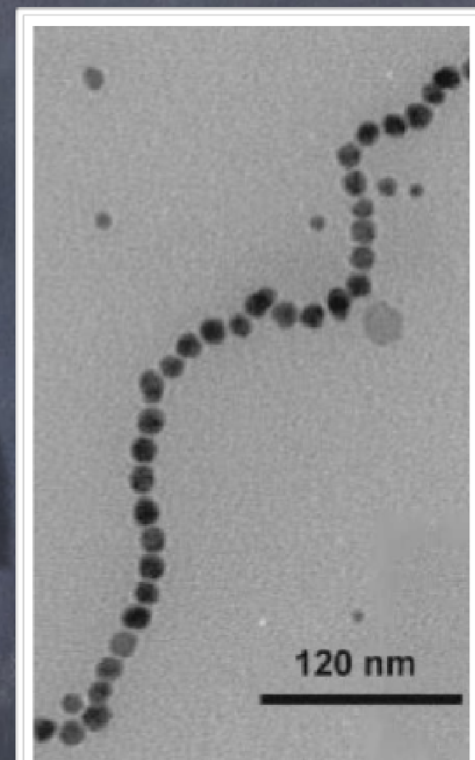
+

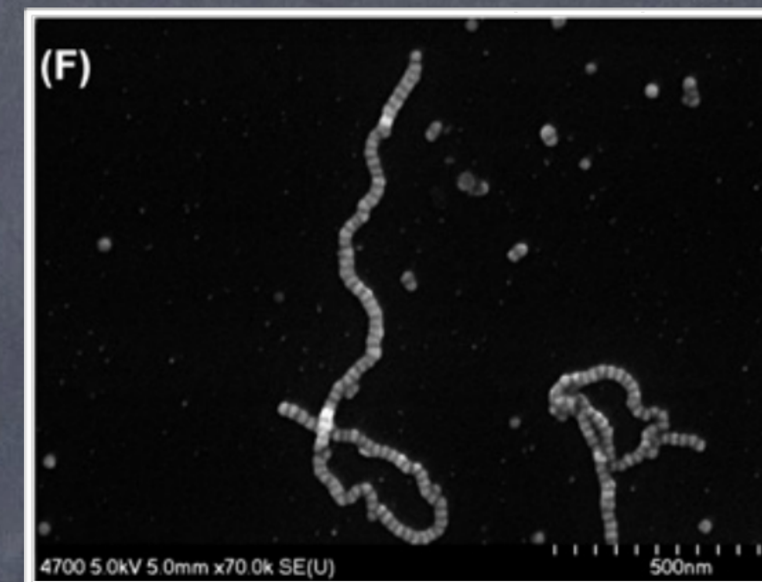
additional bonds/cross-linkers/
hydrodynamics

Carrier

Magnetic Filaments: "simple bonds"

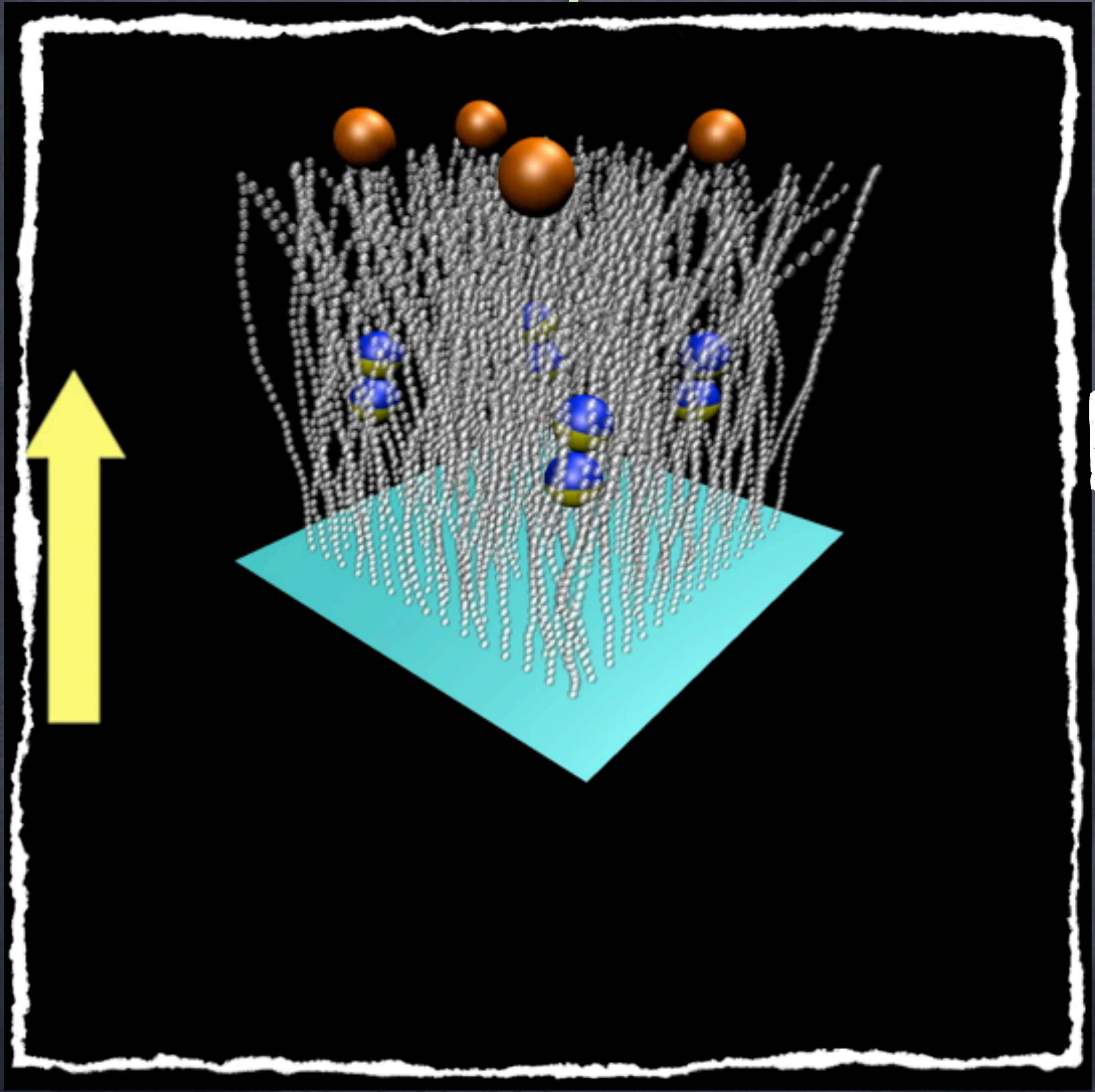






J.J. Benkoski et al, J. Polym. Sci. B 46, 2267 (2008);
J.J. Benkoski et al, Soft Matter 6, 602, (2010);
P. Sanchez et al, Soft Matter, 11, 2963 (2015).

Filaments: possibilities

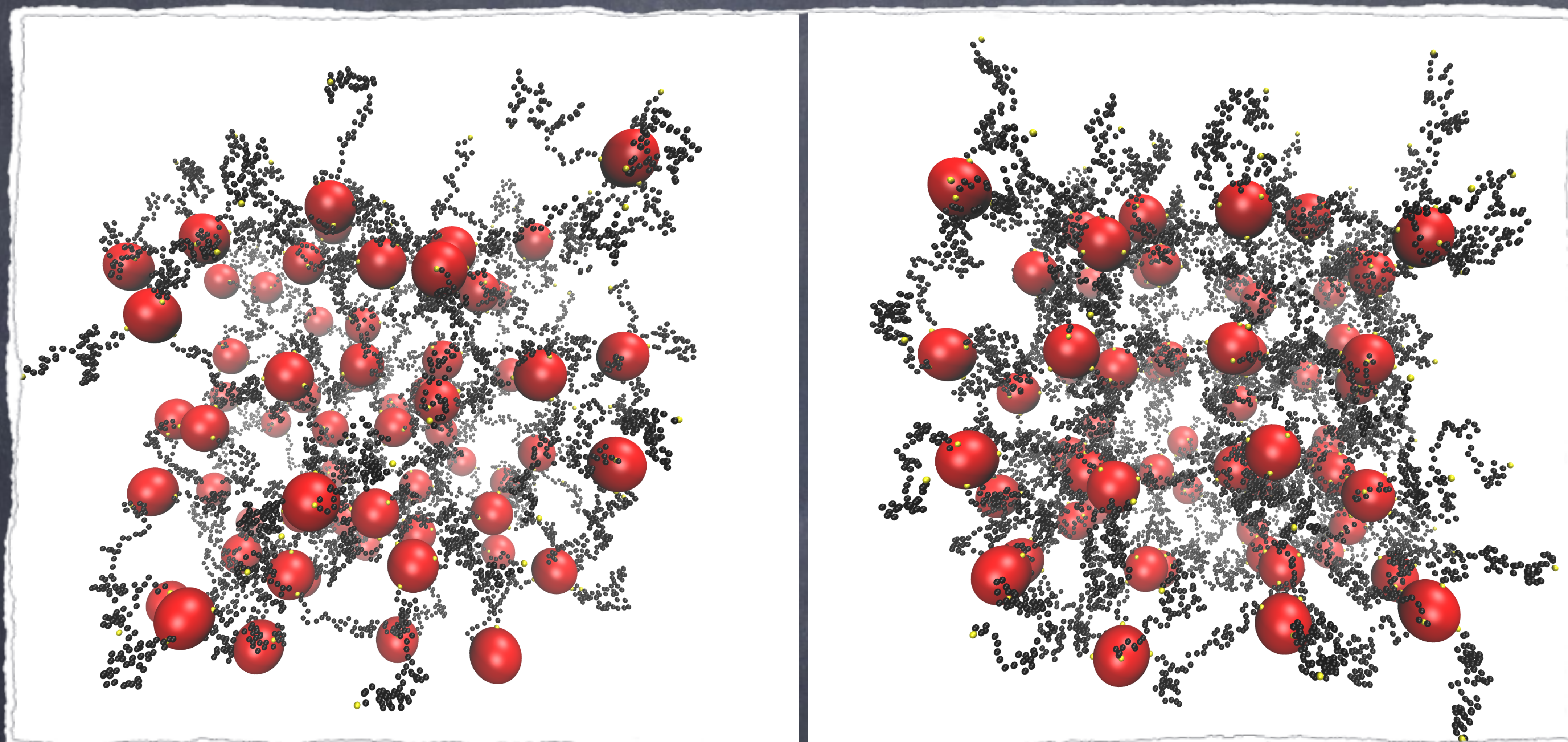


prebuilt chains increase the susceptibility

P. Sanchez et al, Soft Matter, 11, 2963 (2015).

Carrier

Magnetic Gels: linking matrix

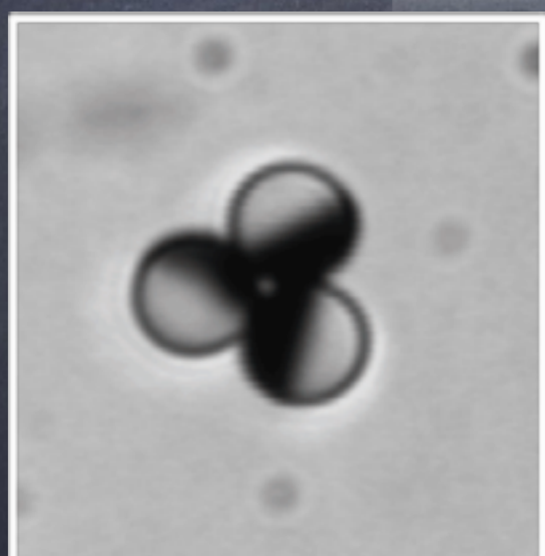


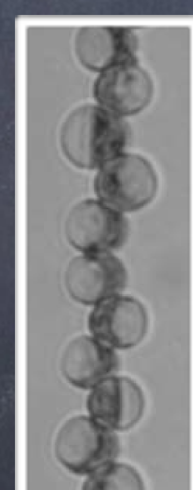
Magnetoelastic coupling

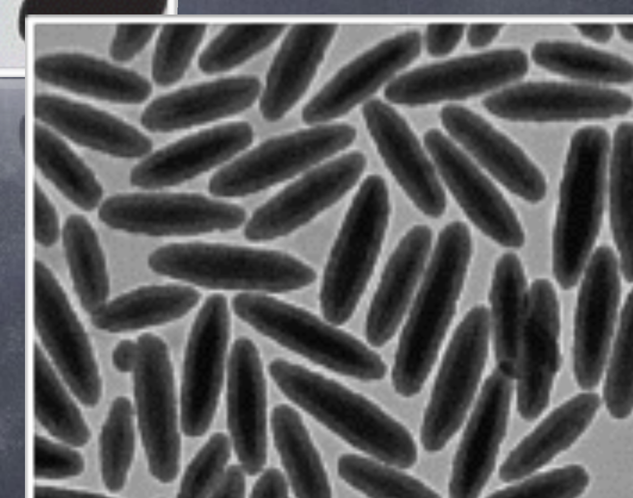
R Weeber et al, Soft Matter, (2012).

Particle

Anisotropy Anisometry



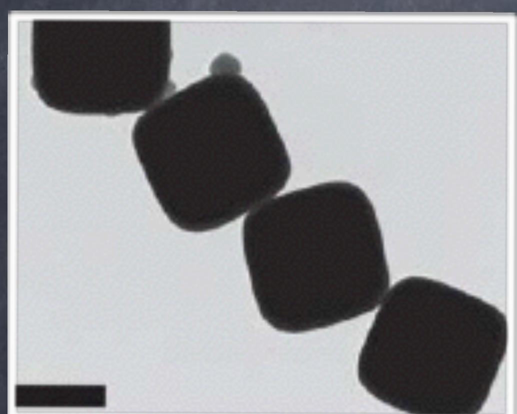


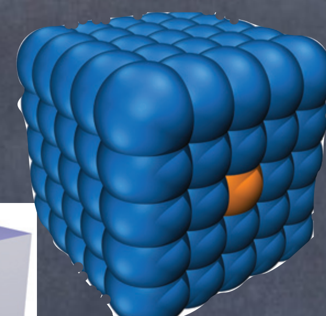


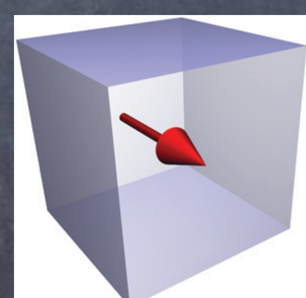
L. Baraban et al., L. Rossi et al., P. Binder et al., Smoukov et al., Jeong et al.

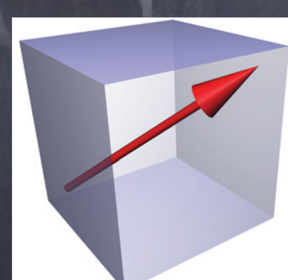
Anisometry:

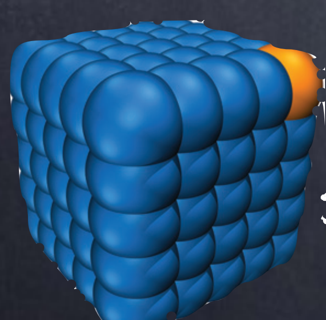
Magnetic Cubes VS Ellipsoids



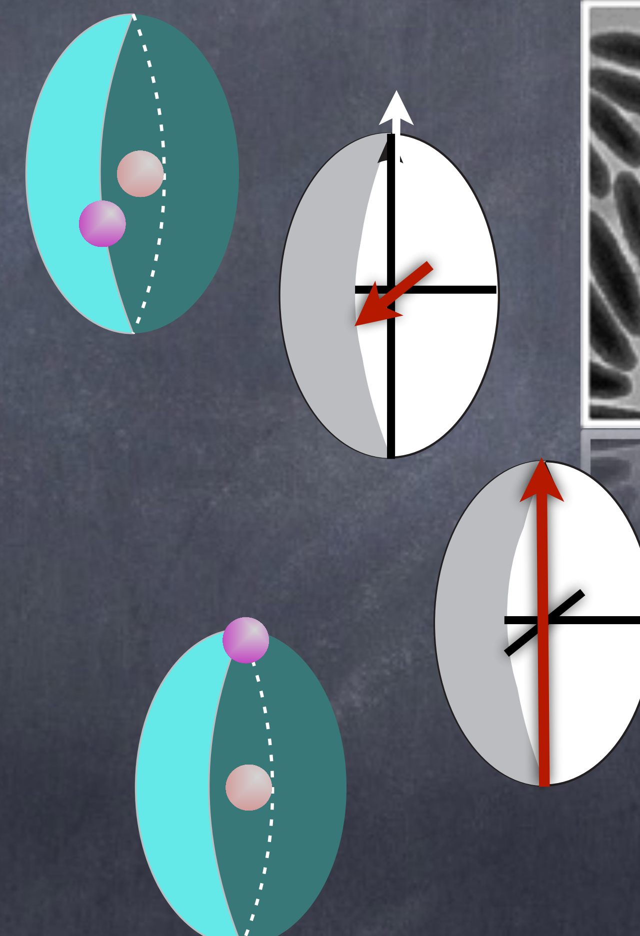


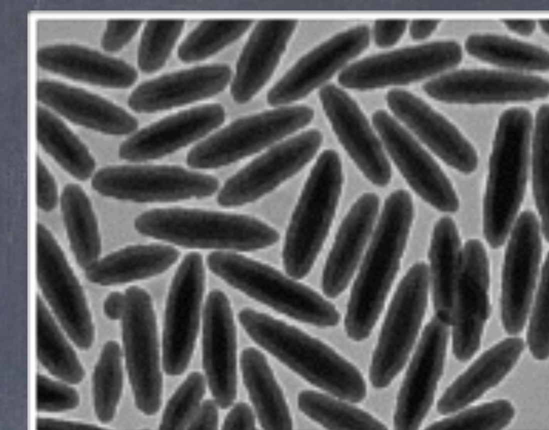






J. G Donaldson and S.K, Nanoscale, 2015, 7, 3217





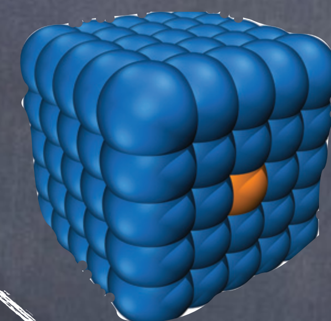
SK, Pyanzina, Sciortino, Soft Matter, 2013;
Donaldson, Novak, Pyanzina, SK, JMMM, 2015

How to model the change of the particle shape?

$$U_d(ij) = -\frac{\mu_0}{4\pi}\left[3\frac{(\mathbf{m}_i\cdot\mathbf{r}_{ij})(\mathbf{m}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i\cdot\mathbf{m}_j)}{r_{ij}^3}\right],$$

+

modified steric potential
(known or combined)

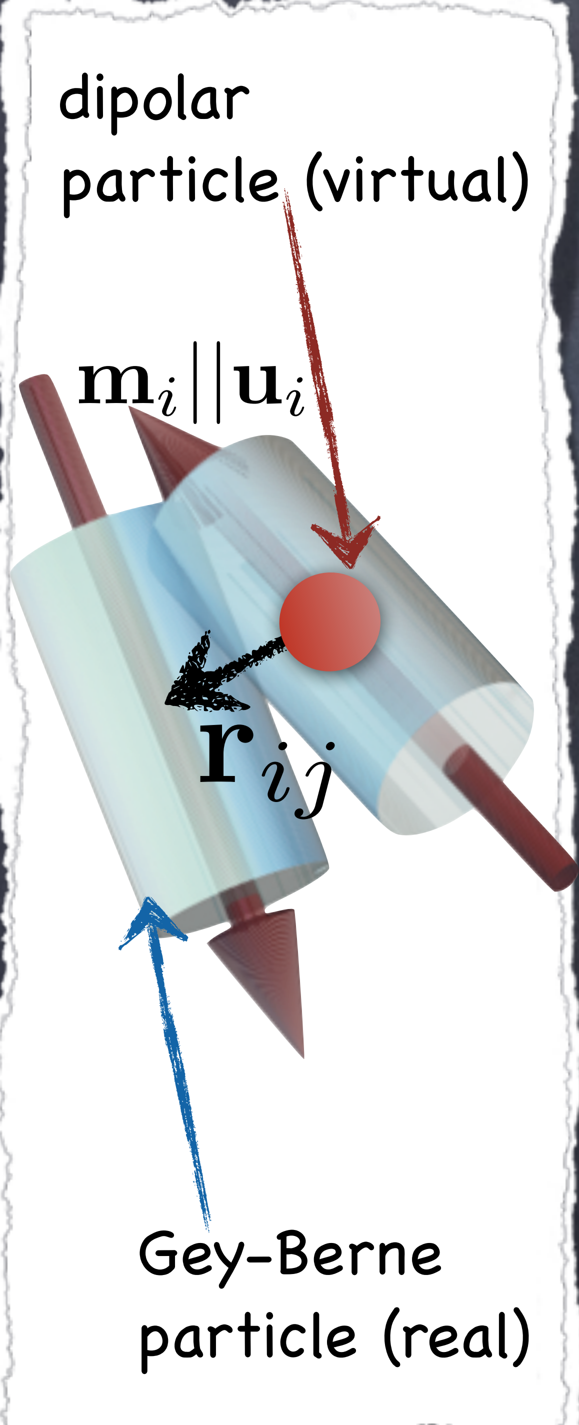


About Cubes:

ask

Joe Donaldson

Magnetic Ellipsoids: Methods



$$U_d(ij) = -\frac{\mu_0}{4\pi}\left[3\frac{(\mathbf{m}_i\cdot\mathbf{r}_{ij})(\mathbf{m}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i\cdot\mathbf{m}_j)}{r_{ij}^3}\right],$$

$$U_{GB}(\mathbf{u}_i,\mathbf{u}_j,\mathbf{r}_{ij}) = \begin{cases} 4\varepsilon(\cdot)\left[\mathrm{A}^{12}(\cdot) - \mathrm{A}^6(\cdot)\right] + \varepsilon(\cdot), & r_{ij} \le r_c \\ 0, & r_{ij} > r_c, \end{cases}$$

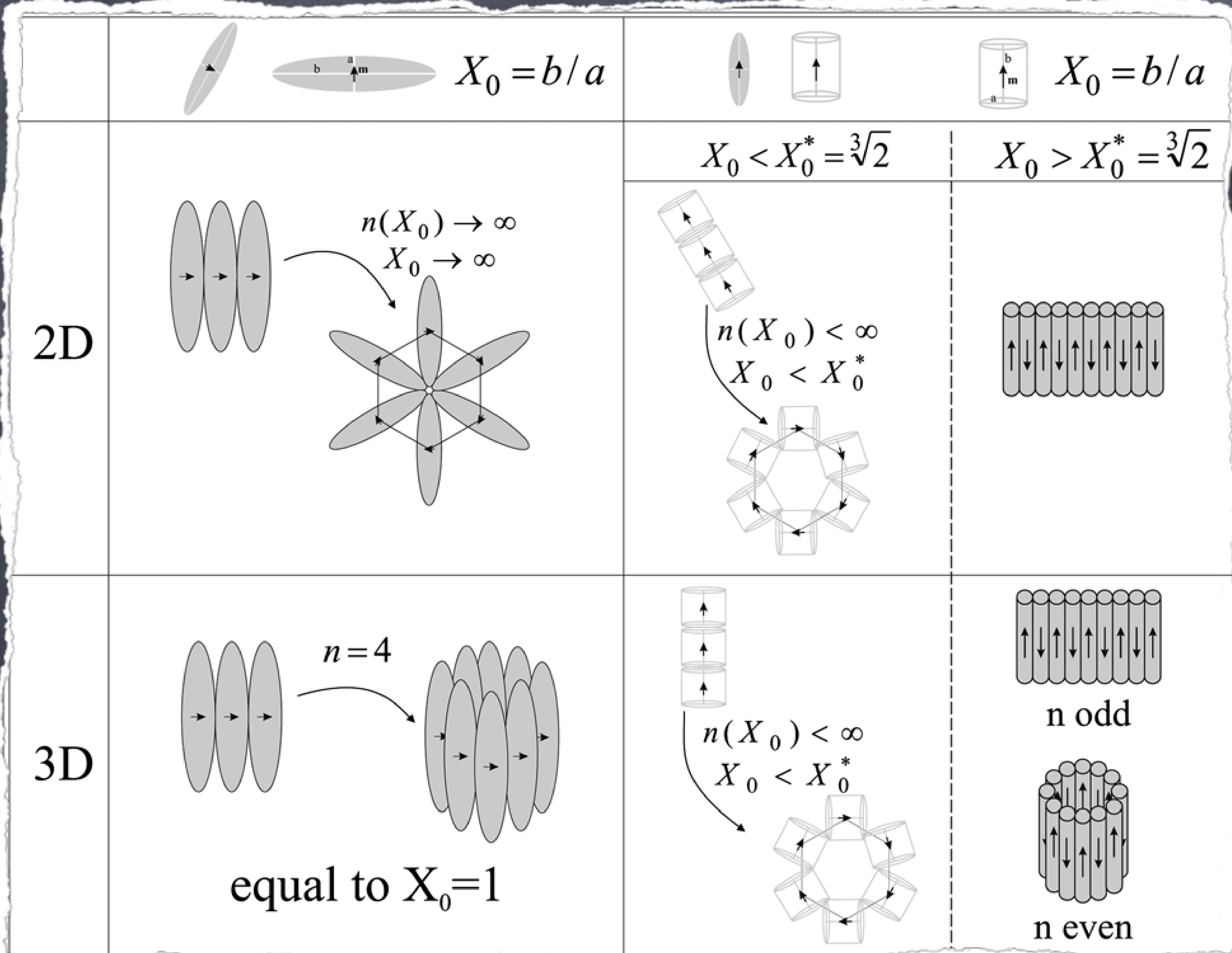
$$\mathrm{A}(\cdot) \equiv \mathrm{A}(\mathbf{u}_i,\mathbf{u}_j,\hat{\mathbf{r}}_{ij}) = \sigma_0/(r_{ij} - \sigma(\mathbf{u}_i,\mathbf{u}_j,\hat{\mathbf{r}}_{ij}) + \sigma_0),$$

$$\sigma(\mathbf{u}_i,\mathbf{u}_j,\hat{\mathbf{r}}_{ij}) = \sigma_0\left[1 - \frac{\chi(X_0)}{2}\times\right.$$
$$\left.\times\left\{\frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i+\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1+\chi(X_0)\;\mathbf{u}_i\cdot\mathbf{u}_j} + \frac{(\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_i-\hat{\mathbf{r}}_{ij}\cdot\mathbf{u}_j)^2}{1-\chi(X_0)\;\mathbf{u}_i\cdot\mathbf{u}_j}\right\}\right]^{-\frac{1}{2}};$$

Here, $\hat{\mathbf{r}} = \mathbf{r}_{ij}/r_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ is the unit vector, coaligned with the vector connecting particle centres, $\mathbf{u}_{i(j)}$ is the unit vector along the b-axis of the particle, $\sigma_0 = 2\sqrt{2}a$, ε_0 denotes the energy parameter, and $\chi(X_0) = [X_0^2 - 1]/[X_0^2 + 1]$. The critical value r_c equals to $(2^{1/6} - 1)\sigma_0 + \sigma(\mathbf{u}_i,\mathbf{u}_j,\hat{\mathbf{r}}_{ij})$.

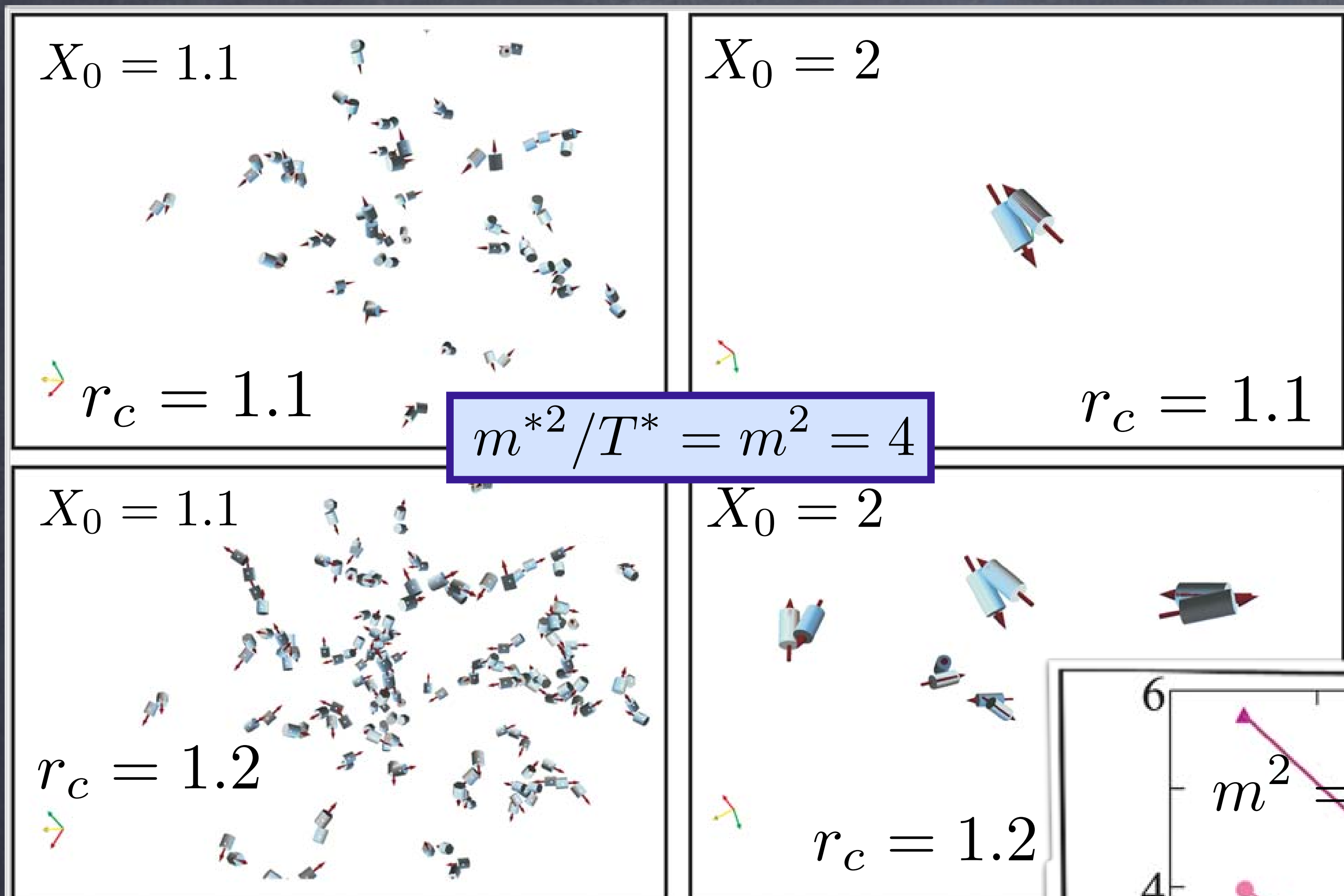
MD Simulations + Analytical Calculations

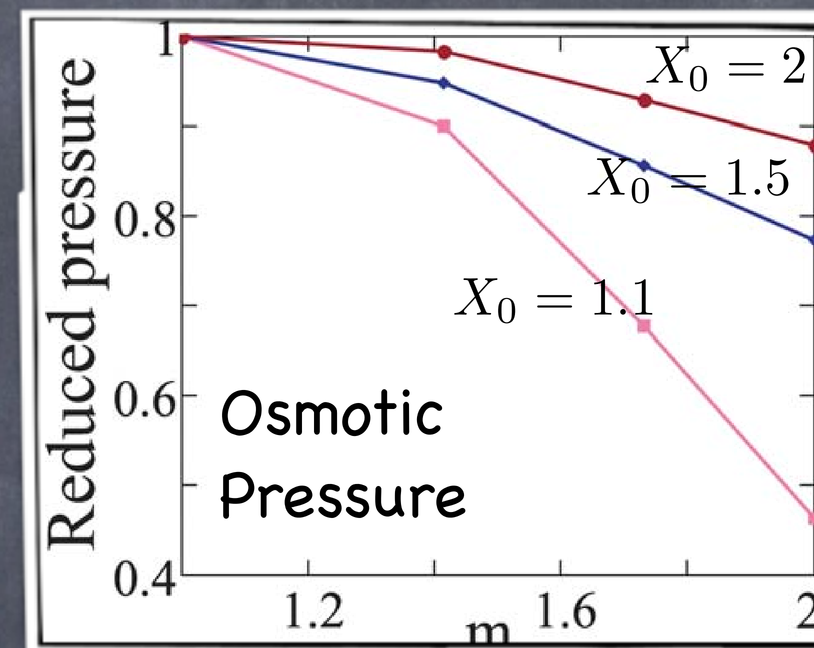
Magnetic Ellipsoids: Ground States

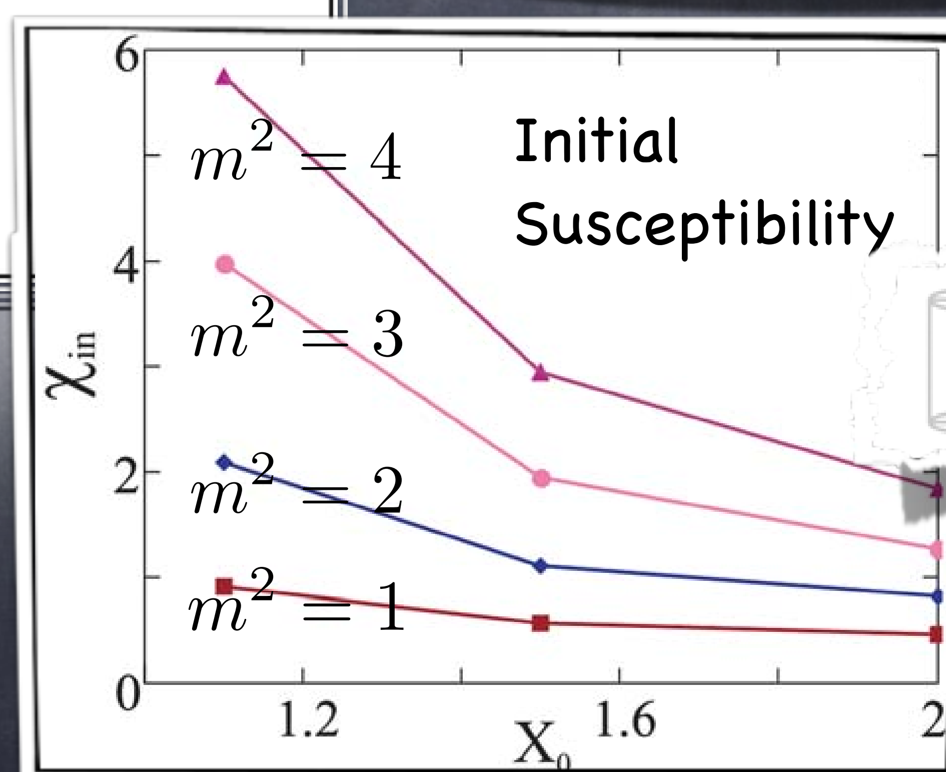


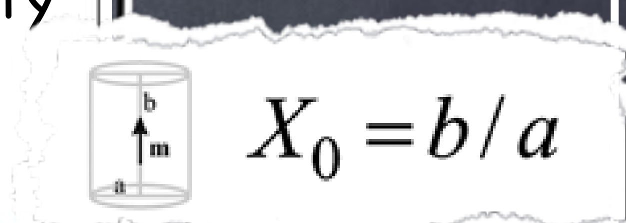
SK, Pyanzina, Sciortino, Soft Matter, 2013

Magnetic Ellipsoids: Temperature up!





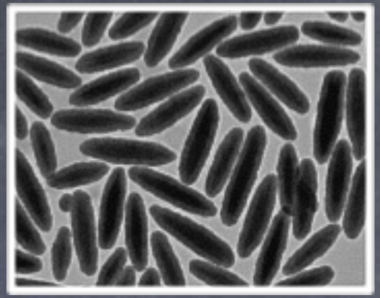




energy+distance (r_c) criteria for the cluster analysis;

only clusters shown

Ellipsoids

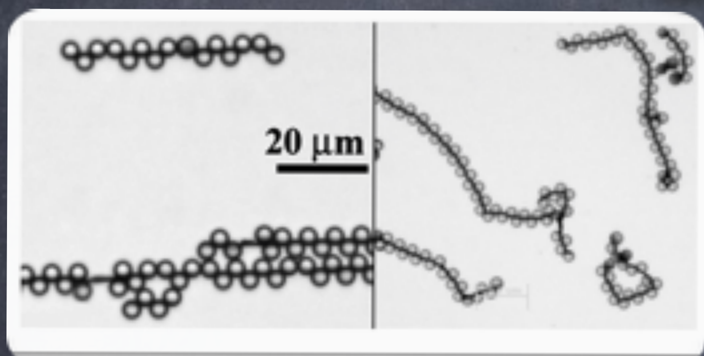


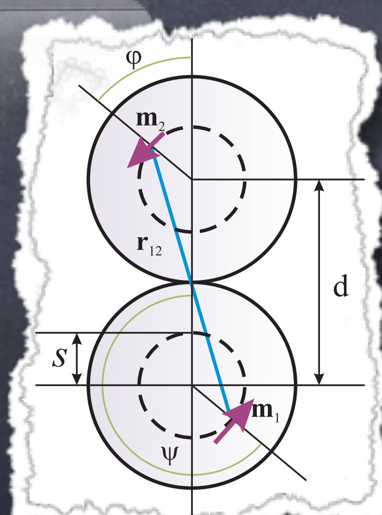
- Antiparallel pair is formed for the ellipsoids with the dipole along the long axes
- All ground state structures of ellipsoids have a vanishing total dipole moment
- The susceptibility decreases with the elongation

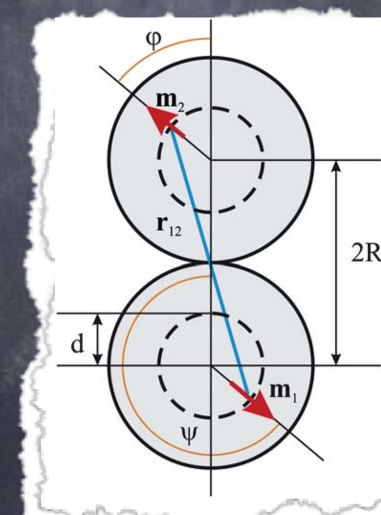
Do not make particles elongated, if you want a magnetically responsive system

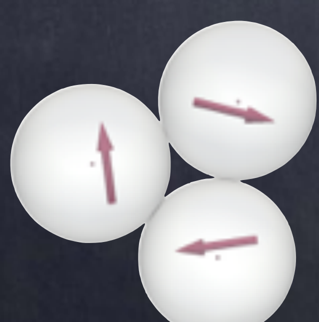
Anisotropy:

Magnetic Janus Particles (MJP) vs Capped Colloids (CC)









* no beer advertisement/propaganda

See also: Aleksey Ruditskiy et al, Soft Matter, 2013

How to model the particle structure?

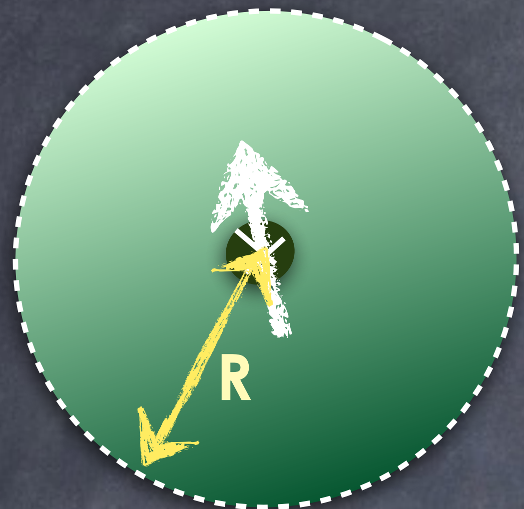
$$U_{\mathrm{LJ}}(r) = 4\epsilon_s[(\sigma/r)^{12} - (\sigma/r)^6],$$

$$U_{\mathrm{WCA}}(r) = \begin{cases} U_{\mathrm{LJ}}(r) - U_{\mathrm{LJ}}(r_{cut}), & r < r_{\mathrm{cut}} \\ 0, & r \geq r_{\mathrm{cut}} \end{cases}$$

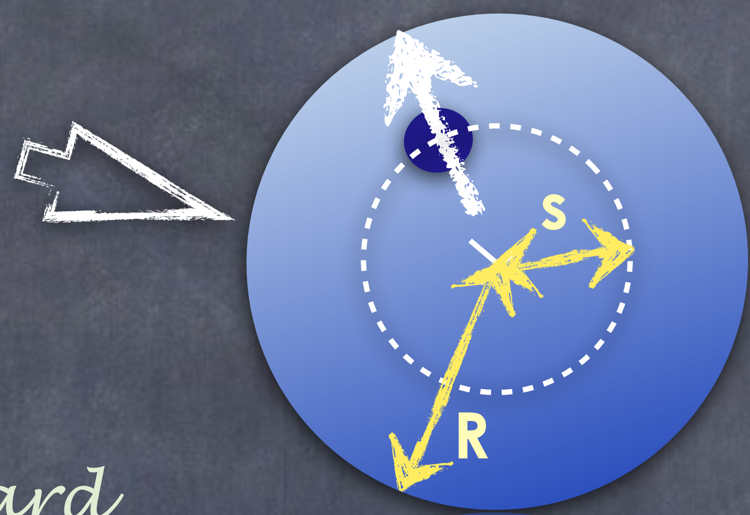
+

modified magnetic interaction
(known or combined)

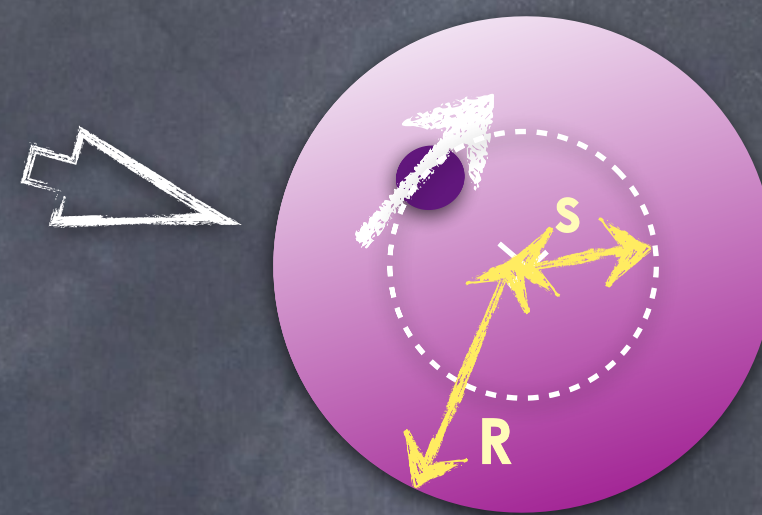
Anisotropy: Simplest Approach



"Regular" soft/hard sphere with the central dipole



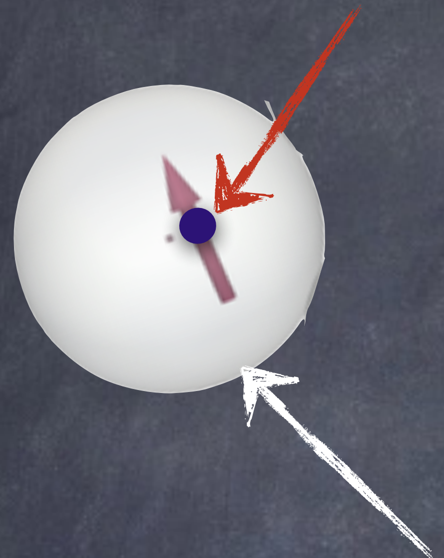
SD-particle: soft/hard sphere with the dipole shifted outwards radially



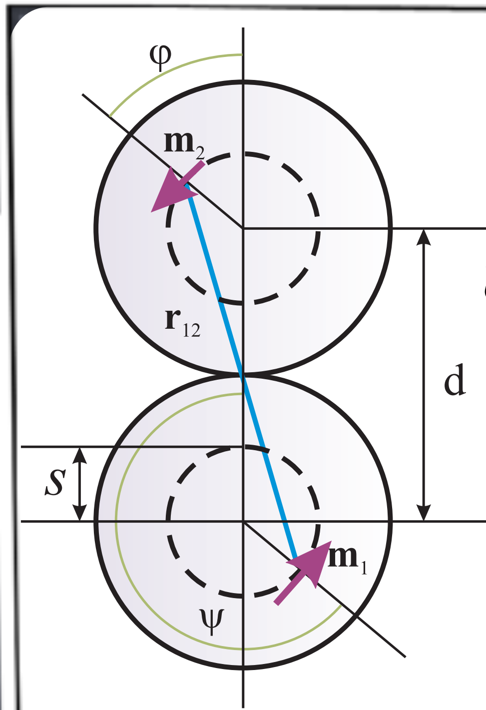
Janus-like particle: soft/hard sphere with the dipole shifted outwards, pointing perpendicular to the radius

MJP: Model

virtual site with the dipole



real soft/hard sphere



$$x = \sin\left[(\psi - \phi)/2\right] \quad y = \sin\left[(\psi + \phi)/2\right]$$

$$U^J_{dd}(s, x, y) = \frac{s^2x^4 - 2sx^3y + (s^2+1)\,x^2 - 2sxy + 3y^2 - 2}{(s^2x^2 - 2sxy + 1)^{5/2}}$$

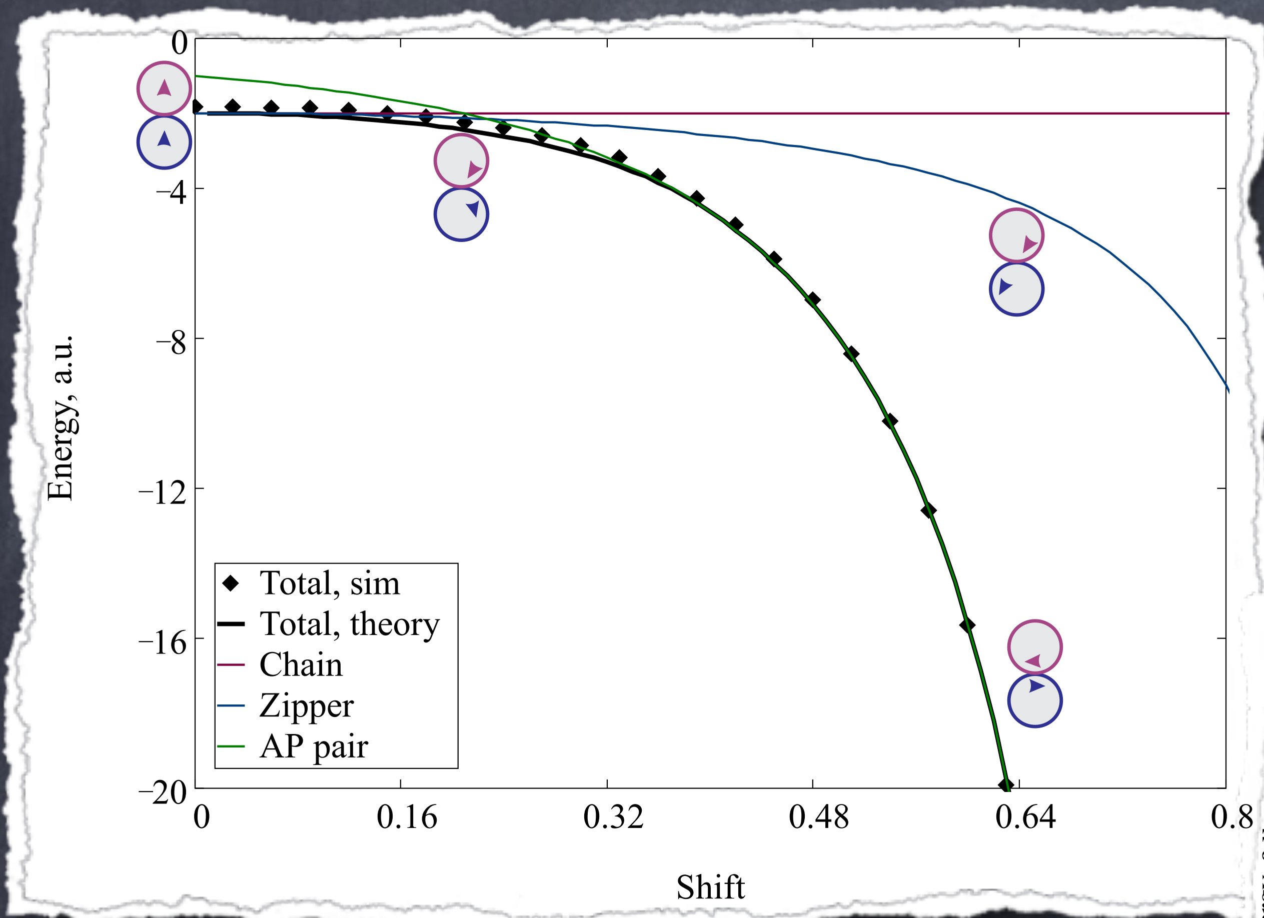
$$U_{\mathrm{WCA}}(r) = $$

$$= \begin{cases} U_{\mathrm{LJ}}(r) - U_{\mathrm{LJ}}(r_{cut}), & r < r_{\mathrm{cut}} \\ 0, & r \geq r_{\mathrm{cut}} \end{cases} .$$

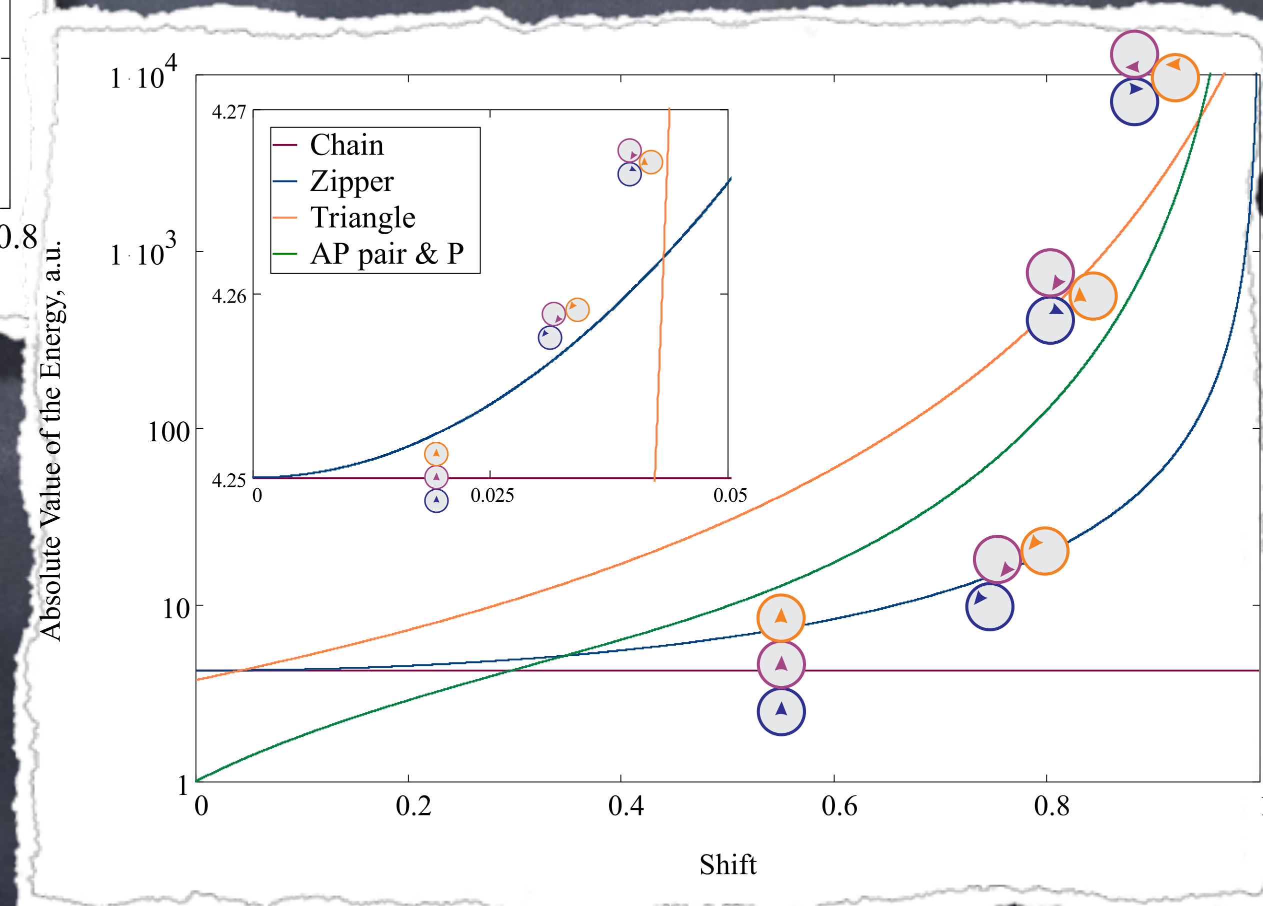
$$U_{\mathrm{LJ}}(r) = 4\epsilon_s[(\sigma/r)^{12} - (\sigma/r)^6],$$

Molecular Dynamics Simulations
(with parallel tempering)
+
Analytical Calculations

MJP: Ground States



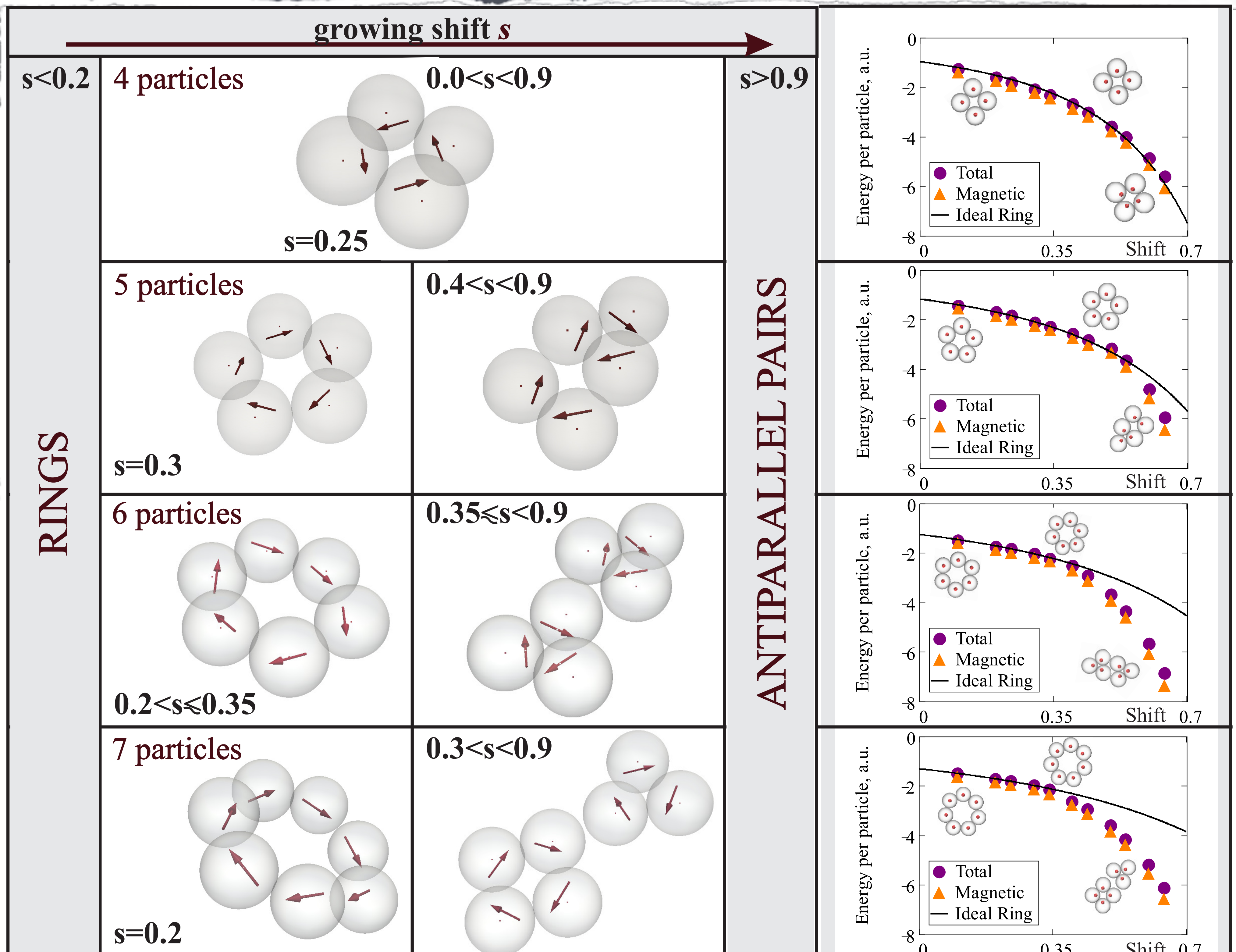
Antiparallel pairs win!
M=0



Zipper exists, but only for a small range of shifts!

E.Novak, E.Pyanzina, SK, JP:CM, 2015

MJP: Ground States



E.Novak, E.Pyanzina, SK, JP:CM, 2015

MJP: Temperature up!

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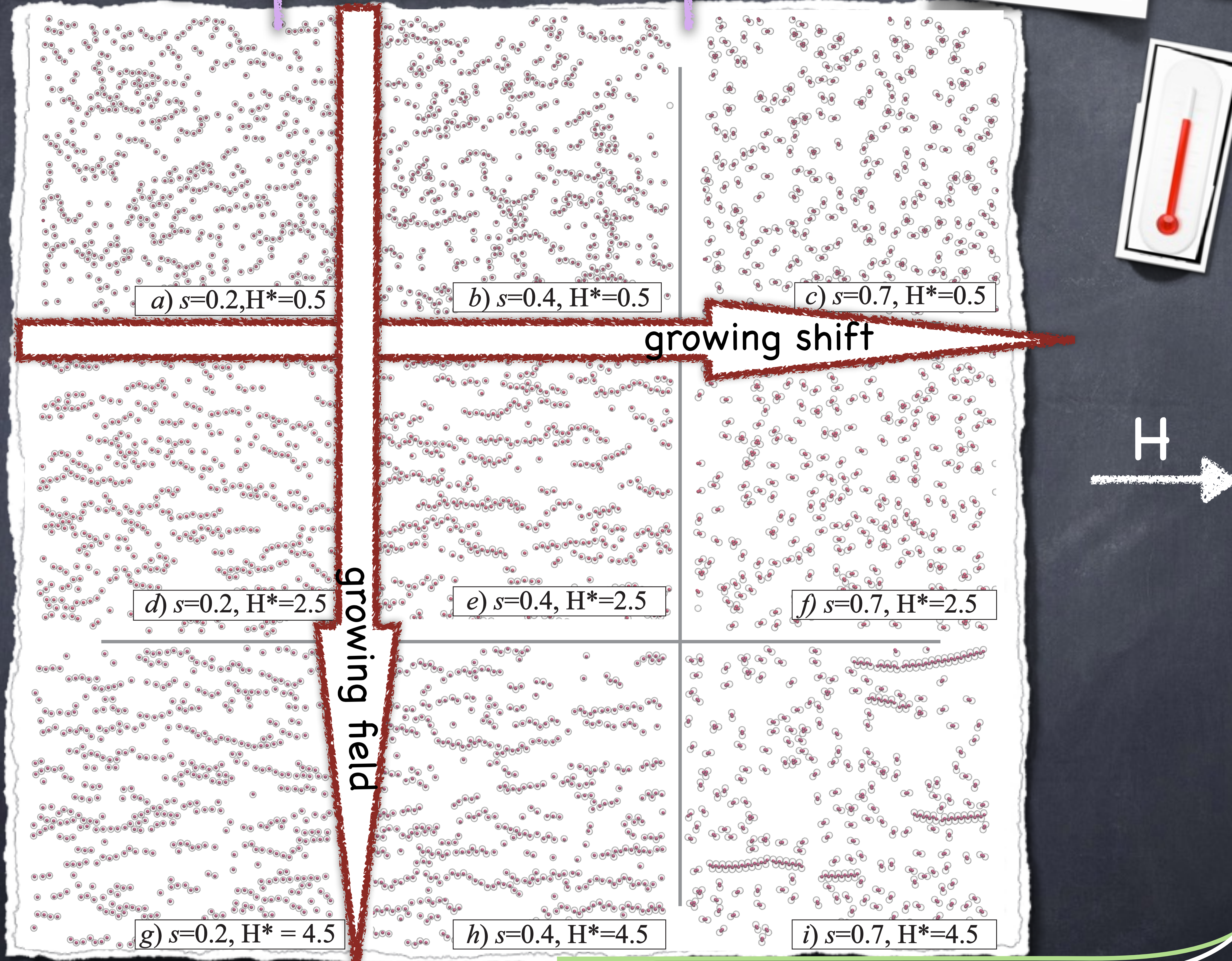
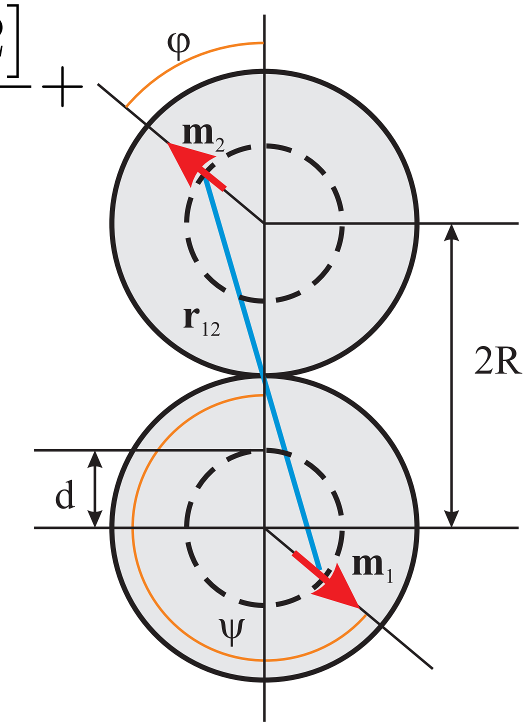


CC: Model

$$U_{dd}(\varphi,\psi,s) = \frac{s^2\cos^2(\psi-\varphi) - 2\cos(\psi-\varphi)\left[2s^2 - s\left(\cos\psi - \cos\varphi\right) - 2\right]}{\left(2s^2\left(1-\cos(\psi-\varphi)\right) + 4 + 4s\left(\cos\varphi - \cos\psi\right)\right)^{5/2}} +$$

$$+\frac{-6\left[s(\cos\psi - \cos\varphi) + 2\cos\varphi\cos\psi\right] + 3s^2}{\left(2s^2\left(1-\cos(\psi-\varphi)\right) + 4 + 4s\left(\cos\varphi - \cos\psi\right)\right)^{5/2}}.$$

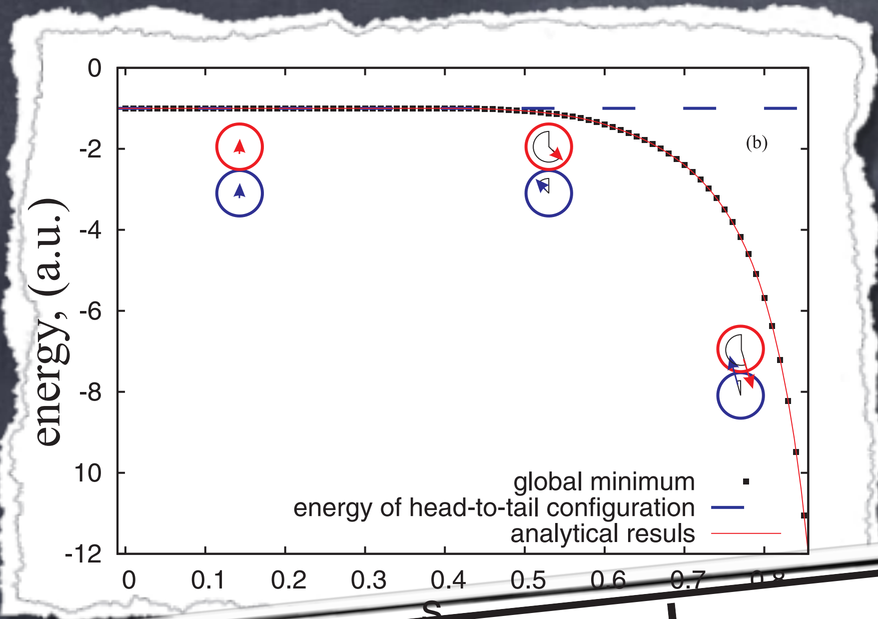


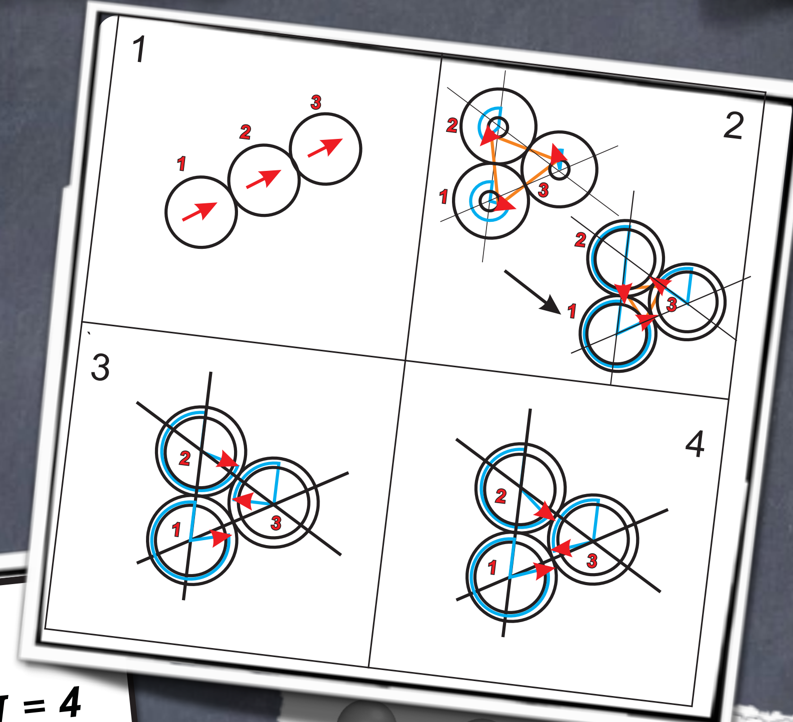
$$U_{\mathrm{WCA}}(r) = \begin{cases} U_{\mathrm{LJ}}(r) - U_{\mathrm{LJ}}(r_{cut}), & r < r_{\mathrm{cut}} \\ 0, & r \geq r_{\mathrm{cut}} \end{cases}$$

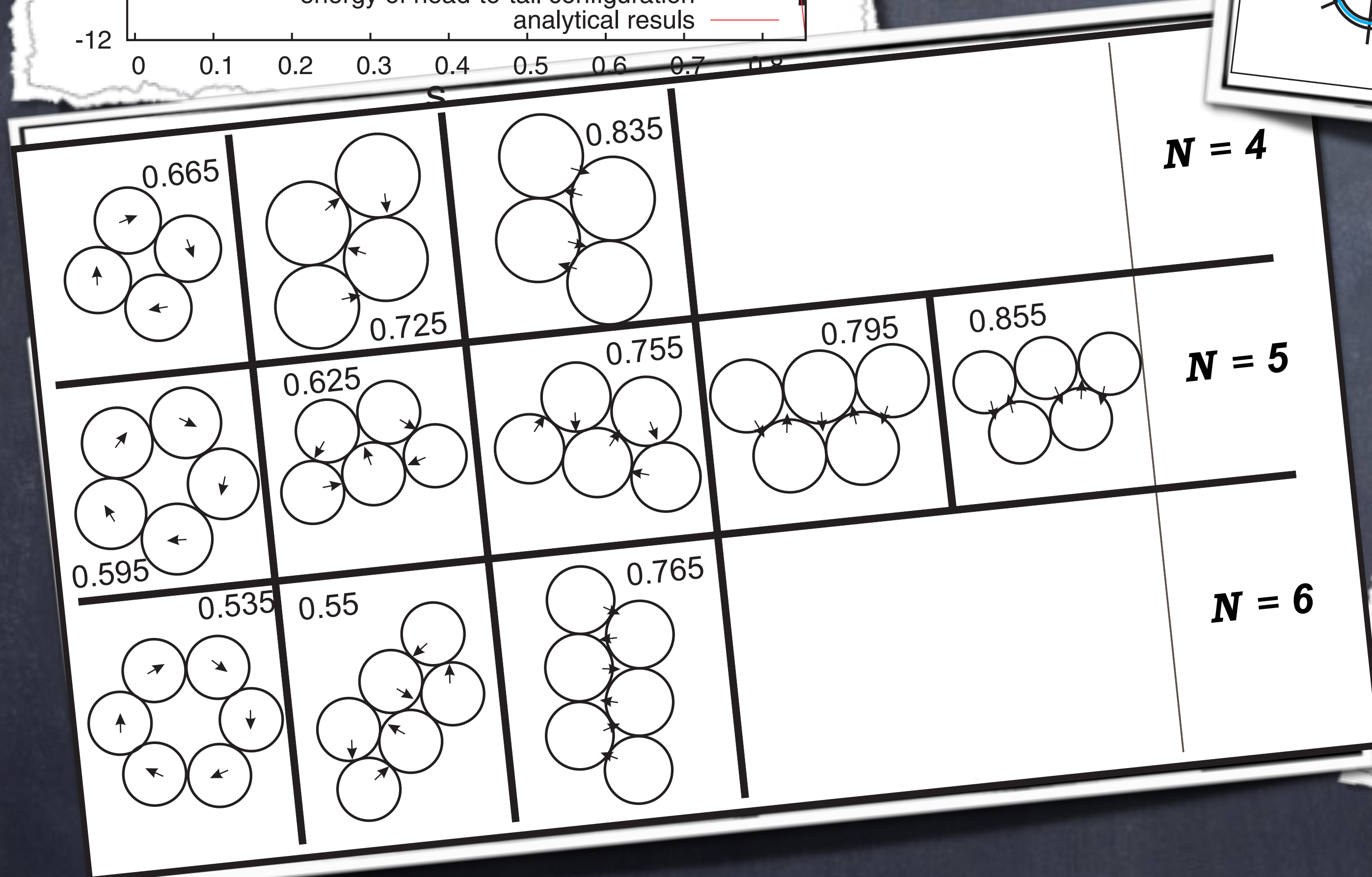
$$U_{\mathrm{LJ}}(r) = 4\epsilon_s\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$$

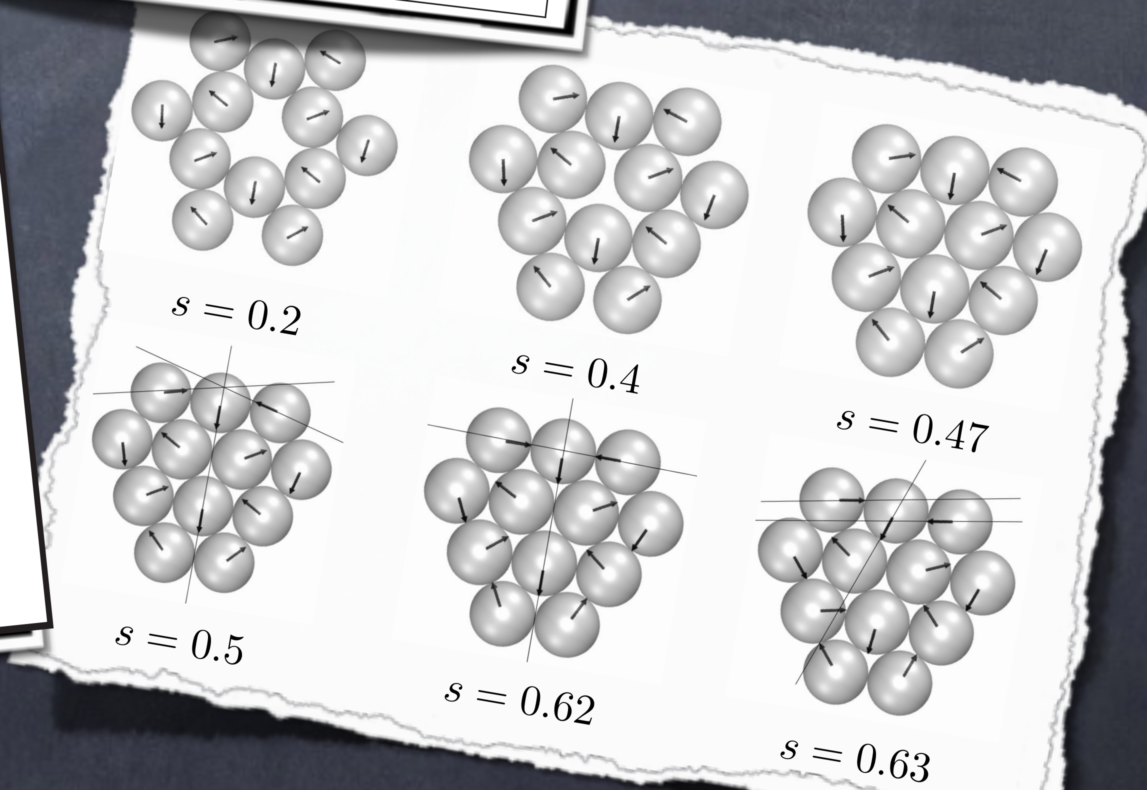
Molecular Dynamics Simulations
+
Analytical Calculations

CC: Ground States







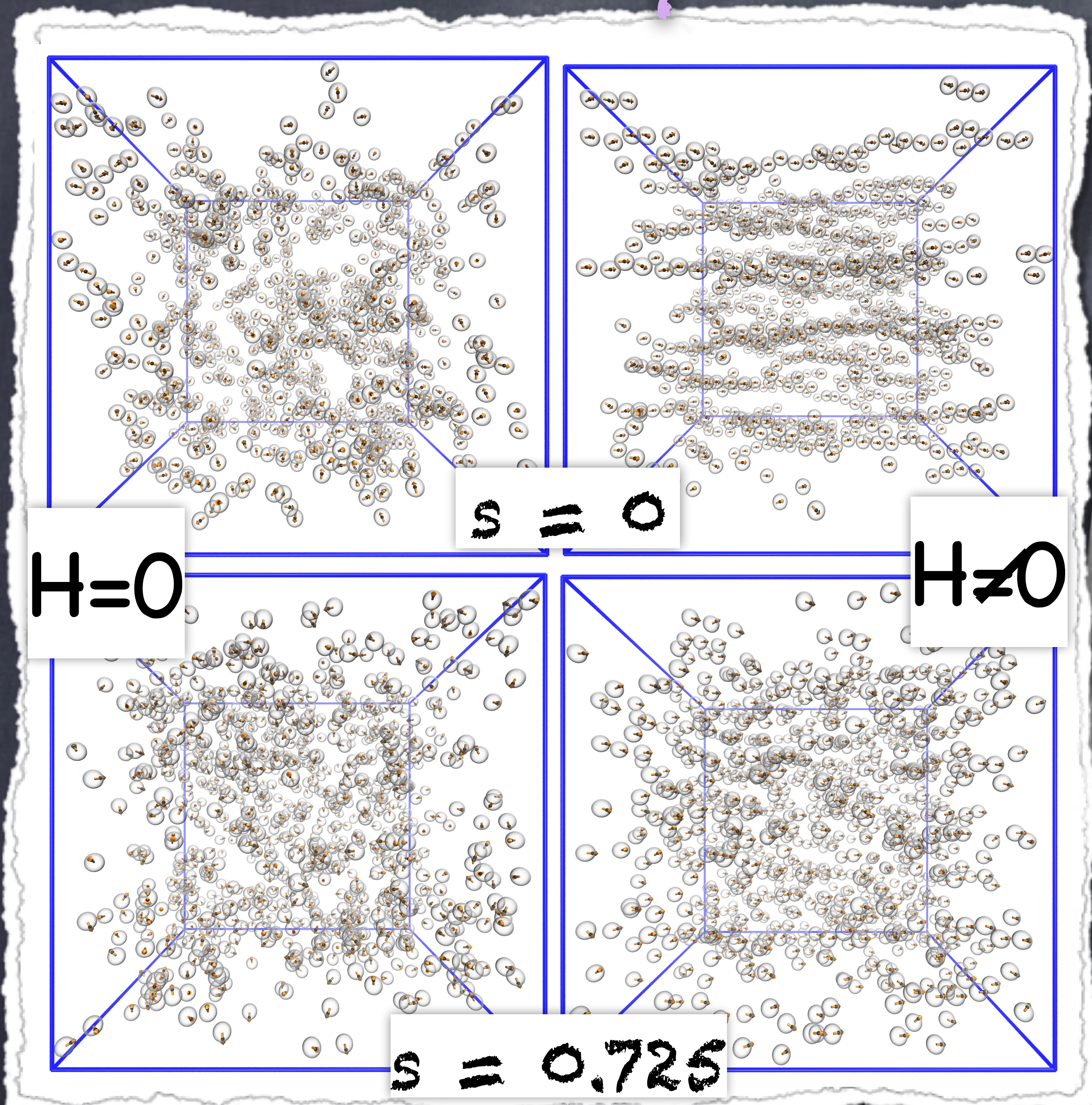


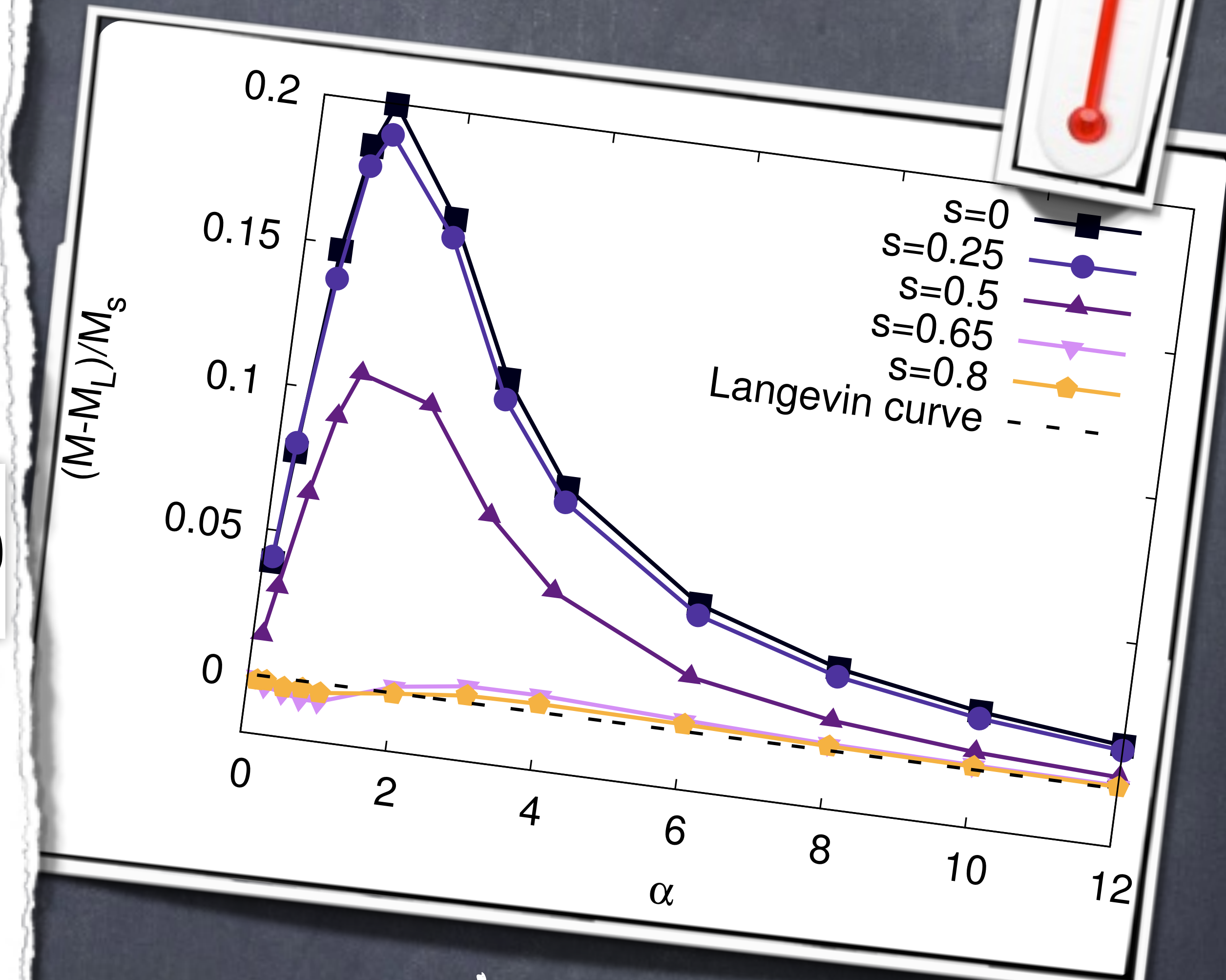
Antiparallel pairs win! M=0

No metastable states!

Klinkigt, Weeber, SK, Holm, 2011-2013

CC: Temperature up!



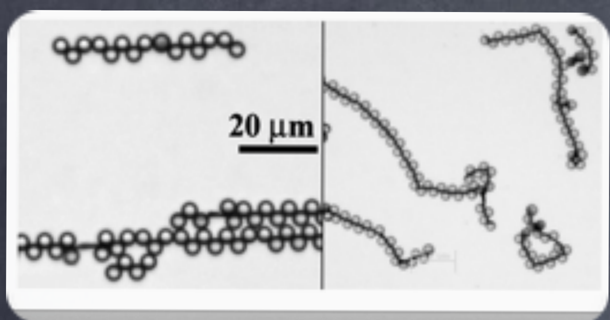


Susceptibility lower than the Langevin one!

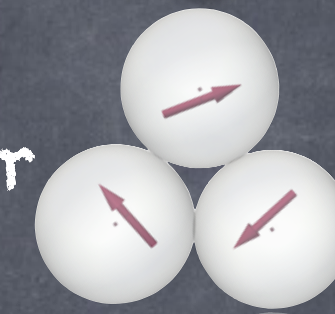
Spatially isotropic in field!

Klinkigt, Weeber, SK, Holm, 2011-2013

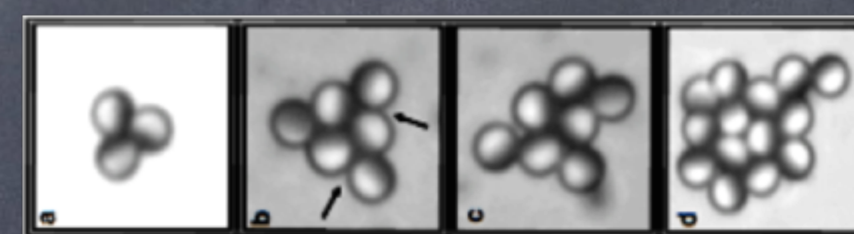
Janus-like magnetic particles



Janus-like particles form rings or antiparallel pairs in the ground states. Zipper is the ground state for a small shift range only



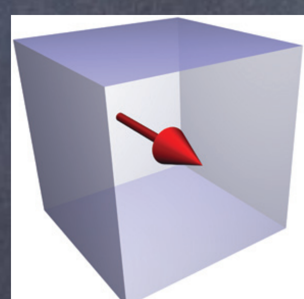
The antiparallel pair and a ring of dipoles become the most favourable configurations

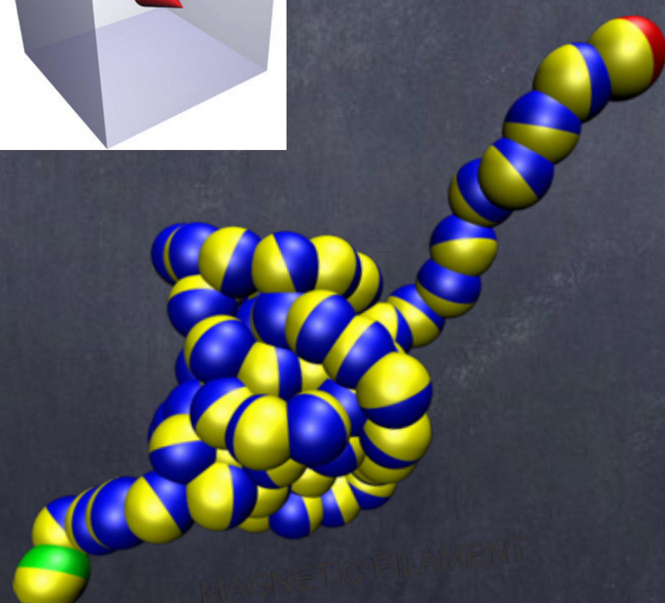


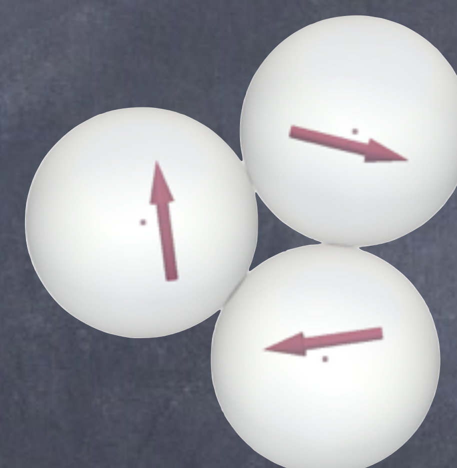
Shift the dipole off-centre to control the self-assembly in strong fields

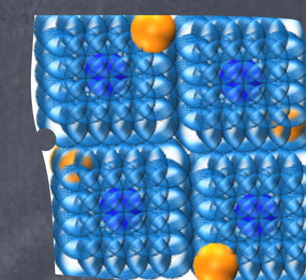
Conclusions

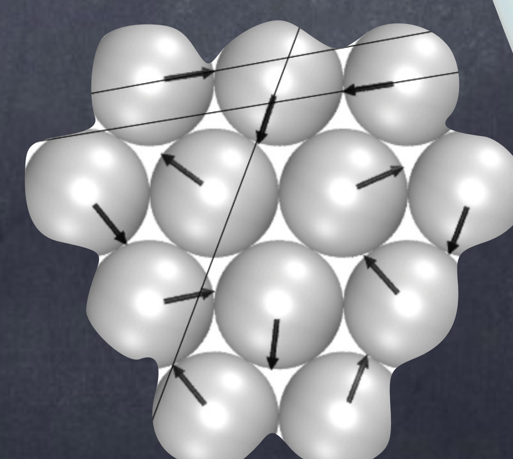
- Self-assembly of various building blocks can be used to control the magnetic response in dipolar soft matter, both to enhance and to weaken

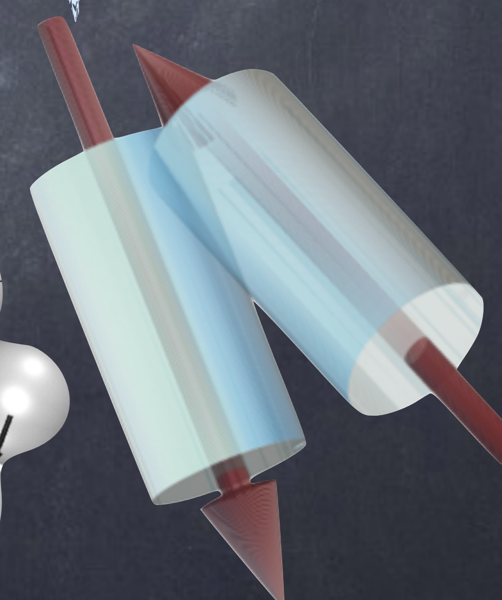






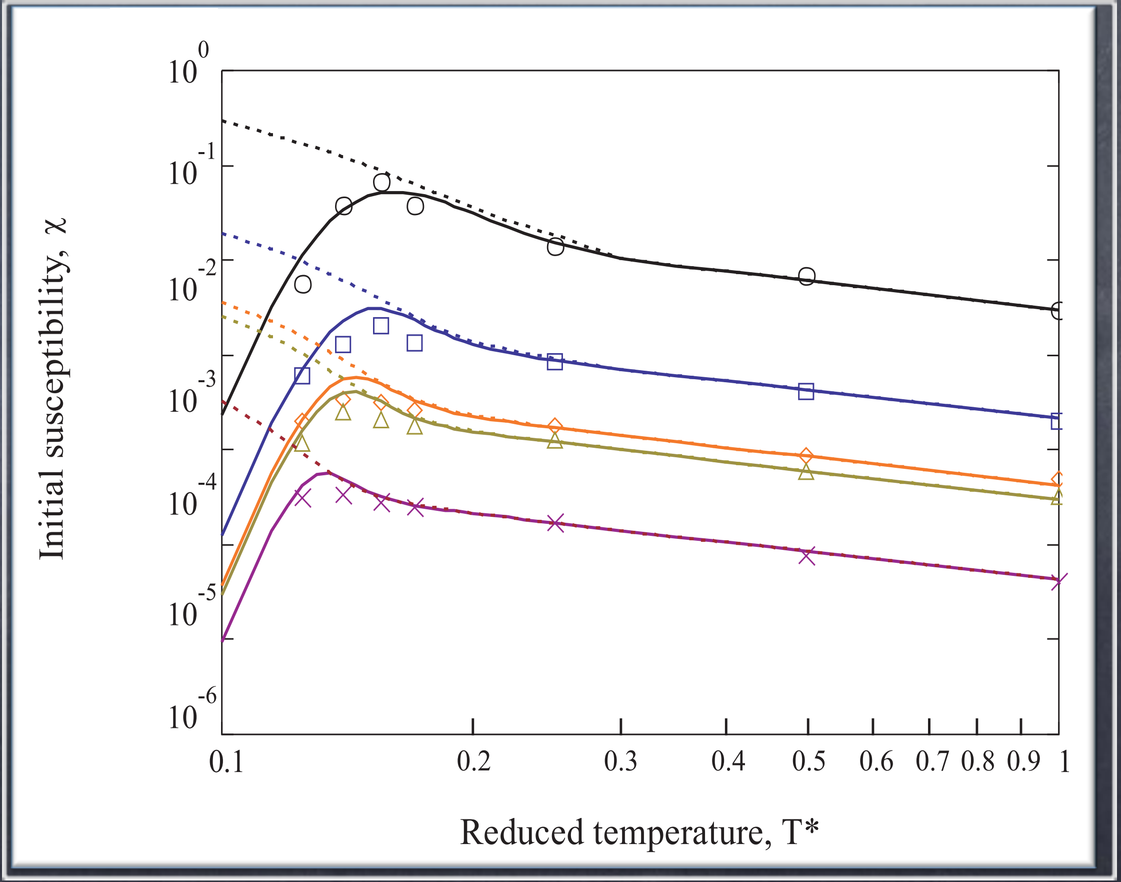






Conclusions

- However, it is difficult to increase the susceptibility, as if the structure's energy grows, it tends to close the magnetic flux



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Ural Federal University
named after the first President of Russia B.N.Yeltsin

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Rudolf Weeber

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Alexey Ivanov

Francesco Sciortino

Thank you!