Temperature-induced hierarchical self-assembly in dipolar hard spheres

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Plan

- Magnetism in SM, basic ideas
- Ideal superparamagnetic gas
- Correlations
- Self-Assembly:
  - Chains
  - Rings
  - Branches
  - Networks...
- Conclusions

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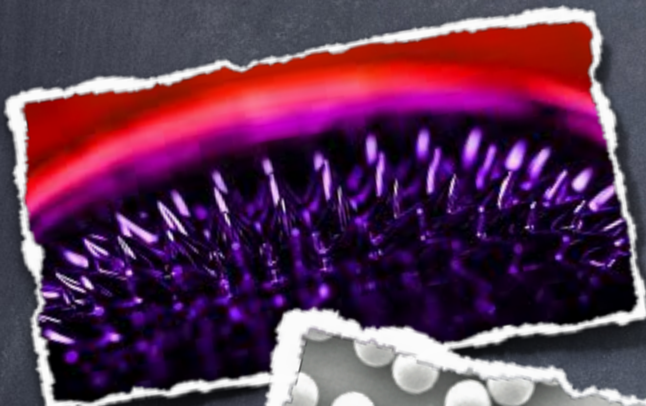
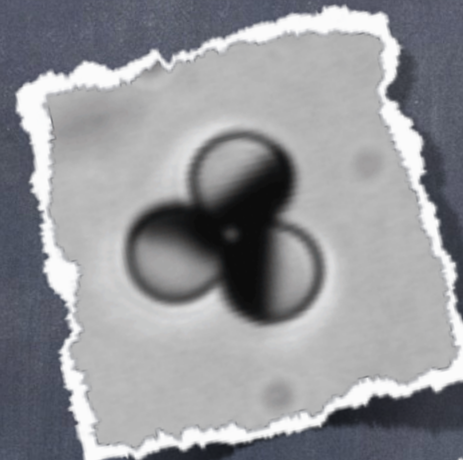
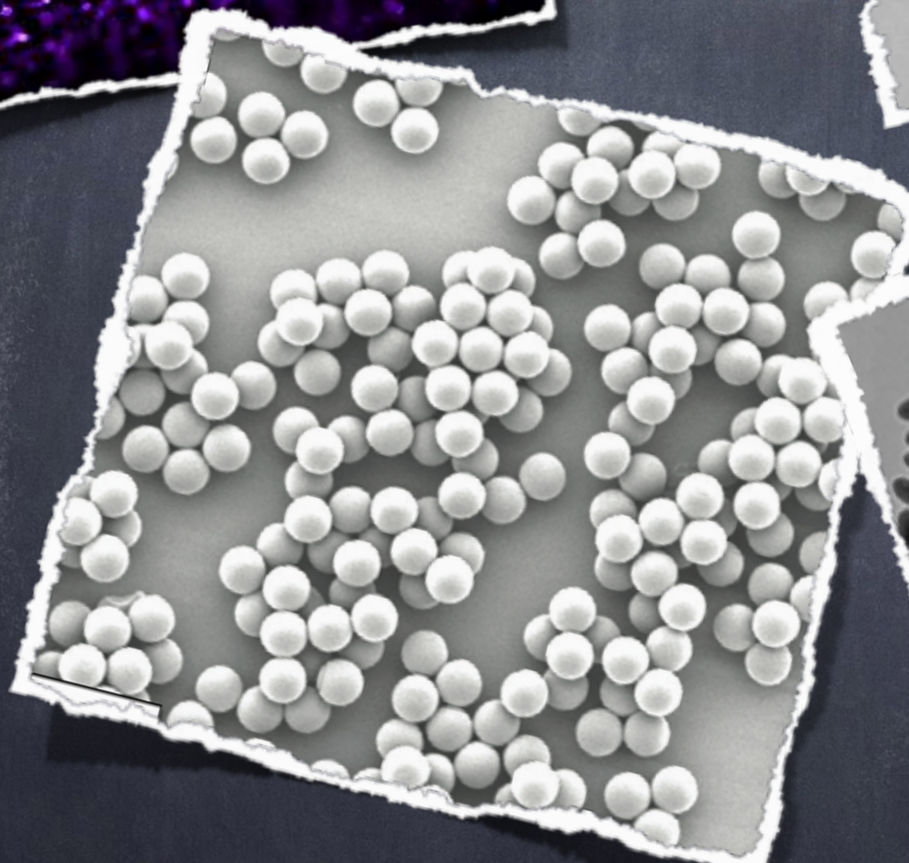
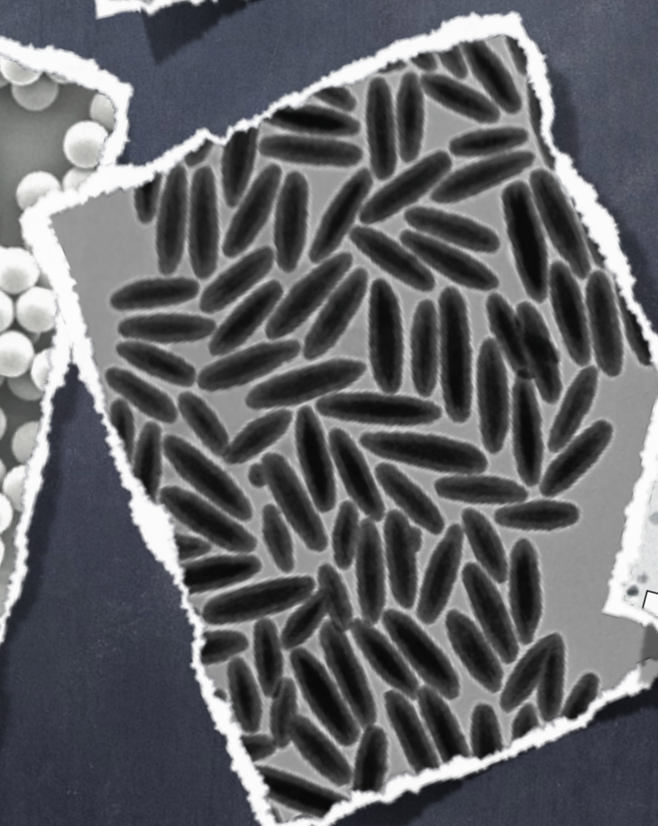
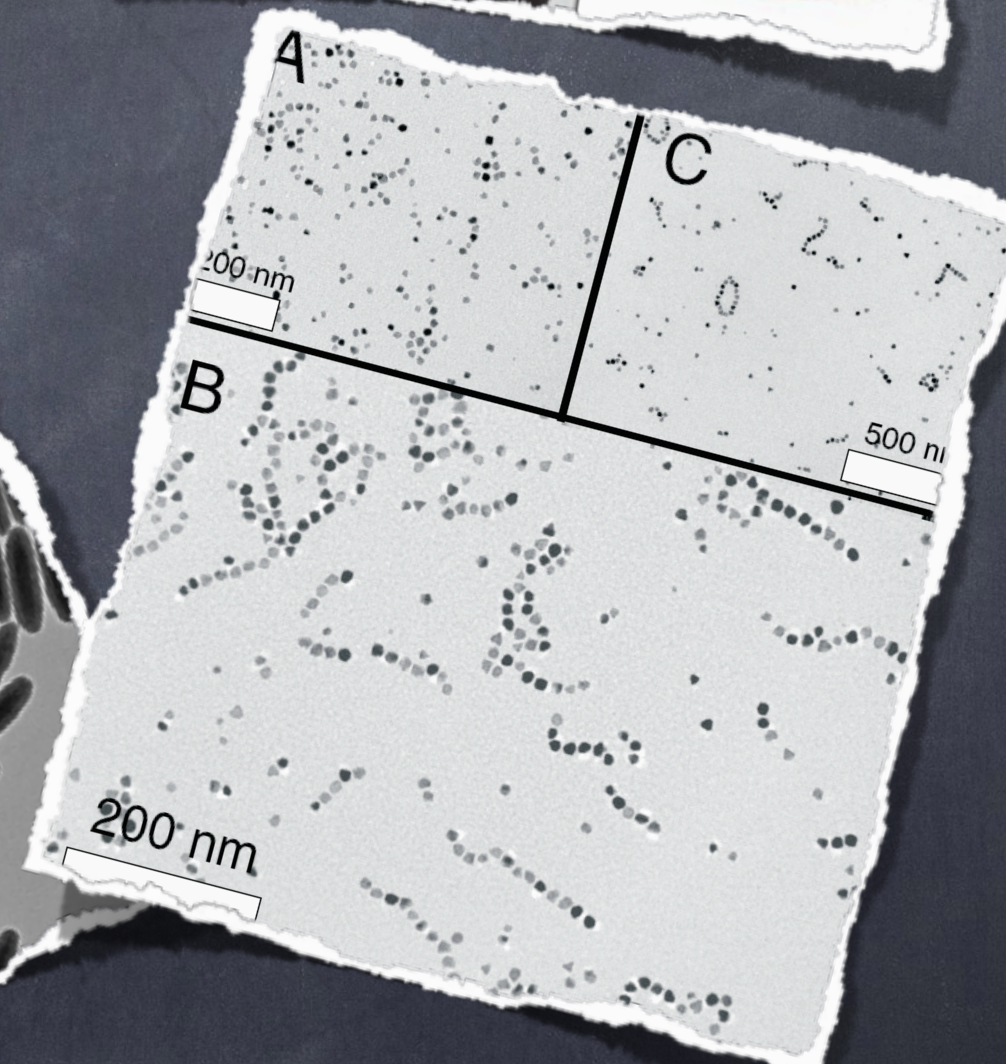
Magnetic soft matter





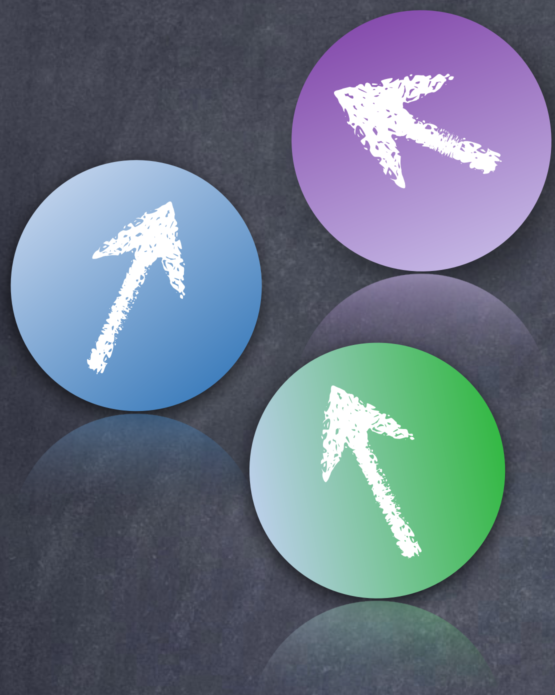






From works of:
Philipse's, Erbe's, Kretchmar's and Tschöpe's groups

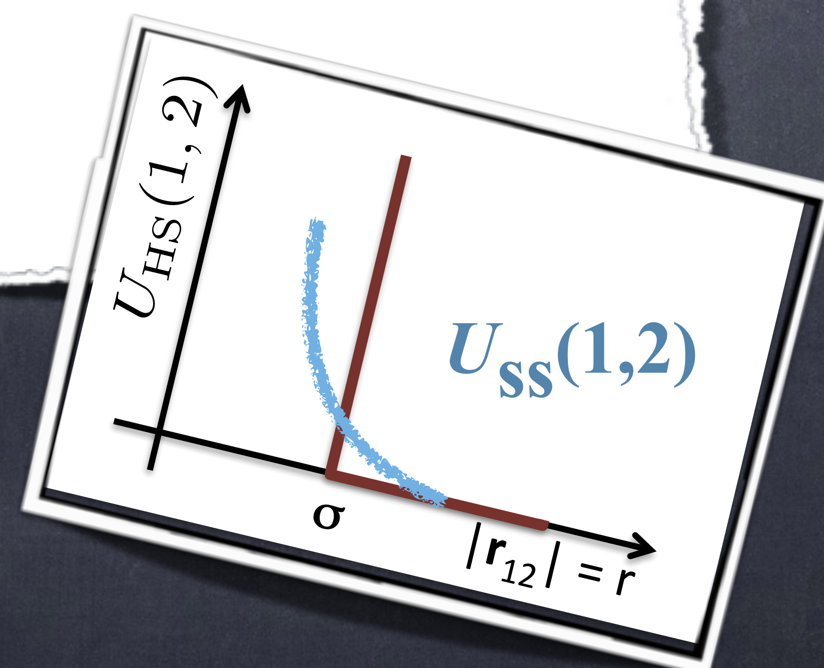
Interactions/Models



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

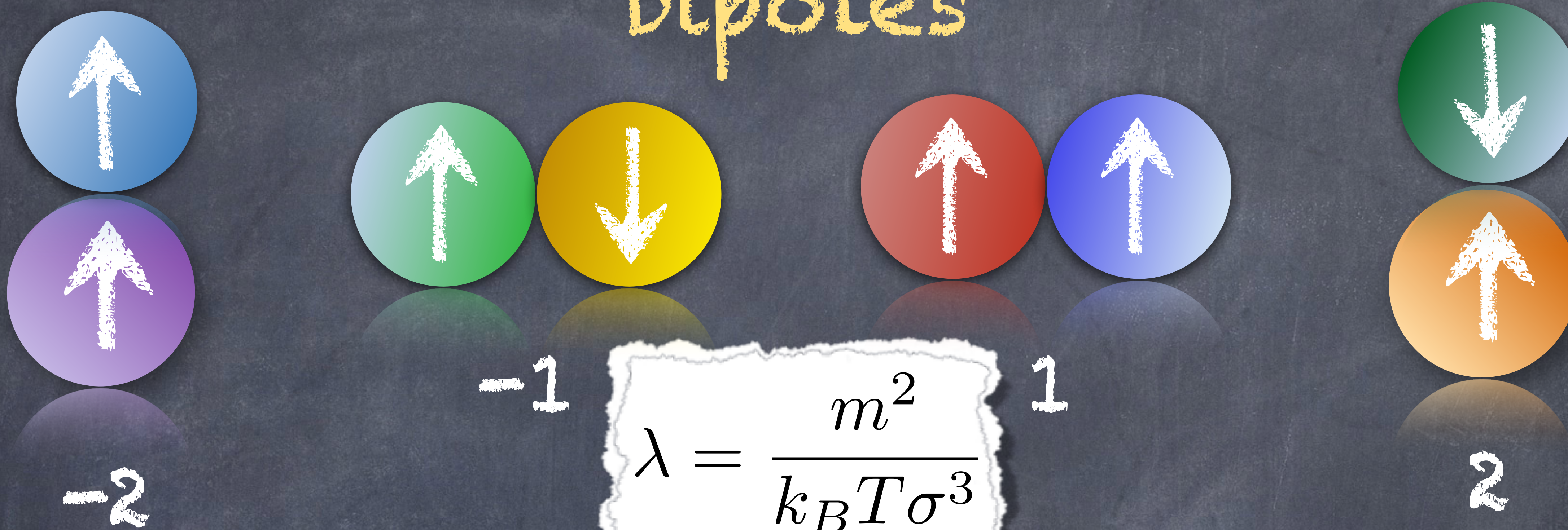
$$U_{\mathrm{DD}}(1,2) = \frac{m^2}{r^3}\left[(\hat{m}_1 \cdot \hat{m}_2) - 3(\hat{m}_1 \cdot \hat{r}_{12})(\hat{m}_2 \cdot \hat{r}_{12})\right]$$

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



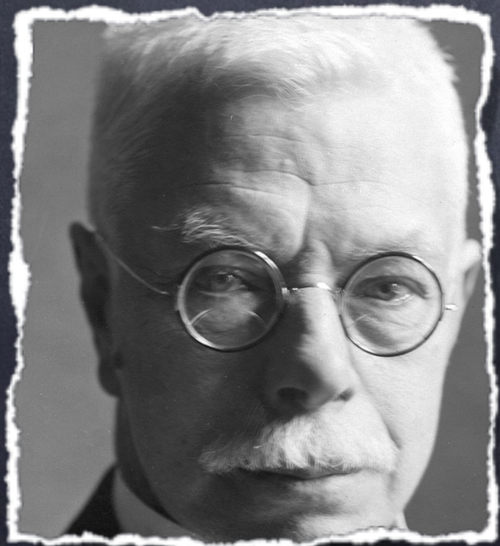
Interactions/Models

Dipoles



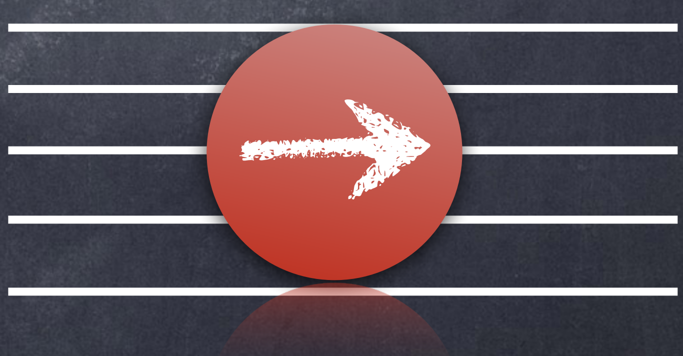
$$\lambda = \frac{m^2}{k_B T \sigma^3}$$

Zeeman



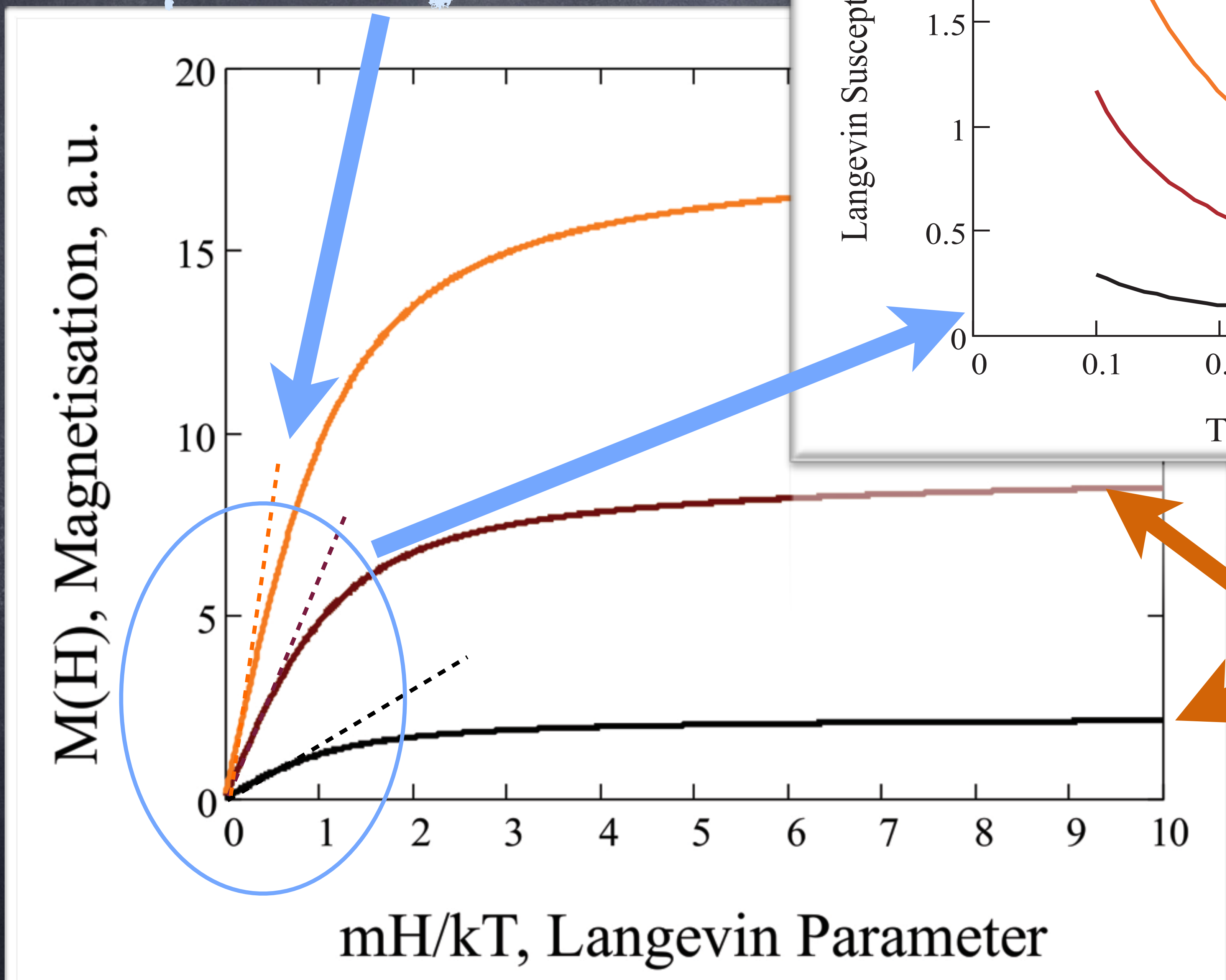
Peter Zeeman

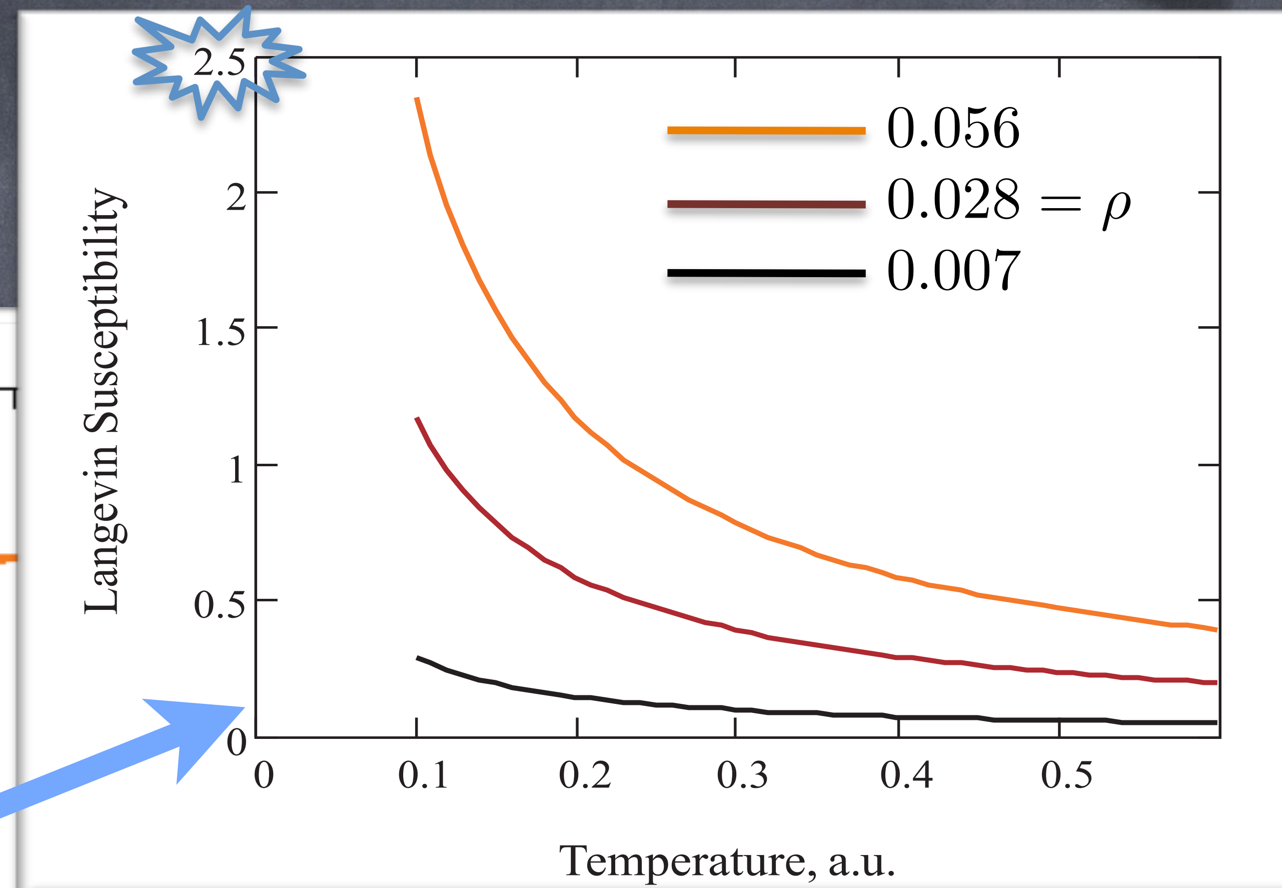
$$E = -(\mathbf{m} \cdot \mathbf{H})$$



Magnetic response

Initial Susceptibility, $\sim<m^2>$



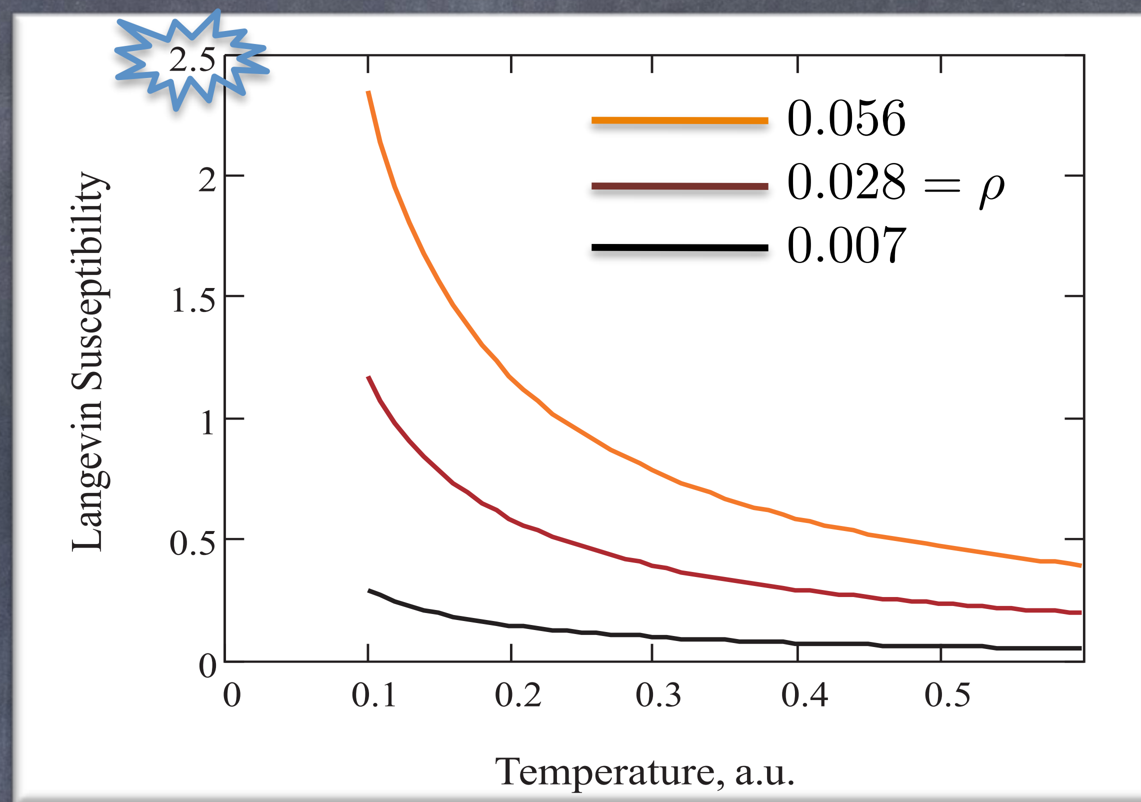


Saturation magnetisation, $\sim<m>$

Susceptibility

...From Langevin

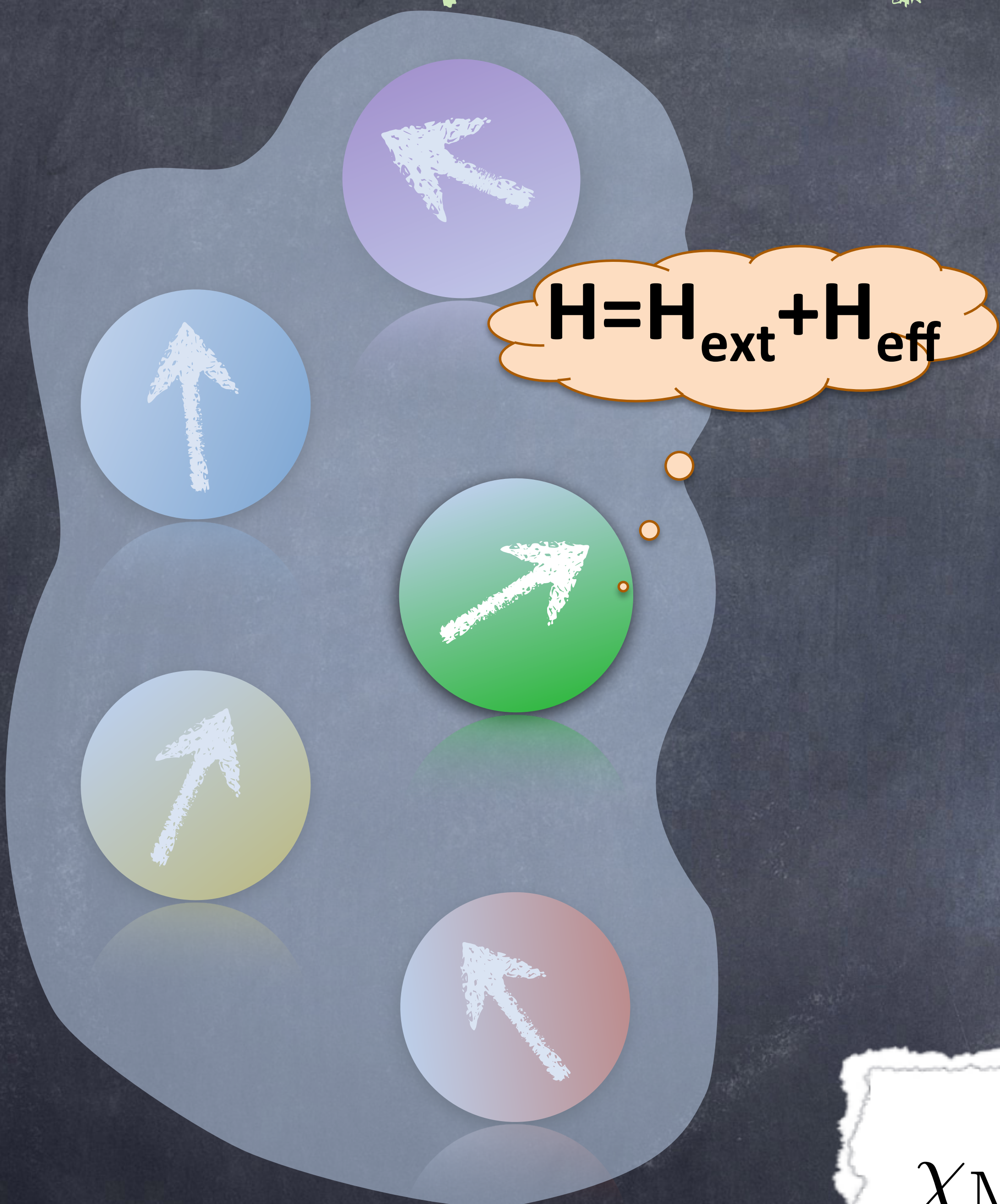
Independent particles



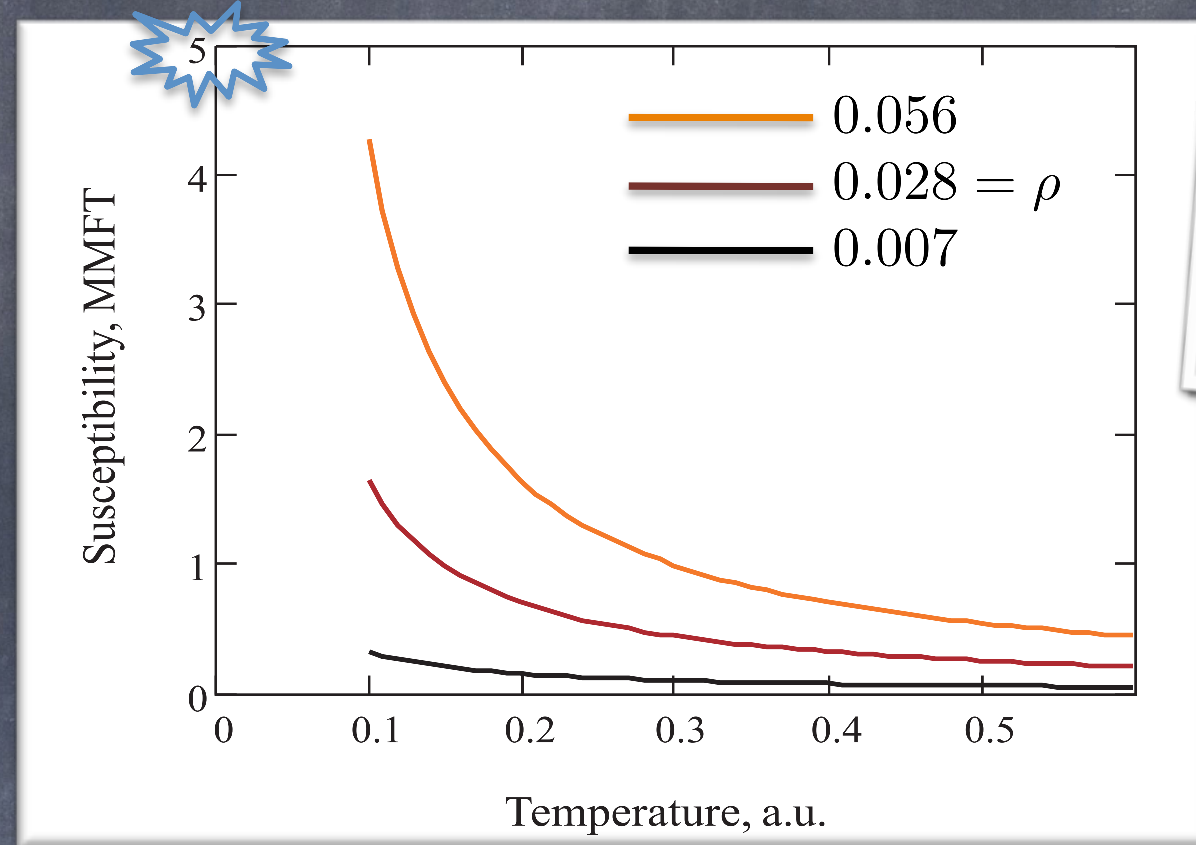
$$\lambda \sim \frac{1}{T} \quad \chi_{\mathrm{L}} = \frac{4\pi}{3}\sigma^3\rho\lambda$$

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

Susceptibility



...to the Mean-Field



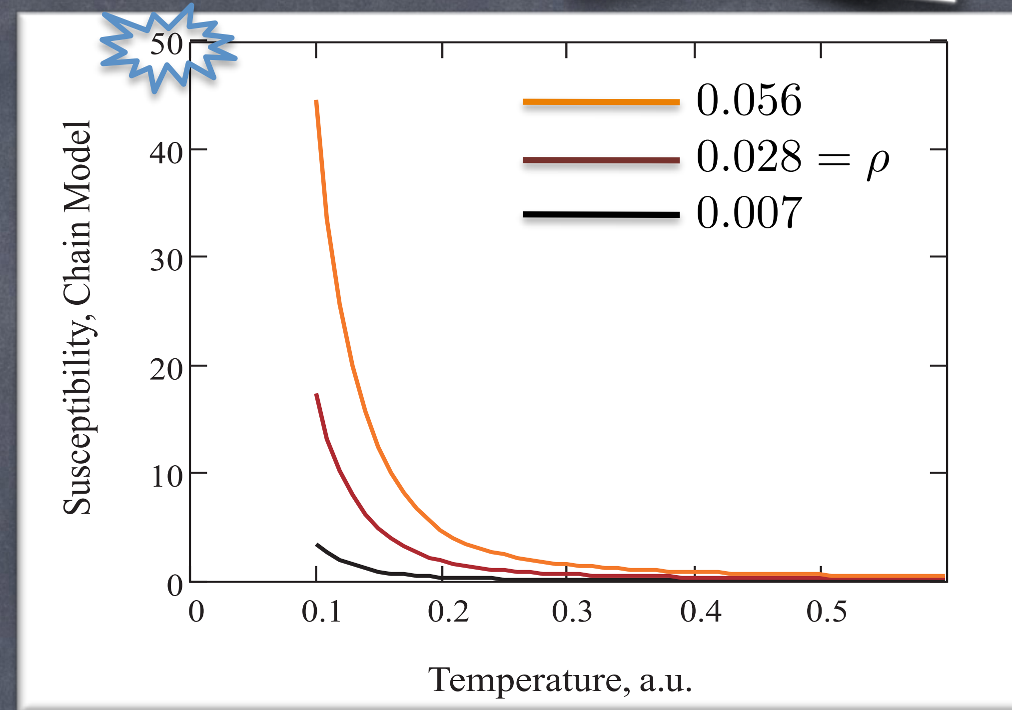
$$\chi_{\mathrm{M}} = \chi_L \left(1 + \frac{\chi_L}{3} + \frac{\chi_L^2}{144}\right)$$

A. Ivanov et al., PRE, 2001.

...CHAINS

Susceptibility

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



$$p(T,\phi) = \frac{1 + 2q(T)\phi - \sqrt{1 + 4q(T)\phi}}{2q(T)\phi}$$

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**

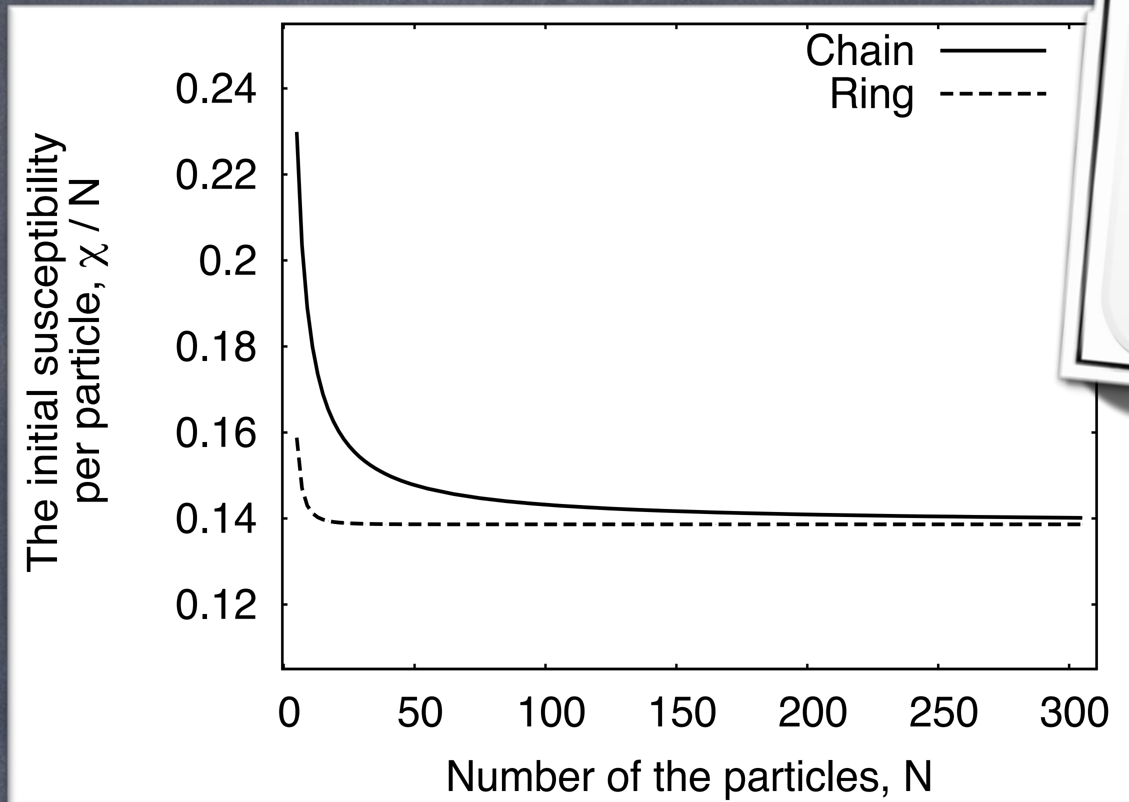
Susceptibility $$\chi_{\text{C}} = \chi_{\text{L}} \frac{1 + p(T,\rho)K(T)}{1 - p(T,\rho)K(T)} \left(1 + \frac{\chi_{\text{L}}}{3}\right)$$

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

Rings

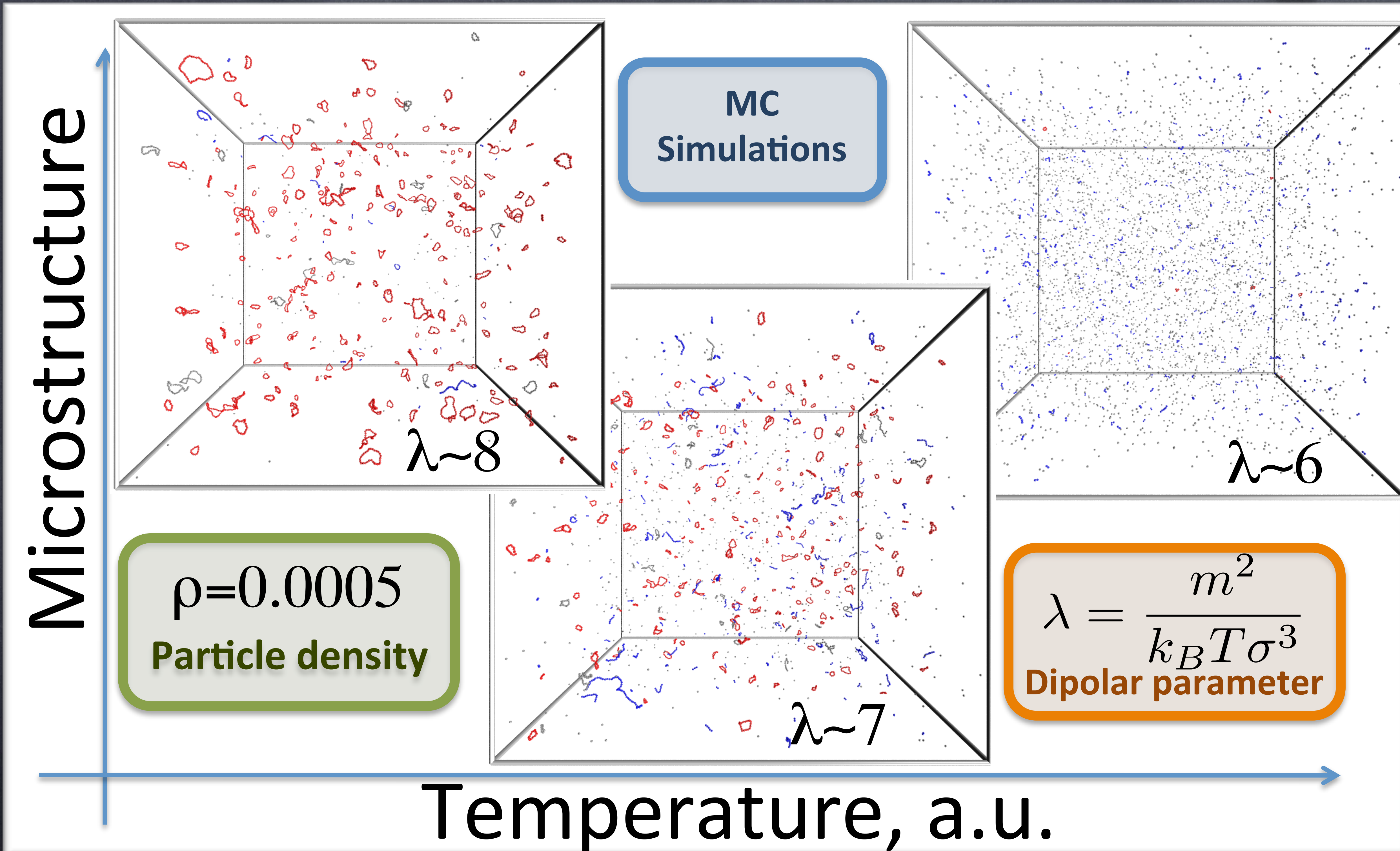
Ground State

T=0



T. Prokopyeva et al., PRE, 2012.

Gas Case

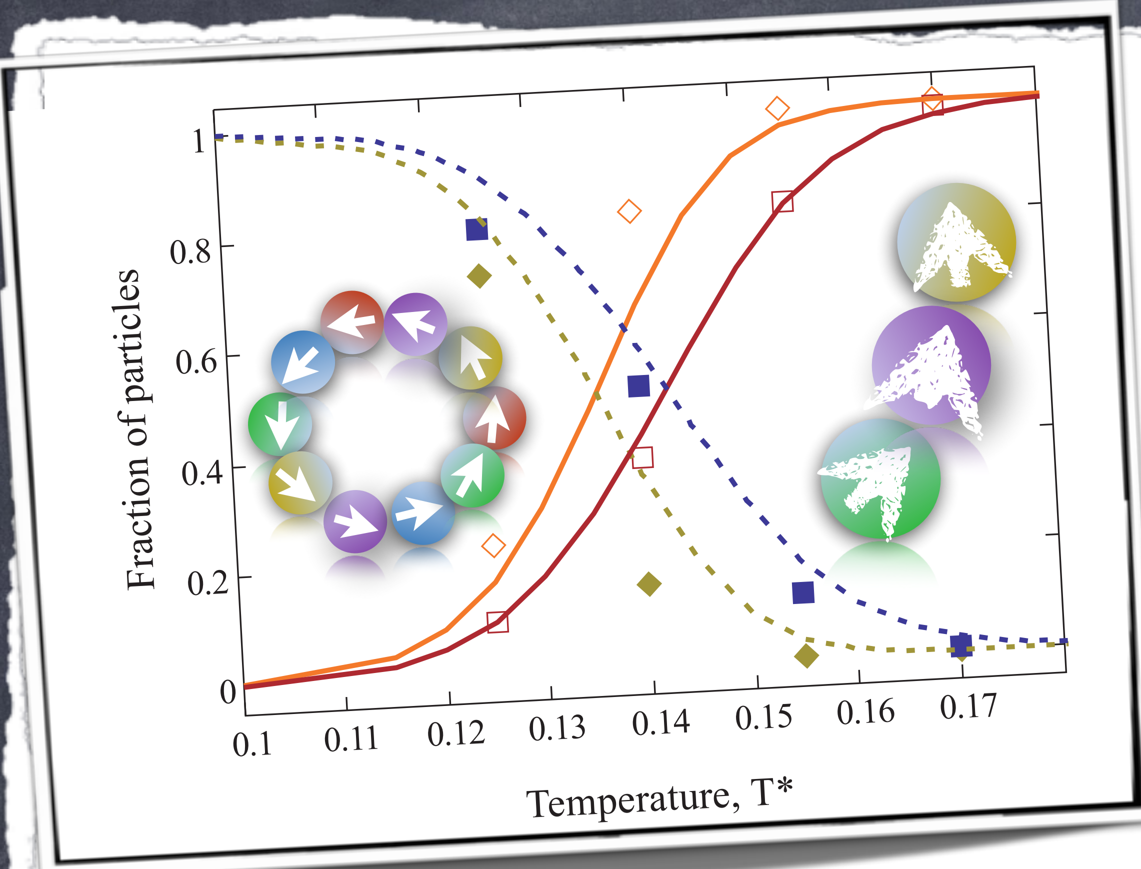


Snapshots provided by L. Rovigatti and F. Sciortino

Gas Case

Chains and Rings!

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

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

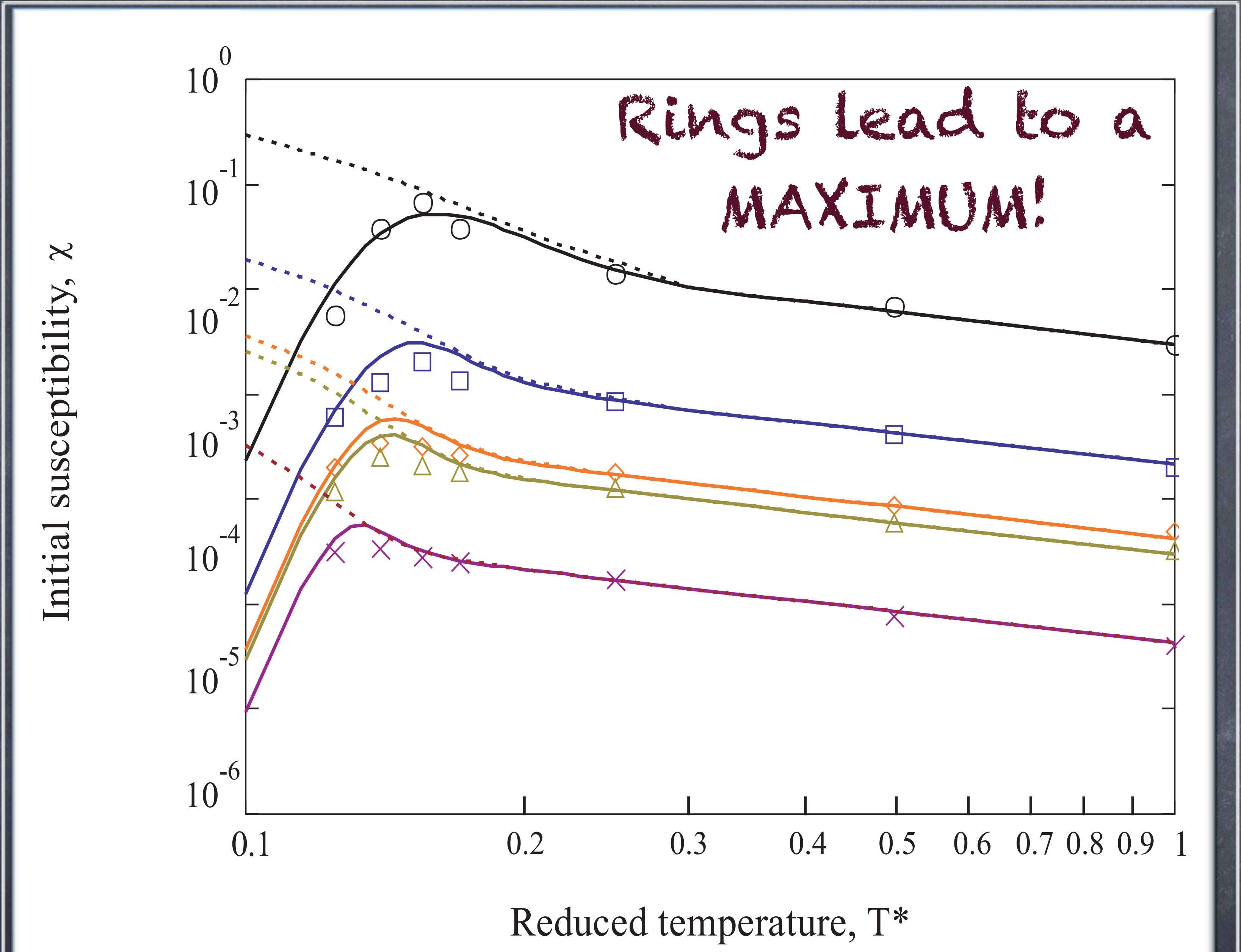
In Eq. (3), $\nu = 0.588$ is the self-avoiding random walk exponent. The term $1/n^{3\nu+1}$ in $W_n(T^*)$ captures the difference in entropy between chains and rings arising from the n ways of opening a ring to form a chain; the difference between the numbers of self-avoiding paths of chains and rings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

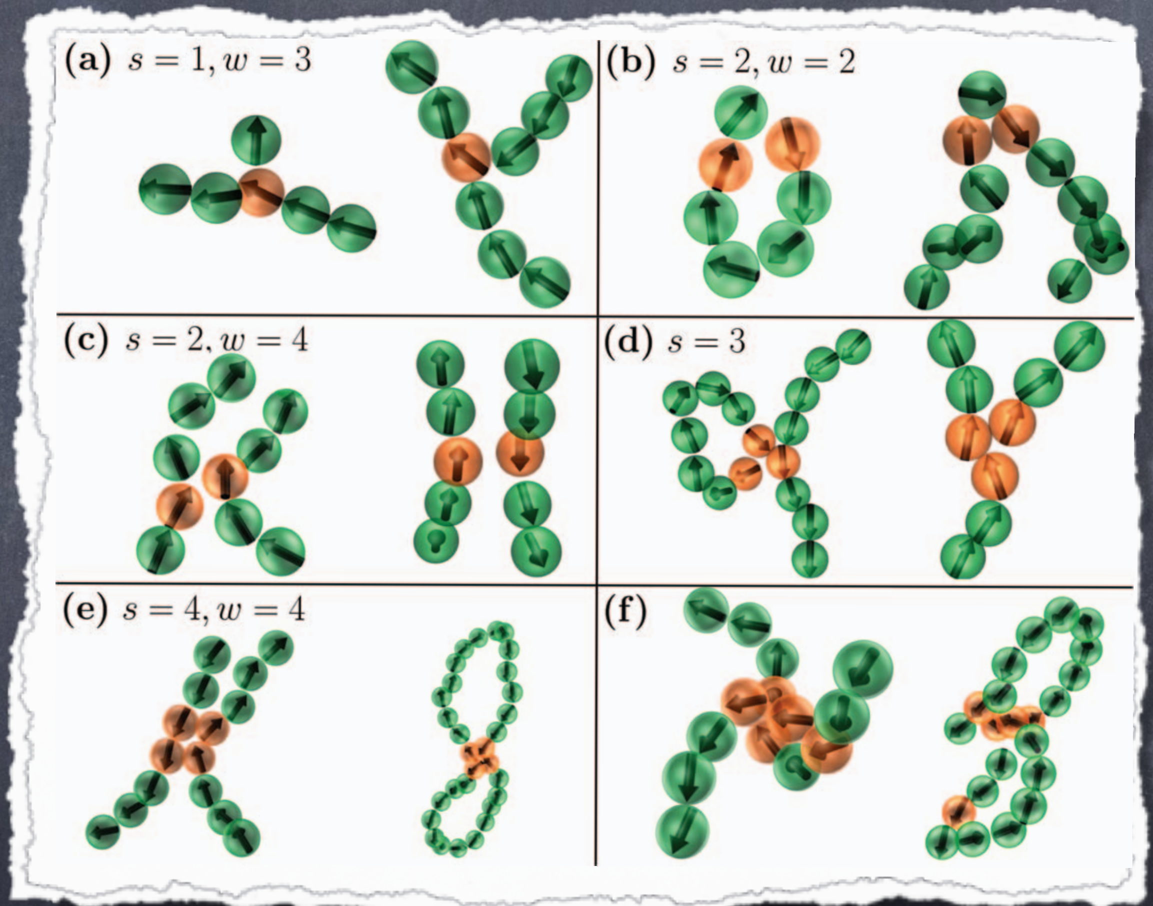
Gas Phase



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

Getting denser

Chains, Rings and various defects!

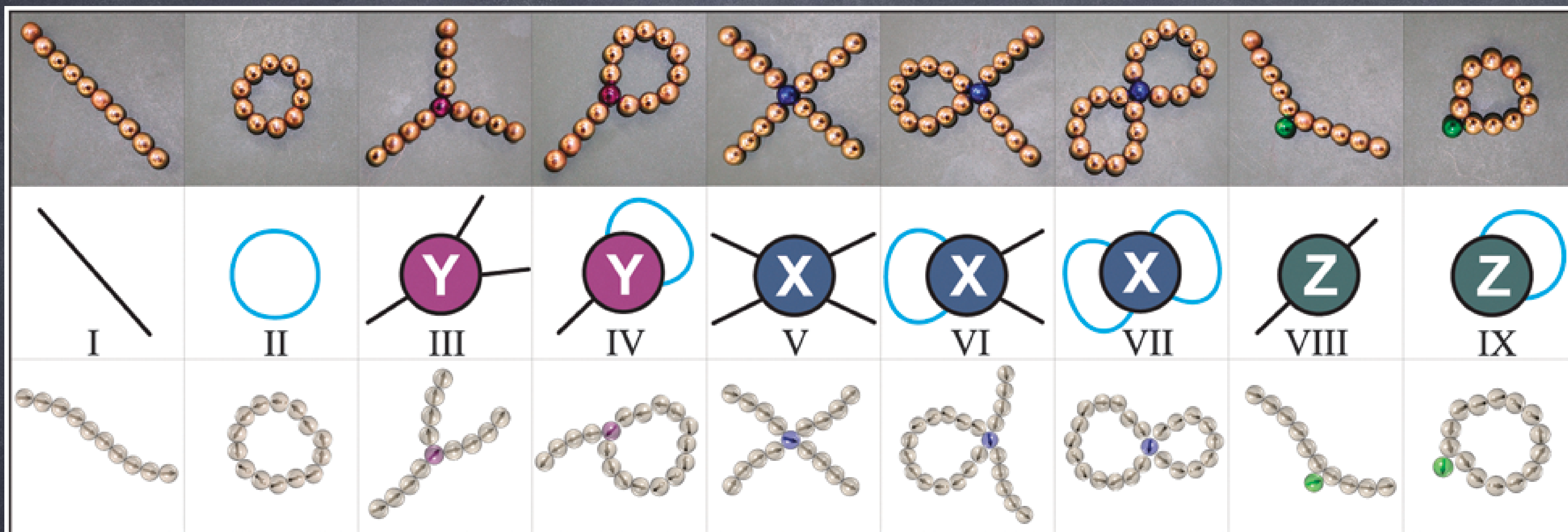


L. Rovigatti et al. J.Chem. Phys. 2013

Moderate DHS concentrations

Branching!

Single defect model



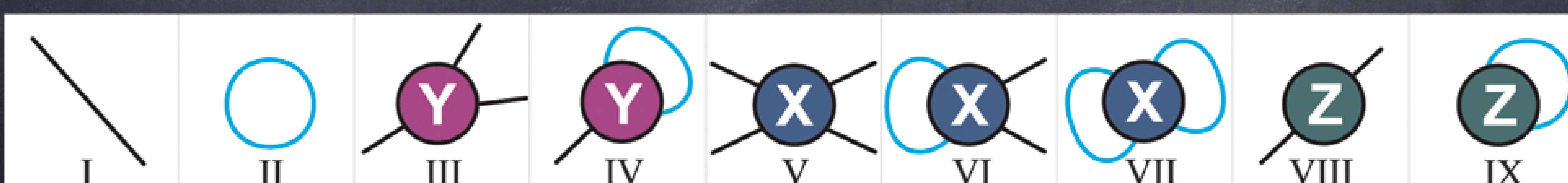
S. Kantorovich et al. PCCP, 2015

Single defect model

$$F = k_B T \sum_i K(\vec{i}\,) g(\vec{i}\,) \ln\left(\frac{g(\vec{i}\,) v(\vec{i}\,)}{eQ(\vec{i}\,)}\right).$$

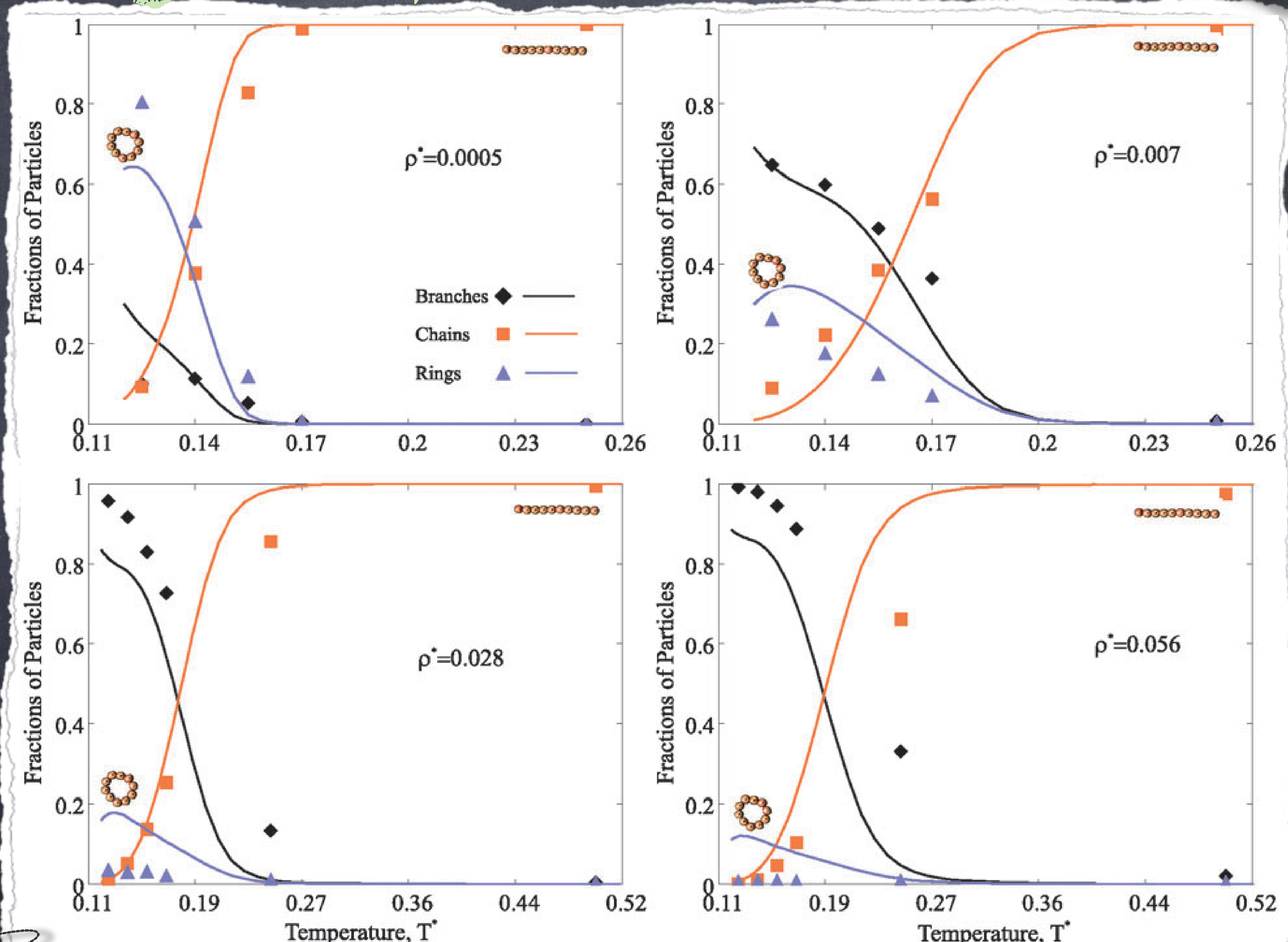
$$\sum_i K(\vec{i}\,) N(\vec{i}\,) g(\vec{i}\,) = \frac{\phi}{v}.$$

$$\vec{i} = (n, k_1, k_2, m_Y, m_X, m_z)$$



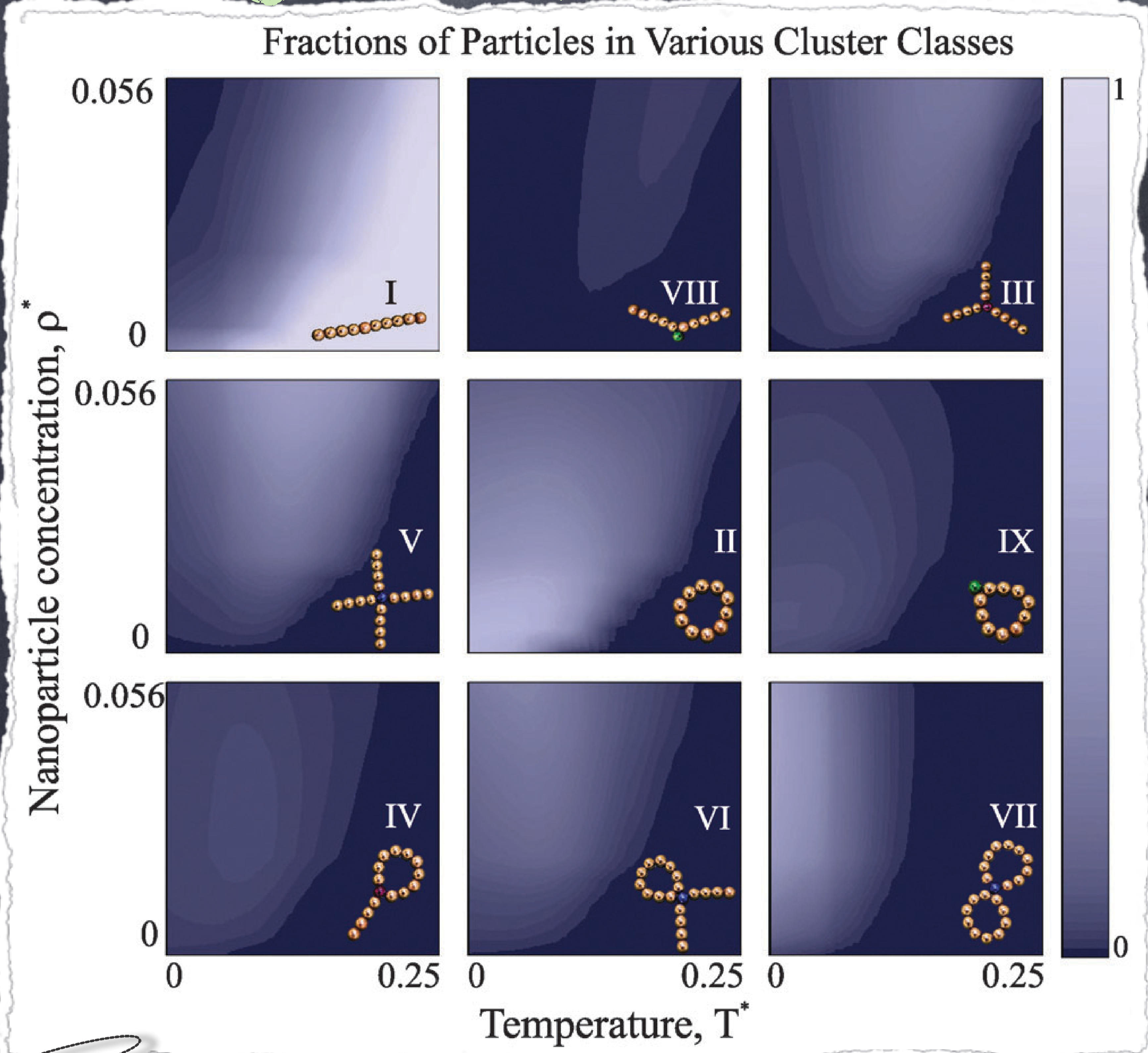
S. Kantorovich et al. PCCP, 2015

Single defect model



S. Kantorovich et al. PCCP, 2015

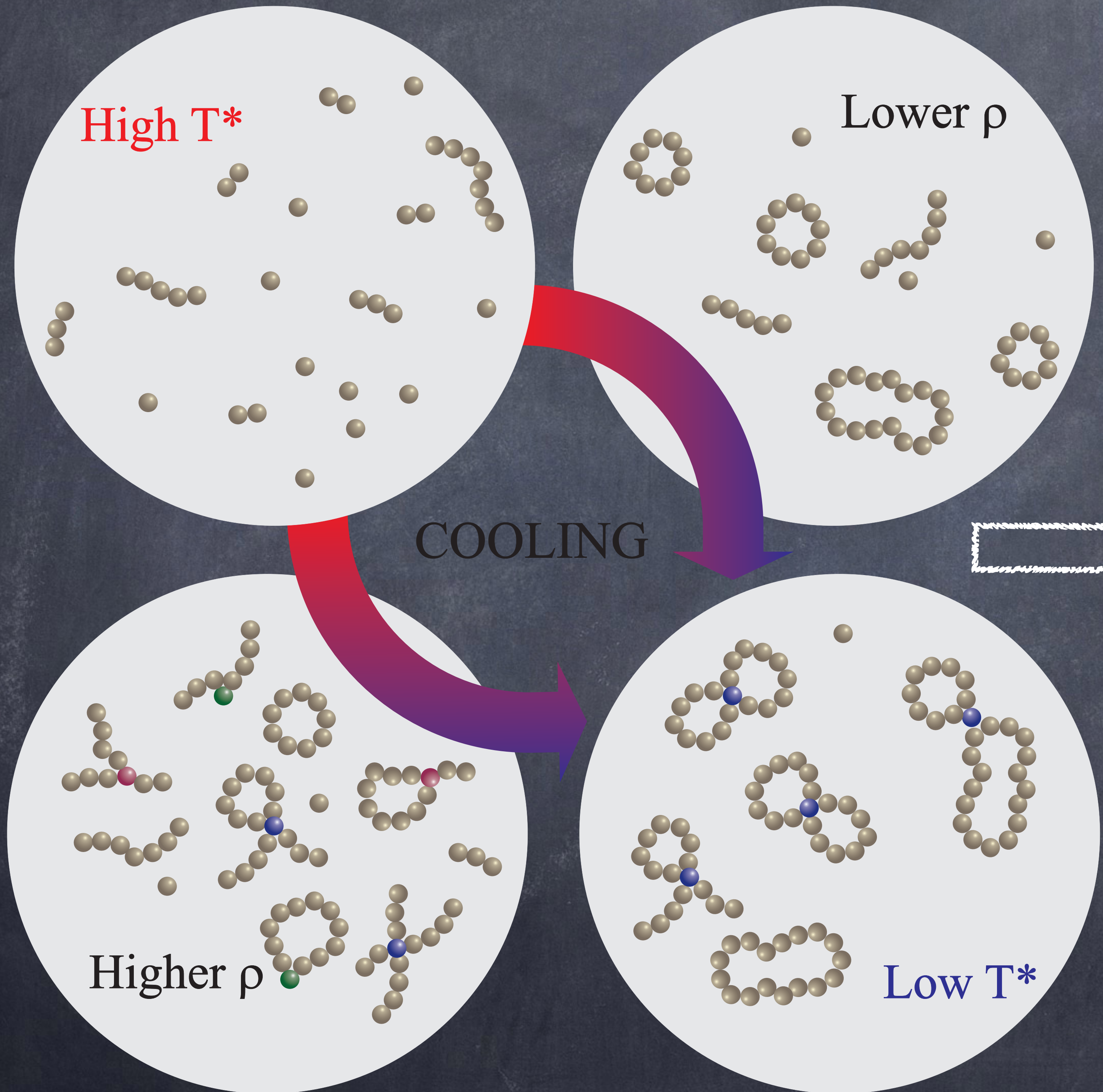
Single defect model

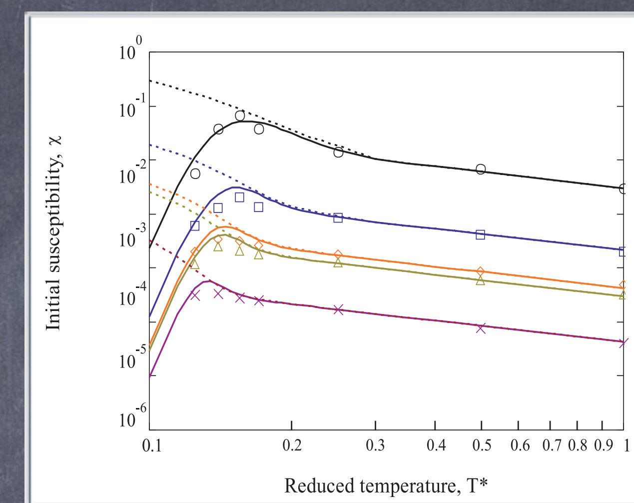


S. Kantorovich et al. PCCP, 2015

Conclusions

DHS as we know them



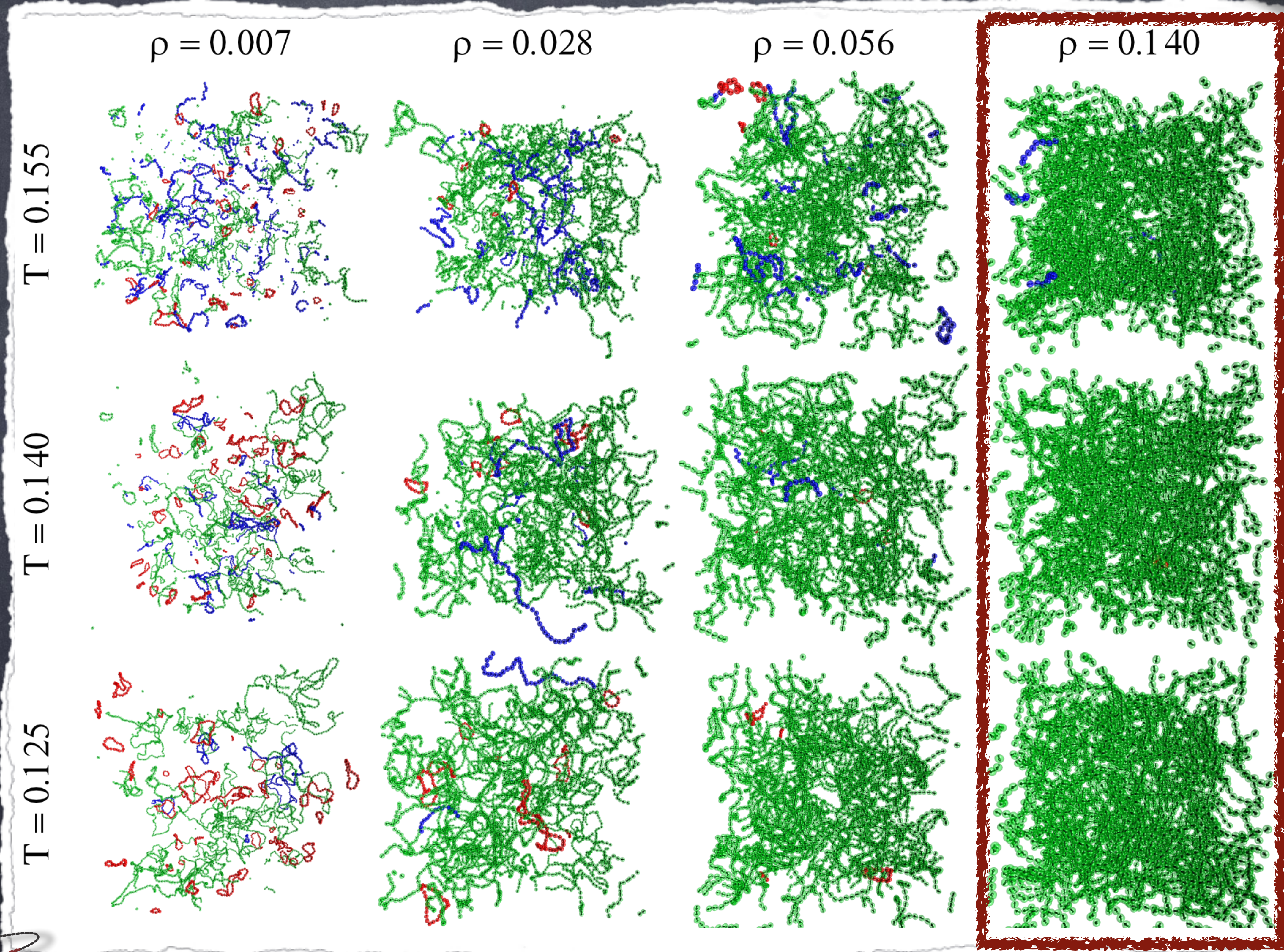


S. Kantorovich et al. PCCP, 2015

What if the DHS concentration is even higher?

Percolating Network!

Challenge:



L. Rovigatti et al.Soft Matter, 2012

Who did the work:

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Francesco Sciortino

Lorenzo Rovigatti

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COLLDENSE
COLLOIDS with DESIGNED RESPONSE

FWF
Der Wissenschaftsfonds.

РФФИ
РОССИЙСКИЙ ФОНД ФУНДАМЕНТАЛЬНЫХ ИССЛЕДОВАНИЙ

VIENNA SCIENTIFIC CLUSTER

Thank you!