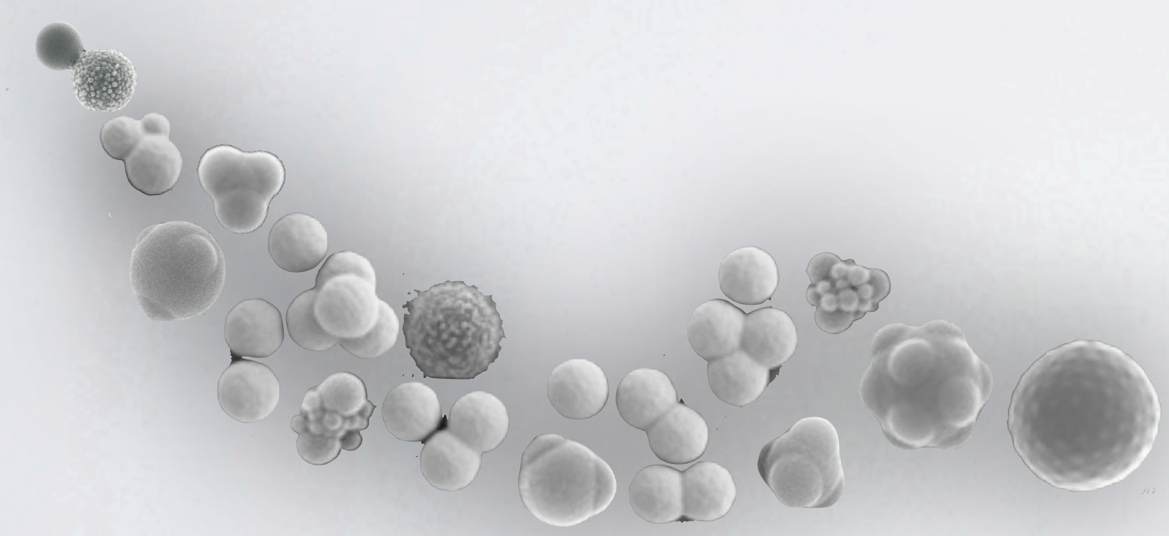
COLLOIDAL SELF-ASSEMBLY



Dr. Daniela J. Kraft

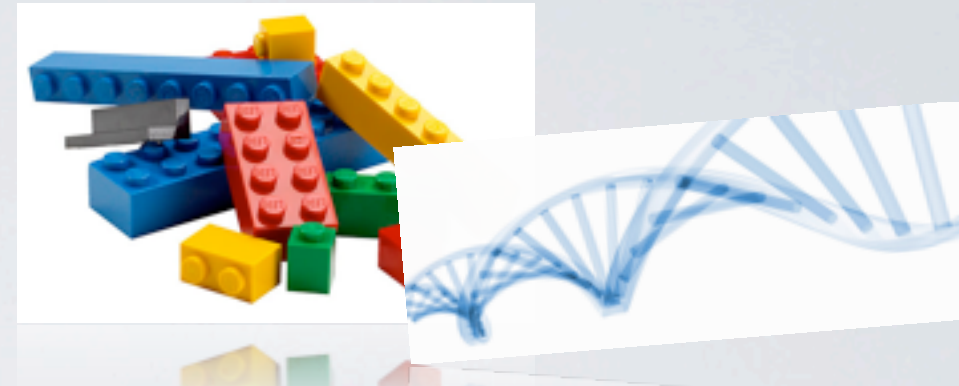
Universiteit Leiden

JMBC workshop Soft and Granular Matter
Soft Matter Physics, LION, Leiden University, The Netherlands
March 23 2016

Leiden Institute of Physics

Liquids

Polymers / DNA

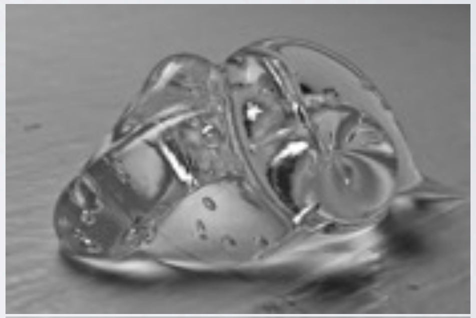


Biophysics

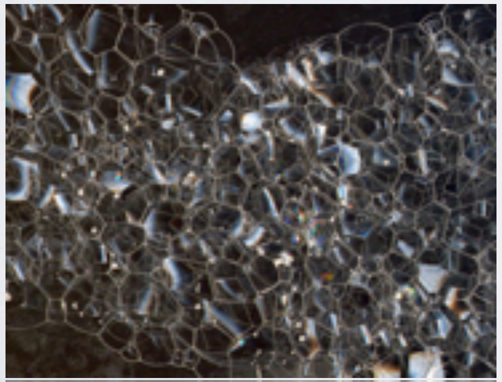
Soft Matter

Relevant energy scale ~ kT
Easily deformed

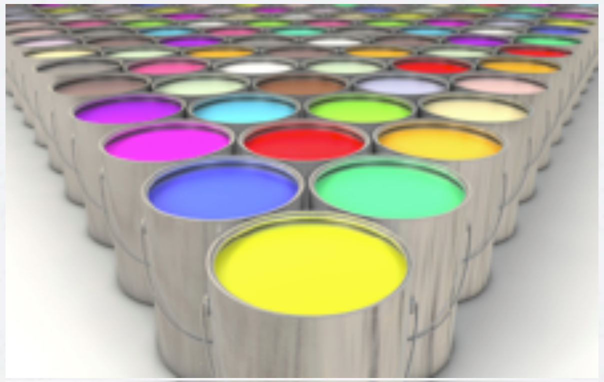
Gels



Foams



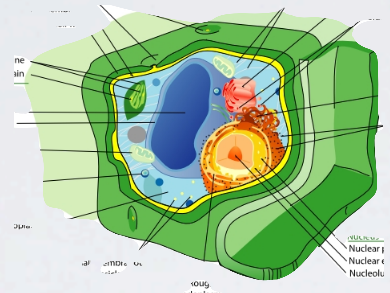
Colloids



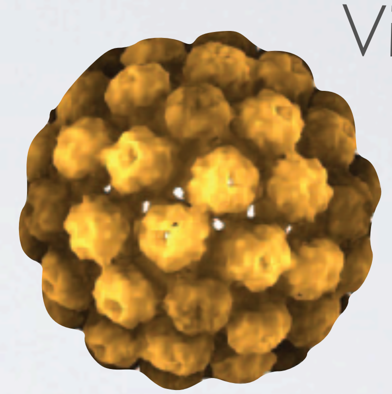
What are Colloids?

Planets

Cells



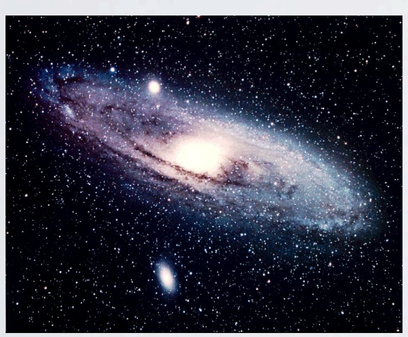
Viruses



10^{5} 10^{-5} 10^{-8}

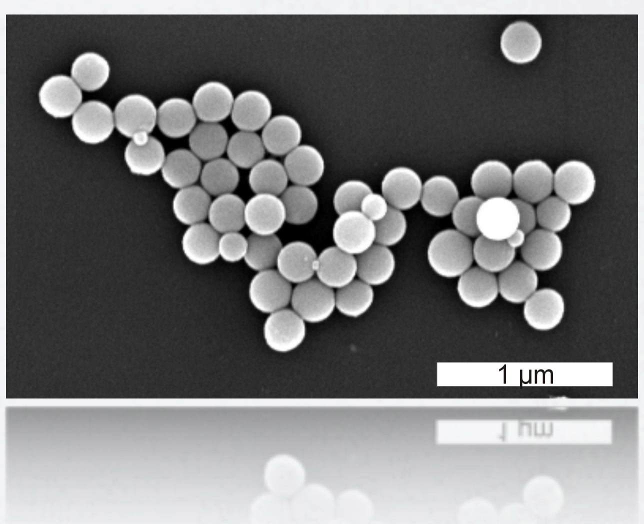
10^{21} 10^{0} $10^{-5}...10^{-9}$ 10^{-10} meter

Galaxies

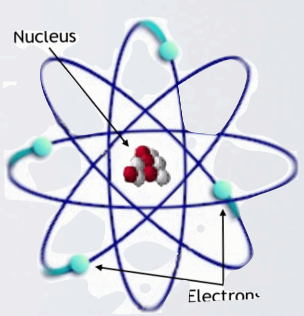


Humans

Colloids

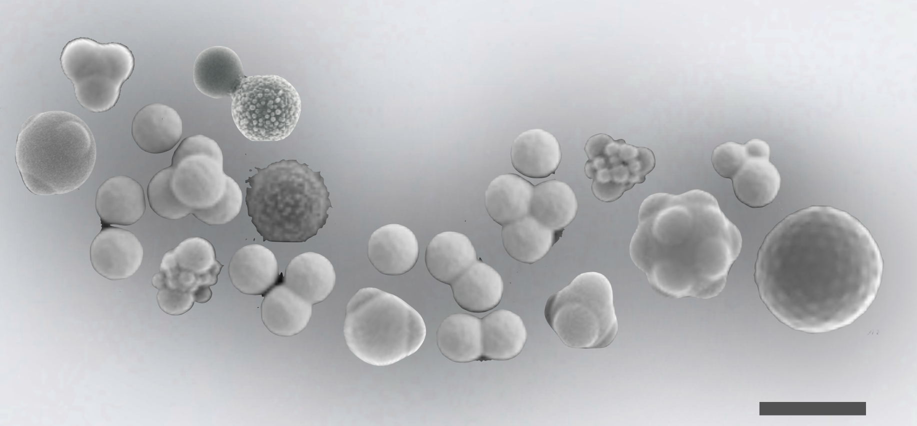


Atoms & molecules



What Are Colloidal Particles?

Colloids
Small particles suspended in a liquid



Size: ~2nm - 10μm
Concentration: ~0.1% to 70% by volume
Materials:

- Plastic: polystyrene, PMMA...
- Inorganic: silica (SiO_2), titania (TiO_2), ...
- Semiconductor: CdSe,...
- Metal: Au, Ag, ...
- Fat, protein,..
- Droplets (emulsions)

Where to find: milk, butter, mayonnaise, blood, ink, paint, toothpaste, coffee,...

Why Are we Interested in Colloids?

Experiment: Latex Paint Stain

Who is That?

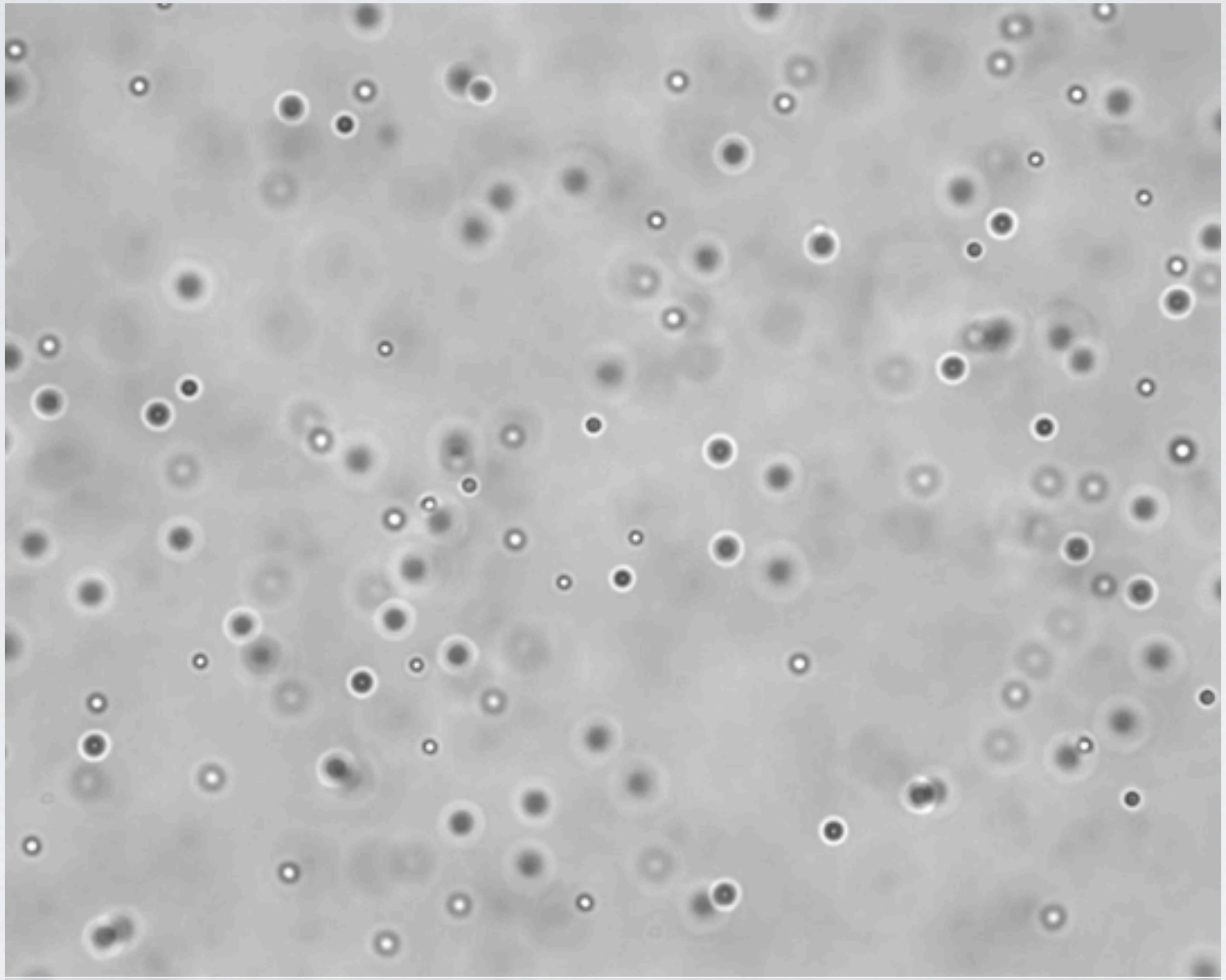
Albert Einstein

Robert Brown

Jean-Baptiste Perrin

Hendrik Casimir

Colloids Undergo Brownian Motion



2μm sized particles

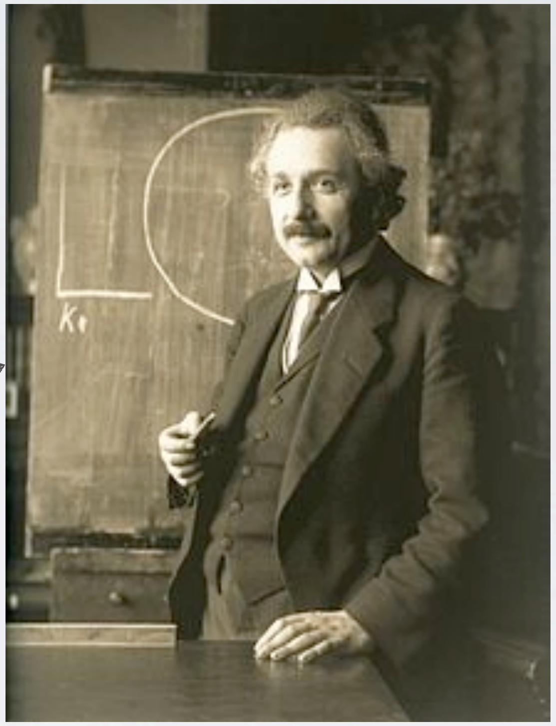
Who is That Scientist?

Albert Einstein

Robert Brown

Jean-Baptiste Perrin

Marian Smoluchowski



Annalen der Physik, 17, 549 (1905)

5. ***Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen;***
von A. Einstein.

Vom Standpunkte der molekularkinetischen Wärmetheorie aus kommt man aber zu einer anderen Auffassung. Nach dieser Theorie unterscheidet sich eingelöstes Molekül von einem suspendierten Körper *lediglich* durch die Größe, und man sieht nicht ein, warum einer Anzahl suspendierter Körper nicht derselbe osmotische Druck entsprechen sollte, wie der nämlichen Anzahl gelöster Moleküle. Man wird anzunehmen haben, daß

"According to this theory, a dissolved molecule is differentiated from a suspended body only by its size, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules."

Colloids = Atoms

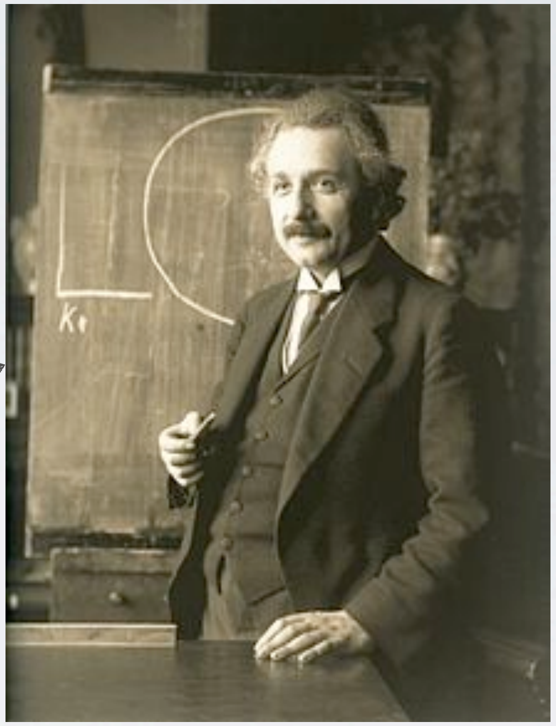
Who is That Scientist?

Albert Einstein

Robert Brown

Jean-Baptiste Perrin

Marian Smoluchowski



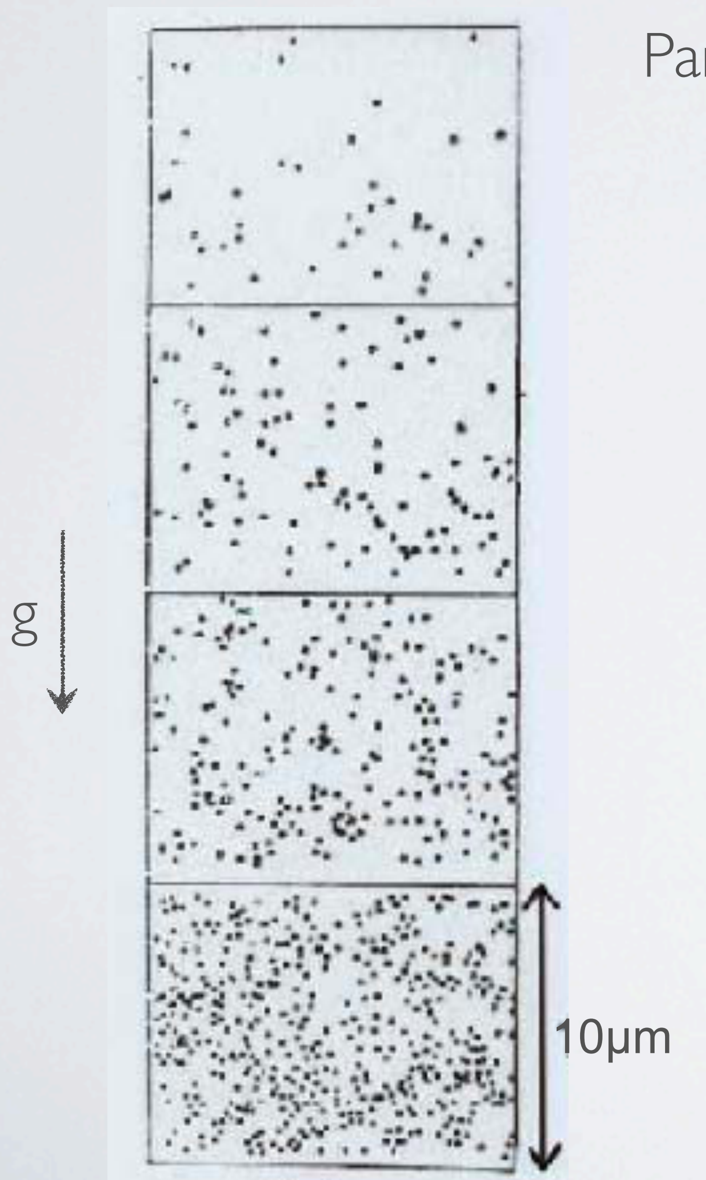
Nobel prize 1926
"For his work on the discontinuous structure of matter, and especially his discovery of the sedimentation equilibrium"

PERRIN'S EXPERIMENT (1907)

Avogadro constant $N_A = 6.02 \cdot 10^{23}$

number of atoms in one gram of hydrogen or 12 g of carbon

Gamboge particles, R=0.3um



Particles are Boltzmann distributed in the gravitational potential

$$\frac{n(z)}{n(0)} = \exp\left[-\frac{V(z)-V(0)}{k_B T}\right]$$

$$V(z) = \Delta m g z$$

Archimedes

$$\Delta m = \frac{4\pi}{3} R^3 (\rho_p - \rho_o)$$

$$\frac{n(z)}{n(0)} = \exp\left[-\frac{\Delta m g z}{k_B T}\right]$$

Number of Avogadro

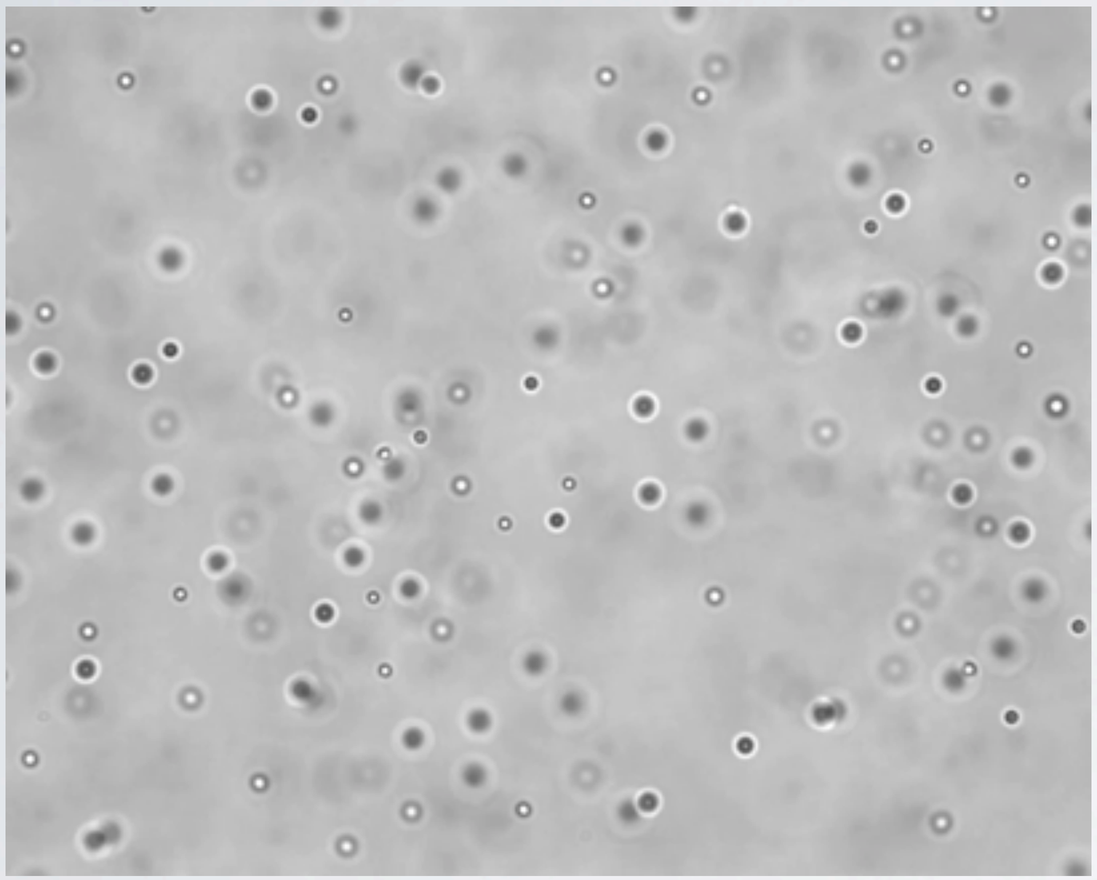
$$N_A = \frac{R}{k_B}$$

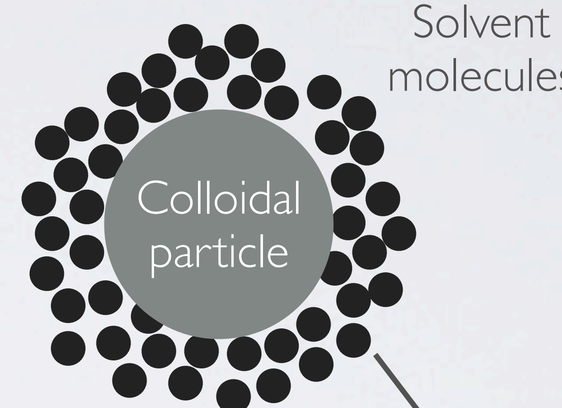
Perrin

$$N_A = 6.82 \cdot 10^{23}$$

Colloids = Atoms

Colloids Undergo Brownian Motion





random fluctuating force from collisions with solvent molecules (10^{-12} s)

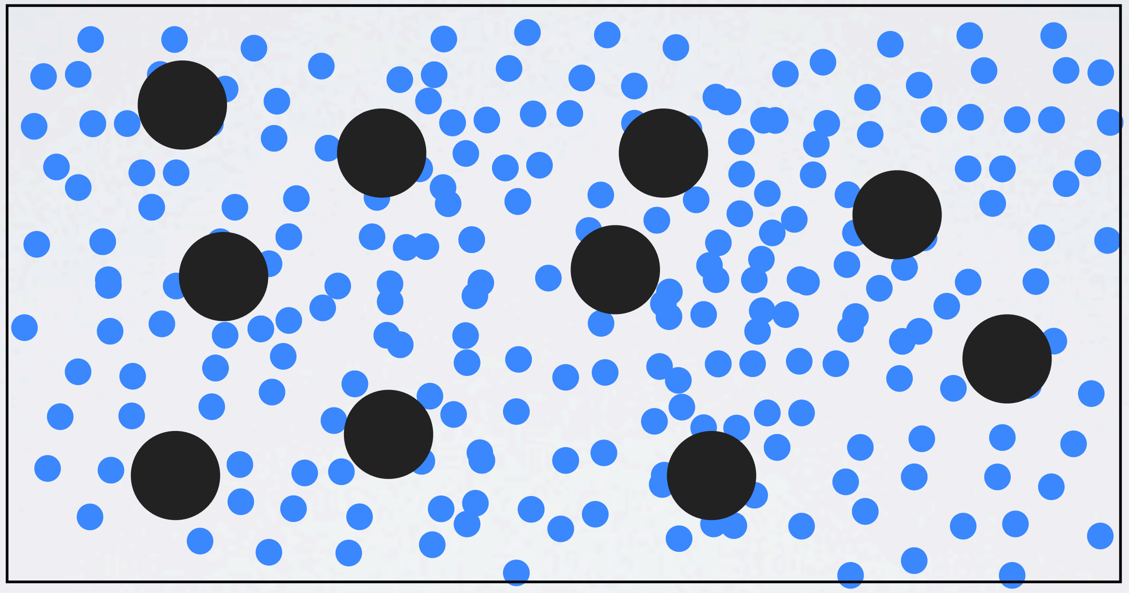
$$m\frac{d\vec{v}(t)}{dt} = -\zeta\vec{v}(t) + \vec{\xi}(t)$$

mass of particle | velocity of particle | viscous friction

For spheres: $\zeta = 6\pi\eta r$

Brownian motion of colloidal particles is just a large-scale manifestation of the thermal motion of the solvent molecules.

Concentrated Colloidal Suspensions



Particle interactions

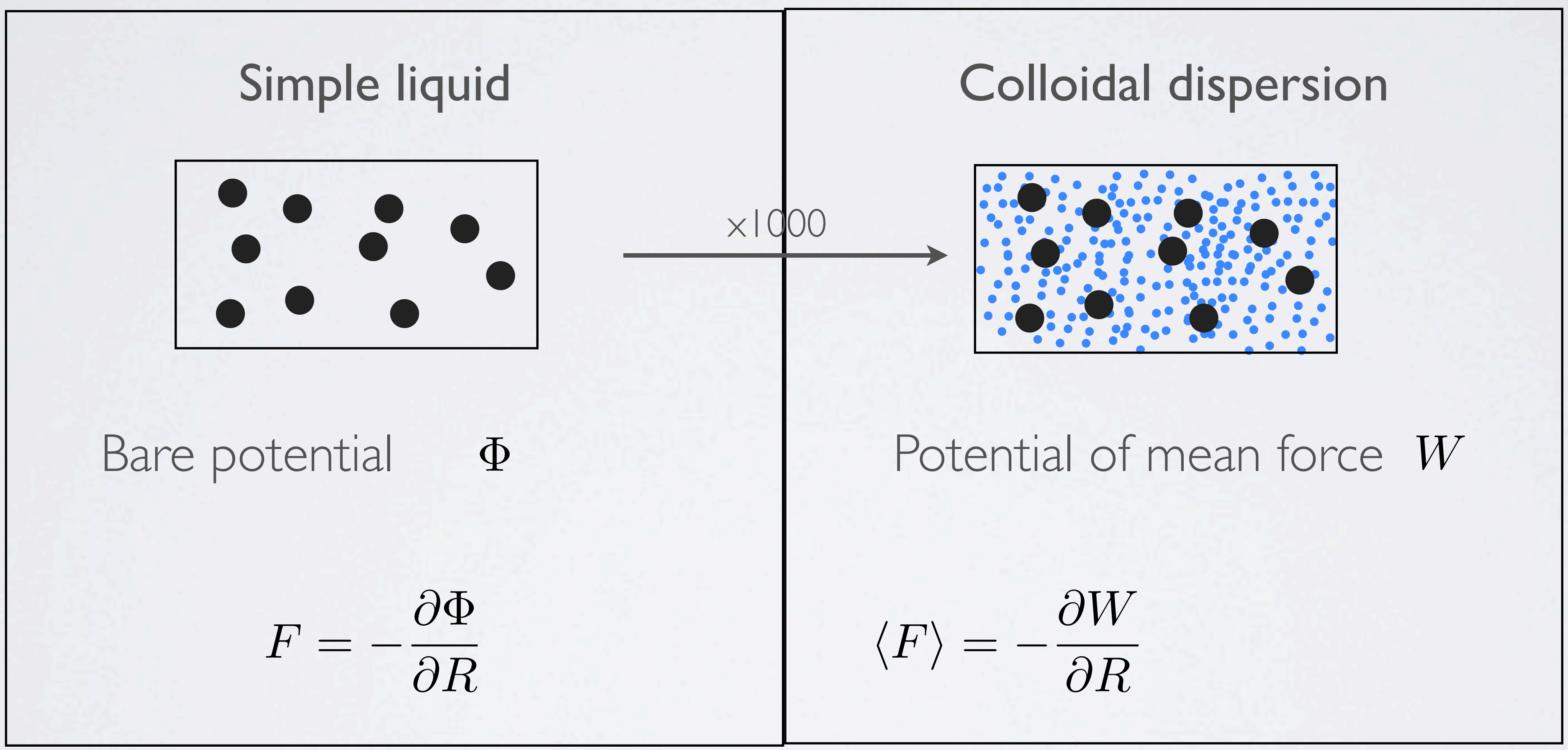
+

Statistical physics

Colloid-Atom Analogy

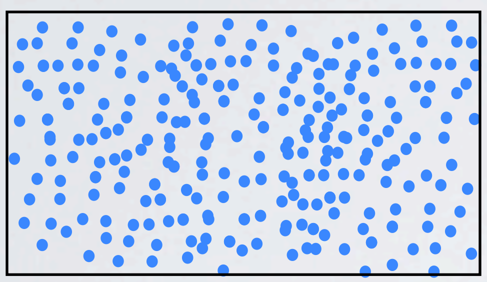
Key concept

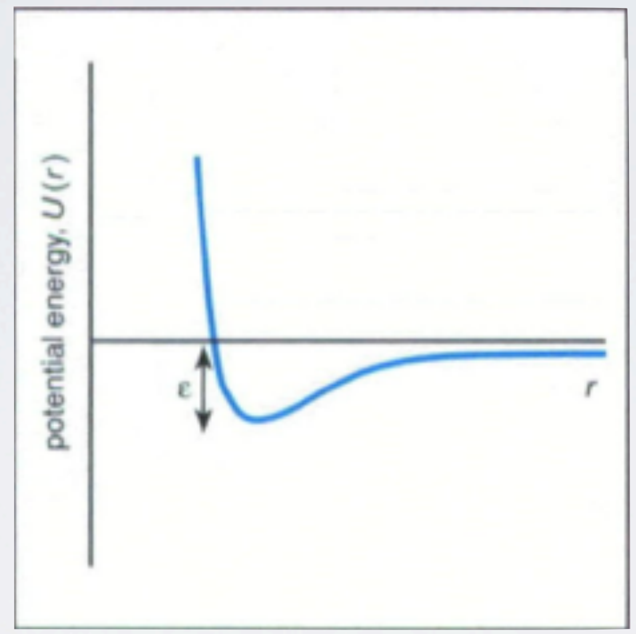
The same concepts and methods of the statistical mechanics of simple liquids can be applied to colloidal suspensions. One must simply replace the bare potential V(r) by the potential of the average force W(r).

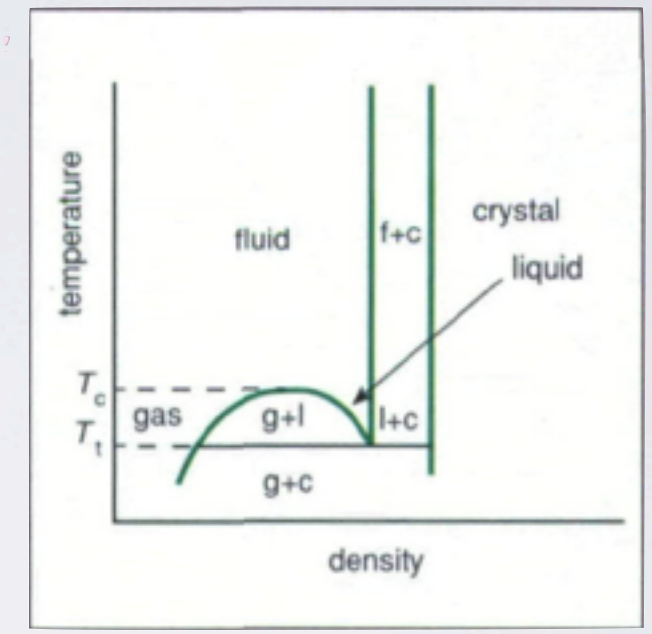


Phase Behavior of Atoms and Colloids

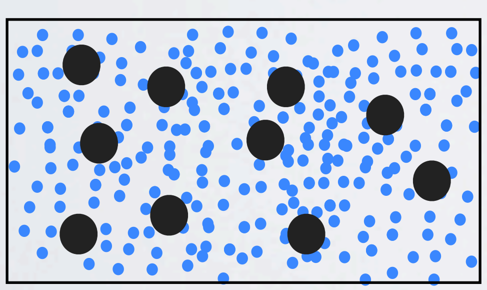
Atoms

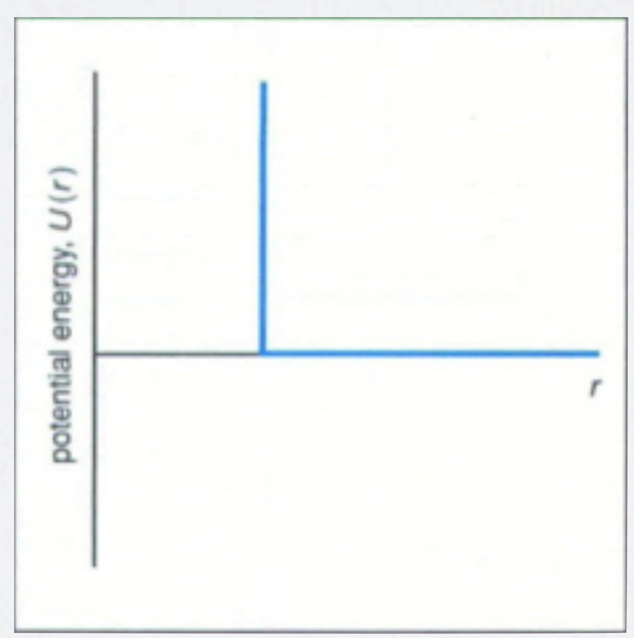


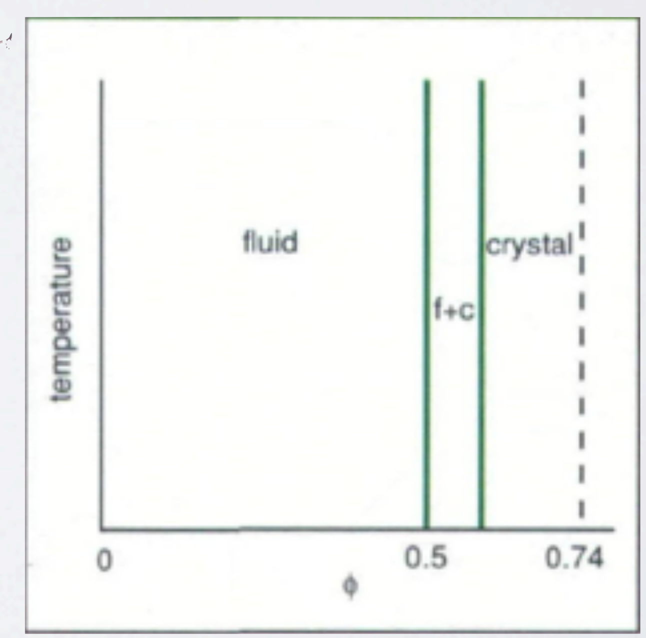




Hard-sphere colloid

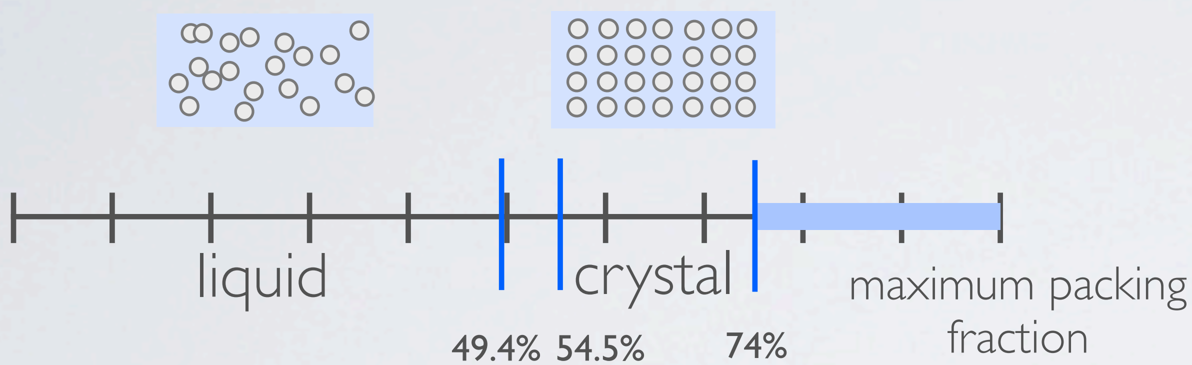


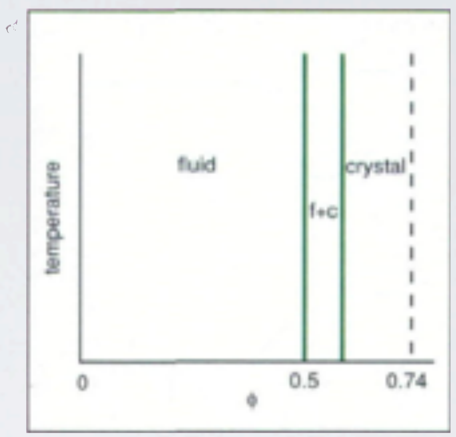


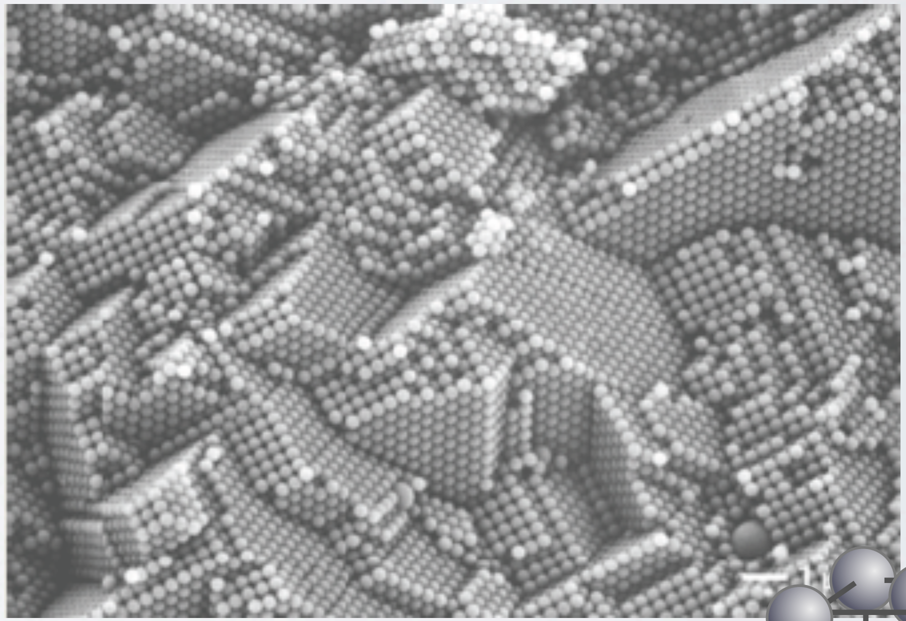


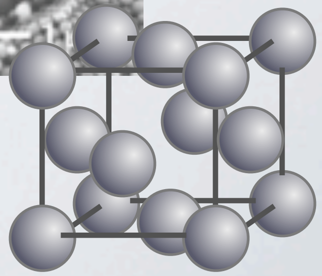
Poon, Pusey, Lekkerkerker, Physics World (1996)

PHASE DIAGRAM OF HARD SPHERE COLLOIDS







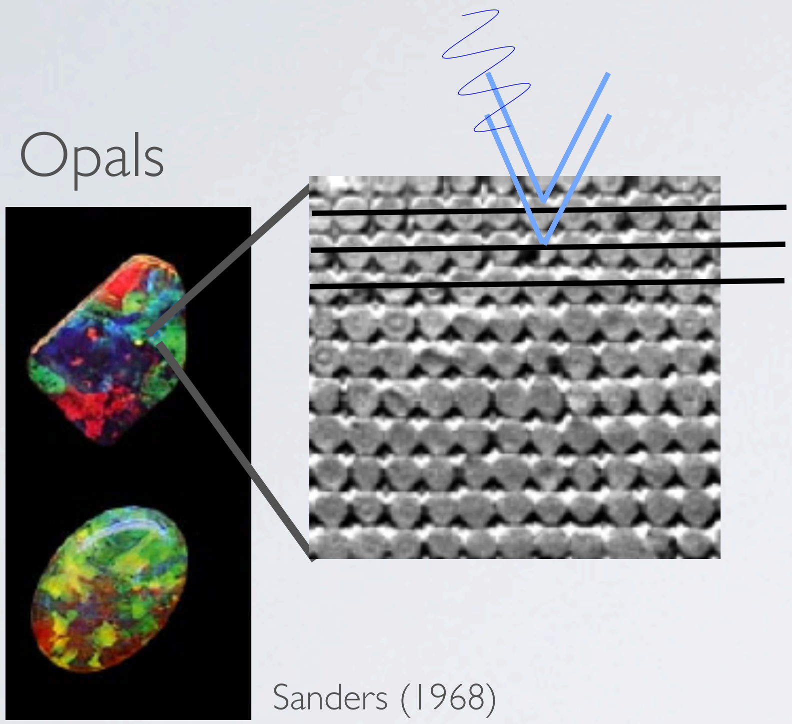


Colloidal fcc crystal made with lattice constant 0.5um

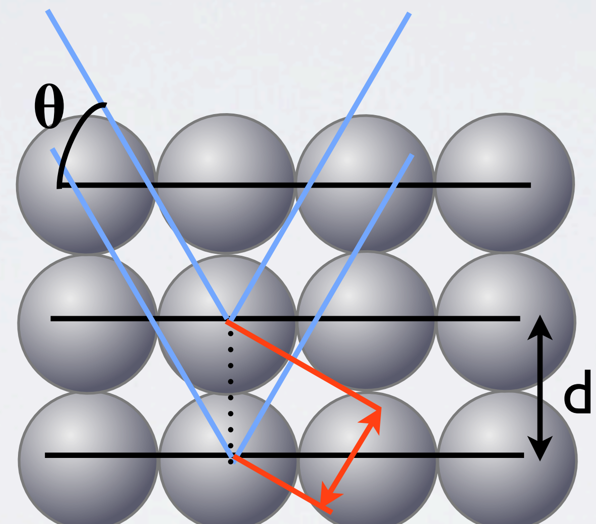
P. N. Pusey, E. Zaccarelli, C. Valeriani, E. Sanz, Wilson C. K. Poon, M.E. Cates, Phil Trans A. (2009)

Experiment: Latex Paint Stain

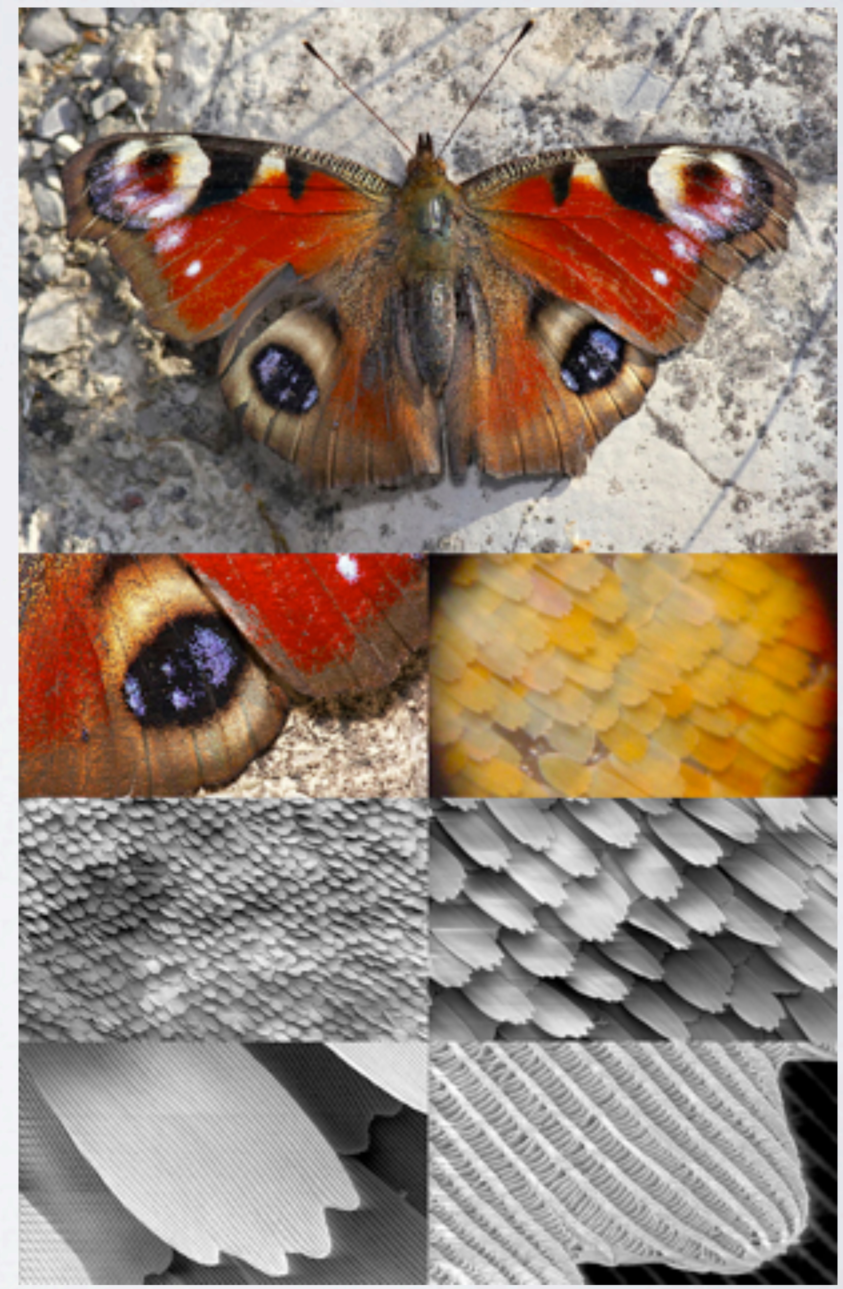
Opals



Sanders (1968)

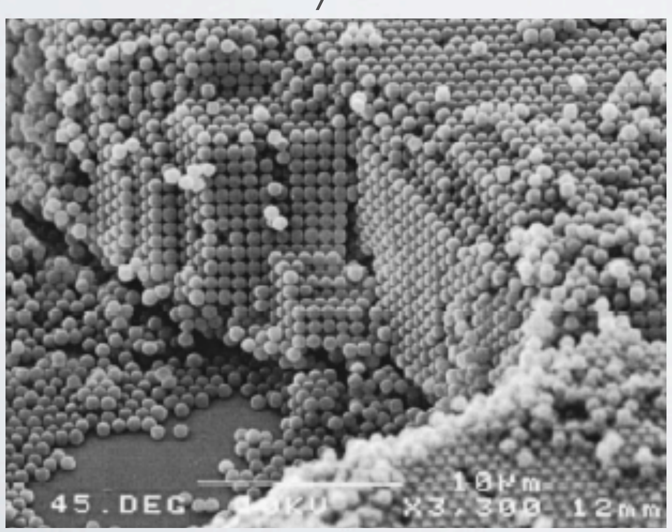


Iridescent feathers, bugs,...



"Butterfly magnification series collage", Wikipedia

Colloidal crystal

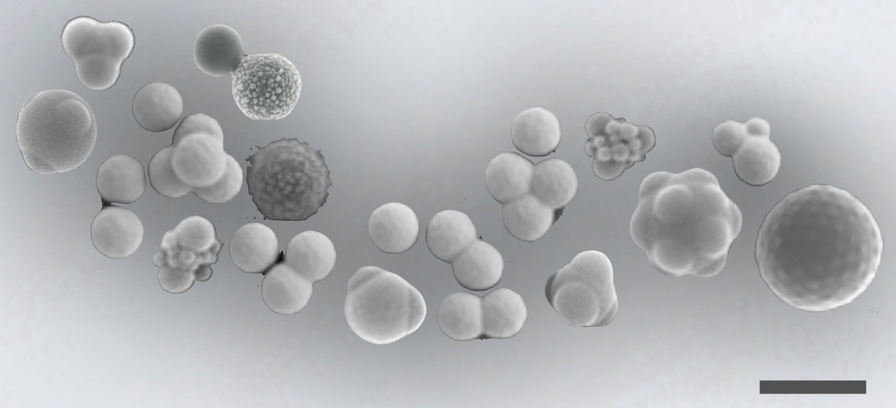


Amos et al., PRE 61, 2929 (2000)

Bragg's law

$$2d\sin\theta = n\lambda$$

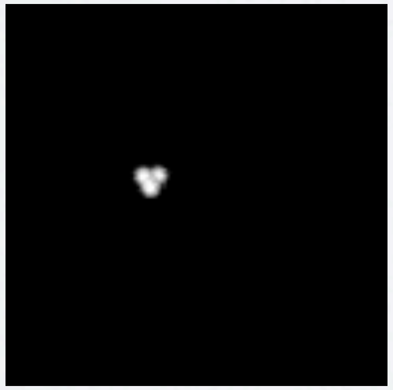
WHY COLLOIDAL PARTICLES?



Size:
~2nm-10μm

- Constant randomization of the sample
  - System reaches energy minimum
  - Self-assembly

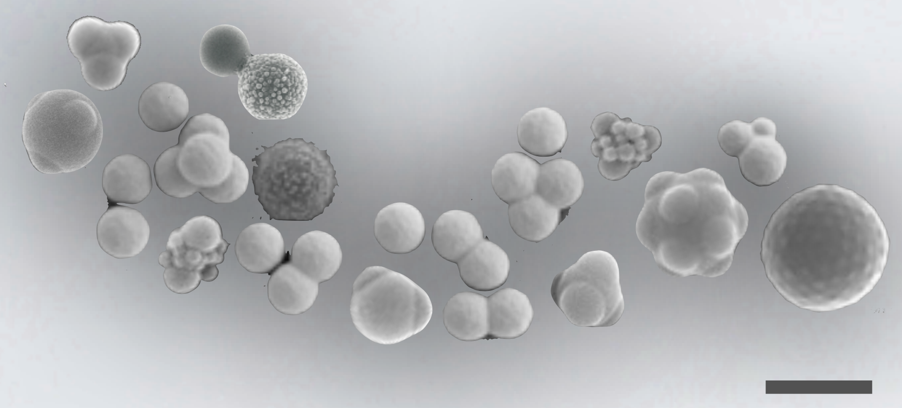
- Observable by microscopy



Kraft et al. PRE 88(2013)

- Tunable interactions

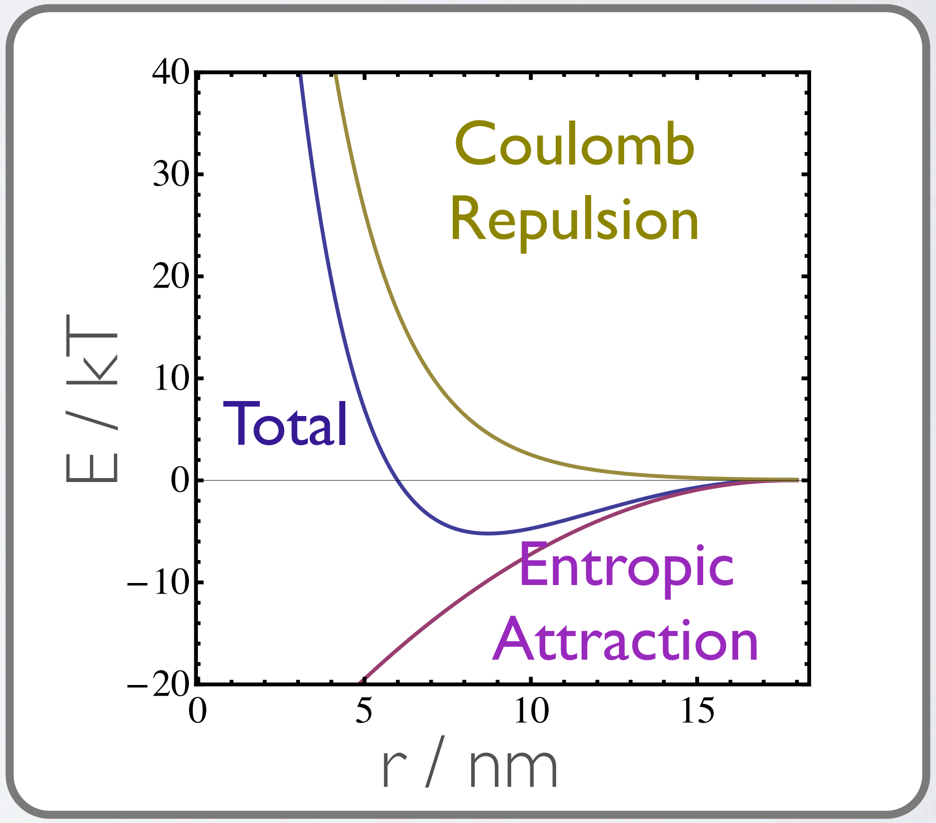
WHY COLLOIDAL PARTICLES?



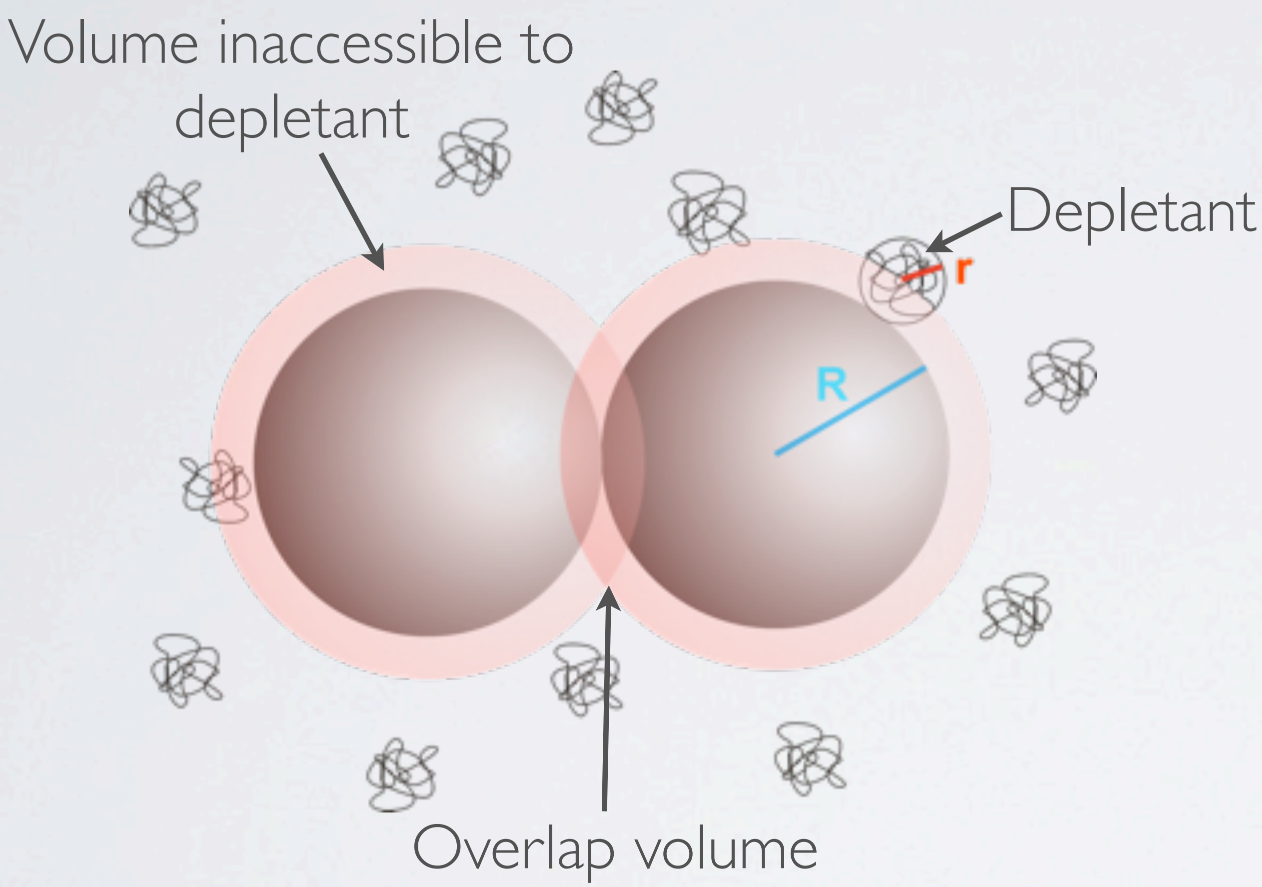
Size:
~2nm-10μm

→ Tunable interactions

- Van der Waals forces
- Coulomb Repulsion
- Magnetic forces
- Entropic forces (depletion)
- Sticky DNA linkers
- Steric repulsion
- ....



The Depletion Interaction



Effective attraction between larger colloid!

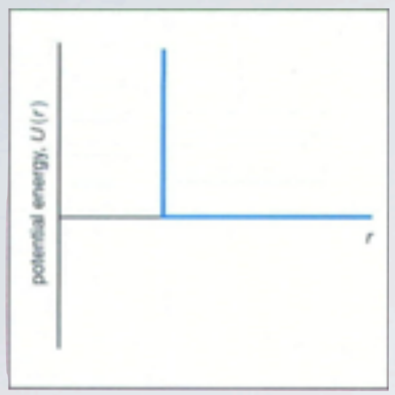
$$u = -\Pi\, V_{overlap}$$
$$= -k_B T\, n_{depl}\, V_{overlap}$$

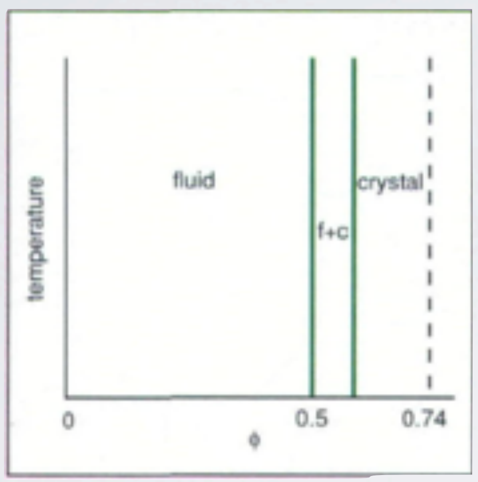
Depletion forces are entropic forces!

Asakura, Oosawa,, J. Chem. Phys. (1954)
Vrij Pure & Appl Chem. (1976)

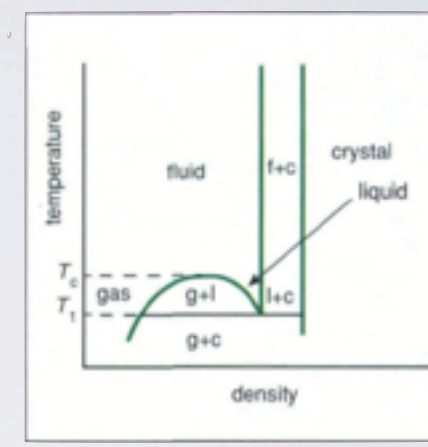
Tunable Interactions
Tunable Phase Diagram

Hard sphere interaction

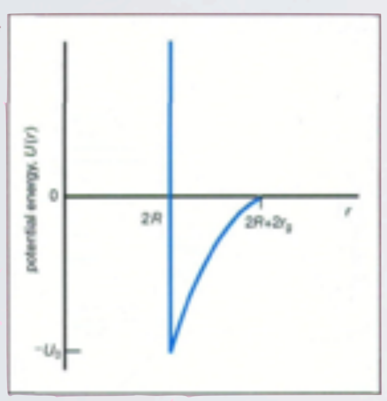


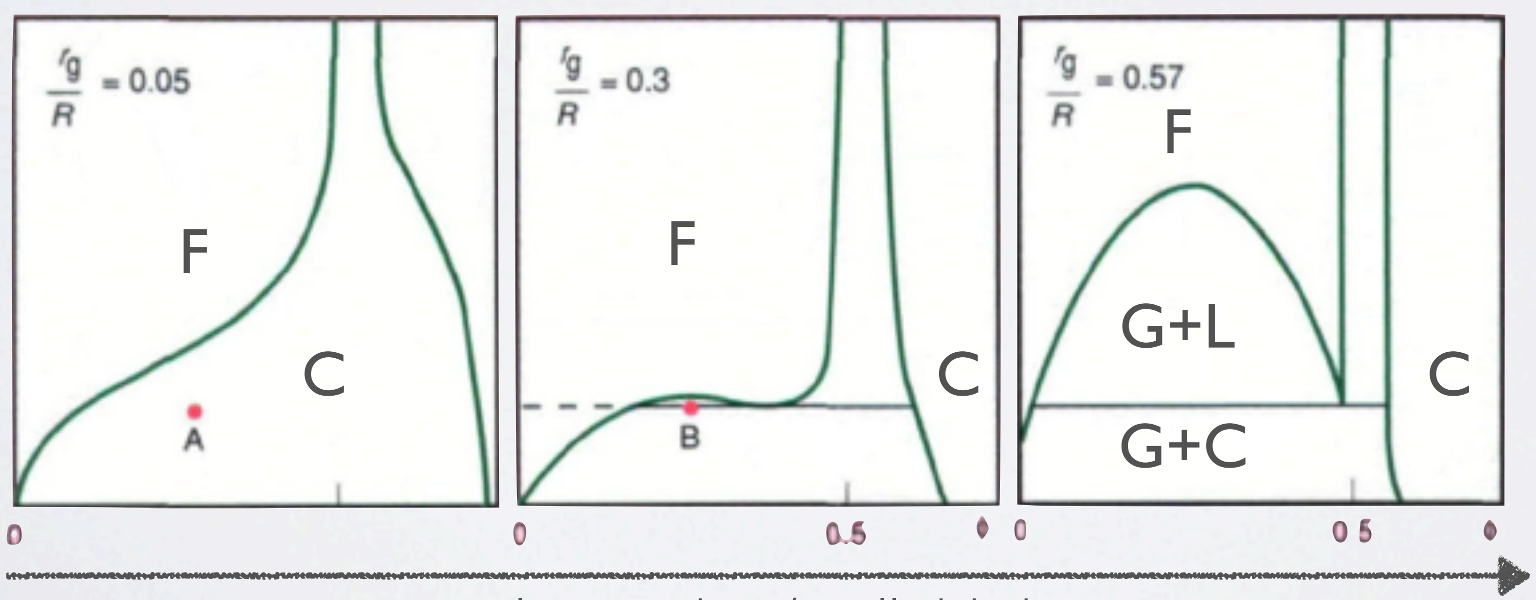


atom phase diagram



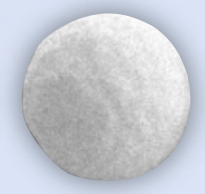
Hard sphere + depletion attraction



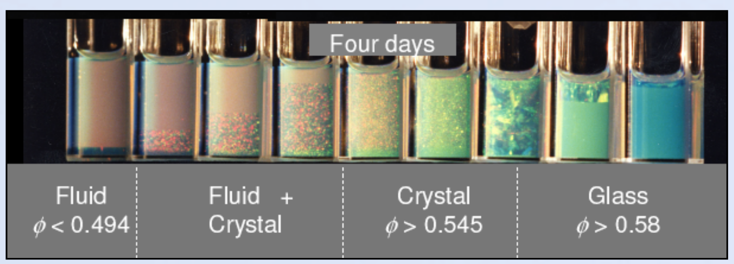


polymer size / colloid size
= interaction range

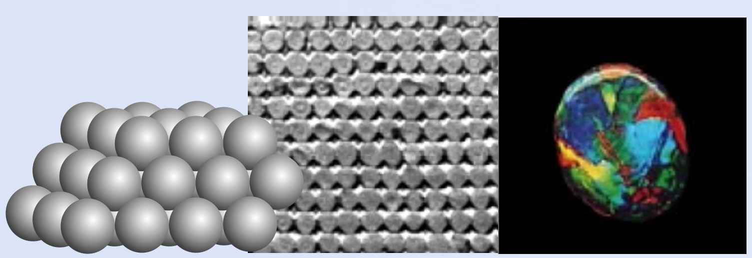
From Spheres to Complex Particles



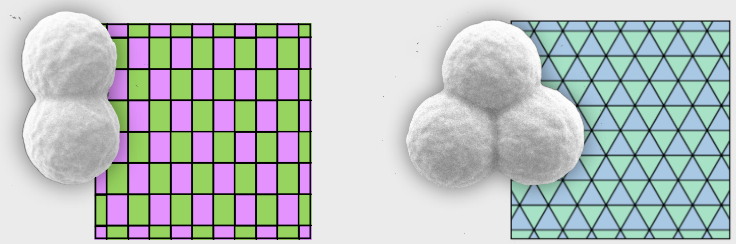
model 'atom'



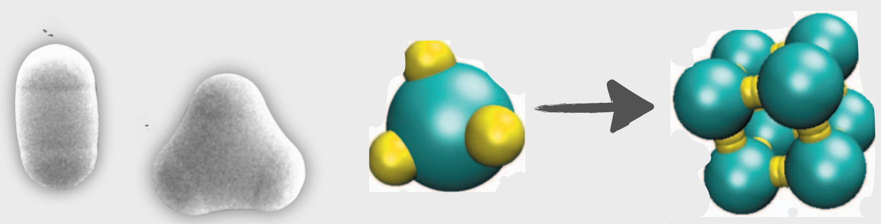
Pusey, van Megen, Nature (1986)



Anisotropic shape

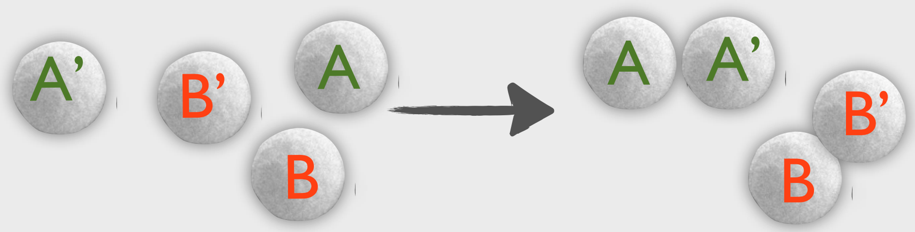


Anisotropic interactions



Wilber et al. JCP (2009)

Highly specific interactions



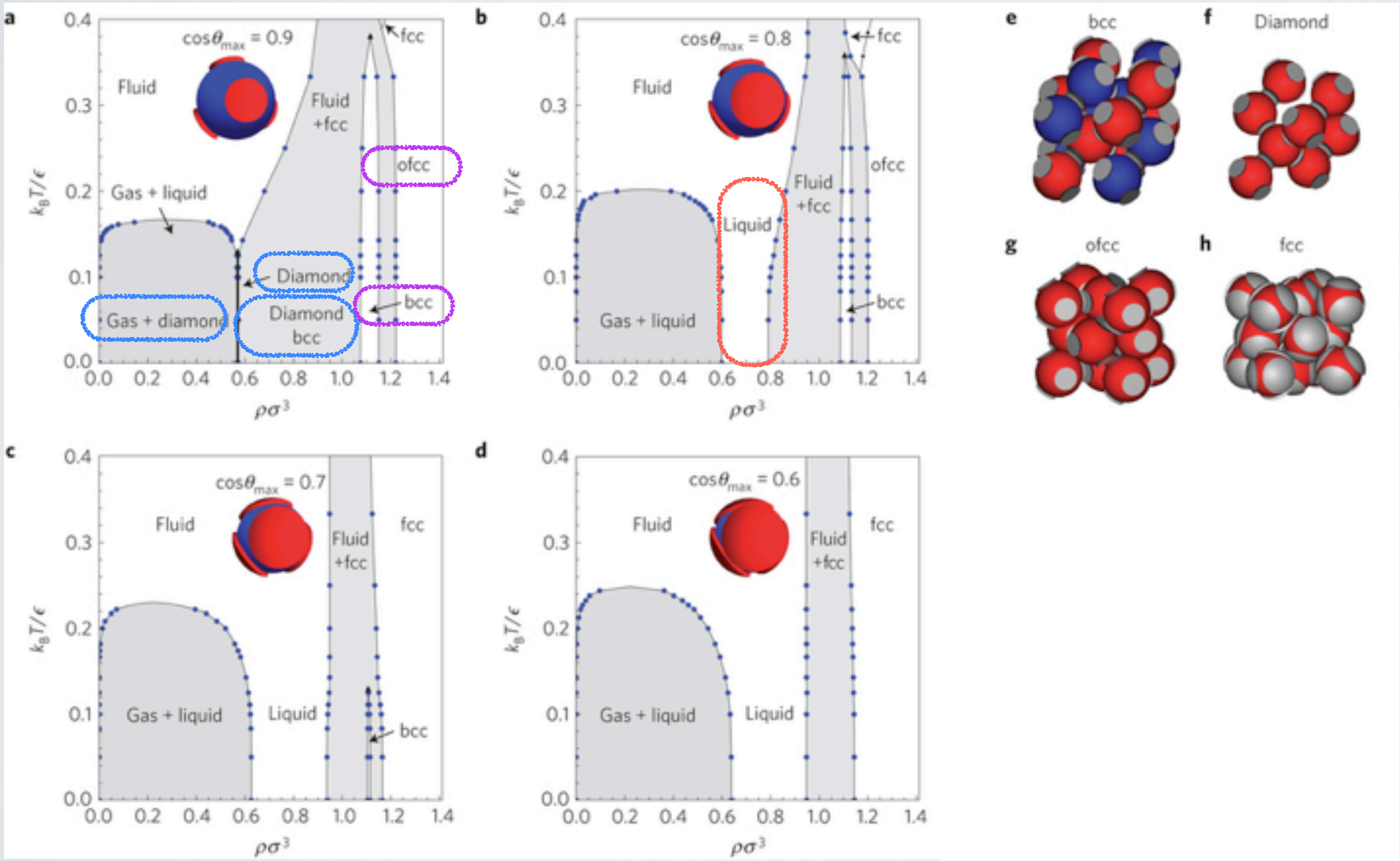
+ External guiding rules
+ activity

Particle shape
and interactions

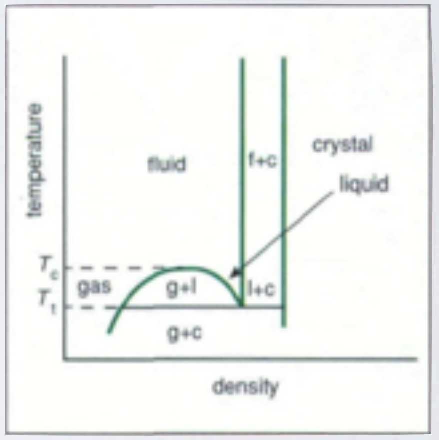
Assembled structure

Understand & Design
self-assembly

Patchy Particles: Liquid Phase can be preferred over the Solid Phase!

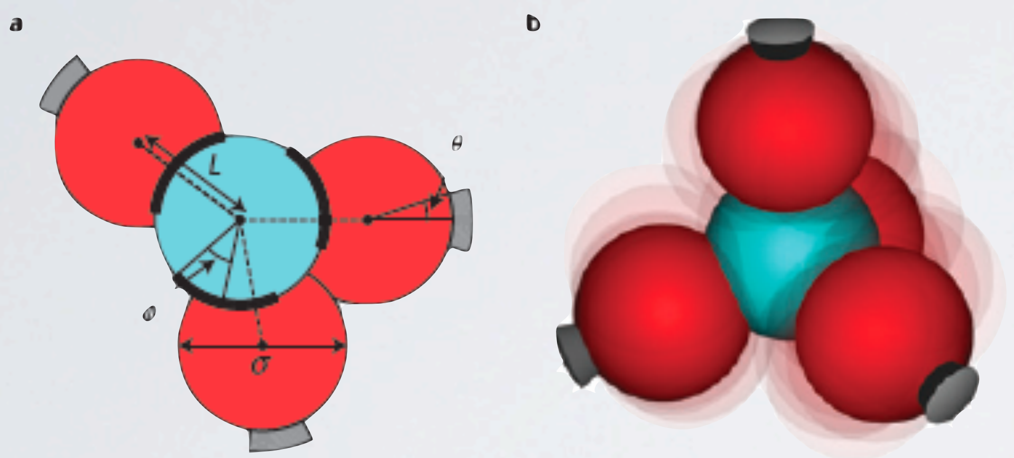


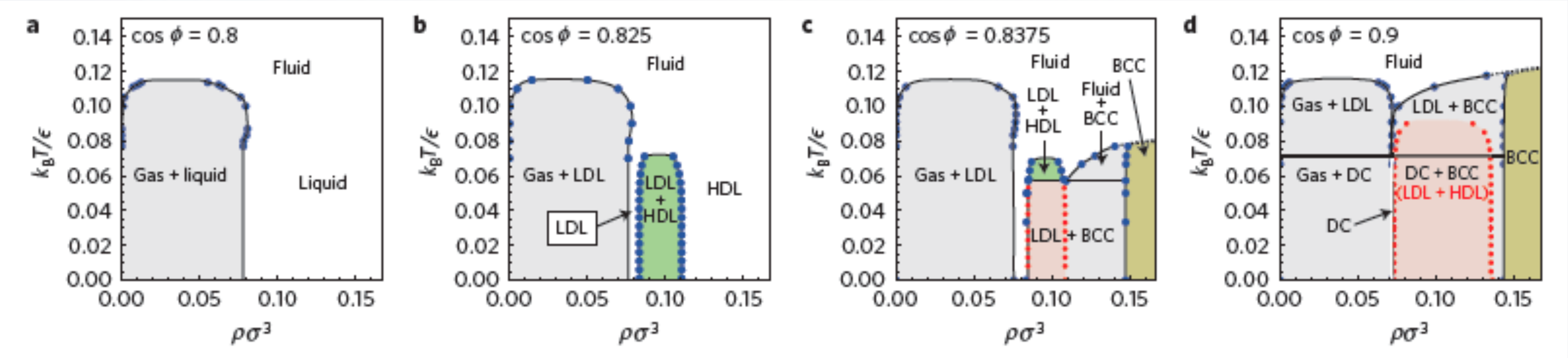
simple liquid phase diagram



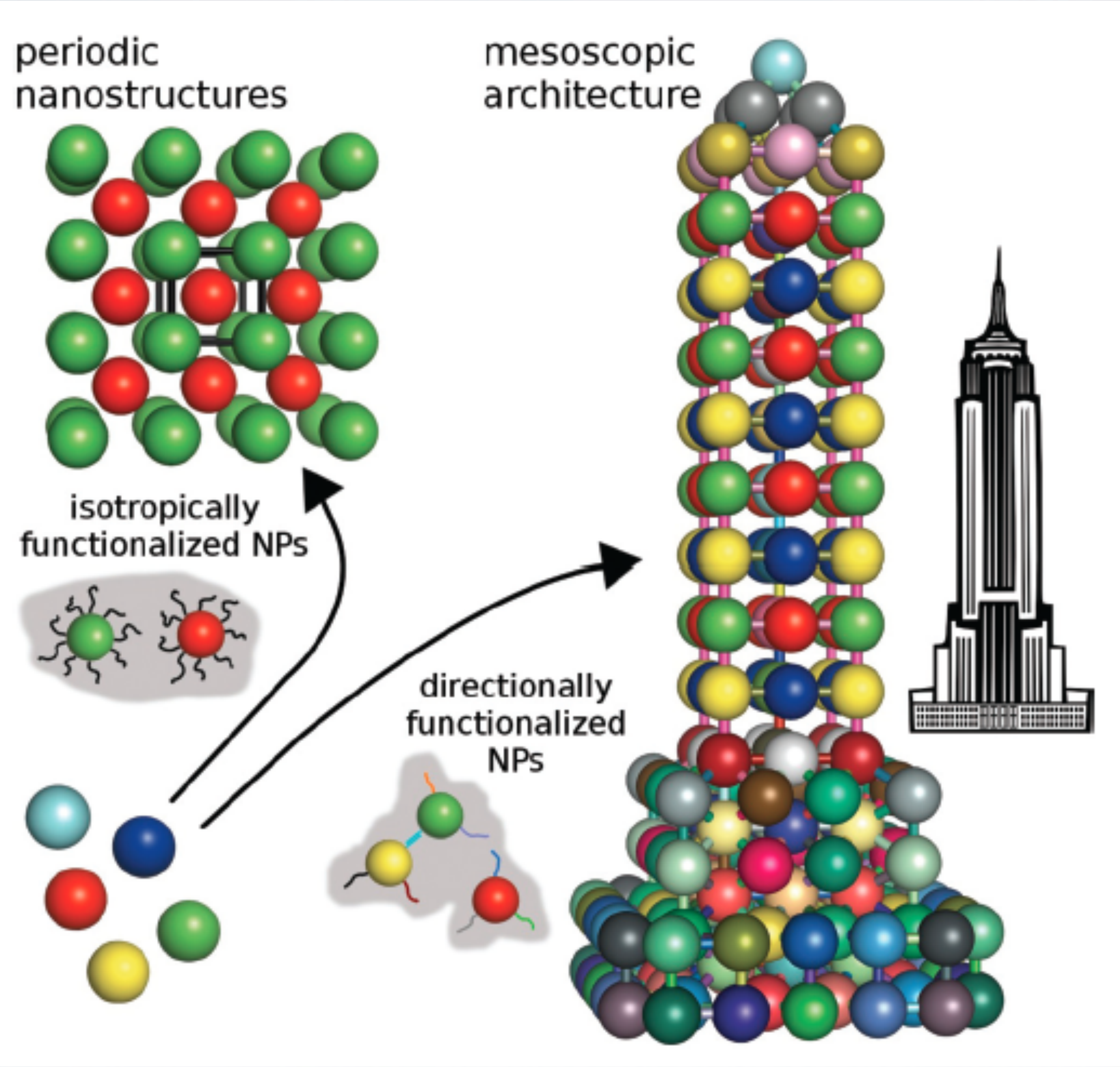
Smallenburg & Sciortino, Nature Physics 9, 554–558 (2013)

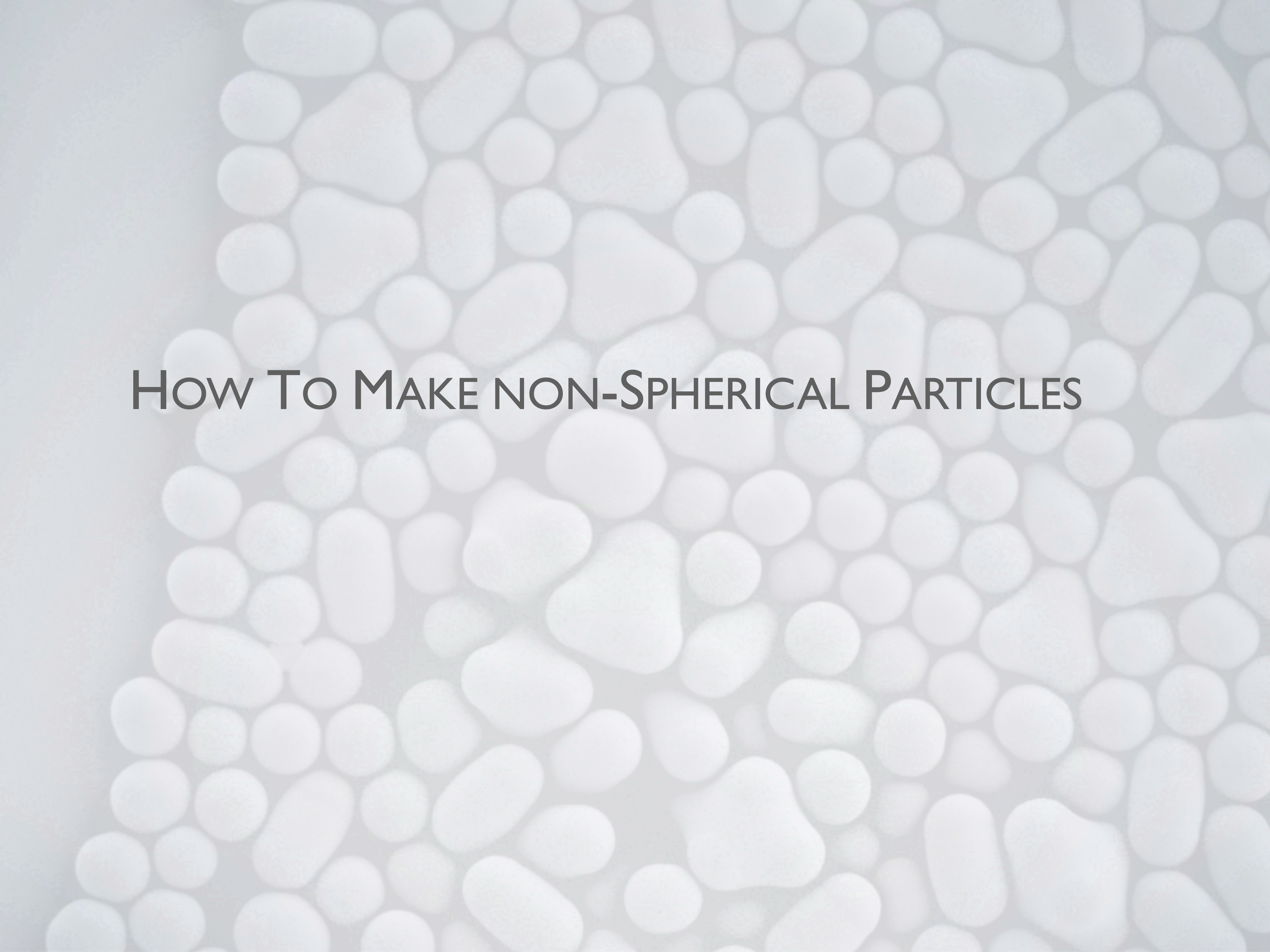
Flexible and Directional Interactions May Lead to Strange New Phase Behavior





DNA-coated Colloids can in Principle Build Arbitrarily complex Structures

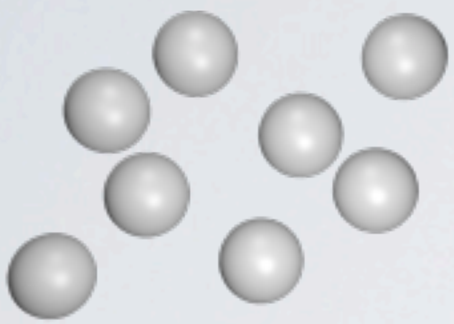




How To Make non-Spherical Particles

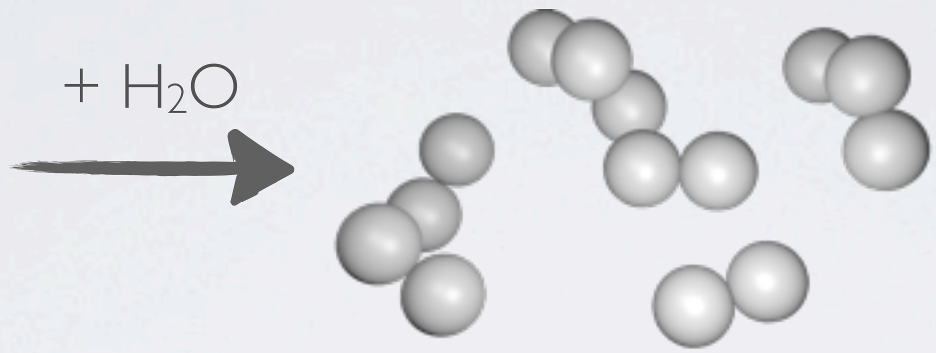
Reshaping Random Colloidal Clusters

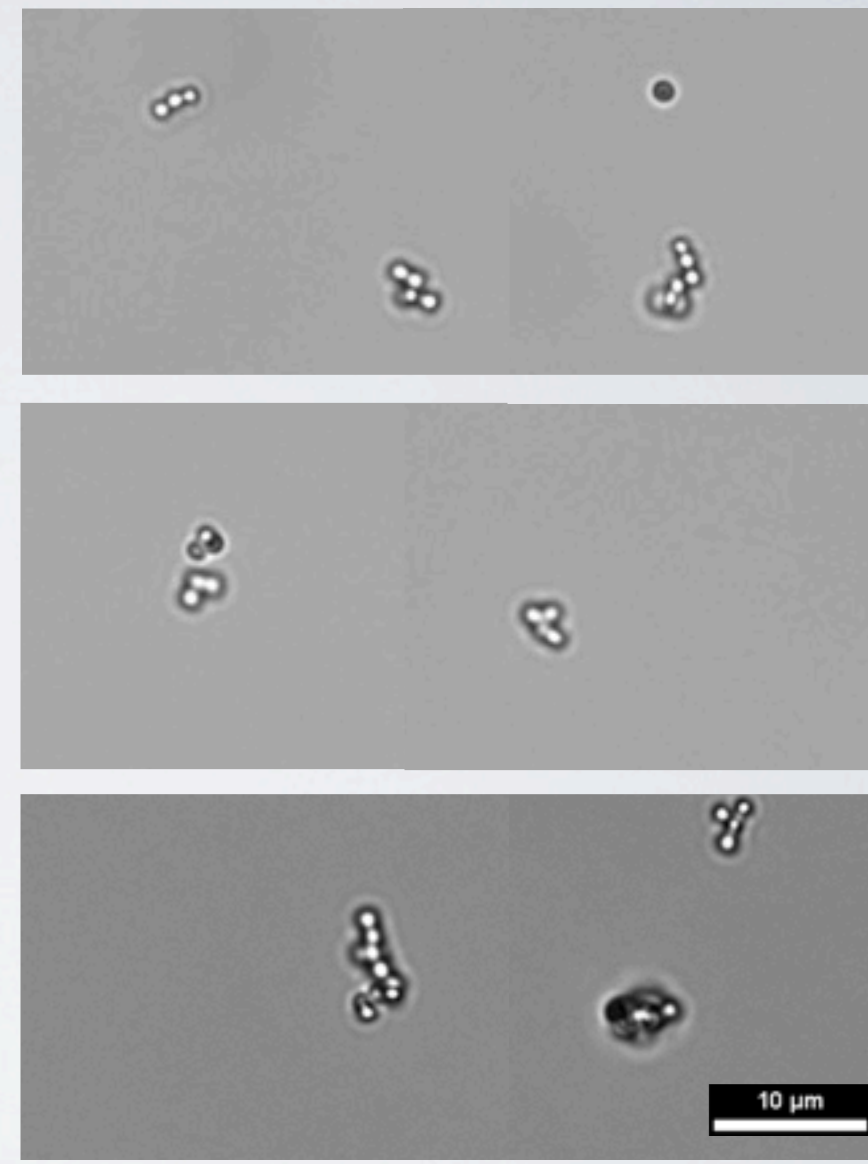
random clusters



+ salt

+ H_2O



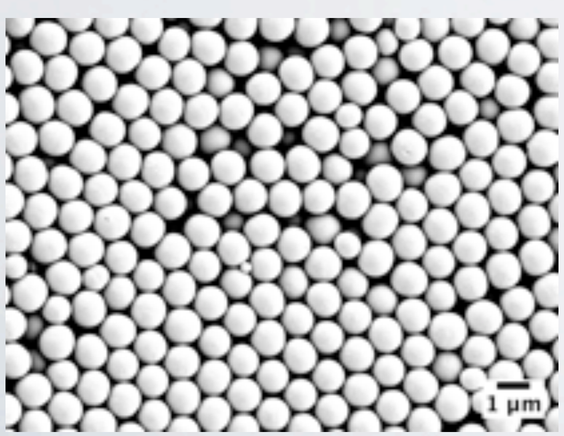


induce aggregation

quench

swelling

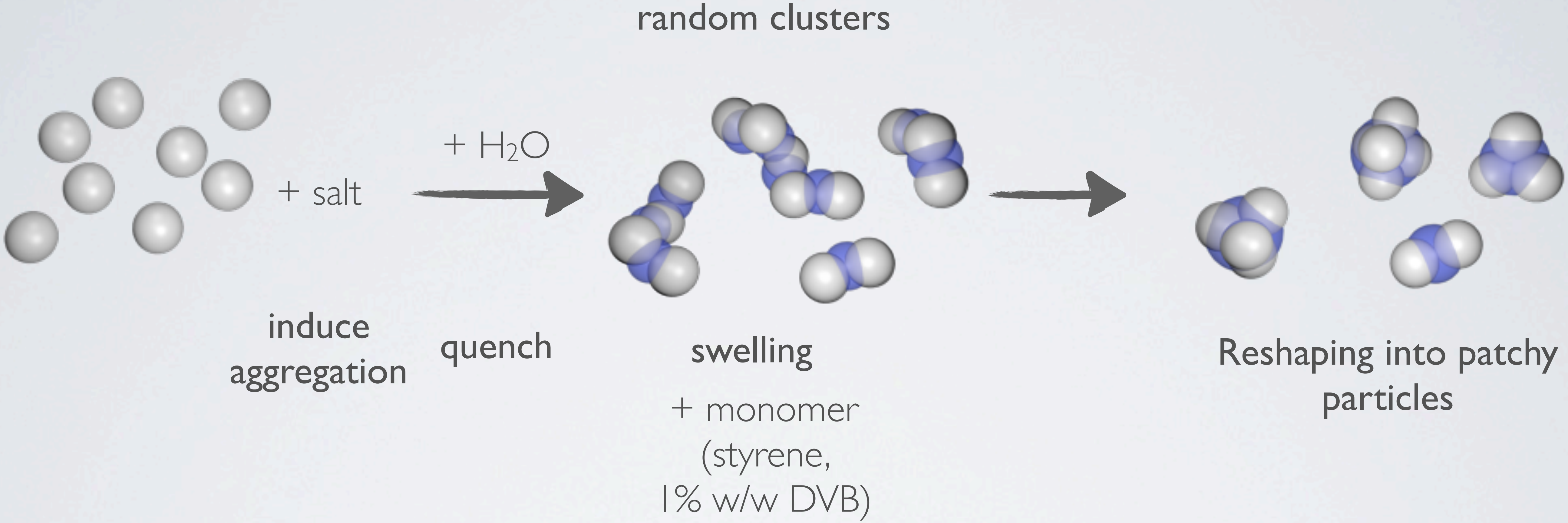
Charge stabilized PS colloids



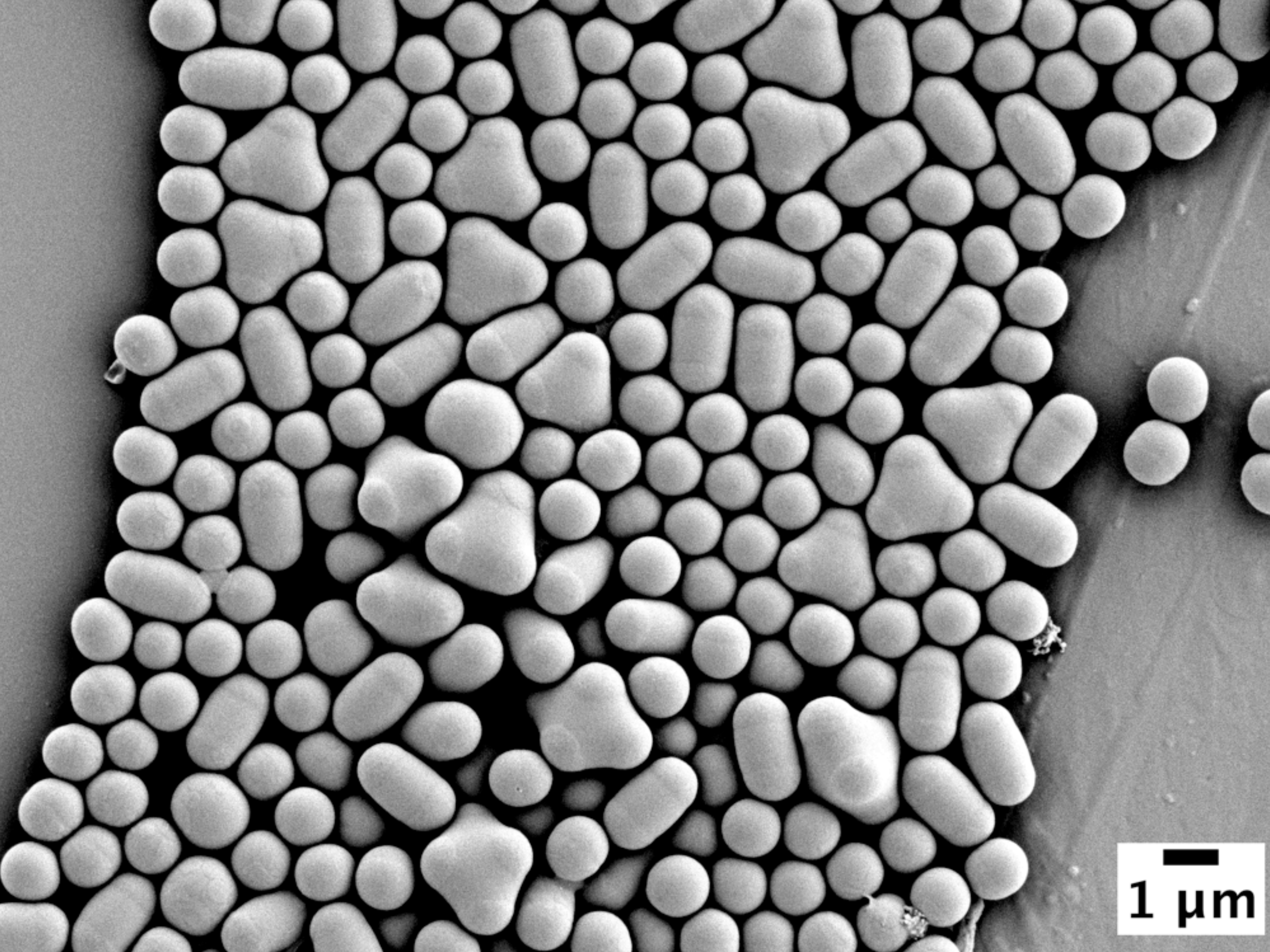
~1µm diameter, 1% crosslink density, purchased from Magsphere

Meester, Verweij, vd Wel, Kraft (ACSNano 2016)

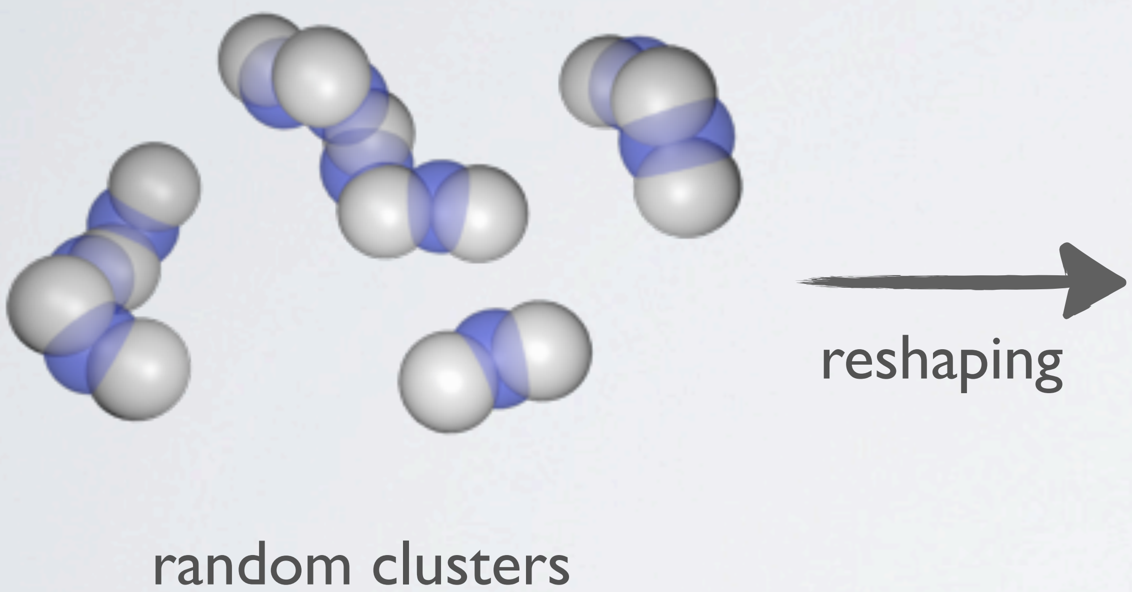
RESHAPING RANDOM COLLOIDAL CLUSTERS

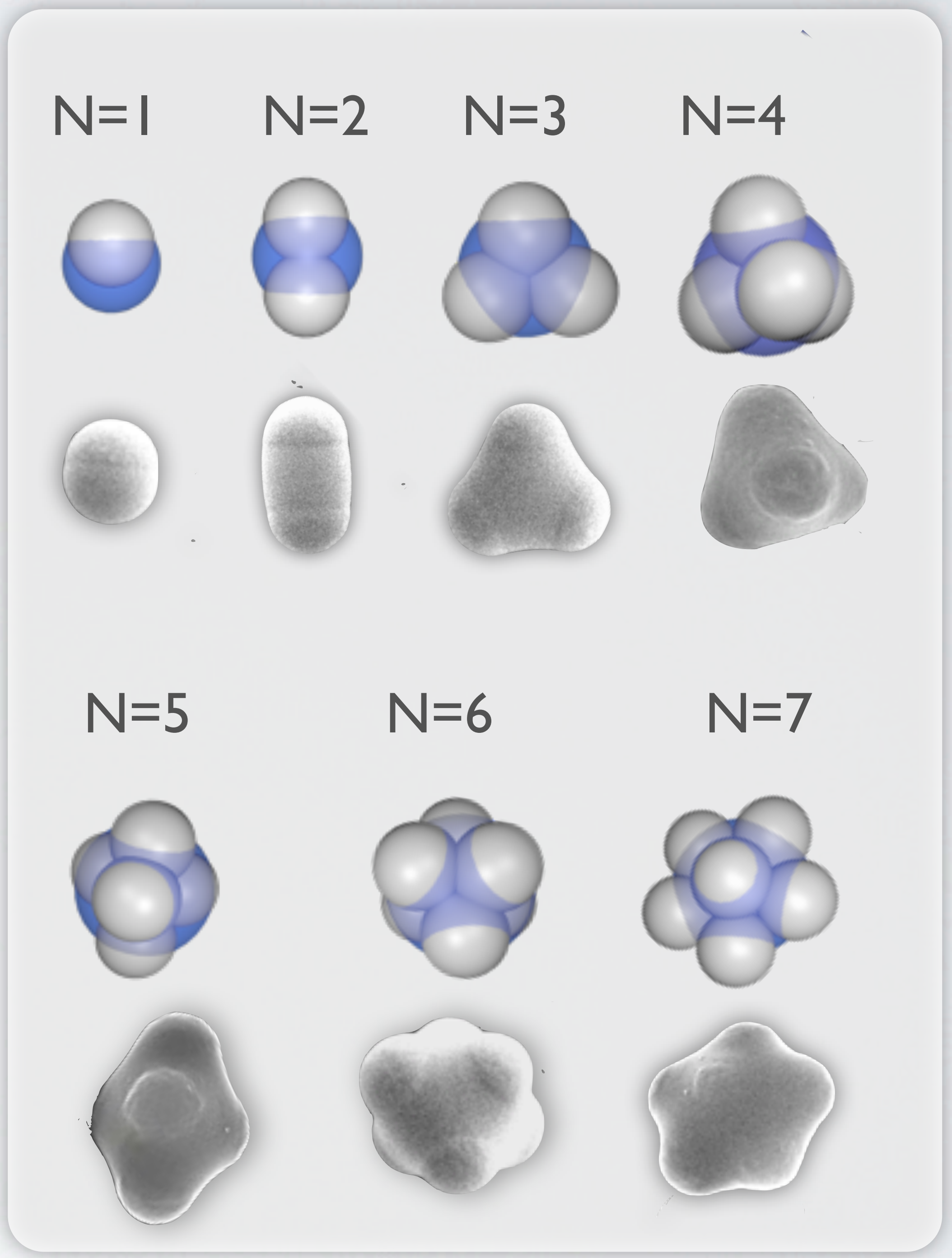


Meester, Verweij, vd Wel, Kraft (ACSNano 2016)


1 μm

Particle Swelling Reshapes the Random Clusters into Uniform Patchy Particles

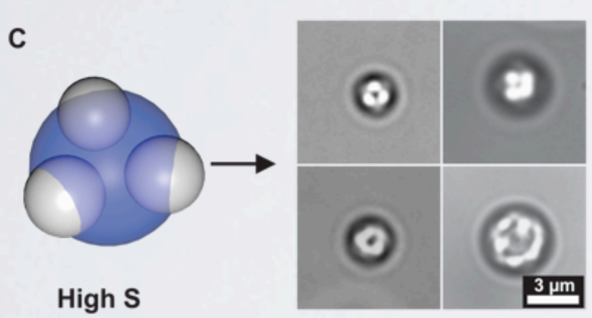




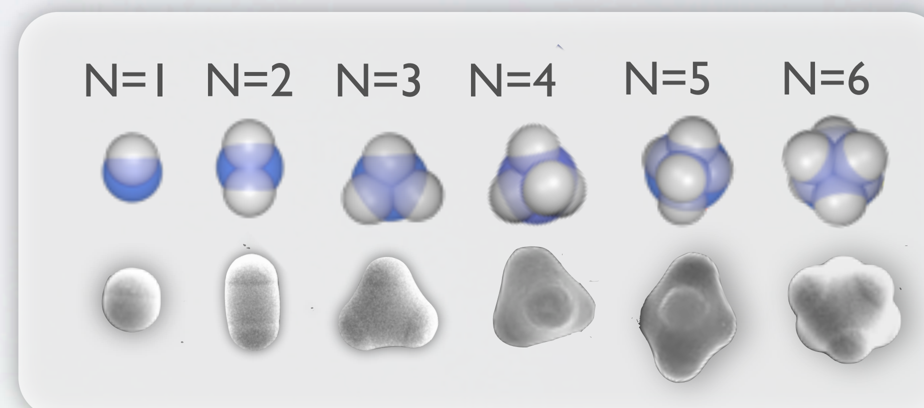
Coalescence driven Reconfiguration

Liquid droplet coalescence drive rearrangement

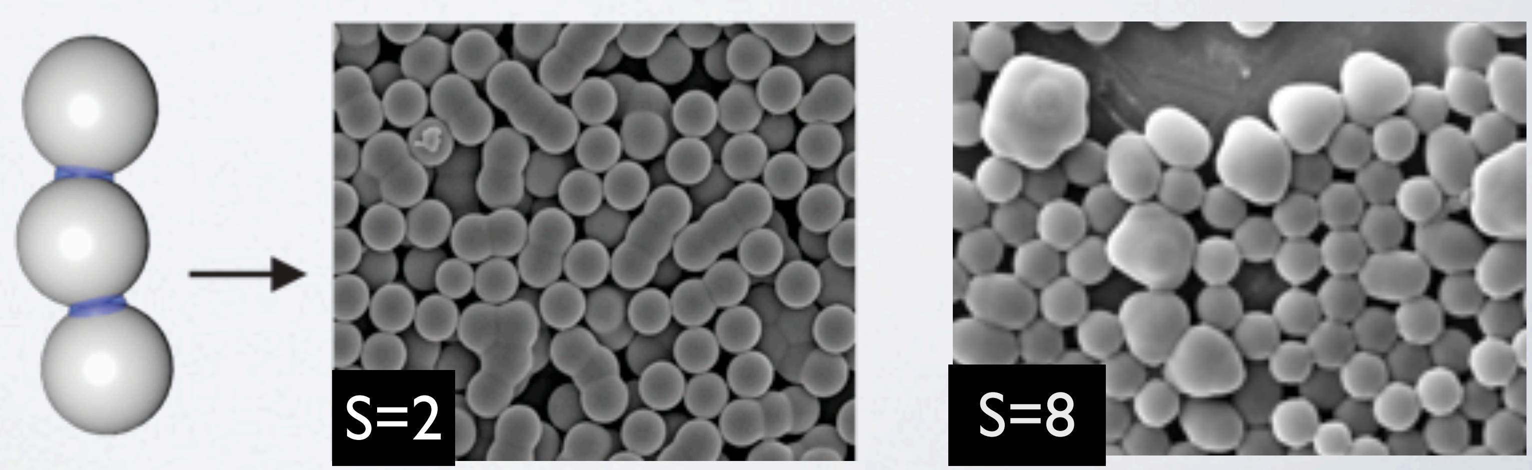
Liquid droplet confines the spheres



Cluster minimize the second moment of the mass distribution

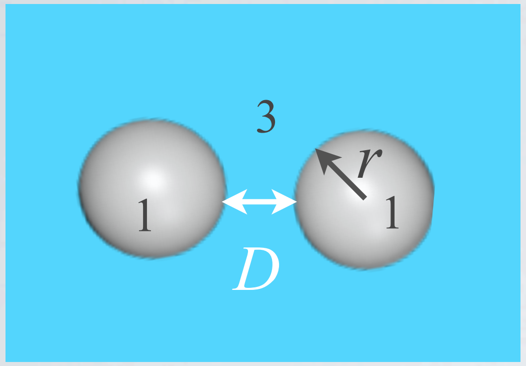


Insufficient swelling
- ➡ no / small liquid bridges
- ➡ no reconfiguration!



Meester, Verweij, vd Wel, Kraft (ACSNano 2016)

What enables Reconfiguration?



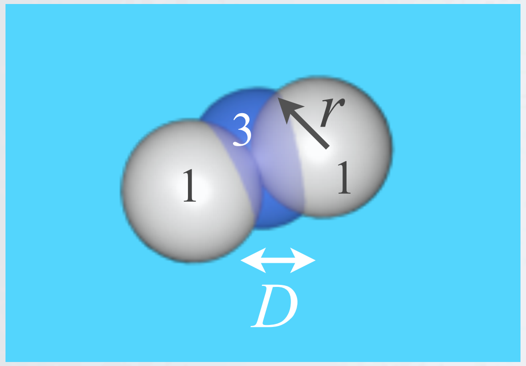
Van der Waals interaction energy $W(D) = -\frac{Ar}{12D}$

with the Hamaker constant A (Lifshitz theory)

$$A = \frac{3}{4}k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}$$

polystyrene spheres: $\epsilon_{PS} = 2.55 \quad n_{PS} = 1.557$

polystyrene spheres in water: $\epsilon_w = 80 \quad n_w = 1.333 \quad A_{PS-w} = 1.5 \cdot 10^{-20} J$



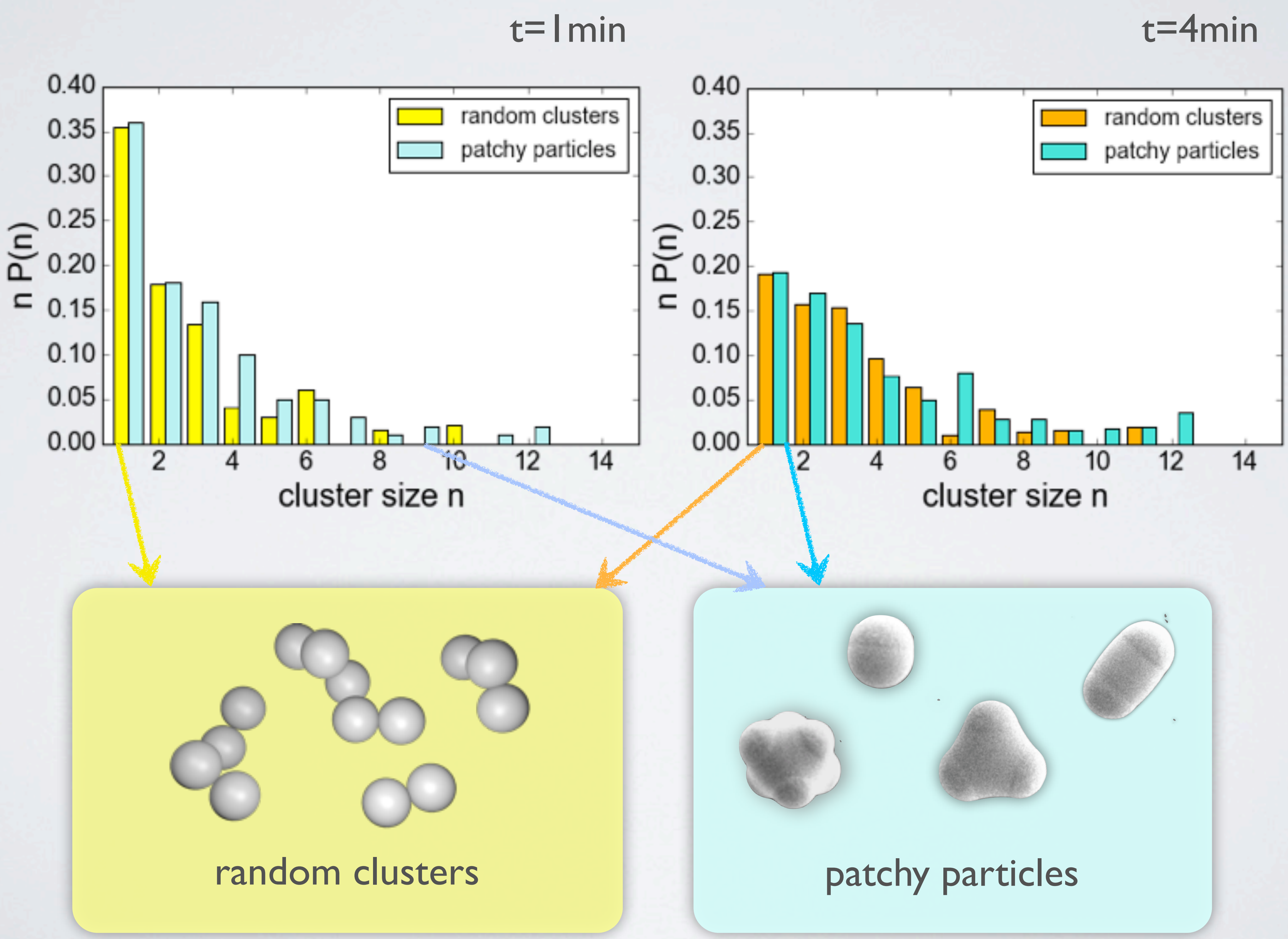
polystyrene spheres in styrene:

$\epsilon_{st} = 2.8 \quad n_{st} = 1.448 \quad A_{PS-st} = 5.3 \cdot 10^{-23} J$

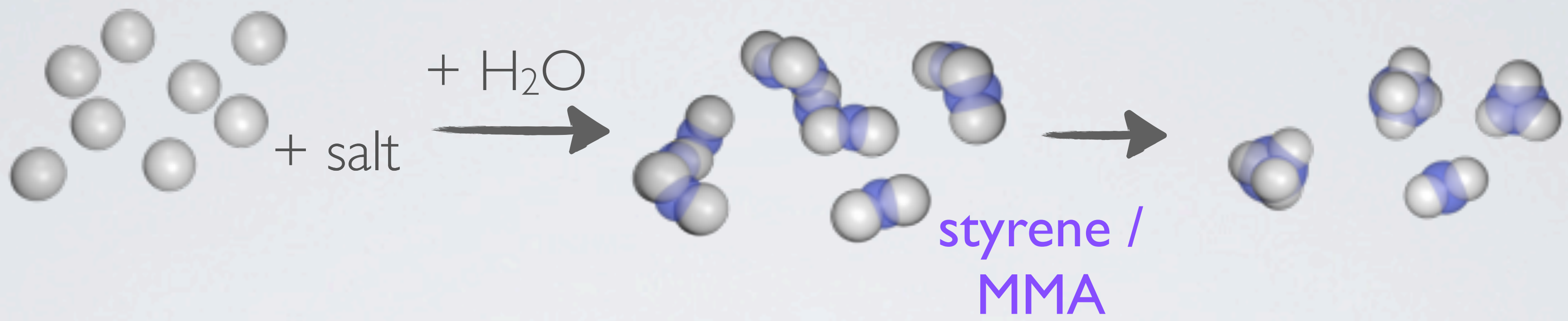
Significant reduction of van der Waals attraction due to liquid bridges!

Meester, Verweij, vd Wel, Kraft (ACSNano 2016)

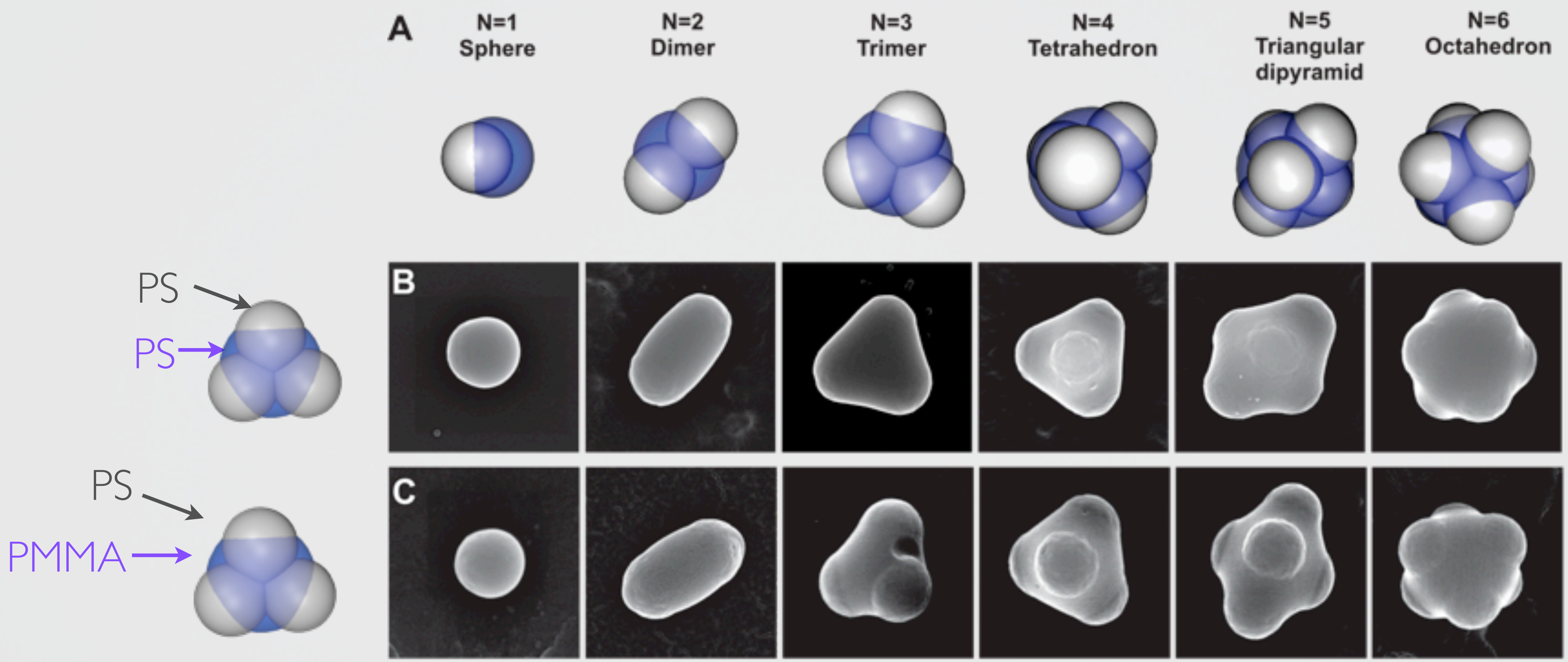
Size Distribution of Random Clusters and Patchy Particles is Equal



Composite PS / PMMA Colloidal Molecules



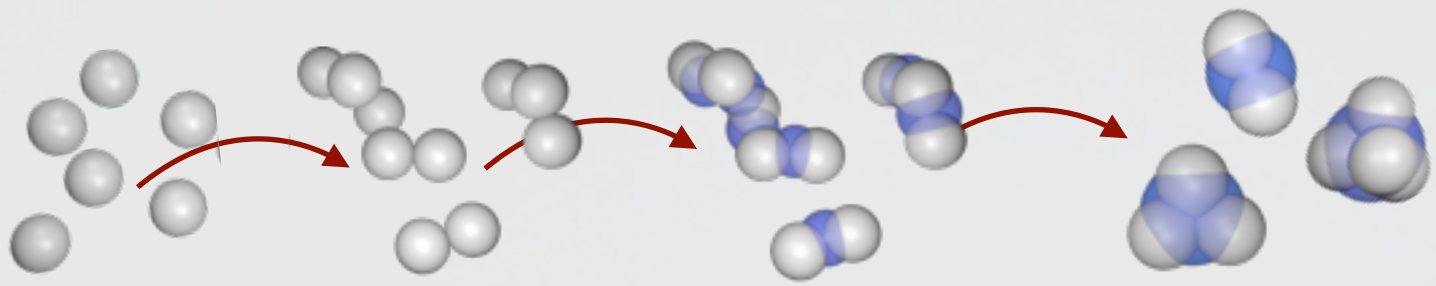
Patchy particles

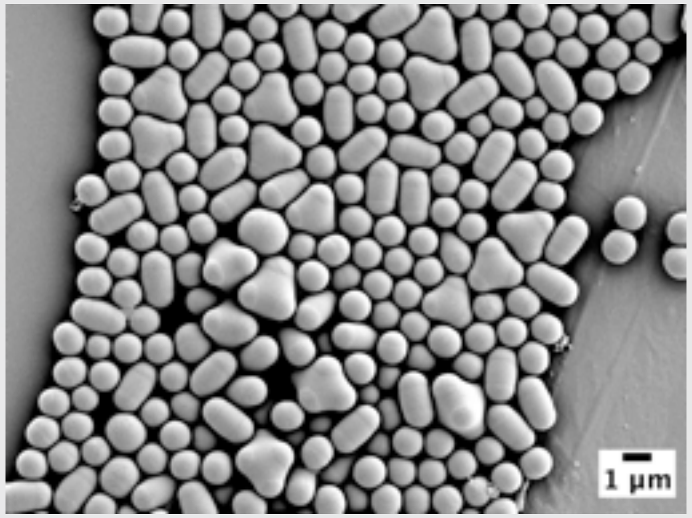


Meester, Verweij, vd Wel, Kraft (ACSNano 2016)

Summary - Recycling Colloidal Aggregates into Patchy Particles

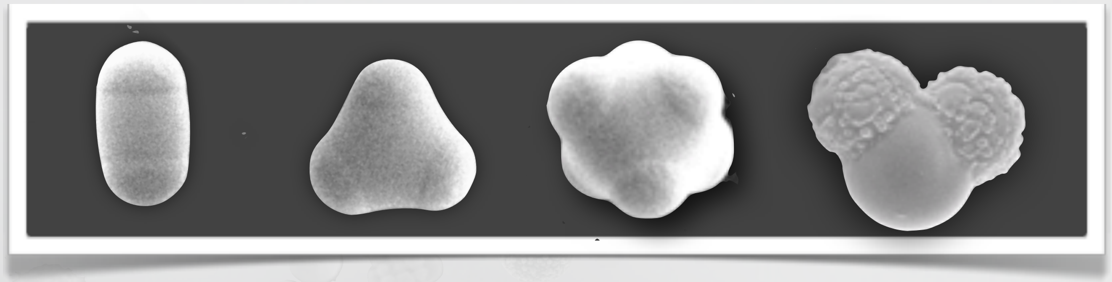
Reorganization of random clusters of spheres



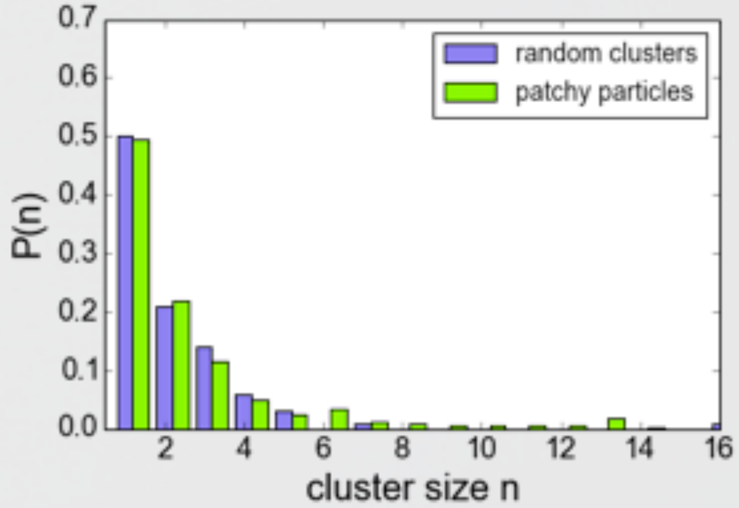


Meester, Verweij, vd Wel, Kraft (ACSNano 2016)

Variety of complex patchy particles

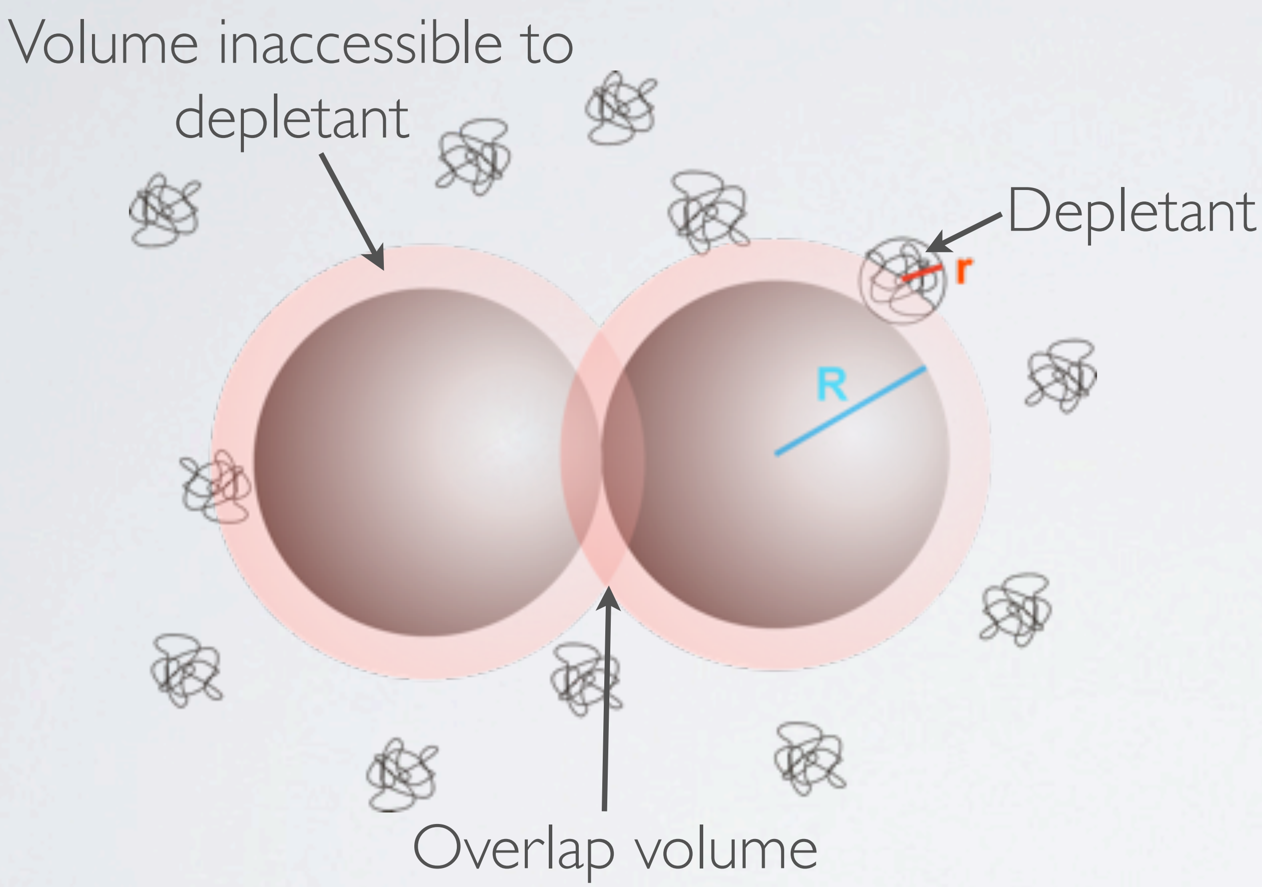


Control over size distribution



Self-Assembly of Patchy Particles
- Tuning Depletion Interactions by Surface Roughness

THE DEPLETION INTERACTION

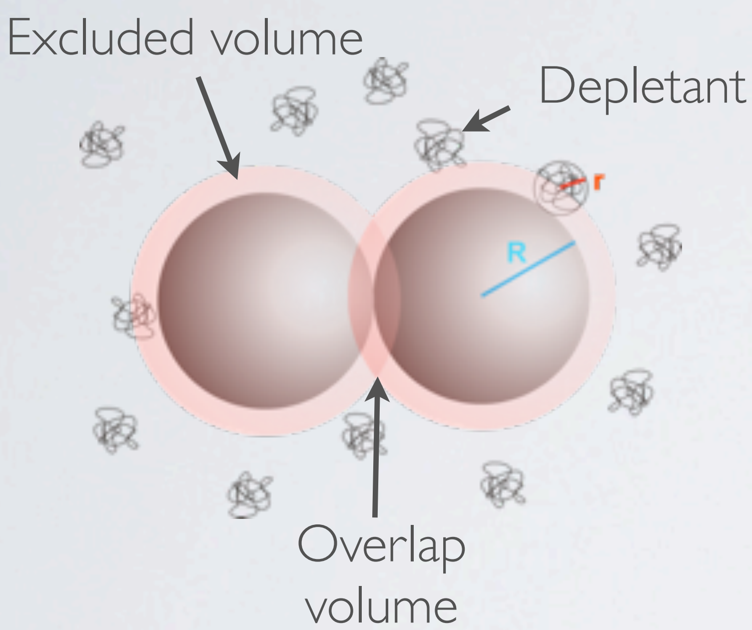


Effective attraction between larger colloid!

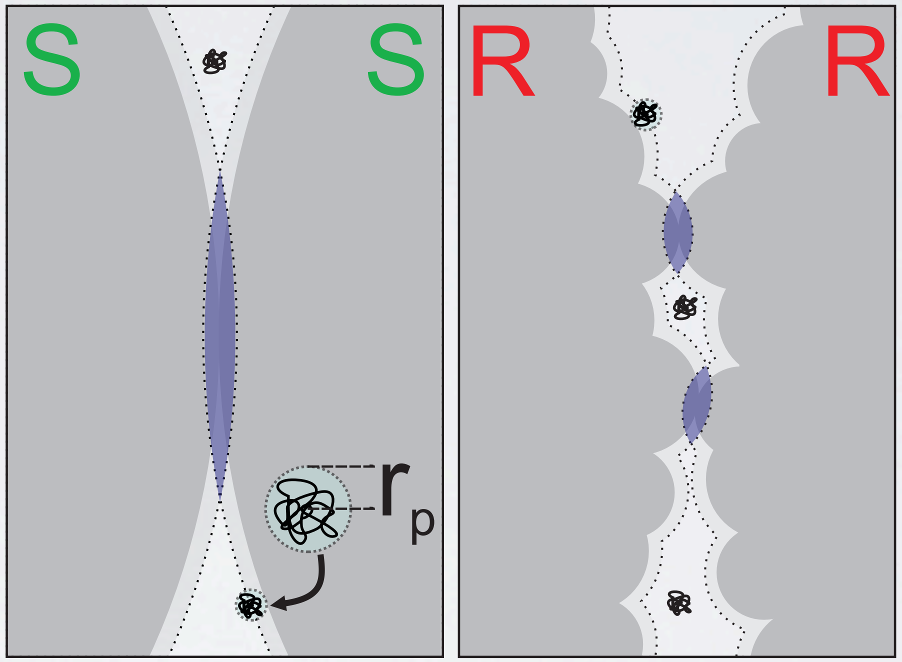
$$u = -\Pi\, V_{overlap}$$
$$= -k_B T\, n_{depl}\, V_{overlap}$$

Asakura, Oosawa,, J. Chem. Phys. (1954)
Vrij Pure & Appl Chem. (1976)

Tuning Depletion Interactions Through the Overlap Volume



$$u = -\Pi \, V_{overlap}$$
$$= -k_B T \, n_{depl} \, V_{overlap}$$



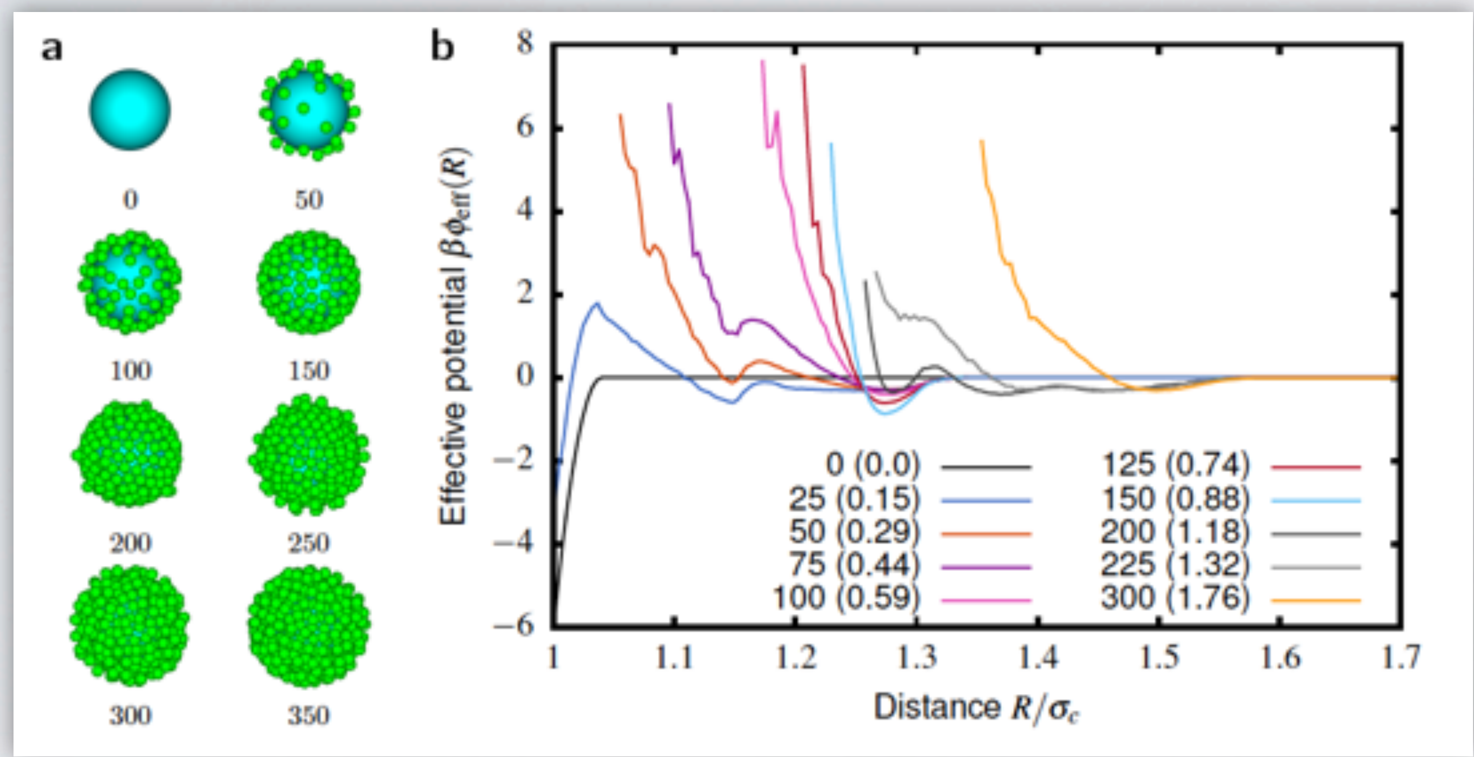
Roughness significant reduces the overlap volume, and thus the depletion attraction.

see also: K. Zhao, T. Mason, PRL 99(2008)

Asakura, Oosawa,, J. Chem. Phys. (1954)

Vrij Pure & Appl Chem. (1976)

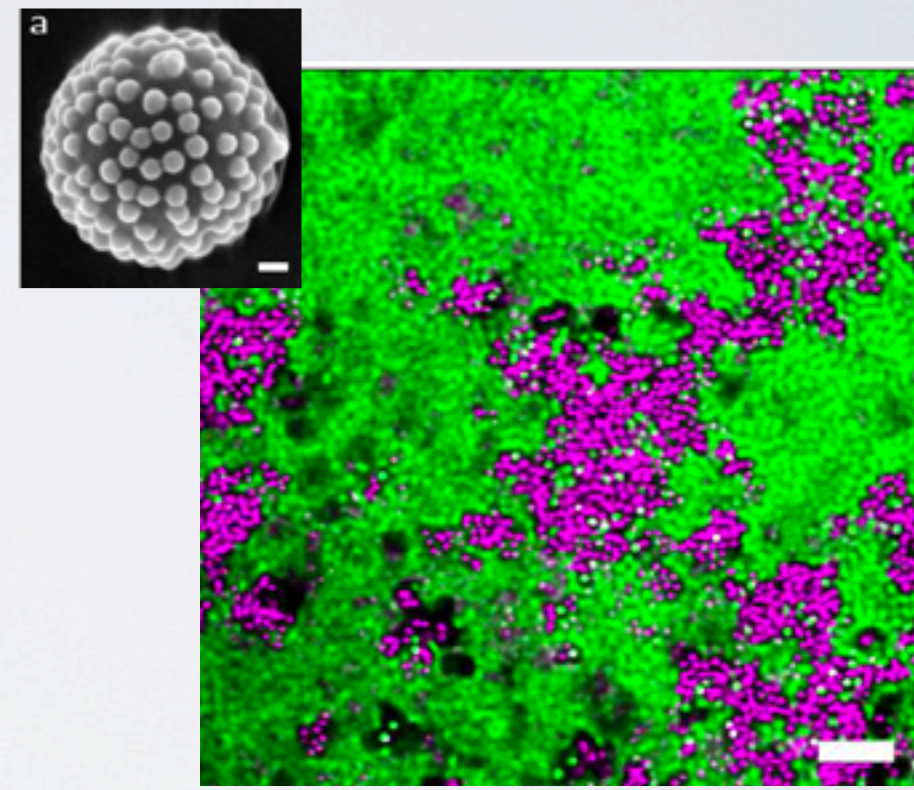
DEPLETION POTENTIAL FOR ROUGH AND SMOOTH SPHERES



Simulations by Michiel Hermes

volume fraction=0.16

σ_p=0.04 σ_c



averaged over 60 frames

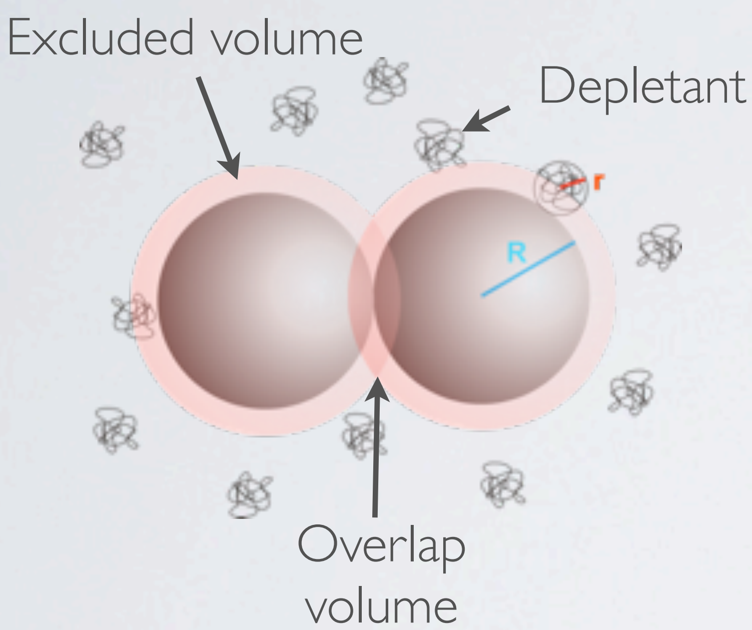
purple: smooth particles

green: rough particles

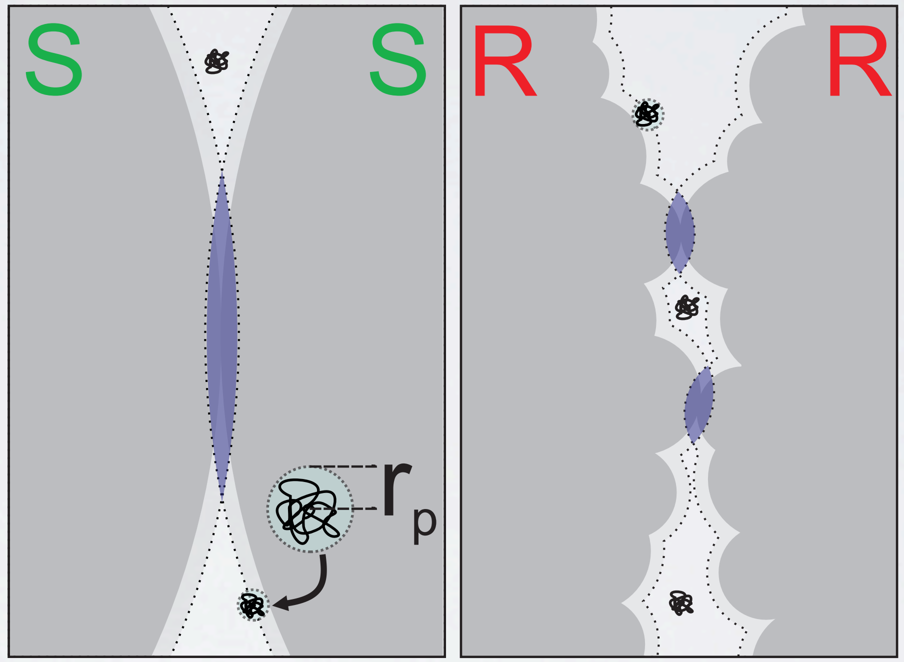
Kamp et al., (Langmuir 2016)

Experiments by M. Kamp

TUNING DEPLETION INTERACTIONS THROUGH THE OVERLAP VOLUME

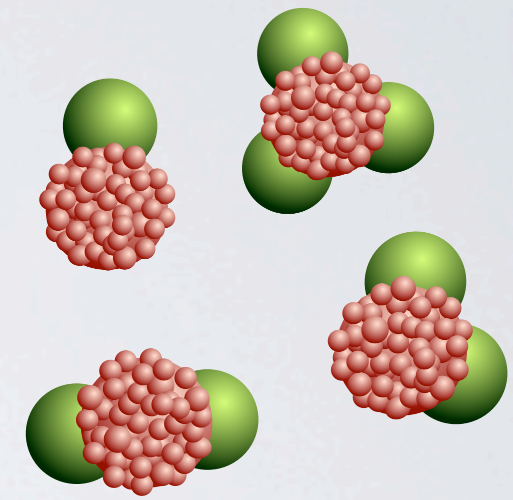


$$
\begin{aligned}
u &= -\Pi\, V_{overlap} \\
&= -k_B T\, n_{depl}\, V_{overlap}
\end{aligned}
$$



Roughness significant reduces the overlap volume, and thus the depletion attraction.

smooth = large overlap volume = attractive



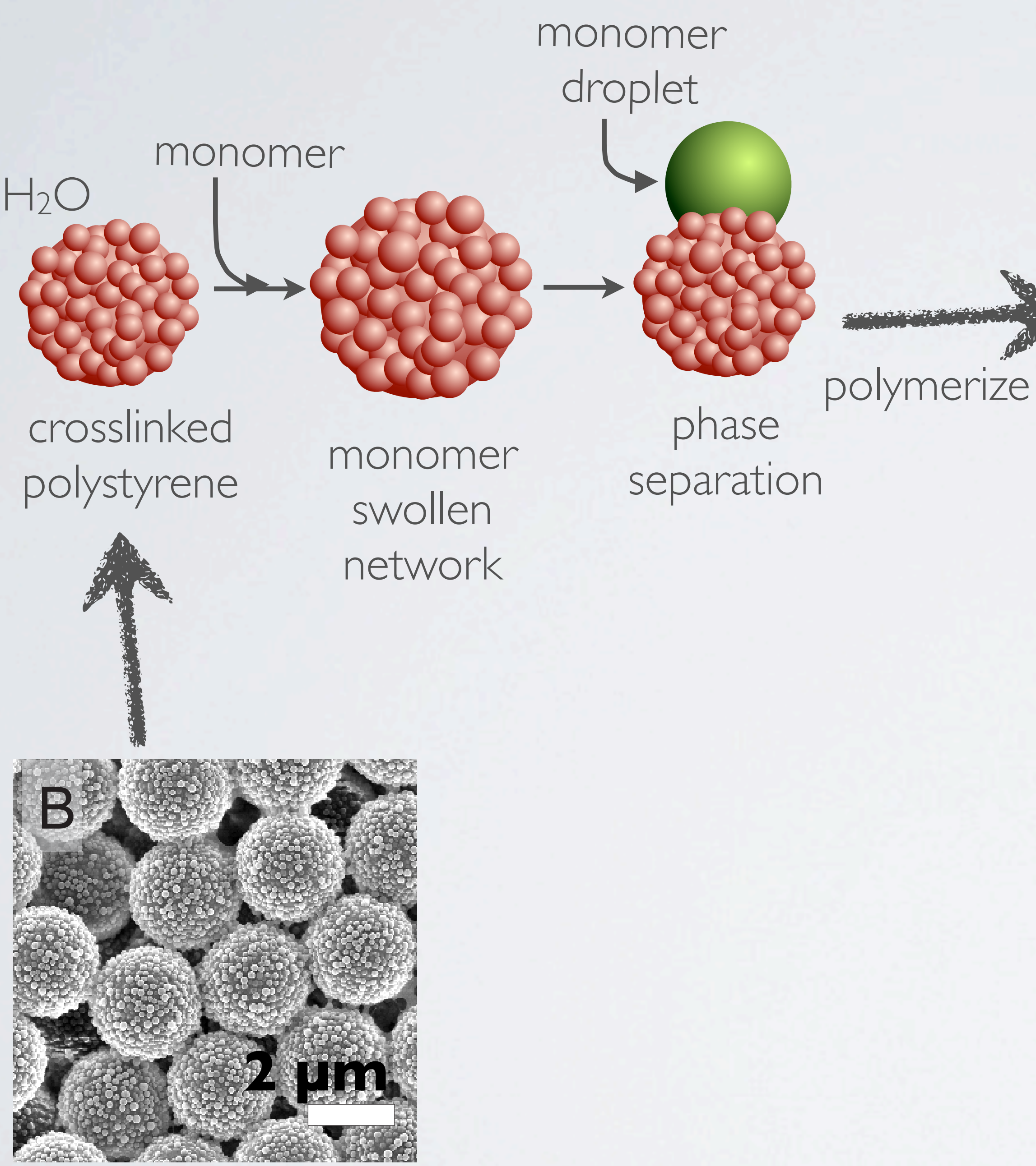
rough = small overlap volume = non-attractive

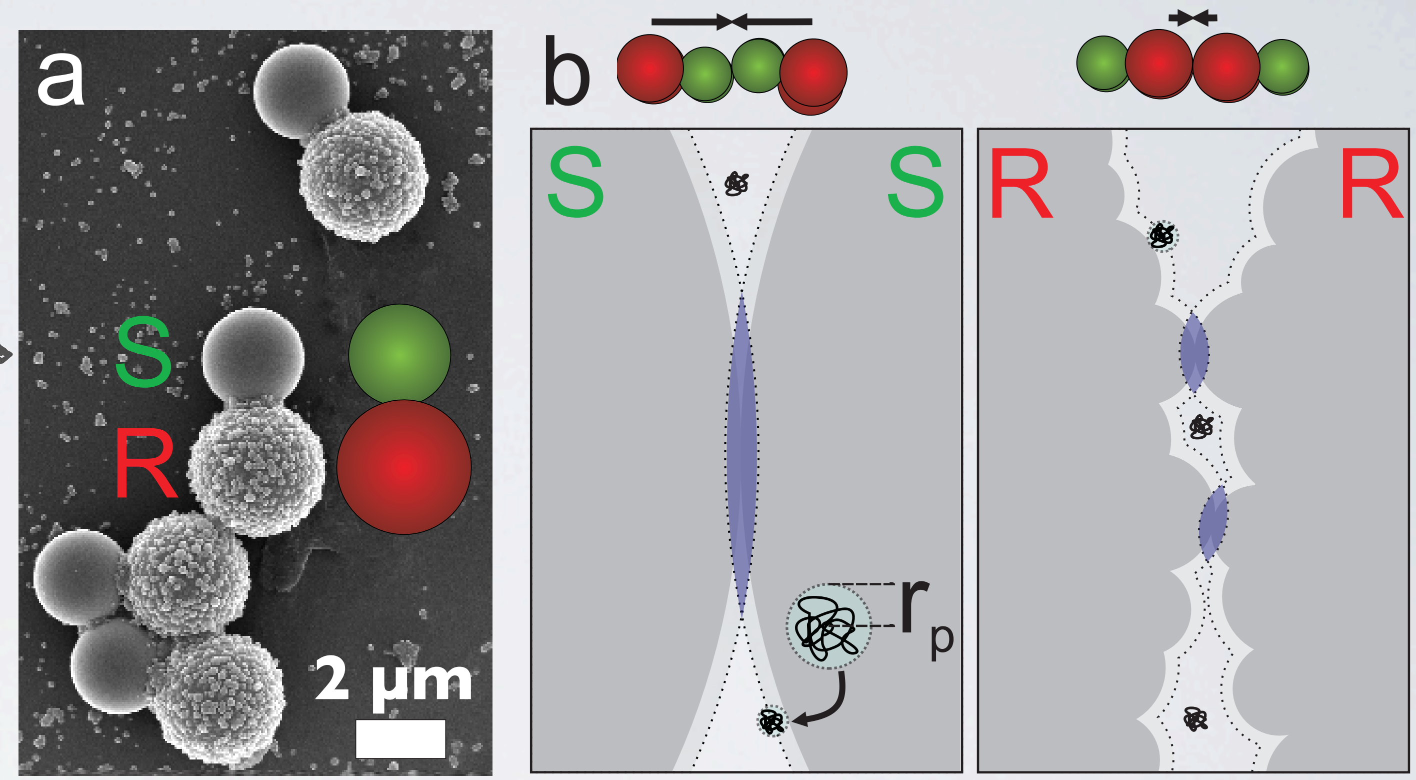
Patchy Particles

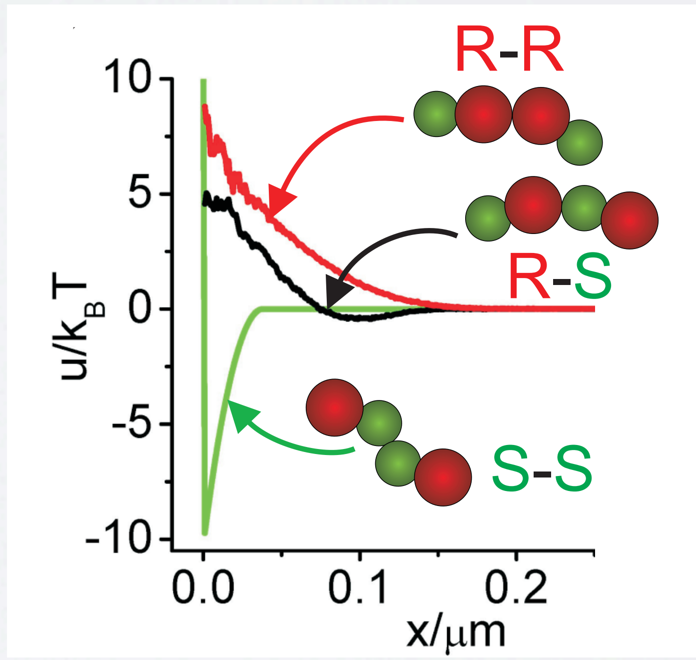
see also: K. Zhao, T. Mason, PRL 99(2008)

Asakura, Oosawa,, J. Chem. Phys. (1954)
Vrij Pure & Appl Chem. (1976)

SYNTHESIS OF ROUGH-SMOOTH COLLOIDS





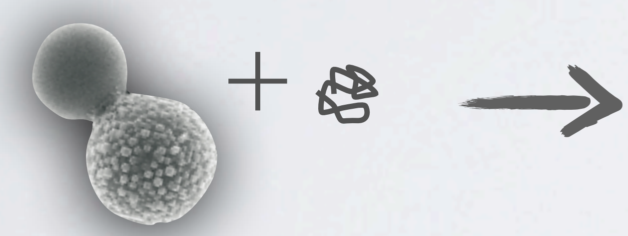


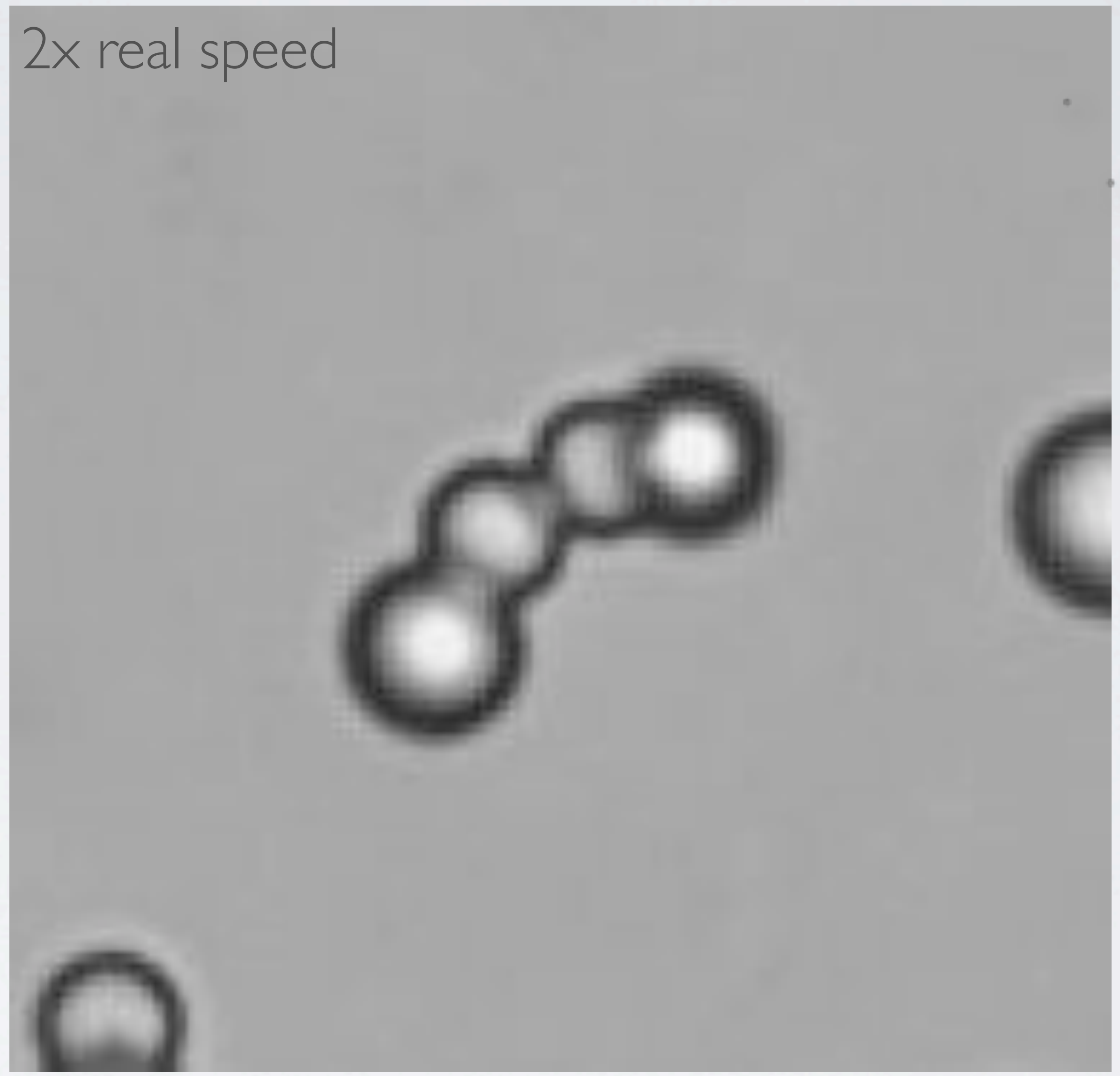
Potential calculated by M. Hermes and M. Dijkstra

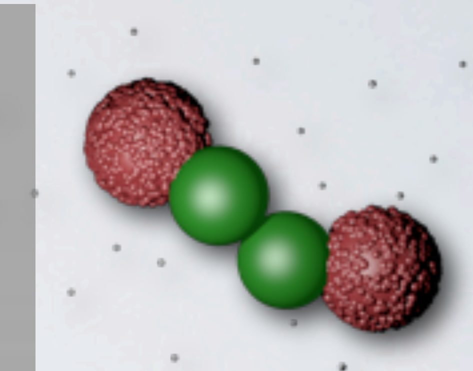
Significant attraction between smooth surfaces only

Bond Formation and Breaking

Roughness anisotropic colloids +
Dextran as depletant (d=38nm)



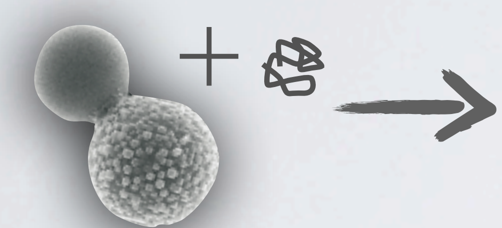


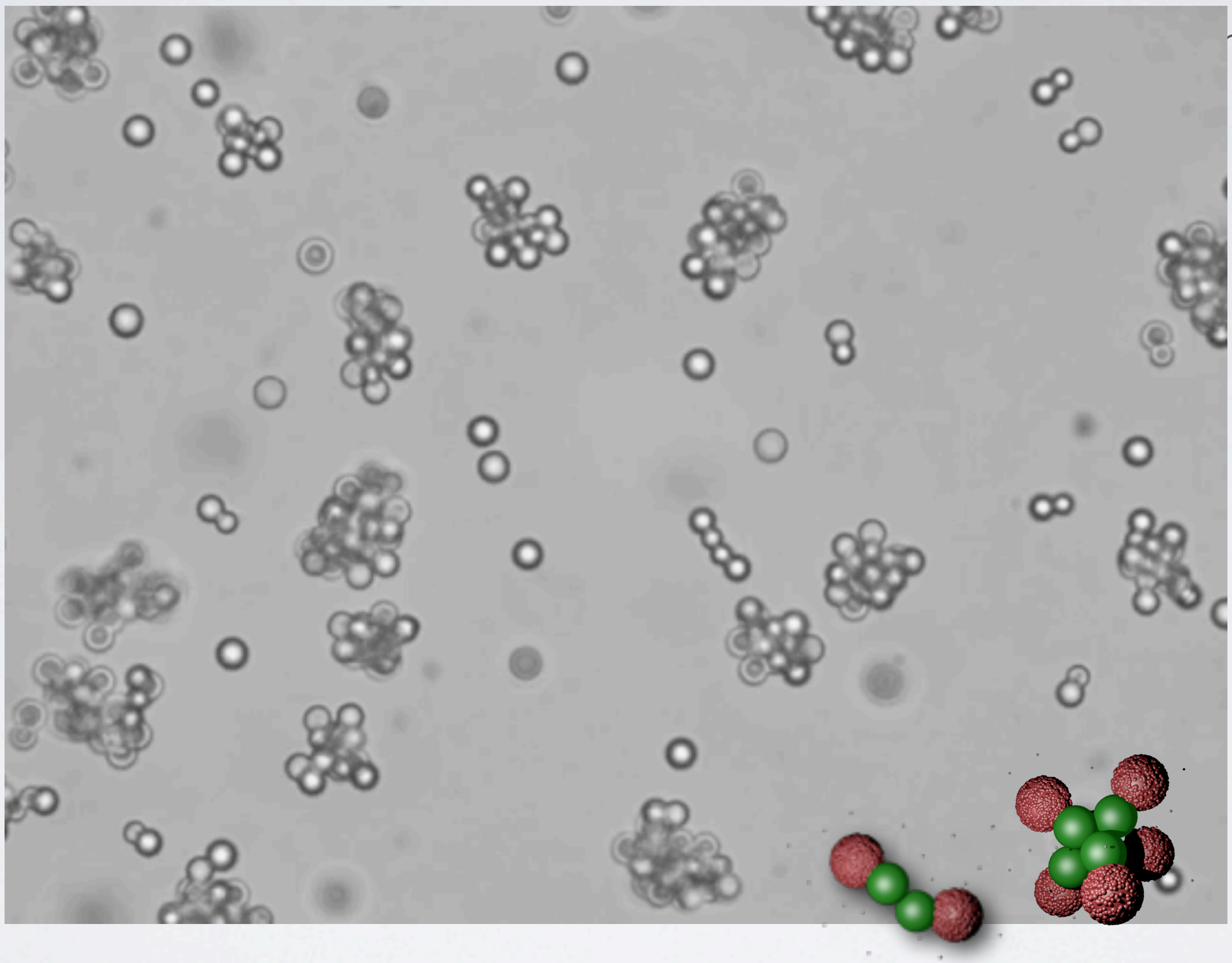


- ☐ Site-specific binding
- ☐ Flexible bonds

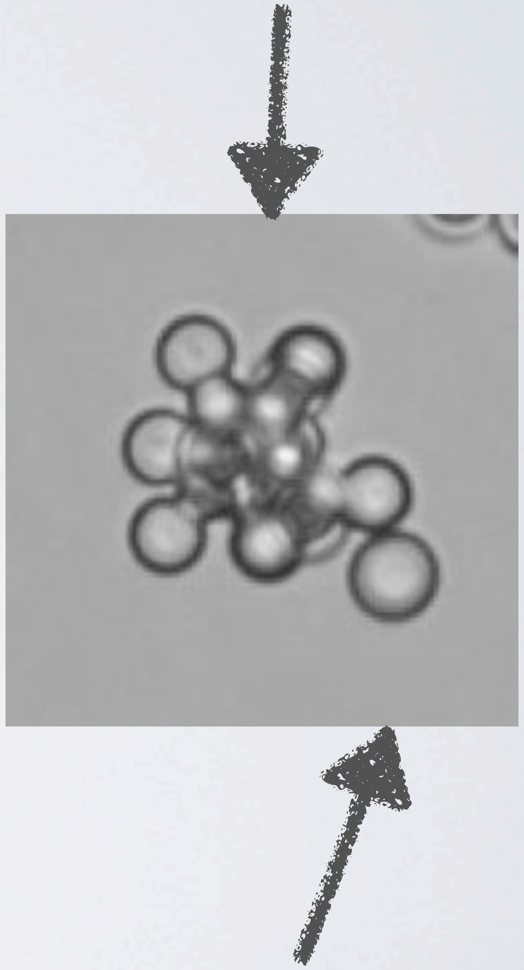
Kraft et al. PNAS (2012)

Colloidal Micelles





Cluster of colloids with
mooth and attractive sides
inside

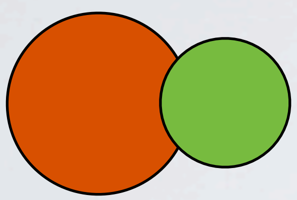


Rough sphere
(not attractive)

Kraft et al. PNAS (2012)

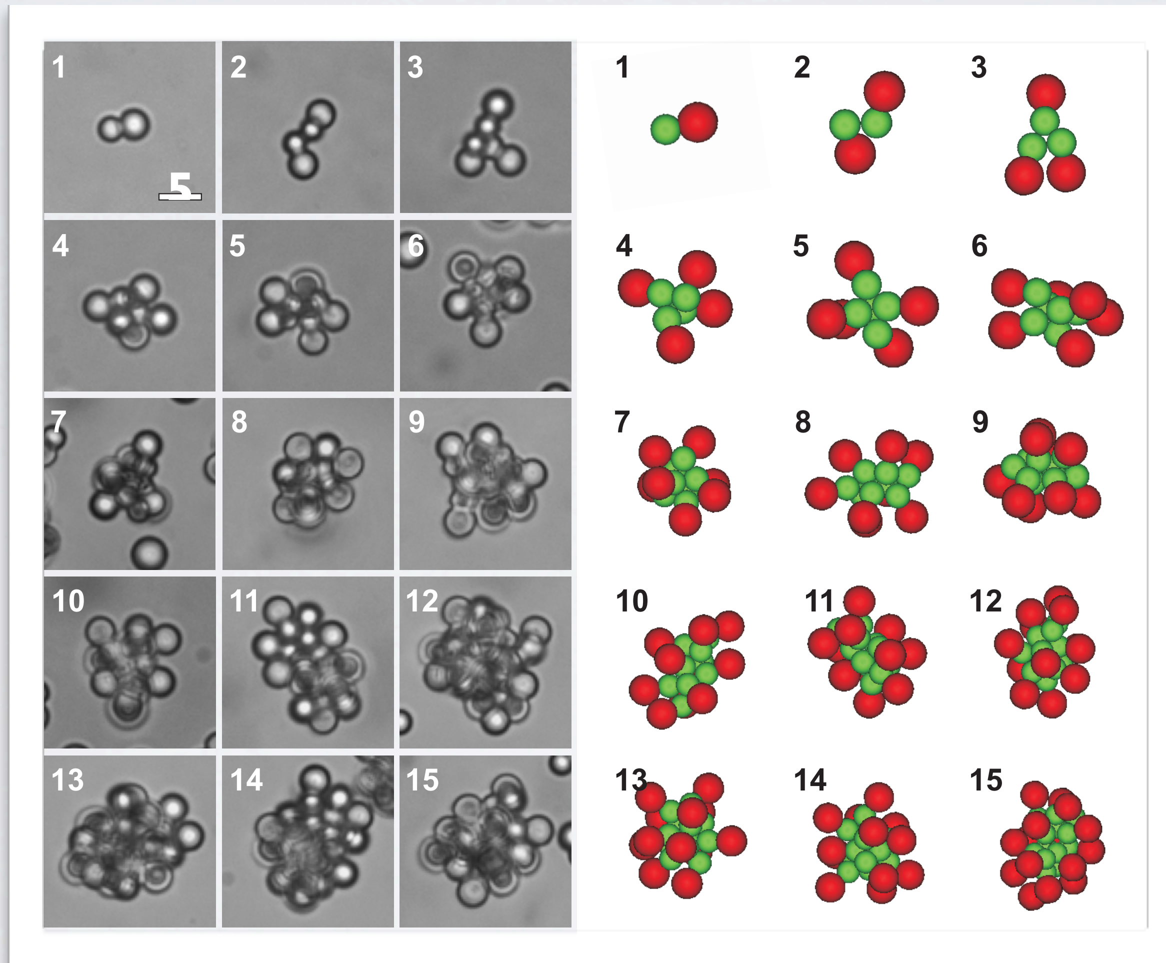
EXPERIMENT & SIMULATIONS

Monte-Carlo Simulations by R. Ni & M. Dijkstra

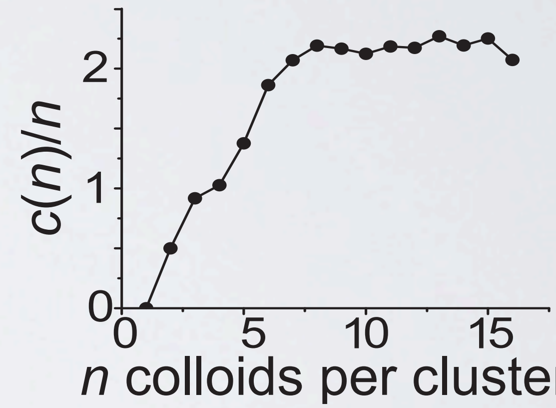


hard sphere repulsion

Asakura-Oosawa-Vrij potential



- Average number of bonds saturates

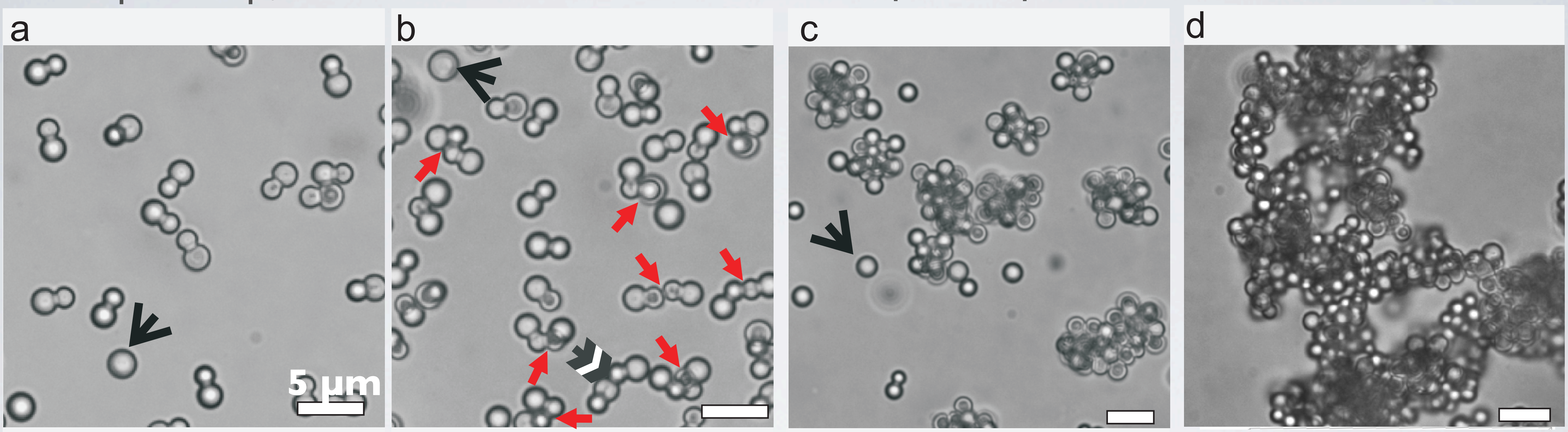


- Interaction potential -9.85kT

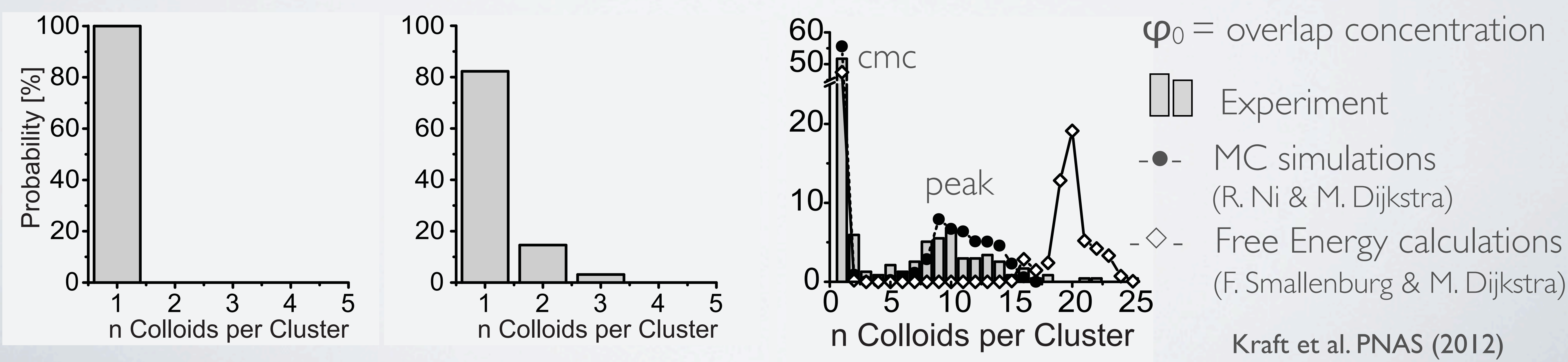
Kraft et al. PNAS (2012)

Increasing Interaction Strength

$\varphi = 0.32\ \varphi_0$ | $\varphi = 0.35\ \varphi_0$ | $\varphi = 0.40\ \varphi_0$ | $\varphi = 0.42\ \varphi_0$



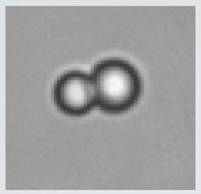
free particles | single bonds | cluster phase | gelation, site-specificity lost



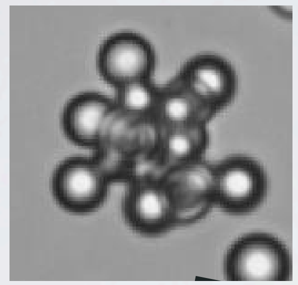
Kraft et al. PNAS (2012)

Critical micelle concentration

Analyze equilibria between monomers and clusters



$$n\mu_1 = \mu_n$$



Critical micelle concentration

volume of a colloid

bonds in a cluster of size n*

bond energy

$$\Phi_{th}^{cmc} = \frac{V_c}{\xi^3} \exp\left[\frac{\beta c(n^*)u}{(n^*-1)}\right]$$

interaction range

≅bond energy per particle in a cluster

Experiments

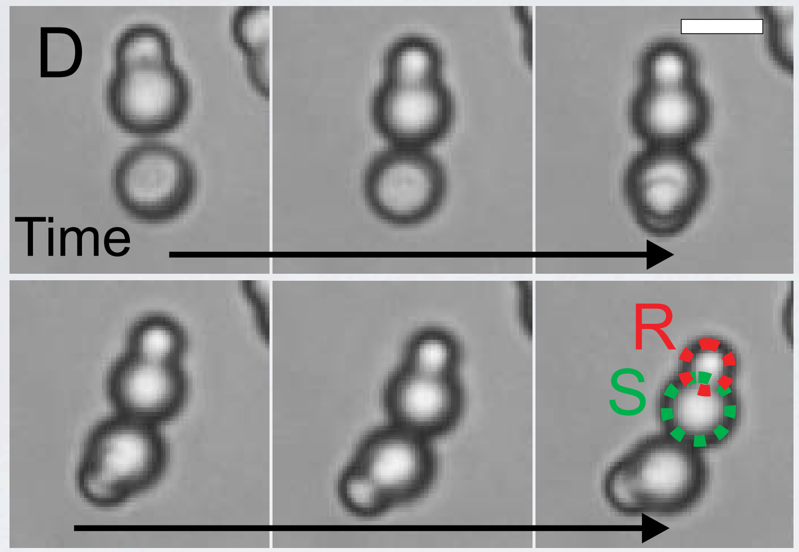
$$\Phi_{exp}^{cmc} = 3.1 \cdot 10^{-5}$$

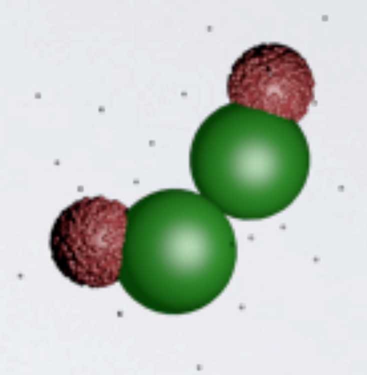
Theoretical prediction

$$\Phi_{MC}^{cmc} = 1.3 \cdot 10^{-5}$$

Interaction range & energy determine the critical micelle concentration

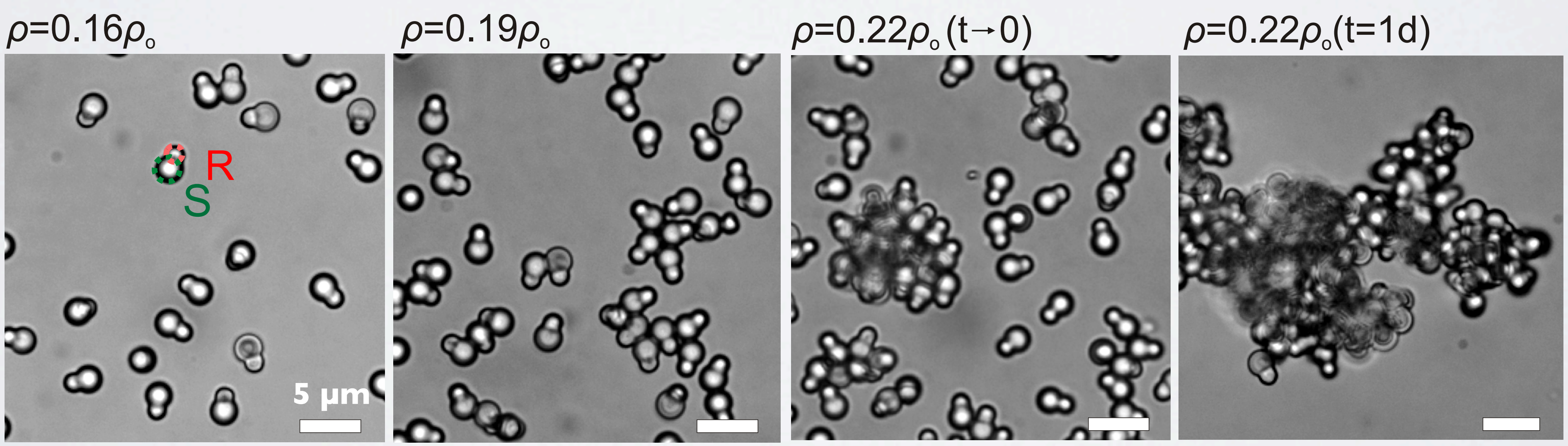
Influence of Patch Size





Site-specific attraction

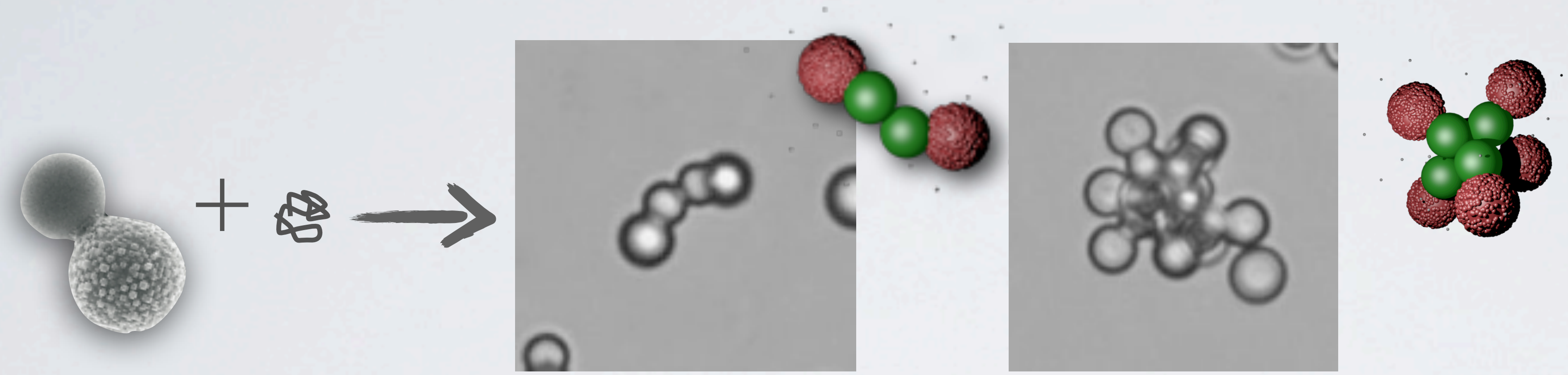
☐ Increasing attraction strength



free particles   single bonds   clusters grow without bounds

φ_0 = overlap concentration

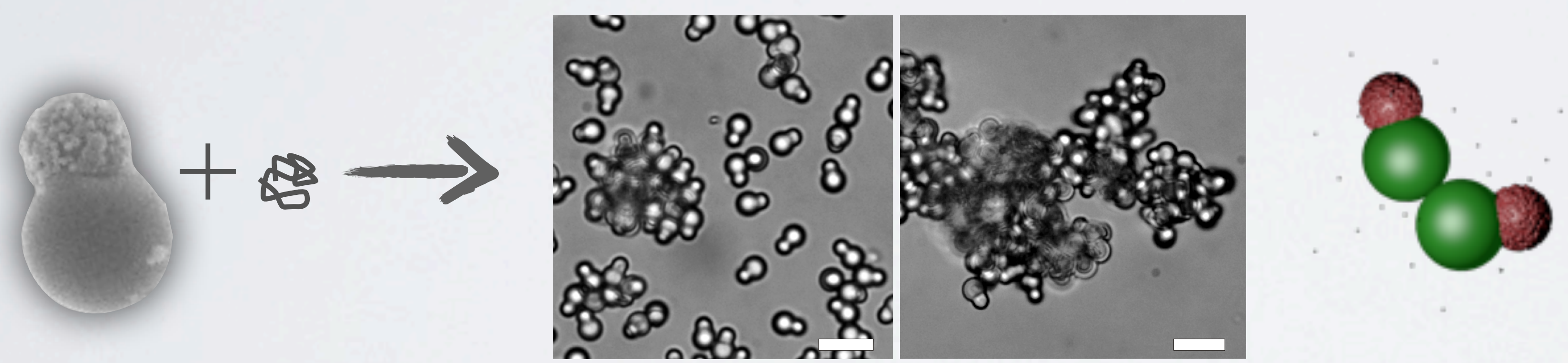
STERIC CONSTRAINTS DETERMINE SIZE AND GEOMETRY OF THE STRUCTURE



Finite size clusters

"Colloidal micelle"

Rough ends sterically constrain assembly size in 3D.

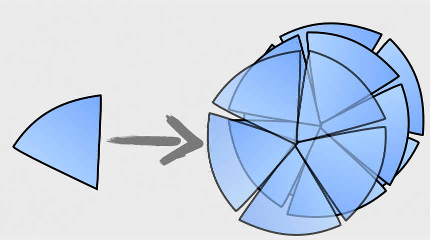


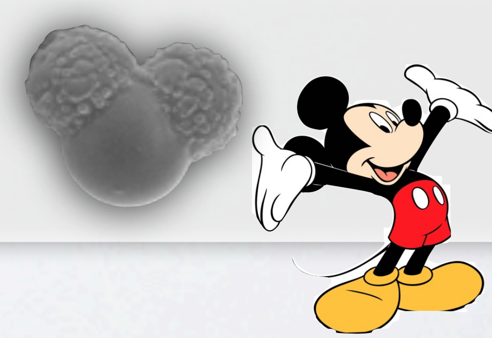
Clusters grow without bounds

Insufficient steric protection leads to unlimited growth.

Kraft et al. PNAS (2012);

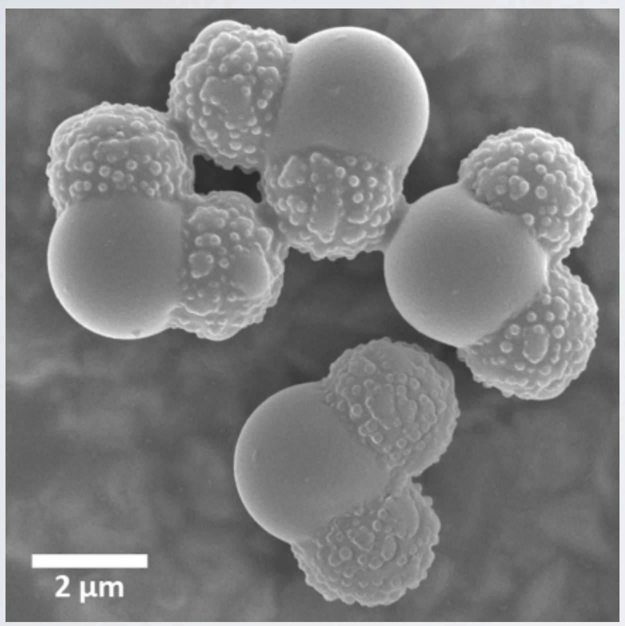
Can we design particles that constrain growth in 2D?





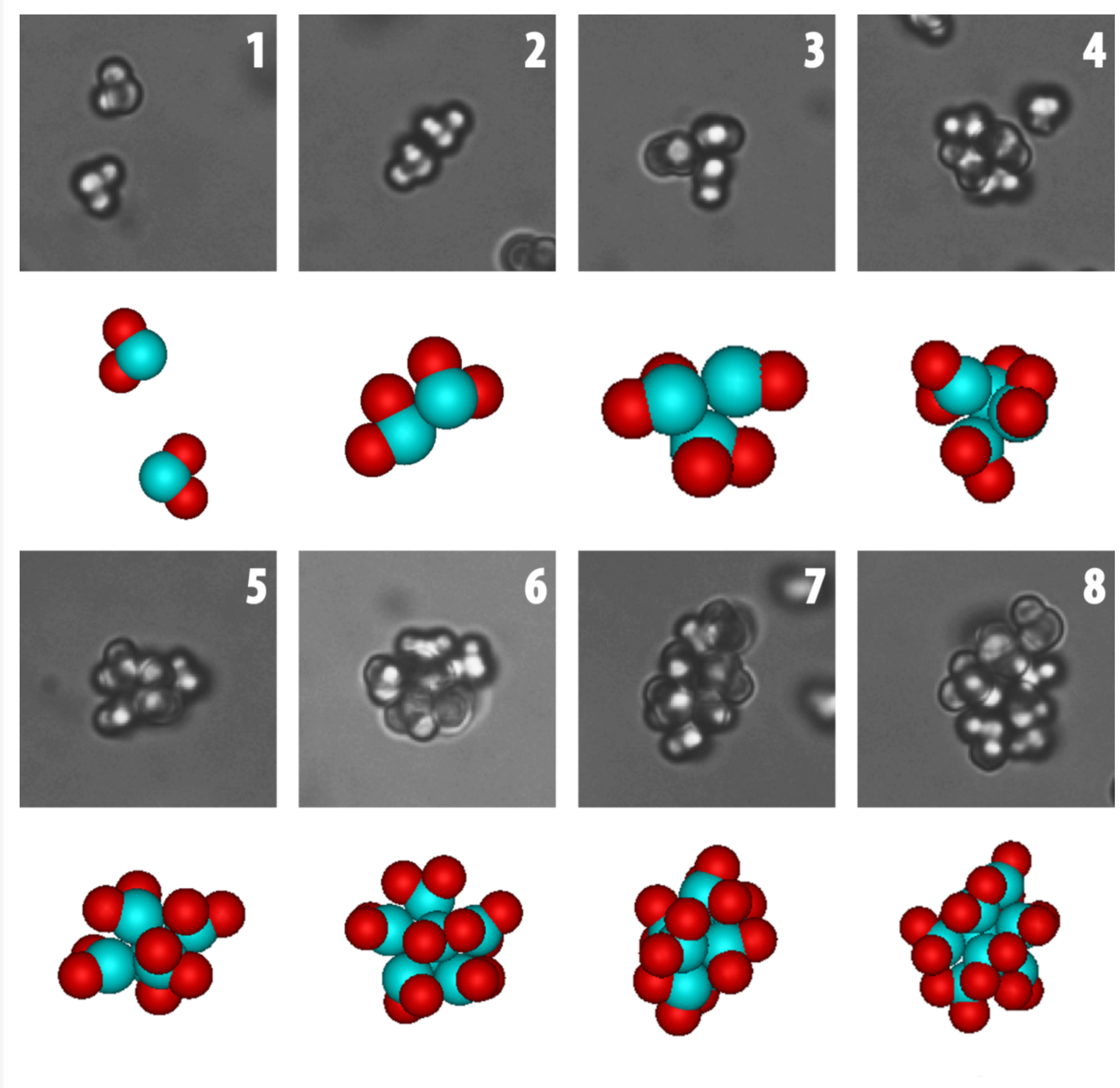
"Mickey Mouse" science

Depletion Induced Assembly of Mickey Mouse Shaped Colloids



Dextran as depletant (d=38nm)

+



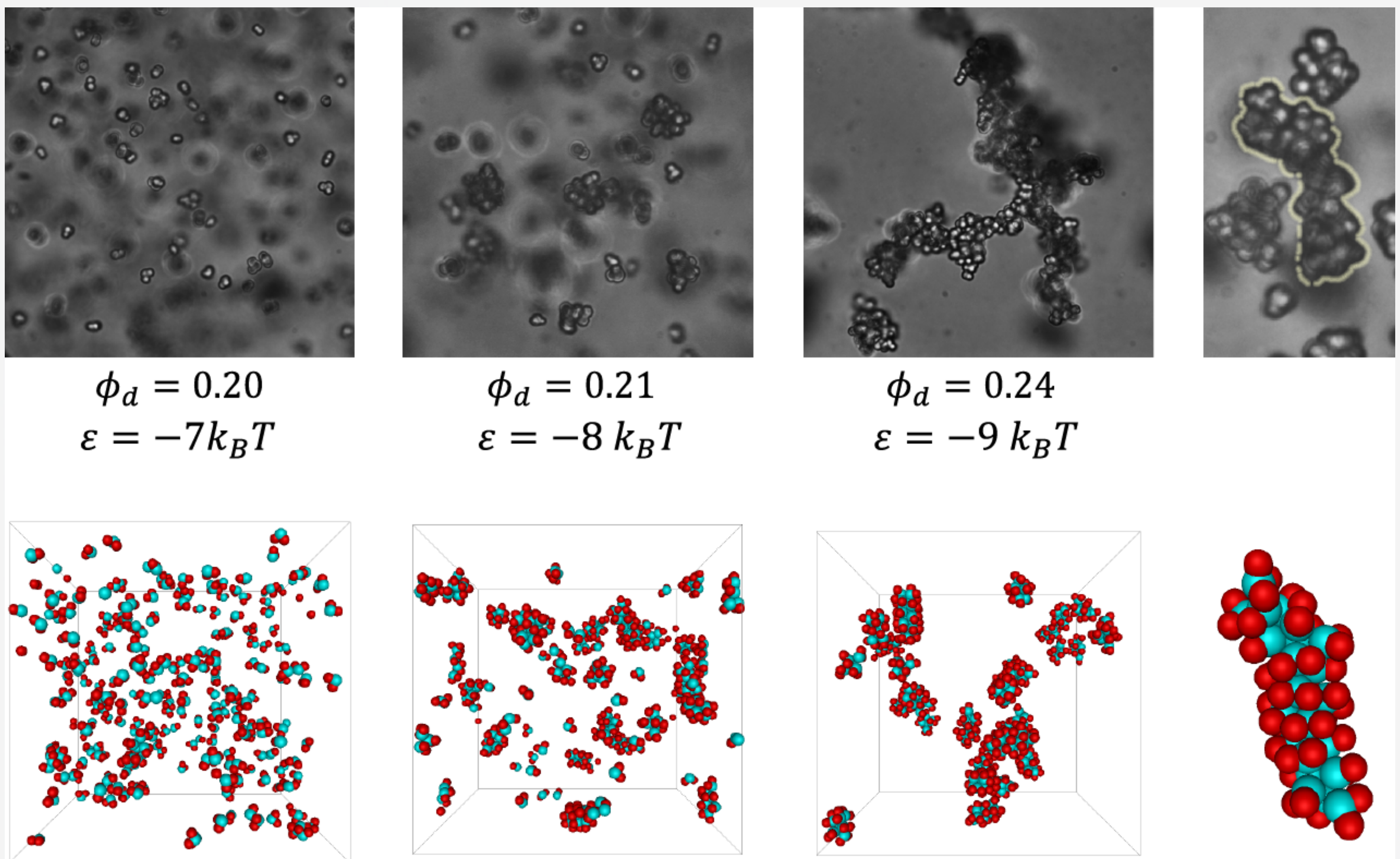
$\phi_{particle} = 0.003$

Experiments headed by J. Wolters, Simulations by G. Avvisati, T. Vissers & M. Dijkstra

Wolters et al. Soft Matter (2015)

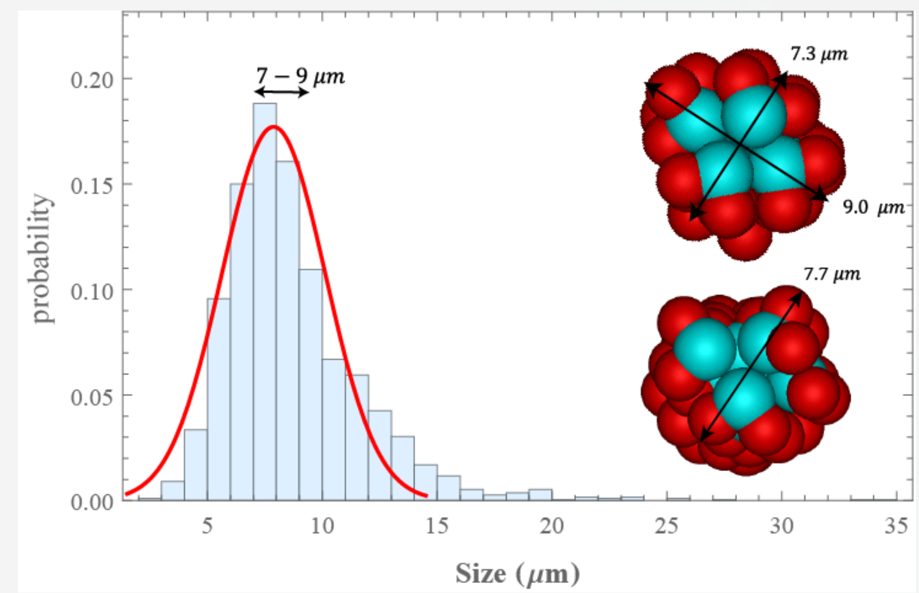
Mickey Mouse Colloids Assemble into Tubular Structures

$\phi_{particle} = 0.01$



interaction strength

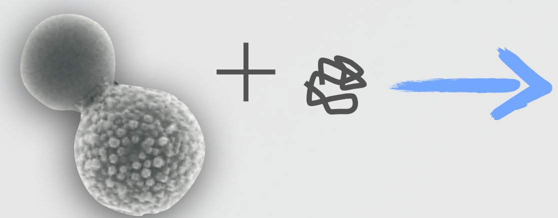
Diameter of tubes

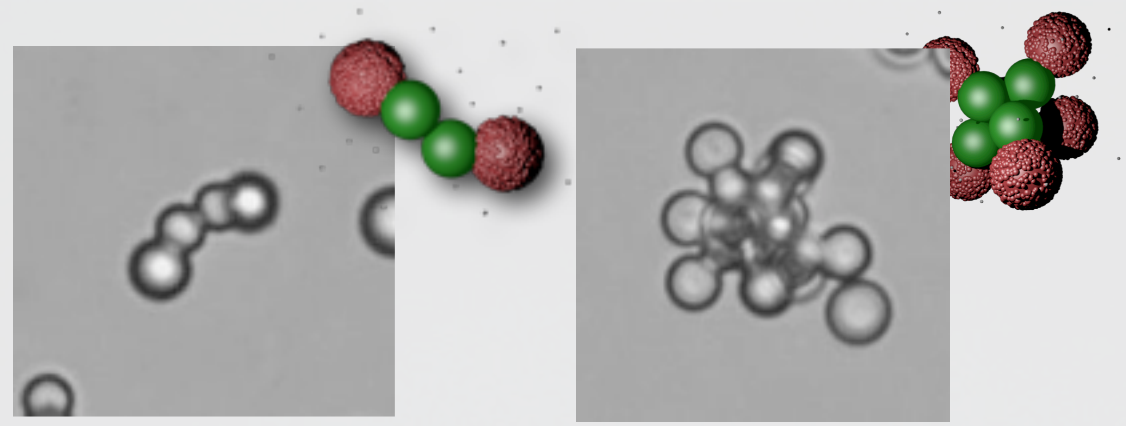


Experiment Simulations

Wolters et al. Soft Matter (2015)

SUMMARY: SELF-ASSEMBLING ONE-PATCH PARTICLES

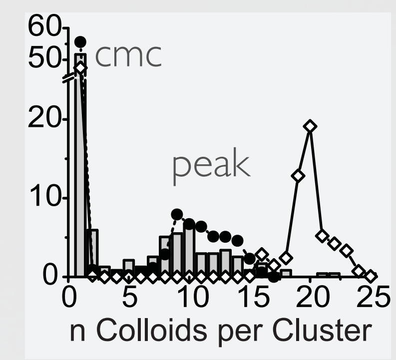


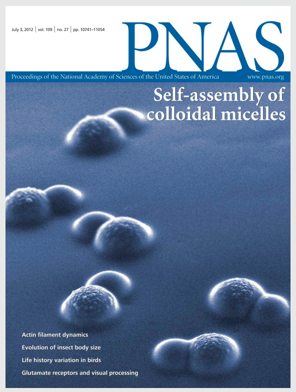


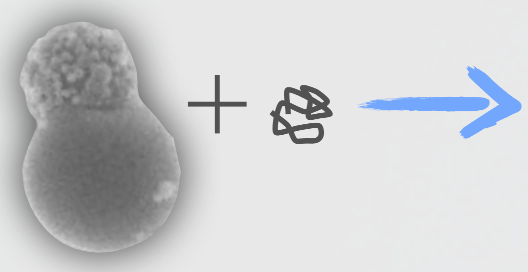
Finite size clusters

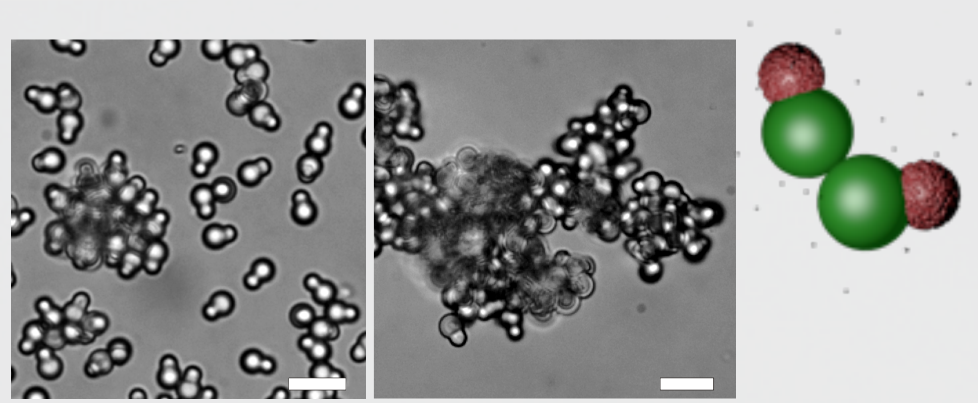
“Colloidal micelle”

Surfactant like behavior!



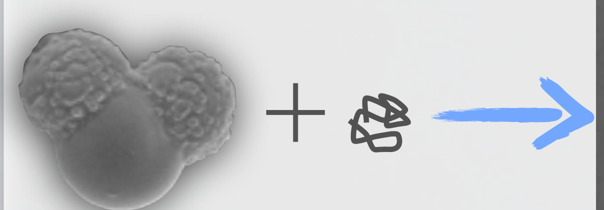


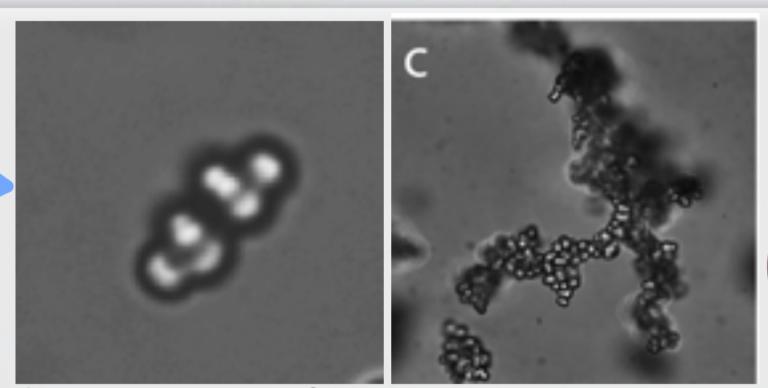




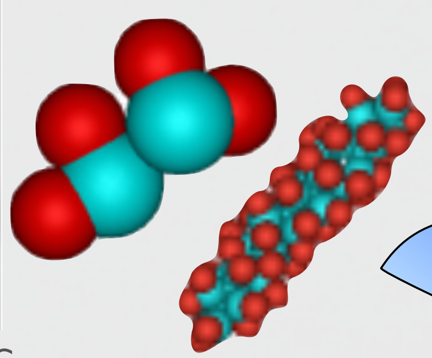
Clusters grow without bounds due to insufficient steric protection.

Kraft et al. PNAS (2012)

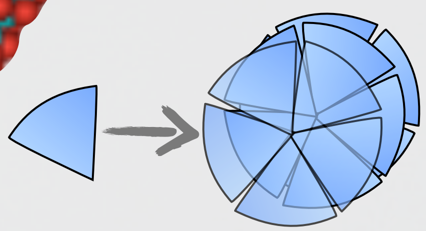




Assembly of tubular structures

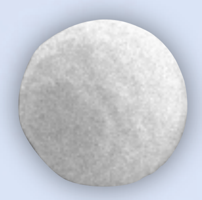


Tube formation due to steric protection in 2 dimensions.

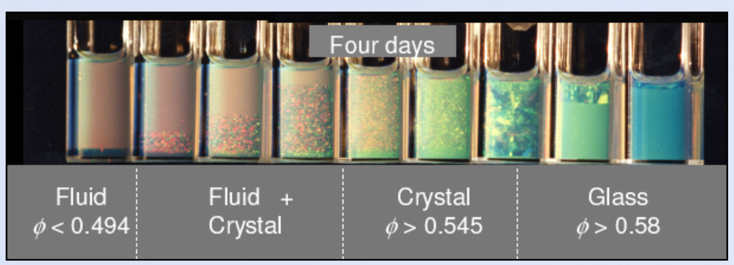


Wolters et al. Soft Matter (2015)

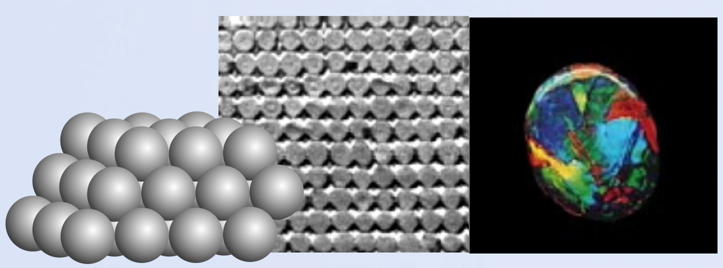
DESIGNED SELF-ASSEMBLY



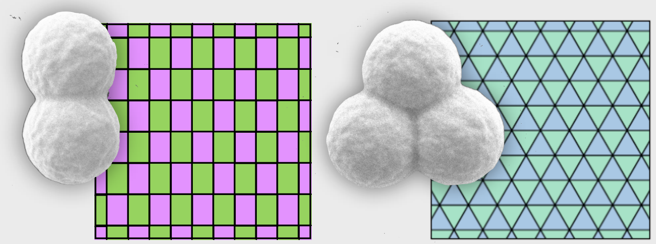
model 'atom'



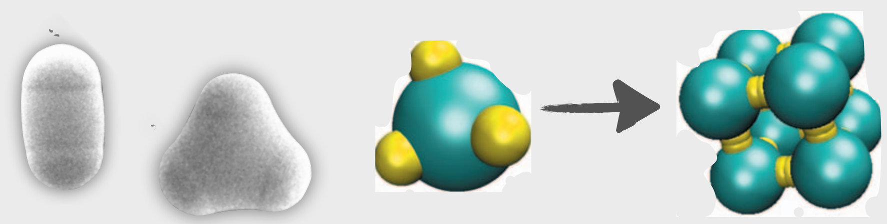
Pusey, van Megen, Nature (1986)



Anisotropic shape

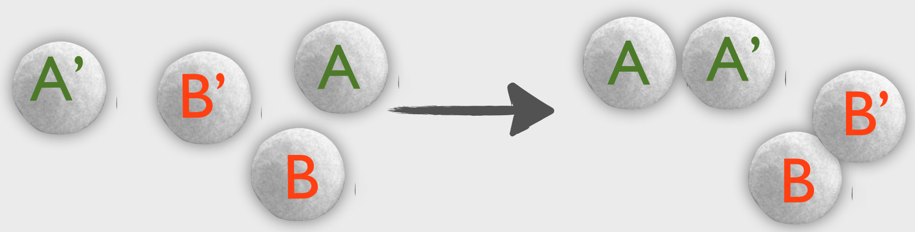


Anisotropic interactions



Wilber et al. JCP (2009)

Highly specific interactions



+ External guiding rules
+ activity

Particle shape
and interactions
↓
Assembled structure

"Designed self-assembly"

THANK YOU ....

Leiden University

Vera Meester
Ruben Verweij
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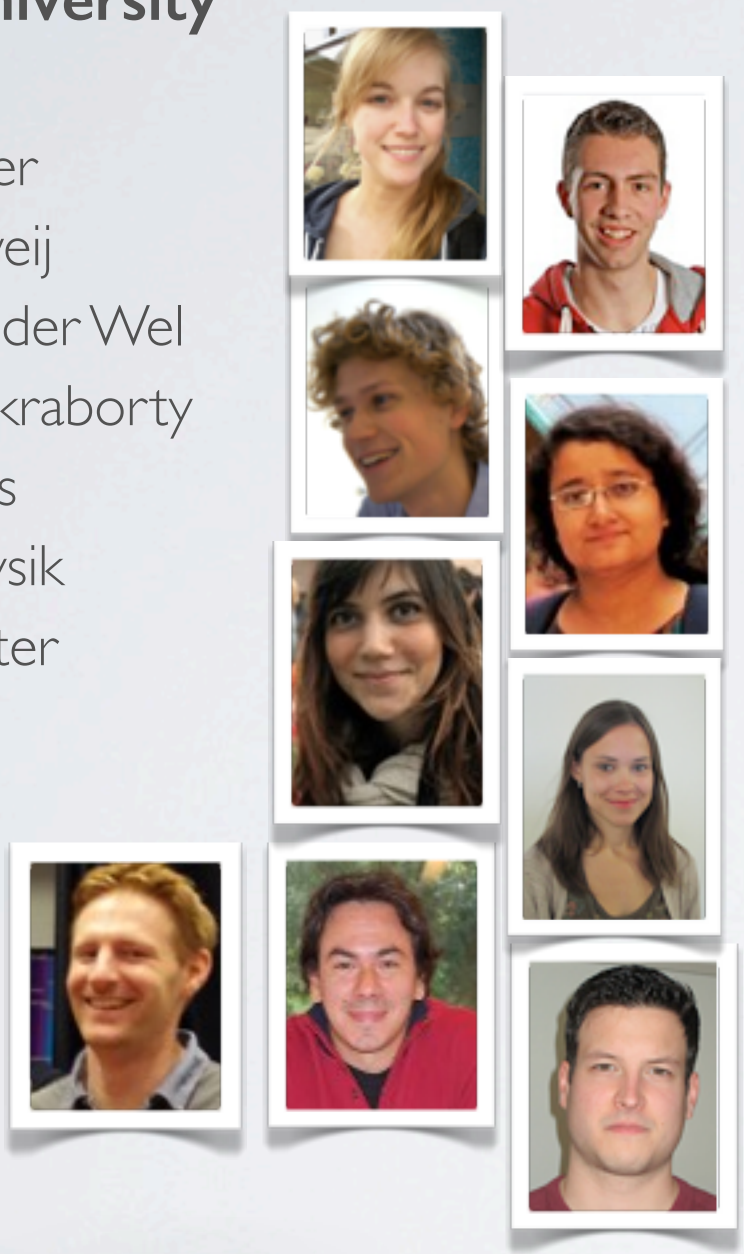
Sabine Matysik
Marcel Winter
Luca Giomi



Experiments

Utrecht University
Willem Kegel
Marlous Kamp
Joost Wolters
Alfons van Blaaderen
Jan Groenewold

Harvard University
Dave Weitz
Kisun Yoon

NYU
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Stefano Sacanna

Simulations

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Ran Ni (now UvA)
Guido Avvisati
Marjolein Dijkstra

University of Edinburgh
Michiel Hermes
Teun Vissers

University of Düsseldorf
Frank Smallenburg

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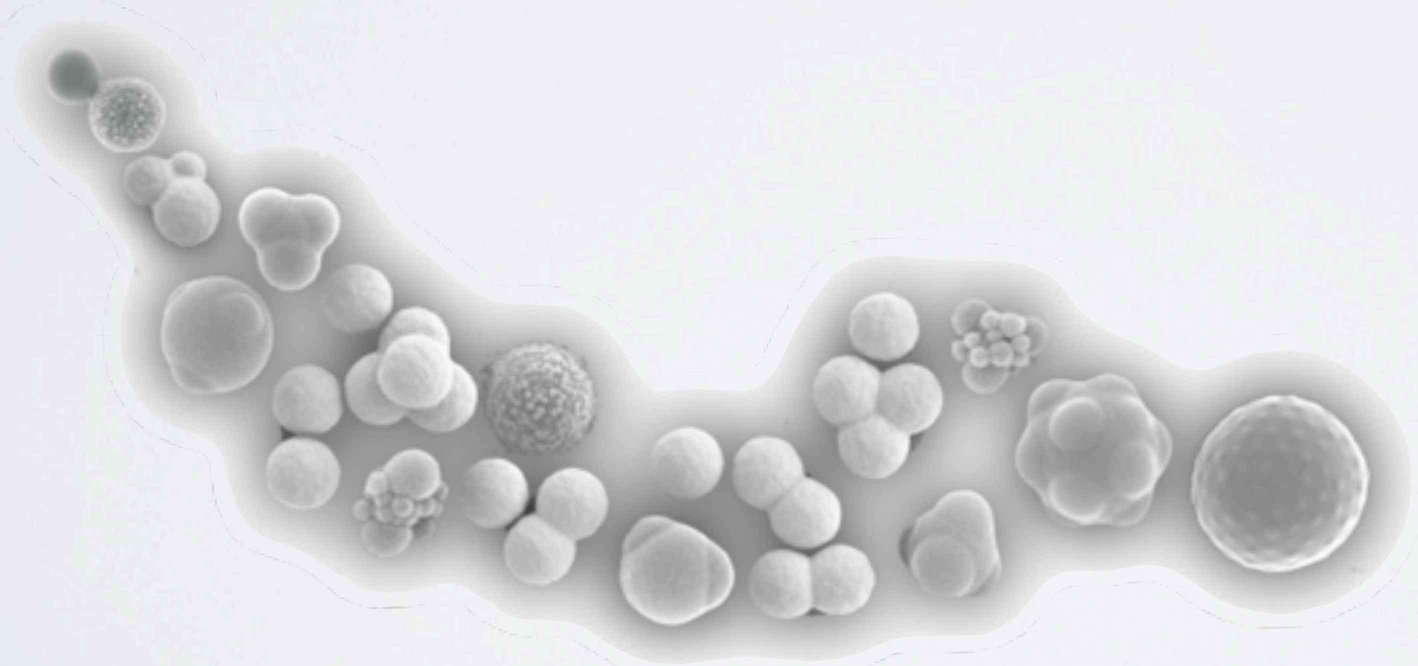
NWO
Rubicon fellowship
VENI grant
Nanofront Gravity grants
DAAD Rise fellowship

Universiteit Leiden
The Netherlands

Thank you for your attention!



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