SOFT SPHERES METALLURGY EXPERIMENTAL APPROACH

Pr B. PANSU
Laboratoire de Physique des Solide UMR-CNRS
University Paris-Sud, ORSAY, FRANCE

1- What nanoparticles?

1-1 The nature of the core

Metallic cores (or bimetallic) with gold, silver, platinium..) :
(Reduction of metallic salts in solution,…)

Surface plasmon resonance

Talapin D.V. Shvchenko : Rev. 2016, 116, 10343−10345

Semi-conducting cores: Quantum dots

Optical properties

Oxydes cores (silica, clays…)

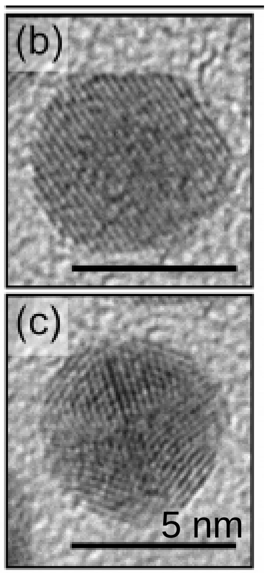
Organic Polymeric cores (polystyrene…)

Many synthesis have been published: reproductibility ?, yield of reaction?
Some are commercially available: not always well controlled.

1- What nanoparticles?

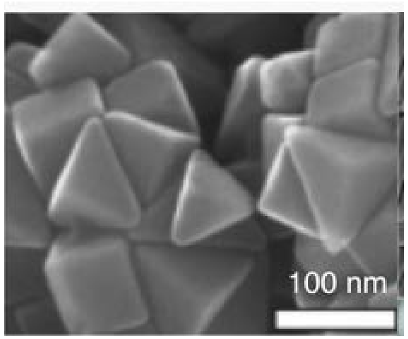
1-2 The core shape and structure

Isotropic

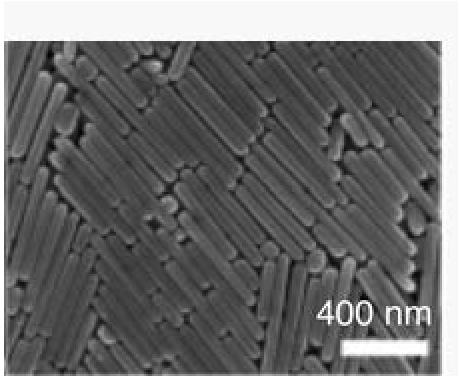


H. Portales, Nano Lett. 2012, 12, 5292

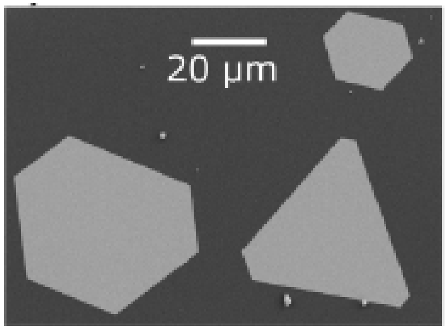
Anisotropic



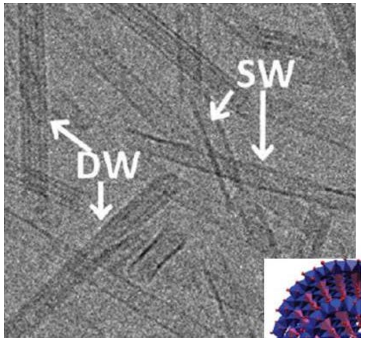
Cubes, pyramids, bi-pyramids…
(picture= Mirkin group)



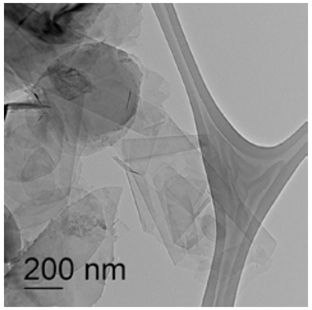
Rods *(picture=Mirkin group)*



Platelets (Cryst. Growth Des. 2018, 18, 1297−1302



Tubes (Iramis CEA)



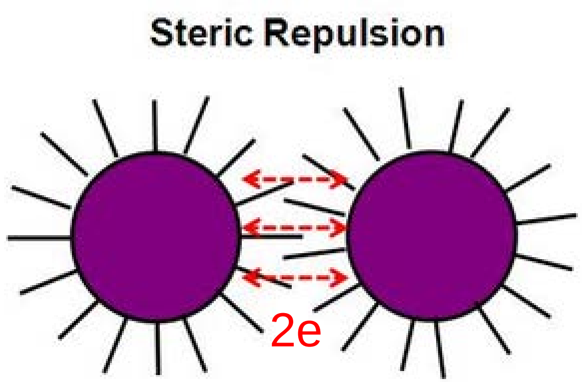
Graphene *(source: graphenox)*

The nanoparticle stabilization/ functionalization

1-3: The nanoparticle stabilization in suspensions

How to prevent irreversible aggregation
due to van der Waals forces?

In oil or in water : ligands



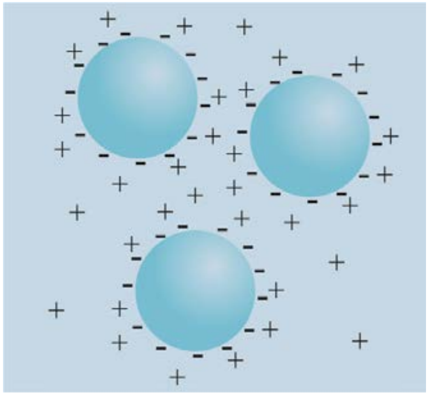
A= Hamaker constant

$$\frac{AR}{12(2e)} < kT$$

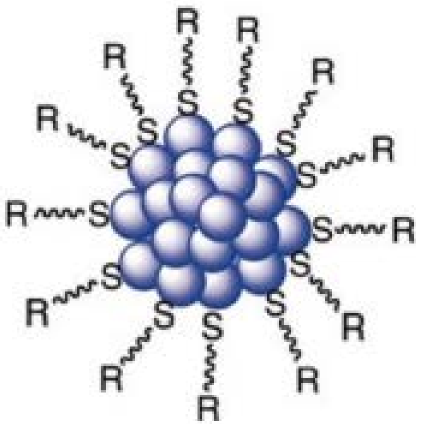
A depends also on the solvant

In water: electrostatic forces
Sensitive to salt concentration
(ionic strength I):
-> exponential screening

$$\lambda_D \, in \, nm = \frac{0.3}{\sqrt{I \, en M}}$$



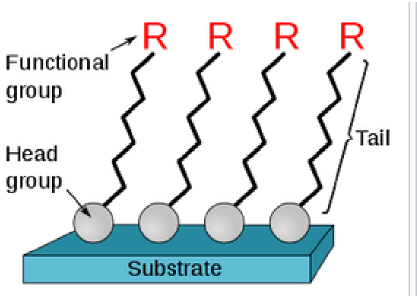
Ligands for gold nanoparticles?



Alkane-thiol:

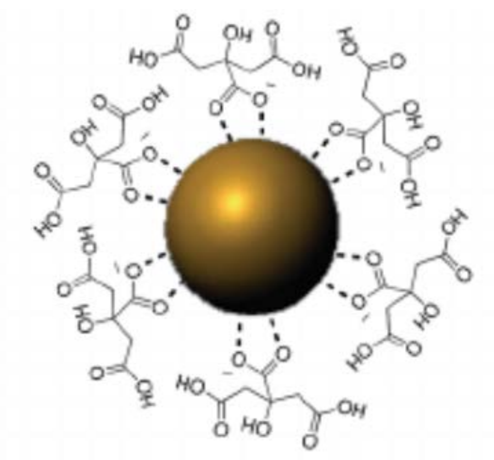
On flat gold surfaces: Self-assembled monolayers (SAM)

bonding energy sulphur-gold ~1 eV



Alkyl-Amine: physisorbtion

Exchange of ligands and maturation is possible at high temperature

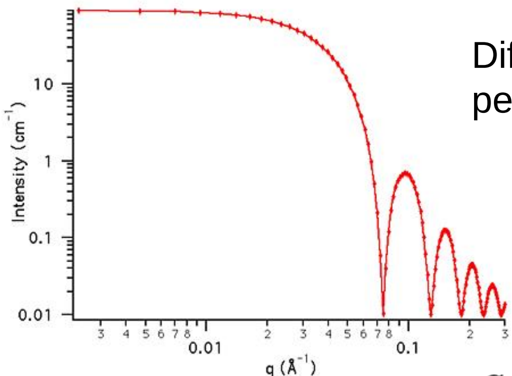


In water: Citrate is largely used

PEG-thiols…

Characterization of the nanoparticles

A- Small Angle Scattering

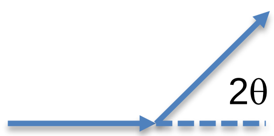


Diffraction by a perfect sphere

$$q = 2\pi \frac{2sin\theta}{\lambda}$$

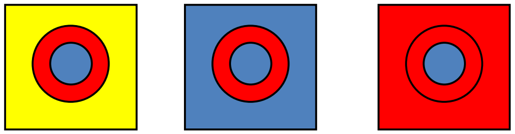
$$qL \approx 2\pi$$

$$sin\theta \approx \frac{\lambda}{L}$$



X-ray: only the core for gold

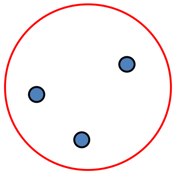
Neutron:



Core +Shell | Shell | Core

For non interactive spheres: I(q) =N F(q)

F(q) Form Factor

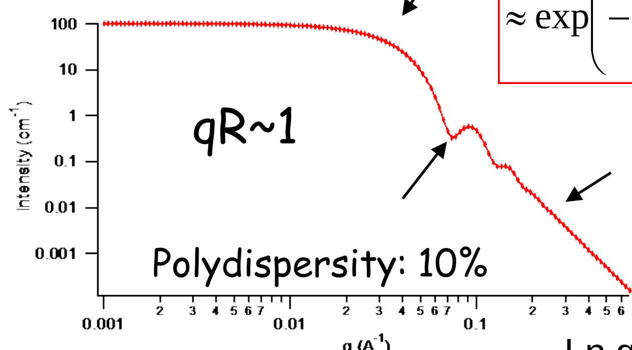


$N>10^{15}$

Very good statistics

Guinier's law:
gyration radius

$$\approx \exp\left(-\frac{q^2 R_g^2}{3}\right) \qquad R_g^{\ 2} = \frac{3}{5} R^2$$



~S/q⁴

Porod's law

$(1/q^{\alpha})$

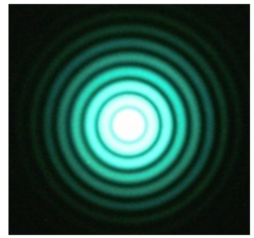
qR>10 with surface rugosity

Ln q

Basic Scattering

Random objects
No interaction

$I = n\, I_0$



$I_0(\theta)$ FORM FACTOR

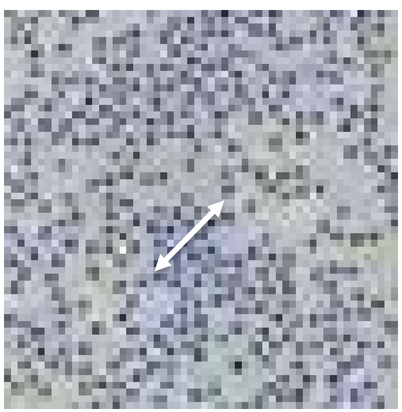
Correlated objects

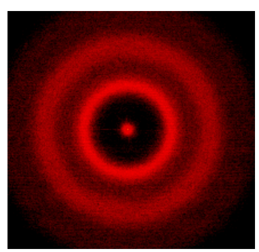
$S(\theta)$

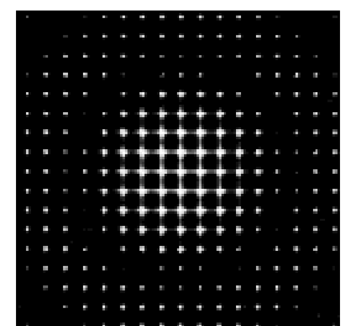
$I(\theta) = n\, I_0(\theta)\, S(\theta)$

Short-range ordered objects ?

Crystalline structure

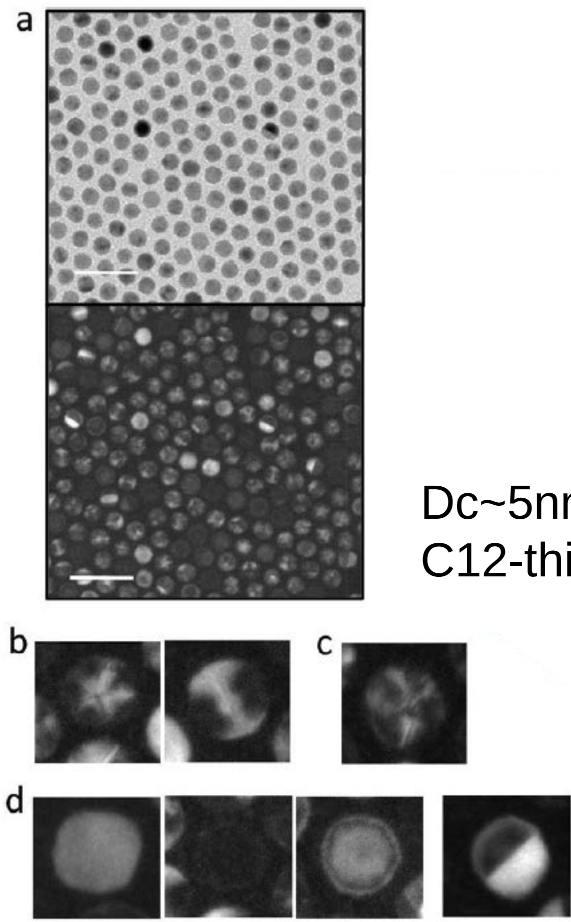






Characterization of the nanoparticles

B- Transmission Electron Microscopy



Dc~5nm
C12-thiol

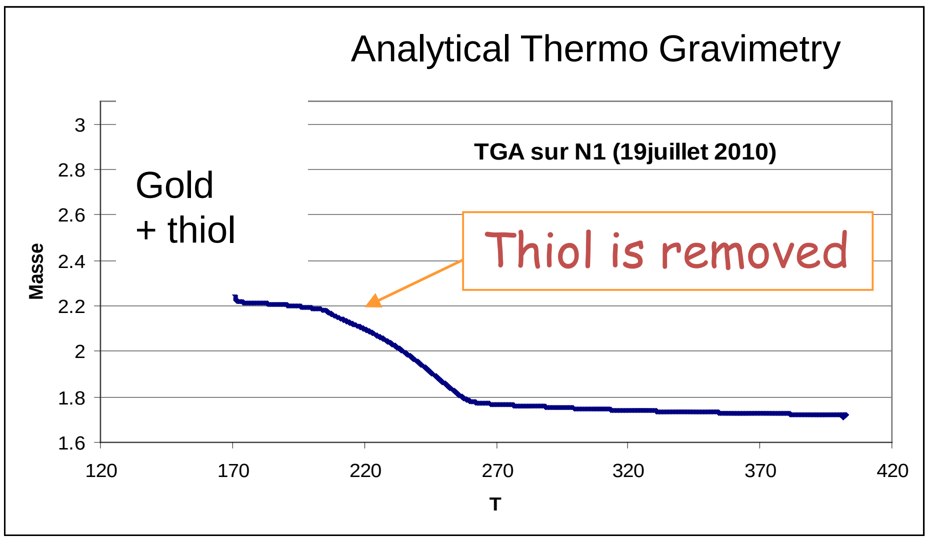
Internal structure:
monocrystalline, twinned…

But very bad statistics

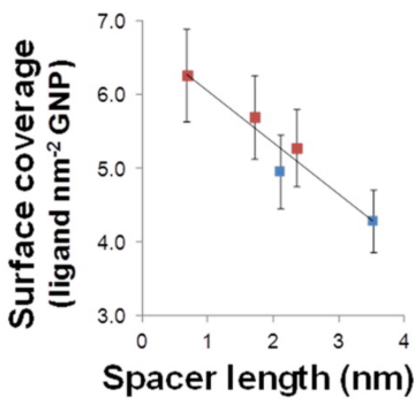
N. Goubet et al, J. Am. Chem. Soc. 2012, 134, 8, 3714-3719

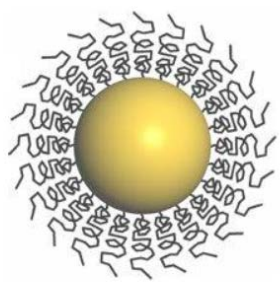
Characterization of the nanoparticles

C- Ligand density



Hydrodynamic radius:
(Pulsed Field gradient NMR
self diffusion, DLS…)





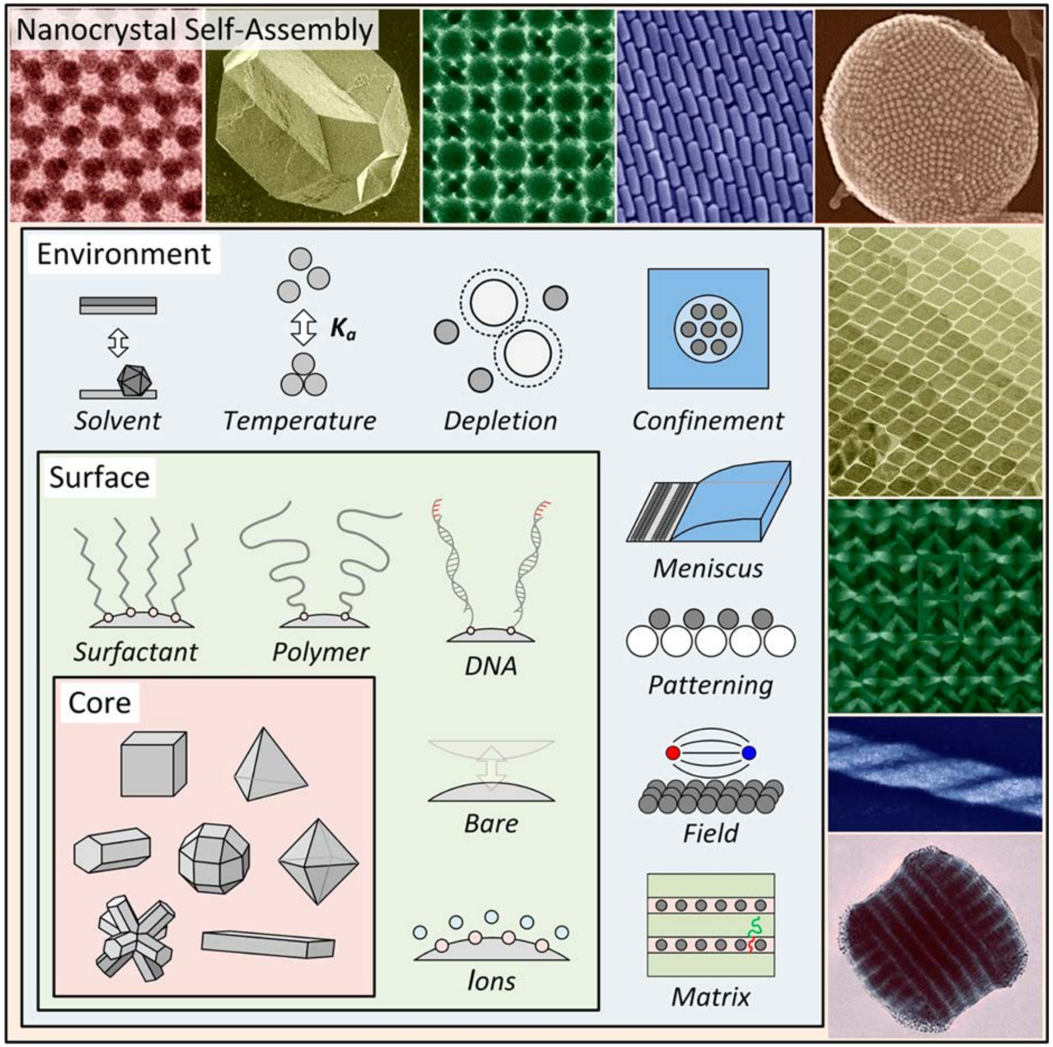
For alkane-thiols
~1/3 Au sites are occupied

-> Dense corona

ACS Nano 2013, 7, 2, 1129-1136

Analyst, 2017,142, 11-29

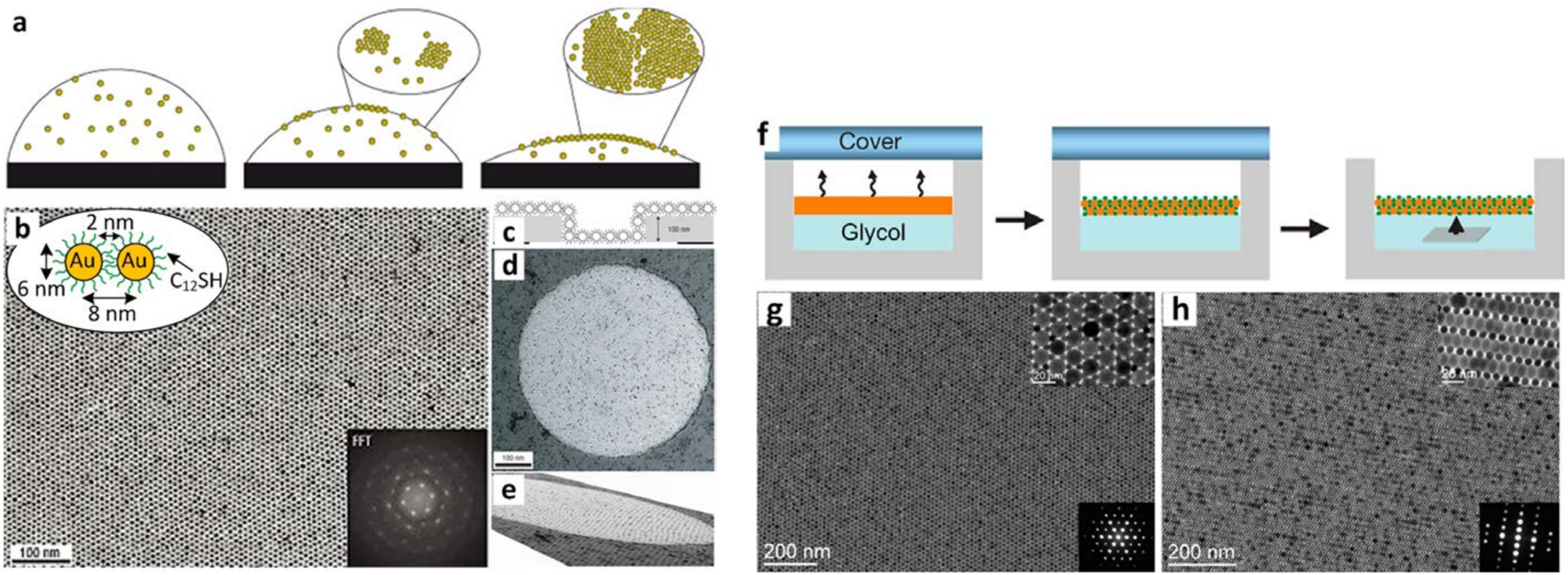
2- Self-Assembly



M. A. Boles, M. Engel, and D. V. Talapin,Chem. Rev. 2016, 116, 11220−11289
Adv. Sci. **2018**, *5*, 1700179

2D- Self-Assembly

Evaporation

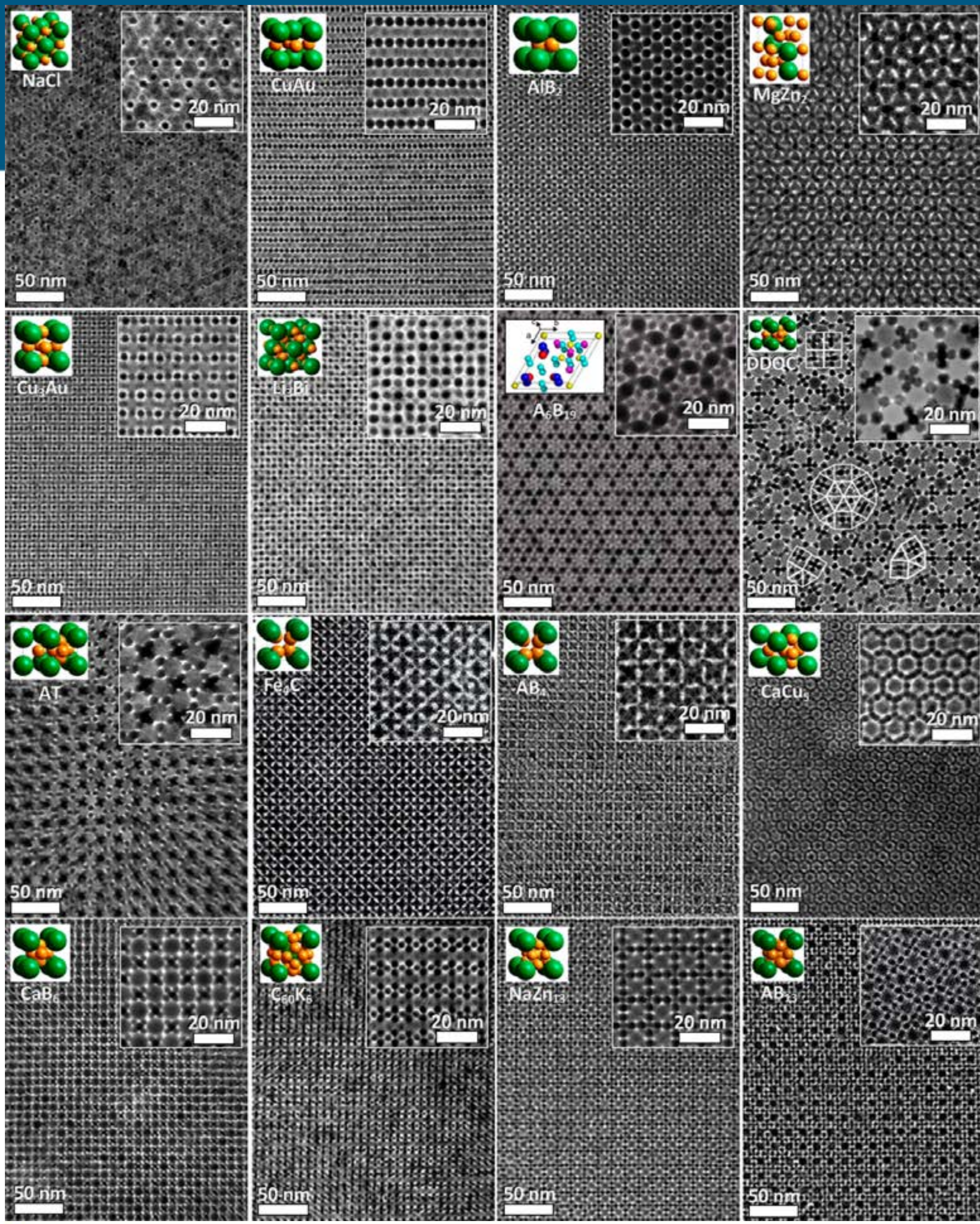


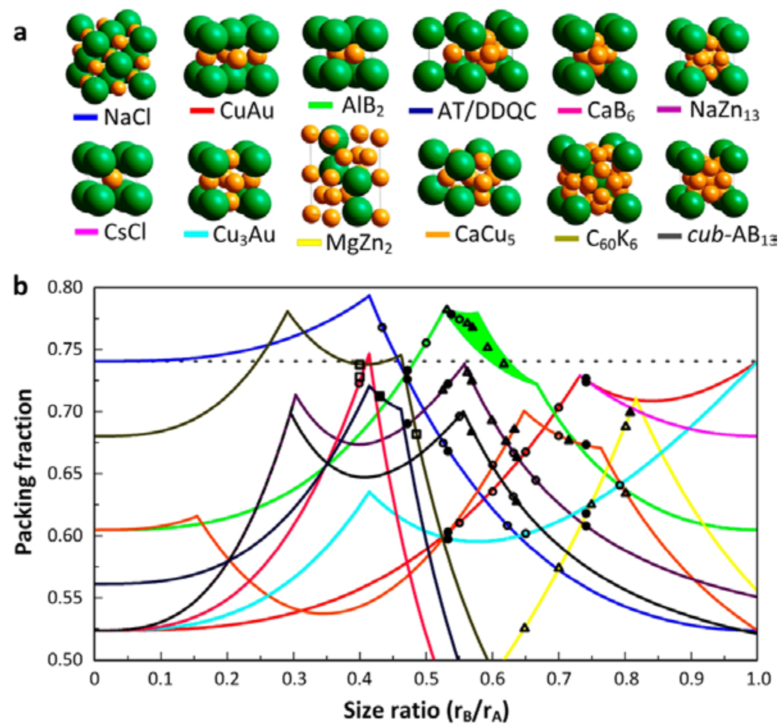
TEM= Electron Microscopy

But wetting problems!

M. A. Boles, M. Engel, and D. V. Talapin,Chem. Rev. 2016, 116, 11220−11289

The structure of alloys
Talapin's group





2D- Self-Assembly-quasi-crystalline phases

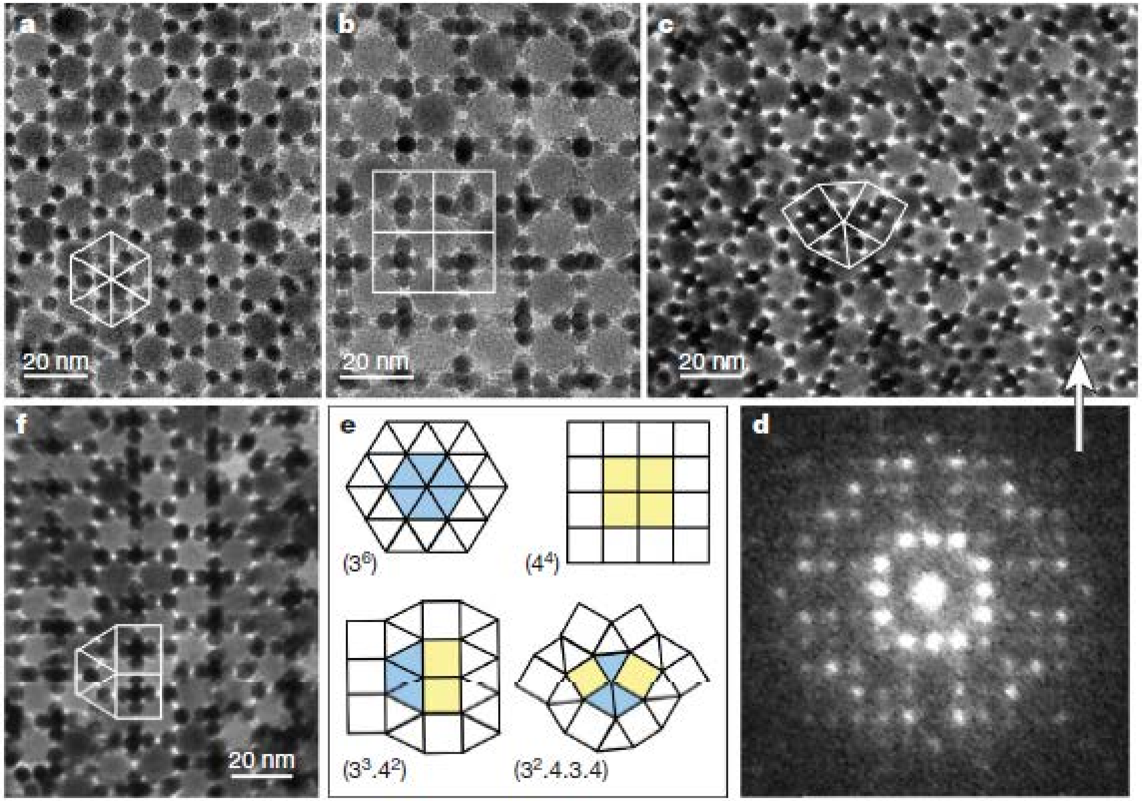
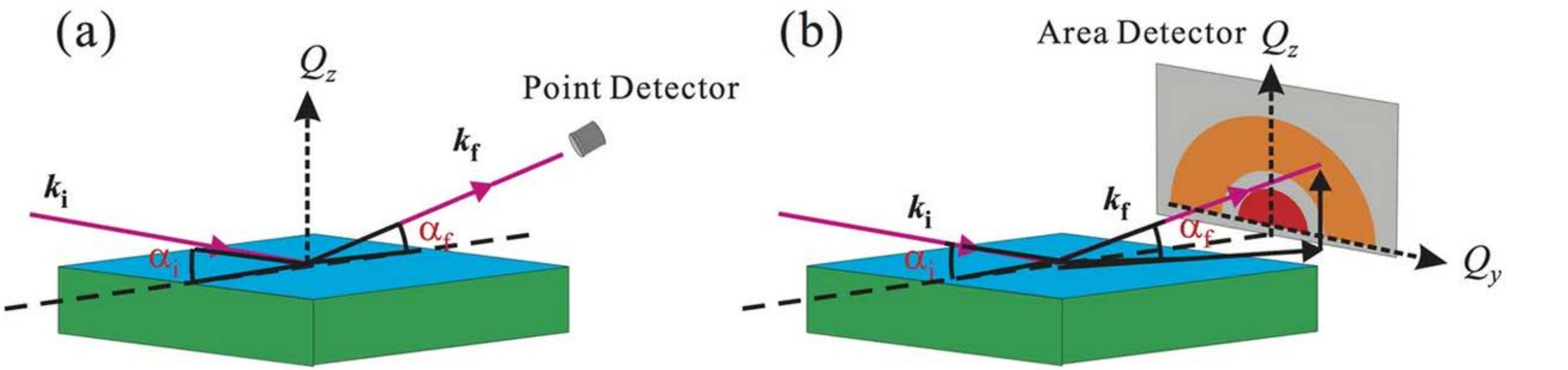


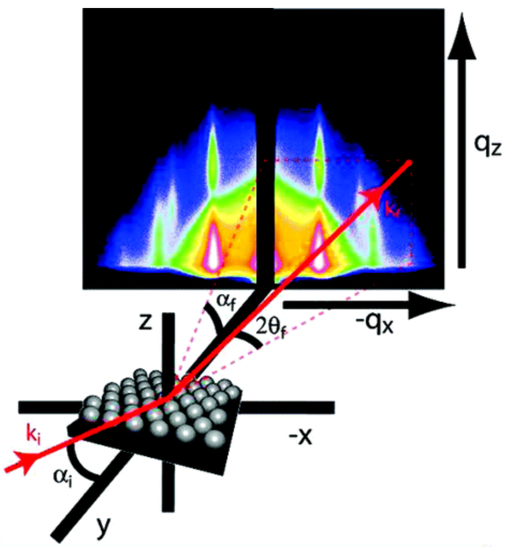
Figure 1 | Periodic binary superlattices self-assembled from 13.4-nm Fe_2O_3 and 5-nm Au nanocrystals. **a**, AlB_2-type superlattice; **b**, CaB_6-type superlattice; **c**, superlattice with AB_4 stoichiometry and the structural motif of the (3^2.4.3.4) Archimedean tiling. **d**, Electron diffraction pattern measured from a ~6-μm^2 domain of the AB_4 superlattice shown in **c**. **e**, Archimedean tilings used to describe the structure of the nanoparticle superlattices. **f**, A fragment of a superlattice corresponding to the ($3^3.4^2$) Archimedean tiling.

Scattering on structured films

XRR reflectivity and GISAXS



Schematic of setup for X-ray (**a**) reflectivity and (**b**) grazing incidence small-angle scattering.

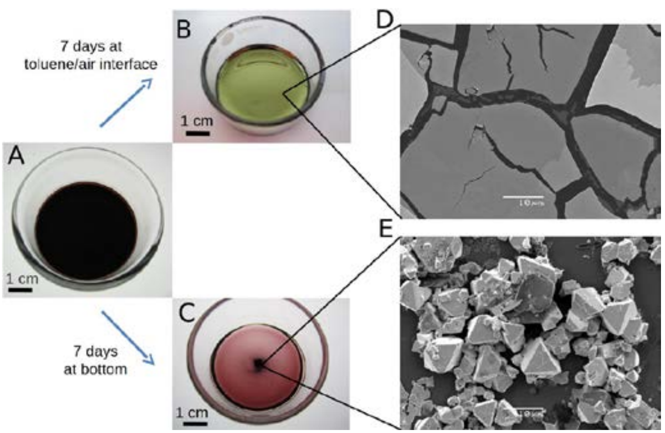


J. Phys. Chem. C 2010, 114, 34, 14427-14432

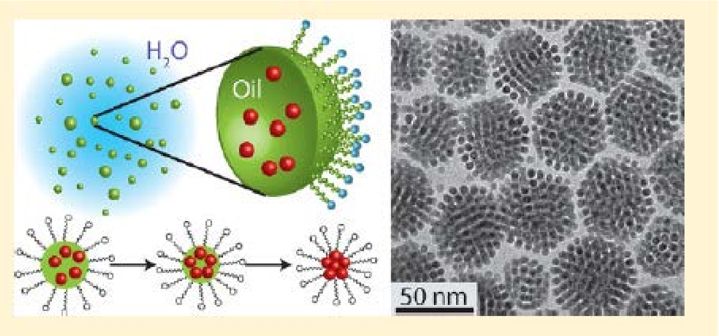
Scientific Reports volume 6, Article number: 26462 (2016)

3D self assembly

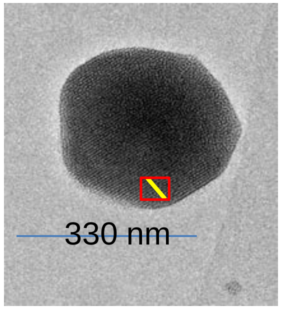
Solvant evaporation



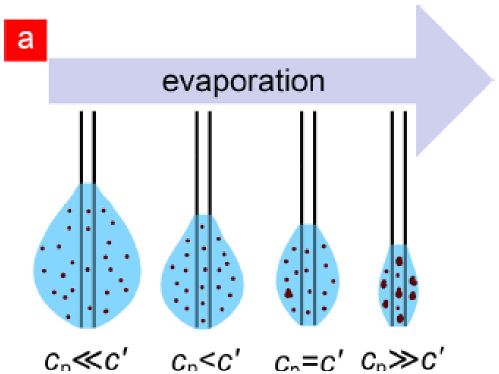
Maturation or evaporation in oil in water emulsion



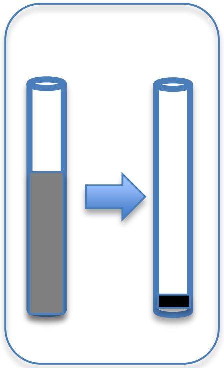
Nano Letters **2012**, 12, 3279



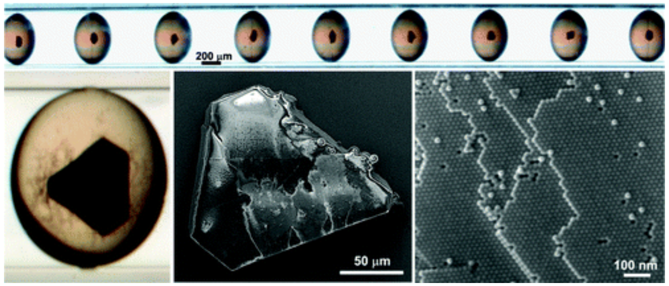
(LPS, Orsay)



Nano Lett. 2019, 19, 5246−5252



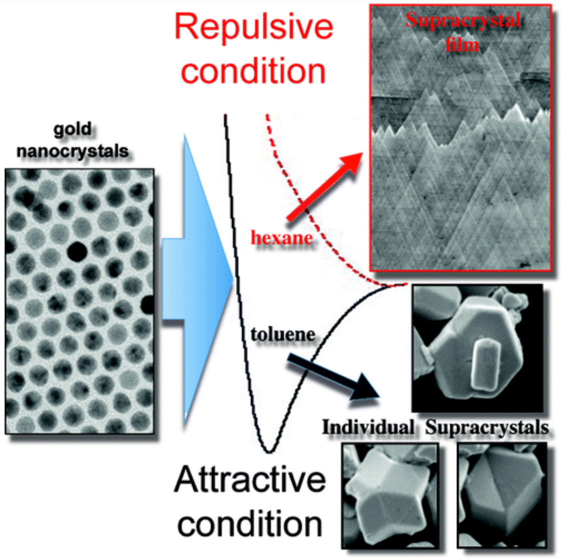
Use of microfuidics



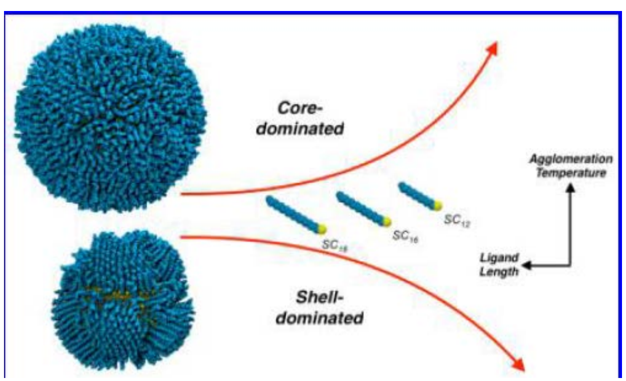
J. Am. Chem. Soc. ,2011,133, 23, 8956

Control of the kinetics?

Interactions-> Aggregation?



N. Goubet et al, Adv. Funct. Mater., 2011, 21, 2693

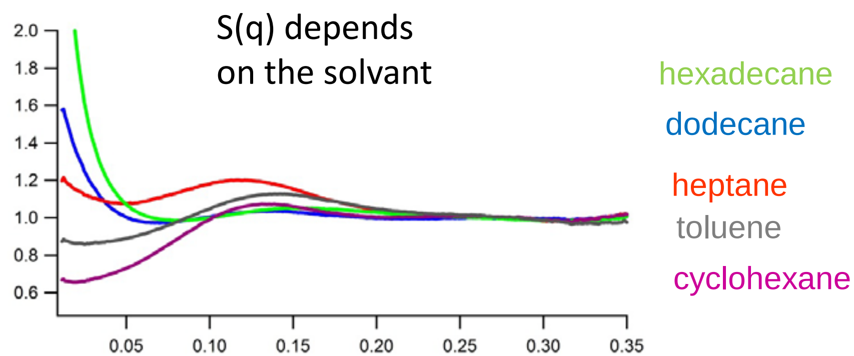


Langmuir 2018, 34, 12982−12989

Using SAXS $I(q) = N\,F(q)\,S(q)$

Form Factor

Structure Factor (=1 in very dilute Suspensions)



Slow solvent evaporation in emulsion

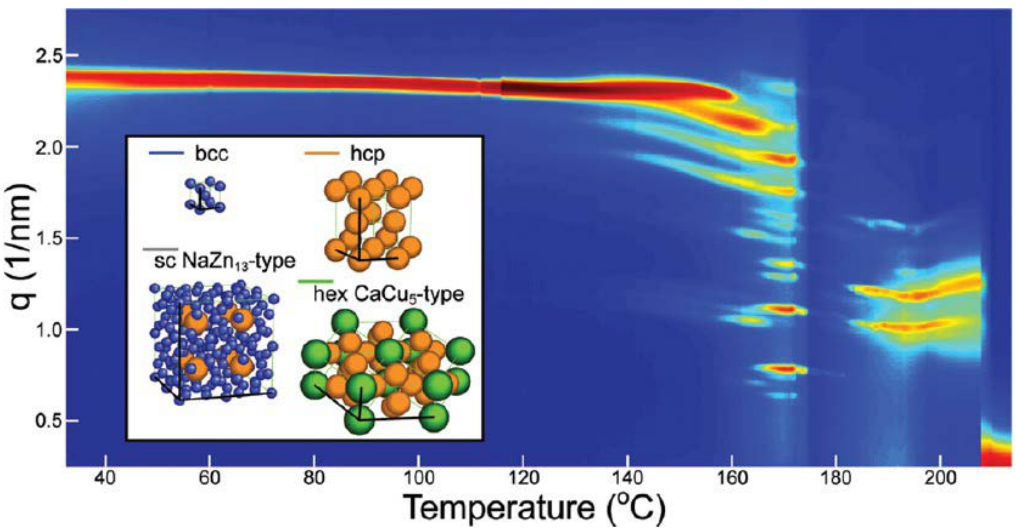
NP volume fraction

Disordered	FCC	BCC

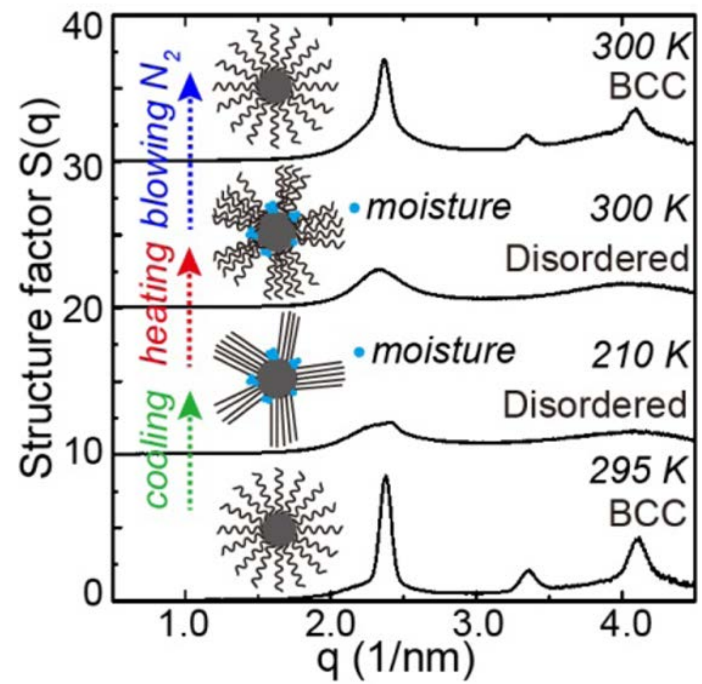
Dc=2nm, ligand C12

J. Phys. Chem. B, 2016, 120 (25), pp 5759–5766

Play with temperature?



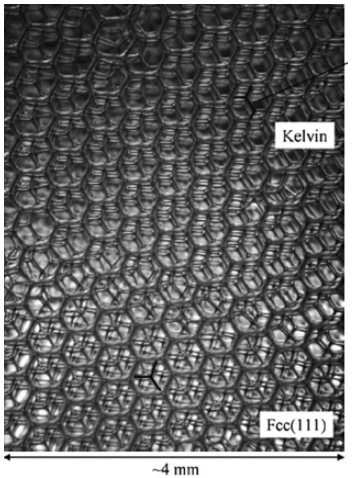
Nano Lett. 2013, 13, 5710−5714



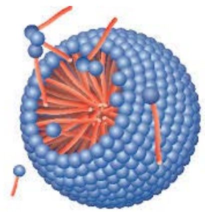
J. Phys. Chem. C 2016, 120, 27682−27687

Freezing the ligands…

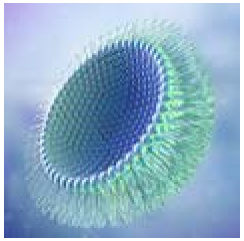
Other soft self-assembled systems



Monodisperse foams

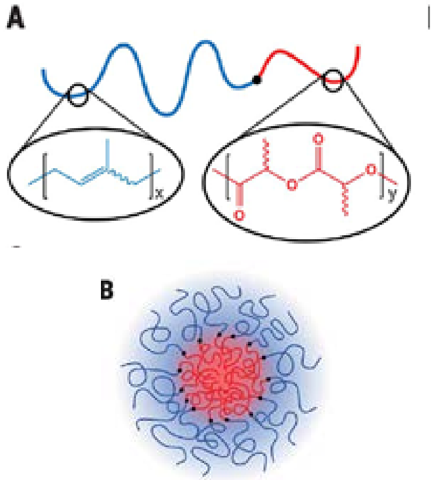


a)

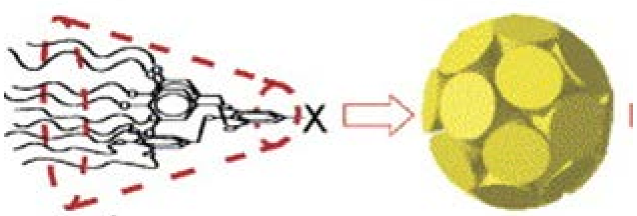


b)

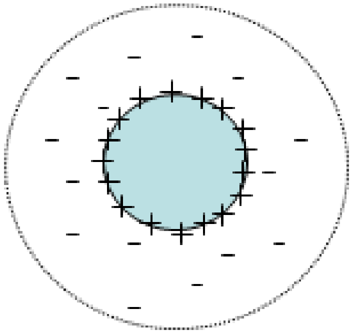
Surfactant Micelles
a) Direct b) Inverse



Co polymer diblocks



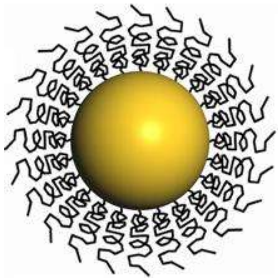
Dendrimers



Charged particles in water

3- What Structures?

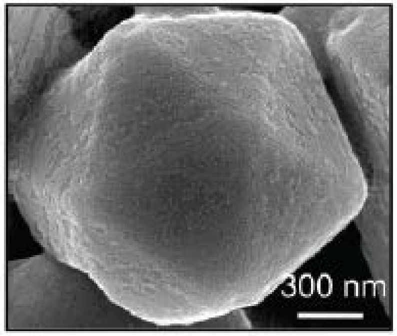
Metallurgy



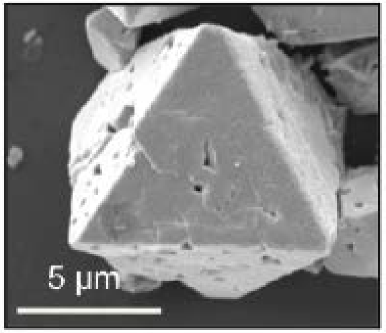
Self-assembly of gold nanoparticles into superlattices

→

What structure and why?



f

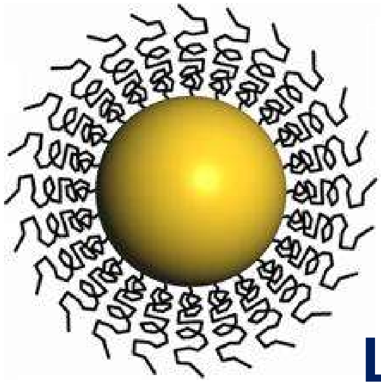


D=5nm

Goubet N. *et al J. Am. Chem. Soc.*, 2012, 134 (8), pp 3714–3719 FCC
(MEB=microscopie électronique à balayage)

Soft spheres

Rigid Core



Soft Corona

More or less spherical
Diameter **D,** Radius **R**

Ligand length **L**
Ligand density **σ**

« Hard » Spheres L<<R

L>>R « Soft » Spheres

FCC

BCC

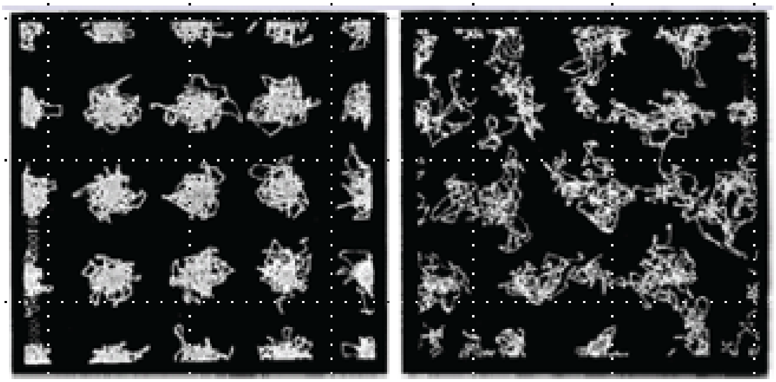
Metallurgy of hard spheres: From hard spheres to soft spheres

Phase Transition for a Hard Sphere System

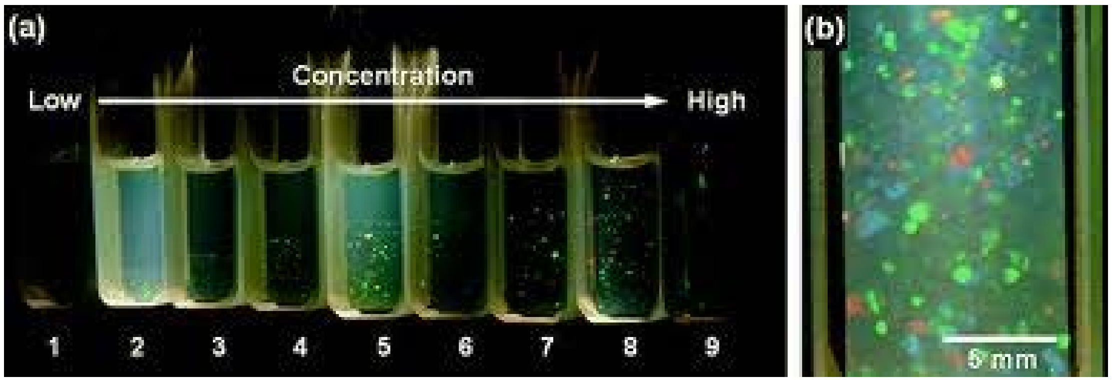
B. J. ALDER AND T. E. WAINWRIGHT
University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

Translational entropy:

FCC structure



Coexistence Disorder-Order ~50%-54%



Colloidal crystals

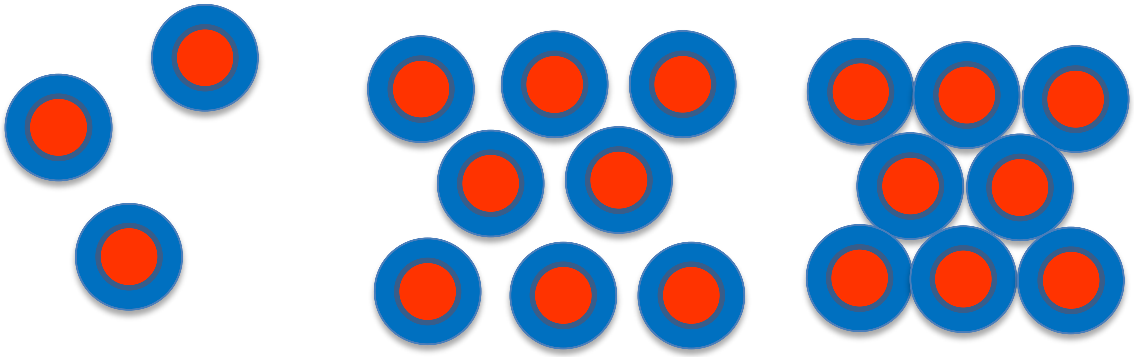
↓

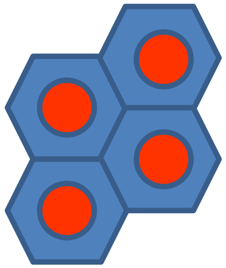
Photonic crystals

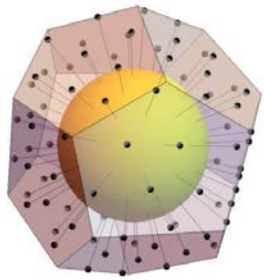
P. Pusey, W Van Megen
Nature **320**, 340 - 342 (27 March 1986)

Metallurgy of hard spheres
From hard spheres to soft spheres

Soft Spheres







50% **74%** **100%**

Not only pair interaction

Soft spheres

Volume fraction

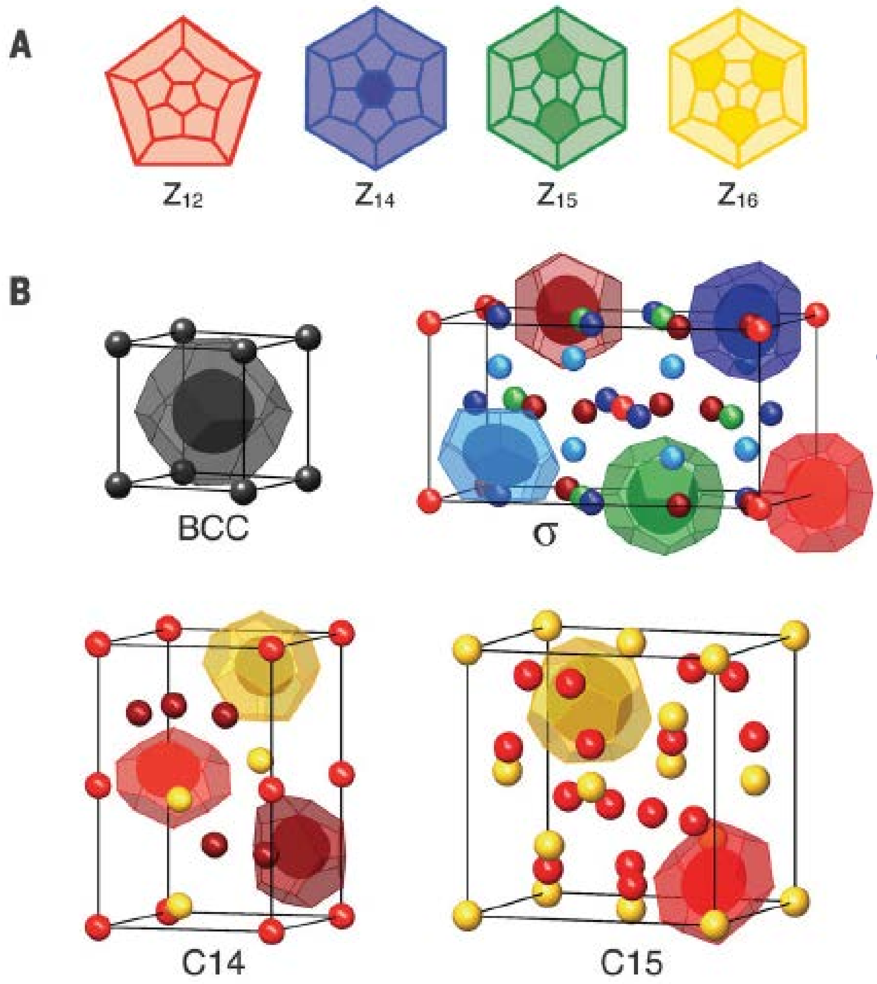
FCC

Surface tension
Soft elasticity
…

BCC

But not only…

Frank et Kasper phases
In block co-polymers



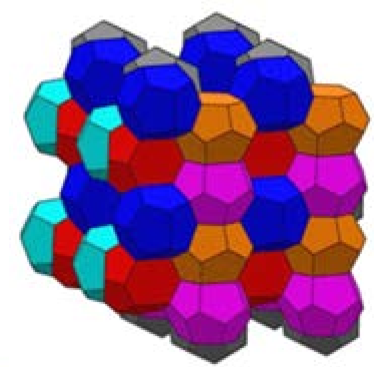
σ sigma phase
= tetragonal

C14= *hexagonal version of the C15 structure*

Kim et al., Science 356, 520–523 (2017)

Many Different
Frank and Kasper phases
recently discovered
in soft spheres system

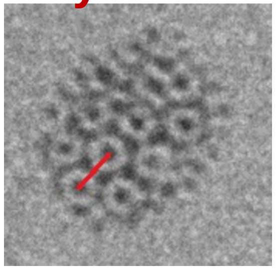
And also A15….



Experiments on gold nanoparticles : L/R~0.7

Gold NPs
D~2 nm
Ligand:
C6-thiol
(Brust synthesis)

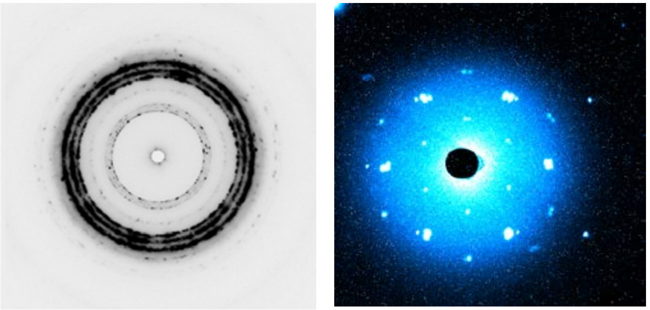
Cryo-TEM



- *METSA*

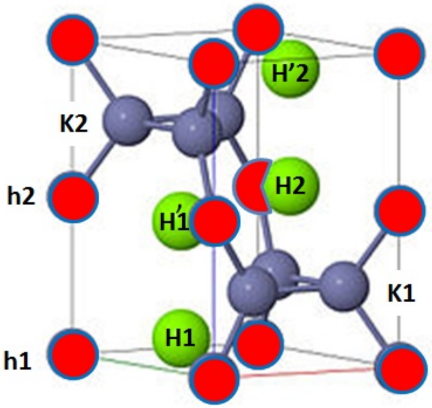
J. Degrouard (LPS)

X-ray scattering



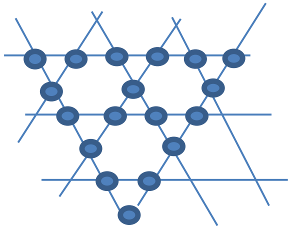
- *SOLEIL; Swing (Fr)*
- *ESRF, BM02 beam line (Fr)*
- *LPS, MOMAC (CEA Fr)*
- *LPS SAXS, MAXS….*

HEXAGONAL STRUCTURE
Lattice parameter= 2* diameter



H=Hexagonal layer

K=Kagome layer

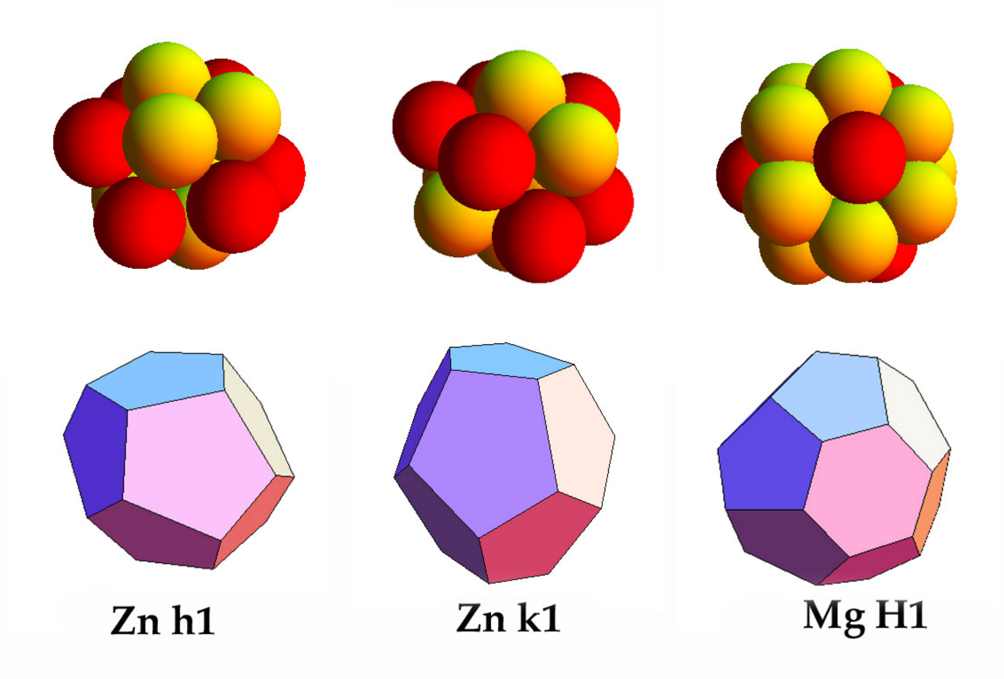


The C14 Structure ($MgZn_2$ type)

One of the Frank and Kasper Phase

Frank and Kasper Phases as closed packed structures

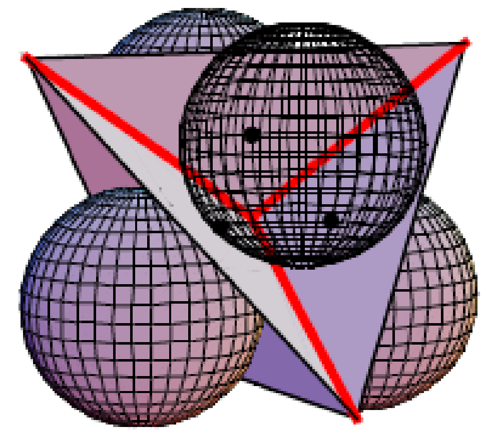
C14 phase: 3 local environments



Z=12 Z=12 Z=16

(deformed icosahedra)

Frank et Kasper phases
Topologically
closed packed structures
=TCP



Local tetrahedral environment

Soft Spheres Self-Assembly a large field that still worth beeing explored

Structure « portrait »

To be published

Why Frank and Kasper Phases in one-size soft NP system?

C14 versus BCC (or FCC)

- Interfacial Energy:

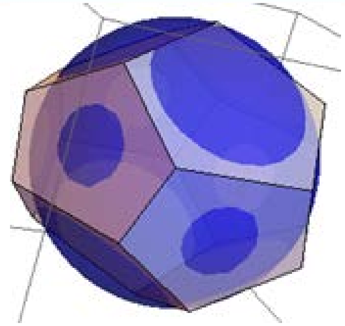
In foams, Frank and Kasper phases (A15) is more stable than BCC (Kelvin) but the difference in energy is very small

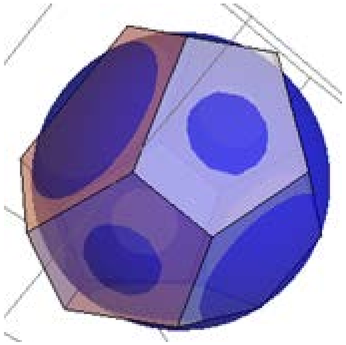
- Ligand distortion: BCC

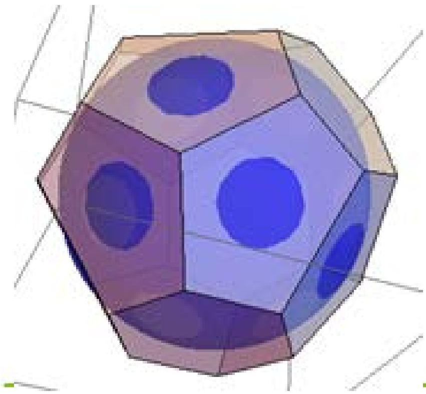
- Van der Waals attraction: ????

- Entropy: requires simulation, not yet done

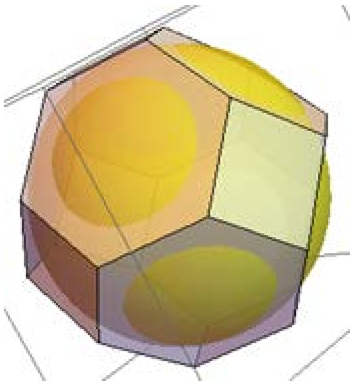
Role of the ligand interfacial energy: C14 versus BCC







	C14	BCC
Voronoi volume	0.11025 0.10941 0.13432	0.11785
Mean radius	0.30415	0.30415
Lmax	0.355371 0.356055 0.356055	0.34531
Lmin	0.25130 0.24575 0.29195	0.26748
Mean area per Voronoi	**1.27114**	**1.2775**



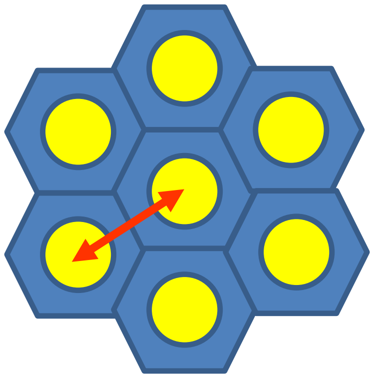
a(C14)=1

→ Close interfacial energy

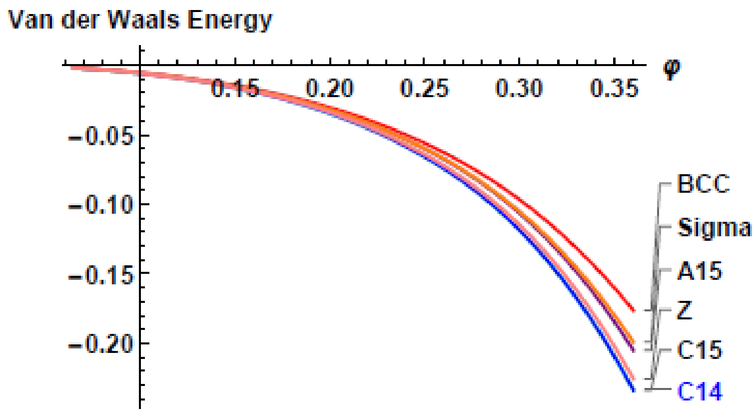
Role of the van der Waals attraction

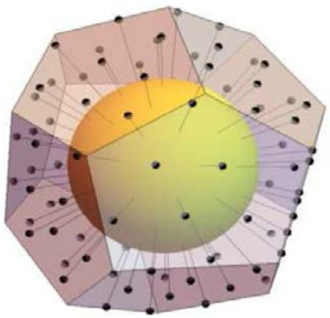
Volume fraction
100%

Competition between the van der Waal attraction
and the elastic ligand repulsion

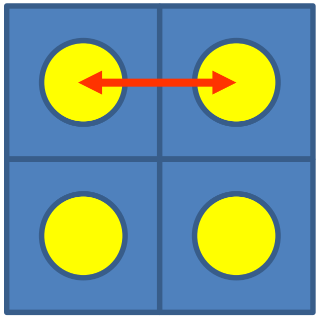


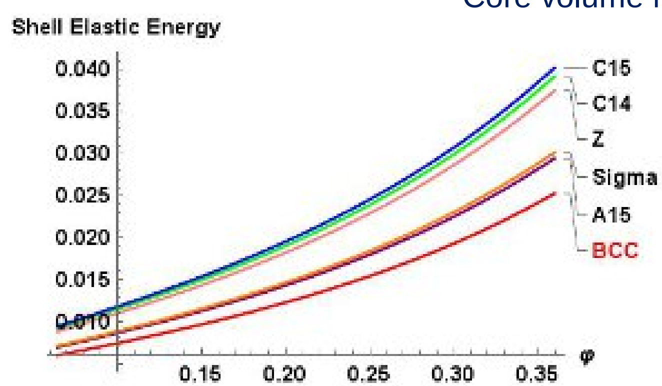
Favors the elastic ligand energ





Core volume fraction





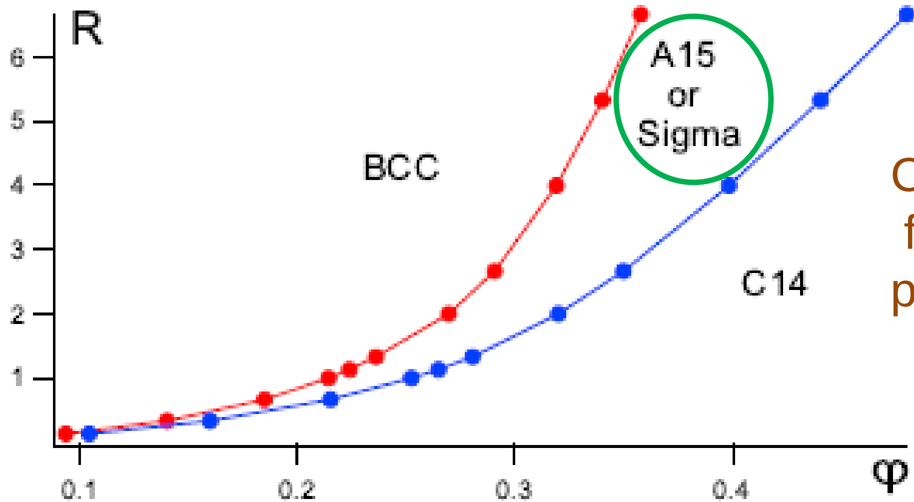
Variation of
the corona thickness
$\ell_0 \to \ell_0 + \delta\ell$

$$E_{el} = \frac{1}{2} K \frac{\langle (\delta\ell)^2 \rangle}{(\ell_0)^2}$$

Favors the van der Waals energy

Which phase and why?

Ratio
Elastic constant/
Hamaker constant

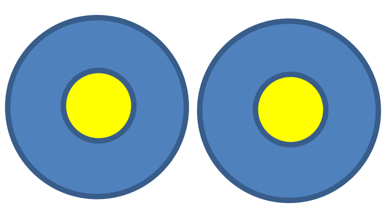


C15 less favorable
from an elastic
point of view

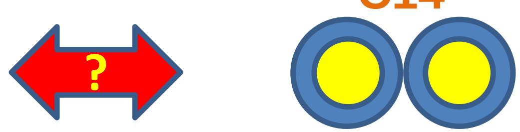
Hard core volume fraction
NP volume fraction=100%

B. Pansu, JF Sadoc EPJE 2017

D=2.2 nm C12 ligands
BCC

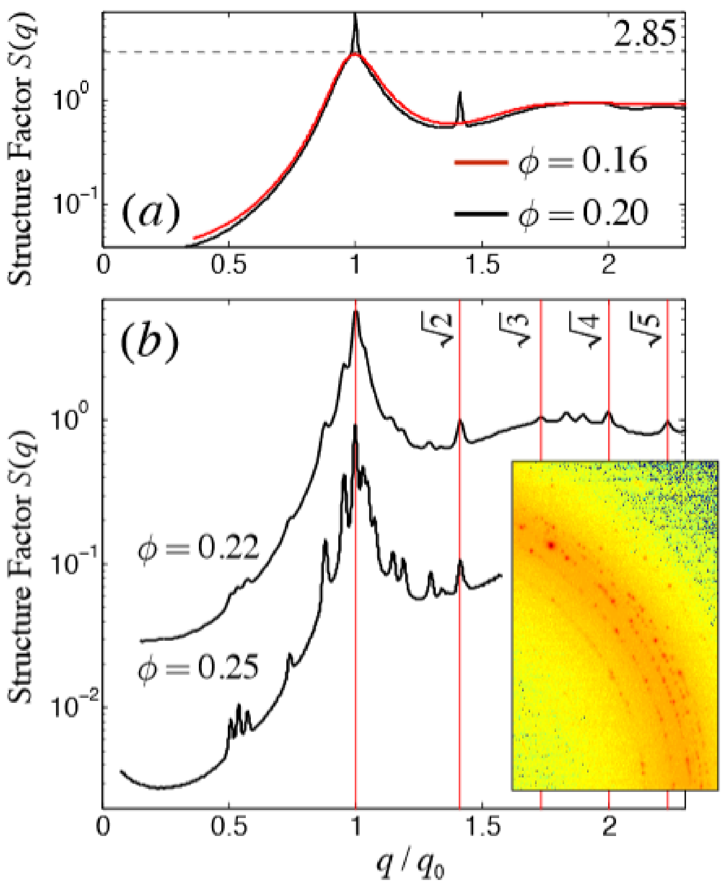


D=2.2 nm C6 ligands
C14



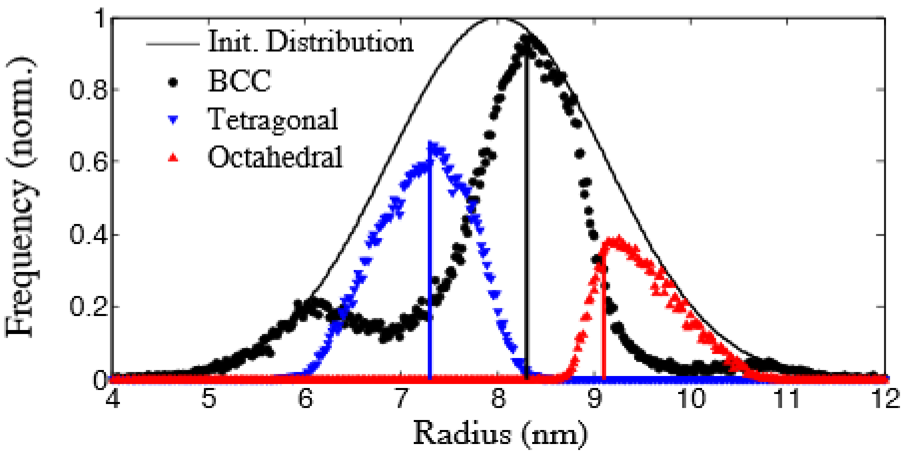
Same behavior for
larger particles

Role of polydispersity?



Silica nanoparticles in water
8 nm 14% 5mM ph=9.5
B. Cabane et al,

Physical Review Letters (2015) 116(20)

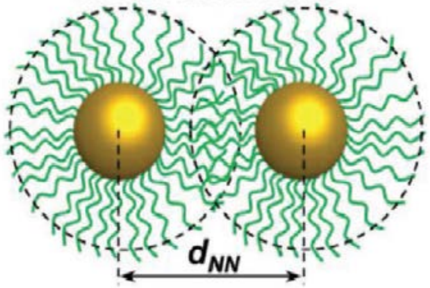


Monte Carlo simulation: fractionation

Opened questions….

- What is the real conformation of the ligands?

  M. A. Boles PhD 2016
  Review K.J. Si, Y. Chen, Q. Shi, W. Cheng
  Adv. Sci. ***2018****, 5, 1700179)*



- What is the role of polydispersity?

  Fractionation of silica particles in C14 structure
  B. Cabane et al, PRL 116, 208001 (2016)

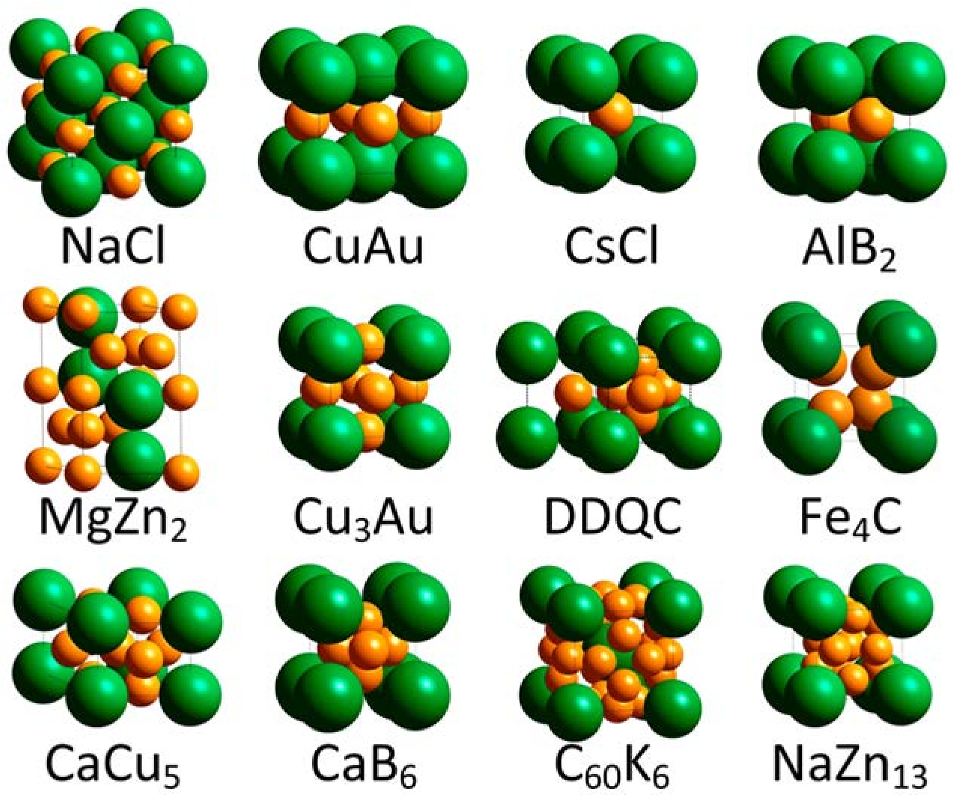
- What is the role of the shape and crystallinity of the NP core?

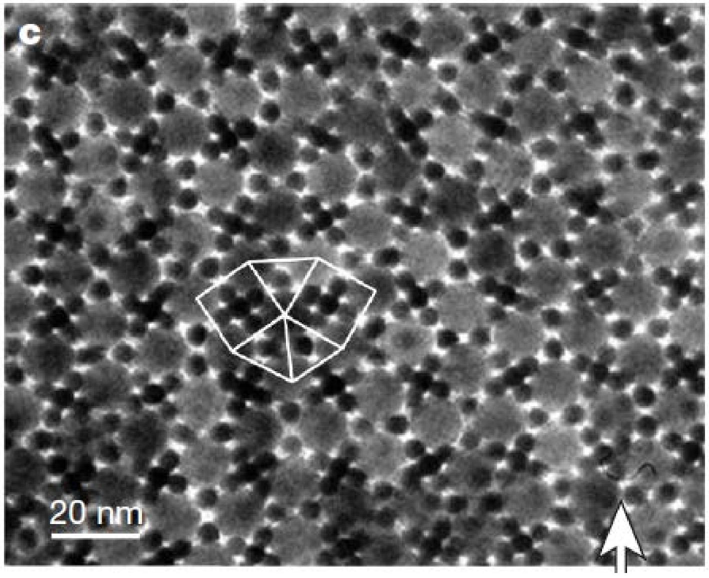
  H. Portales et al NanoLett.2012, 12, 5292-5298

- Temperature: effect on the ligands

  Irreversible phase transition upon heating
  (Nano Lett. 2013, 13, 5710−5714)

In NP Alloys -> same diversity as for classical atoms





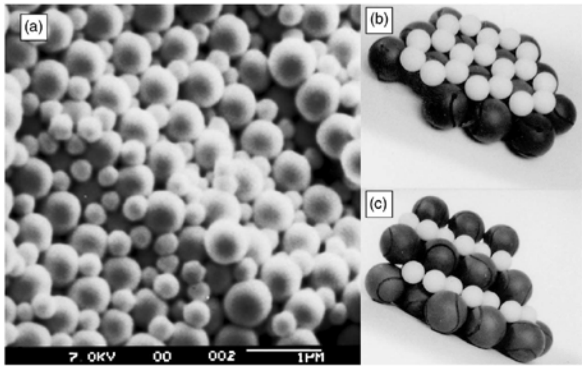
DDQC= dodecagonal quasicrystal

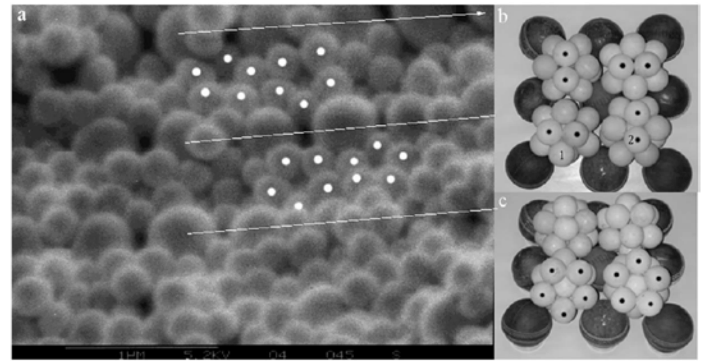
Fe203 (oleic acid) Dc=13.4nm
Au (dodecathiol) Dc=5nm

Michael A. Boles and Dmitri V. Talapin
J. Am. Chem. Soc. 2015, 137, 4494–4502

D.V Talapin and al,
Nature, 461 Oct 2009

In « classical » colloids

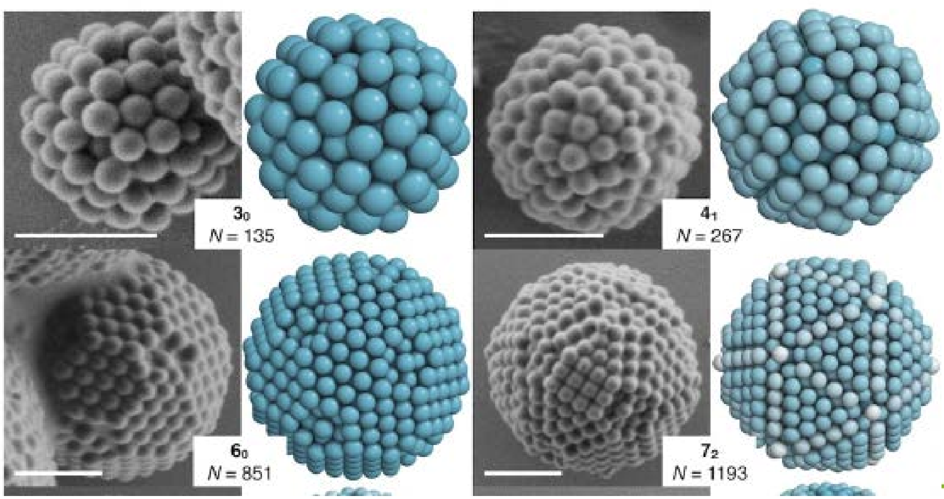




AB2 r=0.428

AB13 r=0.508

A. Schofield, P. Pusey, P. Radcliffe Physical Review E 72(3 Pt 1):031407



D=244 nm
PS

Nature Communications
***volume 9**, 5259 (2018)*

Other open questions

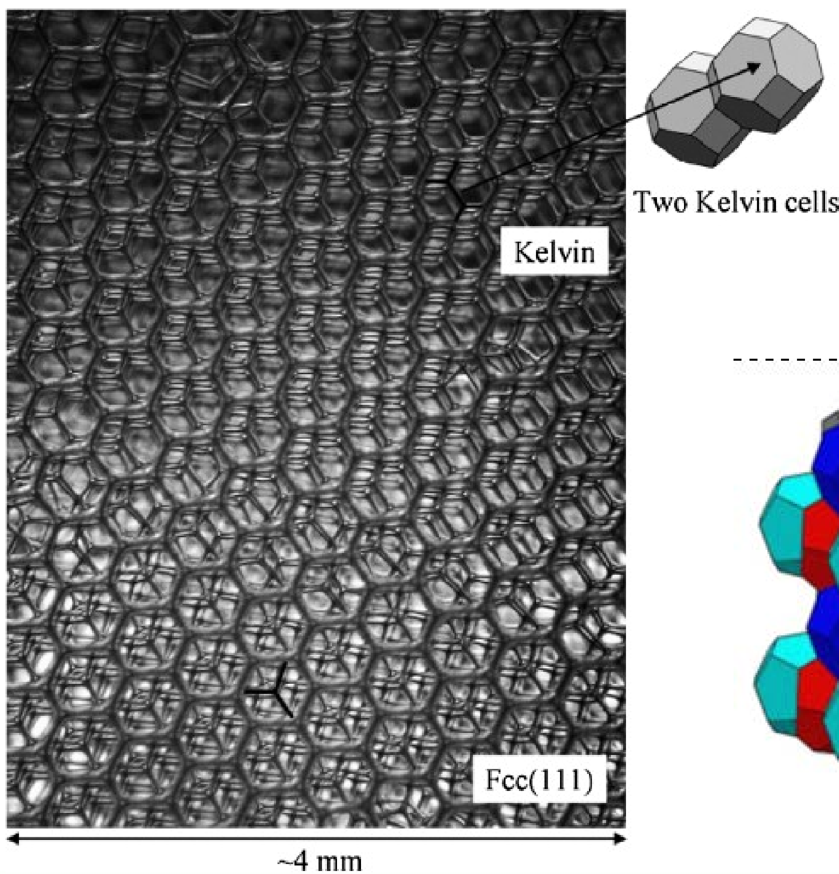
What effect of the structure :

- on the plasmonic properties?
- on the mechanical properties?

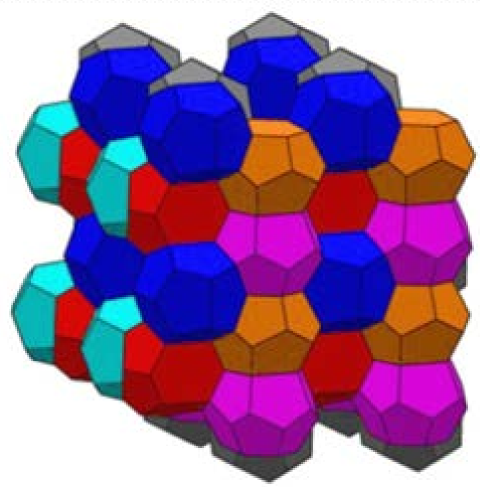
Sup 2: A15 in foams

Lord Kelvin: Minimizing the **interfacial area** with respect of mechanical constraints (1887)

Dry



Kelvin Structure
BCC
One type of cell
Slight distortion of the hexagons
Z=14 (8+6)



Weaire-Mac Phelan Structure (1993)
A15
(Surface Evolver)
Experimental proof: 2012

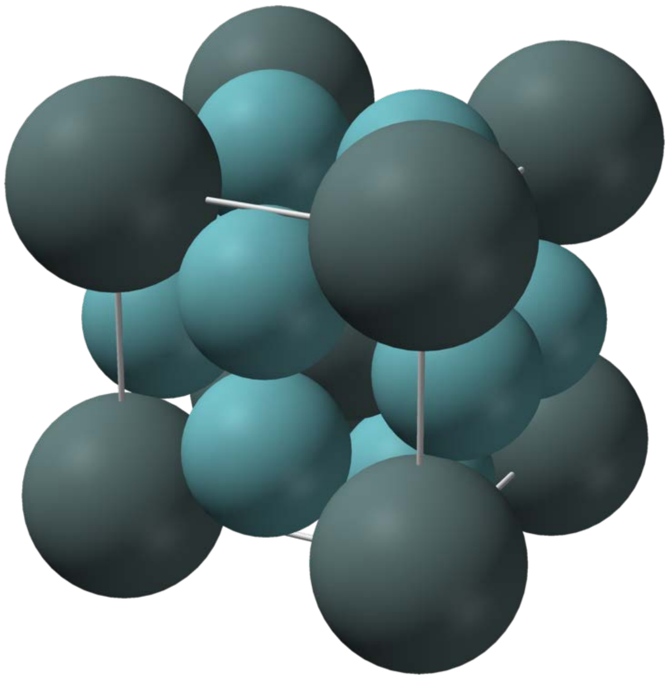
Review: W. Drenkhan, S. Hutzler Adv Colloid Interface Sci. 2015 Oct;224:1-16

A15 structure

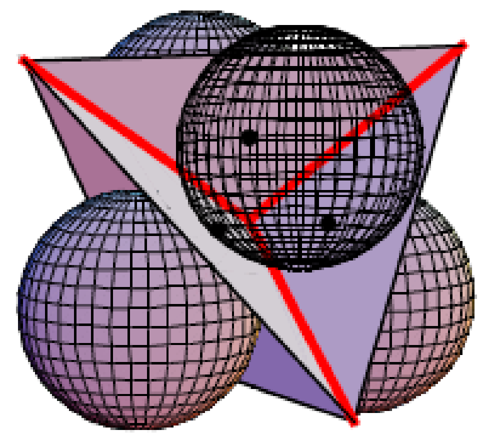
Intermetallic compounds (1931) Cr_3Si

Two different environments: 2 Z12 and 6 Z14

$Pm\bar{3}n$



Frank et Kasper phases
Topologically closed packed structures=TCP



Local tetrahedral environment