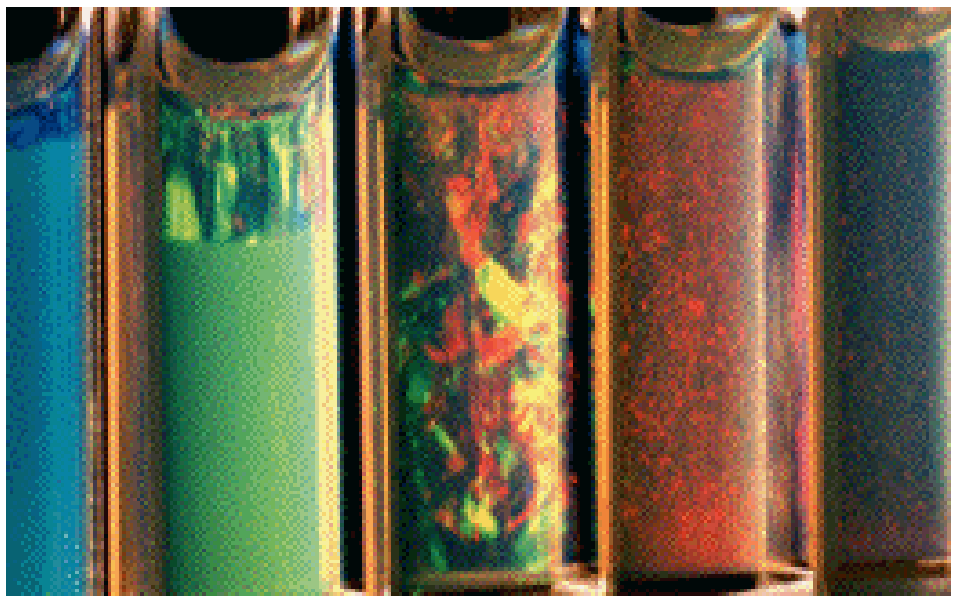
Hard Sphere Crystals

- **Hard Spheres can crystallize: Computer Simulations (Alder, Wainwright 1950's)**
- **Colloid Synthesis -> Monodisperse Silica, Latex -> Sterically Stabilized & Index Matched -> Organic Solvents**

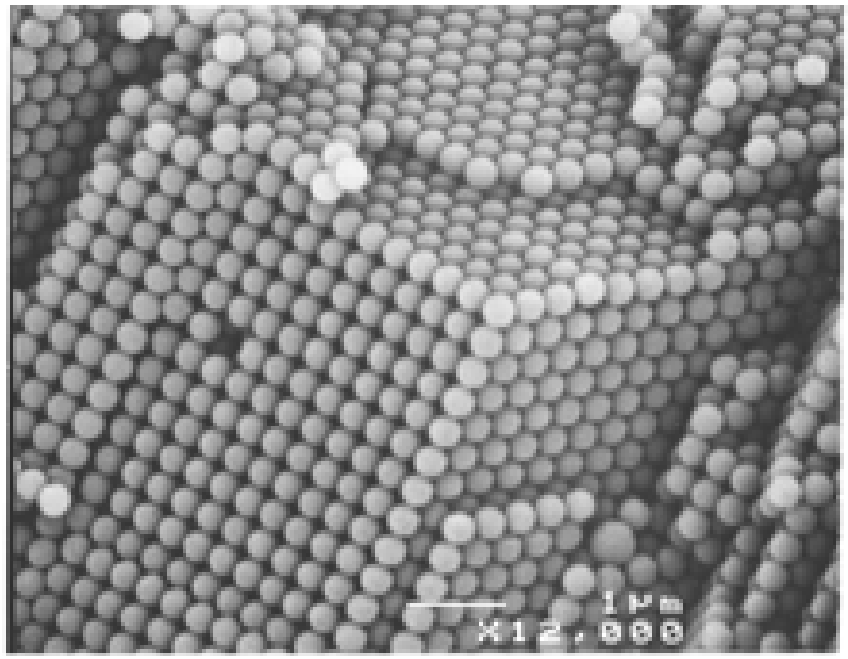


Pusey & Van Megen, Nature (1985)

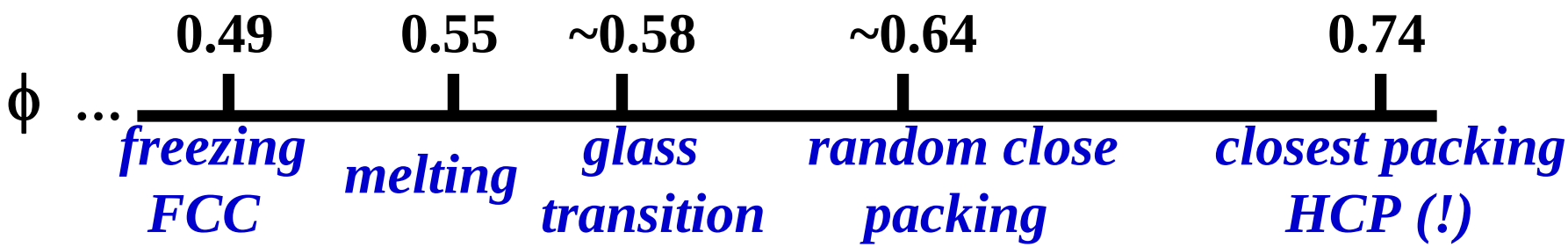
Hard Sphere Crystals

-> Phase Diagram as function of Volume Fraction

Colloids as Hard Spheres



Phase Behavior of Hard Spheres is only Determined by Entropy
-> the volume fraction ϕ



PHSA-PMMA (core-shell) in CHB-cisDec

- **Density & Index Matched (~mg, *No VdW*);** l_B **= 7 nm**
- **$\kappa R<1$ (c~ 10^{-8} – 10^{-11} M):** **Soft Spheres** ⊕
- **With salt (TBA-Cl) additions:** **Charge Reversal** ⊖
  - **more salt: $\kappa R>>1$:** **Hard Spheres**
  - **steric stabilization ~ 15 nm**
- **Surface potential: +100 mV <-> -100 mV**

(*R ~ 1 μm*: several 100e)

DLVO: Screened Coulomb

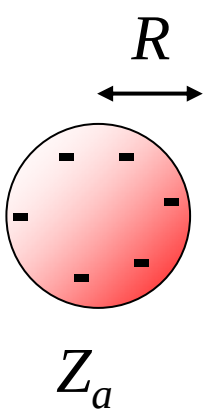
Solution of Poisson-Boltzmann and small DL overlap: Yukawa potential

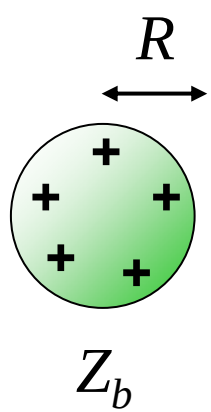
$$V_{Yukawa} = \frac{Z_a Z_b e^2}{4\pi\varepsilon\varepsilon_0}\left(\frac{\exp[\kappa R]}{1+\kappa R}\right)^2 \frac{\exp[-\kappa r]}{r}$$

a,b = +/-

Inverse Debye Screening Length

$$\kappa = \left(\frac{\sum z_i^2 e^2 n_{0i}}{\varepsilon\varepsilon_0 k_B T}\right)^{\frac{1}{2}}$$

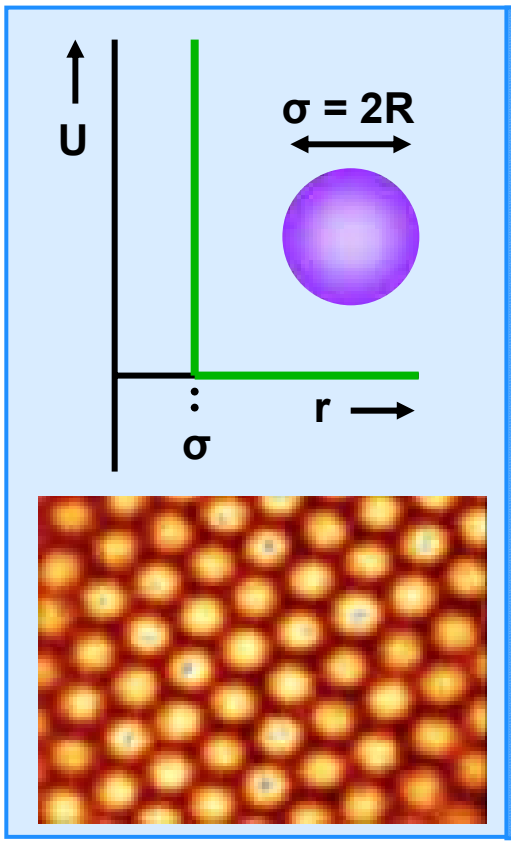


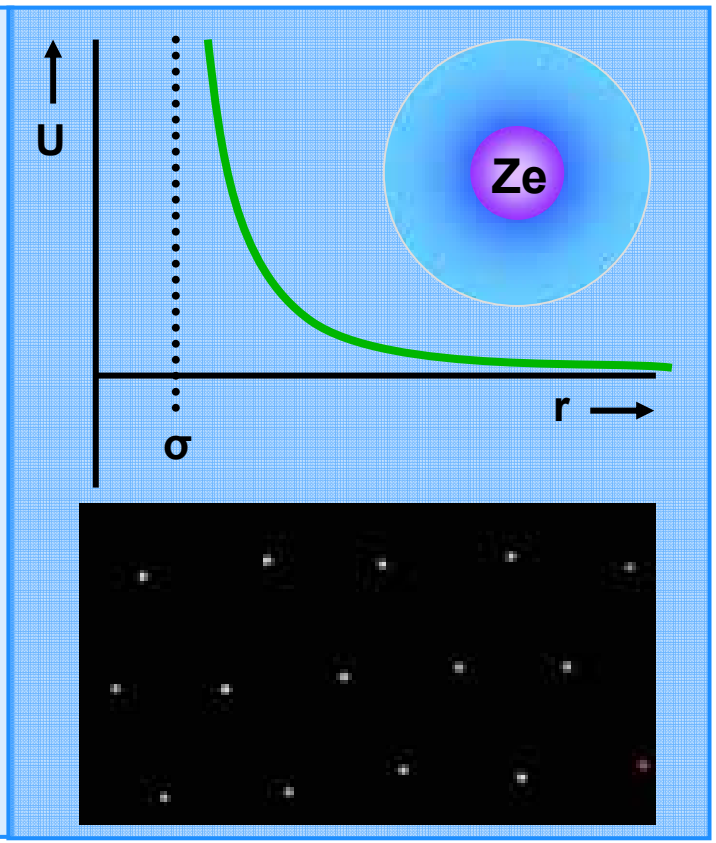


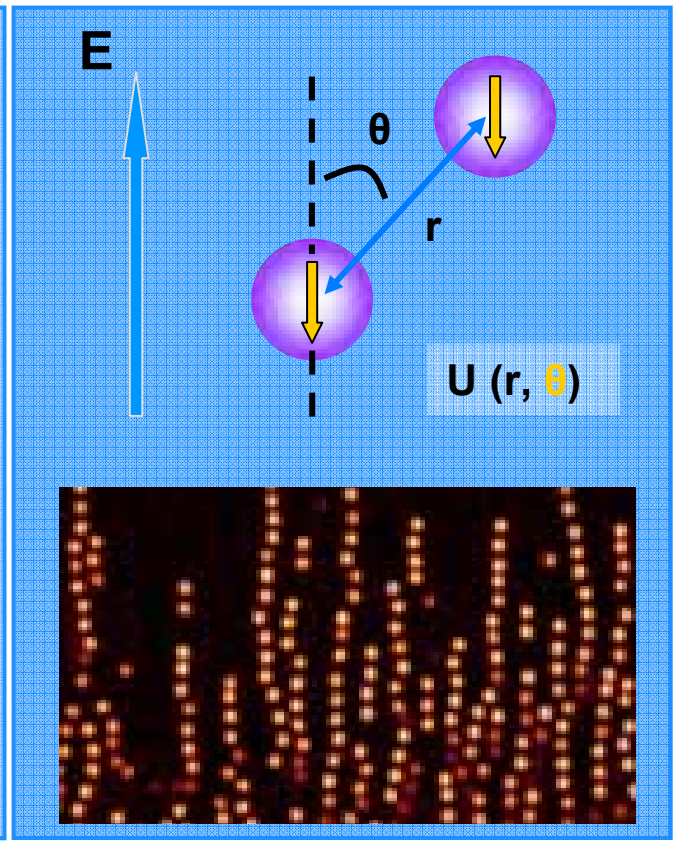
Tunable Interactions: Hard-Soft-Dipolar

PHSA-PMMA in CycloHexylBromide-Decaline with TetrbutylAmmoniumChloride

e.g hard sphere **long-range repulsive** **anisotropic: dipolar**







Density & Index Matched

A.Yethiraj & A.van Blaaderen, *Nature*, (**2003**), 421, 513-517

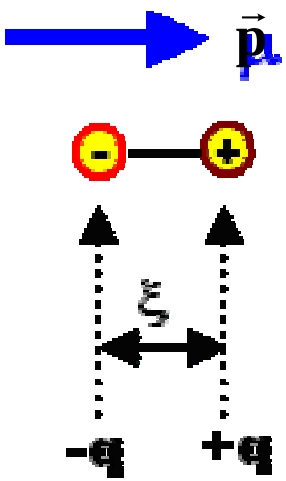
Electric Dipoles

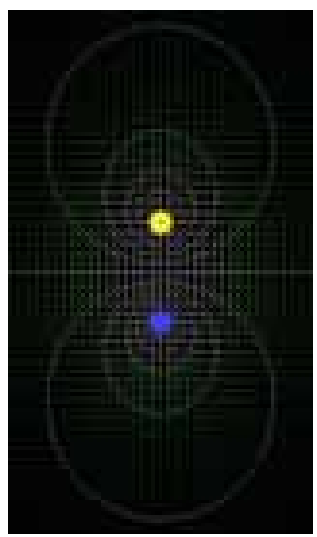
$$\Phi(r) = \frac{(\vec{\mathbf{p}} \cdot \hat{\mathbf{r}})}{4\pi\varepsilon_0 r^2}$$

$$\vec{\mathbf{E}} = -\nabla\Phi$$

$$\vec{\mathbf{E}}(\vec{\mathbf{r}}) = \frac{(3(\vec{\mathbf{p}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \vec{\mathbf{p}})}{4\pi\varepsilon_0 r^3}$$

$$U = -\vec{\mathbf{p}} \cdot \vec{\mathbf{E}}$$

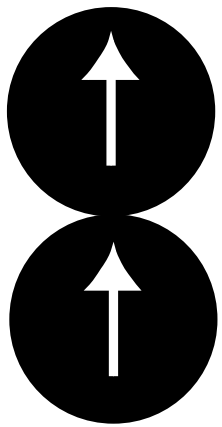




Electric Field at MHz: Dipolar Interactions

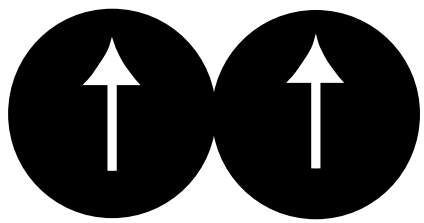
$$\beta u_{\text{dip}}(\mathbf{r}) = \frac{\beta\gamma}{2}\left(\frac{\sigma}{r}\right)^3\left(1-3\cos^2\theta\right) \qquad \gamma = \frac{\pi}{16}\varepsilon_s\varepsilon_0\sigma^3\alpha\left|\mathbf{E}_0\right|^2$$

- Dipoles like to be head-to-toe



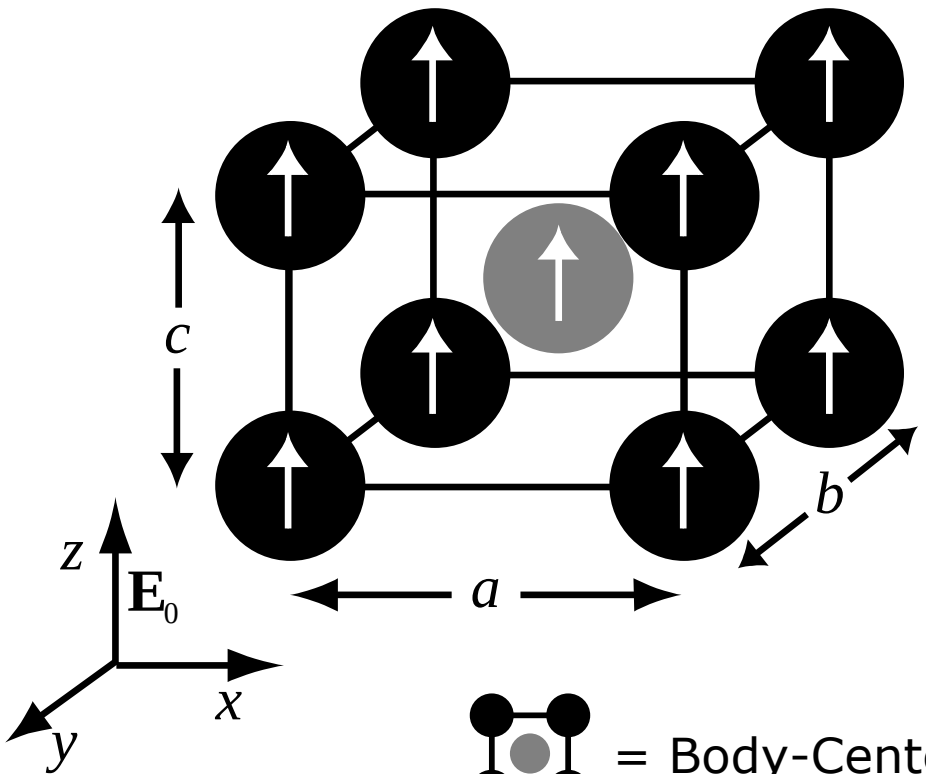
$$u_{\text{dip}}(\mathbf{r}) = -\gamma$$

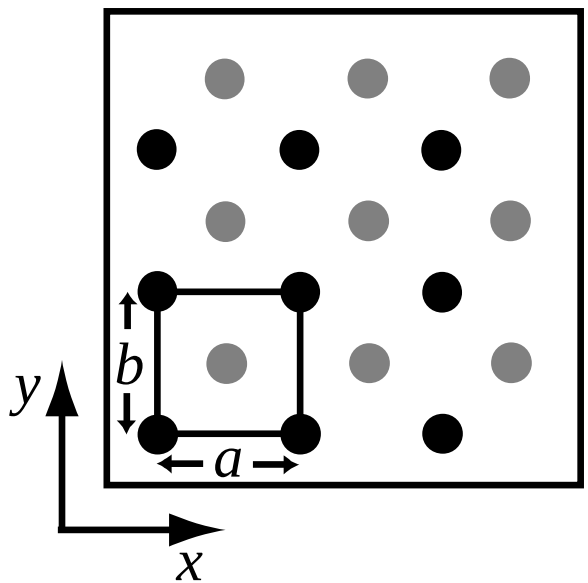
- Dipoles dislike to be side-by-side



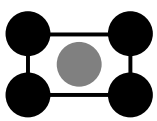
$$u_{\text{dip}}(\mathbf{r}) = \frac{\gamma}{2}$$

Body-Centered Dipolar(-Yukawa) Crystals





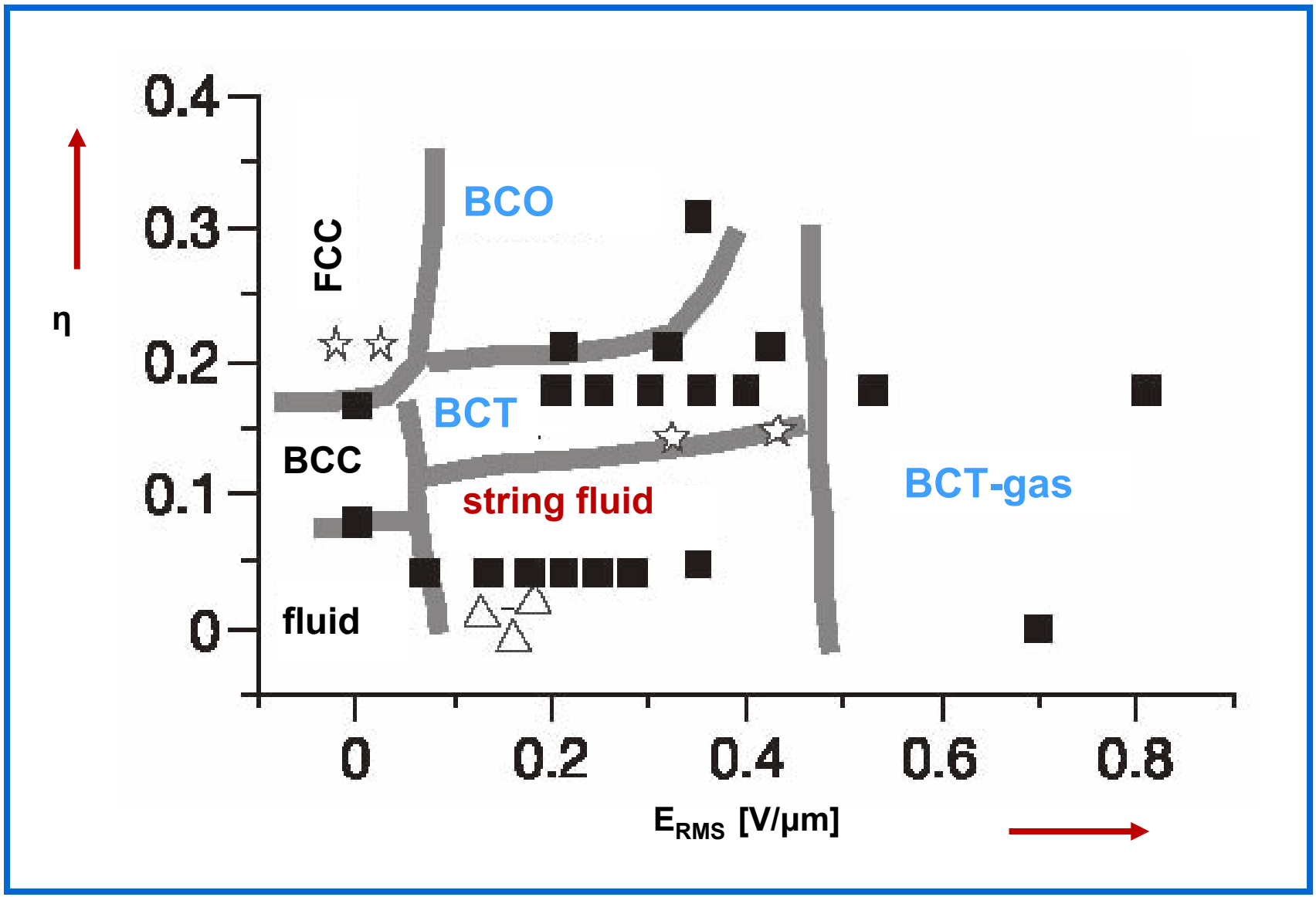
= Body-Centered Tetragonal (bct) a=b≠c



= Body-Centered Orthorhombic (bco) a≠b≠c

(Note: Body-Centered Cubic (bcc) a=b=c)

Rich Phase Behavior f(η,E) (1/κ set)



A.Yethiraj & A.van Blaaderen, *Nature*, **2003**, 421, 513-517

DLVO: Screened Coulomb

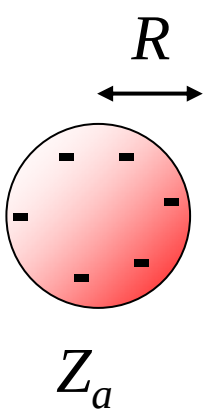
Solution of Poisson-Boltzmann and small DL overlap: Yukawa potential

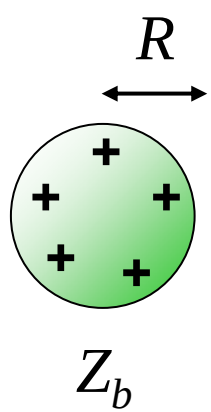
$$V_{Yukawa} = \frac{Z_a Z_b e^2}{4\pi\varepsilon\varepsilon_0}\left(\frac{\exp[\kappa R]}{1+\kappa R}\right)^2 \frac{\exp[-\kappa r]}{r}$$

a,b = +/-

Inverse Debye Screening Length

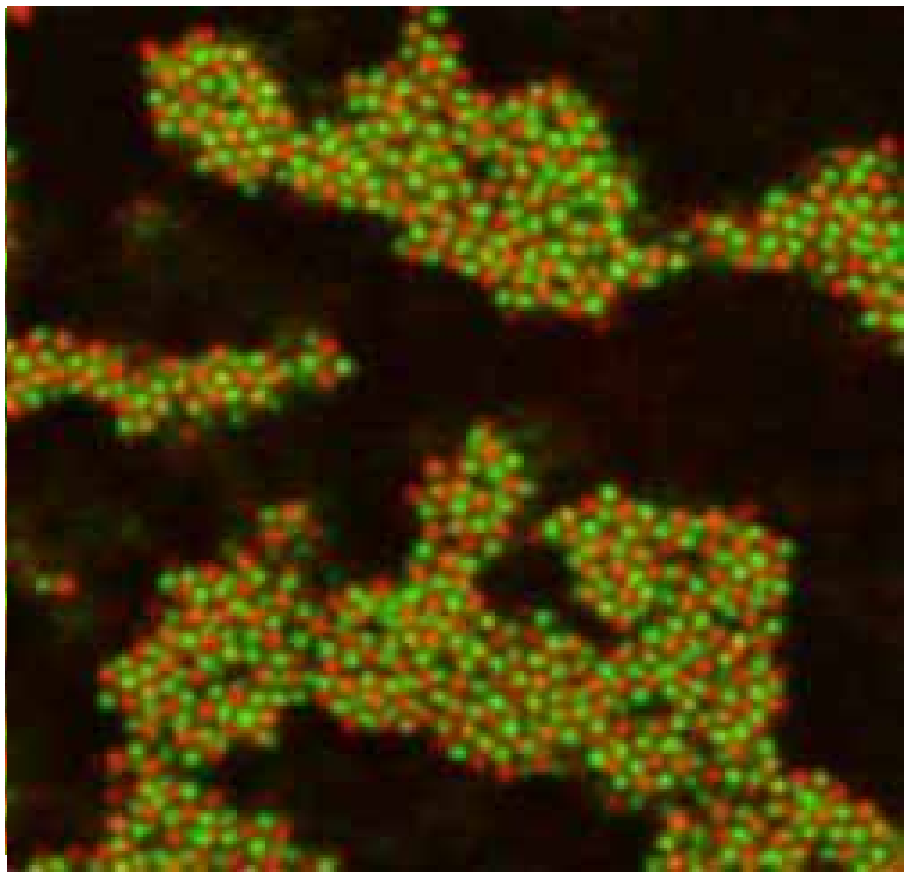
$$\kappa = \left(\frac{\sum z_i^2 e^2 n_{0i}}{\varepsilon\varepsilon_0 k_B T}\right)^{\frac{1}{2}}$$





Ionic Colloidal Crystals

Mixtures of Oppositely Charged Colloids have Contact Energies of Hundreds of kT due to Electrostatic & Van der Waals Forces: <u>HeteroAggregation</u>.



Nature, Sept. (**2005)**

60 x 60 μm

A New Colloidal Model System

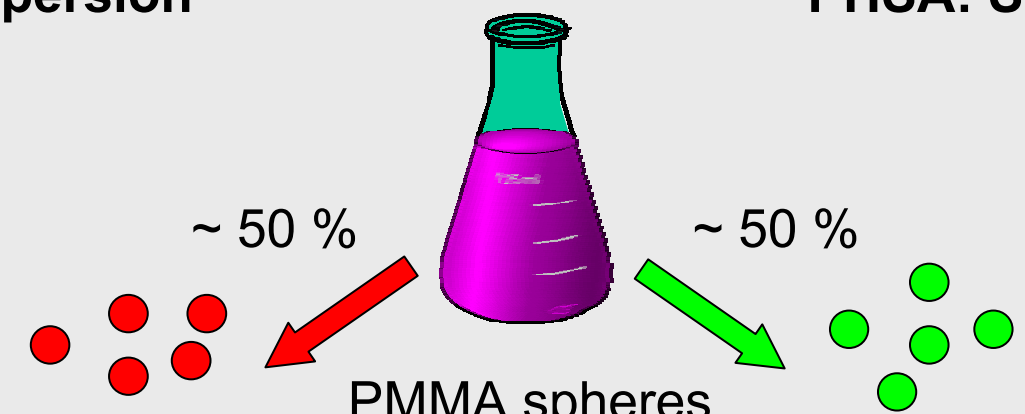
The Solvent

Cyclohexyl bromide (ε ~ 8) , cis-decalin (ε ~ 2)
Low ion concentrations (10^{-7}-10^{-10} M) → long screening lengths, micrometers!

Index matching reduces Van der Waals attractions
Density matching minimizes the role of gravity

The Binary Dispersion

PHSA: Steric Stabiliser



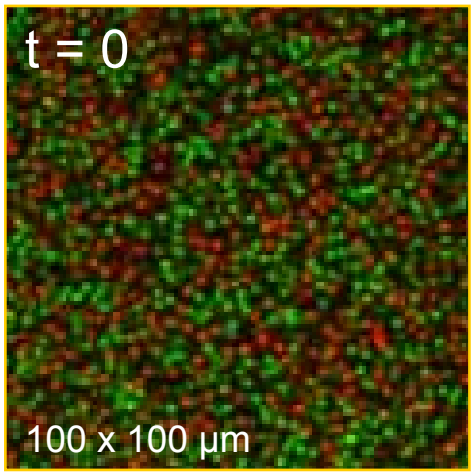
fluorescent RITC label
σ 2.16 μm
+ charge

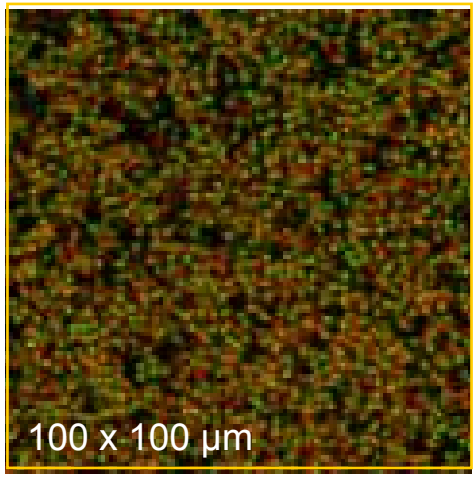
(polydispersity ~ 3%)

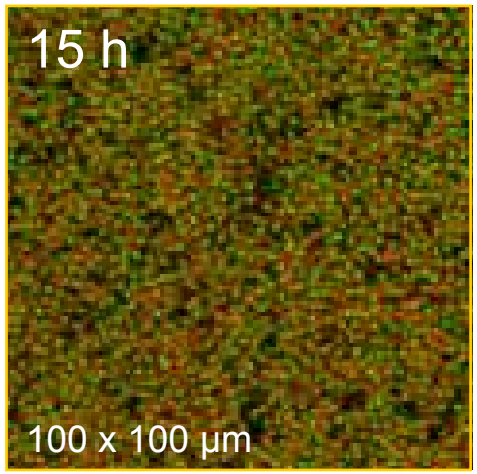
fluorescent NBD label
σ 1.98 μm
- charge

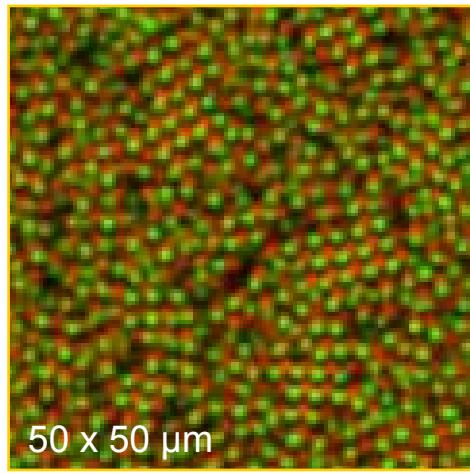
Development in time

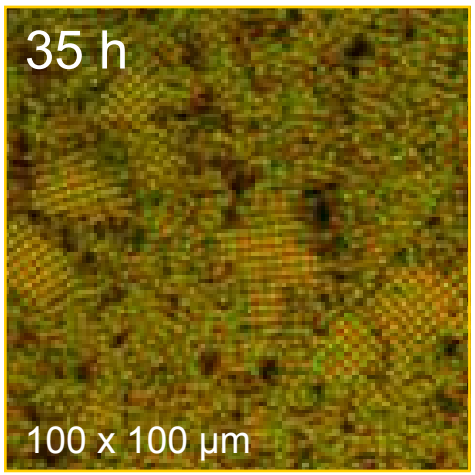
Typical sample: 59.4 μM TBAB
κ-1: 285 nm (κσ ~7.2)
overall volume fraction 0.12
particle number ratio 1.3

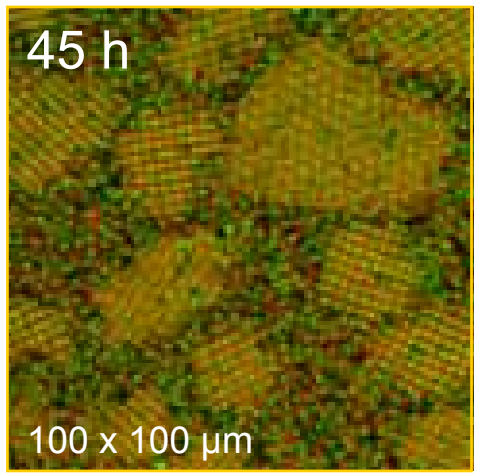


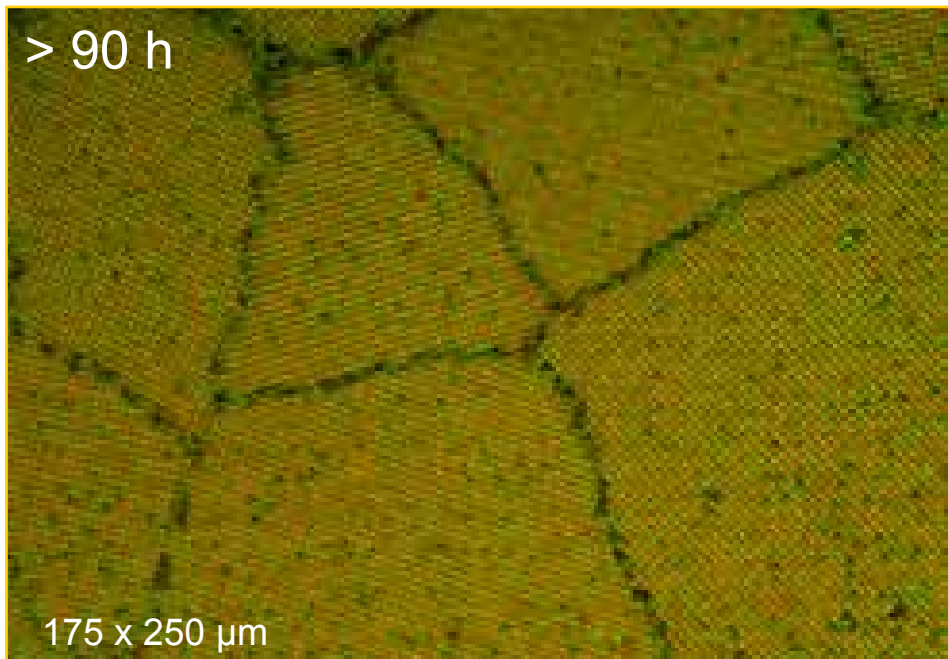








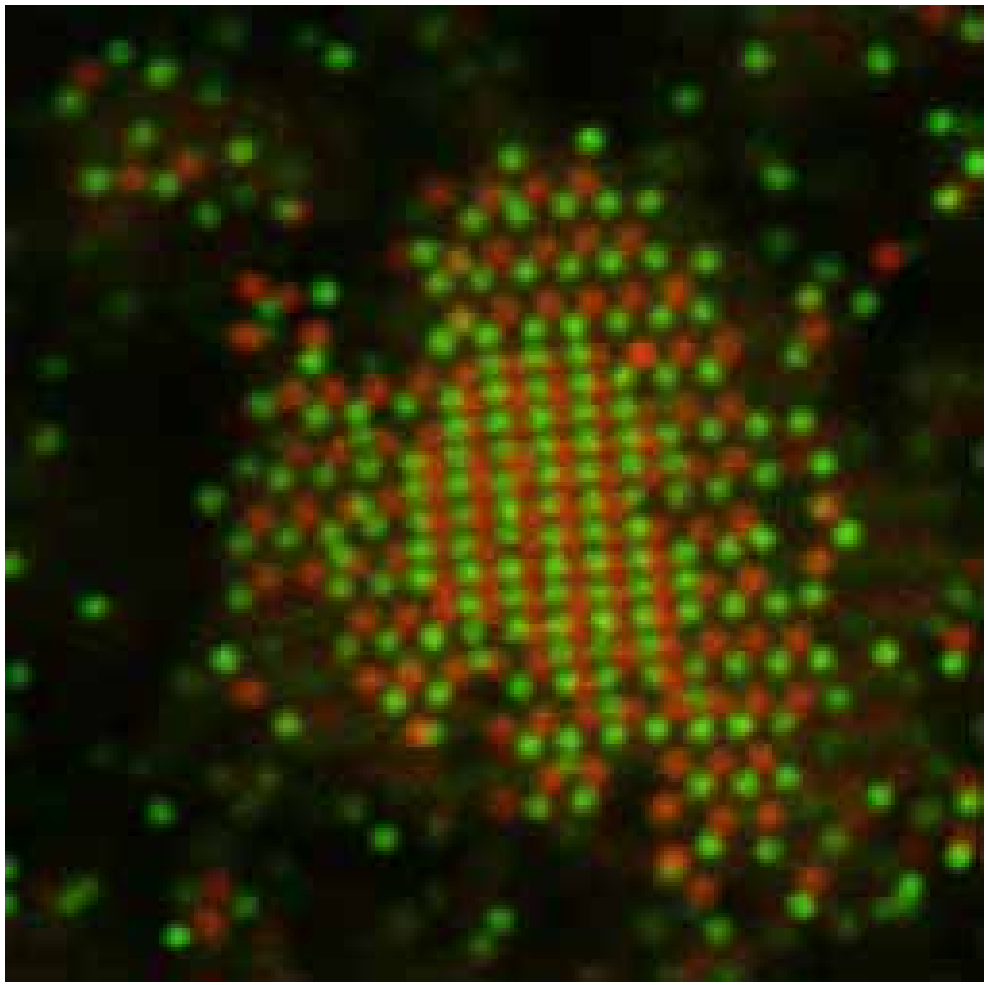




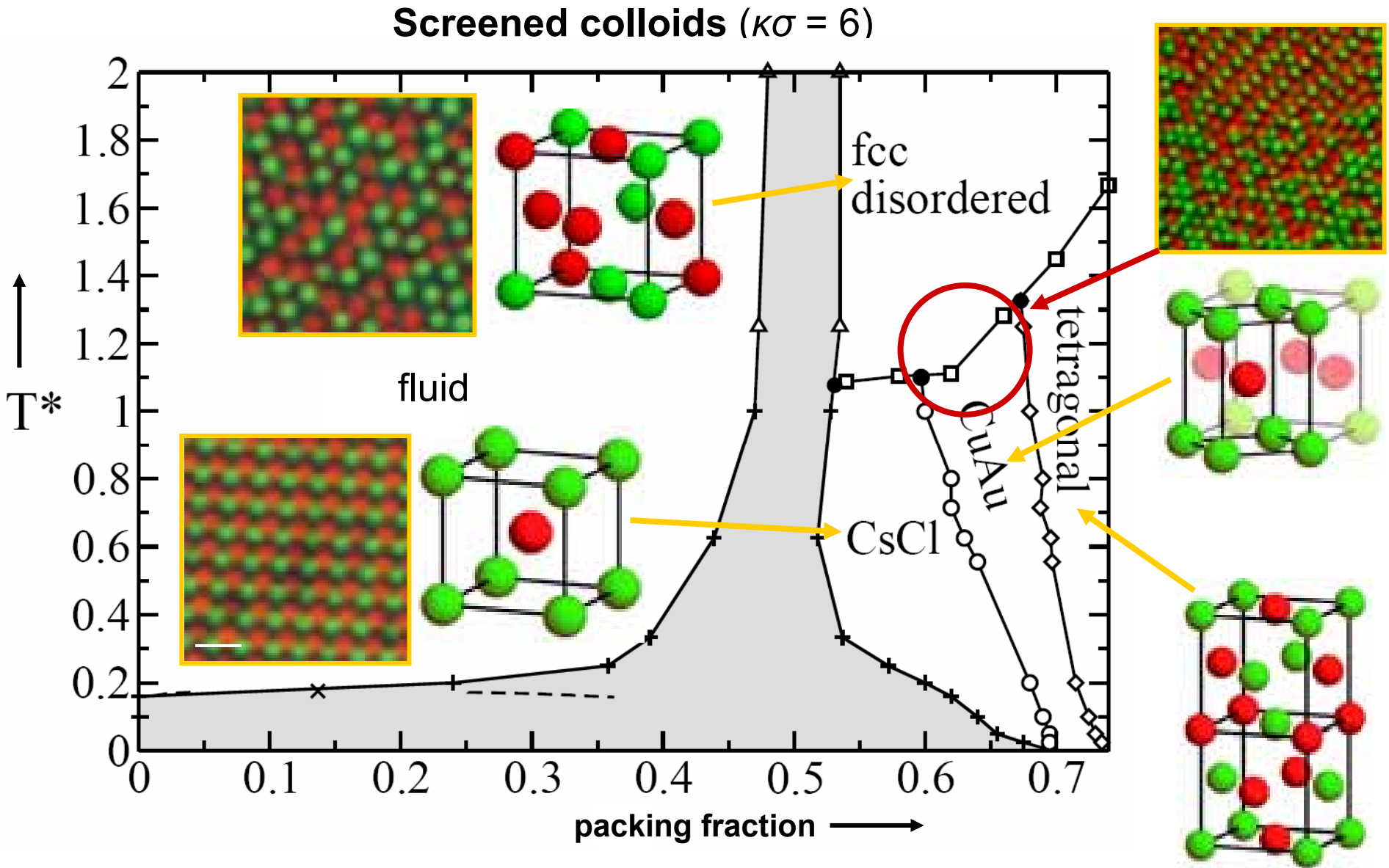
Large, dense crystals !

Coexistence with fluid for months

Time Sequence CsCl

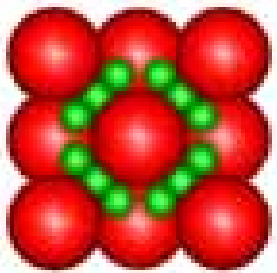


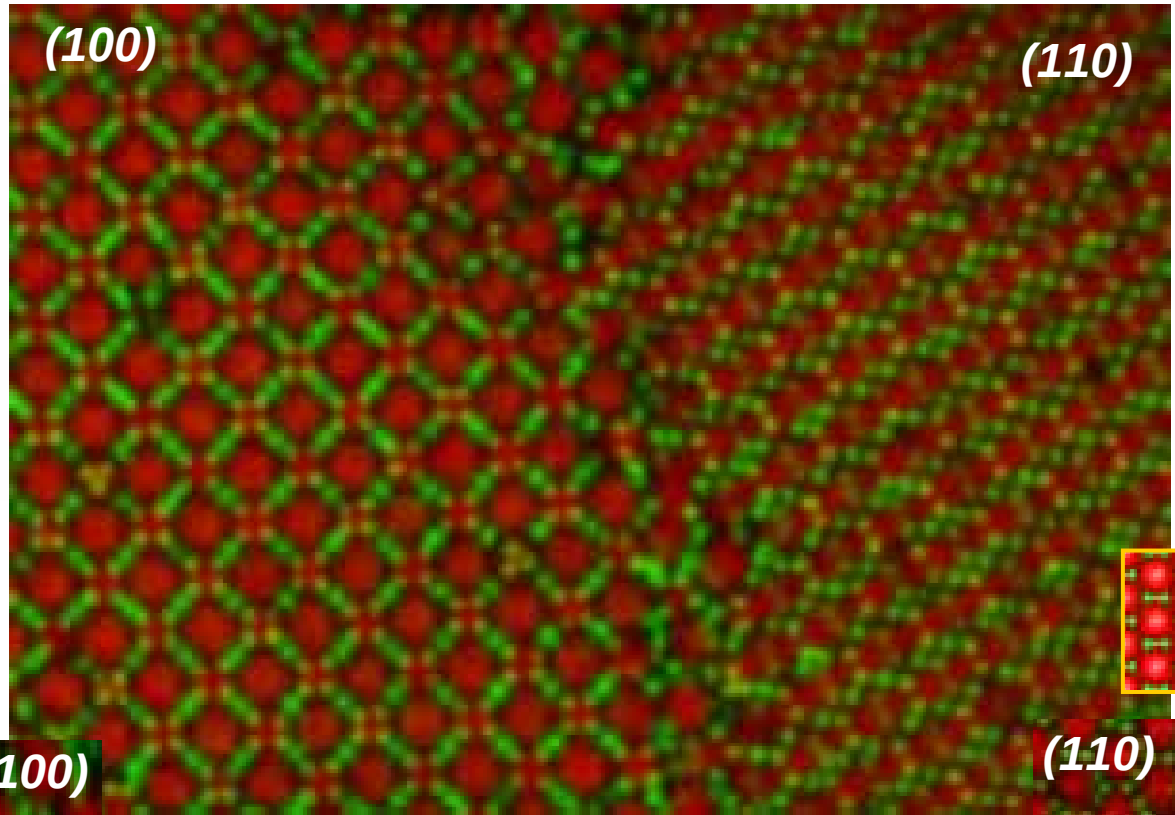
Phase Diagram Contains All Experimentally Observed Structures

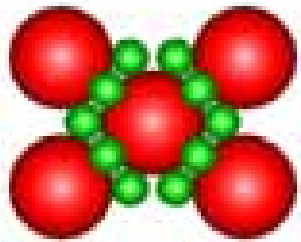


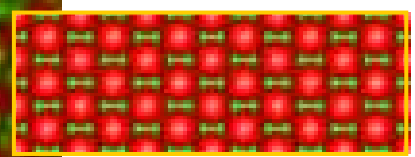
Hynninen, AvB *et al.*, *PRL* (**2006**)

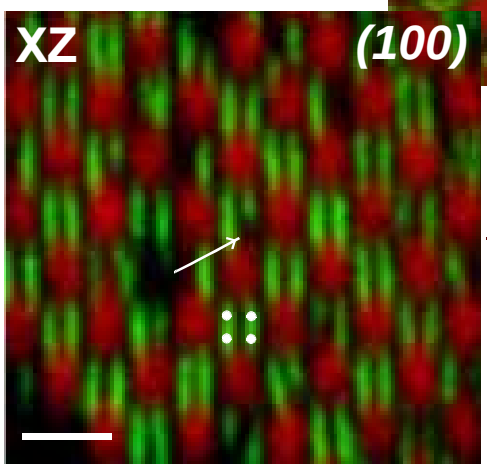
Size Ratio 0.31 LS_6: *isostructural* A_6C_{60}!

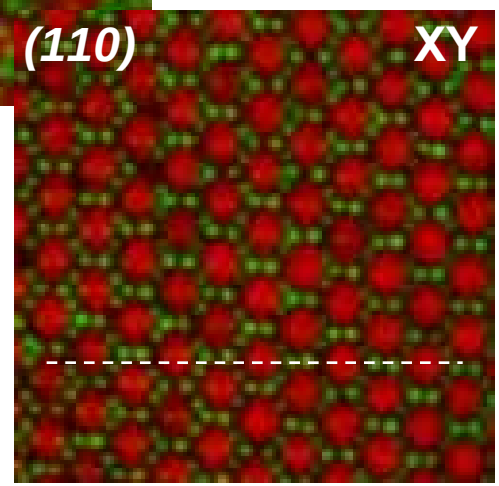


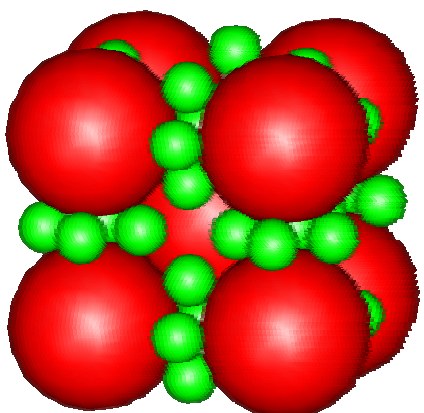






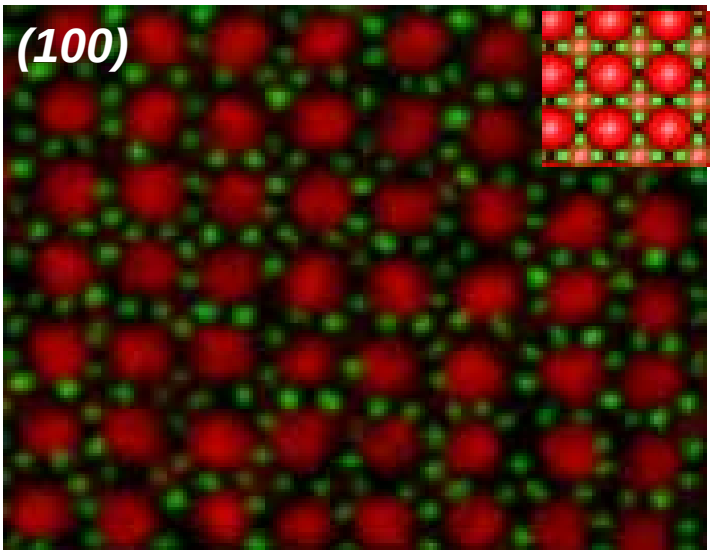


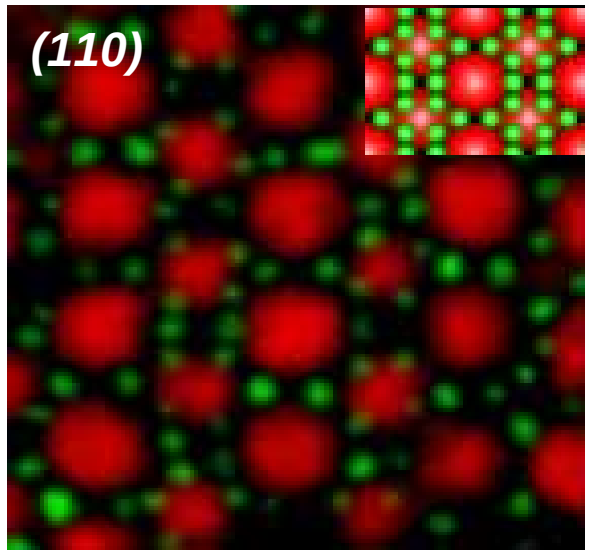


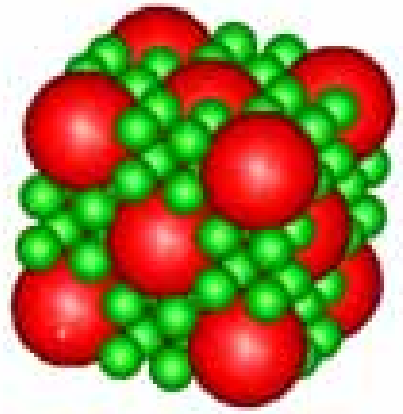


Large: body-centered cubic (***BCC***)
Small: 4 in a plane between each 2 large neighbors

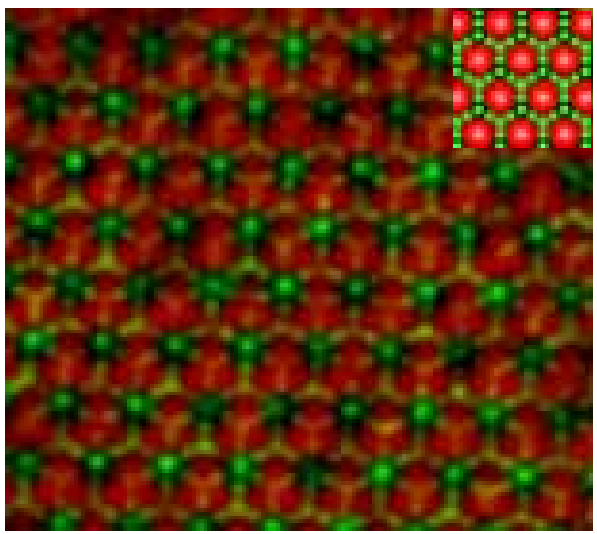
Size Ratio 0.31 LS_8: *New Crystals*!



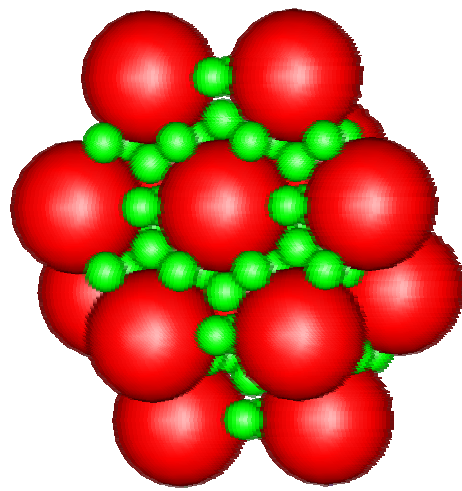




Large: face-centered cubic (***FCC***)
Small: 8 in each octahedral hole

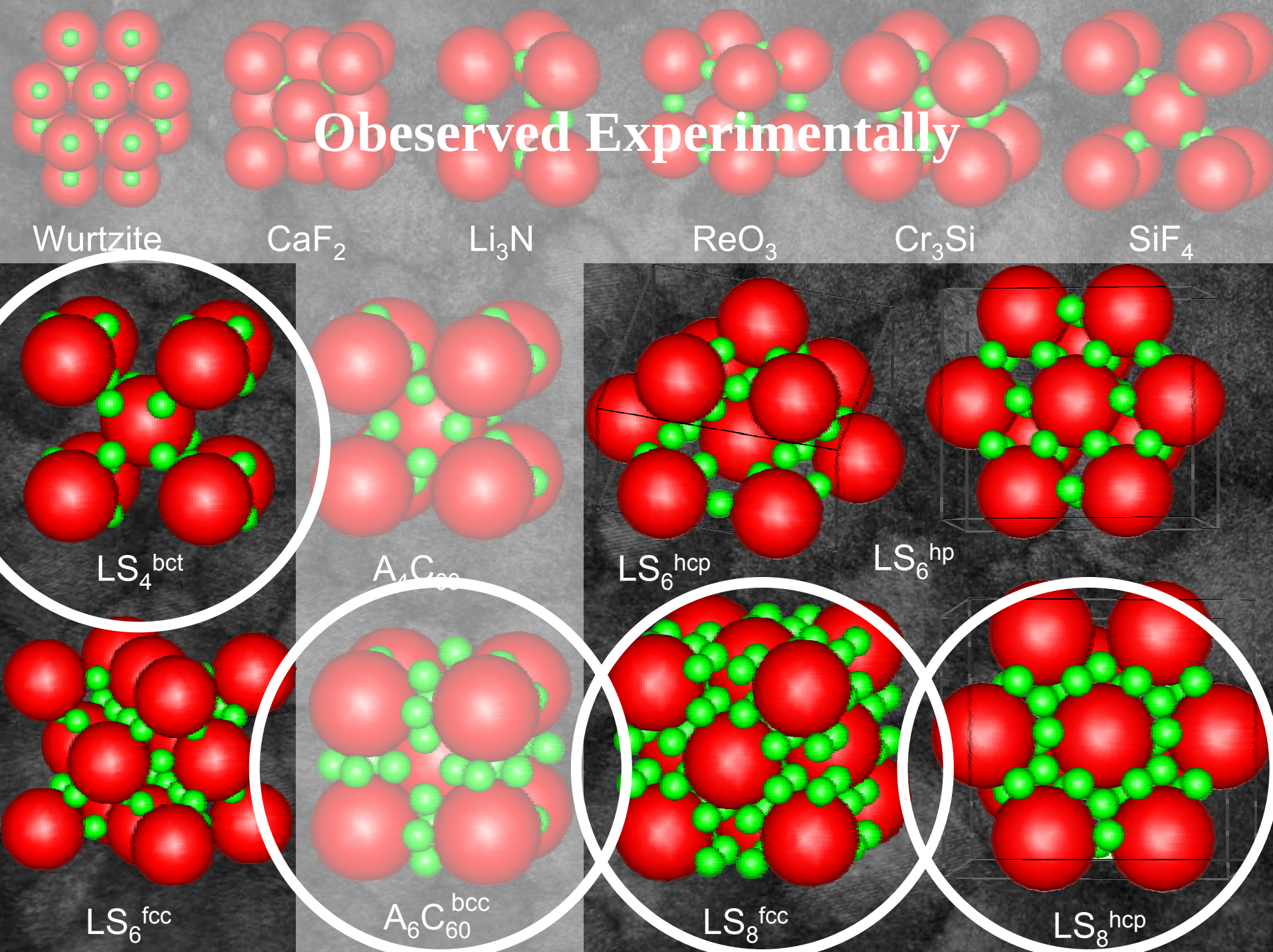


5 layers of *large* and *15* layers of *small* particles



Large: hexagonal close packed (***HCP***)
Small: hexagonal ring around each large one + planes with “kagome” arrangement

Obeserved Experimentally



Oppositely Charged NanoParticles!

e.g. PbSe, Pd, PbS, Au, Ag, Fe_2O_3

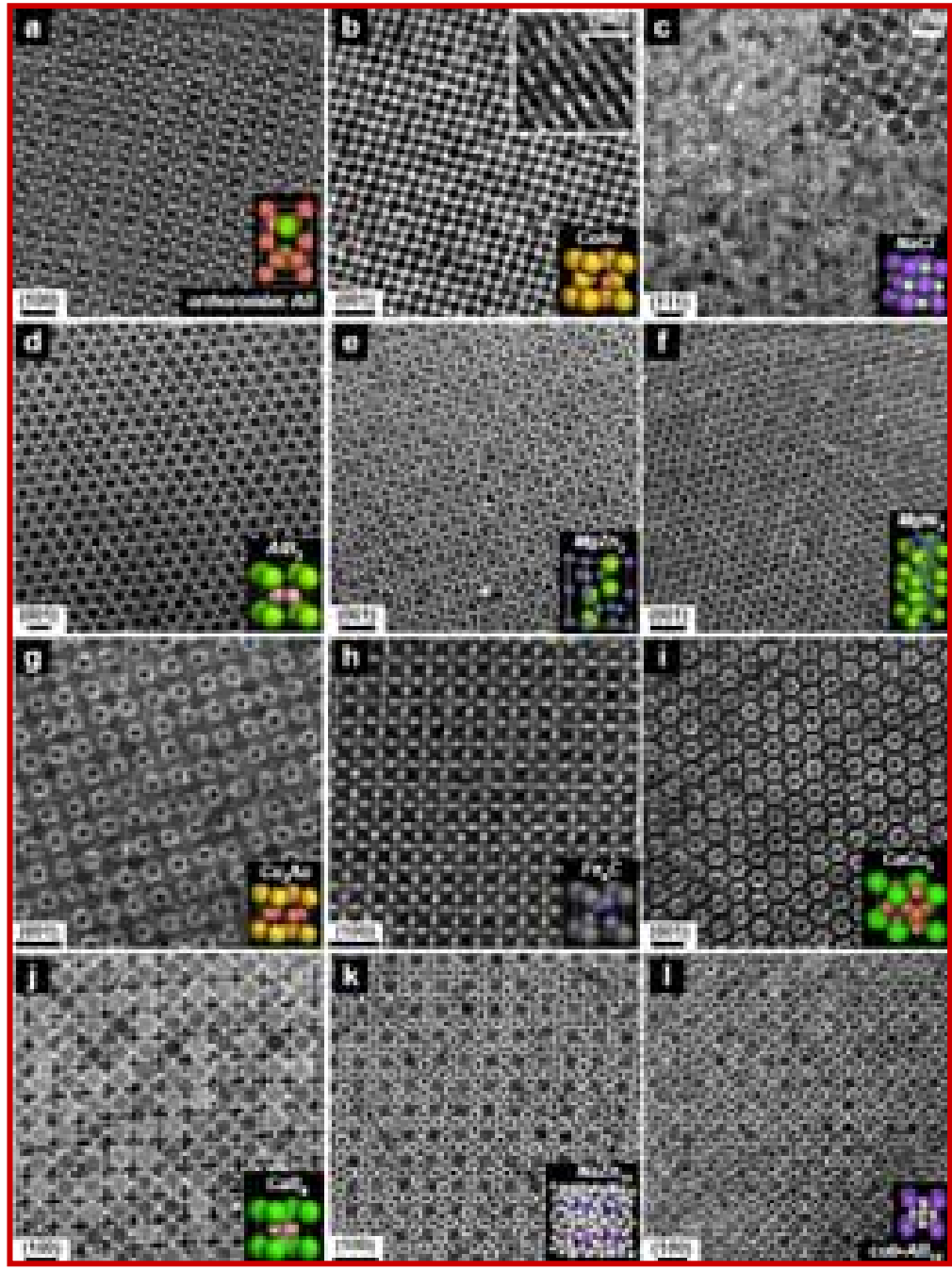
σ : ~ 3 – 14 nm

Z : ± 1, 2 e

Different scale, similar behavior:

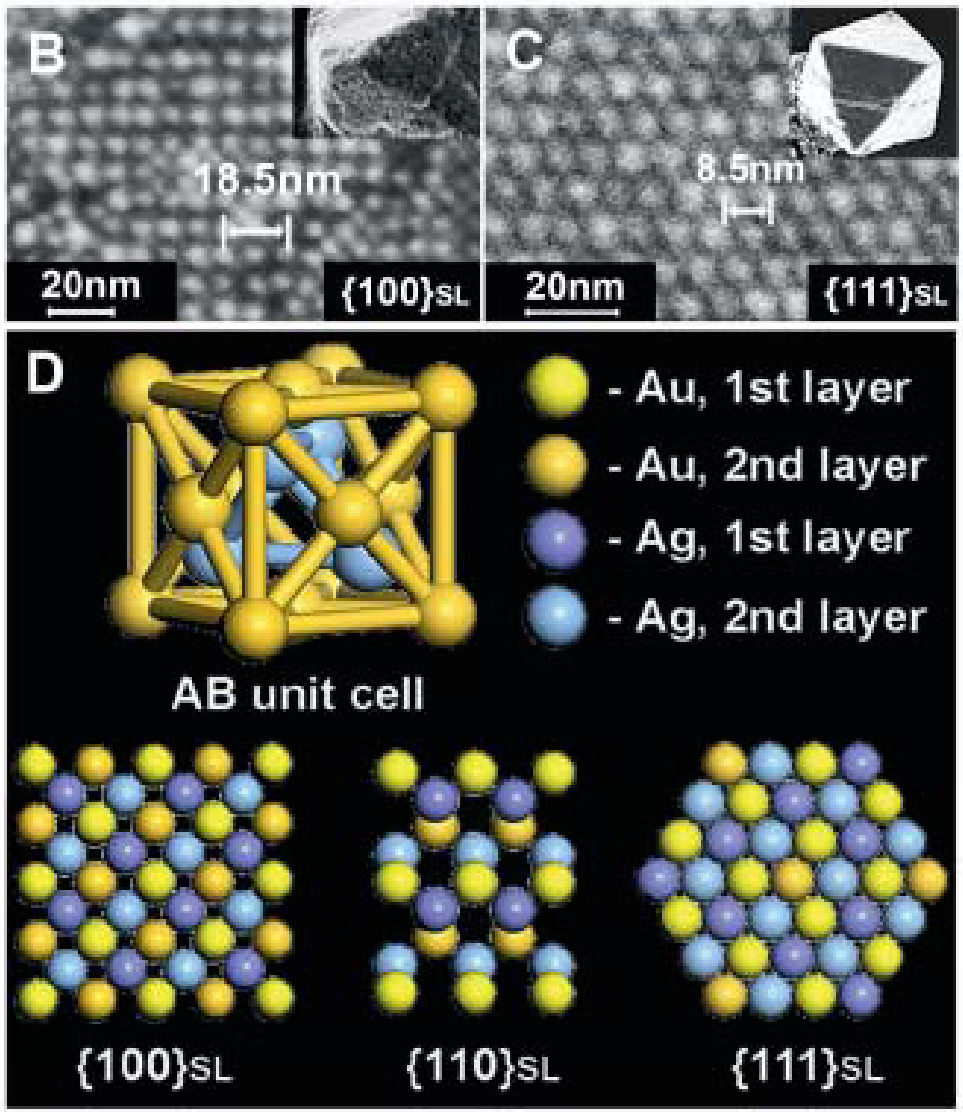
attractions stabilize new,
non-close packed structures

Stoichiometry ***IS*** dictated by charge neutrality



Shevchenko, Talapin, Kotov, O'Brien & Murray, *Nature* 439 (2006)

Gold-Silver NanoParticles: *ZincBlende*

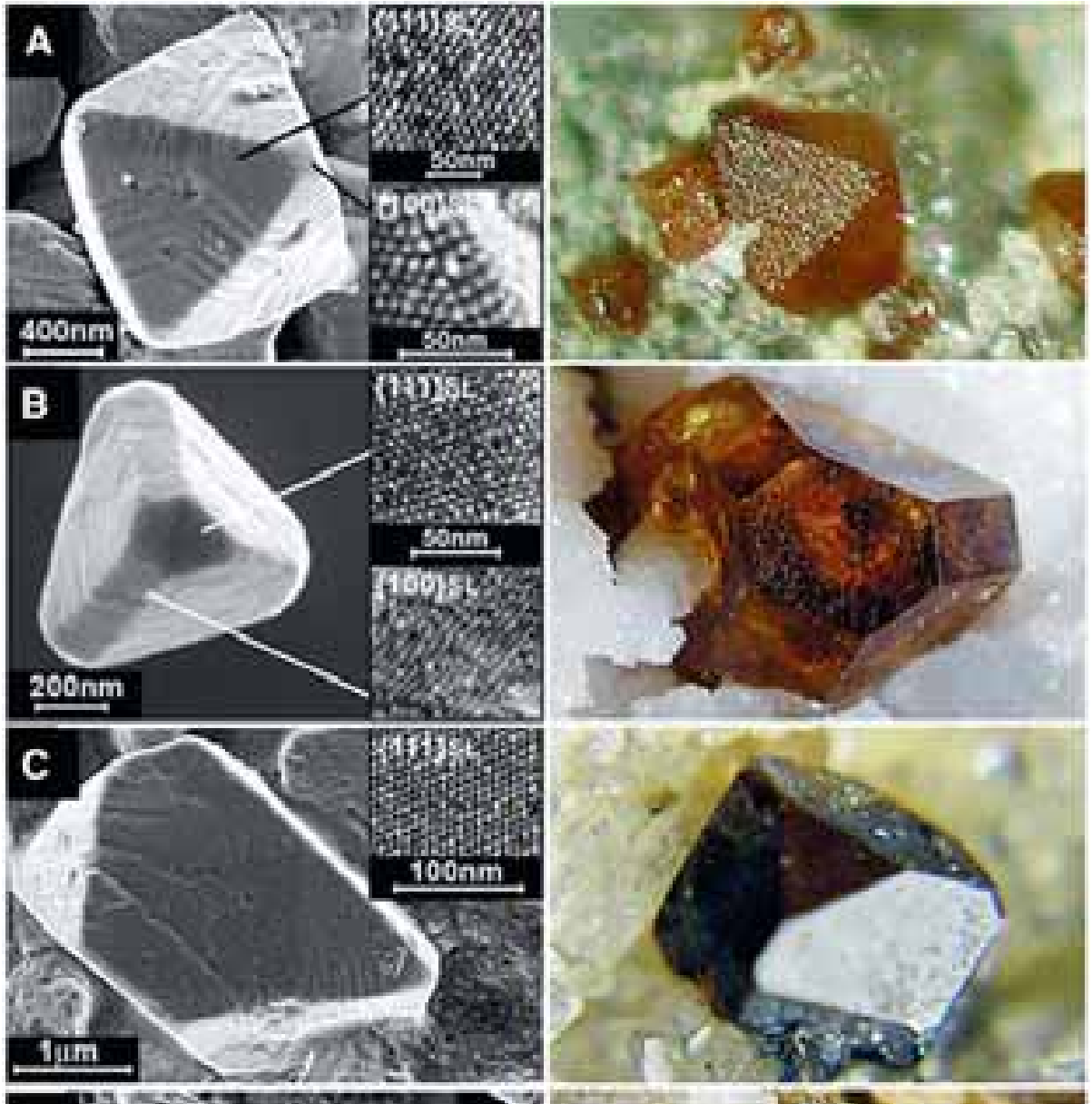


Oppositely Charged nano-Colloids!

Gold and Silver, including the stabilizer, about same size ~10 nm.

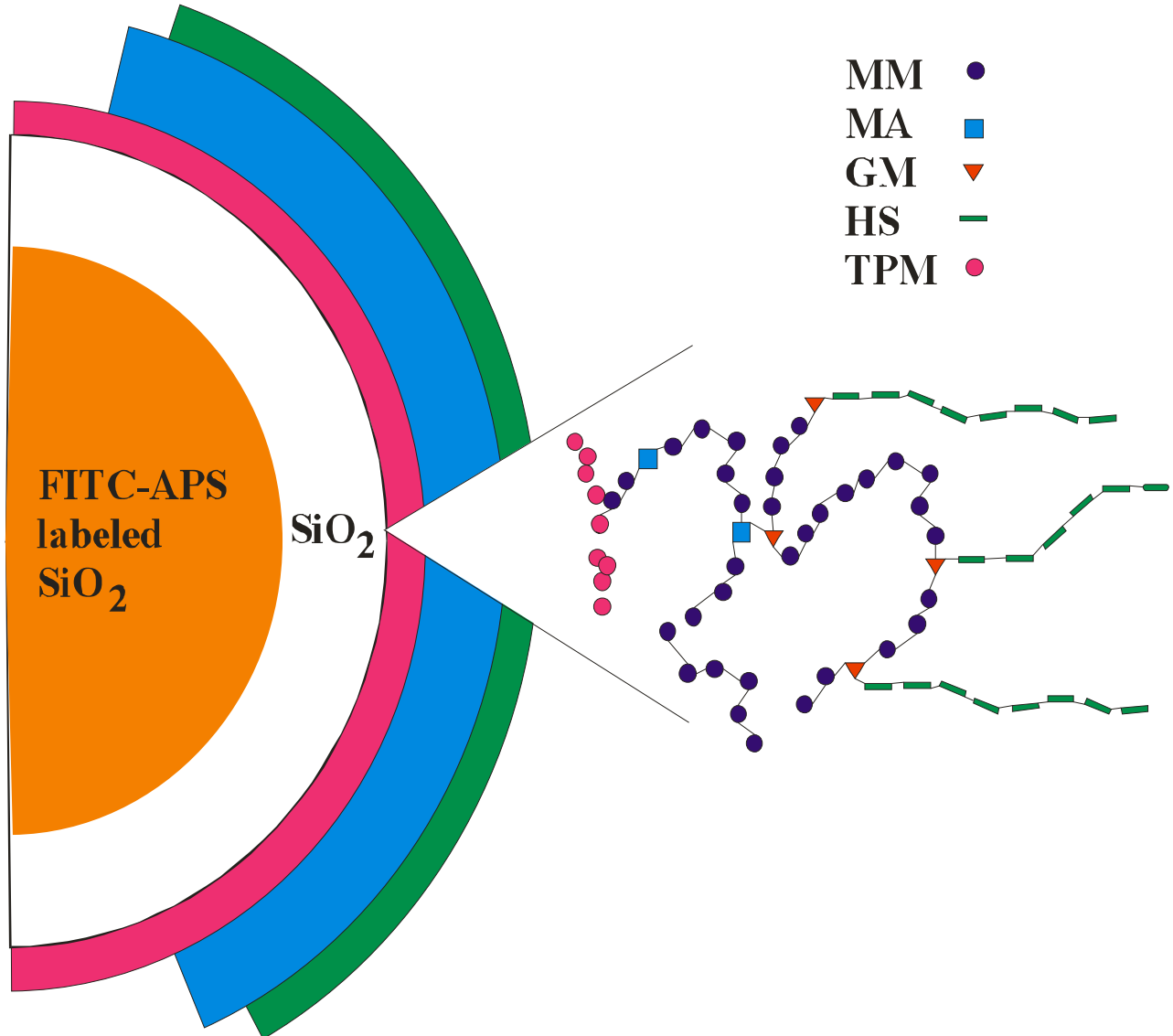
Kalzin et al., *Science* ***312, (2006)***

Diamond-Like: Oppositely Charged

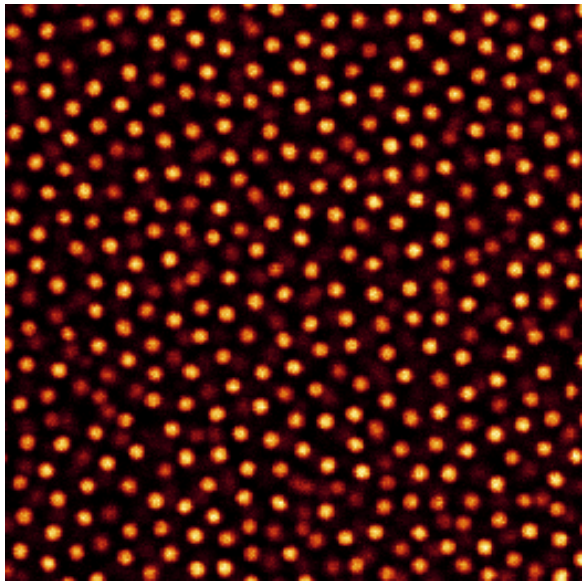


Kalzin et al.,
Science ***312, (*****2006*****)***

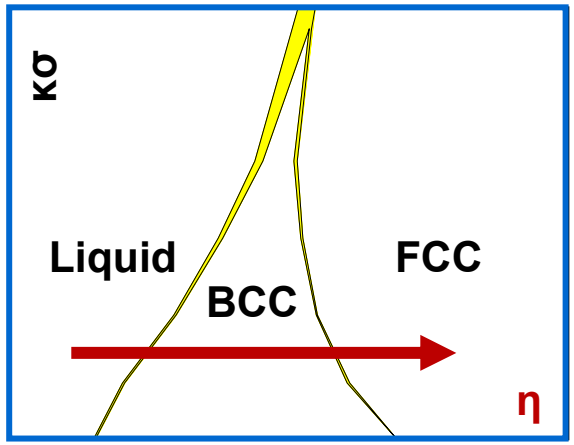
PHSA-PMMA (core-shell) by Dispersion Polymerization



Increasing volume fraction (η)

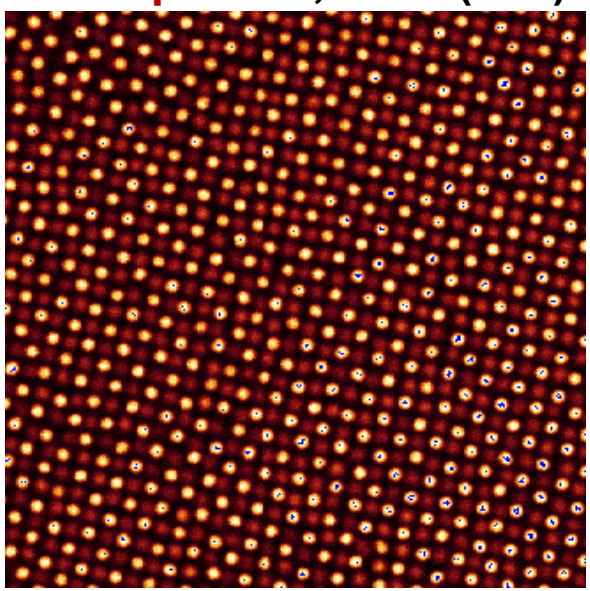


κσ ~ 5

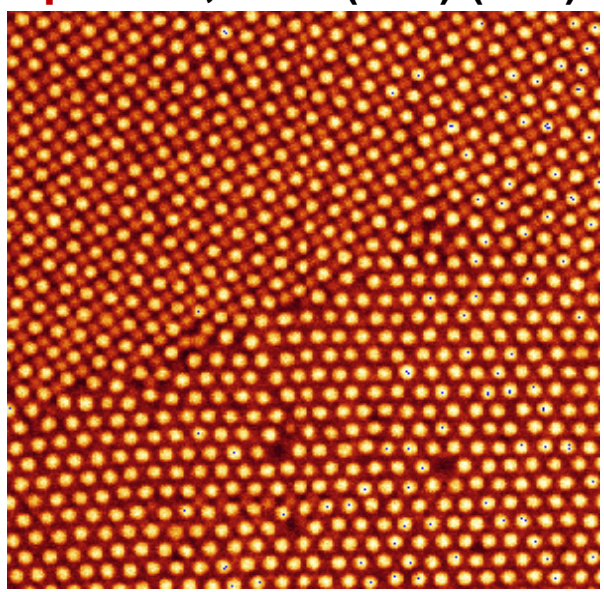


η < 0.10, liquid

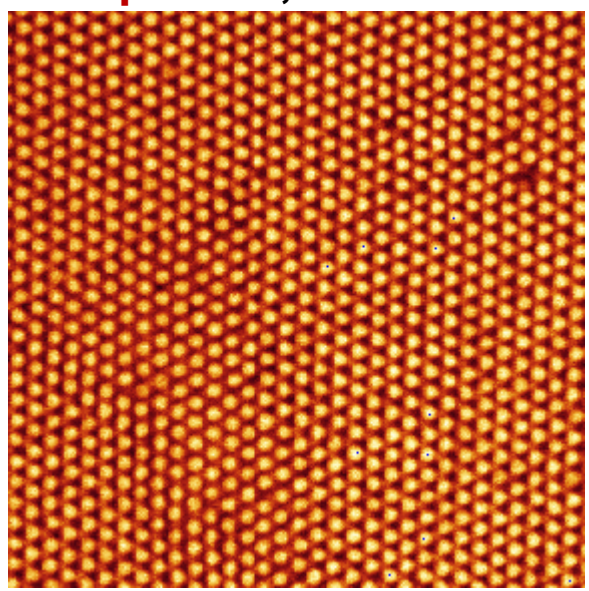
η = 0.15, BCC (110)



η = 0.28, FCC (111)/(100)



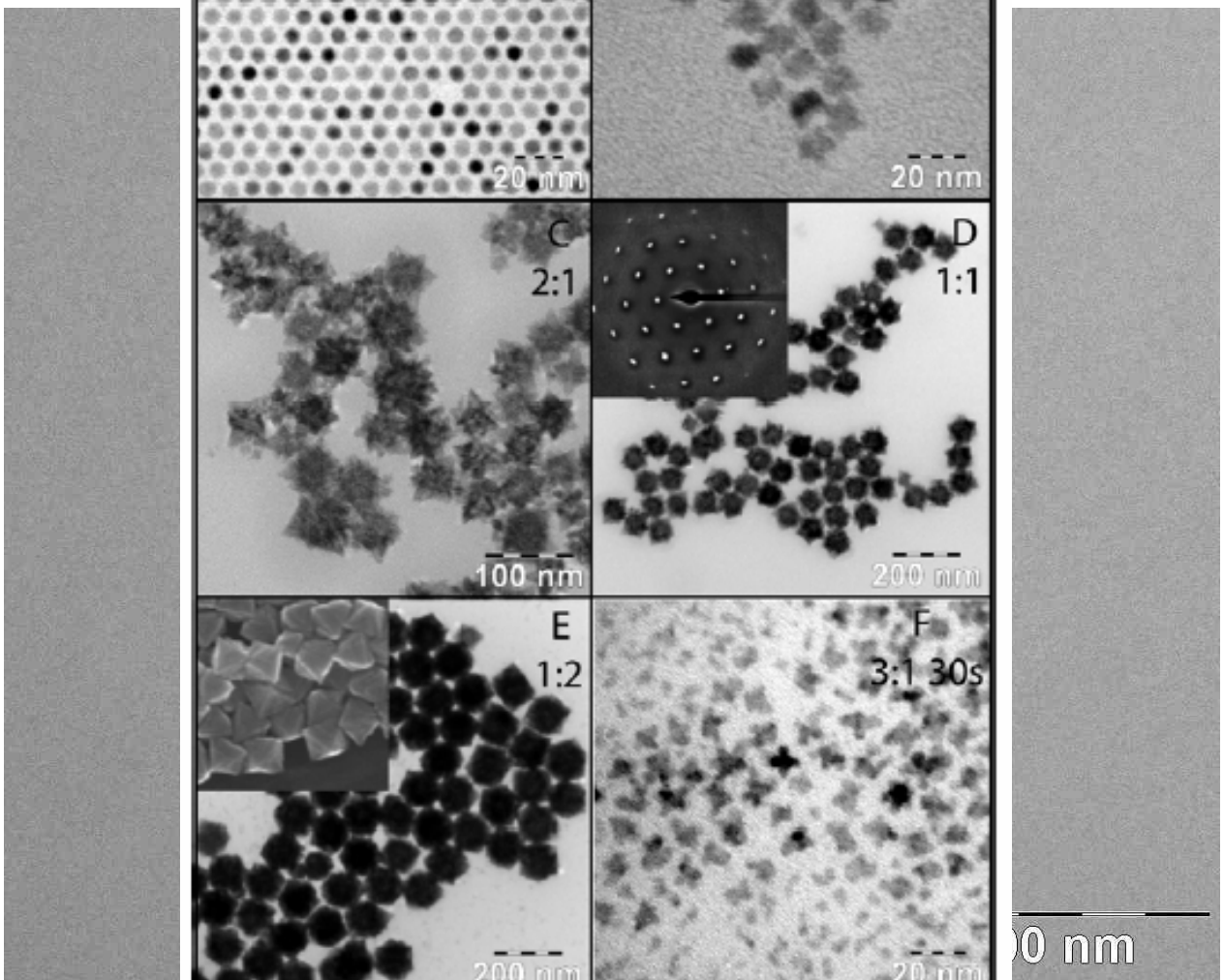
η = 0.38, 'RHCP'



BCC/FCC **~ 0.20** **FCC/'RHCP'**

70 x 70 μm

PbS … rong … E … nt



Strings of Dipoles

Houtepen et al., *JACS*, ***128, (2006)***