Modeling the phase behavior of nanoparticle superlattices with a molecular theory

Mario Tagliazucchi

Department of Inorganic, Analytical and Physical Chemistry
University of Buenos Aires, Argentina

(currently on sabbatical at the Institute for Theoretical Physics,
University of Göttingen, Germany)

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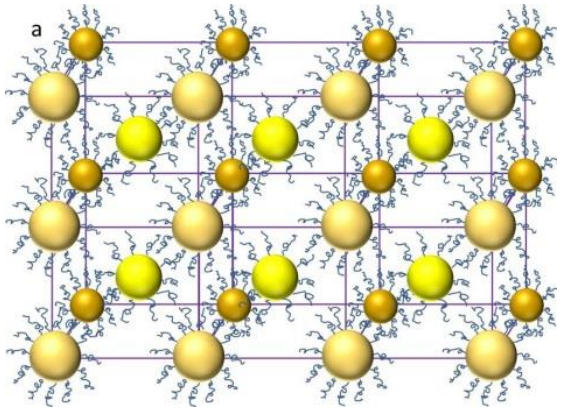
INQUIMAE

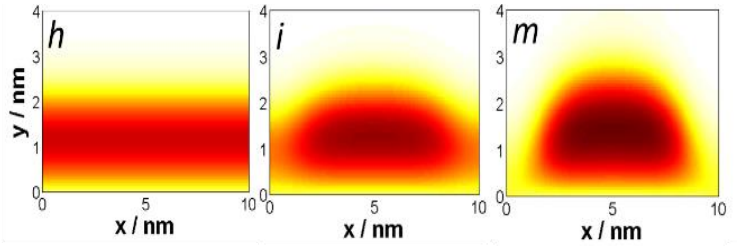
Kavli Reseach Conference - 5/15/2023

Soft Materials Group @ University of Buenos Aires, Argentina

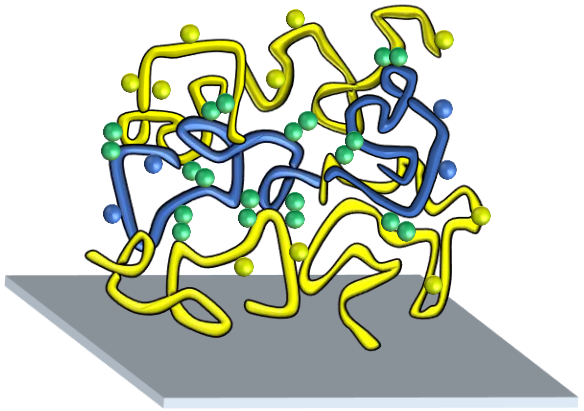
softmaterials.qi.fcen.uba.ar



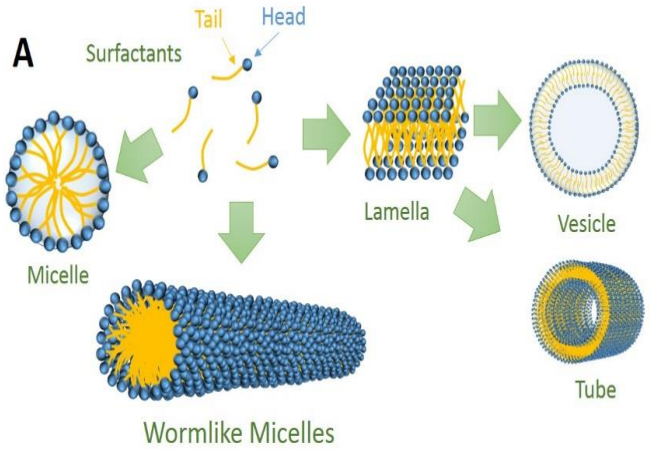
Self-Assembly of NP superlattices



Self-Assembly of Polymeric Systems/Polymer brushes



Polymer Layer-by-layer thin films/Polyelectrolyte coacervates

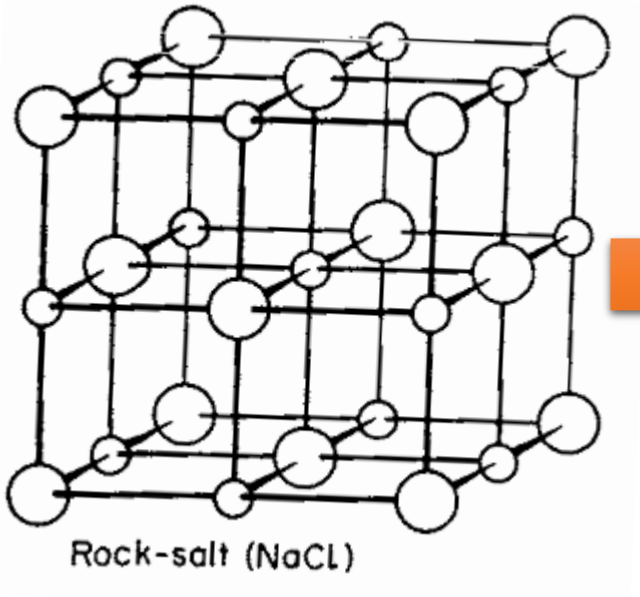


Self-Assembly of Amphiphiles

Atomic crystals

(1912)

— 1 Å



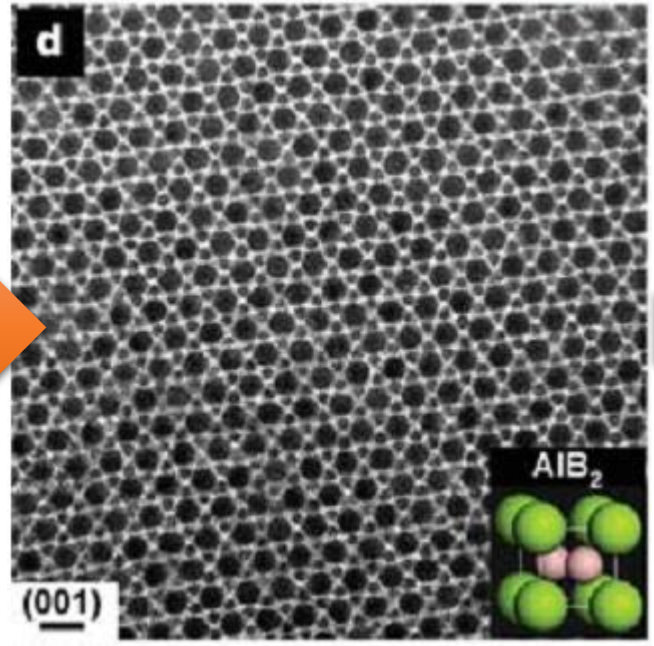
Inorganic Chemistry, Cotton&Willkinson (1972)

X 100

Nanoparticle Superlattices

(1990's)

– 10 nm



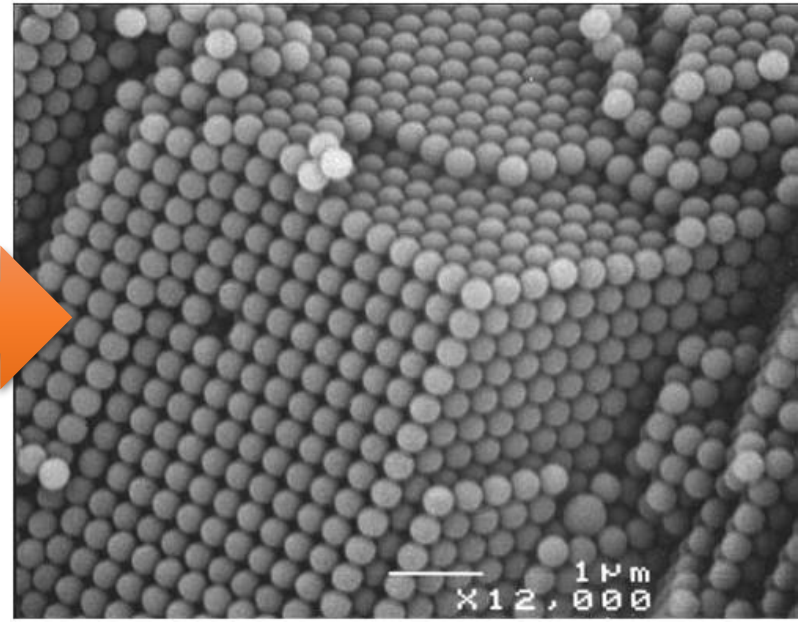
Shevchenko et. al Nature, 439, 2006

X 100

Colloidal crystals

(1930's natural, 1970's synthetic)

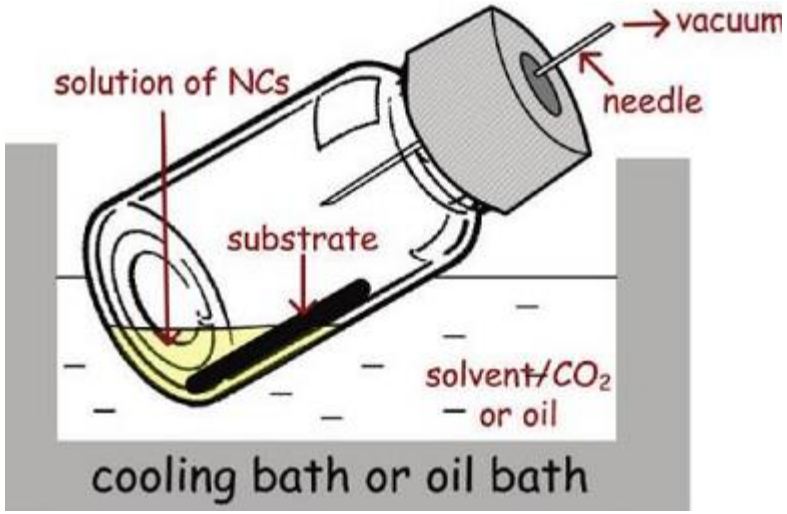
— 1 μm



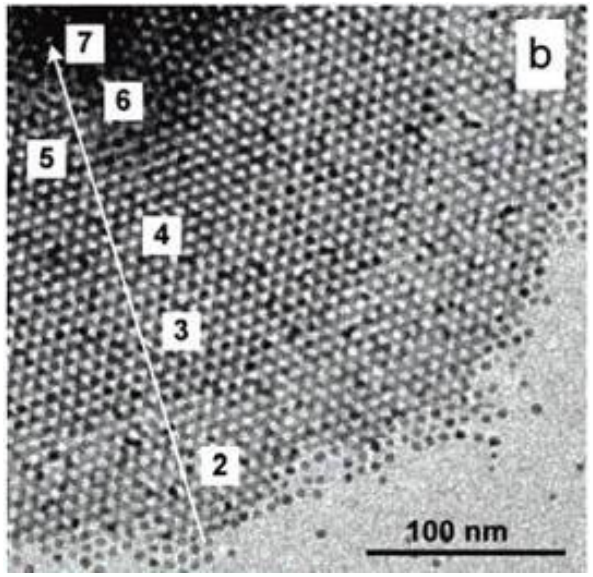
Imhof, A. in Nanoscale Materials, pp.423-454

NP Superlattices

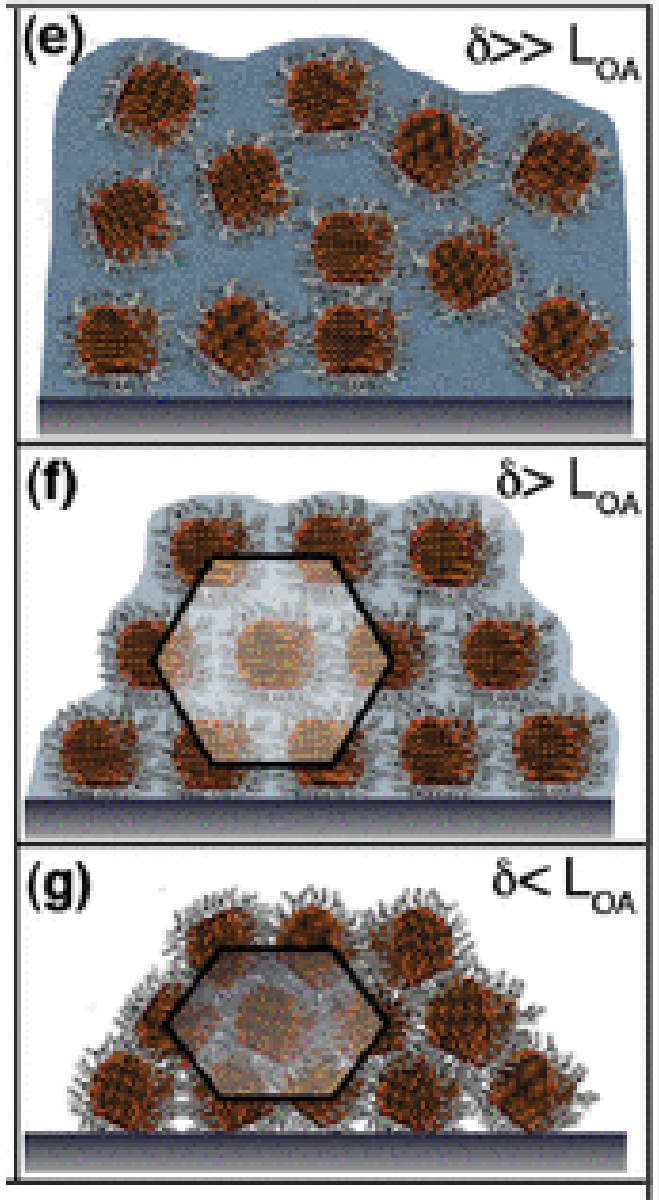
(made of alkanethiol-coated nanocrystals in organic solvents)



Bodnarchuk, et al. JACS **2010**, 132, 11967



Talapin et al, Nano Lett., **2007,** 7.



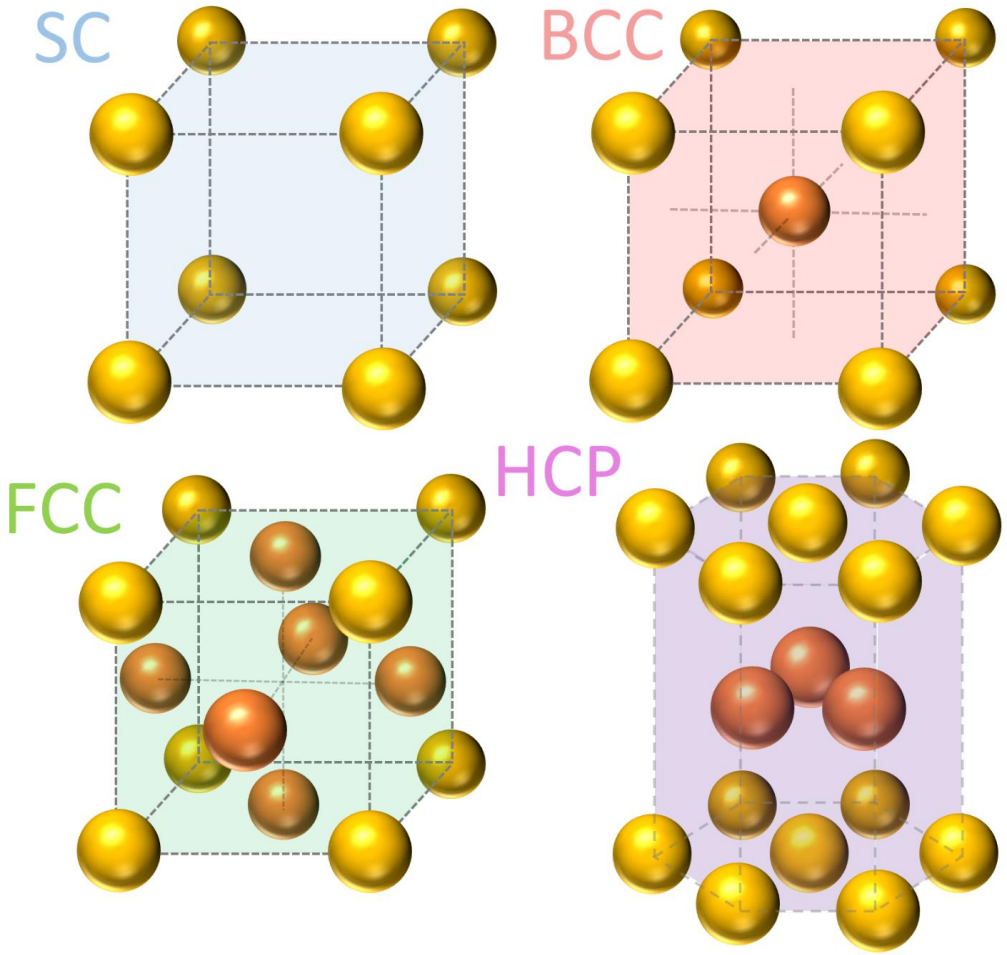
Bian et al, ACS Nano **2011,** 5, 2815

How the properties of the building block dictate the superlattice structure?

What is the role of the amount of solvent in the NPSL?

At which stage is the final superlattice structure determined?

The simplest case: single-component NPSL, spherical NPs



Packing fractions for <u>hard spheres</u>:

FCC/HCP : 0.74

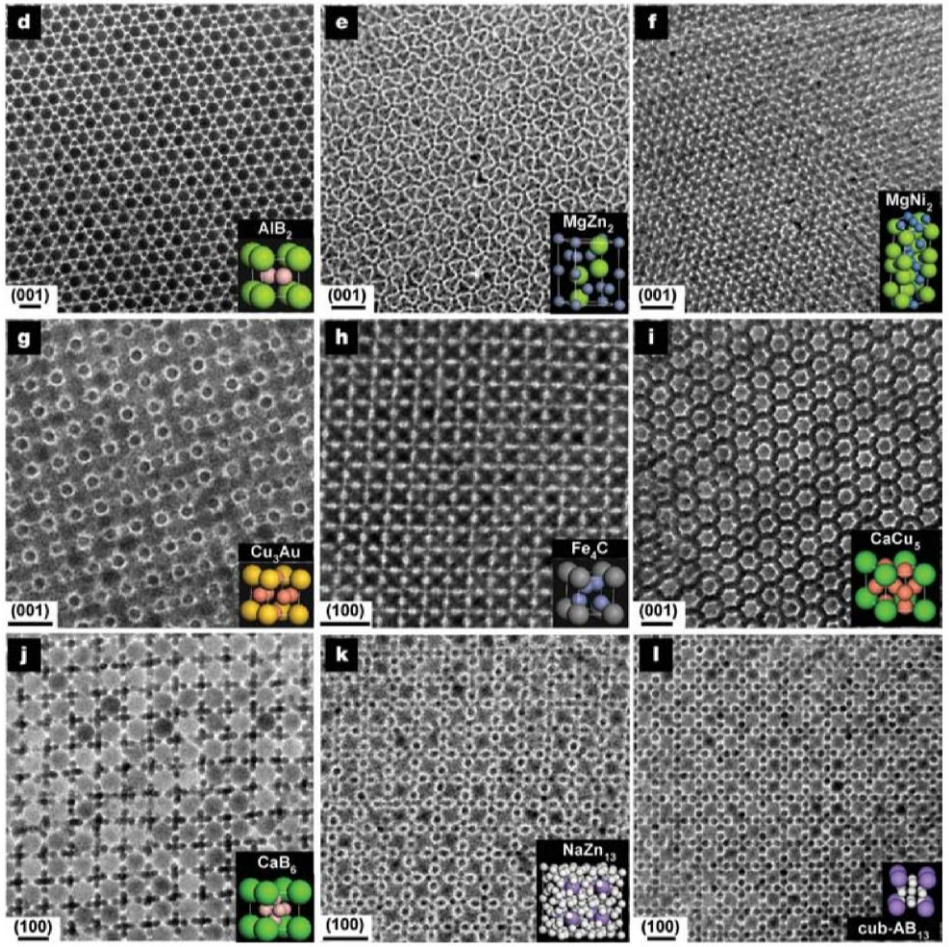
BCC: 0.68

SC: 0.52

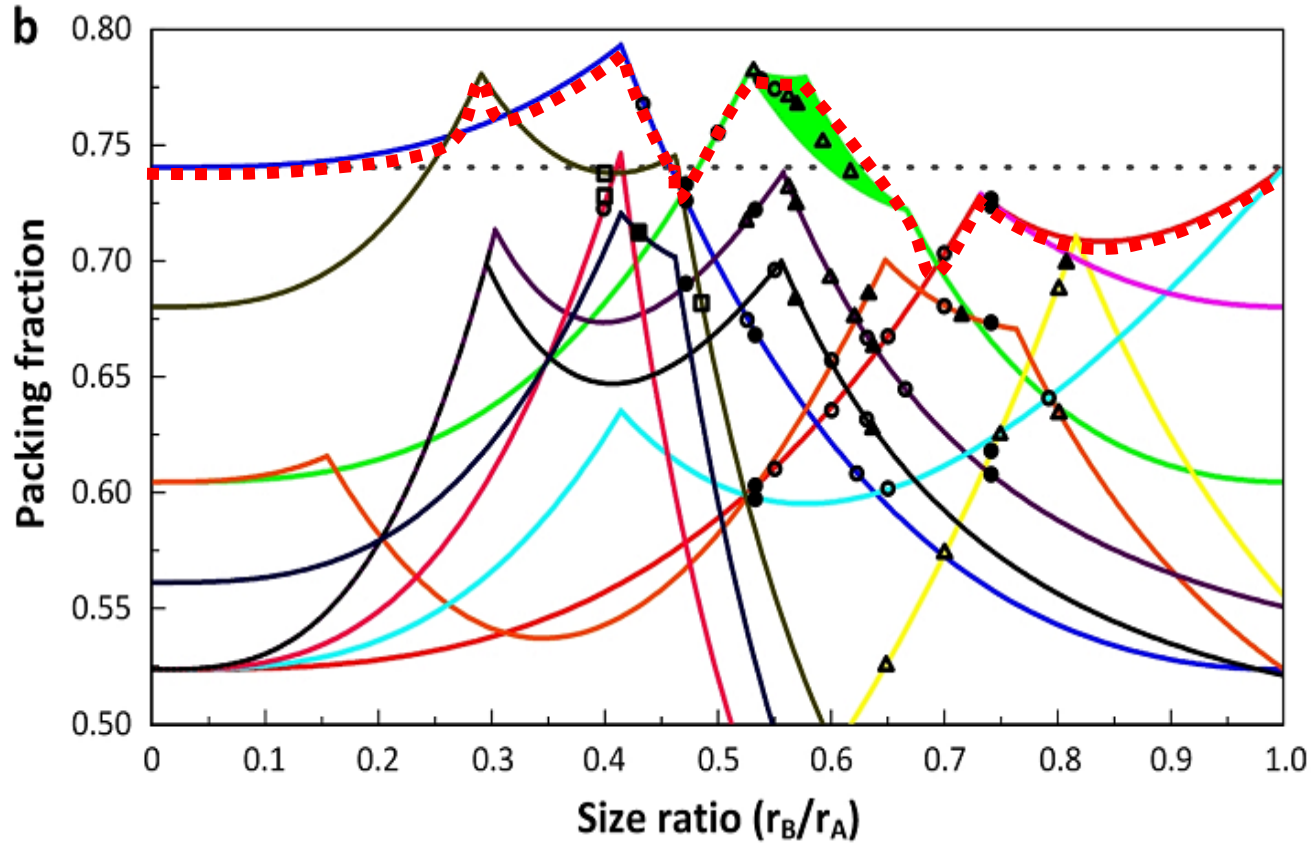
FCC and HCP <u>have maximum packing</u> (FCC is actually ~ 10^{-3} k_BT/particle more stable than HCP)…

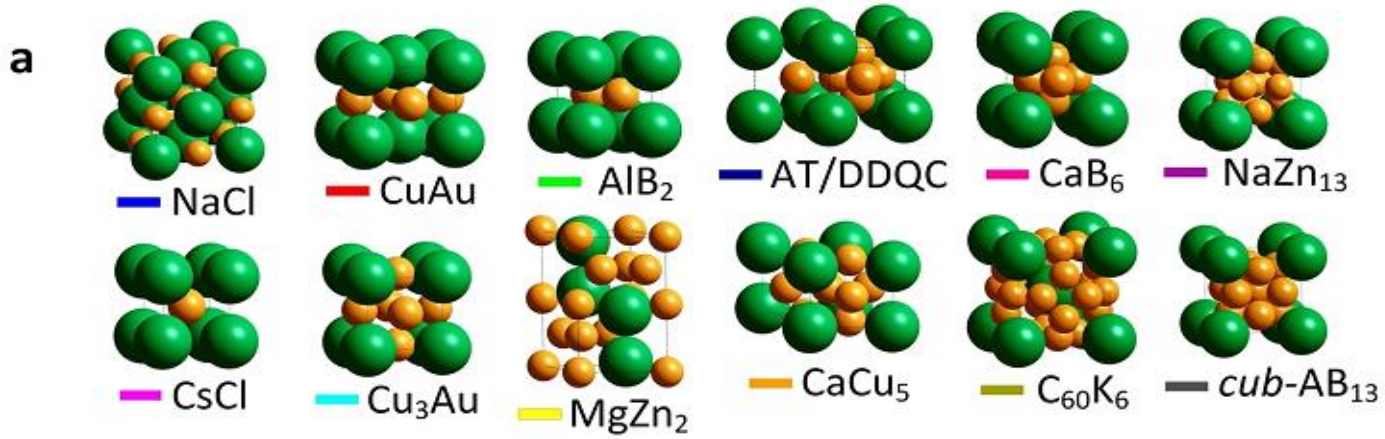
…but in many experiments BCC NPSLs are obtained.

More complex examples: binary superlattices



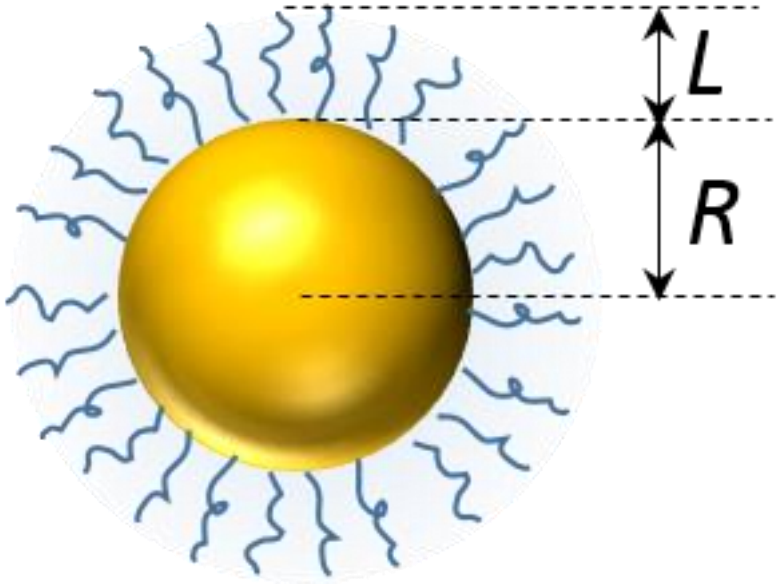
Shevchenko, E. V., et al. Nature **2006** 439, 55

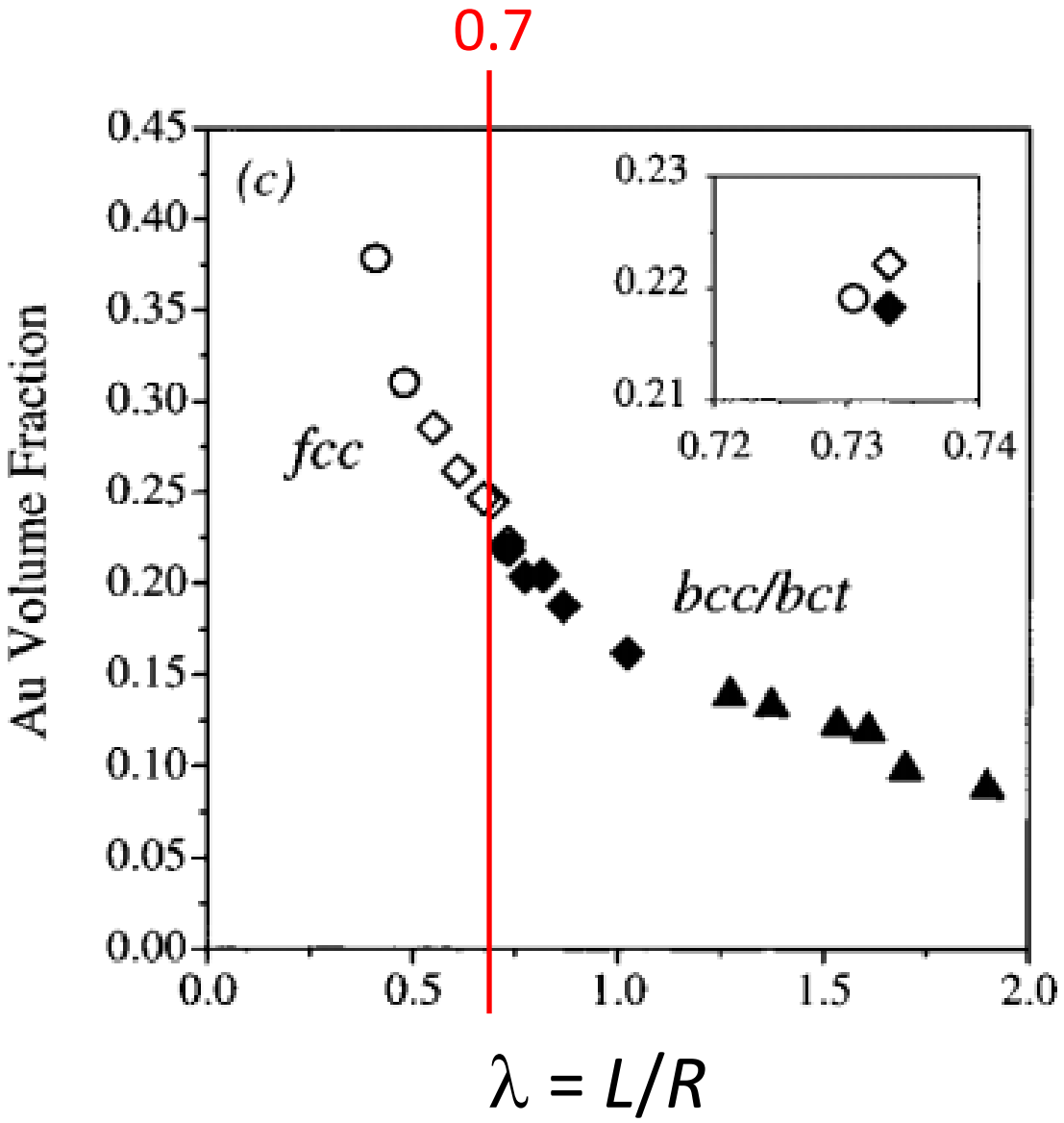




Boles et al. JACS **2015,** 137, 4494-4502.

Nanocrystals are not hard spheres

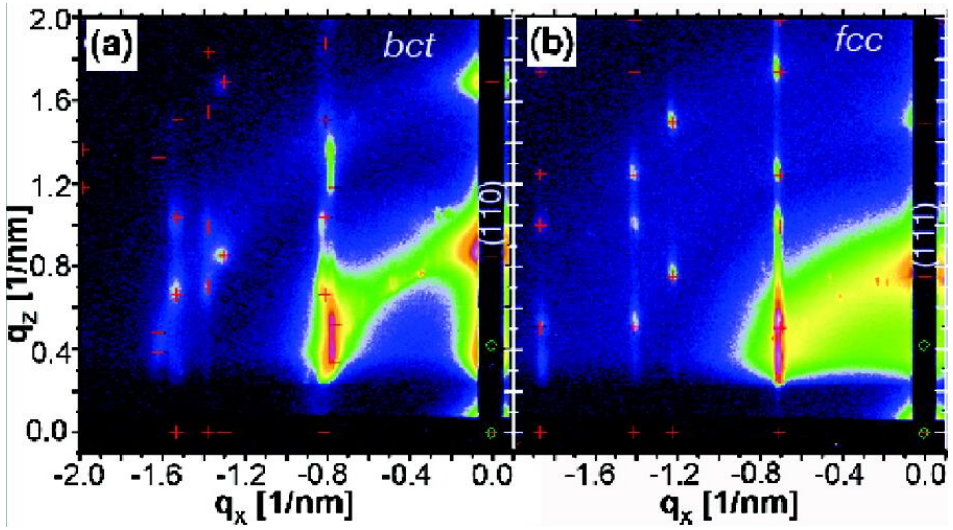




Whetten et al. Acc. Chem. Res. **1999**, 32, 397-406

Solvent-induced BCC↔FCC transition (*in-situ* GISAXS)

Bian et al. ACS Nano **2011**, 5, 2815-2823.

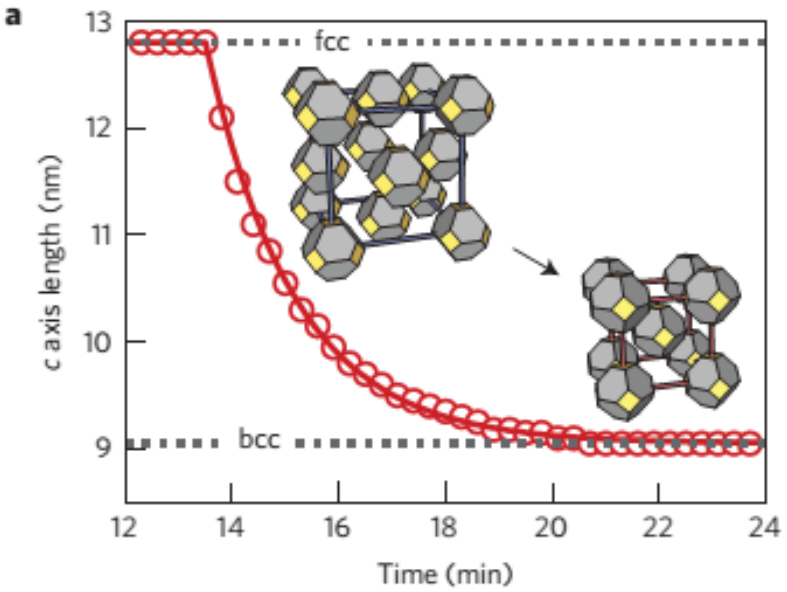


BCT (body centered tetragonal)

Dry superlattice

FCC (face centered cubic)

75% saturated octane vapor



Weidman, M. C., Nat Mater **2016**, 15, 775–781.

Our tool: Molecular Theory

$$\beta F(\mathbf{R}) = \beta F_{Tr,s} + \beta F_{Lig} + \beta F_{Ham}$$

$$\beta F_{Tr,s} = \int \rho_S(\mathbf{r})\left[\ln\left(\rho_S(\mathbf{r})v_S - 1\right)\right]d\mathbf{r}$$

Translational Entropy of the Solvent

$$\beta F_{Lig} = \sigma \int_S \sum_\alpha P(\mathbf{s},\alpha)\left[\ln\left(P(\mathbf{s},\alpha)\right) + \beta u_{gt} N_g(\alpha)\right]d\mathbf{s}$$

Conformational Free Energy of the Ligands

$$\beta F_{Ham} = -\sum_i \sum_{j>i} \frac{A}{12}\left[\frac{D^2}{d_{ij}^2 - D^2} + \frac{D^2}{d_{ij}^2} + 2\ln\left(\frac{d_{ij}^2 - D^2}{d_{ij}^2}\right)\right]$$

Core-core vdW attractions

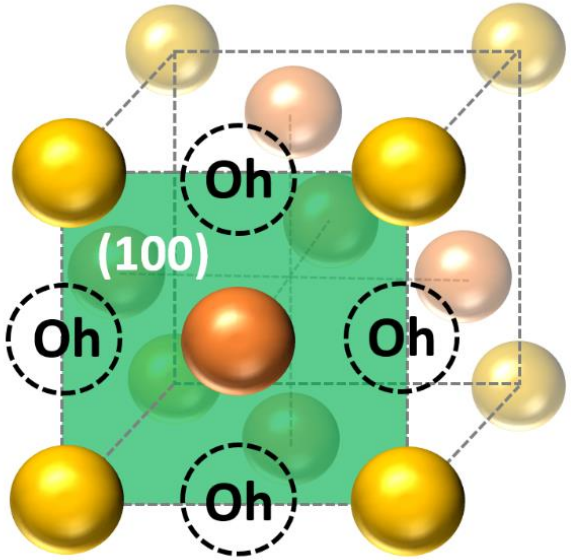
+ Incompressibility:

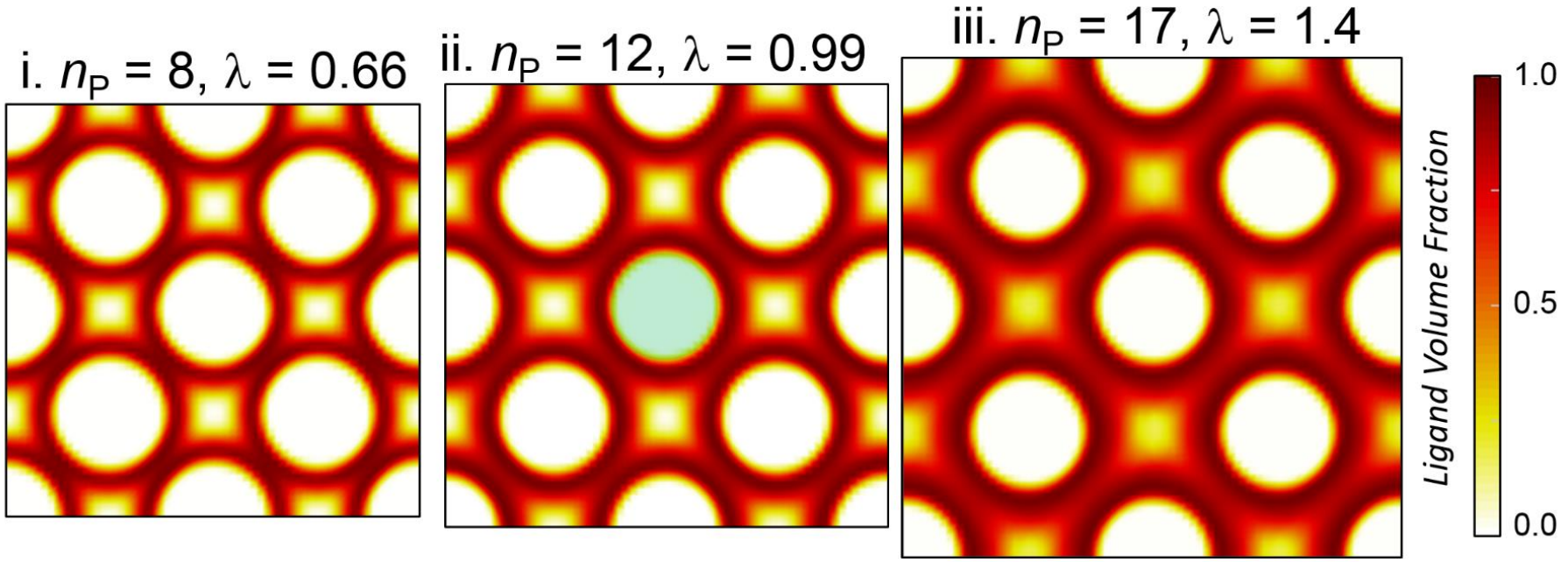
$$\rho_{sv}(\mathbf{r})v_{sv} + \rho_{ligand\ beads}(\mathbf{r})v_{bead} = 1$$

- Free-energy functional approach.
- Includes the degrees of freedom of solvent and ligands. As an output: 3D structural information about their distribution.
- Particles positions (and orientations) are fixed.
- Includes **many-body interactions** between particles by construction.
- Less expensive than MD simulations to obtain **free energies**.
- Includes some "**chemistry**" at a coarse-grained level (ligands length and surface density, molecular volumes, etc).

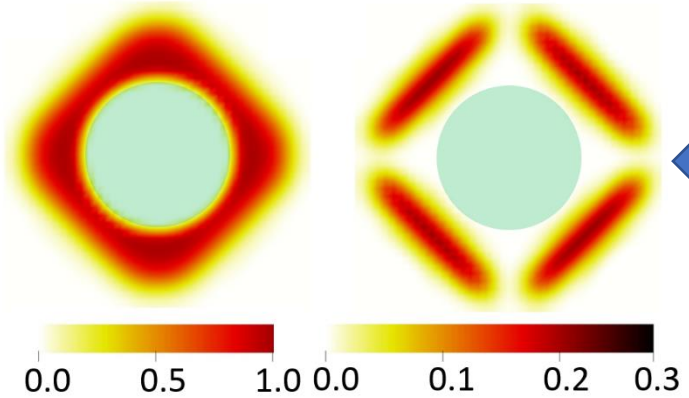
Incompressibility: no "free space" in the system → (can only model "wet" lattices)

Structural Information





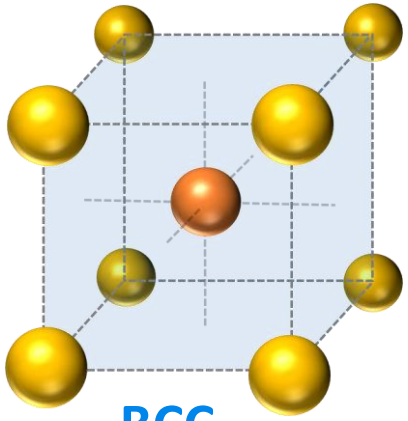
Single particle

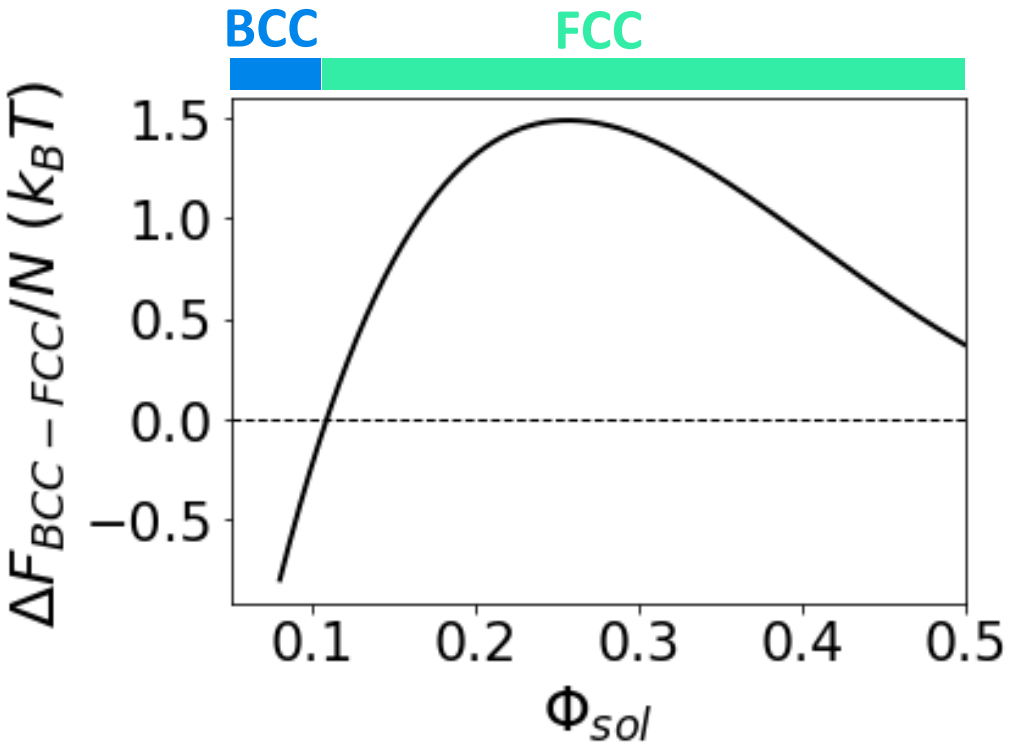


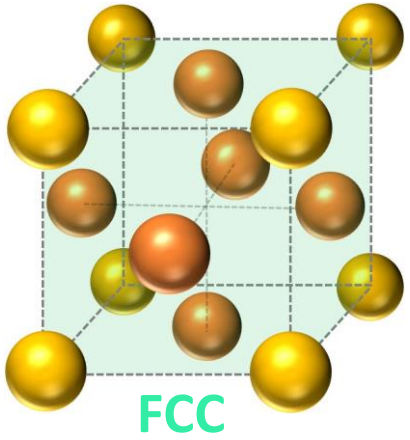
Interpentration

L. Missoni, M. Tagliazucchi, *ACS Nano* **2020**, 14, 5, 5649

Phase behavior: solvent-induced FCC-BCC transition



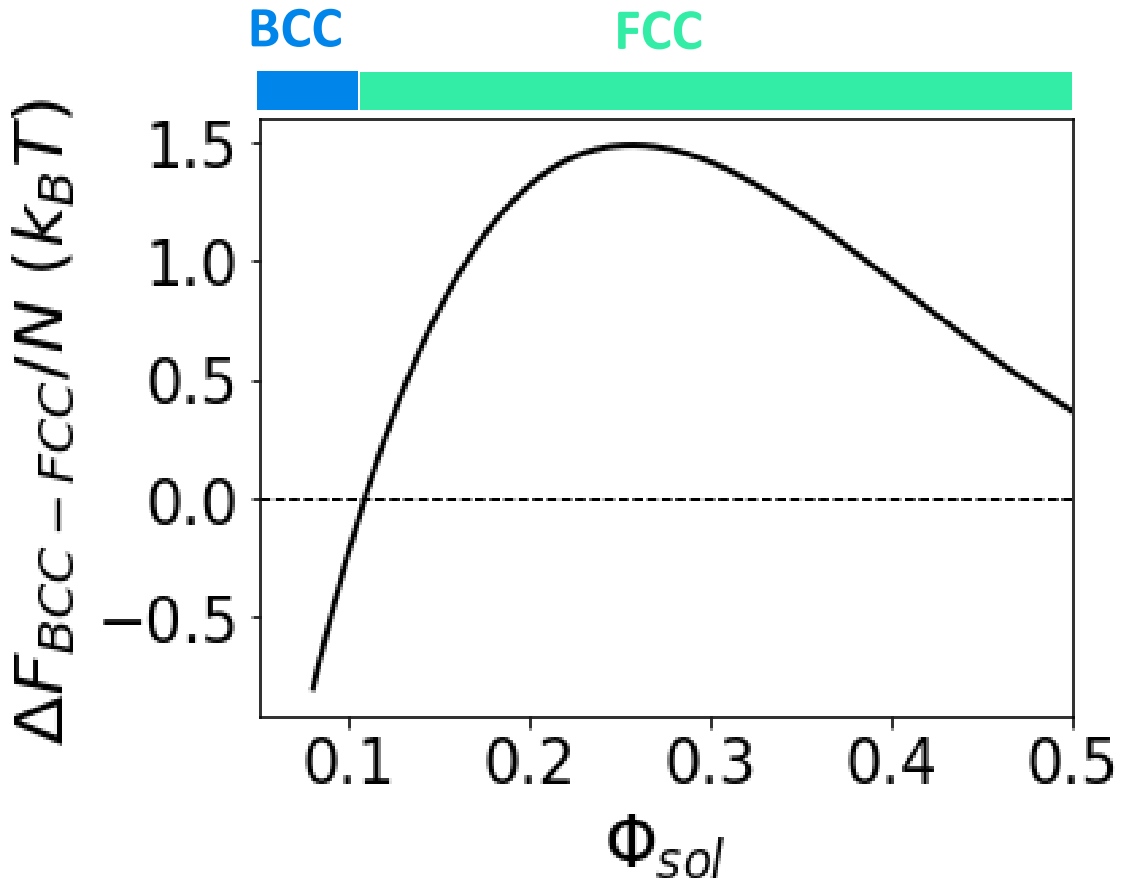




Drying, decrease lattice parameter

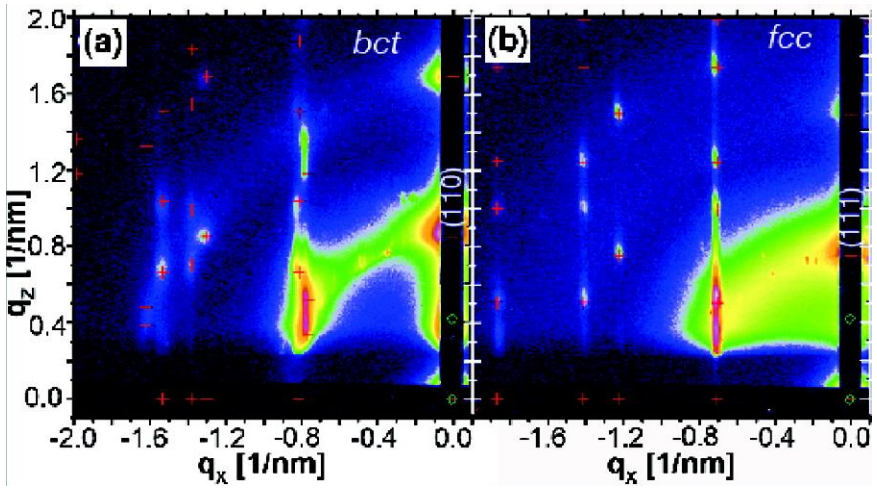
- The comparison between BCC and FCC is at fixed Φ_{sol} (volume fraction of residual solvent).
- For a given Φ_{sol}, NP-NP distance in BCC is ~ 3 % shorter than in FCC. But FCC has 12 near-neighbors and BCC has 8.

Phase behavior: solvent-induced FCC-BCC transition

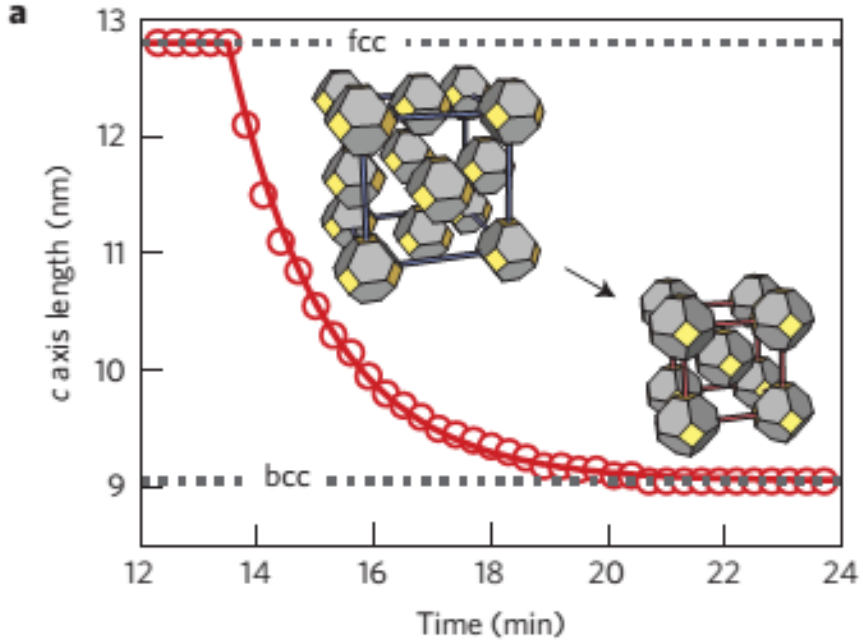


← Drying, decrease lattice parameter

Dry superlattice (BCT) **Octane vapor FCC**

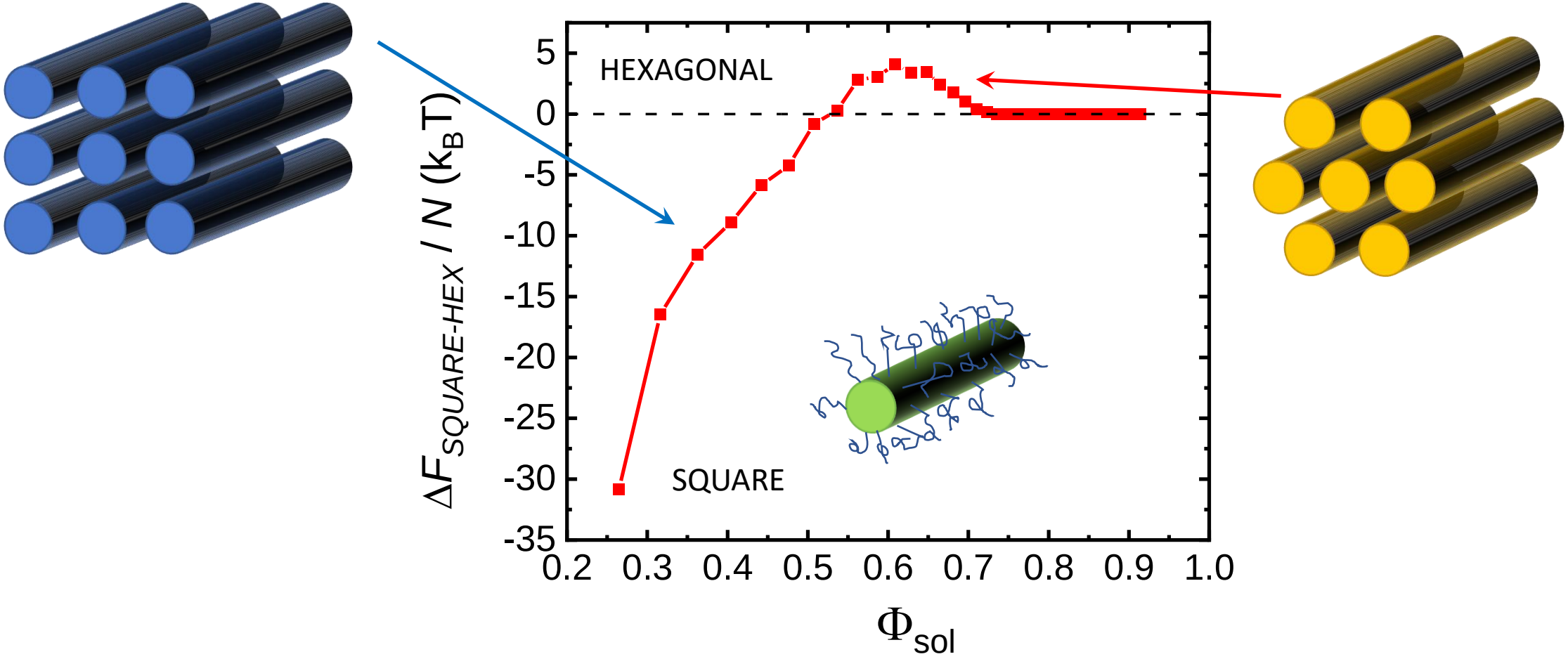


Bian et al. ACS Nano **2011**, 5, 2815-2823.

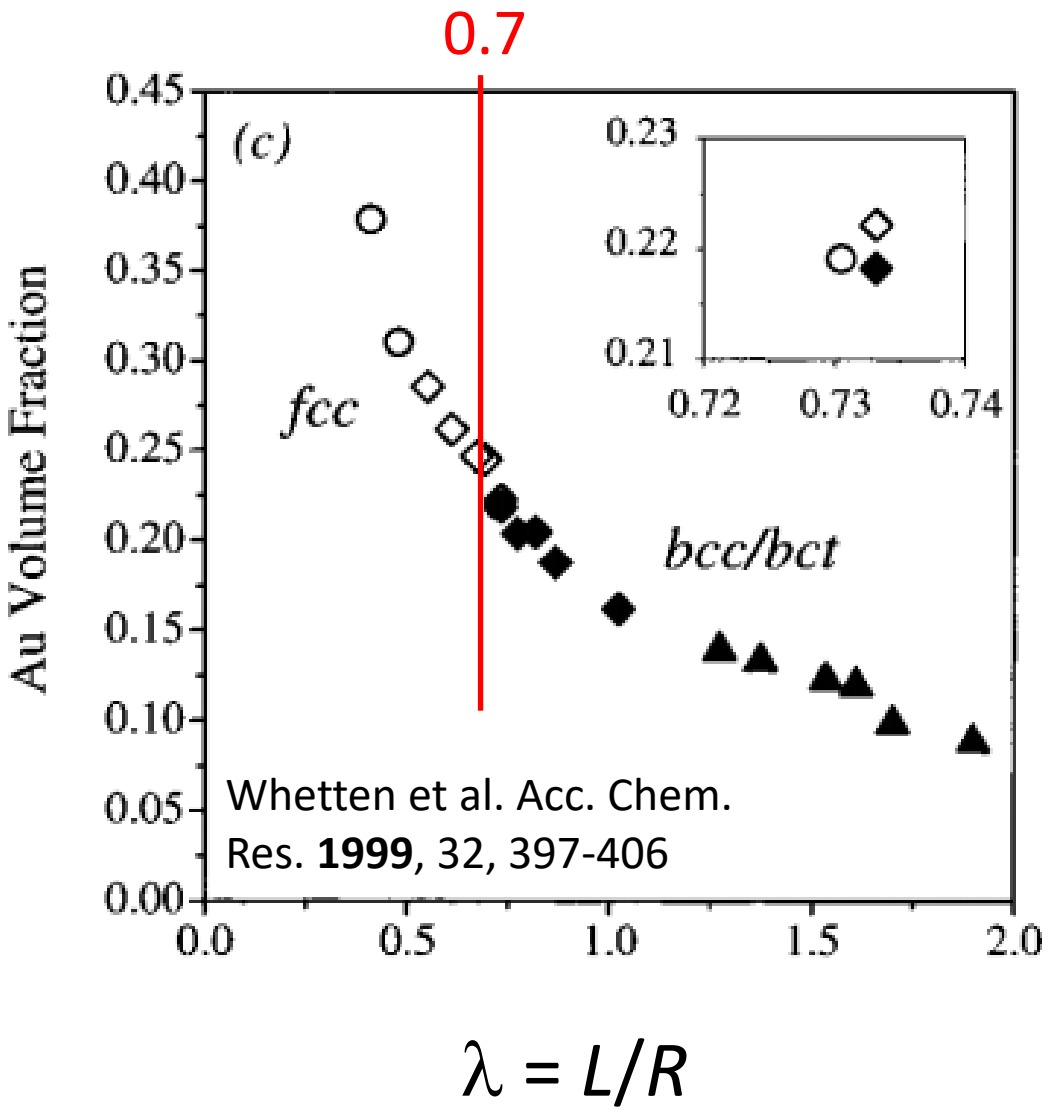


Weidman, M. C., Nat Mater **2016**, 15, 775–781.

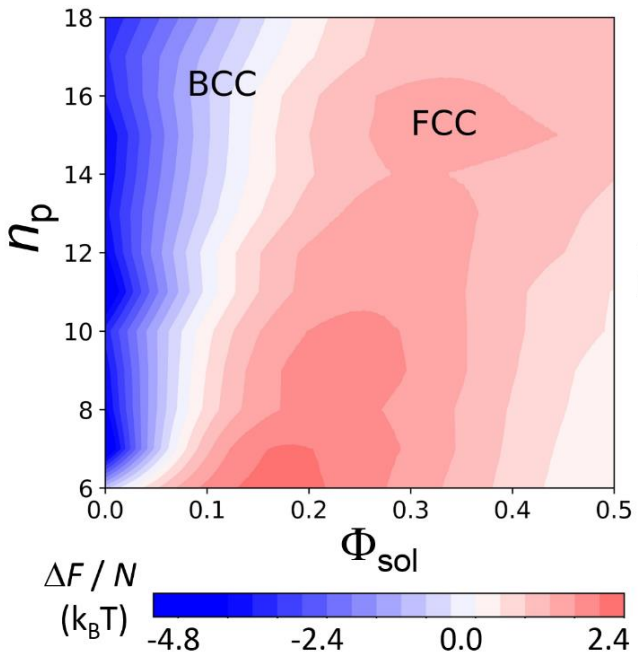
An even simpler system: are evaporation-induced transitions from closed-packed to non-closed-packed structures general?

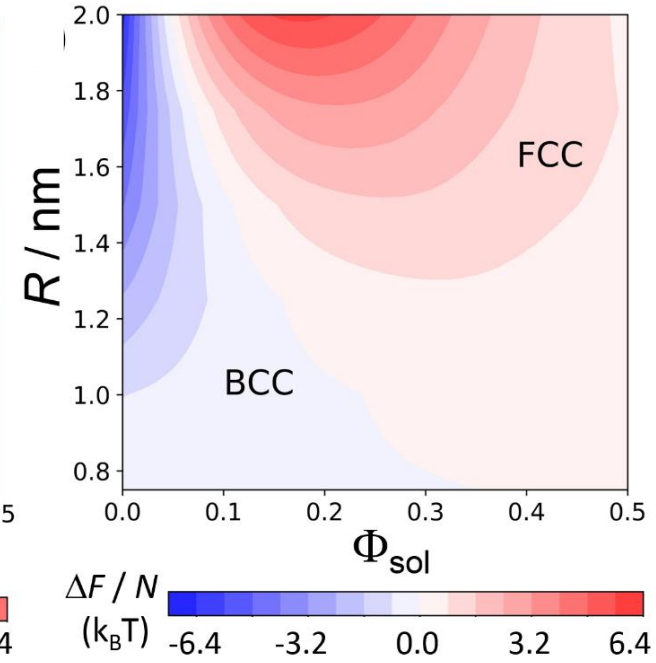


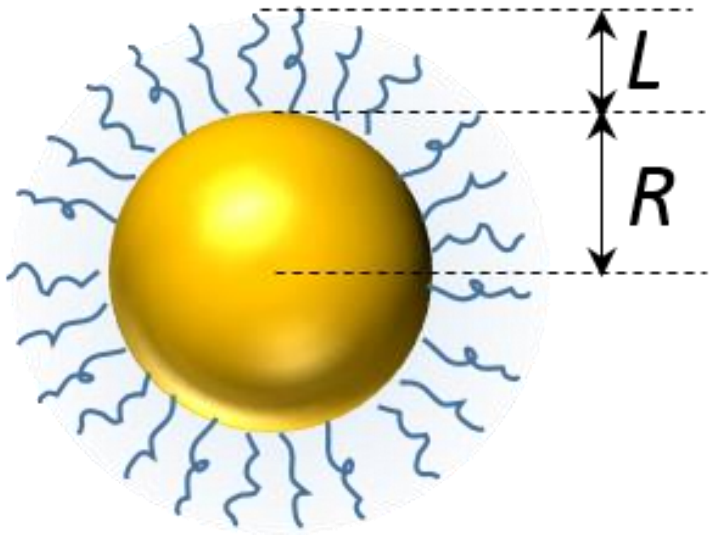
Effect of nanoparticle “softness”

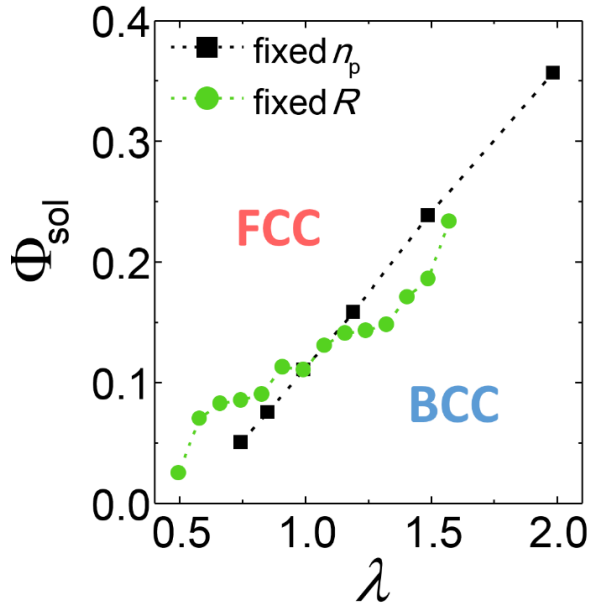


$\lambda = L/R$



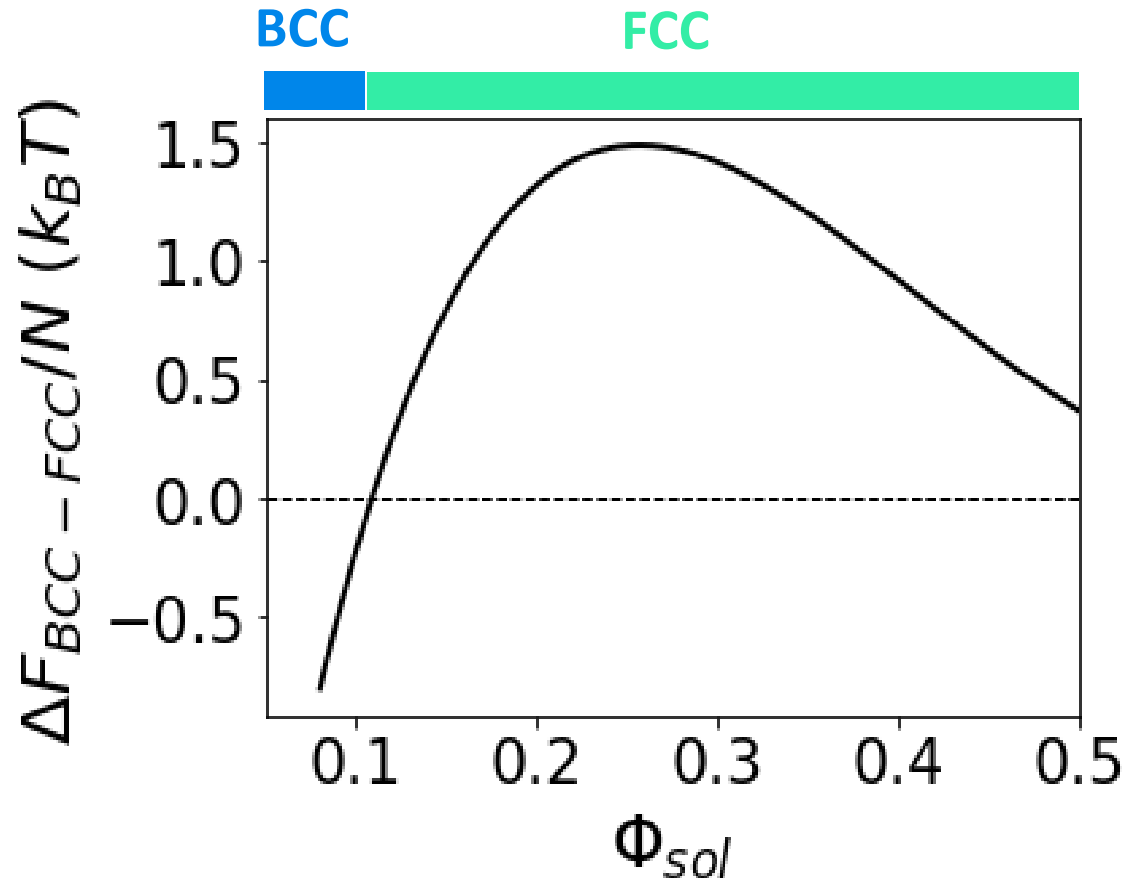




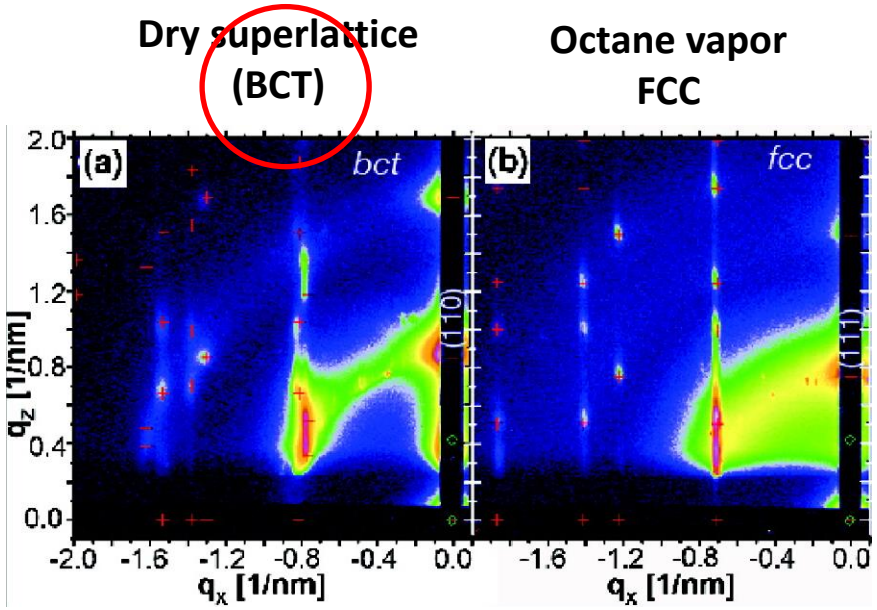


L. Missoni, M. Tagliazucchi, *ACS Nano* **2020**, 14, 5, 5649

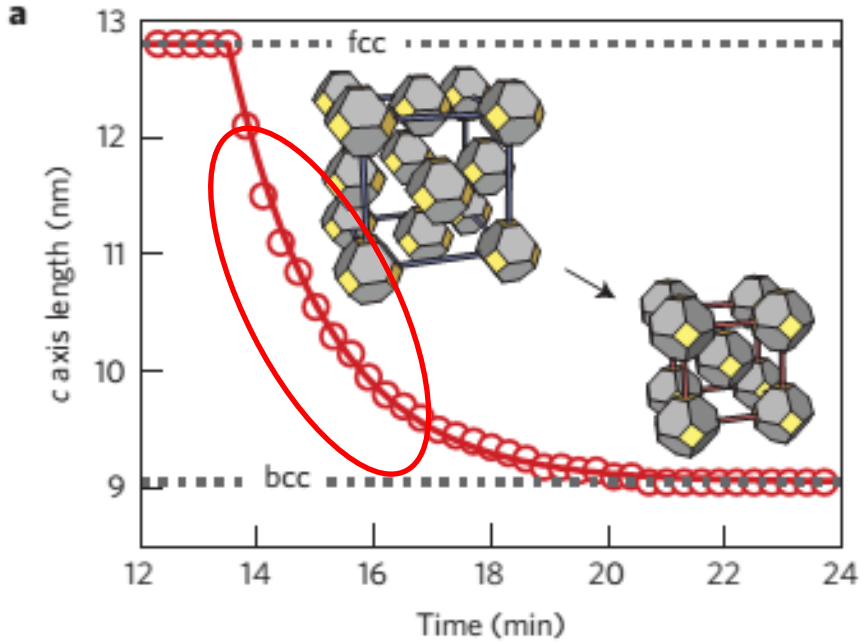
Where is BCT?



← Drying, decrease lattice parameter



Bian et al. ACS Nano **2011**, 5, 2815-2823.



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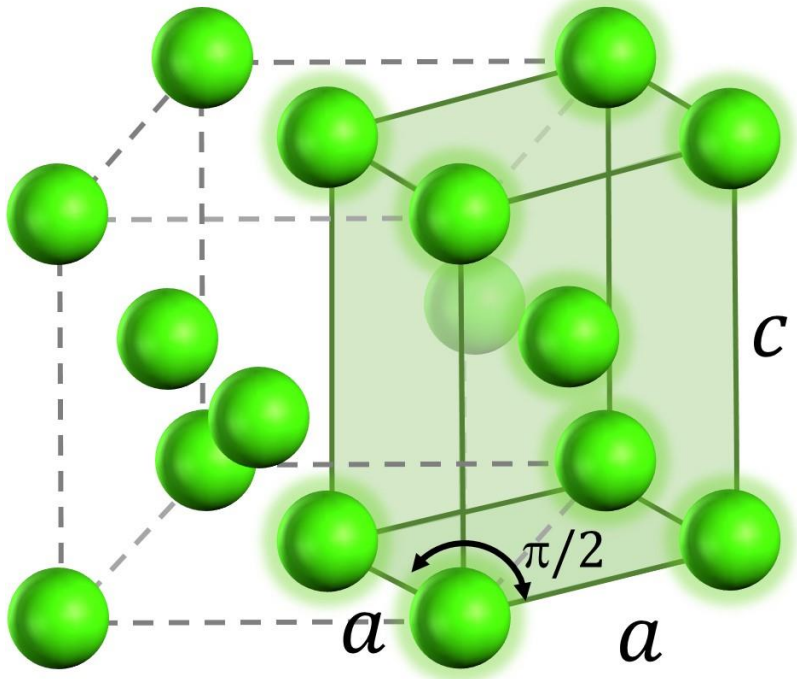
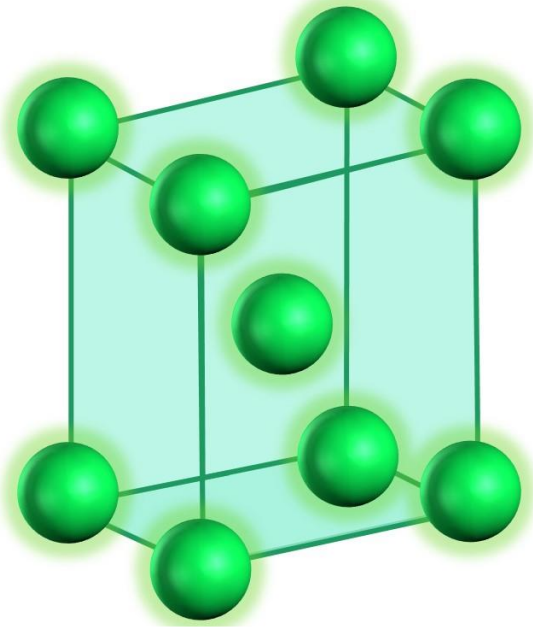
Intermezzo: the Bain transformation

FCC



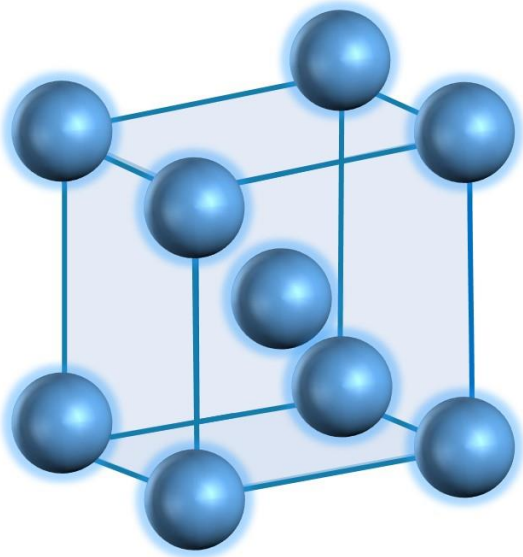
$c / a = \sqrt{2}$

BCT



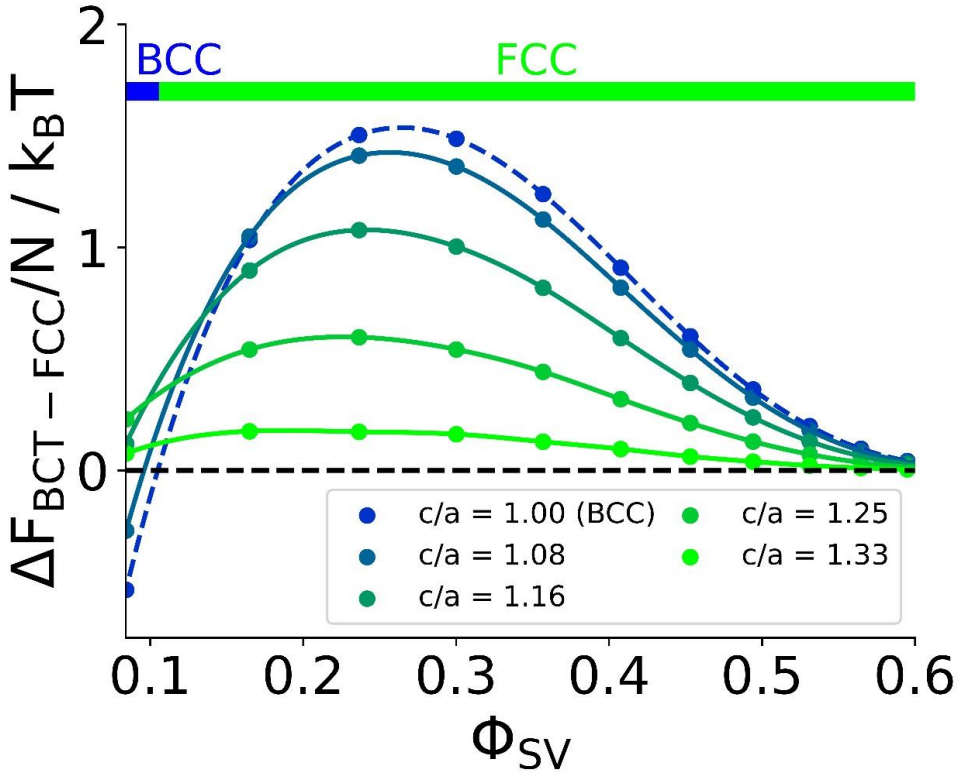
$1 < c / a < \sqrt{2}$

BCC



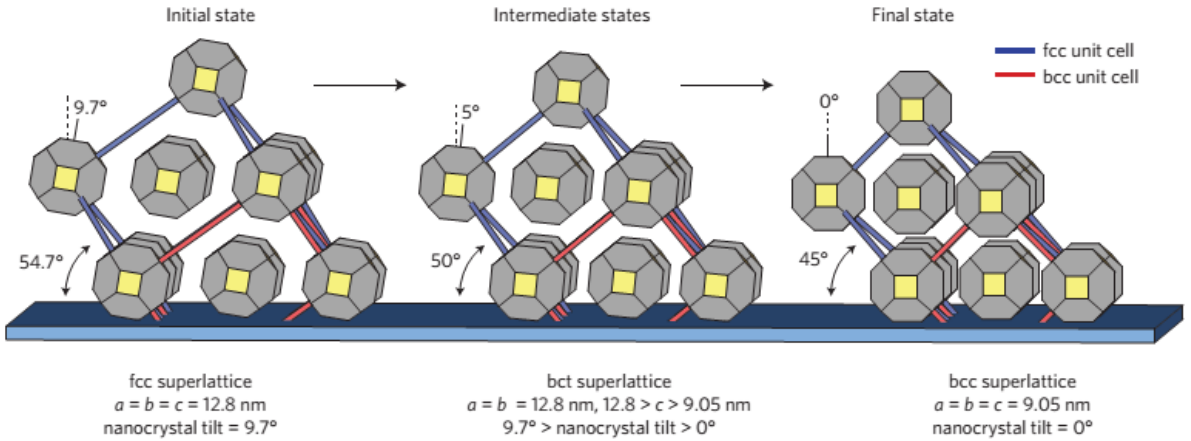
$c / a = 1$

BCT is not predicted by MOLT for spherical NPs in bulk supercrystals

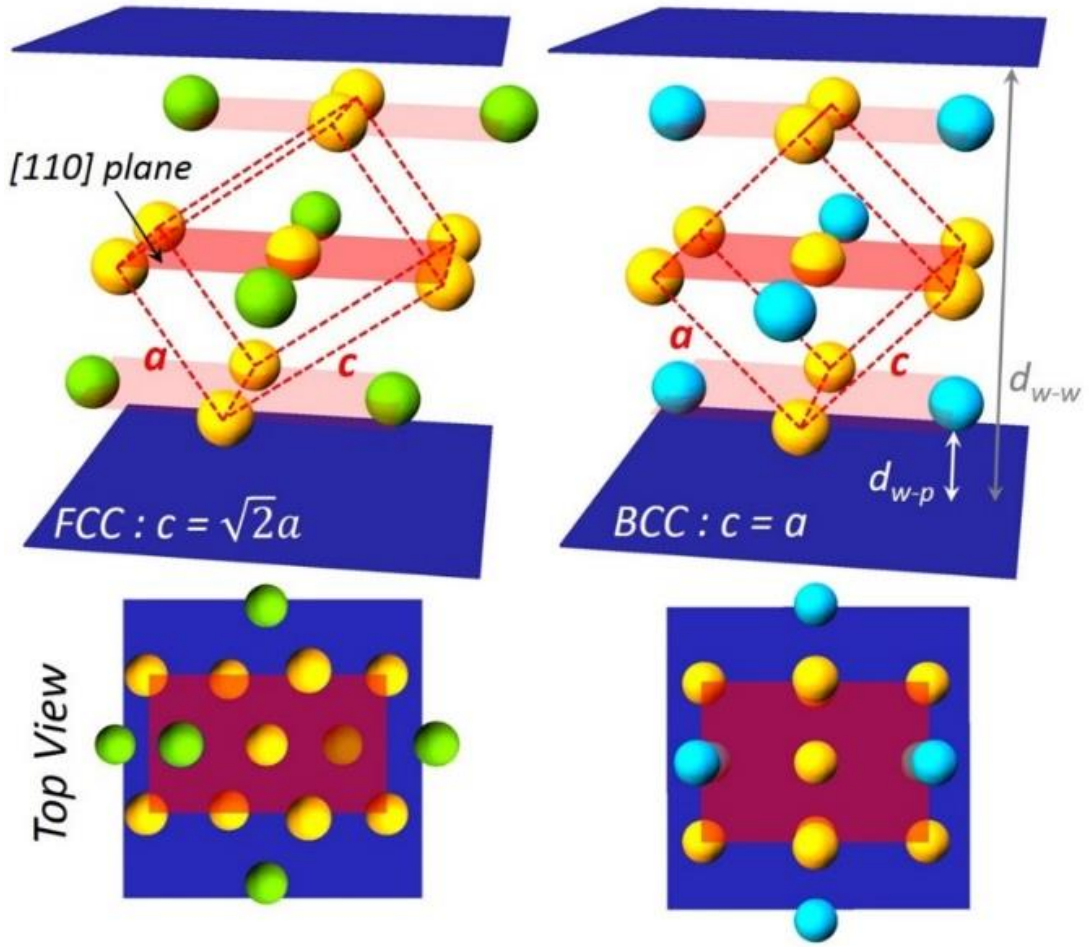


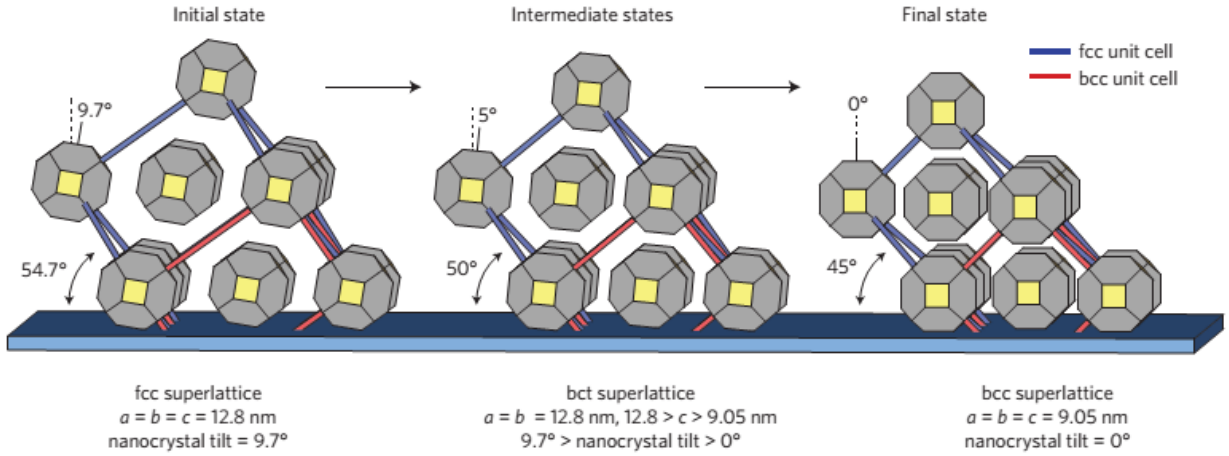
Differences between theory and GISAXS experiments:

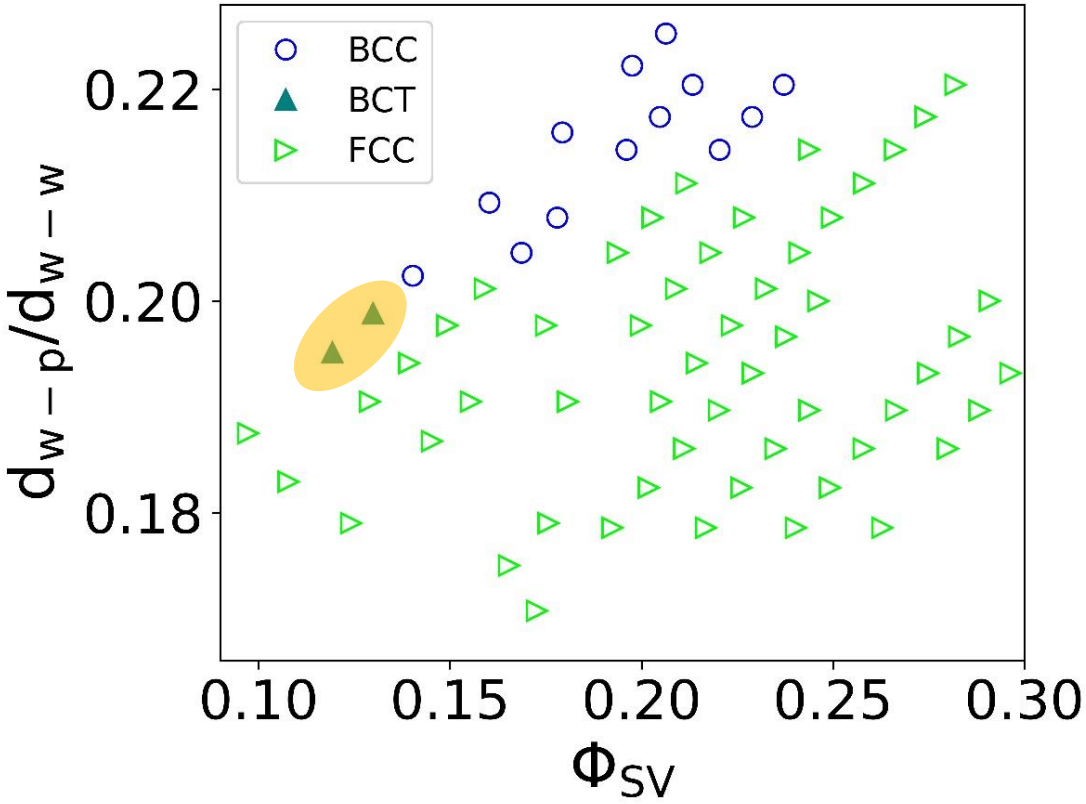
1) Experiments studied thin films
2) Experiments used non-spherical NPs



Surfaces may very weakly favor BCT

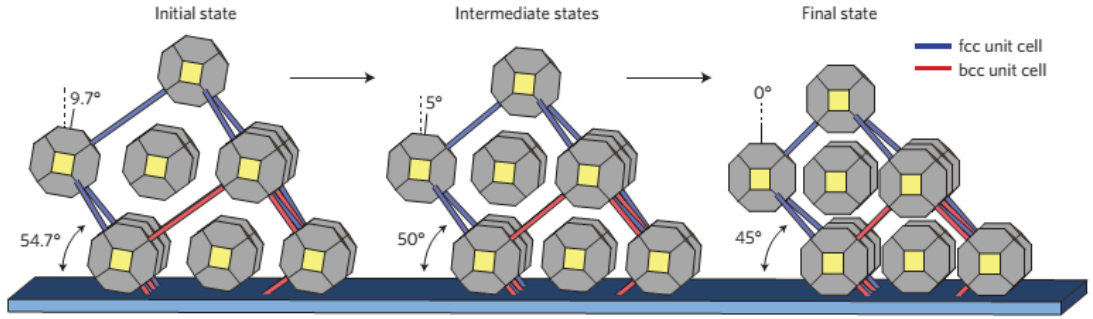


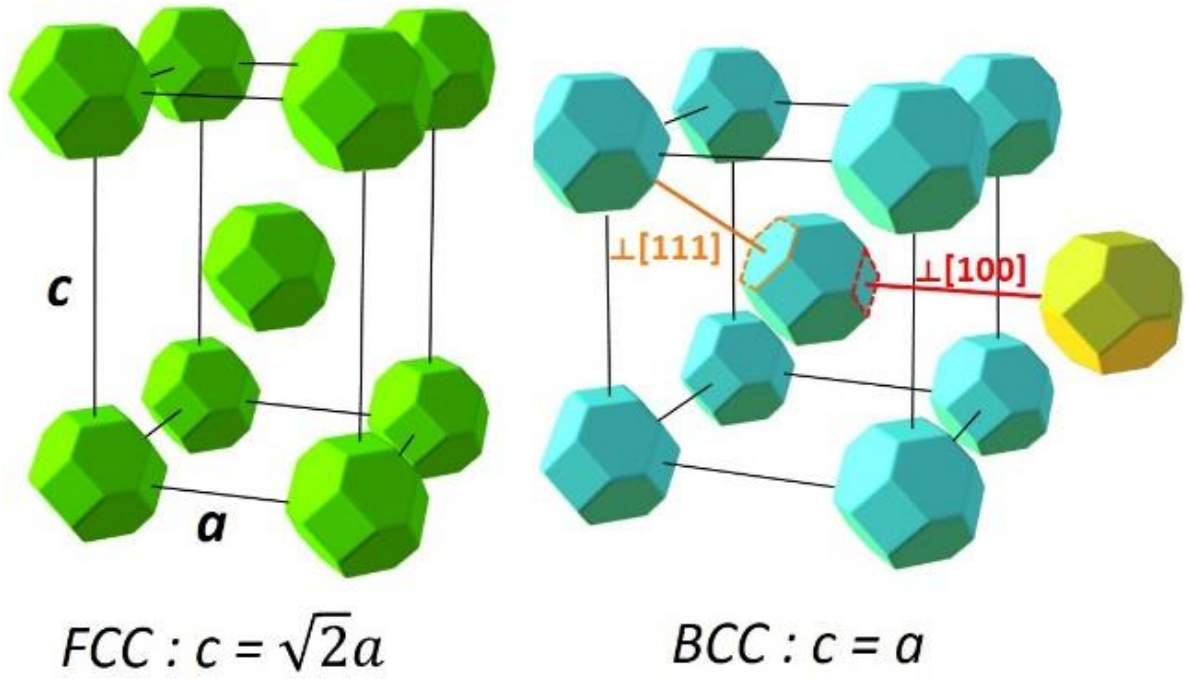


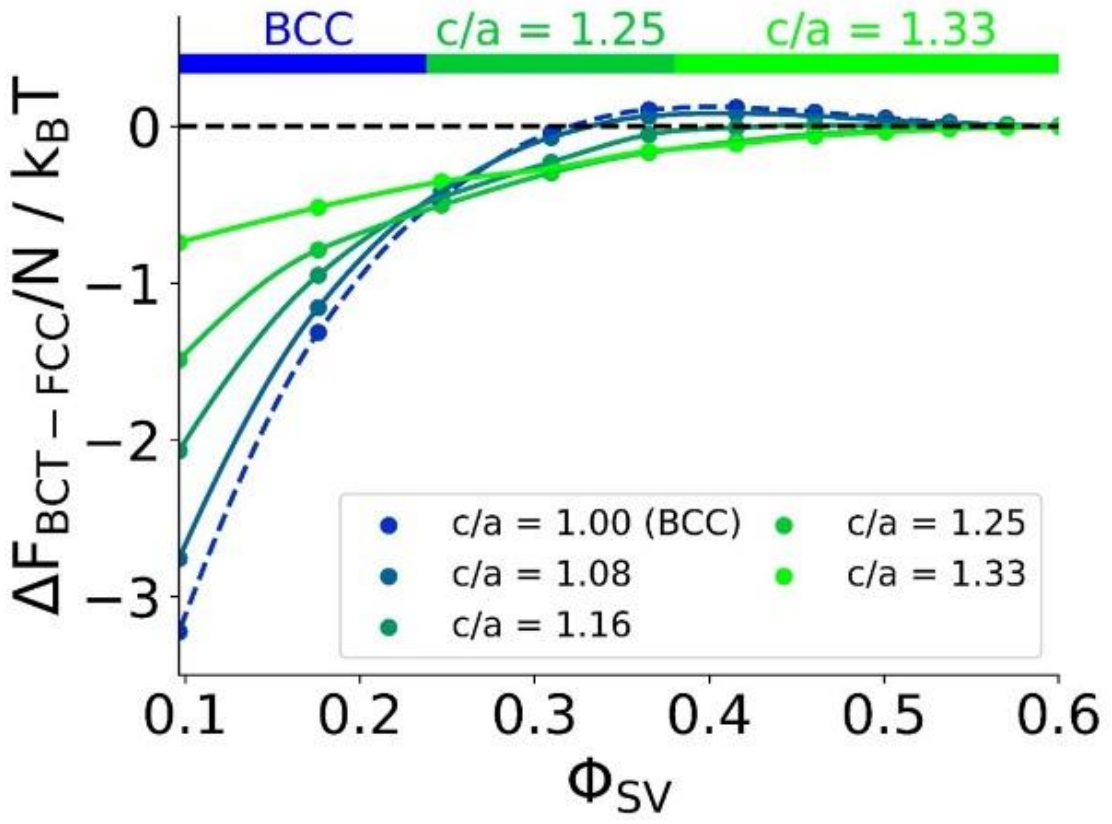


Missoni, L. L., Tagliazucchi, M,
Nanoscale, **2021**,13, 14371-1438

Non-Spherical shapes strongly favor BCT







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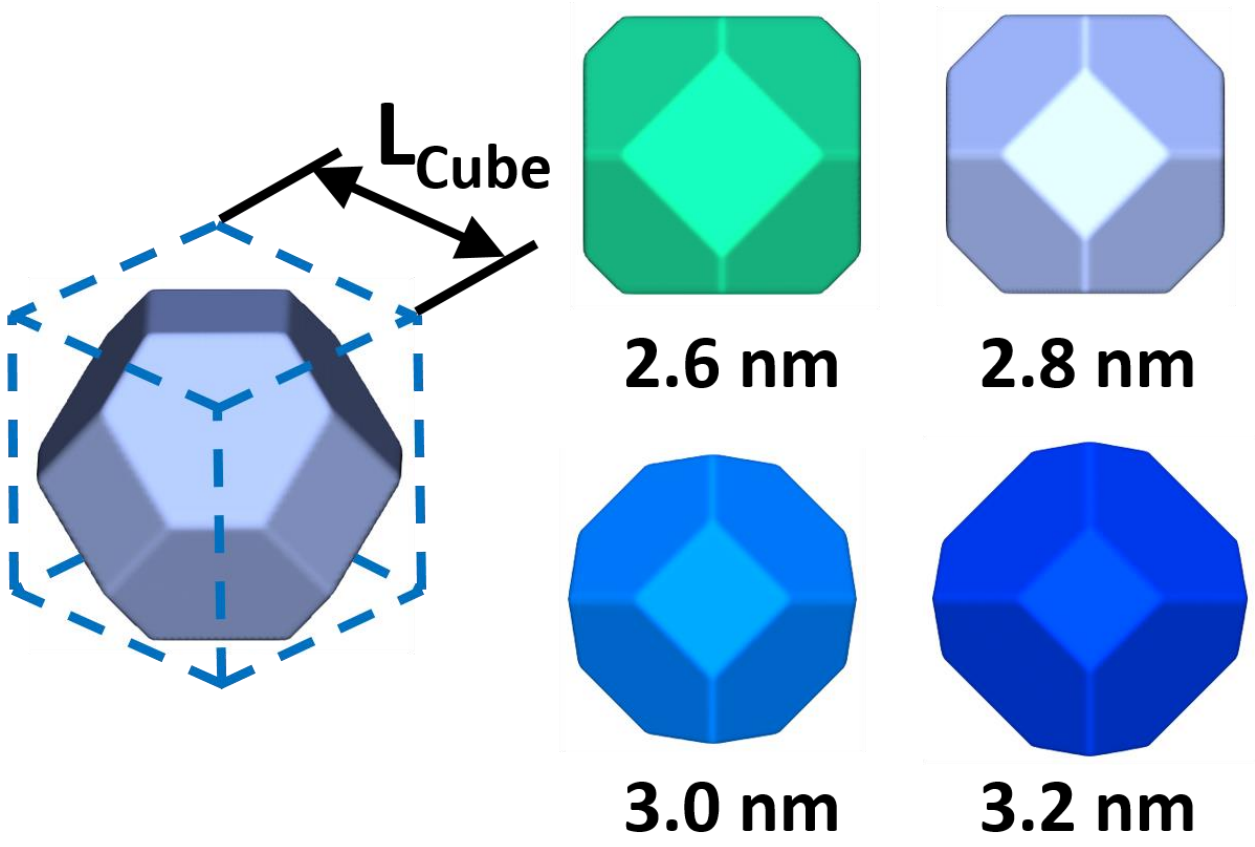
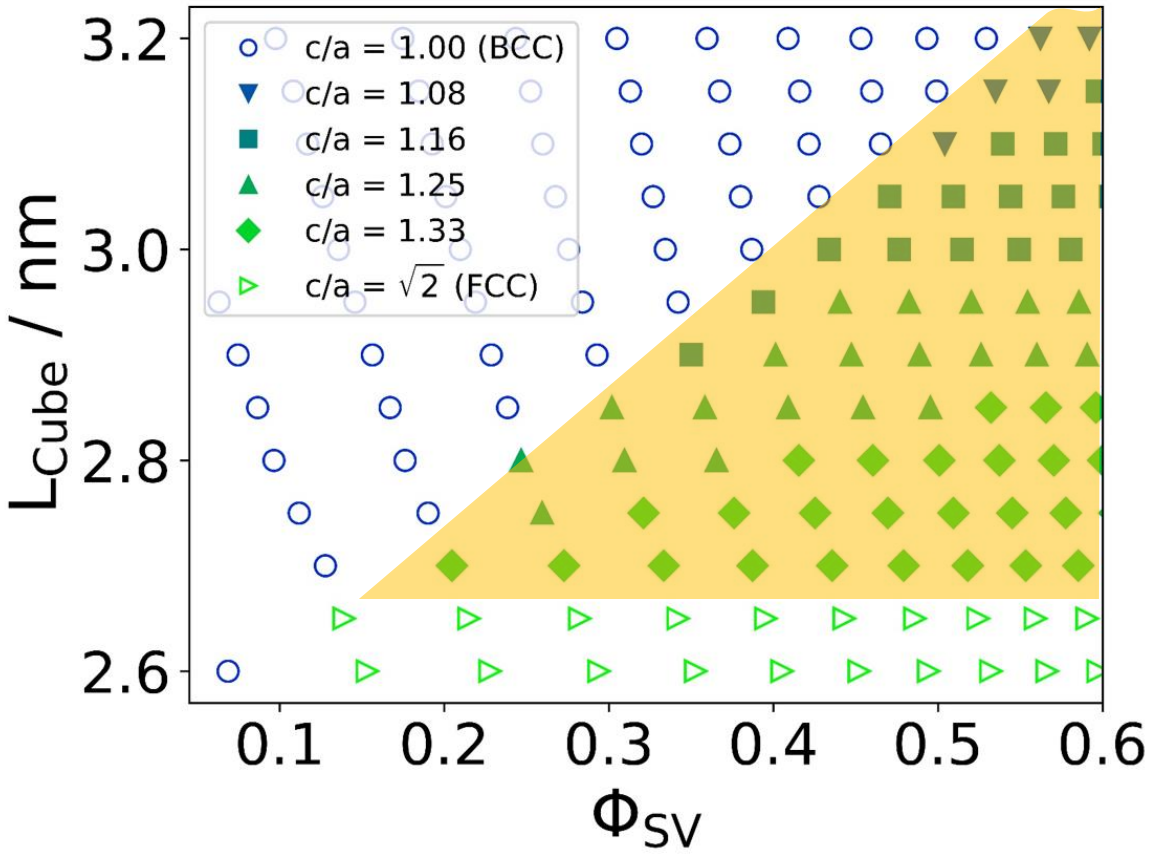
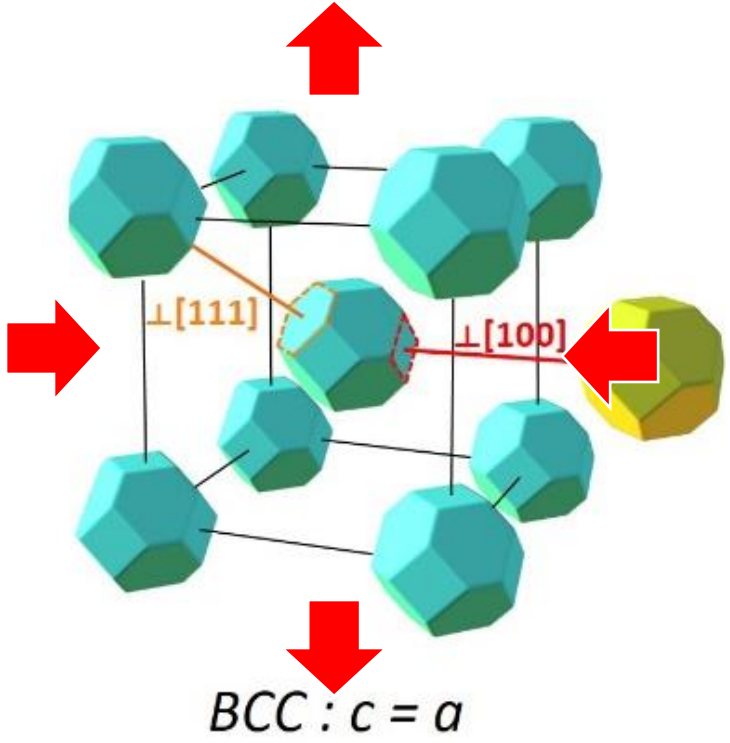
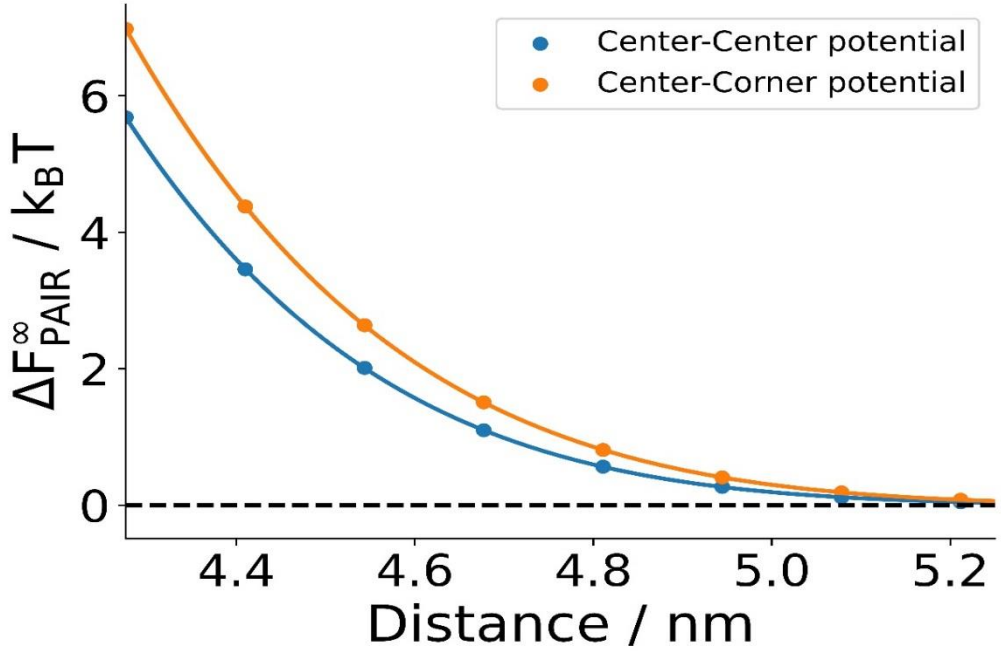
Effect of shape on phase behavior

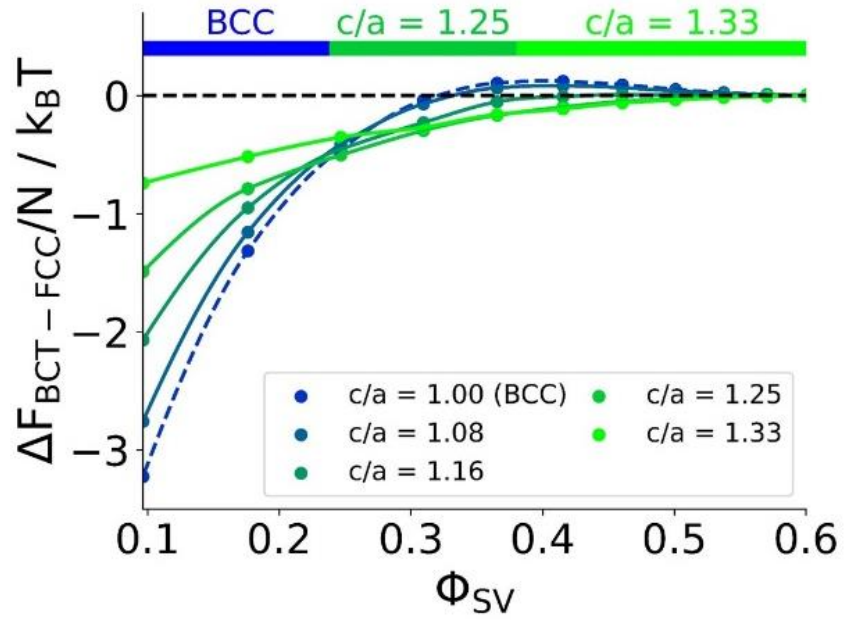




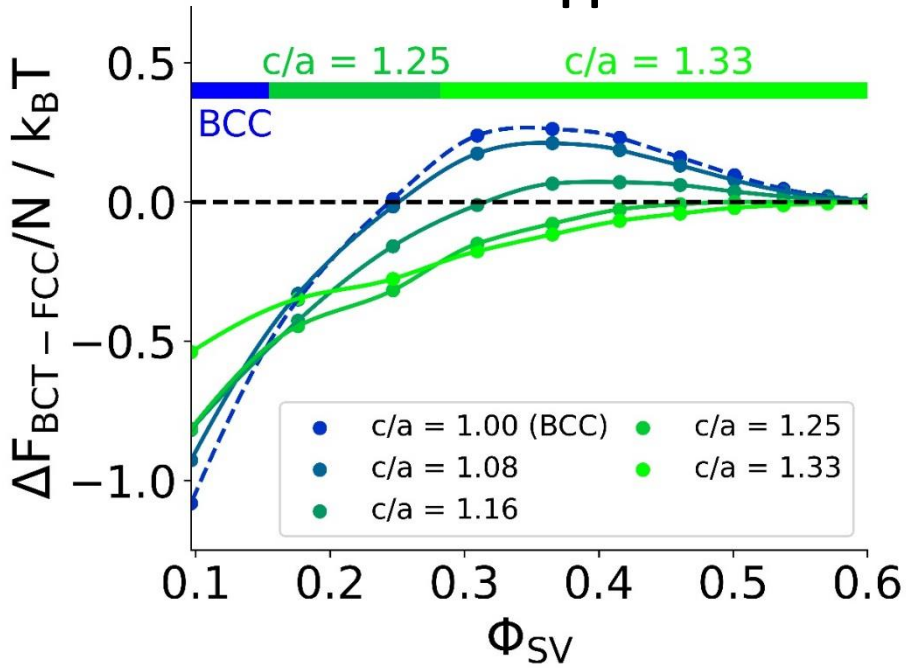
Why a non-spherical shape favors BCT?







Pair-wise additive approximation



Our tool: Molecular Theory

$$\beta F(\mathbf{R}) = \beta F_{Tr,s} + \beta F_{Lig} + \beta F_{Ham}$$

$$\beta F_{Tr,s} = \int \rho_S(\mathbf{r})\left[\ln\left(\rho_S(\mathbf{r})v_S - 1\right)\right]d\mathbf{r}$$

Translational Entropy of the Solvent

$$\beta F_{Lig} = \sigma \int_S \sum_\alpha P(\mathbf{s},\alpha)\left[\ln\left(P(\mathbf{s},\alpha)\right) + \beta u_{gt} N_g(\alpha)\right]d\mathbf{s}$$

Conformational Free Energy of the Ligands

$$\beta F_{Ham} = -\sum_i \sum_{j>i} \frac{A}{12}\left[\frac{D^2}{d_{ij}^2 - D^2} + \frac{D^2}{d_{ij}^2} + 2\ln\left(\frac{d_{ij}^2 - D^2}{d_{ij}^2}\right)\right]$$

Core-core vdW attractions

+ Incompressibility:

$$\rho_{sv}(\mathbf{r})v_{sv} + \rho_{ligand\ beads}(\mathbf{r})v_{bead} = 1$$

- Free-energy functional approach.
- Includes the degrees of freedom of solvent and ligands. Provides 3D structural information about their distribution.
- Particles positions (and orientations) are fixed.
- Includes **many-body interactions** between particles by construction.
- Less expensive than MD simulations to obtain **free energies**.
- Includes some "**chemistry**" at a coarse-grained level (ligands length and surface density, molecular volumes, etc).

Incompressibility: no "free space" in the system → (can only model "wet" lattices)

“Compressible” Molecular Theory for NPSLs

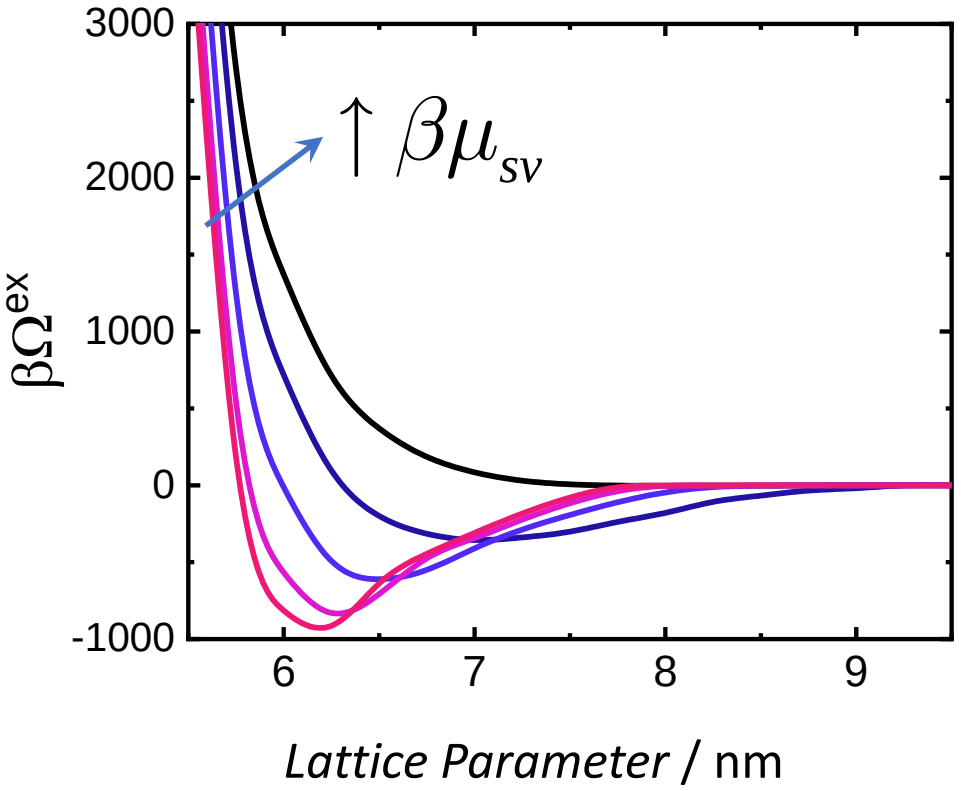
$$\beta\Omega\ \mathbf{R} = \beta F_{Tr} + \beta F_{Lig} + \beta F_{Ham} + \beta F_{HS} + \beta F_{vdW} - \beta\mu_{sv} N_{sv}$$

- βF_{Tr}: Translational Entropy of the Solvent
- βF_{Lig}: Conformational Entropy of the Ligands
- βF_{Ham}: Core-core vdW attractions
- βF_{HS}: sv-sv, sv-ligand and ligand-ligand respulsions
- βF_{vdW}: sv-sv, sv-ligand and ligand-ligand attractions (vdW)
- $-\beta\mu_{sv} N_{sv}$: Chemical potential of the solvent (Grand Canonical ensamble)

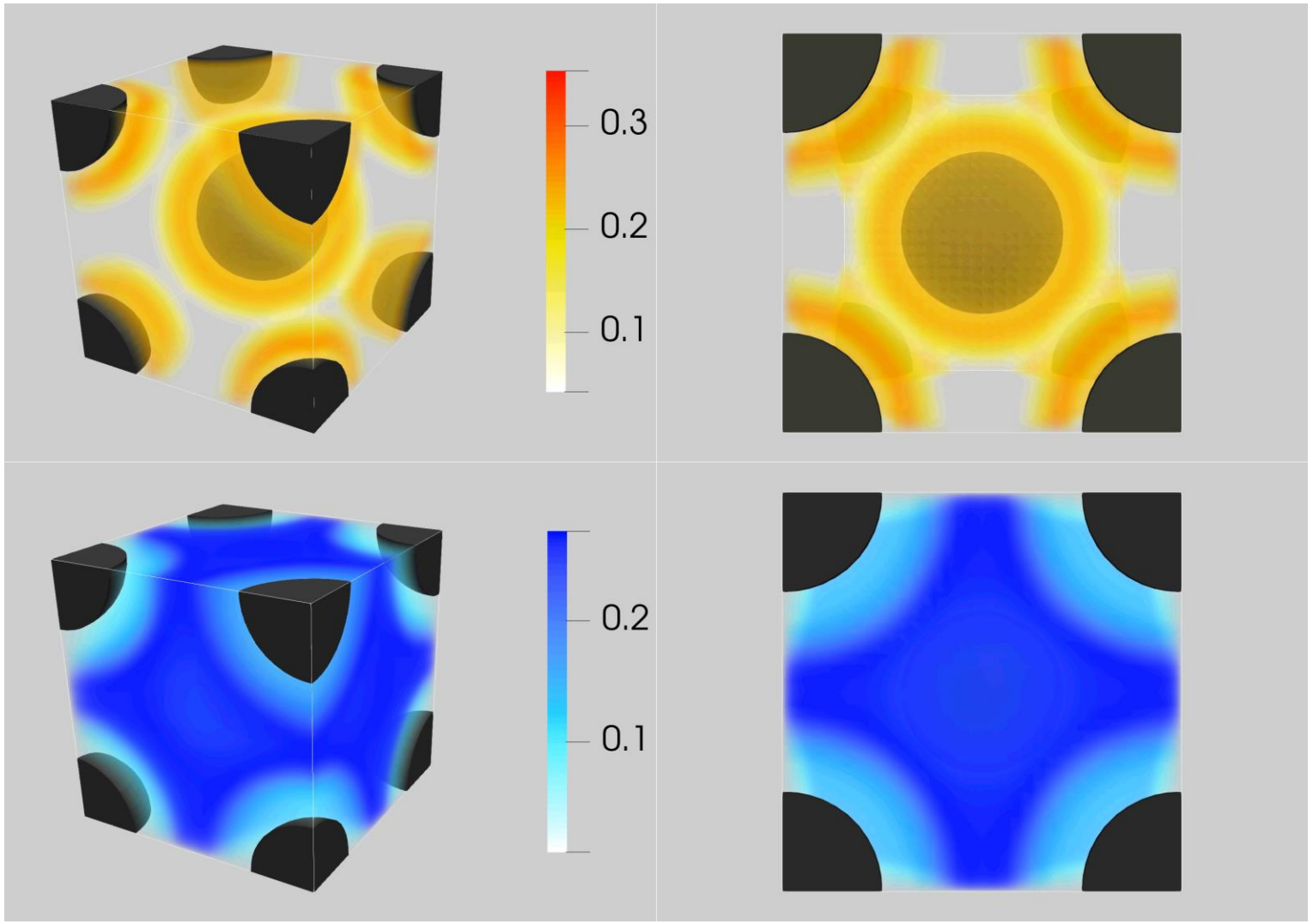
Predicts L↔G phase transition

Allows to study the evaporation of solvent within the SL

Most stable structures during drying

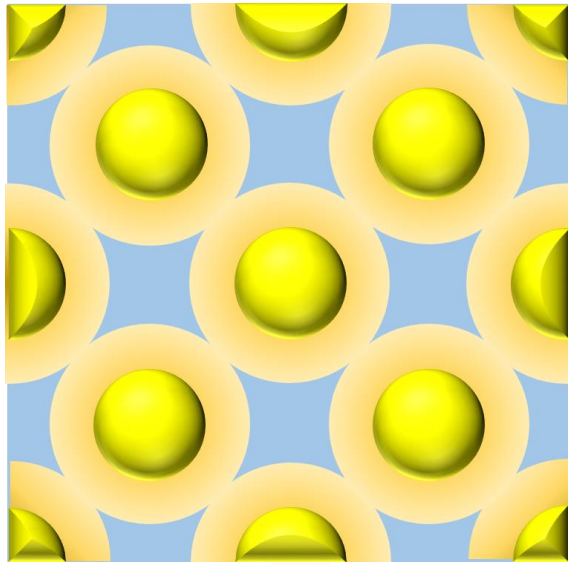


Density of Ligands

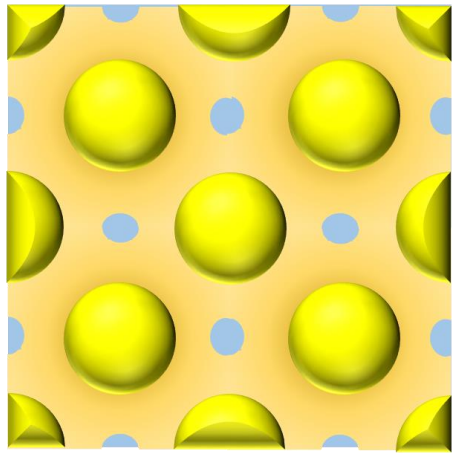


Density of Solvent

Solvent pathways during NPSL assembly

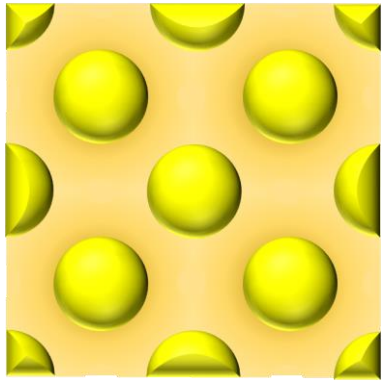


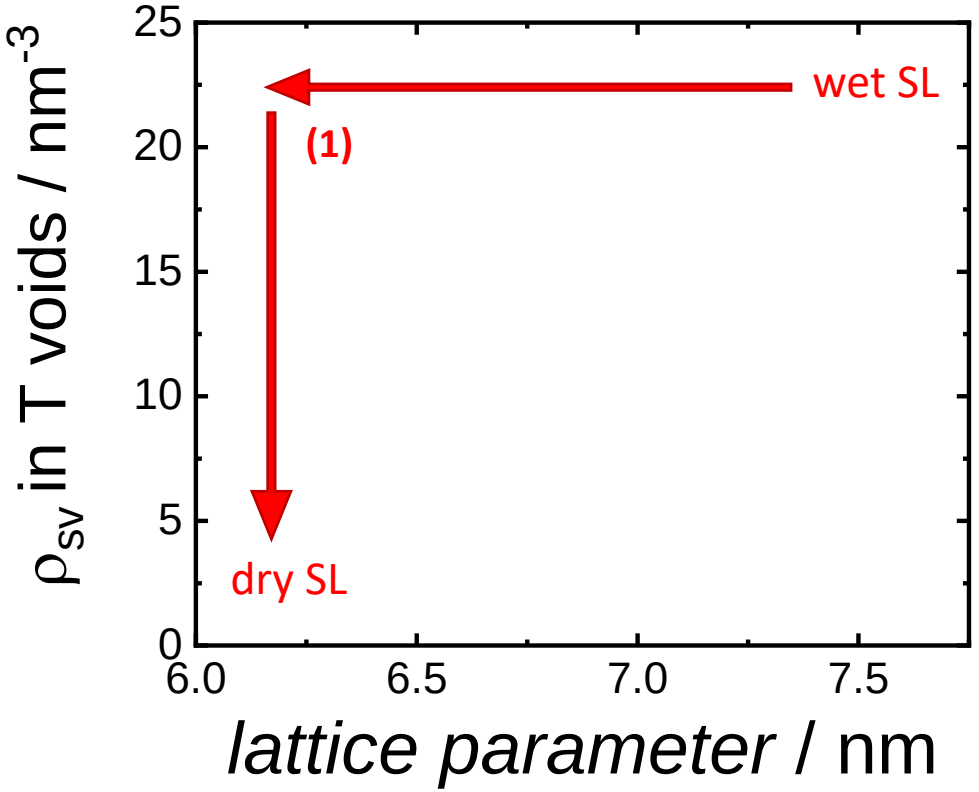
shrink
↓solvent

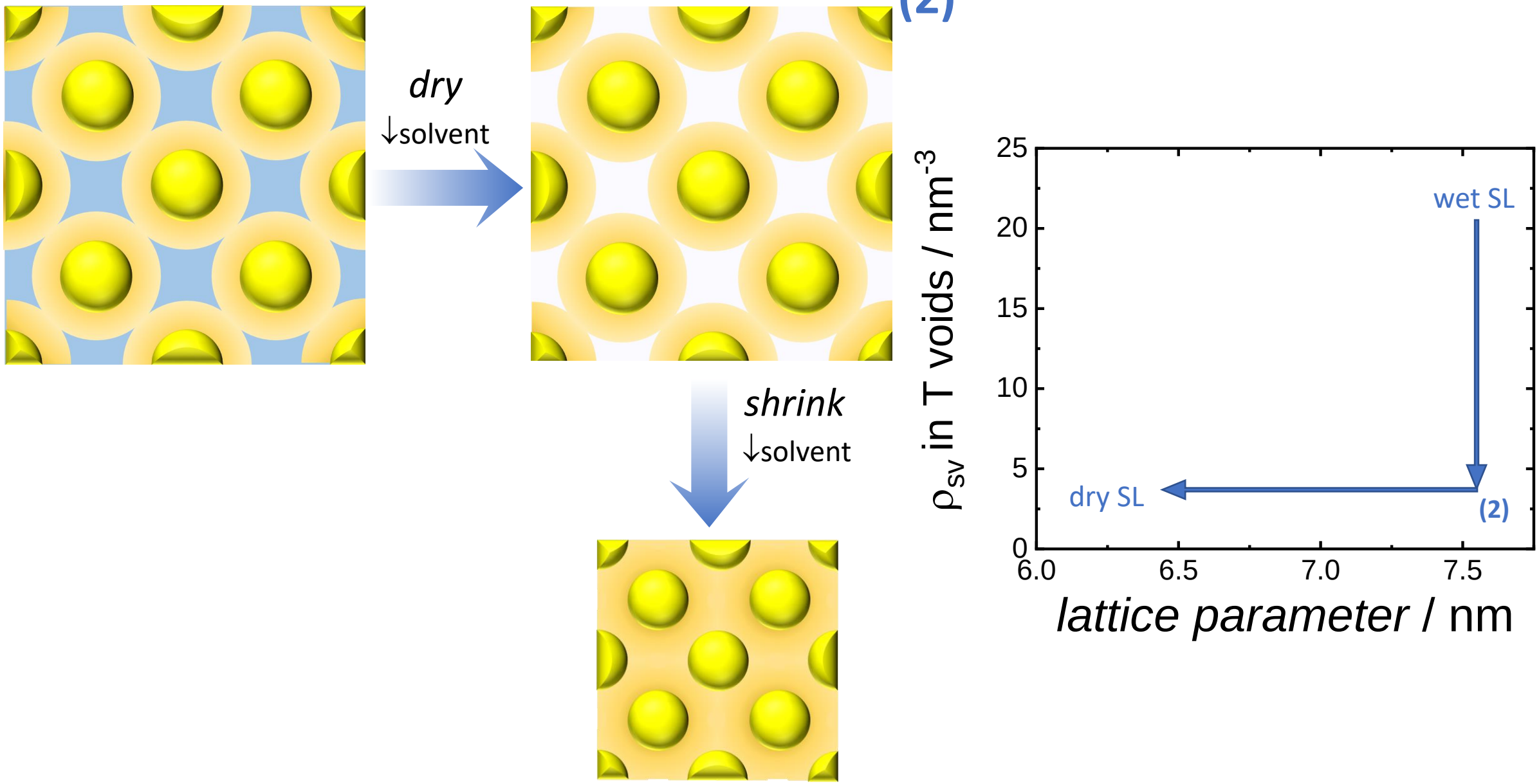


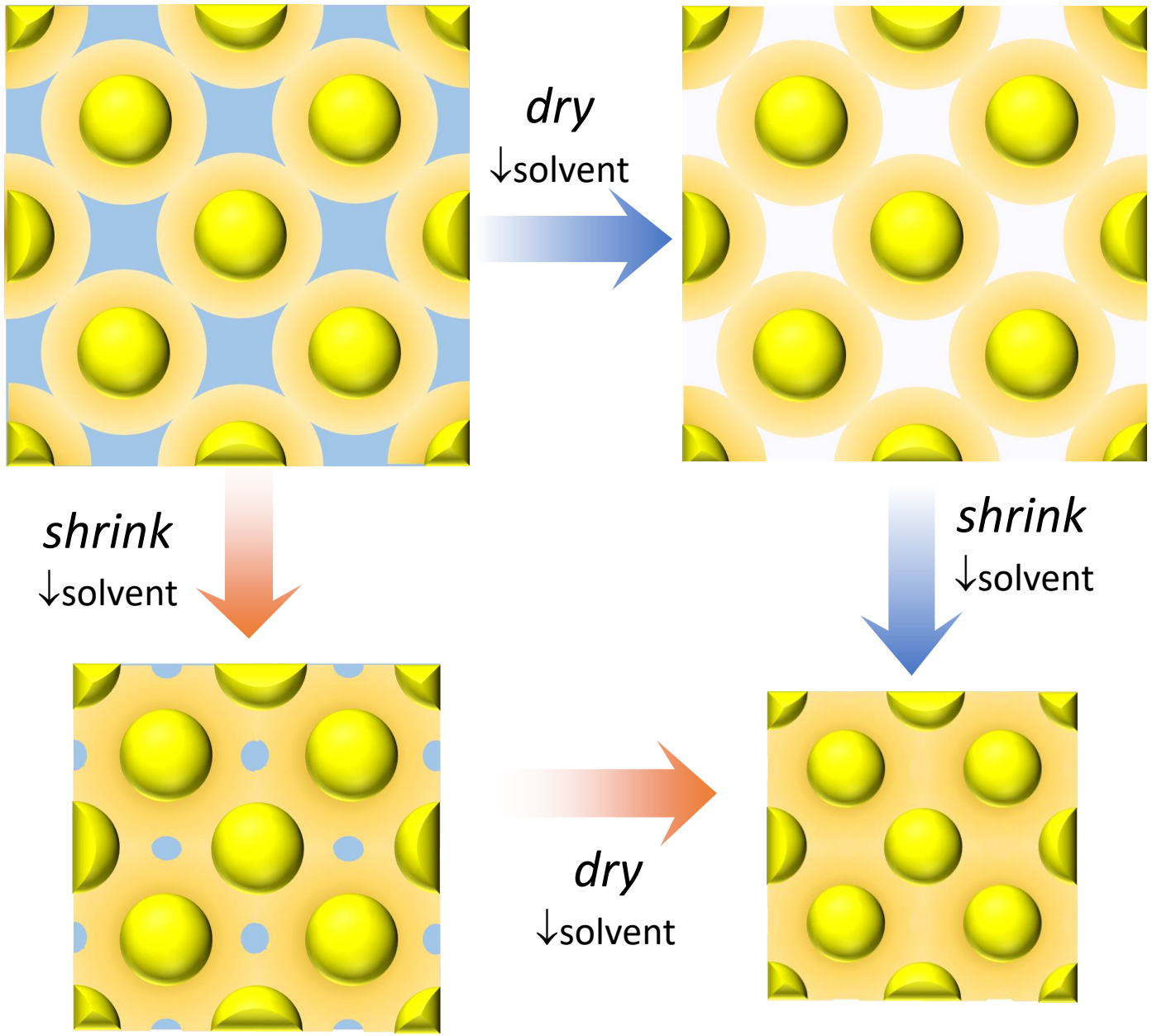
(1)

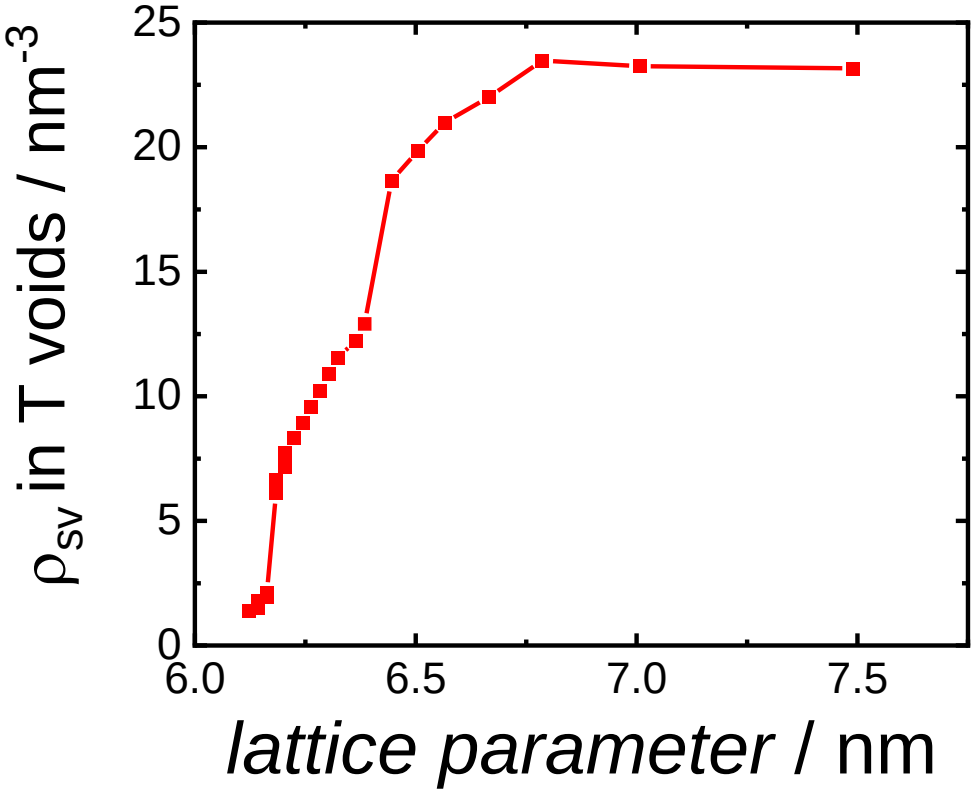
dry
↓solvent





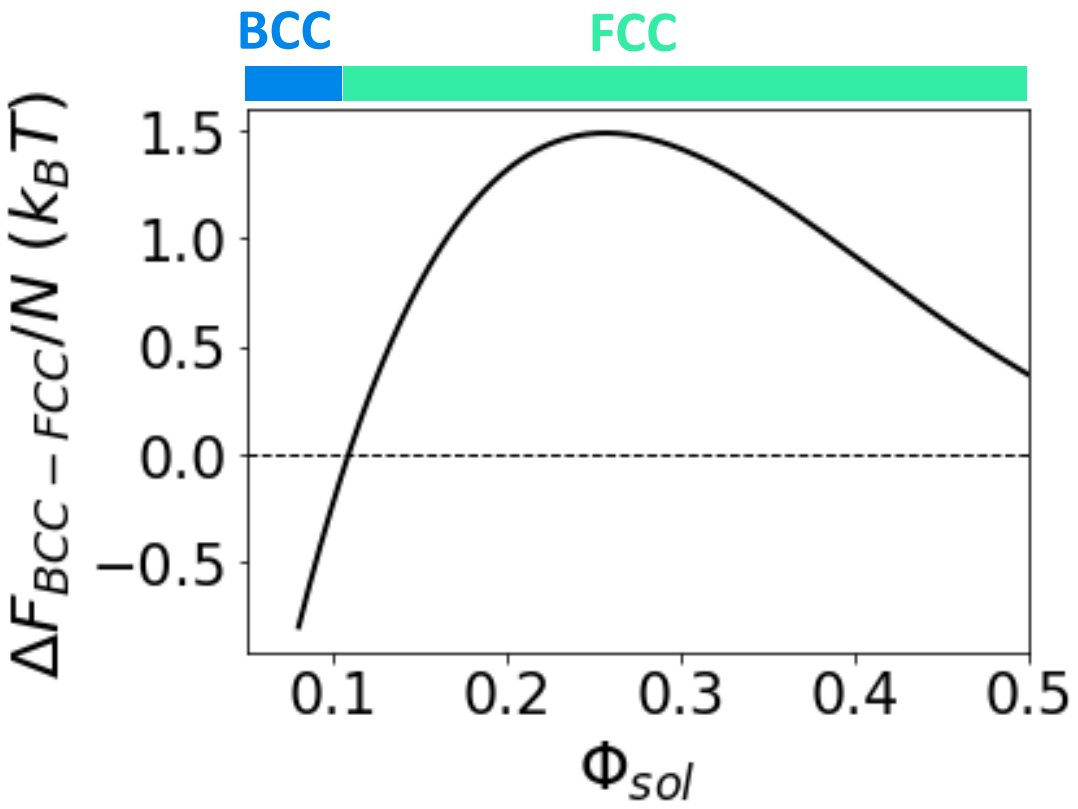

(2)
dry
↓solvent
shrink
↓solvent
ρ_{sv} in T voids / nm^{-3}
25
20
15
10
5
0
6.0
6.5
7.0
7.5
wet SL
dry SL
(2)
lattice parameter / nm



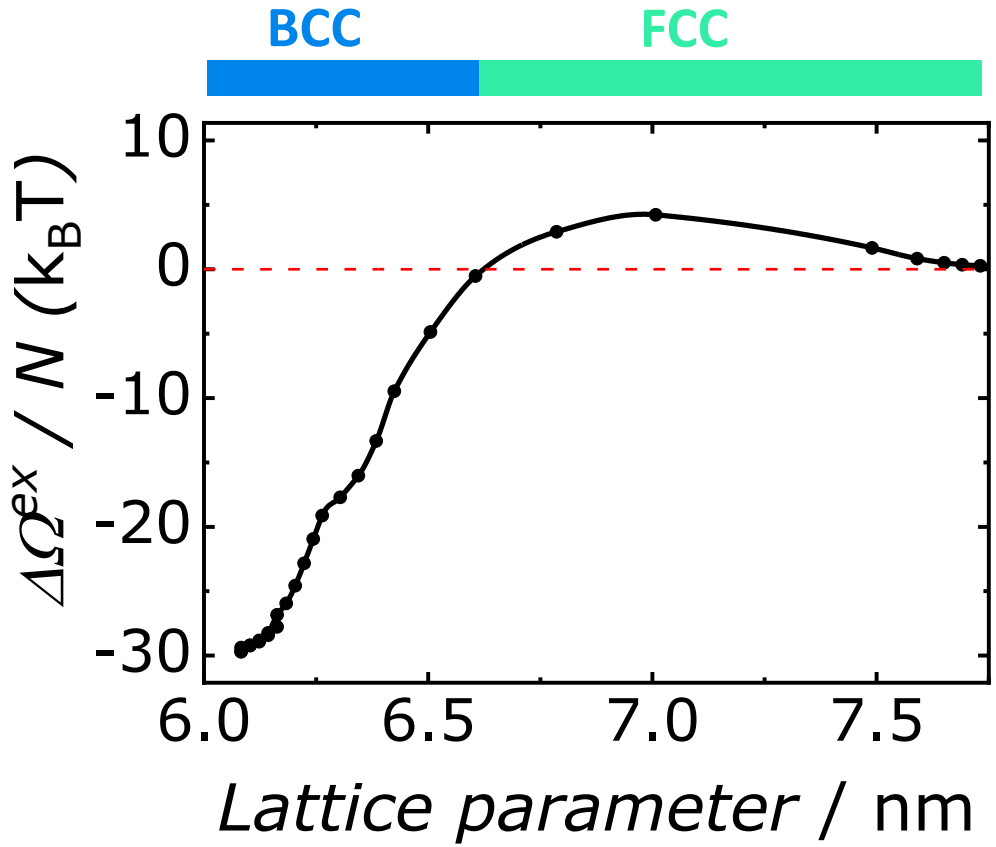


Follows approximately first pathway, first shrink, then dry

We still get the BCC – FCC transition



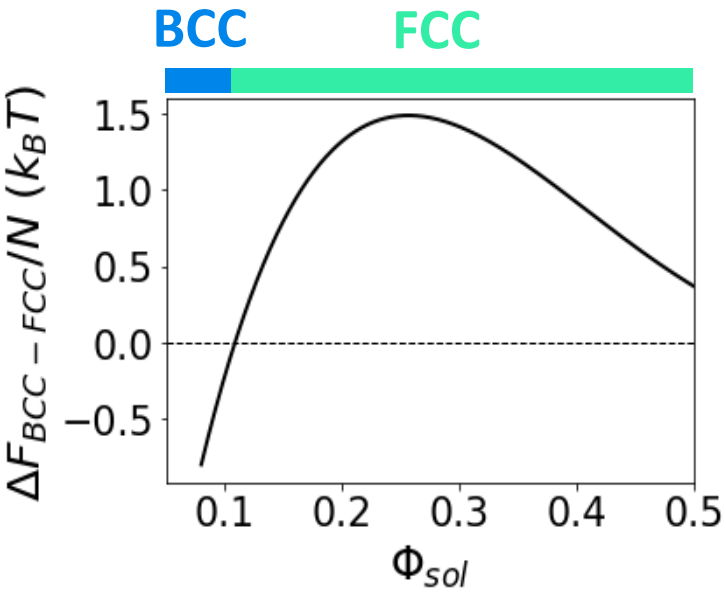
Molecular Theory for NPSLs (no free space)

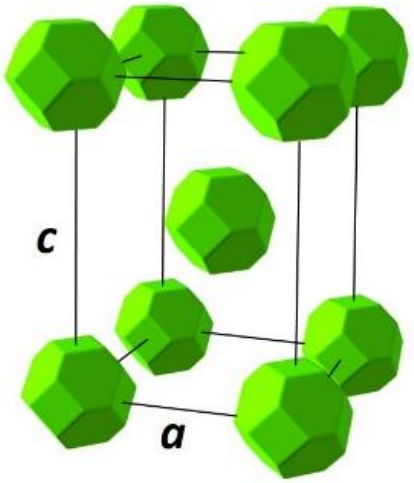


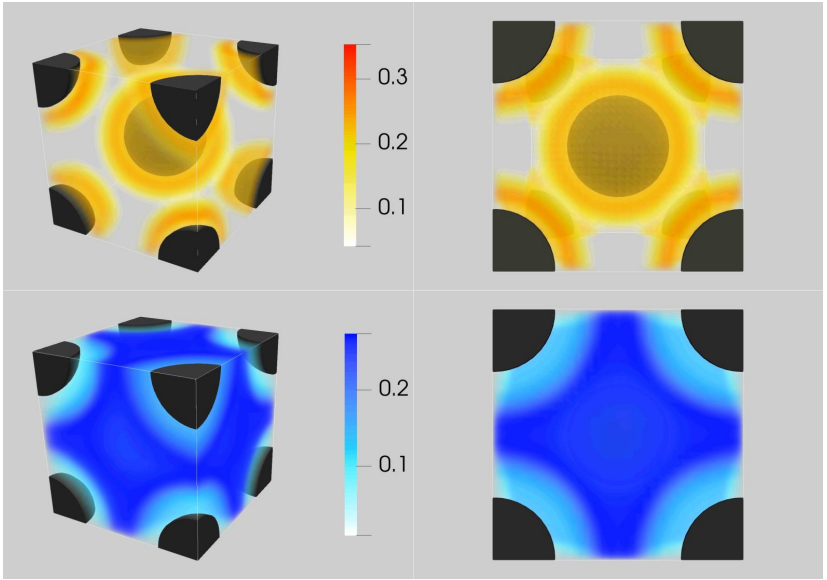
Molecular Theory for NPSLs v2 (models solvent evaporation)

Conclusions

- The MOLT captures the solvent-induced FCC-BCC transition observed in experiments.
- The theory explains the formation of BCT phases from the symmetry breaking of NP-NP interactions in non-spherical NPs.
- Current efforts aimed to understand pathways of solvent evaporation in the formation of NPSLs







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http://softmaterials.qi.fcen.uba.ar/

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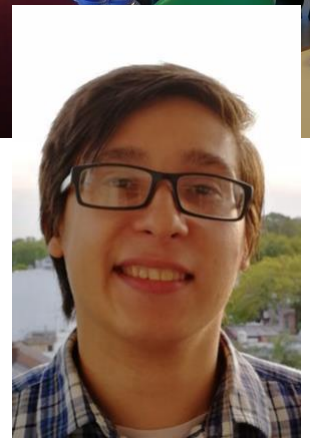

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