Kinetics and Anisotropy in Nanoparticle Assembly (from the perspective of a simulator)

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CRC 1411
DESIGN OF PARTICULATE PRODUCTS

Materials from nanocrystals or colloids

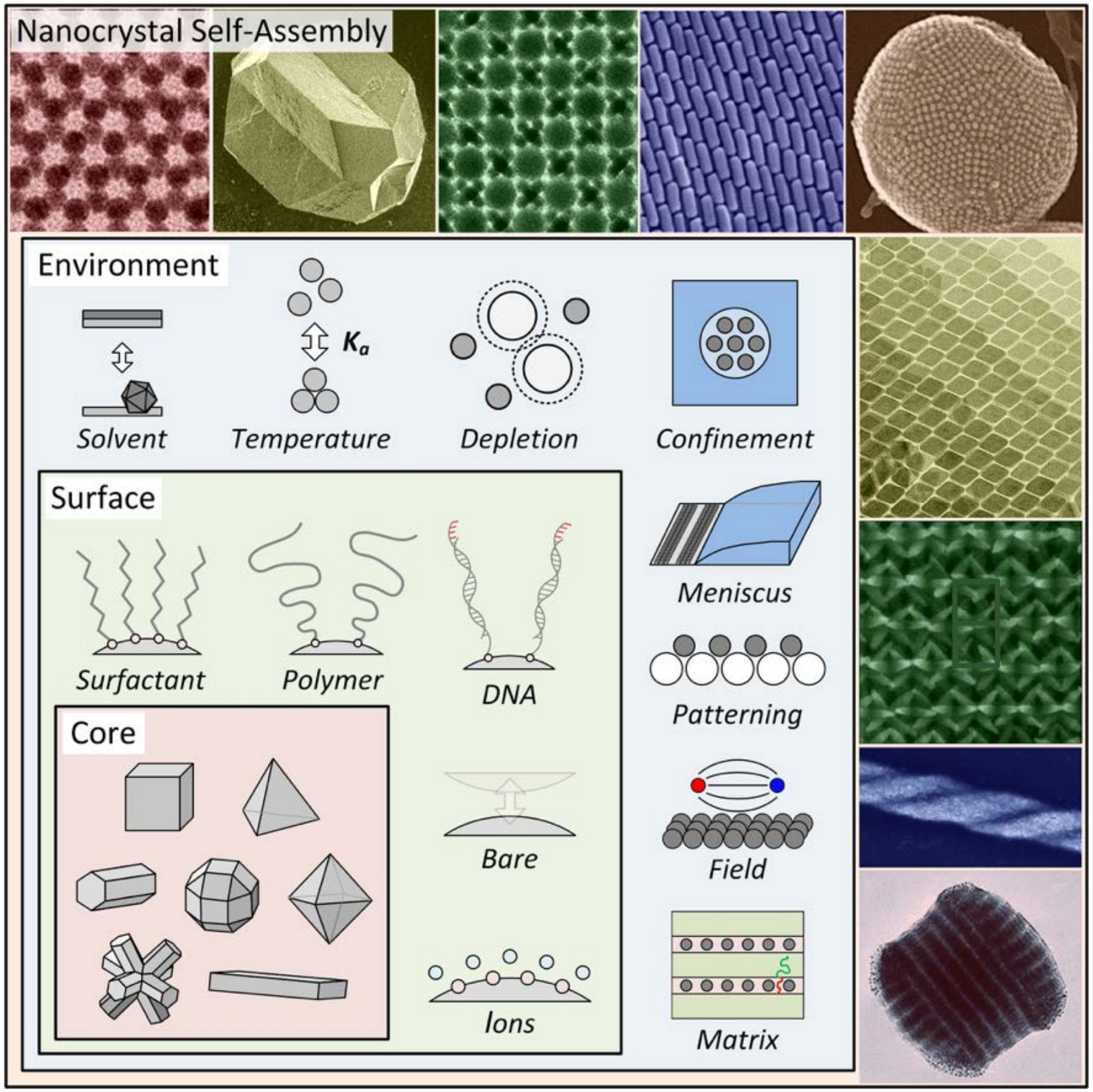
Characteristic length scale

10 µm - 10 mm
assembly
the final product

100 nm - 10 µm
environment
controls the process

1-10 nm
surface
often dominates interaction

5-100 nm
core
the actual particle



Characteristic time scale

minutes - hours - days

milliseconds - seconds

nanoseconds

> microsecond

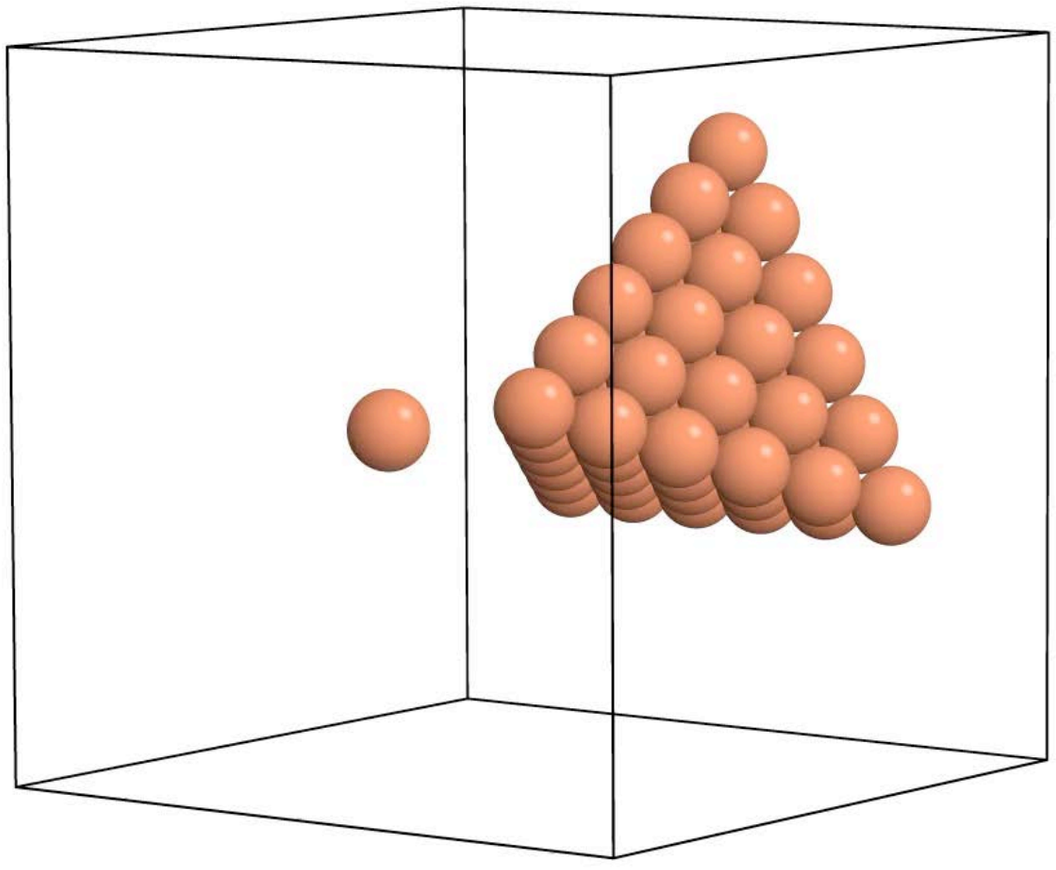
Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials
M. Boles, ME, D. Talapin, *Chem. Rev.* **2016**, 116, 11220-11289

Outline

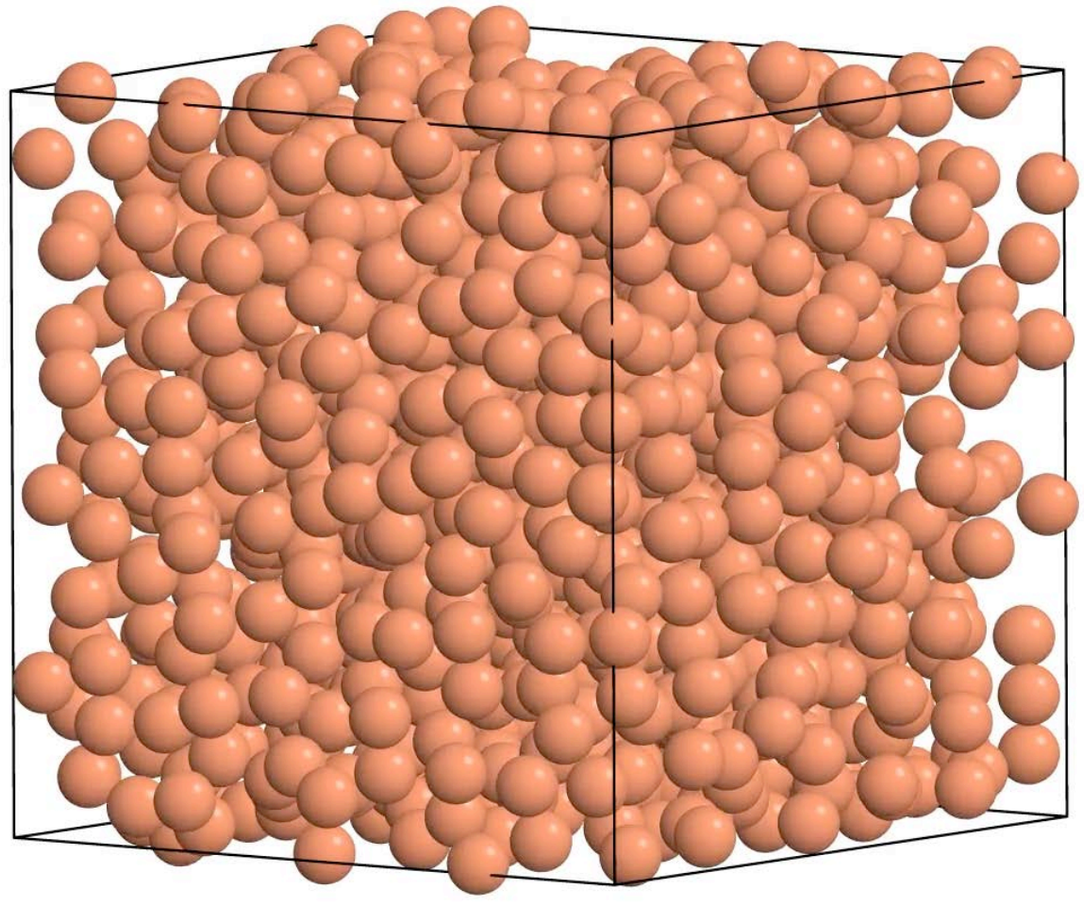
- **Self-assembly of complex crystals on the computer**
- Relationship between structure and formation pathways
- Finite magic number clusters
- Role of polydispersity
- Modeling anisotropic patchy interactions
- Simulating crystal growth (incomplete)

3d billiard in simulation

event-driven molecular dynamics
57 balls (spheres)



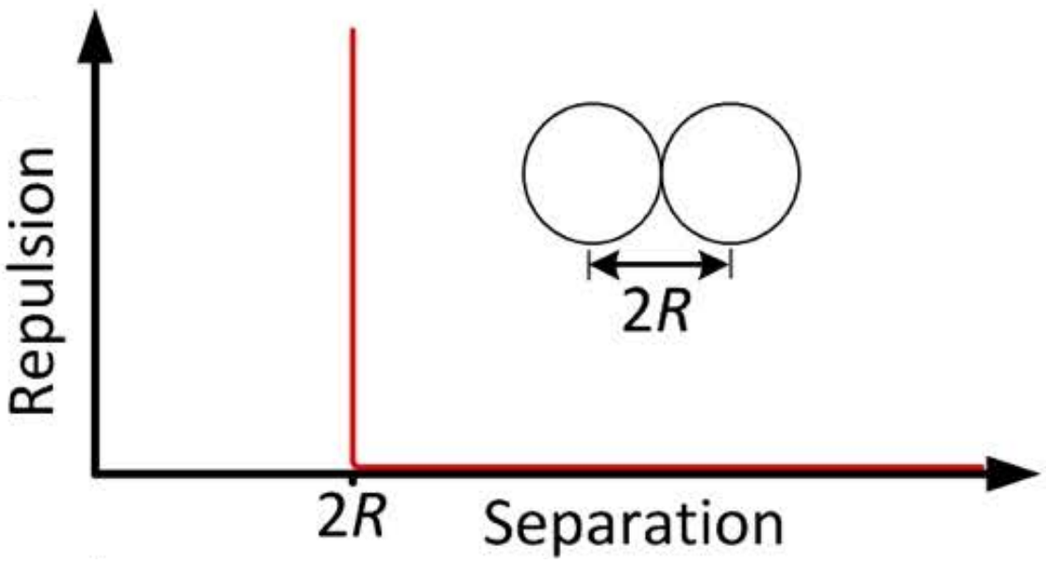
1000 spheres
volume fraction ϕ = 30%



Volume fraction: $\phi = NV_0/V$

particle number — particle volume — system volume

Crystallization in the hard sphere model system

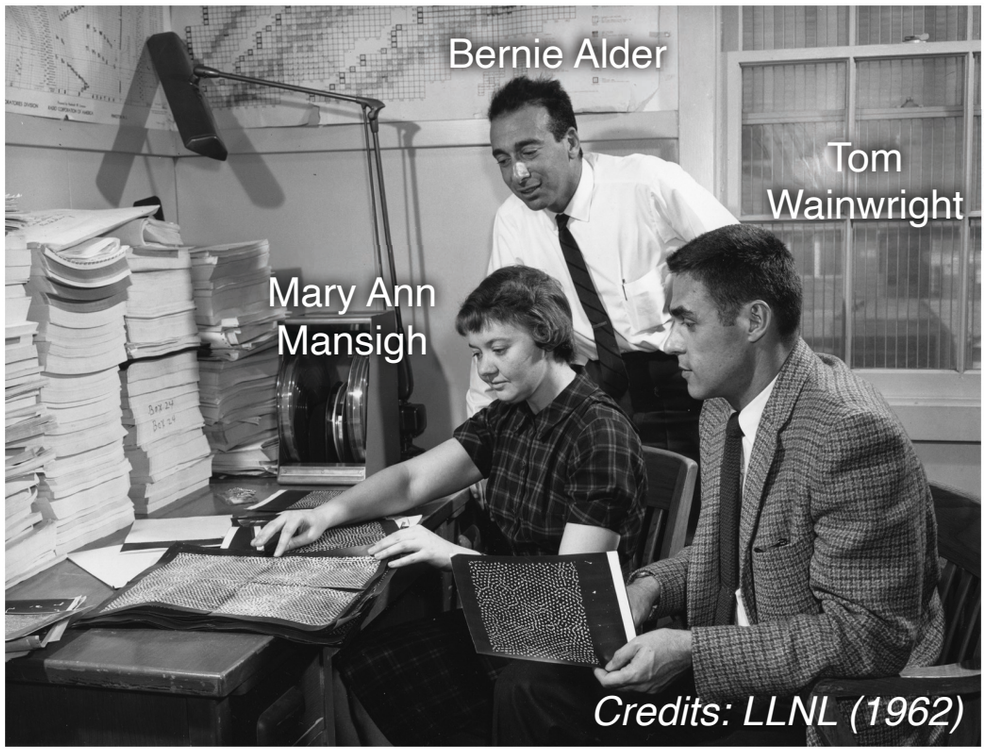


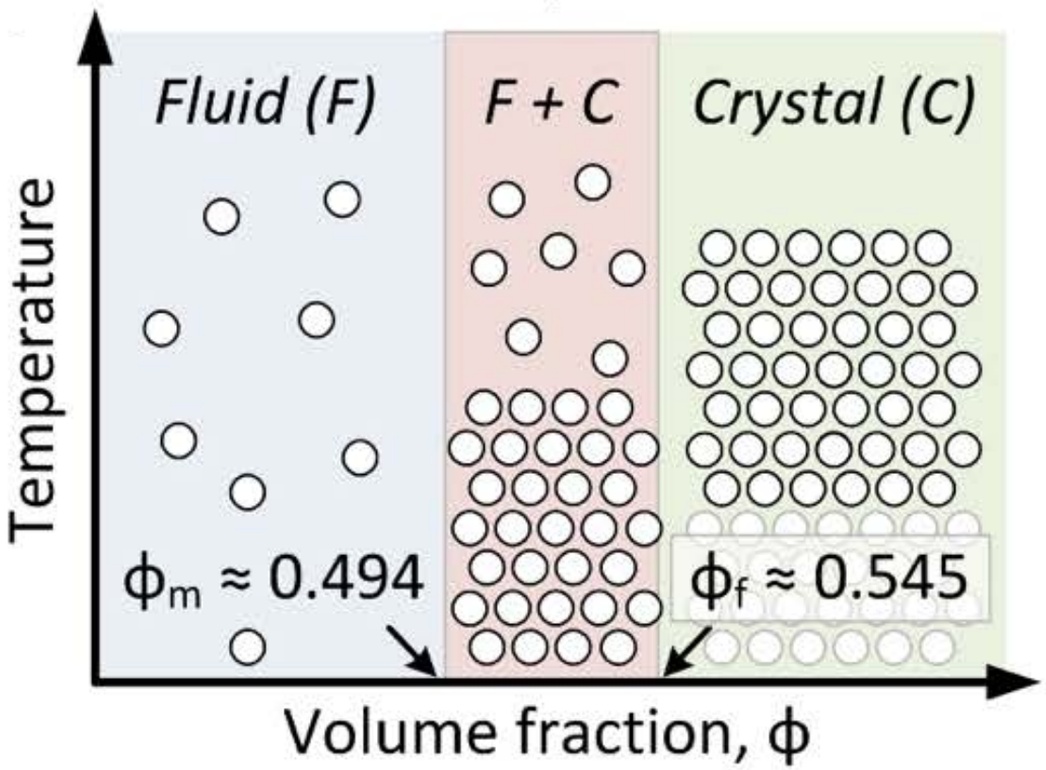
Theoretical prediction:

- Kirkwood, J. Chem. Phys. 1939

Computer simulation:

- Alder, Wainwright, J. Chem. Phys. 1957
  - *UNIVAC, 32 particles, 300 collisions/hour*
- Wood, Jacobson, J. Chem. Phys. 1957

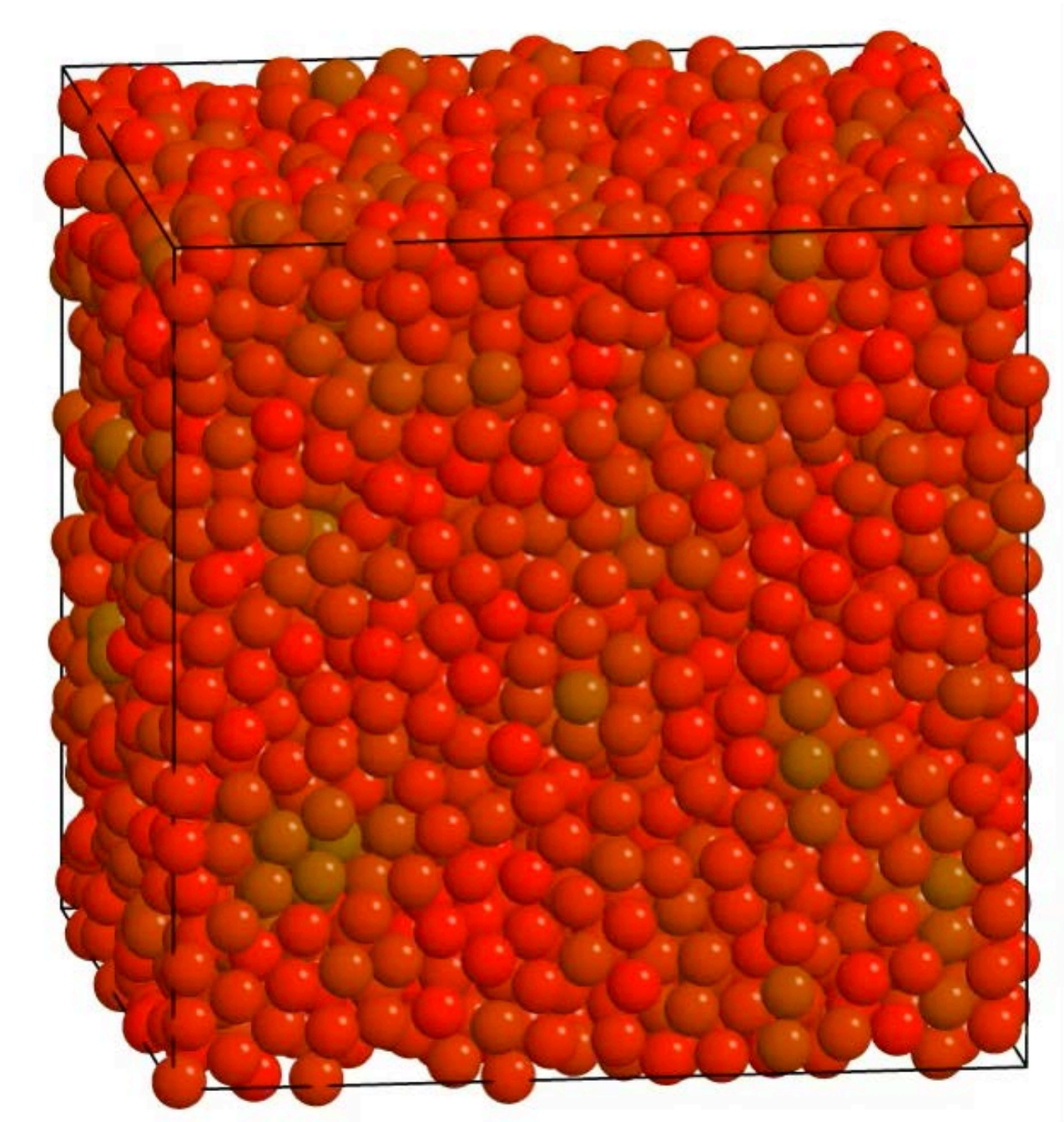




Phase diagram

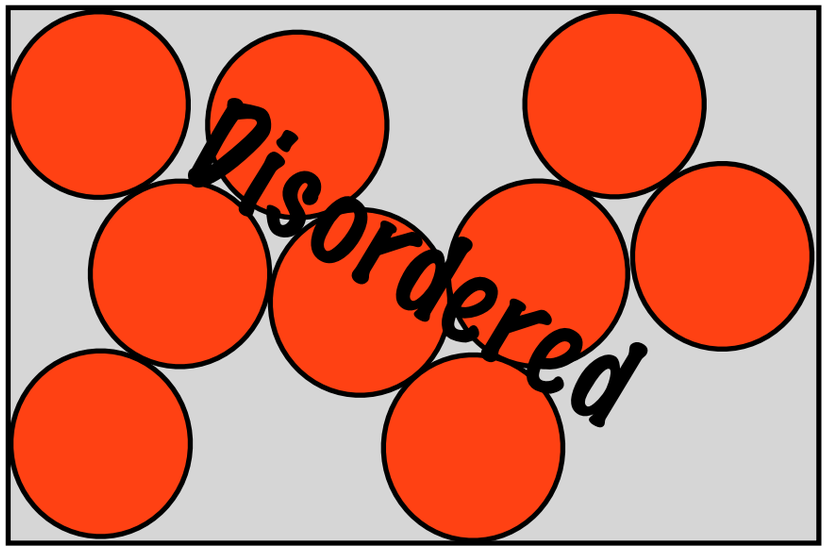
- fluid phase at low density, $\phi < 0.494$
- solid phase at high density, $\phi > 0.545$

Self-assembly simulation of the hard sphere system

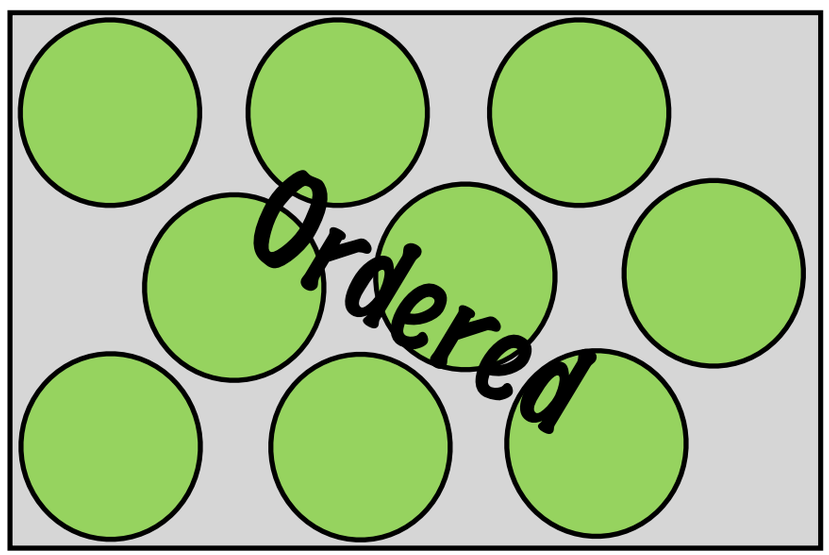


Hard sphere phase transition (1957)

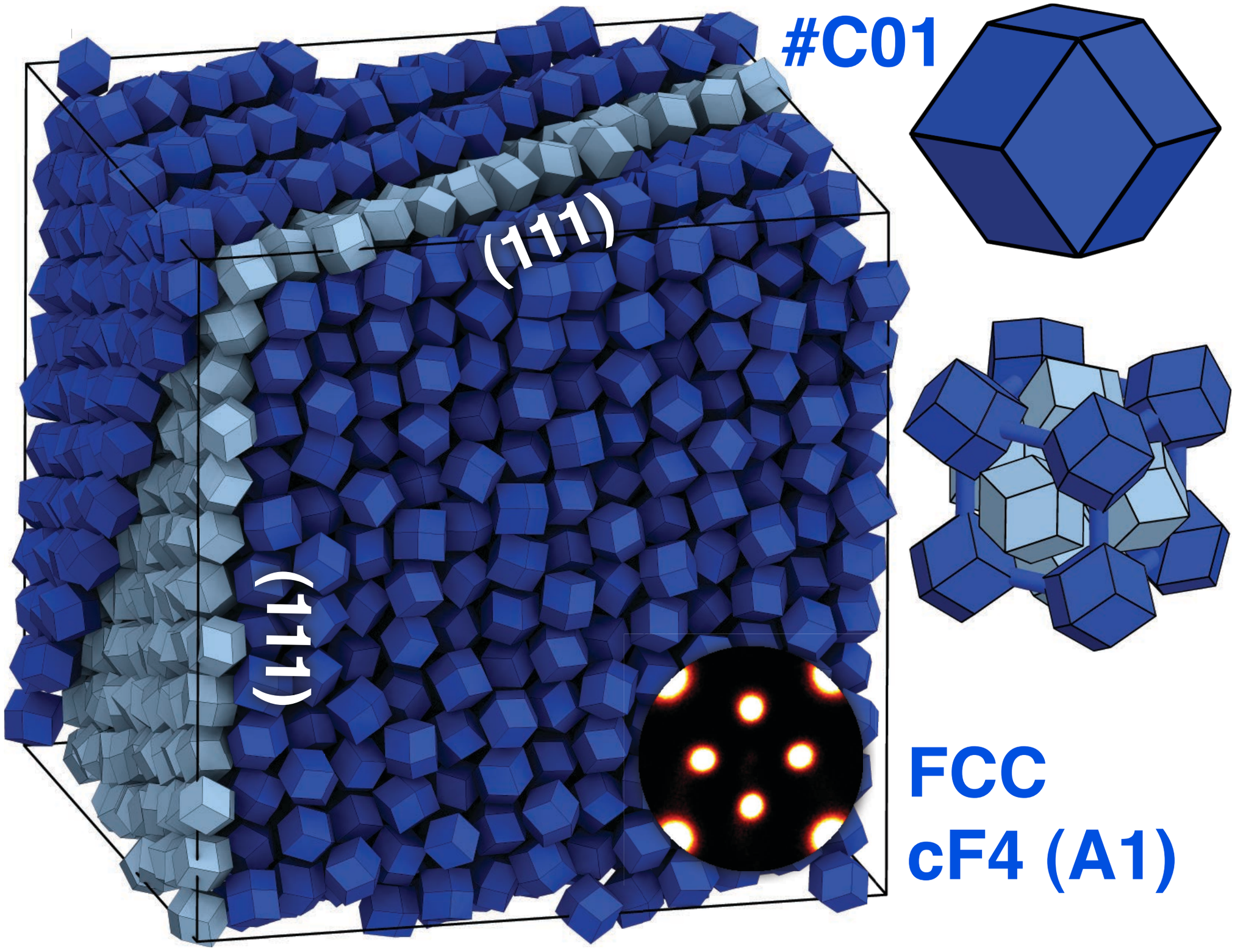
Local bond orientational order parameter:



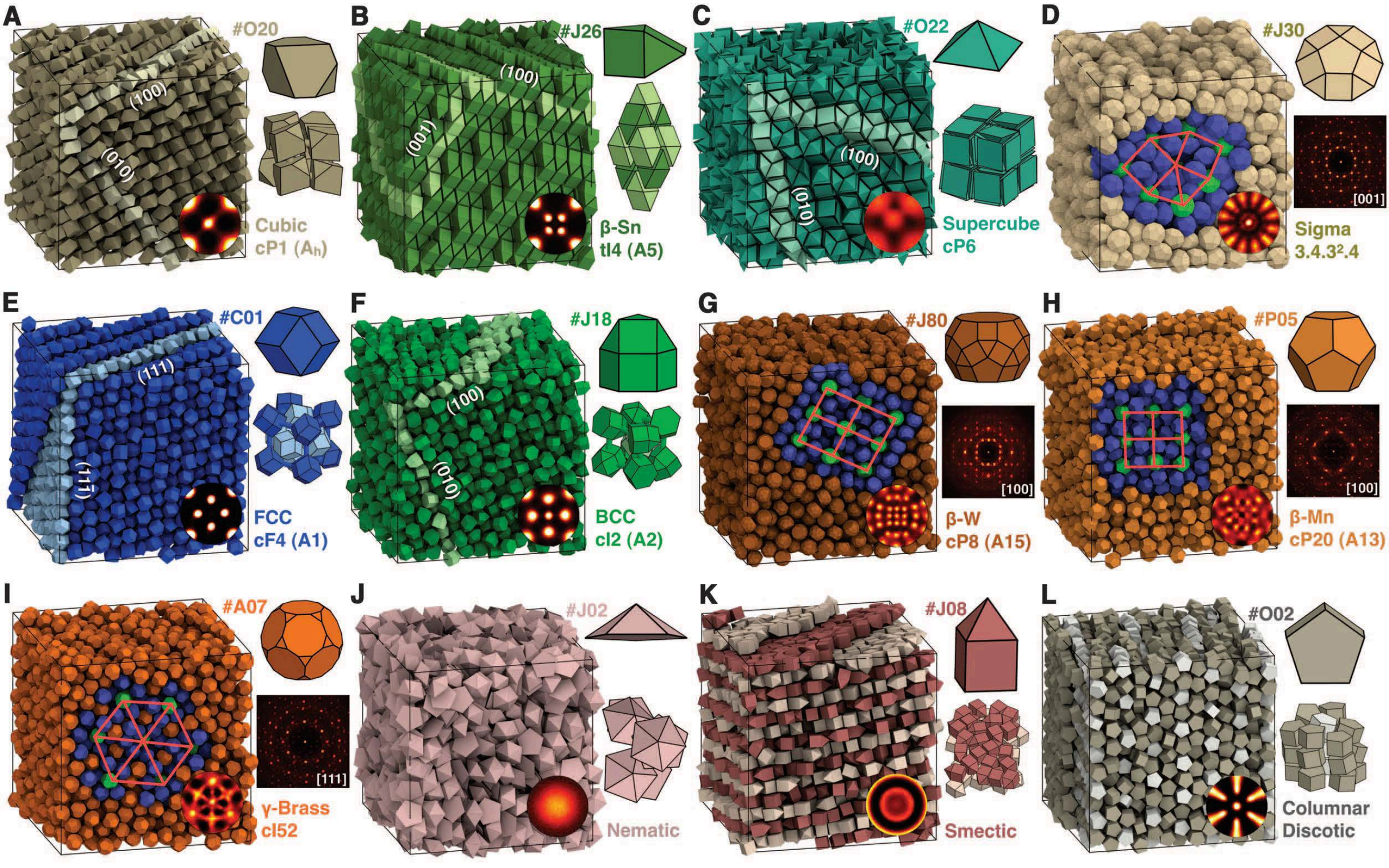
versus



Rhombic dodecahedra (FCC plastic crystal)



Self-assembly of polyhedra ("Polyhedron Zoo")

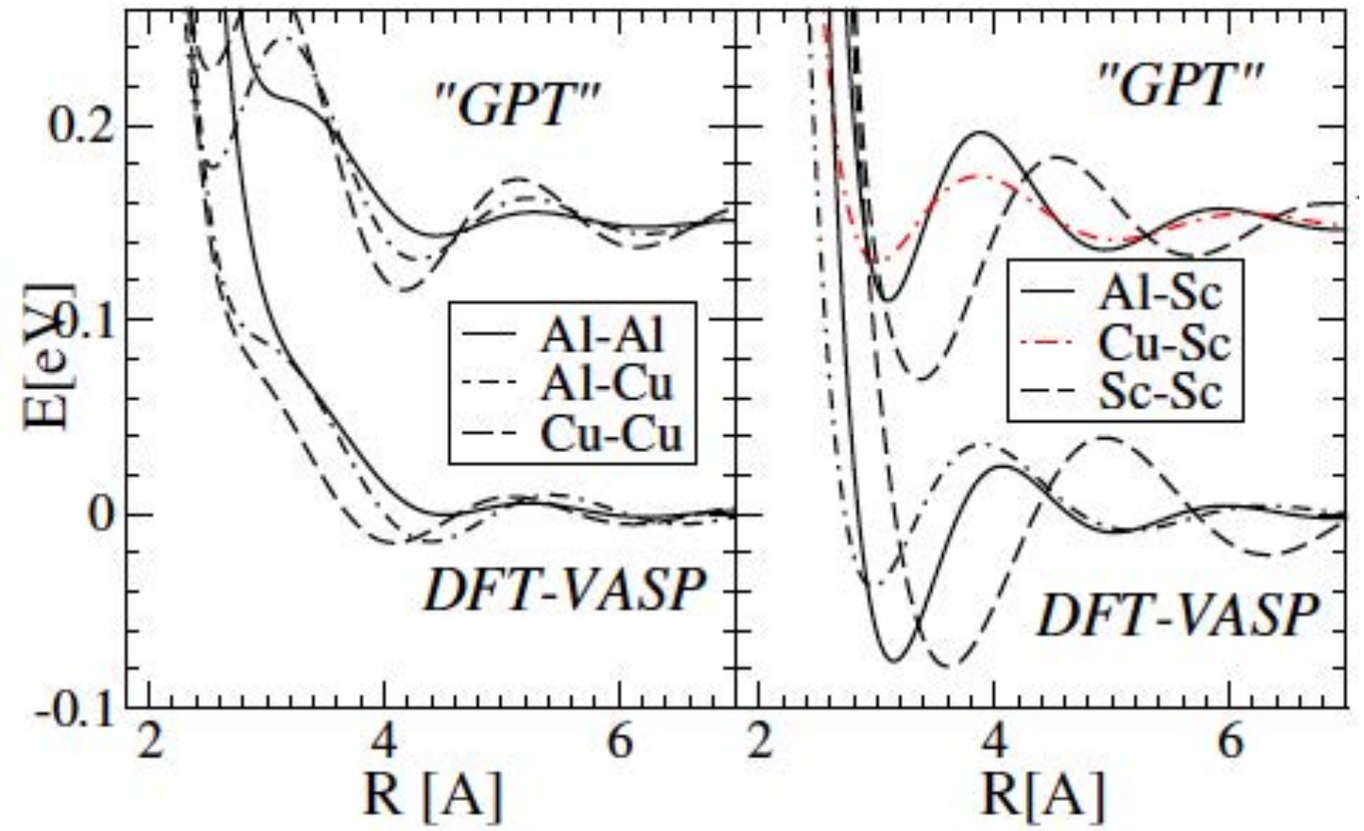


P.F. Damasceno, ME, S.C. Glotzer, *Science* **2012**, 337, 453

Oscillatory pair potential

Fitting to VASP (ab-initio QM)

- effective pseudo-potentials for intermetallics
- Mihalkovic, Henley, PRB 85, 09210 (2012)



Characteristics:

1. short-range repulsion
2. medium-range Friedel oscillations

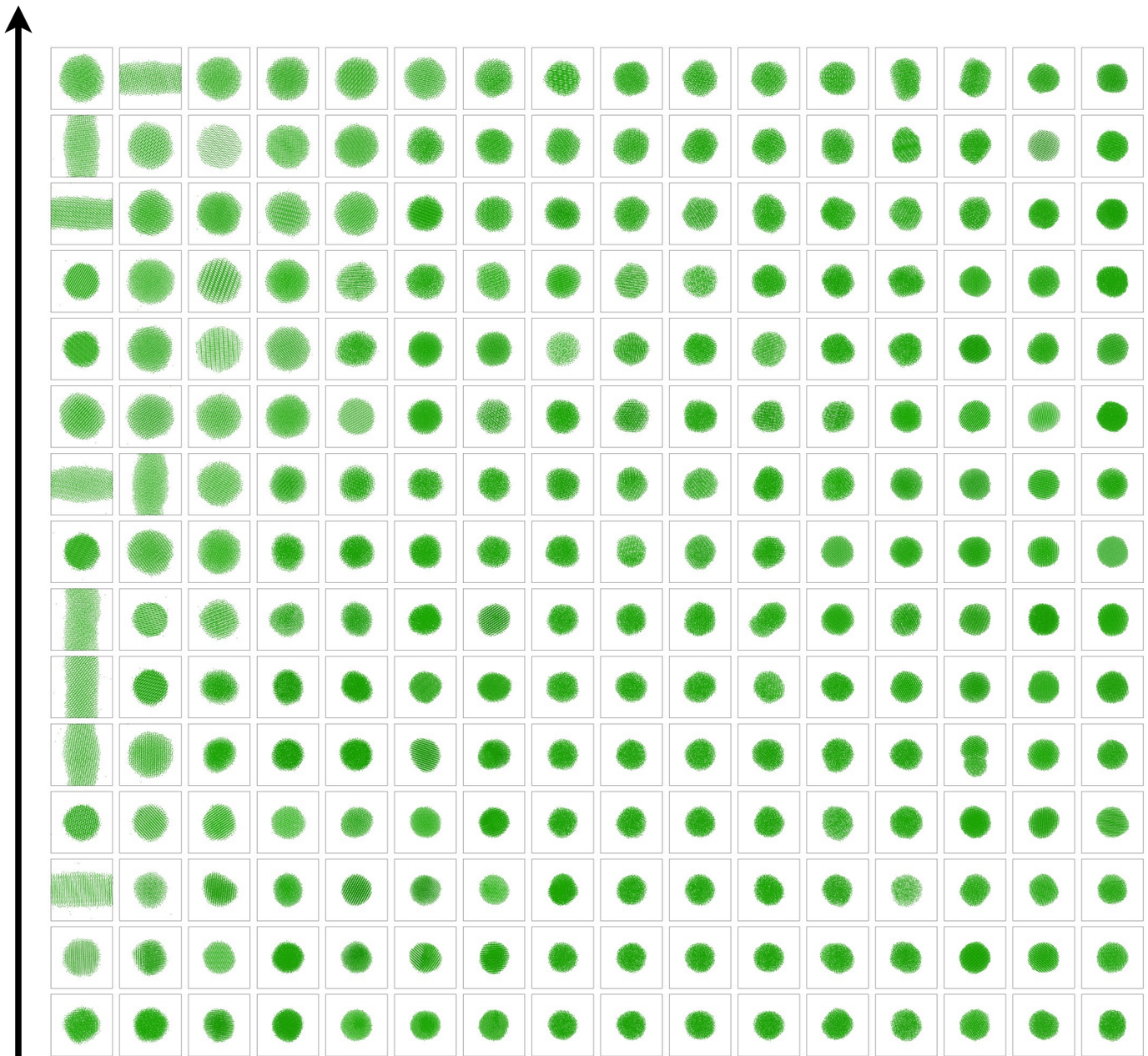
A *good guess* is the Mihalkovic-Henley oscillating pair potential (OPP):

$$V(r) = \frac{C_1}{r^{\eta_1}} + \frac{C_2}{r^{\eta_2}} \cos(kr + \phi)$$

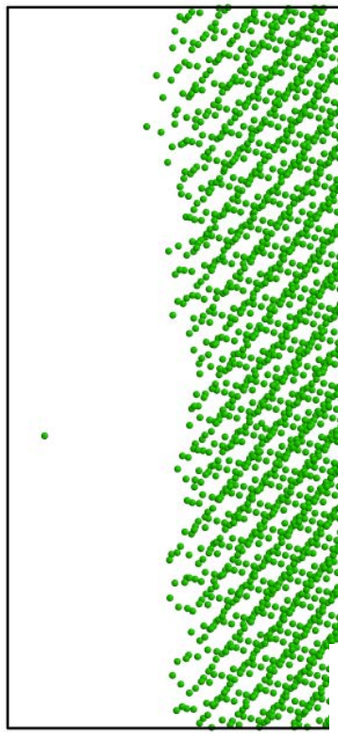
High-throughput simulations

Numerical brute-force phase diagram determination

Parameter 1



Parameter 2

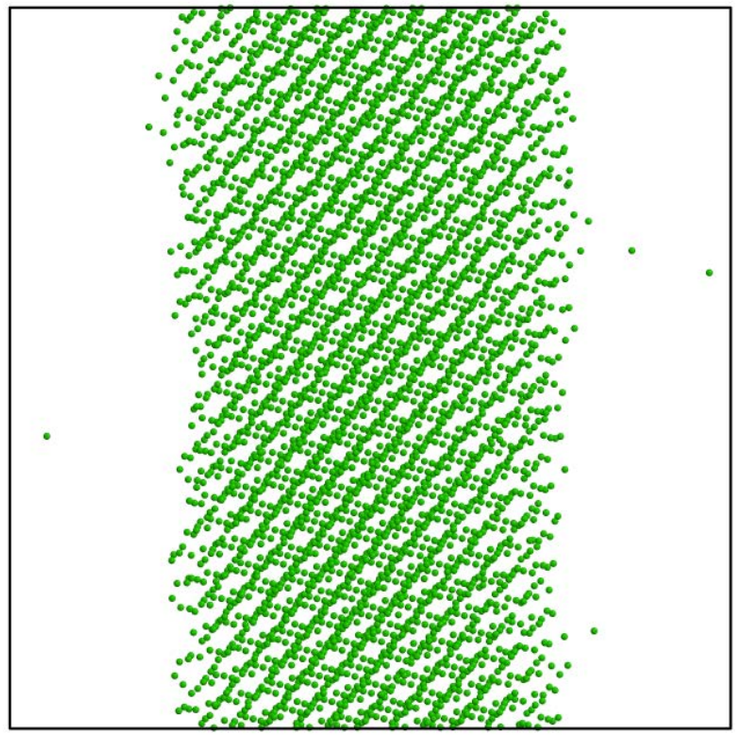


columnar growth

crystal intergrowth

Machine learning approach

Start with test configuration



1) Select order parameter

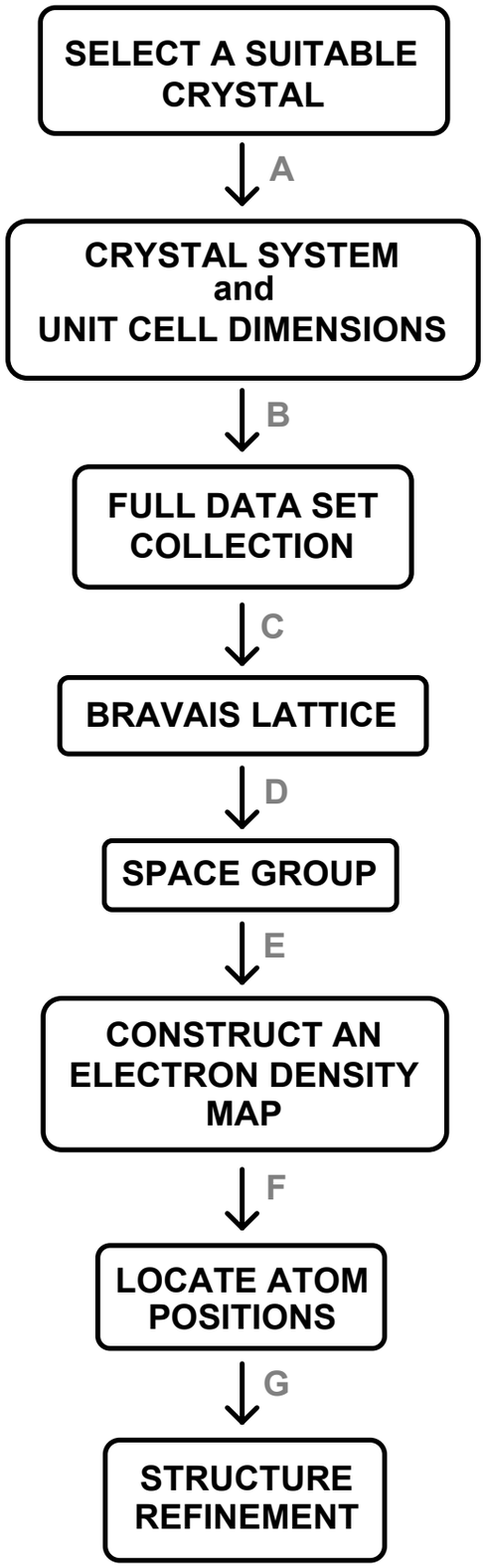
2) Generate list of reference configurations

3) Measure order parameter
   - possibly train neural network
   - include defects? interfaces?

4) Compare test configuration

But:
- Is the list of reference configurations complete?
- What are good order parameters?
- How can we quantify order and symmetry, not just classify?

Structure solution at the atomic scale … in experiment



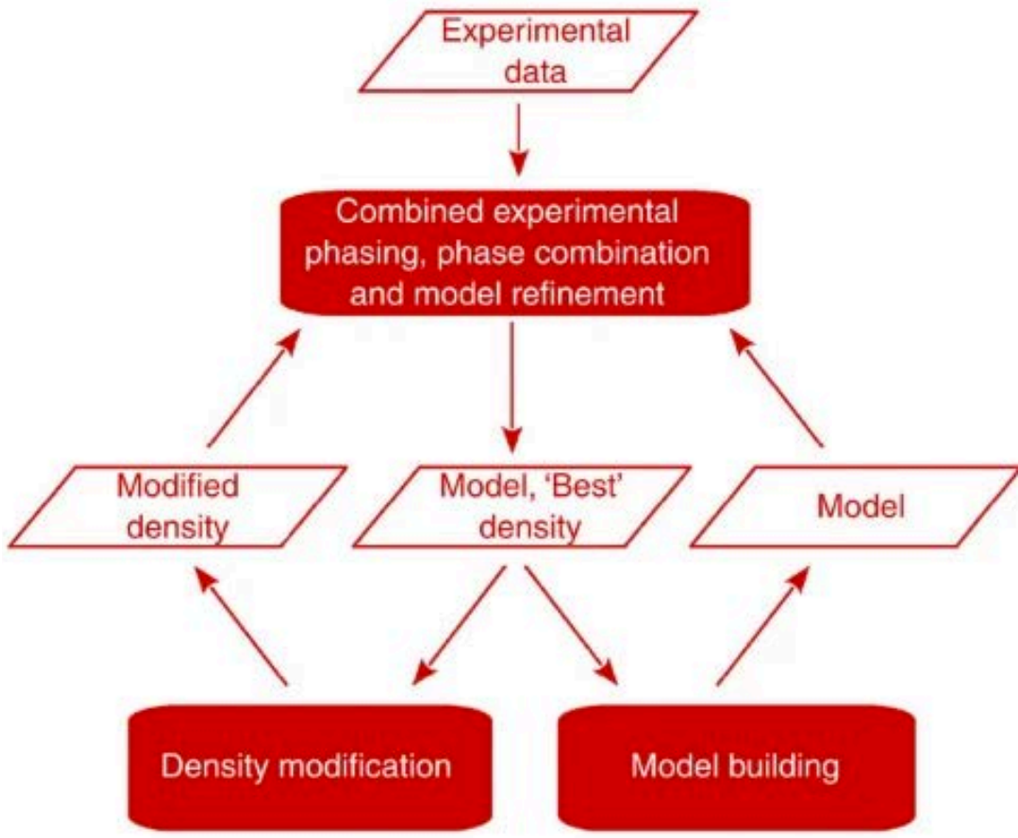
Why not do the same in simulation?

- smaller systems
- less equilibrated

Our advantage:

- we know the positions of all particles
- can avoid detour via reciprocal space
- phase problem is irrelevant

Phase problem



Nature Commun. 4, 2777 (2013)

Is structure solution from simulation data necessary?

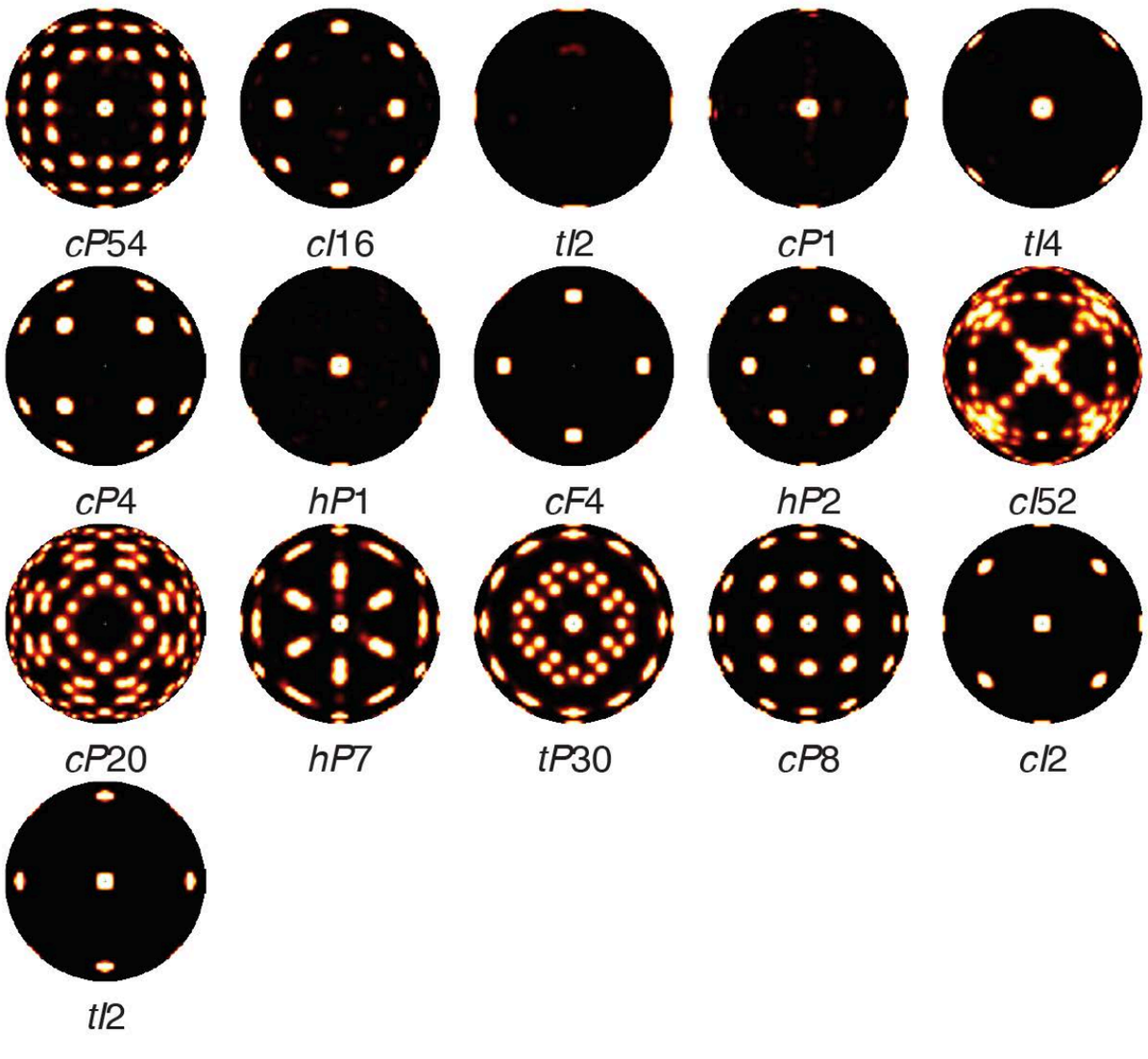
Oscail tutorials on Crystallogtaphy

Bond-orientational order diagrams as “fingerprints”

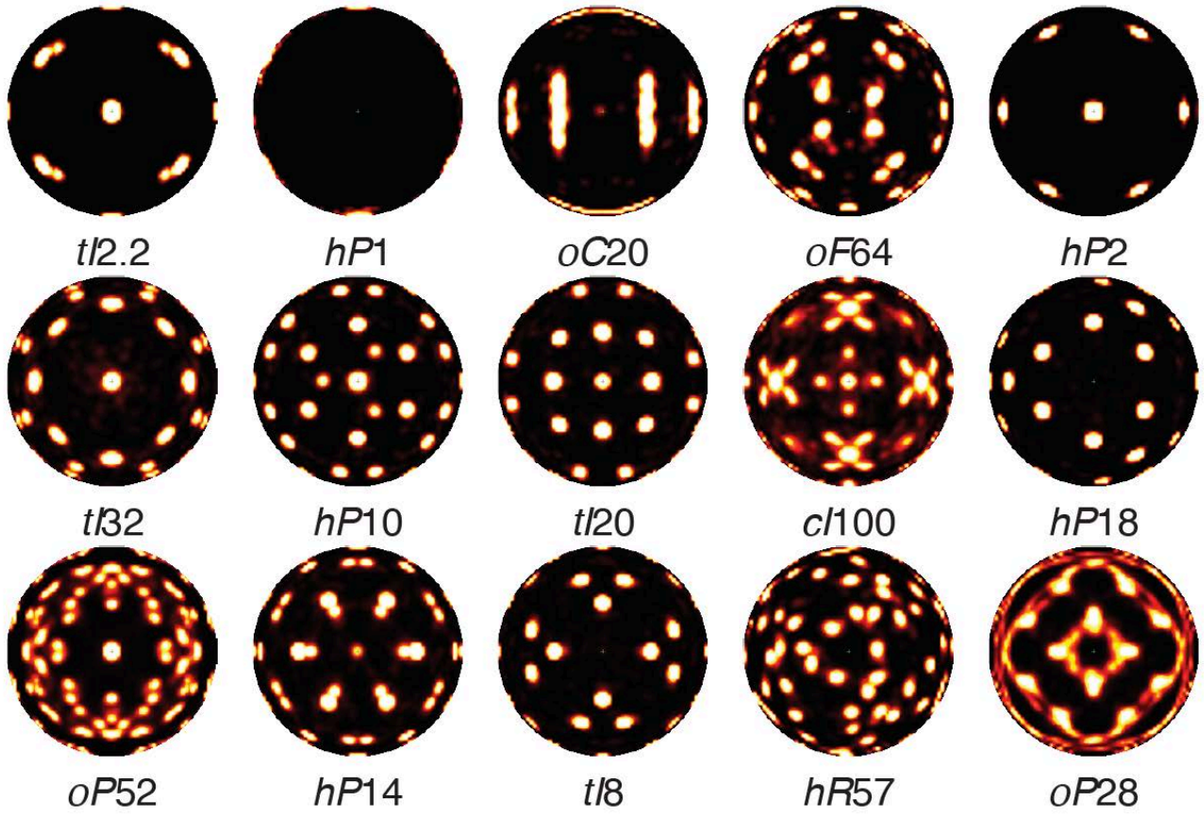
Crystallography on simulation data

- M. Engel, “Point Group Analysis in Particle Simulation Data” https://arxiv.org/abs/2106.14846
- Web applet for particle simulation data
  early glimpse: https://dev.engellab.de/PGquant.html

16 known crystal structures



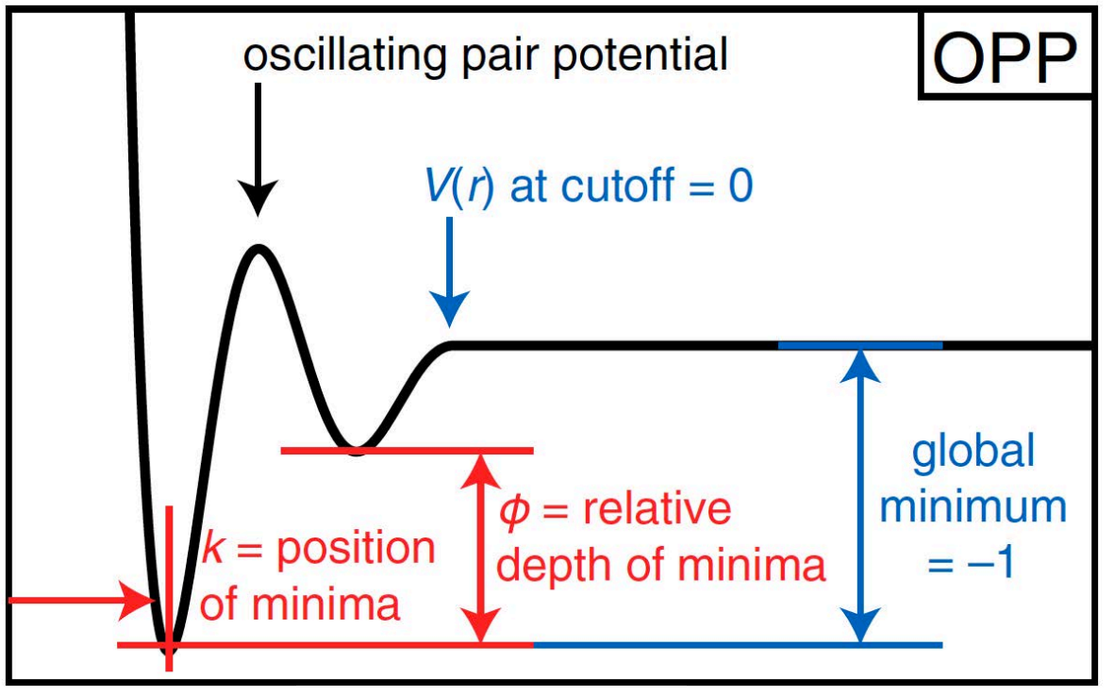
15 “unknown” crystal structures

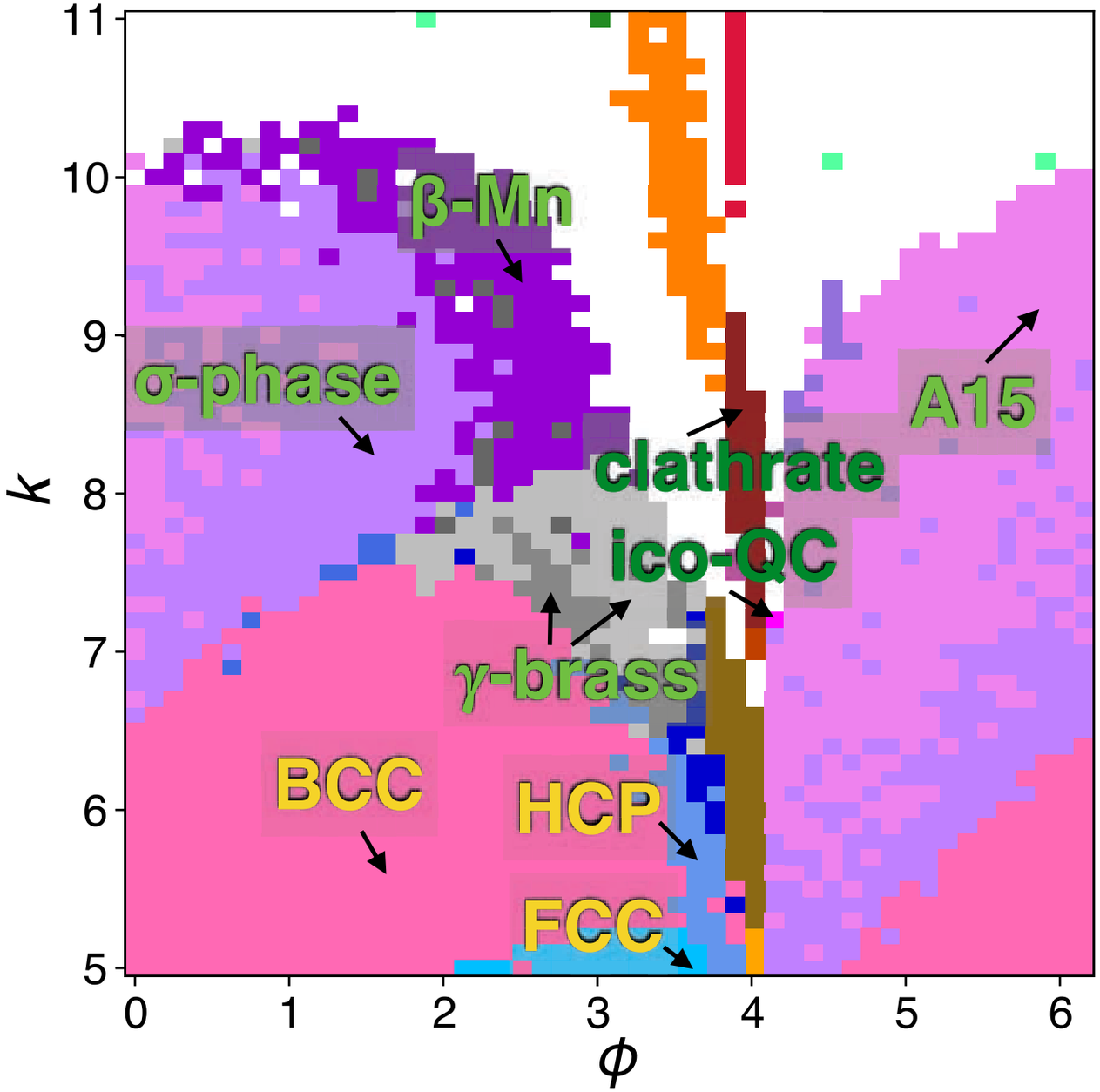


Crystal structure discovery ("Potential Zoo")

Isotropic multiwell pair potential

$$V_{\mathrm{OPP}}(r) = \frac{1}{r^{15}} + \frac{\cos(k(r-1)+\phi)}{r^3}$$





Highlights:

20 000+ simulations

16 known crystal structures

15+ previously unknown crystal structures

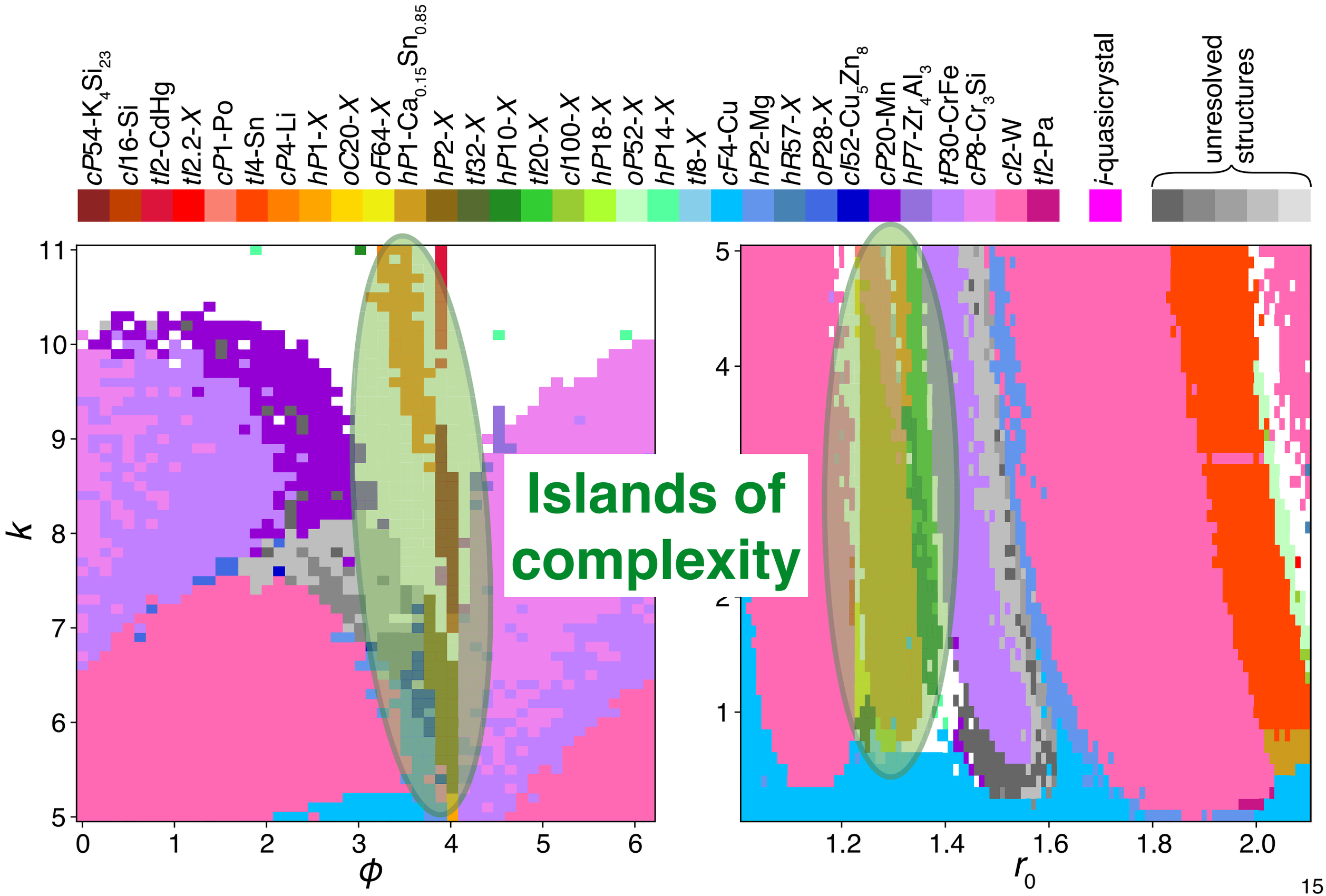
first icosahedral quasicrystal (sim)

most complex crystal structure (sim)

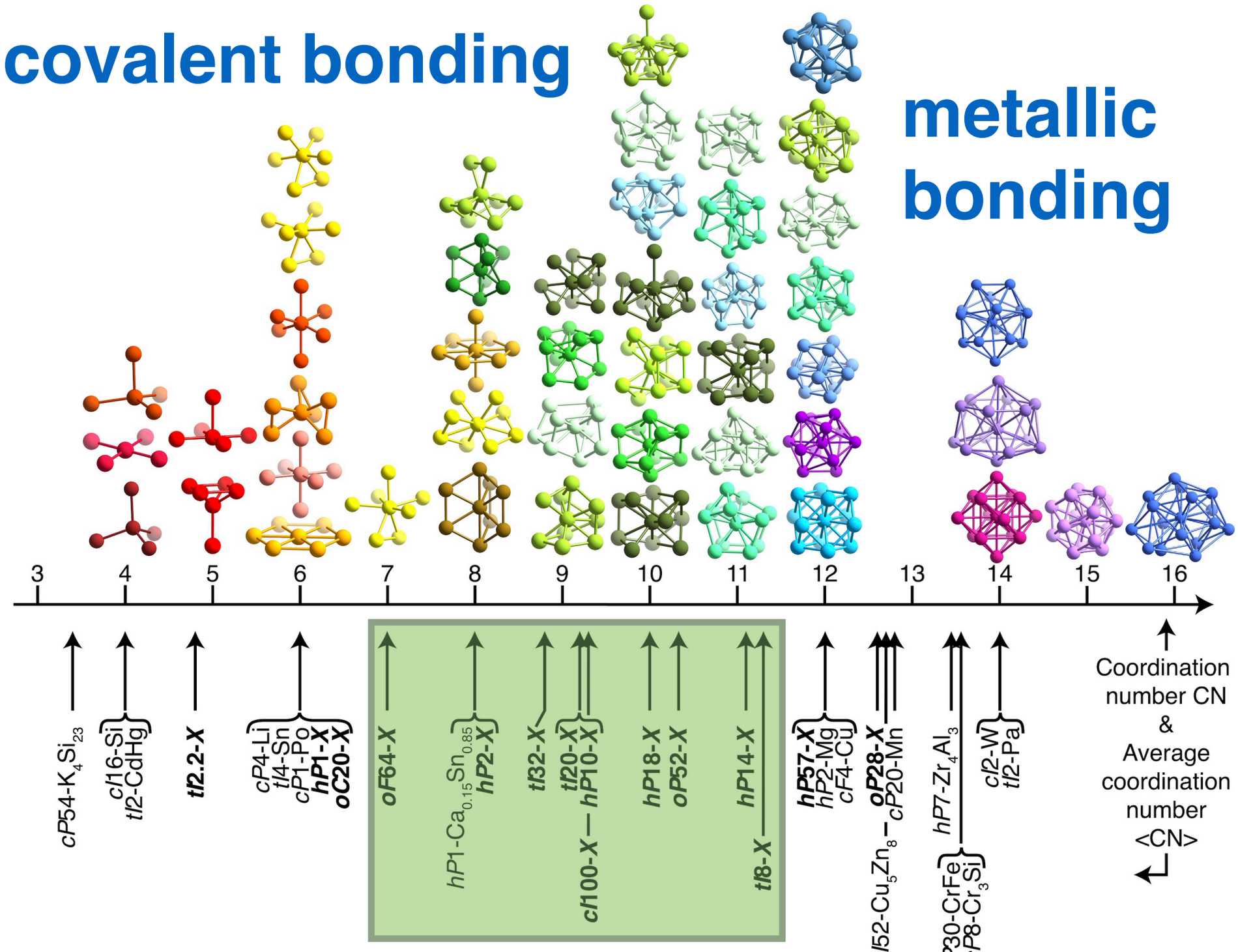
[1] ME, P.F. Damasceno, C.L. Phillips, S.C. Glotzer, *Nature Mater.* **2015**, 14, 109

[2] J. Dshemuchadse, P.F. Damasceno, C.L. Phillips, ME, S.C. Glotzer, *Proc. Natl. Acad. Sci. U. S. A.* **2021**, 118, e2024034118

Phase diagrams (>20000 simulations,)



Overcoming the constraints of chemistry



Constraints of chemistry

Outline

- Self-assembly of complex crystals on the computer
- **Relationship between structure and formation pathways**
- Finite magic number clusters
- Role of polydispersity
- Modeling anisotropic patchy interactions
- Simulating crystal growth (incomplete)

Building block → Structure → Pathway

Building block → Structure ✅

hard spheres (noble metals) form FCC/HCP

soft spheres (micelles, DNA-ligand NPs) form BCC / A15

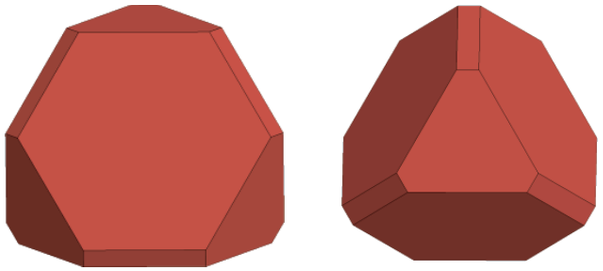
Building block → Pathway ✅ **Structure → Pathway** ❓

icosahedral order (alloys) prefers high-symmetry clusters

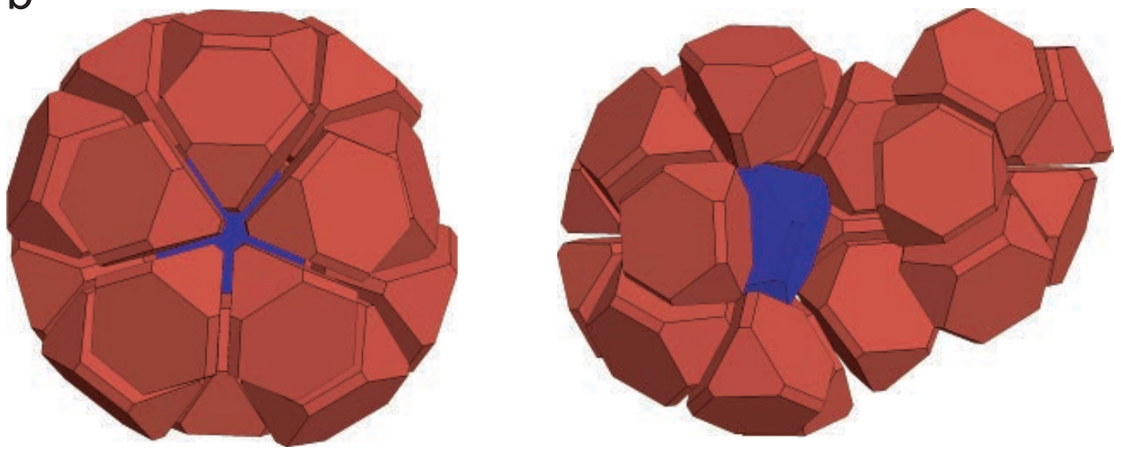
tetrahedral order (water, Si) tends to favor multistep nucleation

Hard polyhedra with good clustering behavior

a

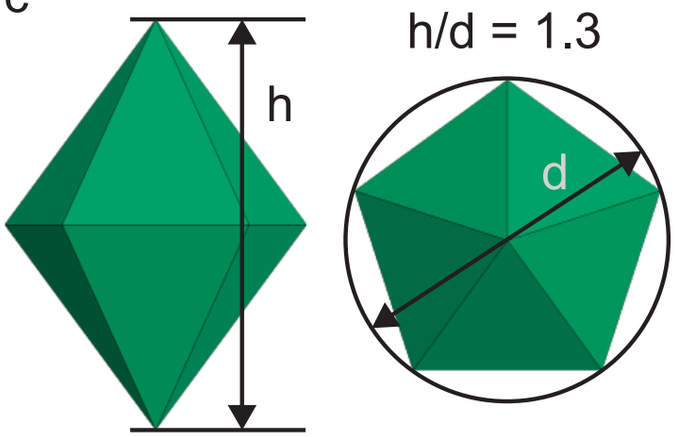


b

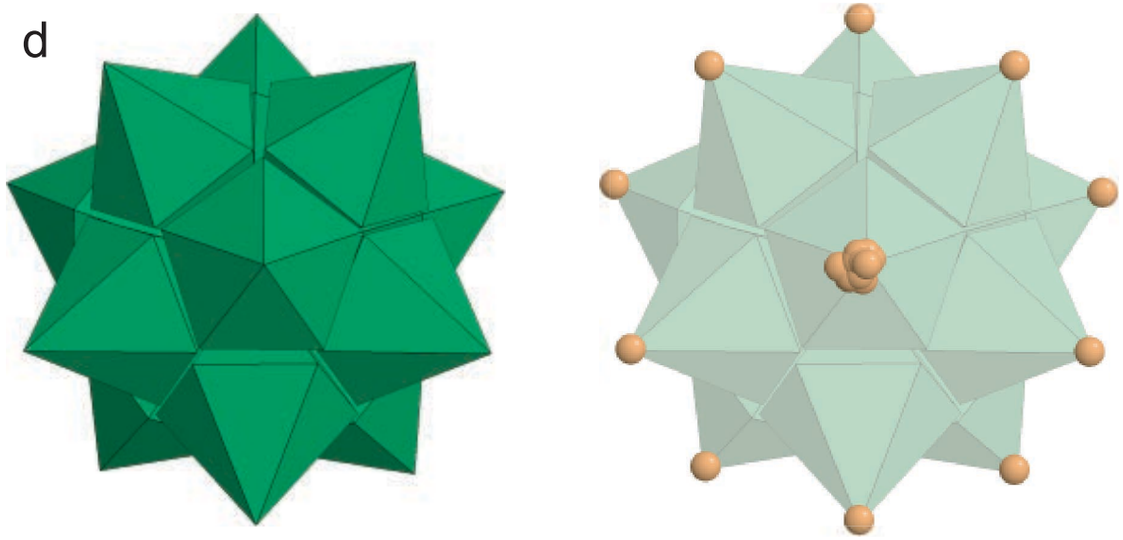


truncated tetrahedron (TT)

c

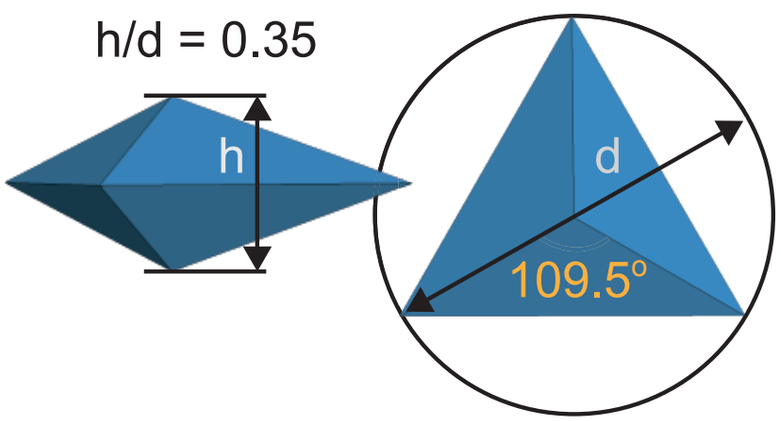


d

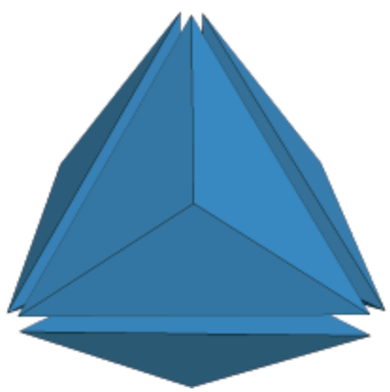


pentagonal bipyramid (PBP)

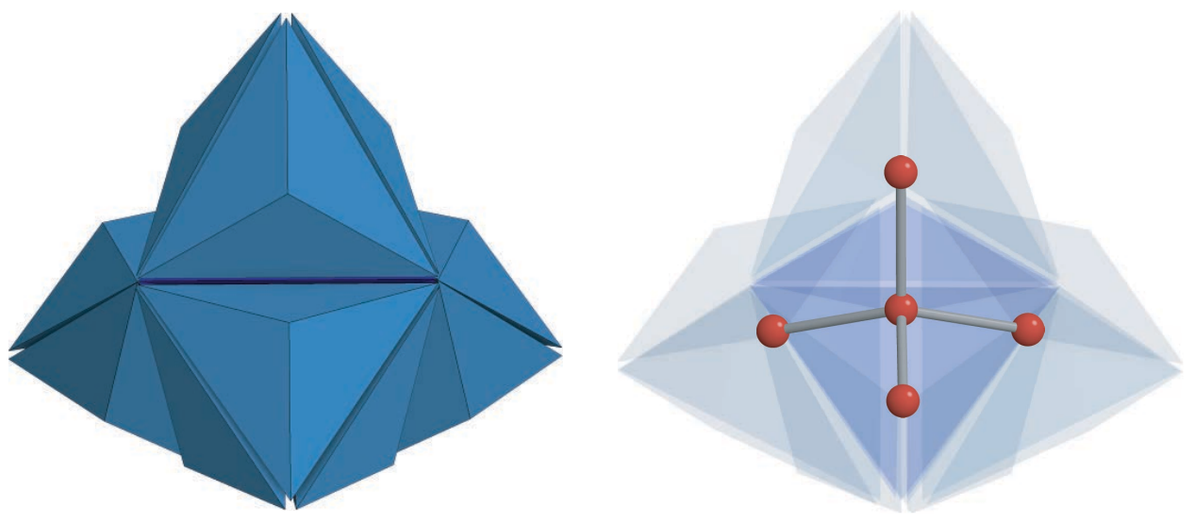
e



f



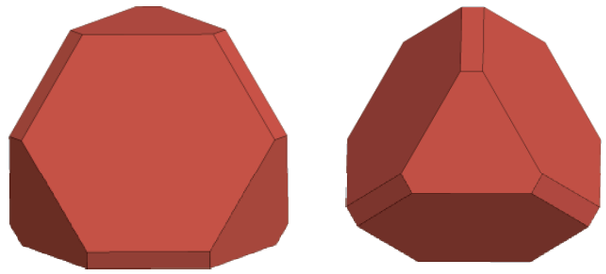
g



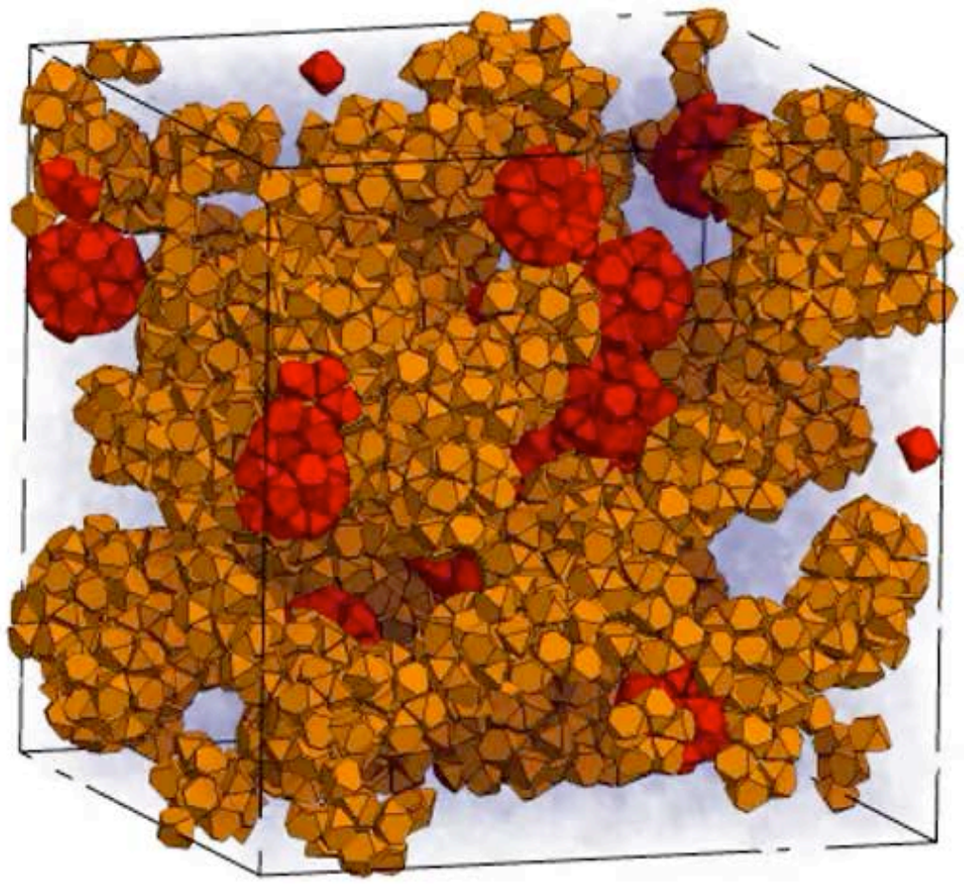
triangular bipyramid (TBP)

Prenucleation clusters forming in the TT system

Icosahedral 20-particle clusters form first, and later convert into a **highly complex crystal**.



a



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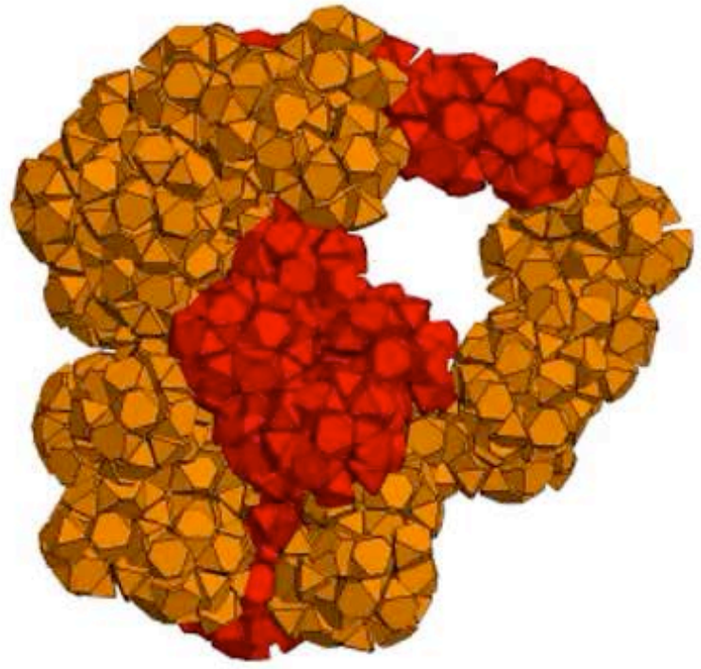
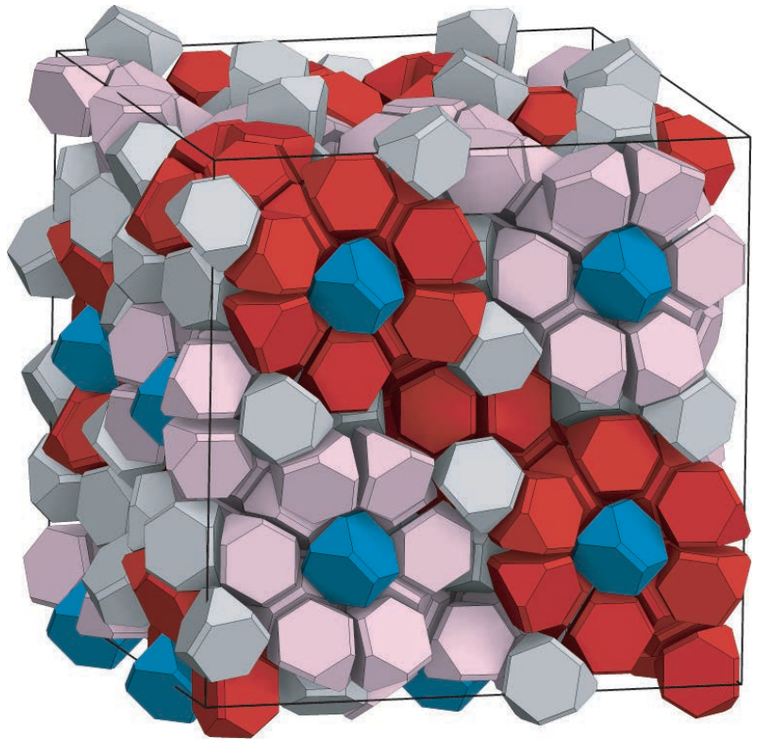


Crystal structure of the cF432 crystal

c



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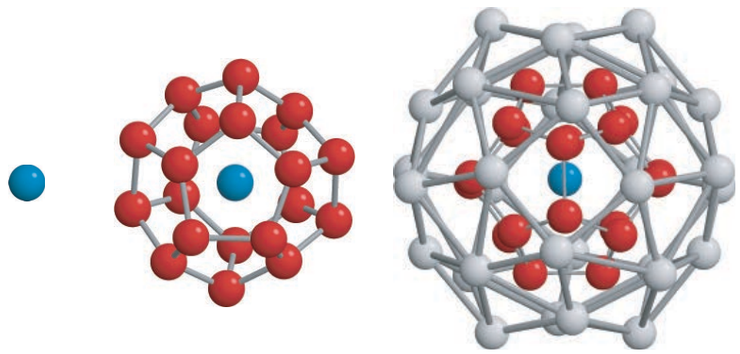


particles in cluster:

- 1 + 20 + 32 = 53

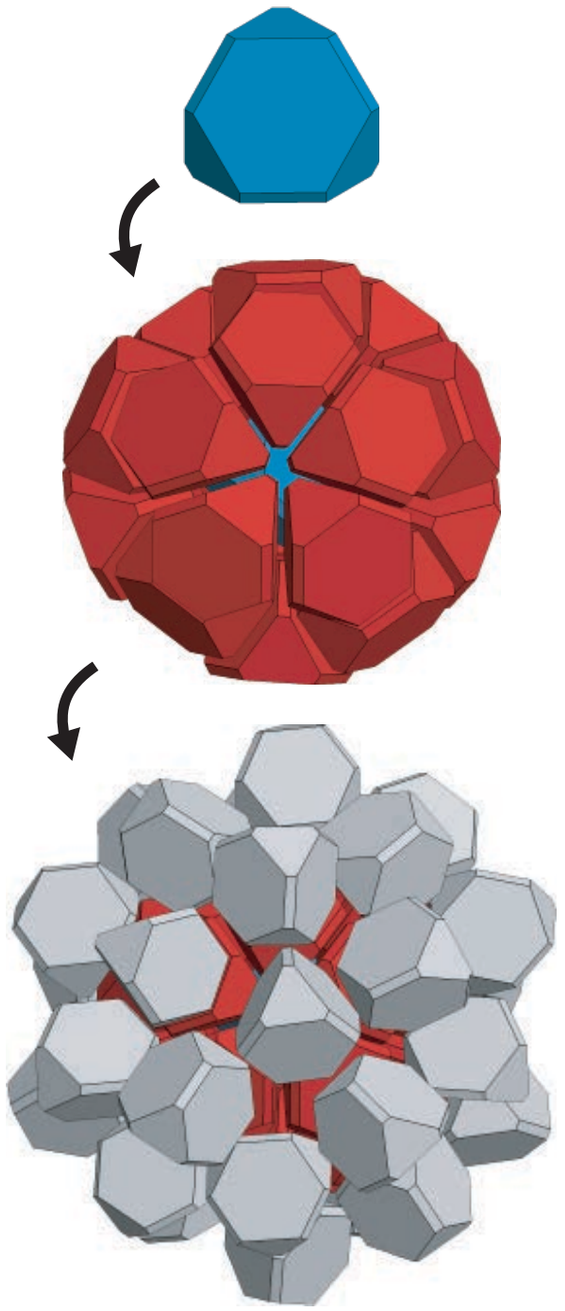
gray particles:

- 1

particles in unit cell:

- 8 x (53 + 1) = 432

Cluster hierarchy

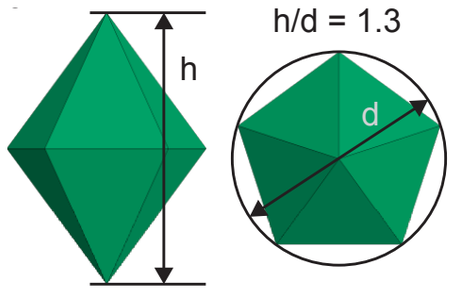


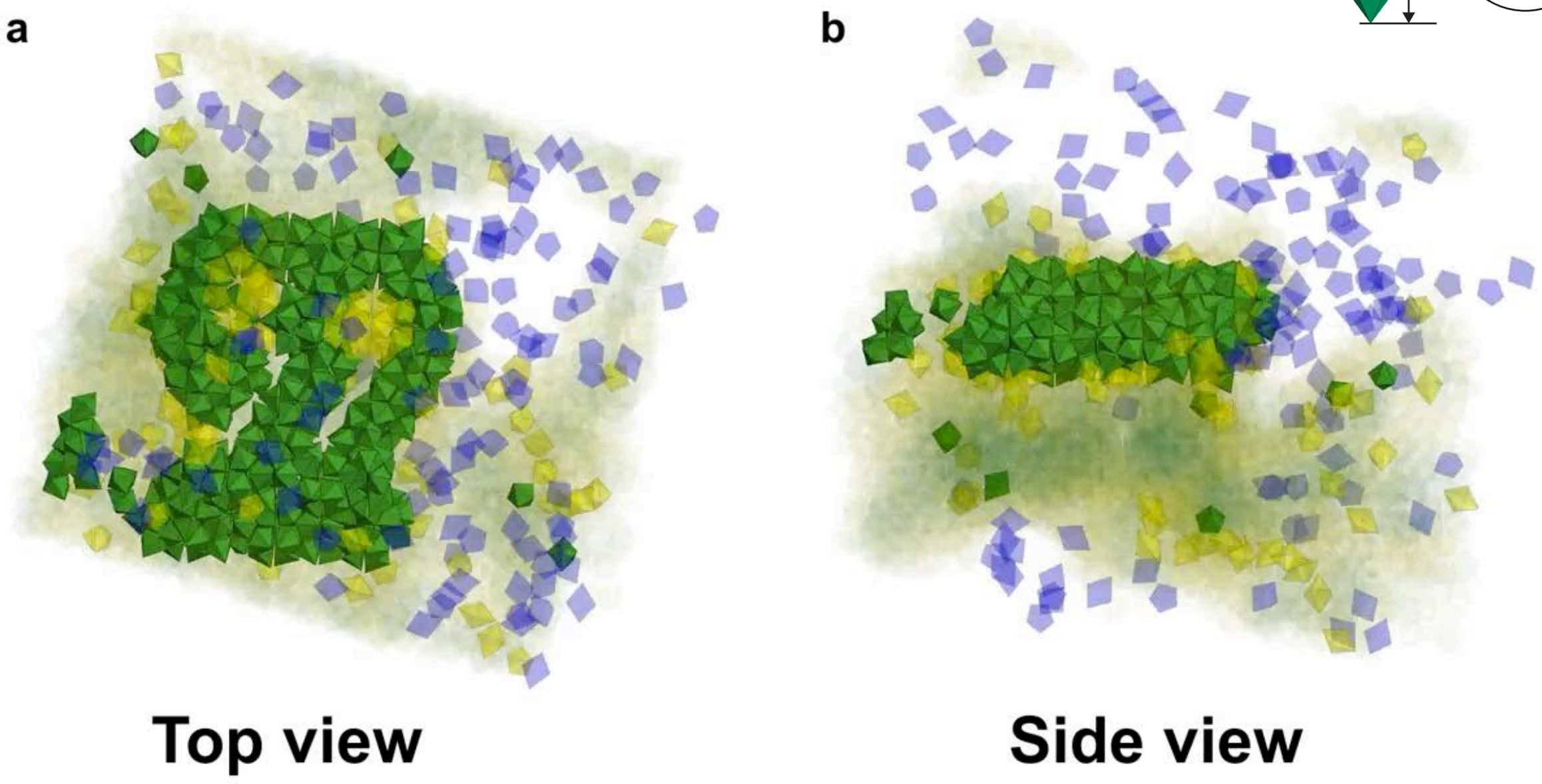
Similar to intermetallic alloys

- e.g.: Bergman phase $Mg_{32}(Al,Zn)_{49}$

Anisotropic growth of the PBP crystal

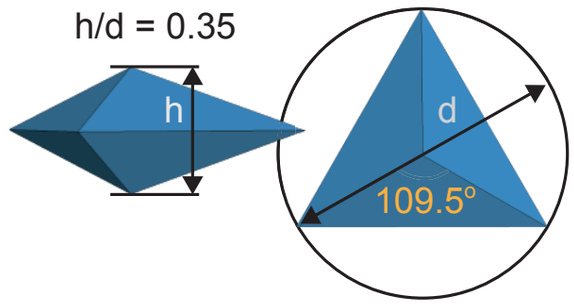
The **low-density fluid** converts to a coexistence of **fiber-like motifs** separated by **weakly ordered dense region**.

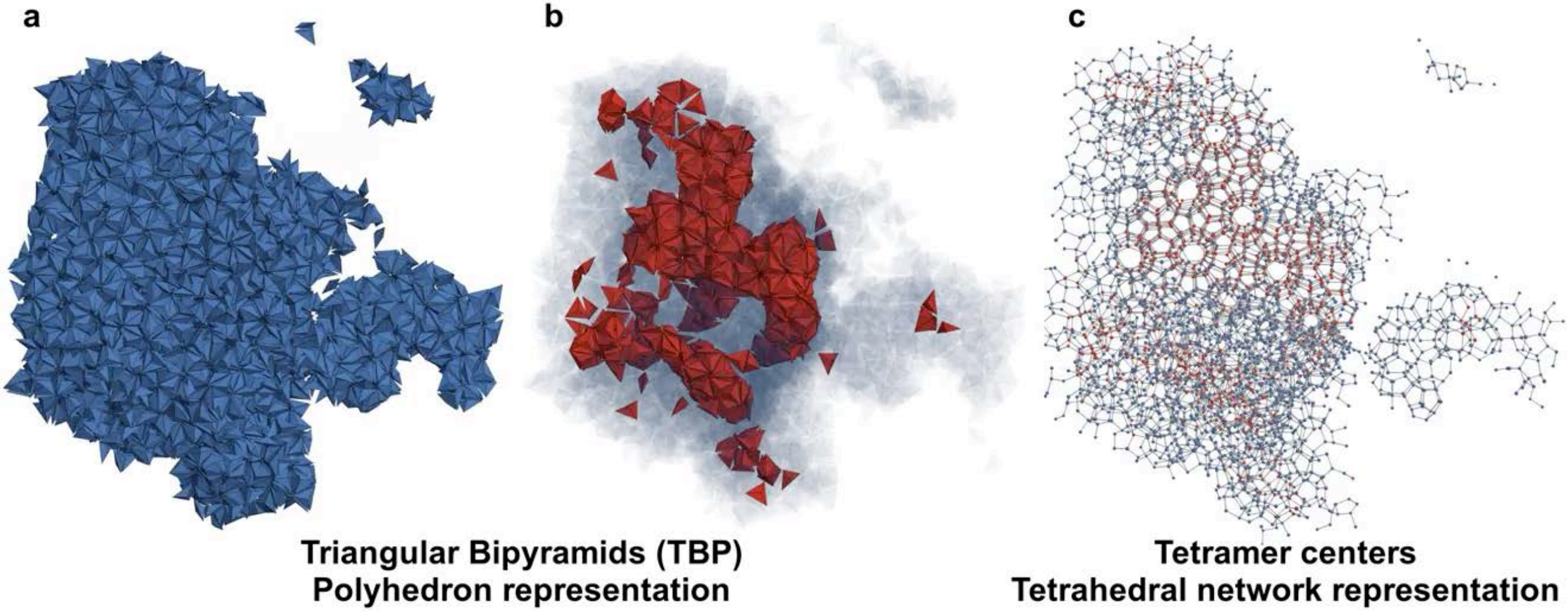




Two-step growth of the TBP crystal

Clathrate crystal from a low-density fluid via an **intermediate amorphous fluid phase**.

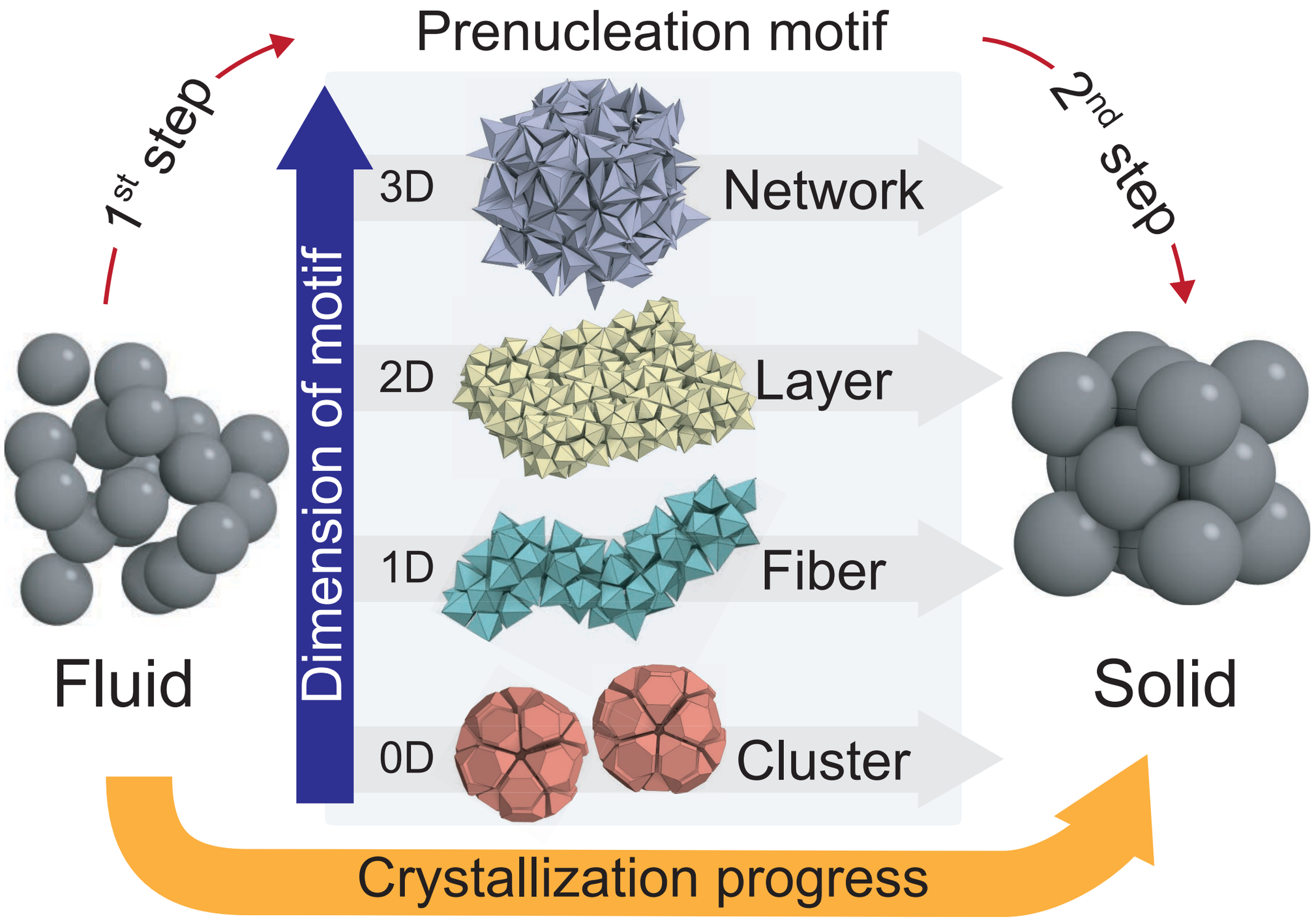




Triangular Bipyramids (TBP)
Polyhedron representation

Tetramer centers
Tetrahedral network representation

Organizing pathways by dimensionality



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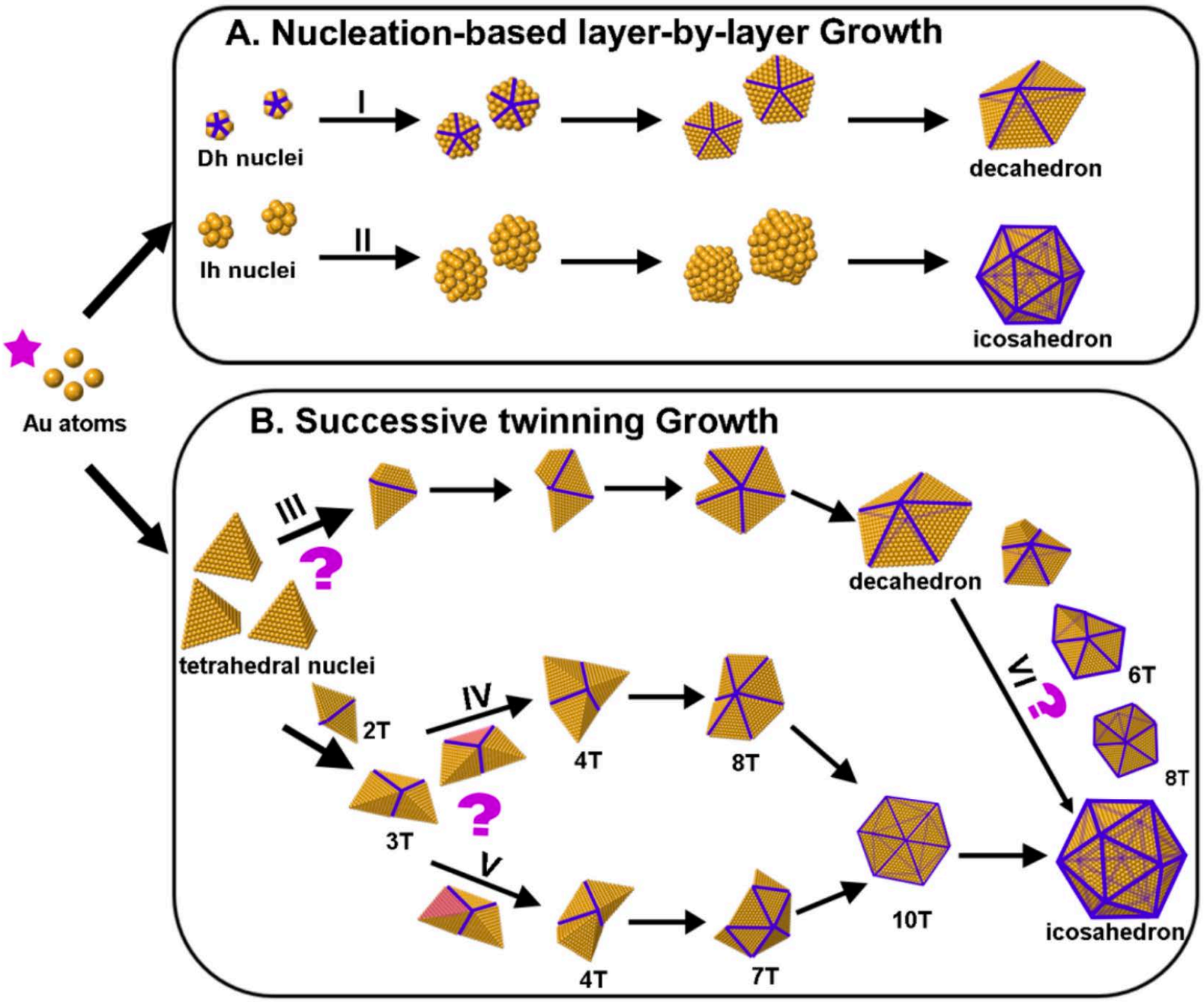
- Simulating crystal growth (incomplete)

Multiply-twinned nanoparticles

Long history, e.g.:

- X. Ma, F. Lin, X. Chen, C. Jin, *ACS Nano* **2020**, 14, 9594
- J.S. Du, W. Zhou, S.M. Rupich, C.A. Mirkin, *Angew. Chem.* **2021**, 60, 6858
- M. Sun, Z. Cheng, W. Chen, M. Jones, *ACS Nano* **2021**, 15, 15953

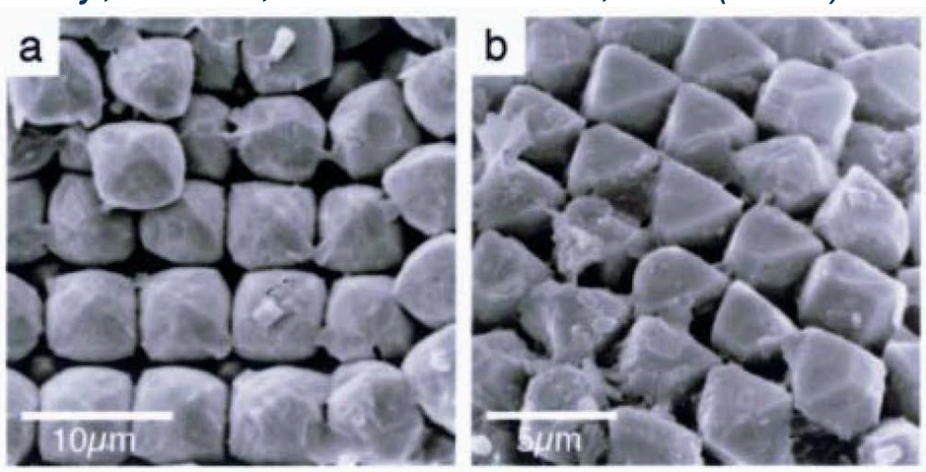


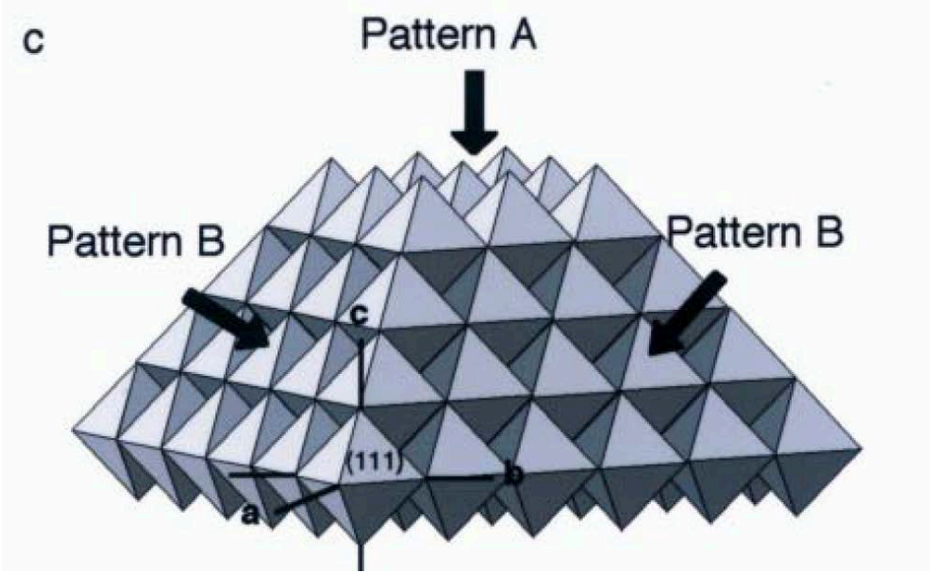
Multi-domain structure in framboidal pyrite (fool's gold)

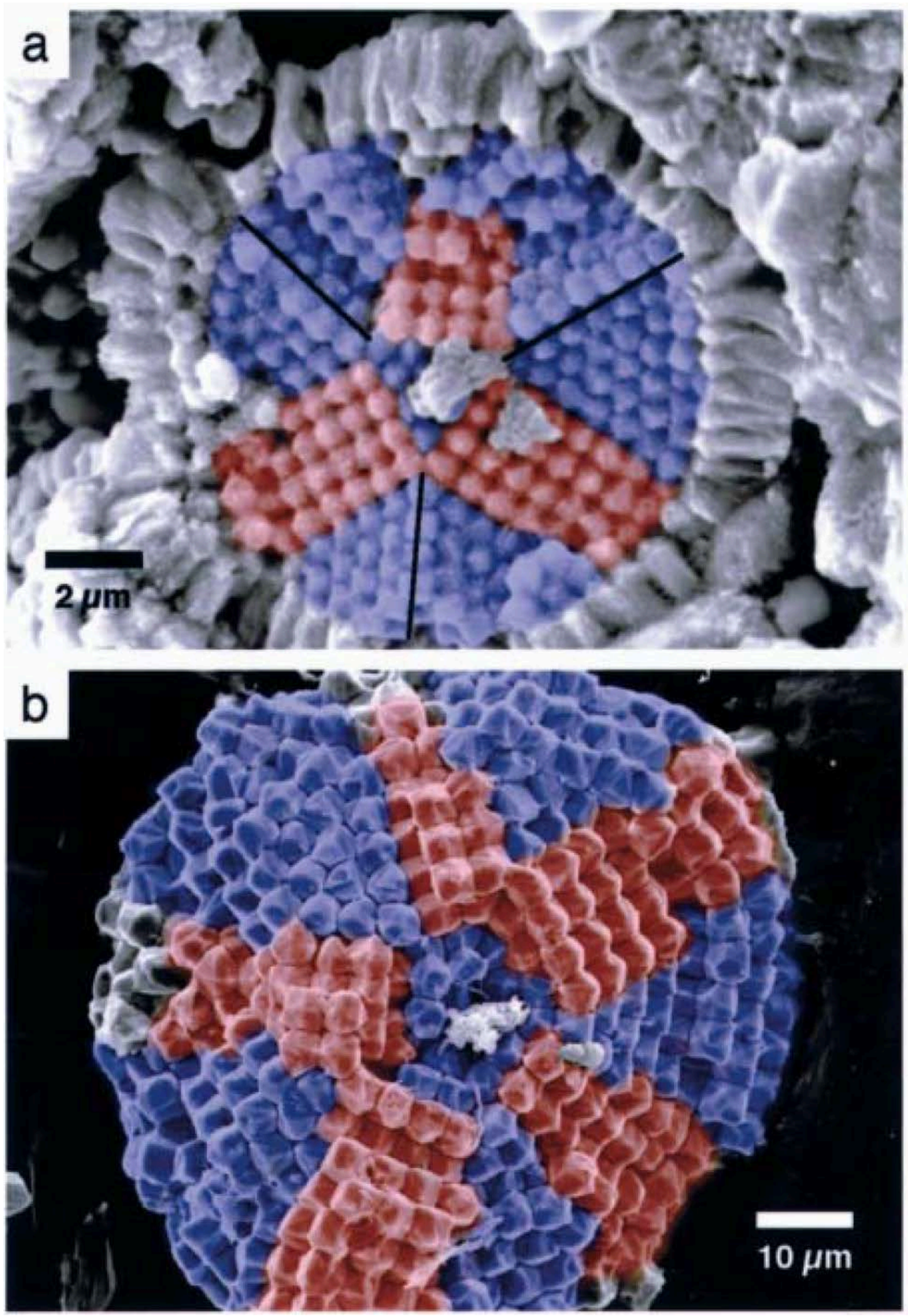
Arrangement of microcrystals in **framboidal pyrite** FeS_2.

Domain structures on sections of framboids from Shirone drill core (31m depth)

H. Ohfuji, J. Akai, Am. Mineral. 87, 176 (2002)

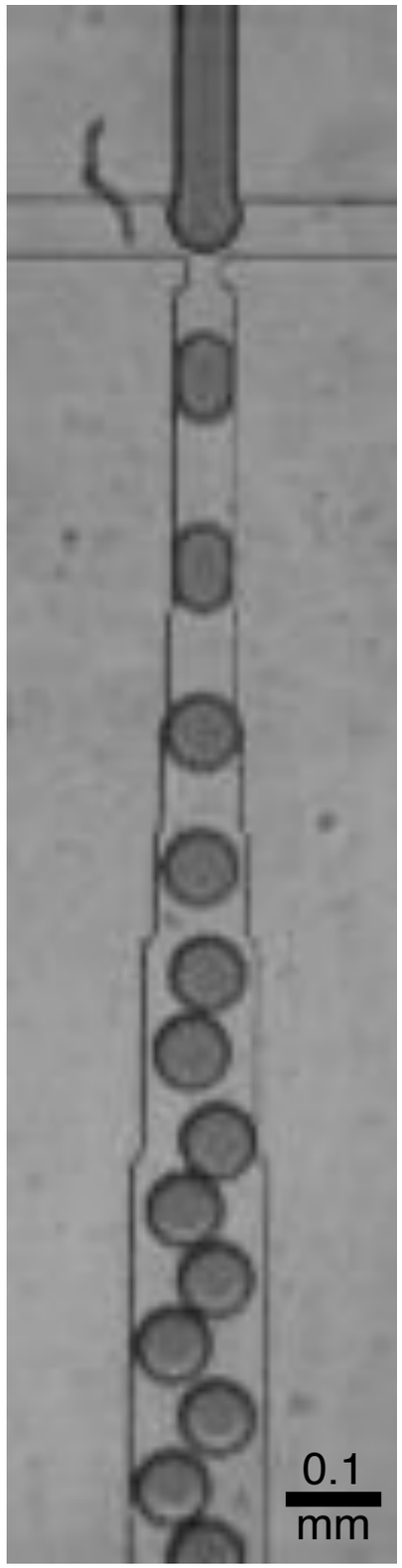






Assembly line for colloid crystals (Vogel group @ FAU)

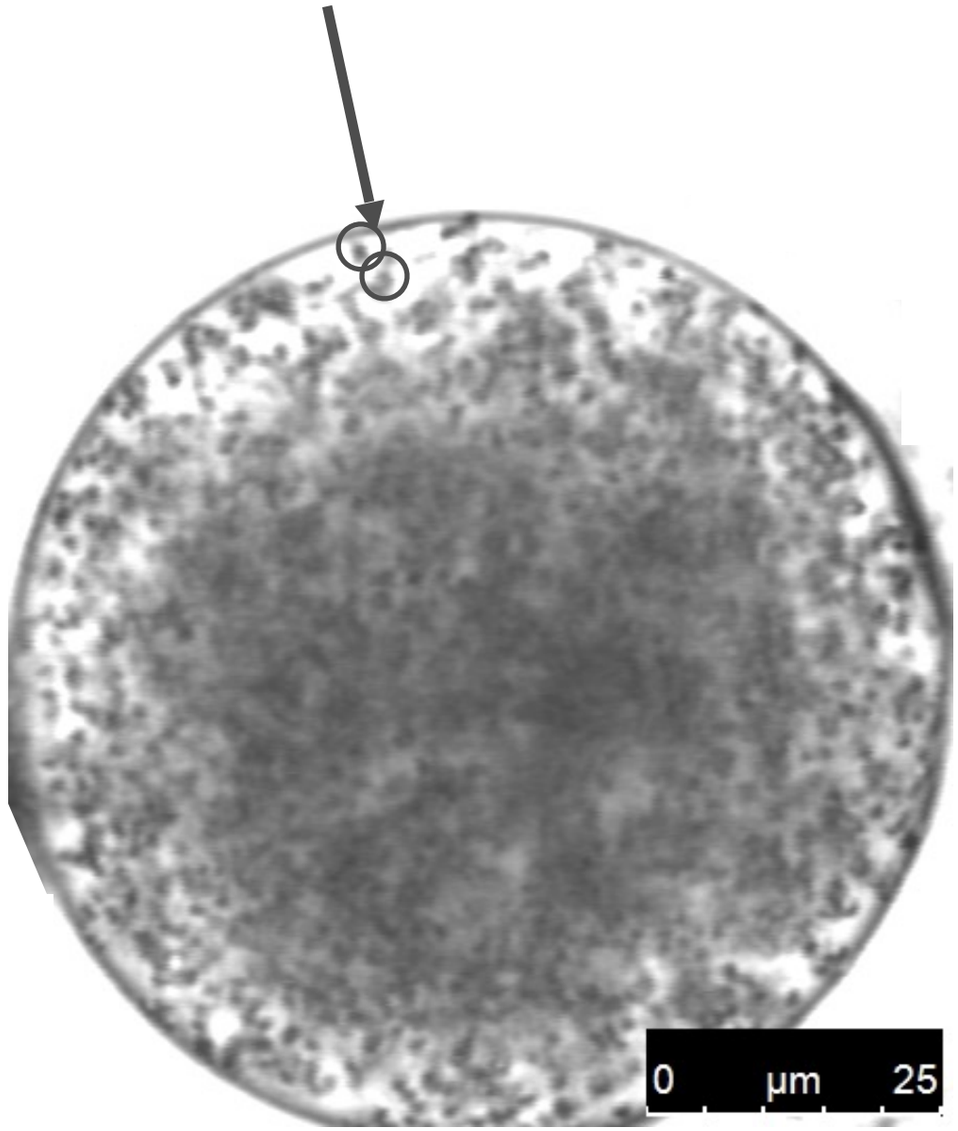
Water-in-oil emulsion droplets with colloidal spheres (polystyrene)

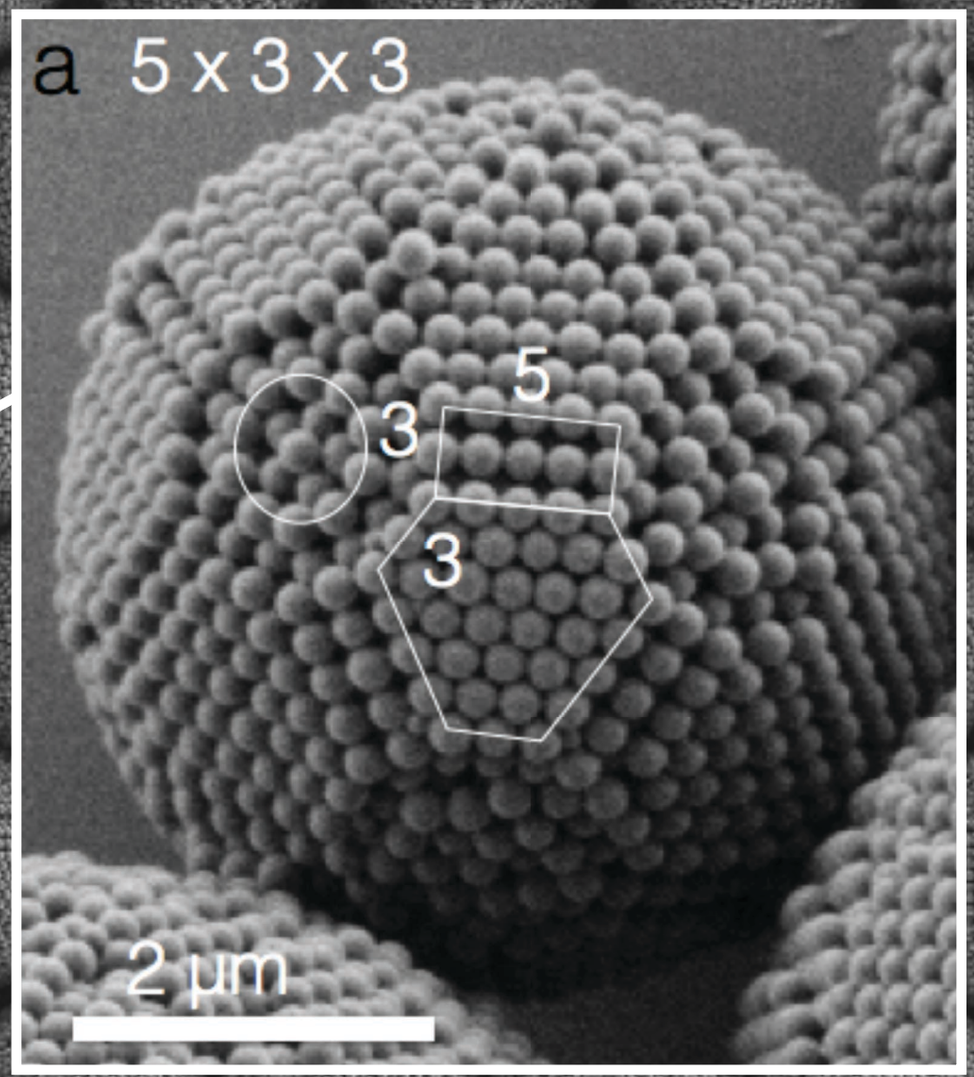


microfluidic
assembly line

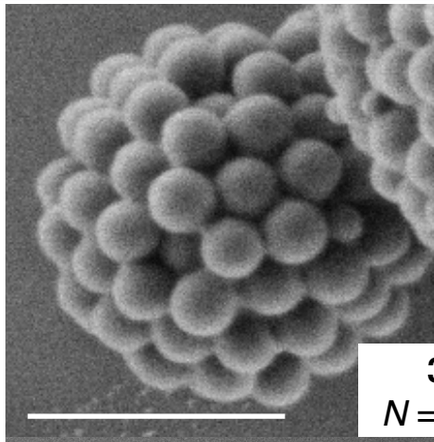
monodisperse
emulsion droplets
(⌀ tens of µm)

100 - 100,000 colloids (⌀ = 100-300 nm)

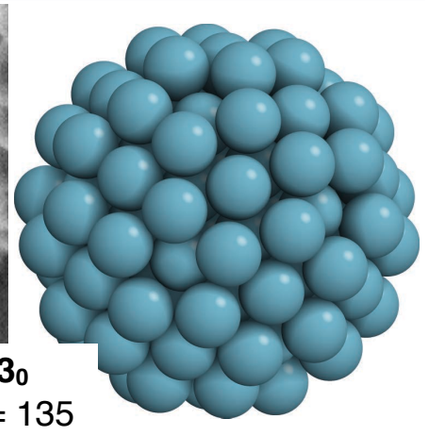


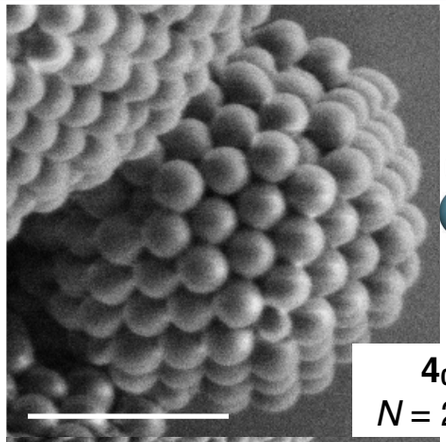

a 5 x 3 x 3
5
3
3
2 µm

Magic number cluster database

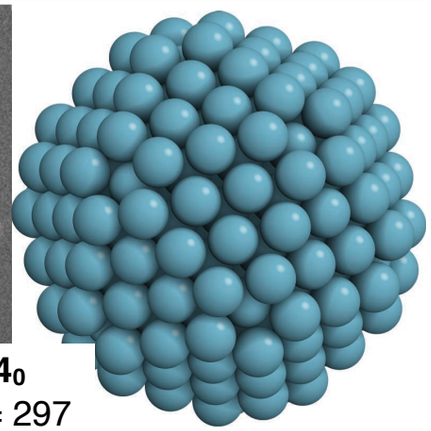


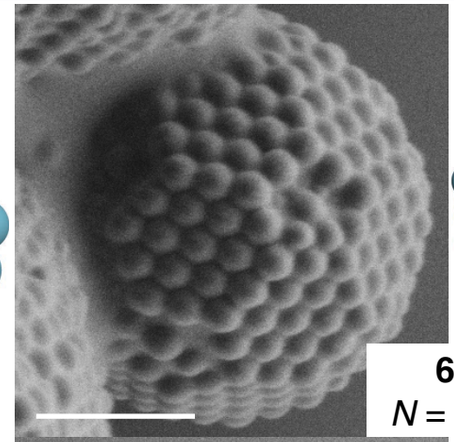
3_0
$N = 135$



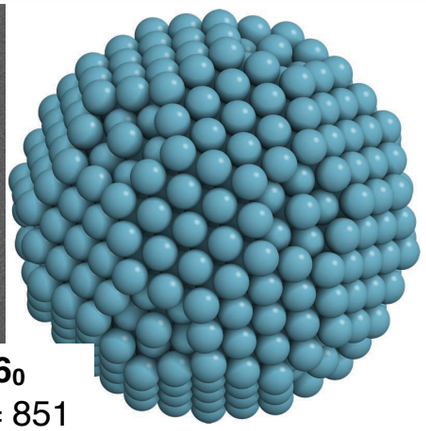


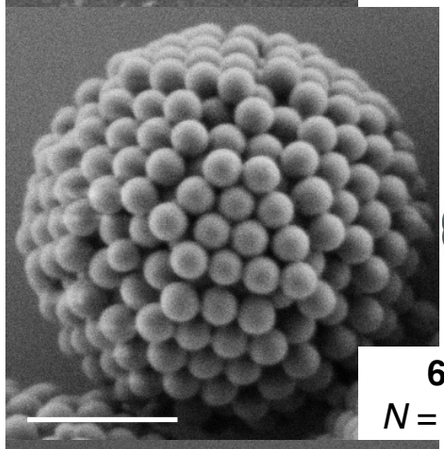
4_0
$N = 297$



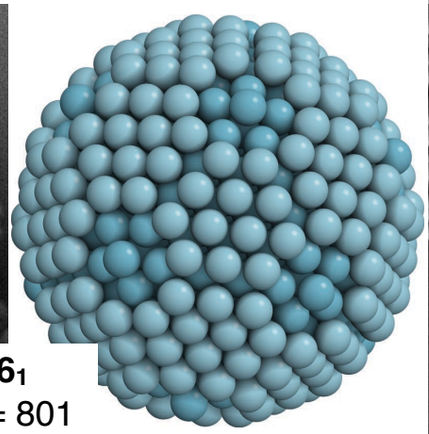


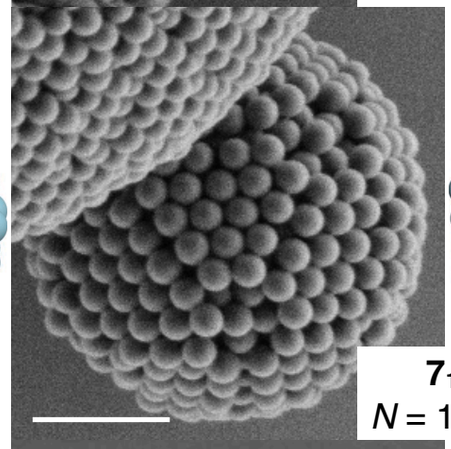
6_0
$N = 851$



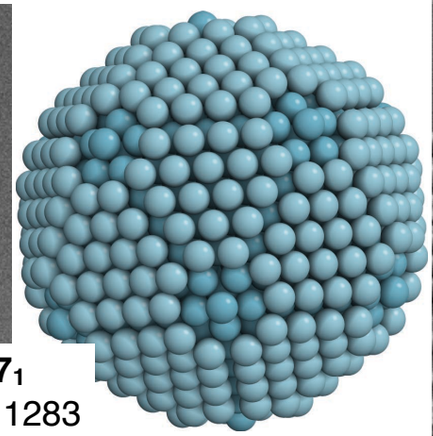


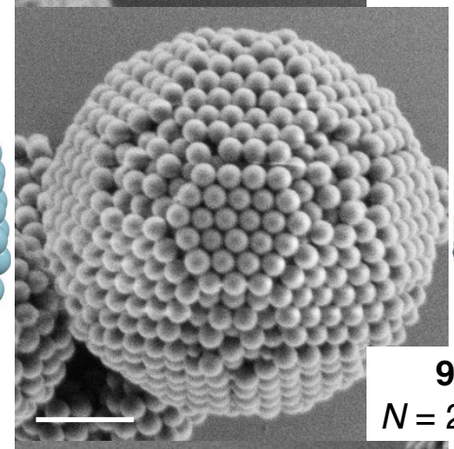
6_1
$N = 801$



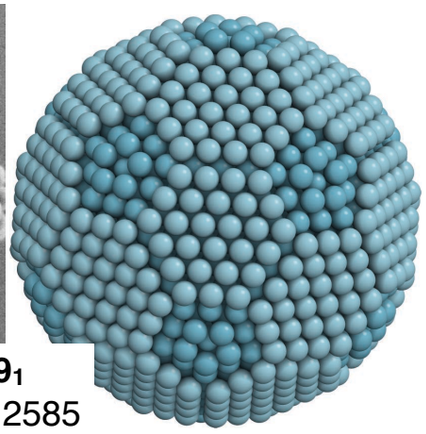


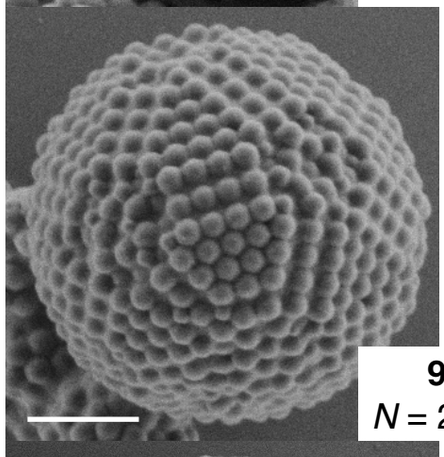
7_1
$N = 1283$



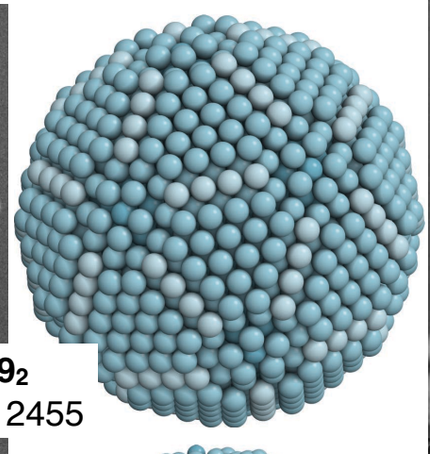


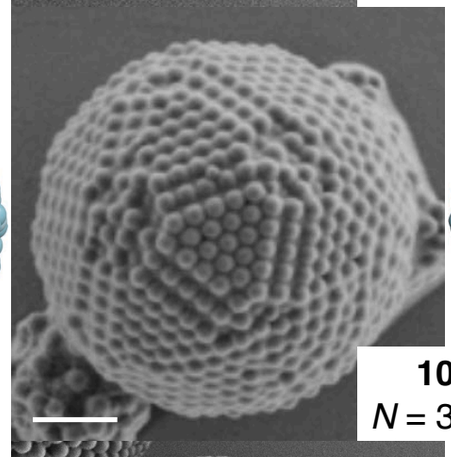
9_1
$N = 2585$



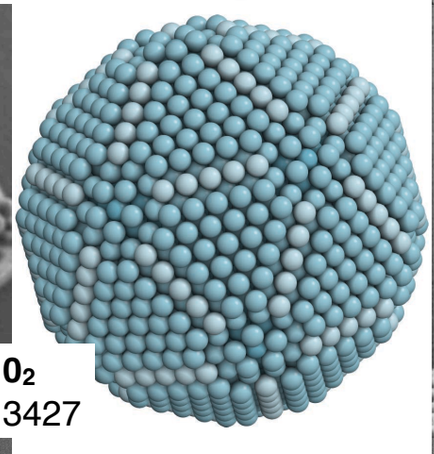


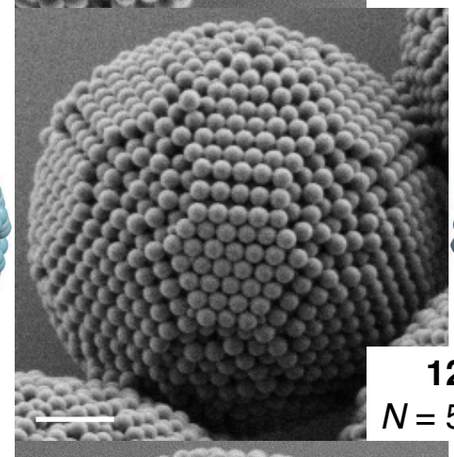
9_2
$N = 2455$



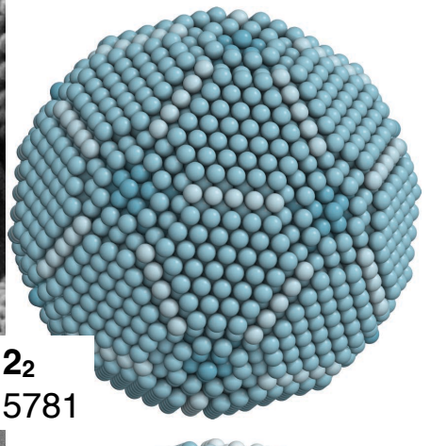


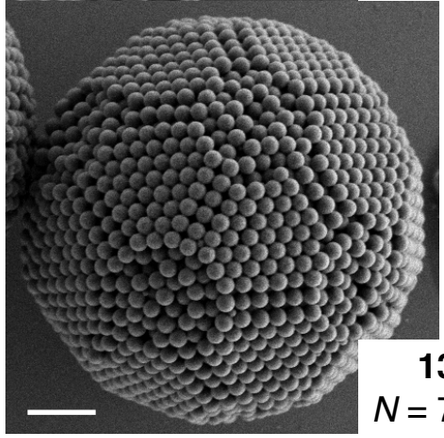
10_2
$N = 3427$



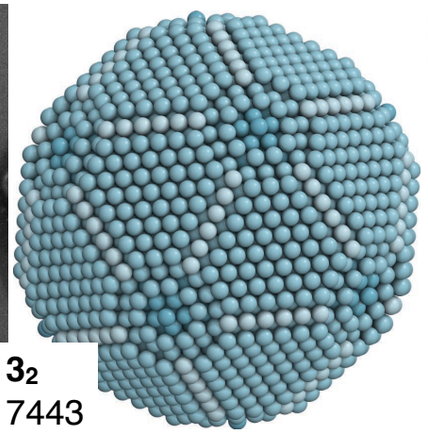


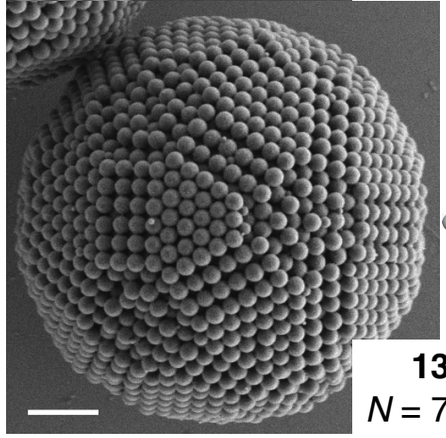
12_2
$N = 5781$



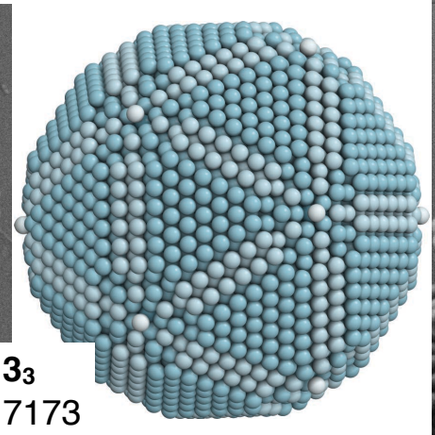


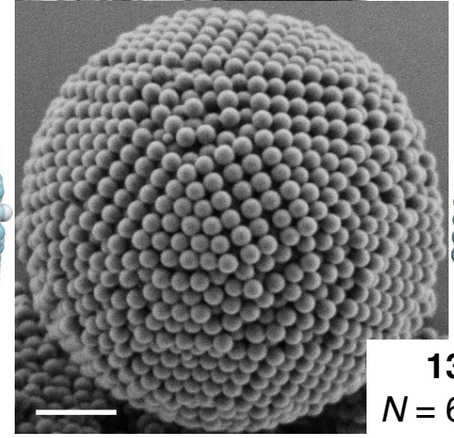
13_2
$N = 7443$



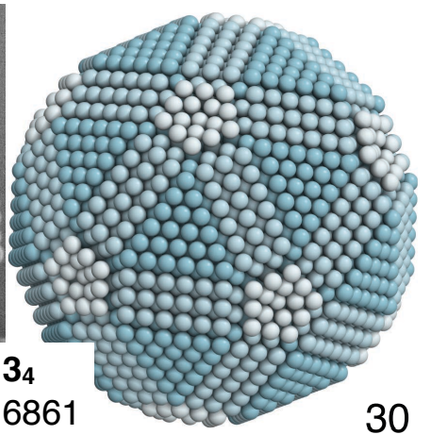


13_3
$N = 7173$



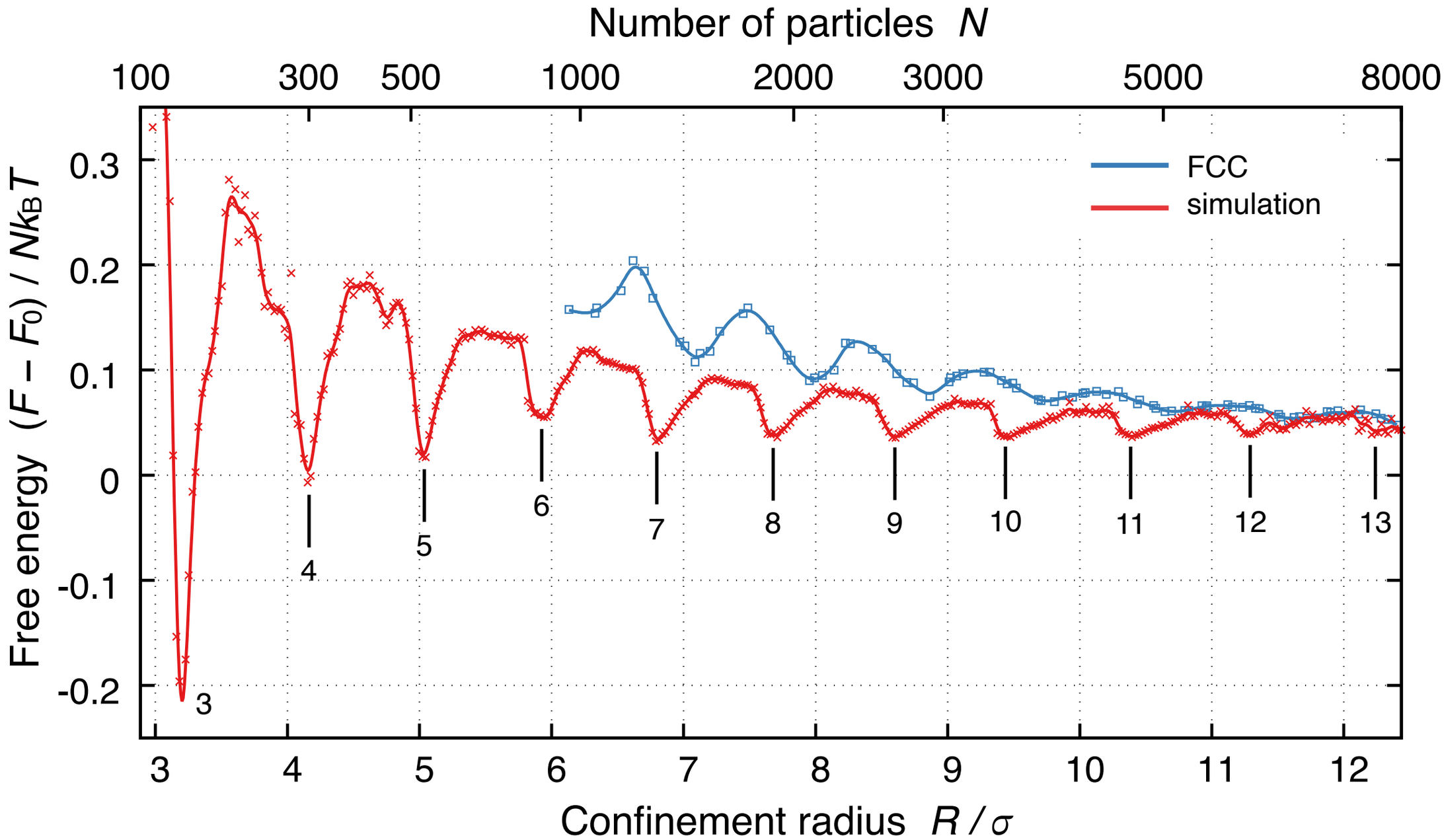


13_4
$N = 6861$



Magic number hard sphere clusters

Thermodynamic stability diagram: high-precision free energy calc.



J. Wang, C.F. Mbah, T. Przybilla, B.A. Zubiri, E. Spiecker, ME, N. Vogel
Nature Comm. **2018**, 9, 5259

Free energy calculations

(1) Existing free energy calculations (FEC):

- work well for solids **with no or few defects**
  - e.g. with Frenkel-Ladd method
- work well for fluids
  - e.g. with thermodynamic integration to ideal gas

How to calculate free energies for partially ordered systems?

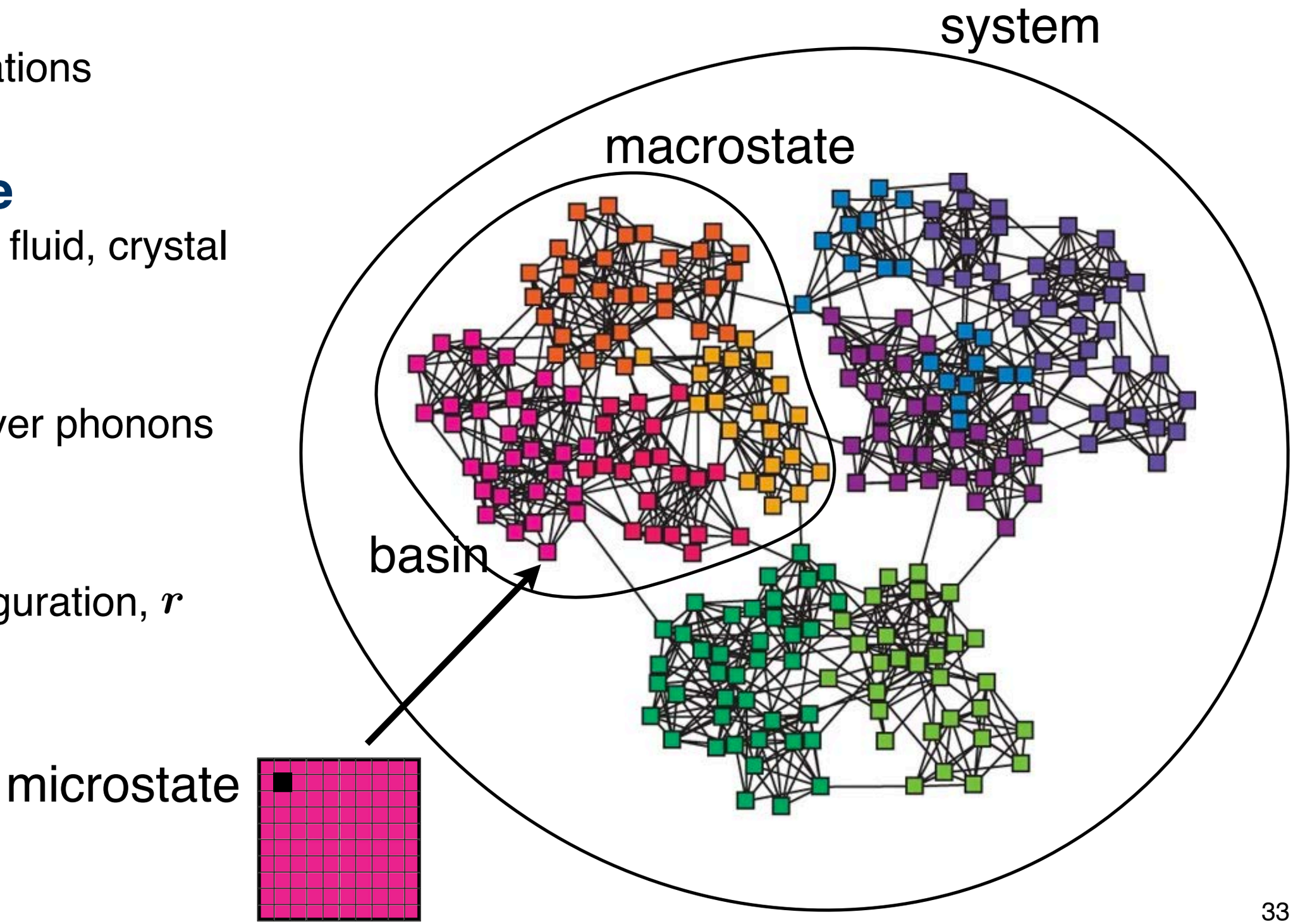
(2) **Why are simulations so much easier than FEC?**

- Systems quickly and consistently move towards lower free energy.
- How can we see this in FEC?

Hierarchy in configuration space

Partition function is hierarchical:

- **system**
  - all configurations
- **macrostate**
  - phase; e.g.: fluid, crystal
- **basin**
  - averages over phonons
- **microstate**
  - single configuration, r



Hierarchy in configuration space

Partition function is hierarchical:

- **system**
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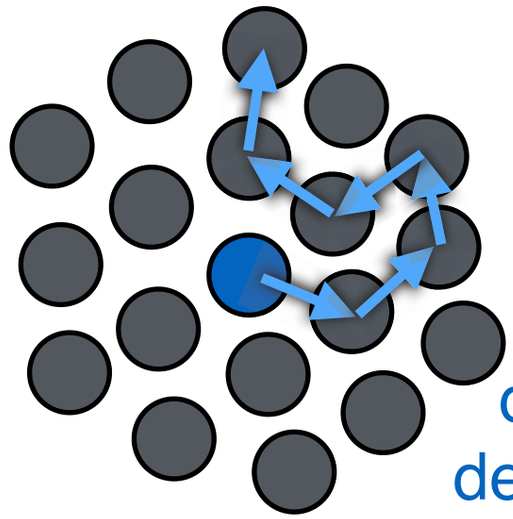
- **macrostate**
  - phase; e.g.: fluid, crystal
- **basin**
  - averages over phonons
- **microstate**
  - single configuration, $\boldsymbol{r}$

configurational entropy

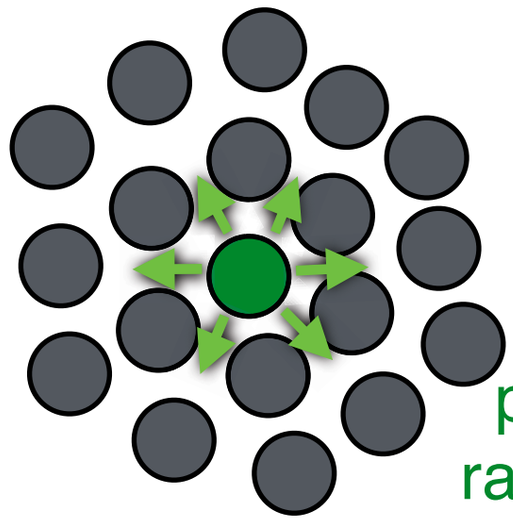
$$\int_{\text{basins} \in \text{macrostate}} d^{3N}\boldsymbol{r}$$



diffusion, defects, etc.

vibrational entropy

$$\int_{\text{microstates} \in \text{basin}} d^{3N}\boldsymbol{r}$$



phonons, rattling, etc.

$$\begin{aligned} S_{\text{macrostate}} &= k_{\text{B}} \log \left(\langle W_{\text{micro} \in \text{basin}} \rangle_{\text{basin}} \times \langle W_{\text{basins} \in \text{macro}} \rangle_{\text{macro}} \right) \\ &= S_{\text{vib.}} + S_{\text{config.}} \end{aligned}$$

Is this separation correct?

Let's assume it is!

Fluid = many basins, few phonons

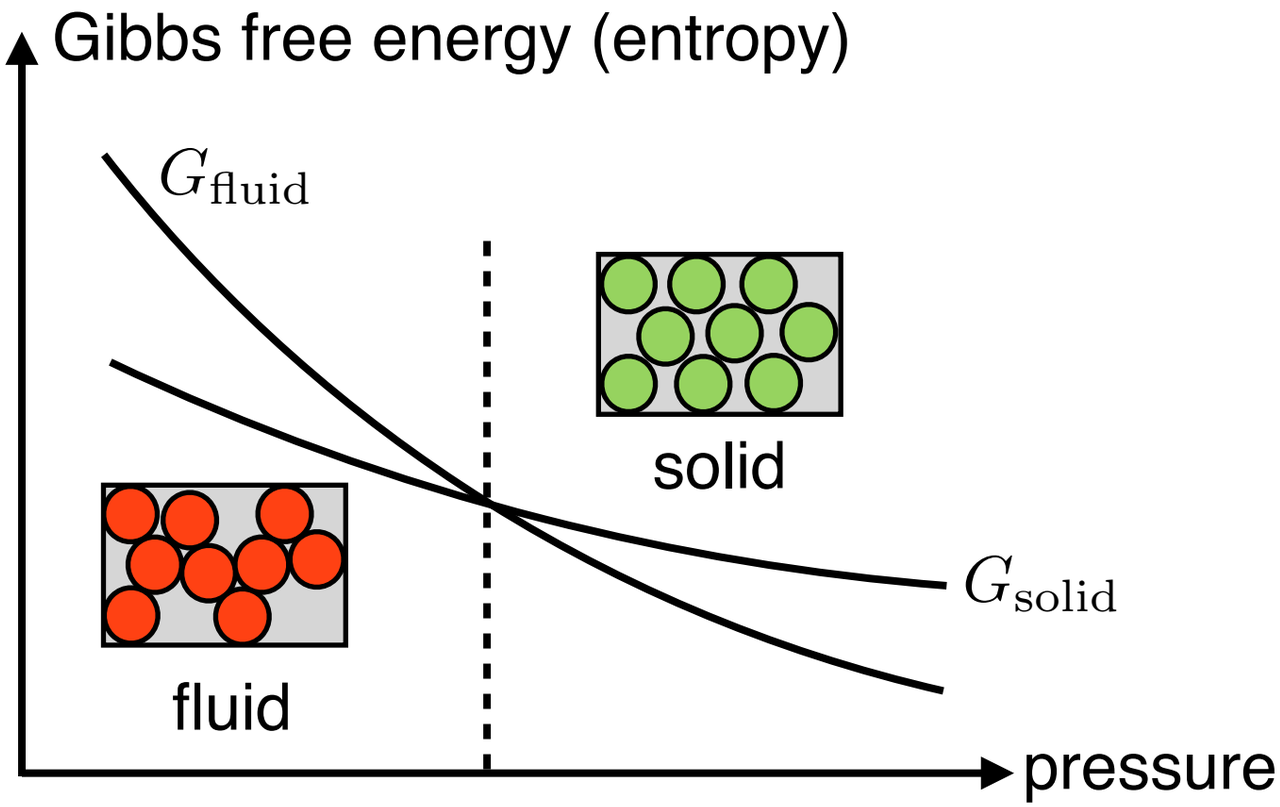
Solid = fewer basins, more phonons

$$S_{\text{conf.}}^{\text{fluid}} > S_{\text{conf.}}^{\text{solid}} \qquad S_{\text{vib.}}^{\text{fluid}} < S_{\text{vib.}}^{\text{solid}}$$

macroscopic (dis)order ***microscopic (dis)order***

Dependence on density

- **configurational entropy** (basins) does <u>not or only slowly</u> change with density
- **vibrational entropy** (phonons) decreases <u>rapidly</u> with density

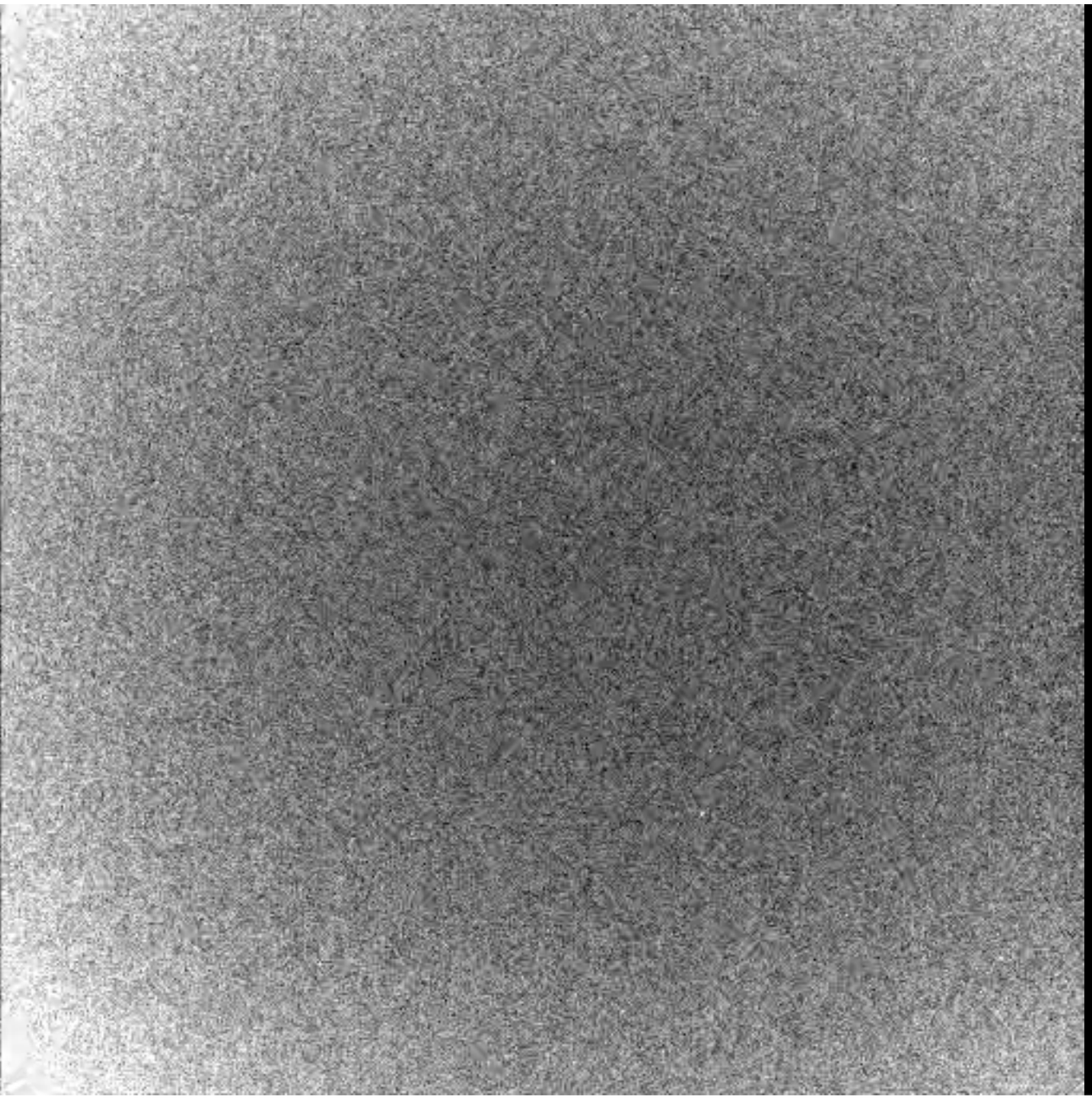


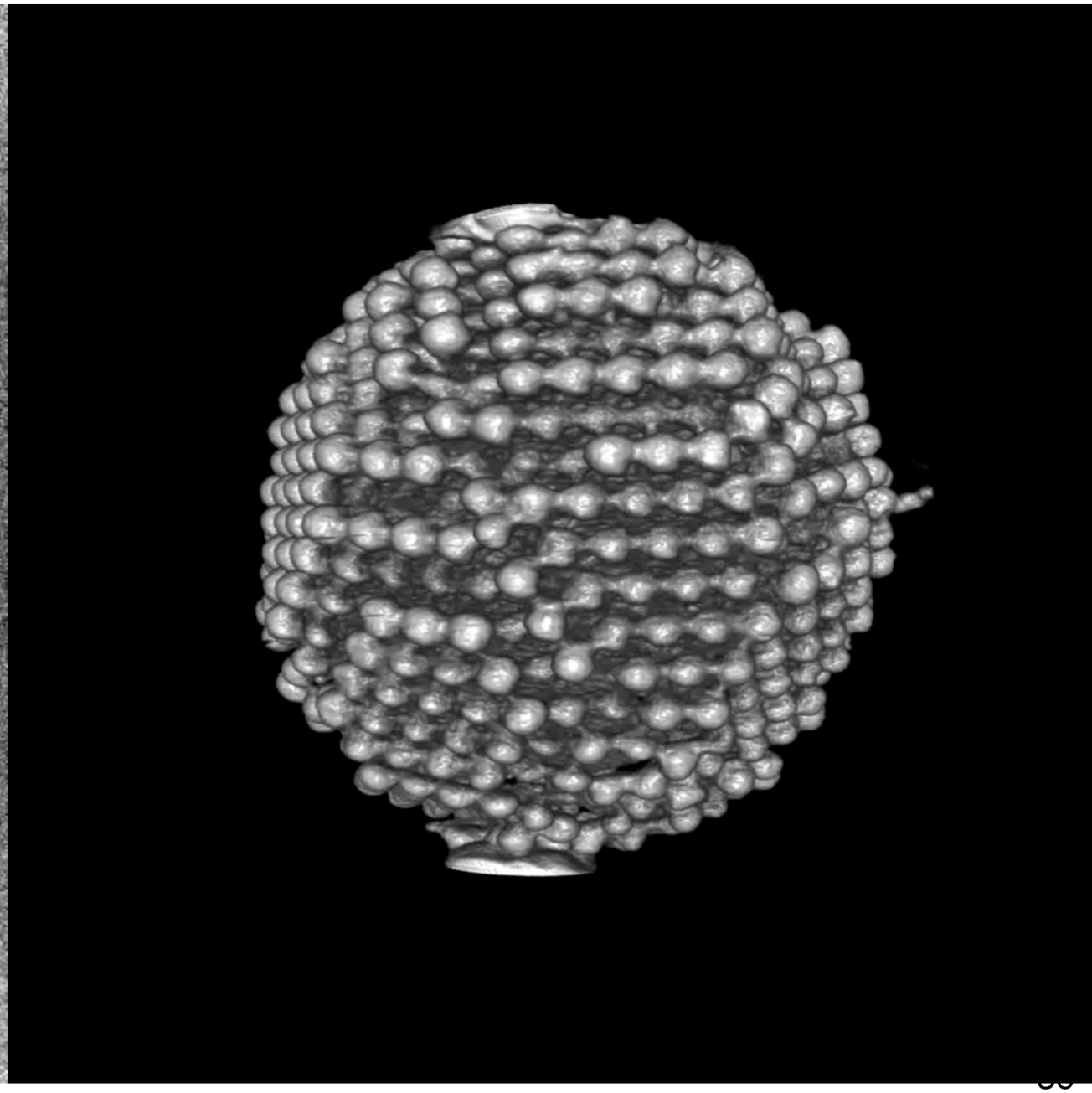
<u>Interpretation:</u>

"At the hard sphere phase transition, the system trades configurational entropy for vibrational entropy."

Transmission X-ray imaging (Spiecker group @ FAU)

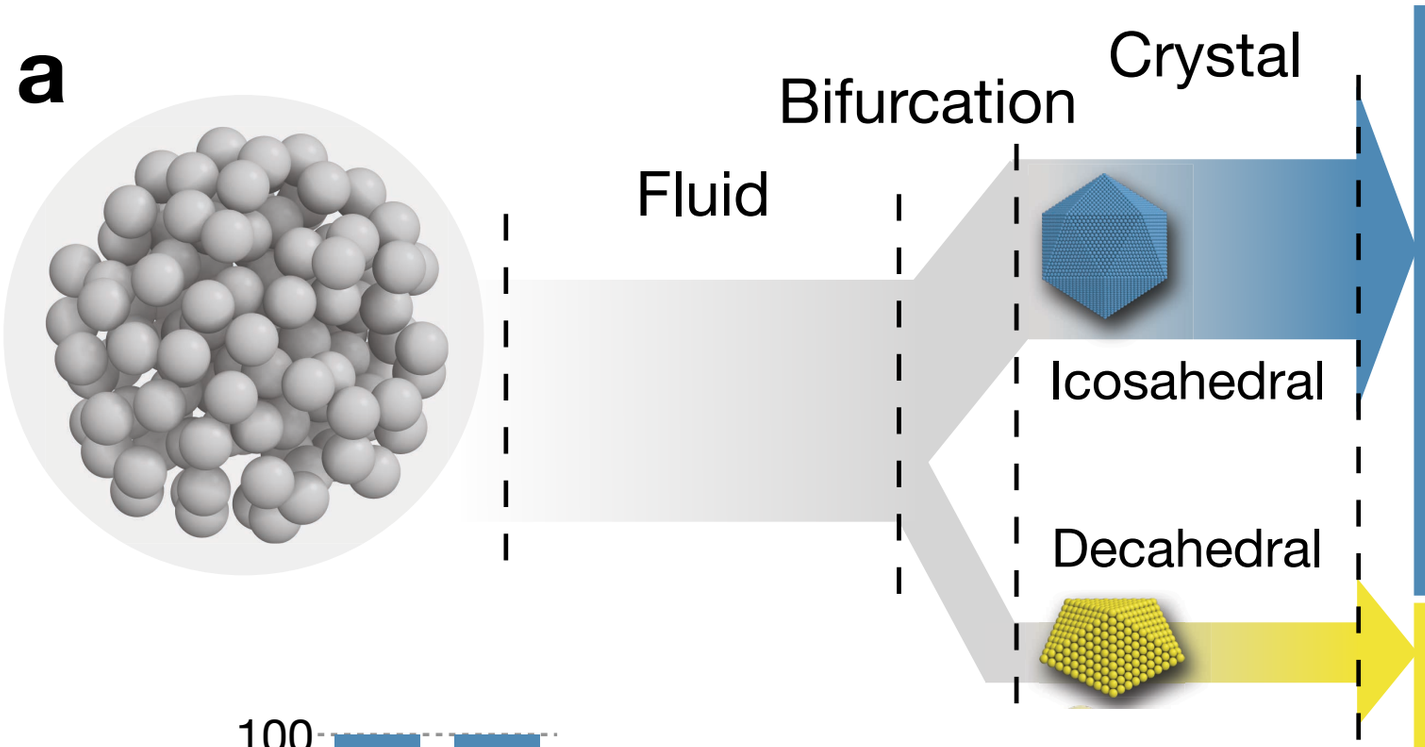
- ZEISS Xradia 810 Ultra X-ray microscope
- imaging of 16 μm x 16 μm large areas
- optical resolutions down to 50 nm (pixel size of 16 nm)

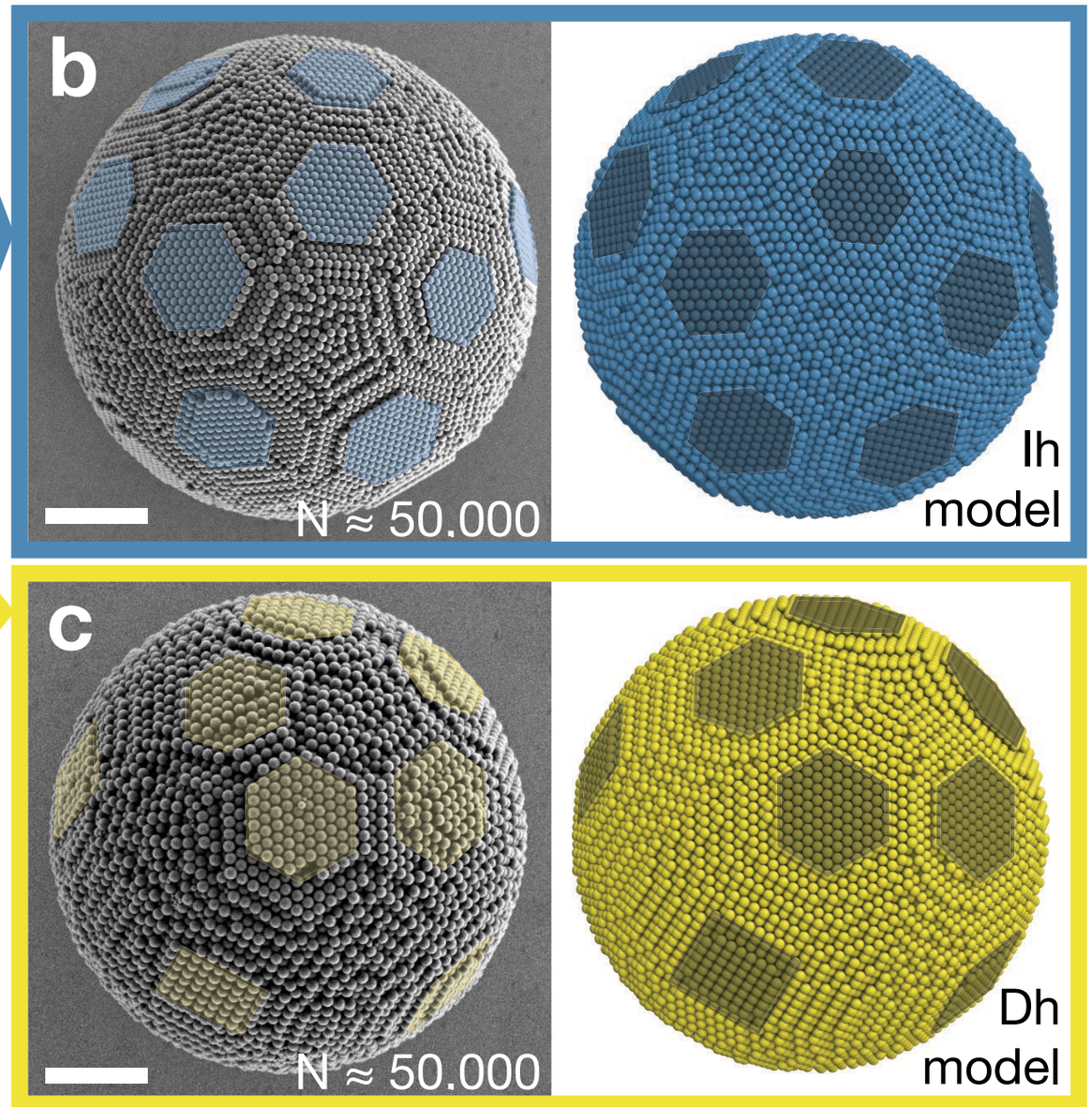


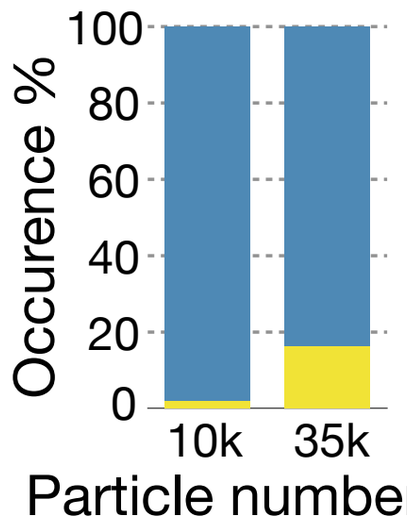


Competing pathways

Structure characterization of icosahedral and decahedral colloidal cluster polymorphs







Icosahedral much more frequent (80-90%)

Why?

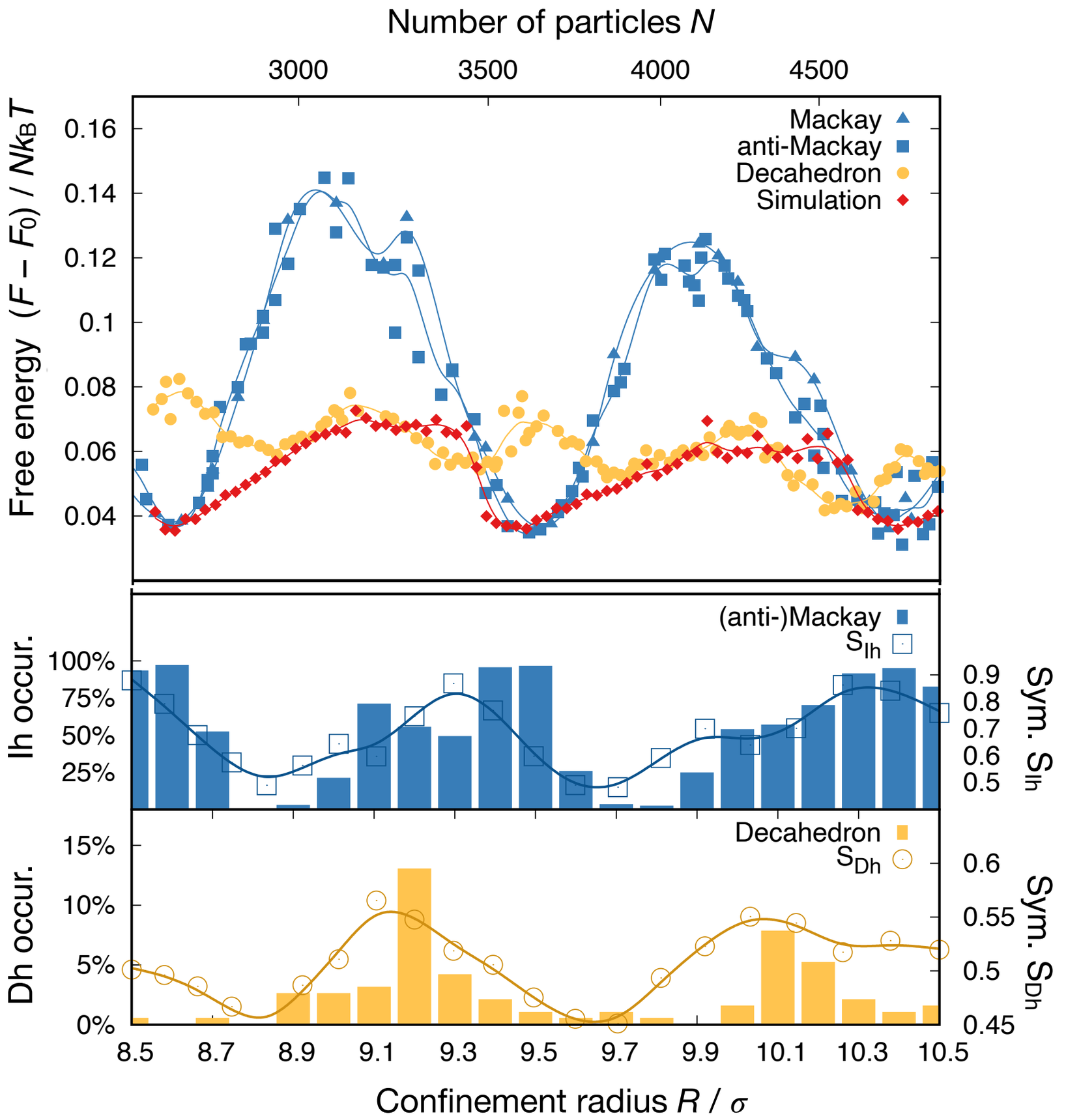
NOT thermodynamics!

C.F. Mbah, J. Wang, S. Englisch, P. Bomminini, N.R. Varela-Rosales, E. Spiecker, N. Vogel, ME *preprint*

Thermodynamics of clusters

Free energy landscape of decahedral and icosahedral clusters

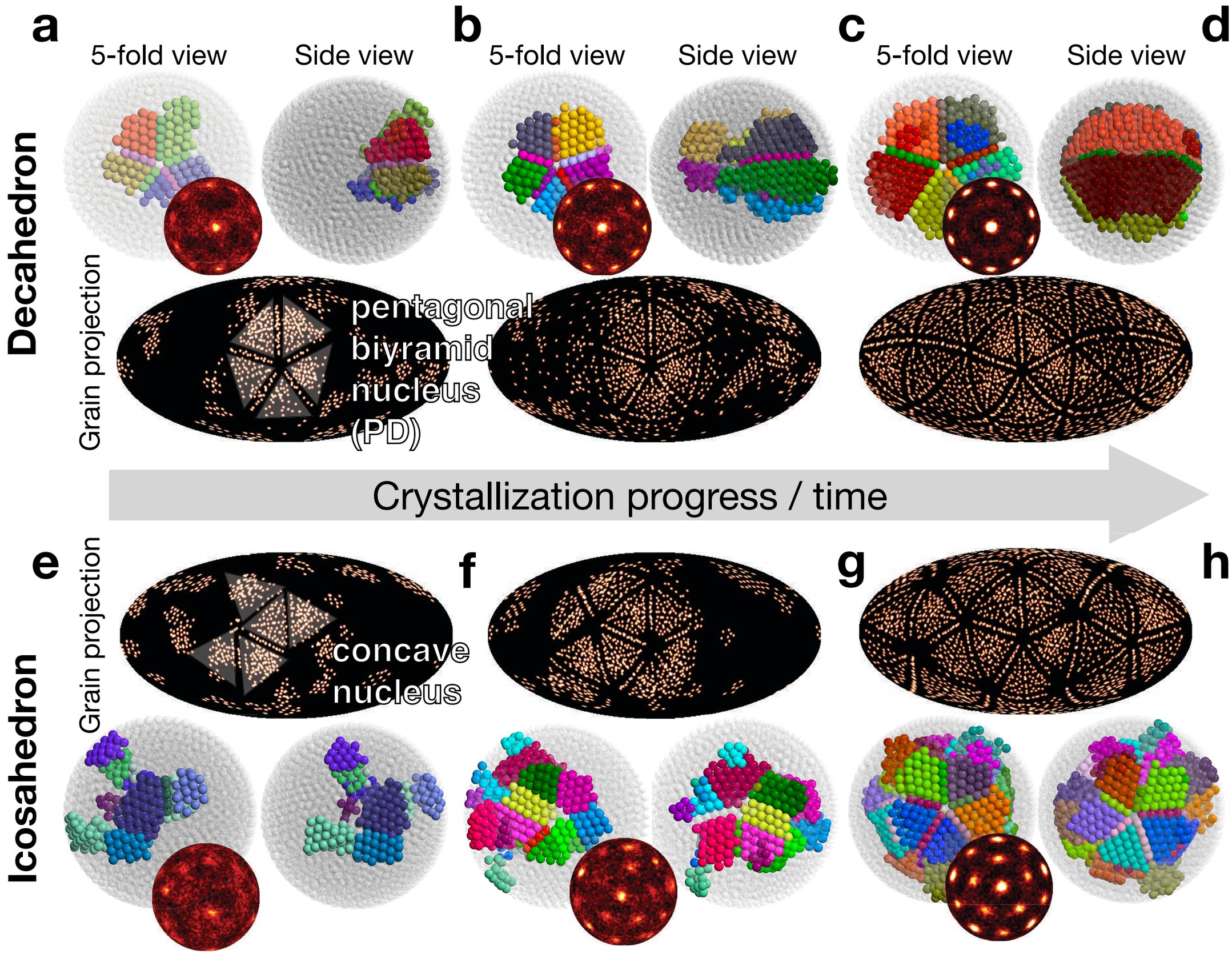
Occurence statistics in simulation contradicts FE calculations



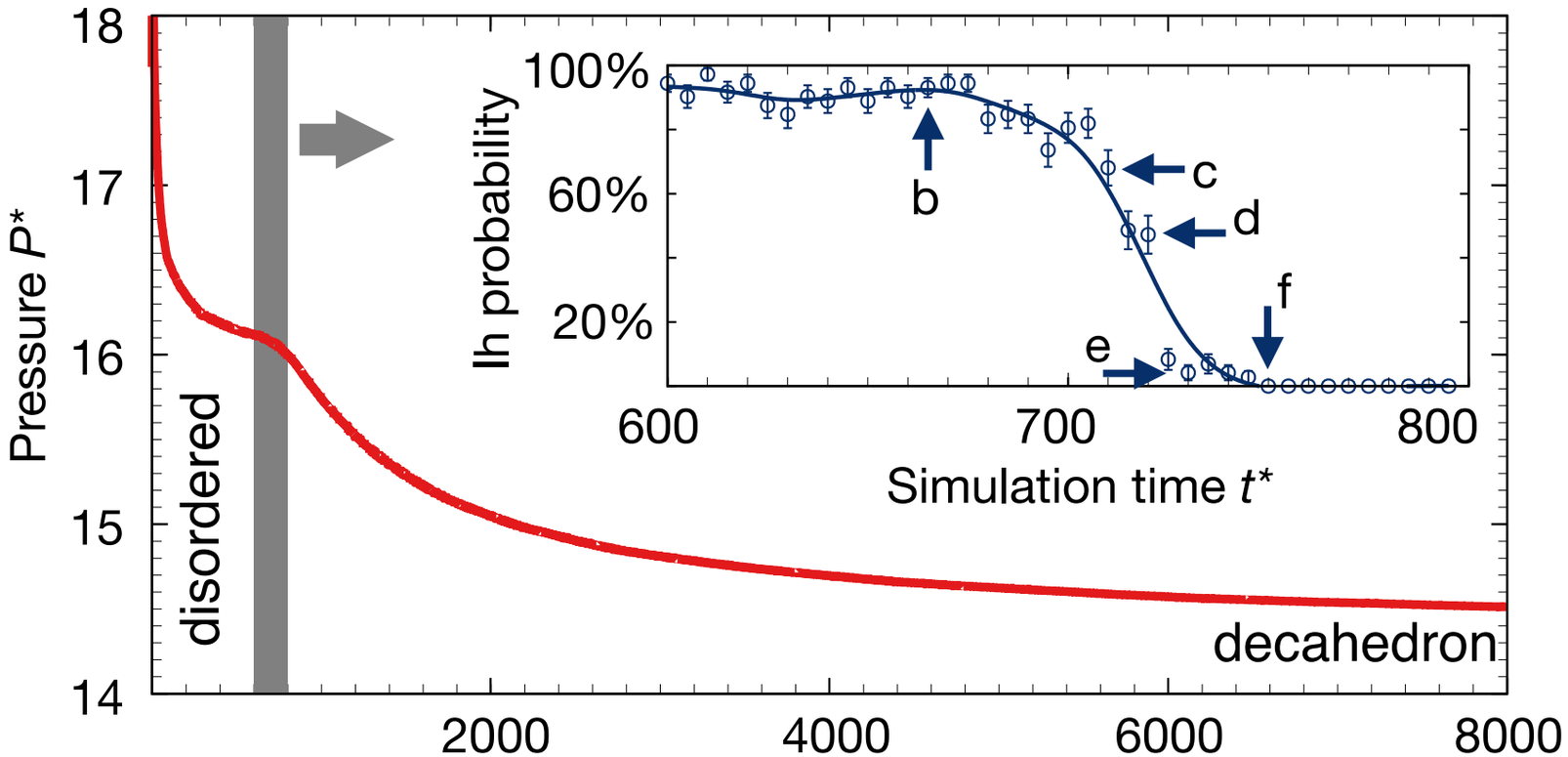
C.F. Mbah, J. Wang, S. Englisch, P. Bomminini, N.R. Varela-Rosales, E. Spiecker, N. Vogel, ME

preprint

Kinetic crystallization pathways



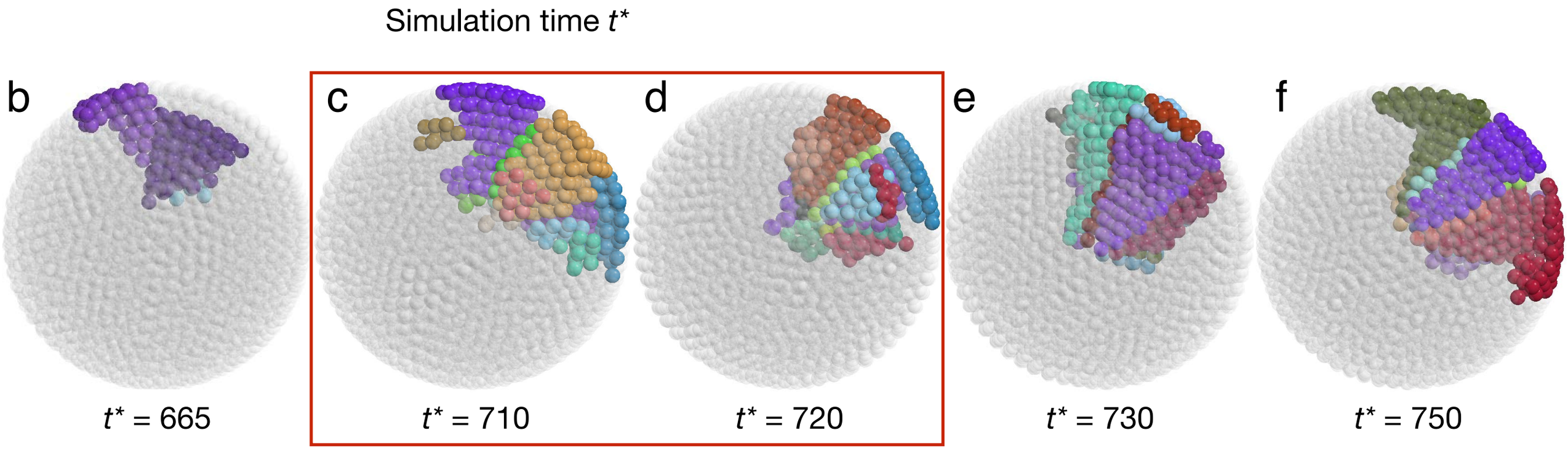
Bifurcation of crystallization trajectories



Probability of forming a compact PD nucleus is:

$$2/5 \times 2/6 \approx 13\%$$

~ probability of observing decahedra



At the critical point, five grains are present in the compact pentagonal bipyramid (PB) configuration.

Outline

- Self-assembly of complex crystals on the computer
- Relationship between structure and formation pathways
- Finite magic number clusters
- **Role of polydispersity**
- Modeling anisotropic patchy interactions
- Simulating crystal growth (incomplete)

Opals are naturally occurring colloidal crystals

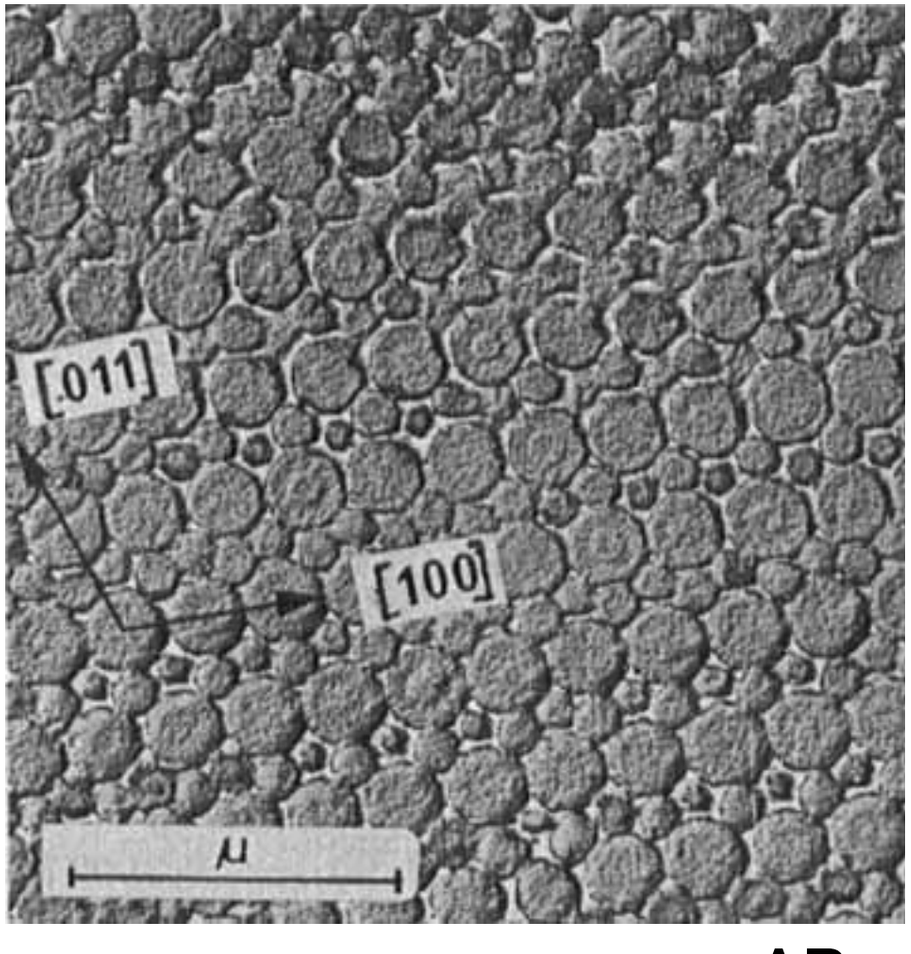
Opal = “hydrated aggregation of silica colloidal spheres ($SiO_2 \cdot nH_2O$)”

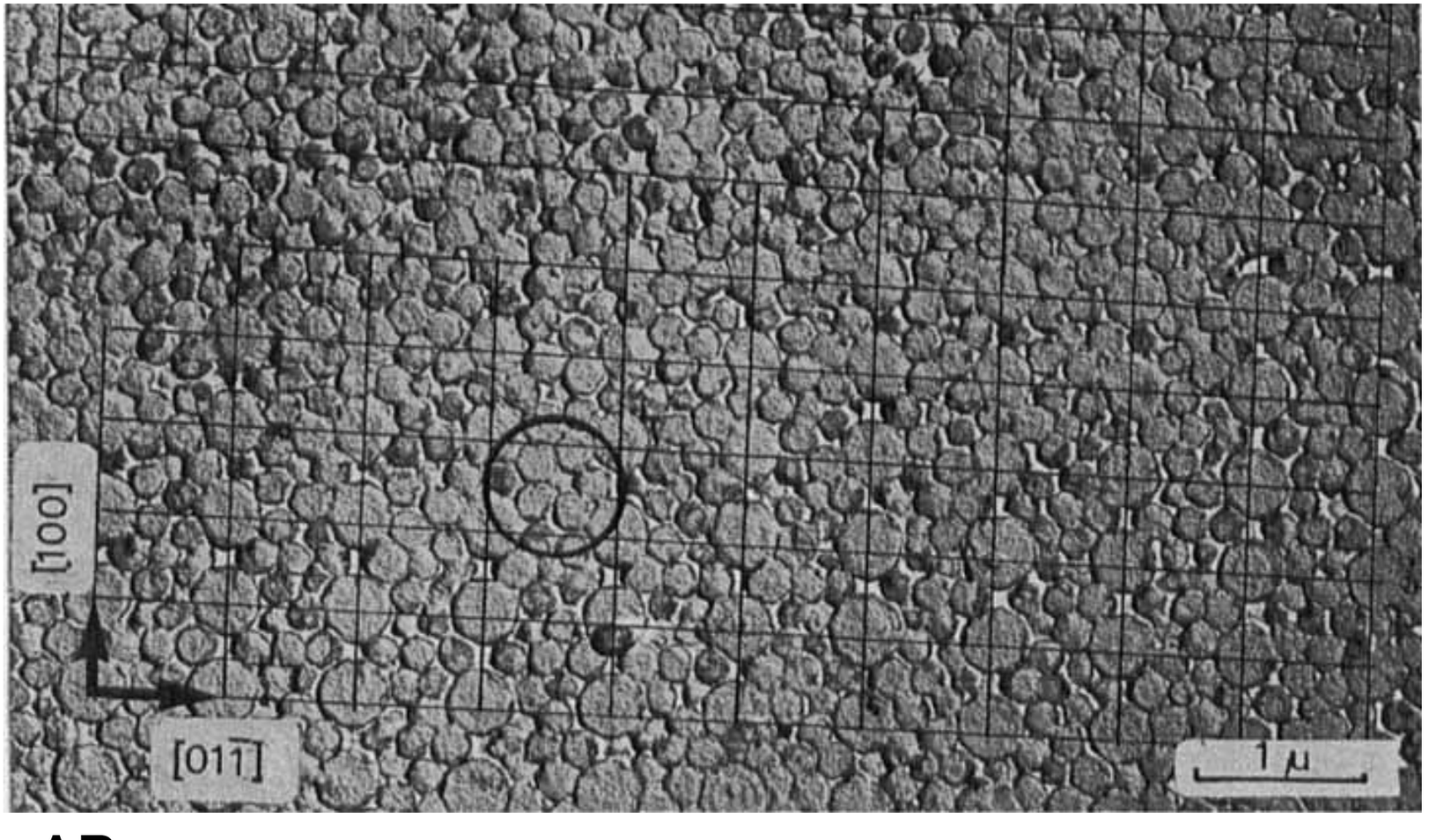
Colloids in nature initially size-disperse (?)

Some opals form binary crystals.

- Sanders, *Phil. Mag. A* **42**, 705 (1980)

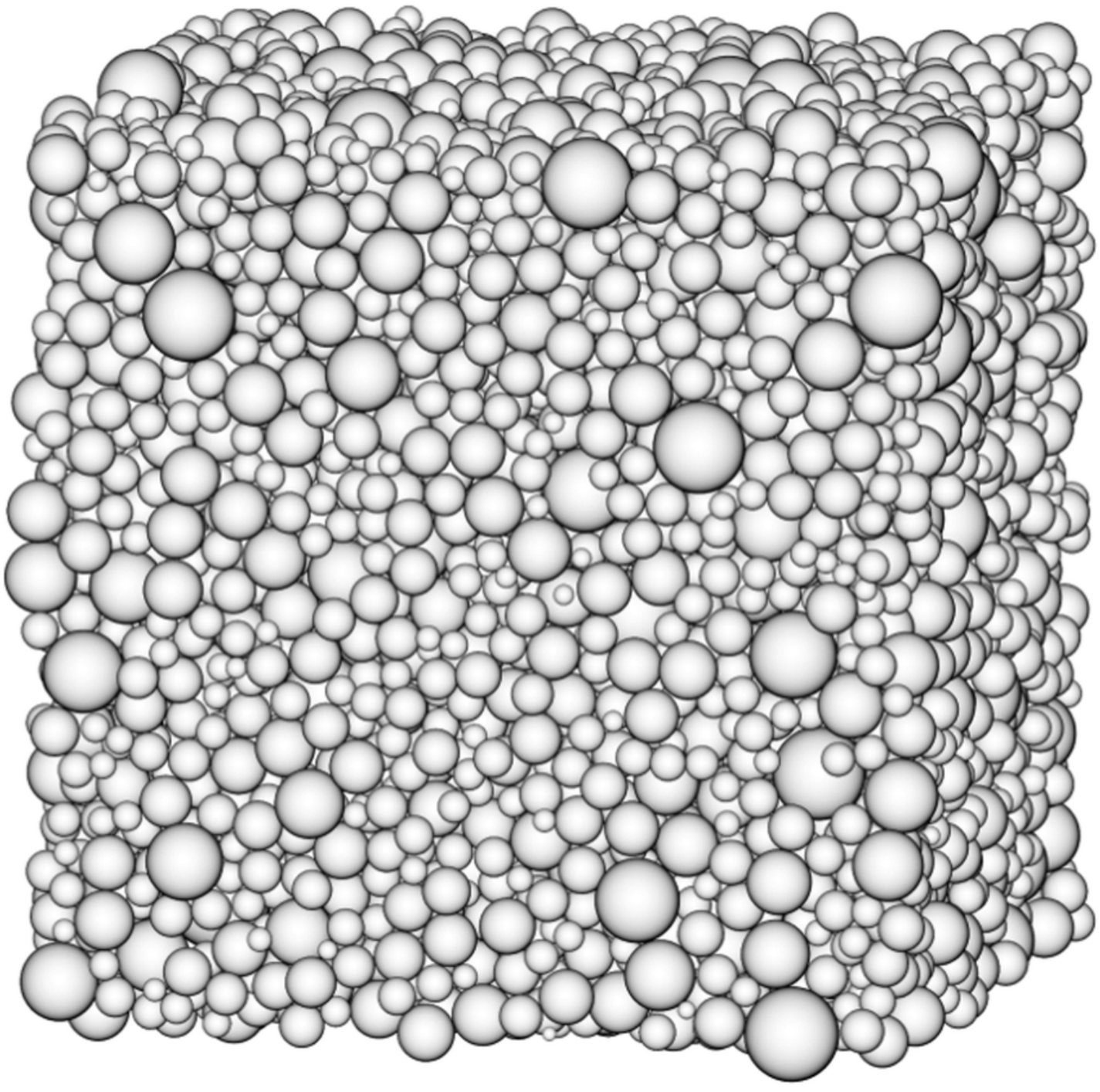
How is this possible?

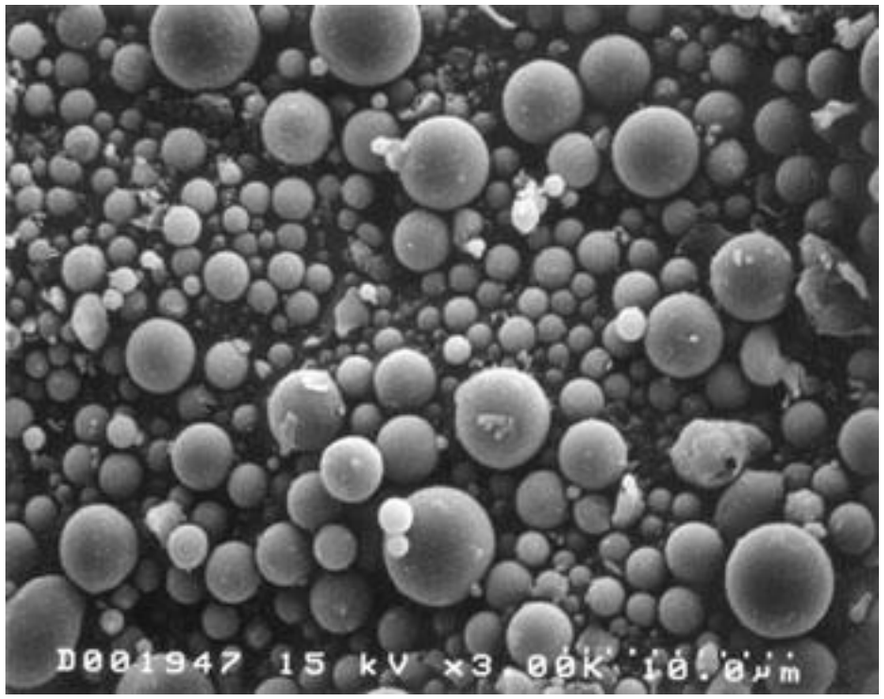




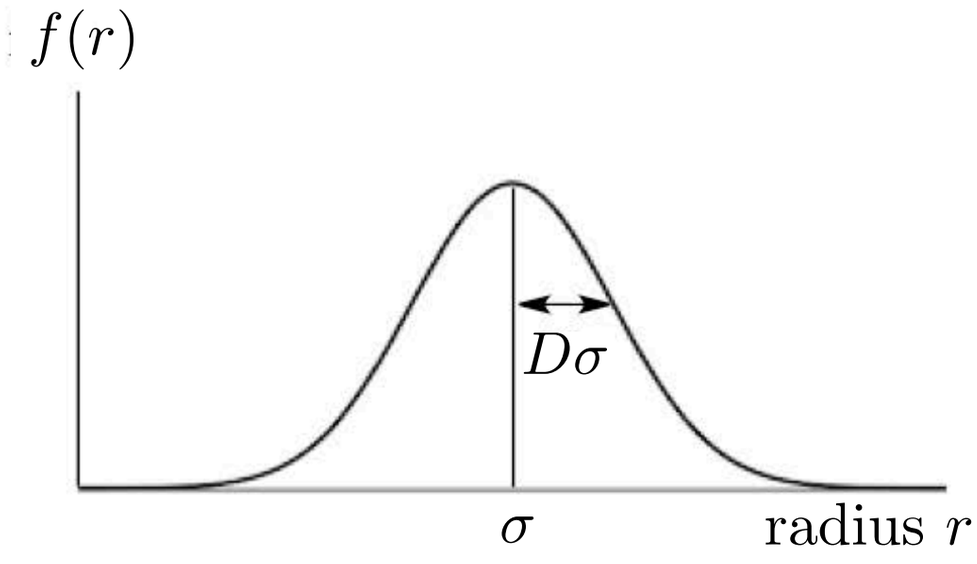
AB_2 AB_{13}

Size-disperse hard sphere mixture



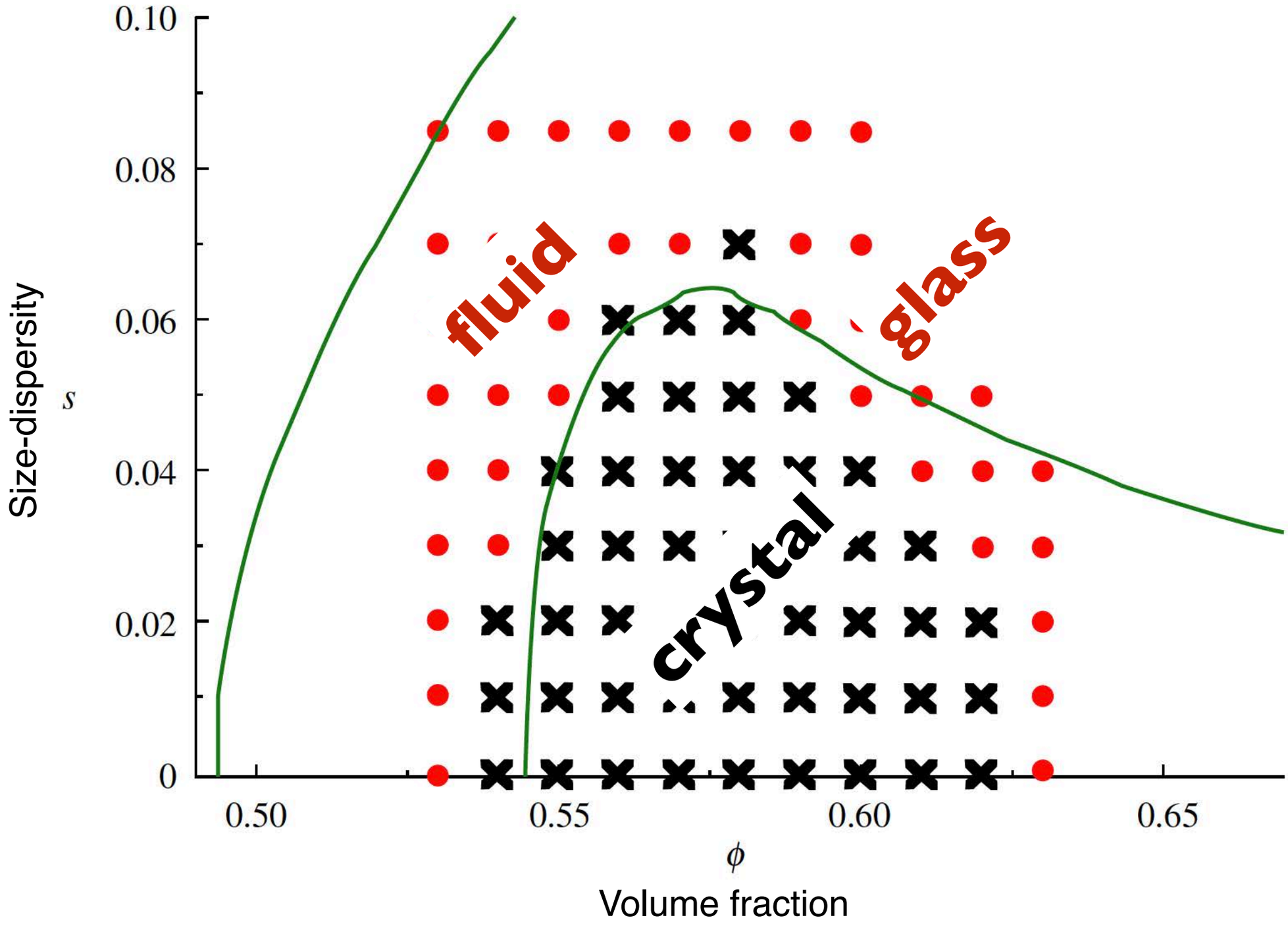


fly ash from combustion
U.S. Department of Transportation



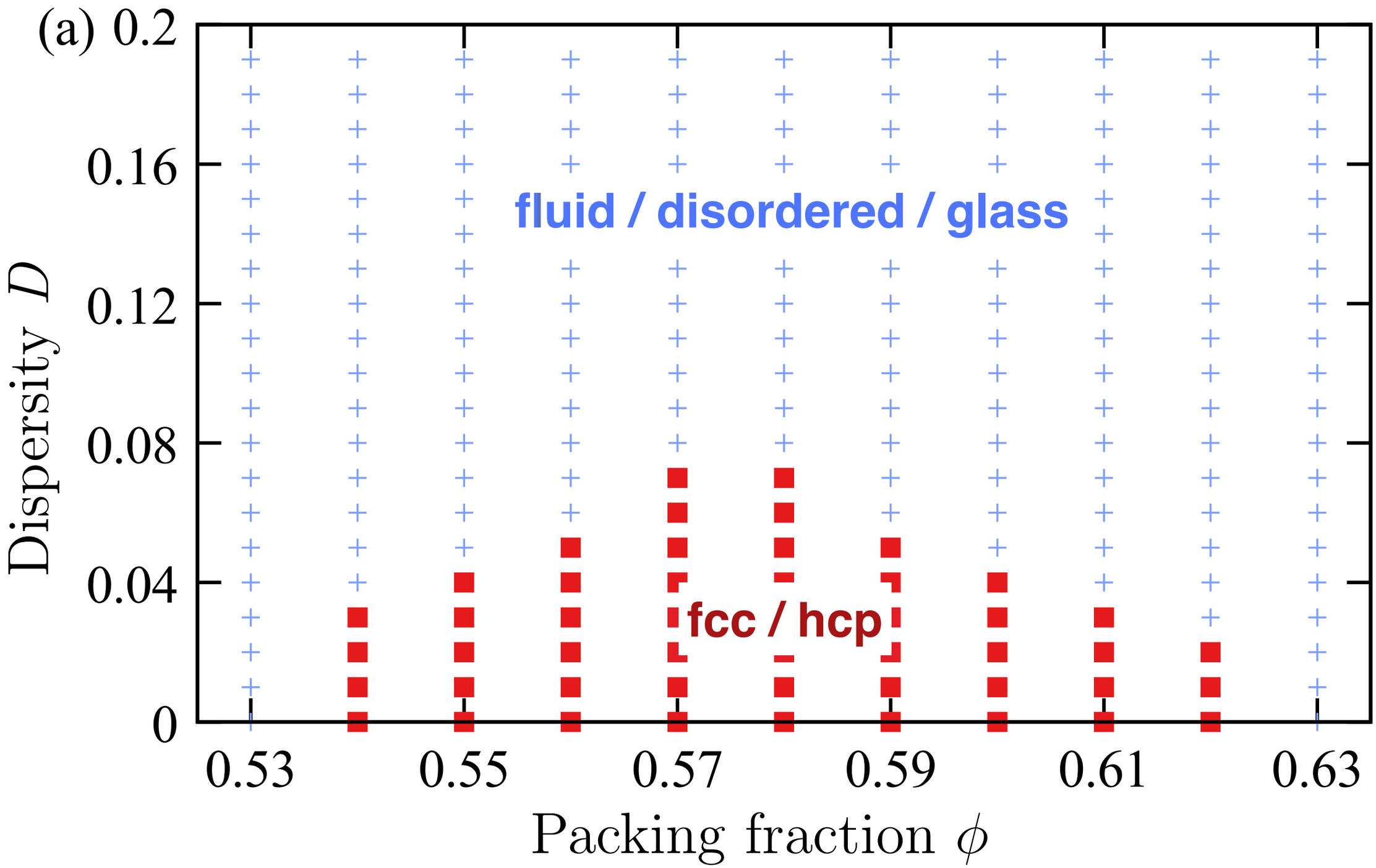
Gaussian radius distribution: $f(r) \propto \exp\left(-\frac{(2r/\sigma - 1)^2}{2D^2}\right)$ ← dispersity

Crystallization diagram from simulation

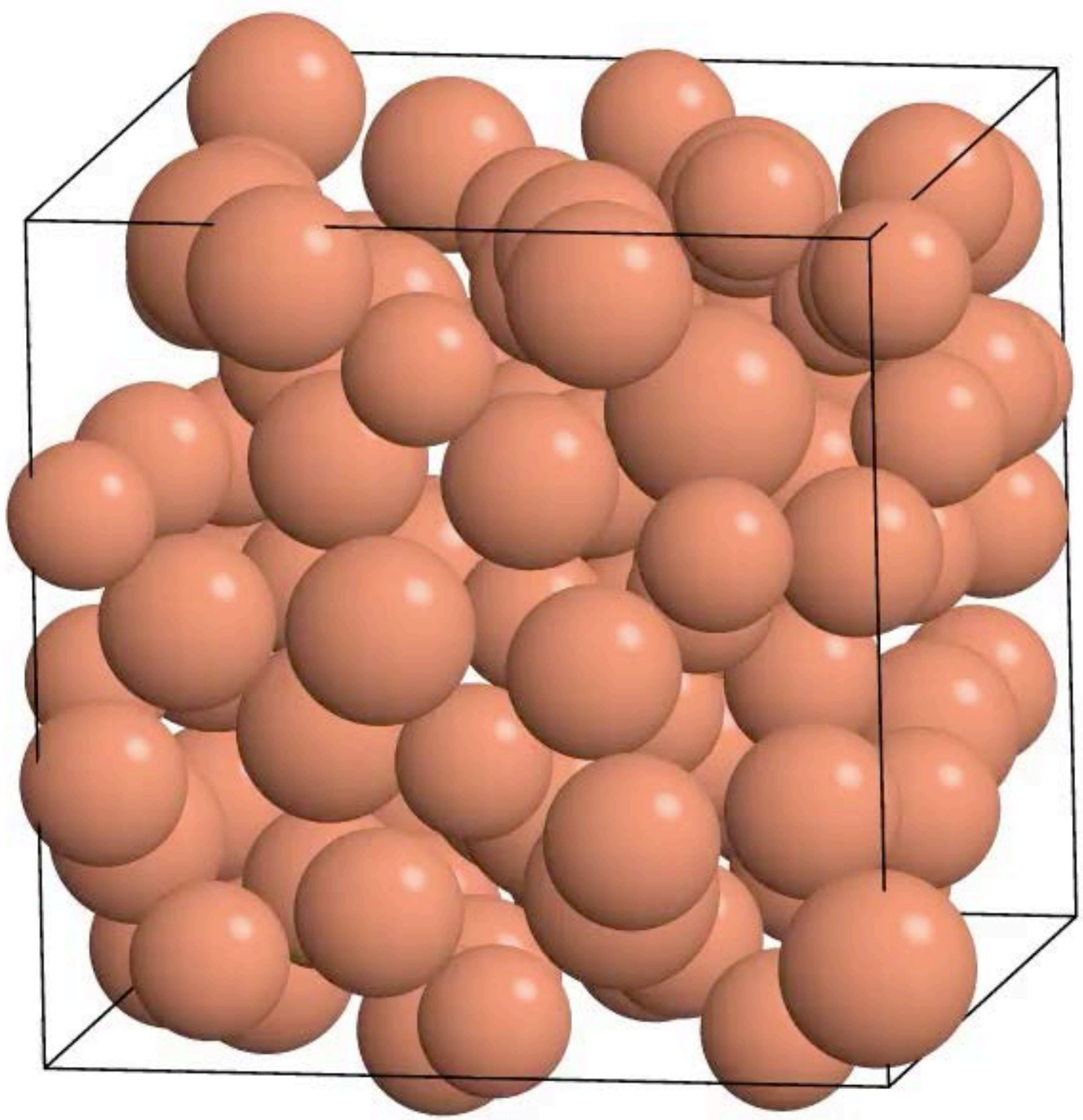


E. Zaccarelli, C. Valeriani, E. Sanz, W.C.K. Poon, M.E. Cates, P.N. Pusey
PRL **2009**, 103, 135704

Molecular dynamics of hard spheres

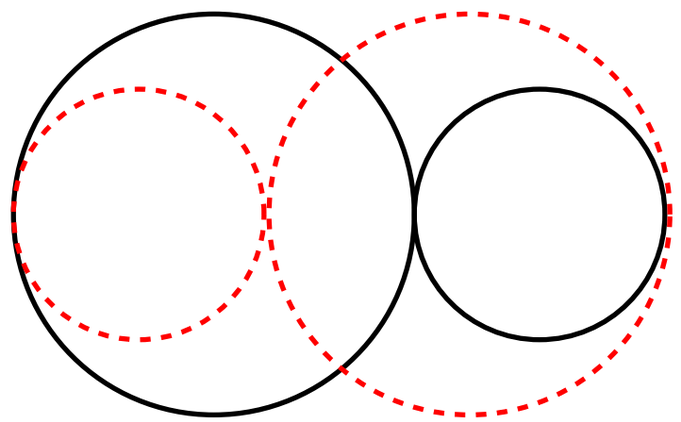


Event-driven molecular dynamics with swap

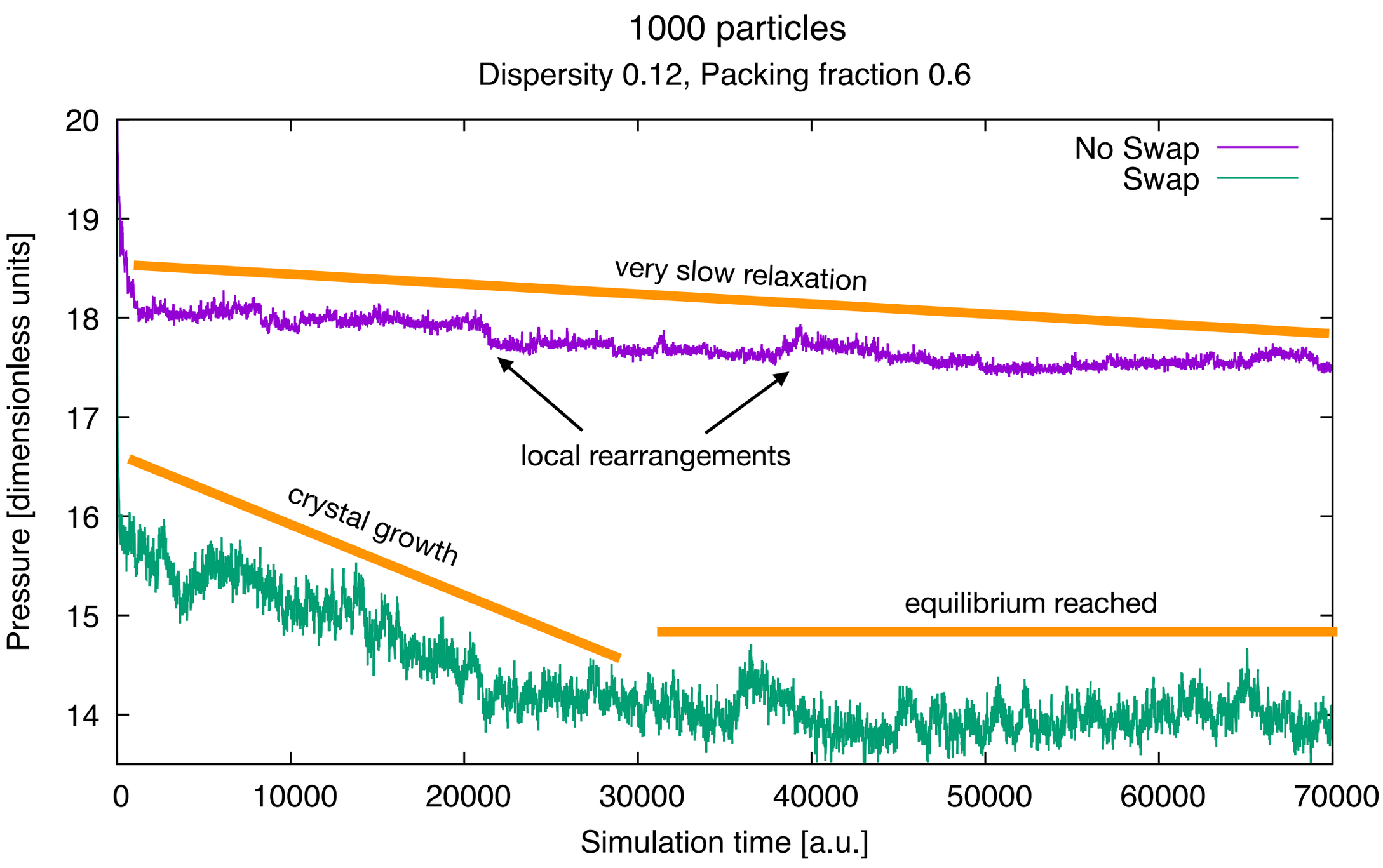


Swap particles at each collision (if possible)

- Kranendonk, Frenkel *J. Phys. Condens. Matter* **1**, 7735 (1989)
- Berthier et al. *Phys. Rev. Lett.* **116**, 238002 (2016)



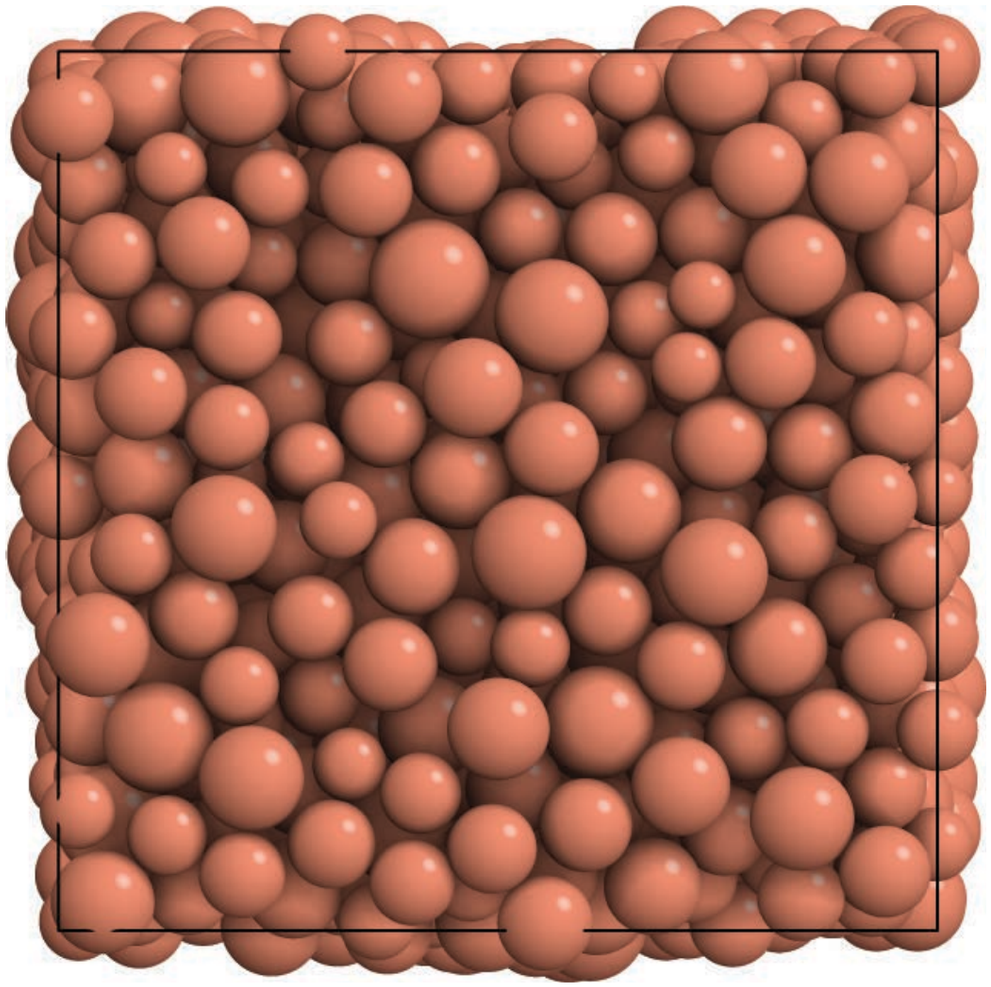
Orders of magnitude speed-up by swap moves

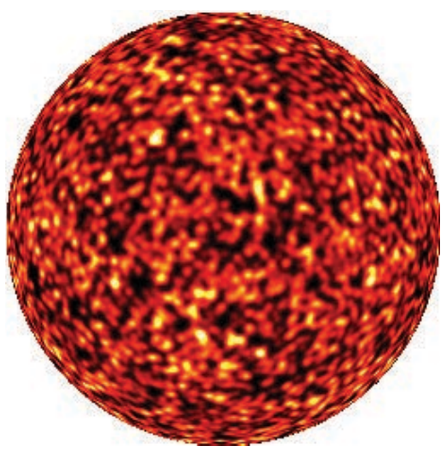


about 1.5 CPU hours in total

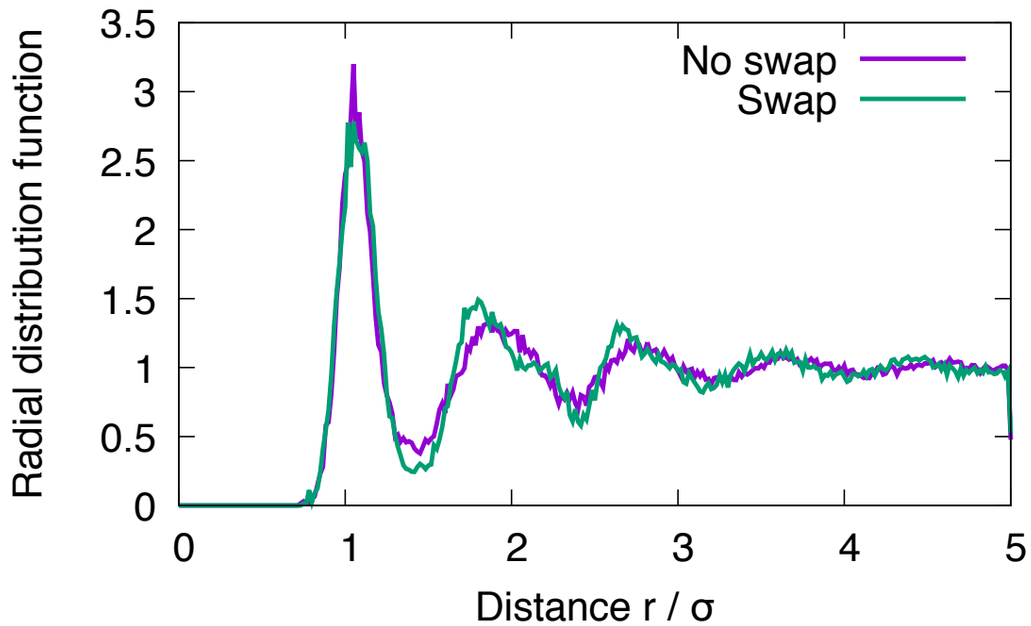
Crystal structure analysis

No swap

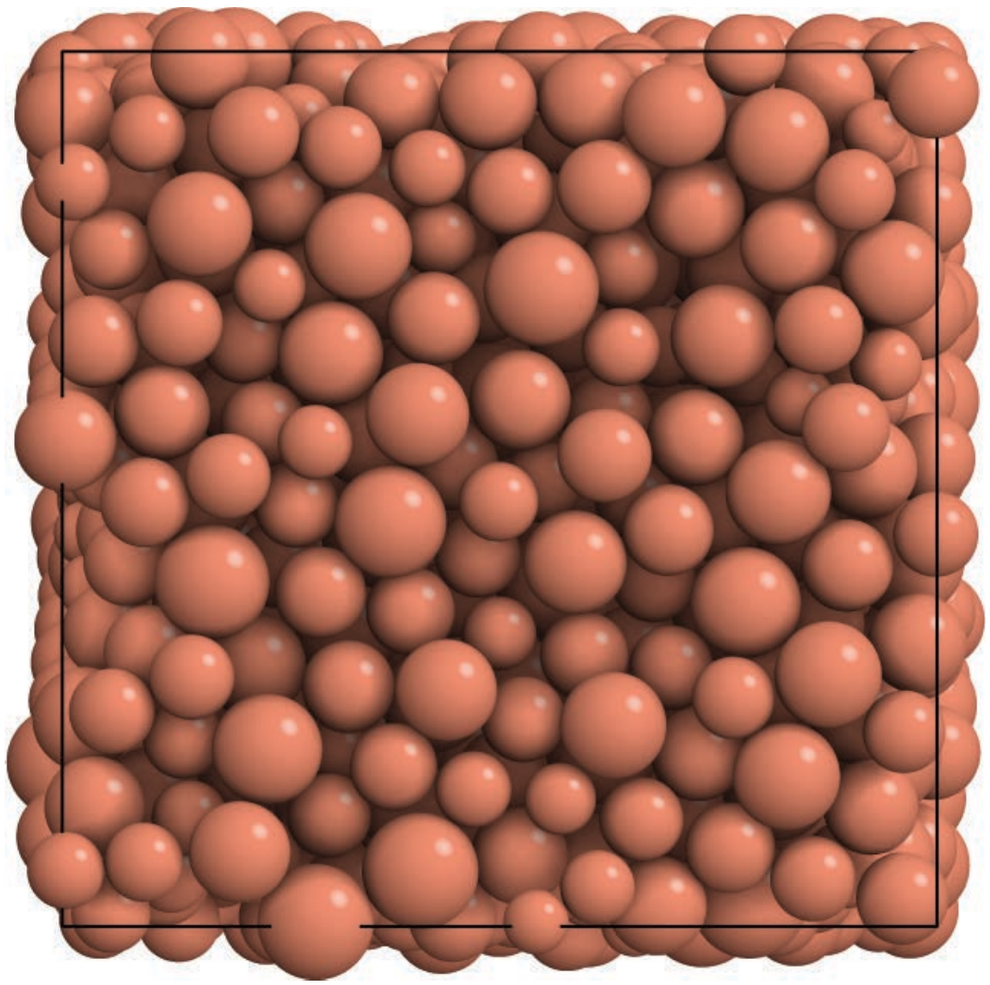


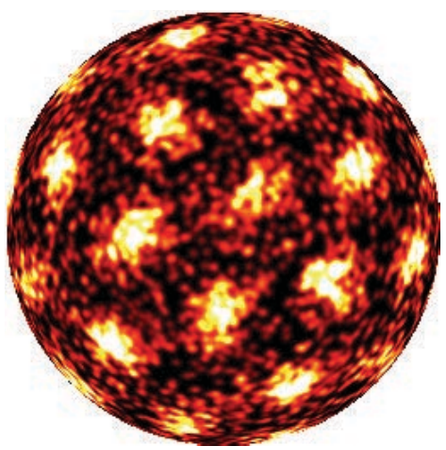


Bond orientational order diagram (BOD)



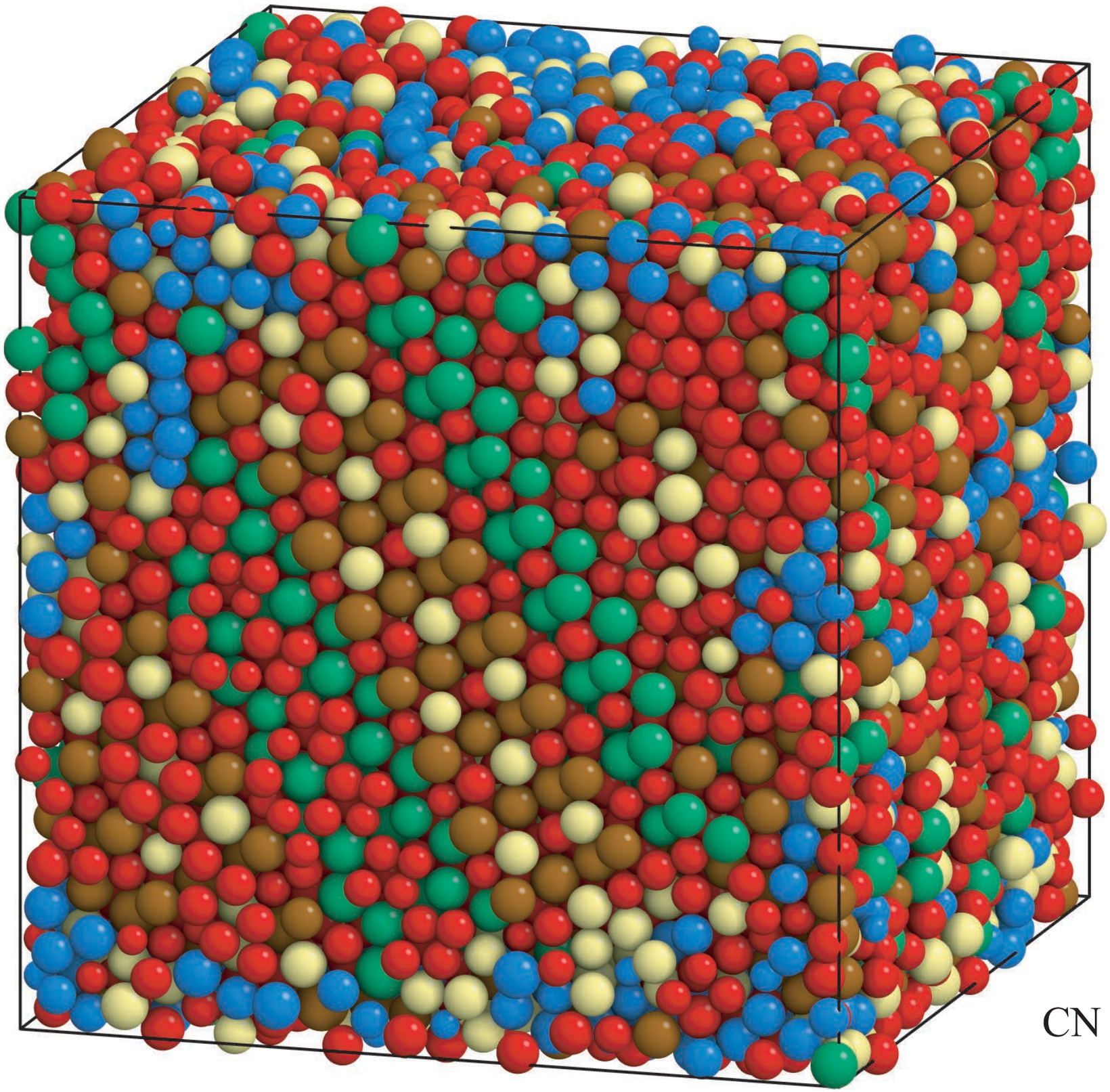
Swap





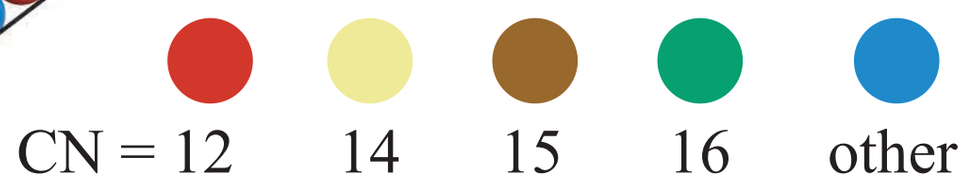
Bond orientational order diagram (BOD)

Ordering observed *via* coordination number



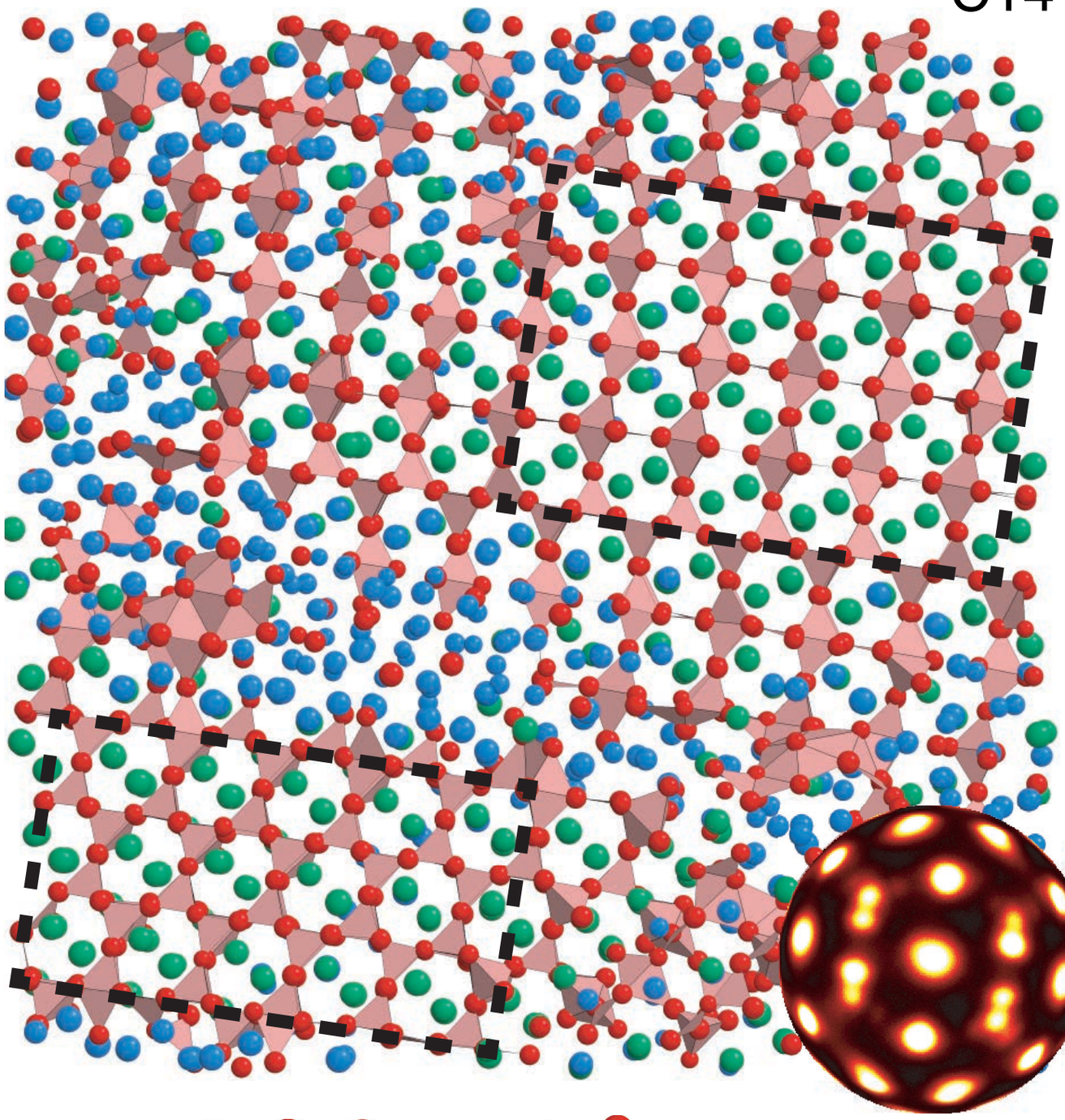
Particles colored by coordination number (CN)

- low CN = small particles
- high CN = large particles



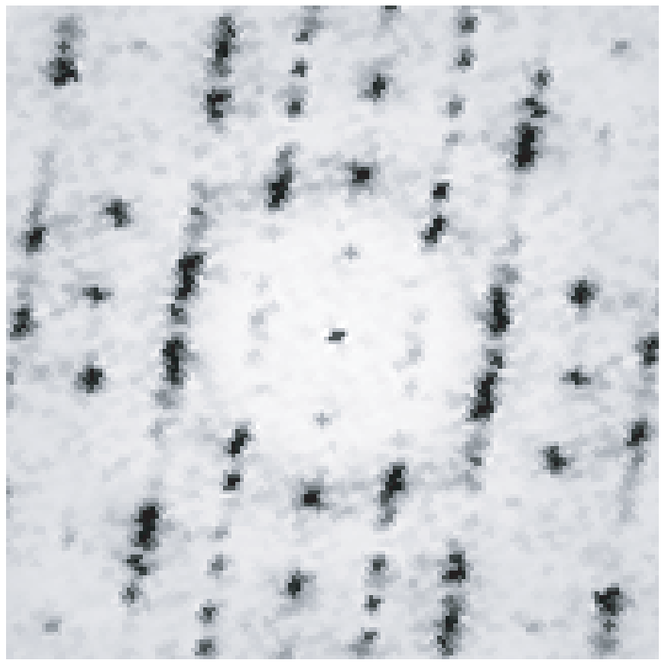
Discovery of Laves phases

C14



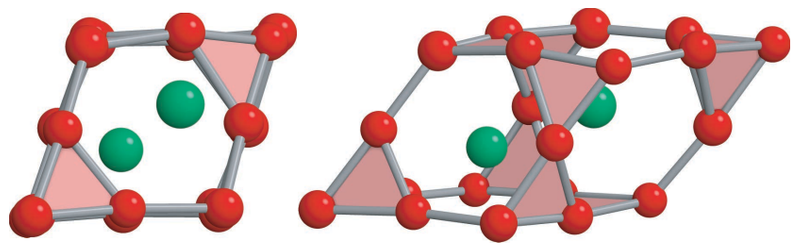
C15

BOD



diffraction (FFT)

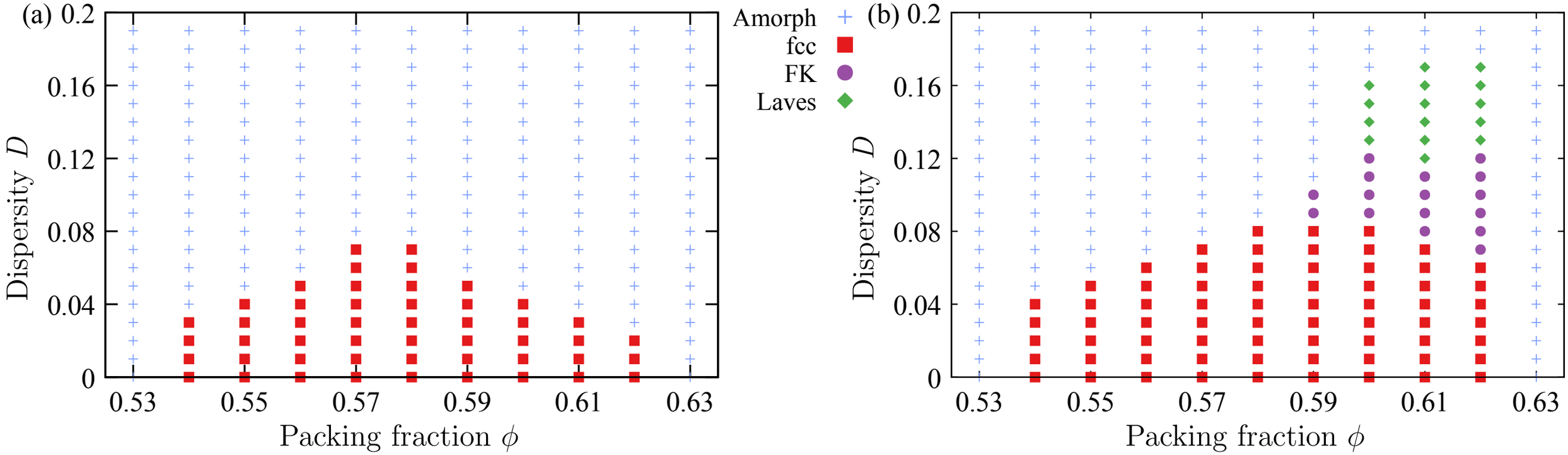
unit cell (C15):



Phase observation diagram with swap algorithm

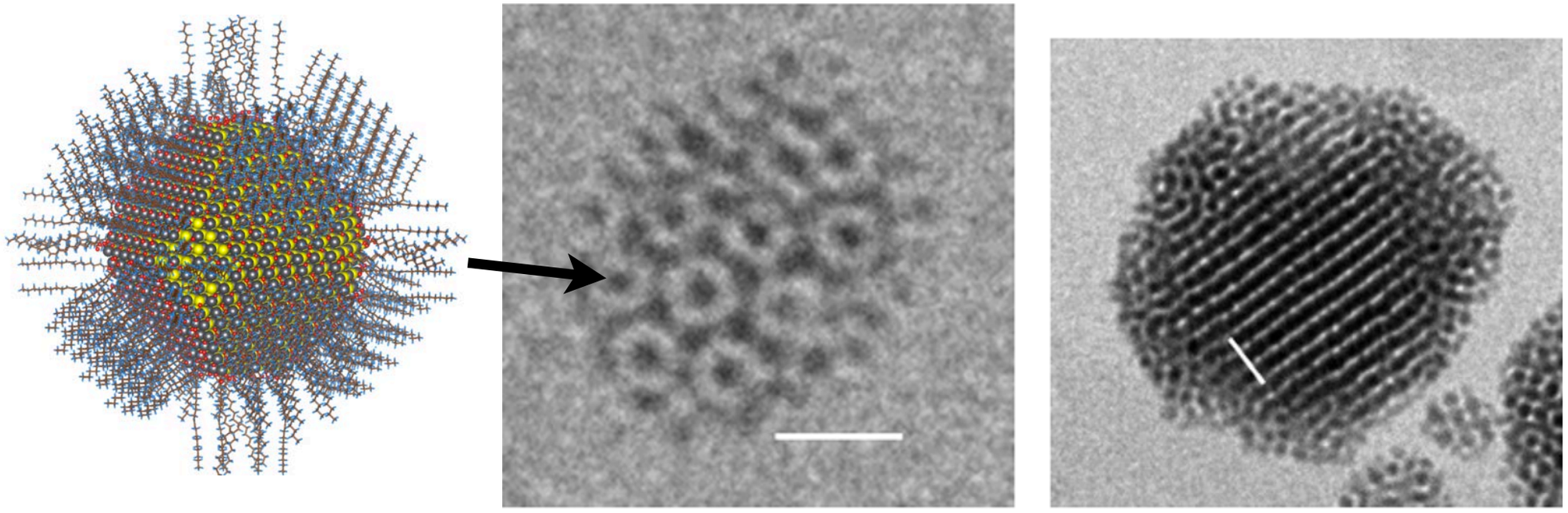
without swap

with swap



Bommineni, Varela-Rosales, Klement, ME, *Phys. Rev. Lett.* **2019**

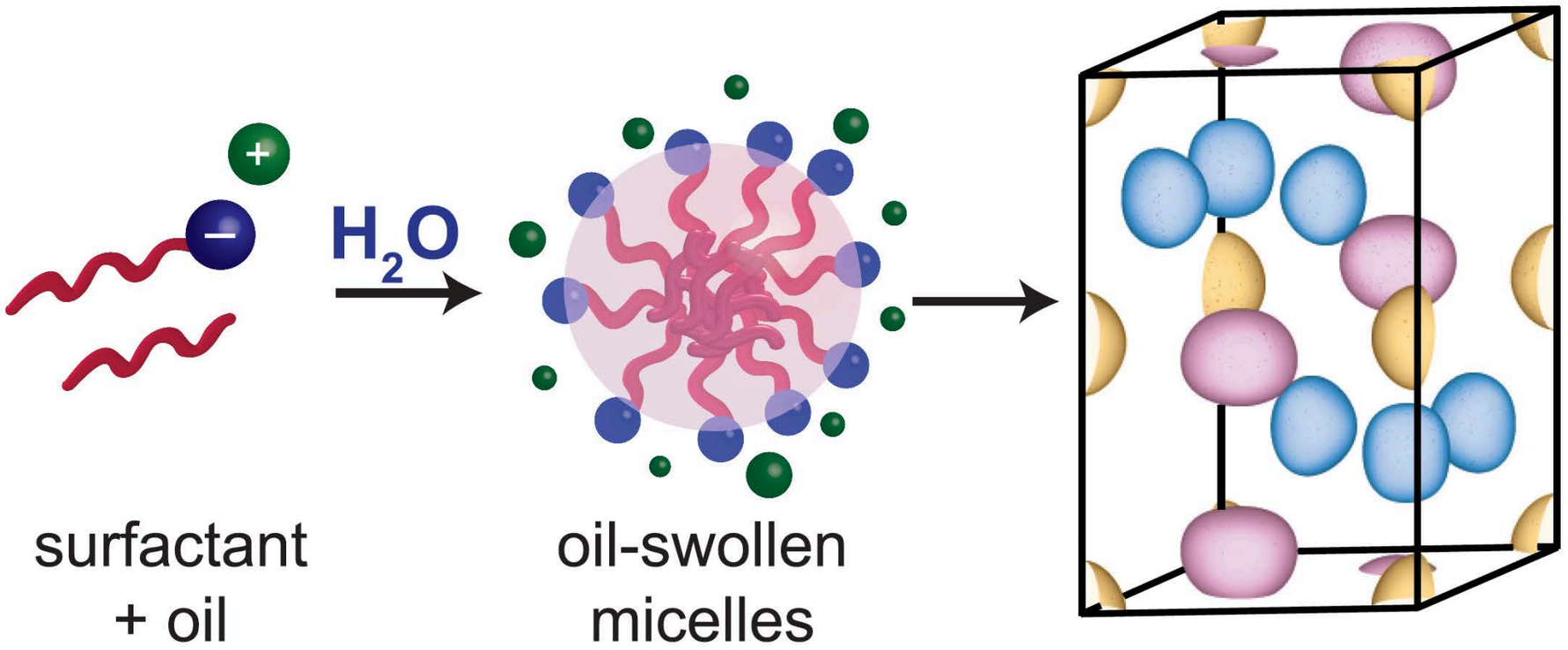
Laves phases in one-component systems



2.5 nm diameter Au nanocrystals

C14 Laves phase

S. Hajiw, B. Pansu, J.-F. Sadoc, *ACS Nano* **2015**, 9, 8116



soft spherical micelles from hydrated mixture TMADec-40

C14 + C15 Laves

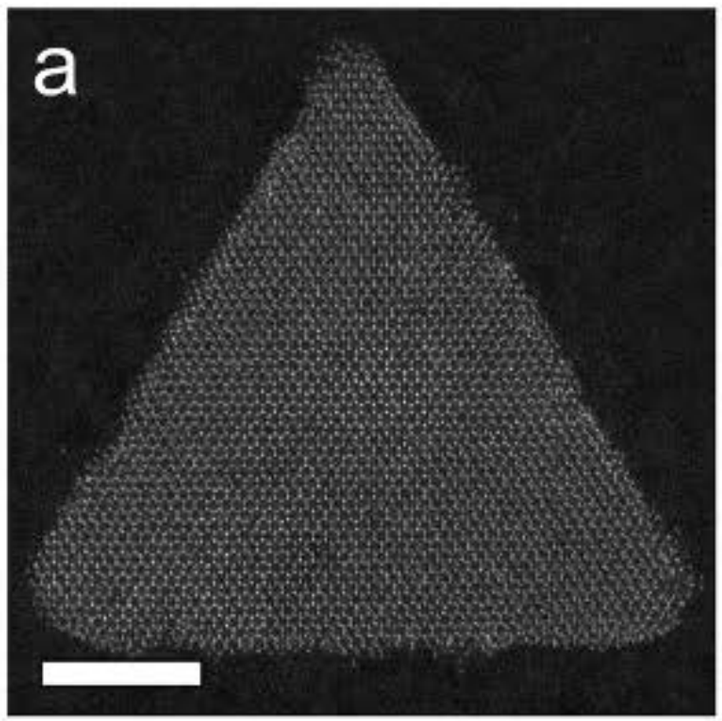
C.M. Baez-Cotto, M.K. Mahanthappa, *ACS Nano* **2018**, 12, 3226

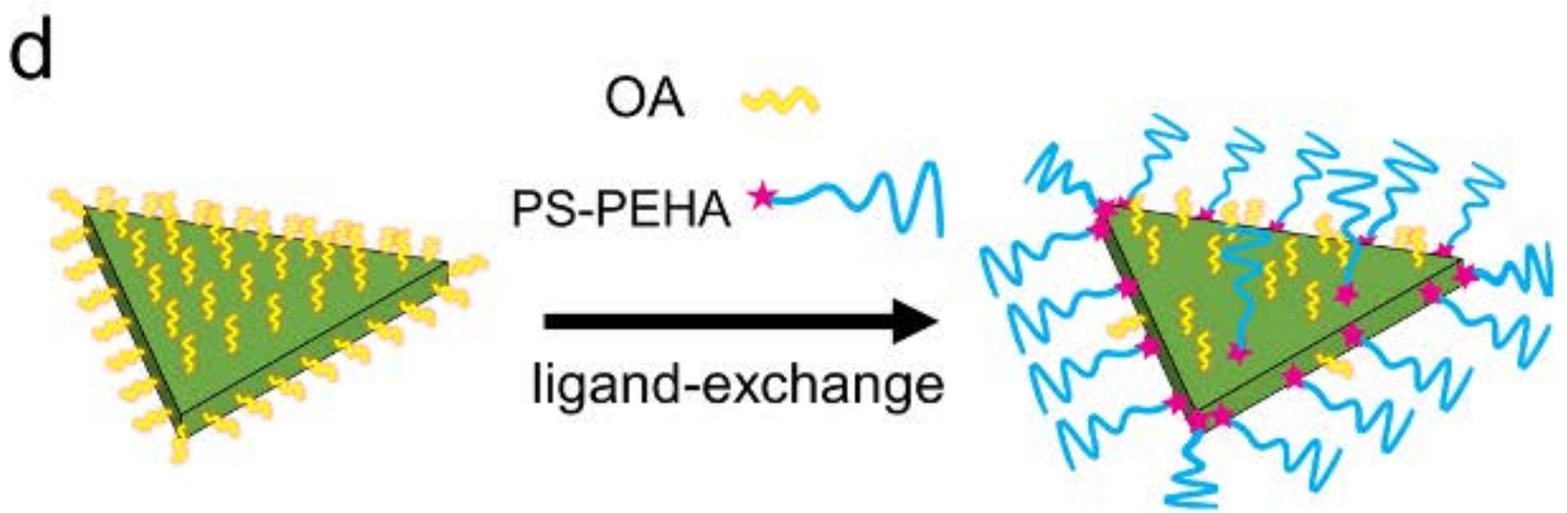
Outline

- Self-assembly of complex crystals on the computer
- Relationship between structure and formation pathways
- Finite magic number clusters
- Role of polydispersity
- **Modeling anisotropic patchy interactions**
- Simulating crystal growth (incomplete)

Anisotropic patchy interactions

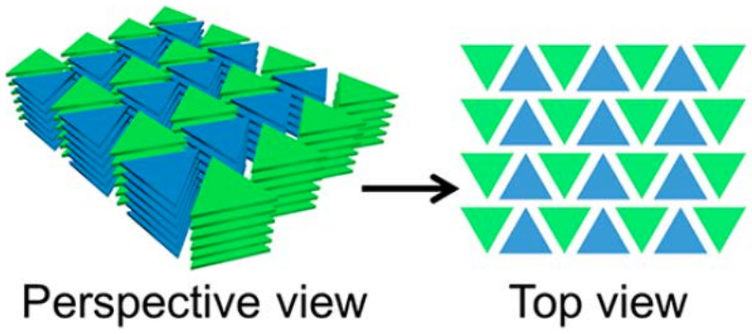
PS-grafted Gd_2O_3 triangular nanoprisms @ Ye lab (Indiana)

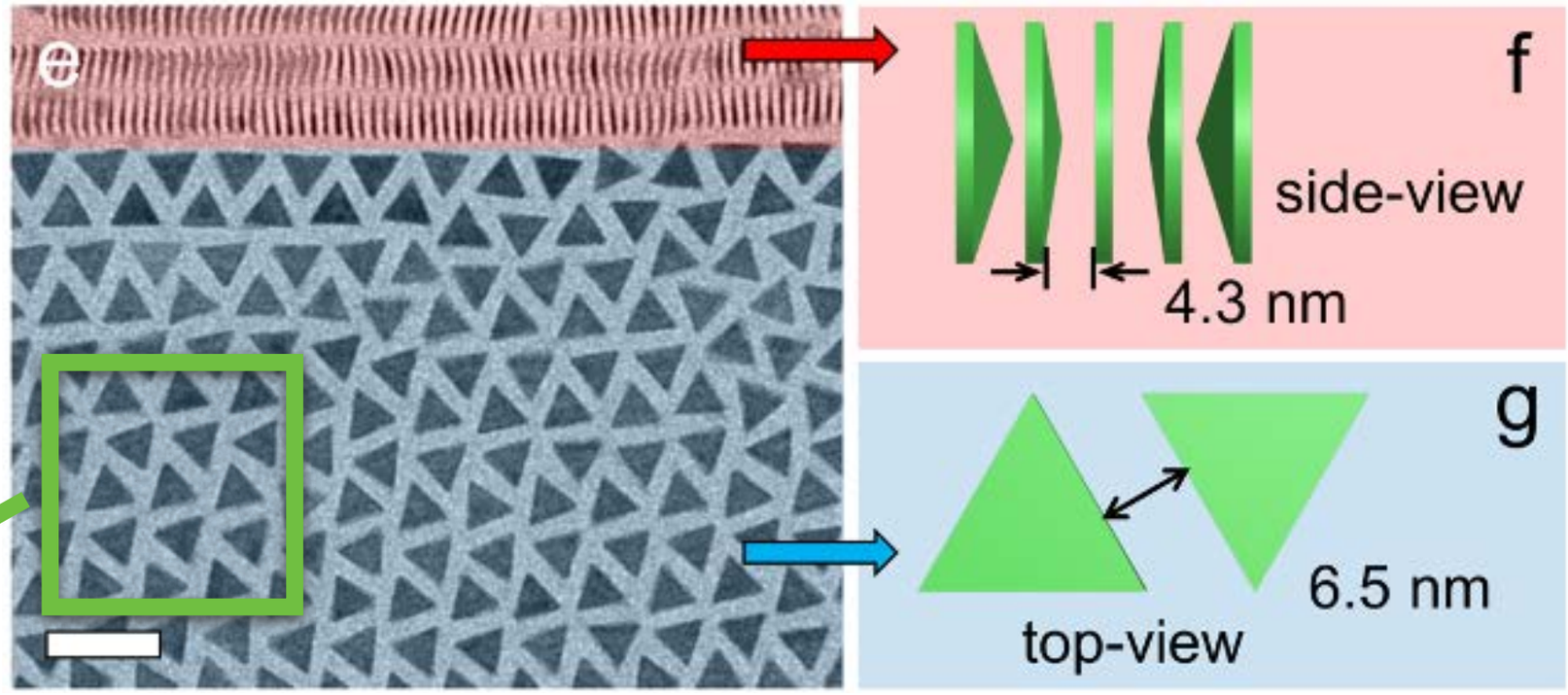




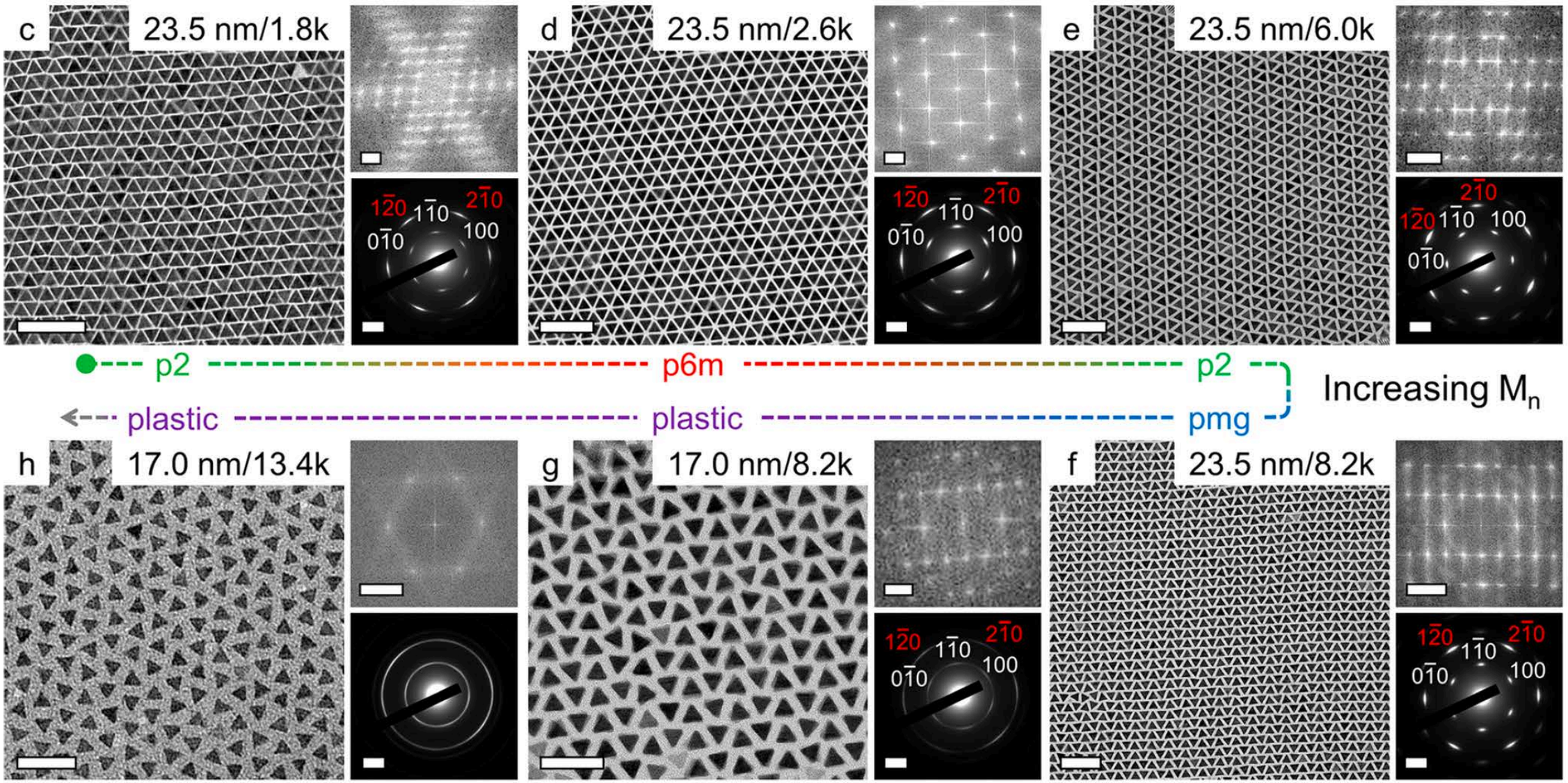
Assembly:

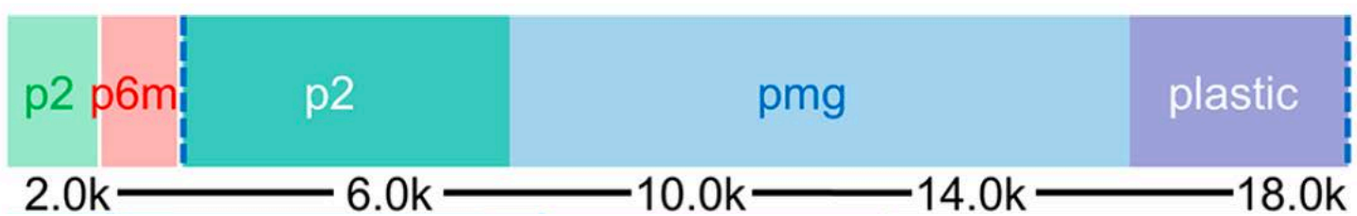
- columns
- laying down (stacked)





Self-assembly of triangles



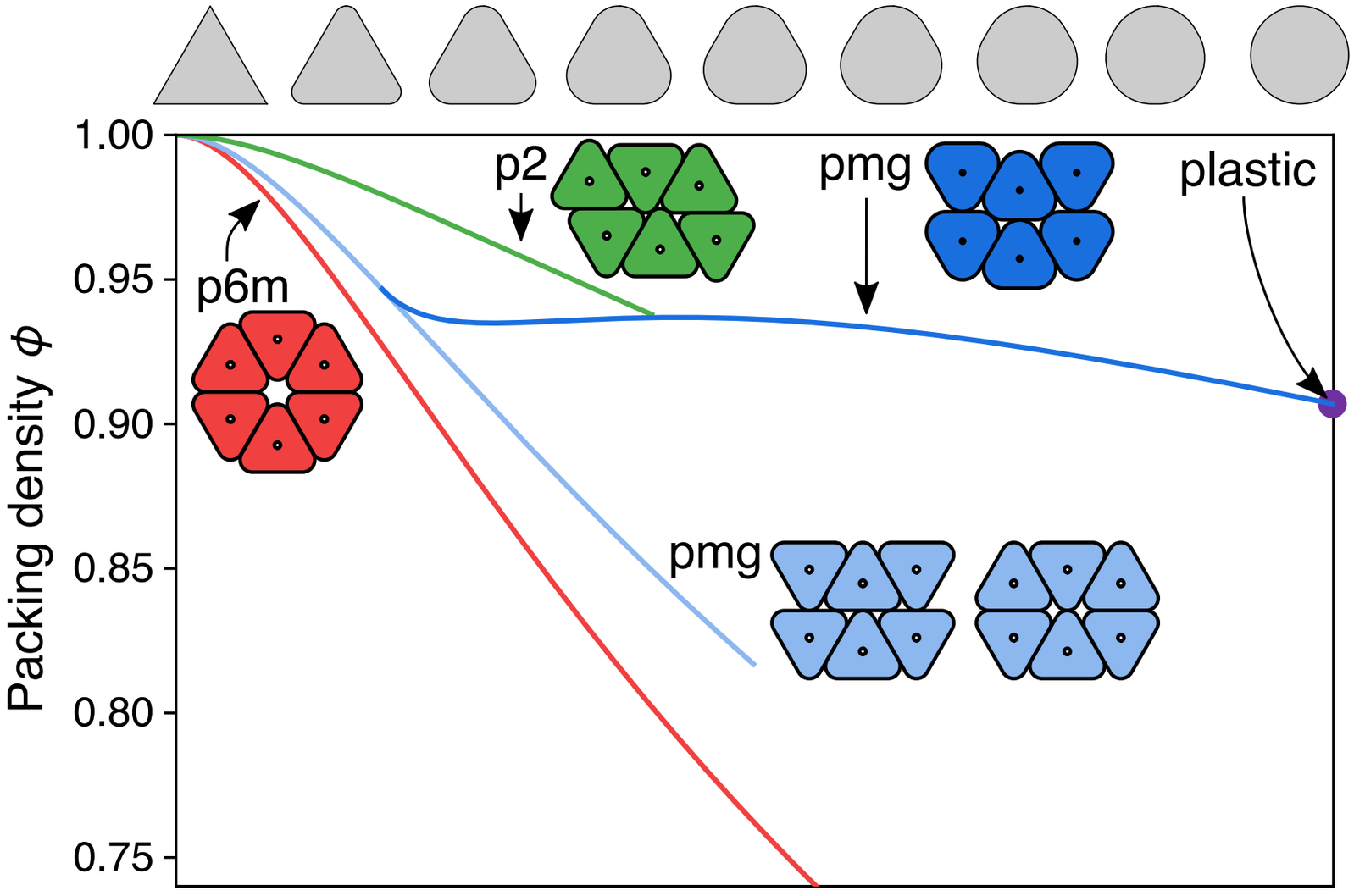


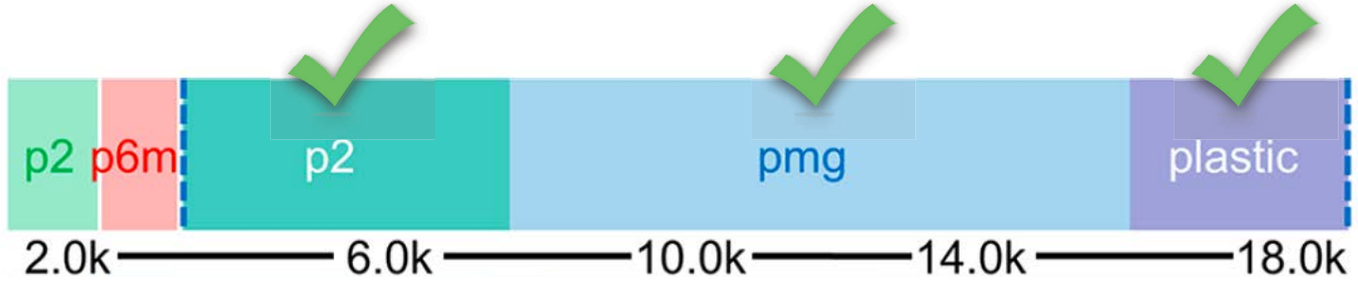
Y. Liu, M. Klement, Y. Wang, Y. Zhong, B. Zhu, J. Chen, ME, X. Ye, *JACS* **2021**, 143 16163

Level 1: Densest packing

Analytic construction

- (1) ligands round particle shape
- (2) results in lattice shear

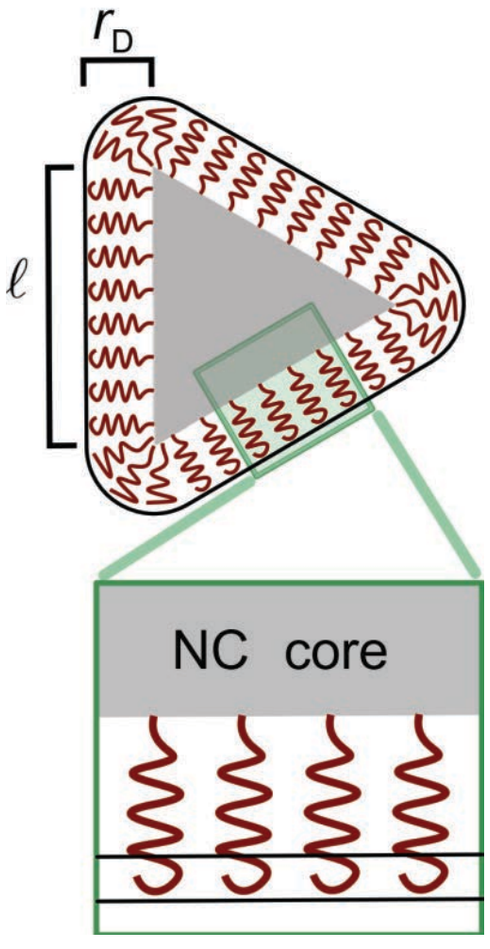


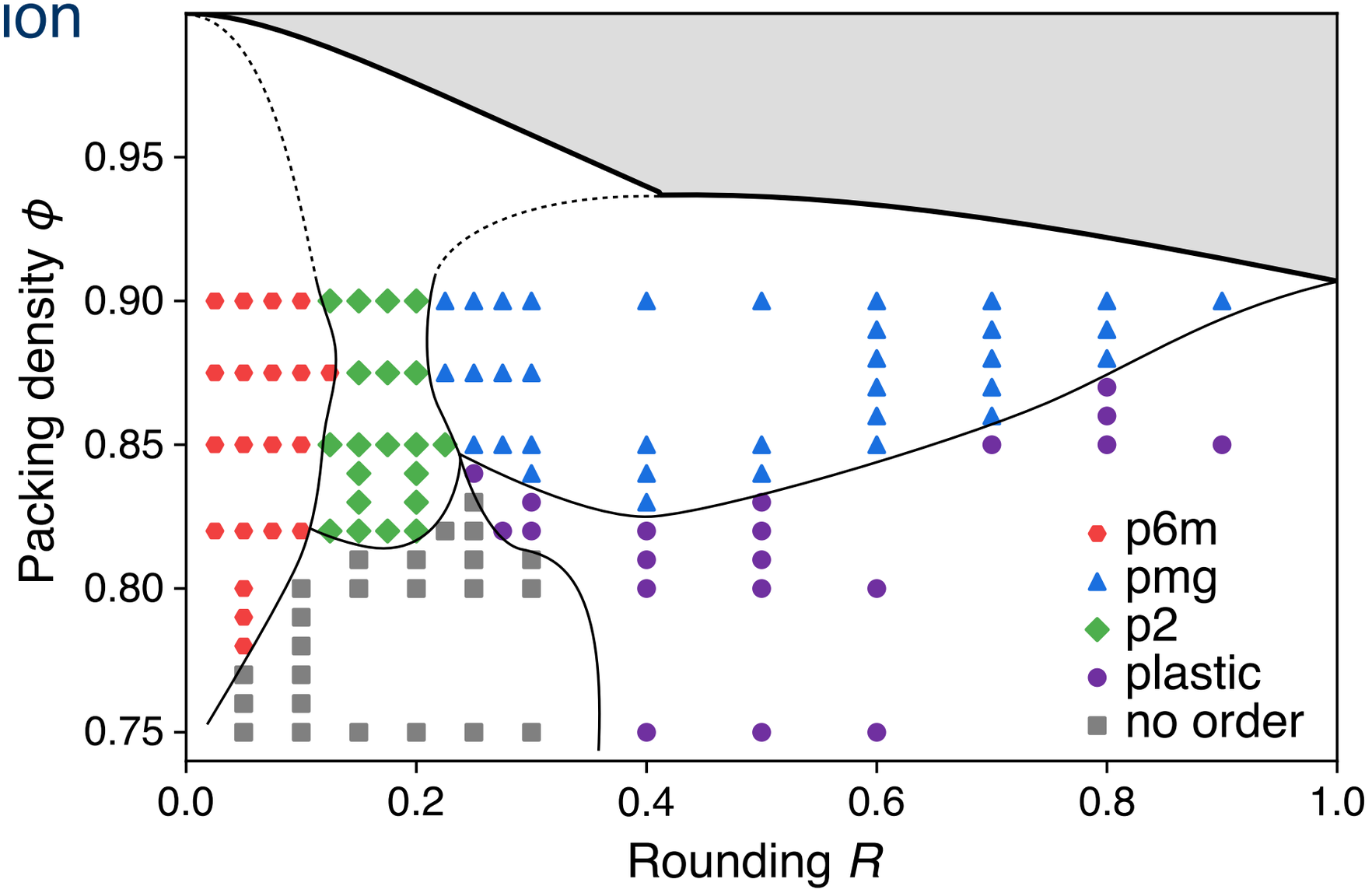


Level 2: Hard particle simulation

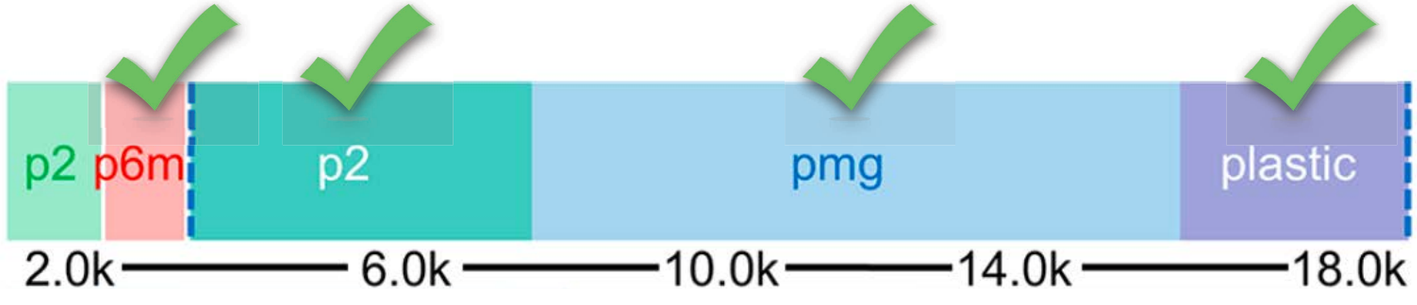
Monte Carlo simulation

- entropy favors high-symmetry lattice p6m





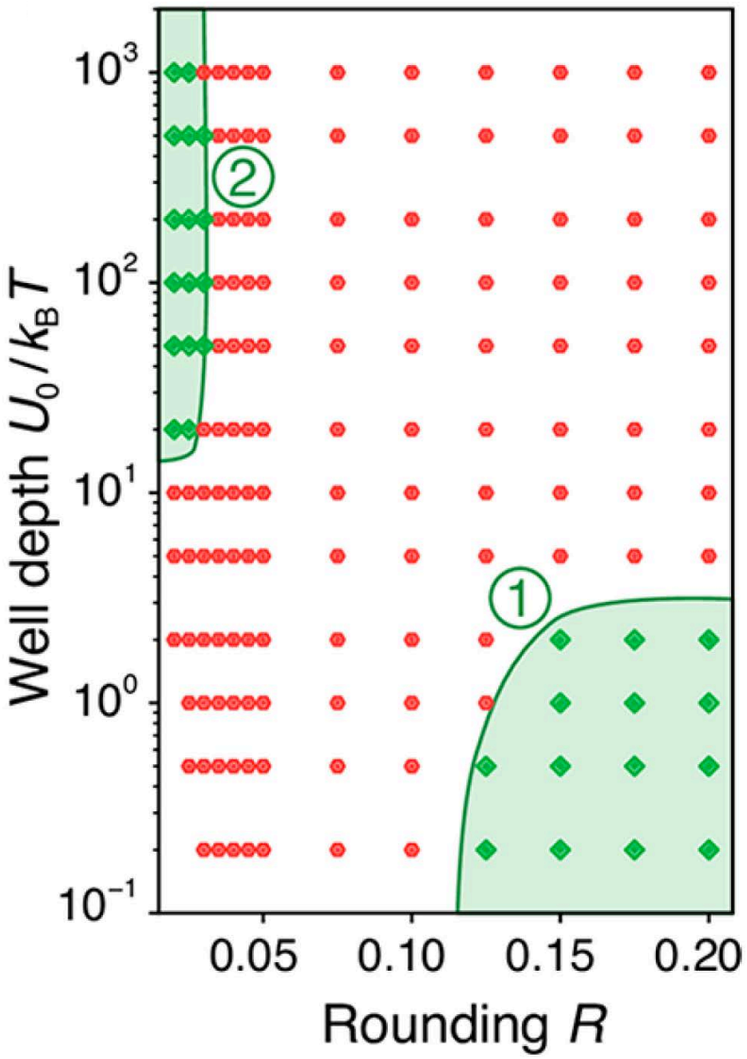
Comparison to experiment:

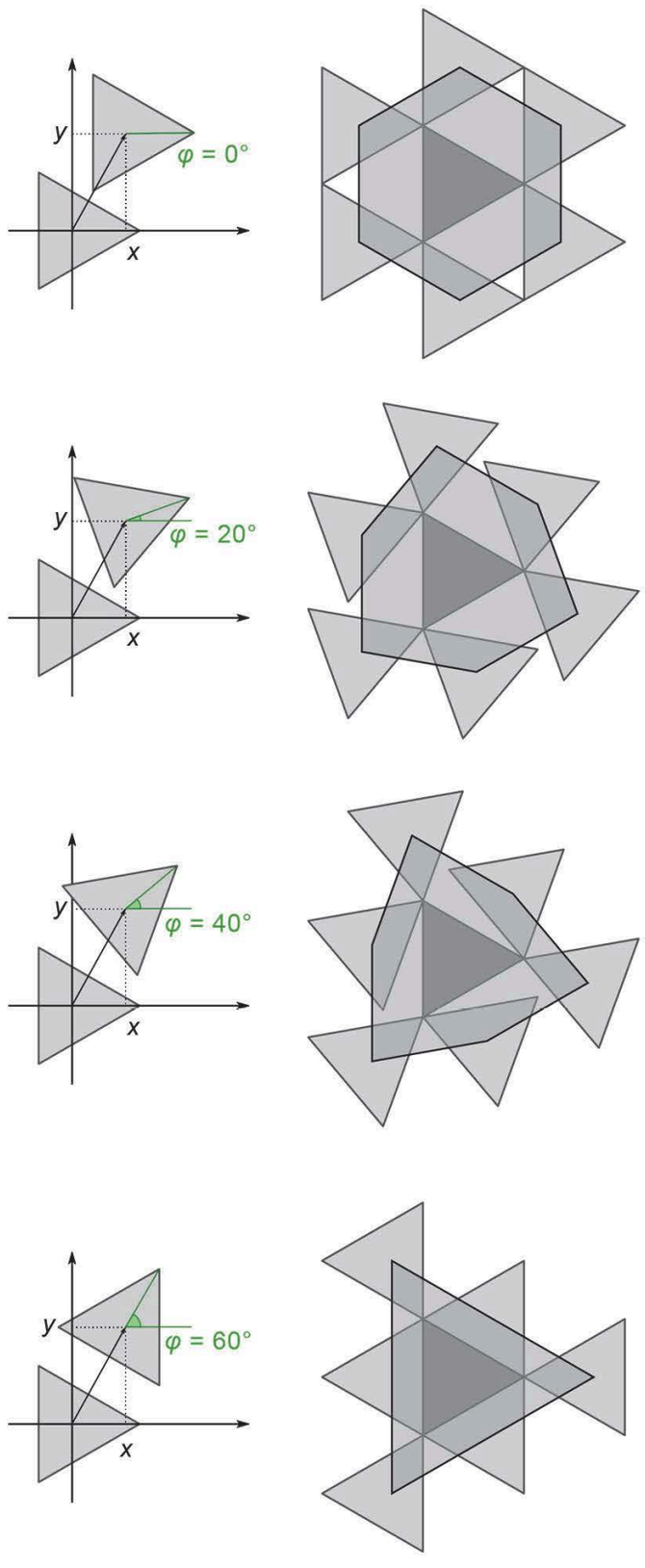


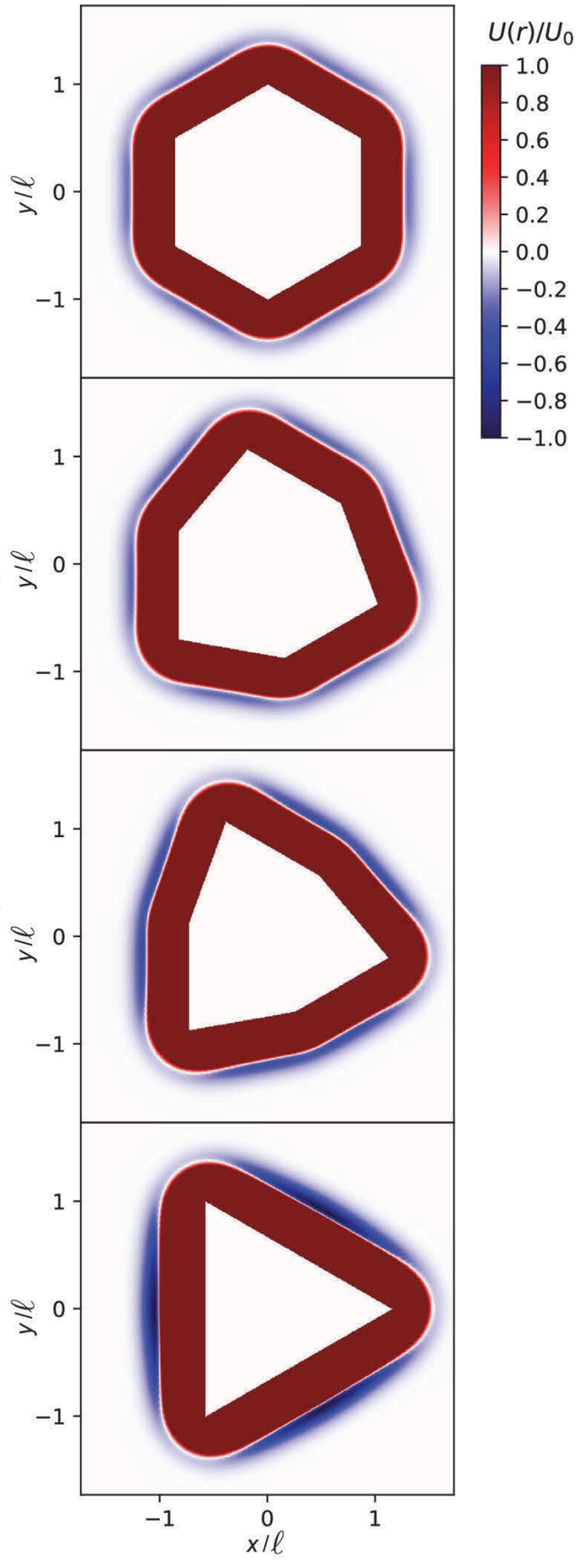
Y. Liu, M. Klement, Y. Wang, Y. Zhong, B. Zhu, J. Chen, ME, X. Ye, *JACS* **2021**, 143 16163

Level 3: Anisotropic patchy interactions (multiscale)

Precomputed tables



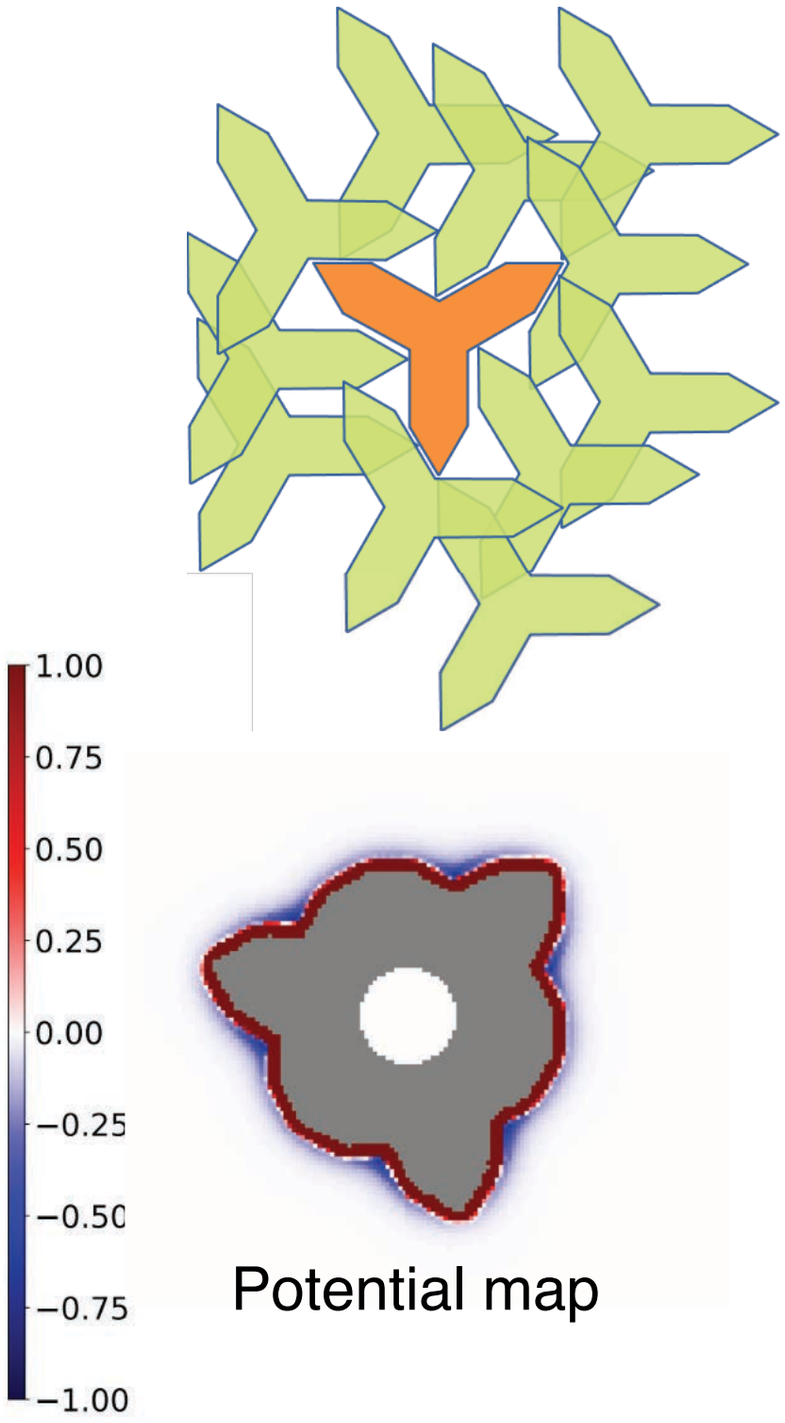




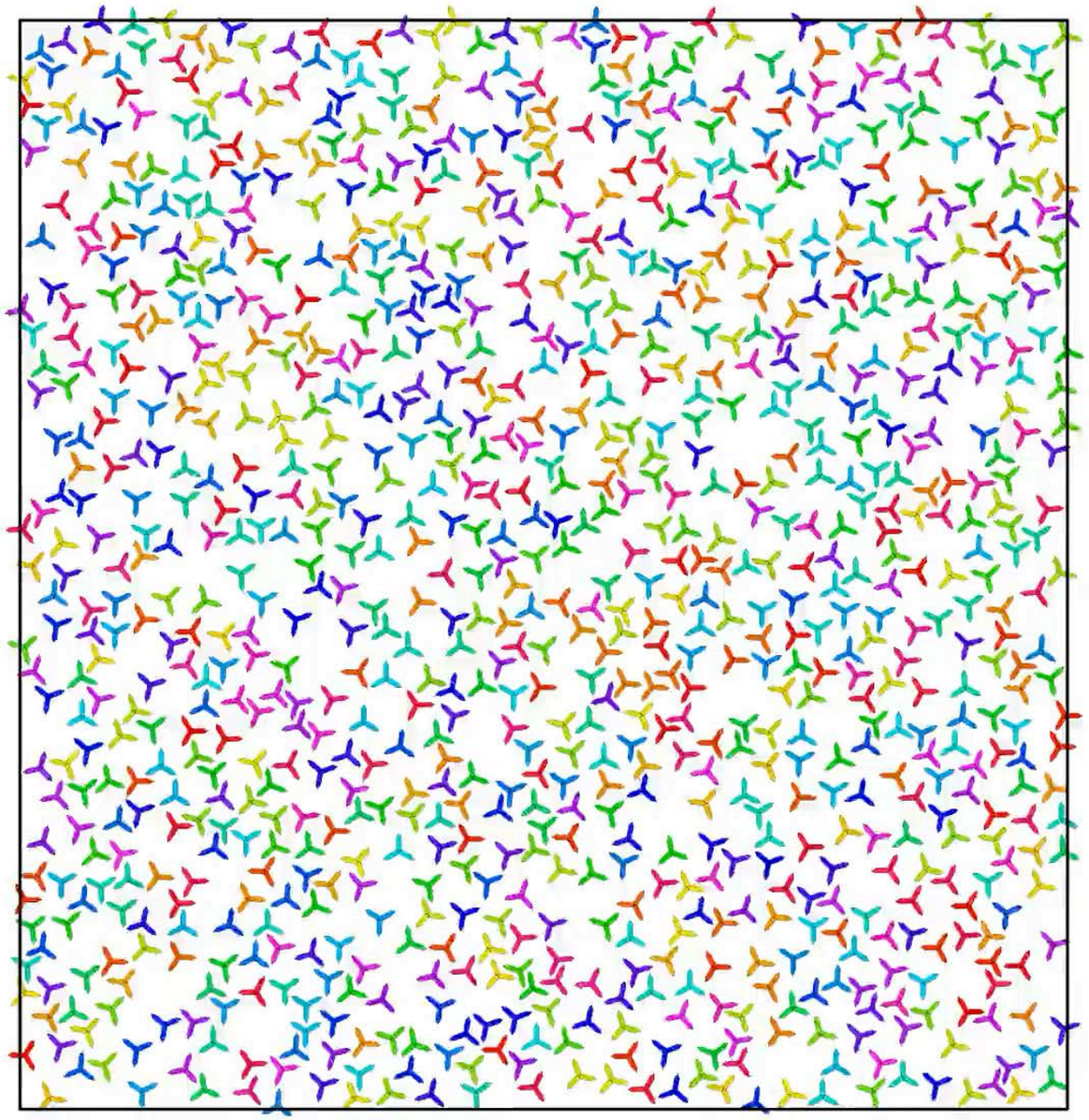
Y. Liu, M. Klement, Y. Wang, Y. Zhong, B. Zhu, J. Chen, ME, X. Ye, *JACS* **2021**, 143 16163

Outlook: More shapes

Tripod particles



Potential map



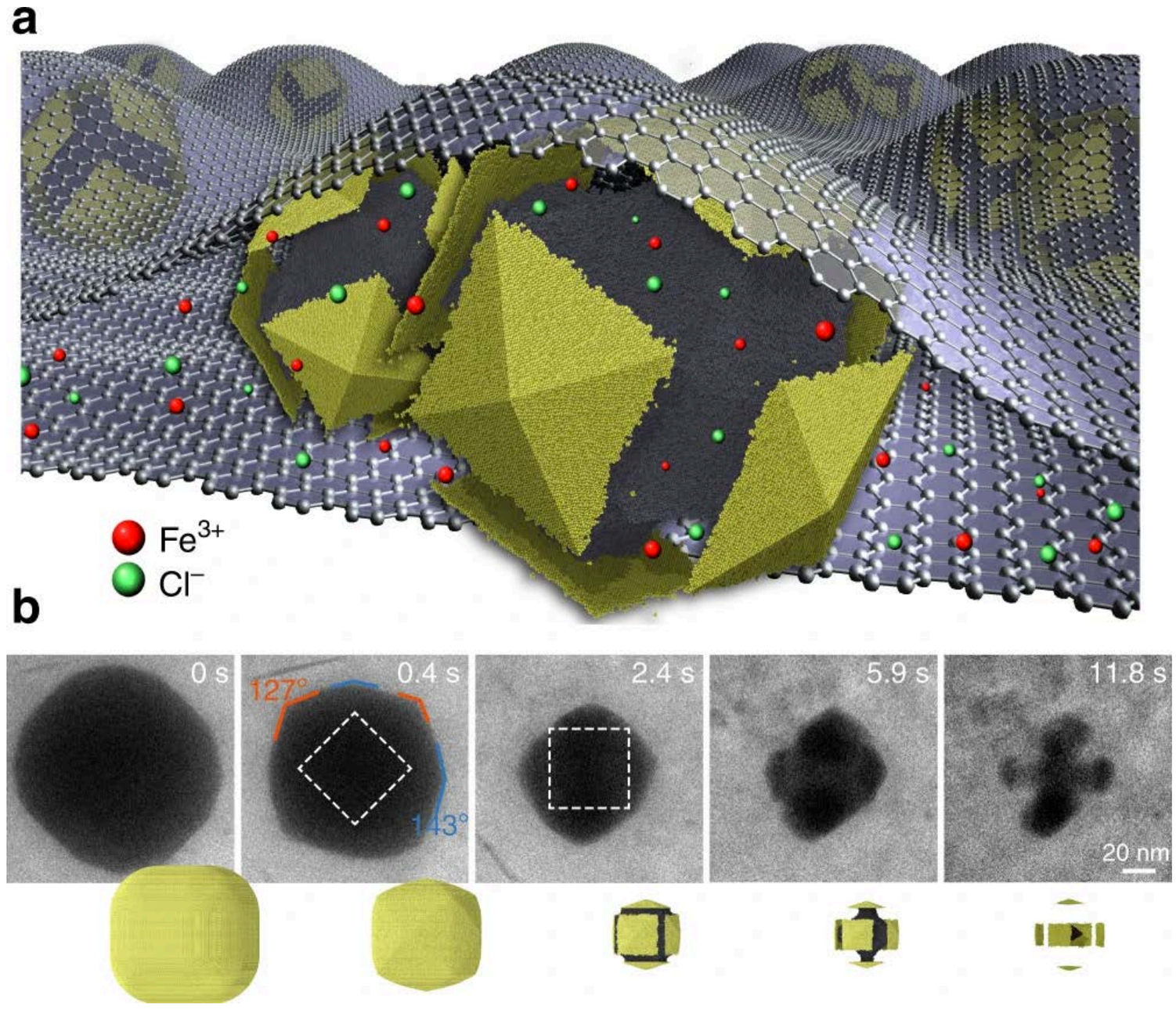
F. Tomazic, M. Engel (unpublished)

Outline

- Self-assembly of complex crystals on the computer
- Relationship between structure and formation pathways
- Finite magic number clusters
- Role of polydispersity
- Modeling anisotropic patchy interactions
- **Simulating crystal growth (incomplete)**

Shape evolution in liquid cell @ Ye lab (Indiana)

Oxidative etching conditions: Pd@Au in H_2O + ferric chloride ($FeCl_3$)



Observations:

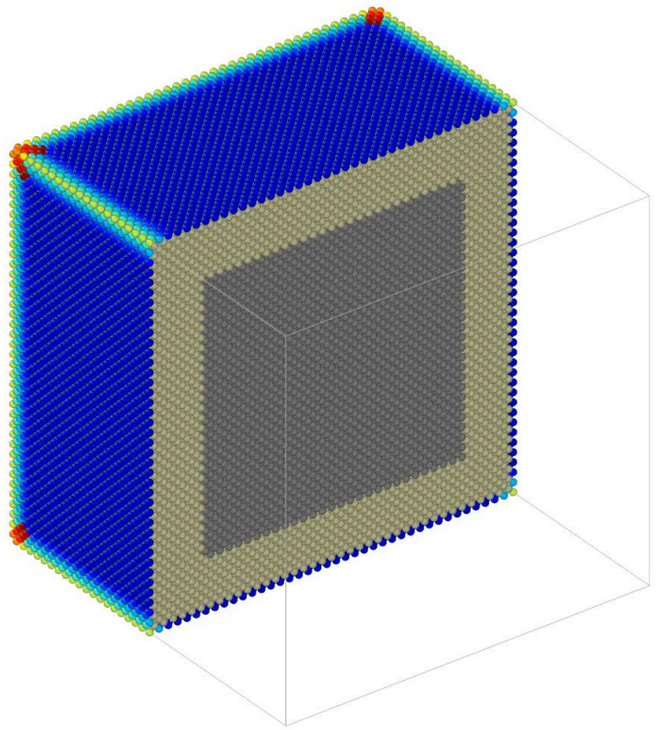
- from edge-selective to layer-by-layer atom removal
- tetrahexahedron intermediate with {310} facets
- concave shapes are achievable

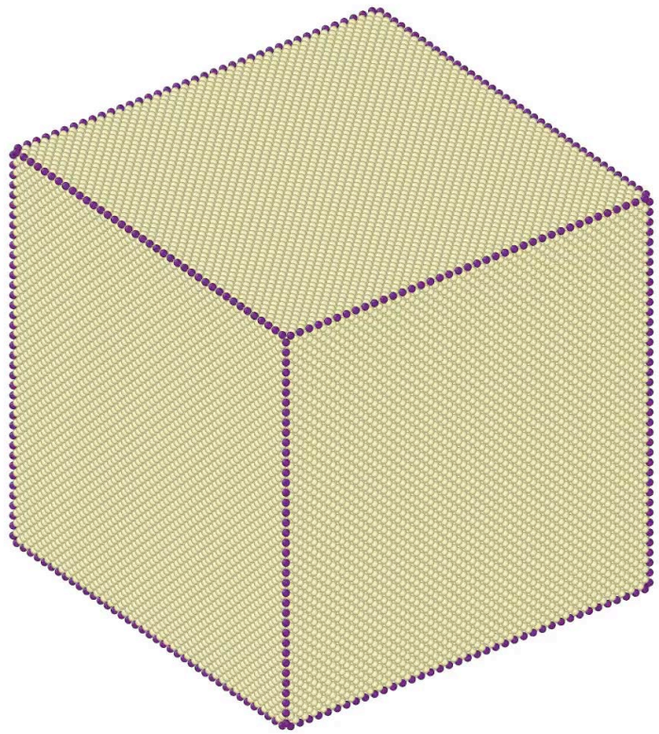
C. Lei, A. Leonardi, J. Chen, …, ME, X. Ye, *Nature Commun.* **2020**, 11, 3041

Appearance of anisotropic shape in core@shell NPs

Chemical etching

- Interaction modeled via embedded-atom method (EAM) potential





A. Leonardi, ME, *ACS Nano* **2018**, 12, 9186

Kinetic Monte Carlo lattice gas

Implementation in C++

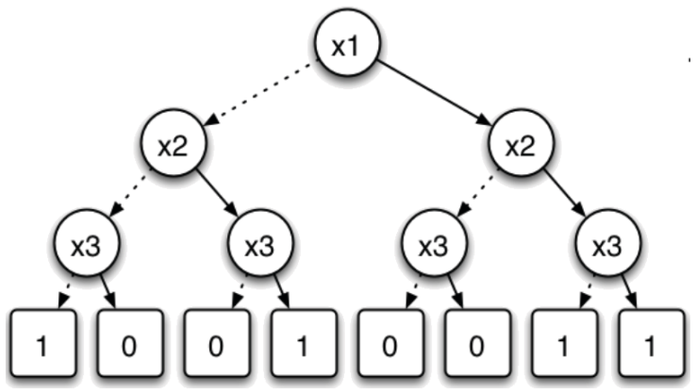
Binary decision tree to store probabilities and choose where to place new particles

Cell linked list:

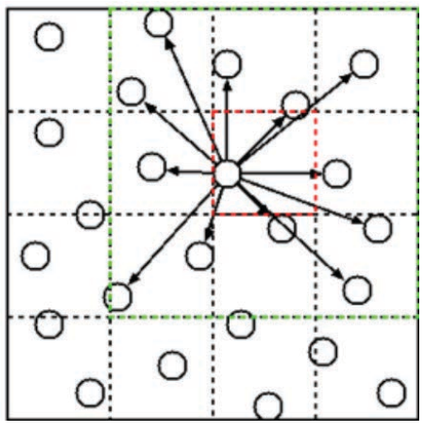
- Only pass over objects spatially close to reference particle (scales with $N \cdot \ln(N)$ instead of N^3)
- Select type of site (particle, position to add particle, bulk buffer layer, or none)

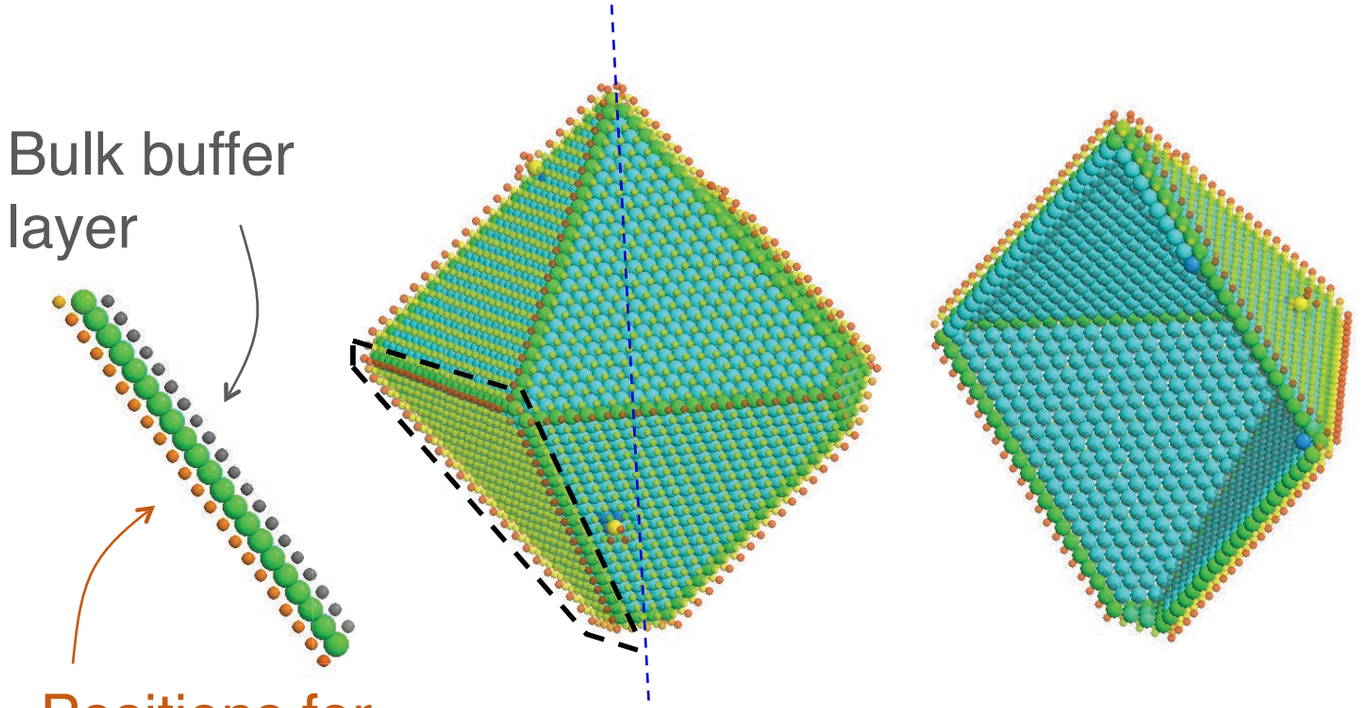
Use of bulk buffer layer: exclude bulk particles from simulation domain to spare memory

Binary decision tree



Cell linked list

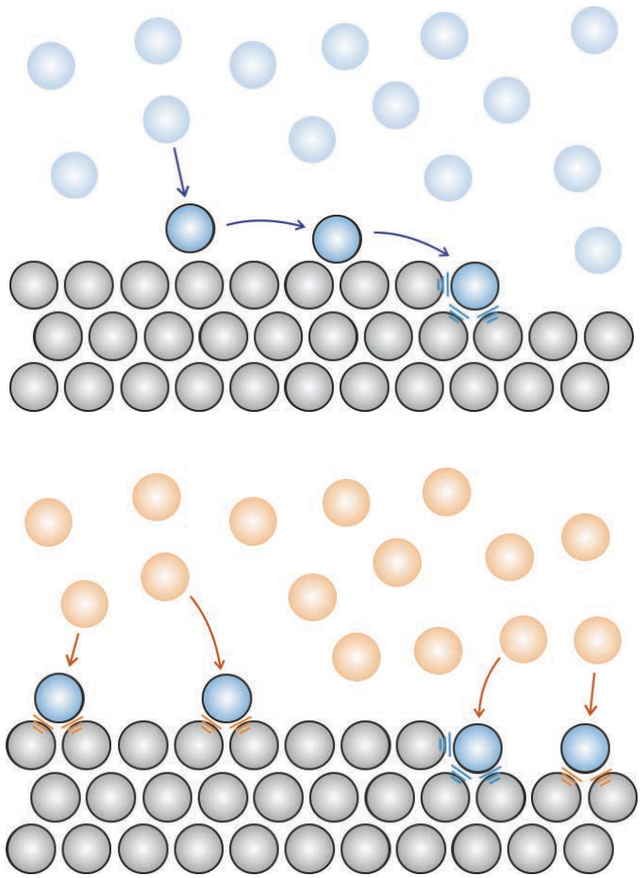


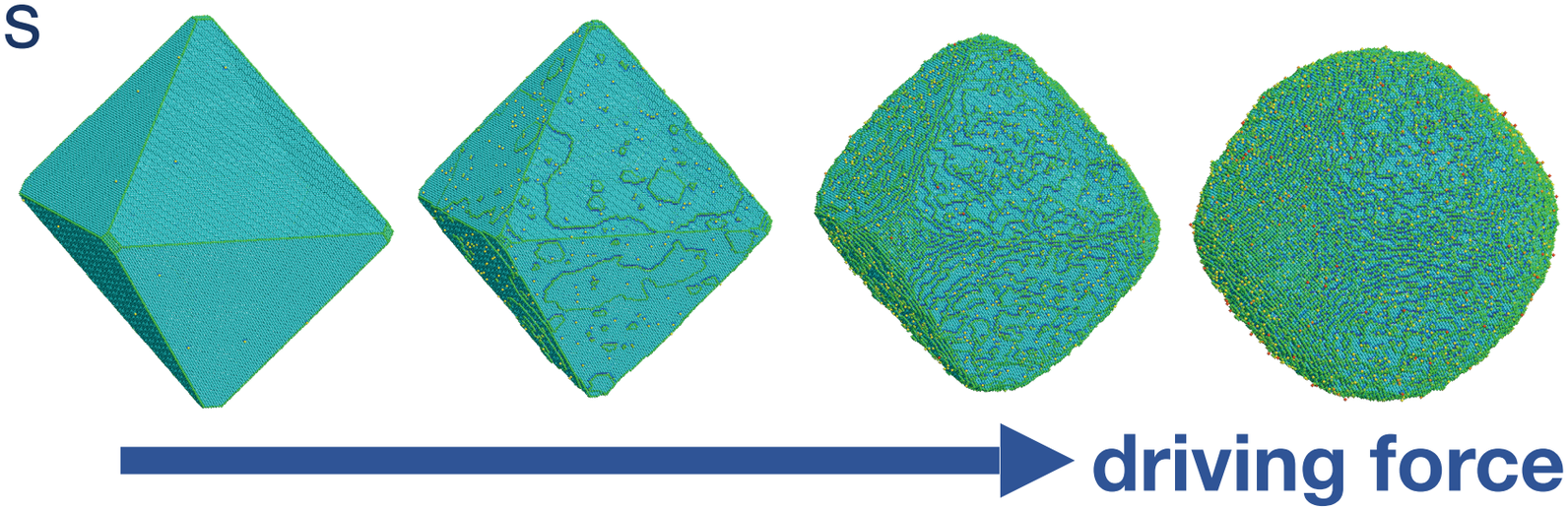


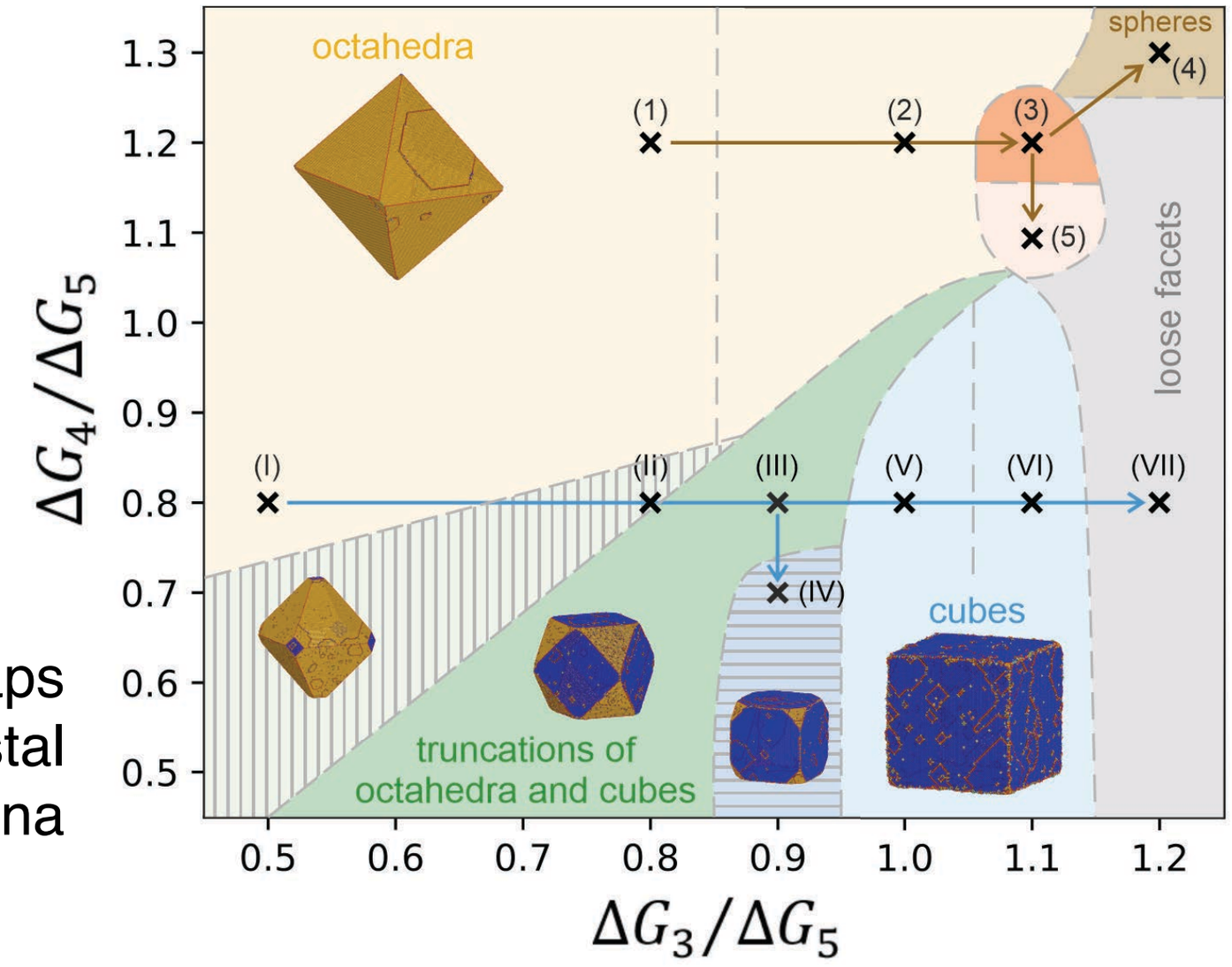
Modeling crystal growth (Carlos Bassani, @ KITP later!)

Varying growth conditions

- thermodynamics *vs.* kinetics







Wulff-shape maps summarize crystal growth phenomena

C. Bassani, M. Engel (unpublished)

Acknowledgements

https://engellab.de

Postdocs

- Alberto Leonardi
- Aswathy Muttathukattil
- Carlos Lange Bassani

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- Nydia Varela-Rosales
- Federico Tomazic
- Navid Panchi

Master/Bachelor students

- Sahib Abdullayev
- Prashanth Kamath
- Isabella Schneider

Background

- Chemical Engineers
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- Physicists
- Chemists
- Computational Engineers