Self-assembly and dynamics in nanoparticle superlattices

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O. Gang (Columbia/Brookhaven)

U.S. DEPARTMENT OF ENERGY

CONTRACT DE-AC02-07CH11358

National Science Foundation

WHERE DISCOVERIES BEGIN

DMR-CMMT (1606336) New!!!

THE Ames Laboratory

Creating Materials & Energy Solutions

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OF SCIENCE AND TECHNOLOGY

Programmable (Self)assembly?

Assembling *ordered* materials, phases, structures from basic *components*, *precisely*

mponents

$k_B T$

Successful self-assembly

$k_B T$

Failed self-assembly

ming of $k_B T$

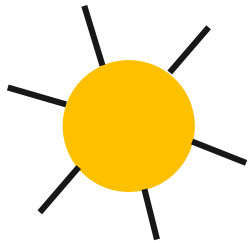
Nanoparticles Assembly

Components: Nanoparticles.

Materials: Crystals (Supercrystals).

How to control super-crystals structure?

- Proper Interactions:



Capping ligands:
Functionalization, passivation

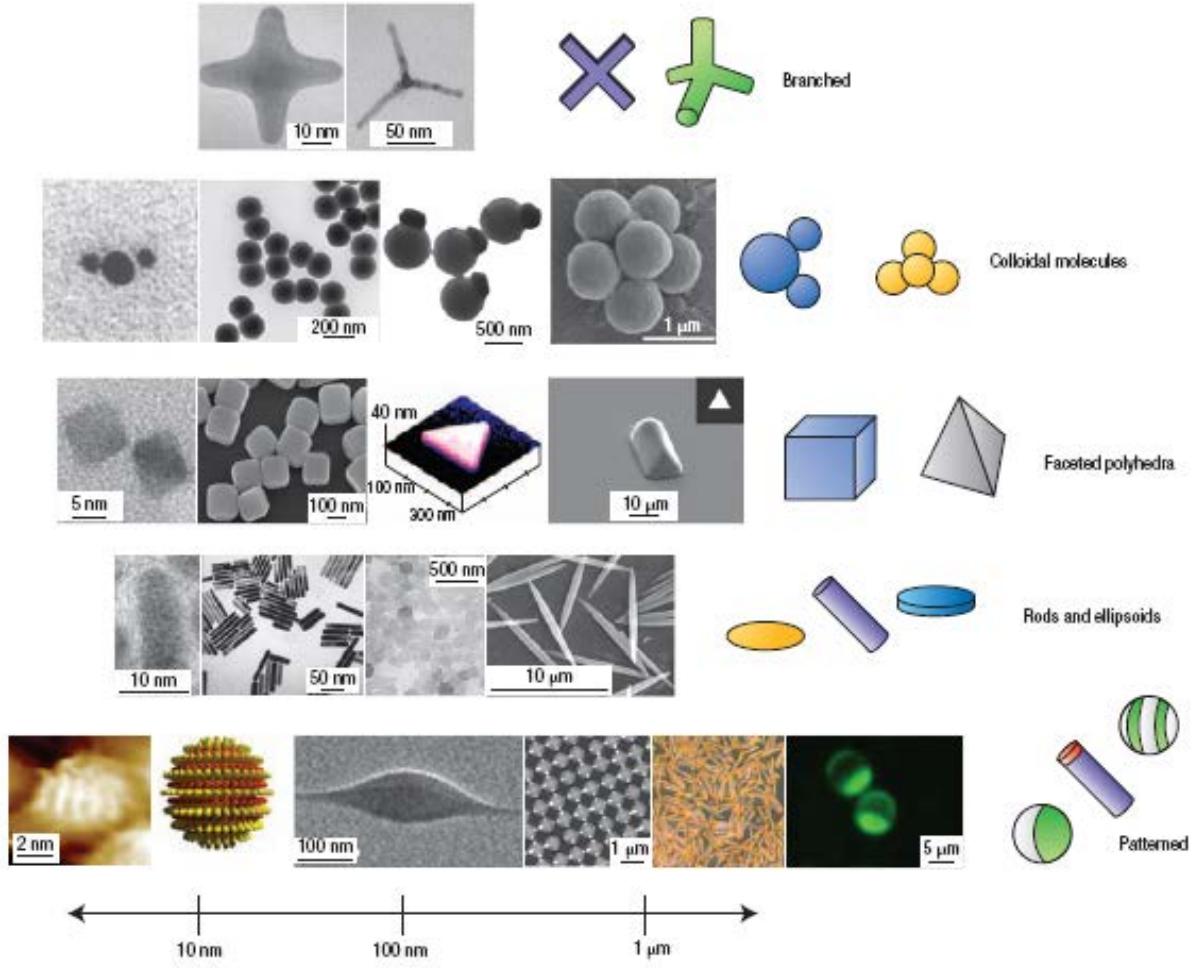
- Control relaxation times

Temperature cycling, annealing..

SUCCESS?

$\varepsilon_F / k_B T$

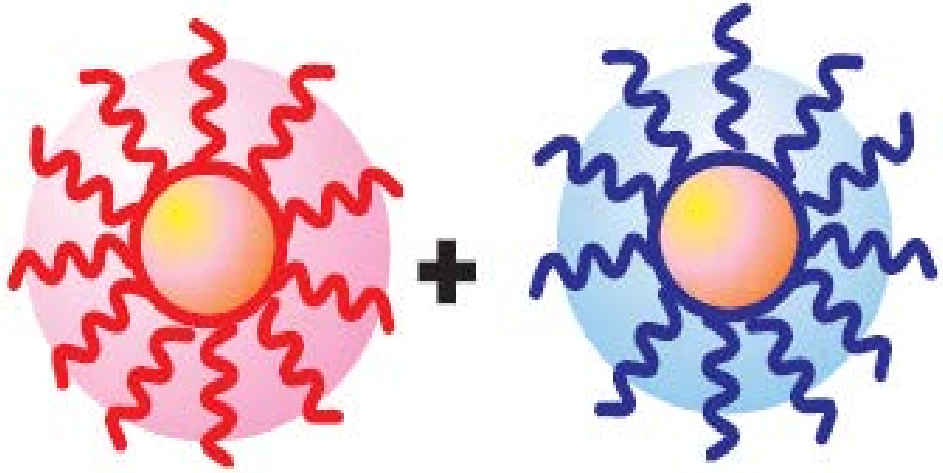
Very narrow success range: Relaxation times grow very fast with characteristic energy.



S. Glotzer and J. Solomon, Nature Materials (2007)

Proper Interactions: Assembling Nanoparticle Superlattices

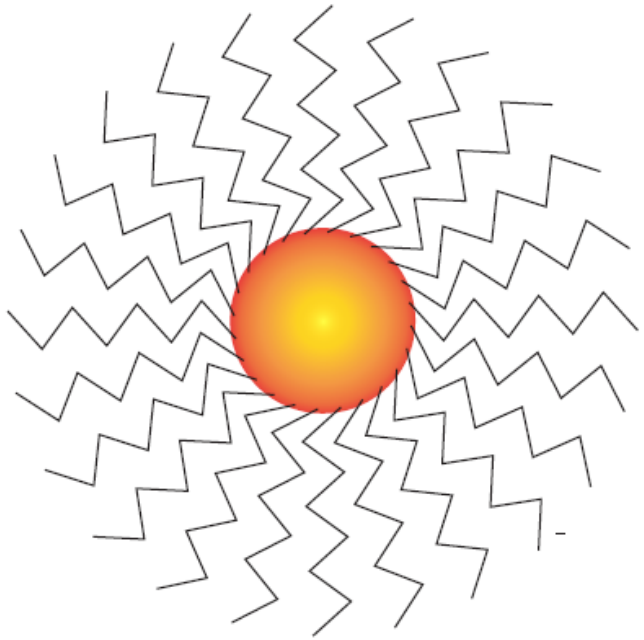
Spherical Nanoparticles functionalized with:



DNA (water)

Nykipanchuck, Maye, Van der lelie and Gang, Nature (2008)

Park, Lytton-Jean, Lee, Weigand, Schatz and Mirkin, Nature (2008)

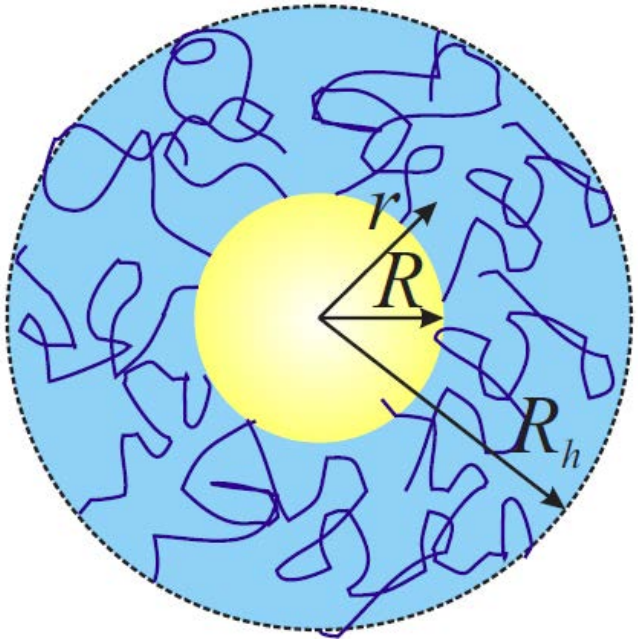


Hydrocarbons (oil)

Whetten et al (Acc. Chem. Res 32 1999)

Shevchenko, Talapin et al. (Nature 2006)

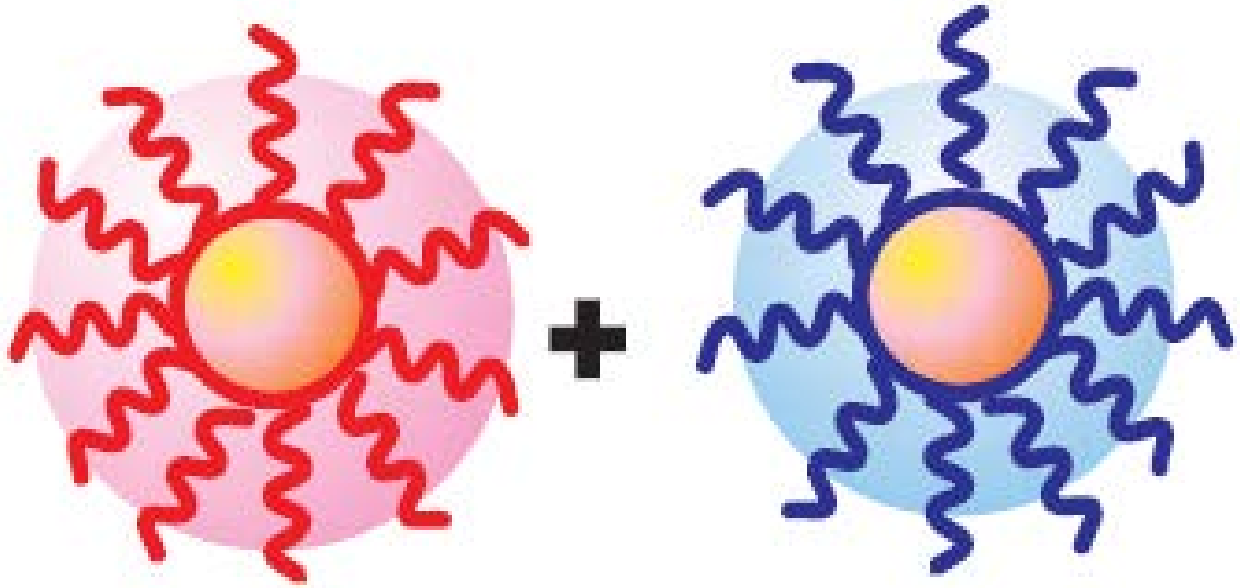
Shevchenko, Talapin, Murray, O'Brien (JACS 2006)



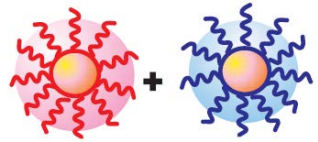
New!!! **Water soluble polymer: Polyethylene glycol (water)**

Zhang,Wang, Mallapragada, A.T, Vaknin, Nanoscale (2017)

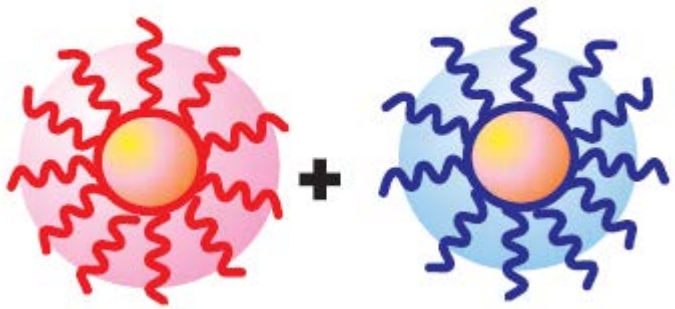
DNA Nanoparticles superlattices



DNA Superlattices



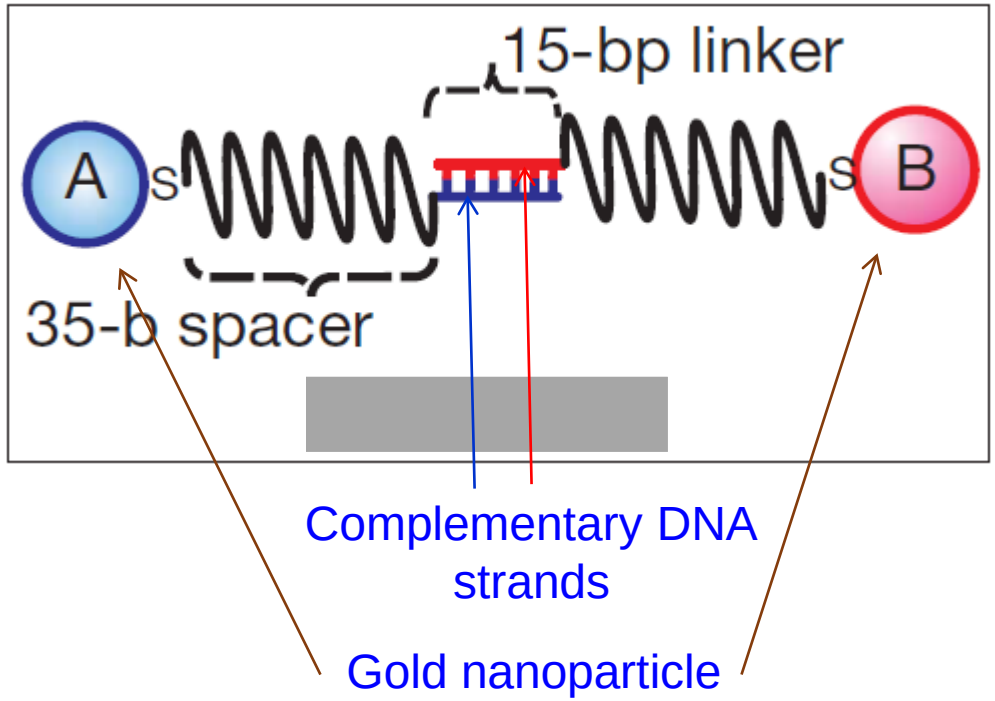
Solution of both A and B



Nykypanchuck, Maye, Van der lelie and Gang, Nature (2008)

Park, Lytton-Jean, Lee, Weigand, Schatz and Mirkin, Nature (2008)

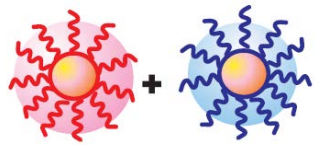
(bcc)



General strategy for programmed self-assembly!

C. Knorowski and A. T., COSSMS (2011)

Predictive theory: Explicit chain

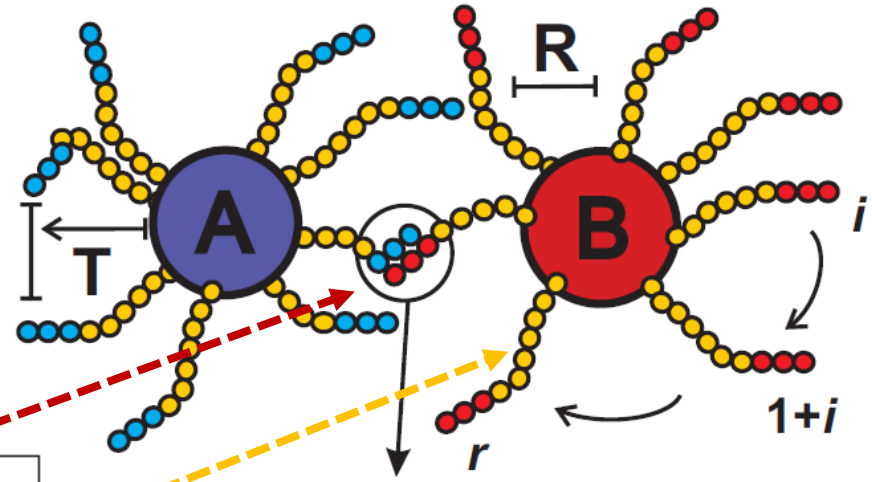


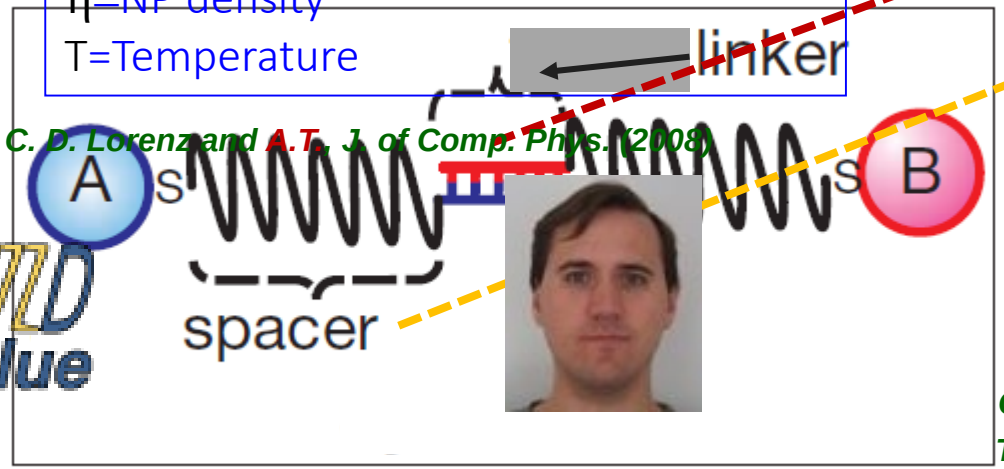
Model consisting of beads (1 bead~ 6 nucleotides)

Hydrogen bond is between complementary base pairs and directional

CT beads=
C-G T-A short-range attraction (HB)
FL,CT beads= hard-core repulsion

PARAMETERS:
R=NP radius (6nm)
r=number of ssDNA strands per NP
η=NP density
T=Temperature



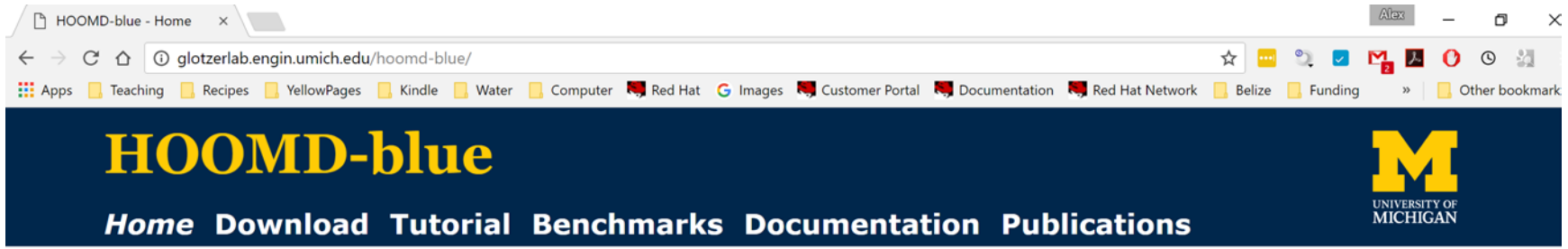


J.A. Anderson, C. D. Lorenz and A.T., J. of Comp. Phys. (2008)

C. Knorowski, S. Burleigh and A. T., PRL (2011)

T. Li, R. Sknepnek, R. Macfarlane, C. Mirkin, M. Olvera de la Cruz, Nano. (2012)

HOOMD-Blue


HOOMD-blue - Home
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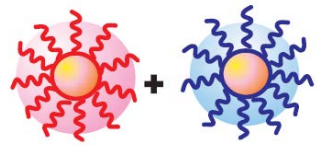
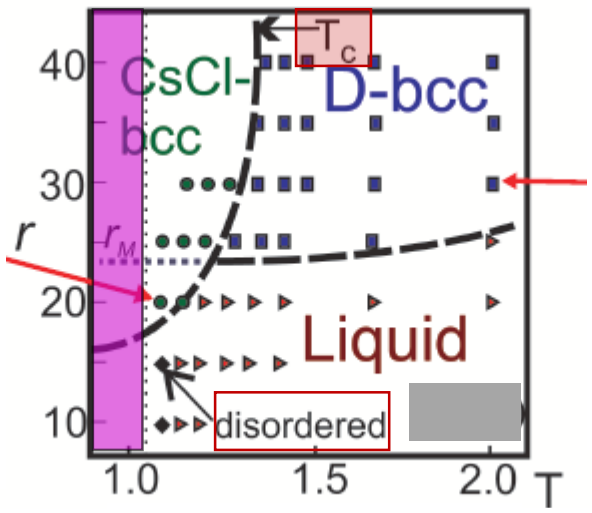
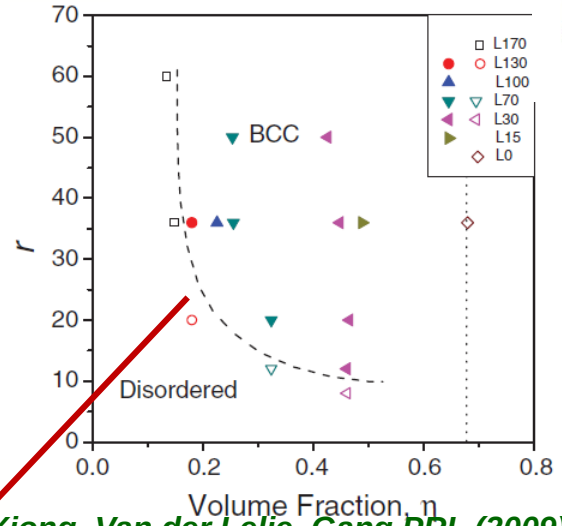
New URL: Update your bookmarks, the HOOMD-blue home page is now http://glotzerlab.engin.umich.edu/hoomd-blue.
HOOMD-blue is a general-purpose particle simulation toolkit. It scales from a single CPU core to thousands of GPUs.
You define particle initial conditions and interactions in a high-level python script. Then tell HOOMD-blue how you want to execute the job and it takes care of the rest. Python job scripts give you unlimited flexibility to create custom initialization routines, control simulation parameters, and perform in situ analysis.
Download and get started using HOOMD-blue today. Please cite HOOMD-blue if you use it published work.
import hoomd, hoomd.md
hoomd.context.initialize()
unitcell=hoomd.lattice.sc(a=2.0, type_name='A')
hoomd.init.create_lattice(unitcell=unitcell, n=10)
nl = hoomd.md.nlist.cell()
lj = hoomd.md.pair.lj(r_cut=3.0, nlist=nl)
lj.pair_coeff.set('A', 'A', epsilon=1.0, sigma=1.0)
all = hoomd.group.all();
hoomd.md.integrate.mode_standard(dt=0.005)
hoomd.md.integrate.langevin(group=all, kT=1.2, seed=4)
hoomd.run(10e3)
$ hoomd run.py --mode=cpu
$ hoomd run.py --mode=gpu
$ mpirun -n 256 hoomd run.py --mode=cpu
$ mpirun -n 64 hoomd run.py --mode=gpu
Fast GPU performance
On a single NVIDIA GPU, HOOMD-blue performs an order of magnitude faster than a
Scalable
HOOMD-blue scales up to thousands of GPUs on Titan and Blue Waters, two of the largest
Flexible
Want to run a Molecular Dynamics simulation using a custom force field? Or maybe you are

Phase Diagram of DNA (from theory)

C. Knorowski, S. Burleigh and A. T., PRL (2011)







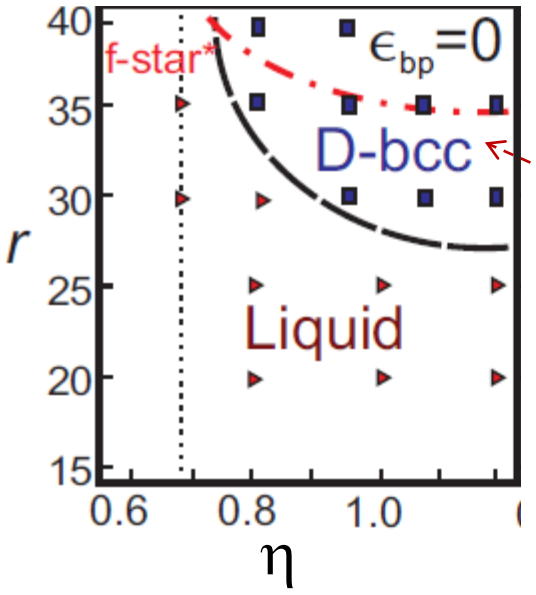
Xiong, Van der Lelie, Gang PRL (2009)

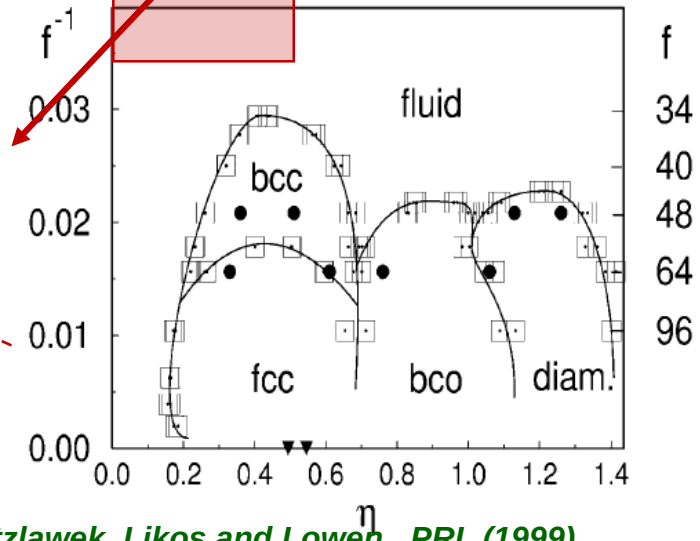
CsCl-bcc

D-bcc

Test case: No hydrogen bonds (ϵ_{bp}=0)

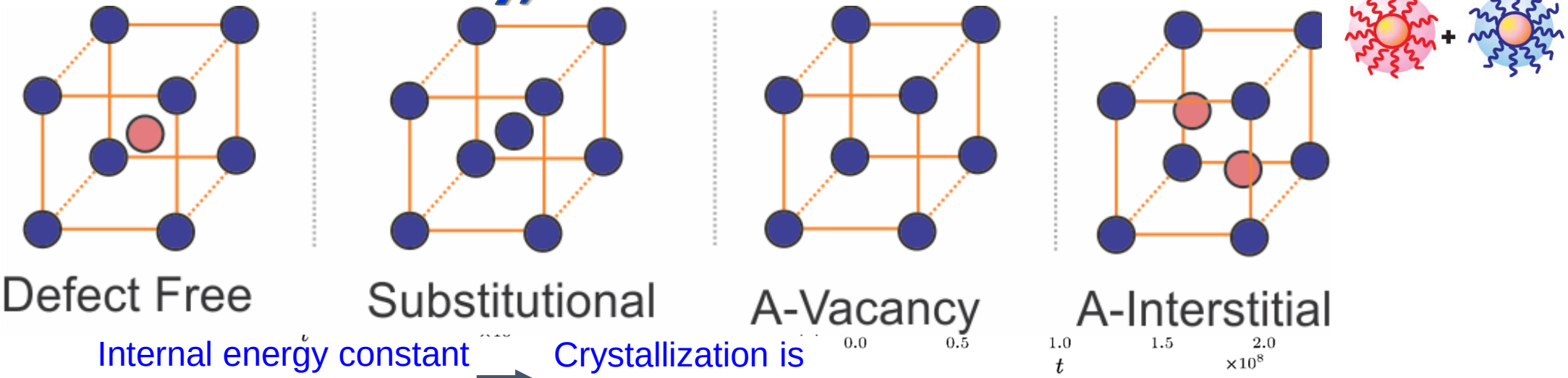
f-star polymer





Watzlawek, Likos and Lowen, PRL (1999)

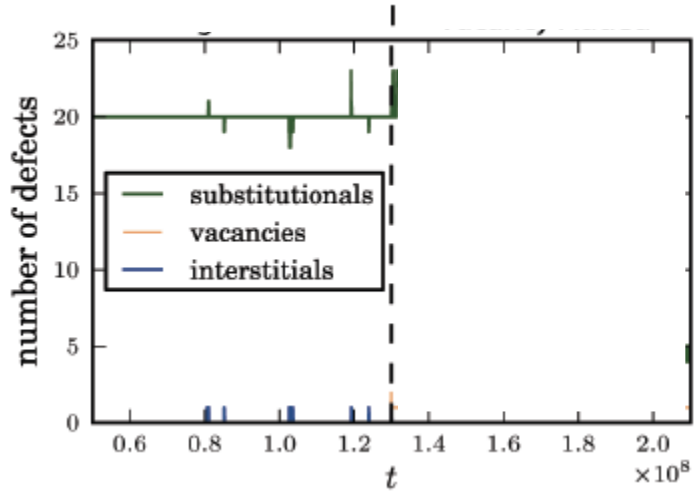
Classical Nucleation Theory, defects



Internal energy constant during nucleation → Crystallization is entropically driven

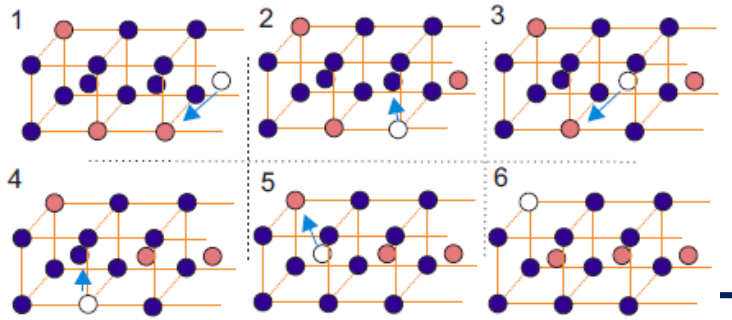
C. Knorowski and A. T., Soft Matter (2012)

DEFECT ANNIHILATION

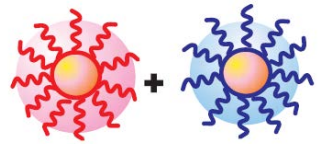


Follows the following elimination reaction:

$$\text{substitutional} + \text{interstitial}\backslash\text{vacancy} \rightarrow \text{interstitial}\backslash\text{vacancy}$$



Hydrophobicity and DNA New!!!



Solution of monodisperse identical DNA-Au Nanoparticles (no hybridization), increase salt concentration.

→ Spontaneous Crystallization (Gibbs monolayer) at the air-water interface.

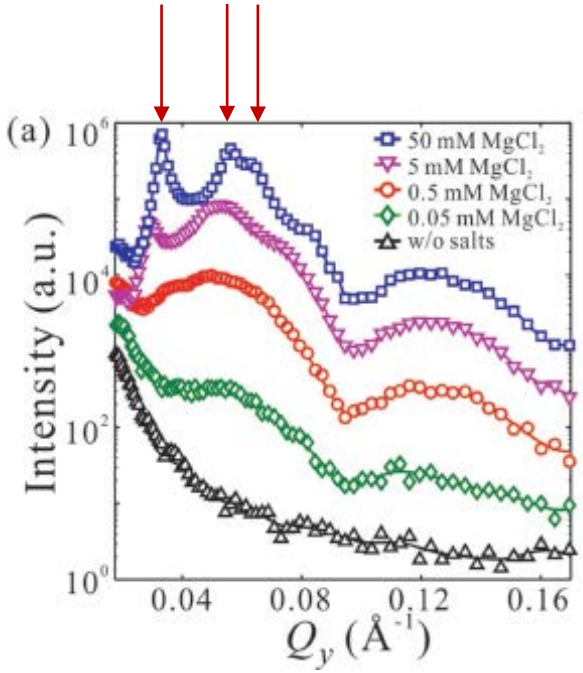
↓

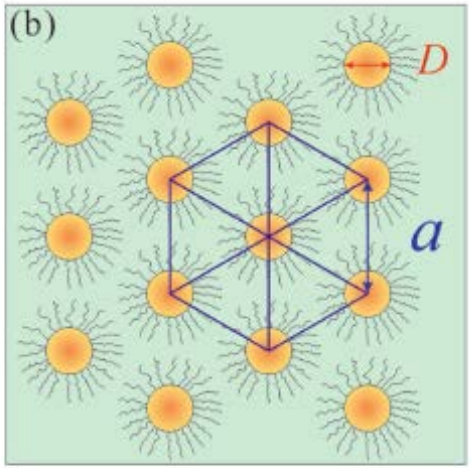
Gibbs monolayer implies hydrophobicity.

↓

Capping ligand does have hydrophobic blocks.

Bragg peaks





Type	Sequence (5' to 3')
Thiol modified DNA – A	HS–C_6H_{12}–TT TTT TTT TTT TCG TTG GCT GGA TAG CTG TGT TCT **TAA CCT AAC CTT CAT**
Thiol modified DNA – A'	HS–C_6H_{12}–TT TTT TTT TTT TCG TTG GCT GGA TAG CTG TGT TCT **ATG AAG GTT AGG TTA**

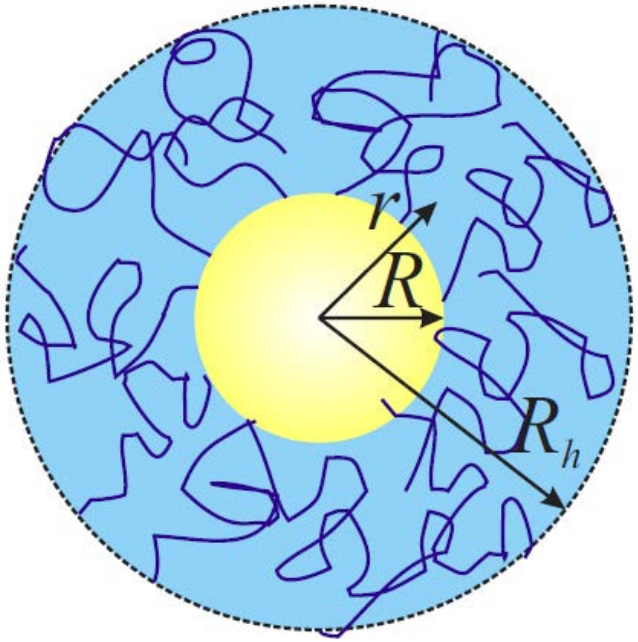
Hydrophobicity is an additional element to consider in the programmable self-assembly of DNA …

What about (mildly) Hydrophilic ligands: PEG ?

H. Zhang, W. Wang, N. Hagen, I. Kuzmenko, M. Akinc, A. T., S. Mallapragada and D. Vaknin, Adv. Mat. and Interf. (2016)

M. Campolongo, S. Tan, D. Smilgies, M. Zhao and Y. Chen, ACS Nano (2011)

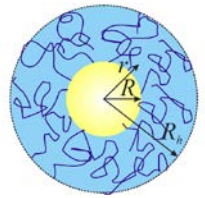
Electrostatic induced superlattices



Water soluble polymer:
Polyethylene glycol (water)

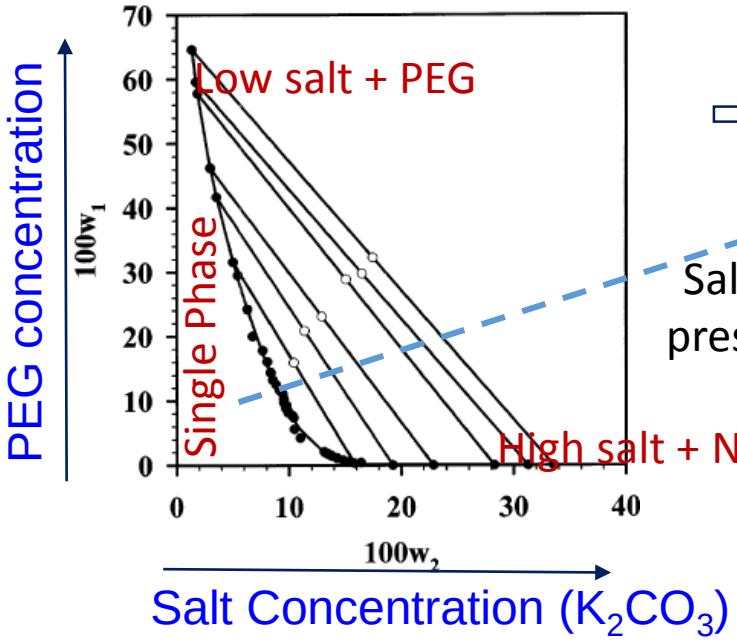
Zhang, Wang, Mallapragada, A.T, Vaknin (2017)
Zhang, Wang, Akinc, Mallapragada, A.T, Vaknin (2017)

Electrostatic induced superlattices

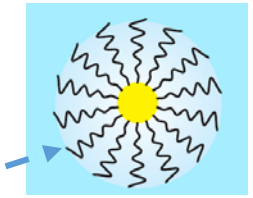


Huddleston, Willauer, Rogers, J. Chem. Eng. Data (2003)

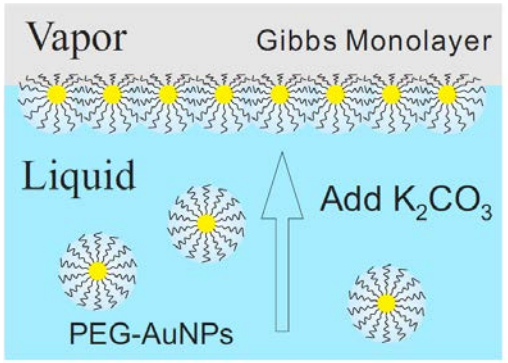
Phase diagram of PEG+salt +water



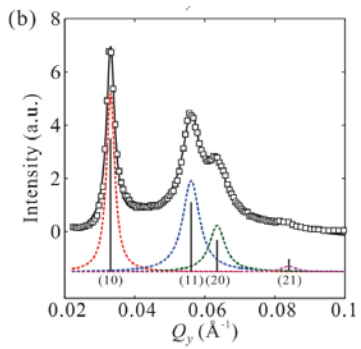
Nanoparticle



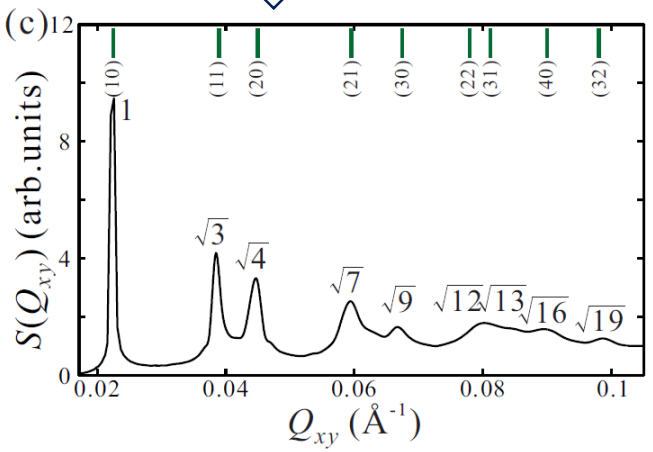
Salt ejected from PEG: Osmotic pressure leads to surface tension



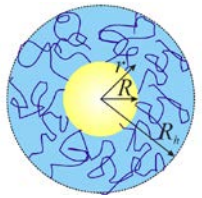
Trading surface tension for polymer stretching



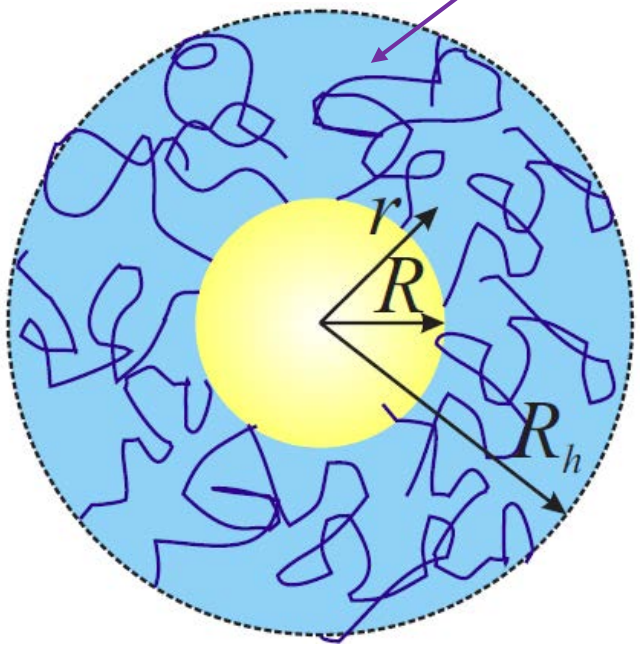
High quality crystals at the air-water interface: ex. DNA



Induced forces



INSIDE: A spherical brush at theta-point



OUTSIDE: high salt, poor solvent

$$\left(\frac{R_h}{R}\right)^2 = 1 + 2\frac{N(\sigma b^2)^{1/2}}{R/b}(2w_0)^{1/4}$$

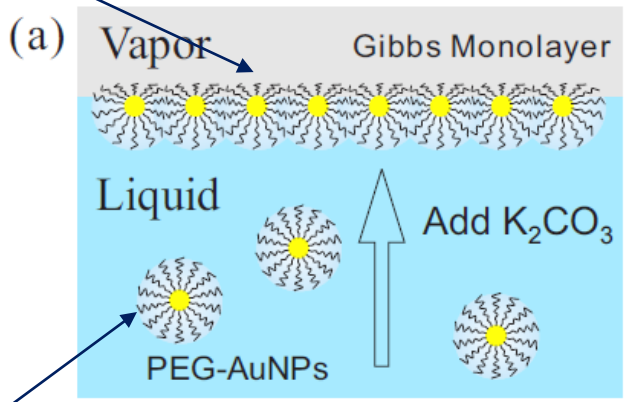
b Kuhn length

σ Grafting density

w_0 Three body interaction

Polymer stretching at the interface

$$\frac{F}{k_BT} \approx \left(\frac{R}{b}\right)^3 (\sigma b^2)^{3/2}(2w_0)^{1/4} H(y) \sim 100 H(y)$$



$$H(y) \sim (1-y)^3$$

$$y = \frac{a_L}{2R_h}$$

a_L Lattice constant

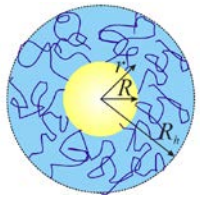
surface tension increases with high salt solution

$$\frac{F}{k_BT} = 4\pi\gamma_{AB}{R_h}^2 \sim 0 - 200$$

$$\gamma_{AB} \approx k_BT/b^2 \log([salt])$$

Lattice constant: Balance between surface tension and stretching: may be tuned by salt.

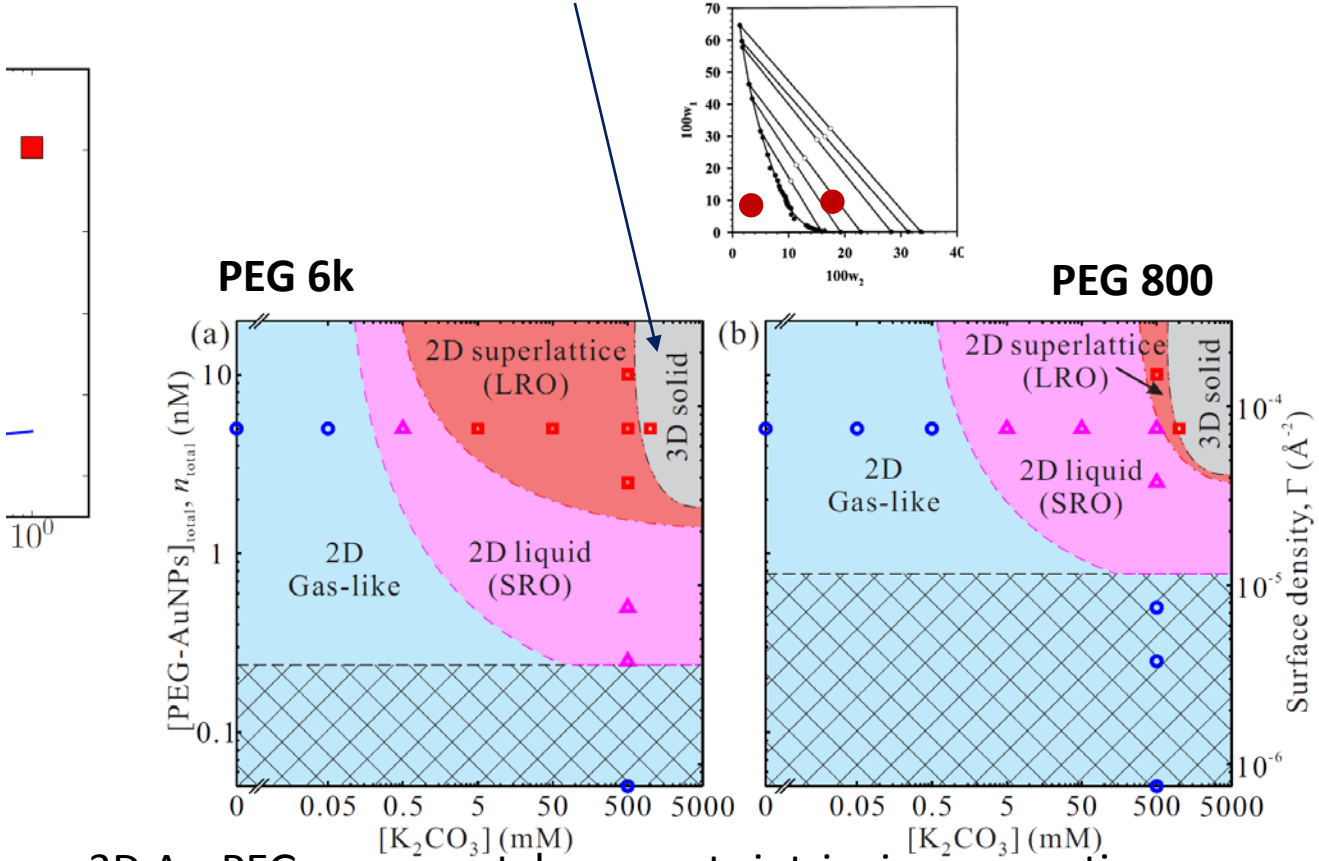
Phase diagram



Lattice constant can be tuned over a very large range:

The softer the shell the more crystals!

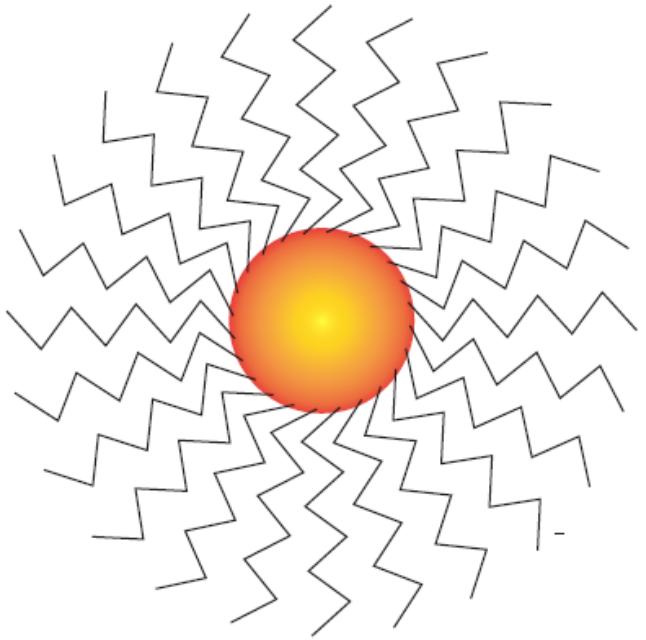
Two phase region: colloidal destabilization: 3D crystals



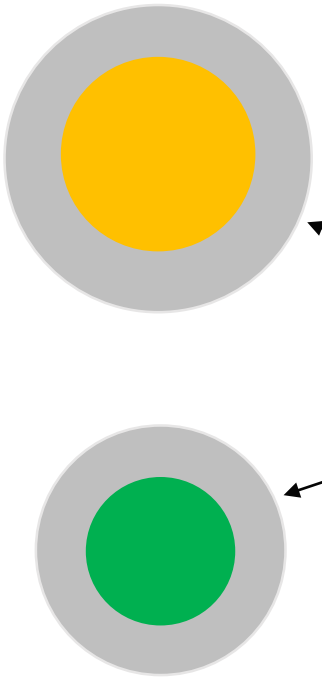
3D Au-PEG supercrystals presents intriguing properties.

H. Zhang, W. Wang, S. Mallapragada, A. T and D. Vaknin (2017)

Superlattices of Hydrocarbon capped ligands



Binary Superlattices by Solvent evaporation



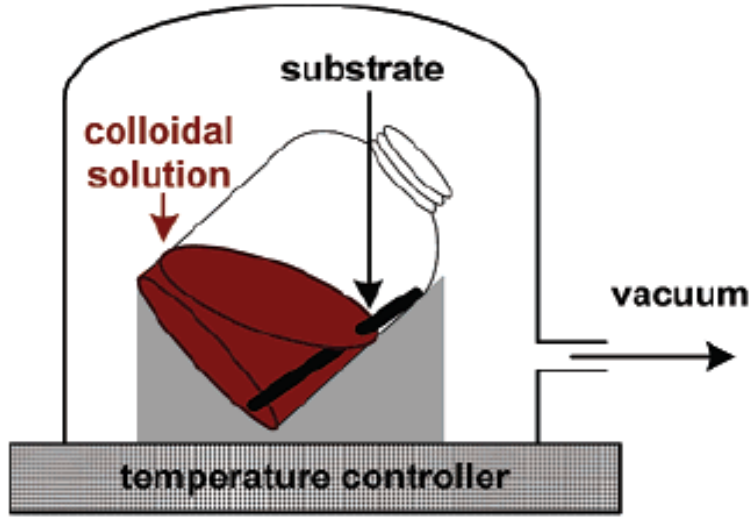
Nanoparticle A

Capping ligand
(hydrocarbon)

Nanoparticle B

Soluble in organic solvent

Solution of both A and B and solvent is evaporated



Shevchenko, Talapin, Murray, O'Brien (JACS 2006)

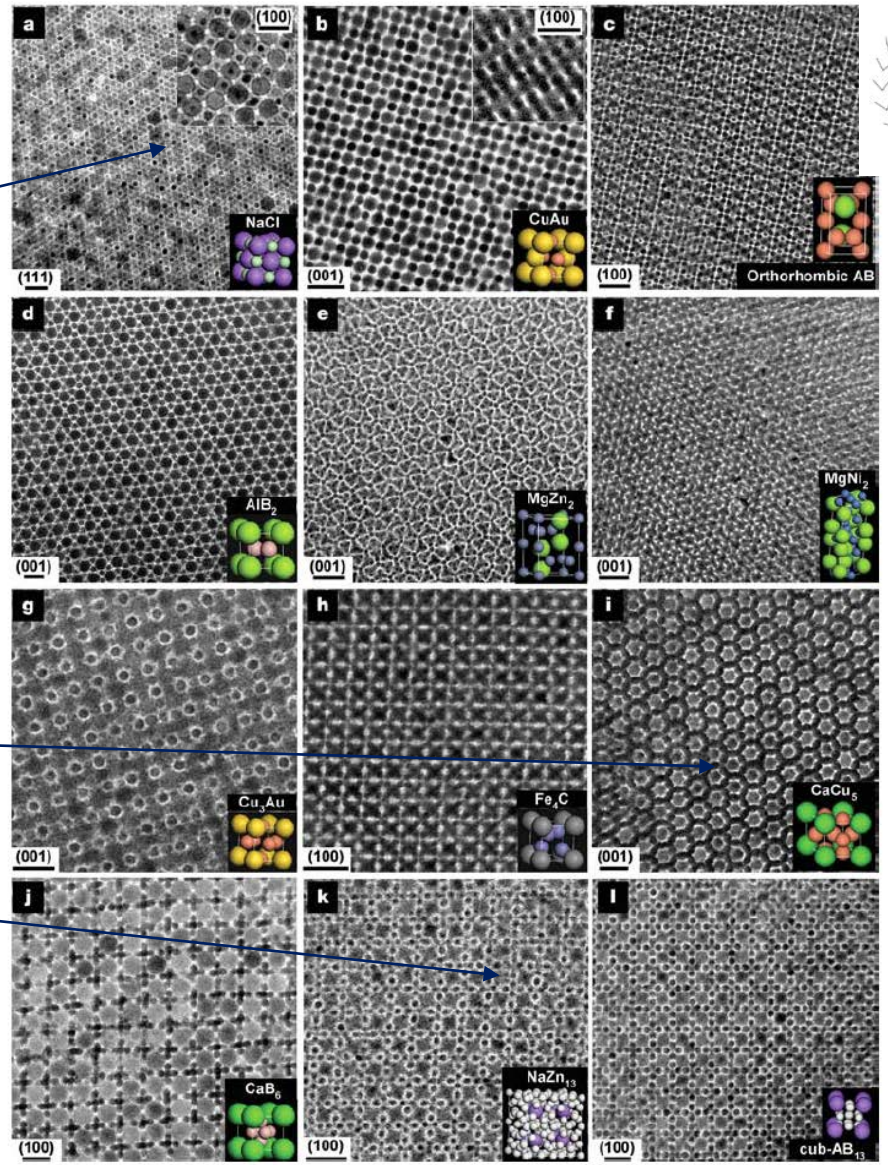
Shevchenko, Talapin, Kotov, O'Brien, Murray (Nature 2006)

Superlattices Examples

Solvent evaporation produces a myriad of super-lattices!!!

These lattices are known from their atomic analogues..

NaCl
CuAu
AlB_2
$MgZn_2$
$MgNi_2$
$AuCu_3$
CFe_4
$CaCu_5$
CaB_6
$NaZn_{13}$
$CubAB_{13}$



Can we predict the structure of these supercrystals?

How many parameters are needed to characterize the phase diagram?

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

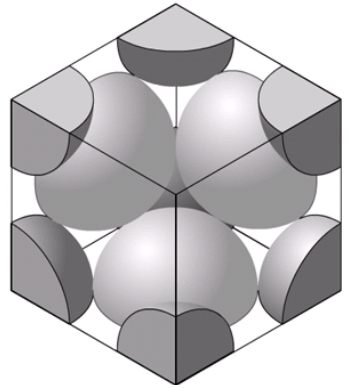
Packing fraction

In 3D

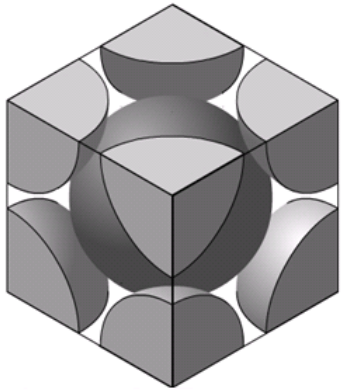
Minimiz

PF= Volu

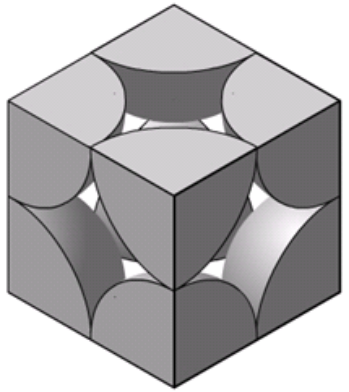
In Binary s



PF= $\pi/18^{1/2} = 0.740$

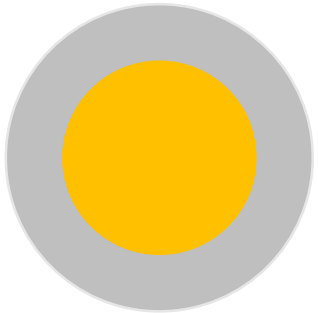


PF= $\pi\ 3^{1/2}/8 = 0.680$

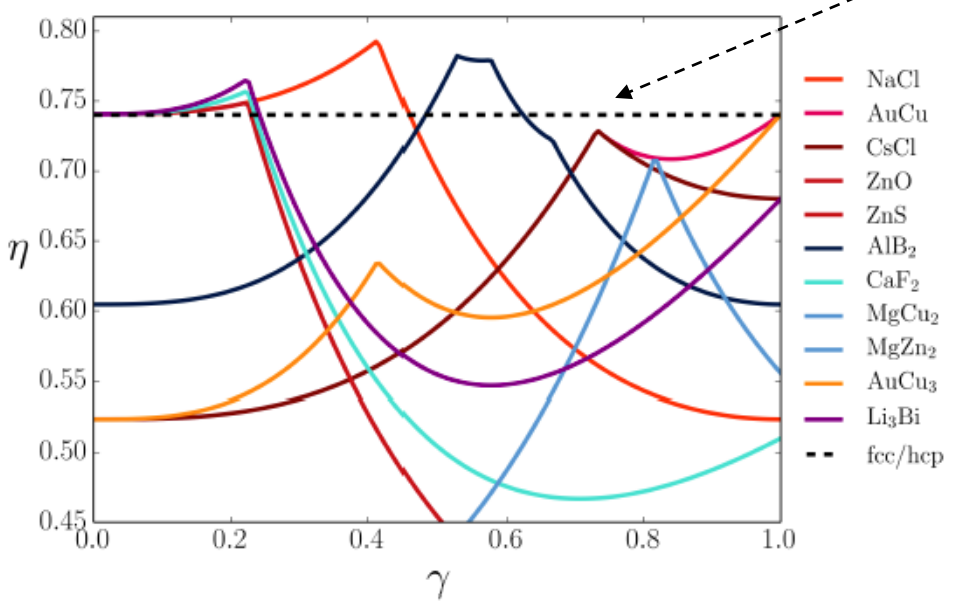


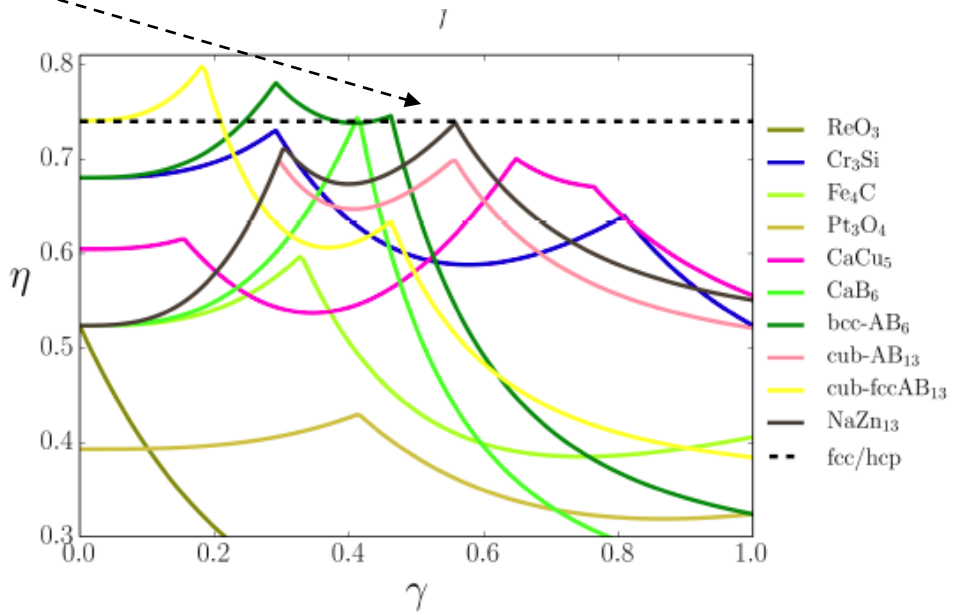
PF= $\pi/6 = 0.524$

Packing fraction of binary lattices, 3D case:



PF does exceeds the fcc/hcp case

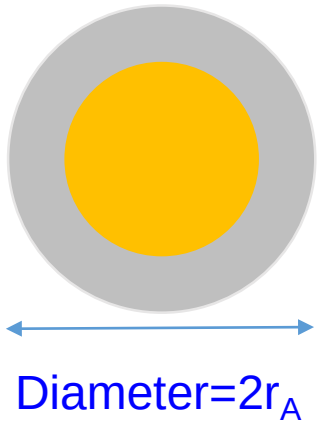




$$\gamma = \frac{r_B}{r_A}$$

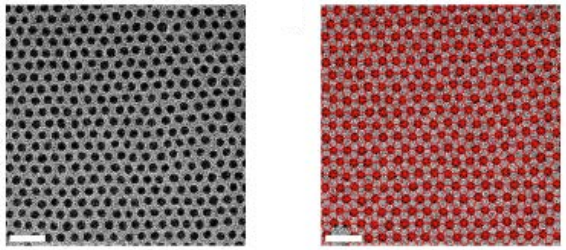
Horst, A.T. , J. Chem. Phys. (2016)

Super-lattices and PF

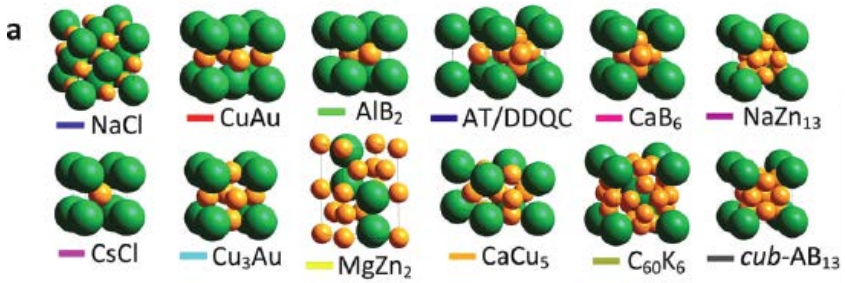


Model the nanoparticles as <u>hard spheres</u>

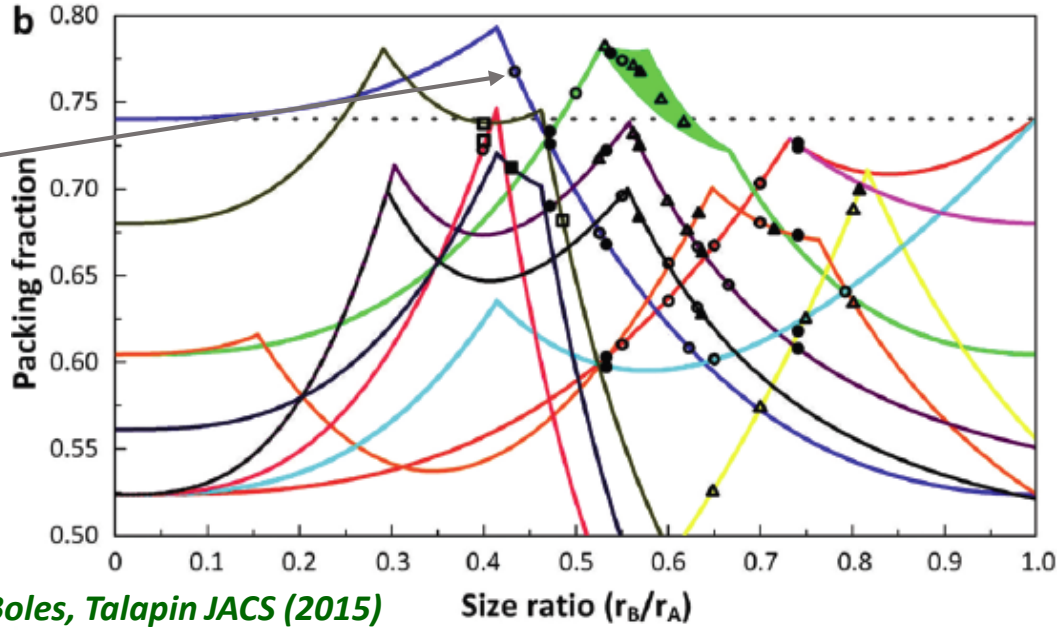
Radius of nanoparticle = half lattice constant of the two-dimensional hexagonal lattice.



Radius of nanoparticle computed from TEM images



Experimental points



Boles, Talapin JACS (2015)

Strong Correlation between PF and experiment!

$$\gamma = \frac{r_B}{r_A}$$

Minimal models

Simplest models whose equilibrium phases correlated with maximum of packing fraction ?

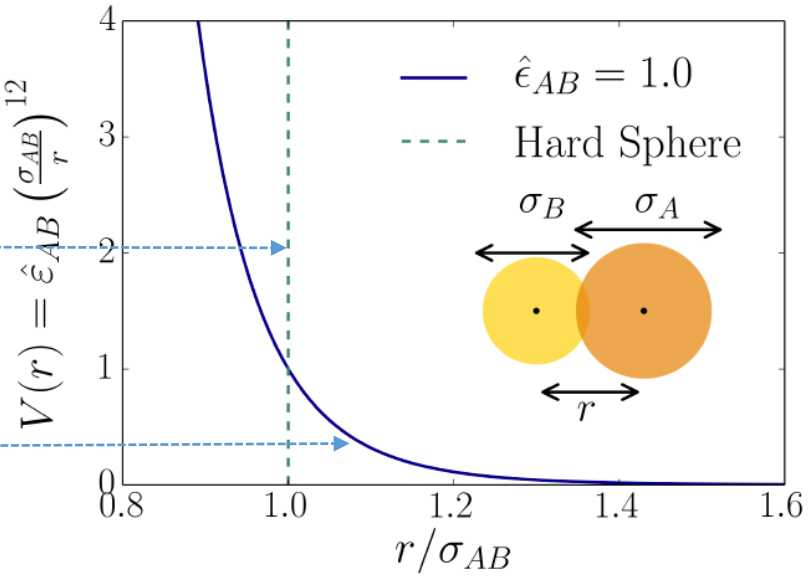
Potential must be short-ranged:

Inverse power law:

$$V_{hf}(r) = \varepsilon_{hf}\varepsilon\left(\frac{\sigma_{hf}}{r}\right)^{p}$$

If p goes to infinity is the hard sphere model:

At p finite is a softer potential:



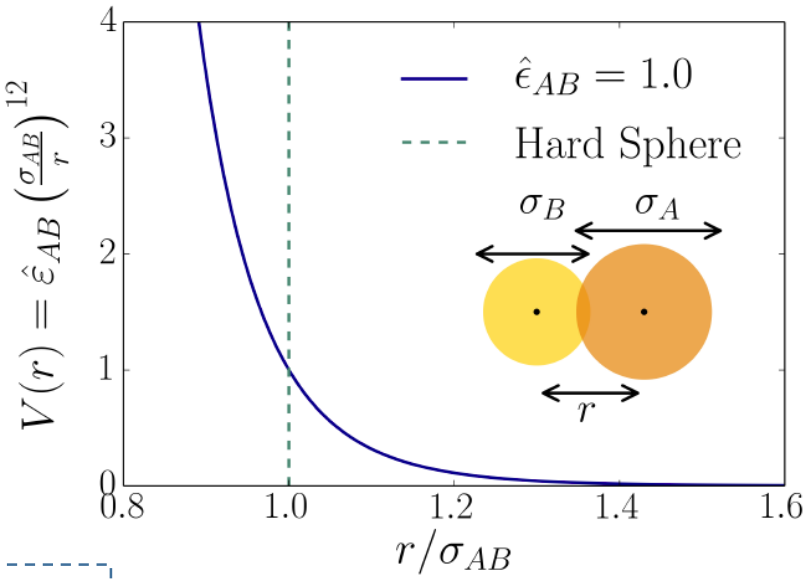
A.T., PNAS (2015)

Binary mixtures of inverse-power law

A.T., PNAS (2015)

Inverse power law:

$$V_{hf}(r) = \varepsilon_{hf}\varepsilon\left(\frac{\sigma_{hf}}{r}\right)^{p}$$



There are 8 parameters :

ε σ_A | $\hat{T} = \frac{T}{\varepsilon}$ $\hat{V} = \frac{V}{\sigma_A^3}$ | σ_B | ε_{AB} ε_{BB} | x_B

Defines units of Length and energy.

Scale invariance

Scale invariance

$$\xi_p = \frac{1}{\hat{T}^{3/p}}\frac{N}{\hat{V}} \qquad \gamma = \frac{\sigma_B}{\sigma_A} \qquad \varepsilon_{AB} \qquad x_B$$

The phase diagram is a function of 4 parameters!

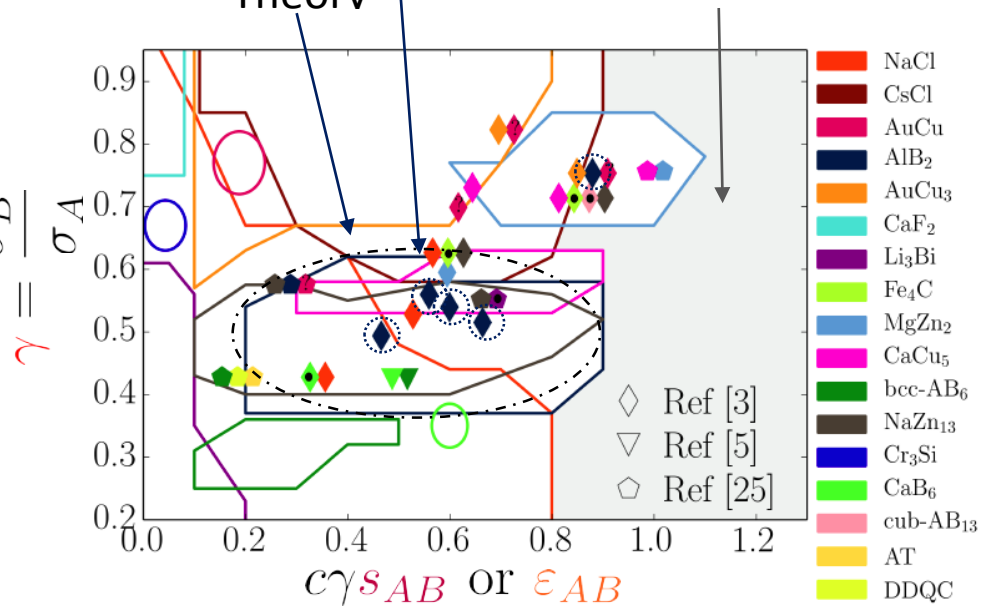
1 more parameter (ε_{AB}) than the hard sphere model.

Comparison to experiments

Data that is not within +/– 0.2 in γ or ε_{AB} is marked with a black dot
(those are points where the theoretical prediction is off)

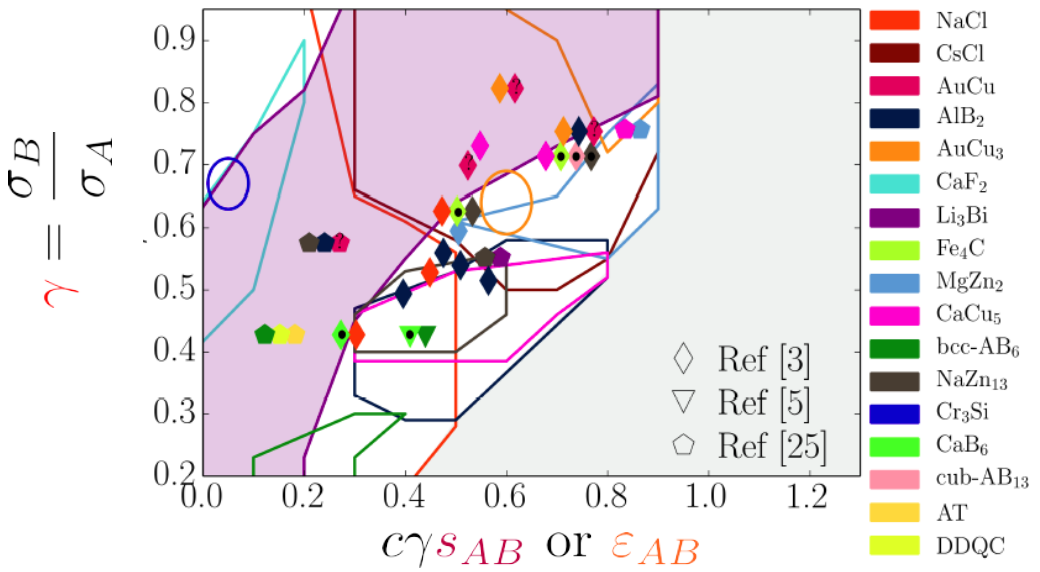
Example AlB_2: Experiment
Theory

No binary phases here:



p = 12

Similar correlation is found with p=6



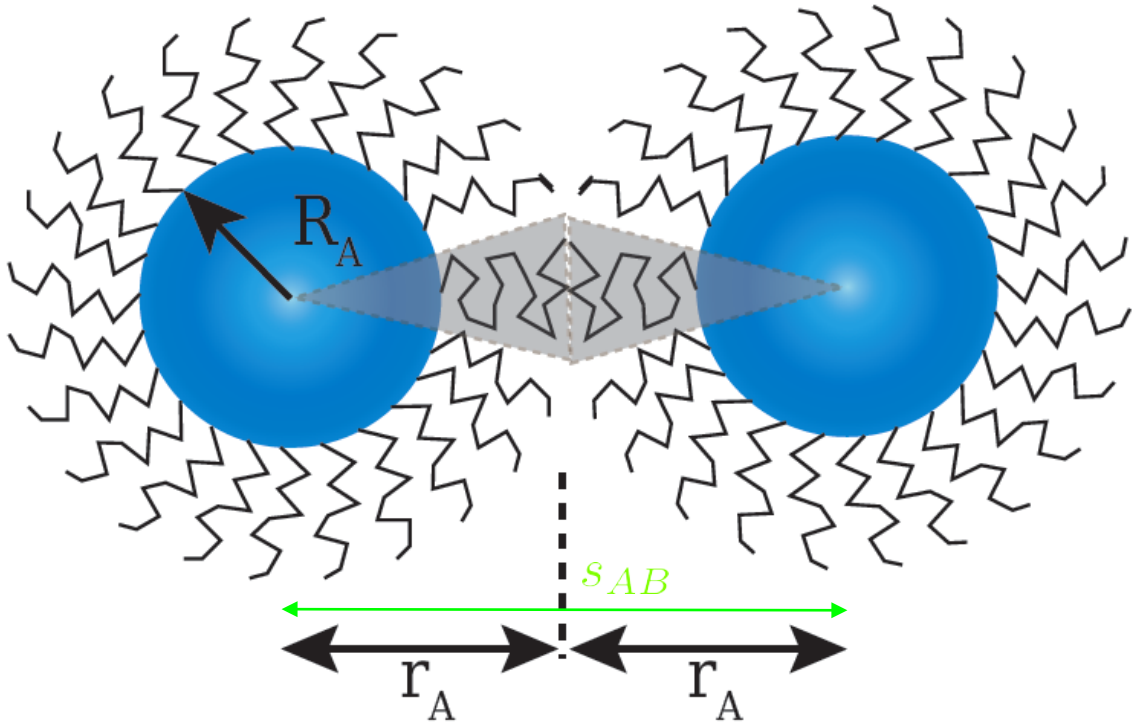
p = 6

Cannot account for low packing fraction phases (eg: Li_3Bi), AuCu does not appear, etc…

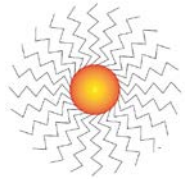
Broad features OK, predictions not specific enough….

The OXM Models (X=P)

L = maximum hydrocarbon extent



Luedtke, Landman J. Phys. Chem. B (2003)



Dimensionless thermodynamics

$\lambda = \frac{L}{R_A}$ Dimensionless hydrocarbon extent

$\tau = \frac{r_A}{R_A}$ Dimensionless radius (lattice constant)

Assume that the shaded chain is space filling:

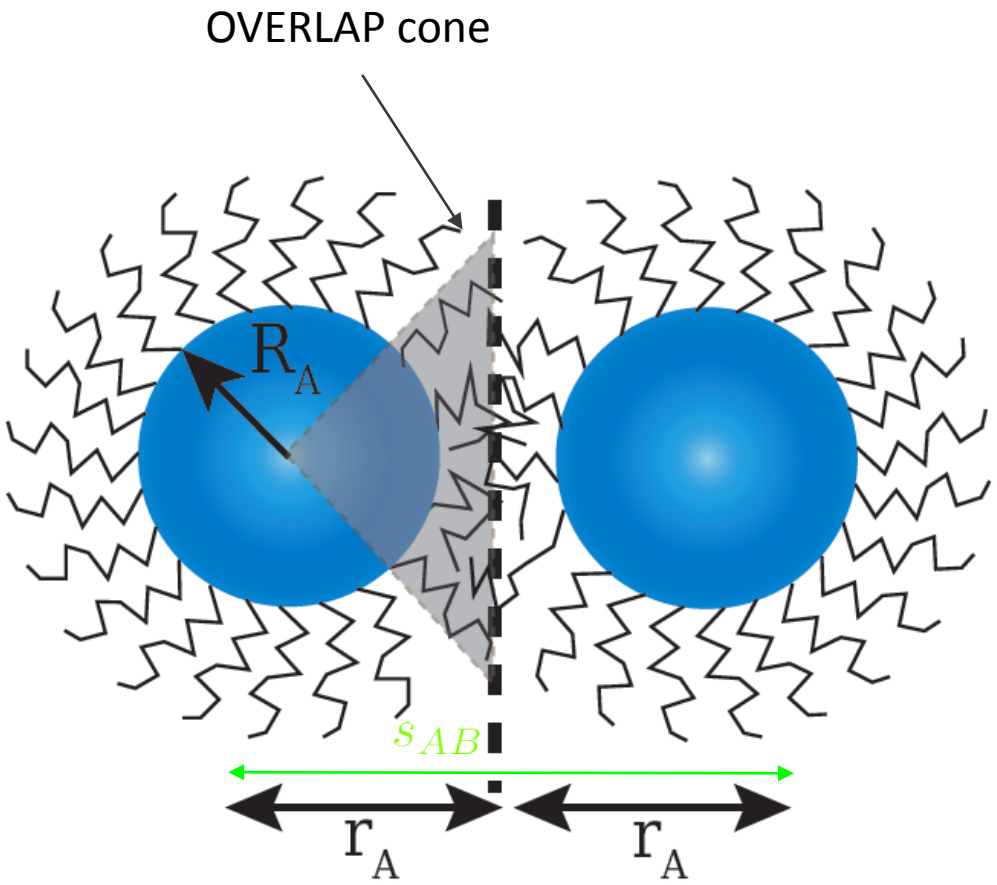
$$\tau^{OPM} = (1 + 3\lambda)^{1/3} \qquad s_{AA} = 2R_A\tau^{OPM}$$

This is the O**P**M formula.

The O**P**M formula for a binary system is:

$$s_{AB}^{OPM} = \tau_A^{OPM} R_A + \tau_B^{OPM} R_B$$

The OXM Models (X=C)



Schapotschnikow, Vlugt, J. Chem. Phys. (2009)

$\lambda = \frac{L}{R_A}$ Dimensionless hydrocarbon extent.

$\tau = \frac{r_A}{R_A}$ Dimensionless lattice constant.

Assume that the OVERLAP cone is space filling:

$$\tau^{OCM} = \eta_{HS}^{1/3}(1+3\lambda)^{1/3} \qquad s_{AA} = 2\tau^{OCM} R_A$$

$$PF = \eta_{HS}$$

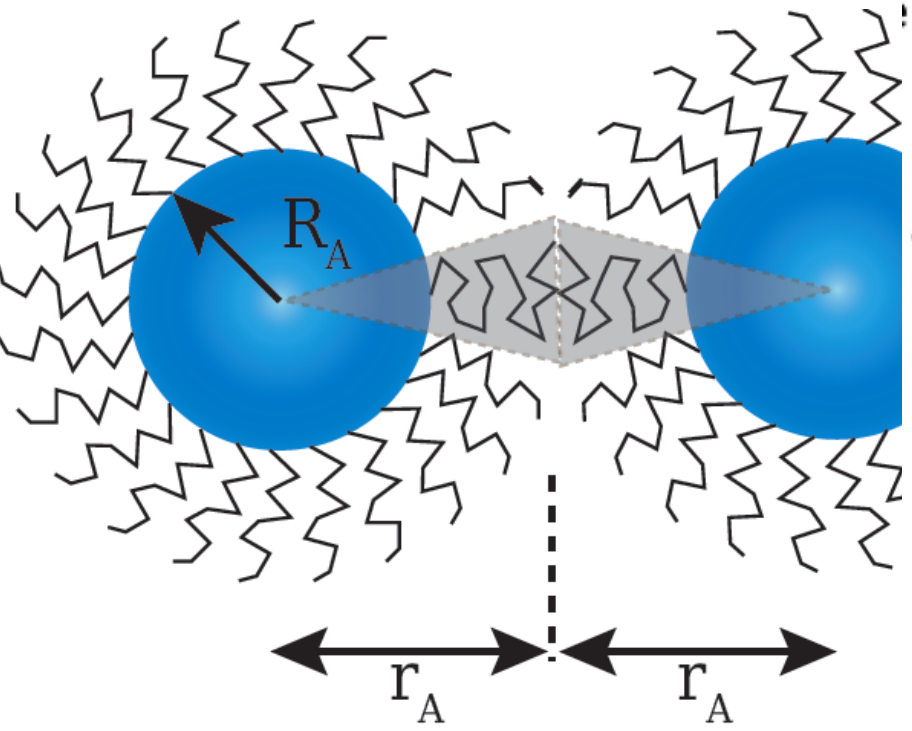
This is the OCM formula.

The OCM formula for a binary system is:

$$s_{AB}^{OCM} = R_A \tau_A^{OCM} + R_B \tau_B^{OCM}$$

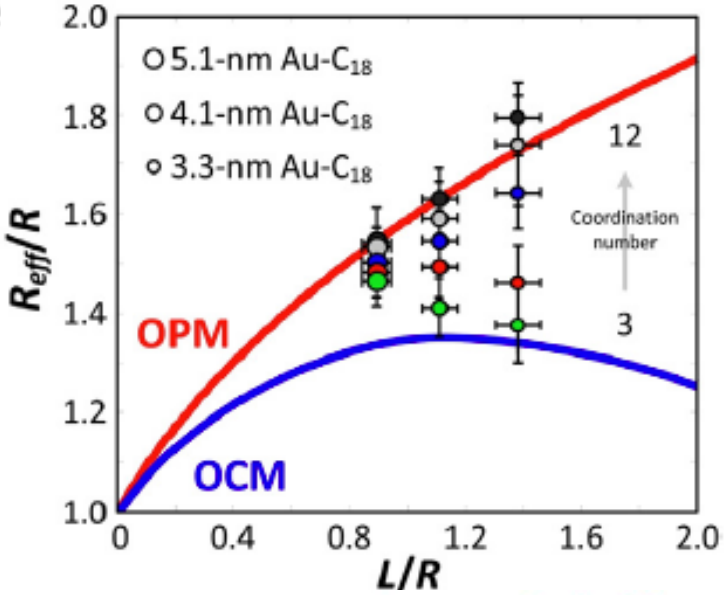
OPM vs OCM

Experimentally: simple lattices:
depends on NC coordination number q



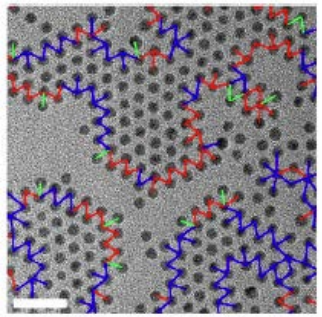
$$\tau^{OPM} = (1 + 3\lambda)^{1/3}$$

Luedtke, Landman J. Phys. Chem. B (2003)

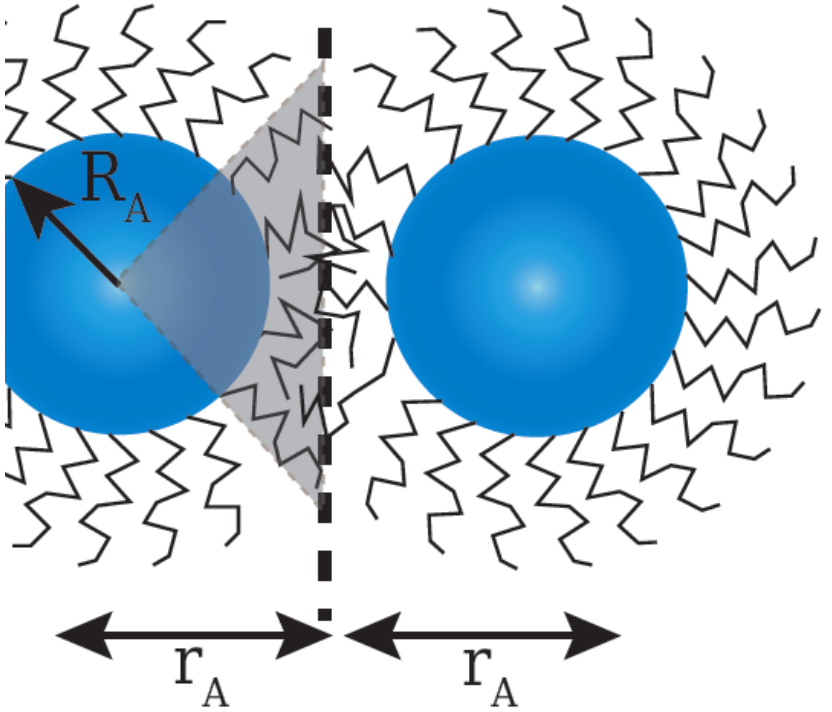


q = 3 OCM

q ≥ 6 OPM



Boles, Talapin JACS (2015)



$$\tau^{OCM} = \eta_{HS}^{1/3}(1 + 3\lambda)^{1/3}$$

Schapotschnikow, Vlugt, J. Chem. Phys. (2009)

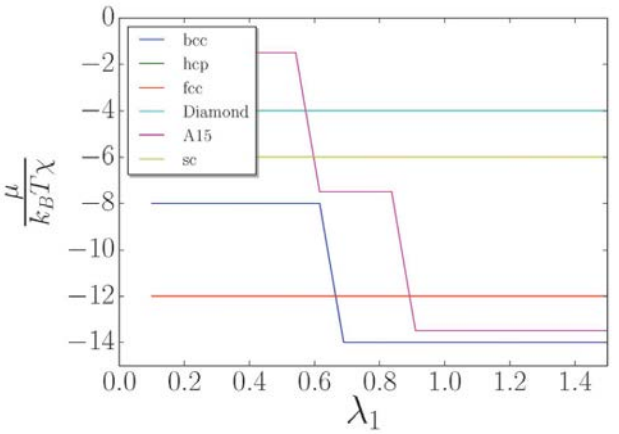
The OPM-FE model

The OPM-model provides selection rules (no free energy).

A free energy (OPM-FE) is constructed by:

- OPM-Spheres of radius $r_A = \tau^{OPM} R_A$
- NCs in contact interact with VdW potential: $V(i,j) = -\frac{A_h}{6D}\frac{r_i r_j}{r_i + r_j} = -\chi \frac{r_i r_j}{r_i + r_j} \equiv -\chi f(i,j)$
- Free energy is:

$$F = -\frac{\chi}{2}\sum_{i=1}^{N}\sum_{j\in\mathcal{N}(i)} f(i,j)$$



Minimum of OPM-FE = Minimum of VdW energy + chain entropy.

bcc to fcc transition in single component systems.

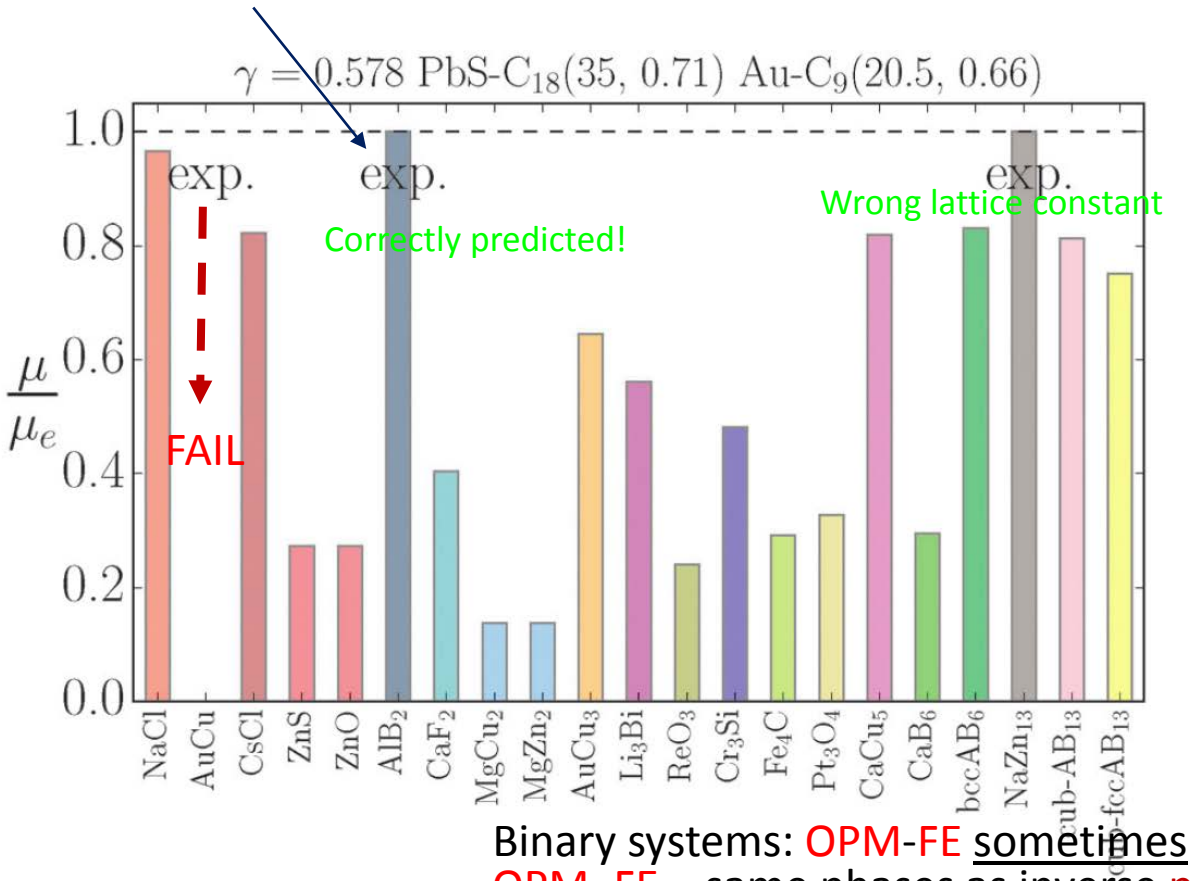
A.T., Soft Matter (2017)

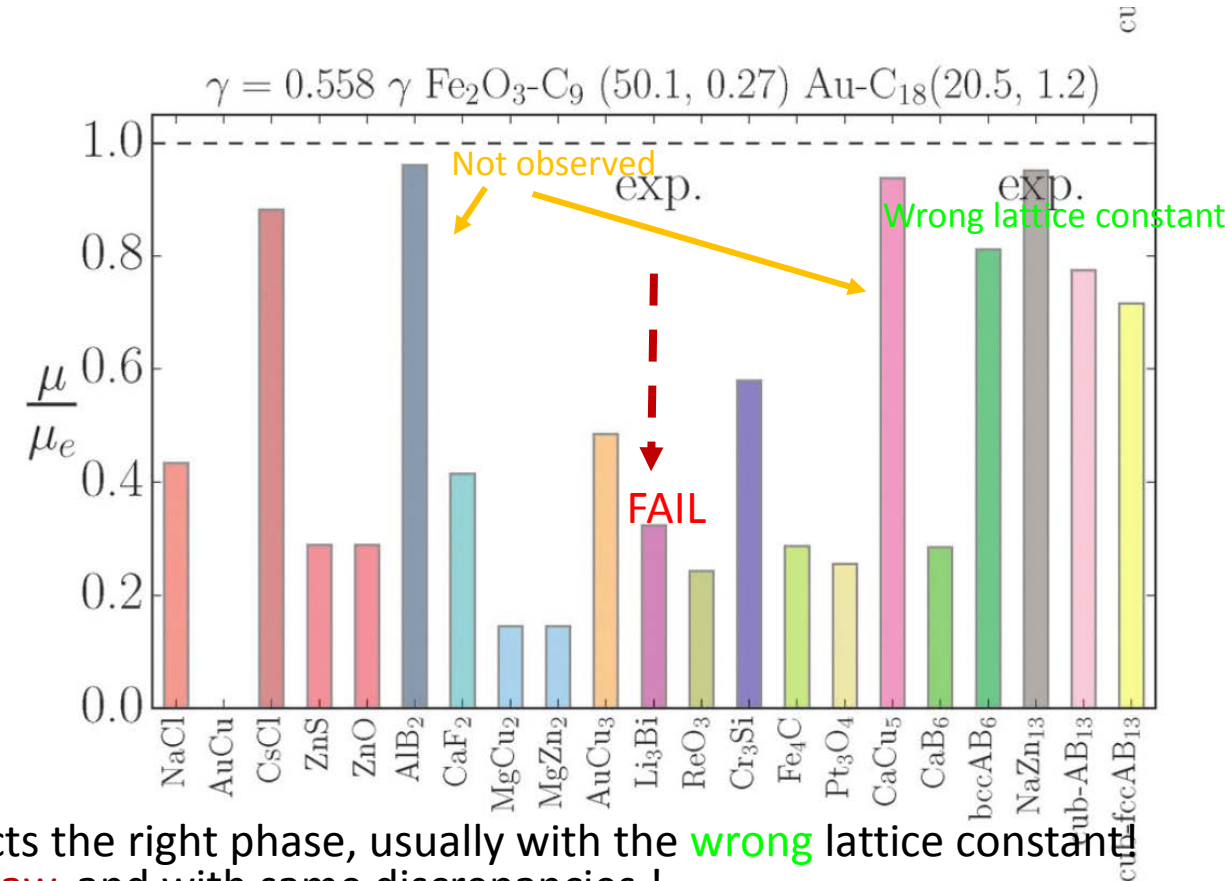
Results for OPM-FE

Model: OPM-FE

exp. *Boles, Talapin JACS (2015)*

Bar =1 (equilibrium) if < 1 how far is from equilibrium.



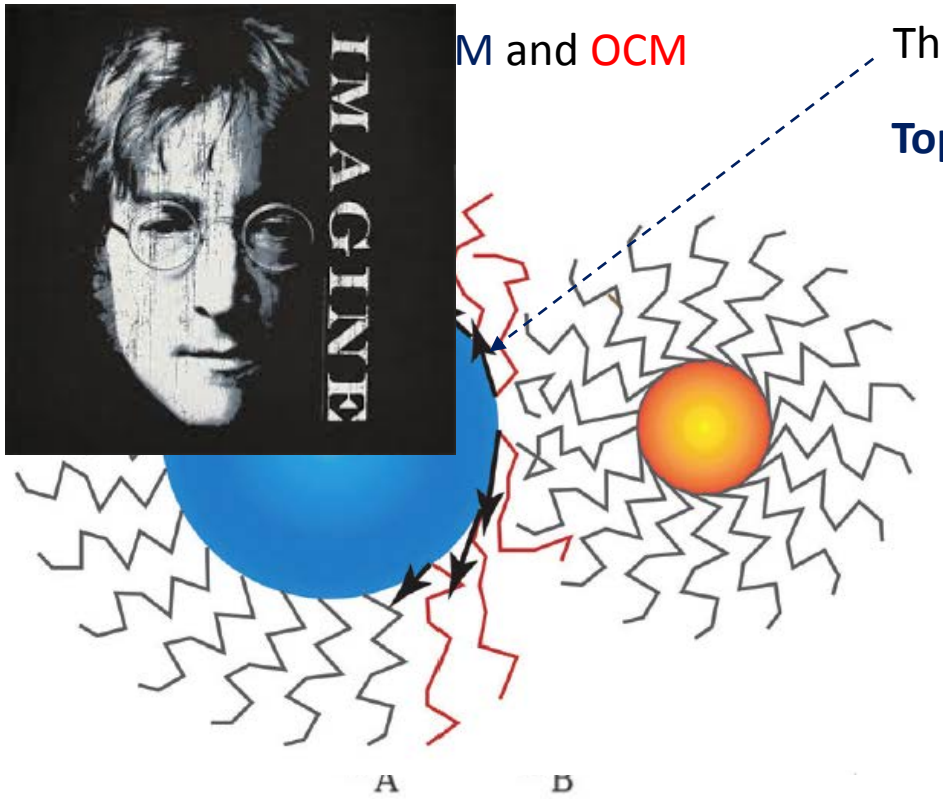


Binary systems: OPM-FE sometimes predicts the right phase, usually with the wrong lattice constant!
OPM–FE = same phases as inverse power law, and with same discrepancies !
OCM not in agreement!

A.T., Soft Matter (2016)

Vortices and Neutral lines

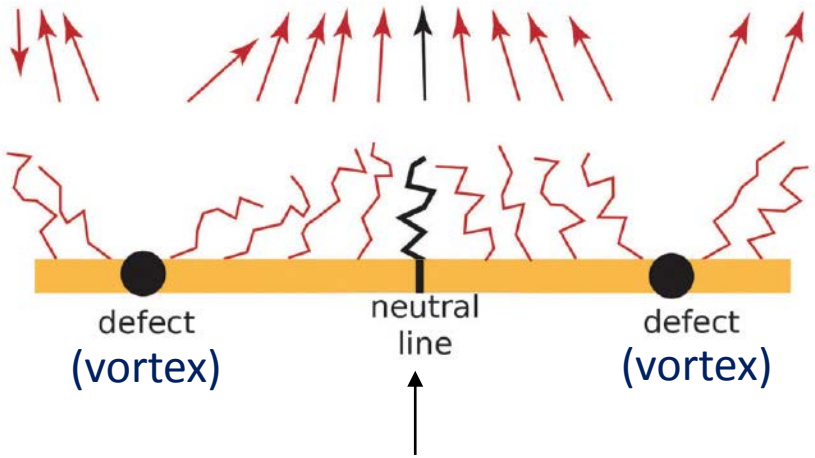
New!!!



Topology (Gauss-Bonnet theorem): There can only be 2 ! (no-anti vortices)

However, vortex = projection of the 3-dimensional hydrocarbon orientation

Vortices can "escape through the third dimension…."



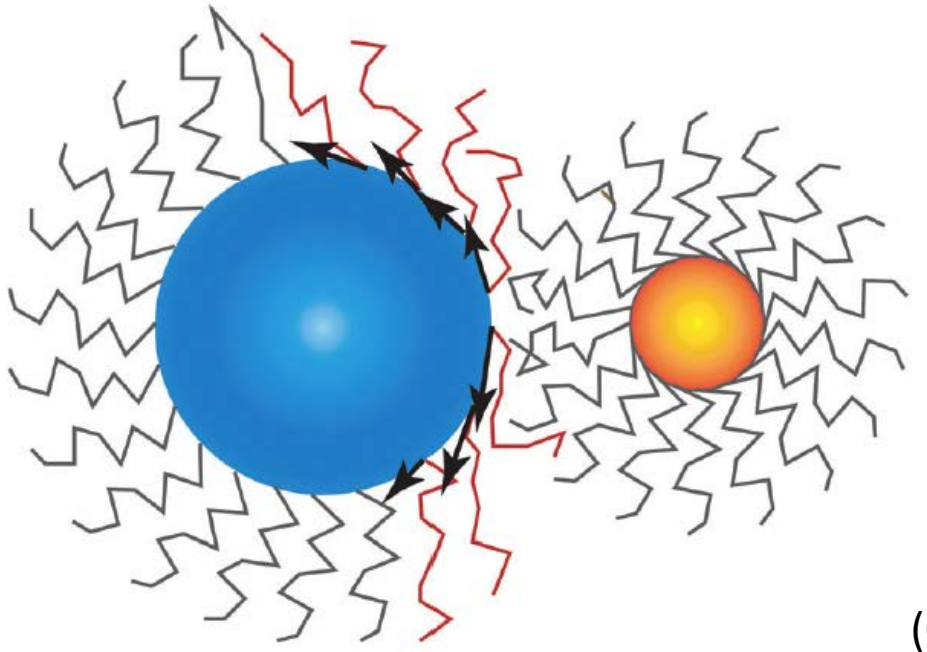
Neutral lines are generated!

NCs as SKYRMIONS WITH topological charge -1:

A.T., Soft Matter (2017)
Selinger, Konya, A.T., Selinger J. Phys. B (2011)
Bowick, Nelson, A.T., Phys. Rev. B (2000)

The OTM model

Topological charge q_T: number of vortices.



q_T=1 q_T=0

What neutral lines look like when $q_T > 1$?

A) vortices

OTM HYPOTHESIS: Neutral lines are costly, need to be MINIMIZED:

q_T = 1,2 One or two vortices (no neutral lines).

q_T = 3 Two vortices and one ½ disclination or 3 vortices.

q_T = 4 Four ½ disclinations or 4 vortices with neutral lines.

$q_T \geq 6$ neutral lines too costly, topological charge is trivial.

(Currently testing this hypothesis with explicit simulations!)

Ratio of nanoparticle radius (hexagonal lattice) is:

$$\gamma \equiv \frac{\tau_B^{OTM}(q_T=0)}{\tau_A^{OTM}(q_T=0)} = \frac{\tau_B^{OPM}}{\tau_A^{OPM}}$$

A.T., Soft Matter (2017)

Prediction of lattice structure within OTM:

Example: $MgZn_2$

Space Group: $P6_3mmc$

Unit cell: 4A 8B

Wyckoff positions: 4f (A) Hex diamond

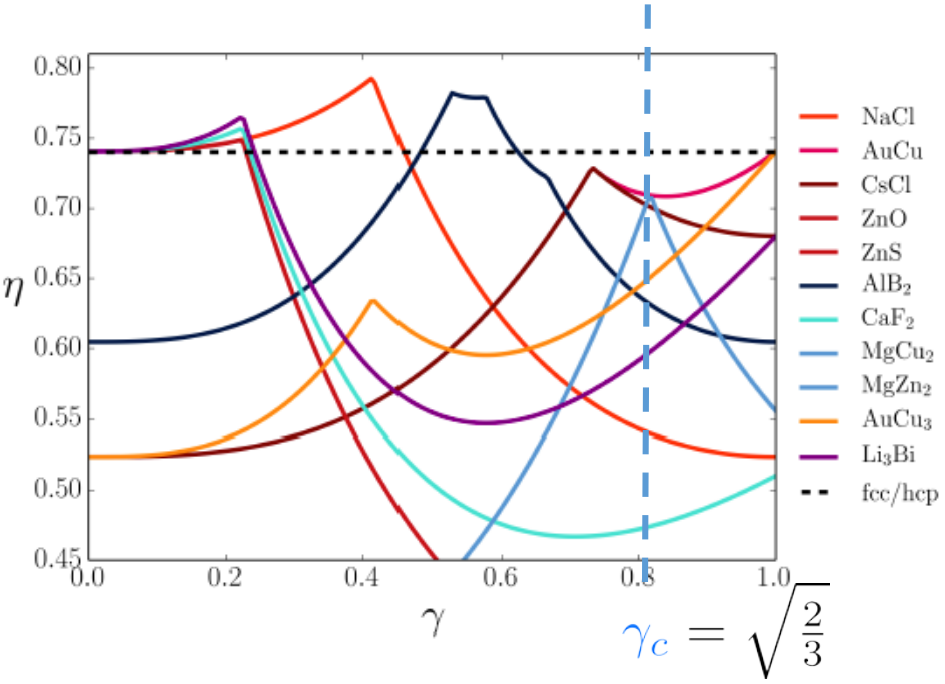
2a, 6h (B) Pyrochlore

$$\gamma \equiv \frac{\tau_B^{OPM}}{\tau_A^{OPM}}$$

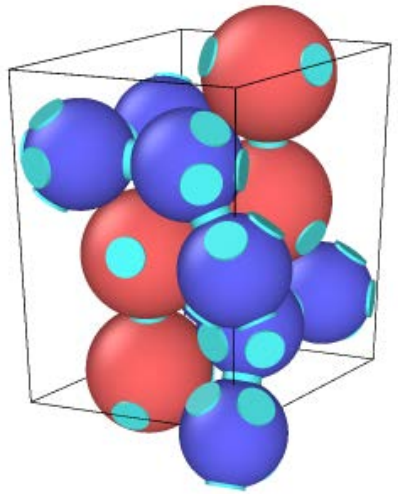
OPM: $q_T = 0$: $\gamma = \gamma_c = \sqrt{\frac{2}{3}}$ A-A contacts (q=4)

B-B contacts (q=6)

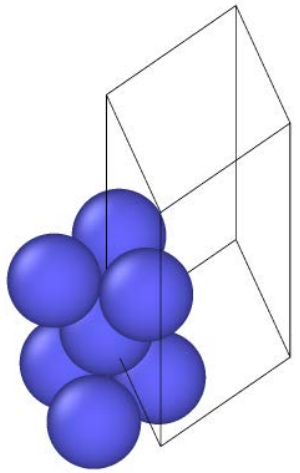
OTM: B-particles can only have $q_T = 0$ $\gamma > \gamma_c = \sqrt{\frac{2}{3}}$



$\gamma_c = \sqrt{\frac{2}{3}}$

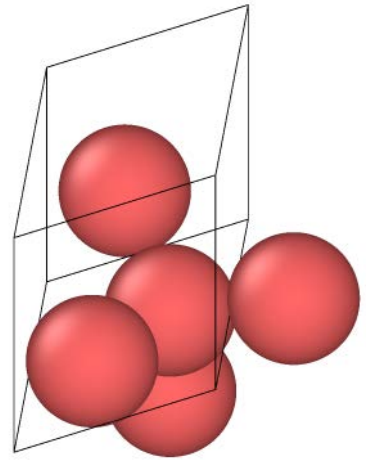


$MgZn_2$



Pyrochlore

$q_T = 0$



Diamond

q_T=0 or 4

A.T., Soft Matter (2017)

Prediction of lattice structure within OTM:

Example: $MgZn_2$

Space Group: $P6_3mmc$

Unit cell: 4A 8B

Wyckoff positions: 4f (A) Hex diamond

2a, 6h (B) Pyrochlore

$$\gamma \equiv \frac{\tau_B^{OPM}}{\tau_A^{OPM}}$$

OPM: $q_T = 0$: $\gamma = \gamma_c = \sqrt{\frac{2}{3}}$ A-A contacts (q=4)

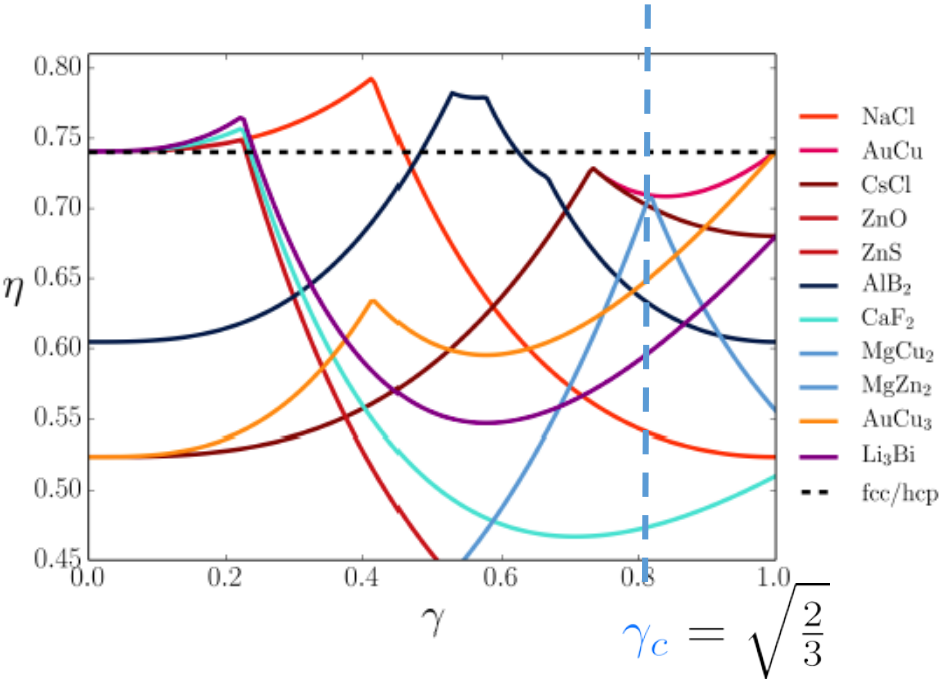
B-B contacts (q=6)

OTM: B-particles can only have $q_T = 0$ $\gamma > \gamma_c = \sqrt{\frac{2}{3}}$

$$\frac{r_A^{OTM}}{r_A^{OPM}} = \frac{r_B}{r_B^{OPM}} = \frac{\gamma}{\gamma_c} < 1 \quad \frac{\gamma}{\gamma_c} r_A^{OPM}$$

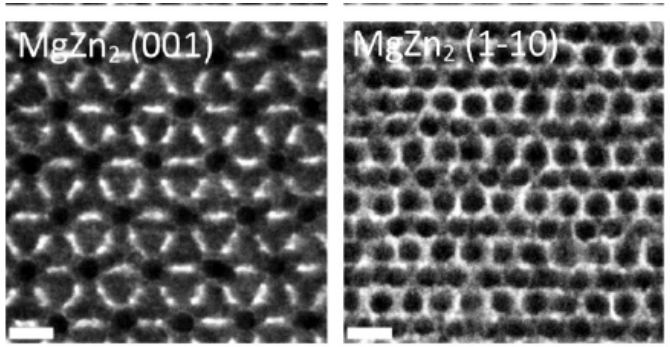
Prediction

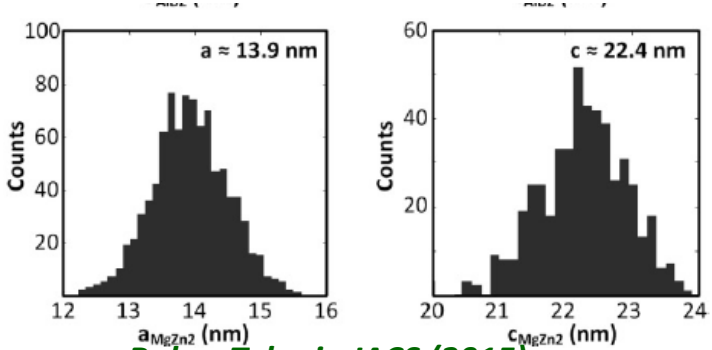
Computed from L, R



A.T., Soft Matter (2016)

Measured experimentally

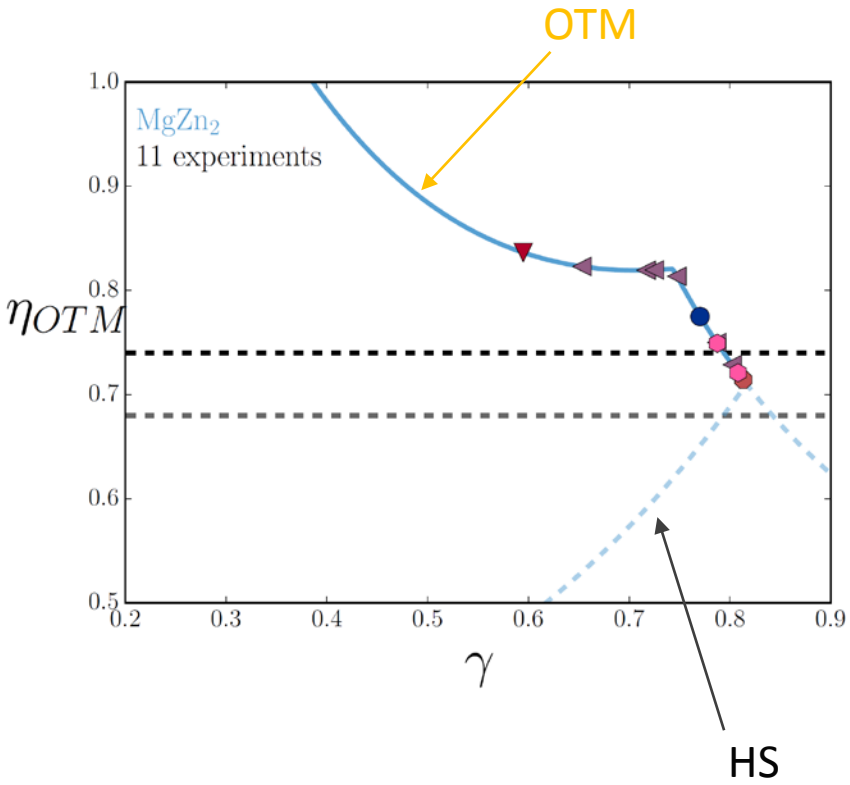


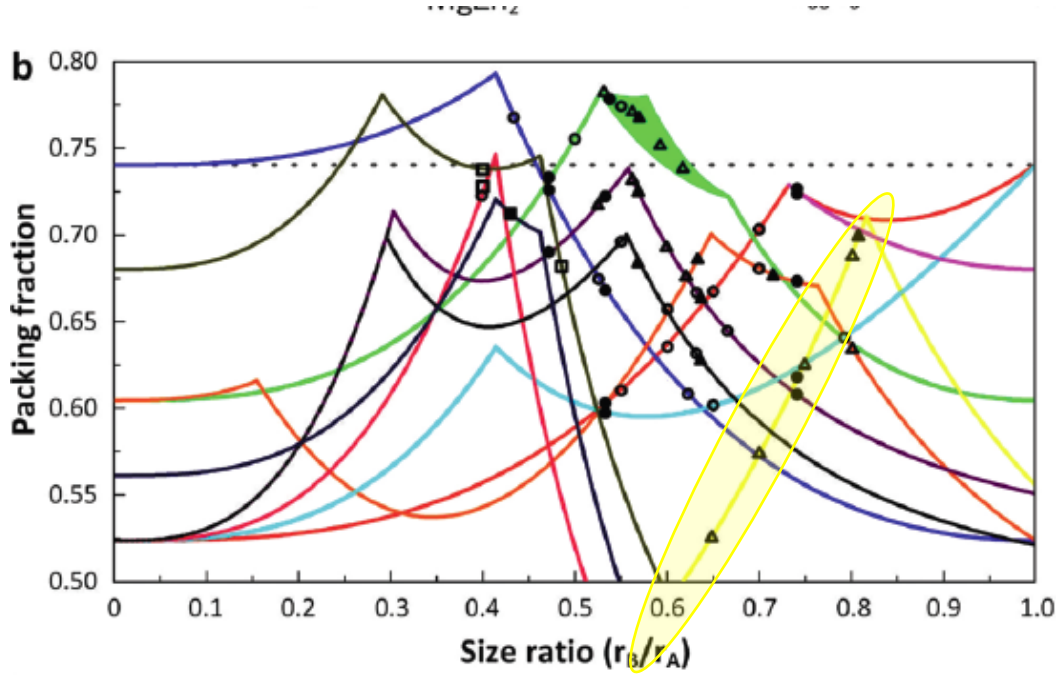


Boles, Talapin JACS (2015)

$MgZn_2$

Within OTM PF widely exceeds the HS prediction for values $\gamma < \gamma_c$

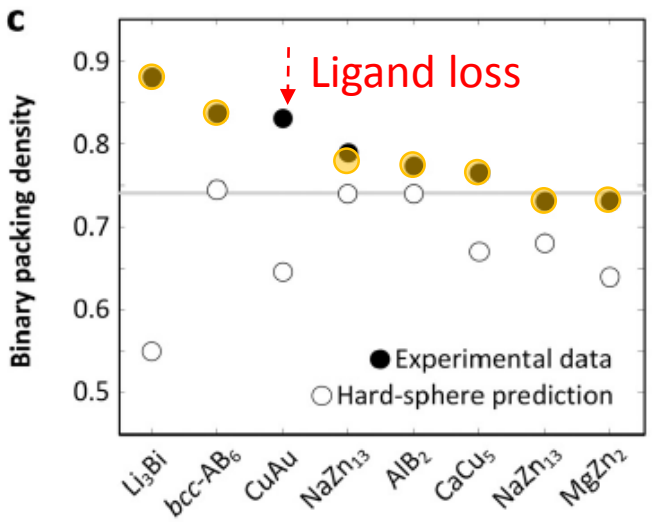




$MgZn_2$ is an example of a low HS PF that becomes High PF within OTM

OTM and experiment

Prediction of Binary Packing density



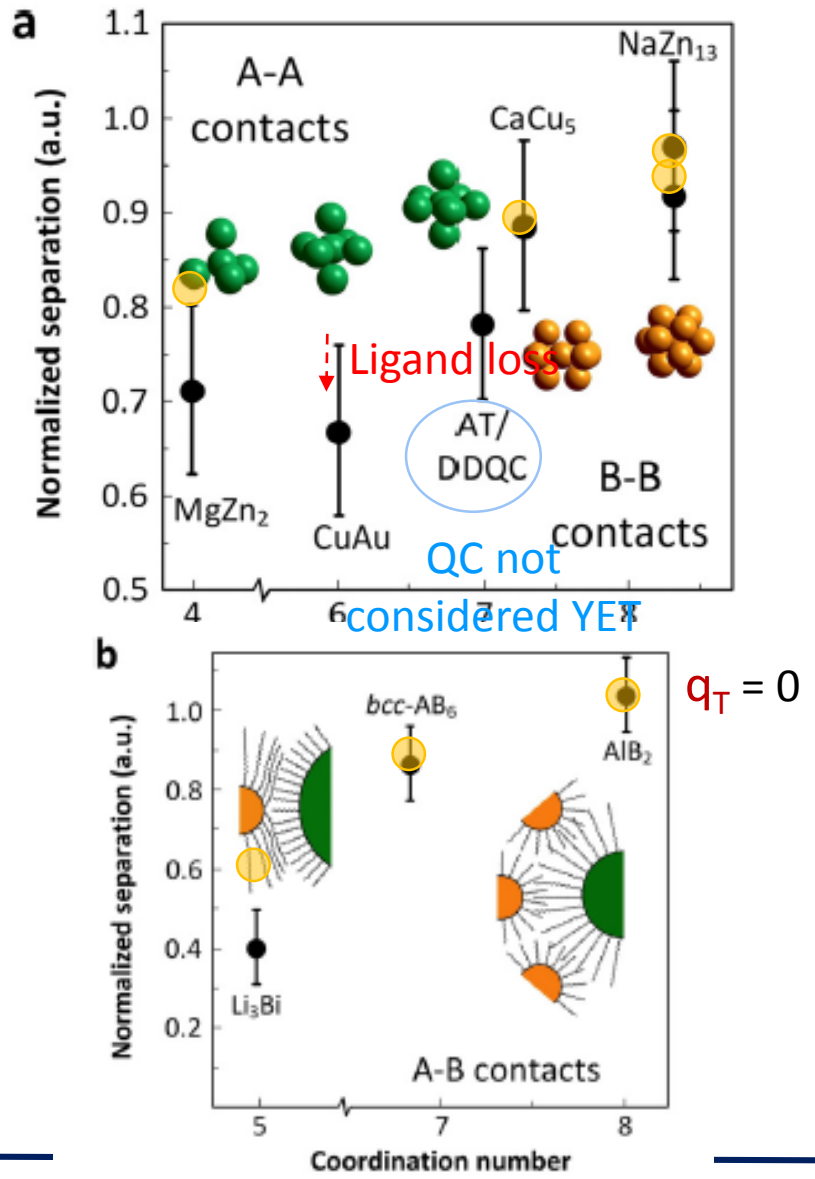
A.T., Soft Matter (2017)

Boles, Talapin JACS (2015)

OTM and experiment

Prediction of lattice structure

Uncertainty in Normalized separation is high …



$q_T = 0$

A.T., Soft Matter (2017)

Boles, Talapin JACS (2015)

Summary of OTM predictions:

Comparison with experiments for both the lattice constant and packing fraction from *Boles, Talapin JACS (2015)*

	η_u			$\bar{d}_{ij}$		
BNSL	exp	OTM	OTM*	exp	OTM	OTM*
$MgZn_2$	0.79	0.77	0.83	1.30	1.35	1.13
Li_3Bi	0.88	0.87	0.86	0.90	0.98	1.01
$bccAB_6$	0.83	0.84	0.86	1.90	2.20	2.00
$CaCu_5$	0.76	0.67	0.70	2.40	2.56	2.50
AlB_2	0.77	0.77	0.78	2.29	2.43	2.33
$NaZn_{13}$	0.73	0.72	0.72	1.75	1.80	1.64
$NaZn_{13}$	0.79	0.74	0.74	2.48	2.72	2.57
AuCu	$0.05^{\dagger}$	0.02	0.01	$(-)^{\dagger}$	>1	>1

There is almost perfect agreement with experiments for all lattices studied in the experiments!

Prediction of ligand loss!

A.T., In preparation (2017)

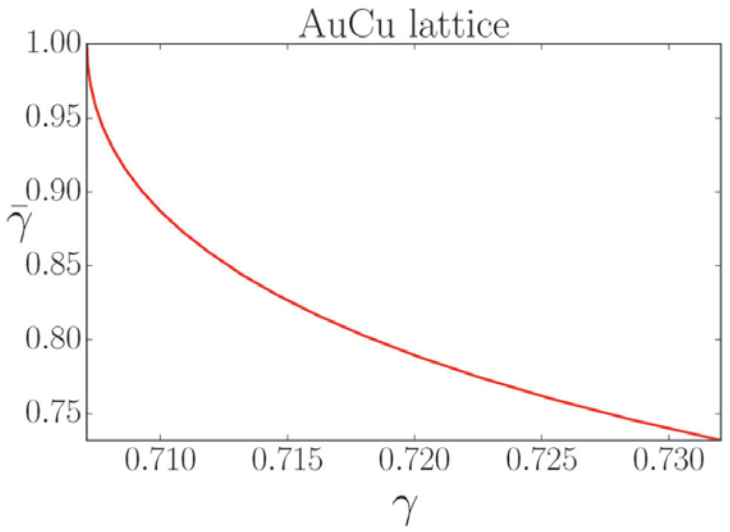
Ligand loss: The case of AuCu

OPM: $q_T = 0$: $\gamma = \gamma_c = \sqrt{3} - 1 \sim 0.73$ A-A contacts (q=4)
A-B contacts (q=8)

OTM: B-particles can only have $q_T = 0$
A-particles can have $q_T = 4$

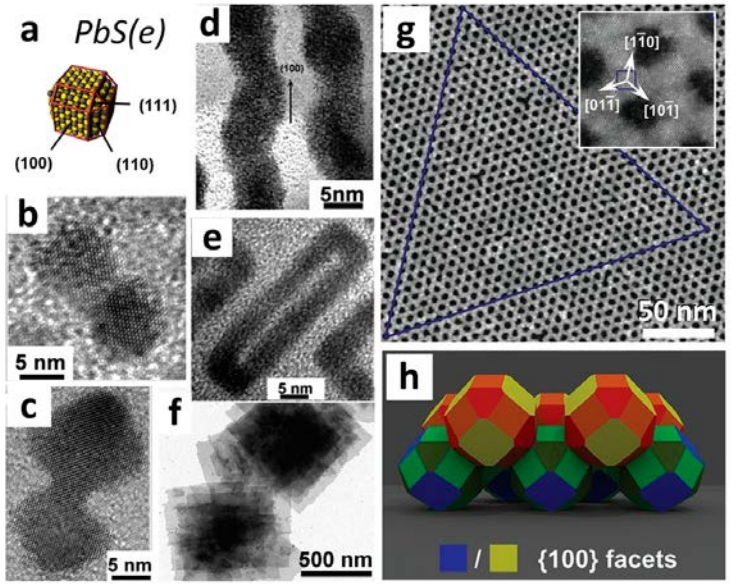
The solution only reaches up to

$$\gamma = \gamma_{c,2} = 1/\sqrt{2} \sim 0.707$$



Experiments report $\gamma_{c,2} \leq 0.57$

Within OTM, experimental results are consistent only if ligands are lost and raw (PbS) are in contact alomg the (1 0 0) faces.



Boles, Engel, Talapin, Chem. Rev. (on-line September 2016)

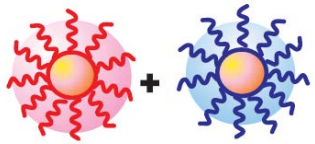
Experimental evidence in complete agreement with OTM prediction. Ligand loss seems a general feature in PbS, includes quasicrystals.

Conclusions

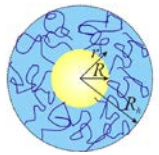
Superlattices: where topology meets geometry meets physics meets chemistry meets materials science!

Superlattice structure prediction for 3 different assembly strategies:

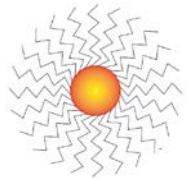
1) DNA-water driven by hybridizations.
2) Hydrocarbons-Organic solvent driven by VdW forces.
3) PEG water driven by electrostatic segregation, and ultimately, by VdW forces.



DNA: Hydrophobicity in linkers influence the resulting phase diagram



Polymers (PEG): crystallization of spherical polymer brushes in 2D and 3D: Controlled lattice constant by salt concentration. Softer ligands (longer polymers) make more mesophases.



Hydrocarbon ligands: skyrmions (hedgehogs) with “non-topological” defects

OTM model explains structure and stability of super-crystal phases

GRAND CHALLENGE to Supercrystal prediction: Understand/Control relaxation times (DYNAMICS): Microfluidics?

Dynamical Lattice Theory

Hoover, Ross, Johnson, Henderson, Barker, Brown J. of Phys. Chem. (1970)

A.T., J. of Phys. Chem. (2014)

This is the harmonic approximation: Write the coordinates of every particle as

$$\vec{R}_a = R_a^0 + \vec{u}_a$$

Position of the particle in the lattice

Displacement from the lattice

The potential energy is:

$$U = \frac{1}{2}\sum_{a,b} V(\vec{R}_a - \vec{R}_b) = \frac{1}{2}\sum_{a,b} V(\vec{R}_a^0 - \vec{R}_b^0) + \frac{1}{2}\sum_{a,b} u_a^i D_{(a,i),(b,j)} u_b^j$$

$$= U_0 + \frac{1}{2}\sum_{a,b} u_a D_{a,b} u_b$$

The free energy is:

$$F^{harm} = U_0 + k_B T \log det D$$

DLT is an approximation because we are neglecting higher order terms…

DLT becomes exact in the limit of very low temperatures!

Computational tools

Calculation of free energies

Self-assembly simulations

MD DYNAMICS

HOODLT

A.T., J. of Phys. Chem. (2014)

HOOMD

J.A. Anderson, C. D. Lorenz and A.T., J. of Comp. Phys. (2008)

C. Knorowski, C. Calero, A.T., almost accepted (2015)

+ GENETIC ALGORITHMS

K. Ho Group collaboration (2016)

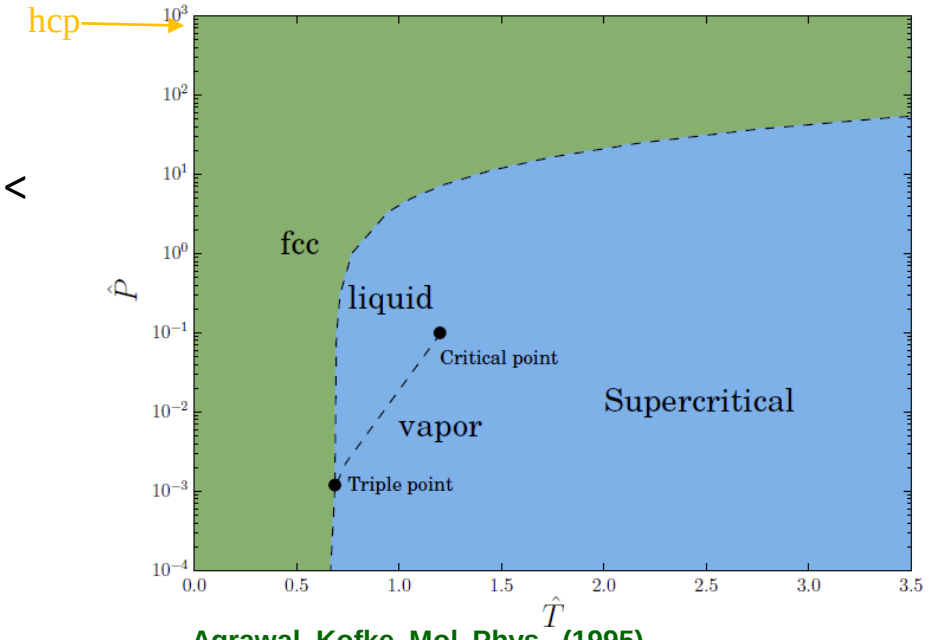
Lennard-Jones Systems

$$V(r) = 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The known phase diagram is given by

At T=0, the equilibrium phase is hcp for P < 878.49

Stillinger, J. of Phys. Chem. (2001)



Agrawal, Kofke, Mol. Phys. (1995)

A.T., J. of Phys. Chem. (2014)

DLT calculation

hcp is the low temperature solid phase!!!

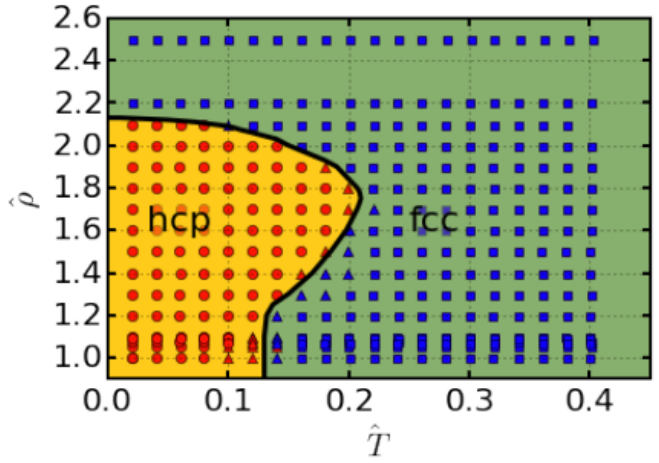
DLT is actually quite accurate!

How results are modified once anharmonic terms are included?

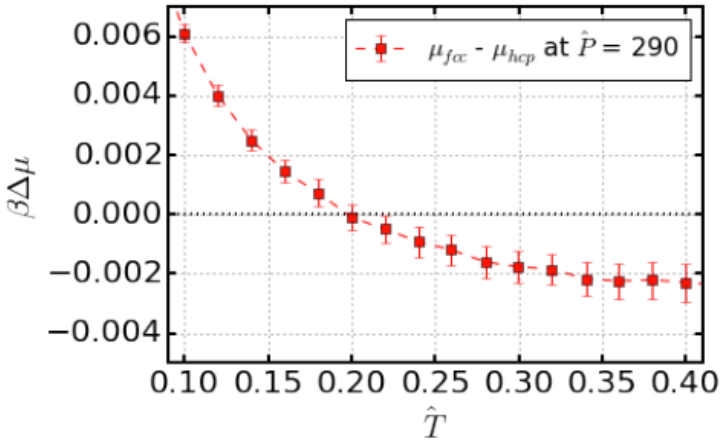
Lennard Jones Systems

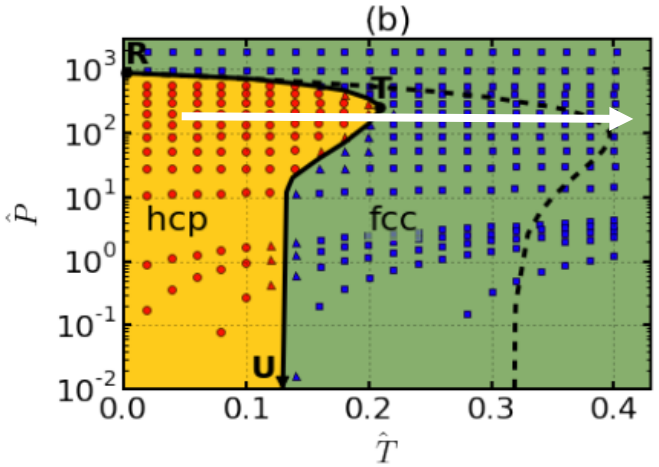
C. Calero, C. Knorowski and A.T., submitted (2015)

The anharmonic contribution is calculated in all these many points…

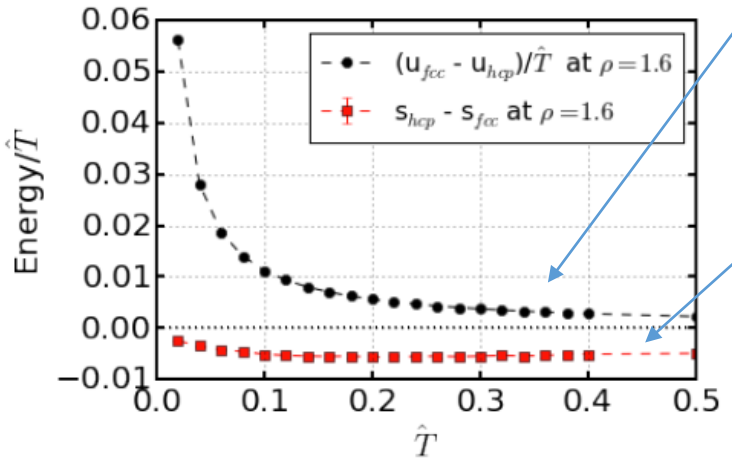


The difference in chemical potential is very small!





The free energy difference is a very subtle balance



Entropy favors fcc

Energy favors hcp

Super-lattices and hard sphere models

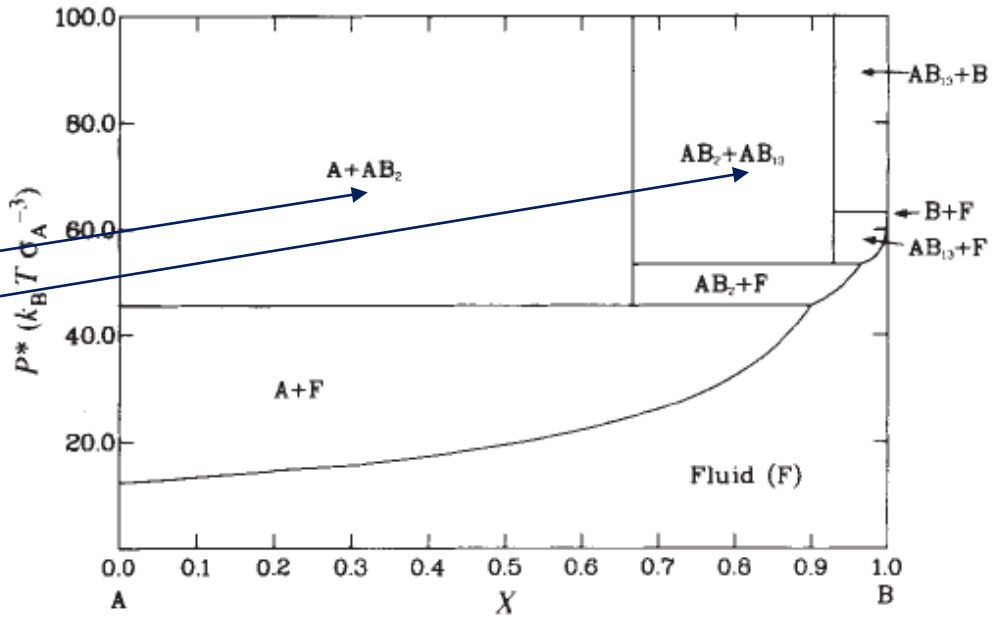
Model the nanoparticles as hard spheres of the respective diameters

$$\gamma = d_A/d_B$$

NaCl
CuAu
AlB_2
$MgZn_2$
$MgNi_2$
$AuCu_3$
CFe_4
$CaCu_5$
CaB_6
$NaZn_{13}$
$CubAB_{13}$
+more

NaCl
AlB_2
$NaZn_{13}$

$$\gamma = 0.58$$

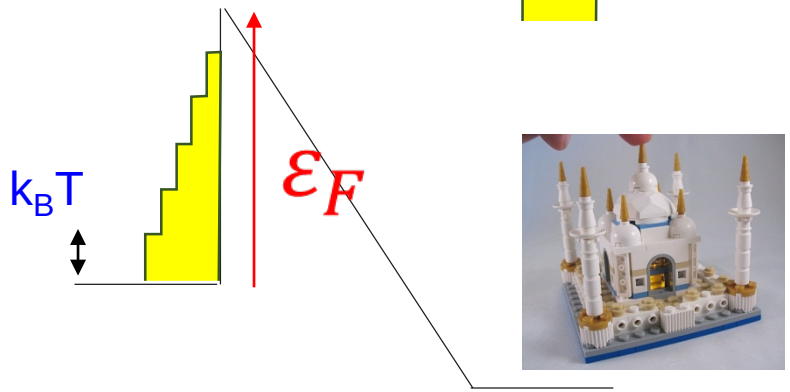


Eldridge, Madden, Frenkel (Nature 1993)

What is mess?

Assembly, when energies >> $k_B T$ does not happen (within available time!)

UNLESS



- CATALYST, enzyme, etc…

NOT ORDERED

SUCCESS?

OUT OF EQUILIBRIUM =

2

$$\varepsilon_F / k_B T$$

Lattices

We compute the free energy for the following 24 lattices:

N	ST	SG	S	P	A
fcc	A or B	Fm-3m	A1	cF4	
hcp	A or B	$P6_3/mmc$	A3	hP2	
bcc	A or B	Im3m	A2	cI2	
NaCl	AB	Fm-3m	B1	cF8	
AuCu	AB	P4/mmm	$L1_0$	cP4	
CsCl	AB	Pm-3m	B2	cP2	
ZnS	AB	F-43m	B3	cF8	
ZnO	AB	$P6_3/mc$	B4	hP4	
AlB_2	AB_2	P6/mmm	C32	hP3	
CaF_2	AB_2	Fm-3m	C1	cF12	
$MgCu_2$	AB_2	Fd-3m	C15	cF24	Laves
$MgZn_2$	AB_2	$P6_3/mmc$	C14	hP12	Laves
$AuCu_3$	AB_3	Pm-3m	$L1_2$	cP4	
Li_3Bi	AB_3	Fm-3m		cF16	
ReO_3	AB_3	Pm-3m	$D0_9$	cP4	
Cr_3Si	AB_3	Pm-3n	A15	cP8	
Fe_4C	AB_4	P-43m		cP5	
Pt_3O_4	A_3B_4	Pm-3n		cP14	
$CaCu_5$	AB_5	P6/mmm	$D2_d$	hP6	
CaB_6	AB_6	Pm-3m	$D2_1$	cP7	
bcc-AB_6	AB_6	Im-3m		cI14	Cs_6C_{60}
$NaZn_{13}$	AB_{13}	Fm3c	$D2_3$	cF112	
cub-AB_{13}	AB_{13}	Pm-3m		cP14	
cub-fcc-AB_{13}	AB_{13}	Fm-3m	$D2_f$	cF56	

Stability (D-matrix positive definite) occurs only for a range of γ

$\gamma_L =$	γ - 0.08	γ	γ + 0.08
NaCl	0.00-0.51	0.00-0.51	0.00-0.51
AuCu	0.86-1.00	0.51-0.75 0.91-1.00	0.86-1.00
CsCl	0.51-0.87	0.51-0.87	0.51-0.87
ZnO	0.00-0.24	0.00-0.24	0.00-0.24
ZnS	0.00-0.24	0.00-0.24	0.00-0.24
AlB_2	—	0.24-0.61	—
CaF_2	—	—	—
$MgCu_2$	0.59-0.88	0.59-0.88	0.59-0.88
$MgZn_2$	0.60-0.88	0.60-0.88	0.60-0.88
$AuCu_3$	0.79-1.00	0.79-1.00	0.79-1.00
Li_3Bi	—	—	—
ReO_3	—	—	—
Cr_3Si	—	—	—
Fe_4C	—	—	—
Pt_3O_4	—	—	—
$CaCu_5$	0.58-0.68	0.52-0.66	0.58-0.68
CaB_6	0.20-0.39	—	0.20-0.39
bcc-AB_6	0.34-0.45	0.34-0.45	0.34-0.45
cub-AB_{13}	—	—	—
cub-fcc-AB_{13}	—	—	0.38-0.41
$NaZn_{13}$	0.43-0.87	0.46-0.86	0.43-0.87

p = 12

$\gamma_L =$	γ - 0.08	γ	γ + 0.08
NaCl	0.00-0.70	0.00-0.70	0.00-0.70
AuCu	—	0.63-1.00	—
CsCl	0.63-1.00	0.63-1.00	0.63-1.00
ZnO	0.00-0.22	0.00-0.22	0.00-0.22
ZnS	0.00-0.22	0.00-0.22	0.00-0.22
AlB_2	—	0.24-0.52	—
CaF_2	0.91-1.00	0.91-1.00	0.91-1.00
$MgCu_2$	—	—	—
$MgZn_2$	—	—	—
$AuCu_3$	0.58-0.92	0.58-0.92	0.58-0.92
Li_3Bi	0.53-1.00	0.53-1.00	0.53-1.00
ReO_3	—	—	—
Cr_3Si	0.63-1.00	0.63-1.00	0.63-1.00
Fe_4C	—	—	—
Pt_3O_4	—	—	—
$CaCu_5$	0.38-0.49	0.39-0.50	0.38-0.49
CaB_6	0.17-0.27	—	0.17-0.27
bcc-AB_6	—	0.22-0.31	—
cub-AB_{13}	—	—	—
cub-fcc-AB_{13}	—	—	—
$NaZn_{13}$	0.29-0.53	—	0.29-0.53

p = 6