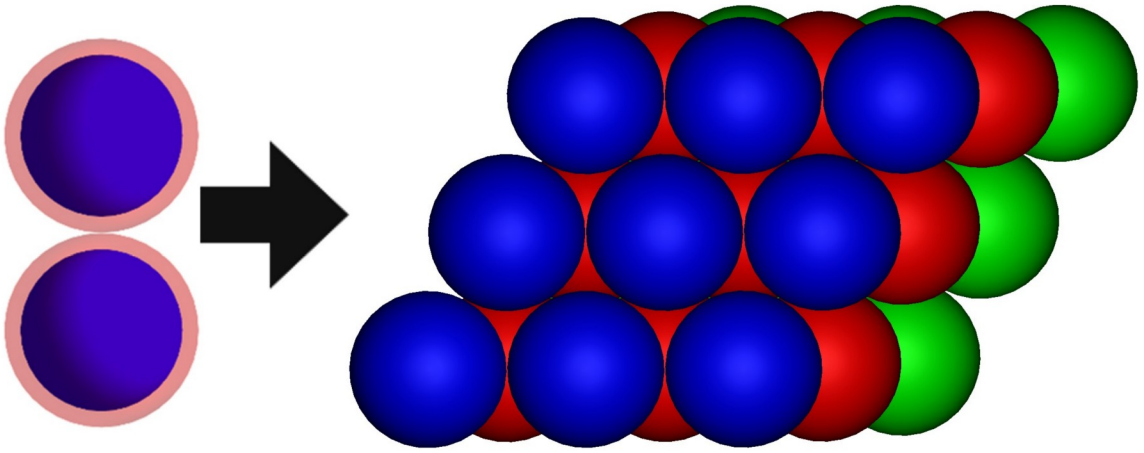
HEINRICH HEINE
UNIVERSITÄT DÜSSELDORF

cnrs

LPS
ORSAY

Predicting self-assembly in simple models with multiple length scales

Frank Smallenburg
Laboratoire de Physique des Solides
Orsay



ANR SoftQC

LABORATOIRE DE CHIMIE ENS DE LYON

LPS ORSAY

- Website : https://softqc.wordpress.com/

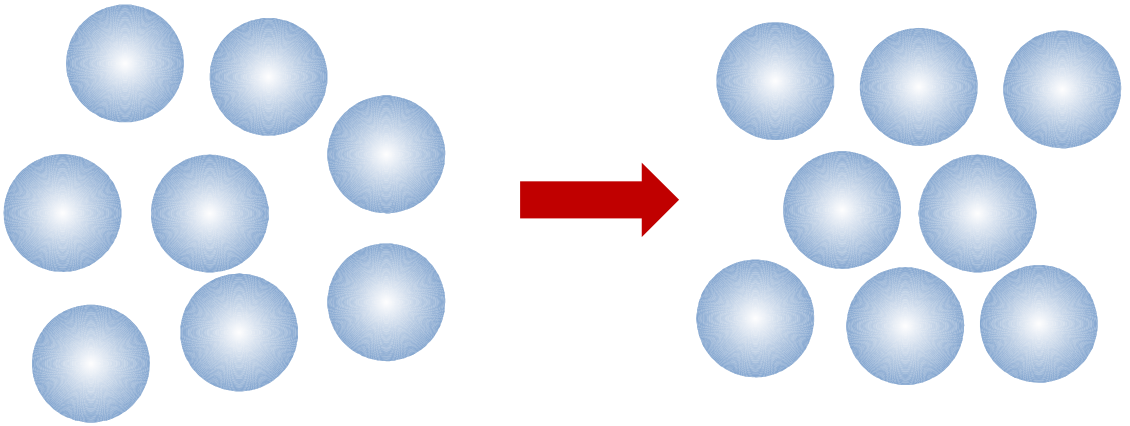
Tackling quasicrystal self-assembly

- Nanoparticle synthesis
- Self-assembly in 2D and 3D
- Structural studies
  - interactions in solution : S(q)
  - superlattices : Bragg peaks
- Simulations
- Theory

Benjamin Abécassis (ENS Lyon)
Claire Goldmann
Brigitte Pansu
Marianne Impéror-Clerc
Giuseppe Foffi
Frank Smallenburg
Anuradha Jagannathan
Jean-François Sadoc

2 PhD students (to start in October 2019) and 1 postdoc (to start in 2020)

How can we predict self-assembly?



We have a set of particle with known interactions and conditions:

What phase(s) can we expect to show up?

Predicting self-assembly with simulations

Direct strategy:

Simulate the system, see what forms

- Usually slow
- Not reliable
- Qualitative results

Predicting self-assembly with simulations

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Simulate the system, see what forms

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Can we be more precise?

Predicting phase behavior

Given:

- Number of particles **N**
- Volume **V**
- Temperature **T**

the thermodynamically stable state for any system is the state with the **lowest Helmholtz free energy *F(N,V,T)***.

This free energy is a combination of potential energy and entropy:

$$F = U - TS$$

For large systems, F is proportional to N and V.
Hence, can be written as $F(\rho, T) = N f(\rho, T)$.

$\rho = N / V$
Number density

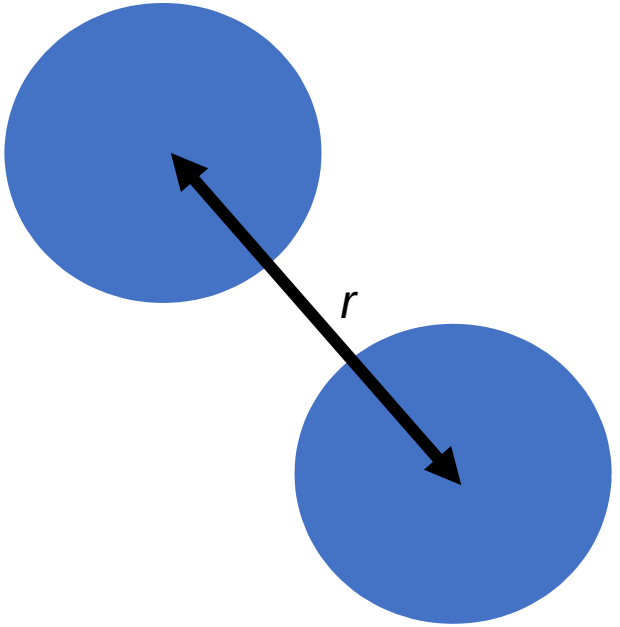
Starting simple: Hard spheres

- **Model:**

$$\beta\phi(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases}$$

(overlap)

(no overlap)



- **Helmholtz Free Energy:**

$$F = \cancel{U} - TS$$

For hard particles, all non-overlapping configurations have the same potential energy (U = 0).

The **entropy** drives the phase transitions.

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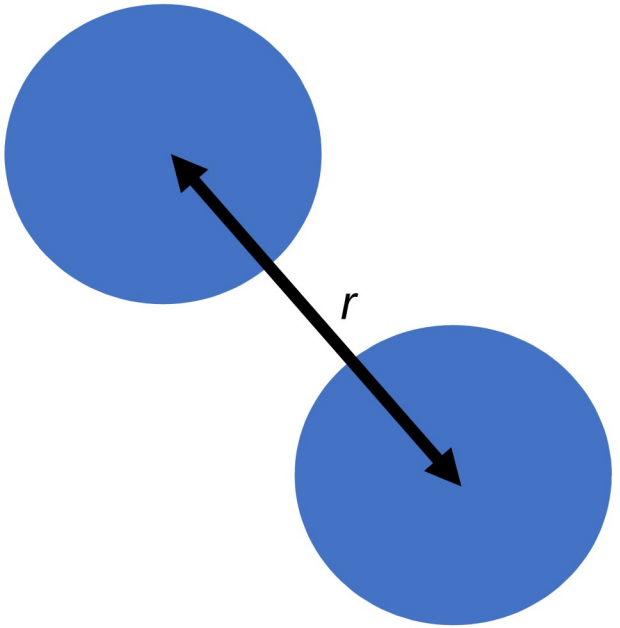

- **Helmholtz Free Energy:**

$$F = \cancel{U} - TS$$

$$F = -k_B T \log Q$$

Boltzmann distribution

$$Q(N, V, T) = \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

Thermal wavelength

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Starting simple: Hard spheres

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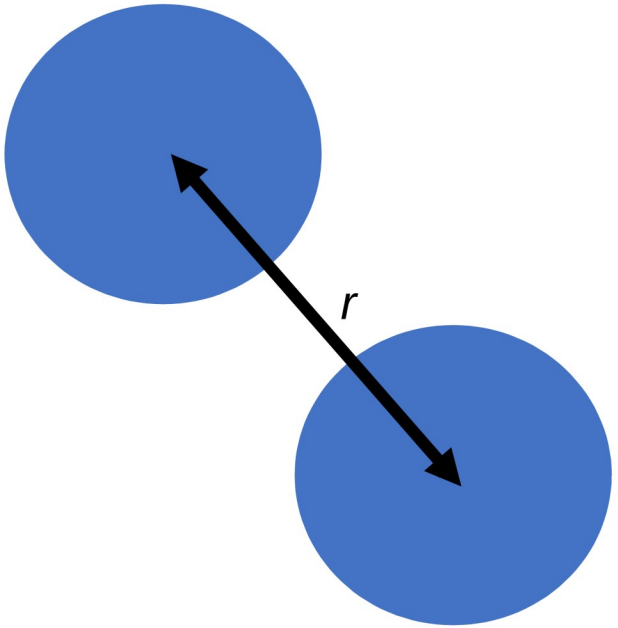

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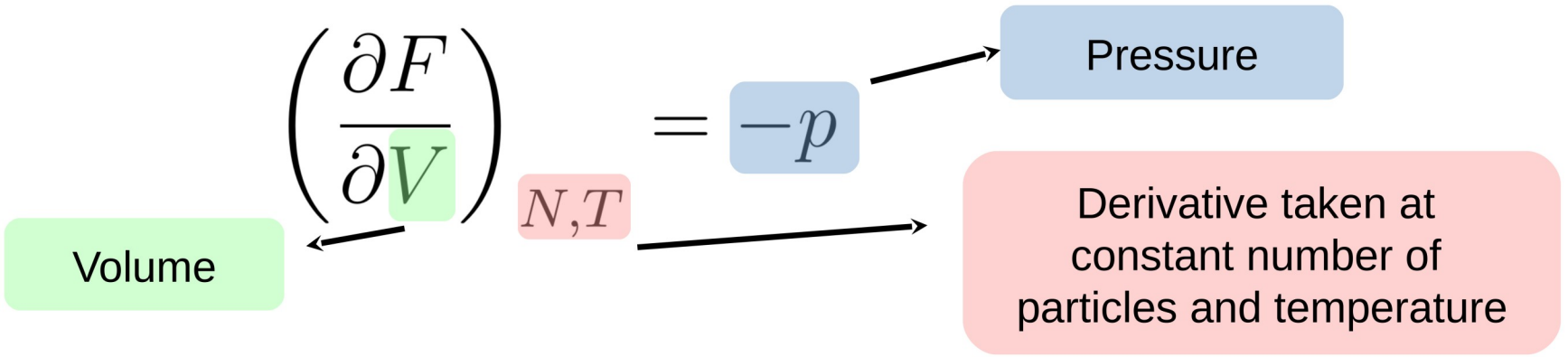
Boltzmann distribution

No overlaps: 1

Overlaps: 0

Thermodynamic integration

Unfortunately, we **cannot** measure this entropy in simulations directly.
However, we can measure **derivatives** of the free energy.
For example the pressure:



Thermodynamic integration

Unfortunately, we **cannot** measure this entropy in simulations directly.
However, we can measure **derivatives** of the free energy.
For example the pressure:

$$\left(\frac{\partial F}{\partial V}\right)_{N,T} = -p$$

Volume

V

N,T

Pressure

$-p$

Derivative taken at constant number of particles and temperature

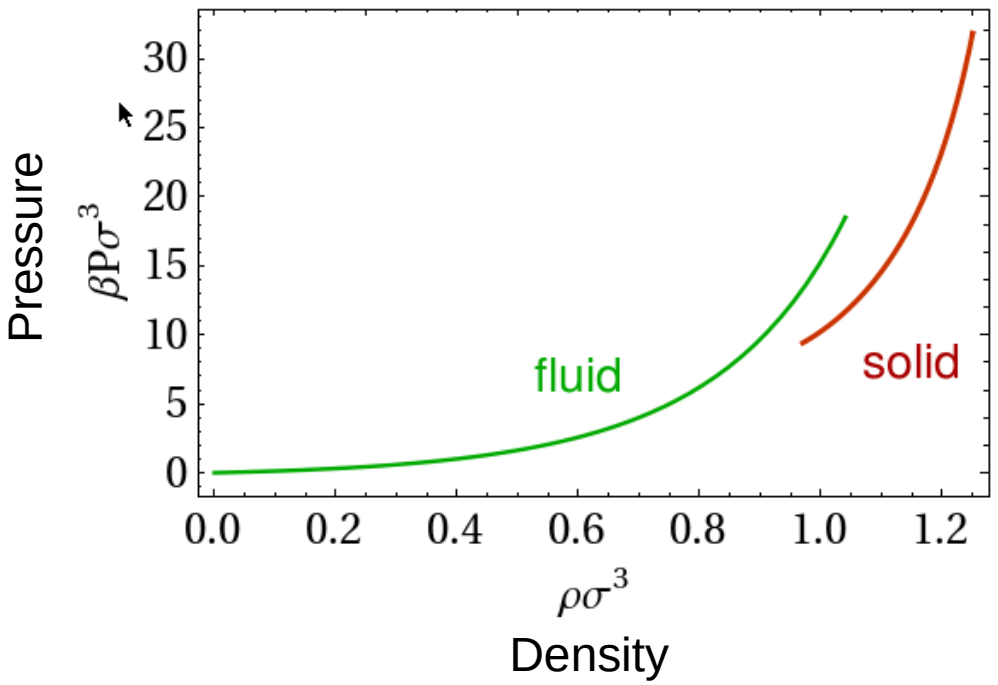
Additionally, in the low-density limit, the system behaves as an ideal gas, with a known free energy:

$$\frac{F_{id}}{Nk_BT} = \log(\rho\Lambda^3) - 1$$

Hence, we can calculate *F* at any density
by integrating the pressure… **for a fluid**

Hard sphere pressure

Measure **equation of state** in simulations:



$\rho = N/V$

$\beta = 1/k_B T$

σ = particle diameter

Hard sphere pressure

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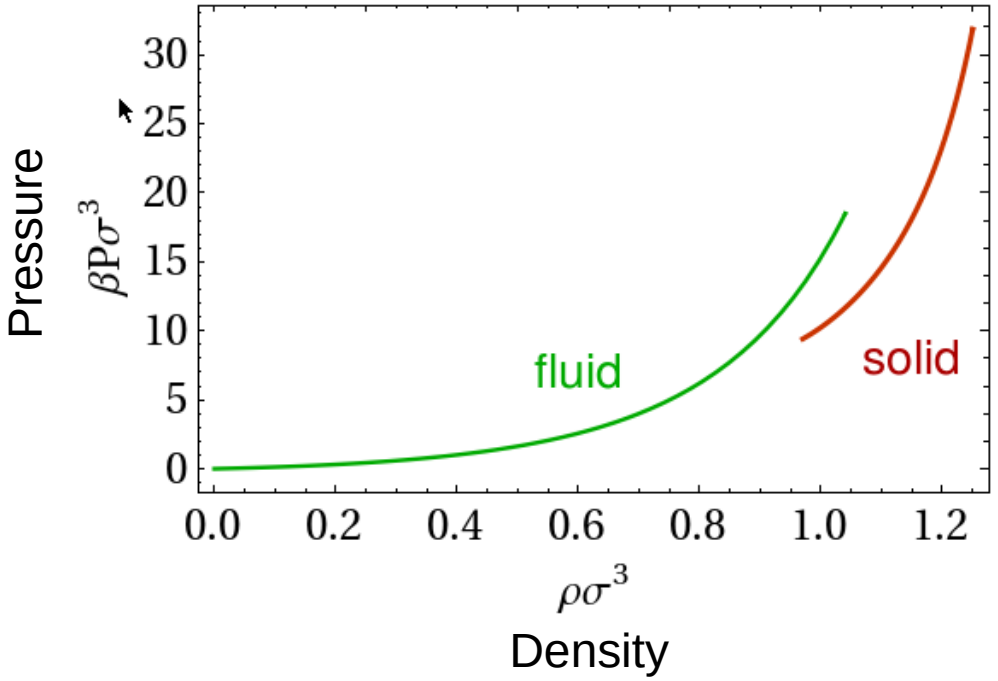

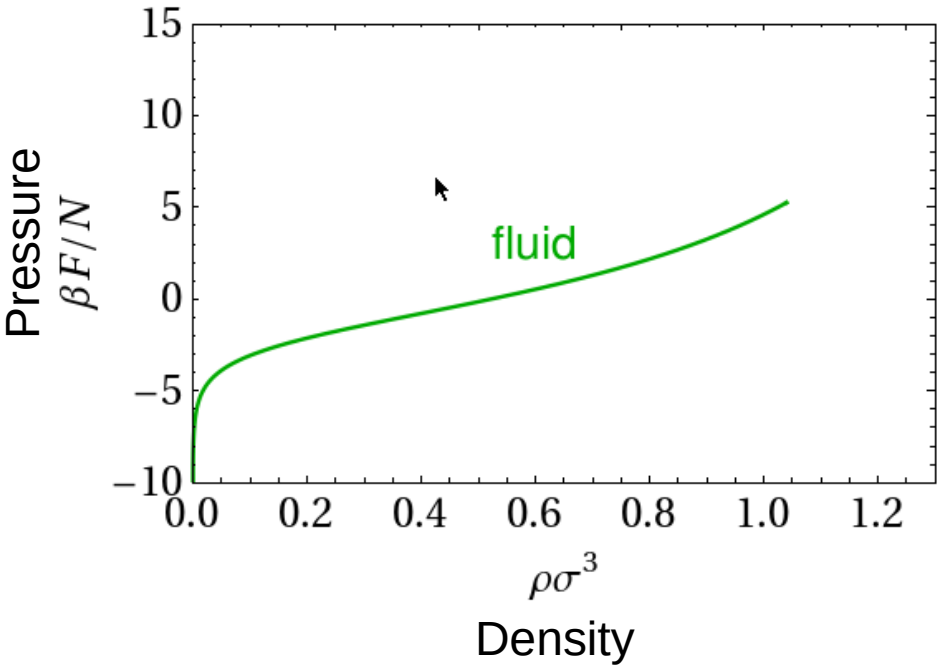

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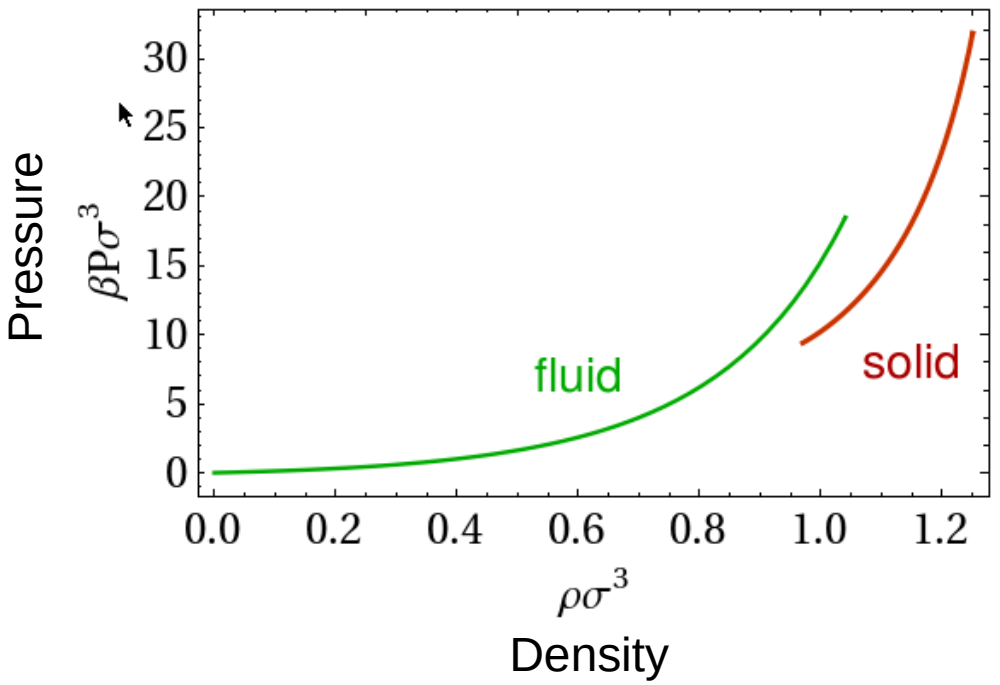

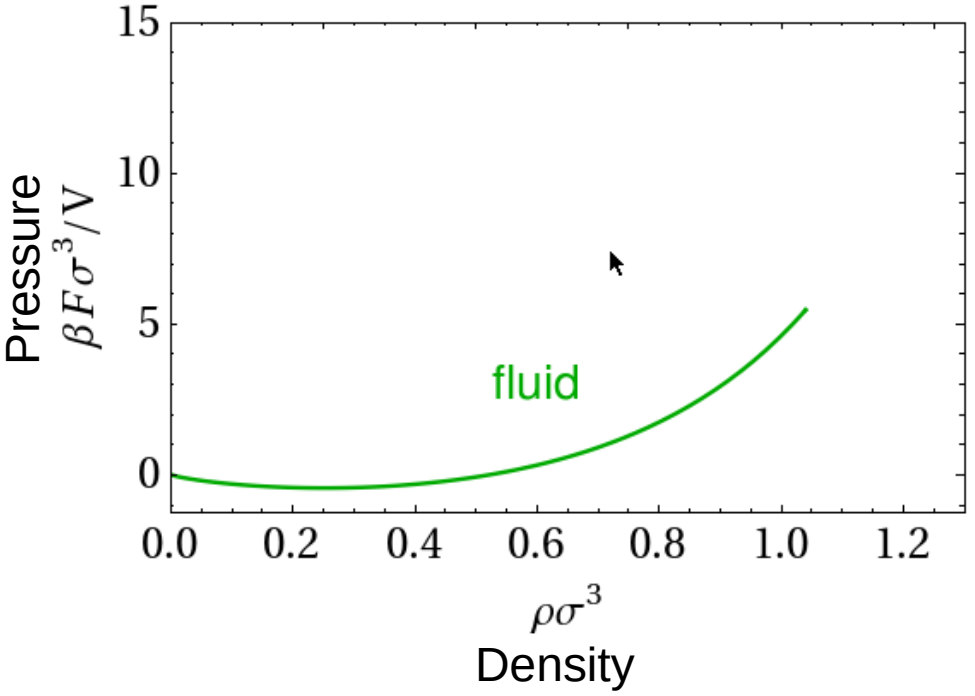

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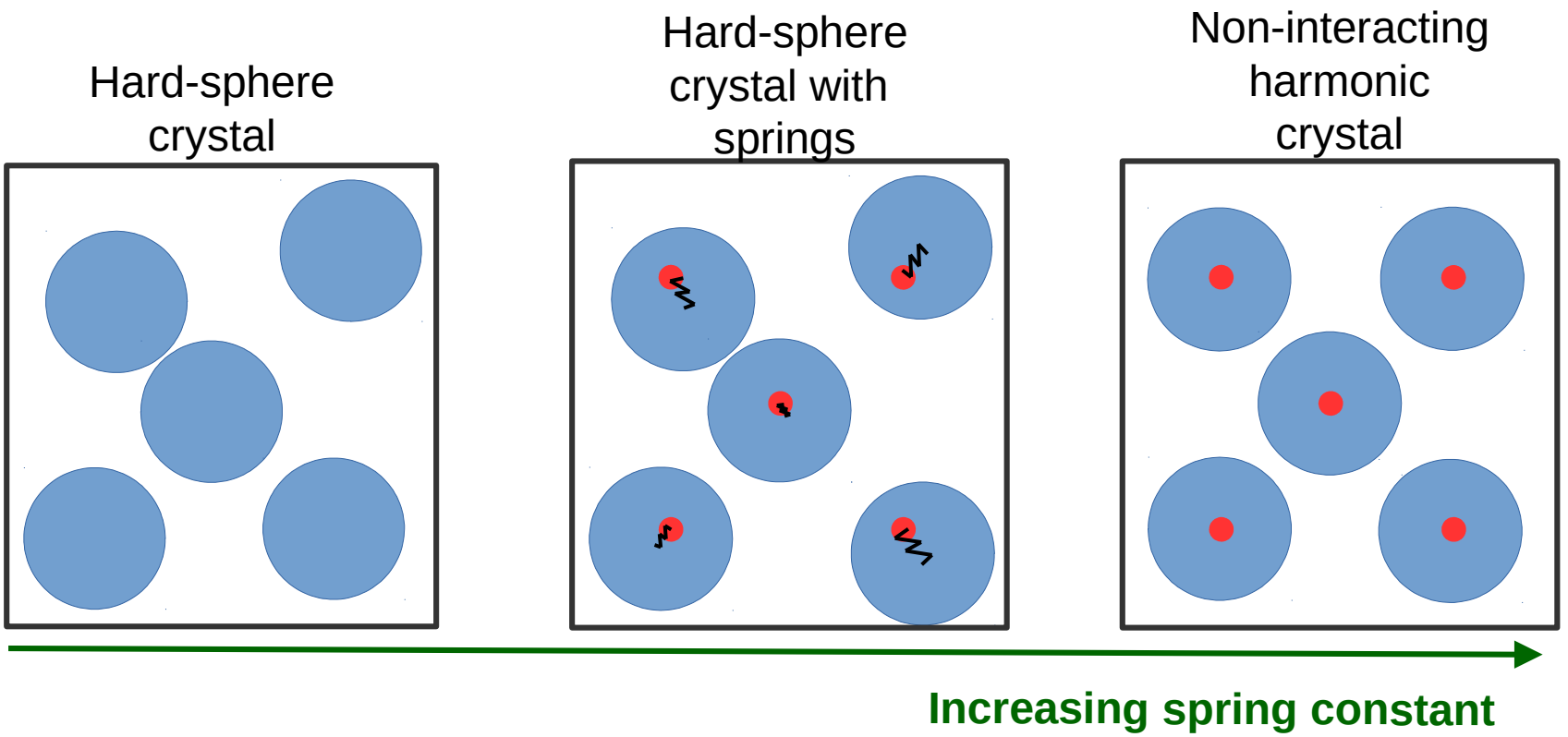
But where do we draw the crystal?

Crystal free energy

For ordered phases, we need a **reference free energy**.

Several routes for obtaining a reference free energy:

1. Thermodynamic integration to an analytically solvable system

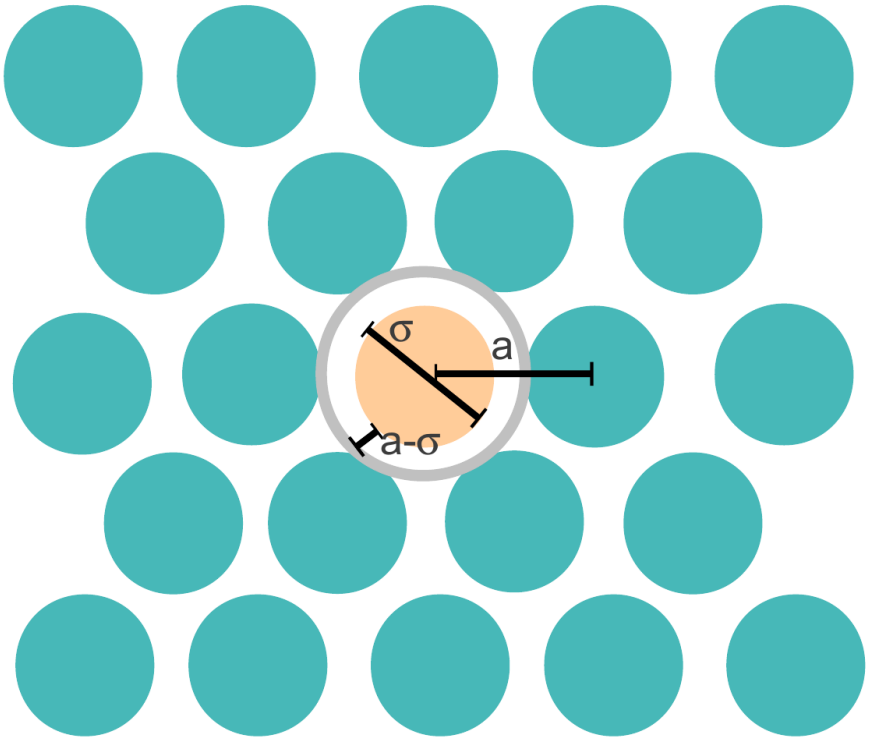


Crystal free energy

For the crystal phase, we can do the same thing, if we know the free energy at some density.

Several routes for obtaining a reference free energy:

2. Theoretical approximations



Simple example: **Cell theory**

- Mean-field approximation of crystal free energy.
- Simple and reasonably accurate for hard particles.

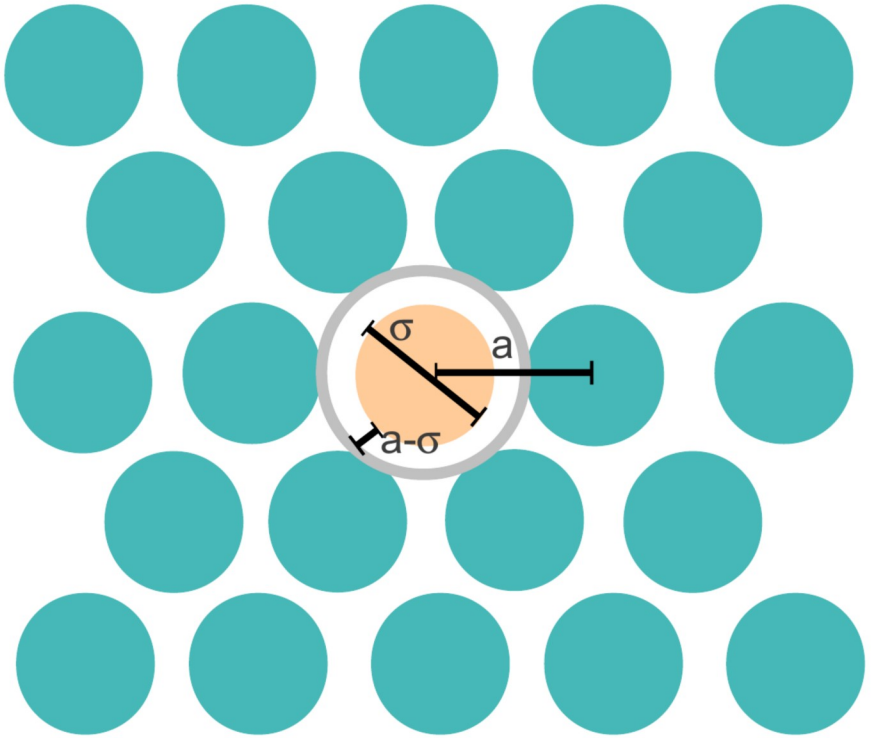
Cell theory

Consider a hard-sphere crystal (e.g. FCC):

- lattice spacing: $a = \left(\frac{\rho}{\rho_{\max}} \right)^{1/3}$

$\rho = N / V$

$\rho_{\max} = \sqrt{2}/\sigma^3$



If we assume all **other particles** are at their average positions, what is the free energy of a single particle?

$$
\begin{aligned}
f_1 &= -k_B T \log Z \\
&= -k_B T \log \left(\frac{1}{\Lambda^3} \int_{V_1} \mathrm{d}\mathbf{r} \exp(-\beta U) \right) \\
&\simeq -k_B T \log \left(\frac{4\pi (a-\sigma)^3}{3} \right)
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Full free energy:

$$F = N f_1$$

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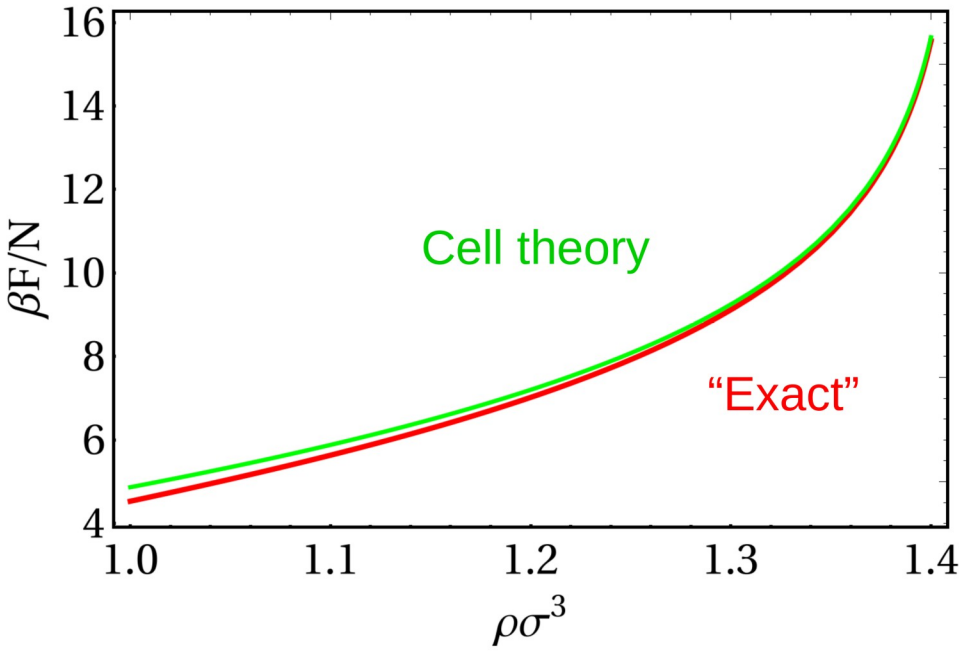

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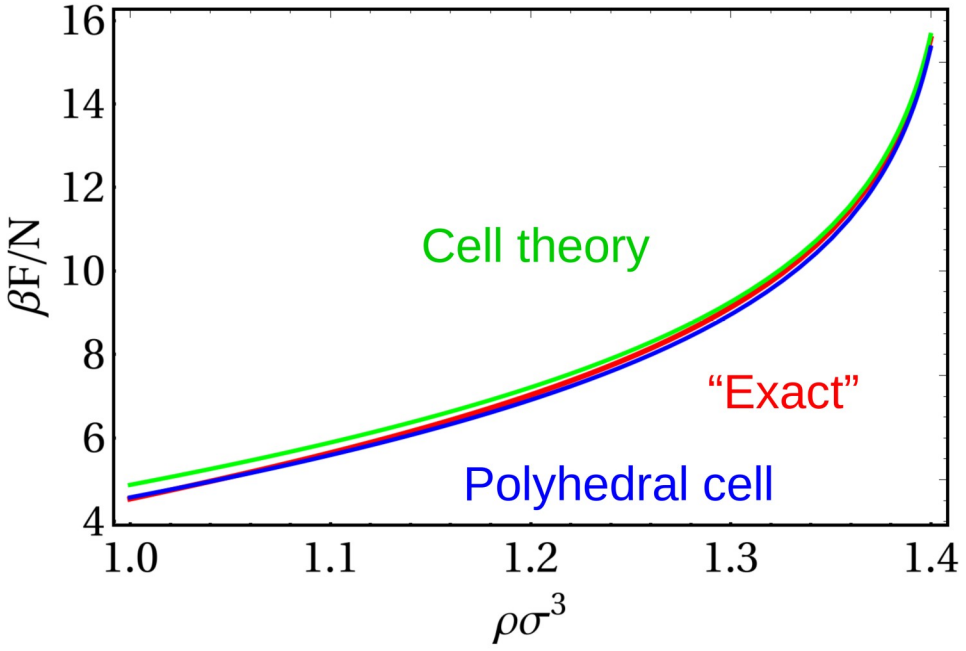

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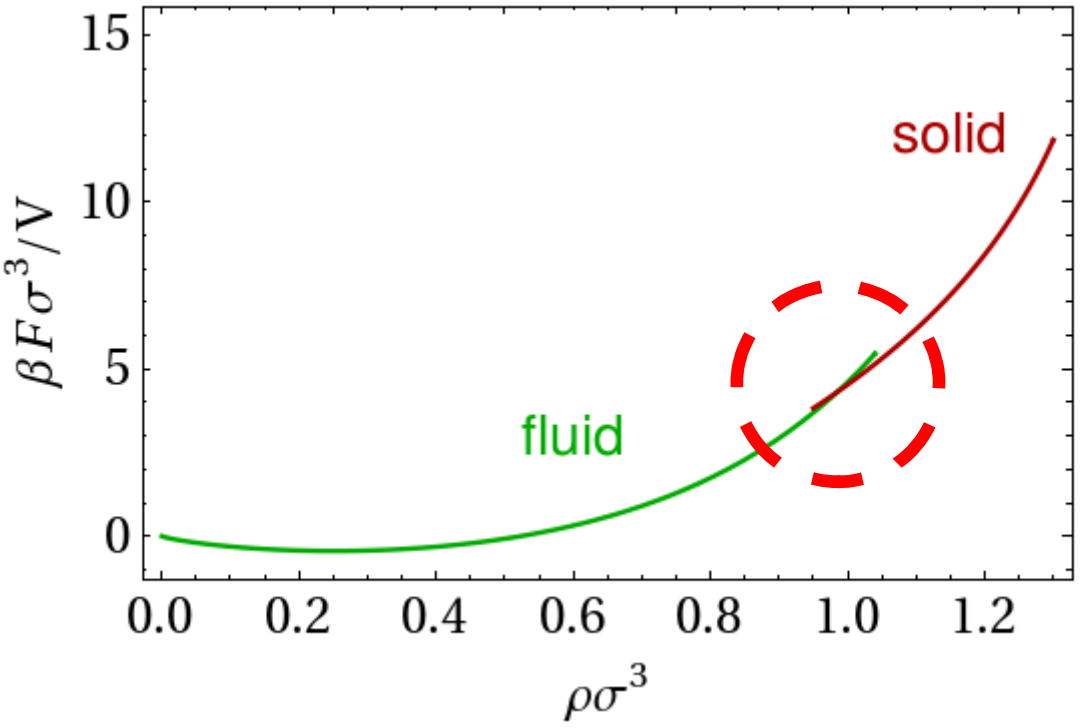
Phase transition

We can now plot the **free energy per unit volume** of both phases:



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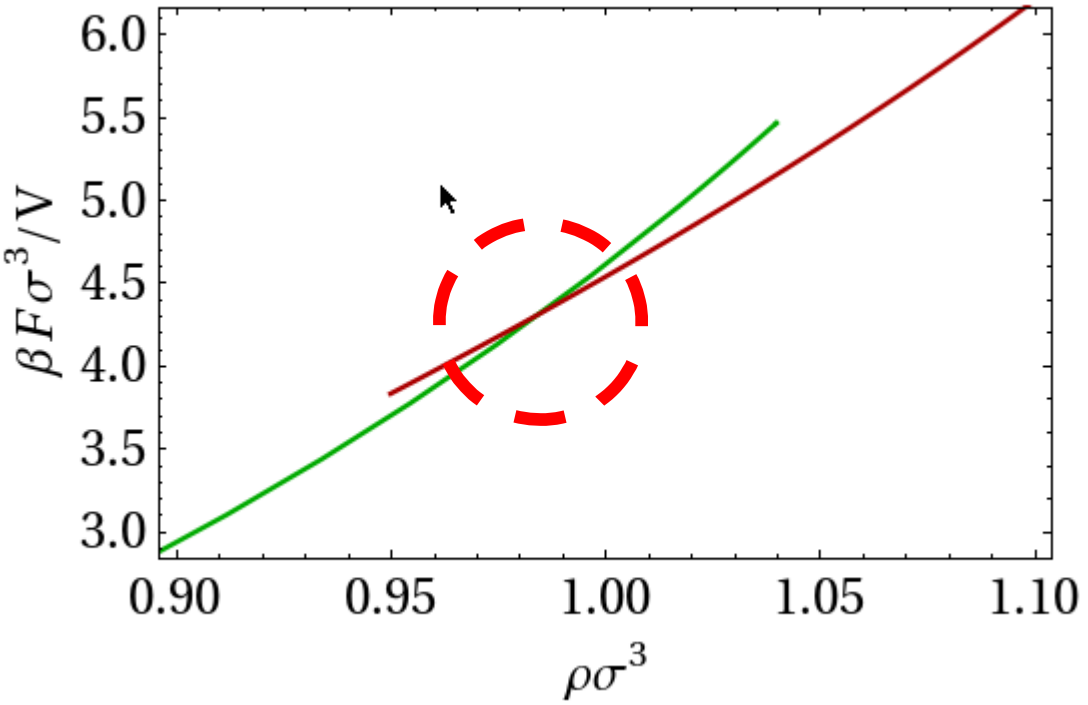

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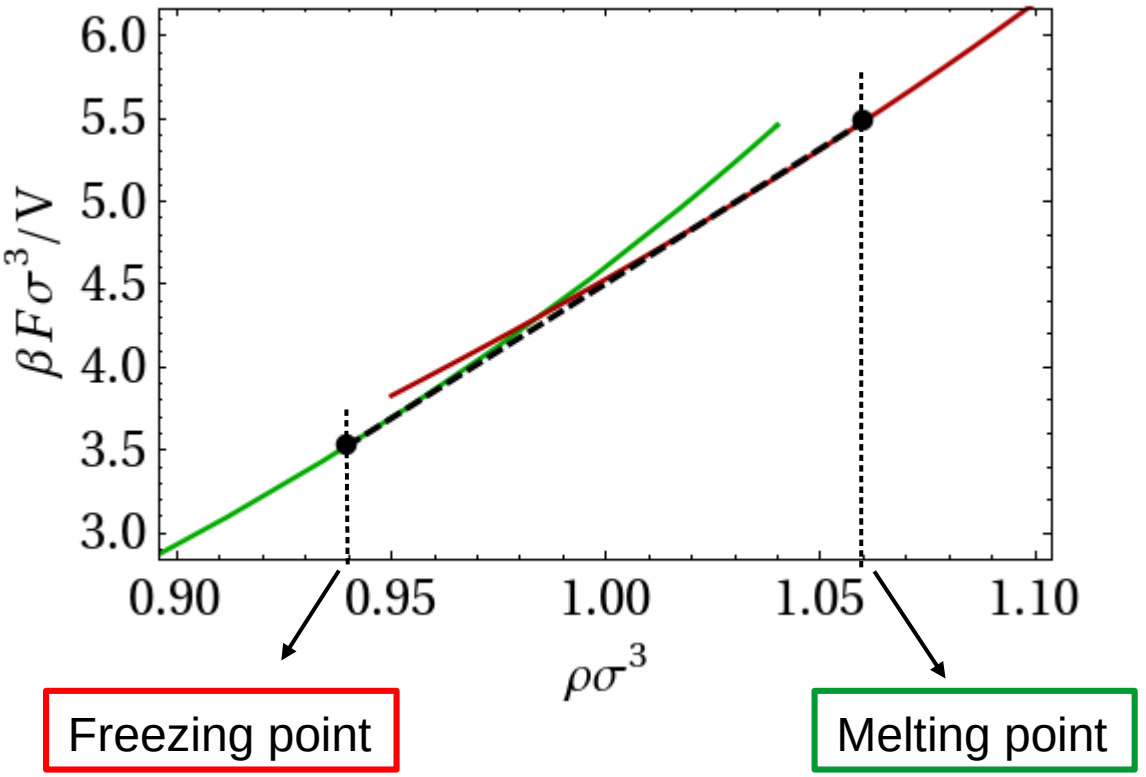


Coexistence region between fluid and solid.

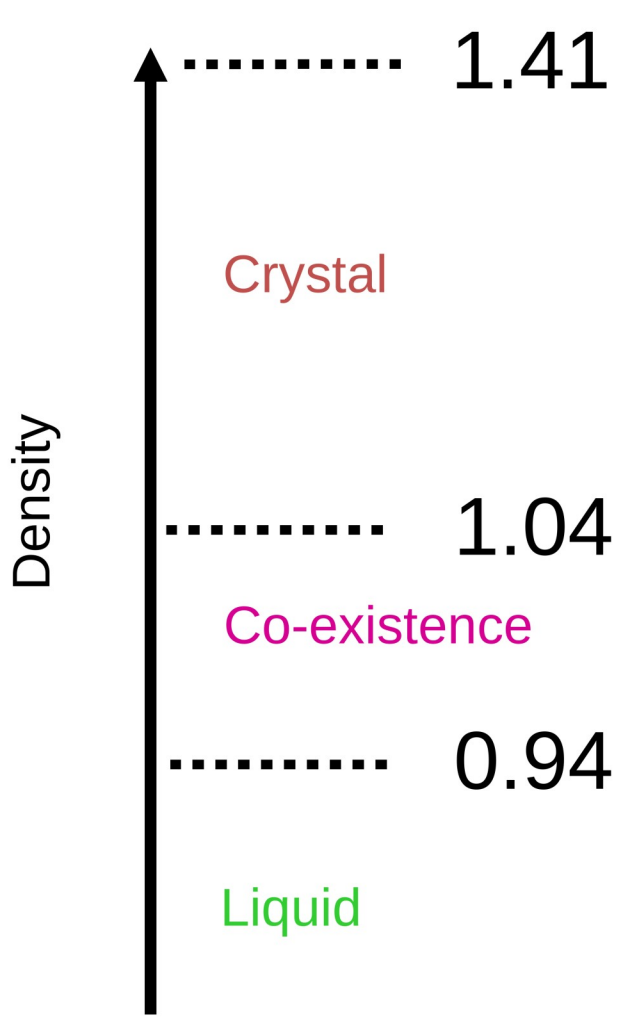
With full simulations:

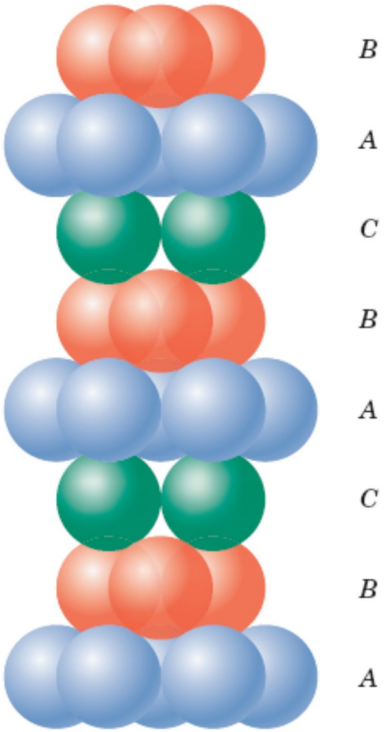
$$\rho_f\sigma^3 = 0.942, \rho_m\sigma^3 = 1.041$$

With (polyhedral) cell theory:

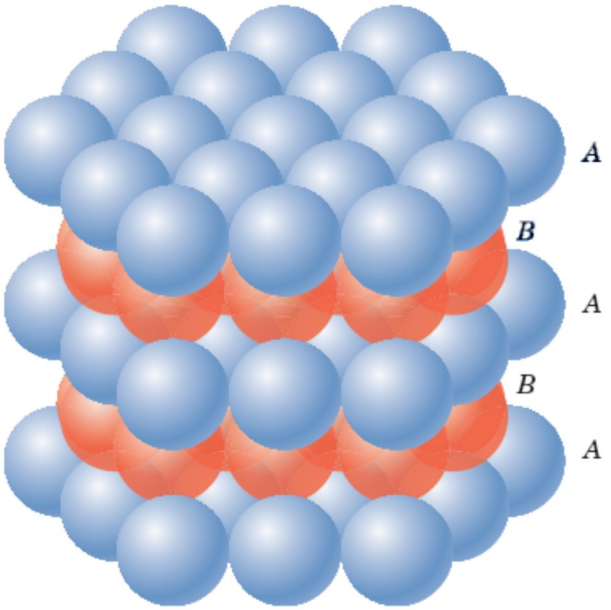
$$\rho_f\sigma^3 = 0.940, \rho_m\sigma^3 = 1.060$$

Hard sphere phase diagram





FCC



HCP

Simulations have shown that the free energy difference (1990s): 0.001KT/particle
FCC wins!

Hard sphere phase diagram

Time

Packing fraction

Figure: Pusey *et al* (2009)
Remade from 1989

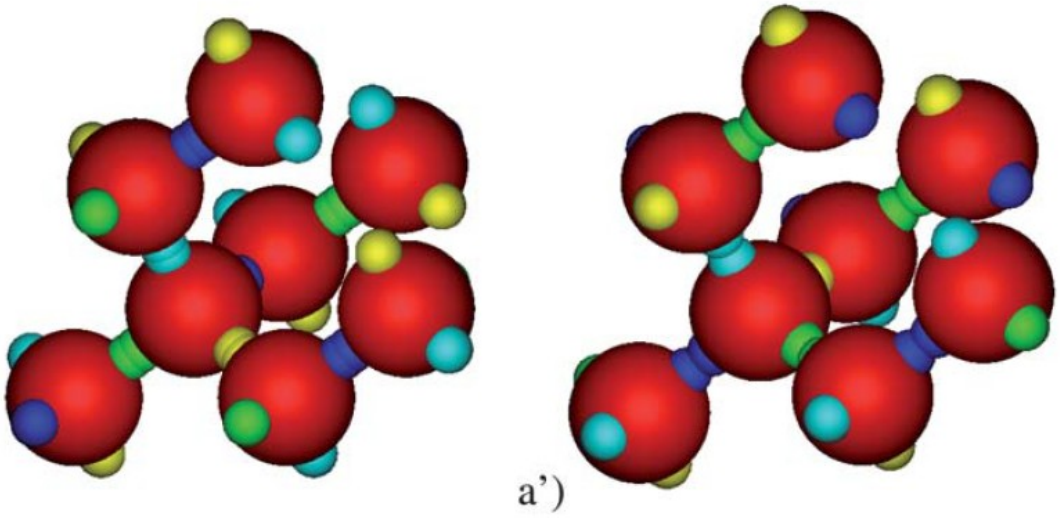
Free-energy calculation using simulations

1) Construct a continuous path from a system where you know the free energy to the system where you want to know the free energy.

2) Measure free-energy derivative along path

3) Calculate free energy

Complications:
- Avoiding phase transitions
- "**Configurational entropy**"

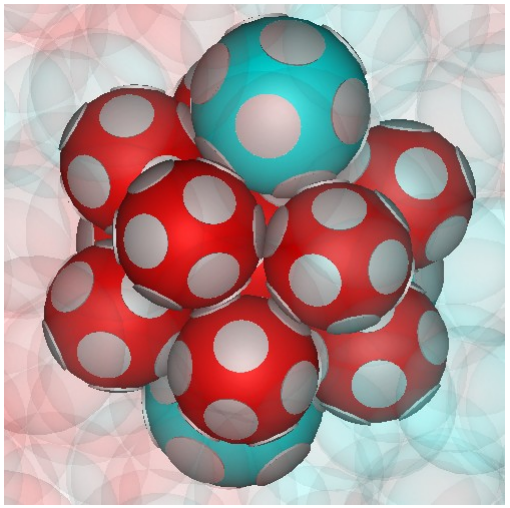


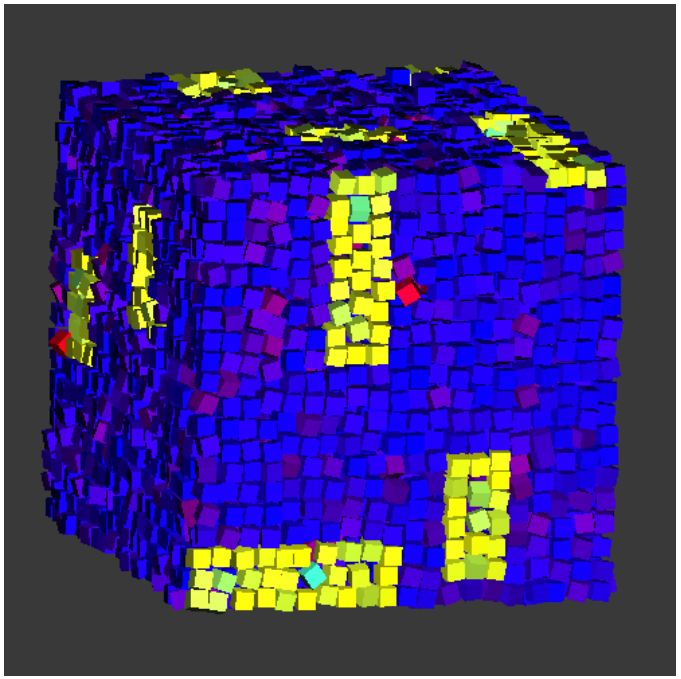
Dorsaz *et al.*
Farad. Discuss. **159**, 9 (2012)

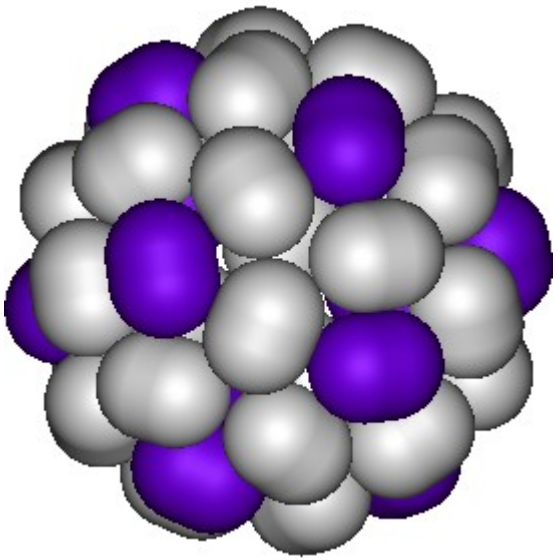
Adding more length scales

Multiple ways of increasing complexity of the geometry:

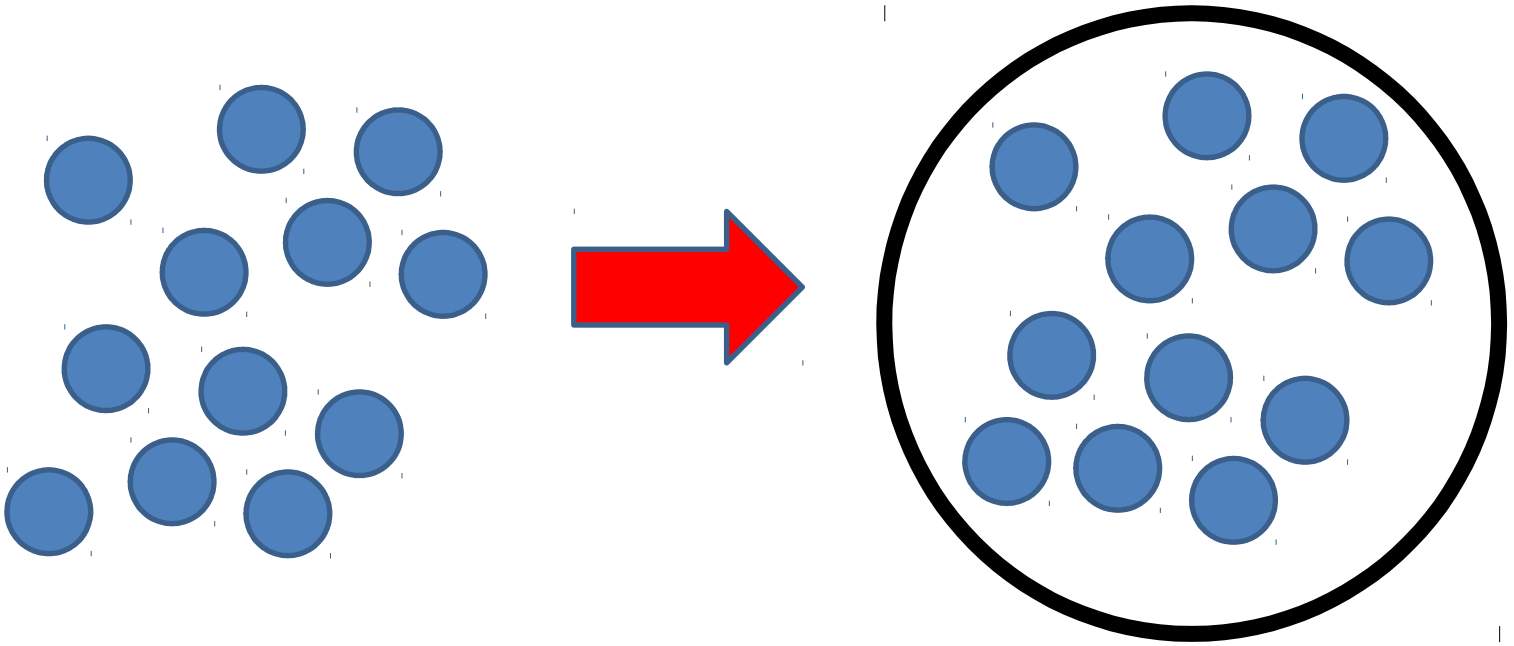
- **Confinement**
- **Size mixtures**
- **Soft interactions**
- **Directional interactions**
- **…**





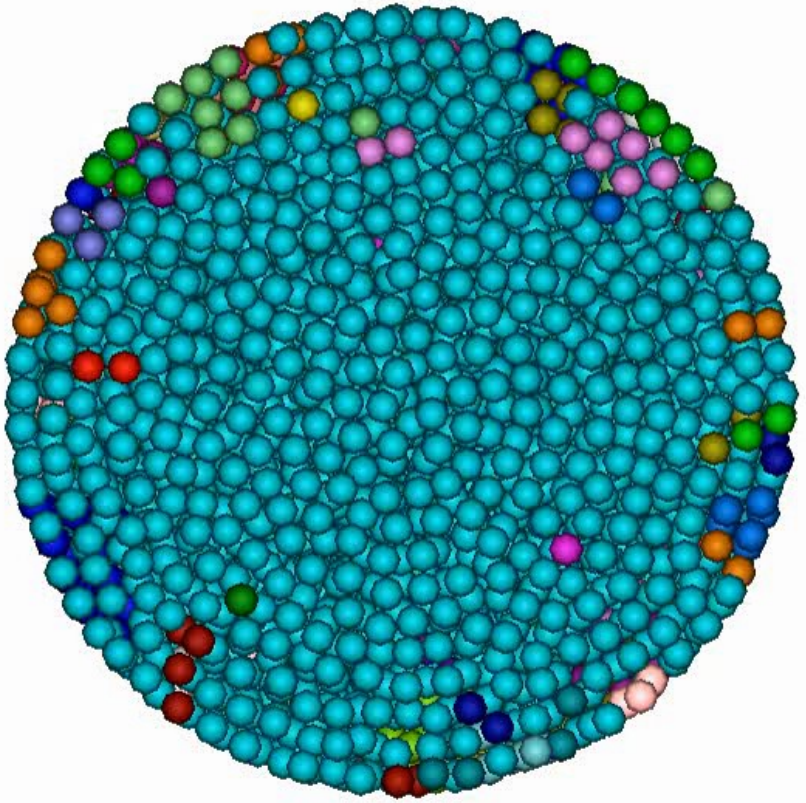


Geometry through confinement



Colloids/nanoparticles confined in shrinking droplets.

Geometry through confinement



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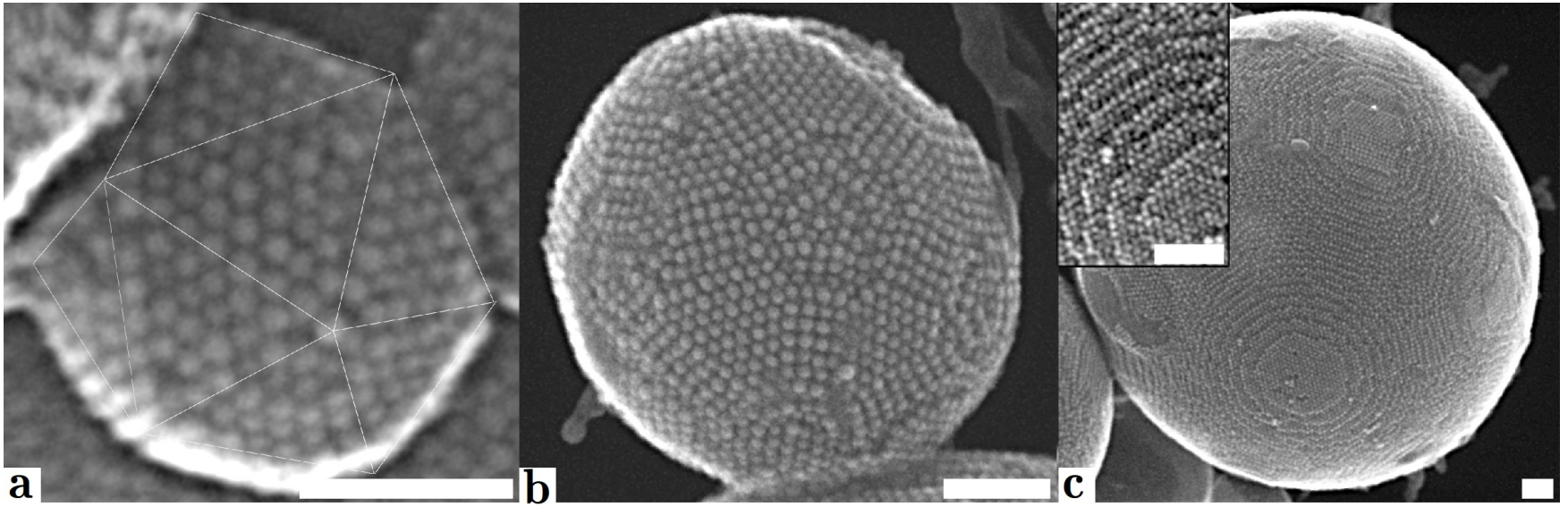
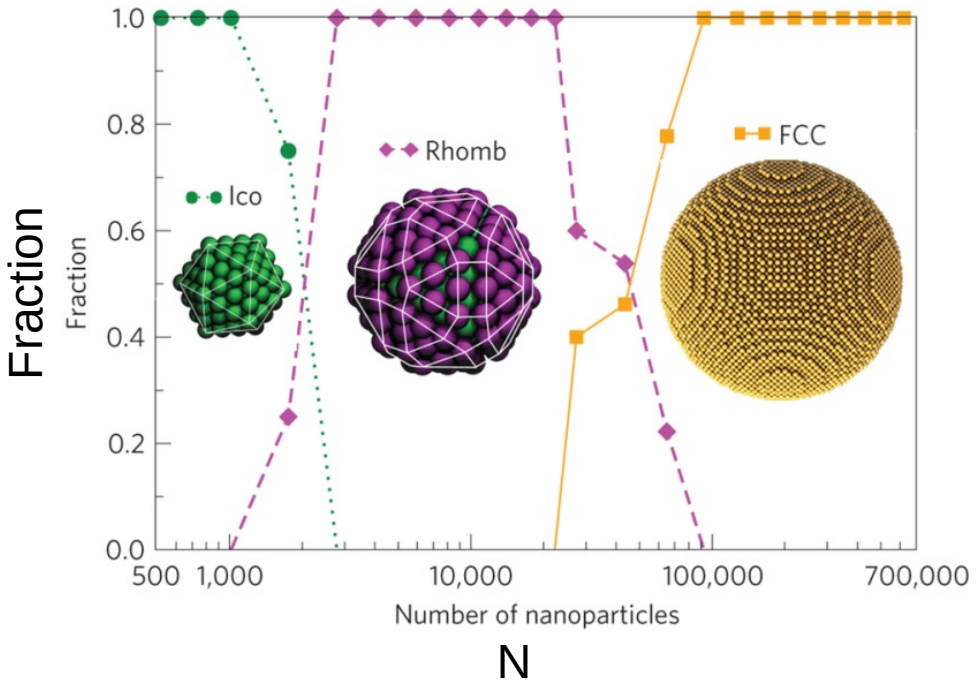
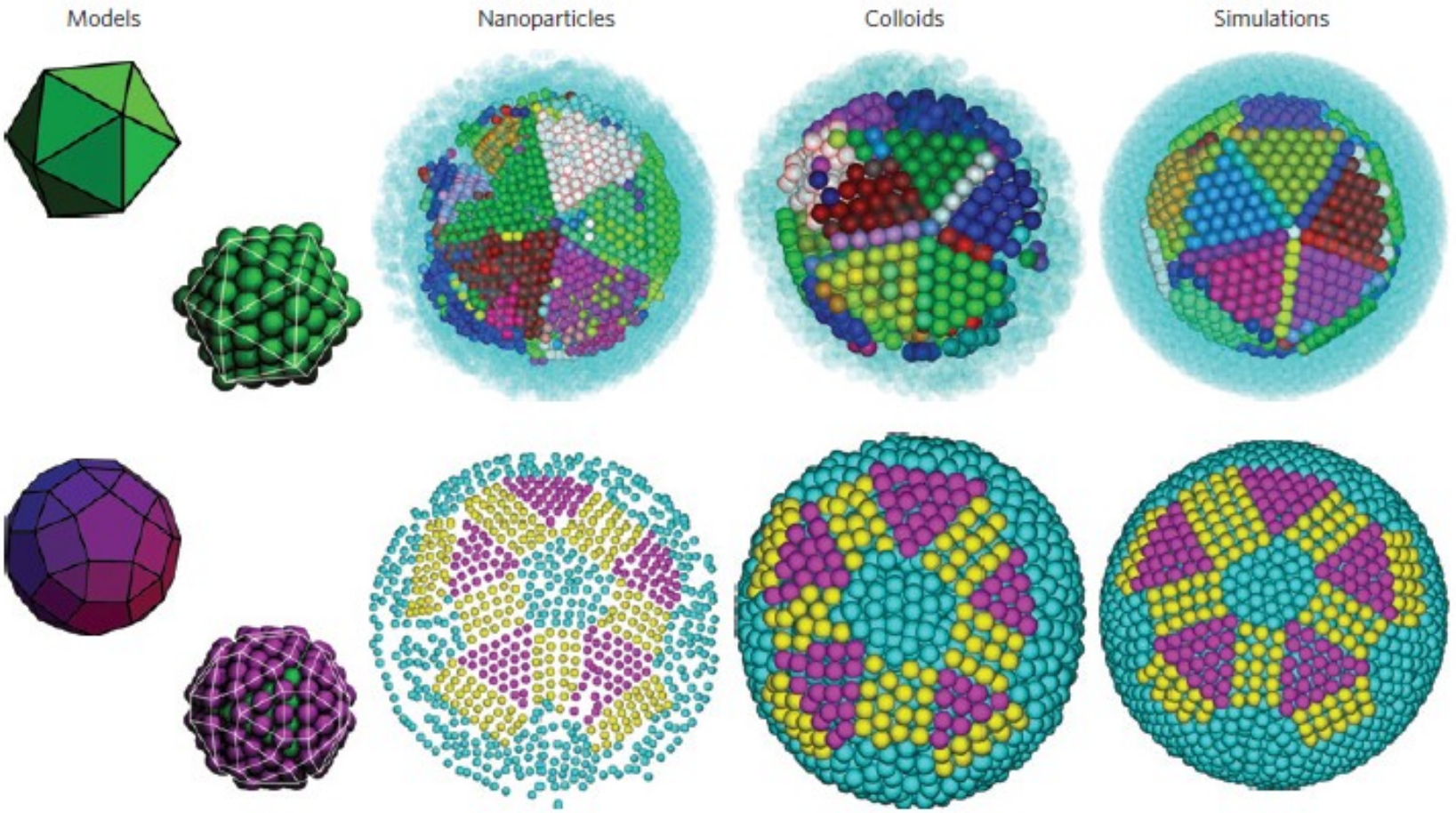




De Nijs et al., Nature Materials ***14****, 56 (2015)*

Geometry through confinement

Simulations vs. experiment:



Candidate crystal structures?

We can (in principle) calculate free energies for any relevant crystal structure.

How to determine **what crystal structures are relevant?**

- **Direct simulation (and hope for the best)**
- **Intelligent guessing**
- **Genetic algorithms**
- **Optimization algorithms**

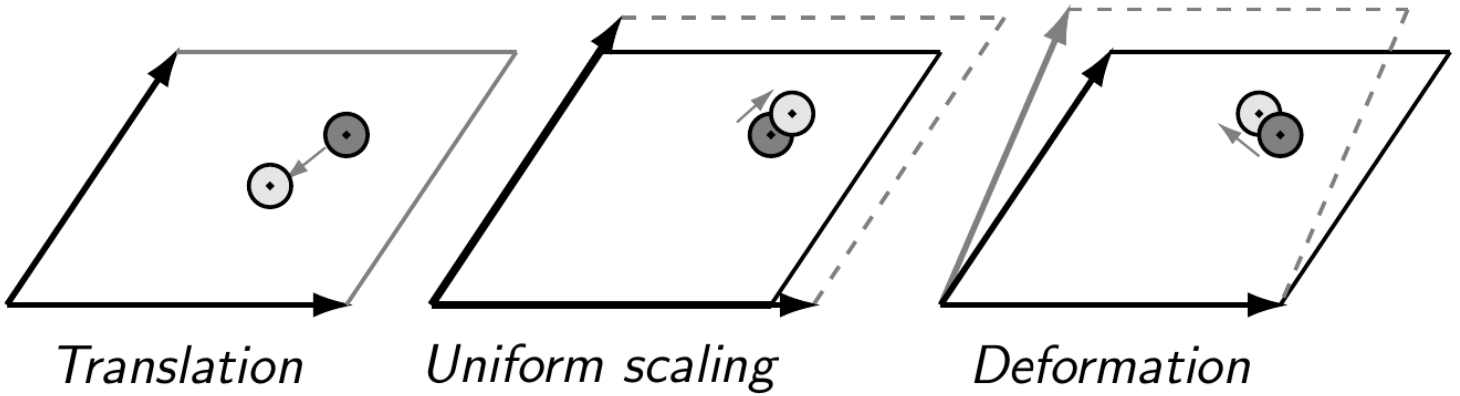
Candidate crystal structures?

We can (in principle) calculate free energies for any relevant crystal structure.

How to determine **what crystal structures are relevant?**

“Floppy box” Monte Carlo:

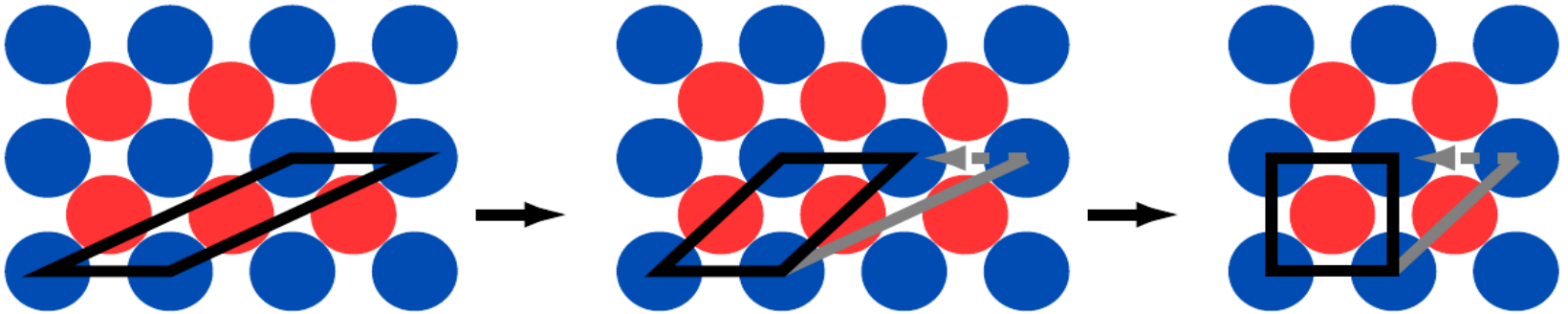
- Simulate very few particles in a simulation cell with variable shape.
- Look for structures with high packing, low energy for a wide range of **pressure**, **temperature**, and **number of particles**.



Filion *et al.* , PRL **103**, 188302 (2009).

Rhombohedral unit cell

- Resulting “unit cell” can in principle represent any periodic lattice if the number of particles is a multiple of the number of particles in the unit cell.
- No quasicrystals!
- To prevent extremely distorted cells, lattice reduction techniques can be used:



Many separate runs to find possible structures.

Each run is relatively short, and ends with a low-temperature annealing step to suppress thermal fluctuations.

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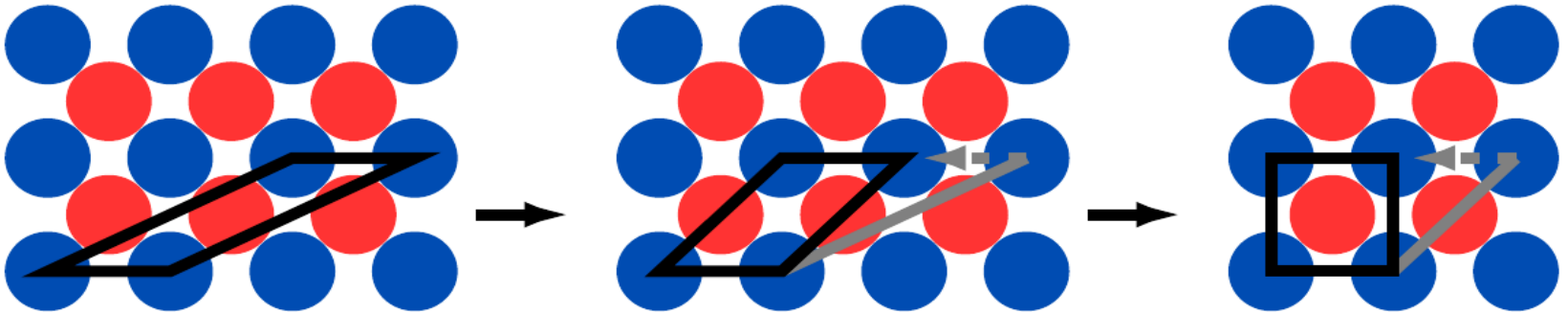

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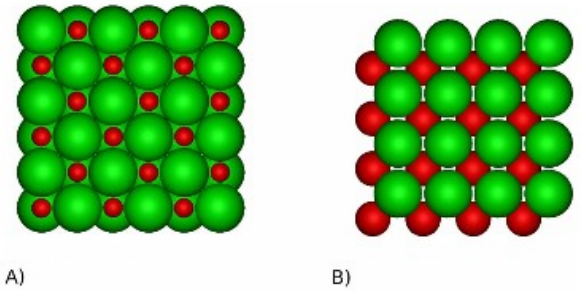
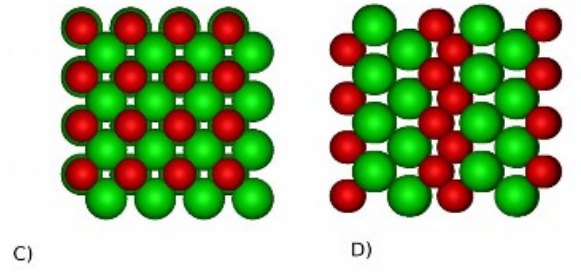
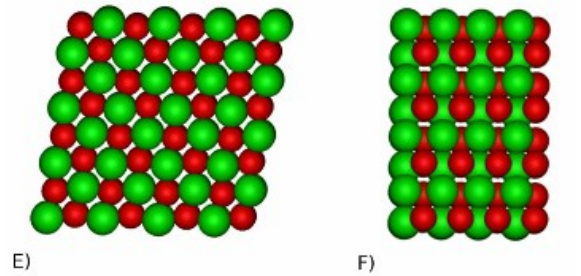
Finding close-packed structures



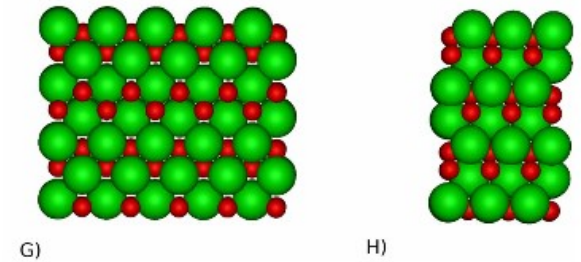
NaCl



CsCl



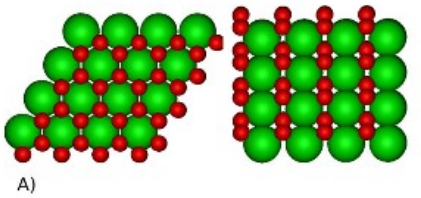
γCuTi



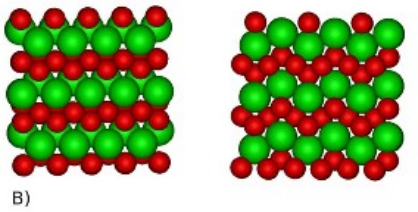
αIrV

Filion & Dijkstra, PRE **79**, 046714 (2009)

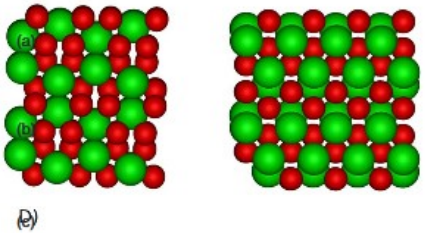
AlB_2

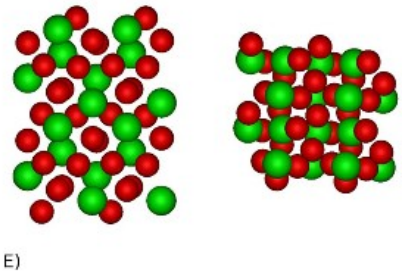


$HgBr_2$



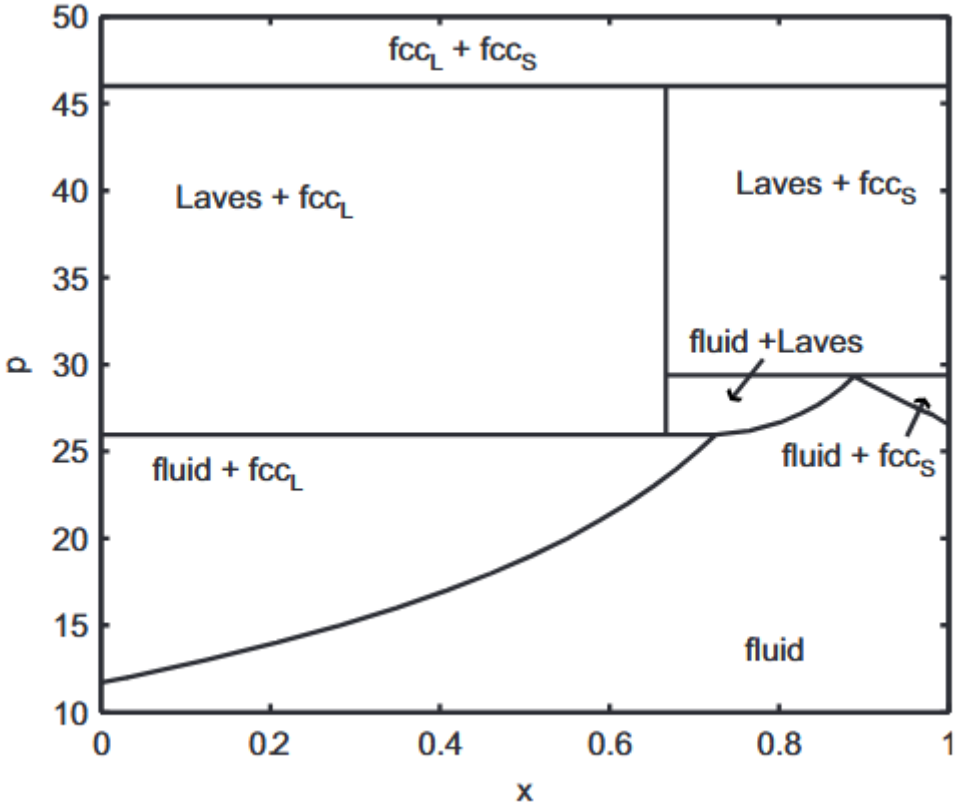
$AuTe_2$

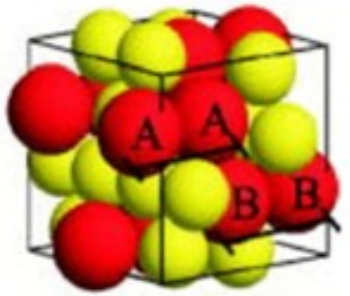




Not all stable phases are close-packed

Entropy can be higher in phases that do not pack as well.

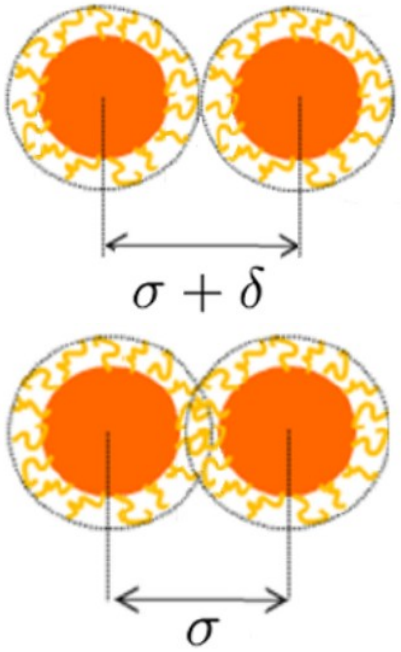




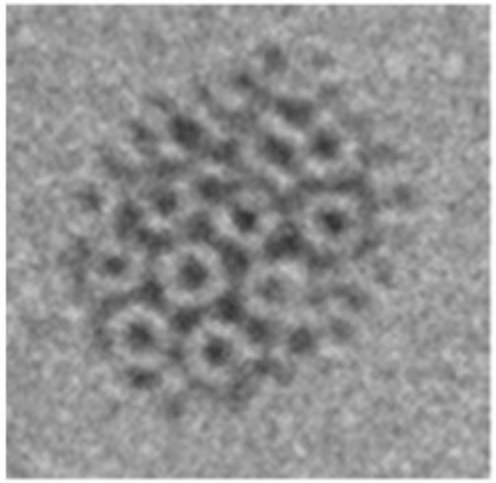
$MgZn_2$

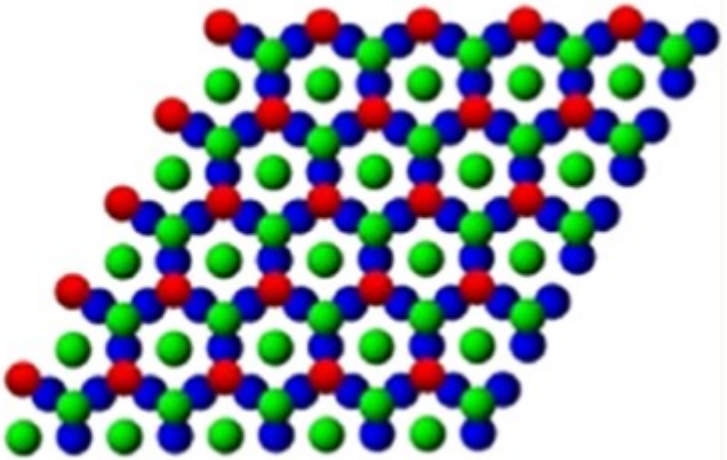
Hynninen, Filion, Dijkstra
J. Chem. Phys. **131**, 064902 (2009)

Geometry through soft interactions

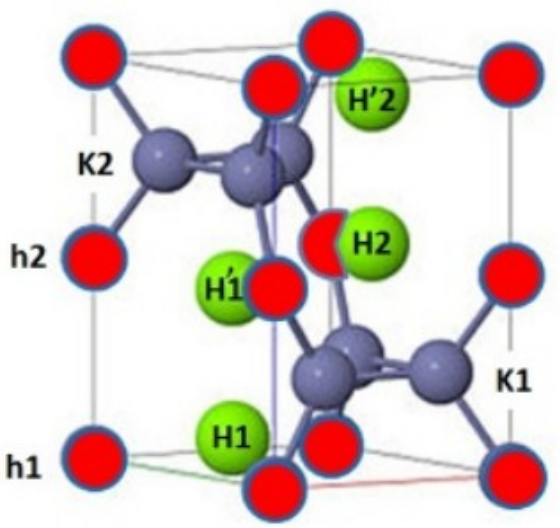


Nanoparticles coated with soft ligands



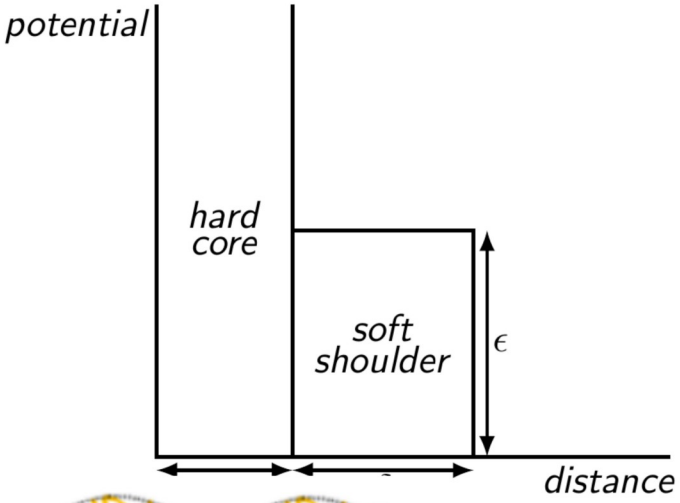


C14

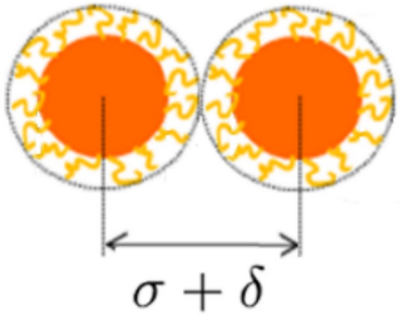


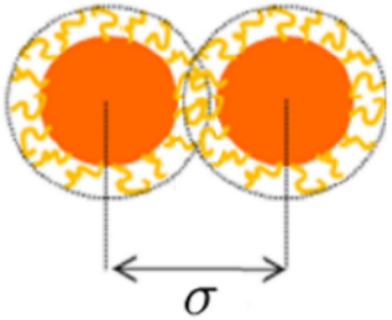
Hajiw, Pansu, Sadoc, ACS Nano 9, 8116 (2015)

Geometry through soft interactions



$$U(r) = \begin{cases} \infty & r < \sigma \\ \epsilon & \sigma < r < \sigma + \delta \\ 0 & r > \sigma + \delta \end{cases}$$





Very rough model for **polymer-coated nanoparticles**:

- fixed energy cost for interpenetration of the polymers

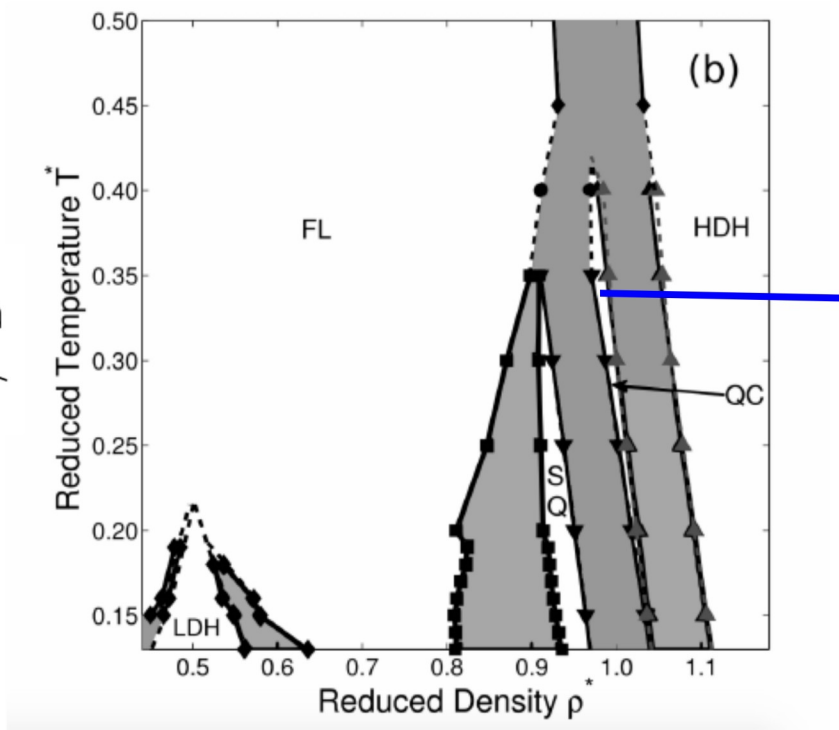
- hard repulsion at some smaller distance σ

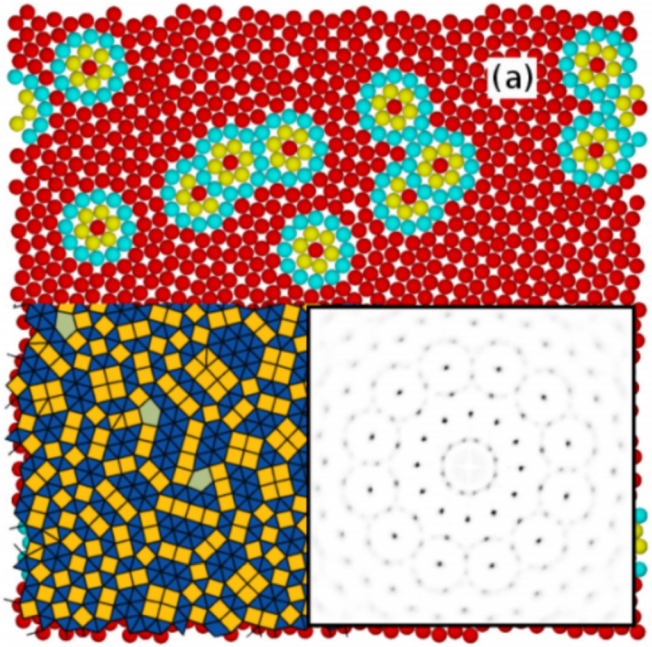
Interesting phase behavior?

In two dimensions: quasicrystals!

ϵ/k_BT

$\delta/\sigma = 0.4$

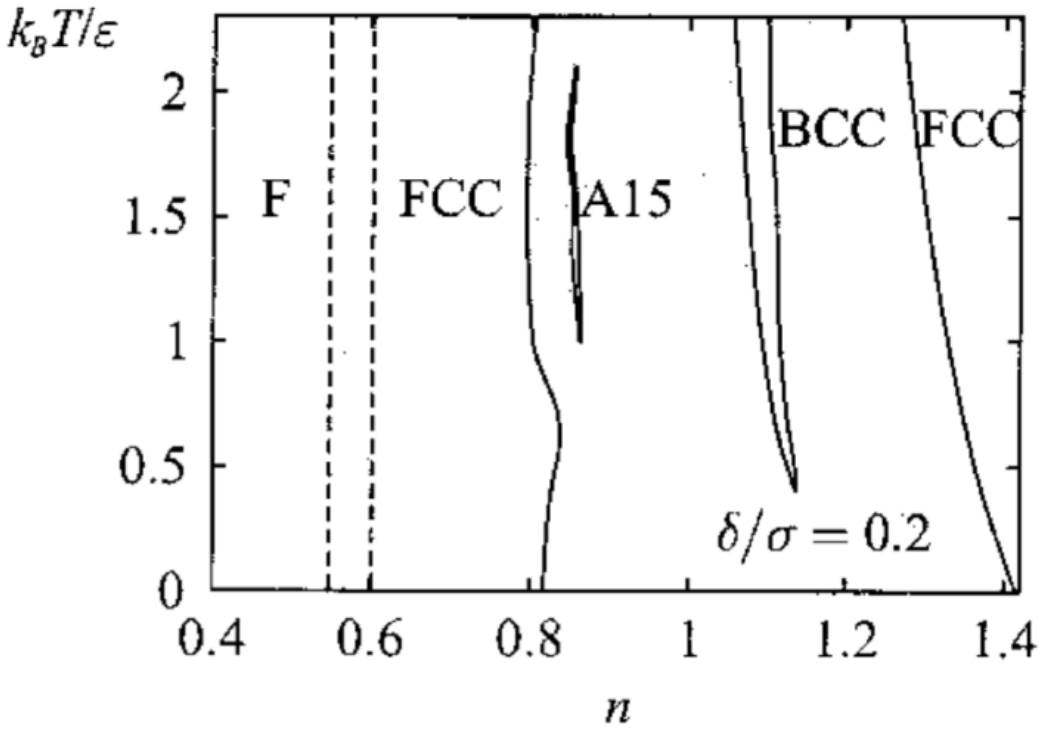




See e.g. Pattabhiraman, et al., J. Chem. Phys. **143**, 164905 (2015).

Interesting phase behavior?

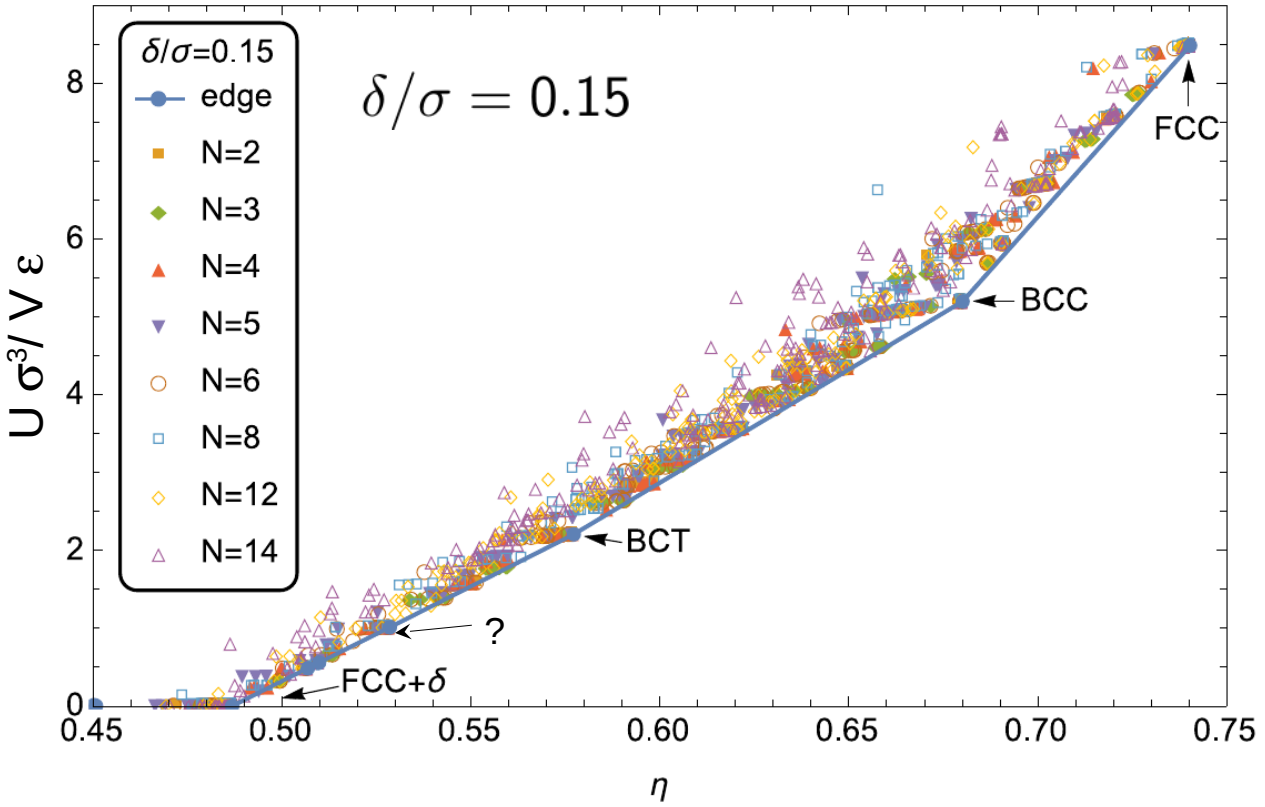
In three dimensions: complex crystals?



- Phase diagram based on a (different) mean-field approach
- Only considered a few different crystal structures
-
- Effect of temperature on fluid stability neglected

Ziherl & Kamien, J. Phys. Chem. B **105**, 10147 (2001).

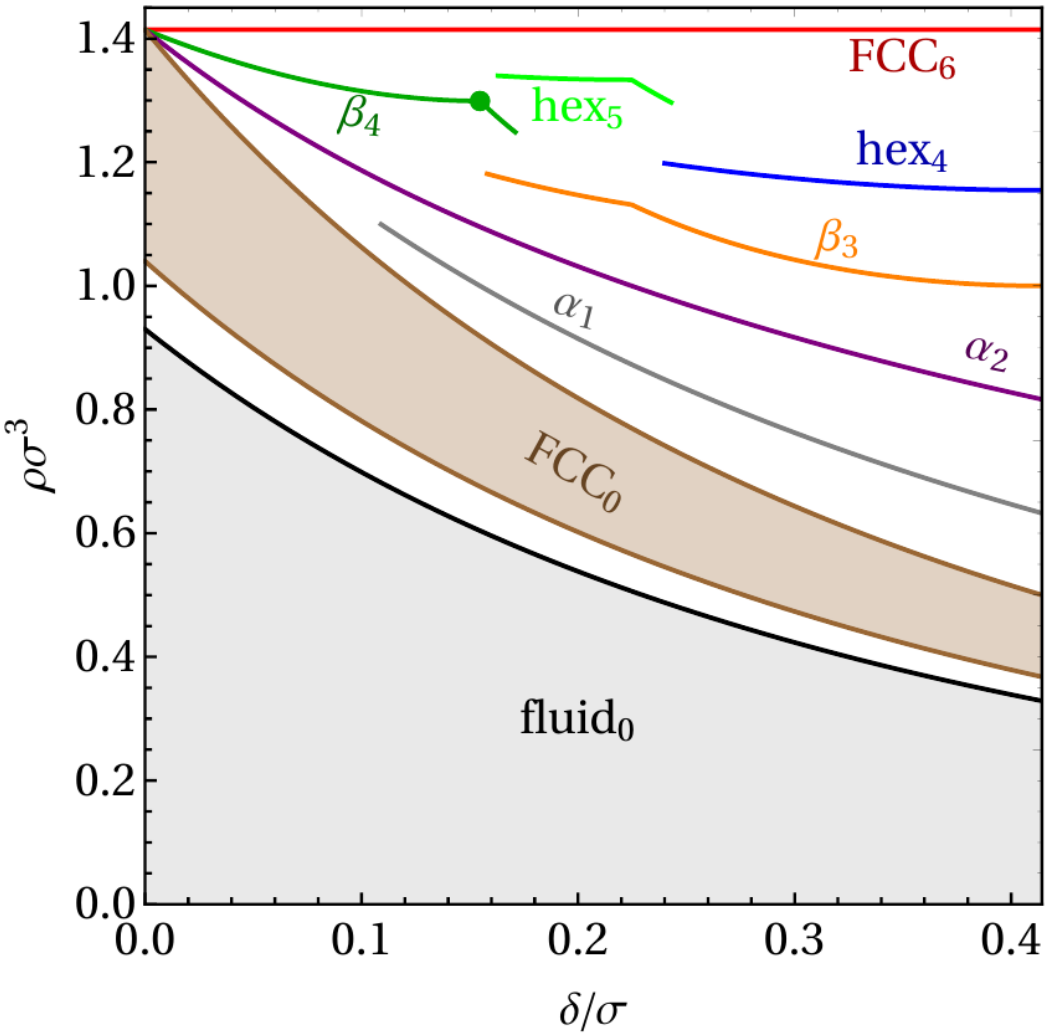
Candidate structures



Sample output:

- Each point is an MC run
- Bottom envelope is the lowest-energy state (or coexistence) possible at each density
- Several structures clearly stable at zero-temperature.

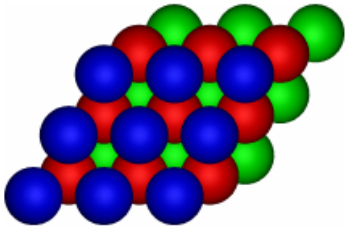
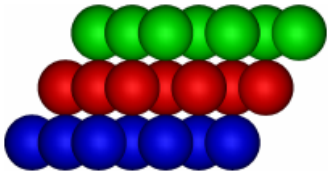
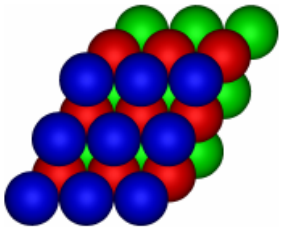
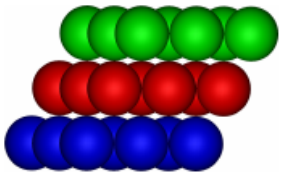
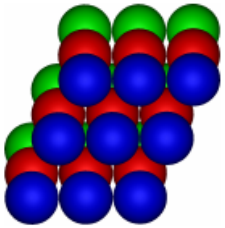
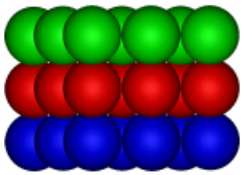
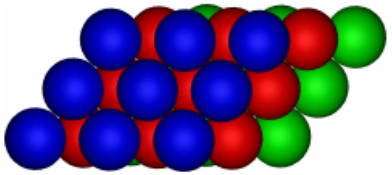
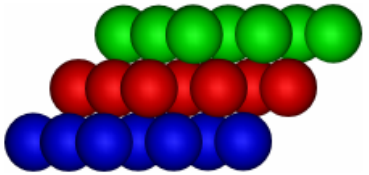
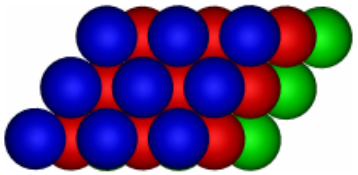
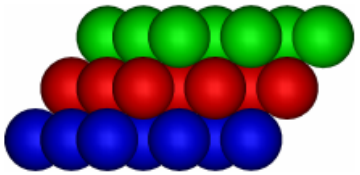
Zero-T structures



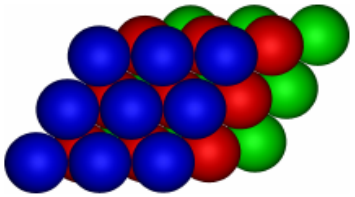
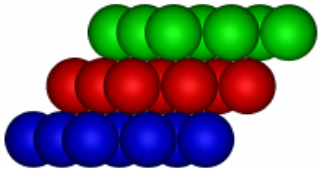
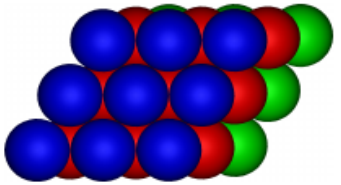
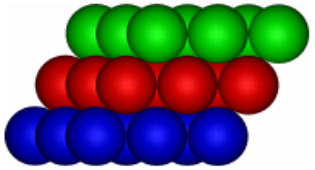
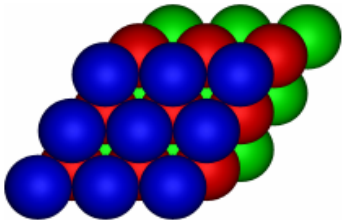
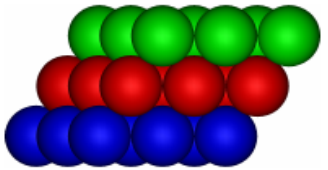
For each shoulder length, we map out all structures found to be stable in the zero-T limit.

- No Frank-Kasper phases found to be stable
- Large variety of structures, but all with simple unit cells
- Subscript indicates energy per particle

Zero-T structures

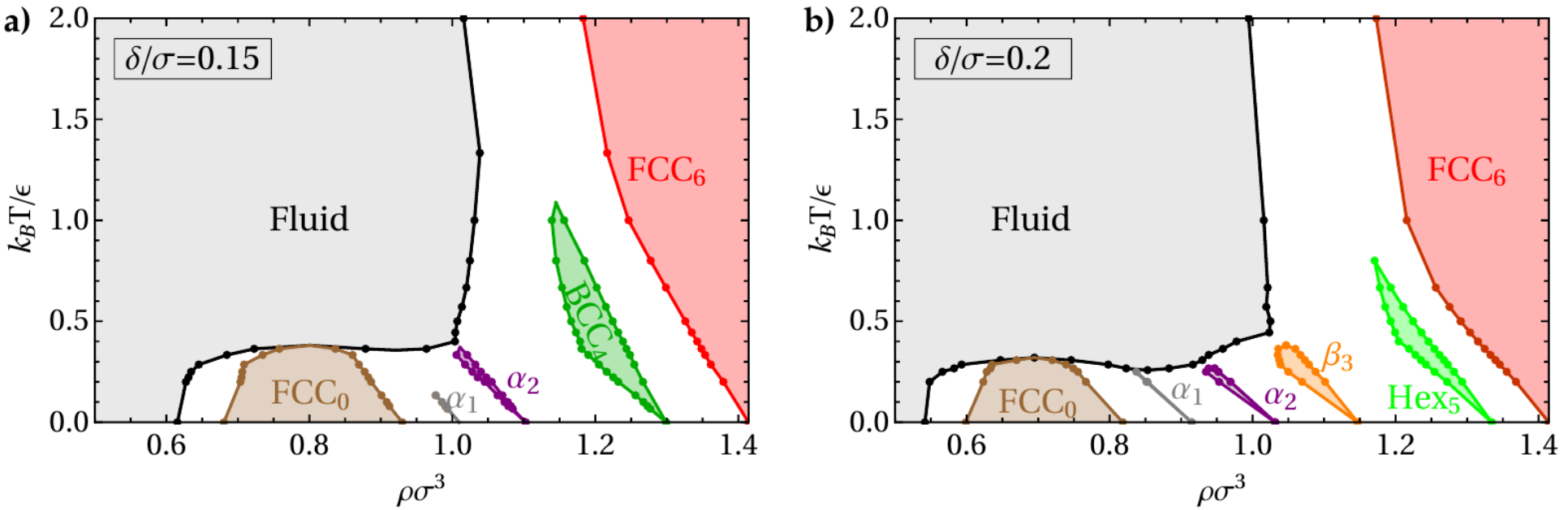
Name	Front view	Side view	$U/N\epsilon$	Notes
FCC_0			0	Low-density FCC.
α_1			1	Body-centered orthogonal (BCO) lattice. Also contains low-density hexagonal planes.
α_2			2	Body-centered tetragonal lattice. Also contains square and β planes.
β_3			3	Also contains α planes.
β_4			4	Body-centered tetragonal (BCT) lattice. Body-centered cubic when $\delta = \frac{2}{\sqrt{3}} - 1 \simeq 0.1547$.

Zero-T structures

Name	Front view	Side view	$U/N\epsilon$	Notes
hex_4			4	Also contains β planes.
hex_5			5	Body-centered orthogonal (BCO) lattice.
FCC_6			6	High-density FCC.

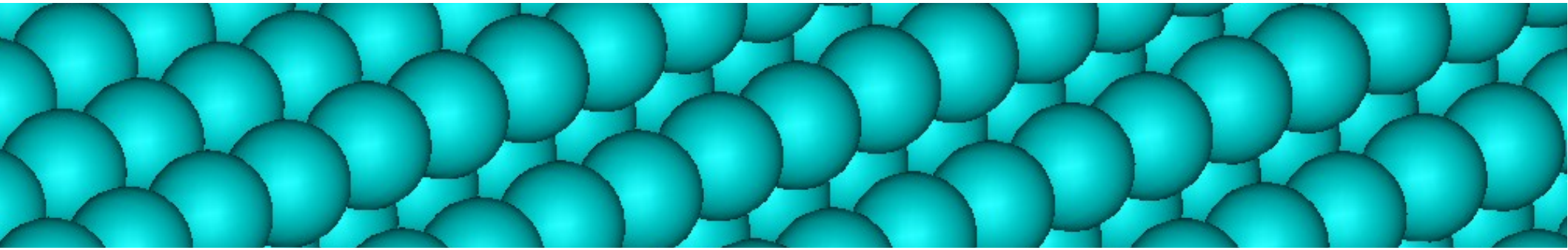
Extension to finite temperature

Using **cell theory**, we can draw the finite-temperature phase diagram for specific shoulder lengths.



Conclusions

- Strong connection between geometry and entropy
- Even simple interactions can lead to complex structures
- Resulting structures can be hard to guess!



Geometry through size mixtures