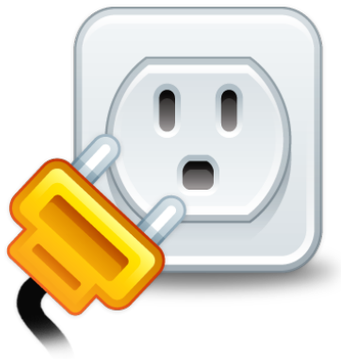
Using enhanced sampling to study the formation of crystals

Gareth Tribello

Atomistic Simulation Centre

Plumed summary

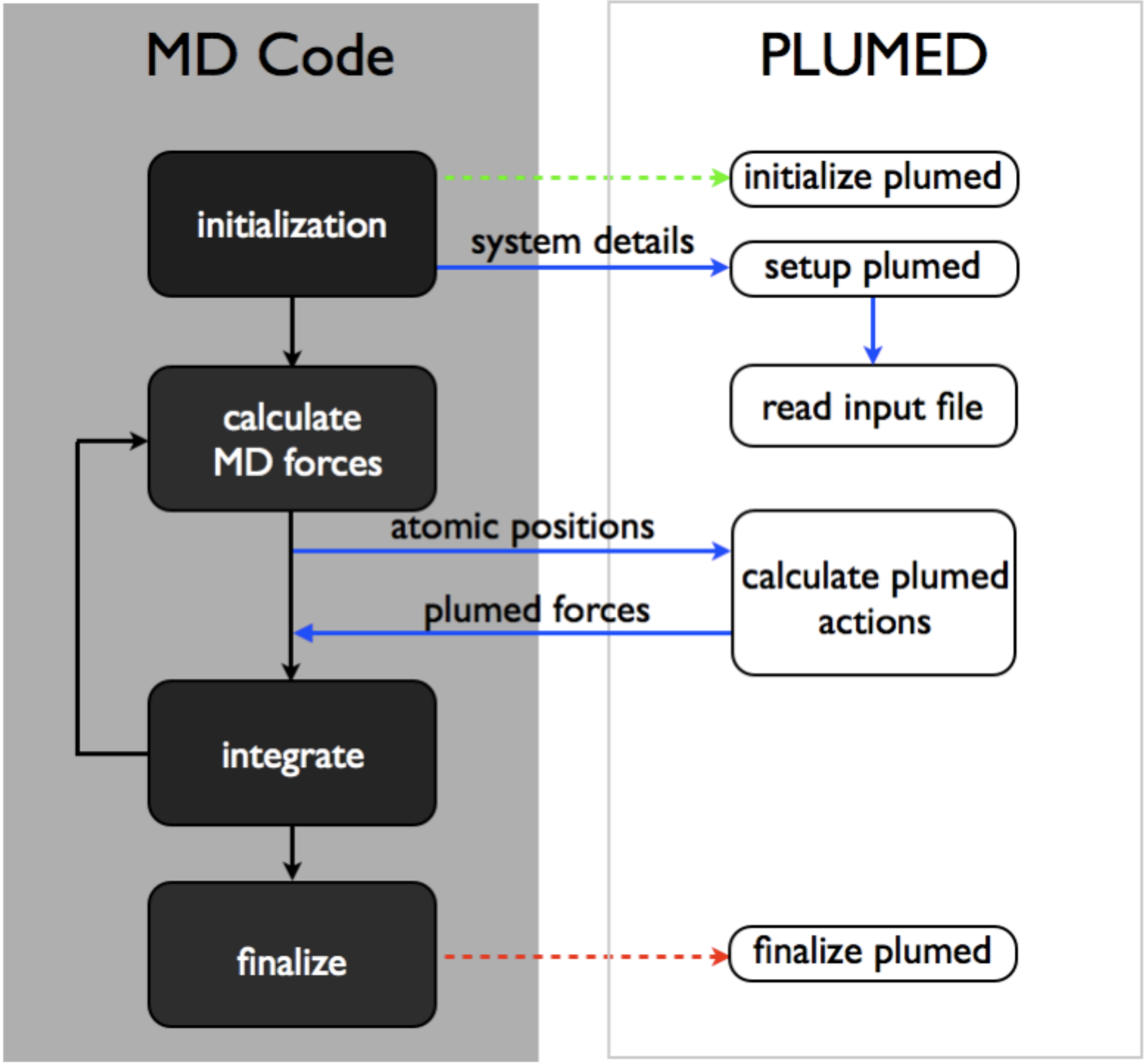
PLUMED



A plugin for any MD code

Analyze your simulation

Enhance sampling


MD Code
PLUMED
initialization
initialize plumed
system details
setup plumed
read input file
calculate
MD forces
atomic positions
calculate plumed
actions
plumed forces
integrate
finalize
finalize plumed

A taxonomy of collective variables

CHEMISTRY

Variables based on contact matrices

Variables based on bonding e.g. distance, angle, torsion

THEORY OF PHASE TRANSITIONS

Variables based on symmetry of coordination sphere

CVs

Variables based on machine learning

CLASSICAL DFT

Variables based degree of homogeneity in system e.g. density gradient, Willard-Chandler surface

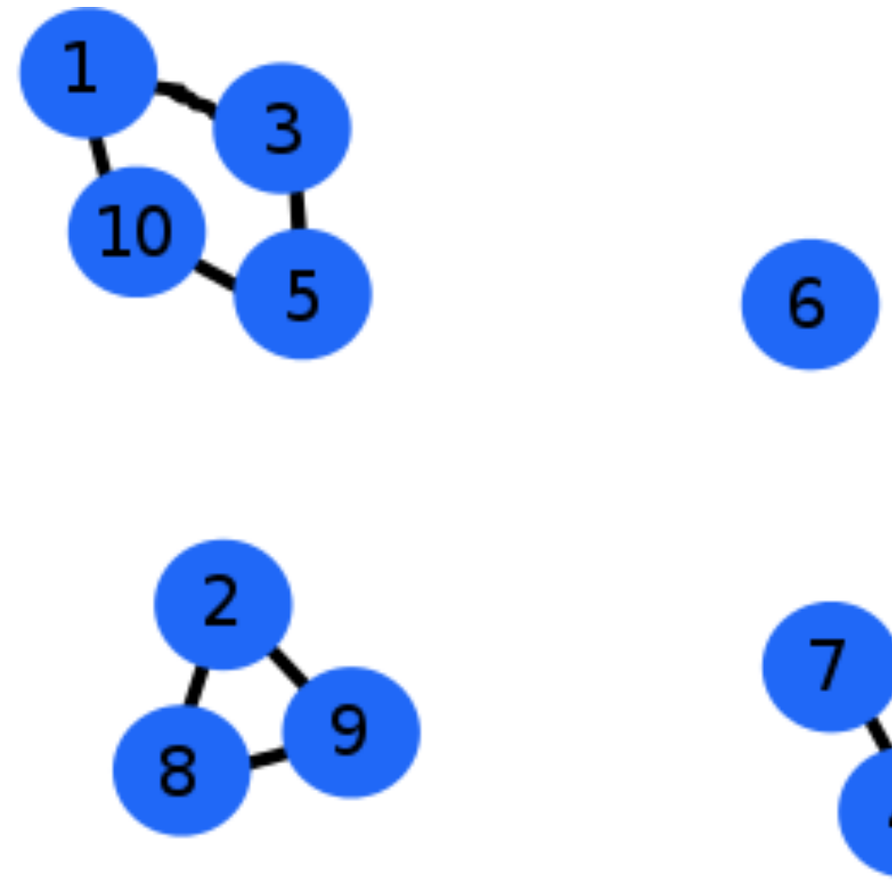
Contact matrix

Fabio Petrucci

Chemistry is about bonding. The contact matrix tells us about whether or not atoms are bonded. Functions of this matrix are natural collective variables

Contact matrix

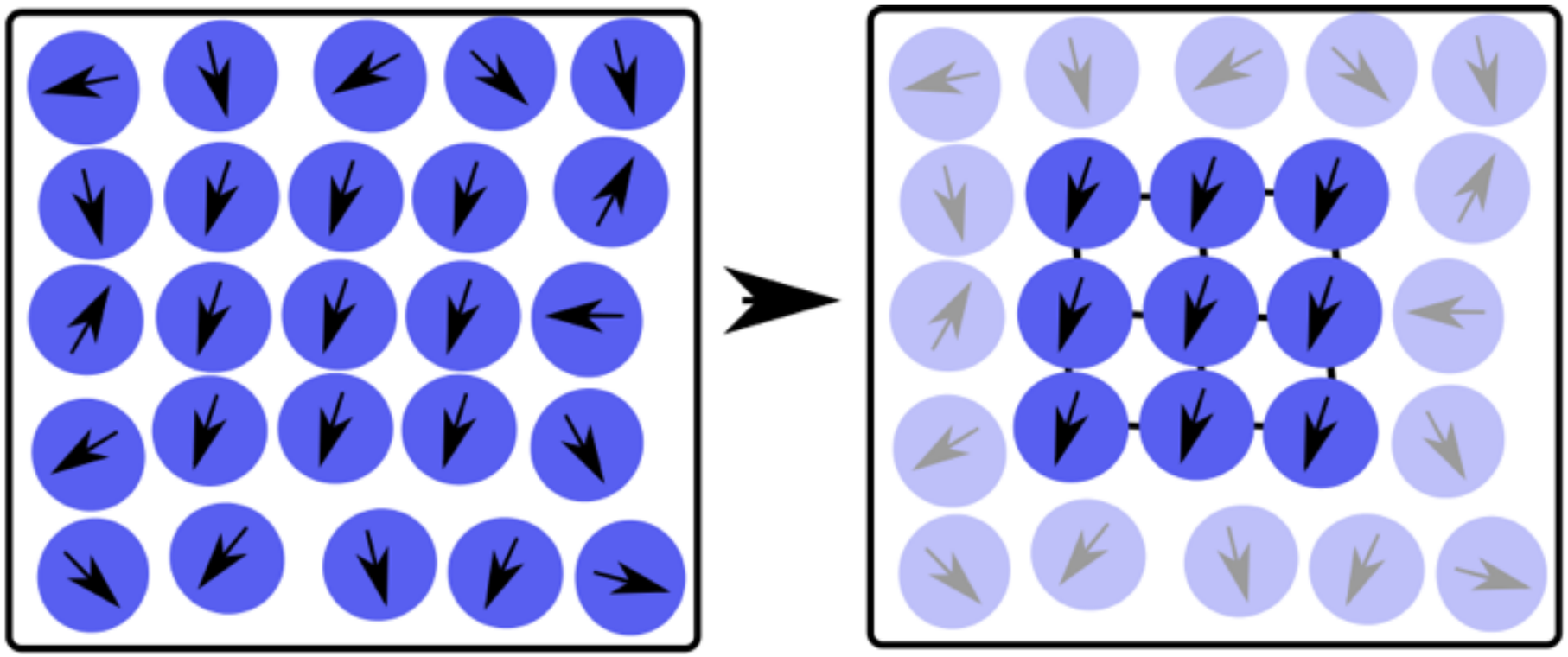
$$\begin{pmatrix}
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\
1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$



Reducible matrix - so reduce to block diagonal form to find clusters using e.g. DFS algorithm

$$\text{property of cluster distribution} = \sum_{j=1}^{M} g\left(\sum_{i=1}^{N_j} s_i\right)$$

“Bonds” between molecules

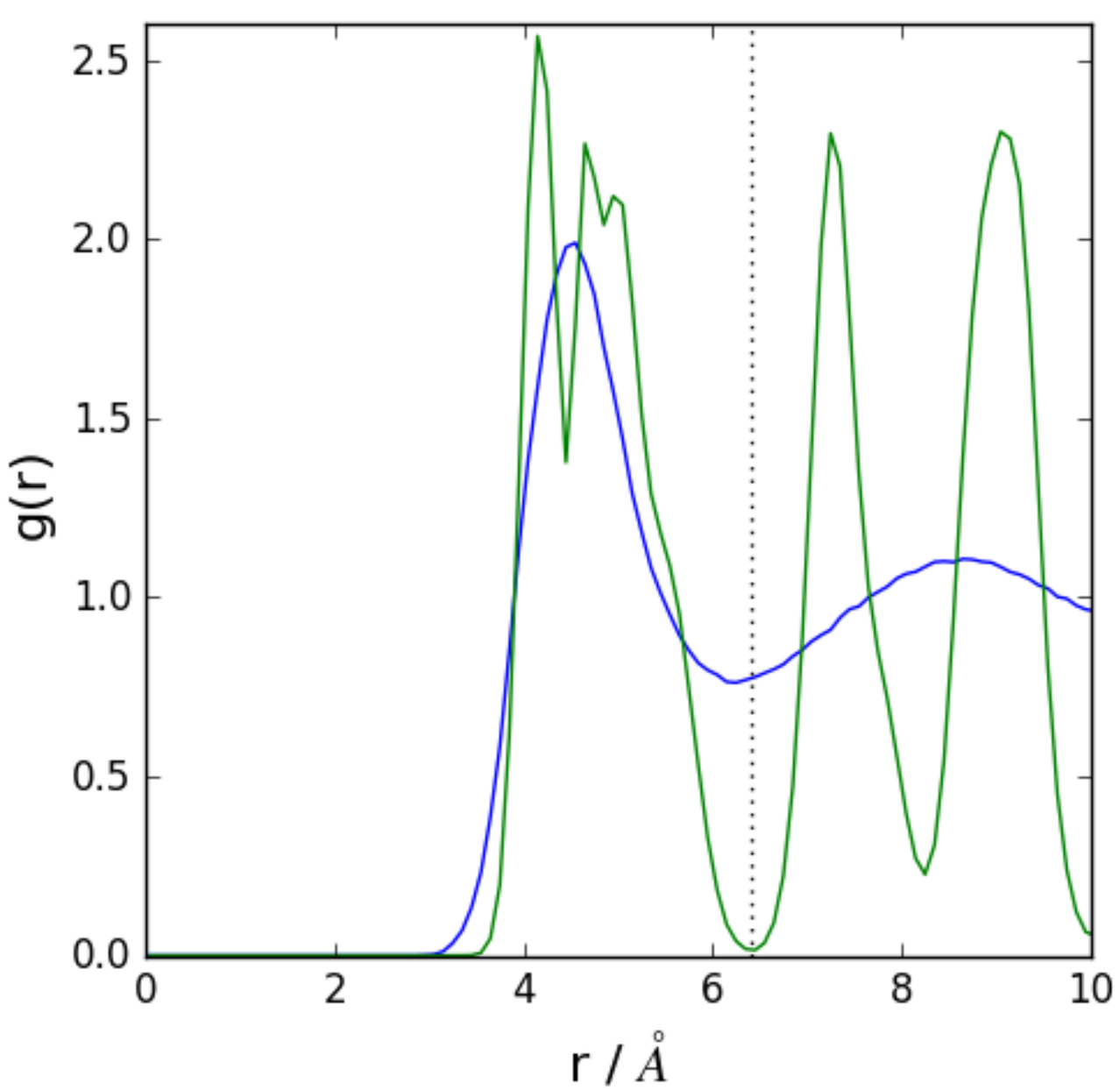


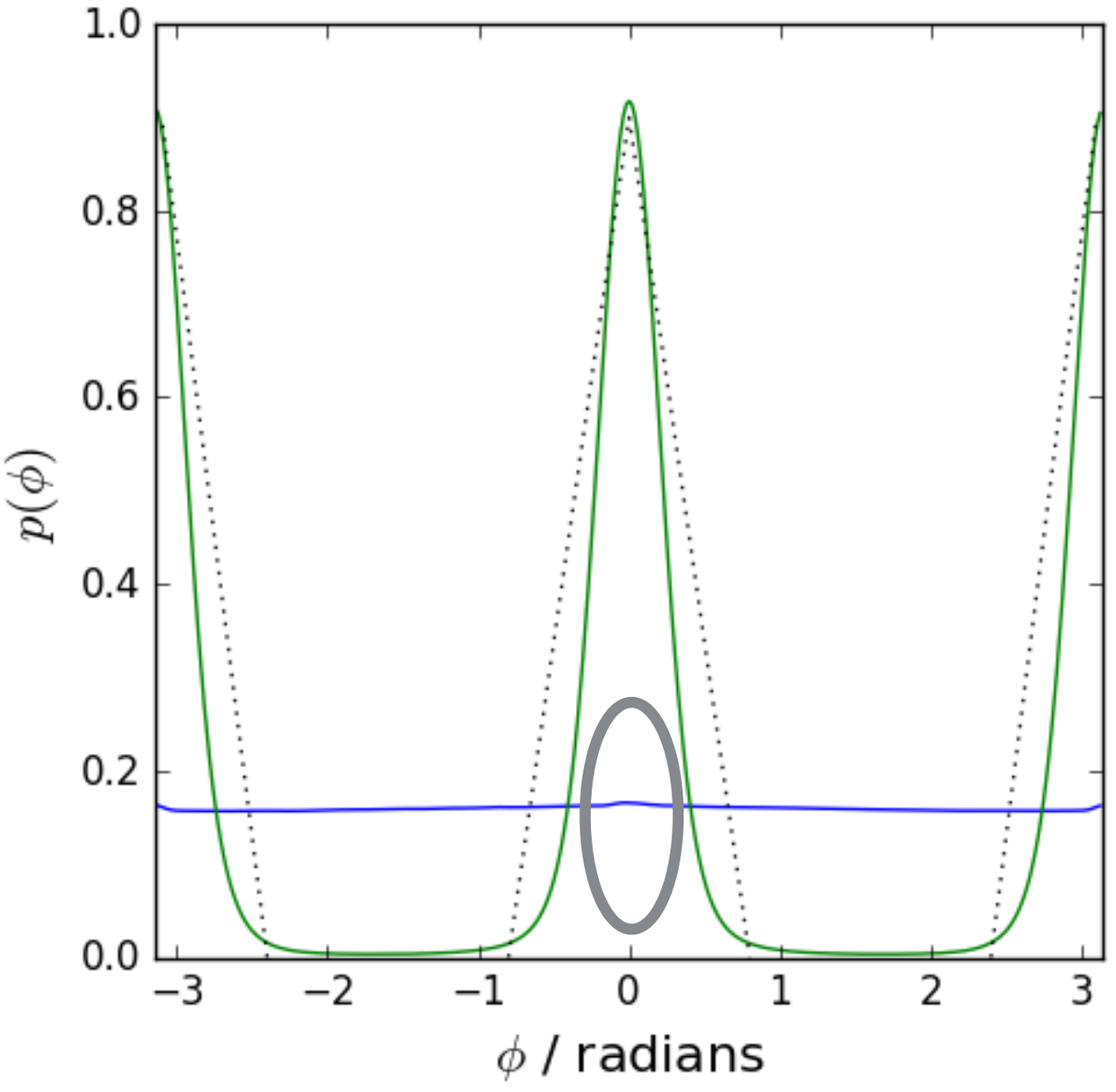
Calculate vector orientation for each of the atoms/molecules in the system

Calculate adjacency matrix which measures whether or not pairs of molecules that are within some cutoff have the same orientation

$$A_{ij} = \sigma(r_{ij})K(\phi_{ij}) \qquad \text{where} \qquad K(\phi_{ij}) = \sum_k \left[1 - \left|\frac{\phi_{ij} - \pi_k}{b_k}\right|\right]$$

Molecule "bonding" in practise





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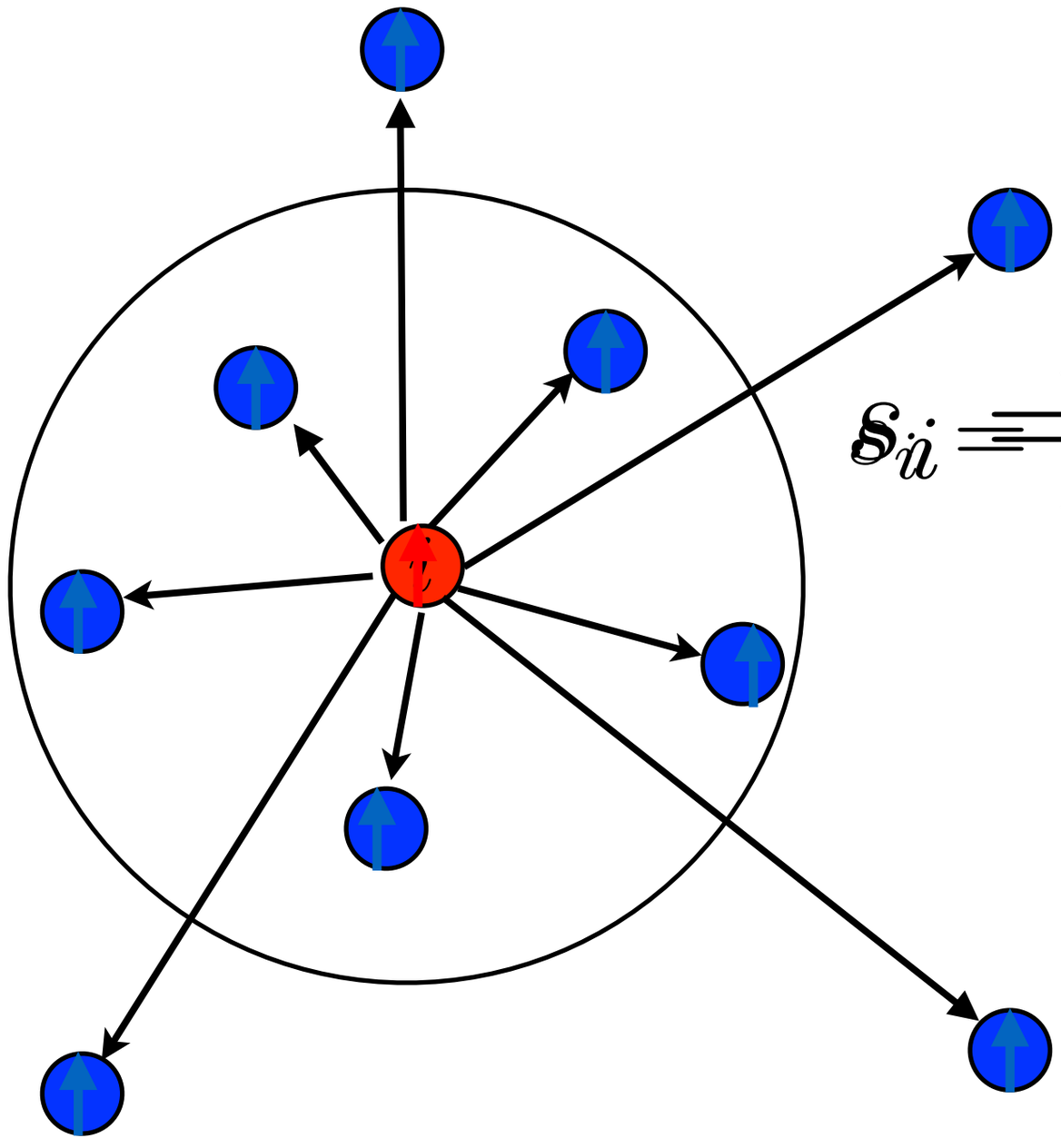
Symmetry functions

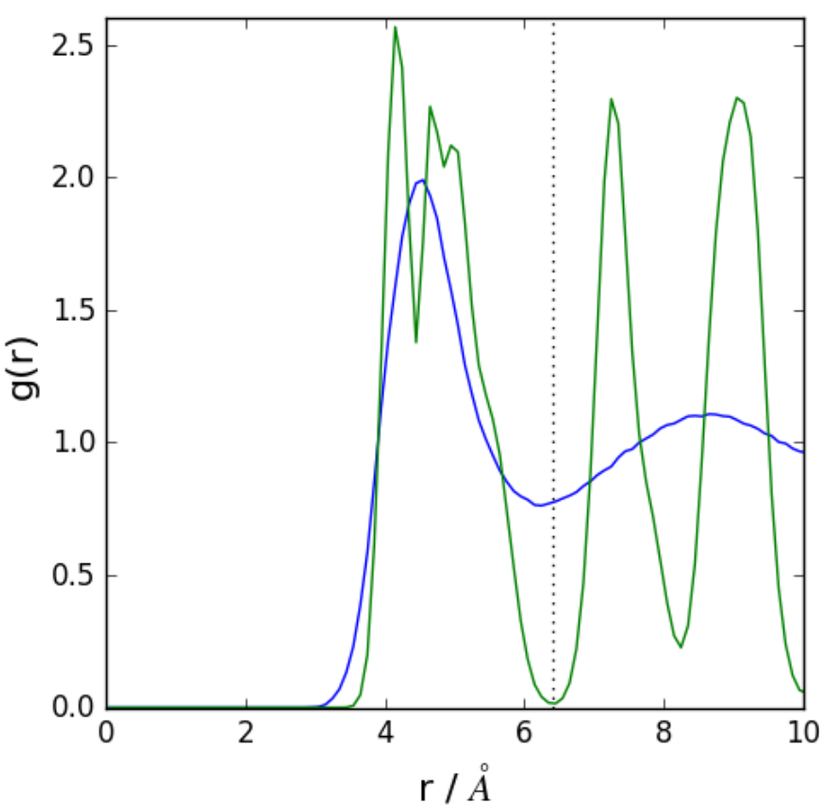


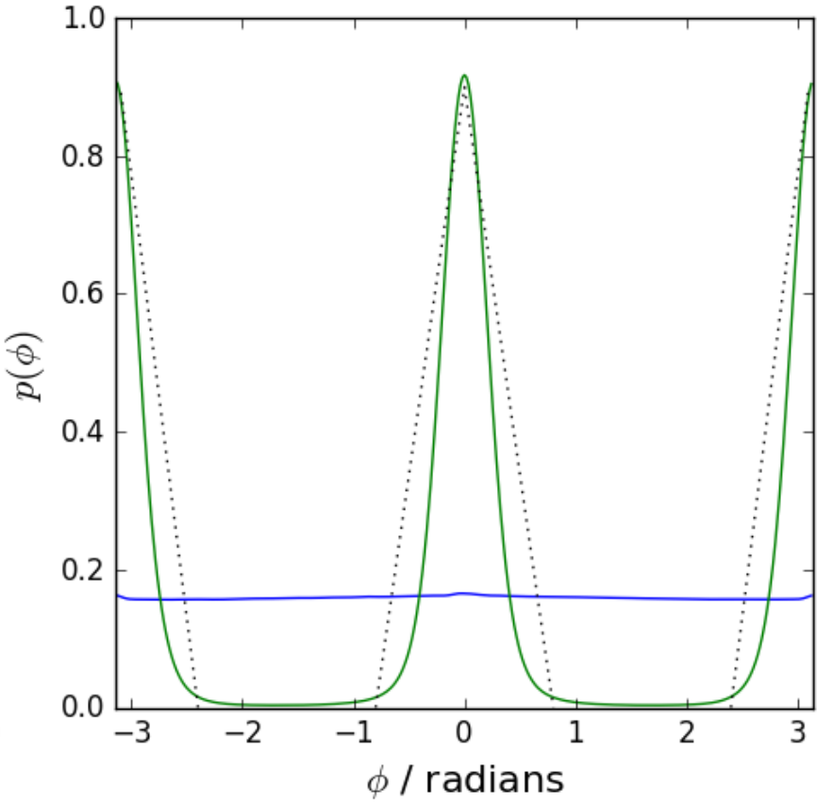
$$s_i = \sum_{i \neq j} \sum_{i \neq j} f(r_{ij}) g(\theta_{ijk}, \phi_{ijk})$$

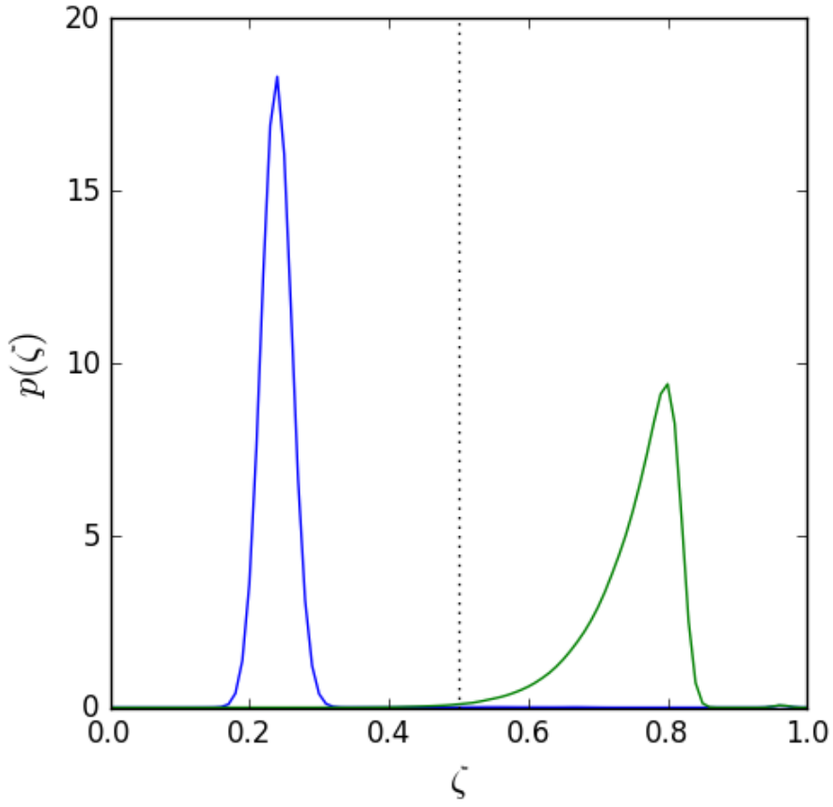
Basis of many cvs e.g:

Coordination number
Steinhardt Q4/Q6 etc
Local Q4/Q6
Cubic Harmonics

A variable for distinguishing solid/liquid

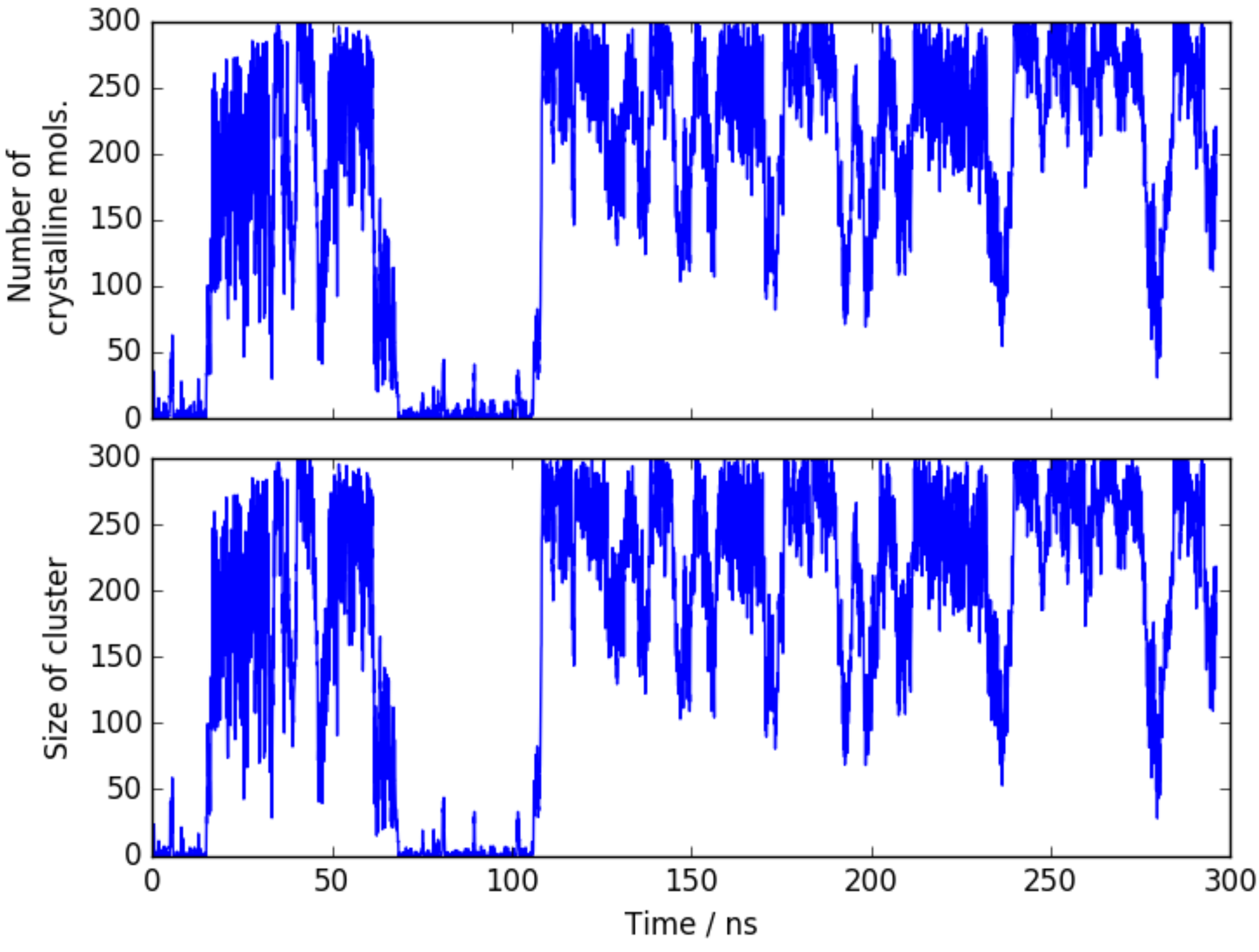




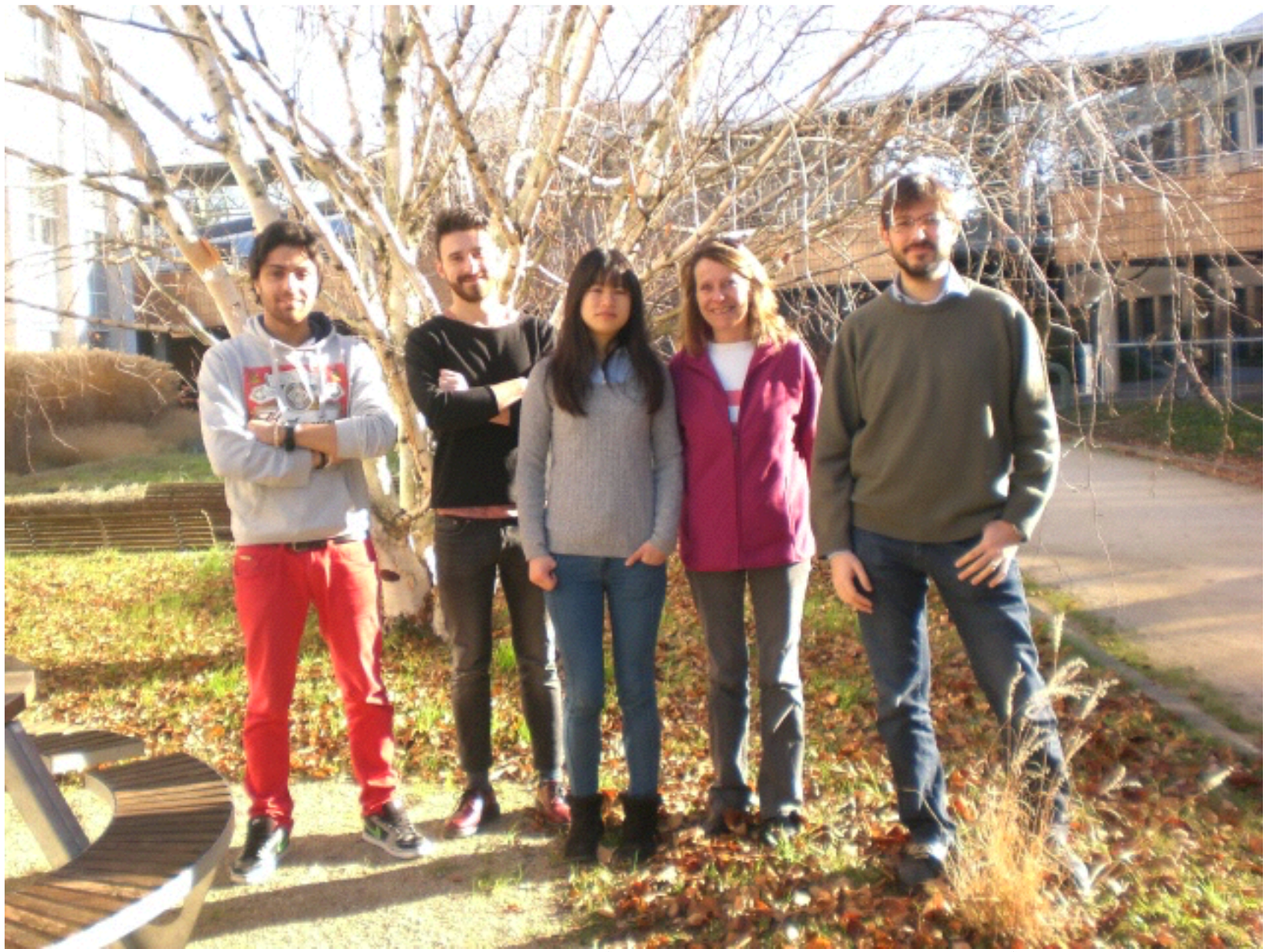


$$C_{ij} = H(s_i)H(s_j)\sigma(|\mathbf{r}_{ij}|)$$

The result


Number of crystalline mols.
300
250
200
150
100
50
0
Size of cluster
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Time / ns

Surface tension



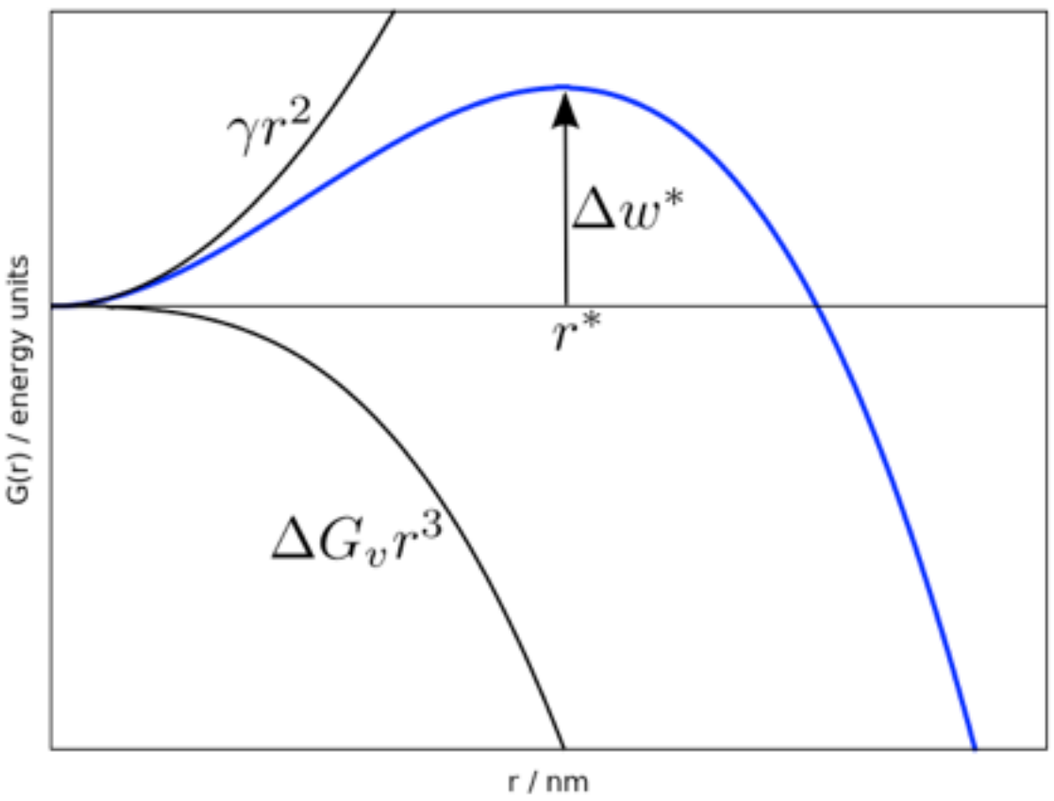
OK but what we need is the surface tension

Bingqing Cheng

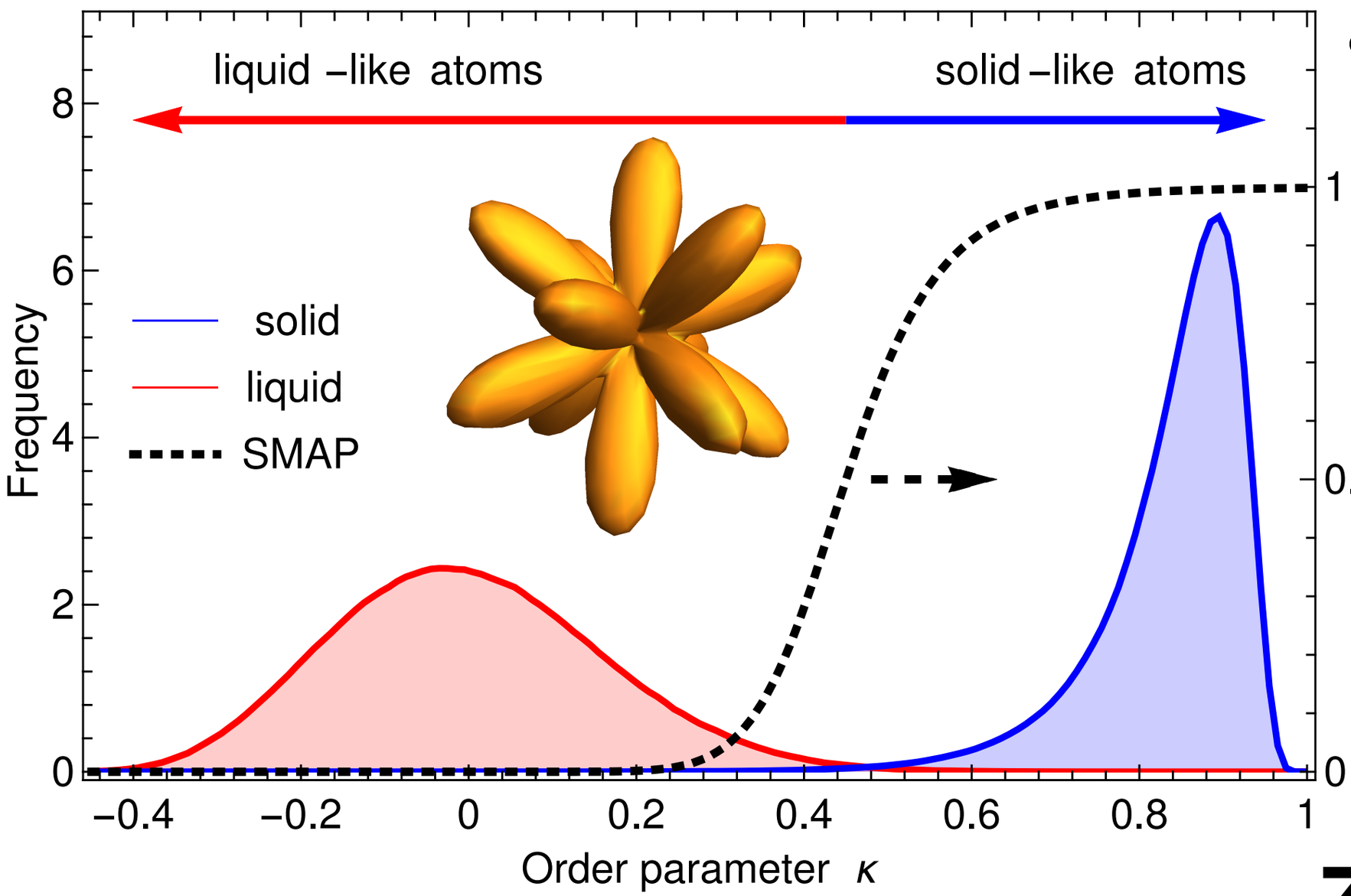
Michele Ceriotti

Classical nucleation theory

$$F(n) = \gamma A(n) + \mu_{sl} n$$



With metadynamics

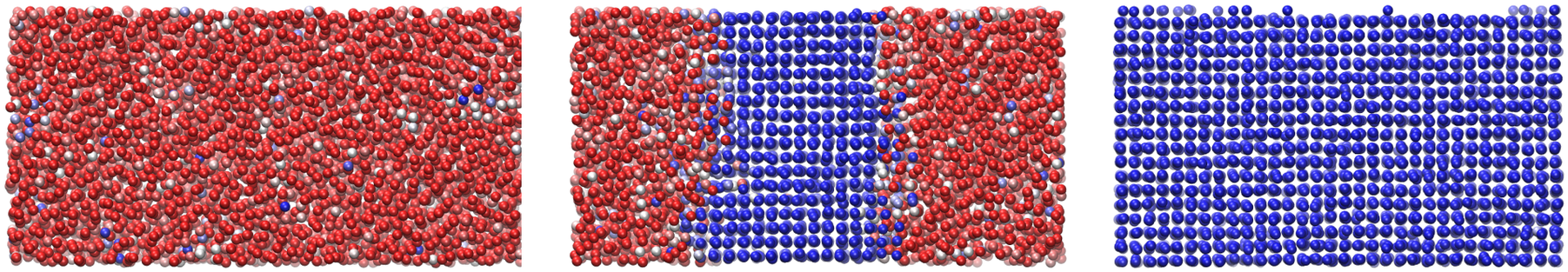


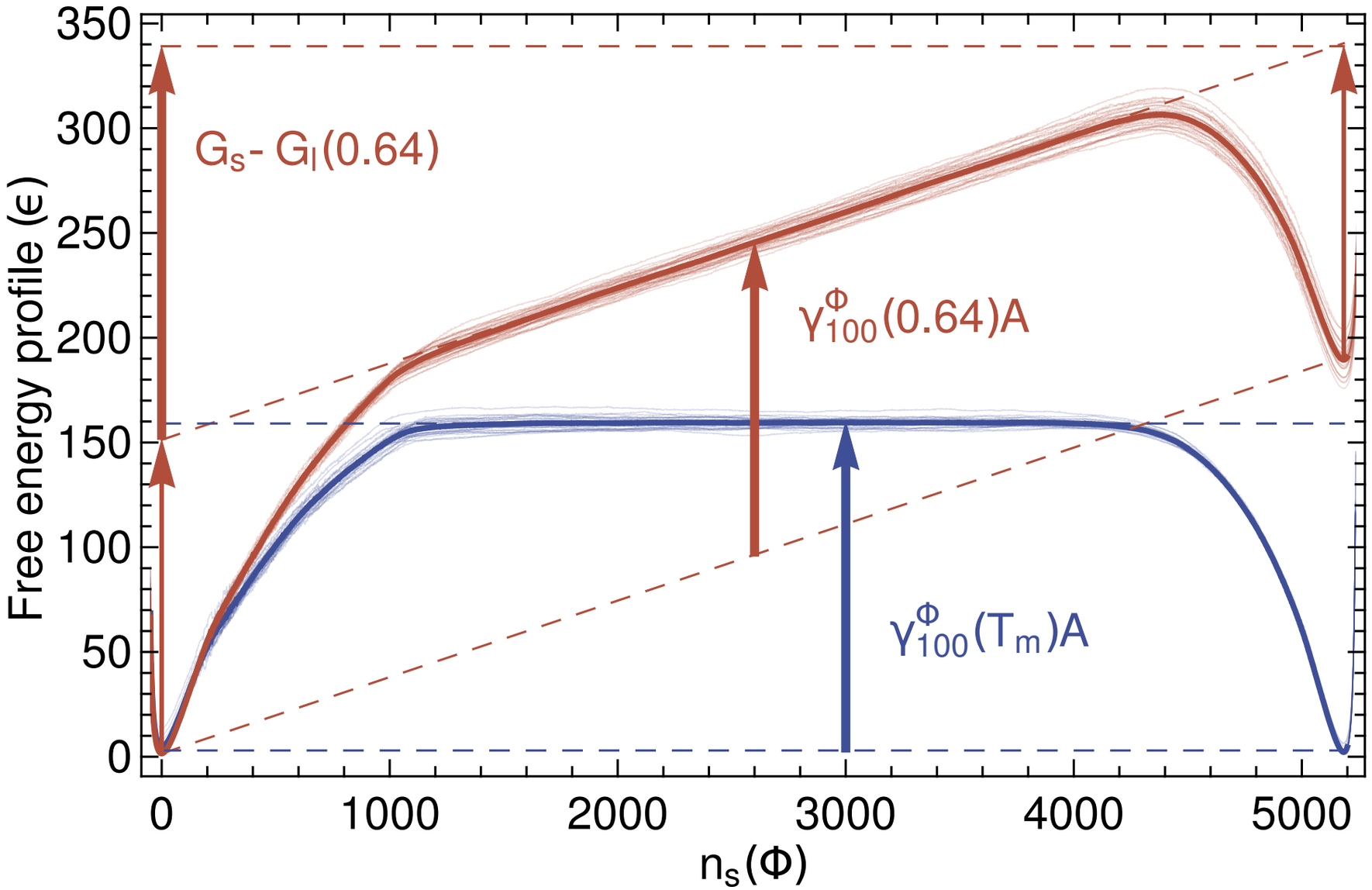
$$\Phi = \sum_i s_i$$

Average value of s in bulk solid and liquid

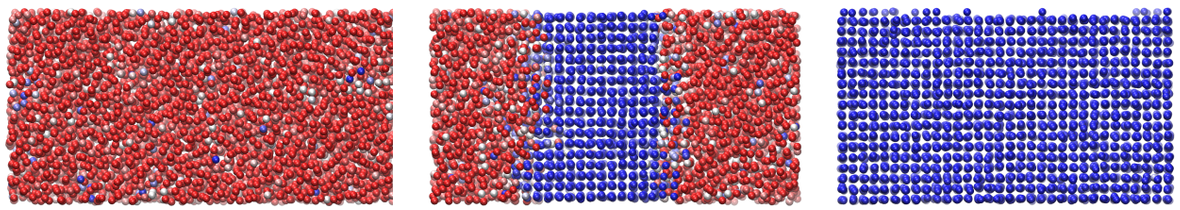
Zero surface excess for Phi

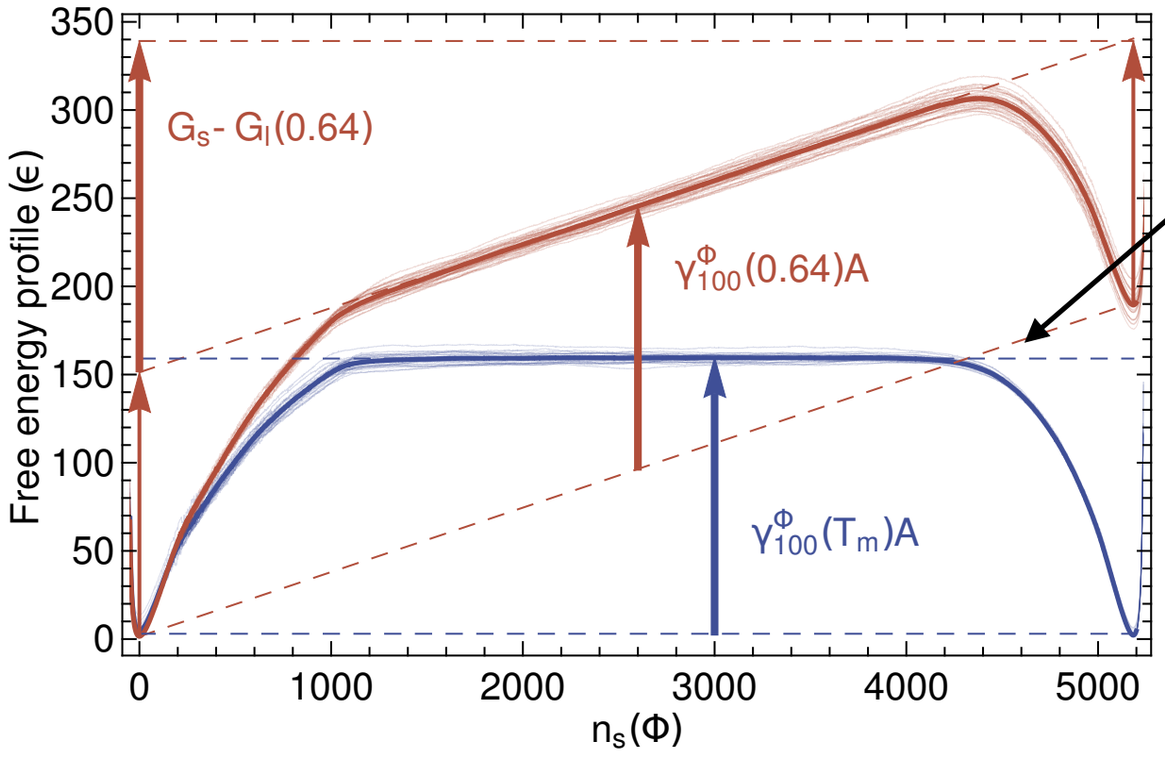
Driving nucleation



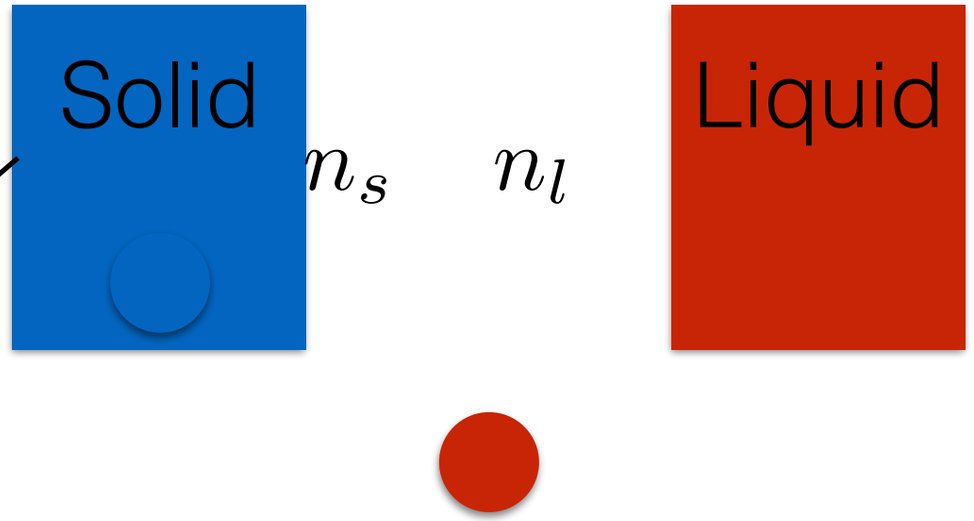


Analysis





Free energy always gives free energy relative to some reference state



$$N = n_s + n_l$$

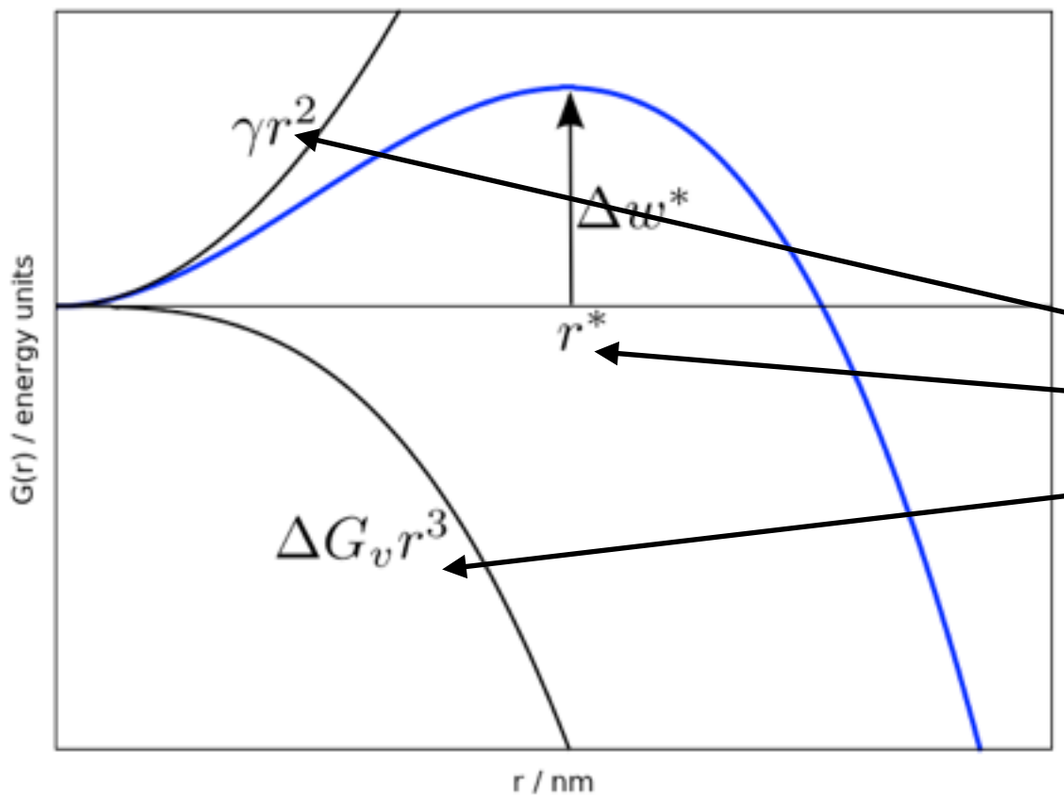
$$\Phi = \phi_s n_s + \phi_l n_l$$

Ensures zero surface excess for phi

$$V \neq n_s v_s + n_l v_l$$

Classical nucleation theory

$$F(n) = \gamma A(n) + \mu_{sl} n$$

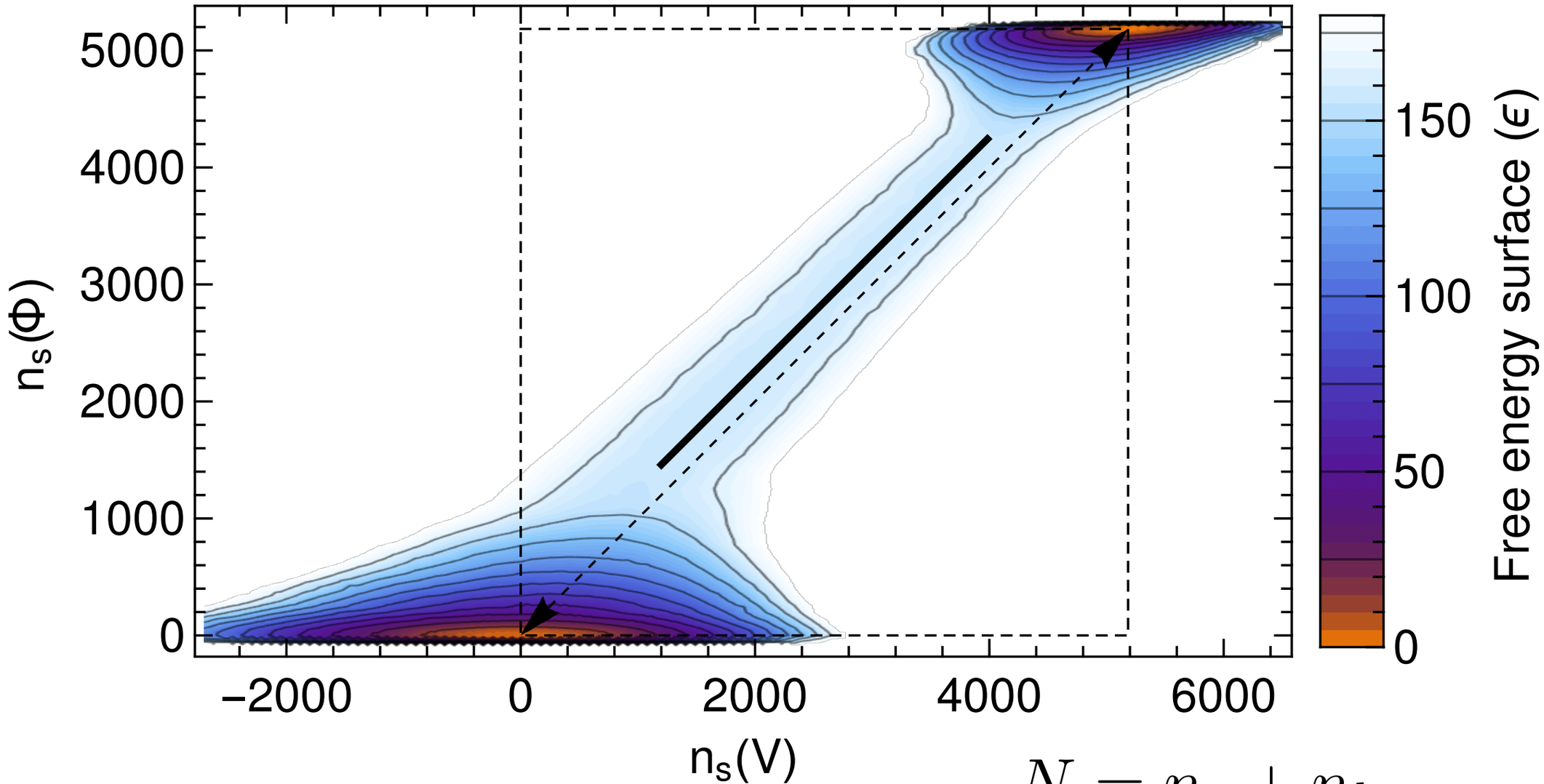


Everything is written in terms of radius. No contribution to volume from surface!!

But does it make a difference?

$$N = n_s + n_l$$

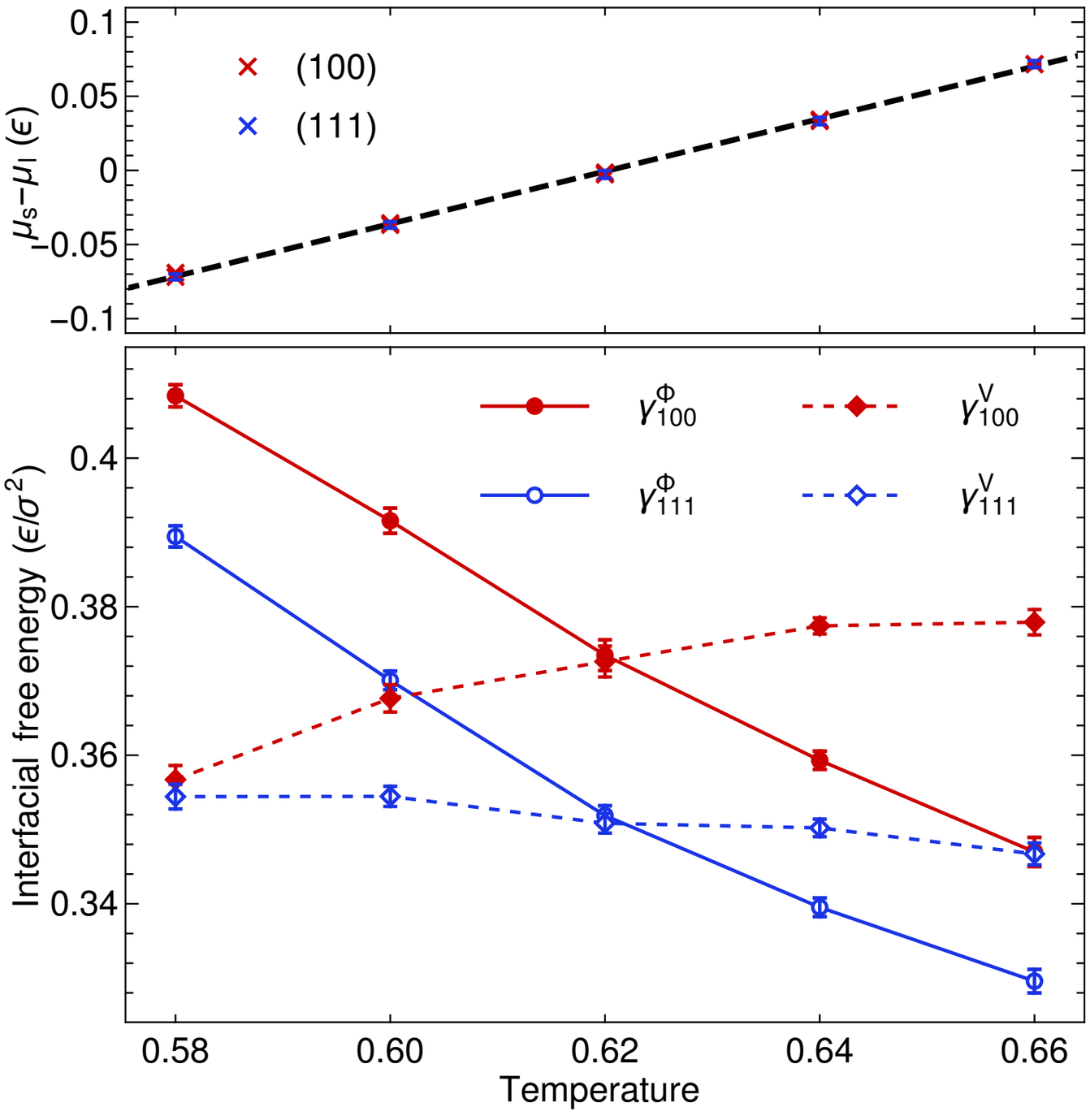
$$\Phi = \phi_s n_s + \phi_l n_l$$



$$N = n_s + n_l$$

$$V = n_s v_s + n_l v_l$$

This really does matter

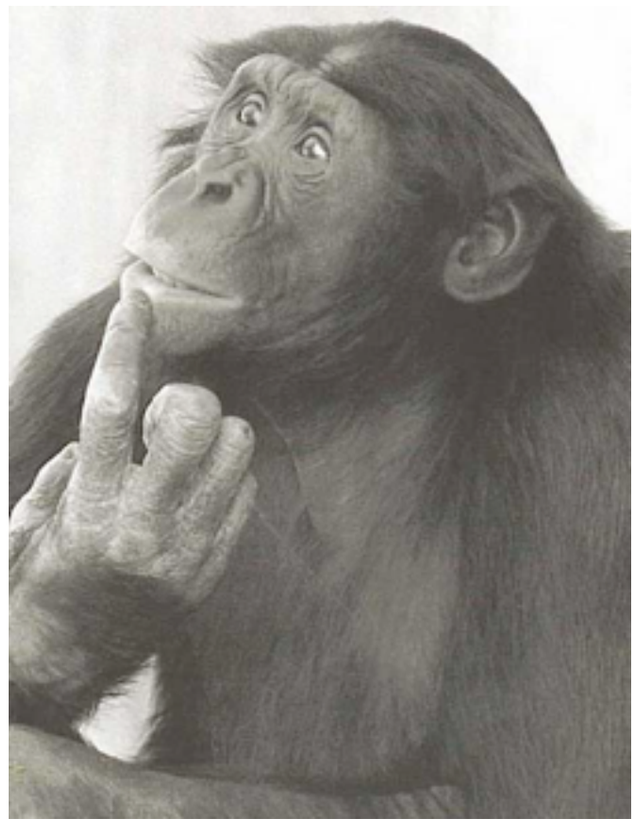


B. Cheng, G. A. Tribello and M. Ceriotti *Phys Rev B* **92** 180102 (2015)

Conclusions

Collective variables are a tool for understanding simulation data. **Many are designed based on established theory**

You need to think about the question you want to answer



Other people help

CLUSTERING

Gabriele Sosso

Federico Giberti

Matteo Savalaglio

PLUMED

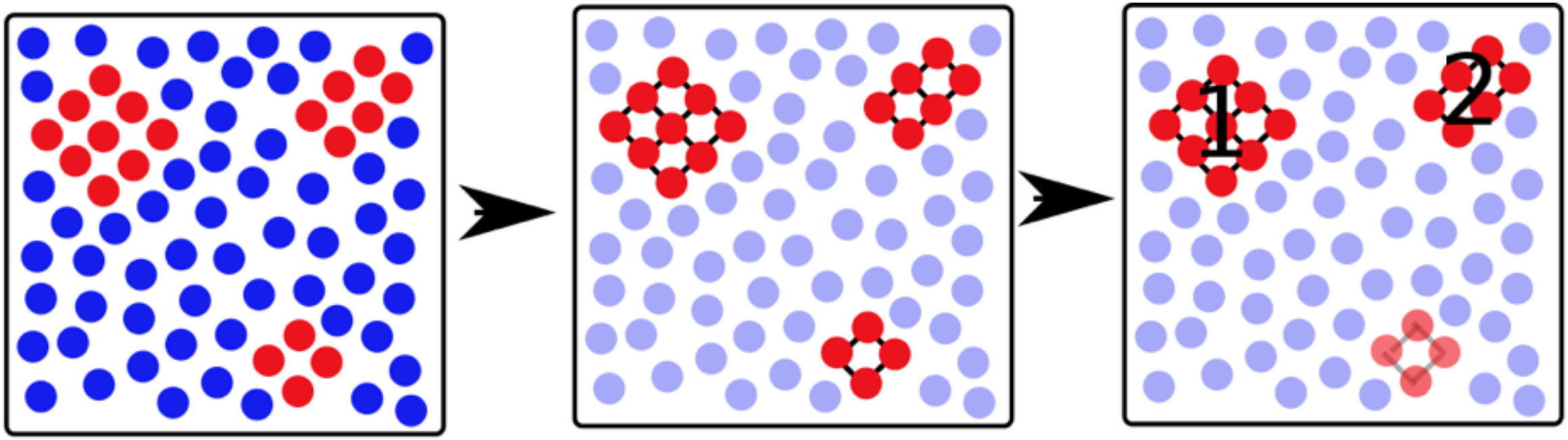
Giovanni Bussi

Carlo Camilloni

Max Bonomi

Davide Branduardi

Filtering



Identify atoms with ordered first coordination sphere using some atom-centered measure of crystallinity

Perform DFS clustering on the set of atoms with a high crystalinity parameter

Count the number of connected components that contain more than 4 atoms

$$C_{ij} = H(s_i)H(s_j)\sigma(|\mathbf{r}_{ij}|)$$