Computational thermodynamics: how to calculate phase diagrams without the fuss

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Outline

- Phase diagrams: Why to calculate them and how?
  overview of some well established tools

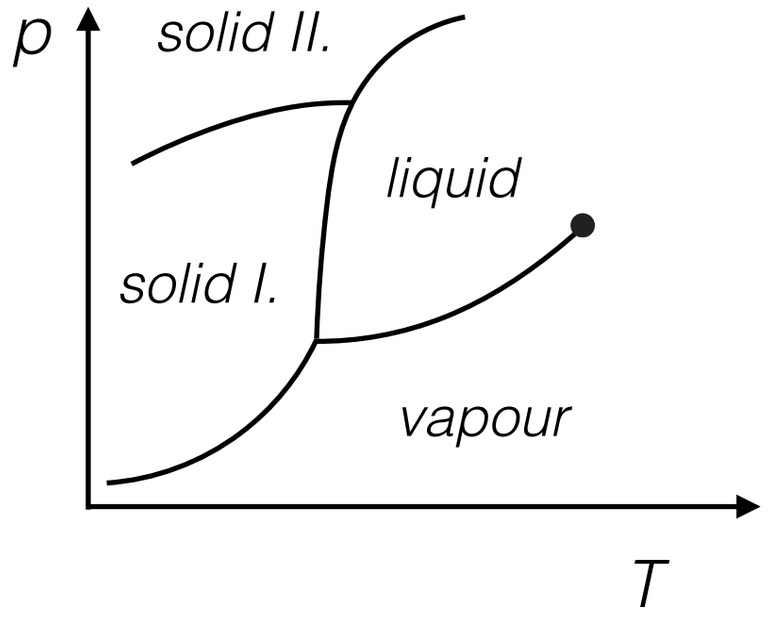
- Nested sampling algorithm

- Some applications
  - metals, alloys
  - clusters
  - molecules

Phase diagrams

A phase diagram is a “map” showing the properties of a given material at specific conditions.

- temperature
- pressure
- density
- composition
- …etc.



- phase boundaries
- critical points
- triple point
- …etc.

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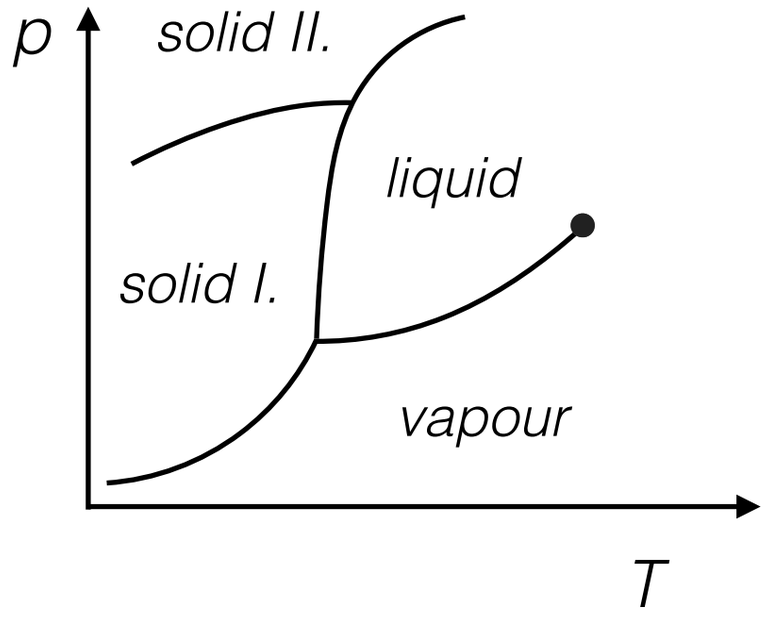

- phase boundaries
- critical points
- triple point
- …etc.

Important in *chemistry*,
materials science,
engineering,
CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry)

Reasons to use computational techniques

- **save time and resources by making predictions**
  (less/no need for expensive experimental equipment, and materials, where to look for phases with specific properties, unique/exotic phases)
- **study phases under extreme conditions**
  (alloys under working conditions,
  planetary interiors (~TPa), critical point of metals…etc.)
- **give an insight to phases on the atomistic level**
  (atomic interactions, driving forces)
- **help to clarify structural properties**
  (provide candidate structures to match experimental findings)

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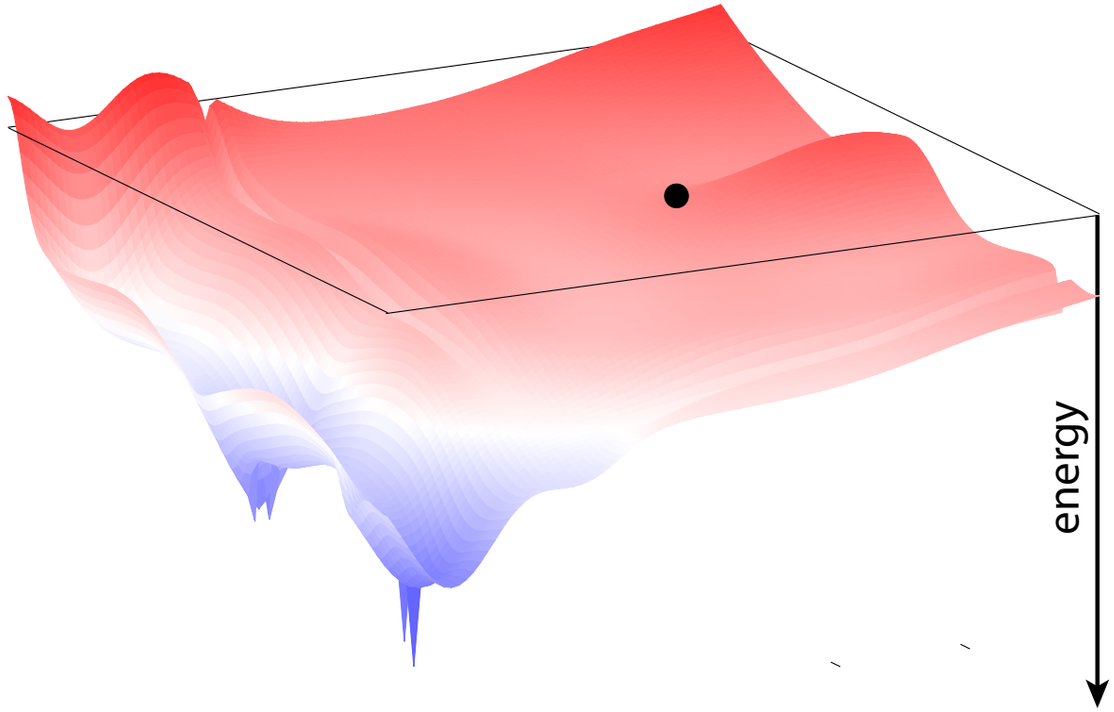
How to generate the relevant atomic configurations?

How to model the interaction between atoms?

Atomic configurations

How to generate relevant atomic configurations?
The number of possible atomic arrangements is enormous even for a very small system.

N particles: 3*N*-dimensional phase space describes the state of every particle in that system, and a point in the phase space is a *microstate* of the system.



Potential energy surface (landscape): potential energy as a function of the atomic configurations.

Atomic configurations

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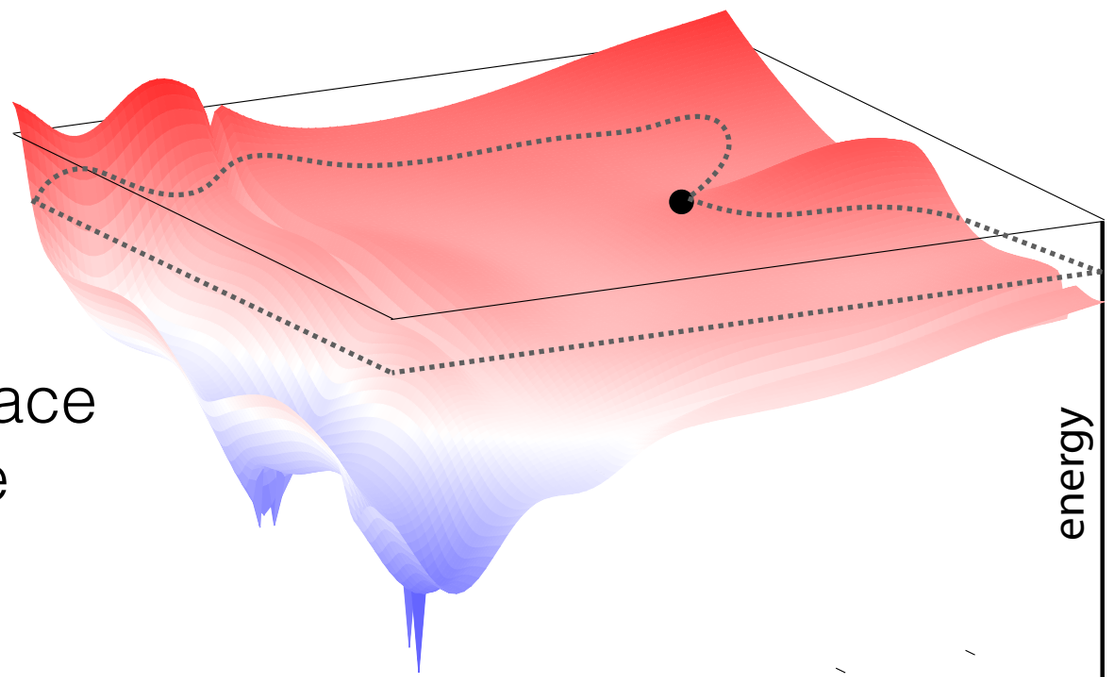
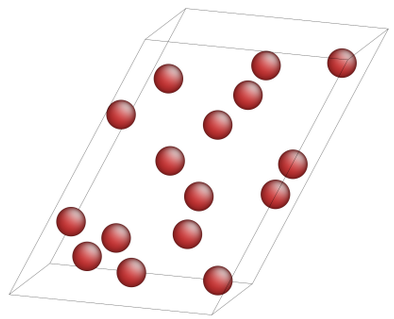
The probability of a *microstate* at given *T* is given by the Boltzmann factor:

exp(-*E*/*kT*)





partition
function

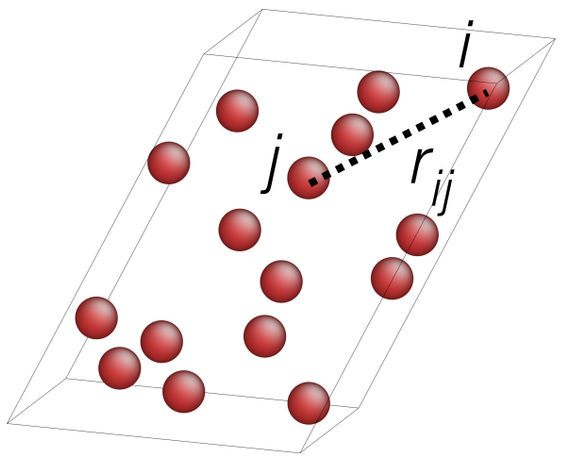
Potential energy surface (landscape): potential energy as a function of the atomic configurations. (minima, transition states, phase transitions)

Interaction models

How to describe atomic interactions?

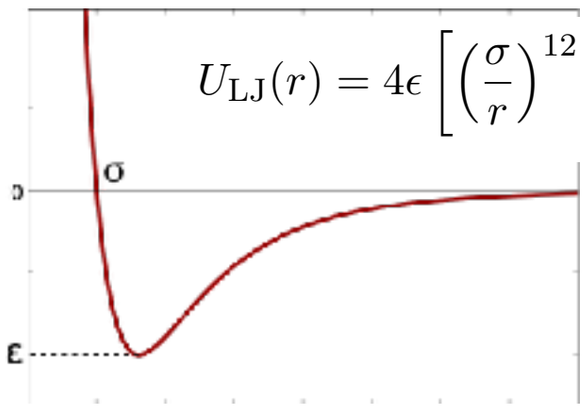
Ab initio, DFT

Classical pair potentials: $E_{\text{tot}} = \sum_i \sum_{j>i} E_{ij}$ where $E_{ij} = V(r_{ij})$

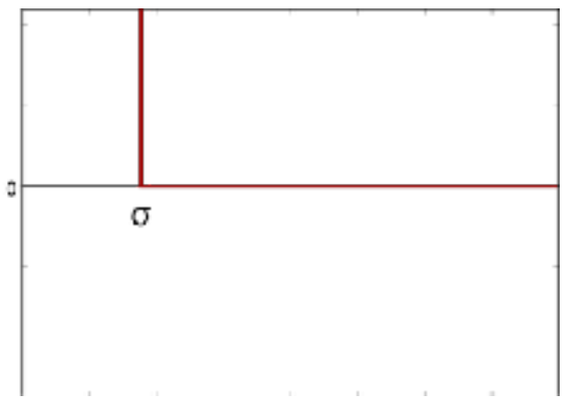


Lennard-Jones potential

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

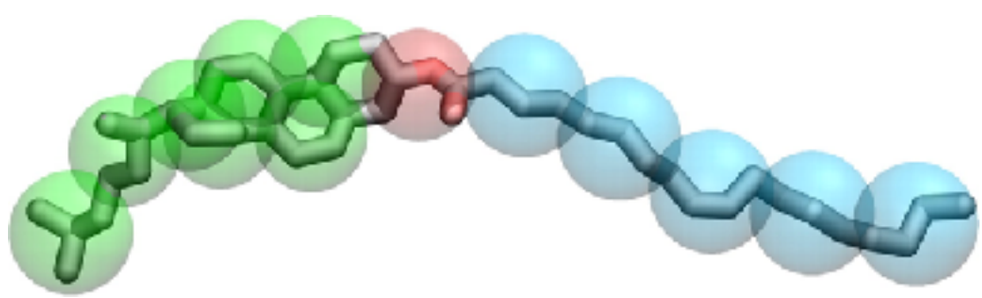


Hard sphere potential



Embedded atom model: $E_i = F\left(\sum_{i\neq j} \rho(r_{ij})\right) + \frac{1}{2}\sum_{i\neq j} V(r_{ij})$

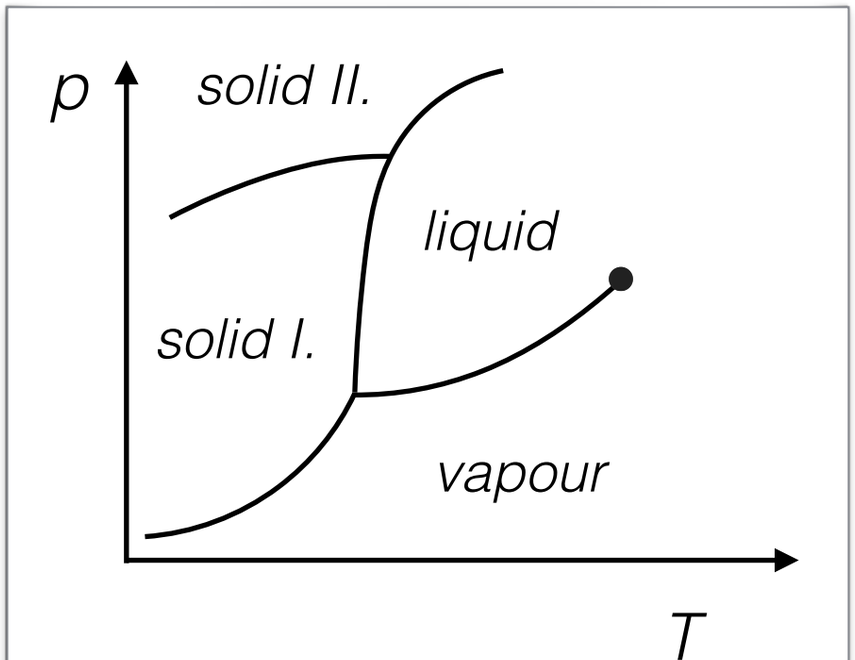
Coarse grain models



(from Shih *et al.*;DOI: 10.1098/rsif.2009.0173)

Calculating a *p*-*T* phase diagram

Methods specific for a given **part** of the phase diagram

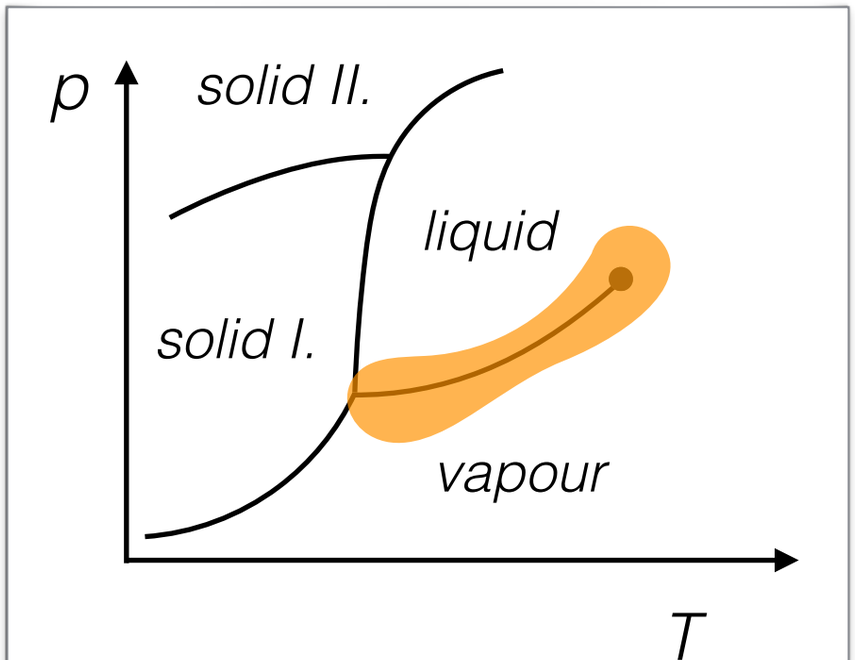


Systematic exploration of the phase diagram

Calculating a *p*-*T* phase diagram

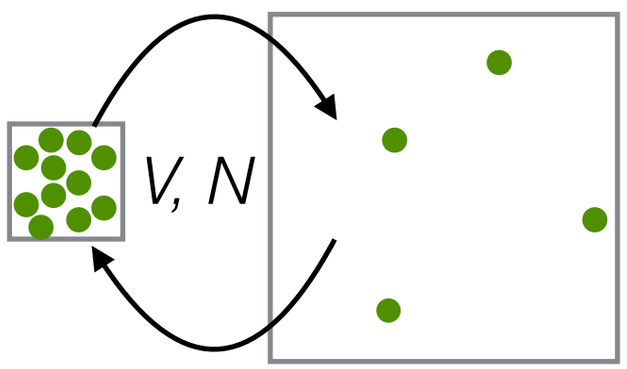
Methods specific for a given **part** of the phase diagram

- **Gibbs Ensemble MC**



Systematic exploration of the phase diagram

sample the equilibrium properties of two fluid phases, without the interface



- limited to fluid phases
- fluctuations become too large nearer the critical point

Calculating a *p*-*T* phase diagram

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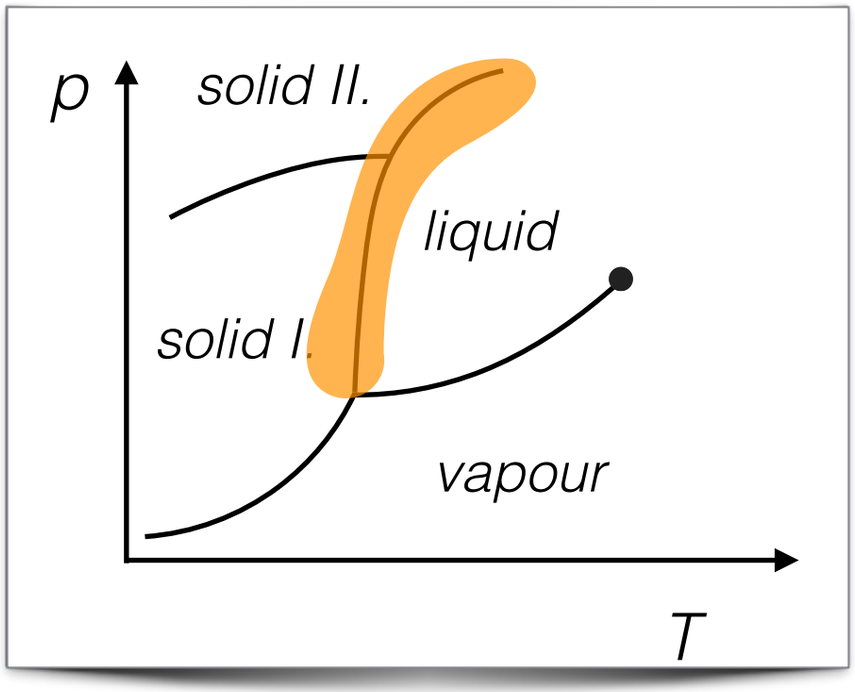
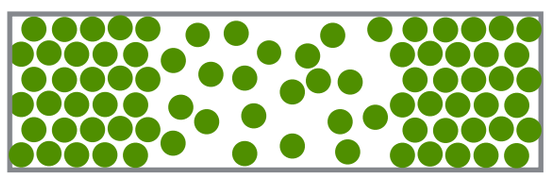
- **coexistence simulations**



Systematic exploration of the phase diagram

equilibrate the coexisting phases by observing the interface



- melting transition
- solid structure has to be known *a priori*
- several simulations needed for a single transition point
- large number of particles needed

Calculating a *p*-*T* phase diagram

Methods specific for a given **part** of the phase diagram

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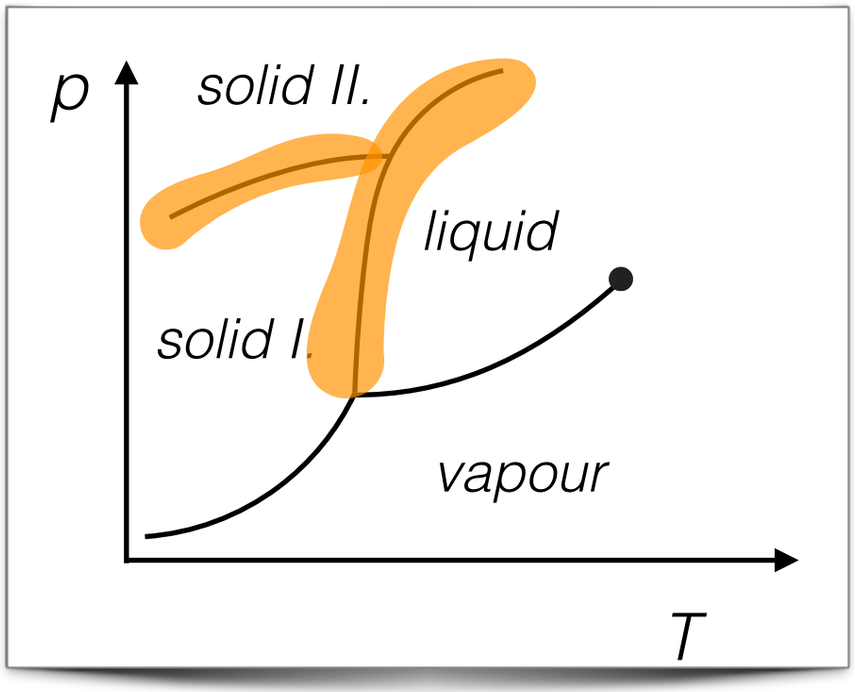
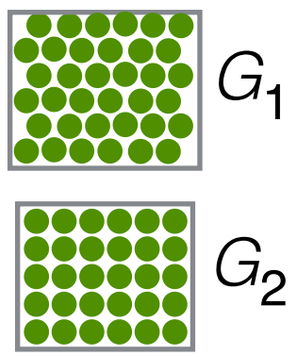
- **free energy comparison**



Systematic exploration of the phase diagram

calculate the free energy of the candidate phases and choose the most favourable



- solid structures have to be known *a priori*

Calculating a *p*-*T* phase diagram

Methods specific for a given **part** of the phase diagram

- **Gibbs Ensemble MC**
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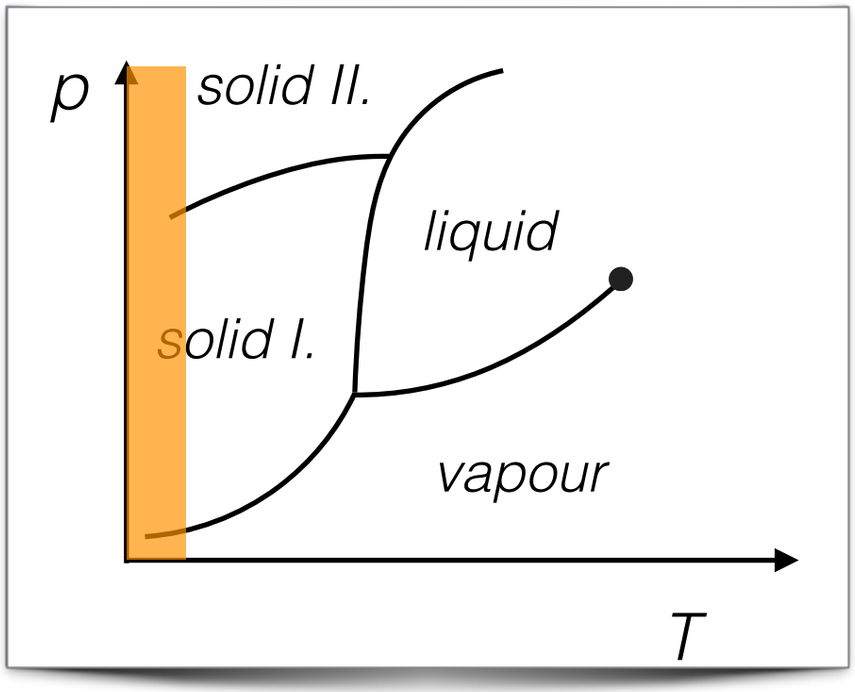
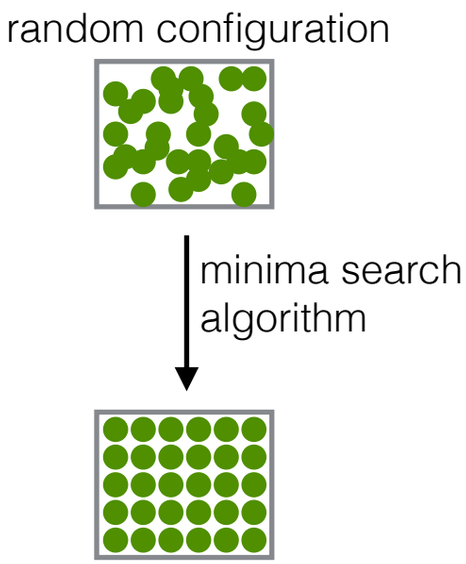
- **free energy comparison**
- **minima search**



Systematic exploration of the phase diagram

use minimisation techniques to find the lowest energy structure



- strong predictive power
- only low temperature phases can be found

Calculating a *p*-*T* phase diagram

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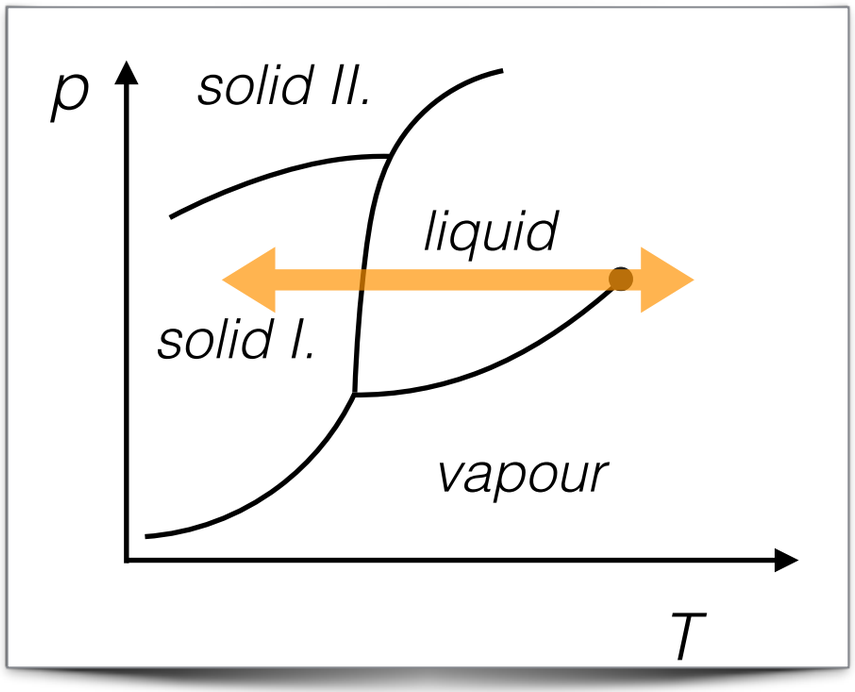
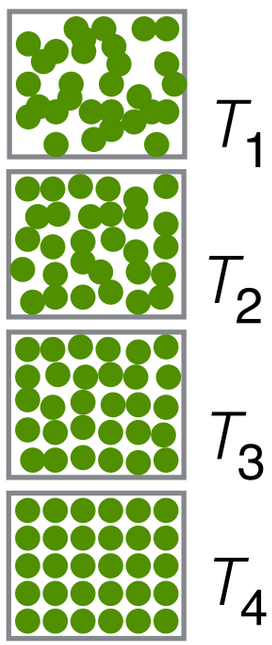


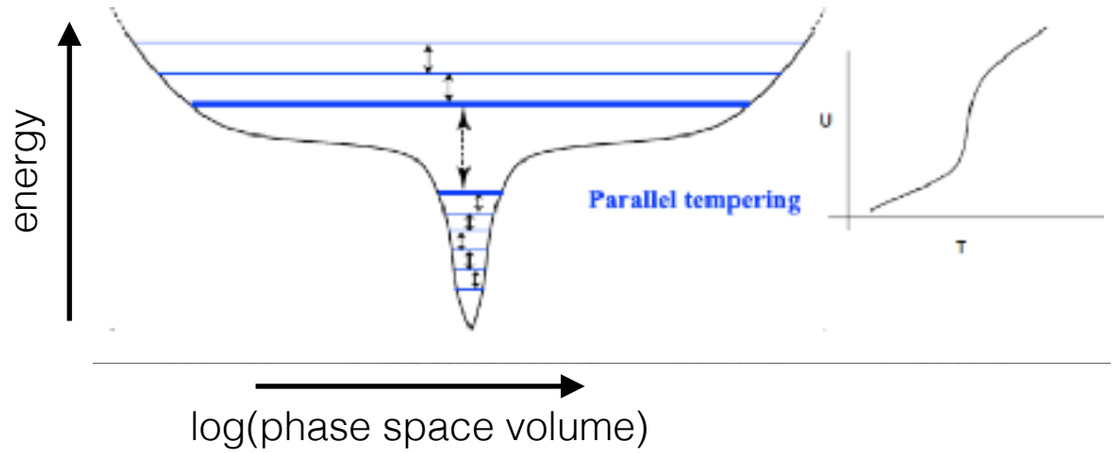
Systematic exploration of the phase diagram

- **Wang-Landau sampling**
- **parallel tempering**

simulate a series of temperature levels simultaneously



- thermodynamic properties can be calculated
- hard to equilibrate around phase transitions



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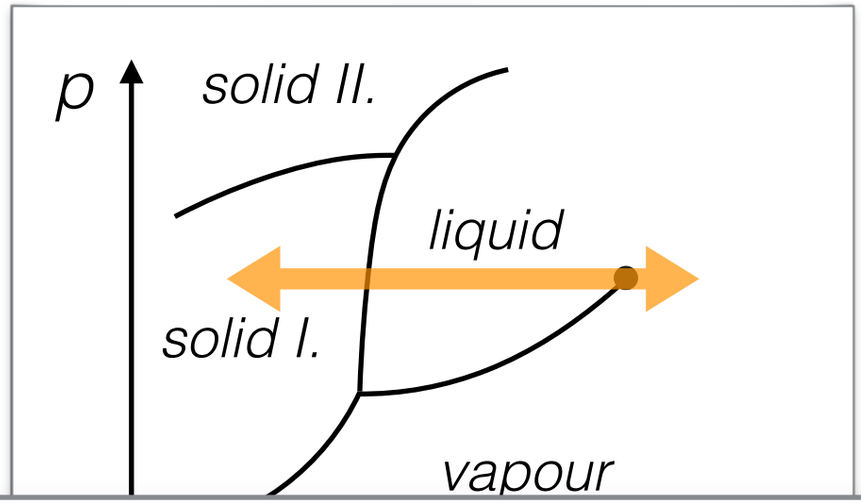


Systematic exploration of the phase diagram

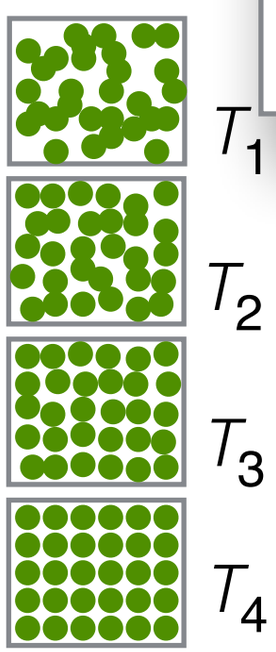
- **Gibbs Ensemble MC**
- **coexistence simulations**
- **free ener**
- **minima s**

- **Wang-Landau sampling**

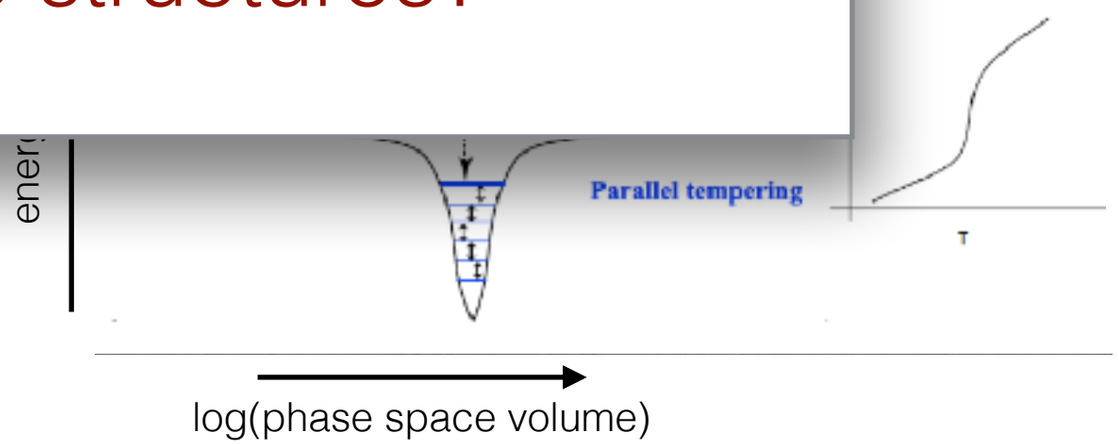
ring

Can't we get the entire phase diagram in a simple, automated way and without prior knowledge of the structures?

simulate



- can be calculated
- hard to equilibrate around phase transitions



Nested Sampling

John Skilling, 2004, Bayesian statistics

"...to sample probability densities in high-dimensional spaces where the regions contributing most of the probability mass are exponentially localised."

evidence (Z) likelihood (L) proportion of the prior distribution

$$Z = \int_0^1 L(X)dX$$

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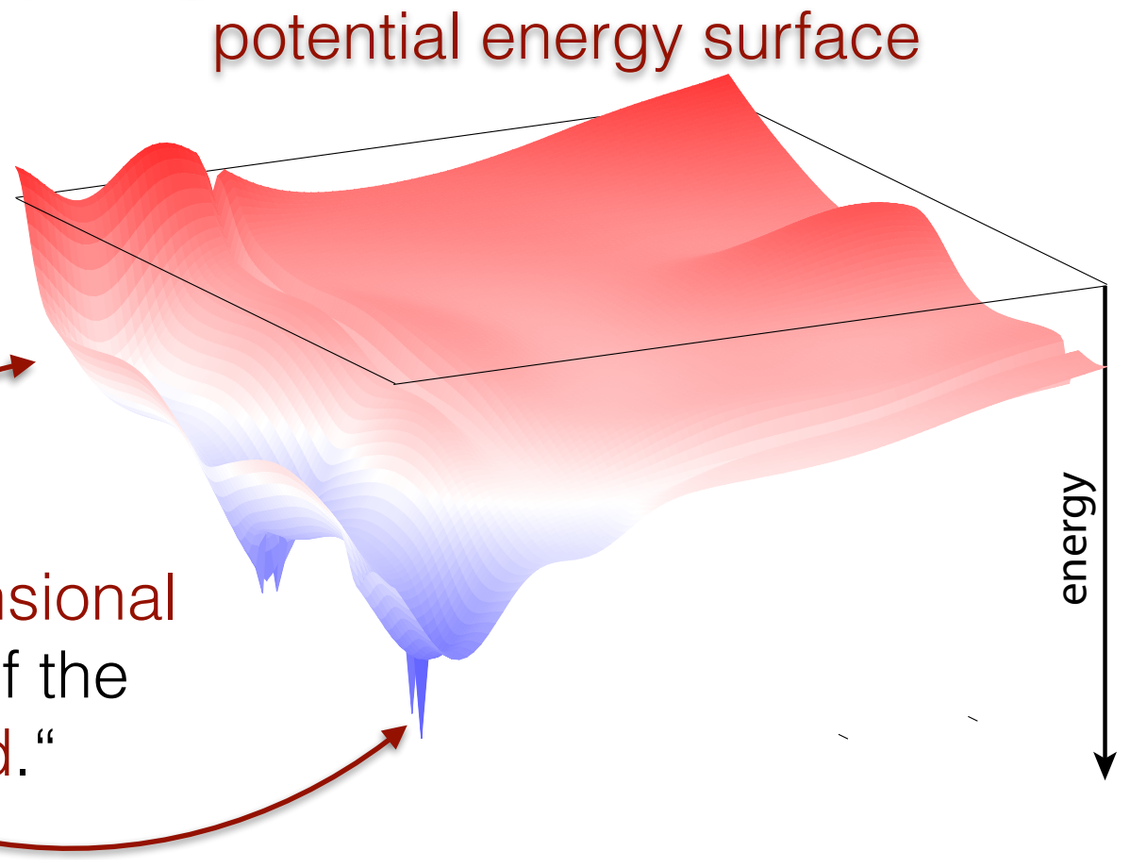

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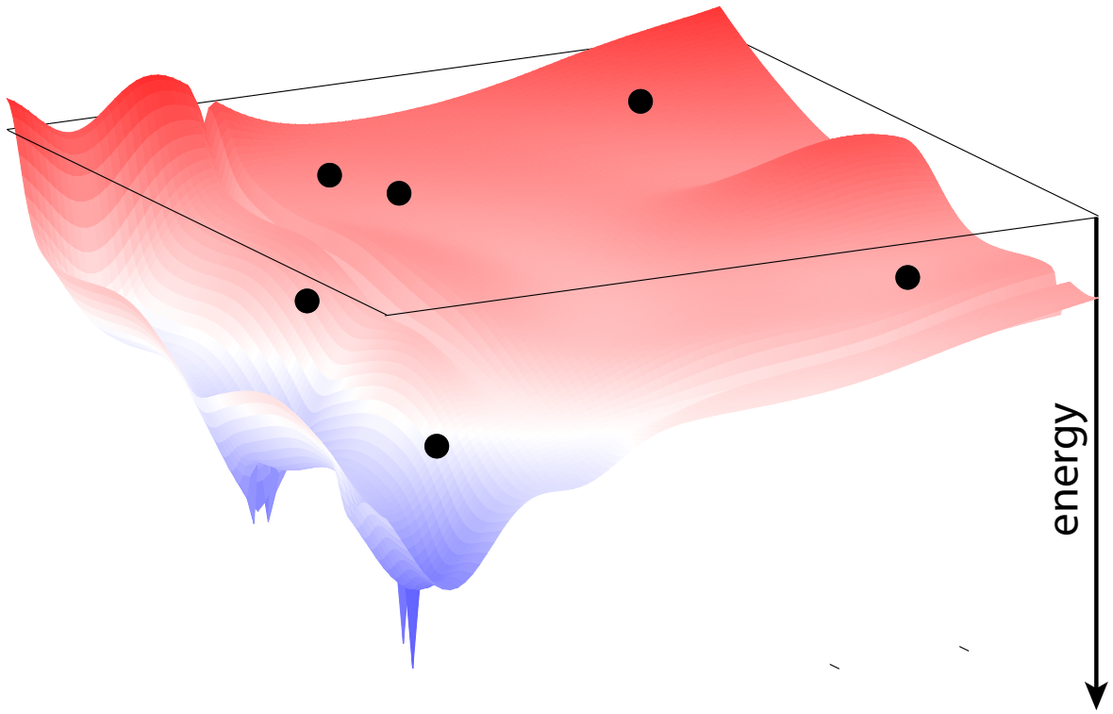
$$Z = \int_0^1 L(X)dX$$

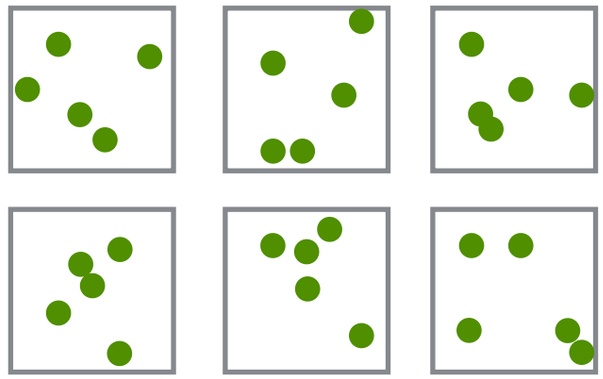
partition function Boltzmann-factor (energy) phase space volume (prior distribution is uniform)

Nested Sampling Algorithm

Iterative algorithm, starting form the “top” (ideal gas) and going towards the “bottom” (global minimum), through a series of nested energy “contours”.

Generate *K* random samples uniformly in the total phase space volume





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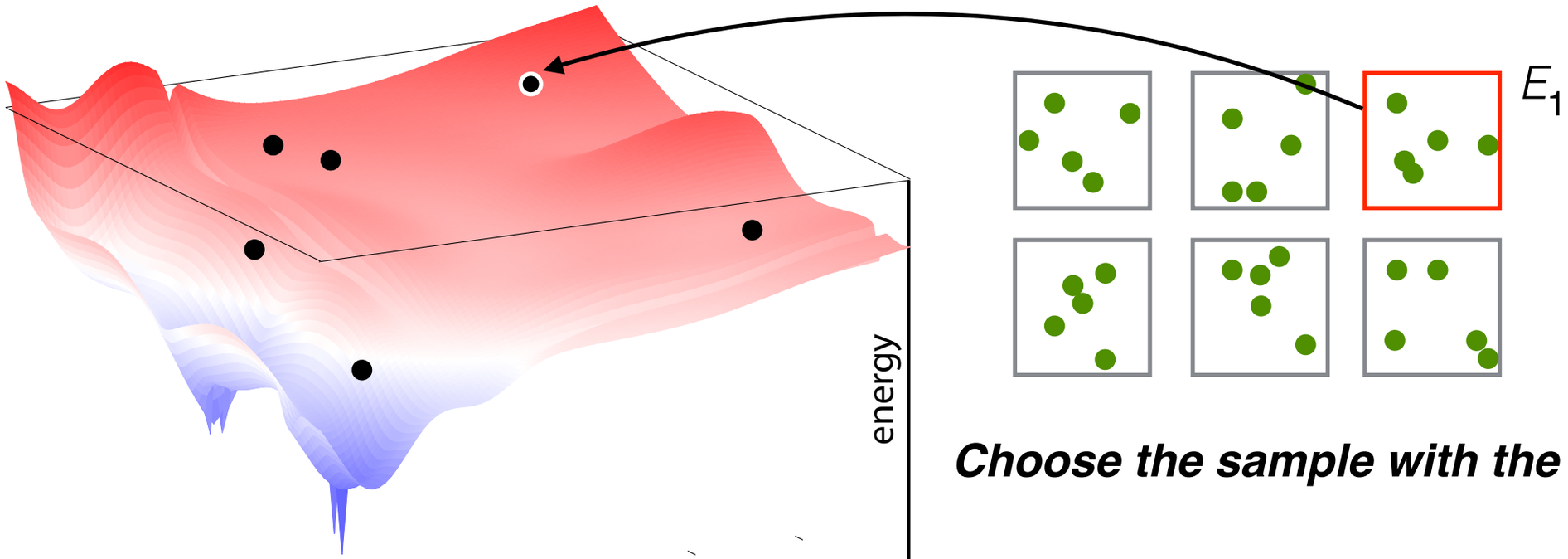

Choose the sample with the highest energy

the rest of the points will have $E < E_1$ and the the phase space volume they occupy is approximately $K/(K+1)$

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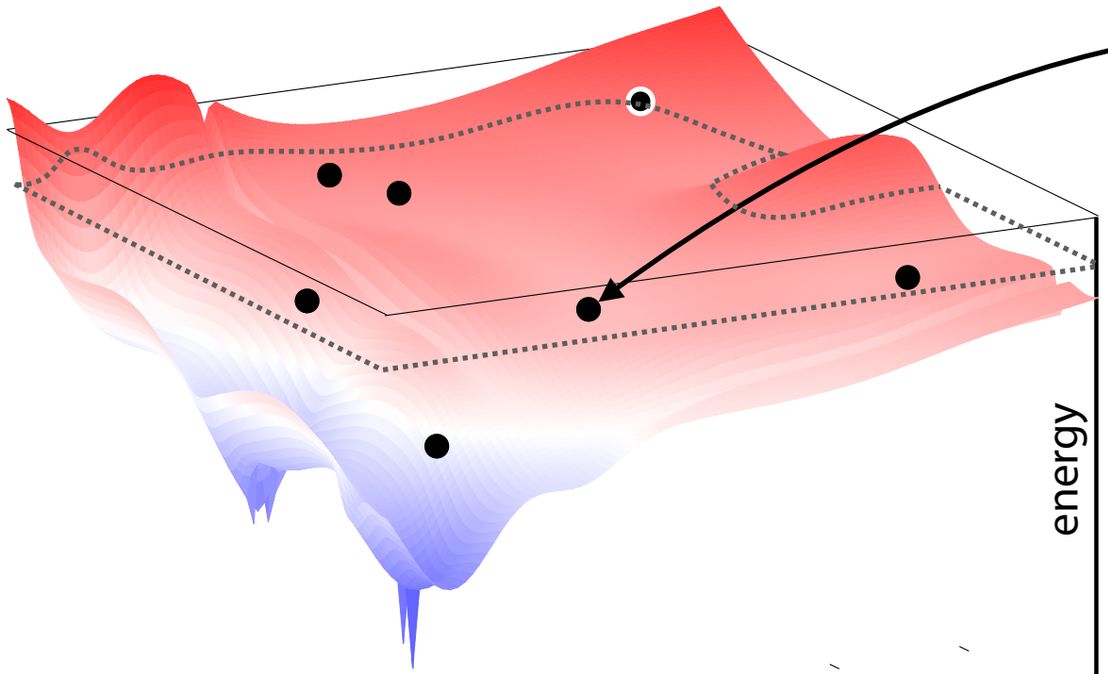

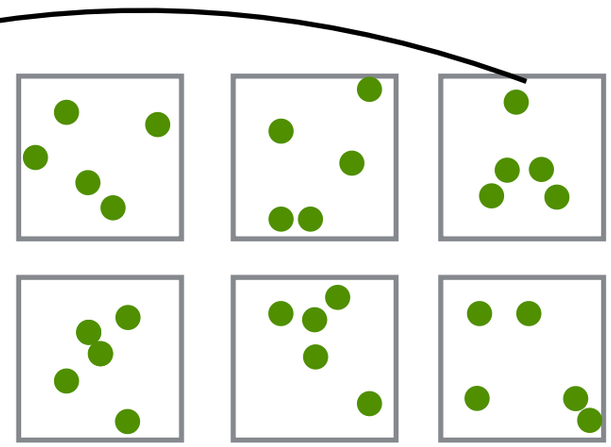

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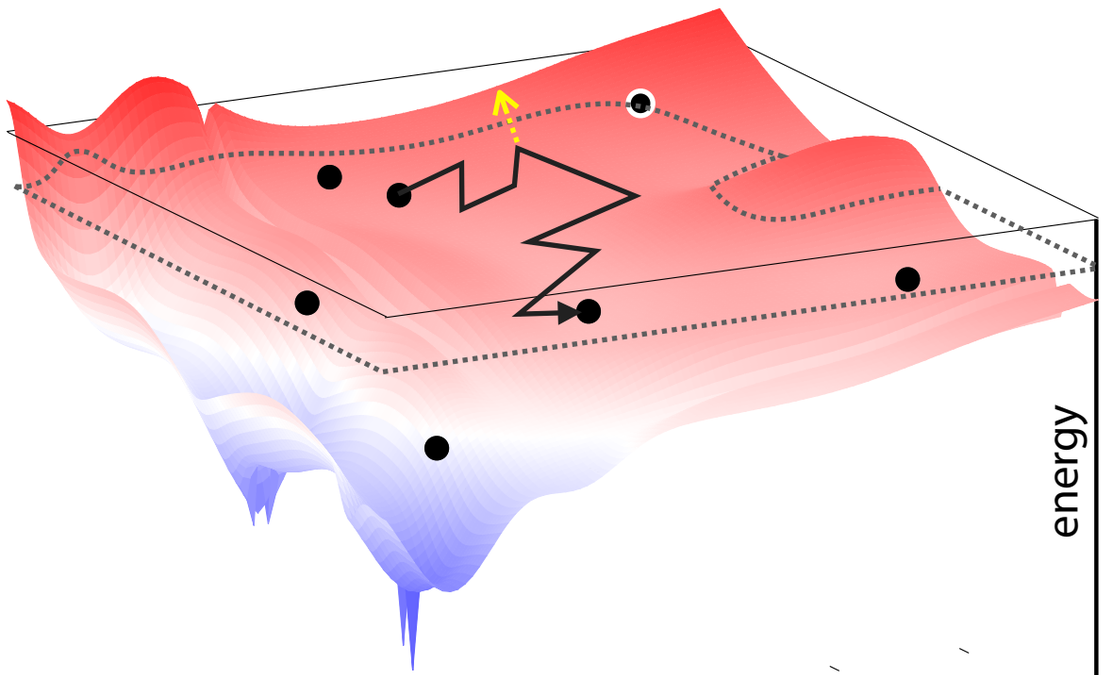
Generate a new sample uniformly with $E < E_1$

How?

Generating a new sample configuration

Iterative algorithm, starting form the “top” (ideal gas) and going towards the “bottom” (global minimum), through a series of nested energy “contours”.

Generate *K* random samples uniformly in the total phase space volume



Clone a randomly selected sample and perform a random walk until it is independent from its parent configuration:

- atomic coordinates
- cell shape
- cell volume
- swap types

- **Markov Chain Monte Carlo (MCMC):**
  single particle and cell moves (volume, shear, stretch)

- **Total Enthalpy Hamiltonian Monte Carlo (TE-HMC)**
  short constant total energy MD trajectories

- **Galilean Monte Carlo (GMC)**
  all-atoms moves, along straight lines between elastic collisions (reflect the velocities to redirect the sample to allowed phase space region)

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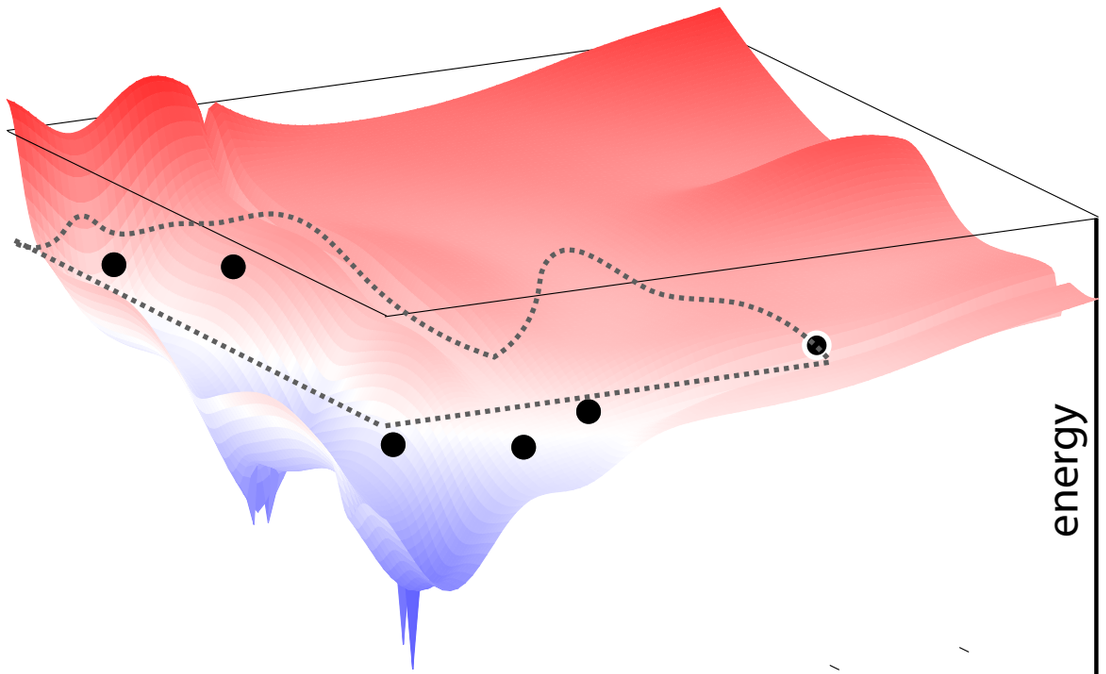

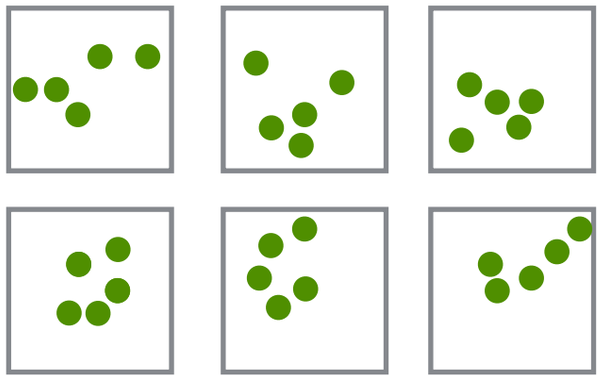

Choose the sample with the highest energy

Generate a new sample uniformly with E < Ei

Repeat this iteration many times…

at the i^{th} iteration the samples will have $E < E_i$ and phase space volume $\sim[K/(K+1)]^i$

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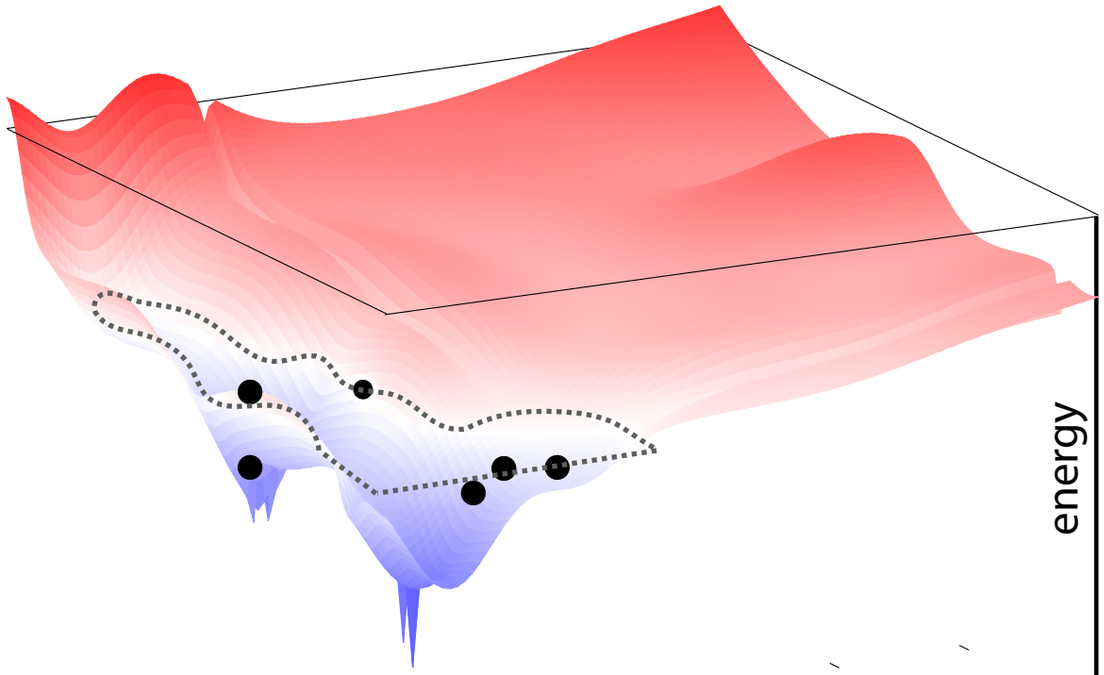

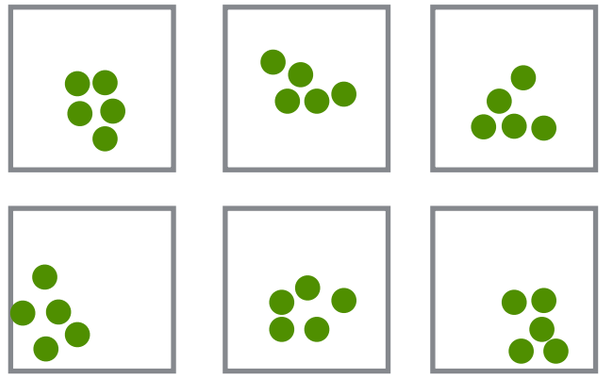

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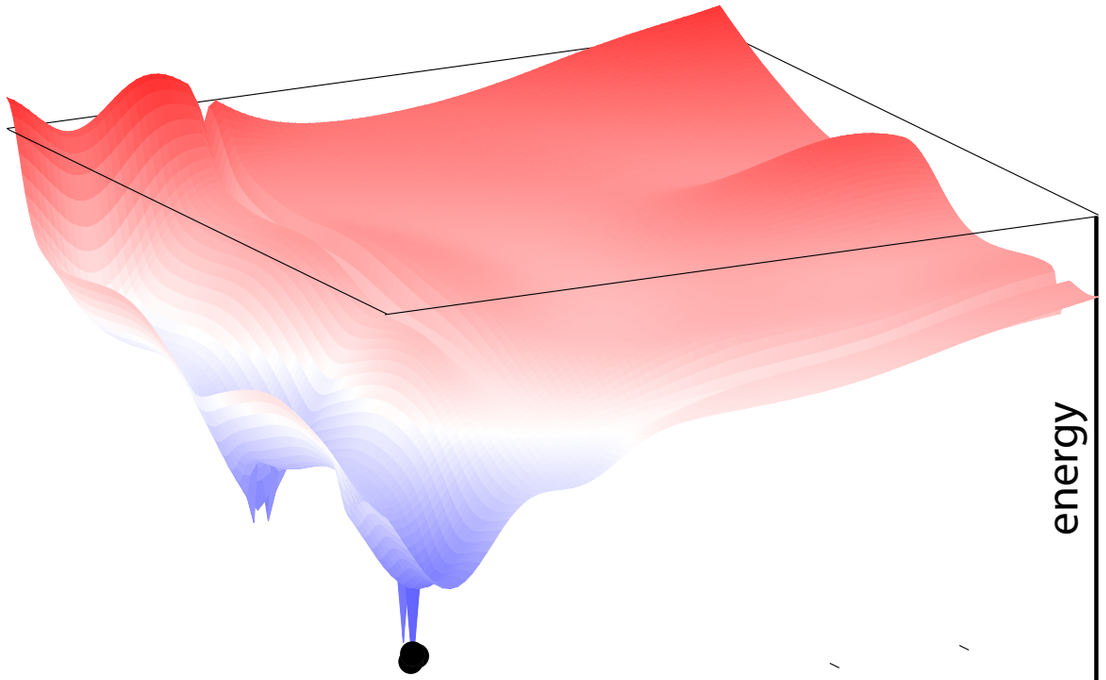

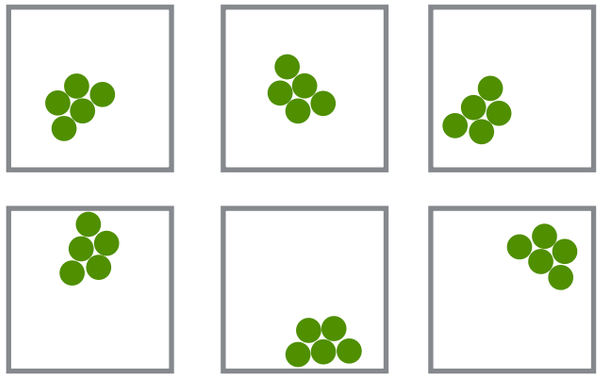

Repeat this iteration many times…

at the i^{th} iteration the samples will have $E < E_i$ and phase space volume $\sim[K/(K+1)]^i$

Until the “bottom” is reached.

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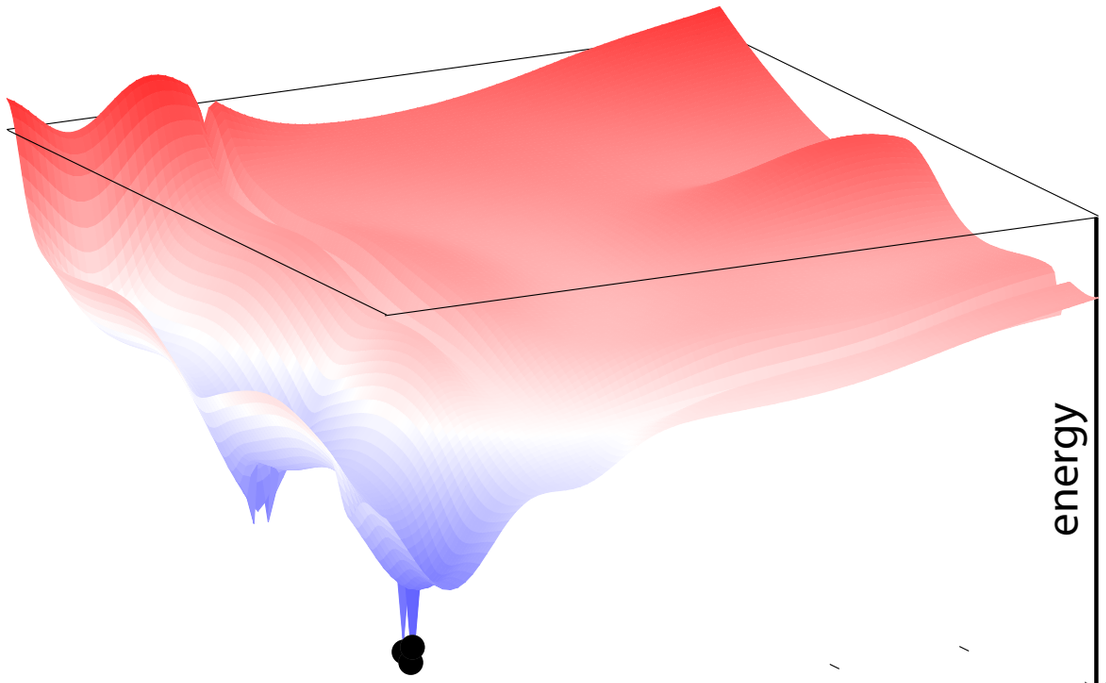

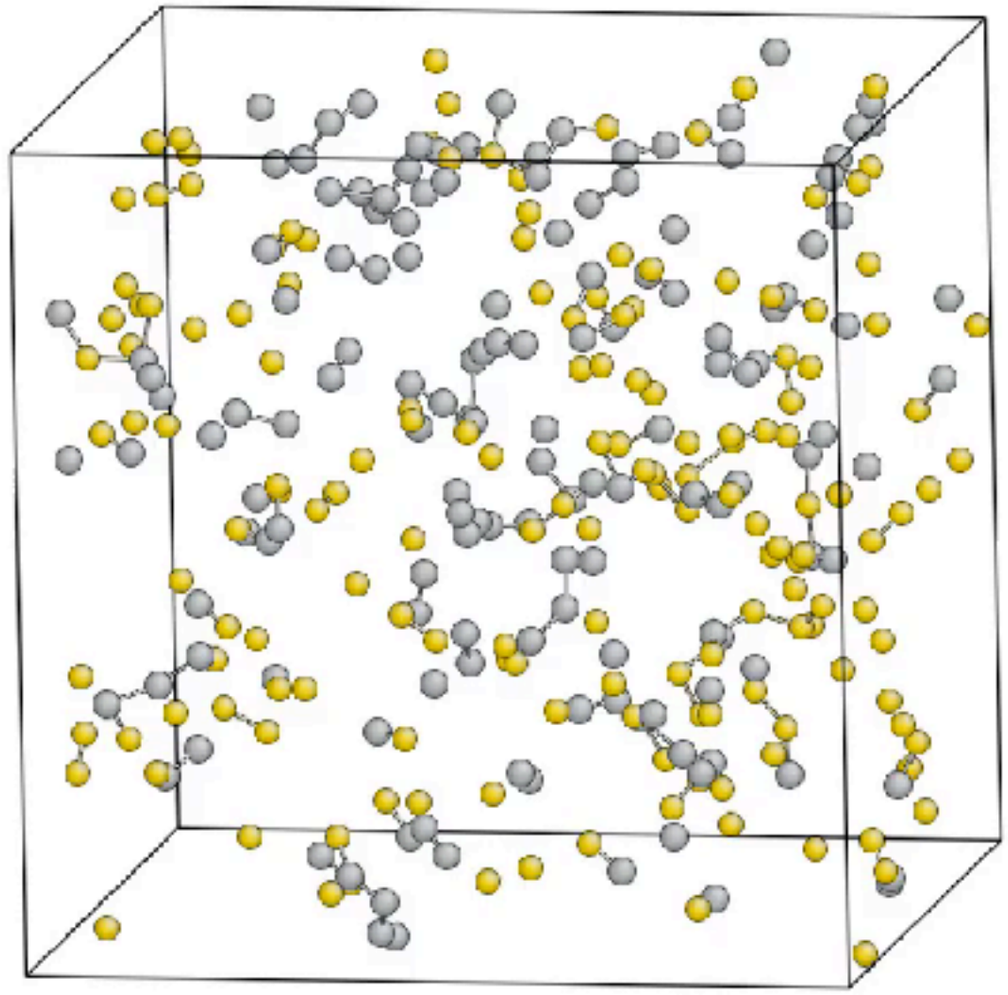

309 atoms (Cu and Pt) in fixed cell: cluster

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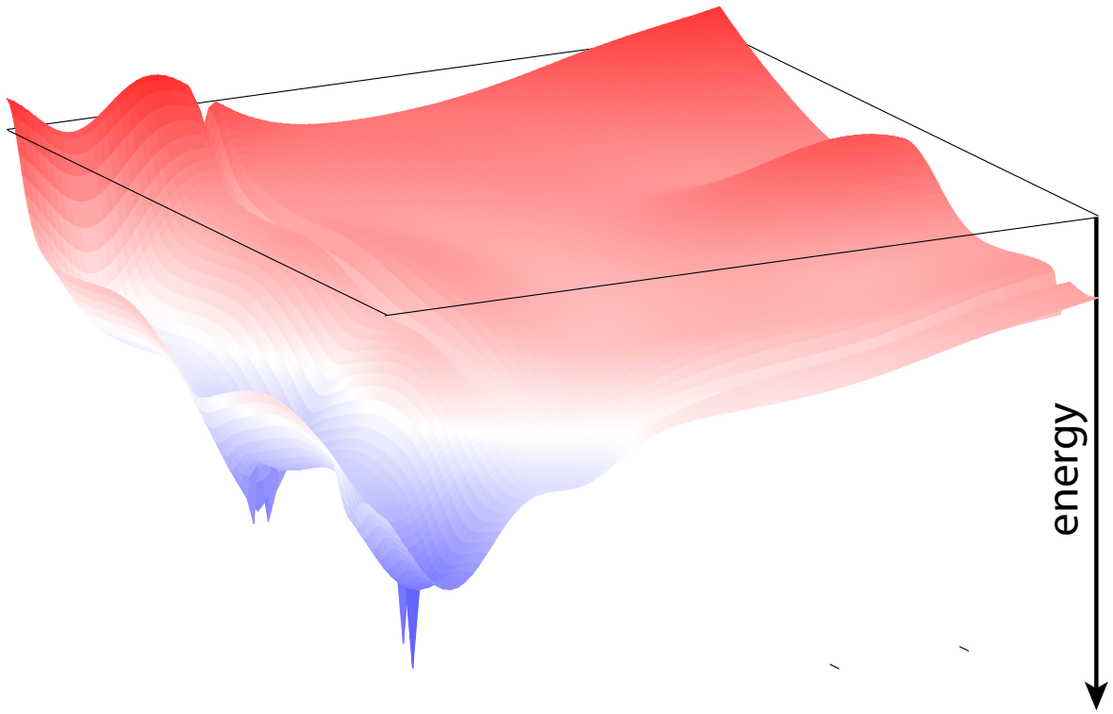


We have a set of $\{E_i\}$ and corresponding volumes $\{[K/(K+1)]^i\}$

$$
\begin{aligned}
Z(\beta) &= Z_{\mathbf{p}} \sum_i w_i e^{-\beta E_i} \\
&= Z_{\mathbf{p}}(\beta) \sum_i \left[(K/(K+1))^i - (K/(K+1))^{i+1} \right] e^{-\beta E_i}
\end{aligned}
$$

- Sampling itself independent from temperature
- Thermodynamic quantities as a simple post processing step

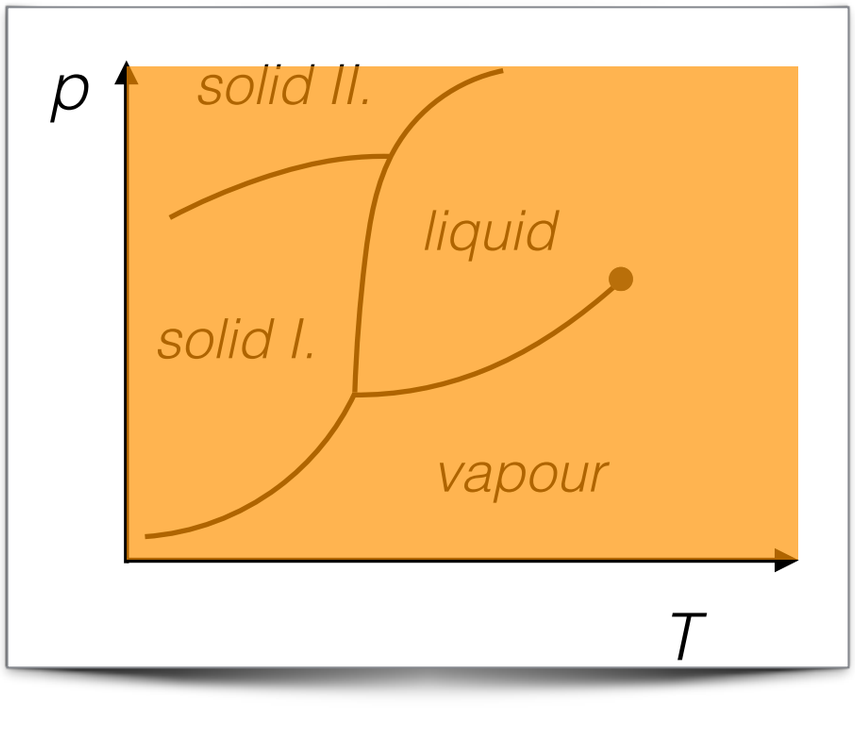
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = - \left(\frac{\partial}{\partial T} \frac{\partial \ln Z}{\partial \beta} \right)_V$$

- Easy control parameter of the sampling is *K*, called the “live set” ~ resolution of the PES
- No need for prior knowledge of the structures
- Can be done with both (N,p,T) and (N,V,T)

Calculating a *p*-*T* phase diagram

Methods specific for a given **part** of the phase diagram

- **Gibbs Ensemble MC**
- **coexistence simulations**
- **free energy comparison**
- **minima search**



Systematic exploration of the phase diagram

- **Wang-Landau sampling**
- **parallel tempering**

Nested Sampling

not specific: entire PES - entire phase diagram

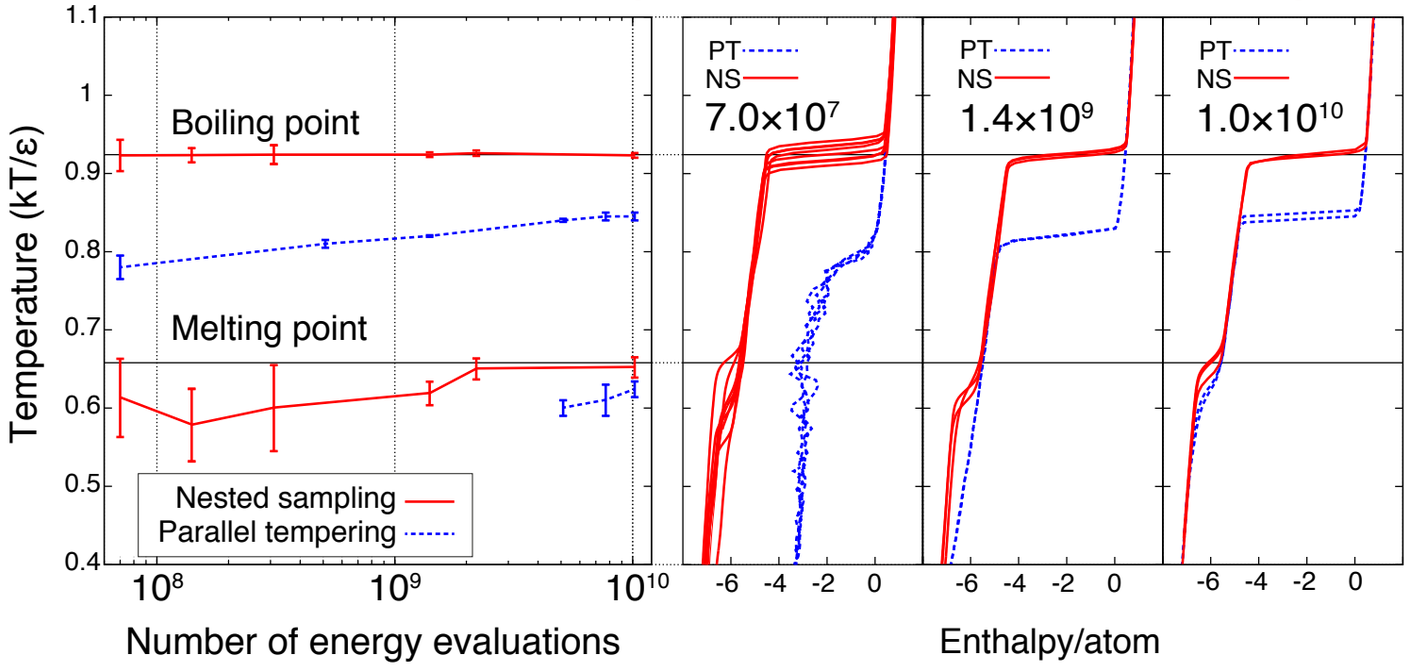
without prior knowledge of the structures

all thermodynamic quantities

can be used as “black box”

Computational cost comparison

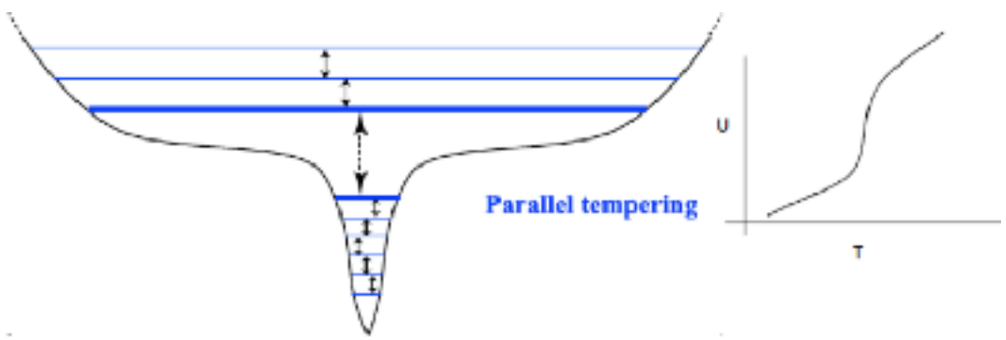
Nested Sampling vs. Parellel Tempering



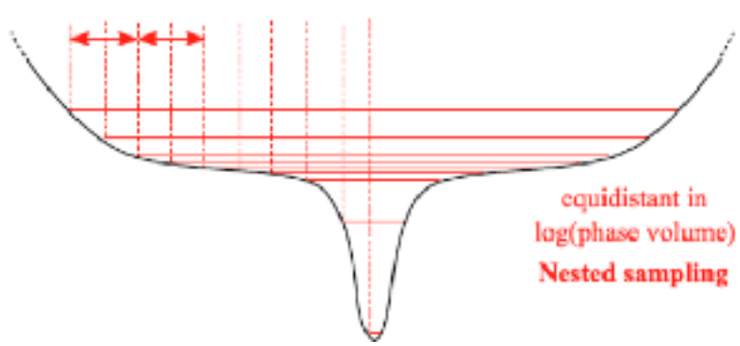
Systematic exploration of the phase diagram:

- Wang-Landau sampling
- parallel tempering

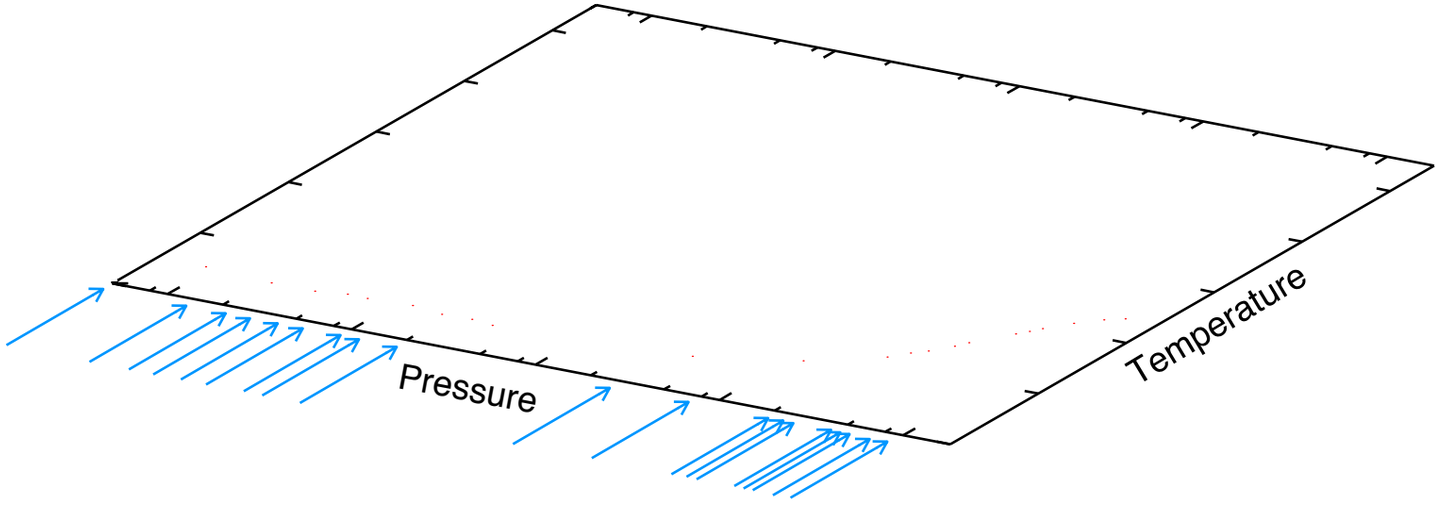
levels equidistant in temperature



levels equidistant in log(phase volume)

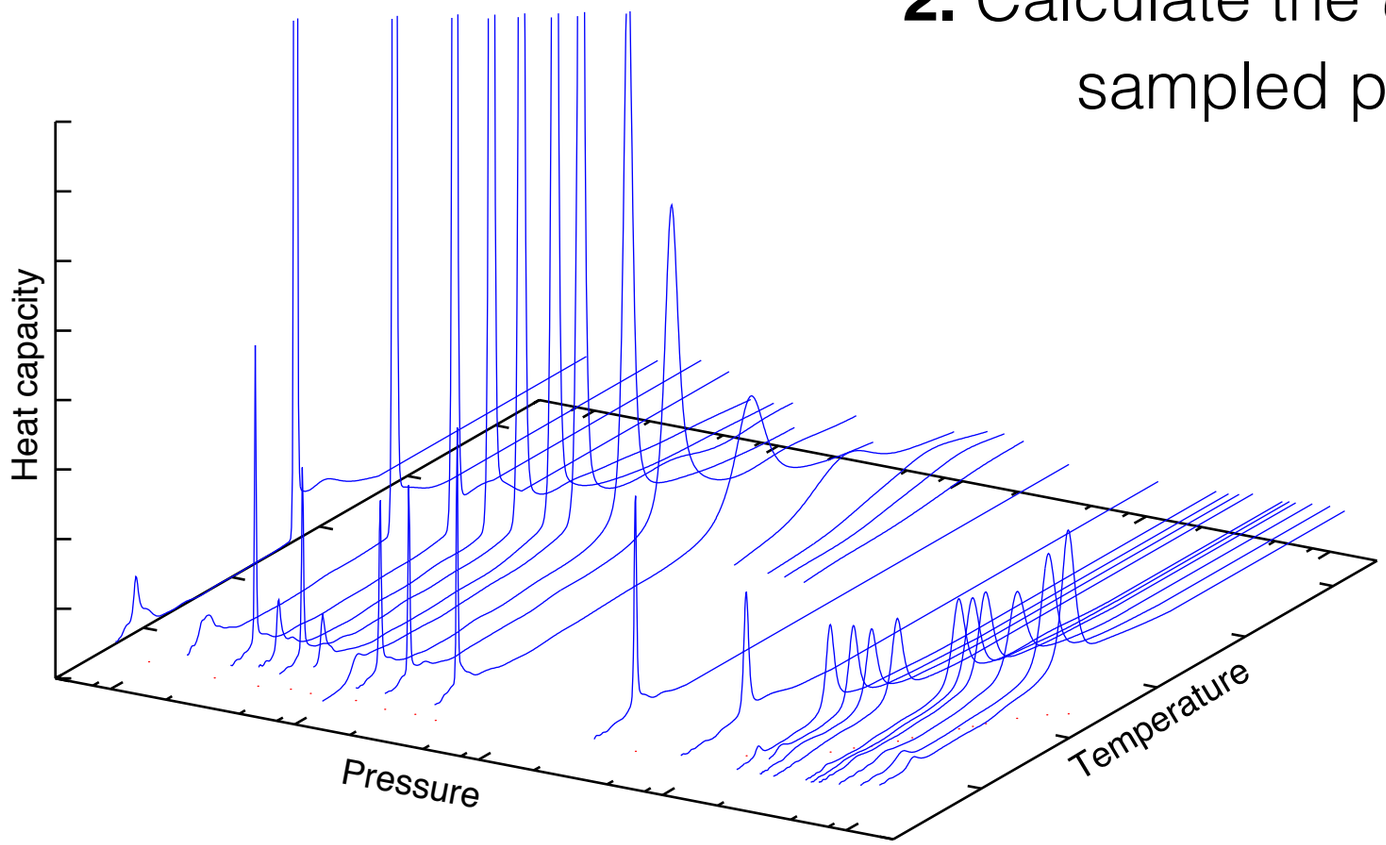


p-*T* phase diagram "in three steps"



1. Choose a system (potential model) and a set of pressures. Perform a *nested sampling* calculation for each.

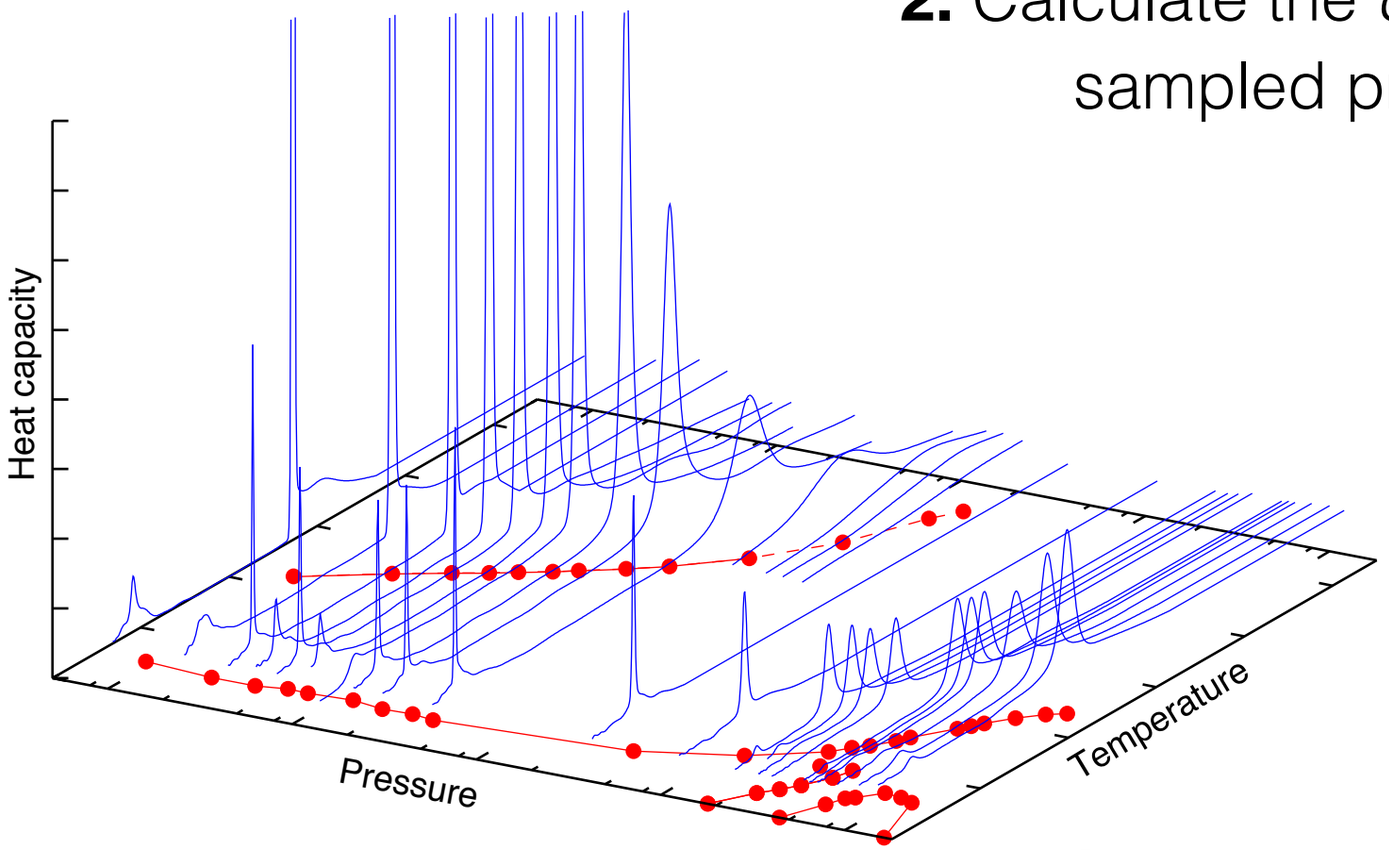
p-*T* phase diagram "in three steps"



2. Calculate the $c_p(T)$ for every sampled pressure.

1. Choose a system (potential model) and a set of pressures. Perform a *nested sampling* calculation for each.

p-*T* phase diagram "in three steps"



1. Choose a system (potential model) and a set of pressures. Perform a *nested sampling* calculation for each.

2. Calculate the $c_p(T)$ for every sampled pressure.

3. Determine the location of maxima on the $c_p(T)$ curve, showing the phase transitions.

p-*T* phase diagram!

Phase Diagram of Aluminium

Embedded atom model by Ercolessi and Adams
64 Al atoms in a simulation cell with variable size and shape

Al

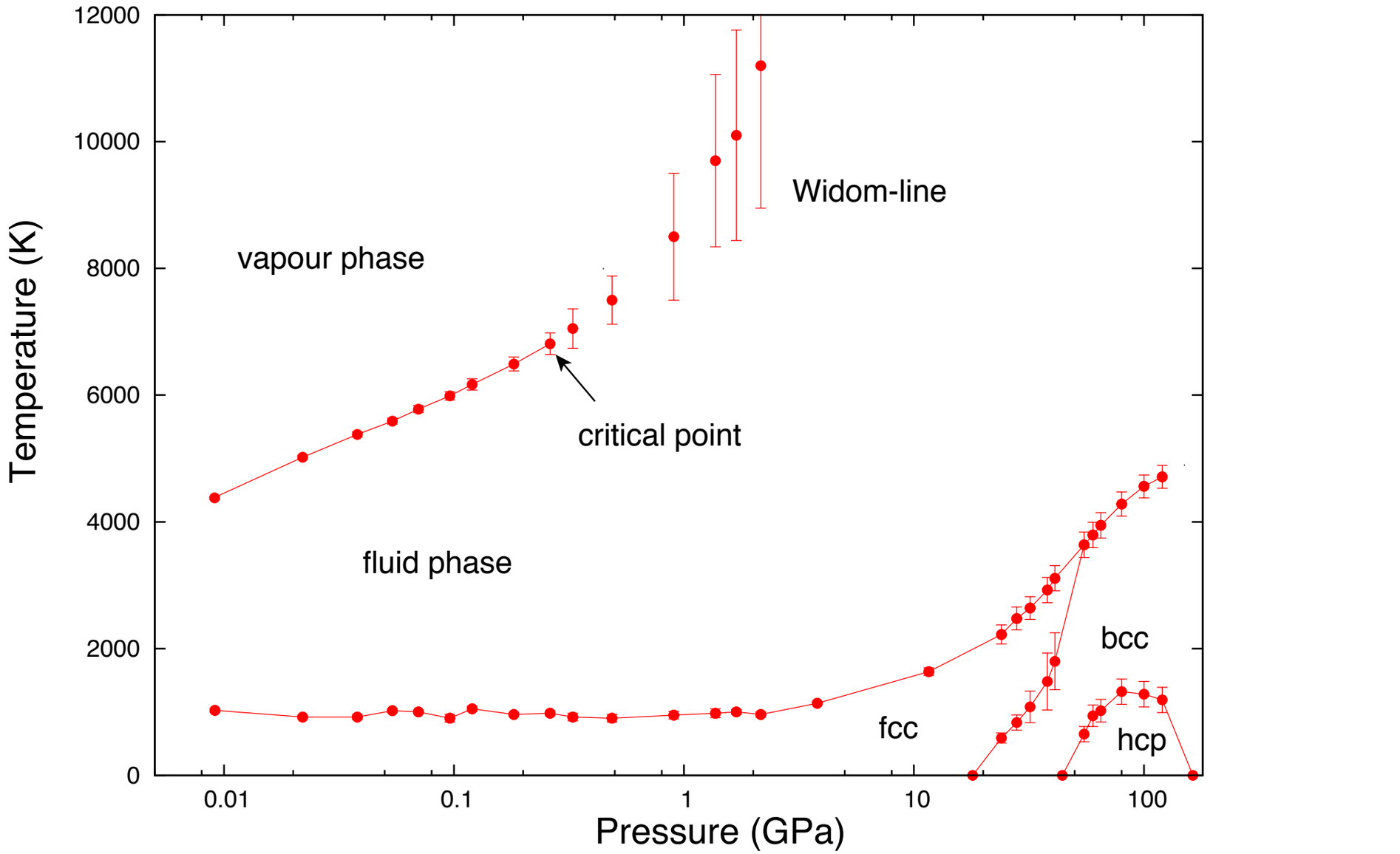
water

BLJ

NiTi

clusters

molecules



Phase Diagram of Aluminium

Al

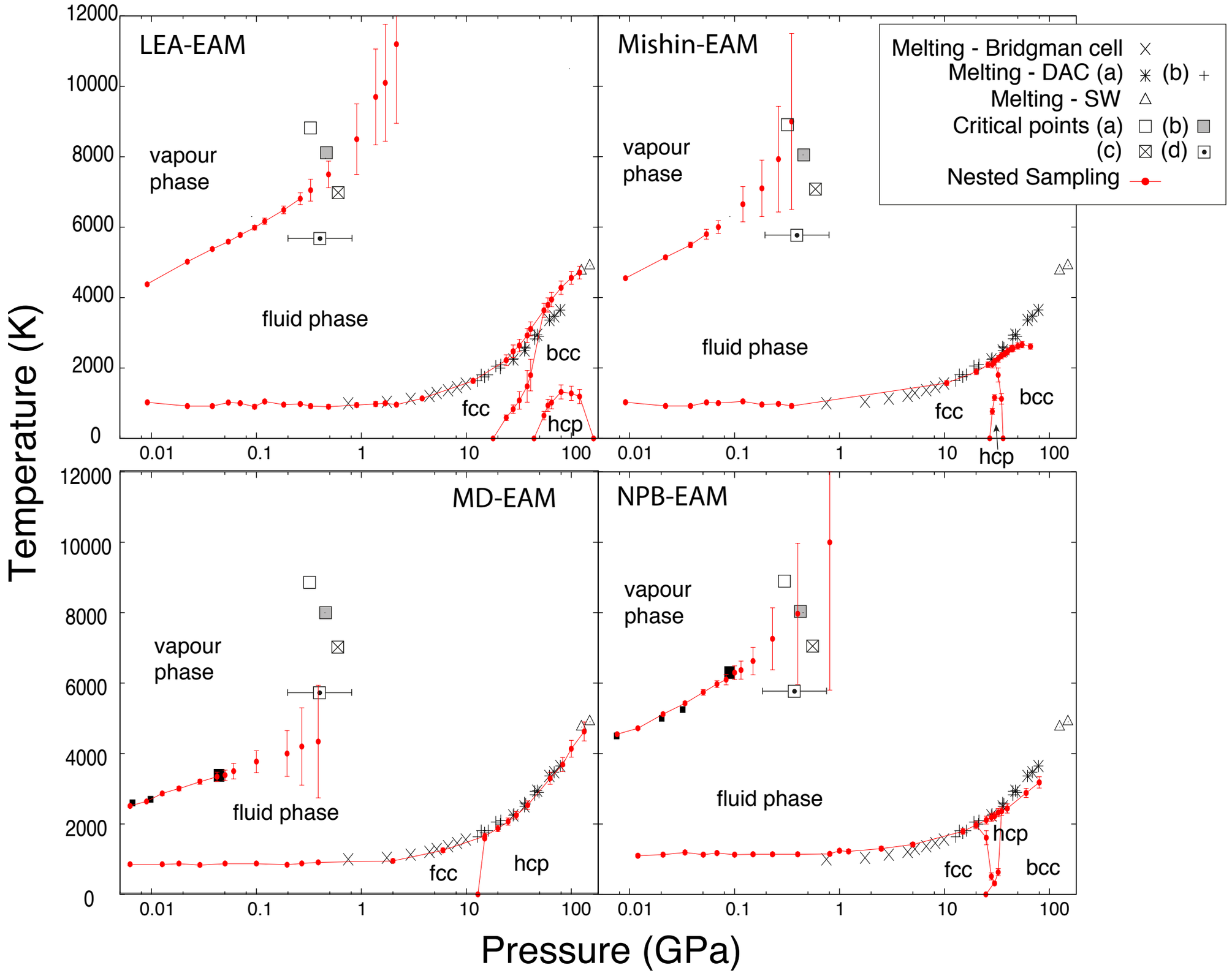
water

BLJ

NiTi

clusters

molecules



Al

water

BLJ

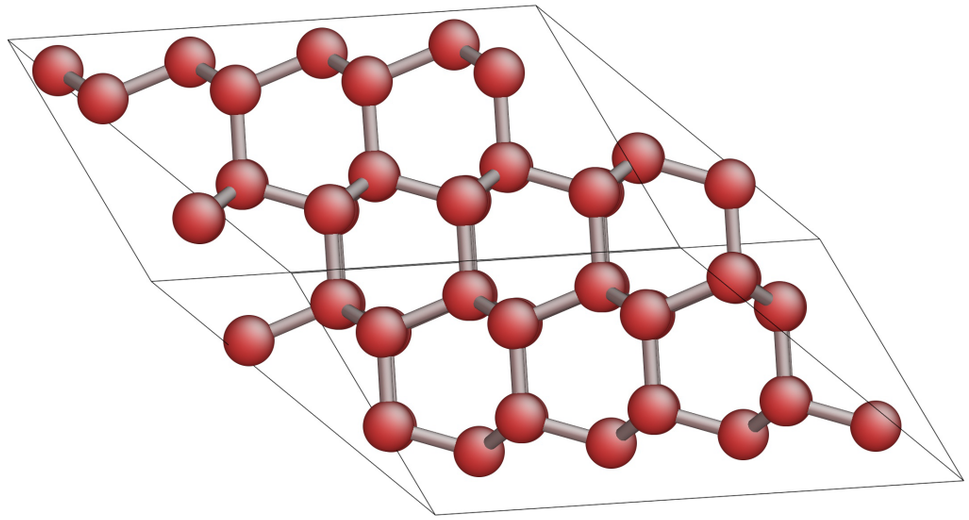
NiTi

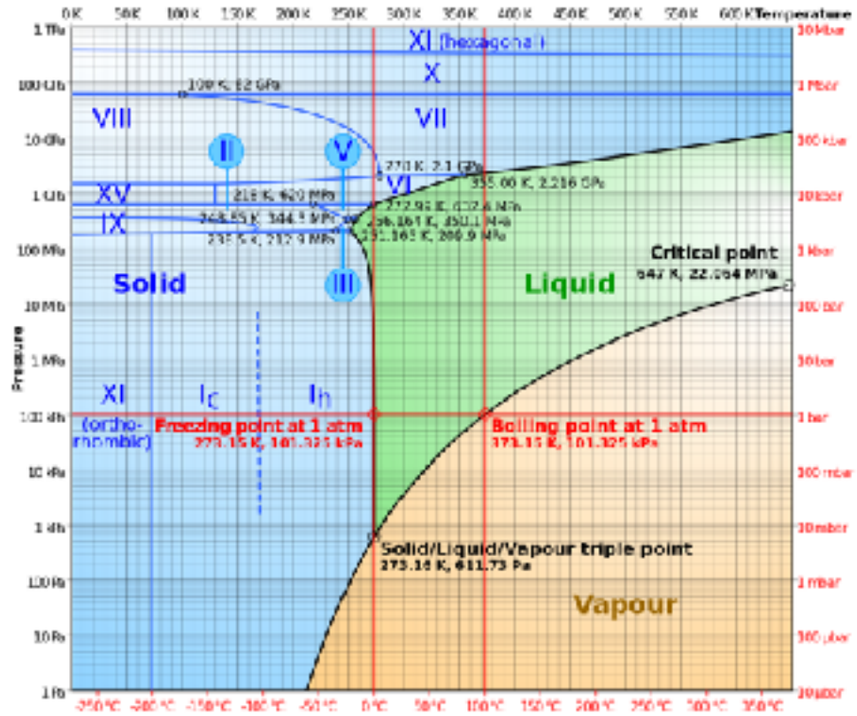
clusters

molecules

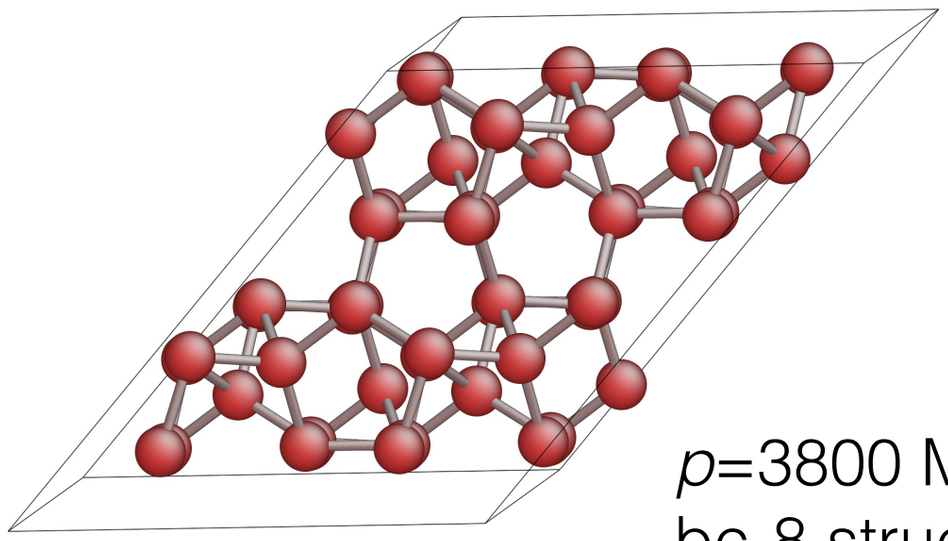
Phase behaviour of water

coarse grain water model: mW (re-parametrised Stillinger-Weber Si)
angular dependent term that encourages tetrahedral configurations





p=1.6 MPa
cubic diamond structure
hexagonal ice (Ih)



p=3800 MPa
bc-8 structure

Al

water

BLJ

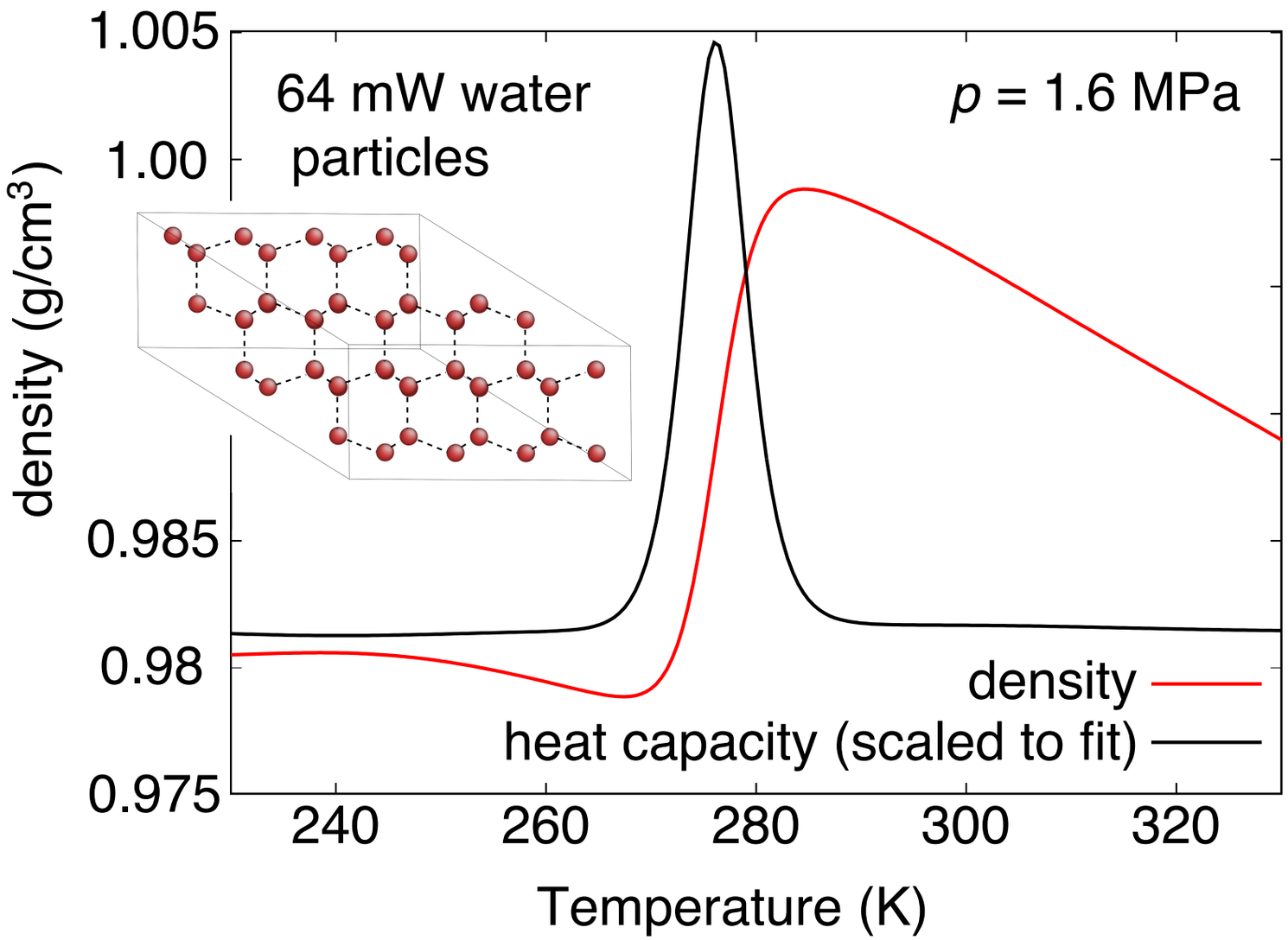
NiTi

clusters

molecules

Phase behaviour of water

coarse grain water model: mW
angular dependent term that encourages tetrahedral configurations



Al

water

BLJ

NiTi

clusters

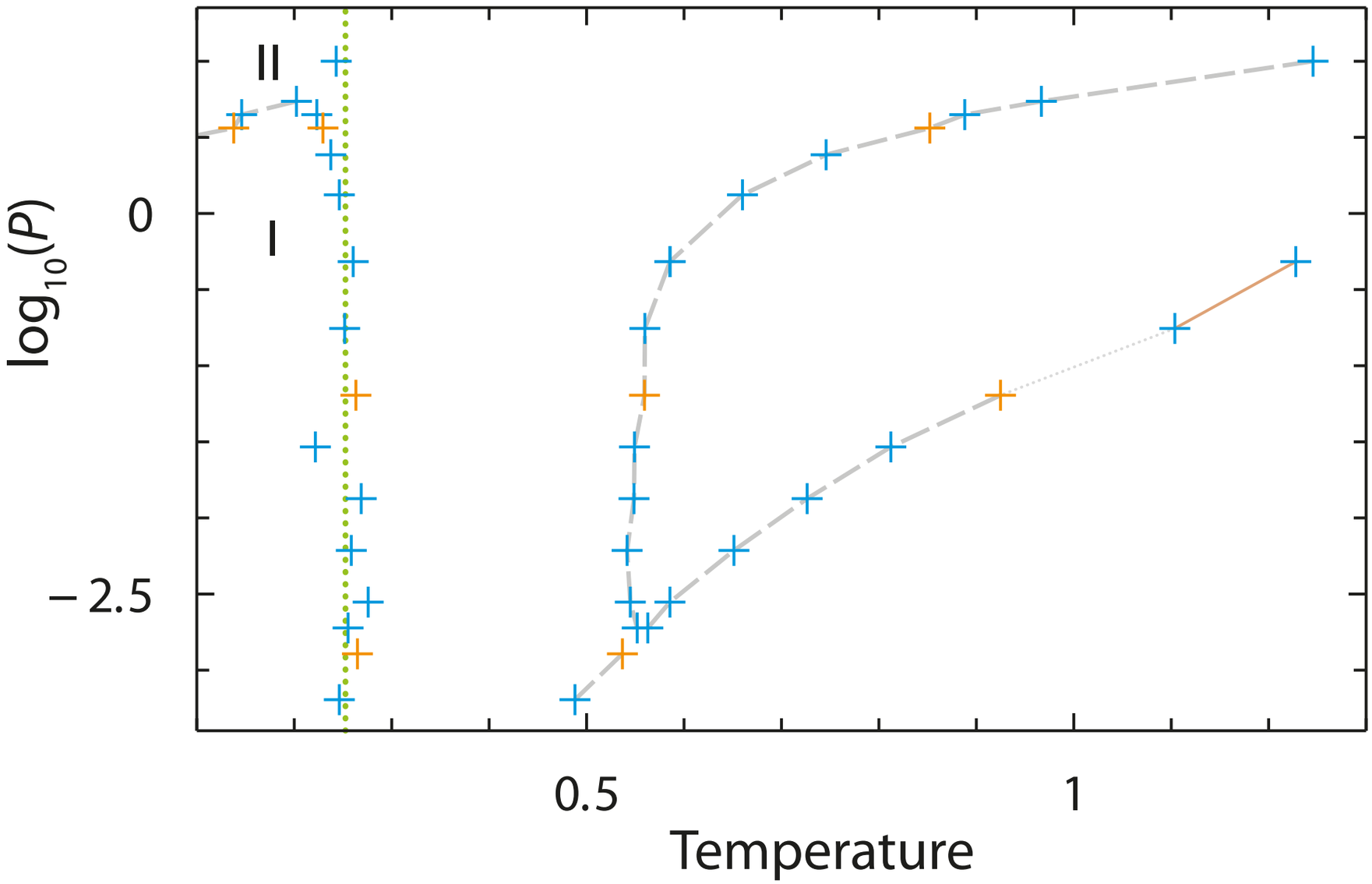
molecules

Binary Lennard-Jones

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

$\sigma_{AA}=\sigma_{AB}=\sigma_{BB}$ → same sizes

$\varepsilon_{AA}=\varepsilon_{BB}=0.5\varepsilon_{AB}$ → same type preference



Al

water

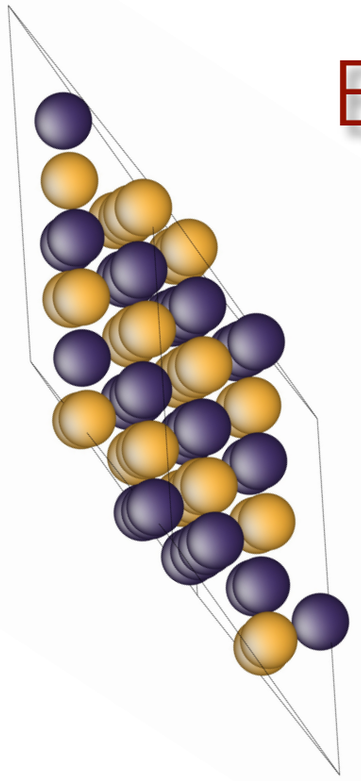
BLJ

NiTi

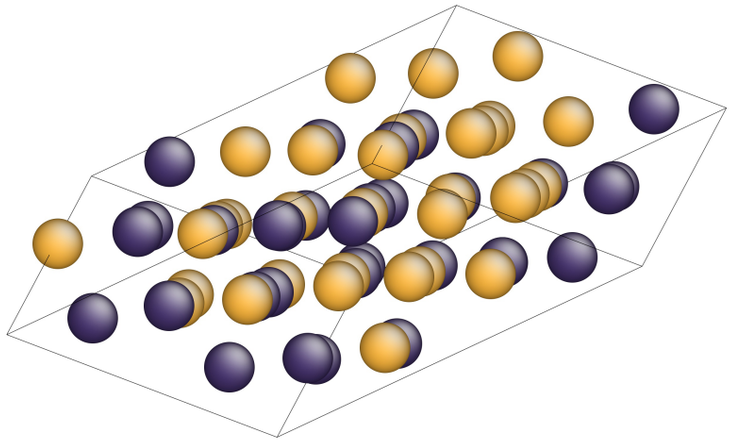
clusters

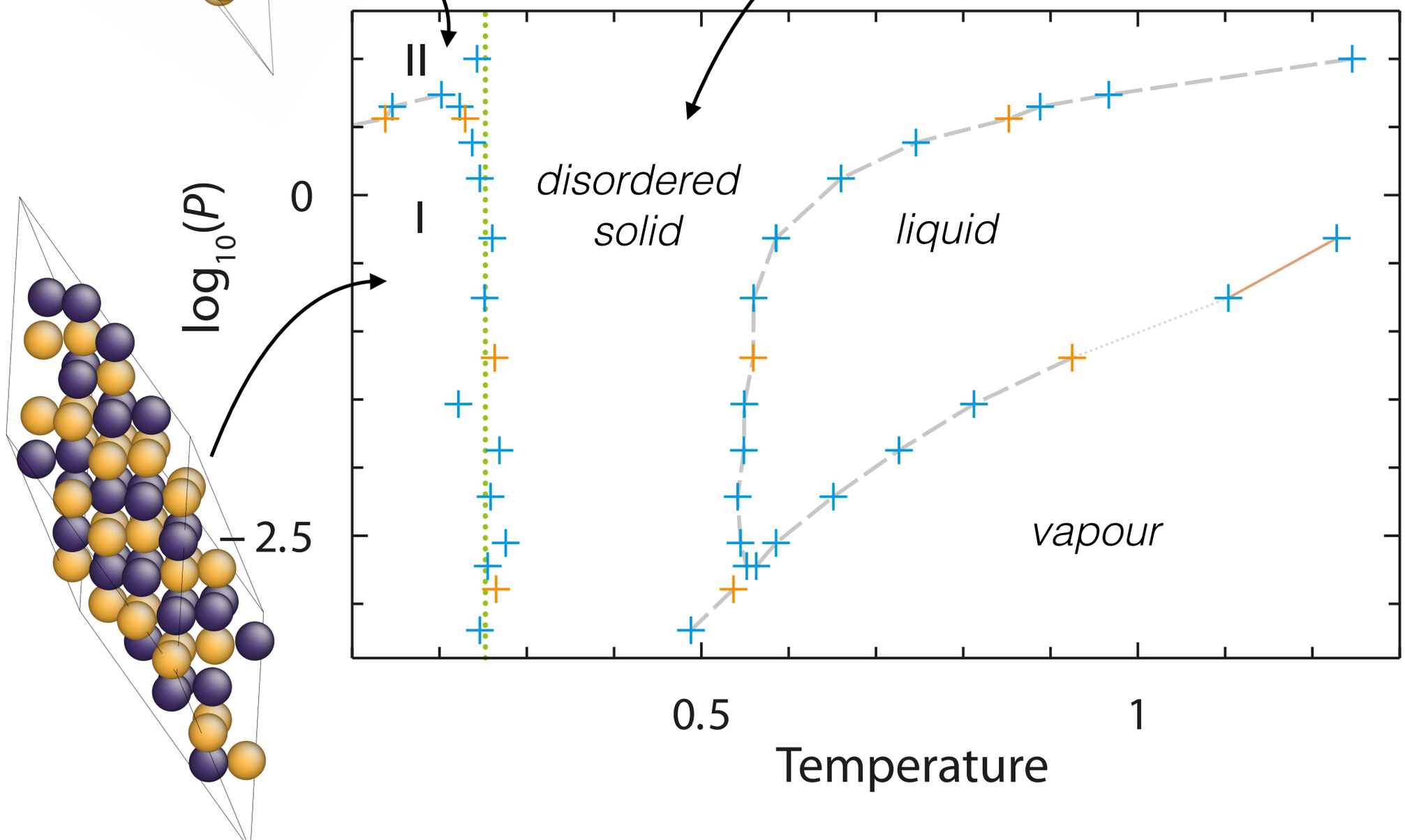
molecules

Binary Lennard-Jones



substitutional alloy, order-disorder transition





Al

water

BLJ

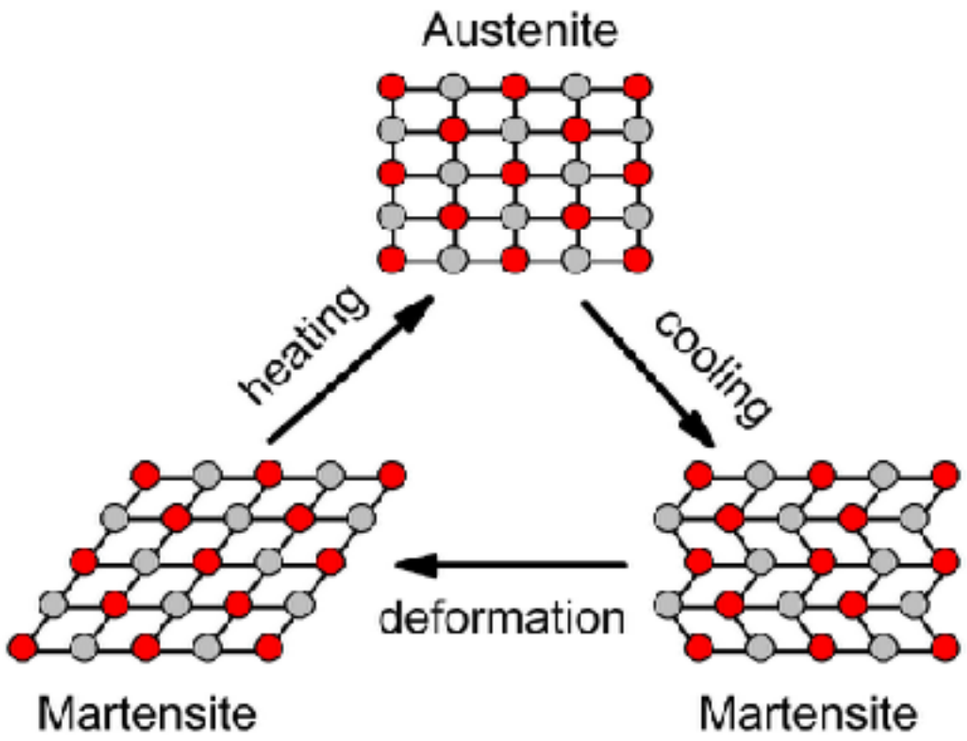
NiTi

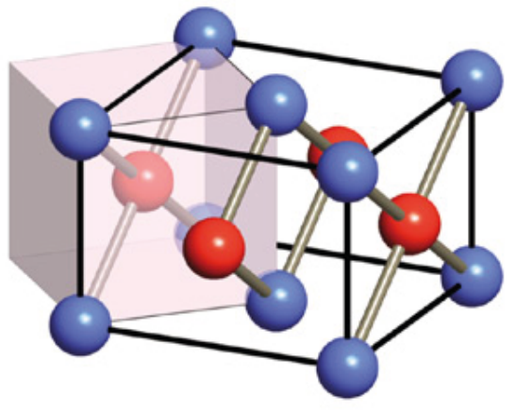
clusters

molecules

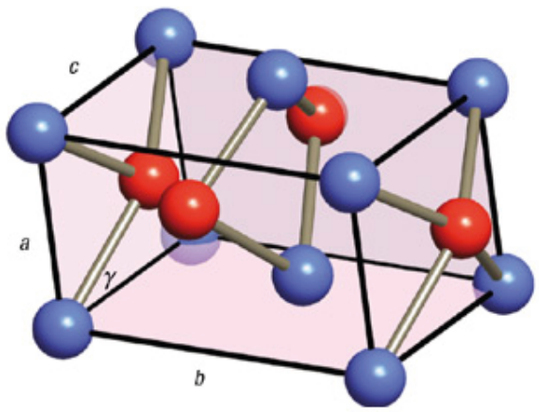
Martensitic Transition in NiTi alloys

shape memory alloy: “remembers” it’s original shape when deformed, and returns to it when heated





B2



B19’

(from Huang et.al. Nat.Mat.2003)

Al

water

BLJ

NiTi

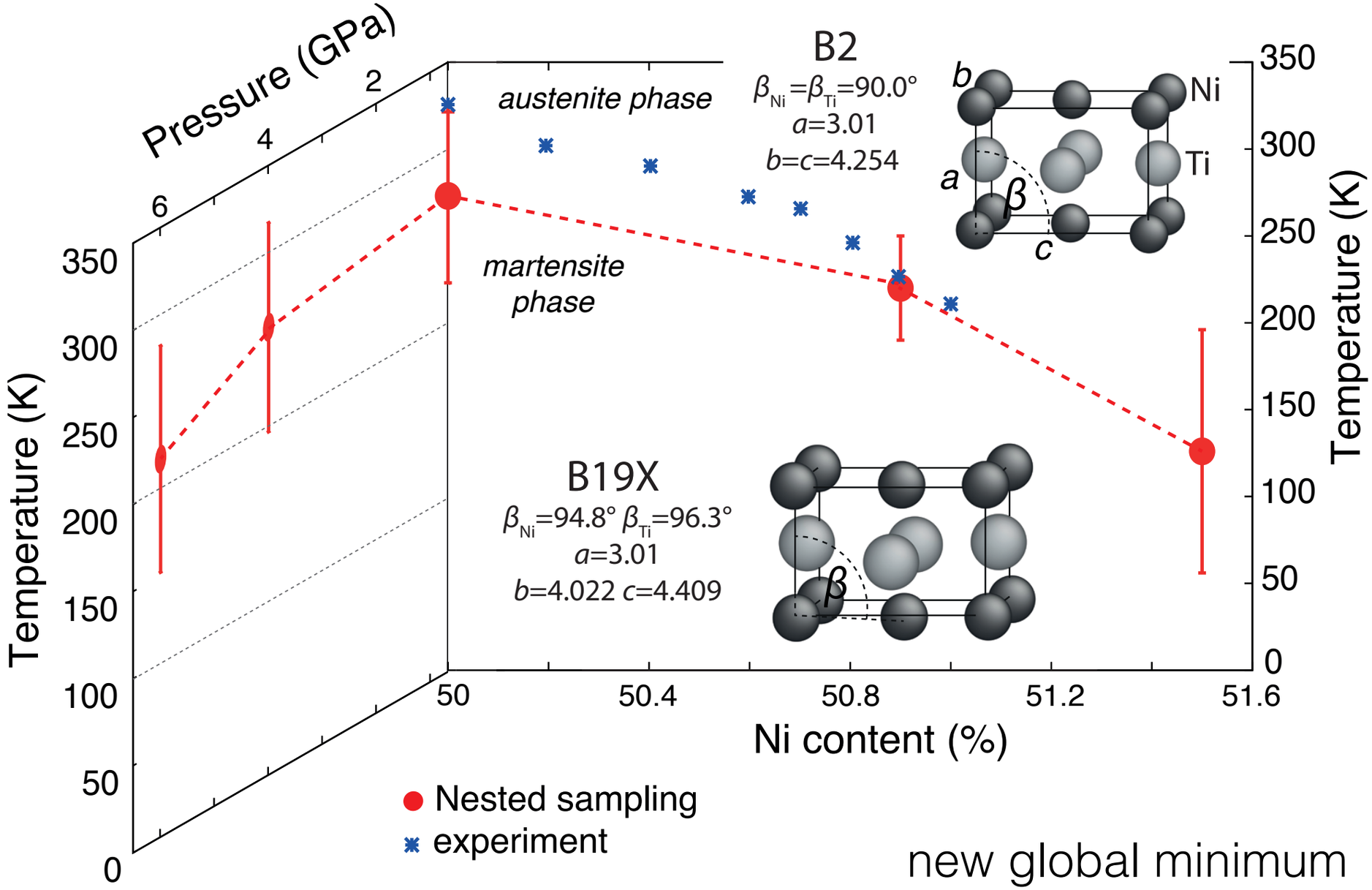
clusters

molecules

Martensitic Transition in NiTi alloys

pressure-temperature-composition phase diagram

Embedded atom model by Zhong et al.
64 and 108 atoms in a simulation cell with variable size and shape



new global minimum structure found!

Martensitic Transition in NiTi alloys

Al

water

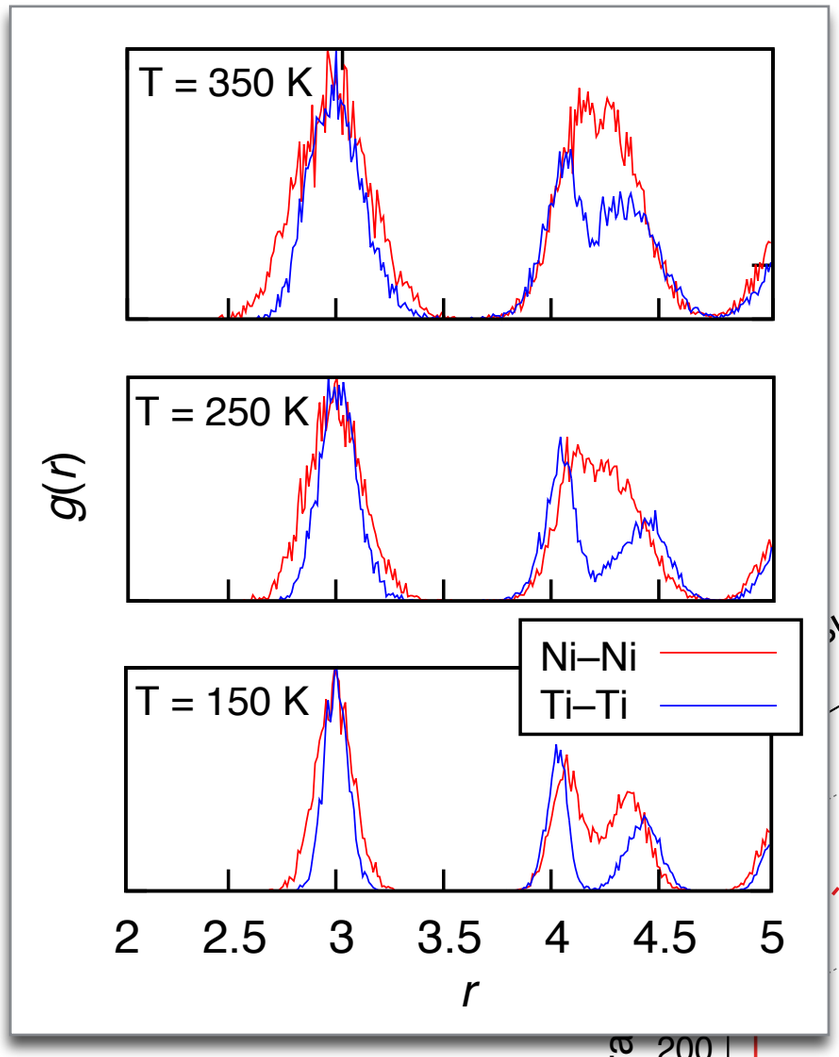
BLJ

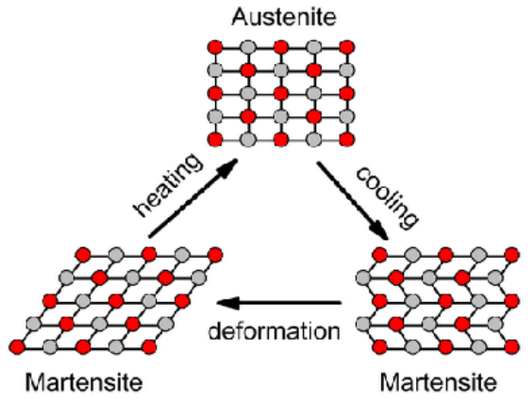
NiTi

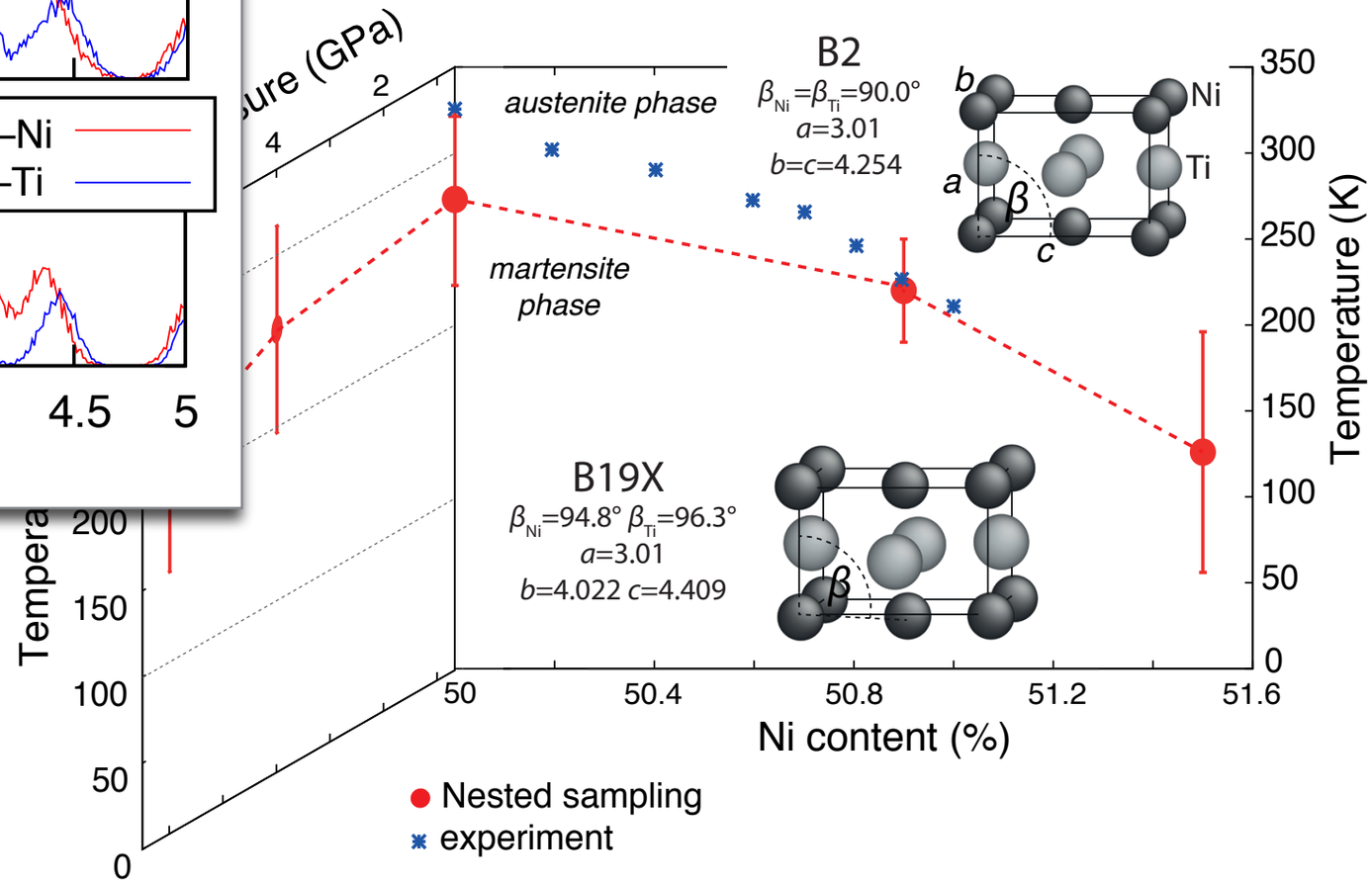
clusters

molecules

radial distribution function







Al

water

BLJ

NiTi

clusters

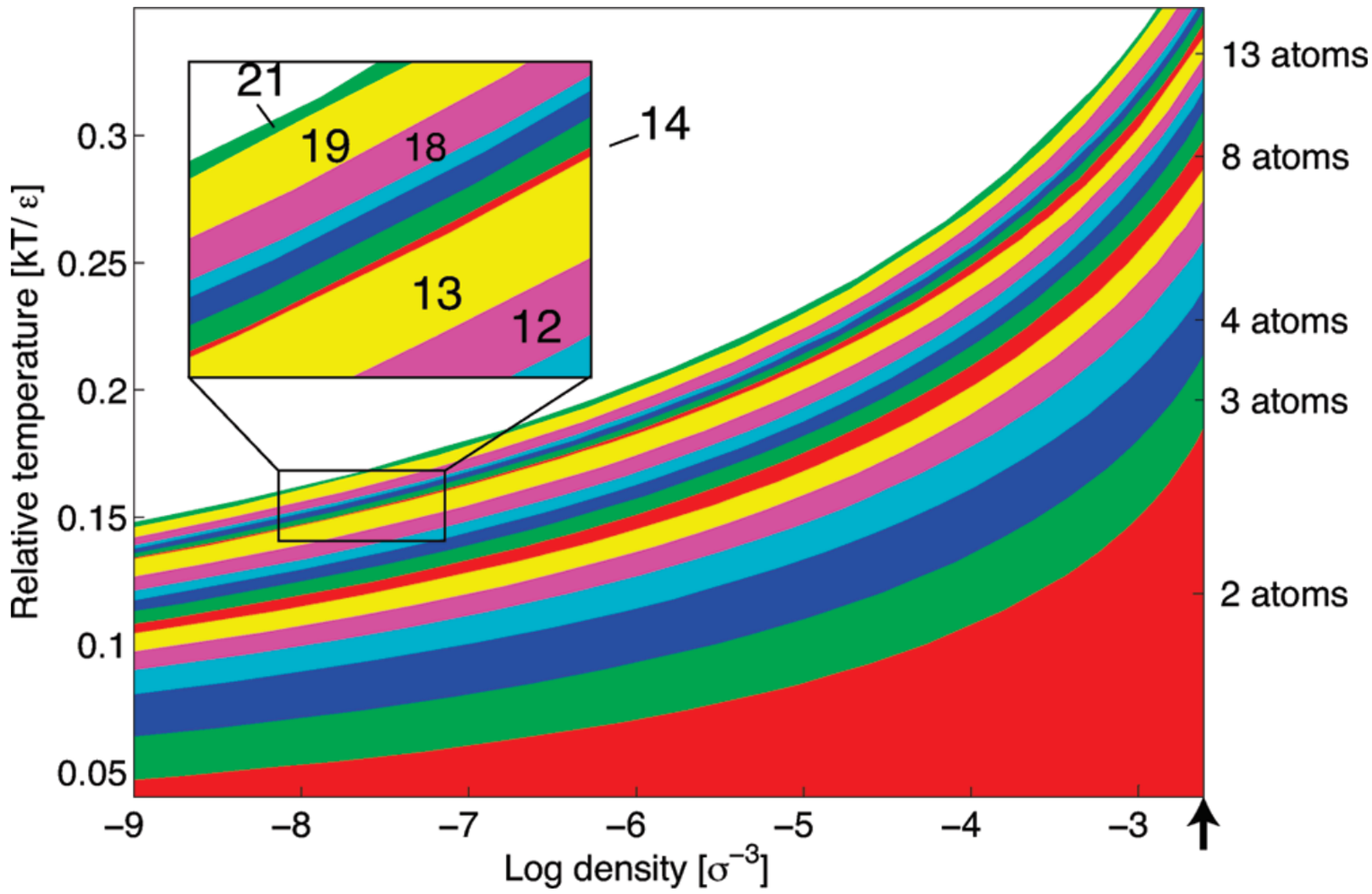
molecules

Lennard-Jones clusters

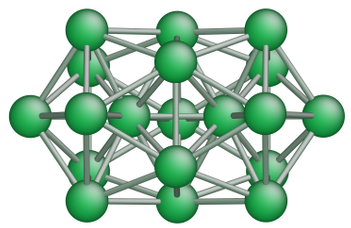
$$U_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Studied clusters from size LJ_2 to LJ_{38}

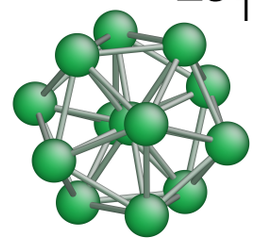
Stability of the Lennard-Jones clusters against the ideal gas



LJ_{19}



LJ_{13}



Al

water

BLJ

NiTi

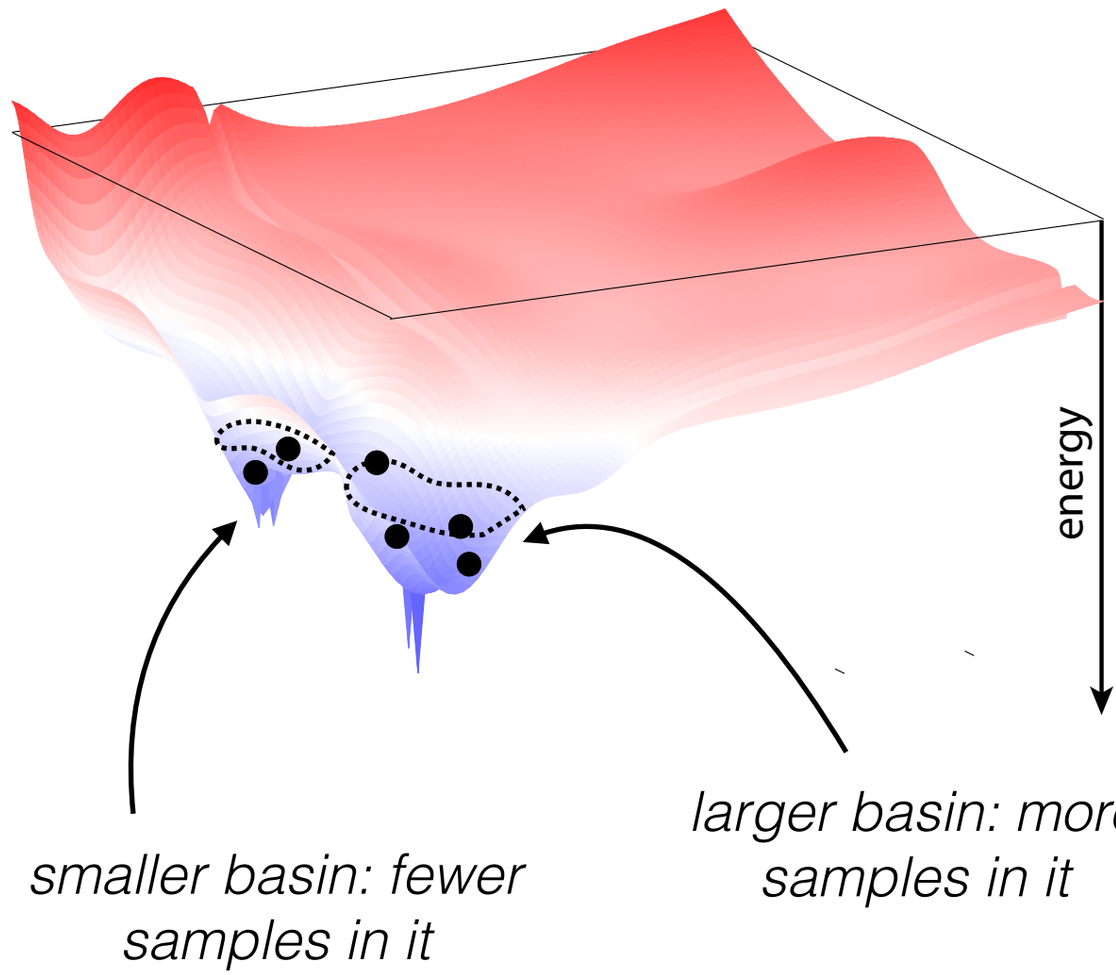
clusters

molecules

Lennard-Jones clusters: visualisation of PES

With a suitable metric categorise configurations and construct a graph

- identify different basins
- estimate saddle points
- sample distribution at a given energy level shows the relative phase space volume ratio of basins



smaller basin: fewer samples in it

larger basin: more samples in it

Al

water

BLJ

NiTi

clusters

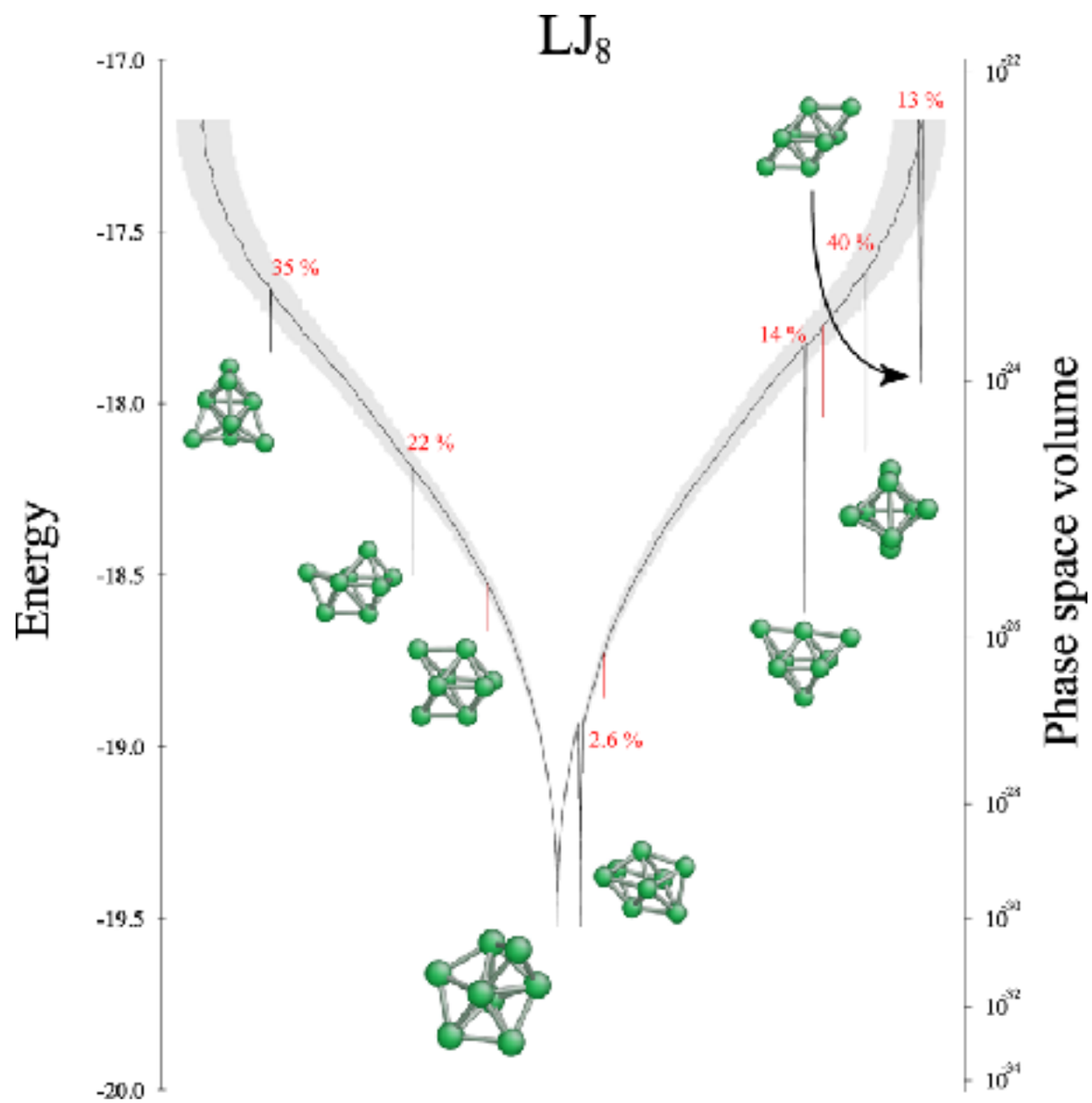
molecules

Lennard-Jones clusters: visualisation of PES

With a suitable metric categorise configurations and construct a graph

- identify different basins
- estimate saddle points
- sample distribution at a given energy level shows the relative phase space volume ratio of basins

Energy landscape chart



Al

water

BLJ

NiTi

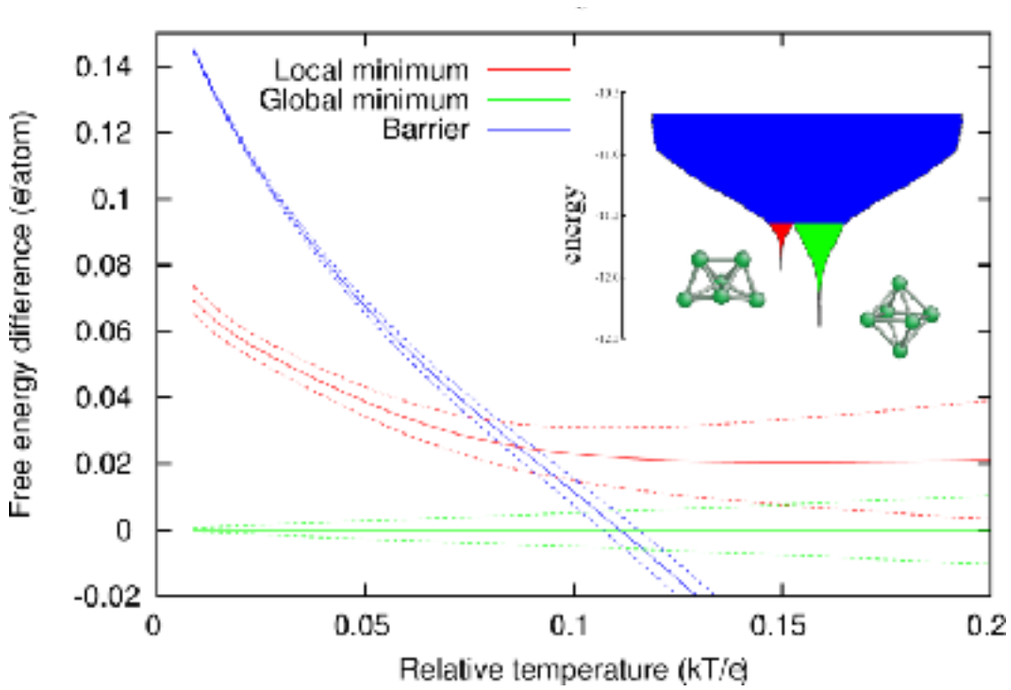
clusters

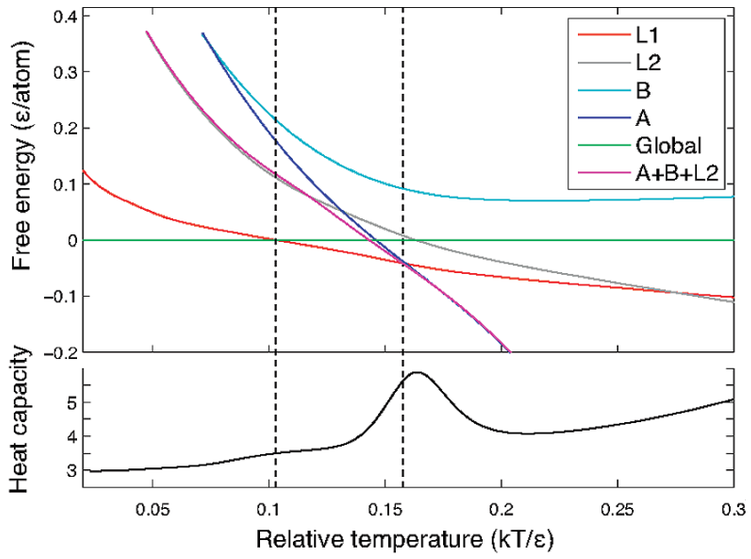
molecules

Lennard-Jones clusters

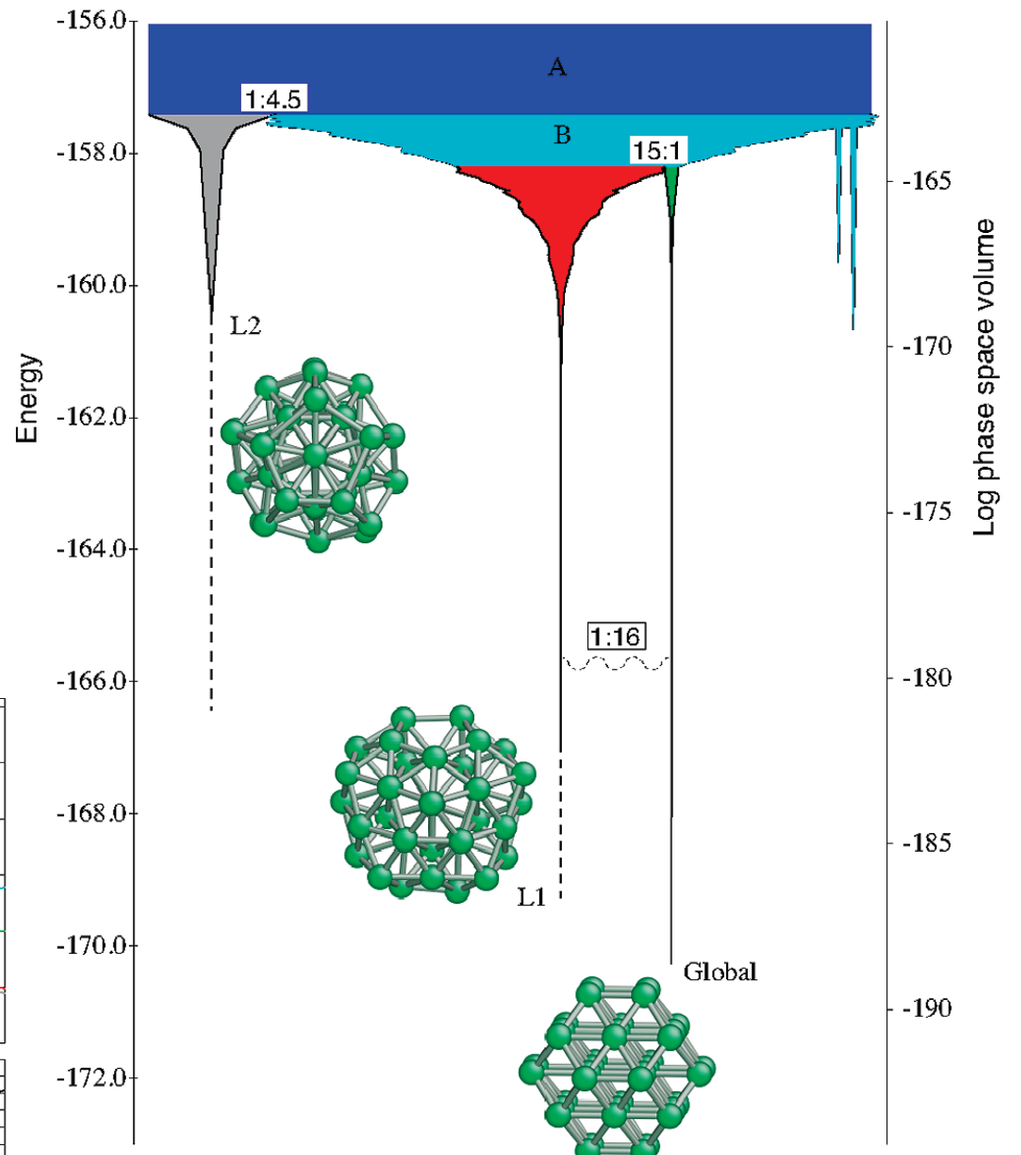
Using the landscape chart, calculate the free energy of the basins, determine the phase transitions without the need of externally defined order parameter.

LJ_6





LJ_{38}



Al

water

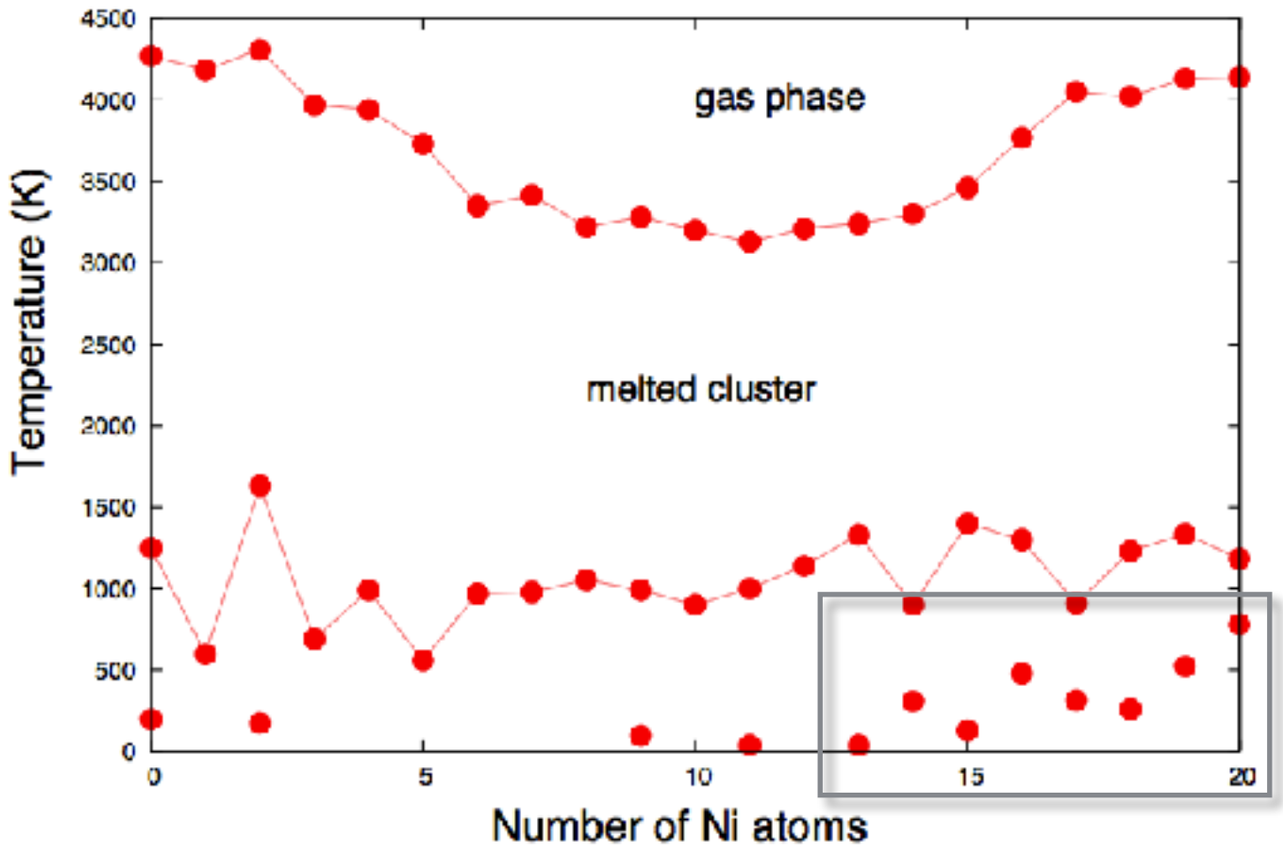
BLJ

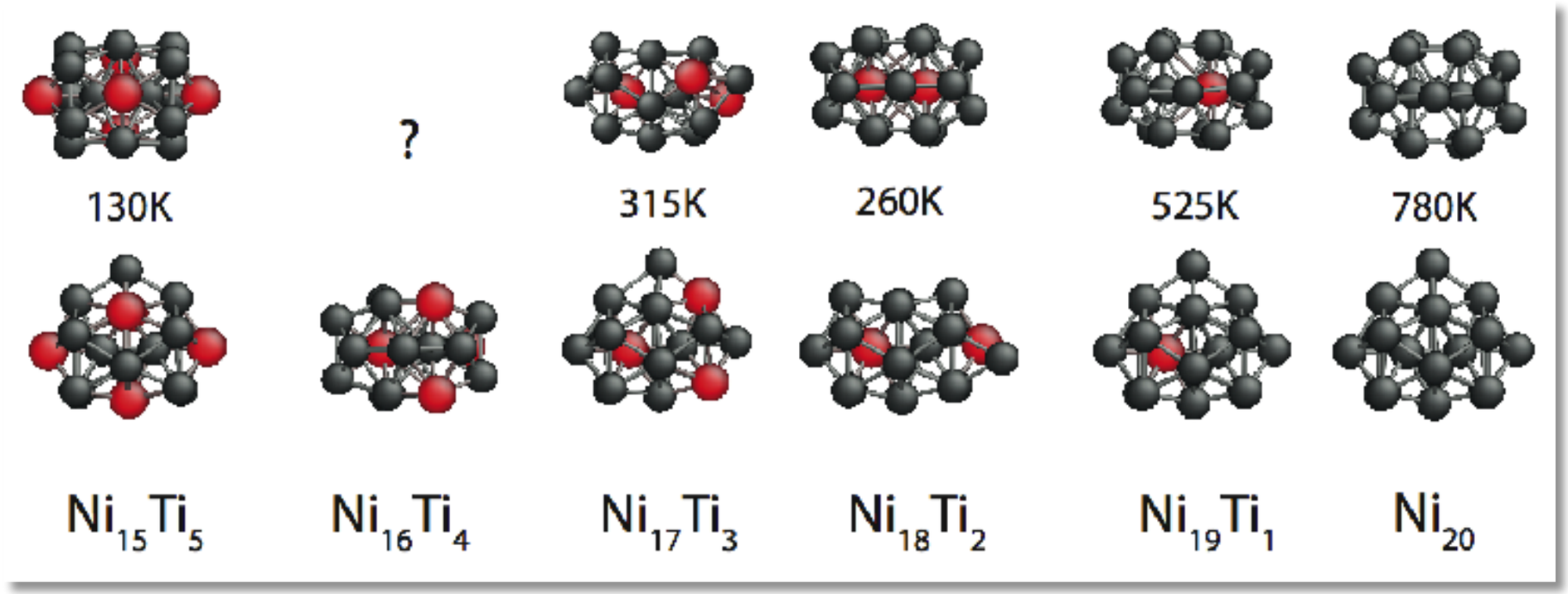
NiTi

clusters

molecules

Phase Diagram of Ni_xTi_y cluster

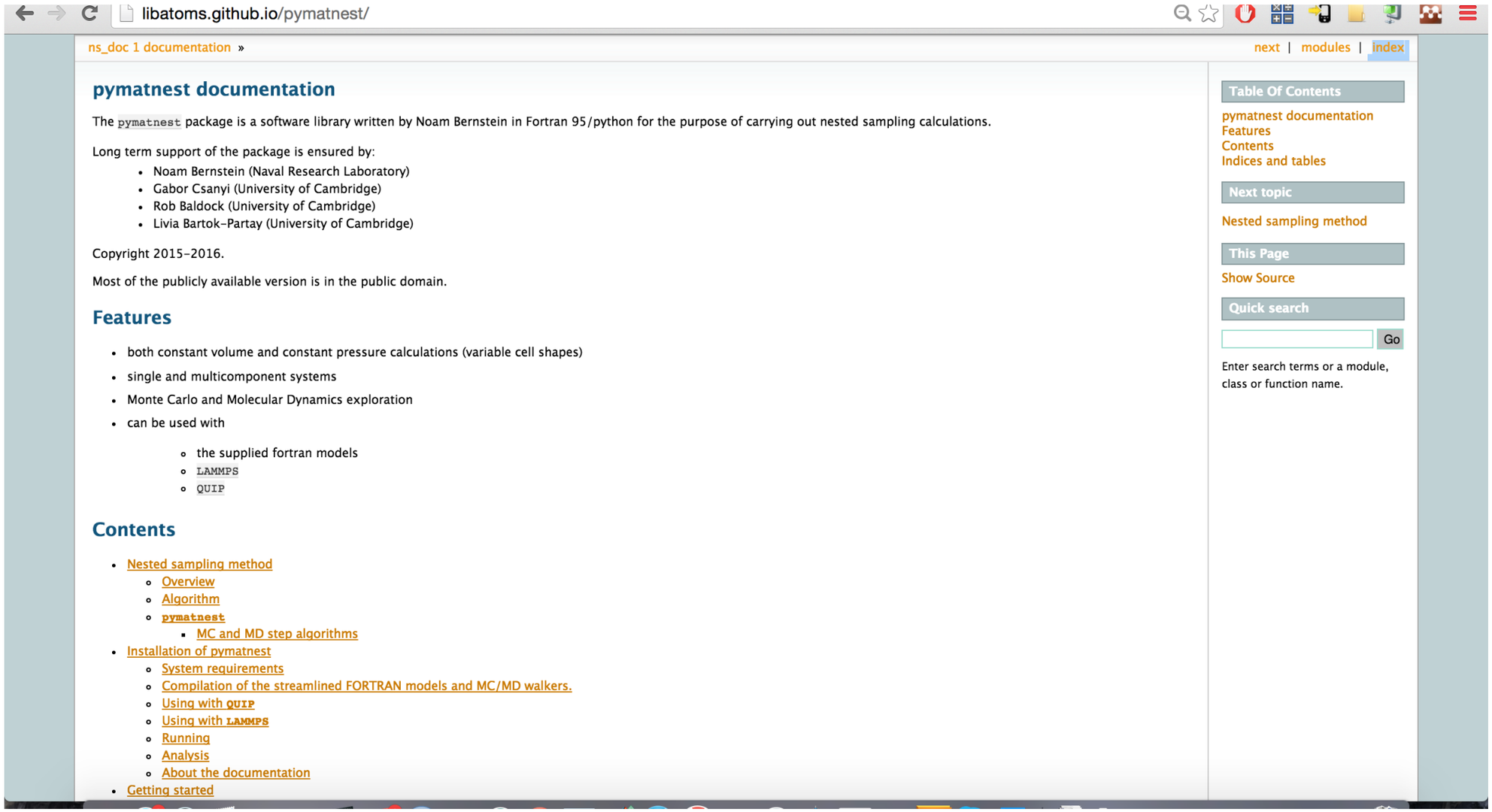




Code release - pymatnest

Python code with an interface to QUIP and LAMMPS

http://github.com/libAtoms/pymatnest
http://libatoms.github.io/pymatnest/



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Martin Schlegel (Cambridge)

St Catharine's College
Cambridge

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