Nested Sampling for computational thermodynamics

(how to calculate phase diagrams without the fuss)

Livia Bartók-Pártay

Department of Chemistry
University of Reading, UK

Nested Sampling

To have an unbiased sampling technique, that can be automated:

not specific to a give part of the PES, where no prior knowledge of structures are necessary.

- Nested sampling algorithm
- Calculate the phase diagram with nested sampling
    - metals, alloys
    - clusters
    - molecules
- Visualise the PES with nested sampling

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

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

Nested Sampling

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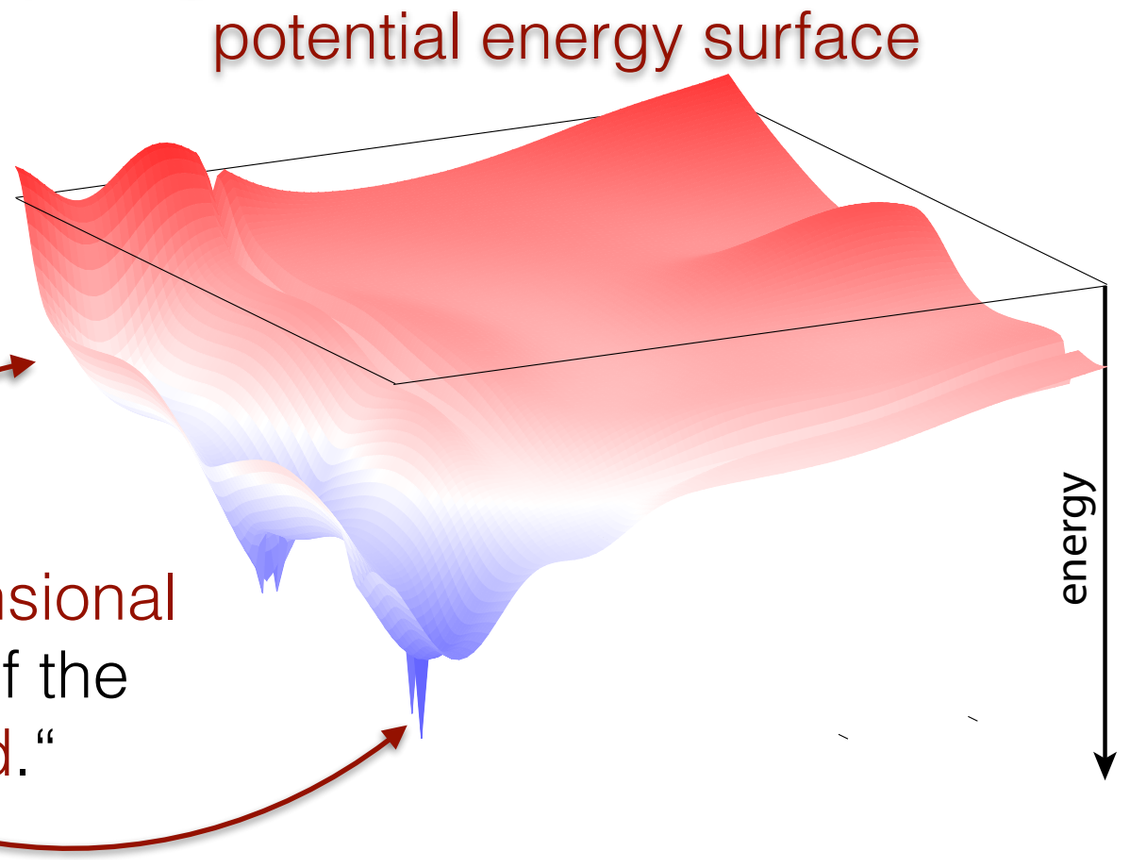


evidence (Z) likelihood (L) proportion of the prior distribution

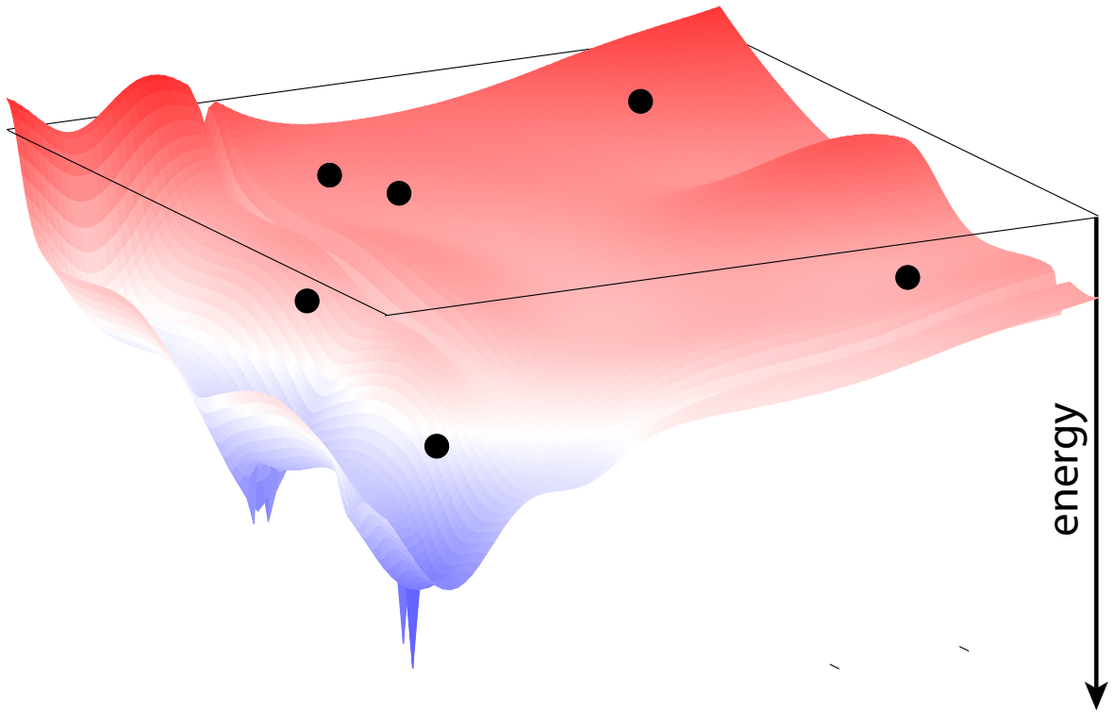
$$Z = \int_0^1 L(X)dX$$

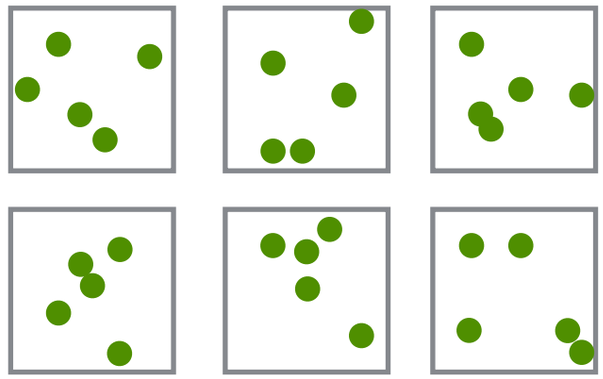
partition function Boltzmann-factor (energy) phase space volume (prior distribution is uniform)

Nested Sampling Algorithm

Iterative algorithm, starting from 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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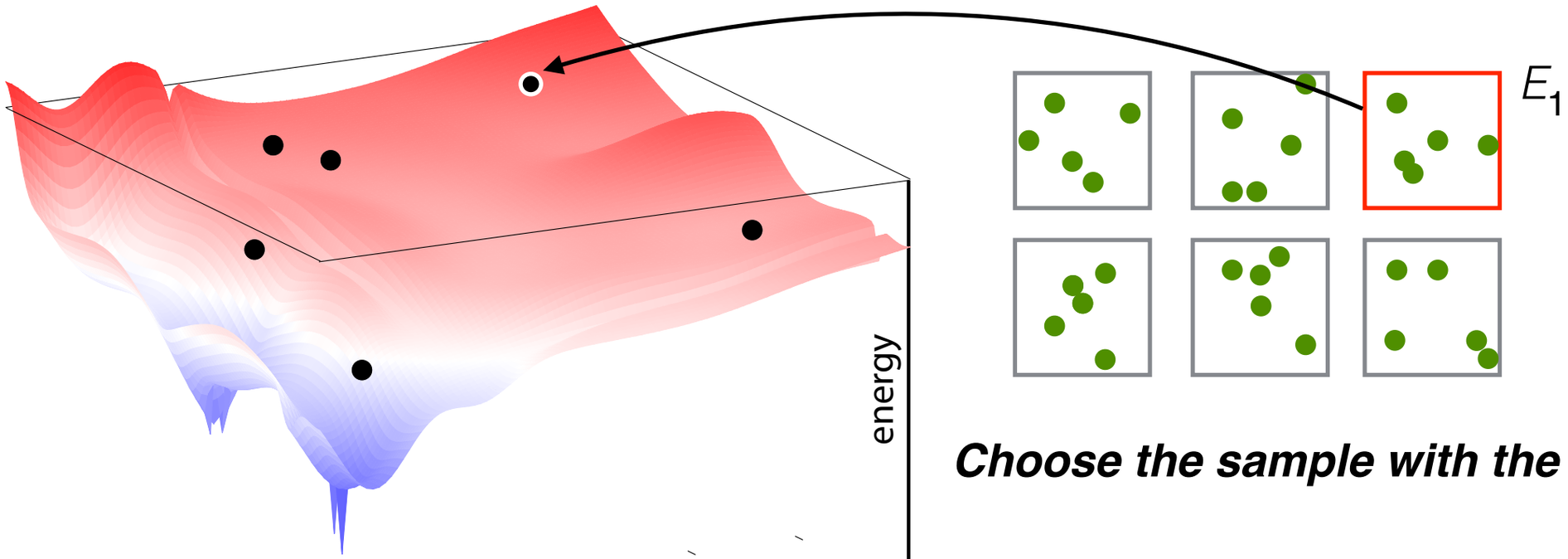

Choose the sample with the highest energy

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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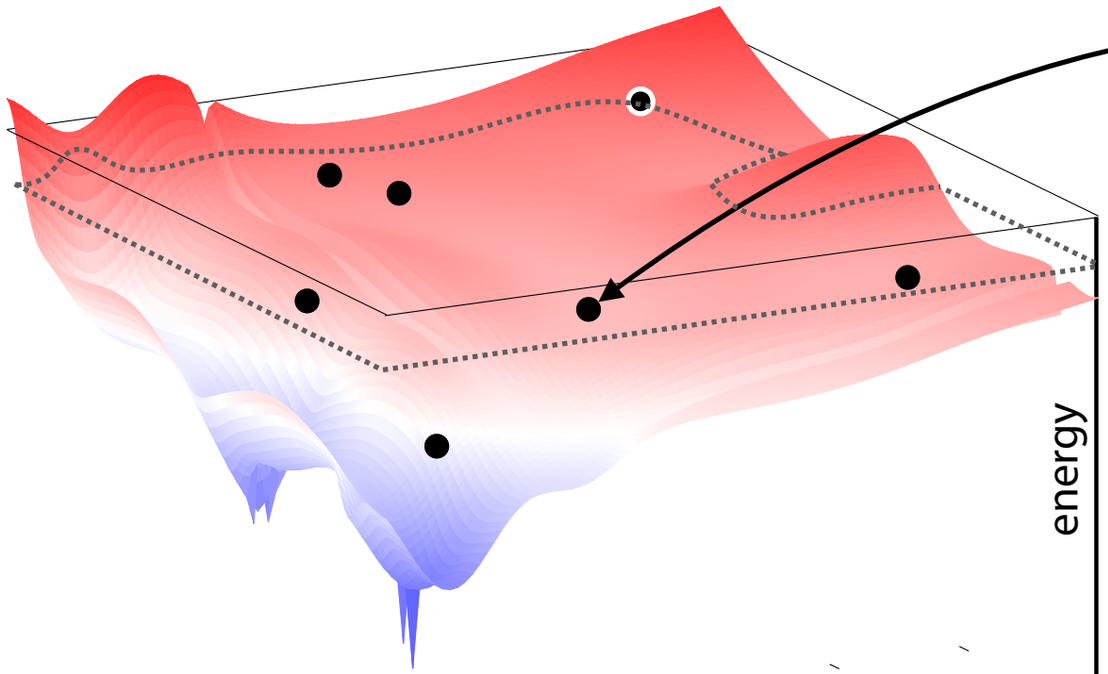

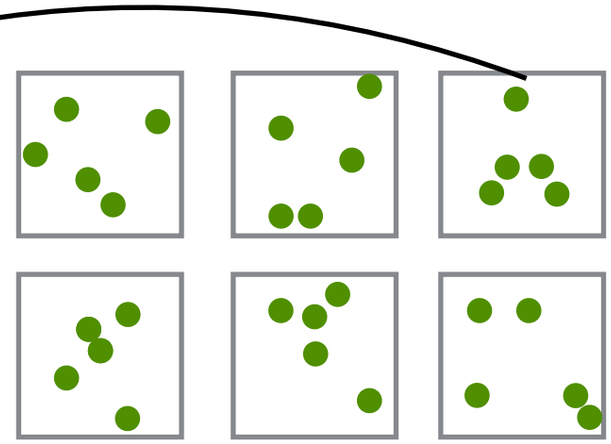

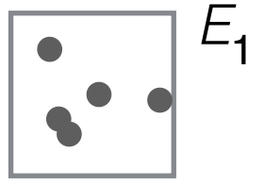

energy

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 $K/(K+1)$

Generate a new sample uniformly with $E < E_1$

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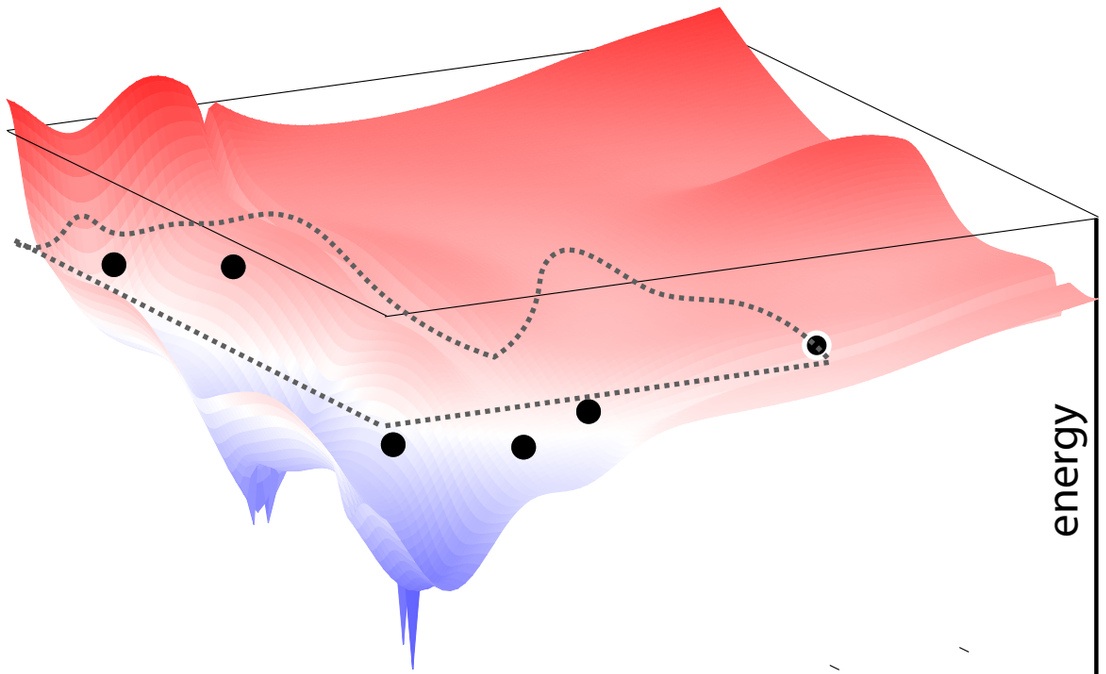

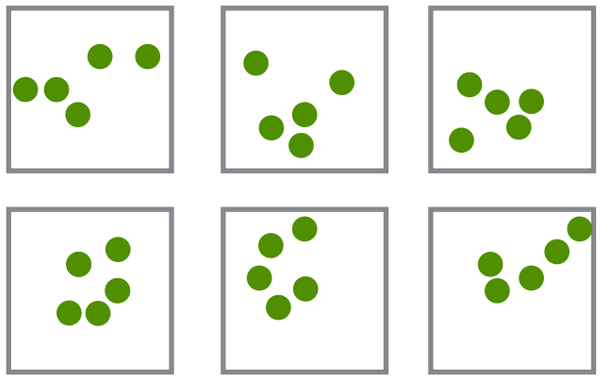

Choose the sample with the highest energy

Generate a new sample uniformly with $E < E_i$

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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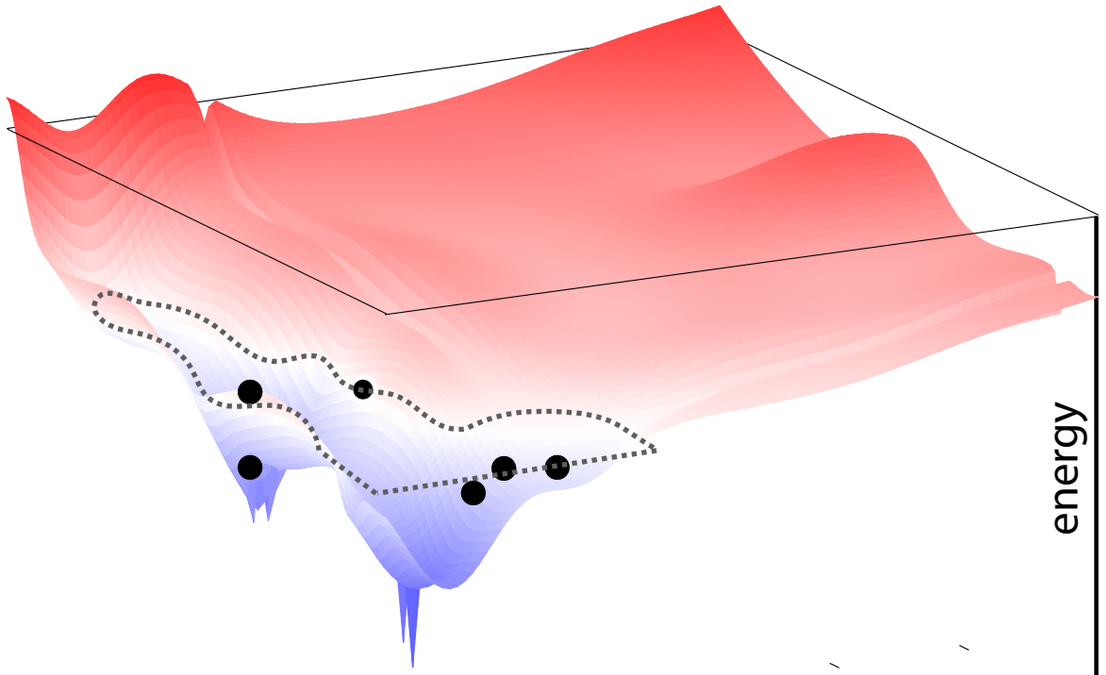

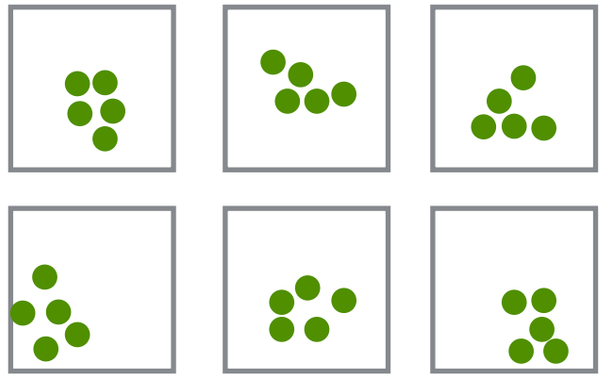

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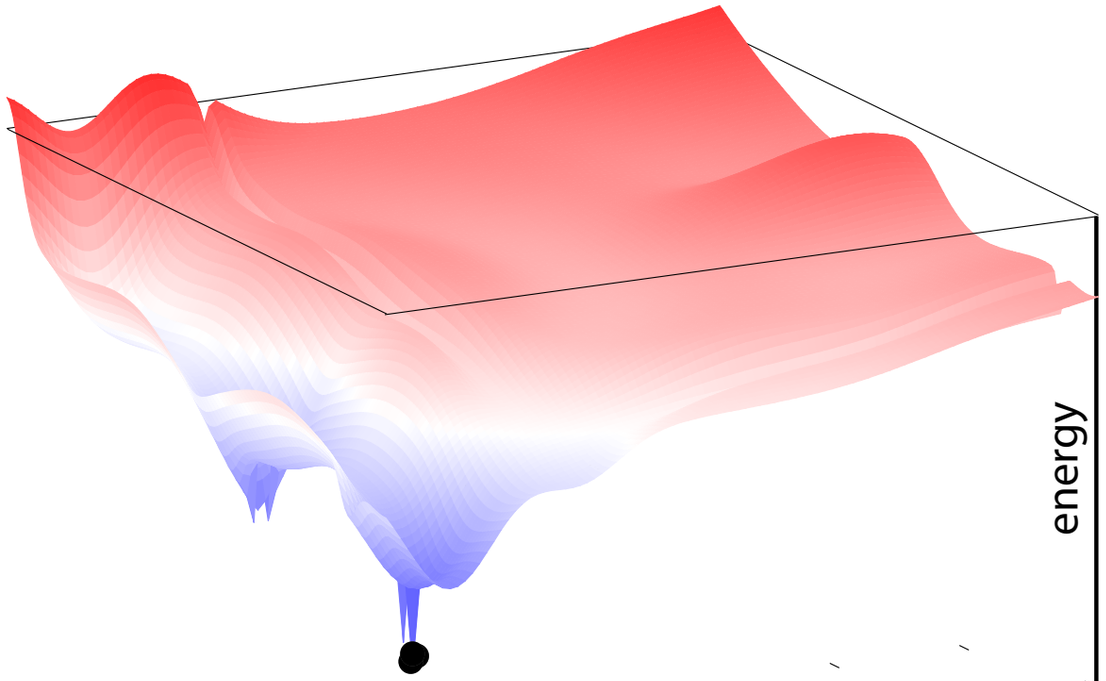

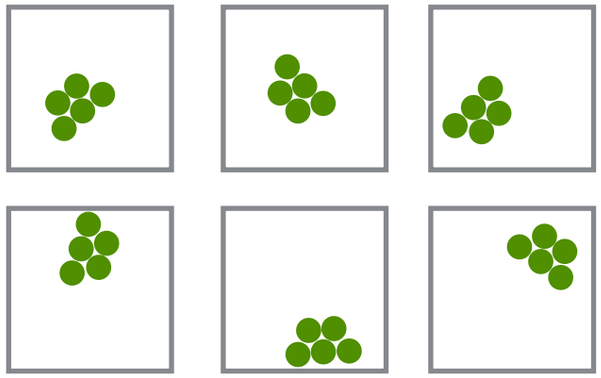

Repeat this iteration many times…

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.

Nested Sampling Algorithm

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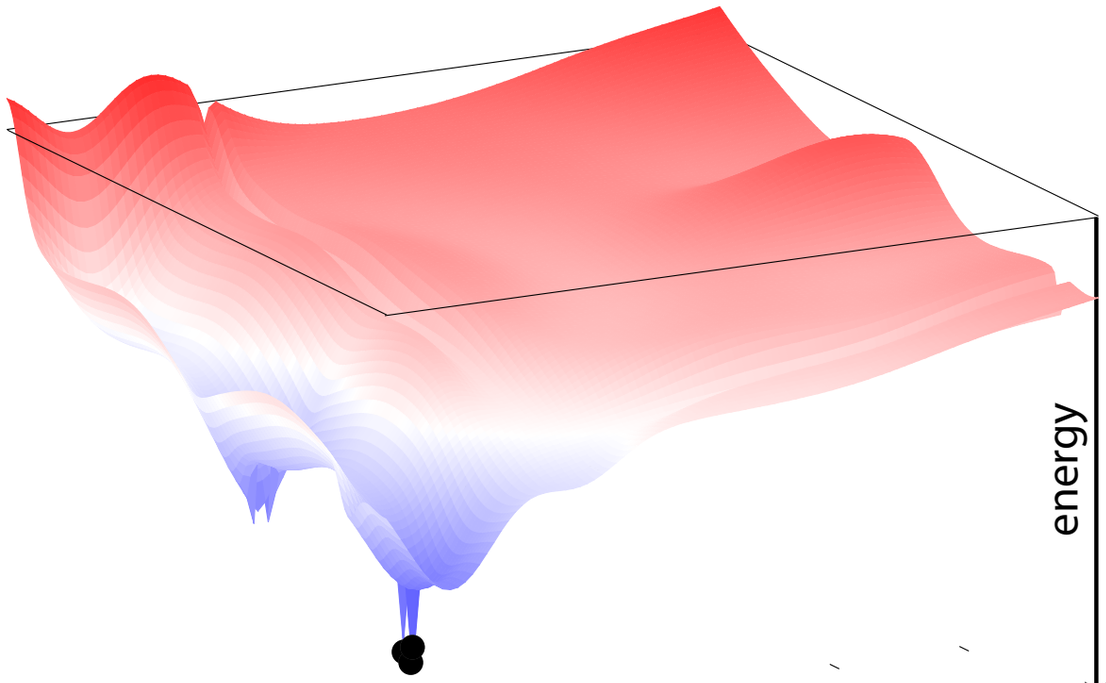
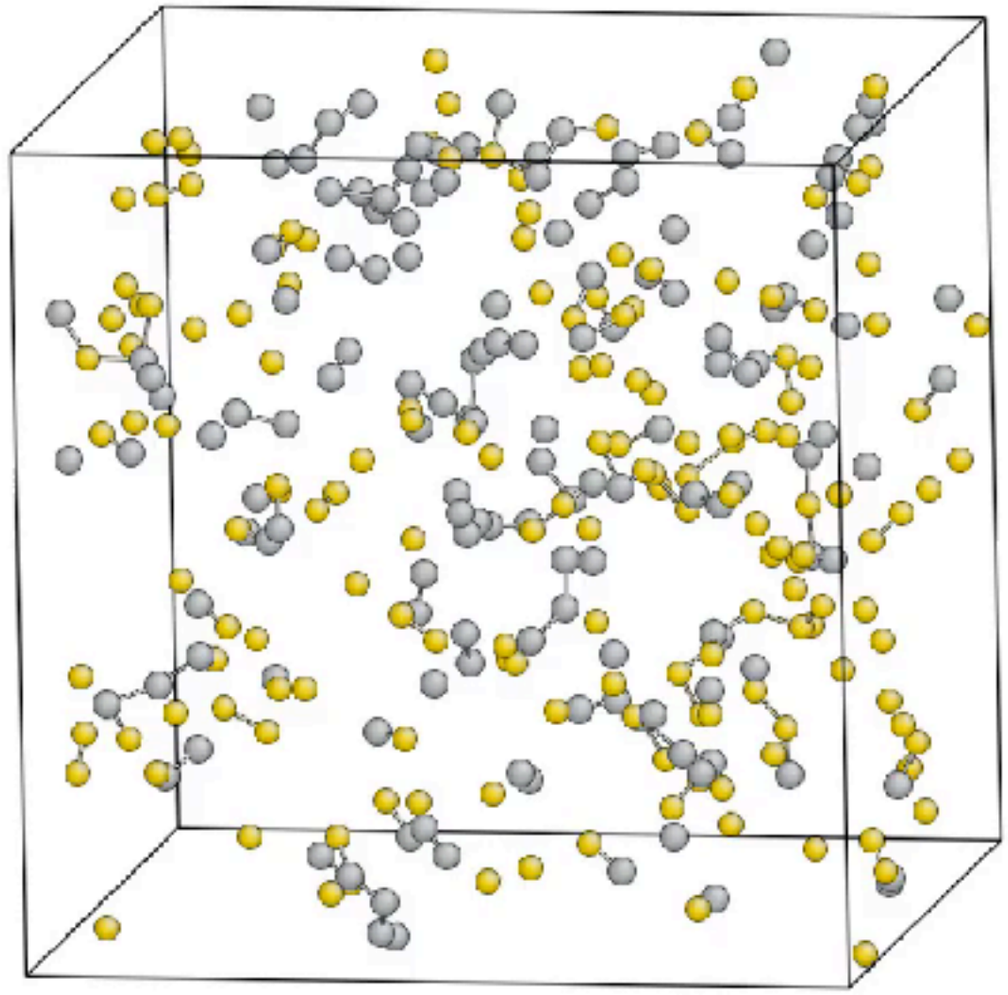
Generate *K* random samples uniformly in the total phase space volume





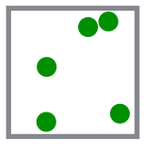
309 atoms (Cu and Pt) in fixed cell: cluster

Nested Sampling Algorithm

At the end we have a set of energies $\{E_i\}$, corresponding volumes $\{[K/(K+1)]^i\}$ and configurations

E_1 $K/(K+1)$

E_2 $K/(K+1)*K/(K+1)$



E_3 $K/(K+1)*K/(K+1)*K/(K+1)$

…

E_i $\{K/(K+1)\}^i$

E_{i+1} $\{K/(K+1)\}^{i+1}$

…

E_n $\{K/(K+1)\}^n$

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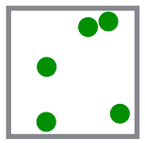

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…

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…

E_n $\{K/(K+1)\}^n$

Partition function:

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

for any temperature

Nested Sampling Algorithm

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

- Thermodynamic quantities as a simple post processing step

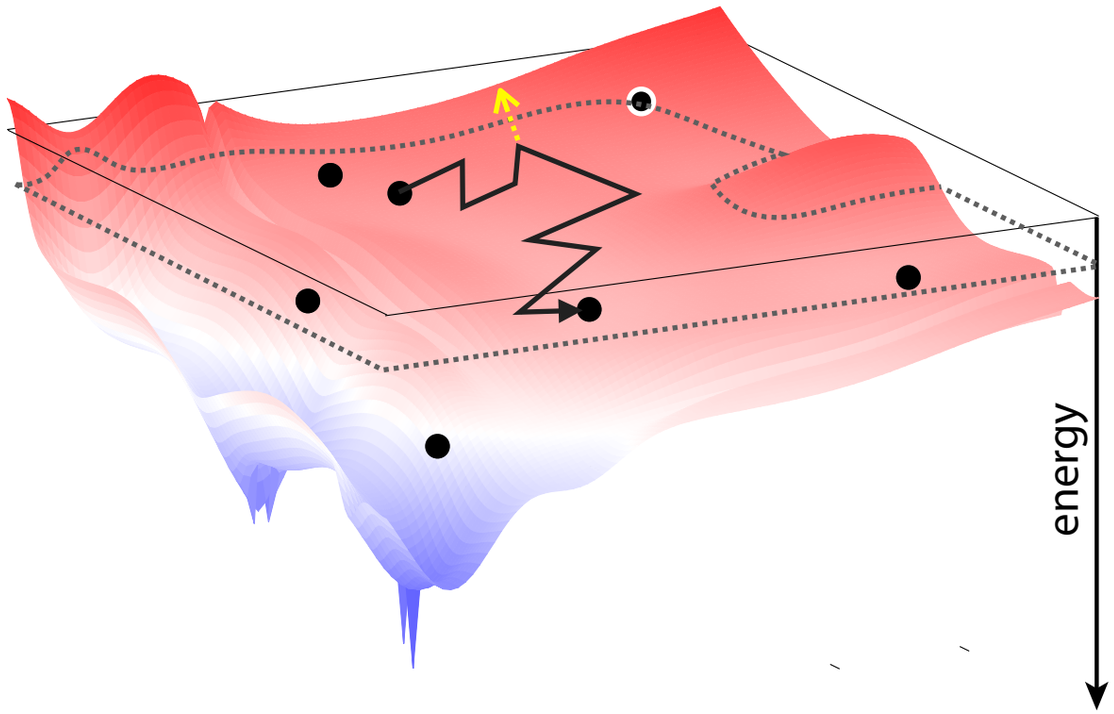
$$
\begin{aligned}
Z(\beta) &= Z_{\mathbf{p}} \sum_i w_i e^{-\beta E_i} \\
&= Z_{\mathbf{p}}(\beta) \sum_i \left[(K/(K+1))^i - (K/(K+1))^{i+1} \right] e^{-\beta E_i}
\end{aligned}
$$

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

- Sampling itself independent from temperature
- No need for prior knowledge of the structures
- Can be done with both (*N,V,T*) and (*N,p,T*)

- Easy control parameter of the sampling is *K*, called the “live set” or the “walkers” (is the resolution of the PES)

Generating a new sample configuration



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)

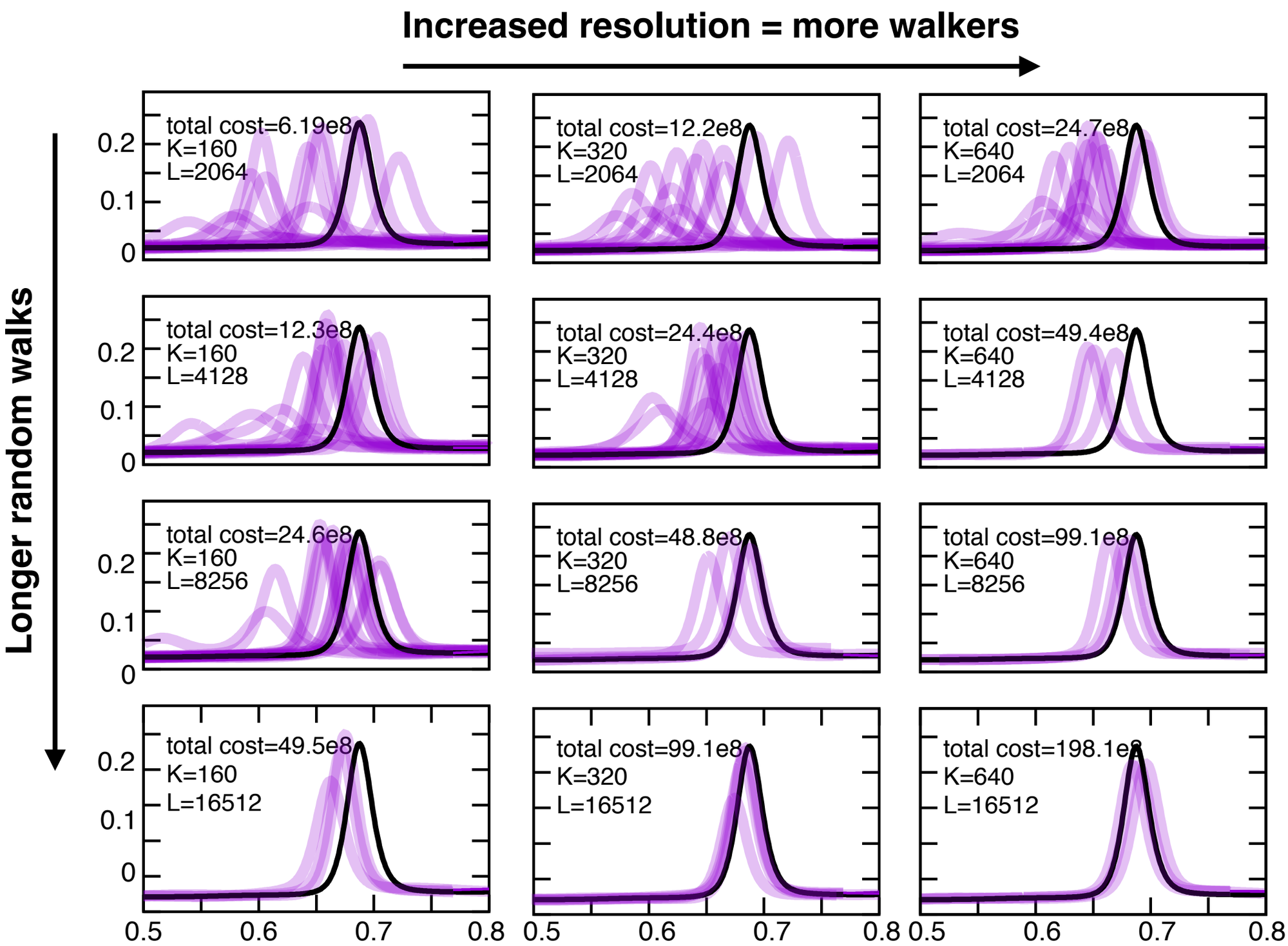
- **Total Enthalpy Hamiltonian Monte Carlo (TE-HMC)**
  short constant total energy MD trajectories

- **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)

Length of the random walk, *L*, is the other control parameter.

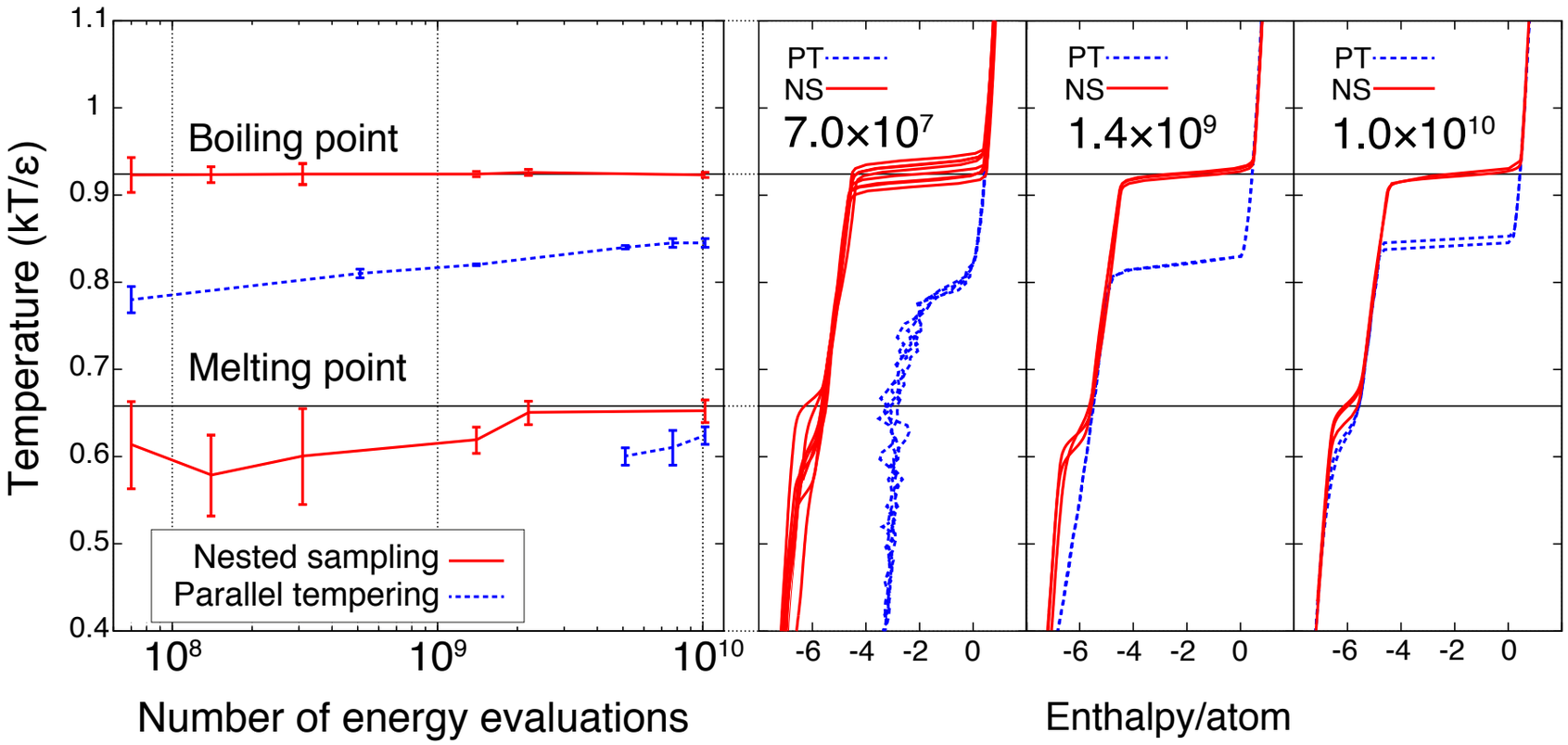
Convergence with *K* and *L*

Melting peak on the heat capacity curve of 64 LJ atoms at constant pressure.



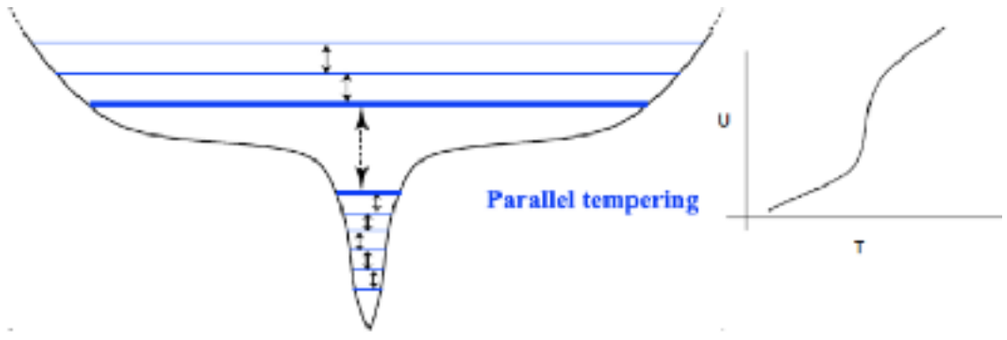
Computational cost comparison

64 LJ atoms at constant pressure

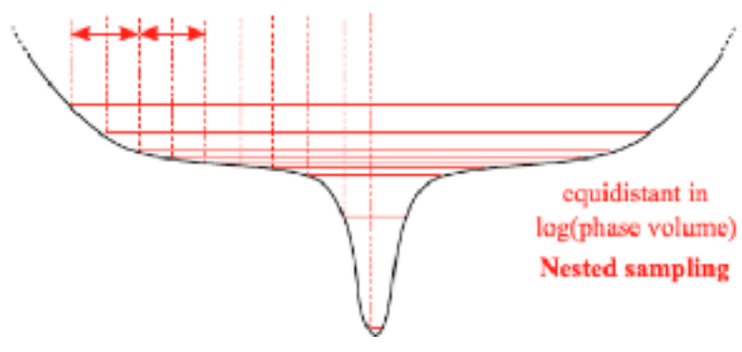


Nested Sampling vs. Parellel Tempering

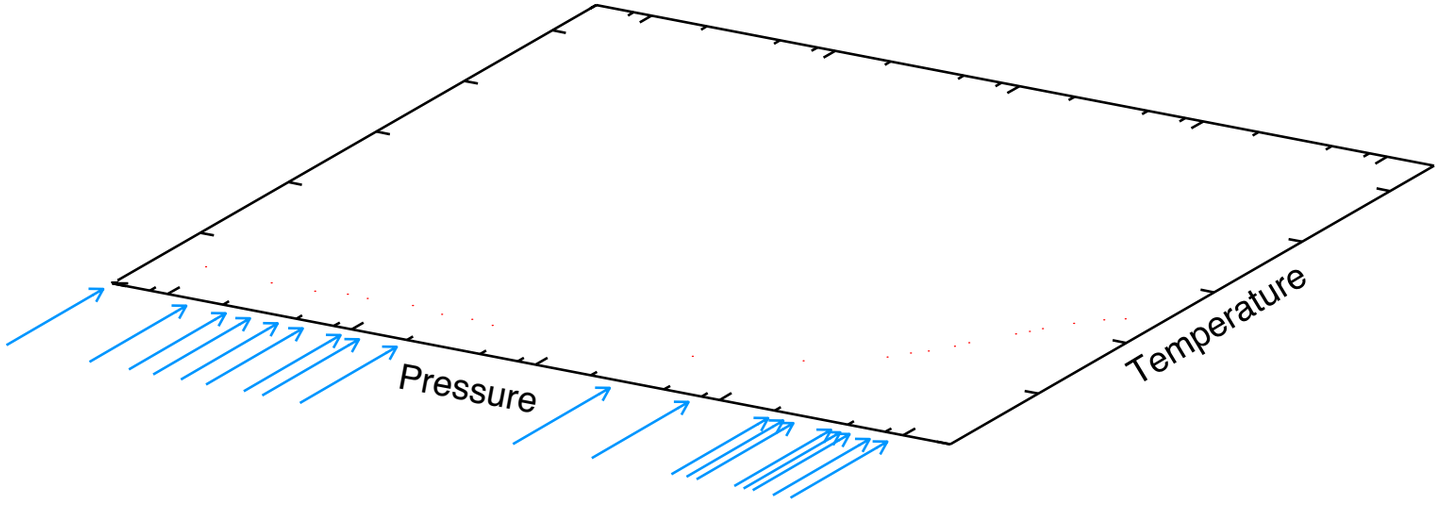
levels equidistant in temperature



levels equidistant in log(phase volume)

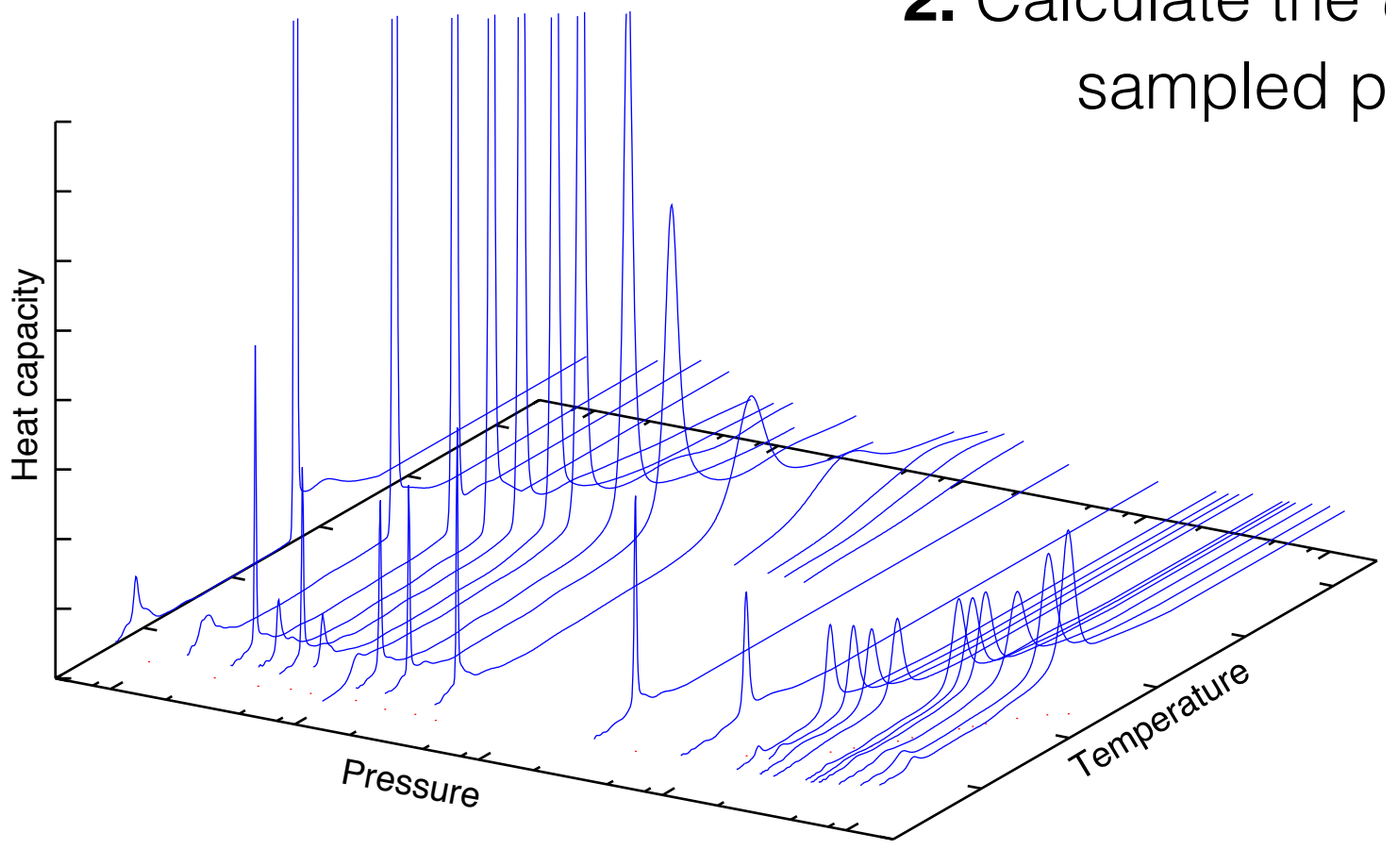


p-*T* phase diagram "in three steps"



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.

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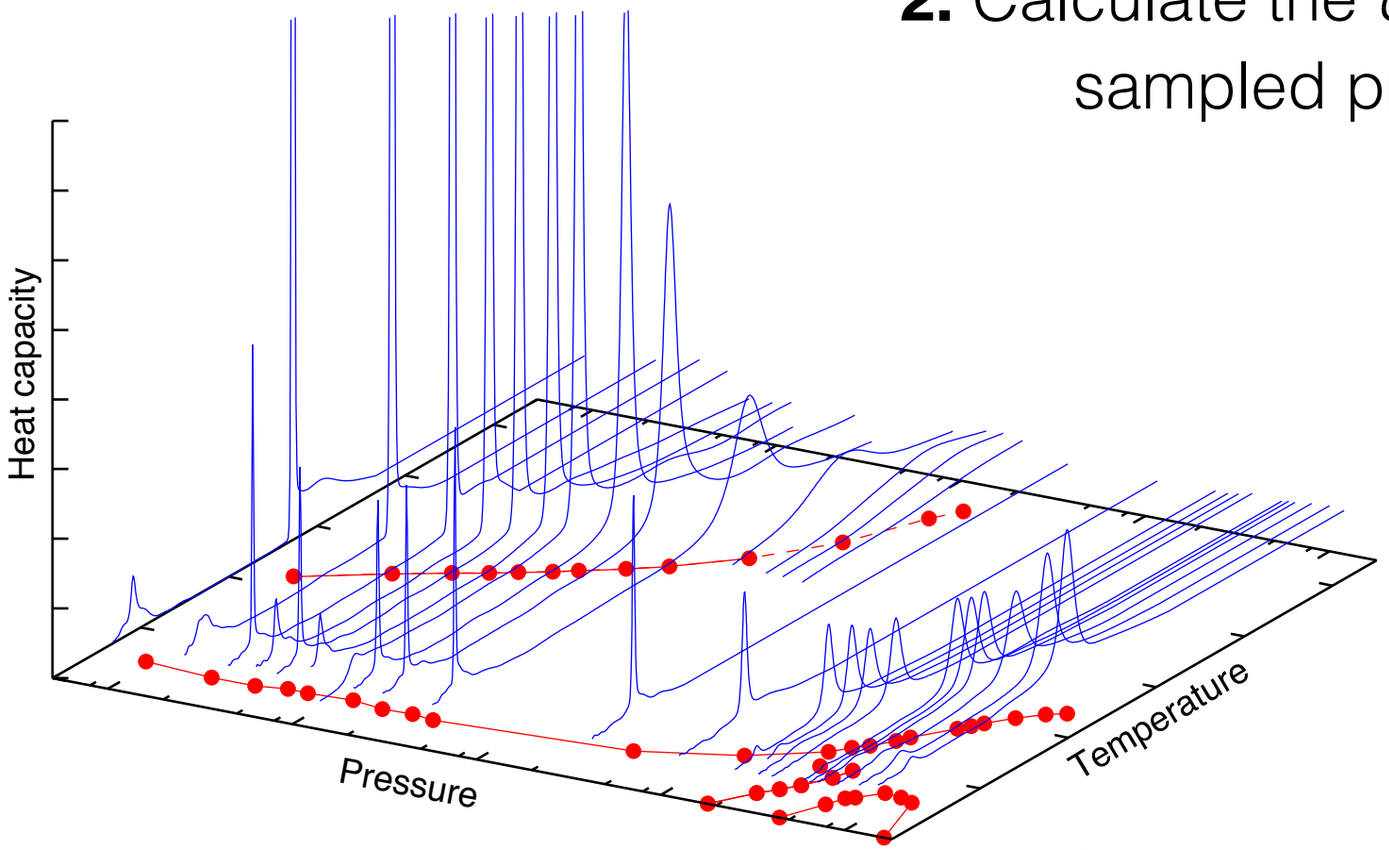


1. Choose a system (potential model) and a set of pressures. Perform a *nested sampling* calculation for each.

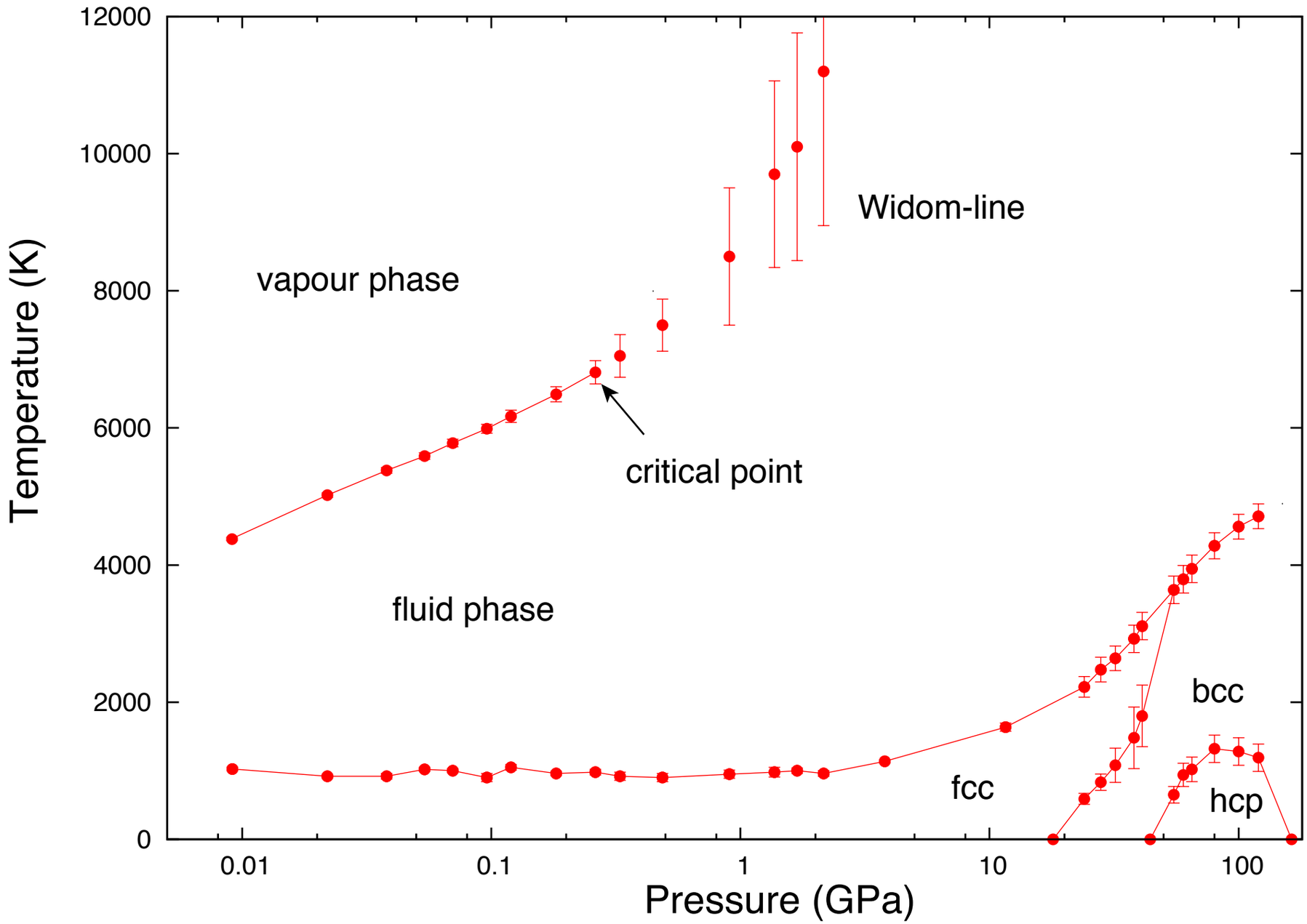
2. Calculate the $c_p(T)$ for every sampled pressure.

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

p-*T* phase diagram!

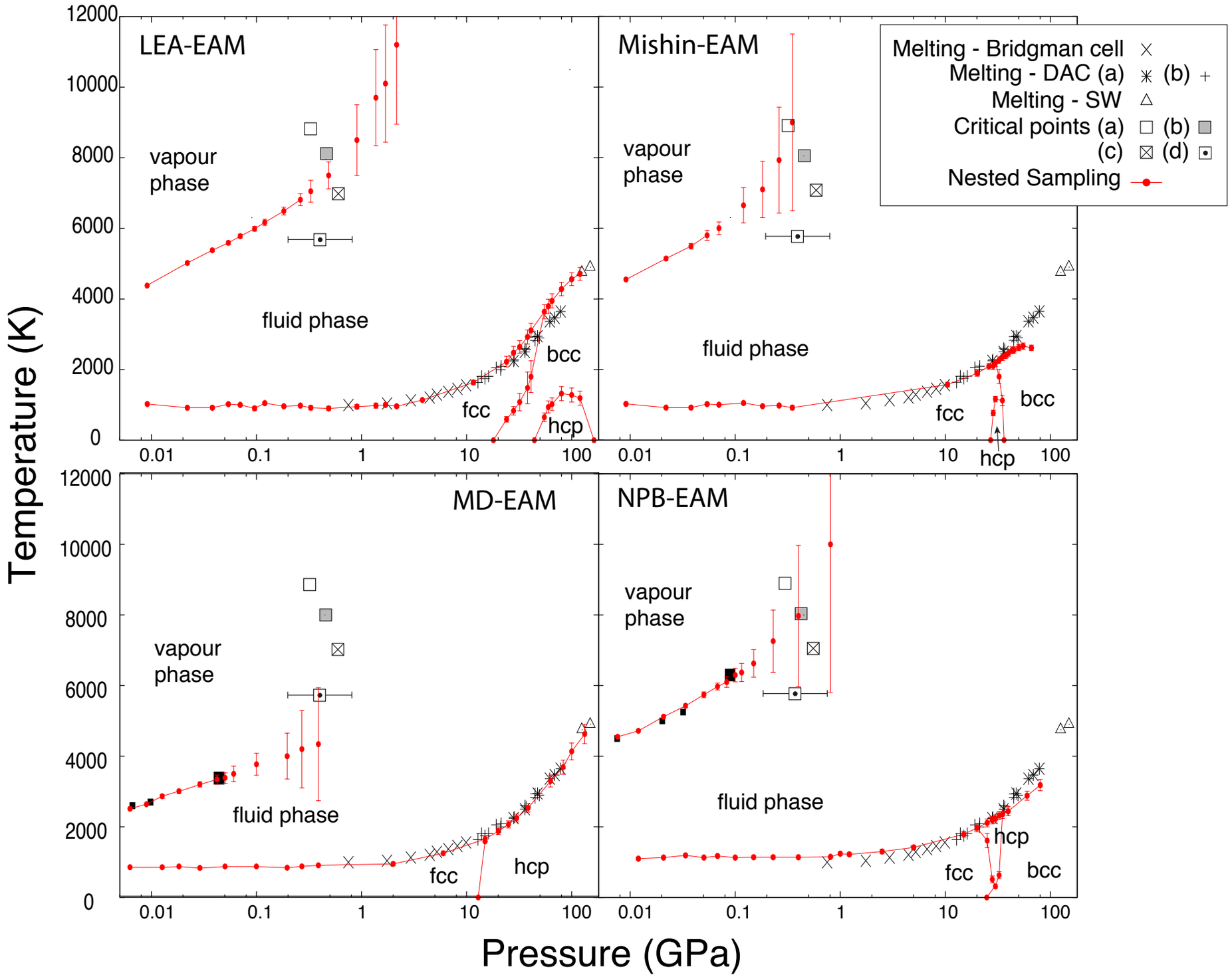
Phase Diagram of Aluminium

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



Baldock *et al.*, PRB **93**, 174108 (2016)

Phase Diagram of Aluminium



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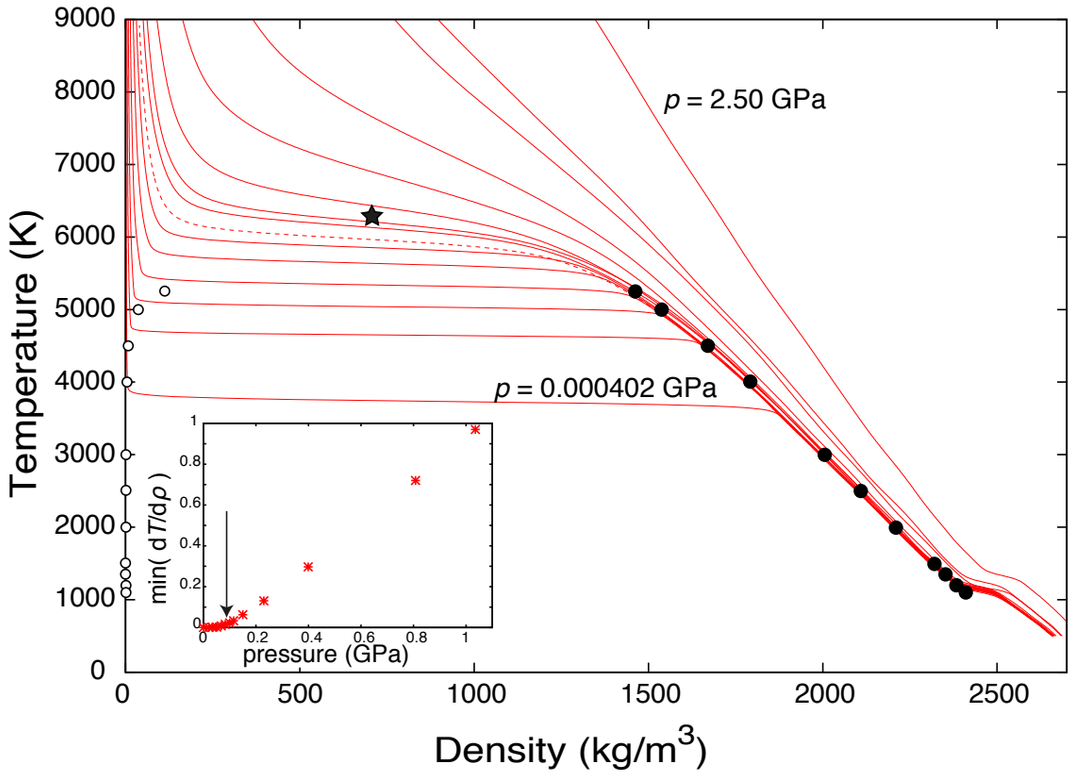
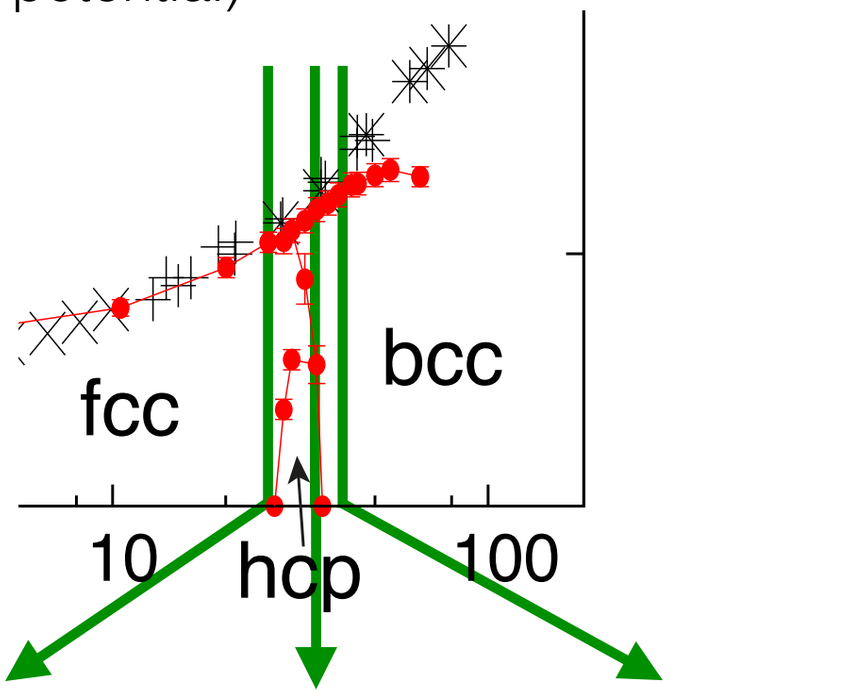
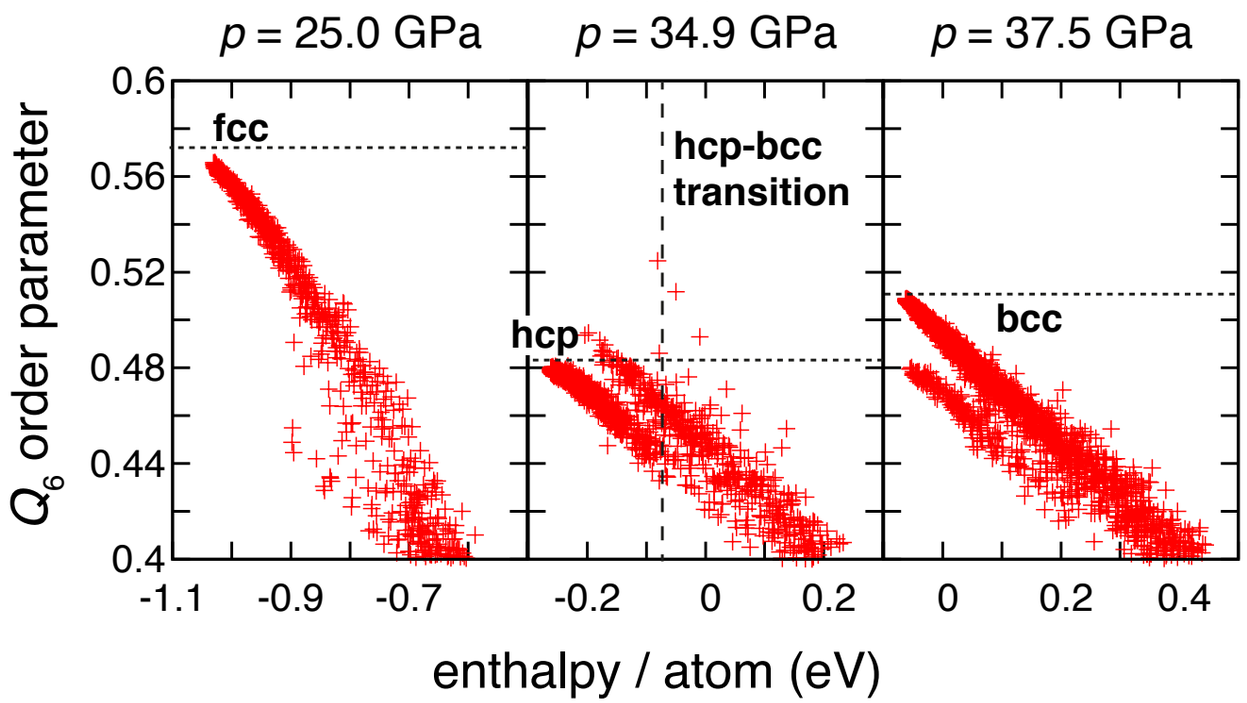
Phase Diagram of Aluminium

Comparison to Gibbs ensemble MC: density-temperature phase diagram (NPB potential)



Solid-solid transition and Q_6 bond order parameter (Mishin potential)





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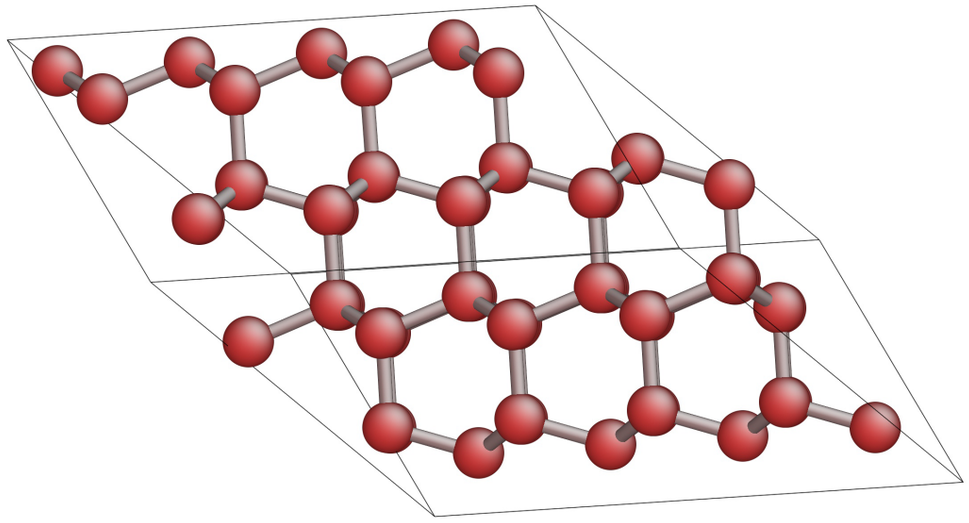
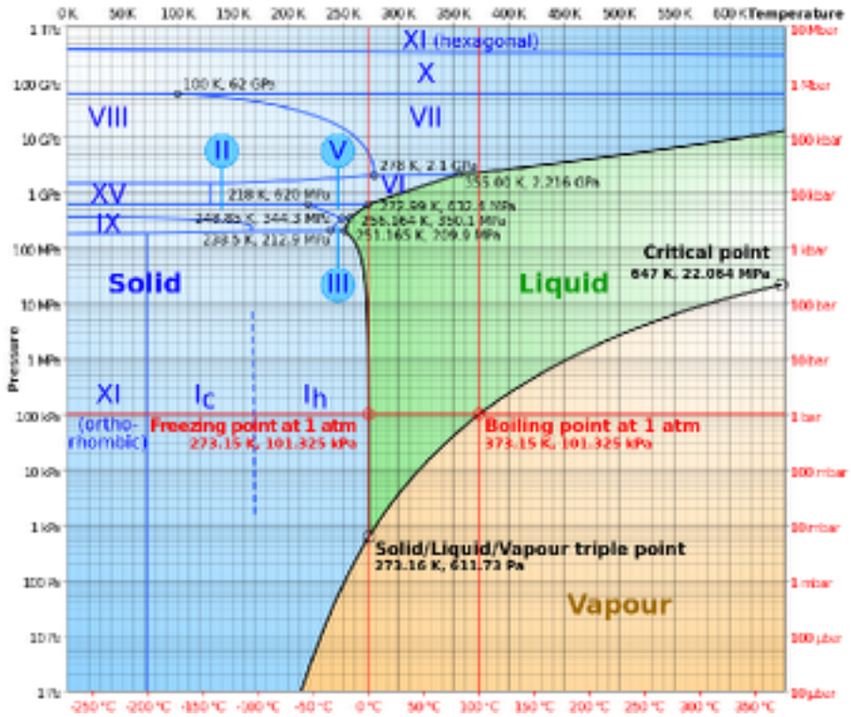
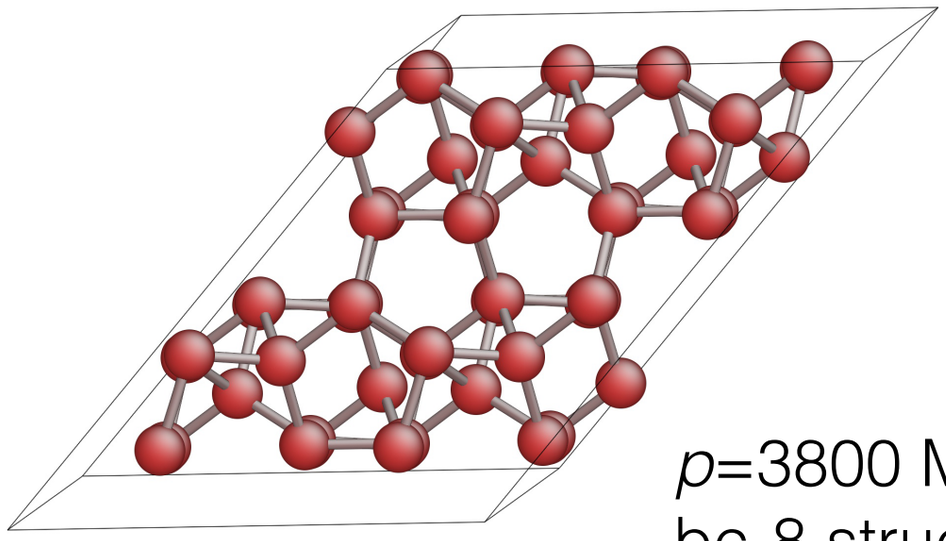
Phase behaviour of water

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

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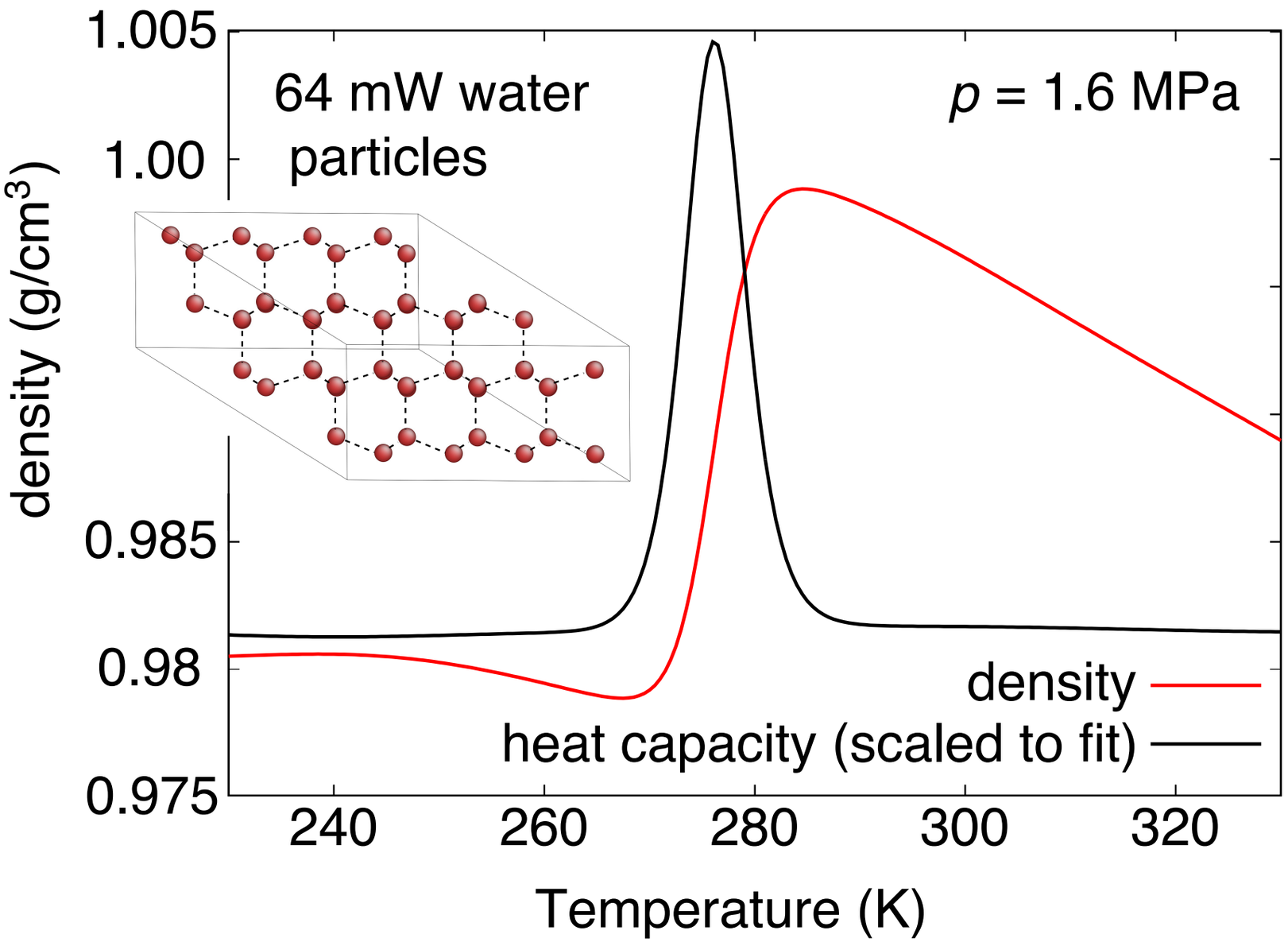


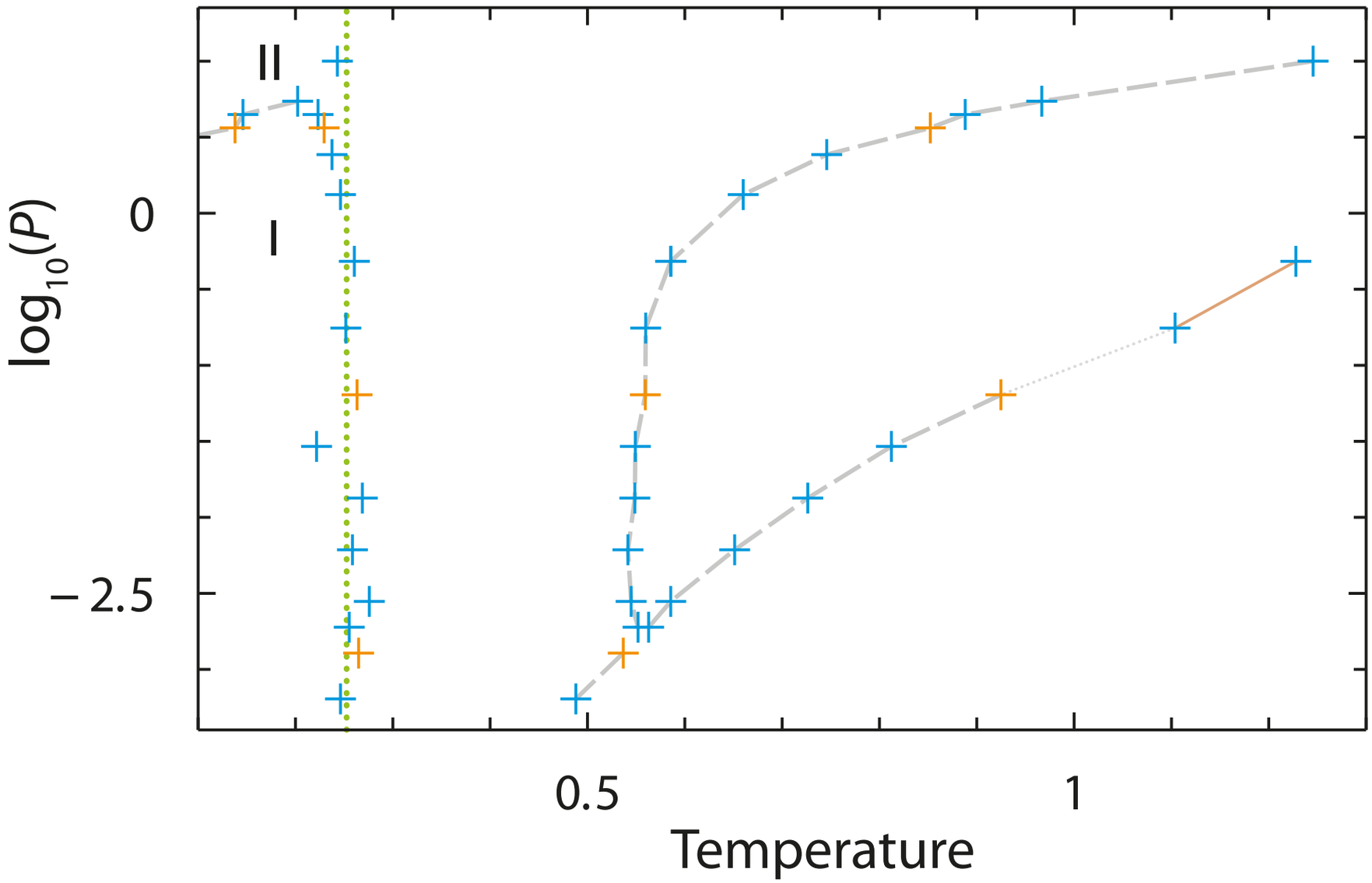
Baldock *et al*., PRE, *in press*

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

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



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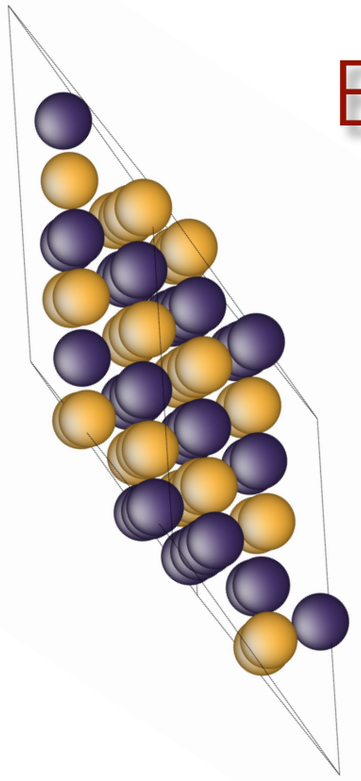
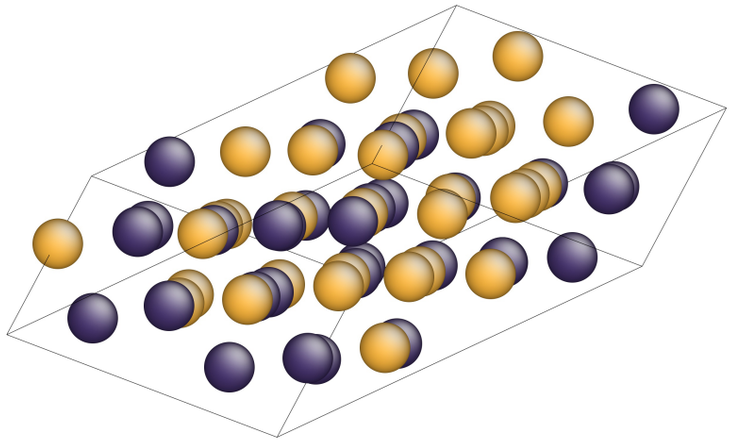
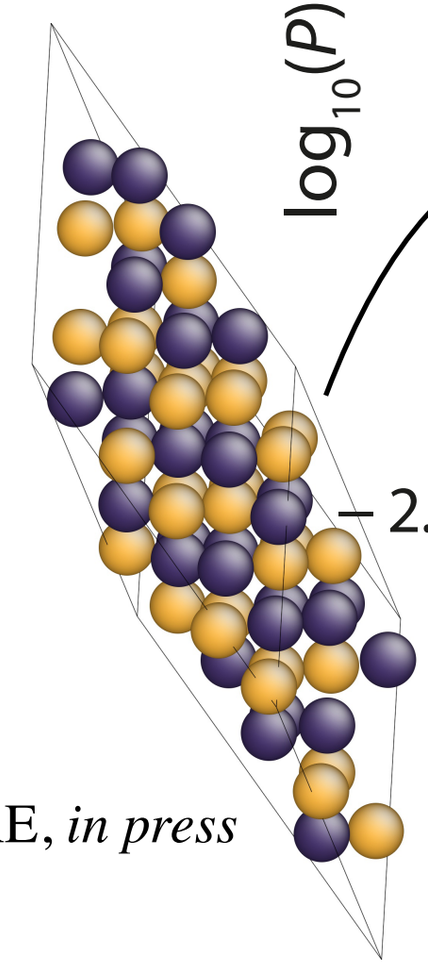
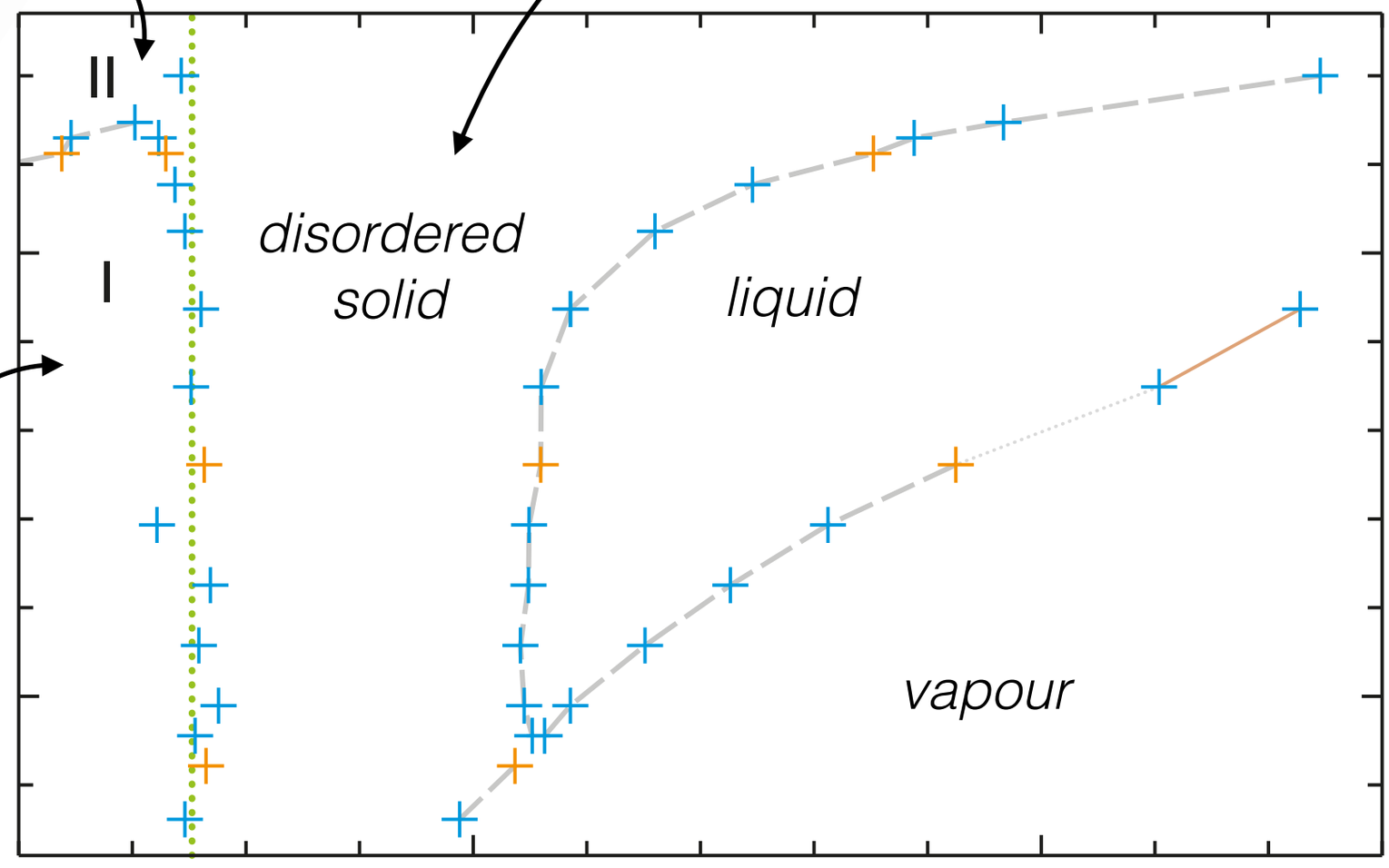


substitutional alloy, order-disorder transition



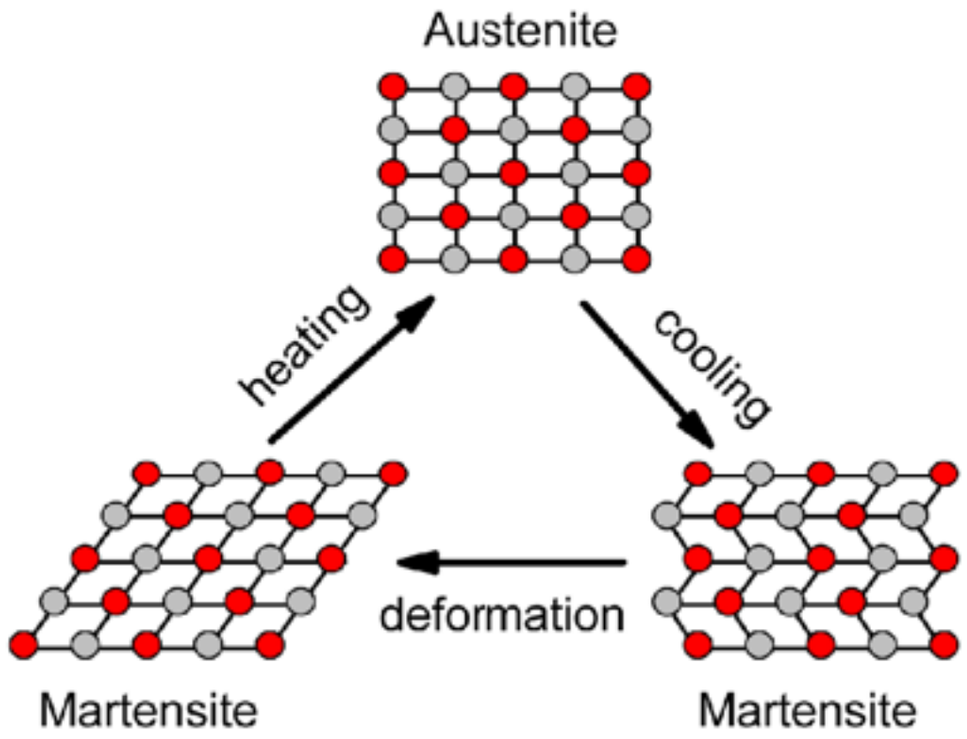


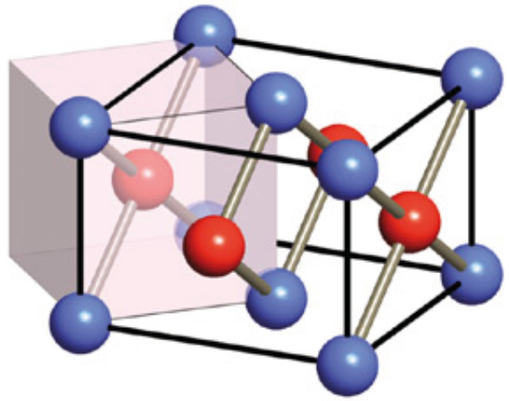


Baldock *et al.*, PRE, *in press*

Martensitic Transition in NiTi alloys

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





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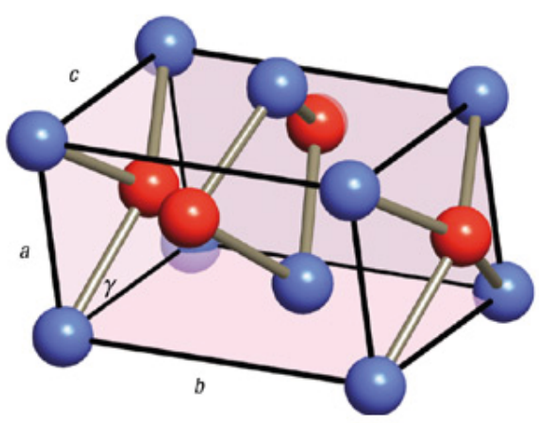


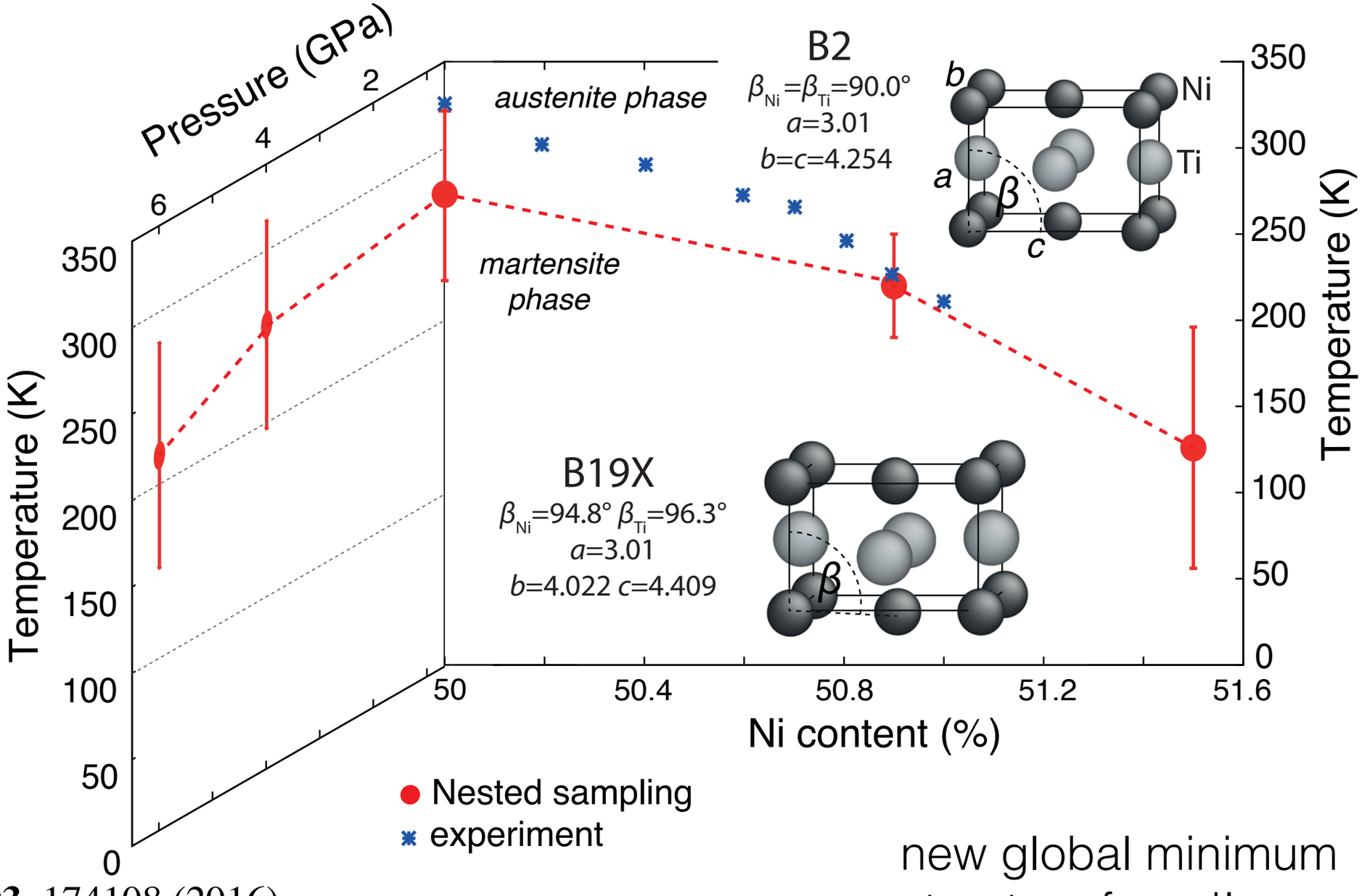
B19’

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

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



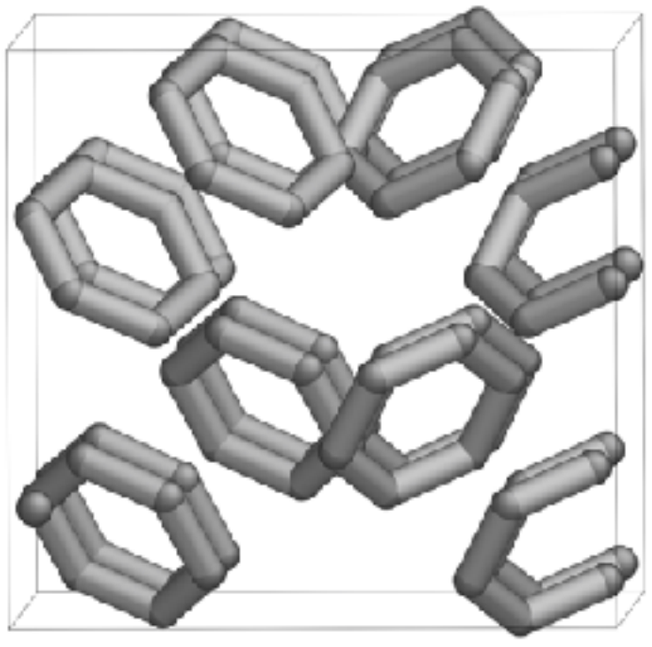
Baldock *et al.*, PRB **93**, 174108 (2016)

new global minimum structure found!

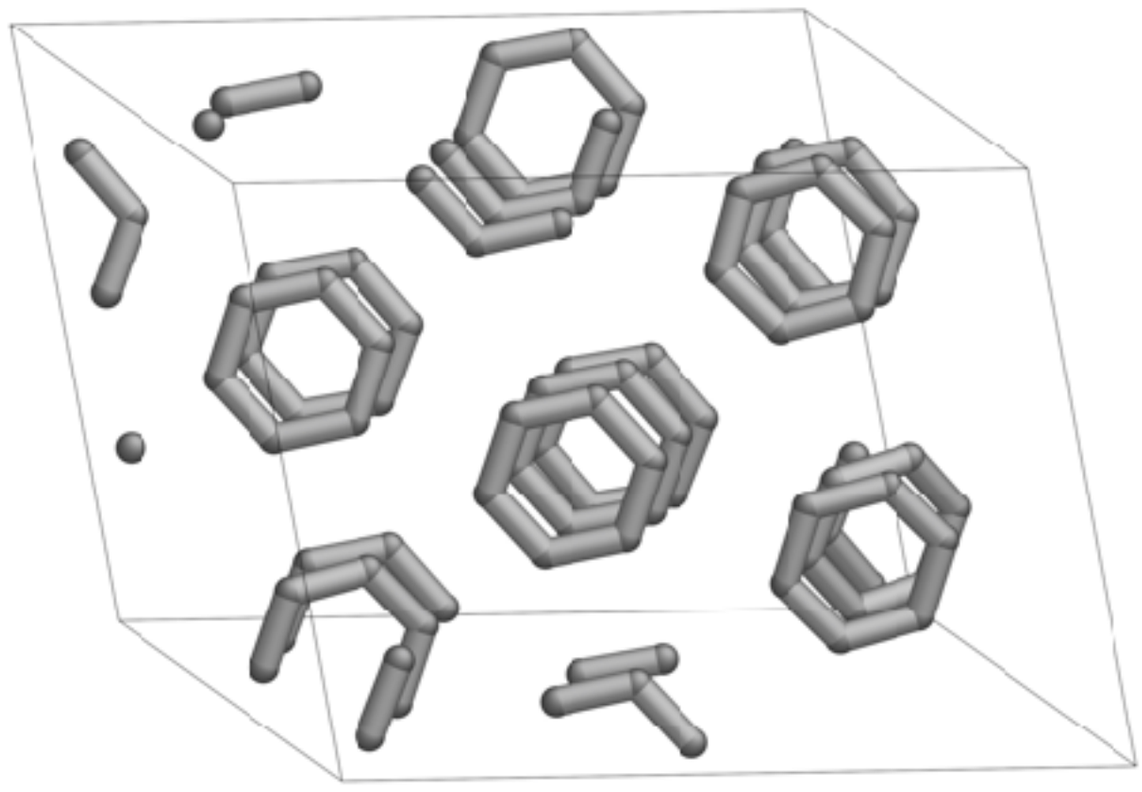
NS with molecular systems

16 benzene molecules (united atom, LJ)

0.5 GPa



5.0 GPa

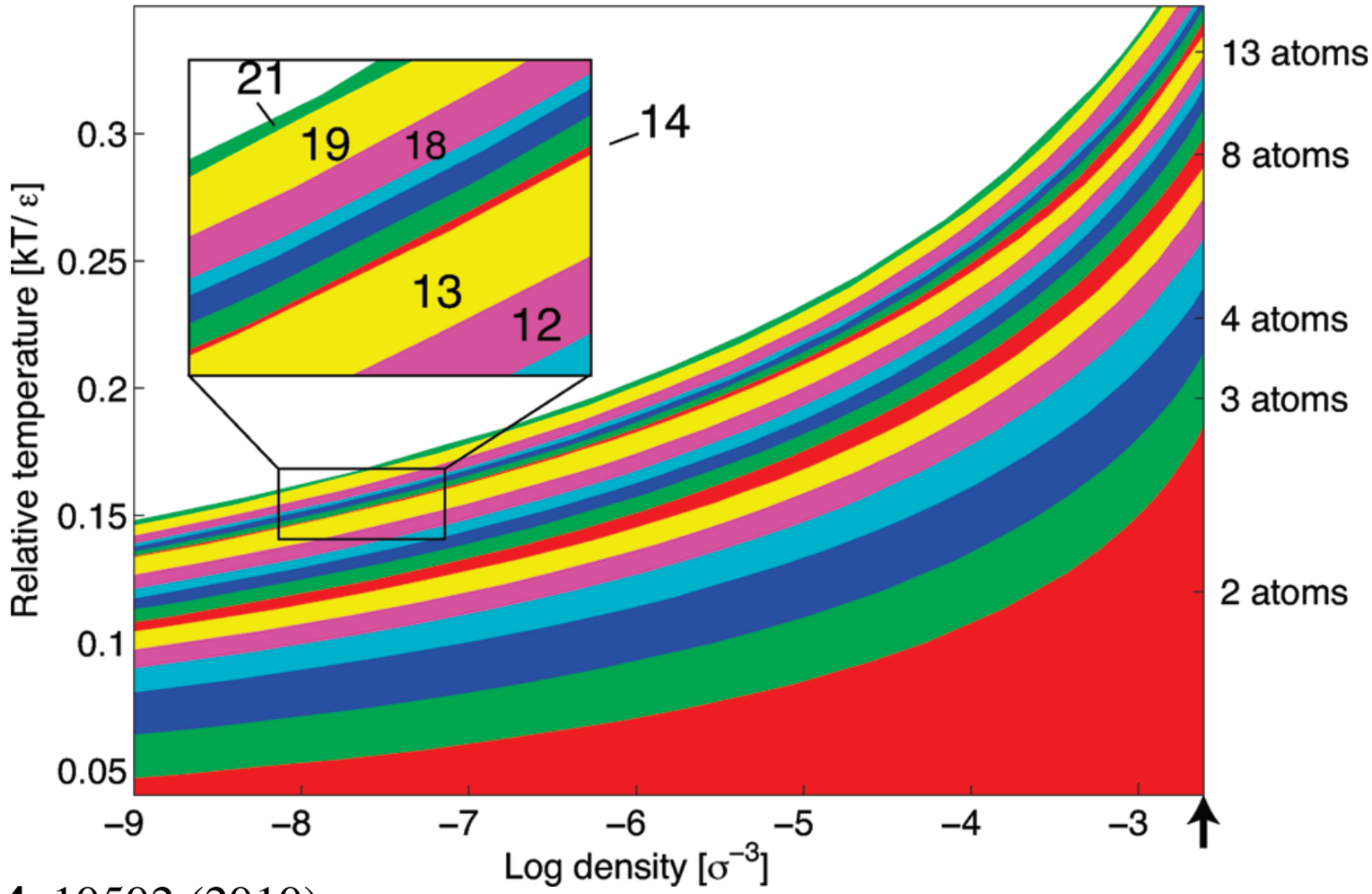


Lennard-Jones clusters

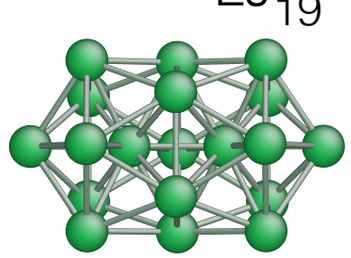
$$U_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Studied clusters from size LJ_2 to LJ_{38}

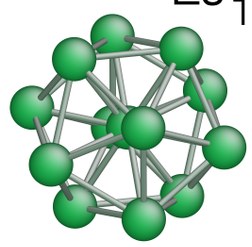
Stability of the Lennard-Jones clusters against the ideal gas



LJ_{19}



LJ_{13}

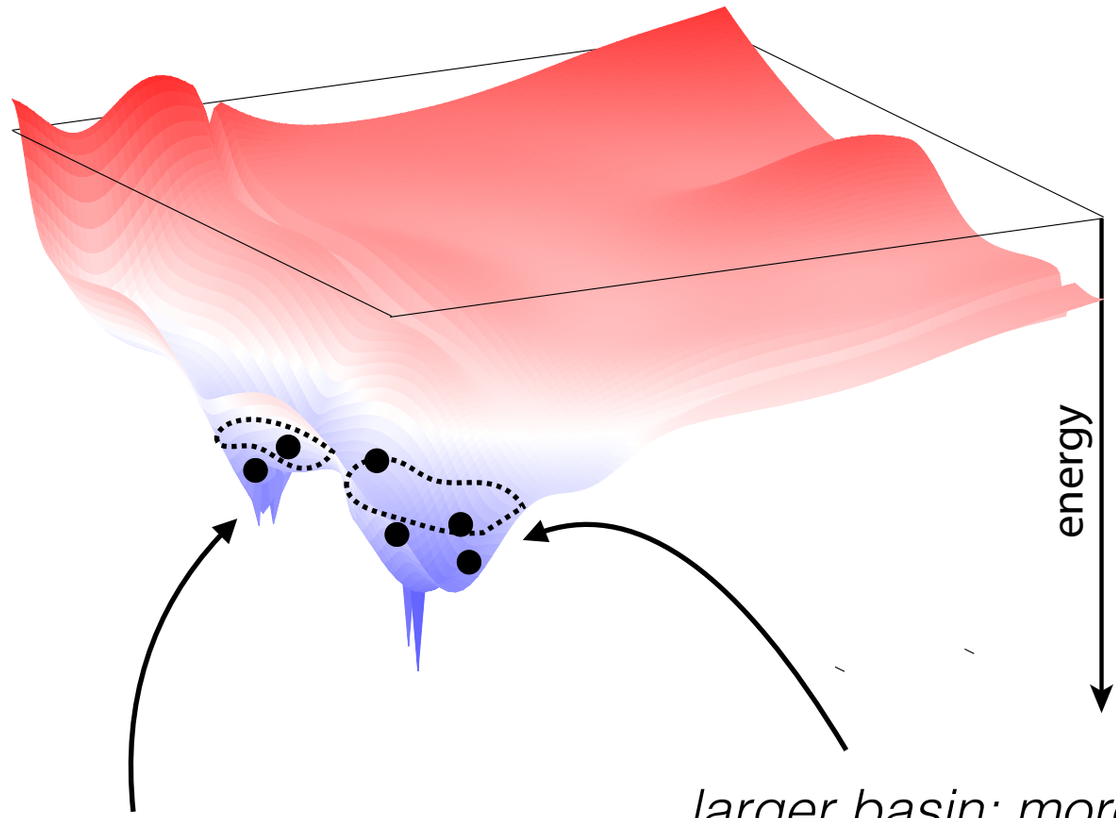


Partay *et al.*, JPC B **114**, 10502 (2010)

Visualising the 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

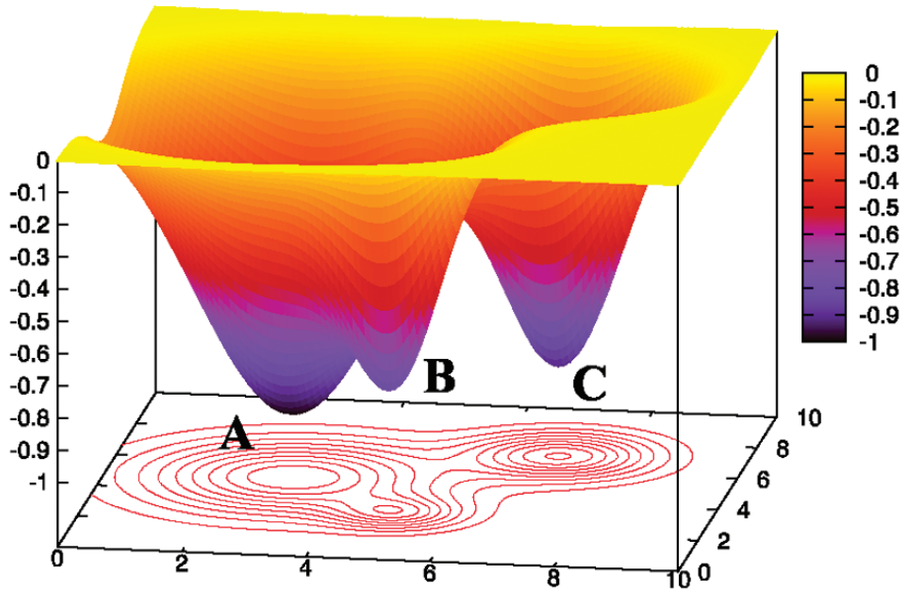


smaller basin: fewer samples in it

larger basin: more samples in it

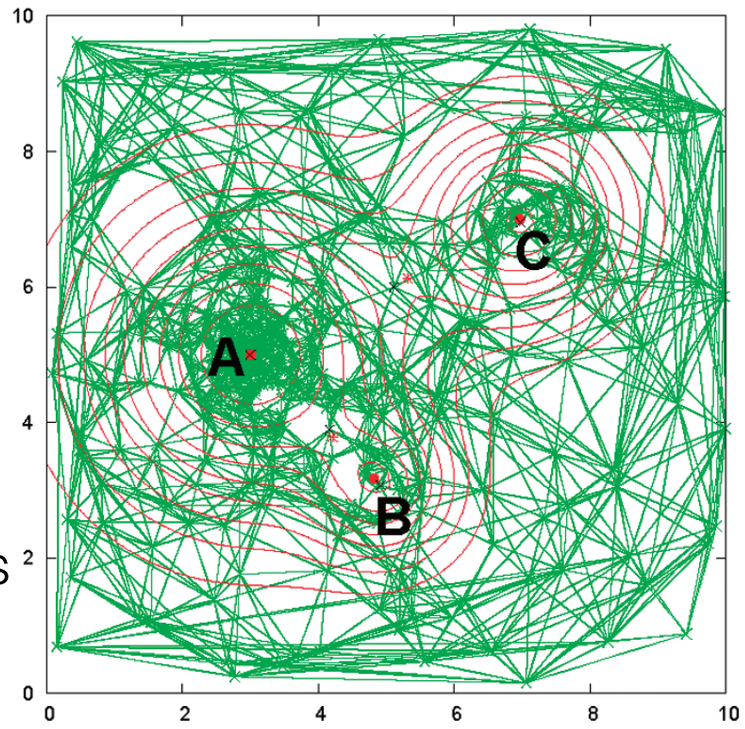
Visualising the PES

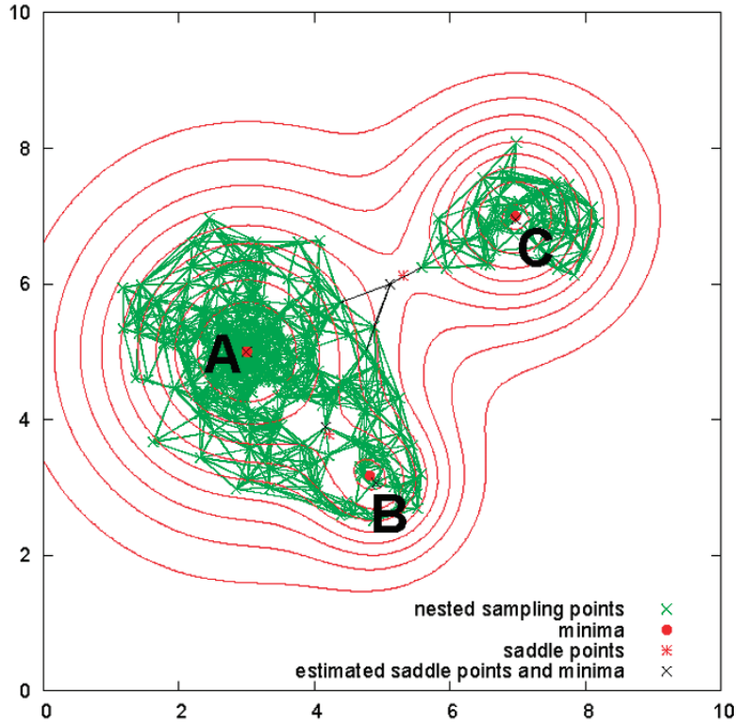
Simple test landscape



After NS:

choose a *good* metric and produce a graph by connecting the *k* closest higher energy neighbours

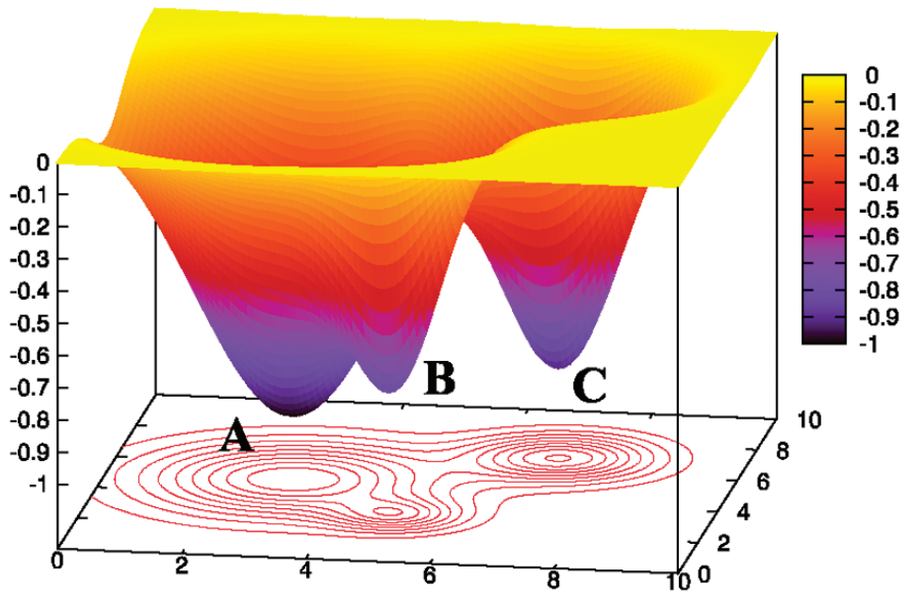




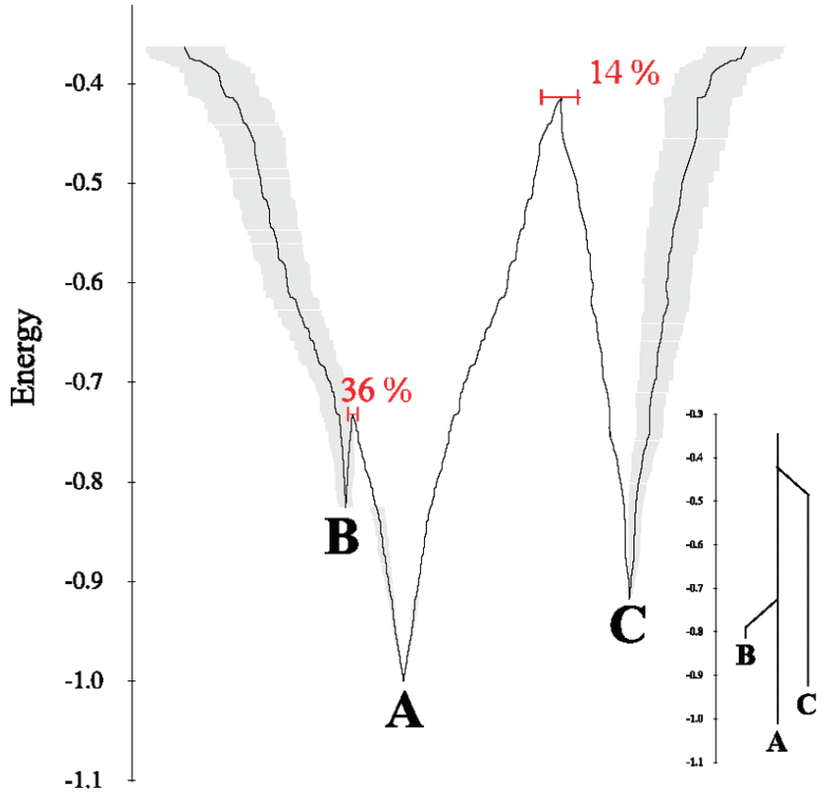
start deleting the points from the top (high energy) and see as the graph to split

Visualising the PES

Simple test landscape

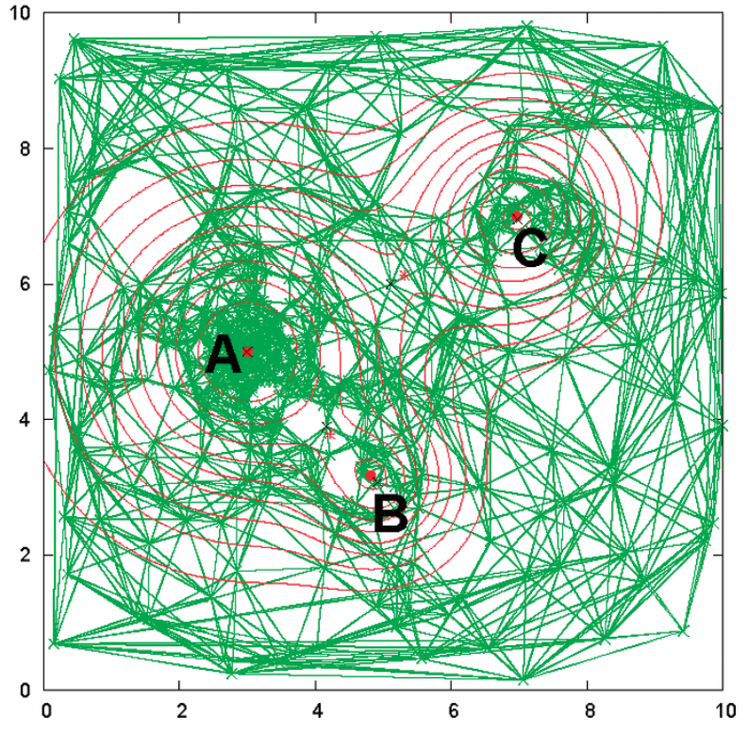


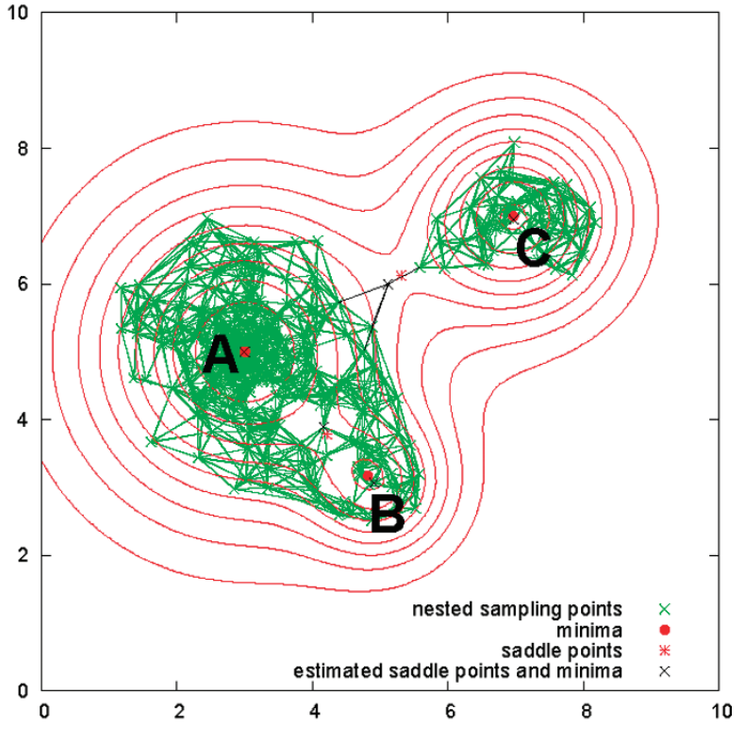
energy landscape chart



After NS:

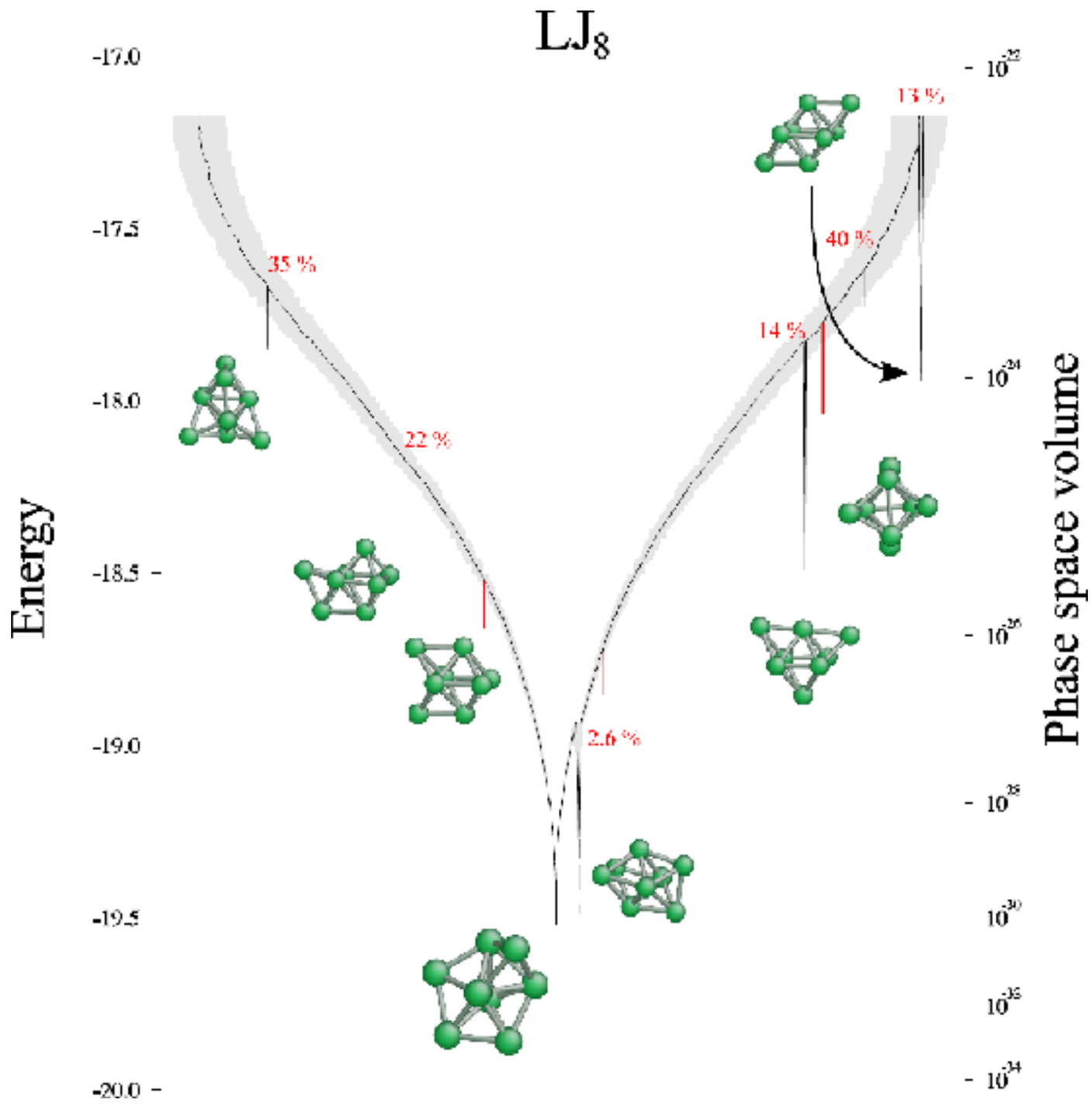
choose a *good* metric and produce a graph by connecting the *k* closest neighbours





start deleting the points from the top (high energy) and see as the graph to split

Energy landscape chart

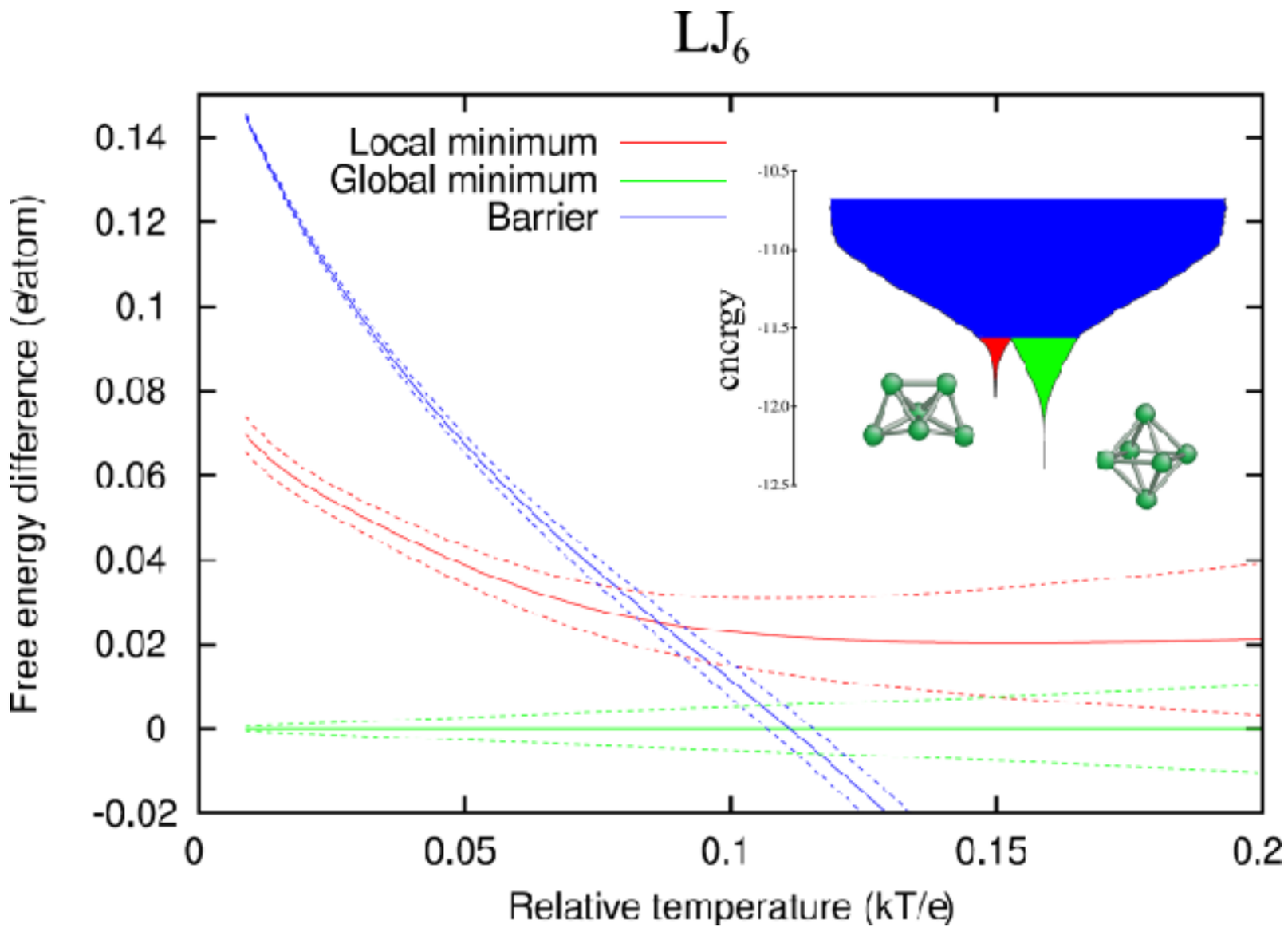


Partay *et al*., JPC B **114**, 10502 (2010)

Energy landscape chart

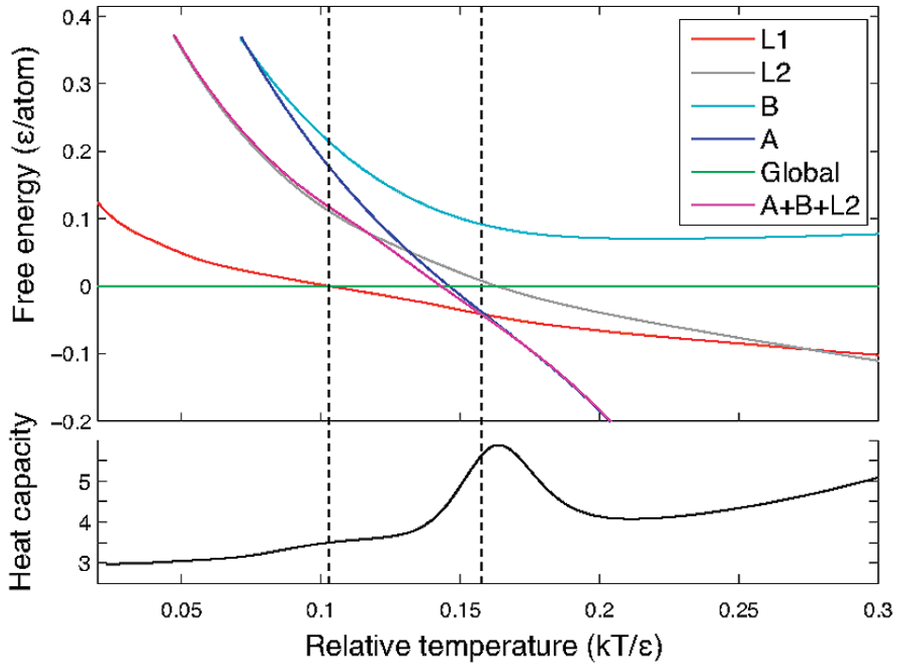
Using the landscape chart, calculate the free energy of the basins, determine the phase transitions without the need of externally defined order parameter.

$$A(\beta) = -\frac{1}{\beta} \ln Z(\beta)$$

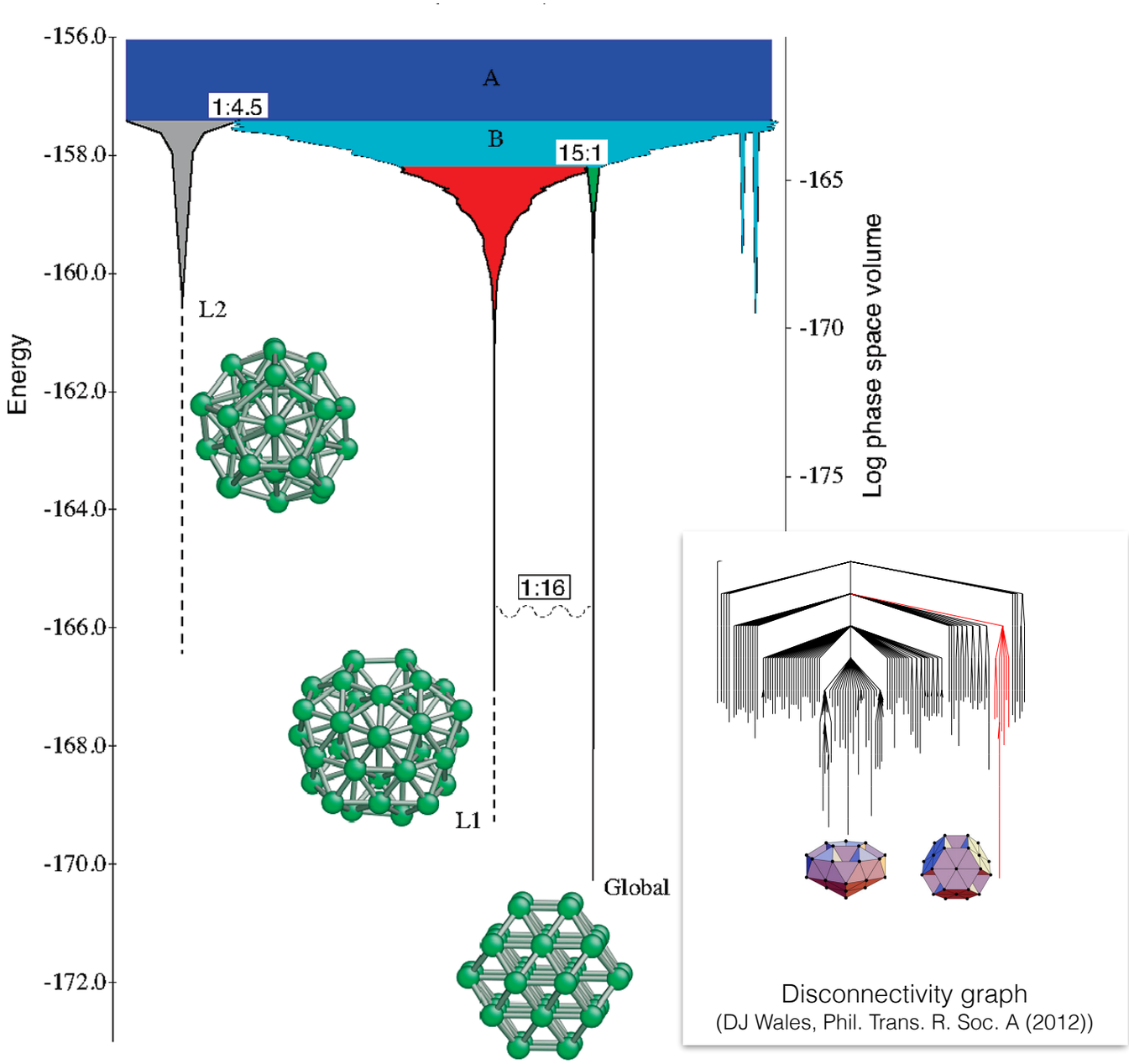


Energy landscape chart

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



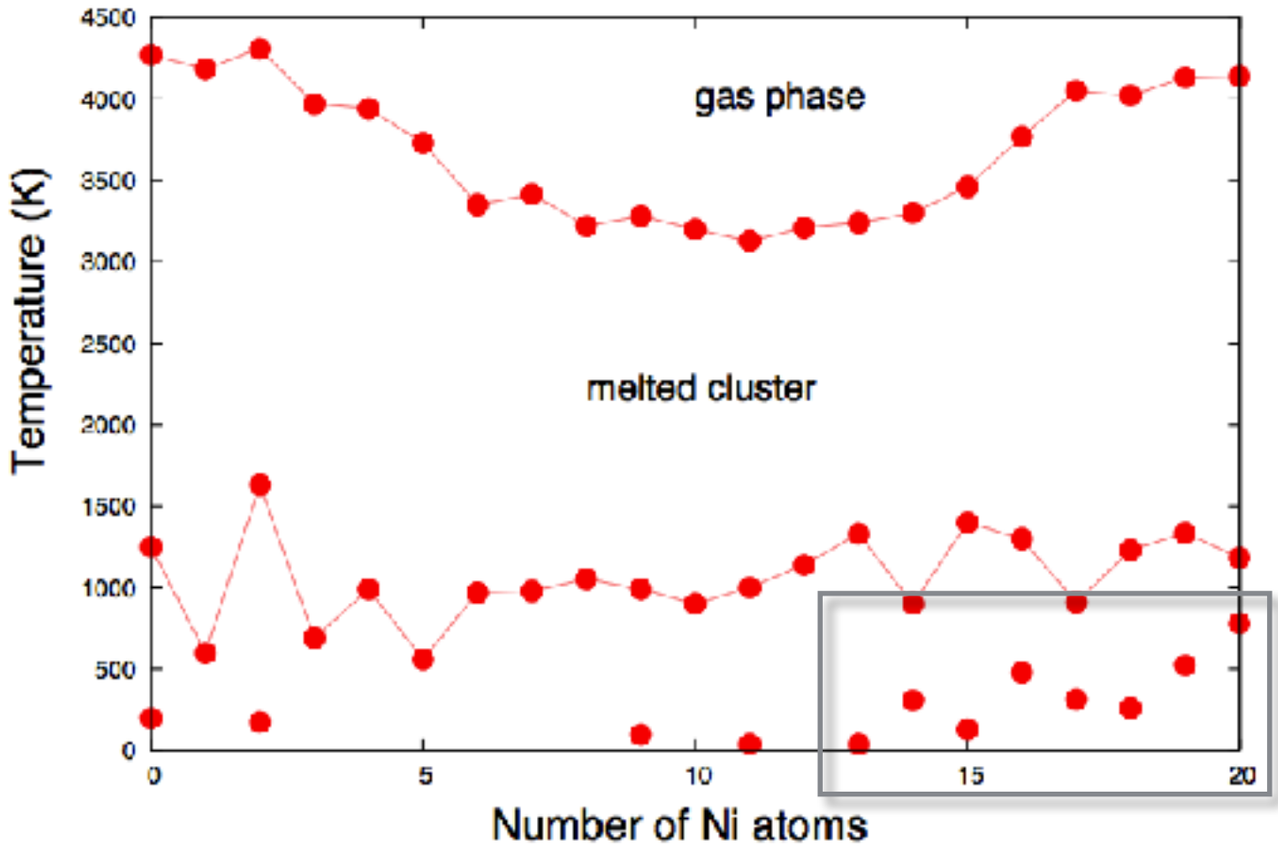
LJ_{38}

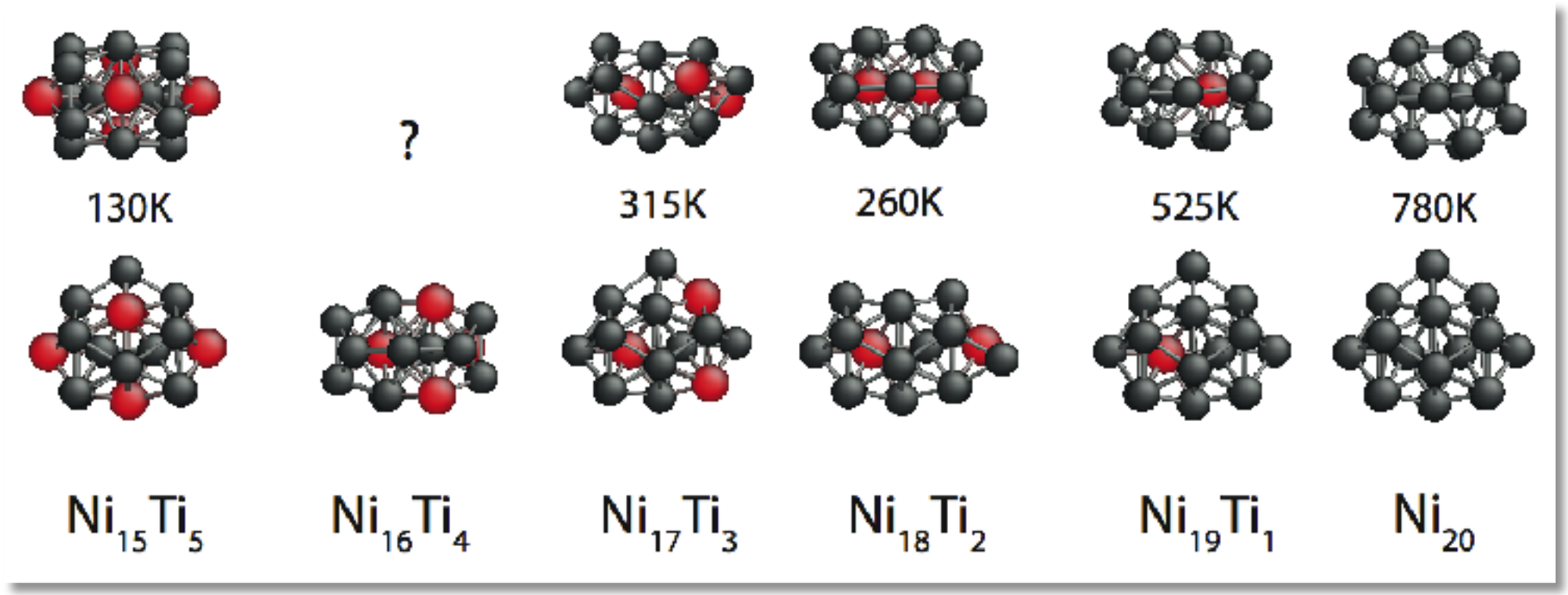


Disconnectivity graph
(DJ Wales, Phil. Trans. R. Soc. A (2012))

Partay *et al*., JPC B **114**, 10502 (2010)

Phase Diagram of Ni_xTi_y cluster





Conclusions

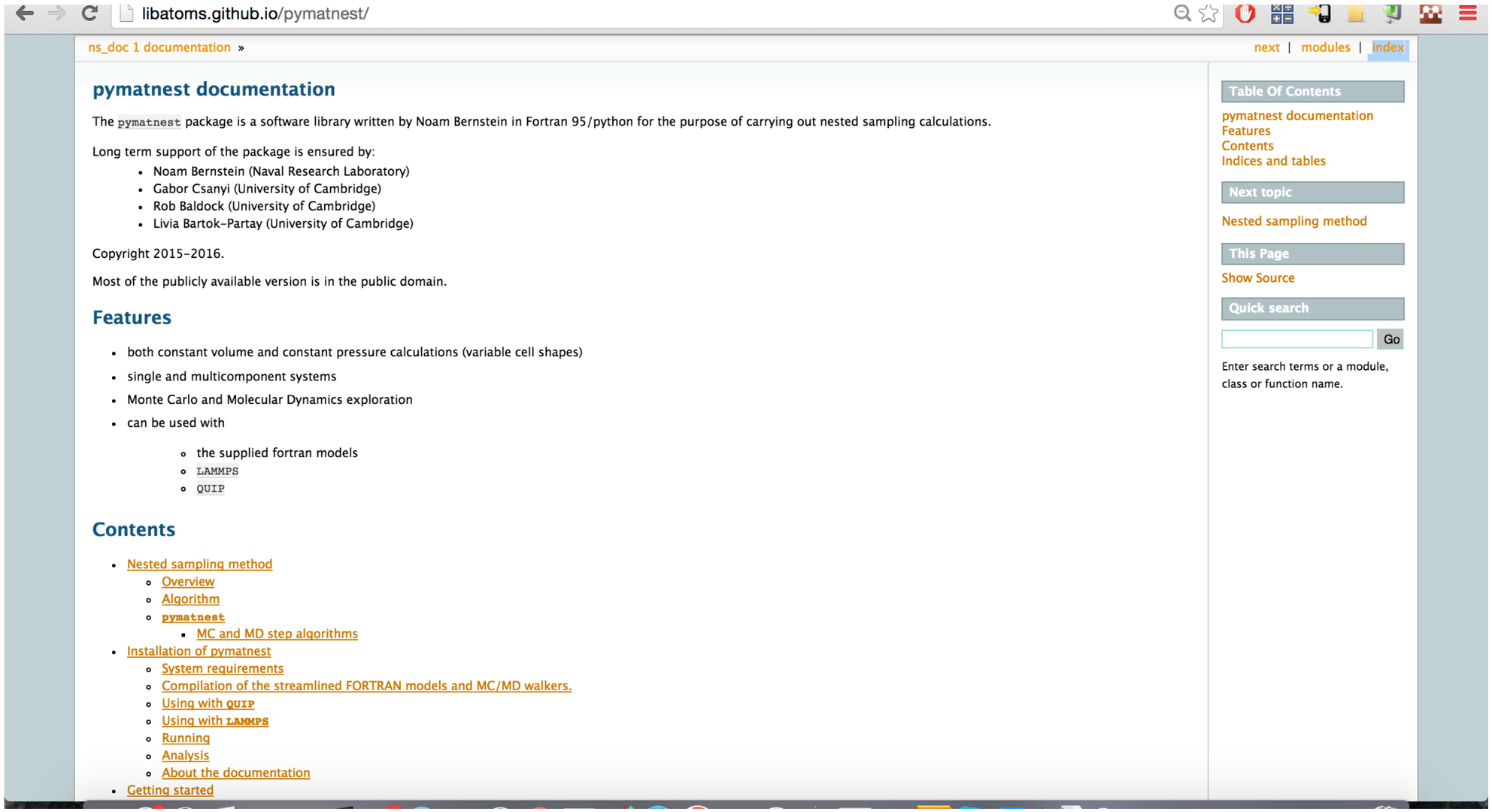
Nested sampling is an unbiased sampling technique,

- sampling independent of temperature
- no prior knowledge of the phases necessary
- entire phase diagram can be calculated
- periodic systems, clusters, multicomponent systems
- next steps:
    - molecules
    - potential development

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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Cambridge

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