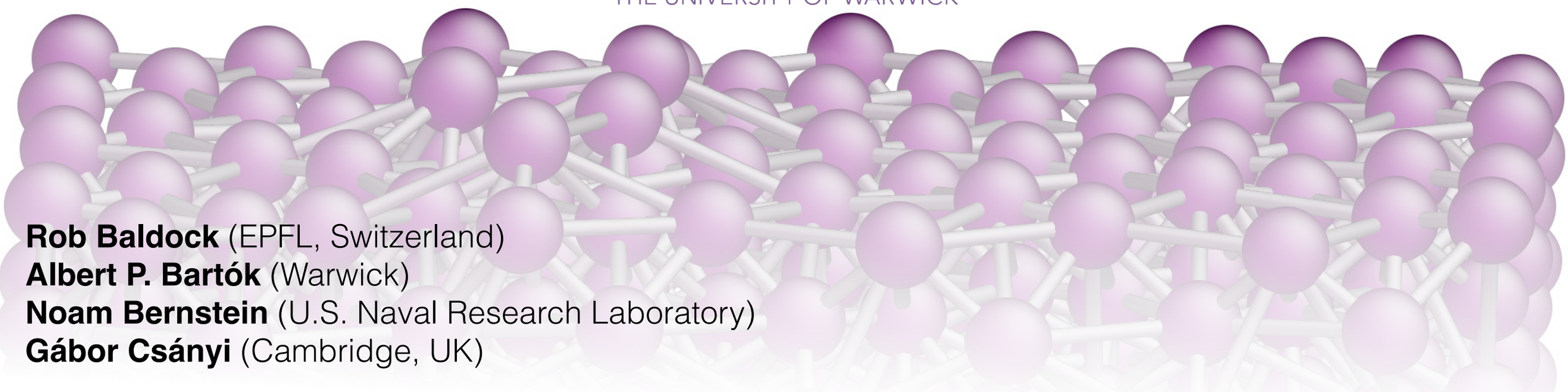
High-throughput computational thermodynamics

* exploring potential energy landscapes with Nested Sampling *

Livia Bartók-Pártay

Department of Chemistry
University of Warwick, UK

WARWICK
THE UNIVERSITY OF WARWICK



Rob Baldock (EPFL, Switzerland)
Albert P. Bartók (Warwick)
Noam Bernstein (U.S. Naval Research Laboratory)
Gábor Csányi (Cambridge, UK)

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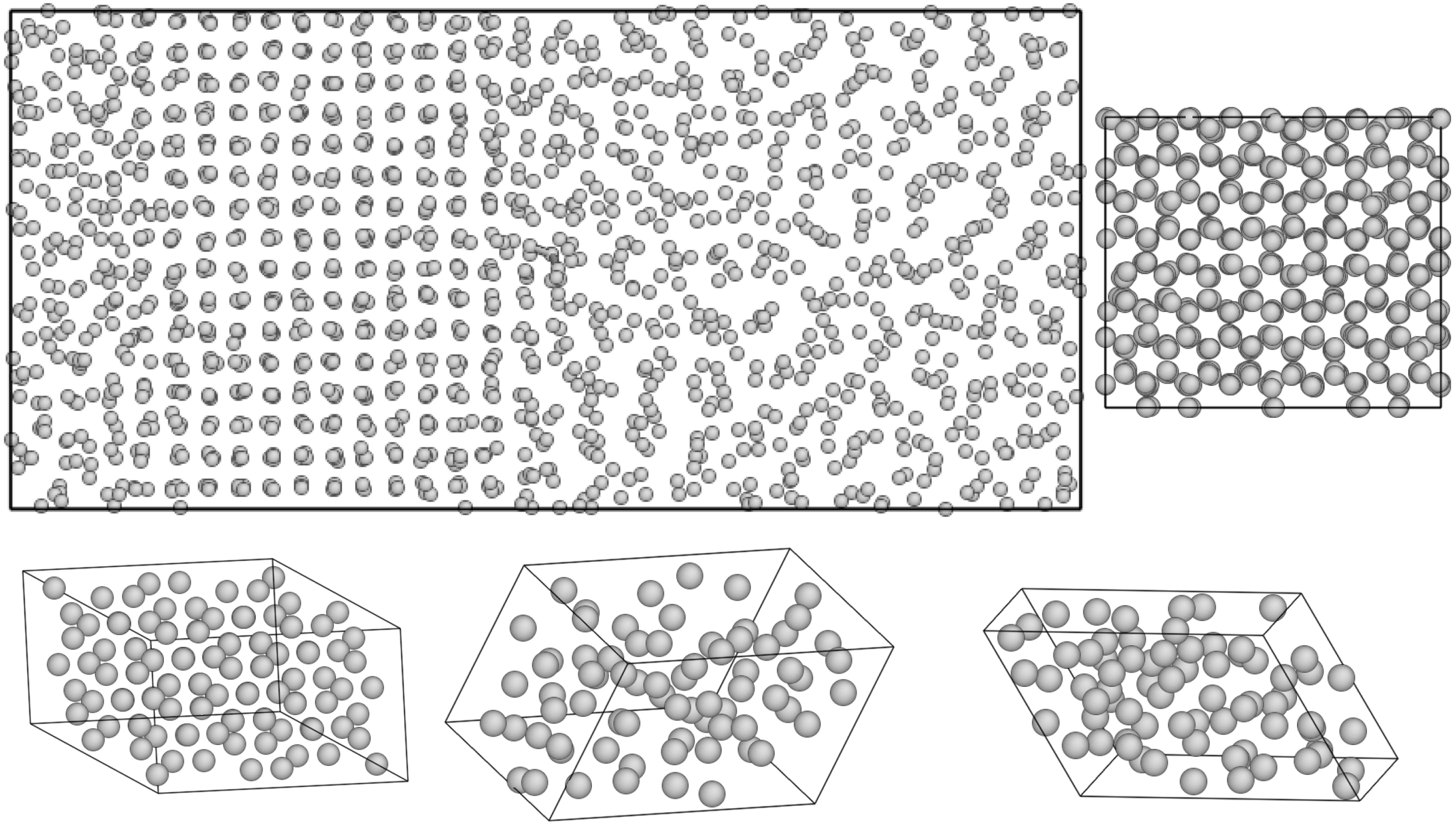
Sampling the Potential Energy Landscape

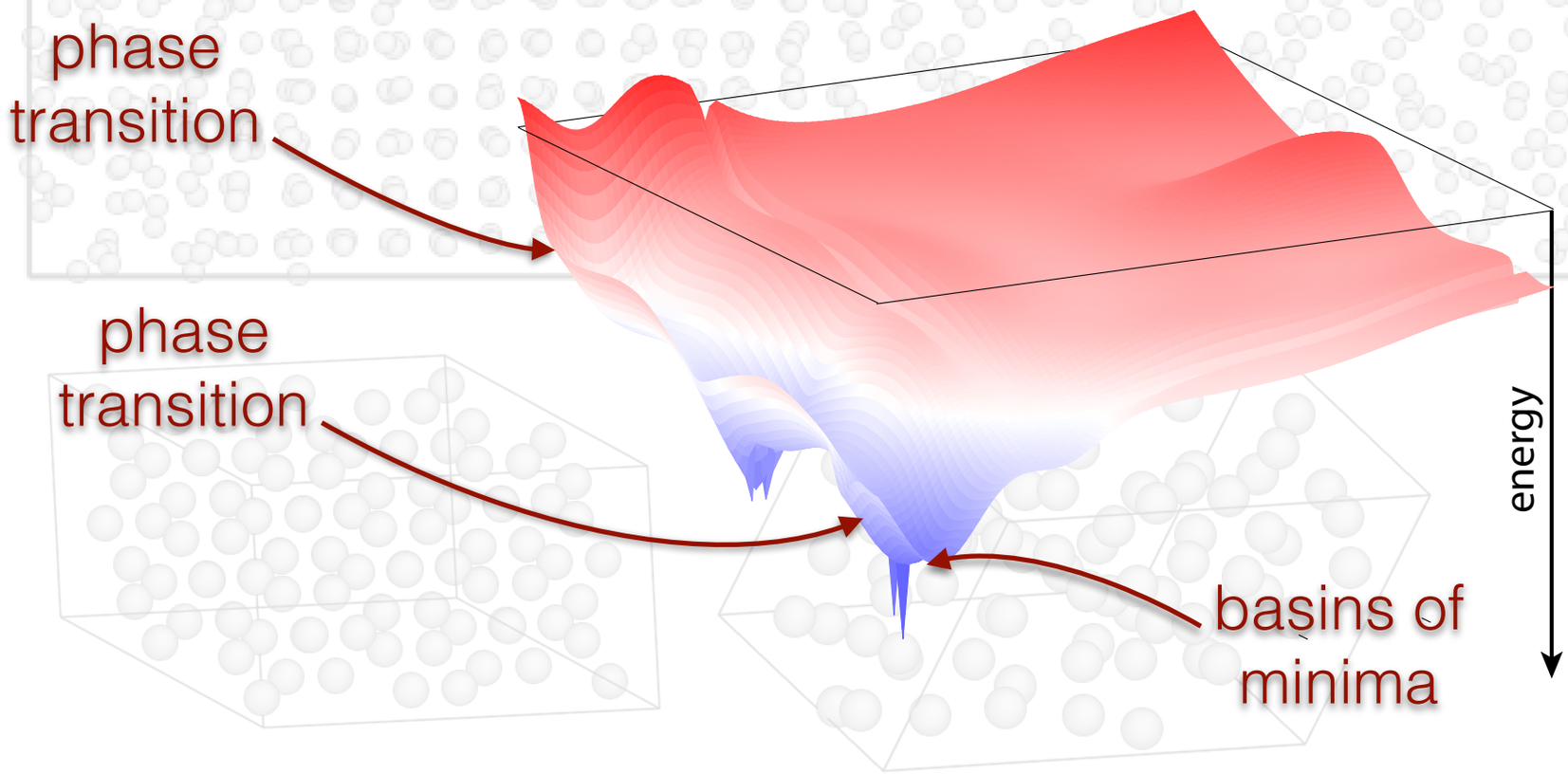
How to generate relevant atomic configurations?



Sampling the Potential Energy Landscape

How to generate relevant atomic configurations?

Aim: To have an unbiased sampling technique which can give an overview of the entire PES (THERMODYNAMICS), and can be automated:
not specific to a given part of the PES (GENERAL), where no prior knowledge of structures are necessary (PREDICTIVE).



Outline

- nested sampling algorithm
- example applications: *p-T* phase diagram of **metals**, **alloys** and **carbon**

How much can we trust potential models?

Nested Sampling

John Skilling, 2004, Bayesian statistics

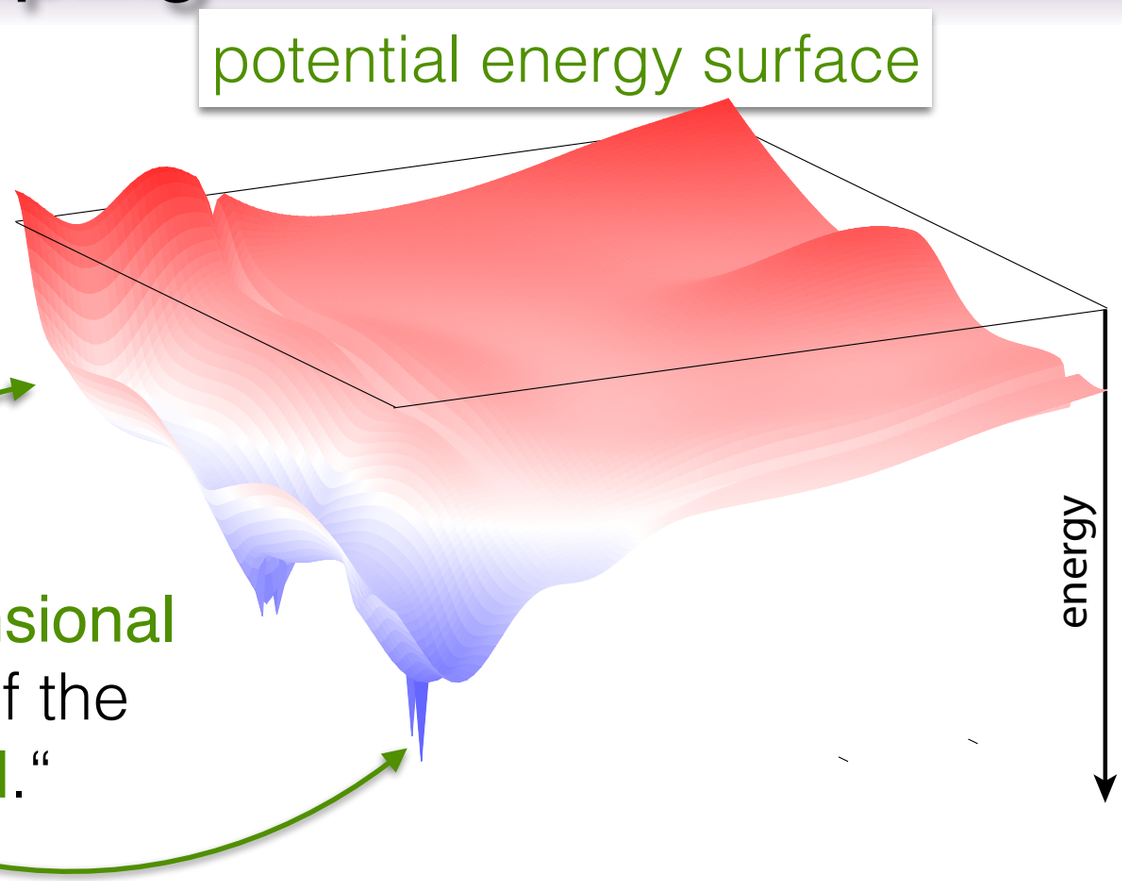
"...to sample probability densities in high-dimensional spaces where the regions contributing most of the probability mass are exponentially localised."

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

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

Nested Sampling

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."

basins of minima, Boltzmann-factor

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

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

partition function

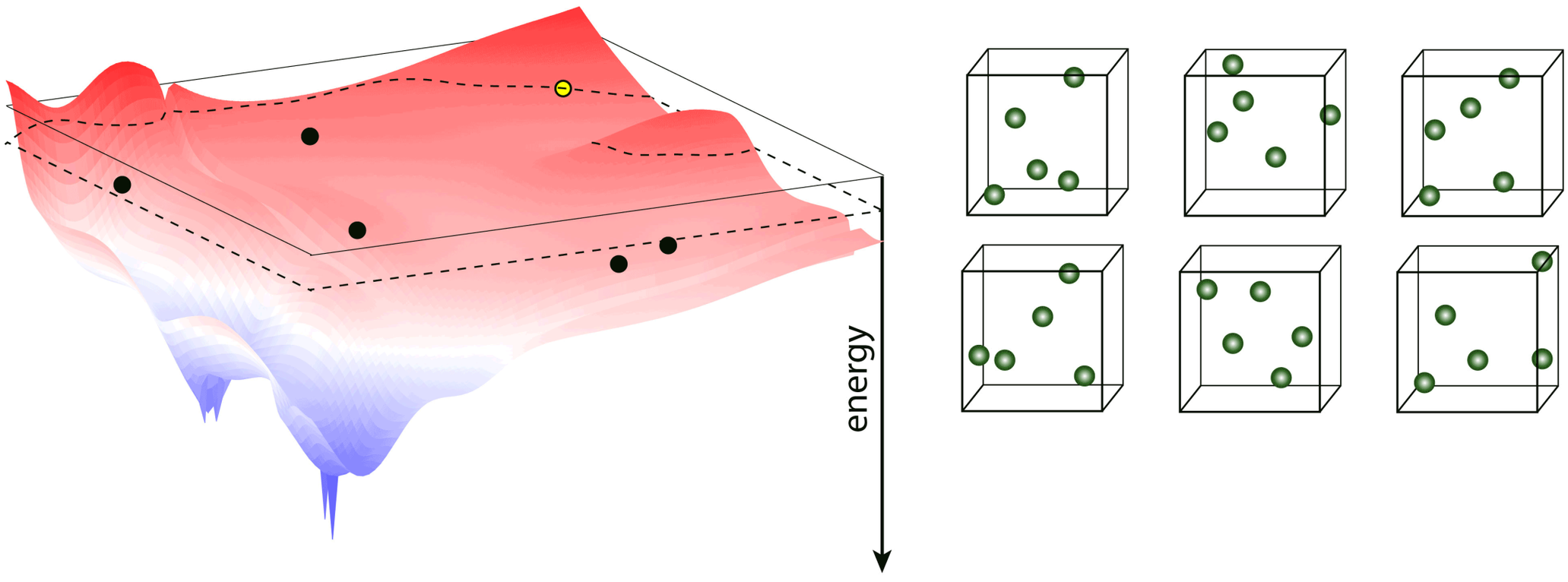
Boltzmann-factor (energy)

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”.

Starting set: generate *K* random samples **uniformly** in the total phase space volume



- Choose the sample (configuration) with the highest energy (the phase space volume within the contour is $K/(K+1)$ fraction of the previous)
- Generate a new point within the current contour (uniformly)
- Repeat until the “bottom” is found

Nested Sampling Algorithm

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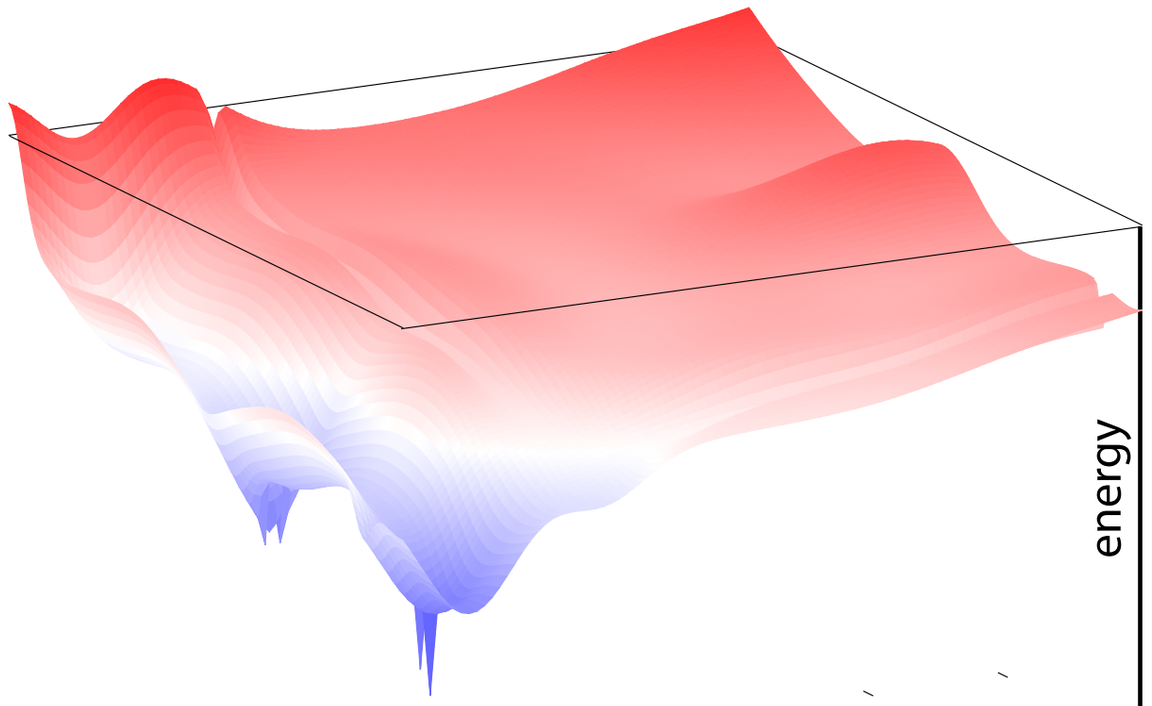
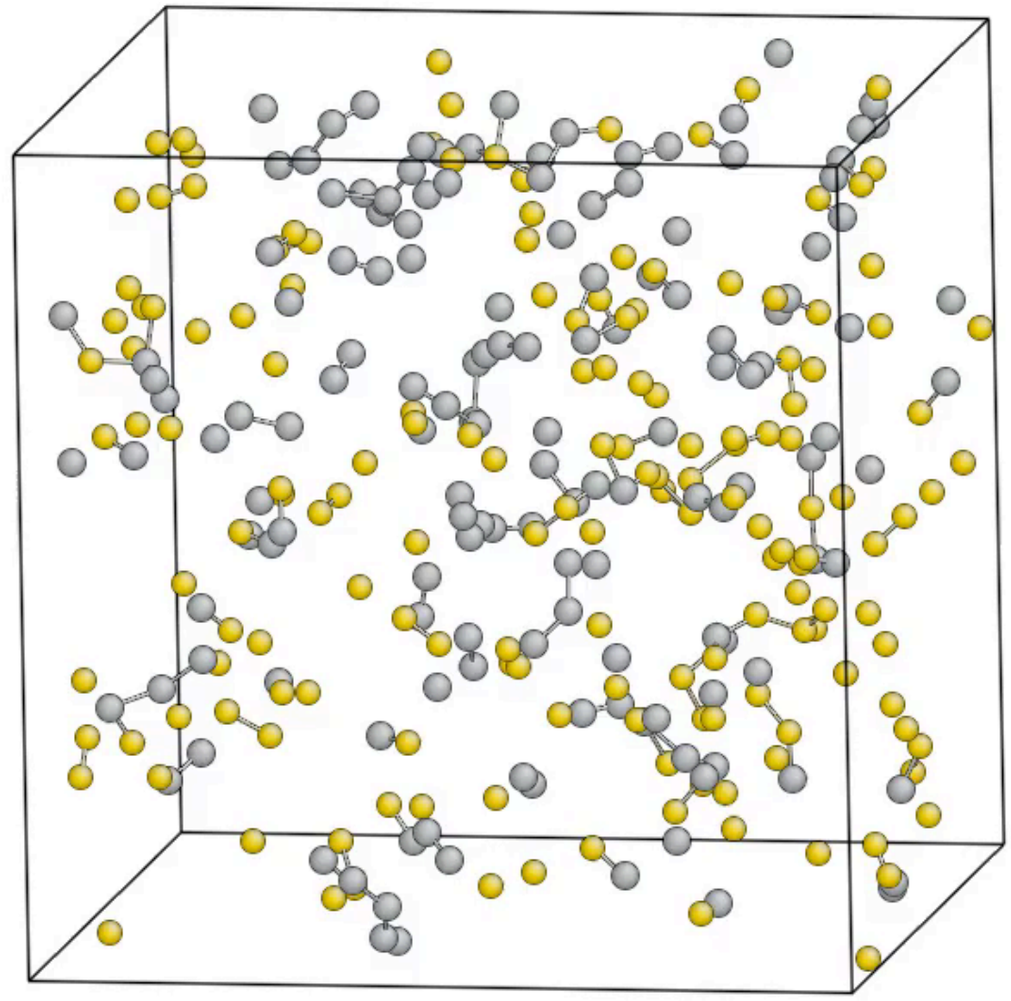




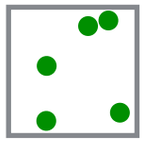
309 atoms (Cu and Pt) in fixed cell: cluster

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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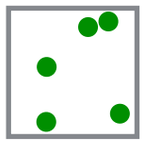

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…

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

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

…

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

Partition function:

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

Heat capacity
Free energy
Compressibility
…etc.

Nested Sampling Algorithm

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

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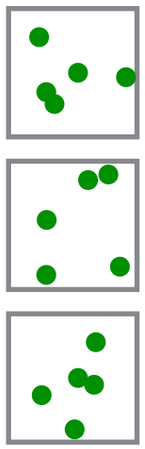

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\end{aligned}
$$

Advantages

- Entire PES is sampled - not specific or limited to a region
- Sampling itself independent from temperature
- Can be done with both (*N,V,T*) and (*N,p,T*)
- Easy control parameter of the sampling is *K*, ca
  or the "walkers" (is the resolution of the PES)
- No need for prior knowledge of the structures

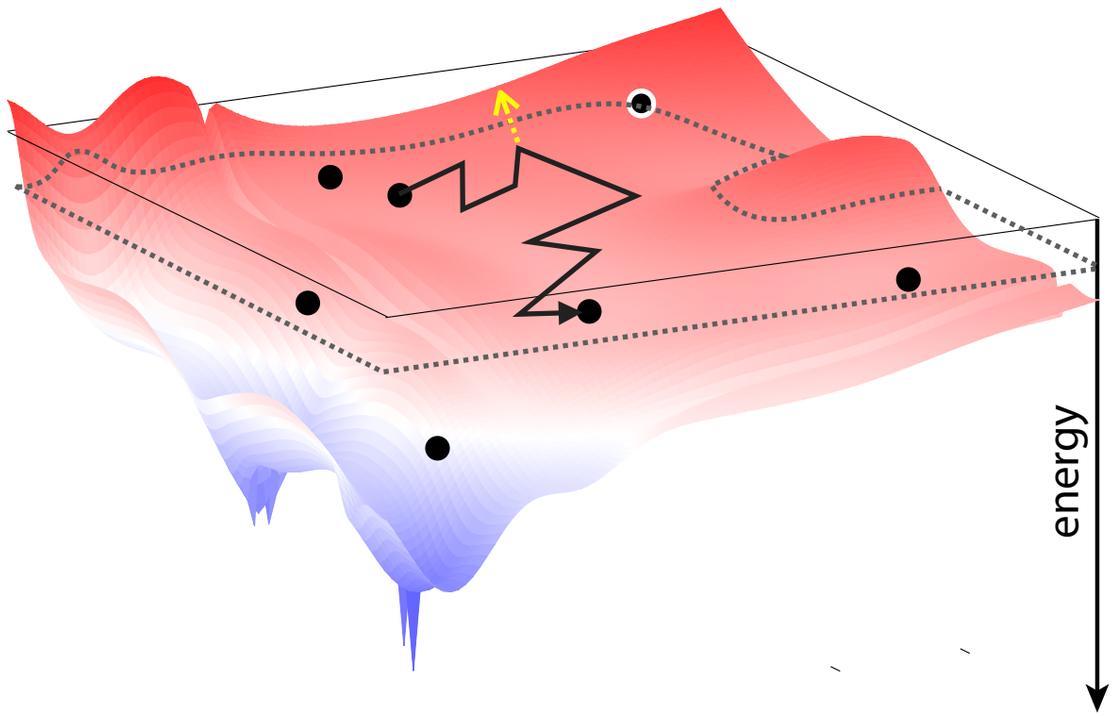
PREDICTIVE!

found new, more stable structure for…

* NiTi (EAM)
* Li (EAM)
* Lennard-Jones

Typical *K*: ~1000-2000
Typically 10^6 iterations

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)

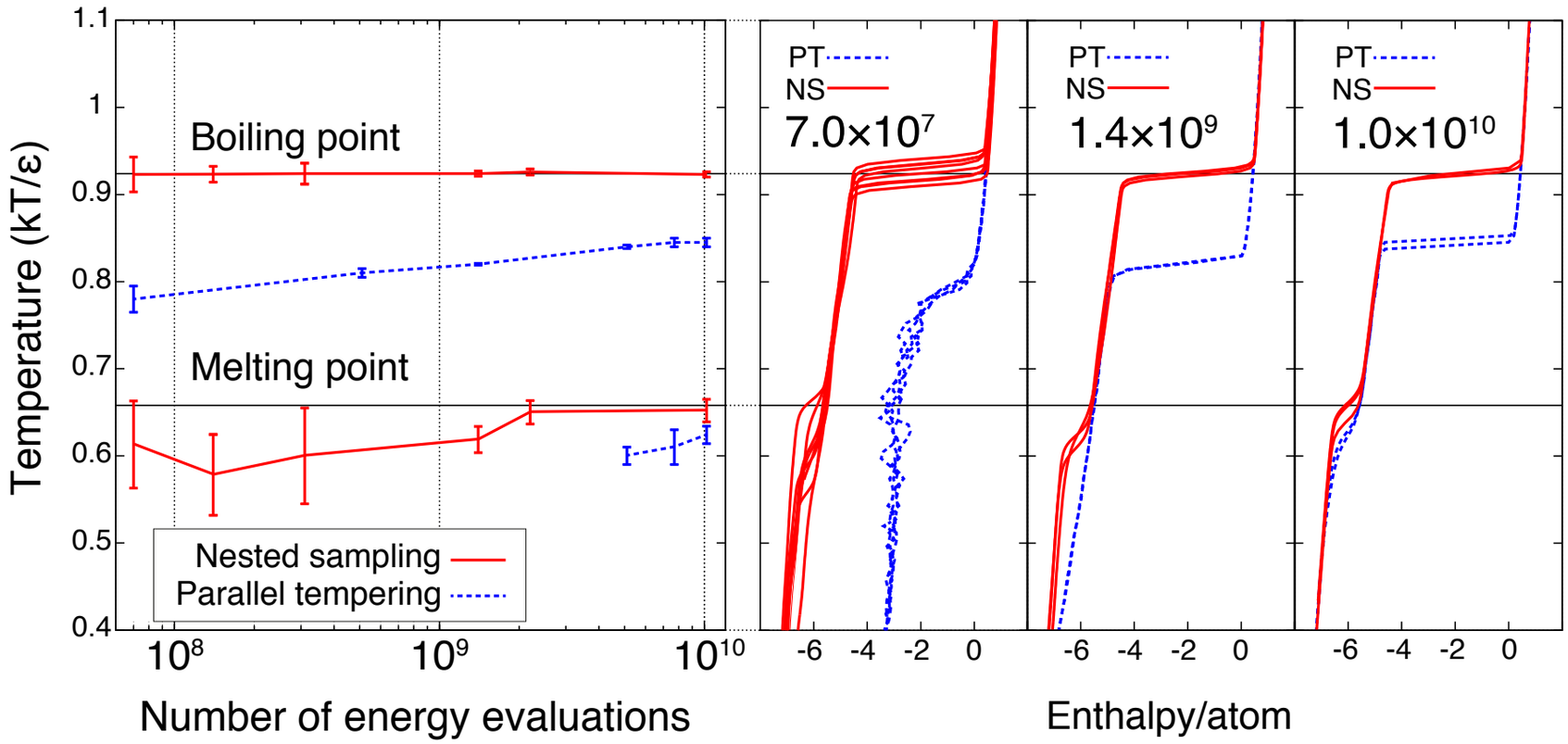
- **Total Enthalpy Hamiltonian Monte Carlo (TE-HMC)**
  short constant total energy MD trajectories

- **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.

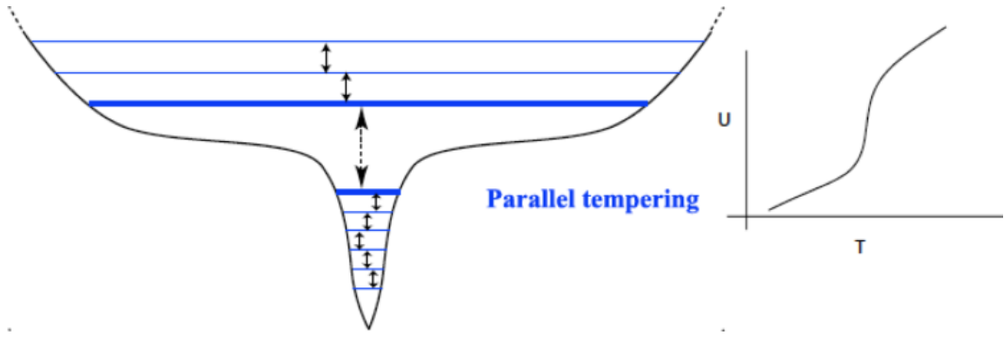
Computational cost comparison

64 LJ atoms at constant pressure

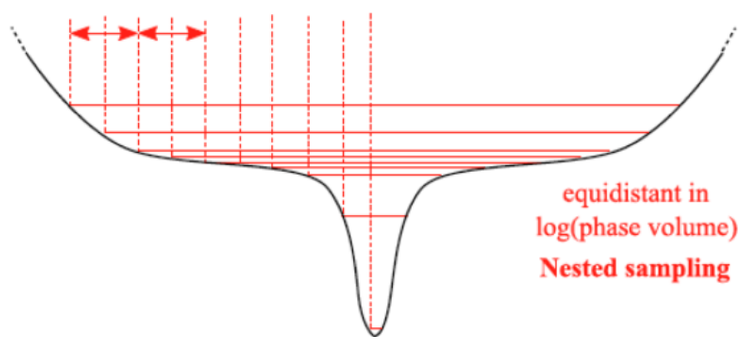


Nested Sampling vs. Parallel Tempering

levels equidistant in temperature



levels equidistant in log(phase volume)



N,P,T (periodic systems)

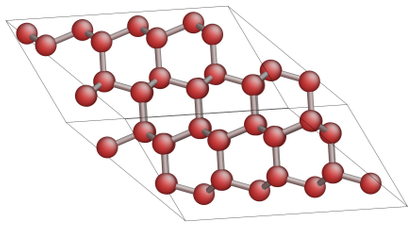
Aluminium [*PRB* (2016),93:174108]

Iron [*Comp.Mat.Sci.* (2018),149:153]

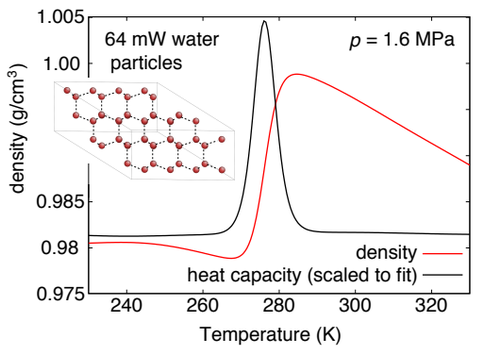
Lithium [J.*Phys.Chem.B* (2020), *in press*]

Hard sphere model system [*PRE* (2014),89, 022302]

coarse grain water: mW [*PRE* (2016),96:043311]



p=1.6 MPa

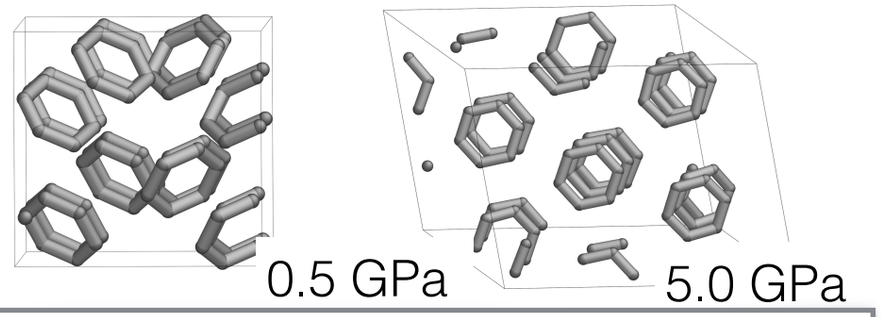


Binary Lennard-Jones [*PRE* (2016),96:043311]

NiTi shape memory alloy [*PRB* (2016),93:174108]

single bead (LJ) spring polymer [*PRE* (2016),96:043311]

Benzene

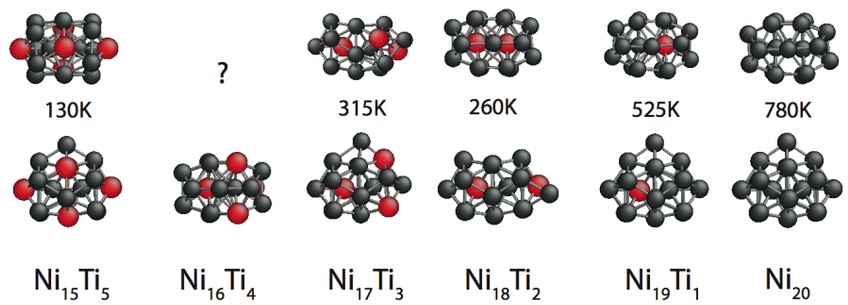


0.5 GPa 5.0 GPa

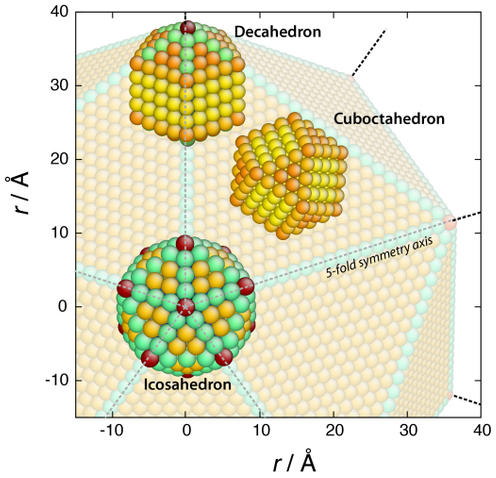
N,V,T (clusters)

Lennard-Jones (LJ_5 - LJ_{38}) [*JPC* (2010),114:10502]

Ni_xTi_y binary clusters



CuPt nanocluster [*Sci.Rep.* (2018),8:9150]



mW and TIP3P water clusters [*PCCP*(2019),21:7305]

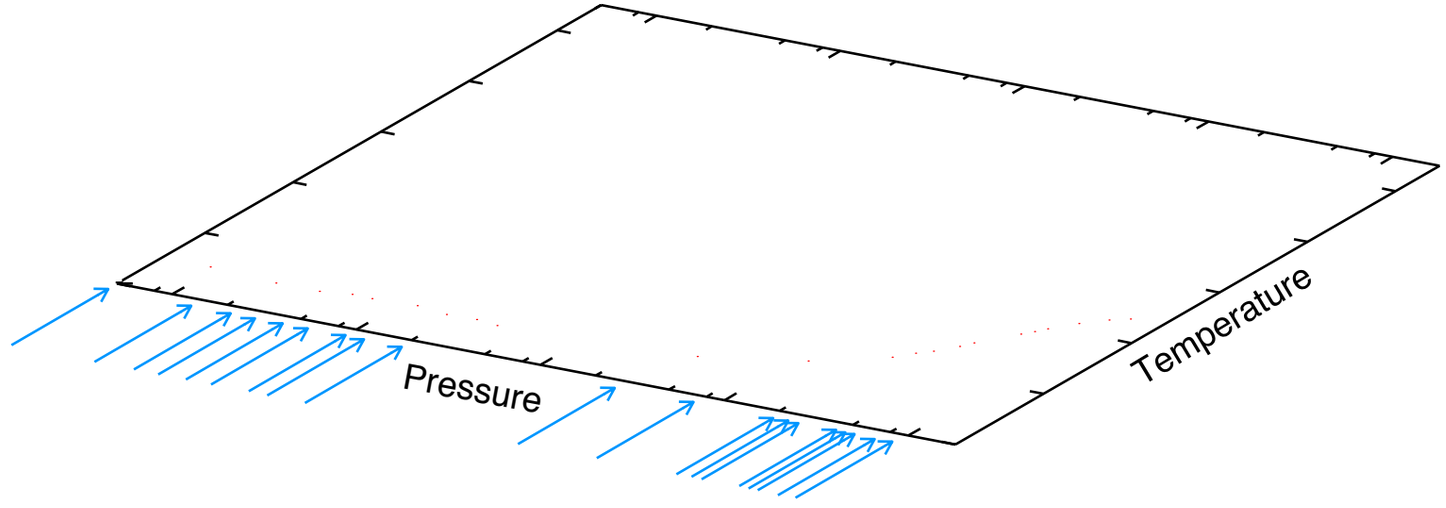
Nested transition path sampling

[*PRL* (2018),120:250601]

Quantum partition function

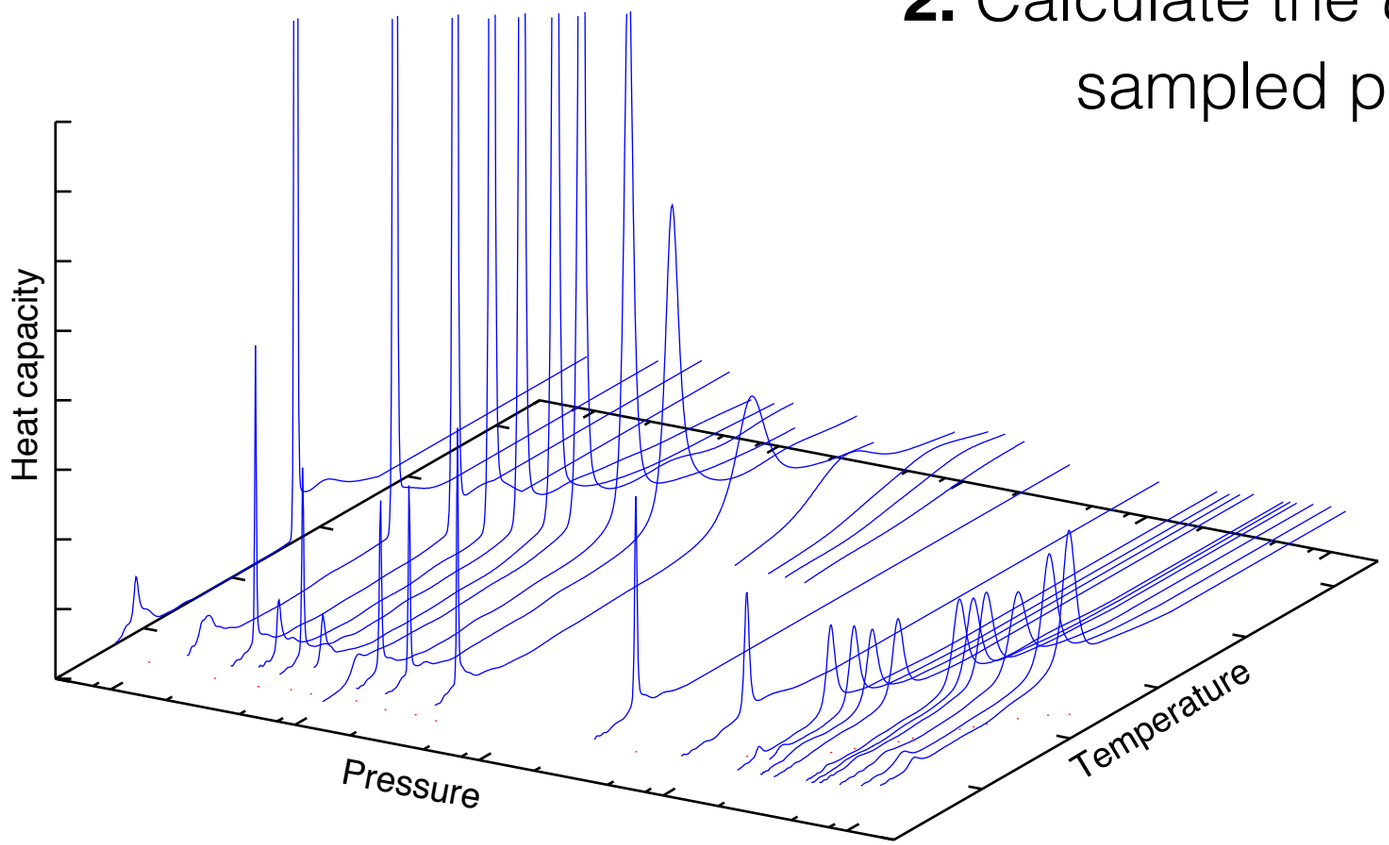
[*JCTC* (2018),14:4353]

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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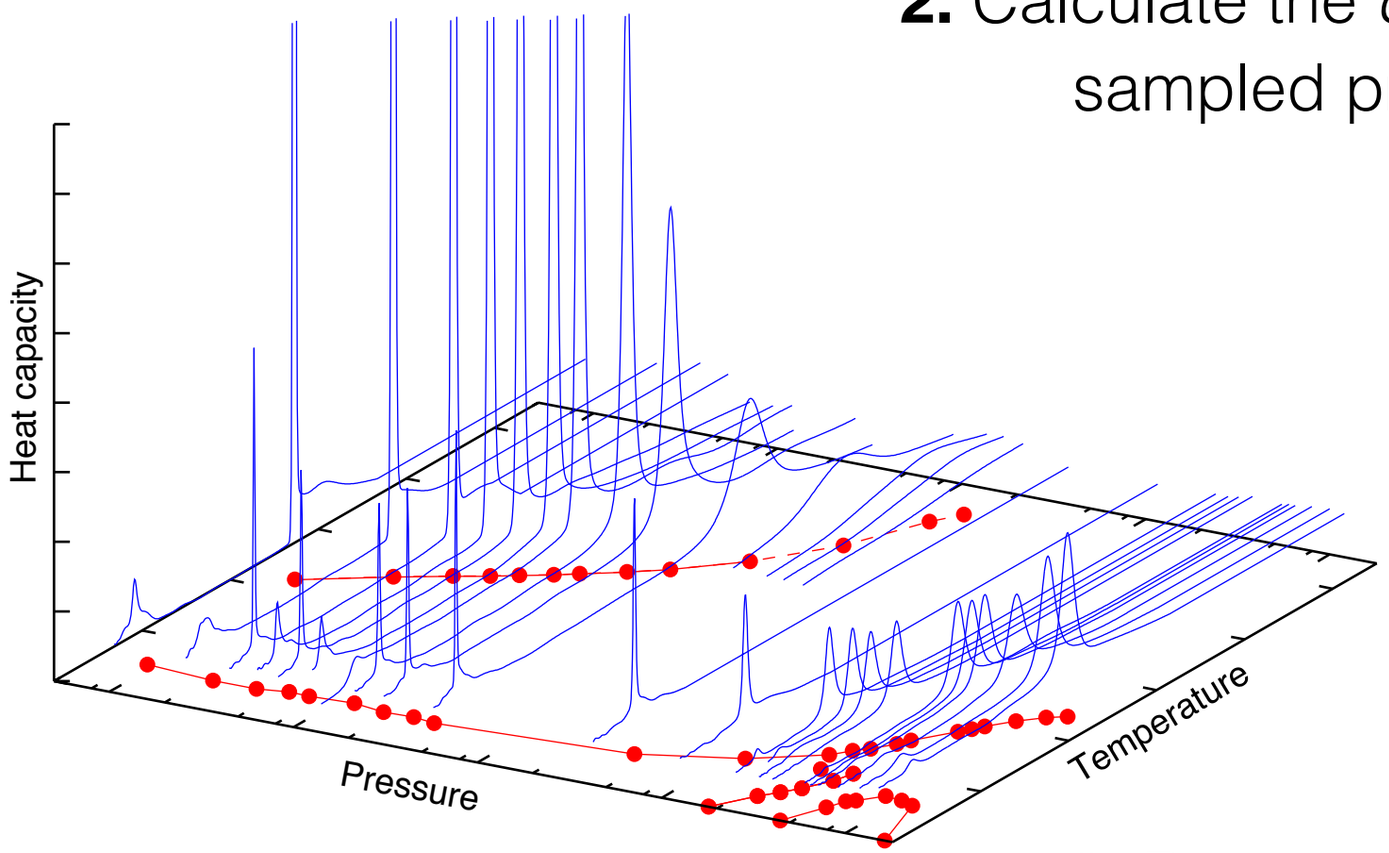
p-T phase diagram “in three steps”



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

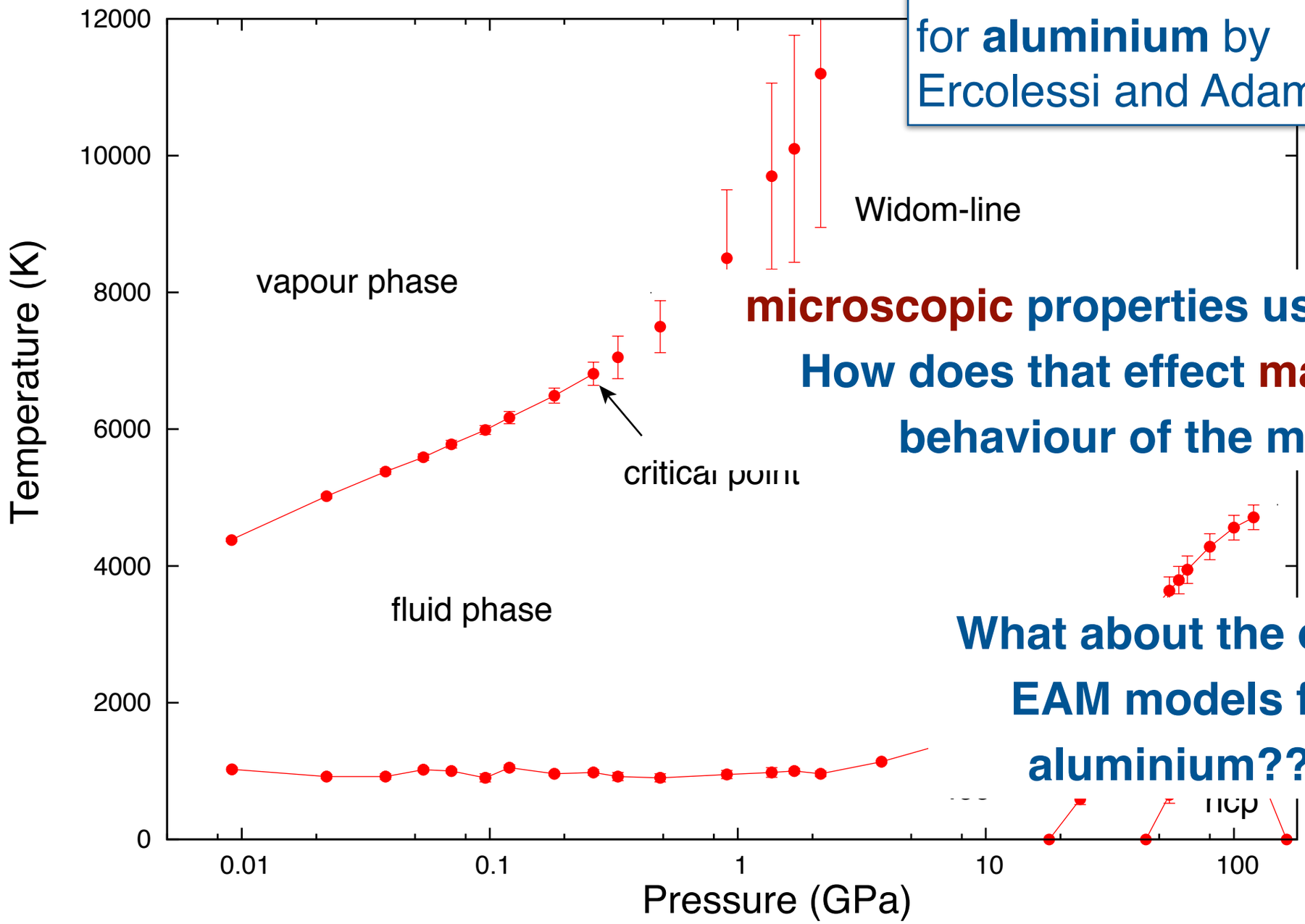
2. Calculate the $c_p(T)$ for every sampled pressure.

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

p-T phase diagram!

p-T phase diagram “in three steps”

Embedded atom model for **aluminium** by Ercolessi and Adams

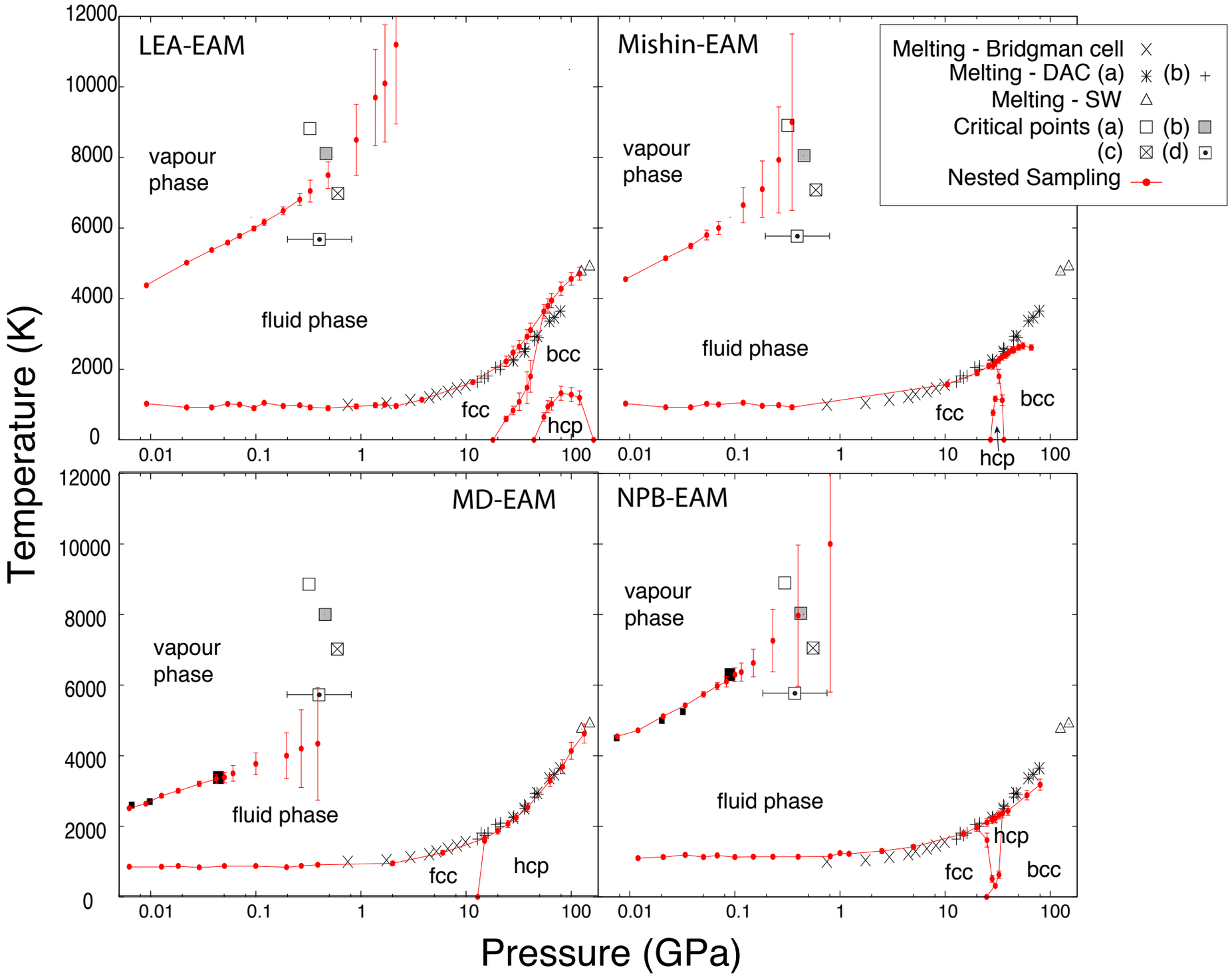


microscopic properties used for fitting

How does that effect macroscopic behaviour of the model?

What about the other EAM models for aluminium???

Phase Diagram of Aluminium



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

Phase Diagram of Lithium

nature physics
LETTERS
PUBLISHED ONLINE: 9 JANUARY 2011 | DOI: 10.1038/NPHYS1864

Cold melting and solid structures of dense lithium

Christophe L. Guillaume[1], Eugene Gregoryanz[1]*, Olga Degtyareva[1], Malcolm I. McMahon[1], Michael Hanfland[2]*, Shaun Evans[2], Malcolm Guthrie[3], Stanislav V. Sinogeikin[4] and H-K. Mao[3,4]

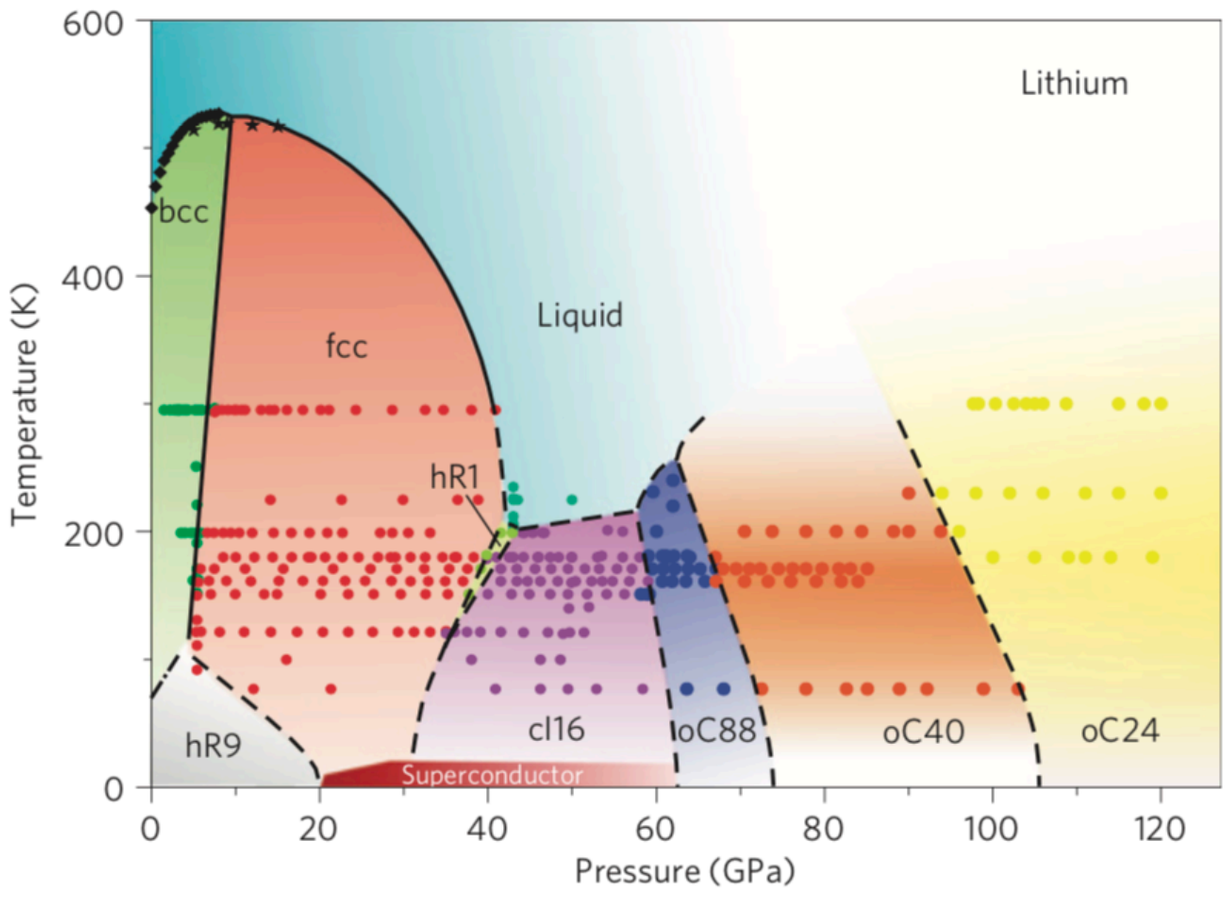


Figure 1 | Proposed phase diagram of lithium over a wide pressure–temperature range. Apart from bcc and fcc, the phases are

Nested sampling calculations:

with 64 and 60 atoms
1000-3000 walkers

EAM by Belashchenko

bcc lattice parameter, elastic constants, vacancy formation energy, surface properties, liquid and solid density, high pressure properties

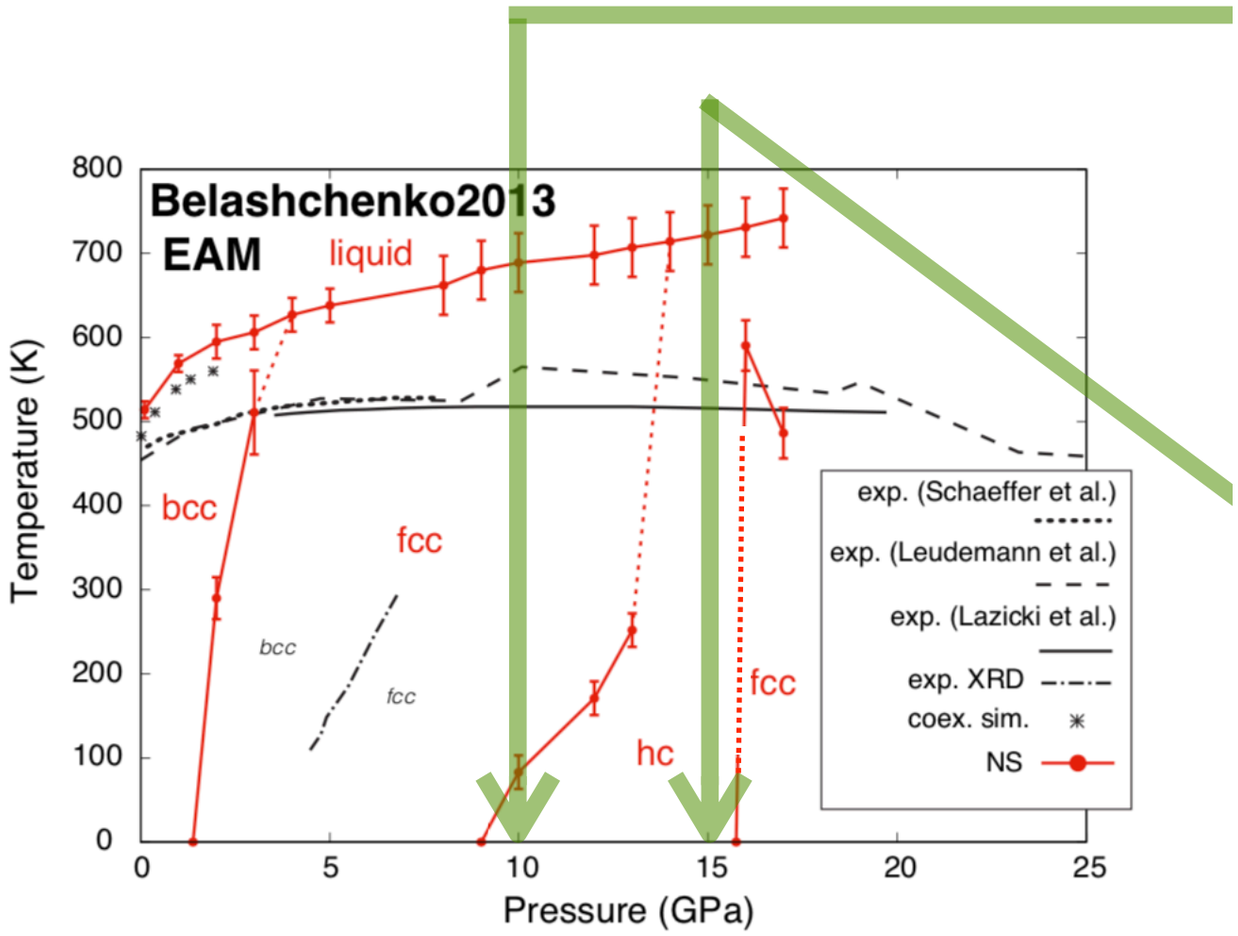
EAM by Nichol and Ackland

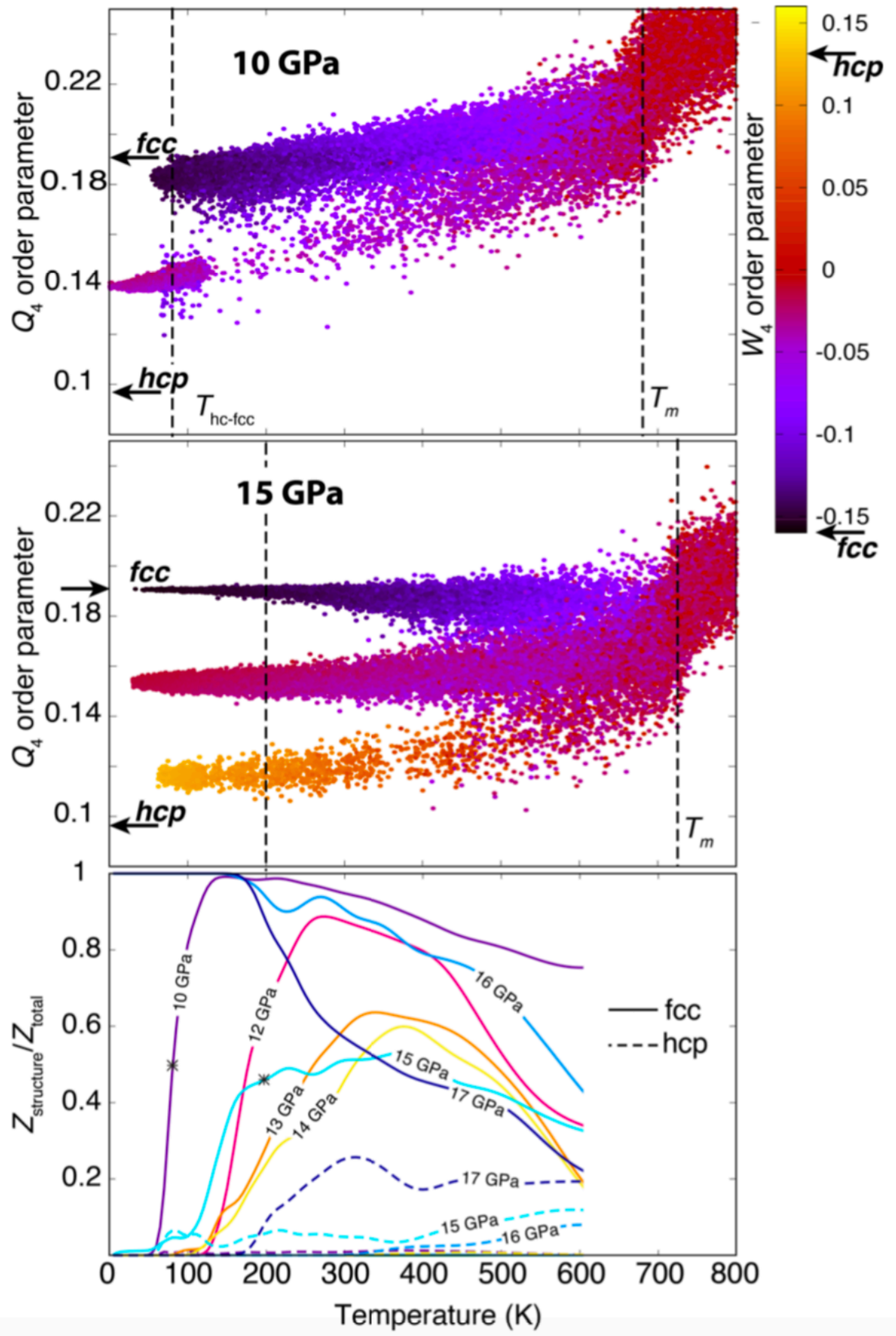
bcc lattice parameter, elastic constants, cohesive energy, unrelaxed vacancy formation energy

2NN-MEAM by Ko and Jeon

force matching algorithm - DFT database of fcc, bcc, hcp configuration 0K and finite temperature

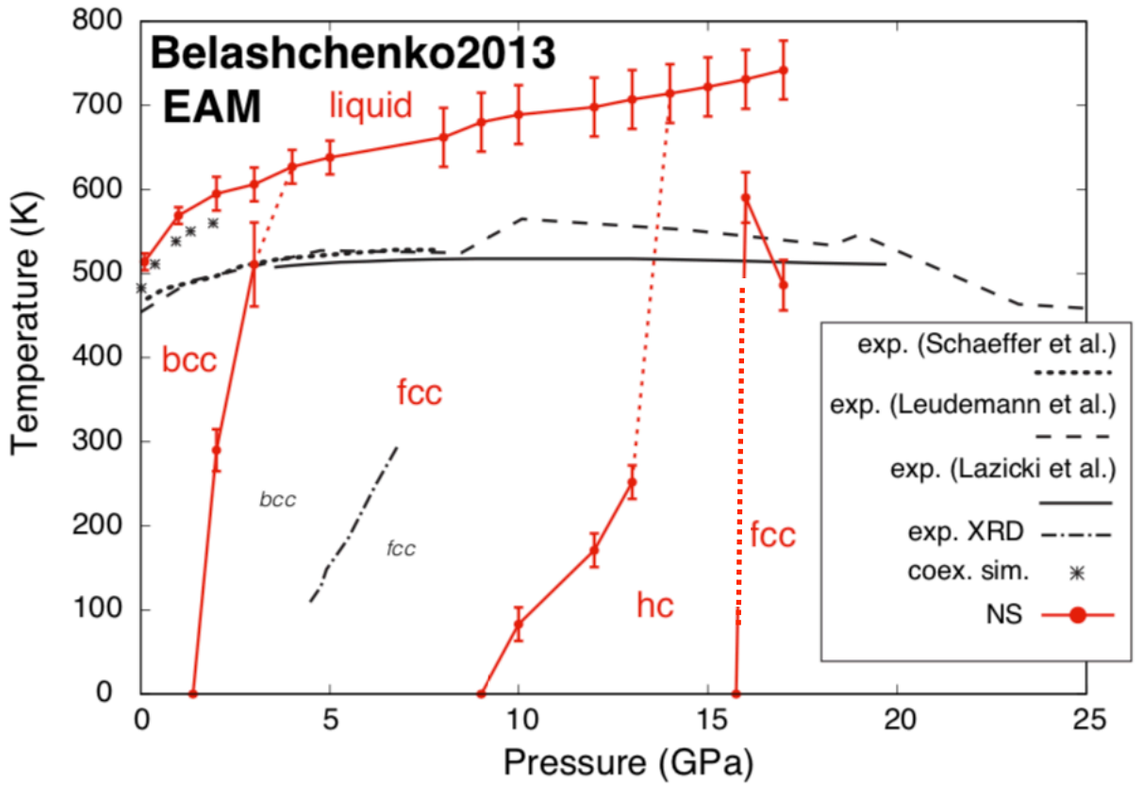
Phase Diagram of Lithium

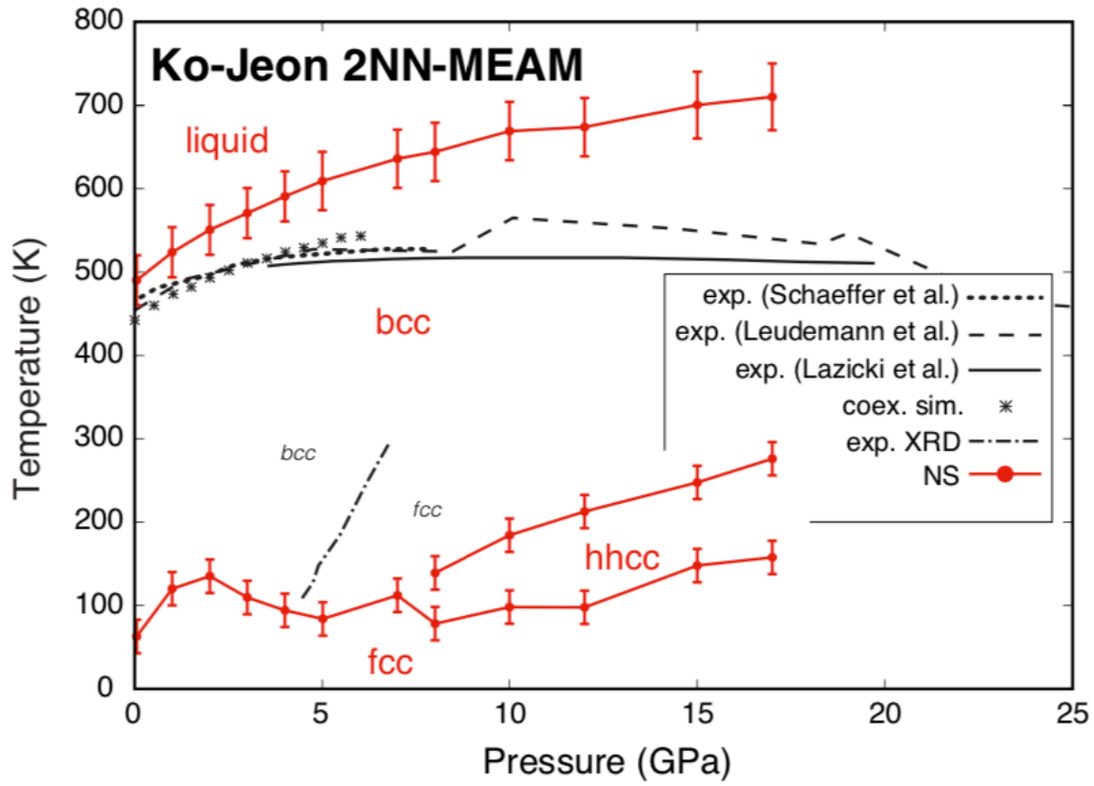




Dorrell and Pártay, *JPCB*. **in press**, (2020)

Phase Diagram of Lithium





Dorrell and Pártay, *JPCB*. **in press**, (2020)

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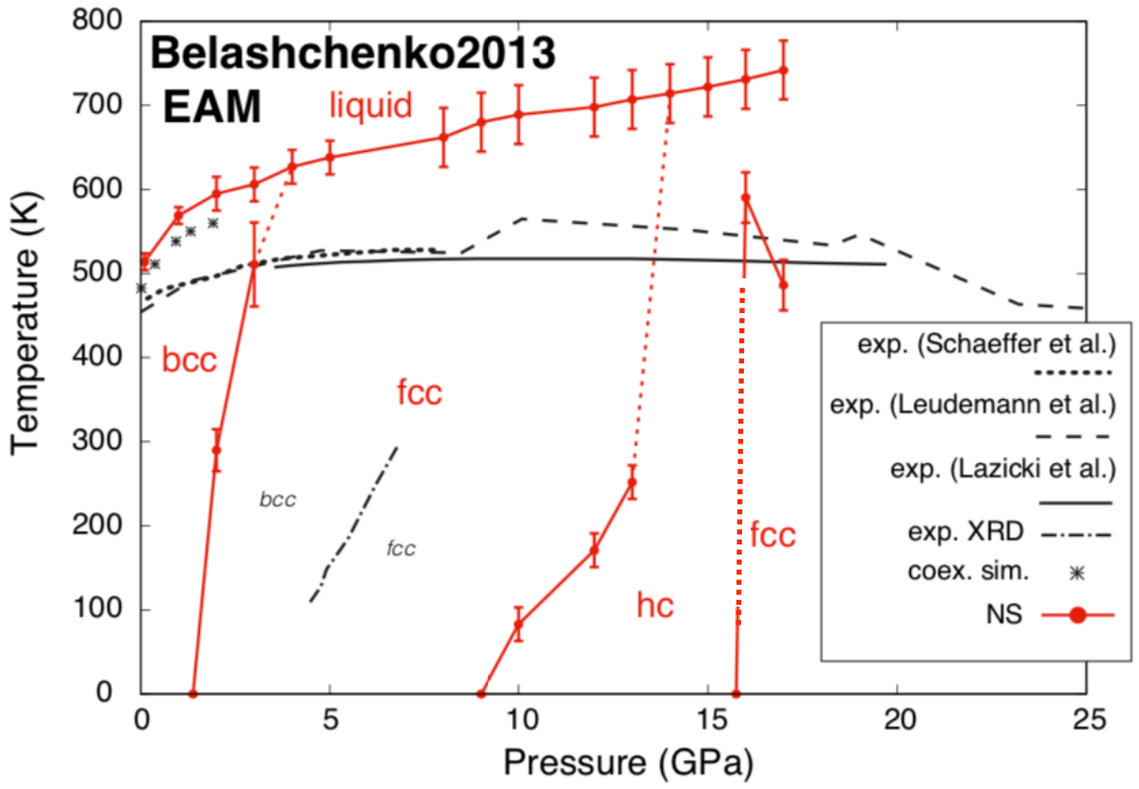

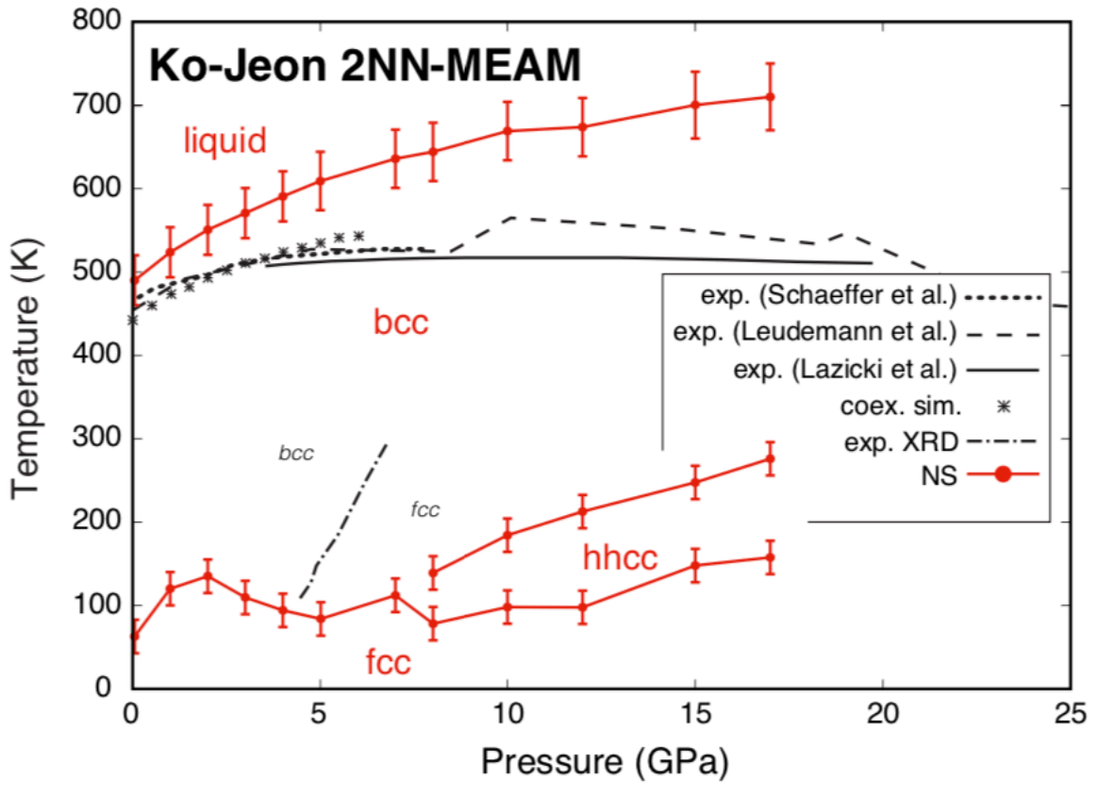

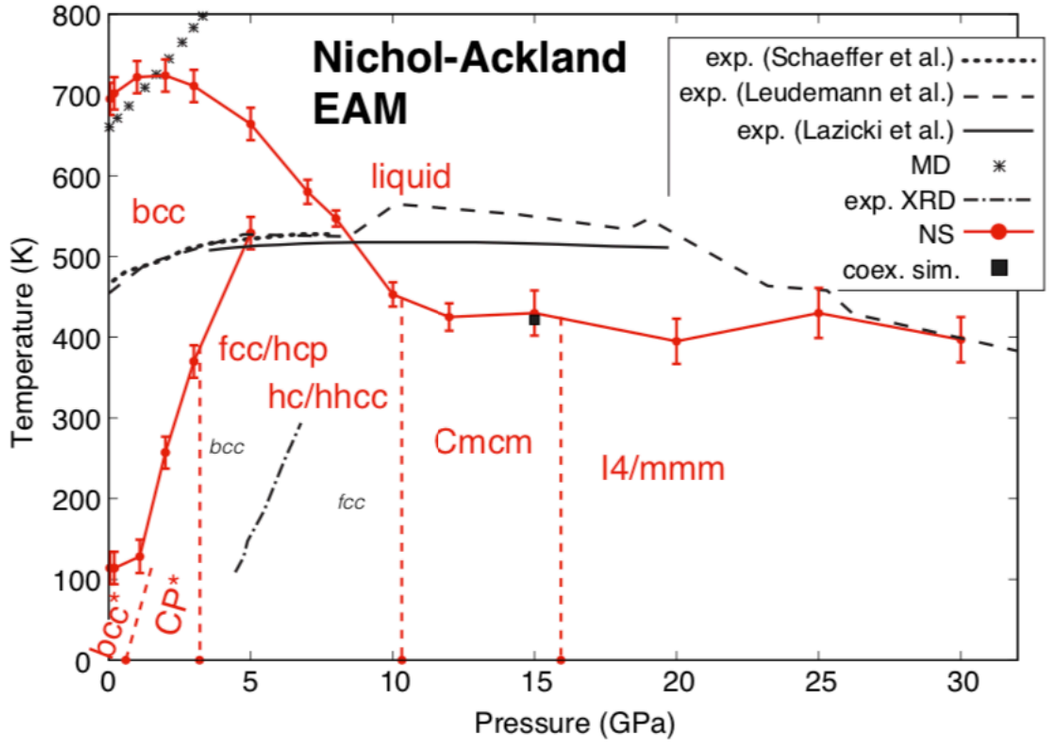

Dorrell and Pártay, *JPCB*. **in press**, (2020)

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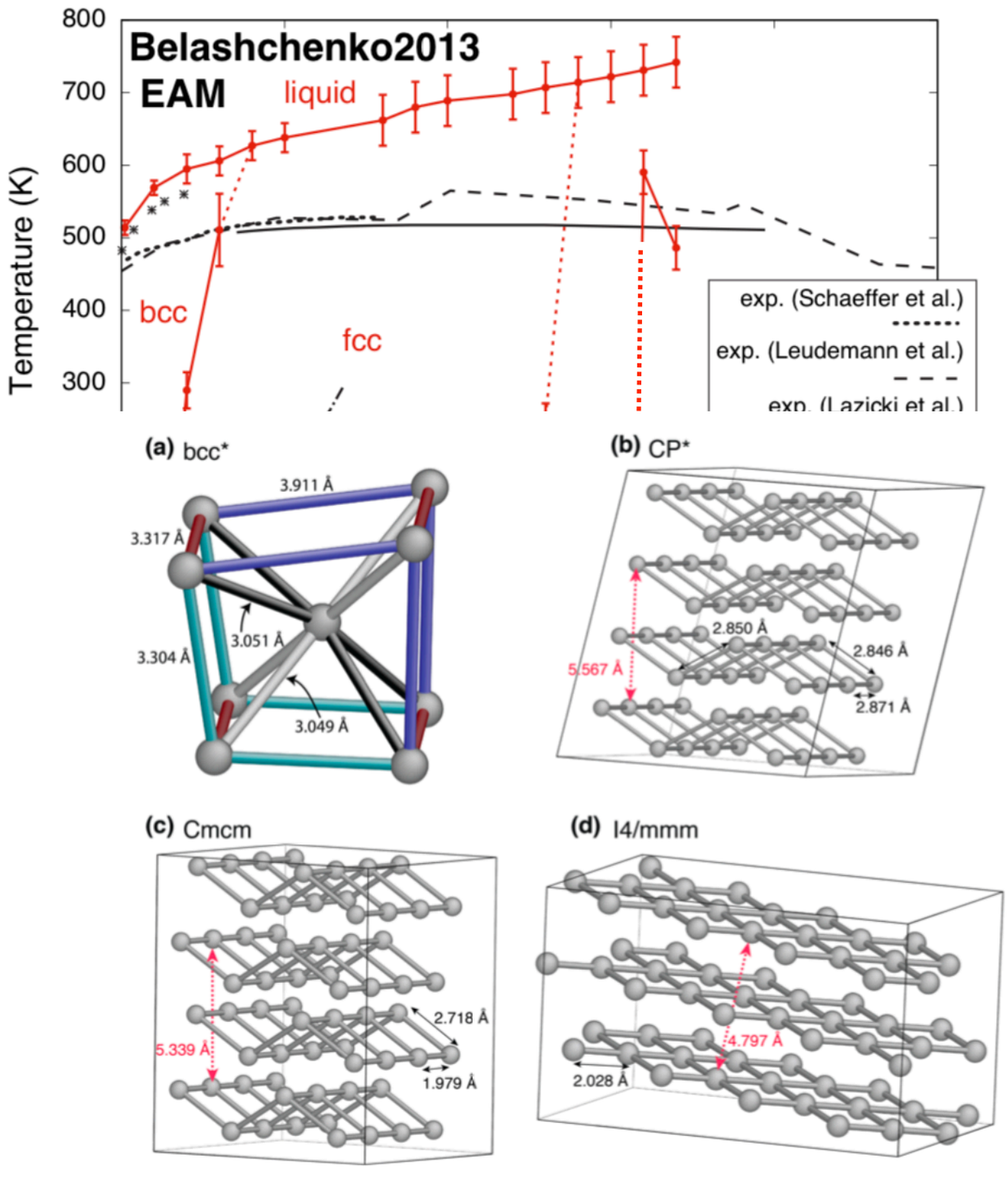
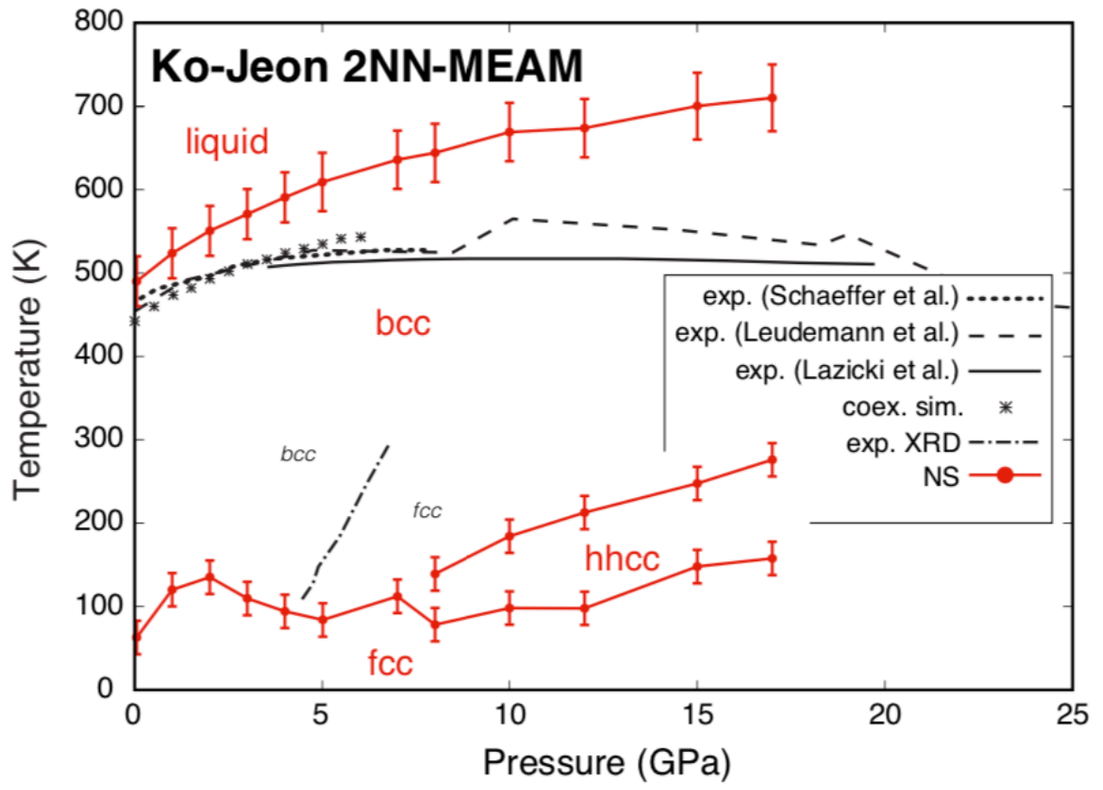
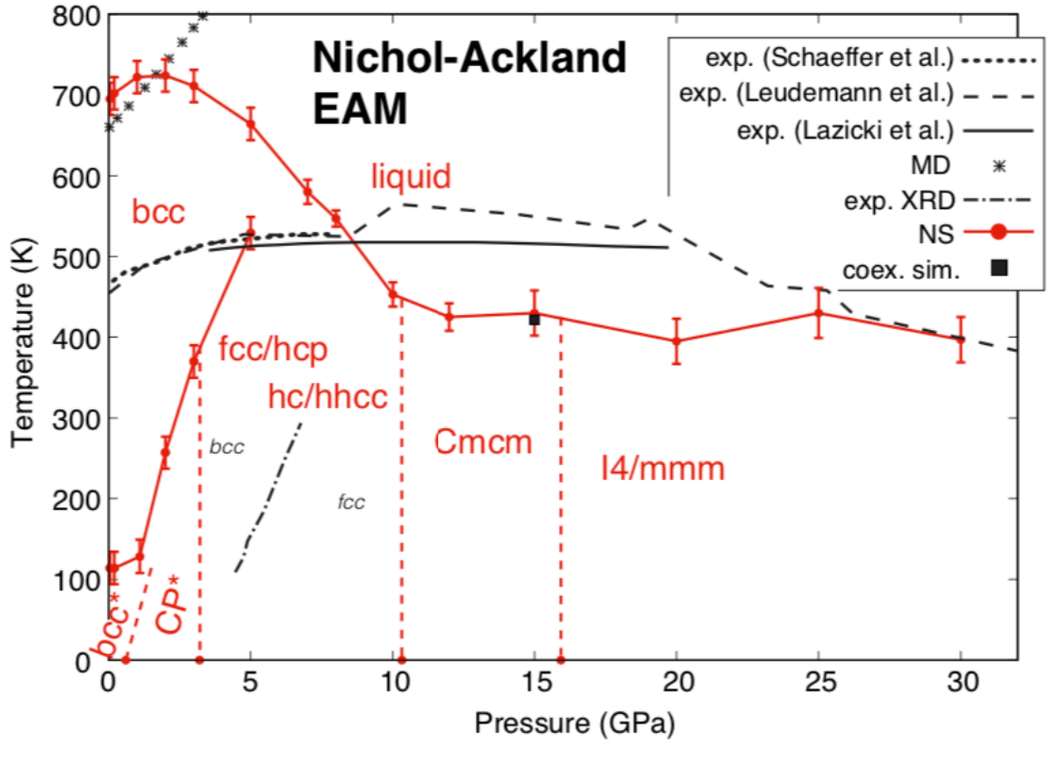


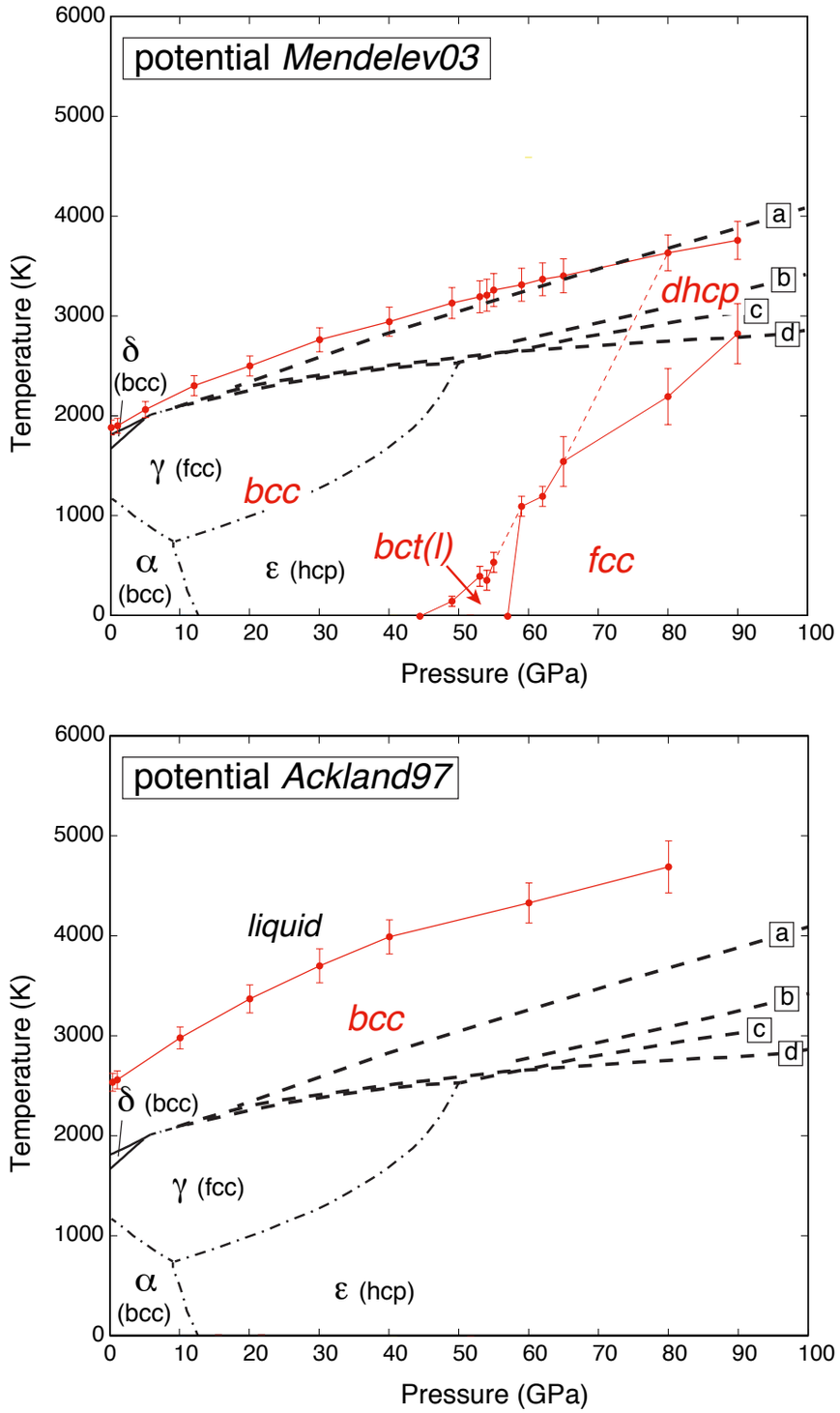


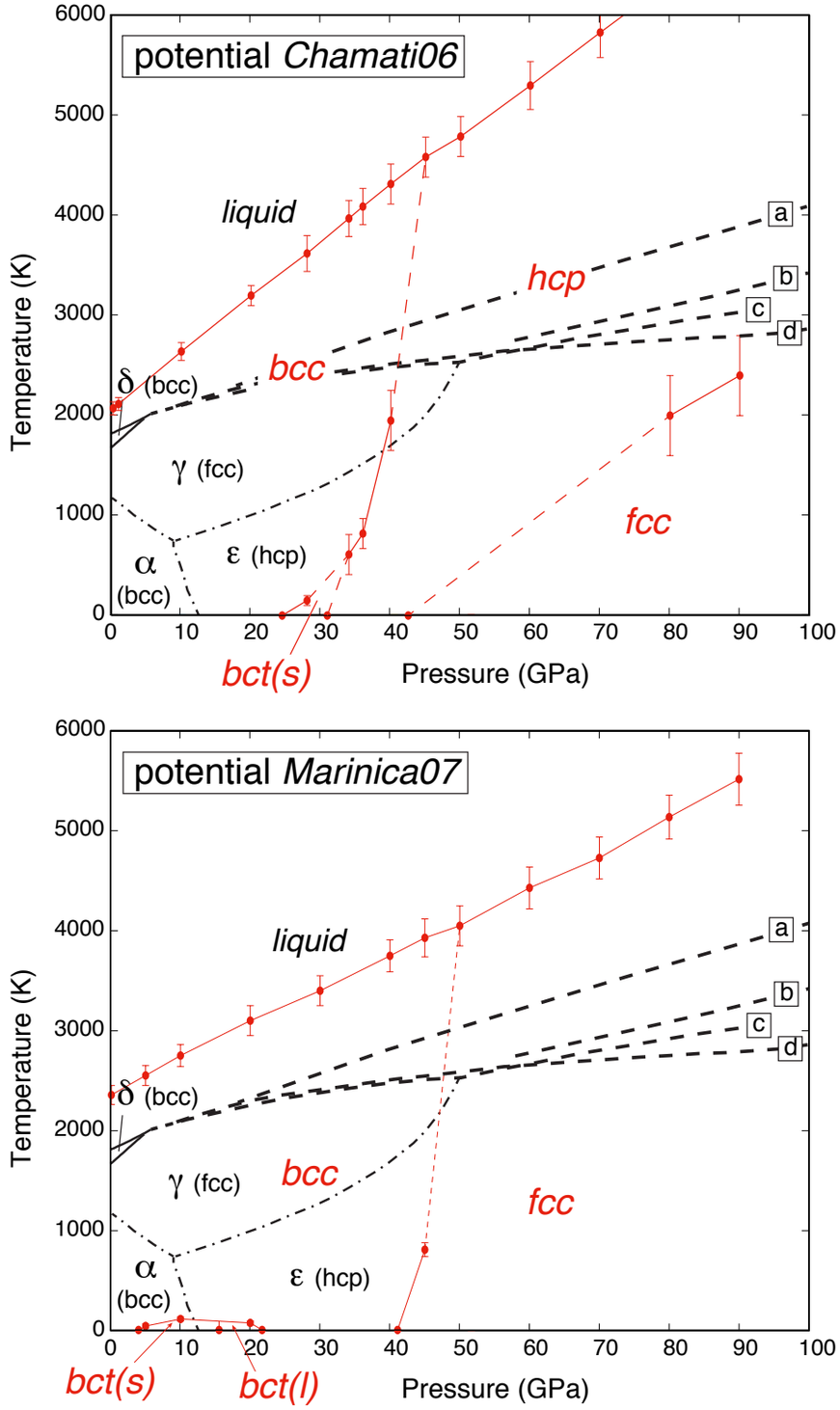


Dorrell and Pártay, *JPCB*. **in press**, (2020)

Phase Diagram of Iron

Embedded atom model of iron, 64 atoms in a simulation cell with variable size and shape

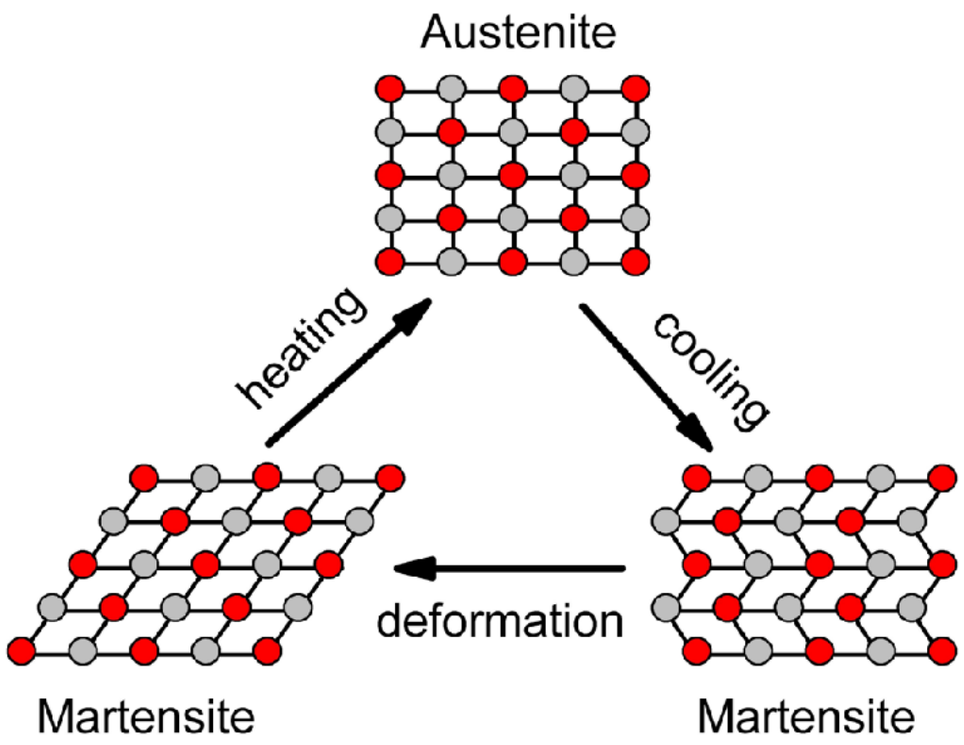


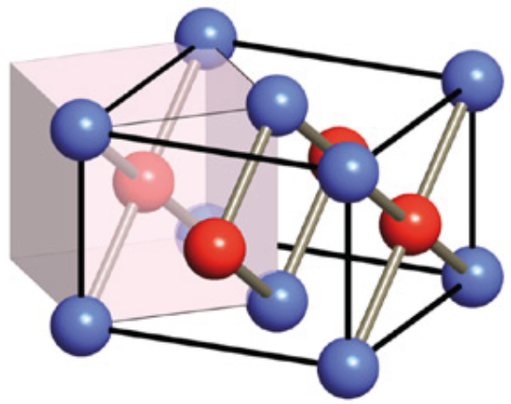


Pártay, *Comp. Mat. Sci.* **149**, 153, (2018)

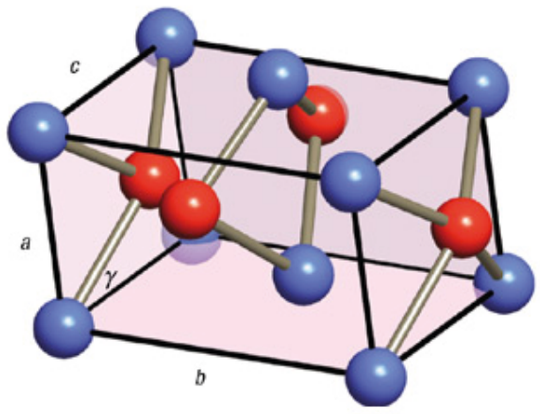
Martensitic Transition in NiTi alloys

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





B2



B19’

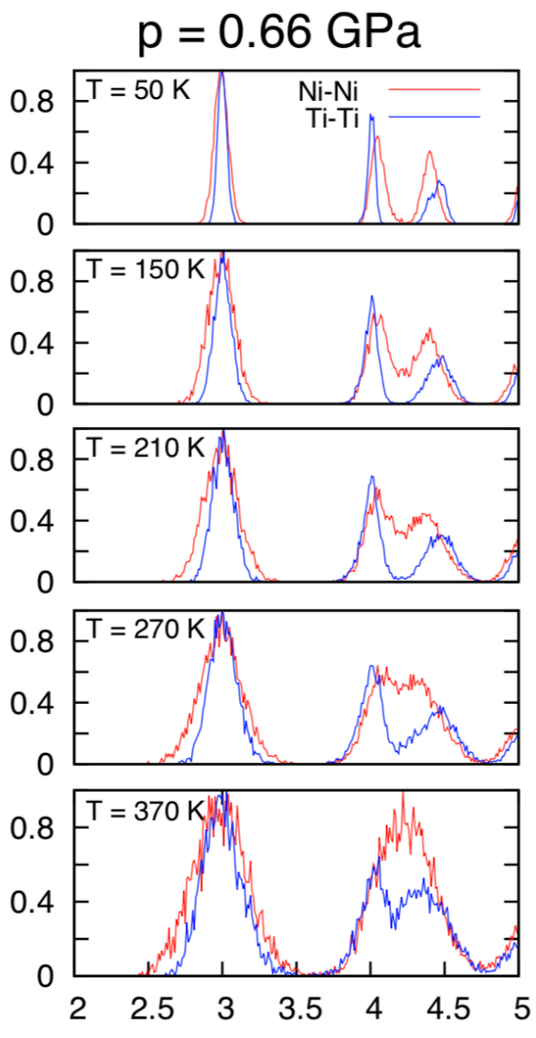
(from Huang et.al. *Nat.Mat.*2003)

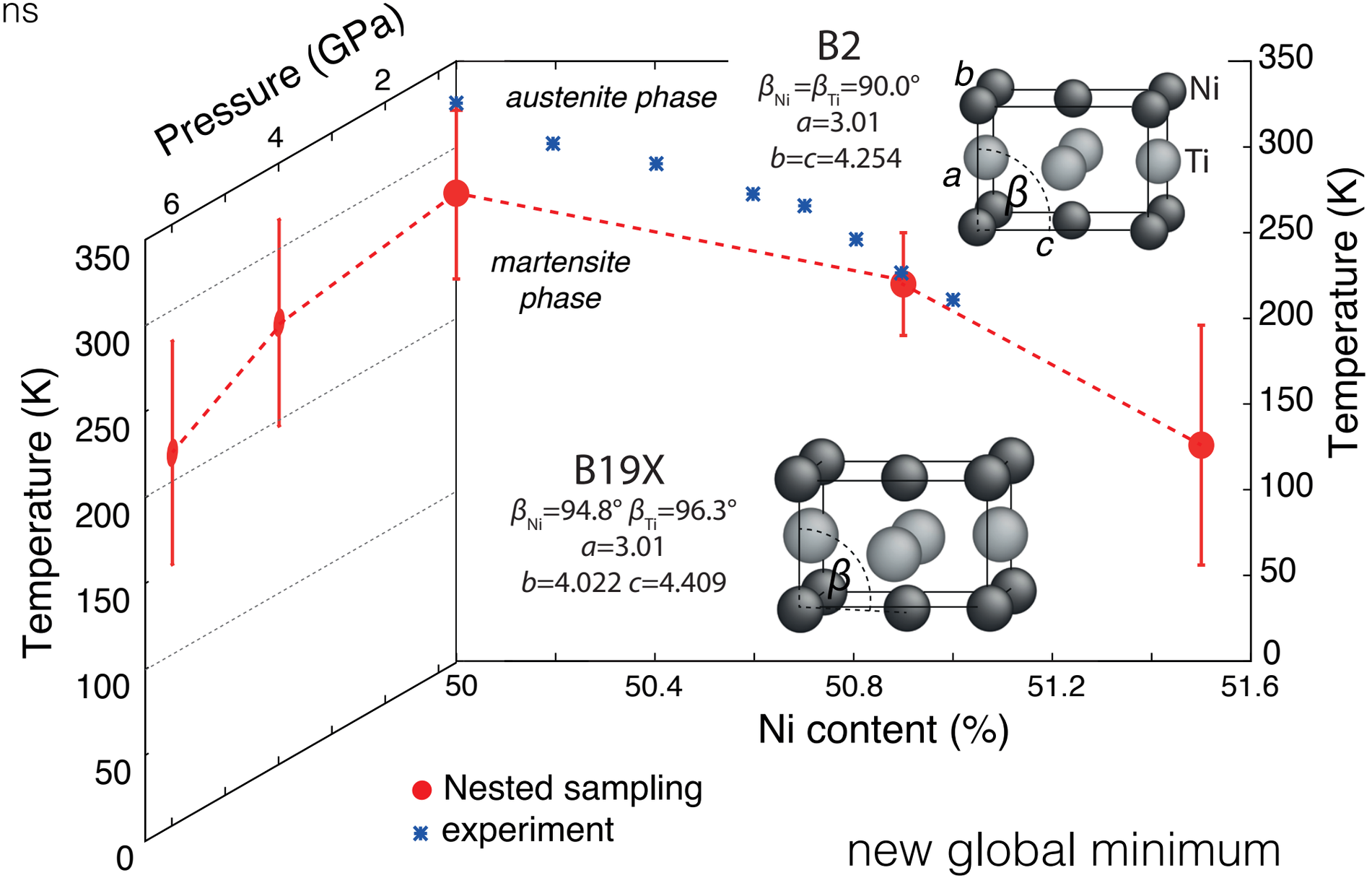
Martensitic Transition in NiTi alloys

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

NS weighted
radial distribution functions



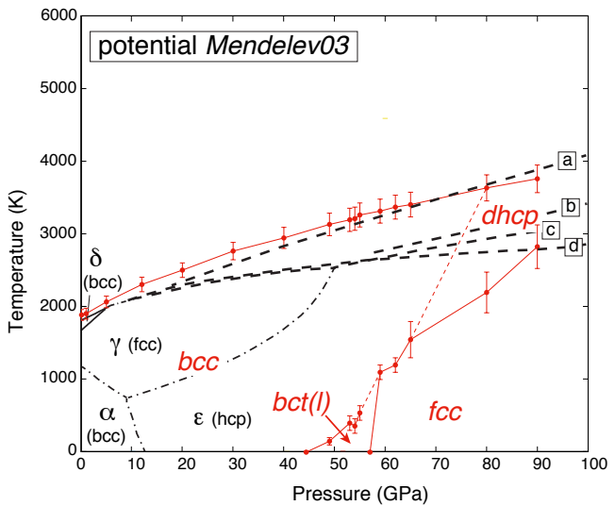


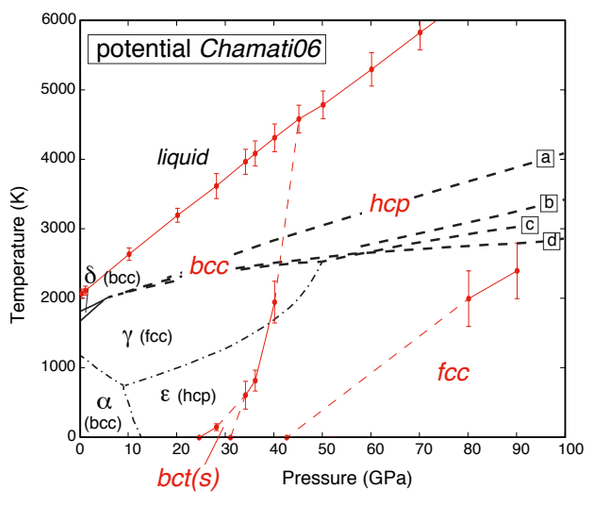
new global minimum
structure found!

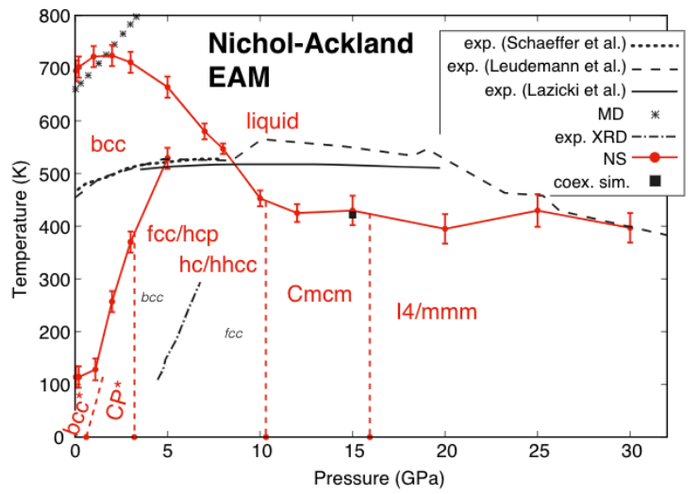
Baldock *et al.*, PRB **93**, 174108 (2016)

Phase Diagram of… models?

Aim: To have an unbiased sampling technique which can give an overview of the entire PES (THERMODYNAMICS), and can be automated:
not specific to a given part of the PES (GENERAL), where no prior knowledge of structures are necessary (PREDICTIVE).



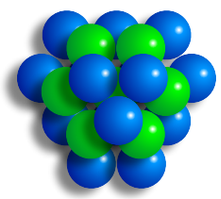




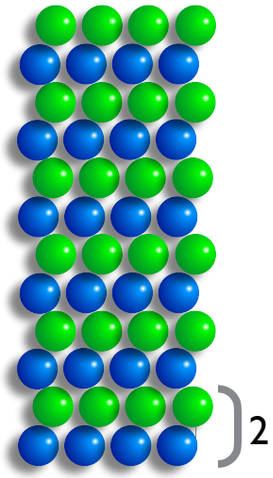
What do we know about the reliability of these models?
How do they perform on reproducing macroscopic behaviour?
How to choose the model we want use for a specific study?
What information to use in the fitting procedure?

What is the global minimum of the Lennard-Jones model?

Everyone knows it's **hcp**!



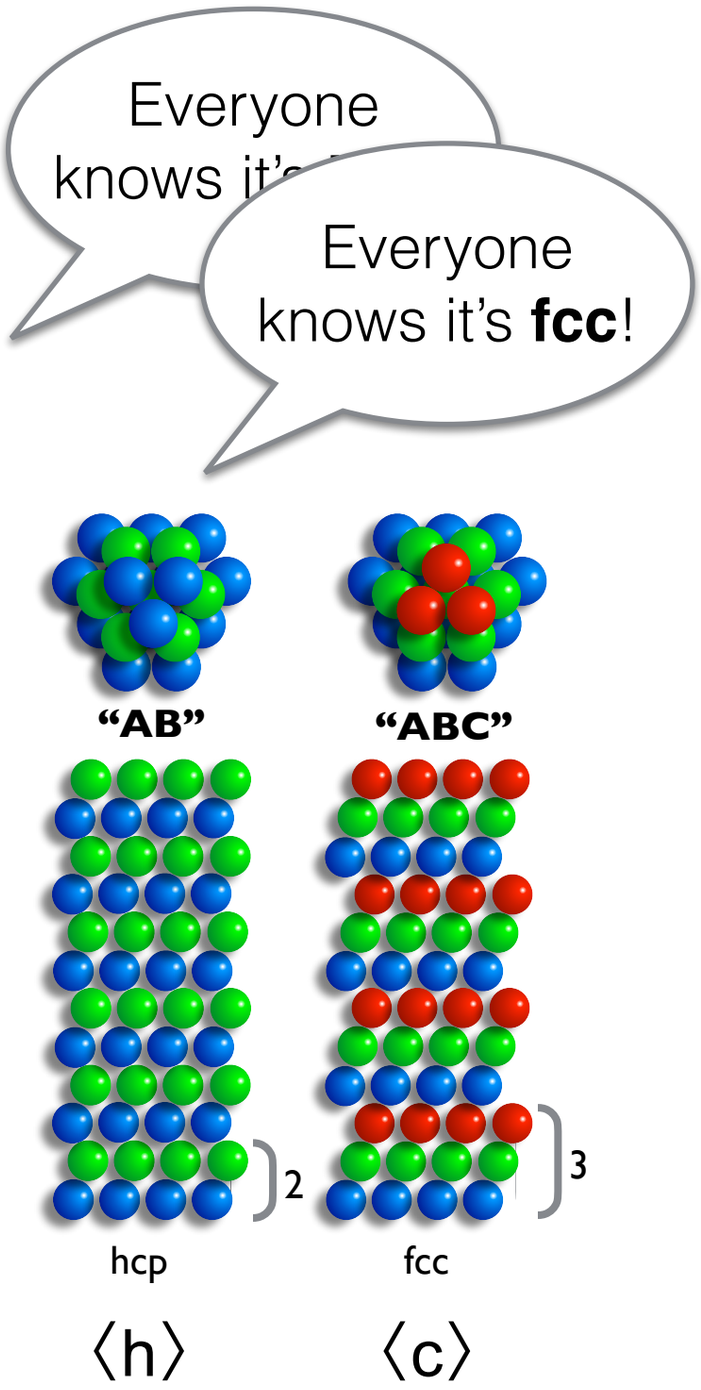
“AB”



hcp

$\langle h \rangle$

What is the global minimum of the Lennard-Jones model?

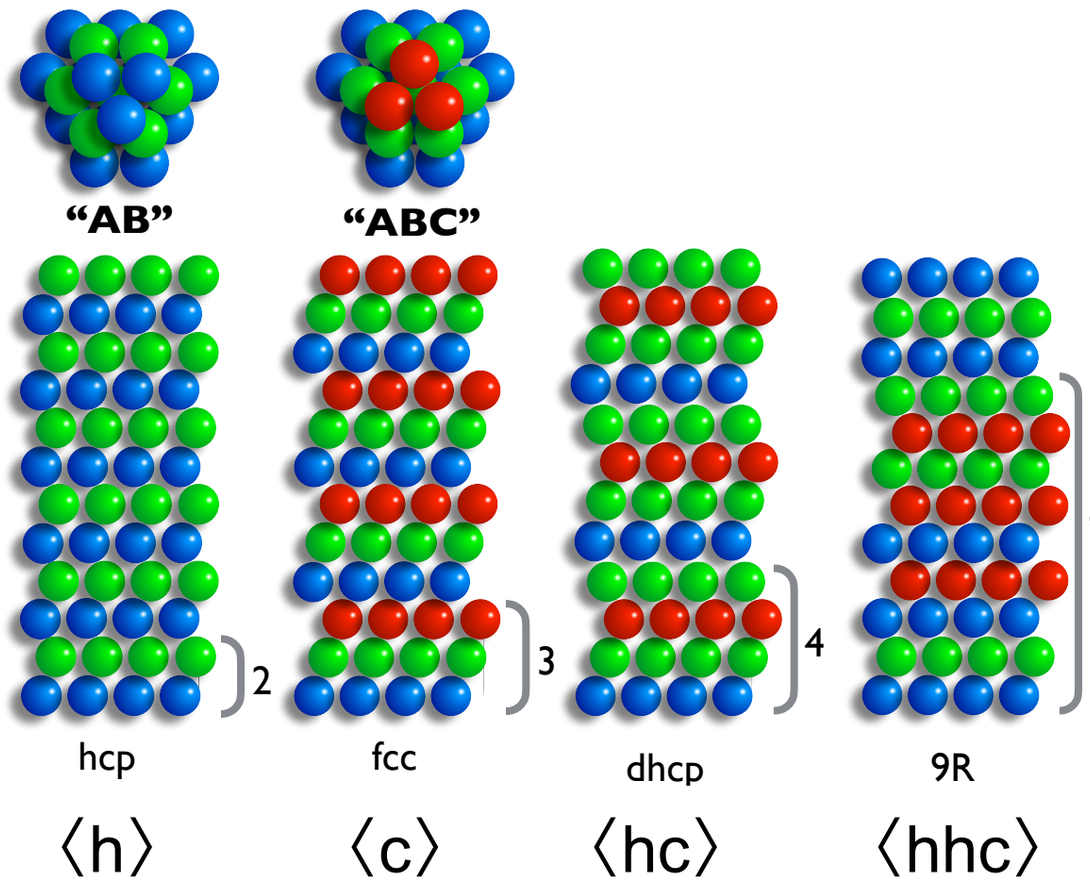


What is the global minimum of the Lennard-Jones model?

Everyone knows it's

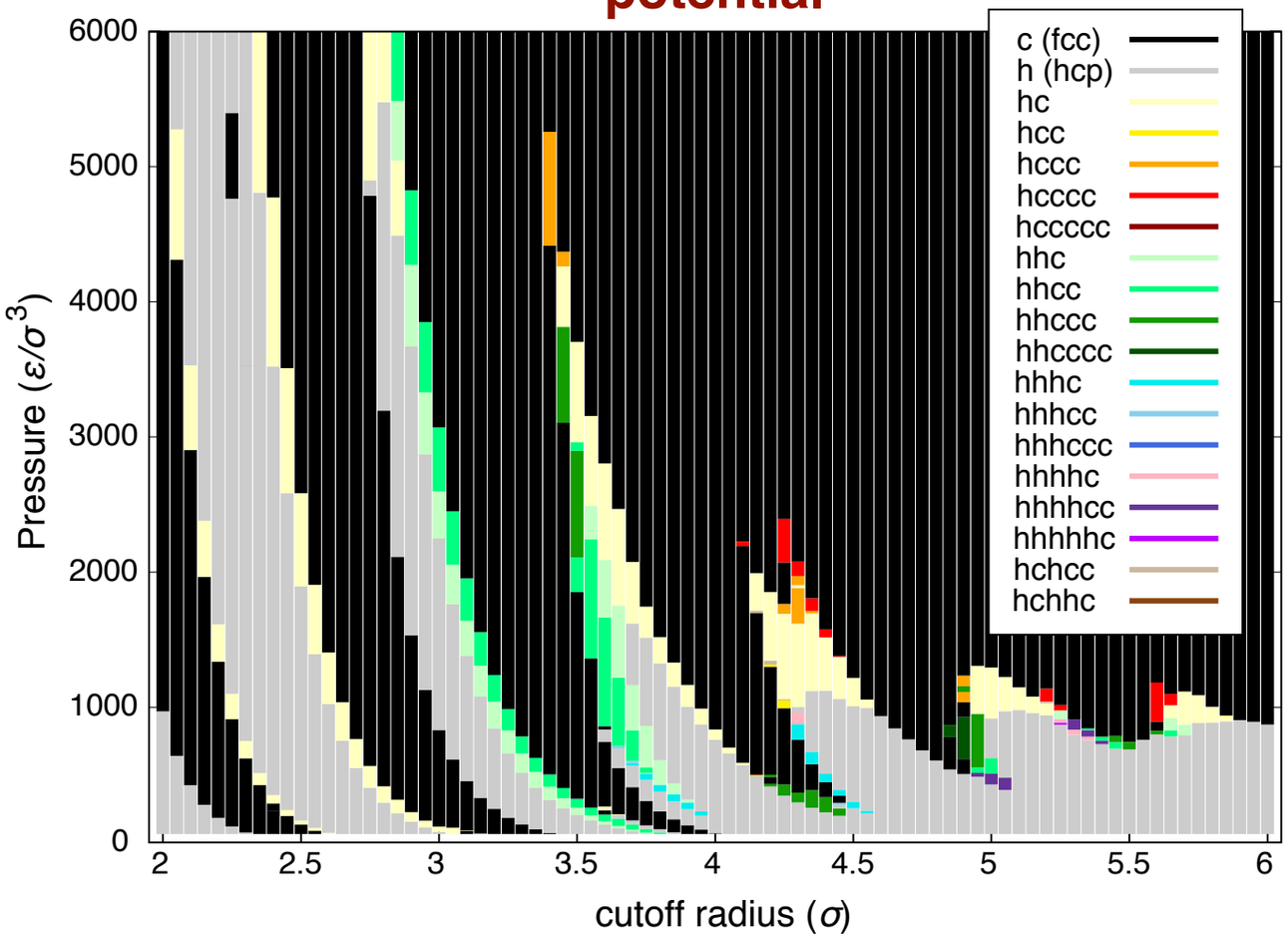
Ev knows

Well, it can be **hcp**, **fcc, dhcp,** … and other close packed **stacking variants**!



depending on the **cutoff distance,** the **smoothness** around the cutoff and the **pressure**, LJ has a ground state of different stacking.

Map of global-minima for energy-shifted LJ potential



Pártay *et al.*, PCCP **19**, 19369 (2017)

Machine Learning Potentials

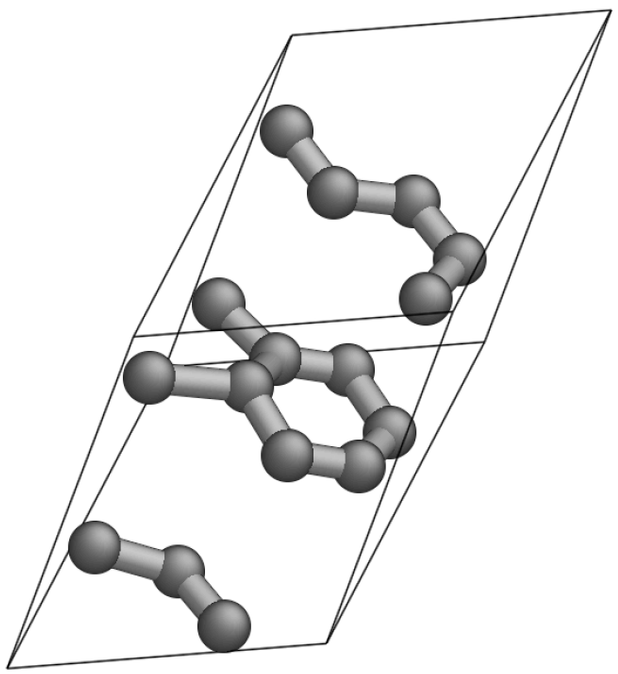
GAP model of carbon (Deringer and Csányi, *PRB*. 95. 094203 (2017))

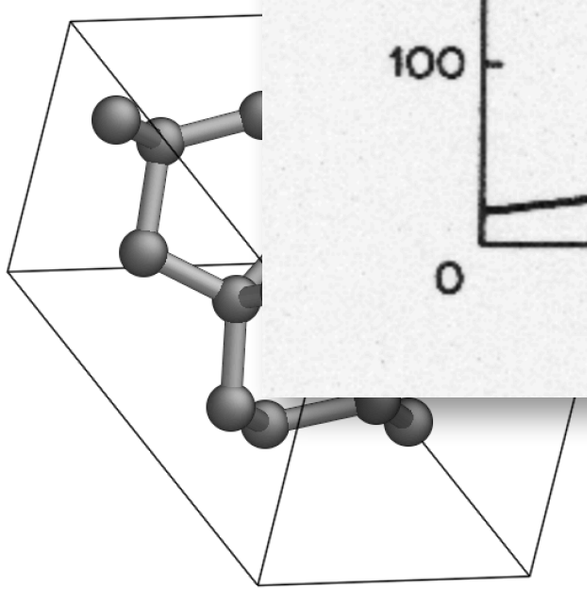
ML Training dataset:

- liquid and amorphous configuration
- amorphous surfaces
- randomly distorted unit cells of grap

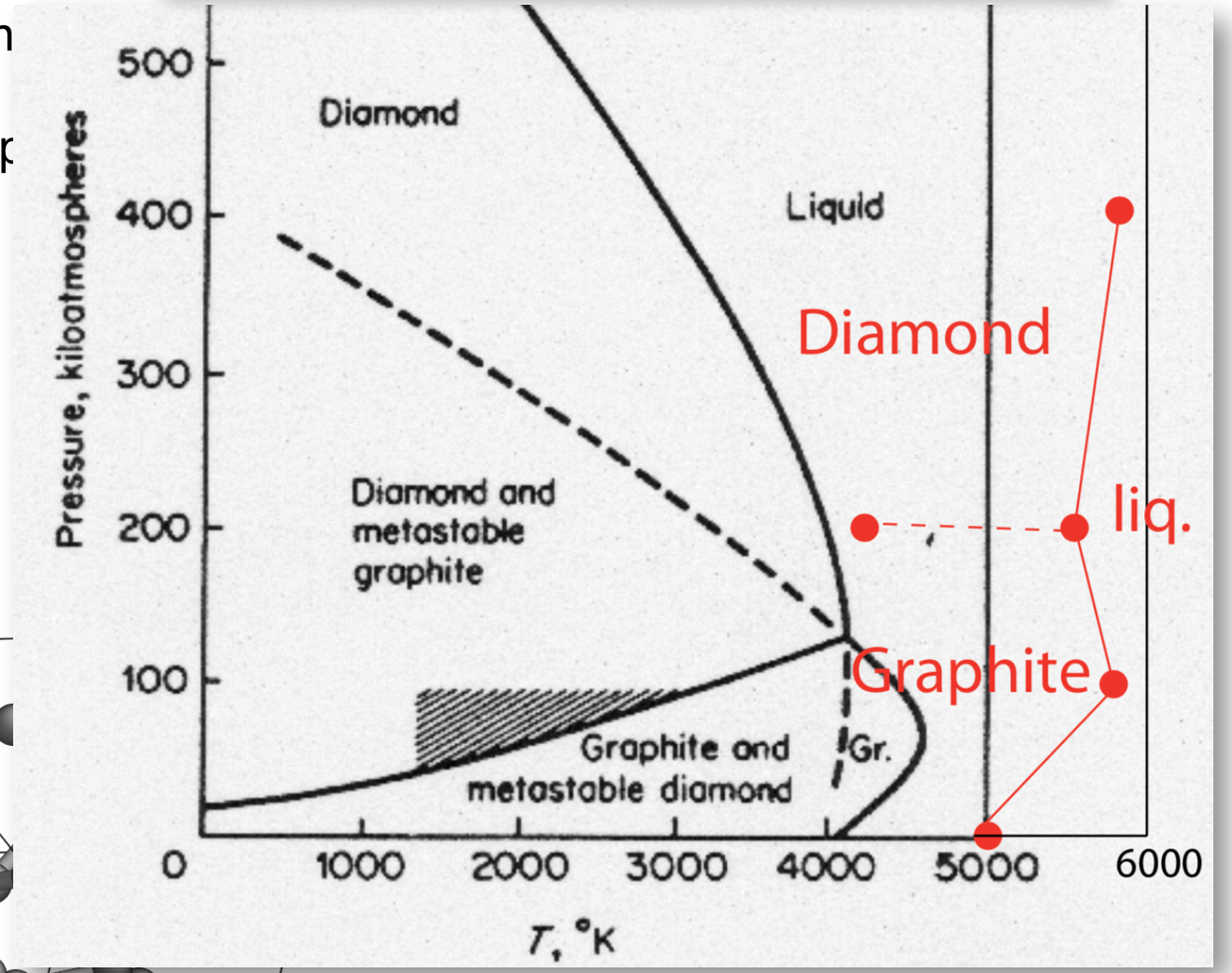
Nested sampling:

- 16 atoms/32 atoms
- 600 walkers





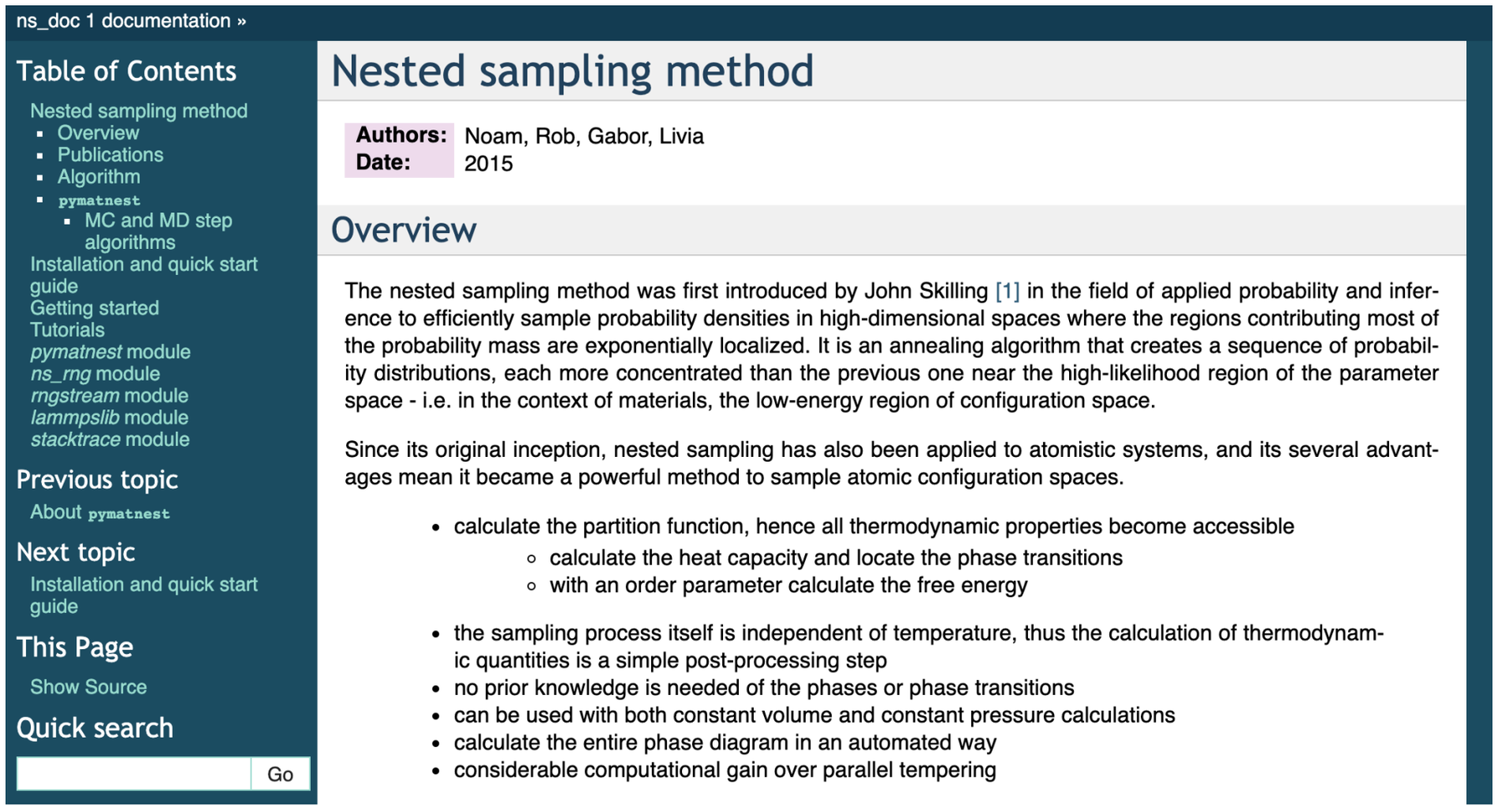
Carbon *p*-*T* phase diagram



Code released - **pymatnest**

Python code with an interface to **QUIP** and **LAMMPS**

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



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