Microscopic origins of complex behavior in carbon and sodium

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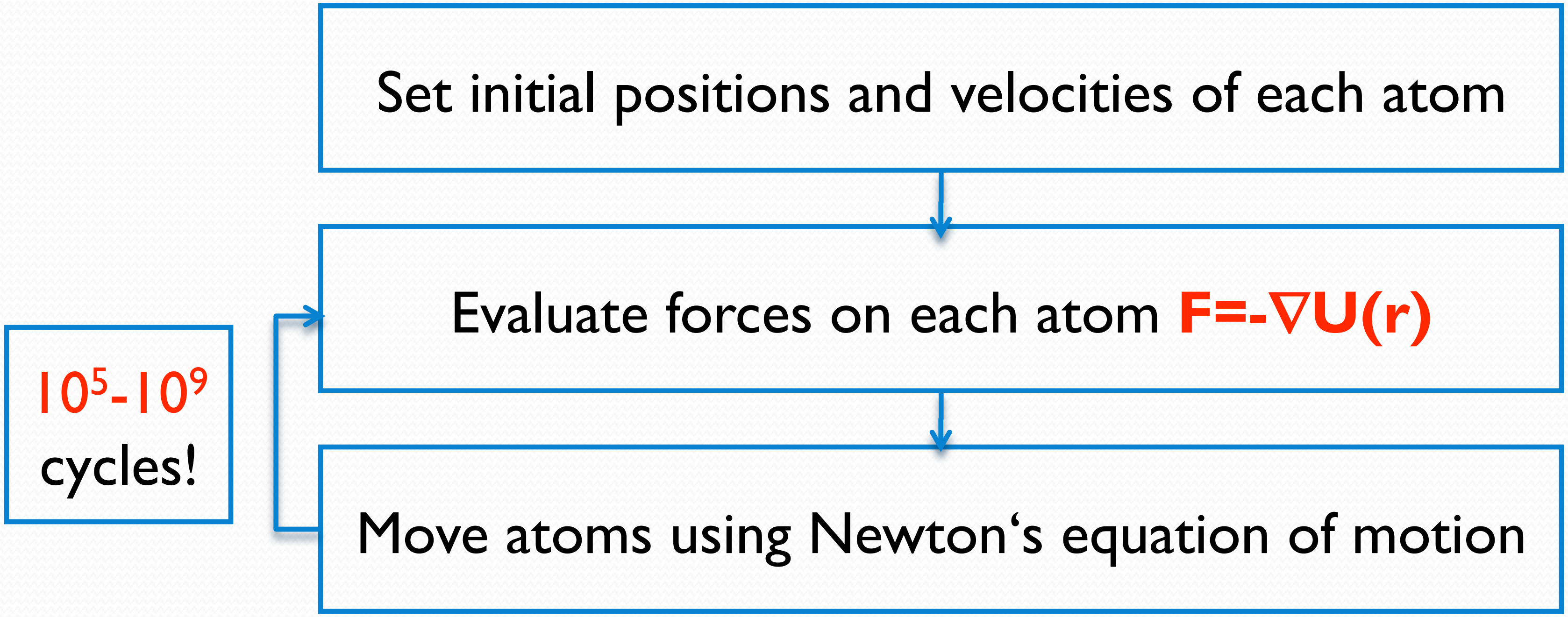
Molecular dynamics (MD)

- MD is a computational method for simulating time evolution of a collection of interacting atoms by numerically integrating Newton's equation of motion.



Set initial positions and velocities of each atom

Evaluate forces on each atom **$F=-\nabla U(r)$**

Move atoms using Newton's equation of motion

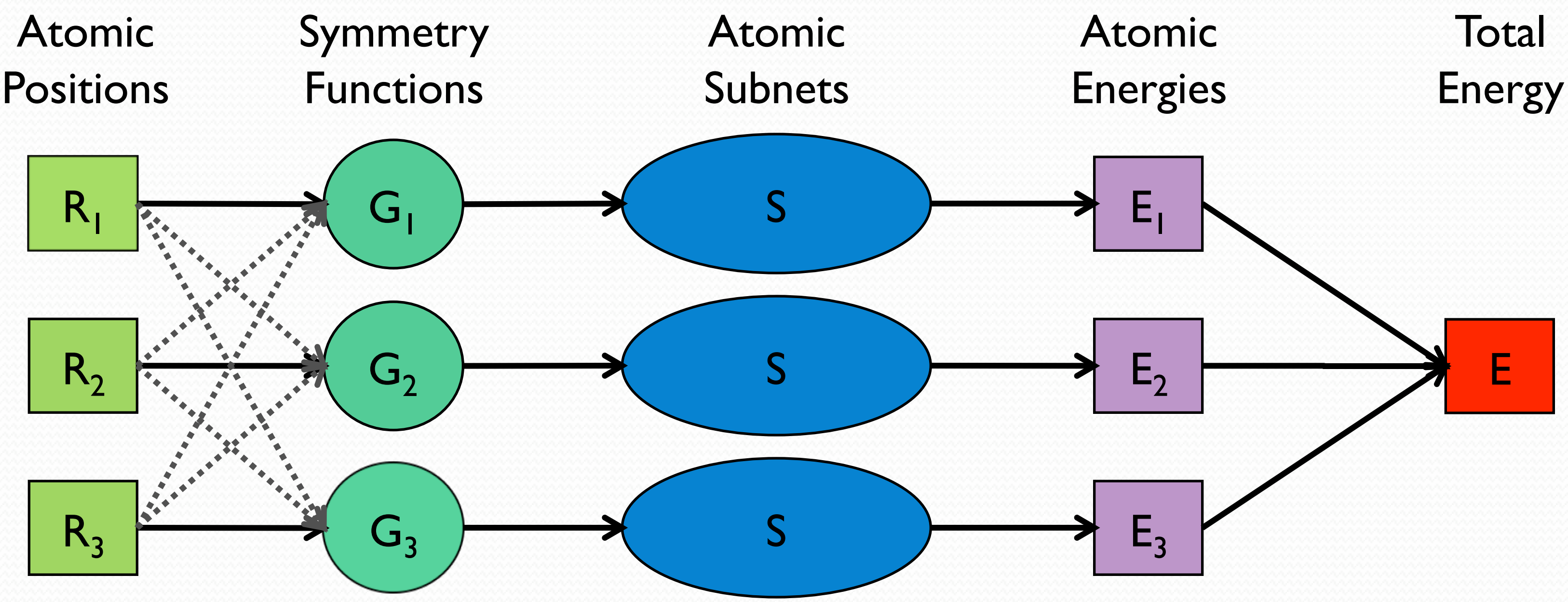
10^5-10^9 cycles!

Evaluation of the potential energy

- ***Ab initio* methods:**
  - based on rigorous principles of quantum mechanics
  - accurate description of a PES
  - not practical for MD simulations because of their computational expense.
- **Empirical potentials:**
  - simple analytical approximation to $U(r)$
  - computationally efficient
  - not capable of describing chemical transformations
- **Alternatives?** Combine the accuracy of an *ab initio* description of a PES with the computational efficiency of empirical potentials.

Neural network representation

J. Behler, M. Parrinello, PRL, 98, 146401 (2007).



Atomic Positions

Symmetry Functions

Atomic Subnets

Atomic Energies

Total Energy

R_1 → G_1 → S → E_1

R_2 → G_2 → S → E_2

R_3 → G_3 → S → E_3

E_1, E_2, E_3 → E

$R_i=\{X_i,Y_i,Z_i\}$

Subnets are identical for atoms of the same type

$$E = \sum_j E_j$$

Input

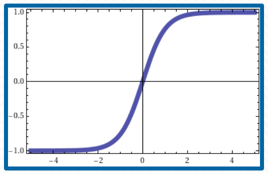
Invisible

Output

Artificial neural network (NN)

- Artificial NN is a mathematical and computational model inspired by the functional aspects of biological structures in the brain that is able to capture and represent complex input-output relationships.

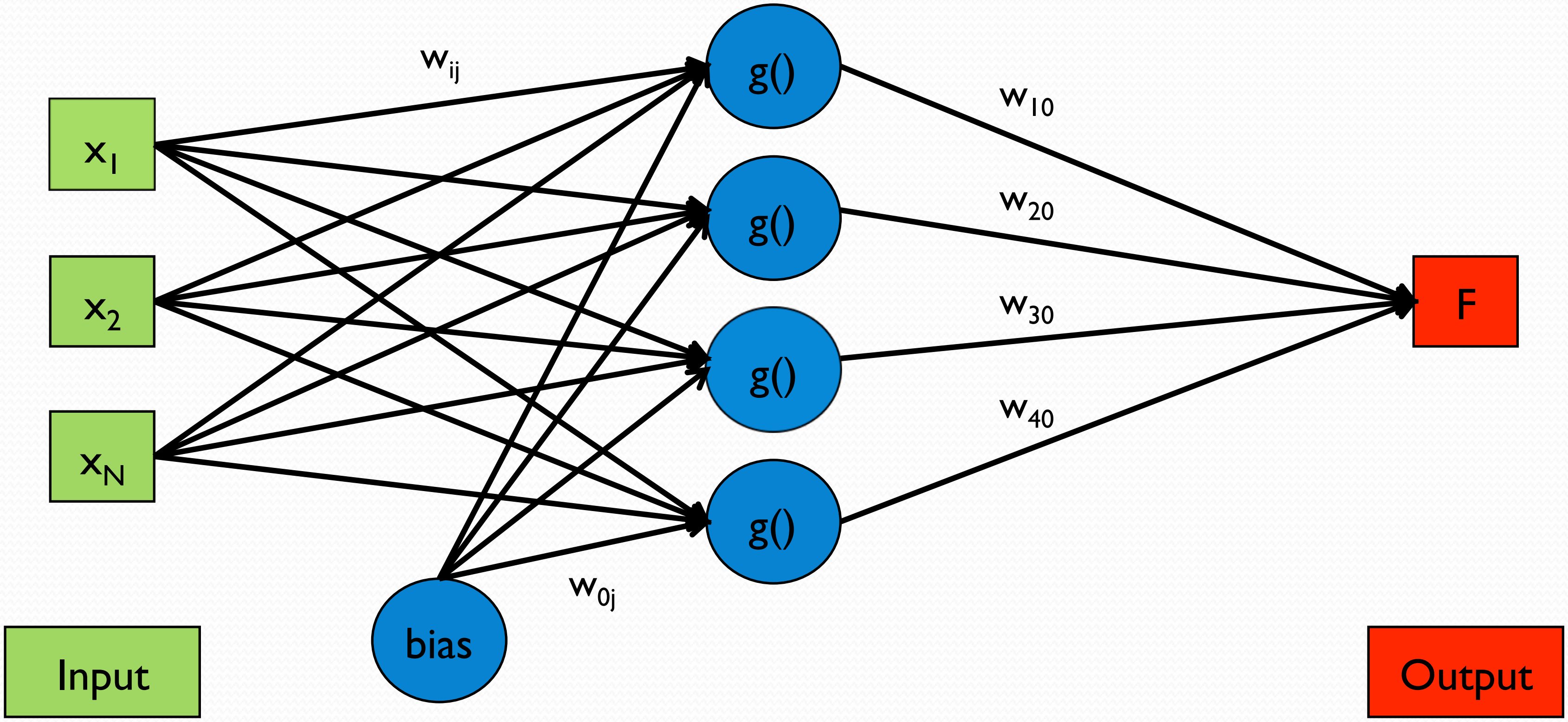
$$F(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{M} w_{i0}\, g\Big(\sum_{j=1}^{N} w_{ij} x_j + w_{0j}\Big), \text{ with } g(x) =$$



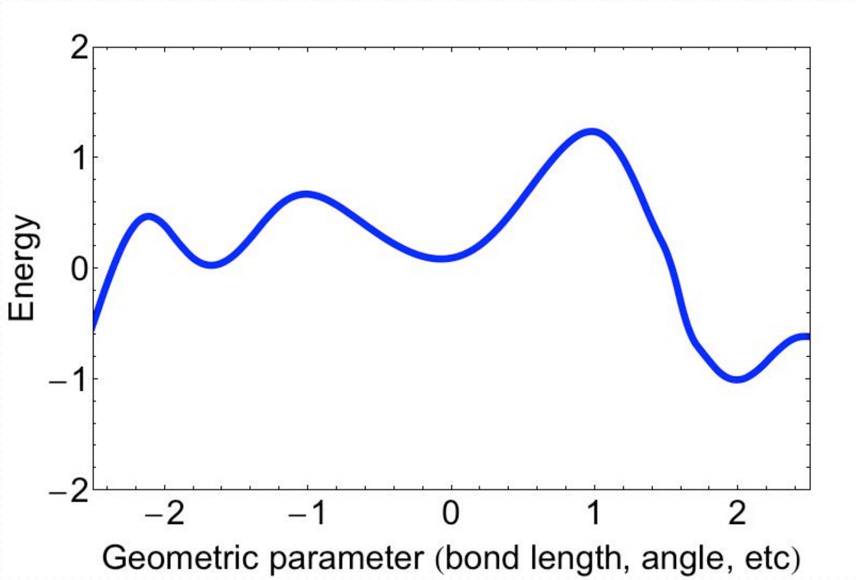
- **The Cybenko theorem:** A neural network represented by the equation above is capable of approximating any continuous, multivariate function to any desired degree of accuracy.

Schematic representation of a NN

$$F(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{M} w_{i0}\, g\left(\sum_{j=1}^{N} w_{ij} x_j + w_{0j}\right)$$

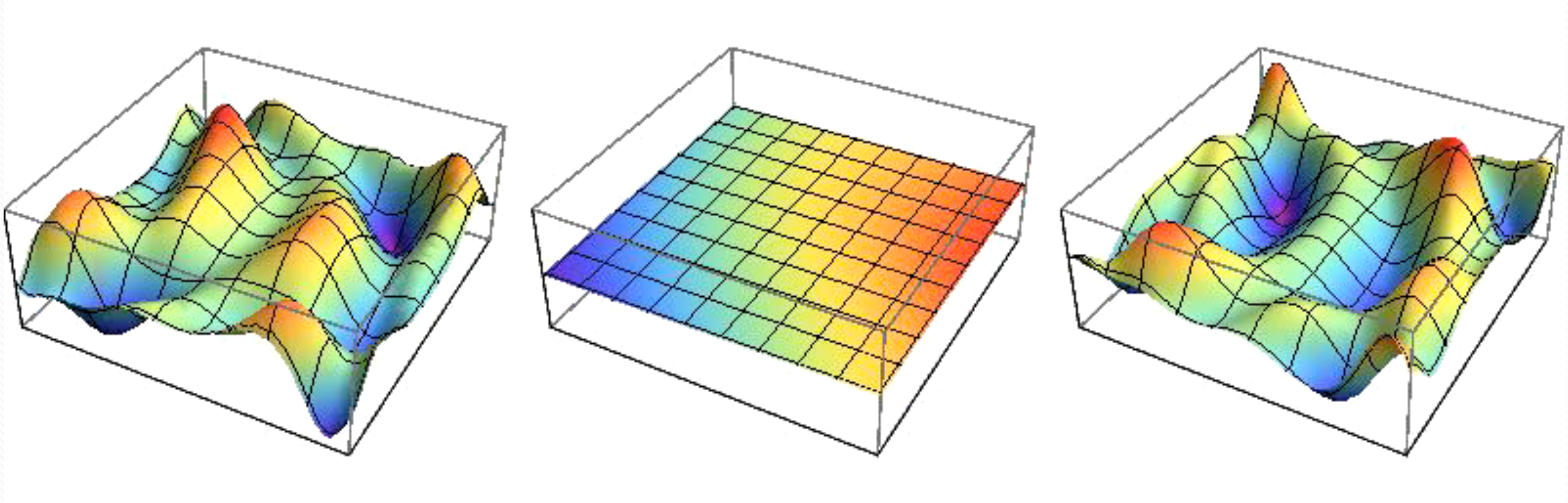


General approach



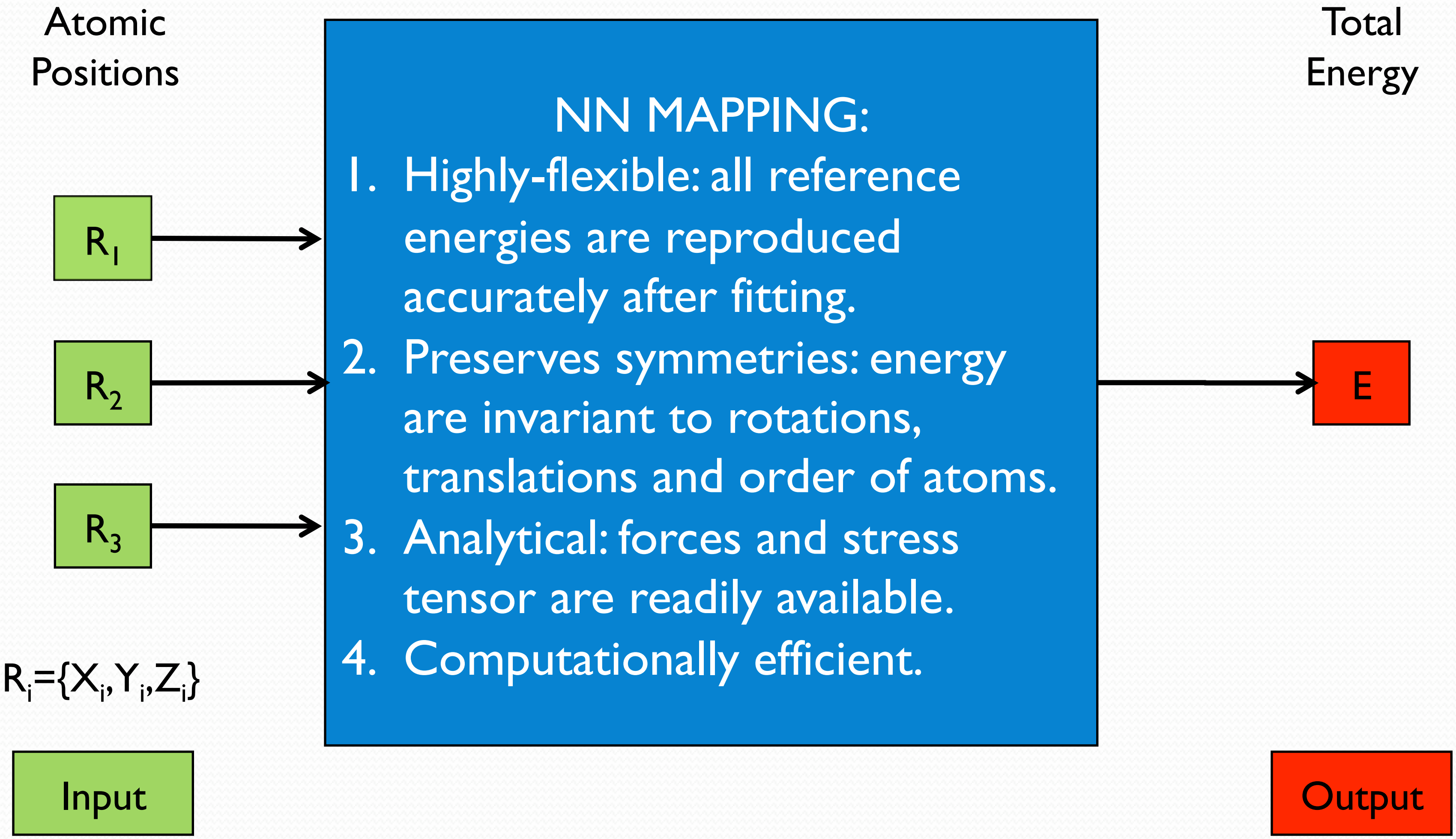
- Calculate accurate *ab initio* energies for a number of atomic configurations.
- Fit a **highly-flexible analytical function represented by a neural network** to reproduce *ab initio* energies for these configurations.
- Use this function to perform **interpolation** and obtain energy and forces for new configurations encountered in the course of lengthy MD simulations.

NN fitting of a 2D function



Target Function | **NN representation** | **Fitting Error**

NN representation of PESs



Atomic Positions

R_1

R_2

R_3

$R_i=\{X_i,Y_i,Z_i\}$

Input

NN MAPPING:

1. Highly-flexible: all reference energies are reproduced accurately after fitting.
2. Preserves symmetries: energy are invariant to rotations, translations and order of atoms.
3. Analytical: forces and stress tensor are readily available.
4. Computationally efficient.

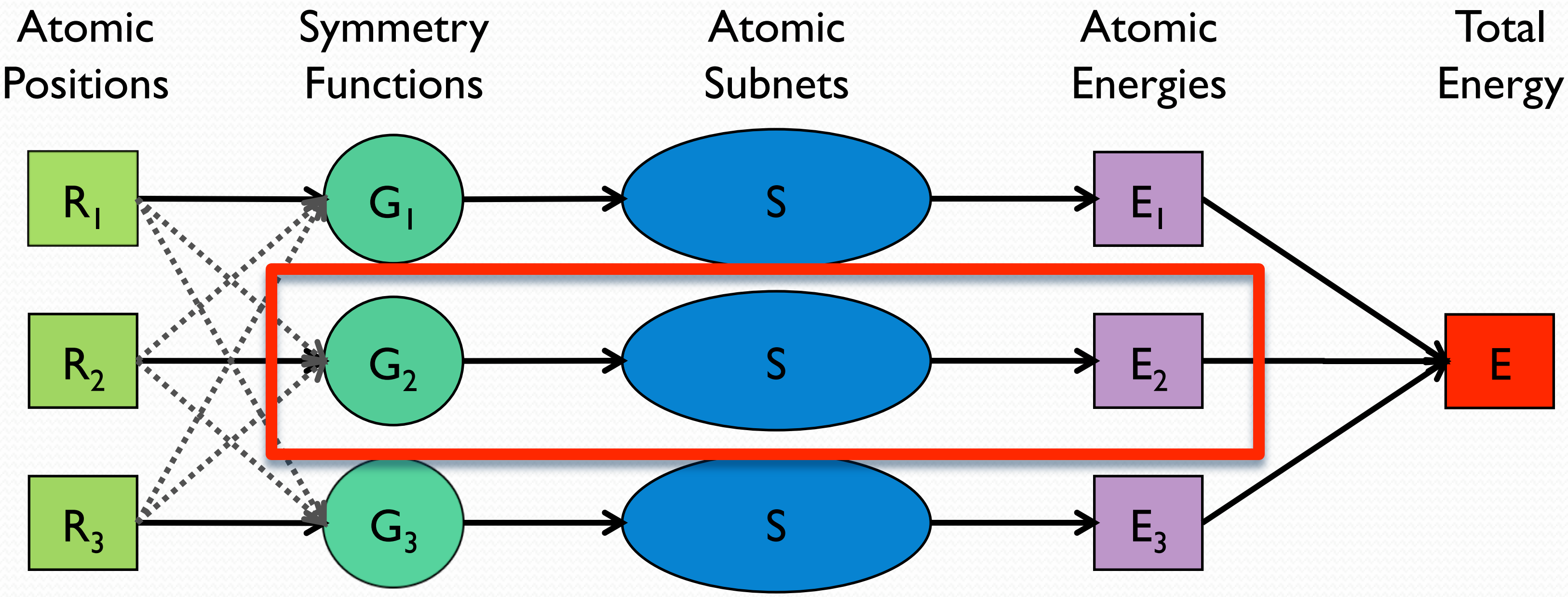
Total Energy

E

Output

Neural network representation

J. Behler, M. Parrinello, PRL, 98, 146401 (2007).



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E

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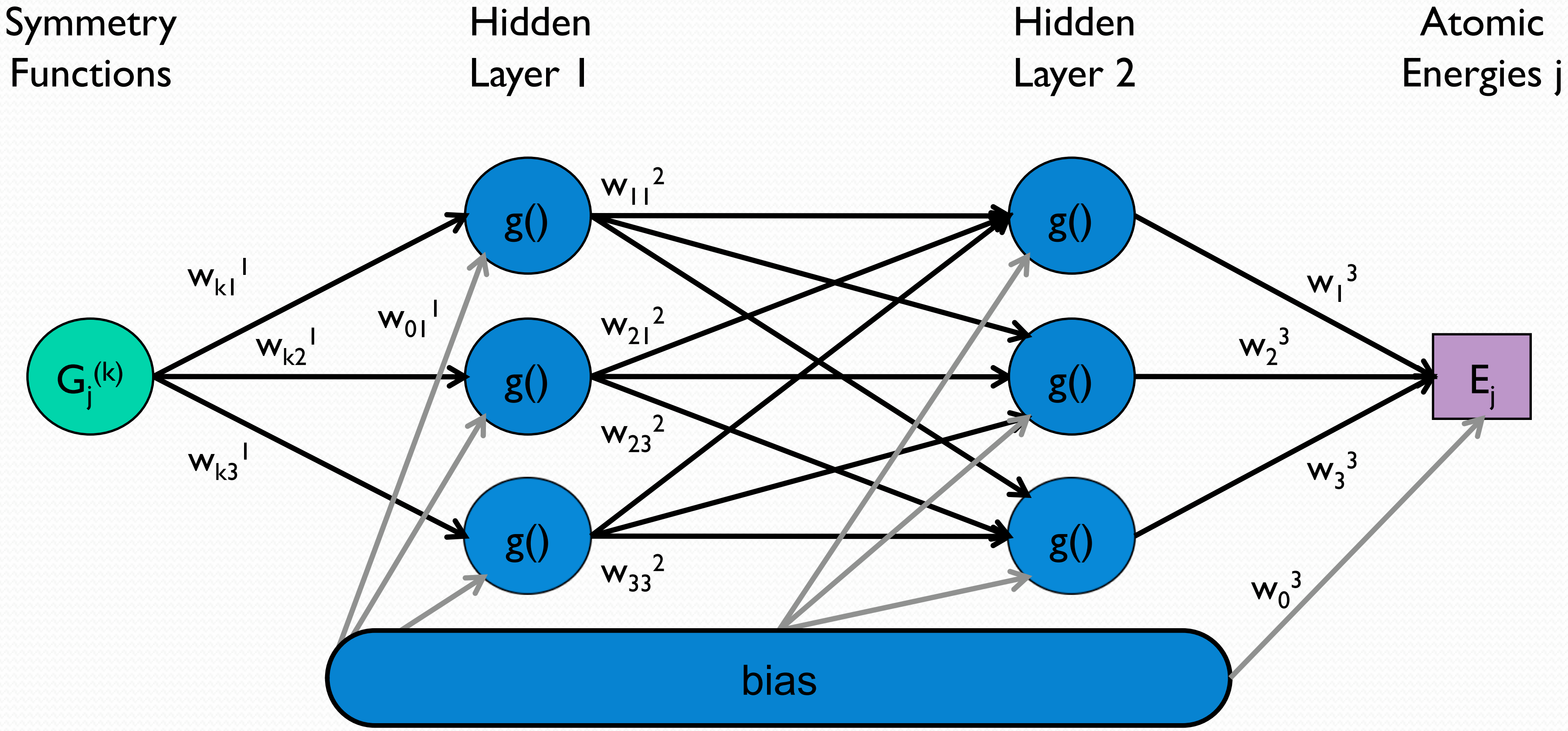
Input

Invisible

Output

Structure of an atomic NN



Advantages of using NNs

- NNs completely obviate the problem of guessing a complicated functional form of the PES. This form is determined automatically by the NN.
- The entire training process is automated so that months of human effort are replaced with a short computer calculation.
- Accurate mapping ensures that all properties determined by the topology of the PES are described with the accuracy comparable with that of *ab initio* calculations.

NN potential for Na and C

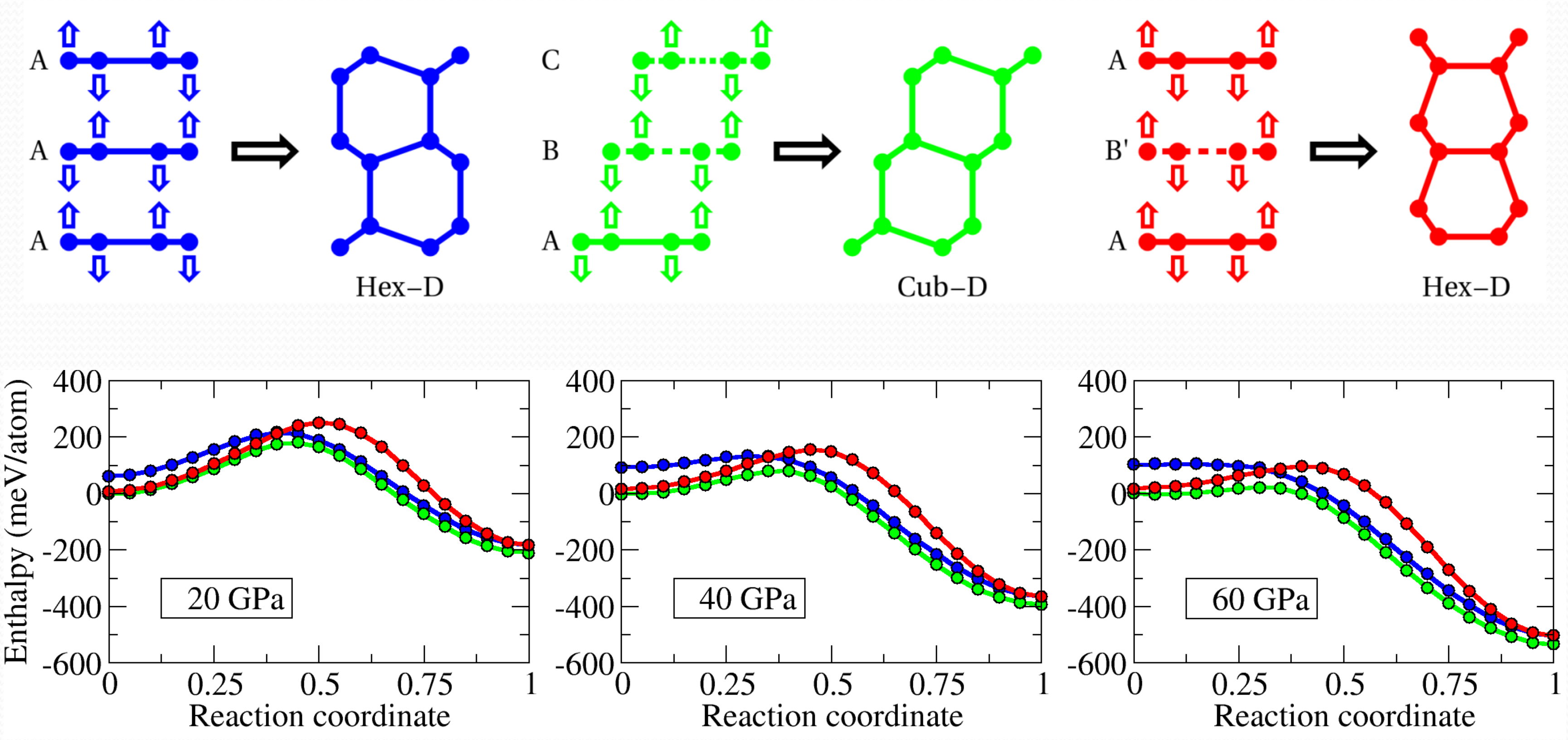
	Sodium	Carbon
Reference energies	PBE density functional	
Pseudopotential	Ultrasoft (2s,2p)-semicore	Dispersion corrected HGH
Convergence (PW cutoff, k-point mesh, etc.)	**1.0 meV/atom**	**1.0 meV/atom**
Training set	17,000 DFT energies (350,000 config.)	60,000 DFT energies (700,000 config.)
Pressure range	0-120 GPa	0-80 GPa
Fitting error of an independent test set	**0.9 meV/atom**	**3.9 meV/atom**

R.Z. Khaliullin, H. Eshet, T. Kuhne, J. Behler, M. Parrinello, PRB, 81, 100103 (2010).
H. Eshet, R.Z. Khaliullin, T. Kuhne, J. Behler, M. Parrinello, PRB, 81, 184107 (2010).

Graphite-to-diamond transition

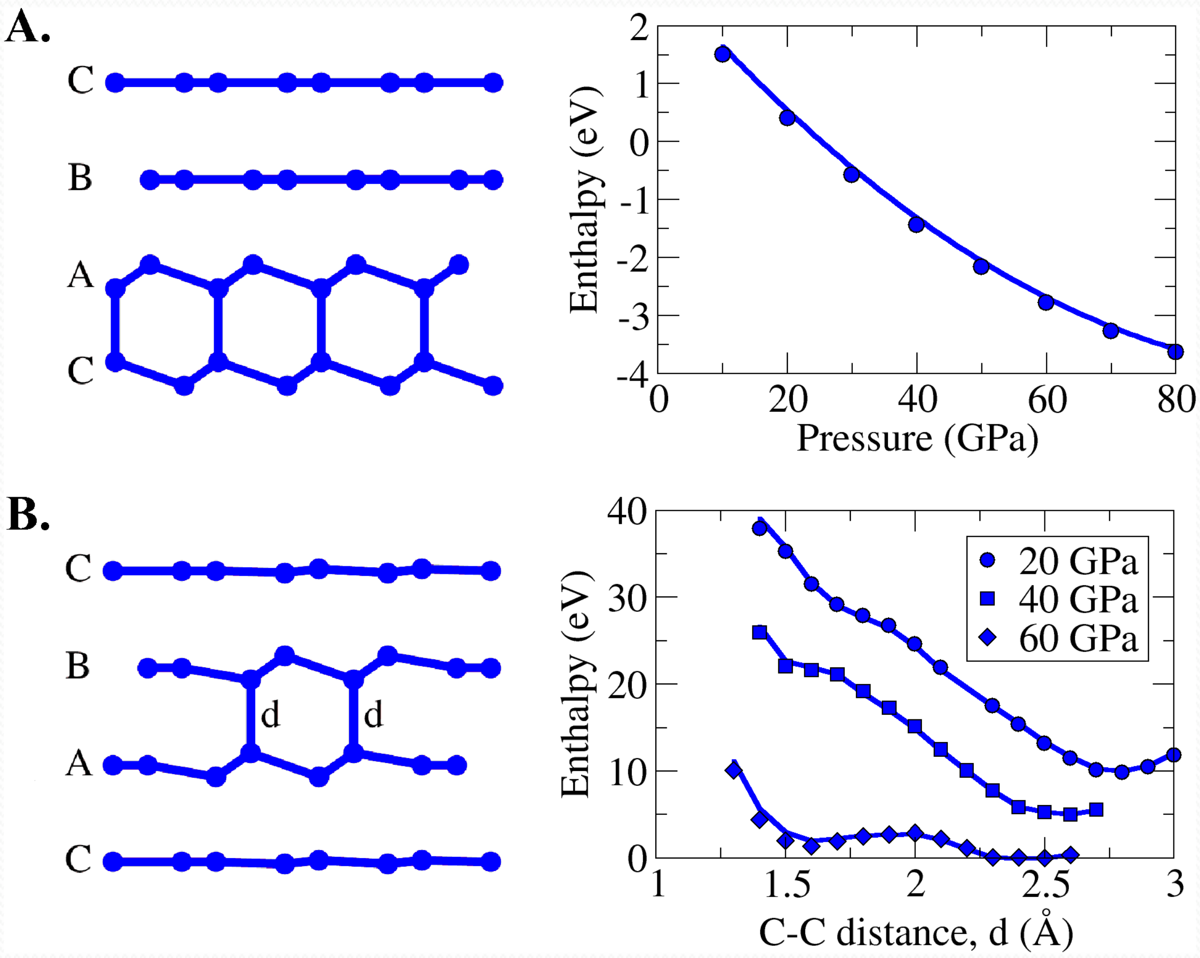
- Severe restrictions on the maximum system size and time scale accessible in simulations have limited theoretical studies of the mechanism to **collective** transformations.
- Many aspects of the transition cannot be explained by the mechanism of collective transformations:
  - the formation of the metastable hexagonal diamond phase,
  - the observation that the transition pressure is considerably higher than the graphite-diamond coexistence pressure: diamond formation is not observed below ~10 GPa
- The NN potential enables us to perform the first atomistic study of homogeneous diamond **nucleation** from graphite.

Barriers for collective paths



Lines – DFT; Dots - NN

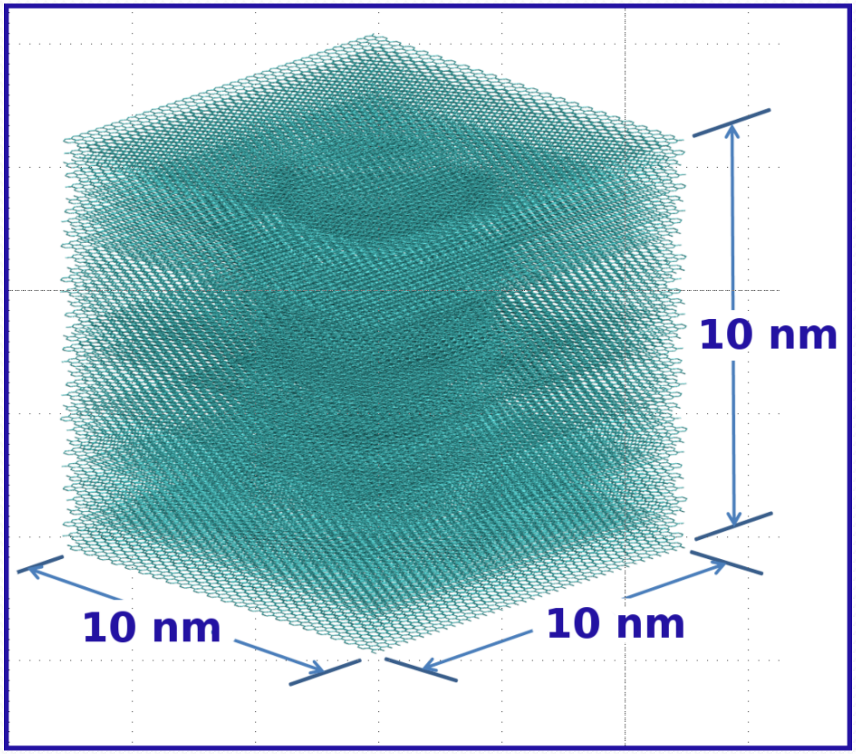
Enthalpy of the interfaces



$[001]_G$ interface

Interfaces around a small nucleus

Model system

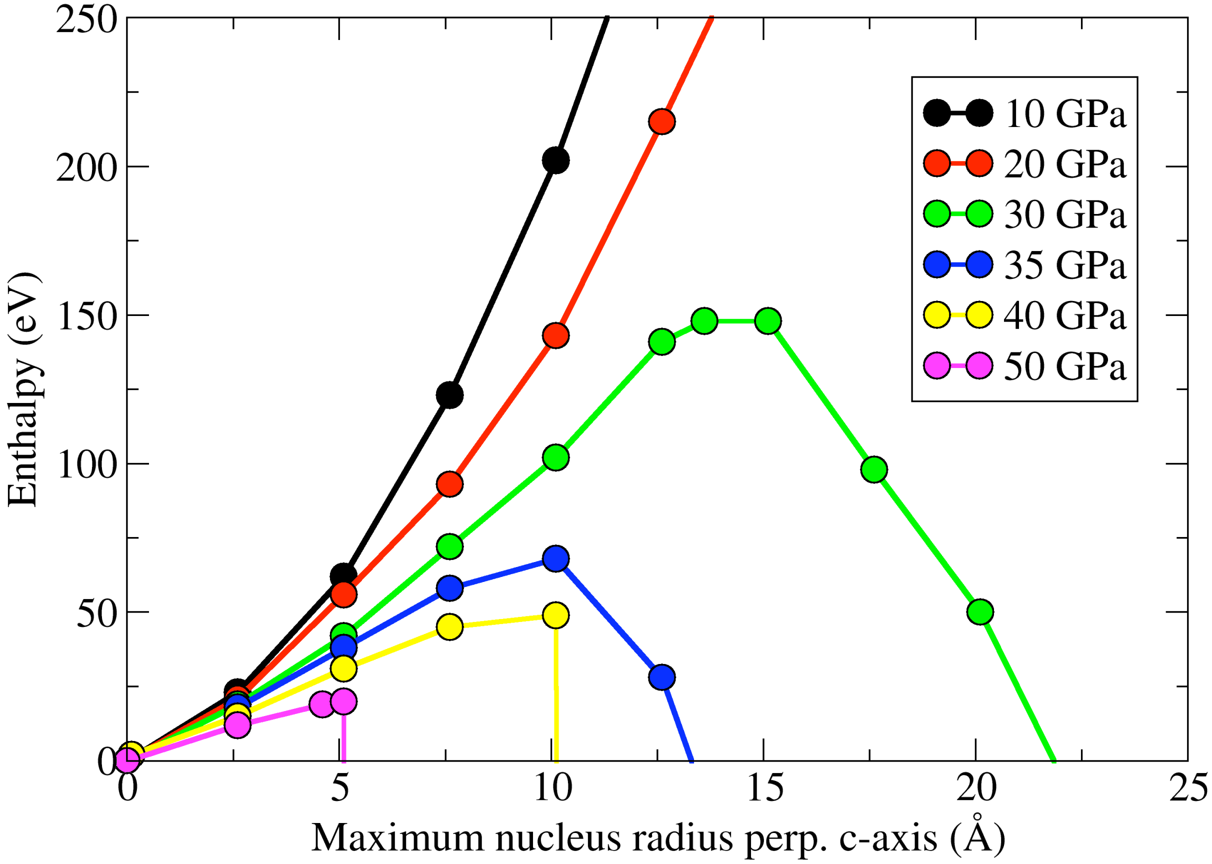


- 145,000 C atoms arranged in the graphite lattice
- Seed a diamond nucleus by constraining interlayer distances between atoms within pre-defined radius R.
- Heat system to T=1500K
- Minimize enthalpy at T=0K and constant pressure

R.Z. Khaliullin, H. Eshet, T. Kuhne, J. Behler, M. Parrinello, Nature Mat, 10, 693, (2011).

Nucleation barriers

$$\Delta G = Vg + S\sigma$$



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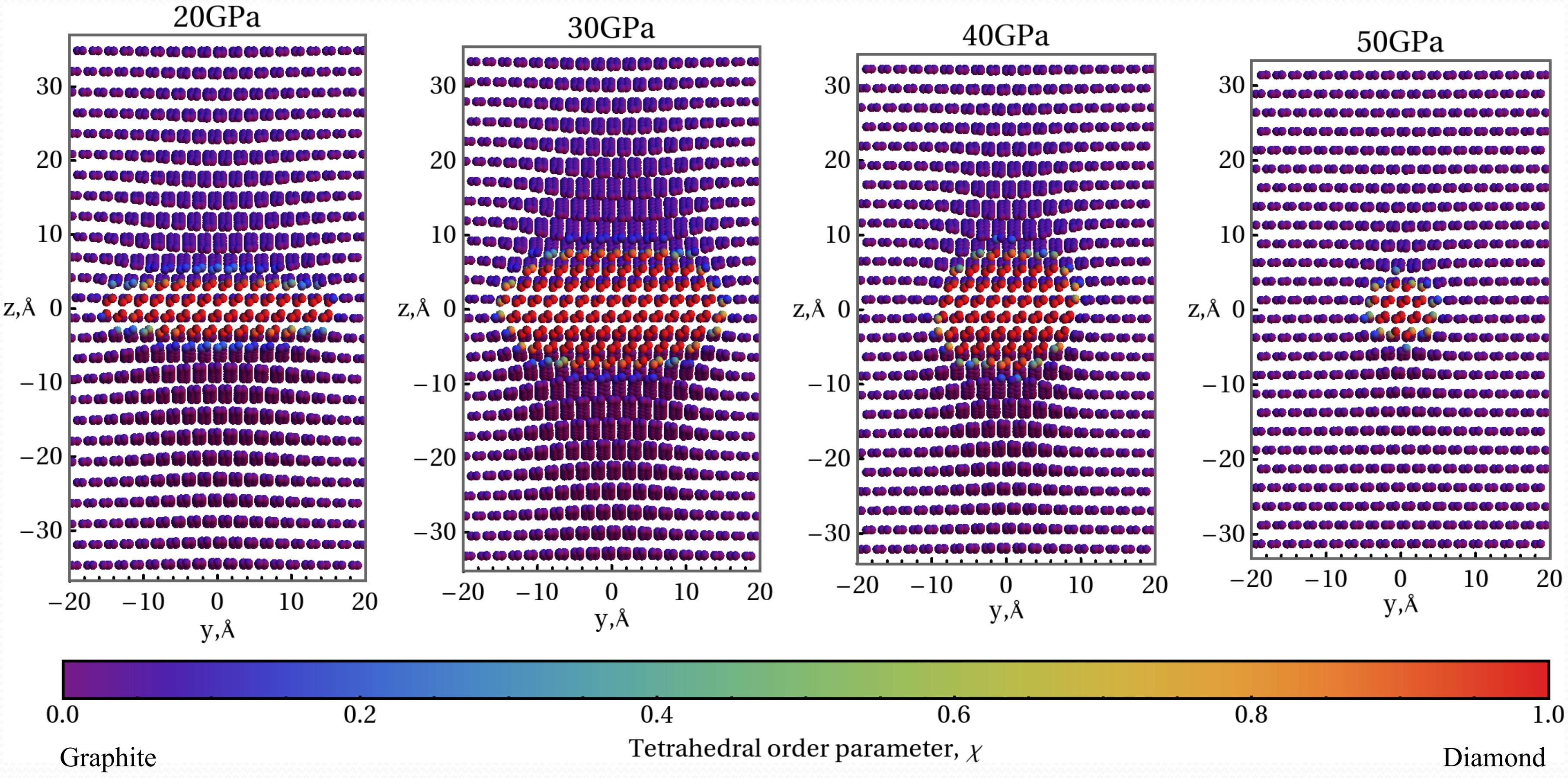
Structure of diamond nuclei



R.Z. Khaliullin, H. Eshet, T. Kuhne, J. Behler, M. Parrinello, Nature Mat, 10, 693, (2011).

Thermodynamics of nucleation

$$\Delta G = V(\Delta g_{\mu} + \Delta g_{s}) + S\sigma$$

Difference in free-energy density of bulk diamond and graphite

POSITIVE
Misfit strain energy per particle volume

POSITIVE
Surface term

- Nucleation is thermodynamically possible if the term in the parenthesis is negative.
- At low pressure (below 10 GPa) misfit strain energy is very large due to large differences in c-axis of graphite and diamond crystals. This explains why diamond formation is not observed below 10 GPa in static compression experiments.

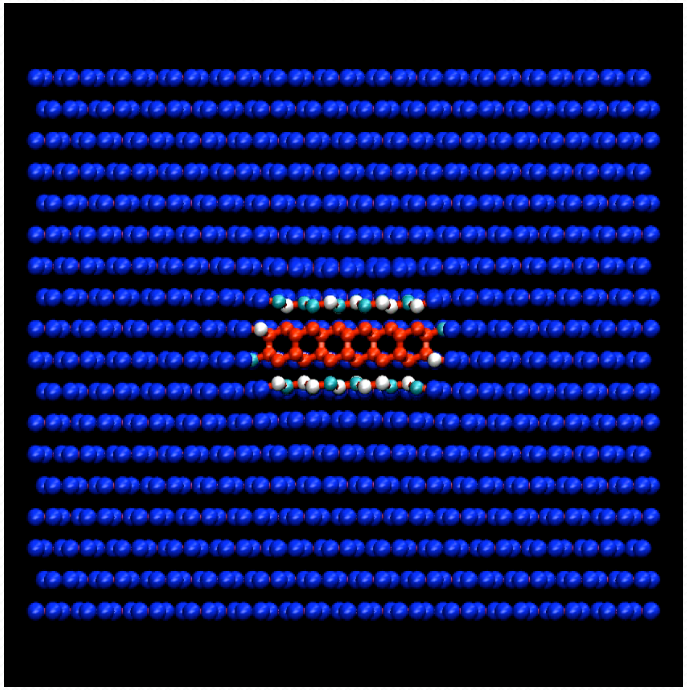
Enthalpy barriers

Pressure	Concerted $\Delta H^{\ddagger}$, meV/atom		Nucleation $\Delta H^{\ddagger}$, meV/atom
	Cubic	Hexagonal	
30 GPa	× 130	× 185	✓ 70-90
40 GPa	× 80	× 140	✓ 40-60
50 GPa	✓ 50	× 93	× 110-280

R.Z. Khaliullin, H. Eshet, T. Kuhne, J. Behler, M. Parrinello, Nature Mat, 10, 693, (2011).

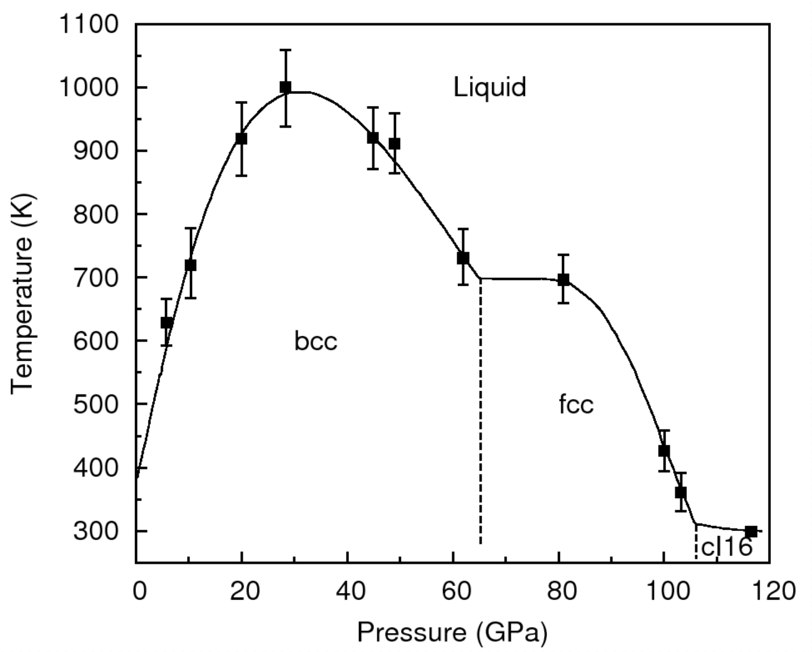
Graphite-to-diamond transition: conclusions

- The transformation does not occur at the graphite–diamond co-existence pressure because of the prohibitively large strains accompanying the formation of diamond nuclei.
- At higher pressures, the nucleation mechanism is favored over the concerted transformation.
- At yet higher pressures, the transition is continuous and proceeds without formation of a well-defined graphite–diamond interface.

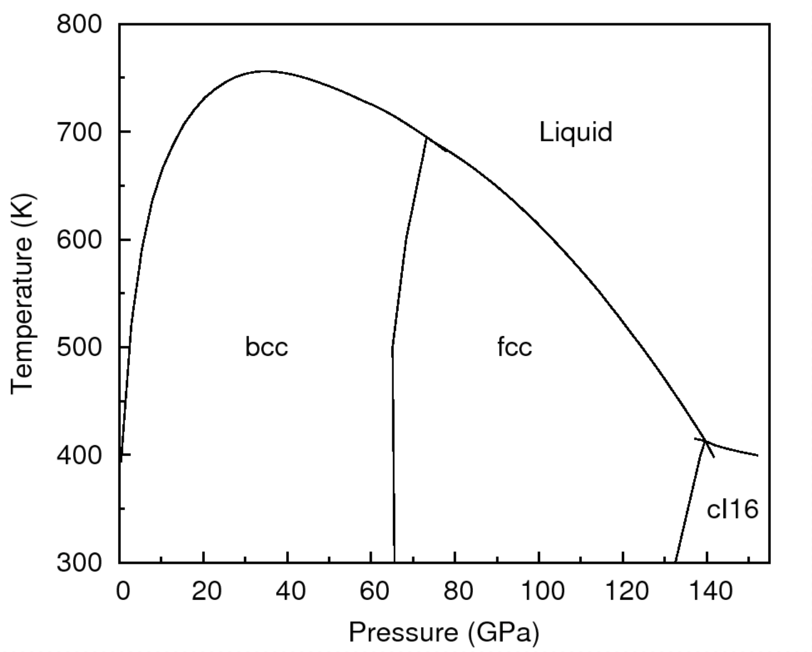


Sodium phase diagram

Experiment

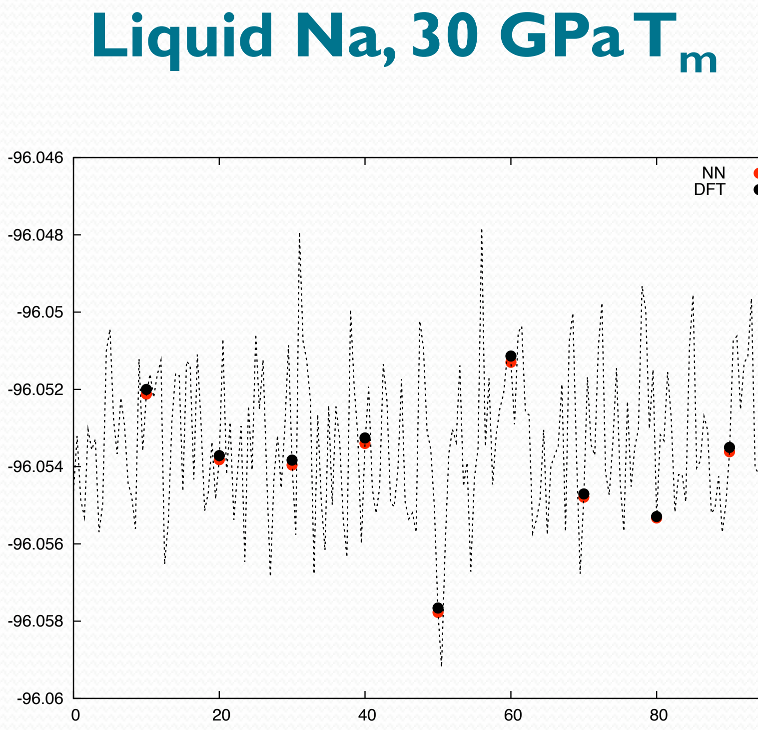


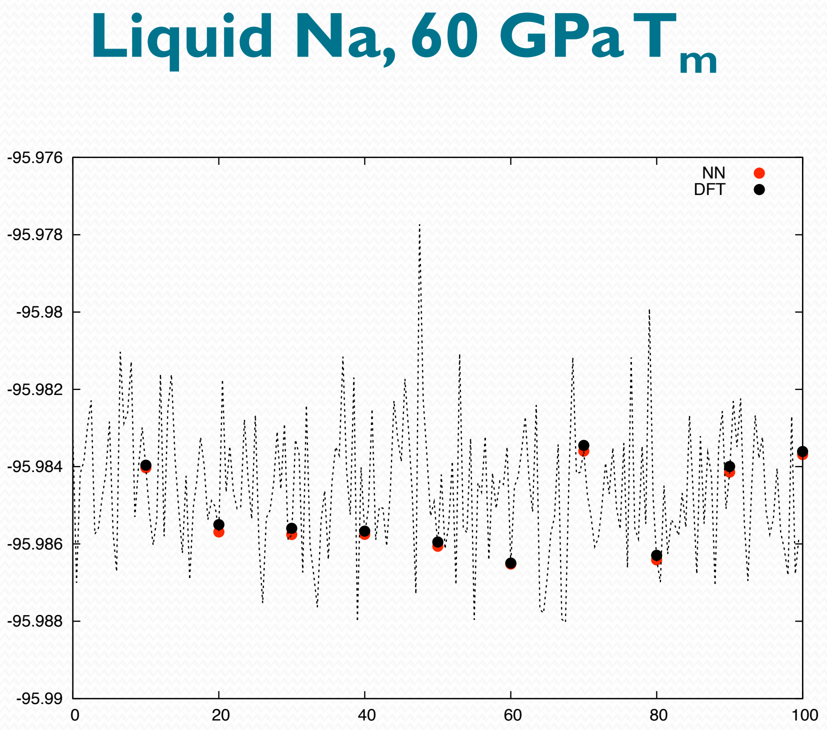
NN simulations



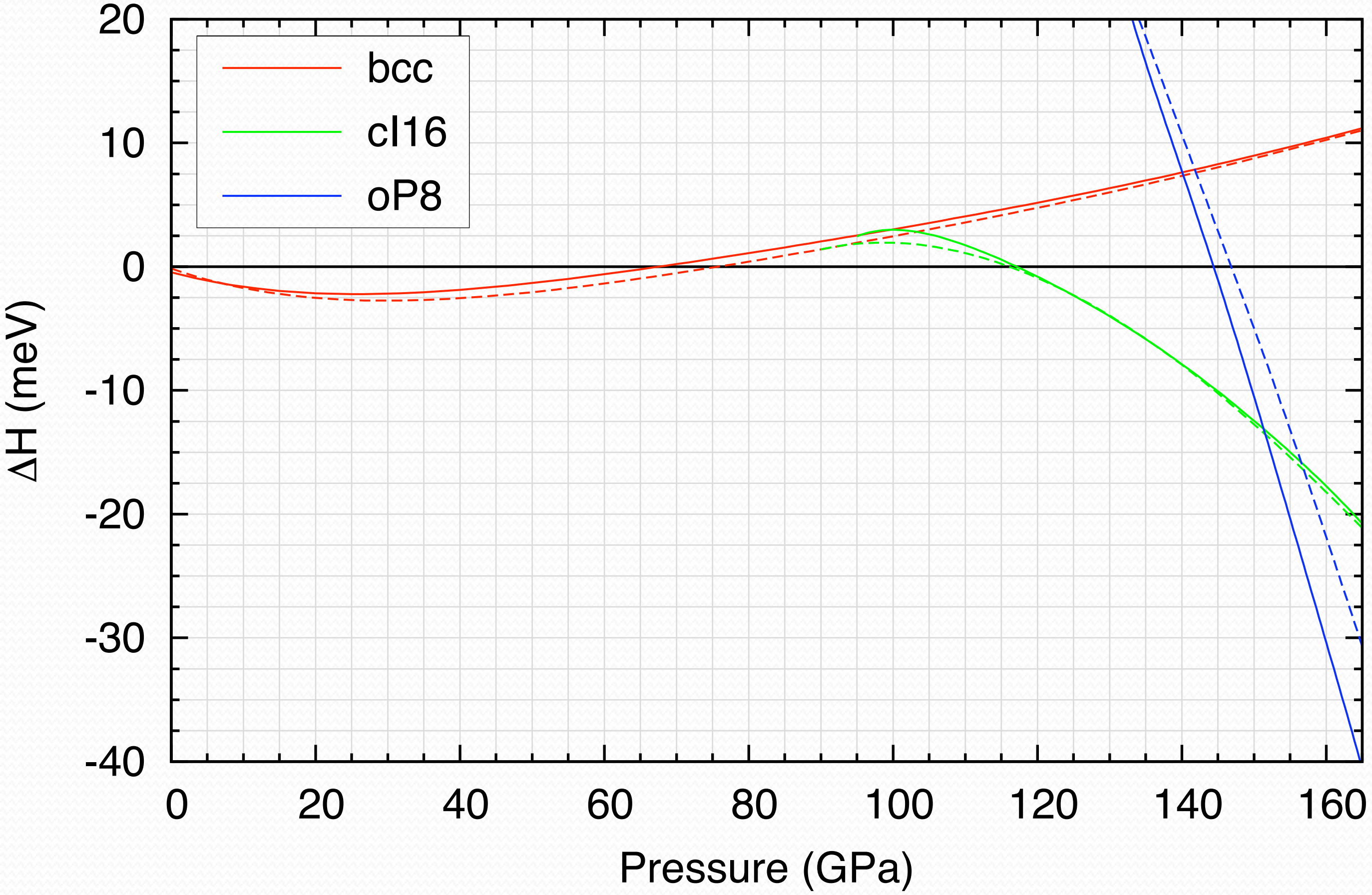
- Sodium undergoes a series of solid-solid phase transitions: bcc → fcc → cI16.
- Nature of the unprecedented pressure-induced drop in melting T is unknown.

Accuracy of the NN potential


Liquid Na, 30 GPa T_m


Liquid Na, 60 GPa T_m

Accuracy of the NN potential



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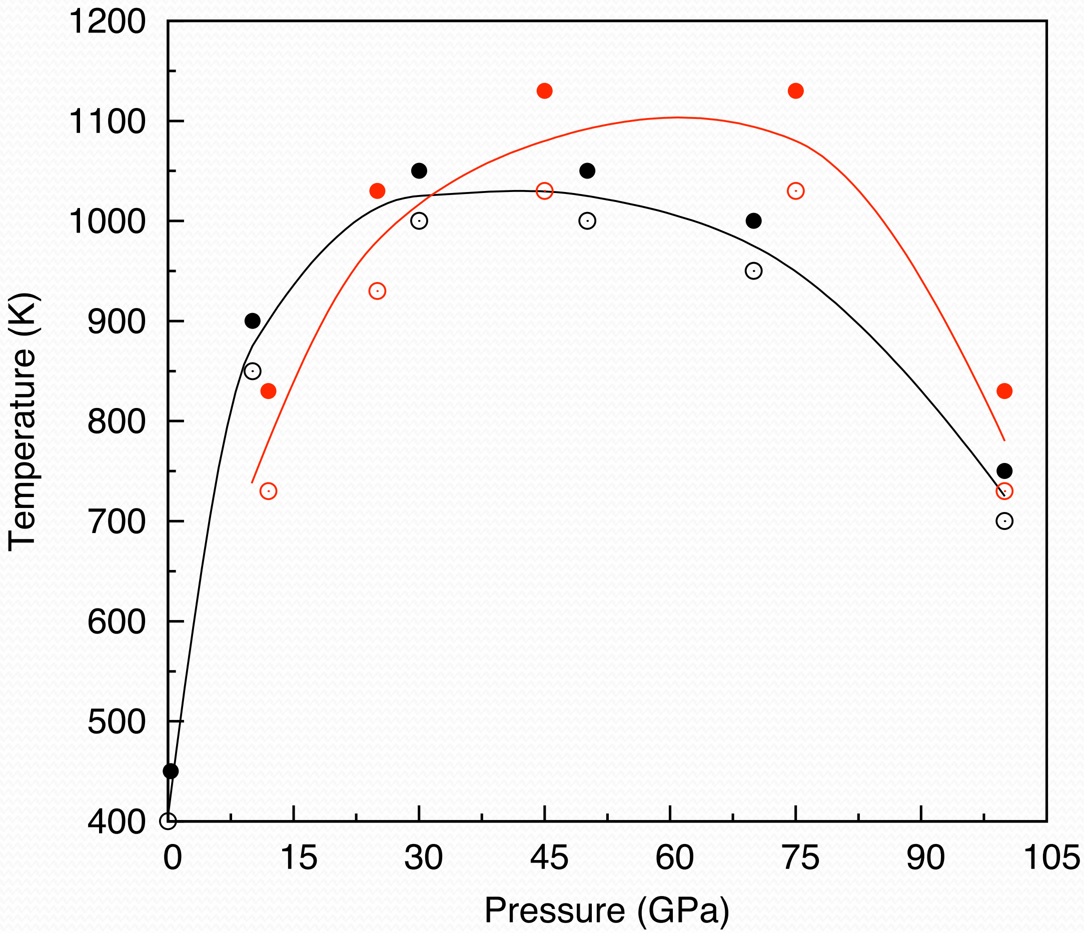
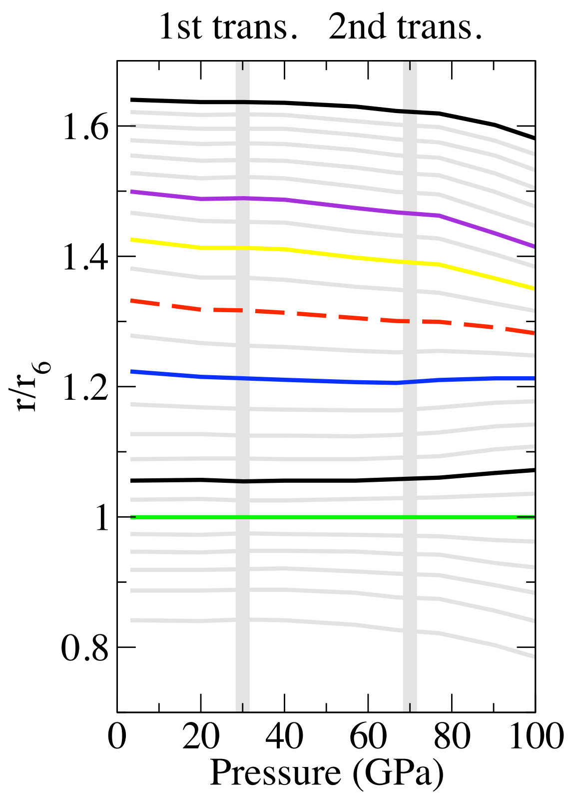
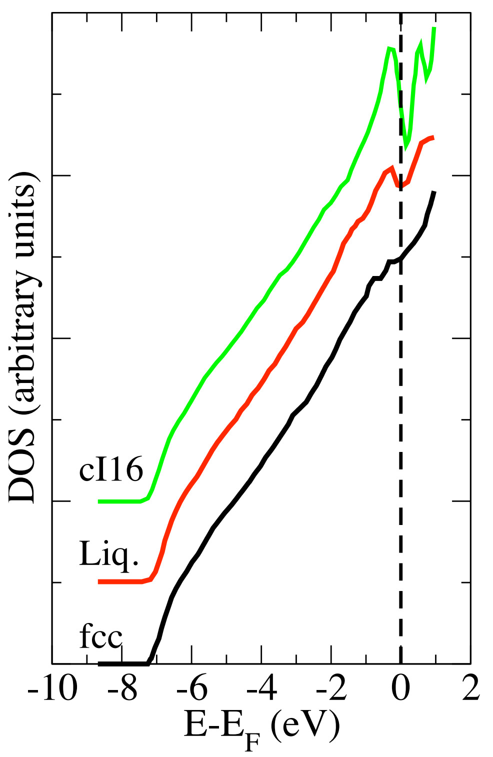


Structural transitions in liquid?

1st, 2nd, 3rd … neighbors



Electronic DOS

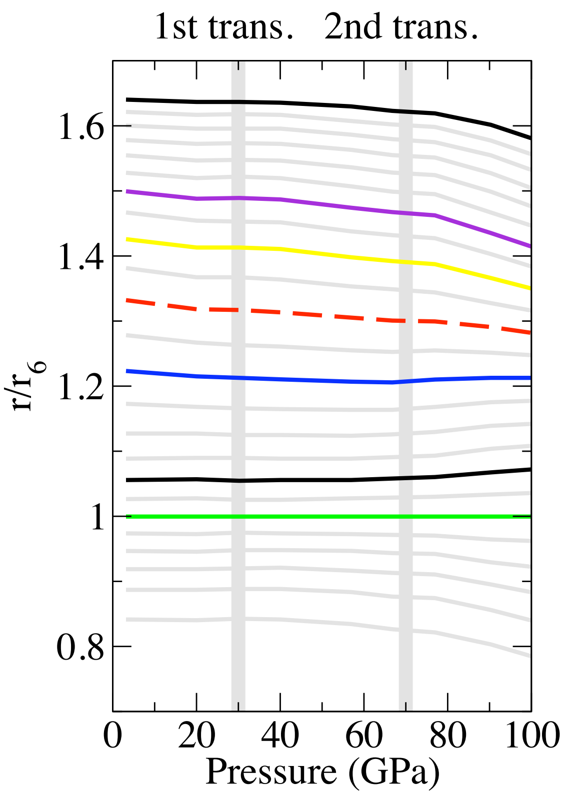


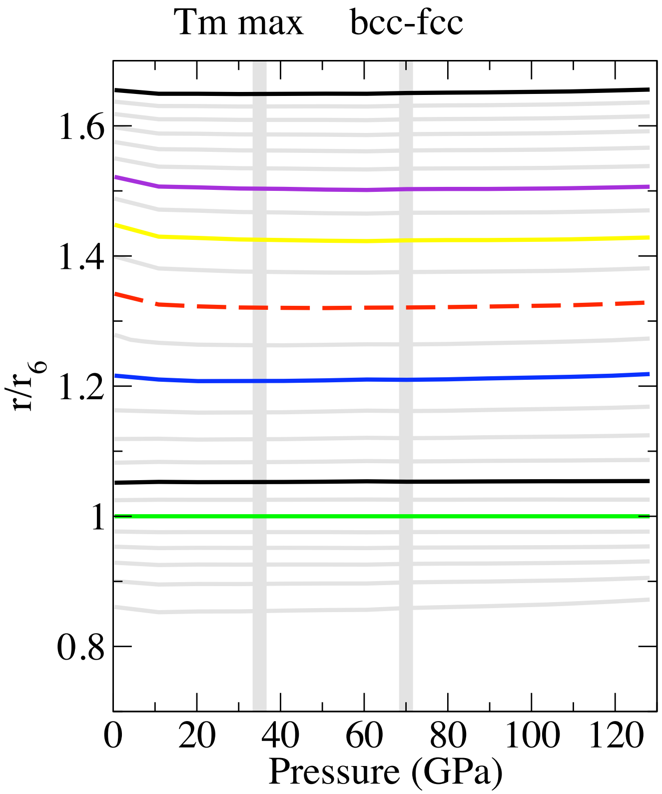
J.-Y. Raty, et al, Nature, 449, 448 (2007).

Structure of liquid Na

Previous simulations

NN simulations





Electronic DOS of liquid Na

Previous simulations

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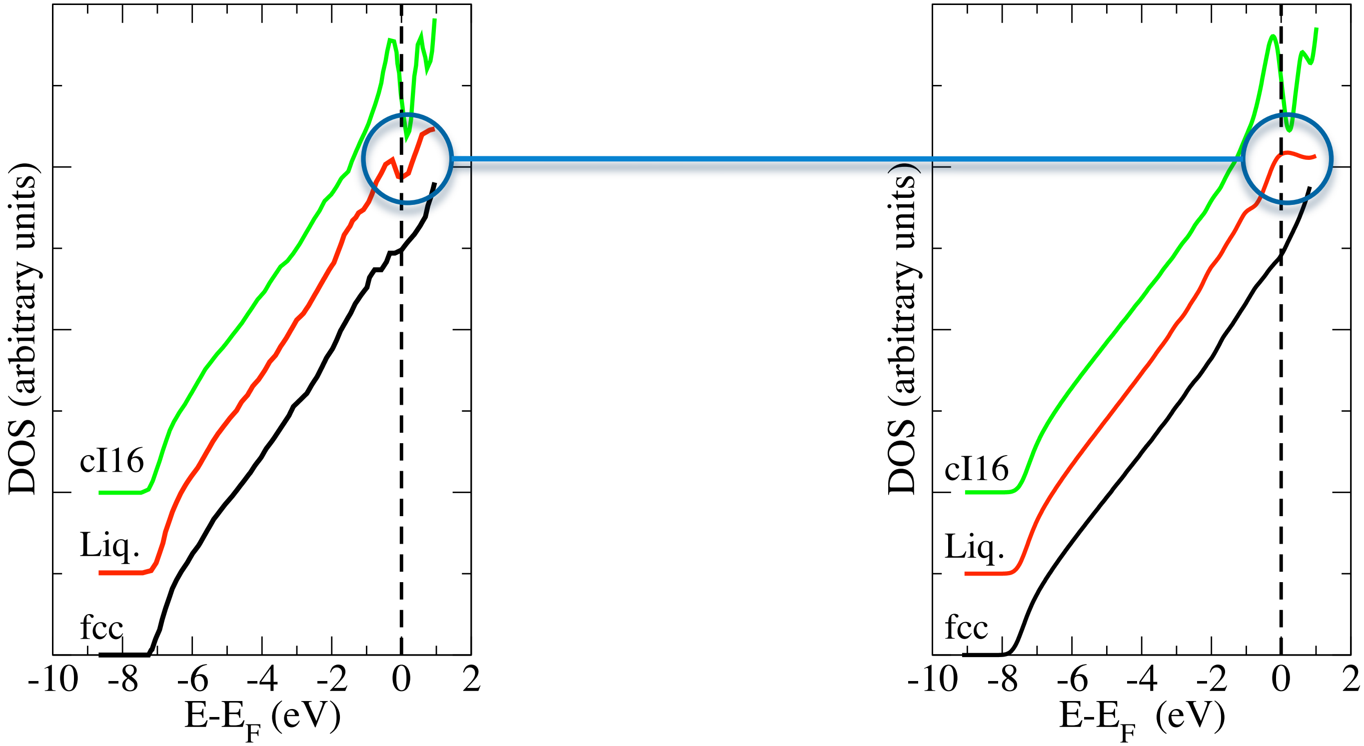
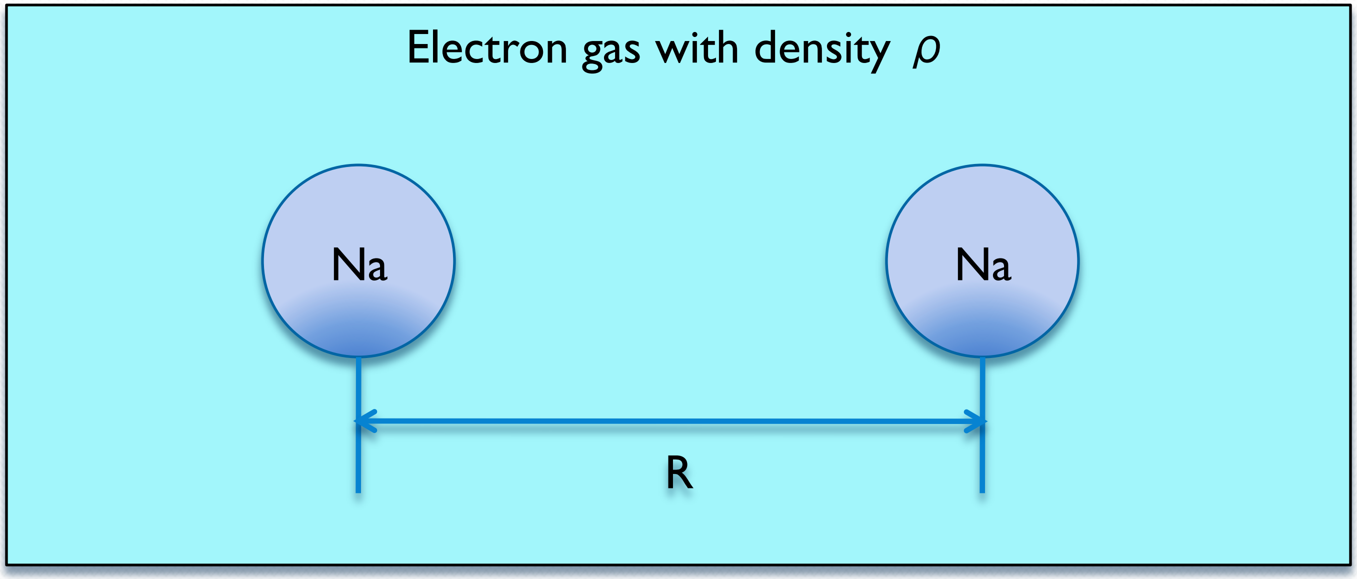
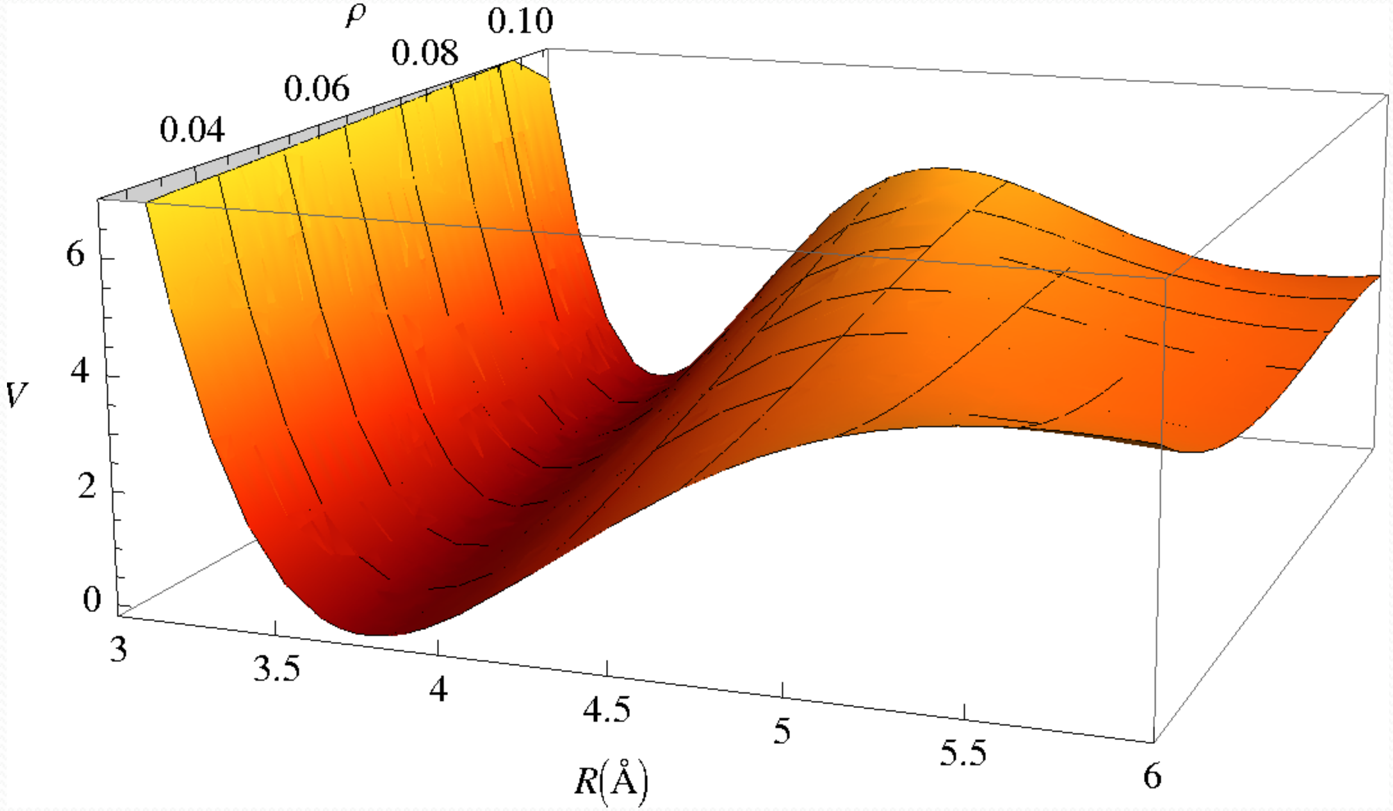


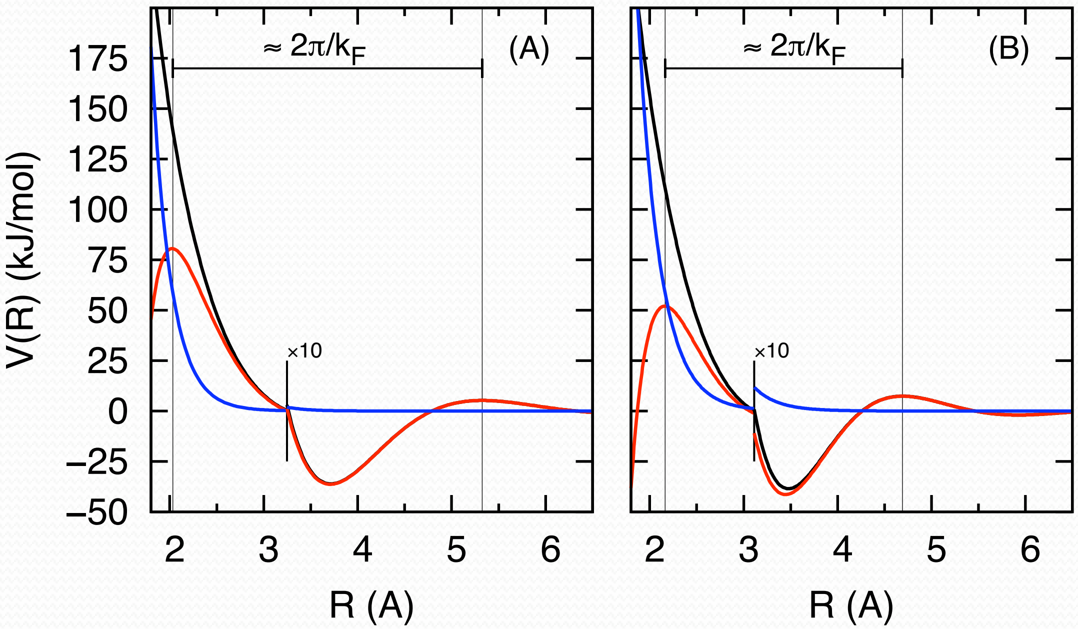
Jellium model



“Jellium” pair potential

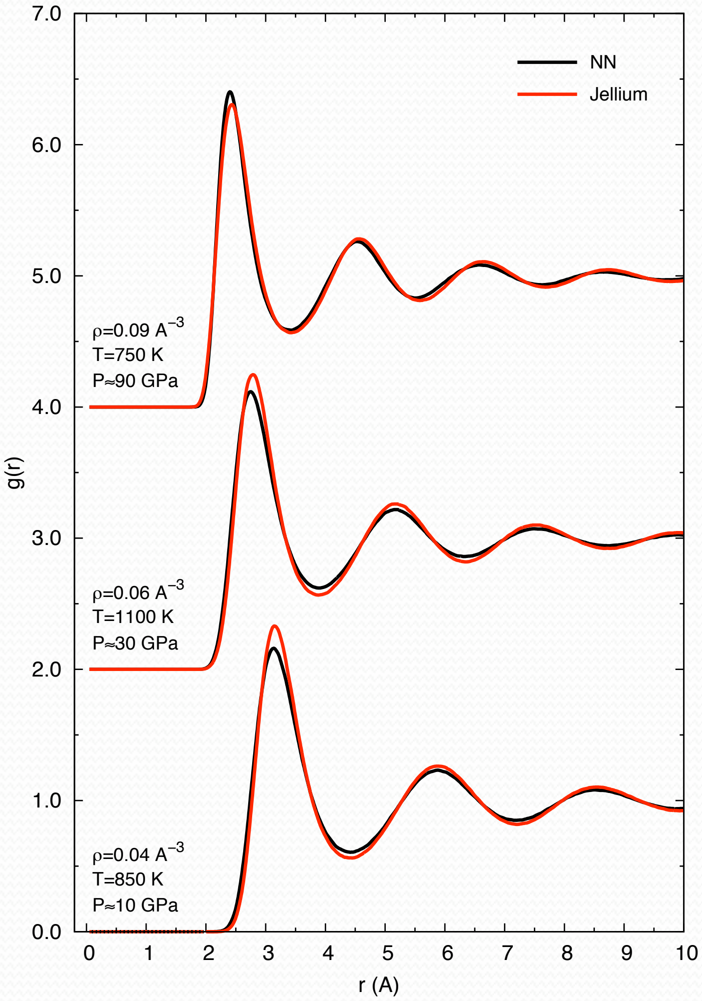


Physical interactions in sodium



$$\phi(r) = \frac{A\exp(-k_0 r)}{r} + \frac{B\cos(2k_F(r - r_0))}{r^m}$$

Accuracy of the pair potential



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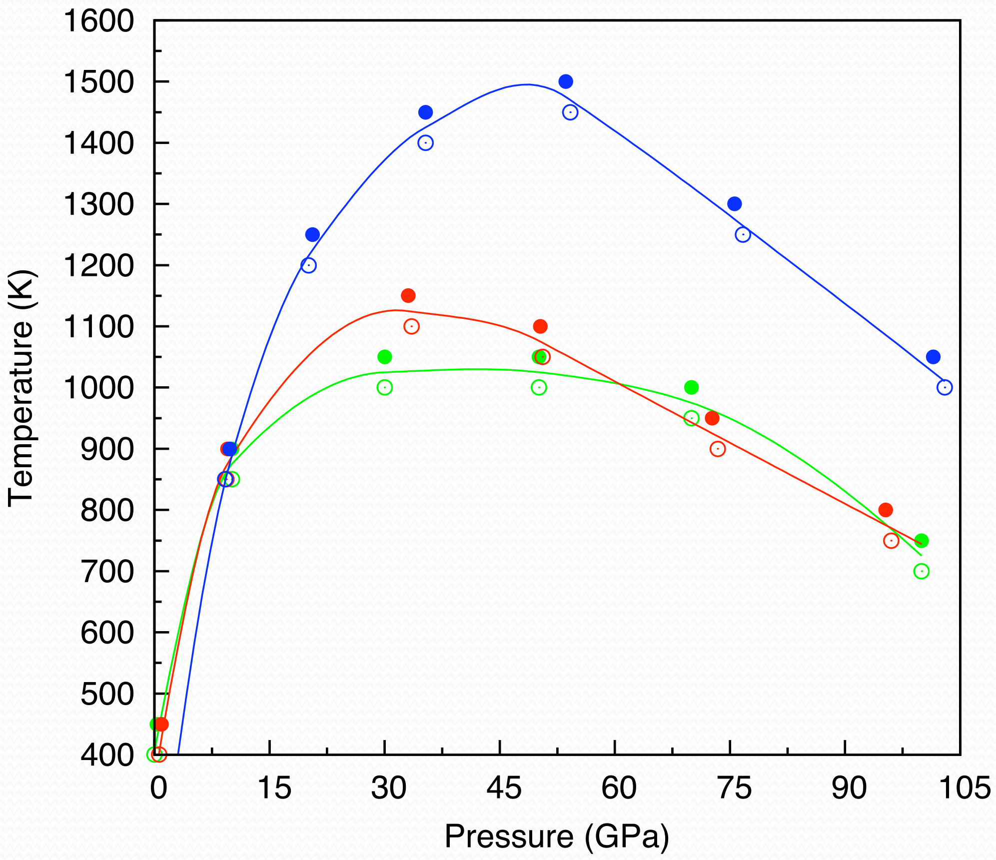
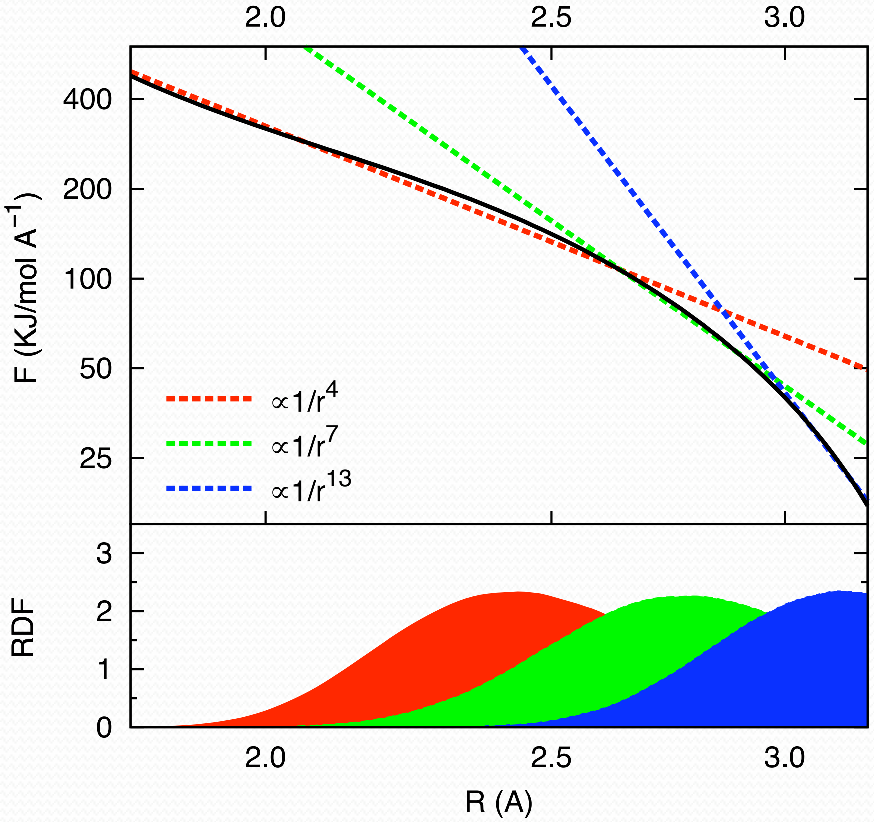


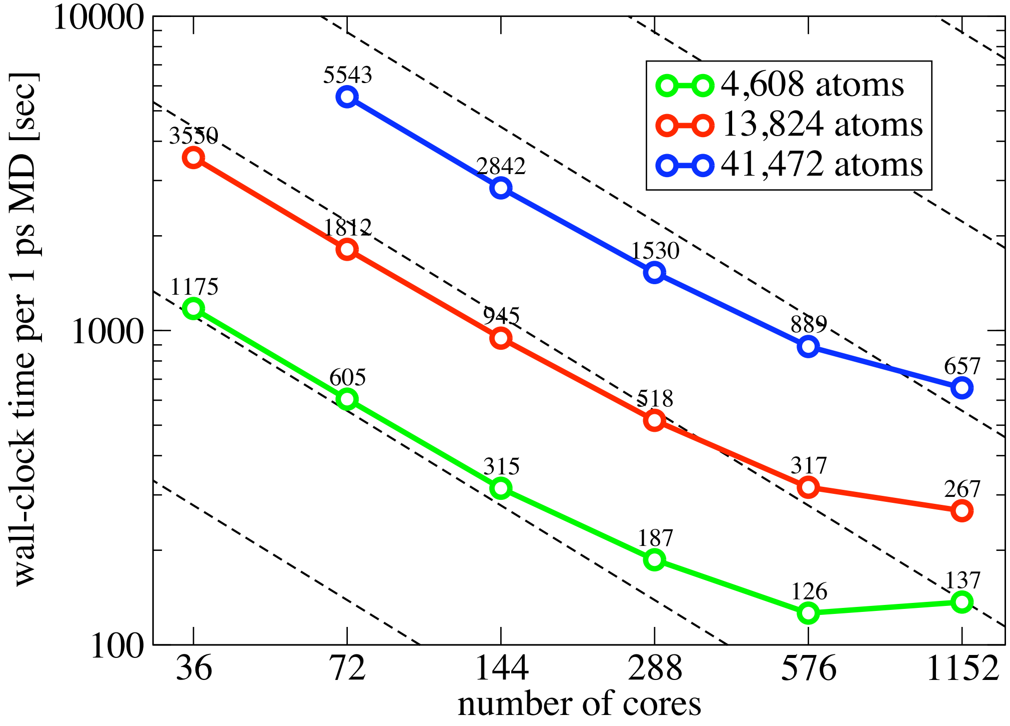
Softening in the repulsive wall



Anomalous melting of Na: conclusions

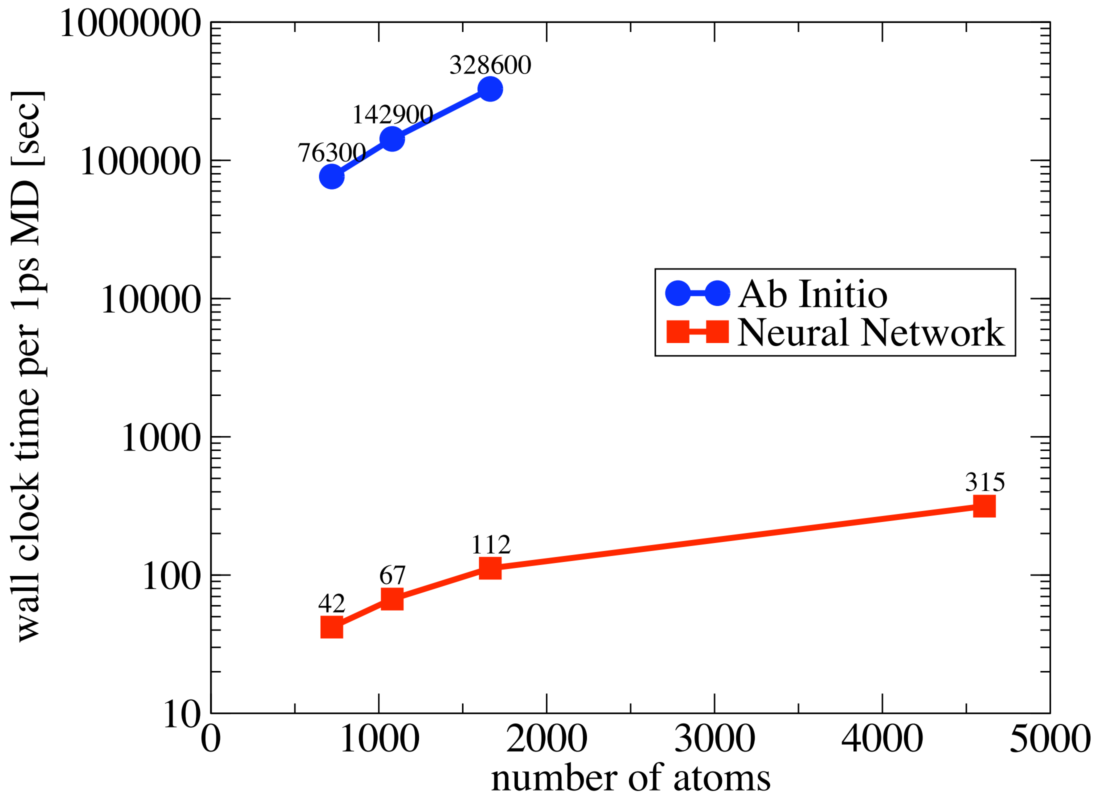
- We reconstructed the phase diagram and showed that the pressure-induced drop in melting temperature is not a consequence of structural transitions in the liquid as previously assumed.
- We demonstrated that the reentrant behavior instead results from the screening of interionic interactions by conduction electrons, which at high pressure induces a softening in the short-range repulsion.

NN implementation



- Interfaced with DLPOLY
  - Thermodynamic integration
  - Metadynamics
- Atomic partitioning of the total energy enables efficient parallel execution
  - now 500-1000 CPUs
- 10^6 atoms can be treated
- One-component systems

Timing: NN vs. *ab initio*



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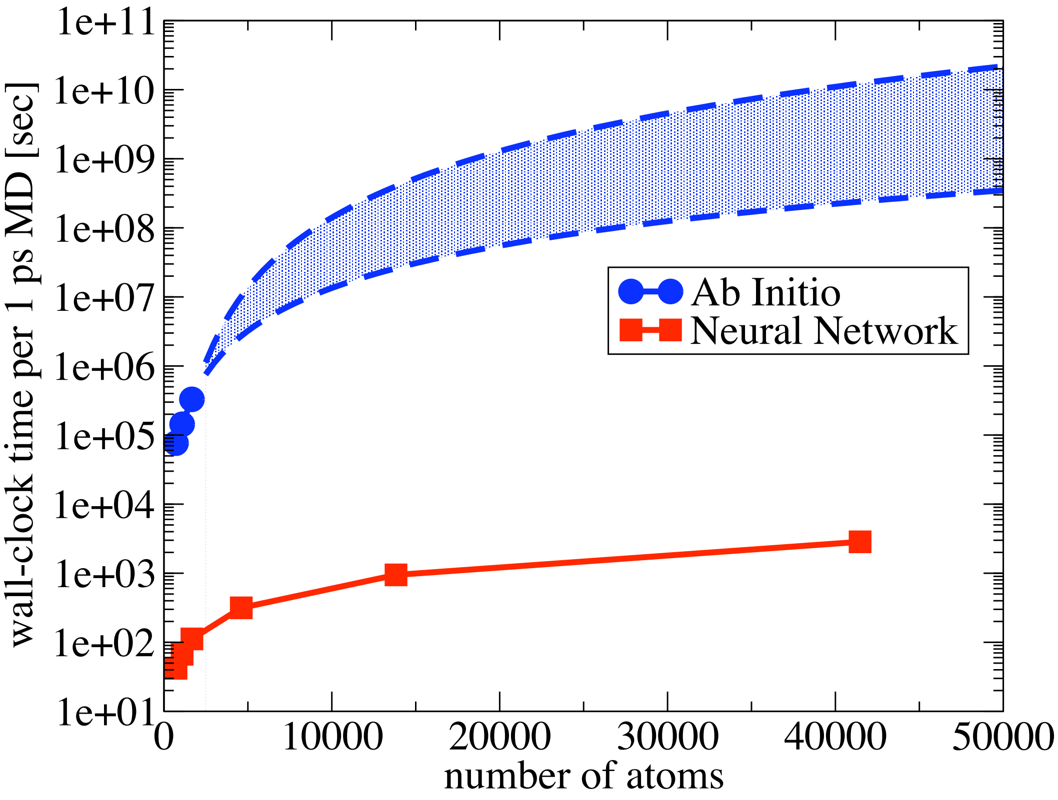

Conclusions

- NN potentials enabled us to perform molecular dynamics simulations of high-pressure high-temperature processes in carbon and sodium on previously inaccessible time and length scales.
- Our simulations offer new insights into the atomistic mechanism of the graphite-to-diamond phase transition and the electronic-structure origin of the anomalous melting behavior of dense sodium.
- NN potentials is an emerging methodology that combines the accuracy of first-principle methods with the high computational efficiency of empirical potentials.

Acknowledgements

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