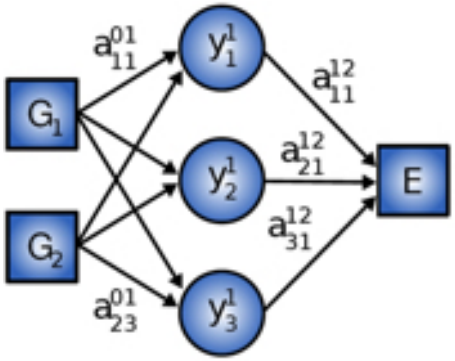
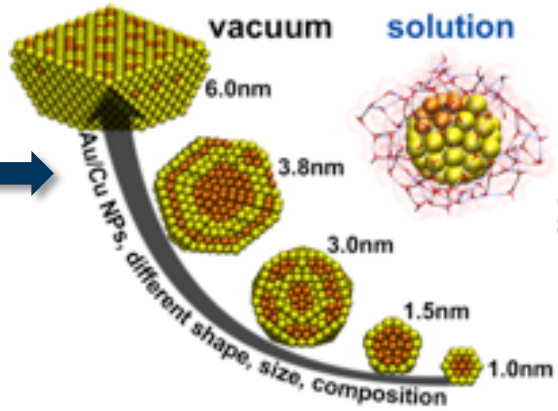
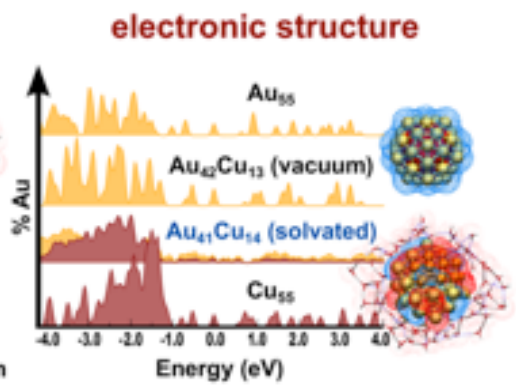
Development of Efficient and Accurate MLPs for the Simulations of Complex Materials



Artificial Neural Network





Comput. Mater. Sci. **114** (2016) 135.
Phys. Rev. B **96** (2017) 014112.

Nano Lett. **14** (2014) 2670.
J. Chem. Phys. **148** (2018) 241711.

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Center for Functional Nanomaterials
Brookhaven National Laboratory

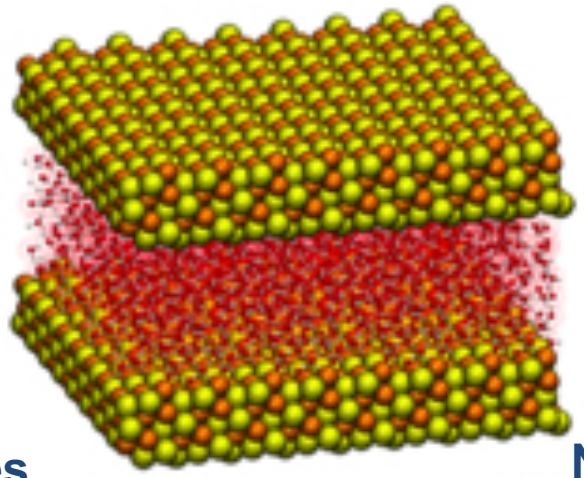
Aalto, Finland, May 6, 2019

Computational Methods and Length Scales

System Size

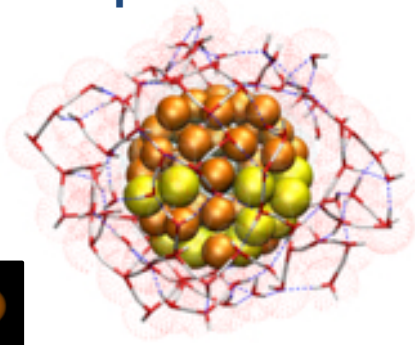
Temperature effects from

- Molecular dynamics simulations (atomic structure)
- Monte Carlo sampling (atomic ordering)

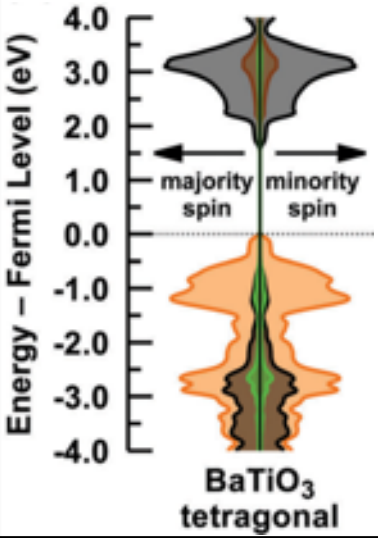


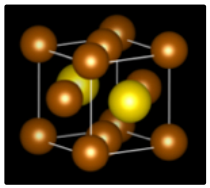
Interfaces and Nanostructures

Nanoparticles

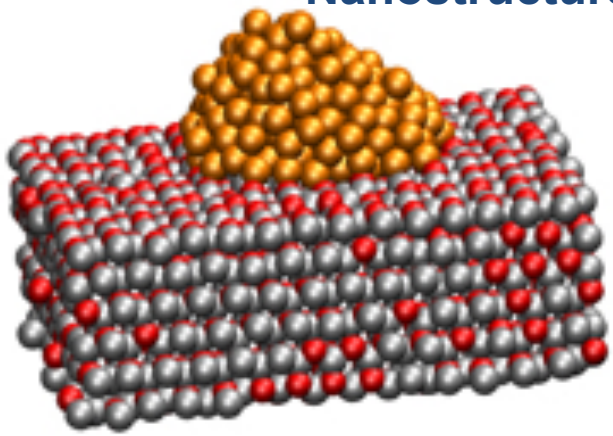


Electronic Structure





Crystal Structure



Approximation

Density Functional Theory — **Atomic Interaction Potentials**

Complex Systems: Challenging for Simulation

Electrochemical Interfaces:

Necessary to describe

⇒ **Breaking and making of bonds**

⇒ **Molecules in gas phase, liquids, solids, and interfaces**

⇒ **Non-ideal surfaces with various kinds of defects**

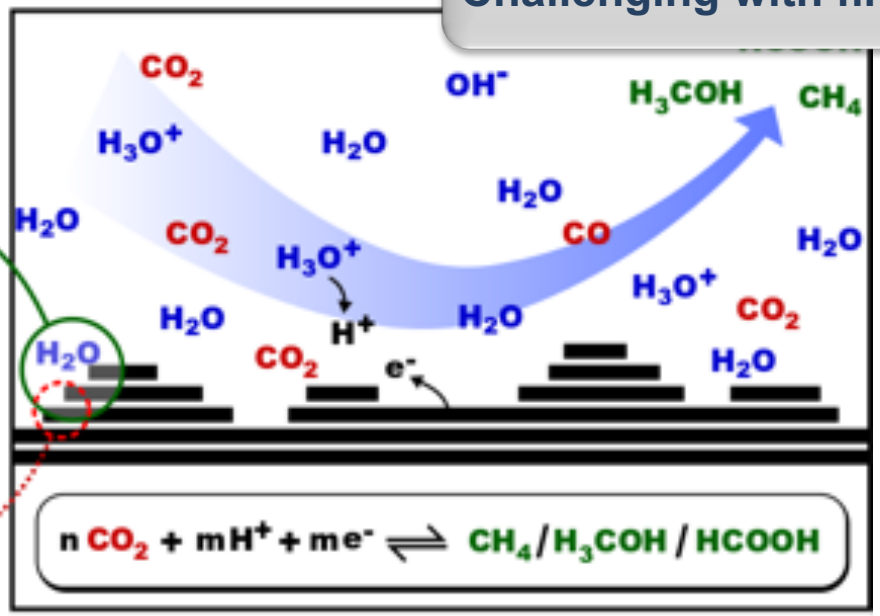
⇒ **Possibly solvent effects and effect of electric field**

No Classical Molecular Potentials

Realistic length scales: Challenging with first principles

Solid-Liquid Interface

Complex Interfaces



Potentials for Materials

- **Empirical Potentials:**
  - ⊕ Efficient
  - ⊖ Simple functional form / usually not reactive
  - ⊖ Transferability problem

- ***Ab initio* (First Principle) MD Potentials:**
  - ⊕ General + Predictive
  - ⊕ Reactive ⇒ proton transfer (chemical reactions)
  - ⊖ No unique combination of, e.g., xc functional + vdW correction
  - ⊖ Computationally demanding

Accelerating Simulations with Machine Learning

State of atomistic simulations

- First-principles methods to compute accurate energies and atomic forces
  → accurate but computationally expensive
- Empirical atomic interaction potentials
  → computationally efficient but only reliable for specific applications

Can machine learning help?

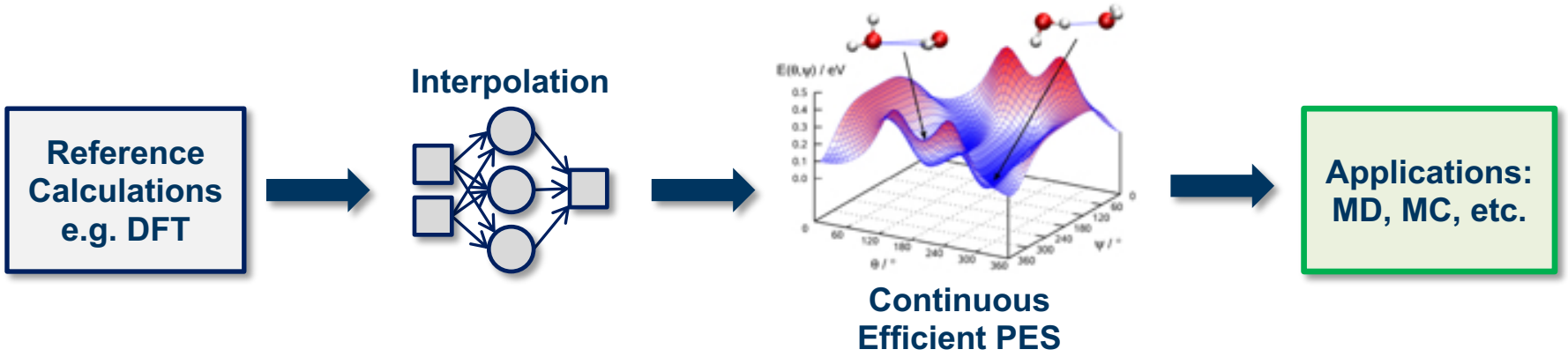
Idea: Train *efficient* machine-learning model to reproduce first-principles results

→ Need **descriptor** of atomic structure as input.

- Model for energy & forces: machine-learning potential
- All kind of structure-property relationships: classification, interpolation

Potentials for Materials

- **Potentials Based on *Ab Initio* Calculations:**



⊕ Accurate + Efficient

Reactive ➡ depends on approach

- **Our Approach:**
  - Artificial neural networks for interpolation ⇒ **Very accurate**
  - Not based on many-body expansion of the PES, no bonds/angles need to be specified ⇒ **Reactive + Full-dimensional**

Machine-Learning Potentials:

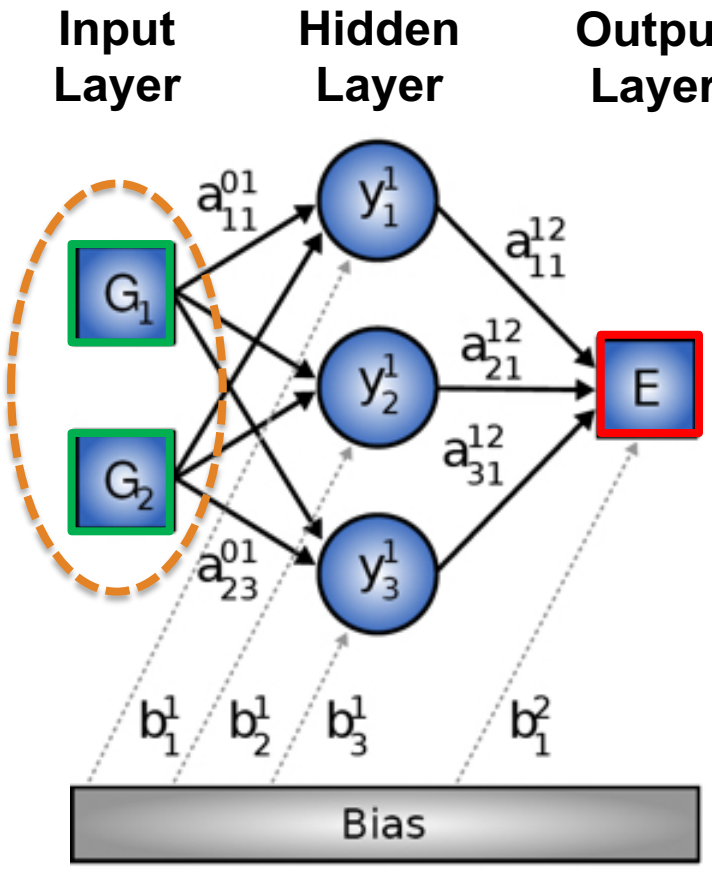
Direct application of ML to MC/MD simulations

Artificial Neural Networks for Regression

- ANNs can approximate arbitrary continuous functions
- *Universal Approximation Theorem*
  G. Cybenko, Math. *Control Signals Syst.* **2** (1989) 303–314.
  K. Hornik, *Neural Netw.* **4** (1991) 251–257.
  B. Hanin (2017) *arXiv* 1708.02691.
- Ideal for the approximation of high-dimensional functions
- Our approach: Use ANNs to approximate the potential energy surface

Machine Learning for Atomic Structures

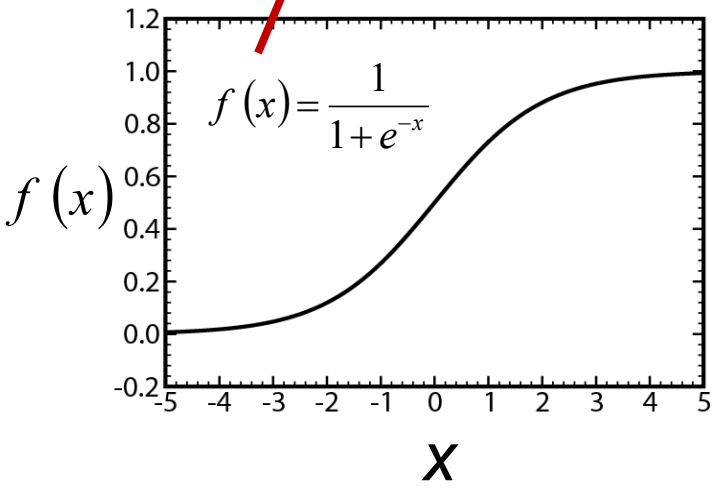
Small Example for a Feed-Forward Neural Network



Total Energy Expression

$$E = f_1^2\left(b_1^2 + \sum_{j=1}^{3} a_{j1}^{12} \cdot f_j^1\left(b_j^1 + \sum_{i=1}^{2} G_i \cdot a_{ij}^{01} \right) \right)$$

Activation Functions

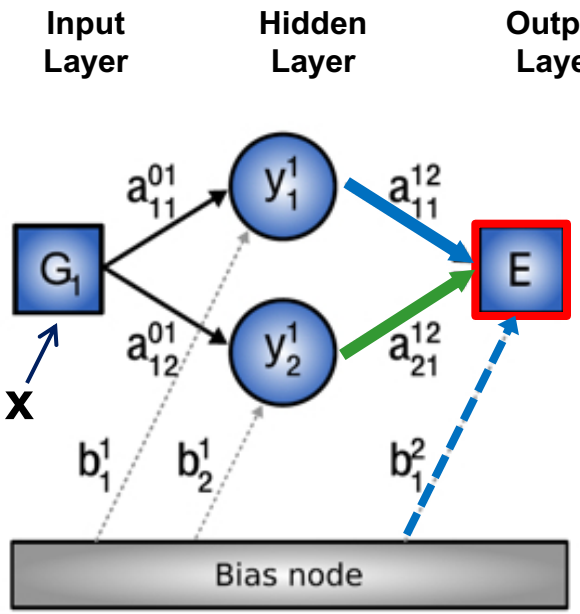


⇒ **Can fit arbitrary functions**

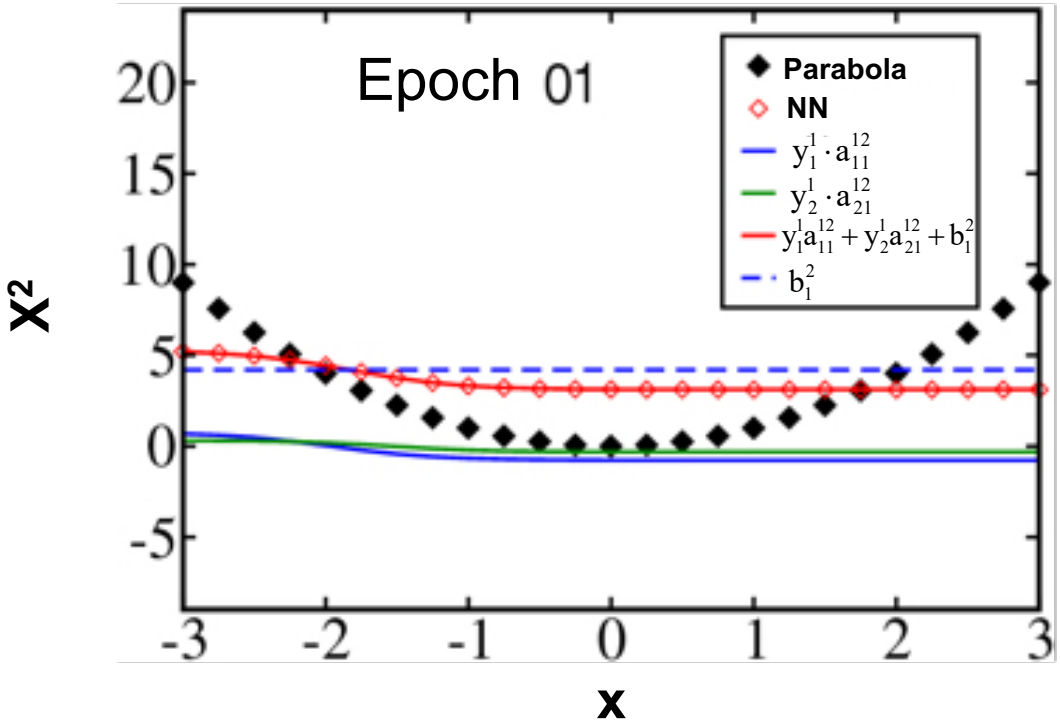
T.B. Blank, S.D. Brown, A.W. Calhoun, and D.J. Doren, *J. Chem. Phys.* 103 (**1995**) 4129.
S. Lorenz, A. Groß, and M. Scheffler, *Chem. Phys. Lett.* 395 (**2004**) 210.

Standard Neural Network

Training the Neural Network:



Parabola: x^2



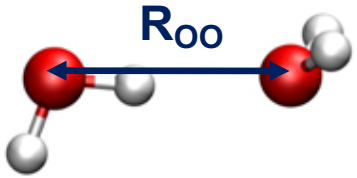
$$E_{NN} = a_{21}^{12} f^1\left(b_2^1 + G_1 \cdot a_{12}^{01}\right) + a_{11}^{12} f^1\left(b_1^1 + G_1 \cdot a_{11}^{01}\right) + b_1^2$$

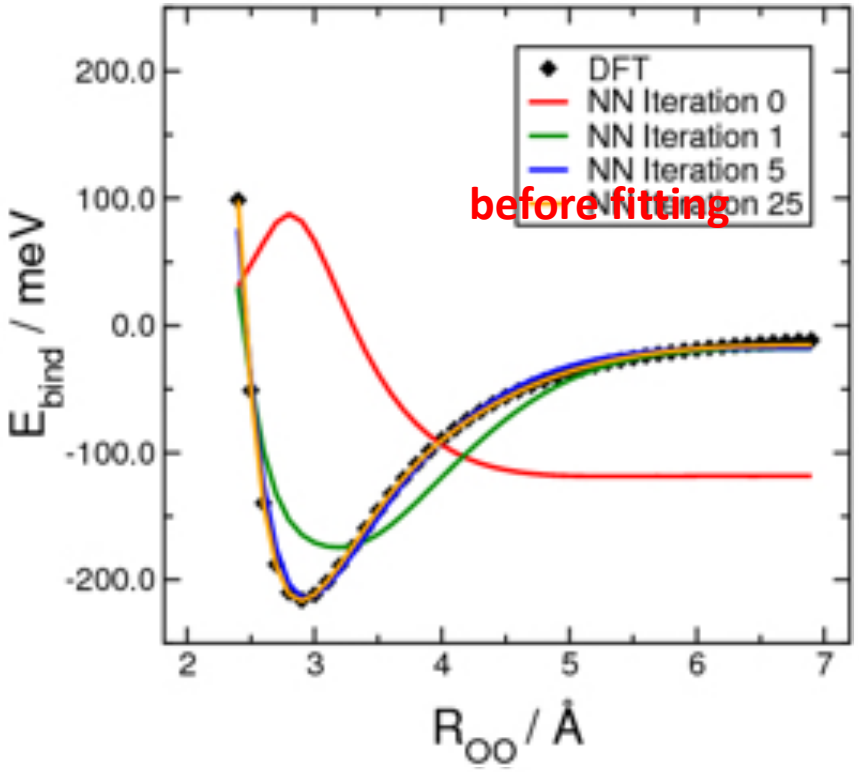
- The NN can learn the functional form of the PES

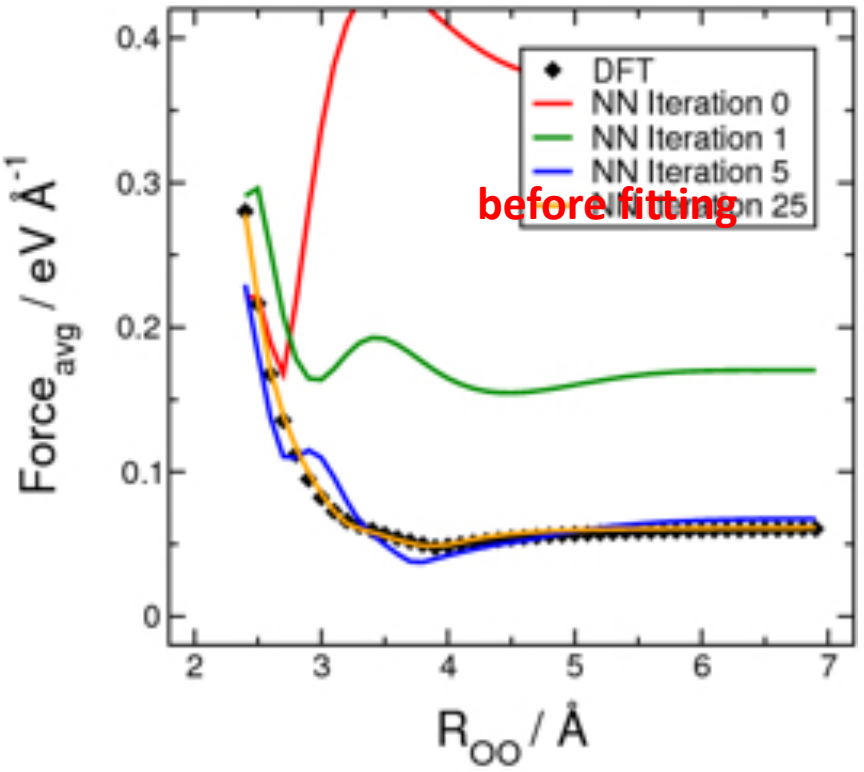
Training the Neural Network

- **Minimize error function for energy (and forces)**
- **Example:**

  1D cut of water dimer PES







⇒ The NN can learn the functional form of the PES

T. Morawietz, A. Singraber, C. Dellago, J. Behler *Proc. Natl. Acad. Sci. U. S. A.* **113**, (2016) 8368-8373.

Conventional ANNs are not Transferable

- ANNs have a fix input dimension
- If the input is atomic coordinates, the ANN can only be used for one specific number of atoms
- Hence, the ANNs are not transferable to atomic structures with different numbers of atoms

→ NOT a replacement for interatomic potentials

Conventional ANNs do not Exhibit Physical Invariants

- ANNs are not automatically invariant with respect to translation & rotation of the atomic structure
- ANNs are not invariant with respect to the exchange of two equivalent atoms

→ NOT a replacement for interatomic potentials

The Behler-Parrinello Approach: Invariant ANN Potentials

1. The total energy is the sum of atomic energies

$$E_{\mathrm{tot}} = \sum_{i}^{\mathrm{atoms}} E_i$$

2. ANNs represent the atomic energies E_i

3. The input for the ANNs are invariant representations of the local atomic environment

→ Suitable replacement for interatomic potentials

J. Behler, and M. Parrinello, *Phys. Rev. Lett.* 98, (**2007**) 146401.

Universal Atomic Energy Function

Decomposition of the total structural energy into atomic contributions

$$E(\sigma) = \sum_{i}^{\text{atoms}} E_i(\sigma)$$

Total energy of structure σ

Energy of the *i*-th atom in structure σ

In embedded atom models (EAM) the atomic energy is

$$E_i(\sigma) = F_\alpha\left(\sum_{i\neq j}\rho_\beta(R_{ij})\right) + \frac{1}{2}\sum_{i\neq j}\phi_{\alpha\beta}(R_{ij})$$

Embedding function

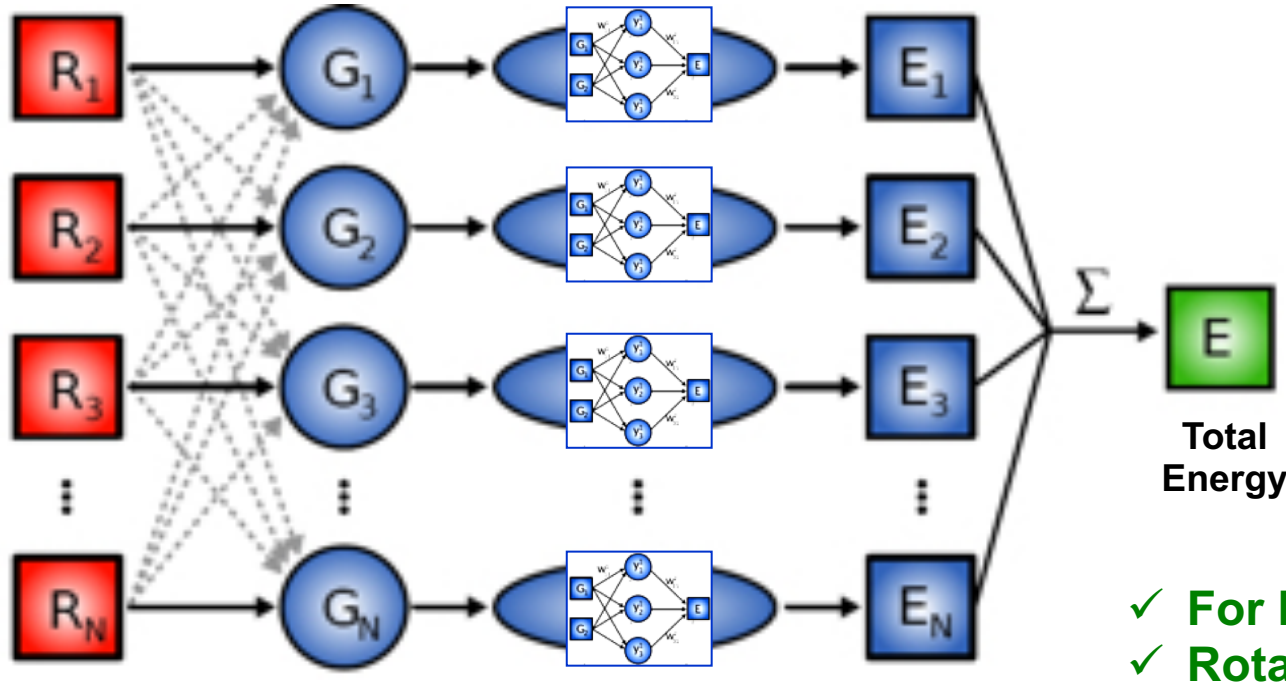
Contribution to charge density

Pair potential

→ Physically motivated functional form, but not flexible. No dependence on bond angles. The model is **not appropriate for every structure/chemical species**.

→ **Use machine learning to determine universal atomic energy function**

High-Dimensional Neural Network



- ✓ For high-D NN
- ✓ Rotation
- ✓ Translation

Set of many-body functions that describes the local environment of each atom "structural fingerprint": **a radius of 6-8 Å**

J. Behler, and M. Parrinello, *Phys. Rev. Lett.* 98, (**2007**) 146401.

J. Behler, R. Martoňák, D. Donadio, and M. Parrinello, *phys. stat. sol. (b)* 245, (**2008**) 2618.

J. Behler, *J. Chem. Phys.* 134, (**2011**) 074106.

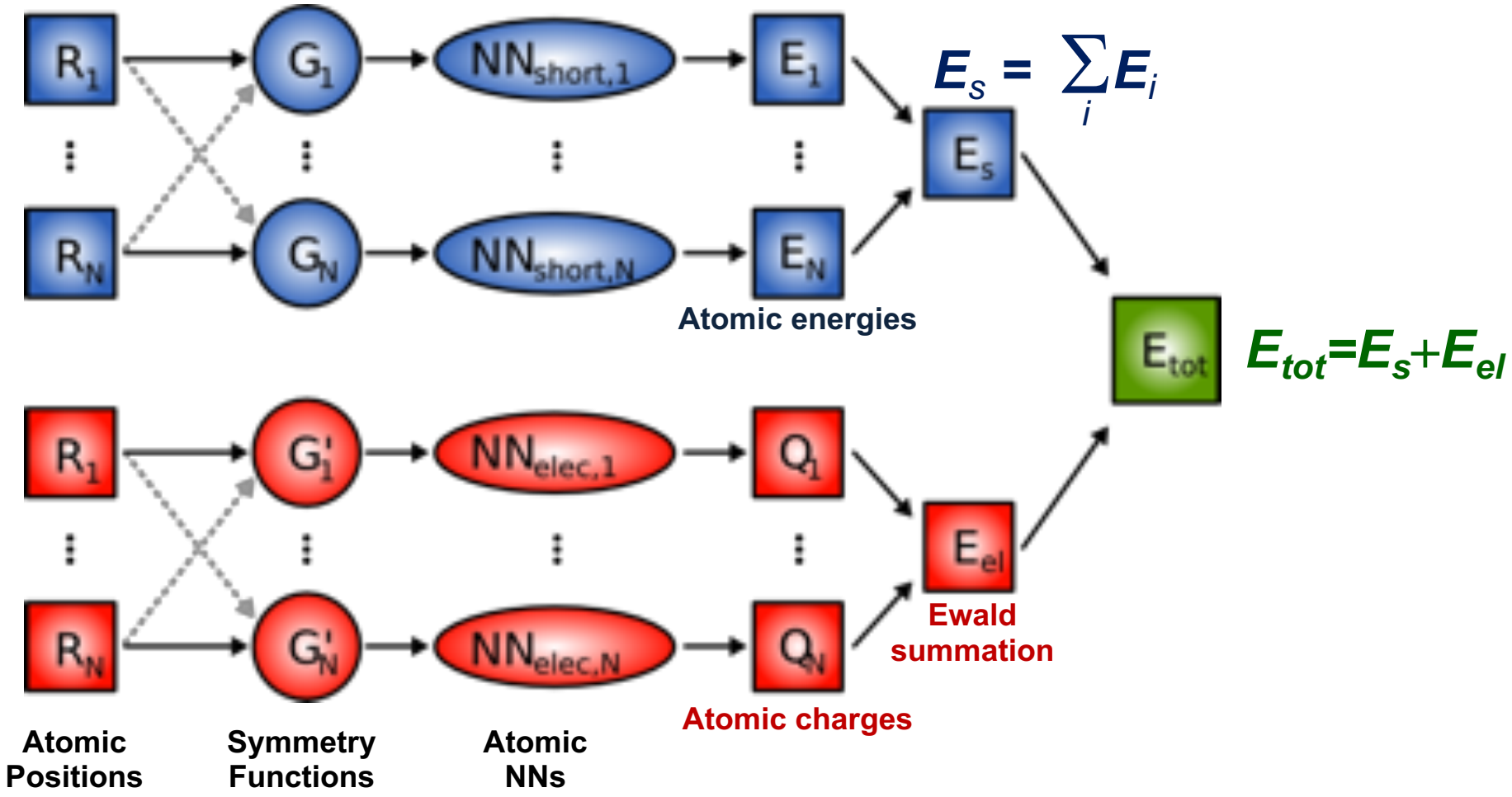
N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* 83, (**2011**) 153101.

Short-Range and Long-Range Energy

- In systems with multiple chemical species, electrostatic interactions may become important
- Electrostatic interactions are **long-ranged**
- Cannot (strictly) decompose the electrostatic energy into atomic contributions
- However, the charge can be calculated
  → no unique way, but consistent recipes
- **Train a separate high-dimensional ANN for the atomic charges**

N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* 83, (**2011**) 153101.

Extension to Multicomponent Systems



N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* 83, (**2011**) 153101.

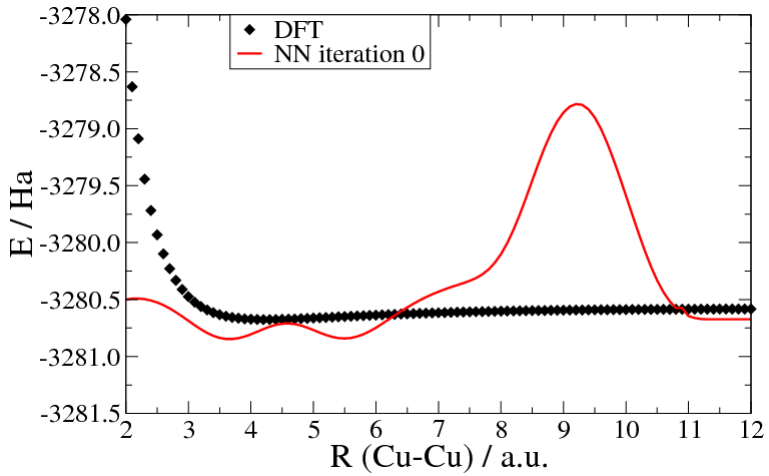
Extension to Multicomponent Systems

- In practice: electrostatic interactions are screened in condensed phases
- **Slightly longer-ranged potentials can often capture the effective electrostatic interactions (e.g., using 8 - 15 Å instead of 6 Å)**
- Confirmed for many different oxide materials

N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* 83, (**2011**) 153101.

Neural Network Fitting

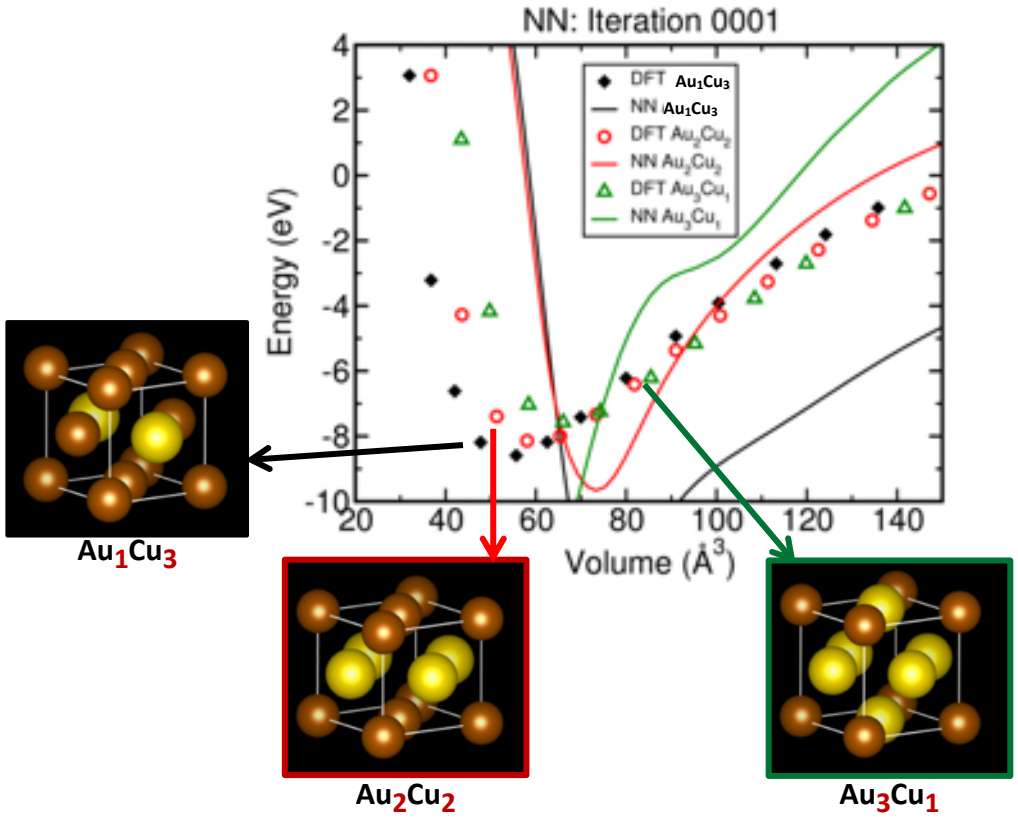
Example: Copper Dimer



"Before fitting"
Random parameters

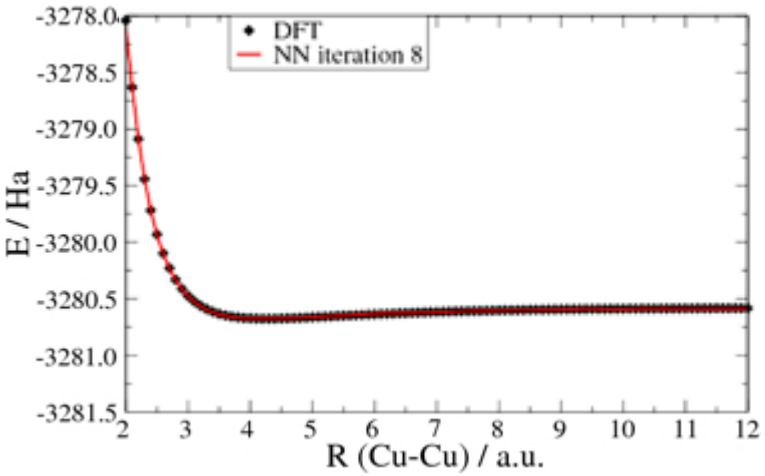
High-Dimensional:

Au_xCu_y Crystal Structures



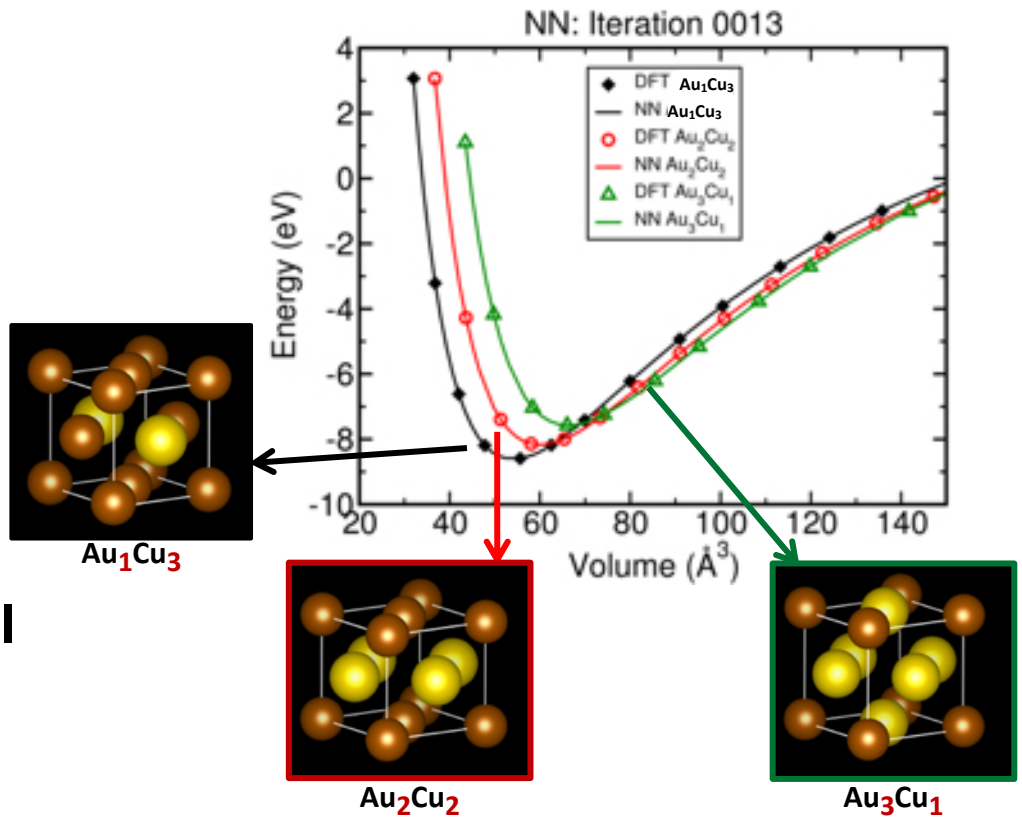
Neural Network Fitting

Example: Copper Dimer



High-Dimensional:

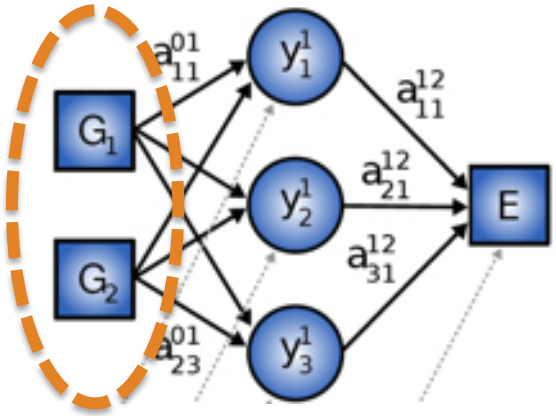
Au_xCu_y Crystal Structures



⇒ **Conclusion:**

NNs can establish a functional relationship between the structure and its energy

Descriptors of the Local Structural Environment



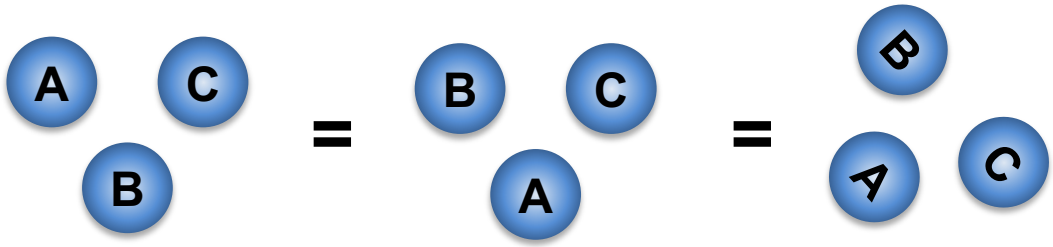
Properties of the Atomic Energy

$$E(\sigma) = \sum_{i}^{\text{atoms}} E_i(\sigma)$$

Like the structural energy, the atomic energy is invariant with respect to

- Exchange of equivalent atoms (order of counting) and
- Translation/rotation of the entire structure.

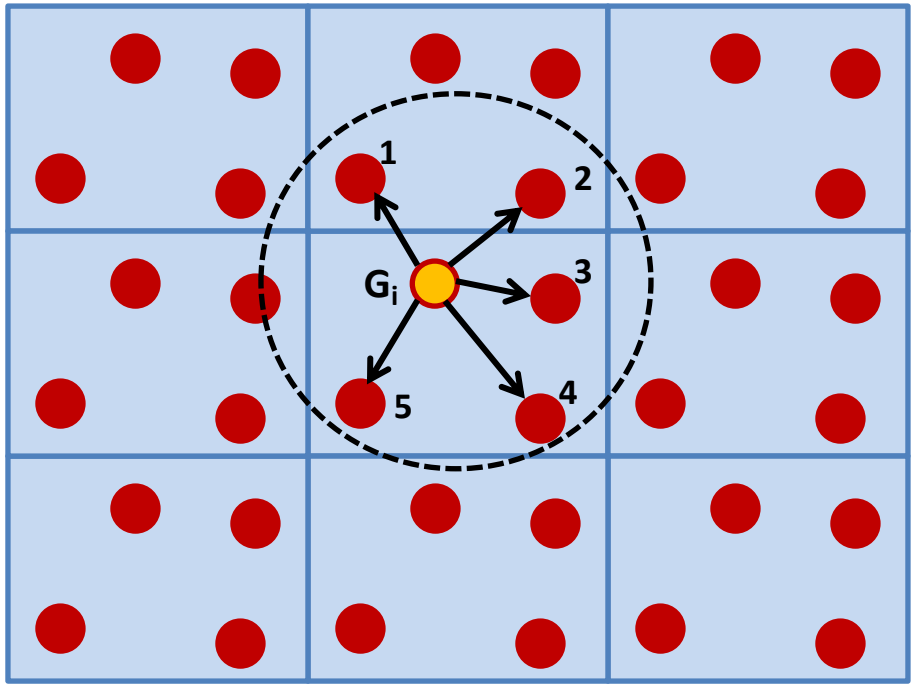
Any (machine-learning) model must obey these invariants.



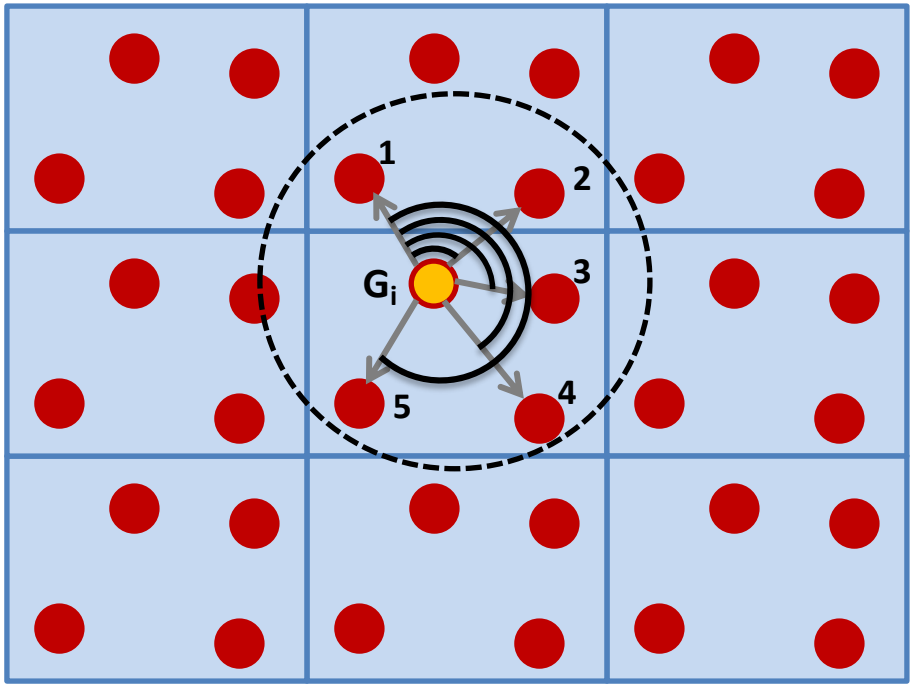
Radial & Angular Distribution Functions

Approach: Use the radial and angular distribution of atoms and atom types as descriptor.

Atomic Radial Distribution Function



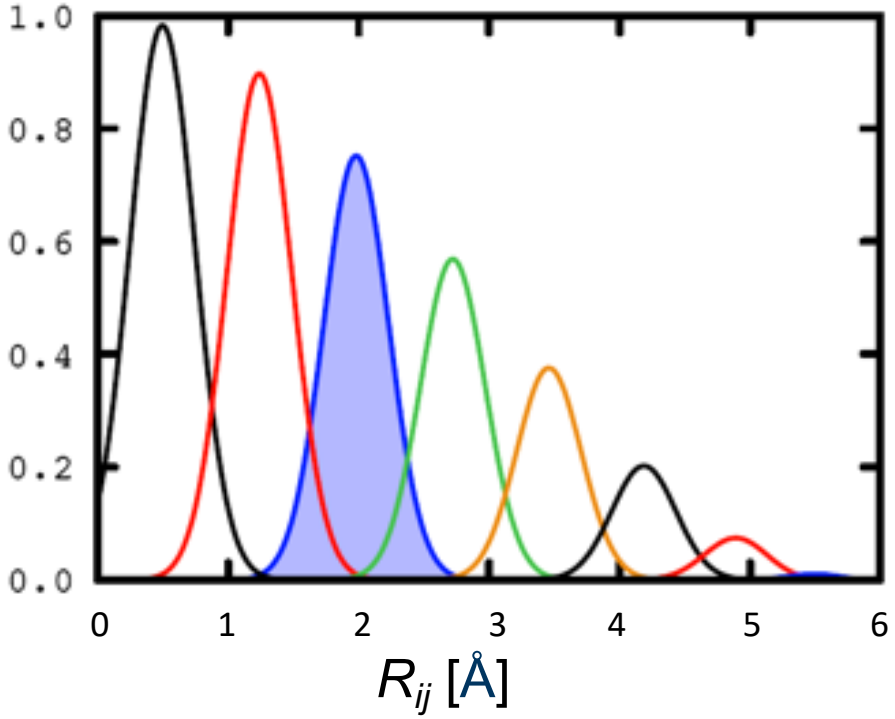
Atomic Angular Distribution Function



Behler-Parrinello Symmetry Functions

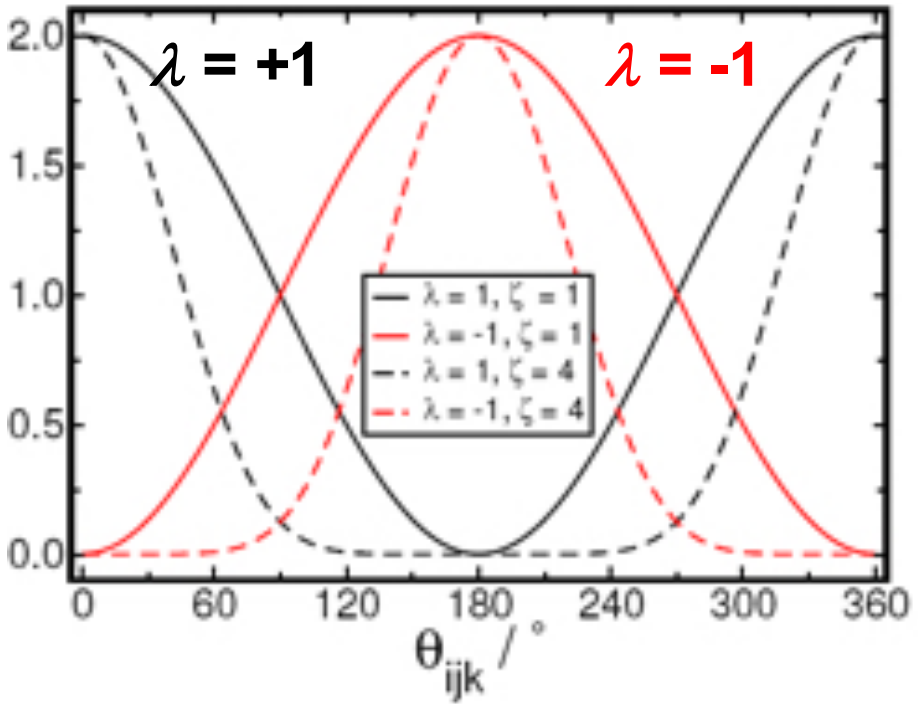
Radial symmetry functions

$$G_i^2 = \sum_j e^{-\eta\left(R_{ij}-R_s\right)^2} \cdot f_c\left(R_{ij}\right)$$



Angular symmetry functions

$$G_i = 2^{1-\zeta} \sum_j \sum_k \left[\left(1 + \lambda \cdot \cos\theta_{ijk}\right)^\zeta \cdot e^{-\eta\left(R_{ij}^2+R_{ik}^2+R_{jk}^2\right)} \cdot f_c\left(R_{ij}\right) \cdot f_c\left(R_{ik}\right) \cdot f_c\left(R_{jk}\right)\right]$$



J. Behler, and M. Parrinello, *Phys. Rev. Lett.* 98, (**2007**) 146401. J. Behler, *J. Chem. Phys.* 134, (**2011**) 074106. **N. Artrith**, T. Morawietz, J. Behler, *Phys. Rev. B* 83, (**2011**) 153101.

Challenge: Multicomponent Materials

Behler- Parrinello (BP) uses parameters for all possible combinations of species.

Example BP descriptor for 3 atomic species A, B, and C
(potential for species A):

- Radial: A-A, A-B, A-C → factor of N
- Angular: A-A-A, A-A-B, A-A-C, A-B-B, A-B-C, A-C-C → factor of $O(N^2)$

→ **Descriptor size scales with $N(N+1)/2$ where N is the number of species**

Quadratic scaling!

Very challenging to construct MLPs with more than 4 atomic species using BP descriptor.

ML does not Require Complete Descriptors

BP functions are **not complete in the structural space** but are suitable for the construction of ANN potentials.

Machine-learning techniques are useful when only incomplete descriptors are available!

- The descriptor does not have to distinguish between all possible sets of 3-D coordinates. It is sufficient to distinguish between relevant atomic arrangements.
- Similarly, not all chemical combinations occur in real materials. There is no need for a complete descriptor of the chemical space!

→ **Construct a simple, incomplete yet refinable descriptor of the local atomic structure $\{R\}$ and chemistry $\{t\}$**

Descriptor for Many Species: Structure $\{R\}$ and Chemistry $\{t\}$

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Descriptor to Describe Structure $\{R\}$

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Structure $\{R\}$: Expansion of RDF and ADF

Expansion of radial (bond length) and angular (bond angle) distribution functions

Pairs $$\mathrm{RDF}_i(r) = \sum_{j \neq i} \delta\left(r - R_{ij}\right) f_c(R_{ij})$$

Triplets $$\mathrm{ADF}_i(\theta) = \sum_{j,k \neq i} \delta\left(\theta - \theta_{ijk}\right) f_c(R_{ij}) f_c(R_{ik})$$

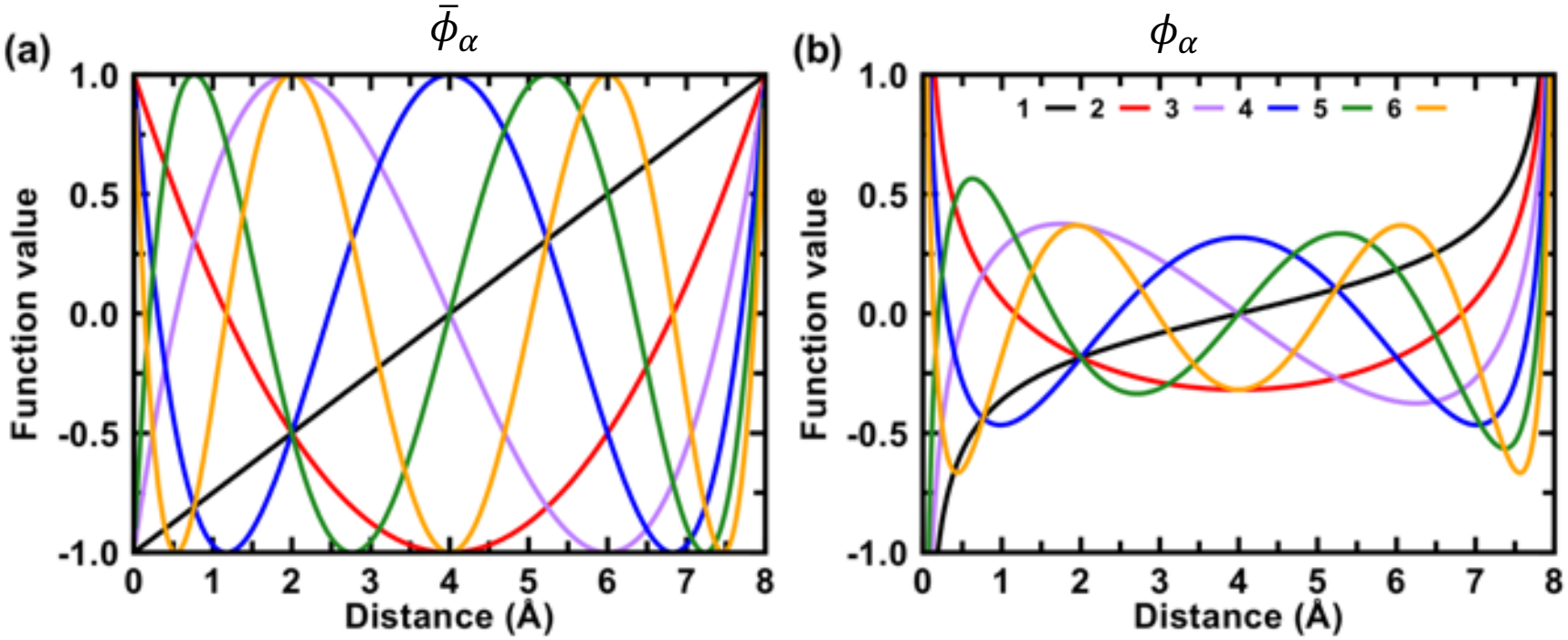
in an orthonormal basis set $\{\phi\}$ (**we use Chebyshev polynomials for their faster convergence properties compared to Fourier series**).

$$\mathrm{RDF}_i(r) = \sum_{\alpha} c_{\alpha}^{(2)} \phi_{\alpha}(r) \text{ for } 0 \leq r \leq R_c \qquad \mathrm{ADF}_i(\theta) = \sum_{\alpha} c_{\alpha}^{(3)} \phi_{\alpha}(\theta) \text{ for } 0 \leq \theta \leq \pi$$

Both RDF and ADF are invariant wrt. rotation, translation, and exchange of equivalent atoms, so the coefficients $\{c_\alpha\}$ can be used as descriptor.

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Visualization of the Chebyshev Polynomials



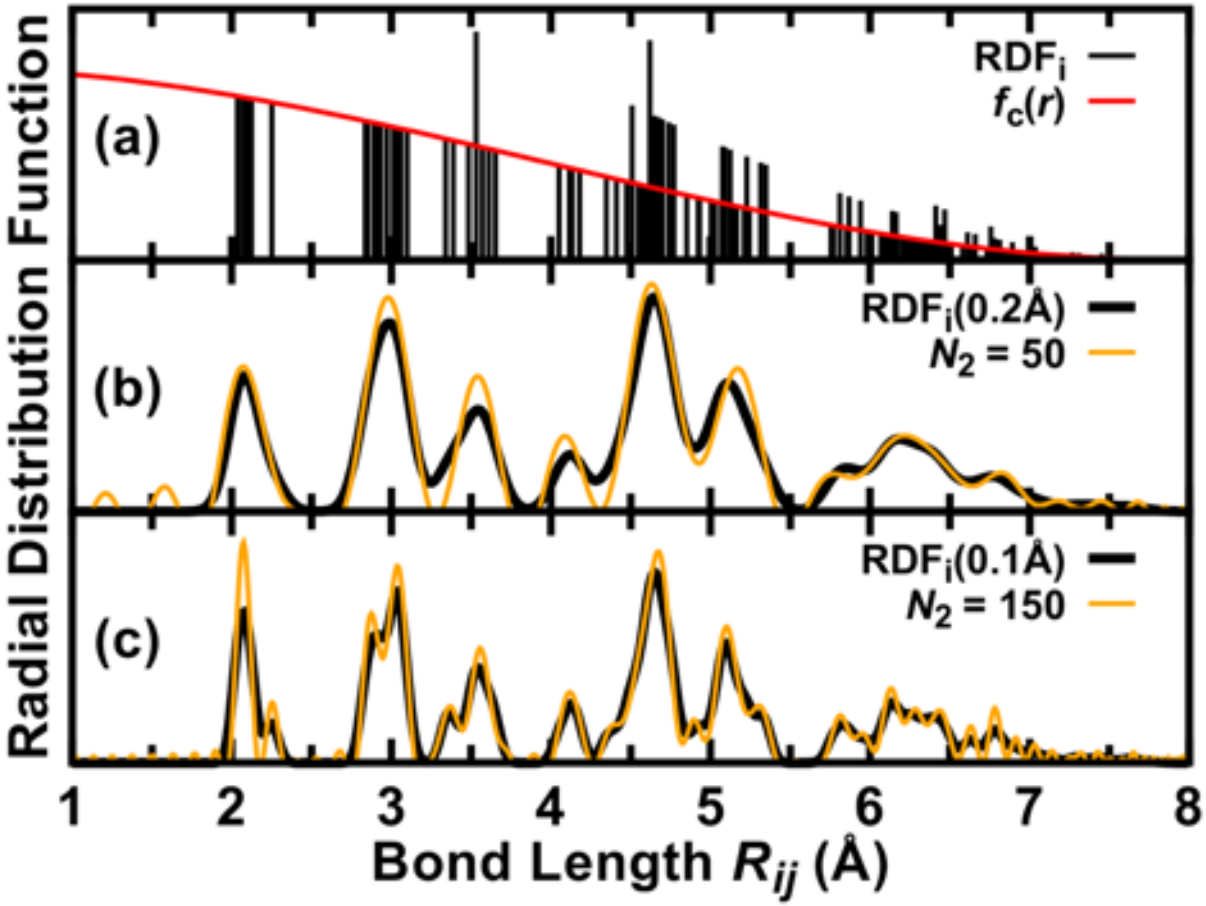
(a) Basis functions (i.e., rescaled Chebyshev polynomials) up to order α = 6 for a catoff radius R_c = 8.0 Å. The polynomial of order α = 0 is constant 1 and not shown. **(b)** The corresponding basis functions are only needed for the reconstruction of the RDF or ADF.

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Descriptor is Systematically Refinable

The resolution of the descriptor is determined by the expansion order.

Example convergence for the radial distribution function (Li_2MnNiO_4):



Discrete RDF multiplied with cutoff function.

RDF broadened by convolution with Gaussians, (b): 0.2 Å, (c): 0.1 Å, compared to Chebyshev expansions of orders (b):50 and (c):150.

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Descriptor for Many Species: Chemistry $\{t\}$

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

Chemistry $\{t\}$: Second Set of Coefficients

To describe the local chemistry, we include a species-dependent weight:

Pairs $$ {}^{\{t\}}\mathrm{RDF}_i(r) = \sum_{j\neq i} \delta\big(r - R_{ij}\big) f_c\big(R_{ij}\big)\, w_{t_j} $$

Triplets $$ {}^{\{t\}}\mathrm{ADF}_i(\theta) = \sum_{j,k\neq i} \delta\big(\theta - \theta_{ijk}\big) f_c\big(R_{ij}\big) f_c(R_{ik})\, w_{t_j} w_{t_k} $$

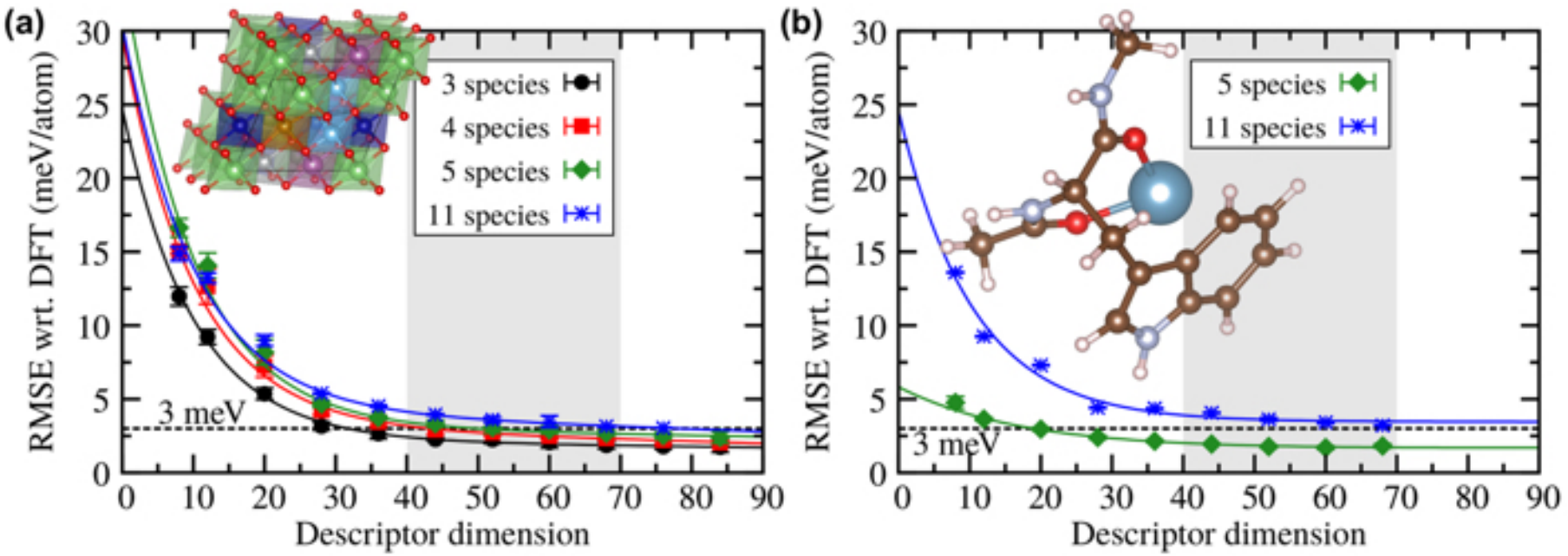
So that the expansion coefficients become

$$ {}^{\{t\}}c_\alpha^{(2)} = \sum_{j\neq i} \bar{\phi}_\alpha\big(R_{ij}\big) f_c(R_{ij})\, w_{t_j} \qquad {}^{\{t\}}c_\alpha^{(3)} = \sum_{j,k\neq i} \bar{\phi}_\alpha\big(\theta_{ijk}\big) f_c(R_{ij}) f_c(R_{ik})\, w_{t_j} w_{t_k} $$

The descriptor of the local chemistry is then $$ {}^{\{t\}}\hat{\sigma}_i^{R_c} = \begin{pmatrix} {}^{\{t\}}c_0^{(2)} \\ {}^{\{t\}}c_1^{(2)} \\ \vdots \\ {}^{\{t\}}c_0^{(3)} \\ {}^{\{t\}}c_1^{(3)} \\ \vdots \end{pmatrix} $$

The Same Descriptor Size is Optimal for 3-11 Species

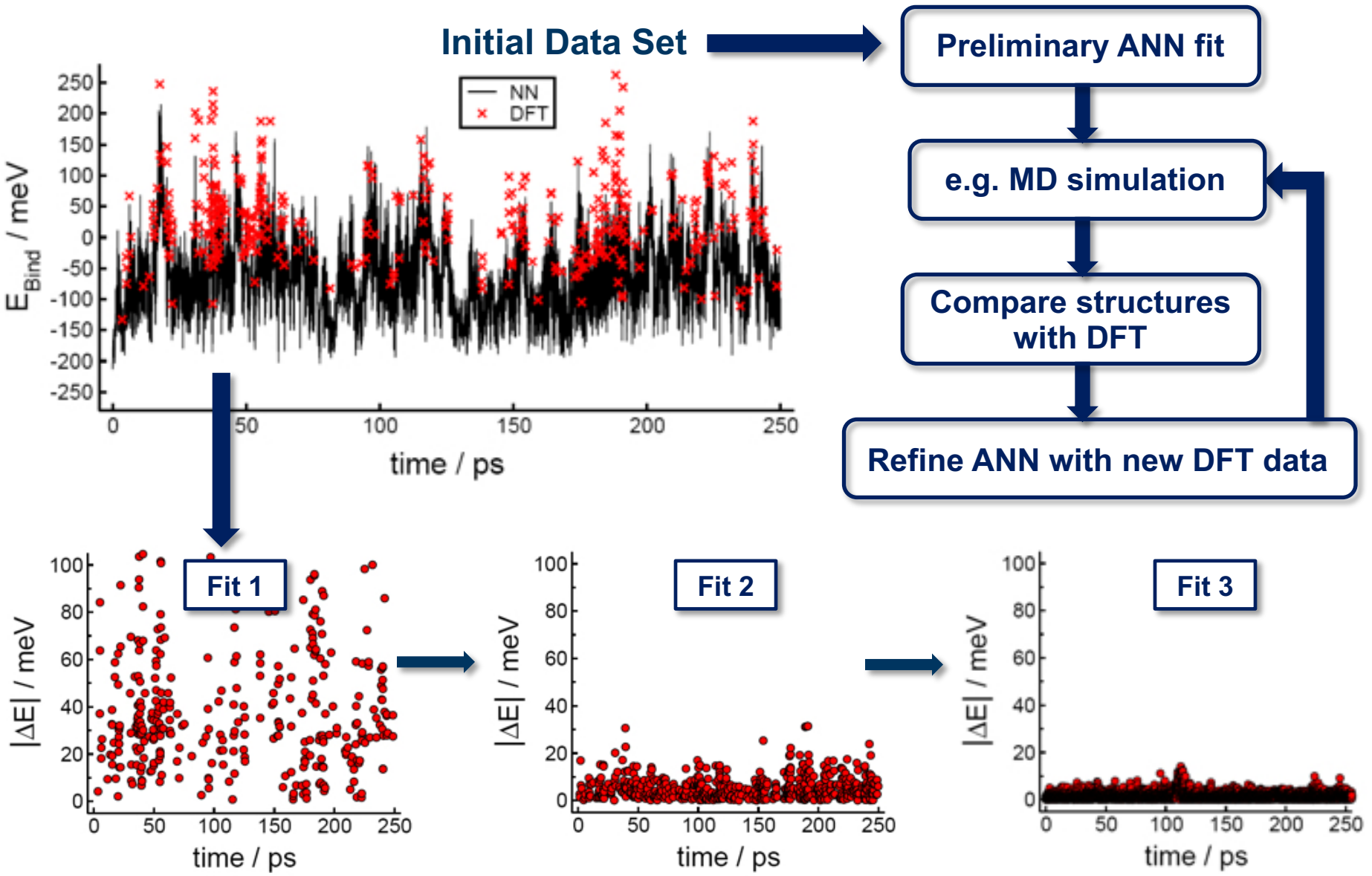
The combined descriptor is appropriate for Li-TM oxides and amino acid complexes with **11 chemical species**. The size of the descriptor is constant.



The RMSE was evaluated after 3000 training iterations for 3-5 species and after 5000 iterations for 11 species.

N. Artrith*, A. Urban, and G. Ceder, *Phys. Rev. B* **96** (2017) 014112.

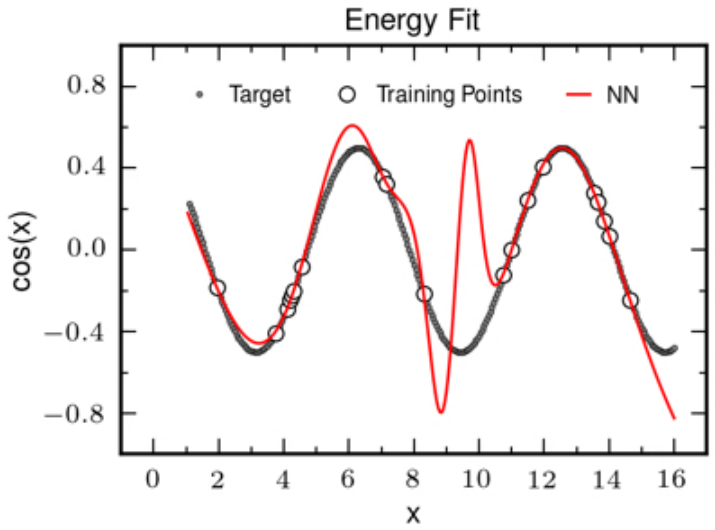
Systematic Construction of the Training Set

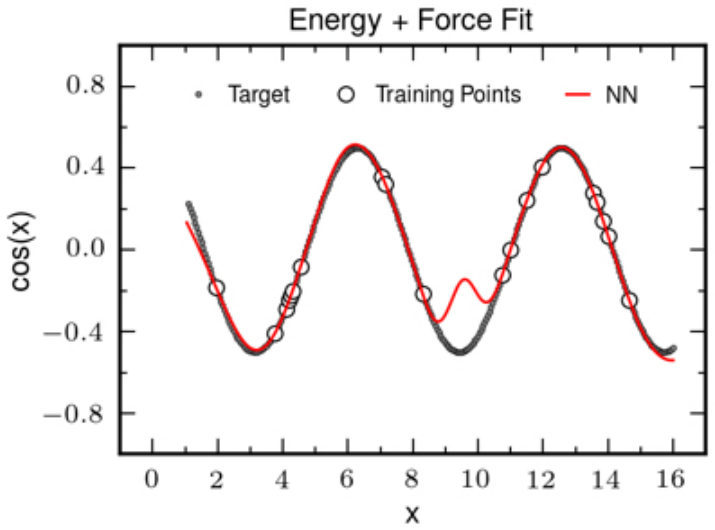


N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* **83**, (2011) 153101.
T Morawietz, A Singraber, C Dellago, J Behler *Proc. Natl. Acad. Sci. U. S. A.* **113**, (2016) 8368-8373.

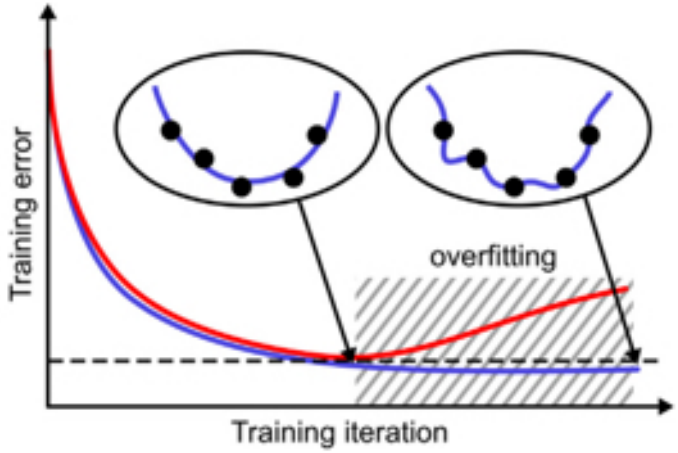
Caution: Overfitting and Extrapolation

Overfitting:

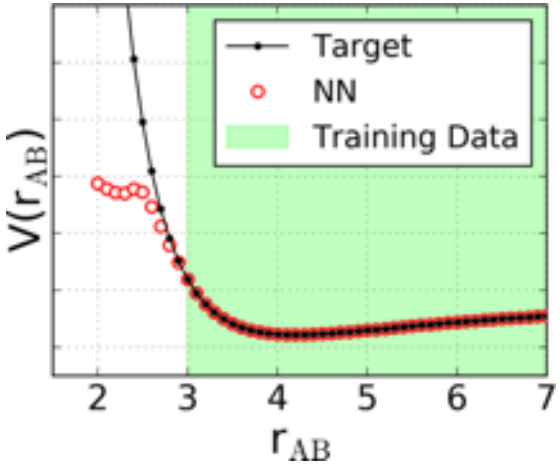




- **Solutions:**
  - * Early stopping
  - * Use gradient info



Extrapolation:



- **Solutions:**
  - * Carefully sample repulsive regions
  - * Output "extrapolation warnings" during MD

N. Artrith, T. Morawietz, and J. Behler, *Phys. Rev. B* **83**, (2011) 153101.
N. Artrith and A. Urban, *Comput. Mater. Sci.***114** (2016) 135.

Summary of Part I – Theory of ANN Potentials

- ANN potentials are interatomic potentials based on artificial neural networks
- The ANNs represent atomic energies as function of the local atomic environment
- Input of the ANNs are invariant descriptors (feature vectors) of the local atomic environment
- Construction/training is done by iterative sampling of the relevant structure and composition space

Part II
Complex Inorganic Materials for Energy Applications

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250 · No. 6 June
1065–1244 (2013)

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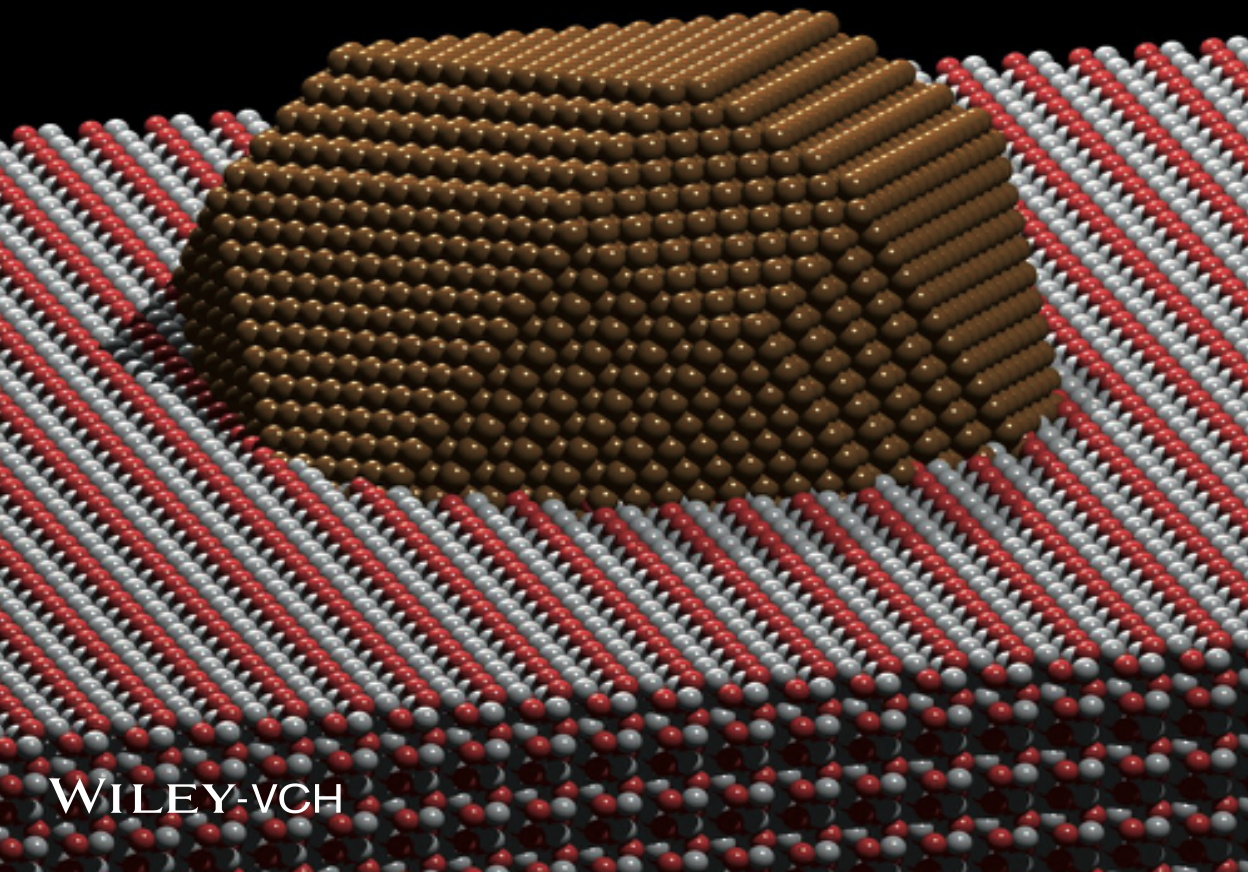
www.pss-b.com
basic solid state physics

6
2013

Feature Article

Neural network potentials for metals and oxides – First applications to copper clusters at zinc oxide

Nongnuch Artrith, Björn Hiller, and Jörg Behler



WILEY-VCH

N. Artrith, B. Hiller, J. Behler
Phys. Stat. Sol. B 250 (**2013**) 1191 (invited feature article).

Journal Cover

Neural Network Potential for Copper

Training of the ANN potential

DFT code: FHI-aims (PBE) [a]

Cu Structures:

- **Bulk:** 15,400
- **Clusters :** 8,400
- **Surfaces :** 13,800

RuNNer code [b]

Fitting points: **32,000**

RMSEs E_{total} = **0.0036** eV/atom

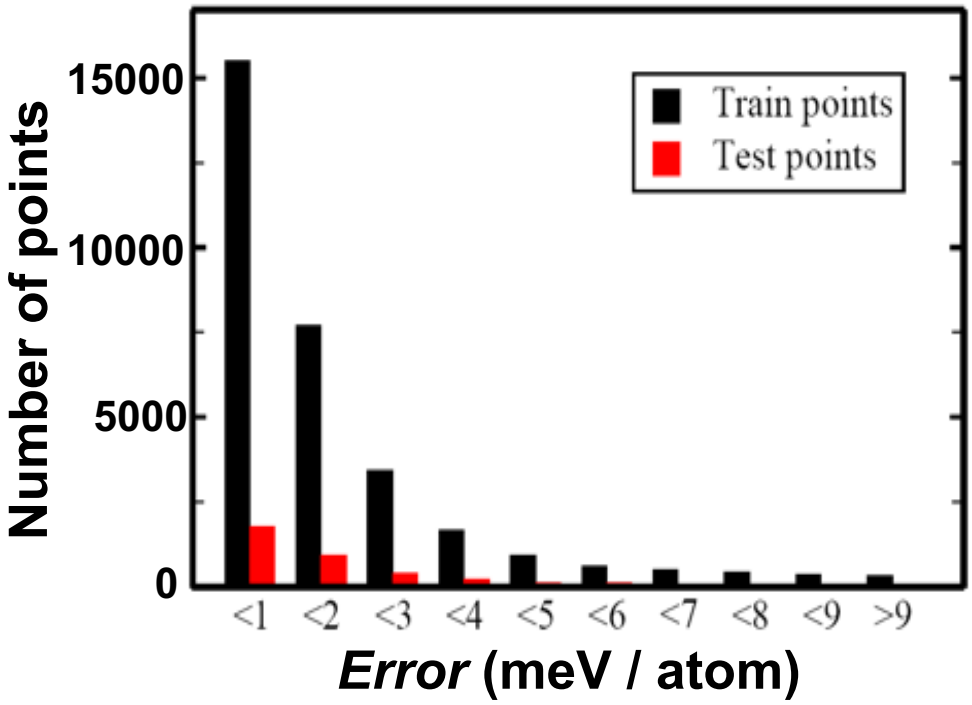
Forces = **0.0415** eV/Bohr

Testing points: **3,600**

RMSEs E_{total} = **0.0034** eV/atom

Forces = **0.0416** eV/Bohr

Training data: 2 - 100 atoms



[a] V. Blum et al., *Comp. Phys. Comm.* 180, **(2009)** 2175 - 2196.

[b] J. Behler, RuNNer – A Neural Network Code for High-Dimensional PESs, Ruhr-University Bochum

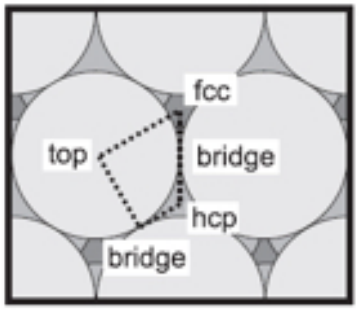
Low-Index Copper Surfaces

Surface Energies (fcc):

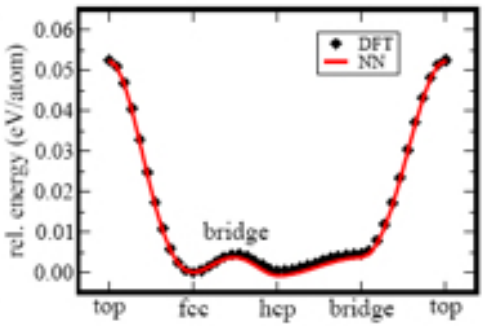
Surface	DFT (meV/Å²)	NN (meV/Å²)
Cu(111)	93.16	92.74
Cu(100)	100.53	100.99
Cu(110)	102.39	103.92
Cu(110)mr	109.93	111.69

Energy Profile for Cu Adatom Diffusion:

Cu(111)

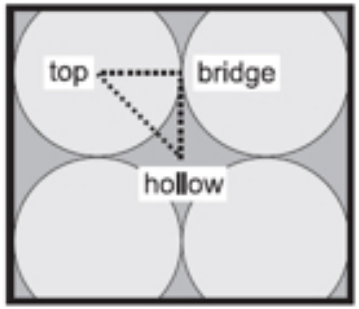


Path

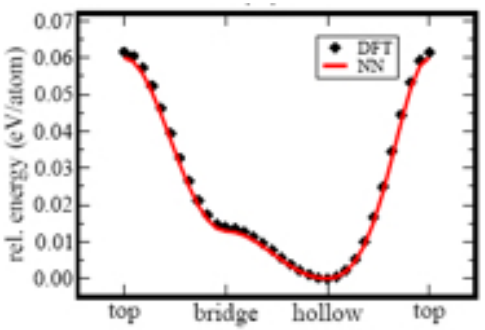


Energy profile

Cu(100)



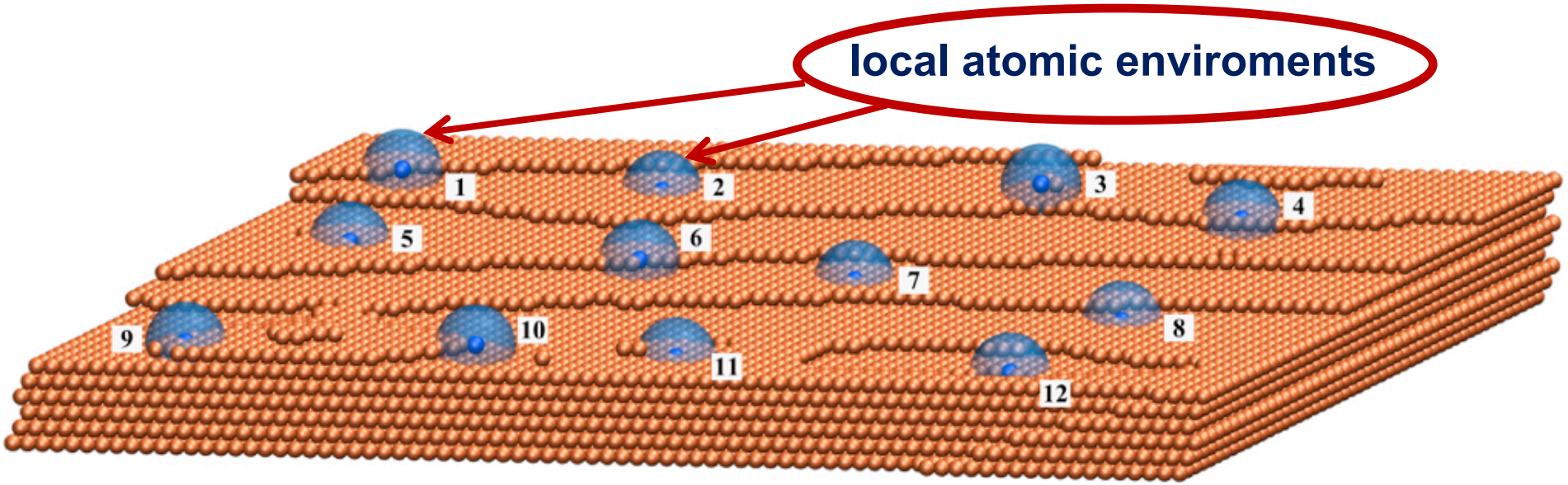
Path



Energy profile

Cu(111): Complex Realistic Model

Model of a real surface with steps, kinks, and adatoms (29,443 atoms).



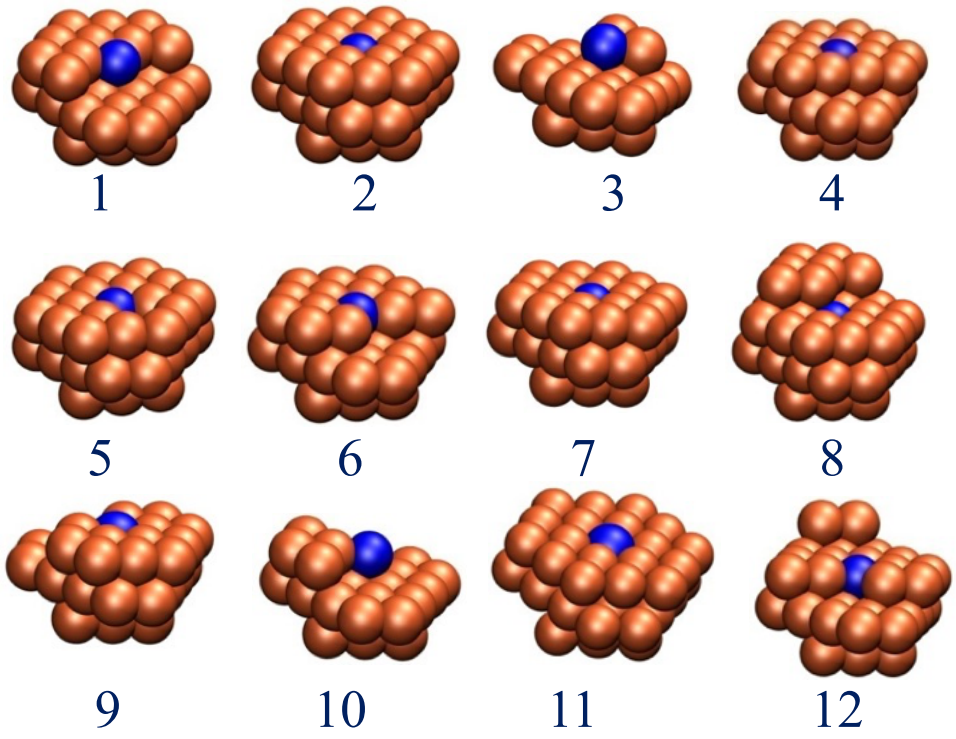
DFT ⇒ impossible
NN ⇒ ≈ few minutes (1 core)

⇒ NN potentials can be used to study systems of this size.

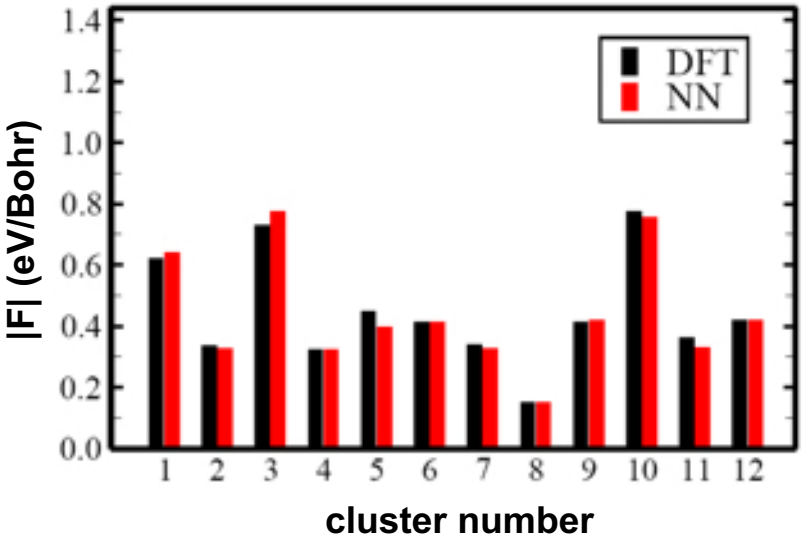
N. Artrith, and J. Behler, *Phys. Rev. B* 85, (**2012**) 045439.

Checking the Accuracy for Large Systems

Comparison of the DFT and neural network (NN) forces acting on the central atoms of clusters cut from the slab.



Forces:



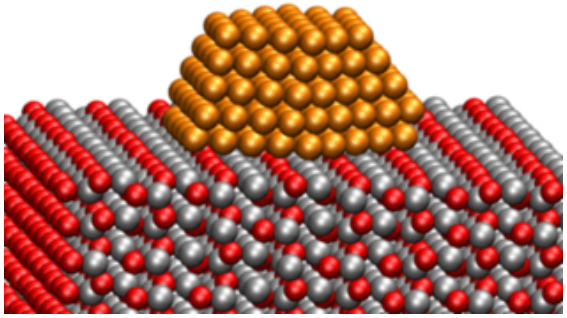
⇒ **Very good agreement**
⇒ **NN PES is reliable**

N. Artrith, and J. Behler, *Phys. Rev. B* 85, (**2012**) 045439.

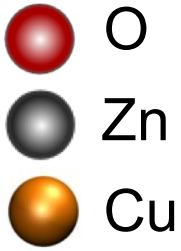
Cu@ZnO Catalyst for Methanol Synthesis

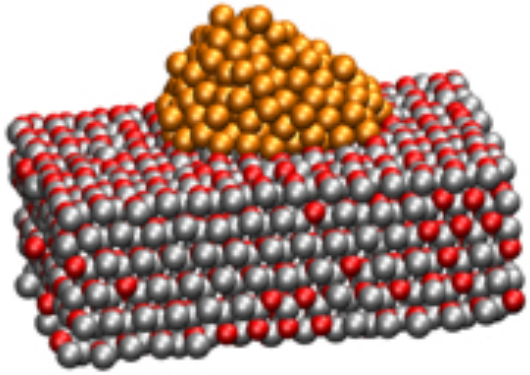
ANN-MD Simulation: Slab model ~8,000 atoms: NVT, MD at 1000 K

Training and testing sets for the ANN potential:
Cu/Zn/O structures: (e.g. ideal, vacancies, defects)
~100,000 structures (90% train, 10% test)
RMSEs E_{total} : **0.005** eV/atom
Forces: **0.090** eV/Bohr



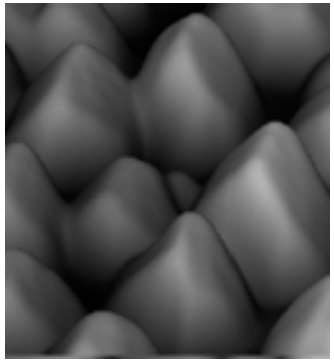
Initial configuration/ MD movie





Configuration at 300 ps

N. Artrith, B. Hiller, J. Behler
Phys. Stat. Sol. B 250 (**2013**) 1191 (invited feature article).



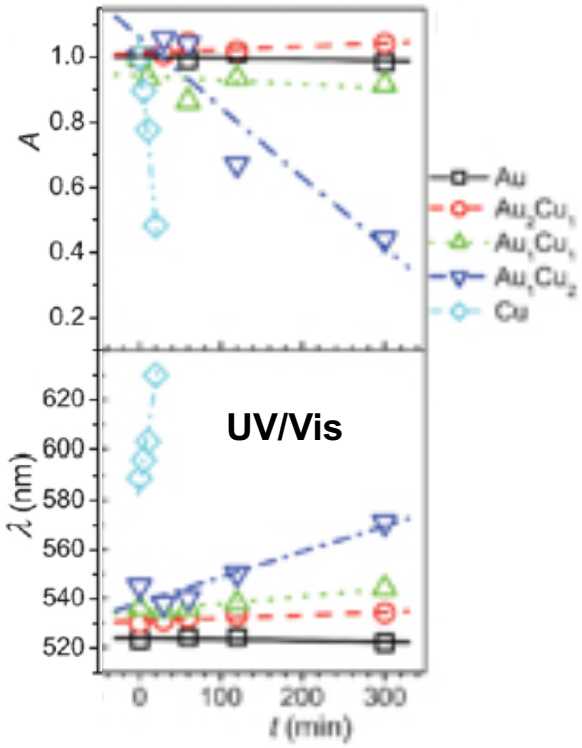
STM image of Cu@ZnO(10$\bar{1}$0), T= 290 K

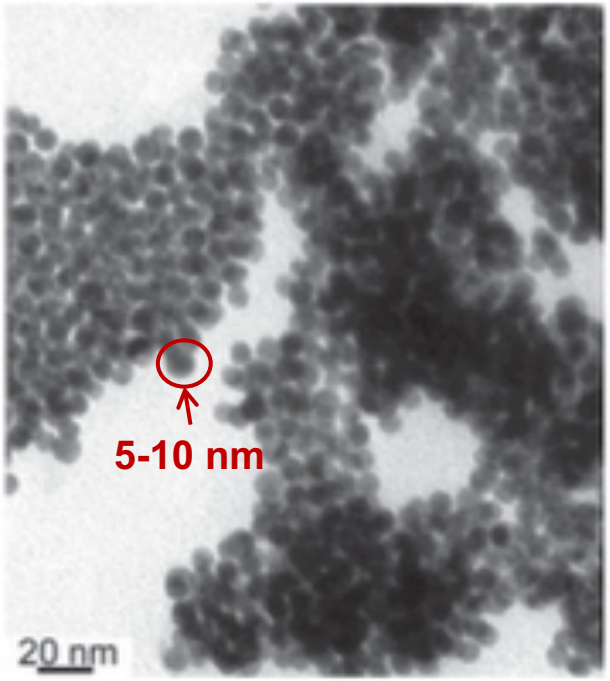
U. Köhler, et. al,
Phys. Status Solidi B 250 (**2013**) 1122.

- **ANN potentials allow to simulate structural models with thousands of atoms while providing high accuracy close to the reference method**

ANN Potential: Cu/Au/O/H System

Au/Cu is an efficient and stable catalyst for the ORR and CO_2 reduction





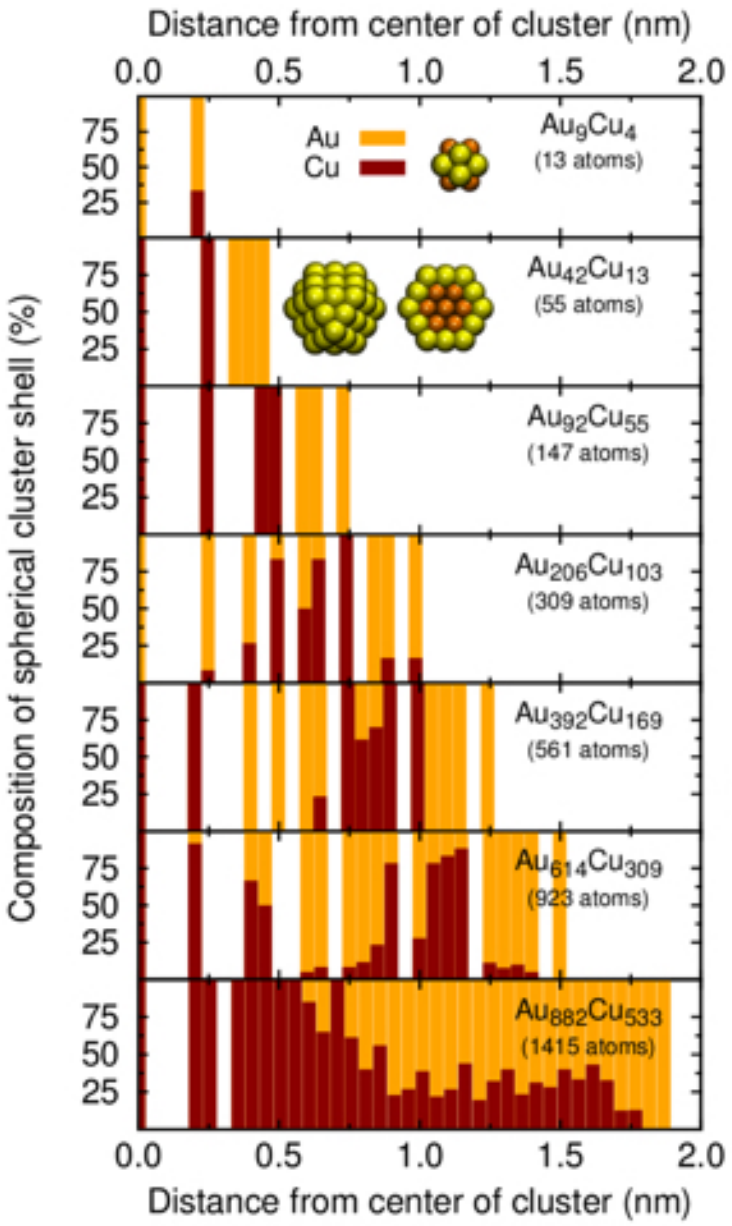
TEM: Au_1Cu_1 NPs after oxidation

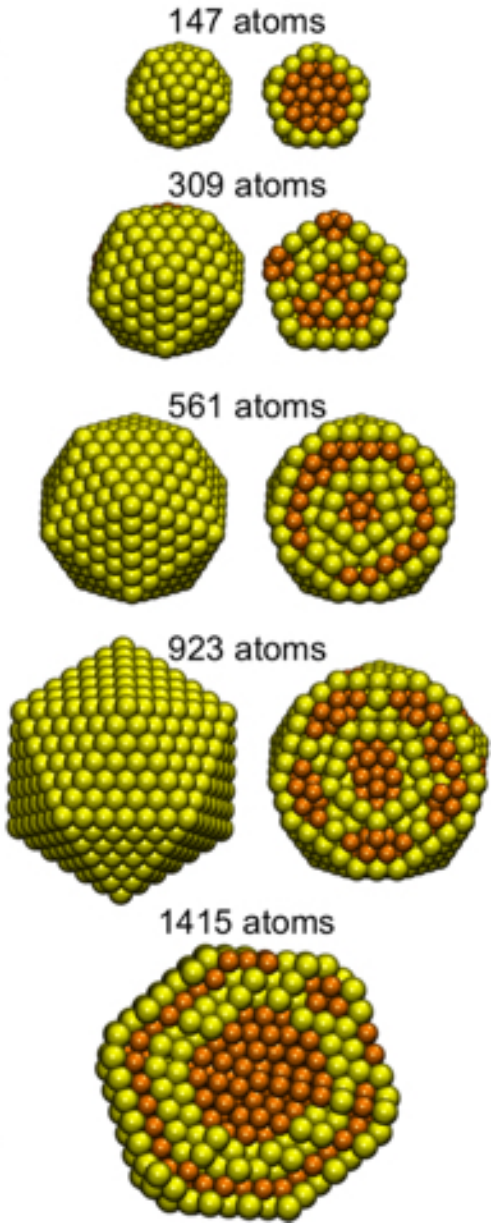
Shao-Horn, Hamad-Schifferli, et. al, *Chem. Commun,* 48, (**2012**) 5626.

Oxidation rates of Au_xCu_y NPs: depend on composition,
where *k*A and *k*λ exhibited a trend of **Au_2Cu_1** < Au < Au_1Cu_1 < Au_1Cu_2 < Cu

- **How can we identify relevant compositions and (surface) structures?**

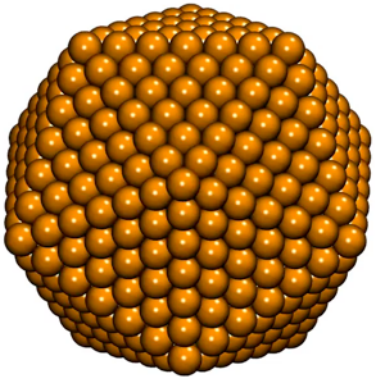
Optimized Compositions and Ordering of Au/Cu: MC

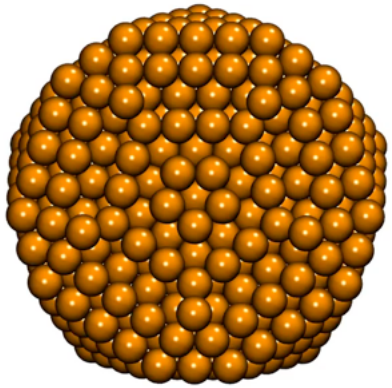




MC Annealing (movies):
T= 5,000-300 K

Cluster 923 atoms



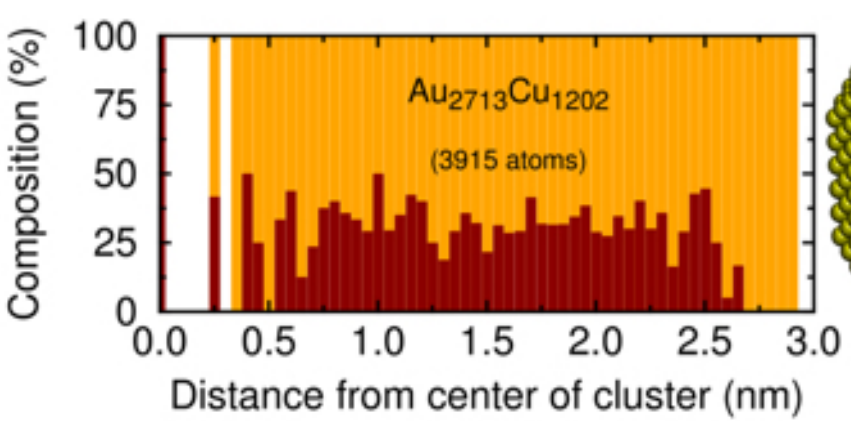


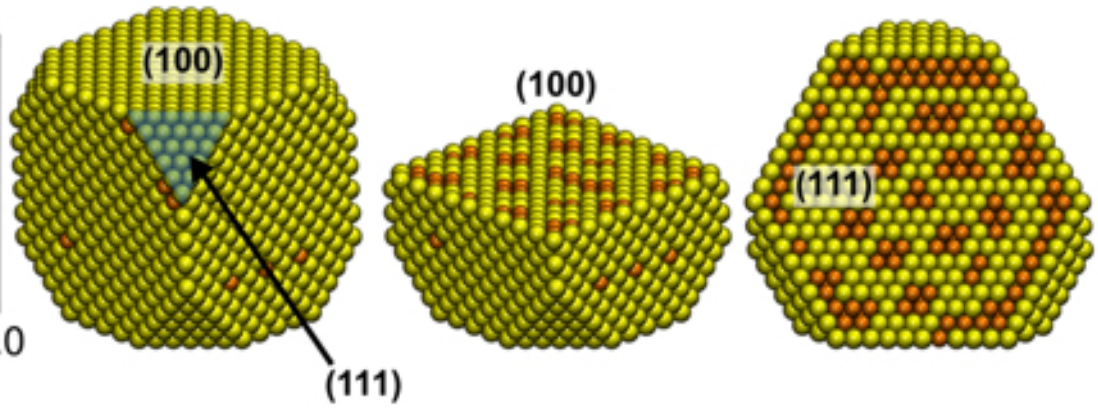
Cross-section
Cluster 923 atoms

Optimized Compositions and Ordering of NPs: 3,915 atoms

MC Annealing: T= 5,000-300 K

⇒ **Composition of Au/Cu NP (~6 nm) and cut-through in (100) and (111) directions**





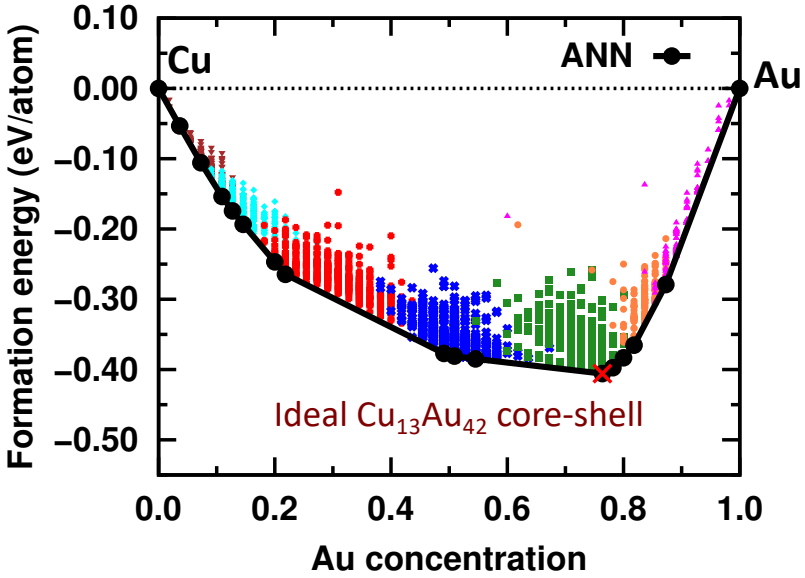
⇒ **No longer a core-shell morphology**
⇒ **Outer layer of the NP is gold-terminated (as expected from the surface-energy)**
⇒ **Interior bulk Au and Cu atoms form a solid solution**

CPU time/structure: 147 atoms
NN << DFT : 10^4
DFT : 3.0 hours (16 cores)
NN : < 1 second (1 core)

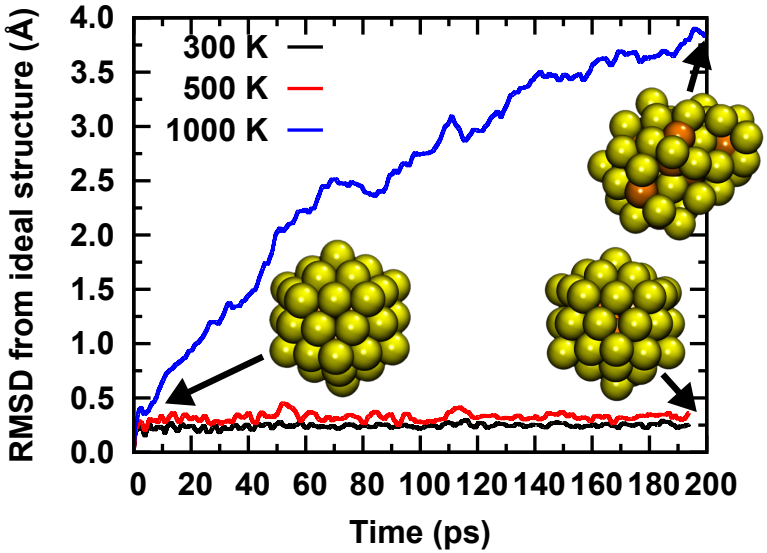
CPU time/structure: 3,915 atoms
DFT : Very difficult
NN : 59 seconds (1 core)

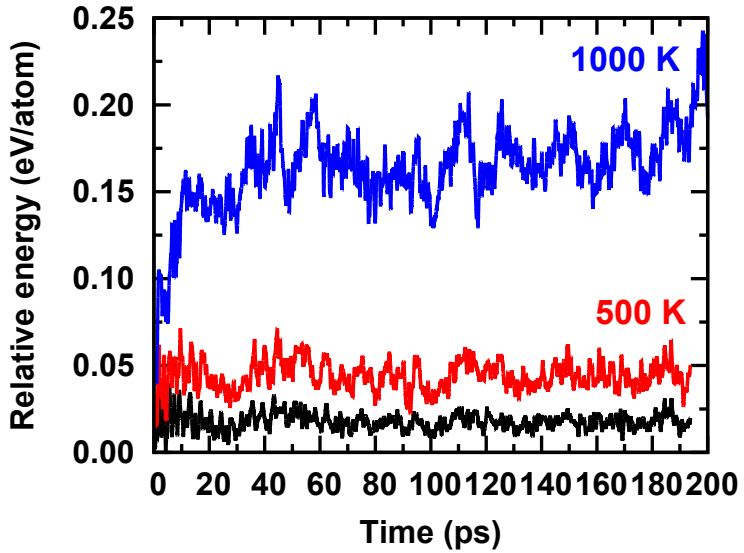
N. Artrith and A. Kolpak, *Nano Lett.*,14, (**2014**) 2670.

Formation Energies of 55-Atom Cluster and Thermal Stability



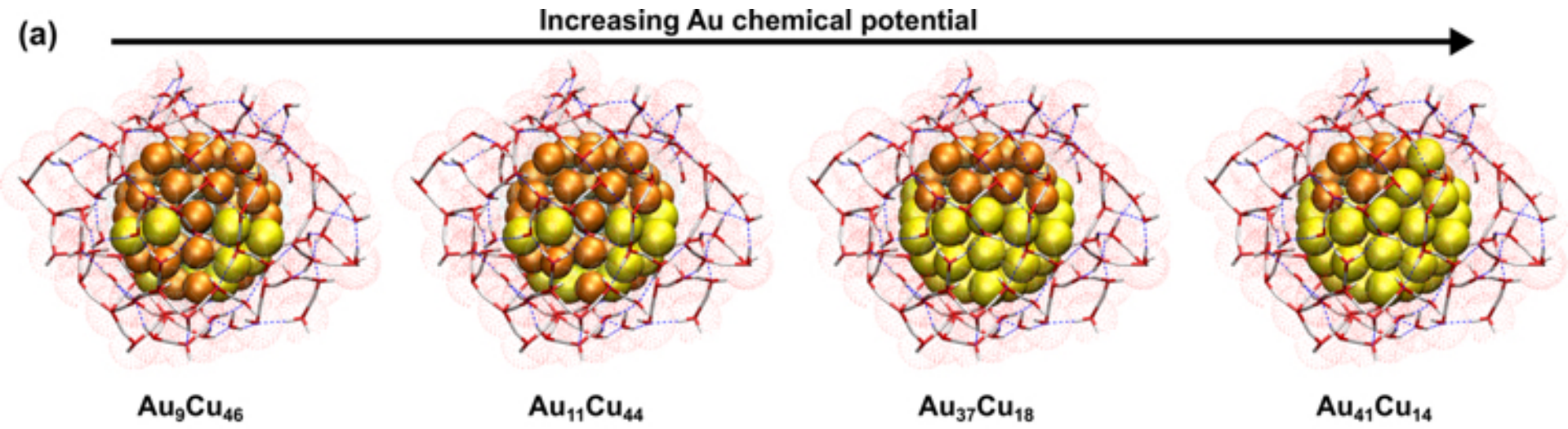
- Grand canonical MD
- Stable configurations: derived from core-shell structure
- At 1000K: cluster melts
- 300K & 500K: below melting point

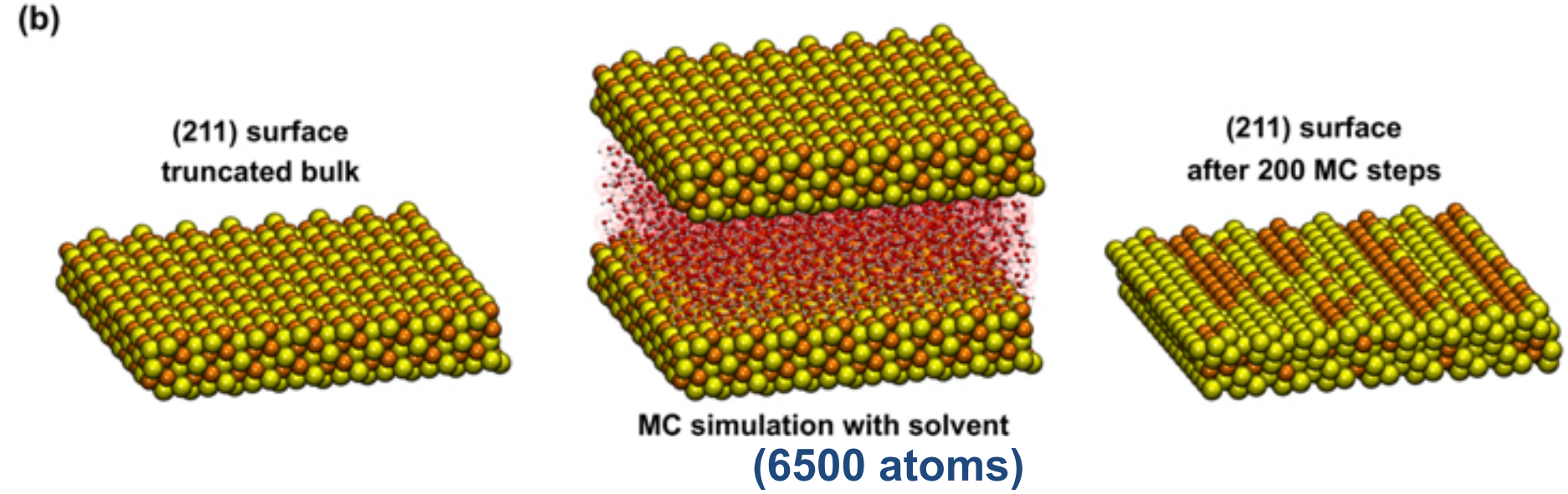




N. Artrith and A. Kolpak, *Comput. Mater. Sci.*,110, (**2015**) 20-28.

55-Atom Cluster in Water and (211) Surface Slab





N. Artrith and A. Kolpak, *Nano Lett.*,14, (**2014**) 2670.

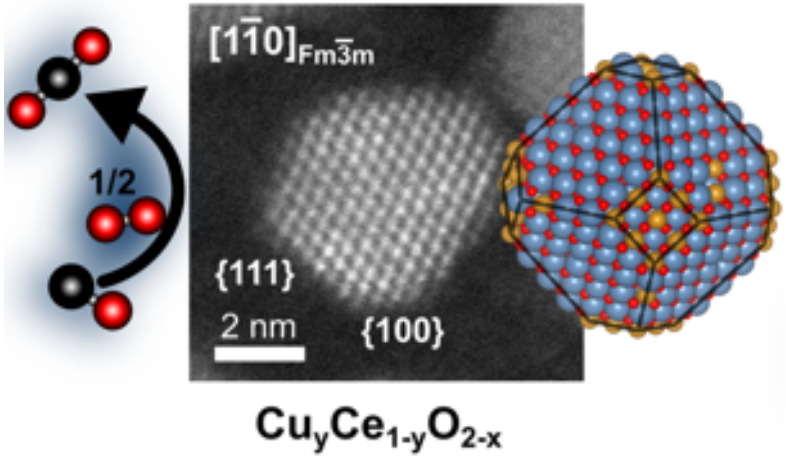
Specialized ML Potentials for Assisting DFT Calculations

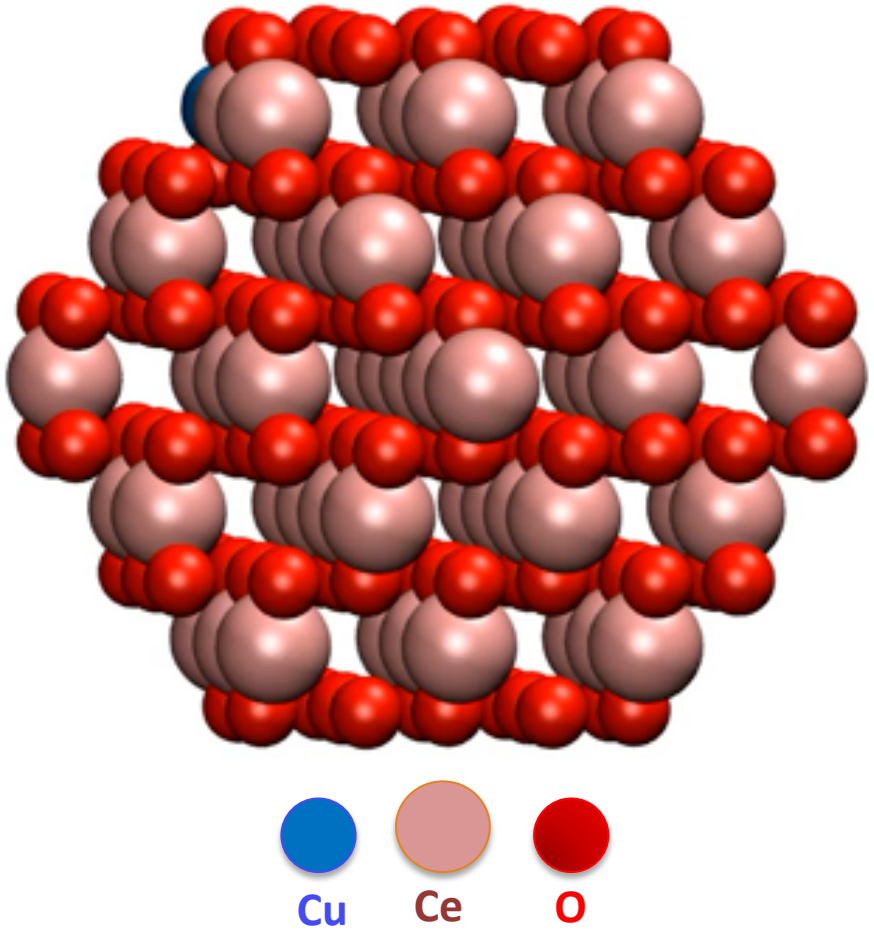
- Often, a general ML potential is not necessary
- ML potential for specific structure space sufficient for accelerated sampling

Active Site in CuO/CeO_2 for CO Oxidation

Cu Distribution in the particles

- MC simulations of a **3.5 nm (~1,300 atoms, $Cu_{54}Ce_{405}O_{834}$)**: Cu is most stable near surface
- Cu adsorption on (100) surface and on edges favorable





J.S. Elias, **N. Artrith**, M. Bugnet, L. Giordano, G. A. Botton, A.M. Kolpak, and Y. Shao-Horn*
ACS Catalysis **6**, (2016), 1675-1679

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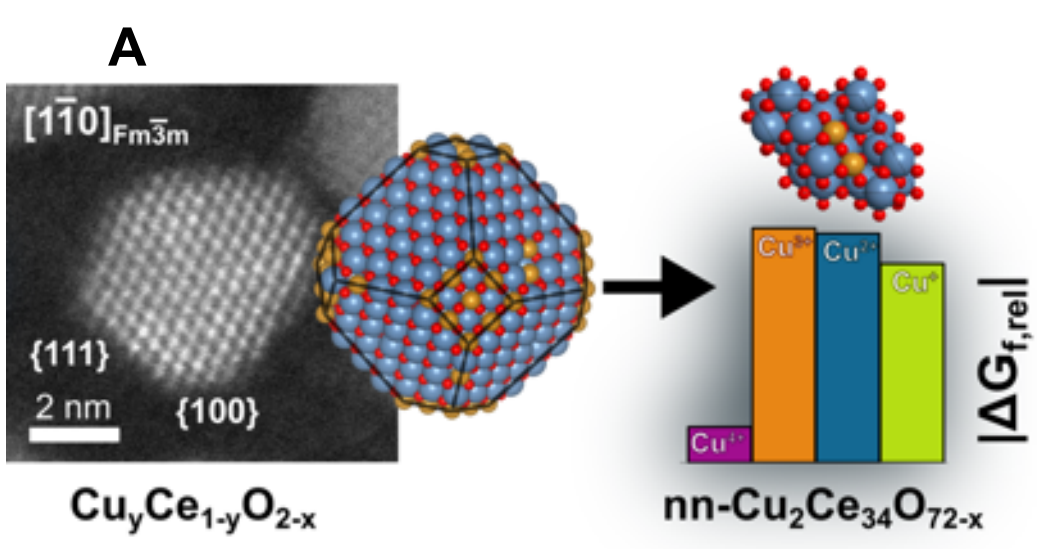
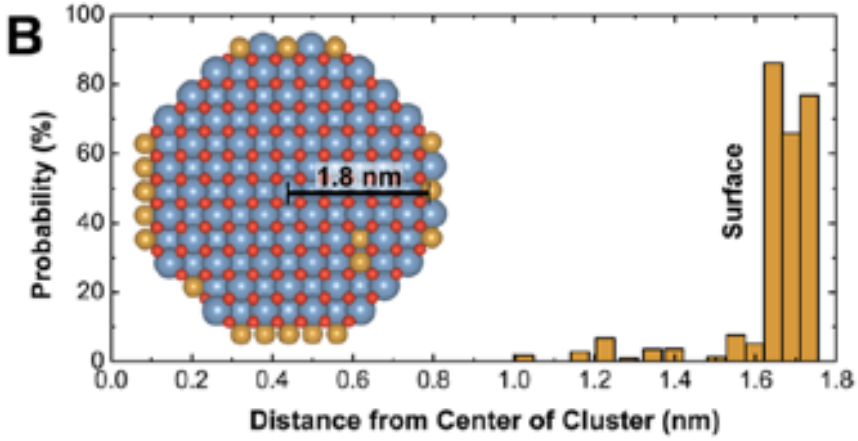
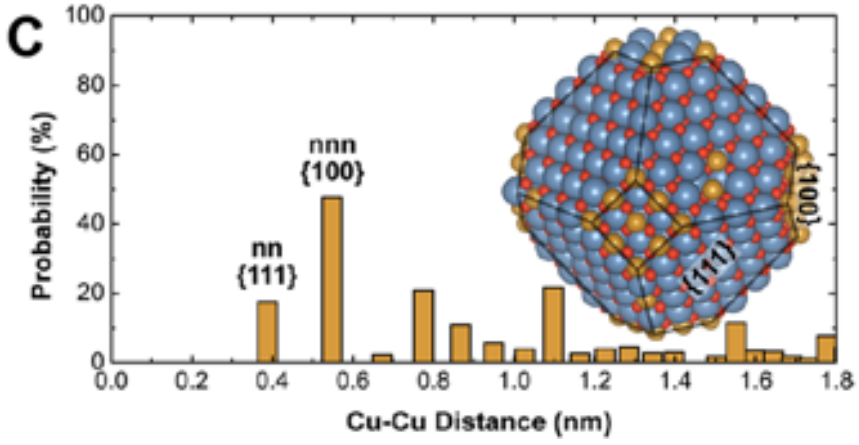






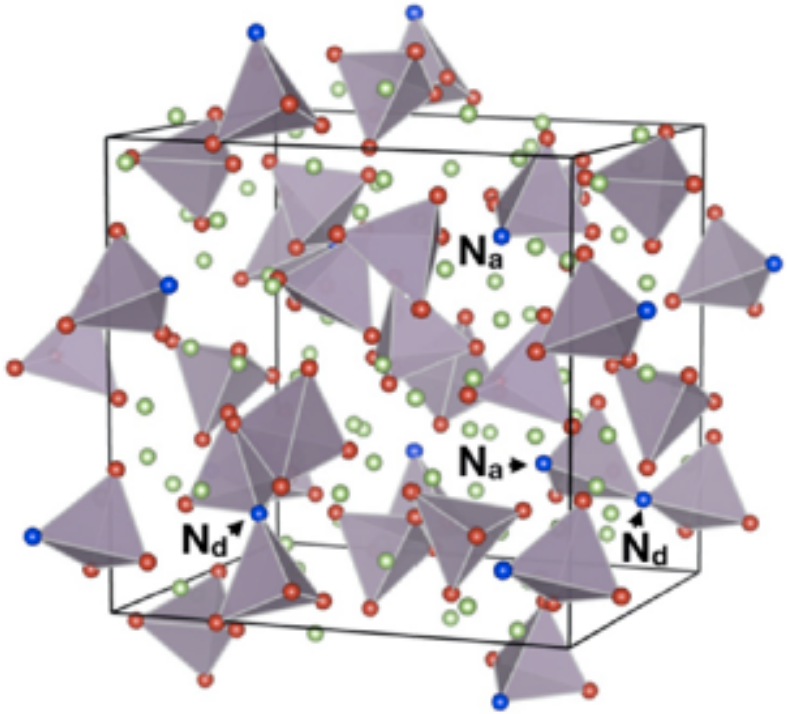
Cu-Cu pair distribution

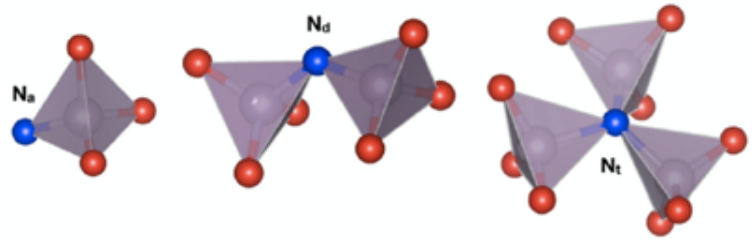
- Cu clustering: Cu-Cu pair distribution
- Combined probability that either the nearest neighbor (nn) or next-nearest neighbor (nnn) site of a Cu defect is also a Cu defect is around 70%

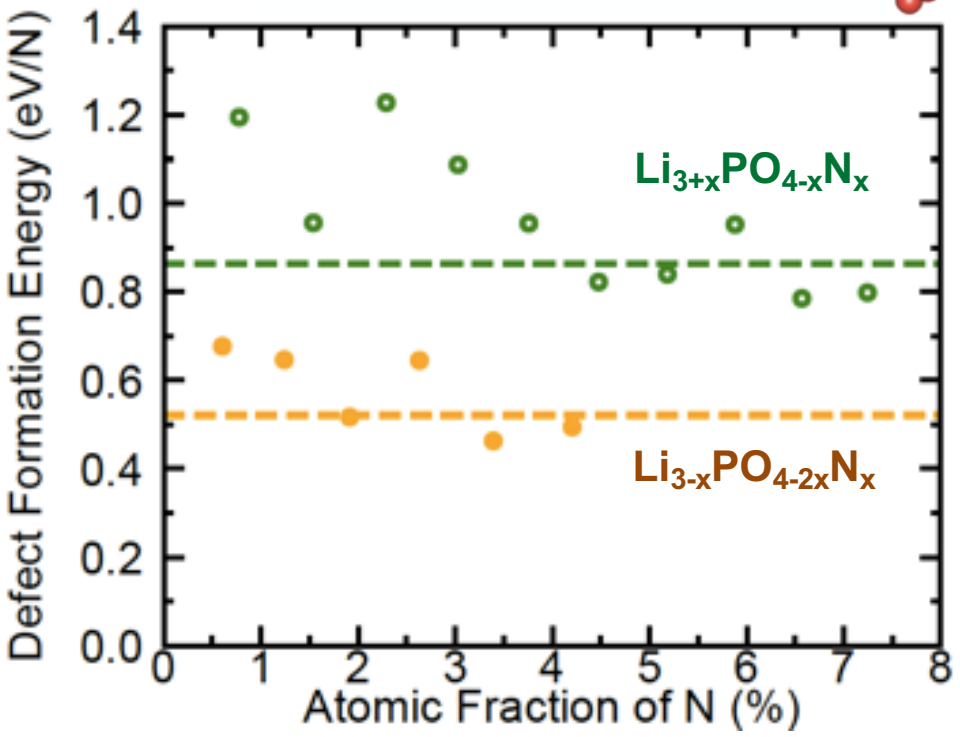
J.S. Elias, **N. Artrith**, M. Bugnet, L. Giordano, G. A. Botton, A.M. Kolpak, and Y. Shao-Horn*
ACS Catalysis **6**, (2016), 1675-1679

MLP: Application to Amorphous LiPON

- Genetic Algorithm with MLP:
- Amorphous N doped Li_3PO_4: **Solid Electrolyte Material for Li-ion batteries**
- With N improving the conductivity and diffusivity (from MD simulations of amorphous structure models)







Diffusity : LiPO = 10^{-13} cm^2s^{-1}

: LiPON = 10^{-10} cm^2s^{-1}

V. Lacivita, **N. Artrith**, and G. Ceder, *Chem. Mater.* **30** (2018), 7077-7090. DOI: 10.1021/acs.chemmater.8b02812

AIMD: Application to Amorphous LiPON

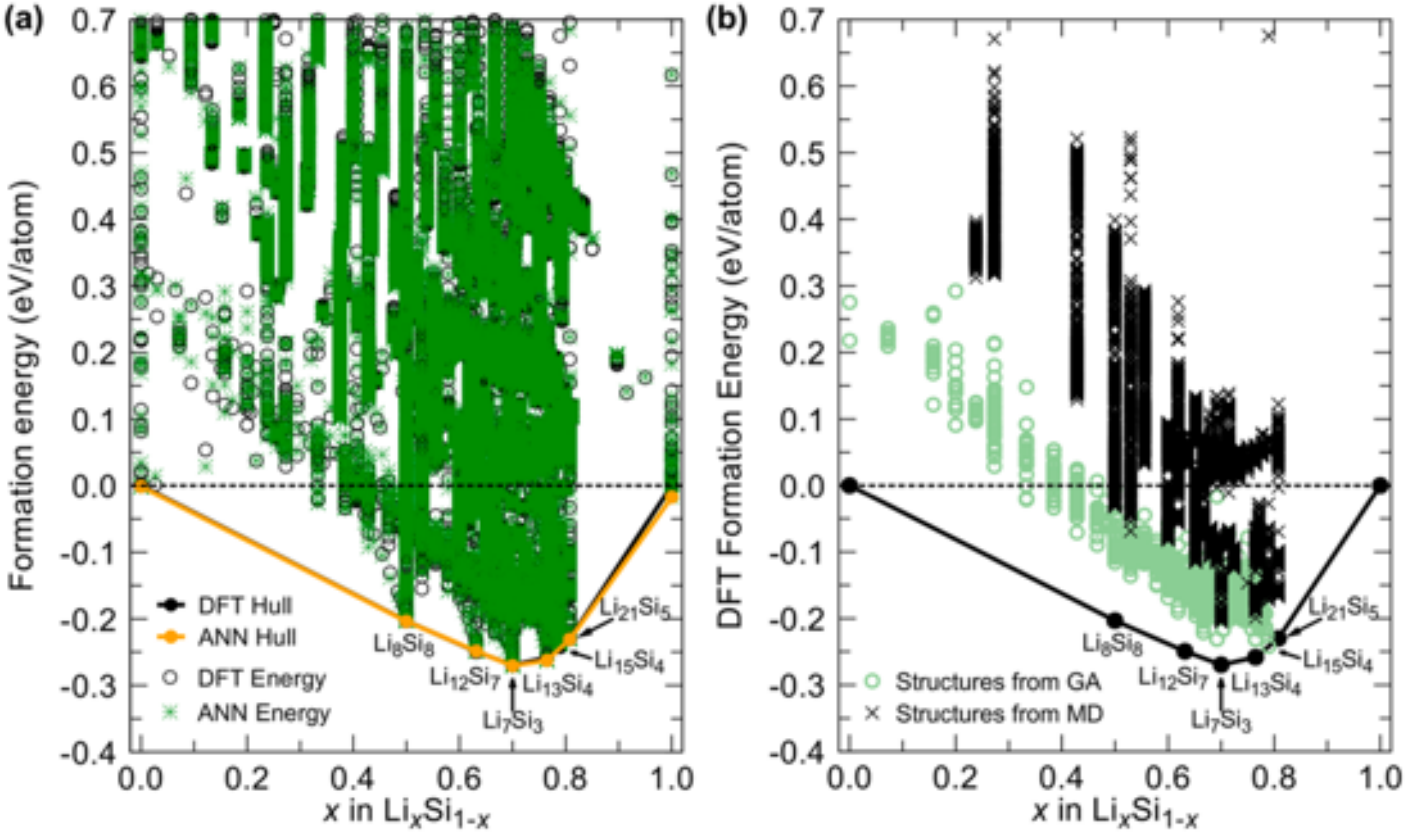
- Genetic Algorithm with MLP:
- Amorphous N doped Li_3PO_4: **Solid Electrolyte Material for Li-ion batteries**
- With N improving the conductivity and diffusivity (from MD simulations of amorphous structure models)

	at. % N	# N_a	# N_d	ρ		D
				computed		
$Li_{2.69}PO_{3.38}N_{0.31}$	4	1	4	2.04		5×10^{-10}
$Li_{2.94}PO_{3.50}N_{0.31}$	4	2	3	2.33	LiPON	7×10^{-10}
$Li_{3.31}PO_{3.69}N_{0.31}$	4	3	2	2.30		3×10^{-12}
$Li_{3.38}PO_{3.62}N_{0.38}$	5	6	0	2.31		2×10^{-12}
				experimental		
$Li_{2.7}PO_{3.9}$ [1]	0					
$Li_{2.9}PO_4$ [49,50]	0				LiPO	6×10^{-13}
$Li_{3.1}PO_{3.8}N_{0.16}$ [4]	2					
$Li_{3.3}PO_{3.8}N_{0.22}$ [4]	3					
$Li_{2.9}PO_{3.3}N_{0.46}$ [4]	6					

V. Lacivita, **N. Artrith**, and G. Ceder,
Chem. Mater. **30** (2018), 7077-7090. DOI: 10.1021/acs.chemmater.8b02812

LiSi Alloys for High-Capacity Li-Ion Battery Anodes

- A specialized ANN potential: **GA samples only a limited structure space**
- Only ~1,000 reference structures needed for the construction of a specialized ANN potential
- Identified low-energy structures are then recomputed using DFT
- The result is a first-principles phase diagram based on extensive sampling



N. Artrith*, A. Urban, and G. Ceder, *J. Chem. Phys.* **148,** (2018) 241711 **(Editor's Choice)**.

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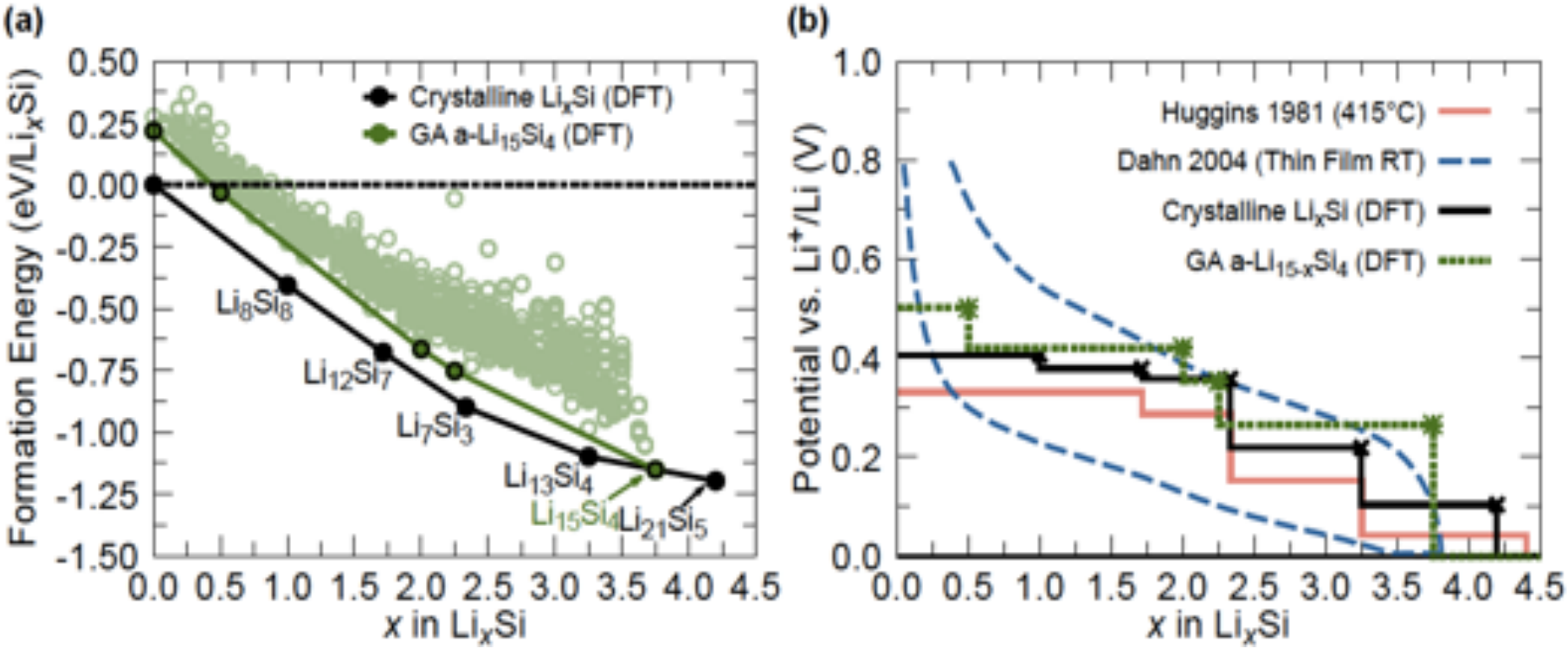
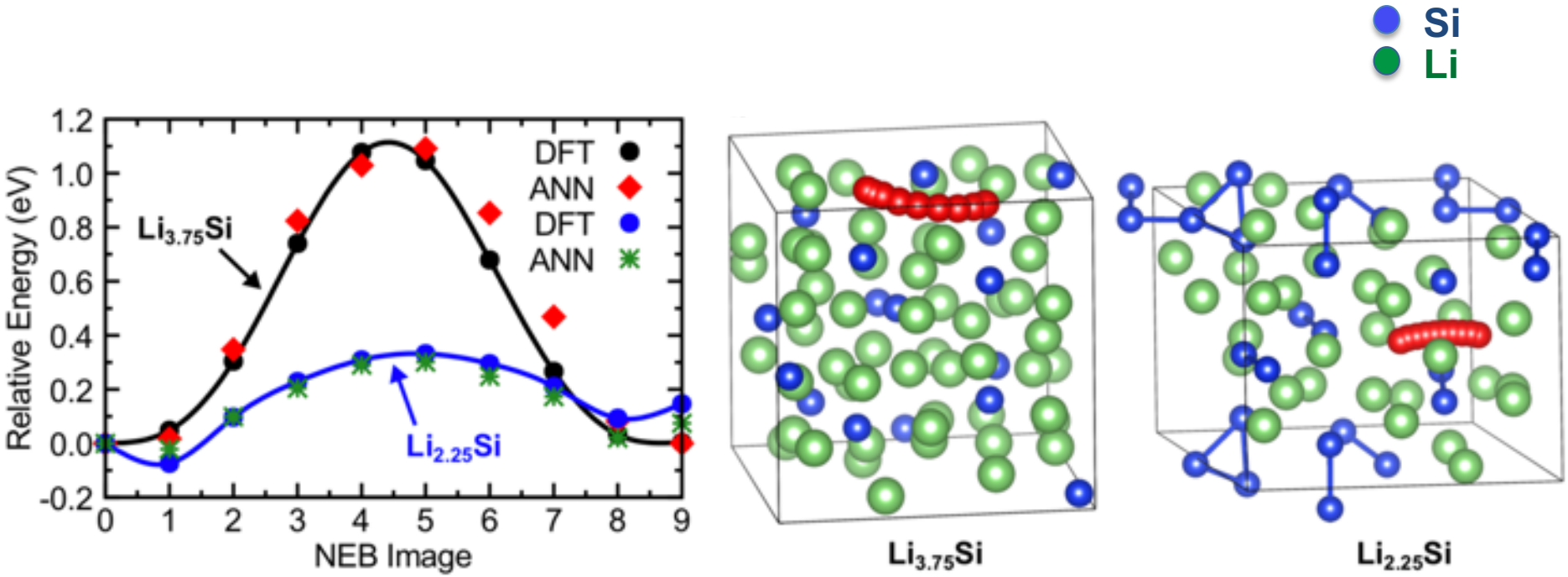


N. Artrith*, A. Urban, and G. Ceder, *J. Chem. Phys.* **148,** (2018) 241711 **(Editor's Choice)**.

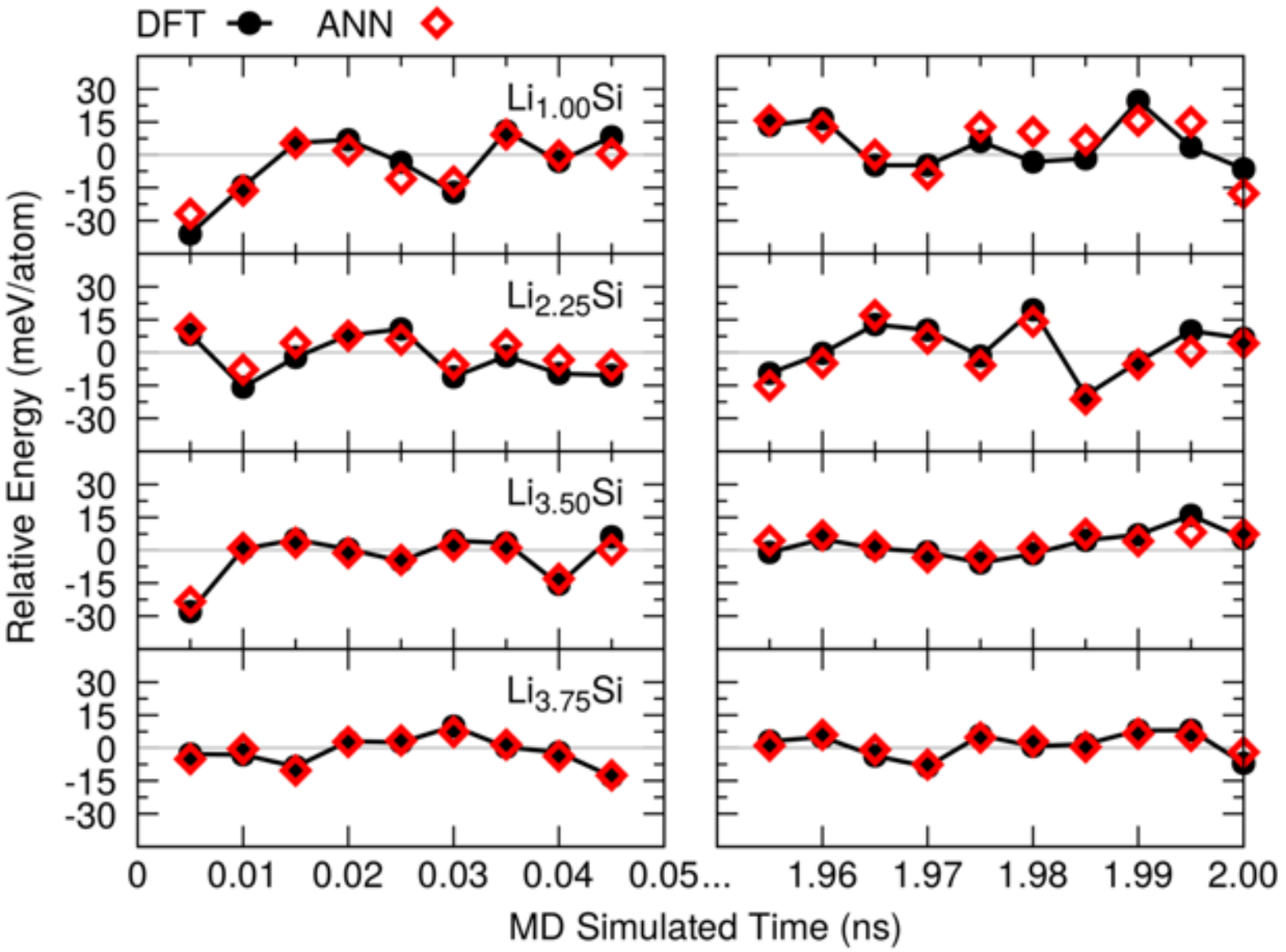
A General Machine Learning Potential for LiSi

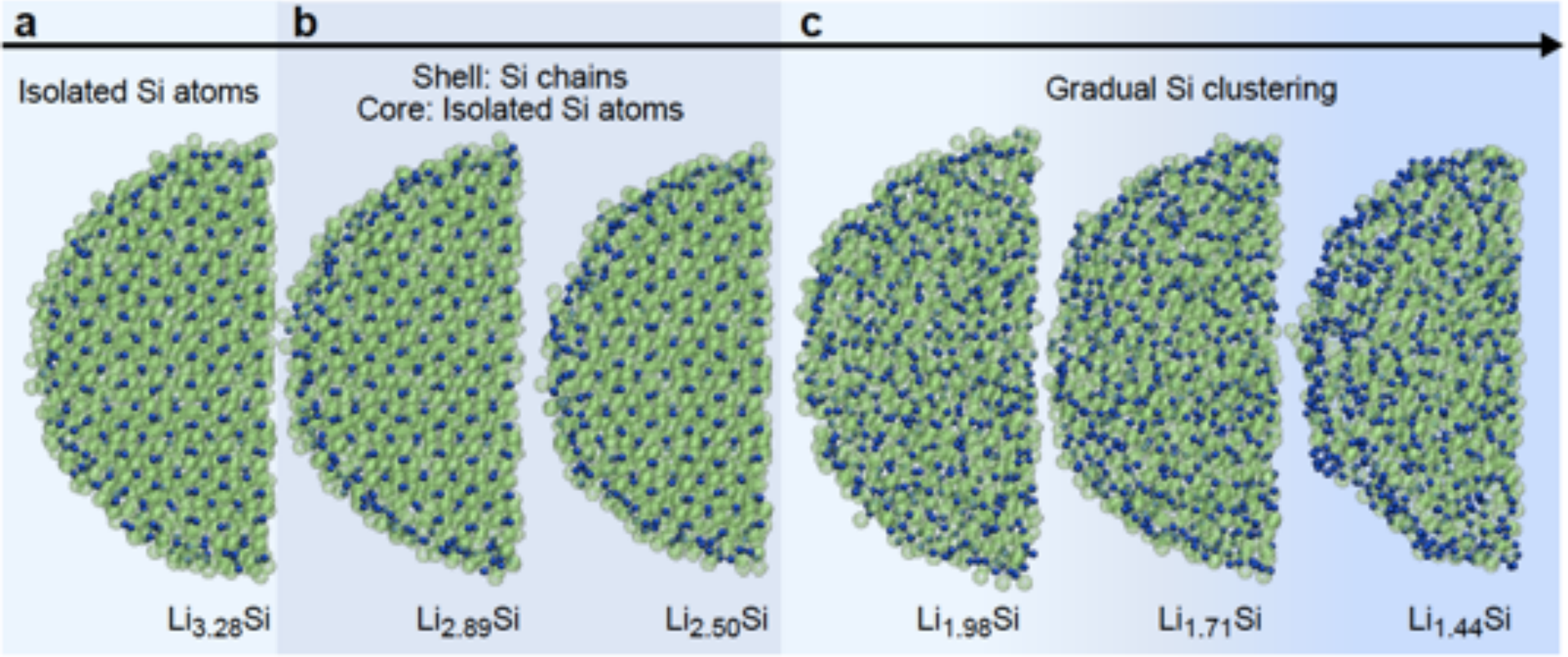
The LiSi ANN Potential is Accurate for Diffusion

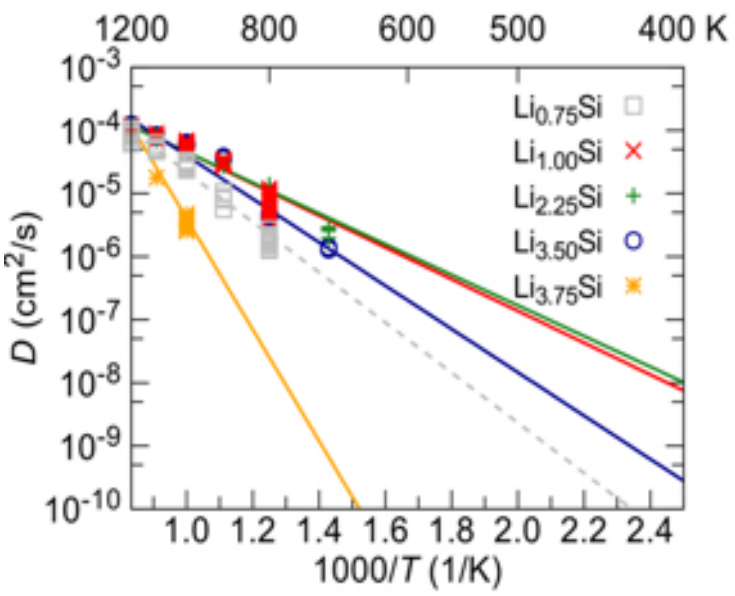


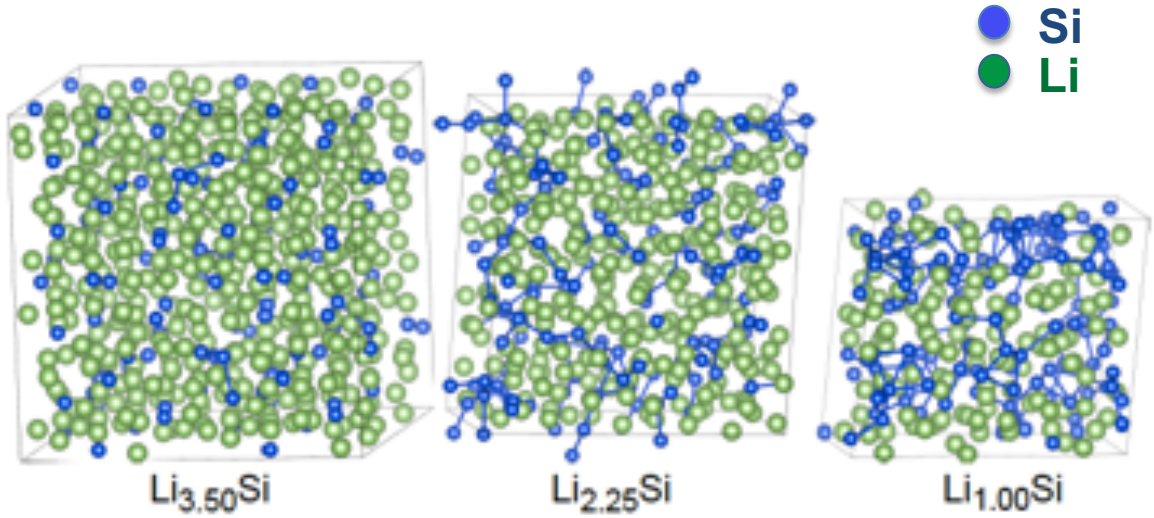
- Structures not in training set
- **Tested many different diffusion pathways in different alloy compositions**

And it is Accurate for Long MD Trajectories







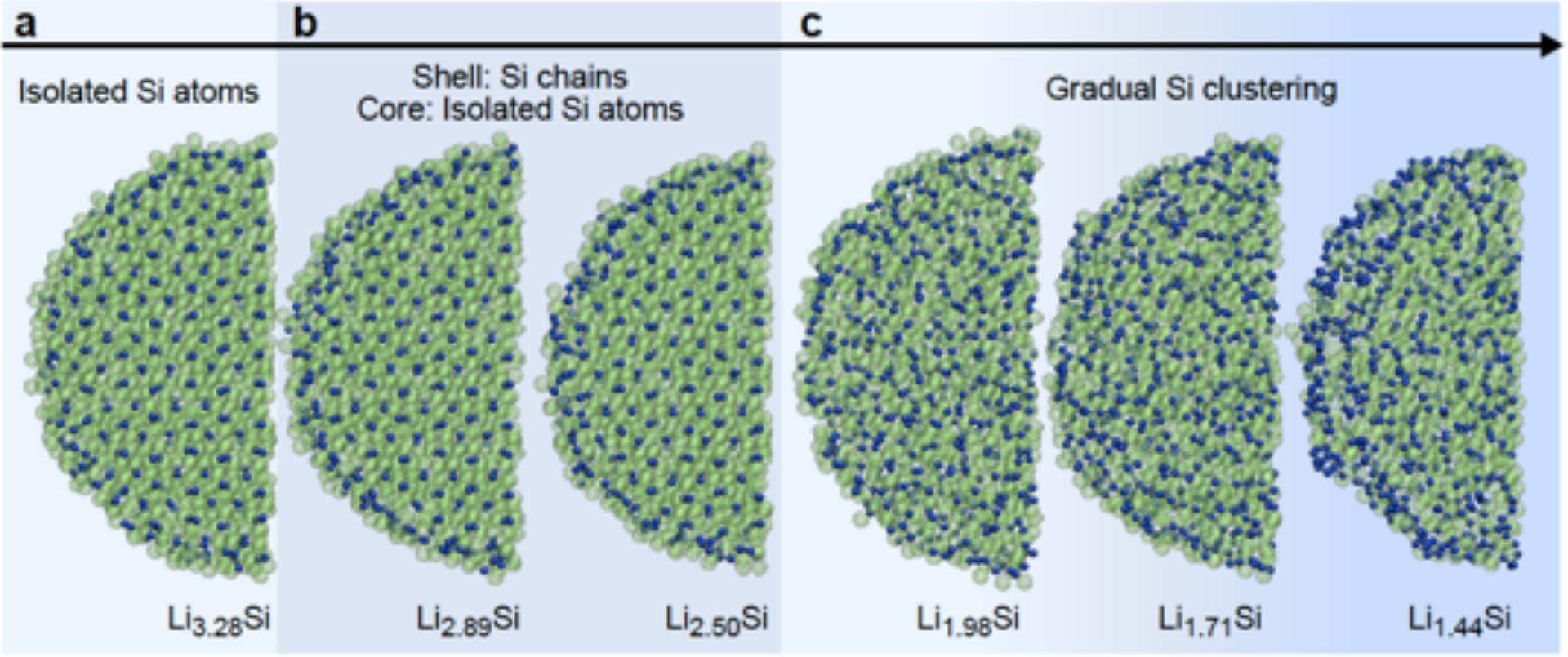


N. Artrith et al. arXiv:1901.09272 **(2019)**

NP Delithiation (d≈8nm) Shows Si Clustering

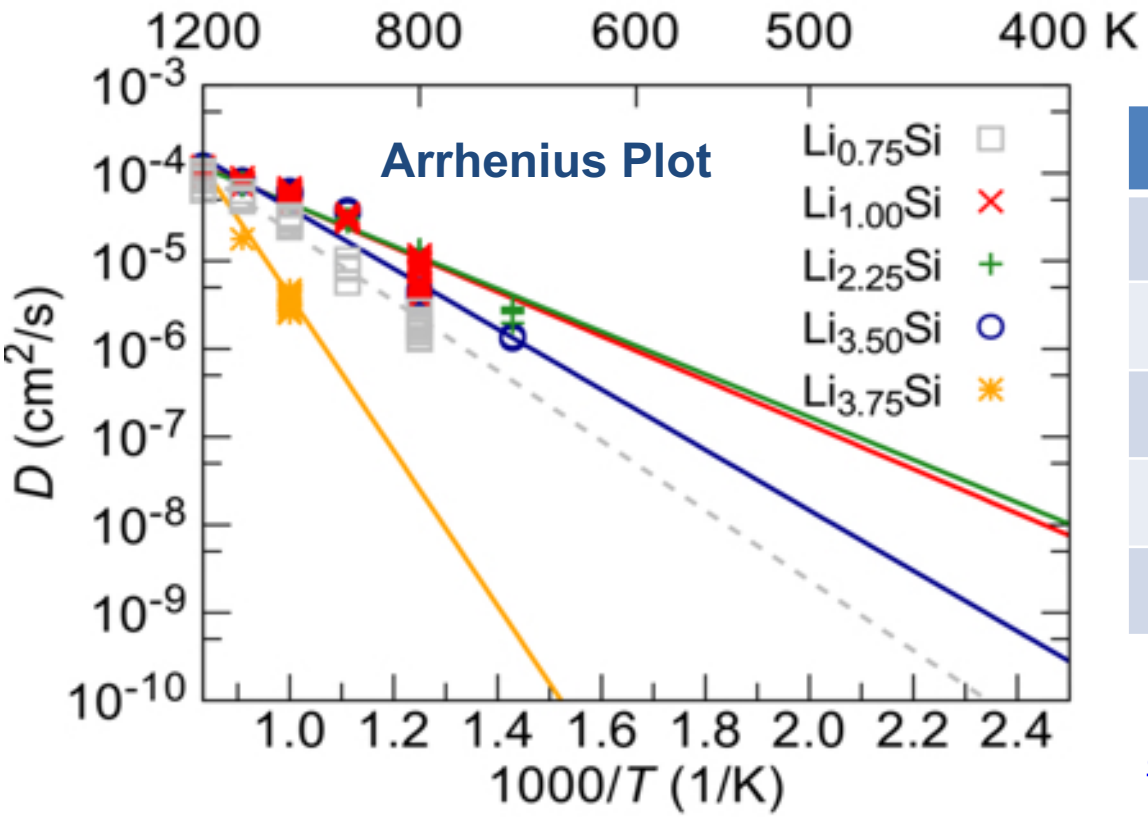
- MD simulations, over **4 ns at 500 K** at each composition, based on nanoparticle (NP) structures with **~12,000 atoms**.
- For composition within the two-phase region a core-shell structure is most stable: in the nanoparticle bulk Si atoms are isolated and near the surface Si is clustered into short Si chains.
- Further Li extraction results in Si clustering throughout the entire NP.

Si
Li



ANN MD: The Li Diffusivity Varies with Li Content

- MD simulations (5 ns) of **$Li_{480-x}Si_{128}$** structures using the ANN potential show that structures with Si clusters (Li_xSi with $1.0 \le x \le 2.25$) exhibit the highest Li diffusivities with $D \approx 5\text{-}10\times10^{-11}$ cm^2s^{-1}.
- Isolated Si atoms ($Li_{3.50}Si$ and $Li_{3.75}Si$) and structures in which Si forms three-dimensional networks (Li_xSi with $x < 1.0$) exhibit much lower diffusivities of $D < 5\times10^{-13}$ cm^2s^{-1}.



x_{Li}	E_a (eV)	D (cm^2s^{-1})
0.75	0.789	1.154×10^{-14}
1.00	**0.500**	**5.986×10^{-11}**
2.25	**0.483**	**9.607×10^{-11}**
3.50	0.682	3.820×10^{-13}
3.75	1.750	0.107×10^{-25}

N. Artrith et al.
arXiv:1901.09272 **(2019)**

ANN MD: The Li Diffusivity Varies with Li Content

Experimental References

D (cm^2/s)	Method	Reference
10^{-10}	EIS	[1]
10^{-12}	CV, EIS, GITT	[2]
10^{-14}	EIS, PITT	[3]
10^{-14}–10^{-13}	PITT	[4]

ANN Results

x_{Li}	E_a (eV)	D (cm^2s^{-1})
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[1] R. Ruffo, S. S. Hong, C. K. Chan, R. A. Huggins, and Y. Cui, *J. Phys. Chem. C* **113**, 11390 (2009).
[2] N. Ding, J. Xu, Y. Yao, G. Wegner, X. Fang, C. Chen, and I. Lieberwirth, *Solid State Ionics* **180**, 222 (2009).
[3] J. Xie, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda, and O. Yamamoto, *Mater. Chem. Phys.* **120**, 421 (2010).
[4] J. Li, X. Xiao, F. Yang, M. W. Verbrugge, and Y.-T. Cheng, *J. Phys. Chem. C* **116**, 1472 (2012).

Summary Part II – ANN Potentials in Applications

- **ANN potentials are a versatile tool for the modeling of complex materials** such as amorphous alloys and non-ideal oxides
- With new improved structure descriptors, the method can now be used with **compositions with more than 10 chemical species**
- Training accurate ANN potentials for general applications may require large reference libraries (>10,000 structures), but **often specialized potentials for smaller configuration spaces are sufficient** if combined with DFT

http://ann.atomistic.net

Outlook

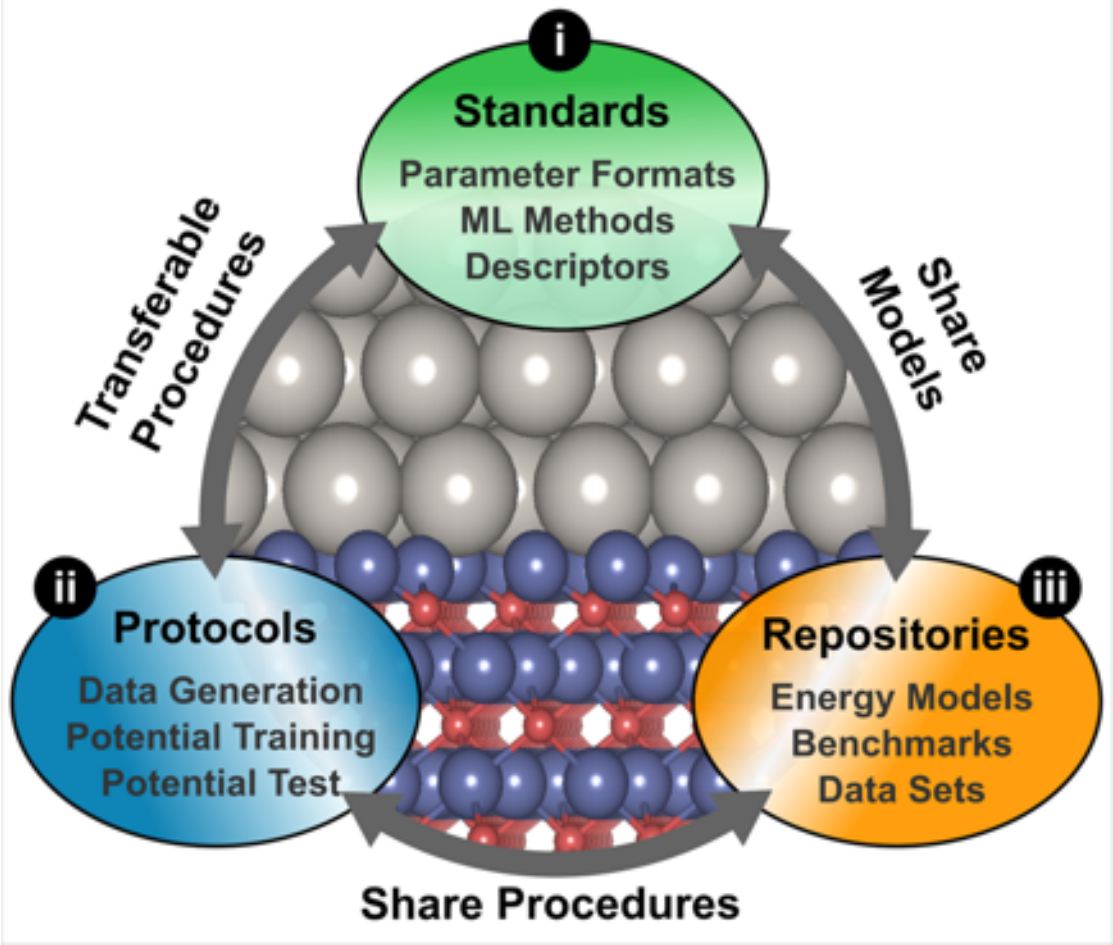
- **More systematic tests needed** to understand for which materials and applications the MLP method is successful
- Now that several implementations exist, we should have **a transferable format for ANN potentials** (collaborate on standardized format)
- How to **sample large chemical and configuration spaces** in the most efficient way?
- Including a **physically motivated baseline** could reduce the size of the reference library needed

Outlook

Some more steps required for ANN potentials to become a standard tool (like other potentials):

- **Interfaces with standard simulation software** are needed
  → aenet interfaces in development:
  ASE, Tinker, DL_POLY, LAMMPS, PIMD
- Implementations have to become compatible so that ANN potentials can be shared
- **Model construction (training) has to be made easier**
- **ANN potential parameter formats should be standardized**

Outlook



N. Artrith, *J. Phys. Energy* (**2019**) just accepted (invited review)

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The Behler group, RUB, Germany
: DFG SFB 558 Collaborative Project

Computational resources
: Extreme Science and Engineering Discovery Environment (**XSEDE**)
: Brookhaven National Laboratory (**CFN Computer Cluster**)

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NERSC
National Energy Research Scientific Computing Center

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- And others

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