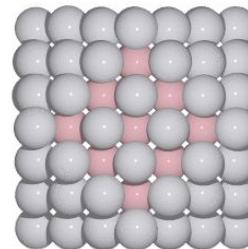
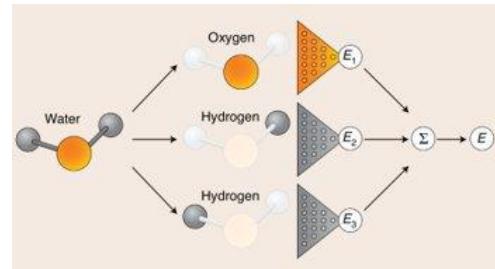


Optimizing Nanoparticle Structures via Neural-Network-Enhanced Genetic Algorithms and Monte-Carlo Simulations

Cheng Zeng, PhD

Jan 11, 2023

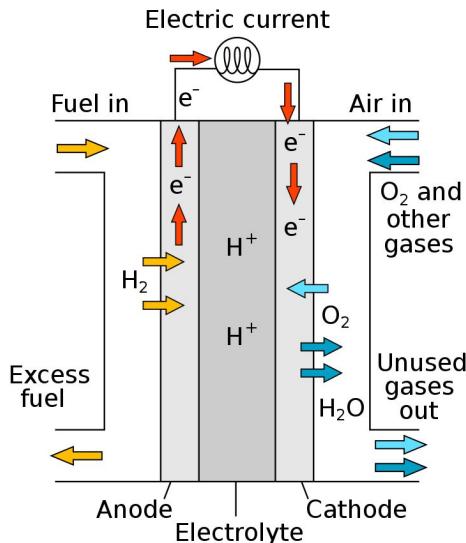


Outline

- Background and Motivation
 - Fuel Cell & Oxygen Reduction Reaction
 - Pt–Co Nanoparticles for Enhanced Oxygen Reduction
 - Nanoparticle Morphology: Packing of Atoms
- Technical Approaches
 - Potential Energy Surfaces
 - Atom-centered Neural Network (NN) Potential
 - A Nearsighted Force-Training (NFT) Approach
 - Advanced Algorithms to Optimize Nanoparticle Structures
 - Genetic Algorithms
 - Monte-Carlo Simulations
- Results and Discussion
 - Validation of Neural Network Potentials
 - Energy Convex-Hull of 147-atom Co–Pt Icosahedra
 - Morphology Crossover among Pt and Pt–Co Nanoparticles
 - Order–disorder Phase Transition of Pt–Co Truncated Octahedrons
- Conclusions

Background & Motivation

Fuel Cell & Oxygen Reduction Reaction (ORR)



Advantages

- CO₂ emission free
- High power density

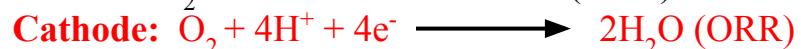
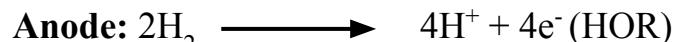
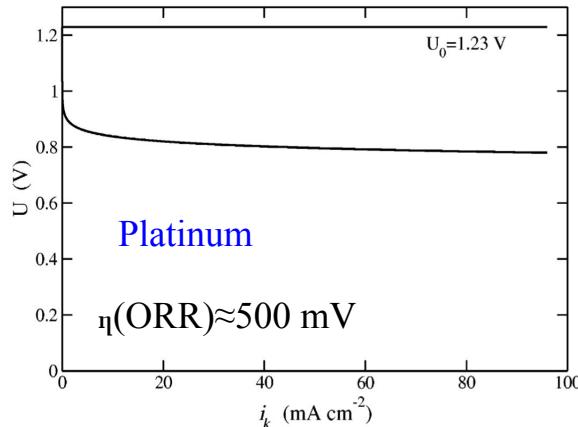
Disadvantages

- Sluggish ORR kinetics

Solution?

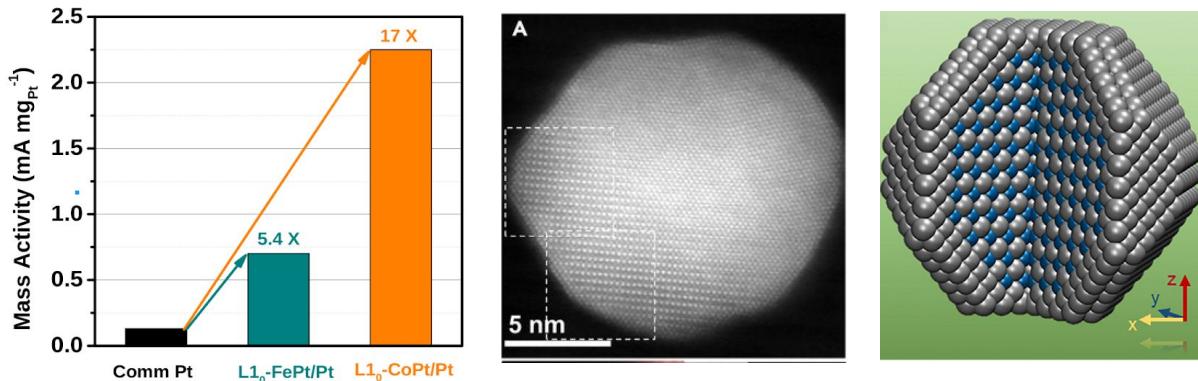
Pt alloys as ORR catalysts

Platinum is considered to be the best elemental catalyst for ORR.



Pt-Co Nanoparticles for Enhanced ORR

CoPt core-shell nanoparticle surpasses DOE targets for both ORR activity and stability

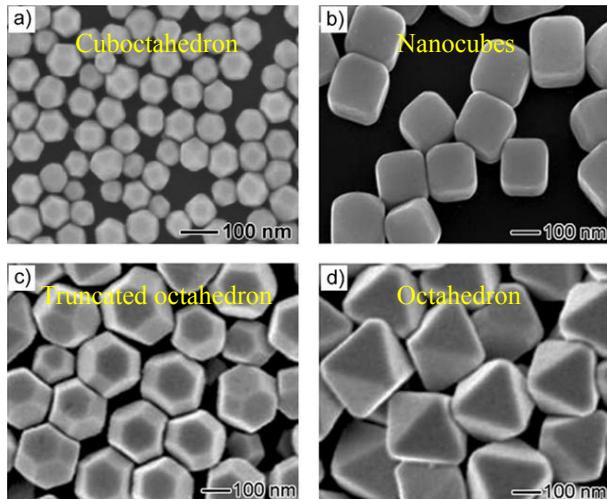


J. Li et al., Joule, 3: 124-135 (2019)

- The entire nanoparticle has around 20,000 atoms (~9 nm).
- Quantum mechanical calculations for physical systems are limited to ~500 atoms.
- Why this type of nanoparticle appears in experiments?

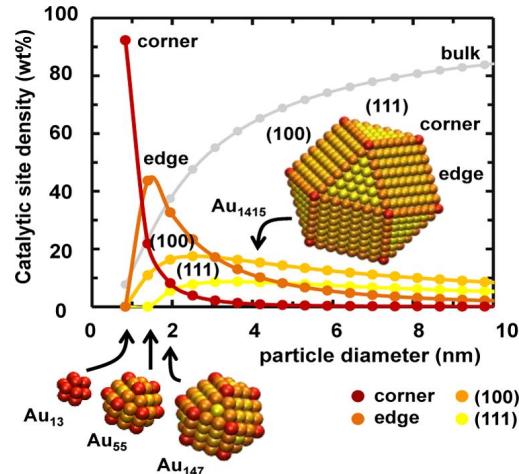
Nanoparticles (NPs) Morphology: Packing of Atoms

Ag nanocrystals in various shapes

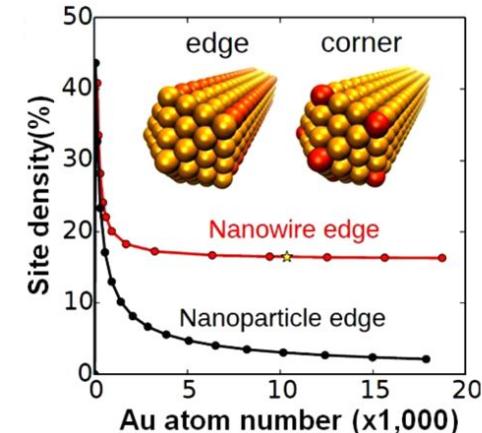


Xia et al., *JACS*, **48** (2009)

Shape and size play key roles in catalysis

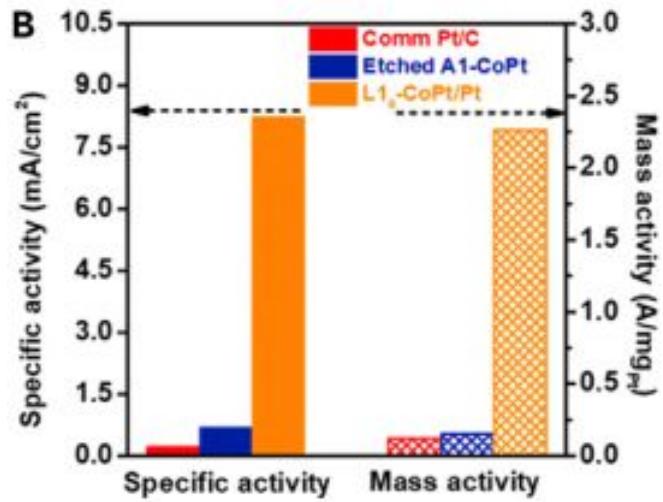


Zhu et al., *JACS*, **135** (2013)

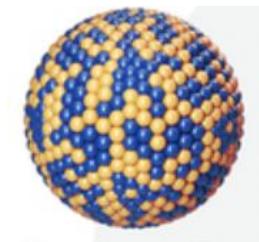


Zhu et al., *JACS*, **136** (2014)

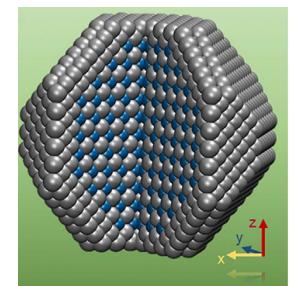
Order–Disorder Phase Transition in NPs



J. Li et al., Joule, 3: 124-135 (2019)



Random alloy

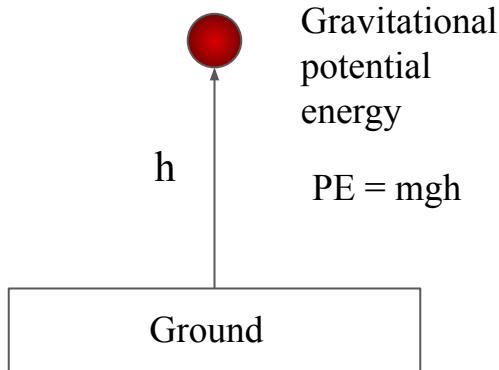


Ordered alloy

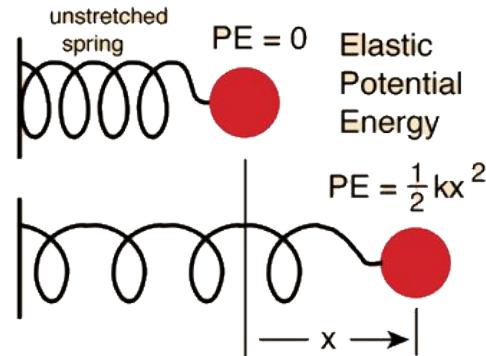
- Ordered CoPt NP shows higher ORR stability and catalytic activity.
- How to decide NP morphology and orderliness computationally?

Technical Approaches

Potential Energy (PE)



Force of gravity: $f = - mg$



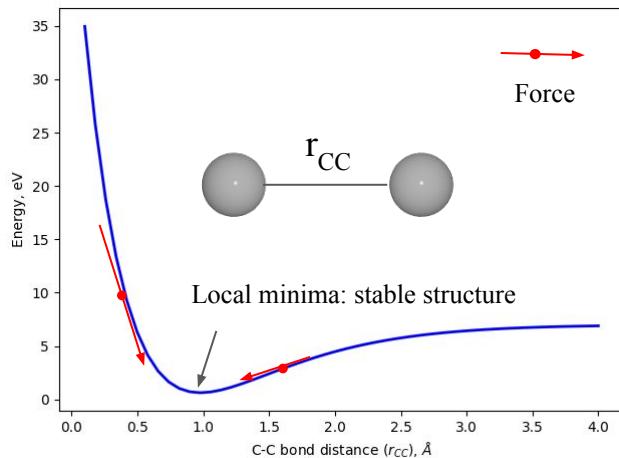
Force of spring: $f = - kx$

- Potential energies depend only on relative positions.
- Forces drive the state to lower potential energies (more stable states); Forces are negative derivative of energy with respect to positions.

Potential Energy Surfaces

Potential energy surfaces (PES) provide a numerical framework to describe chemistry. Each structure (geometry) is associated with a unique energy. Since geometry changes are smooth, the energy landscape created is also smooth. In this way, chemistry becomes topology.

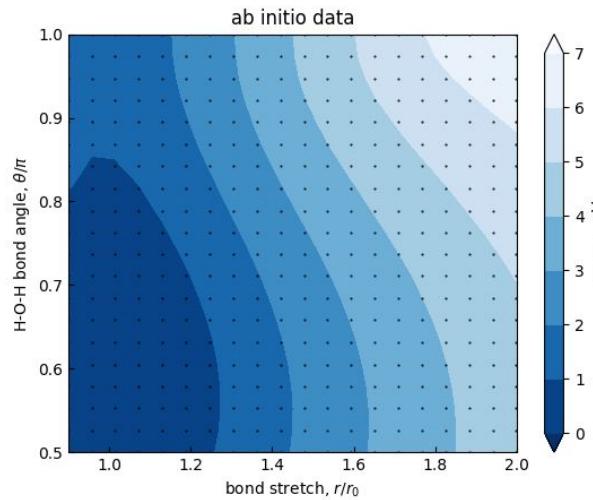
The simplest example: 1D PES



$$E = E(\{\vec{R}\})$$

$$\mathbf{F}_i = - \left(\frac{\partial E}{\partial \mathbf{R}_i} \right)_{j \neq i}$$

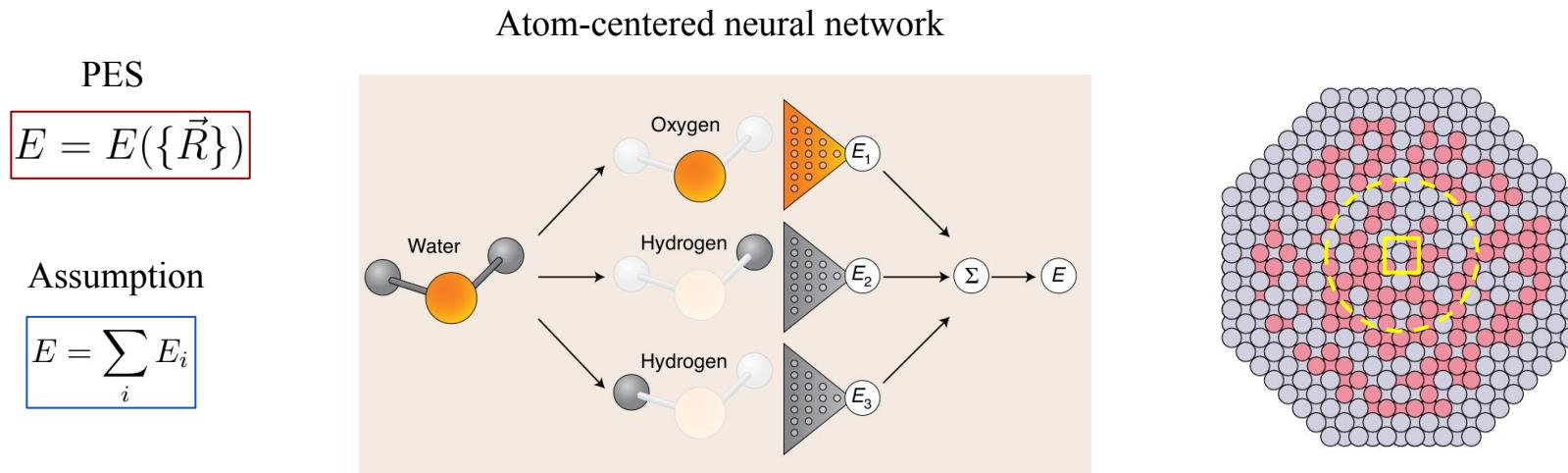
Single water molecule: 2D PES



- More stable structures have lower potential energies.
- Forces indicate how close the current structure is to a local minima.

Atom-centered Neural Network Potential

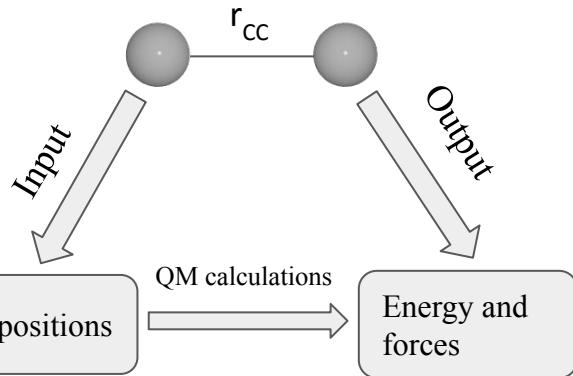
Neural network (NN) math fitting has gained its momentum in the last two decades because it can fit any arbitrary function, which makes it ideal for fitting PES whose function form is unknown.



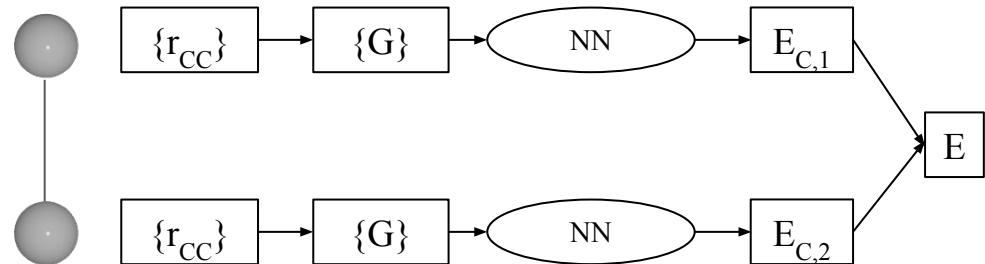
- Each atomic energy comes from the atom interacting with its neighbors (local chemical environment).
- Local chemical environments are the building blocks of atom-centered NN potentials.

How Atom-centered NN Potential Works?

Example training data



Journey of a structure in atom-centered NN



$$\text{Forces: } \mathbf{F}_i = - \left(\frac{\partial E}{\partial \mathbf{R}_i} \right)_{j \neq i}$$

Loss function

$$Loss = \frac{1}{2} \sum_{j=1}^M \left\{ \left(E_j/N_j - \hat{E}_j/N_j \right)^2 + \frac{\alpha}{3N_j} \sum_{k=1}^3 \sum_{i=1}^{N_j} \left(F_{ik} - \hat{F}_{ik} \right)^2 \right\}$$

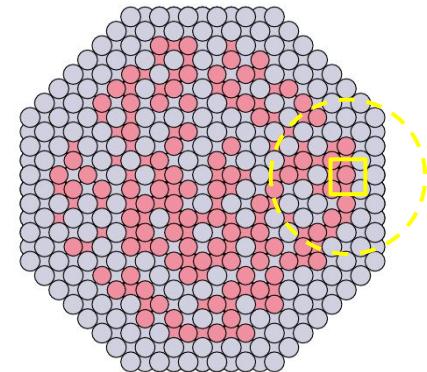
Challenges in NN Potentials

Normally a large amount of training data are needed.

- On-the-fly learning to minimize the number of expensive quantum mechanical calculations

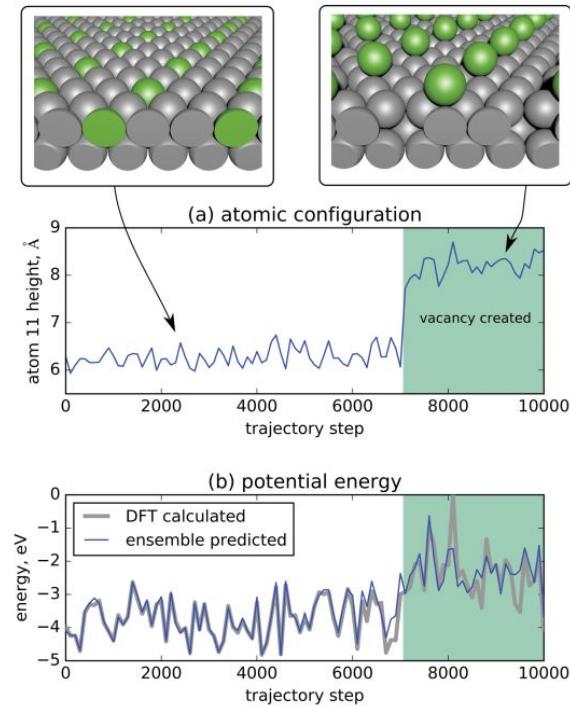
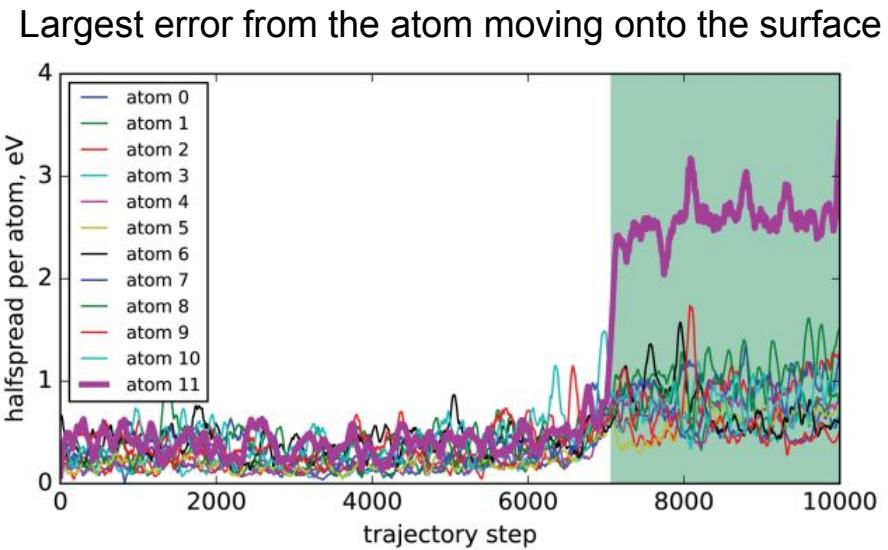
How to generate *small atomic structures* when ML predictions *fail on a large structure*?

- Per-atom uncertainty quantification



Localizing Prediction Uncertainty to Atoms

Ensemble models can isolate prediction errors to atoms.



An Active Learning Protocol

□ Integration of ensemble uncertainty metric and nearsighted force training

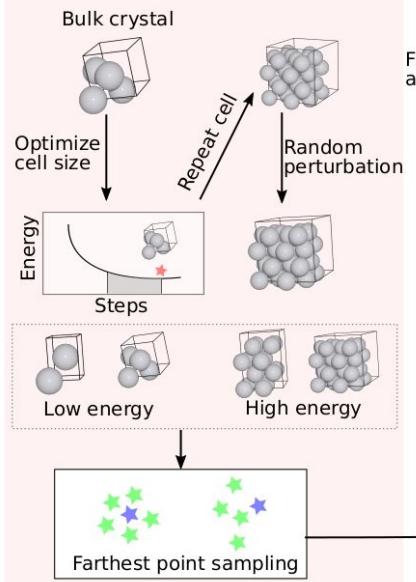
Atomic uncertainty

$$\delta_i = 2.58\sigma_f = 2.58\sqrt{\frac{\sum_{j=1}^M \|\mathbf{f}_i^{(j)} - \bar{\mathbf{f}}_i\|^2}{M-1}}$$

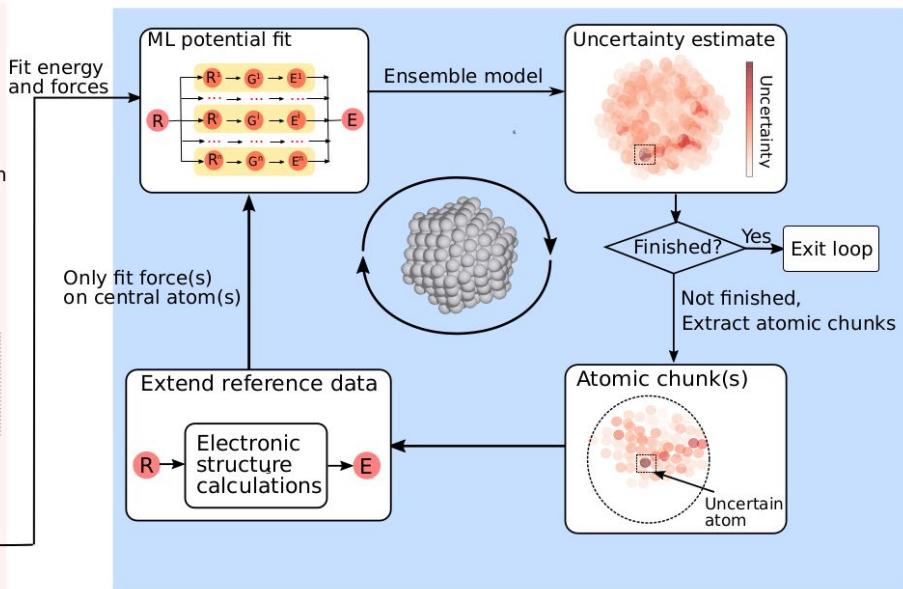
Structure uncertainty

$$\delta = \max_i(\{\delta_i\})$$

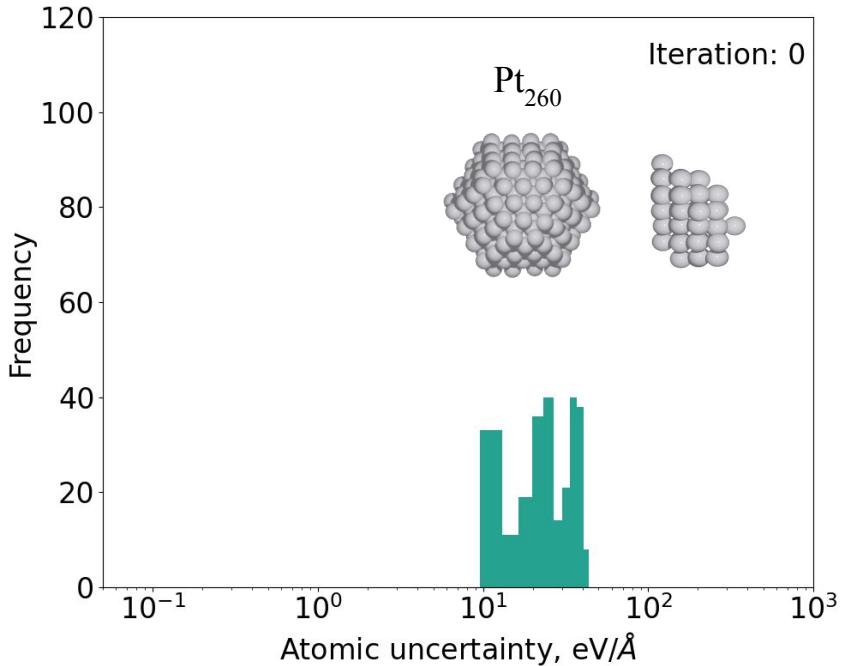
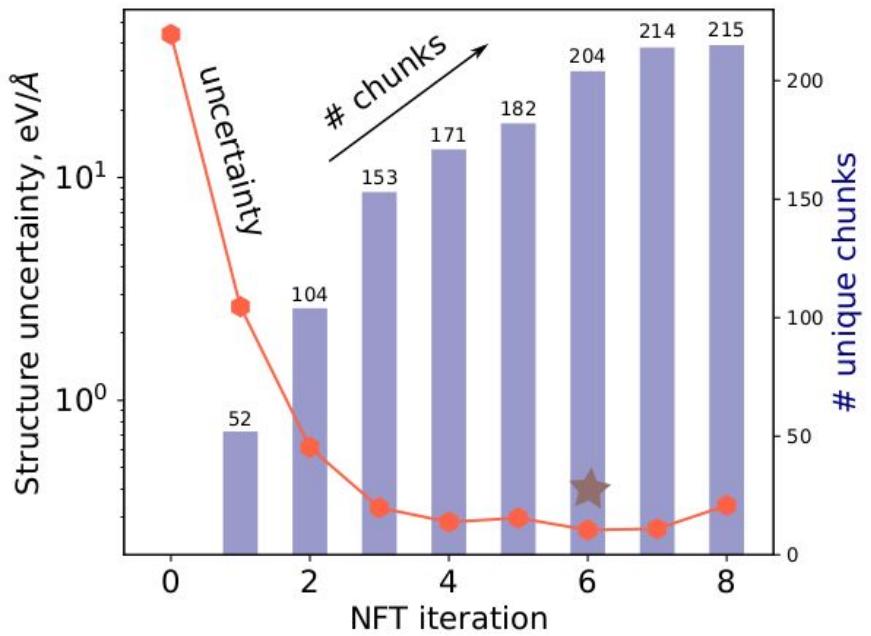
Initialization



Nearsighted Force Training Iteration

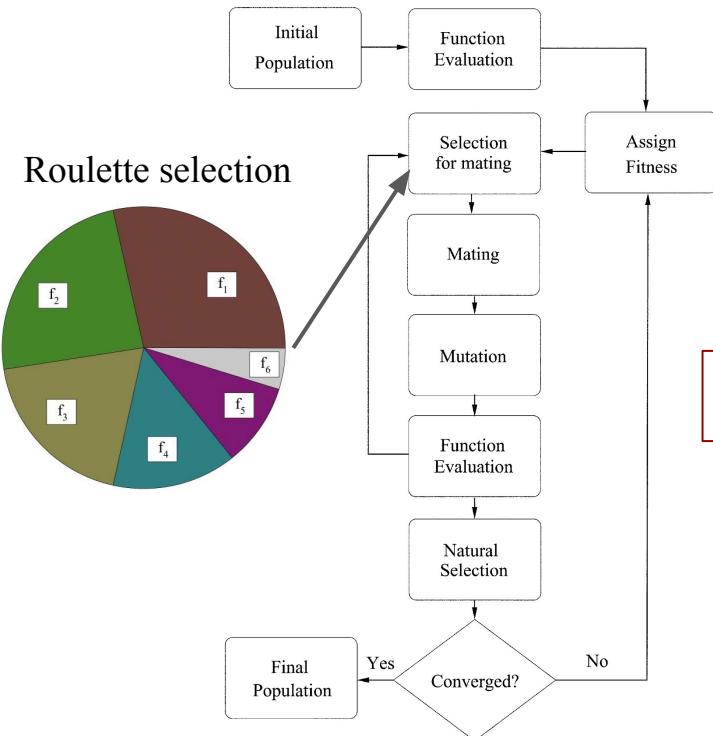


Benchmark on a Pt Nanoparticle with 260 Atoms



Genetic Algorithm

Flow chart

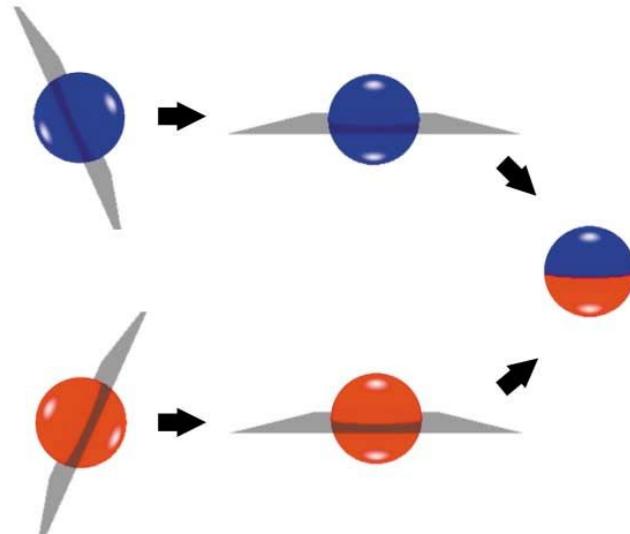


Fitness score: Formation energy of a Pt–Co system

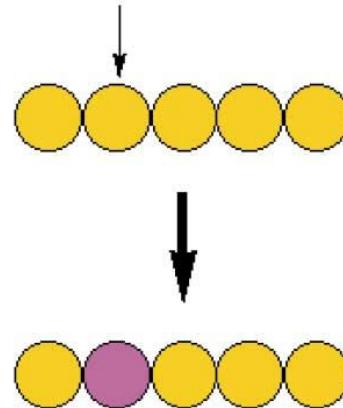
$$E_f(\text{Pt}_x\text{Co}_y) = \bar{E}(\text{Pt}_x\text{Co}_y) - \frac{x}{x+y}\bar{E}(\text{Pt}_{x+y}) - \frac{y}{x+y}\bar{E}(\text{Co}_{x+y})$$

Genetic Algorithm Operators

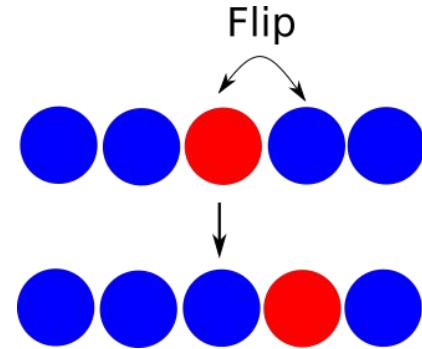
Crossover: cut and splice



Mutation



Permutation



Monte-Carlo (MC) Simulations

Classical Metropolis-Hastings (MH) Algorithm

Table 3: The MH algorithm

1. Initialization: Choose an initial state θ_0 .
 2. FOR $t = 1, \dots, T$:
 - (a) Draw a sample $\theta' \sim q(\theta | \theta_{t-1})$. ← proposed probability function
 - (b) Accept the new state, $\theta_t = \theta'$, with probability ← target probability function (to be sampled)
 - Otherwise, set $\theta_t = \theta_{t-1}$.
 3. Return: $\{\theta_t\}_{t=1}^T$.
- $$\alpha(\theta_{t-1}, \theta') = \min \left[1, \frac{\pi(\theta') q(\theta_{t-1} | \theta')}{\pi(\theta_{t-1}) q(\theta' | \theta_{t-1})} \right], \quad (6)$$
- $$\theta_0 \rightarrow \theta_1 \rightarrow \theta_2 \rightarrow \dots \rightarrow \theta_T$$

Boltzmann distribution of system states

$$p_i \propto e^{-\epsilon_i/k_b T}$$

The probability of a system being in a certain state i is associated with the energy of the state and the temperature.

Results & Discussion

Training Data: Selected Atomic Chunks

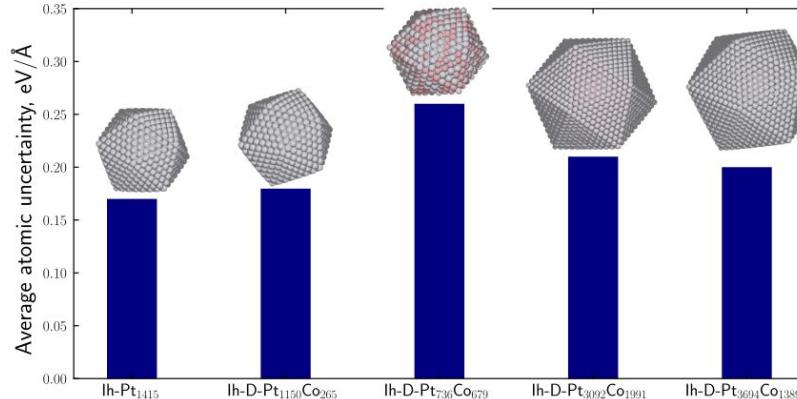
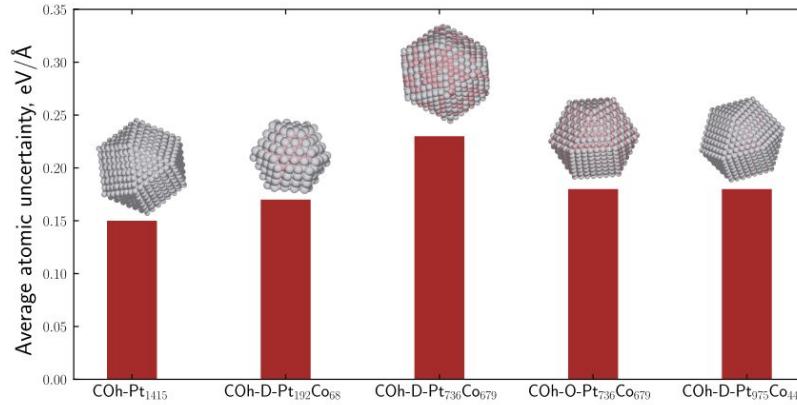
Atomic uncertainty

$$\delta_i = 2.58\sigma_f = 2.58\sqrt{\frac{\sum_{j=1}^M \|\mathbf{f}_i^{(j)} - \bar{\mathbf{f}}_i\|^2}{M-1}}$$

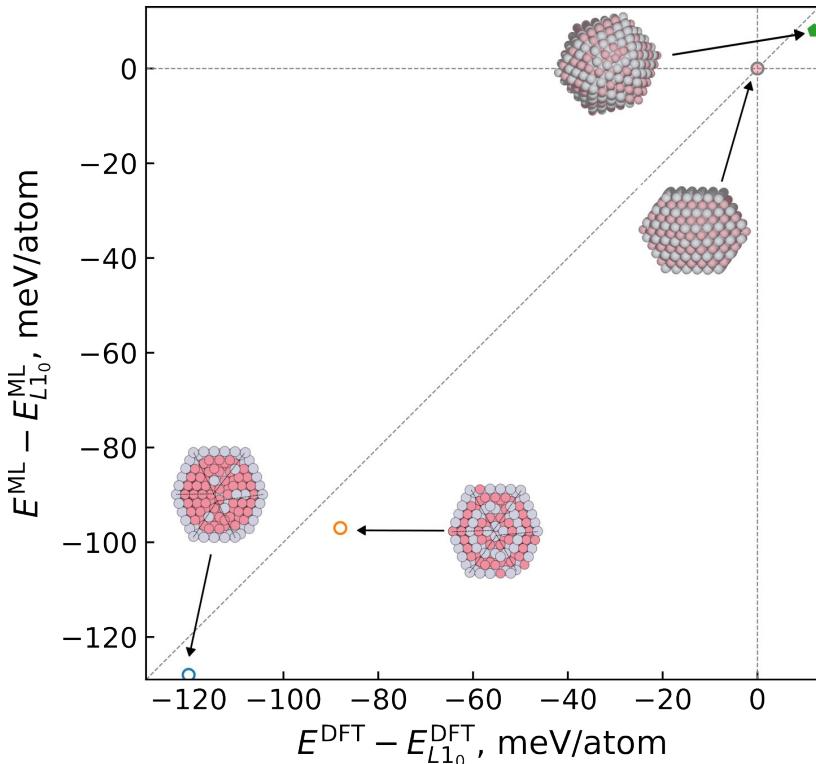
Training data: ~2000 chunks
in sizes of 46-150 atoms

NN topology: (20, 5, 5, 1)

Average atomic uncertainty of force predictions



Validation of NN Potentials



DFT data from: M. E. Gruner et al., *Phys. Rev. Lett.*, **100** (2008)

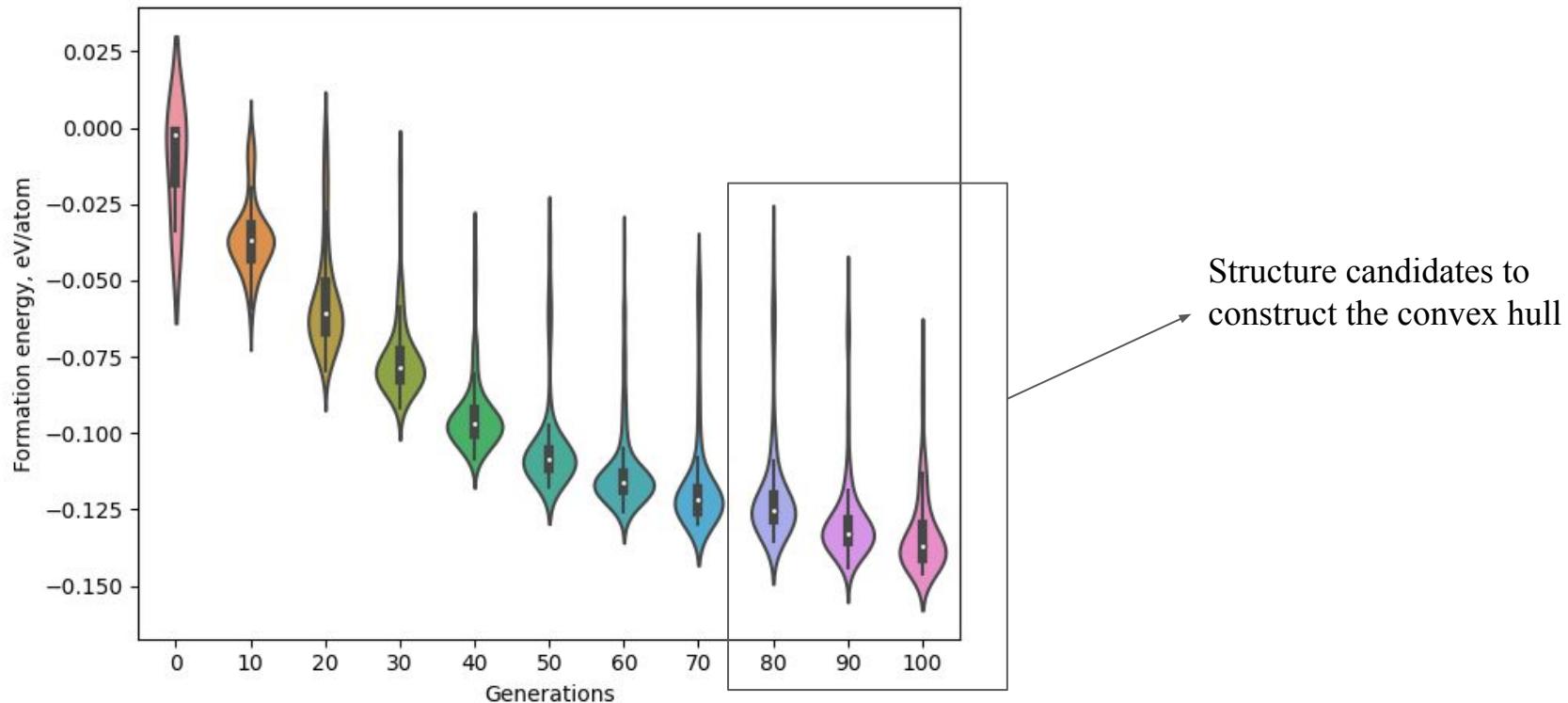
Pt₂₉₆Co₂₆₅ thermodynamic stability

- Core-shell icosahedron (Ih) with depleted surfaces
- Icosahedron with alternating Co/Pt shells
- L1₀-ordered cuboctahedron (COh)
- Disordered icosahedron

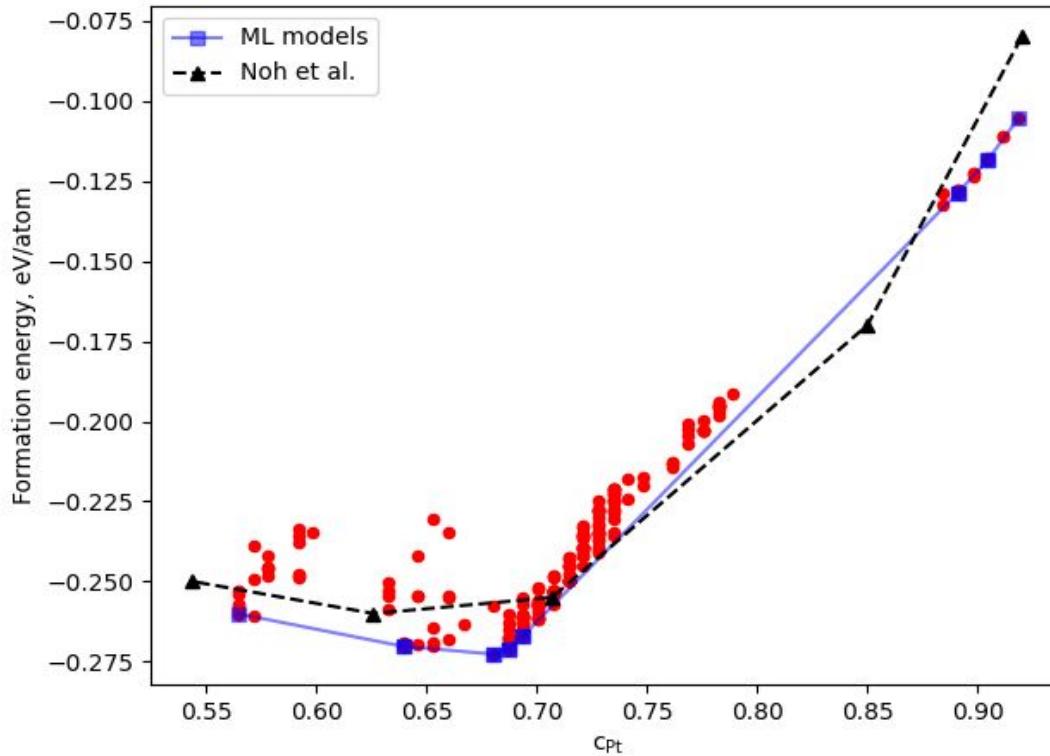
*DFT data using PW cutoff of 268 eV; ML models trained on DFT data using PW cutoff of 350 eV

Genetic Algorithms on 147-Atom Co–Pt Icosahedra

- Formation energy distributions at every 10th generation



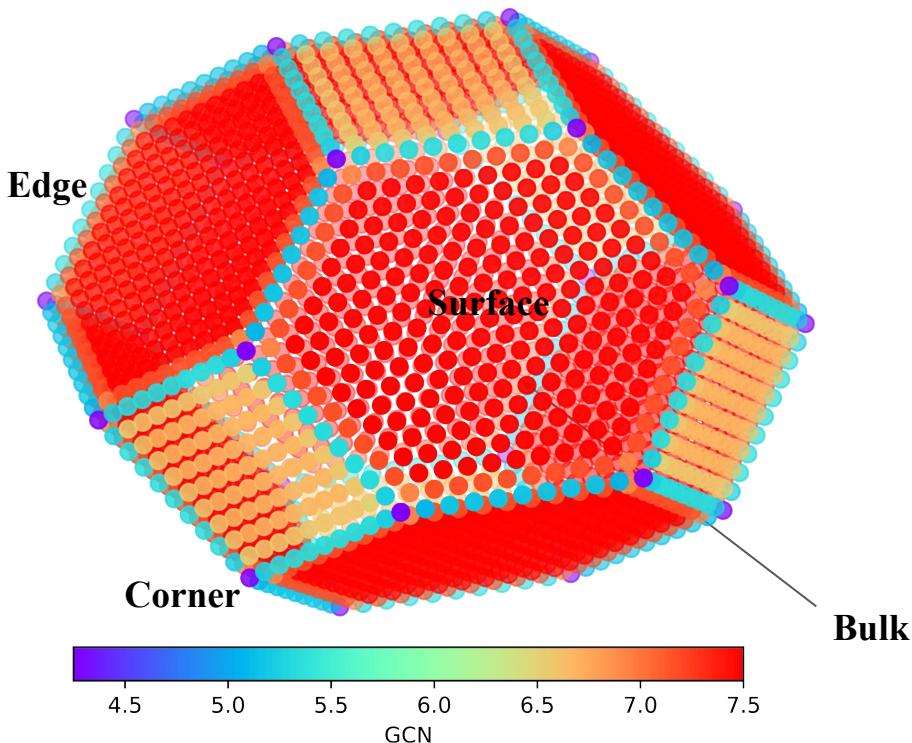
Energy Convex Hull: Predictions vs First-principles



$$E_f(\text{Pt}_x \text{Co}_y) = \overline{E}(\text{Pt}_x \text{Co}_y) - \frac{x}{x+y} \overline{E}(\text{Pt}_{x+y}) - \frac{y}{x+y} \overline{E}(\text{Co}_{x+y})$$

An Empirical Model for Nanoparticle Stability

Site coordination number in a truncated octahedron



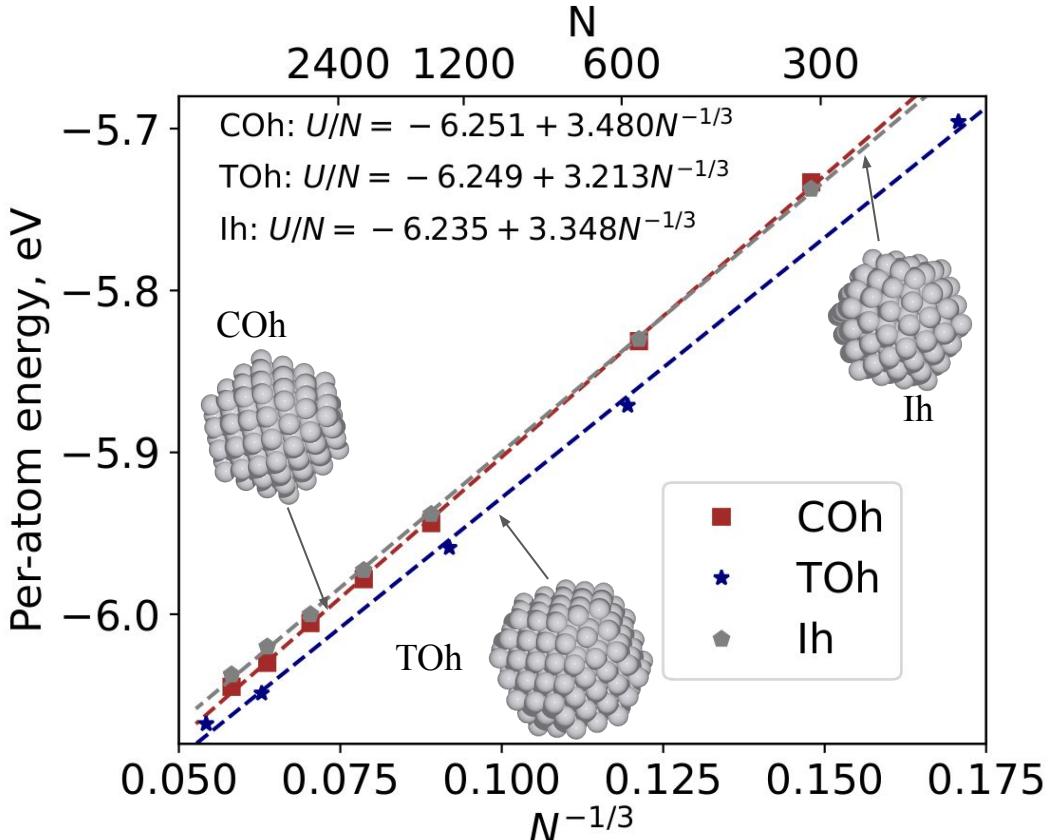
$$U = AN + BN^{2/3} + CN^{1/3} + D$$
$$\approx AN + BN^{2/3}$$

- A, B, C and D are coefficients.
- N is the number of atoms in the NP.
- When N is large only bulk and surface contributions are significant, hence dropping other terms.

A linear relationship

$$\frac{U}{N} = A + BN^{-1/3}$$

Crossovers among Morphologies of Pt NPs

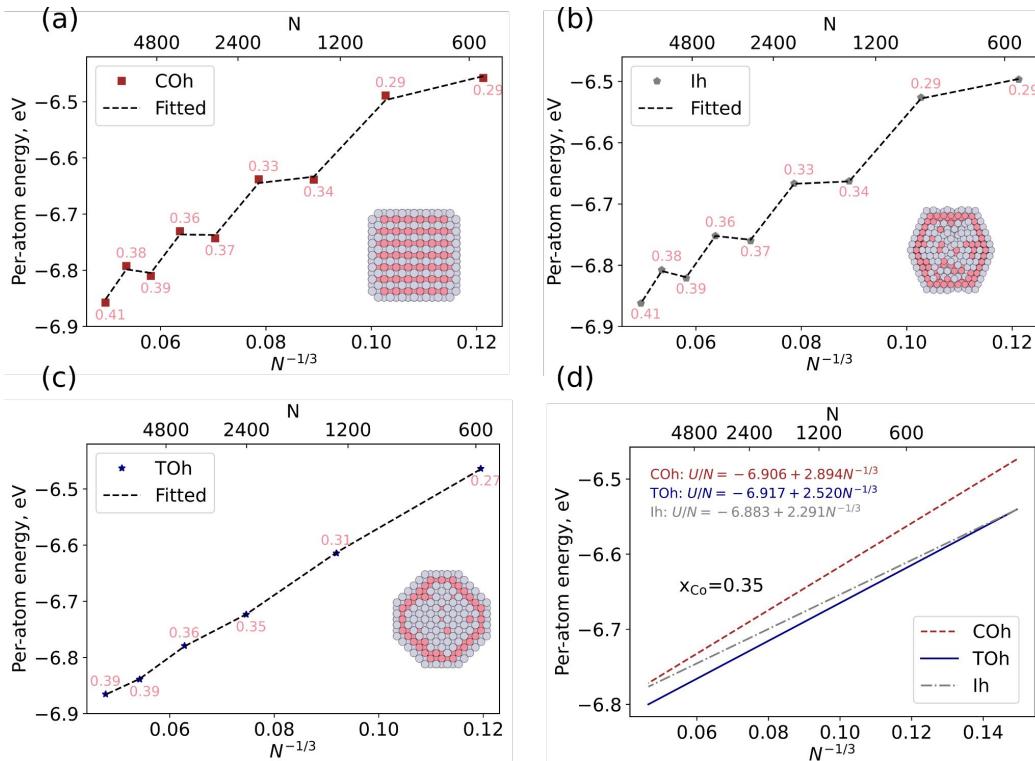


$$\frac{U}{N} = A + BN^{-1/3}$$

- Crossover from Icosahedron to Cuboctahedron happens at **N=538**.
- **Truncated octahedron** is the most stable morphology across all sizes because of its low bulk and surface energy contributions.

*TOh: Truncated (regular) octahedron

Crossovers for PtCo Core–Shell Nanoparticles



$$\frac{U}{N} = A + BN^{-1/3}$$

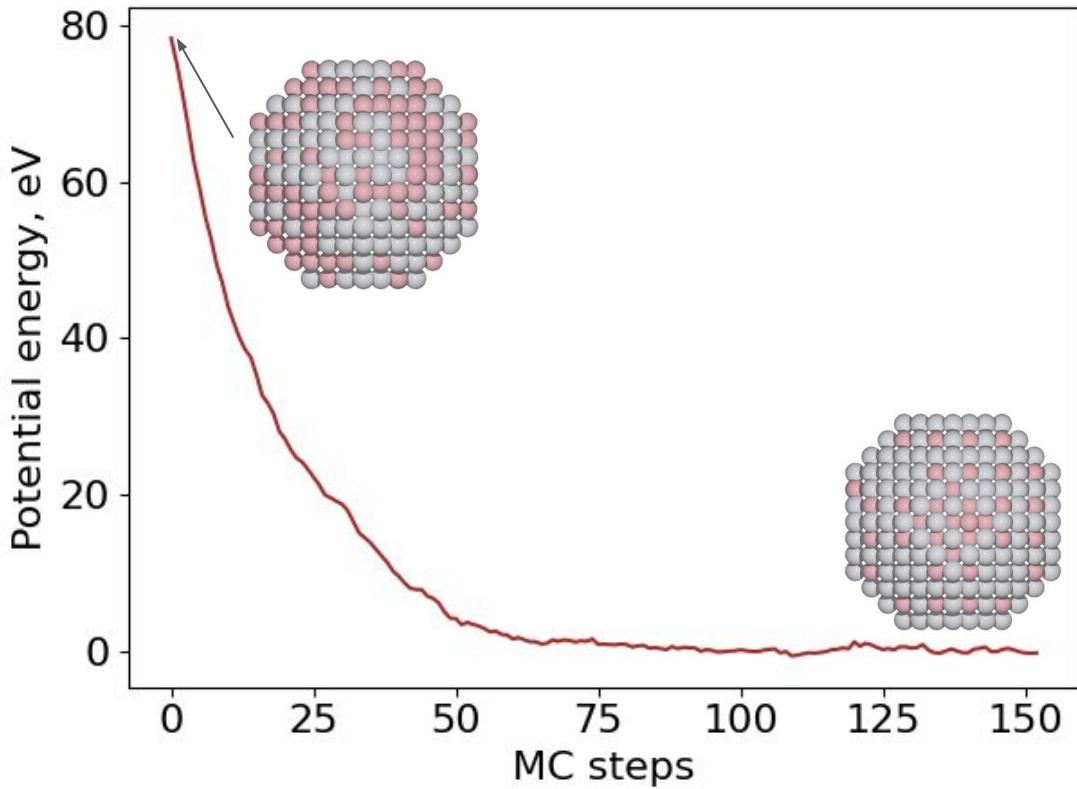
$$A = A_0 (x_{\text{Co}} E_{\text{Coh}}^{\text{Co}} + (1 - x_{\text{Co}}) E_{\text{Coh}}^{\text{Pt}} - \alpha x_{\text{Co}}(1 - x_{\text{Co}}))$$

$$B = B_0(1 - \kappa x_{\text{Co}})$$

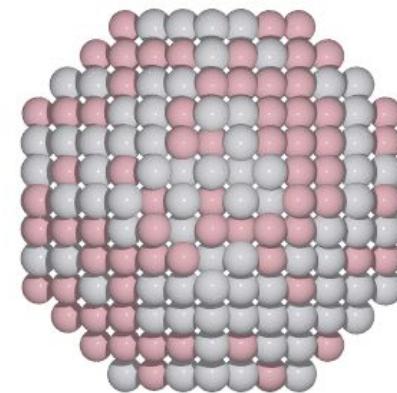
- Crossover from Ih to TOh happens at **N=303**.
- Crossover between Ih and TOh occurs because of the larger downshift of surface energy for Ih upon Co alloying in pure Pt NPs.

*Dashed curves are fitted with the revised empirical equations.

Monte-Carlo Simulations: An Example

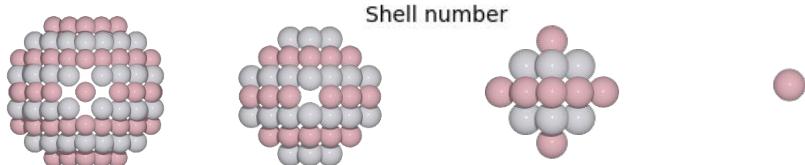
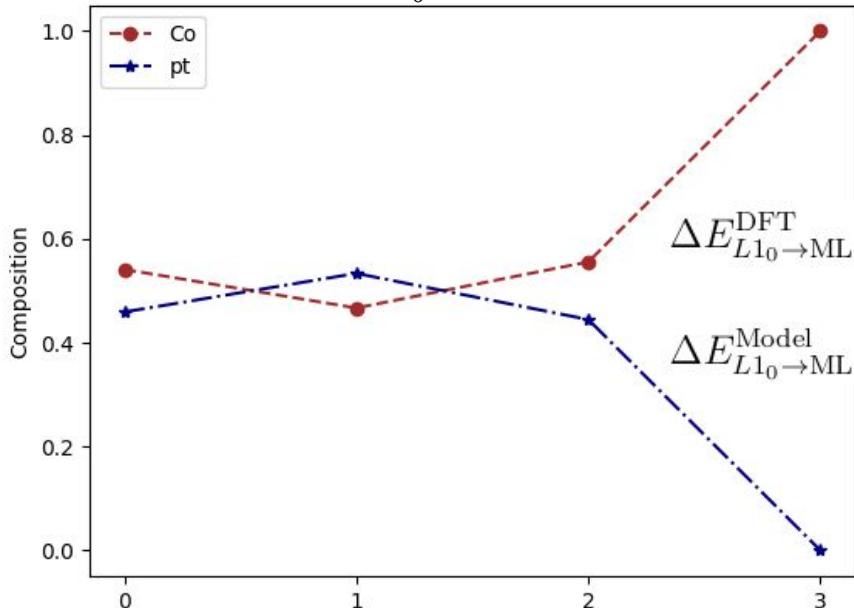


$\text{Pt}_{300}\text{Co}_{286}$, $T=500 \text{ K}$

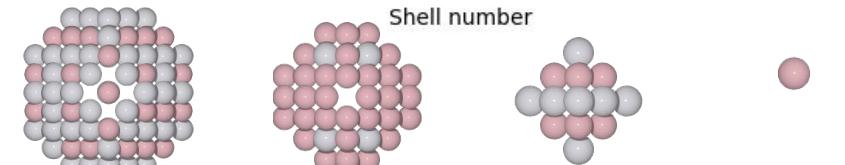
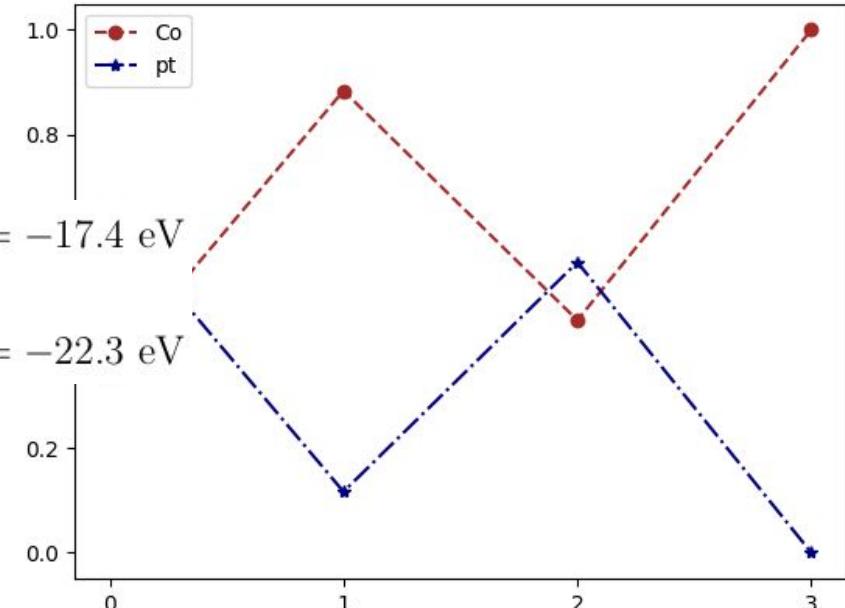


Putative Global Minima of $\text{Pt}_{96}\text{Co}_{105}$ TOh

Fully L1_0 ordered



Putative GM by ML models



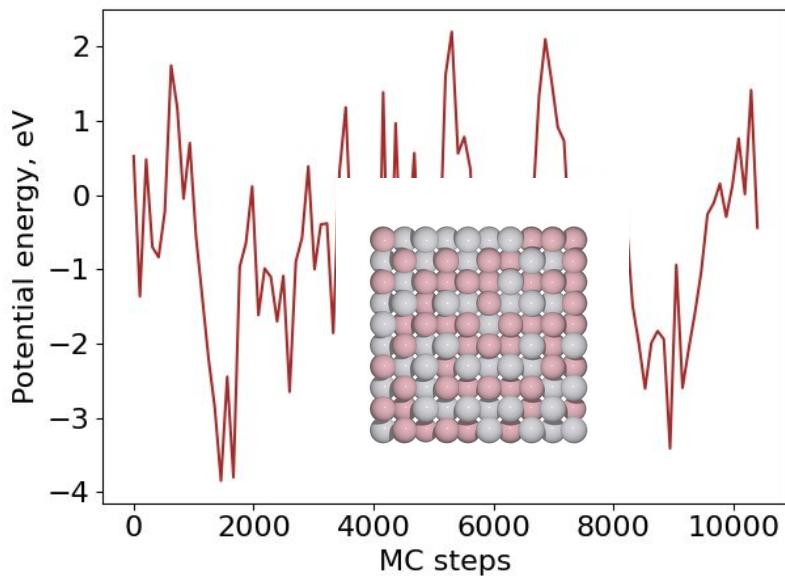
*DFT results using PW cutoff of 268 eV

Order–Disorder Phase Transition: An Example

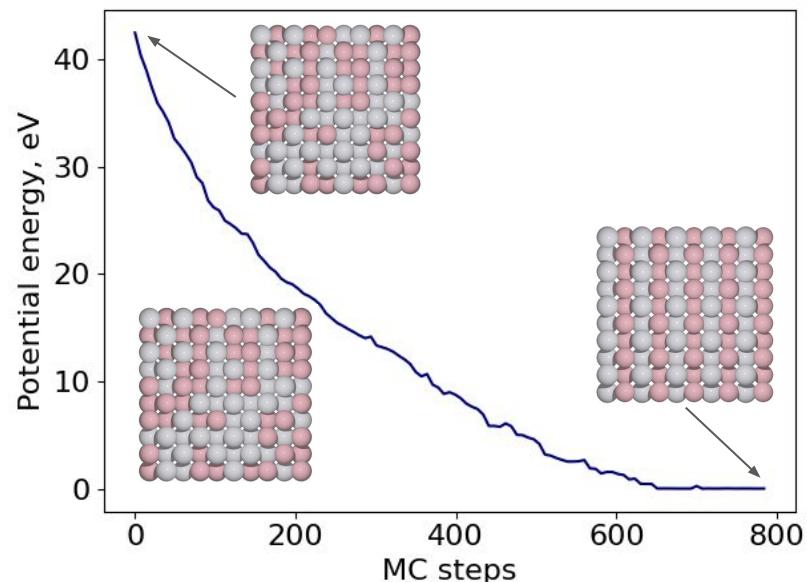
❑ Bulk Pt₂₅₀Co₂₅₀

$$p_i \propto e^{-\epsilon_i/k_b T}$$

Temperature: 1800 K, entropy dominant

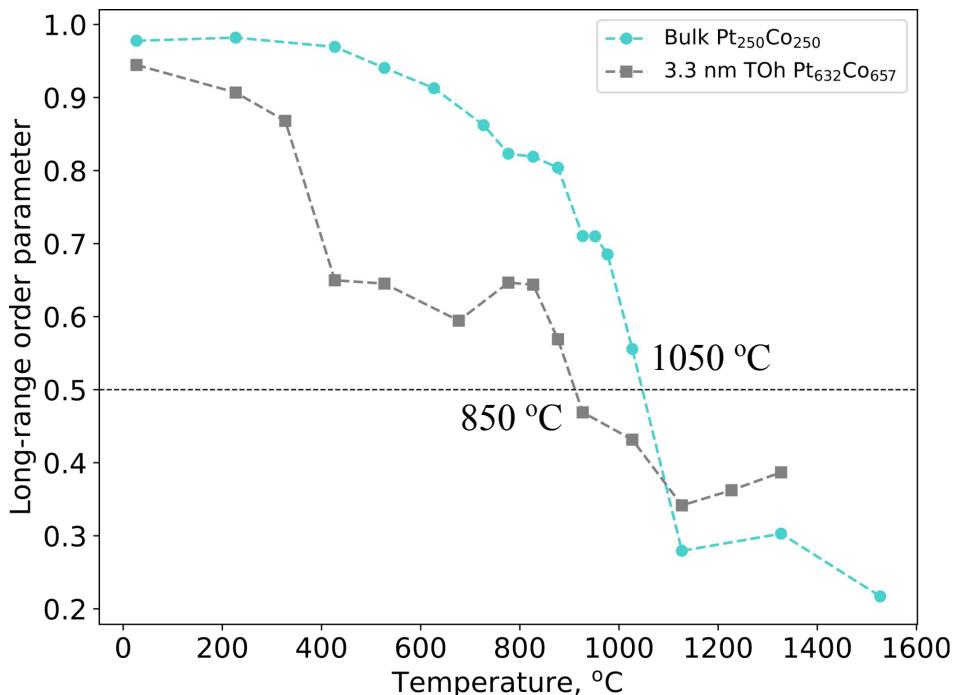


Temperature: 500 K, energy dominant



Order–Disorder Phase Transition

Bulk alloy $\text{Pt}_{250}\text{Co}_{250}$ and a 3.3-nm PtCo NP



Long-range order parameter

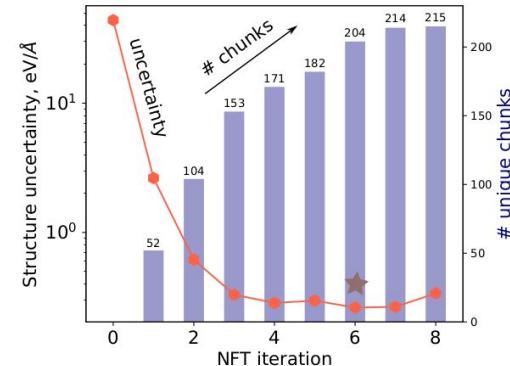
$$\Phi = \max_{i \in \{x,y,z\}} (\{\Phi_i\}) \quad \Phi_i = |p_{A,i} - 1/2| + |p_{B,i} - 1/2|$$

- Order–disorder transition of a bulk alloy is at ~ 1050 °C.
- The transition of a 3.3-nm PtCo NP is around ~ 850 °C, 200 °C lower than that of a bulk alloy.

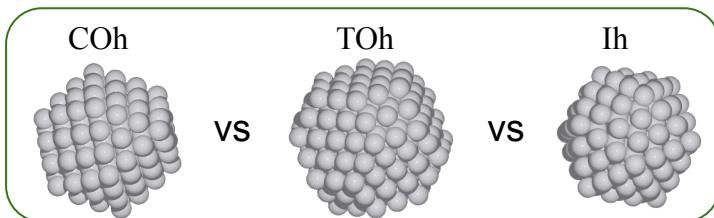
Take Home Messages

Phase stability of PtCo nanoparticles is studied via neural network potentials (NNPs).

- Models—NNPs trained with NFT are robust in that
 - Training is on small-size atomic chunks, hence fast and cheap.
 - Models can be easily improvable by feeding uncertain atomic chunks.
 - Predictions in extrapolation regions show *ab initio* accuracy.
- Applications—Design of nanoparticles in various shapes, morphology, compositions and orderliness



Morphology crossover



Order–disorder phase transition

