

The phase stability of large-size nanoparticle alloy catalysts at *ab initio* quality using a nearsighted force-training approach

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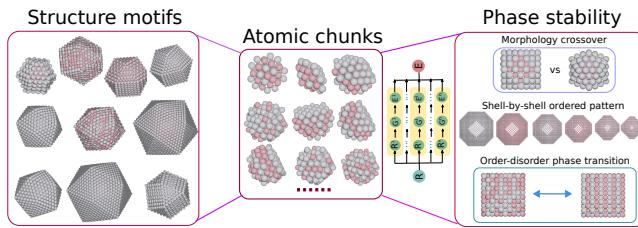
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Abstract

Co–Pt alloyed catalyst particles are integral to commercial fuel cells, and alloyed nanoparticles are important in many applications. Such systems are prohibitive to fully characterize with electronic structure calculations due to their relatively large sizes of hundreds to thousands of atoms per simulation, the huge configurational space, and the added expense of spin-polarized calculations. Machine-learned potentials offer a scalable solution; however, such potentials are only reliable if representative training data can be employed, which typically also requires large electronic structure calculations. Here, we use the nearsighted-force training approach that allows us to make high-fidelity machine-learned predictions on large nanoparticles with >5,000 atoms using only small and systematically generated training structures ranging from 38–168 atoms. The resulting ensemble model shows good accuracy and transferability in describing the relative energetics for Co–Pt nanoparticles with various shapes, sizes and Co compositions. It is found that the fcc(100) surface is more likely to form a L1₀ ordered structure than the fcc(111) surface. The energy convex hull of the icosahedron shows the most stable particles have Pt-rich skins and Co-rich underlayers, and is in quantitative agreement with one constructed by brute-force first-principles calculations. Although the truncated octahedron is the most stable shape across all sizes of Pt nanoparticles, a crossover to icosahedron exists due to a large downshift of surface energy for CoPt nanoparticle alloys. The downshift can be attributed to strain release on the icosahedron surface due to Co alloying. We introduced a simple empirical model to describe the role of Co alloying in the crossover for Co–Pt nanoparticles. With Monte-Carlo simulations we additionally searched for the most stable atomic arrangement for a truncated octahedron with equal Pt and Co compositions, and also we studied its order-disorder phase transition. We validated the most stable configurations with a new highly scalable density functional theory code called SPARC. From the outermost shell to the center of a large Co–Pt truncated octahedron, the atomic arrangement follows a pattern: Pt → Co → L1₂(Pt₃Co) → L1₂(PtCo₃) → L1₀(PtCo) → ⋯ → L1₀(PtCo). Lastly, the order-disorder phase transition for a Co–Pt nanoparticle exhibits a lower transition temperature and a smoother transition, compared to the bulk Co–Pt alloy.

Keywords: Co–Pt nanoparticles, Nearsighted force training, Global optimization, Morphology crossover, Order-disorder transition

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1 Introduction

Bimetallic nanostructures have received increasing attention in the past two decades [1–3]. Among the family of bimetallic nanostructures, Co–Pt nanoparticles have a wide range of applications in heterogeneous catalysis and magnetic storage [4–7]. Moreover, Co–Pt nanoparticles have been commercialized in electric vehicles such as Toyota Mirai [8, 9]. The size, composition, shape, and orderliness of Co–Pt nanoparticles all play a pivotal role in controlling the structure and hence the chemical and physical properties. For example, the magnetic and optical properties are closely associated to the orderliness of the structure [10, 11]. Li et al have shown that a core-shell Co–Pt nanoparticle with an ordered core loses fewer Co atoms than that with a random core [4]. Yang et al used Monte-Carlo simulations to reveal that disordering is initiated at the surface due to the reduced coordination, hence lowering the ordering temperature [12]. Muller and Albe pointed out that surface segregation of one element can have a large impact on the ordering [13]. Alroyeau et al showed in both experiments and simulations that the shape and size affect the order–disorder transition, indicating that a larger nanoparticle tends to show a higher transition temperature and the size effect is uniquely determined by the smallest length of a nanoparticle [14]. Alroyeau’s large-scale simulation was based on tight-binding potentials fitted to experimental and first-principles calculations, and the most stable structure for an equal-composition nanoparticle was identified to be a fully L₁₀ ordered truncated octahedron [14]. However, first-principles calculations by Gruner et al suggested that the most stable shape of a Co–Pt nanoparticle at small sizes is not the L₁₀ ordered regular truncated octahedron, but a multiply twinned icosahedron. Therefore, there is a discrepancy between the *ab initio* calculations and well-parameterized empirical models.

The above discrepancy points to another important question for nanoparticle design: pure Pt nanoparticles are normally stable in the single crystal structure, such as truncated octahedron, whereas Pt alloy nanoparticles can exist in the multiply-twinned structures such as icosahedron [15–18], although the shape of Pt nanoparticles can be controlled by capping materials [19]. It is thus crucial to understand the characteristics of structure motifs, such as icosahedron and octahedron. The icosahedron structure is created by packing twenty tetrahedra sharing a common vertex, leading to a close-packed surface but distorted tetrahedra. The distorted structure experiences a high-internal strain while displaying a lower surface energy [20]. Thus icosahedron is normally more stable at small sizes, where the surface energy prevails over the volume contribution [21]. In contrast, the octahedron structure preserves the bulk lattice symmetry and it is directly obtained by cutting a single crystal. The normal octahedron only has fcc(111) facets. To lower the total energy, truncated octahedron is a more reasonable structure motif [22], which presents no internal strain but a higher surface energy. That is why truncated octahedron is more stable at larger sizes [23]. The trade-off between surface and volume contributions lead to possible crossovers among structural motifs, and a simple empirical thermodynamic model was used to account for this interesting phenomenon [22–25]. Nevertheless, crossovers among various shapes of bimetallic nanoparticles have been barely reported. Zhu et al used an empirical model fitted to density functional theory (DFT) calculated properties to show that alloying of Pd can extend the stability of icosahedron PdAu nanoparticle beyond that of pure Au nanoparticles because of the stress release when two different metals are mixed [26]. Since the empirical potential was fitted to a small number of properties, the prediction accuracy over a large range of different nanoparticle structures is questionable. The crossovers in bimetallic nanoparticles will not be fully understood without reliable interatomic potentials.

Electronic structure calculations based on DFT offer a good compromise between accuracy and computational cost. However, model systems of practically-sized nanoparticles, with sizes of 1,000–10,000 atoms, are notoriously expensive for even single calculations, due to the famous $\mathcal{O}(N^3)$ scaling, where N indicates the system scale, such as the number of electrons, number of atoms or number of basis functions. For nanoparticle structure exploration, the picture is more grim due to the huge combinatorial space that must be explored to describe the range of sizes, crystal structures, facets, and alloy (dis-)ordering that may be encountered. Further, as a magnetic system, Co–Pt particles have an added expense in electronic structure due to the requirement for spin-polarized calculations. These combinations of factors make the rigorous exploration of Co–Pt structure–function relationship out of reach for methods like DFT.

Machine-learned inter-atomic potentials have gained momentum in fitting potential energy surfaces calculated by *ab initio* calculations [27–33]. However, a fundamental problem arises in using atomistic machine learning to perform large-scale simulations: for high-fidelity potentials, the training data should closely resemble the ultimate structures being predicted, and the generation of such training data for nanoparticles can be very costly, as described above. To circumvent this issue, we recently released a “nearsighted force-training” (NFT) [34] approach to generate small-size training data to systematically learn the forces and energies of large structures. In this approach, a bootstrap ensemble [35] (or any other reasonable uncertainty metric) is used to identify the most uncertain atoms in a particular structure. Atomic “chunks” centered on these uncertain atoms are removed, and calculated at large enough size that the central atom’s force can be calculated with fidelity by DFT. Only the force on the central atom is used in the loss function, thus adding targeted data and avoiding noise associated with boundary atoms. We demonstrated that this approach successfully built and relaxed nanoparticles containing up to 1,415 atoms in previous work.

Here we apply the NFT approach to build a robust ensemble model for Co–Pt nanoparticles. Using these well-validated neural network models, we optimize the structures of Co–Pt alloys of simple bulk, fcc(111) surfaces, fcc(100) surfaces, icosahedron and octahedron nanoparticles of various sizes and compositions. Moreover, we aim to address a number of key problems regarding the thermodynamic stability of Co–Pt nanoparticles, including the crossover among Pt and Co–Pt structure motifs, the most stable atomic arrangement of a Co–Pt truncated octahedron, and the order–disorder phase transition of Co–Pt truncated octahedron.

2 Methods

2.1 Training data

The training data were found by a nearsighted force-training approach, as briefly described in the Introduction and fully in Zeng et al. [34]. Note that unlike in the prior publication, in this work we deal with a magnetic system. The underlying assumption for NFT to be applicable for magnetic systems is that the ground-state spin states have a unique mapping from atomic positions to spin states (or magnetic moments) which also display a strong locality. In general, forces may depend on the initial guess of magnetic moments, since a poor initial guess may lead to a different local-minimum spin configuration. Thus, we have used a consistent initial-guess strategy for all calculations, with an initial magnetic moment of $0 \mu_B$ for Pt atoms and $2.1 \mu_B$ for Co atoms.

A cutoff of 8 Å was used to carve out atomic chunks; that is, when an uncertain atom was

extracted, all neighbors within 8 Å were used in the small-scale DFT calculation to find the central force. We focus on a variety of octahedron and icosahedron nanoparticles and we performed structure optimization on these representative structures, aiming to find atomic chunks representing diverse local chemical environments that are unique and informative for potential energy surfaces of Co–Pt nanoparticles. The icosahedron nanoparticles include Pt_{1415} , fully disordered $\text{Pt}_{736}\text{Co}_{679}$, $\text{CoPt}/2\text{Pt}$ core-shell with a disordered core ($\text{Pt}_{1150}\text{Co}_{265}$), $\text{CoPt}/1\text{Pt}$ core-shell with a disordered core ($\text{Pt}_{3092}\text{Co}_{1991}$), and $\text{CoPt}/2\text{Pt}$ core-shell with a disordered core ($\text{Pt}_{3694}\text{Co}_{1389}$). The cuboctahedron nanoparticles include $\text{Pt}_{192}\text{Co}_{68}$ with a disordered core, a Pt_{1415} , a core-shell CoPt/Pt cluster $\text{Pt}_{975}\text{Co}_{440}$ with a disordered core, a fully L1_0 ordered Co–Pt cluster $\text{Pt}_{736}\text{Co}_{679}$ and a fully disordered Co–Pt cluster $\text{Pt}_{736}\text{Co}_{679}$. In total, 2064 atomic “chunks” in sizes from 38 to 168 atoms were extracted from those nanoparticles. Adding the 18 bulk cells, we have 2082 training images. We trained a force ensemble model and an energy ensemble model on these 2082 images. For brevity, the force ensemble model and energy ensemble model will be denoted as force model and energy model, respectively. The force model was trained on forces of central atoms of atomic chunks and on both energy and forces of bulk cells. The energy model was trained on only total energies of the bulk cells and atomic chunks. The configurations of the cuboctahedron and icosahedron nanoparticles and the corresponding average atomic uncertainties of forces are presented in the supporting information (SI). The statistics of those generated atomic chunks are discussed in the SI, including the distributions of forces on the central atom, number of atoms, force prediction residuals and energy prediction residuals. The nanoparticle trajectories, training images (atomic chunks), force and energy ensemble models are included as supporting datasets.

2.2 Procedure for generating chunks in the NFT approach

All atomic “chunks” were generated in an iterative and sequential manner by gradually lowering overall prediction uncertainties of the force model on small to large nanoparticles. All active learning procedure is terminated if either criteria is met: the target uncertainty (e.g. structure uncertainty for a NFT procedure on one structure or trajectory uncertainty for structure optimization) is below the convergence criterion, the number of retraining steps exceeds a pre-defined number, or the target uncertainty has not been lowered for two continuous steps. We primed the procedure by obtaining an initial ensemble model trained on forces and energies of 18 Co–Pt bulk structures sampled following the initialization procedure implemented in Zeng et al. [34] Then we performed an NFT active learning on a “rattled” cuboctahedron $\text{Pt}_{192}\text{Co}_{68}$ This procedure was terminated after 9 NFT steps because the structure uncertainty did not improve for two consecutive steps. Till then, we carved out 225 unique atomic “chunks”, and the lowest structure uncertainty was 0.51 eV/Å. We trained a force model on the bulk cells and the selected atomic “chunks”. Next, we carried out an active learning for the structure optimization of the $\text{Pt}_{192}\text{Co}_{68}$ until a termination criterion was satisfied. We continued the active learning for structure optimization for a larger nanoparticle until we had included all the nanoparticles mentioned in the above section.

2.3 ML models

Either force model or energy model is a bootstrap ensemble of 10-member neural network models. We took a bootstrap approach to sample the training images for each neural network model, details

of which can be found in the work by Peterson et al. [35] Ensemble averages were used as the predictions for both energy and forces. Atomic uncertainties were proportional to standard deviations of the ensemble force predictions, as used in Zeng et al. [34] Each member of neural network models is a Behler-Parrinello type. [27] Neural network models were constructed using an open-source atomistic machine learning package (AMP) developed in our group. [36] Fast force and energy inferences were carried out with n2p2, which is mainly developed by Singraber et al. [37] Fast fingerprinting was performed with SIMPLE-NN implemented with AMP-Torch. [38, 39] Gaussian symmetry functions with a cutoff radius of 6.5 Å were used to encode the local chemical environments. For the feature vector of Co elements, it consists of 12 G2 and 8 G4 symmetry functions, where Pt feature vector comprises 13 G2 and 7 G4 symmetry functions. Full details of the symmetry functions are included in the supporting data set in the JSON format. 3000 epochs were used for training. A simple structure of (20, 5, 5, 1) was employed for the neural network topology to mitigate overfitting. A L₂ regularization ($L_2 = 0.001$) was used to avoid large atomic neural network weights, hence alleviating the overfitting.

2.4 Computational settings of DFT calculations

DFT calculations for bulk, atomic chunks and 201-atom nanoparticles were carried out with the Grid-based projector-augmented wave code (GPAW) [40]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with a plane wave cutoff of 350 eV was used [41]. To achieve a fast convergence, a Fermi-Dirac smearing of 0.1 eV was utilized and the energetics were extrapolated to 0 K. Calculations for atomic chunks were sampled at the Γ -point of the Brillouin zone, where calculations for bulk cells used a k-point grid of $12 \times 12 \times 12$. For atomic structures including Co, spin polarization was included. Otherwise, the calculations were spin-paired. The lattice constant of bulk Pt was found to be 3.936 Å. Atomic chunks were placed in a non-periodic box where the shortest distance to the box wall is at least 5 Å. Structure optimizations used a MDMIn algorithm until the maximum atomic force was not larger than 0.05 eV/Å. Self-consistent field (SCF) calculations were considered to be converged when the energy difference between the last three steps is less than 0.0001 eV/electron.

DFT calculations of the 586-atom particles were done using the highly parallel “Simulation Package for Ab-initio Real-space Calculations” (SPARC) code. [42–44] To the best of our knowledge, this calculation represents the largest size of Co–Pt nanoparticles that has ever been studied directly with DFT. A mesh spacing of 0.13 Å (0.25 Bohr radii) was used in a Gamma-point calculation with the PBE functional and the PseudoDojo pseudopotentials [45], and all calculations were run until the energy converged to within 2.7×10^{-4} eV/atom (1×10^{-5} Ha/atom). Atomic forces were computed and compared with GPAW results for smaller systems, confirming that the mean absolute force error between codes is below 0.025 eV/Å for all systems tested (see Figure S3 in the SI). Particles were surrounded by 3.5 Angstrom of vacuum in each direction with Dirichlet boundary conditions in all directions.

2.5 Genetic algorithms

We aimed to explore a wide range of the potential energy surface with an emphasis on structures of nanoparticles in various shapes. We were particularly interested in the global minima for a given shape, size and alloy composition. However, searching global minima (GM) using a brute-force

approach is computationally prohibitive. For example, if we consider a small fixed-shape 147-atom nanoparticle with 73 Co and 74 Pt atoms, the number of possible atomic arrangement is already as large as $147!/(73! \times 74!) \approx 10^{44}$. Although symmetry can reduce the complexity, attempting to exhaust the search space is inaccessible, especially for large nanoparticles in the size of thousands of atoms. Instead, we seek advanced global optimization techniques such as genetic algorithms (GA) and Monte-Carlo simulations. GA, inspired from evolutionary theory, has become popular in the past two decades for optimizing structures. [46–50] The GA was performed on both Co–Pt surfaces and a type of Co–Pt icosahedron to construct energy convex hulls. The GA was set up with the atomic simulation environment (ASE) [51] using the ML models based on the procedure implemented by Lysgaard et al [49] and Bossche et al [50]. Our GA used a rigid structure; that is, all derived structures are not allowed to relax. The structural relaxation is only performed afterwards if needed. To make comparisons between different compositions, we define the negation of the mixing energy $E_f(Pt_xCo_y)$ of a structure Pt_xCo_y as the fitness score to propagate the GA algorithm:

$$E_f(Pt_xCo_y) = \overline{E}(Pt_xCo_y) - \frac{x}{x+y}\overline{E}(Pt_{x+y}) - \frac{y}{x+y}\overline{E}(Co_{x+y}) \quad (1)$$

where $\overline{E}(Pt_xCo_y)$, $\overline{E}(Pt_{x+y})$, and $\overline{E}(Co_{x+y})$ denote the ML model calculated per-atom energies of the corresponding structures. We first studied fcc(111) and fcc(100) surfaces. For the fcc(111) and fcc(100) surfaces, we used a $4 \times 4 \times 5$ supercell in size of 80 atoms with 13 Å separation between slabs in the direction orthogonal to the surface. The initial generation was populated with 120 surfaces using randomly chosen compositions. The lattice constants of pure Co and Pt slabs were determined by the force model, and for the mixed slabs, the lattice constant is linearly interpolated based on Vegard’s law. We used three ASE operators to create the next generation. “CutSplice-Crossover”, as introduced by Deaven and Ho [46], takes two parent structures, then cuts them in a random plane and combine the halves from two parent slabs together to form an offspring. The second operator “RandomSlabPermutation” was used to randomly permute two atoms of different types. The last “RandomCompositionMutation” changes the composition of the slab by mutating one element to the other. The probability of the above three operators are respectively 0.6, 0.2, and 0.2. In addition, we used a variable function named “RankFitnessPopulation” to uphold the composition diversity at each generation so that optimization is on a full range of compositions. The GA was run for 100 generations.

The GA was also used to build the convex hull of a 147-atom PtCo icosahedron nanoparticle. The initial generation was populated with 100 members, and the composition is randomly chosen and lattice constant used was obtained by a linear interpolation. For the icosahedron nanoparticle, we are interested in the fittest Co/Pt composition, hence we do not restrict the algorithm to keep a wide range of compositions in each generation. For the nanoparticles, four types of operations were utilized to create the offspring, including “CutSpliceCrossover”, “RandomSlabPermutation”, “MirrorMutation” (To mirror half of the cluster in a randomly oriented cutting plane while discarding the other half) and “SymmetricSubstite” (To permute all atoms within a shell of the symmetric particle), and the corresponding operation probabilities are 3/6, 1/6, 1/6, 1/6, respectively. The GA was also run for 100 generations. After the GA runs were completed, we chose to study structures after 80th generation. We pinpointed the Co–Pt icosahedron with the most negative formation energy, which is named as the fittest Co–Pt icosahedron. We calculated the c_{Pt} of the fittest structure, and we selected structures whose mole fractions of Pt are close to the fittest one based on

a Gaussian function. In total, 232 Co–Pt icosahedron nanoparticles were selected, and energetics of their relaxed structures were used to construct the energy convex hull for the 147-atom Co–Pt icosahedra.

2.6 Monte Carlo simulations

Previous works suggest that GA was more efficient to search at a wide range of compositions, whereas for a structure with a fixed composition, Monte Carlo (MC) simulations were found to be more effective [12,13,52]. All MC calculations were conducted in the canonical ensemble. At each elementary MC step, two neighboring atoms are exchanged and the energy change is calculated for this exchange. The new structure is then accepted if the energy change is negative, or it is accepted based on the Boltzmann probability if the energy change is positive. The number of MC steps has been determined in a way that on average at least 40 times of swap were performed for each atom in the structure. We used MC simulations to find the putative global minima of TOh $\text{Pt}_{96}\text{Co}_{105}$ and $\text{Pt}_{300}\text{Co}_{286}$, and we compared them to the fully L1_0 ordered counterpart at full DFT levels of theory. We also used MC simulations to study the order–disorder phase transitions for Co–Pt bulk and nanoparticles with nearly equal compositions of Co and Pt. For each MC trajectory at a given temperature, the order parameter was calculated as the average over configurations after a burn-in period.

3 Results & Discussion

The key objective of this study is to train robust machine learning models that can predict stable structures of nanoparticles and can also distinguish the phase stability of nanoparticles with various shapes and atomic arrangements.

3.1 Validation of ML predictions

Before describing the phase stability findings of this study, we first validated our ML models by a comparison with *ab initio* calculations. Gruner et al used first-principles calculations to compare the energetics of a dozen structural motifs for Fe–Pt and Co–Pt alloy nanoparticles in reference to an L1_0 ordered cuboctahedron [53]. Since the current work focuses on the Co–Pt nanoparticle, we created some 561-atom nanoparticles for $\text{Pt}_{296}\text{Co}_{265}$ that are either identical or close in atomic arrangements to those used in Gruner’s *ab initio* calculations. The nanoparticles included a L1_0 ordered cuboctahedron, disordered icosahedron, icosahedron with alternating Co and Pt shells and core–shell icosahedron with a Co-rich second shell. We relaxed those structures with the force model and then we calculated the energetics with the energy model. One should note different randomness may play a negligible role in the energetics because only a small fraction of atoms are randomly positioned. Another thing to note is that the work of Gruner et al used a smaller cutoff (268 eV) than the one (350 eV) used for DFT calculations on atomic chunks. The comparison between ML predictions and *ab initio* calculations by Gruner et al is shown in the Figure. 1. One can see a very good agreement for both cubocahedron and icosahedron nanoparticles, and the overall order for all structures presented is exactly captured by the ML models. In addition, we compared the energy difference between a ML-relaxed 147-atom Pt icosahedron and cubocahedron to that

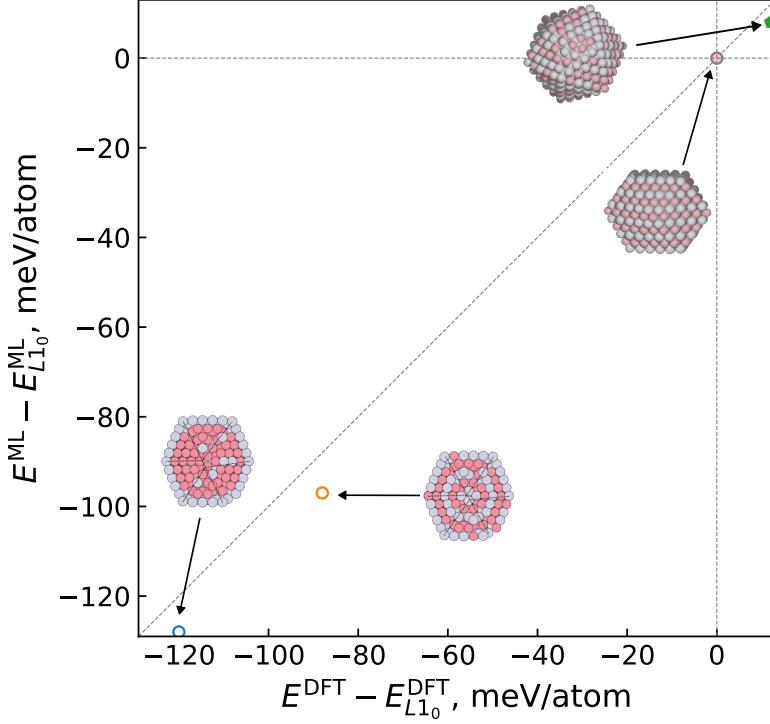


Figure 1: Energetics of $\text{Pt}_{296}\text{Co}_{265}$ nanoparticles in various shapes in reference to the L1_0 ordered cuboctahedron: ML predictions versus DFT calculations by Gruner et al [53]. The DFT calculations used a smaller cutoff (268 eV) compared to 350 eV used to obtain the training data for ML models.

obtained by DFT calculations. Although the exact energetics for each shape differs by up to 2–4 eV (13.6–27.2 meV/atom) between ML predictions and DFT calculations, the relative energy difference between those two shapes is much closer; Pt icosahedron is more stable than Pt cuboctahedron by 1.03 eV (7 meV/atom) using ML models versus 1.27 eV (8.6 meV/atom) using DFT calculations. It suggests that the ML models are able to distinguish the thermodynamic stability across various shapes of nanoparticles, and different atomic arrangements for a given shape.

3.2 Energy convex hull of Co–Pt surfaces and nanoparticles

We first examined the formation energy of two ordered bulk alloys, PtCo and Pt_3Co . The formation energy for PtCo and Pt_3Co are -0.24 and -0.14 eV/atom, respectively, close to values by experiments and empirical potentials [11, 54]. As a comparison, the DFT-calculated formation energies for PtCo and Pt_3Co are respective -0.10 and -0.06 eV/atom. It indicates that Co and Pt atoms have a strong tendency of being mixed.

To gain insights into atomic arrangement of a Co–Pt surface, we built energy convex hulls for 5-layer Co–Pt fcc(100) and fcc(111) surfaces using the neural-network-enhanced GA. Figure 2(a) shows the energy convex hull for fcc(100), where c_{Pt} represents the mole fraction of Pt atoms. We extracted the fittest fcc(100) surface with the lowest formation energy, and its composition is around $c_{\text{Pt}} = 0.6$. Side view of the global minima implies that it is an L1_0 ordered structure, forming alternating Pt and Co layers with the outermost layer being Pt. In addition, the convex

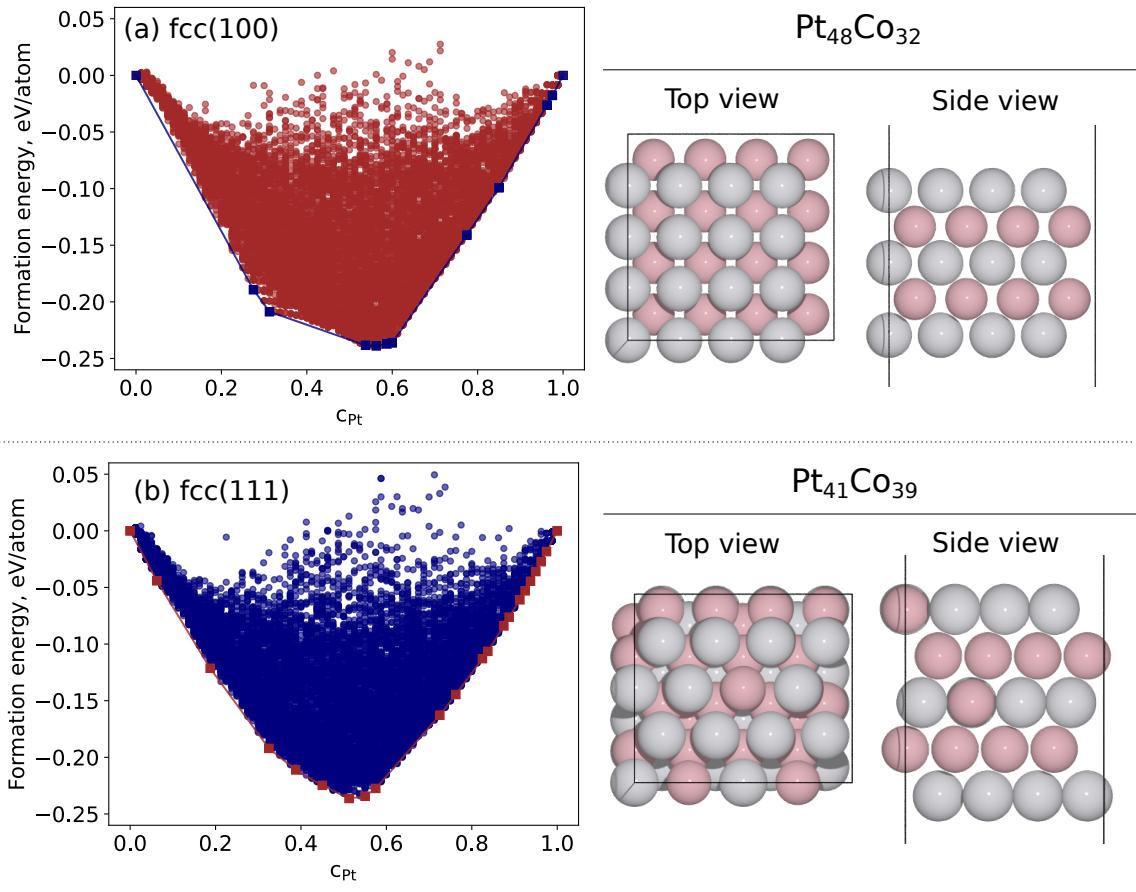


Figure 2: Energy convex hulls of fcc(100) (a) and fcc(111) (b) surface PtCo alloys as a function of Pt compositions. Solid squares are the stable structures and circles refer to unstable structures. Top and side views of the fittest configurations are shown on the right.

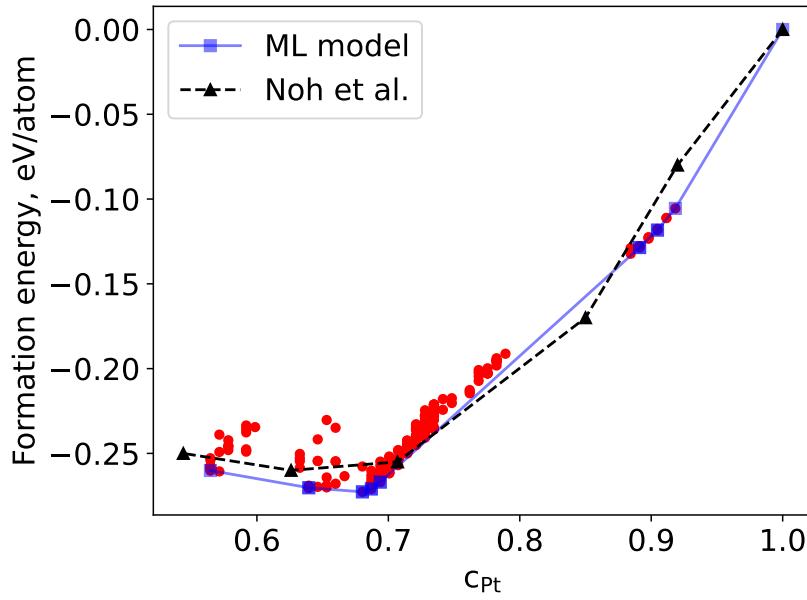


Figure 3: Energy convex hull of a 147-atom Co–Pt Ih as a function of Pt compositions. Solid squares are the stable structures found by ML models, and circles refer to unstable structures of ML predictions. Up-triangles refer to the stable structures excerpted from Noh et al [55].

hull of fcc(100) is not symmetric, and it experiences a sharp change at $c_{\text{Pt}} = 0.3$. The structure at $c_{\text{Pt}} = 0.8$ is close to L1₂ ordered, which suggests the atomic arrangement in a fcc(100) surface is inclined to form an ordered structure. We anticipate that compositions of stable structures may change if we increase thickness of the surface where bulk contributions become more dominant (e.g., global minima closer to 0.5 for an infinitely thick surface). Yet, atomic arrangement patterns, in particular near surfaces, should hold for thicker surfaces.

In comparison, the convex hull of fcc(111) surface alloys is much smoother, representing more flexibility in atomic arrangements in this more closely-packed facet. In terms of the fittest configuration Pt₄₁Co₃₉, the general trend still holds that Pt tends to segregate at the surface while being depleted at the subsurface. A small amount of Co shows up at the surface, although Co–Co direct connections are prohibited. In brief, the main features of atomic arrangements for both fcc(100) and fcc(111) surfaces are a surface Pt layer and a subsurface Co layer. Besides, the fcc(100) surface is more likely to form an ordered structure than the fcc(111) surface.

Next we turned to build the convex hull of a 147-atom Co–Pt icosahedron. The convex hull in Figure 3 shows the formation energy of 147-atom Co–Pt icosahedra as a function of mole fractions of Pt atoms, centered on the Pt-rich region where the global minimum lies. Results of Noh et al [55] are also included for comparison. The trend of formation energy versus composition demonstrates that the ML-predicted convex hull agrees very well with the *ab initio* results. The prediction discrepancy of formation energies is less than 0.03 eV/atom across the composition range shown in Figure 3. The discrepancy is probably due to the insufficiency of training data, which can be improved by adding additional atomic chunks extracted from uncertain 147-atom Co–Pt icosahedra—we do not seek such an improvement as it takes many additional DFT computations

and as demonstrated, the prediction accuracy for Co–Pt structures in this work is satisfactory.

On the Pt-rich side (decreasing from $c_{\text{Pt}} = 1$), the formation energy rapidly drops with the addition of Co. In contrast, there exists a wide flat region ($0.5 \leq c_{\text{Pt}} \leq 0.7$) where either addition or removal of Co atoms barely changes the formation energy. Moreover, the most significant feature is shared between ML-predicted and DFT-calculated global minima; that is, a Pt skin forms on the surface and an inner Co-rich layer is attached directly to the Pt skin. Among eight stable Co–Pt icosahedra found by ML models in Figure 3, seven structures are covered by a full Pt skin except the one at $c_{\text{Pt}} = 0.56$, where the Pt percentage on the skin is 78%. The average Co composition of the second shell is 0.74.

It is well-known in fuel-cell catalysis that Pt–Co alloyed catalysts exhibit a platinum skin, the compression on which increases the catalyst’s activity. This skin is generally considered to be formed by dealloying of the cobalt under electrochemical conditions, due to the difference in electrodeposition potential between Co and Pt. However, these results show that Pt is also thermodynamically most stable on the surface, for a fixed Pt:Co composition, adding to the stability of these catalysts.

On the left side of convex hull, the ML model identifies a stable structure with composition $\text{Pt}_{83}\text{Co}_{64}$, where Co atoms on the surface occupy the center of fcc(111) surfaces. In this same region, the DFT calculations show a structure with composition $\text{Pt}_{80}\text{Co}_{67}$, where Co atoms on the surface sit at the corners. To validate whether the center occupancy represents a stable atomic arrangement, we constructed icosahedron structures with stoichiometry $\text{Pt}_{80}\text{Co}_{67}$ where surface Co atoms occupy both types of sites, and compared the energies with both DFT and ML calculators. In both cases, the corner occupancy was predicted to be more favorable, with DFT energies showing a difference of ~ 14 meV/atom, which indicates that the terrace center occupancy is a low-energy state as well. However, this configuration is not captured in the DFT calculations by Noh et al [55]. The configurations of two types of $\text{Pt}_{80}\text{Co}_{67}$, together with their ML and DFT energies, are provided in the SI. Since both calculators correctly show the corner site to have lower energy, this indicates that the two calculators captured different structures purely by the stochasticity of the genetic algorithm itself, and not due to an issue with the ML fidelity.

3.3 Crossovers among morphology in Pt and Co–Pt nanoparticles

The predictions based on the GA runs further demonstrate the accuracy and transferability of the ML models. We decided to study the crossover among morphology in Pt and Co–Pt nanoparticles, aiming to provide physical insights into the distinct crossover behavior of Co–Pt nanoparticles. The crossover between different shapes of Pt nanoparticles has been extensively investigated based on well-parameterized empirical potentials [22,23,56]. Those studies were established on an empirical thermodynamic model, dividing the total potential energy (U) of a nanoparticle in a specific shape into the contributions of volume, surface and edges, which reads as:

$$\frac{U}{N} = A + BN^{-1/3} + CN^{-2/3} \quad (2)$$

where N is the total number of atoms, A corresponds to the volume contribution, B describes the surface contribution and C is related to the edge contribution; these parameters will differ with nanoparticle shape. As N increases, the edge contribution becomes less important, hence it can be dropped for large-size nanoparticles. However, discrepancy exists even for the crossover of

pure Pt nanoparticles. For example, Uppenbrink et al used Sutton–Chen potential to conclude that the crossover between icosahedron and cuboctahedron occurs at around a size of 550 atoms for either pure Au or Pt nanoparticles, and a decahedron is found in a narrow range of sizes [22]. In contrast, Baletto et al used a different empirical potential to conclude that the crossover between icosahedron and regular truncated octahedron should occur in a small size (< 100 atoms) and decahedra can exist in a wider range of sizes [23]. For simulations on small-size Pt nanoparticles, either cuboctahedron or regular truncated octahedron has been used in previous works [14, 18, 57]. Although controlling experimental conditions can open up possibilities for a variety of shapes of pure Pt nanoparticles, it is well acknowledged that multiply-twinned structures rarely form [16]. In order to clear those uncertainties, we used the well-validated ML models to predict energetics of typical structure motifs of Pt nanoparticles, including seven cuboctahedron, five truncated octahedron, and seven icosahedron nanoparticles; Decahedron is not considered because it is usually only an intermediate state and it has been barely reported in experiments [16, 58]. We then fit the predicted energetics of each structure type, as a function of numbers of atoms, to a simplified equation (2) dropping the edge contributions, and a crossover exists if the fitted lines intersect at a certain nanoparticle size. The results are shown in Figure 4. From the fit parameters displayed on the plot, one can see that volume contributions of single-crystal cuboctahedron and truncated octahedron are almost identical, while that of icosahedron is larger due to the distorted internal structure. As for the surface contribution, it always remains positive for all structure motifs, with the order of cuboctahedron $>$ icosahedron $>$ truncated octahedron, implying that the surface tends to destabilize the system. It is reasonable that the surface contribution of cuboctahedron is larger than that of icosahedron because more fcc(100) facets are exposed on the cuboctahedron surface compared to all fcc(111) facets on the icosahedron surface. Besides, it was found that the surface contribution of truncated octahedron is lower than icosahedron, probably because the distorted internal structure of icosahedron also has a profound impact on its surface energy (i.e. the icosahedron surface is somehow distorted as well). As a result, there exists a crossover between cuboctahedron and icosahedron, which is estimated to be at $N = 538$, and truncated octahedron is the most stable Pt shape across all sizes. The crossover point between cuboctahedron and icosahedron is in agreement with the result of Uppenbrink et al. [22] To the best of our knowledge, it is the first time that the unique high stability of truncated octahedron is identified, and it explains the observation that truncated octahedron is the structure of pure Pt nanoparticles most frequently found in experiments. [16, 18]

Using a similar logic, we extended this analysis to study the crossover in Co–Pt nanoparticles. Results in Section 3.2 point out that the most outstanding feature of the atomic arrangement for Co–Pt nanoparticles are an outermost Pt skin and a Co-rich second shell. Thus for truncated octahedron and icosahedron, we created Co–Pt structure motifs enforcing the above feature, and with the remaining Co atoms randomly placed in the core. As a comparison, we also included a core-shell CoPt/1Pt cuboctahedron with a L₁₀ ordered core. To account for the Co composition effect on the energetics, we introduced a revised empirical model, as shown in the following equations.

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

where

$$A = x_{\text{Co}}A_{\text{Co}} + (1 - x_{\text{Co}})A_{\text{Pt}} - \alpha x_{\text{Co}}(1 - x_{\text{Co}}) \quad (4)$$

and

$$B = B_0(1 - \kappa x_{\text{Co}}) \quad (5)$$

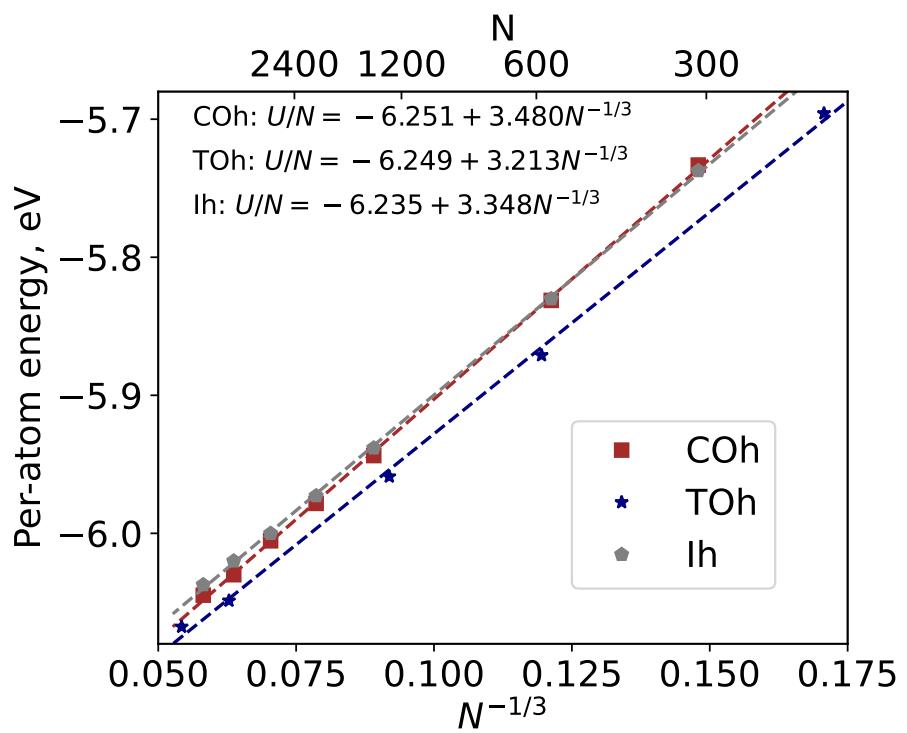


Figure 4: Energies of relaxed structure motifs of Pt nanoparticles, plotted as per-atom energy (U/N) versus $N^{-1/3}$. COh, TOh and Ih represent cuboctahedron, truncated octahedron and icosahedron, respectively.

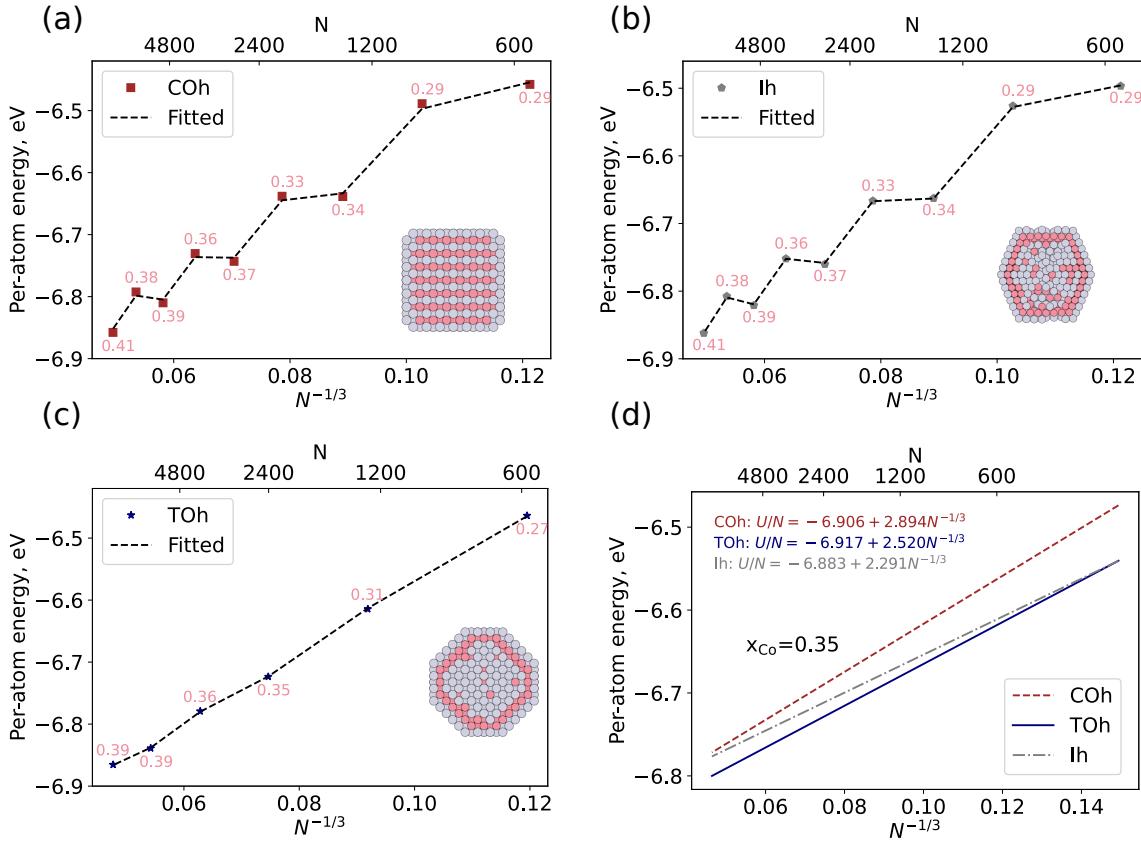


Figure 5: Energies of relaxed structure motifs of Co–Pt nanoparticles, plotted as per-atom energy (U/N) versus $N^{-1/3}$. COh, TOh and Ih represent cuboctahedron, truncated octahedron and icosahedron, respectively. (a) Cuboctahedron, (b) Icosahedron, (c) Truncated octahedron, (d) Fitted results using Eq. 3, at a Co composition of 35%. The Co compositions are indicated by texts next to each data point. The fitted lines are indicated by dash lines. Cross-sectional view of the structure motif for Co–Pt nanoparticles are included as an inset. The number of atoms are presented in the twin axis at the top.

Here, A_{Pt} and B_0 are the respective volume and surface contribution in a Pt nanoparticle, A_{Co} is the cohesive energy of a fcc Co bulk, equivalent to the volume contribution in a pure Co nanoparticle, α describes the mixing of enthalpy, and κ for the reduction of a Pt surface energy due to Co alloying. The ML calculated energetics for cuboctahedron, icosahedron and truncated octahedron are shown in Figure 5(a–c), and the fitted result for each shape is represented by the dashed line. Note that those lines in Figure 5(a–c) are jagged because the Co composition for each data point is not the same, as pointed out the text nearby. Then the fitted results are summarized in Figure 5(d), using a Co composition of 35%. Obviously, Co alloying lowers both volume and surface contributions, suggesting a strong tendency of mixing Co and Pt atoms. But the dependencies differ with Co–Pt nanoparticle shapes.

A crossover between icosahedron and truncated octahedron is observed at a size of around 303 atoms because the addition of Co in the core of icosahedron lowers the surface energy by a much larger magnitude than that of truncated octahedron, even though the difference between volume contribution is enlarged from 0.014 to 0.034 eV. It can be explained by the strain/stress release

on the distorted surface of icosahedron when a smaller element such as Co is introduced into the subsurface and core. Specifically, we define the average local strain for a surface atom i as:

$$\varepsilon_i = \frac{1}{M} \sum_{j \in \text{NN}_i} \frac{d_{ij} - d_{\text{Pt}}}{d_{\text{Pt}}} \quad (6)$$

where d_{ij} is the interatomic distance between atoms i and j , d_{Pt} is the DFT-calculated lattice constant for an optimized bulk Pt (3.936 Å), NN_i represents the summation over the surface neighbors of atom i , and M is the number of surface neighbors. We calculated the average local strains on the terrace fcc(111) sites, denoted as $\bar{\varepsilon}_{\text{T}111}$, for cuboctahedron and icosahedron particles in sizes of 561, 923, 1415, 2057, 2869, 3871 and 5083 atoms with and without Co alloying. The standard deviation of local strains over all nanoparticle sizes is denoted as $\sigma_{\text{T}111}$. $\bar{\varepsilon}_{\text{T}111} \pm \sigma_{\text{T}111}$ for pure Pt cuboctahedron and icosahedron are respectively $-1.321\% \pm 0.176\%$ and $+2.333\% \pm 0.215\%$. Adding the same amount of Co atoms for both Co–Pt cuboctahedron and icosahedron, the $\bar{\varepsilon}_{\text{T}111} \pm \sigma_{\text{T}111}$ changes to $-3.116\% \pm 0.068\%$ and $-1.244\% \pm 0.190\%$, respectively. As a result, the absolute changes of $\bar{\varepsilon}_{\text{T}111}$ for cuboctahedron and icosahedron due to Co alloying are -1.8% and -3.6% , confirming the more significant stress release in icosahedron nanoparticles upon Co alloying. If we increase the Co composition to 40%, we find that the crossover between icosahedron and truncated octahedron is shifted to a larger size of 504 atoms, further extending the range of stability for icosahedron. Nevertheless, the crossover may also depend on the kinetics and experimental conditions, which are not considered in this study. One should also keep in mind that this study is mainly aimed at providing the physical insights for differences in crossover for Pt and Co–Pt nanoparticles, and the structures used to analyze the crossover for Co–Pt alloy systems can probably be further optimized. The method presented here can however be easily extended to more exhaustive searches.

3.4 Order-disorder phase transition in Co–Pt truncated octahedrons

Before discussing the order–disorder phase transition, we need to first investigate the stable structure of a Co–Pt nanoparticle. Two questions should be answered in this regard—first, is the stable structure ordered? Second, if it is ordered, how? The truncated octahedron structure was chosen for this analysis based on the crossover analysis, as it is the most thermodynamically stable shape for large sizes and is also the structure most commonly reported in experiments [4, 16, 59]. First, we performed MC simulations at a temperature of 500 K on particles with composition $\text{Pt}_{300}\text{Co}_{286}$. We picked a structure after more than 58,600 MC steps and we treated it as the putative global minima. We relaxed the structure using the force model, and then we compared the results to the fully $\text{L}1_0$ ordered counterpart with both the ML energy model and with DFT, using the highly-scalable SPARC code. To our knowledge, this DFT calculation on a spin-polarized 586-atom structure represents the largest Co–Pt nanoparticle that has even been directly validated by a full *ab initio* method. The shell-by-shell atomic arrangement of both structures are shown in Figure 6. For the ML-found minimum, an alternating preference for Pt and Co atoms can be seen starting with a Pt-rich surface with the subsurface layer fully occupied by Co. Co atoms on the surface of this structure are more likely to occupy terrace fcc(111) sites and to connect with Pt atoms on the surface, consistent with the previous findings in the GA study. This observation is validated by aforementioned SPARC DFT calculations to prove that $\text{L}1_0$ ordered Co–Pt truncated octahedron alloy is not the most stable structure, but ordered in a different pattern as shown in the configurations in Figure 6(a). The

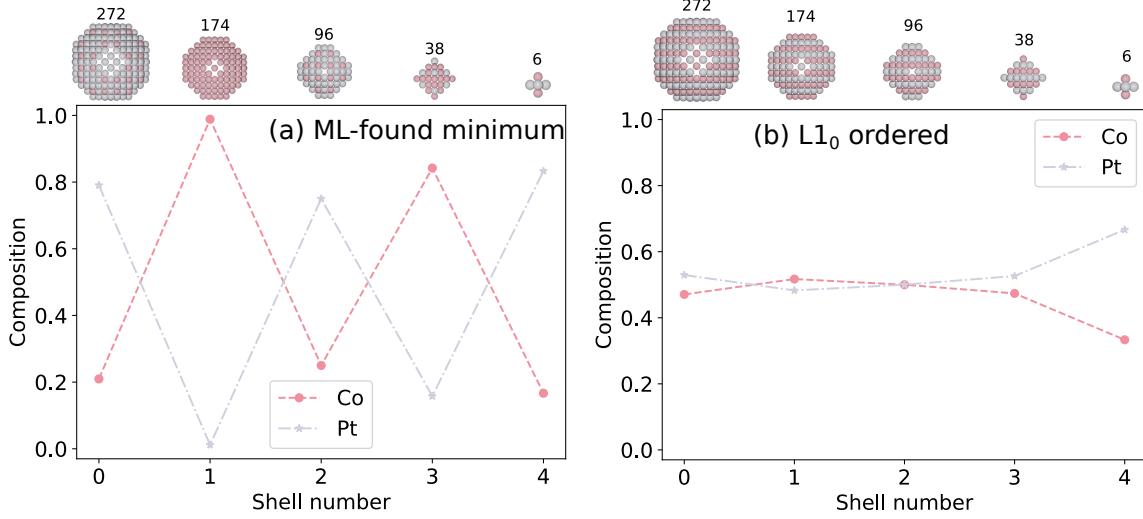
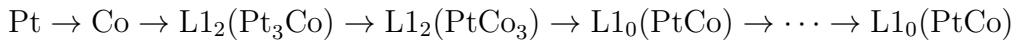


Figure 6: Composition depth profile of a truncated octahedron $\text{Pt}_{300}\text{Co}_{286}$: the putative global minima found by ML models (a), and the fully L1_0 ordered Co–Pt nanoparticle alloy (b). Atomic arrangement at each shell and the total number of atoms are provided at the top.

SPARC DFT calculations suggest that the DFT-calculated energy of the MC structure found by ML models is lower than the L1_0 structure by 0.057 eV/atom. As a comparison, the ML-calculated energy difference is 0.097 eV/atom. Therefore, the relative stability predicted by the ML models is (semi-)quantitatively accurate. The DFT-maximum atomic forces for the ML-found minimum and L1_0 ordered structures are 0.42 and 0.27 eV/ \AA , respectively, which are larger than conventional relaxation criteria but are within ML-predicted maximum atomic uncertainty of forces, 0.43 and 0.42 eV/ \AA , respectively. The larger maximum force for the MC structure indicates that the DFT energy difference is expected to be slightly larger for the DFT fully relaxed structures, hence it is closer to ML predictions. We performed a similar study on a smaller Co–Pt truncated octahedron $\text{Pt}_{96}\text{Co}_{105}$, and the comparison between ML predicted putative minima against the L1_0 one is included in the SI.

We also performed MC simulations at a temperature of 500 K on a much larger nanoparticle with 6266 atoms ($\sim 6 \text{ nm}$). We started with a fully L1_0 ordered structure, and we would like to see where the small thermodynamic fluctuation will lead the structure. We took out a structure after 330,000 MC steps, showing the configuration for each shell in Figure 7. It is clear that that the first four outermost shells changes to a distinct orderliness compared to the almost unchanged L1_0 -like structures going from the 5th shell to the center of the truncated octahedron. The optimized structure for a truncated octahedron with nearly equal compositions of Pt and Co follows a pattern of atomic arrangement as:



Then we carried out a series of MC simulations using the ML model at various temperatures to find the temperature for order–disorder phase transition. We studied the order–disorder phase transition for two structures; one is a 500-atom bulk cell $\text{Pt}_{250}\text{Co}_{250}$ and the other is a 1289-atom truncated octahedron $\text{Pt}_{632}\text{Co}_{657}$. We employed a long-range order (LRO) parameter (Φ) introduced by Cowley [60] to describe the order–disorder transition, and it takes the form of:

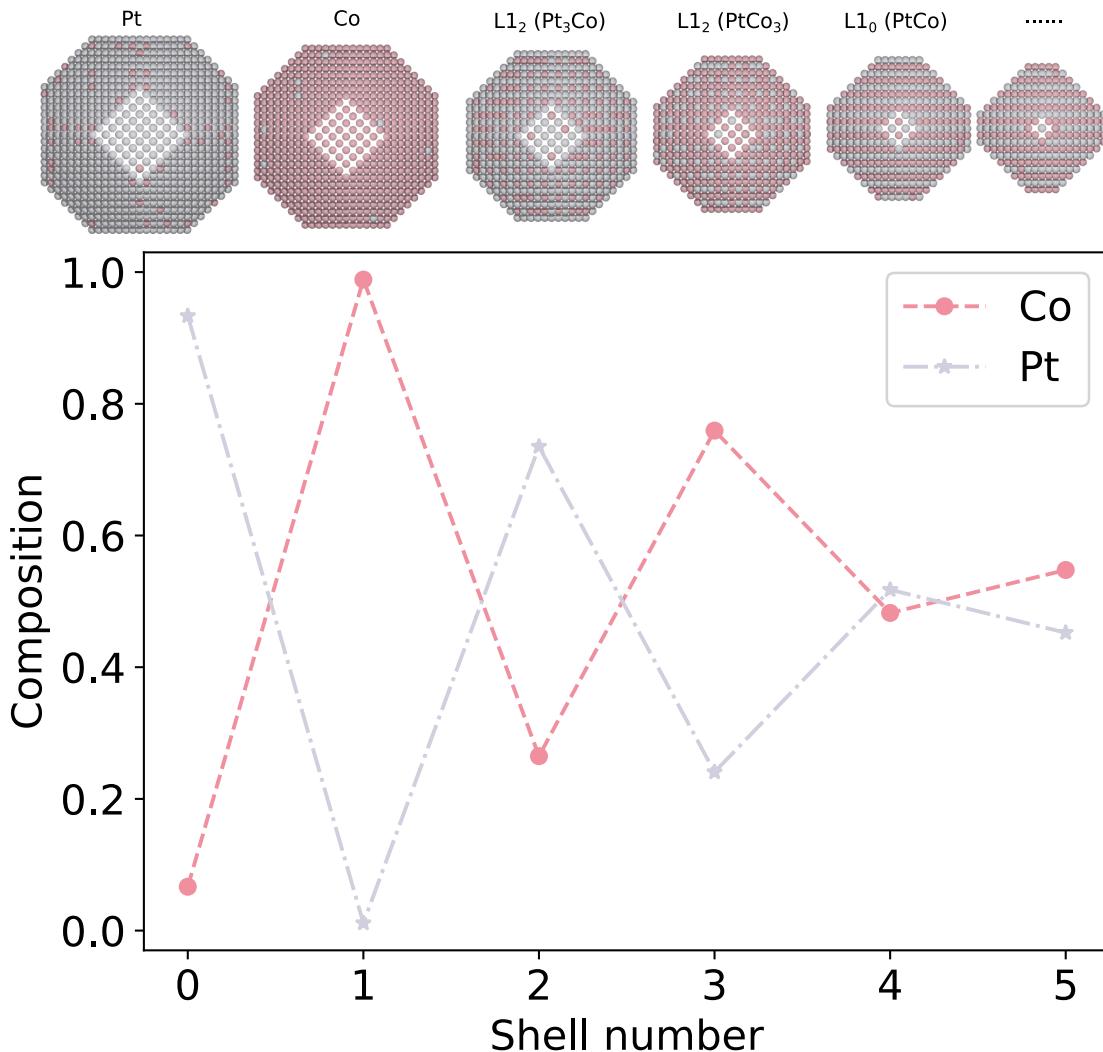


Figure 7: Depth profile of compositions and configurations at each shell for a 6 nm $\text{Co}_{3102}\text{Pt}_{3164}$ optimized by MC simulations.

$$\Phi = \max_{i \in \{x,y,z\}} (\{\Phi_i\}) \quad \text{where } \Phi_i = |p_{A,i} - 1/2| + |p_{B,i} - 1/2| \quad (7)$$

where $p_{A,i}$ and $p_{B,i}$ are the occupation probabilities on each sublattice of the L1₀ phase evaluated in an ordering direction i . As the stable structure of truncated octahedron only exhibits L1₀ ordering from the 5th shell to the center, we only consider those L1₀ ordered shells for the order-disorder transition in the 3.3-nm truncated octahedron nanoparticle. Figure 8 shows the order parameters calculated at various temperatures by MC simulations on a bulk cell and a nanoparticle. The phase transition temperature was estimated to be the point where $\Phi \approx 0.5$. It can be seen that phase transition for a bulk occurs at around 1050°C, overestimating the experimental transition temperature by $\sim 200^\circ\text{C}$ [61, 62]. This large deviation is similar to what has been found by well-validated empirical inter-atomic potentials. [14] The deviation in this work can be due to two possible reasons—one is the insufficient representation of machine learning models for the underlying *ab initio* potential energy surfaces of Co–Pt nanoparticles, and the other one is the intrinsic difference between *ab initio* calculations and experiments. Provided that the *ab initio* potential energy surfaces are not known, the exact origin of this large deviation to experiments cannot be fully understood. Adding more data to further reduce prediction uncertainties may give us a hint, but we elected not to take such an approach since the objectives of this work are to understand basic physics and the trend of transition temperatures for bulk alloy and nanoparticles. For the 1289-atom truncated octahedron, there exists a much smoother transition region where the transition temperature is found to be around 900°C, which is 150°C lower than that of a bulk. The size effect agrees well with experimental observations and simulations in the work of Alloyeau et al [14], in which order-disorder phase transition temperature is lowered by at least 175 °C. This phenomenon can be understood by the surface induced disordering due to the reduced coordination hence an overall lowered order-disorder transition temperature [12].

4 Conclusions

Based on a NFT approach, robust neural network models have been developed for Co–Pt nanoparticles. It demonstrates that the NFT approach is applicable to multi-element metallic magnetic nanoparticles. The resulting neural network models can be easily improved by addressing uncertain local chemical environments when necessary. Using neural-network-enhanced genetic algorithms and Monte Carlo simulations, we have presented a thorough study in optimizing structures of Co–Pt nanoparticles. The models and methods presented/used in this work are general and transferable to other types of multi-element nanoparticles. A number of key findings have been discovered, which not only refine existing understandings of the thermodynamic stability of Co–Pt nanoparticles, but also offer guidelines for the synthesis of nanoparticle catalysts in experiments.

1. Co–Pt fcc(100) surfaces exhibit a strong tendency to form an L1₀ ordered structure featuring alternating Pt and Co layers. Co–Pt fcc(111) surfaces show more flexibility of the atomic arrangement while the major feature is also the alternating layers.
2. The energy convex hull for a 147-atom Co–Pt icosahedron constructed by neural network models is quantitatively accurate compared to brute-force *ab initio* calculations, and a new low-energy atomic arrangement for Pt₈₀Co₆₇ is identified.

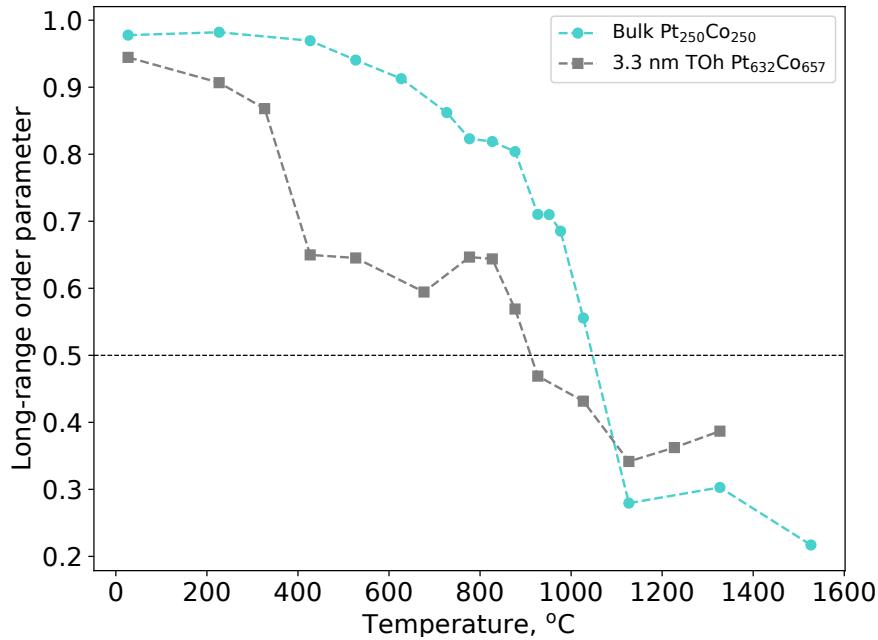


Figure 8: Long-range order parameter for a 500-atom bulk cell and a 1289-atom 3.3 nm truncated octahedron calculated by MC simulations at various temperatures. TOh is short for truncated octahedron.

3. In terms of the crossover among Pt structure motifs, the truncated octahedron is the most stable shape across all sizes because of its low surface and volume energies, and the crossover from icosahedron to cuboctahedron occurs at a size of \sim 538 atoms.
4. A revised empirical model is proposed to study the crossover among structural motifs in Co–Pt nanoparticles. The addition of Co improves the stability of icosahedron, leading to a crossover between icosahedron and truncated octahedron at the size of \sim 343 atoms for a given Co composition of 35%. It can be rationalized by the significant stress release on the distorted fcc(111) surfaces of icosahedron when a smaller element is introduced in the core. Also, the crossover moves to a larger size when more Co atoms are added.
5. MC simulations reveal that the most stable atomic arrangement of a Co–Pt truncated octahedron with nearly equal Co and Pt compositions is not fully L1₀ ordered, as often found by well-parameterized empirical potentials. Instead, it displays a more complex pattern going from the outermost shell to the center of truncated octahedron, which is confirmed by large-scale DFT calculations on SPARC. The outermost shell is Pt segregated, followed by a Pt depleted second shell. The third and fourth shells are L1₂-like structures rich in Pt and Co, respectively. Deeper shells all exhibit L1₀-like atomic arrangement.
6. The order-disorder phase transition for a bulk and nanoparticle has been studied based on a long-range order parameter. Nanoparticles show a lower transition temperature and a much smoother transition compared to a bulk Co–Pt alloy.

SUPPORTING INFORMATION

Representative cuboctahedron and icosahedron structures used to generate the training data (atomic chunks) and the corresponding average atomic uncertainties for the relaxed structures of those full-size nanoparticles (Section I), statistics for the atomic chunks (Section II), validation of force consistency between GPAW and SPARC (Section III), energies and configurations for two Pt₈₀Co₆₇ icosahedra (Section IV), and shell-by-shell compositions and configurations of a Pt₉₆Co₁₀₅ truncated octahedron (Section V) are included in the supporting information.

Data and code availability

Data generated in this work and example scripts are saved in a private repository and will be made available to public after the manuscript is accepted for publication.

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References

- [1] Ristau, R.A.; Barmak, K.; Lewis, L.H.; Coffey, K.R.; Howard, J.K. On the relationship of high coercivity and L10 ordered phase in CoPt and FePt thin films. *Journal of Applied Physics* **1999**; 86, 4527–4533. Publisher: American Institute of Physics.
- [2] Sun, S.; Murray, C.B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **2000**; 287, 1989–1992. Publisher: American Association for the Advancement of Science.
- [3] Ferrando, R.; Jellinek, J.; Johnston, R.L. Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles. *Chemical Reviews* **2008**; 108, 845–910. Publisher: American Chemical Society.
- [4] Li, J.; Sharma, S.; Wei, K.; Chen, Z.; Morris, D.; Lin, H.; Zeng, C.; Chi, M.; Yin, Z.; Muzzio, M.; Shen, M.; Zhang, P.; Peterson, A.A.; Sun, S. Anisotropic Strain Tuning of L10 Ternary Nanoparticles for Oxygen Reduction. *Journal of the American Chemical Society* **2020**; 142, 19209–19216.
- [5] Sun, X.; Huang, Y.; Nikles, D.E. FePt and CoPt magnetic nanoparticles film for future high density data storage media. *International Journal of Nanotechnology* **2004**; 1, 328–346.

- [6] Jun, Y.w.; Choi, J.s.; Cheon, J. Heterostructured magnetic nanoparticles: their versatility and high performance capabilities. *Chemical Communications* **2007**; , 1203–1214.
- [7] Christodoulides, J.A.; Huang, Y.; Zhang, Y.; Hadjipanayis, G.C.; Panagiotopoulos, I.; Niarchos, D. CoPt and FePt thin films for high density recording media. *Journal of Applied Physics* **2000**; 87, 6938–6940.
- [8] Yoshida, T.; Kojima, K. Toyota MIRAI Fuel Cell Vehicle and Progress Toward a Future Hydrogen Society. *The Electrochemical Society Interface* **2015**; 24, 45.
- [9] Wang, C.; Spendelow, J.S. Recent developments in Pt–Co catalysts for proton-exchange membrane fuel cells. *Current Opinion in Electrochemistry* **2021**; 28, 100715.
- [10] Mehaddene, T.; Kentzinger, E.; Hennion, B.; Tanaka, K.; Numakura, H.; Marty, A.; Parasote, V.; Cadeville, M.C.; Zemirli, M.; Pierron-Bohnes, V. Lattice dynamics and migration enthalpies in CoPt₃ and FePd. *Physical Review B* **2004**; 69, 024304. Publisher: American Physical Society.
- [11] Andreazza, P.; Pierron-Bohnes, V.; Tournus, F.; Andreazza-Vignolle, C.; Dupuis, V. Structure and order in cobalt/platinum-type nanoalloys: from thin films to supported clusters. *Surface Science Reports* **2015**; 70, 188–258.
- [12] Yang, B.; Asta, M.; Mryasov, O.N.; Klemmer, T.J.; Chantrell, R.W. The nature of A1–L10 ordering transitions in alloy nanoparticles: A Monte Carlo study. *Acta Materialia* **2006**; 54, 4201–4211.
- [13] Müller, M.; Albe, K. Lattice Monte Carlo simulations of FePt nanoparticles: Influence of size, composition, and surface segregation on order-disorder phenomena. *Physical Review B* **2005**; 72, 094203. Publisher: American Physical Society.
- [14] Alloyeau, D.; Ricolleau, C.; Mottet, C.; Oikawa, T.; Langlois, C.; Le Bouar, Y.; Braidy, N.; Loiseau, A. Size and shape effects on the order–disorder phase transition in CoPt nanoparticles. *Nature Materials* **2009**; 8, 940–946. Number: 12 Publisher: Nature Publishing Group.
- [15] He, D.S.; He, D.; Wang, J.; Lin, Y.; Yin, P.; Hong, X.; Wu, Y.; Li, Y. Ultrathin Icosahedral Pt-Enriched Nanocage with Excellent Oxygen Reduction Reaction Activity. *Journal of the American Chemical Society* **2016**; 138, 1494–1497. Publisher: American Chemical Society.
- [16] Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S.E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angewandte Chemie International Edition* **2009**; 48, 60–103. eprint: <https://onlinelibrary.wiley.com/doi/10.1002/anie.200802248>.
- [17] Wu, J.; Qi, L.; You, H.; Gross, A.; Li, J.; Yang, H. Icosahedral Platinum Alloy Nanocrystals with Enhanced Electrocatalytic Activities. *Journal of the American Chemical Society* **2012**; 134, 11880–11883. Publisher: American Chemical Society.
- [18] Shao, M.; Peles, A.; Shoemaker, K. Electrocatalysis on Platinum Nanoparticles: Particle Size Effect on Oxygen Reduction Reaction Activity. *Nano Letters* **2011**; 11, 3714–3719. Publisher: American Chemical Society.

- [19] Ahmadi, T.S.; Wang, Z.L.; Green, T.C.; Henglein, A.; El-Sayed, M.A. Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles. *Science* **1996**; 272, 1924–1925. Publisher: American Association for the Advancement of Science.
- [20] Mackay, A.L. A dense non-crystallographic packing of equal spheres. *Acta Crystallographica* **1962**; 15, 916–918. eprint: <https://onlinelibrary.wiley.com/doi/10.1107/S0365110X6200239X>.
- [21] Cleveland, C.L.; Landman, U. The energetics and structure of nickel clusters: Size dependence. *The Journal of Chemical Physics* **1991**; 94, 7376–7396. Publisher: American Institute of Physics.
- [22] Uppenbrink, J.; Wales, D.J. Structure and energetics of model metal clusters. *The Journal of Chemical Physics* **1992**; 96, 8520–8534. Publisher: American Institute of Physics.
- [23] Baletto, F.; Ferrando, R.; Fortunelli, A.; Montalenti, F.; Mottet, C. Crossover among structural motifs in transition and noble-metal clusters. *The Journal of Chemical Physics* **2002**; 116, 3856–3863. Publisher: American Institute of Physics.
- [24] Nishioka, K. Thermodynamics of a liquid microcluster. *Physical Review A* **1977**; 16, 2143–2152. Publisher: American Physical Society.
- [25] Northby, J.A.; Xie, J.; Freeman, D.L.; Doll, J.D. Binding energy of large icosahedral and cuboctahedral Lennard-Jones clusters. *Zeitschrift für Physik D Atoms, Molecules and Clusters* **1989**; 12, 69–71.
- [26] Zhu, B.; Guesmi, H.; Creuze, J.; Legrand, B.; Mottet, C. Crossover among structural motifs in Pd–Au nanoalloys. *Physical Chemistry Chemical Physics* **2015**; 17, 28129–28136. Publisher: The Royal Society of Chemistry.
- [27] Behler, J.; Parrinello, M. Generalized Neural-Network Representation of High-Dimensional Potential-Energy Surfaces. *Physical Review Letters* **2007**; 98, 146401.
- [28] Bartók, A.P.; Payne, M.C.; Kondor, R.; Csányi, G. Gaussian Approximation Potentials: the accuracy of quantum mechanics, without the electrons. *Physical Review Letters* **2010**; 104, 136403.
- [29] Rupp, M.; Tkatchenko, A.; Müller, K.R.; von Lilienfeld, O.A. Fast and Accurate Modeling of Molecular Atomization Energies with Machine Learning. *Physical Review Letters* **2012**; 108, 058301.
- [30] Behler, J. Four Generations of High-Dimensional Neural Network Potentials. *Chemical Reviews* **2021**; 121, 10037–10072. Publisher: American Chemical Society.
- [31] Deringer, V.L.; Bartók, A.P.; Bernstein, N.; Wilkins, D.M.; Ceriotti, M.; Csányi, G. Gaussian Process Regression for Materials and Molecules. *Chemical Reviews* **2021**; 121, 10073–10141. Publisher: American Chemical Society.

- [32] Unke, O.T.; Chmiela, S.; Sauceda, H.E.; Gastegger, M.; Poltavsky, I.; Schütt, K.T.; Tkatchenko, A.; Müller, K.R. Machine Learning Force Fields. *Chemical Reviews* **2021**; 121, 10142–10186. Publisher: American Chemical Society.
- [33] Botu, V.; Batra, R.; Chapman, J.; Ramprasad, R. Machine Learning Force Fields: Construction, Validation, and Outlook. *The Journal of Physical Chemistry C* **2017**; 121, 511–522. Publisher: American Chemical Society.
- [34] Zeng, C.; Chen, X.; Peterson, A.A. A nearsighted force-training approach to systematically generate training data for the machine learning of large atomic structures. *The Journal of Chemical Physics* **2022**; 156, 064104. Publisher: American Institute of Physics.
- [35] Peterson, A.A.; Christensen, R.; Khorshidi, A. Addressing uncertainty in atomistic machine learning. *Physical Chemistry Chemical Physics* **2017**; 19, 10978–10985.
- [36] Khorshidi, A.; Peterson, A.A. Amp: A modular approach to machine learning in atomistic simulations. *Computer Physics Communications* **2016**; 207, 310–324.
- [37] Singraber, A.; Behler, J.; Dellago, C. Library-Based LAMMPS Implementation of High-Dimensional Neural Network Potentials. *Journal of Chemical Theory and Computation* **2019**; 15, 1827–1840.
- [38] Lee, K.; Yoo, D.; Jeong, W.; Han, S. SIMPLE-NN: An efficient package for training and executing neural-network interatomic potentials. *Computer Physics Communications* **2019**; 242, 95–103.
- [39] Shuaibi, M.; Lei, X.; Comer, B.; Chen, R.Q.; Musa, E.; Adams, M. AMPtorch: Atomistic Machine Learning Package (AMP) - PyTorch. <https://github.com/ulissigroup/amptorch> **2020**.
- [40] Enkovaara, J.; Rostgaard, C.; Mortensen, J.J.; Chen, J.; Dułak, M.; Ferrighi, L.; Gavnholt, J.; Glinsvad, C.; Haikola, V.; Hansen, H.A.; Kristoffersen, H.H.; Kuisma, M.; Larsen, A.H.; Lehtovaara, L.; Ljungberg, M.; Lopez-Acevedo, O.; Moses, P.G.; J Ojanen; Olsen, T.; Petzold, V.; Romero, N.A.; Stausholm-Møller, J.; Strange, M.; Tritsaris, G.A.; Vanin, M.; Walter, M.; B Hammer; Häkkinen, H.; Madsen, G.K.H.; Nieminen, R.M.; Nørskov, J.K.; Puska, M.; Rantala, T.T.; Schiøtz, J.; Thygesen, K.S.; Jacobsen, K.W. Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method. *Journal of Physics: Condensed Matter* **2010**; 22, 253202.
- [41] Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**; 77, 3865–3868.
- [42] Xu, Q.; Sharma, A.; Comer, B.; Huang, H.; Chow, E.; Medford, A.J.; Pask, J.E.; Suryanarayana, P. SPARC: Simulation Package for Ab-initio Real-space Calculations. *SoftwareX* **2021**; 15, 100709.
- [43] Ghosh, S.; Suryanarayana, P. SPARC: Accurate and efficient finite-difference formulation and parallel implementation of Density Functional Theory: Isolated clusters. *Computer Physics Communications* **2017**; 212, 189–204.

- [44] Ghosh, S.; Suryanarayana, P. SPARC: Accurate and efficient finite-difference formulation and parallel implementation of Density Functional Theory: Extended systems. *Computer Physics Communications* **2017**; 216, 109–125.
- [45] van Setten, M.J.; Giantomassi, M.; Bousquet, E.; Verstraete, M.J.; Hamann, D.R.; Gonze, X.; Rignanese, G.M. The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table. *Computer Physics Communications* **2018**; 226, 39–54.
- [46] Deaven, D.M.; Ho, K.M. Molecular Geometry Optimization with a Genetic Algorithm. *Physical Review Letters* **1995**; 75, 288–291. Publisher: American Physical Society.
- [47] Johnston, R.L. Evolving better nanoparticles: Genetic algorithms for optimising cluster geometries. *Dalton Transactions* **2003**; , 4193–4207 Publisher: The Royal Society of Chemistry.
- [48] Vilhelmsen, L.B.; Hammer, B. Systematic Study of $\{\mathrm{Au}\}_{6}$ to $\{\mathrm{Au}\}_{12}$ Gold Clusters on MgO(100) F Centers Using Density-Functional Theory. *Physical Review Letters* **2012**; 108, 126101.
- [49] Lysgaard, S.; Landis, D.D.; Bligaard, T.; Vegge, T. Genetic Algorithm Procreation Operators for Alloy Nanoparticle Catalysts. *Topics in Catalysis* **2014**; 57, 33–39.
- [50] Van den Bossche, M.; Grönbeck, H.; Hammer, B. Tight-Binding Approximation-Enhanced Global Optimization. *Journal of Chemical Theory and Computation* **2018**; 14, 2797–2807. Publisher: American Chemical Society.
- [51] Hjorth Larsen, A.; Jørgen Mortensen, J.; Blomqvist, J.; Castelli, I.E.; Christensen, R.; Dułak, M.; Friis, J.; Groves, M.N.; Hammer, B.; Hargus, C.; Hermes, E.D.; Jennings, P.C.; Bjerre Jensen, P.; Kermode, J.; Kitchin, J.R.; Leonhard Kolsbjerg, E.; Kubal, J.; Kaasbjerg, K.; Lysgaard, S.; Bergmann Maronsson, J.; Maxson, T.; Olsen, T.; Pastewka, L.; Peterson, A.; Rostgaard, C.; Schiøtz, J.; Schütt, O.; Strange, M.; Thygesen, K.S.; Vegge, T.; Vilhelmsen, L.; Walter, M.; Zeng, Z.; Jacobsen, K.W. The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter* **2017**; 29, 273002.
- [52] Boes, J.R.; Kitchin, J.R. Modeling Segregation on AuPd(111) Surfaces with Density Functional Theory and Monte Carlo Simulations. *The Journal of Physical Chemistry C* **2017**; 121, 3479–3487. Publisher: American Chemical Society.
- [53] Gruner, M.E.; Rollmann, G.; Entel, P.; Farle, M. Multiply Twinned Morphologies of FePt and CoPt Nanoparticles. *Physical Review Letters* **2008**; 100, 087203. Publisher: American Physical Society.
- [54] Oriani, R.; Murphy, W.K. Thermodynamics of ordering alloys—IV heats of formation of some alloys of transition metals. *Acta Metallurgica* **1962**; 10, 879–885.
- [55] Noh, S.H.; Seo, M.H.; Seo, J.K.; Fischer, P.; Han, B. First principles computational study on the electrochemical stability of Pt–Co nanocatalysts. *Nanoscale* **2013**; 5, 8625–8633. Publisher: The Royal Society of Chemistry.

- [56] Baletto, F.; Ferrando, R. Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects. *Reviews of Modern Physics* **2005**; 77, 371–423. Publisher: American Physical Society.
- [57] Tang, L.; Han, B.; Persson, K.; Friesen, C.; He, T.; Sieradzki, K.; Ceder, G. Electrochemical Stability of Nanometer-Scale Pt Particles in Acidic Environments. *Journal of the American Chemical Society* **2010**; 132, 596–600. Publisher: American Chemical Society.
- [58] Wang, X.; Vara, M.; Luo, M.; Huang, H.; Ruditskiy, A.; Park, J.; Bao, S.; Liu, J.; Howe, J.; Chi, M.; Xie, Z.; Xia, Y. Pd@Pt Core–Shell Concave Decahedra: A Class of Catalysts for the Oxygen Reduction Reaction with Enhanced Activity and Durability. *Journal of the American Chemical Society* **2015**; 137, 15036–15042. Publisher: American Chemical Society.
- [59] Li, J.; Sun, S. Intermetallic Nanoparticles: Synthetic Control and Their Enhanced Electrocatalysis. *Accounts of Chemical Research* **2019**; 52, 2015–2025. Publisher: American Chemical Society.
- [60] Cowley, J.M. Short- and Long-Range Order Parameters in Disordered Solid Solutions. *Physical Review* **1960**; 120, 1648–1657. Publisher: American Physical Society.
- [61] Leroux, C.; Cadeville, M.C.; Pierron-Bohnes, V.; Inden, G.; Hinz, F. Comparative investigation of structural and transport properties of L10-NiPt and CoPt phases: the role of magnetism. *Journal of Physics F: Metal Physics* **1988**; 18, 2033–2051. Publisher: IOP Publishing.
- [62] Le Bouar, Y.; Loiseau, A.; Finel, A. Origin of the complex wetting behavior in Co-Pt alloys. *Physical Review B* **2003**; 68, 224203. Publisher: American Physical Society.