RUHR-UNIVERSITÄT BOCHUM

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MATERIALS RESEARCH DEPARTMENT





FOCUS ON: ATOMISTIC SIMULATION

Atomistic simulation builds on fundamental physical laws for the prediction, analysis and design of materials and their properties. Atomistic simulation is universal, applicable across disciplines and a cornerstone of research in materials science, chemistry and biology.

The present newsletter showcases atomistic simulation in the Materials Research Department and highlights the strength and breadth of MRD research in this area.

Like all previous newsletters, this 17th issue is also accessible through the MRD website at www.mrd.rub.de.

Enjoy reading,

Ralf Drautz and Anjana Devi MRD Speakers Anastasiia Petrova and Denisa Voicu MRD Science Managers

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LIQUIDS IN METALLIC NANOCON-FINEMENT

Structure, dynamics and thermodynamics from atomistic simulations

Properties of liquids at interfaces and in confinement are different from those in bulk and are relevant to a series of phenomena of natural and technological interest. Water interfaces are key to atmospheric and geochemical processes, while confined electrolyte solutions and confined ionic liquids (IL) play a crucial role in energy devices. A microscopic, atomistic understanding of solid/liquid interfaces is therefore crucial to advance both our fundamental understating of natural phenomena, as well as to improve technological devices.

 Image: Contract of the state of the sta

Molecular dynamics simulations, at atomistic resolution and at different level of theory, can provide a dynamical picture of interfaces "in operando" and help the microscopic interpretation of experiments.

In this short contribution I would like to highlight some recent work from our group on atomistic simulation of metal/liquid interfaces at the nanoscale. Peculiar to these systems is the role of electronic polarization which needs to be accurately included in the simulations.

We have recently developed a simple method to introduce metal polarization in atomistic simulations, where harmonically coupled core-shell charge pairs are combined to Lennard Jones potentials on each metal atom. Such approach proved accurate in reproducing image charge potentials, compatible with atomistic simulations packages and inexpensive, so it can be used on large scale simulation containing hundred thousands atoms [1].

We have used this approach to investigate IL confined between gold electrode and observed quite some interesting phenomena. For example, we have shown that although structural modifications affect the interfaces only for a couple of nanometers, dynamical properties are instead modified on much longer scale, and e.g. bulk diffusion is only recovered 10 nm away from the gold surface [2]. Simulations also permitted to compute interfacial free energy and to evaluate the impact of the metallic polarization on the shift of the freezing temperature in confinement. Extending the simulation to the non-equilibrium realm, we have also investigat-

ed the impact of shear flow on the same type of systems, finding that the portion of fluid closer to the metal surface behaves as a glassy solid, which extends for a few nanometres. An analysis of friction showed that, thanks to the strong interaction with the surface, the confined IL resists the "squeeze out" and remains in place at higher pressures [3]. We have also shown, for different electrolyte solutions, that the metal polarisation enhances the interfacial capacitance with differences between the cathode and anode, depending on the ion's size and solvation shell structures [4].

To explicitly consider reactivity, a description which also includes the electronic structure is required, as in ab initio molecular dynamics simulations. Electronic structure-based simulations permit to describe chemisorption at interfaces, as well charge transfer, also as function of a variable interfacial potential. In our recent work [5] we used ab initio molecular dynamics simulations in combination with the charge unbalance method to obtain the atomistic structure of the Pt-water double layer in response to an applied potential, in realistic solution conditions. The simulations permitted to evaluate the interface capacitance and the absolute electrode potential for different values of the charge on the electrodes. We showed that the metal polarisation is responsible for interfacial charge transfer and oscillations, which modulate the water coverage at the surface and in turn the interface dipole. Our results pave the way to the development of realistic models for catalytic processes at the Pt-water interface.



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COMPUTATIONAL DISCOVERY AND CHARACTERIZATION OF NEW INORGANIC COMPOUNDS

Unleashing the power of computational high-throughput screening and machine learning

Most of the experimental knowledge painfully accumulated over centuries concerning the crystal structure of (inorganic) materials is nowadays gathered in databases. The most famous of these, the Inorganic Crystal Structure Database (ICSD) contains more than 250000 entries pertaining to around 50000 different compounds. Looking at these 50000 materials, the first question that comes to our mind is if this set is representative of the compounds that we can synthesize in a lab. The answer to this question is probably no. It is true that elementary substances and binary compounds are relatively well studied, but present knowledge of ternary and multinary materials is far less complete. The second pertinent question is if these materials are sufficient for all desired technological applications of materials science. Unfortunately, the answer is certainly no. There are several areas where we do not know any material with the desired properties, or sufficiently good materials are known but are composed of expensive, rare, or toxic elements. For example, we still do not have an industry-grade transparent p-type conductor that would enable completely transparent electronics, or a room-temperature transparent ferromagnet, or a room-temperature superconductor (or even an industry-friendly superconductor at liquid nitrogen temperature).

The endeavor to experimentally synthesize and characterize all possible inorganic phases is a monumental and resource-intensive task. It is for this task that numerical simulations appear as the most cost-effective path to explore the gigantic search space of materials at our disposal. In our group we follow this computational approach to discover new stable inorganic compounds that may be used in energy-related technologies.



Figure 1: Ternary phase diagram of La-W-N, showing the perovskite phase of LaWN₃ we discovered in 2015, Ref. [1].



Figure 2: Diversity of structures obtained in our search of two-dimensional compounds. We found examples that can be built by decorating nearly all Platonic and Archimedean tesselations as well as their dual Laves or Catalan tilings, Ref. [2].

Materials design has gained a game-changing tool with the advent of computational high-throughput screening of large sets of materials. Using efficient and accurate numerical methods, such as density functional theory, promising stable compounds for synthesis can be identified and used as a guideline for experimental efforts. Unfortunately, these calculations are costly from the numerical point of view, which limits the number of materials to be investigated to the tens of thousands. This problem can be circumvented by the use of machine learning methods, that in recent years have drastically accelerated the process of discovering and characterizing new materials. In fact, new developments in neural networks, and in particular crystal-graph neural networks, now allow for speedup-factors of at least two orders of magnitude in the search for new compounds.

Using these techniques, we have constructed databases containing tens of thousands of novel

compounds, some with unique physical properties. An example are nitride perovskites, that we predicted in 2015 [1] and that were synthesized in 2021 with interesting piezoelectric and ferroelectric properties. Another interesting example are two-dimensional systems, where our methodology unveiled an unexpected structural richness. In fact, we could find two-dimensional layers constructed from nearly all Platonic and Archimedean tesselations as well as their dual Laves or Catalan tilings.

The marriage of traditional computational methods and machine learning has opened exciting avenues for materials design, providing us with powerful tools to uncover novel compounds and push the boundaries of what is possible in the realm of materials science. These advances hold great promise for addressing pressing technological challenges and continue to shape the future of materials research.



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ATOMISTIC SIMULATIONS WITH HIGH-DIMENSIONAL NEURAL NETWORK POTENTIALS

Using machine learning in molecular dynamics simulations of complex systems

Today, computer simulations are the key to advances in many fields, from chemistry via physics to materials science, because they can provide important atomic-level information complementing experimental data. The reliability and predictive power of these simulations crucially depend on the quality of the description of the atomic interactions, which determine the properties and reactivity of molecules and materials. While accurate electronic structure methods can in principle provide these interactions directly based on the laws of quantum mechanics, the computational costs of such calculations are prohibitively high and applications are restricted to small systems even when the most powerful supercomputers are used. Simple empirical force fields, on the other hand, have been successfully used for decades to study large systems containing thousands of atoms, but they lack the required accuracy for highly reliable simulations and in some cases can yield even qualitatively incorrect predictions.

Since about two decades we are working on the development of methods to overcome this dilemma by combining modern machine learning algorithms with quantum mechanical electronic structure calculations with the aim to "learn" the atomic interactions, i.e., the shape of the potential energy surface. The resulting machine learning potentials are able to provide the multidimensional potential energy surface, which contains all information about the atomic interactions, at strongly reduced computational costs while the



Figure 1: Simulation of a solid-liquid interface between water and the lithium intercalation compound $LiMn_2O_4$, Ref. [4] (figure courtesy of Nikolas Lausch).

reliability of quantum mechanics is maintained. In this way they allow to perform predictive molecular dynamics simulations beyond the system size that is accessible by conventional ab initio molecular dynamics. An important step in the development of machine learning potentials for complex condensed systems has been our development of high-dimensional neural network potentials in 2007 [1, 2], which can now be termed second-generation machine learning potentials [3]. The key idea of these potentials is to represent the total potential energy of a system as a sum of environment-dependent atomic energies. The local geometric environments need to be transformed to a set of translationally, rotationally and permutationally invariant features that are suitable as input for neural networks. To achieve this goal, we have developed so-called atom-centered symmetry functions [1], which meet all these requirements. However, for some systems also long-range electrostatic interactions beyond the local atomic environments are important, which can be explicitly included in third-generation high-dimensional neural network potentials [3]. Here, the atomic partial charges are learned by atomic neural networks as a function of the chemical environment. In a second step they can then be used to compute the long-range interactions without truncation based on Coulombs law. In the fourth generation of high-dimensional neural network potential, a global charge equilibration step is employed to determine the global charge distribution in the system. This enables the inclusion of non-local phenomena like long-range charge transfer, which is omnipresent in many molecules and materials. Thus, over the years, the capabilities of machine learning potentials, which are now a very active field in the area of atomistic simulations with many different and very accurate methods being constantly proposed, have substantially grown and step by step the complexity of systems, which can be studied with first principles accuracy, has been extended.

Apart from our focus on method development, in our group we have applied high-dimensional neural networks to many different types of systems including materials like silicon, carbon and copper, but also oxides like zinc oxide and metal-organic frameworks. As part of the cluster of excellence RESOLV, we are particularly interested in aqueous systems, like liquid water and electrolyte solutions, but in particular also solid-liquid interfaces, which are of central importance for catalysis and electrochemical energy storage and conversion. An example is the solid-liquid interface of the lithium intercalation compound $LiMn_2O_4$ depicted in Figure 1, which is of interest for catalytic water splitting.

Recently, in November 2022, our group has moved to Ruhr-Universität Bochum, to establish the new Chair for Theoretical Chemistry II as part of the Research Center Chemical Sciences and Sustainability of the Research Alliance Ruhr. We are now looking forward to many fruitful collaborations in the very dynamic and active research environment in the Ruhr area, which offers a plenty of opportunities to further improve and apply our methods.



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PREDICTING ELECTRONIC PROPERTIES OF FUNCTION-AL INTERFACES THROUGH COMPUTATIONAL SIMULATIONS

Interface-controlled technologies for electronic devices

The core functionality of electronic devices, spanning from transistors and solar cells to sensors and light-emitting diodes, relies on precise control of electron dynamics at interfaces between distinct materials. For example, within a photovoltaic cell, incident light energy excites an electron-hole pair, necessitating efficient separation to produce an external current. Such a process is typically aided by a potential gradient or appropriate alignment of energy levels at an interface.

Manipulating and shaping potential gradients at interfaces presents a unique opportunity to guide electrons and pioneer new technologies. At the Research Center for Future Energy Materials and Systems, our group has embraced this challenge, focusing on the development and application of computational materials modeling to energy materials. Our goal is to facilitate the creation of enhanced electronic and quantum materials by constructing heterostructures with specific functionalities for energy production, storage, and saving.

However, understanding and mastering the intricate physics of interfaces still pose significant challenges, both experimentally and theoretically. On the theoretical front, state-of-the-art methods relying on density functional theory (DFT) can be either unreliable or too computationally intensive to evaluate the electronic band structures of complex interfaces in energy devices. To tackle this issue, we recently optimized two density functionals explicitly for computing electronic and optical properties of interfaces and two-dimensional ma-



Figure 1: Atomic structure and local density of electronic states of SGO on a Si substrate, calculated with a modified hybrid density functional, Ref. [3].



terials: a local hybrid [1] and a local meta-GGA functional [2]. Our functionals achieve the accuracy of more involved Green's function methods while retaining the computational efficiency of standard DFT calculations. Consequently, our methods are tailored to enable predictive high-throughput calculations of the spectral and transport properties of various functional interfaces.

As an example, we demonstrate the investigation of the suitability of an epitaxial layer of strontium germanate (SGO) on a silicon (Si) surface with (100) orientation as a photocathode [3]. Photocatalytic water splitting holds promise as a strategy for large-scale clean energy production. However, the lack of efficient and low-cost solid-state photocatalysts remains a challenge. Our calculations confirm a type-III band line-up of energy levels at the interface (Figure 1). We observe that both redox potentials reside within the local band gap of SGO and below the Fermi energy of the supercell. Consequently, photogenerated electrons from the Si bulk reaching the SGO-capped surface are anticipated to traverse the interface and partake in water reduction. We conclude that the thin SGO layer, with a partially occupied lowest conduction

band, would function as a metallic electrode in the system.

In collaboration with experimental groups, we are currently engaged in several projects that involve extensive calculations across various types of interfaces. To maximize the value of these efforts, we are aggregating the resulting valuable data into an open-access materials database, the NOMAD Lab, developed by the FAIRmat NFDI consortium [4]. In the near future, our aim is to leverage artificial intelligence to meticulously analyze and extract critical patterns from this data. This analysis will enable us to construct predictive models for interface design, aiding in the identification of essential structural and chemical characteristics for specific functionalities at the interface [5].

Our endeavor encompasses not only the accumulation of calculations for interfaces but also the advancement of machine learning models to predict properties across a broader spectrum of interfaces. This data-centric approach shows great promise in guiding the future trajectory of interface design and promoting sustainable research practices.



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Figure 2: Schematic representation of the band edges of the SGO/Si system extracted from the local density of states of Figure 1, plotted together with the redox potentials of water splitting reactions, Ref. [3].



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INTERFACE EFFECTS ON DEFORMATION AND FRACTURE IN FULLY LAMELLAR TI-AL ALLOYS

Identifying processes and interaction mechanisms

Strengthening of metals by incorporating nano-scale twin boundaries is one of the important approaches of recent years to overcome the strength-ductility trade-off of metals and metallic alloys. To this effect, also nano-lamellar microstructures of lightweight Ti-Al alloys promise a great potential, e.g. for high temperature applications. However, for designing optimal microstructures, the contribution of the interfaces to the overall deformation and fracture behavior needs to be better understood. Generally speaking, interfaces in microstructures alter the mechanical properties due to their interaction with lattice dislocations and other interfaces via their stress fields. They can act as sink, barrier, or trap for lattice dislocations, but also as dislocation source. Unless they are perfectly coherent, interfaces exhibit misfit and/or compatibility stresses and are likely to nucleate cracks and alter crack paths. Last not least, especially at high temperatures and in interface-dominated microstructures, they can contribute to the plastic deformation by interfacial sliding and migration.

The dominant structures in two-phase lamellar Ti-Al are $\gamma\text{-TiAl}$ with a tetragonal L_{10} crystal structure, and the α_2 -Ti₂Al phase with a hexagonal DO_{10} lattice. These phases are arranged in parallel lamellae with a thickness of a few tens of nm up to some µm, depending on the composition and processing route. Three types of y/y(111)[111] twist grain boundaries exist, the true twin (TT; misorientation 180°), rotational boundary (RB; 120°) and the pseudo-twin (PT; 60°). The γ and $\alpha_{_2}$ phases are aligned such that the close packed planes and directions match, i.e. $\{111\} \gamma$ || (0001) α_2 and <110] γ || <1120] α_2 . There are 6 possible variants formed by rotating the two phases around [0001] α_2 and <111> γ respectively, by multiples of 60°. Of all these interfaces only the TT is intrinsically coherent, all others exhibit coherency strains and/or misfit dislocation structures.



Figure 1: Crack advancement of a penny-shaped crack under tensile load. The crack was initiated in the vicinity of an interface, the position of which is marked by the red line. The crack advancement in an ideal γ -TiAl single crystal is shown for comparison. The interfaces are the intrinsically coherent γ/γ true twin (γ -TT C), the strained and coherent γ -TiAl/ α_2 -Ti₃Al interface (γ - α C), the partially relaxed and semi-coherent γ - α_2 interface (γ - α_2 PSC), and the semi-coherent γ -TiAl pseudo-twin (γ -PT SC). The diagram shows that the semi-coherent interfaces are effective in blocking the crack propagation.



To identify the relevant processes and interaction mechanisms in nano-lamellar Ti-Al alloys we have investigated deformation and fracture by means of large-scale atomistic simulations. Bicrystals, fully lamellar samples, as well as polycrystals were studied to clarify whether the different boundaries are effective and equal strengtheners, what is the role of the interface coherency in these processes, and which structural length scale dominates the deformation behavior, i.e. what are critical values for lamella thickness and lamella spacing to enable / suppress twin migration / dislocation motion. The simulations were carried out with a well established empirical potential for the interatomic interactions [1] using the open-source software LAMMPS [2].

In a series of bicrystal studies of crack-interface interactions with different loading scenarios, we observed that, although the crack-tip mechanisms differ and there is a strong directional anisotropy, all internal boundaries increase the fracture toughness - in particular the semi-coherent ones. This can be seen e.g. from Figure 1, where the advancement of a penny-shaped crack in the vicinity of different interfaces is shown. Here the minimum advancement is observed for the interfaces labelled with SC (semi-coherent) or PSC (partially semi-coherent). An example of crack-tip blunting of an initially sharp, brittle crack at the pseudo-twin y/y interface is shown in Figure 2 (from [3]).

The role of the misfit dislocation network at semi-coherent interfaces was further investigat-

Figure 2: Snapshot of an atomistic simulation of crack tip blunting at the γ -TiAl Pseudotwin boundary. Green atoms are bulk γ -TiAl atoms, pink atoms mark the PT boundary and magenta atoms the crack tip surface. Orange, blue and yellow atoms represent typical stacking faults and defect atoms in TiAl. The initially sharp crack gets blunted and arrested at the PT boundary (adapted from Ref. [3]).

ed via computational tensile/compression tests [4, 5]. Among other things, we were able to show that e.g. at a semi-coherent γ/γ PT interface the misfit interfacial dislocations cause nucleation events, as exemplarily shown in Figure 3 (adapted from [4]). These events are responsible for lowering the overall dislocation nucleation stress and cause localized or early plasticity. While this could be detrimental to the tensile strength of a lamellar sample, it does improve its fracture toughness by dissipating energy without further crack advancement. The toughening effect as a function of lamella spacing in a fully lamellar sample has two contributions: The crack-initiation toughness, which exhibits a Hall-Petch type, "smaller is stronger" behavior, and the crack propagation toughness, which actually increases with increasing lamella spacing [6].

Summarizing, the spacing and the degree of lattice misfit of/at lamellar interfaces in two-phase Ti-Al alloys represent two important material parameters, which can also be adjusted experimentally e.g. by varying the processing route as well as the chemical composition. Tuning the lamella spacing provides the means to improve the fracture toughness of a material, whereas the lattice misfit and the resulting coherency stresses govern dislocation nucleation at the interfaces. Last not least, such studies demonstrate how large-scale atomistic simulations can be employed to separate and analyze microscopic mechanisms which are otherwise hard to disentangle.



Figure 3: Three snapshots of an atomistic simulation of a TiAl lamella, bordered by a PT interface, under strain. Atoms are colored according to centrosymmetry; those with perfect bulk coordination are not shown. Blue atoms mark the dislocation lines of the misfit dislocation network and red atoms the stacking fault region in between. The sequence shows how the network deforms under strain and finally nucleates dislocation loops into the lamella (adapted from Ref. [4]).



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ENTROPIC SHAPE MEMORY EFFECT: SIMPLE MODELS FOR COMPLEX SYSTEMS

The mechanisms of shape recovery in polymers

Shape memory (SM) materials have the remarkable property that, after being deformed, can return to their original undeformed shape under a suitable stimulus. In metallic SM alloys, this effect is based on a first order phase transition between two crystalline structures (austenite versus martensite). In shape memory polymers (SMPs), on the other hand, quite a different mechanism is at work.

Due to conformational degrees of freedom, entropy plays a key role for mechanical behavior of polymeric materials: The number of isotropic chain conformations is much larger than those corresponding to a stretched state [1]. As a result, when a polymeric sample is elongated, its entropy reduces. The tendency to increase entropy gives rise to restoring forces. This mechanism can be effective only if the system is at least partially ergodic, e.g., if polymer chains are sufficiently mobile to explore the available configurations. Consequently, if one stretches a polymeric sample and cools it well below the glass transition temperature, the sample will remain in the deformed state due to the lack of mobility. To trigger the recovery of the original shape, the sample is heated above a switching temperature (which is often close to the glass transition temperature) in order to increase the chains' mobility.

The activation of shape recovery can be also achieved in other ways. A promising route here is to use the plasticizing effect of small molecules (often referred to as additives) [2]. Moisture, for example, can enhance chain mobility and thus trigger the recovery process without the need to raise temperature. Indeed, as shown by the experimental materials scientists at the Ruhr-University Bochum, diffusion of small molecules such as water, acetone and ethanol into a shape memory sample can lead to shape recovery at room temperature, where the pure sample would keep its elongated form for long periods of time [3].

Figure 1 shows the structure formula of a polyurethane-based shape memory polymer used in experiments of [3] (ESTANE ETE 75DT3, henceforth referred to as SMP-E). As illustrated in this figure, a SMP-E molecule can be viewed as a sequence of "hard" segments (which stabilize the shape) and "soft" ones (responsible for entropic elasticity). To study this complex system via molecular dynamics (MD) simulations, each of these segments is represented by a sphere. Remarkably,



Figure 1: (a) Switching temperature for shape recovery versus concentration of additive molecules inside the SMP-E as for water, acetone and ethanol. For comparison, the reference data for the pure (dry) sample is also shown, Ref. [3]. The gray band gives the experimental uncertainty.

(b) The experimental setup for the observation of shape recovery. In the case shown here, shape recovery can do work against an external load, Ref. [3].



Figure 2: A bead-spring molecular dynamics model for ESTANE ETE 75 DT3, referred to here as SMP-E, Ref. [4].

as illustrated in Figure 2, MD simulations shows that, despite its simplicity, the model is capable of reproducing the shape memory effect. As visualized by a representative polymer in this plot, the polymer chains are elongated when the sample is stretched and remain in this low entropy state after the sample is cooled below the glass transition point of the hard segments. Shape recovery is activated either by reheating or by adding small molecules into the samples [3, 4].

Molecular dynamics simulations also reveal that the size of additive molecules plays an important role for chain mobility. Indeed, there seems to be an optimum size for the additive-induced enhancement of the chains' relaxation dynamics [5].

These new findings deserve a thorough experimental investigation. One could, for example, use alcohols of various molecular length (methanol, ethanol, propanol, etc.) to systematically study the effect of molecular size. Moreover, the present MD simulations shall be complemented by fully atomistic investigations to explore the important role of functional groups and their mutual interactions (e.g. hydrogen bonds) on the structural integrity and shape recovery [6].



Figure 3: Molecular dynamics simulations showing different stages of a shape memory cycle. A chain from the sample is shown on the right to highlight conformational changes, Ref. [4].



Figure 4: Non monotonic effect of the size of small molecules on glass transition temperature, T_g , the mode coupling critical temperature, T_c , and the Vogel-Fulcher-Taman temperature, T_0 . All these quantities show a minimum at an additive diameter of 0.5 in units of a segment length, Ref. [5].



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SIMULATION OF FUNCTIONAL FERROELECTRICS

Microscopic insights into ferroelectric domain walls

The name ferroelectric is derived from the Latin word for iron. Analogous to that well-known magnetic material, ferroelectrics have a spontaneous order parameter which shows characteristic field hysteresis and multi-domain structures (Figure 1).

Analogous to magnetic materials, ferroelectrics bear a high potential for application ranging from non-linear optics, energy harvesting, capacitors, sensors, non-volatile memories, and neuromorphic computing to future cooling devices [1]. There are, however, important differences between these material classes: oxidic ferroelectrics such as $BaTiO_3$, (Figure 1b), are brittle insulating materials with mixed ionic-covalent bonds and the order parameter is the spontaneous polarization, i.e. ordered electric dipoles. Furthermore, the polarization is strongly coupled to the lattice which shows displacive structural phase transitions with exceptional functional properties [2].

The design of optimized ferroelectrics requires a fundamental understanding of the interplay between different elements of microstructure, particularly domain walls and inhomogeneities. In recent years, microscopic simulations have contributed to major breakthroughs [1]. The main challenges in simulations are to correctly reproduce polarizability, phase stability at finite temperatures, and the coupling to external fields.

In our group we apply different ab initio based molecular dynamics simulation methods. To access



Figure 1: (a) Ferroelectric field hysteresis showing the time evolution of polarization (P, solid line) and global strain (η , dotted line) during field-induced switching. Switching is related to an intermediate domain structure and the shift of domain walls. (b) Oxidic ferroelectric perovskites based on

the prototypical material $BaTiO_3$ with alternating BaO and TiO_2 layers. Material properties can be designed by substitution, e.g., $Ba \rightarrow Sr$, $Ti \rightarrow Cu$.



Figure 2: (a) In the effective Hamiltonian approach, the degrees of freedom are coarse grained to the local dipole moment \mathbf{u}_i and the local strain \mathbf{w}_i .

(b) In core-shell potentials, each ion is split into a core and a shell to model the polarizability. The interaction between ions includes short-range and Coulomb interactions.

the microscale or to sample statistical processes, we use the so-called effective Hamiltonian approach (Figure 2). The degrees of freedom are coarsegrained to local dipole moments and local strain being essential to ferroelectricity. Phase diagrams and functional properties can be correctly described. However, this method does not explicitly include atomistic information needed for substituents or defects. Therefore, we supplement and cross-check our results with atomistic core-shell potentials.

Figure 3 summarizes recent research examples from our group: (a)—(b) Ferroelectric domains

can be stabilized up to few unit cells and their motion is related to the nucleation and growth of 2D clusters on the walls. (c)—(d) Fast changes of external fields increase the number of nucleation centers on the moving wall and thus the domain wall velocity. As these centers are high in energy, they switch back with time and the domain wall velocity decreases. (e)—(f) Inhomogeneities locally modify the domain wall dynamics. For example, the energy barrier to shift the domain wall across a TiO₂ centered plane increases at SrTiO₃ inclusions, which may pin walls.







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EXPLORATION OF COMPLEX INTERMETALLIC PHASES WITH MACHINE LEARNING

Predicting Fe-Mo R-phase formation energy

Intermetallic phases are one of the most commonly observed groups of crystal structures. They exhibit peculiar properties like high strength and play an important technological role as beneficial precipitates in light-weight steels, as detrimental precipitates in single-crystal superalloys and as potential crystal-structures for hydrogen storage. In this project we focus on a subgroup of intermetallic phases, the topologically close packed (TCP) phases. The set of TCP phases contains the crystal structures A15, μ, σ, χ, C14, C15, C36, R, M, P, and δ . These crystal structures of the TCP phases are geometrically closely related and can be understood as different periodic arrangements of the Frank-Kasper polyhedrons of the nearest neighbor shells with coordination numbers from 12 to 16. These TCP phases form in numerous binary, ternary and multi-component compounds. The major factors that govern their thermodynamic stability are the average number of valence electrons and the differences in atomic size of the constituent elements as well as entropy contributions. The computational prediction of their thermodynamic stability requires the computation of the formation energy of the possible permutations of constituent elements on the inequivalent lattice sites (Wyckoff sites or sublattices). This leads very quickly to a combinatorial explosion as it requires to permutate the chemical elements on a number of sublattices that ranges from 2 (A15, C15), 3 (C14), 4 (χ), and 5 (C36, σ , μ) for the simpler TCP phases to 11 (R, M), 12 (P), and 14 (δ). The computational cost for computing the thermodynamic stability with a quantum-accurate method like density functional theory (DFT) limits the range of exploration of TCP phases to binary or ternary compositions of the simpler TCP phases (A15, C15, C14, χ , C36, σ , and μ) while chemically complex TCP phases or the structurally complex R, M, P and δ phases are out of reach.

Here we present a machine learning (ML) approach to overcome this limitation and demonstrate a complete sampling of the R-phase in the Fe-Mo binary system with very high accuracy. This system is particularly well suited as it forms several simpler TCP phases and it is one of the few binary systems that exhibit a complex TCP phase. The training data for the ML model are magnetic and non-magnetic DFT calculations with full structural relaxation for complete chemical samplings of



Figure 1: Workflow from DFT calculations for simple TCP phases to the training of ML models with domain knowledge of the interatomic bond to predictions of the structural stability of the complex R-phase in Fe-Mo.



Figure 2: Performance of different combinations of domain knowledge and regression algorithms in terms of root mean square error (RMSE) on formation energies of test structures.

the simpler TCP phases A15, C15, C14, χ , C36, σ , and μ in the Fe-Mo system. This data set provides a systematic coverage of all coordination polyhedrons but the small size of only few 100 structures poses a challenge for constructing a ML model with sufficient transferability for robust predictions. To enforce reliable predictions, we train the ML models not only with conventional features of geometry and chemical composition but additionally we include domain knowledge at several levels. At the geometry level, we include domain knowledge of the crystal structures by taking polyhedron-resolved averages of atomic features. At the chemistry level we include domain knowledge of the interatomic bond in terms of approximate atom-resolved electronic density-of-states information computed with coarse-grained electronic-structure methods. The vector with all features from different levels is the basis for training the ML models to reproduce the formation energies of the differ-

ent lattice occupations of the simple TCP phases obtained by DFT. This overall workflow is shown in Figure 1 and repeated for different numerical regression methods. We find a systematic shift of the learning curve towards improved performance with increasing domain knowledge, fairly independent of the chosen regression scheme (Figure 2). With the trained models the formation energy of the Fe-Mo R-phase can be predicted for the first time across the full range of chemical compositions as shown in Figure 3. The predictions are very robust with a root-mean-square-error of less than 25 meV/atom and in very good agreement with punctual DFT calculations of the identified relevant compositions of the Fe-Mo R-phase. This approach will be rolled out further for other complex TCP phases in multi-component compounds in the German-French collaboration "Artificial Intelligence for Intermetallic Materials" funded by DFG and ANR.







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18/MRD NEWS

ATOMIC CLUSTER EXPANSION FOR PT-RH CATALYSTS

From ab initio to the simulations of nanoclusters in few steps

Noble metals platinum (Pt) and rhodium (Rh) have been extensively employed as heterogeneous catalysts in various applications, such as vehicle exhaust catalysts and fuel cells, due to their remarkable activity and stability. These catalysts are often used in the form of nanoparticles, which maximize the active surface area for chemical reactions. Notably, the internal microstructure of these nanoparticles can be tailored to enhance their functional properties and structural stability. One popular approach involves creating core-shell nanoparticles, where a core of one metal (e.g., Rh) is enveloped by a shell of another metal (e.g., Pt). This core-shell design can boost catalytic activity and stability.



Figure 1: A preferential segregation of Pt atoms (in blue) at surfaces of an Pt-Rh nanocluster. Left: the initial cluster configuration with a random distribution of both metals (containing 30% of Pt); right: the final configuration after equilibration performed using a hybrid MD-MC simulation.

However, maintaining the stability of non-equilibrium nanoparticles under operational conditions can be a challenge.

Atomic-scale simulations can provide deeper insights into the thermodynamic and kinetic phenomena governing the structure of these nanoparticles. These simulations can provide information about the energetic aspects of specific structural features as well as the dynamical evolution of the entire system. However, to perform accurate simulations, reliable interatomic interaction models are essential.

The atomic cluster expansion (ACE), developed at ICAMS by Prof. Drautz and his colleagues [1-3], presents a state-of-the-art approach for description of interatomic interactions. ACE combines machine learning methods and physically based models of interatomic interactions, offering superior accuracy and computational efficiency. One of the key features of ACE is a complete and hierarchical set of basis functions that span the space of local atomic environments. This enables to expand an atomic property, such as the energy of atom, with outstanding accuracy.

Recently, we have developed an ACE parametrization for the Pt-Rh system using a semi-automatic workflow [4]. This workflow involves generating a training dataset based on density functional theory (DFT) calculations, fitting the model, and carrying a series of fundamental validation tests. The workflow also employs active learning (AL) algorithms to improve the model's accuracy. The parameterization of ACE models was based on about 30 000 reference DFT calculations. The considered atomic structures span a wide portion of the configuration space for both elemental metals and their binary compounds. After initial training, AL was employed to ensure a reliable description of Pt-Rh surfaces as these are crucial for simulations of core-shell nanoclusters. The validation of the parameterized potential included various fundamental properties of the elemental metals as well as the phase stability and other thermodynamic properties of various Pt-Rh phases.

Finally, the ACE parametrization was applied in a series of atomistic simulations to investigate structural stability of various Pt-Rh nanoclusters. The primary focus of the simulations was to examine the role of surface segregation that may play a role in stabilization of the core-shell geometry. Largescale molecular dynamics (MD) and Monte Carlo (MC) simulations were used to explore the thermodynamic stability and the dynamical evolution of realistic clusters at various temperatures and chemical compositions. We observed a strong tendency of the Pt atoms to segregate at cluster surfaces and to form a single monolayer coverage of the whole cluster (see Figure 1). While the formation of a Pt surface layer can be related to low surface energies of Pt, experimental observations of the core-shell particles show a thicker coverage of 3-5 layers of Pt at the surface. By carrying out additional simulations at elevated temperatures (see Figure 2), we showed that the core-shell cluster morphologies consisting of a Rh core with a thicker Pt shell observed in experiments are not thermodynamically favorable but rather kinetically stabilized. This corroborates with the fact that the experimental synthesis procedure creates the core first followed by the coating of the surface element. However, the ACE predictions may be also affected by the limited accuracy of the DFT calculations for Pt surface energies. It is therefore necessary to reexamine the defect energetics in Pt using advanced DFT functionals in order to fully resolve this issue.



Figure 2: Core-shell nanoclusters after 2 ns MD annealing at 1000 K (left) and 1500 K (right). The intermixing of Rh atoms (in green) into the Pt shell (transparent blue) takes place only at elevated temperatures and is therefore kinetically prohibited at ambient conditions.



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MACHINE LEARNING **MODELS: ARE YOU SURE?**

Controlling the reliability of machine learning models

Machine learning (ML) has gained widespread popularity in various scientific disciplines, including materials science, thanks to its universal approach: if you can represent an object, process, or signal as a collection of numbers, i.e. featurize it, and you have corresponding target properties, then you can train machine learning model for it.

ML models are recognized for their ability to make accurate predictions within established input data ranges. However, they face challenges when attempting to make predictions beyond these known limits. These two scenarios are simply known as interpolation and extrapolation and they represent fundamental concepts in the world of ML. Interpolation means making predictions within the confines of existing data. To put it simply, it's like estimating what lies between two data points on a graph. In this scenario, ML models perform exceptionally well, providing accurate predictions when they can rely on past observations. Extrapolation, on the other hand, pushes the boundaries, requiring predictions beyond the scope of existing data. Imagine trying to predict what happens far beyond the last data point on that graph. Even highly advanced ML models frequently encounter challenges in this domain. So, can we address this inherent limitation in ML models? Can we enhance their extrapolation capabilities?

One approach to improving the extrapolation capabilities of ML models is to employ a more "physical" approach to feature engineering. This involves creating representations of objects that encapsulate underlying physical principles and fundamental symmetries, such as translations, rotations, inversions, etc. While this approach can







Figure 2:

Active Exploration: Schematic representation of artificially generated liquid water configurations aimed at maximizing extrapolation grades across the majority of atoms. The spontaneous emergence of hydrogen transfer configurations is observed. This technique allows for the efficient generation of training configurations for ACE.

significantly broaden the applicability of the model, it may not guarantee absolutely accuracy in all situations.

Another approach is based on the intriguing ability of certain ML models to provide their degree of confidence or uncertainty regarding their own predictions. This confidence can be expressed as a continuous value, providing valuable insights into the reliability of the model's output. The method of the uncertainty indication strongly depends on the type of model, with one approach applicable to neural networks, another suited for linear models, and thirds one is natural for Gaussian processes.

Among the various applications of ML in materials science, one interesting role is played by machine learning interatomic potentials (MLIP) - models that can predict the energy of arbitrary atomic configurations and corresponding forces acting on atoms. These potentials combine the accuracy of electronic structure methods like density functional theory (DFT) with computational efficiency comparable to classical force-fields. One of the recent remarkable example of such models is the Atomic Cluster Expansion (ACE) [1]. ACE efficiently utilizes translational, rotational, inversion and permutation symmetries real space. It also exploits density trick to efficiently compute manybody interactions and provides a formally complete basis set for local atomic environments. ACE can represent local atomic neighborhoods of each atom within a specific cutoff distance as point in a high-dimensional space. The atomic environments from the training set collectively form a region of certain shape in this space. At this point, one can identify most representative points that outline the boundaries of this complex region and refer to them as an "active set" [2]. When new atomic environments are encountered during a molecular dynamics simulation with ACE, they are also mapped into this high-dimensional space. This is where the crucial aspect comes into play: measuring how closely these new points align with the active set. If they fall within the perimeter defined by the active set, the predictions made by ACE are reliable—this is the realm of interpolation.

However, if these new points lie beyond the active set's boundaries, it signals that corresponding atomic environments are quite distinct from what the model has seen before, and the model extrapolates. To quantify this "novelty", one can compute the so-called extrapolation grade – a value that is less than one for interpolation and greater than one for extrapolation cases.

Here's where it becomes exciting: when we see new atomic structures with extrapolative atomic environments, we can pause our simulations and perform more precise calculations, such as DFT, for this new configurations, to obtain new reference data. These new data are then added to the training set, and the ACE model is updated, becoming more accurate. This iterative self-improvement process is known as "active learning" and it can effectively address the extrapolation problem of ML models.

In conclusion, machine learning models inherently excel at interpolating within familiar data domains but encounter limitations when extrapolating into uncharted territories. This intrinsic limitation may limit the applicability of ML models. However, the ability of models to signal their uncertainty offers a solution. By taking these uncertainty signals into account, we can avoid using models in scenarios where their reliability is reduced. Moreover, through active learning, we can systematically improve these models, ensuring their extrapolation strength. Thus, the usage of the machine learning models is not just about their accuracy, it is also about using uncertainty to continually improve and expand their predictive capabilities.



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FROM THE STRUCTURE OF GRAIN BOUNDARIES TO THEIR THERMODYNAMICS AND PROPERTIES

Bridging experiments and atomistic simulations

Almost every crystalline material in nature or in engineering applications is in fact polycrystalline, i.e., it consists of many differently-orientated crystallites. This fact strongly influences the material properties: The grain boundaries (GBs) separating the crystallites can, for example, act as obstacles for dislocation movement, serve as weak planes for crack propagation, provide pathways for fast diffusion, or affect thermal and electrical conductivity. GBs are characterized by five macroscopic parameters, describing the orientation of the abutting crystallites to each other as well as the geometry of the GB plane. Here, we were more interested in the so-called microscopic degrees of freedom, which describe the atomic arrangements that occur on the nanoscale. Advances in imaging techniques, especially (scanning) transmission electron microscopy (TEM, STEM), have increasingly provided a picture of the structure of special GBs.

At the Max-Planck-Institut für Eisenforschung, such STEM experiments could recently prove an old hypothesis: In pure copper, different GB structures can (co-)exist on the same grain boundary plane (see e.g. [1]). Such a finding requires atomic resolution, good sample preparation, and some luck to find several structures under experimental conditions; not many such results have been reported to date. These different structures do not, however, occur randomly: In order to understand their stability conditions, one can treat them as thermodynamic interface phases. (It must be noted that these "phases" are quite different to bulk phases, given that they cannot exist on their own, but only at interfaces. In parts of the literature, they are therefore called complexions instead of GB phases.) A thermodynamic description of GBs is unfortunately not accessible via STEM experiments. Here, atomistic simulations are invaluable for understanding and interpreting the experimental observations.

Our research currently concentrates on [111] tilt GBs, which exhibit a rich GB phase landscape. Figure 1 shows the two GB phases of a Σ 37c [111] [1 10 11] GB, which we termed "domino" and "pearl" [1]. Using evolutionary algorithms, we



Figure 1: The domino (top) and pearl (bottom) GB phases in a Σ 37c grain boundary. The insets show the perfect fit between experimentally-observed and simulated structures. Adapted from Ref. [1] under CC-BY 4.0.



Figure 2: Grain boundary excess free energies of the pearl (blue) and domino phase (red) show a grain boundary phase transition at around 460 K. Adapted from Ref. [1] under CC-BY 4.0.

could find the same structures in the computer using EAM potentials. This allowed us to perform free-energy calculations and predict a GB phase transition at 460 K (Figure 2). Reality, however, turns out to be more complicated: Experimentally, an alternating pattern of domino and pearl structures was found. Here, we propose that inherent defects of the necessarily non-ideal experimental GBs might (meta-)stabilize such a pattern, highlighting that pure defect thermodynamics are insufficient to explain the complex state of GBs in real materials [1].

Such a detailed investigation of a single GB type naturally poses the question of transferability: Are we just looking at special cases—interesting, but ultimately not significant for macroscopic properties—or can we learn something about more than the Σ 37c GB? Atomistic simulations enable the easy screening of several GB types and chemical elements. We thus investigated several [111] tilt GBs for a range of fcc metals, namely Ni, Cu, Pd, Ag, Au, Al, and Pb [2]. The result was that the same structural motifs of the domino and pearl phases occur in all of them, indicating that GB phase transitions are likely abundant across

different systems. Model simulations with simpler interatomic potentials (switching from EAM to medium-ranged pair potentials and then to pair potentials with only next-neighbor interaction) revealed that the GB motifs can be reproduced with medium-ranged interactions—but not next-neighbor interactions—even if the model potential is not material specific (Figure 3). The GB energies and properties are, however, very material specific [2].

Of course, most GB phases would in practice be tailored by introducing alloying elements and not by temperature and/or stress. We are undertaking investigations in this direction, but could already correlate GB structure and segregation sites for a single copper GB phase with silver as an alloying element [3]. Detailed analyses of the STEM data allowed us to directly connect the experimental GB state with hybrid molecular dynamics/Monte Carlo simulations [3].

Future work will also have to consider how these GB phases/complexions do affect the material properties of macroscopic samples. We already have some data on the effect of different GBs on electrical resistance [4] and studies of the micromechanics of bicrystals are in progress.



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Figure 3: A Σ 7 [111] grain boundary modeled with successively simpler models (EAM, medium-ranged pair potential, next-neighbor pair potential), showing that only medium-ranged pair interactions are required to reproduce the structure. Adapted from Ref. [2] under CC-BY 4.0.





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