

CALCULATION OF METALS PHASE DIAGRAMS FROM FIRST PRINCIPLES USING MACHINE LEARNING INTERATOMIC POTENTIALS

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Calculation of phase diagrams of materials at finite temperatures from first principles is of great importance in materials science and is inherently linked to the challenge of predicting material properties and novel materials design. When studying first-order equilibrium phase transitions, the Helmholtz free energy plays a key role. Unfortunately, this quantity cannot be directly computed in numerical experiments.

Modern theoretical materials science employs various methods for calculating free energy at finite temperatures from first principles, differing in accuracy and computational intensity. The harmonic approximation is one approach for determining vibrational properties of materials at zero temperature. This method provides reasonable accuracy for calculating phonon properties (density of states, dispersion curves) at relatively low temperatures for materials stable at 0 K. The quasi-harmonic approximation actually accounts for only volume dependence of vibrational properties but can be useful for calculation of temperature-dependent properties such as heat capacity, thermal expansion coefficient, and vibrational entropy. However, this approach fails for strongly anharmonic lattices or crystalline phases stabilized dynamically only at finite temperatures. A solution to this problem involves calculating phonon properties at finite temperatures using data from *ab initio* molecular dynamics (AIMD).

One method for determining crystal phonon properties is the Temperature-Dependent Effective Potential (TDEP) approach [1–2]. This method directly optimizes force constant matrix coefficients based on trajectories obtained from AIMD. We evaluated the accuracy of the TDEP against the more rigorous but computationally expensive Thermodynamic Integration Method (TIM) [3–4]. It was shown that the second-order harmonic force constants introduce errors exceeding 10 meV/atom in thermodynamic potentials, leading to unacceptable uncertainties in equilibrium phase boundary calculations. Incorporating higher-order force constants in the TDEP yields more reliable results. The TDEP method was applied to AIMD simulations of zirconium (Zr) in various crystalline allotropes. The phase diagram of zirconium was calculated for three solid phases: HCP α -Zr, BCC β -Zr, and ω -Zr (simple hexagonal lattice). A comparison was made between the computed zirconium phase diagram, experimental data, and results from other theoretical studies.

The work further presents results for the uranium phase diagram. AIMD simulations of thermodynamic properties were performed for four uranium phases (α , γ , γ' , and liquid) across broad pressure and temperature ranges. These AIMD results were used to compare two approaches for phase diagram calculations. The first is direct TDEP application to first-principles data for calculation Gibbs free energies. The second approach is based on training of machine learning MTP potentials based on AIMD results and the following calculation of thermodynamic potentials via the TIM. Notably, this study marks the first construction of uranium's phase diagram over wide pressure and temperature ranges using the AIMD+TDEP framework. Comparisons with existing experimental and theoretical literature data revealed significant discrepancies in equilibrium line positions. A key finding is the identification of an α - γ - γ' triple point, absent in earlier theoretical studies and located in a region lacking experimental data. This region, however, is accessible for exploration using modern laser heated diamond anvil cell experiments.

References

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