

# Thermodynamics from first-principles: Phase diagram of oxygen adsorbed on Ni(111) and thermodynamic properties

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## Abstract

Thermodynamic properties and the surface phase diagram of O/Ni(111) have been calculated from Metropolis and Wang-Landau Monte Carlo simulations based on lateral interactions derived from density functional theory (DFT) calculations. The DFT energies were mapped onto an Ising-like Hamiltonian according to the cluster expansion technique formalism. Both, fcc and hcp adsorption sites were included in the Hamiltonian. Different criteria were used to evaluate competing parameter sets: cross-validation score  $CV$ , Mallows'  $C_p$  statistics and adjusted  $R^2$  statistics. The parameter space was searched using genetic algorithms in order to find optimum sets. The different parameter sets obtained from different criteria lead essentially to the same transition temperatures. Excellent agreement is found when comparing the shape and stability regions of the theoretical and experimental (from the literature) phase diagrams. Additionally, we were able to elucidate the nature of the  $p(2 \times 2)$  phase transition at  $\frac{1}{4}$  ML oxygen coverage (experimental results in the literature disagree about the nature of this transition). Differences arise when comparing the values of the calculated and experimental transition temperatures owing to imprecision in present-day DFT calculations.