# 510b Alloy Surface Segregation in Reactive Environments Via Density Functional Theory and Atomistic Thermodynamics

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The chemical and materials properties of an alloy surface depend sensitively on its detailed surface composition and structure, which can differ substantially from the that of the bulk alloy due to segregation of one species to the surface. The surface composition and structure can further be modified by the partial pressures and temperatures in the surrounding environment, if one alloy component interacts more strongly with a gas-phase species than the other. Thus, in order to predict the chemical and materials properties of an alloy surface under reactive conditions, such as catalytic or corrosive conditions, one requires a theory that explicitly considers the effect of the reactive environment on the alloy surface.

As a first step towards this predictive capability, we are extending the concepts of *ab initio atomistic thermodynamics* to address segregation in binary transition metal alloys in the presence of a reactive gas phase. We apply the approach to the (111) surface of $Ag_3Pd$ in an $O_2$ atmosphere, and find that contrary to the situation in ultra-high vacuum where Ag segregation is observed, Pd segregates to the surface at high oxygen pressures. Furthermore, the oxygen partial pressure required to induce Pd segregation depends on the bulk reservoir, i.e. the bulk composition and structure, that the surface is in equilibrium with. We discuss the difficulties and possible inaccuracies of the *ab initio atomistic thermodynamic approach* with respect to the limited exploration of configuration space and the steps necessary to proceed beyond it.