Thermodynamic properties of Au-Pd nanostructured surfaces studied by atomic scale modeling

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The understanding of equilibrium Au-Pd nanostructures is important in view of catalytic applications. The composition and ordering properties in the vicinity of Au-Pd cluster surfaces at equilibrium are studied using the Metropolis Monte Carlo importance sampling and a popular version of the embedded atom method (EAM). The clusters contain about 1000 atoms.

The thermodynamic stability of the ordered phases in the bulk and at the cluster surfaces is discussed on the basis of simulations in the semi-grand canonical ($\Delta\mu$, NPT) statistical ensemble. A stable ordered phase in this case is evidenced by a constant composition within a certain interval of values of the chemical potential difference $\Delta\mu = \mu_{Au} - \mu_{Pd}$. (Fig. 1)

Surface enrichment in Au is systematically predicted, accompanied by partial sub-surface enrichment in Pd, best enhanced around the equiatomic overall composition. Clusters display similar segregation and ordering properties as flat infinite surfaces. However, no thermodynamic stability of the ordering at cluster surfaces could be evidenced.

We also address the question about the sensitivity of the segregation and ordering properties on the surface energy. To this purpose, the parameterization of the EAM potential used has been modified in order to predict surface energies closer to the experimentally measured ones, 1.5 J/m^2 and 2.0 J/m^2 for Au and Pd respectively, as shown in the following table.

Surface		Standard EAM, J/m^2	Modified EAM, J/m^2
Au	{111}	0.884	1.407
	{100}	0.973	1.497
	{110}	1.027	1.582
Pd	{111}	1.610	1.903
	{100}	1.722	2.011
	{110}	1.841	2.148

The new parameterization does not induce significant changes with regard to the results shown in Fig. 1. It is therefore concluded that surface energy is not of a major importance in segregation and ordering properties of nanostructured Au-Pd alloy surfaces.

Figures:

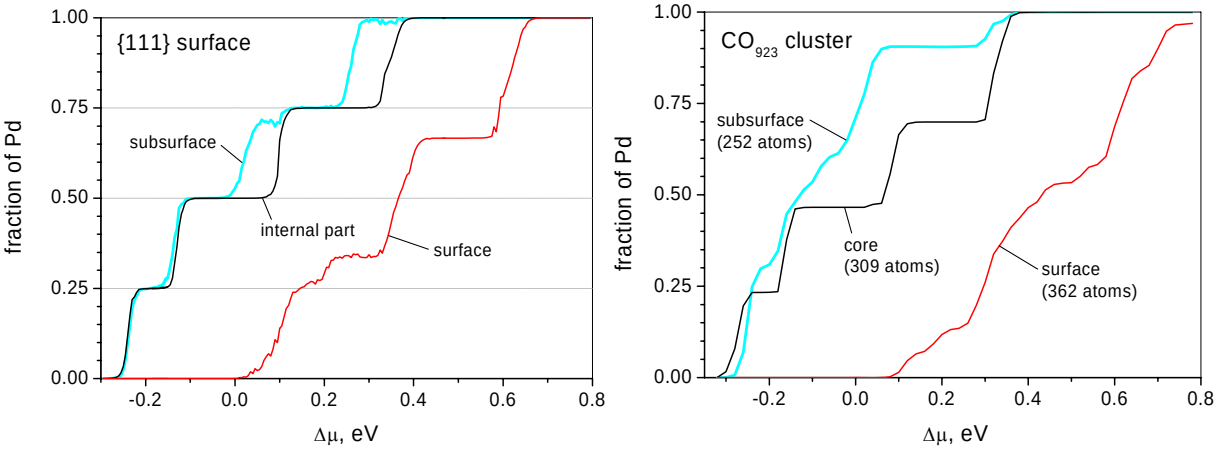

Figure 1. Composition versus Δμ in an infinite {111} surface and in a cuboctahedral cluster containing 923 atoms at T = 100 K. The surface, subsurface and the internal part of the system are separately shown.