

MM 36: Topical Session: Thermodynamics at the nano scale IV - Electrochemistry and strain

Time: Wednesday 10:15–11:45

Location: BAR 205

Topical Talk MM 36.1 Wed 10:15 BAR 205

First-principles prediction of the equilibrium shape of nano particles under realistic electrochemical conditions — ●NICOLA MARZARI¹ and NICEPHORE BONNET² — ¹Theory and Simulations of Materials, EPFL — ²AIST and University of Tokyo

A first-principles model of the electrochemical double layer is applied to study surface energies and surface coverage under realistic electrochemical conditions and to determine the equilibrium shape of metal nanoparticles as a function of applied potential. The potential bias is directly controlled by adding electronic charge to the system, while total energy calculations and thermodynamic relations are used to predict electrodeposition curves and changes in surface energies and coverage. This approach is applied to Pt surfaces subject to hydrogen underpotential deposition. The shape of Pt nanoparticles under a cathodic scan is shown to undergo an octahedric-to-cubic transition, which is more pronounced in alkaline media due to the interaction energy of the pH-dependent surface charge with the surface dipole.

References: N. Bonnet and N. Marzari, Phys. Rev. Lett. 110. 086104 (2013).

MM 36.2 Wed 10:45 BAR 205

Calculation of pourbaix diagrams combining DFT and experimental data as descriptor for high-throughput screening —

●IVANO E. CASTELLI, KRISTIAN S. THYGESEN, and KARSTEN W. JACOBSEN — Technical University of Denmark, Kgs. Lyngby, Denmark

Stability is the most important criterion for a material to be used in any type of application. It is often calculated relative to experimentally known structures in which the candidate material can separate. This method gives no information about corrosion in water. Stability in a realistic electrochemical environment can be investigated using Pourbaix diagrams that combine experimental information, namely dissolution energies, with computational data from density functional theory (DFT) total energies [1].

With this approach, the stability in water of 20 cubic perovskites previously screened for one-photon water splitting device [2] has been investigated. These materials are usually stable at pH = 7 and U = 0 V. Oxides and oxyfluorides are also stable at high potential, while oxynitrides at low potential [3].

Furthermore, the stability in water is efficiently used as a descriptor, together with size and position of the bandgap, for high-throughput screening for energy related applications of known materials from the Materials Project database [4,5].

References [1] K.A. Persson et al., Phys Rev B 85, 235438 (2012). [2] I.E. Castelli et al., Energy Environ. Sci. 5, 5814 (2012); Energy Environ. Sci. 5, 9034 (2012). [3] I.E. Castelli et al., Topics in Catalysis (2013). [4] <http://materialsproject.org/> [5] <https://cmr.fysik.dtu.dk/>

Topical Talk MM 36.3 Wed 11:00 BAR 205

Interface stress effects and critical behavior in nanocrystalline materials — ●RAINER BIRRINGER — Universität des Saarlandes, Saarbrücken

We discuss the concept of interface stress in nanocrystalline (nc) materials made up of grain- and/or phase boundaries. Interface stress is an inherent property of any interfacial material manifesting solid-solid or solid-liquid interfaces. In nc metals the stress exerted by interface stress on the abutting crystallites scales as one over grain size and may assume values of the order of several GPa in the limit of small grain sizes. We present data for grain boundary stress in noble metals and address the issue of interface stress at the Ni-Ag phase boundary.

The critical behavior at the para- to ferromagnetic phase transition is usually considered not being dependent on the microstructural details of the system but depends only on the respective universality class, the dimensionality of the space and the symmetry of the order parameter. We studied nc Gadolinium to scrutinize whether or not the randomness and disorder associated with nanocrystallinity may act as a relevant scaling field and so make the system change its universality class, derived from the single crystalline state, when approaching the asymptotic critical regime in the limit of small grain sizes.

MM 36.4 Wed 11:30 BAR 205

Surface excess elasticity in nanostructures: fact or fiction? — ●NADIA MAMEKA¹, JÜRGEN MARKMANN^{1,2}, and JÖRG WEISSMÜLLER^{1,2} — ¹Helmholtz-Zentrum Geesthacht, Institut für Werkstofforschung, Werkstoffmechanik, Geesthacht, Germany — ²Technische Universität Hamburg-Harburg, Institut für Werkstoffphysik und -technologie, Hamburg, Germany

Solid surfaces interact with the underlying bulk via a capillary force, the surface stress, which varies as the solid is strained. This variation defines a surface excess elastic modulus, which is well documented in theory. For nanoscale structures, the excess elasticity implies a size-dependent effective elastic response of the entire structure. While experimental observations of this phenomenon have been claimed, no agreement has been reached about magnitude or even sign of the excess modulus. One may therefore ask if there is a measurable impact at all. Here, we use experiments with dynamic mechanical analysis (DMA) on nanoporous gold to probe the issue. We focus on reversible changes in the elastic response when the surface is electrically charged or adsorbate monolayers deposited and lifted in electrolyte. The results reveal a significant variation in macroscopic stiffness. This conclusively confirms the important role of the surface excess elasticity phenomena in materials with large specific surface area. As an example, the reversible variation of the elastic modulus in the presence of weakly binding ClO₄⁻ ions to the Au surface reached up to 10% for a ligament size of 40 nm in mm-sized samples.