

# A theoretical assessment of the reported increase in the mean inner potential of Au clusters with decreasing particle size

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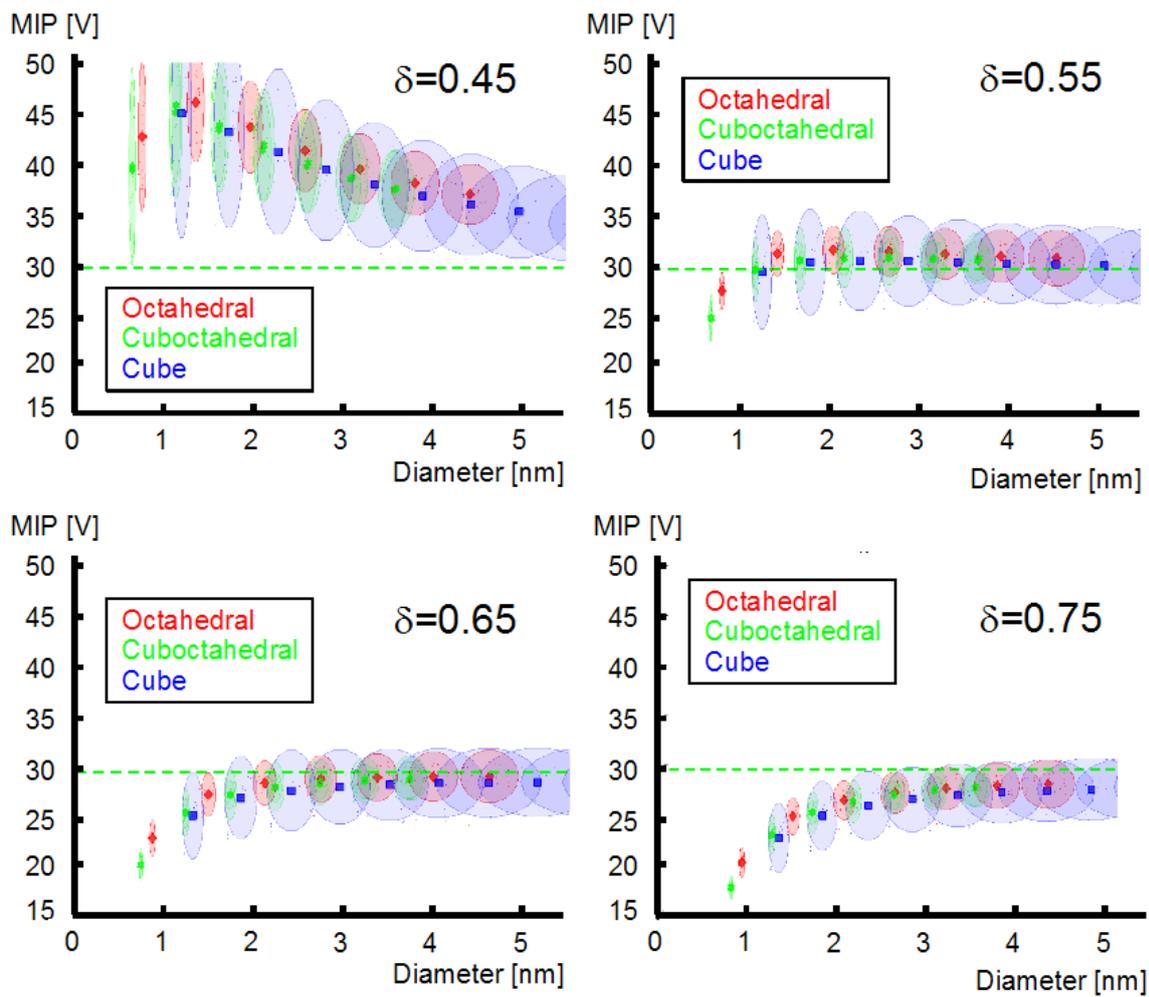
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In recent years, a series of papers has appeared reporting a large increase in the measured mean inner potentials (MIPs) of nanoparticles and thin films with decreasing specimen thickness (up to 85 V for thicknesses smaller than 1 nm) [1, 2, 3]. These results have been explained empirically by introducing a constant phase offset [1], charge transfer between the particles and the substrate [2] or the presence of strain in the specimen surface layer [3]. We note here that an apparent increase in MIP could also be caused by dynamical diffraction [4], dipoles on the specimen surface [5], a systematic error in the measured specimen thickness or the presence of a surface adatom layer consisting of O or C [6].

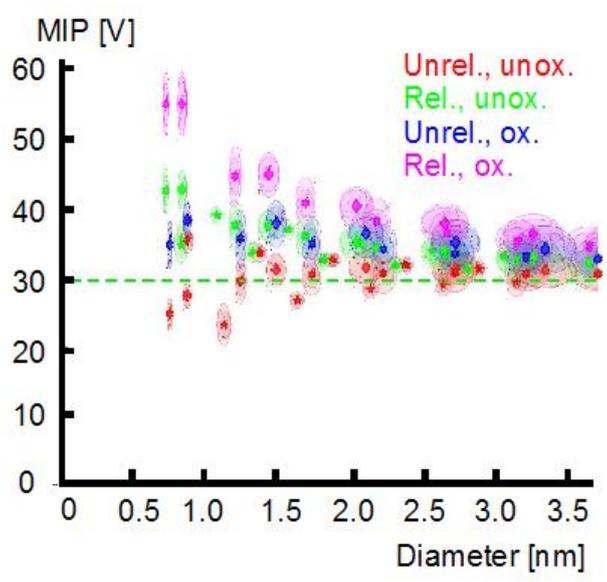
We have carried out simulations of the phase of the undiffracted beam and evaluated the MIP from the simulated phase in order to investigate the influence of some of the above mentioned effects on the evaluated MIP. The calculations are performed for octahedral, cuboctahedral, cube-like, Mackay icosahedral and Marks decahedral clusters with sizes ranging from approximately 0.5 nm to 4 nm. The clusters are decorated with a thin layer of oxygen or carbon and the atom positions are relaxed using the embedded atom method (EAM) [7] within the LAMMPS code [8] in order to include surface relaxation. The relaxed and unrelaxed clusters are used in multislice simulations in the StemSim software [9] with an incident parallel plane wave using scattering factors from Ref. [10]. The MIP is then evaluated from the phase of the undiffracted beam derived in real space from the object exit wave function and compared with the MIP evaluated from thin Au slabs.

In contrast to a crystalline slab, the extension of a cluster is not well defined. We assumed spheres around the atom positions with radius  $r_k = \delta a$ , with  $a$  being the lattice parameter of Au and  $\delta$  being an adjustable parameter. From the sphere model of the cluster, the local cluster thickness and the projected area of the cluster can be reconstructed. Variation of the free parameter  $\delta$  mimics the error resulting from the freedom in the choice of the area used for retrieval of the experimental phase shift in the cluster. Fig. 1 shows the inferred MIP plotted as a function of cluster thickness for different choices of  $\delta$ . An incorrect choice of  $\delta$  yields deviations in the MIP of  $\pm 10$  V. For further investigations we took  $\delta = 0.55$ , since deviations were lowest for this choice. For each cluster, a series of calculations starting from an [001] orientation for tilts about [100] and [010] were performed for specimen tilt angles in a square array of range  $\pm 12^\circ$ . The resulting variation in the apparent MIP is visualized in Fig. 1 in the form of colored ellipses. Strong outliers due to dynamical diffraction at zone axis orientations have been excluded from this visualization. Fig. 2 depicts the dependence of MIP on cluster diameter for clusters with and without relaxed surfaces, as well as with and without an additional surface layer. (The additional O layer does not resemble the true chemical state of the surface of the cluster, but only accounts for the additional phase shift due to adatoms). In the present calculations only a combination of a relaxed surface and an additional phase shift due to an adatom layer can come close to accounting for the experimental measurements of MIPs of about 60-80 V [3] for clusters with sizes smaller than 1 nm. It should be noted that many of the other possible factors described above could also account for the reports in the literature. These possibilities will be discussed in full elsewhere.

1. M. Wanner et al., *Ultramicroscopy*, **106** (2006), p. 341.
2. S. Ichikawa et al., *Jeol News*, **38** (2003), p. 6.
3. R. Popescu et al., *Phys. Rev. B*, **76** (2007), p. 235411.
4. M. Gajdardziska-Josifovska et al., *Ultramicroscopy*, **50** (1993), p. 285.
5. M. O'Keefe and J. C. H. Spence, *Acta Cryst. A*, **50** (1993), p. 33.
6. H. Lichte et al. *Ann. Rev. Mater. Res.*, **37** (2007), p. 539.
7. M.S. Daw and M. I. Baskes, *Phys. Rev. Lett.*, **50** (1983), p. 1285.
8. S. Plimpton, *J. Comp. Phys.*, **117** (1995), p. 1
9. A. Rosenauer and M. Schowalter, *Springer Proc. Phys.*, **120** (2007), p. 169.
10. A. Weickenmeier and H. Kohl, *Acta Cryst. A*, **47** (1991), p. 590.



**Figure 1.** Evaluated MIPs plotted as a function of cluster diameter for octahedral, cuboctahedral und cubic clusters. Comparison of dependencies for different parameters  $\delta$  shows the sensitivity of the evaluated MIP to the region used for evaluation of the MIP. Ellipses depict the range over which the MIPs varied for a cluster with different orientations. Orientations leading to strong deviation due to dynamical diffraction were not visualized. The dashed green line is the MIP of the scattering data set used for the simulations.



**Figure 2.** Dependence of MIP on the cluster diameter for unrelaxed unoxidized, relaxed unoxidized, unrelaxed oxidized and relaxed oxidized clusters..