HAADF-STEM simulations of gold nanoclusters utilizing site-dependent Debye-Waller factors

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Keywords: HAADF-STEM, Nanoclusters, Simulation

The study of nanoclusters has been motivated by their importance to the catalysis industry. Whilst there has been found to be a strong correlation between particle size and catalytic activity, the relationship is yet to be fully understood [1]. Gold is of specific interest for its capacity to function as a highly effective catalyst for the oxidation of carbon monoxide in nanocluster form, in stark contrast to the inert nature of bulk gold.

The structural characterization of nanoscale specimen is paramount to studying the causes of transitions from bulk to nancluster structural motifs and the concurrent changes in catalytic properties. The use of electron microscopy techniques in producing atomic resolution images in two-dimensions is now well established but extending their abilities to determining the three-dimensional structure of specimens is more challenging. In 2008, Li *et al* reported the successful three-dimensional characterization of gold nanoclusters[2]. This work relies on the relationship between HAADF-STEM image intensities and the number of atoms in the cluster as described by Young et al. [3]. In Li's work, 3D characterization was achieved through the comparison of experimental images with simulated images of test structures. A good match between experimental and simulated images was found, however, there were discrepancies which were attributed to a simplistic consideration of thermal vibrations in the image simulations.

In this work, image simulations are produced with a more extensive approach to the thermal vibrations of atoms. Conventionally, thermal diffuse scattering is accounted for using frozen phonon algorithms in which a number of STEM images of static perturbed structures are averaged to generate the final image. The perturbed structures are generated using random offsets of atomic positions weighted by Debye-Waller factors. This method has been found to work well for bulk crystalline samples. However, molecular dynamics simulations suggest that this method will be less well suited to nanoscale structures in which the variety in local conditions such as coordination and bond-length makes the use of homogeneous, isotropic Debye-Waller factors inappropriate. Fig.1 shows the a Marks-decahedron cluster of 887 gold atoms with one additional surface atom which clearly illustrates the variety in local conditions within a single cluster. In the new technique reported here the variety and anisotropy of thermal vibrations are accounted for by taking frozen structure configurations during the course of molecular dynamics simulations rather than using randomly generated configurations.

Fig.2 shows a simulated HAADF-STEM image of a gold Marks-decahedron nanocluster, generated using the new technique. Molecular dynamics simulations were performed using the DL_POLY package [4] with interatomic interactions modelled by an empirical Gupta potential [5]. The simulations were performed at a temperature of 300K for 0.5ns including an equilibration period of 0.1ps. A Hoover NVT ensemble was used. The HAADF-STEM images were simulated using a program based on the multi-slice technique of Kirkland [6]. The STEM simulation program utilizes highly parallel GPU architecture which reduces simulation times so that images such as fig.2 can be produced in a matter of hours on a desktop PC fitted with a Nvidia Tesla C2075 GPU. The simulations were performed for an accelerating voltage of 200keV, a convergence angle of 20mrad, defocus of 52 Å with an annular detector with response at an angular range from 90 to 230mrad.

In summary, *ab-initio* molecular dynamics simulations have been successfully used to account

for the thermal motion of atoms in an extensive manner in configuration-averaged multi-slice simulations for high-angle annular dark field scanning transmission electron microscopy of nanoclusters.

References

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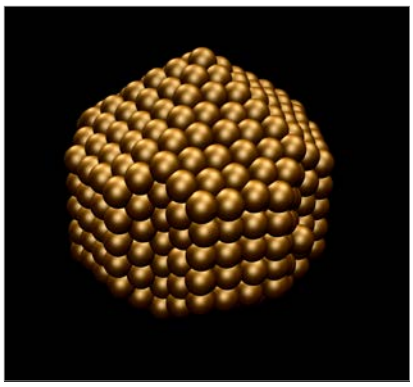

Figure 1. *887 atom Au nanocluster with Marks-decahedron structure illustrates the diversity of local geometries within a single cluster*

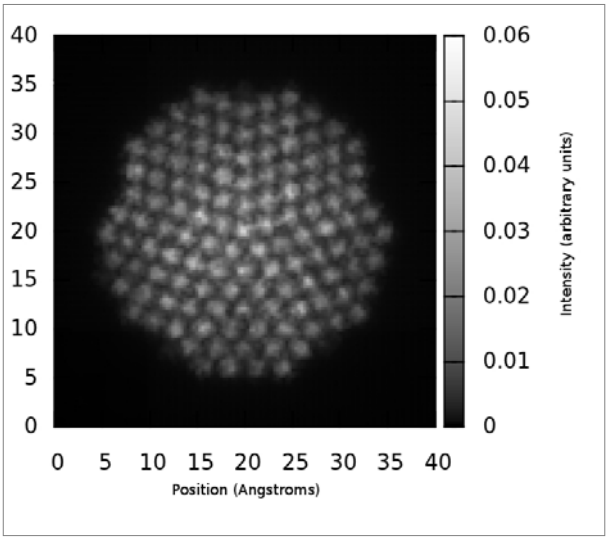

Figure 2. *Simulated HAADF-STEM image of Marks-decahedron gold cluster utilizing molecular dynamics-based frozen phonon algorithm*