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Integrated Computational and Experimental Structure Determination for Nanoparticles

Min Yu[1], Andrew B. Yankovich[1], Amy Kaczmarowski[1], Dane Morgan[1] and Paul M. Voyles[1]

[1.] Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA.

Atomic details of nanostructures are important to materials performance for catalysis, solar energy, optoelectronics, sensing and many other fields. However, solving the three-dimensional (3D) structure of nano-scale materials at the atomic level is challenging, especially for predicting metastable, out-of-equilibrium systems. Scanning transmission electron microscopy (STEM) provides structural images of materials at atomic resolution, but a single image provides only a two-dimensional (2D) projection of the structure, and three-dimensional tomographic imaging at atomic resolution with single-atom sensitivity remains challenging. Experimentally driven structural refinement approaches typically rely on minimizing the error between forward simulation from atomic models and the experiment data. Such optimizations are difficult with limited data and rely on knowing good initial guesses for the structure. They also typically make no direct use of information about the energy of the potential structures. Purely computational techniques, such as genetic algorithms (GAs) [1], have proven to be extremely effective at predicting the ground state structures of a wide range of complex structures, including clusters, crystals, and grain boundaries. However metastable configurations are often neglected by methods designed to find the global minimum of the system energy.

We have developed an integrated GA optimization tool [2] that can reverse engineer the 3D structure of a nanoparticle by matching forward modeling to experimental STEM data [3,4] and simultaneously minimizing the system energy. This tool integrates the power of GAs for complex optimization and can find metastable structures guided by experimental data. We validated the algorithm by reproducing the structure and orientation of stable and metastable 309-atom Au nanoclusters using simulated STEM images with better than 0.5 pm fidelity for every atom. Then we determined the 3D structure of a ~6000 atom Au nanoparticle on amorphous carbon substrate based on a high precision STEM image [5].

STEM experiments were conducted on a FEI Titan microscope equipped with a CEOS probe aberration corrector. The experimental high angle annular dark field STEM image in Figure 1a shows a [110] oriented, ~8nm diameter Au nanoparticle having 2 distinct grains separated by a $(\bar{1}12)$ twin boundary. In order to achieve better image signal to noise ratio and remove image distortions caused by instabilities in the probe and sample during image acquisition, we acquire a series of STEM images and utilize the non-rigid (NR) registration technique [4]. Inside the optimization, we simulate the STEM image using a computationally efficient convolution method with a non-linear scaling factor to counteract the over-estimation of intensities in thick sample, instead of frozen-phonon multislice simulations [3]. Based on the STEM image, we started GA optimization from a family of single crystals along Au (110). After 4000 generations, we find a structure of 4998 atoms shown in Figure 1b, which shows the same ellipsoid shape, twin boundary, and surface facets as experiment. The atomic column positions in the experimental and simulated STEM images differ by 0.18 Å on average (Figure 1c). The fitness function decays monotonically through the GA evolution, while the energy term fluctuates (Figure 2). Overall, the integrated GA tool successfully optimizes the metastable Au nanoparticle atomic

positions to match experimental STEM data while simultaneously achieving a locally stable structure. [6]

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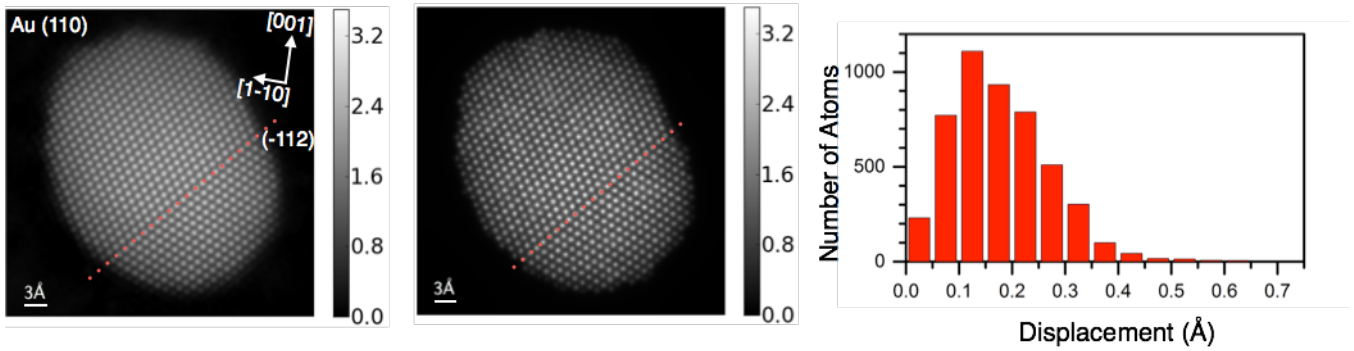

Figure 1. Experimentally measured STEM image of Au nanoparticle (left); Simulated STEM image of the GA optimized structure (middle); Comparison of atomic column displacements between experiment and simulation (right).

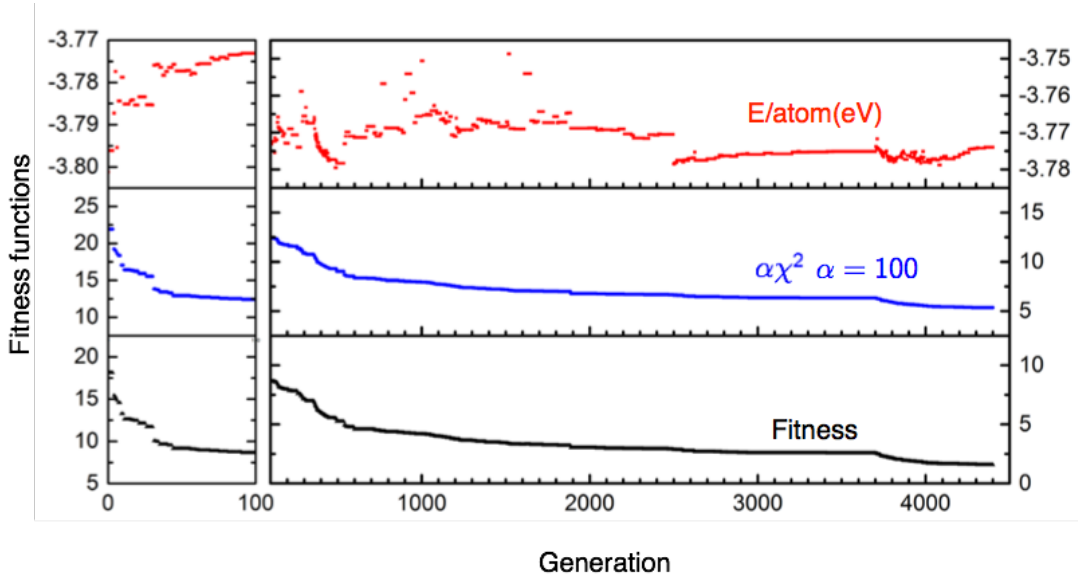

Figure 2. The energy, discrepancy between simulations and experiments, and total cost function over the course of the GA optimization.

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