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A Model Based Method for Tomographic Reconstructions of Nanoparticle Assemblies

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Small angle X-ray scattering is a primary tool for resolving the crystal structures of self-assembled nanoparticle superlattices [1]. However, it is not quite informative when periodic lattices are broken into clusters due to their inhomogeneity. Therefore, it is desirable to develop a method to rapidly reconstruct the three-dimensional architecture of cluster ensembles in real space. Conventional tilt-series electron tomography is well poised for this task; it is, yet, limited by its low throughput. For instance, a reasonable reconstruction generally requires 70-140 tilt images, which would need 40 minutes or 2-4 hours to record a BF-TEM or an ADF-STEM tilt series, respectively. In addition, the intensity of BF-TEM images is not a linear or any simple monotonic function of the sample thickness particularly when gold nanoparticles are imaged; this could dramatically lower the resolution and interpretability of the reconstructed tomograms. Here, we present a model based tomographic method that only relies on the projected centroids of the nanoparticles and bypasses the image intensity. This method only requires 5-10 tilt images and it is useful for calibrating a TEM goniometer and field/scan distortions.

This method is based on measuring the geometric centers $(x^i(\theta), y^i(\theta))$ of nanoparticles in the projected images as a function of the tilt angle θ, where the superscript i is the label for each individual particle. The frame of reference/rotation axis can be shifted to a specific particle n by a pre-subtraction procedure, i.e., $\left(x^i(\theta), y^i(\theta)\right) = \left(x^i(\theta), y^i(\theta)\right) - \left(x^n(\theta), y^n(\theta)\right)$. The three-dimensional (3-D) positions of the particles at zero degree tilt in the particle n reference frame can be retrieved by a nonlinear least squares fitting of the below equation.

$$\begin{pmatrix} x^i(\theta) \\ y^i(\theta) \\ z^i(\theta) \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x_0^i \\ y_0^i \\ z_0^i \end{pmatrix} \quad (1)$$

where, α is the image/scan rotation with respect to the projected tilt axis, and β is the offset angle between the 3-D tilt axis and the projection plane (Fig. 1a). There are five unknowns— α, β, (x^i_0, y^i_0, z^i_0) —in the above equation. At each tilt, two linearly independent equations can be provided— $(x^i(\theta), y^i(\theta))$ are observables. Therefore, in principal, only three tilt images are needed to solve all the unknowns; in practice, however, a couple of tilt images are needed to average out drift and scan distortions.

Fig. 1 shows the measured and modeled trajectories of gold nanoparticles supported on a carbon grid. The actual 3-D tilt-axis has a 1.5 degree take-off angle from the projection plane as evidenced by the $(x^i(\theta), y^i(\theta))$ plot in Fig. 1b. Using the model based fitting method, particles positions and their rotational trajectory can be reconstructed (Fig. 1c). This method can be further applied to a hetero-particle system (Fig. 2). Using prior knowledge of the system—i.e. the center particle of the cluster is cubic—a model based reconstruction of the seven-particle cluster can achieved (Fig. 2c).

References
[1] Y. Zhang, F. Lu, *et al*, Nature Nanotechnology, **8,** 865 (2013)
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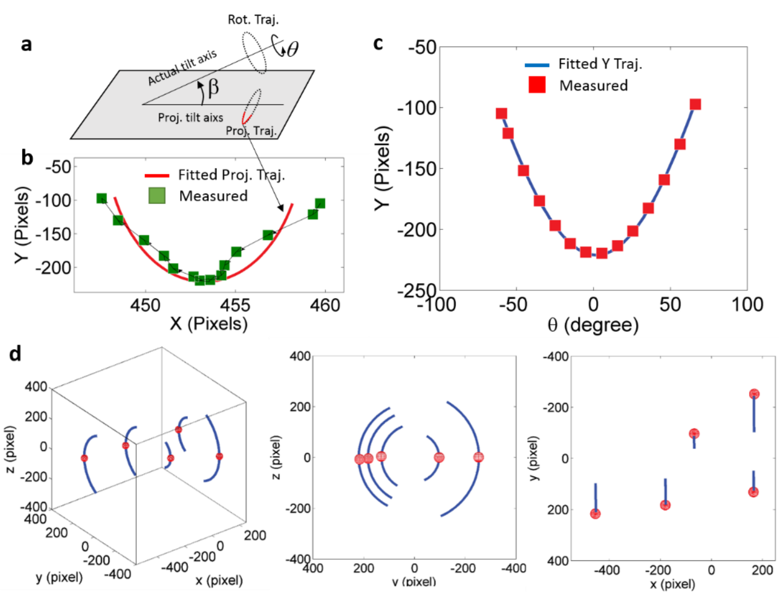

Fig. 1. Model based fitting of the 3-D particle positions using Eq. (1). (a) A schematic plot showing the geometry of the actual tilt axis and the projected tilt axis. (b) Measured and modeled projected trajectory of a particle from -60 degrees to +66 degrees. The offset angle between the tilt axis and the projection plane is determined to be 1.5 degrees. (c) The projected Y movement of the particle overlaid with the fitted model. (d) Reconstructed 3-D positions of five nanoparticles.

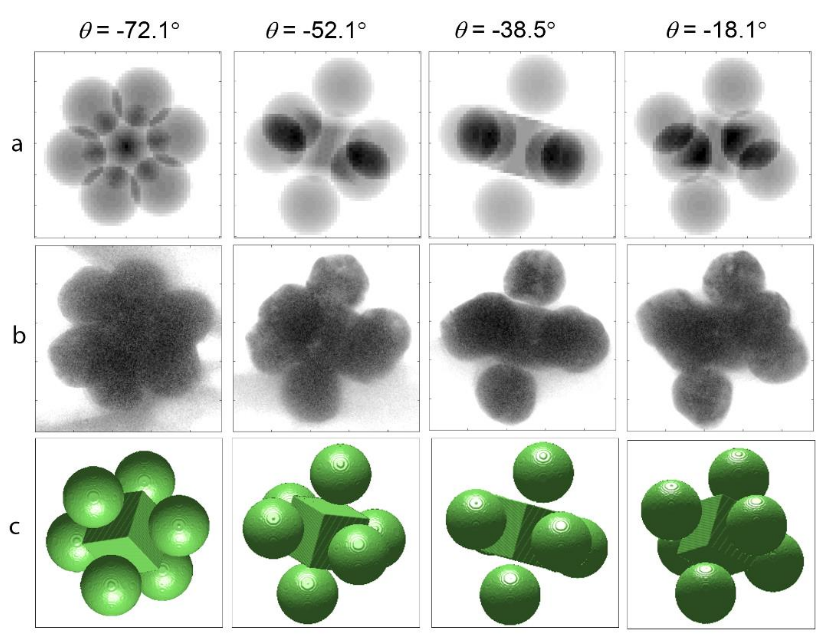

Fig. 2. A model based reconstruction of a heteo-particle cluster. (a) The modeled projection images at specified tilt angles. (b) BF-TEM images recorded in a 120 keV TEM. (c) The isosurface rendering of the reconstruction at the specified tilt angles.

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