Quantitative techniques for aberration corrected HAADF STEM of nano-materials

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Abstract. Electron microscopy is a powerful tool for directly visualising structure and with the advent of aberration correction, atomic columns and even individual atoms are now routinely imaged. HAADF STEM offers a great sensitivity to atomic number - the well known Z-dependence in the measured intensity. By calibrating the HAADF detector, putting images on an absolute scale, and using an absolute HAADF scattering cross section comparison, it is possible to compare experiment with simulations in a parameter robust manner. We show how the cross section method relieves the use of a fitting parameter for the probe and is insensitive to experimental parameters such as defocus. Finally, we test our analysis method using a 2-dimensional nano-structure to identify the composition of atomic columns in thin layered materials. We also discuss some of the potential sources of error in quantifying small, thin, low-scattering and beam sensitive samples.

1. Introduction
Using a high angle annular dark field (HAADF) detector in the scanning transmission electron microscope (STEM), it is possible to directly image the atomic configuration of nanostructures. This technique has often been chosen for heavy elements on light supports or structures with a combination of light and heavy elements for the strong correlation between atomic number and imaged intensity, known as Z contrast. The major advantage of HAADF STEM over conventional high resolution transmission electron microscopes (HRTEM) is its incoherence. In HAADF STEM there are no contrast reversals often seen in HRTEM due to the phase contrast nature of the imaging [1]. However, though it offers many advantages, meaningful quantitative compositional information is less than straight-forward to extract from HAADF images because intensities are dependent on both composition and thickness [1].

In this paper we show that by comparing detector calibrated experimental images with simulations, it is possible to compare the absolute scattering from a thin layered sample without fitting parameters or modelling of the whole structure. We show that this method is robust to experimental parameters such as defocus, which are often difficult to determine accurately. Finally, we discuss briefly the main sources of errors in routine HAADF quantification of beam sensitive samples.

2. Absolute HAADF Scattering Cross Section
“Cross sections” is a term often used in X-ray and neutron diffraction and also electron energy loss spectroscopy in electron microscopy, but not applied to image analysis. Earlier studies using HAADF-STEM showed interest in the idea of cross sections but without detailed description of the calibrations.
necessary to fully quantify them [2] and without the resolution needed to isolate individual atomic columns [3]. Since detector calibrations have been formalized to put imaging on an absolute scale and careful matching of experiment to simulations shown to be possible [4], other similar parameters have been used such as column mean-intensities to match experiment and theory for the heights of individual columns [5].

Since HAADF STEM is an incoherent technique by the nature of its detection method [1], we can consider the final image as a convolution in two dimensions of the probe \( P(r_0 - r) \) and an object function \( O(r) \):

\[
I(r_0) = \int P(r_0 - r) O(r) d^2r
\]

At atomic resolution, so long as the columns are well resolved and the sample is sufficiently thin such that there is minimal “cross-talk” between columns, this can allow us to understand the image intensity intuitively: once the image intensity is calibrated as a function of the incident beam [5], we can then integrate around an isolated column contained in pixels \( i \) each of area \( A \) and intensity \( I \) such that:

\[
\sum_i I_i A_i = \int \sum_i A_i P(r_0 - r) O(r) d^2r
\]

Due to the fact that the detector calibration expresses the intensity as a fraction of the incident probe, the summed probe function \( \sum_i A_i P(r_0 - r) \) normalises to 1. Thus, the summed object function of that column is measured as:

\[
A \sum_i I_i = \int O(r) d^2r
\]

What remains is an integration of the object function which has no dependence on the probe and has dimensions of \([L^2]\). We call this parameter the absolute HAADF scattering cross section [5] and can use this to compare simulations to experiments without concerns about the probe.

3. Parameter Robustness

When comparing experimental images to simulations quantitatively, some experimental parameters that affect the imaged intensity must be known accurately and thus their identification and calibration is vital. Some of the most influential and difficult to determine experimental parameters are defocus and source effects of the finite probe [7]. Optimum focus is usually found by manual adjustment of experimental conditions or choosing the image which maximises contrast in a through focal series. However, the latter often requires prolonged exposure and issues of damage in beam sensitive samples are paramount, and the former is prone to human error. Thus it is essential to have a metric for comparing experiments to simulation which is robust to this experimental parameter.

This work was originally born out of investigation of catalyst nanoparticles of Pt/Pd. Thus we used an absorptive potential multislice simulation which takes into account phonons and TDS and is ideally suited for thin and small nano-materials. Simulations show that the peak value for a single atom drops significantly (Figure 1) with defocus, as is expected when imaging with a broadened defocused beam. However, the cross section is insensitive to defocus so long as the area of column integration is sufficiently such that the entire column is included.

Such large variations in peak intensity over a small range of defocii means that accurate comparison with simulations is limited unless an independent measure of that parameter is done. Cross-sections are more robust.

However, other parameters such as local sample mistilt, accurate knowledge of the Debye-Waller thermal factor still remain as concerns in the object function. We note also that the incoherence is only transverse and this approach is no longer valid for thicker crystals, especially where cross-talk and probe tails mean that imaged intensity cannot be clearly attributed to one atomic column.
4. Thin 2D Layered Material

MoS$_2$ is a thin 2D layered material and thus offers the ideal test-bed for elemental identification, as shown previously [8]. We apply our method to show that this parameter robust method allows for identification of elements by matching experiment to theory. The sample was prepared by liquid exfoliation [9] and imaged using a C$_s$-probe-corrected JEOL ARM-200F at 80kV with inner and outer detector angles of 55mrad and 180mrad respectively. The small probe of the C$_s$-corrected instrument ensures that individual columns can be well resolved, eliminating issues of cross-talk. The detector was calibrated for quantitative imaging using different probe currents to allow the nonlinear digital to analogue converter gain to be kept constant between detector maps and imaging while also allowing a good dynamic range to be used for the imaging of such a low scattering sample [10]. We used 2.6pA for the detector map and 33.8pA for imaging, giving a ratio of 1:13. The probe current was measured immediately prior to and post imaging both the detector and sample, with a Faraday cage, to ensure that there was no significant probe current decay from the cold FEG.

Careful background subtraction was necessary since the sample showed contamination in some areas (Figure 2, bottom) which would greatly affect the measured cross section value. Four line profiles were taken from the vacuum into the monolayer (Figure 2, dashed lines) and the vacuum “black level” was subtracted. The intensity between the columns is attributed to probe tails and thus included in the final cross section value. Only atoms far from edges and steps were considered as areas close to the edges of thin 2D sheets often have ad-atoms [8]. Only those in the top half of the image were investigated, where the sample was cleaner.

The measured values from 42 atoms gave a mean cross section of 0.0098Å$^2$. The main sources of calculable errors were due to the accuracy of the pico-ammeter in the measuring of the small 2.6 ± 0.1pA current used to map the detector and also the large variance of integrated intensities due to noisy data. The standard deviation of the cross section was ±0.0031Å so a large sample size of Mo atoms was taken and the measured cross sections averaged. Thus the error on the mean was much lower: ±0.0006Å$^2$.

Comparison with theoretical cross section values revealed that the mid area atoms were single Mo (calculated cross section of 0.0092Å$^2$), confirming that this is a monolayer. It was not possible to identify the S$_2$ as the columns of S$_2$ were not well resolved above the background. They would have had a much smaller cross section of 0.0022Å$^2$.

Cross sections of other columns (Figure 2, right) showed that these were either two S on top of one Mo or one Mo on top of two S, confirmed by the open hexagon structure of multilayer MoS$_2$. It is not possible to distinguish between the two stacking configurations as in such thin materials, channelling of the probe has not been established. Thus the scattering from both stacking orientations is identical.
5. Conclusions
We have shown that analysis of quantified HAADF STEM images can be carried out by summing around well resolved columns and that this can be understood very intuitively in terms of the cross-sections of scattering. We have shown that this approach is more robust to imaging parameters, such as defocus, which may be experimentally difficult to determine. This is especially useful when imaging conditions are limited such as for beam sensitive specimens so rapid acquisition of images is necessary before beam damage occurs.

Applying this analysis to an ideal sample of a thin 2D layered material of MoS$_2$ prepared by liquid exfoliation; we show that it is possible to match with excellent agreement the cross sections of Mo in experimental images with simulations of single atoms, removing the need to do large, time consuming calculations of the whole image. We highlight some of potential sources of error in quantifying images, especially in detector calibrations and background subtraction.

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