The nanoworld through aberration corrected lenses

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Abstract The advent of aberration correction for electron microscope lenses has produced a significant advance in the improvement of resolution in microscopy. This improvement, while significant in itself, promises to have its most profound impact in materials science when it delivers quantitative information to challenge models and modellers. This capability for an electron microscope-modelling synergy to deliver useful results at the atomic level is not yet firmly established. For this reason, one of the major challenges for electron microscopy in materials science over this decade is to study systems where electron microscopists and modellers can work collaboratively. This paper explores some examples.

1. Microscopy and modelling
The history of microscopy has many important milestones, but certainly the most significant of the past decade is the realization of aberration corrected electron lenses. Unlike the step change in resolution which electron lenses brought, the advantages of aberration correction are being more slowly realized and even more slowly brought to bear upon solving materials problems.

Discussions about aberration correction should involve far more than its effect upon resolution, but that is a reasonable place to start. The improvement in achievable resolution, however defined, while significant in itself, promises to have its most profound impact in materials science when it delivers quantitative information (e.g. atom positions, occupancy, local strain) to challenge models and modelers. This is because reliable predictive modeling is a powerful tool for developing new materials, revealing how a material might organize itself and respond to its environment – stress, temperature, local inhomogeneities. The reliability of modeling at the atomic scale is often in question because of the many parameters used (e.g. cell size, potentials, code), and it is this which can be tested against precise and accurate atomic-level experimental data (e.g. images) or high energy resolution EELS. Confirmation of modeling capability gives confidence in predictive modeling. For this reason, a major focus and one of the major challenges for electron microscopy in materials science over this decade should be to study systems where electron microscopists and modelers can work collaboratively, but where the free parameters (i.e. excuses for disagreement) are few.
Success in this collaboration will require an objectivity about the interpretation and reporting of results which has, unfortunately, been somewhat lacking in our field in recent years. The pressures that the culture of “impact factors” brings sometimes result in the objective reporting of uncertainty, essential to the effective comparison between modeling and experiment, being lost. As an example, progress requires a clear reporting of experimental errors and their basis of determination, and, on the modeling side, a thorough understanding of the limitations of the code used. The increasing use of short Letters, with no follow-up substantive paper, contributes to this problem; however the opportunities for depositing the tedious but essential details on archived sites, or in methodology sections or supplements as an appendix to a paper, offer a solution and should continue to be explored.

Resolution and visibility

Rayleigh’s criterion is always a starting point for considering resolution, even though it was established for a topic far from the consideration of electron microscope images – the distinguishability of two stars [1] – which accounts for the frequent reappraisal of a suitable definition for our subject. Many use ad hoc definitions to suit particular circumstances, but O’Keefe [2] has argued that the determination of resolution in atomic resolution electron microscopy should be based upon the distinguishability of atoms or atoms columns that exist in the sample, and by this definition resolution beyond the Rayleigh criterion has been achieved (e.g. [3]). Provided that “distinguishability” is well-defined, this is an objective approach. However “distinguishability of atoms or atoms columns” is not the same as “separation of atom peaks in the image” [2] unless one is certain that peak positions accurately reflect atom positions. Unfortunately the traffic-stopping outcome if this assumption cannot be made sometimes allows the traffic to flow where it should not. The precise determination of atomic positions in strained systems or studies of defect structures which depend upon a direct relationship between image intensity and projected potential are areas where this comment applies in particular. The question should be, what accuracy and precision is necessary to solve a particular problem? In this context, chasing resolution for its own sake is a sterile activity.

The ability to not only reduce but also choose particular values of aberrations has opened up the possibility of tuning lenses (TEM) and detectors (STEM) for particular purposes – both to improve resolution and to improve contrast. With the availability of computer codes (e.g. multislice codes) to simulate both STEM and TEM images, simulated images from model structures can be compared with the image, or with a set of images, to differentiate between candidate models, even for relatively complicated materials systems. This can be done even when there is no obvious relationship between the image detail and the model, even though then many parameters have to be determined (e.g. sample thickness, orientation, defocus, lens aberrations). Of particular interest, however, are those situations in which the image is directly interpretable in terms of structure. For TEM, we consider image formation as a two step process – formation of the exit wave function $\psi(r)$ and transfer of the exit wave function to the image, involving the aberration function $\chi(u) = 0.25C_3 \lambda^3 u^4 + 0.5 \Delta f \lambda u^2$, with the parameters having their usual meanings. For phase objects (i.e. $\psi(r)$ $\psi^*(r) = \text{constant}$), visibility of any detail in
the image depends upon using $\chi(u)$ to shift the phase of some Fourier components at frequency $u$. If the sample is sufficiently thin to be a weak phase object and if the phase is proportional to the projected potential, then a uniform phase shift for all $u$ (except $u=0$) results in an image wave function in which the contrast is linearly proportional to the projected potential. In HRTEM the value of defocus $\Delta f$ is generally chosen to make the aberration function $\chi(u) \approx \frac{\pi}{2}$ over as large a range $\Delta u$ of $u$ as possible, as in phase contrast light microscopy using a phase plate. Despite the attractive simplicity of this argument, the majority of samples, even those studied by HRTEM, are not weak phase objects. Then the transfer function reports the phase shift at frequency $u$ caused by aberrations and defocus. For some purposes, (e.g. C nanotube imaging) uniform transfer of frequencies might be optimum, but, since there is often a complex relationship between the exit wave and the object, the ability to differentially phase shift particular frequencies could be useful. This is nowhere better illustrated than in the technique of through-focus series reconstruction, in which a set of images, each with particular frequencies enhanced, is used to reconstruct the complex exit wave function.

Maximum resolution is not the only aim of HRTEM – visibility of high resolution detail is also important. The recent work of Jia et al [4] discusses the image intensity

![Defocus-thickness map for [110] SrTiO$_3$ for $C_s = -40$ micron (200kV) (courtesy S-J Shih)](image)
from a weak phase object in the case where $\chi(u) \sim -\pi/2$ over a wide range of $u$, achieved with negative $C_s$ and defocus positive. The important outcome was that atomic columns of low-Z atoms showed high relative contrast using this technique, as seen in Figure 1 for [110] SrTiO$_3$ for values of $C_s$ (- 40 micron) and defocus (10 nm) (rather than $C_s$ positive and defocus negative) set to give $\chi(u) \sim -\pi/2$ for the JEOL aberration corrected MCO2200. It is seen that the map is a good representation of the projected structure up to 5.5 nm, after which the Sr columns fade.

Jia et al [4] emphasized that such an analysis is only valid for very thin samples, but their full dynamical simulations supported the idea that negative $C_s$ combined with positive defocus can be used to enhance contrast from light atom columns. Other authors have discussed the opportunities offered for enhancing contrast and/or resolution by using negative $C_s$. Figure 2 shows the thickness defocus map for [001] SrTiO$_3$ for a small negative $C_s = -2 \mu$ (a value close to that proposed by Chang et al [5] for optimising the contrast transfer function for the JEOL 2200MCO).

![Defocus-thickness map of [001] SrTiO$_3$ for $C_s = -2\mu$ (courtesy S-J Shih)](image)

It is seen that for the thicknesses of ~19.5 nm (well beyond the validity of the weak phase object approximation) and defocus near zero, only O columns appear bright. These are the parameters chosen by Shih [6] to successfully study the atomic structure of interfaces in SrTiO$_3$.  

![Sr Ti-O O](image)
Urban et al [7] commented upon the observed advantage of the negative $C_s$ technique for thicker samples in terms of the sample being a mixture of a phase object and an amplitude object. For the amplitude object, where the exit wave amplitude (at appropriate thicknesses) is maximum (or minimum) at the atomic columns (through channeling), then perfect transfer ($\chi(u) = 0$) is optimum. So, they argued, for the sample of intermediate thickness, optimum contrast is achieved for some $C_s$ and defocus intermediate between those appropriate for the weak phase object (-40 $\mu m$ and 10 nm respectively in their microscope) and the thick sample (zero $C_s$ and zero defocus).

Aberration correction also provides new opportunities for improved contrast and resolution in STEM, by allowing use of larger beam convergence and detector angles. For example recently Okunishi et al [8] reported improved imaging of light elements in STEM using an annular detector positioned within the bright field cone.

### Interfaces

Planar interfaces provide possibilities for collaboration between modeling and high resolution electron microscopy, of the kind discussed above, particularly if the crystallography of the material on either side of the interface is well-characterised.

![Figure 3](image)

**Figure 3** High resolution HAADF images (periodically averaged parallel to the interface) of rare-earth dopants on {100} faces of Si3N4 grain boundaries [9]

| Position | $x$ (nm) | $y$ (nm) | $z$ (fractional coordinate) |
|----------|----------|----------|-----------------------------|
| La(1)    | 0.35 ± 0.02 | 0.50 ± 0.02 | 0.25                        |
| La(2)    | 0.72 ± 0.03 | 0.61 ± 0.02 | 0.25                        |
| La(3)    | 0.71 ± 0.04 | 0.80 ± 0.03 | 0.75                        |
| La(4)    | 0.34 ± 0.02 | 0.84 ± 0.04 | 0.75                        |

| Position | $x$ (nm) | $y$ (nm) | $z$ (fractional coordinate) |
|----------|----------|----------|-----------------------------|
| Lu(1)    | 0.52 ± 0.02 | 0.54 ± 0.02 | 0.25                        |
| Lu(2)    | 0.69 ± 0.02 | 0.55 ± 0.02 | 0.25                        |
| Lu(3)    | 0.81 ± 0.05 | 0.81 ± 0.04 | 0.75                        |

**Table 1** Coordinates of dopant atom sites on interfaces in Figure 3 (the errors shown are standard deviations; the coordinate system is marked in Figure 3).
As an example, Figure 3 shows an interface between a Si$_3$N$_4$ grain and a glassy intergranular pocket (admittedly, the glassy phase was not well-characterised – see below). The question to be answered initially was whether dopant atoms (in this case Lu and La) segregated to the boundary, and if so, whether to particular crystallographic sites. As can be seen from the figure, La and Lu do segregate to specific sites (different for the two dopants). By imaging in two directions in the boundary plane normal to each other, Winkelman et al [9] measured the 3-D coordinates of the dopant sites, as shown in Table 1. They paid particular attention to the error estimates, to facilitate comparison with modeling. Early attempts to predict these observed positions through modeling were only partially successful, the problems being attributed to how to account for the interatomic potentials due to the glassy intergranular film abutting the boundary and surrounding the dopant atoms. Recently Painter et al [10] have reported new modeling results in better agreement with the experimental observations.

Grain boundaries in SrTiO$_3$ have proved to be a fertile ground for refining structures by comparing experimental and model structures. Dudeck et al [11, 12] have used through focal series reconstruction to investigate the structure of the Σ3 {112} GB, for which there were two competing models of indistinguishable energy. A detailed quantitative comparison of experiment and theory (DFT) of the GB led to a refined structural model of the GB plane [12]. Shih et al [6, 13] made a direct comparison of individual experimental images and images simulated from model structures to solve a problem concerning the role of planar {100} GB surfaces in abnormal grain growth in SrTiO$_3$. In this material, many abnormal grains, important to grain growth during sintering, have {100} surfaces which are observed to be “atomistically planar” (e.g. Figure 4). HREM imaging using the conditions suggested by Figure 2 to enhance the contrast on O columns allowed a detailed study to be made of the atomic structure of these surfaces [12]. Comparison of experimental and simulated images led to the conclusion that the {100} surfaces have significant Ti vacancies, which could play a role in explaining the unexpected mobility [14] of these faces.

Nanoparticles
Nanoparticles, and in particular catalytic nanoparticles, are a fertile ground for collaboration between modeling and imaging. For single element particles (e.g. Au, Pt),
there is the question of structure, particularly surface structure, and of strain. In the case of alloys, the distribution of atomic species within, and especially at the surface of, the particle is of primary interest. A study of elemental distribution in GeSi quantum dots [15] demonstrated the influence of strain and surface energies on such distributions, and warned of ignoring strain or inhomogeneous distribution in analyzing images from nanoparticles. Recent studies of elemental distributions in nickel-doped and yttrium-doped ceria particles [16] have shown layering to be determined mainly by diffusion of the precursor ions, which in turn can be related to their hydration energy. These results make it clear that any analysis requiring the interpretation of images as though they show the projected potential needs to be approached cautiously, and especially for images taken along zone axes. The greatest advances in understanding and then controlling nanoparticle structures will be achieved when tomographic or confocal imaging [17] give reliable 3D structures at the atomic level.

**Selected area diffraction**
The contribution of high resolution microscopy to understanding the structure of amorphous materials has been relatively small, despite the importance of amorphous phases in controlling the growth and properties of many technologically important materials. The reason is clear – the difficulty of interpreting images of amorphous material at or near the atomic level. Fluctuation electron microscopy appears to be sensitive to medium range order [18], even though it cannot be said to give a measure of it. Short range order can now be studied to high precision and accuracy using electron diffraction combined with RMC refinement of models based on DFT [e.g. 19, 20]. Attempts to investigate inhomogeneities in amorphous structure at the nanoscale were hindered by the dispersion of the selected area in the sample plane caused by spherical aberration (an aberrated objective lens causes the selected area diffraction intensity at scattering angle $\alpha$ to arise from an area of the sample displaced by $C_\alpha \alpha^3$). This obstacle is overcome in an aberration corrected system, and has proved to be of importance in the study of amorphous nanovolumes by RDF electron diffraction analysis, where diffraction data is collected to high scattering angles [21].

**Conclusion**
The aberration corrected high resolution electron microscope is a tool for investigating the structure of materials to below the 1 Å level. It is however a tool which can as easily mislead as it can clarify. Because it gives results in pictorial form, they can be seductively misleading, especially to the biased eye. To use the instrument confidently, it is essential to have a thorough understanding of diffraction and imaging theory, the basis of which is clearly laid down in the literature of the past 50 years. Research into this literature provides a means for avoiding many of the pitfalls of interpretation which await the unwary.

At the same time, properly used, the high resolution microscope gives quantitative data about structure suitable for linking into, and challenging, atomistic models. In combination, high resolution microscopy and modeling can reveal the structure of the nanoworld at an unprecedented level of detail.
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