Imaging Materials at the Space-Energy-Time Limit

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At its core, Materials Science and Engineering is concerned with developing an understanding of fundamental structure-property relationships of materials so that performance can be traced back to atomic-scale features and so elements of rational processing to obtain desired behaviors can be applied. In order to generate a comprehensive view of how atomic-scale structure and nanoscale morphology influence macroscopic behaviors, a large range of space, energy, and time must be explored. As an illustrative example, if we take the speed of sound as the limit at which materials can undergo change (*e.g.*, transformation or deformation), and if we wish to study the origins of such phenomena, then we must operate on the combined angstrom (10^{-10} m) and femtosecond (10^{-15} s) scales. Owing to decades of research and development, transmission electron microscopy (TEM) is now capable of (dare I say) routinely reaching angstrom and even sub-angstrom spatial scales. Indeed, imaging atoms is now fairly commonplace, and many consider modern TEM spatial resolution to have reached the limit of what most want and need for materials research. Likewise when considering energy resolution, those familiar with TEM will point out that, in addition to imaging and diffraction, spectroscopy is an at-least equally powerful capability and, therefore, as deserving of the attention of instrument developers. Accordingly, recent developments have made major strides in improving TEM energy resolution, and there are now instruments capable of resolving energies below 0.01 electron volts (*i.e.*, much lower than the energies of molecular bond vibrations). Imagine, atomically-resolved vibrational spectroscopy relying only on the interaction of an energetic electron with an atom! Though still far from routine, such energy resolutions are – like spatial resolution – nearing the limits of what most materials scientists and engineers would deem sufficient.

But what of time? Unlike space and energy, this dimension has received far less attention – but that is changing. First, why bother with time-resolved TEM studies at all? It does not require much thought to realize that individual snapshots of materials at equilibrium (or literally frozen in a transition state) tell only a small part of the story. This requires one to piece together dynamic behaviors by filling in the gaps. Thus, direct imaging of materials processes – as they happen in real time – can immediately reveal otherwise hidden behaviors. Indeed, the atoms and molecules comprising materials are always in motion, and we rely on the ability to move these constituents around in ways that enable useful macroscopic properties to emerge. At first pass, one might approach time-resolved TEM by developing fast cameras capable of capturing a series of images in a brief amount of time. Such an approach does work, but only to a point, and that point currently is roughly on the order of milliseconds (*i.e.*, ~1,000 frames per second). Recalling our simple example of the speed of sound, such temporal resolution falls well short of reaching the limits of what materials science and engineering ultimately wants and needs. Thus, an entirely new approach to time-resolved TEM is needed. In addition to the points made above, here I will discuss how the frontier of time-resolved TEM has shifted focus to pulsed electron sources rather than fast cameras for reaching continuous coverage of femtosecond to millisecond timescales. By gaining strict control over the electron emission process from the TEM source, one can conduct stroboscopic imaging experiments capable of exceeding current camera temporal resolutions *by ten orders of magnitude*. I will explain the concept behind this breakthrough, and I will describe

how this can be practically implemented in an otherwise standard, commercially-available TEM. Further, I will provide a specific, illustrative example of how this approach – dubbed Ultrafast Electron Microscopy (UEM) – has been used to directly probe very fast materials processes that operate on timescales far shorter than accessible with state-of-the-art fast cameras. Finally, I will conclude by noting the current challenges and limitations to this approach, and I will describe how instrument developers – with support from both government and industrial funding agencies – are feverishly working to overcome these limitations and push electron microscopy to the point where angstrom-femtosecond studies become commonplace.

Suggested Reading:

1. Zewail, A. H.; Thomas, J. M. "4D Electron Microscopy: Imaging in Space and Time" Imperial College Press: London, 2009.

2. Zewail, A. H. "Filming the Invisible in 4-D" *Scientific American* **2010**, *303*, 74-81.

3. Flannigan, D. J.; Zewail, A. H. "4D Electron Microscopy: Principles and Applications" *Accounts of Chemical Research* **2012**, *45*, 1828-1839.

4. Plemmons, D. A.; Suri, P. K.; Flannigan, D. J. "Probing Structural and Electronic Dynamics with Ultrafast Electron Microscopy" *Chemistry of Materials* **2015**, *27*, 3178-3192.