Low Loss EELS

Notes to accompany the lectures delivered by David A. Muller at the Summer School on Electron Microscopy: Fundamental Limits and New Science held at Cornell University, July 13-15, 2006.

Additional Reading and References:
How Delocalized is an EELS Signal?

For $E_0=100$ keV electrons, $\lambda=0.037$ Å, $v=1.64\times10^8$ m/s

For dipole scattering, the cross section is

$$\frac{d^2\sigma}{d\Omega dE} \propto \frac{1}{\theta^2 + \theta_E^2} \left| \langle f | r | i \rangle \right|^2 \rho_f(\Delta E)$$

with the characteristic angle at energy loss $\Delta E$ of

$$\theta_E \equiv \frac{\Delta E}{2E_0}$$

By analogy with the Raleigh resolution criterion, we might expect a resolution of

$$r_{inel} \approx \frac{\lambda}{\theta_E}$$

(this would assume that all the scattering lies inside $\theta_E$, which is not true).

For an energy loss $\Delta E=20$ eV, we get $r_{inel} = 6.5$ nm
An upper limit to the cutoff angle is the maximum momentum transfer in the small-angle approximation. This is also the peak of the Bethe Ridge at

$$\theta_B \approx \sqrt{2\theta_E}$$

Which gives

$$r_{\text{min}} \approx \lambda \sqrt{\frac{E_0}{\Delta E}}$$

or 0.26 nm for $\Delta E=20$ eV which is a little too small.

The real answer seems to lie between $r_{\text{inel}}$ and $r_{\text{min}}$ (and closer to $r_{\text{min}}$)

Dipole Theory Calculations of Inelastic Resolution

\[ \langle \theta \rangle \approx \theta_E^{3/4} \]

Fig. 1: Localization diameter for 100 keV electrons and a 10 mrad on-axis detector [6].

Comparison of Dipole and Full Atomic Calculations

For a free atom, agreement is \( \sim 10\% \) or better. Crystal channeling could cause problems.
Consider a fast e\textsuperscript{-} that passes a free, target charge and is deflected through a small angle.

Momentum transfer \[ \Delta p = \int_{-\infty}^{\infty} e E_2(t) \, dt = \frac{2e^2}{bv} \]

Energy Loss \[ \Delta E(b) = \frac{(\Delta p)^2}{2m} = \frac{2e^4}{mv^2} \frac{1}{b^2} \]

Energy loss is a function of impact parameter.
Quantum Treatment (Single scattering, linear imaging)

For a probe wavefunction \( a(b) \), detector function \( D \) and transmission function \( w(x,x',E) \)

The probability of losing energy \( E \) at distance \( b \) from the atom is

\[
P(b, E) = \frac{4R_y}{E_0} \int a(\rho - b) a^*(\rho' - b) \times w(\rho, \rho', E) D(\rho - \rho') \, d^2\rho \, d^2\rho'.
\]

The detector controls overlap of the wavefunction from different positions in the sample, i.e. it controls the coherence volume (optics) or degree of nonlocality of the probe (QM)

For a tiny aperture on axis,

\[
D(\rho - \rho') = \frac{2\pi\beta_0^2 J_0(k\beta_0 |\rho - \rho'|)}{k\beta_0 |\rho - \rho'|} \to \pi\beta_0^2,
\]

which allows coherence over the entire sample, i.e. a phase sensitive image

For large aperture on axis,

\[
D(\rho - \rho') = \to 2\pi\beta_0^2 \delta(|\rho - \rho'|),
\]

which removes non-local overlap, i.e. an incoherent image

**EELS with a Large Collector Aperture**

\[ P(b, E) = \frac{4R_y}{E_0} |a(b)|^2 \otimes w(\rho, \rho, E). \]

Convolution of probe intensity with response function.  

\[ |a(b)|^2 \text{ has the same form as elastic incoherent imaging, but } w \text{ is quite delocalized} \]

For a dipole excitation

\[ P_D(b, E) = \frac{\beta_0^2 R_y}{\pi^2 E_0} |a(b)|^2 \]

\[ \otimes \left( \frac{1}{b_{\text{max}}} \right)^2 \left[ \left| K_0\left( b/b_{\text{max}} \right) \right|^2 z_{fi} \right] \]

\[ + \left| K_1\left( b/b_{\text{max}} \right) x_{fi} \cdot \cos \gamma \right|^2 \]

i.e. \( w(r, E) \) has the same form as the classical loss function for a dipole

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*D.A. Muller, J. Silcox / Ultramicroscopy 59 (1995) 195–213*
EELS with a Tiny Collector Aperture

For a dipole excitation

\[
P_D(b, E) = \frac{\beta_0^2}{2\pi^2} \frac{R_y}{E_0} \left( \frac{1}{b_{\text{max}}} \right)^2 |a(b) \otimes [K_0(k_0\rho\theta_E)z_{\text{fi}} + iK_1(k_0\rho\theta_E)x_{\text{fi}} \cos \gamma]|^2
\]

Convolution of probe wavefunction with response function has the same form as elastic coherent imaging, but again the “inelastic object” is quite delocalized. Expect phase contrast and contrast reversals.
Effect of the Collector Aperture

Donut or volcano shape

Long tails
In both cases

Small Collector

Large Collector

(narrower central peak)

Fig. 2. Spatial distribution of the probability for a 25 eV energy loss by a 100 keV electron beam in a STEM with $C_s = 1.3$ mm, 700 Å defocus and a 10 mrad objective aperture; (a) for a 1.6 mrad collector aperture and (b) for a 10 mrad collector aperture. The dotted line shows the component of $P(b, E)$ perpendicular to the optic axis while the dot-dashed line shows the $P(b, E)$ along the optic axis. $b_{\text{max}}$ is at 43 Å but the semiclassical approximation holds to within 5 Å of the dipole where the “donut” shape appears.
Delocalization has long tails and a sharp central peak.

Inelastic Point Spread Function for a 100 kV STEM

- Energy loss has little effect on the FWHM.
- But a LARGE effect on the FW 10th maximum.

Radially Integrated Point Spread Functions for Energy Loss Images in a 100 kV STEM ($C_s = 3.3\text{mm}$)

- Si-L edge: 80% from a 7 Å Radius
- O-K edge: 80% from a 3 Å Radius
- Cu-L edge: 80% from a 2.4 Å Radius
Delocalization has long tails and a sharp central peak

Fig. 8. Measures of spatial resolution for a 100 kV STEM at 1100 Å defocus with $C_z = 3.3$ mm, a 8.18 mrad objective aperture and a 10 mrad collector aperture. The full width at half maximum (FWHM), full width at tenth maximum and the radius of the disk containing 80% of the scattered electrons are shown for $P(b, E)$ from a single dipole, calculated using Eq. (13).

**Bulk and Surface Plasmons**

**Screening inside a solid**
\[
\frac{1}{\varepsilon(\omega)}
\]

**Screening outside a solid**
(screening of the image charge)
\[
\frac{1}{\varepsilon(\omega)+1}
\]

**Bulk energy loss:**
\[
P(\omega) \alpha \text{Im}\left( \frac{-1}{\varepsilon(\omega)} \right)
\]
Plasmon pole \(\omega_p\), at \(\varepsilon=0\)

**Surface energy loss:**
\[
P(\omega) \alpha \text{Im}\left( \frac{-2}{\varepsilon(\omega)+1} \right)
\]
Plasmon pole \(1/\sqrt{2}\omega_p\), at \(\varepsilon=-1\)
Plasmons at an interface

\[ b_{\text{max}} = \frac{v}{\omega} \]

Is the natural length scale

Where plasmon effects become noticeable (a few nm for plasmons)
EELS across a 50 nm thick Silicon edge
Valence EELS from a thin interlayer?

When layer A becomes thinner than $\chi_v/\omega$, the bulk mode from A is suppressed. (i.e. can’t measure the bulk dielectric function of a grain boundary phase – must use Interface formula)

Valence EELS on Nanoparticles

When a nanoparticle is smaller than $\nu/\omega$, the probe will also excite spherical, multipole plasmon modes.

**Spherical Cavity Modes**

$$\omega_{\text{void}} = \left[ \frac{l + 1}{2l + 1} \right]^{1/2} \omega_p ,$$

**Spherical Modes**

$$\omega_s = \left[ \frac{l}{2l + 1} \right]^{1/2} \omega_p .$$

*FIG. 2. Typical low-energy-loss spectra of silicon particles: (a) over a particle; (b) grazing incidence.*

Valence EELS on Nanoparticles

Electron Energy Loss Spectrum at Edge of 4 nm Silicon Tip

- Data Fit with 3 Lorentzians
- Data after Background Subtraction
- Data before Background Subtraction
- Individual Lorentzians

Cherenkov Radiation

B.W. Reed et al, Phys Rev B60 (1992) 5641
Summary

• The EELS signal is localized to within a few Angstroms for core edges and on the order of 1-6 nm for valence (1-30 eV) excitations.

• Valence EELS on small particles measures more than just the bandgap
• Surface plasmons, Cherenkov radiation are just as important