Designing *in-situ* experiments in gas and liquid environments for the DTEM

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The study of dynamic processes under controlled environmental conditions

- Many dynamic phenomena require the ability to reproduce localized extreme conditions around the specimen – such as high-temperature, high-pressure, specific oxidizing or reducing atmosphere or a liquid environment:
  - Corrosion of materials for high temperature applications (eg. grain boundaries and defects).
  - Catalysis.
  - Nucleation and growth from solutions.
  - Dynamics in structural biology

- Localized gas/fluid conditions are created around the sample and separated from the high vacuum inside the microscope using hermetically sealed windowed-cells.
For all experiments we need to control the environment inside the microscope.

Image aberration-corrected environmental Titan - <20 torr, temporal resolution ~25 ms

Probe aberration-corrected and monochromated Titan – temporal resolution ~ 500 ms

Double Cs-corrected JEOL-2200 - Converting into a DTEM with ~1µs temporal resolution
Accommodates any kind of sample.

Currently achieve global specimen heating using a non-translatable fiber-based laser with \(1/e^2\) diameter ~ 150 micrometers.

Working on getting localized specimen heating using a translatable fiber-based laser with 20 micrometer beam diameter. It will allow for systematic studies in the same specimen and minimize thermal drift.
Gas Pressure vs. Resolution

Atomic resolution possible at ambient pressure (gas path lengths up to 20 µm – 15nm membranes)
Hollow nanoparticles by localized laser heating

Ex-situ heating of Zn/ZnO nanoparticles with an infrared laser leads to vaporization of the Zn core, leaving the laser-transparent ZnO shell unchanged. K.Y. Niu et al., Langmuir (2010)

Same observations using the in-situ stage—demonstrates that localized temperatures up to ~900°C are feasible. S. Mehraeen, et al. Microscopy & Microanalysis, In Press
In-situ continuous flow fluid stage

- Atomic resolution and chemical analysis is possible.
- Improved resolution for thinner membrane thicknesses and fluid path lengths.
- Flow rates across the membrane windows up to 0.01 – 10 mL per minute
- Imaging conditions that eliminate beam induced reactions (due to radiolysis damage) are needed.

Induction threshold dose for Nucleation

Beam current, pixel dwell time and magnification can be varied to keep the dose under a critical value.

An average cumulative electron dose is needed to initiate nucleation $<d_{\text{ind}}>$ ≈ 28 electrons/Å²

Below a dose rate of 0.5 electrons/(Å²s) no nucleation or growth is observed.
Observing controlled growth of nanoparticles

X3 speed (1:30 min real time)
Magnification: 100,000 kx
Pixel dwell time: 5 µs
Beam current 7 pA
Electron dose rate: 0.59 electrons/(Å²s)
Using Dose to Control Growth

Reaction limited growth follows LSW growth mode.

Diffusion limited growth slower than predicted by Classical Nucleation Theory. Finite confinement of liquid by cell may play a role. DTEM could help explaining this discrepancy.
Conclusions

• In-situ studies with gas and liquid stages can be strongly affected by the electron beam. Its effect can be controlled for each system.

• Identified different parameters that can be optimized:
  • Membrane thickness and Fluid/Gas path length – increase electron scattering and degrade image quality. Image conditions simulations may help designing experiments (David A. Welch et al. In preparation).
  • Mobility from charging effects, bubbles formation – minimized by low dose imaging conditions.
  • Brownian motion – Faster read-out speeds will limit blurring artifacts.

• Different growth regimes have been determined under various dose conditions. DTEM will help decouple growth from electron beam effects.

• Faster temporal resolution will also enable studies into transient states and provide better kinetics (critical nuclei diameter observation, initial reaction rates currently missed, ...).