Links between Theory and Experiment II

Essential Collaborations
Clean Lab versus Real World

Structure of Clean Oxide Surfaces
"God made solids, but surfaces were the work of the Devil."
Wolfgang Pauli, 1900-58.

"Direct Observation of Charge Transfer at a MgO(111) Surface"

Low angle transmission electron diffraction combined with direct methods have been used to study the $\sqrt{3}\sqrt{3}R\cdot30^\circ$ reconstruction on the polar (111) surface of MgO and refine the valence charge distribution.
• A 'simple' relation exists between X-ray Scattering factors and charge density:

\[
F(K) \sim \int \text{dr } \rho(r) e^{iKr}
\]

However, only a finite number of \( K \) are measured, only \( |F|^2 \) is measured, and finite-T motion induces broadening/weakening.

Data fitting by 'Direct Methods' infers phase relations and incorporates atom positions along with model atom/ion charge distributions with scaling and charge-transfer capability. A Deformation Density can be defined as:

\[
\rho_{\text{model, surface}} - \rho_{\text{bulk}}
\]


• The results:

The crystal is Mg terminated, nonstoichiometric, with two Mg vacancies in first layer relative to bulk, with a compensating electron hole in the next Oxygen layer. The reconstruction can be thought of as built from octopolar units \((\text{MgO})_4\) with two additional O atoms in the fourth layer. Charge transfer from O to Mg is observed, indicating reduced ionicity in the surface layers and indications of a weak covalent component in the bonding. DFT band structure calculations of atom position relaxations confirm the experimental x,y coordinates, and reveal the vertical z-coordinate locations.

• Observation:

Oxide surfaces are almost never what one would imagine from trivial cleavage of bulk. Theory and experiment must work together closely at several stages, to reach a successful conclusion.
"Surface Structures of SrTiO₃ (001): A TiO₂-rich Reconstruction with a c(4x2) Unit Cell"  

Schematic top-view and structural relaxed side-view of three cation distribution patterns with (4x1) unit cell. Courtesy: O. Warschkow, submitted for publication.

- **Lesson:** Don't assume you 'know' what the oxide will do!

- For years theorists calculated and experimentalists assumed that the 'obvious' cleavage of SrTiO₃ (001) would yield SrO₂⁻ terminated or TiO₂⁻ terminated surfaces. Dozens of papers 'decorate' the literature with this theme. However, given the chance, the material will form TiO₂-rich surfaces, with 1, 2, 3… extra titania layers tending toward the anatase structure. This is of importance in device design/fabrication for electronic and electro-optic applications - e.g., SrTiO₃ is a favorite 'buffer layer' to support growth of additional materials like high-Tₚ superconductors.

- The presence of several reconstructed surfaces is confirmed, and a common feature of the most stable surfaces is 'dangling oxygen' over narrow channels which will be sites of high chemical reactivity.

- Tight control over surface preparation conditions, DF theory, plus high-resolution electron or X-ray microscopy, plus clever fitting schemes form essential collaborative elements for success.
Grain Boundaries – Composition, Chemical Gradients

Grain Growth – Ostwald ripening

"Great Oaks From Little Acorns Grow"
Chaucer (c.1343-1400)

Les petits ruisseaux font les grande rivières
Parvis e glandibus quercus

A nanocrystalline copper sample containing 100,000 atoms after 10% deformation.

Left: Atoms in the grain boundaries are colored blue, atoms at stacking faults are colored red. We clearly see stacking faults left behind by partial dislocations that have run through the grains during the deformation processes.

Right: The atoms have been colored depending on how far they have moved, relative to a homogeneous deformation of the solid. Blue atoms have moved downwards relative to what would be expected if the deformation had been homogeneous and elastic, red atoms have moved upwards. The grains are blue in the upper part and red in the lower, indicating that they have not deformed as much as the sample. The major part of the deformation has been in the grain boundaries.

"Softening of nanocrystalline metals at very small grain sizes"
The average stress versus strain for each grain size. Each curve is the average over several simulations. The curves show the response of the material to mechanical deformation. We see a clear grain size dependence: the maximal flow stress and the yield stress decrease with decreasing grain size, resulting in a reverse Hall-Petch effect.

"Interatomic interactions in the effective-medium theory"
"A semi-empirical effective medium theory for metals and alloys"

MD simulations were used, for the first time, to study grain-boundary diffusion creep of a model polycrystalline silicon microstructure. Our fully dense model microstructures, with a grain size of up to 7.5 nm, were grown by MD simulation of a melt into which small, randomly oriented crystalline seeds were inserted. In order to prevent grain growth and thus to enable steady-state diffusion creep to be observed on a time scale accessible to MD simulations (of typically 10-9s), our input microstructures were tailored to (i) have a uniform grain shape and a uniform grain size of nm dimensions and (ii) contain only high-energy grain boundaries (GBs) which are known to exhibit rather fast, liquid-like self-diffusion. Our simulations reveal that under relatively high tensile stresses these microstructures, indeed, exhibit steady-state diffusion creep that is homogenous (i.e., involving no grain sliding), with a strain rate that agrees quantitatively with that given by the Coble-creep formula, \( s\dot{\gamma} = D_{GBD}d_0^3 \), according to which (i) the creep rate has the same activation energy as the GB self-diffusion flux, \( D_{GBD} \), (ii) for small values of \( s \), is proportional to \( s \), and (iii) increases with decreasing grain size, \( s \), as \( d^{-3} \).
Typical plot of the total (elastic + plastic) strain and associated system volume vs. simulation time for a system with a grain size of 5.4 nm. The slopes of the linear $e(t)$ curves yield constant strain rates.

Monitoring of the center-of-mass coordinates (normalized to the instantaneous lengths $L_x$, $L_y$ and $L_z$ of the rectangular simulation cell) of each grain vs. simulation time revealed a homogenous deformation process and the absence of GB sliding.

This work demonstrates that atomistic simulations for polycrystalline model systems with a grain size of only nm dimensions, albeit with an appropriately designed microstructure, can be used to elucidate the evolution of coarse-grained polycrystalline microstructures. This result is particularly remarkable given that, in order to be observable by MD simulation, the strain rates in these simulations are typically about ten orders of magnitude higher than typical Coble-creep rates - and yet capture the same physics.

Since GB-diffusion creep is a relatively slow process compared to the rather fast deformation processes involving grain-sliding (for example, in superplastic deformation or in the inverse Hall-Petch effect), we are now able to systematically determine the fundamental mechanisms of GB sliding in plastic deformation, particularly the interplay between GB diffusion and GB sliding.

Arrhenius plot for the creep rate between 1100 and 1400K for our model Si microstructure with a grain size of 5.4 nm. The activation energy thus obtained agrees quantitatively with that obtained from the Arrhenius plot for the GB diffusion flux, $D_{GB}d_{D}$, for the same system, however, under zero external stress.

(Here $D_{GB}$ and $d_{D}$ are, respectively, the GB diffusion coefficient and the GB width)
Molecular dynamics simulations of the zipping process have also been carried out. So far, only islands bound to substrates without interface traction have been investigated. Islands composed of up to 360 Ag atoms have been modeled using embedded atom potentials. Island-substrate interactions are modeled using a Leonard-Jones potential. We find that grain boundary formation occurs over time scales that are accessible through MD simulations, in that zipping occurs at very high rates [Figures 8 and 9]. The observed zipping height is consistent with the results of finite element modeling, suggesting that the physical model on which the finite element calculations are based, grain boundary formation through island straining, is valid.

We are further developing molecular dynamics simulations that will account for traction at the island-substrate interface. We also plan to carry out experiments involving in-situ Transmission Electron Microscope (TEM) observations of the early stages of polycrystalline film formation, using micromachined membranes.
Fig. 6: When islands impinge, grain boundaries form as islands strain to close the gap between them, zipping a distance $z_0$ to replace two surfaces of energy $\gamma_s$ with a boundary of energy $\gamma_{gb}$.

Fig. 9: Molecular dynamics results showing the distance between the centers of mass of coalescing islands as a function of time. A distance of roughly two atomic diameters is closed in approximately 0.5 nanoseconds.
MgSiO$_3$ perovskite is thought to be the dominant phase of the Earth's lower mantle and hence accounts for approximately 40% of the earth by volume. The conductivity of the material has been investigated by experiment and simulation although the experiments are subject to large error and competing experimental groups have not been able to agree on their conclusions. An alternative is to study analogue fluorides which require much lower temperatures and lower pressures to produce the same volume contraction and to melt.

We have simulated, using molecular dynamics, the effect of temperature and pressure on the fast ionic conductivity of such an isostructural analogue; KCaF$_3$. The effect of pressure results in a decrease in the critical temperature for conduction relative to the melting point indicating that conductivity may be possible deep within the mantle.

"A molecular dynamics simulation of the effect of high pressure on fast-ion conduction in a MgSiO$_3$ - perovskite analogue; KCaF$_3$"


"Molecular dynamics simulation in fluoride perovskites"

Important take-home lesson:

Many diffusion processes involve correlated motion involving two or more particles.

Simple 1-body Monte Carlo moves will completely miss these processes, or will take excruciating time to discover the relevant phase space.

Solution: modify procedure to randomly select n-tuples, n=1,2… using a neighbor tree to select relevant pairs, trimers...

A snapshot from a molecular dynamics simulation showing the molecular order in a smectic-A* twist grain boundary phase. Also shown is a close up view of molecules within a grain boundary showing a screw dislocation defect

By dissolving right-handed or left-handed chiral molecules in a liquid crystal, the director can be made to twist in a helical fashion uniformly through space. On cooling such a system, a chiral smectic phase is formed, but it is no longer possible for the layered system to support a uniform twist. Instead, to relieve the strain energy, the phase splits into domains of untwisted smectic, separated by twist grain boundaries.

Very large systems are required in order to allow these structures to develop properly. The overall cell length from front to back determines the helical pitch, which must be several hundred nanometres for a realistic comparison with experiment; twisted structures of the order of the wavelength of visible light are of technological interest, because of their potential applications in optical device design. The transverse dimensions of the simulation cell must also be very large, otherwise the orientation of smectic layers is dictated by the requirement that they fit with the periodic boundary conditions, rather than being driven by the physics. It is also necessary to simulate the system for a relatively long time (of the order of nanoseconds) to allow these structures to develop spontaneously. The close comparison with experimental results is indicated in the table.

Comparison with experimental data:

<table>
<thead>
<tr>
<th>Property</th>
<th>Simulation (arb units)</th>
<th>Experiment/nm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectic layer spacing</td>
<td>4.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Helix pitch</td>
<td>320</td>
<td>500</td>
</tr>
<tr>
<td>Smectic domain size</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Dislocation line separation</td>
<td>11</td>
<td>15</td>
</tr>
</tbody>
</table>