Mass Spectrometry from a Theorist’s View

- Conventional mass spectrometry involves heating, vaporizing, & ionizing a compound
  - Issues arise when compound is not volatile

- Two approaches to get non-volatile molecules in the gas phase as ions
  - **Secondary ion mass spectrometry - SIMS**
    - Smash a several 1000 eV particle into the solid
  - **Matrix assisted laser desorption ionization – MALDI**
    - Zap a solid with a pulsed laser

- Both techniques involve fast energy deposition at a surface
- Can we obtain a microscopic view?

**Secondary Ion Mass Spectrometry (SIMS)**

- Secondary Species: Neutrals and Ions (+/-)
- Incident Cluster

**MALDI - Biological Mass Spectrometry**

MALDI: Matrix Assisted Laser Desorption Ionization

MALDI: Franz Hillenkamp, Michael Karas
Figure: M. Karas, Proc. SPUT92, Matematisk-fysiske Meddelelser, 43, 623 (1993)
Computer View of the SIMS Process

Organic Molecules on a Metal Surface

How make all hits successful?

- Use cluster beams... SF₅, Au₃
- C₆₀ is currently attractive, source designed by J. C. Vickerman (UMIST) & Ionoptika (UK)
  - New physics of motion! (More need for simulations)
  - Increased total ejection yield – higher sensitivity
  - Greater ion fraction – higher sensitivity
  - More removed material than damaged material, intrigue – molecular depth profiling
  - Smoother surface
- Simulations courtesy of Zbigniew Postawa, Jagellonian University, Krakow, Poland

Vision Picture: Concepts apply to Molecular Systems

Experimental data is an average over all aiming points on the surface.


Tt=29 ps

Larger volume is altered, i.e. more damage, for Ga
15x more material removed with C₆₀
Depth Profiling a Molecular System with $C_{60}$

Key point in successful molecular depth profiling is the ratio of the sputtering yield to the thickness of the altered layer created by the incident ion beam.

$0.35\text{ml} 1\text{M trehalose} + 0.35\text{ml} 10\text{mM VGDE}$

*(100:1)* spincast on a Si Substrate

Juan Cheng and Nick Winograd

What is the molecular dynamics (MD) method?

Sophisticated game of billiards where the atoms are the ‘balls’ and move according to Newton’s or Hamilton’s equations of motion. The key is to use forces that describe the appropriate chemistry.

$$\frac{dr}{dt} = v, m \frac{dv}{dt} = F(r) = -\nabla V(r)$$

Where the forces are obtained from the potential, $V(r)$, which is the solution to the electronic Schrödinger equation within the Born-Oppenheimer approximation.

Once the potential is assumed, all atomic motions follow.

How do we implement the equations?

Treat each atom classically and integrate Newton’s or Hamilton’s equations of motion.

$$\frac{dv}{dt} = F/m$$

$$\frac{dr}{dt} = v$$

Simple integrator for a fixed timestep $\delta t$ ...

$$v(t+\delta t) = v(t) + F(t)*\delta t/m$$

$$r(t+\delta t) = r(t) + v(t)*\delta t$$

Computer time issues

Pick $\delta t$ such that $F(t)$ and $v(t)$ = constant

$\delta t \approx 0.01-5$ fs (fast particle, CH vib, thermal motion)

Force calculation goes as

(complexity & range of potential) $\times$ (number of particles)

What are the assumptions?

- Classical mechanics
  - No electronic excitations
  - No ionization
  - No quantized vibrational motion
  - No tunneling

- Interaction potential or force field
  - Approximation to lowest adiabatic electronic state
  - Really tough to construct good potentials especially if one wants correct reaction chemistry
**How does the computer time get consumed?**

- CPU time is proportional to the number of time steps
  - The number of time steps to cover a specific time is *inversely* proportional to the time step, $\delta t$
  - Because of errors limited to between $10^6$ to $10^8$ steps thus total time is limited

- The force calculation takes the most time
  - Proportional to the number of particles
  - Proportional to the number of neighbors of an atom, or $r_{cut}$, where $r_{cut}$ is the range of the potential
  - Depends on the complexity of the functional form
  - Limits size of system

**Examples of time steps**

<table>
<thead>
<tr>
<th>System</th>
<th>Energy of Primary Ar Particle</th>
<th>Range of Time Steps in fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanethiols on Au</td>
<td>700 eV</td>
<td>0.01 - 0.15</td>
</tr>
<tr>
<td>Silicon</td>
<td>1 keV</td>
<td>0.05 - 0.50</td>
</tr>
<tr>
<td>Ag</td>
<td>5 keV</td>
<td>0.03 – 10.</td>
</tr>
</tbody>
</table>

- Smaller time steps needed for hard collisions and H vibrations
- Larger time steps ok for thermal processes and heavier particles
- We use a variable time step integrator – automatically readjusts

**Typical number of neighbors**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Potential</th>
<th>Typical number of neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Brenner CH – chemical reactions!</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>Brenner CH</td>
<td>4</td>
</tr>
<tr>
<td>Si</td>
<td>Stillinger-Weber or Tersoff</td>
<td>4</td>
</tr>
<tr>
<td>Ag</td>
<td>Sandia EAM or MD-MC/CEMA</td>
<td>80</td>
</tr>
<tr>
<td>C or H</td>
<td>AIREBO – very complex functional form, condensed organic films with reactions</td>
<td>300</td>
</tr>
</tbody>
</table>

**Examples of CPU time for 1 ion hit**

<table>
<thead>
<tr>
<th>System</th>
<th>$N_{atoms} / 10^6$</th>
<th>$N_{molecules} / 10^6$</th>
<th>Vol/1000 nm$^3$</th>
<th>Incident Energy/eV</th>
<th>Time of Traj.</th>
<th>CPU Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$/Ag</td>
<td>0.17</td>
<td></td>
<td>2.7</td>
<td>15000</td>
<td>15 ps</td>
<td>15 days</td>
</tr>
<tr>
<td>C$_{60}$/ice</td>
<td>1.2</td>
<td>0.4</td>
<td>18.8</td>
<td>5000</td>
<td>15 ps</td>
<td>2 months</td>
</tr>
<tr>
<td>C$_{60}$/Atomic benzene</td>
<td>0.3</td>
<td>0.025</td>
<td>2.6</td>
<td>500</td>
<td>25 ps</td>
<td>6 months</td>
</tr>
<tr>
<td>C$_{60}$/Coarse-grained benzene</td>
<td>0.15</td>
<td>0.025</td>
<td>2.6</td>
<td>500</td>
<td>25 ps</td>
<td>4 days</td>
</tr>
</tbody>
</table>
MALDI - Biological Mass Spectrometry

MALDI: Matrix Assisted Laser Desorption Ionization

MALDIE: Franz Hillenkamp, Michael Karas
Figure: M. Karas, Proc. SPUT92, Matematisk-fysiske Meddelelser, 43, 623 (1993)

Processes in UV MALDI
Primarily "Thermal Ablation"

- Laser excitation of absorbing molecules
- Intramolecular vibrational equilibration
- Intermolecular energy transfer
- Formation of a highly energetic high-T/high P region
- Photomechanical and photochemical effects
- Explosive disintegration and ejection of a volume of material
- Intensive processes in the ejected plume
- Formation and propagation of pressure waves
- Ionization
- ??? More????

Relative Length & Time Scales:
MALDI vs. SIMS

One sphere = 20 atoms

Add some Chemistry!

- Shorter wavelength (often less than 200 nm)
- Electronic transition to a level above the dissociation limit
- Photon energy is sufficient to break chemical bonds
- Newly formed radicals can undergo subsequent reactions
  - Changes heat energy available for ablation
  - Changes composition of the material
Different Lasers gives Different Physics & Chemistry

Cross section of the luminal side of an aortal wall

Thermal, charring, damage

Cool cutting, bond cleavage, volatile gas formation

0.4-mm crater produced by 532-nm (green) radiation

0.35-mm trench produced by 193-nm (far UV) radiation

Cross section of the luminal side of an aortal wall


One Application of UV ablation

- Laser Assisted In-Situ Keratomeleusis (LASIK) technique

Pictures taken from http://www.visionforlife.com / Emory Vision Correction Center, Atlanta, Georgia

Would love to do a full atomistic, microscopic Molecular Dynamics simulation!

Length Challenge

- System too big (collective process, molecules rather than atoms, Beer’s law absorption into non-ablating material, pressure wave into material), need 100K or more molecules or 2M+ atoms!

Time Challenge

- Physics demands a longer real time to be simulated (mechanical vs thermal relaxation times vs laser pulse width, evolution of plume) need at least 150 ps laser pulse, at least 1 ns plume evolution

Chemistry Challenge

- No interaction potential available for all the photo-induced reaction intermediates and products
  
  Many 1 ns simulations (i.e. many fluences) of millions of particles are required

Strategy for Modeling Ablation

Lots of individual & coupled events but…. Ablation occurs in many different systems

**Isolate the essential physics & chemistry! Ignore time consuming details**

- Coarse grain breathing sphere MD model for thermal ablation (Leonid Zhigilei, now at Univ. Virginia)
  - Strategy developed specifically for ablation of organic solids
  - Many results applicable to laser ablation of other materials

- Coarse grain chemical reaction model (CGCRM) (Yaroslava Yingling, now at National Cancer Institute – ICS Minor)
  - No chemically correct potential surface needed
  - Strategy is applicable to many problems where effects of chemistry needs to be included
Think Molecules rather than Atoms

- ~20 times fewer particles
- Factor of 50 times larger time step because no H-vibration
- Each molecule is a breathing sphere


Simulation Setup

- Excitation of randomly chosen molecules based on:
  - wavelength
  - penetration depth (Beer’s law)
  - pulse width
  - laser fluence
- Photon absorption by molecule:
  - Vibrational excitation
  - Photochemical fragmentation

Total Yield - UV MALDI

- Desorption
- Mainly single molecules
- Thermal process
- Ablation!
- Lots of clusters
- Volume ejection

UV MALDI animation

- Melting is fast (<1ps) vs normal boiling and vaporization
- Radiation overheats material to limit of thermodynamic phase stability
- Phase explosion occurs and becomes visible at ~225 ps
- Phase explosion leads to a mixture of vapor and liquid droplets
- Transient structure (~300 ps) of interconnected clusters
- Finally individual molecules and well-defined liquid droplets

Compare, explain, guide experiment

**Coarse grained chemical reaction model (CGCRM) for incorporation of photochemistry**

- Philosophically a combination of MD and KMC calculations
- Need compound with known chemistry
- Identify from the literature all possible (important) reactions
- Take literature information on heats of formation, rates of reaction
- Assign a mass, radius, interaction potential for all reactants, intermediates and products
- Define rates and probabilities
- Monitor energy balance

Assess effects of chemistry on the ablation process


**Photochemical Processes in Organic Solids**

- 248-nm laser ablation of chlorobenzene, simple fragmentation, available ablation data at 248-nm
  
  $\text{C}_6\text{H}_5\text{Cl} + h\nu \rightarrow \text{C}_6\text{H}_5^\text{•} + \cdot\text{Cl}$
  
  - Model allows simulations of both vibrational excitation and photochemical fragmentation processes. Combined effects can be examined too.

- All reactants and products are spherical particles.

**Laser Excitation**

$\Delta H_{\text{rxn}} = -482 \text{ kJ/mol}$

$\Delta H_{\text{rxn}} = -80 \text{ kJ/mol}$
Current Group Members & Projects

• NSF Chemistry – Energetic Particle Bombardment of Solids
  – Mike Russo – C\textsubscript{60} and Au\textsubscript{n} bombardment of ice
  – Ed Smiley – C\textsubscript{60} bombardment of benzene, coarse-grained simulations
  – Kate Ryan – ionization effects in sputtering
  – Christin Palombo – DESI – cluster bombardment mass spec in air

• NSF - ITR – Modeling Polymer Ablation
  – Pat Conforti & Manish Prasad, UV ablation of polymers

• AFOSR – Multiple University Research Initiative (MURI), collaboration with scientists from six other universities to examine the synergistic effects of UV radiation and 5 eV O atom bombardment in low earth orbit
  – Manish Prasad & Pat Conforti, UV & O atom radiation of PMMA

Publication, graphics and animations are available from our web site –
http://galilei.chem.psu.edu/