Ultrafast X-Ray-Matter Interaction

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Stanford • June 20, 2007
Thanks to many collaborators!

<table>
<thead>
<tr>
<th>LLNL</th>
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<tbody>
<tr>
<td>S. Hau-Riege</td>
<td>M. Bogan</td>
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<td>A. Szoke</td>
<td>S. Boutet</td>
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Uppsala: J. Hajdu, M. Bergh & C. Caleman
Prague: L. Juha, J. Chalupsky
Warsaw: J. Krzywinski & R. Sobieraski
Krakow/Hamburg: B. Ziaja
Hamburg: every one at FLASH
Outline of talk

• Introduction to XFELs
• X-ray/matter interaction physics
• Application to x-ray optics damage
• Application to x-ray imaging of biomolecules
• Conclusions
Introduction to XFELS
This talk concerns the interaction of XFEL pulses with matter.

**XFEL schematic diagram**

- **electron injector** → **linac** → **undulator** → **x-ray optics** → **experiments**
  - **electrons** → **x rays**

**x-ray parameters**

<table>
<thead>
<tr>
<th>Facility</th>
<th>Date</th>
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<tbody>
<tr>
<td>Hamburg FLASH</td>
<td>2005</td>
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<tr>
<td>Triest FERMI</td>
<td>2008</td>
</tr>
<tr>
<td>Stanford LCLS</td>
<td>2009</td>
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<td>Japan SCSS</td>
<td>2010</td>
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<tr>
<td>Euro XFEL</td>
<td>2013</td>
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</table>

- Photon energy: 40 eV – 30 keV
- # photons/pulse: $10^{12} - 10^{13}$
- Output energy: 10 µJ - 3 mJ
- Output fluence: 10-100 J/cm²
- Pulse length: 10-250 fs
- Spectral bandwidth: $10^{-3}$
- Spatial coherence: near 100%
- Repetition rate: 10-100 Hz
X-ray matter interaction physics
Focus on small samples of condensed matter

- samples are nm to µm in size
  - $10^3$ to $10^{12}$ atoms
- clusters, biomolecules, nano-particles and structures, and surface regions of bulk materials.
Fundamental x-ray interaction processes

- absorption
  - bound-bound, bound-free, free-free
  - bound-free (photo-ionization) tends to dominate
    - single photon (linear)
    - multi-photon (nonlinear)
- scattering
  - coherent (Thomson, forward scattering)
  - incoherent (Compton)
- emission
  - inverse of these processes
  - generally occurs for hot plasmas on longer timescales
Atomic physics and x-ray absorption

Hydrogenic energy level diagram

Periodic table:

- **K shell**: 1 electron (max. no. 2)
- **L shell**: 8 electrons (max. no. 18)
- **M shell**:...

Energy level diagram:

- Vertical axis: Energy
- Horizontal axis: Principal quantum no.

- **1**: K shell (1 electron)
- **2**: L shell (8 electrons)
- **3**: M shell (max. no. 18 electrons)
## Typical atomic ionization energies

<table>
<thead>
<tr>
<th>element (Z)</th>
<th>shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (1)</td>
<td>K</td>
<td>0.0136</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C (2)</td>
<td>L</td>
<td>0.28</td>
<td>.011</td>
<td>-</td>
</tr>
<tr>
<td>Si (14)</td>
<td>M</td>
<td>1.84</td>
<td>0.1 – 0.15</td>
<td>-</td>
</tr>
<tr>
<td>Fe (26)</td>
<td></td>
<td>7.1</td>
<td>0.71 – 0.84</td>
<td>.05 – .09</td>
</tr>
<tr>
<td>Au (79)</td>
<td></td>
<td>81</td>
<td>12–14.4</td>
<td>2.2–3.4</td>
</tr>
</tbody>
</table>
Typical photo-ionization cross sections

cross-section $\text{cm}^2/\text{atom}$

$E$ (keV)
Much of the real interest lies in what happens immediately following x-ray interactions

- inner shell photo-ionization
- e-e slowing down
- auger ionization
- e-ion coupling
- collisional ionization
- recombination
Energy-time picture of x-ray material interaction

- x-ray absorption
- auger emission
- electron slowing down
- non-thermal ion motion
- electron-ion thermalization
- spallation
- thermal fracture
- FEL pulse duration
- melting

Particle energy:
- 10 keV
- 1 keV
- 10 eV
- 1 eV
- 0.1 eV

Time:
- 1 fs
- 10 fs
- 100 fs
- 1 ps
- 10 ps
- 100 ps
- 1 ns
Methods and computer programs for simulating x-ray interaction with solids

- Monte Carlo
- Rate equations
- Molecular dynamics
- Continuum ("hydro") dynamics

**Particle energy**
- 10 keV
- 1 keV
- 10 eV
- 1 eV
- 0.1 eV

**Time**
- 1 fs
- 10 fs
- 100 fs
- 1 ps
- 10 ps
- 100 ps
- 1 ns
Monte Carlo simulations have been used to study the time and space development of electron cascades.

- many \((10^3-10^6)\) electron trajectories are tracked in space and time
- collision events are simulated from known cross sections using probability weighted random numbers to choose location and scattering angle.
Simulated spatial distribution of electrons

Carbon, primary electron energy = 250 eV

Spatial distribution of absorbed energy resulting from surface x-ray absorption

Time dependent evolution of electrons after absorption of a 10 keV photon in diamond

Conclusions from Monte Carlo study
- It is important to include effects of both electron and holes.
- Cascade timescale ~ 10 fs.
- ~ 800 secondary electrons are generated per photo-electron.
- Cascade cloud is ~ 0.2 µm in diameter.

Ziaja, et al., JAP (2005)
X-ray energy deposition in materials

- We are primarily concerned with single pulse effects

- **Dose** = absorbed energy per unit mass, volume, or atom.

- Natural units are eV/atom, since binding energies of solid materials are of this order.

- In most cases, the time to transport energy out of x-ray deposition region is longer than XFEL pulse duration.
  - absorbed dose remains confined during pulse.

- In some cases, electron transport broadens the energy deposition region and reduces the dose.
X-ray matter interaction spans a wide range of dose and applications.

- x-ray optics
- hot solids
- Warm Dense Matter
- Dense plasmas
- Biomolecular imaging
- high field interactions

energy density ("dose", eV/atom)
Application: X-ray Optics
Layout of LCLS X-ray areas

- Linac
- Undulator
- Optics enclosure
- Near experimental hall
- Far experimental hall

Distance (m)
There are variety of x-ray optics in the LCLS Front End Optics Enclosure.
Damage and melting

• Damage is defined as anything that will cause degradation or failure of an optic.

• possible damage mechanisms
  – melting
  – phase change
  – high pressure effects (spallation, shear)
  – thermal stress, thermal fatigue
  – photo-chemical processes

• Theoretical analysis of x-ray processes and experience from optical laser-matter studies suggest that we should avoid melting the optics surface in a single pulse.
  – Calculation of the melt dose

\[
D_m = \int_{T_r}^{T_m} C(T) dT + H_m
\]

- \( T_r \) = room temp.
- \( T_m \) = melting temp.
- \( C \) = heat capacity
- \( H_m \) = latent heat of melting
Melting damage threshold

<table>
<thead>
<tr>
<th>Material</th>
<th>Be</th>
<th>C</th>
<th>Si</th>
<th>B₄C</th>
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<tbody>
<tr>
<td>Quantity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T_melt (K)</td>
<td>1560</td>
<td>3800</td>
<td>1690</td>
<td>2620</td>
</tr>
<tr>
<td>D_melt (eV/atom)</td>
<td>0.41</td>
<td>2.1</td>
<td>0.91</td>
<td>0.74</td>
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</table>
Expected dose from LCLS (normal incidence)

Gaussian beam model: \[ F = F_0 \left(1 + \frac{L\lambda}{w^2}\right)^2 \]

Cold opacity model for dose: \[ D = F \sigma_a \]

unfocused dose at 20 m from LCLS undulator

\[ F = \text{fluence} \]
\[ D = \text{dose} \]
\[ L = \text{distance} \]
\[ \lambda = \text{wavelength} \]
\[ w = \text{beam waist} \]
\[ \sigma_a = \text{abs. xsect/atom} \]
Compare melt dose to x-ray dose

x-ray dose = maximum over LCLS energy range (0.8 - 8 keV)

- light, refractory elements must be used near XFEL
- many other materials can be used in far hall
The dose can be decreased by using grazing incidence optics

Three factors lead to a greatly reduce dose at grazing incidence:
• evanescent wave limit to x-ray range.
• high reflectivity.
• electron transport.

\[ d_x = \text{x-ray range} \]
\[ d_e = \text{photo-electron collisional range} \]
\[ d_h \approx [d_x^2 + d_e^2]^{1/2} \]
The x-ray range is determined from solution of wave equation

\[ d_x = \frac{\lambda \rho}{4\pi \beta}, \quad \rho = \sqrt{\frac{1}{2} \left[ \sin^2 \theta - 2\delta + \sqrt{\left(\sin^2 \theta - 2\delta\right)^2 + 4\beta^2} \right]} \]

refractive index = \( 1 - \delta - i\beta \)

<table>
<thead>
<tr>
<th>( \theta_{\text{crit}} ) (deg)</th>
</tr>
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<tbody>
<tr>
<td>Be</td>
</tr>
<tr>
<td>1.52</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>1.78</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>1.71</td>
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</table>

\( E_x = 1 \text{ keV} \)
The photo-electron range is determined from “universal” fit to experimental data.

\[ d_{\text{elec}} = 5.4 \frac{E_e}{\rho} \left(1 + \frac{0.98}{1 + 0.0031E_e}\right) \mu m \]

The dose can be reduced by a factor of 5 or more with grazing incidence optics.

Analytic estimate of the surface dose

Design for LCLS Soft-X-ray Offset Mirrors

• Operation range is to be between 0.8 and 2 keV.
• Design criteria
  – maximize reflectivity (> 90%)
  – minimize length (i.e. maximize grazing angle)
  – minimize dose
• 2 options have been considered: Si and B\textsubscript{4}C coating on Si
• Findings
  – B\textsubscript{4}C/Si provides good solution for full 0.8 to 2 keV range.
    • $\theta = 0.8$ deg.
    • $L = 25$ cm
  – Si provides an alternate solution for 0.8 to 1.8 keV
    • This option may be considered if manufacturing or damage is a problem for B\textsubscript{4}C layer.

M. Pivoraroff, R. Soufli, LLNL
Reflectivity and Dose for grazing incidence mirrors

Reflectivity

Dose (eV/atom)

E (keV)

E (keV)
Recent experiments at FLASH
We have recently performed damage experiments on the FLASH facility in Hamburg collaboration with groups at Hamburg, Warsaw, Prague, Uppsala and Essen.

**Laser parameters**
- Wavelength = 32, 22 and 14 nm (photon energy = 39–91 eV)
- Pulse length ≈ 25 fs
- Focal spot diameter ≈ 20 µm
Goals and setup for FLASH experiments

- determine damage thresholds at shortest available wavelengths
- relate this to XFEL damage through calculated dose.

Samples: C, Si, SiC, B₄C

- Samples were exposed to pulses at various fluences.
- Samples were analyzed post-shot with various microscopes.
Damage craters measured by optical interferometry

Images of SiC samples exposed to 32 nm radiation
gray scale = surface height

(a) F < 0.28 J/cm²
(b) F = 0.72 J/cm²

Images of damage craters measured by optical interferometry:

- (a) F < 0.28 J/cm²
- (b) F = 0.72 J/cm²

Images with lineouts through center:

- (a) depth (nm)
- (b) position (µm)
- (c) position (µm)

September 2006 experiments

- Experiments done at 3 wavelengths: 32, 22, and 14 nm.

Focus on low-fluence region

Crater depth at 14 nm (preliminary data)
Low fluence region yields damage thresholds

- Damage threshold increases as wavelength decreases.
- Threshold for bulk SiC ≈ melt.
- Thin films have lower threshold.

Preliminary observations
XFEL imaging of biomolecules
The central idea is obtain images of single biomolecules with ultra-short pulses, before the absorbed energy has time to alter the molecular structure.

- A key question is: how short must the pulses be?
- The following slides present theoretical models to address this question

see lecture by Henry Chapman

Before pulse

25 Å

~ 50 fs pulse

After pulse

Diffraction pattern
A hydrodynamic model for x-ray irradiated molecules

“real” molecule

spherical, hydro model

atoms
calculate the ionization and motion of Lagrangian shells within the model molecule
First consider a pure Coulomb explosion

- X-ray photo-ionization ejects electrons from the sample
- Explosive motion is caused by repulsion of the ions.
- Assume uniform distribution of ionization
- Assume a very short pulse and look at motion after pulse
Analytic solution for Coulomb explosion

The motion of a shell at radius $r$ can be found from the energy form of the equation of motion:

$$\frac{dr}{dt} = \sqrt{\frac{2}{m}} (E - U)$$

- $r = \text{mass per unit charge}$
- $U = \text{potential energy per unit charge} = eQ \left(\frac{r_o}{R}\right)^3 \frac{1}{r}$
- $E = \text{total energy} = U(r_o)$

Solution:

$$t = \sqrt{\frac{2\pi}{3} d^{1/2} \left(\frac{R^3}{Q}\right)} \frac{1}{\rho_o} \int_{\rho_o}^{\rho} \frac{x^{1/2} dx}{(x - \rho_o)^{1/2}}; \quad \text{where} \quad \rho \equiv \frac{r}{R}$$

$$\equiv T f(\rho, \rho_o)$$

- $T = Hau-Riege, \ et \ al. \ Phys. \ Rev. \ E. \ (2004)$
Trajectories of radial shells in Coulomb explosion

- Motion is self-similar
- Analytic solution is useful for scaling and to check numerical calculations.

\[ R \approx 10 - 300 \text{ Å} \]
\[ T \approx 10 \text{ fs} \]

For short times: \( t = 5.3 \text{ fs} \)

\[
\left[ d \left( \frac{R}{10 \text{ Å}} \right) \right]^{-1/2} \left( f_i \right)^{-1} \left( \frac{\Delta r}{1 \text{ Å}} \right)^{1/2}
\]
A more complete numerical model extends the pure Coulomb explosion model

- Finite duration x-ray pulse.
- Time dependent photo and Auger ionization.
- Trapped electrons:
  - Determine spatial distribution of trapped electrons by a balance between pressure and electrostatic forces.
  - Calculate secondary collisional ionization using time and space dependent rate equations.
  - Solve partial-differential equation for material expansion via finite difference method.

\[
electrons \text{ escape if } E > \frac{3eQ}{2R} = 2 \text{ keV} \left( \frac{Q}{10^3} \right) \left( \frac{R}{100 \text{ Å}} \right)
\]

\[
electrons \text{ are trapped if energy is smaller}
\]
The trapped electrons shield the core of the molecule, forming 2-layer configuration

charged layer

neutralized hot core

similar to Debye shielding in a plasma
Extended model shows faster expansion of outer region, but slower expansion of inner core.
Complete model shows rapid ionization

- photo-ionization initiates a cascade.
- collisional ionization very quickly dominates.
- By 10 fs, carbon is stripped of 3 electrons.

**Graph Details**

- **Color Code**
  - Black = neutral carbon
  - Blue = valence ionization
  - Red = inner shell ionization

- **Equation**
  
  \[(k,l) = (\text{# K-shell,} \, \text{# L-shell}) \text{ electrons}\]

- **Graph Axes**
  - **X-axis**: Time (fs)
  - **Y-axis**: Ion density \(10^{22} \text{/cm}^3\)

- **Graph Labels**
  - Carbon

- **Graph Notes**
  - \((1,0)\), \((1,1)\), \((1,2)\), \((1,3)\), \((1,4)\), \((2,0)\), \((2,1)\), \((2,2)\), \((2,3)\), \((2,4)\)
The structure of a molecule with trapped electrons has lead to the concept of a molecular tamper

Fluence = $3 \times 10^{12}$
Radius = 20 Å
Tamper = 10 Å, H$_2$O
Pulse length = 20 fs

Tracer atoms
Results on x-ray imaging of biomolecules

- pulse lengths ~ 10 - 50 fs necessary to avoid damage
- incorporation of a molecular tamper helps extend the allowable pulse length
- incorporation of a ionization repair technique in the data analysis also helps.
X-ray interaction with nano-particles at FLASH: modeling and experiment

• Experiments were designed to gain an understanding of nano-particle dynamics relevant to future experiments on biomolecules.

• Differences between FLASH and (future) LCLS experiments
  - lower energy photons (100 eV vs 8 keV)
  - larger particles (100 nm vs 2-10 nm)
    • photo-electrons do not escape the particles
    • radiation absorption is inhomogeneous within particle

• We have used a Livermore radiation hydrodynamics code ("HYDRA", M. Marinak) to model the particle dynamics.
Energy deposition in 140 nm polystyrene sphere at 32 nm

Calculated properties of irradiated polystyrene spheres

Experimental results and comparison to calculations

- Experimental results will be posted upon publication, expected in Nature, 2007.
Conclusions

• The advent of XFELs will open an exciting new field of ultra-short, high intensity, x-ray material interaction.

• A large range of energy densities and physical phenomena can be accessed.

• X-ray optics must be designed to withstand damage.
  – Melting is an important threshold damage mechanism.
  – To avoid damage use:
    • low-Z materials
    • grazing incidence
    • placement at a large distance from the XFEL.

• Experiments on new FELs (i.e. FLASH) are helping to design XFEL optics and provide a glimpse of the interesting new physics in the x-ray future.

• Studies of x-ray interaction with biomolecules have helped define the necessary pulse parameters (e.g. pulse-length) for future imaging experiments.
References

• x-ray matter interaction
    • henke.lbl.gov/optical_constants

• Monte Carlo electron cascades

• XFEL optics

• x-ray imaging of biomolecules

• email me for more references: (rlondon@llnl.gov)