Interaction of energetic particles with surfaces: insight from molecular-dynamics simulations

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Thanks to: Chr. Anders, S. Zimmermann, A. Friedrich, Y. Rosandi, C. Engin E. Bringa (LLNL), R. E. Johnson (U Virginia)
5 keV Cu $\rightarrow$ Cu after 1 ps
color: temperature (kinetic energy in the center-of-mass frame)
Particle-solid interaction: applications:

- materials production:
  - implantation
  - ion-beam mixing
- surface technology:
  - thin-film growth
  - etching
  - surface modification
- micro- and nano-fabrication
- surface analysis:
  - depth profiling
  - SIMS, RBS, ...
- biotechnology:
  - desorption of biomolecules
- plasma-wall interaction:
  - thermonuclear fusion
- astrophysics:
  - erosion of planets, comets, dust grains
Characteristics of molecular dynamics

Solve Newton’s equations.

Think of:

**Potentials:** empirical many-body potentials

**Electrons:** no excitation or: friction-like energy loss

**Boundary conditions:** sufficiently large crystallite

**Detectors:** atomistic

**Statistics:** sufficiently many atoms
**Advantages**

- as realistic as possible in comparison to analytical theory or Monte Carlo simulations
  - for many-body simulations
  - for thermal nonequilibrium situations
- easy visualization / animation:
  appeals to imagination

**Disadvantages**

- slow
- cannot handle time scales $\gtrsim 1$ ns
- cannot handle space scales $\gtrsim 100$ nm
Metallic many-body potentials

(EAM potentials, tight-binding potentials, ...)
Describe for fcc metals reasonably:

- lattice constant, cohesive energy
- elastic constants
- defect energies
- extended defects, impurities
- surface structure
Outline:

- 'spikes' in metals induced by keV atom impact
- change in surface topography by ion bombardment
- cluster-induced cratering: linking nano- and microscales
High-density cascades: Spikes

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A spike is a limited volume with the majority of atoms temporarily in motion.

Spike effects may be important when the spike lifetime is larger than the duration of the initiating cascade. Spikes have been considered as the origin of a variety of experimental results over the years. The more compelling evidence seems to come from sputtering experiments.

Peter Sigmund, Appl. Phys. Lett. 1974
Energy density and time constant of heavy-ion-induced elastic-collision spikes in solids
### Spikes used to explain:

<table>
<thead>
<tr>
<th>Sputtering</th>
<th>enhancement, esp. under cluster bombardment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damage</td>
<td>reduction of point defect production</td>
</tr>
<tr>
<td></td>
<td>defect structure (<em>cascade collapse</em>)</td>
</tr>
<tr>
<td></td>
<td>amorphization</td>
</tr>
<tr>
<td></td>
<td>surface topography (<em>craters</em>)</td>
</tr>
<tr>
<td></td>
<td>chemical disorder (<em>ordered alloys</em>)</td>
</tr>
<tr>
<td>Mixing</td>
<td>enhancement</td>
</tr>
<tr>
<td></td>
<td>in molten cascade core</td>
</tr>
<tr>
<td>Conceptual</td>
<td>use of macroscopic concepts</td>
</tr>
<tr>
<td></td>
<td>(n, T, p)</td>
</tr>
</tbody>
</table>
\( n, T, p: \)

**System:**

- 1 keV Cu → Cu
- many-body potential
- no electronic stopping
- \( \approx 10^4 \) atoms
- 5 ps simulated

**Data analysis:**

- macroscopic quantities as *gliding averages* over sphere with radius \( r_c = 4.7 \, \text{Å} \) containing \( \approx 43 \) atoms
- temperature from

- only potential contribution to pressure from virial
movie:
1 keV Cu -> Cu

Cross section through a Cu(100) crystal after bombardment with a 1keV Cu ion.
Kinetische energi ("temperature") in units of \( \frac{1}{2} kT \), shown as an ellipse averaged around each atom.
E_{pot} - E_{kin} : L_{melt} = 0.14 \text{ eV /atom}

latent heat of melting
Cascade melting

Check:
- latent heat
- temperature
- diffusion
- pair correlation

10 keV Au -> Au temperature vs distance from spike center
Averback & Ghaly, 1994

mean square displacement
Averback et al 1988
Radial distribution functions for copper at (a) 600 K, (b) superheated to 2200 K and (c) liquid at 2200 K. Compare with (d) the core of a 2 keV cascade after 0.6 ps.
Cascade melting: Conclusions:

- liquid at low density
- low lattice heat capacity $\rightarrow$ long spike lifetime
- importance of latent heat of melting $\rightarrow$ long spike lifetime
- Pressure relaxation at free surface
Changes in surface topography
due to single ion impact

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Thanks to: Th. Michely, H. Hansen, C. Busse
(RWTH Aachen)
Outline:

• Erosion of Pt (111)
• Growth of Al (111)
• Grazing incidence bombardment:
  step-edge sputter yield
• Case study:
  Fluence dependent sputtering of Pt (111) by 5 keV Ar $\theta = 83^\circ$
Erosion of Pt (111)

1 keV Xe -> Pt (111) @ 650 K
Formation of
\[ Y_{ad} \quad \text{adatoms} \]
\[ Y_{sp} \quad \text{sputtered atoms} \]
\[ Y_{sv} \quad \text{surface vacancies} \]
\[ Y_{bv} \quad \text{bulk vacancies} \]
\[ Y_{i} \quad \text{interstitials} \]

Conservation of mass:
\[ Y_{sp} + Y_{ad} + Y_{i} = Y_{sv} + Y_{bv} \]

If diffusion possible:
bulk vacancies, interstitials, (part of) surface vacancies anneal:
\[ Y_{sv,\text{eff}} = Y_{sp} \]
(measurement of \( Y_{sp} \))

100 eV Cu → Cu
defects formed:
2 surface vacancies
2 interstitials
Karetta & Urbassek (1992)
Prediction from collision-cascade theory:

\[ \frac{Y_{ad}}{Y_{sp}} = 2 \frac{U_{sp}}{U_{ad}} - 1 \]

where \( U_{sp} \): energy dispensed to sputter an atom
\( U_{ad} \): energy dispensed to lift an atom to adatom position

bond-counting argument:
\( Z=9 \) bonds of atom in fcc(111) surface plane
\( Z=3 \) bonds of adlayer

pair potentials: \( \frac{U_{sp}}{U_{ad}} = \frac{9}{6} \) \( \frac{Y_{ad}}{Y_{sp}} = 2 \)

many-body: \( \frac{Y_{sp}}{Y_{ad}} = \frac{\sqrt{9}}{\sqrt{9} - \sqrt{3}} \) \( \frac{Y_{ad}}{Y_{sp}} = 4 \)
Conclusions:
PR B 50 (1994) 11167

- rough quantitative agreement of expt and simul
- $Y_{ad}/Y_{sp} \approx 4$
- at low energy: deviations due to steeper energy spectrum
Growth of Al (111):

1 keV Xe -> Al (111) @ 300 K
(+ marks height of original surface

ion fluence: 0.03 ML 0.20 ML 0.50 ML 1.5 ML
net growth net erosion

2400 Å
Experiment and MD simulation:

- preponderance of adatom over surface vacancy formation
- spike-induced local melting
- outflow of liquid (swelling)
- rapid resolidification -> amorphous zones hinder diffusion
- formation of vacancy clusters: hinders diffusion
Preponderance of adatom over surface vacancy formation

Surface vacancies separated from bulk vacancies
Formation of vacancy clusters: hinders diffusion

Probability that a vacancy is part of a vacancy cluster of $n$ vacancies
Outflow of liquid (swelling):

- prompt (ballistic)
- delayed (thermal spike)
outflow of liquid (swelling)
rapid resolidification → amorphous zones
movie
1 keV Ne impact for comparison:

no swelling
no amorphization
Top views:
Preponderance of adatom over surface vacancy formation

- surface atom
- adatom
- ion (impact point)
Experiment and MD simulation:

- preponderance of adatom over surface vacancy formation
- spike-induced local melting
- outflow of liquid (swelling)
- rapid resolidification -> amorphous zones hinder diffusion
- formation of vacancy clusters: hinders diffusion
Grazing incidence bombardment: step-edge sputter yield


5 keV Xe → Pt (111)
B-step = {111} micro-facetted step = along [1-1 0] direction
ion impact along [-1 -1 2]

\[ \xi = \frac{x}{\Delta x} \]
Flat terrace: $Y_{sp}, Y_{ad} = 0$ for $\vartheta \geq 80^\circ$
Near Step ($\xi=-1$): substantial sputtering and damage

$Y_{ad}/Y_{sp} \cong 4$
Dependence of damage and sputter yield on distance $\xi$ to step roughly a rectangular function

$Y_{ad} = \text{const.}$ for $-x_c < \xi < 0$

$x_c = 2 \Delta h \tan \vartheta$: distance where ion reflects clear from the step
Top views, $\theta = 80^\circ (\xi = -1)$:

- average event: $Y_{ad} = 126$
- productive: $Y_{ad} = 169$
- poor: $Y_{ad} = 34$
Beschuss der flachen Terrasse in einem Polarwinkel von 80°
Beschuss der B-Stufe in einem Polarwinkel von 80° in Zelle $\xi = -1$
Beschuss der B-Stufe in einem Polarwinkel von 80° in Zelle $\xi = -9$
Beschuss der B-Stufe in einem Polarwinkel von 80° in Zelle $\xi = -11$
Conclusions: 5 keV Xe -> Pt (111)

- Flat terrace: $Y_{sp}, Y_{ad} = 0$ for $\vartheta \geq 80^\circ$
- Near Step: substantial sputtering and damage
- Dependence of damage and sputter yield on distance $\xi$ to step roughly a rectangular function
- Influence of step reaches a distance $x_c = 2 \Delta h \tan \vartheta$ before the step
- Damage preferentially produced on upper terrace (behind step)
- Step edge smears out
Fluence dependent sputtering of Pt (111) by 5 keV Ar at $\theta = 83^\circ$

STM topographs at ion fluences of F = 0.25, 0.5, 1.0, 1.75 ML @ 720 K

Removed material vs fluence.
Line: model
Hatched: sputter yield of terraces
Interpretation:

\[ Y = Y_{\text{step}} \cdot A_{\text{step}} + Y_{\text{terrace}} \cdot (1 - A_{\text{step}}) \]

- \( Y_{\text{step}} \): average yield in front of steps
- \( Y_{\text{terrace}} \): average yield of terraces
- \( A_{\text{step}} \): area fraction of island impact areas

Fit of \( Y(F) \) yields:

- \( Y_{\text{step}} = 8.4 \pm 1.5 \) MD: 8.3
- \( Y_{\text{terrace}} = 0.08 \pm 0.03 \) MD: 0

Note:
- For \( A_{\text{step}} \) use \( d \cdot x_c \) if island diameter \( d > x_c \)
- \( A_{\text{island}} \) if \( d < x_c \)

At large fluence \( F \), island coalescence decreases sputter yield

![Graph showing removed material vs. fluence](image)
Cluster-induced cratering: linking nano- and microscales

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E. Bringa
Lawrence Livermore Natl Labs, CA

Thanks to: R. E. Johnson (Univ Virginia)
Cluster-surface interaction:

- materials production:
  - cluster deposition of materials
  - thin-film growth
    - crystalline nuclei, increased adatom mobility

- surface technology:
  - surface modification
  - surface cleaning
  - soft landings: preparation of supported clusters
  - surface smoothing (by lateral cluster spreading)

- planetary sciences
  - solar wind, dust, ... impact -> surfaces of icy moons, comets etc
  - collisions within planetary ring systems
  - dust analysis by spacecraft: CASSINI, STARDUST
cluster deposition of materials
nucleus of comet Halley
Giotto (1986)
dust grain (20 µm) collected by airplane
Abb. 1: Die Raumsonde Cassini/Huygens während der Endmontage in Cape Canaveral. Oben ist die in Italien gebaute Hauptantenne zu sehen, links die Huygens-Sonde, direkt darüber der in Heidelberg entwickelte Staubbefug der Cosmic Dust Analyzer (CDA), unten die beiden Haupttriebwerke, rechts die Fernerkundungsinstrumente einschließlich der beiden Kameras, die vom Betrachter wegblicken.


dust analysis on the Cassini mission
Outline:

I. Craters at the nano-, micro-, macroscale

II. Crater simulations by molecular dynamics

   A) Cratering: systematic results for Ar system
   B) Cratering: pictorial results for Cu system

III. Comparison to experiment
I. Craters at the nano-, micro-, macroscale

- nano: cluster impacts
- micro: dust particles
- macro: (micro-) meteorites, ...
Cratering experiments at the nanoscale:

\[ \text{Diameter of Crater [Å]} \]

\[ \sim V^{1/3} a \]

Yamada, Insepov et al

Xe -> Au: Donnely & Birtcher
Craters at the microscale: metal projectiles (d = 0.1 – 5 µm)

Abb. 9. Das eigentliche Kratervolumen $V(T')$ in Al als Funktion der Projektilenergie $E_{\text{kin}}$. Die Meßpunkte entsprechen verschiedenen Projektilmassen und verschiedenen Projektilgeschwindigkeiten (für $v > 1 \text{ km/sec}$).

Rudolph, Z Naturforsch 24a (1969) 326

Fig. 6. Crater volume vs kinetic energy from different experiments. The current experiment is the data point at $10^{12} \text{ eV}$, at $10^{10} \text{ eV}$ the data from Frisch (1992) and at $10^{22} \text{ eV}$ the data from Lange and Ahrens (1987). Each data point is the average value of all data points from the author. The error bars represent the standard deviation.

$$V(E_{\text{kin}}) = 2.34 \times 10^{-20} E_{\text{kin}}^{0.98}.$$

Planet Space Sci 41 (1993) 429
Craters at the microscale


Crater in solar cell of Hubble space telescope

Quinones & Murr, Phys Stat Sol A 166 (1998) 763

Al : v=2.6 km/sec, R=1.6 mm -> Cu
Barringer-Krater, Arizona: 1200 m Durchmesser, 200 m tief entstanden vor 50 ka durch 50m-Meteorit

Cratering experiments at the macroscale:

Gaspra
Galileo-Beiflug in 1200 km Entfernung
19 x 12 x 11 km
Figure 3. Voyager 1 images of crater-pocked Mimas reveal two different hemispheres of this inner, 400-km-diameter satellite of Saturn. Craters are spaced closely and overlap each other, indicating that the surfaces seen are ancient. The relatively large, 130-km-diameter crater Herschel is named after Mimas’s discoverer. Several fissures or grooves (best seen in the right image) may be a consequence of Herschel’s formation, heat-driven expansion of the crust, or tidal forces from Saturn.
Crater morphologies diameters are for Moon (approximate)

Copernicus
II Crater simulations by molecular dynamics

Notation:

- $E$  total cluster energy
- $E/n$ impact energy / projectile atom
- $Y$  total sputter yield
- $Y/n$ sputter yield / projectile atom

- $U$  cohesive energy
- $\varepsilon = E/U$  scaled cohesive energy
Cratering simulations by MD:

- 100 keV Xe$_1$ -> Au
  Bringa & Nordlund

- 10 keV Cu$_{13}$ -> Cu
  Aderjan & Urbassek

- 5.5 keV Cu$_{55}$ -> Cu
  Muramoto & Yamamura

- 20 keV Ar$_{2000}$ -> Si
  Aoki et al
Interest

Here:

- sputter yield $Y$
- crater size $V$

Further:

- surface modification: post-impact hardness
- ejecta: energy, angle, mass distribution
- etc
Anders (Univ. Kaiserslautern):

- amorphous Ar target
- Lennard-Jones potential
- 19 000 - 1 280 000 atoms
- up to 100 ps simulation time
- $\text{Ar}_n$ cluster size $n = 1 \ldots 10 000$
- cluster energy $E = 1 \text{ eV} \ldots 50 \text{ keV}$

Bringa (LLNL):

- $\text{Cu}_n \rightarrow \text{Cu}$
- cluster size $n = 50 \ldots 250 000$
- target size: $0.25 \ldots 25 \times 10^6$
- cluster energy: $10 \text{ eV} / \text{atom}$
- $0.5 \text{ keV} \ldots 2.6 \text{ MeV}$
- cluster velocity: $5.3 \text{ km} / \text{sec}$
Molecular dynamics simulations: how to measure crater shape and volume

\[ \text{Vol}_{cr} = \frac{2}{3} \pi z_{cr} R_{cr}^2 \]

circular damage area
II.A. Cratering: systematic results for Ar system

Notation:

- $V$: crater volume (below reference plane), expressed as number of missing atoms
- $z$: crater depth
- $r$: crater radius
- $r/z$: aspect ratio
crater volume linear in energy

\[ \text{Ar}_{100} \]
threshold energy to linear behavior
aspect ratio: nearly hemispherical craters
threshold energy to hemispherical crater
dependence of thresholds on cluster size $n$
Crater formation mechanism:

Cratering: pictorial results for Cu system

$R_{cl} = 9 \text{ nm}$
$n = 250,000$
$E = 2.5 \text{ MeV}$

(stress coloring)

movie

Tensile stress leads to break-up
splashing:
III Comparison to experiment

- Previous experiments on crater volumes:
  - Rudolph 1969:
    - µm-sized projectiles
  - Eichhorn and Grün, 1993:
    - ice targets
  - Quinones and Murr, 1998; Murr et al 1998:
    - mm-sized projectiles

- Previous simulations on crater volumes:
  - Bringa et al, 2001
  - Colla et al, 2000
  - Aderjan et al, 2000
Crater volumes:
Synopsis (selection) of experiments and simulations
data scaled to cluster size n

dependence on cluster size n
Conclusions

crater volume $V$

- linear in total energy $E$
- threshold energy to linearity $\approx$ hemispherical shape
  only minor dependence on cluster size
- results are "approximately" independent of projectile size and only
  scale with total cluster energy
- BUT: experiment for $\mu$m- and mm-sized projectiles give larger
  craters than simulations for nm-sized projectiles
- simulations for larger clusters show similar behavior
- probable reason: different dynamics for larger clusters
  - instead of "microexplosion" for small projectiles
  - stress effects (rebound pressure) within projectile important