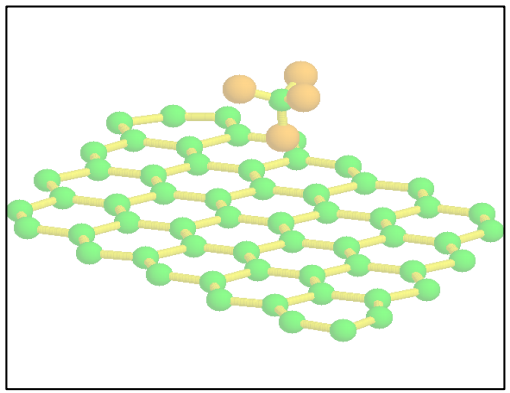
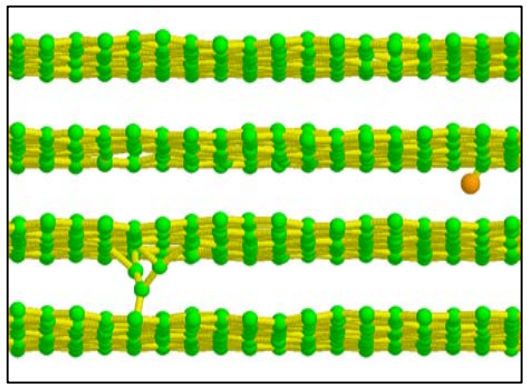
Atomistic simulations of plasma-surface interactions

E.M. Bringa, G. Gilmer, J. Marian and L. Zepeda-Ruiz

PSIF workshop
ORNL, Oak Ridge, March 2005





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S. Stuart (Clemson), K. Nordlund (Helsinki)

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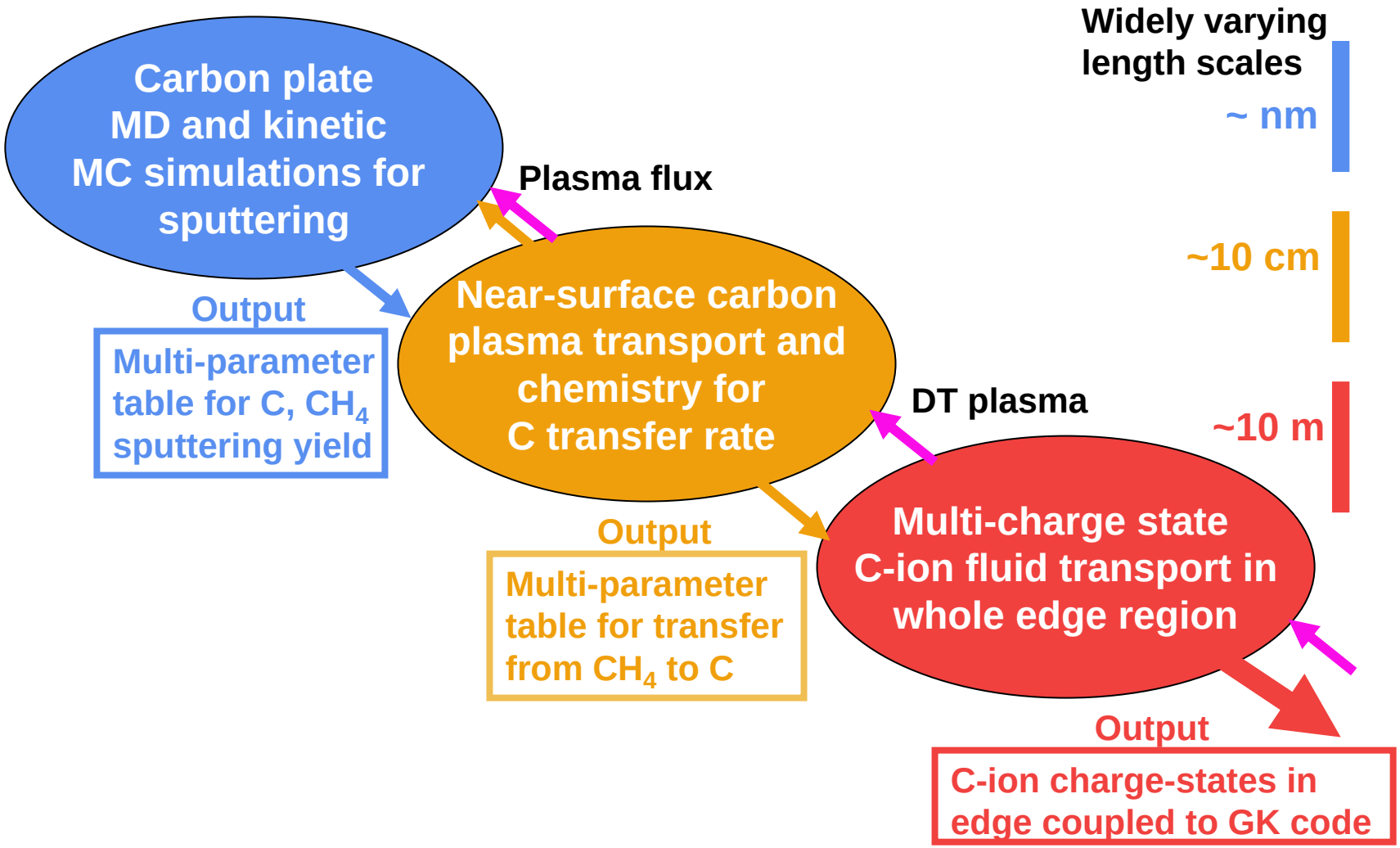
Outline

- **Motivation**
- **On potentials and MD codes …**
- **Sputtering yield as a function of energy and angle for both REBO and AIREBO**
- **To do list …**
- **Summary**

Overall picture:
Edge plasma impurities from plasma/wall interactions

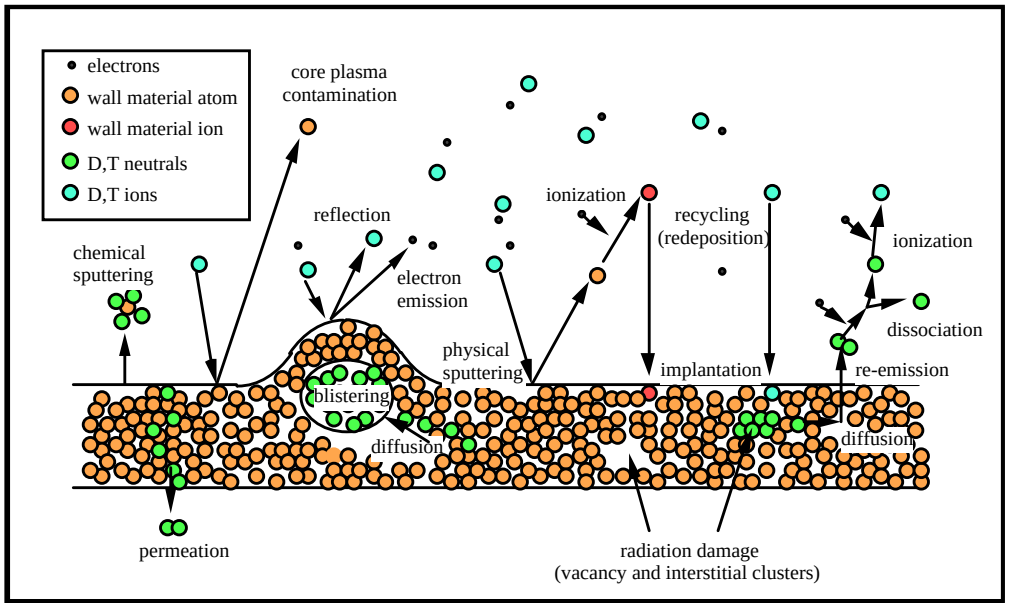
Impurities in the edge plasma are important for power balance



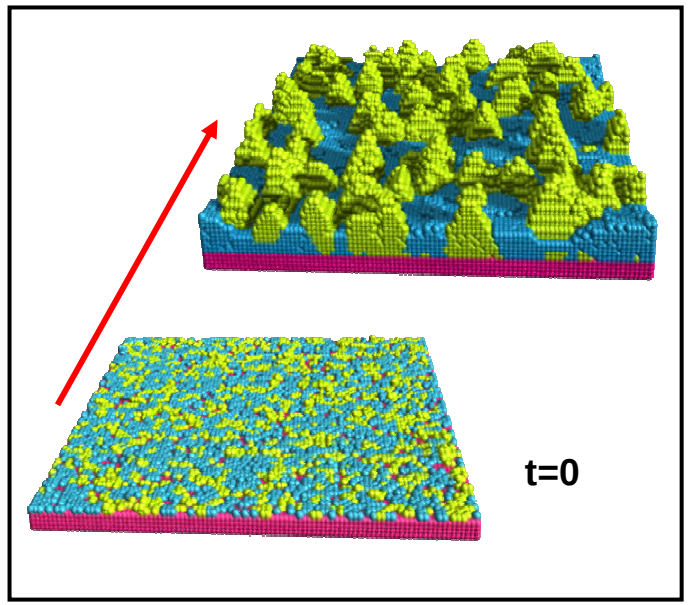
Modeling plasma-wall interactions requires understanding complex physical and chemical processes

Carbon contamination of the plasma results from erosion of the surface by chemical and physical sputtering.

Divertor surface processes



Topographical evolution



Molecular Dynamics and surface Monte Carlo simulations enable fundamental understanding and determine required sputtering-yield data

Goal: generate table of erosion as function of many variables

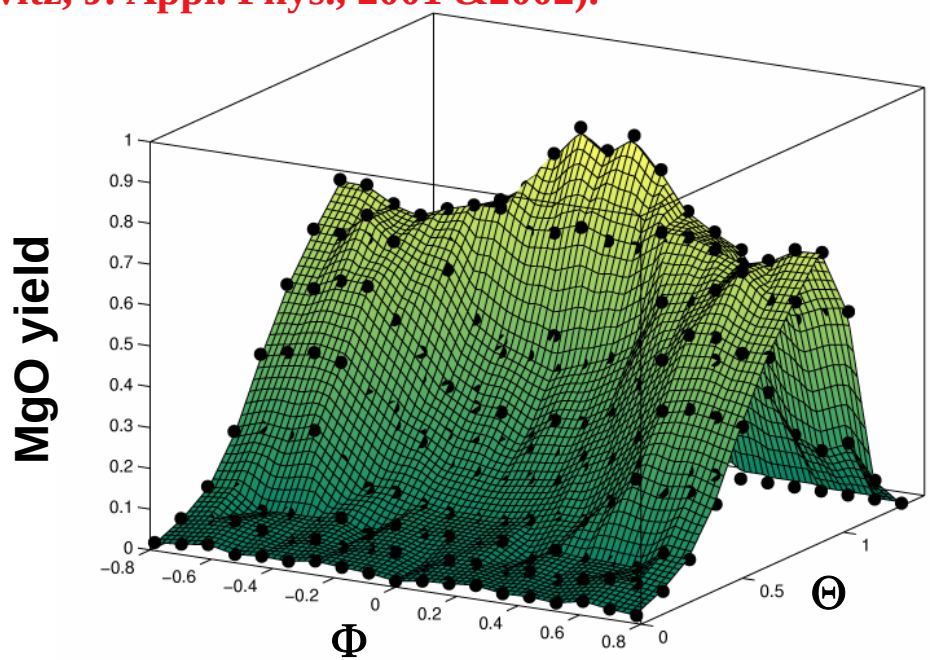
$$\text{Sputtering Yield } Y = \frac{\text{Species ejected from the surface}}{\text{Energetic ion impacting the surface}}$$

We are calculating carbon and hydrocarbon yields similar to the MgO example below (Zepeda-Ruiz & Srolovitz, J. Appl. Phys., 2001 &2002).

Yield as a function of:

- **ion/neutral type**
- **incident energy**
- **incident angle**
- **particle flux**
- **surface temperature**
- **surface topography**

Large number $O(10^5\text{-}10^6)$ of MD simulations required – use accelerated or rare event methods (future).



MgO sputtered by 600 eV Ar ions

How do we get started with MD of hydrocarbons?

Need good reactive empirical (fast) potentials ➔ "chemistry"

REBO I (Reactive-Empirical-Bond-Order, R_{cut}=2 Å)

Brenner *et al.* 1990-1992. Bond-order term has 3-body contributions. No dispersion forces (long range), no repulsion/attraction term for non-bonded atoms ➔ Graphite planes not bonded (distance between planes ~ 3.3 Å).

REBO I + (dispersion/non-bonded), R_{cut}~10 Å)

Various implementations. MDCASK (LLNL): *parallel implementation (A. Kubota)*

REBO II, Rcut=2 Å

Brenner *et al* 2002. Re-parametrization of Brenner I, including new functional forms

AIREBO (Adaptative-Intermolecular REBO, R_{cut}=10 Å)

Stuart *et al.*, 2000-2003: REBOI + LJ-(bond-order) + torsion (4-body)

Tight-Binding based BOP (R_{cut}=2.4 Å)

Pettifor+Oleynik (1999-2003): new version has both 3 and 4 body terms. SLOW

ReaxFF [REActive Force Field, R_{cut}=3.9 (LJ) / ∞ (Coulomb)]

Van Duin *et al.* (2001-2003): BOP+LJ+torsion+Coulomb. VERY SLOW, but available for several species (H,C,O,N, Si, Al,…). BRAND NEW parallel version (GRASP –SNL, P. Vashista -USC), not yet widely available.

MD simulation of sputtering from hydrocarbons

• 500 eV-few keV C→ graphite bombardment, R. Smith, K. Beardmore, several papers, Tersoff/REBOI

• 10 keV C_{60} bombardment of C_6H_5 molecules adsorbed on graphite: M. Kerford and R.P. Webb, Nucl. Inst. Meth. Phys. Res. B **153**, 270 (1999). REBOI

• low energy (<35 eV) H bombardment of hydrogenated amorphous carbon surfaces that can lead to ejection of CH_x molecules: E. Salonen *et al*., Phys. Rev. B **60** (1999) R14005 and **63** (2001) 195415, etc. REBOI / Tight-Binding

Up to date there is no systematic desorption study in the range 35-150 eV

What are bond-order potentials?

***One route is through a* MANY–BODY EXPANSION:**

$$U = \underbrace{\sum V^{2B}(R_i,R_j)}_{\text{two-body}} + \underbrace{\sum V^{3B}(R_i,R_j,R_k)}_{\text{three-body}} + \underbrace{\sum V^{4B}(R_i,R_j,R_k,R_l)}_{\text{four-body}} + \underbrace{\ldots\ldots}_{\text{higher order}}$$

They are a way to improve on two-body interactions

Assume potential energy can be expanded in terms of bond stretches and angle bends:

$$U = \underbrace{\sum \text{bond stretch}}_{\textit{two-body}} + \underbrace{\sum \text{angle bend}}_{\textit{three-body}} + \underbrace{\sum \text{stretch-bend}}_{\textit{three + higher}}$$

$$+ \underbrace{\sum \text{stretch-stretch}}_{\textit{three-body}} + \underbrace{\sum \text{bend-bend}}_{\textit{four + higher}} + \ldots.$$

The energy is written in a form similar to a pair potential but with a many–body bond–order function that modulates the attractive pair term:

$$U_{atom} = \sum_{ij} [A e^{-a r_{ij}} - b e^{b r_{ij}}] \; ; \; U_{tot} = \sum U_{atom}$$

b: many–body bond–order function

REBO ➔ only interactions within ~0.2 nm

Adapted from D. Brenner's web site

http://www.mse.ncsu.edu/CompMatSci/Tutorial/listing.html

What can AIREBO do better than REBO?

(besides graphite planes being bonded!)

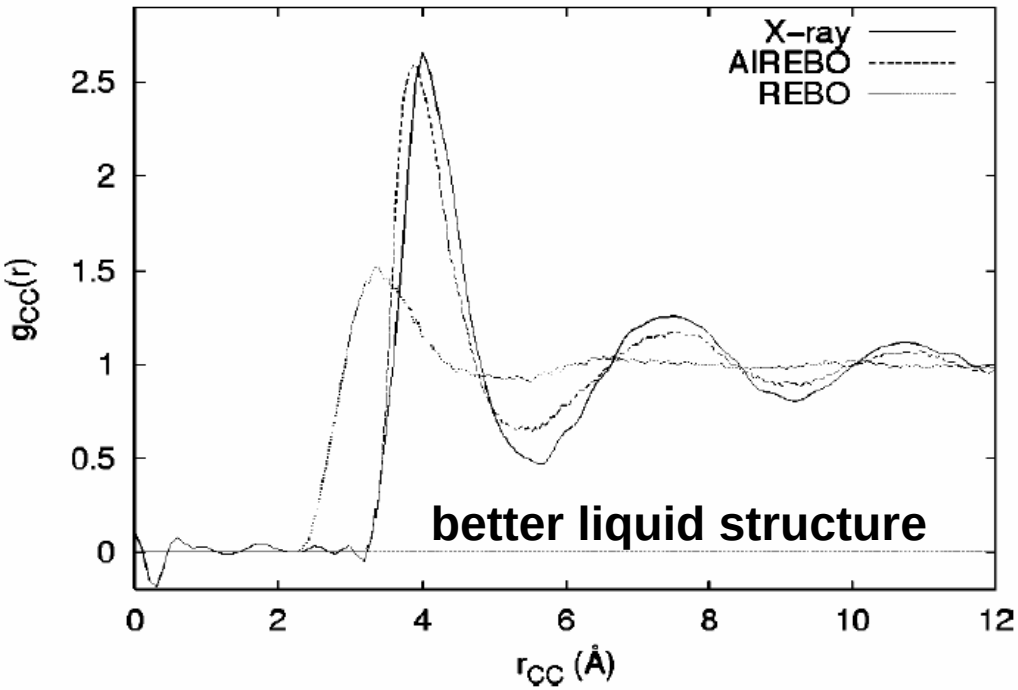


FIG. 2. Carbon–carbon pair correlation function $g_{CC}(r)$ for liquid methane at 92 K. Curves represent results from x-ray diffraction (Ref. 48), the AIREBO model, and the REBO model.

Stuart *et al*, J. Chem. Physics **112** (2000) 6472

Better description of radicals than REBO

REBO+ torsion + dispersion (LJ)+nonbonded repulsion via an adaptive method

⇩

suitable for studying reactivity in molecular condensed phases.

Overcomes the limitations of the REBO potential in studying systems with intermolecular interactions.

It has been designed for molecular systems such as liquid hydrocarbons (specially alkane liquids), thin films, and small hydrocarbon molecules

What can AIREBO do better than REBO?

Graphite planes are bonded!

Distance between graphite planes

TABLE IV. Structural, mechanical, and energetic properties of graphite.

Property	REBO	AIREBO	Experiment
r_{CC} (Å)	1.420	1.396	1.415[a]
r_I (Å)	···	3.354	3.354[a]
c_{11} (GPa)	1060[b]	1150	1060(20)[c]
c_{12} (GPa)	150[b]	150	180(20)[c]
c_{13} (GPa)	···	10	15(5)[c]
c_{33} (GPa)	···	40[d]	36.5(1.0)[c]
$\Delta_{sub}H_{298}$ (kcal/mol)	170.2	172.3	171.9[a]
$\Delta_f H_{298}$(rhomb) (kcal/mol)	0	0.0006	0.14(4)[a]
Vacancy formation E (eV)	7.5	7.7	7.6[e]

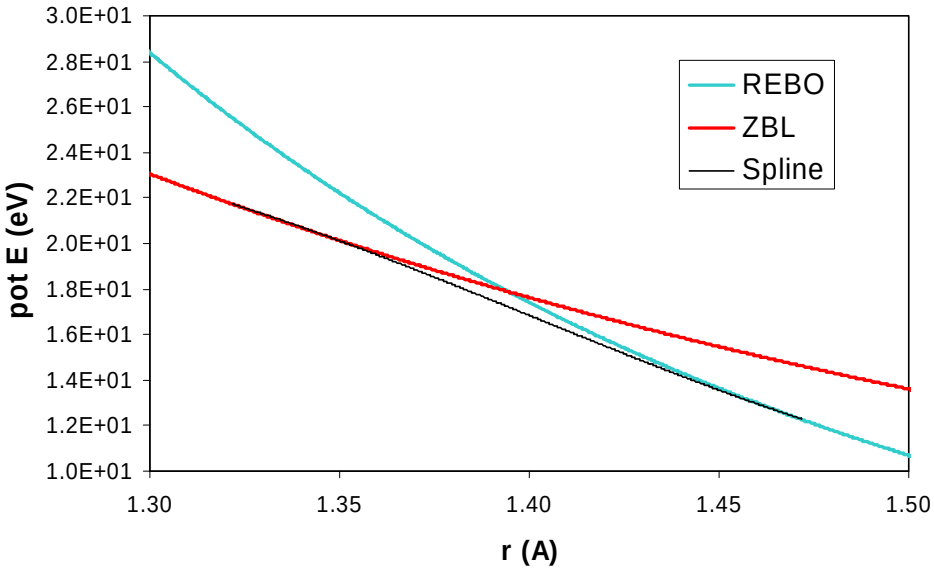
[a]Reference 62.
[b]The experimental r_I value was used in evaluating elastic constants for the REBO model.
[c]Reference 65.
[d]c_{33}=40 GPa at equilibrium geometry, 36 GPa at experimental geometry.
[e]Reference 44.

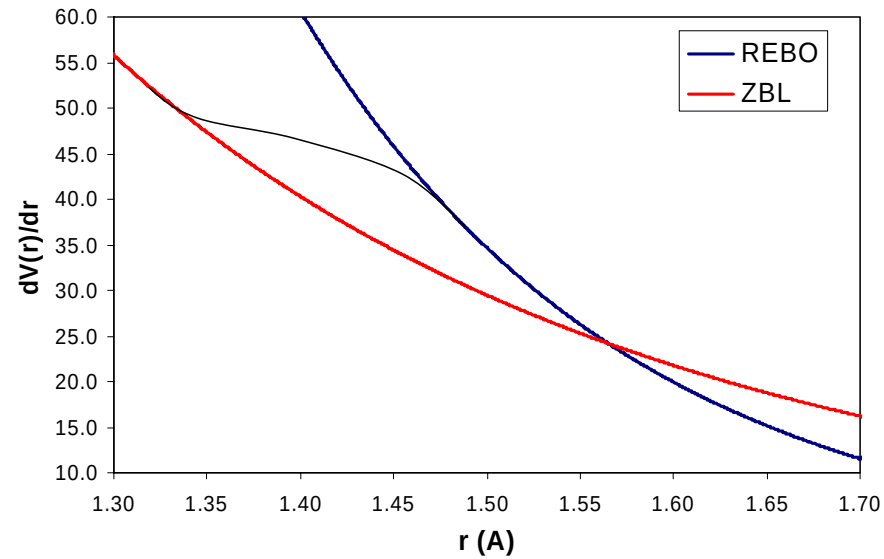
Stuart *et al.*, J. Chem. Physics **112** (2000) 6472

Using AIREBO potential to calculate sputtering yields

- Serial Source code obtained directly from the author (S. Stuart, Clemson University).
- Code can do both REBO and AIREBO
- Can turn off/on LJ and torsion
- Added capability to do ion bombardment: ZBL potential at high energies + multiply impact points
- Parallel wrapper (T. Oppelstrup, LLNL) to run 20-100 impacts/CPU. Run in 20-128 CPU's, during 2-12 hours

High energy simulations:
Smooth joining of ZBL with REBO (J. Marian)





REBO has a "Morse" repulsive potential given by 1 exponential
ZBL [$V=Z_1Z_2/r\ \Phi(r)$] has screening function Φ composed of 4 exponentials➔

Use 3rd order exponential spline ➔ continuity of the 0th and 1st derivatives

$$V(r) = \exp\left(B_0 + B_1 r + B_2 r^2 + B_3 r^3\right)$$

$$\text{for } 1.3216 < \mathrm{r} < 1.4718$$

Parallel AIREBO code

- Advantages: number of simulated atoms only limited by the number of available CPU's.
- Necessary to study ELMS erosion (keV) ions, when targets of ~0.1-1 million are needed.
- Other problems that can be tackled with this code: a) shocks in diamond and hydrocarbons, of interest to DOE ICF program; b) laser ablation of diamond; etc.

- Parallel version available from NRL, but uses particle decomposition ➔ VERY slow.
- **Implement parallel version of AIREBO using domain decomposition. Collaboration with S. Zybin (CalTech).**

Funded by DOE-OFES

How to transform serial AIREBO into a parallel code? I

Solution:

A) use domain decomposition. Only cells of size r_{cut} are considered when calculating forces. MDCASK has excellent parallelization, with scaling proven up to 400 CPU's and several hundred million atoms.

B) AIREBO force routines very efficient

➔ use AIREBO force routines within MDCASK domain decomposition.

Problem: Force routines assume a GLOBAL list of interacting pairs ➔ impossible to achieve efficiency in parallel code ➔ need to build "local" pair list for each "cell".

Funded by DOE-OFES

How to transform AIREBO into a parallel code? II

Usual pair list easy for repulsive, pair potential. Simple for 3 body bond-order terms in REBO, because all interacting atoms are within the (short) cut-off.

Problems:

1) Need very large cut-off for LJ (1 nm, versus 0.2 nm for other interactions)

2) 4-body terms (ijkl) may include atoms which are NOT included in "cell" or neighbor "cells".

Solution:

A) If LJ cut-off is used, no problem with 4^{-body} terms.

B) If want to save more time, then define a re-normalized "short" cut-off ($r_{new} = 2\ r_{old}$) ➔ all atoms will be included in pair list.

Still a few bugs in the code, stay tuned

Funded by DOE-OFES

Carbon sputtering yield as a function of energy

First sputtering calculations using AIREBO

Runs in MCR (LLNL, 11 TFs, Pentium III), using 500-2000 atoms, and 1-128 CPUs

Potential/code	t_o=CPU time (μs/atom/step) / time for Y(E) point
EAM/MDCASK	5 (parallel) / 0.9 days
Tersoff/MDCASK	25 (parallel) / 4.3 days
REBO+LJ/MDCASK	300 (parallel) / 52 days
REBO/AIREBO	5 (serial) / 0.9 days
REBO+LJ+torsion/AIREBO	300 (serial) / 52 days

1 sputtering point: ~2000 iterations, 500 atoms, 15000 steps ➔
Time for 1 Y(E) point=1.5 10^{10} t_o

Need parallel runs

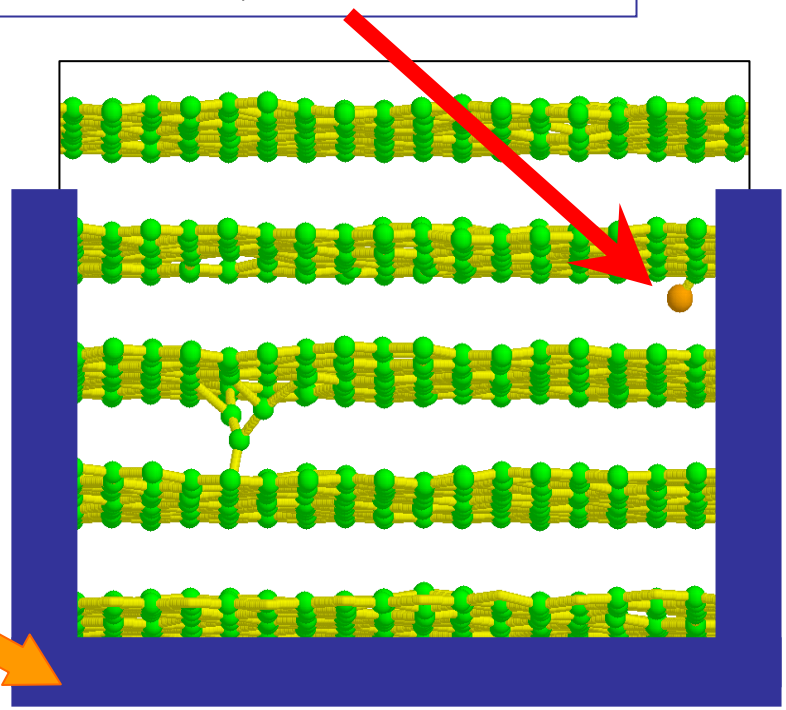
Bombardment simulations at LLNL

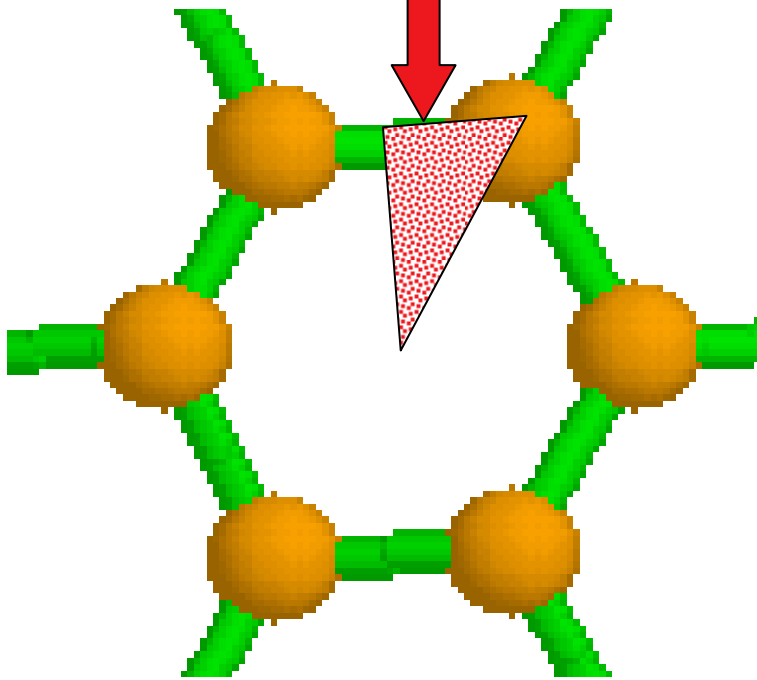
GRAPHITE

MDCASK (LLNL): highly parallel, variable time step, Potential: REBO+long range+ZBL
Targets: 500-40,000 C atoms, 300-600 K

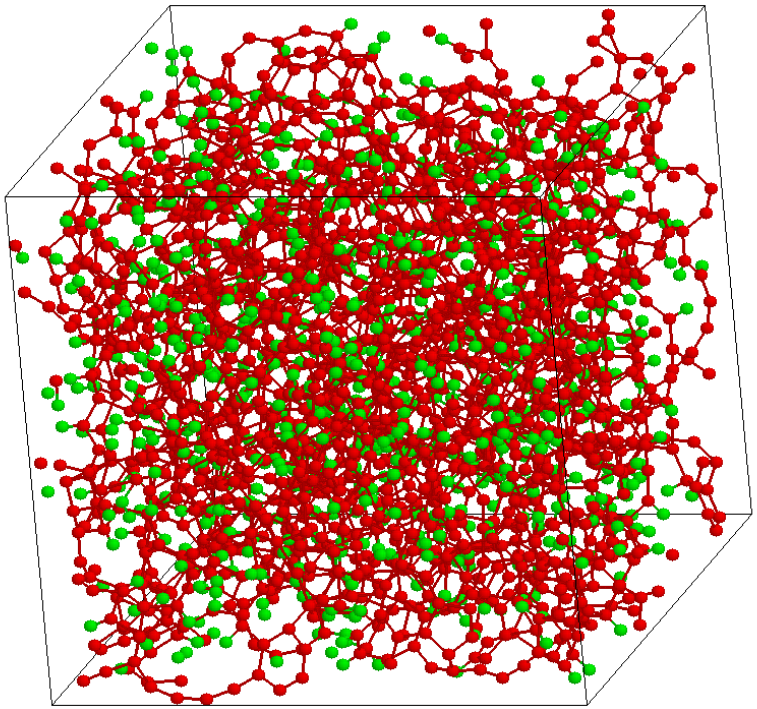
H/D/T projectiles, 5-300 eV, several angles of incidence, hitting an irreducible region on the surface.

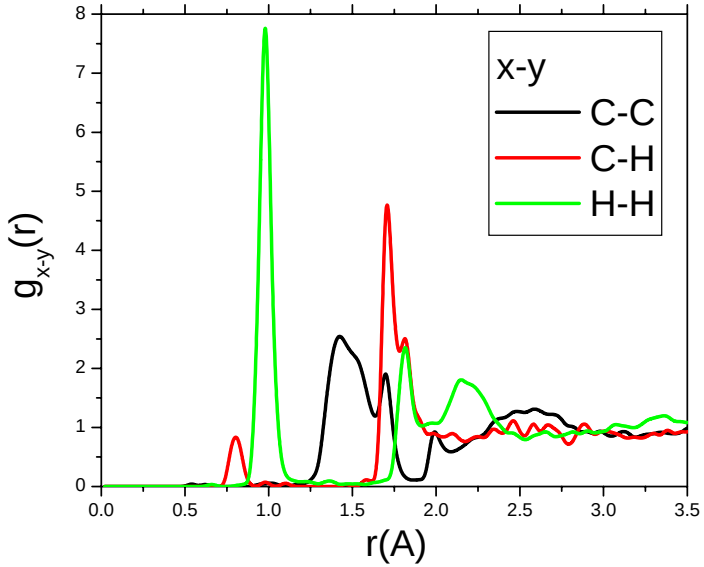
Thermostat at sides and bottom to minimize boundary effects





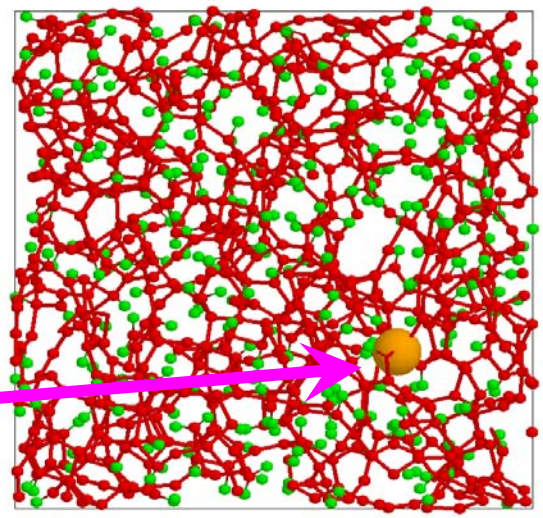
We have produced several amorphous carbon MD "sample" to model steady-state divertor surfaces



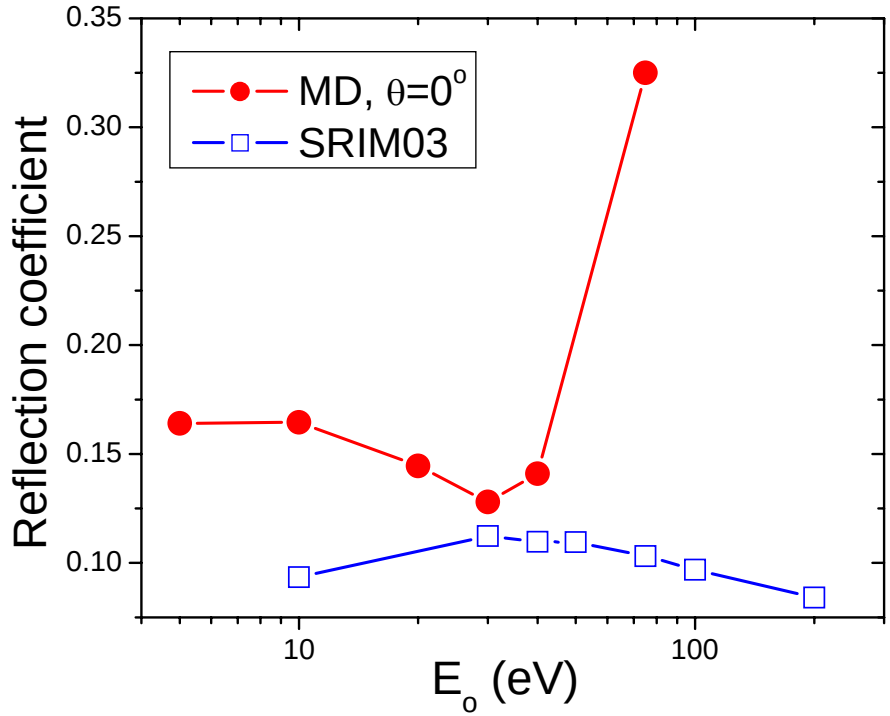


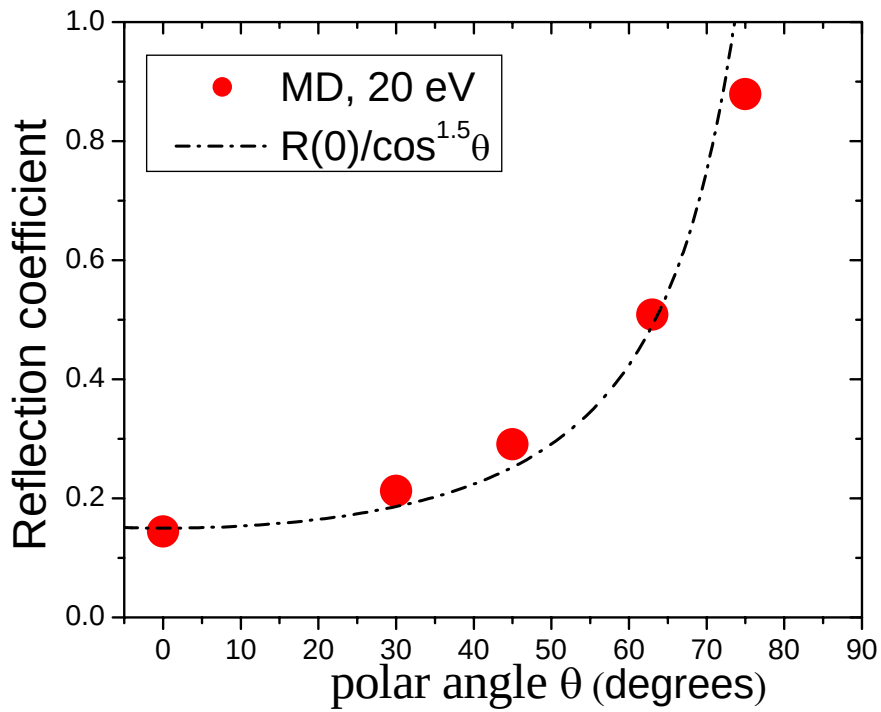
aC:H sample with 30%-40% H content
g(r) matches published results, sp^2/sp^3 ratio ~60%/40% at 300 K

100 eV D → aC:H sample, 45°, 300 K
No sputtering for this event. D gets trapped in the amorphous sample.



Calculation of reflection coefficients
T → aC:T

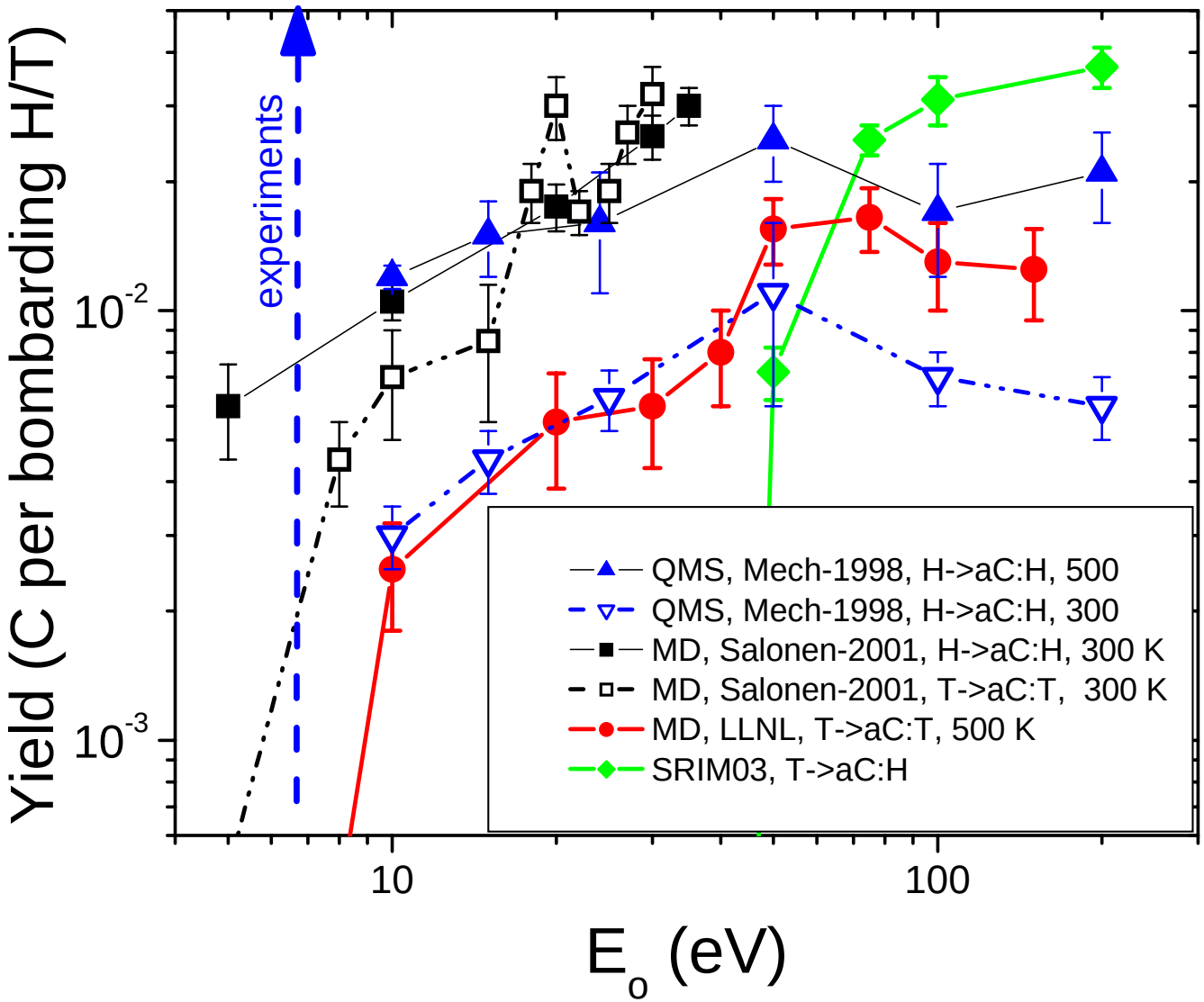




- Large differences between BCA (SRIM2003) and MD results.
- Smooth dependence with polar angle at low energies
- FUTURE: compare with reflection coefficients from Alman *et al*. (UIUC/ANL) at lower energies.

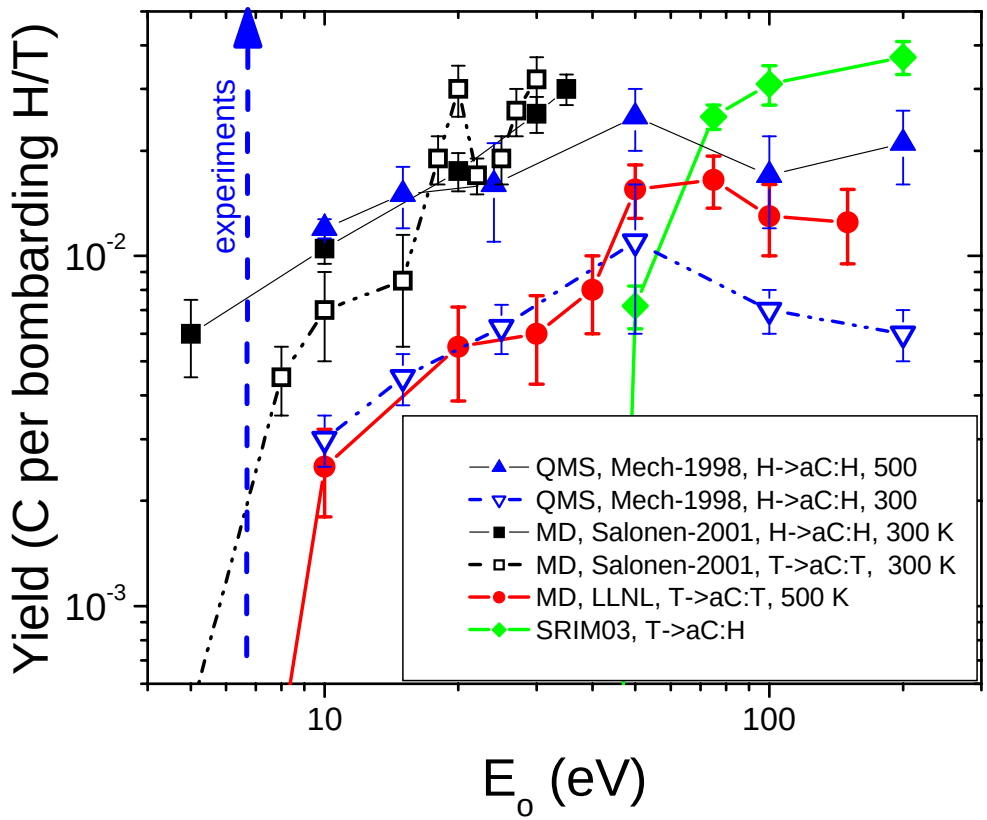
Carbon sputtering yield as a function of energy

First sputtering calculations above 35 eV



Carbon sputtering yield as a function of energy

First sputtering calculations above 35 eV



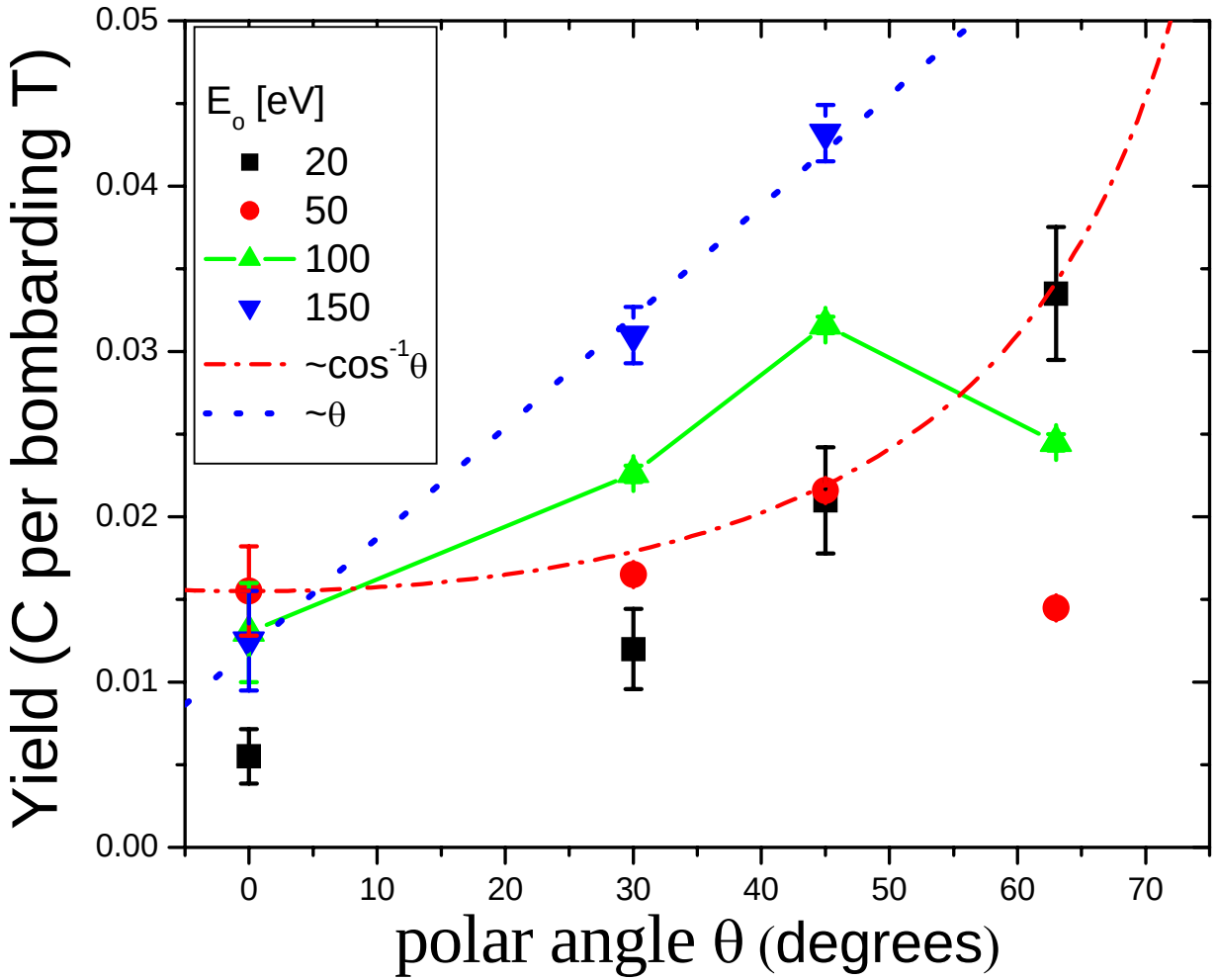
- TRIM gives totally different behavior even for physical sputtering (maximum at much higher energies)
- Clear evidence of chemical erosion at low energies
- Calculated value within range of existing experimental values for H, D bombardment.

- MD reproduces maximum in yield seen in experiments!
- MD values within range of existing experimental values for H, D bombardment.
- No experimental results for T bombardment, but from D,H experiments, expect Y(T) >Y(H) (isotope effect).

Yield is 2-8 times lower than low energy yield from Salonen *et al*., PRB **63** (2001) 195415, for T→aC:T. Possible reasons: 1) different surface "topologies" give different ejection probabilities; 2) different temperatures, 3) Salonen *et al*. used small spread in incident angle+Maxwellian velocities.

Carbon sputtering yield as a function of angle

First sputtering calculations as a function of incident angle



No available experimental data

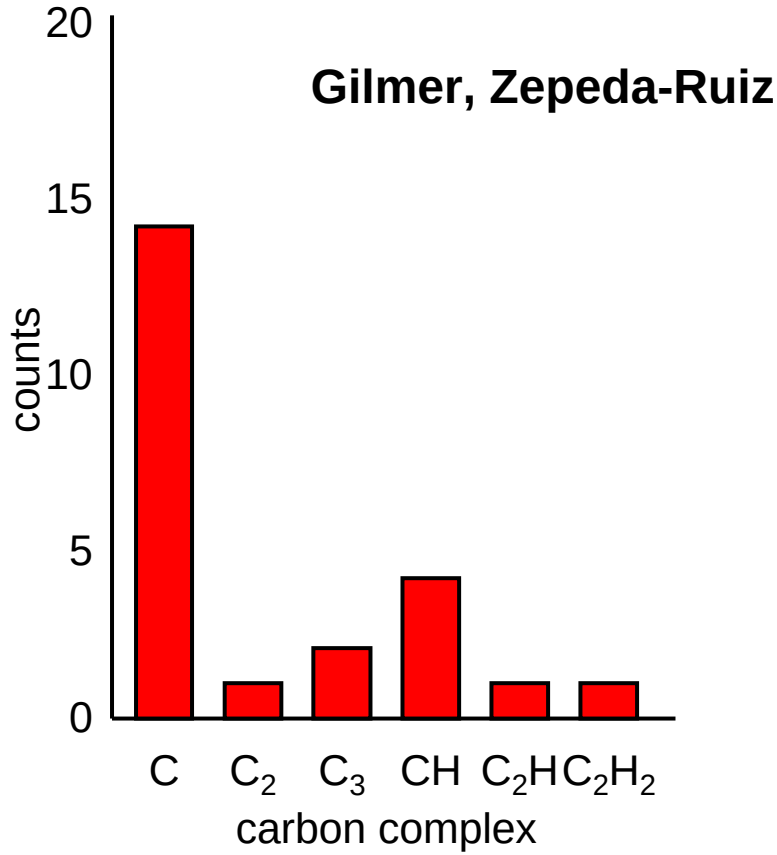
- Yield increases with the incident angle, as expected, BUT …
- There seems to be no simple functional form to fit the angular dependence.
- At high polar angles the yield decreases (very glancing incidence becomes ineffective)

Near future calculations:

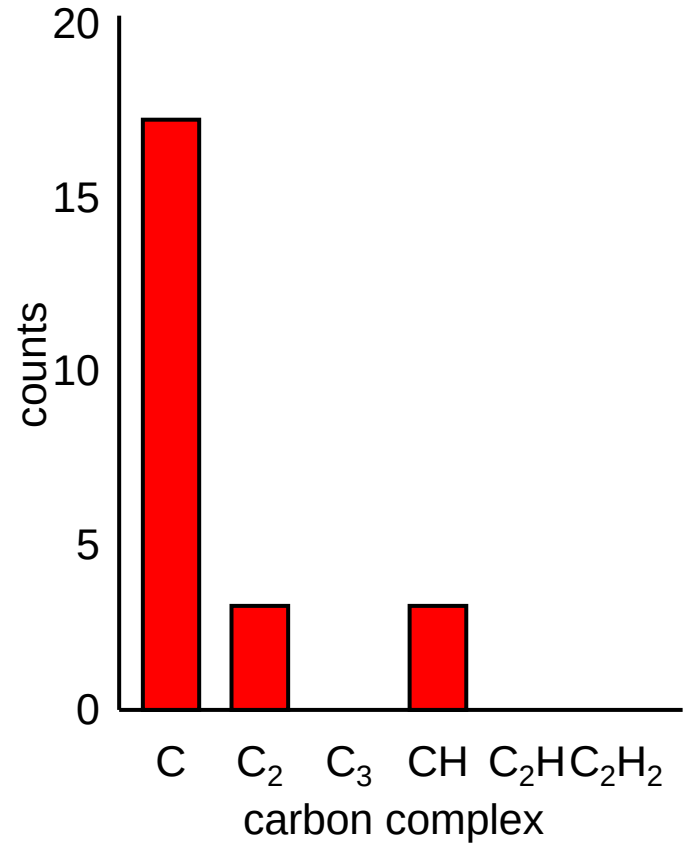
- calculation for additional angles
- to evaluate role of the surface topology, build several different surfaces and re-calculate.

Impacts produce a variety of ejected carbon complexes

case I: 50 eV at 0°, 1.55% → 31 C ejected



case II: 100 eV at 0°, 1.30% → 26 C ejected

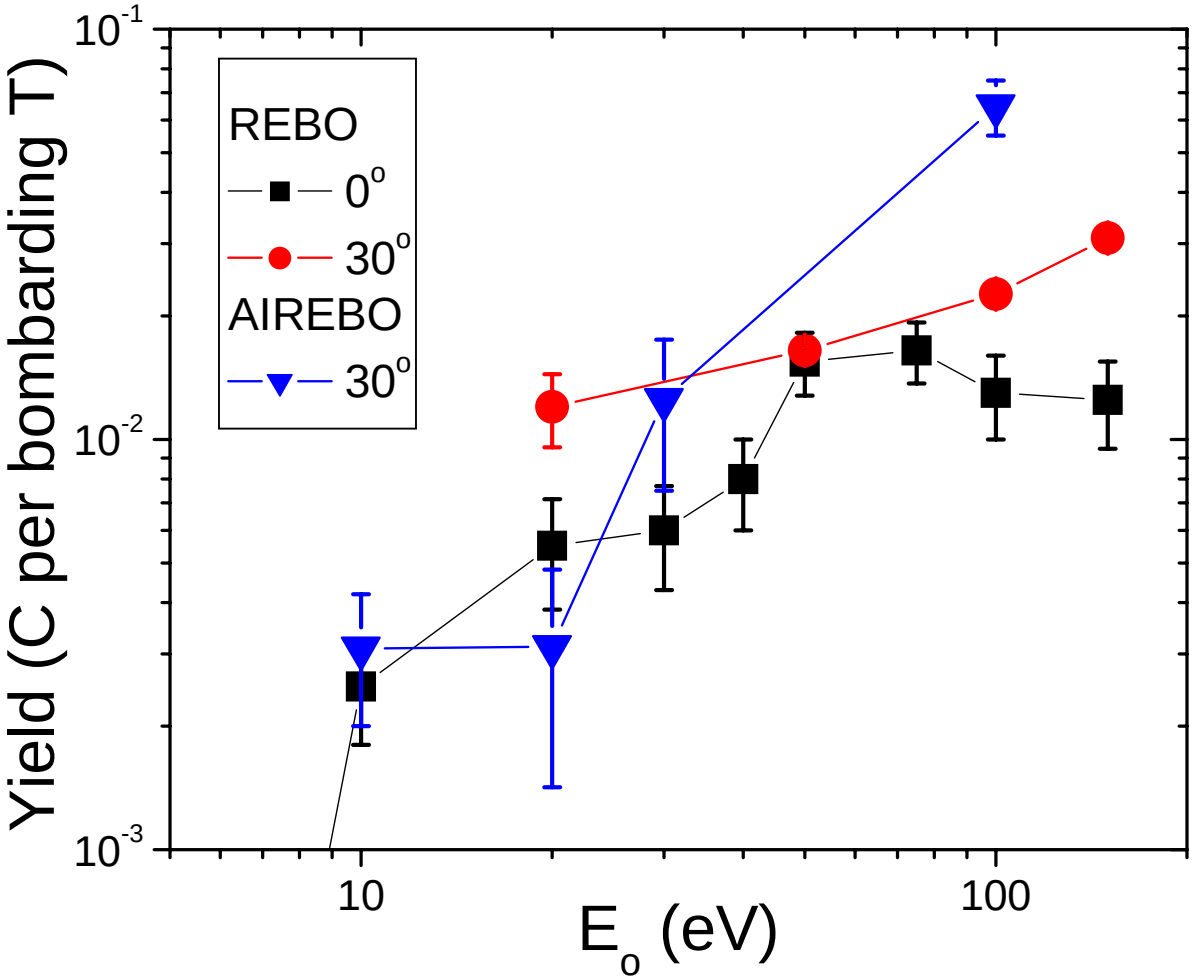


No observation of "methane" formed directly by impact/chemical sputtering

- For this particular sample topology, there are no CT_3 groups dangling on the surface that would lead to CT_4 formation.
- CT_4 may form/eject much later on, on the surface or directly above the surface ➔ use chemical kinetics code to evaluate this possibility.

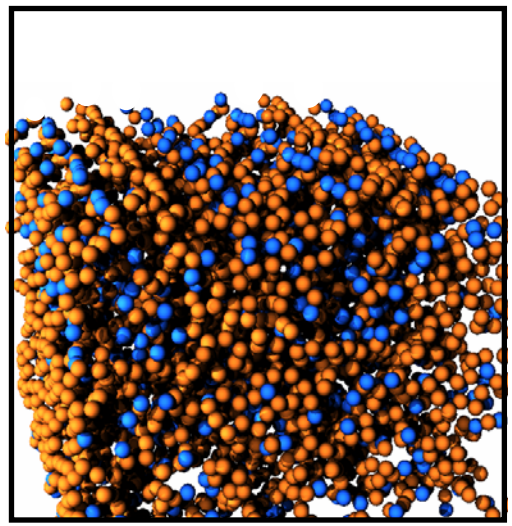
Carbon sputtering yield as a function of energy

First sputtering calculations using AIREBO runs with 500-2000 atoms



REBO and AIREBO yields are the same within a factor of 2-4.

Runs with bigger/different samples in progress



Carbon sputtering yield
REBO vs. AIREBO
runs with 500-2000 atoms

target/sputtering (100 eV T) \ angle	30°	45°
Quenching: REBO, Sputtering: REBO	2.26 %	3.16 %
Quenching: REBO, Sputtering AIREBO	8.35 %	10.05 %
Quenched: REBO, Sputtering: REBO + torsion		8.25 %
Quenched: REBO, Sputtering: REBO + LJ	1.30 %	1.89 %
Quenched: AIREBO, Sputtering AIREBO	0.93 %	1.30 %
Quenched: REBO, Sputtering: REBO, 2nd target	1.75 %	2.80 %

REBO and AIREBO yields are the same within a factor of 2-4.

Variability from sample to sample as large as variability from REBO to AIREBO

Some open questions

•For MD, are we using appropriate "model" surfaces? In experiment surface is dynamically changing, including long term relaxation processes difficult to include in MD. Can MD+MC give us some hints? Need experiments on surface/near surface structure!

•Can we understand the differences between the erosion rates at different devices only as a function of flux/ion temperature? NOTE: Salonen *et al*. found shielding at "high" fluxes.

• Is bombarding with dimers (with 2 E_o) the same as bombarding with monomers (E_o)?

• How does ion bombardment enhance chemistry? How far can radicals/neutrals diffuse in the highly damaged aC:H? Can radicals form 2-4 nm below the surface, travel towards the surface, and then induce desorption?

• What is the effect of impurities? Is it only shielding/geometric? Be experiments indicate huge effect … Are there 'drastic' electronic effects (➔ classical simulations may not work?)

Summary and future work

CARBON SPUTTERING YIELDS:

- **MD calculations using REBO/AIREBO potential include both physical and chemical effects.**
- **Calculated sputtering and reflection for graphite**
- **Constructed amorphous C:H sample for MD sputtering**
- **Obtained sputtered species and erosion rates for amorphous C**

- **First sputtering calculations at energies above 35 eV ➔ reproduces experimental maximum in energy**
- **First study as a function of incident polar angle➔ complex behavior**
- **REBO-AIREBO differences "small", but more detailed study needed**

Future MD calculations:

- **Sample energy and angle more finely**
- **Sample surface topology**
- **NEW: Sample target content of H/D/T**
- **NEW: Sample surface temperature**

→ **sputtering/reflection/sticking tables as input for near-surface chemistry/plasma codes**

MD simulations of diffusion in aC:H → **Input for KMC simulations**