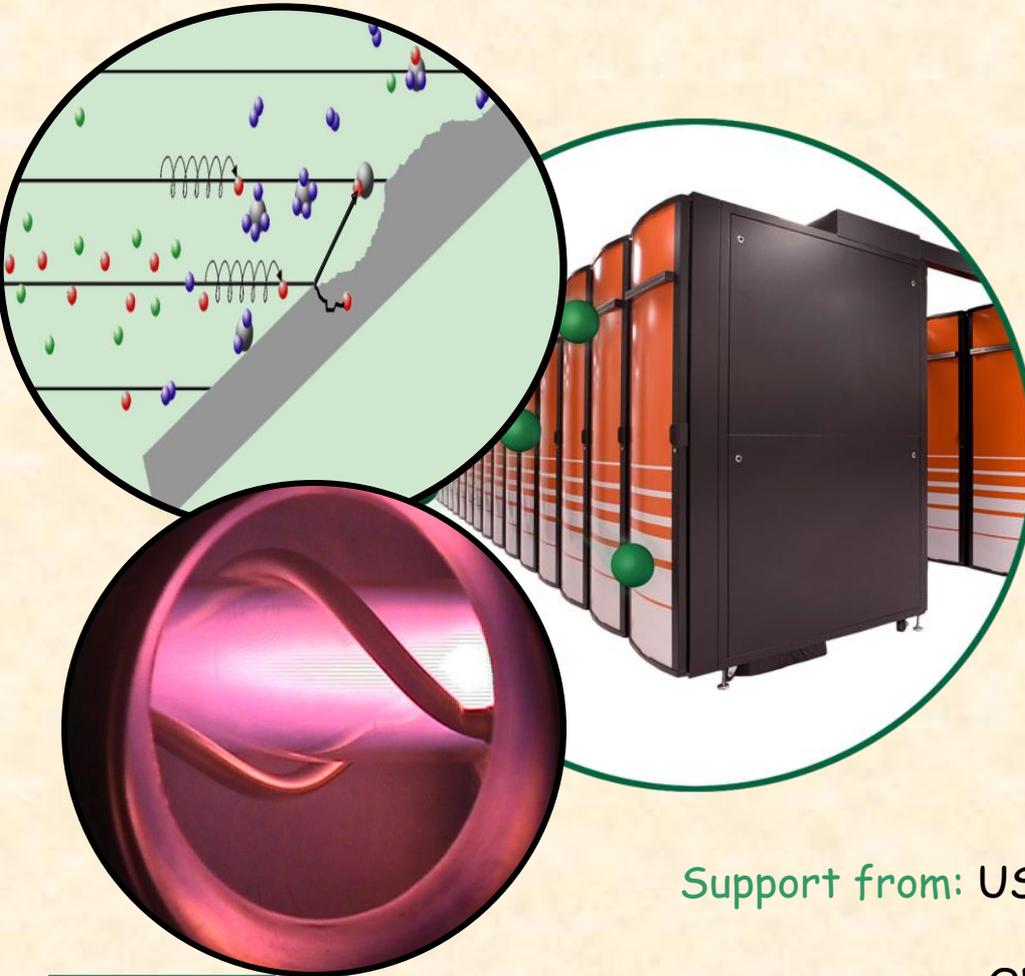


# Bottom-up Integrated Theoretical-Experimental Science for the Plasma-Material Interface



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Support from: US DOE (OFES and OBES)  
and  
ORNL LDRD program





Our thanks to John Hogan (FED, ORNL)

# Close collaborators:

## Theory:

CMD

Mat.

PWDFT

TBDFD modeling



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Kyoto U. NICS

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Taiwan

## Experiment:

jpg

Stephan Irle, Nagoya U

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(Purdue)

Chase Taylor  
Purdue

beam

plasma

beam and plasma

, Jeff Harris, Rick Goulding, FED, ORNL



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Jae  
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(UTK)  
PhD

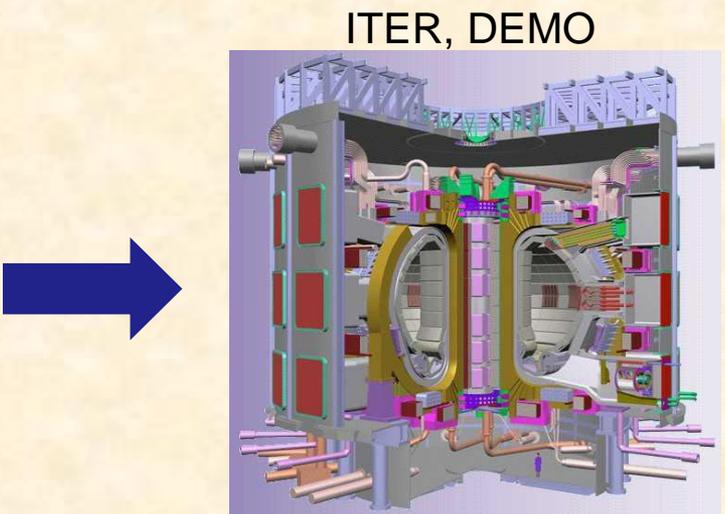
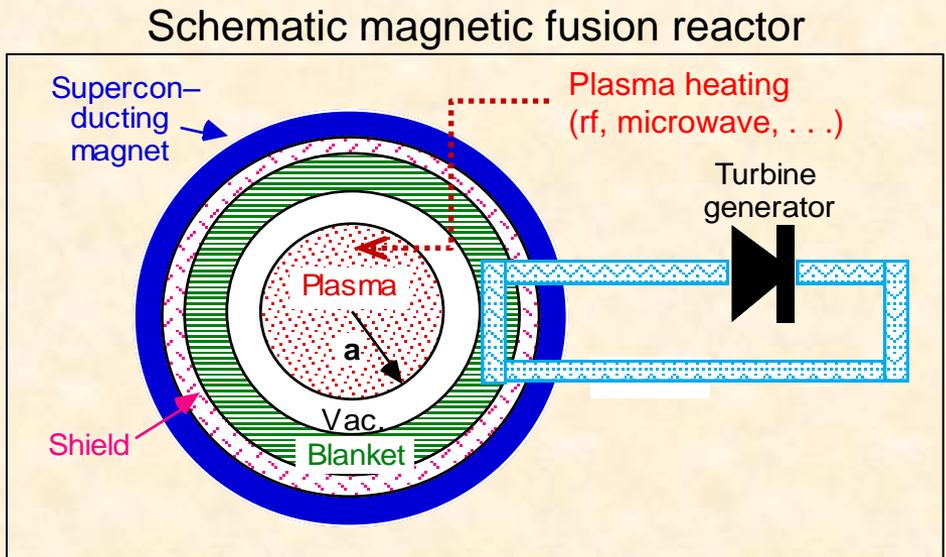
Chris  
(MTSU)



Why PLASMA-MATERIAL INTERFACE  
is such an important problem?

# All energy from D-T fusion reactions passes through first wall

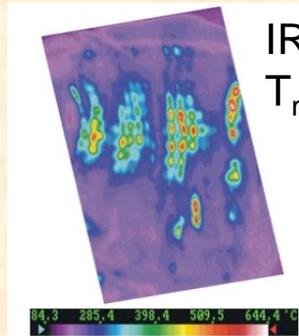
- Flux of (particles + heat + 14 MeV neutrons)  $\sim 10 \text{ MW/m}^2$



Unlike nuclear fission where energy is volume-distributed

- Plasma-material interactions limit performance in present non-DT experiments

TORE SUPRA (France)



IR image of wall,  $T_{\text{max}} \sim 600^\circ \text{ C}$

# How to build an effective science of PMI?

## Guiding principle:

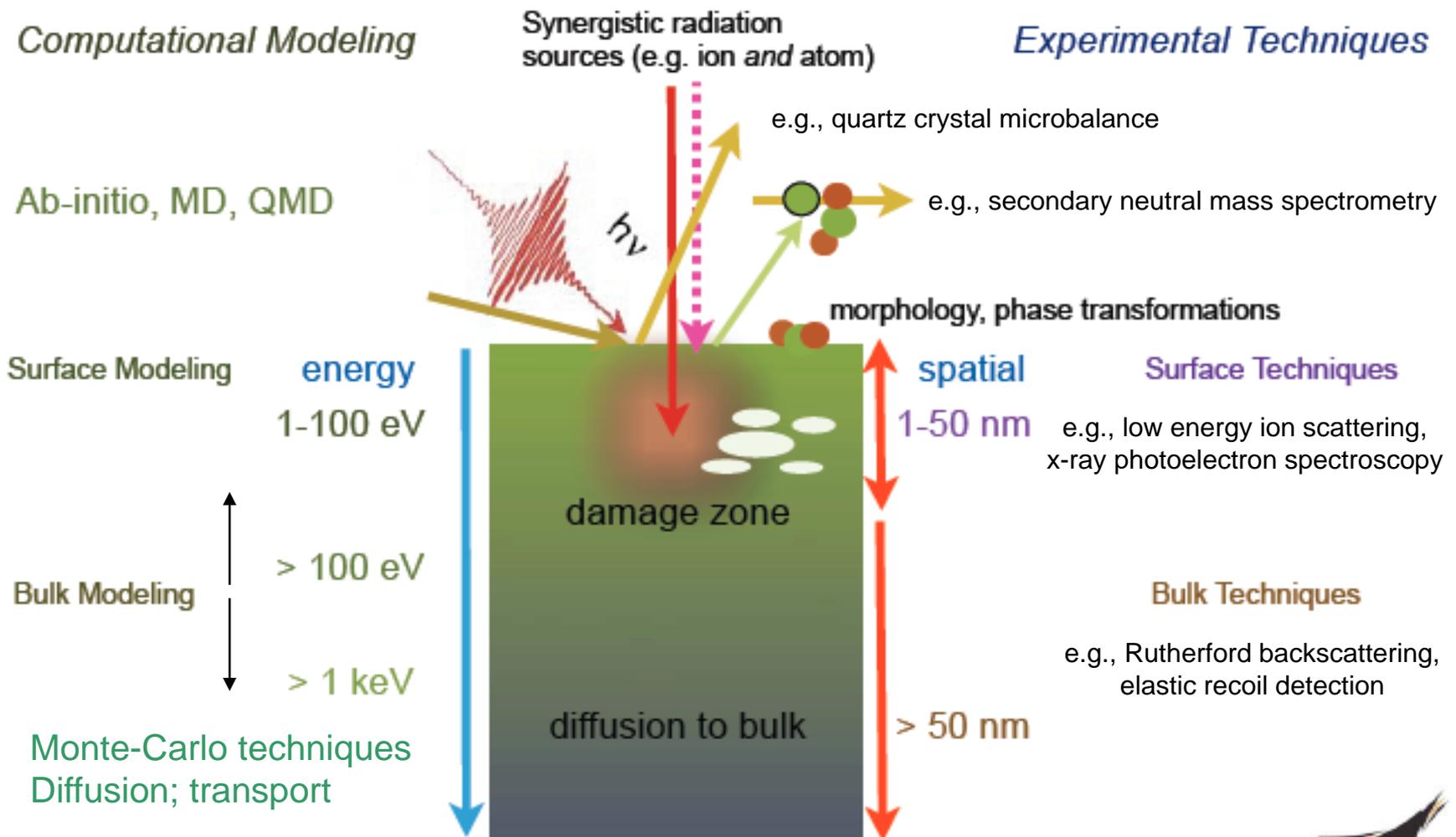
*If Edison had a needle to find in a haystack, he would proceed at once with the diligence of the bee to examine straw after straw until he found the object of his search... I was a sorry witness of such doings, knowing that a little theory and calculation would have saved him 90% of his labor.*

–Nikola Tesla, New York Times, October 19, 1931

The traditional trial-and-error approach to PMI for future fusion devices by successively refitting the walls of toroidal plasma devices with different materials and component designs is becoming prohibitively slow and costly

# Why bottom-up science?

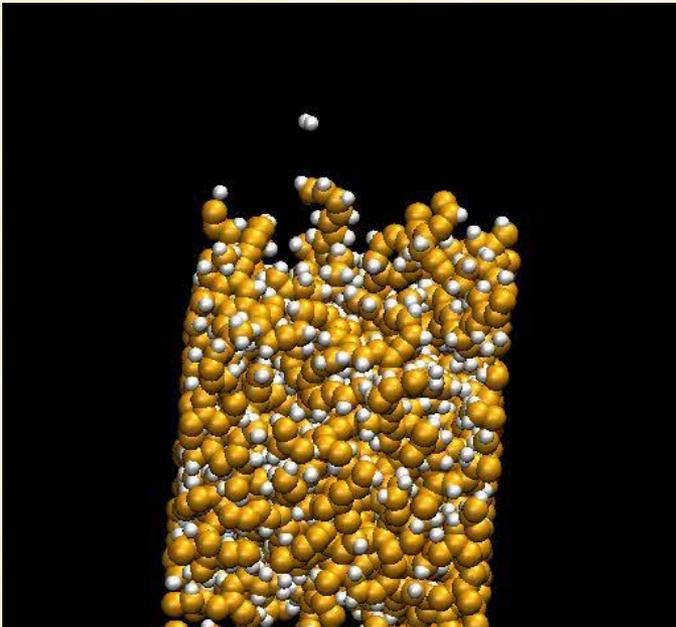
# Probing the PMI requires integration of many experimental and theoretical techniques spanning orders of magnitude in time, length, and energy scales



Courtesy of J.P. Allain



# What does flux of $10^{25}$ particles/m<sup>2</sup>s mean (ITER) for a typical atomistic (MD) simulation?



At a box of surface of 3 nm lateral dim?  
a few thousands atoms (carbon)

The flux is 0.01 particle/nm<sup>2</sup>ns

1) 1 particle at the interface surface of  
the cell each 100 ps.

But for deuterium with impact energy less  
then 100 eV: Penetration is less than 2 nm,  
typical sputtering process takes up to  
50 ps

Each impact independent, uncorrelated!

In effect interaction of an impact particle with nanosize macromolecule functionalizes it!

News is that each particle will change the surface for the subsequent impact!

# PMI simulations: Erosion, sputtering, retention, redeposition, reflection, displacement... originated from atomic processes

- **Atomistic approaches therefore natural starting poi**
  - **Quantum computational chemistry :**
    - *Individual chemical reactions (and dynamics) for a few tens of atoms; electronic excitations.*
  - **Quantum (DFTB) and Classical Molecular dynamics (CMD):**
    - *Processes with hundreds and thousands of atoms; classical dynamics on a predefined potential surface; as good as the potential is good*
    - *DFTB parameterized QMD, 1000x slower than CMD, 1000x faster than DFT based QMD*
      - (a good fit to current supercomputers, we already parameterized DFTB for all fusion materials)*
  - **Binary collision approximation :**
    - *Good for physical sputtering cascades, elastic processes (TRIM), displacement damage*
  - **Kinetic Monte Carlo (KMC):**
    - *For long time-scale processes*
    - *Diffusion of impurities in surfaces and bulk; depends on the probability rates for individual processes determined by atomistic approaches above*
- **... Material science: Continuum approaches**
- Since irradiation creates dynamical surface (a modified interface), cumulative bombardment is the key for modeling experiment (learned from previous PMI work)

# Classical MD is only as good as the interatomic potential model used

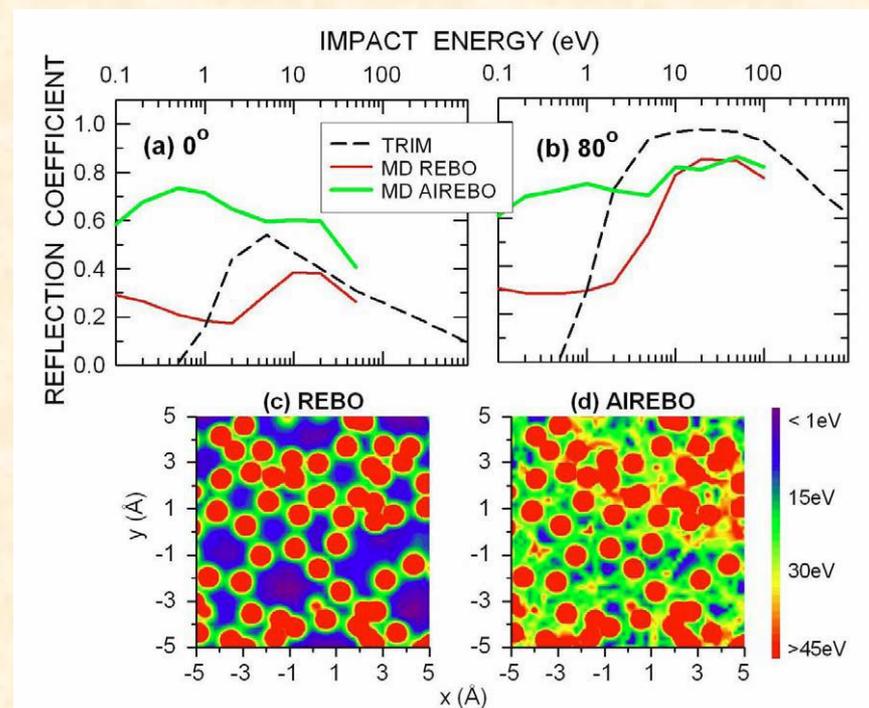
## Most advanced: hydro-carbon potential developed for chemistry

- Brenner, 1990 , 2002 : REBO, short range, 0.2nm
- more sophisticated AIREBO (Stuart, 2000, 2004, 1.1 nm)
- > 400 semi-empirical parameters, “bond order”, chemistry

$$E = \sum_{i,j} V_{rep}(r_{ij}) - b_{ij}(r_{ij})V_{attr}(r_{ij})$$

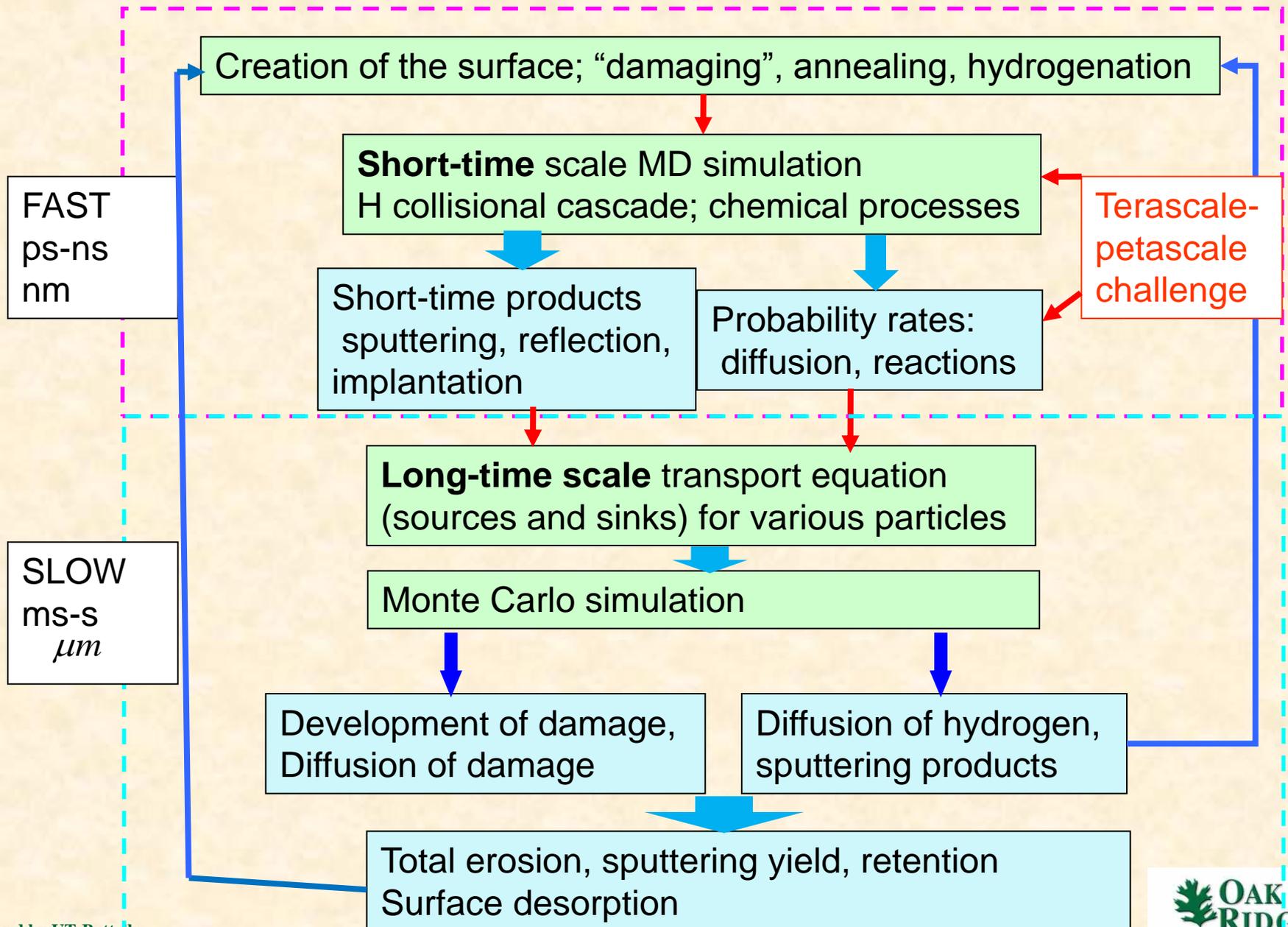
## EX: MD calc. of reflection coeff.

- Significant sensitivity to changes in potential model for some processes
- Experimental validation essential to establish credible MD simulation.
- Interatomic potentials for W and Be are less mature than for carbon and require more experimental validation.



Reinhold & Krstic, 2008

# Simulation is computationally intensive and multi-scale



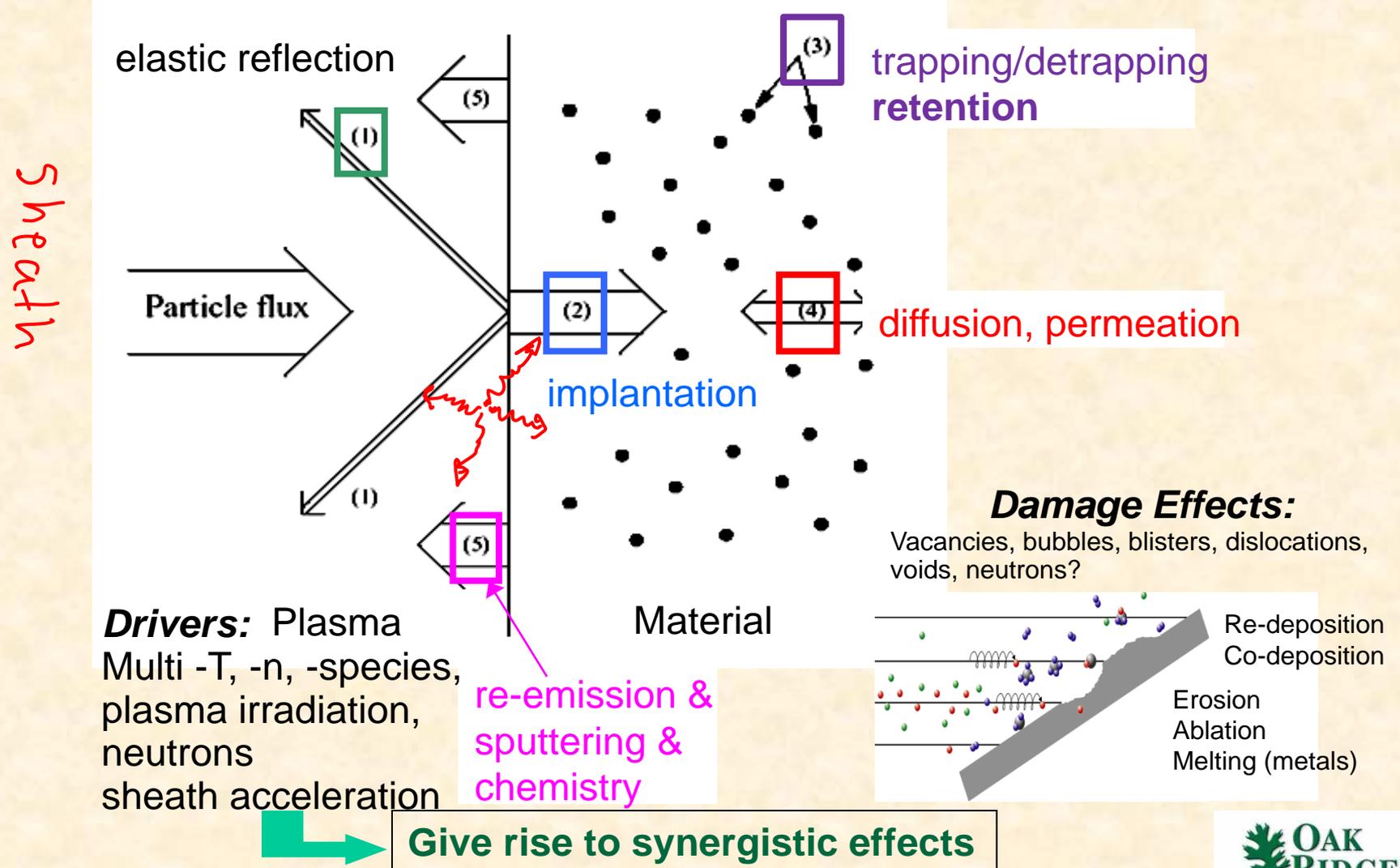
# Why is PMI so difficult problem?

*Interfacial physics, “when the two worlds meet” : traditionally the most challenging areas of science*

*Dynamical surface communicates between two worlds: Plasma and Material*

# PMI has many fundamental processes & synergies

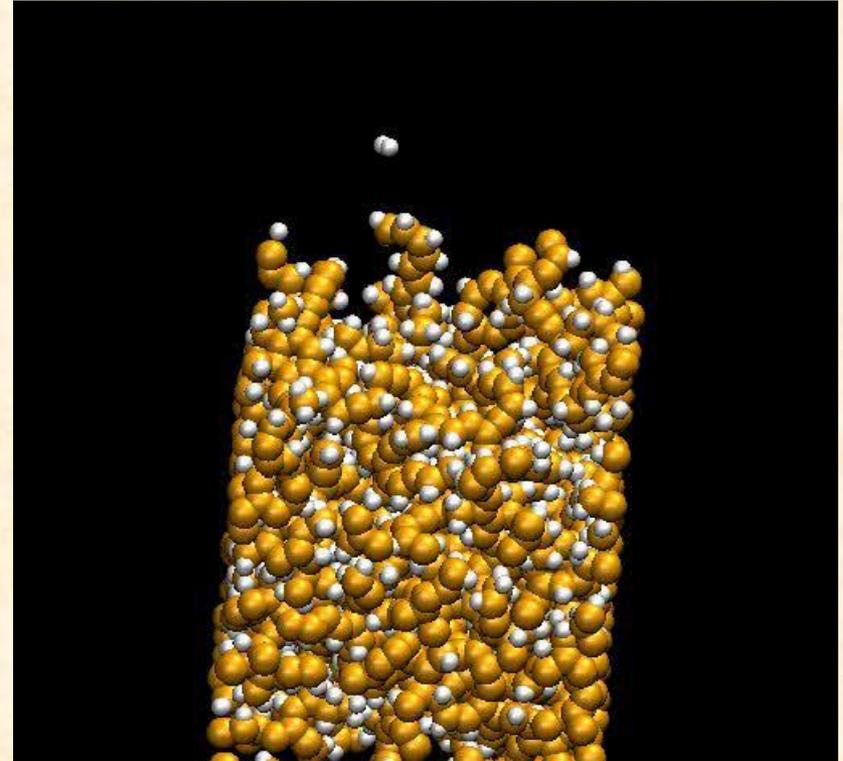
When an ion or neutral arrives at a surface it undergoes a series of elastic and inelastic collisions with the atoms of the solid.



## *Function of :*

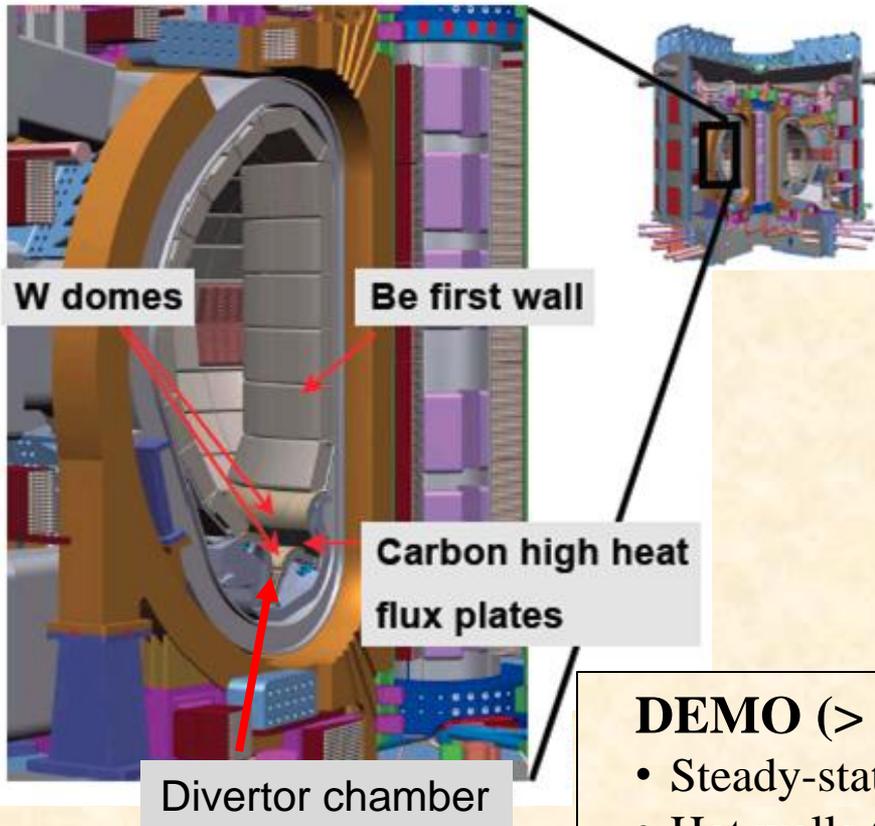
- Type (H, H<sub>2</sub>, Ar, N, He)
- Impinging projectile energy (1-100 eV), angle
- Internal state of the projectile
- Isotopic effect (D, T)
- Flux density ( $10^{21}$ - $10^{25}$  m<sup>-2</sup>s<sup>-1</sup>)
- Surface microstructure
  - Crystalline, amorphous a-C, polycrystalline); Doping (Si, B)
  - Hydrogenation level (H/C ratio)
  - Hybridization level (sp/sp<sup>2</sup>/sp<sup>3</sup> ratio)
  - Surface morphology; preparation
  - Surface temperature (300-1500K)

- Predefined classical potentials (Brenner, REBO, AIREBO (Stuart))  
*Limit to < 100 eV (D-D,D-C); <30 eV (C-C)*



*Possible mechanism: Swift bond breaking*

# PMI strategy is evolving thru ITER towards DEMO reactor



## ITER (> 2020) uses multi-matl walls

Pulses ~ hundreds of sec

~Be Main chamber wall (700m<sup>2</sup>)

Low Z + oxygen getter

~W Baffle/Dome (100 m<sup>2</sup>)

Funnels exhaust to *divertor chamber*

Low erosion, long lifetime

~C Divertor Target (50 m<sup>2</sup>) (Graphite)

Minimize high-Z impurities

(which lead to large radiative losses)

## DEMO (> 2030?):

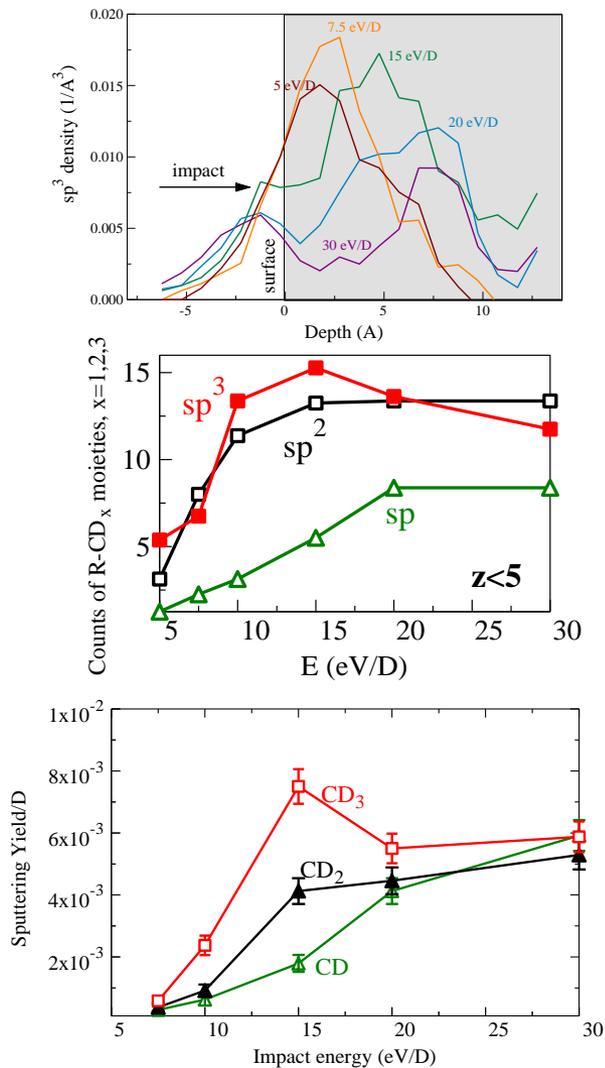
- Steady-state, power flux ~ 10 MW/m<sup>2</sup>
- Hot walls (>600 C)
- Refractory metals
- Neutron irradiation 14.1 MeV (> 100 dpa)

Parameter range inaccessible in present devices

☞ **valid extrapolation needed!**

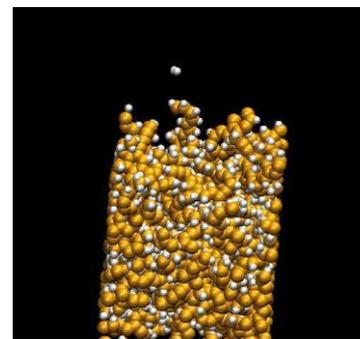
# Materials exposed to plasma are modified, resulting in a "dynamical" surface

## Amorphization depends on penetration depth rather than of deposited energy

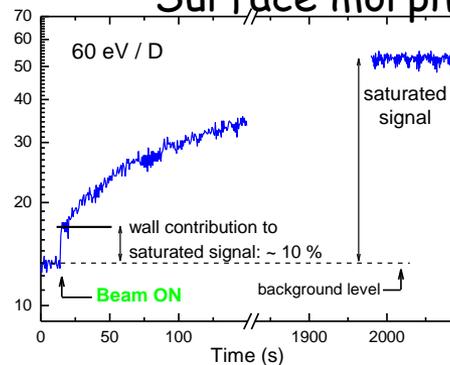


Krstic et al, New J. of Phys. 9, 219 (2007).

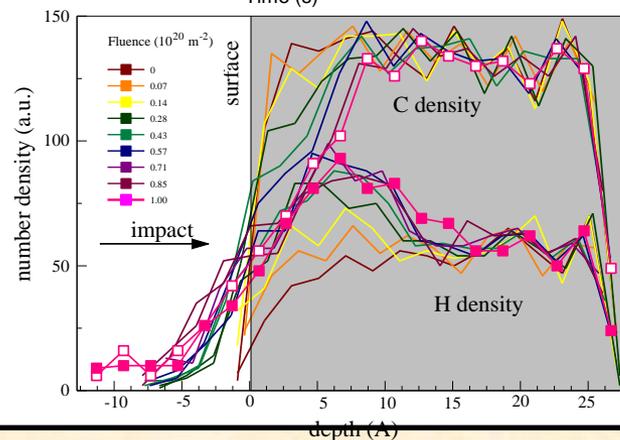
## Chemical sputtering of hydrocarbons



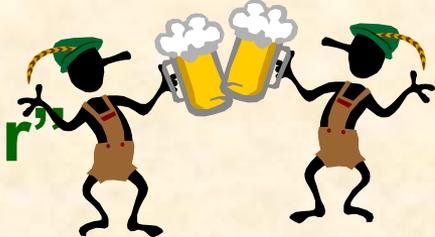
### Surface morphology



Reaching "steady state"

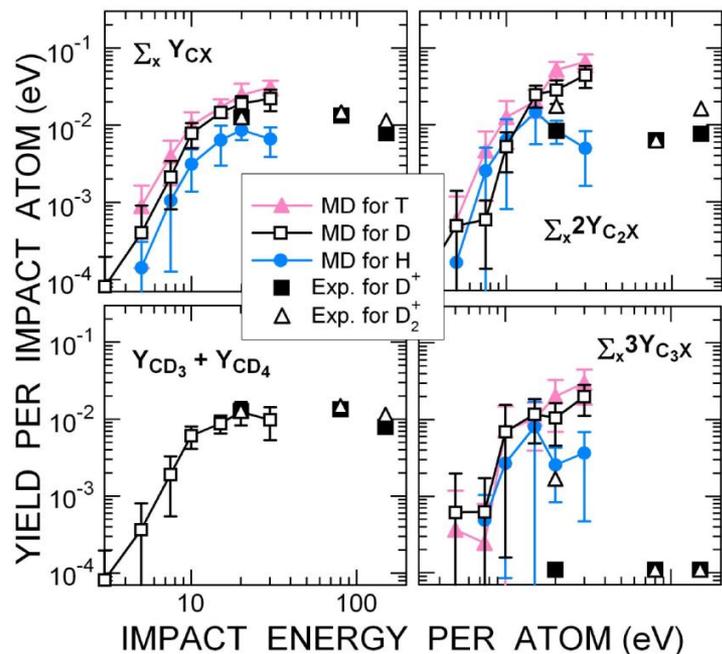


# How to validate theory with experiments (and vv)?



# What have we learned from the “next door beam-surface experiments?”

Beam-surface exp’t: precision control of projectiles & targets . . .  
 . . . enabled development & validation of MD approach

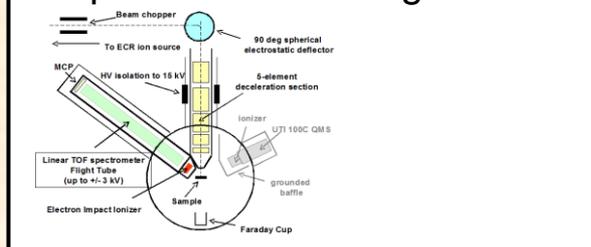


**Remarkable agreement of theory & exp’t when simulation mimics exp’t. No fitting parameters!**

Key: simulation prepares surface by bombardment!

- Fluence (not flux) like that in experiment
- Type, internal state, energy, angle as in exp’t

Beam-surface experiments:  
Prepared beam & target

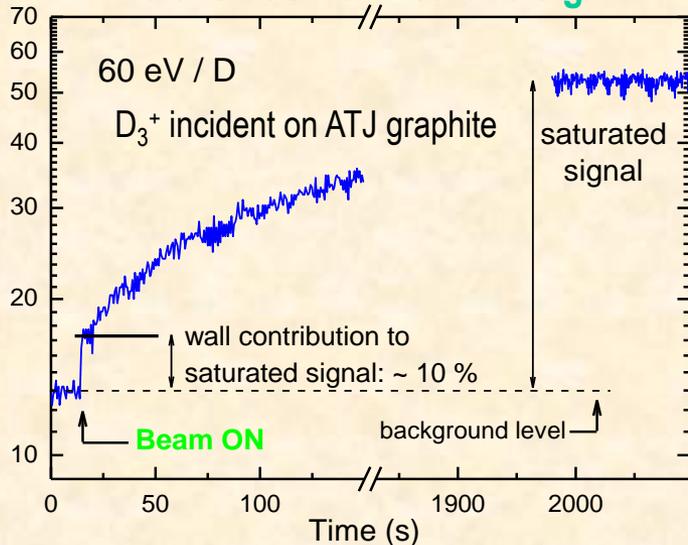


Meyer et al,  
Physica Scripta T128, 50 (2007).

# Chemical sputtering creates a dynamic, evolving surface

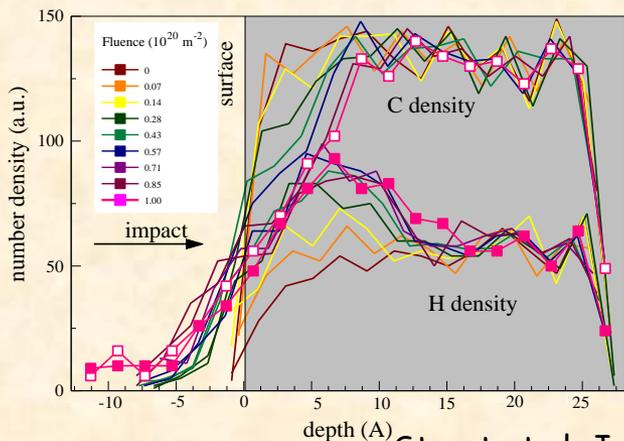
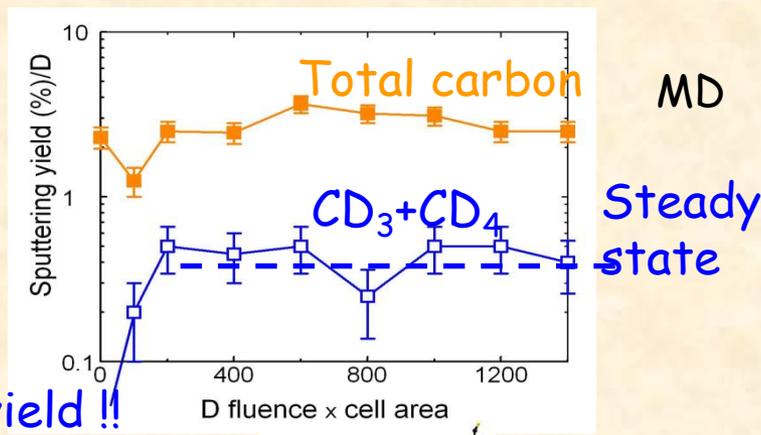
- Competition between beam induced C=C bond breaking, H passivation, HC precursor formation, and H loss, HC product emission
- At steady state dynamic equilibrium between H loading and H<sub>2</sub> loss has been reached

## Time evolution of methane signal

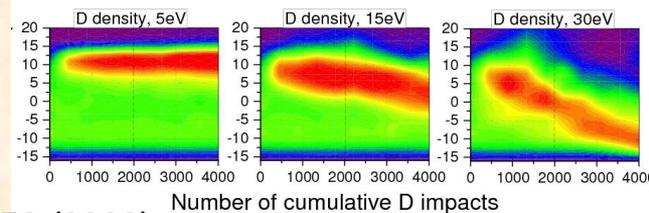
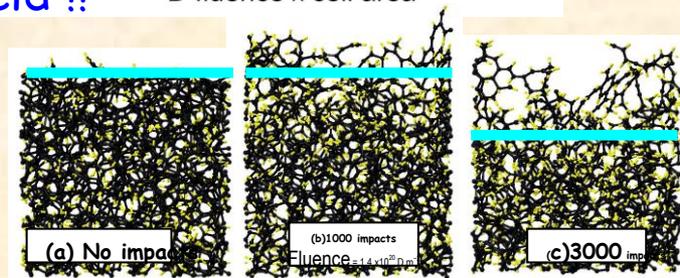


Vergara et al., 2006

## Steady state methane yield/D



## Evolution of the density profile

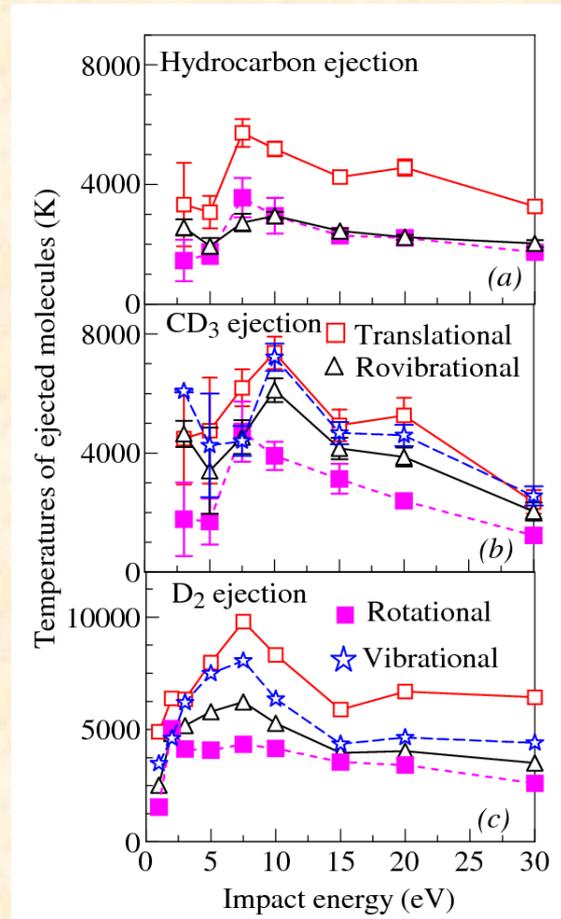
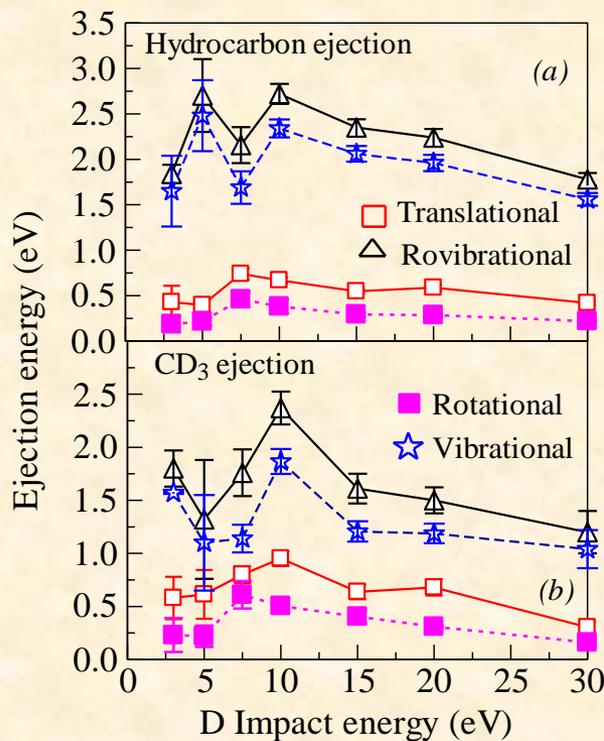
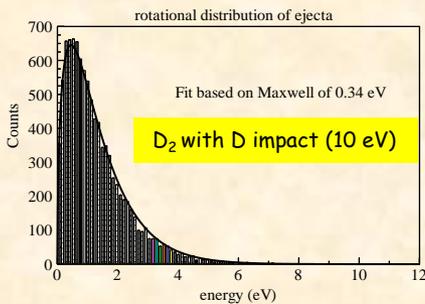
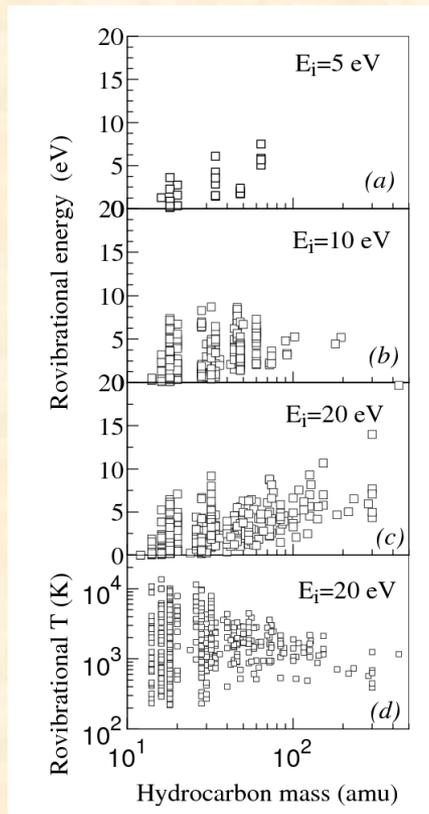


Stuart et al, J. Phys. Conf. Ser. 194, 012059 (2009)

IPAM, April 2012

# New physics from theory-experiment cannot reach

hydrocarbon chemistry  
in plasma!



Ejection energy

Ejection temperature

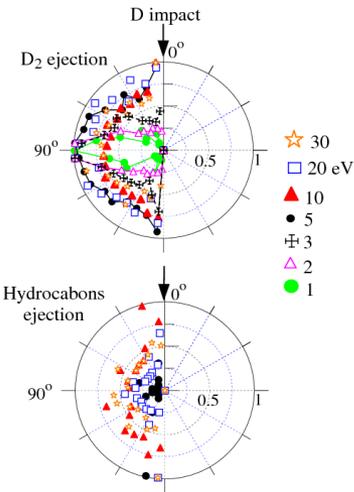
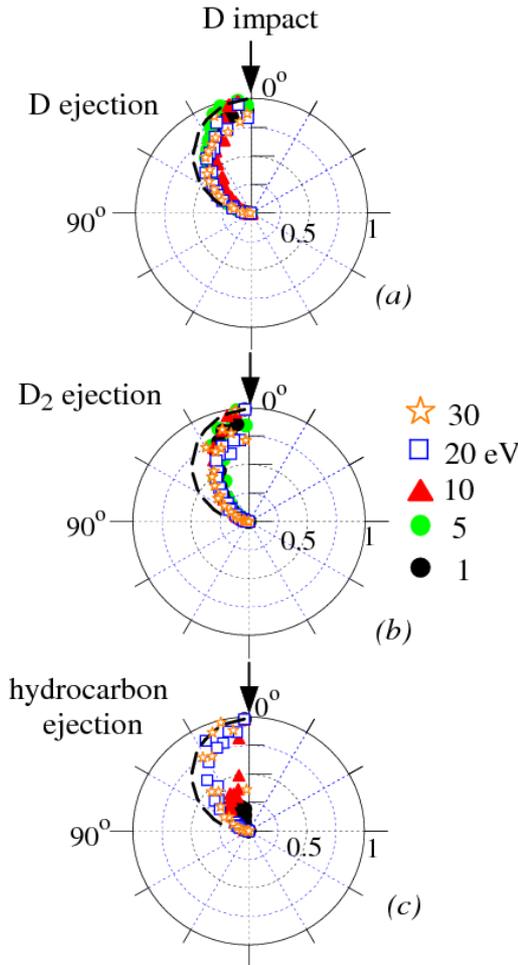
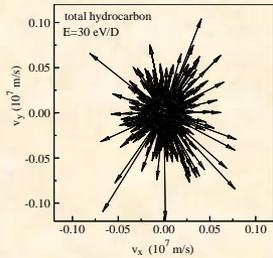
Approximate thermalization indicated

Functions of hydrocarbon mass and impacting D energy

Krstic et al, J. Appl. Phys. 104, 103308 (2008).



### 3) Angular distributions $dn/d\Omega$

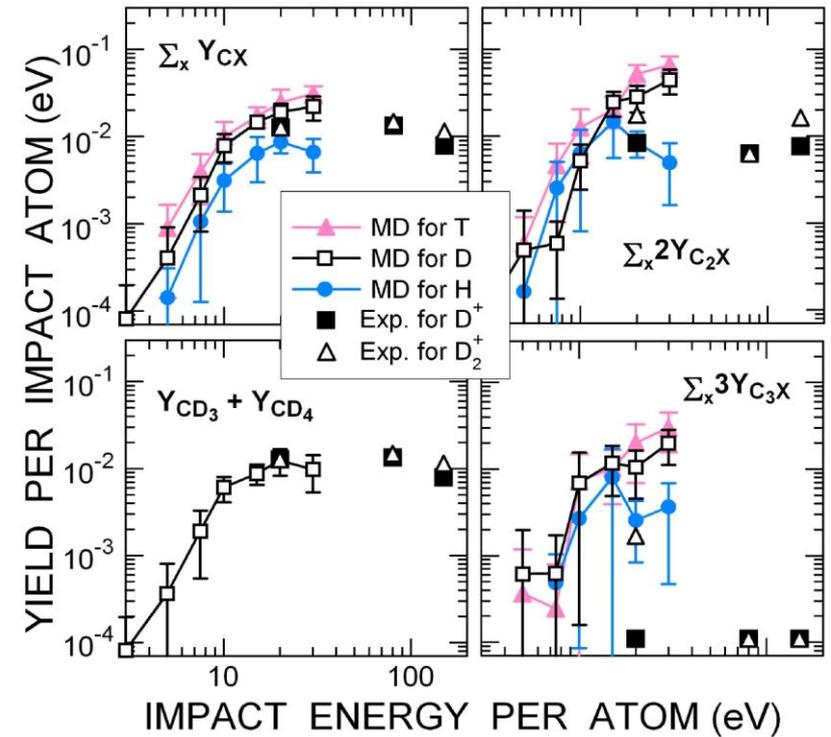


Angular moments  $L$   
sin law or isotropic

CM velocities follow cos-law

Krstic et al, J. Appl. Phys. 104, 103308 (2008).

4) Isotope effects increase with the mass of the projectile  
 • Bond-breaking threshold are nearly mass independent and are dominated by associative-dissociative reactions

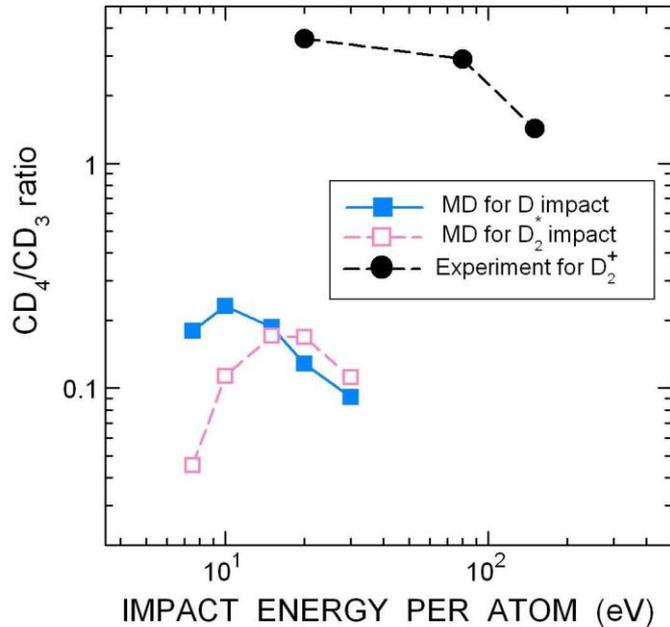


Reinhold et al, J. Nucl. Mat. 401, 1 (2010).

# Where MD Fails?

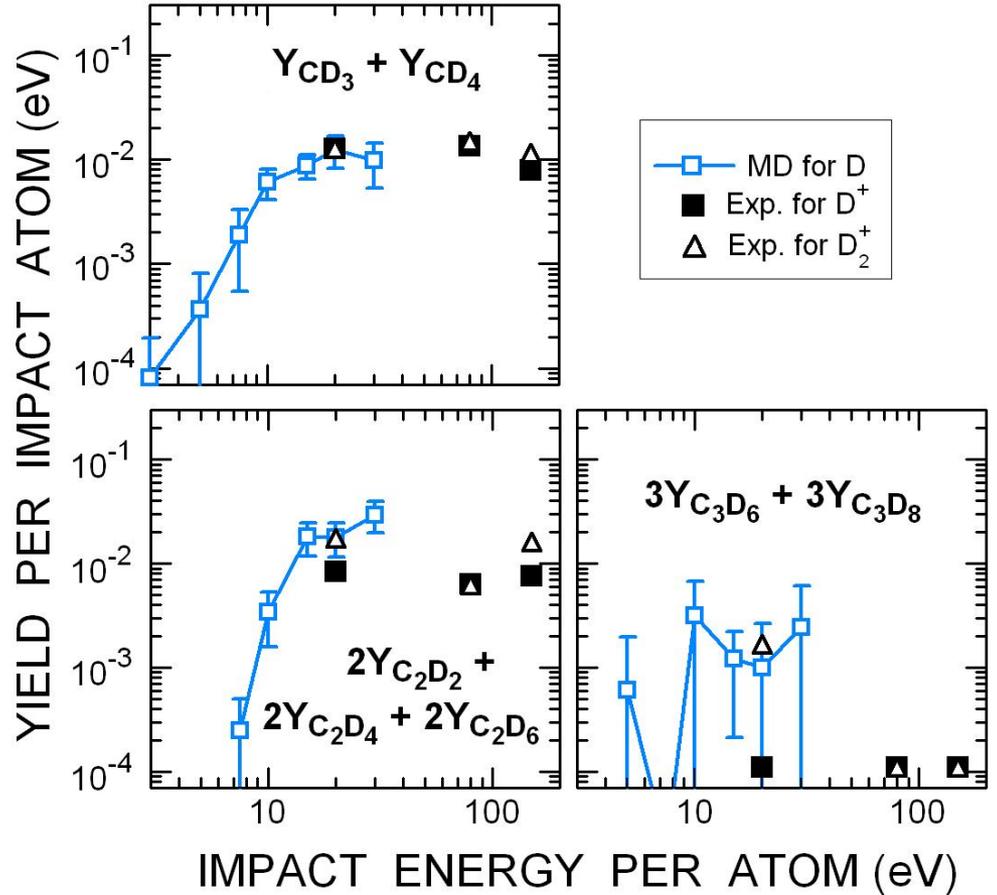
Do we need better potentials?

Do we need direct line of sight experiments?



Open problem: simulations overestimates the yield of large molecules

->Erosion of carbon oversized at higher energies



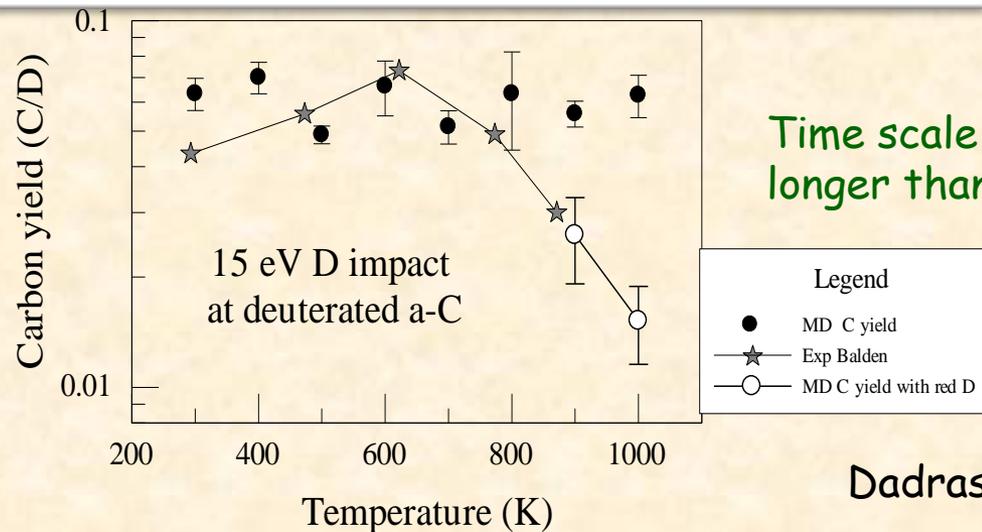
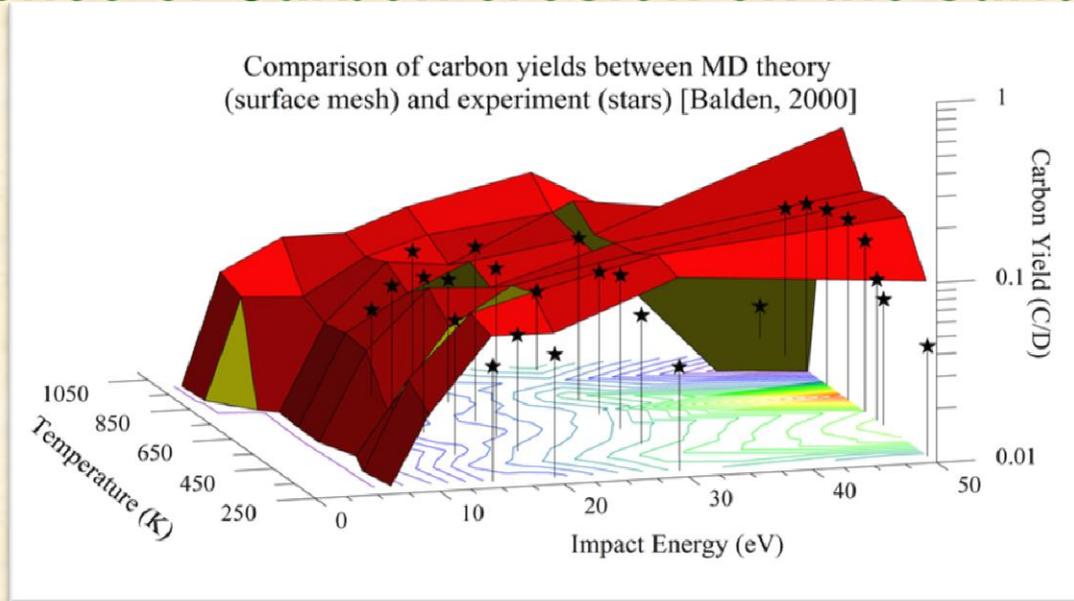
Krstic et al, Nuc. Instr. Meth. B 267, 704 (2009).

We have developed a new hydrocarbon potential which includes ZBL corrections for higher impact energies and additional hydrocarbon params

IPAM, April 2012

# Example : Where MD fails?

## Dependence of Carbon erosion on the surface temperature



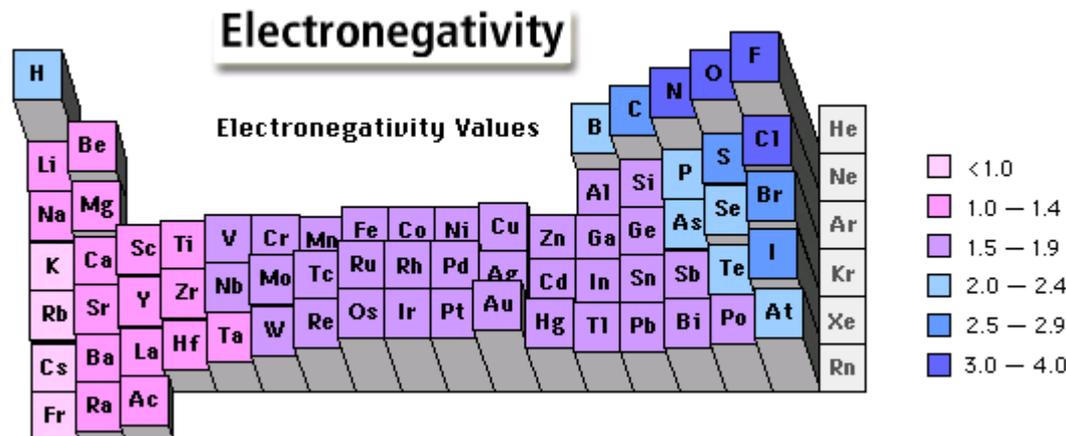
Time scale of thermal D-release longer than ps-ns scale

Dadras et al, 2010

# Lithium wall conditioning improves confinement! Why?

- Controlled experiments on many toroidal devices demonstrated reduced recycling, improved energy confinement time  $\tau_E$ , and a reduction of edge instabilities known as edge localized modes (ELMs)
- Initially the experimentalists conjecture was that there was some "functionality" that governed the behavior of the Li-C-O-H system observed indirectly by analyzing the O(1s) and C(1s) peaks. For "some reason" the Li(1s) peaks didn't show much information.

Lithium dynamics is difficult to study theoretically because Li polarizing features when interacting with other elements



Consequence: Bonding between Li and other atoms covalent and polar;  
Long-range nonbonding:  
Coulomb : $1/R$   
Lenard-Jones : $1/R^6$ ,  $1/R^{12}$

# Goals:

- Chemistry and sputtering/reflection dynamics in lithiated carbon material, bombarded by slow deuterium atoms is studied.
  
- The objectives of this research are two-fold:
  - 1) To develop the realistic methods for computational simulation of the Li-C-H-O, validated by experiments.
  
  - 2) To explain the specifics of the chemistry of deuterium bonding in lithiated carbon. Experiments from Purdue indicate that bonded C-Li-O? sites are preferable for H bonding:

## Quaternary system Li-C-O-H

Currently our biggest efforts in th!! (6 members of the team on it):

- Li-C , Li-H and Li-O are of very different electronegativities and therefore these could be considered as ionic solids.
- The implication is that, as a result of partial charge transfer from one element to the other, the dominant long-distance binding force between particles is the Coulombic attraction between opposite charges.

Total energy in LiXY mixture

$$E_{tot} = E_{bound} + E_{nbound}$$

$$E_{nbound} = E_{coul} + E_{vdW}$$

$$E_{coul} = \sum_i \sum_{j>i} \frac{q_i q_j}{r_{ij}}$$

$$E_{vdW} = \sum_i \sum_{j>i} D_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

# Charging changes at each simulation step: Quantum-Classical Molecular dynamics a must

**Electrons:** Quantum mechanically at each step, resulting in charges and forces  
**Nuclei:** Classical motion

Employed the **Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB)** method (developed by [Bremen Center for Computational Materials Science](#), Germany)

It is an **approximation to the DFT method** in which only valence orbitals are considered, and difficult Integrals parameterized in advance.

In comparison to other TB methods: Improved self-consistent interaction of electronic charges

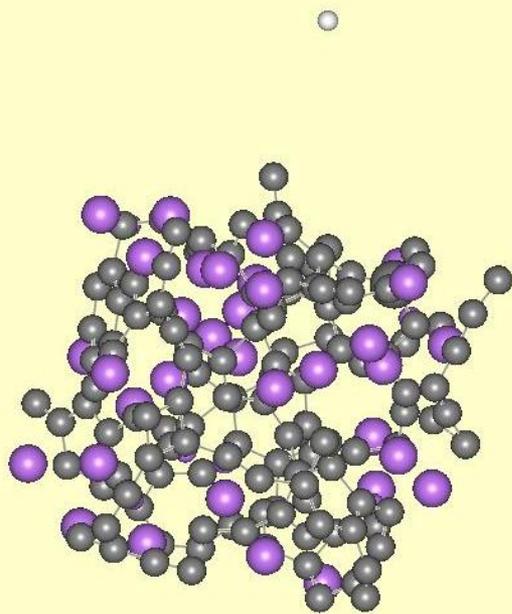
This enables computational efficiency about 1,000 time faster than ab initio quantum methods (and about 1,000 time slower than Classical Molecular Dynamics)

Parameterization for Li-C-H-O provided by K. Morokuma group (Kyoto-ORNL-Emory)  
Inclusion of Mo and He in parameterization: H. Witek (Taiwan U.)

[1] M. Elstner, D. Porezag, G. Jungnickel, et al, Phys. Rev. B 58, 7260 (1998)

[2] G. Zheng, M. Lundberg, J. Jakowski, et al, Int. J. Quantum Chem. 109, 1841 (2007).

# Simulation of deuterium impact to lithiated and oxidated carbon surface



- Cell of a **few hundreds of atoms** of lithiated and oxidated amorphous carbon ( $\sim 30\%$  of Li,  $< 10\%$  of O), at **300K**
- By random seed of Li and O in **amorphous carbon** and **energy minimization**, followed by thermalization
- bombarded by **5 eV D** atoms and **2.5 eV H**,
- **Perpendicularly** to the shell interface
- **5004 random trajectories**

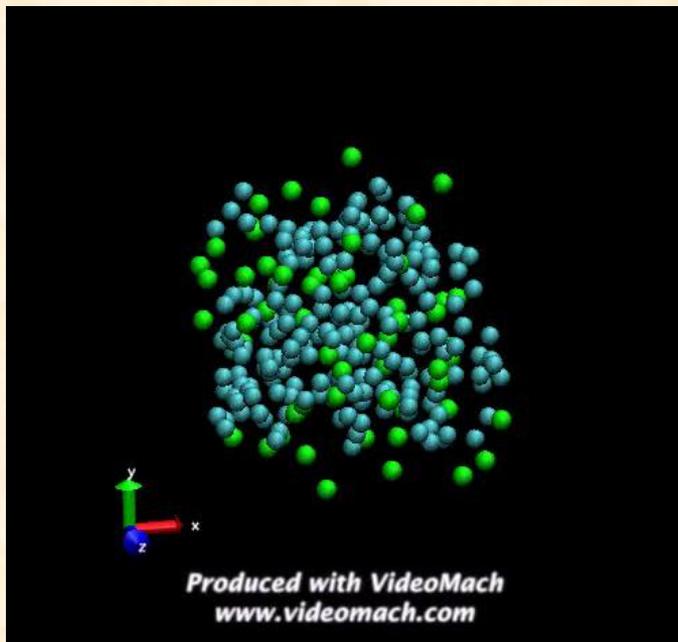
**The cell swelled during the structure optimization**

5004 processors of Cray XT5 (Jaguar, Kraken),

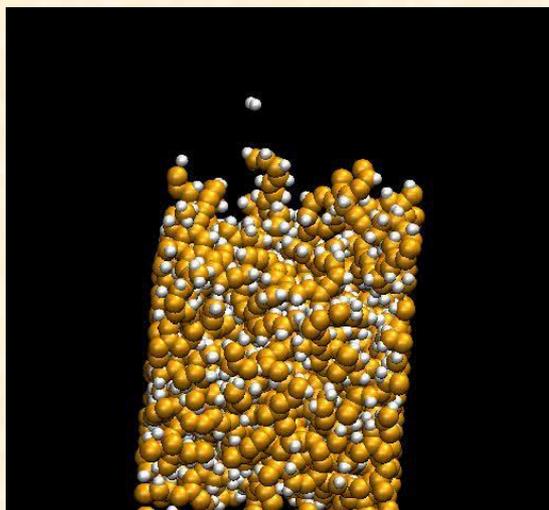
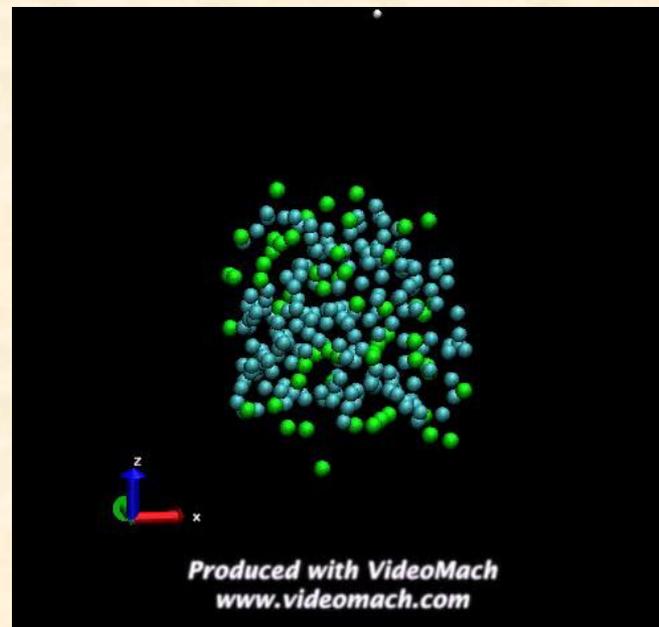
Time step 0.2-1fs, 24 hours: 200-400 fs.

One run over 120,000 CPU hours (TeraGrid project)

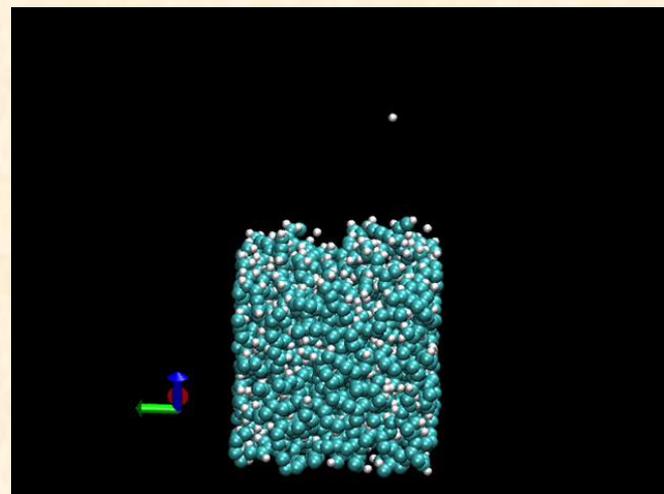
# Slabs studied: Periodicity in x-y



C-Li-O

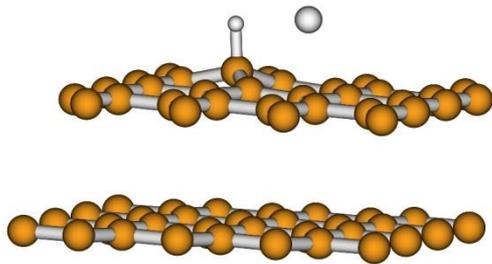


Only C+H



# Quantum-mechanical, PWDFFT “static” calculations of Alain Allouche of CNRS (Marseille) finger -point in the same direction:

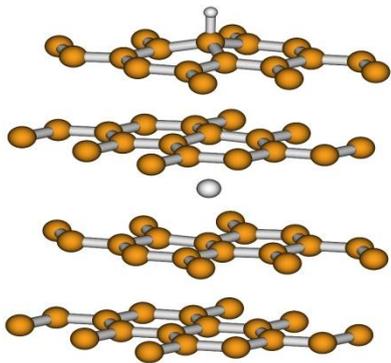
## •graphene bilayer with Li and H on the surface



When a lithium atom is co-adsorbed on surface bonding energy of H grows up to values ranging from -2.2 to -2.5 eV, with decreasing the Li-H distance. (compared with -1.9 eV for pure graphite)

Another remarkable finding of Allouche: With inclusion of defects the energy shows similar shift like in XPS exper.

## •graphene 4-layers, Li inside the slab, H on surface



The bonding E enhancement is also observed when Li is sandwiched 1 layer below the surface layer, but disappears when Li is 2 layers below the surface.

A. Allouche, Carbon (2012)

# Surface contains much more Oxygen than expected

Our quantum-classical molecular dynamics predictions showed that if there is comparable quantity of oxygen in the surface, O takes over and dominates the Retention chemistry

Here comes the experiment  
J.P. Allain, C. Taylor, Purdue U):

- 1) At most 5% oxygen content on the surface of NON-LITHIATED graphite... AS EXPECTED.
- 2) With lithium it increases to 10% of Oxygen
- 3) With LOW-ENERGY IRRADIATION over 20-40% oxygen AT the surface.

It is not Lithium that suppresses erosion of C, and increases retention of H

OXYGEN plays the key role in the binding of hydrogen.

Lithium is the oxygen getter

If there is a SIGNIFICANT amount of oxygen on surface with lithium present in the graphite matrix, OXYGEN becomes the main player; NOT LITHIUM!!!

... consistent with the XPS data!!

Submitted to Nature Communications (2012)

Is the PMI phenomenology with plasma  
Irradiation different than with a beam  
irradiation?

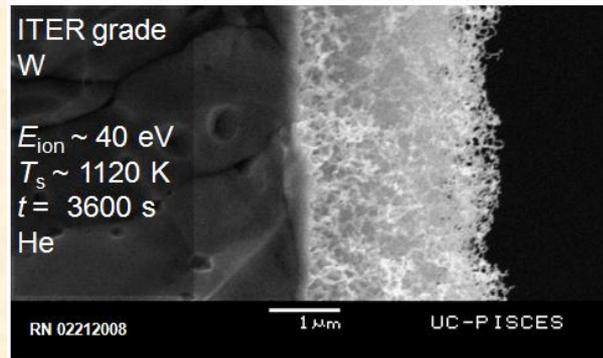
Can we derive plasma-irradiated PMI from the  
beam-PMI?

Can we model plasma irradiation?

*Answer is: Yes, No, Yes...*

# Synergies in tungsten: dramatic effects in plasma experiments

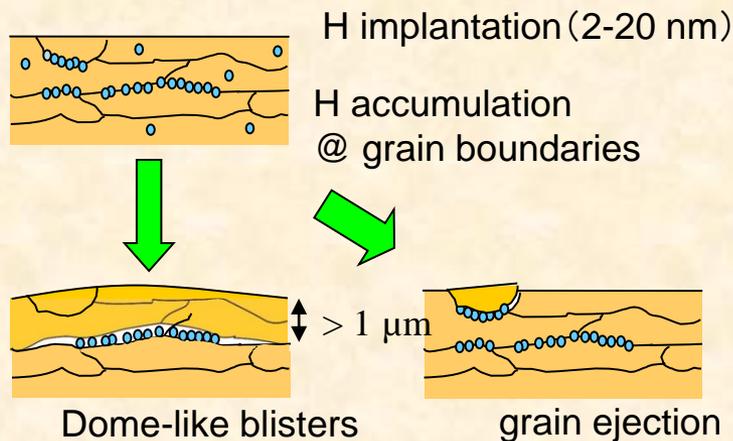
**“Fuzz” nanostructures**  
on W irradiated by He  
high W temperatures ( $>1000\text{K}$ )



Baldwin,  
2008

**Blistering related to D, H retention**

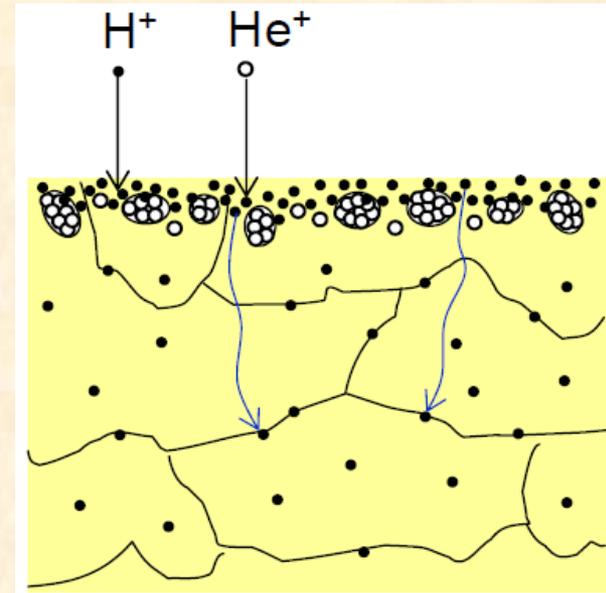
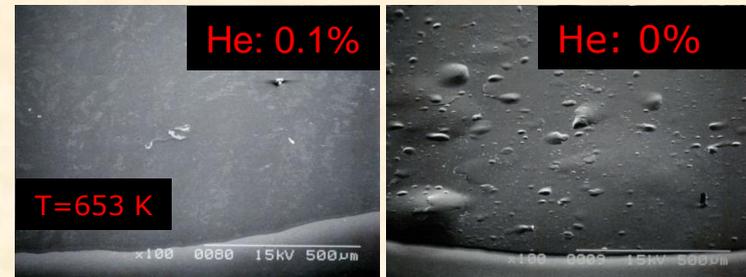
- Sparser for  $T > 600\text{K}$



*Ueda et al, 2008*

**He suppresses H retention**

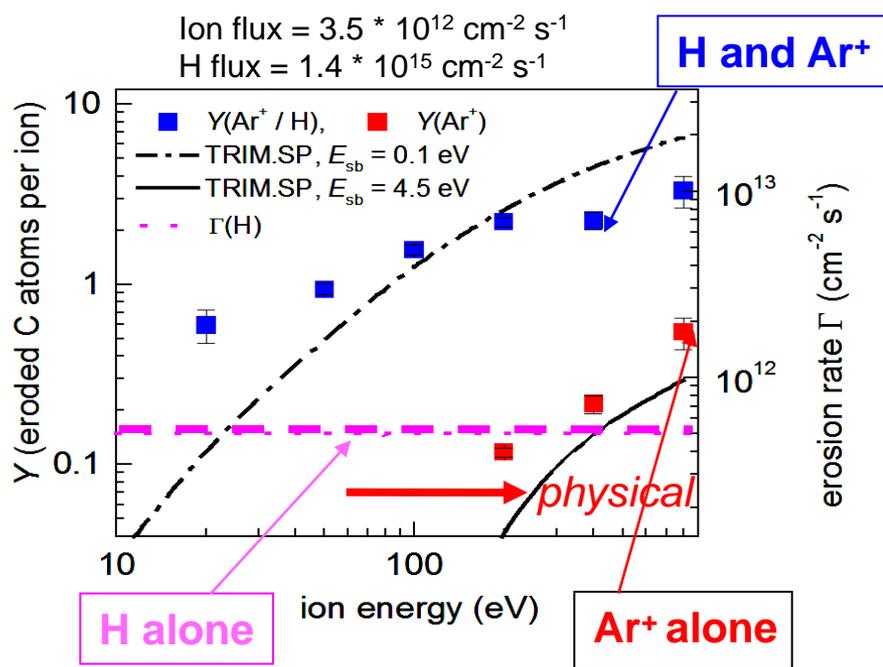
- He penetrates deeper than H
- Strong dependence on energy
- He bubbles: barrier to H diffusion?



# Goal: Study synergy in the evolution of surface irradiated by plasma

## Experiments with Ar+ and H:

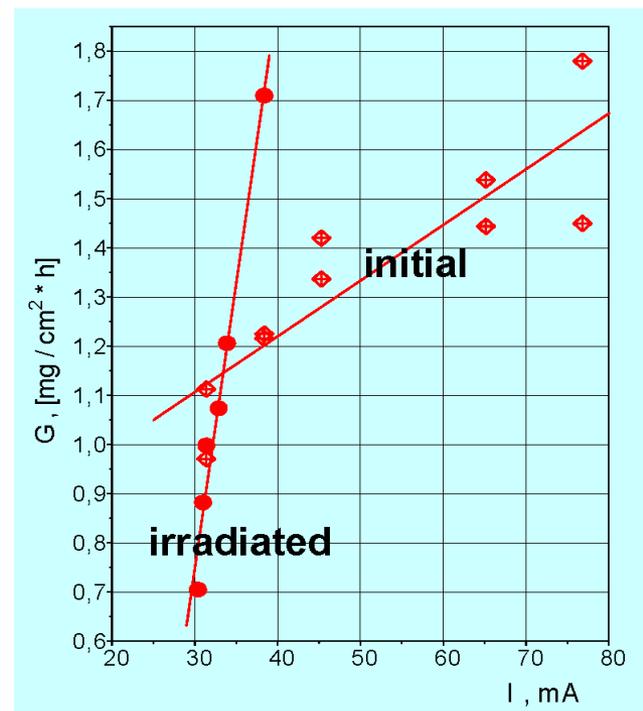
- Sputtering = (chemical) + (physical)
- Surface preparation by H impact for chemical sputtering
- Impurity atoms in plasma are efficient precursors for erosion
- **PM processes very dependent on inventory of H in the material**



Hopf & von Keudell, 2003

## Exposure of pyrolytic graphite to 5 MeV C+ simulates **NEUTRON DAMAGE**:

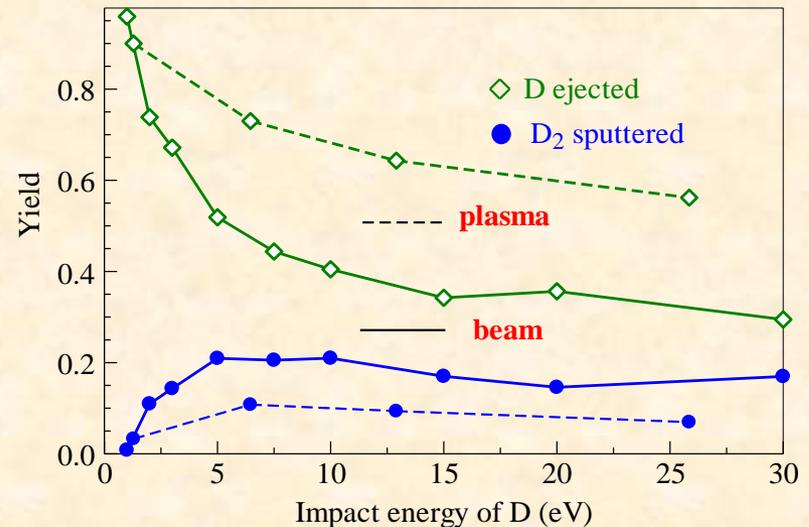
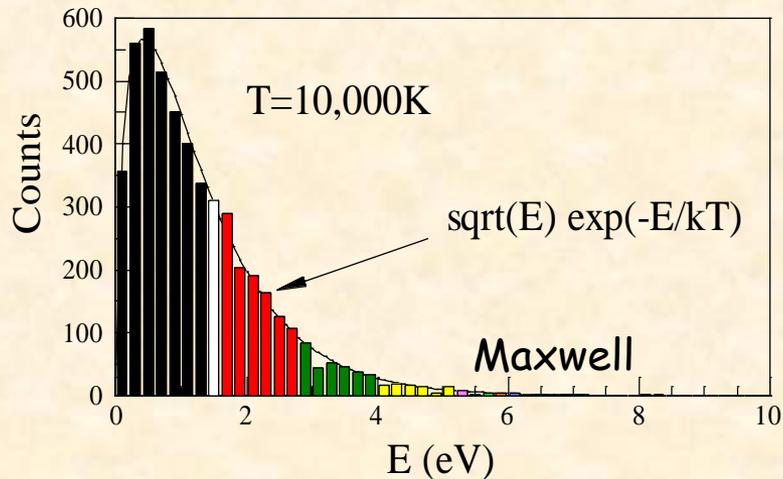
- more nucleation  $\Rightarrow$  enhanced erosion
- sites for H retention
- increased HC density?
- increased ejection probability?



B.I. Khripunov et al. 2009

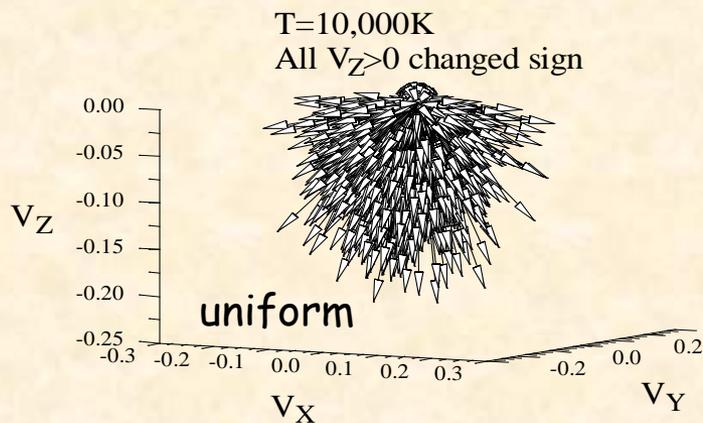
# Simulations of the plasma irradiation (D atoms)

HOW?



Krstic et al, 2009

Impact distributions



Krstic et al, AIP Conf. Proc. 1161, 75 (2009).

**With plasma irradiation:  
Reflection significantly higher than  
beam, sputtering suppressed !!!**

# CONCLUSIONS:

- PMI extremely difficult **interfacial problem** (Material mixing create **SURFACE entity**; its scale depends on impact energy: for sub-100eV => nm-ns scales)
- PMI science can be built from bottom-up recognizing its **multiscale** character and building from shortest time/spatial scales (fs/Angstrom) up
- Theory&modeling of PMI has to be validated by experiment (and v.v.)
- Irradiation create **dynamical surface**, changing interface, cumulative bombardment is the key for agreement with experiment
- Surface responds to **synergy** in plasma irradiation (angles, energies, particles), NOT following linear superposition principle; NEED plasma irradiation modeling and experiments; **dedicated plasma devices** a must
- Oxygen is doing D chemistry in lithiated carbon surfaces