

Classical or Quantum Molecular Dynamics?

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IAEA Technical Meeting of the International Atomic and Molecular Code Centre Network on Simulation of Plasma-Material Interaction Experiments

29-31 July 2015, IAEA Headquarters, Vienna, Austria



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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

Need bottom-up approach arising from the fundamental atomistic and nano science

Conventional solution

- Problem statement + brain
→ algorithm
- Algorithm + language + brain
→ program
- Compile program
→ executable
- Computer + executable + input
→ result
- The brain is
 - Expensive
 - Finite
 - Not growing exponentially

←
The only step currently
employing HPC in most
applications



- 250,000 processors running for 12 hours
- 342 processor years

Big Picture:

“State of the Art” Plasma Simulation Codes Use Rudimentary PMI Models

- SOLPS = B2 (2-D fluid plasma transport) + EIRENE (3-D kinetic neutral transport) used to simulate JET, design ITER, etc.
 - Reflection, physical sputtering data from TRIM (BCA) calculations,
 - User specified absorption coefficients,
 - Empirical or calibrated chemical sputtering yields.
- UEDGE (2-D fluid plasma transport) & XGC (kinetic plasma turbulence & transport) use specified recycling coefficients,
 - Can be coupled to DEGAS 2 kinetic neutral transport to use TRIM reflection data.
- PMI do not evolve in response to plasma \Rightarrow no consistent solution to plasma-material system.
- Replacing with dynamic, first principles, multi-scale model:
 - Consistent treatment of D retention & recycling,
 - Surface morphology evolution through erosion & redeposition,
 - Kinetic characterization of impurity sources,
 - Etc.

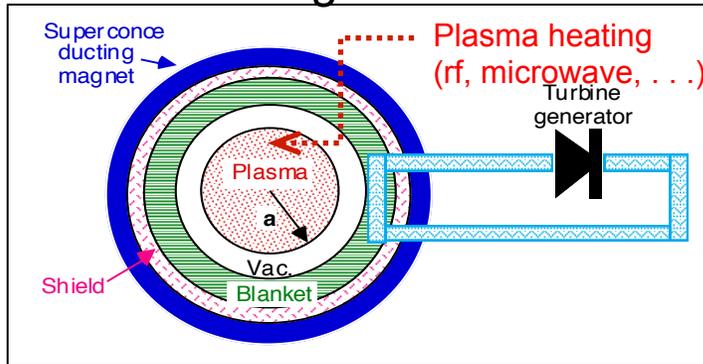
Challenges at the Plasma-Material Interface

This is not the material science

Science of the **interface** has many fundamental processes & synergies

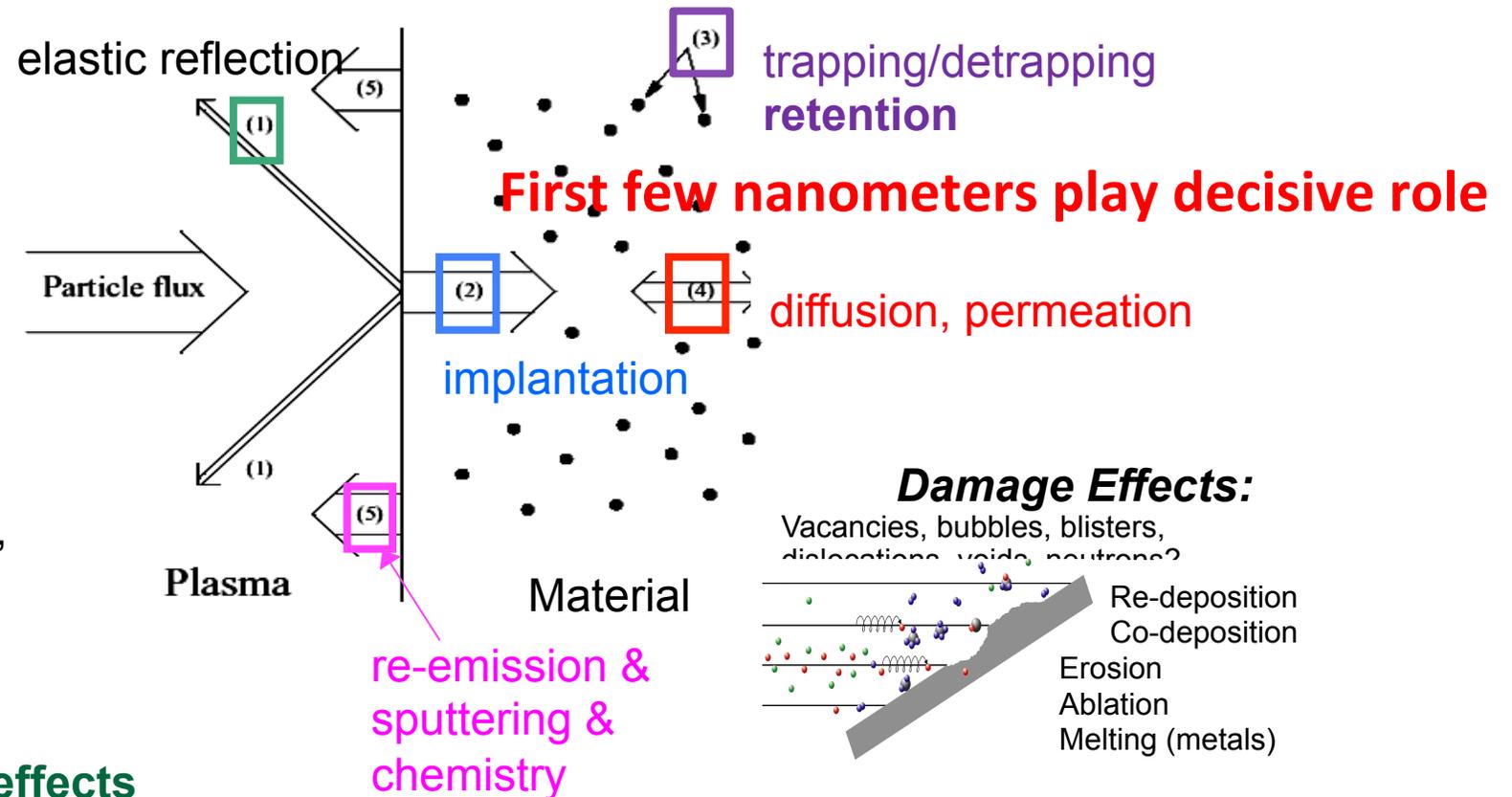
Emphasis on integrating the simulation of a fusion plasma with the material boundary falls inherently on the plasma material interface because the phenomenology of the interface evolves much faster than plasma time scales and because the interface traverses a wider range of scales, which overlap with the scales of the plasma.

Schematic magnetic fusion reactor



Drivers: Plasma
Multi -T, -n, -species,
plasma irradiation,
neutrons
sheath acceleration

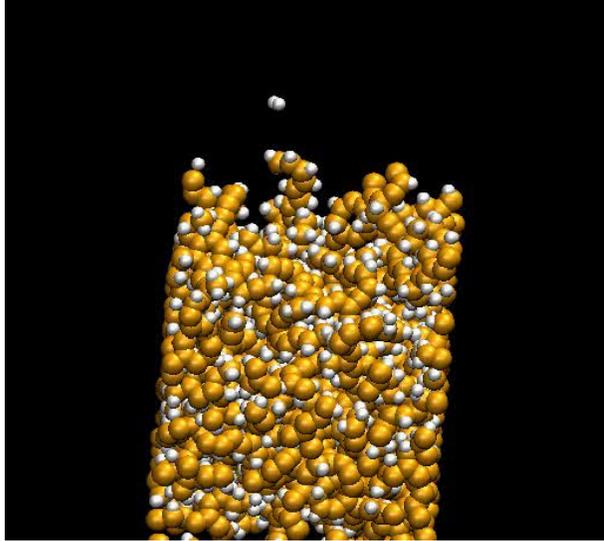
Give rise to synergistic effects



Multiscale nature of the physical processes at interface

How does PMI see a flux of 10^{25} particles/m²s mean (ITER)?

The flux is 0.01 particle/nm²ns, i.e. **1 particle each 10 ns at 10 nm²**



A typical evolution of **deuterium impact at 100 eV** even with chemical sputtering in carbon takes no more than **50 ps**, and penetration no more than **2 nm**; in tungsten events even faster

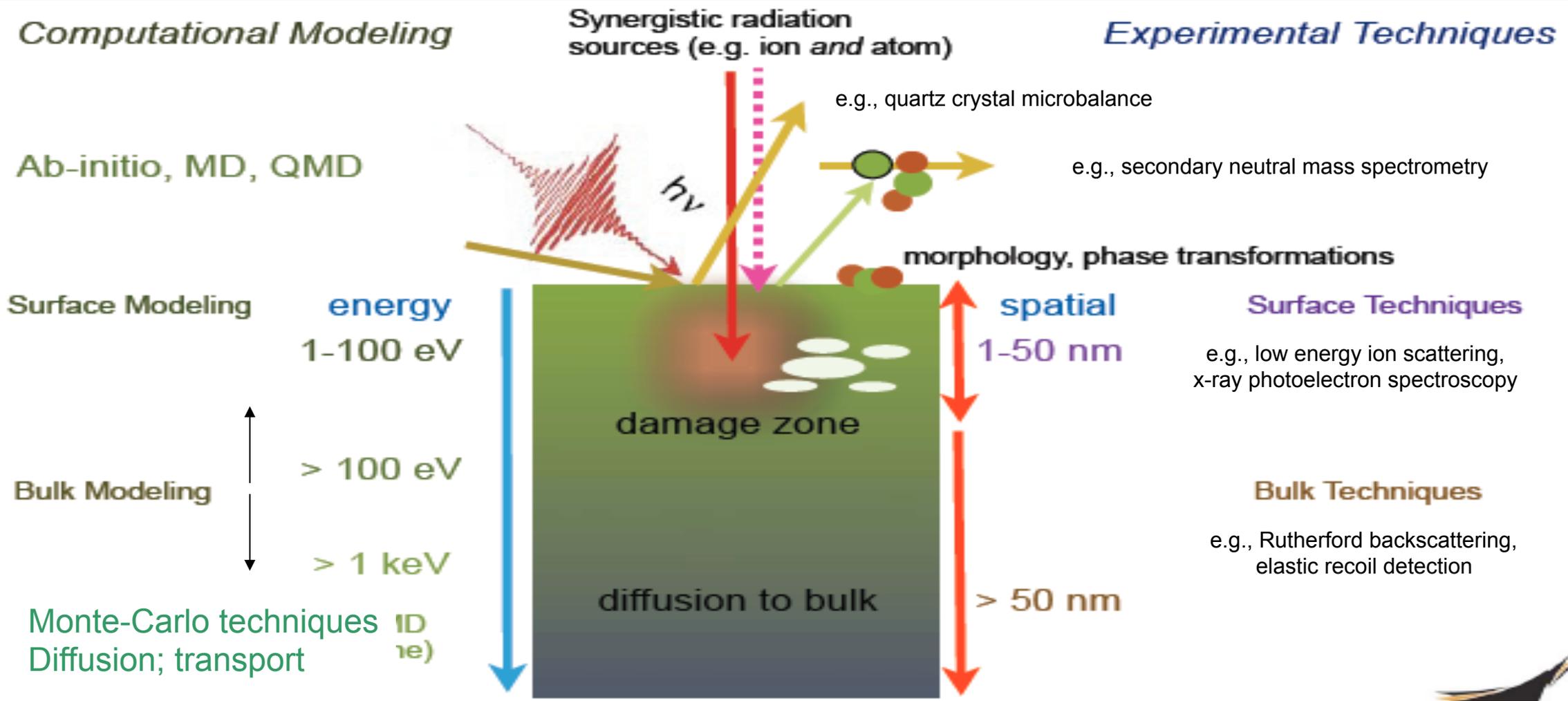
Each particle will functionalize the material, change the surface for the subsequent impact!

Processes essentially discrete  **Atomistic Happening at nanoscale in both time and space, scales determined by impact plasma particle energy**

The interface at which plasma and material meet is a dynamic entity, a mix of material and plasma that is governed by the history of their interaction,

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. **Need bottom-up approach arising from the fundamental atomistic and nano science**

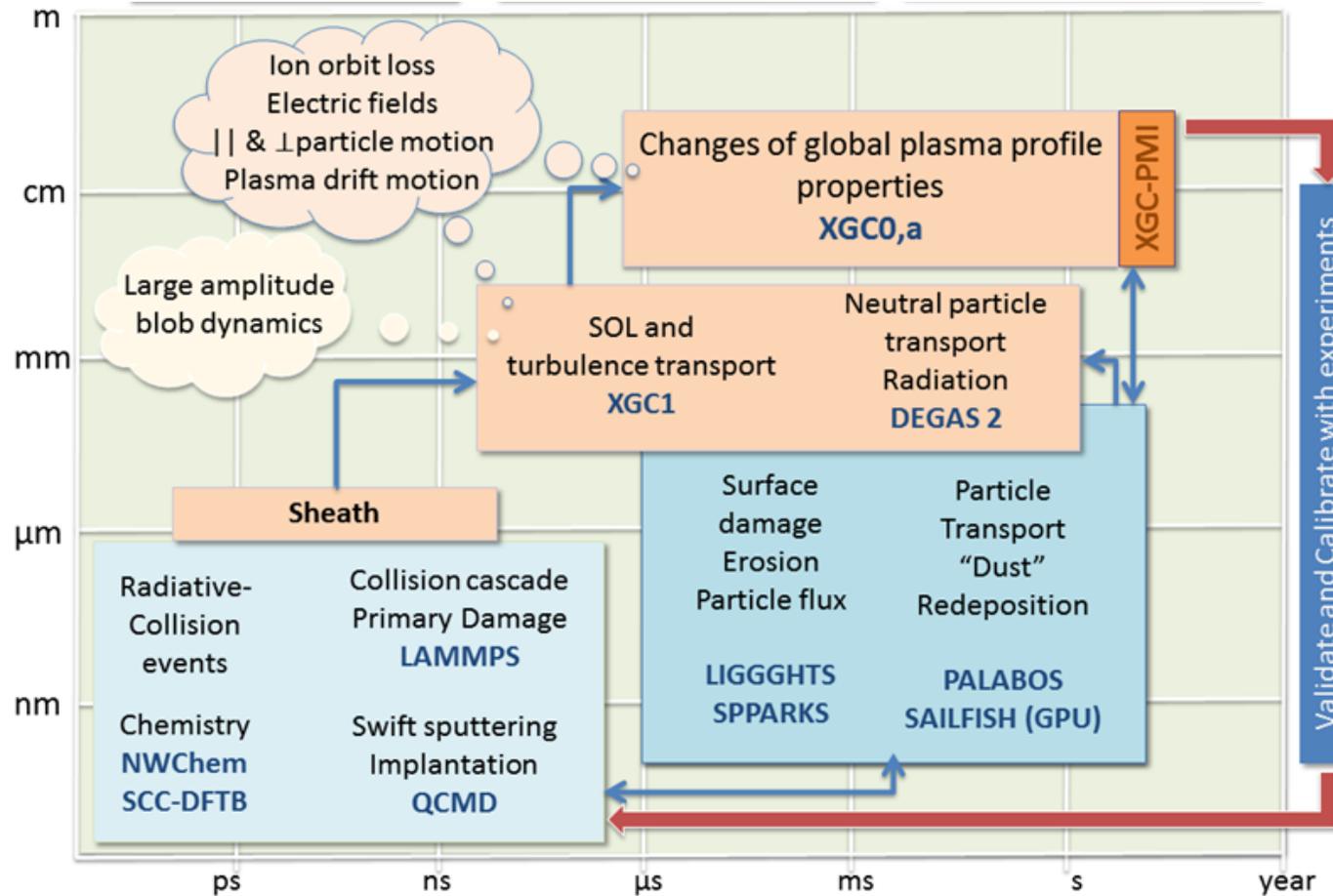
Probing the PMI requires integration of many experimental and theoretical techniques spanning orders of magnitude in time, length, and energy scales



Strategic objectives: Integrated plasma & material modeling system

Plasma codes resolve events at the scale of μs

At shorter than μs time: Study phenomenology, provide parameters for MC approaches at longer time scale!!!



Atomistic PMI codes (Computational chemistry NWChem, Approximate DFT: SCC-DFTB, Quantum-Classical Molecular Dynamics, Classical Molecular Dynamics, LAMMPS)

Mesoscopic PMI codes (DEM: LIGGGHTS and KMC:SPPARKS, referenced in the text, and Lattice-Boltzmann codes [PALABOS] and [SAILFISH]),

Plasma codes (XGC family and DEGAS 2)

Study PMI separately, with plasma drivers

Integration of PMI and plasma at the “same footing”, with nano PMI drivers

Basic Problem of Computational Chemistry

Schrodinger equation for electrons: 2nd order, linear partial differential equation in $3*N$ dimensions for N electrons

$$\hat{H} \Psi (r) = E \Psi (r)$$

$$\hat{H} \Psi (r, t) = i \frac{d \Psi (r, t)}{dt}$$

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{\mu} \sum_i \frac{Z_{\mu}}{|r_{\mu} - r_i|} + \sum_{i>j} \frac{1}{|r_i - r_j|}$$

For dynamics add time dependent derivative (additional scalar dimension)

Where are we with its solution after trying for 90+ years?:
can do only very simple systems

Various approaches:

- Ab initio theory

Goal to construct approximate wave functions that can be systematically improved toward exact solution – if we have large enough computer

How to do it? –subject of the first 40 years of computational chemistry

- Density functional theory (cannot systematically improve toward exact)
- Quantum Monte Carlo ?

What many electron systems can we solve?

- A non-interacting system

$$\hat{H} = \sum_i \hat{h}(r_i) \rightarrow \Psi = A \prod_i \psi_i(r_i)$$

$$\hat{h}\psi_i(r) = \varepsilon_i \psi_i(r) \rightarrow E = \sum_i \varepsilon_i$$

- Hartree-Fock: Simplest possible electronic wave function is an antisymmetric product of one-electron wave functions

Each electron is assumed to move in the average potential of all other electrons – but no instantaneous, direct coupling of electrons

This is somewhat related to much more used DFT

- DFT

A lot of problems that are outweighed by the success; Came into chemistry from solid-state physics

Must be applied with calibration against ab initio wave function methods;

Done for many system types

DFT problems

Weak interactions missing (long range correlation, dispersion)

Excited states, open shells missing

True-time dependence missing

Relativistic effects missing

Size-dependence of calculations?

No systematic path for improvement

Ab initio hierarchy

- Configuration interaction
 - A linear expansion

$$\Psi = |0\rangle + \sum_i^{\text{occ}} \sum_a^{\text{virt}} c_i^a |i \rightarrow a\rangle + \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} c_{ij}^{ab} |i j \rightarrow ab\rangle + \dots$$

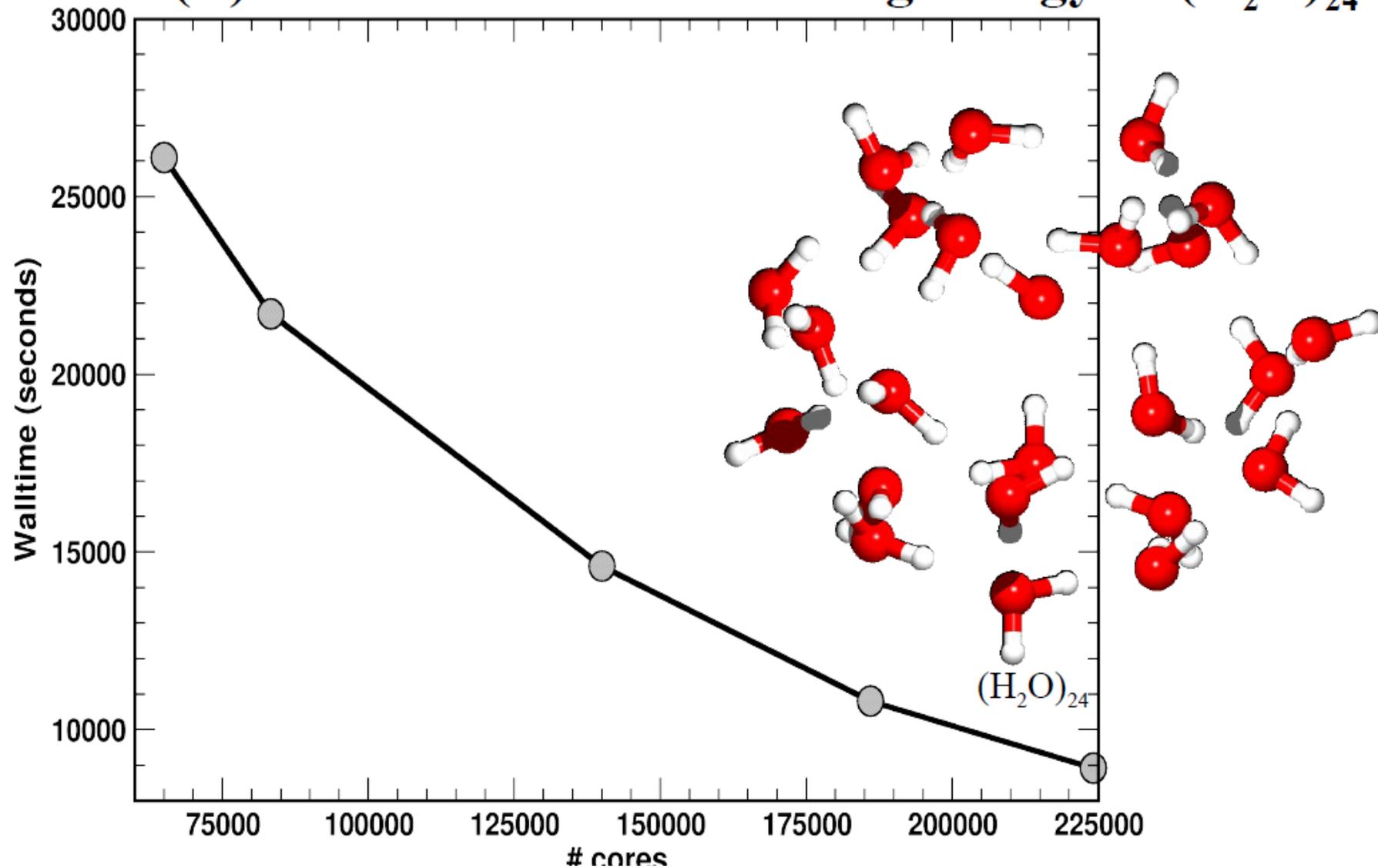
- Coupled cluster theory
 - A non-linear expansion
 - CCSD(T) is the “gold standard” - cost is $O(N^7)$

$$\Psi = \exp(\hat{T})|0\rangle = \left(1 + \sum_i^{\text{occ}} \sum_a^{\text{virt}} t_i^a \hat{a}_a^\dagger \hat{a}_i + \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \dots \right) |0\rangle$$

NWChem CCSD(T) – 1.31 PFLOP/s

E. Aprà, R.J. Harrison, W.A. deJong, A.P. Rendell, V. Tipparaju and R.M. Olson

CCSD(T) benchmark of the binding energy of $(\text{H}_2\text{O})_{24}$



NWChem: General Computational Chemistry package – open source

NWChem aims to provide its users with computational chemistry tools that are **scalable** both in their ability to treat **large scientific computational chemistry** problems efficiently, and in their **use of available parallel computing resources** from high-performance parallel supercomputers to conventional workstation clusters.

NWChem software can handle (all mentioned methods):

- Biomolecules, nanostructures, and solid-state
- From quantum to classical, and all combinations
- Ground and excited-states
- Gaussian basis functions or plane-waves
- Scaling from one to thousands of processors (250,000)
- Properties and relativistic effects

MADNESS

Multiresolution Adaptive Numerical Scientific Simulation

*George I. Fann¹, Diego Galindo¹, Robert J. Harrison^{1,2},
Rebecca Hartman-Baker¹, Judy Hill¹, and Jun Jia*

¹Oak Ridge National Laboratory

²University of Tennessee, Knoxville

In collaboration with

*Gregory Beylkin⁴, Lucas Monzon⁴, Hideo Sekino⁵ and Edward
Valeev⁶*

⁴University of Colorado

⁵Toyohashi Technical University, Japan



What is MADNESS?

<http://en.wikipedia.org/wiki/Madnes>

A general purpose numerical environment for reliable and fast scientific simulation

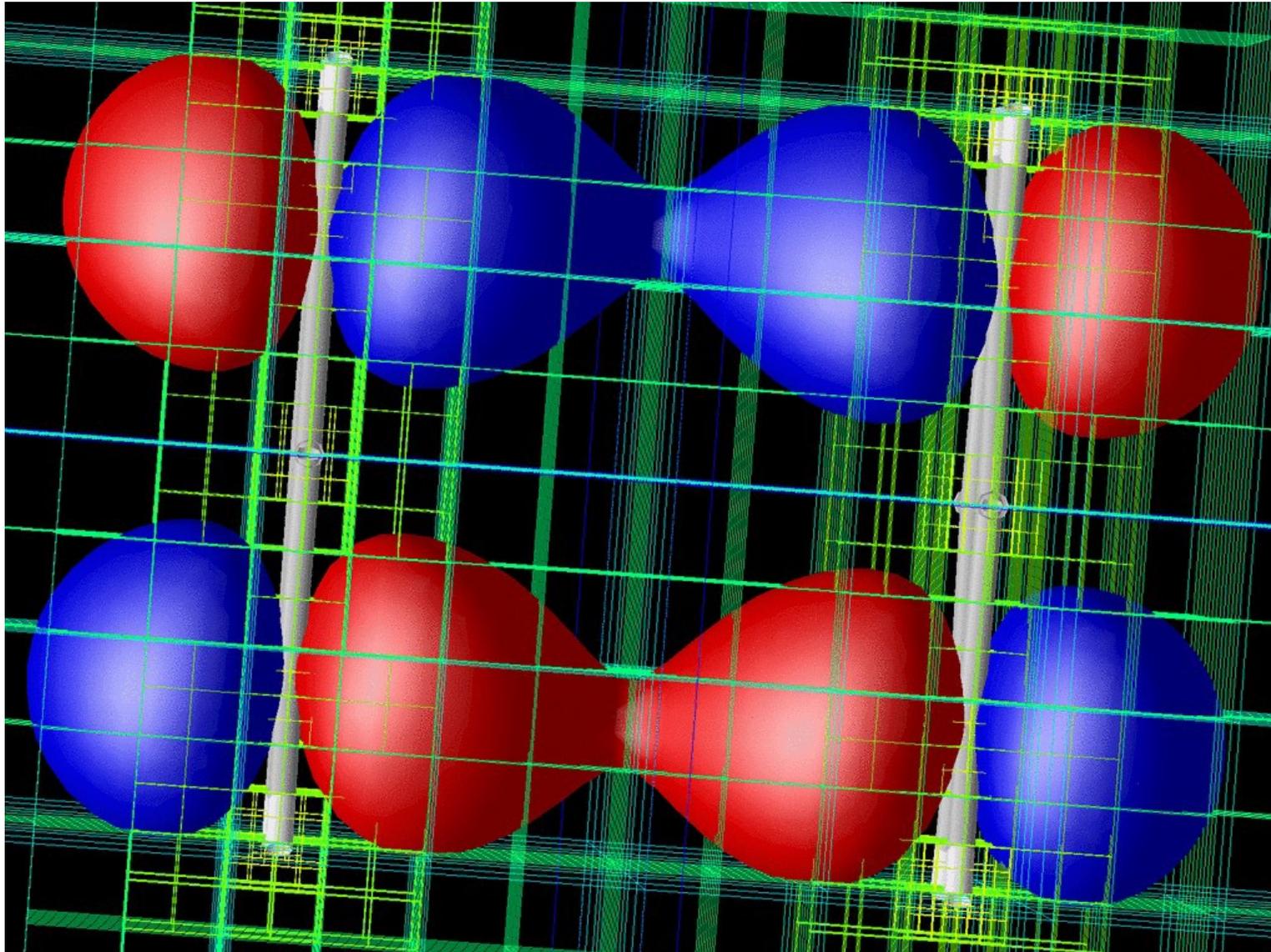
– Chemistry, nuclear physics, atomic physics, material science, nanoscience, climate, fusion, ...

• A general purpose parallel programming environment designed for the peta/exa-scales

Addresses many of the sources of complexity that constrain the HPC ambitions

High-level software environment for the solution of integral and differential equations in many dimensions using adaptive and fast harmonic analysis methods with guaranteed precision based on multiresolution analysis and separated representations . Solution of integral not differential equations. Wavelet representation of operators.

The user chooses accuracy, and the simulation box size, system changes mesh (even 100,000 times during calculation) to reach the required accuracy of the wave function.



SCC-DFTB method:
A cheap QM alternative to DFT
for
QCMD

“1000 times faster than DFT-MD, 1000 times slower than CMD”

1. <http://www.dftb.org>
2. DFTB Porezag, D., T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, *Construction of tight-binding-like potentials on the basis of density-functional theory: application to carbon*. Phys. Rev. B, 1995. 51: p. 12947-12957.
3. DFTB Seifert, G., D. Porezag, and T. Frauenheim, *Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme*. Int. J. Quantum Chem., 1996. 58: p. 185-192.
4. SCC-DFTB Elstner, M., D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, and G. Seifert, *Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties*. Phys. Rev. B, 1998. 58: p. 7260-7268.
5. SCC-DFTB-D Elstner, M., P. Hobza, T. Frauenheim, S. Suhai, and E. Kaxiras, *Hydrogen bonding and stacking interactions of nucleic acid base pairs: A density-functional-theory based treatment*. J. Chem. Phys., 2001. 114: p. 5149-5155.
6. SDFTB Kohler, C., G. Seifert, U. Gerstmann, M. Elstner, H. Overhof, and T. Frauenheim, *Approximate density-functional calculations of spin densities in large molecular systems and complex solids*. Phys. Chem. Chem. Phys., 2001. 3: p. 5109-5114.
7. DFTB3 Gaus, M.; Cui, C.; Elstner, M. *DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB)*. J. Chem. Theory Comput., 2011. 7: p. 931-948.

Implementations

DFTB+



Standalone fast and efficient DFTB implementation with several useful extensions of the original DFTB method. It is developed at the Bremen Center for Computational Materials Science (Prof. Frauenheim) and is the successor of the old Paderborn DFTB and Dylax codes. Free for non-commercial use.

DFTB+/Accelrys

DFTB+ as part of Accelrys' Materials Studio package, providing a user friendly graphical interface and the possibility to combine DFTB with other higher or lower level methods.

deMon

DFTB integrated in the ab initio DFT code deMon

GAUSSIAN G09

DFTB in the Gaussian code

AMBER

Amber is a package of molecular simulation programs distributed by UCSF, developed mainly for biomolecular simulations. The current version of Amber includes QM/MM support, whereby part of the system can be treated quantum mechanically, and DFTB is among the quantum mechanical methods available. Amber also has a stand-alone (pure QM) implementation.

CHARMm

CHARMm (Chemistry at HARvard Macromolecular Mechanics)

ADF

DFTB integrated in the Amsterdam Density Functional (ADF) program suite.

Alternative to DFT: Approximate DFT

Density-Functional Tight-Binding: Method using atomic parameters from DFT (PBE, GGA-type), diatomic repulsive potentials from B3LYP

- Seifert, Eschrig (1980-86): minimum STO-LCAO; **2-center approximation**
- Porezag, Frauenheim, *et al.* (1995): efficient parameterization scheme: **NCC-DFTB**



Helmut
Eschrig



Gotthard
Seifert



Thomas
Frauenheim

- Elstner *et al.* (1998): charge self-consistency: **SCC-DFTB**
- Köhler *et al.* (2001): spin-polarized DFTB: **SDFTB**

$$E^{(NCC-)DFTB} = \sum_i^{valence\ orbitals} n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B}^{atoms} E_{AB}^{rep}$$

$$E^{(SCC-)DFTB} = E^{(NCC-)DFTB} + \frac{1}{2} \sum_{A \neq B}^{atoms} \gamma_{AB} \Delta q_A \Delta q_B$$



Marcus Elstner

$$E^{S(pin-polarized)DFTB} = E^{(SCC-)DFTB} + \frac{1}{2} \sum_A^{atoms} \sum_{I \in A} \sum_{J \in A} P_{AI} P_{AJ} W_{AIJ}$$



Christof Köhler

DFTB and SCC-DFTB methods

$$E^{\text{DFTB}} = \underbrace{\sum_i^{\text{valence orbitals}} n_i \varepsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2} \sum_{A \neq B}^{\text{atoms}} E_{\text{rep}}^{AB}}_{\text{terms 2-6}}$$

$$E^{\text{SCC-DFTB}} = \underbrace{\sum_i^{\text{valence orbitals}} n_i \varepsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2} \sum_{A \neq B}^{\text{atoms}} \gamma_{AB} \Delta q_A \Delta q_B}_{\text{terms 7-8}} + \underbrace{\frac{1}{2} \sum_{A \neq B}^{\text{atoms}} E_{\text{rep}}^{AB}}_{\text{terms 2-6}}$$

❖ where

- n_i and ε_i – occupation and orbital energy of the i^{th} Kohn-Sham eigenstate
- E_{rep} – distance-dependent diatomic repulsive potentials
- Δq_A – induced charge on atom A
- γ_{AB} – distance-dependent charge-charge interaction functional; obtained from chemical hardness (IP – EA)

SCC-DFTB: general comparison with experiment

*Performance for small organic molecules
(mean absolute deviations)*

- Reaction energies: ~ 5 kcal/mole
- Bond-lengths: ~ 0.014 Å
- Bond angles: $\sim 2^\circ$
- Vib. Frequencies: $\sim 6-7$ %

OUR Investigation of the parallel efficiency of the SCC-DFTB (one node use of up to 8 cores at Titan)

CPU only	OMP-1	OMP-2	OMP-4	OMP-8
Total time	702.8	372.5	338.0	205.5
Time for Forces	2.9	2.0	1.9	1.5
* Form E.Weight dens	1.9	1.0	0.9	0.5
Time for SCF energy	524.5	370.0	335.6	203.5
* Form density matr	28.1	14.6	13.1	7.3
* Diagonalization	667.8	351.9	319.0	192.7
CPU+GPU	OMP-1	OMP-2	OMP-4	OMP-8
Total time	102.7	96.5	74.8	71.5
Time for Forces	2.9	2.6	1.9	1.6
* Form E.Weight dens	1.9	1.6	0.9	0.6
Time for SCF energy	99.2	93.3	72.4	69.4
* Form density matr	27.4	24.0	12.8	69.4
* Diagonaliz	68.5	65.9	56.3	56.4
- magma_dsygvd_m	62.3	61.7	52.1	52.3

Table 1 . Time in seconds for one MD step (energy+ forces evaluations) for 900 Carbons with SCC-DFTB+ code. Comparison with only CPU and hybrid CPU+GPU with different number of OpenMP threads (see columns) is shown. Here we used `-cc=numa_node` flag in apron call.

1000 and 5000 nodes at Titan for the statistics (cannot help time causality!!!)

Ncores	16,000	80,000
CPU-only	N=1000	N=5000
800 atoms	339.0s	365.4s
1600 atoms	2062.7s	2781.5s
Atom factor	6.1	7.6
CPU+GPU	N=1000	N=5000
800 atoms	70.7s (4.8)	90.5s (4.0)
1600 atoms	263.6s (7.8)	391.4s (7.1)
Atom factor	3.7	4.3

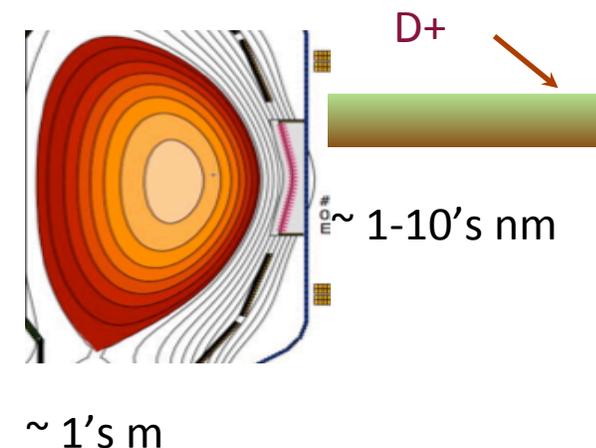
Table II. Times for one step, varying number of atoms and number of cores. N is the number of nodes at Titan. N_{cores} is the number of cores of Titan used for the calculations.

Our application of SCC-DFTB: Lithium wall conditioning improves confinement! Why?

- From in-situ experiments labs, and more than 7 different tokamak machines (TFTR , CDX-U, FTU, DIII-D, TJ-II, EAST , and NSTX): Graphite with thin lithium coatings have a "significant" effect on plasma behavior: Reduced hydrogen recycling, erosion and ELMs, improved energy confinement time

Noticeable is the ratio of the dimensions of the plasma and Li layer!!!

“Nano-control of macro device”

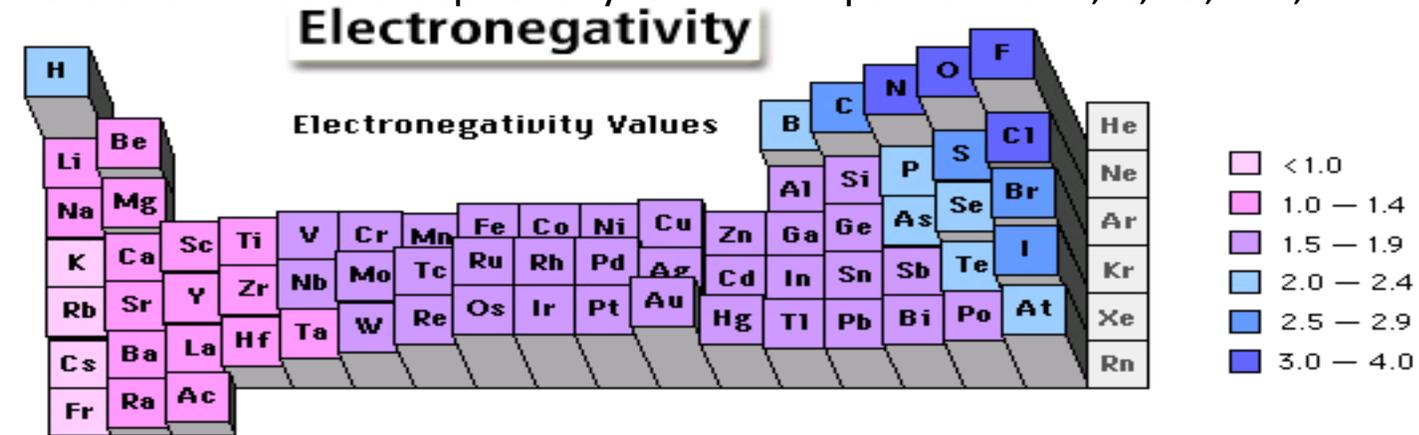


- Initially the experimentalists conjecture was that there was some "functionality" that governed the behavior of the Li-C-O-H system observed indirectly by analyzing the O(1s) and C(1s) peaks.

Working assumption was that the main generator was Li-H chemistry

Lithium dynamics: Difficult to study theoretically by usual classical MD because of Li polarizing features when interacting with other elements

Electronegativity is chemical property of an element defining its tendency to attract electrons: Li has it exceptionally low in comparison to H, C, O, Mo, W.

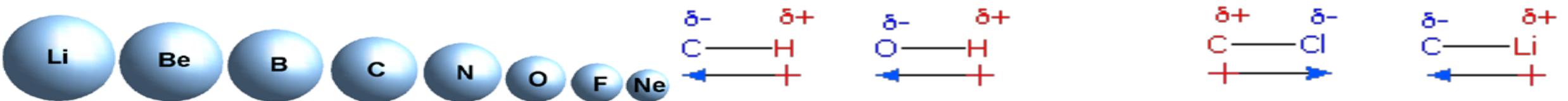


Consequence: Bonding between Li and other atoms covalent and polar;

Long-range nonbonding:

Coulomb : $1/R$

Lennard-Jones : $1/R^6$, $1/R^{12}$



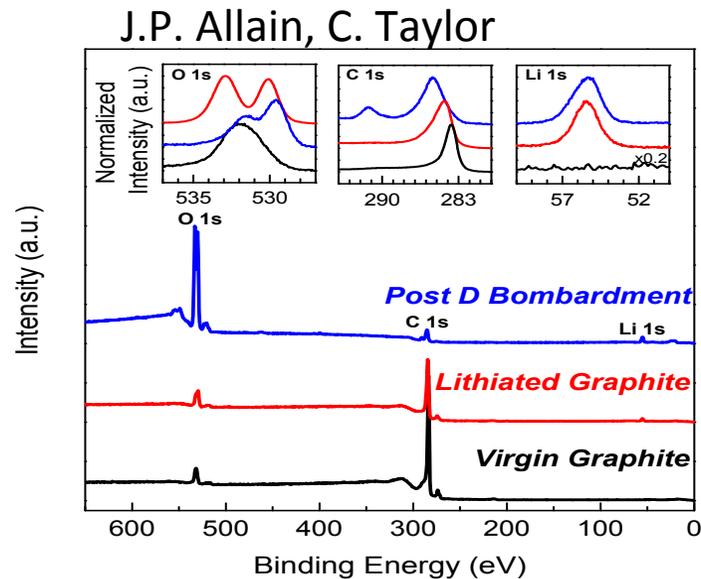
Quantum-mechanical approach a must

Quantum-Classical MD based on Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB) method (developed by Bremen Center for Computational Mat. Science, Germany) a possible answer for qualitative phenomenology is our choice

What did experiments teach us?

From experiments: There was correlation between hydrogen retention and the behavior change of the O(1s) and C(1s) peaks ONLY IN THE PRESENCE OF LITHIUM

The Li(1s) peak was always invariant????

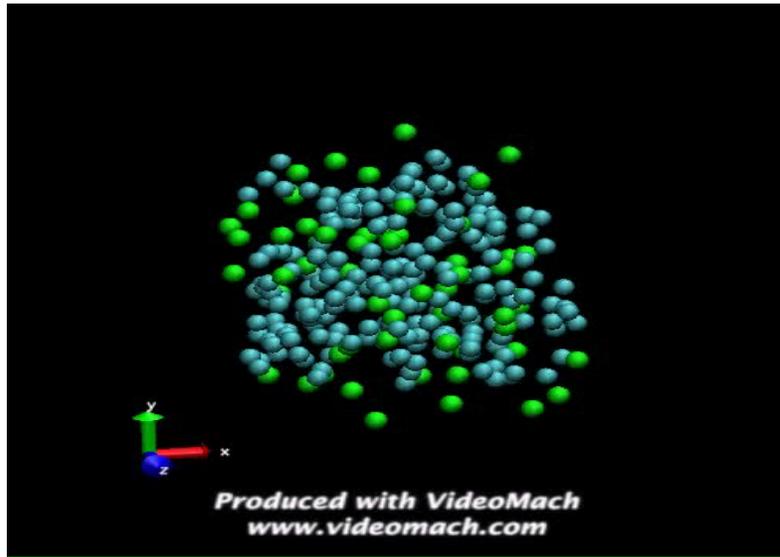


But theory said:

D has a slight preference for interacting with Li rather than with C when small concentrations of O present

Krstic et al., FED (2012)

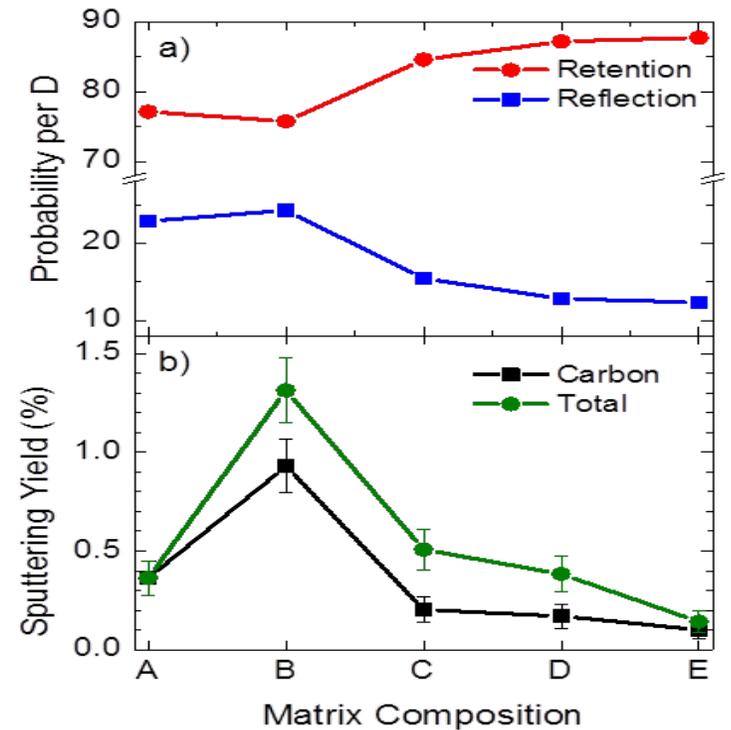
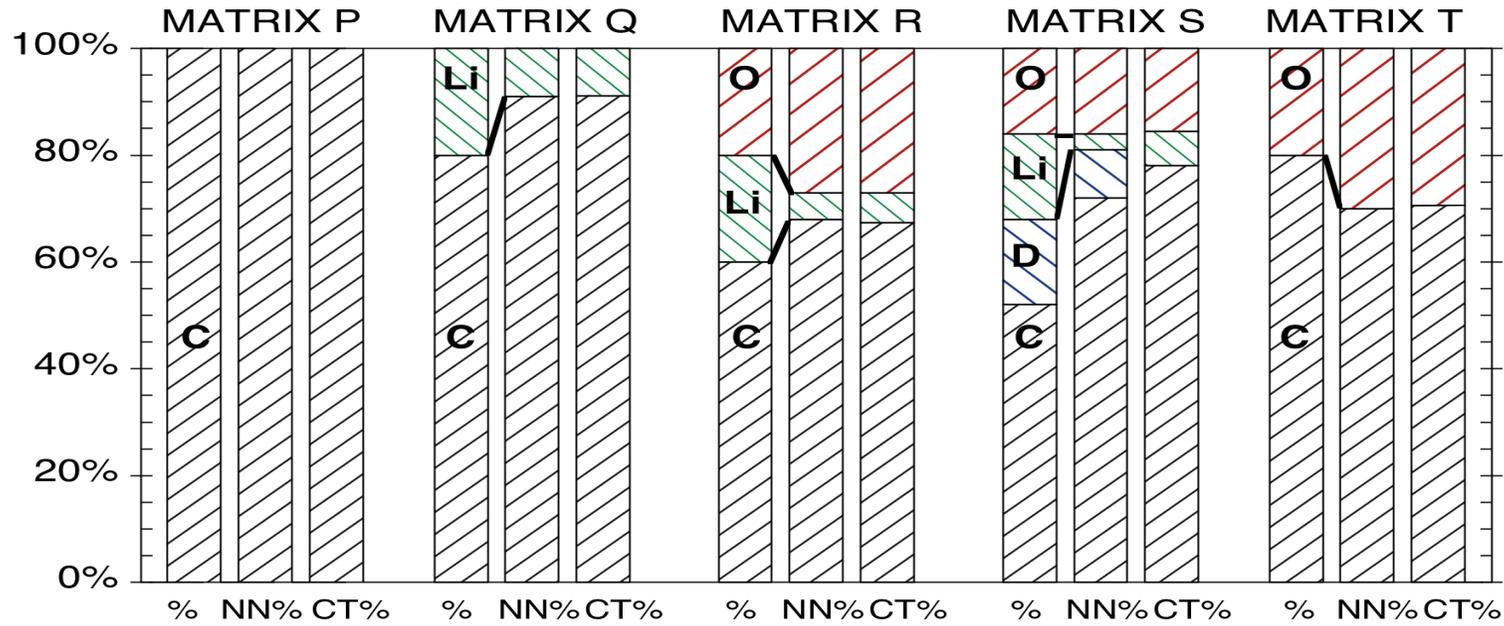
Simulation of deuterium impact to lithiated and oxidized carbon surface (quantum-classical approach, SCC-DFTB) – larger O concentrations



- Cell of a **few hundreds atoms** of lithiated and oxidated amorphous carbon
- (~20% of Li, **and/or** ~20% of O), at **300K**
- How?
- By random seed of Li and O in **amorphous carbon** and **energy minimization**, followed by thermalization
- bombarded by **5 eV D** atoms, up to 500fs for the full evolution
- **Perpendicularly** to the shell interface

• **5004 random trajectories** (embarrassingly parallel runs at Jaguar, Kraken); Time step **1 fs**; 30,000-50,000 CPU hours per run, number of runs > 20.

Simulations: How much is uptake of D correlated to O and Li contents?



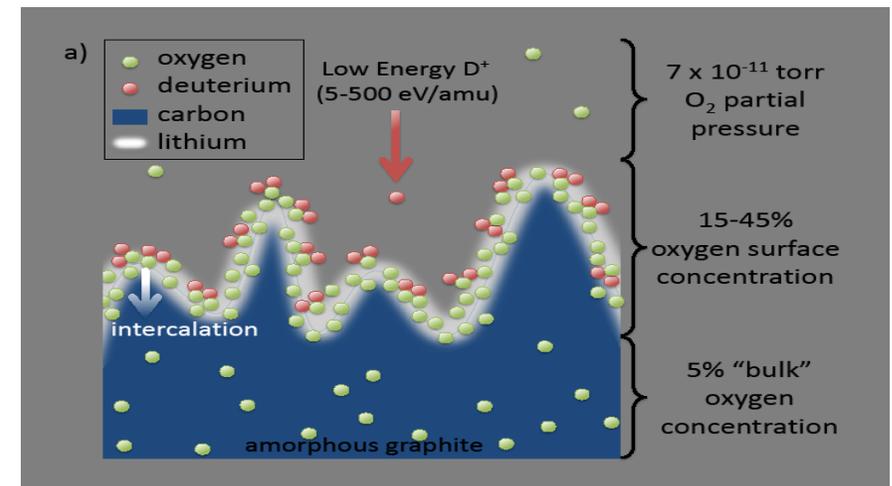
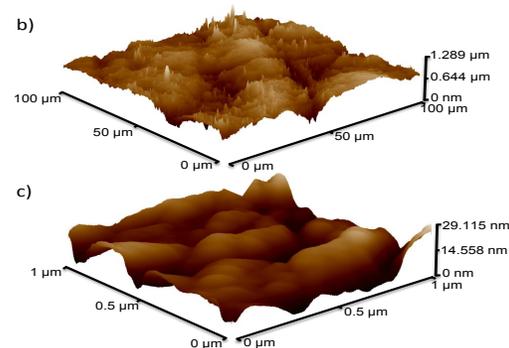
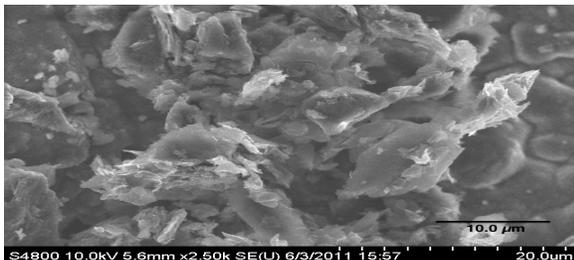
Prediction from simulation:

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

Experimental validation

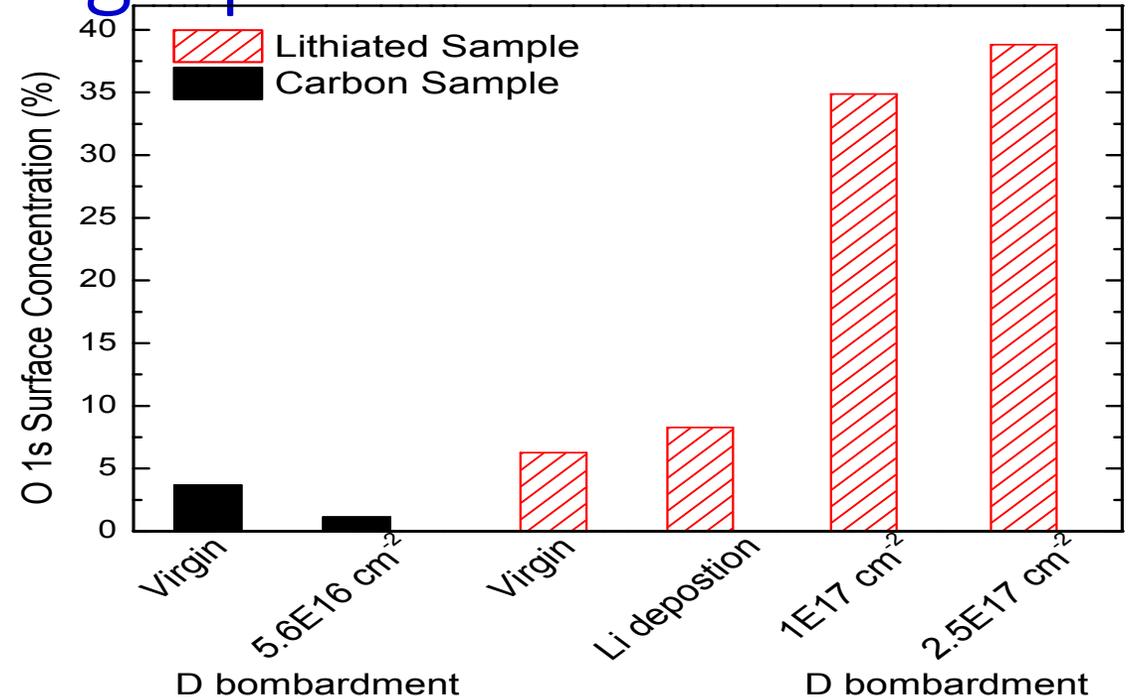
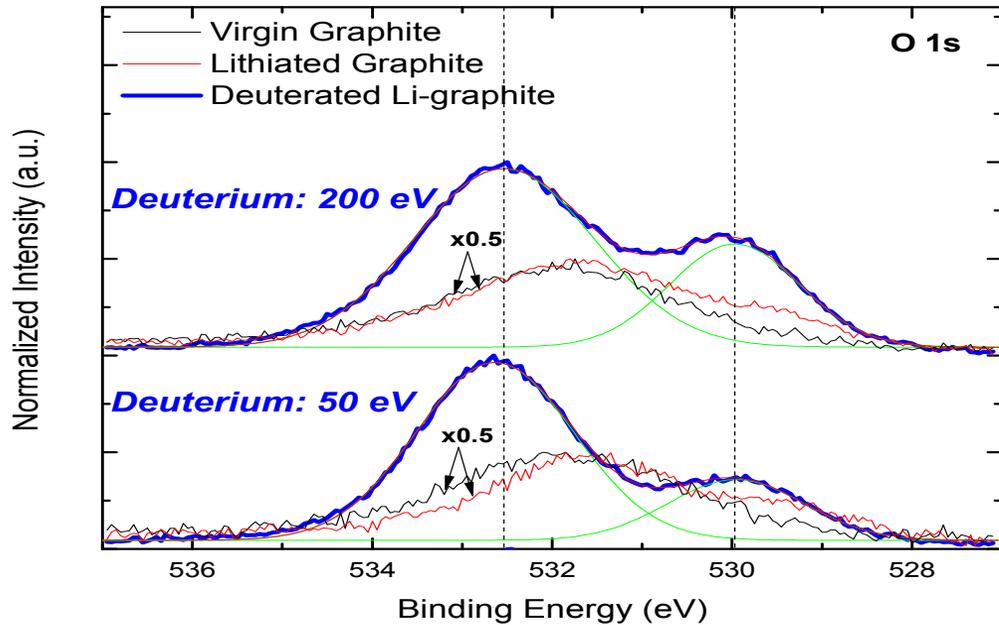
Here came the experiment again (C. Taylor, J.P. Allain):

- 1) At most 5% oxygen content on the surface of NON-LITHIATED graphite... AS EXPECTED.
- 2) With lithium one gets 10% of Oxygen
- 3) **IMPORTANT**: LOW-ENERGY IRRADIATION of D promotes 20-40% oxygen on the surface.
..... (only when LITHIUM present in GRAPHITE!!)



How to get high concentrations of Oxygen in the surface?
How could we study 100's of eV and keV impacts with 5 eV D?

D interactions with lithiated graphite



- (left) The surface chemistry is found independent of the incident energy
- (right) With lithium on graphite, surface concentration of Oxygen increased upon bombardment by D

What we learn from this T&E corroboration?

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

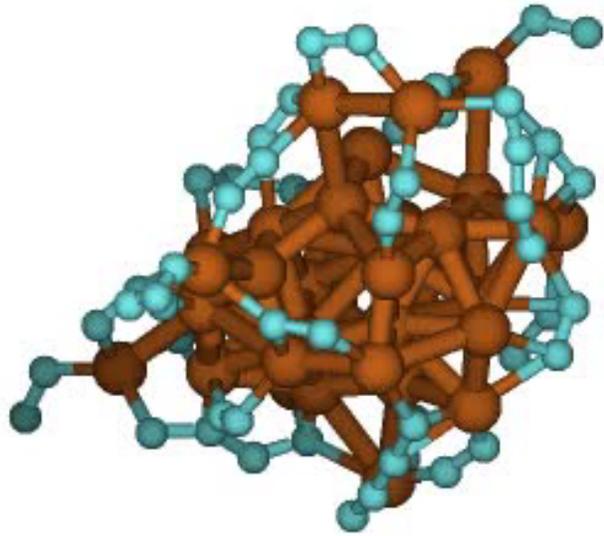
OXYGEN plays the key role in the binding of hydrogen.

**Lithium is the oxygen getter: Lithiation of C brings
A LOT OF Oxygen inside C and this the main role of Li.**

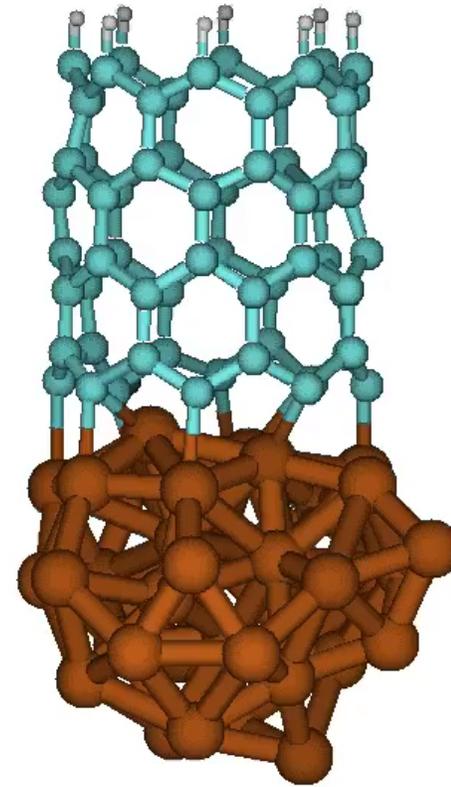
If there is a **SIGNIFICANT amount of oxygen** on surface with lithium present in the graphite matrix, OXYGEN becomes **the main player**; NOT LITHIUM!!! Oxygen and Oxygen-Carbon bond D strongly: suppressing erosion & increasing D retention.

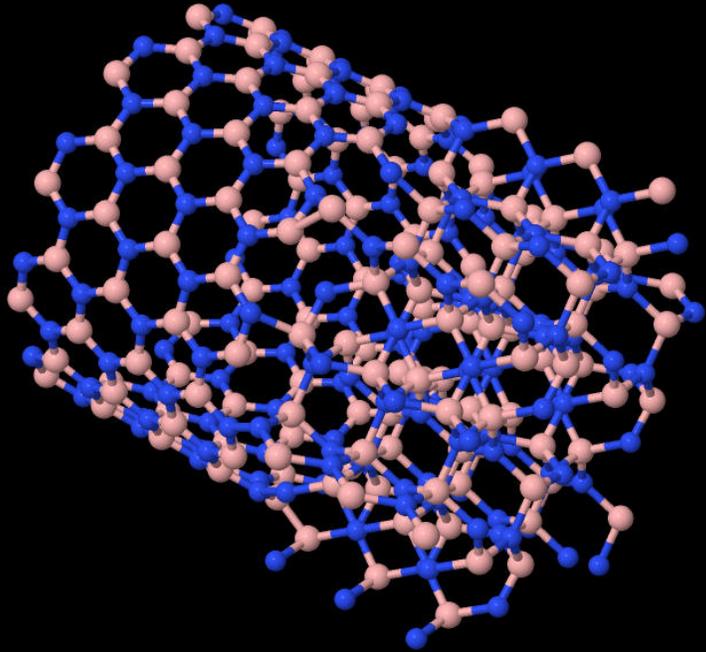
... **consistent with the XPS data!!**

How to do nanosynthesis in plasma: of a SWCNT QCMD with SCC-DFTB



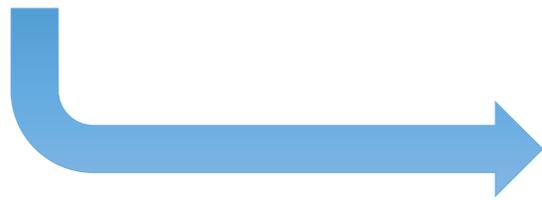
Iron catalyst



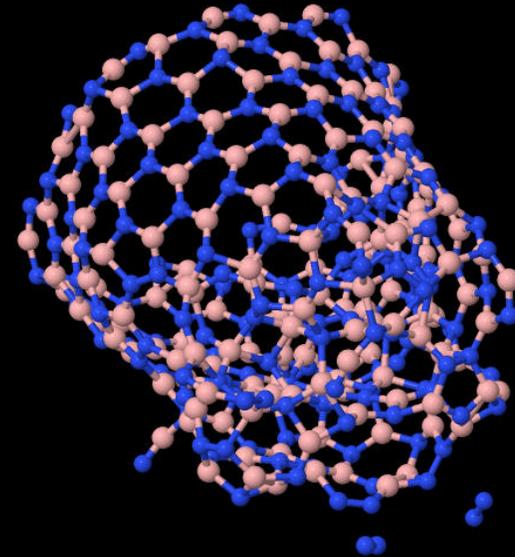


Synthesis of BN nanotubes

Covalent-ionic bonding of BN



Self-organization of the NT layers



Jmol

Jmol

CMD TOOLS

<http://lammps.sandia.gov>

**LAMMPS is classical molecular dynamics code
For ensemble of particles in a liquid, solid, or
gaseous phase**

**Highly efficient, GPU functionality recently too
Highly parallelized, up to millions of atoms**

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

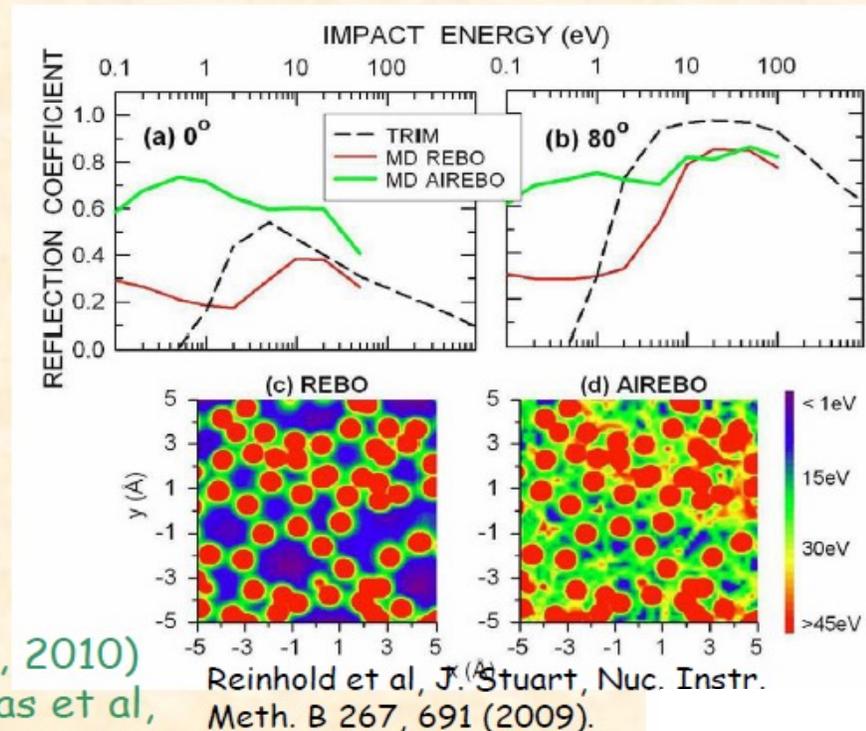
Most advanced: hydro-carbon potential developed for chemistry

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

Adaptive Intermolecular Reactive Bond Order (**AIREBO**) potential : **torsion, dispersion, Van der Waals**,
Even for hydrocarbons problems visible

EX: MD calc. of reflection coeff.

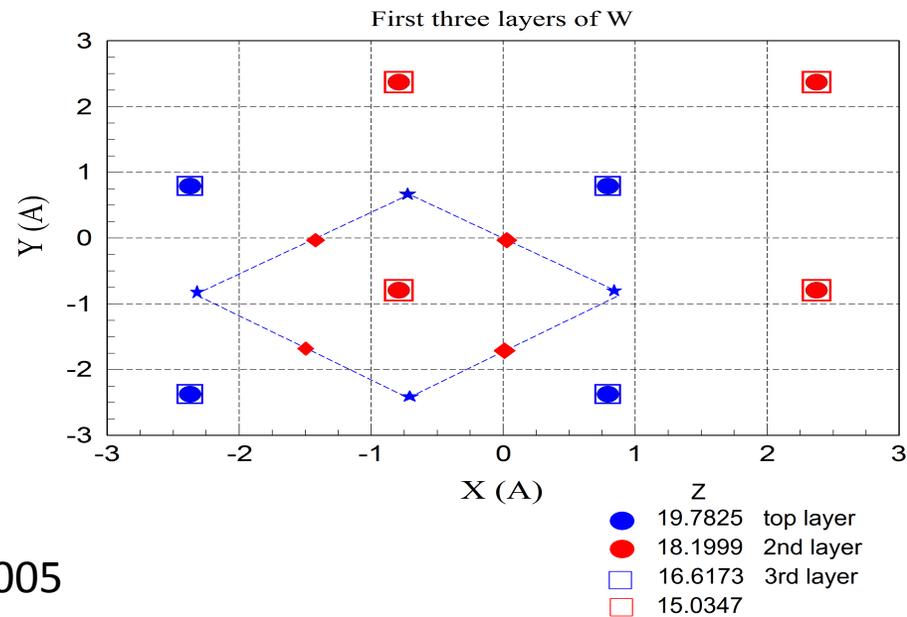
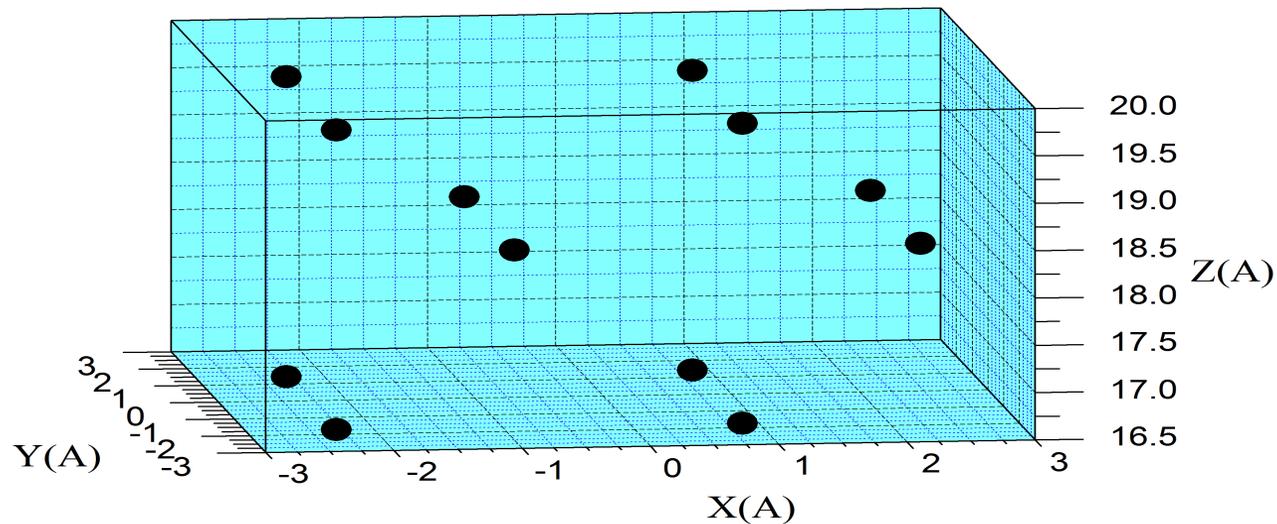
- **Significant sensitivity to changes in potential model for some processes**
- Experimental validation essential to establish credible MD simulation.
- Interatomic potentials for W, Be, C exist (talk of Nordlund)
- Experimental validation?



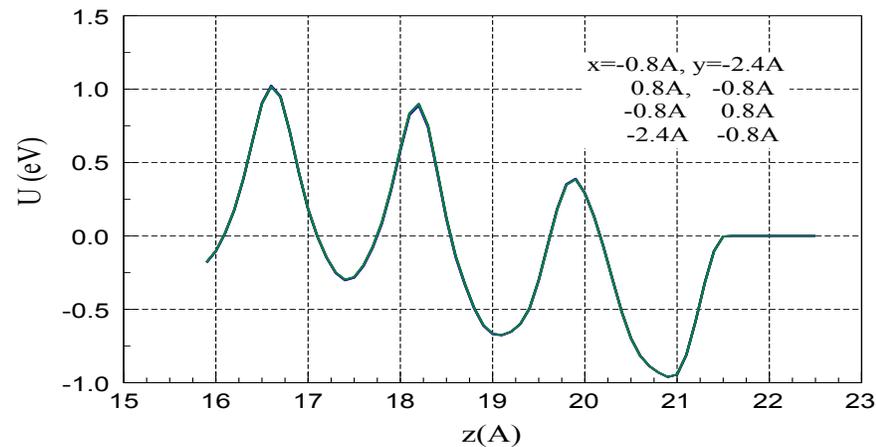
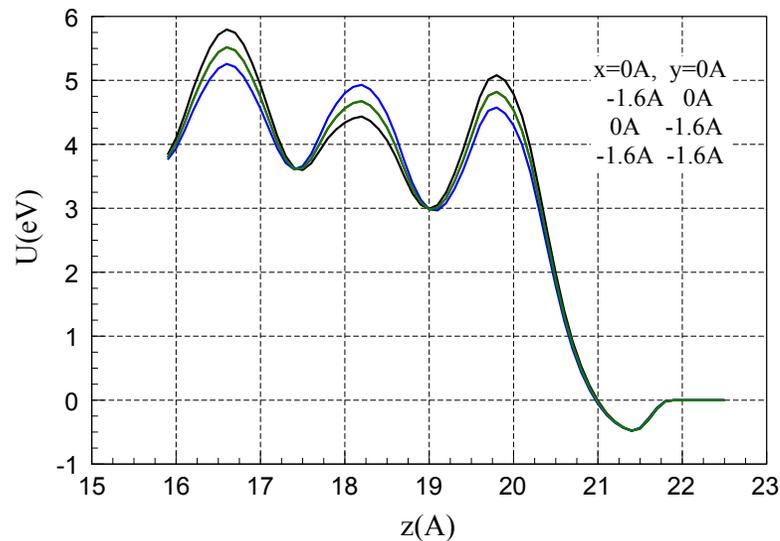
Improvements to CH potentials done (Kent et al, 2010)
New Li-C-H-O potentials being developed (Dadras et al,

Perfect monocrystal of W

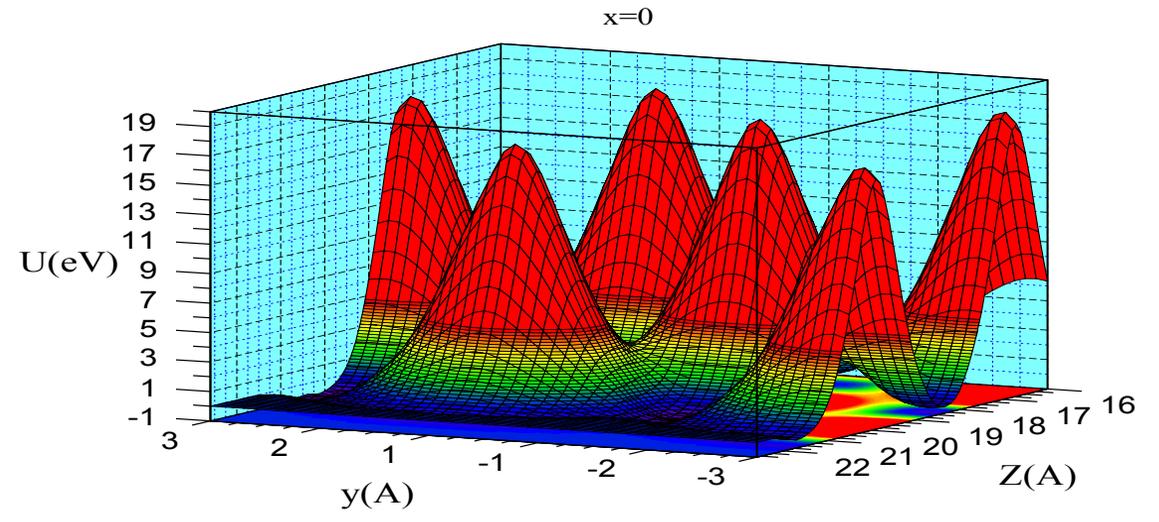
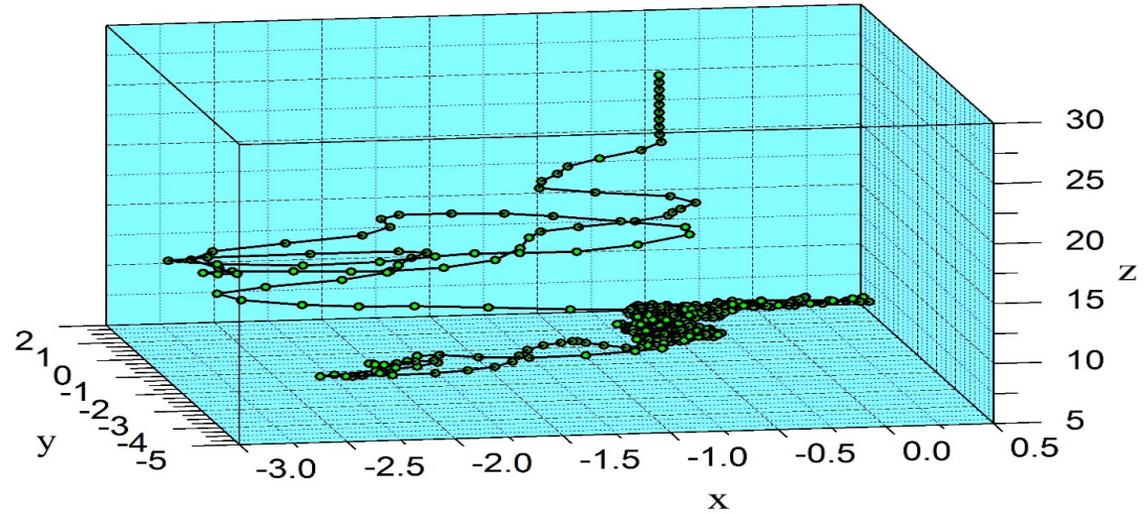
First three layers of W



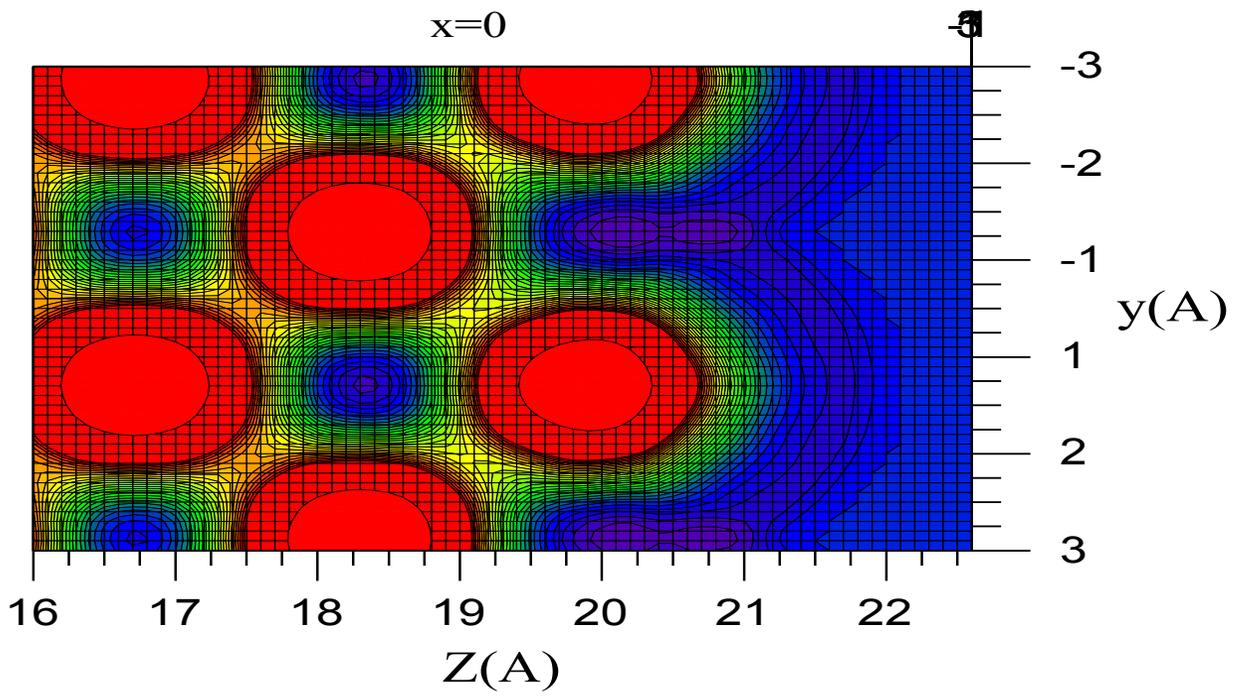
BOP of Juslin, 2005



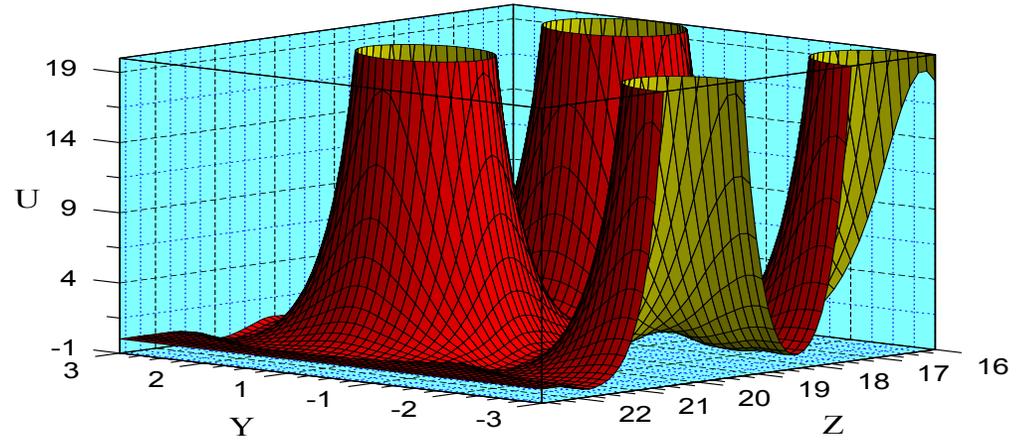
trajecotry of a retained D #8



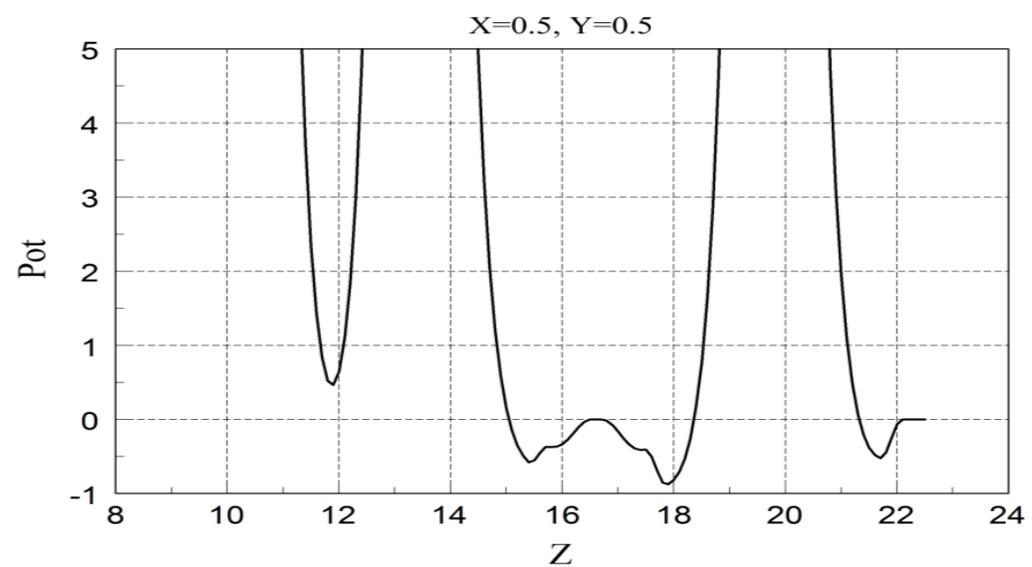
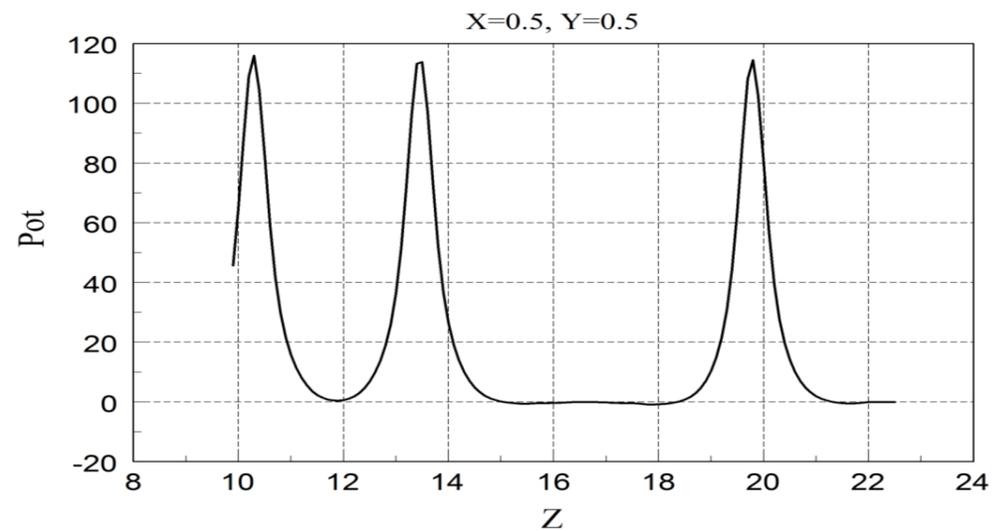
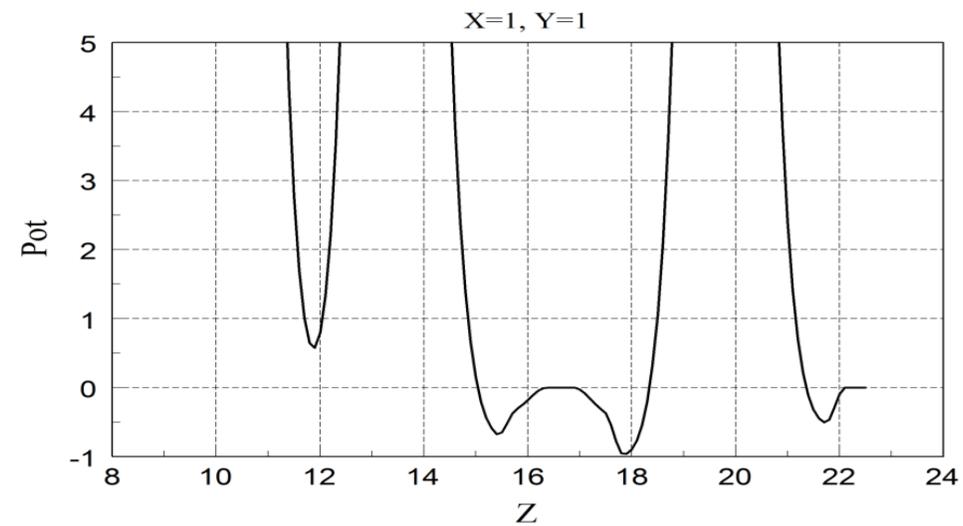
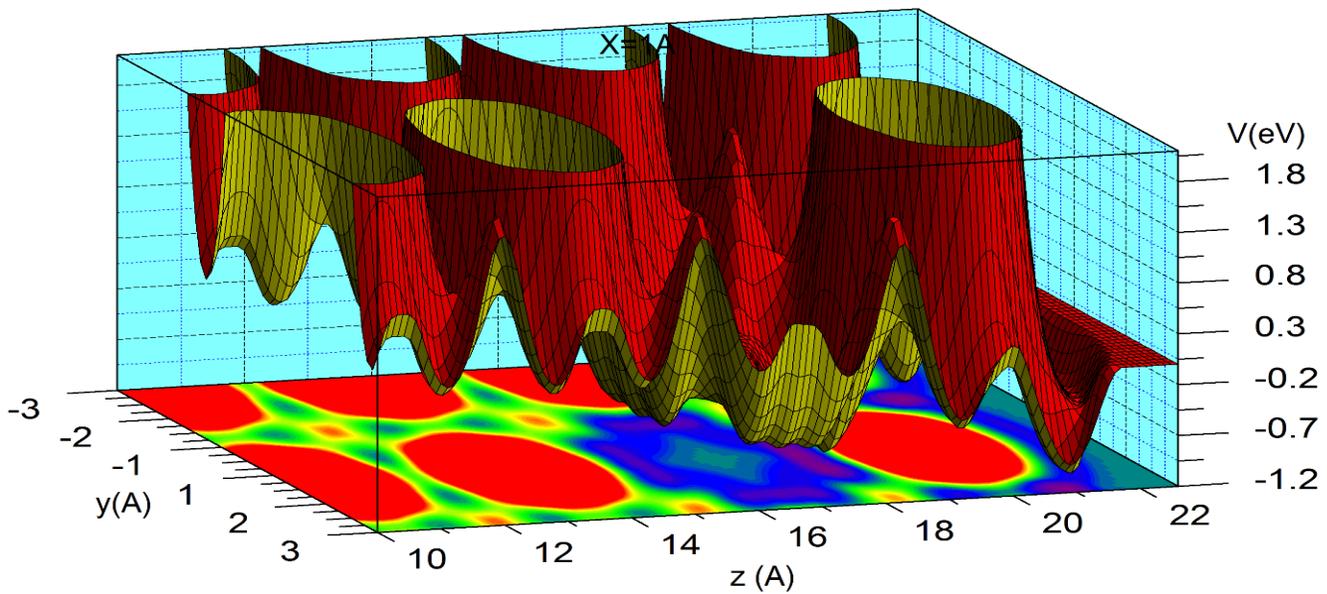
$x=0$



$x=0.5$



With a vacancy present (J.C. Wells, 2014)



How much is LAMMPS parallelization efficient for Tersoff-type potentials

N:number of nodes	1000	1750	2500	3750	5000
$N_{\text{atoms}}=26582$	220.4s	207.8s	172.8s	225.9s	223.1s
Speed up Ratio (T_{1000}/T_{5000})	1.00 (100%)	1.06 (60%)	1.27 (51%)	0.98 (26%)	0.99 (20%)
$N_{\text{atoms}}=351232$	1224.7s	894.2s	694.2s	635.6s	607.7s
Speed up Ratio (T_{1000}/T_{5000})	1.00 (100%)	1.37 (78%)	1.76 (70%)	1.93 (51%)	2.02 (40%)
Atom-factor	5.6	4.3	4.0	2.8	2.7

Table III. Time for one loop of 75,000 steps with variation of number of atoms and number of nodes. Speed up ratios and parallel efficiencies (in %) are also presented, starting from 8000 cores.

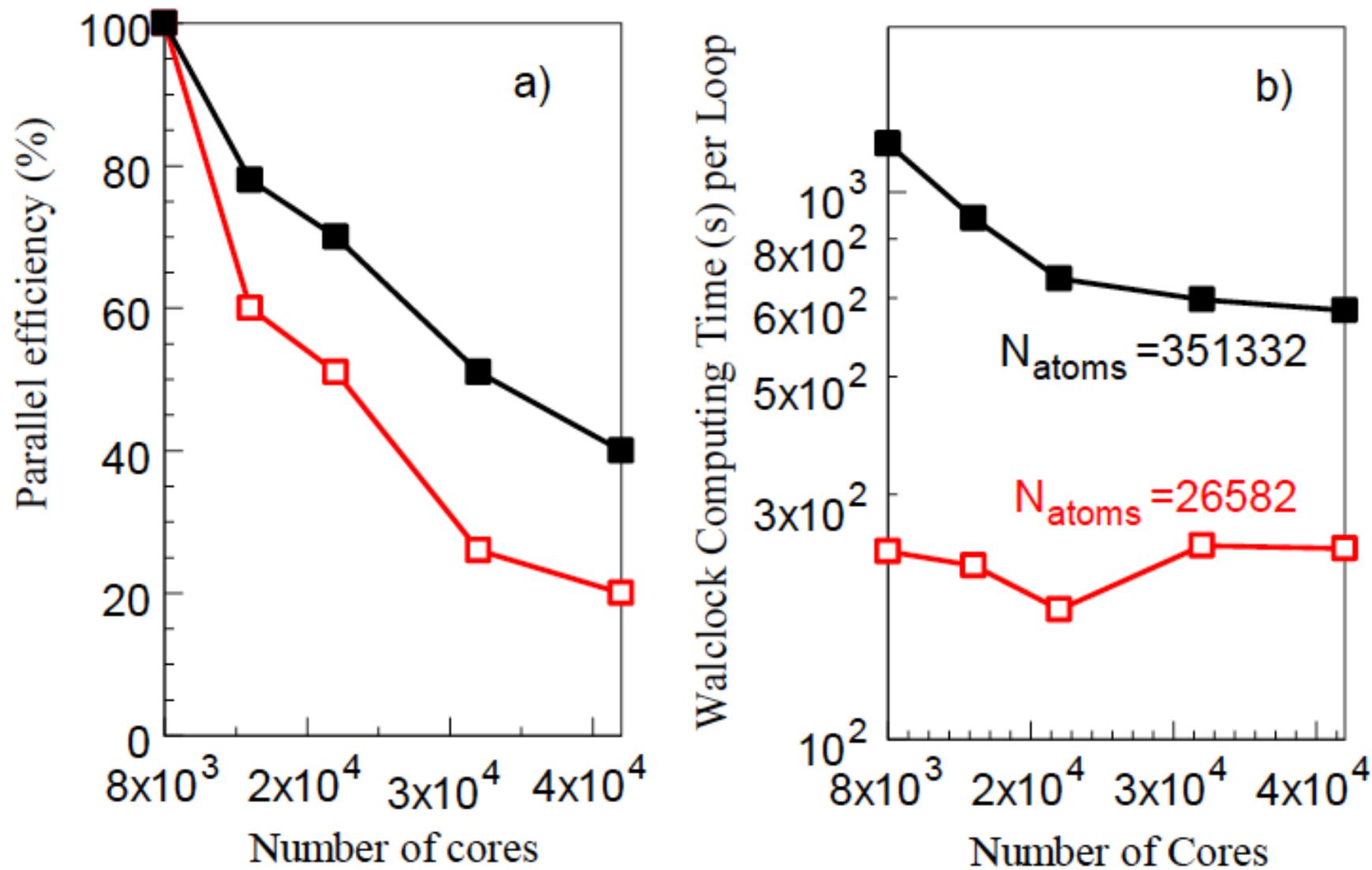
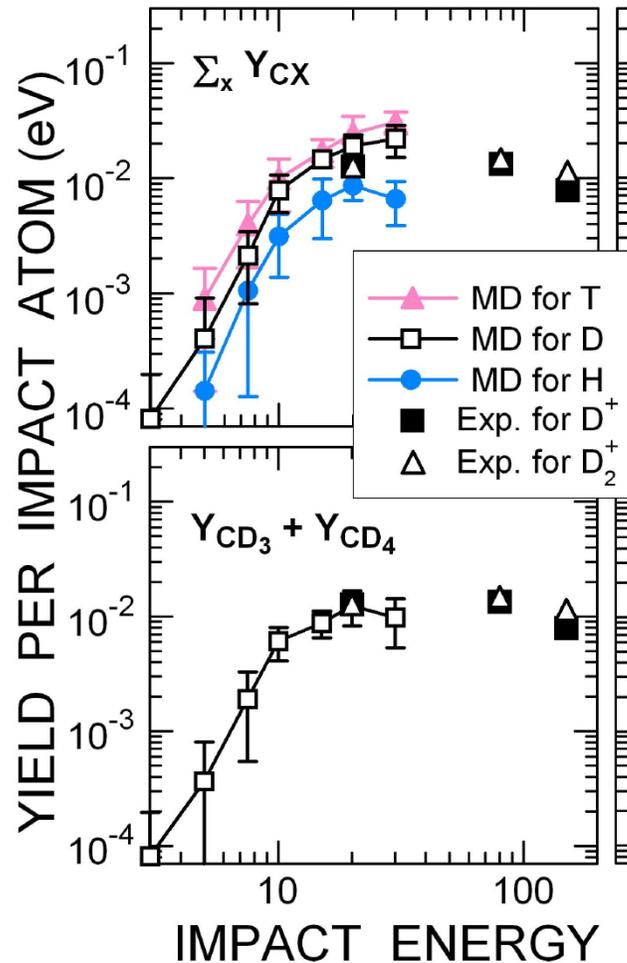


Fig. 1 Parallel efficiency normalized to 8000 cores (100%) and wall-clock time for one loop of 75,000 steps as a function of number of cores, for two different sizes of the computation cell.

EXAMPLES of (SUCCESFUL) use of CMD

Examples of the successes : Hydrocarbons



Remarkable agreement of theory & beam exp't when simulation prepare the sample at the level of nanoscale (fluence) to mimic exp't. No fitting parameters!

CARBON

Meyer et al, PS T128, 50 (2007).

Chemical sputtering of carbon

Neutron-caused defects simulated by effects of *W* self-atom (ion in exp.) damage

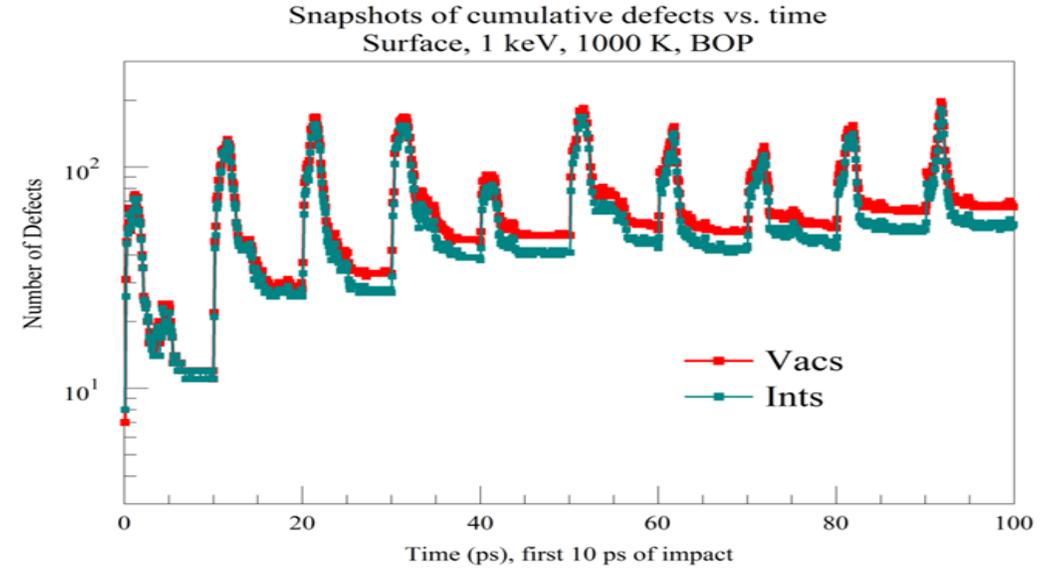
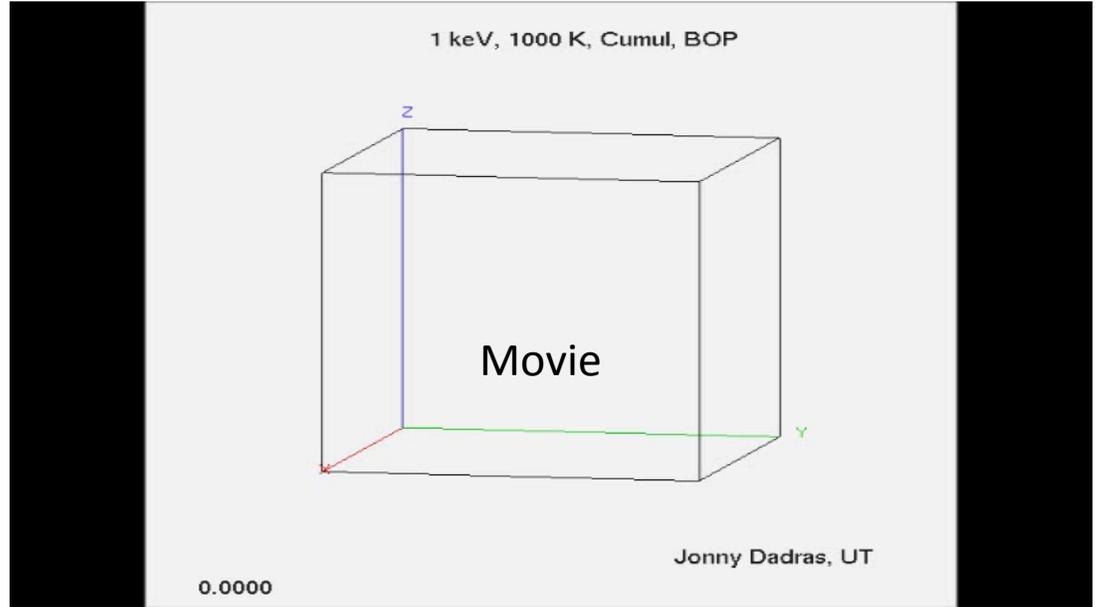
One way to study impact of 14 MeV neutrons and other light energetic particles

$$\frac{4M_1M_2}{(M_1 + M_2)^2} E_{k0}$$

- Virgin *W* has very low density of intrinsic defect sites at which to trap He
- 30 keV *W* ion exposure creates extrinsic near-surface defects that should facilitate He trapping during subsequent He ion exposures, perhaps even amorphize surface, and/or accelerate fuzz growth, but effect is small

Exp::

Why so small effects?

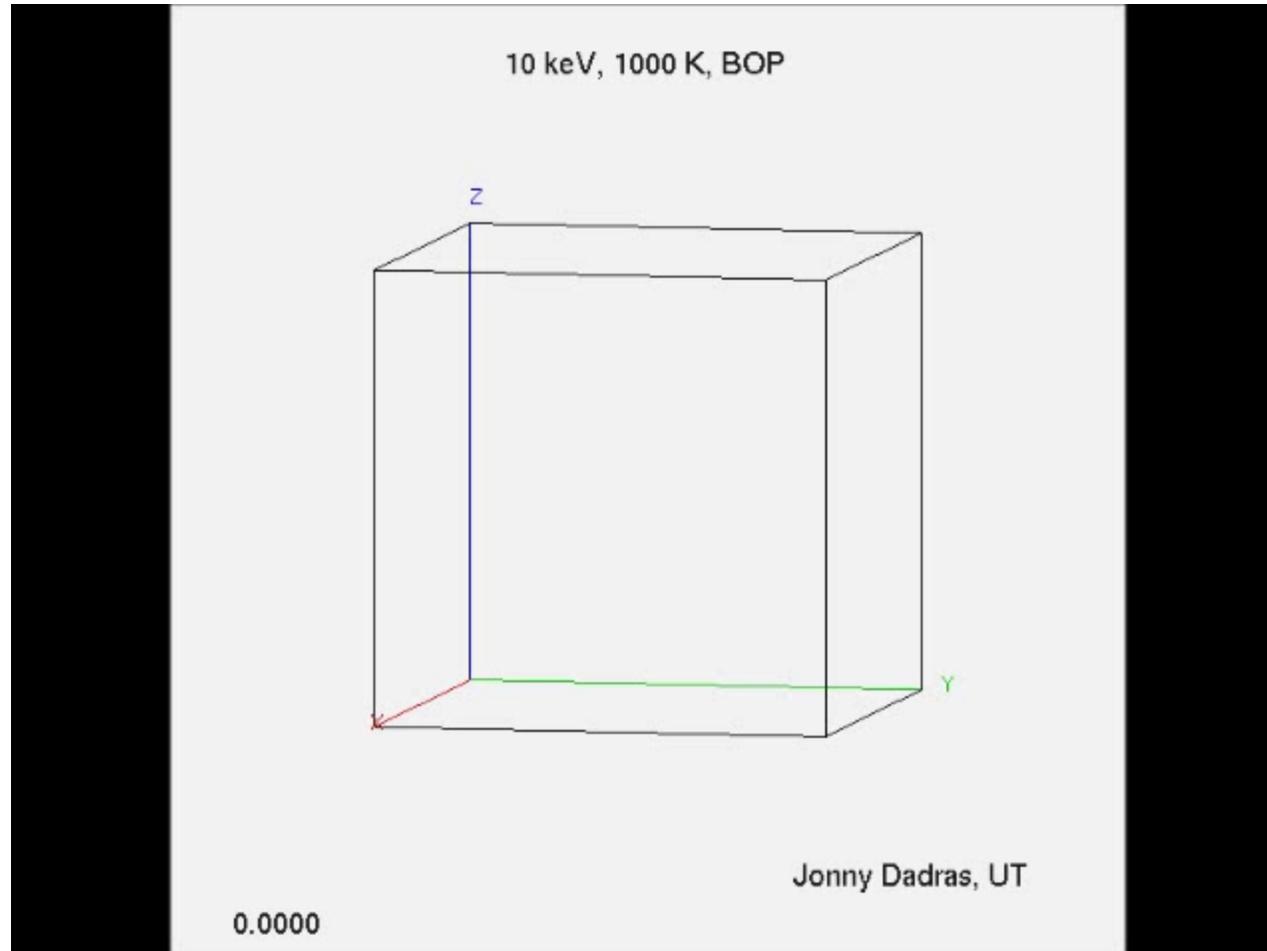


Strong recombination of Frenkel pairs

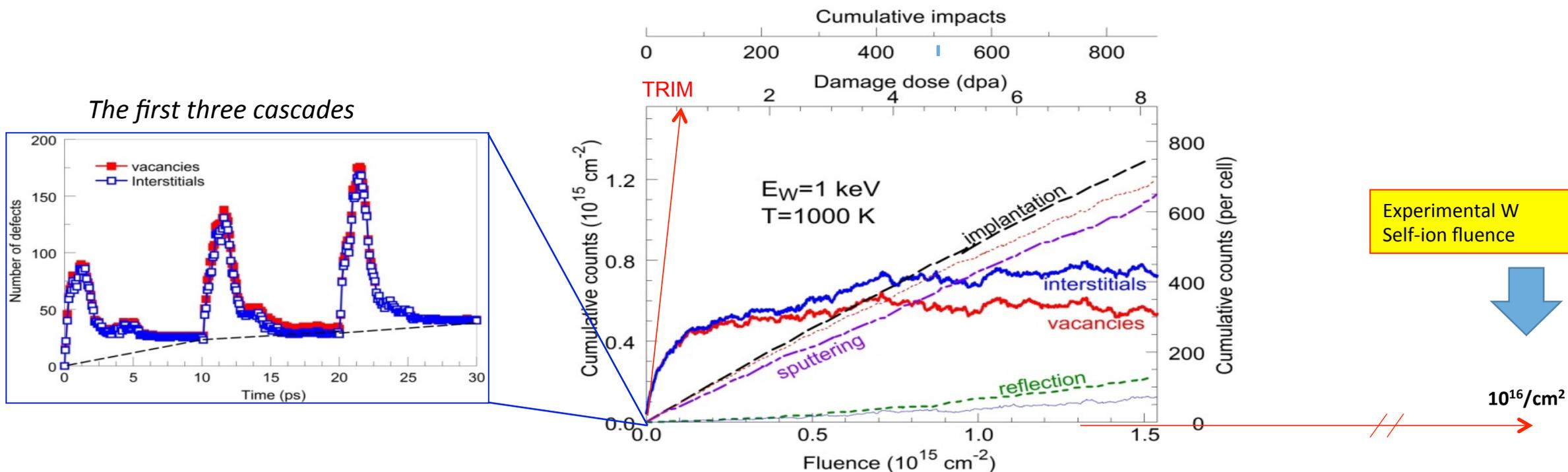
Evolution of Defects in a Tungsten Surface by Cumulative Bombardment with Self-Atoms: **Classical MD is here a good tool !!! We choose LAMMPS and BOP**

Krstic

TUNGSTEN DEFECT RECOMBINATION



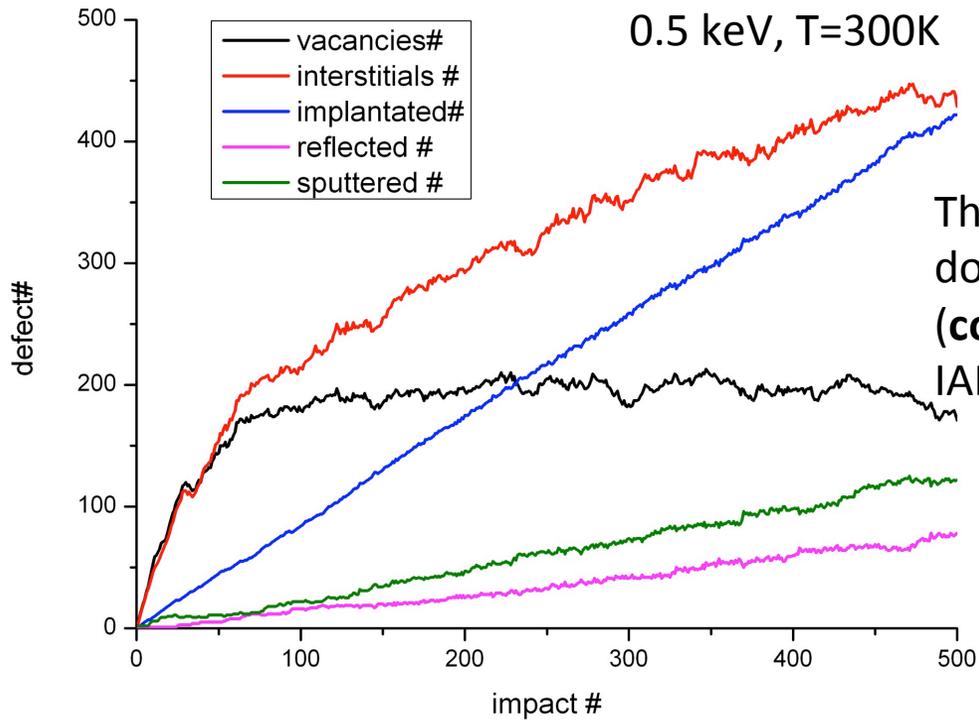
MD simulation of self-atom damage 1 keV



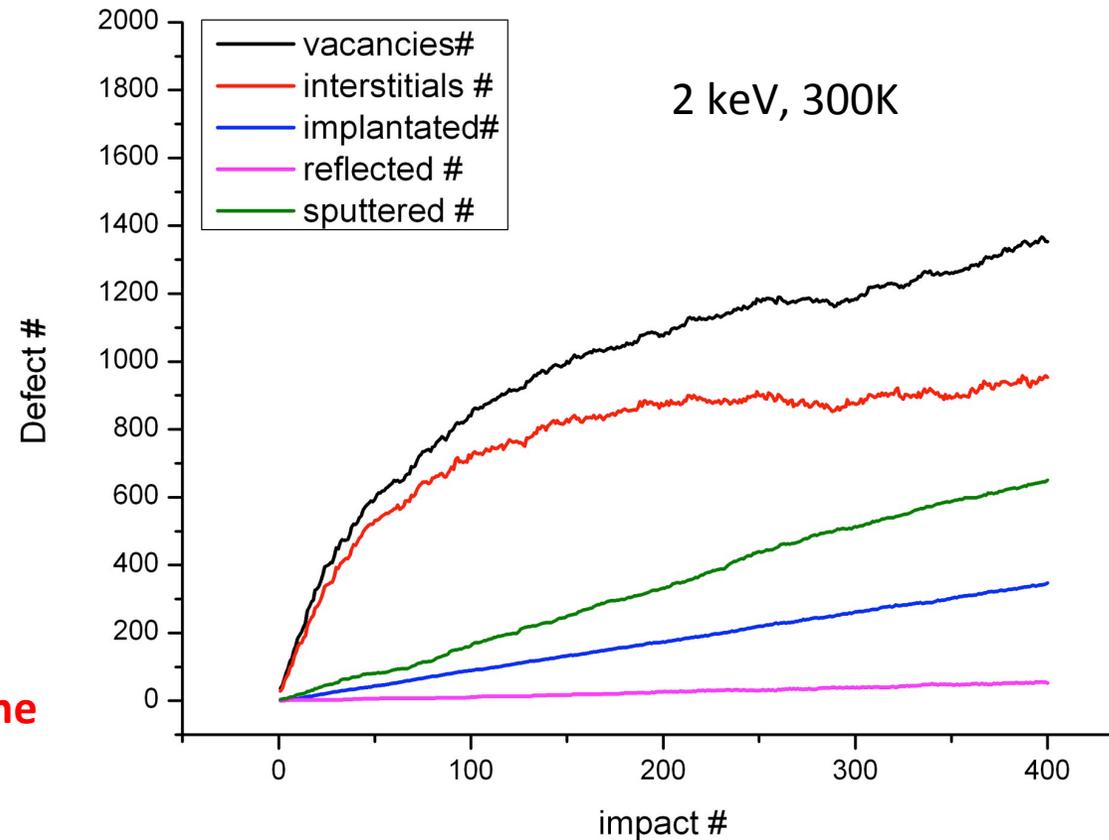
Molecular dynamics results of damage accumulation for consecutive W impacts:

- Unlike TRIM, accumulated damage is not linear with dose (# of impacts)
- In fact, accumulated damage saturates at much smaller doses than applied in expt.
- Evidence for spontaneous recombination of Frenkel pairs inside critical distance

Recent experiments on deuterium retention in pre-damaged W by self-ions show saturation about 1 dpa!!!

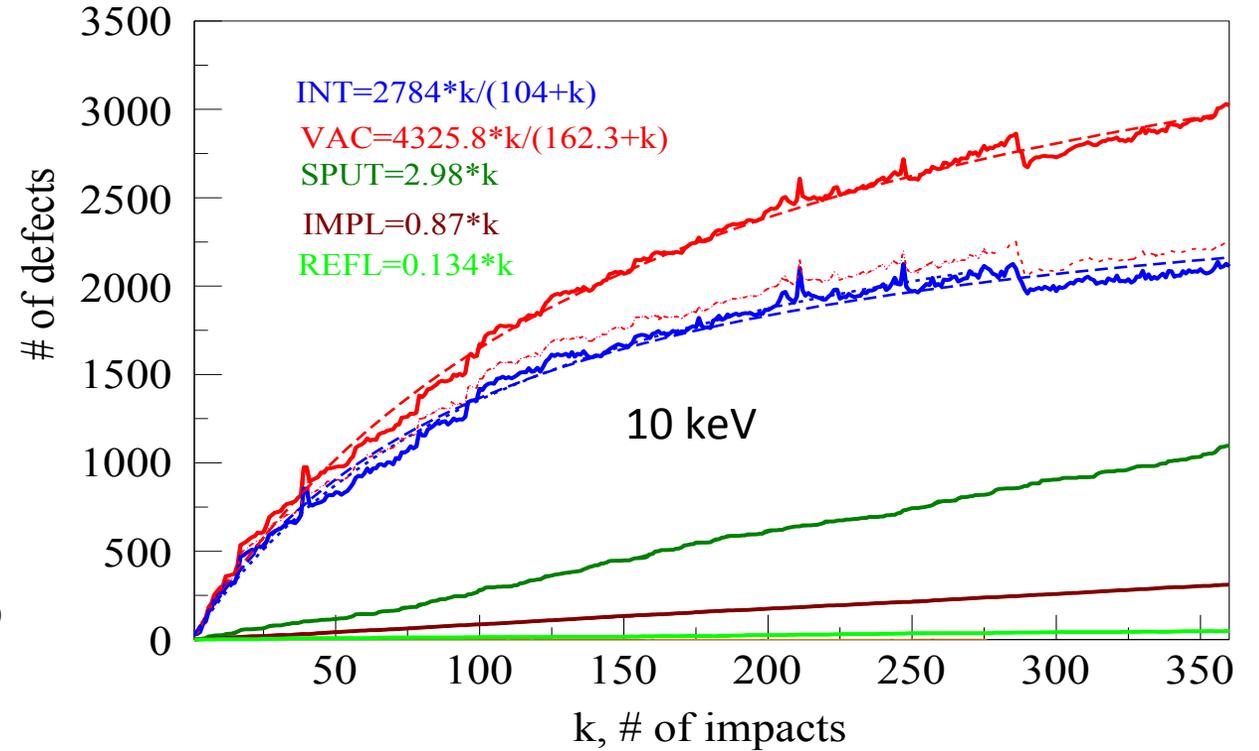
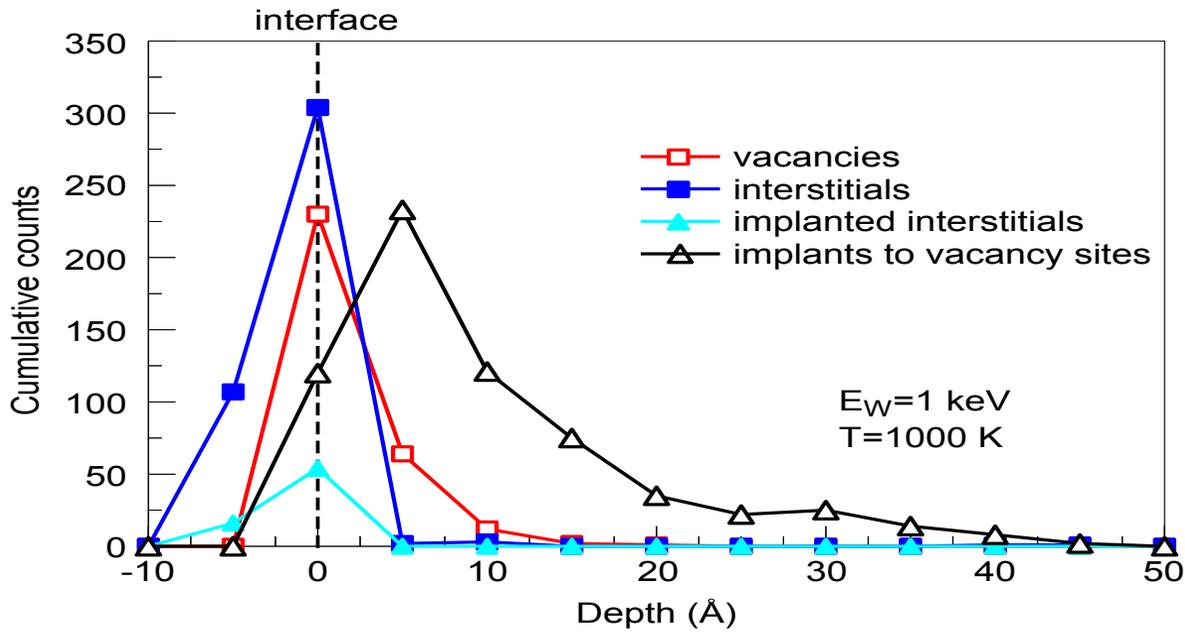


The calculations of self-damage in tungsten done in range 250 eV -10 keV (collaboration with Yong Wu, IAPCM, Fu Yong Zhao (2014) IAPCM, Beijing)



- **For impact energies < 2 keV implantation dominates over sputtering:**
 - Interstitials dominates vacancies
- **At higher energies the trend inverts**
- At large fluences:
 - **The dominant defect linearly increases with increase of the dominant one of the Implanted and sputtered;**
 - **Sub-dominant defects saturates into a constant**

Significant fraction of “defects” located in surface layer, and
 •contribute to surface roughening, rather than creating He trap sites.

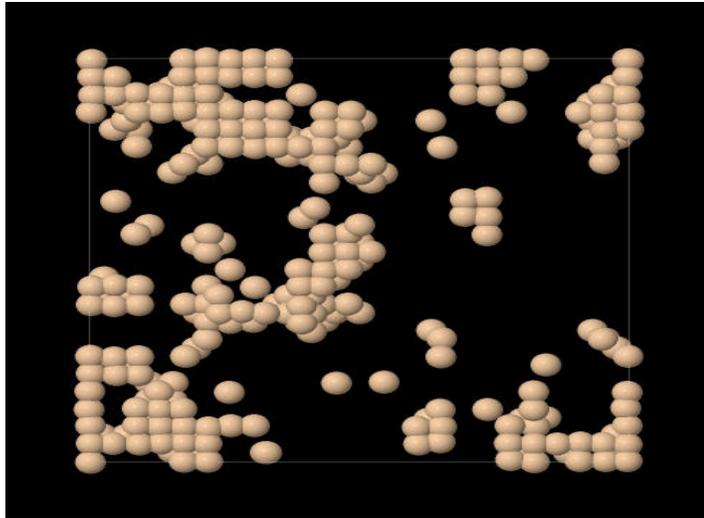
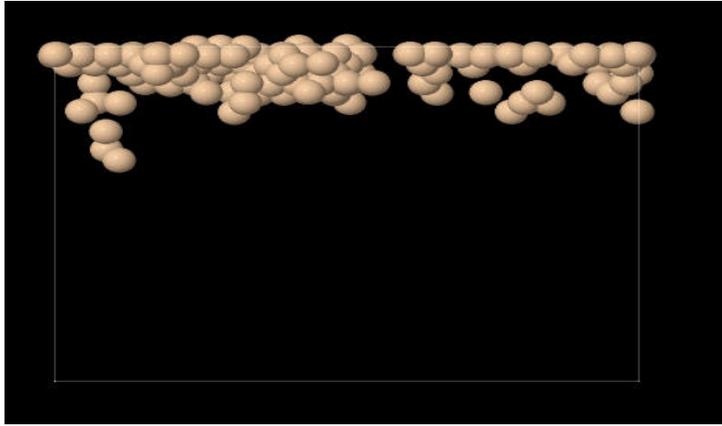


E (keV)	Spurt. yield	Implant. Yield	Reflect. probability
1	0.73	0.85	0.14
10	2.98	0.87	0.13

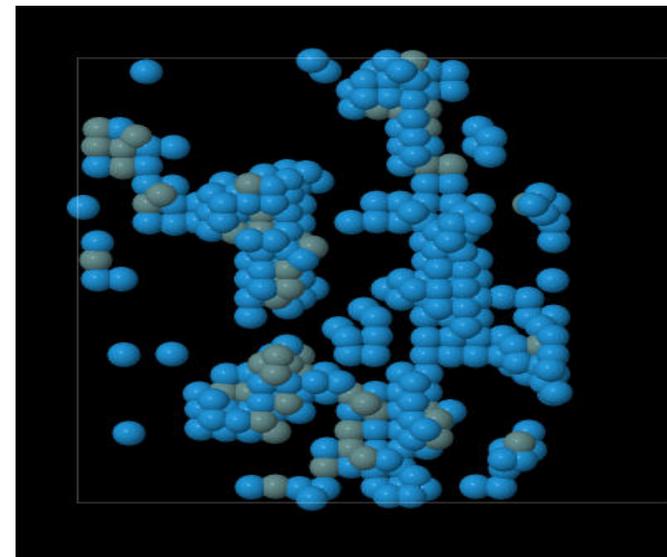
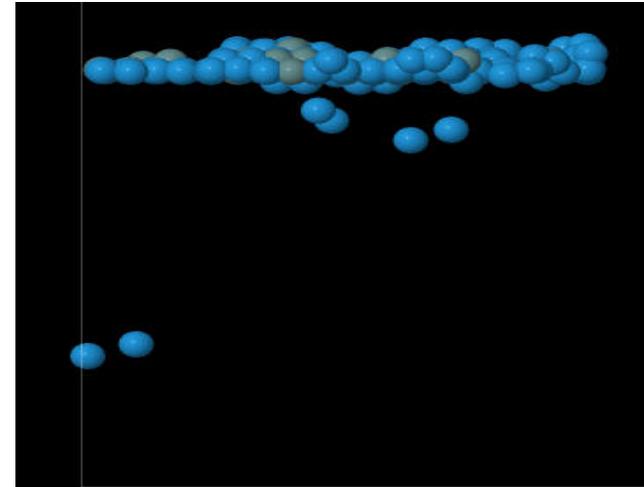
Defect clustering (1 kev, !000K)

After 888 impacts of W

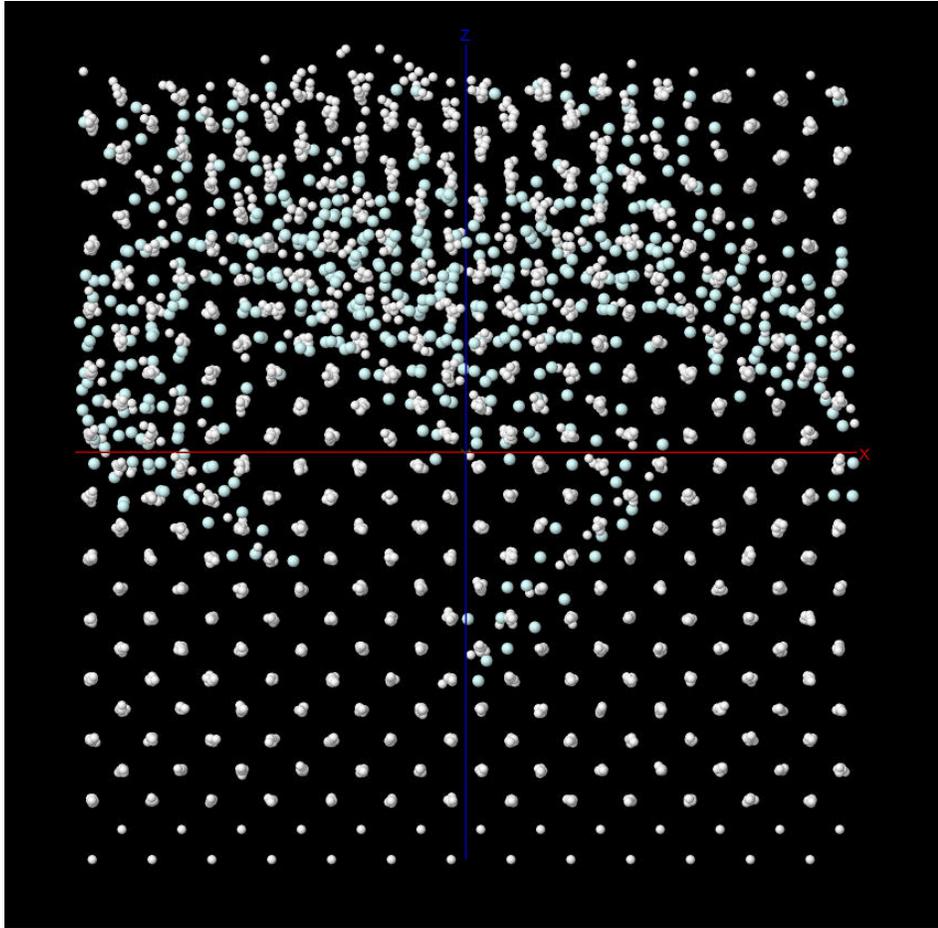
Vacancies



Interstitials



DIFUSION of D in Tungsten



Previously bombarded tungsten cell (~4400 W atoms) with 25 eV D impact: about 500 retained D atoms;

The atoms in the cell thermostated to various temperatures in the range 500K-2500K and relaxed

In order to calculate diffusion of deuterium in W we use the expression which relates macroscopic transport coefficient D with microscopic information on the mean square distance of atom migration

We apply MD with LAMMPS:

Mobility of atoms in MD is described by the means square displacement

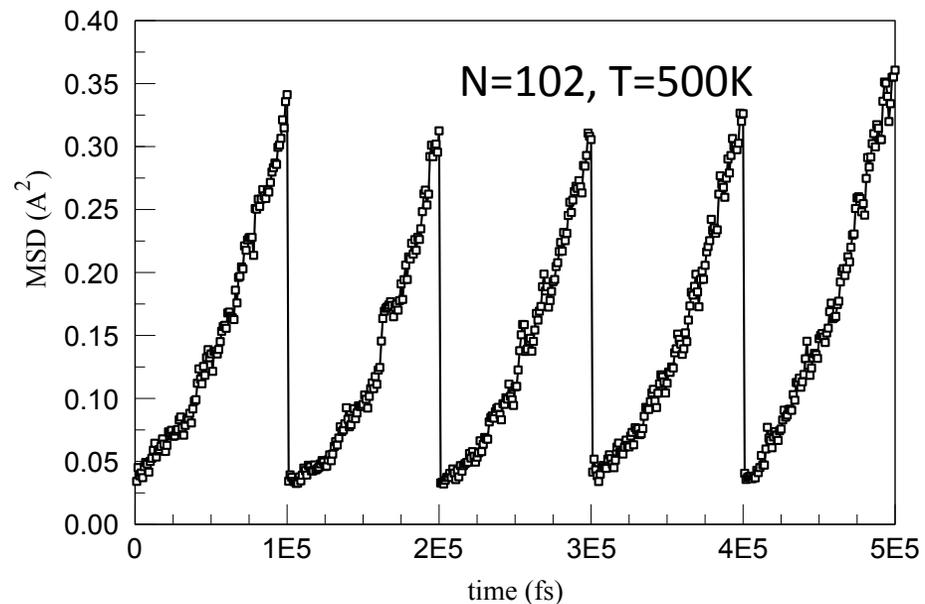
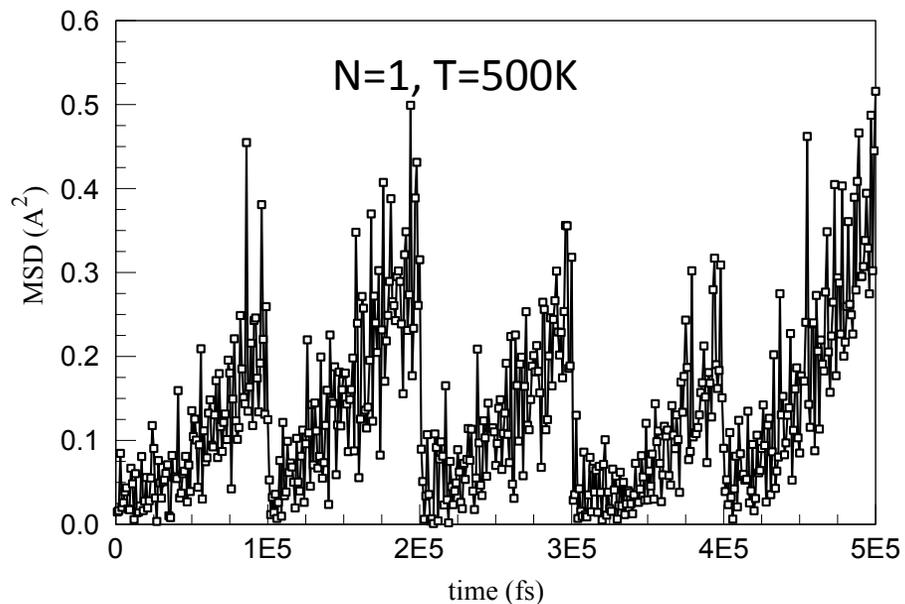
$$MSD = \langle \Delta \vec{r}(t)^2 \rangle = \frac{1}{N} \sum_{i=1}^N (\vec{r}_i(t) - \vec{r}_i(0))^2$$

MSD contains information on diffusion coefficient D through Einstein Relation

$$MSD = \langle \Delta \vec{r}(t)^2 \rangle = A + 2n_d Dt + \text{fluctuations}$$

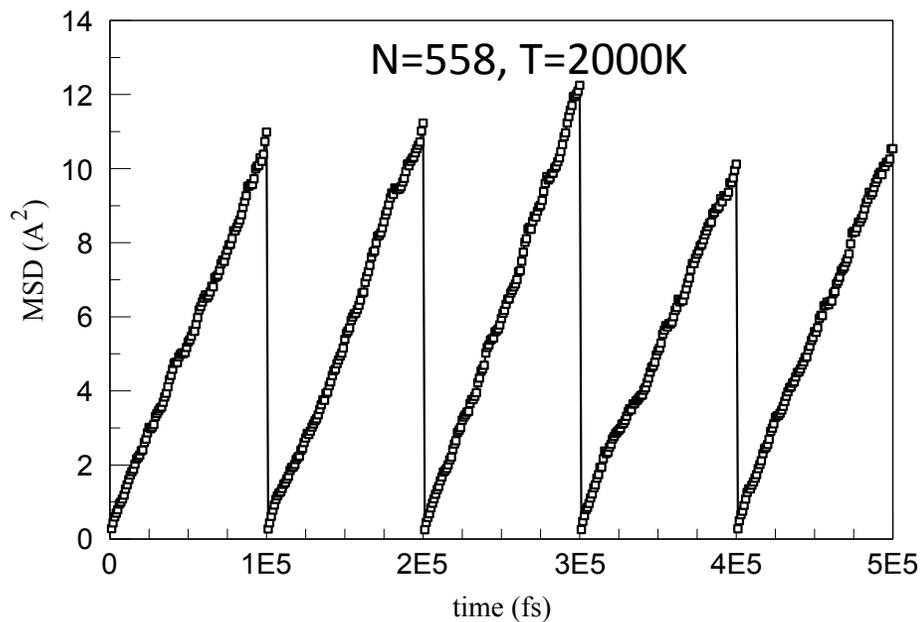
n_d Is the number of dimensions

For long time, the slope of the MSD vs time is proportional to the diffusion coefficient D

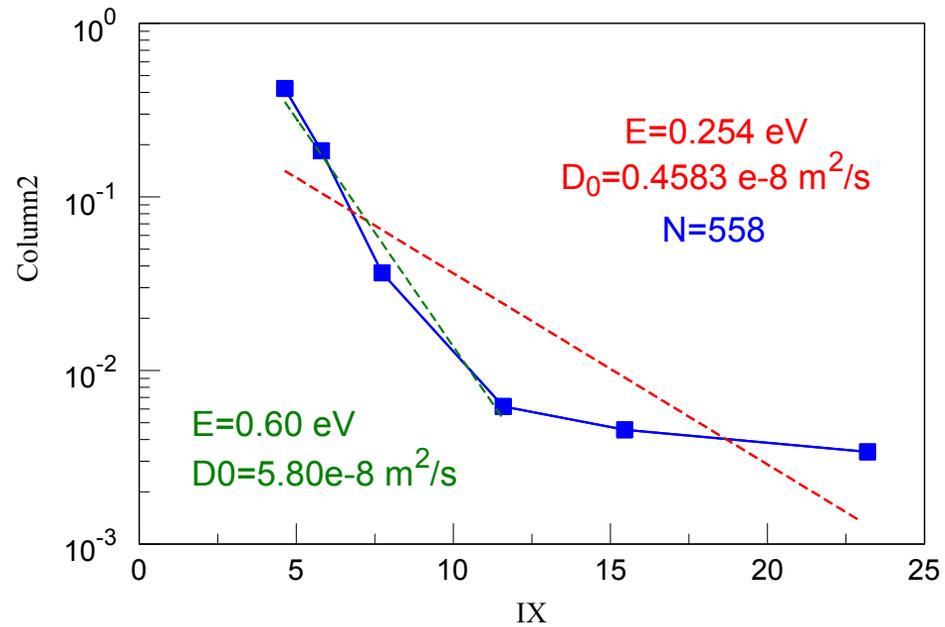
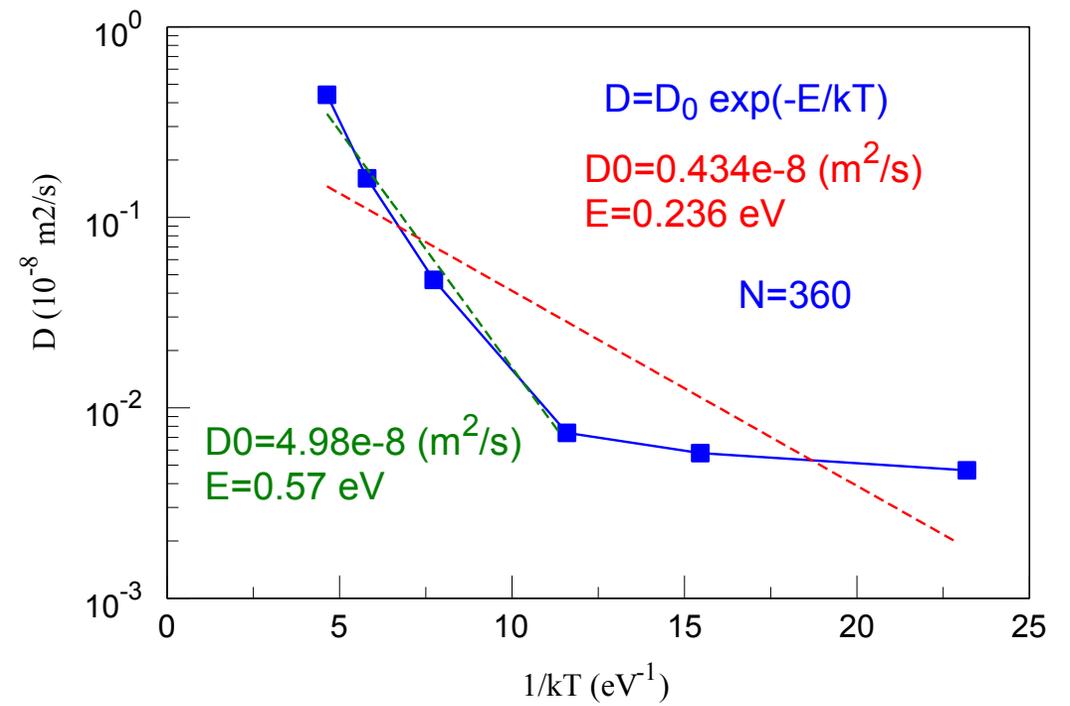
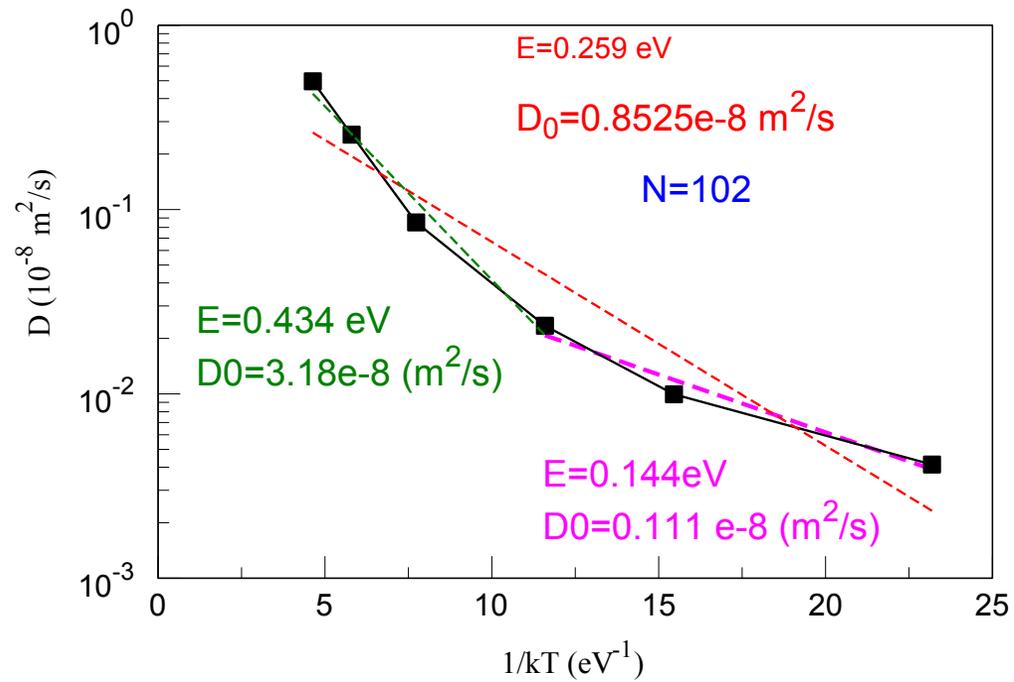


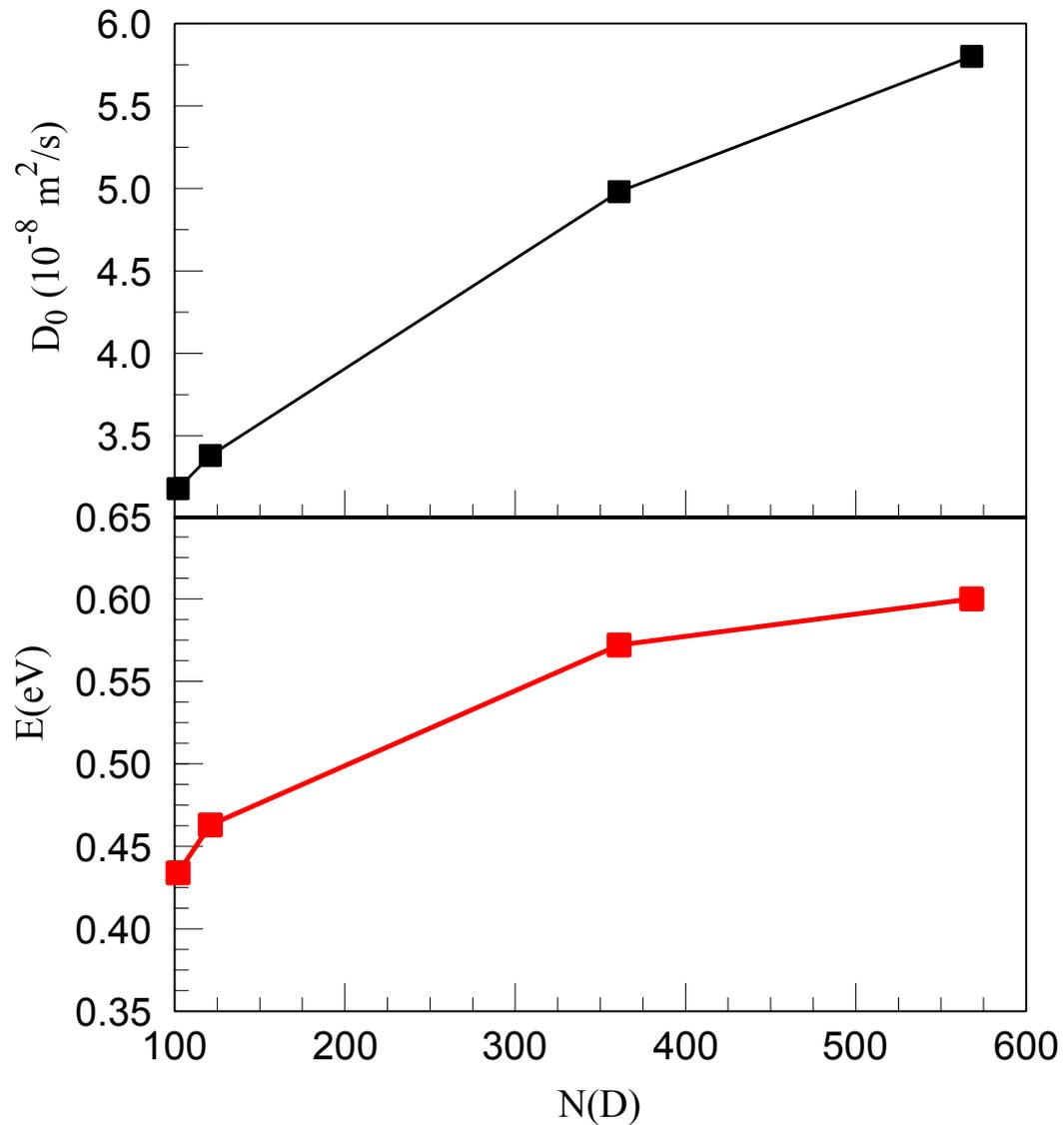
In principle it is enough 1 D atom for calculating diffusion coefficient, but the fluctuations are too high.

Averaging MSD over 100 atoms significantly pacifies fluctuations;

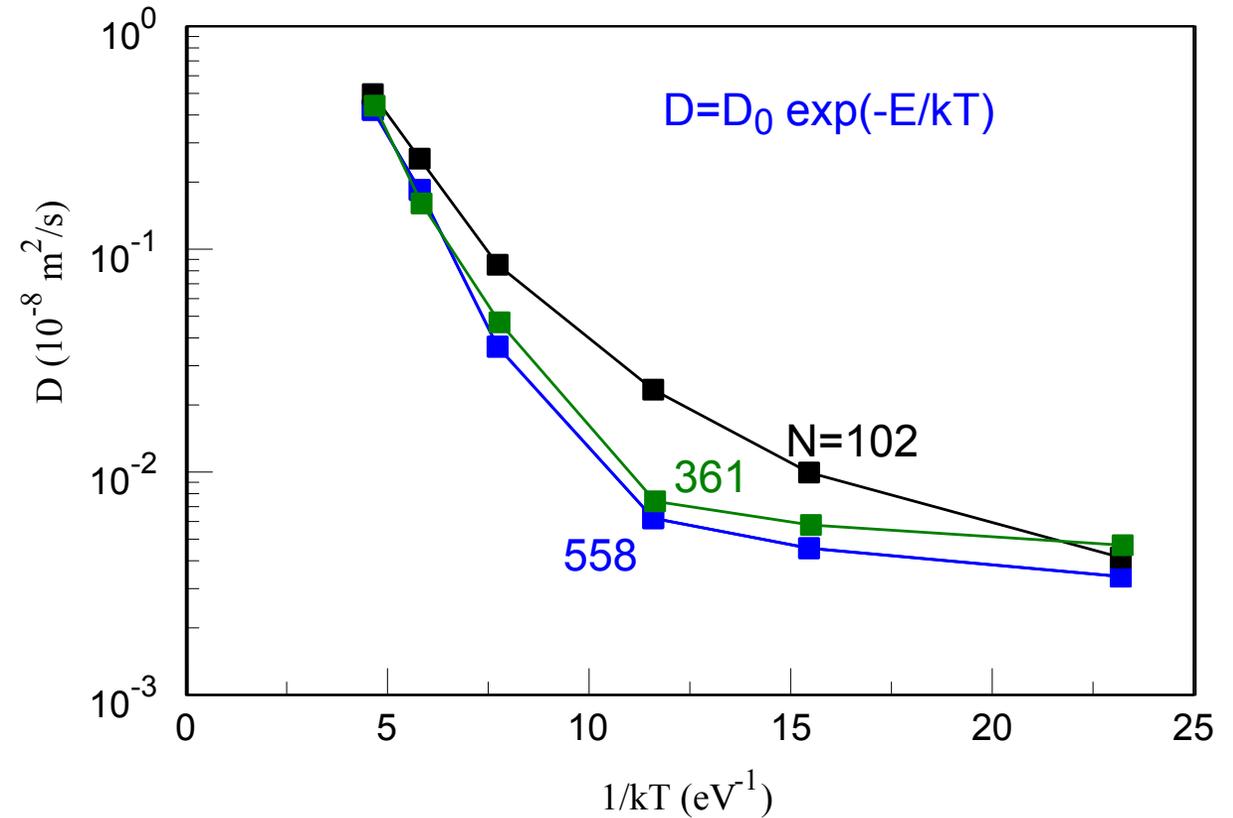


Results improved at higher temperatures due to the faster diffusion and by choosing various initial times and then averaging

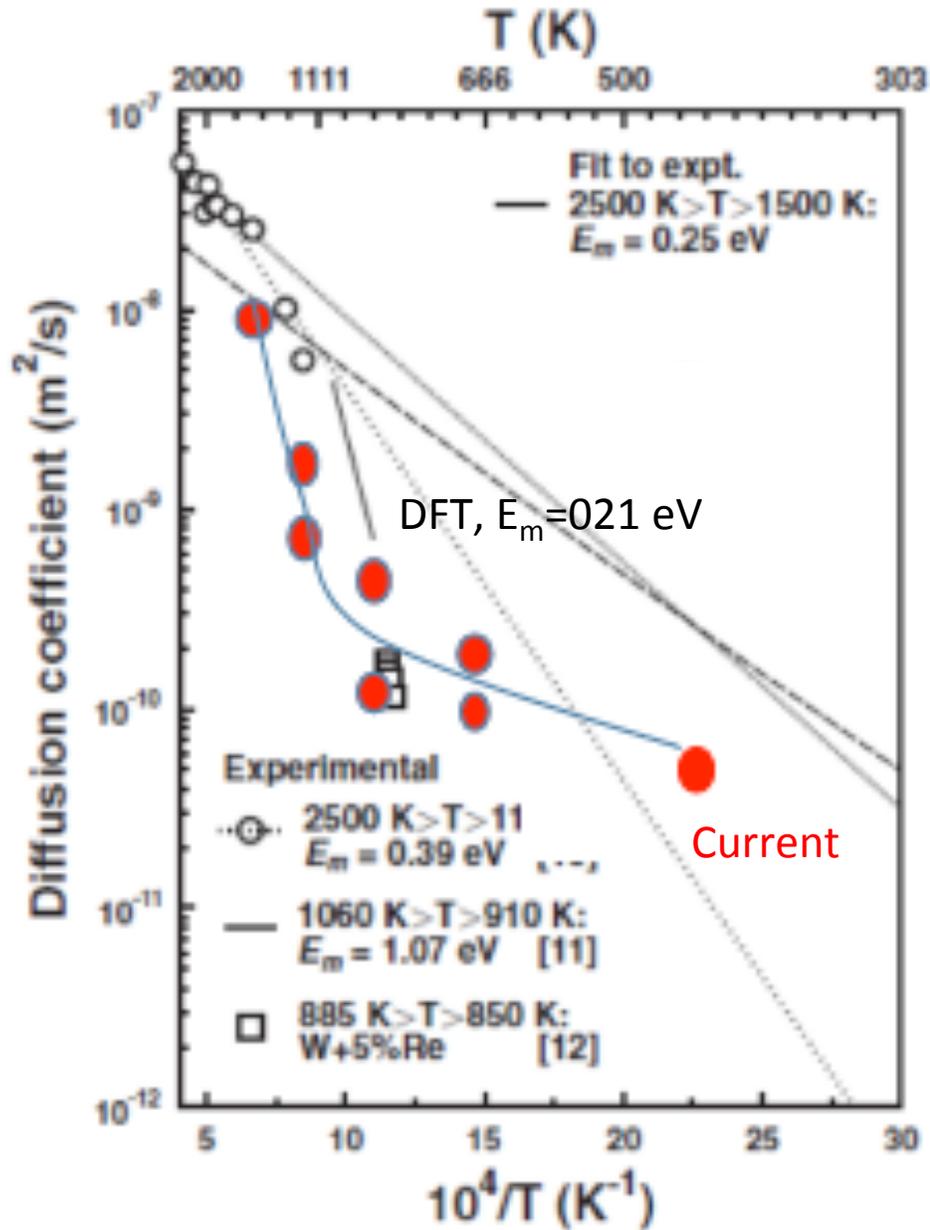




Both E and D_0 are increasing with deuterium density
 Exponent increase expresses stronger D-D than D-W interaction.

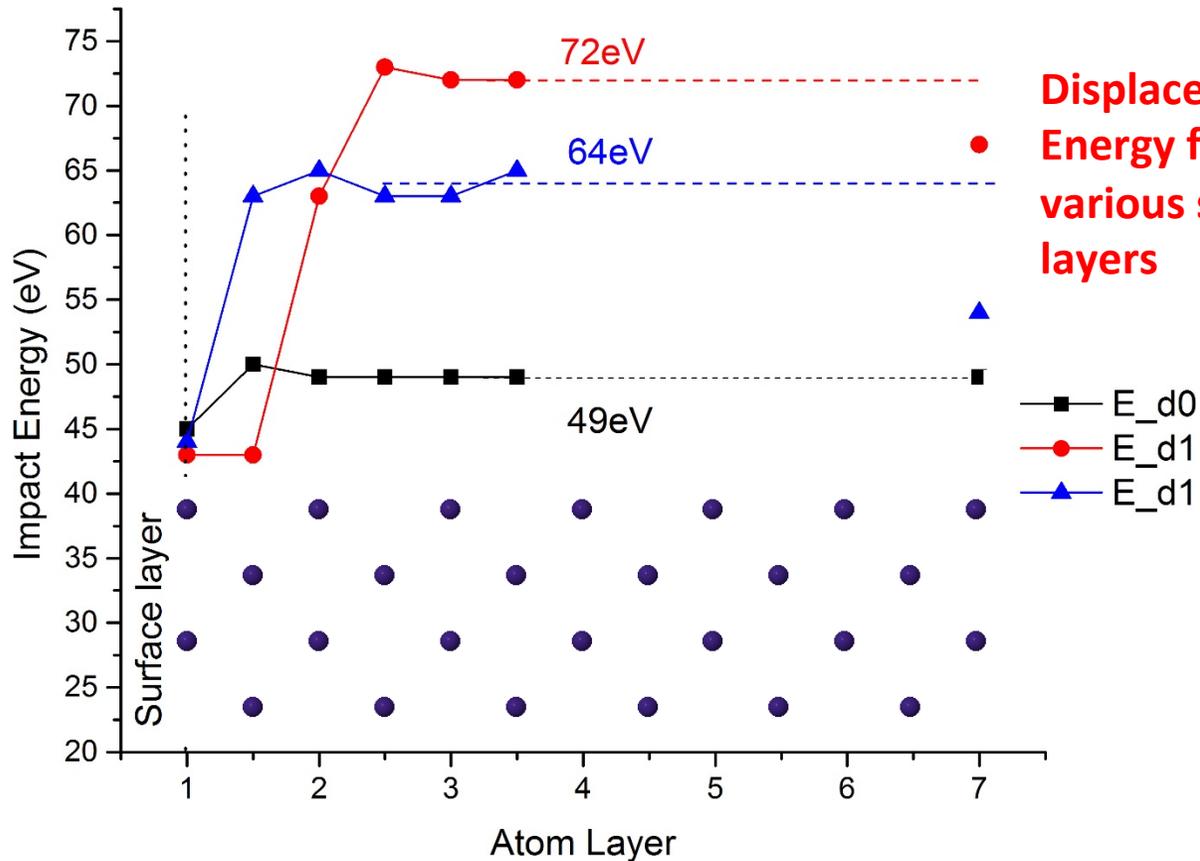


Still, diffusion is reduced with increase of density,
 Due to the faster change of the exponential
 than prefactor.



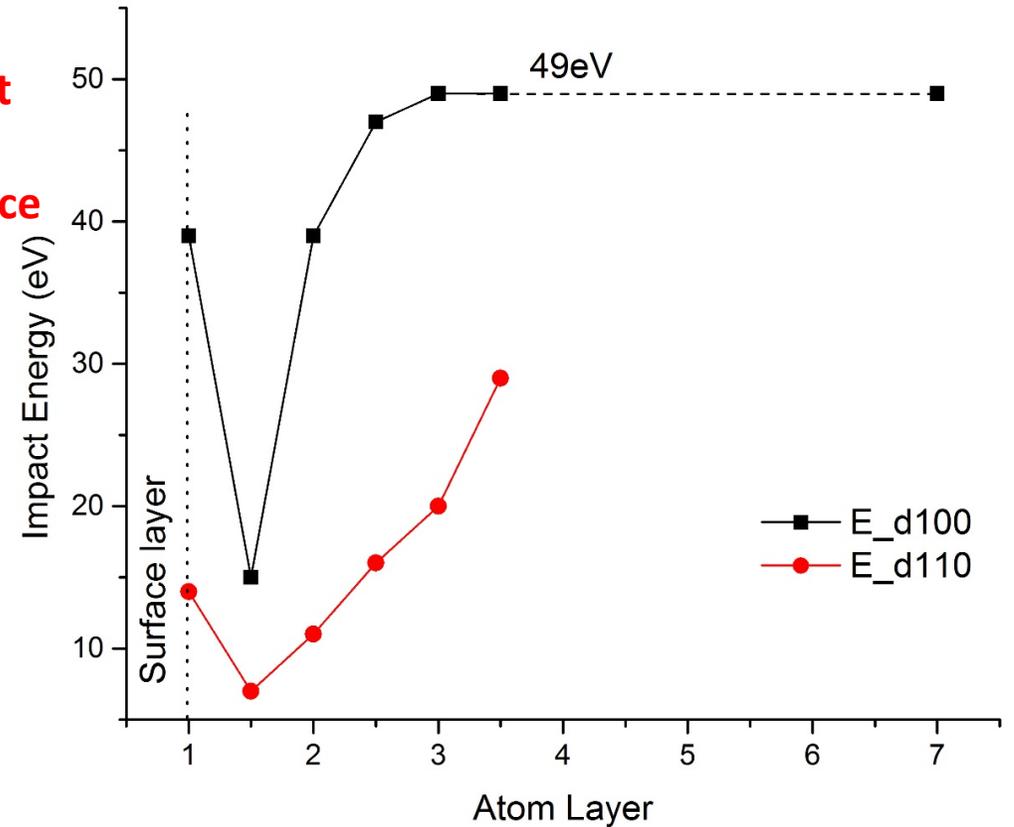
Comparison of experimental data and previous simulations with the the new MD simulations Experimental references (from up to down): R. Frauenfelder, J. Vac. Sci. Technol. **6**, 388 (1969); A.P. Zakharov et al, Fiz.-Khim. Mekh. **9**, 29 (1973); G. Benamati et al, J. Nucl. Mater. 283-287, 1033 (2000). DFT calculations Heinola JAP 107, 113531

Energy for stable defects formation



Impact energy needed to form stable defects in the crystal. X axis represents the original position of impinging atom. Black, red and blue line represents the energy profile for impact along (001), (101) and (111) direction, respectively. Dashed lines represent extrapolated energy value, ideally for impact on bulk atoms.

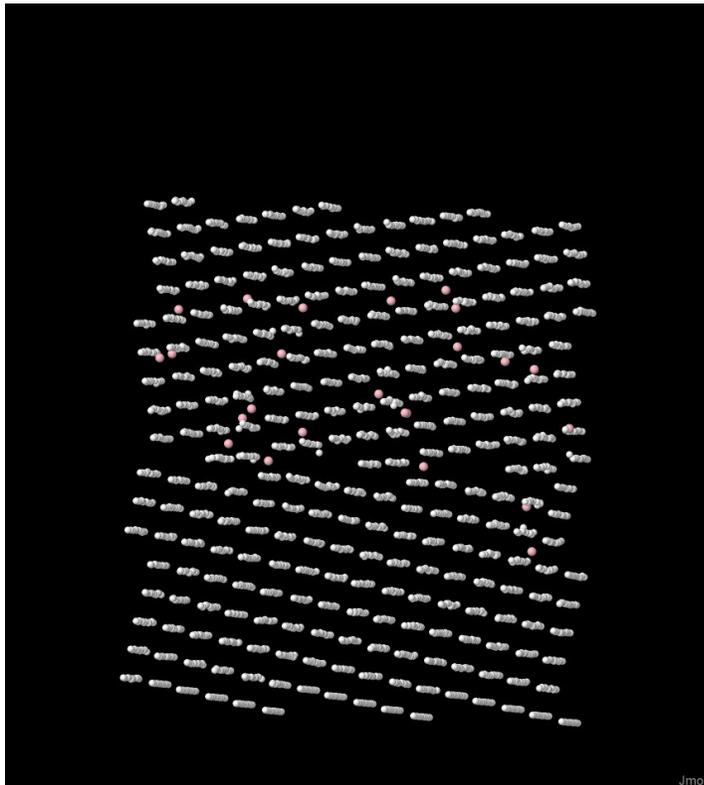
Energy for stable defects formation



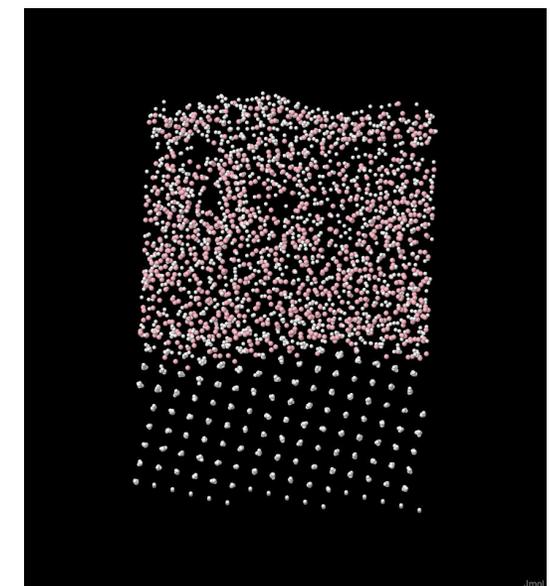
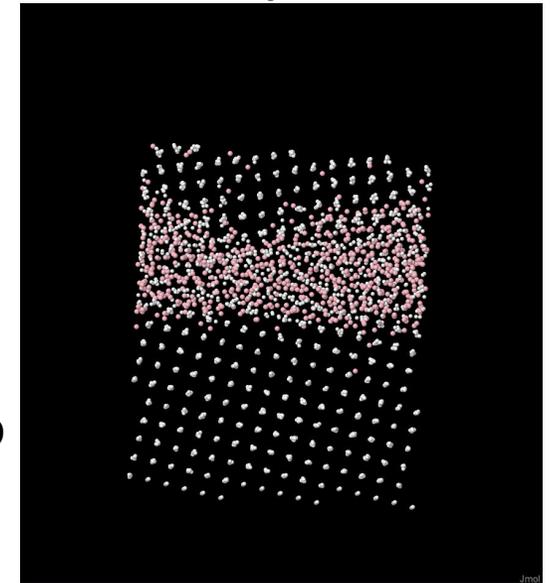
Impact energy needed to form stable defects in the crystal. X axis represents the original position of impinging atom. Black and red line represents the energy profile for impact along (100) and (110) direction, respectively. Dashed lines represent extrapolated energy value, ideally for impact on bulk atoms. No stable defects observed for inner atom layers for whatever high impact energy, because the recombination of defects by diffusion (rotation mechanism) always takes effect.

Possible to control surface diffusion by tungsten morphology

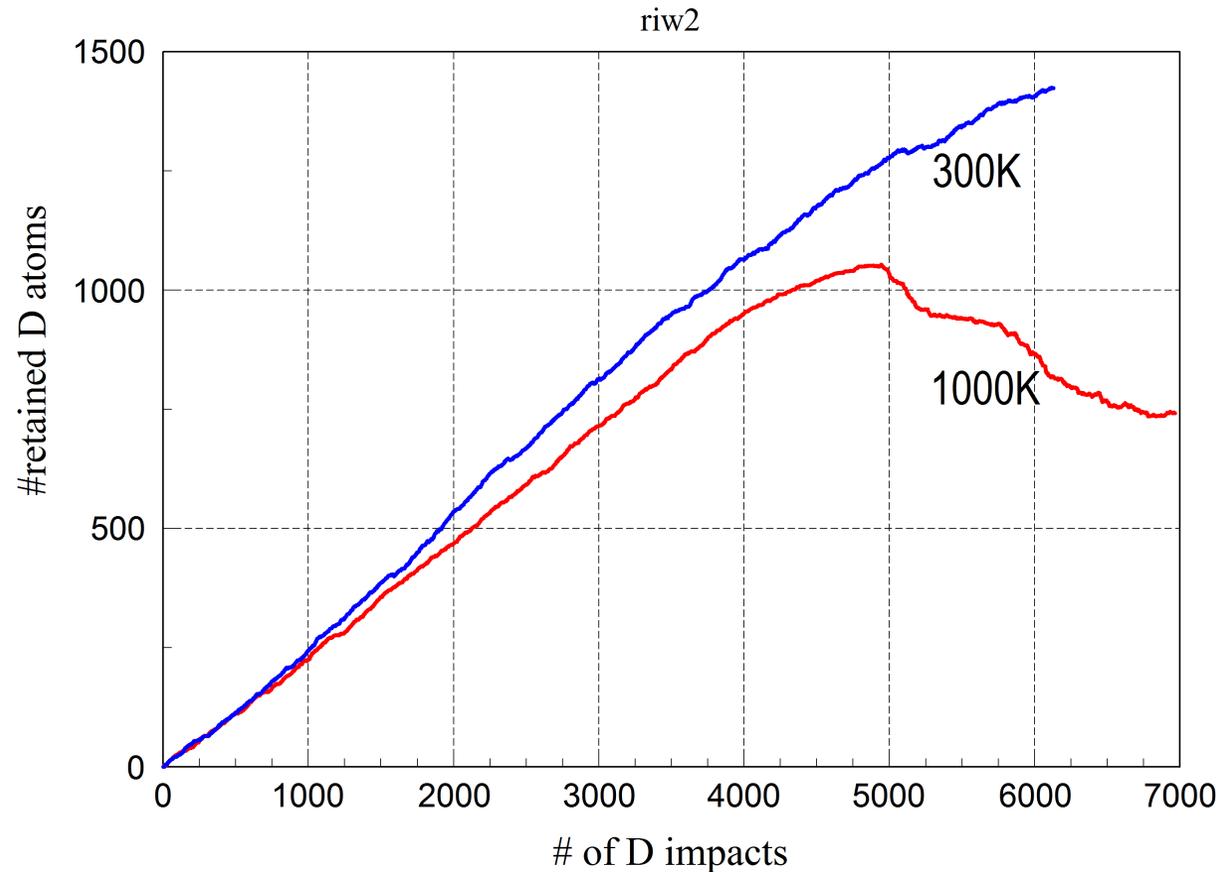
- Examples: Two nano- film layers, nanograins,...



The nano-boundary 3000 D
Slows down the diffusion
If in the direction
Orthogonal to impact
The upper layer filled
with D, further filling 5500D
amorphizes W



THE SATURATED UPPER MAY START DEGASING AND PREVENT FURTHER D INPUT



Stimulated high-T diffusion
Can help to see this effect
At the MD scale of time

Conclusions

- The plasma-material interface has a big effect on the plasma performance, and we don't understand why! The answers can be found in the plasma-PMI integration science.
- The main weight in the science of integration of fusion plasma and its interfacial surface boundaries is carried by PMI because 1) the basic PMI phenomenology evolves much faster than the plasma time scale, and 2) it evolves through wider range of the scales, which partially overlap with the scale of plasmas. The PMI has to be understood and parameterized at nanoscale before integrating it with plasma at the “same footing” at micro-scale.
- Bringing together the various scales of PMI and plasma is the fundamental multidisciplinary question, covering plasma science, surface science, atomic physics, computer science and applied mathematics.
- We are now capable to do this integration by combining nano, meso and continuum scales: Computer resources, computer codes, knowledge “how-to” and quality manpower are available.
- Quality validation of the simulations is the key for the “right track”. Mimicking the experiments by simulation is the key for the successful validation. High quality experiments, well suited for the purpose do exist.
- **Need systematic improvement of understanding of PMI processes in order to reduce epistemic uncertainties. Only then we will be able to apply the apparatus of aleatoric uncertainties in order to have a controlled UQ for the PMI processes.**