Max-Planck-Institut
für Plasmaphysik

Influence of deuterium on damage in tungsten

Udo v. Toussaint
With Input from M. Zibrov, T.Schwarz-Selinger, L. Gao, J. Dominguez, ...

MAX PLANCK
GESELLSCHAFT

Outline

- Motivation
- Direct Simulation of WH with Artificial Dynamics Approach
- Self-damaging (super-threshold) : MD and KMC-Simulations
- DSSL/HSSL (sub-threshold) : Insights from MD
- Conclusions /Outlook

Motivation

- **Influence of Hydrogen (isotopes) on defect concentration (Exp.)**

  - Strong experimental evidence of significant effects of hydrogen on material
    - Repeated irradiation of H-loaded tungsten increases H-retention (T. Schwarz-Selinger et al [1])
    - Sequential loading increases vacancy concentration (indicated by TDS) (M. Pecovnik et al [2])
    - Formation of *stable* H-supersaturated W-layer at subthreshold energies (L. Gao et al [3])
    - C.f. presentations of T. Schwarz-Selinger, L. Gao and others in this workshop
  - Understanding important
    - Indication that relevant mechanisms may be missed
    - Prediction for DEMO conditions…
  - Atomistic modelling still lacking...

Artificial Dynamics (MD/MC)-Approach

- **Modelling: Molecular Dynamics**
  - Relevant time scales
    - Collision cascades : fs - ps
    - Diffusion times: ns - ms
    - Structural relaxation: micro-sec++
    - Molecular Dynamics simulations : sub-fs (!)

    → Direct simulation challenging

  - Approach: keep atomistic potentials, but omit time scale separation: merge with Monte Carlo approach
    - Basic sequence: **(a) Drag-and ‚drop' atoms at random; (b) relax system**(by MD)**; repeat** until equilibrium
    - Commonly used e.g. to prepare amorphous samples – typically cross-checked using some reference value
    - Result: steady-state structure f with <df/dt> = 0

Artificial Dynamics (MD/MC)-Approach

- **E.g. recent publication using this approach for defect modelling (no temperature):**

PHYSICAL REVIEW MATERIALS **4**, 023605 (2020)

Editors' Suggestion

Microscopic structure of a heavily irradiated material

P. M. Derlet[1,*] and S. L. Dudarev[2,†]

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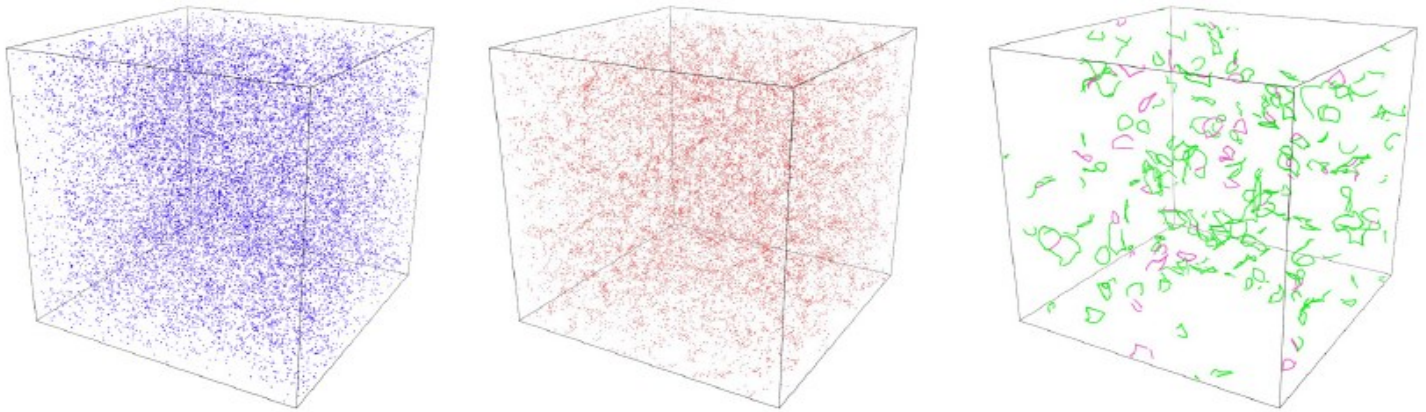
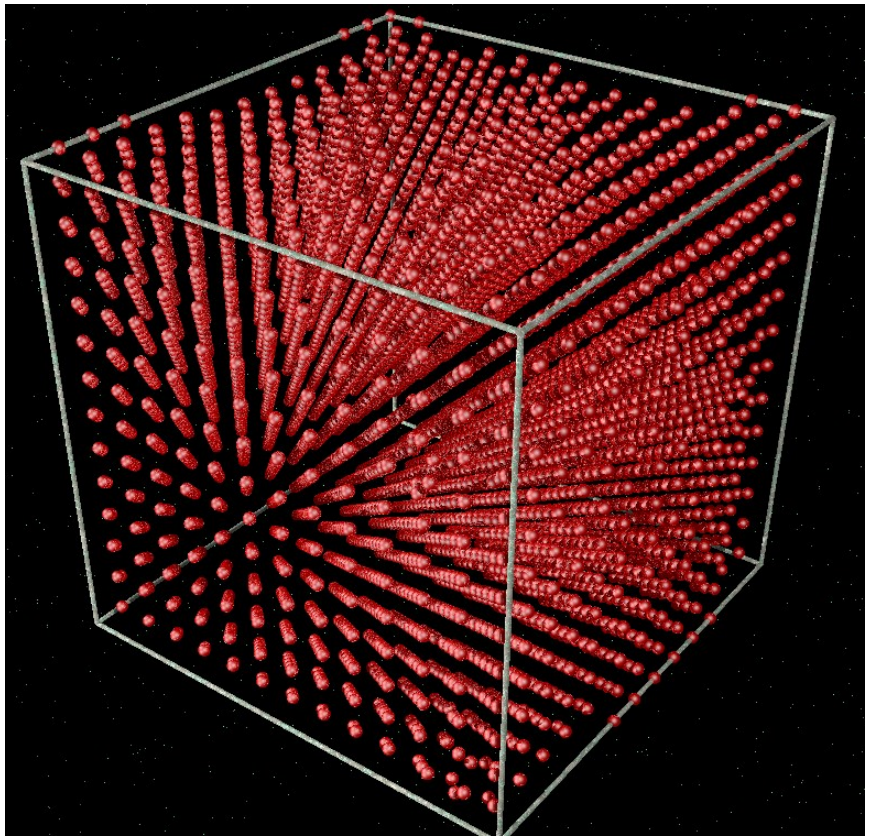
[2]*UK Atomic Energy Authority, Culham Centre for Fusion Energy, Oxfordshire OX14 3DB, United Kingdom*



- See also eg. A. Chartier [9] and further references therein
- Key difference: Relaxation using thermostated sample

System Description

- **Modelling: Apply AD-approach to W and W-H/D-systems**
  - Comparison of equilibrium structures and the fluence-dependent approach to steady-state
    - Parameters:
      - System size
      - System temperature
      - Hydrogen concentration
      - MD-potentials (i.e. Wang et al [7], Juslin et al [8])
      - Relaxation scheme
    - Main quantities of interest:
      - Energy of system as function of displacements of atoms (dpa)
      - Defect-formation
      - Defect-lifetimes
      - Defect-sizes
      - ...



W atoms in red, H in blue

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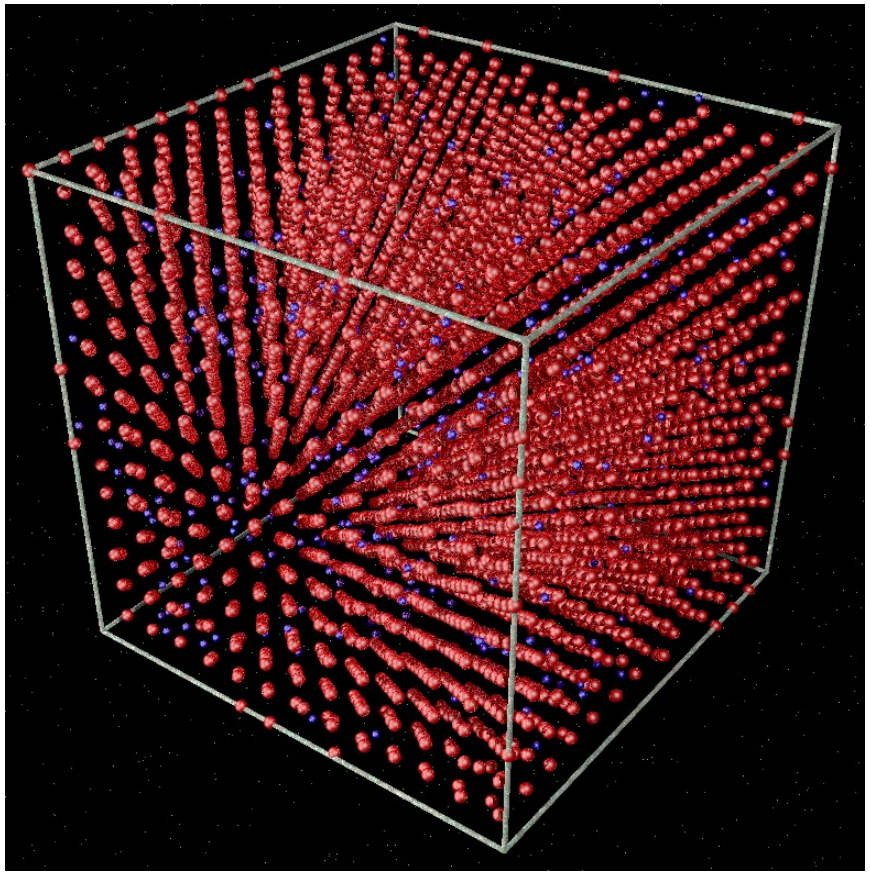
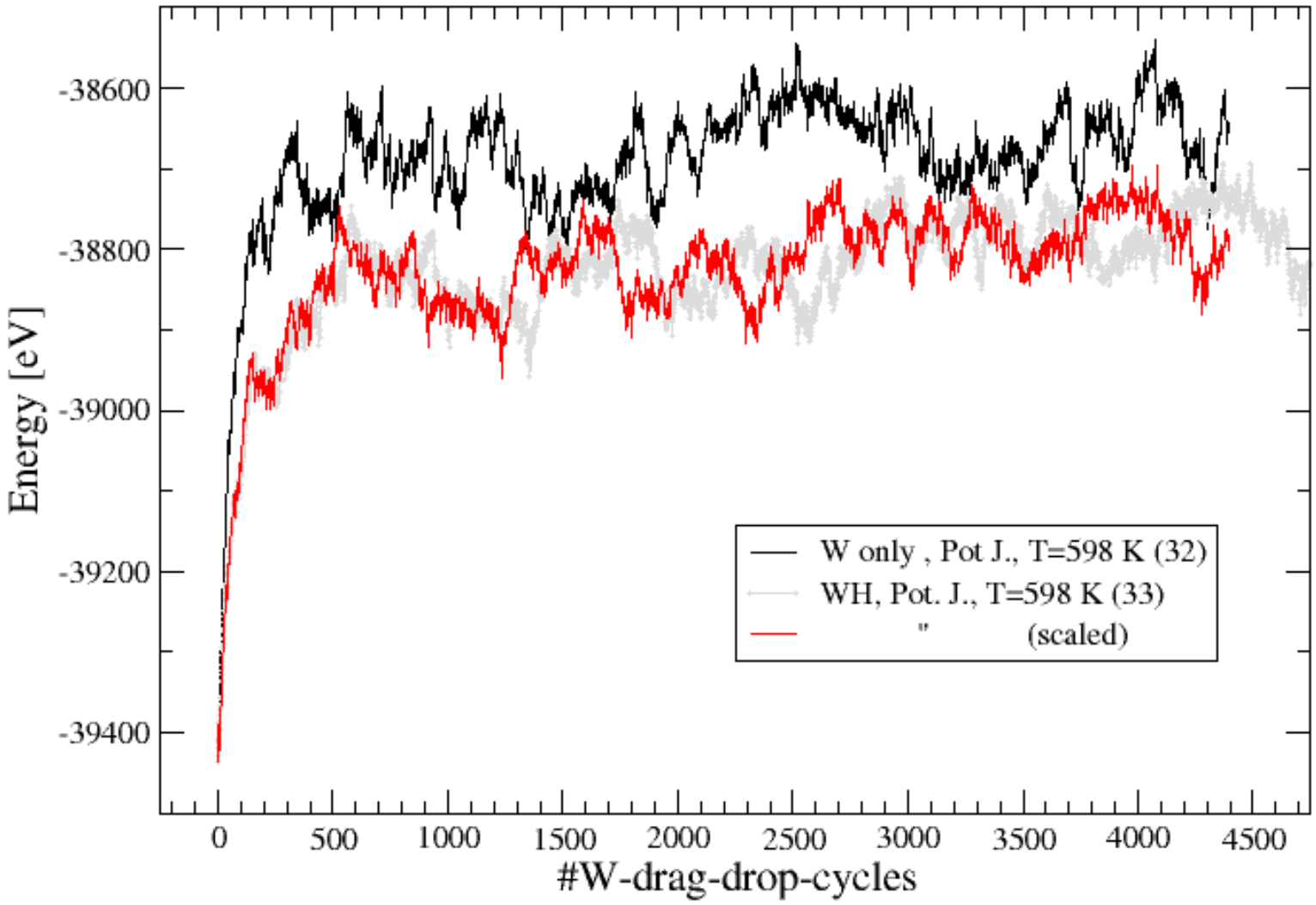


W atoms in red, H in blue

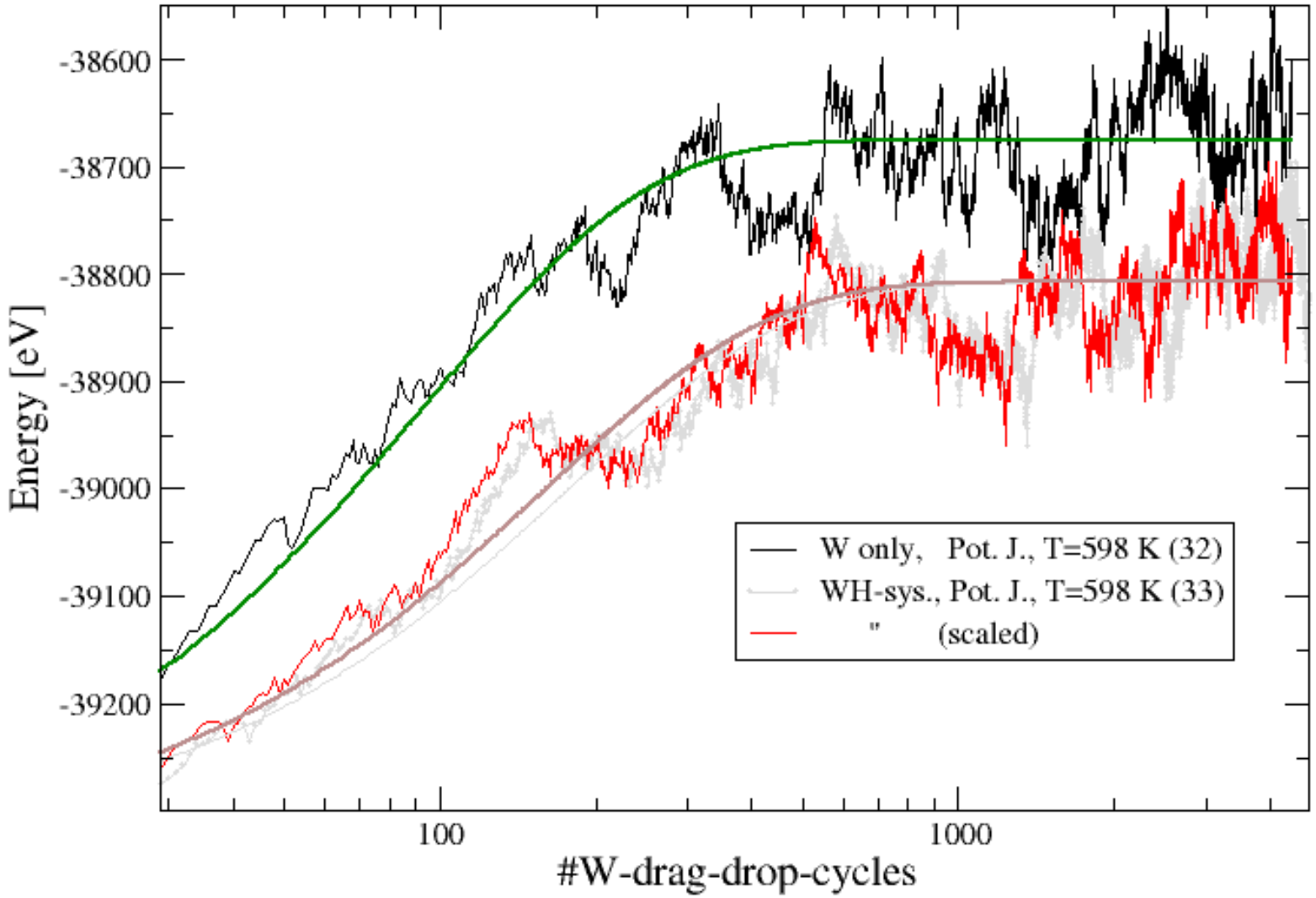
Results: System Energy

- **I) System energy : Overview**
- System sizes O(1000-5000) atoms
  - Fast convergence (<1dpa)
  - No extreme outliers (jumps)
  - Different MD-potentials yield roughly similar energies



Results: System Energy

- **I) System energy : Overview**
- System sizes O(1000-5000) atoms
  - Fast convergence (<1dpa)
  - $E(t) \sim (1 - \exp(-\lambda t)) + E_\infty$
  - $\lambda \leq O(0.1)$ dpa
  - weakly influenced by H



Results: System Energy

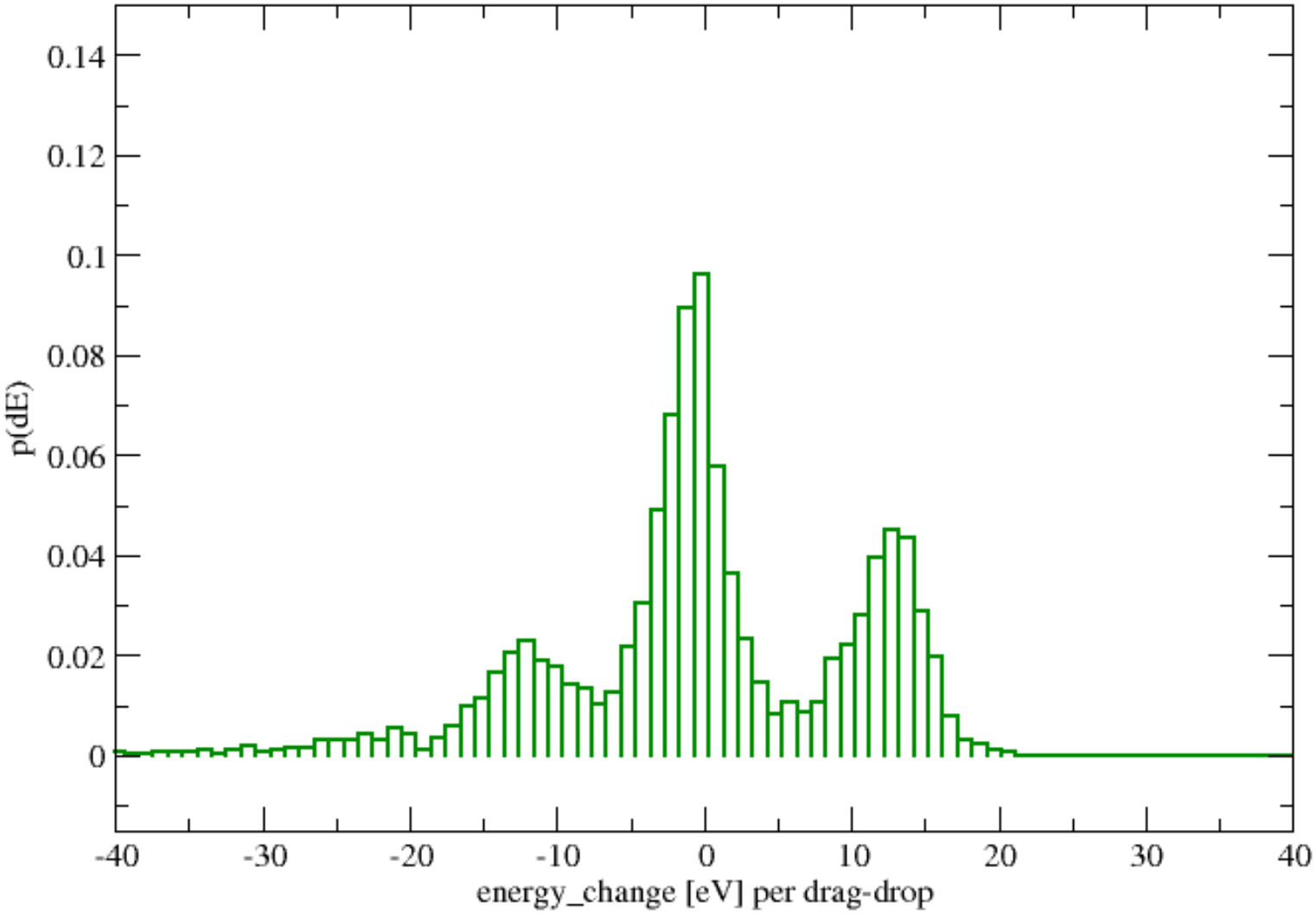
- **I) System energy :**

  W only, steady-state

  - Energy *change* **multi**modal:
  - Drag-drop-cycle:

    relaxed Frenkel-pair generation:

    E_{FP}= 12.6 eV [5]
  - induced system relaxation



Results: System Energy

- **I) System energy : steady-state (W)**
  - Energy *change* **multi**modal:
  - Drag-drop-cycle:
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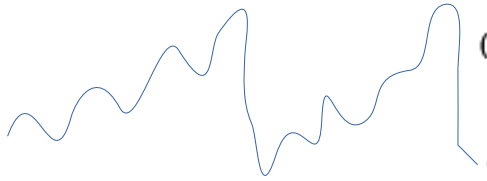
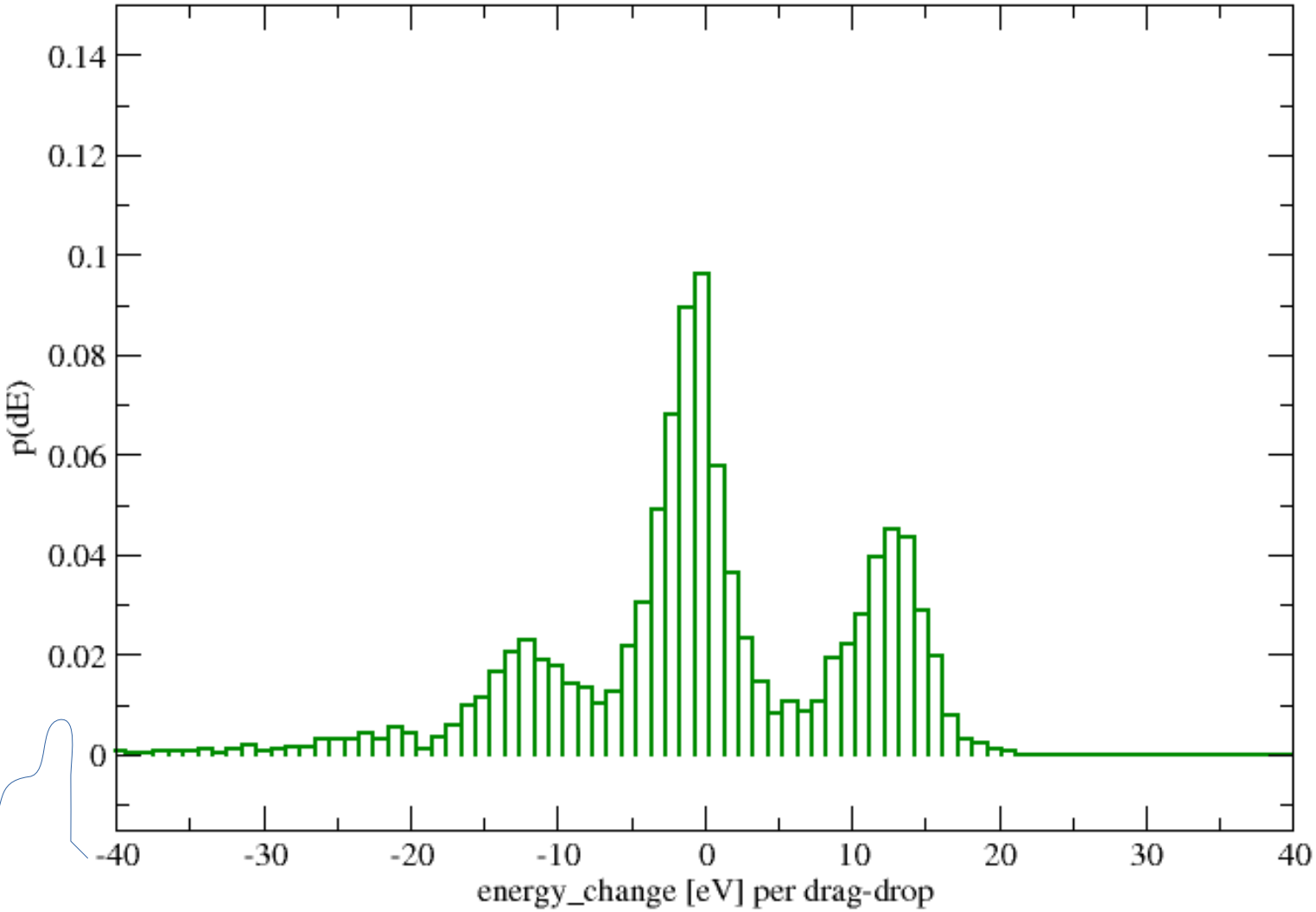
  - induced system relaxation

Heavy tail:





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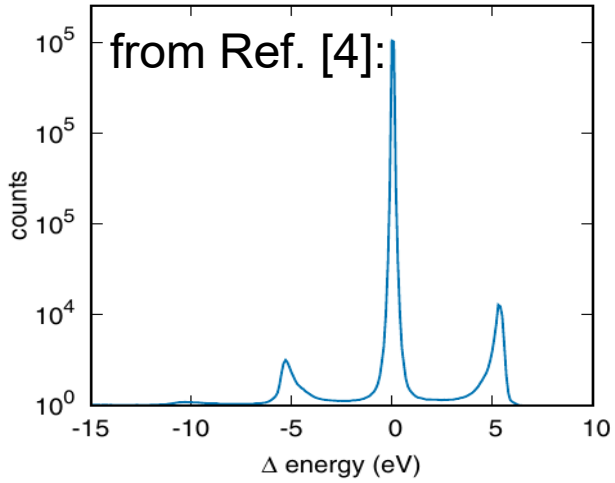

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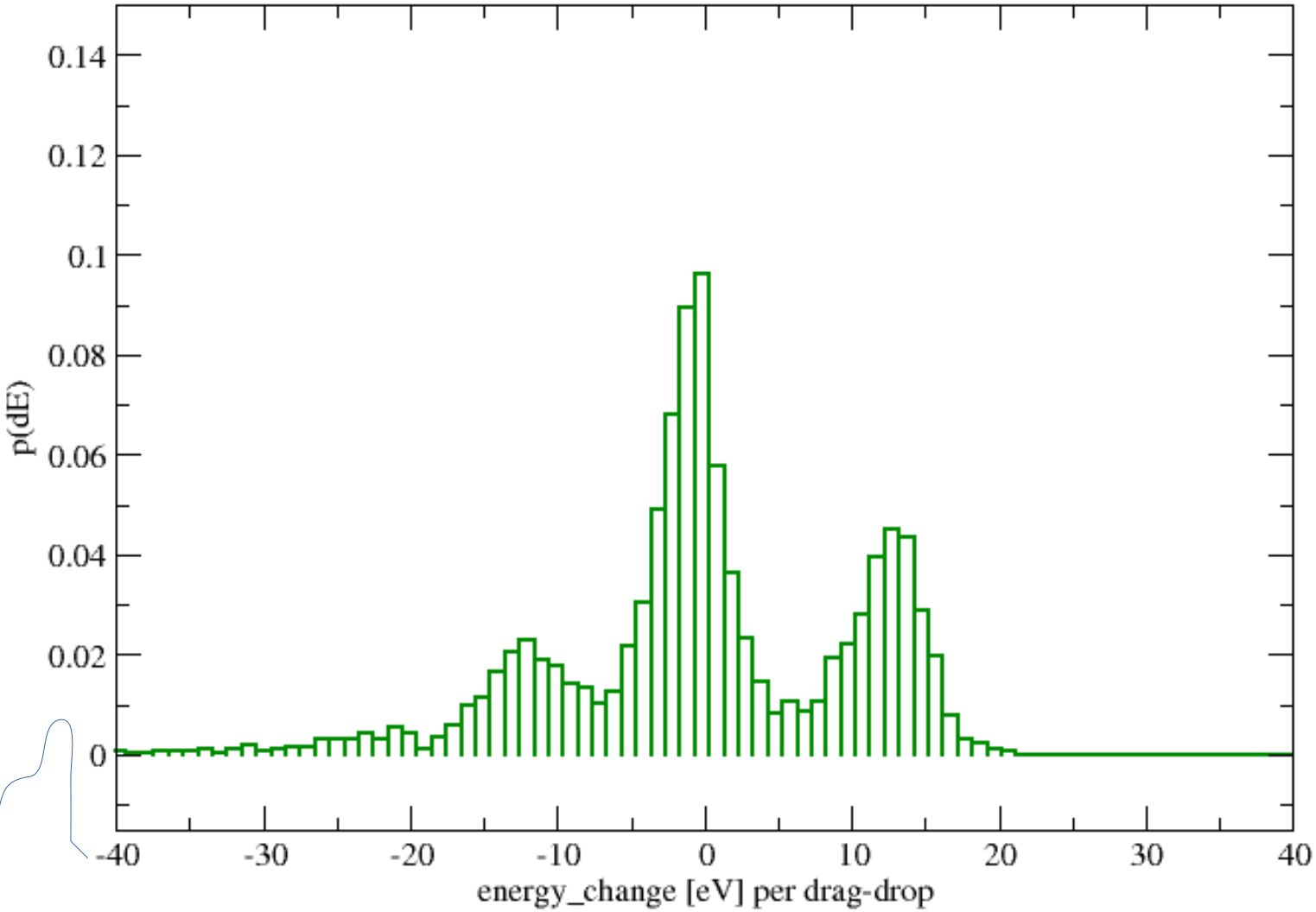


Results: System Energy

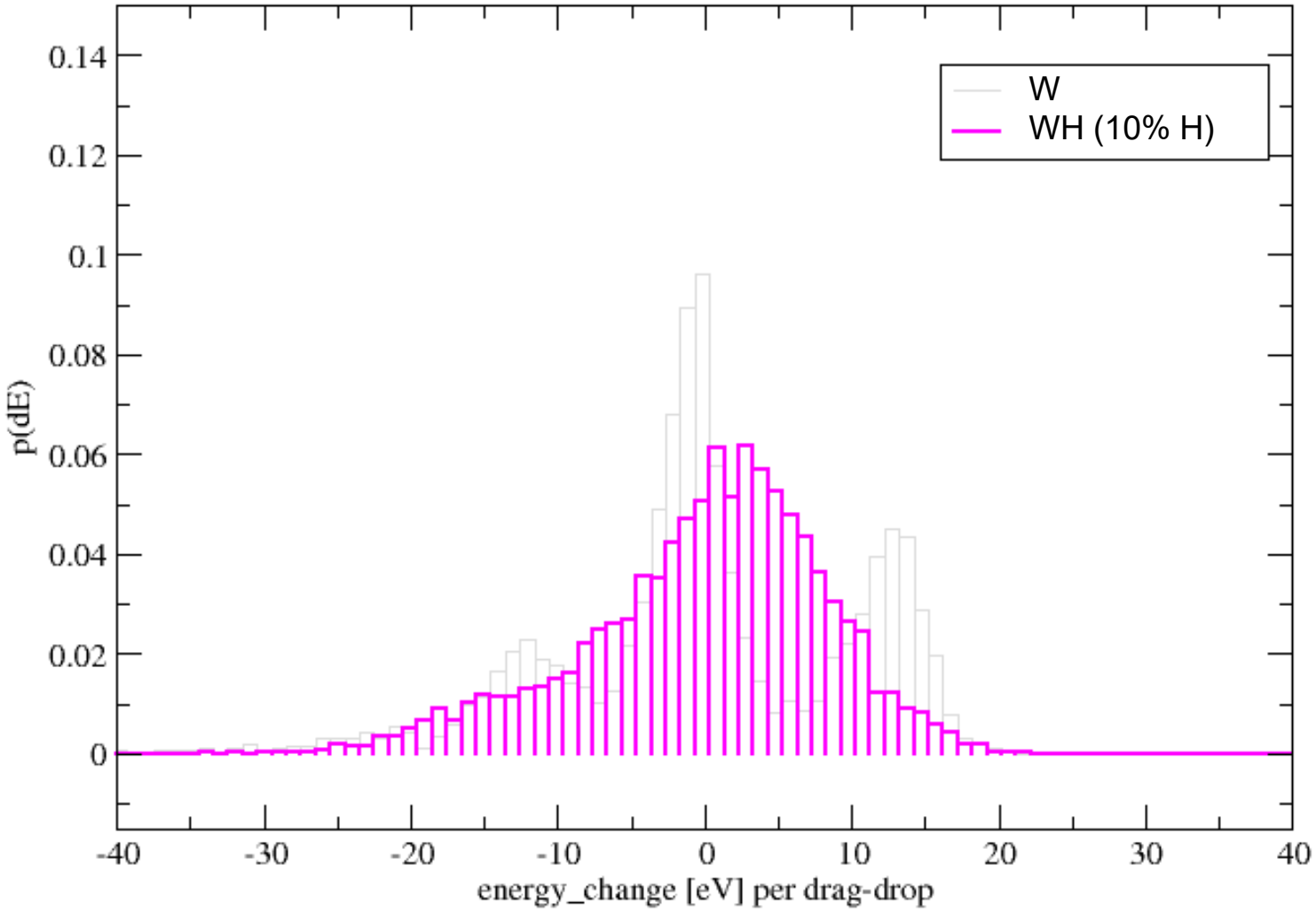
- **I) System energy : steady-state (W-H)**

  Presence of H significant:

  – Energy *change* now **uni**modal:

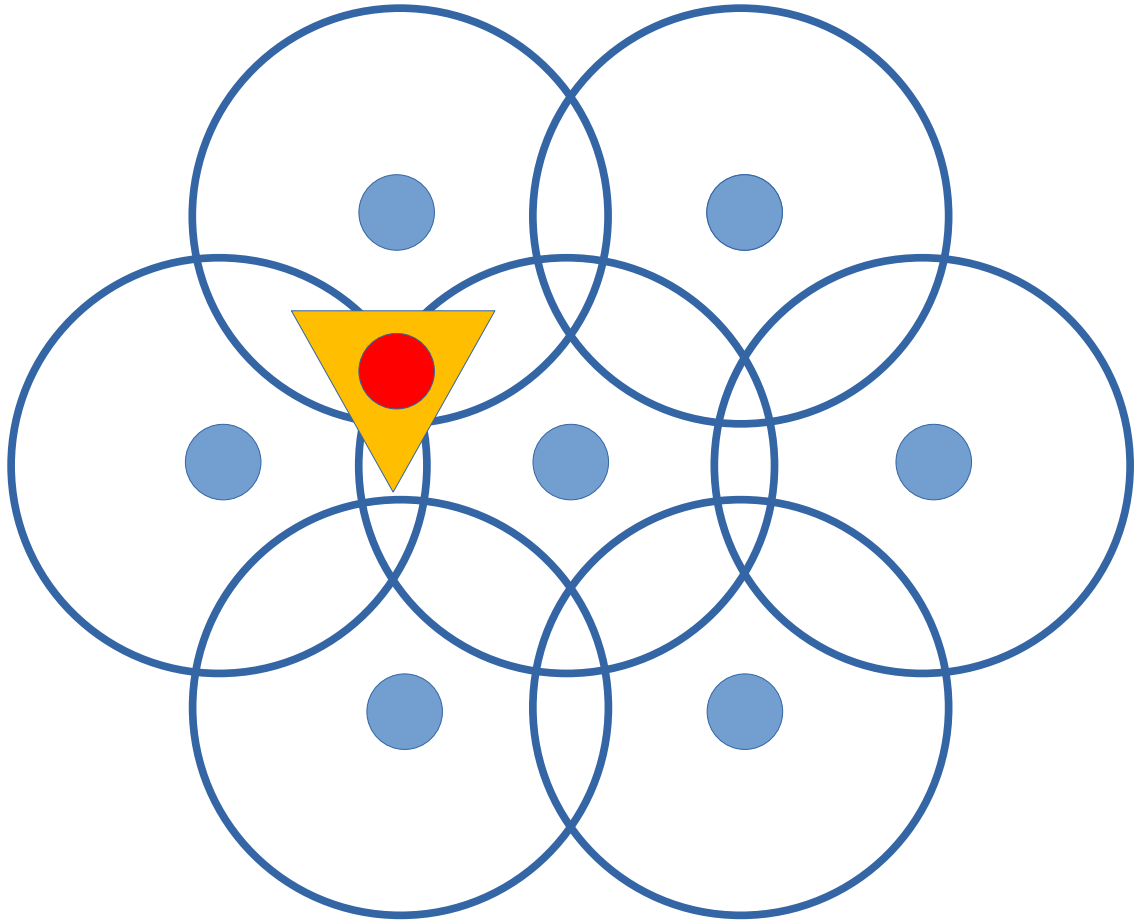
  – Hydrogen broadens energy change

  – induced system relaxation stays



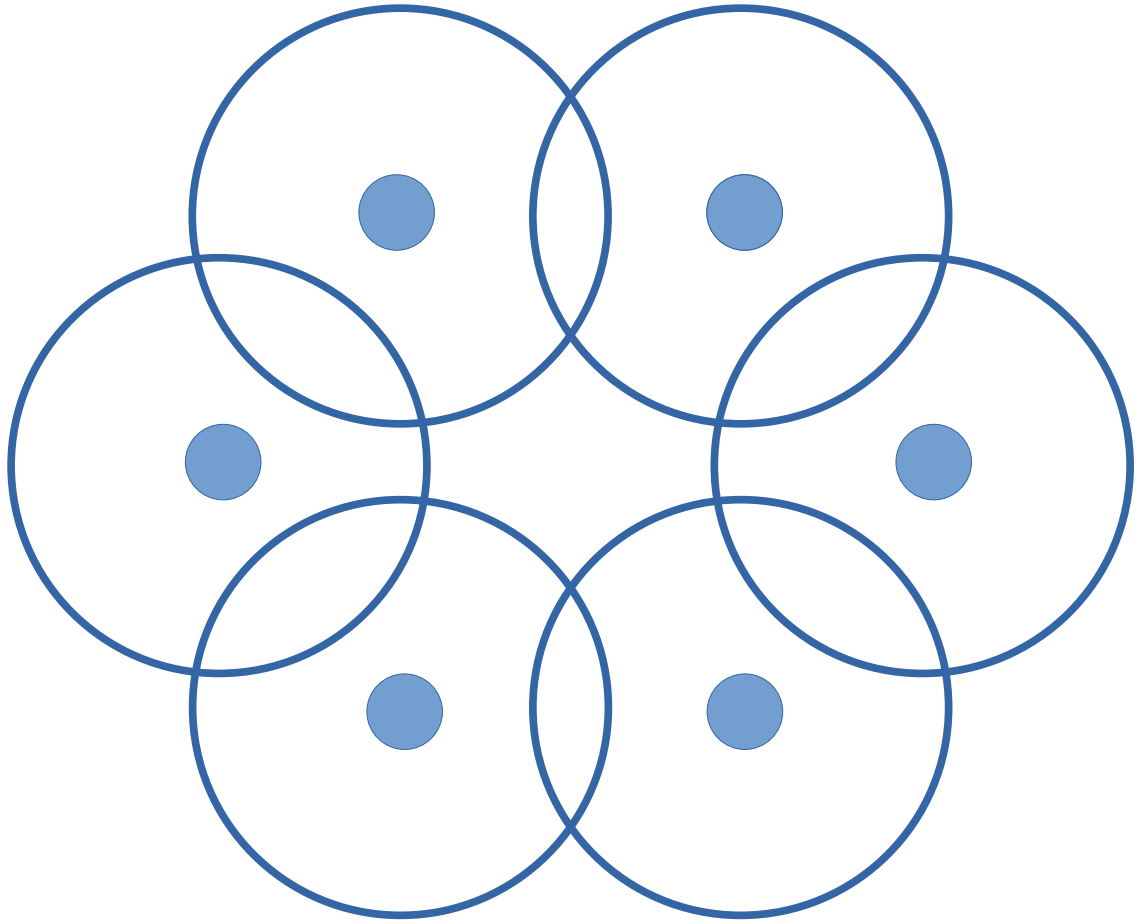
Results: Defect-formation

- **II) Defect-formation: Analysis**
  - Interstitial detection:
    - Straightforward based on
      - Voronoi-cell volumes
      - (Wigner-Seitz-cells)



Results: Defect-formation

- **II) Defect-formation**
- Analysis:
  - Interstitial detection:
    - Straightforward: Voronoi-cell volumes
  - Vacancies/Voids:
    - Voronoi approach error prone (shared excess volume)
    - Computationally expensive approach is needed: ‚free volume accounting‘



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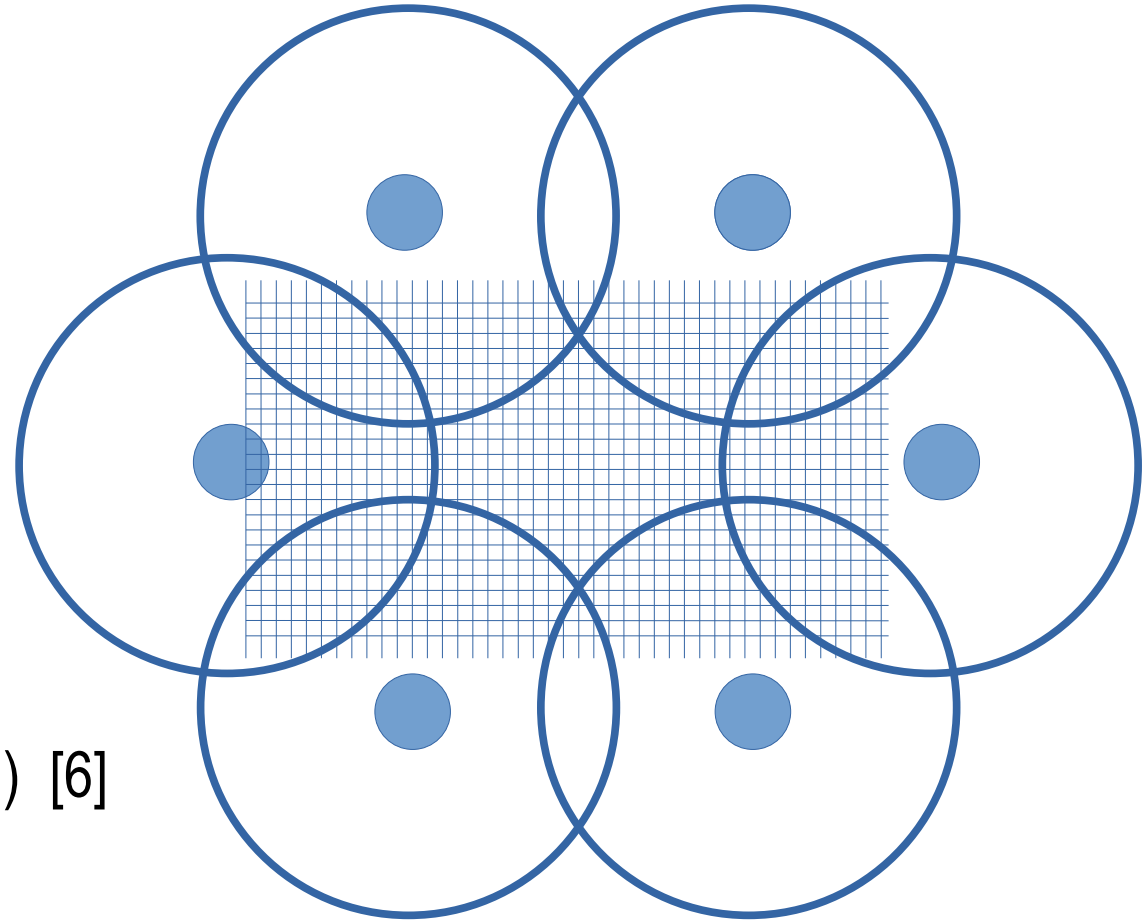
    - KDTree-approach (O(N^2)⟶ O(N log(N))) [6]



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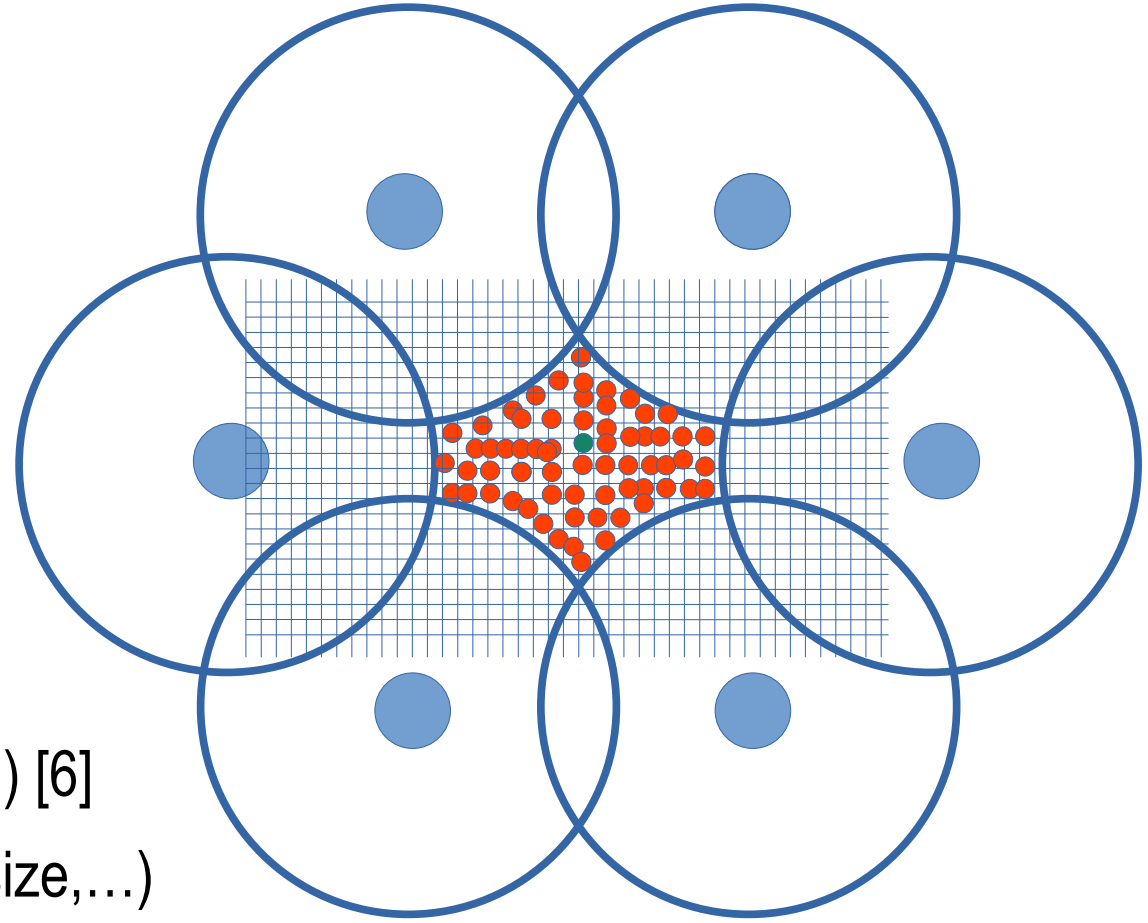
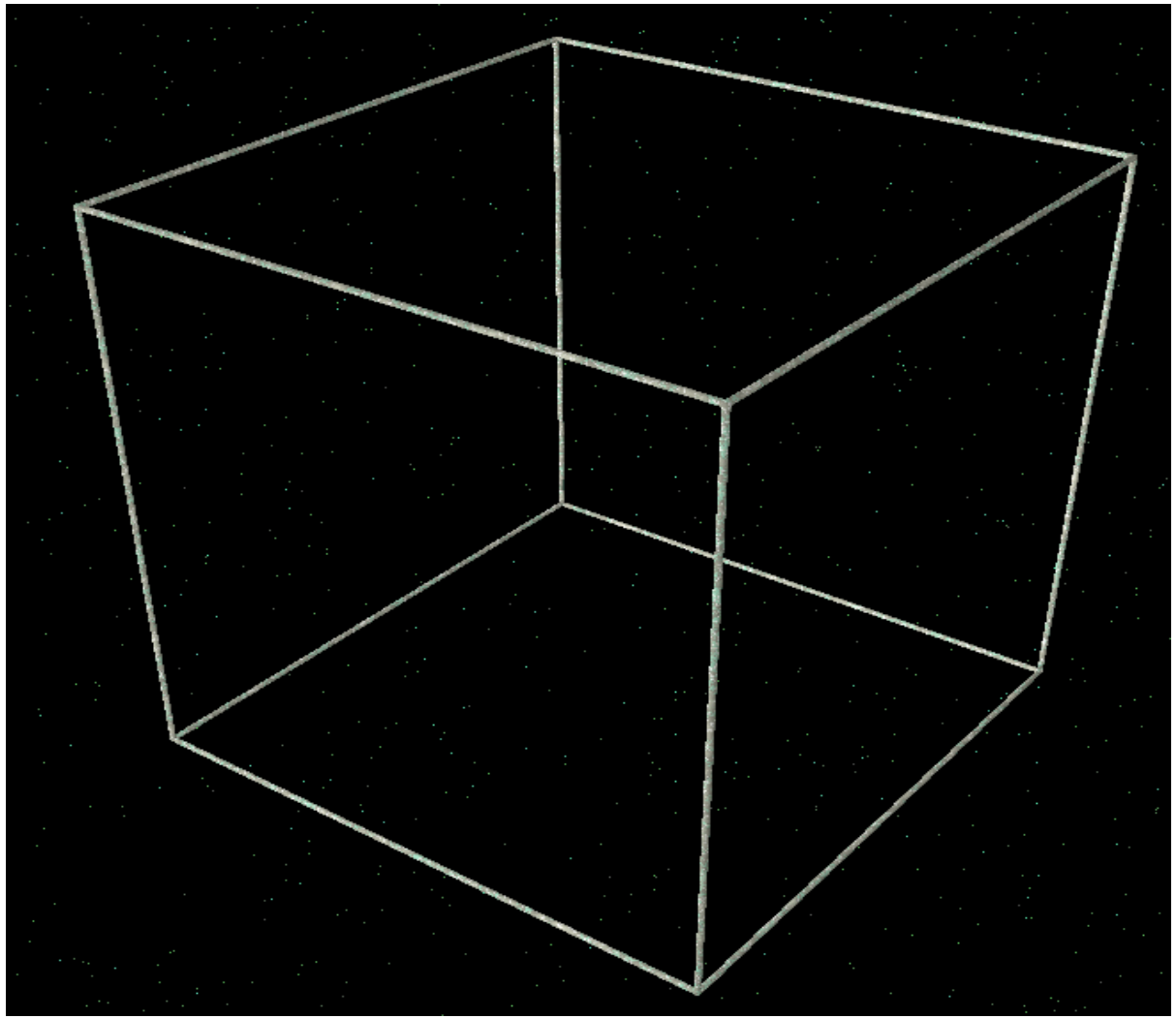
  - Vacancies/Voids:
    - Voronoi approach error prone
    - (shared excess volume)
    - KDTree-approach (O(N^2)⟶ O(N log(N))) [6]
    - Cluster-analysis of free volumes (center, size,…)



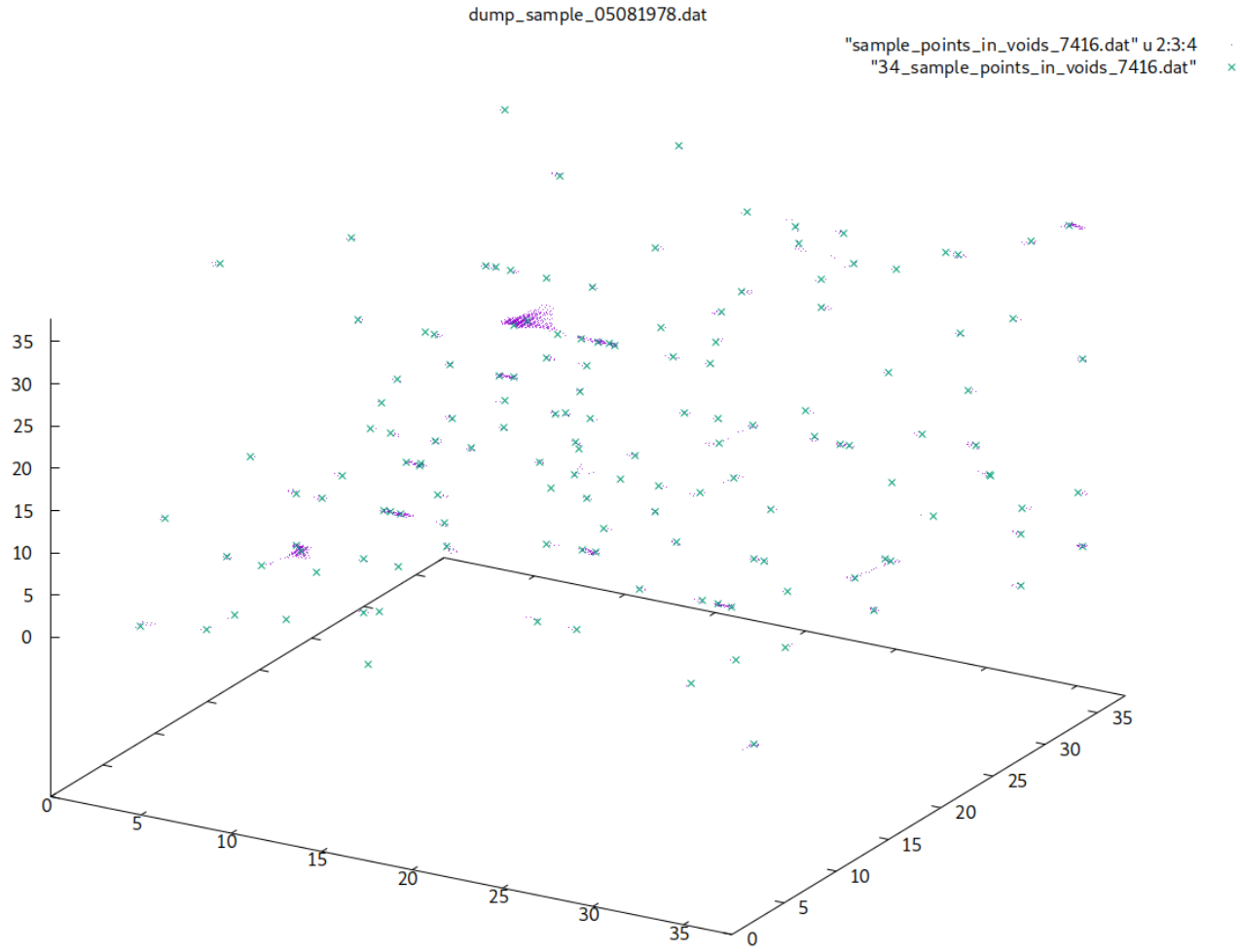
Results: Defect-formation

- **II) Defect-formation: Results**
- Void-volumes:



Results: Defect-formation

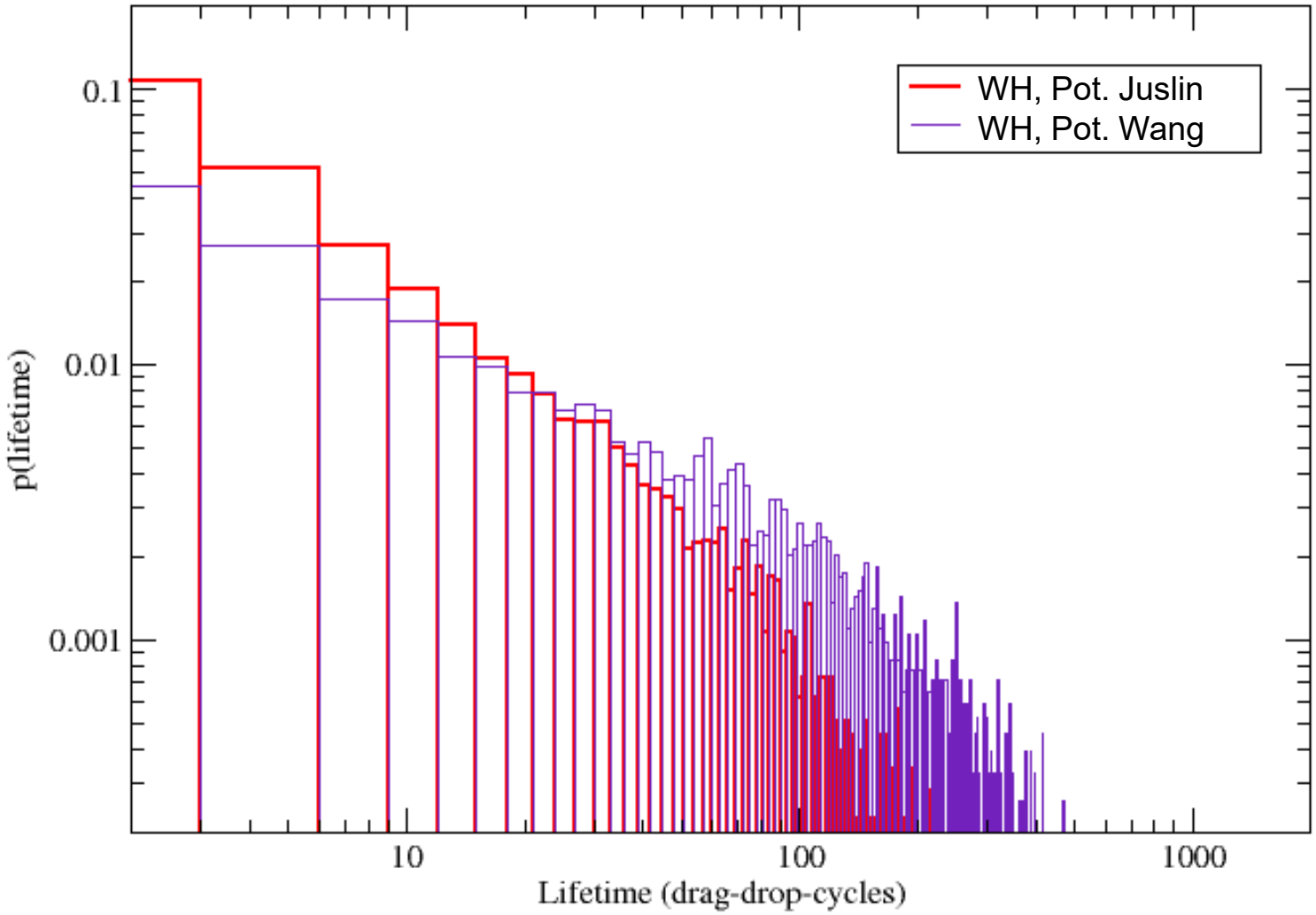
- **II) Defect-formation: Results**
- Void-volumes
- Tracking of
  - Position
  - Size
  - Lifetime
  - Density



Results: Defect-formation

- **II) Defect-formation:**
- **Lifetimes** of vacancies:
  (log-log-plot)

- MD-potentials have noticeable effect on result

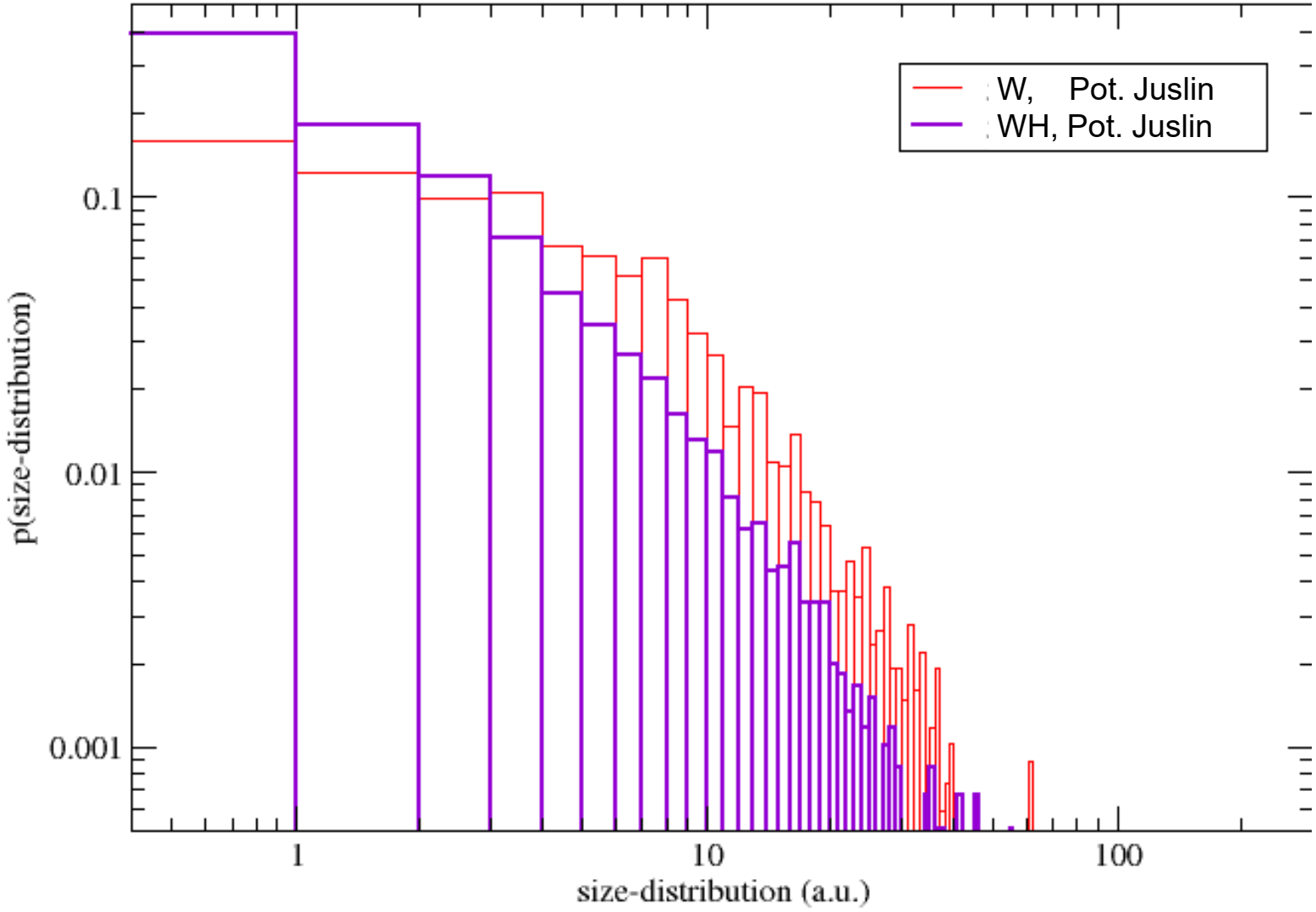


Results: Defect-formation

- **II) Defect-formation:**
- **Size-Distributions** of vacancies (log-log-plot)

- Influence of H presence is *significant :* ***smaller*** void size(!)

- Different MD potentials are internally consistent

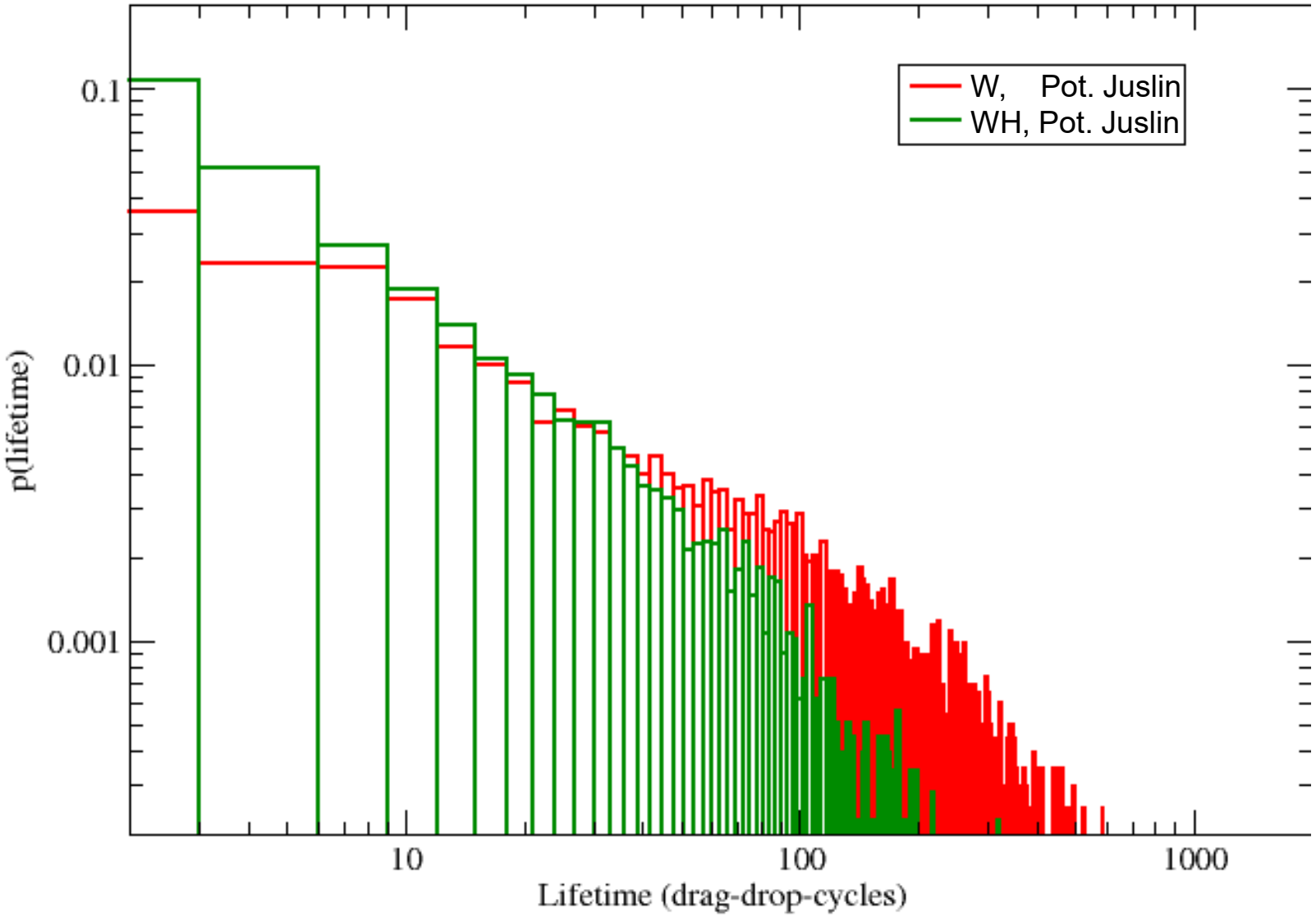


Results: Defect-formation

- **II) Defect-formation:**
- **Lifetime**-Distributions:
  (log-log-plot)

- Tendency towards *shorter* lifetime

- Magnitude depends on MD pot.



Conclusion & Outlook

- Modelling results:
  - Convergence to ‚equilibrium' (steady-state) structure with fluence-constant of ≤O(0.1) dpa
  - Simulation results robust under intrinsic parameter variation
  - Effect of presence of Hydrogen : reduced lifetime and size of considered defects
  - MD-potentials affect observed properties of WH-system

No supporting evidence for structural effects of H (?!)

- Difference of experimental results and simulation results emphasize importance of **dynamic model** aspects
  - Urgent need to look into fundamentals : Equilibrium C(S) or steady-state $C(S,C_0)$
  - System description: Relevant system parameters : S=S(E) ?

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- **Self-damaging (super-threshold) : MD and KMC-Simulations**
- DSSL/HSSL (sub-threshold) : Insights from MD
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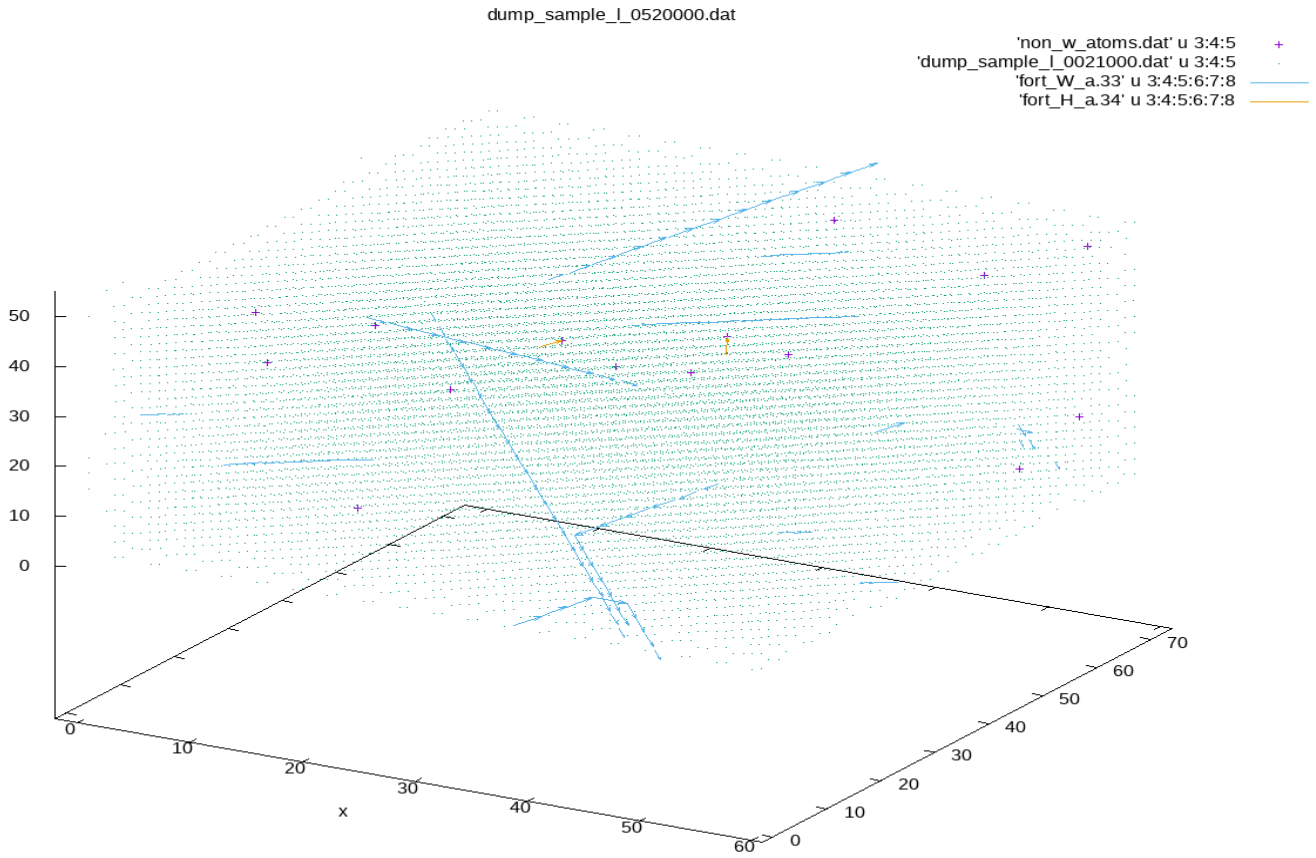
Self-Damaging with/without H

- **Ansatz: Consider basic processes with MD and derive rates**

#processes not small : $I_A + V \rightarrow 0$ vs. $I_A + VH \rightarrow H$; $I_A + I_BH \rightarrow I_2H$; $VH_n + H \rightarrow VH_{n+1}$,...



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Check some of the movies… (out_573_vh7_052.mp4) : hydrogen filled vacancy recombines with incoming interstitial

Mechanism : Stabilisation of defects by hydrogen effective against interstitials?

Please distinguish
‚**stabilisation**‘ of vacancies by hydrogen (against interstitial atoms) from ‚**demobilisation**‘ of vacancies by hydrogen

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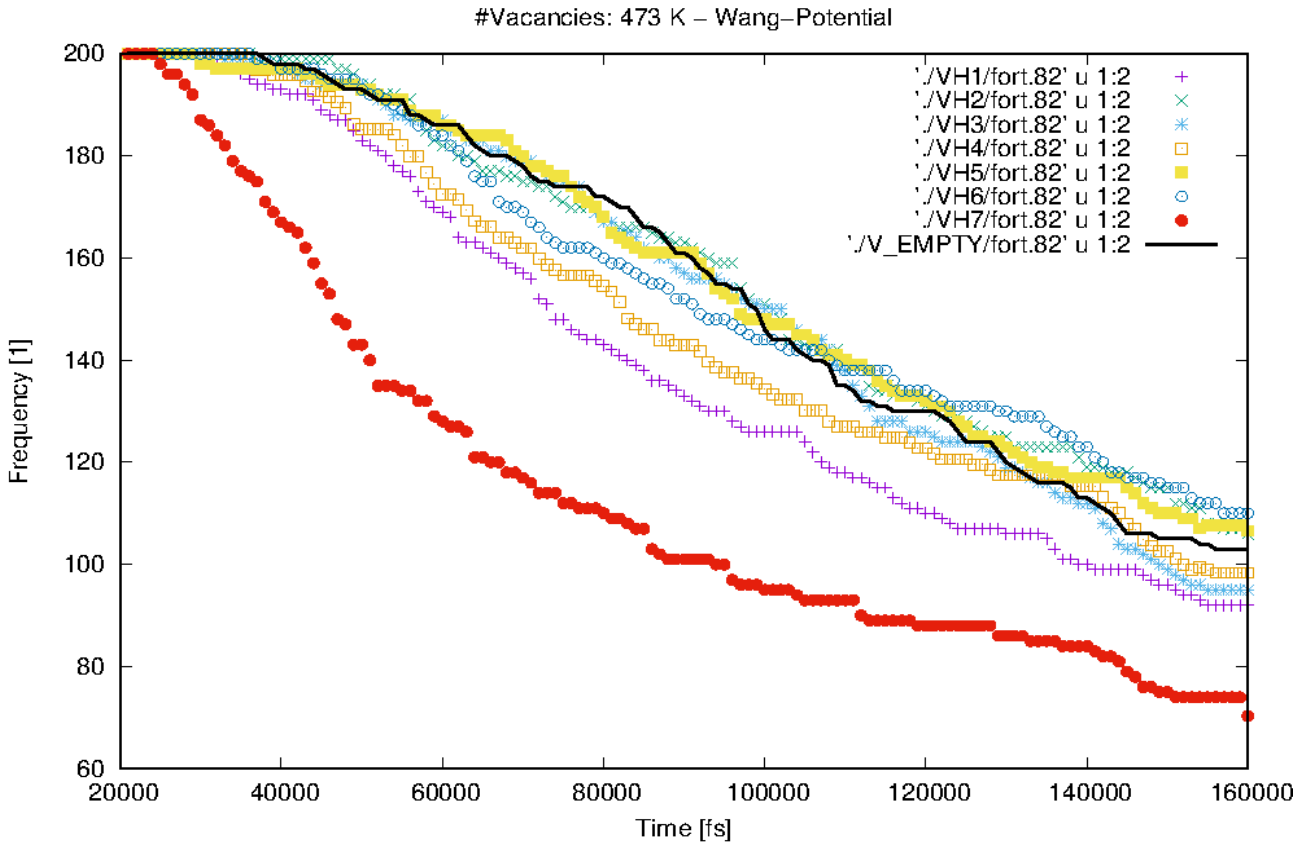
- **Stabilization** effect for V only for $N_H \sim 6$ observable
- But: 'Trapping' of Interstitials with solute H
- followed by Interstitial cluster formation
- Note : No $I_A + I_A$ – Interactions observed
- Put everything together in KMC-simulation



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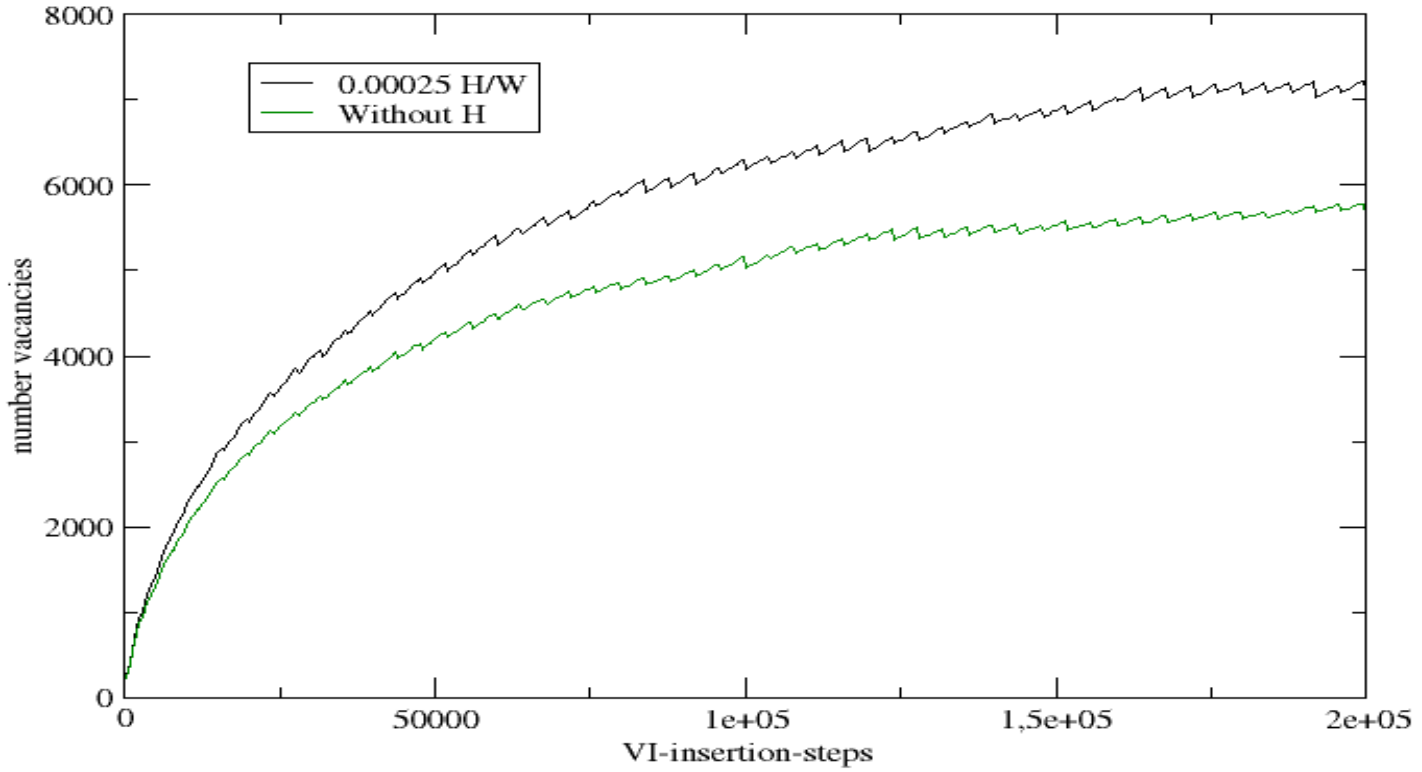
  - But: 'Trapping' of Interstitials with solute H
  - followed by Interstitial cluster formation
  - Note : No $I_A + I_A$ – Interactions observed
  - Put everything together in KMC-simulation: c.f. KMC/combined_movie_H_wo_H.mp4

Self-Damaging with/without H

- **Ansatz: Consider basic processes with MD and derive rates**
- KMC-result: Increased number of vacancies already for relatively small amounts of (solute) H
- Key process: Immobilization of I (by IH-cluster formation) enhances survival probability of vacancies



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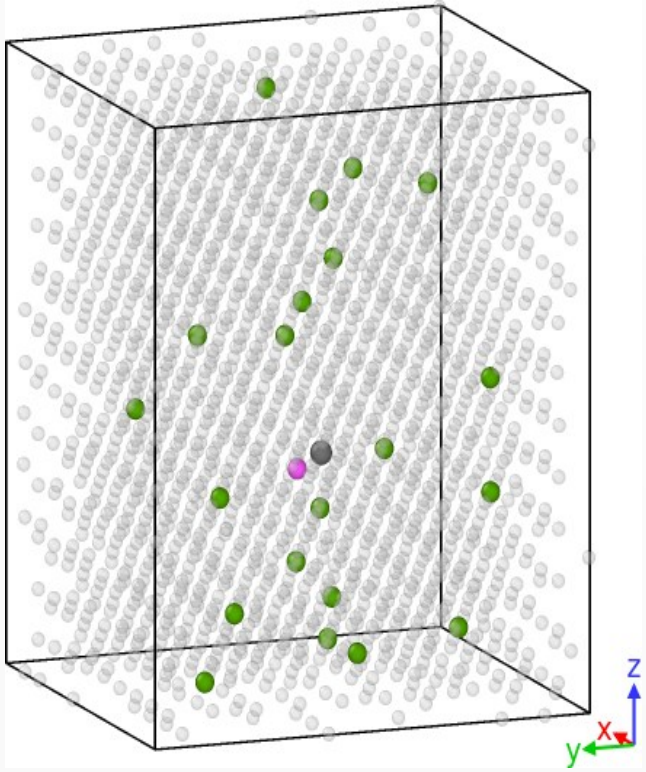
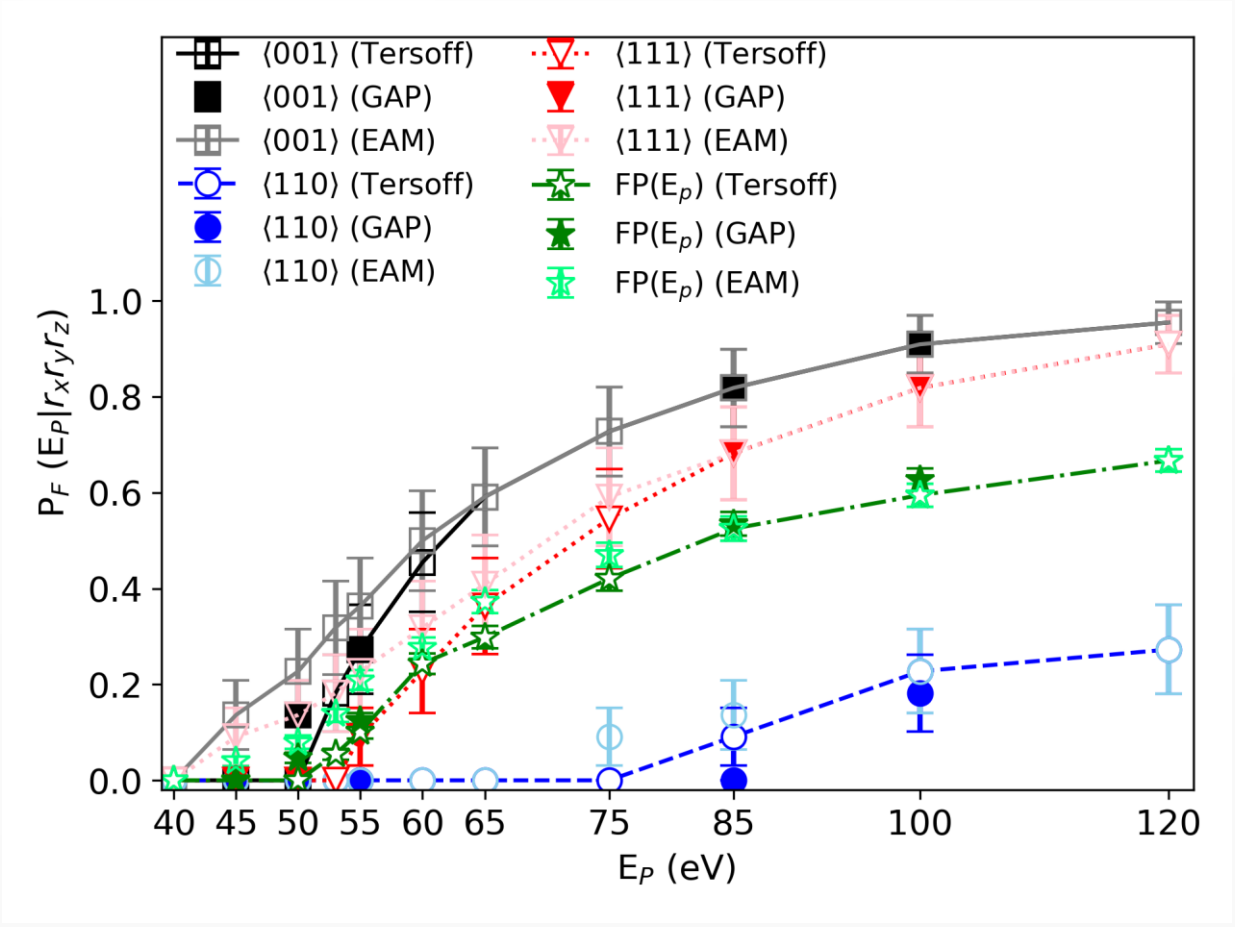
DSSL

- H/DSSL
  - DSSL: a distorted hydrogen-rich W-layer at the surface (cf. Presentation by Liang)
  - DSSL is formed under sub-threshold energy hydrogen exposure of tungsten [1]
- DSSL-Formation is unexpected:
  - Energy transfer to W-atoms is below displacement energy: lattice should stay undamaged
  - Other experiments with ‘H-supersaturated’ tungsten (quenching) did not show similar patterns
- Possible explanations
  - Reduction of displacement threshold energy by presence of hydrogen, e.g. by
    - Stress
    - Three-body interactions
  - Processes without displacement

DSSL

- H/DSSL : Reduction of displacement threshold energy by presence of hydrogen
- Molecular Dynamics study of the influence of H : scan over all directions (by J. Dominguez)





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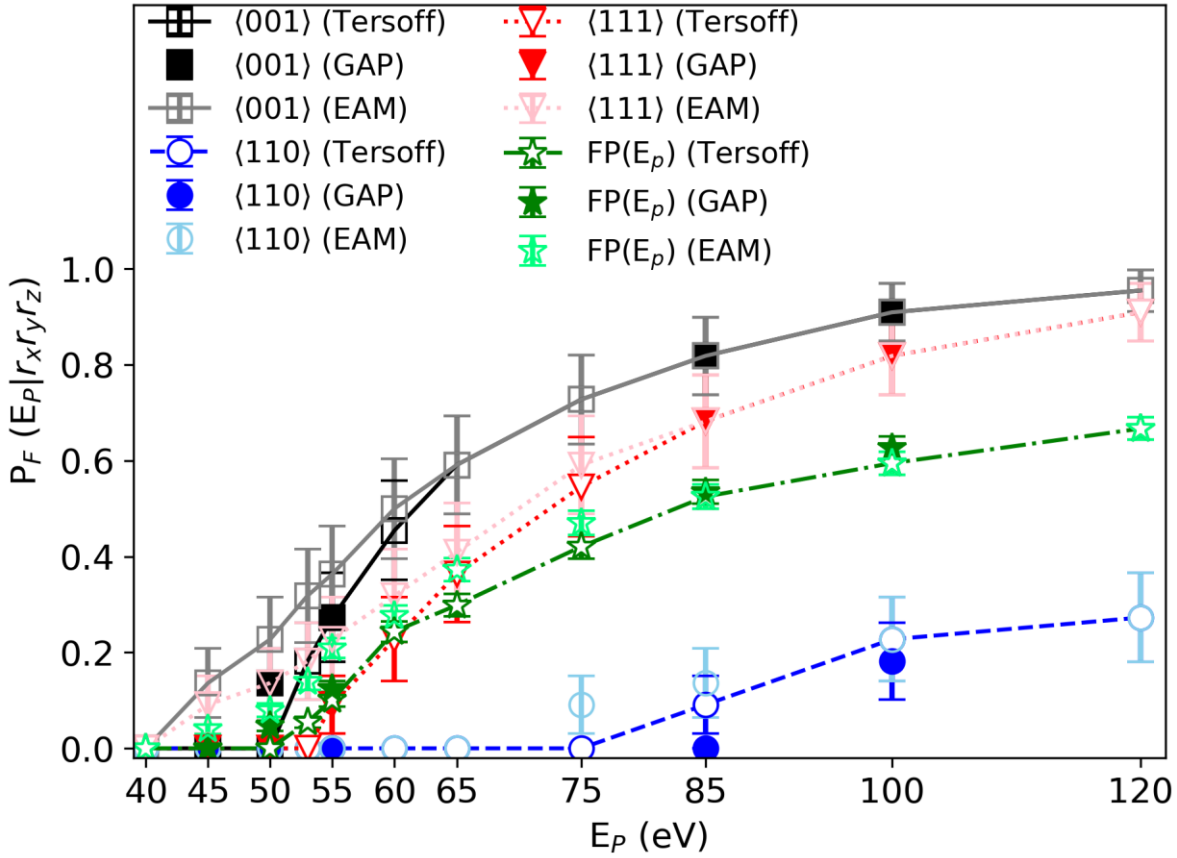
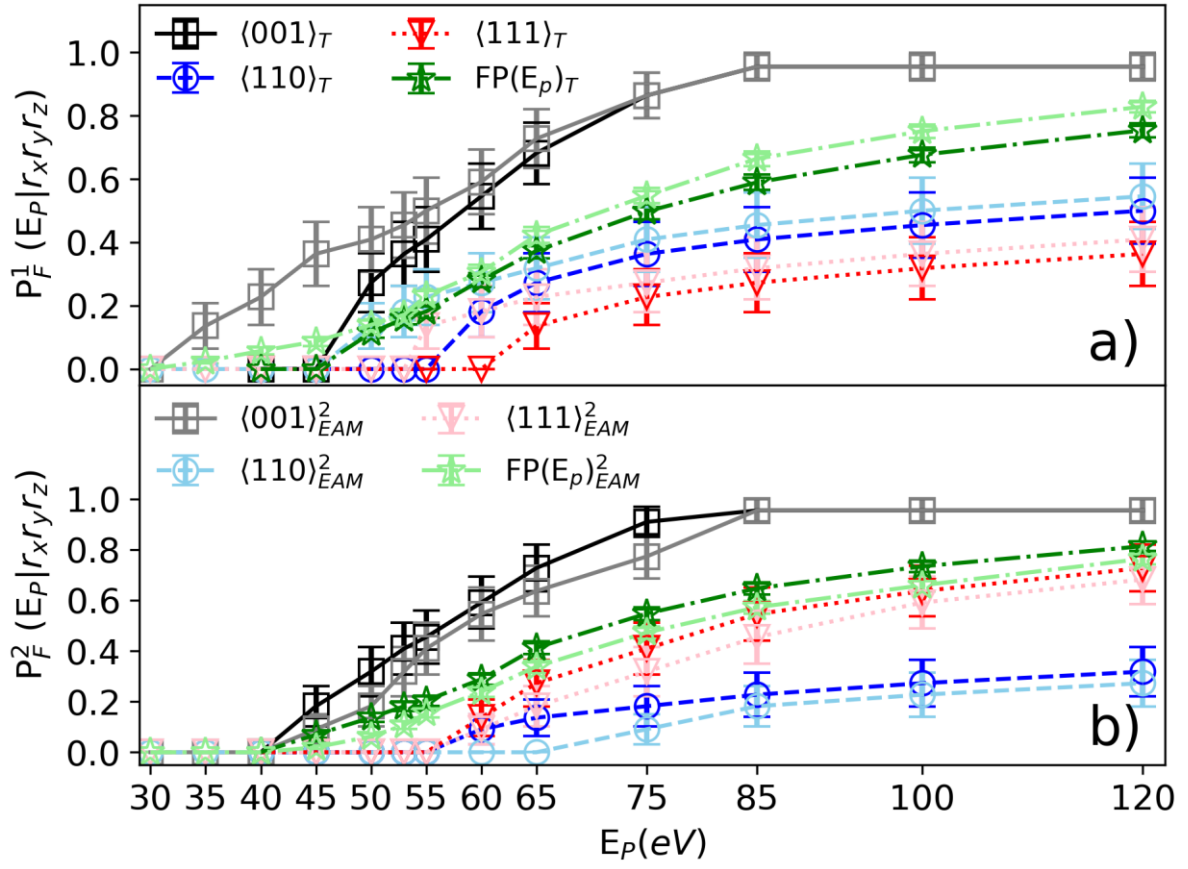
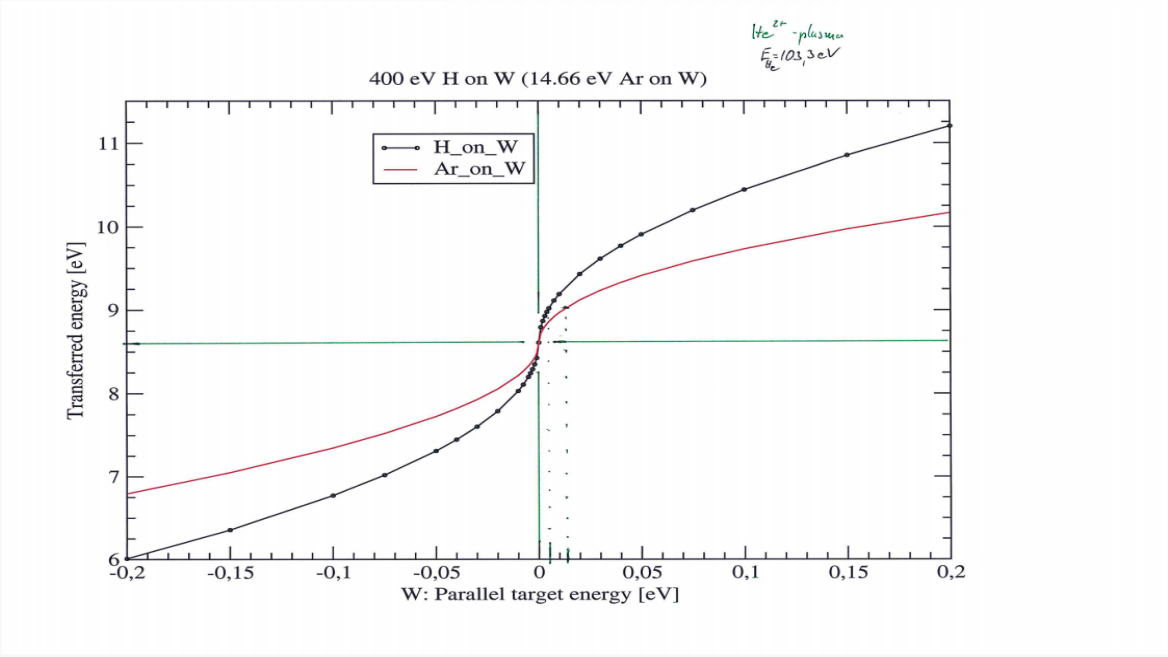




DSSL

- H/DSSL : Other kinetic mechanism?
- Max-E-transfer (E_H = 415 eV) on W: E ~ 8.9 eV : in the range of surface vacancy formation
- Equation for Max-Energy-transfer **only** approximation : $K = \frac{4M_1M_2}{(M_1+M_2)^2}$ (target atom at rest)
-



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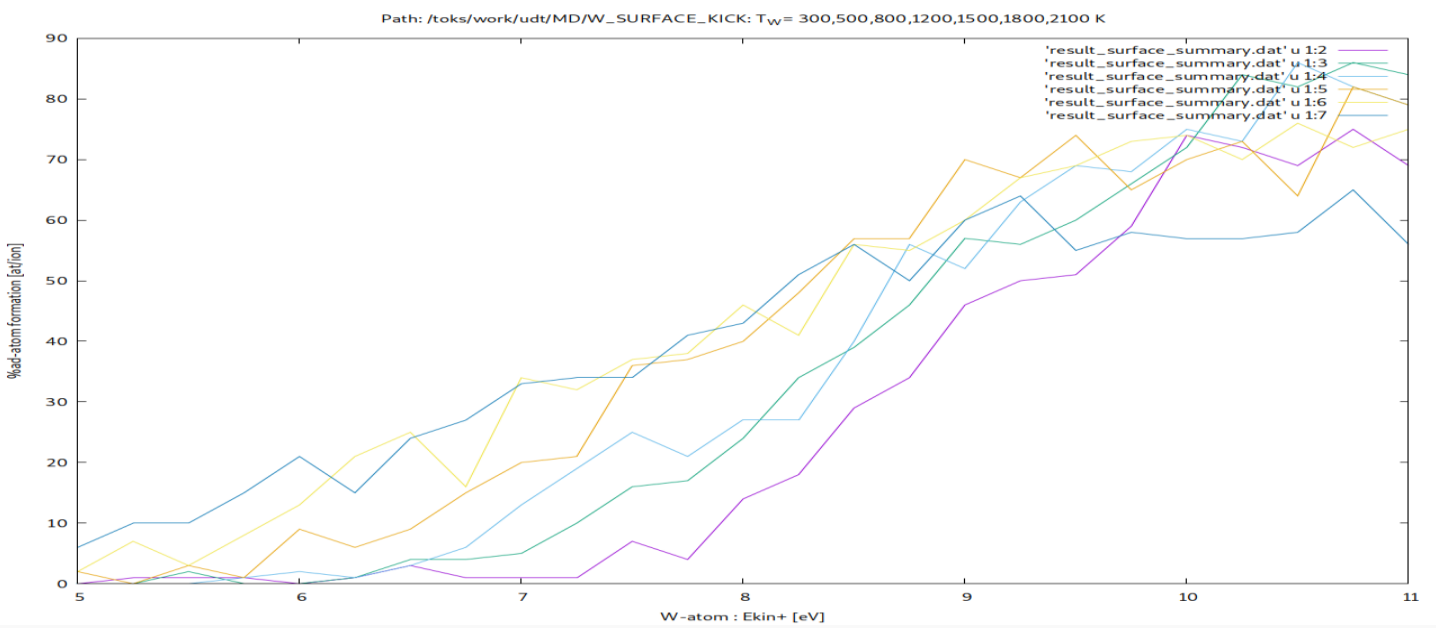
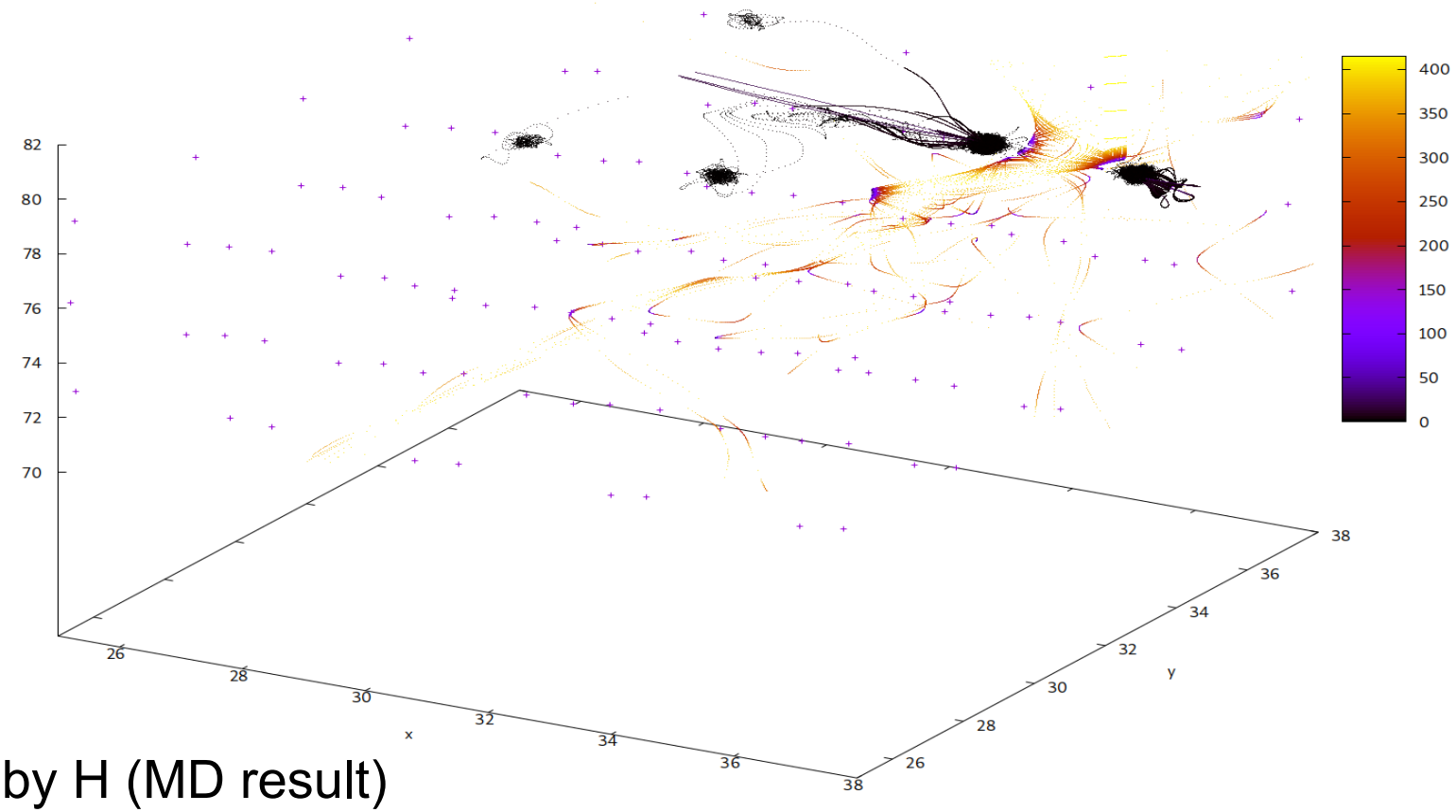
- Equation for Max-Energy-transfer only approximation : $K = \frac{4M_1M_2}{(M_1+M_2)^2}$ (target atom at rest)
- Deviation for large mass ratios:



DSSL

- H/DSSL : Other kinetic mechanism?
- Direct MD validation:
- 500 K, 415 eV H
- Wang potential



- Vacancy production
- mechanism confirmed!

- Propagation into bulk:
- Vacancies are demobilized by H (MD result)

Model for DSSL-formation

- Basic assumptions
  1) Vacancy (V) formation at surface : formation enthalpy O(3.6 eV, E_k higher) [2]
     f(ion-flux, E)
  2) VH_n mobility : $E_A(VH_0) \sim 2$ eV [3], mobility lower for n>0
     f(T, n, E)
  3) VH_n-Hydrogen interaction: uptake and release $VH_n \pm H$ [4]
     $f(c_H, T)$
  4) Conversion of VH_N into stable (&immobile) defect (SD): $VH_N + H \rightarrow SD$ f(T)
- Physics model
  - Enhanced formation of vacancies at surface(s) under energetic particle influence
  - VH mobility results in propagation
  - H-uptake and release $VH_0 \leftrightarrow VH_1 \leftrightarrow VH_2 \leftrightarrow \ldots \leftrightarrow VH_n \rightarrow SD$
- Yet unspecified:
  - a) Nature of SD b) Saturation process of SD-concentration

Model for DSSL-formation

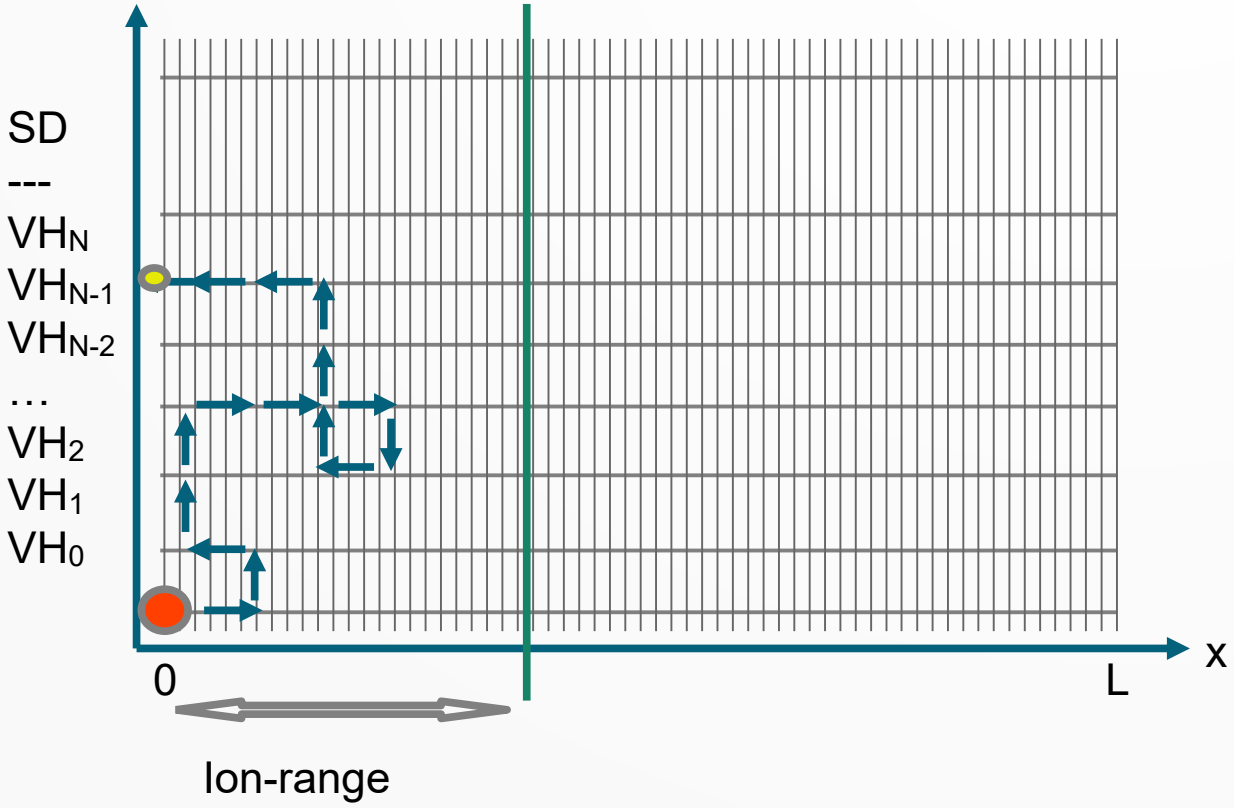
- Some numbers
  - Jump frequency of hydrogen atoms (300K) : $\nu_H = 2.7*10$ 1/s
  - Equilibrium-concentration of D (PLAQ-conditions[1]): $c_H = 2.3*10^{-5}$ H/W
  - Jump frequency of vacancies (thermal) : $\nu_V = 6.3*10$ 1/s
  - Kicks by ions (flux 10^{20} H/(m^2s), range 100 A) : O(0.1-1000) 1/s
- Initial reasoning
  - Thermal diffusion of VH_n-complexes is negligible (even for VH_0) at ~room temperature
  - VH mobility is determined by kicks or local non-equilibrium temperature: stopping ~ 1eV/A
  - Ion-induced processes will result in
    - Enhanced diffusion of VH_n
    - Biased vacancy movement (with (weak) preference *back* to surface)

Simulation

- Discrete particle (VH_n) simulation with flux kept constant:
  - Phase-space: vacancy position and number of hydrogen atoms in it
    - Time and spatially constant hydrogen concentration $c_H(T)$
    - Insertion of VH_0 at x=0
    - No interaction between vacancy complexes
  - Input parameters:
    - temperature T (affects the hydrogen concentration and H-uptake/release processes)
    - kick-frequency f (inducing a vacancy step) & H-binding energies in VH
    - directional bias p (0..1; 0.5 is unbiased) of vacancy movement: ~ 0.48
    - Loss of hydrogen from VH_n due to a step : q = O(<~0.3): RW-return prob in 3D: 0.34… (Polya)
    - $VH_n \rightarrow VH_{B(k;q=0.3*n,n)}$ with B(k;q,n) binomial distribution :
      - $B(k;q,n) = n!/(k! * (n-k)!) * q^k (1-q)^{n-k}$

Simulation

- Simulation output:
  - Phase-space density as function of fluence:



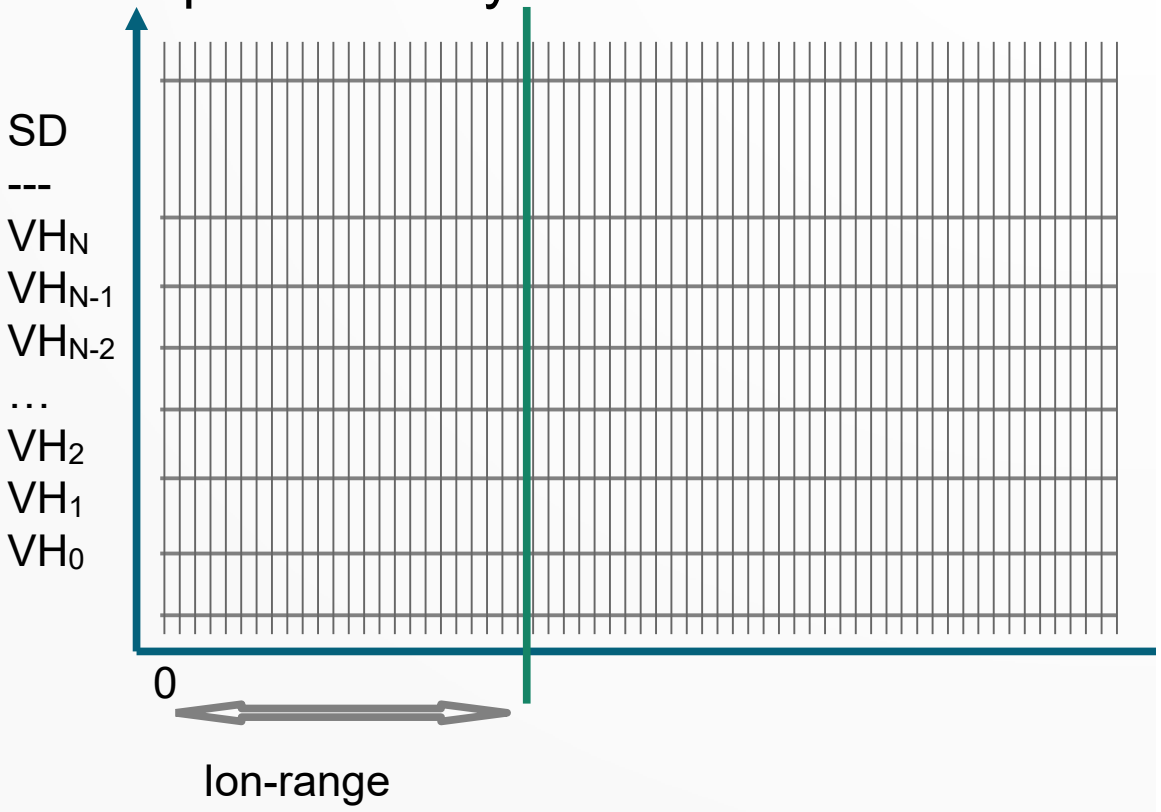
Processes:

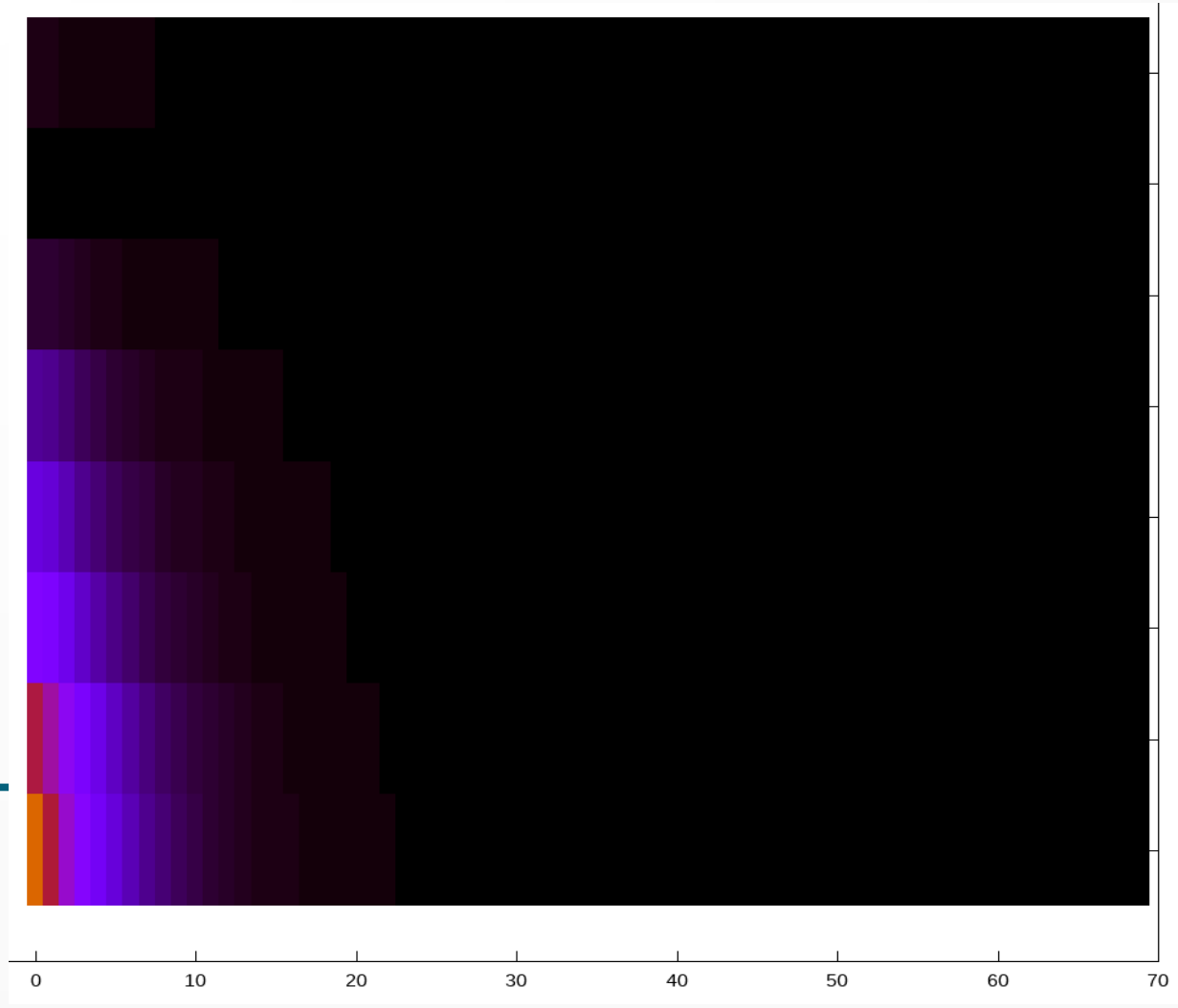
- Migration of vacancy complex
  - Thermal diffusion
  - Kicked (within ion-range)
- Uptake of hydrogen by VH_n
- Loss of hydrogen (thermal) by VH_n
- Conversion of VH_N to SD (terminal)
- Loss of VH_n complex (terminal) at
  - Front surface (x=0)
  - Rear-surface (x=L)

Simulation

Simulation output:

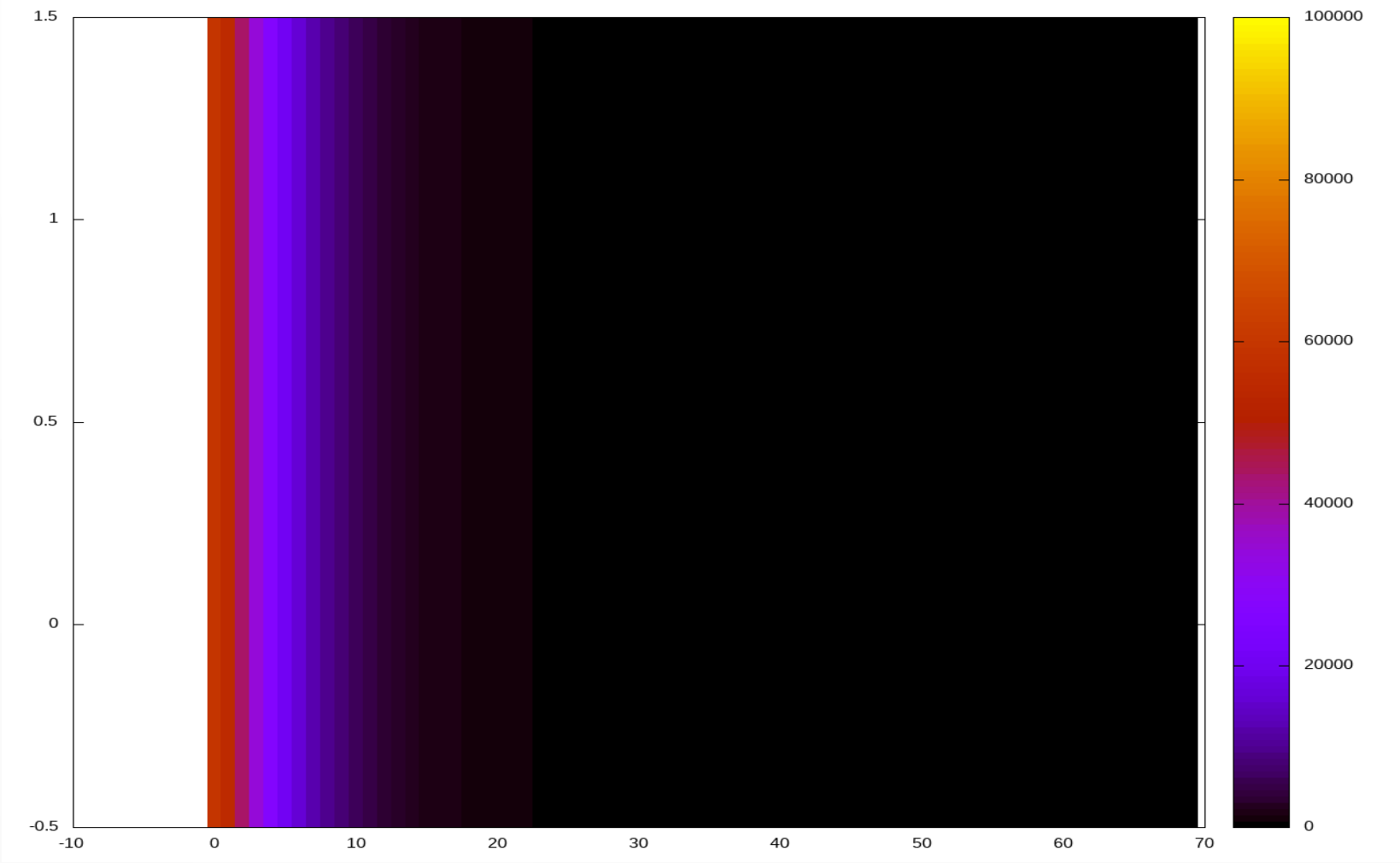
- Phase-space density as function of fluence:





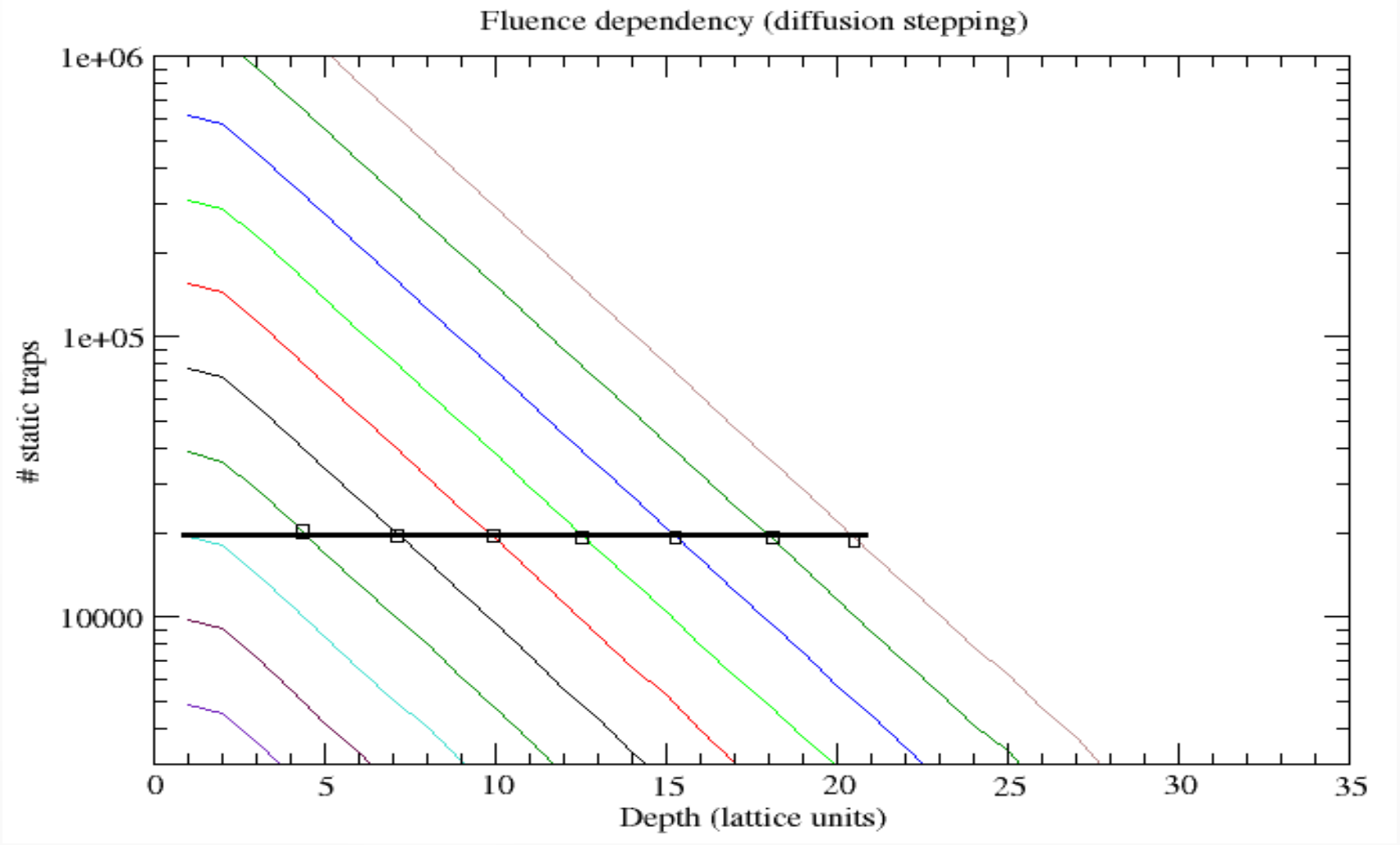
Simulation

Fluence dependence of static defect (SD) profiles



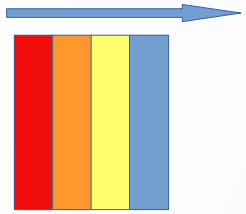
Simulation

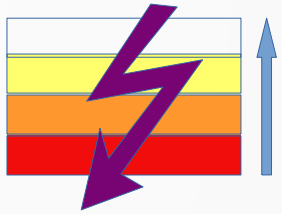
Fluence dependence of static defect (SD) profiles



Simulation results & Consequences

- Static defects are being developed
  - Static defect formation *propagates from surface into the bulk*
  - High eff. hydrogen concentration is crucial (step-ladder)
  - Defect layer is *restricted to ion range* due to limited mobility at low temperatures
  - Restricted parameter windows: e.g. layer vanishes at too high temperatures; balance of kick and H-interaction
  - Layer build up slows (as expected) with thickness – but: can formed defect layer act as vacancy source itself?





- Validation aspects: possible falsification by
  - (low-) fluence series experiments: Surface vs. bulk (ion-range) phenomena
  - Decoupling of hydrogen loading and kicking: simultaneous exposure to ions and e-beam?
  - High/Low-temperature exposures (but competing effects: stability of SD?)
  - ...
  -

Outline

- Motivation

- **Direct Simulation of WH with Artificial Dynamics Approach: Needs refinement**

- **Self-damaging (super-threshold) : MD and KMC-Simulations: Interstitial trapping**

- **DSSL/HSSL (sub-threshold) : Insights from MD : Vacancy formation at surface**

- **Conclusions /Outlook : Falsifikation: E.g. experiment with simultaneous hydrogen exposure and low-energy Xe-ion surface irradiation**

References:

[1] L. Gao, W. Jacob et al., Deuterium supersaturation, Nucl. Fus. 57(1) (2016) 016026

[2] J.N. Mundy, S.T. Ockers, L.C. Smedskjaer, Vacancy migration enthalpy in tungsten at high temperatures, Argonne National Laboratory

[3] G. Bonny et al., Many-body central force potentials for tungsten, Mod. Simul. Mater. Sci. 22 (2014) 053001 and references therein

[4] D. Kato, H. Iwakiri, K. Morishita, First-principle study on binding energy of vacancy-hydrogen clusters in tungsten, Plasma Fusion Res. Series Vol 8 (2009), p. 404-407

[5] L. Gao, M. Wilde, A. Manhard, U. von Toussaint, W. Jacob, Hydrogen atom-ion synergy in surface lattice modification at sub-threshold energy, Acta Materialia 201 p. 55-62 (2020)

Parameters

- Simulation parameters for displayed data:

e_trap=(/1000.0,1.3,0.8,0.7,0.6,0.6/) ! Hydrogen trapping-energies [eV] in VH-complexes

e_diff_vac=(/1.5,1.8,2.3,2.5,2.6,2.6/) !mobility of VH_i
Conc_H0 (300K) = 2.3d-5
H-Diffusion: Frauenfelder (D0=4.1d-7 m**2/s , Ea=0.39 eV)
p_forward=0.47
Kicks = 800 1/s
T = 300 K
Time-step = 2.677d-8 s