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Molecular Dynamics of H Cottrell Atmosphere Formation in Al—Influence of Non-Dilute Concentration at Dislocation Cores

H-Mat Hydrogen Materials Compatibility Consortium

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U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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Hydrogen + Dislocations: How do they get along?

H is important fuel and proper storage is important, however it also leads to Hydrogen Embrittlement (HE)

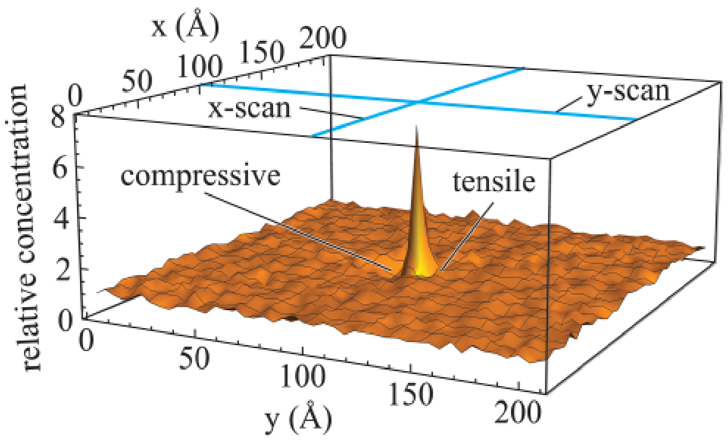
To understand HE we must understand where H is going. Even with typically low H solubilities, enrichment near defects can result in HE.

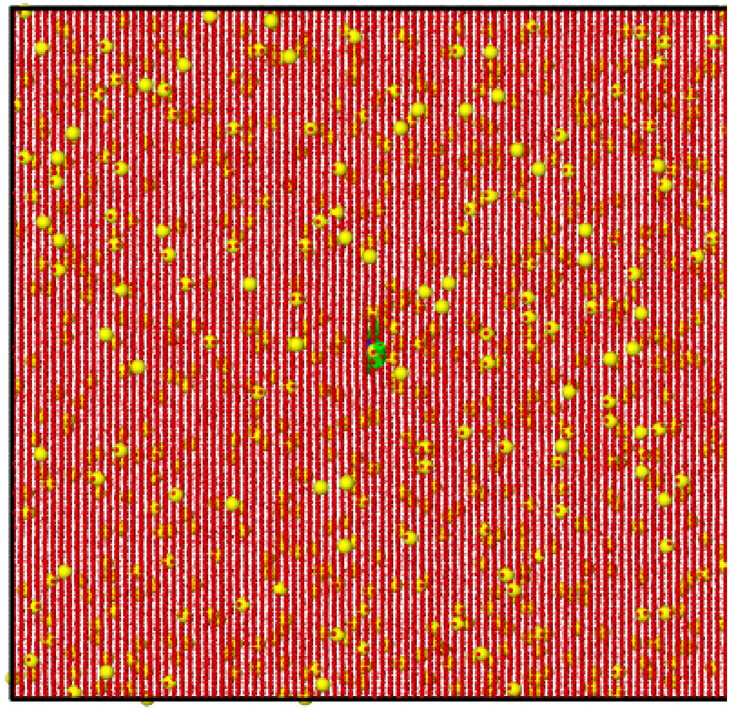
H-enhanced local plasticity(HELP) is a common theory used to explain the origin of HE that is concerned with Cottrell atmosphere.

To better understand HELP we focus on the formation of atmospheres in Al

Outline

- MD simulation setup
- Transient formation of a H Cottrell atmosphere
- Compare and contrast to theoretical expressions
- Solute-Solute interactions at the core





Manuscript for the presented work has been submitted

Previous work

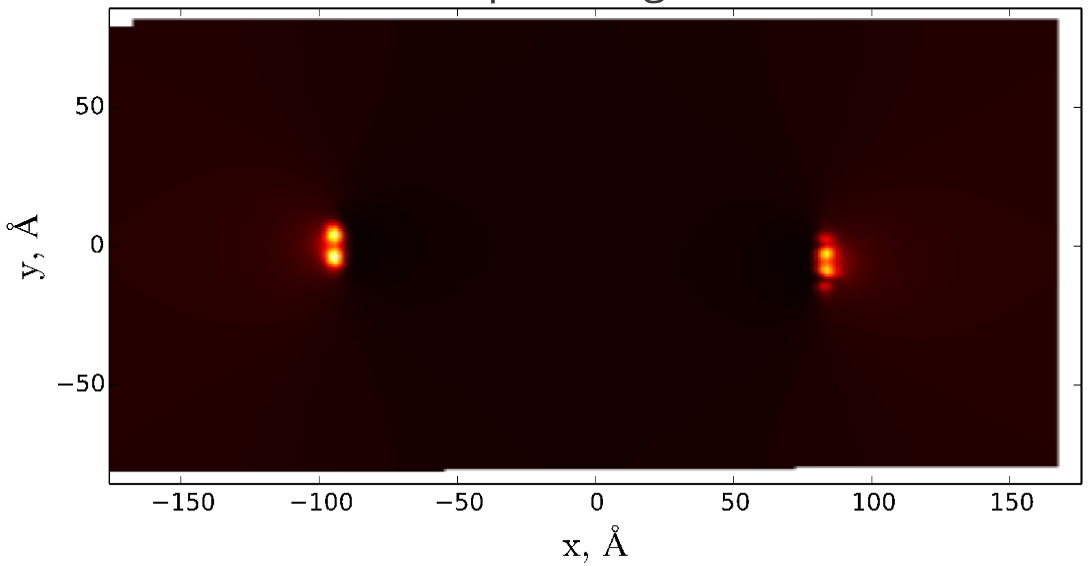
Molecular statics can calculate H insertion energy, E_{ins}

Models and theories rely on E_{ins} to understand atmosphere behavior

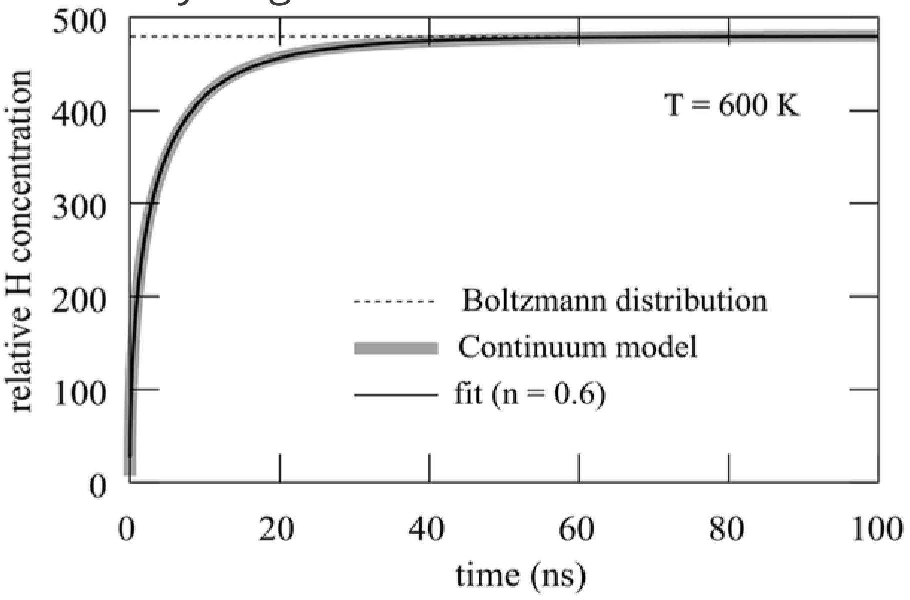
MD work with Cottrell atmospheres has been done but not on the transient formation

Understanding formation helps inform HELP

Boltzmann Heatmap for Edge Dislocation: Al-H



Peak Hydrogen Concentration Saturation



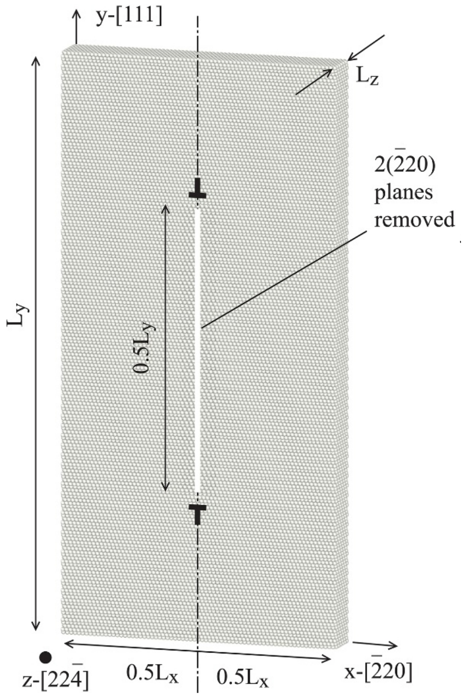
Difficulty simulating atmosphere

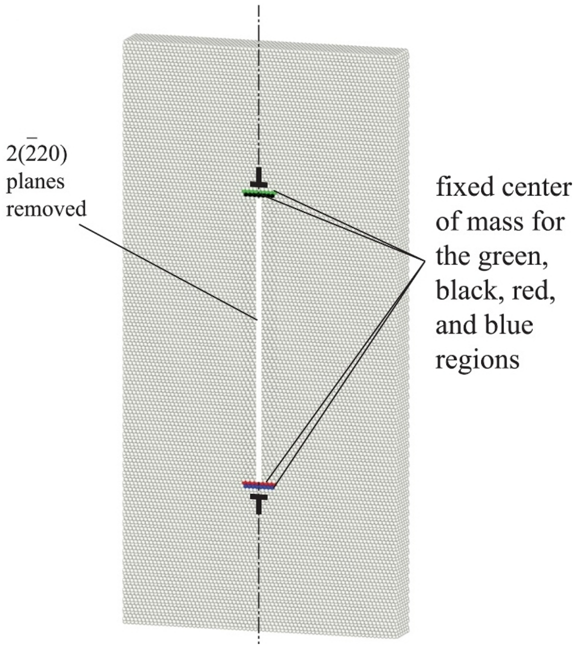
On MD time scales, 300K shows slow H diffusion

Low Peierls stress materials edge bounces around

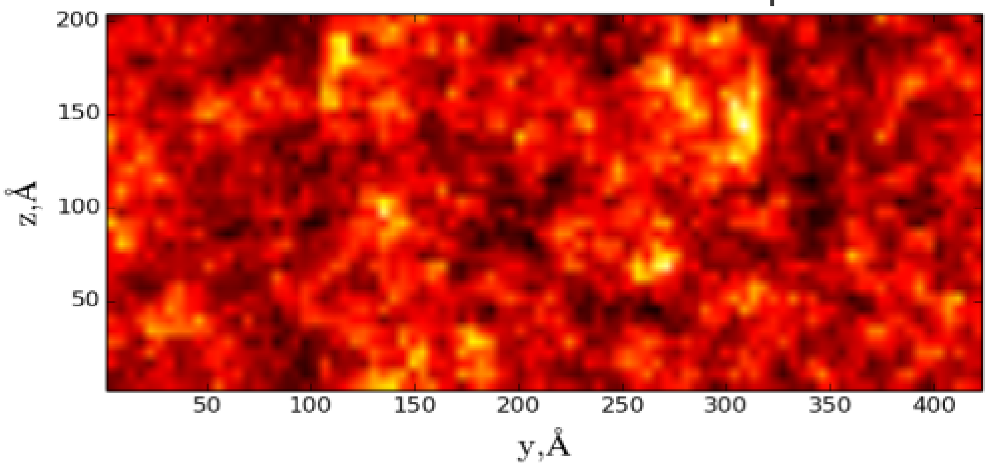
Dislocation needs to stay stationary.

Recenter the c.o.m. on partial planes to keep in place

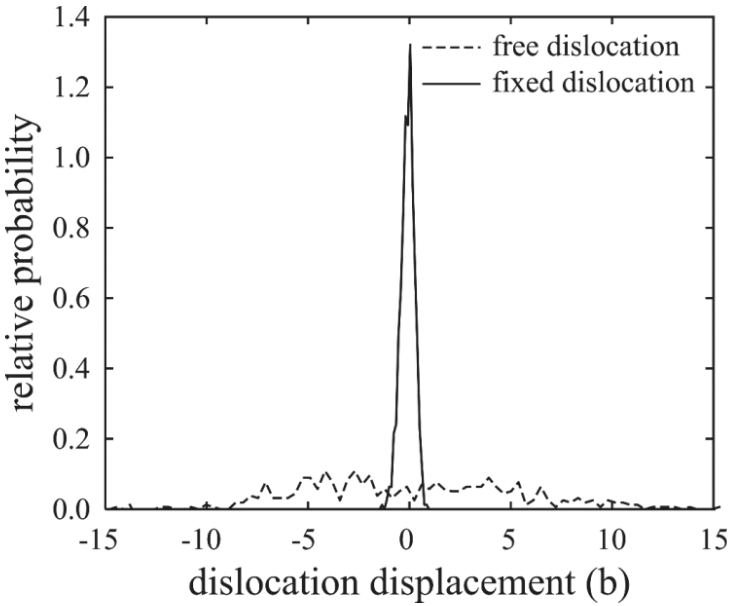


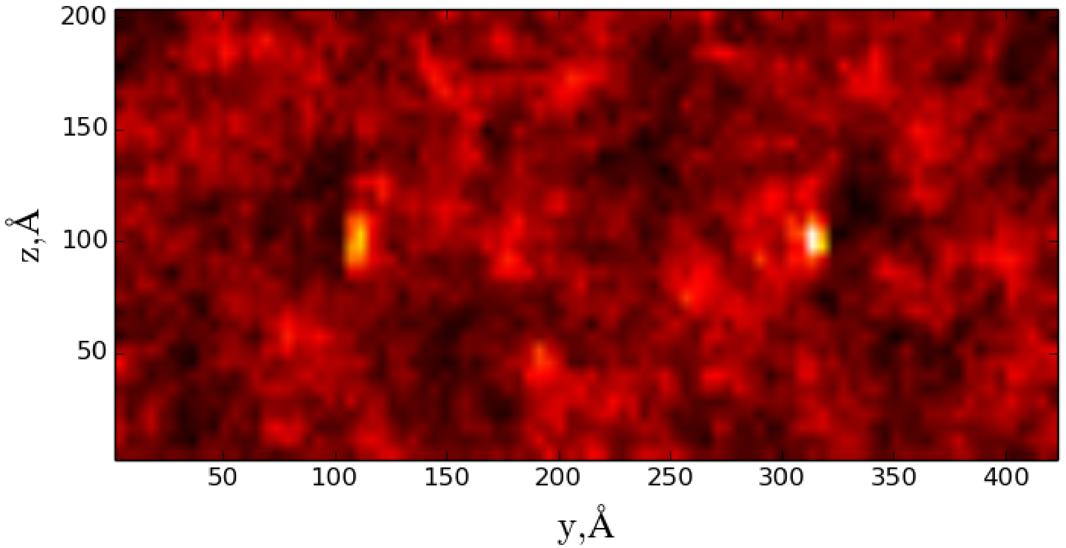


H Concentration Map



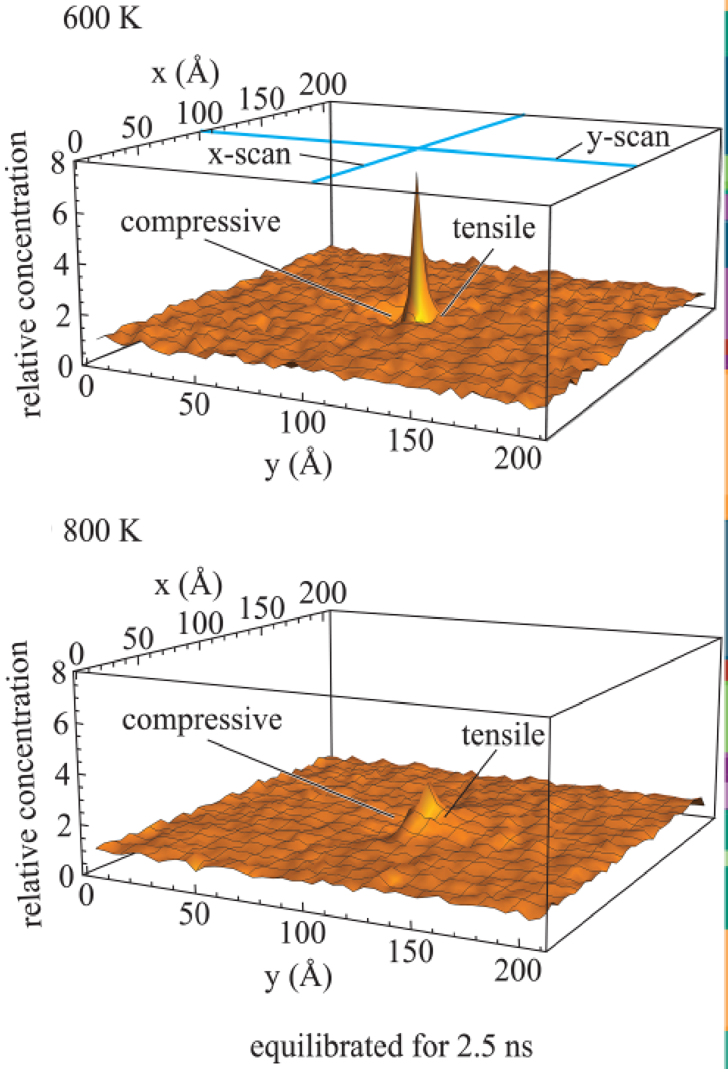
MD mediated atmosphere formation





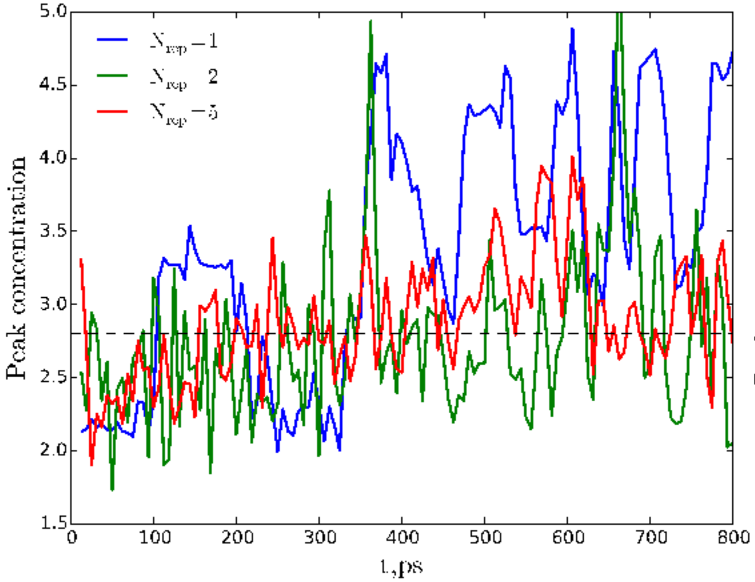
Dislocation remains in same spot

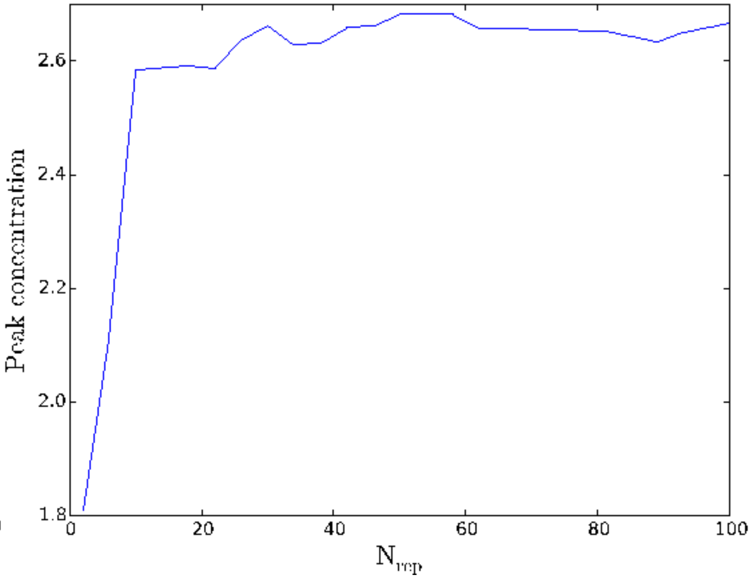
Shows characteristics of edge strain field



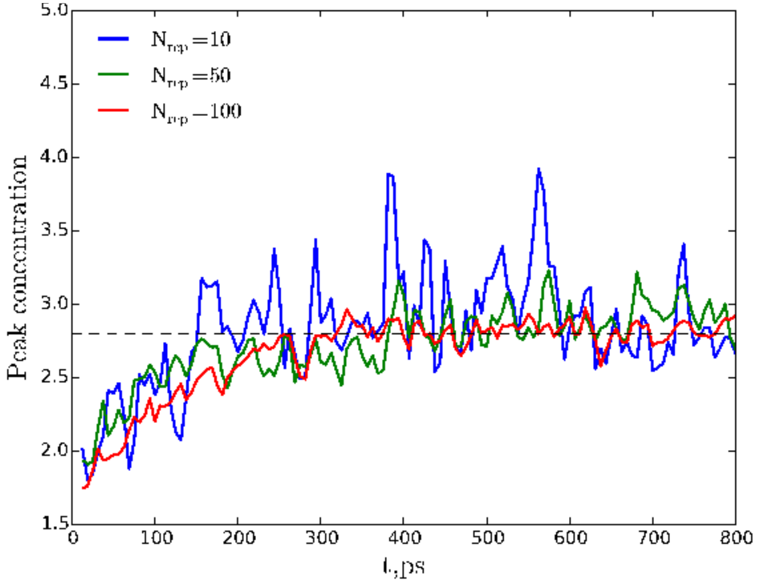
Convergence Calculations

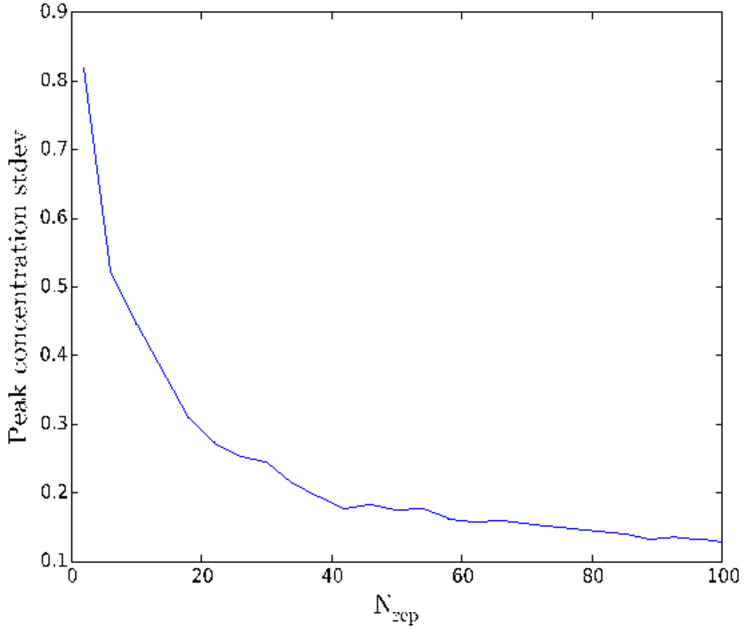
With more replicas the trend becomes apparent





With more replicas the curves smooths out





Alloying will increase the noise

How does it match theory?

Fit to Cottrell theory shows good agreement

$$\hat{X}(t) = X_0 + (X_{sat} - X_0)\left\{1 - e^{-(t/t^*_{cl})^{2/3}}\right\}$$
$$t^*_{cl} = \sqrt{2}b^2\, k_B T / DW (X_{sat}/X_0)^{3/2}$$

$$\frac{t^*_{cl}(600\text{K})}{t^*_{cl}(800\text{K})} \sim 27$$

800 K plateaus ~0.25 ns → ~6.7 ns at 600K

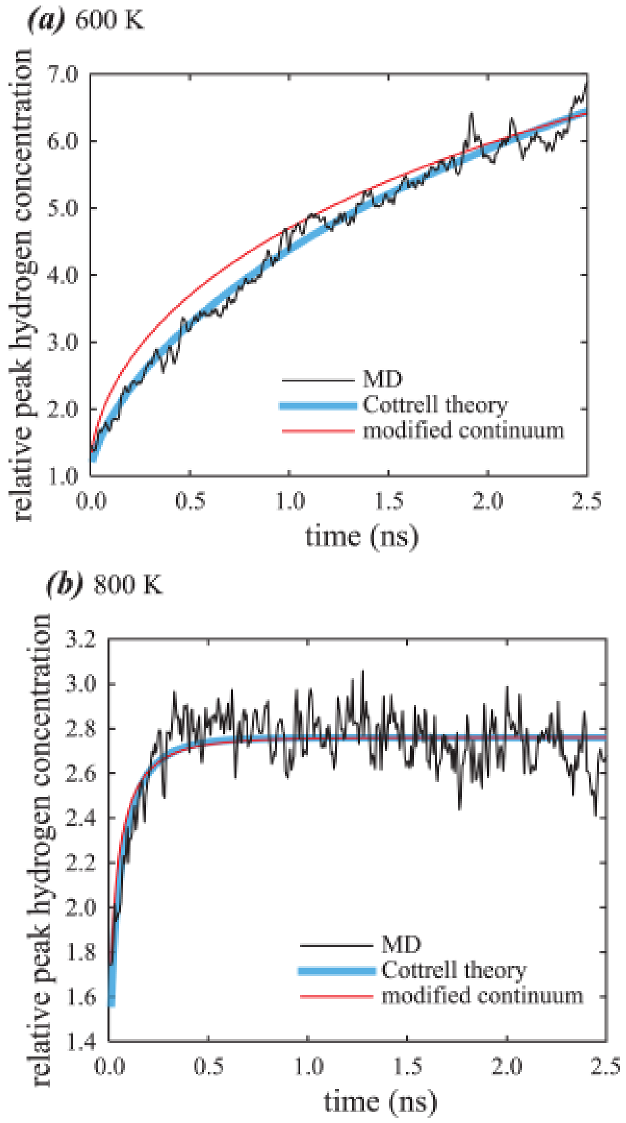
Epperly and Sills theory accounts for finite atmosphere also shows good agreement

$\hat{X}(t)$=peak concentration
X_{sat} =saturation concentration
X_0 =background concentration
t=time

b=Burgers magnitude
k_B =Boltz const
T =temp
D =diffusivity
$W = |min_x p_d(\boldsymbol{x})\Delta V|$

$X_0 = 1$
$X_{sat}(800\text{K}) \approx 2.8$
D ≈ 2.73 nm²/ns
W ≈ 0.2 eV
t^*_{cl}(800K)=0.0684 ns

600K fit data with X_{sat} as a free param
$X_{sat}(600\text{K}) = 8.3$
$t^*_{cl}(600\text{K}) = 1.830$ ns



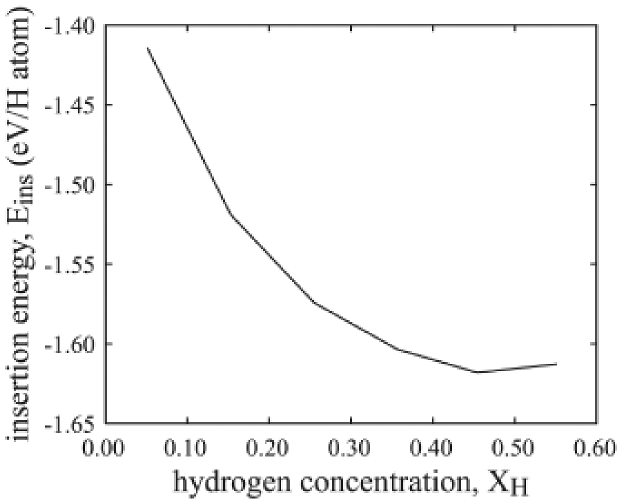
Cottrell & Bilby *Proc. Phys. Soc.* **62**, 49 (1949)
Epperly & Sills *J. Mech. Phys. Solids* ***141***, 103944 (2020)

Theoretical Overestimation of Peak Concentrations

The peaks estimated by MD are much lower than predicted

E_{ins} must be less favorable near dislocation

Bulk Al E_{ins} more attractive with more H

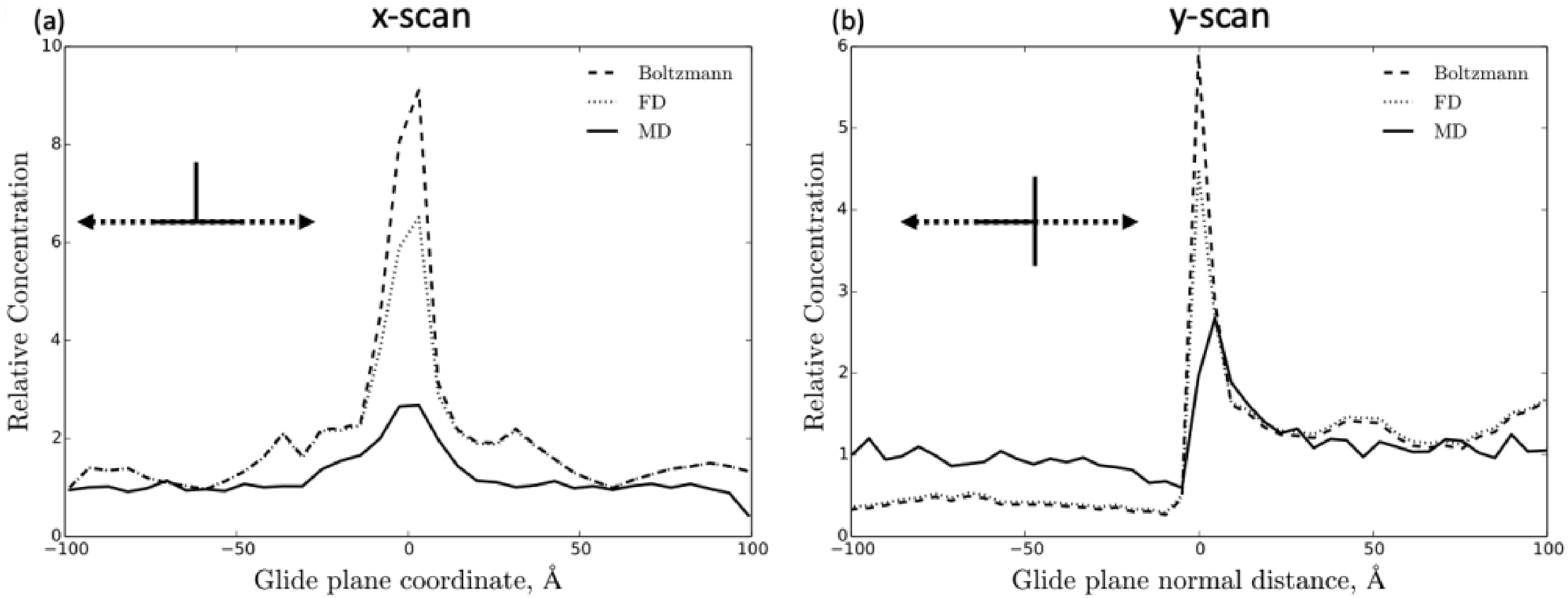


Boltzmann:

$$p_i = e^{-\frac{E_i}{k_b T}}$$

Fermi-Dirac:

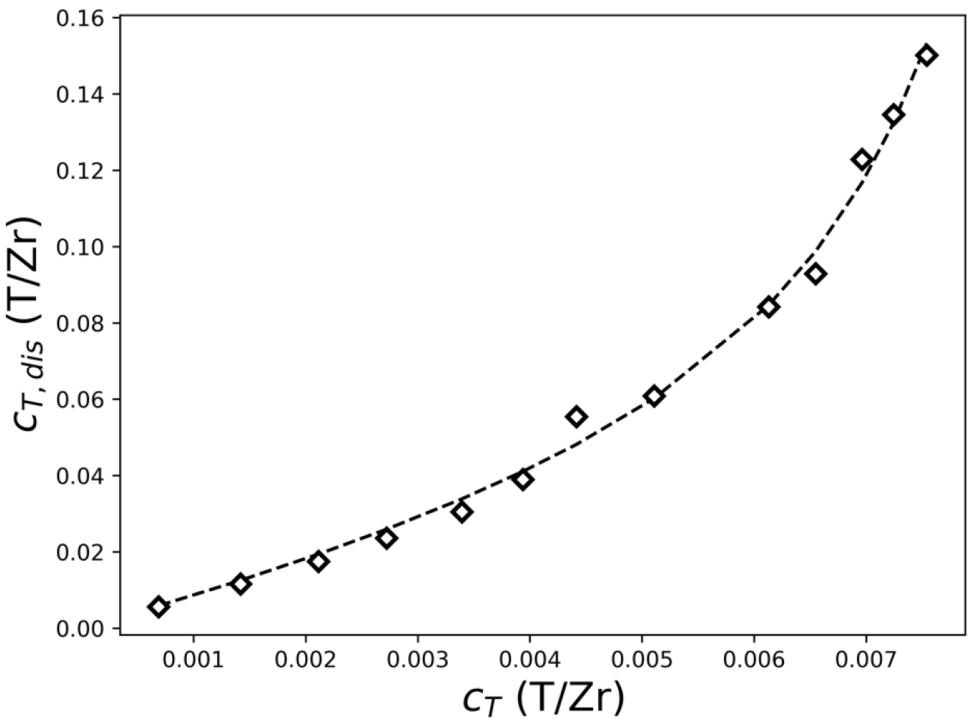
$$n_i = \frac{1}{e^{-(E_i - \mu)/k_b T} + 1}$$



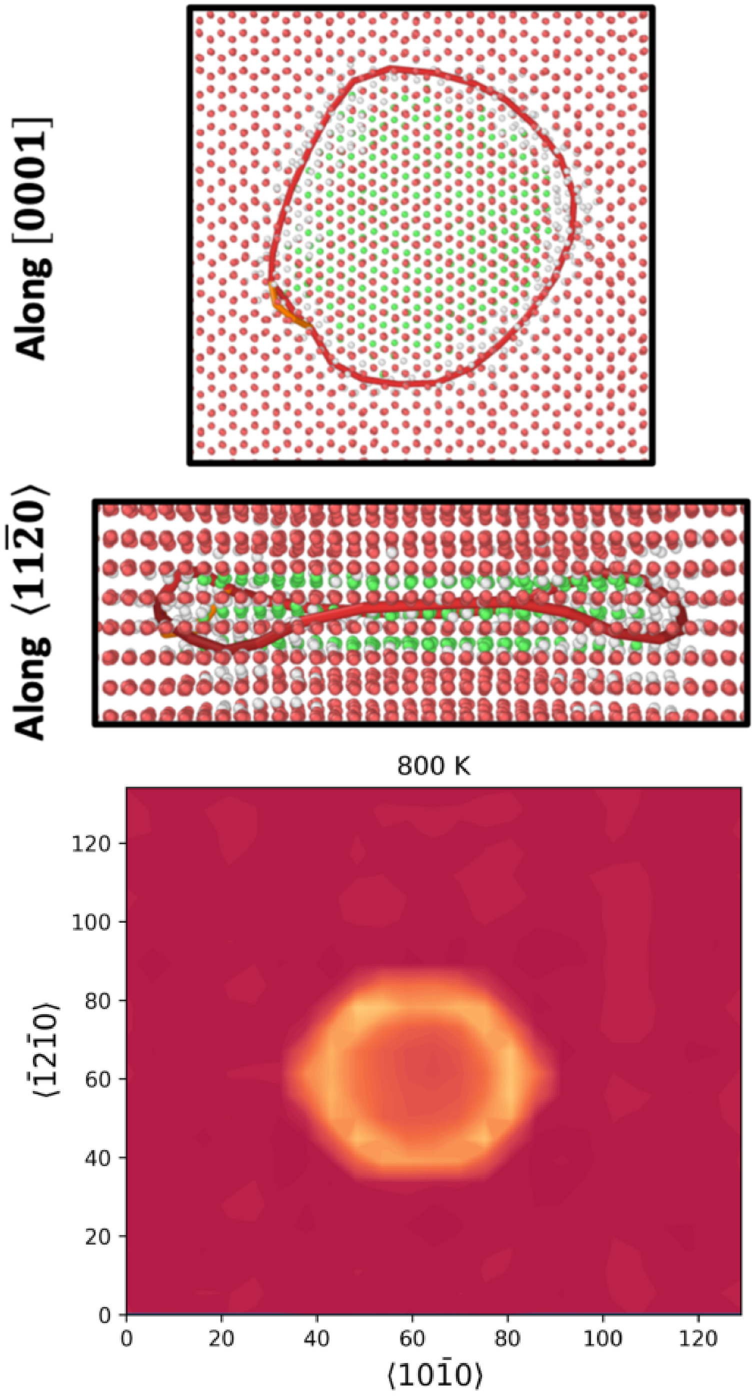
Solute-Solute Interaction in Zr-T*

T-T interactions in HCP Zr also show a solute-solute effect

With more T loading enrichment increases at vac-type dislocation loop.



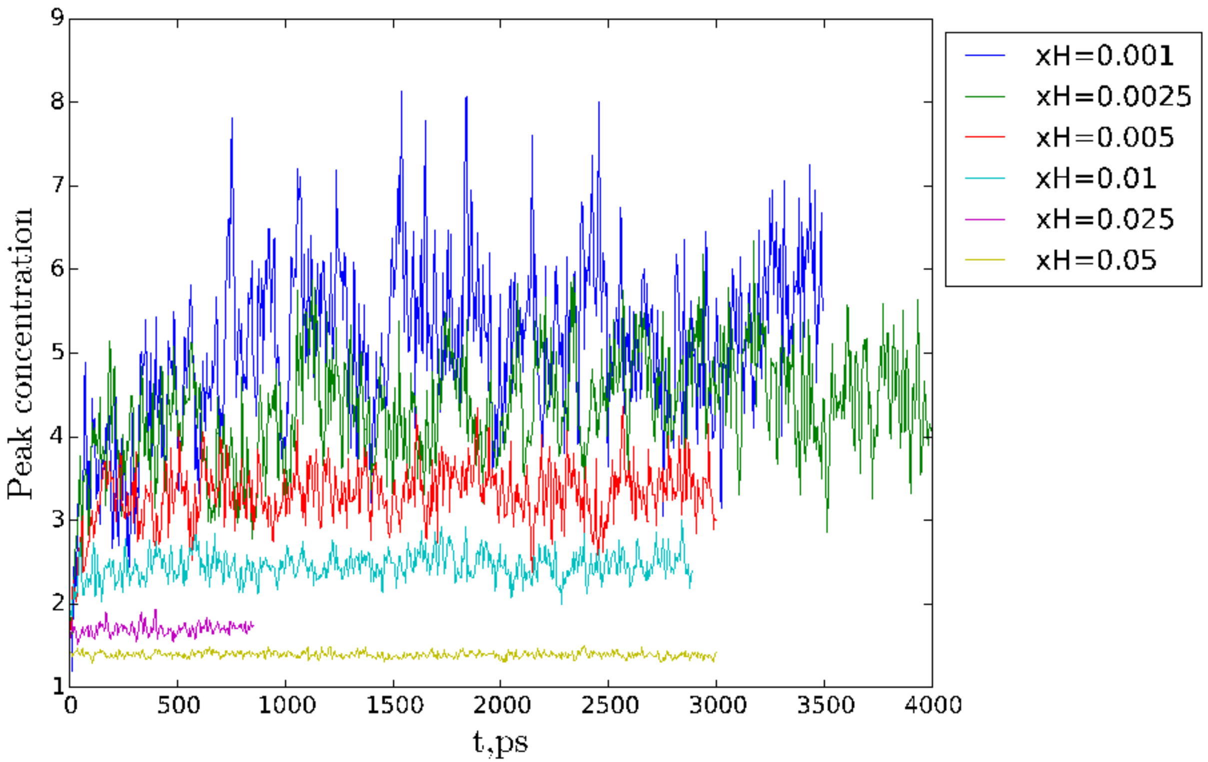
Fitting to equations reveals a strong T-T interaction.

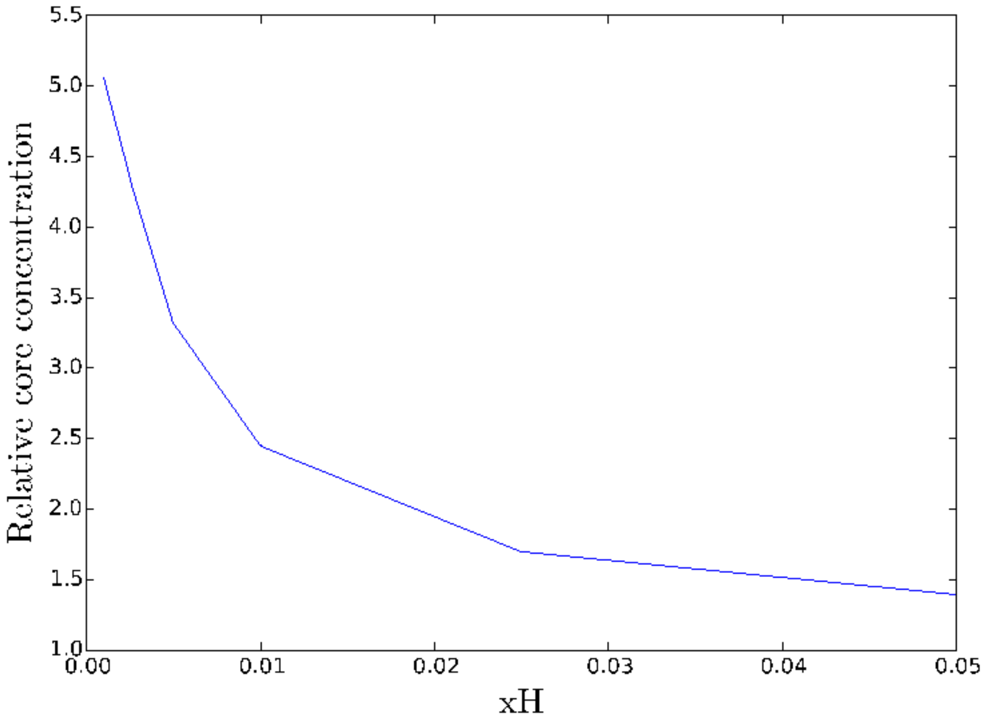


*Skelton, et. al. manuscript submitted

Solute-Solute Interaction in Ni-H

- This phenomenon is observed in systems outside of Al-H
- Ni-H systems with variable loading of H show different enrichment at the core



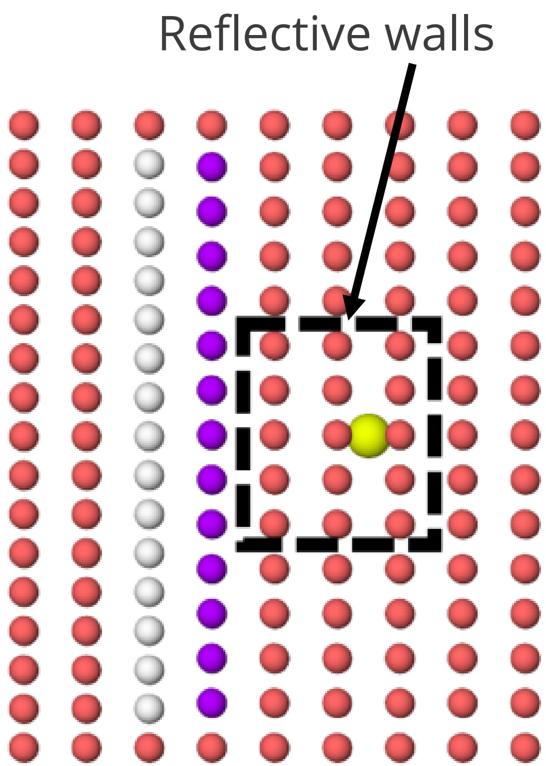


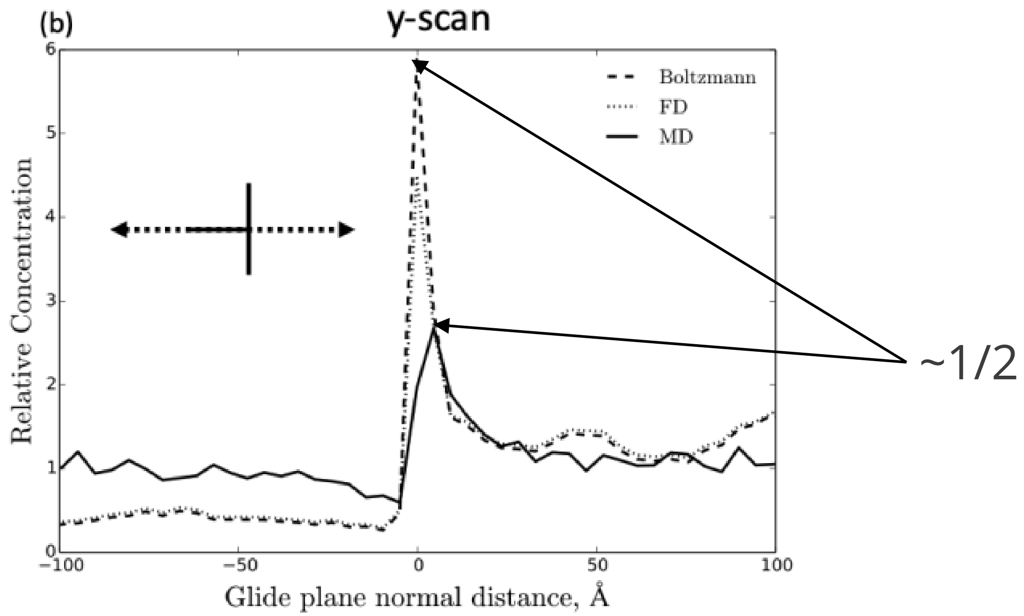
Measuring Solute-Solute Interactions

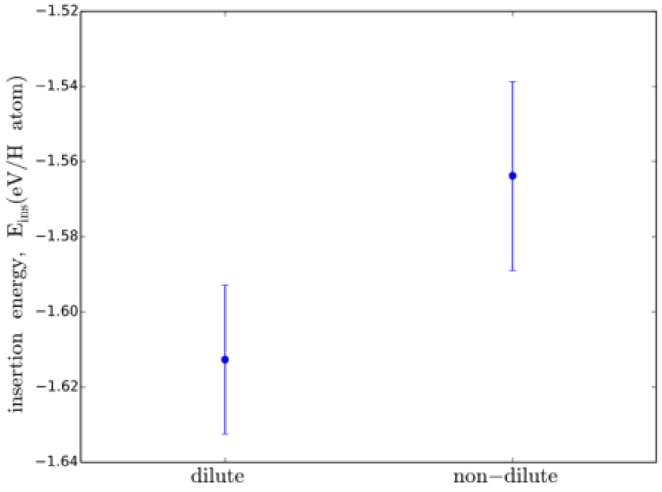
To measure the effects of having nearby H, use reflective walls

Time-average simulation with 1 (dilute), or 2(xH~.01) H in the box

A change of 50meV leads to the enrichment at the dislocation of ~1/2 the dilute enrichment

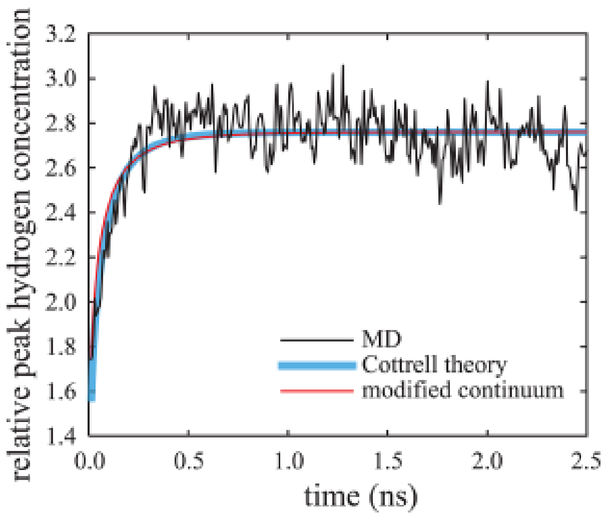


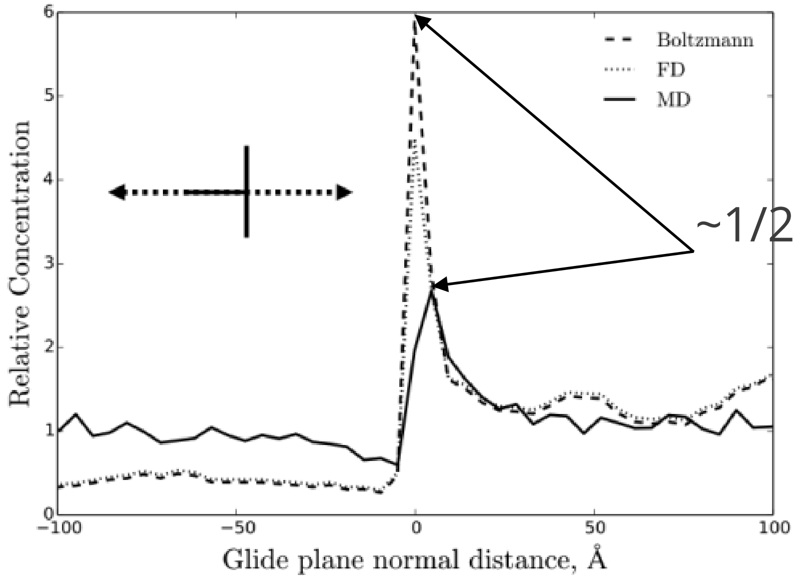




Conclusions

- Simulated the transient formation of hydrogen Cottrell atmospheres
- Compared to theoretical expressions
- Calculated the solute-solute interactions near a dislocation
- Solute-Solute Interactions should be considered



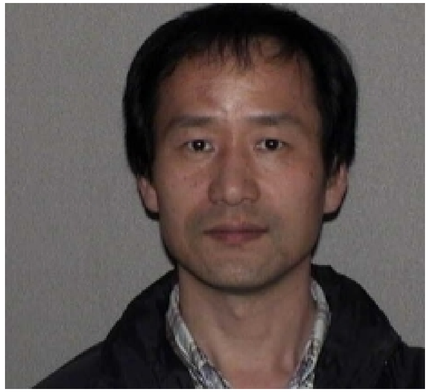


Acknowledgements*

*Due to work from home, hair/facial hair may have changed

Catalin Spataru (SNL)

Kevin Chu(Ga. Tech)



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Chris San Marchi (SNL)

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Thank you to DOE's H-MAT program for funding this work.

Thanks for your time, questions?

Extra Slides

Running average to Instantaneous value

$$\overline{X_H}(x,y,t) = \frac{1}{t}\int_0^t X_H(x,y,t)dt$$

$$X_H(x,y,t) = \frac{\partial[t \cdot \overline{X_H}(x,y,t)]}{\partial t}$$

$$\mathrm{X}_{H,exp}(\mathrm{x},\mathrm{y},\mathrm{t}) = \mathrm{C}_H \mathrm{X}_H(\mathrm{x},\mathrm{y},\mathrm{t})$$

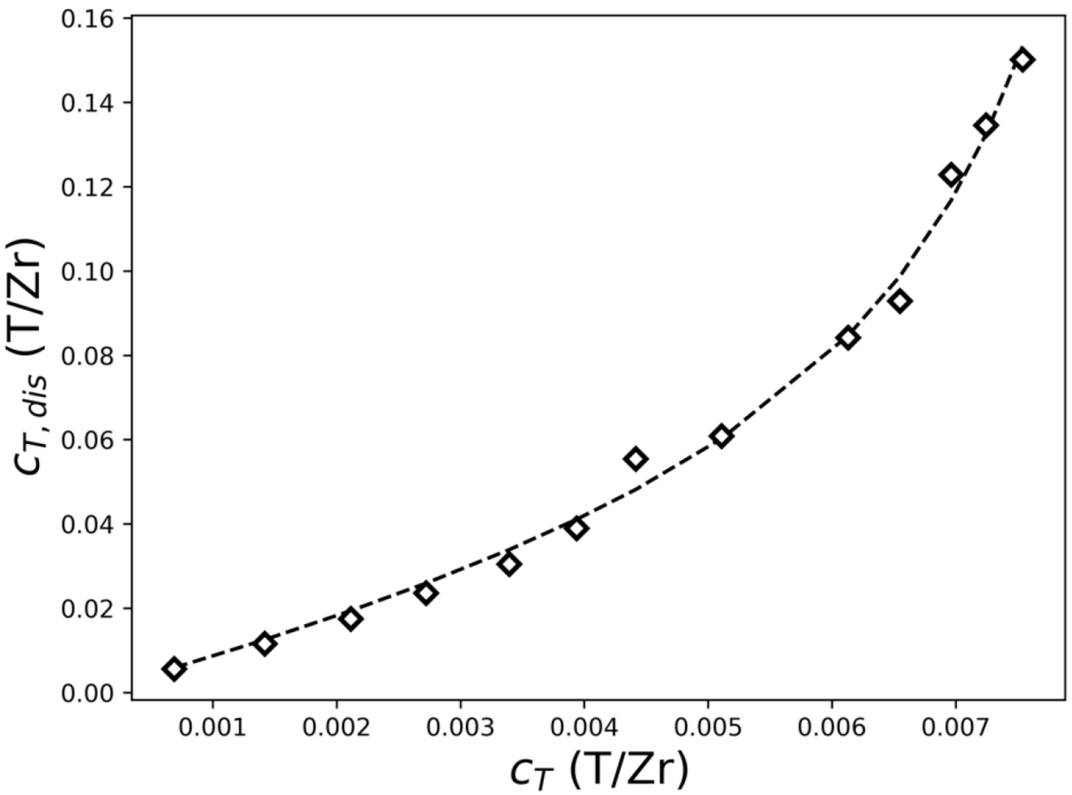
$$\frac{\partial f_i}{\partial t} = \begin{cases} d_{i,1,0}, i = 2 \\ d_{i,1,-1}, i = 3 \\ \frac{15d_{i,1,-1} - 6d_{i,2,-2} + d_{i,3,-3}}{10}, 4 \le i \le N-2 \\ \frac{4d_{i,1,-1} - d_{i,2,-2}}{3}, i = N-1 \\ d_{i,1,-1}, i = N \\ d_{i,0,-1}, i = N+1 \end{cases}$$

Zr-T Solute-Solute Interactions

$$E\left(c_{T,dis}\right) = E_0 + c_{T,dis}E_{TT}$$

$$c_{T,dis}/(1 - c_{T,dis}) = c_T/(1 - c_T)\exp\left[-\frac{E_0 + c_{T,dis}E_{TT}}{k_B\mathrm{T}}\right]$$

E_0 = -0.127±0.002 eV and E_{TT} = -0.363±0.024 eV



Example of out-of-date Pictures