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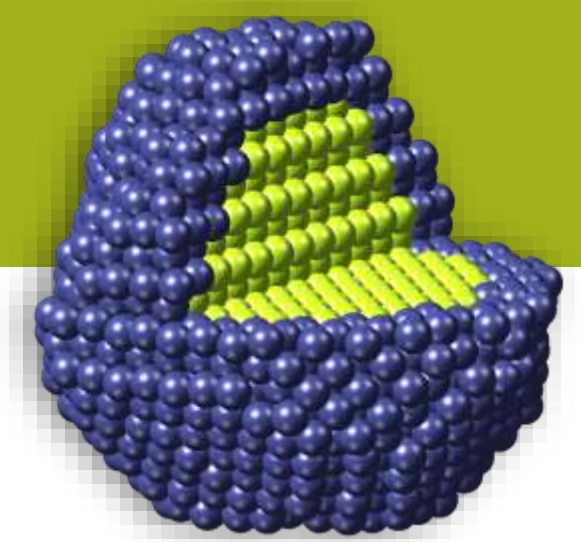

WEBINAR

Diffusion and You:
Batteries, Catalysis, Alloys, Corrosion, and the Stock Market

Erich Wimmer and Benoît Minisini
Materials Design

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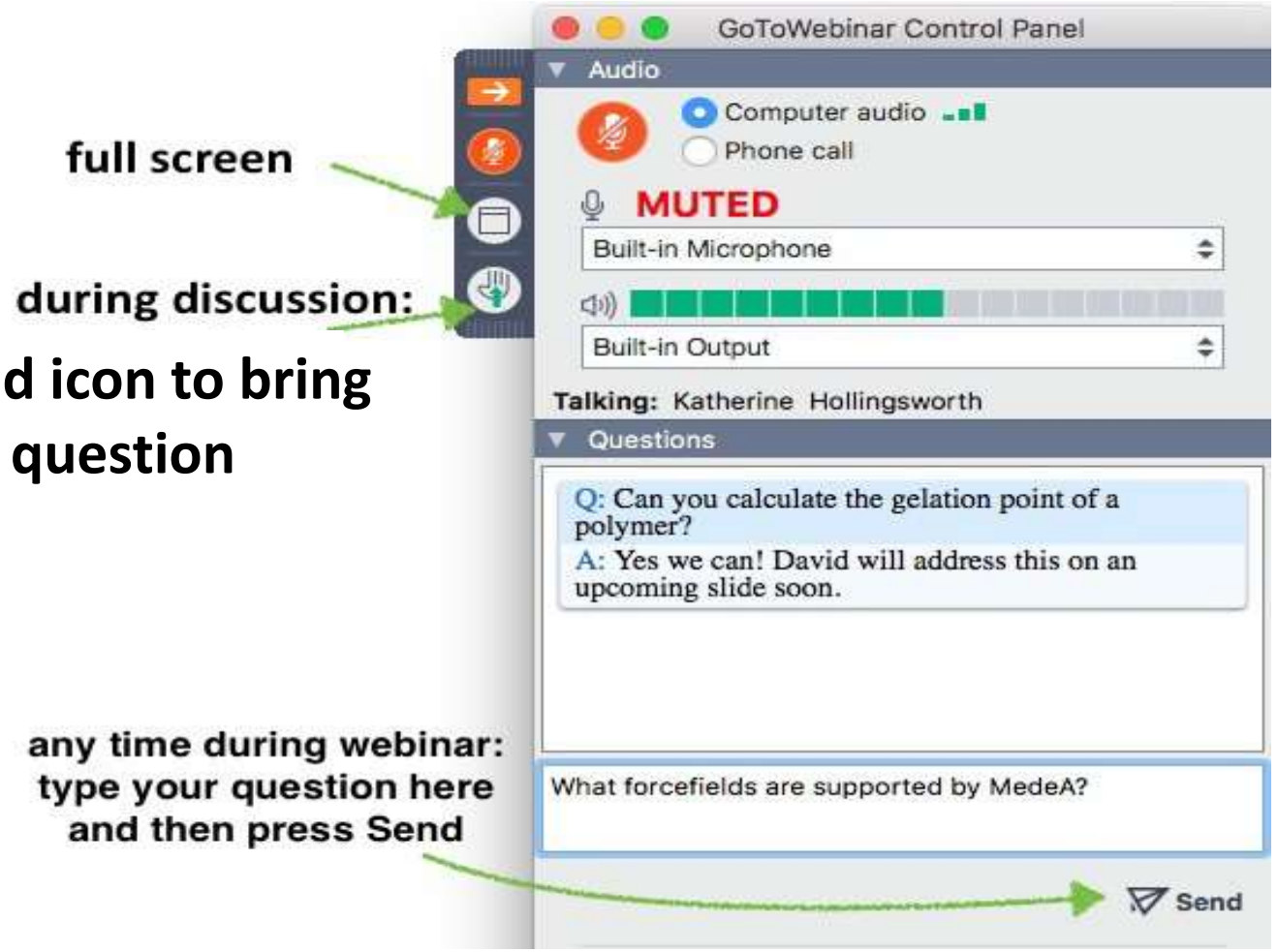


Use the raise hand icon to bring attention to your question

Webinar Speakers

Katherine Hollingsworth
khollingsworth@materialsdesign.com

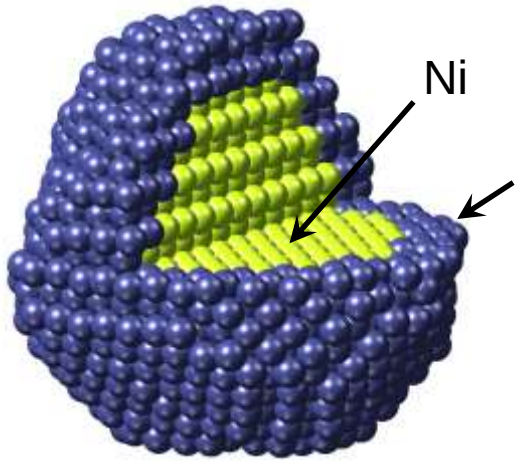
Erich Wimmer
ewimmer@materialsdesign.com

Benoît Minisini
bminisini@materialsdesign.com

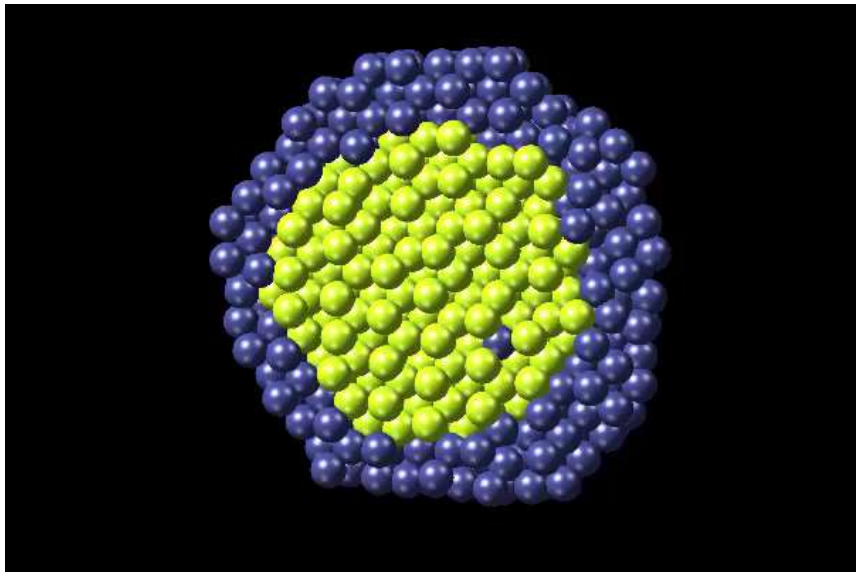
Outline

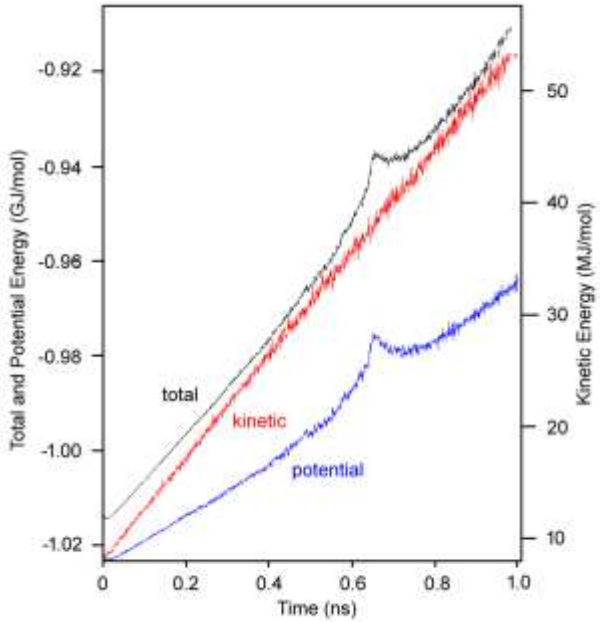
- The omnipresence of diffusion processes
- Specific systems
  - Catalysis: Core-shell nanoparticles
  - Organic liquids
  - Li ion batteries: diffusion in
    - polymers
    - solid state electrolytes
  - Metal alloys:
    - ballistic diffusion
    - Soret effect
    - Diffusion in Au alloys
  - Diffusion and the stock market
  - Corrosion
- Summary and Conclusions

Catalysis: Core-Shell Nanoparticles

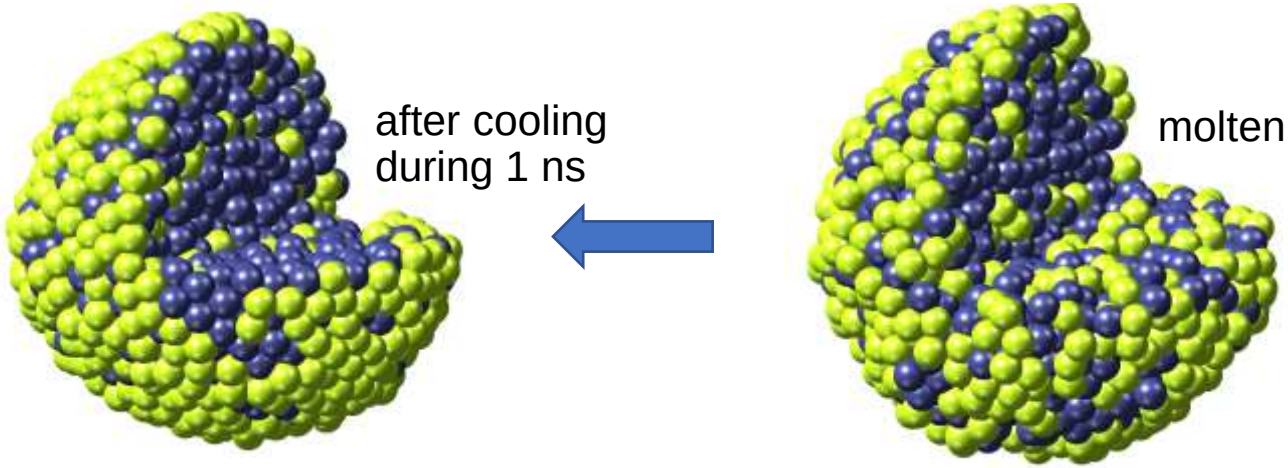


$Pt_{1356}Ni_{808}$



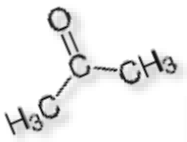


Molecular Dynamics with interatomic potential of Francis et al. [1] using *MedeA LAMMPS*

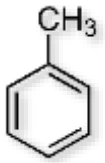


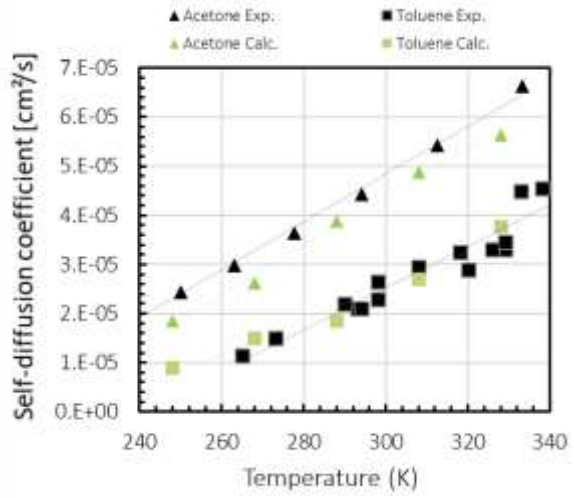
1. M. F. Francis, M. N. Neurock, X.W. Zhou, J.J. Quan, H.N.G. Wadley, and E.B. Webb, Journal of Applied Physics 104, no. 3: 034310 (2008)

Self-Diffusion in Organic Liquids

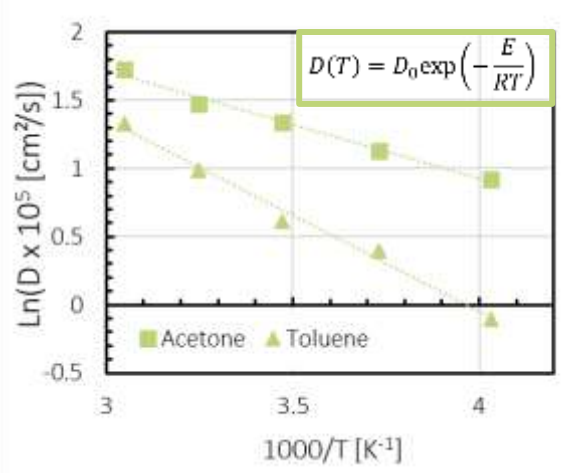


Dependence in temperature

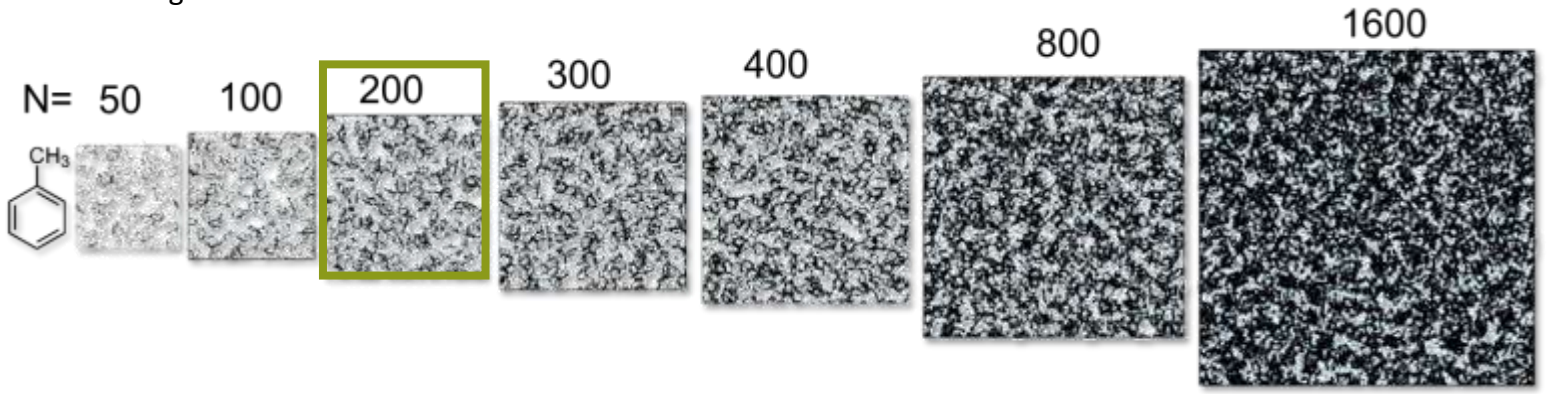




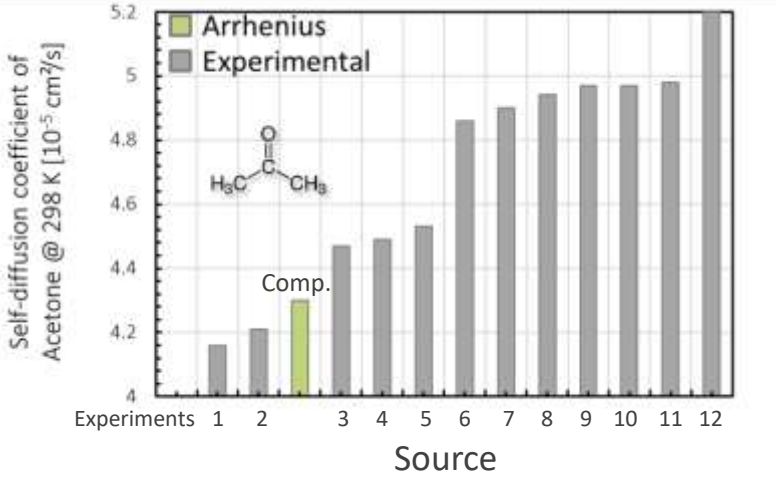
Acetone: Ertl H. et al. AICHE Journal, 1973, Vol. 19. 6, p. 1215-1223.
Toluene: Guevara-Carrion G et al. J. Chem. Phys., 2016, Vol. 144. p. 124501



MedeA LAMMPS, PCFF+, *MedeA LAMMPS Diffusion* module
2ns 1 configuration L ~ 30 Å

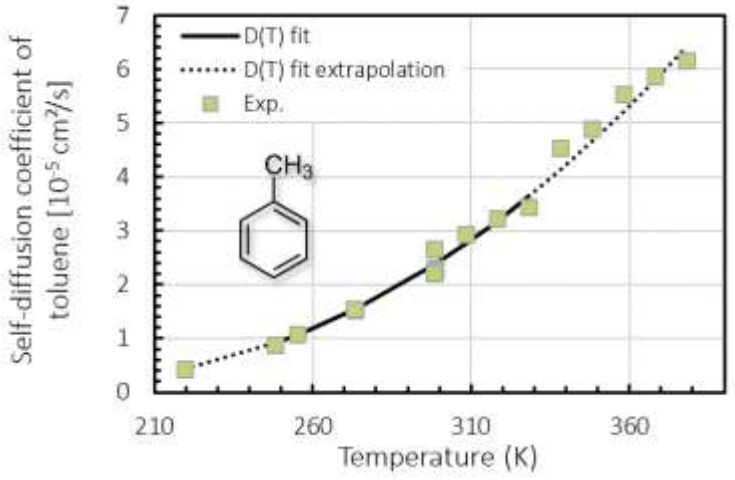


Interpolation



Exp.: Suarez-Iglesias O., Medina I., de los Angeles Sanz M., Pizarro C., Bueno J.L. : J. Chem. Eng. Data, 2015, Vol. 60. 10, p. 2757-2817

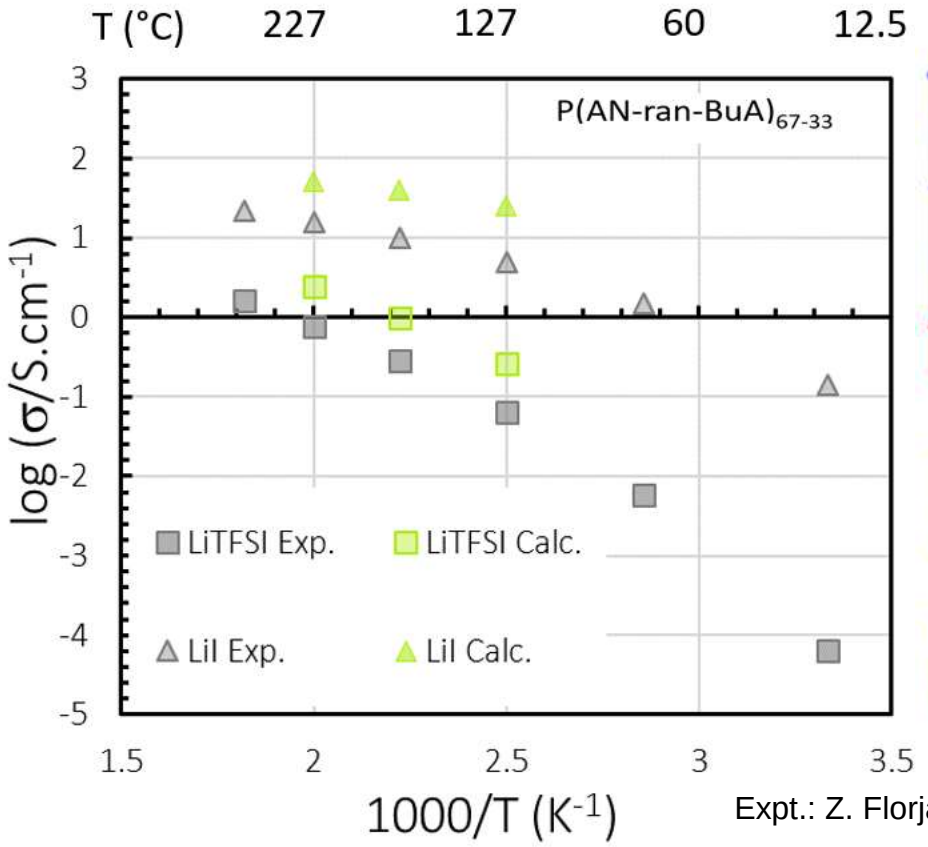
Extrapolation

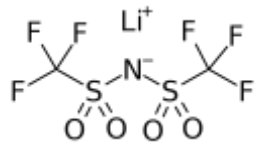


Exp: F.D., Pickup S et al. Technical Report # UMR-FDB-1 0, 1989

Li Ion Conductivity in Polymer Electrolytes

Random copolymer of acrylonitrile (AN) with butyl acrylate (BuA) in Li bis(trifluoromethanesulfone)imide (LITFSI) and Li iodide (LiI)

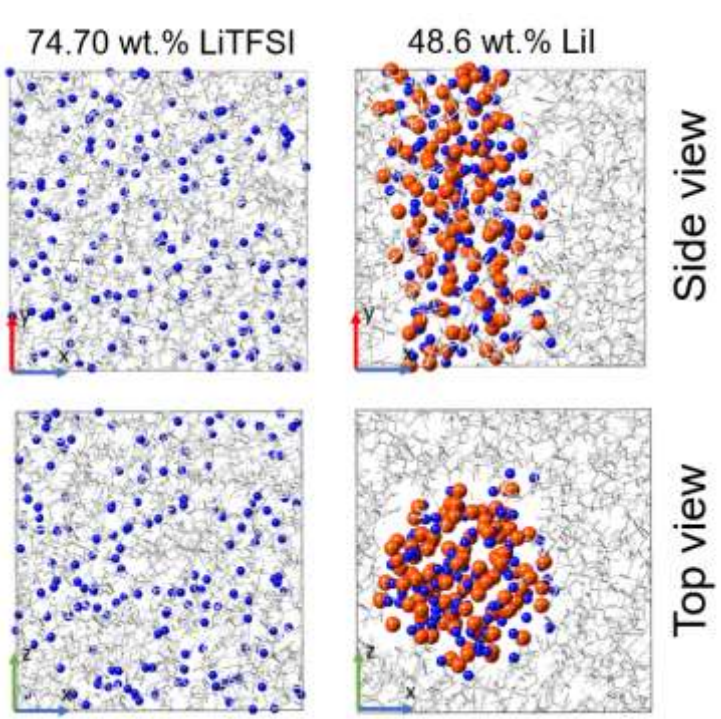


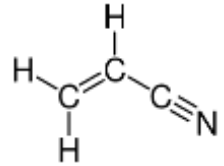


LiTFSI

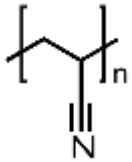
Li^+ I^-

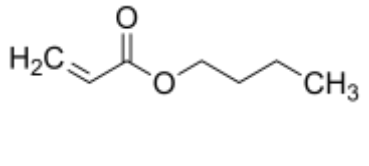
Lithium iodide



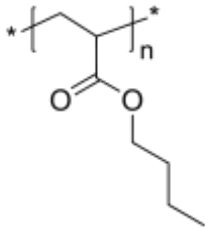


acrylonitrile





butyl acrylate

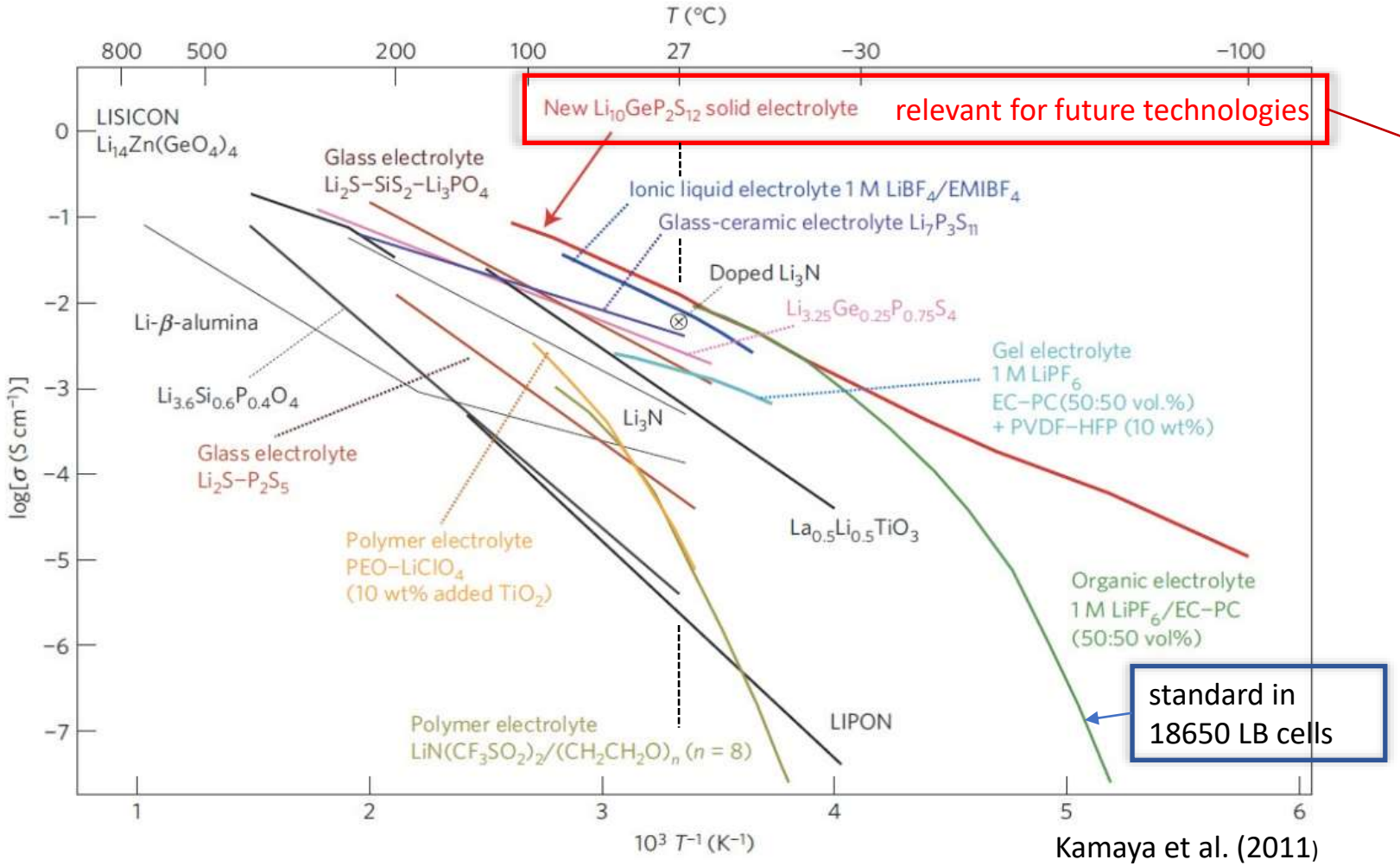


- LiTFSI is dispersed in the polymer matrix
- In the presence of LiI, molecular dynamics simulations reveal a phase separation leading to anisotropic diffusion and ionic conductivity.
- MD simulations in an electric field cause heating, which is used to determine the ionic conductivity.

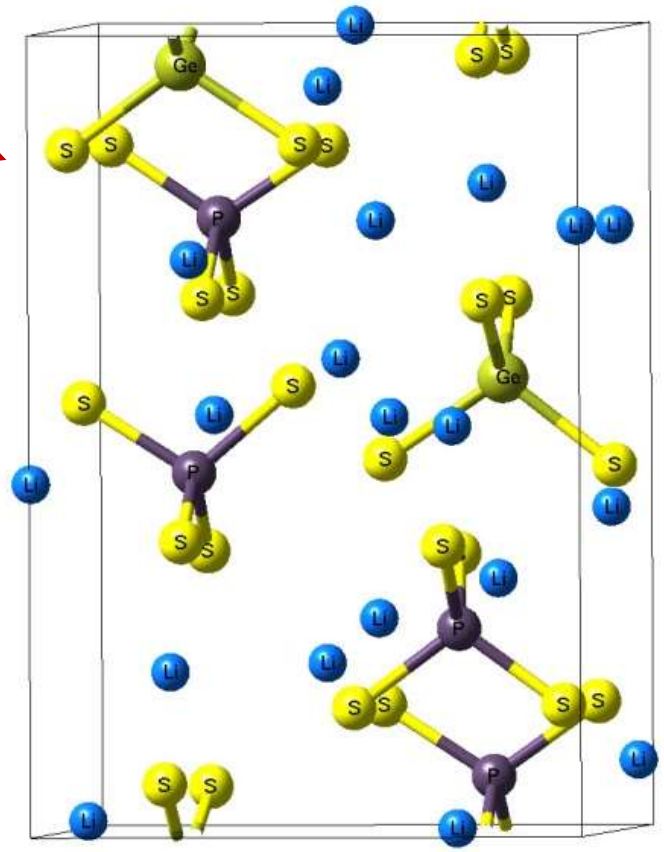
R. Windiks, B. Minisini, and A. Mavromaras, Advanced Automotive Battery Conference, Wiesbaden (2020)

Expt.: Z. Florjanczyk *et al.*, J. Phys. Chem. B 108 (2004) 14907-14914

Li Diffusion in Solid State Electrolytes

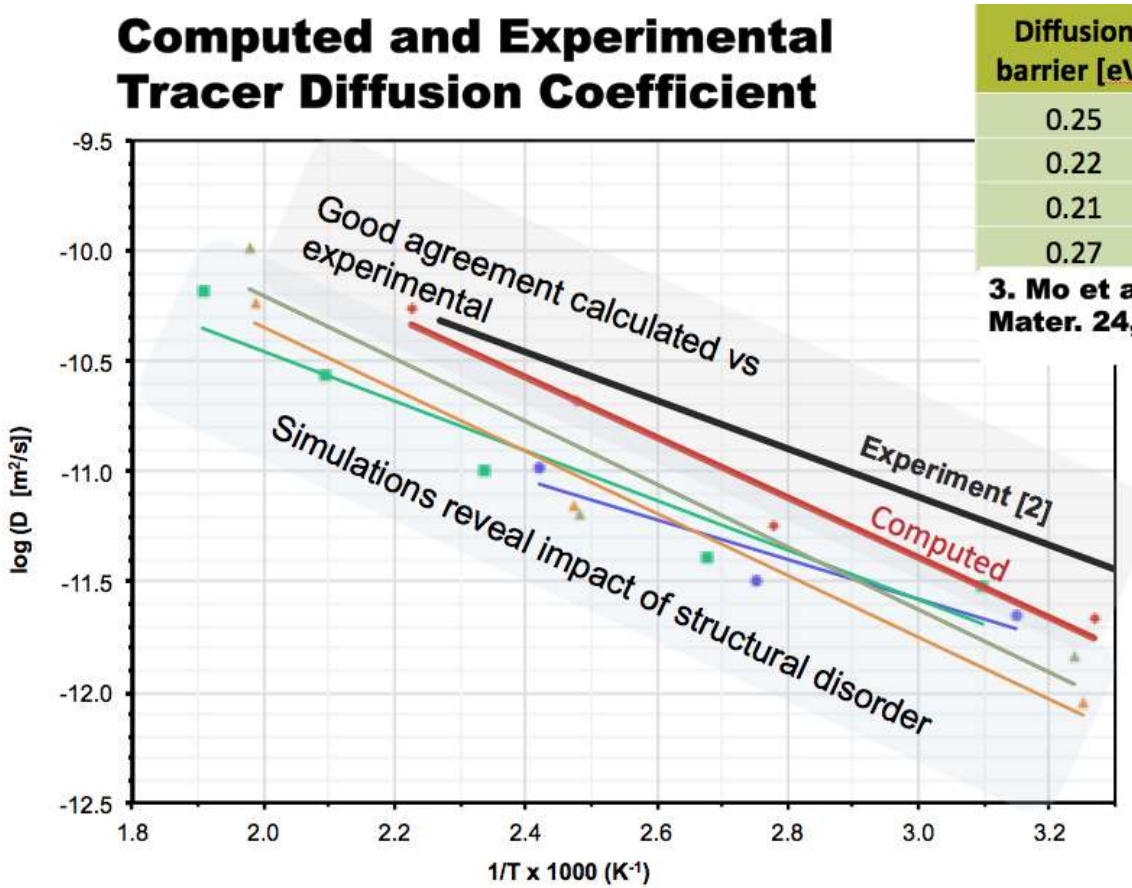


Kamaya et al. (2011)



Crystal structure of LGPS

Li Diffusion in Solid State Electrolytes



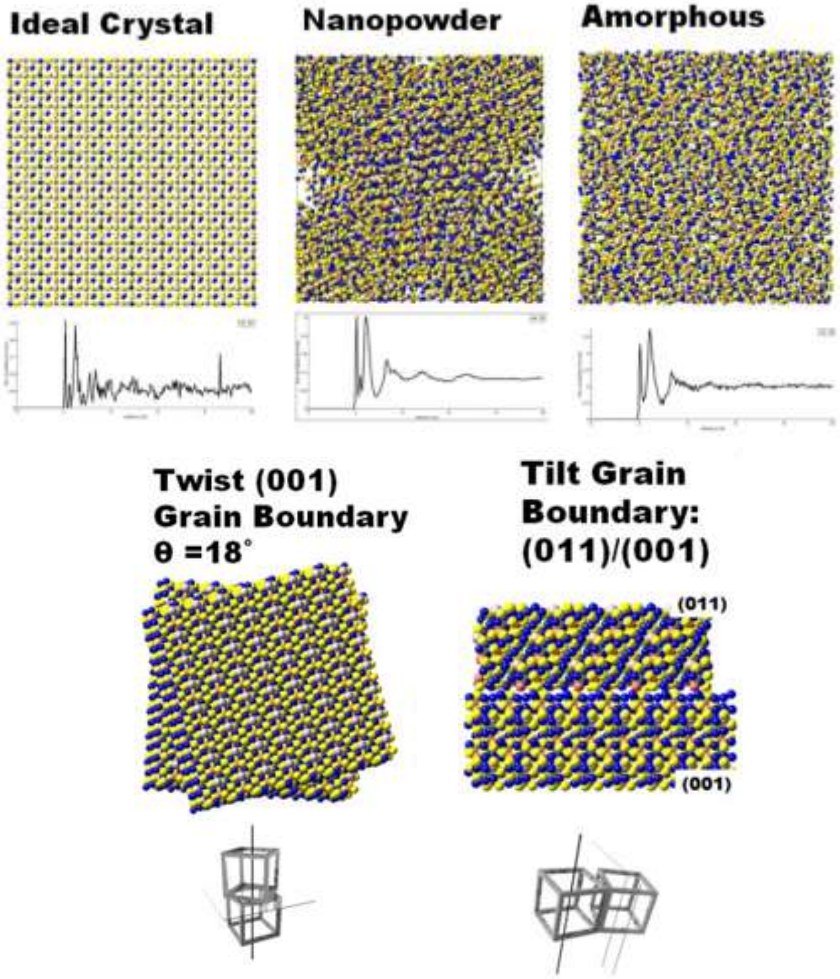
Diffusion barrier [eV]	Ref.
0.25	[1]
0.22	[2]
0.21	[3]
0.27	This work

Kamaya et al. (2011)
Kuhn et al. (2016)

3. Mo et al. Chem. Mater. 24, 15 (2012).

Computed Data

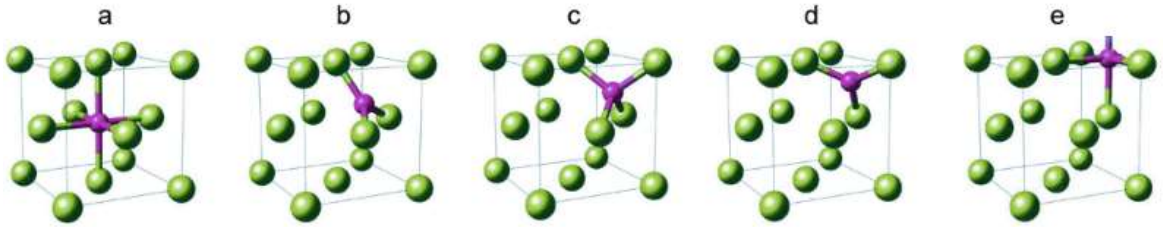
- Crystal
- Nanopowder
- Amorphous
- Tilt Grain Boundary:
- (011)/(001)
- Twist (001) Grain Boundary

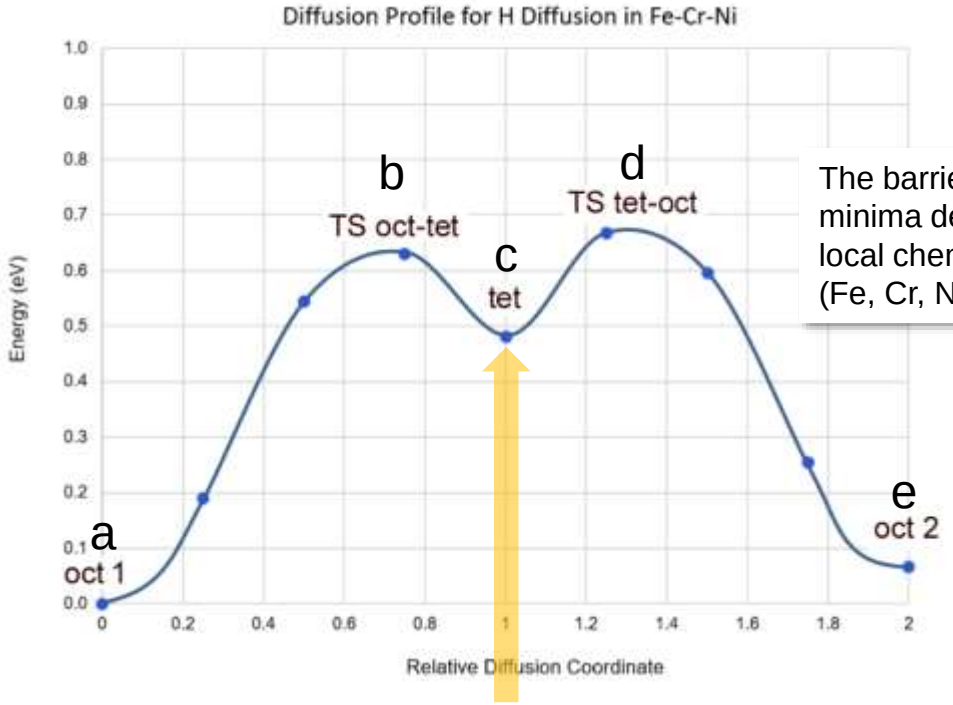


MedeA VASP
MedeA LAMMPS
MedeA Forcefield Optimizer

Nernst-Einstein relation
Ionic conductivity (σ) ∝ Diffusivity (D)

Diffusion of H in Steel

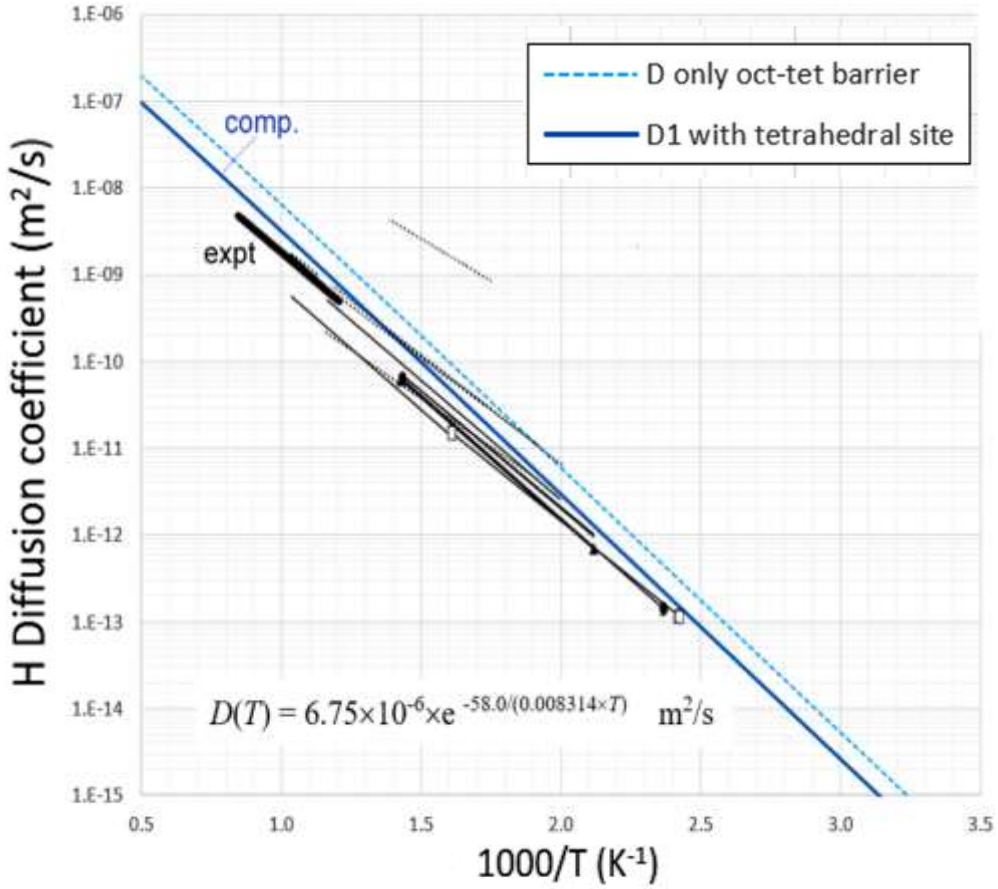




The barrier and local minima depend on the local chemical composition (Fe, Cr, Ni)

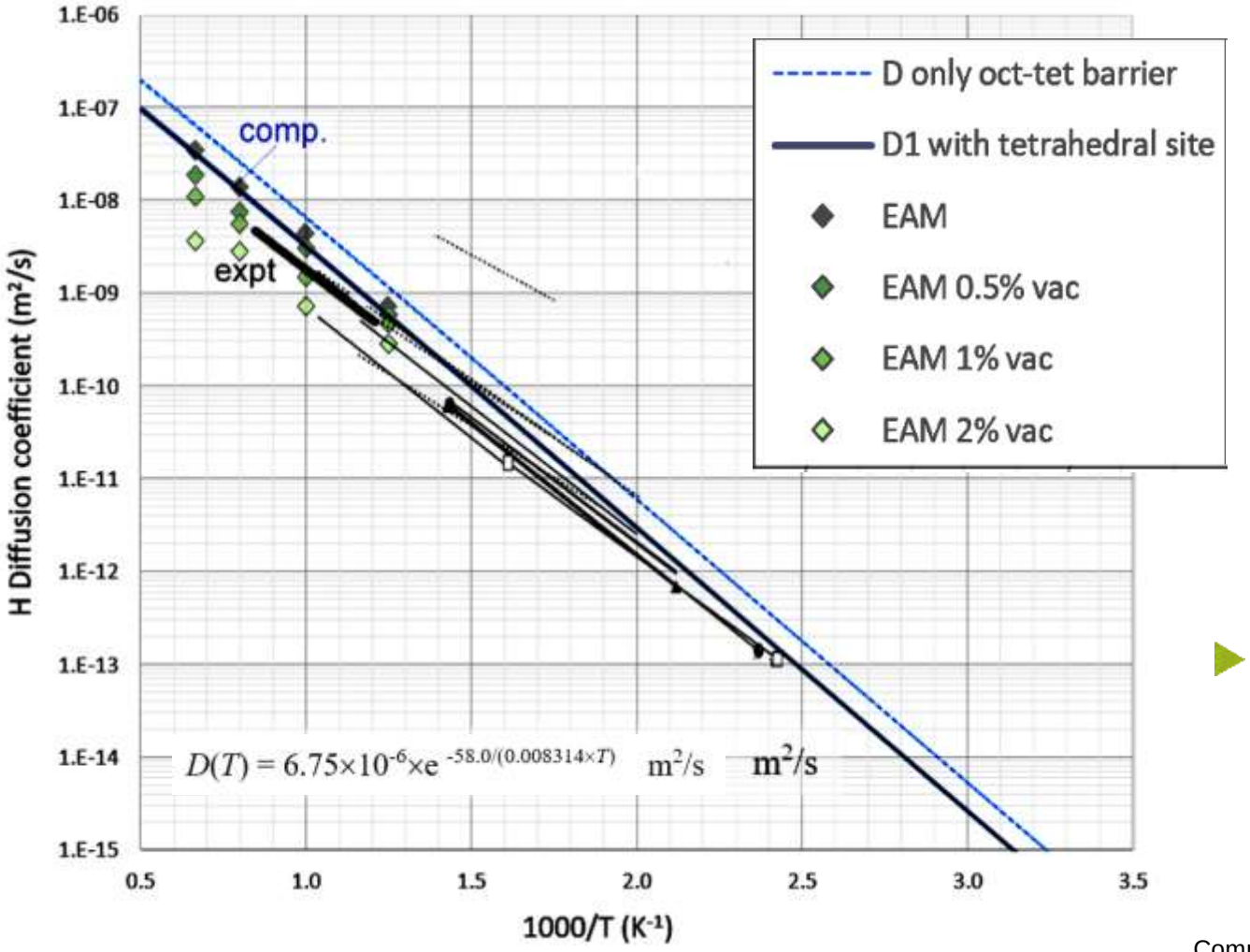
The diffusion coefficient D_1 includes an equilibration of the H atom in the intermediate tetrahedral site.

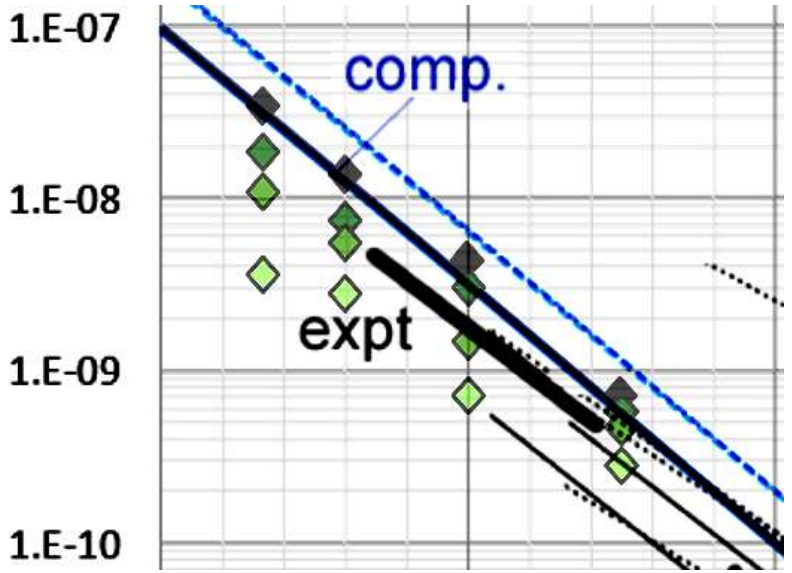
DFT using *MedeA VASP* and *MedeA Phonon*



Computations: M. Christensen and E. Wimmer (Materials Design), unpublished
Experiments: H. Katsuta and K. Furukawa, J. Nucl. Sci. Techn. **18**, 143 (1981), C. San Marchi, B.P. Somerday, and S.L. Robinson, Int. J. of Hydrogen Energy **32**, 100 (2007)

Diffusion of H in Steel





- Trapping of H in vacancies reduces the apparent diffusion coefficient.

DFT using *MedeA VASP* and *MedeA Phonon*
MedeA Diffusion using molecular dynamics with EAM interatomic potentials

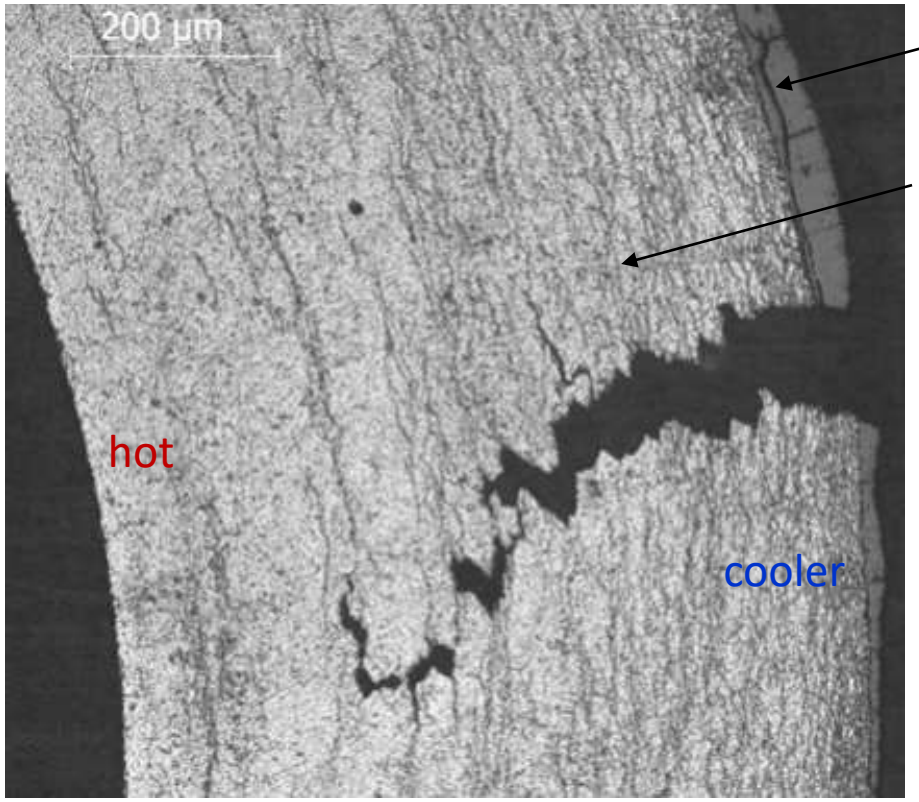
Experimental: H. Katsuta and K. Furukawa, J. Nucl. Sci. Techn. **18**, 143 (1981), C. San Marchi, B.P. Somerday, and S.L. Robinson, Int. J. of Hydrogen Energy **32**, 100 (2007)

Computations: M. Christensen and E. Wimmer (Materials Design), unpublished
Experiments: H. Katsuta and K. Furukawa, J. Nucl. Sci. Techn. **18**, 143 (1981), C. San Marchi, B.P. Somerday, and S.L. Robinson, Int. J. of Hydrogen Energy **32**, 100 (2007)

Hydride Formation in Zr Alloys

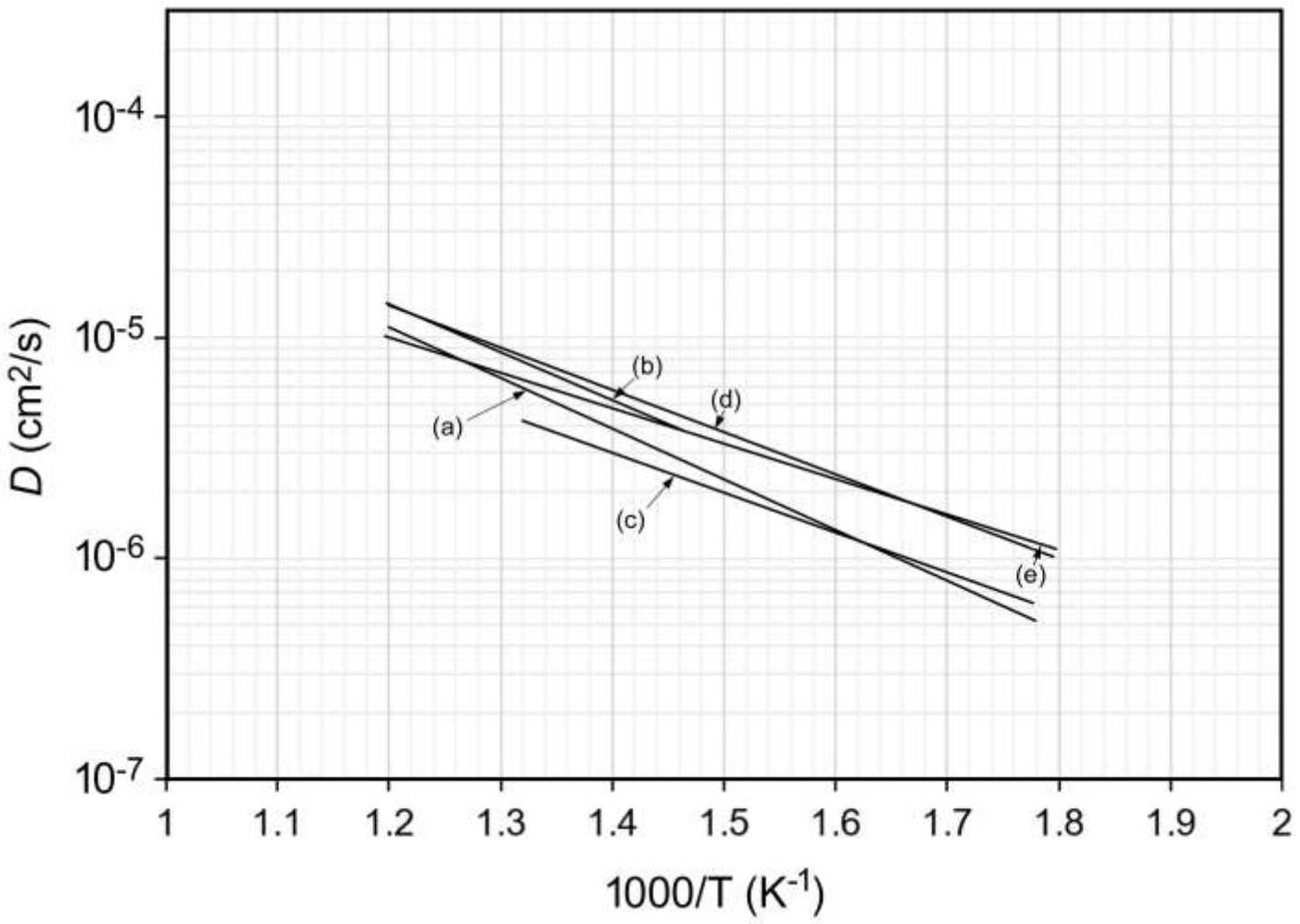
$$Zr + H_2O \rightarrow ZrO_2 + H_2$$

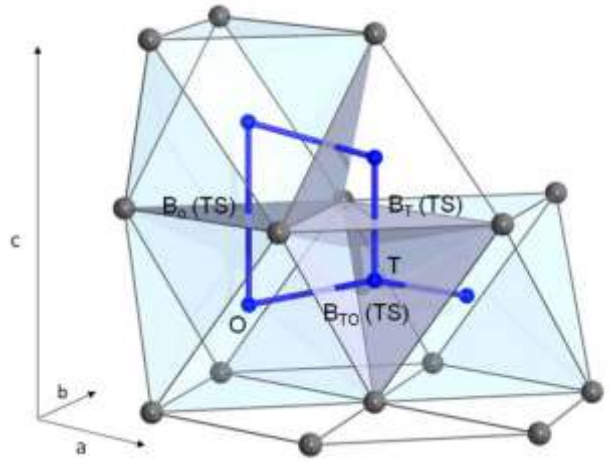
$$H_2 + Zr \rightarrow ZrH_2$$



Cross section of fuel rod, Zr alloy

H Diffusion in Zirconium





Experimental results

(a) J. J. Kearns, J. Nucl. Mater 43 (1972) 330

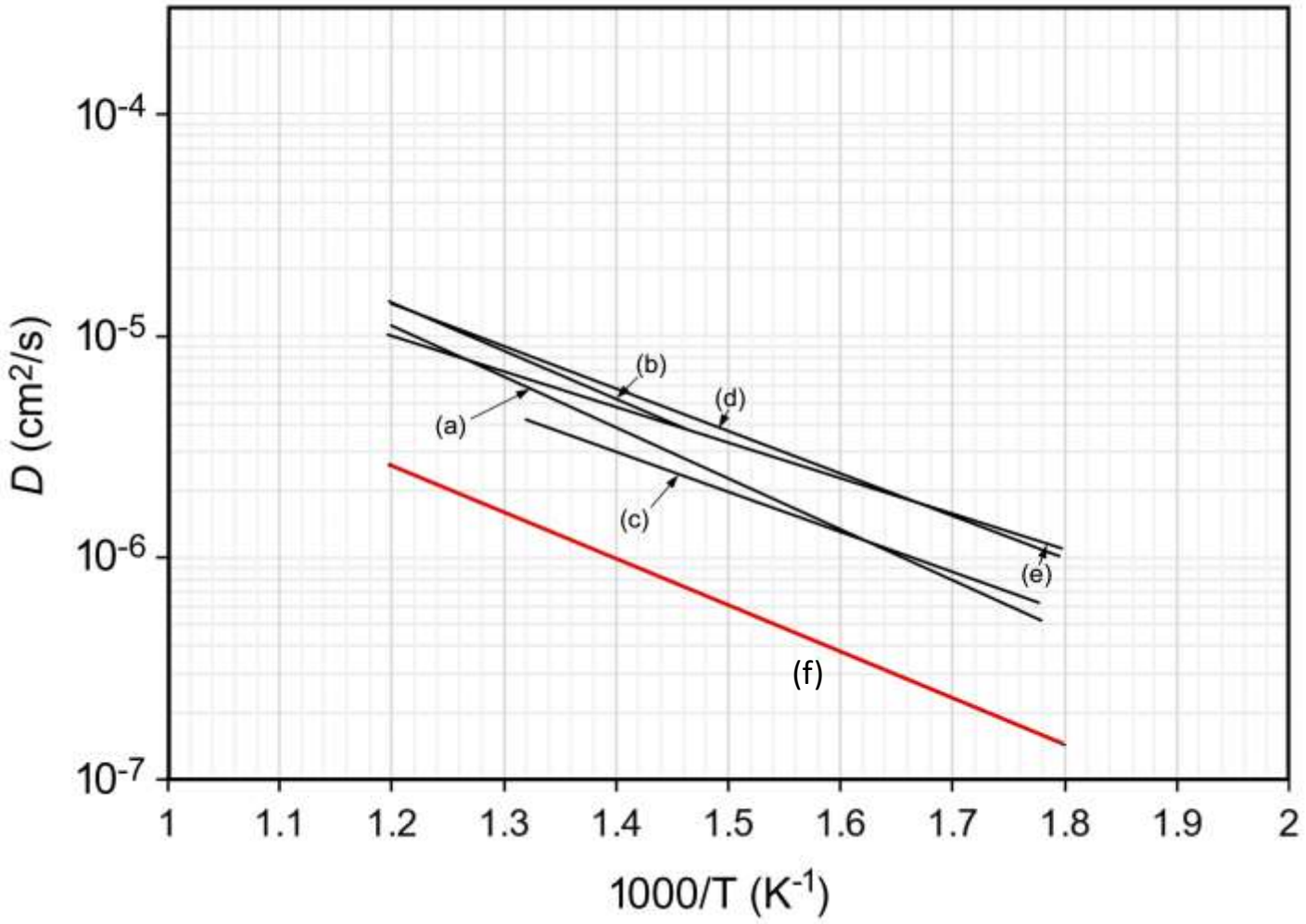
(b) M. Someno, Nippon Kinzoku Gakkaishi 24 (1960) 249

(c) B. F. Kammenzind et al. 11th Intl. Symposium vo. 1295 ASTM Intl. (1996) 338.

(d) A. Sawatzky, J. Nucl. Mater. 2 (1960) 62

(e) M. W. Mallett and W. M. Albrecht, J. Electrochem. Soc. 104 (1957) 142

H Diffusion in Zirconium



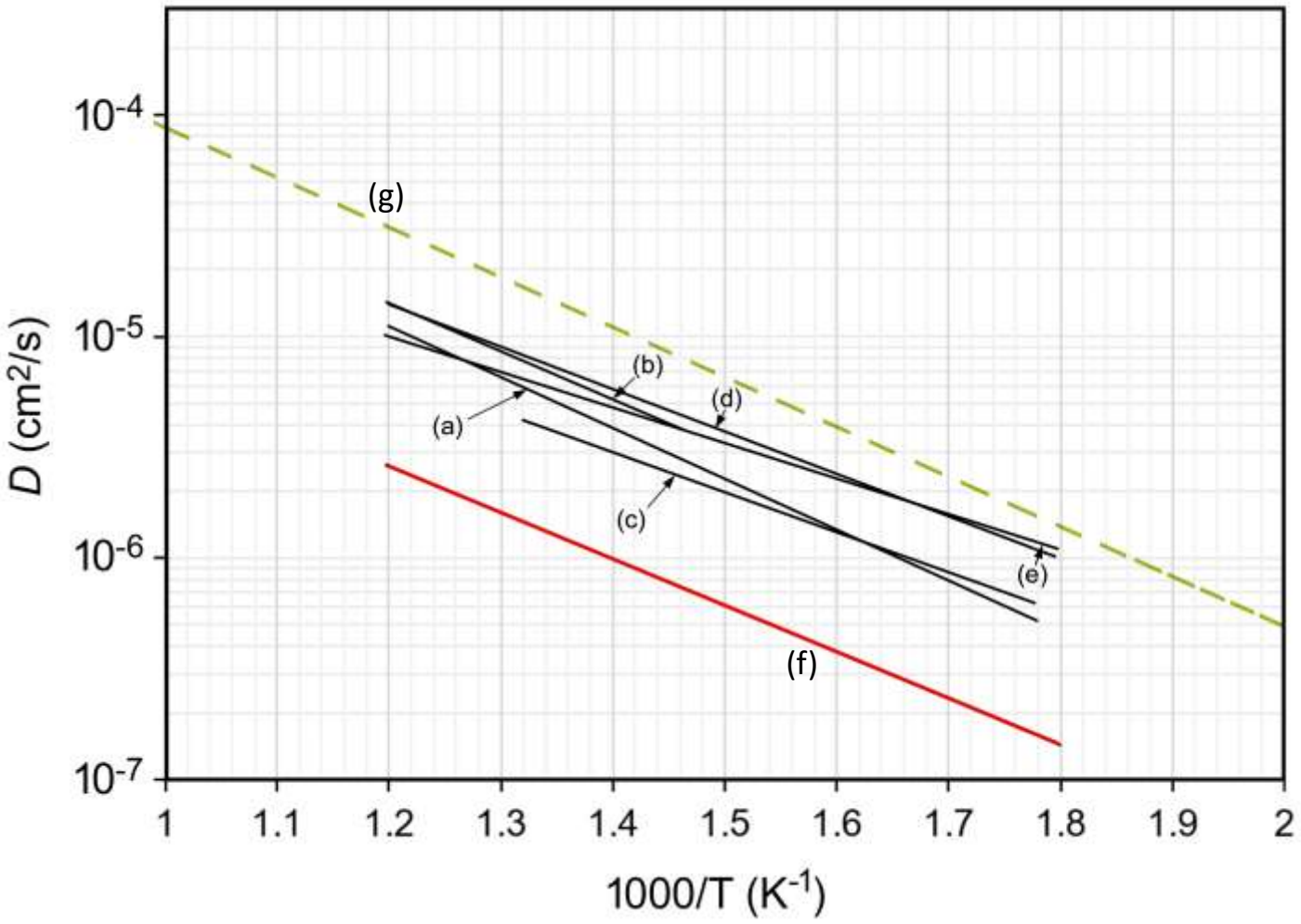
DFT calculations and kinetic Monte Carlo

(f) M. Christensen et al., J. Nucl. Mater. 460 (2015) 82.

The slope (activation barrier) agrees with experiment, but the predicted diffusion is too slow.

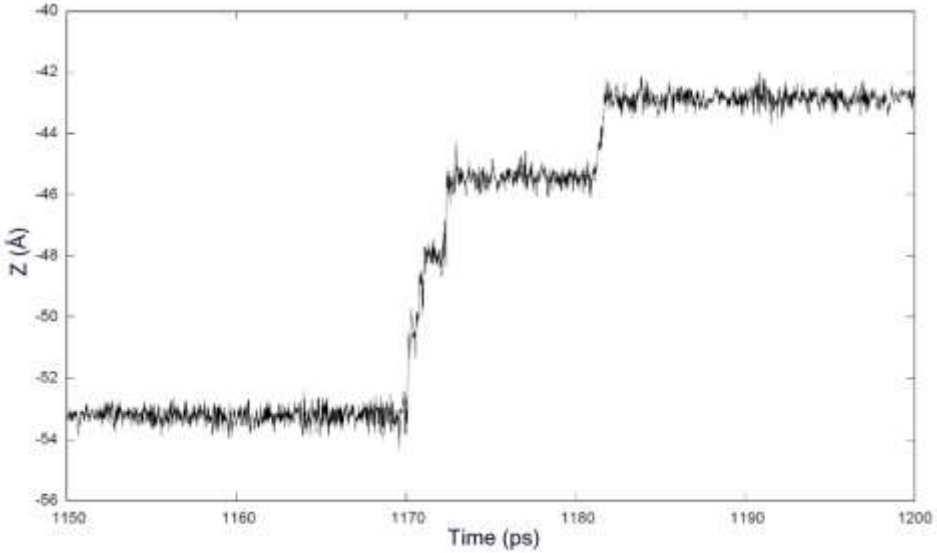
This model assumes equilibrium after each jump, i.e. no ballistic effects are included.

H Diffusion in Zirconium



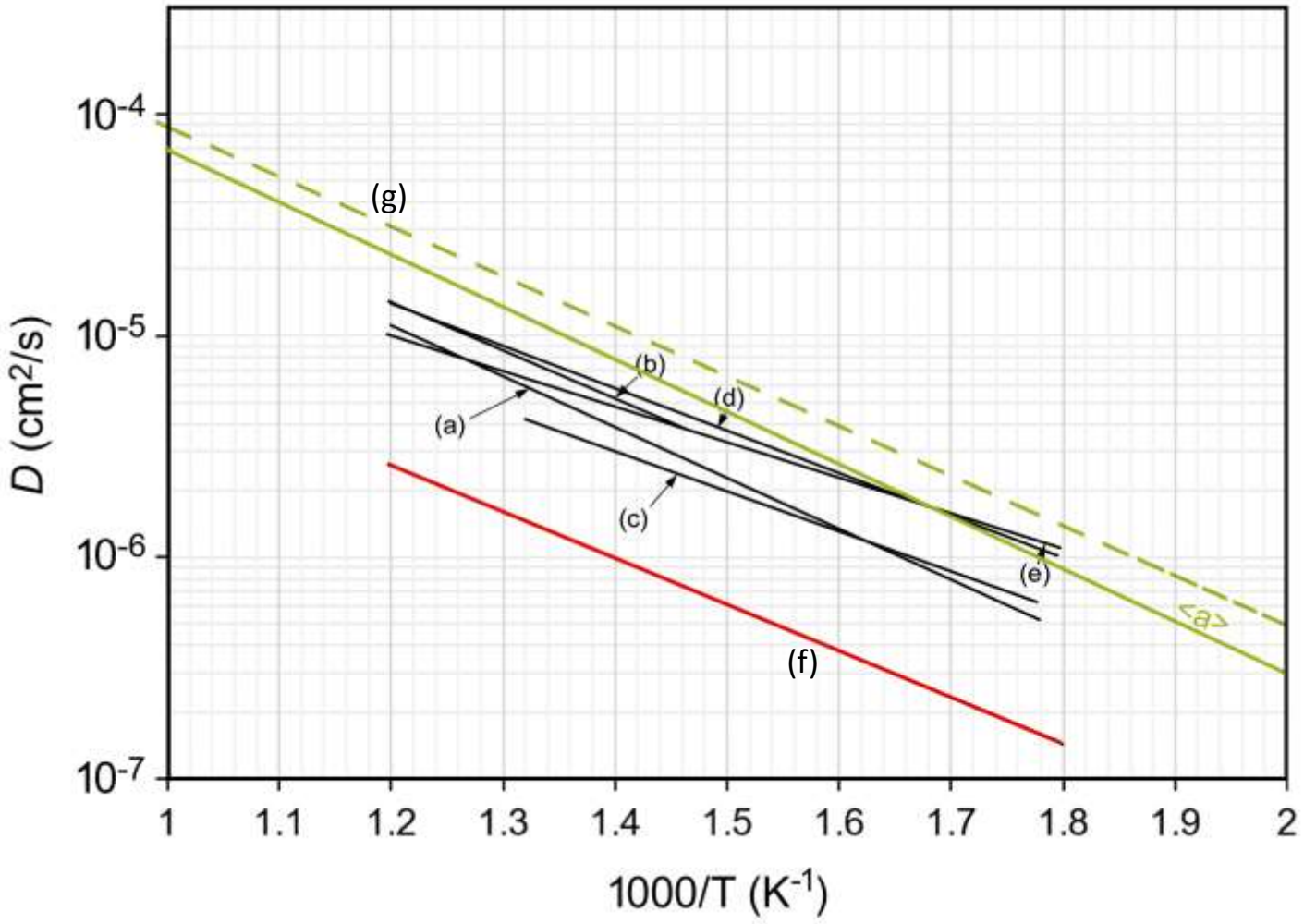
Molecular dynamics with interatomic potential including ballistic effects.

(g) E. Wimmer, M. Christensen, W. Wolf, W. H. Howland, B. Kammenzind, and R. W. Smith, J. Nucl. Mater. 532 (2020) 152055



Position in the z-direction of diffusing H atom at 922 K

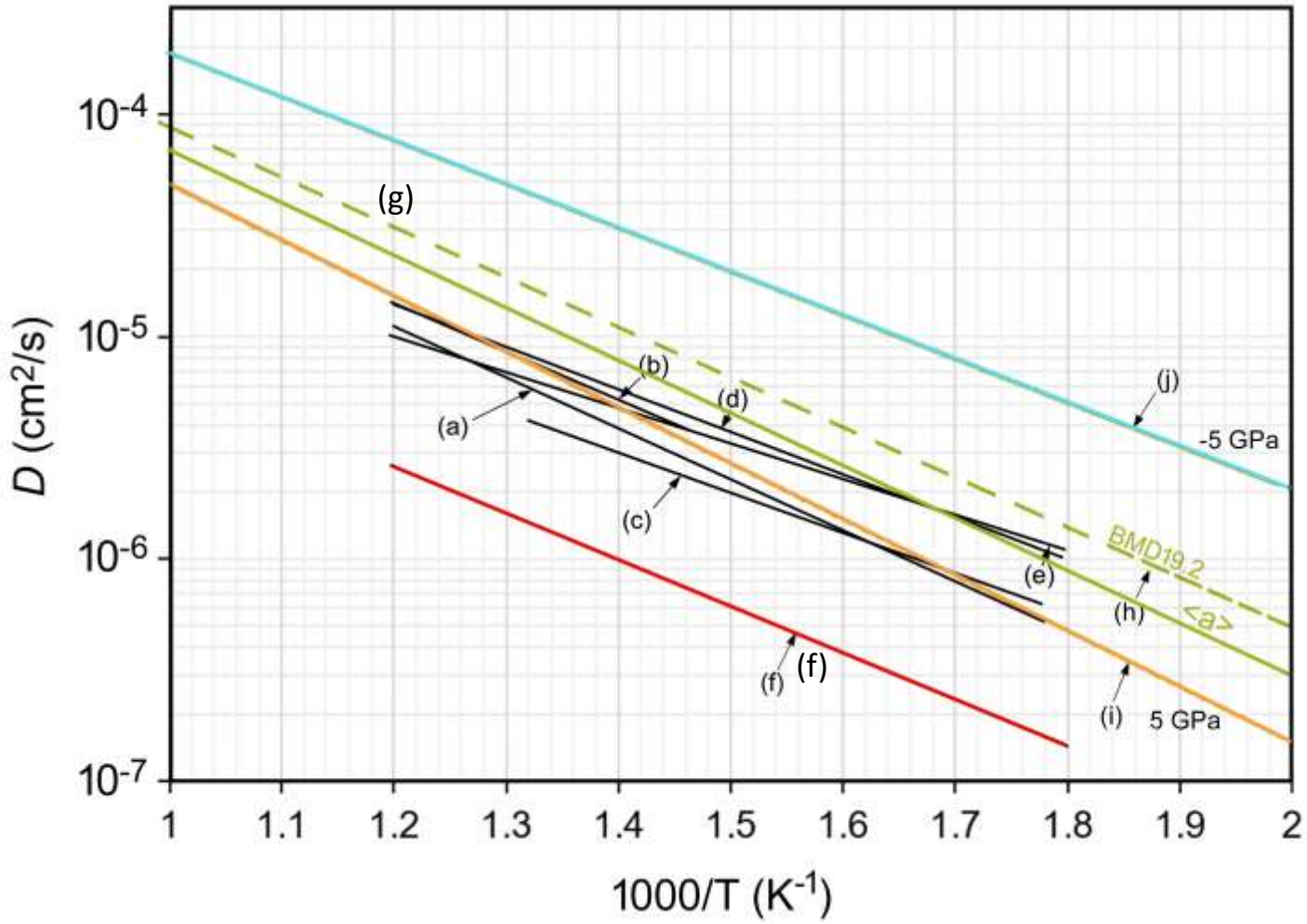
H Diffusion in Zirconium



Experiments measure mostly diffusion in the <a>-direction of the hcp Zr crystals. The diffusion in this direction is slower than in the <c> direction.

<a> The agreement with experiment is improved.

H Diffusion in Zirconium

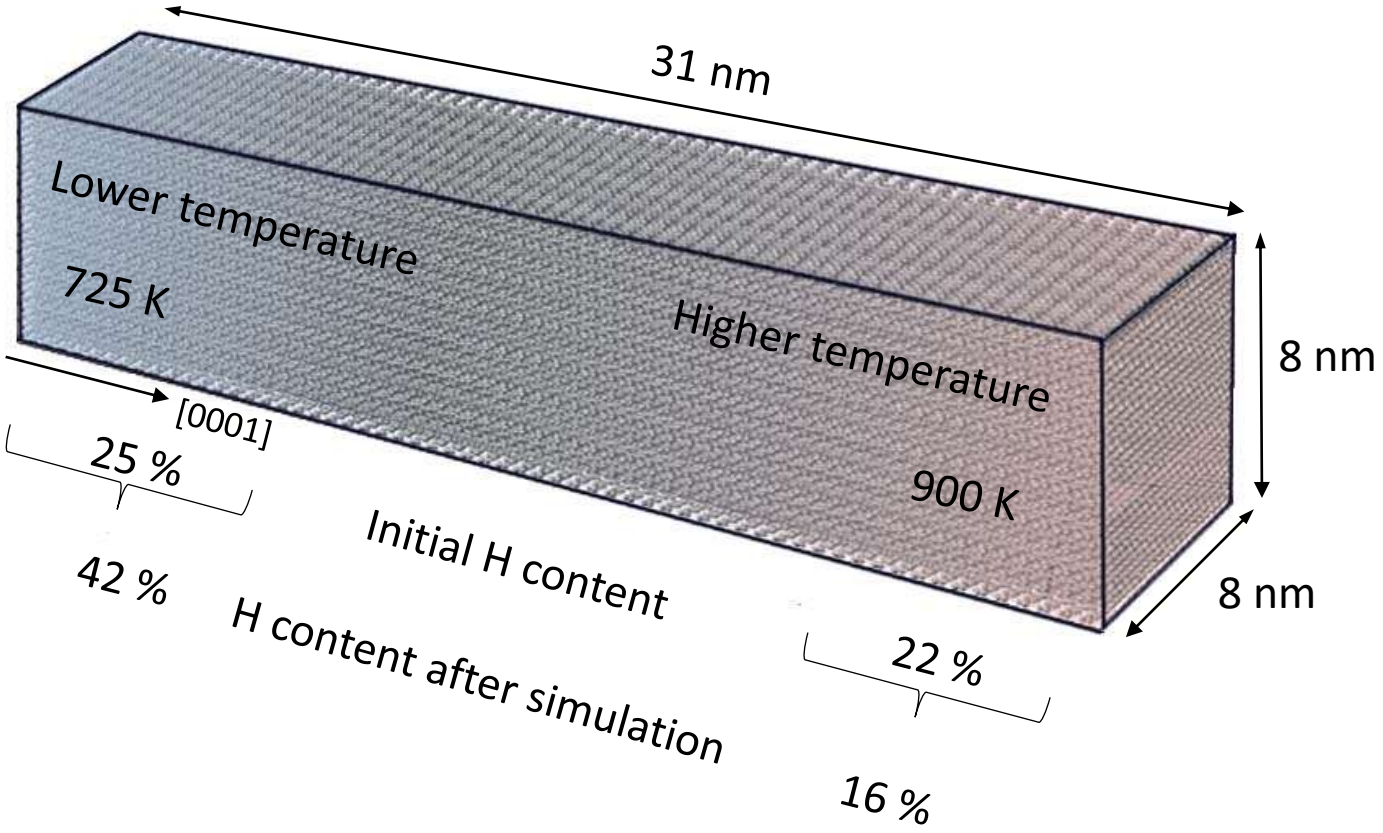


(j) Tensile strain (negative pressure) increases the diffusivity of H in Zr;

(i) Compressive strain (positive pressure) reduces the diffusivity

H Diffusion in Zirconium: Soret Effect

Hydrogen diffuses from hot to cold regions



Computational method:

Molecular dynamics using an EAM potential [1]

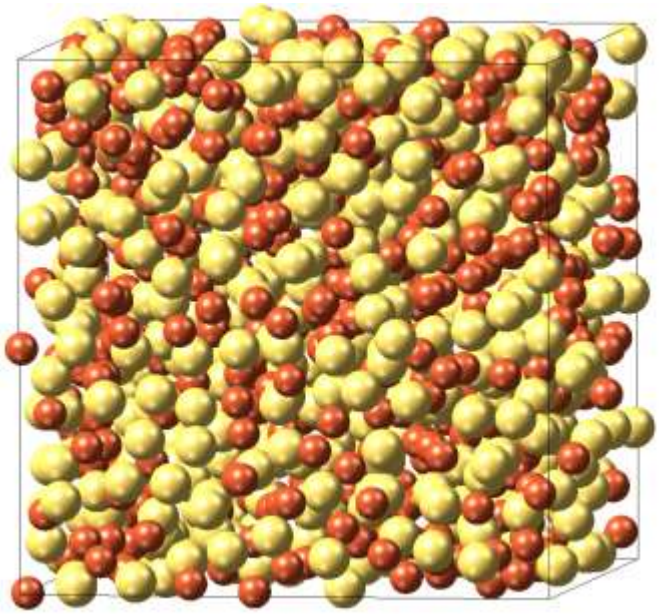
Software: *MedeA LAMMPS*

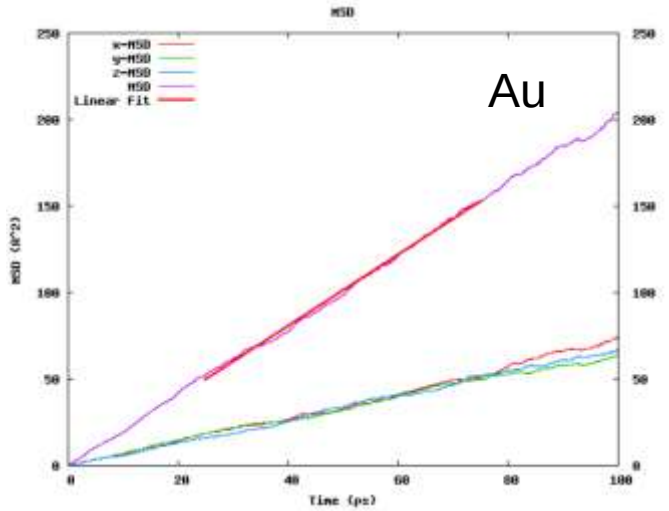
[1] E. Wimmer, M. Christensen, W. Wolf, W. H. Howland, B. Kammenzind, and R. W. Smith, J. Nucl. Mater. 532 (2020) 152055

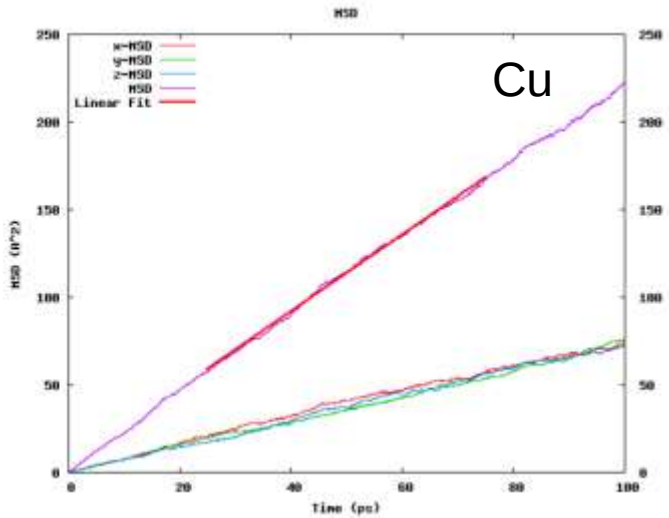
https://www.materialsdesign.com/Publications/Wimmer2020

Diffusion in Molten Metals

Model of molten Au-Cu







Au50% Cu50% $Au_{512}Cu_{512}$

T = 1470 K

D(Au) = 3.4×10^{-5} cm^2/s

D(Cu) = 3.7×10^{-5} cm^2/s

Cu diffuses only slightly faster than Au

Computational approach:

Molecular dynamics

Embedded Atom Potential (EAM) of Zhou (2004)

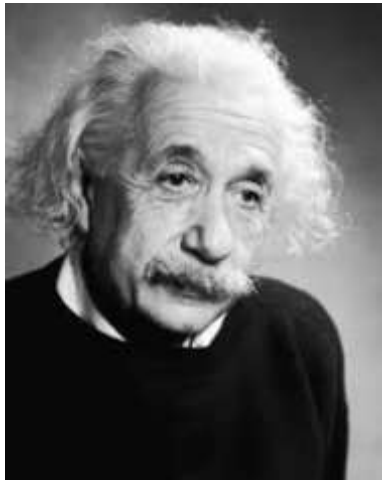
MedeA LAMMPS

Theoretical Foundation

Adolf Fick 1829 - 1901

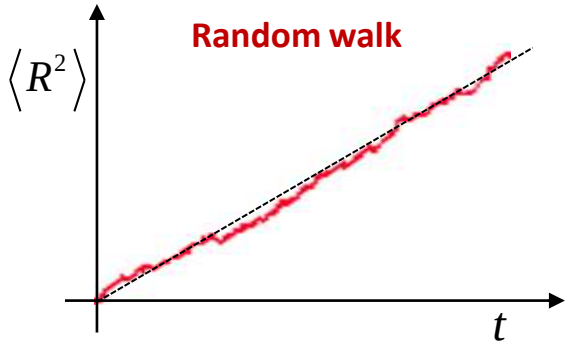
1855: A. Fick $j_x = -D\frac{\partial c}{\partial x}$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$



Albert Einstein 1879 - 1955

1905: A. Einstein $\left\langle R^2 \right\rangle = 6Dt$

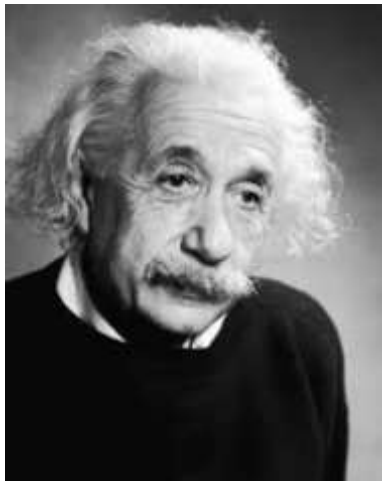


Theoretical Foundation and the Stock Market

Adolf Fick 1829 - 1901

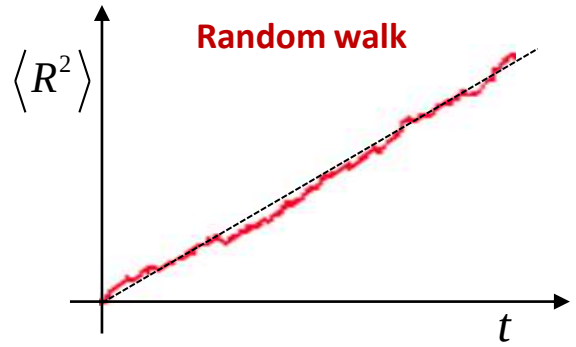
1855: A. Fick $j_x = -D\frac{\partial c}{\partial x}$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$



Albert Einstein 1879 - 1955

1905: A. Einstein $\langle R^2 \rangle = 6Dt$



1900: L. Bachelier

Random fluctuations of stocks with time are mathematically equivalent to a **diffusion** process

$$c^2 \frac{\partial^2 \mathfrak{P}}{\partial t} - \frac{\partial^2 \mathfrak{P}}{\partial x^2} = 0.$$

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}$$

Louis Bachelier 1870 - 1946

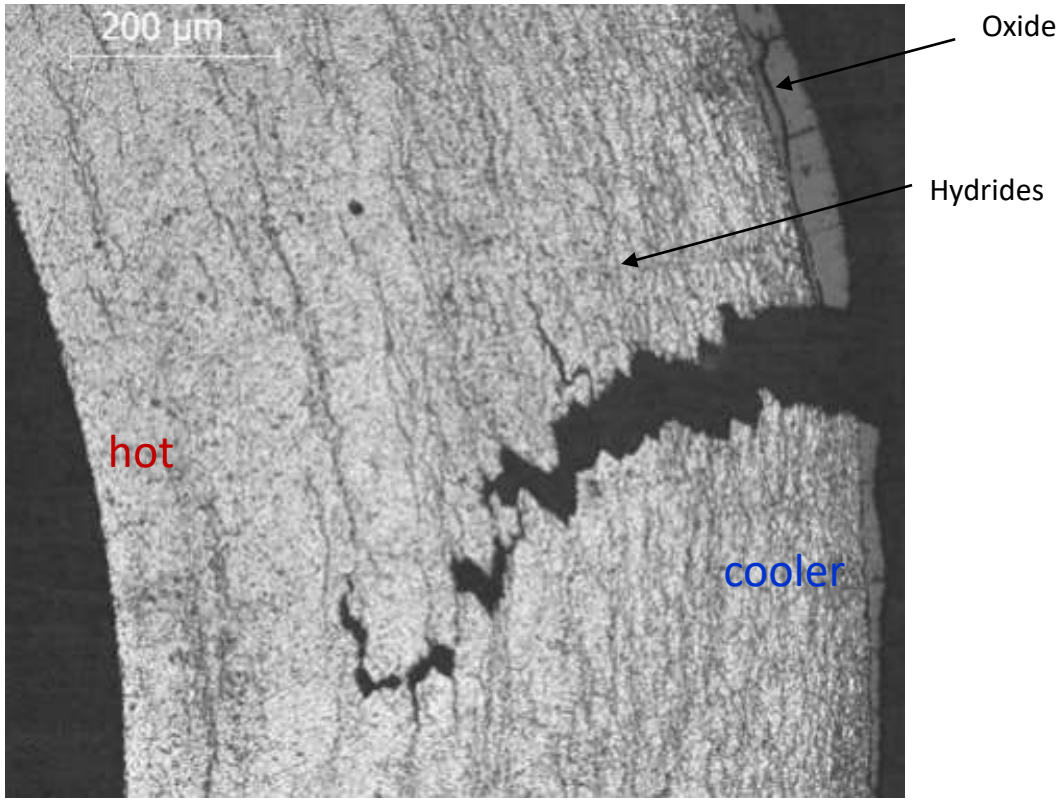
L. Bachelier, Théorie de la spéculation, Annales scientifiques de l'E.N.S. 3e série, tome 17 (1900) p.21-86
http://www.numdam.org/item?id=ASENS_1900_3_17__21_0

Thanks to Prof. Jörg Kärger for the reference to L. Bachelier

Corrosion of Zr

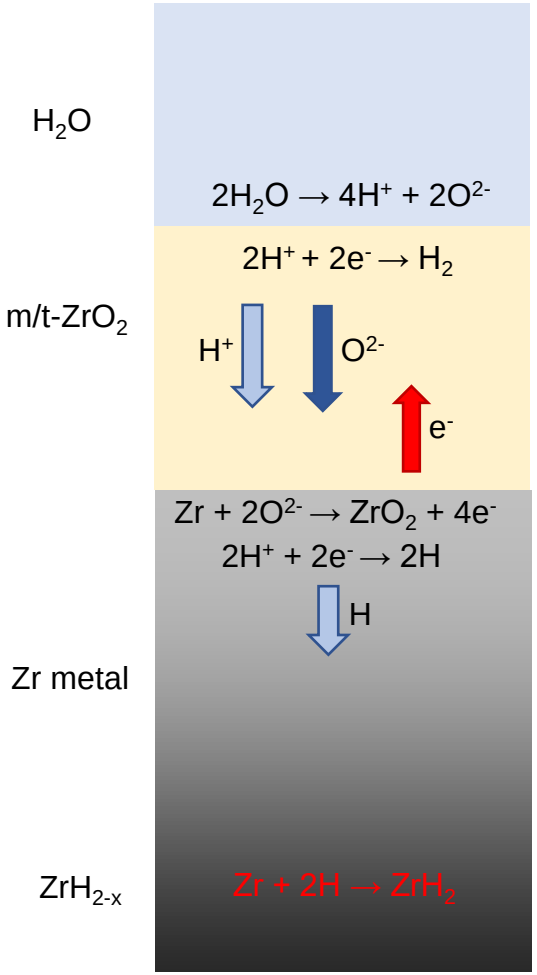
$$Zr + H_2O \rightarrow ZrO_2 + H_2$$

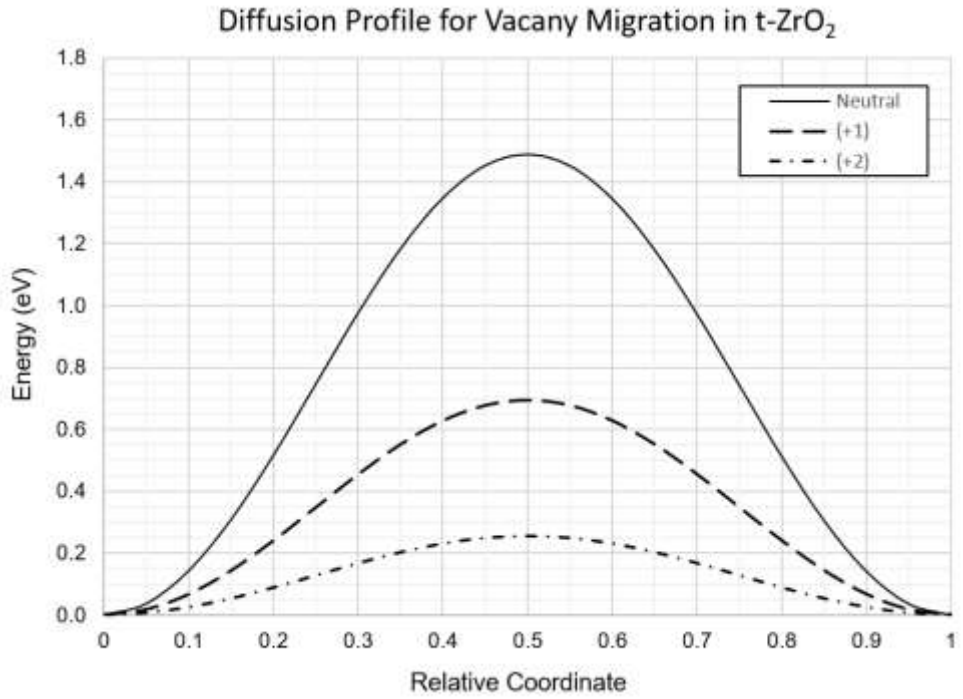
$$H_2 + Zr \rightarrow ZrH_2$$

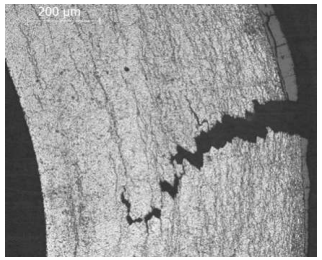


Cross section of fuel rod, Zr alloy

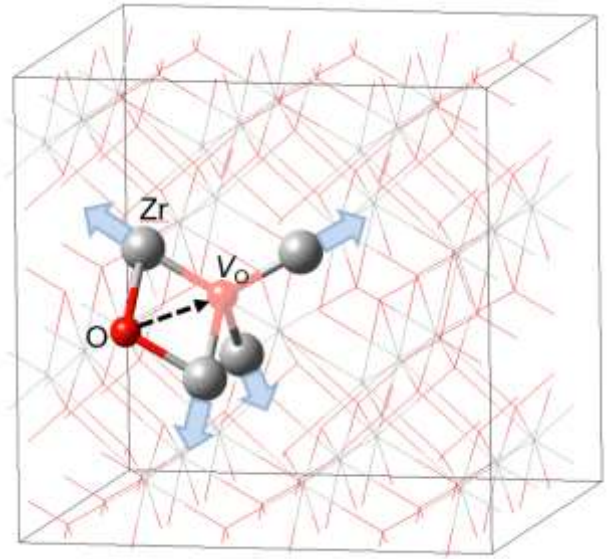
Corrosion of Zr





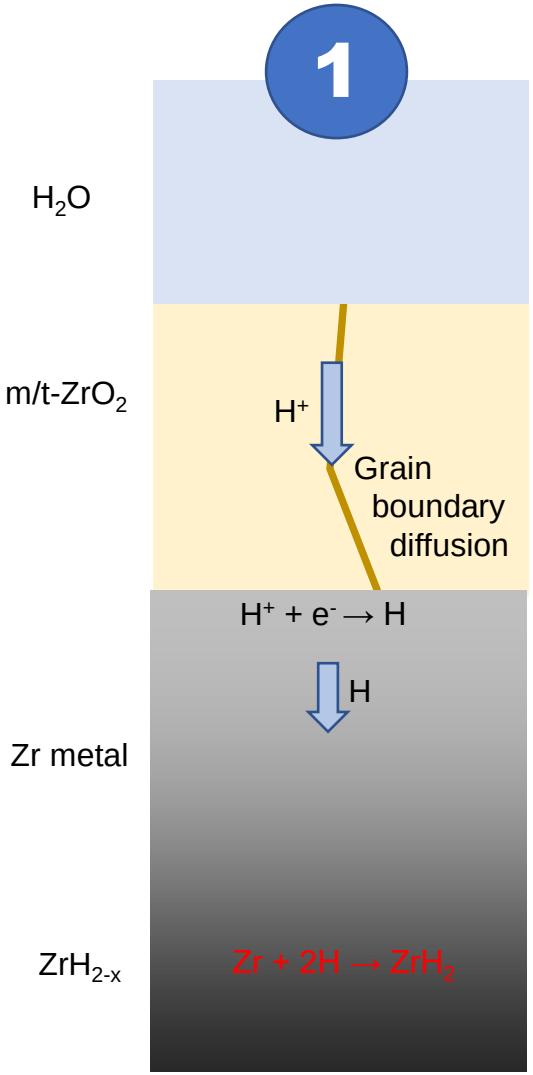


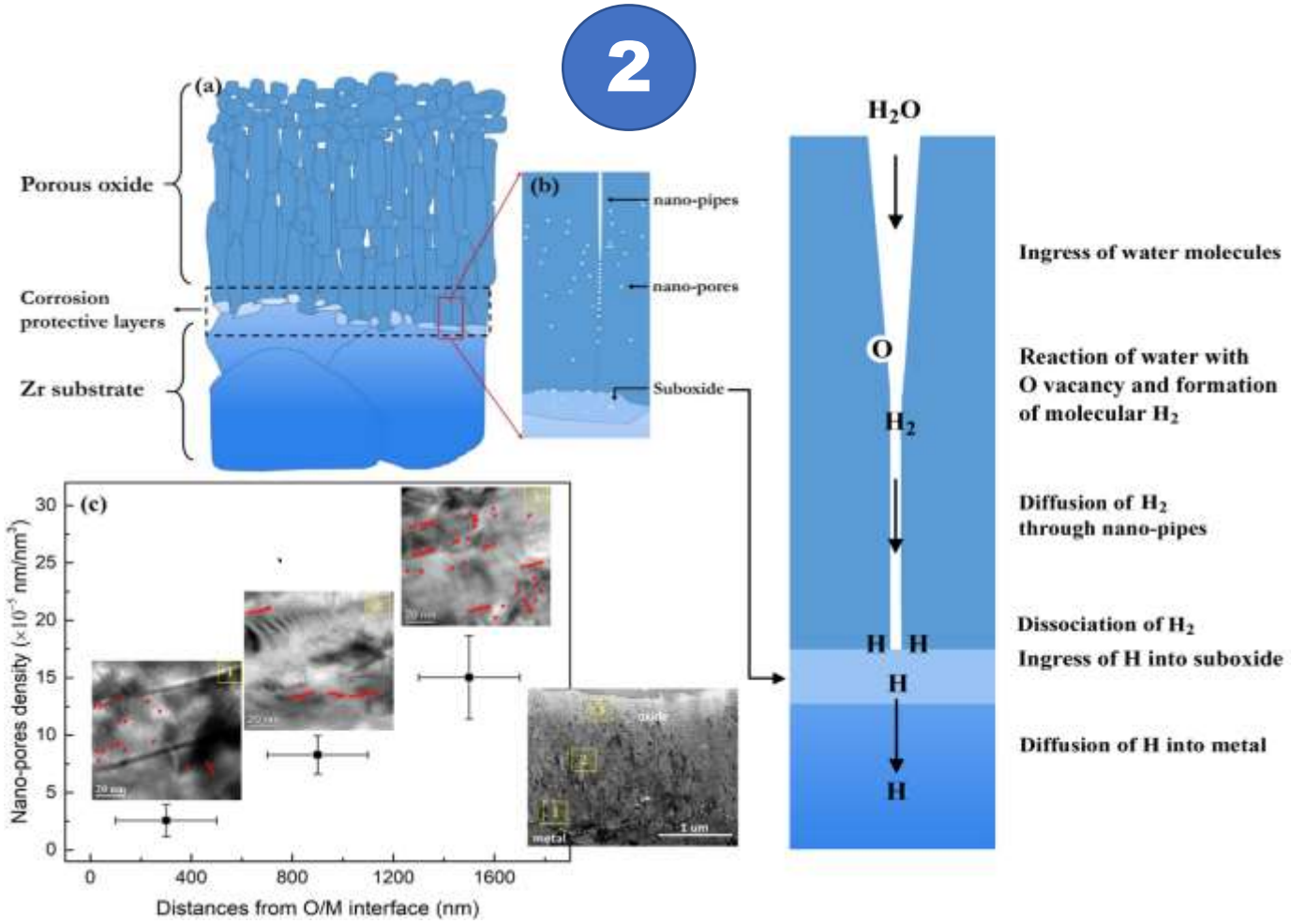
- In pure t-ZrO_2, the energy barrier for O vacancy migration (*i.e.* oxygen diffusion) decreases from 1.49 eV for a neutral vacancy to 0.25 eV for a doubly positively charged vacancy.



A. Eichler, Phys. Rev. B64, 174103 (2001)

Hydrogen Pickup Mechanisms

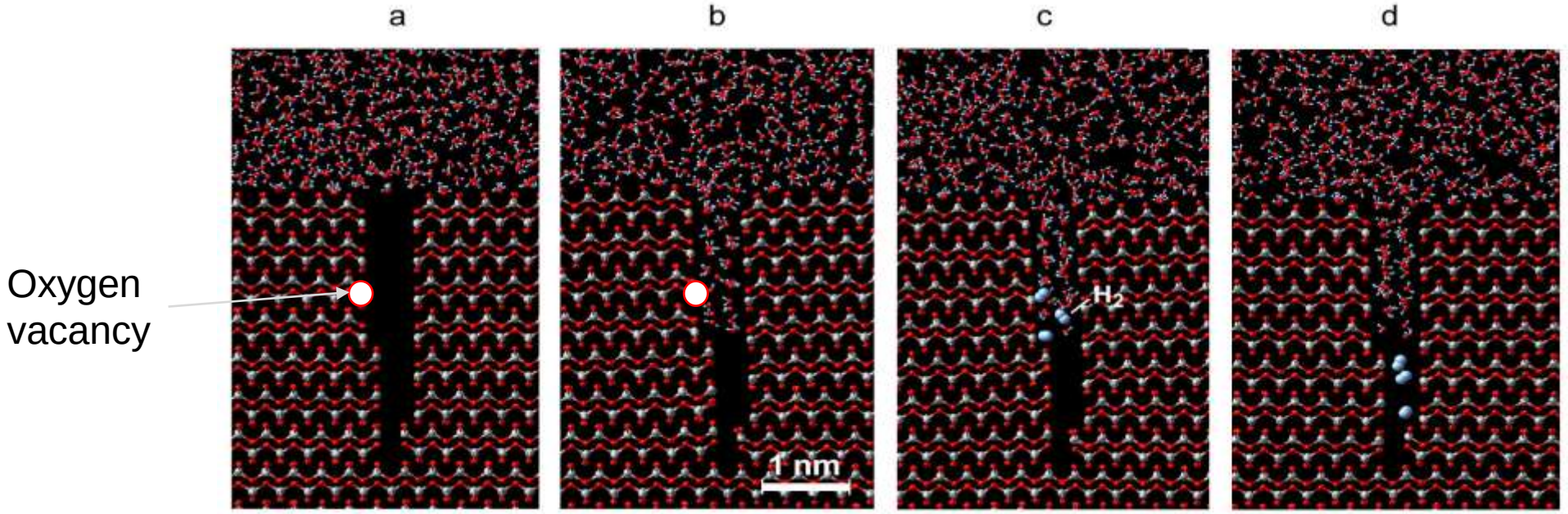




J. Hu, Junliang Liu, S. Lozano-Perez, C. R. M. Grovenor, M. Christensen, W. Wolf, E. Wimmer, E. V. Mader, Acta Mater. 180 (2019) 105

A Possible Mechanism of H Diffusion

1. Oxygen vacancies diffuse from the metal/oxide interface to the surfaces of nanopipes
2. Water diffuses into cracks and nanopipes in the oxide layer
3. Water molecules react with vacancies and form H_2 molecules
4. H_2 molecules diffuse through nanopores (as narrow as 0.5 nm), reach the sub-oxide or Zr(O-sat region), dissociate, and enter the metal
5. HPU is reduced if the reduction to H_2 occurs close to the water/oxide interface.



J. Hu, J. Liu, S. Lozano-Perez, C. R. M. Grovenor, M. Christensen, W. Wolf, E. Wimmer, and E. V. Mader, Acta Materialia 180, 105-115 (2019)

Summary and Conclusions

- Diffusion processes are omnipresent and important.
- The basis for atomistic simulations is the link between random motion and diffusion (Bachelier, Einstein, Smoluchowski).
- Atomistic simulations based on quantum mechanical total energy calculations and classical molecular dynamics simulations provide **understanding** of diffusion mechanisms and **quantitative predictions** of diffusion coefficients as shown for
  - Catalysis: diffusion in core-shell nanoparticles
  - Diffusion in organic liquids
  - Li-ion batteries: diffusion of Li ions in polymers and solid-state electrolytes
  - H diffusion in steel and zirconium
  - Au and Cu atoms in molten alloy
  - Corrosion of Zr
- Atomistic simulations expand the scope of experiments.

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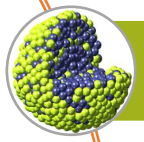
MedeA 3.1 Webinars

June 2020: Elasticity and beyond – Predicting Mechanical Properties with *MedeA*, by Ray Shan



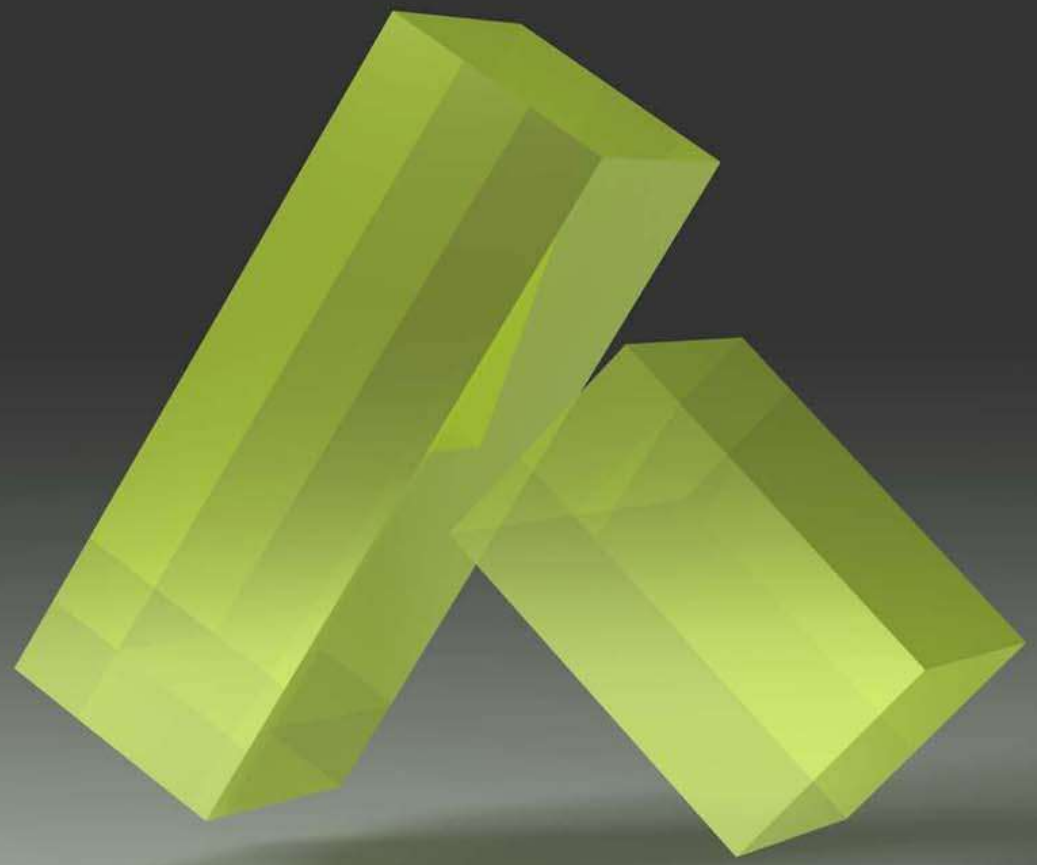
June 2020: Diffusion by Erich Wimmer and Benoît Minisini

July 2020: VASP 6 by Martjin Marsman

July 2020: Mesoscale modeling by Jörg-Rüdiger Hill

August 2020: *MedeA* 3.1 by Marianna, Walter and Jörg-Rüdiger Hill

Upcoming in the fall of 2020: Additional webinars addressing accuracy and larger scales



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