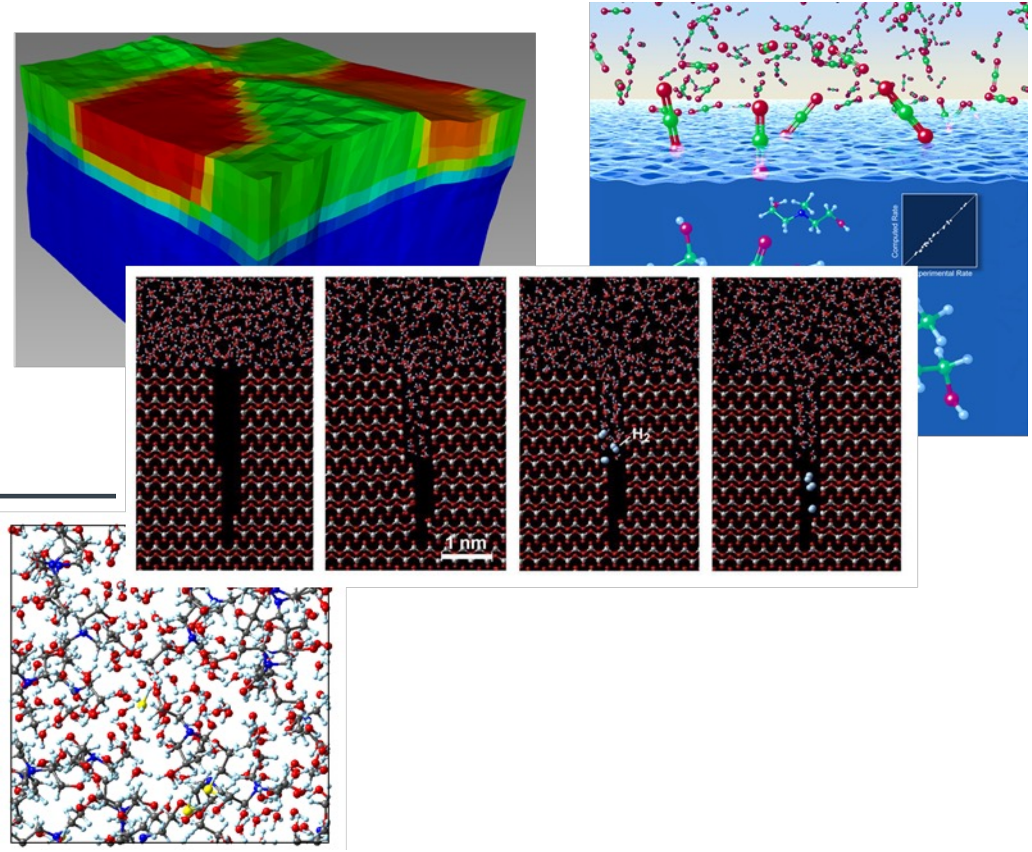
materials design

Webinar

Lessons Learned Solving Industrial Problems

Xavier Rozanska



Outline

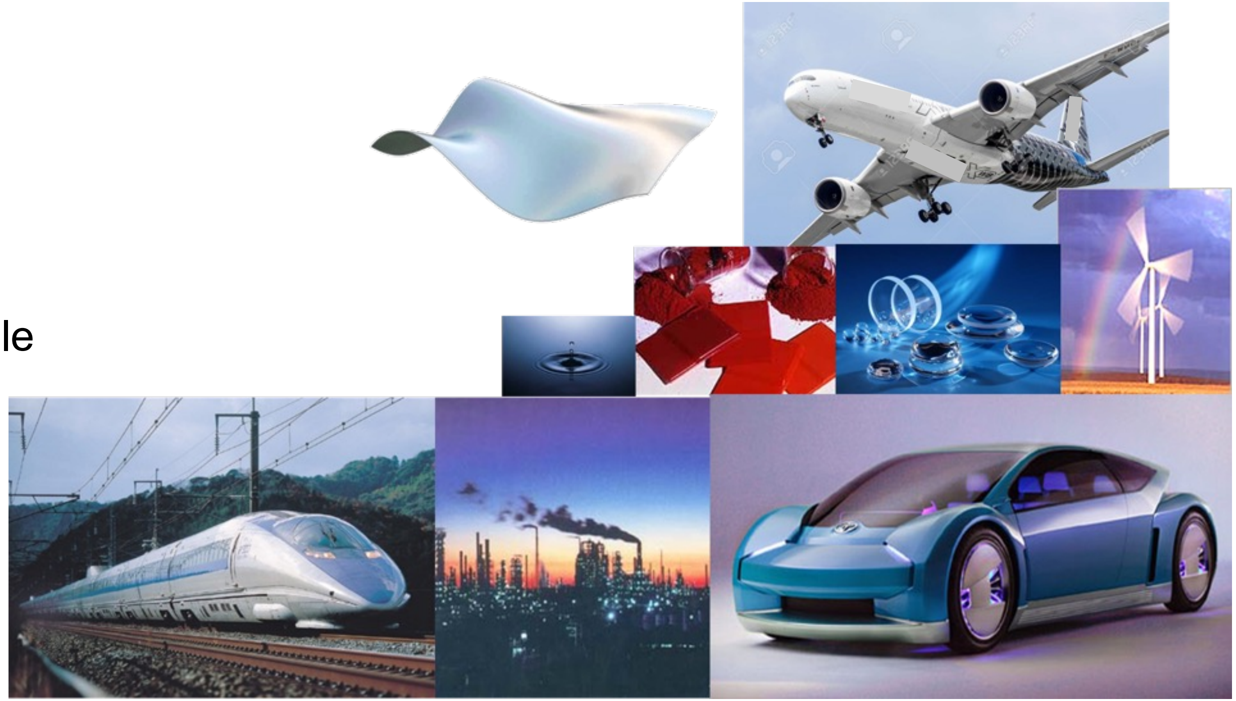
- Research and Atomistic Simulations in Industrial Environment
- Application Examples
  - Metallurgy
  - Batteries
  - Composite materials
  - Fluids
- Summary and Conclusions

Research and Atomistic Simulations in Industrial Environment

Industrial Value

Creation of products which are:

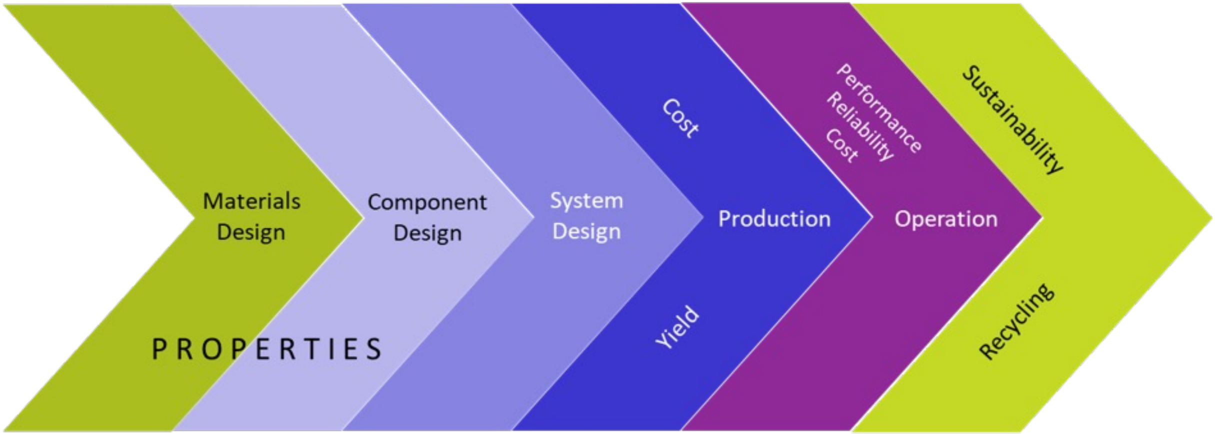
- Valuable for customer
- Innovative
- Efficient to manufacture
- Safe and reliable
- Environmentally responsible
- Meeting the regulations



Value of Modeling and Simulation

- Understanding mechanisms
- Prediction of properties

→ Optimal design and processes



Materials Design

Component Design

System Design

Production

Operation

PROPERTIES

Cost

Yield

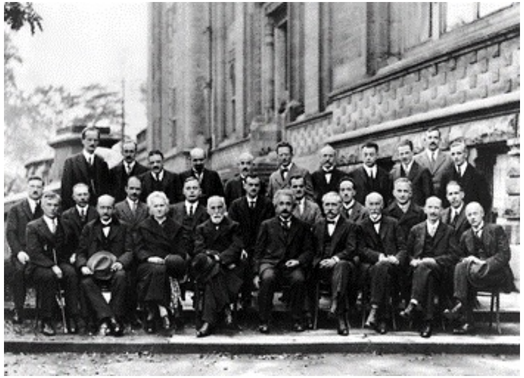
Performance
Reliability
Cost

Sustainability

Recycling

- Improvement of industrial products is a long-term iterative process
- Materials modeling and simulation are catalysts of this process

Research in Industry and Academia



Fifth Solvay Conference on Physics, 1927

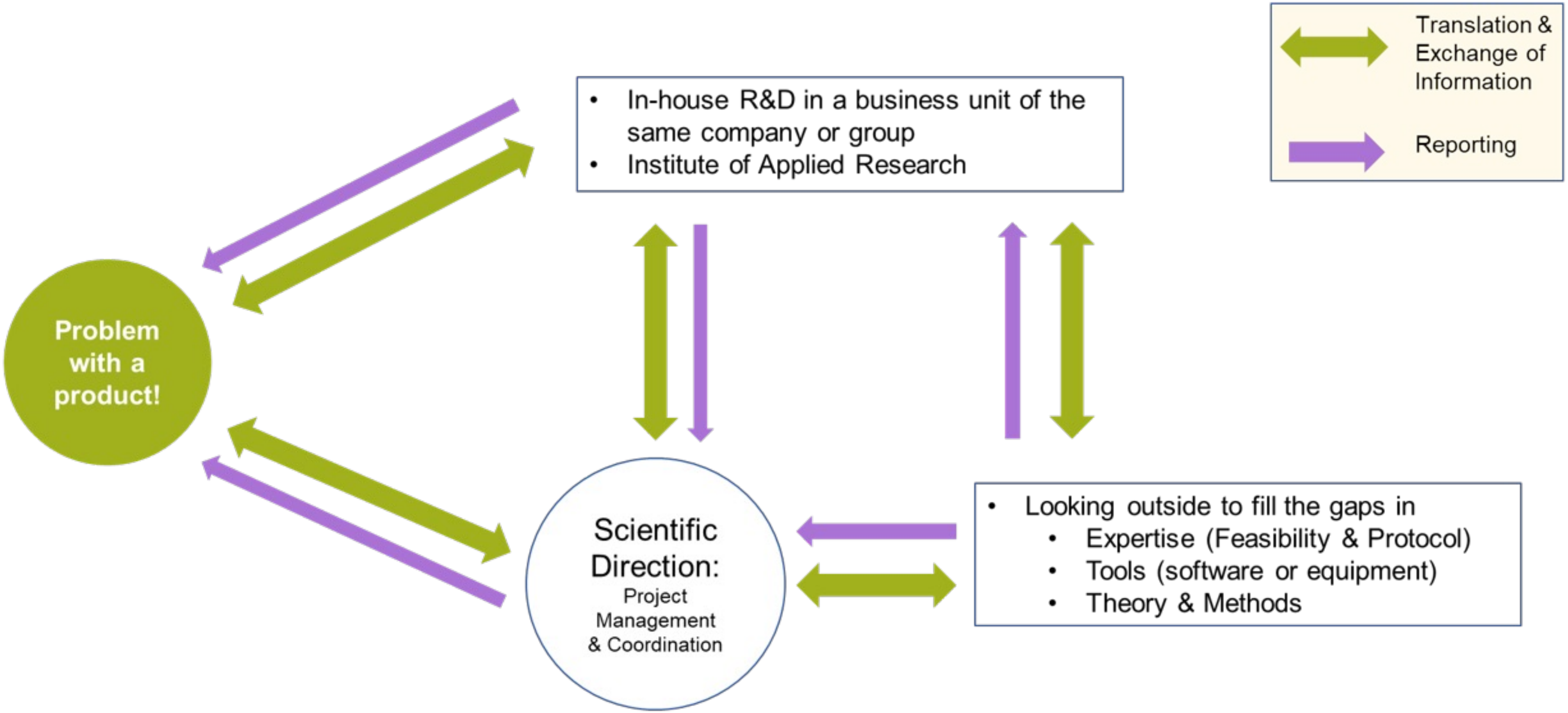
Academia

- Driven by new methods to solve known problems
- Breakthrough discoveries
- Knowledge driven
- Mostly long-term
- Challenging – failure is part of the learning process
- New theory and method
- Push the limits of the state of the art in a field or a discipline

Industry

- Driven by ‘new’ or given problem and flexible with methods
- Mostly incremental (or opening new business)
- Application driven with visible and direct societal impact (e. g. vaccine)
- Mostly short-term, long-term for strategic goals
- Challenging – Failure is possible and acceptable: complexity of systems or property
- Extensions or integrations of theories and methods (interdisciplinary and multiscale)
- Prefer to stay within the limits of the state of the art

Research in Industry



Translation & Exchange of Information

Reporting

- In-house R&D in a business unit of the same company or group
- Institute of Applied Research

Problem with a product!

Scientific Direction: Project Management & Coordination

- Looking outside to fill the gaps in
  - Expertise (Feasibility & Protocol)
  - Tools (software or equipment)
  - Theory & Methods

Additional readings: Westmoreland *et al.* (**2002**). *Applications of molecular and materials modeling* (pdf online)

Scientific Foundation of Simulation

Classical Mechanics | Electrodynamics | Statistical Mechanics | Quantum Mechanics

$$\boldsymbol{F} = m\boldsymbol{a}$$

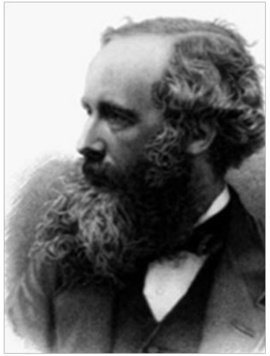
$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

$$S = \mathrm{k} \ln W$$

$$\Delta G = \Delta H\text{-}T\Delta S$$

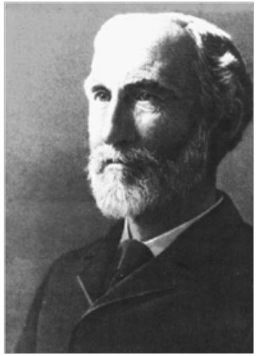
$$\mathbf{H}\,\Psi = E\,\Psi$$

Isaac Newton
1687



James C. Maxwell
1864

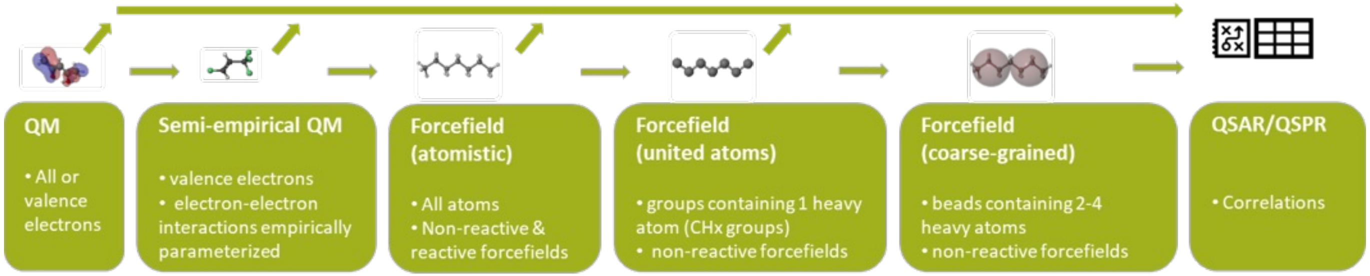
Ludwig Boltzmann
1871



Josiah W. Gibbs
1876

Erwin Schrödinger
1926

Scientific Foundation of Simulation



QM
- All or valence electrons

Semi-empirical QM
- valence electrons
- electron-electron interactions empirically parameterized

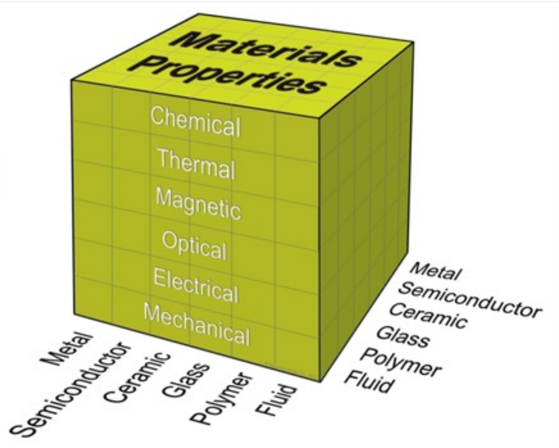
Forcefield (atomistic)
- All atoms
- Non-reactive & reactive forcefields

Forcefield (united atoms)
- groups containing 1 heavy atom (CHx groups)
- non-reactive forcefields

Forcefield (coarse-grained)
- beads containing 2-4 heavy atoms
- non-reactive forcefields

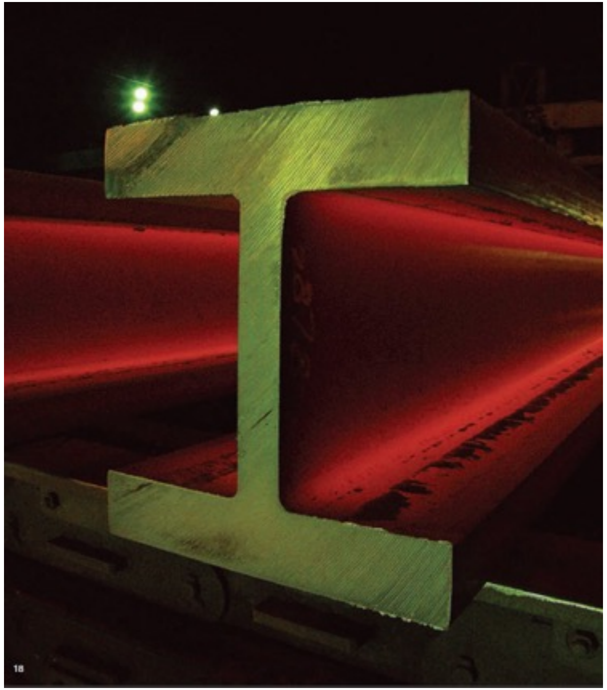
QSAR/QSPR
- Correlations

Prediction of materials properties of engineering value

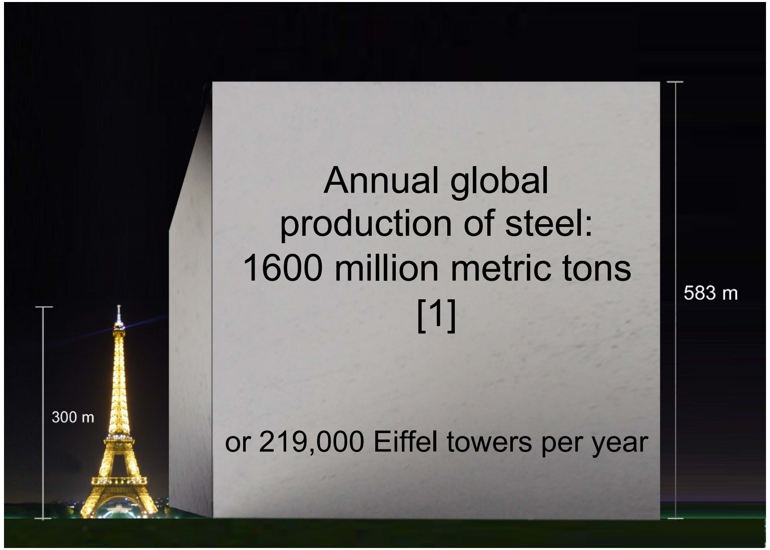


Research Application Examples

Properties of Steel



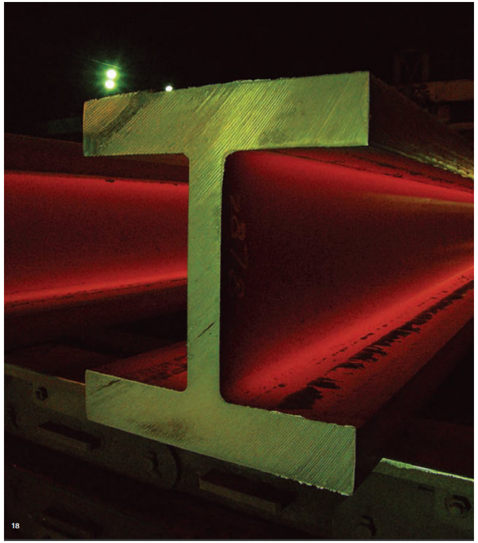
The Importance of Steel



Value:
Carbon steel: ~ \$500 per ton
Stainless steel: ~ \$2500 per ton
Global value ~ \$1000 billion [2]

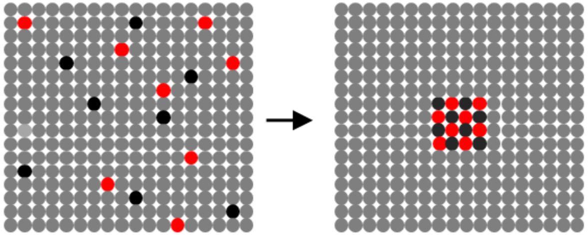
1. A mass of 1.6×10^{12} kg with a density of 8.050×10^{3} kg m^{-3} gives a volume of 1.99×10^{8} m^{3} or a cube with a length of 583 m on each side
2. As reference: the Volkswagen group produces annual revenues of \$ 225 billion with 610,000 employees

Precipitation Hardening of Steel



- Long-term creep resistance can be a critical safety factor.
- Certain precipitates cause hardening and reduce creep.
- Which precipitates are most appropriate for a given alloy composition?
- Experimental tests are costly and take long time.
- DFT calculations can provide understanding and quantitative data.

Precipitation



$$\mathrm{MX}_{\mathrm{solid}} \rightleftharpoons \mathrm{M}_{\mathrm{maxtrix}} + \mathrm{X}_{\mathrm{matrix}}$$

$$K_{eq} = [M][X]$$

$$K_{eq} = \exp\left(\frac{-\Delta G}{RT}\right)$$

Equilibrium constant

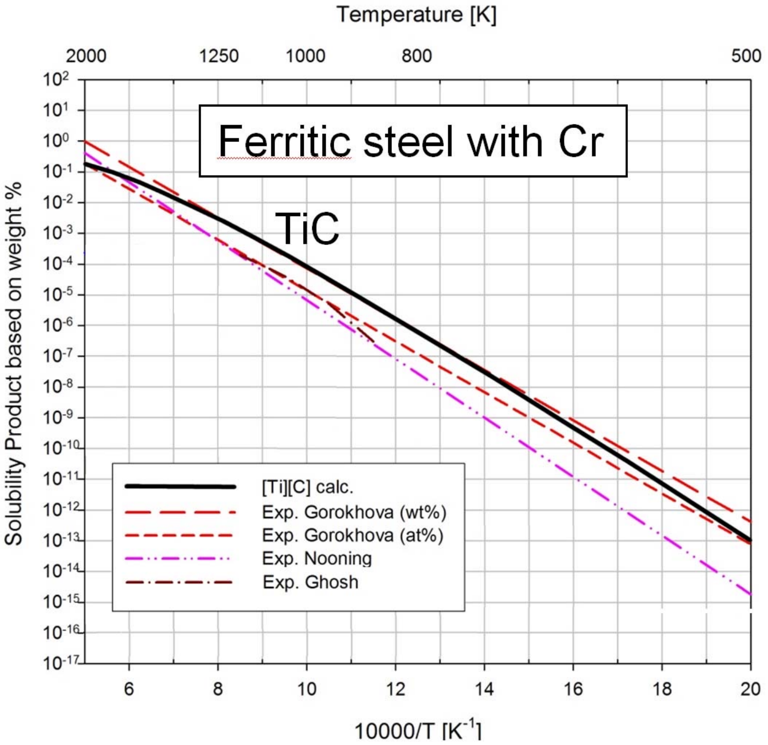
Solubility product $[M][X] = \exp\left(\frac{-\Delta G}{RT}\right)$

At 500 K an error of 10 kJ/mol in *ΔG* results in an error of about a factor of 10 in the solubility product

Typically reported as logarithmic plot

$$\log[M][X] = A - \frac{H}{T}$$

Computed vs. Experimental Solubility Product



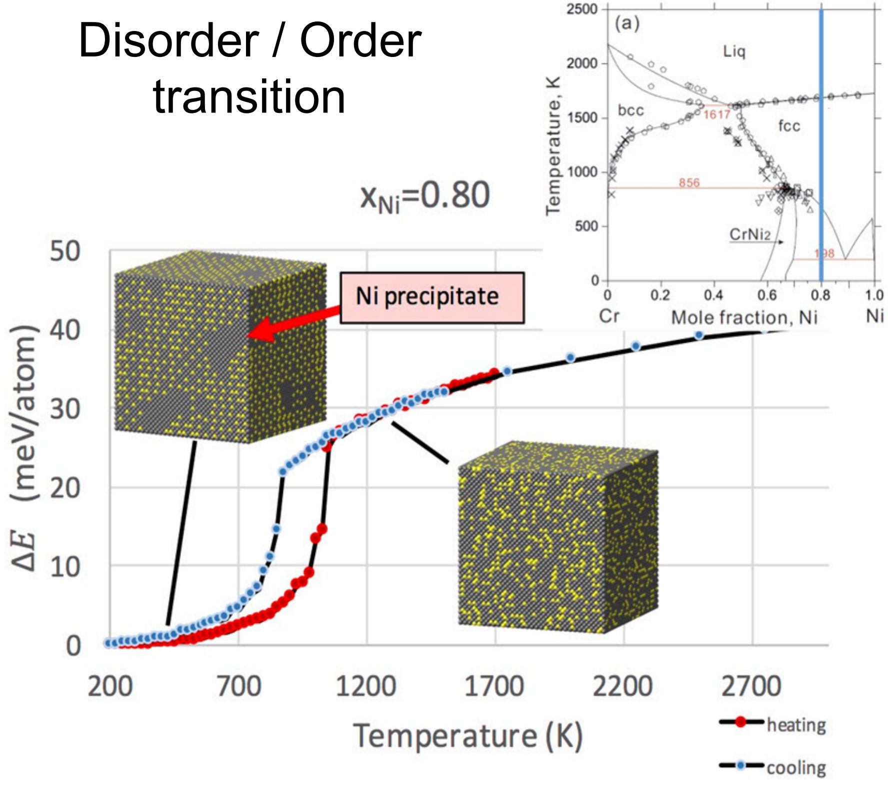
$$\log[M][X] = A - \frac{H}{T}$$

- Computed solubility product of TiC in ferritic Fe-Cr steel is similar to available experimental data
- Accurate electronic energies, inclusion of vibrational entropy (full phonon spectra) and thermal expansion are critical
- Ab initio calculations provide quantitative materials property data for alloy engineering

Source: W. Wolf *et al.* - Materials Design - Internal Report

Formation of Non-Cubic Ni_2Cr Phase in Ni-Cr Alloys

Disorder / Order transition



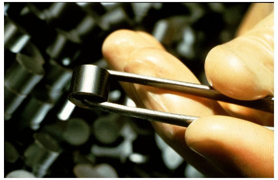
- Cluster expansion using UNCLE with a training based on VASP data
- UNCLE Monte-Carlo simulation based on cluster expansion for fcc Ni-Cr system
- The simulations capture the disorder / order transition

Source: D. Reith - Materials Design - Internal Report

Safety of Nuclear Reactors

Advanced Materials for Nuclear Power

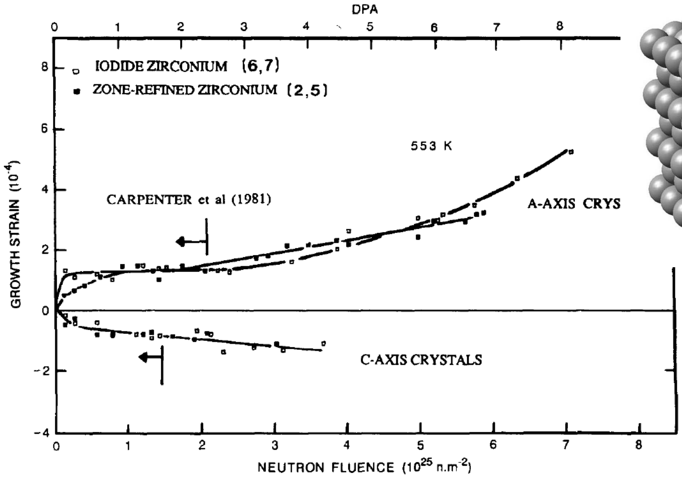
- Objective: increase the life-time of materials in the reactor while maintaining their safe operation
- Problems:
  - Irradiation-induced degradation of structural materials
  - Oxidation
- Approach
  - Use materials modeling to gain deeper understanding of
    - irradiation-induced degradation mechanisms
    - Oxidation and hydrogen pickup in the metal (hydride formation)
    - Role of alloying elements (Sn, Fe, Cr, Ni, Nb)
  - Predict the performance of improved and new alloys prior to experimental testing which is expensive and time consuming

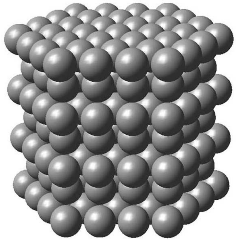


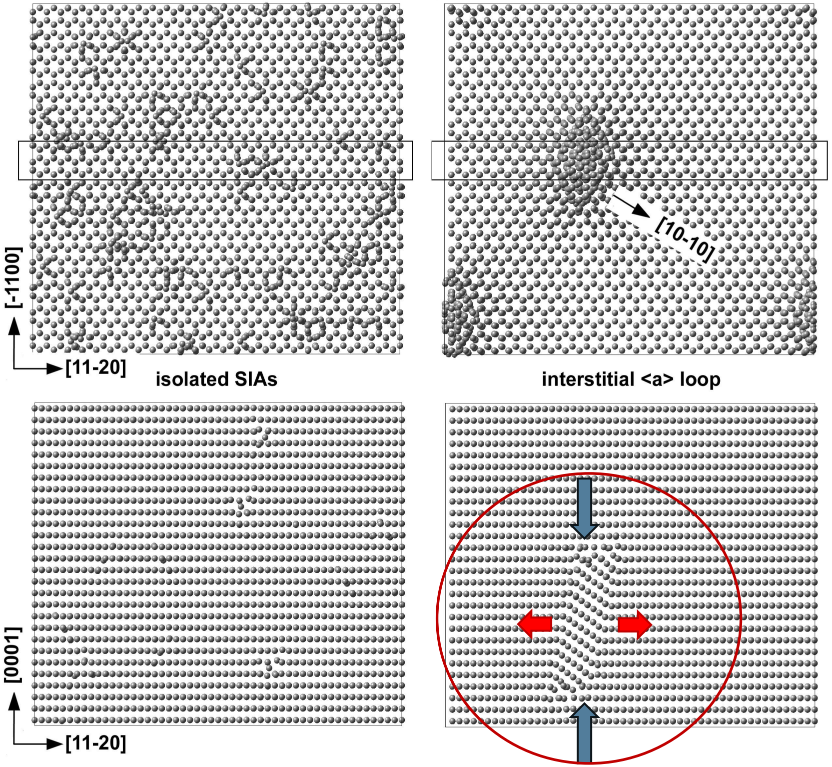
UO_2 fuel pellet

Zr cladding

Swelling of Zr under Neutron Irradiation

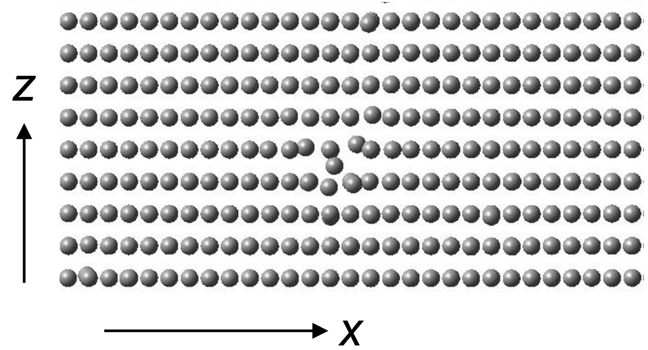






- Under irradiation, zirconium alloys deform anisotropically
- Large-scale molecular dynamics simulations provide atomistic understanding of the underlying atomic-scale phenomena
- Computations performed with LAMMPS in *MedeA* environment

Diffusion of Interstitials in Zr



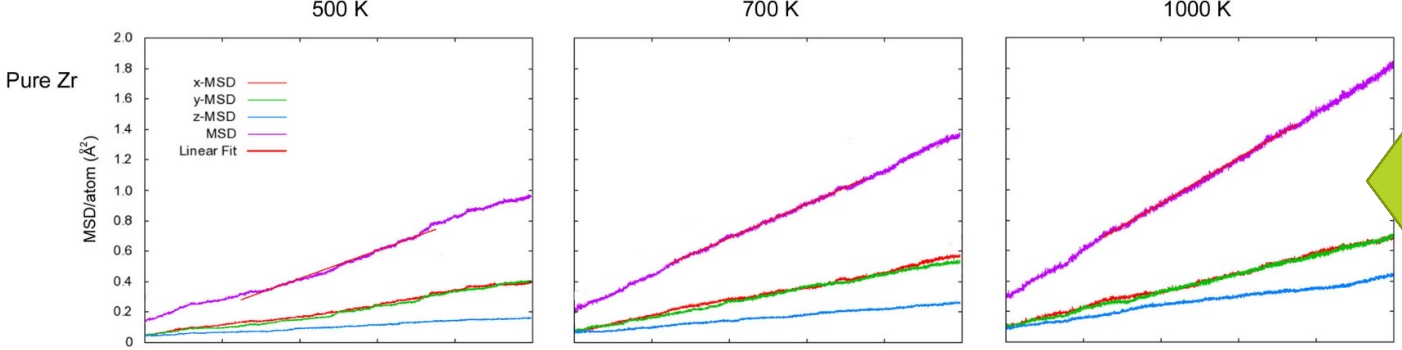
The simulations reveal:

- Fast diffusion of interstitials
- Anisotropic diffusion: faster in *x* & *y*-directions than *z*
- Build-up of <*a*> dislocation loops

MedeA® LAMMPS/EAM

1 ns molecular dynamics

Diffusion of interstitial Zr

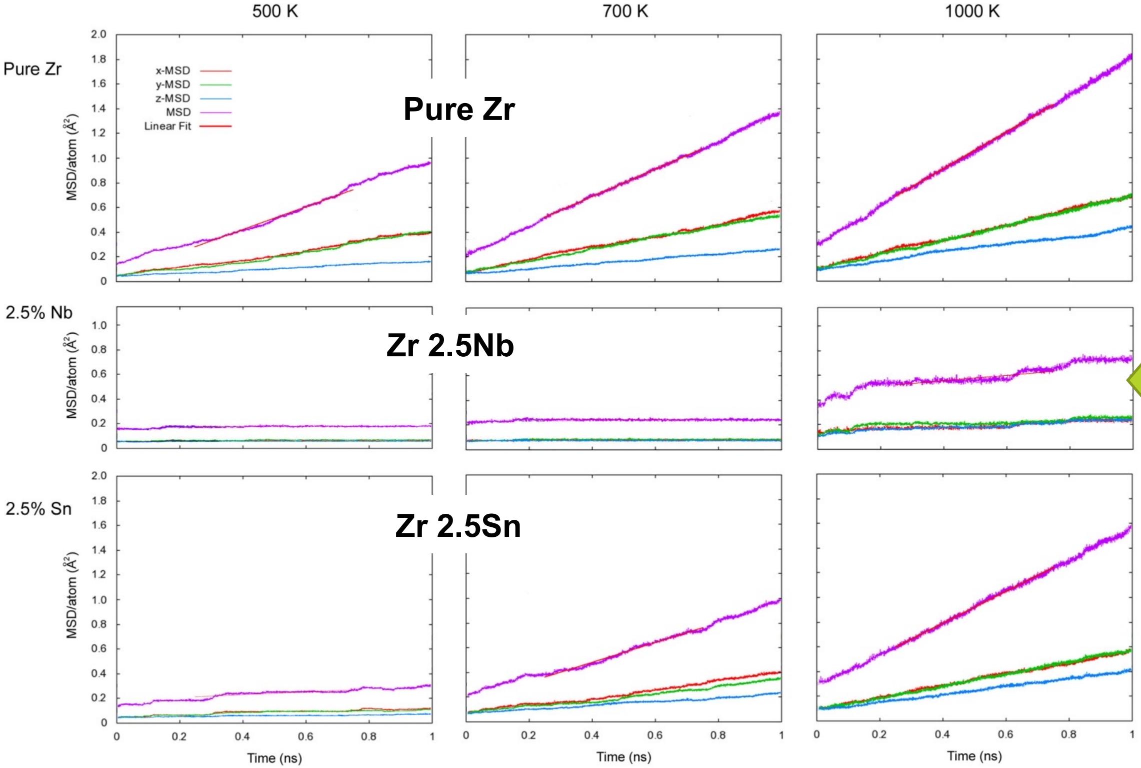


The slope of the mean square displacement vs. time is proportional to the diffusion coefficient

Effect of Alloying with Nb and Sn

MedeA$^{®}$-LAMMPS/EAM

Diffusion of interstitial Zr



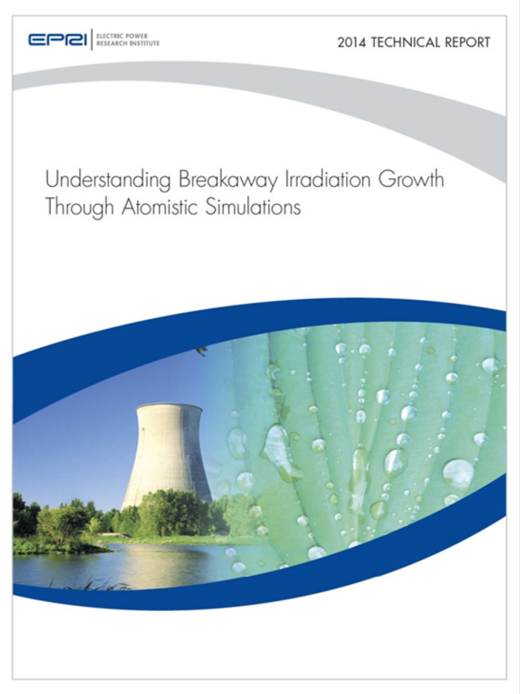
Pure Zr

Zr 2.5Nb

Zr 2.5Sn

Nb suppresses the interstitial diffusion

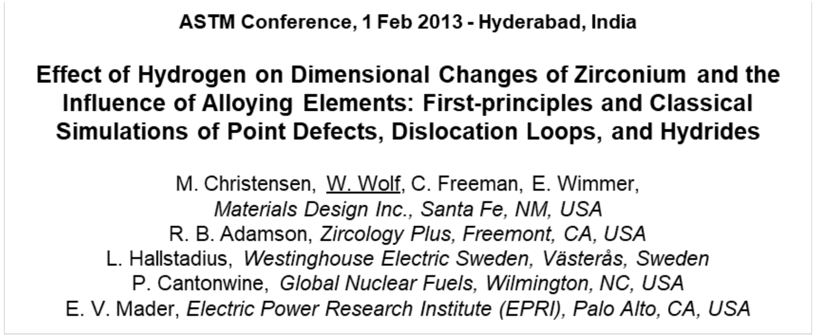
Reference



2014 TECHNICAL REPORT

Understanding Breakaway Irradiation Growth
Through Atomistic Simulations

http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000003002003185

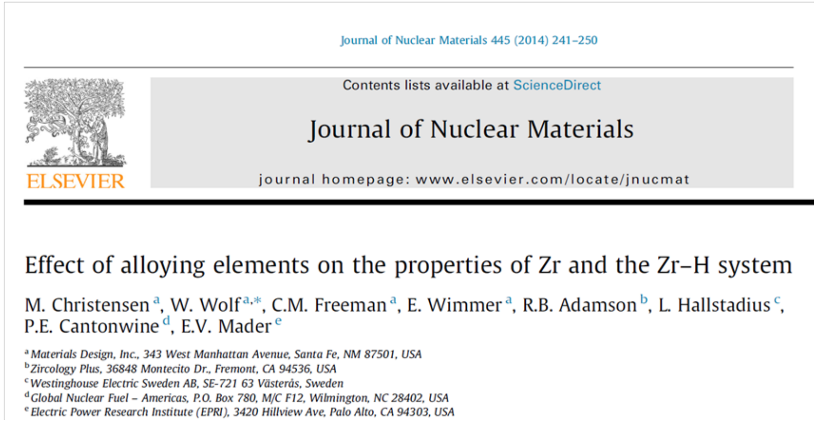


ASTM Conference, 1 Feb 2013 - Hyderabad, India

Effect of Hydrogen on Dimensional Changes of Zirconium and the Influence of Alloying Elements: First-principles and Classical Simulations of Point Defects, Dislocation Loops, and Hydrides

M. Christensen, W. Wolf, C. Freeman, E. Wimmer,
Materials Design Inc., Santa Fe, NM, USA
R. B. Adamson, *Zircology Plus, Freemont, CA, USA*
L. Hallstadius, *Westinghouse Electric Sweden, Västerås, Sweden*
P. Cantonwine, *Global Nuclear Fuels, Wilmington, NC, USA*
E. V. Mader, *Electric Power Research Institute (EPRI), Palo Alto, CA, USA*

John H. Schemel Best Paper Award



Journal of Nuclear Materials 445 (2014) 241–250

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

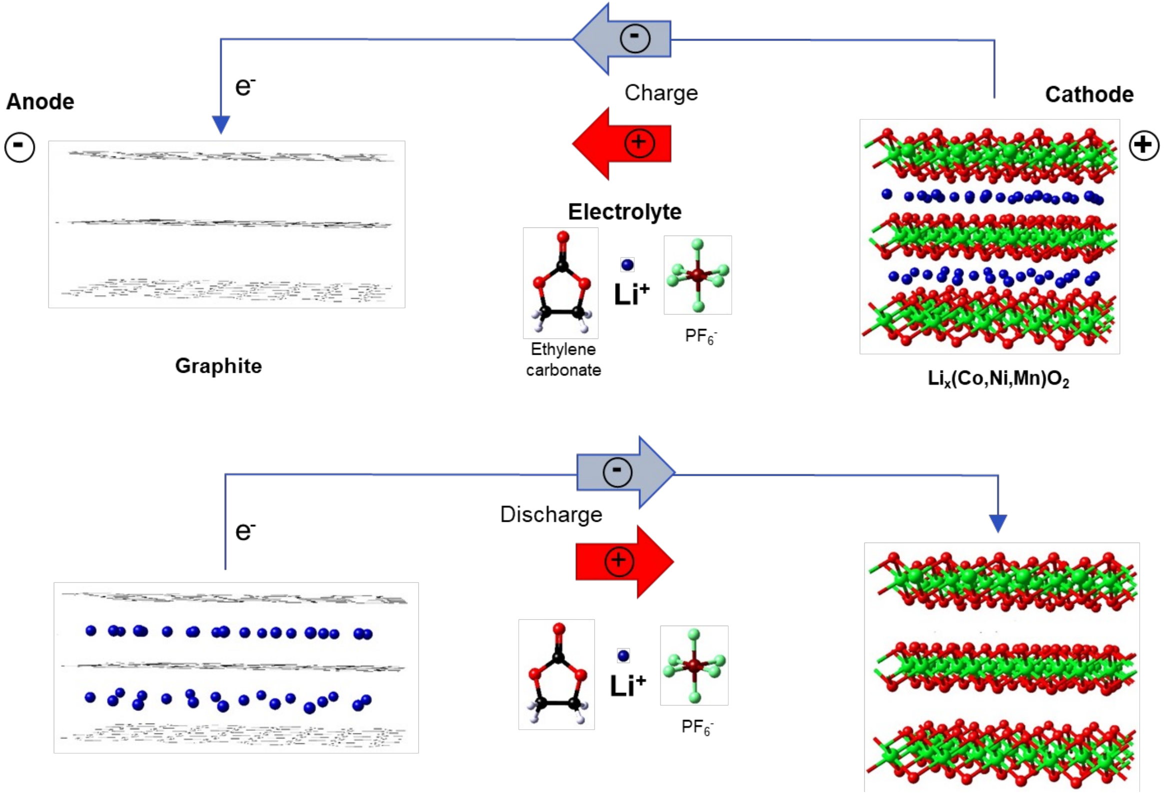
Effect of alloying elements on the properties of Zr and the Zr–H system

M. Christensen [a], W. Wolf [a,*], C.M. Freeman [a], E. Wimmer [a], R.B. Adamson [b], L. Hallstadius [c], P.E. Cantonwine [d], E.V. Mader [e]

[a] *Materials Design, Inc., 343 West Manhattan Avenue, Santa Fe, NM 87501, USA*
[b] *Zircology Plus, 36848 Montecito Dr., Fremont, CA 94536, USA*
[c] *Westinghouse Electric Sweden AB, SE-721 63 Västerås, Sweden*
[d] *Global Nuclear Fuel – Americas, P.O. Box 780, M/C F12, Wilmington, NC 28402, USA*
[e] *Electric Power Research Institute (EPRI), 3420 Hillview Ave, Palo Alto, CA 94303, USA*

Batteries

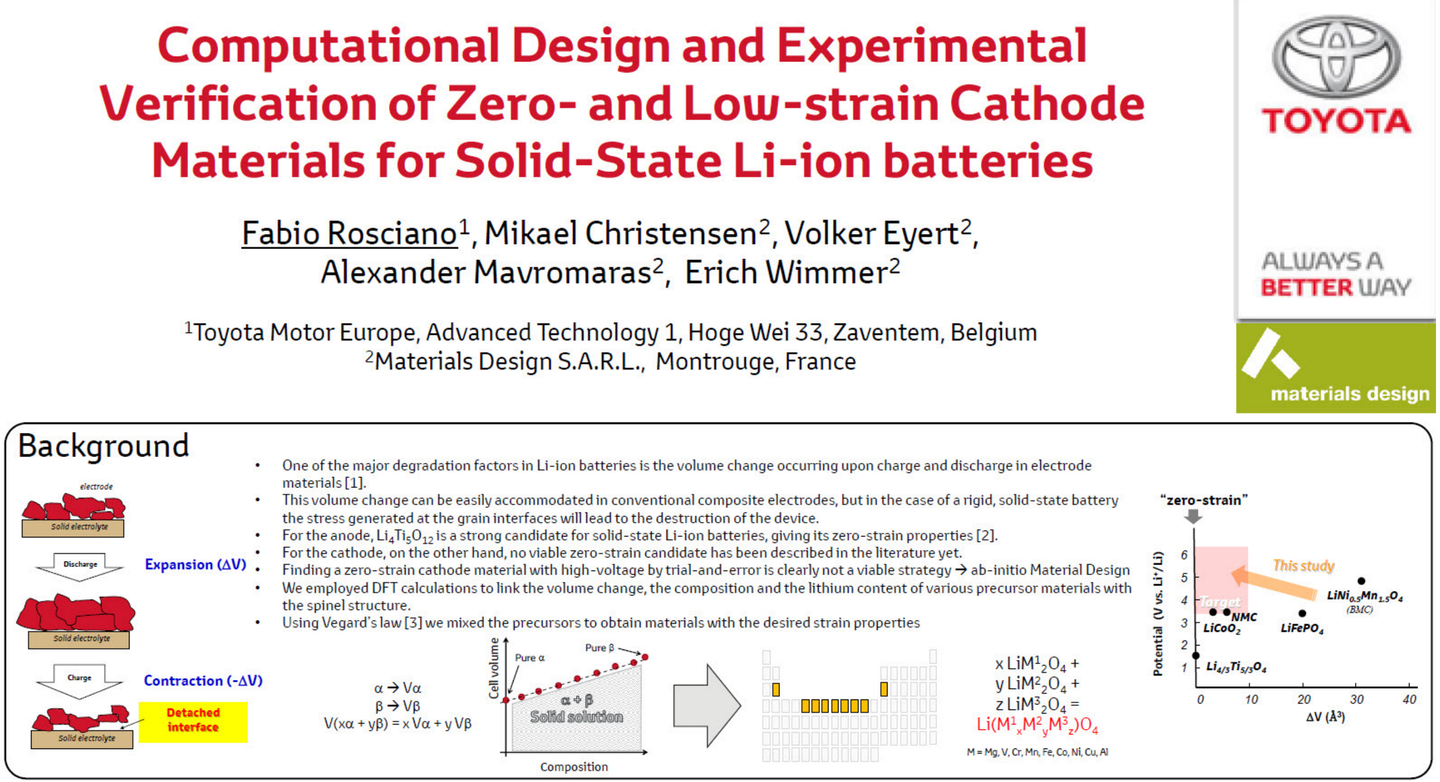
Li-Ion Battery



Engineering Issues

- Limited capacity: Li_xCoO_2 is unstable if more than half of Li is removed. Practical operation is restricted to $0.5 \le x \le 1$ → half of the capacity is not used.
- Li_xCoO_2 expands when Li is removed and contracts when Li is inserted → degradation
- The liquid electrolyte is flammable
- Each cell behaves differently → serious issue in battery packs

Low-Strain Cathode Materials



Computational Design and Experimental Verification of Zero- and Low-strain Cathode Materials for Solid-State Li-ion batteries

Fabio Rosciano[1], Mikael Christensen[2], Volker Eyert[2],
Alexander Mavromaras[2], Erich Wimmer[2]

[1]Toyota Motor Europe, Advanced Technology 1, Hoge Wei 33, Zaventem, Belgium
[2]Materials Design S.A.R.L., Montrouge, France

Background

- One of the major degradation factors in Li-ion batteries is the volume change occurring upon charge and discharge in electrode materials [1].
- This volume change can be easily accommodated in conventional composite electrodes, but in the case of a rigid, solid-state battery the stress generated at the grain interfaces will lead to the destruction of the device.
- For the anode, $Li_4Ti_5O_{12}$ is a strong candidate for solid-state Li-ion batteries, giving its zero-strain properties [2].
- For the cathode, on the other hand, no viable zero-strain candidate has been described in the literature yet.
- Finding a zero-strain cathode material with high-voltage by trial-and-error is clearly not a viable strategy → ab-initio Material Design
- We employed DFT calculations to link the volume change, the composition and the lithium content of various precursor materials with the spinel structure.
- Using Vegard's law [3] we mixed the precursors to obtain materials with the desired strain properties

$\alpha \rightarrow V\alpha$
$\beta \rightarrow V\beta$
$V(x\alpha + y\beta) = x\,V\alpha + y\,V\beta$

$x\,LiM^1{}_2O_4 +$
$y\,LiM^2{}_2O_4 +$
$z\,LiM^3{}_2O_4 =$
$Li(M^1{}_xM^2{}_yM^3{}_z)O_4$

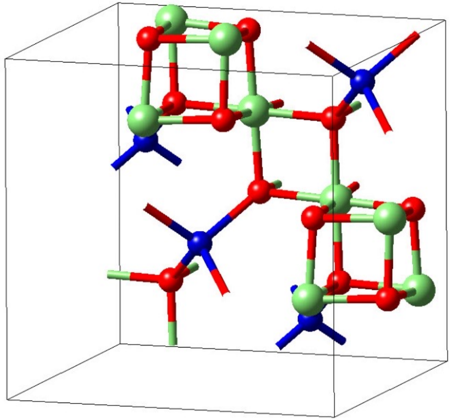
M = Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Al

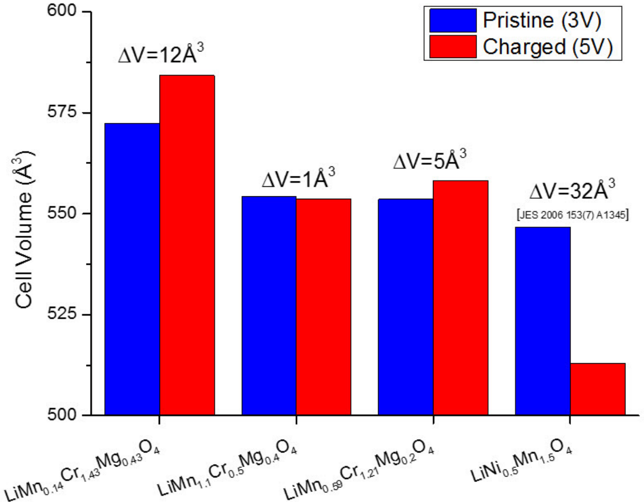
Simulations

- *ab initio* methods are used to compute equilibrium volume of spinel structures and identify compounds that shrink or expand when Li is removed

Active Space: $\mathrm{Li}(\mathrm{M}^1_x, \mathrm{M}^2_y, \mathrm{M}^3_z)\mathrm{O}_4, \quad \mathrm{M} = \mathrm{Mg}, \mathrm{V}, \mathrm{Cr}, \mathrm{Mn}, \mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Al}$

- Find compounds close to zero expansion when Li atoms are inserted





Patent

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 December 2014 (04.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/191018 A1

(51) **International Patent Classification**:
C01G 45/12 (2006.01) *H01M 10/052* (2010.01)
H01M 4/505 (2010.01) *H01M 10/0562* (2010.01)

(21) **International Application Number**: PCT/EP2013/060881

(22) **International Filing Date**: 27 May 2013 (27.05.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(71) **Applicant**: **TOYOTA MOTOR EUROPE NV/SA** [BE/BE]; Avenue du Bourget 60, B-1140 Brussels (BE).

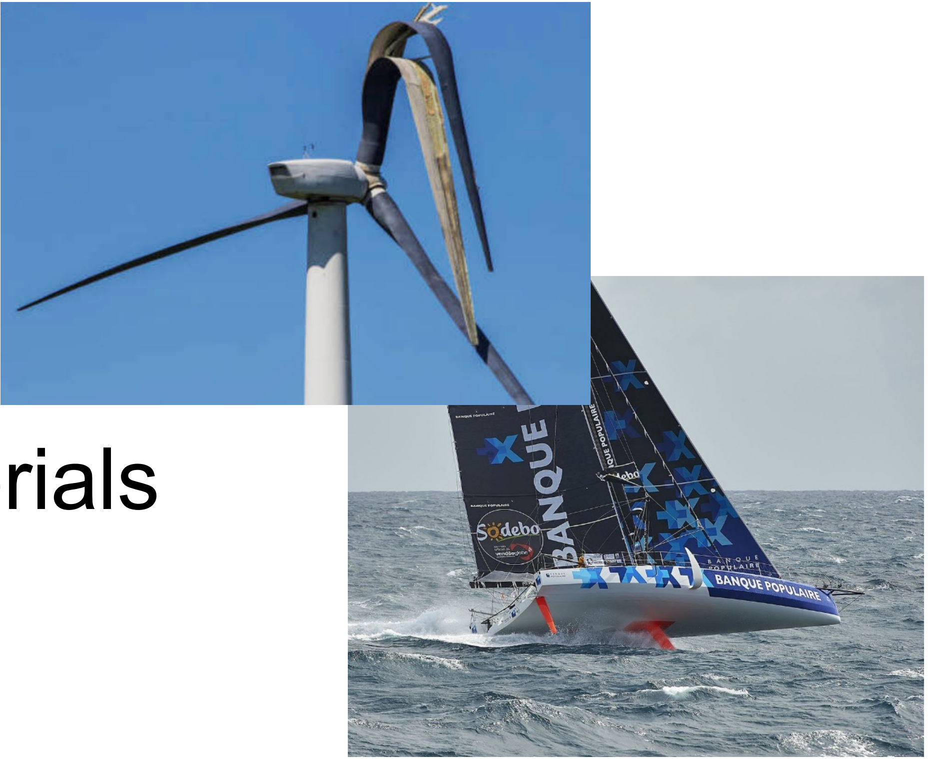
(72) **Inventors**: **ROSCIANO, Fabio**; Milcampslaan 127, B-1030 Schaarbeek (BE). **CHRISTENSEN, Mikael**; Branningevagen 1, S-120 54 Arsta (SE). **EYERT, Volker**; Baumschulenweg 6A, 14469 Potsdam (DE). **MAVROMARAS, Alexander**; Bergandsgatan 43, S-133 41 Saltsjobaden (SE). **WIMMER, Erich**; 3 avenue du Commerce, F-78000 Versailles (FR).

(74) **Agents**: **HART-DAVIS, Jason** et al.; Cabinet Beau de Lomenie, 158 rue de l'Université, F-75340 Paris Cedex 07 (FR).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

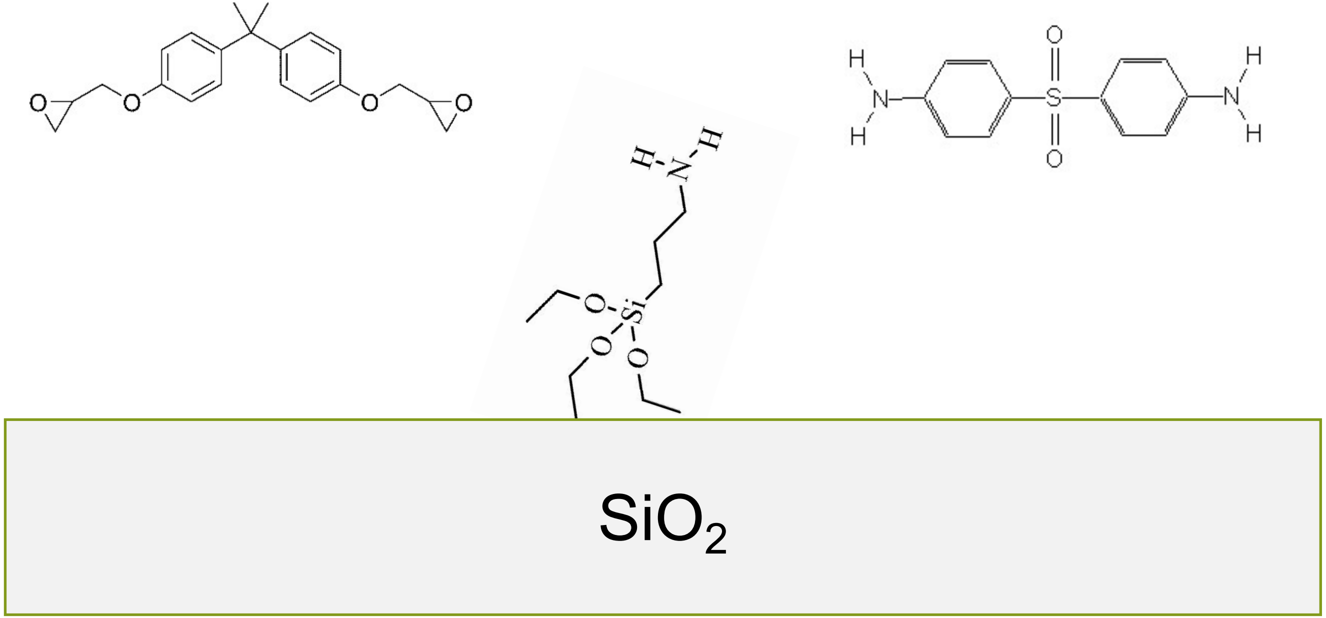
Published:
— *with international search report (Art. 21(3))*



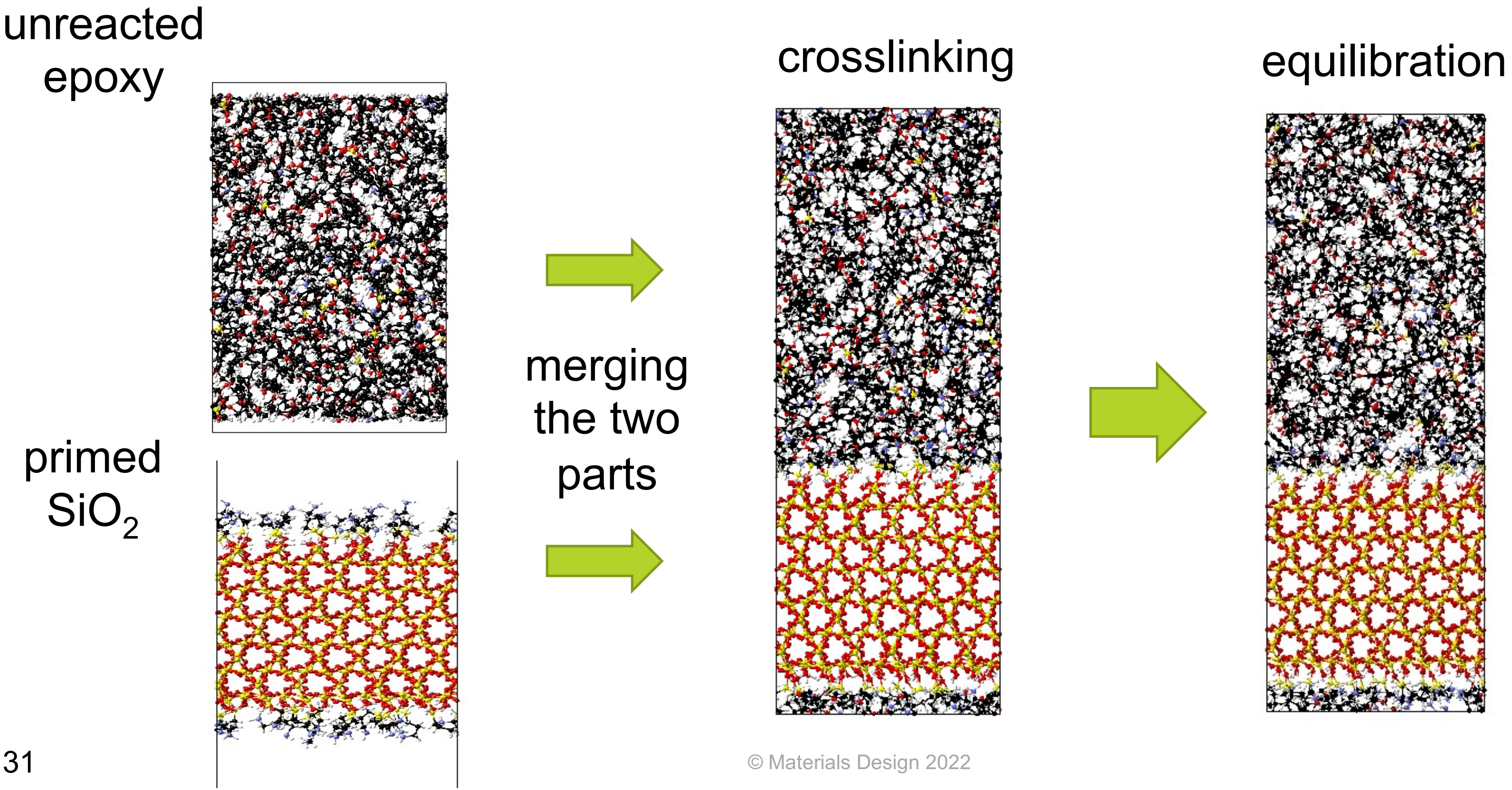
Composite Materials

Epoxy-Oxide Interfacial Systems

How much primer (coupling between SiO_2 surface and polymer) is optimal?



Epoxy-SiO_2 Interfaces – Model Building



unreacted epoxy

primed SiO_2

merging the two parts

crosslinking

equilibration

Epoxy-SiO_2 Interfaces – Mechanical Properties

Stiffness coefficient C_{33} for SiO_2 - epoxy composite layer systems with various levels of primer coverage:

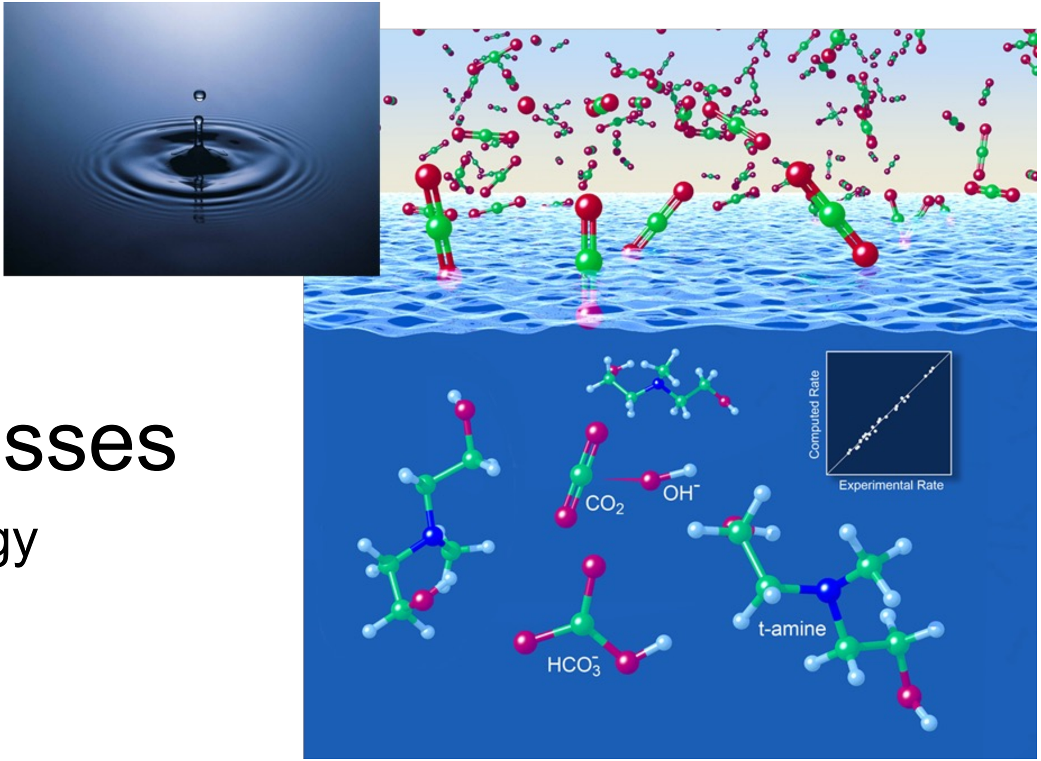
Primed surface sites (%)	C_{33} (GPa)
0	7.2
12.5	7.8
25	8.8
50	5.0
Reference: Bulk Cured Resin	5.97 ± 0.29

Intermediate primer coverage produces optimal enhancement in small strain mechanical behavior.

Source: D. Rigby - Materials Design - Internal Report

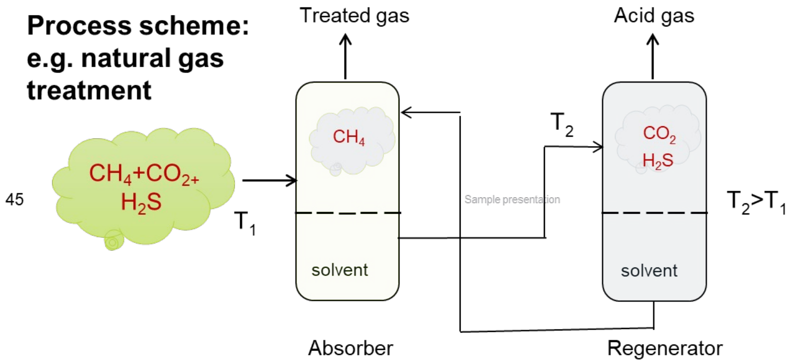
Chemical Processes

Reducing Cost and Energy Consumption



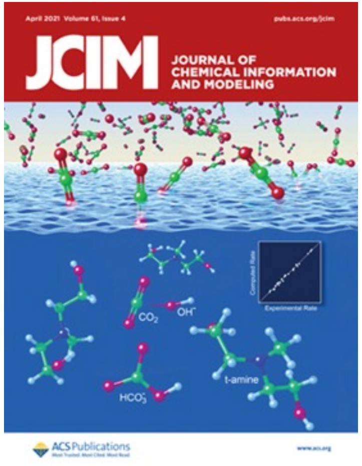
Carbon Capture and Storage Technology

- CO_2 is removed from natural gas in a carbon capture unit



- The solvent is an aqueous amine
- How to select the amine to control the efficiency of the CO_2 capture and reduce cost and energy consumption?

Rates of CO_2 Absorption in Aqueous Amine Solvents

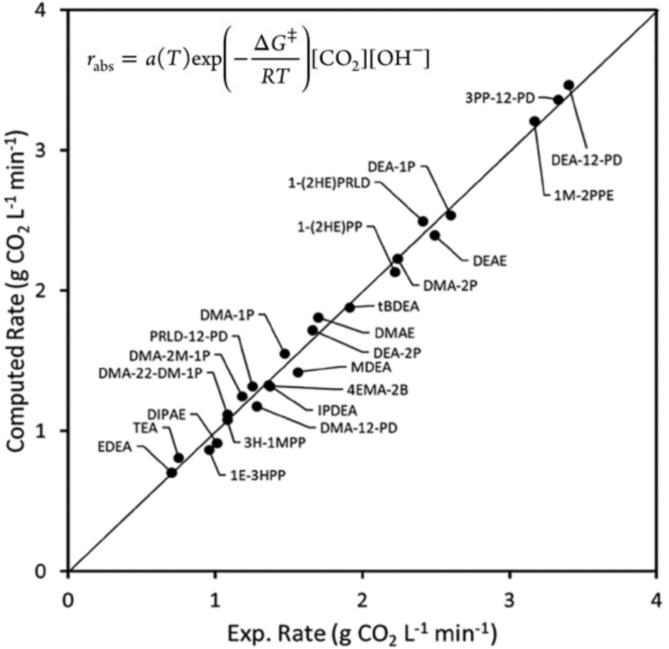


April 2021 Volume 61, Issue 4

pubs.acs.org/jcim

JCIM JOURNAL OF CHEMICAL INFORMATION AND MODELING

ACS Publications



$$r_{abs} = a(T)\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)[CO_2][OH^-]$$

Challenge for simulation:

- The experimental distribution of the activation energies of CO_2 absorption is around 1.3 kJ mol^{-1}
- To be fully predictive the simulation method must be one order of magnitude more precise than 1 kJ mol^{-1}
- A Bell-Evans-Polanyi relation and long MD simulations to compute the energies of reaction of:

$OH^- + CO_2 \rightarrow HCO_3^-$

permitted an accuracy of 0.1 kJ mol^{-1}

Source: *J. Chem. Inf. Model*. **2021**, *61*, 1814 – Together with TotalEnergies, SE