From nano to macro: Introduction to atomistic modeling techniques

Lecture series, CEE, Fall 2005, IAP, Spring 2006

Unifying chemistry and mechanics: Modeling fracture mechanics of chemically complex materials using reactive force fields

Lecture 4

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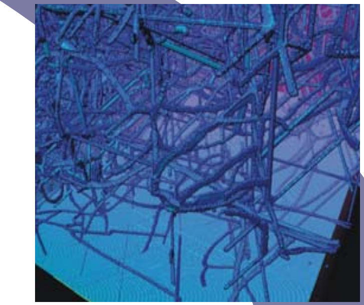
Mechanical behavior of different materials…

"brittle": Materials that experience little, if any, plastic deformation before the onset of fracture

(Buehler *et al.*, *Nature*, 2003)

"ductile": Materials that experience significant plastic deformation before the onset of fracture

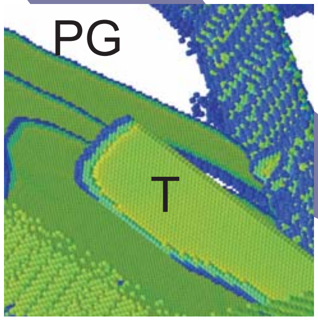


(Buehler *et al.*, *CMAME*, 2004)

Use large-scale computing within framework of multi-scale modeling

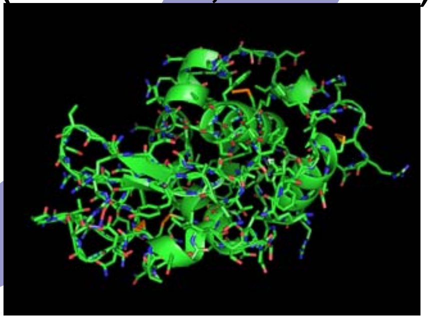
Develop fundamental understanding

"geometric confinement"
Nanostructured materials, carbon nanotubes



(Buehler *et al.*, *JMPS*, 2003)

"biological materials"
(Proteins, DNA …)



(Buehler *et al.*, *MRS Proceedings*, 2004)

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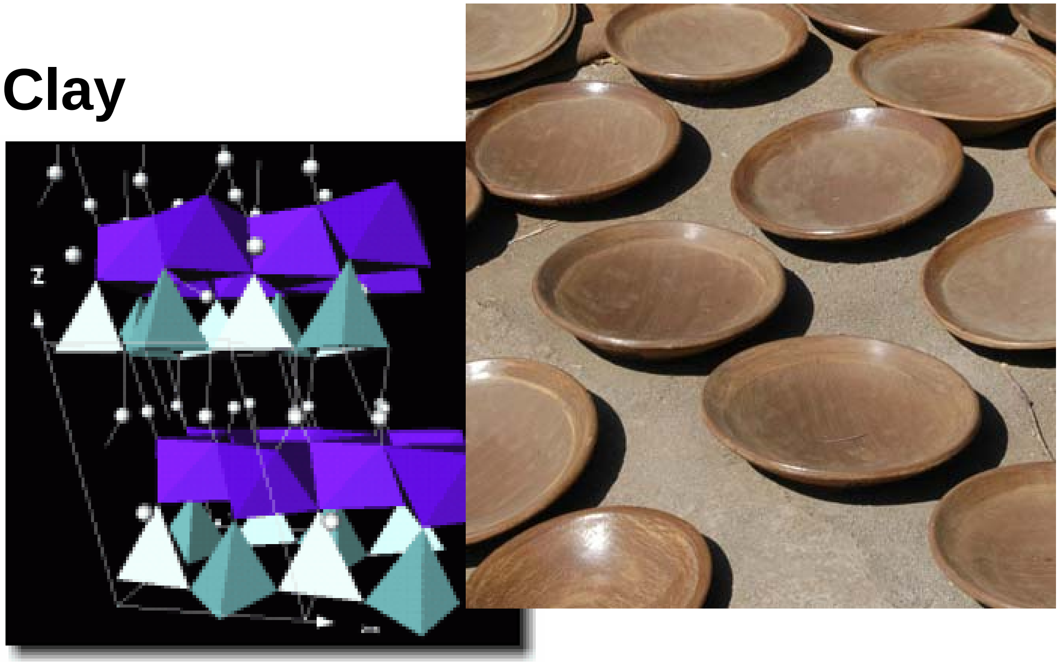
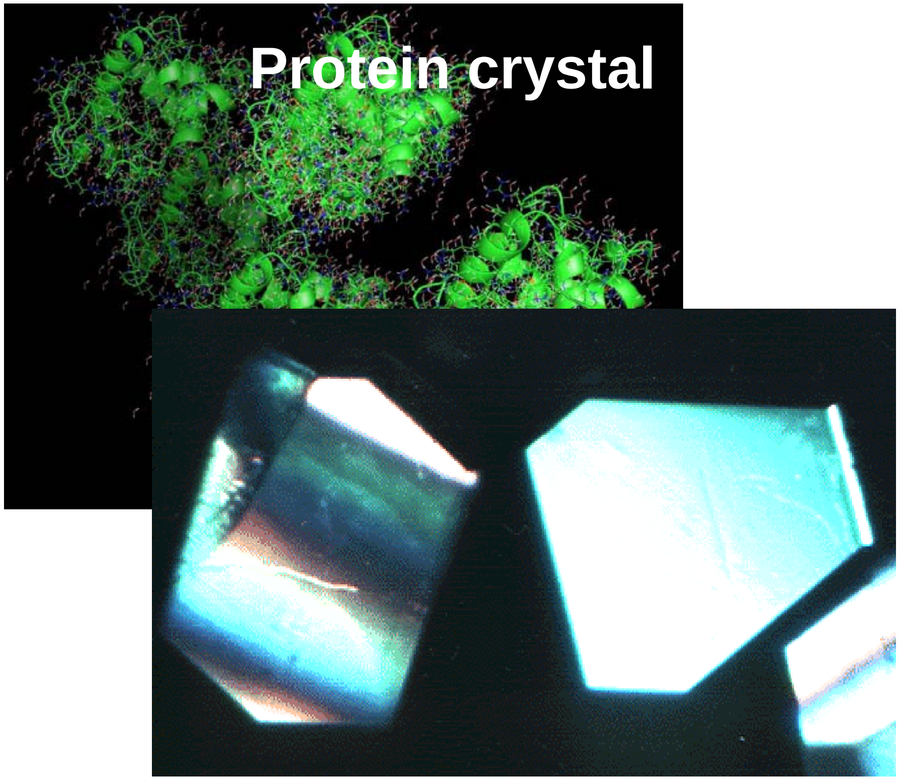
I: Materials with high chemical complexity

- Natural materials, like C-S-H (cement), wood, clay
- Biological materials, like proteins, bone

- Feature: Chemical bonds or interactions, and competition between different kinds of chemical bonding governs the material behavior

Clay





http://www.geology.uiuc.edu/~jwang7/RD/publications/The%2010A%20phase-04.pdf,
http://www.ill.fr/dif/3D-crystals/layers.html
http://www.tropicalisland.de/lombok/images/AMI%20Lombok%20Masbagik%20Timur%20pottery%20village%20clay%20plates%203008x2000.jpg

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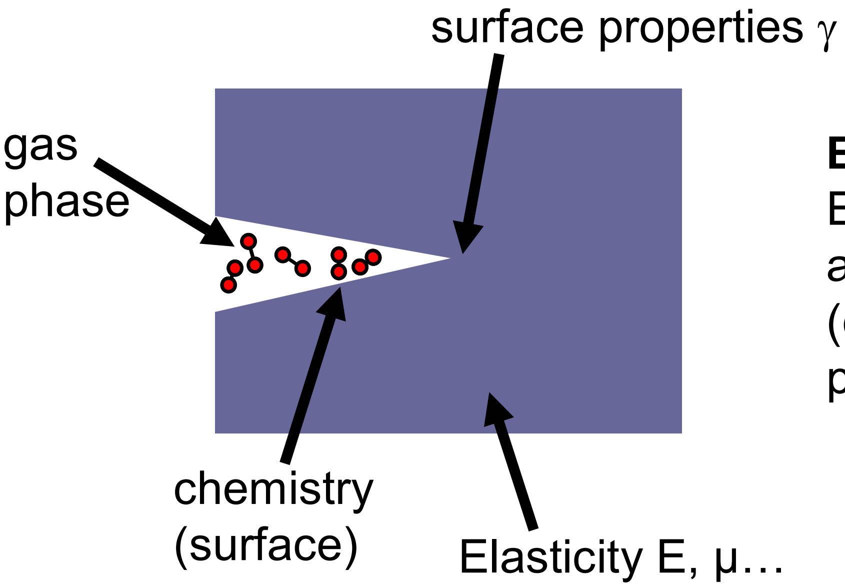
II: Chemistry and mechanics…

- Develop atomistic models that enable seamless integration of chemistry and mechanics:
  - ☐ Chemistry: Bond breaking and formation, flow of charges, paradigms such as molecules, atoms, electrons etc., “chemistry governs hyperelastic behavior”
  - ☐ Mechanics: Fracture, critical SIF, theoretical strength etc.
- Goal: Unified treatment in computational environment
- Requires treatment of thousands of atoms near defects and at reaction cores: Can not be done with existing methods

Stress corrosion cracking, hydrogen embrittlement



Example: Environmentally assisted cracking (coupling mechanical properties-chemistry)

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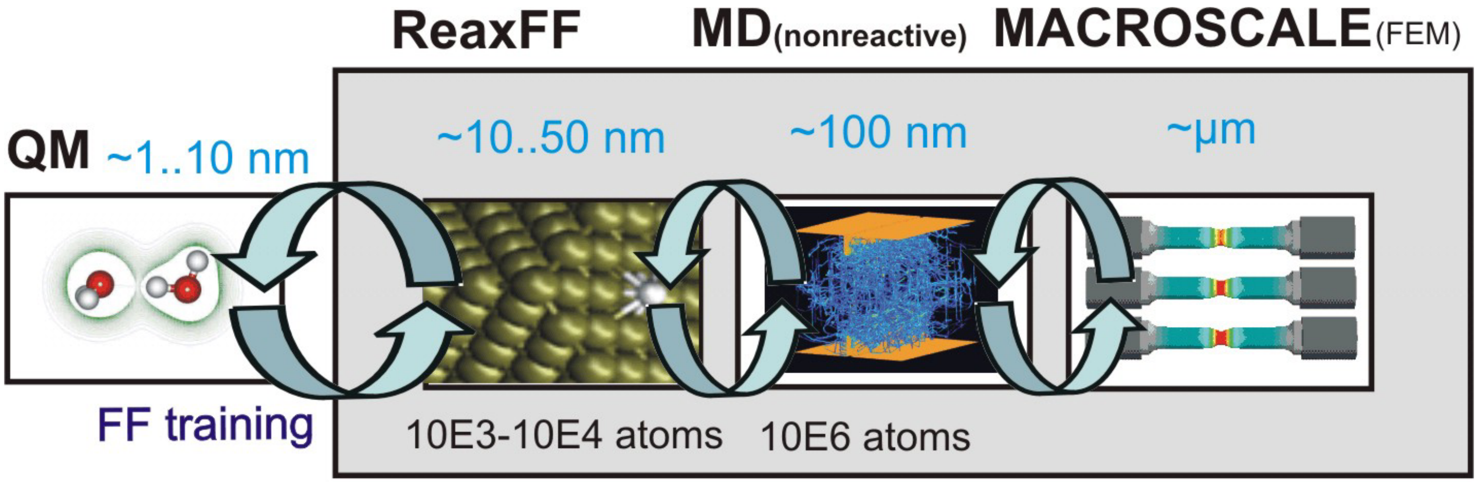
Objectives

- Develop atomistic based, fundamental theoretical models of chemically complex materials, both in terms of microstructure (class I, multitude of chemical bonds), or in terms of interaction of materials with chemical environments (class II)

- Strategy: Transfer information from quantum mechanics (DFT) to larger scales, by using empirical potentials



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Outline

- Introduction (previous slides)

- Part A:
  Nonreactive force fields (CHARMM, AMBER, DREIDING etc.)
- Part B:
  Reactive force fields: A new bridge between QM and MD
- Part C:
  Application of reactive force fields (enzymes, fracture, water formation)

- Conclusion and outlook,
  discussion points for future work or collaboration

Main objective: Provide introduction into modeling techniques and some of our research interests and examples

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Part A: Nonreactive force fields

Development started ~1960, ongoing research effort

Goal: Model (mainly) organic chemistry

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Common empirical force fields

Class I (<u>experiment derived</u>, simple form)

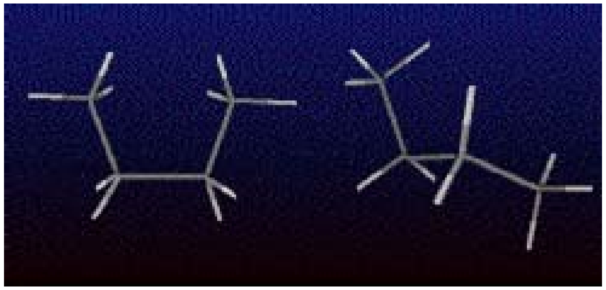
- CHARMM
- CHARMm (Accelrys)
- AMBER
- OPLS/AMBER/Schrödinger
- ECEPP (free energy force field)
- GROMOS

Harmonic terms;
Derived from vibrational spectroscopy, gas-phase molecular structures
Very system-specific

Class II (more complex, <u>derived from QM</u>)

- CFF95 (Biosym/Accelrys)
- MM3
- MMFF94 (CHARMM, Macromodel…)
- UFF, DREIDING

Include anharmonic terms
Derived from QM, more general



http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm
http://amber.scripps.edu/

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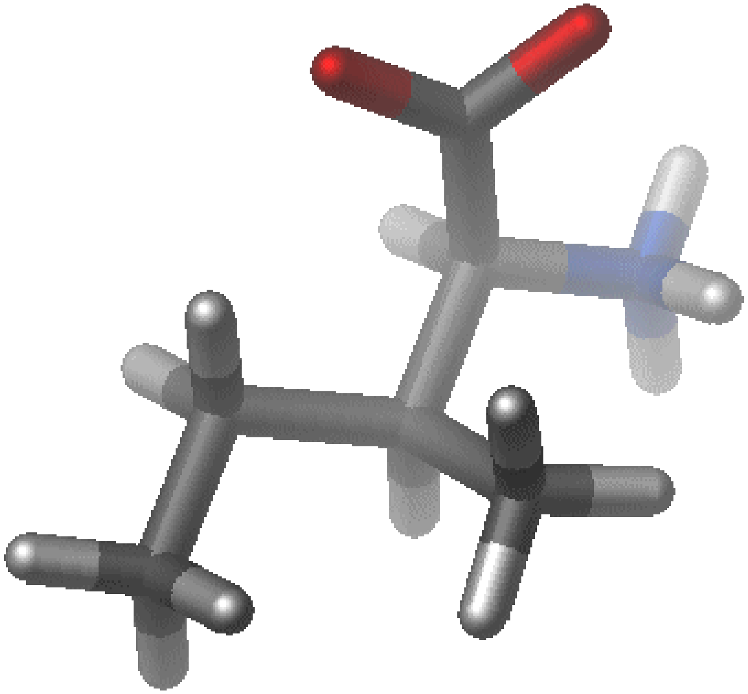
Review: CHARMM potential

$$V(R) = E_{bonded} + E_{non-bonded}$$

$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

Bonding between atoms described as combination of various terms, describing the angular, stretching etc. contributions



http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

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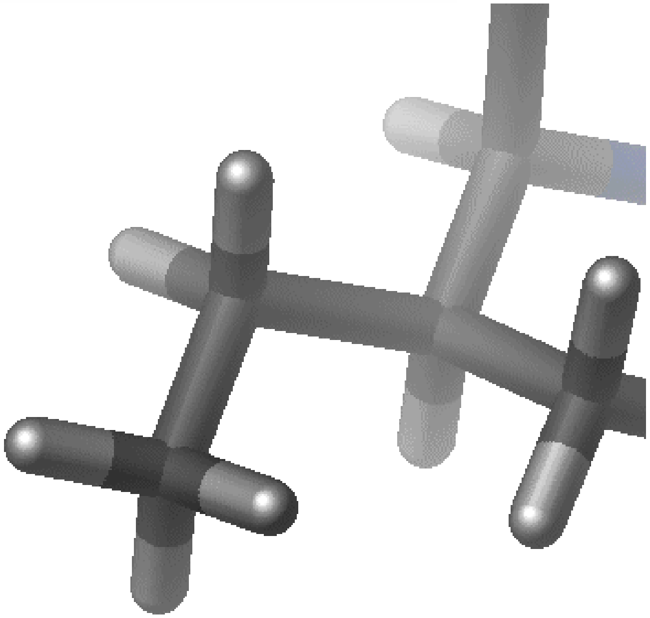
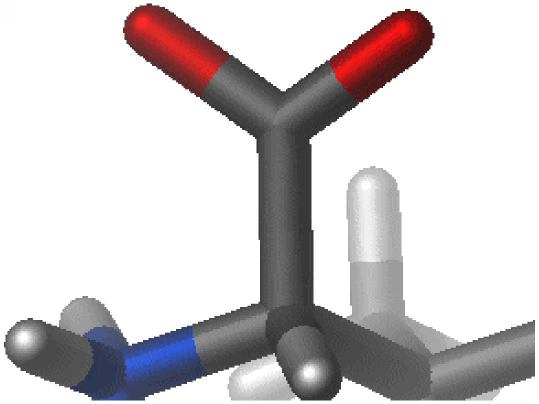
Review: CHARMM potential

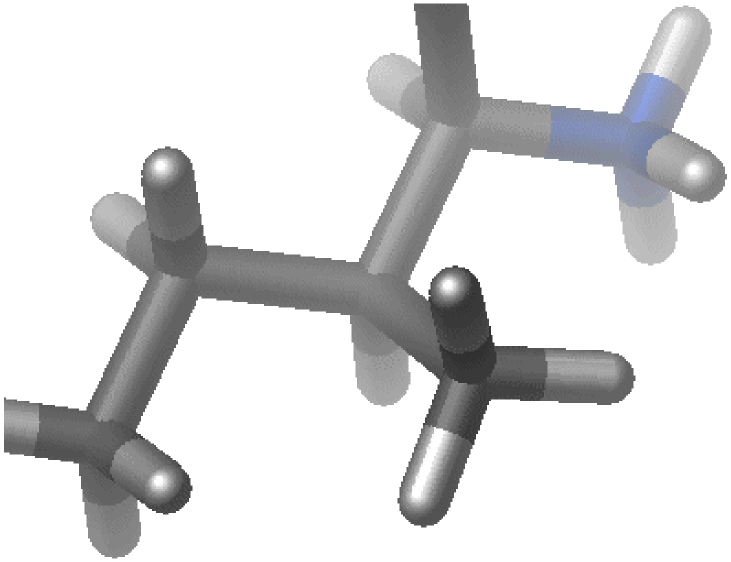
$$E_{bond-stretch} = \sum K_b (b - b_0)^2$$



$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$



$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_\phi (1 - \cos(n\phi))$$



http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html

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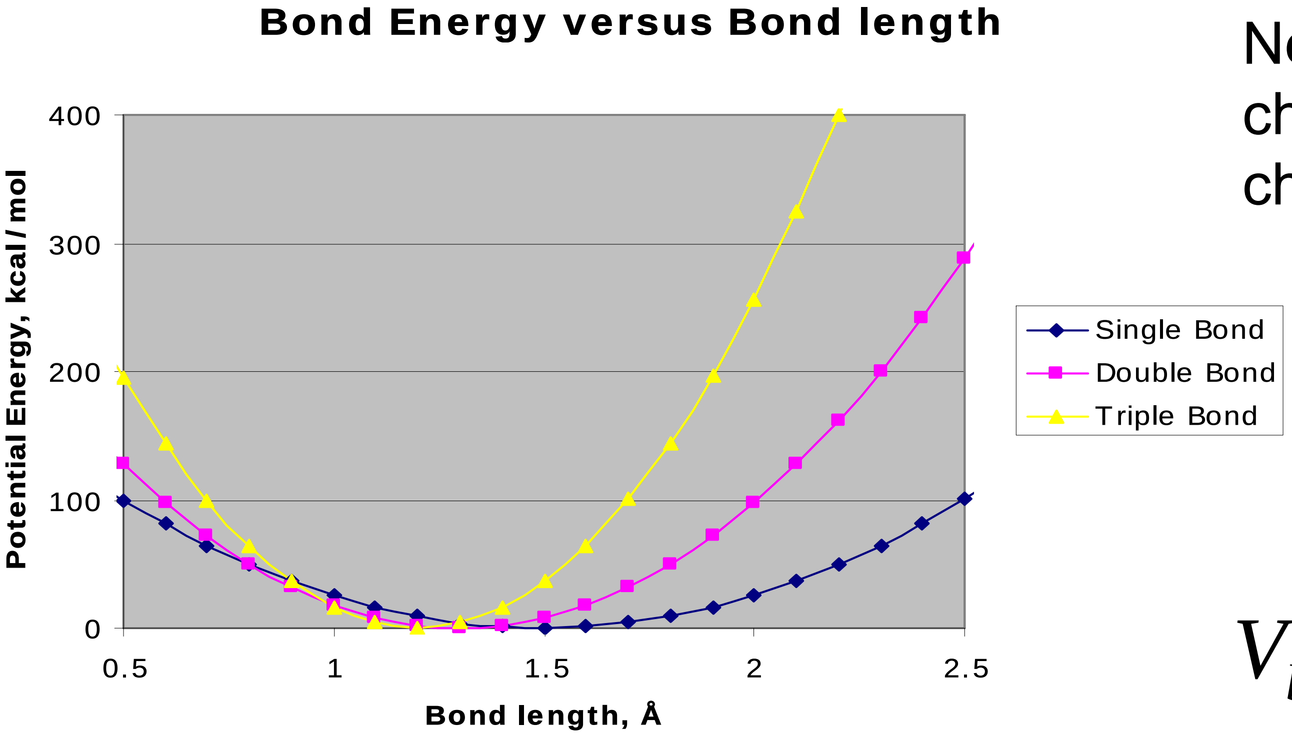
Review: CHARMM potential

Chemical type	K_{bond}	b_o
C−C	100 kcal/mole/Å^2	1.5 Å
C=C	200 kcal/mole/Å^2	1.3 Å
C≡C	400 kcal/mole/Å^2	1.2 Å



Different types of C-C bonding represented by different choices of b_0 and k_b;

Need to retype when chemical environment changes

$$V_{bond} = K_b (b - b_o)^2$$

http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

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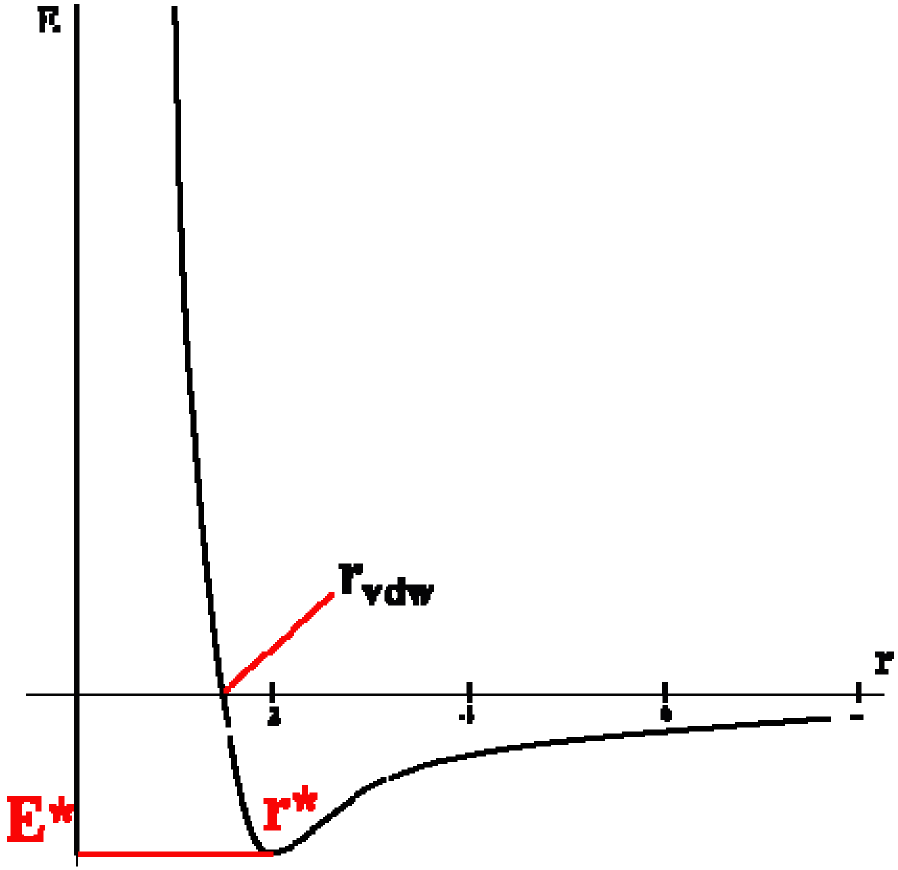
Review: CHARMM potential

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$

$$E_{van-der-Waals} = \sum_{\substack{nonbonded \\ pairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^{6}} \right)$$

$$E_{electrostatic} = \sum_{\substack{nonbonded \\ pairs}} \frac{q_i q_k}{D r_{ik}}$$



Nonbonding interactions

vdW (dispersive)

Coulomb (electrostatic)

H-bonding

http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html

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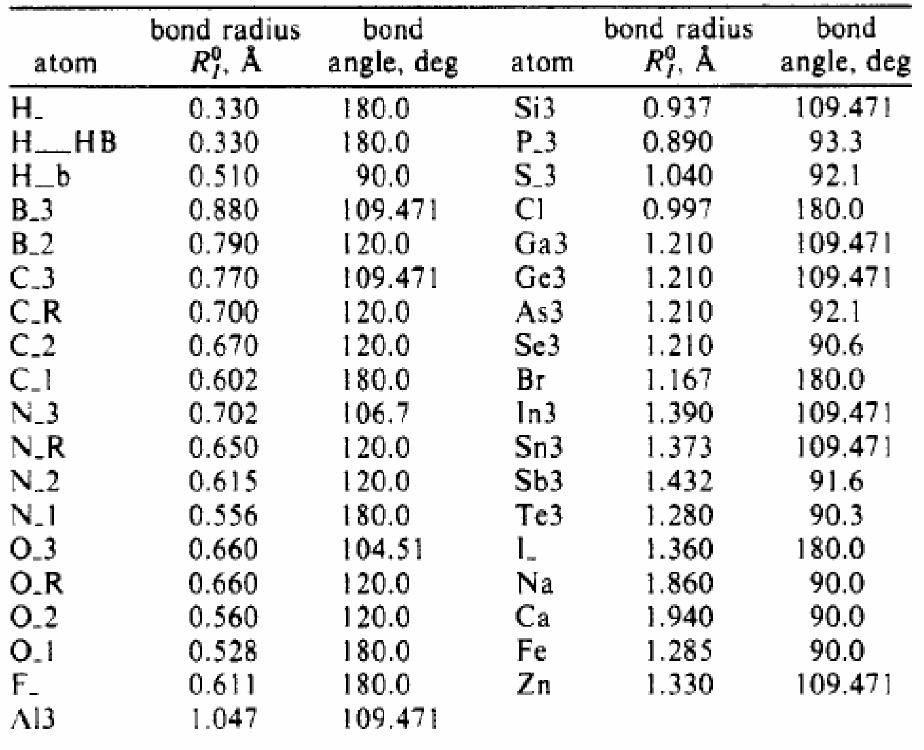
DREIDING



atom	bond radius R_I^0, Å	bond angle, deg	atom	bond radius R_I^0, Å	bond angle, deg
H_	0.330	180.0	Si3	0.937	109.471
H__HB	0.330	180.0	P_3	0.890	93.3
H_b	0.510	90.0	S_3	1.040	92.1
B_3	0.880	109.471	Cl	0.997	180.0
B_2	0.790	120.0	Ga3	1.210	109.471
C_3	0.770	109.471	Ge3	1.210	109.471
C_R	0.700	120.0	As3	1.210	92.1
C_2	0.670	120.0	Se3	1.210	90.6
C_1	0.602	180.0	Br	1.167	180.0
N_3	0.702	106.7	In3	1.390	109.471
N_R	0.650	120.0	Sn3	1.373	109.471
N_2	0.615	120.0	Sb3	1.432	91.6
N_1	0.556	180.0	Te3	1.280	90.3
O_3	0.660	104.51	I_	1.360	180.0
O_R	0.660	120.0	Na	1.860	90.0
O_2	0.560	120.0	Ca	1.940	90.0
O_1	0.528	180.0	Fe	1.285	90.0
F_	0.611	180.0	Zn	1.330	109.471
Al3	1.047	109.471			

$$E = \tfrac{1}{2}k_e(R - R_e)^2$$

$$K_{IJ}(1) = 700\ (\mathrm{kcal/mol})/\text{Å}^2$$

$$K_{IJ}(n) = nK_{IJ}(1)$$

$$E_{IJK} = \tfrac{1}{2}C_{IJK}[\cos\theta_{IJK} - \cos\theta_J^0]^2$$

$$C_{IJK} = \frac{K_{IJK}}{(\sin\theta_J^0)^2}$$

$$K_{IJK} = 100\ (\mathrm{kcal/mol})/\mathrm{rad}^2$$

Depending on chemistry different atoms are assigned different labels

C_3 = carbon sp^3

C_1 = carbon sp

Use combination rules to determine bonds between different elements

Mayo *et al.*

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UFF “Universal Force Field”

- Can handle complete periodic table
- Force constants derived using general rules of element, hybridization and connectivity

$$E_R = \tfrac{1}{2} k_{IJ} (r - r_{IJ})^2$$

$$r_{IJ} = r_I + r_J + r_{BO} + r_{EN}$$

Features:

- Atom types=elements
- Chemistry based rules for determination of force constants

Pauling-type bond order correction

$$r_{BO} = -\lambda (r_I + r_J) \ln(n)$$

$$r_{EN} = r_I r_J (\sqrt{\chi_I} - \sqrt{\chi_J})^2 / (\chi_I r_I + \chi_J r_J)$$

$$k_{IJ} = \left(\frac{\partial^2 E_r}{\partial R^2} \right)_0 = 2G \frac{Z_I^* Z_J^*}{R^3} = 664.12 \frac{Z_I^* Z_J^*}{r_{IJ}^3}$$

Rappé *et al.*

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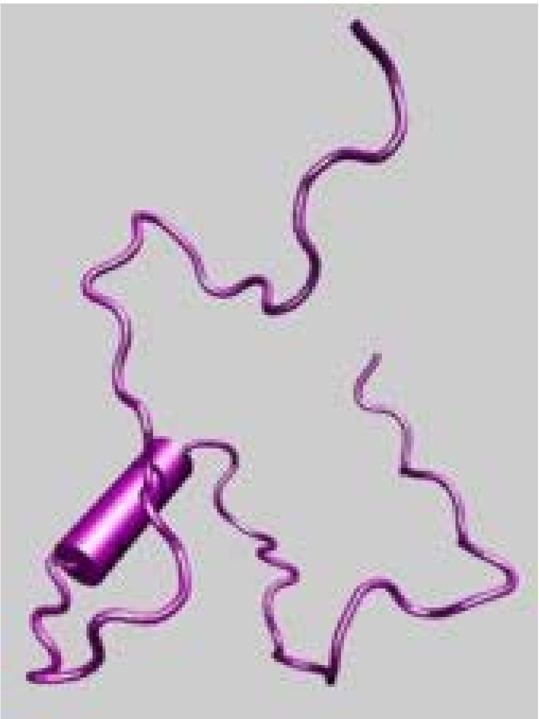
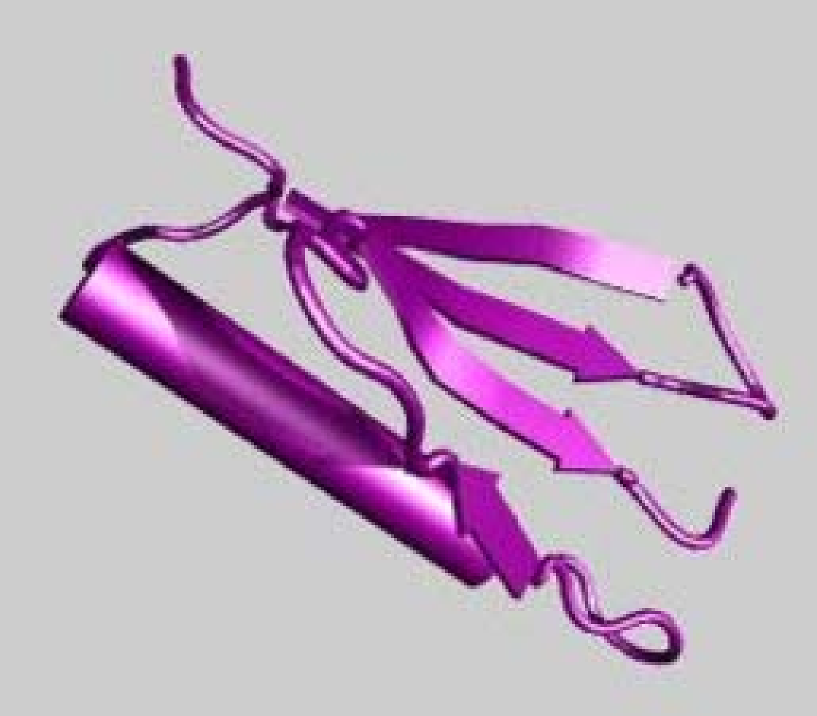
Applications…



Protein L Unfolded



Protein L Folded According to CHARMM Computation

http://www.npaci.edu/online/v5.5/protein-folding.html

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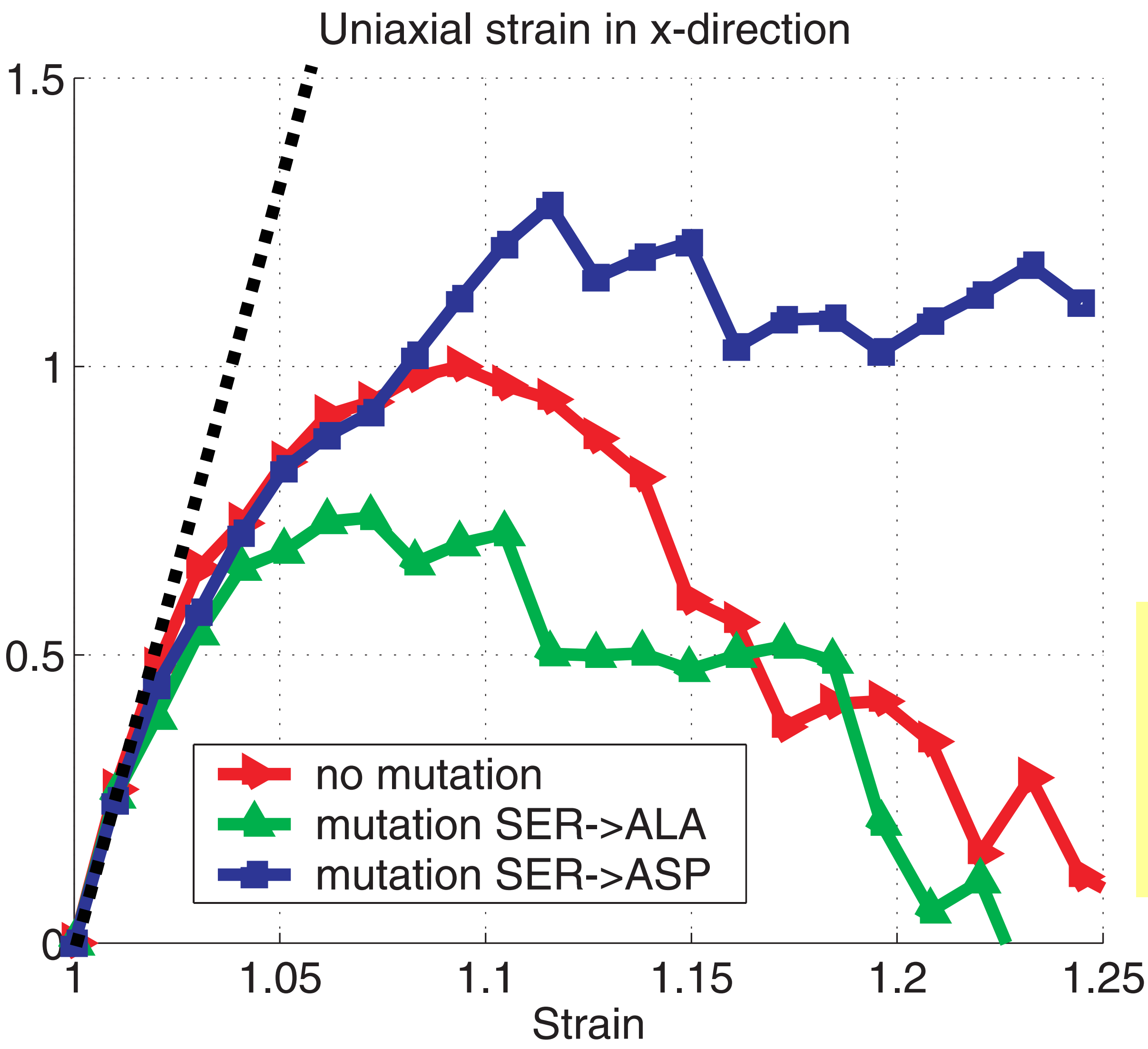
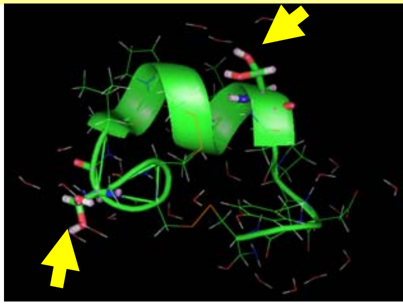
Effect of double point mutations on elasticity of protein crystals*



* α–Conotoxin PnIB From Conus Pennaceus

- Change in maximum strain (ca. ±30%)
- Change in maximum stress (ca. ±25%)
- Change in shape of stress-strain behavior
- Impact mainly on hyperelasticity of protein crystal (preserve small-strain elasticity)



Possible explanation: Replacing polar groups by non-polar residues reduces electrostatic interaction: Thus “weaker” crystal

Buehler, under submission

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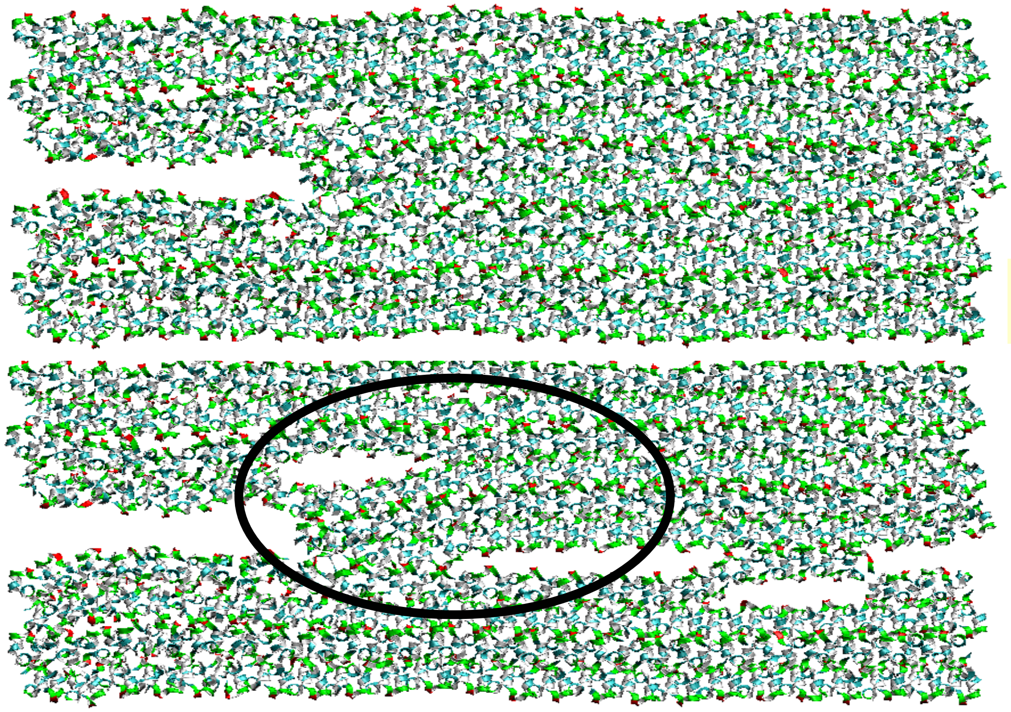
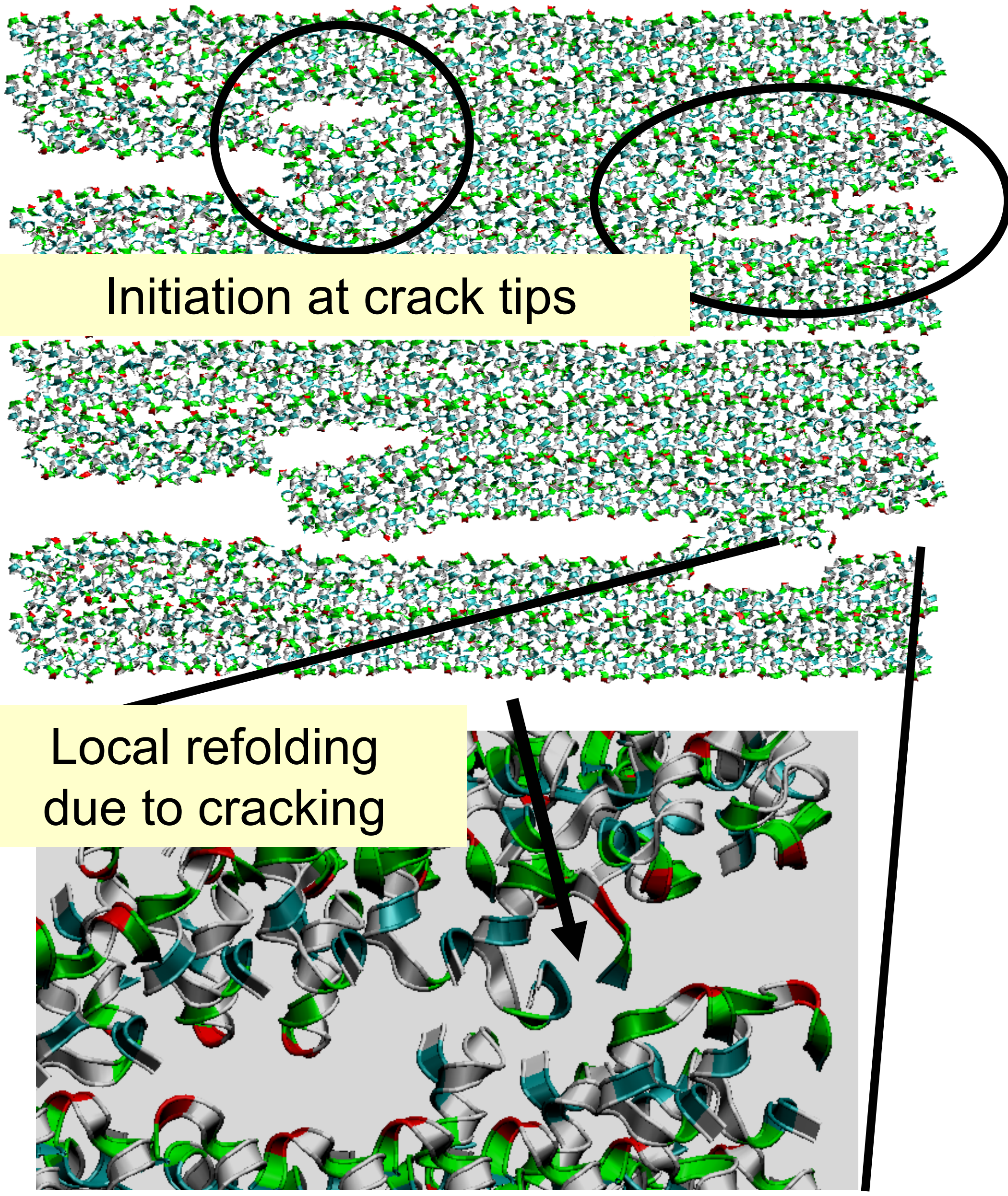
Crack dynamics in protein crystals



Coalescence of cracks



Initiation at crack tips

Local refolding
due to cracking

Comparison fracture initiation theory-MD simulation

$$\varepsilon_f^{MD} \approx 12\% \qquad \varepsilon_f^{theory} \approx 5\%$$

$$\xi_{cr} \propto \frac{\gamma E}{\sigma_{\max}^2} \approx 13\,\mathbf{nm} \qquad \xi \approx 12\mathbf{nm}$$

Buehler, under submission

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Conclusions

- Potentials like CHARMM, AMBER, DREIDING etc. are well advanced and widely used to describe biophysical or organic systems, including water
- They do not allow correct modeling formation and breaking of covalent bonds
- In many biophysics applications, this is a reasonable approximation; however, in some case, this assumption is not suitable (e.g. fracture, chemistry)

- From many formulations and ideas, a few concepts are most widely used in the community, and the results are trusted in

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Part B: Reactive force fields

A new theory to couple the QM scale to classical MD

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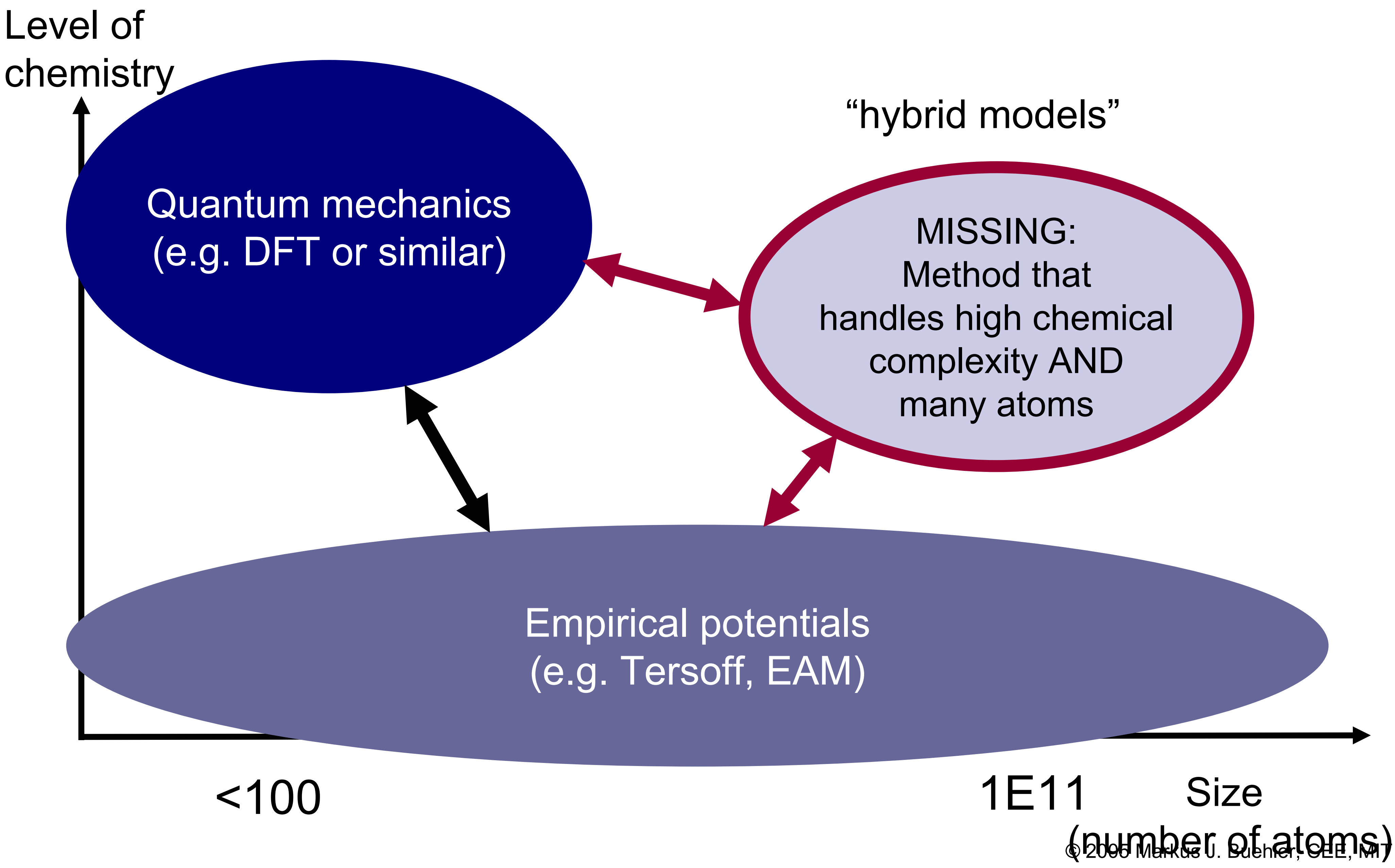
The missing link…



Level of chemistry

Quantum mechanics
(e.g. DFT or similar)

“hybrid models”

MISSING:
Method that
handles high chemical
complexity AND
many atoms

Empirical potentials
(e.g. Tersoff, EAM)

<100

1E11

Size
(number of atoms)

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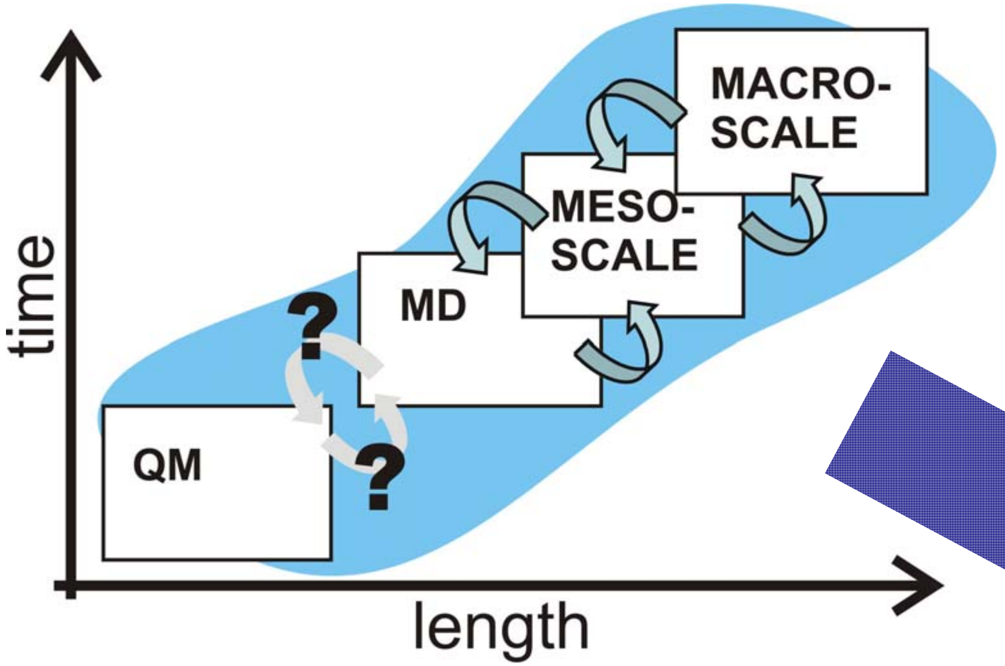
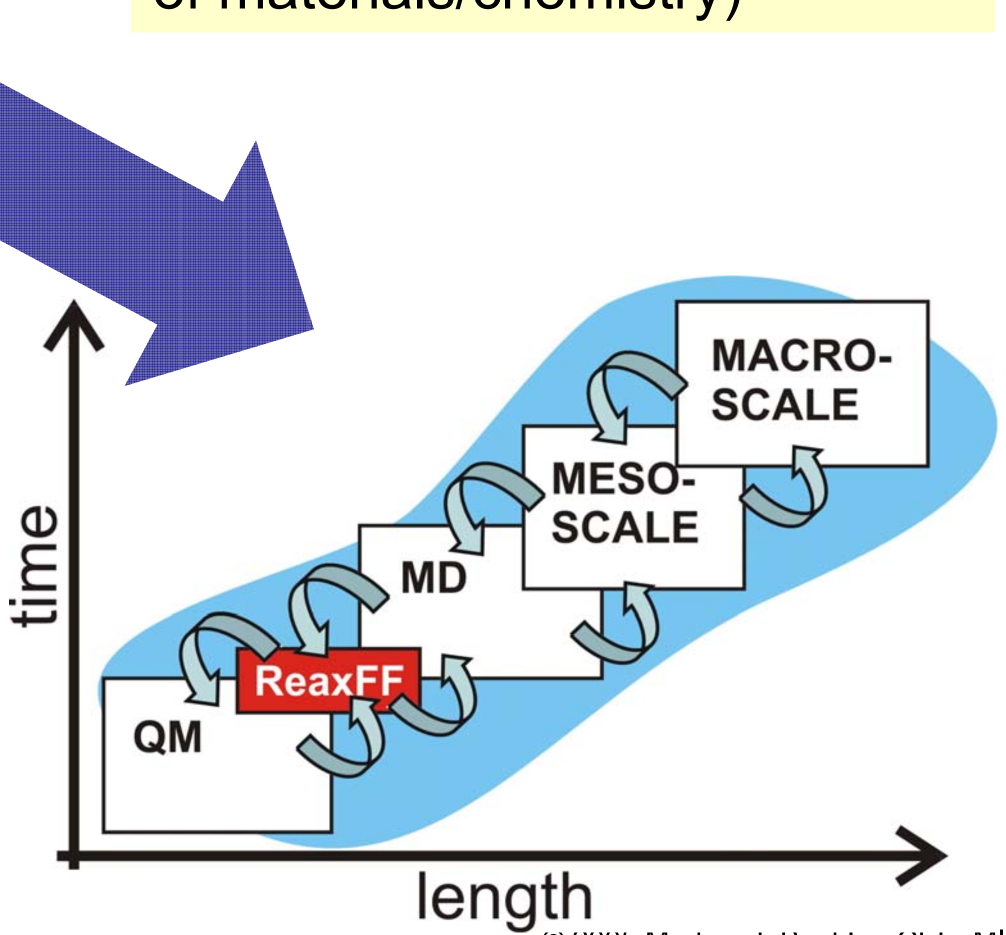
ReaxFF: A new bridge between QM and MD



DFT: ~500 atoms (ps)

ReaxFF: ~10,000 atoms (ns) (needed for realistic description of materials/chemistry)



There exists a huge gap in performance between QM and empirical MD

ReaxFF (van Duin *et al.*) is a possible bridge *(fully first principles trained)*

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Why reactive potentials?

- Materials with high chemical complexity and their fracture/deformation behavior
  - ☐ Natural materials such as C-S-H, clay, minerals,…
  - ☐ Biological materials, e.g. those based on proteins
- Interaction of metals or other mono-atomic crystals with chemicals, e.g. oxidation of surfaces or enhancing/reducing likelihood for failure in stress corrosion cracking
- Description of enzymatic processes
- Materials processing: Energy consumption

In all those systems: Critical to include correct description of relative bond strength (covalent vs. dispersive and others), type of bonding.

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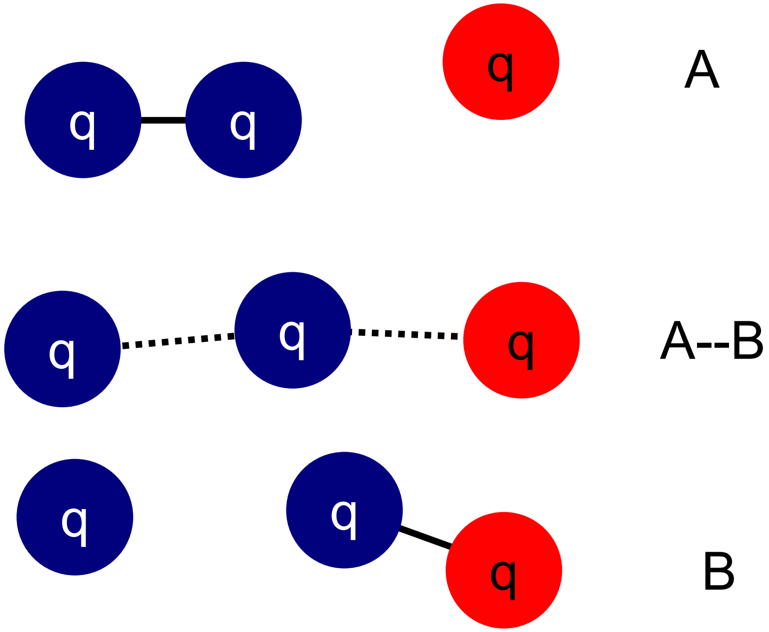
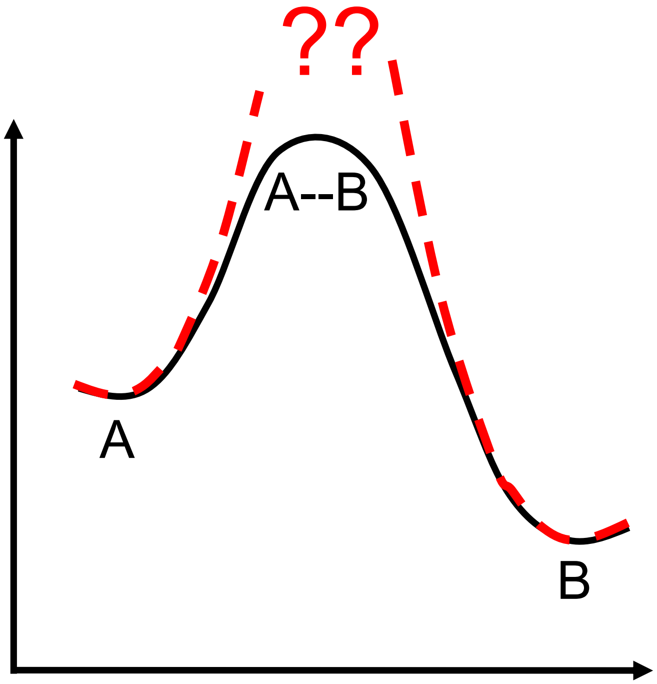
Key features of reactive potentials
Chemistry and state transitions

- Although numerous empirical interatomic potentials exist that can describe thermodynamic equilibrium states of atoms, so far, attempts have failed to accurately describe the transition energies during chemical reactions using more empirical descriptions than relying on purely quantum mechanical (QM) methods.





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Historical perspective of reactive potentials

- 1985: Abell: General expression for binding energy as a sum of near nieghbor pair interactions moderated by local atomic environment

- 1990s: Tersoff, Brenner: Use Abell formalism applied to silicon (successful for various solid state structures)
- 2000: Stuart *et al*.: Reactive potential for hydrocarbons
- 2001: Duin *et al*.: Reactive potential for hydrocarbons "ReaxFF"
- 2002: Brenner *et al*.: Second generation "REBO" potential for hydrocarbons

- 2003-2005: Extension of ReaxFF to various materials including metals, ceramics, silicon, polymers and more in Goddard's group

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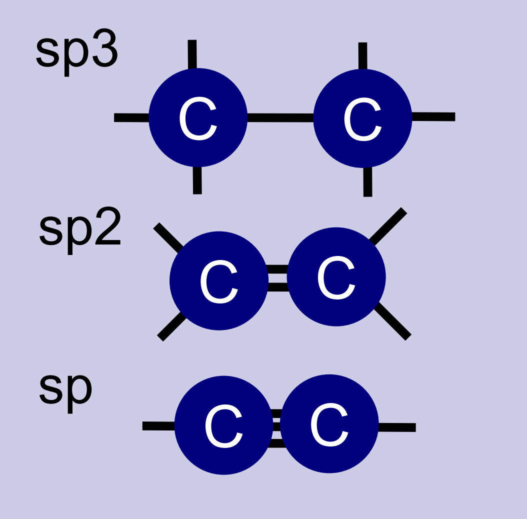
ReaxFF: A reactive force field in CMDF

$$E_{system} = \underbrace{E_{bond} + E_{vdWaals} + E_{Coulomb}}_{\text{2-body}} + \underset{\text{3-body}}{E_{val,angle}} + \underset{\text{4-body}}{E_{tors}}$$

$$+ \underbrace{E_{over} + E_{under}}_{\text{multi-body}}$$



- A **bond length/bond order relationship** is used to obtain smooth transition (Pauling) from **non-bonded to single, double, and triple bonded systems**.
- All connectivity-dependent interactions (*i.e.* valence and torsion angles) are made bond-order dependent
  - Ensures that their energy contributions disappear upon bond dissociation
- Feature **non-bonded interactions** (van der Waals, Coulomb): **Shielded**
- ReaxFF uses a geometry-dependent **charge calculation scheme** (similar to QEq) that accounts for polarization effect
- Most parameters in the formulation have **physical meaning**

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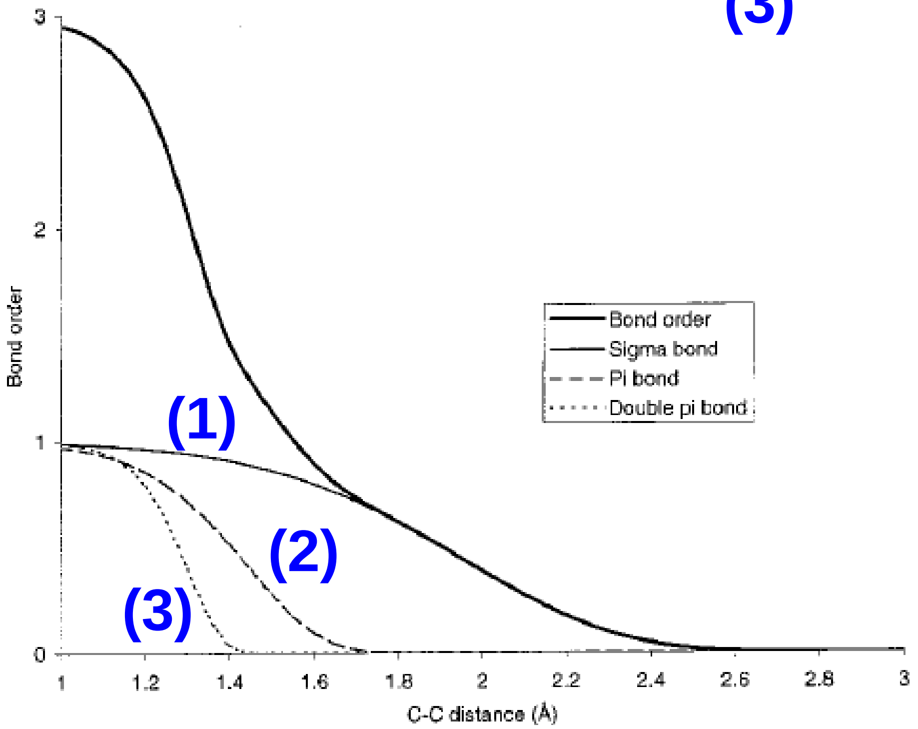
Bond order and bond energy

$$E_{system} = \boxed{E_{bond}} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

$$\mathrm{BO}'_{ij} = \exp\left[\underset{(1)}{p_{\mathrm{bo},1} \cdot \left(\frac{r_{ij}}{r_{\mathrm{o}}}\right)^{p_{\mathrm{bo},2}}}\right] + \exp\left[\overset{(2)}{p_{\mathrm{bo},3} \cdot \left(\frac{r^{\pi}_{ij}}{r_{o}}\right)^{p_{\mathrm{bo},4}}}\right] + \exp\left[\underset{(3)}{p_{\mathrm{bo},5} \cdot \left(\frac{r^{\pi\pi}_{ij}}{r_{\mathrm{o}}}\right)^{p_{\mathrm{bo},6}}}\right]$$



Duin et al., 2001

$$\Delta'_i = \sum_{j=1}^{n\mathrm{bond}} \mathrm{BO}'_{ij} - \mathrm{Val}_i$$

$$\mathrm{BO}_{ij} = \mathrm{BO}'_{ij} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, \mathrm{BO}'_{ij}) \cdot f_5(\Delta'_j, \mathrm{BO}'_{ij})$$

$$f_1(\Delta_i, \Delta_j) = \frac{1}{2} \cdot \left(\frac{\mathrm{Val}_i + f_2(\Delta'_i,\Delta'_j)}{\mathrm{Val}_i + f_2(\Delta'_i,\Delta'_j) + f_3(\Delta'_i,\Delta'_j)} + \frac{\mathrm{Val}_j + f_2(\Delta'_i,\Delta'_j)}{\mathrm{Val}_j + f_2(\Delta'_i,\Delta'_j) + f_3(\Delta'_i,\Delta'_j)}\right)$$

$$f_2(\Delta'_i,\Delta'_j) = \exp(-\lambda_1 \cdot \Delta'_i) + \exp(-\lambda_1 \cdot \Delta'_j)$$

$$f_3(\Delta'_i,\Delta'_j) = \frac{1}{\lambda_2} \cdot \ln\left\{\frac{1}{2} \cdot [\exp(-\lambda_2 \cdot \Delta'_i) + \exp(-\lambda_2 \cdot \Delta'_j)]\right\}$$

$$f_4(\Delta'_i,\mathrm{BO}'_{ij}) = \frac{1}{1 + \exp(-\lambda_3 \cdot (\lambda_4 \cdot \mathrm{BO}'_{ij} \cdot \mathrm{BO}'_{ij} - \Delta'_i) + \lambda_5)}$$

$$f_5(\Delta'_j,\mathrm{BO}'_{ij}) = \frac{1}{1 + \exp(-\lambda_3 \cdot (\lambda_4 \cdot \mathrm{BO}'_{ij} \cdot \mathrm{BO}'_{ij} - \Delta'_j) + \lambda_5)}$$

$$\boxed{E_{\mathrm{bond}} = -D_{\mathrm{e}} \cdot \mathrm{BO}_{ij} \cdot \exp[p_{\mathrm{be},1}\,(1 - \mathrm{BO}_{ij}^{p_{\mathrm{be},1}})]}$$

Over-/undercoordination

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + \boxed{E_{over} + E_{under}}$$

- Valence theory of bonding: Total bond order for C should not exceed 4 and that of H should not exceed 1 (except in hypervalency)
- Thus: Penalty term in FF to correct for over/undercoordination

Valency

$$\Delta_i = \sum_{j=1}^{n\text{bond}} \text{BO}_{ij} - \text{Val}_i$$

Degree of deviation of BO from atomic valency

$$\boxed{E_{\text{under}} = -p_{\text{under}} \cdot \frac{1 - \exp(\lambda_7 \cdot \Delta_i)}{1 + \exp(-\lambda_8 \cdot \Delta_i)} \cdot f_6(\text{BO}_{ij,\pi}, \Delta_j)}$$

$$f_6(\text{BO}_{ij,\pi}, \Delta_j) = \frac{1}{1 + \lambda_9 \cdot \exp\left(\lambda_{10} \cdot \sum_{j=1}^{\text{neighbors}(i)} \Delta_j \cdot \text{BO}_{ij,\pi}\right)}$$

$$\boxed{E_{\text{over}} = p_{\text{over}} \cdot \Delta_i \cdot \left(\frac{1}{1 + \exp(\lambda_6 \cdot \Delta_i)}\right)}$$

Duin et al., 2001

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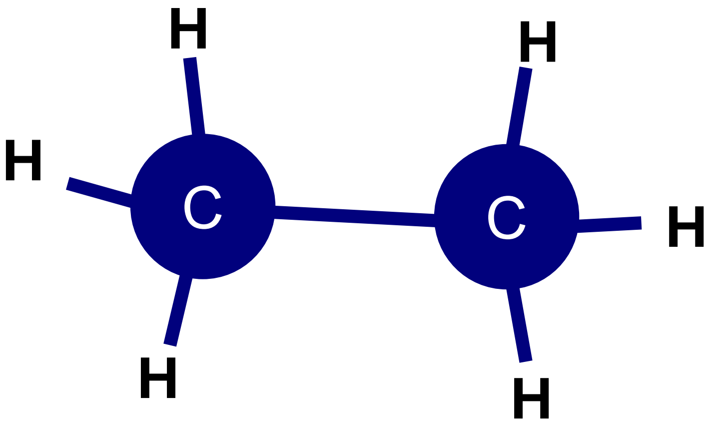
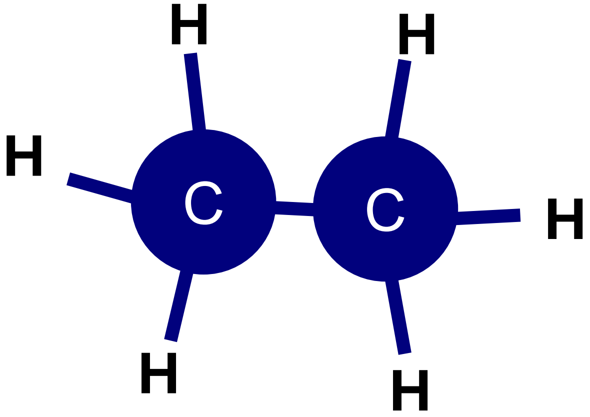
Concept: Stabilization of molecules



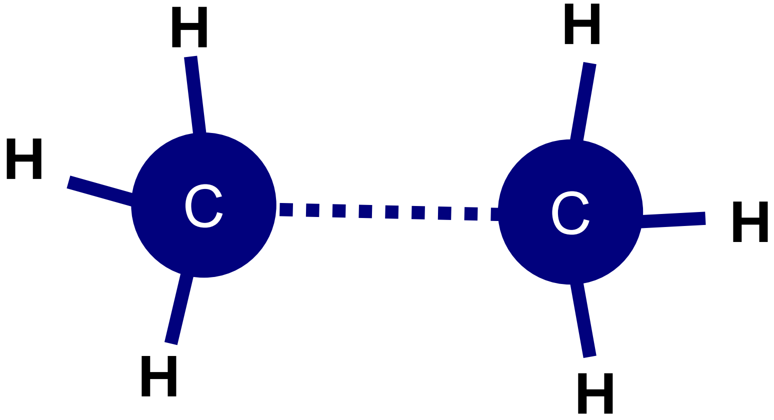
C-C Bond order = 1
Eqilibrium

“squeeze”



C-C Bond order = 2
Total bond order = 5
Valency = 4
Thus: Penalize; repulsion

“pull”



C-C Bond order → 0
Total bond order = 3
Valency = 4
Thus: Penalize; attraction

Duin et al., 2001

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Valence angles

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + \boxed{E_{val,angle}} + E_{tors} + E_{over} + E_{under}$$

- Similar to bond terms: Calculated depending on bond orders
- Equilibrium angle depends on hybridization: 109.47° sp3, 120° sp2, 180° sp (carbon)

$$\boxed{\begin{aligned} E_{\mathrm{val}} = f_7(\mathrm{BO}_{ij}) \cdot f_7(\mathrm{BO}_{jk}) \cdot f_8(\Delta_j) \cdot \\ \{k_a - k_a \exp[-k_b(\Theta_{\mathrm{o}} - \Theta_{ijk})^2]\} \end{aligned}}$$

$$f_7(\mathrm{BO}_{ij}) = 1 - \exp(-\lambda_{11} \cdot \mathrm{BO}_{ij}^{\lambda_{12}})$$

$$f_8(\Delta_j) = \frac{2 + \exp(-\lambda_{13} \cdot \Delta_j)}{1 + \exp(-\lambda_{13} \cdot \Delta_j) + \exp(p_{v,1} \cdot \Delta_j)} \cdot \left[\lambda_{14} - (\lambda_{14} - 1) \cdot \frac{2 + \exp(\lambda_{15} \cdot \Delta_j)}{1 + \exp(\lambda_{15} \cdot \Delta_j) + \exp(-p_{v,2} \cdot \Delta_j)}\right]$$

$$\mathrm{SBO} = \Delta_j - 2 \cdot \left\{1 - \exp\left[-5 \cdot \left(\frac{1}{2}\Delta_j\right)^{\lambda_{16}}\right]\right\} + \sum_{n=1}^{\mathrm{neighbors}(j)} \mathrm{BO}_{jn,\pi}$$

↑

Sum of bond orders

$$\Delta_{j,2} = \Delta_j \text{ if } \Delta_j < 0$$

$$\Delta_{j,2} = 0 \text{ if } \Delta_j \geq 0$$

$$\mathrm{SBO2} = 0 \text{ if } \mathrm{SBO} \leq 0$$

$$\mathrm{SBO2} = \mathrm{SBO}^{\lambda_{17}} \text{ if } 0 < \mathrm{SBO} < 1$$

$$\mathrm{SBO2} = 2 - (2 - \mathrm{SBO})^{\lambda_{17}} \text{ if } 1 < \mathrm{SBO} < 2$$

$$\mathrm{SBO2} = 2 \text{ if } \mathrm{SBO} > 2$$

$$\Theta_0 = \pi - \Theta_{0,0} \cdot \{1 - \exp[-\lambda_{18} \cdot (2 - \mathrm{SBO2})]\}$$

Duin et al., 2001

Torsion angles

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + \boxed{E_{tors}} + E_{over} + E_{under}$$

- Similar to bond and angle terms: Calculated depending on bond orders

$$\boxed{E_{\text{tors}} = f_{10}(\text{BO}_{ij}, \text{BO}_{jk}, \text{BO}_{kl}) \cdot \sin\Theta_{ijk} \cdot \sin\Theta_{jkl}}$$

$$\Big[\frac{1}{2}V_2 \cdot \exp\{p_l(\text{BO}_{jk} - 3 + f_{11}(\Delta_j,\Delta_k))^2\} \cdot (1 - \cos 2\omega_{ijkl}) + \frac{1}{2}V_3 \cdot (1 + \cos 3\omega_{ijkl})\Big]$$

$$f_{10}(\text{BO}_{ij}, \text{BO}_{jk}, \text{BO}_{kl}) = [1 - \exp(-\lambda_{23} \cdot \text{BO}_{ij})] \cdot [1 - \exp(-\lambda_{23} \cdot \text{BO}_{jk})] \cdot [1 - \exp(-\lambda_{23} \cdot \text{BO}_{kl})]$$

$$f_{11}(\Delta_j, \Delta_k) = \frac{2 + \exp[-\lambda_{24} \cdot (\Delta_j + \Delta_k)]}{1 + \exp[-\lambda_{24} \cdot (\Delta_j + \Delta_k)] + \exp[\lambda_{25} \cdot (\Delta_j + \Delta_k)]}$$

$$\Theta_0 = \pi - \Theta_{0,0} \cdot \{1 - \exp[-\lambda_{18} \cdot (2 - \text{SBO2})]\}$$

Duin et al., 2001

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vdW/Coulomb interactions

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

- Accounts for short distance repulsion (Pauli principle orthogonalization) and attraction energies at large distances (dispersion)
- Included for all atoms with shielding at small distances

$$E_{\text{vdWaals}} = D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{\text{vdW}}} \right) \right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{\text{vdW}}} \right) \right] \right\}$$

$$f_{13}(r_{ij}) = \left[r_{ij}^{\lambda_{29}} + \left(\frac{1}{\lambda_w} \right)^{\lambda_{28}} \right]^{1/\lambda_{28}}$$

$$E_{\text{Coulomb}} = C \cdot \frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$$

Partial charges are calculated using the electron equilibration method (EEM); similar to QEq

Duin et al., 2001

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Summary: Reactive versus nonreactive potentials

	Nonreactive FFs	**Reactive FFs**
Ground state energies (e.g. distinguish sp3-sp2-sp…)	Yes (few states)	Yes
Excited / transition states (go from one to another ground state; see also Figure 4)	No	Yes
Breaking of bonds and continuous energies during reactions	No (sometimes: Morse functions for bond breaking but energetics are typically wrong)	Yes
Formation of bonds	No	Yes
Charge flow during reactions	No	Yes
Organo-Inorganic interfaces (or between other materials)	No (mostly)	Yes (bridging FFs)
Retyping necessary after reaction	Yes (have C2,C3 etc. for different hybridization)	No (atom types are element types)

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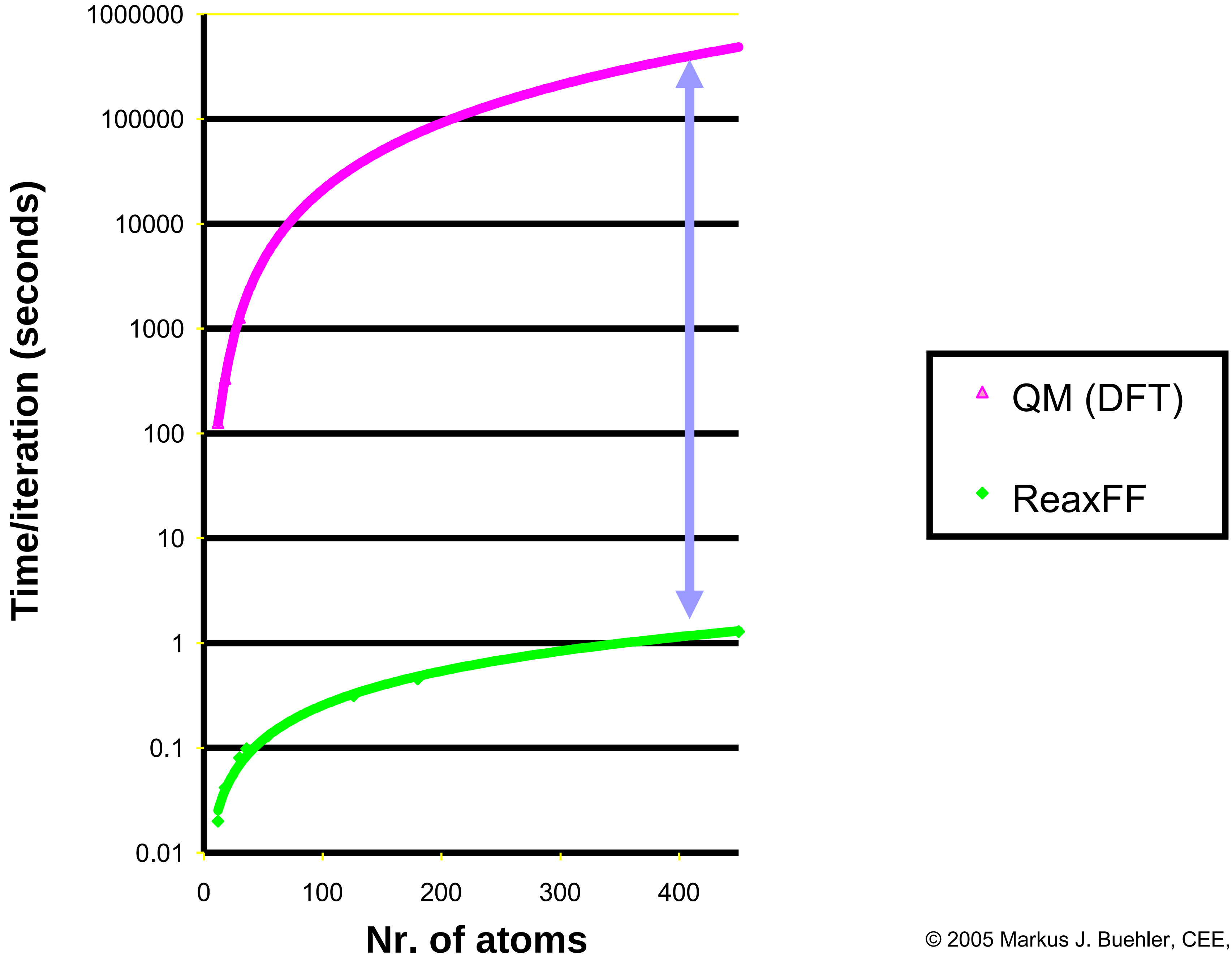
Computational cost: Compare ReaxFF with DFT



Duin *et al.*

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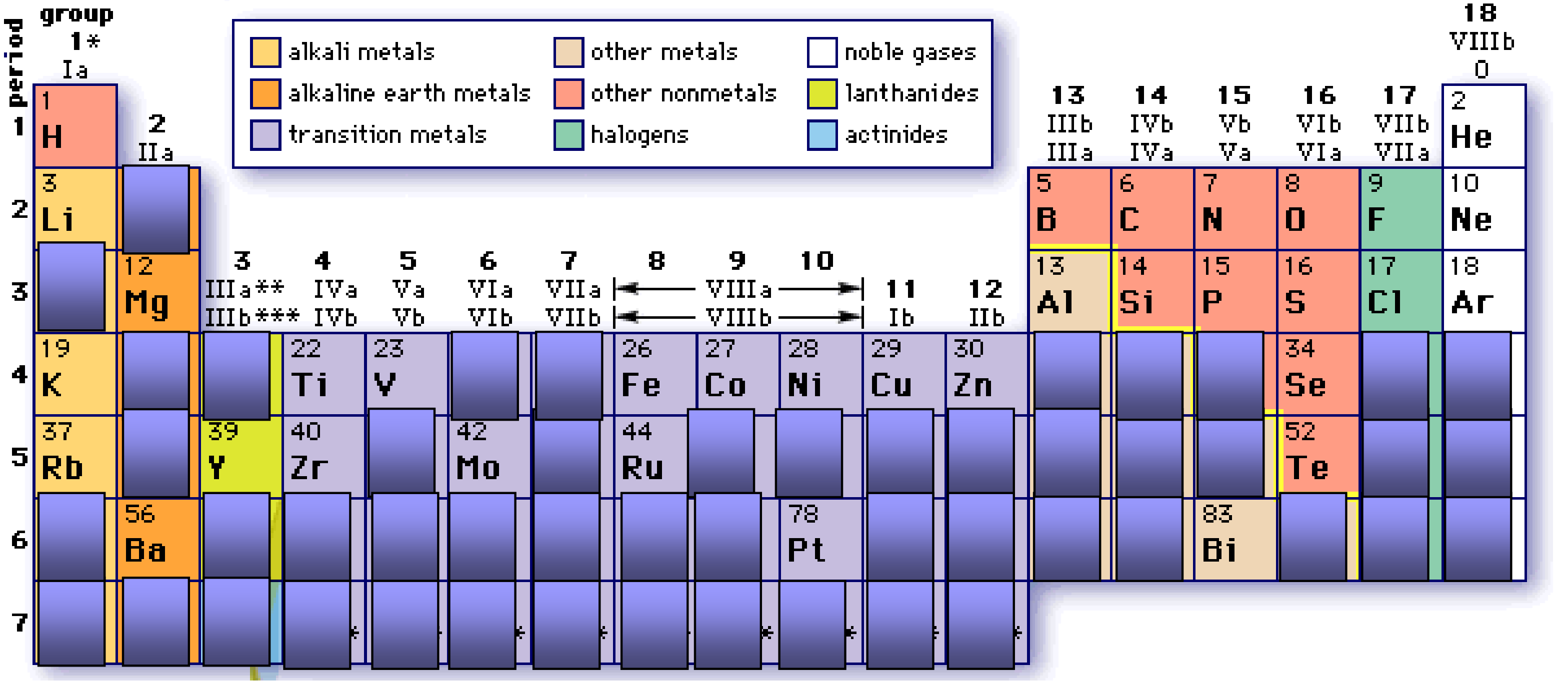
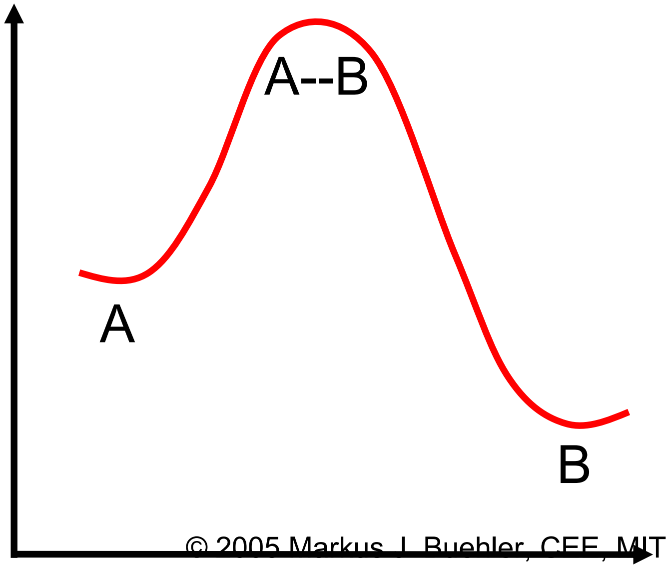
Current development status of ReaxFF



■ : not currently described by ReaxFF

Allows to interface metals, ceramics with organic chemistry: Key for complex materials, specifically biological materials



Duin et al., 2001

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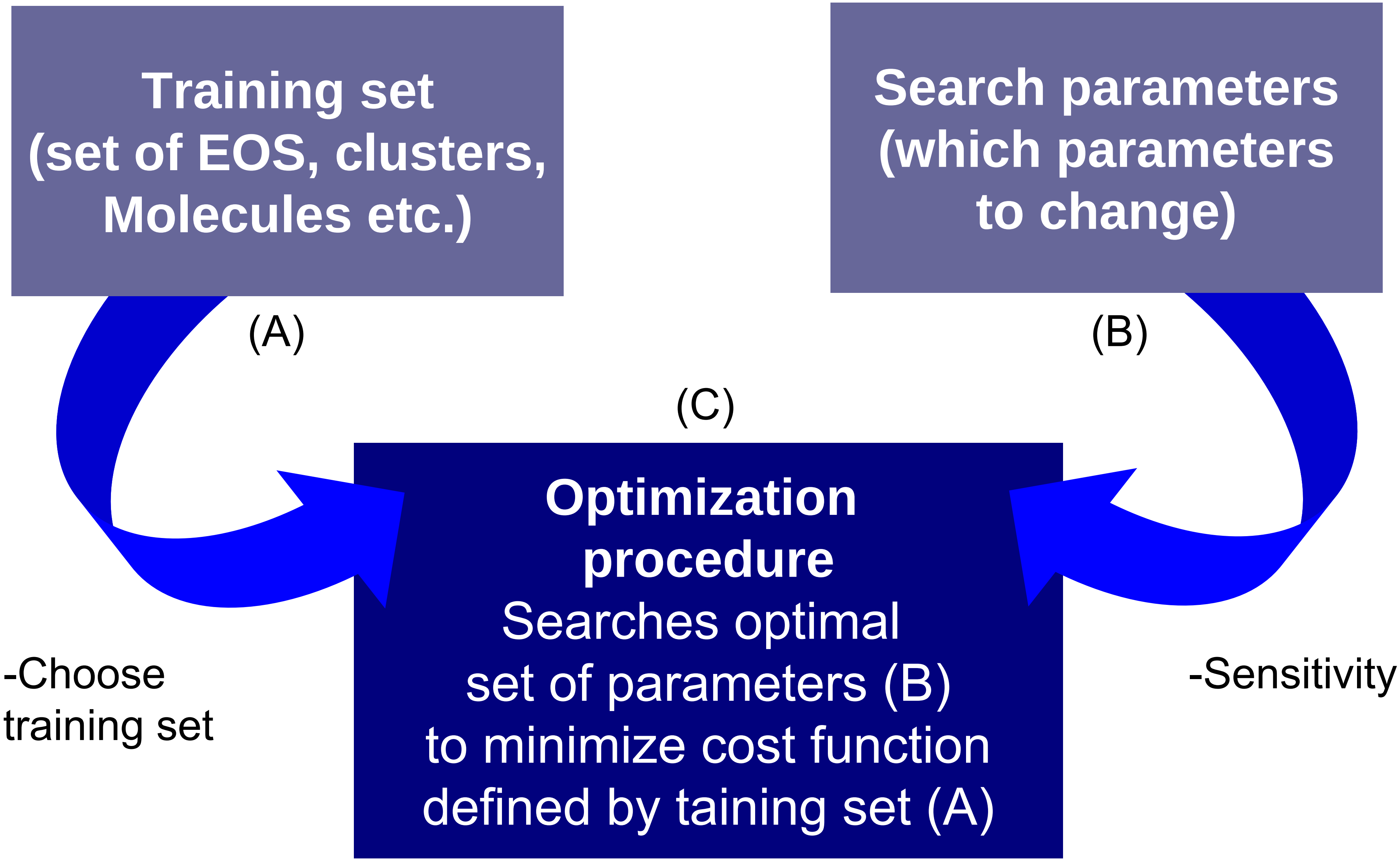
Training of ReaxFF Force Field



Training set (set of EOS, clusters, Molecules etc.)

Search parameters (which parameters to change)

(A)

(B)

(C)

Optimization procedure

Searches optimal set of parameters (B) to minimize cost function defined by taining set (A)

-Choose training set

-Sensitivity

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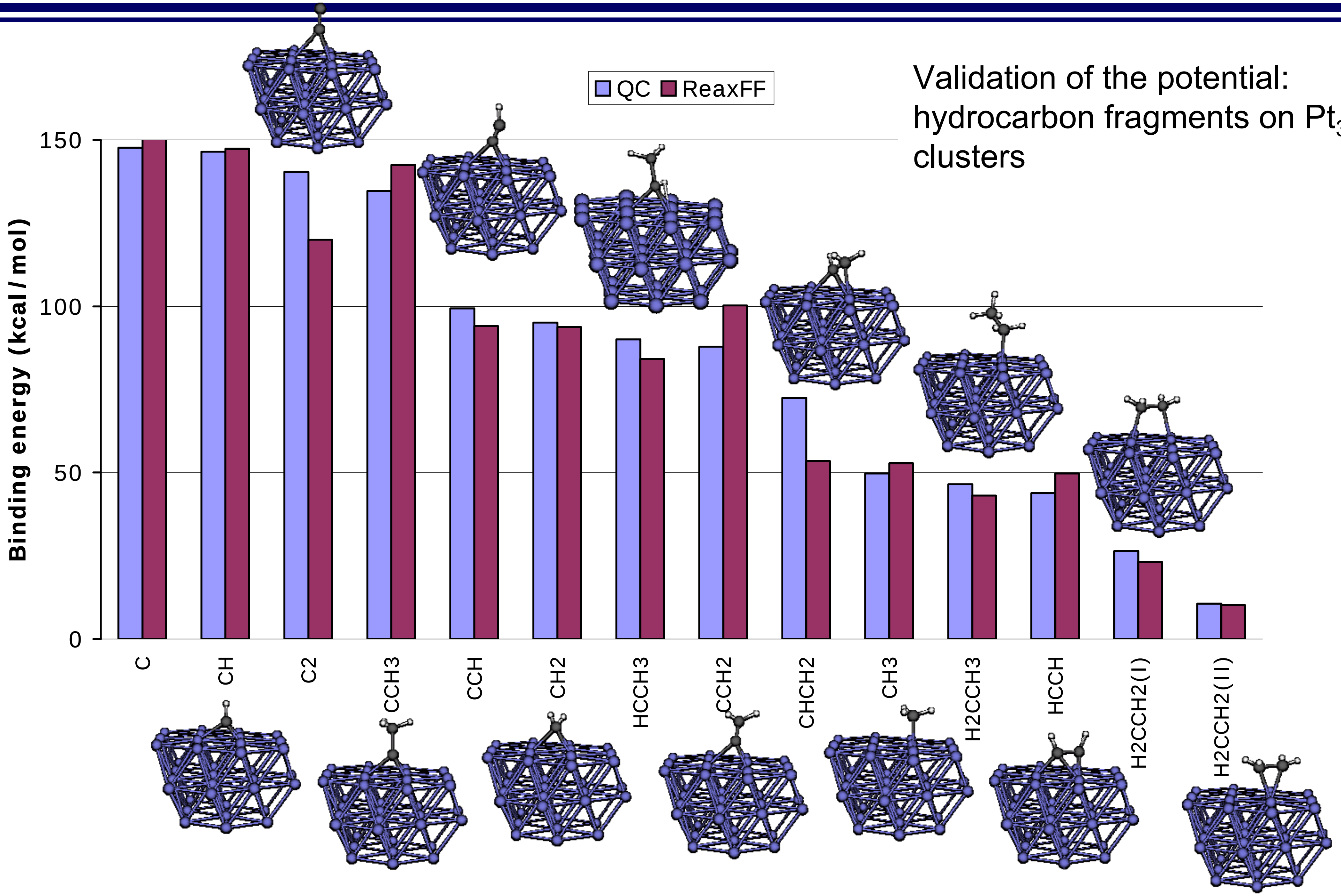
Training of ReaxFF Force Field: Hydrocarbon-Pt interactions

Validation of the potential: hydrocarbon fragments on Pt_{35}-clusters



ReaxFF can describe different C-Pt bonding modes

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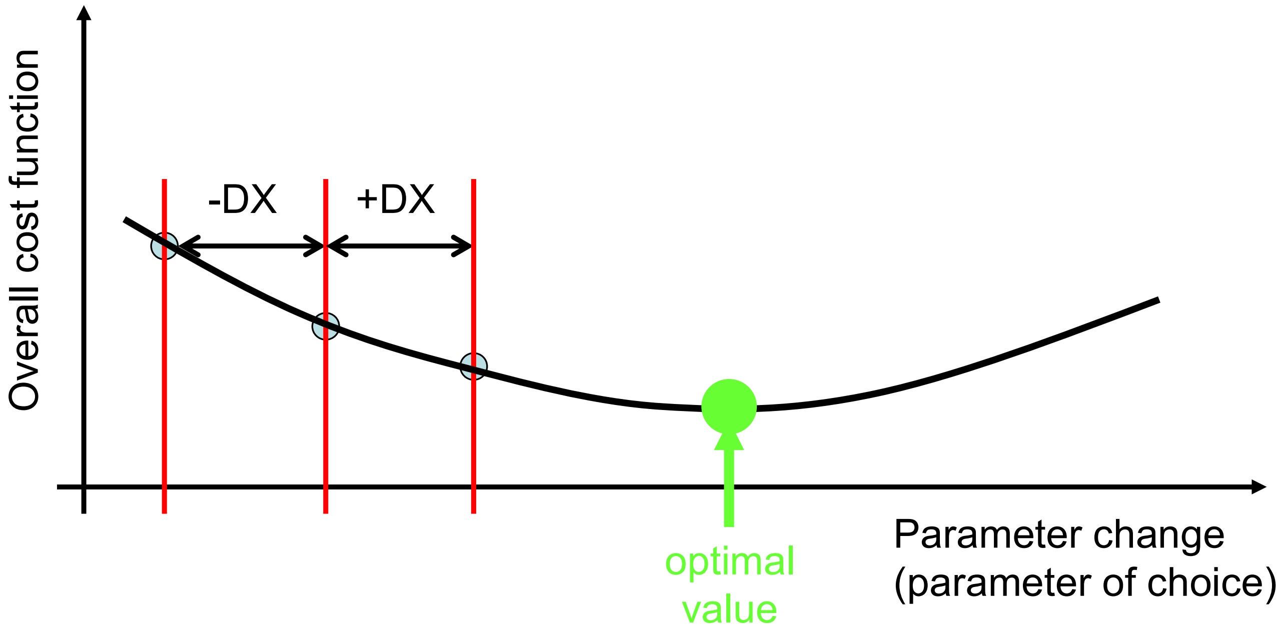
Force field training: Parabolic extrapolation

Parabolic extrapolation



Concept of parabolic expansion. ReaxFF calculates the cost function at 3 parameter values, then extrapolates to the optimal value.

ENERGY #Here we compare relative energies, including EOSs: i.e., using a weight of 1.5 we want the energy difference "+ butbenz/1 - butbenz_a/1" to be exactly -90 kcal/mol

```
#Weigh op1 Ide1 n1 op2 Ide2 n2 Lit
#alfa vs. beta vs. gamma cleavage in butylbenzene
1.5 + butbenz/1 - butbenz_a/1 -90.00
1.5 + butbenz/1 - butbenz_b/1 -71.00
1.5 + butbenz/1 - butbenz_c/1 -78.00
#cyclohexane heat of vaporization
1.0 + chex_cryst/16 – chexane/1 -11.83
ENDENERGY
```

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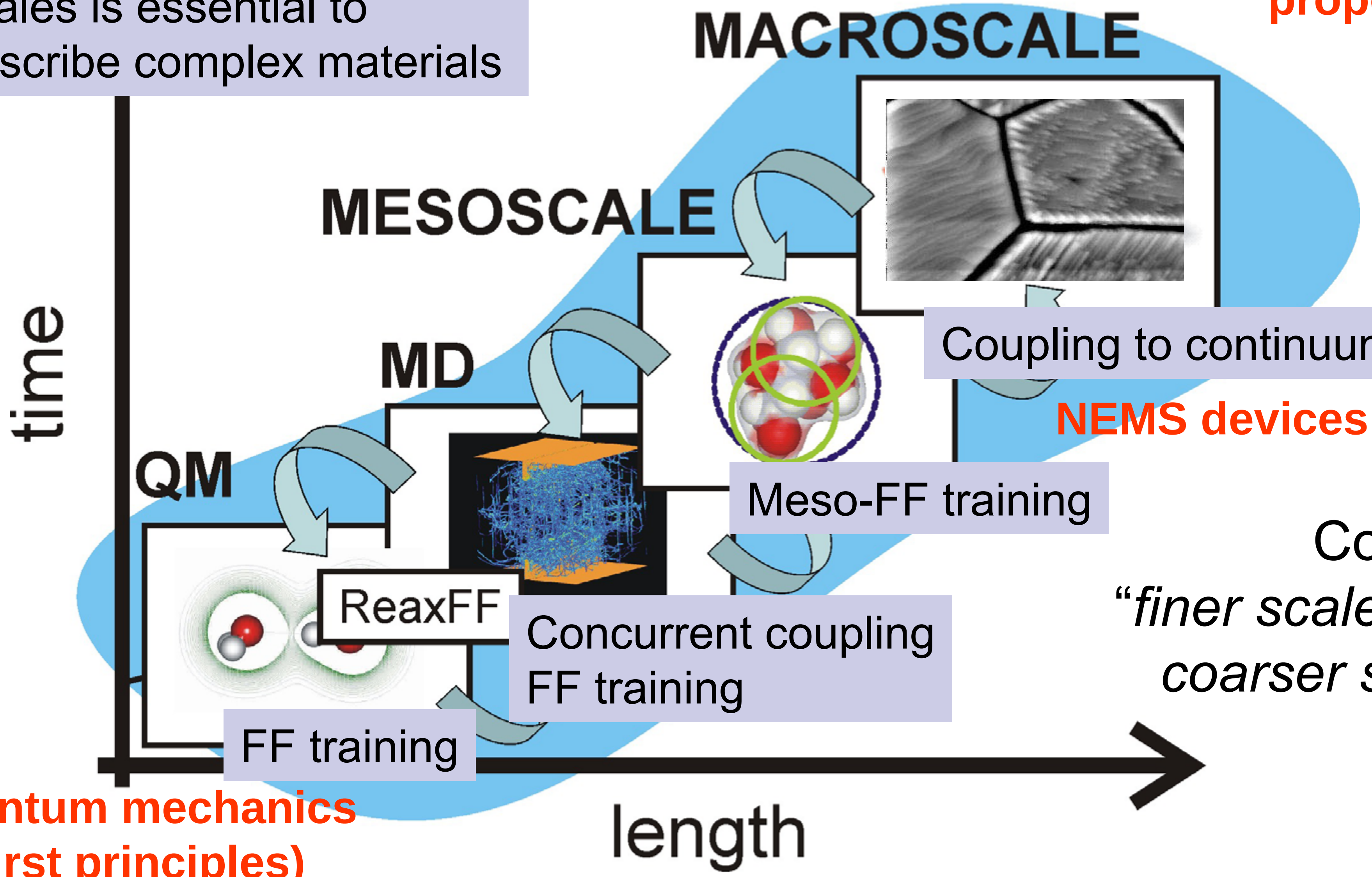
Challenge: Coupling of various scales
From QM to Macroscale

Integration of various scales is essential to describe complex materials

Engineering properties



Coupling to continuum

NEMS devices

Meso-FF training

Concurrent coupling FF training

FF training

Quantum mechanics (first principles)

Concept:
“finer scales train coarser scales”

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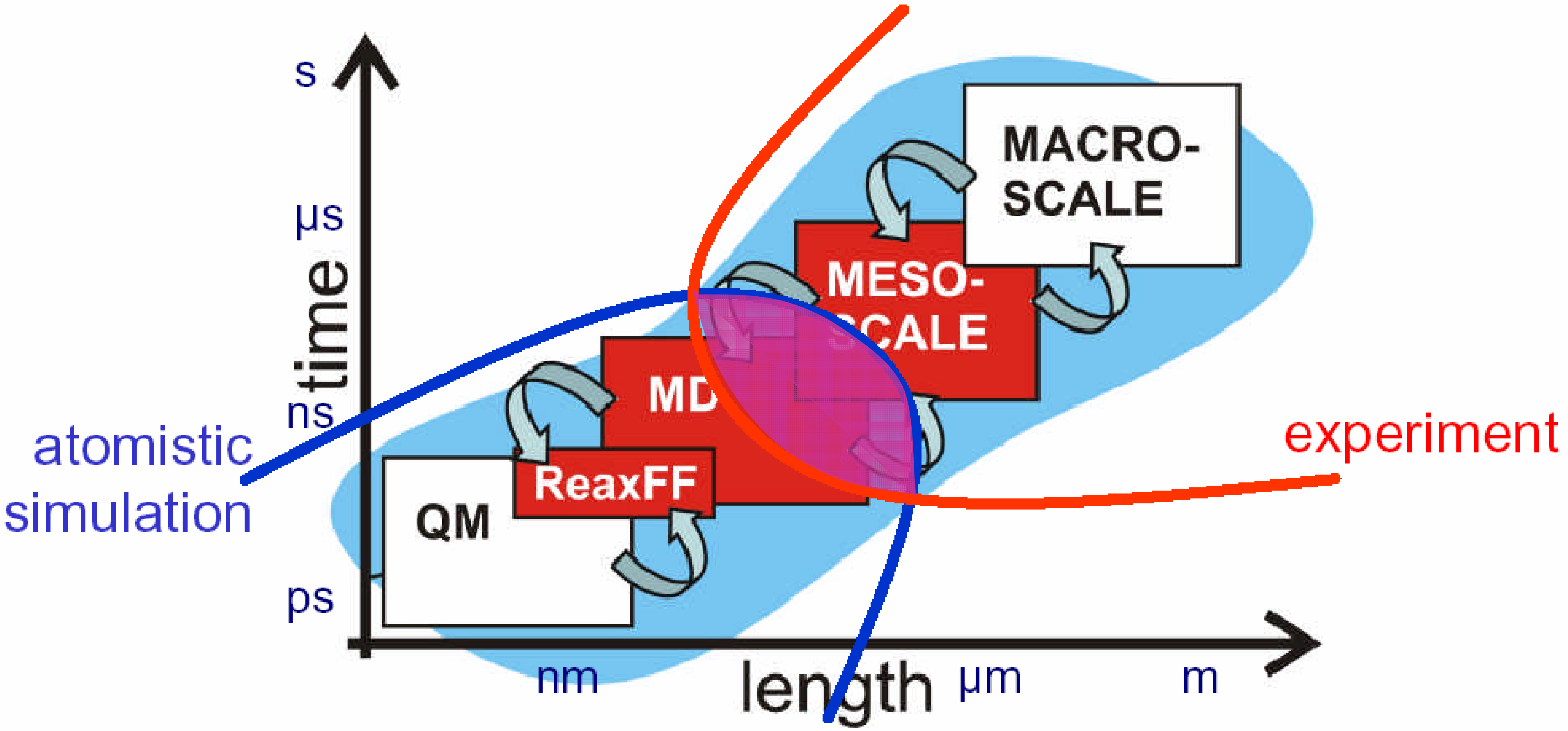
Multi-scale modeling of complex materials
Length and time scales covered



- Focus: Reactive force fields, empirical MD and mesoscopic methods are used to bridge the scales to the macroscopic regime (**nm..μm and ps..μs**)
- This allows to overlap with experimental results and enables application to solve engineering problems

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Code development status for ReaxFF

At present we have the following codes:

- Standalone ReaxFF FORTRAN code for simulation and training of force fields
  up to 3,000 atoms, n^2 scaling
- GRASP (MIT-Caltech-Sandia collaboration): Parallelized version of ReaxFF
  up to 100,000 atoms (depends on total CPU numbers), n scaling
- Integration of ReaxFF into the multi-paradigm multi-scale modeling framework "CMDF" for hybrid simulations with mixed potentials
  up to 100,000 atoms in mixed calculations (3,000 reactive atoms)
  can mix with QM, future mix with FEM

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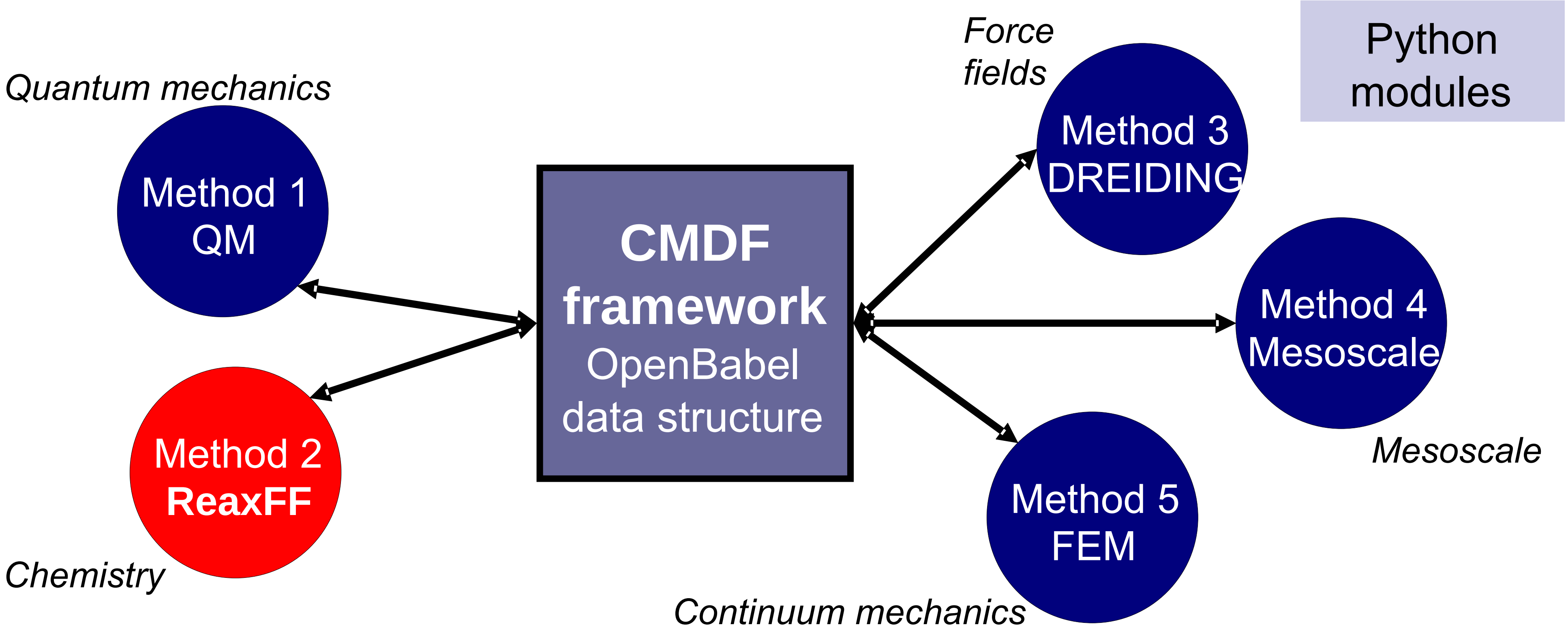
The CMDF framework



- The development of CMDF bases on the concept of calling simulation modules (libraries) from a Python scripting environment
- This technology allows reuse of existing codes within a modern scripting environment without “touching” the individual source codes

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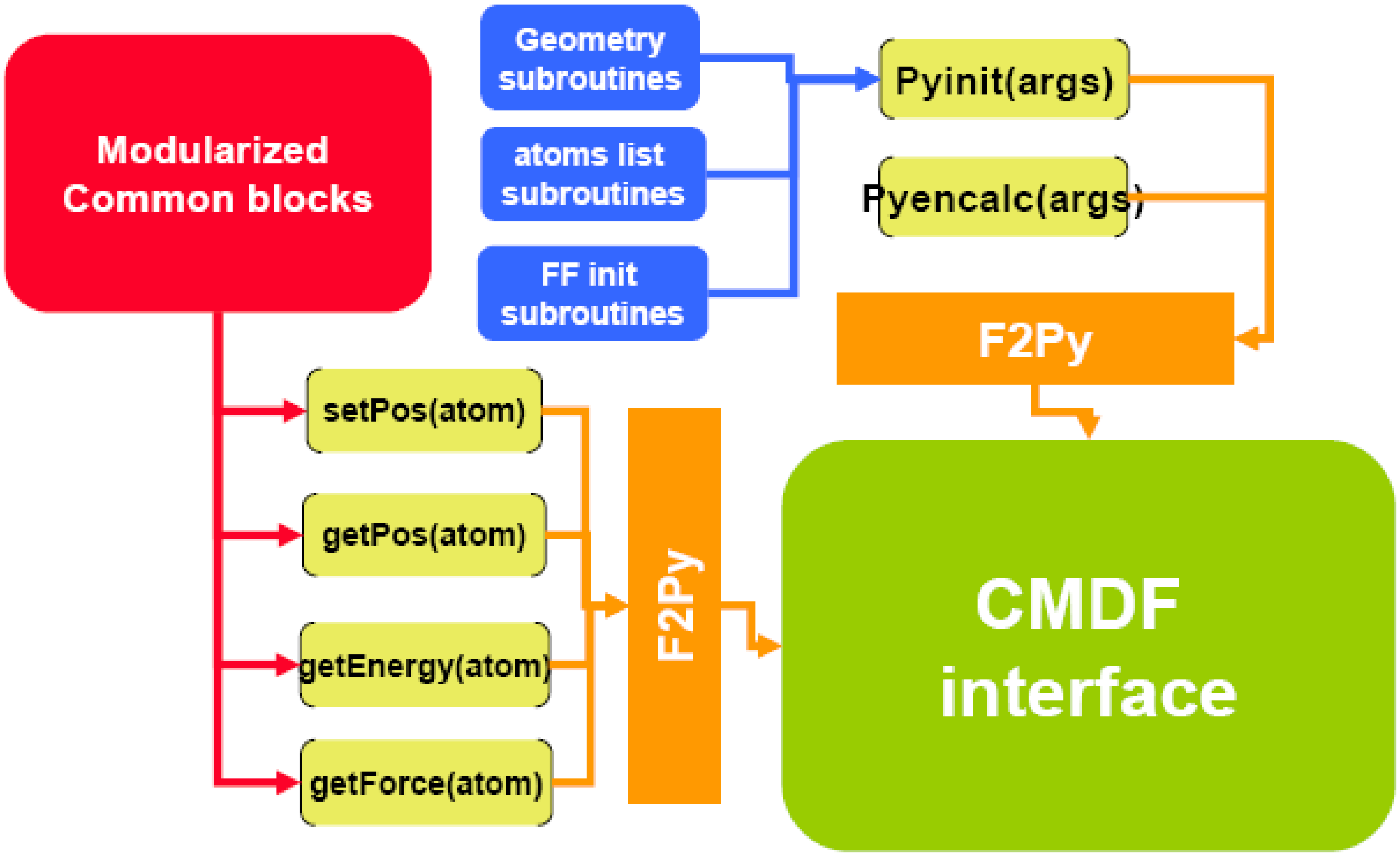
ReaxFF in the CMDF framework



Modularized Common blocks

Geometry subroutines

atoms list subroutines

FF init subroutines

Pyinit(args)

Pyencalc(args)

F2Py

setPos(atom)

getPos(atom)

getEnergy(atom)

getForce(atom)

F2Py

CMDF interface

Si-ping Han, Caltech

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The CMDF framework

```
OBMol=tools.readbgf (“water.bgf”)
OBMol=tools.build_MWNT (10, 8, 4)
tools.insertcrack(OBMol, 10, 20, 2.3)
Loop { tools.forces(OBMol, ???)
       dynamics.IntegrateNVE(OBMol)
tools.printfracture (OBMol)
```

`tools.forces(OBMol, EAM)`

or

`tools.forces(OBMol, ReaxFF)`

or

`tools.forces(OBMol, Tersoff)`

or

`tools.forces(OBMol, JAGUAR DFT X,B3LYP)`

✓ The scale agnostic design using the central data structure allows simple replacement of different simulation methods: Design methods that operate on OpenBabel objects

✓ This can be used to “try” different simulation engines during a simulation to find the most efficient method required to achieve a desired accuracy

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Part C: Application areas

Application of ReaxFF and hybrid simulations to various topics

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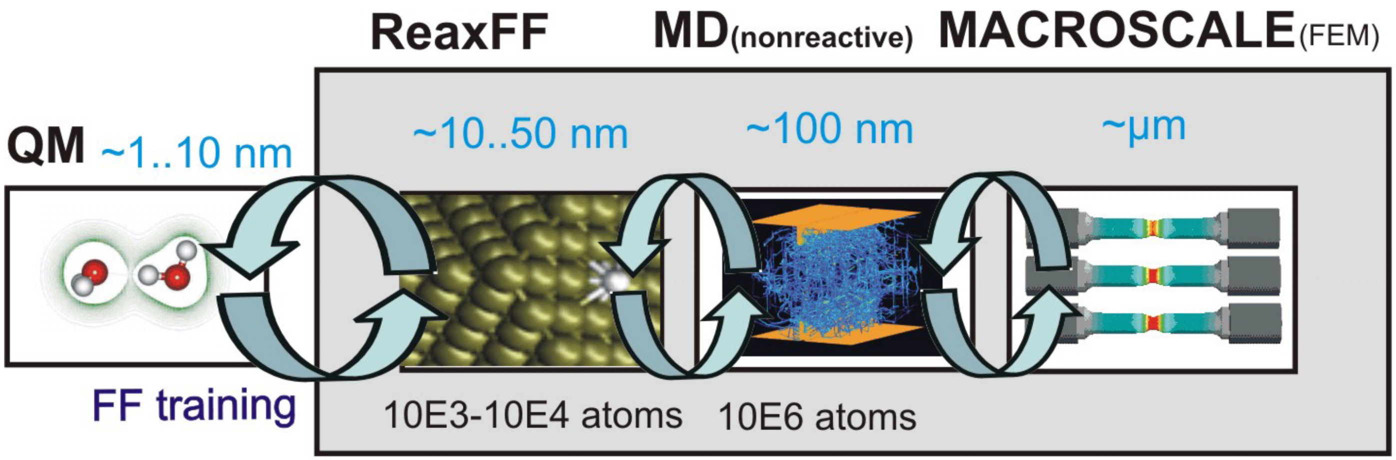
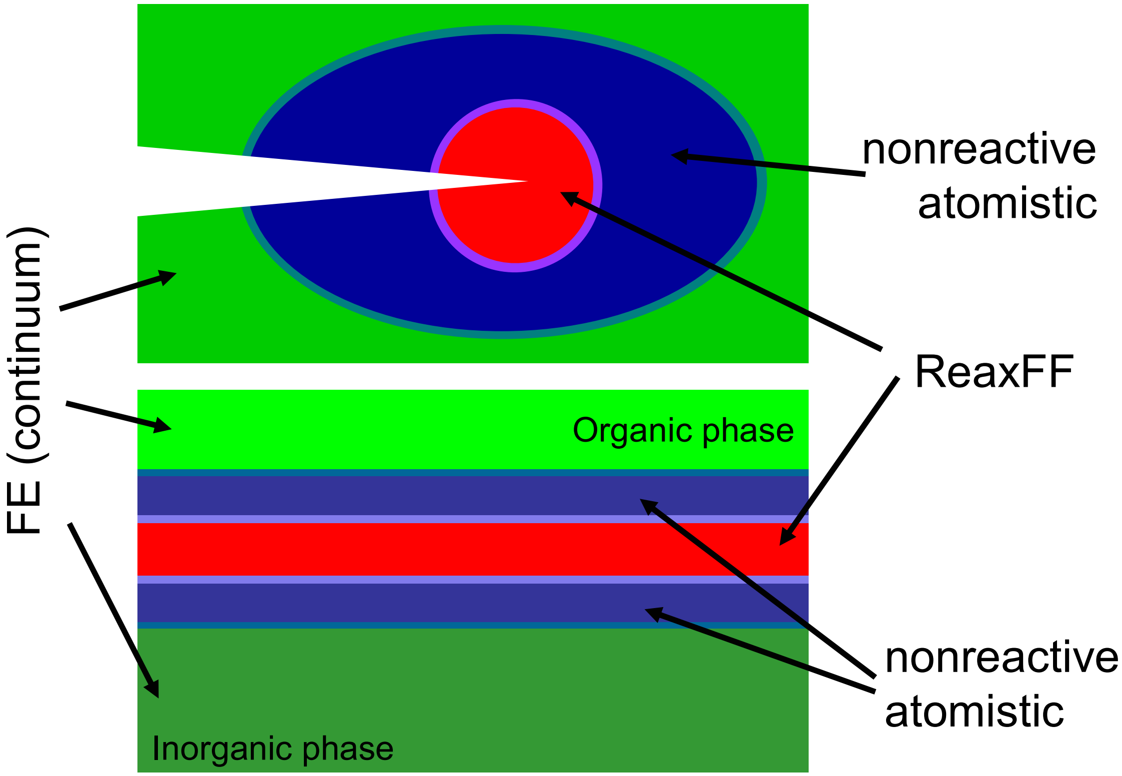
Concurrent multi-scale simulations

Concurrent integration of various scales and paradigms





- Concurrent FE-atomistic-ReaxFF scheme in a crack problem (crack tip treated by ReaxFF) and an interface problem (interface treated by ReaxFF).
- Highlighted transition regions as handshake domains between different scale and methods.

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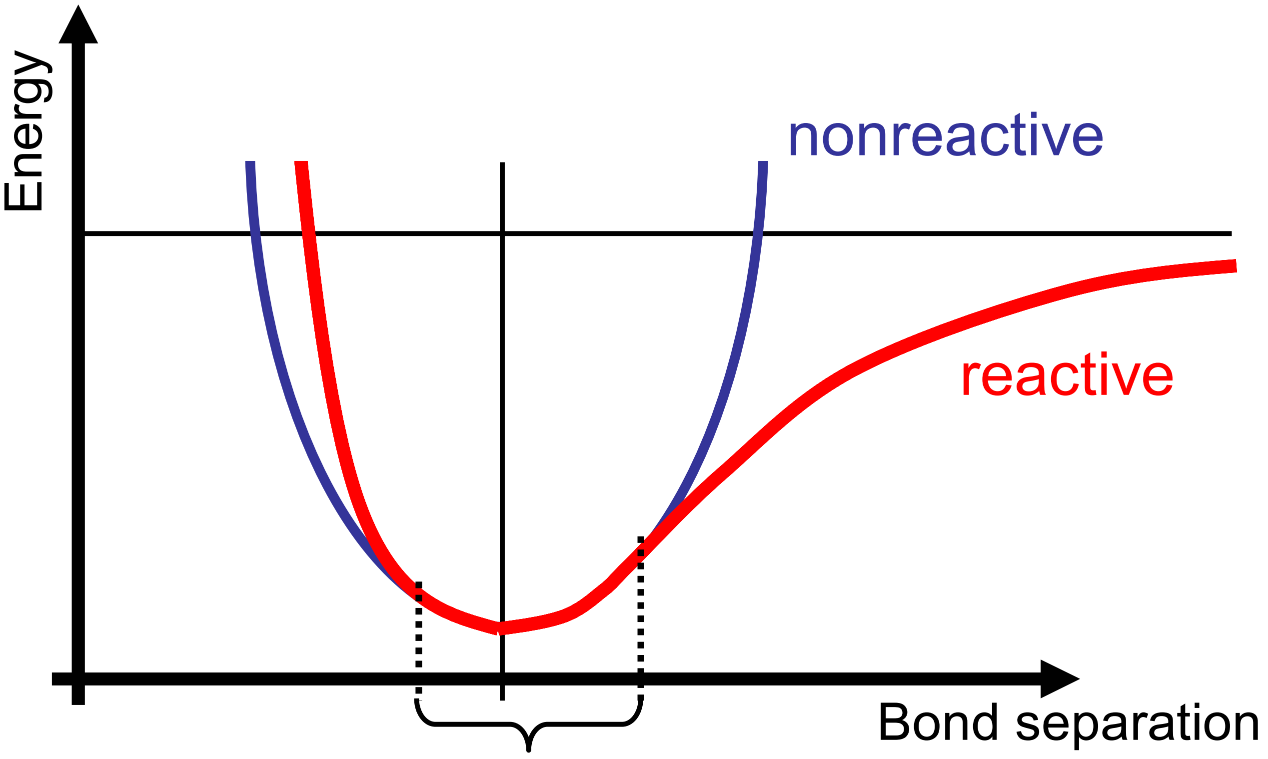
Example for code coupling: Concept of mixed Hamiltonian



reactive≈nonreactive
small-strain approximation

- Schematic showing the coupling of reactive and nonreactive potentials
- The simpler nonreactive potential is trained to resemble the reactive potential for small deviations from the equilibrium configuration.

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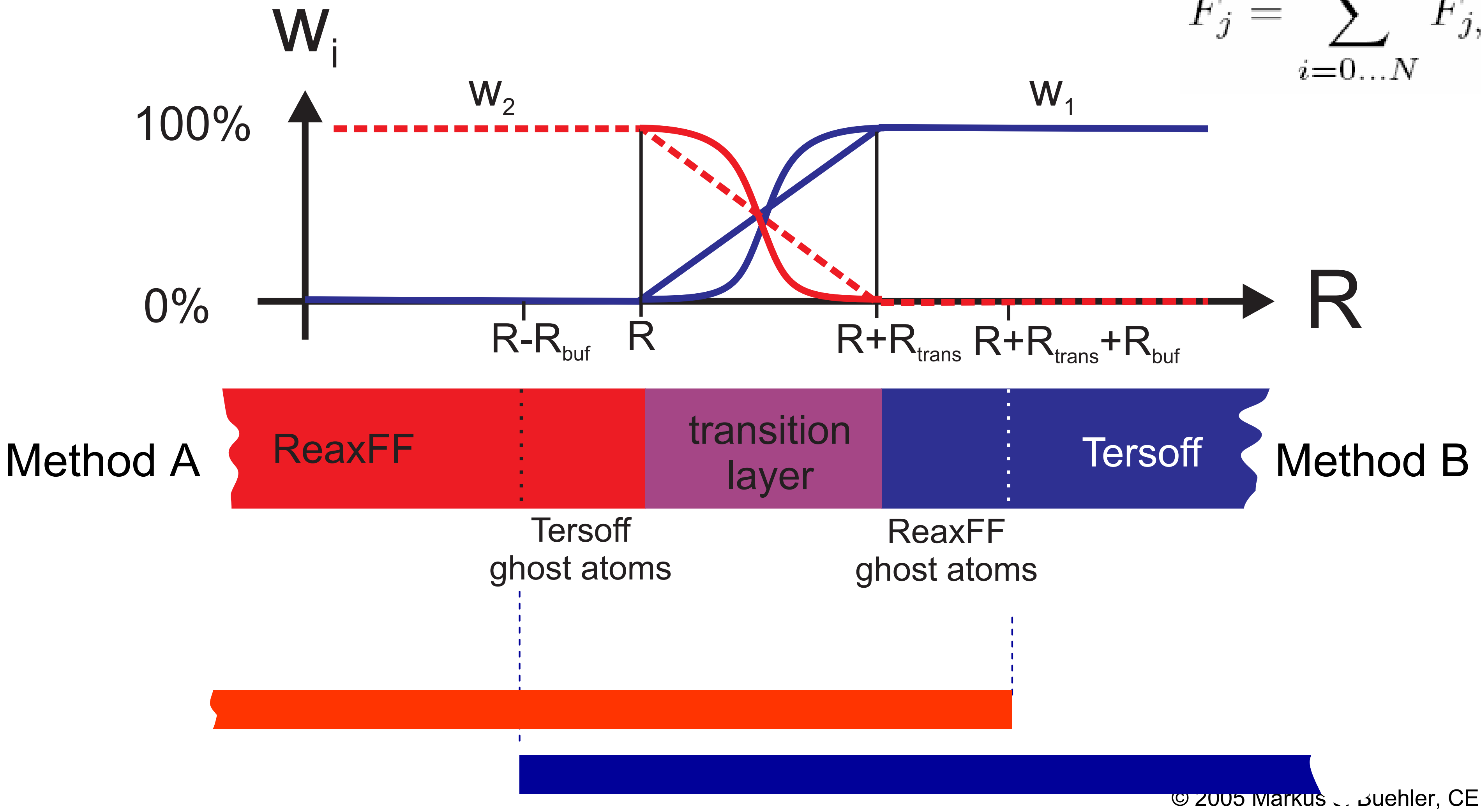
Example for code coupling: Concept of mixed Hamiltonian

- Use **scheme to couple different codes** with each other based on **weights describing the amount of force and energy contribution of different force engines: Works well for certain force fields**

$$\sum_{i=0\ldots N} w_i = 1$$

$$\vec{F}_j = \sum_{i=0\ldots N} \vec{F}_{j,i} w_i$$



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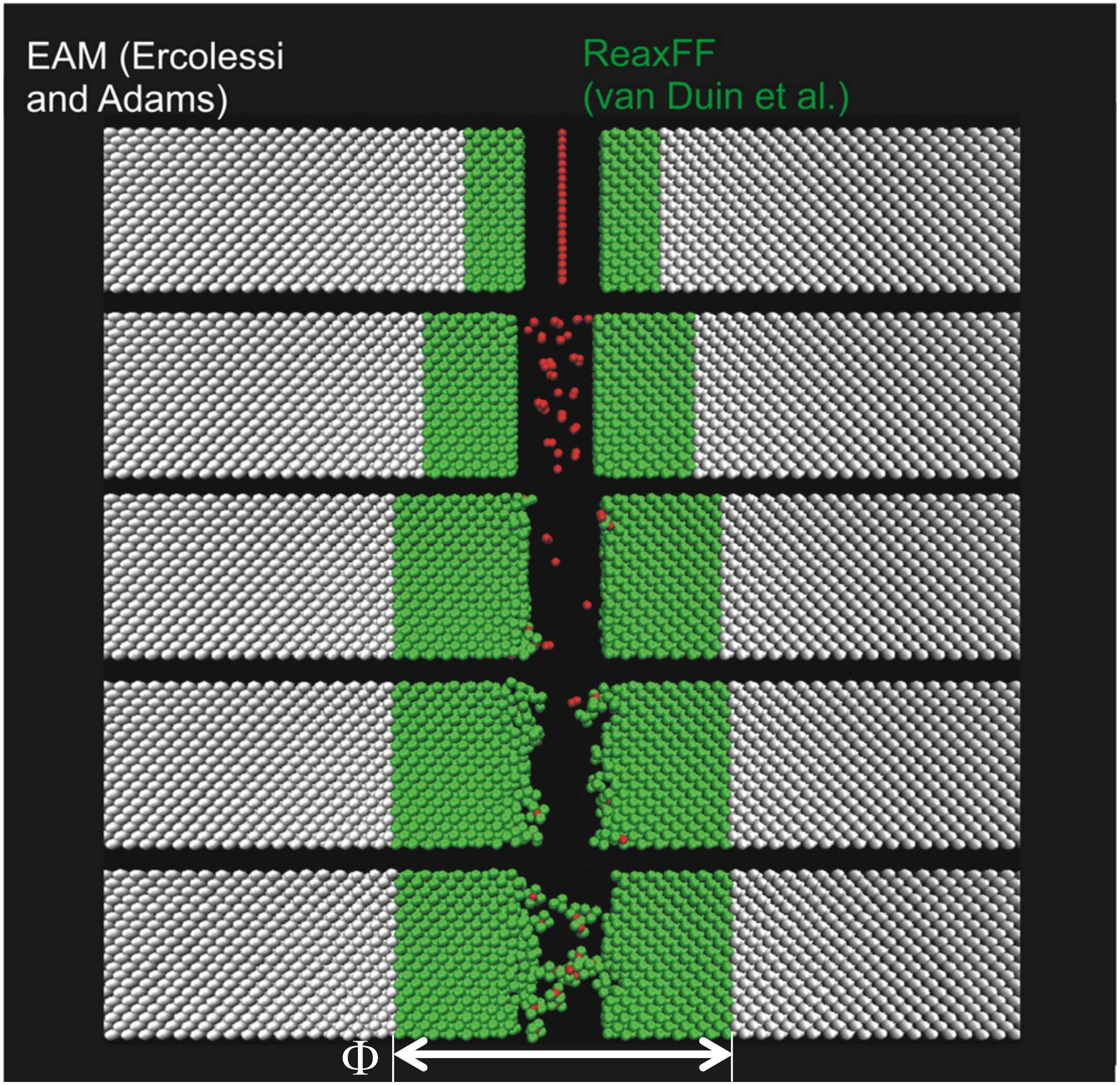
Oxidation of a metal (Al) surface

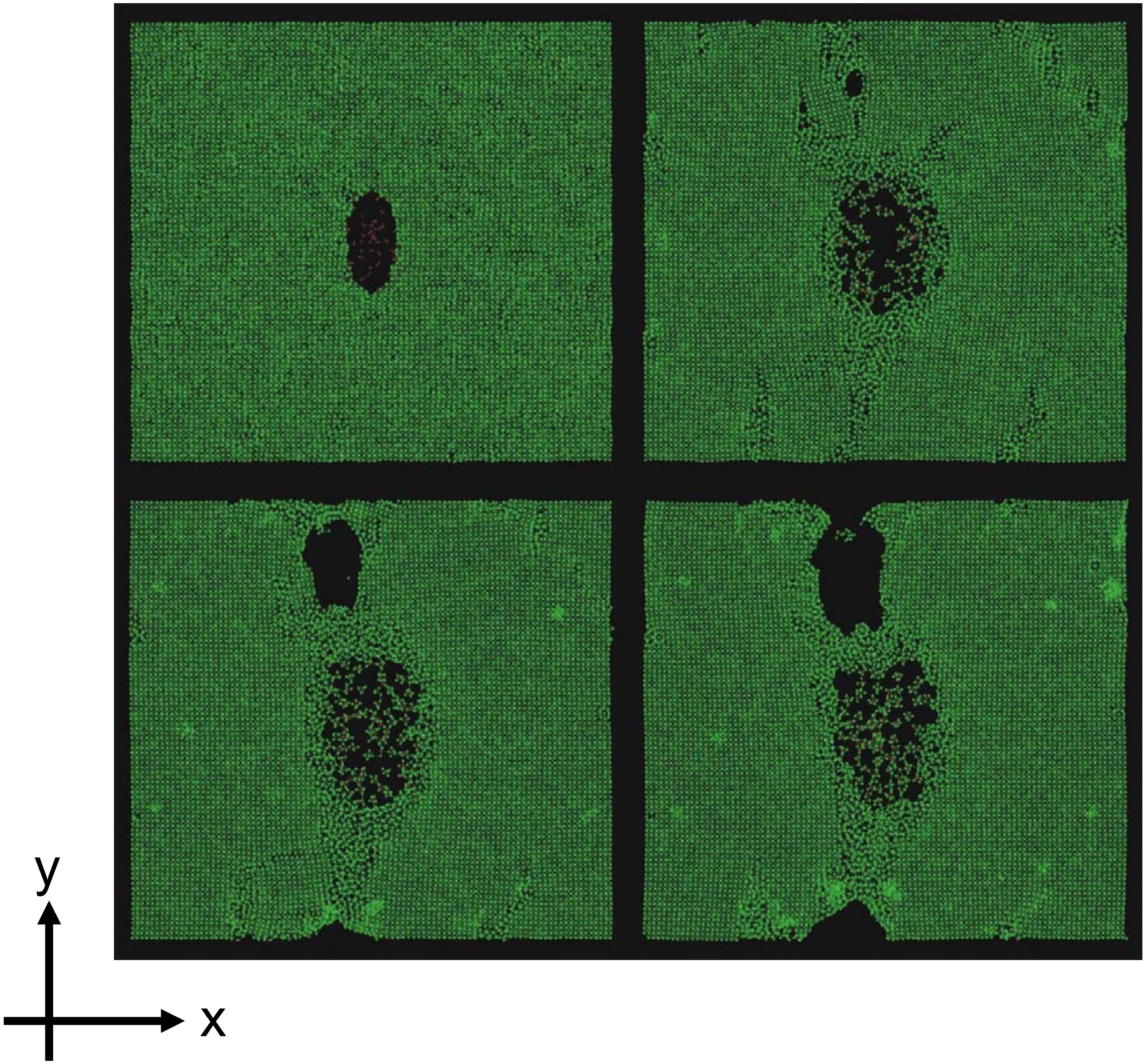
- Examples demonstrates the concept of the moving boundary between different computational engines

- Boundary location determined by position of oxygen atoms

- Iterative procedure to find Φ



Deformation of Al and Al oxidation



- Nano-void in Aluminum filled with O_2: Load applied in the x-direction

- The system is under 10% strain in the *x*-direction (orthogonal to the long axis of the elliptical defect).

- The results demonstrate our capability to couple complex chemistry competing with fracture events.

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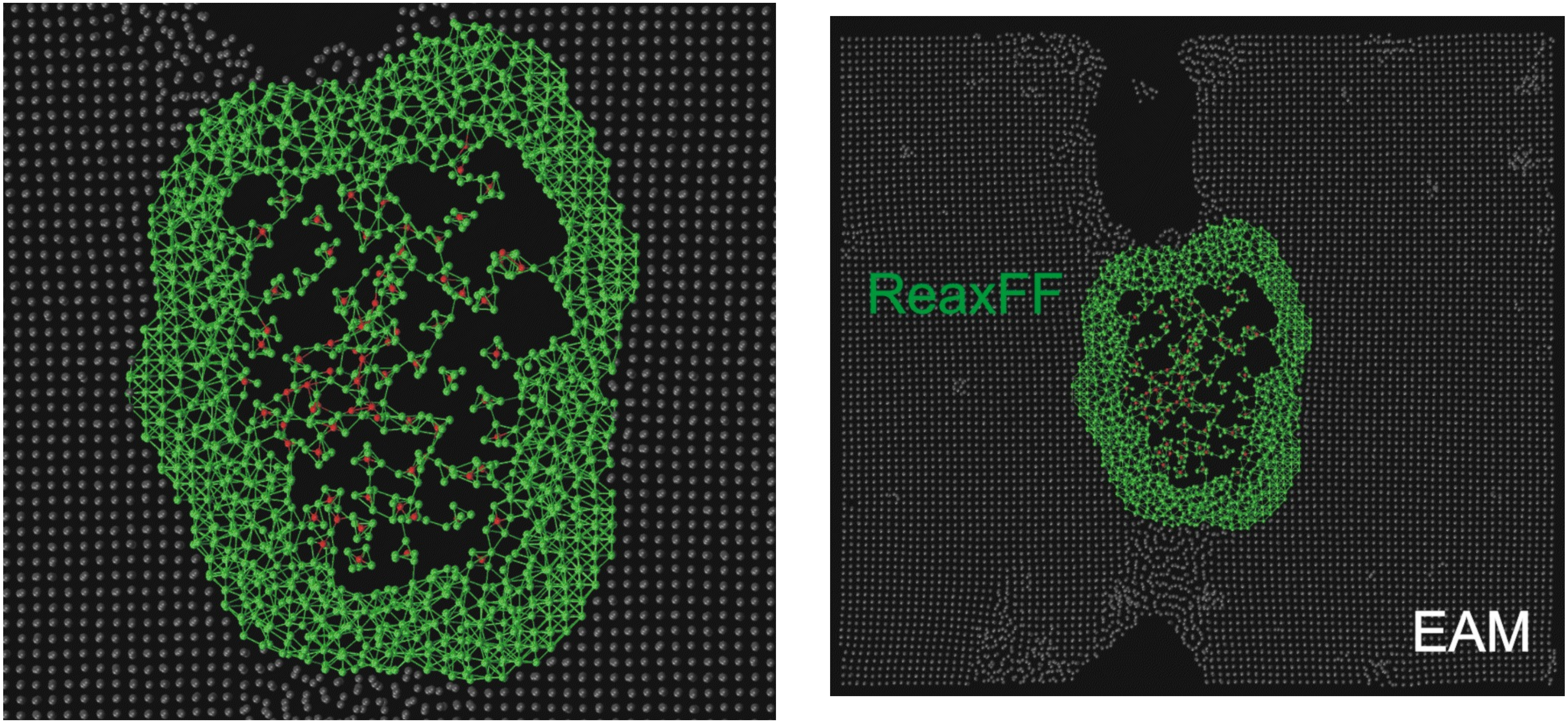
Deformation of Al and Al oxidation



Close-up view of the interface between the EAM and the reactive region.

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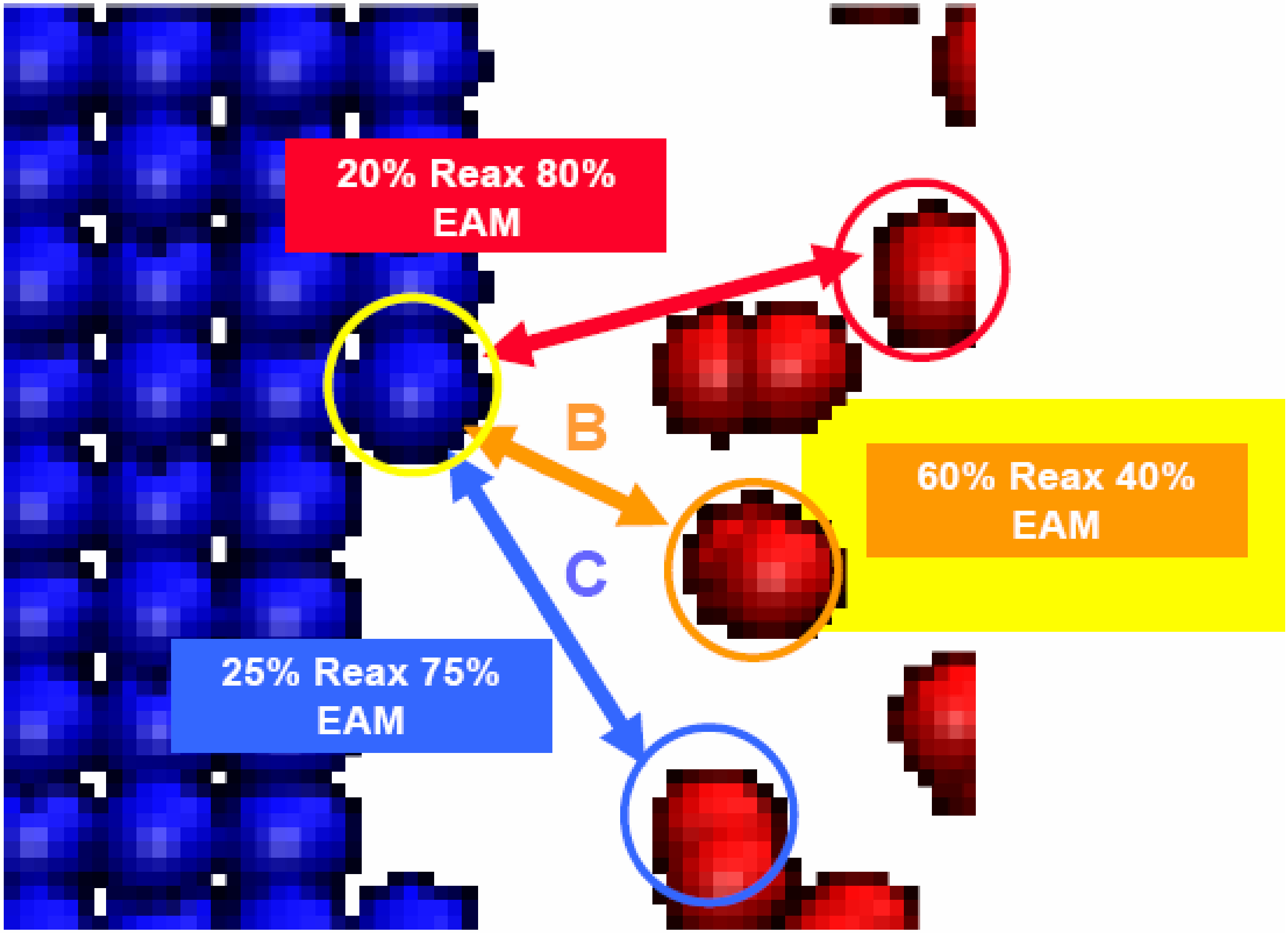
Decomposition into EAM/ReaxFF regions



Si-ping Han

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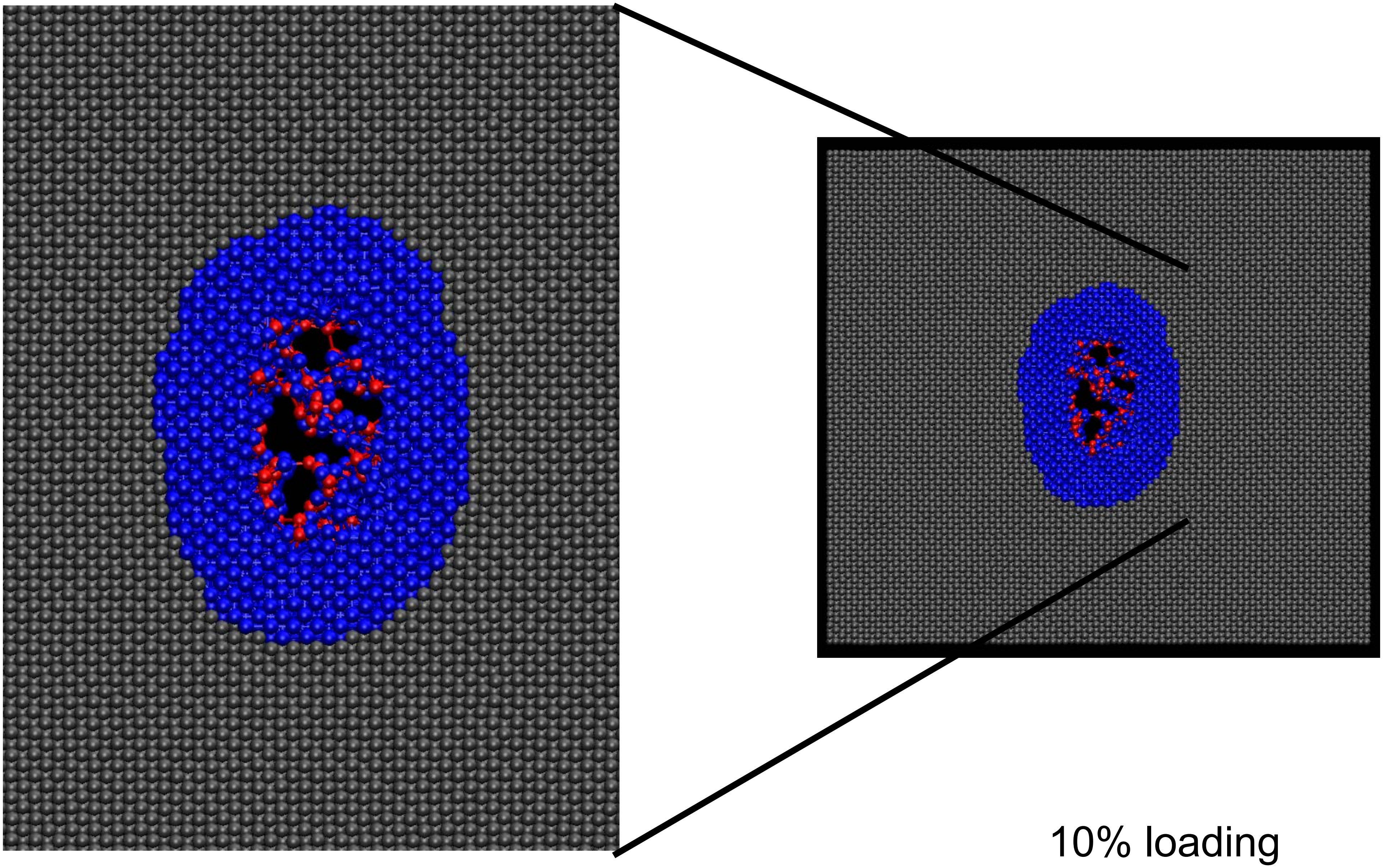
Deformation of Ni and Ni oxidation



10% loading

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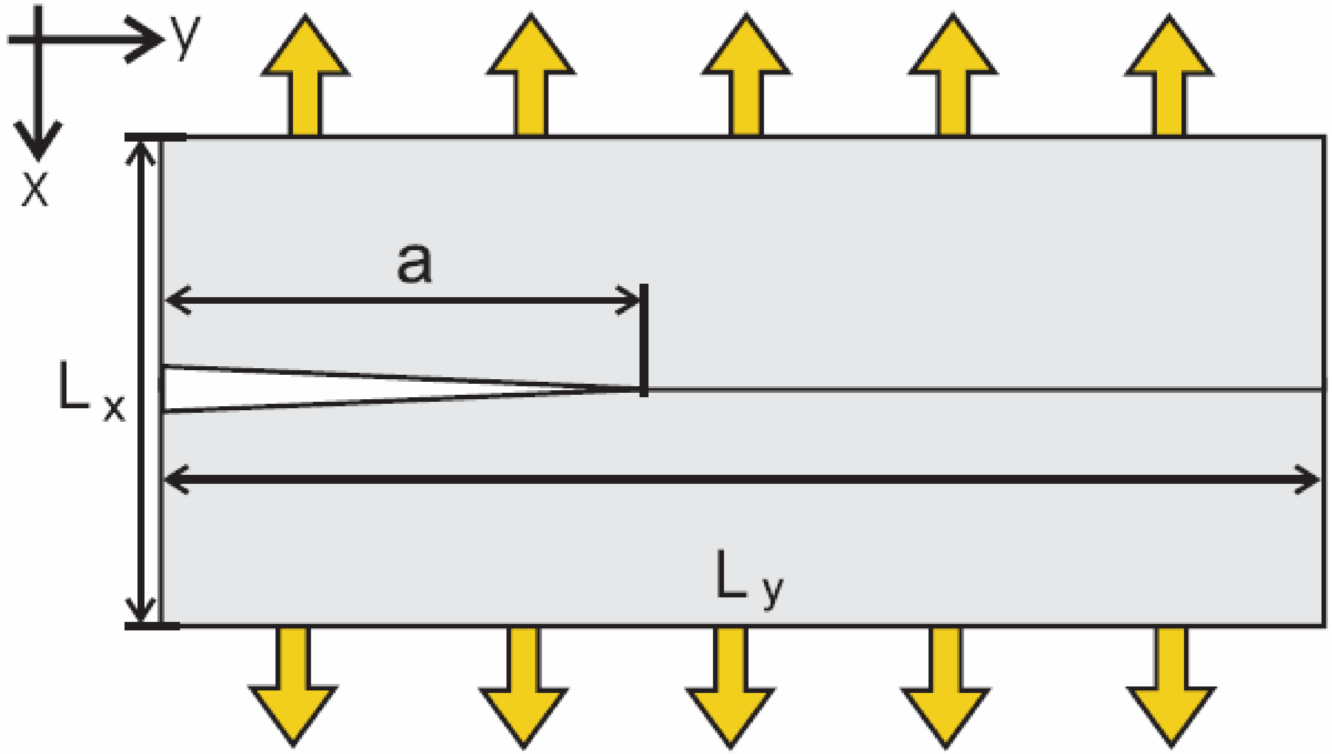
Simulation Geometry: Cracking in Silicon



- We consider a crack in a silicon crystal under mode I loading.
- We use periodic boundary conditions in the *z* direction corresponding to a plane strain case.

- The smallest system contains 13,000 atoms and the largest system over 110,000 atoms.
- In the largest system, $L_x \approx 550$ Å and $L_y \approx 910$ Å.
- The number of reactive atoms varies between 500 and 3,000.
- Calculation of forces and energies in the reactive region is the most expensive part

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Cracking in Silicon: Model within CMDF

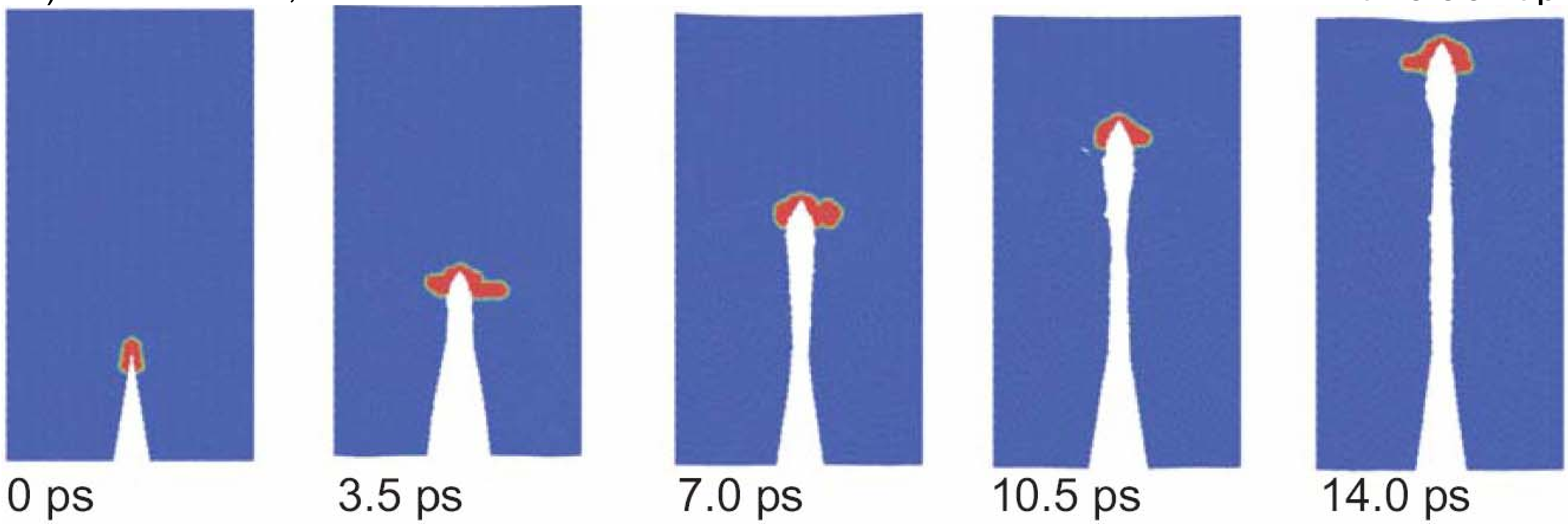
- To model cracking in Silicon more efficiently, we developed a multi-paradigm scheme that combines the Tersoff potential and ReaxFF

- The ReaxFF region is moving with the crack tip (region determined based on local atomic strain)

New hybrid scheme within CMDF

Reactive region is moving with crack tip

(110) crack surface, 10 % strain



ReaxFF 🟥
Tersoff 🟦

- CMDF reproduces experimental results (e.g. Cramer, Wanner, Gumbsch, 2000)

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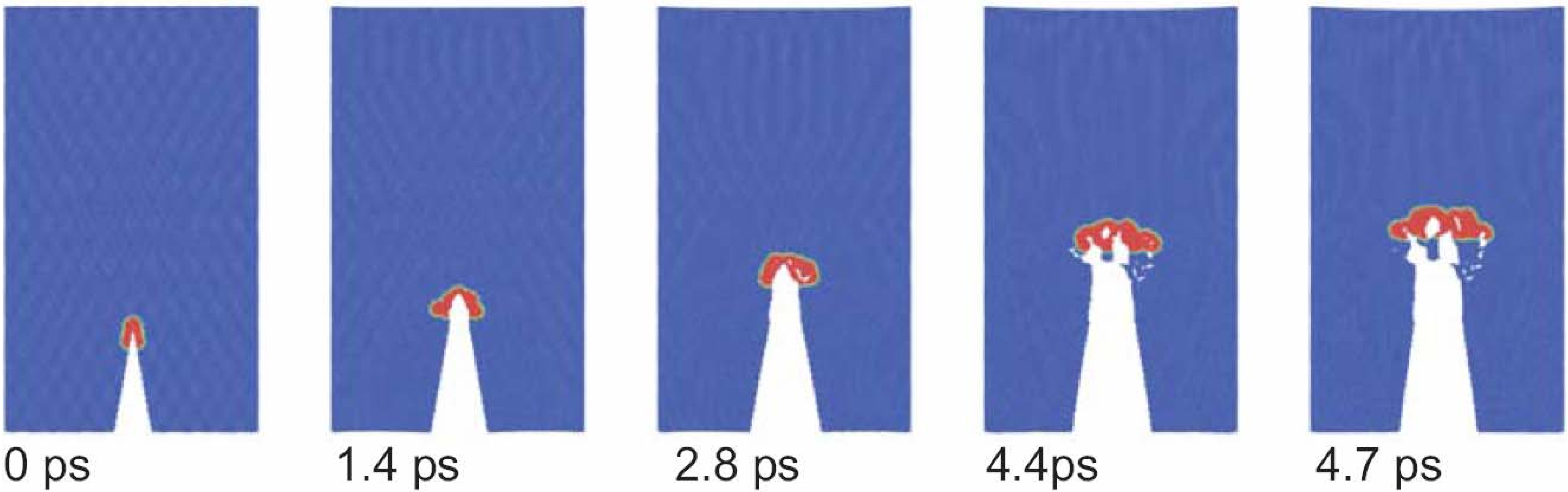
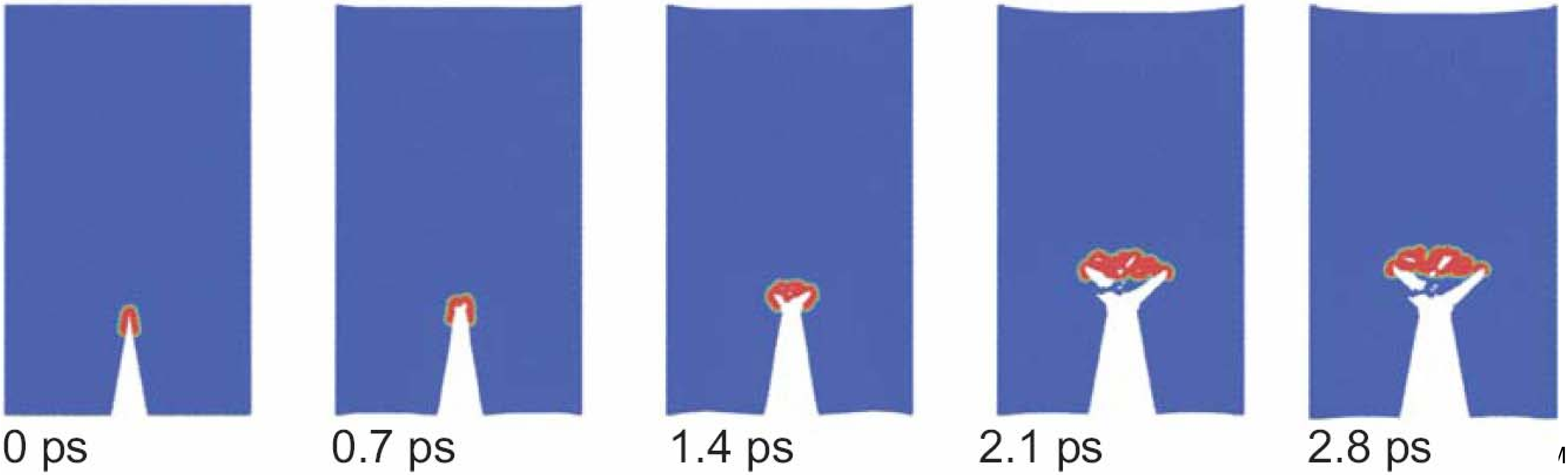
Cracking in Silicon: Model within CMDF

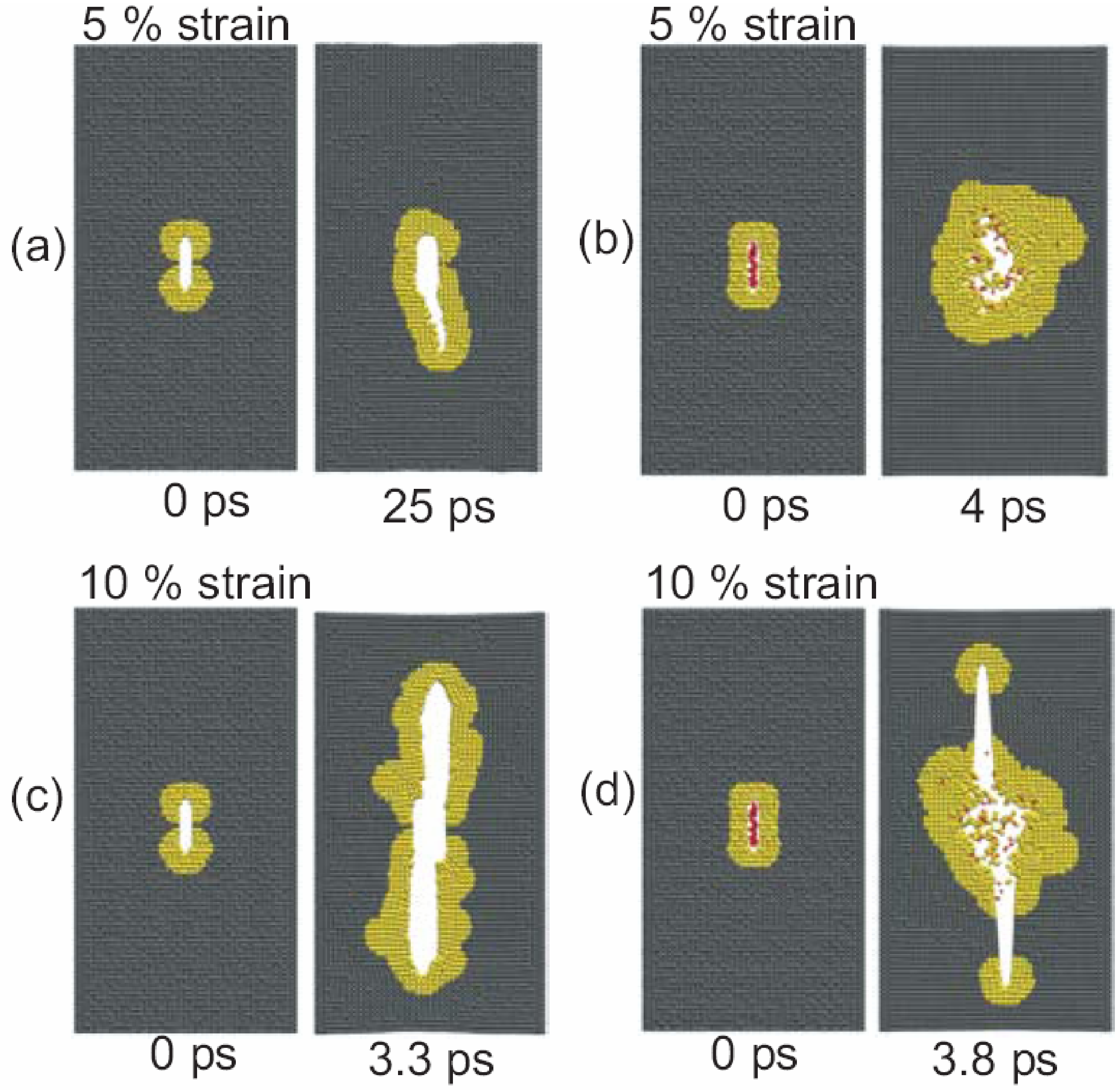
(110) crack surface, 20 % strain



(100) crack surface, 10 % strain



Oxidation versus brittle fracture
Including complex chemistry



- Crack dynamics in silicon without (subplots (a) and (c)) and with oxygen molecules present (subplots (b) and (d))
- Subplots (a) and (b) show the results for 5 percent applied strain, whereas subplots (c) and (d) show the results for 10 percent applied strain.
- The systems contain 13,000 atoms and $L_x \approx 160$Å and $L_y \approx 310$Å.

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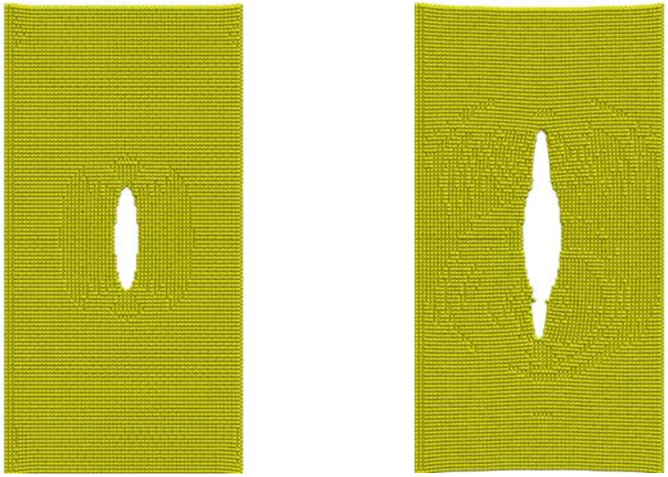
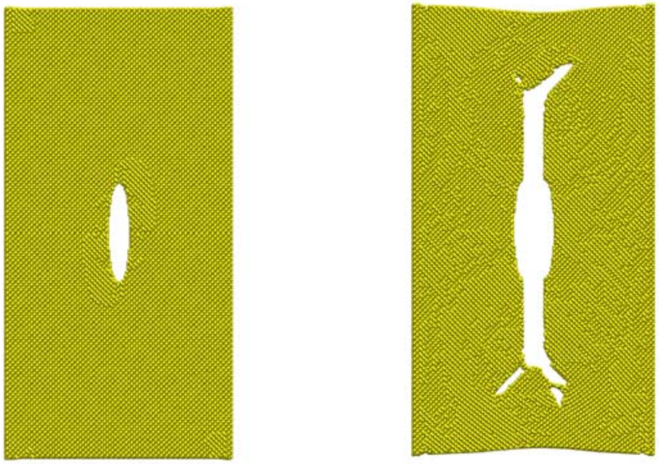
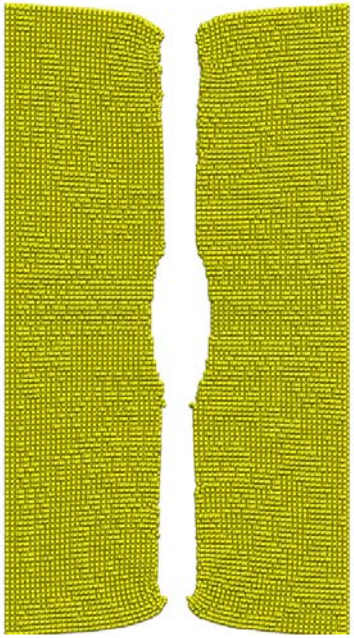
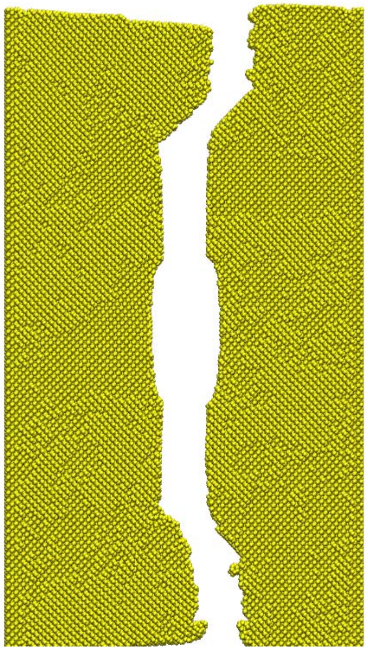
GRASP calculations
32 CPUs, 30,000 atoms, ca. 8 hours









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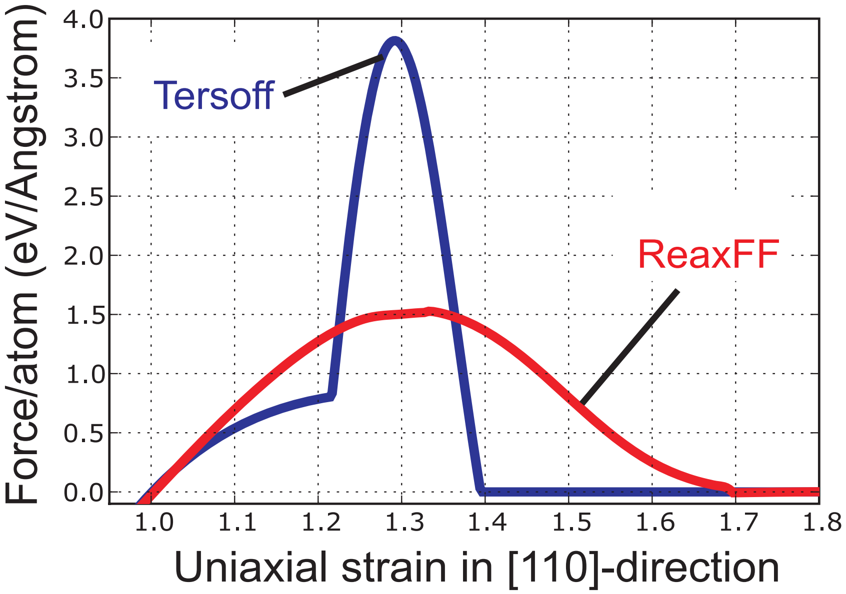
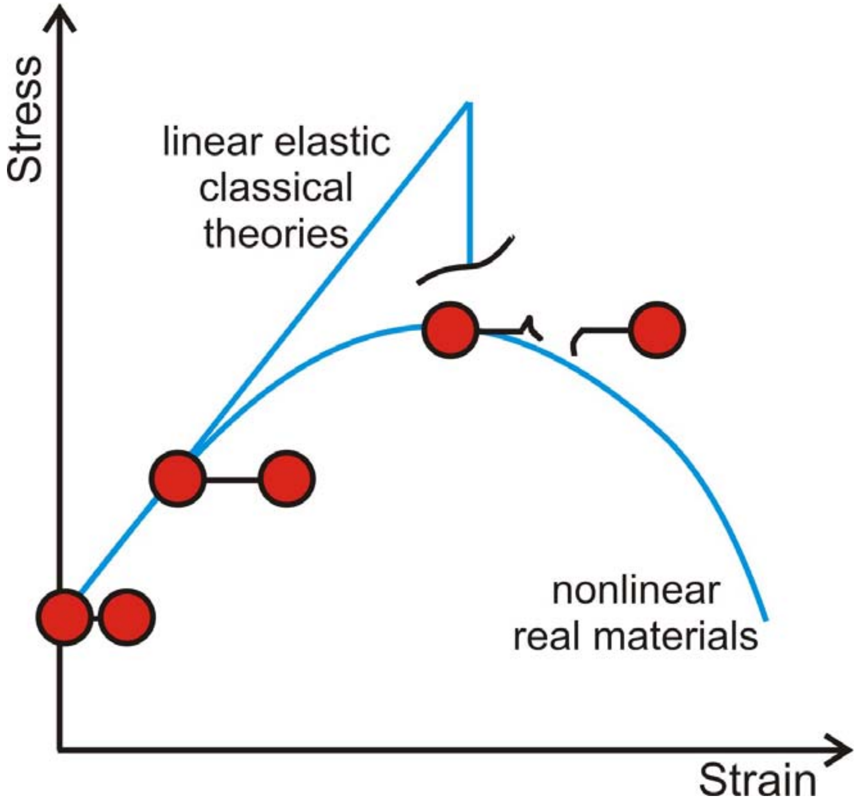
Conclusions

- Underlines importance of large-strain elasticity in fracture mechanics of materials
- “Properties at bond breaking are critical”… therefore chemistry, at the finest scale!





(Buehler and Gao, Nature, in press)

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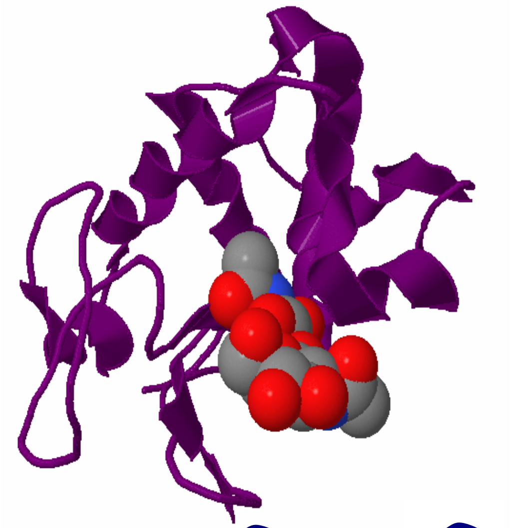
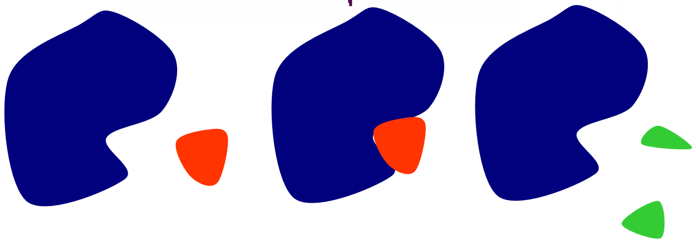
Modeling enzymes

- Perform **atomistic simulations at finite temperature** to develop accurate and predictive models of **chemical properties of complex biological materials**

- **Objective**: Develop atomistic model of enzymes to "observe" and study the details of the "<u>protein at work</u>", clarify mechanism





- **Issue:** How to incorporate chemistry into modeling of biological materials:
  - ☐ Classical generic, empirical force fields do **not** allow treatment of chemical reactions (e.g. AMBER, CHARMM, DREIDING…)
  - ☐ Thus: Development of new generic, reactive force field **ReaxFF** that can model complex chemistry (treats ~3,000 atoms)

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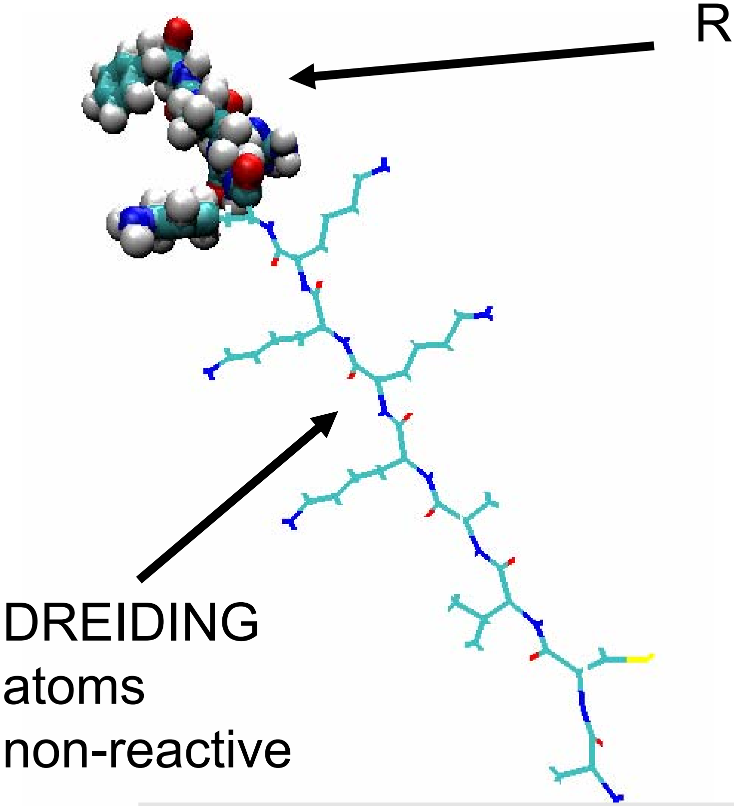
Combination of ReaxFF and DREIDING Hybrid Simulations for organic systems



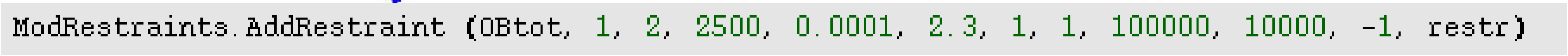
ReaxFF atoms

DREIDING atoms non-reactive

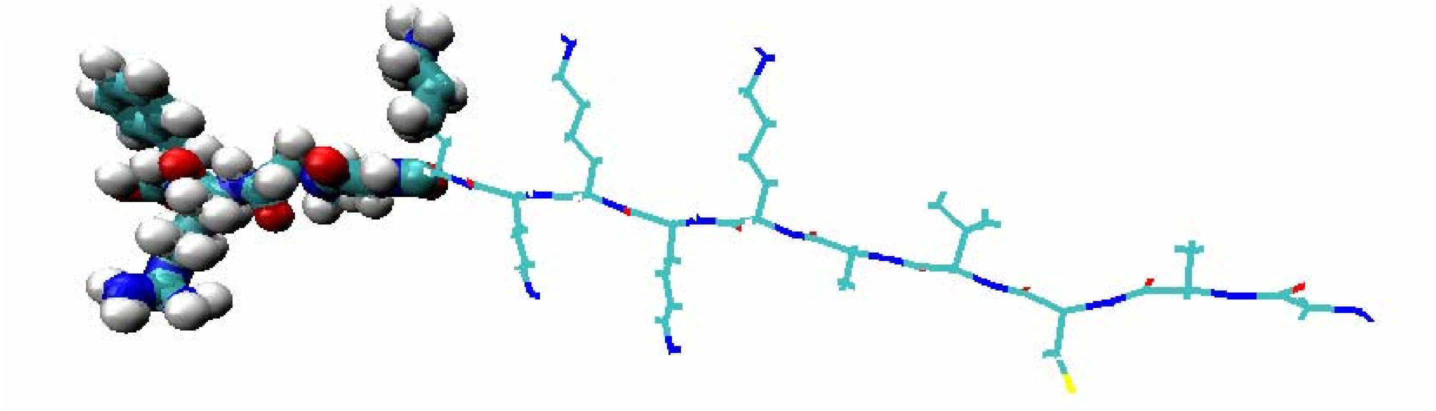
- Goal: Couple ReaxFF and classical force field (e.g. DREIDING) to develop a new ReaxFF/MM scheme
- Intention: Provide alternative to QM/MM scheme

Key capabilities:

- Update of reactive regions
- Restraints (harmonic)



```
ModRestraints.AddRestraint (OBtot, 1, 2, 2500, 0.0001, 2.3, 1, 1, 100000, 10000, -1, restr)
```



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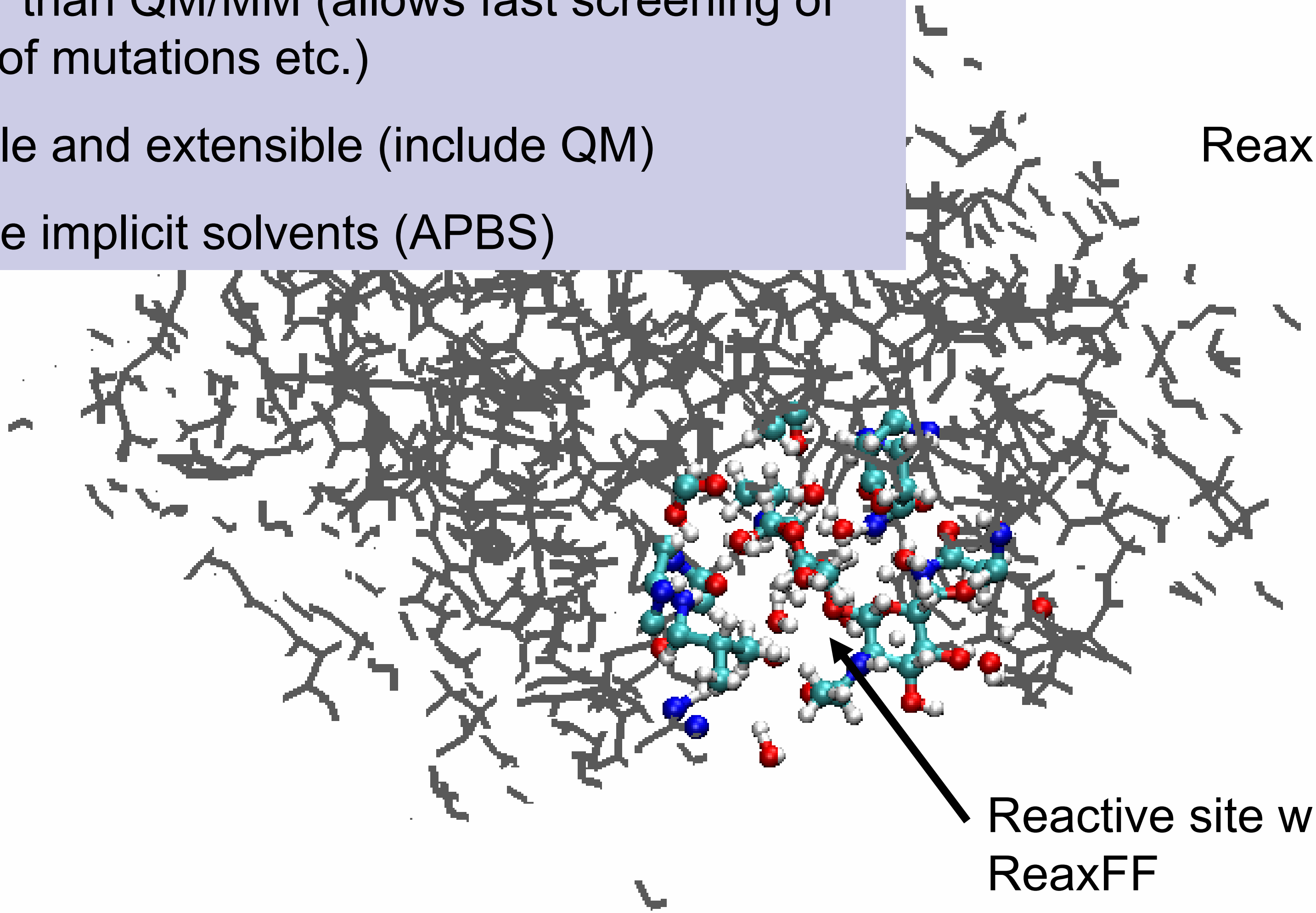
Reactive modeling of active site in protein

Advantages over classical QM/MM schemes:

- No ghost atoms
- Faster than QM/MM (allows fast screening of effects of mutations etc.)
- Flexible and extensible (include QM)
- Include implicit solvents (APBS)



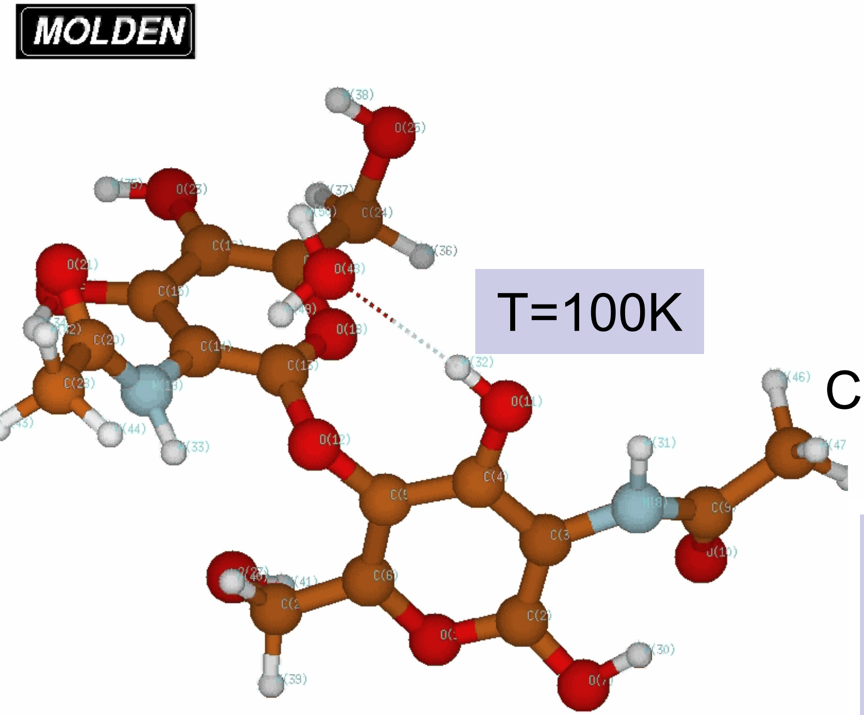
Non-reactive region
(Biograf, DREIDING)

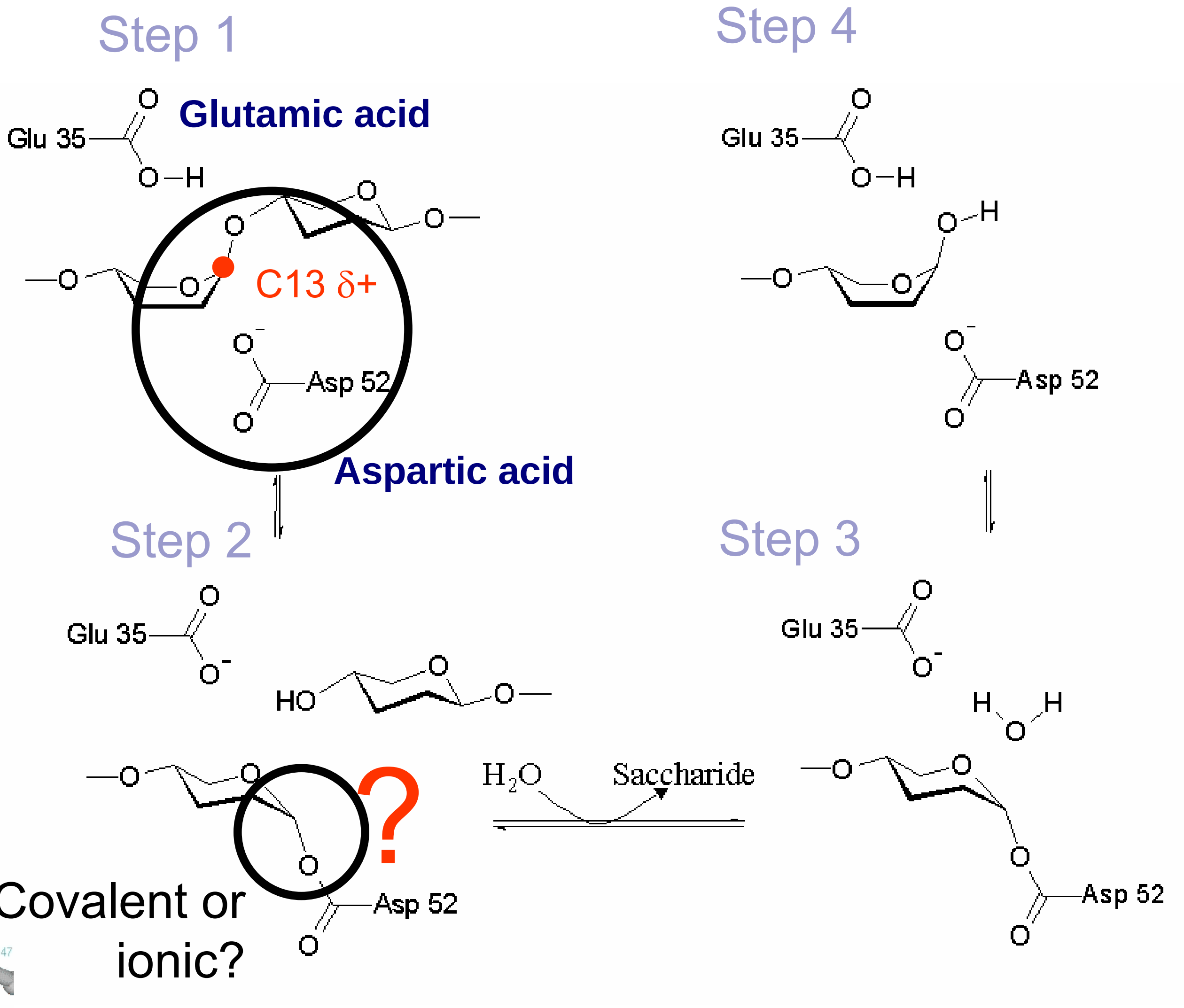
ReaxFF/MM scheme

Reactive site with
ReaxFF
Contains substrate

The Philips mechanism in Lysozyme Example (2)

- Hen Egg White Lysozyme (HEWL)
- **Function**: Destruction of bacterial (and fungi) cell walls-through hydrolysis of glycosidic linkages





Covalent or ionic?

Controversy: Is a covalent bond formed or not? Vocadlo *et al.*, *Nature*, 2001, propose: Covalent bond is formed (as proposed by Koshland, 1951)!

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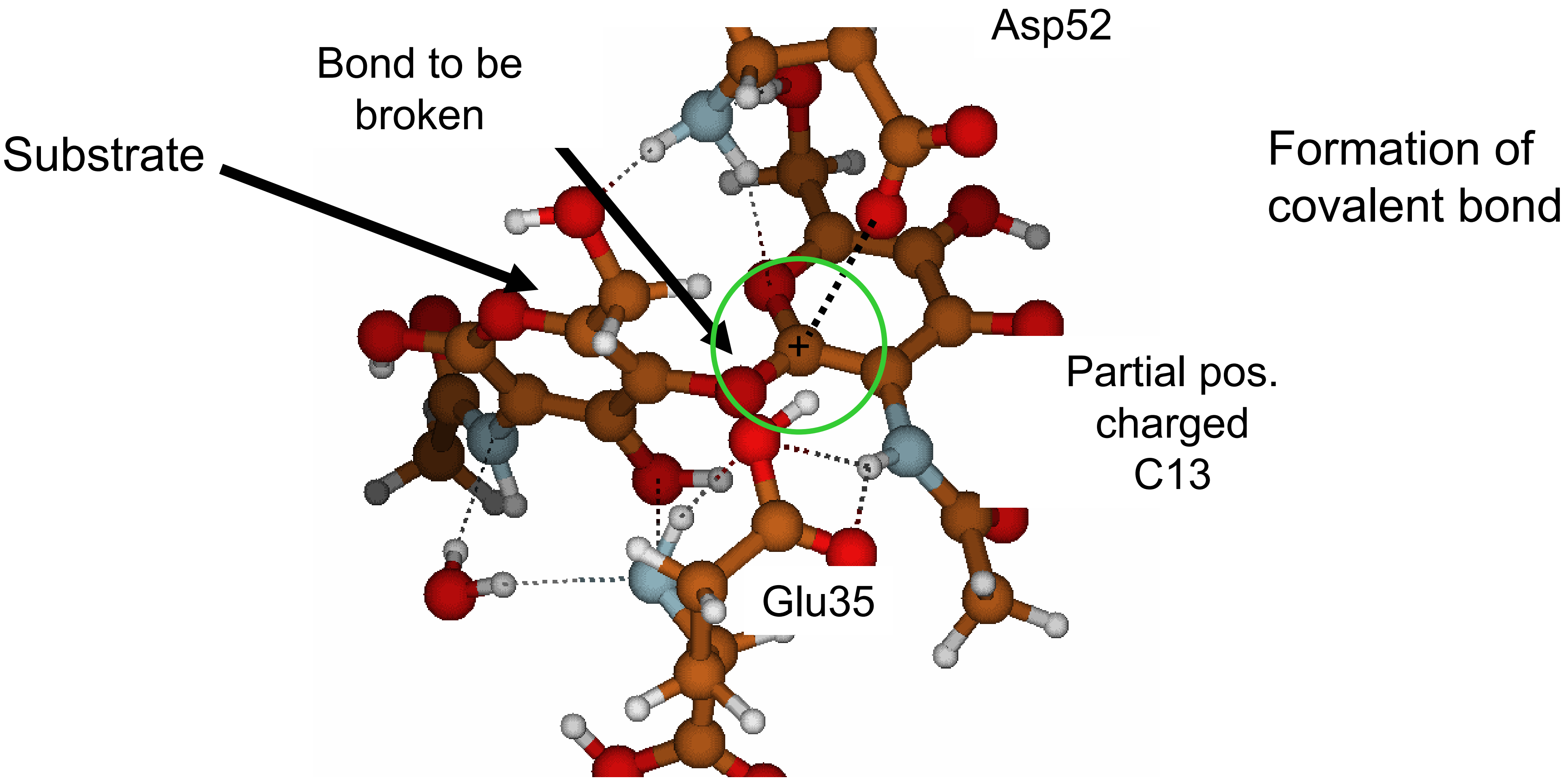
Protein at work: Simulation with ReaxFF



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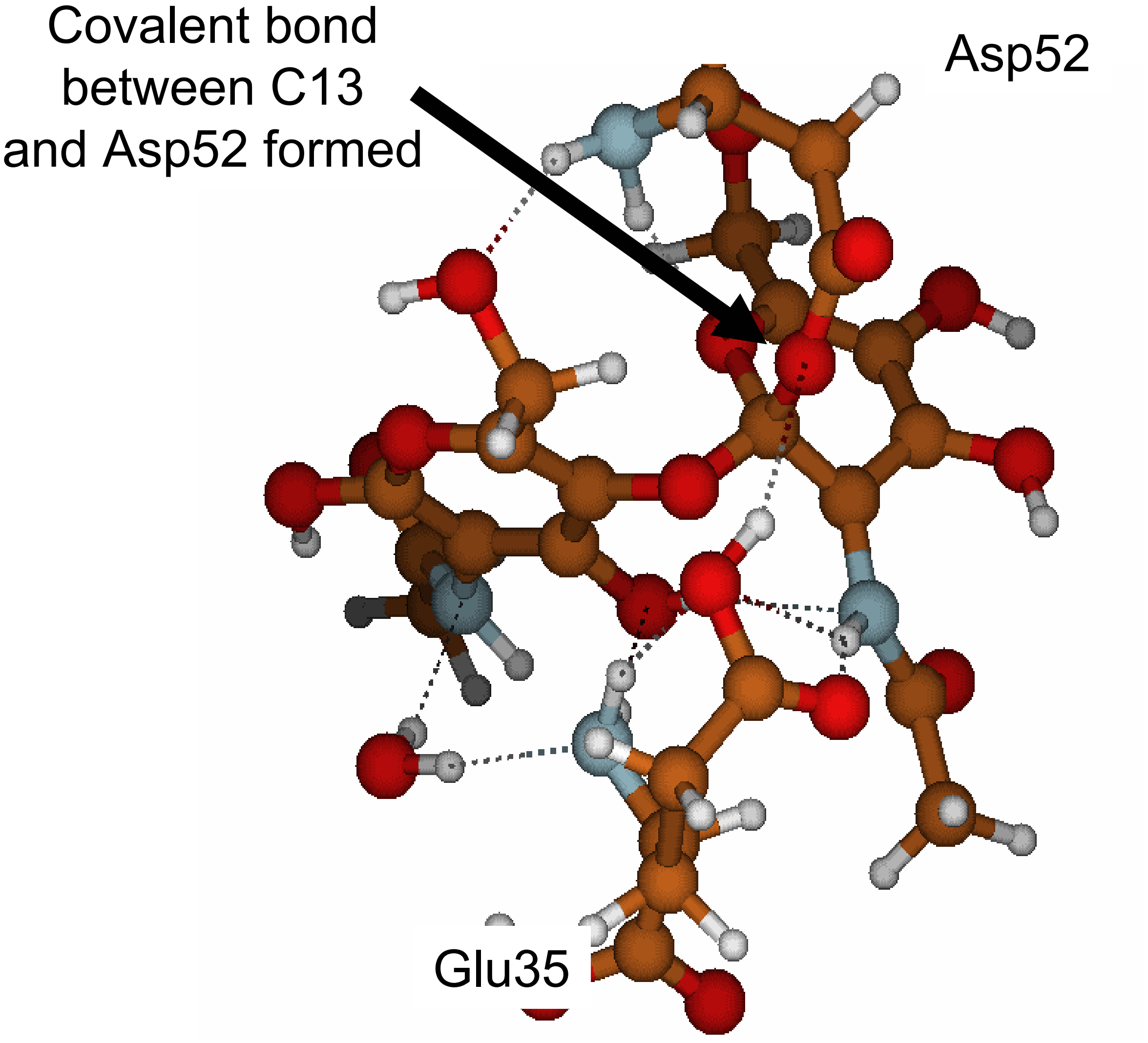
Protein at work: Simulation with ReaxFF



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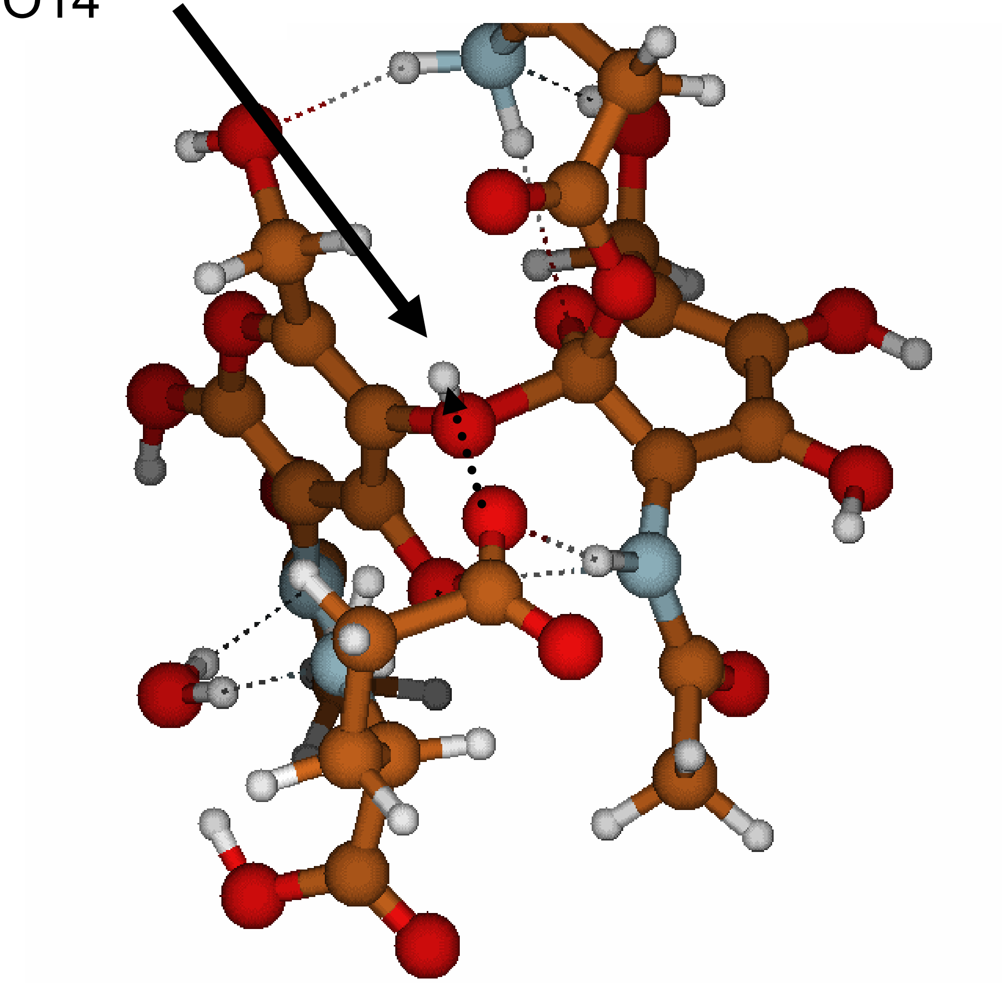
Protein at work: Simulation with ReaxFF



Proton transferred from Glu35 to O14

Proton transfer

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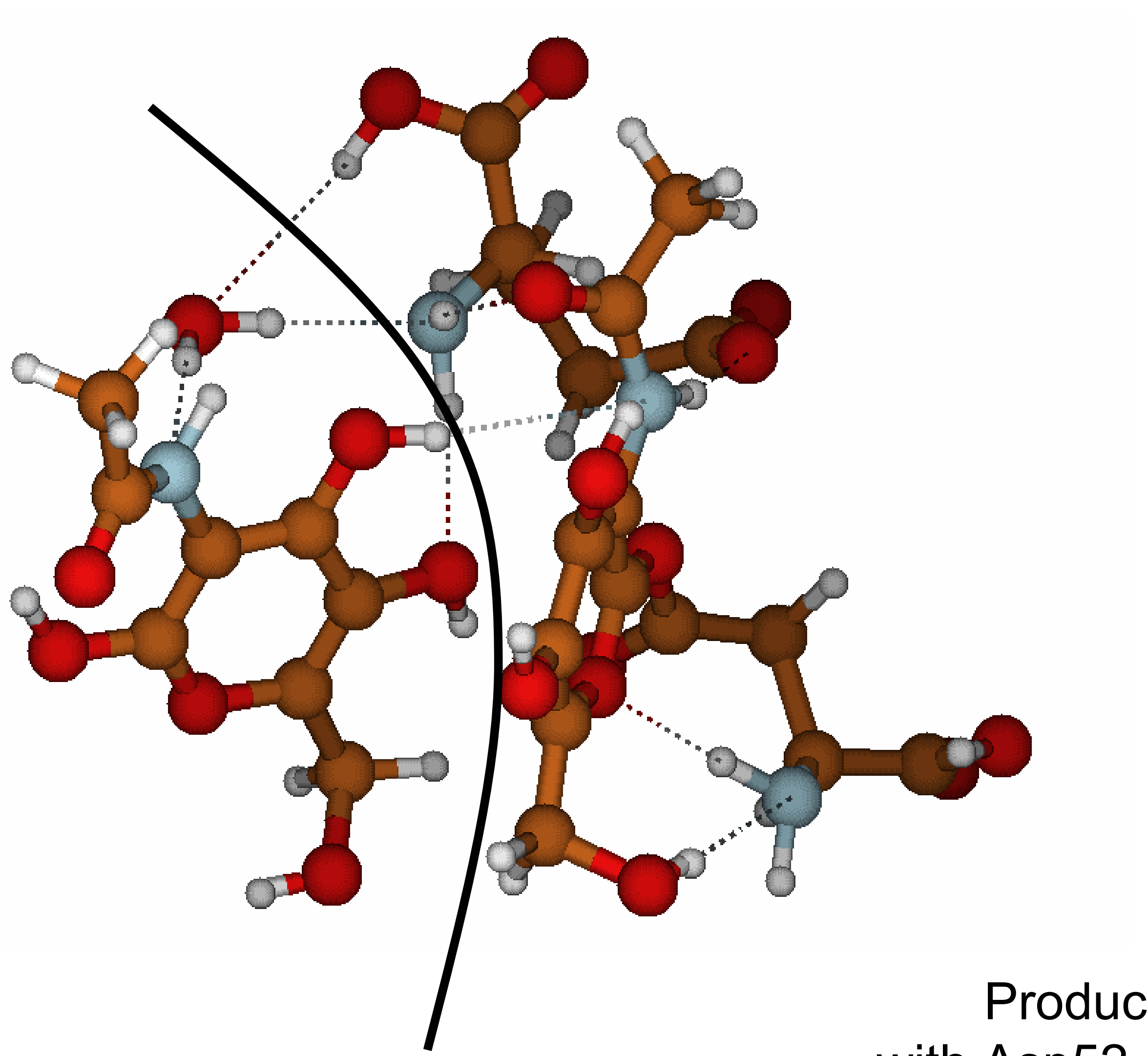
Protein at work: Simulation with ReaxFF



Product #1

Product #2
with Asp52 attached

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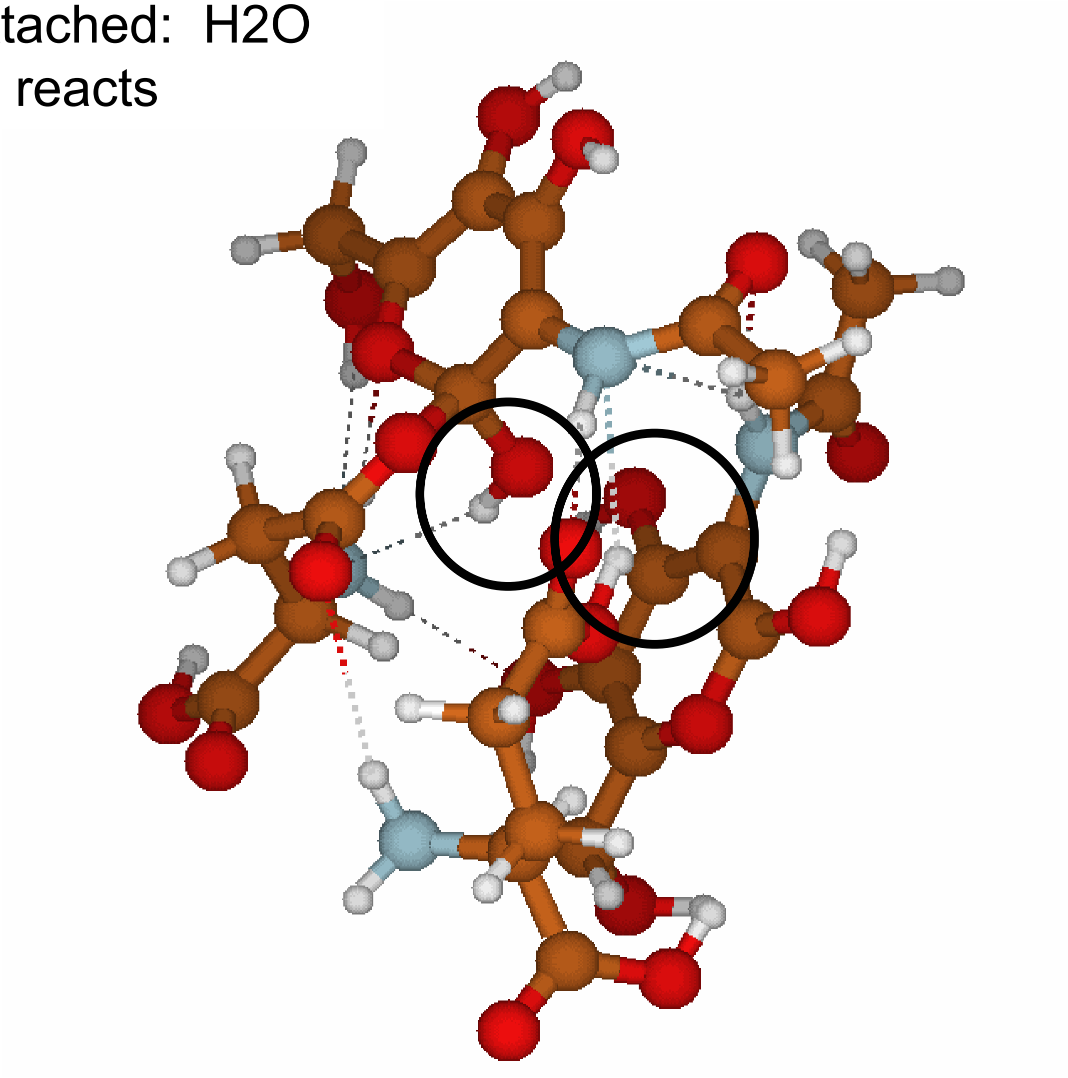
Protein at work: Simulation with ReaxFF

“Transition state”
OH attached: $H2O$
reacts



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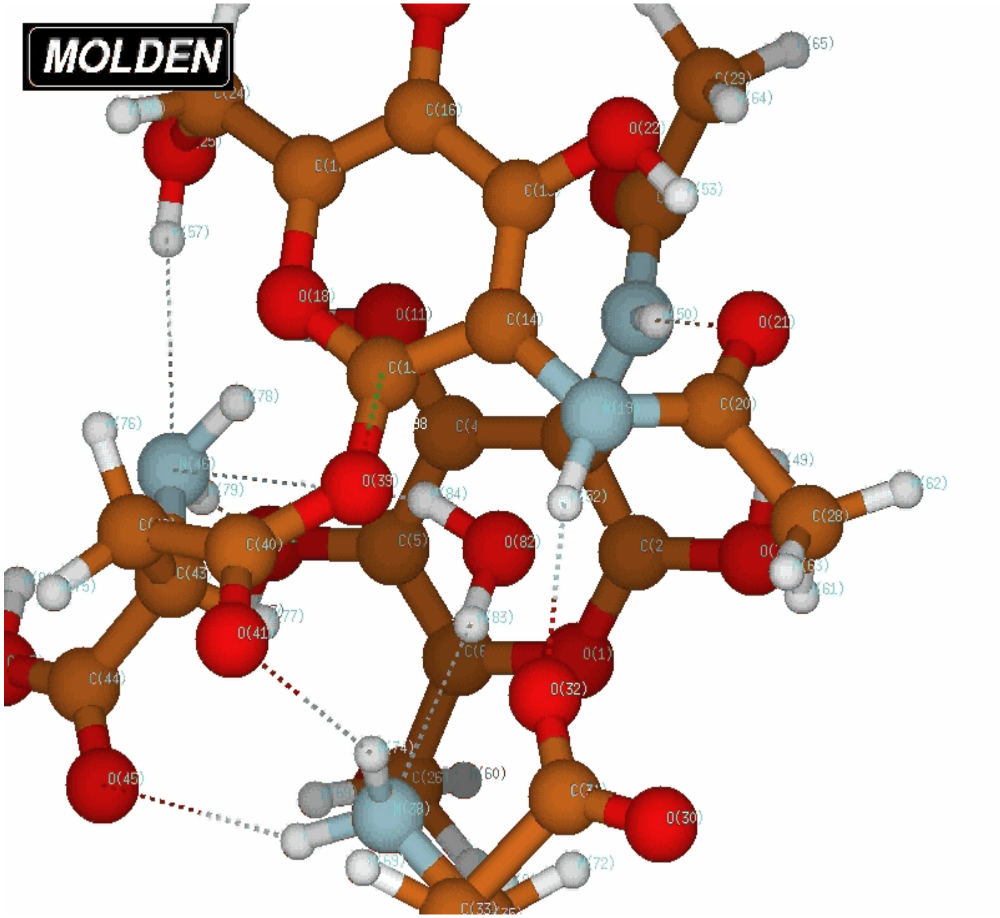
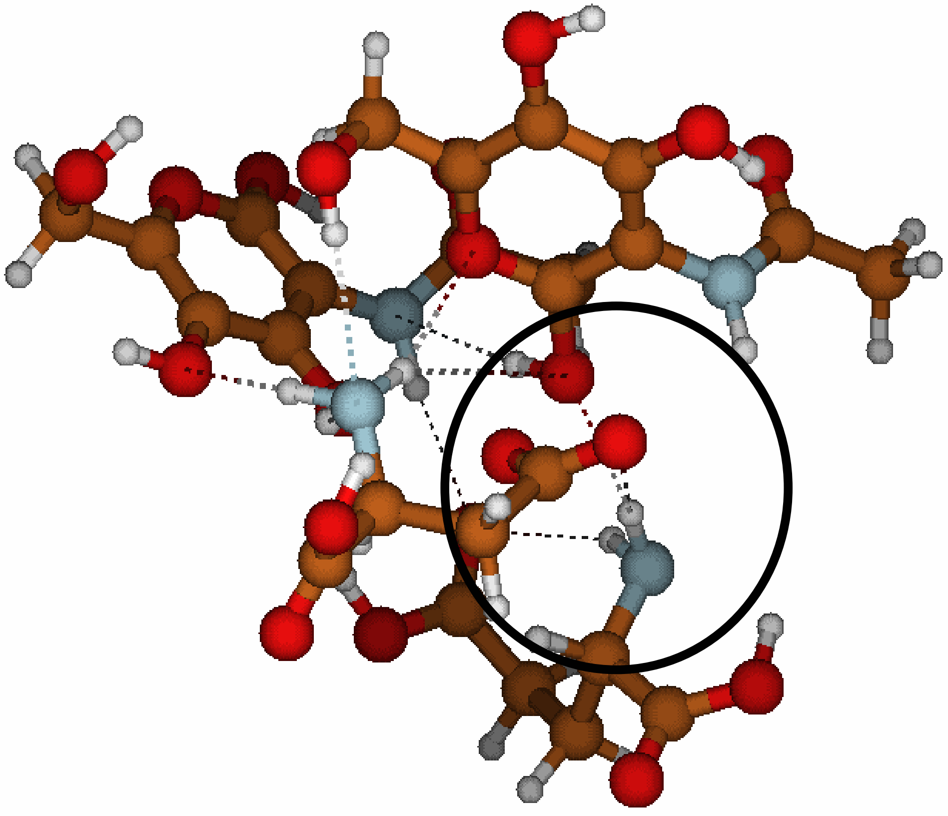
Protein at work: Simulation with ReaxFF





Have broken bond between
C13 and Asp52
Hydrolized water

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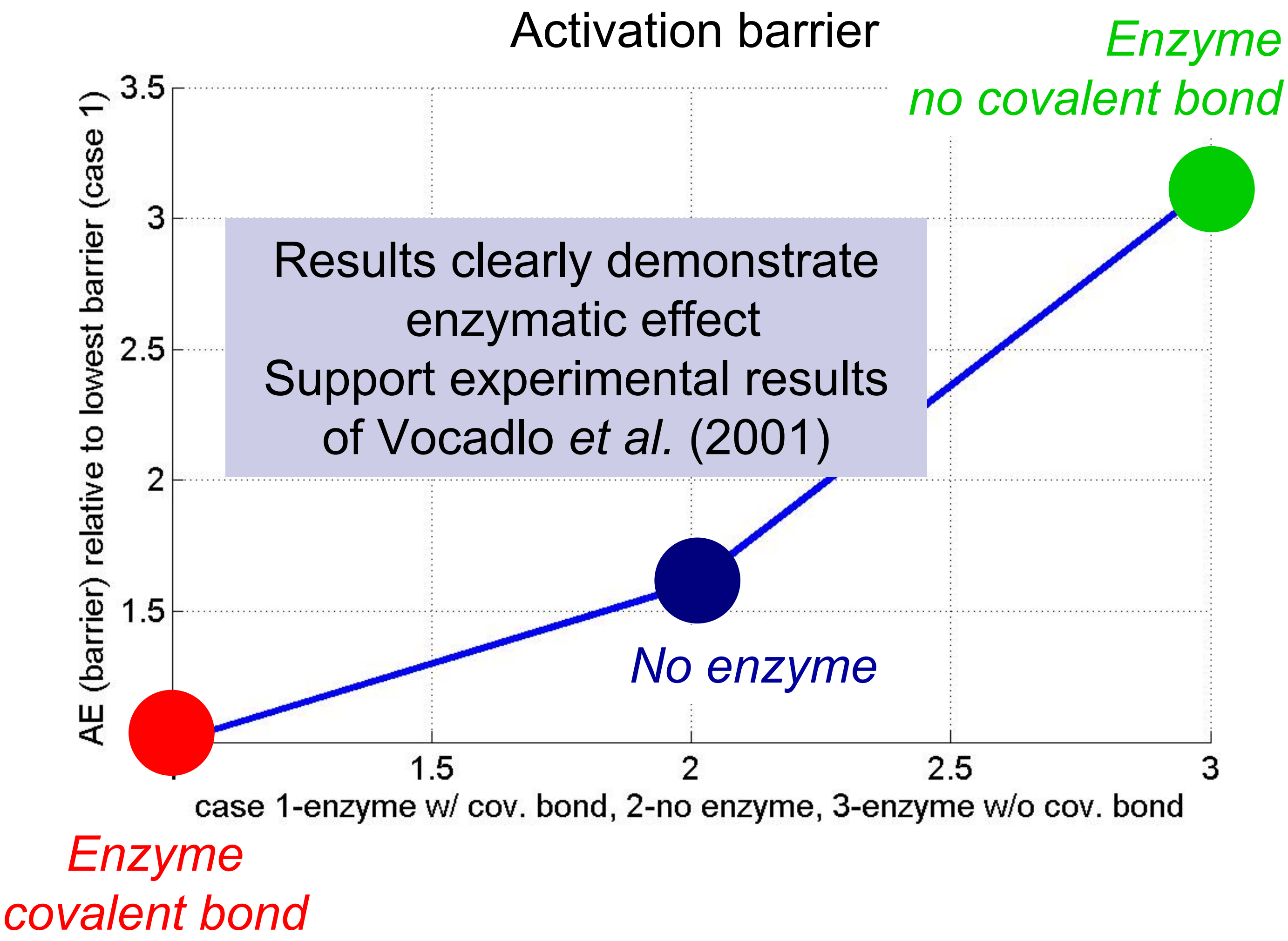
Result: Clarify reaction mechanism in Philips mechanism

- Using the reactive force field we have shown the catalytic effect of enzymes

- This suggests that the method can be applied to other biological systems as well

- Allows quick screening of different paths, different reactions to find optimal solution



Results clearly demonstrate enzymatic effect
Support experimental results of Vocadlo *et al.* (2001)

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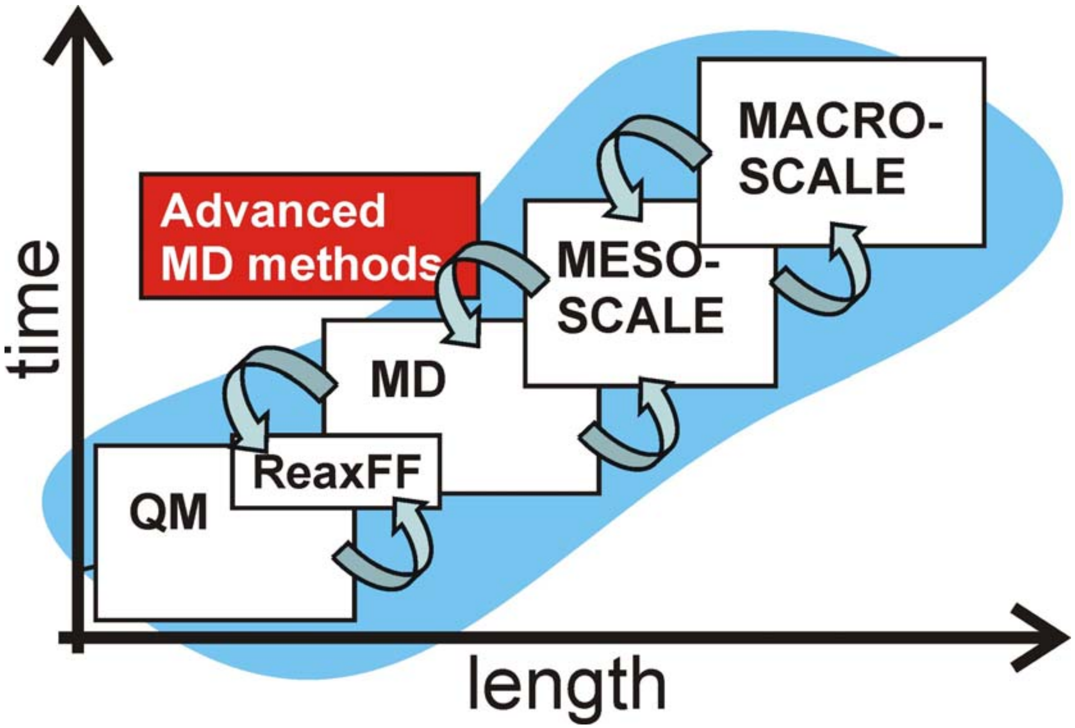
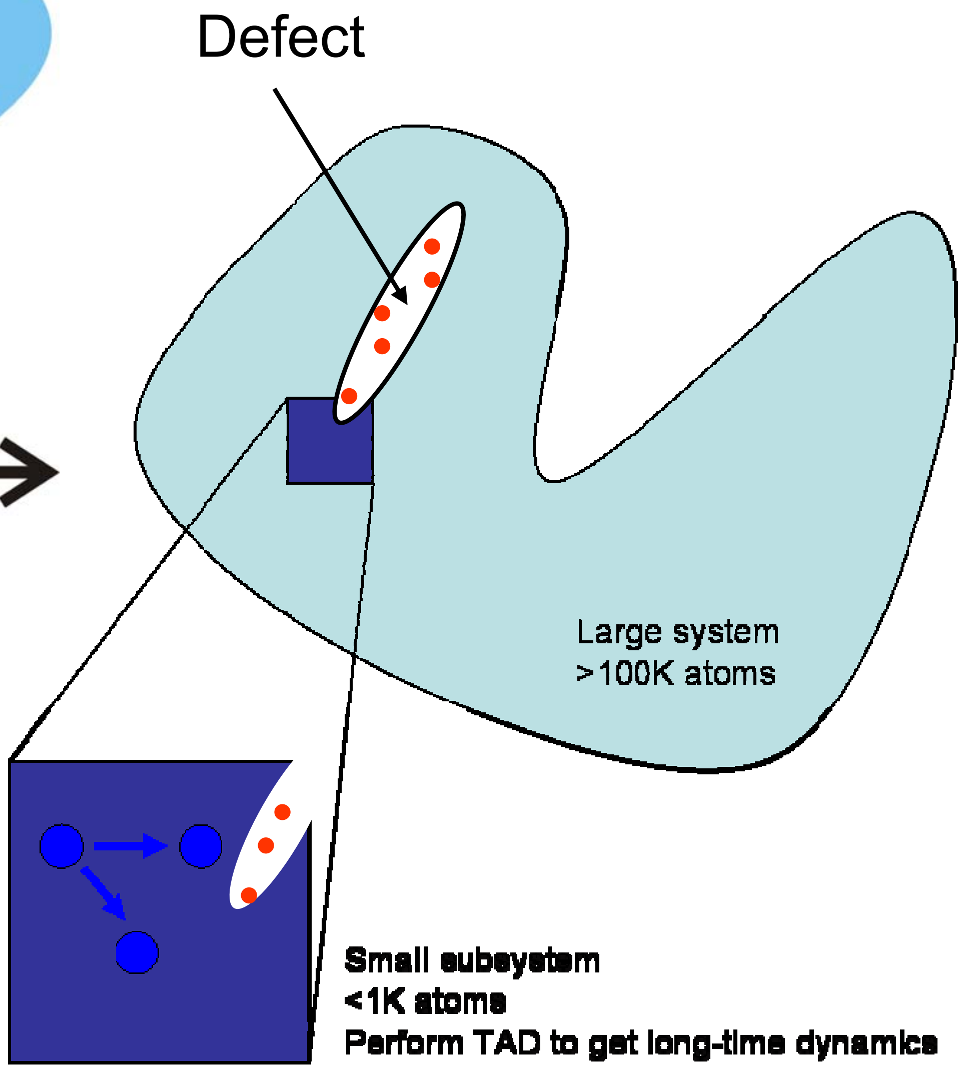
Extension to large time scales



Collaboration with
Art Voter, LANL



- Long time dynamics at crack tip using TAD
- Boundary conditions “elasticity” provided by large background system

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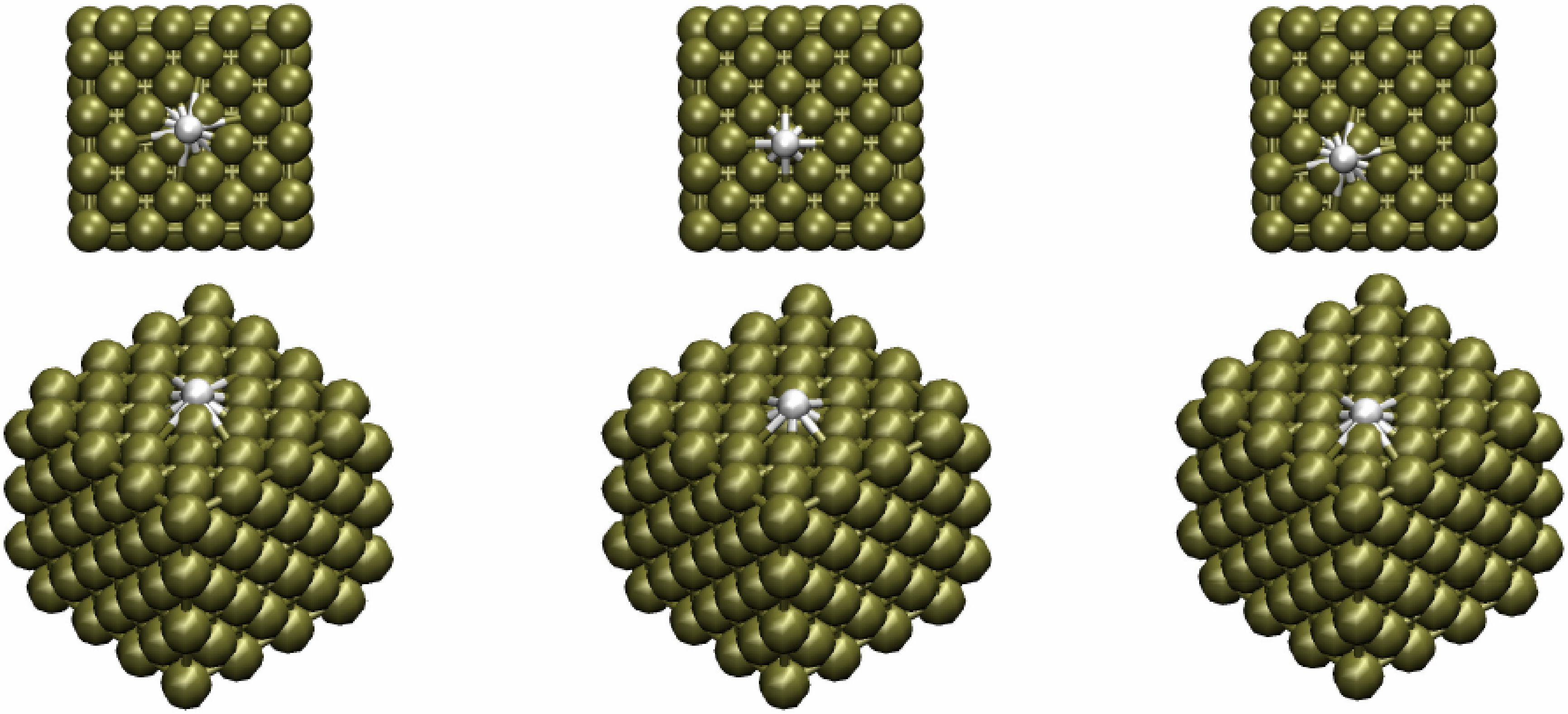
Diffusion of H on Pt

TAD low temperature 400 K (high sampling temperature 1300 K)



State 1 → State 2 → State 3

(equiv. to state 1)

State 1 → State 2:
Δt = 1.33E-8 sec
AE = 0.512 eV

State 2 → State 3:
Δt = 2.131E-10 sec
AE = 0.252 eV

ReaxFF interfaced with TAD through CMDF

(Collaboration with Art Voter, LANL)

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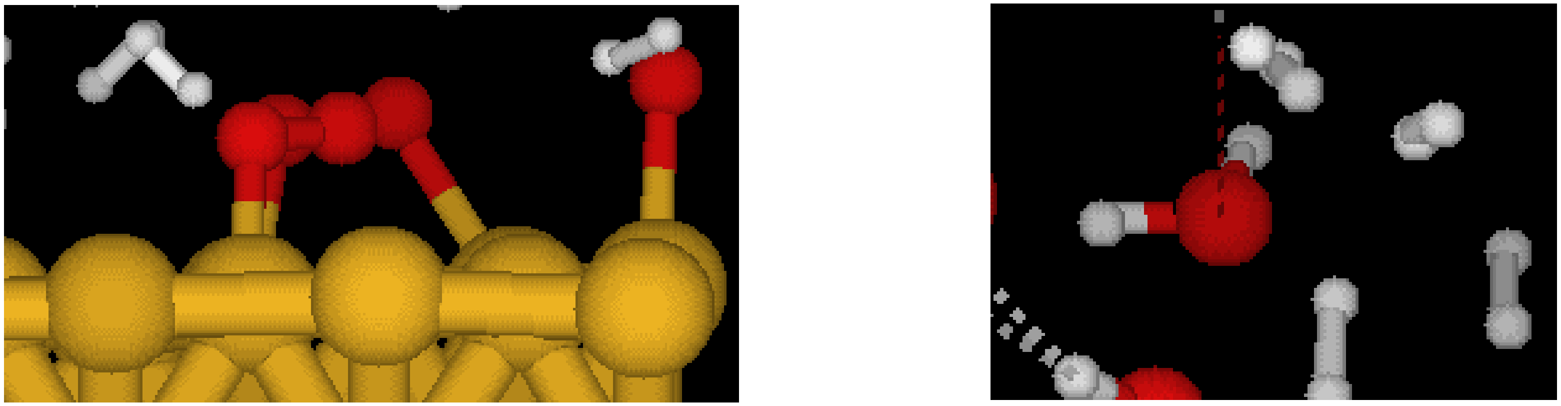
Formation of water

- Motivation
  - Water formation is one of the most fundamental chemical reactions
  - Water plays a critical role in biological systems
  - Need an atomistic model that allows proper description of chemistry of water formation
  - Water formation also important in fuel cells (hydrogen economy)
- Objective: Use the reactive force field applied to this simple system

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$



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Questions

- Can ReaxFF model the finite temperature dynamics of chemical reactions, in particular solid-gas phase interface reactions?
- Can we estimate the activation barriers from the dynamical runs, and does it agree with QM and experimental results?
- Can we demonstrate the effect of catalysts based on first principle modeling?

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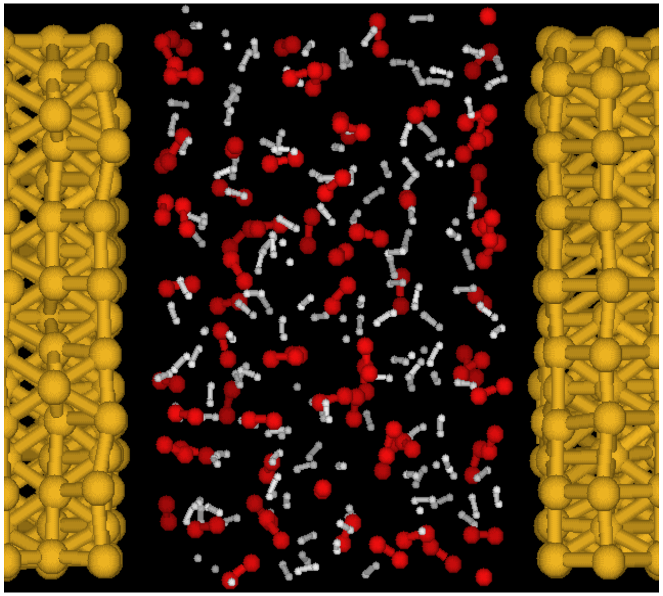
Simulation procedure

- ReaxFF force field
- NVT dynamics: temperature control, constant volume
- Time step Δt=0.25 fs, Velocity Verlet and Berendsen
- Simulation procedure: Set up initial structure according to desired pressure, relax using minimizer, then start finite temperature NVT dynamics
- Several runs with nonreactive force field to EQ, then use as variations in ICs for statically relevant runs (around 10 copies)



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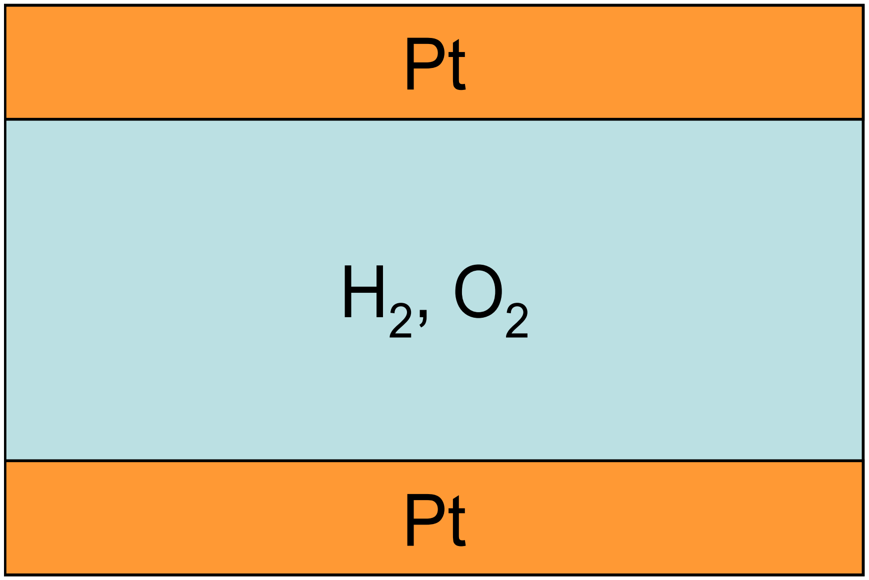
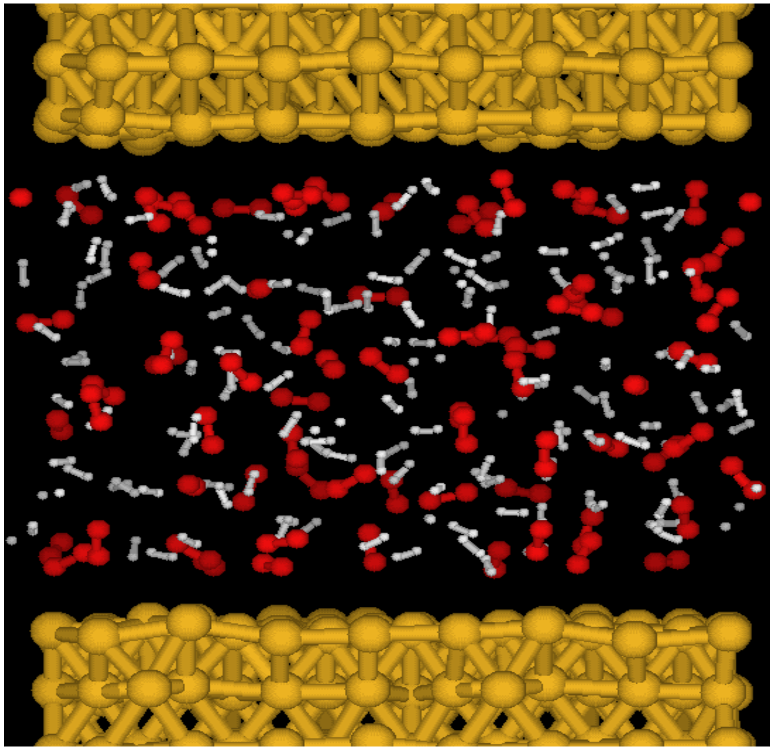
Simulation geometry





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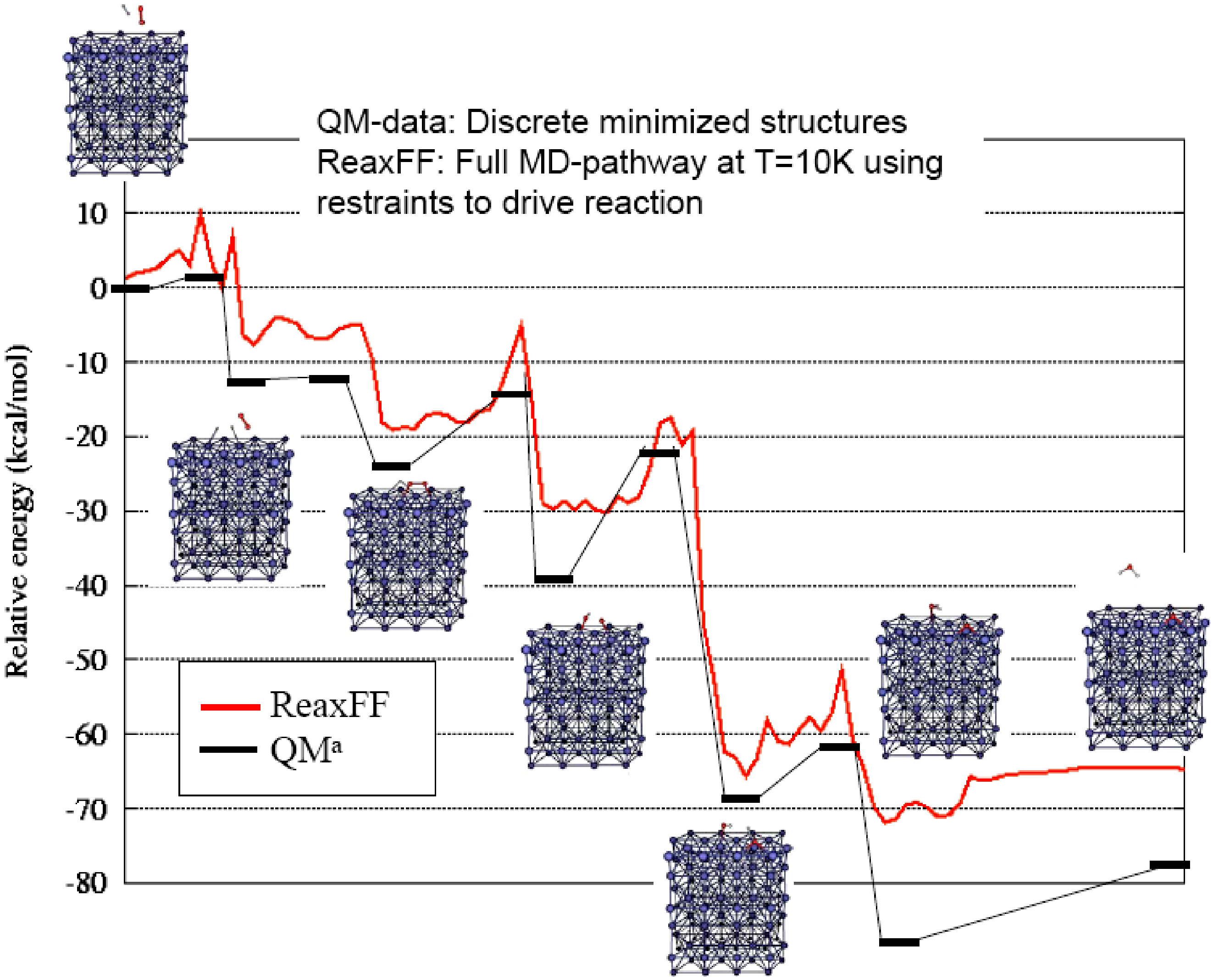
QM data: Training set (subset)



a:T. Jacob and W.A. Goddard (2004)

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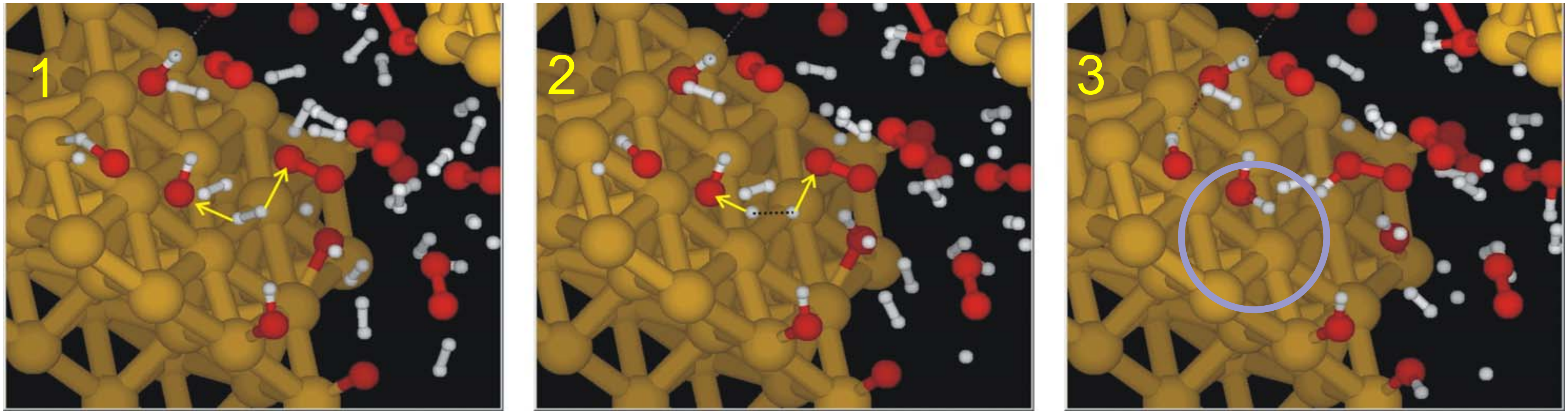
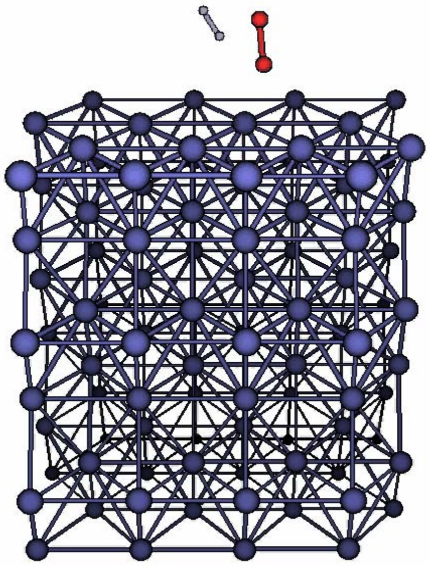
Formation mechanism



- •O2 close to Pt surface
- •Chemisorption of O2 (Pt-O-O)
- •Dissociation Pt-O´and formation of Pt-O-H (stable)
- •Formation of Pt-O-H2 as another H2 approaches → leads to water and H-O-O molecule

- •A lot of water leads to numerous hydrogen bonds



H2O forms at the Pt (111) surface

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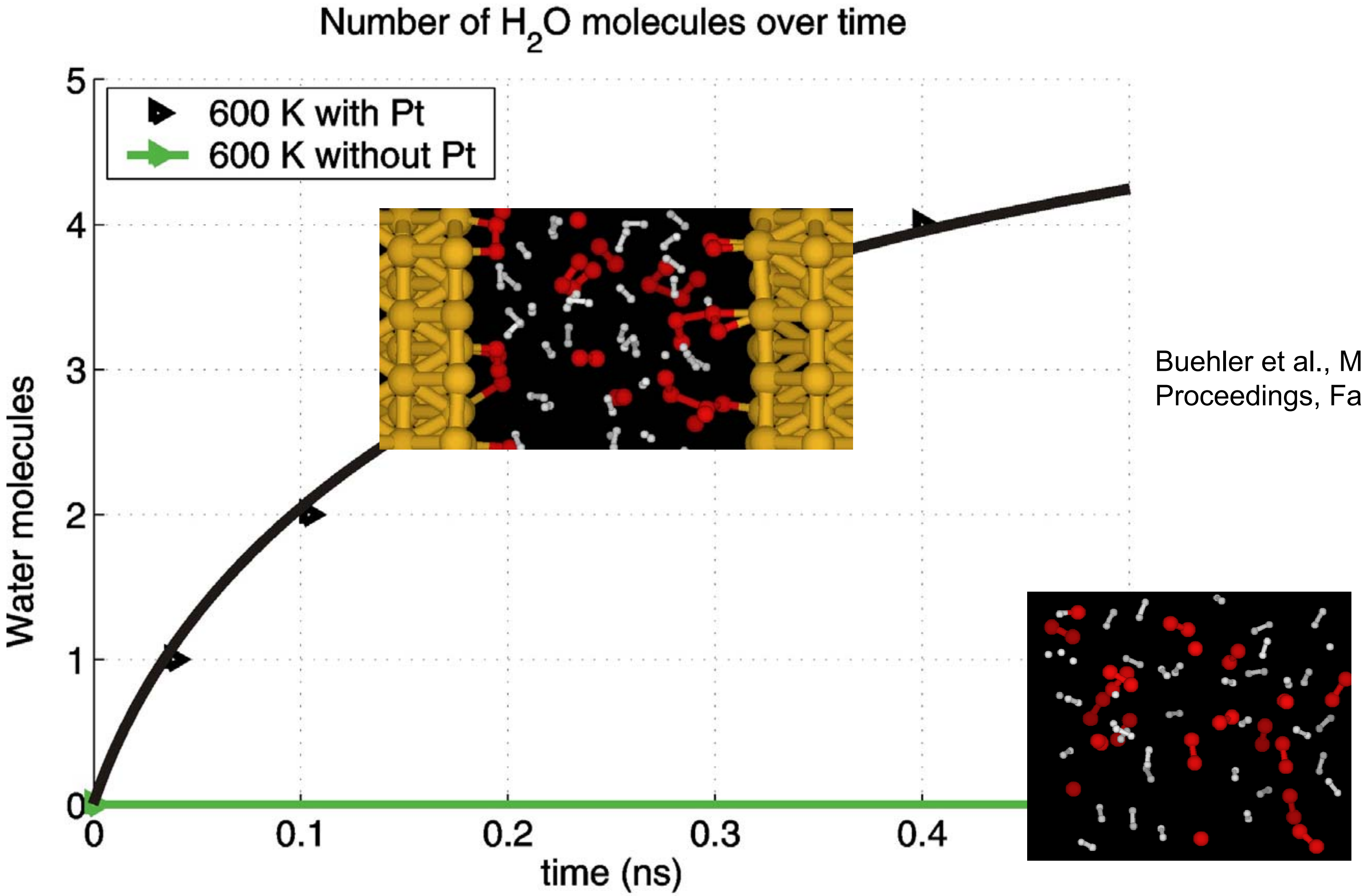
Effect of Pt catalyst



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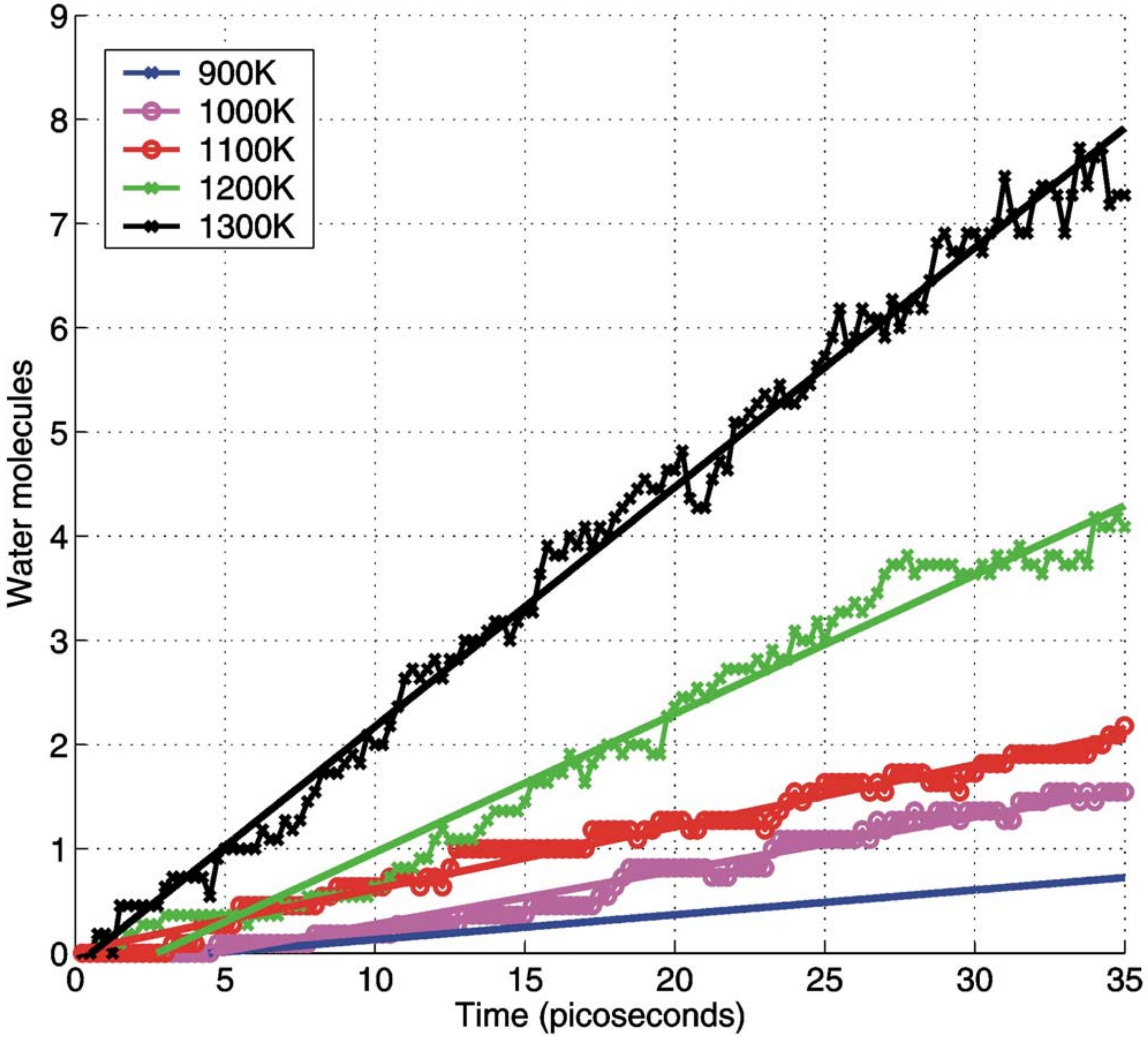
MD simulation clearly proves the effect of the catalyst in greatly enhancing the reaction rate

It also leads to **more controlled reaction conditions**

Reaction rate versus temperature



- Observe formation of water molecules at a time scale of several picoseconds
- The higher the temperature, the higher the production rate of water molecules
- The rates depend on concentration: The higher the concentration, the higher the rates.
- Need to be in the right MD window (time scale)

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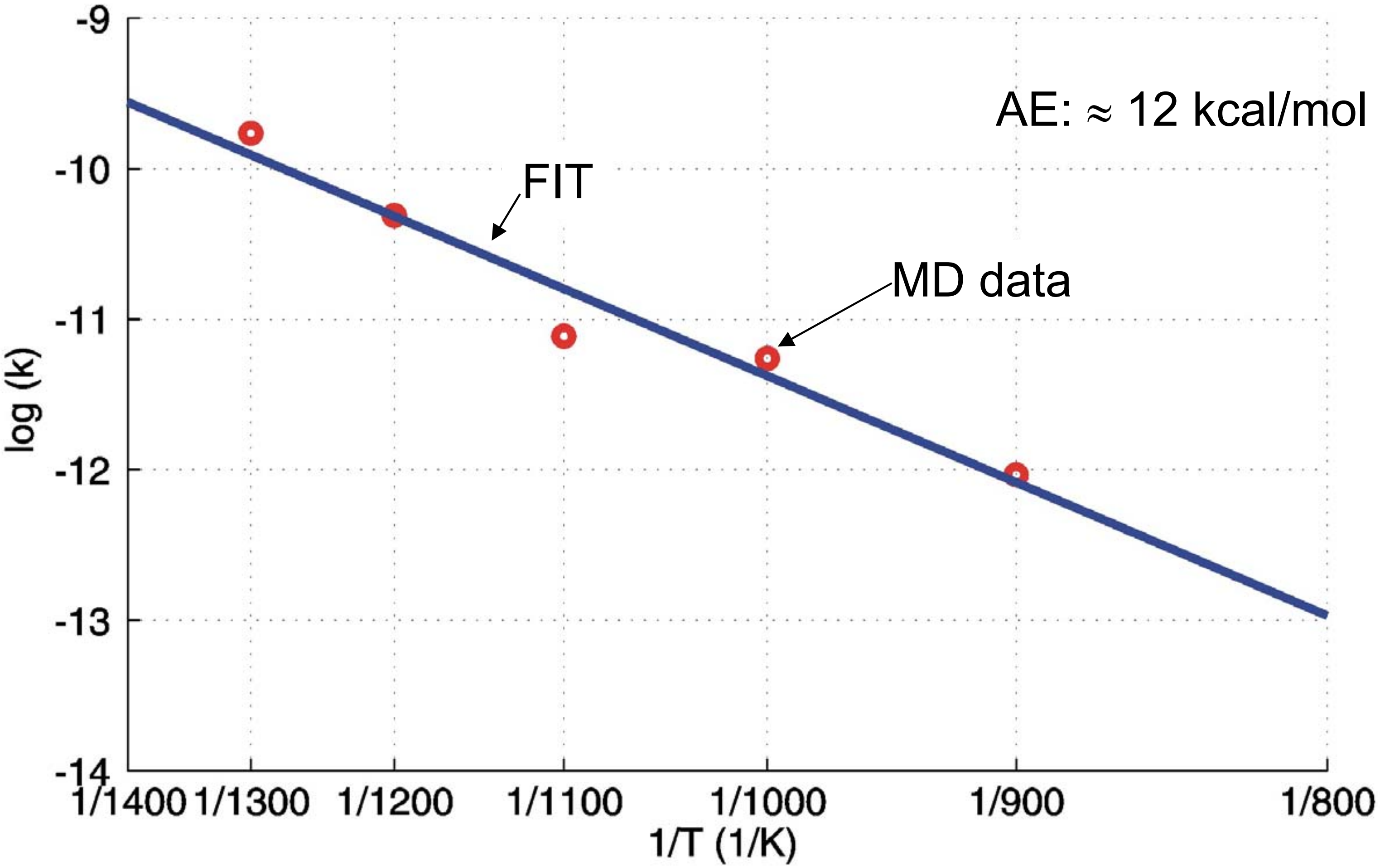
Arrhenius plot for AE



- Simulations at different temperatures and measurement of rates allows to plot the data in an Arrhenius plot (log of reaction rate)

- Fit linear curve to the data to obtain prefactors and activation barrier

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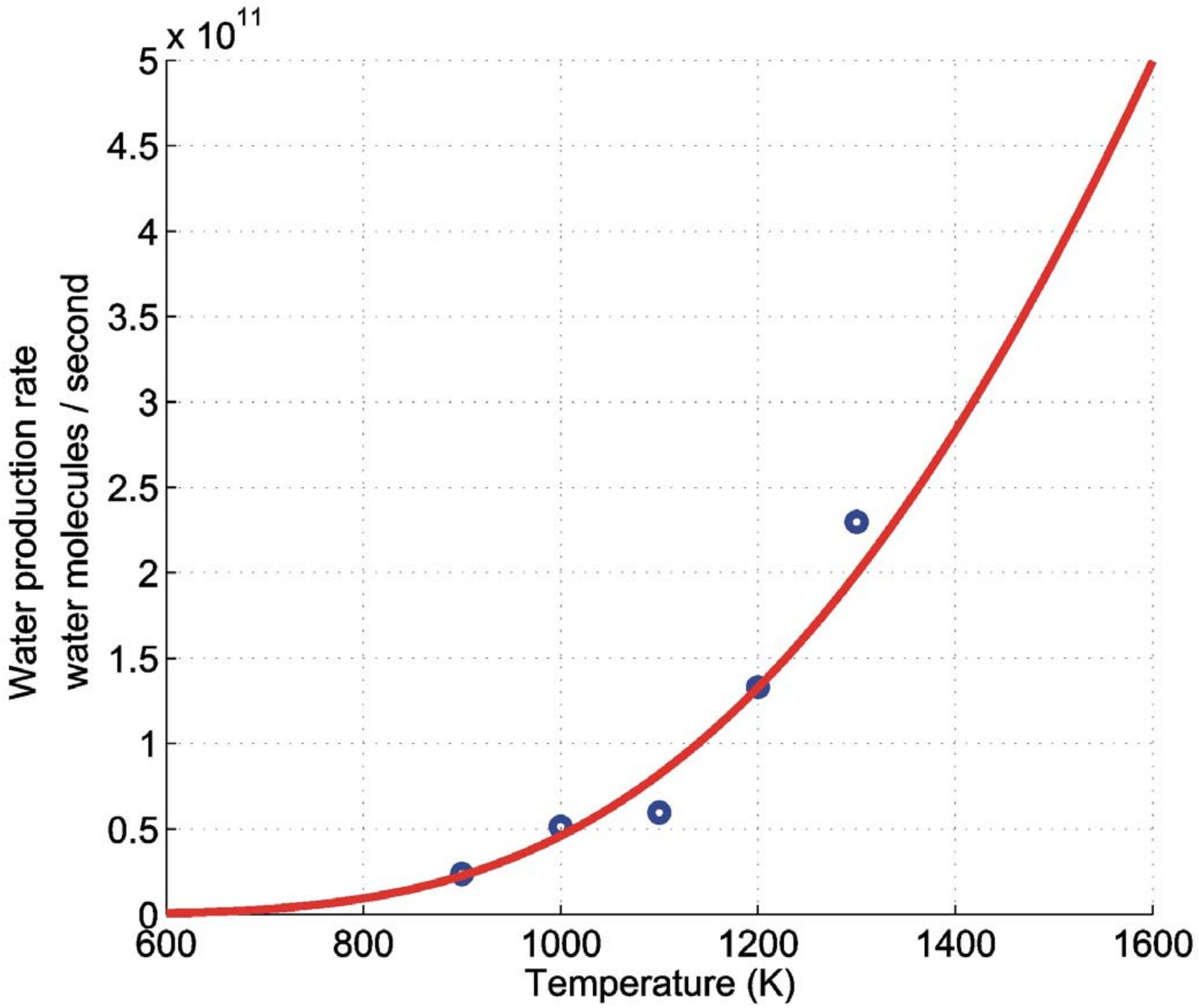
Reaction constants versus temperature



- Compare fitted result and MD simulation data

- Allows to extract to experimental results (work in progress)

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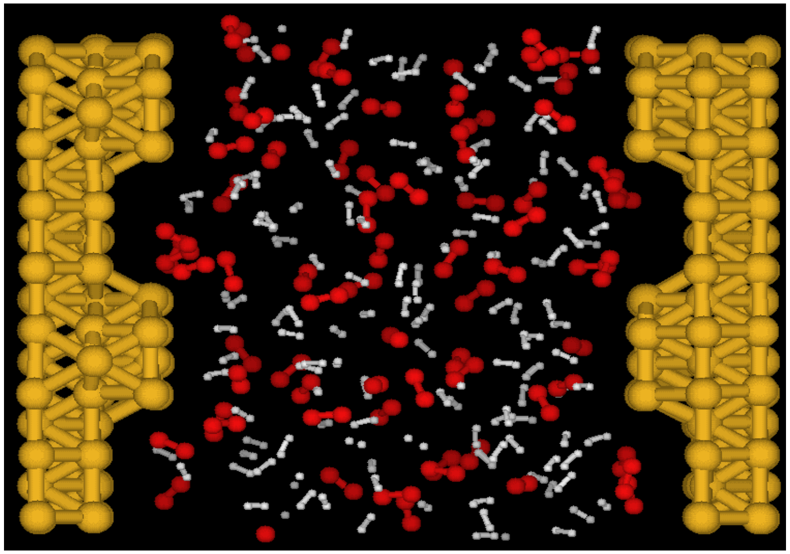
Outlook



“Engineer a new nano-surface”

- Study change in dynamics at defects (e.g. due to surface steps)
- Influence of strain in Pt on water production rate

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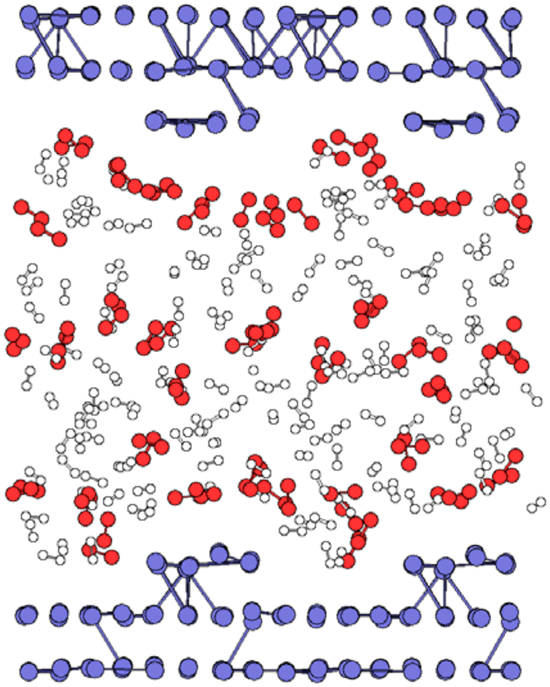
Summary and Outlook

- Observe that water formation rates are dependent on temperature
- Could link atomistic simulation to "continuum description" and extract barriers and prefactors
- Reaction barriers from dynamical runs in good agreement with the prediction by restraint MD simulation with ReaxFF ("close the loop")
- Have shown clear catalyst effect (first time by pure MD simulation of this process)



Main result: ReaxFF can be successfully applied to model chemical solid-gas-phase reactions and can reproduce predictions by quantum mechanics and experimental results.

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Conclusion and wrap-up

- The combination of large-scale computing and new multi-scale simulation paradigms is a promising approach to solve critical questions in the field of chemically complex materials
- Combination of ReaxFF and empirical force fields enables coupling of mechanical properties and chemistry
- Progress in this field has potentially high impact in the materials and modeling community
- Activities to address complex materials with rigorous computational (first principles based) methods are important to evolve engineering principles towards a new generation of tools, beyond FEM/continuum methods
- Particle-based methods can also include principles of living systems at a meso-scale (e.g. involving concepts of cellular automata to model cell growth and related matters)

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Some additional references

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The DREDING force field:
[6] Mayo, S. L.; Olafson, B. D.; Goddard III, W. A. J. Phys. Chem., 1990, 94, 8897

Lecture topics: Outline

Fall 2005

- Oct. 27, 1 PM, Room 1-134: Introduction to atomistic modeling techniques: Do we need atoms to describe how materials behave?
- Nov. 3, 1 PM, Room 1-134: Methods and techniques for modeling metals and their alloys and application to the mechanics of thin metal films
- Nov. 17, 1 PM, Room 1-134: Concurrent scale coupling techniques: From nano to macro
- Dec. 5, 1 PM, Room 1-150: Reactive versus nonreactive potentials: Towards unifying chemistry and mechanics in organic and inorganic systems

IAP 2006: From nano to macro: Introduction to atomistic modeling techniques and application in a case study of modeling fracture of copper (1.978 PDF)

- Jan. 9 (Monday): Introduction to classical molecular dynamics: Brittle versus ductile materials behavior
- Jan. 11 (Wednesday): Deformation of ductile materials like metals using billion-atom simulations with massively parallelized computing techniques
- Jan. 13 (Friday): Dynamic fracture of brittle materials: How nonlinear elasticity and geometric confinement governs crack dynamics
- Jan. 16 (Monday): Size effects in deformation of materials: Smaller is stronger
- Jan. 18 (Wednesday): Introduction to the problem set: Atomistic modeling of fracture of copper
- The IAP activity can be taken for credit. Both undergraduate and graduate level students are welcome to participate. Details will be posted on the IAP website (http://web.mit.edu/iap/).

Spring 2006

- TBD. Atomistic modeling of biological and natural materials: Mechanics of protein crystals and collagen
- TBD. Mechanical properties of carbon nanotubes: Scale effects and self-folding mechanisms
- TBD. Atomistic and multi-scale modeling in civil and environmental engineering: Current status and future development

http://web.mit.edu/mbuehler/www/Teaching/LS/

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