



3.22 Mechanical properties of materials

Reactive Potentials: Chemistry and MD

Lecture 4/4



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Outline: 4 Lectures on Molecular Dynamics (=MD)



- Lecture 1: Basic Classical Molecular Dynamics
General concepts, difference to MC methods, challenges, potential and implementation
- Lecture 2: Introduction to Interatomic Potentials
Discuss empirical atomic interaction laws, often derived from quantum mechanics or experiment
- Lecture 3: Modeling of Metals
Application of MD to describe deformation of metals, concepts: dislocations, fracture
- Lecture 4: Reactive Potentials
New frontier in research: Modeling chemistry with molecular dynamics using reactive potentials

Summary of important concepts



- Reviewed some analysis techniques and basic MD concepts
- Modeling vs. Simulation for Molecular Dynamics
- Metallic bonding: Basics and motivation for multi-body interactions
- Models for metallic bonding – EAM (=embedded atom method)
(electron gas etc.)
- Plasticity and Concept of dislocation nucleation and motion; at a crack tip: Dislocations are responsible to carry plasticity

MD updating scheme: Complete



(1) Updating method (integration scheme)

$$r_i(t_0 + \Delta t) = \underbrace{-r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{2r_i(t_0)\Delta t}_{\text{Positions at } t_0} + \underbrace{a_i(t_0)(\Delta t)^2}_{\text{Accelerations at } t_0} + \dots$$

Positions
at $t_0 - \Delta t$

Positions
at t_0

Accelerations
at t_0

(2) Obtain accelerations from forces “Verlet central difference method”

$$f_i = ma_i \quad a_i = F_i / m$$

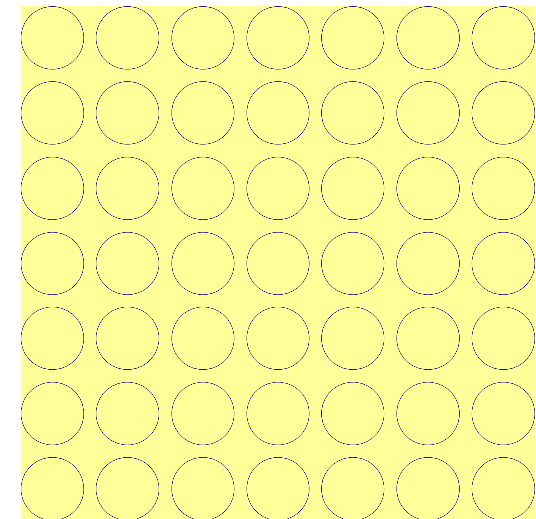
(5) Crystal (initial conditions)
Positions at t_0

(3) Obtain forces from potential

$$F = -\frac{dV(r)}{dr} \quad F_i = F \frac{x_i}{r}$$

(4) Potential

$$\phi_{weak}(r) = 4\varepsilon \left(\left[\frac{\sigma}{r} \right]^{12} - \left[\frac{\sigma}{r} \right]^6 \right)$$



Deformation of crystals



- Deformation of a crystal is similar to pushing a sticky tape across a surface:

$$F \sim \tau \cdot L$$

“homogeneous shear”



$$F \approx F_{\text{ripple}}$$

“localized slip (ripple)”



$$L_{\text{crit}} \approx \frac{F_{\text{ripple}}}{\tau}$$

Beyond critical length L it is easier to have a localized ripple...

Theoretical shear strength



- Perfect crystal: Deformation needs to be cooperative movement of all atoms; the critical shear stress for this mechanism was calculated by Frenkel (1926):

$$\tau_{th} = \frac{b}{a} \frac{G}{2\pi} \approx \frac{G}{30}$$

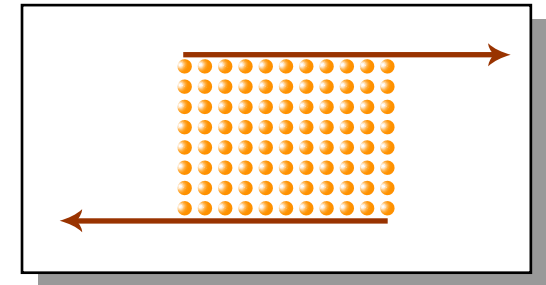


Figure by MIT OCW.

- Although this is an approximation, the shear strength measured in experiment is much lower:

$$\tau_{exp} = \frac{G}{10,000 \dots 100,000,000}$$

- Difference explained by existence of dislocations by Orowan, Polanyi and Taylor in 1934
- Confirmed by experiments with whiskers (dislocation free crystals)

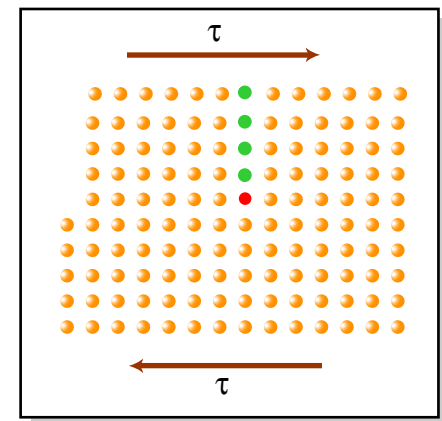
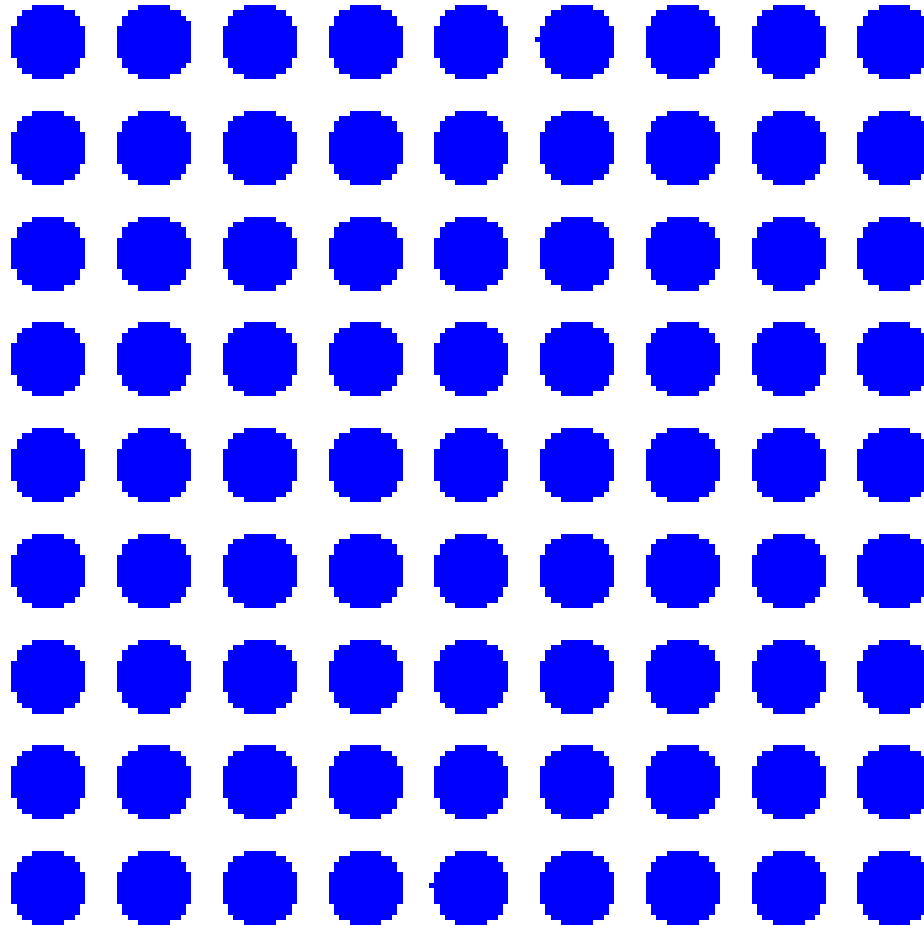


Figure by MIT OCW.

Animation: Dislocation motion



Courtesy of Dr. Helmut Foell. Used with permission.

Animation online:

http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_5/illustr/a5_1_1.html

Geometry of a dislocation (3D view)



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See: Fig. 2 at <http://www.kuleuven.ac.be/bwk/materials/Teaching/master/wg02/I0310.htm>

Slip direction and plane in FCC

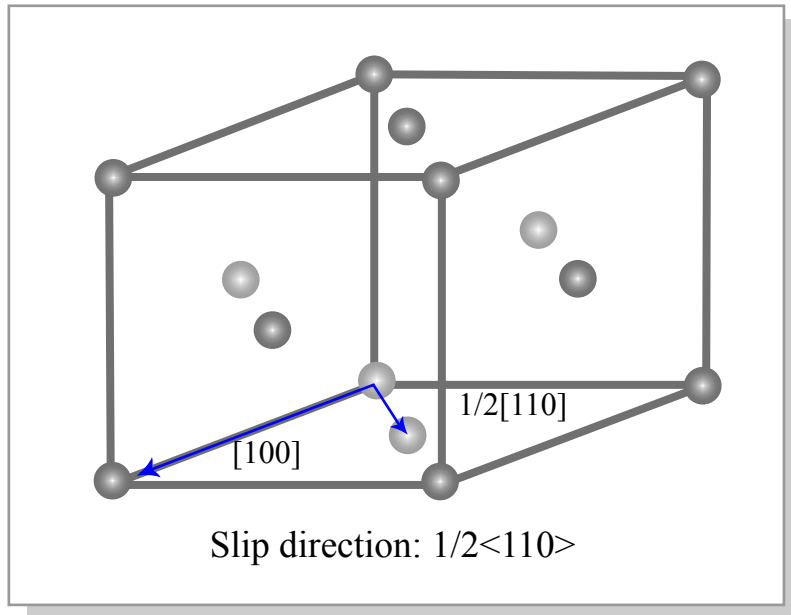


Figure by MIT OCW.

For specific crystals, there are certain directions of Burgers vectors and slip planes that are energetically favored

FCC:

Slip directions are $\frac{1}{2}\langle 110 \rangle$

Glide planes are $\{111\}$

The slip planes and directions are those of highest packing density

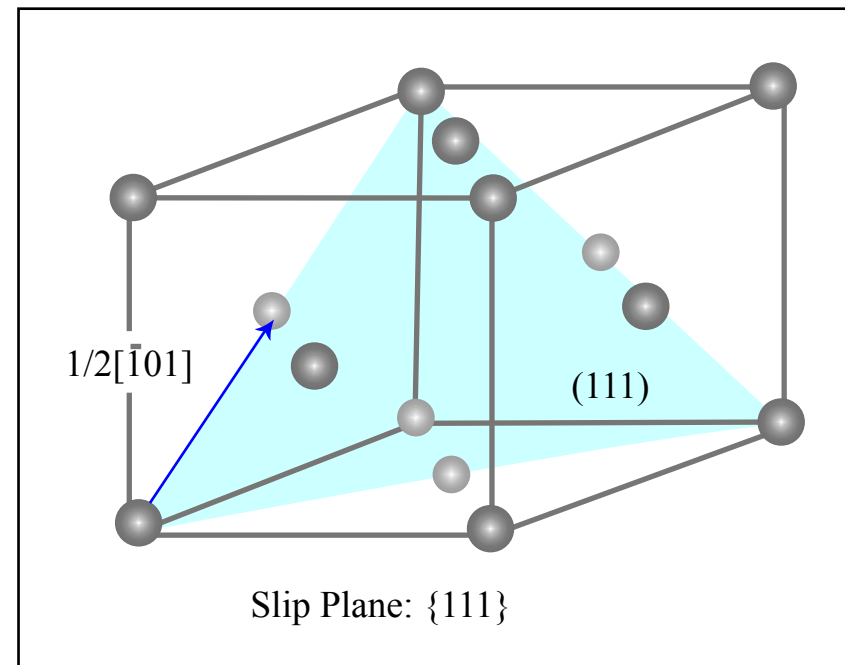


Figure by MIT OCW.

Other crystallographic defects



- Point defects: Vacancies and interstitials
- Can be produced by plastic deformation

- Vacancy formation energy ca. $E_v \sim 1-3$ eV/atom, scale with melting temperature T_m :

$$E_v \sim 8kT_m$$

- Impurity either substitutional (other atom species on lattice site) or interstitial (non-lattice site)

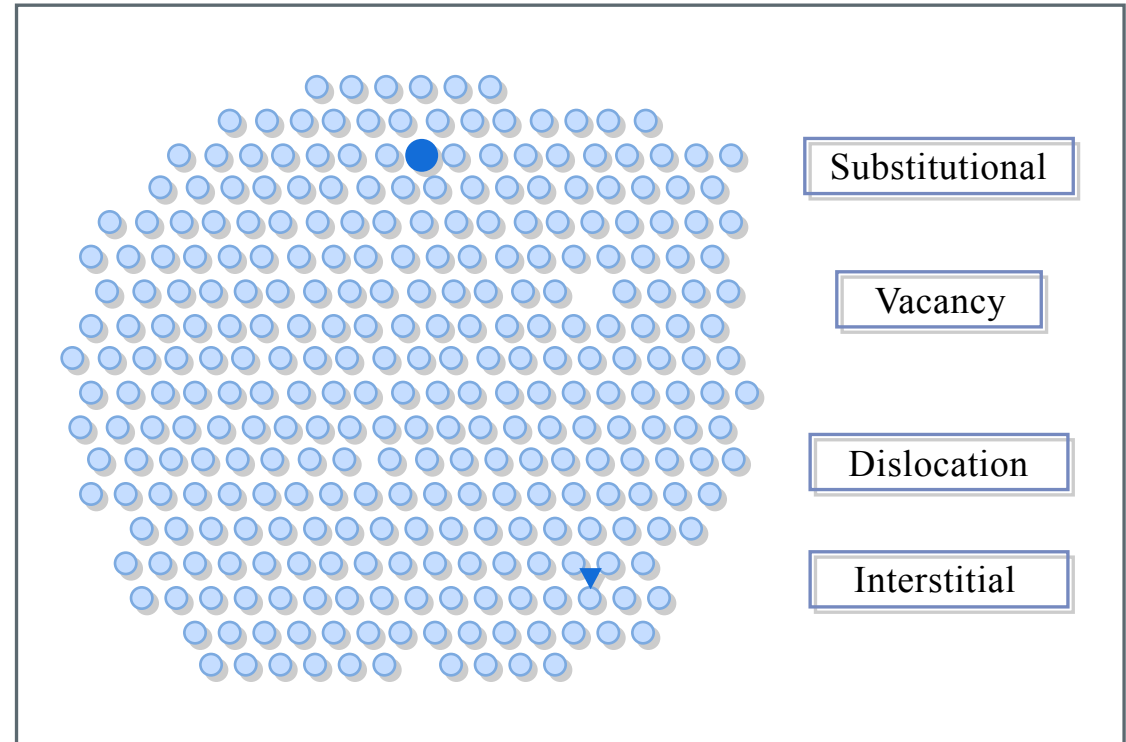
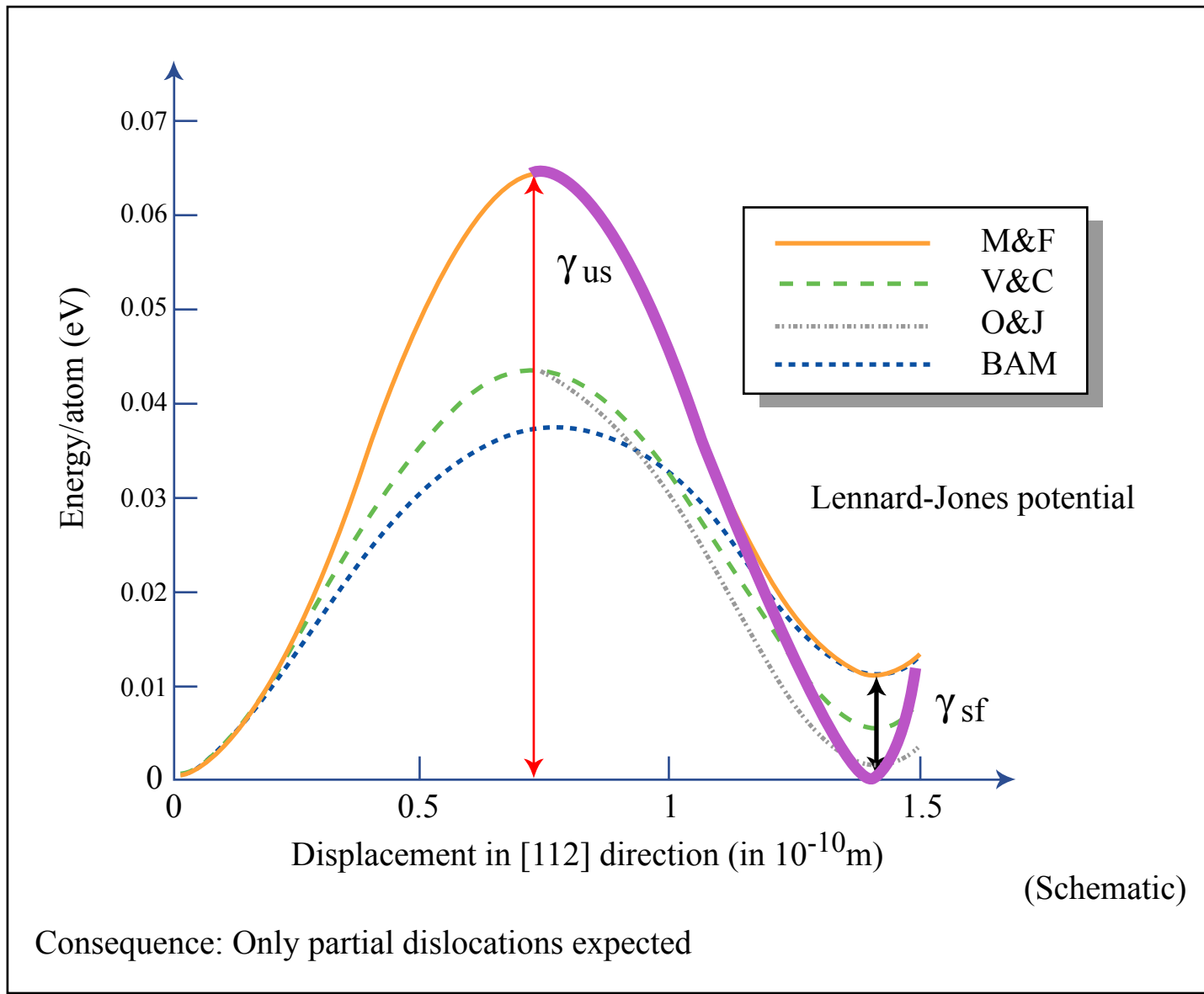


Figure by MIT OCW.

Stacking fault energy: LJ potential vs. EAM potential



Ductile versus brittle materials

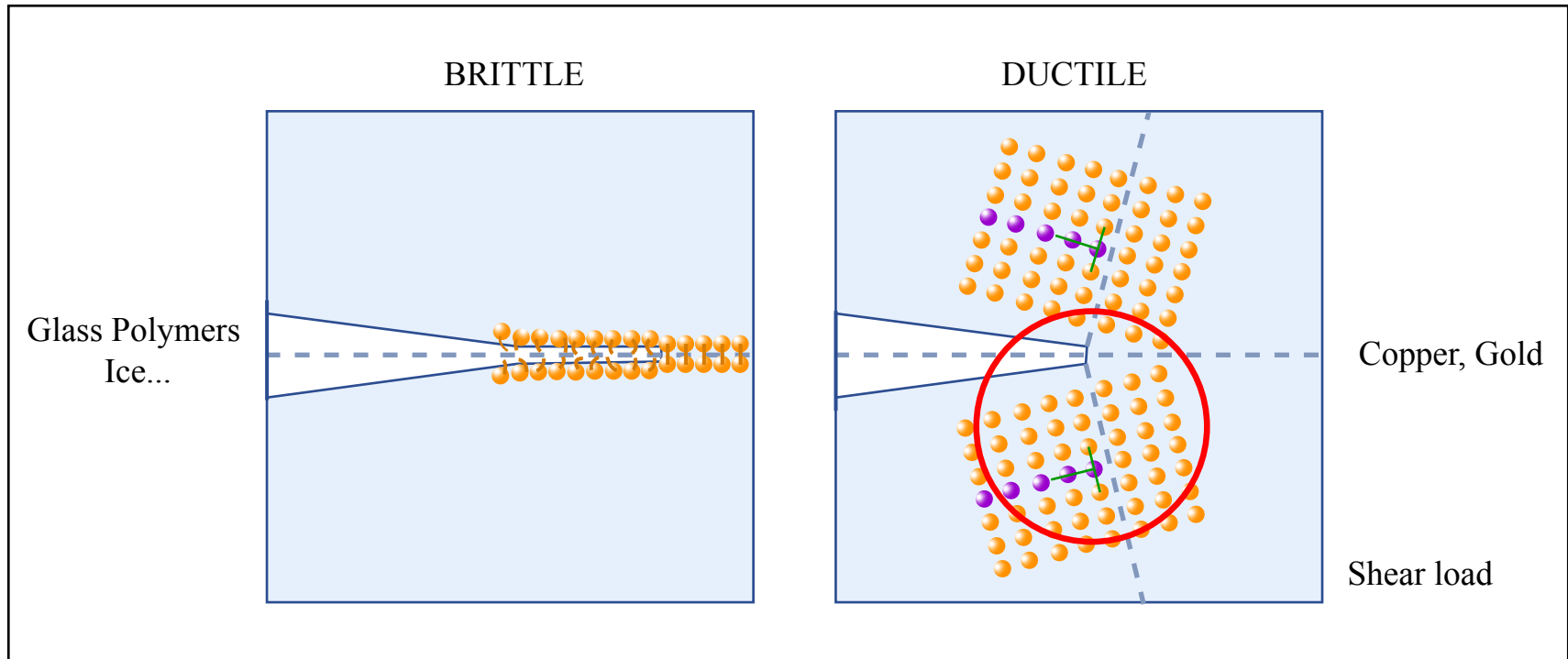
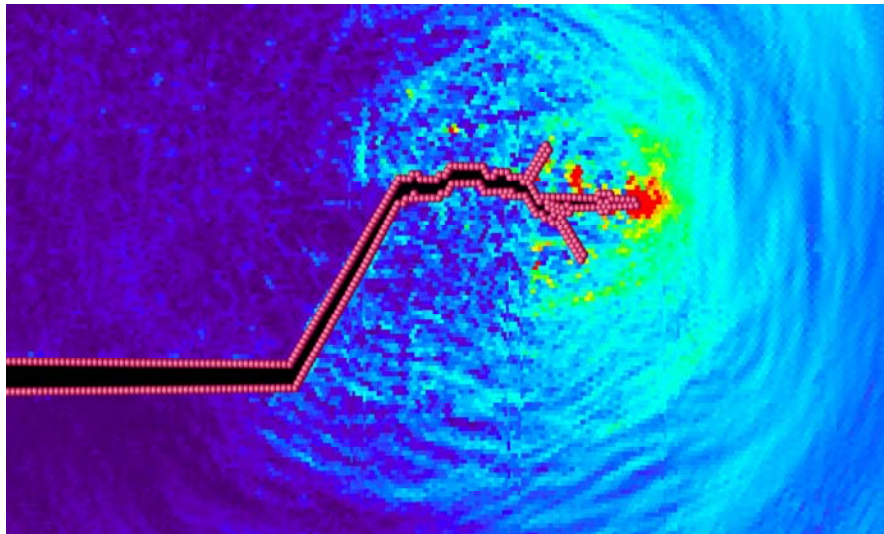
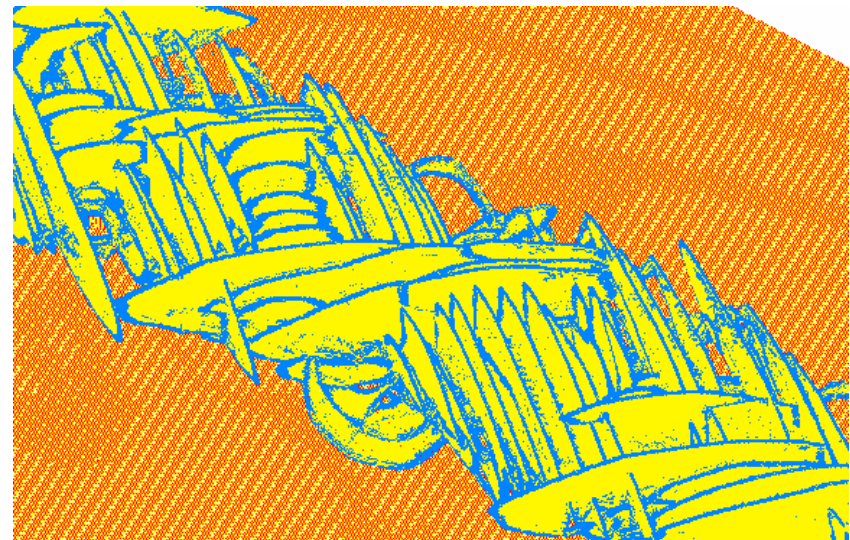


Figure by MIT OCW.



(a)



(b)

Atomistic details of dislocation nucleation



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Source: Figure 16 in Buehler, Markus J., Balk, John, Arzt, Eduard, and Gao, Huajian. "Constrained Grain Boundary Diffusion in Thin Copper Films." Chapter 13 in *Handbook of Theoretical and Computational Nanotechnology*. Edited by Michael Rieth and Wolfram Schommers. Stevenson Ranch, CA: American Scientific Publishers, 2006.

- Dislocation nucleation from a traction-free grain boundary in an ultra thin copper film
- Atomistic results depict mechanism of nucleation of partial dislocation

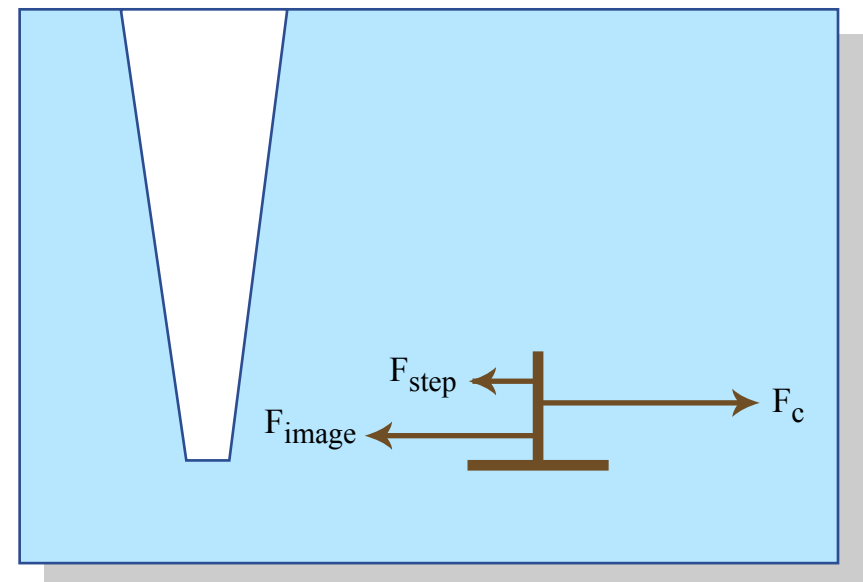


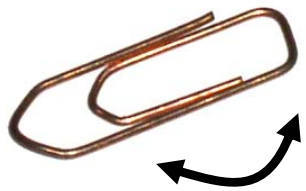
Figure by MIT OCW.

Analysis of a large-scale simulation of work-hardening



- Can computer simulation be used to study work-hardening (“feasibility study”)?
- How can the results of ultra-large scale atomistic computer simulation be analyzed (1,000,000,000 atoms!) – reach cube w/ μm side length
- What are the fundamental, atomistic mechanisms of work-hardening in ductile materials, and how do these mechanisms compare with the classical picture of work-hardening?

„bending a paper clip until it breaks“



1



2



3



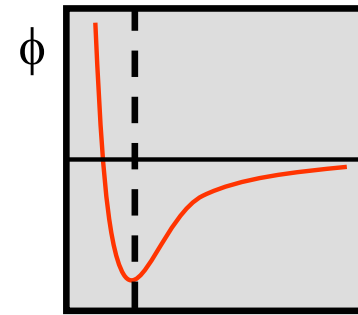
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Analysis of a large-scale simulation of interaction of MANY dislocations



Simulation details

- Approximately 250,000,000 to 1,000,000,000 atoms



Generic features of atomic bonding: „repulsion vs. attraction“

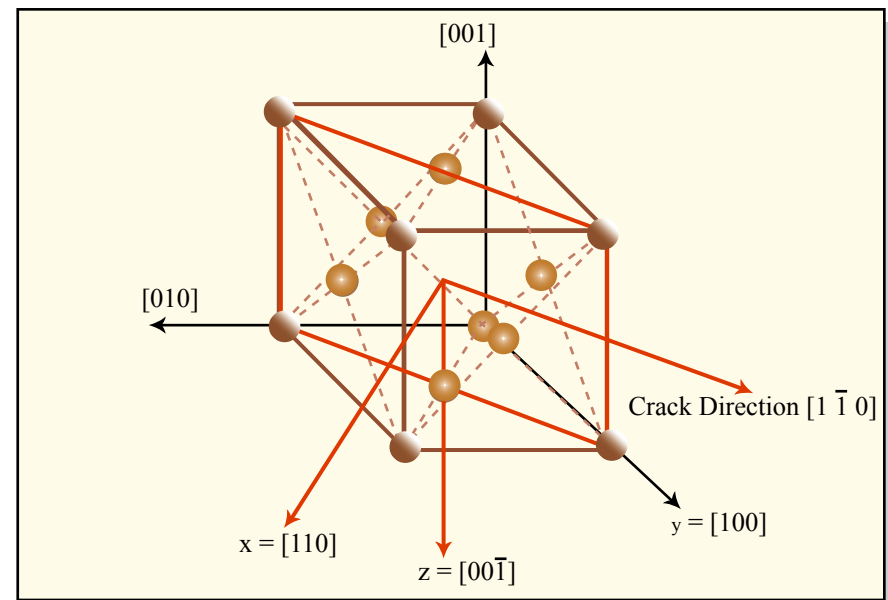
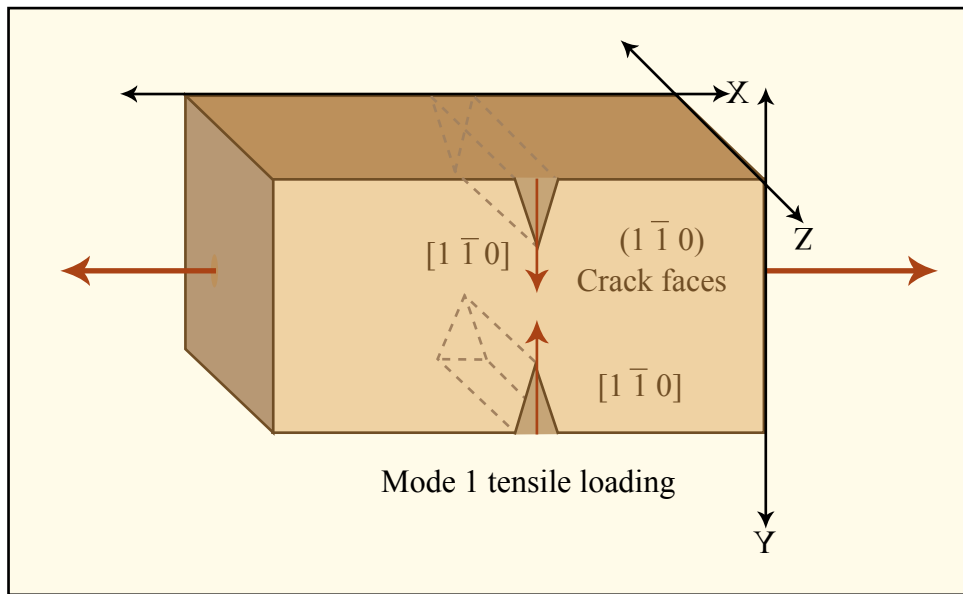


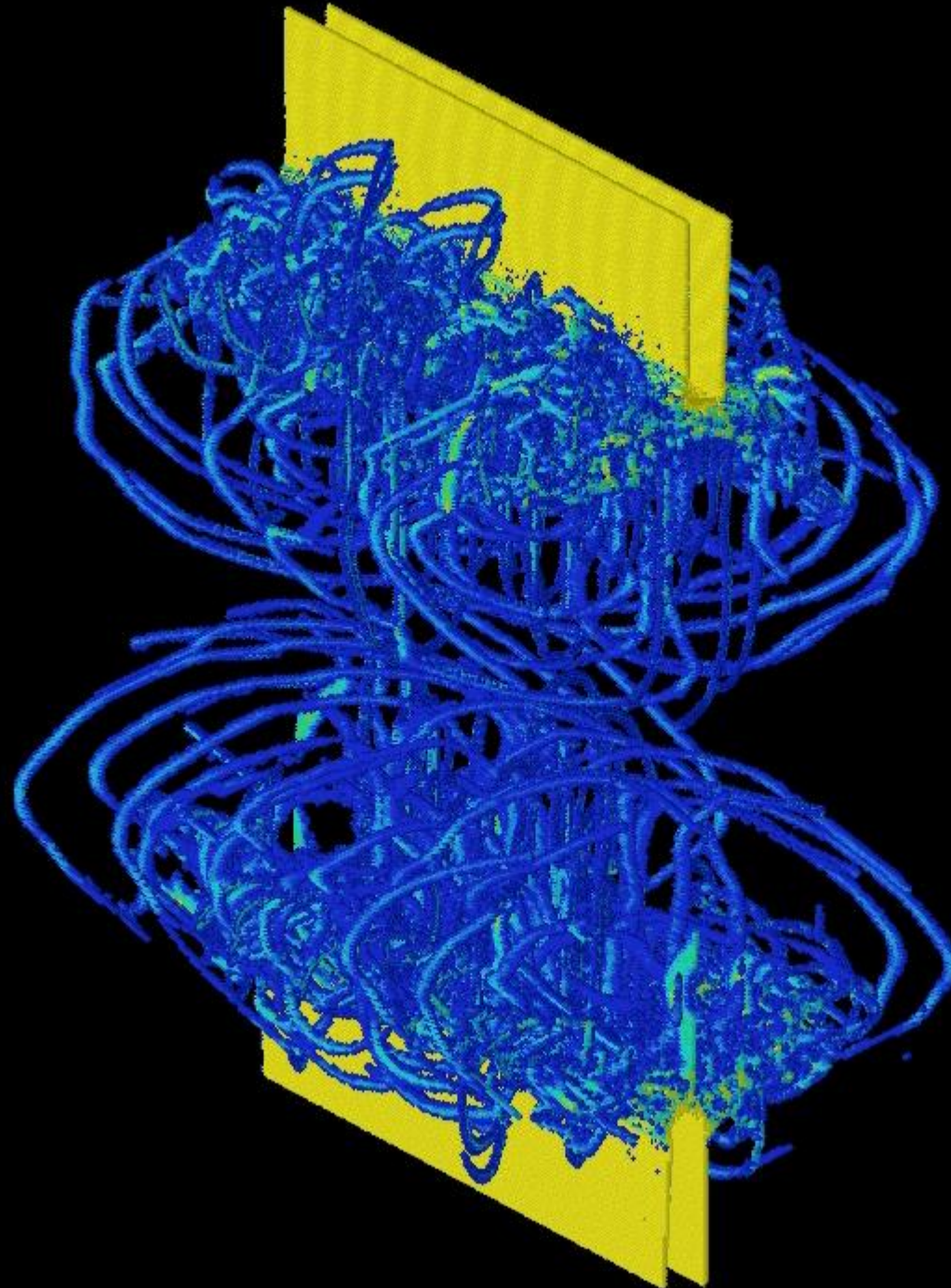
Figure by MIT OCW. After Buehler, et al. 2005.

Figure by MIT OCW. After Buehler, et al. 2005.

The purpose of scientific computing is insight, not numbers.

(Richard Hamming)

Cracking of a copper crystal: Thousands of dislocations

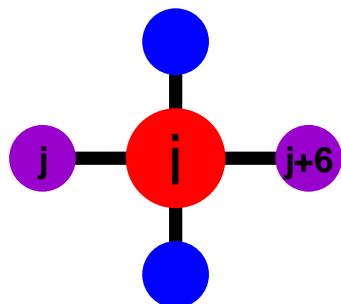


Critical:
Atomic interaction
(potential)

(Buehler, 2006)

- Energy method: Dislocation core has higher energy (e.g. different number of “bonds”)
Difficult to “see” stacking faults
- Centrosymmetry method – geometric method that can distinguish many different defects

$$c_i = \sum_{j=1}^6 \left\{ \left| \sum_{k=1}^3 r_{k,j} + r_{k,j+6} \right|^2 \right\}$$



(Kelchner et al.)

Centrosymmetry Parameter c_i for Various Types of Defects in Copper

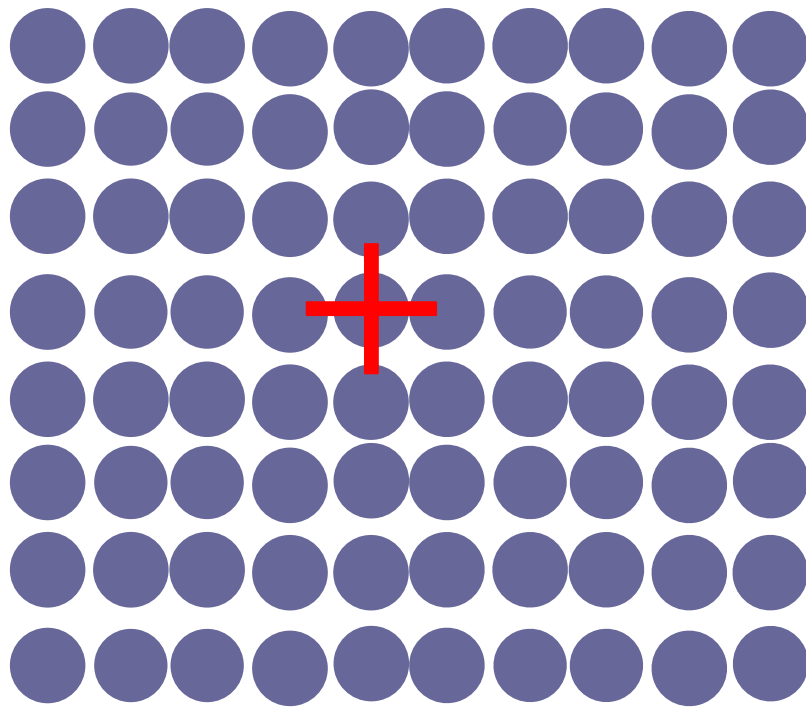
Defect	c_i (in \AA^2)	Range Δc_i (in \AA^2)
Perfect lattice	0.00	$c_i < 0.1$
Partial dislocation	1.86	$0.1 < c_i < 5$
Stacking fault	6.49	$5 < c_i < 18$
Surface atom	22.06	$c_i > 18$

Intervals of c_i were used to separate different defects.

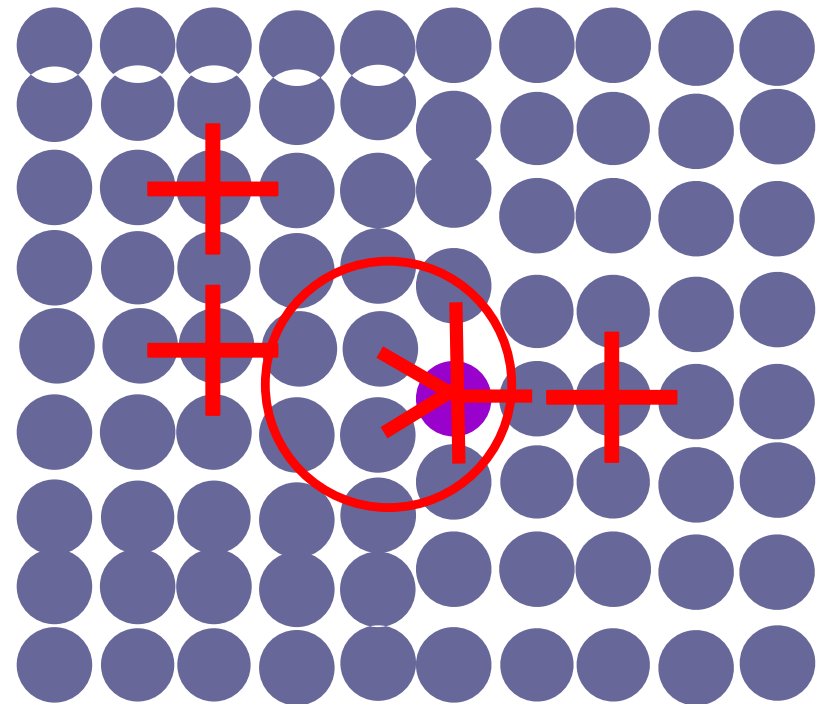
“Visualize” the centrosymmetry method



All centrosymmetric atoms



No dislocation

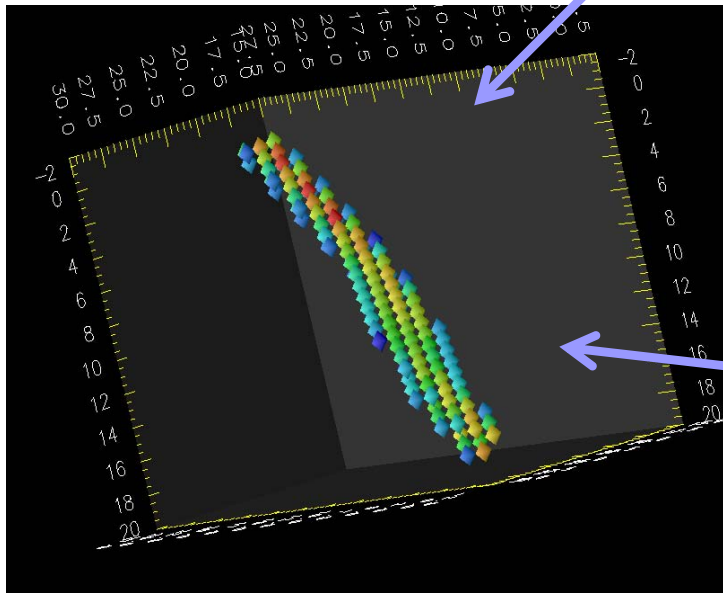
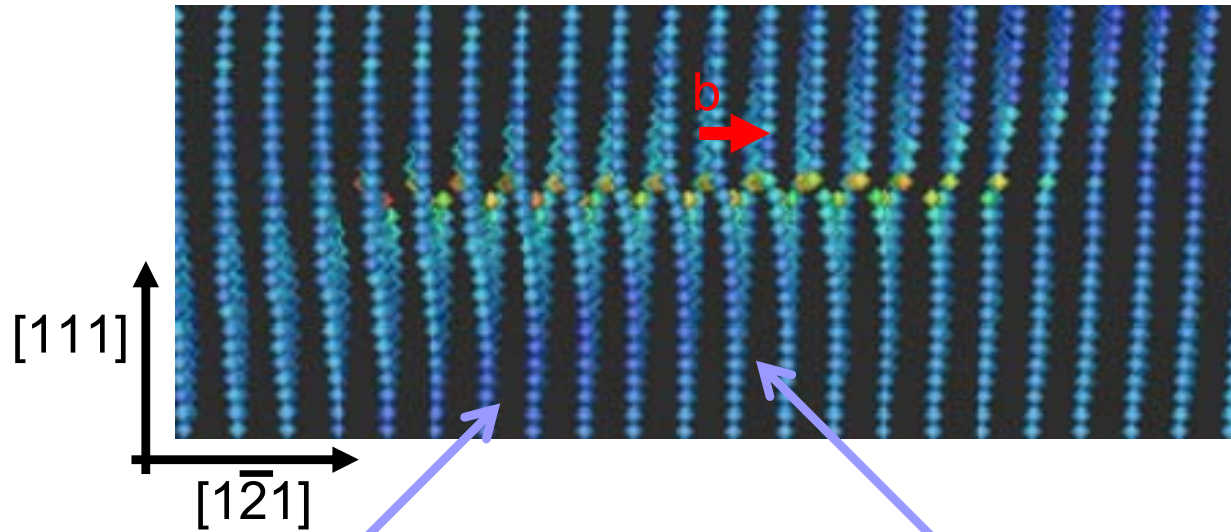


Dislocation

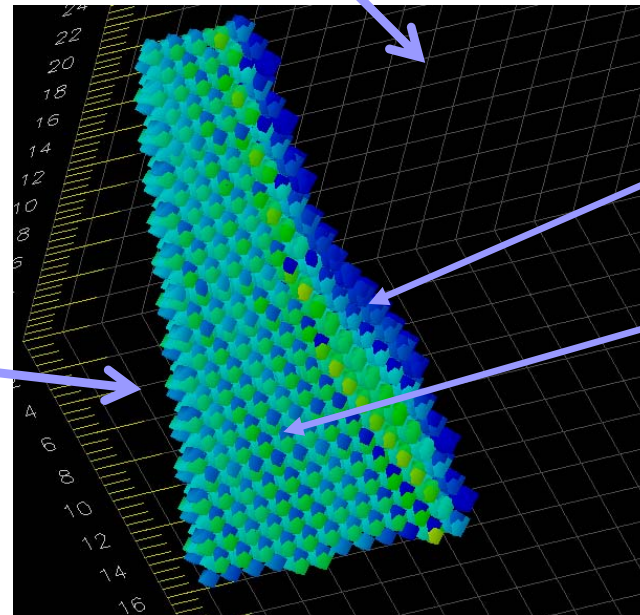
Analysis of glide plane and Burgers vector





Lattice
around
dislocation



Atoms with higher energy
than bulk are highlighted



Centrosymmetry method

-  partial dislocation
-  Stacking fault

Hardening mechanisms creation of sessile structure

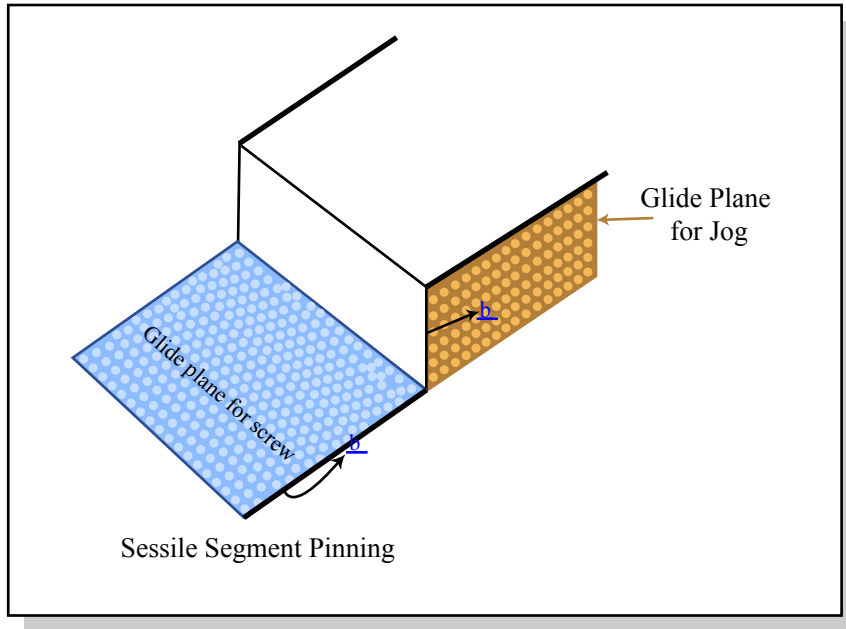


Figure by MIT OCW.

Sessile segment Pinning

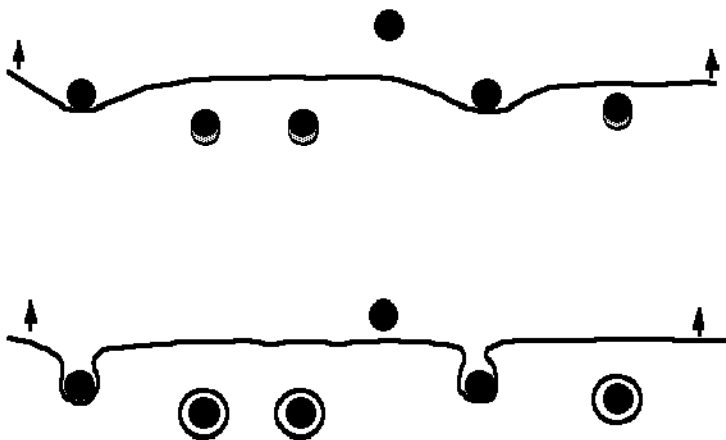


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See Fig. 4 in Buehler, M., et al. "The dynamical complexity of work-hardening: a large-scale molecular dynamics simulation." *Acta Mech Sinica* 21 (2005): 103-111.

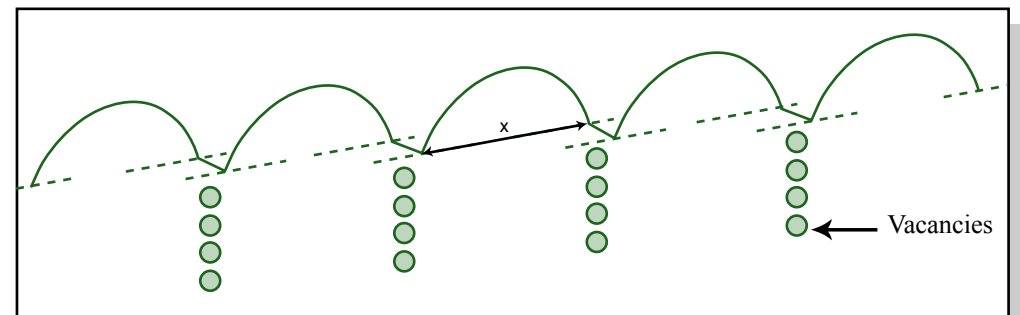


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See:

1. Buehler, M. J., et al. "The dynamical complexity of work-hardening: a large scale molecular dynamics simulation." *Acta Mechanica Sinica* 21, no. 2 (2005): 103-111.
2. Buehler, M. J., et al. "Atomic plasticity: description and analysis of a one-billion atom simulation of ductile materials failure." *Computer Methods In Applied Mechanics And Engineering* 193, no. 48-51 (2004): 5257-5282.

Dislocations in Nickel ([AVI](#))
Movie by Professor Buehler.

Summary of important concepts



- Plasticity and Concept of dislocation nucleation and motion; at a crack tip: Dislocations are responsible to carry plasticity
- Demonstrated and visualized dislocations from MD simulation; discuss “centrosymmetry technique” to visualize the geometrical defects
- Examples of MD modeling of dislocations
- Describe interaction of dislocations – MD can model this phenomenon of mutual interaction that makes it more difficult to deform materials – they break

Increase in computing power Classical molecular dynamics

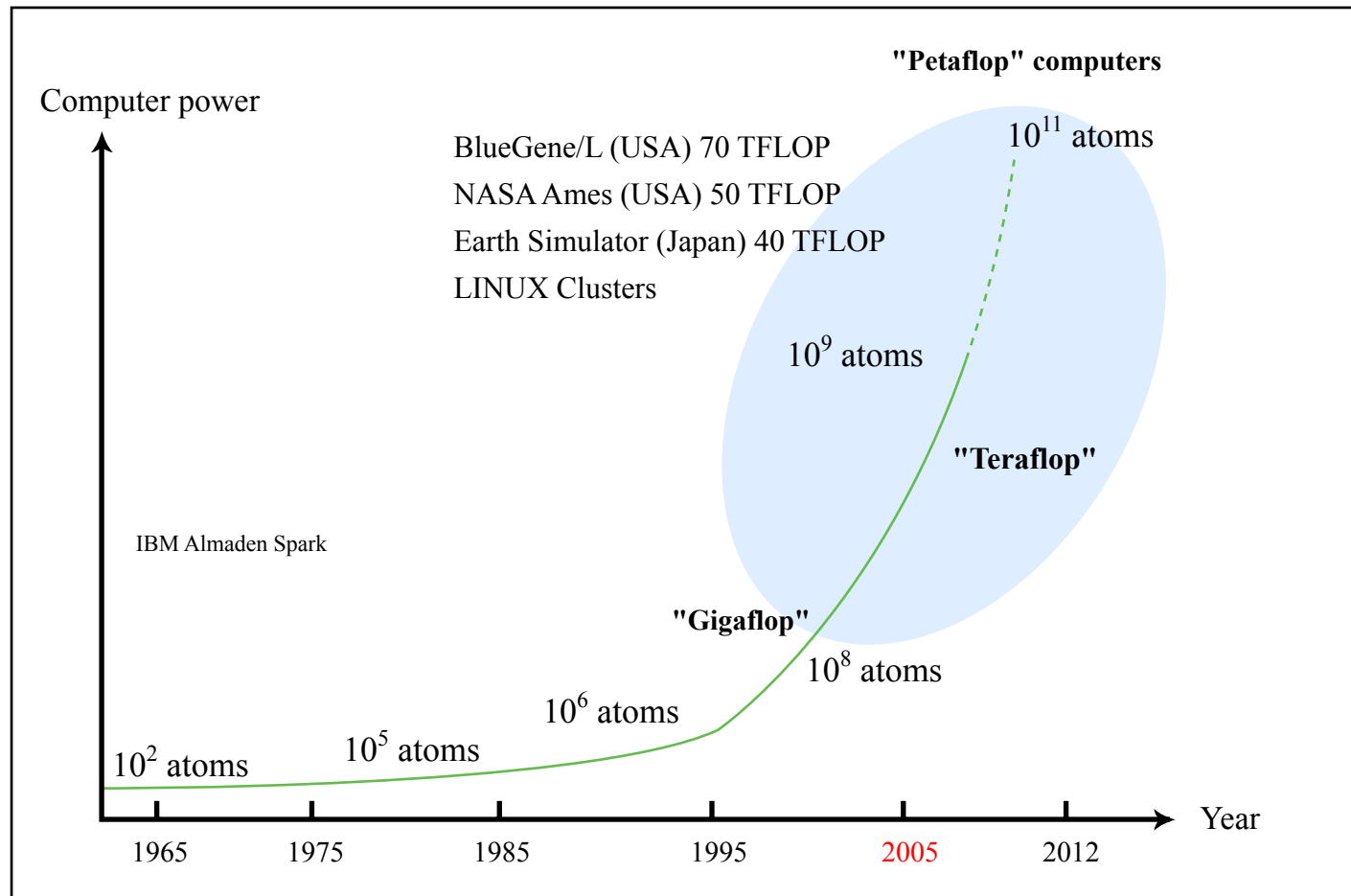


Figure by MIT OCW.

Parallel Molecular Dynamics

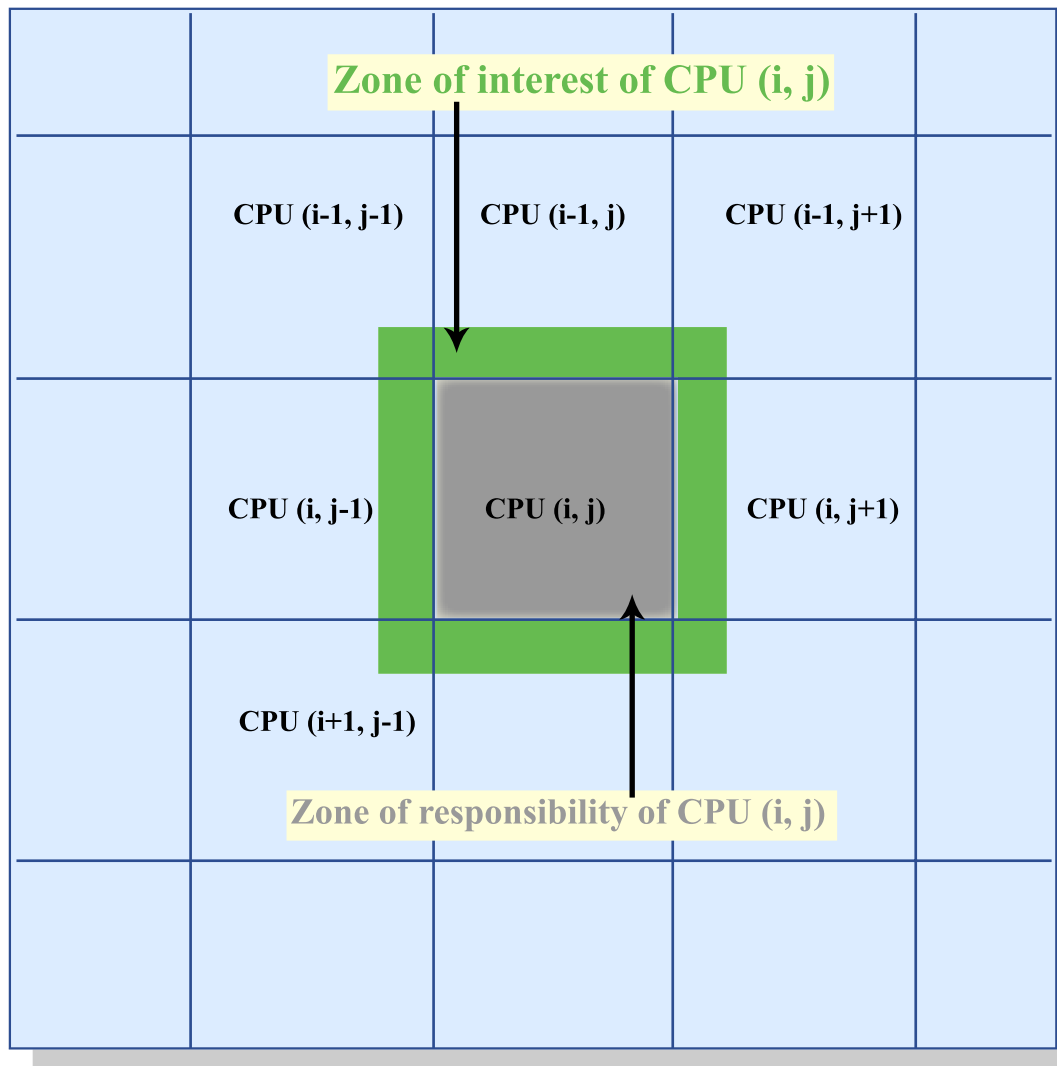


Figure by MIT OCW.

(after Schiotz)

Concept:

Divide the workload

No (immediate) long range interaction (only via dynamics)

- Each CPU is responsible for part of the problem
- Atoms can move into other CPUs (migration)
- Need to know topology or the geometric environment on other CPUs (green region)
- 1,000,000,000 particles on 1,000 CPUs: Only 1,000,000 atoms/CPU

Implementation of parallelization



- Shared memory systems (all CPUs “see” same memory)
 - OpenMP (easy to implement, allows incremental parallelization)
 - POSIX threads
- Distributed memory systems
 - MPI (=Message Passing Interface)
Most widely accepted and used, very portable, but need to parallelize whole code at once
- Parallelization can be very tedious and time-consuming and may distract from solving the actual problem; debugging difficult
- **Challenges:** Load balancing, different platforms, input/output, compilers and libraries, modifications and updates to codes, “think parallel” as manager
- Strategy for your own code: Find similar code and implement your own problem

Review:

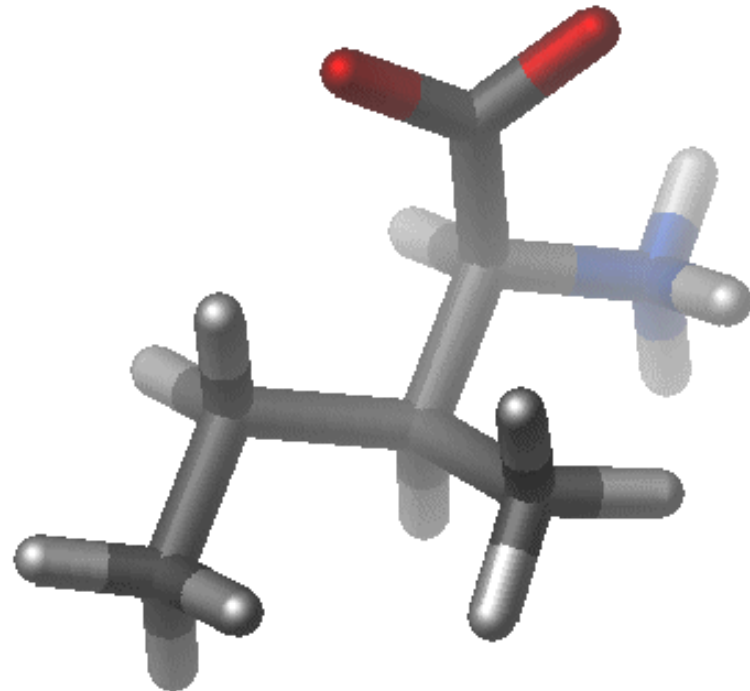
Model for covalent bonds



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

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

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



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Images created for the CHARMM tutorial by Dr. Dmitry Kuznetsov (Swiss Institute of Bioinformatics)

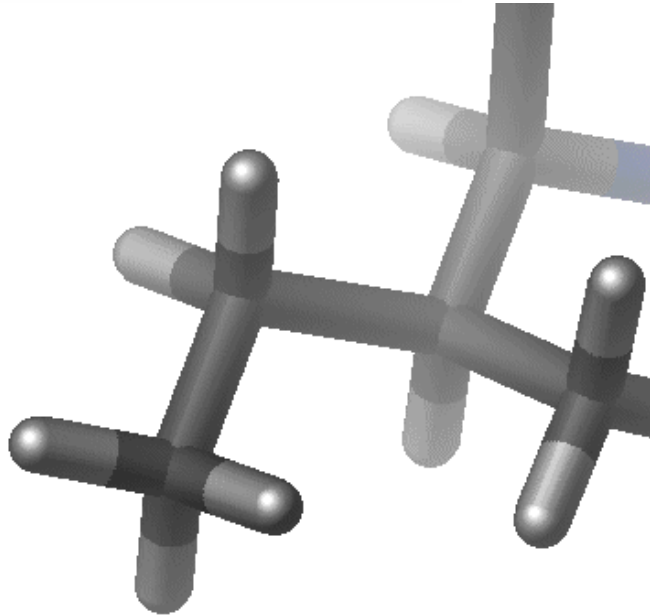
http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html for the EMBnet Education & Training committee (<http://www.embnet.org>) □□

http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm

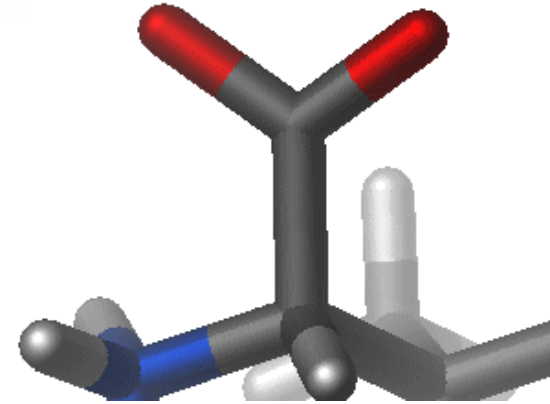
Review: Model for covalent bonds



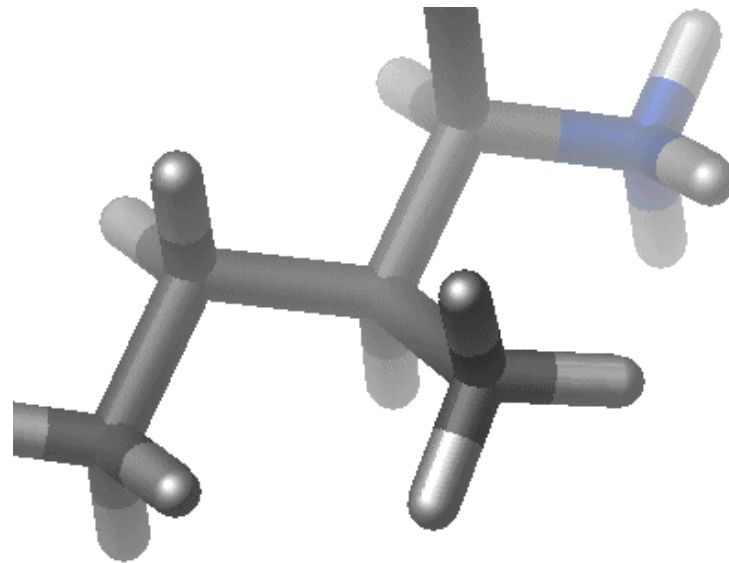
$$E_{\text{bond-stretch}} = \sum K_b (b - b_0)^2$$



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



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

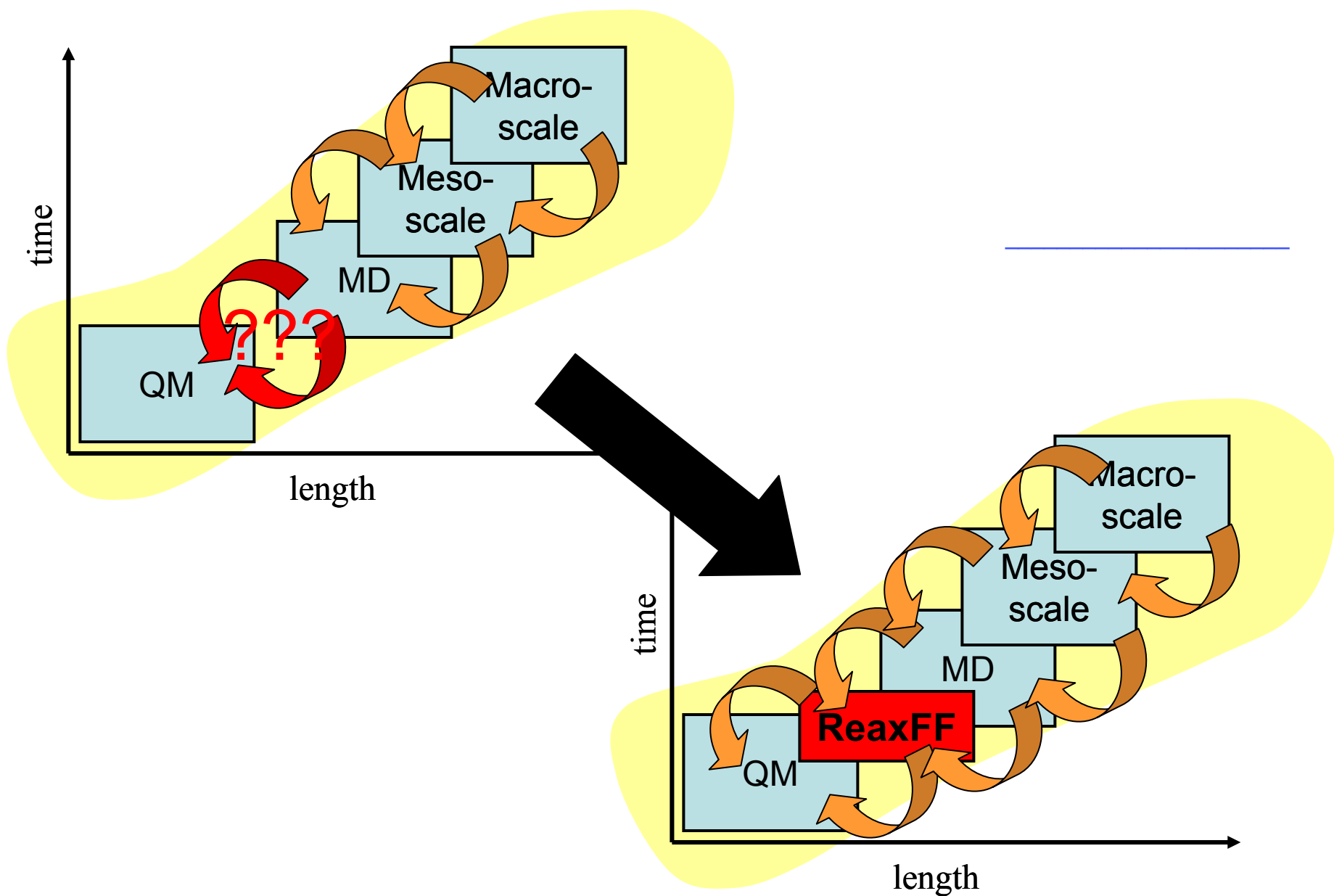


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ReaxFF: A new bridge between QM and MD



Why do we need reactive potentials?

- Materials with high chemical complexity
 - 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
- Materials processing: Energy consumption

In all those systems: Critical to include correct description of relative bond strength, type of bonding.

Historical perspective of reactive potentials

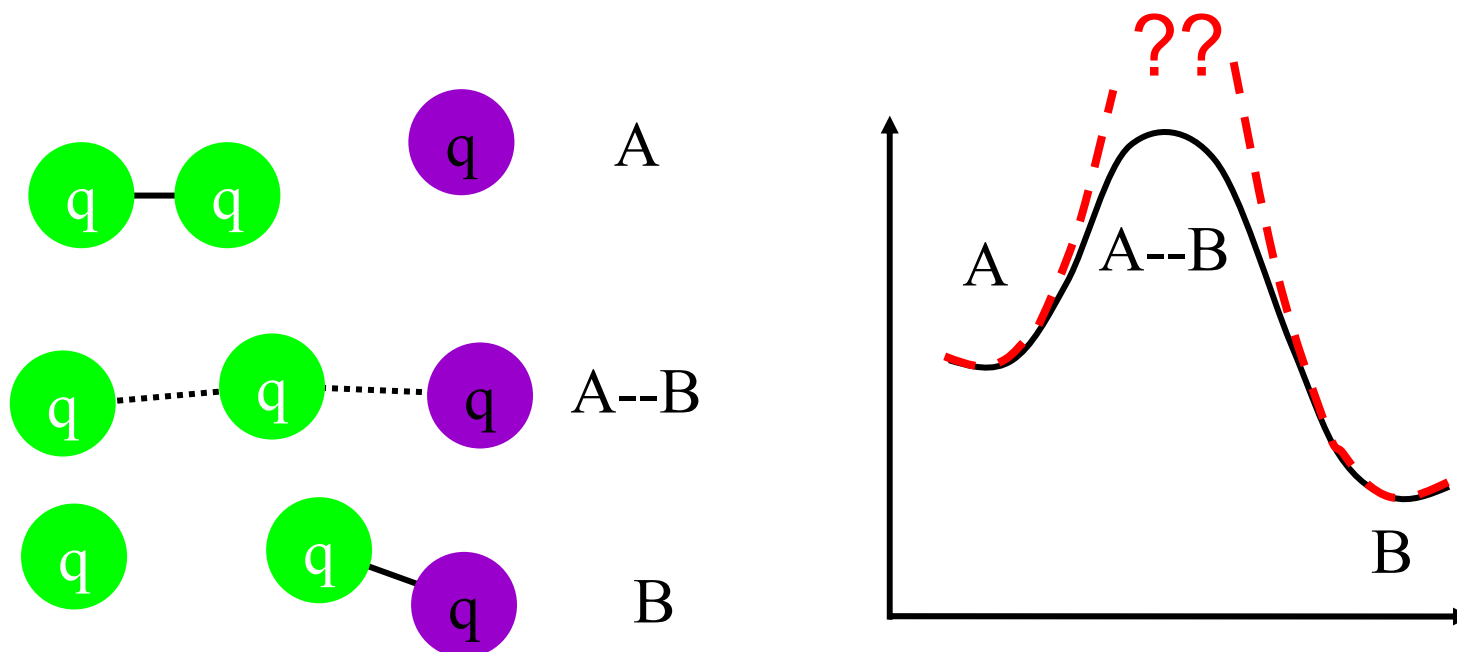


- **1985: Abell:** General expression for binding energy as a sum of near neighbor pair interactions moderated by local atomic environment
- **1990s: Tersoff, Brenner:** Use Abell formalism applied to silicon (successful for various solid state structures)
- **2000: Stuart et al.:** Reactive potential 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

Key features of reactive potentials



- 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.

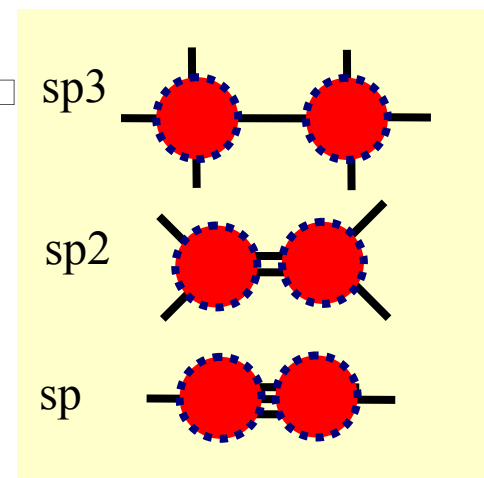


ReaxFF: A reactive force field in CMDf

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

2-body *3-body* *4-body*

multi-body

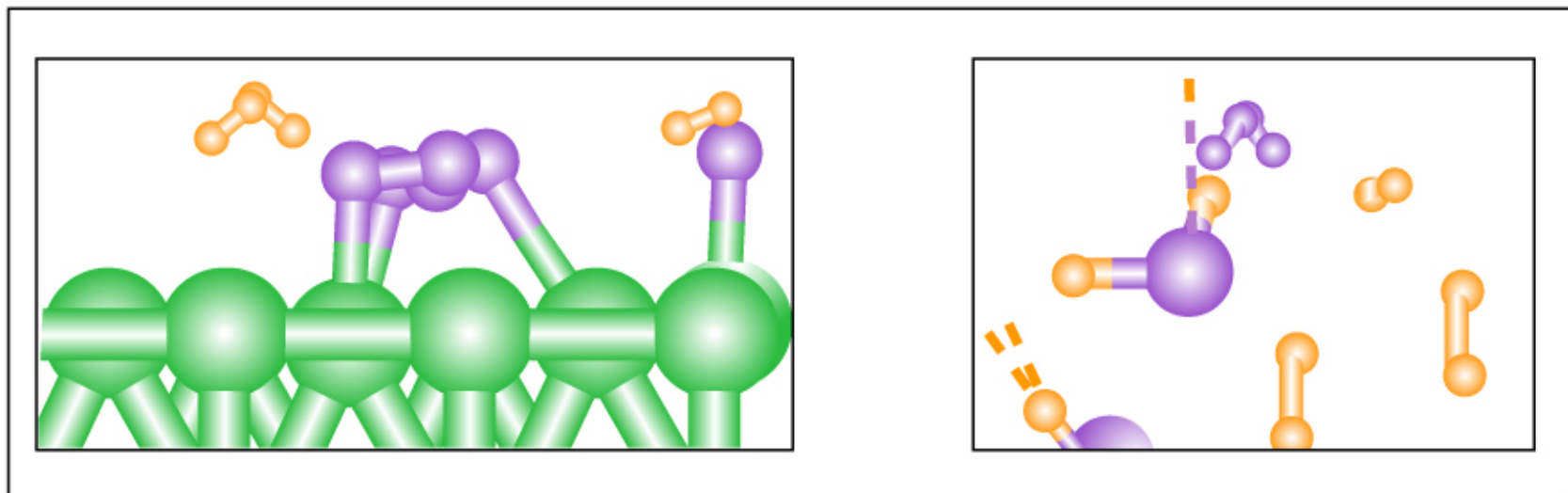


- A **bond length/bond order relationship** is used to obtain smooth transition (Pauling) from **non-bonded to single, double, and triple bonded systems**.
- All connectivity-dependent interactions (*i.e.* valence and torsion angles) are made bond-order dependent
 - Ensures that their energy contributions 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**

■ 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



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?

Simulation procedure



- ReaxFF force field
- NVT dynamics: temperature control, constant volume
- Time step $\Delta t=0.25$ 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)

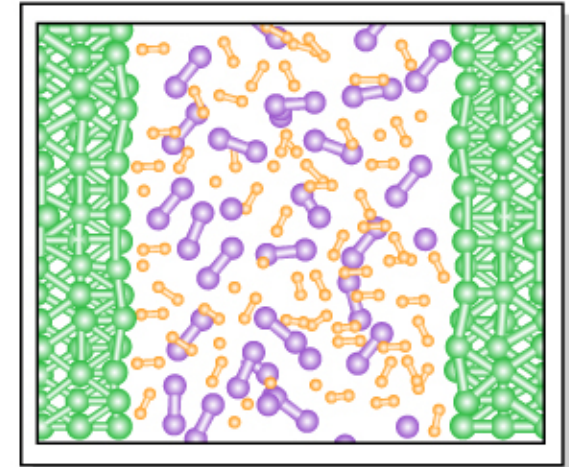


Figure by MIT OCW.

Formation mechanism

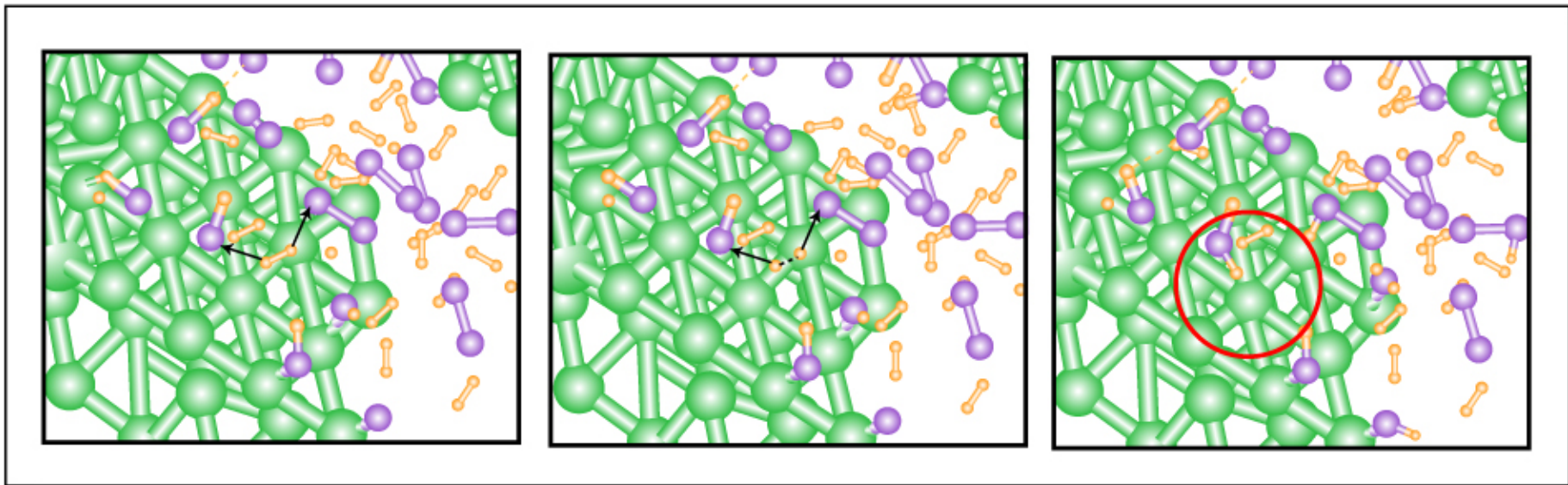


Figure by MIT OCW.

- 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

Effect of Pt catalyst

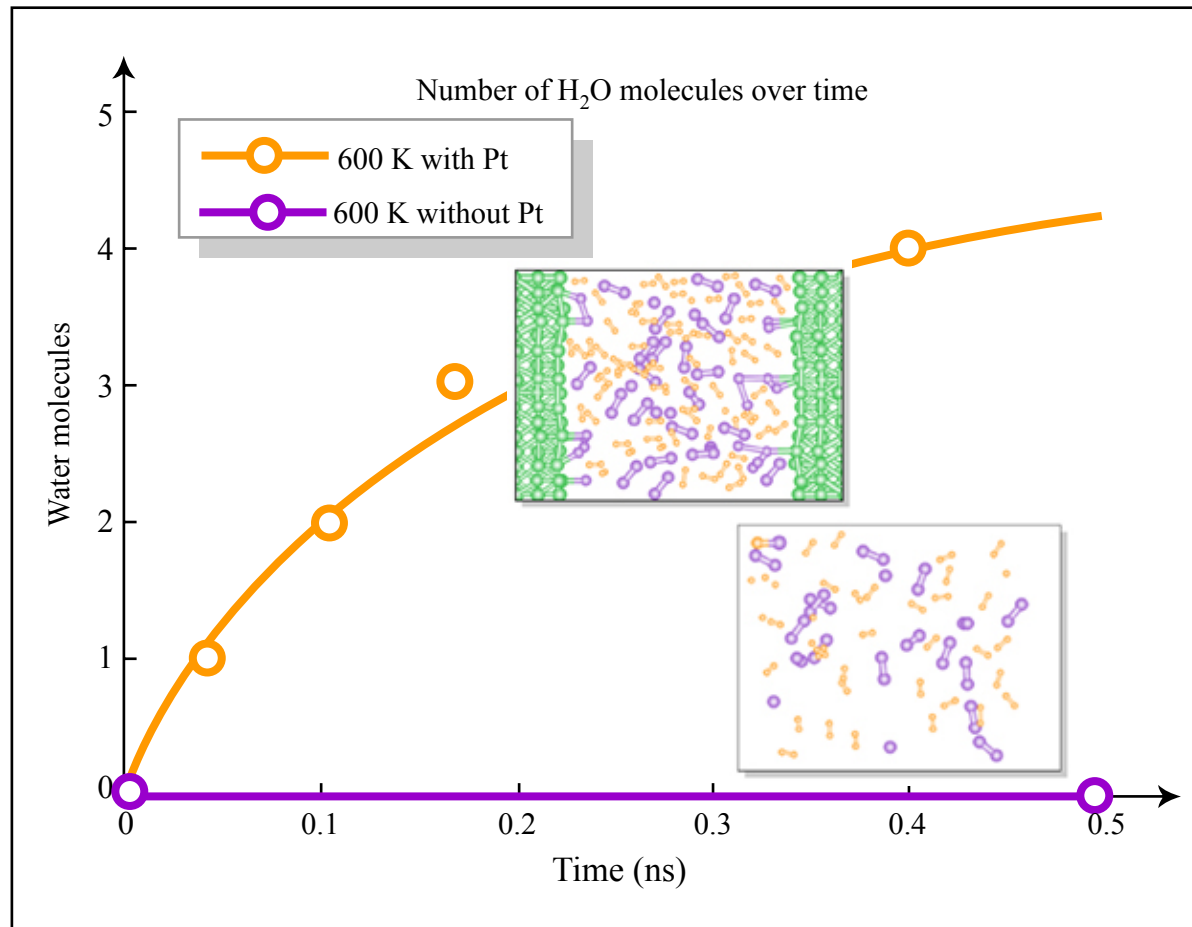


Figure by MIT OCW.

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

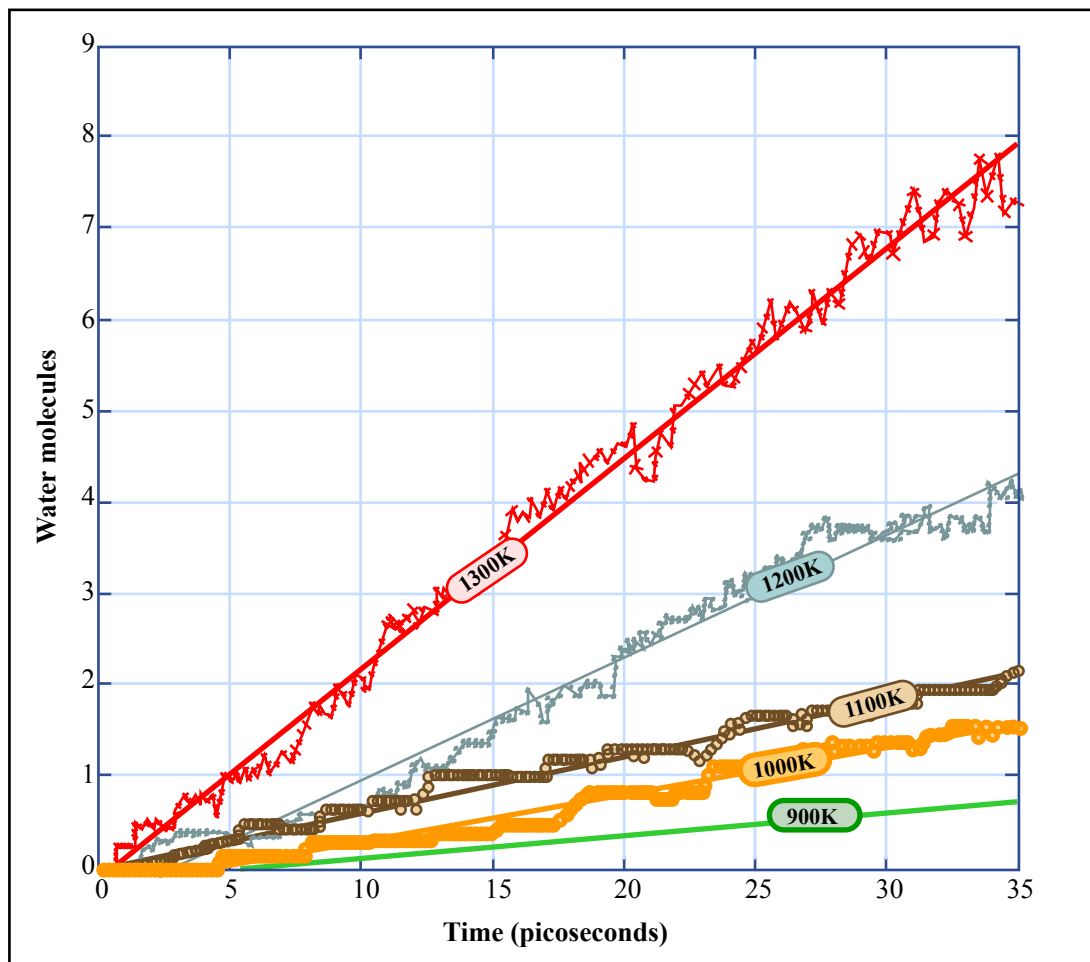


Figure by MIT OCW.

- 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)

Arrhenius plot for AE

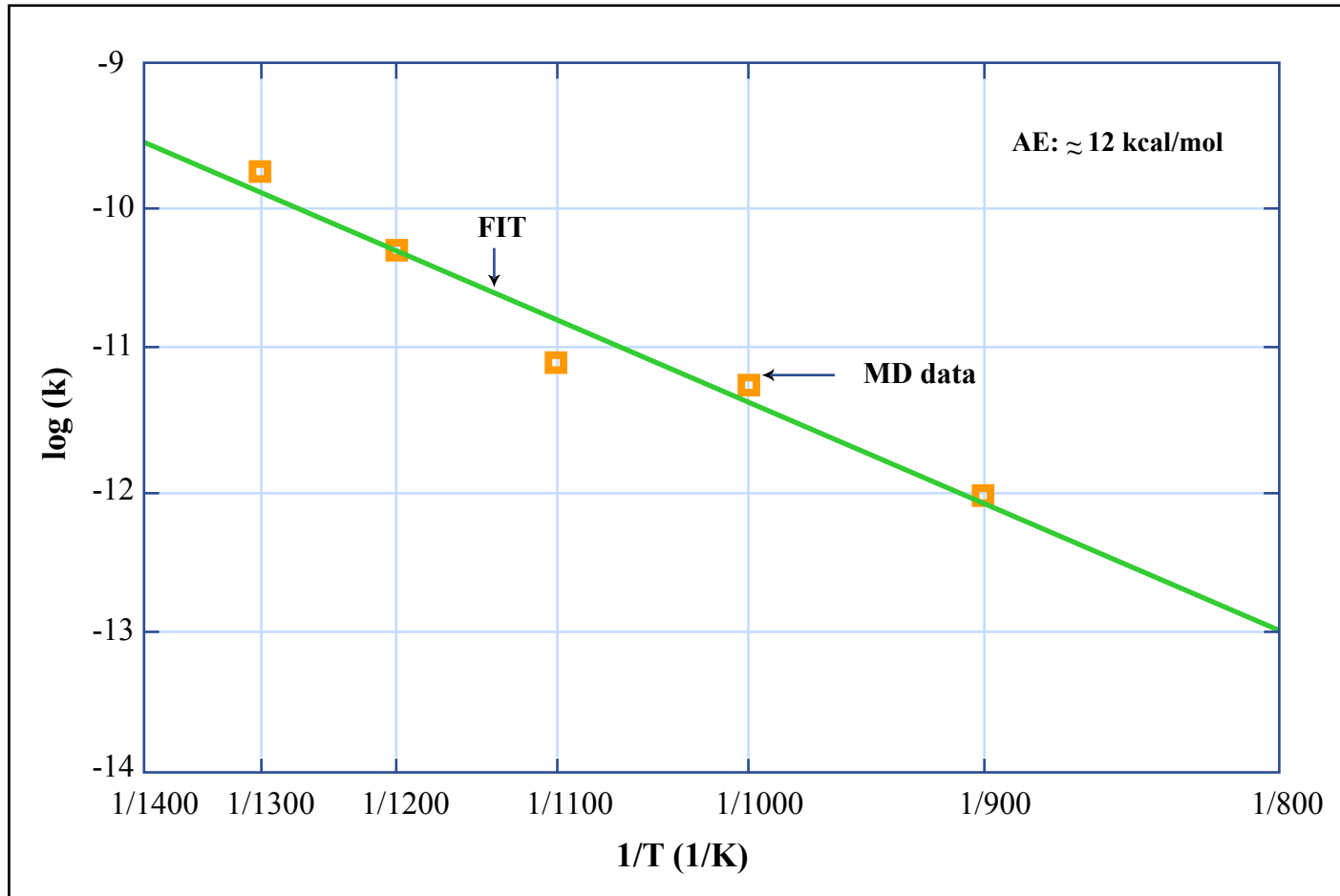
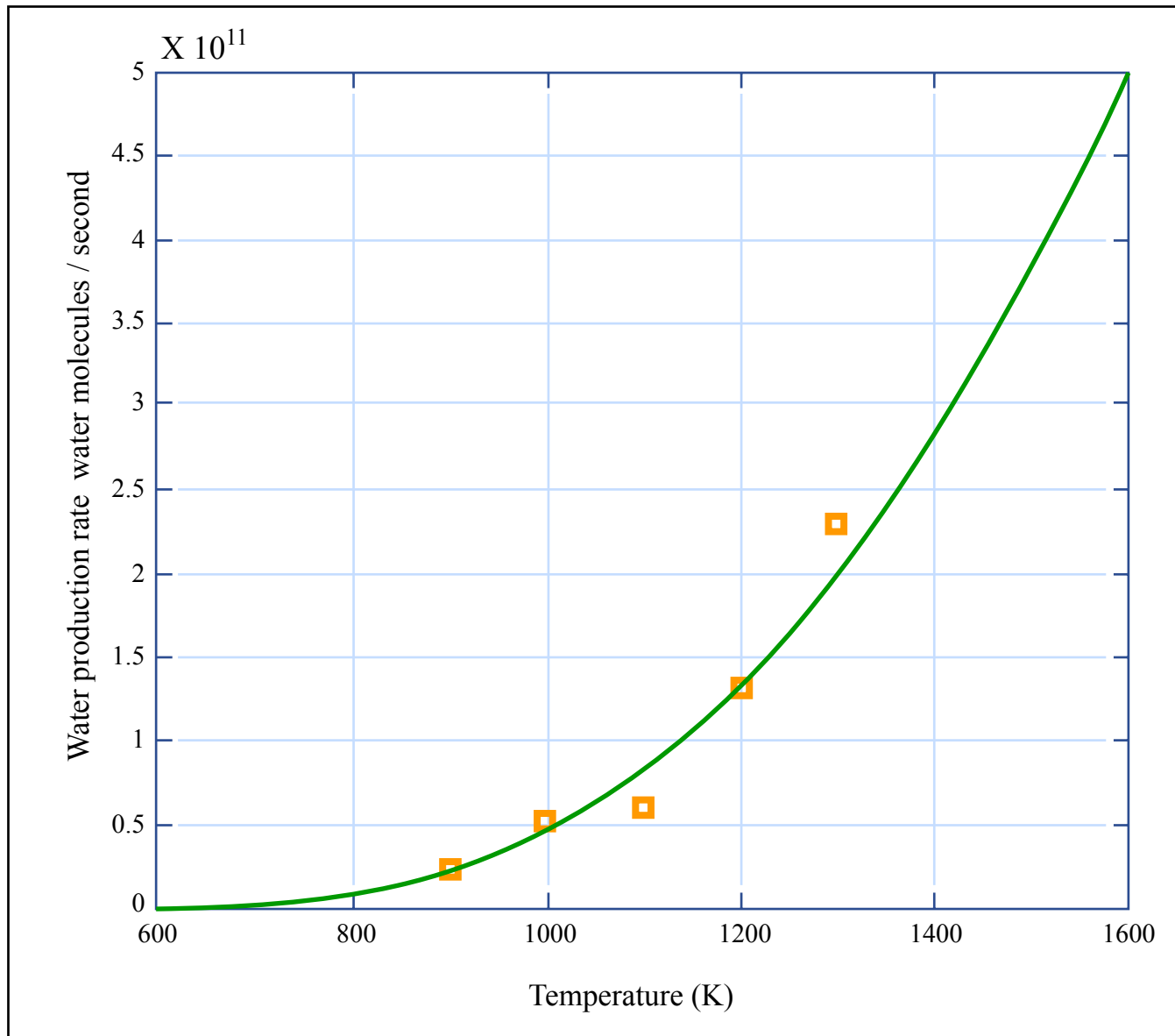


Figure by MIT OCW.

- 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

Reaction constants versus temperature



- Compare fitted result and MD simulation data

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

Figure by MIT OCW.

Summary of important concepts



- Reactive force fields are capable of treating various kinds of chemical bonds; including covalent bonds, weak (dispersive) interactions, and others
- These force fields are based on the idea to decompose the different chemical bond effects into individual contributions to the energy, while having cross-terms (penalty for over- and undercoordination)
- Reactive potentials – in particular newer formulations such as ReaxFF – can be used to simulate chemical reactions, i.e. formation and breaking of new chemical bonds
- We demonstrated this concept in a study of water formation
- This represents one of the frontiers in atomistic modeling

Additional references

<http://web.mit.edu/mbuehler/www/>

1. Buehler, M.J., *Large-scale hierarchical molecular modeling of nano-structured biological materials*. Journal of Computational and Theoretical Nanoscience, 2006. **3**(5).
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