



**From nano to macro: Introduction to atomistic modeling techniques**

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

**Introduction to atomistic modeling techniques: Do we need atoms to describe how materials behave?**

**Lecture 1**



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**Civil & Environmental Engineering**  
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# Introduction: Lecture series



- Introduce large-scale atomistic modeling techniques and motivate its importance for solving problems in modern engineering sciences.
- Demonstrate how atomistic modeling can be successfully applied to understand dynamical materials failure of:
  - Metals (Cu, Ni, Al, Fe...) and alloys (NiAl...),
  - Semiconductors (Si),
  - Thin films (of metals or other materials),
  - Ceramics ( $\text{Al}_2\text{O}_3$ , SiC),
  - and biological materials (e.g. collagen) as well as natural materials (clay, C-S-H; ongoing and future studies).
- Find potential collaborations and synergies within the CEE Department and at MIT as a whole
- **Target group:** Undergraduate / graduate students, postdocs, faculty interested in atomistic methods and scale coupling



# Format



- Ca. 10 lectures 45-50 minutes each, with time for discussion and questions
- Clustered lectures during IAP and workshop (course 1.978, for credit)
  - Lectures (introduction and methods)
  - Modeling and simulation of fracture and deformation of copper (Dislocation nucleation, fracture, brittle versus ductile, comparison with theory and experiment..)
- Two UROP projects posted (fracture of silicon and modeling of collagen)
- Course material posted on the website (introductory papers, books, etc.)

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

Check for updates and supplementary material



# Outline and content (Lecture 1)



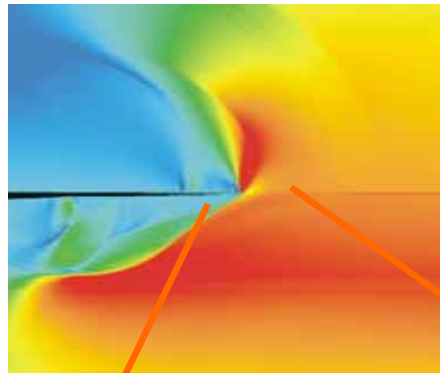
- The BIG challenge to couple nano with macro
- Historical perspective: Understanding behavior of materials
- How atomistic simulations are carried out, including:
  - Definition and numerical issues
  - Time scale dilemma
  - Pre-processing and input parameters
  - Atomic interactions (potential energy surface)
  - Computing strategy: MD codes, parallelization, supercomputing
  - Analysis and visualization, data extraction
- Research examples using atomistic methods
- Discussion and conclusion:  
Are all atoms necessary to describe how materials behave?
- Outlook



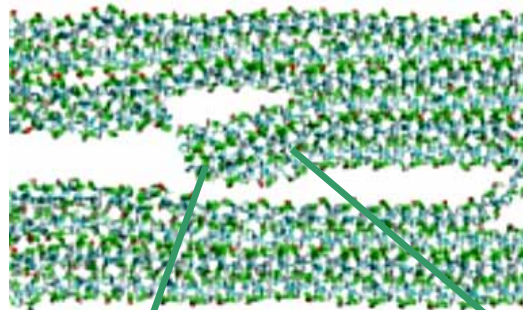
# Introduction



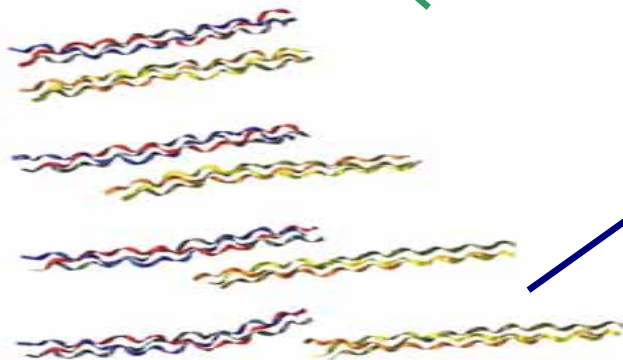
# From nano to macro



Crack dynamics at micrometers (**macroscale**)

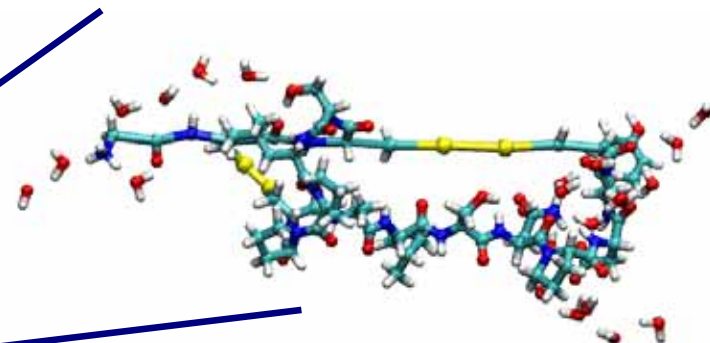


Dynamics of fracture in protein crystals (**mesoscale**)



Mechanics of individual collagen fibers/proteins (**nanoscale**)

- Materials are made out of atoms
- Depending on the scale looked at materials, these atoms are “visible” or not
- Nevertheless, the atomic structure always plays an essential role in determining material properties (in particular under certain conditions)
- **Example:** Structure of a complex biological material (levels of hierarchies)



Chemistry (**atomic scale**)



# The BIG problem ...

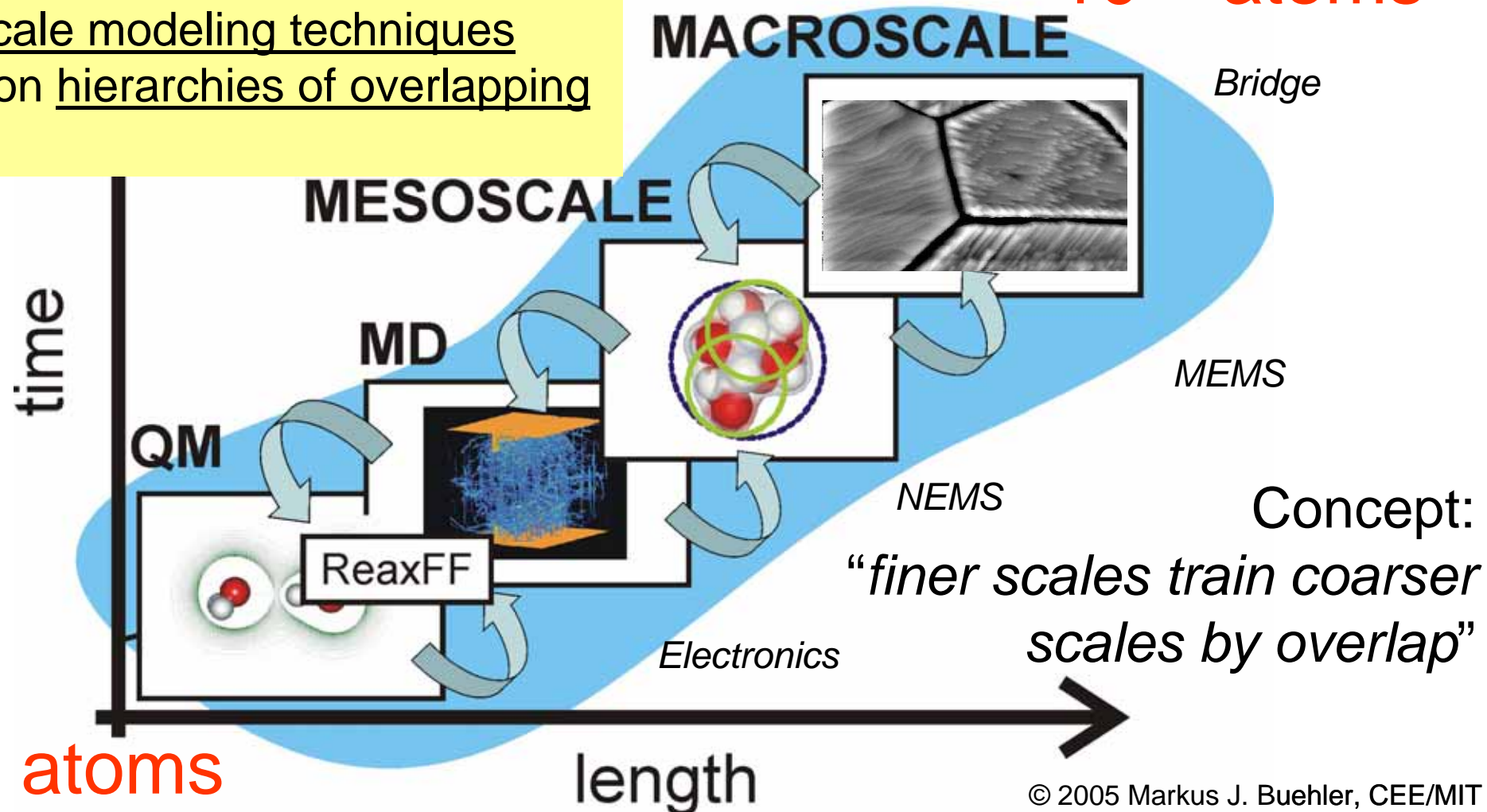


**Want:** Accuracy of quantum mechanics (QM) in  $10^{23}$  atom systems...

This is impossible (today and in the foreseeable future)

Possible solution:  
Multi-scale modeling techniques  
based on hierarchies of overlapping  
scales

$\sim 10^{23}$  atoms







# Historical perspective: Modeling of mechanics (behavior) of materials



- 1500-1600s: L. da Vinci, Galileo Galilei
- 1700-1800: Euler, Bernoulli
- Beam theories, rods (partial differential equations, continuum theories)
- Continuum mechanics theories
- Development of theories of fracture mechanics, theory of dislocations (1930s)
- 1960..70s: Development of FE theories and methods (engineers)
- 1990s: Marriage of MD and FE via Quasicontinuum Method (Ortiz, Tadmor, Phillips)
- 20th century: Atoms discovered (Jean Perrin)
- MD: First introduced by Alder and Wainwright in the late 1950's (interactions of hard spheres). Many important insights concerning the behavior of simple liquids emerged from their studies.
- 1964, when Rahman carried out the first simulation using a realistic potential for liquid argon (Rahman, 1964).
- Numerical methods like DFT (Kohn-Sham, 1960s-80s)
- First molecular dynamics simulation of a realistic system was done by Rahman and Stillinger in their simulation of liquid water in 1974 (Stillinger and Rahman, 1974).
- First fracture / crack simulations in the 1980s by Yip and others, 1990s Abraham and coworkers (large-scale MD)
- Now: MD simulations of biophysics problems, fracture, deformation are routine
- The number of simulation techniques has greatly expanded: Many specialized techniques for particular problems, including mixed quantum mechanical - classical simulations, that are being employed to study enzymatic reactions ("QM-MM") or fracture simulations (Kaxiras and others, Buehler and Goddard).

Continuum

Atomistic

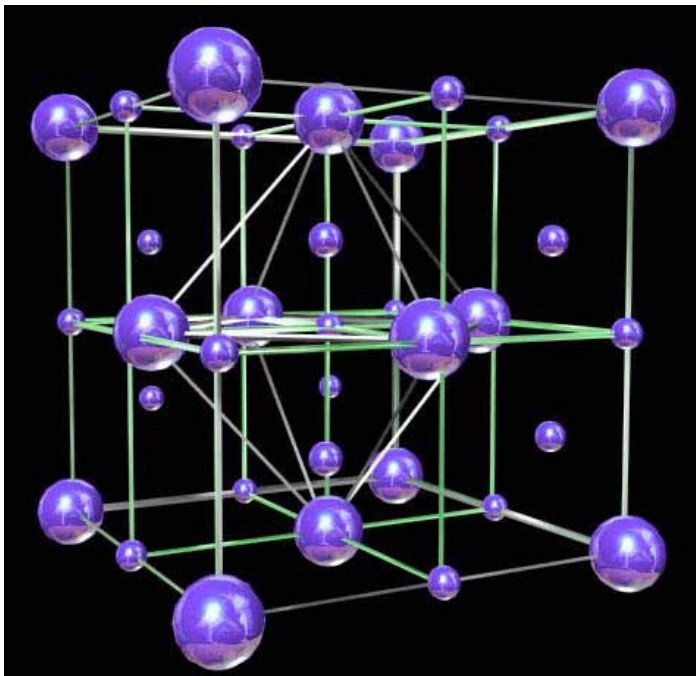




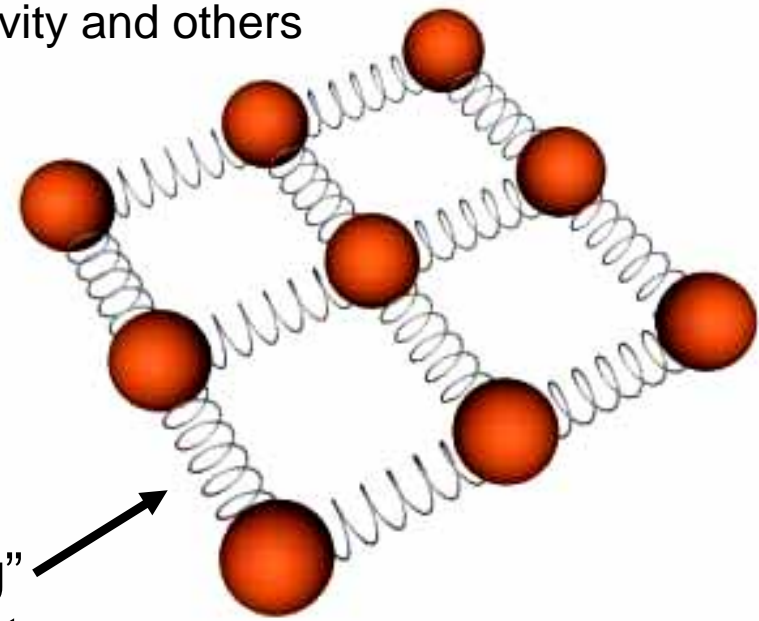
# The problem to solve



- In atomistic simulations, the goal is to understand and model the motion of each atom in the material
- The collective behavior of the atoms allows to understand how the material undergoes deformation, phase changes or other phenomena, providing links between the atomic scale to meso/macro phenomena



Vibration, change of location, connectivity and others



“Spring”  
connects  
atoms...

[http://www.sr.bham.ac.uk/xmm/images/structures/spherespring\\_300\\_248.jpg](http://www.sr.bham.ac.uk/xmm/images/structures/spherespring_300_248.jpg)



# Classical molecular dynamics (MD)



- Classical MD calculates the time dependent behavior of a molecular system by integrating their equations of motion ( $F$ =force vector,  $a$ =acceleration vector)

$$F = ma$$

- The word “classical” means that the core motion of the constituent particles obeys the laws of classical mechanics
- Molecular dynamics simulations generate information at the microscopic level, which are: Atomic positions, velocities, forces
- The conversion of this microscopic information to macroscopic observables such as pressure, stress tensor, strain tensor, energy, heat capacities, etc., requires theories and strategies developed in the realm of statistical mechanics
- Statistical mechanics is fundamental to the study of many different atomistic systems

Important: The Ergodic hypothesis states

$$\langle A \rangle_{ensemble} = \langle A \rangle_{time}$$

Ensemble average = Time average (atomistic data usually not valid instantaneously in time and space)



# Integrating the equations of motion



- Verlet algorithm
- Leap-frog algorithm
- Beeman's algorithm

Update of positions

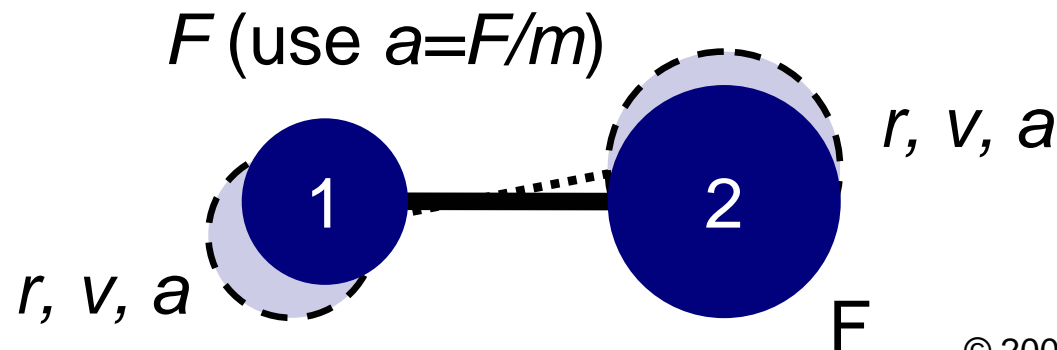
$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2$$

- Velocity Verlet (popular)

Update of velocities

$$v(t + \delta t) = v(t) + \frac{1}{2}[a(t) + a(t + \delta t)]\delta t$$

- Algorithms to control the temperature of a system, pressure, stress, etc. exist (e.g. Nosé-Hoover, Berendsen, etc.)
- NVE, NVT, NPT calculations
- Most calculations in mechanics field are NVE (nonequilibrium phenomena such as fracture)



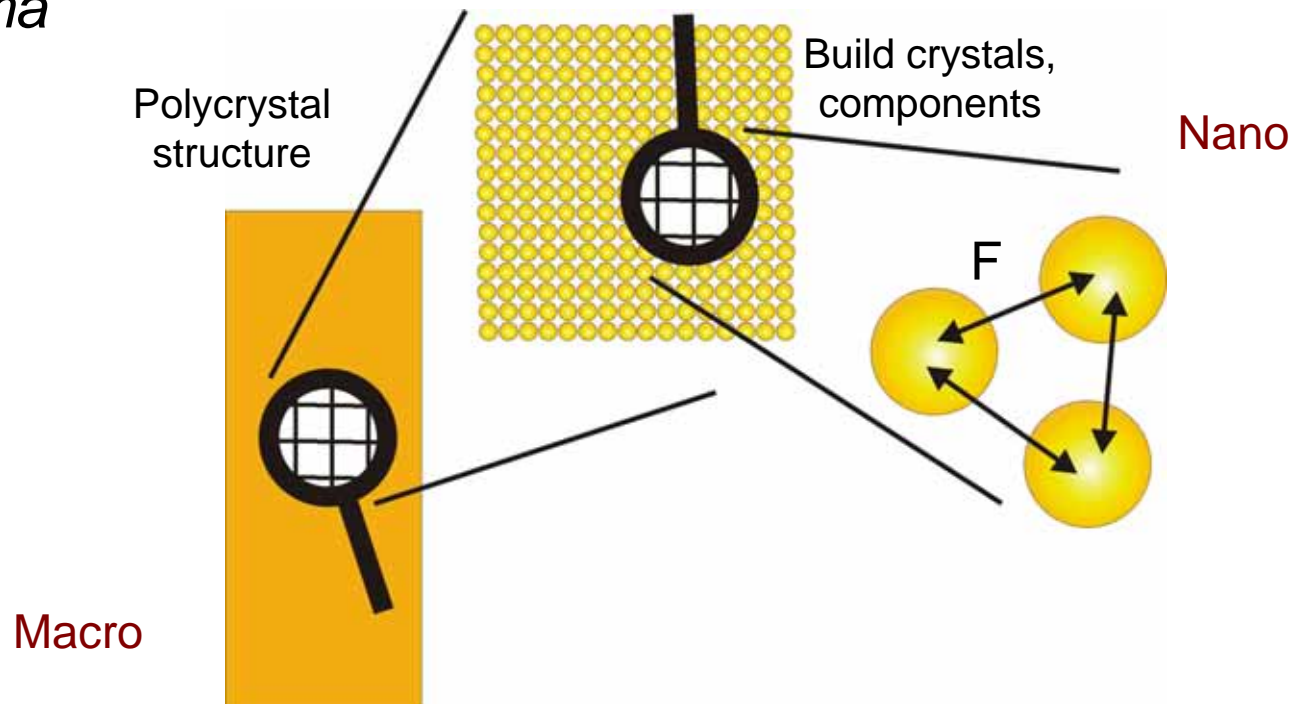


# Time scale dilemma...



- Calculate timely evolution of large number of particles (integrate using Velocity Verlet, for example)

$$F = ma$$



- Need to resolve high frequency oscillations, e.g. C-H bond (at nanoscale)

Time step:  
0.1..3 fs

Time scale range of MD: Picoseconds to several nanoseconds

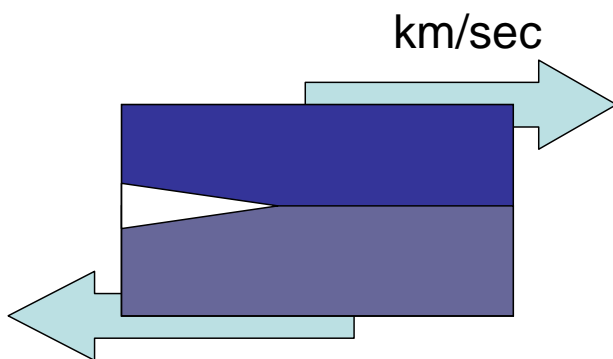
Timescale dilemma: No matter how many processors (**how powerful the computer**), can only reach nanoseconds: **can not parallelize time**



# Consequences of the time scale dilemma



- Very high strain rates in fracture or deformation (displacement km/sec)
- Limited accessibility to diffusional processes or any other slow mechanisms
- Unlike as for the scale problem (ability to treat more atoms in a system) there is no solution in sight for the time scale dilemma
- MD has to be applied very carefully while considering its range of validity (window, niche: fracture ideal, since cracks move at km/sec)
- When valid, MD is very powerful and nicely complements experiment and theory, but it has limitations which need to be understood



	yes	yes w/ limitations	no
Fracture in model materials	×		
Fracture in real materials		×	
GB diffusion at high temperatures		×	
GB diffusion at low temperatures			×
Plasticity in model materials	×		
Plasticity in real materials		×	

(Buehler, 2004)



# Monte Carlo (MC) techniques



- Monte Carlo (MC) techniques and alike have been developed to overcome some of the limitations of dynamical (MD) atomistic calculations
- Instead of integrating the EOM, MC performs a random walk to measure properties: Randomly probing the geometry of the molecular system (configuration space, acceptance depends on “cost function”)
- MC enables modeling of diffusion and other “slow” processes (slow compared to the time scale of atomic vibrations)
- There exist many different flavors, including
  - Classical MC (no information about dynamics, only about mechanisms and steady state properties, e.g. thermodynamical variables)
  - Kinetic MC (get information about dynamics)
  - Advanced MD methods (marriage between MC and MD, e.g. Temp. Acc. Dyn.)
  - Bias potentials (e.g. restraints) to facilitate specific events by reducing the barriers
- Generally, MC techniques require more knowledge about the system of interest than MD

<http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf>

D. Frenkel and B. Smit *Understanding Molecular Simulations: from Algorithms to Applications*, Academic Press, San Diego, 2nd edition (2002).

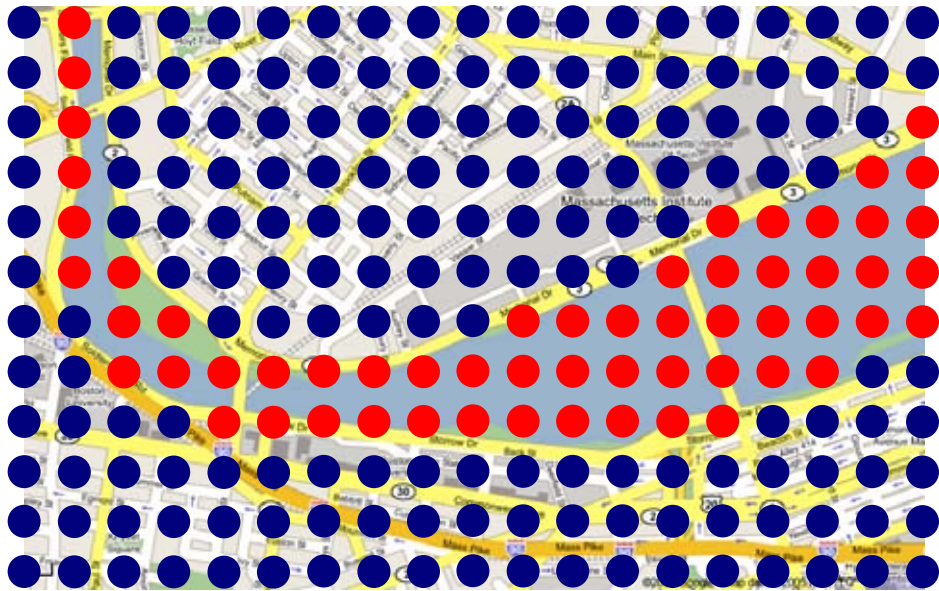
<http://www.ccl.net/cca/documents/molecular-modeling/node9.html>

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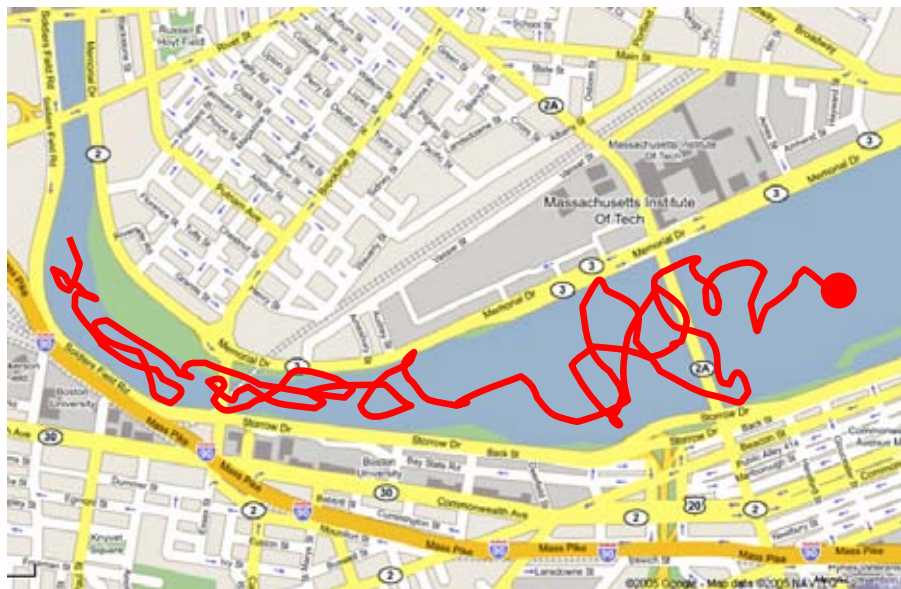


# Example: Measuring the average depth of the Charles River



Classical grid-based quadrature scheme:

*Discretize problem and perform measurements at grid points*



Monte Carlo:

*Perform random walk through the river; measurements are performed only at accepted locations*

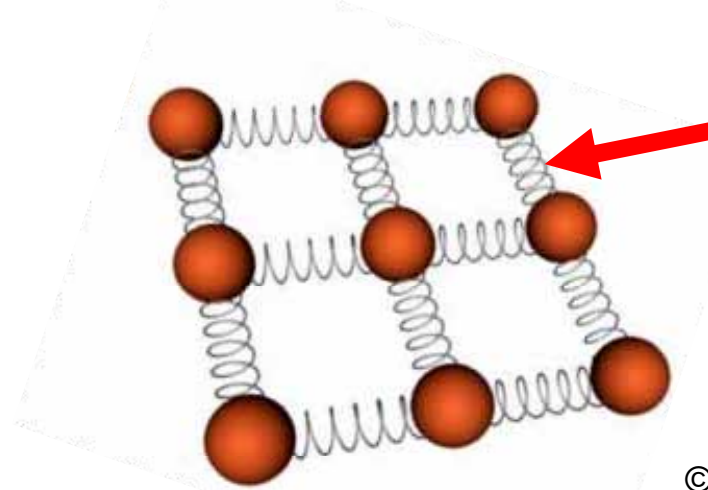
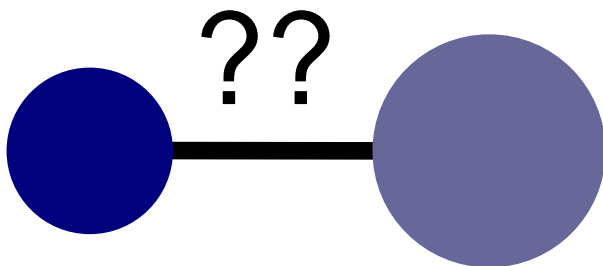




# Characteristics of MD (and MC)



- Atomistic or molecular simulations (molecular dynamics, MD) is a fundamental approach, since it considers the basic building blocks of materials as its smallest entity: Atoms
- At the same, time, molecular dynamics simulations allow to model materials with dimensions of several hundred nanometers and beyond: Allows to study deformation and properties, mechanisms etc. with a very detailed “computational microscope”, thus bridging through various scales from “nano” to “macro” possible by DNS
- Sometimes, MD has been referred to as a “first principles approach to understand the mechanics of materials” (e.g. dislocations are “made” out of atoms...)
- With the definition of the interatomic potentials (how atoms interact) all materials properties are defined (endless possibilities & challenges...)



DFT or  
Empirical or  
Semi-empirical...

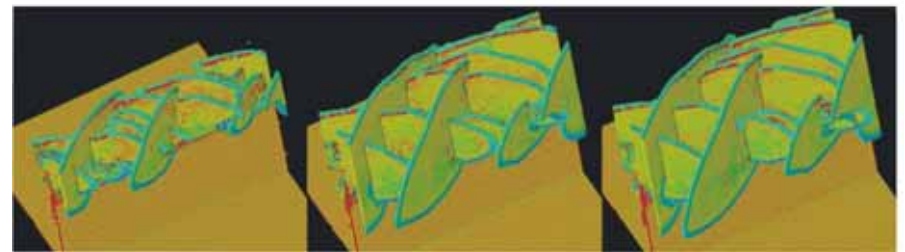
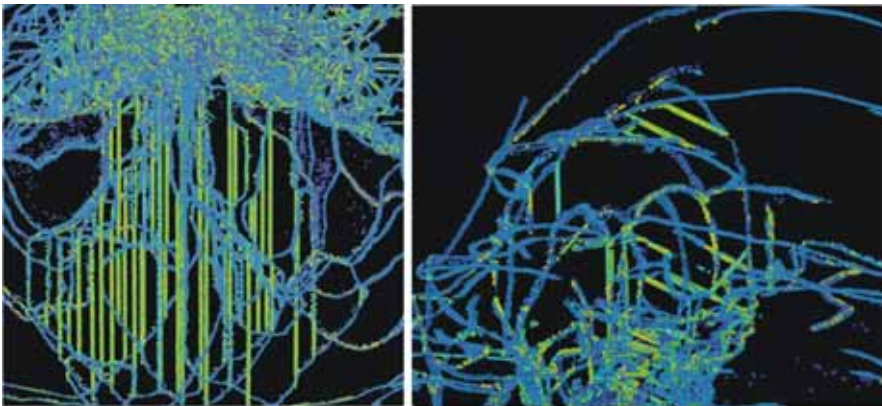
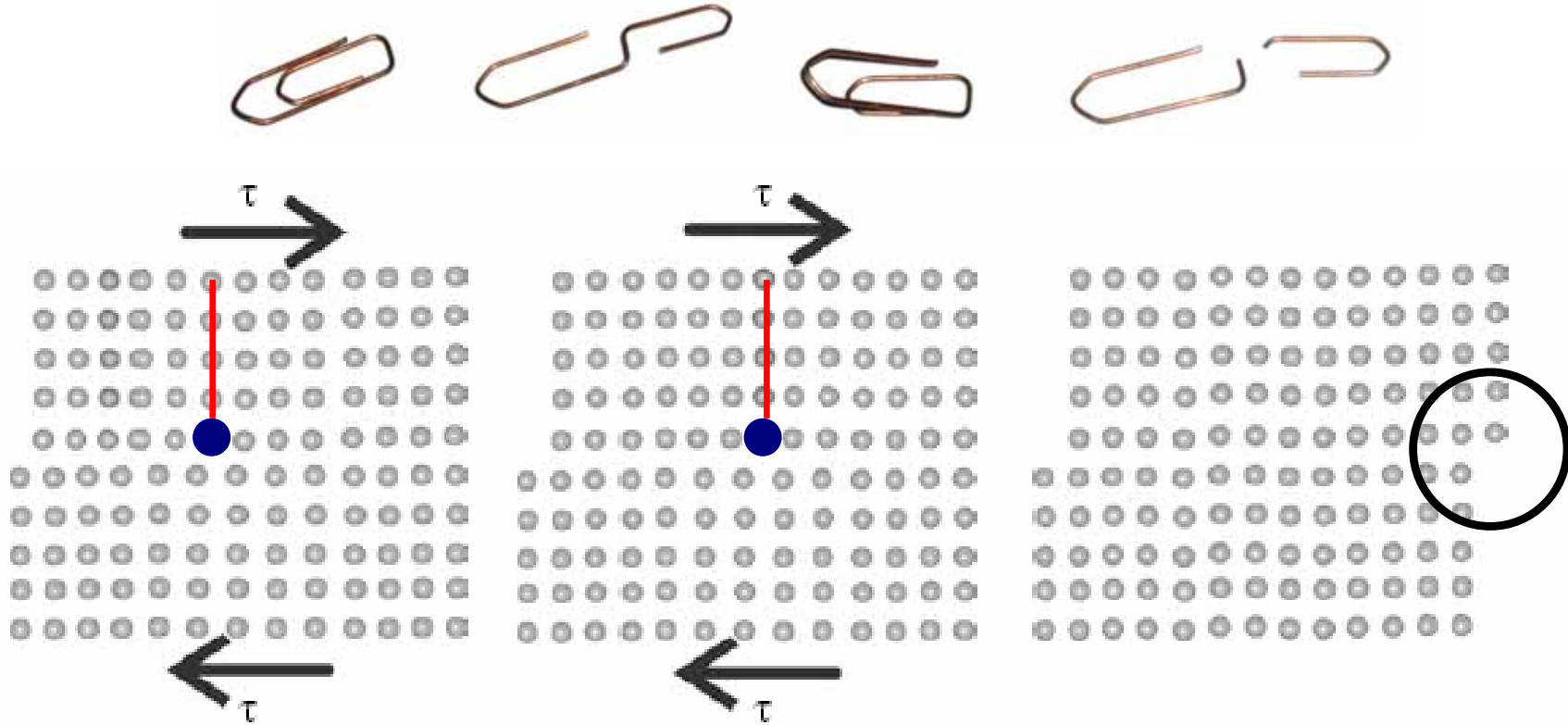
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# First principles description of mechanics: Dislocations carry plasticity in metals



Dislocations  
are made  
out of atoms

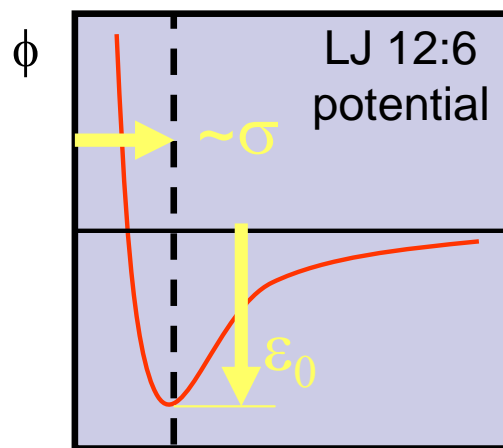
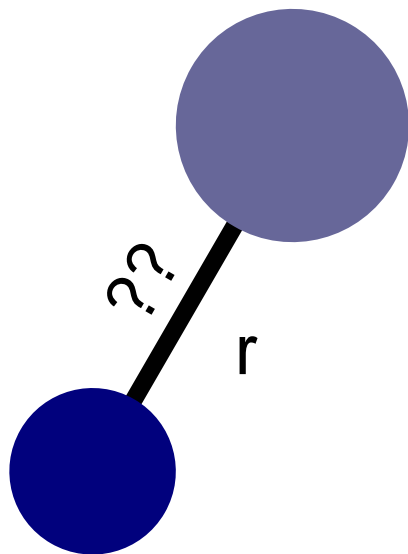




# The interatomic potential



- The fundamental input into molecular simulations, in addition to structural information (position of atoms, type of atoms and their velocities/accelerations) is provided by definition of the interaction potential (equiv. terms often used by chemists is “force field”)
- MD is very general due to its formulation, but hard to find a “good” potential (extensive debate still ongoing, choice depends very strongly on the application)
- Popular: Semi-empirical or empirical (fit of carefully chosen mathematical functions to reproduce the energy surface...)



Forces by  $d\phi/dr$

Parameters

Lennard-Jones

$$\phi(r) = 4\epsilon_0 \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

Or more sophisticated potentials  
(multi-body potentials EMT,  
EAM, TB...)

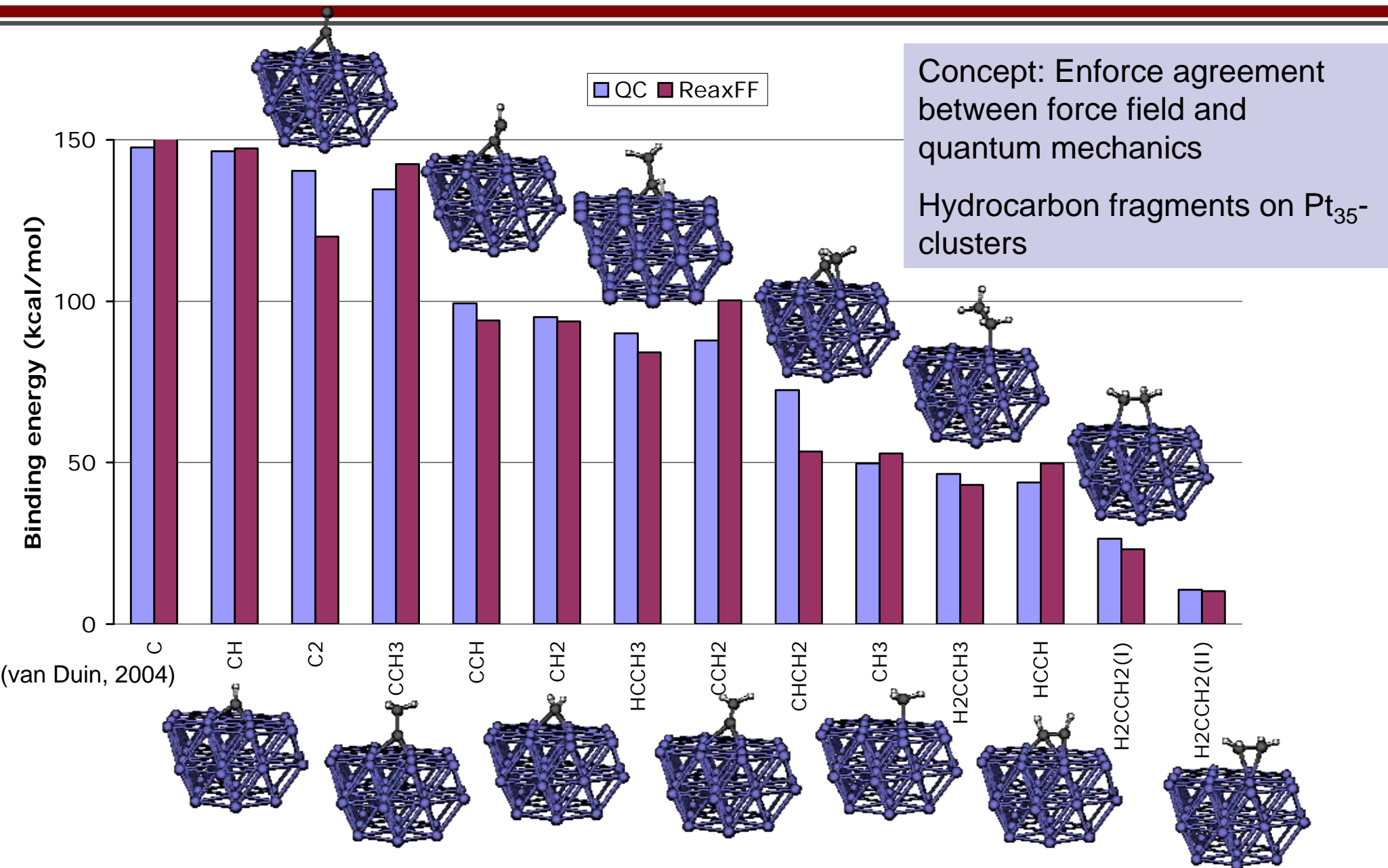


# Training of Force Fields: Hydrocarbon-Pt interactions



Concept: Enforce agreement between force field and quantum mechanics

Hydrocarbon fragments on Pt<sub>35</sub>-clusters



ReaxFF can describe different C-Pt bonding modes



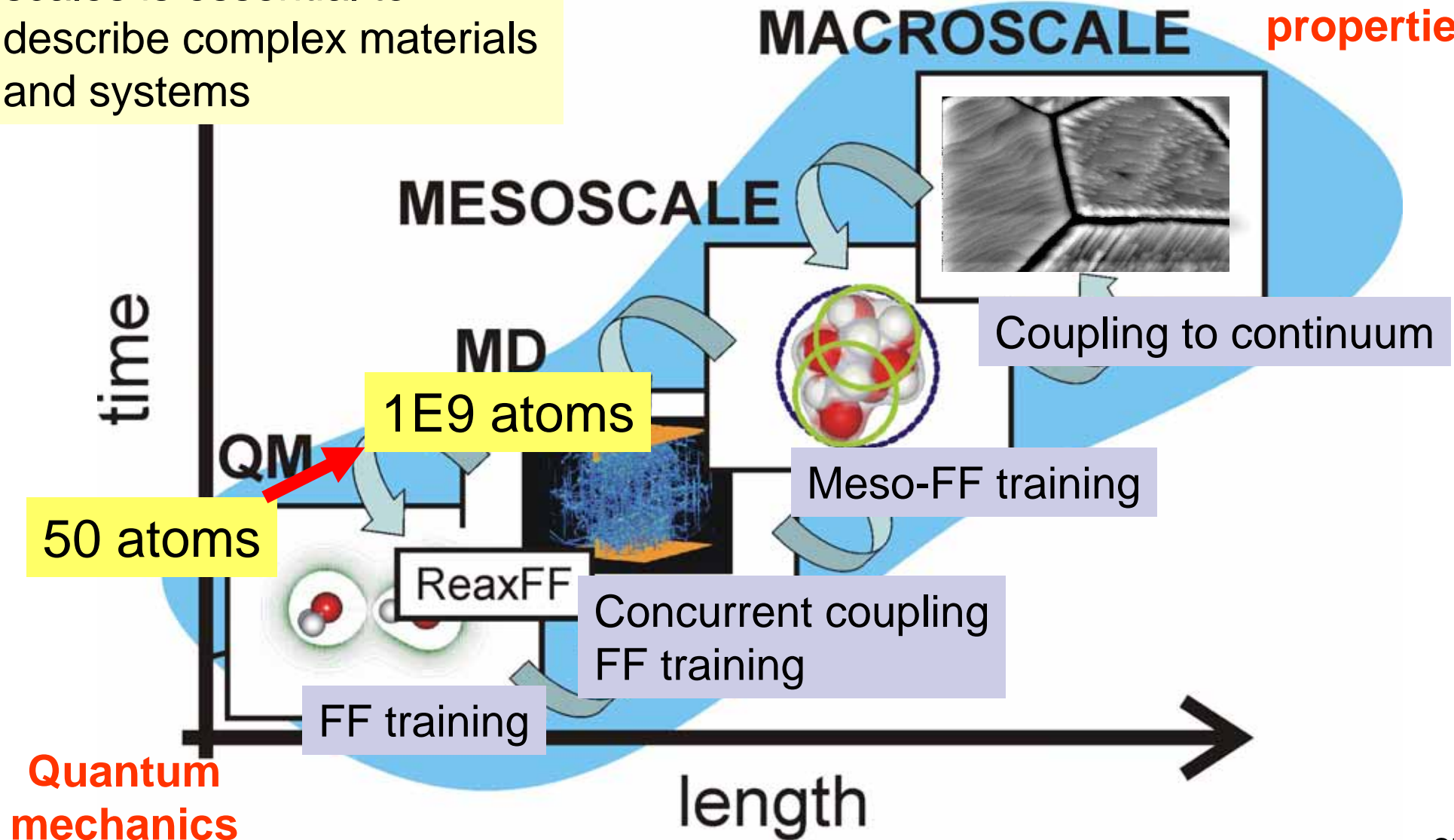


# Challenge: Coupling of various scales From QM to Macroscale



Integration of various scales is essential to describe complex materials and systems

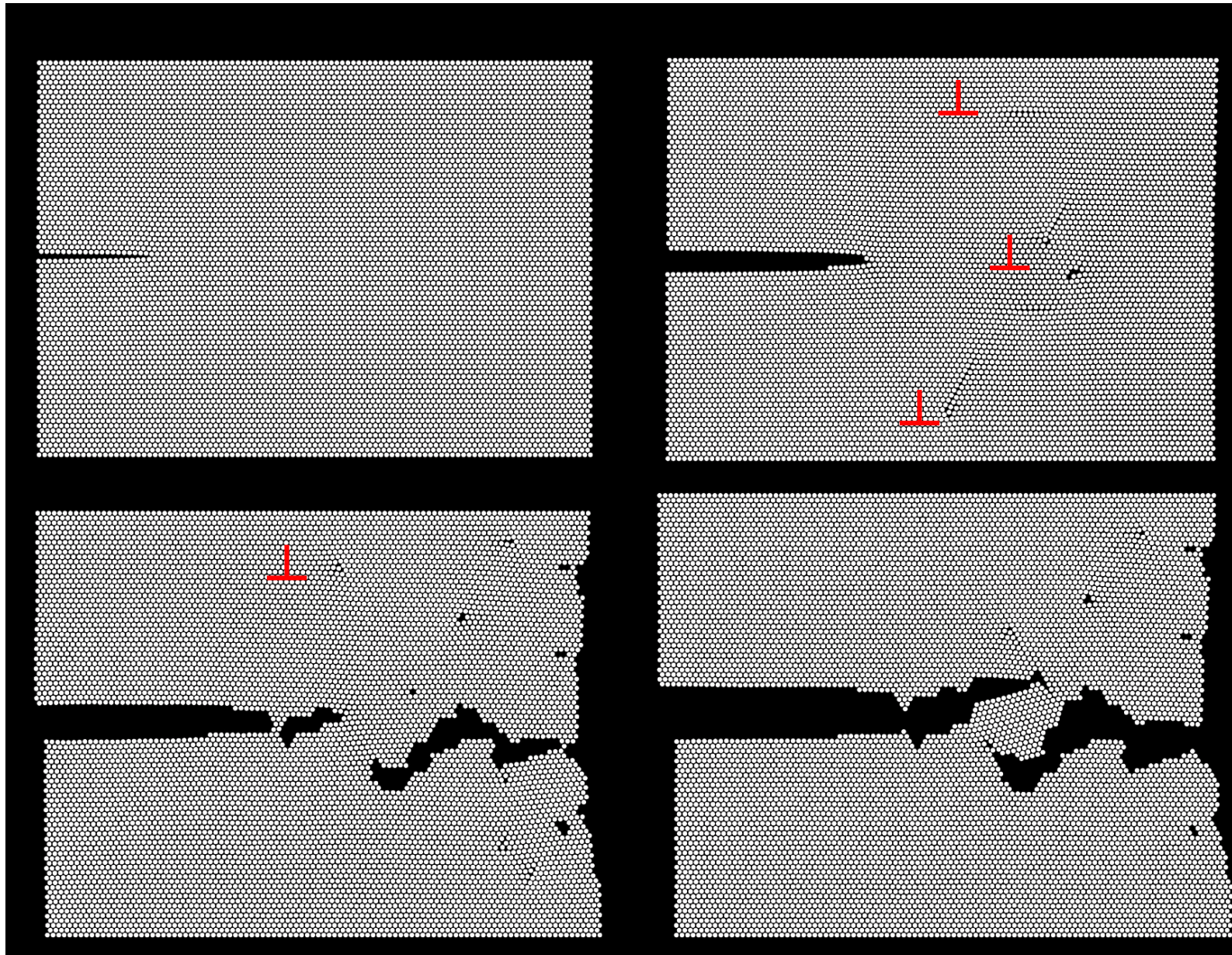
Engineering properties







# Atomistic model of fracture (small-scale)



LJ  
2D  
Mode I



# Example: Potentials for metals



$$\phi_i(r) = \sum_{j=1}^{N_i} \phi_{ij}(r_{ij})$$

[http://phycomp.technion.ac.il/~p\\_hsorkin/thesis/node18.html](http://phycomp.technion.ac.il/~p_hsorkin/thesis/node18.html)

$$\phi_{ij}(r_{ij}) = \sum_{j=1}^{N_i} 4\epsilon_0 \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

$$\phi_{ij}(r_{ij}) = D \{ 1 - \exp[-\beta(r_{ij} - r_0)] \}^2$$

Pair potentials

Good for gases, but don't describe metallic bonding well

Lennard-Jones 12-6

$C_{12} \neq C_{11}$

Morse

$$\phi_{ij}(r) = \sum_{i=1}^{N_i} \phi_{ij}(r_{ij}) + \sum_i \sum_j f(\rho)$$

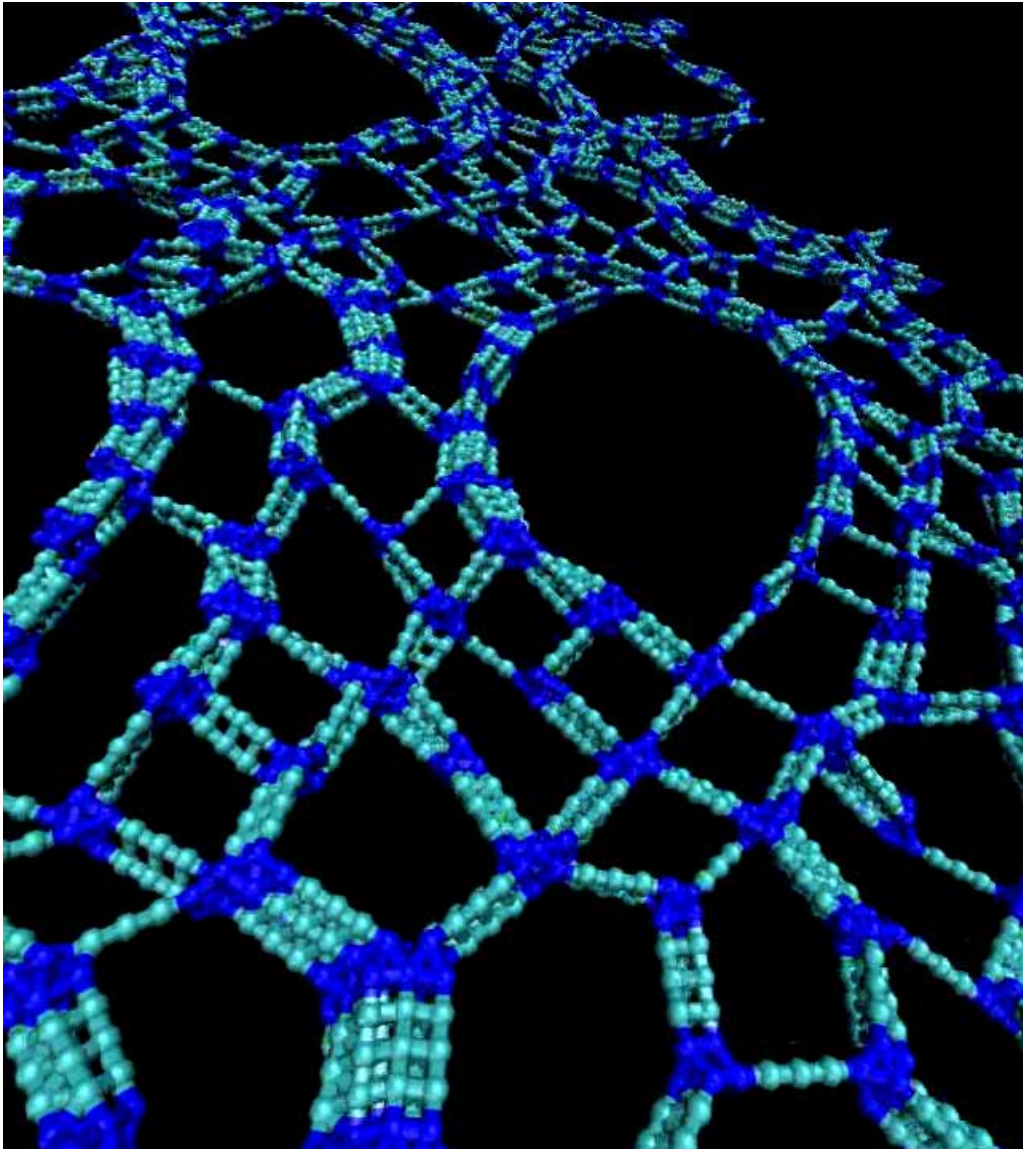
Electron density  
↓

EAM potentials (1980s), Finnis-Sinclair method, Effective medium theory: All based on QM arguments

Quality varies: Good for copper, nickel, to some extent for aluminum ...

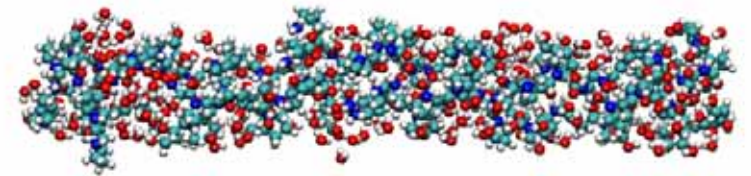
M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984); S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 1986.  
 M. W. Finnis and J. E. Sinclair, Philos. Mag. A **50**, 45 (1984).  
 K. W. Jacobsen, J. K. Nørskov and M. J. Puska, Phys. Rev. B **35**, 7423 (1987).





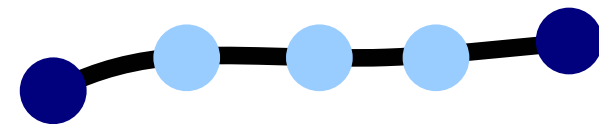
(Buehler, to be published)

Fully atomistic (MD)  
(based on QM)



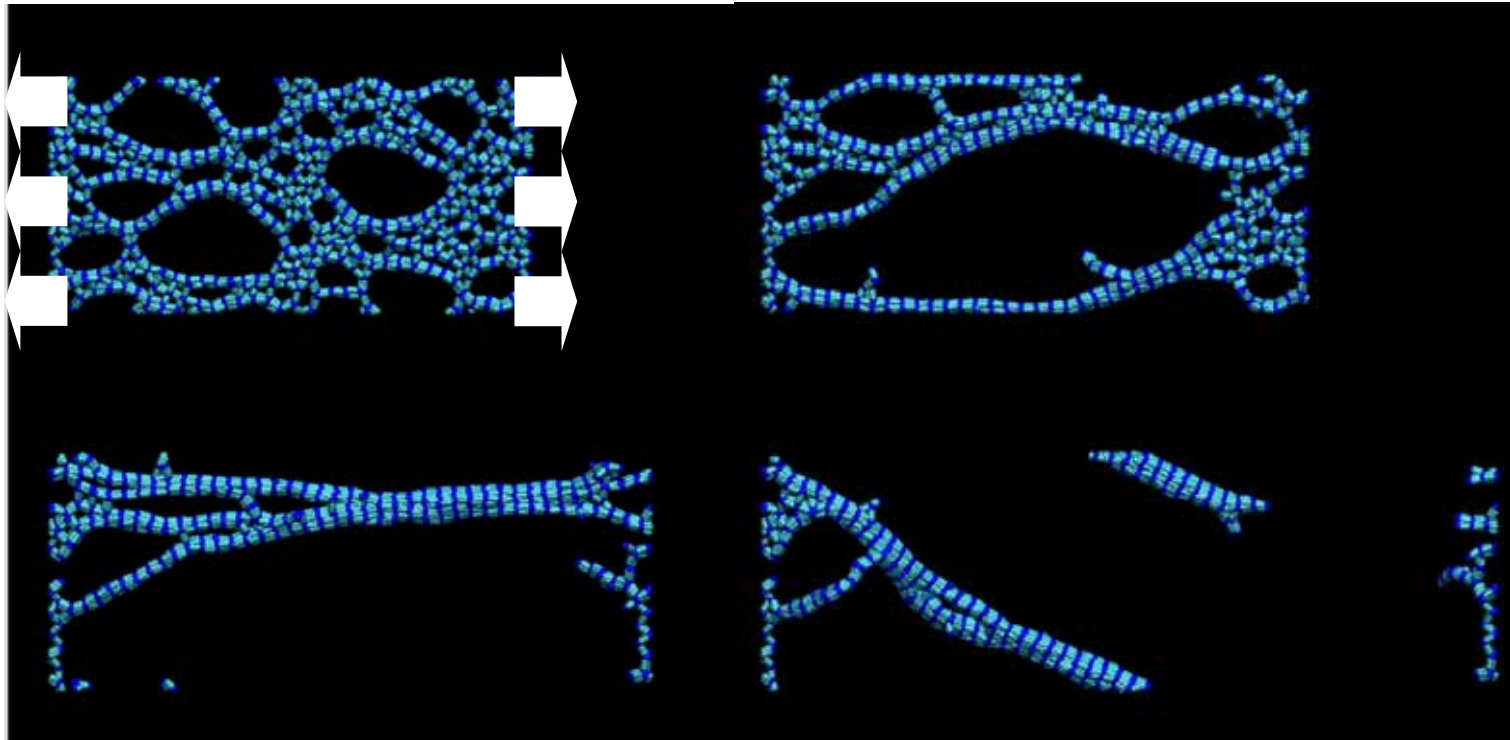
+H<sub>2</sub>O skin

Elasticity,  
Plasticity,..  
of single fiber  
assemblies  
(cross-links)

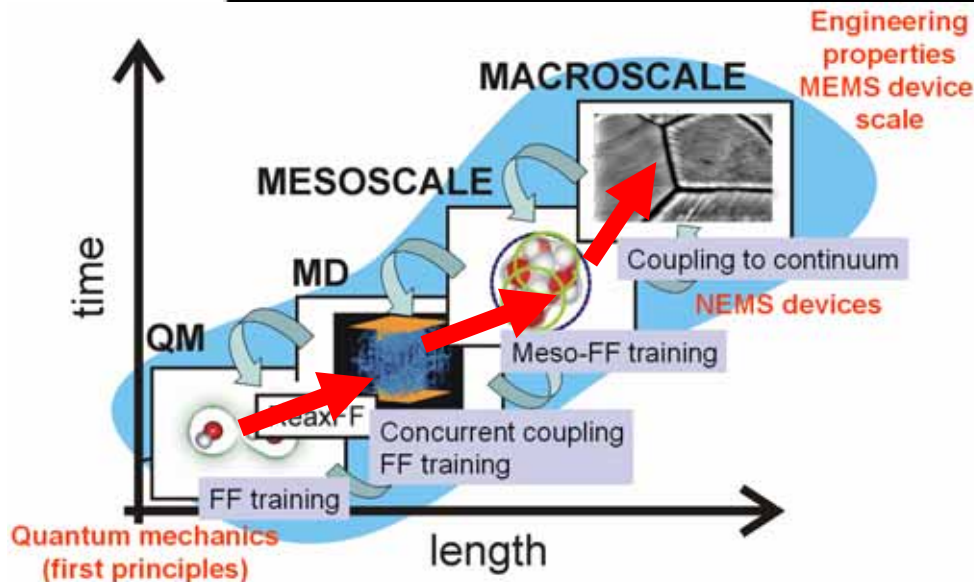


Mesoscale (parametrization)  
Long-range, short-range  
interactions

# Nano-meso-macro transition: Biopolymer



(Buehler, to be published)



- Concept of hierarchical coupling works well for some systems
- Challenge: “Which level of detail” to leave out & what information to transport (and how)?



# Interatomic potential concepts, materials and simulation codes



**QM (not much material specific):** DFT (electronic structure information), codes: JAGUAR, GAUSSIAN, GAMES, CPMD...

**Electron FF:** Electrons as particles (Gaussians moving according to classical EOMs), codes: CMDP

**Tight binding:** Orbitals, semi-empirical, has fitting parameter obtained from QM (codes: EZTB and many more)

**ReaxFF:** Bridge between QM and empirical FFs (charge flow)

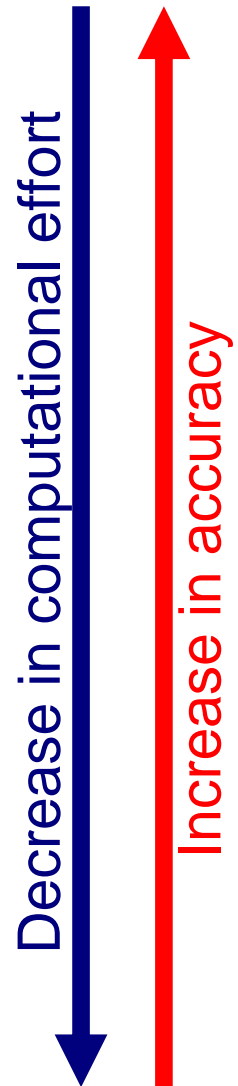
**EAM:** Metals, alloys; semi-empirical expressions (QM derived); Codes: IMD, LAMMPS, XMD and many others

**MEAM:** Silicon, metals and other covalently dominated materials (codes: IMD, CMDP)

**Tersoff:** Bond order potentials (covalent systems), simple

**Organic force fields (harmonic):** Proteins, organics etc., CHARMM, DREIDING, AMBER (codes: NAMD, GROMACS, CHARMM...)

**Pair potentials:** Noble gases (Ar) or model materials

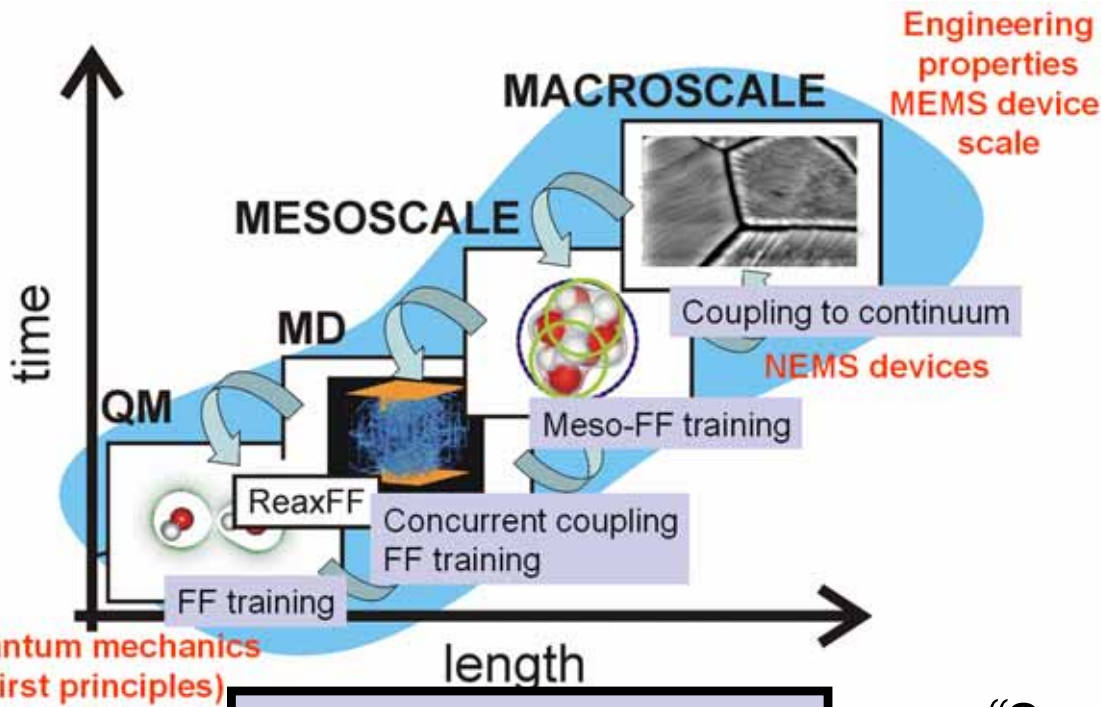
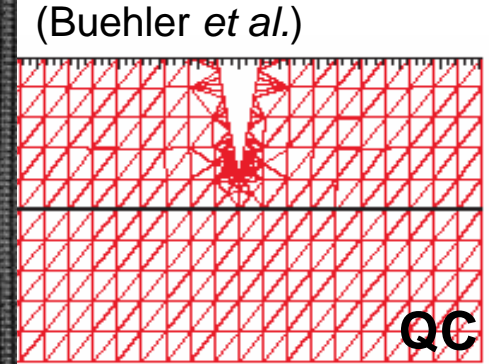
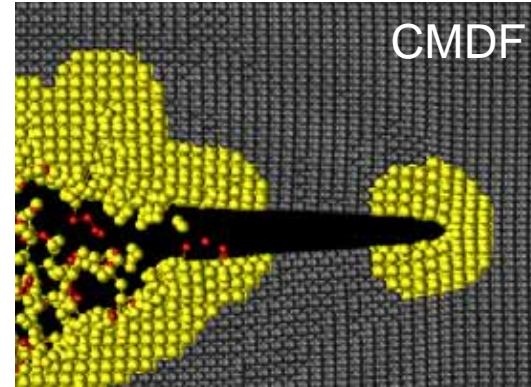
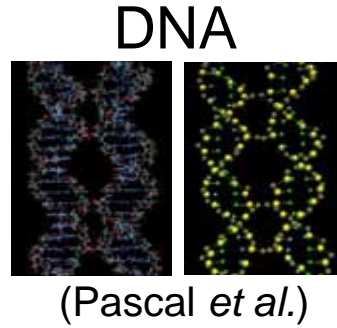
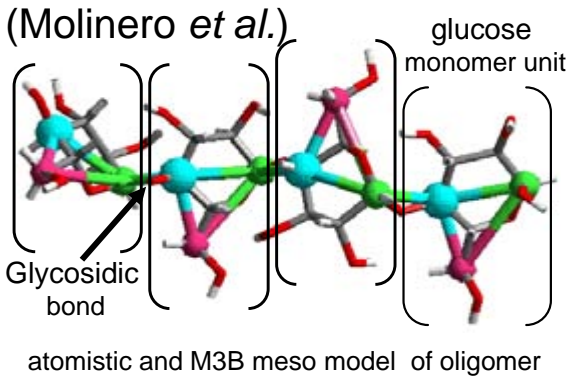


Less accuracy does not mean less science can be done

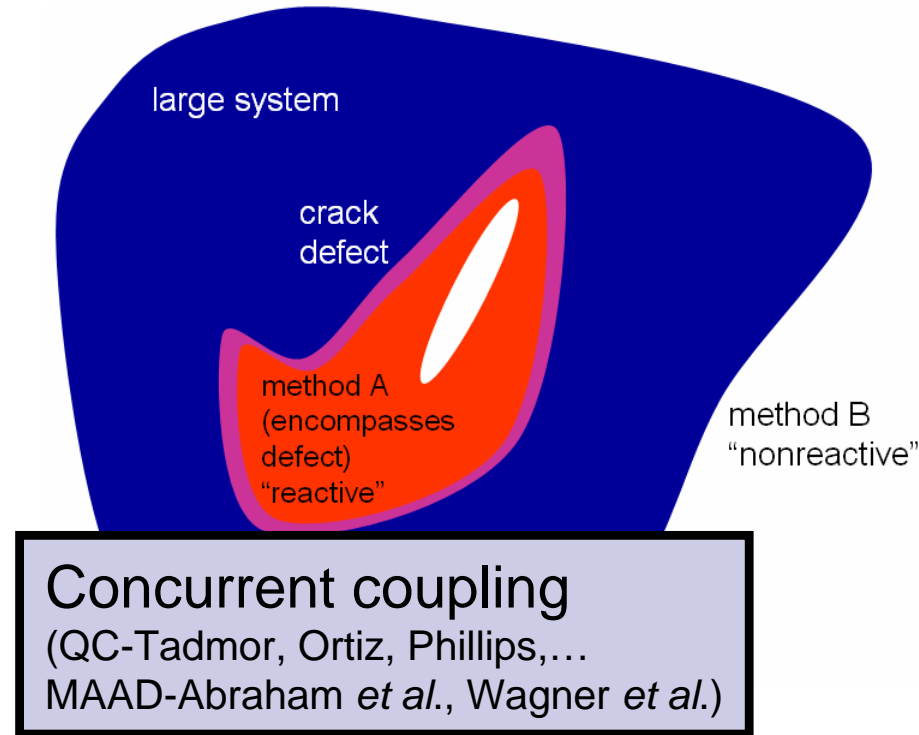




# Concurrent versus hierarchical multi-scale simulations



Hierarchical coupling

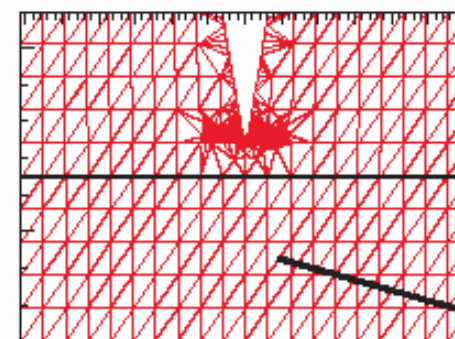
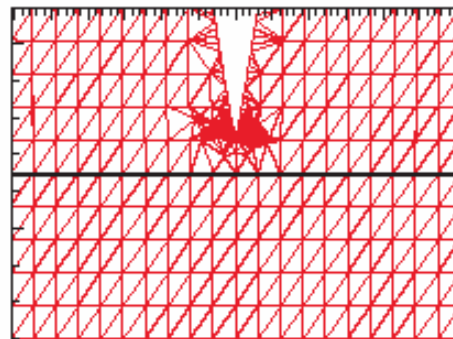
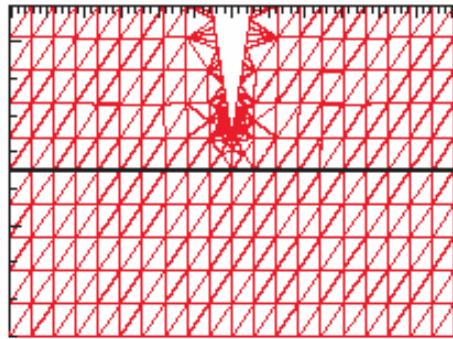


"Spatial variation of resolution and accuracy"

"finer scales train coarser scales"



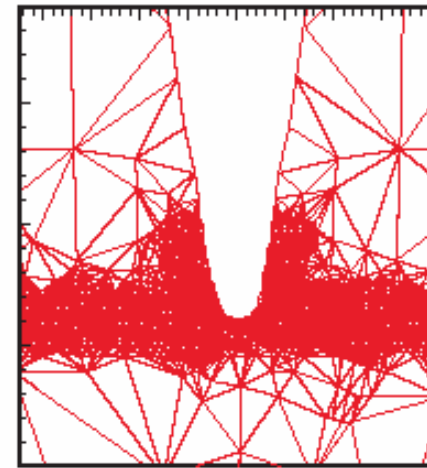
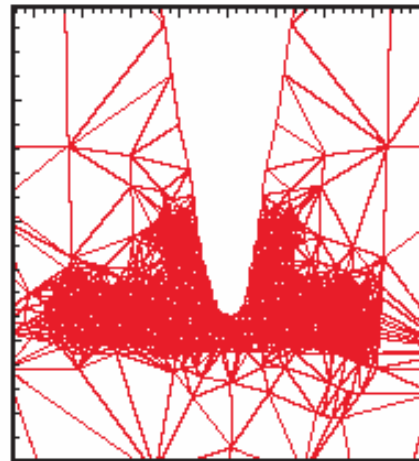
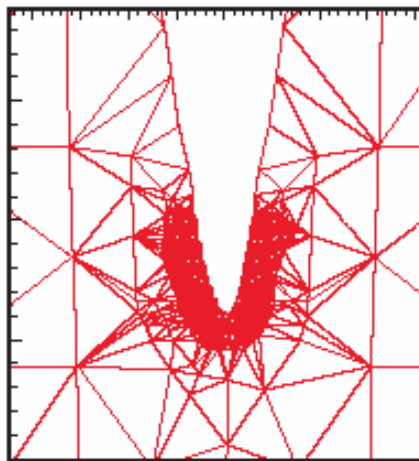
# The Quasi-Continuum (QC) Method



Thin copper film

rigid substrate

(a)



(b)

$y[111]$   
↑  
x [110]

Combine atomistic regions embedded  
in continuum region



# Atomic stress tensor: Cauchy stress



Virial stress:

$$\sigma_{ij} = \frac{1}{2} \sum_{\alpha, \beta} \left( -\frac{1}{r} \frac{\partial \phi}{\partial r} r_i r_j \Big|_{r=r_{\alpha\beta}} \right)$$

where  $r_i$  is the projection of the interatomic distance vector  $\mathbf{r}$  along coordinate  $i$ .

- We only consider the force part, excluding the part containing the effect of the velocity of atoms (the kinetic part).
- It was recently shown by Zhou *et al.* that the virial stress including the kinetic contribution is not equivalent to the mechanical Cauchy stress.
- The virial stress needs to be averaged over space and time to converge to the Cauchy stress tensor.

D.H. Tsai. Virial theorem and stress calculation in molecular-dynamics. *J. of Chemical Physics*, 70(3):1375–1382, 1979.

Min Zhou, A new look at the atomic level virial stress: on continuum-molecular system equivalence, Royal Society of London Proceedings Series A, vol. 459, Issue 2037, pp.2347-2392 (2003)

Jonathan Zimmerman *et al.*, Calculation of stress in atomistic simulation, MSMSE, Vol. 12, pp. S319-S332 (2004) and references in those articles by Yip, Cheung, .



# Atomic strain tensor



Atomic virial strain

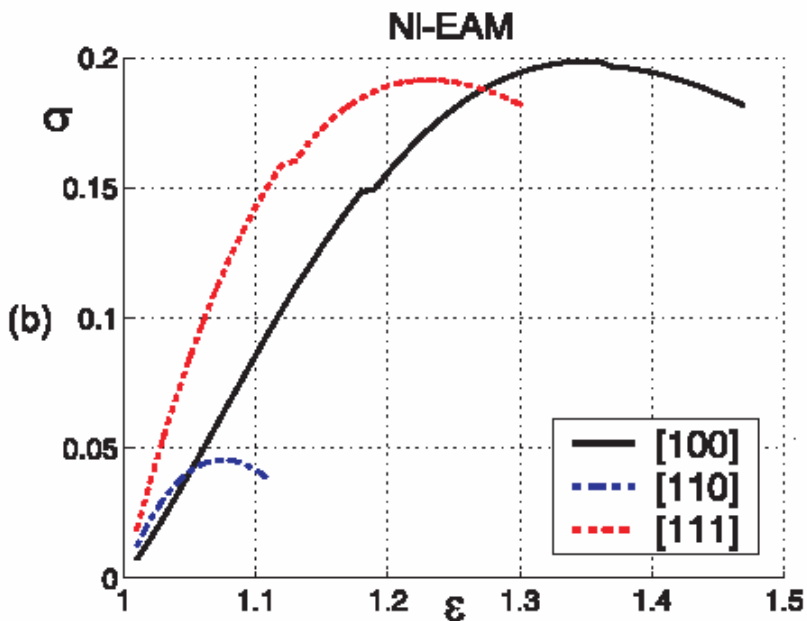
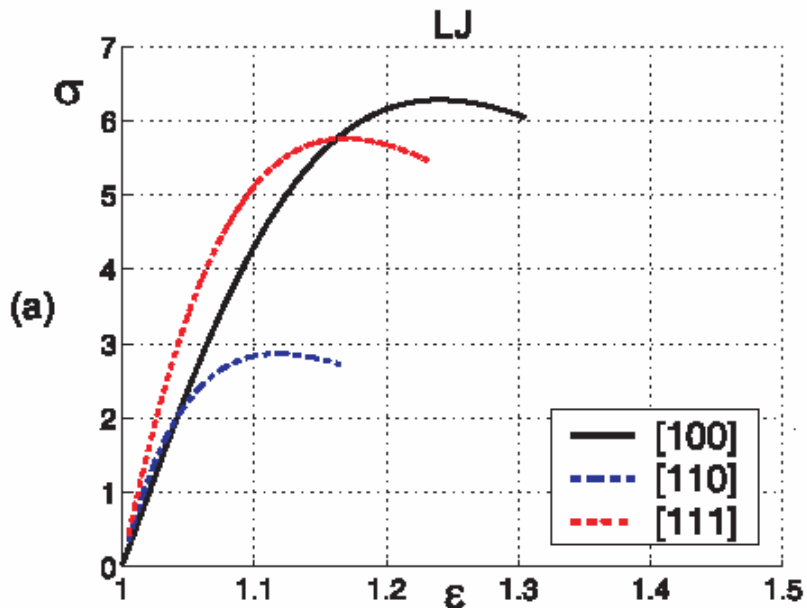
$$q_{ij}^l = \frac{1}{N} \sum_{k=1}^N \left( \frac{\Delta x_i^{kl} \Delta x_j^{kl}}{r_0^2} \right) \quad b_{ij}^l = \frac{N}{\lambda} q_{ij}^l = \frac{1}{\lambda} \sum_{k=1}^N \left( \frac{\Delta x_i^{kl} \Delta x_j^{kl}}{r_0^2} \right)$$

- The strain field is a measure of geometric deformation of the atomic lattice
- The local atomic strain is calculated by comparing the local deviation of the lattice from a reference configuration.
- Usually, the reference configuration is taken to be the undeformed lattice.
- In the atomistic simulations, the information about the position of every atom is readily available, either in the current or in the reference configuration and thus calculation of the virial strain is relatively straightforward.
- Unlike the virial stress, the atomic strain is valid instantaneously in space and time. However, the expression is only strictly applicable away from surfaces and interfaces.

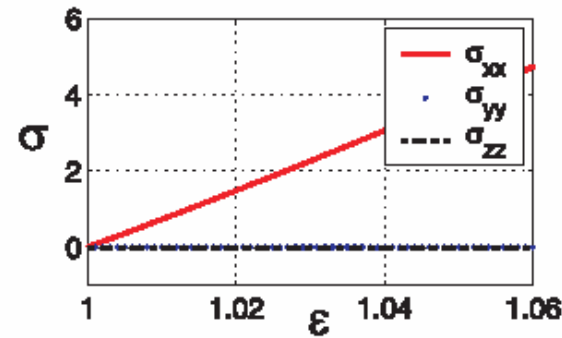




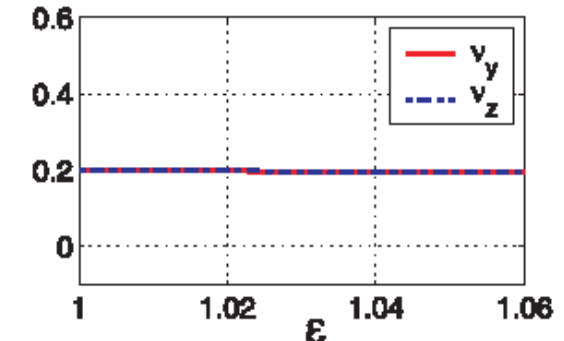
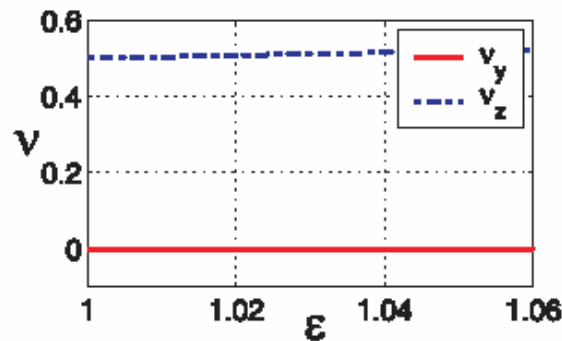
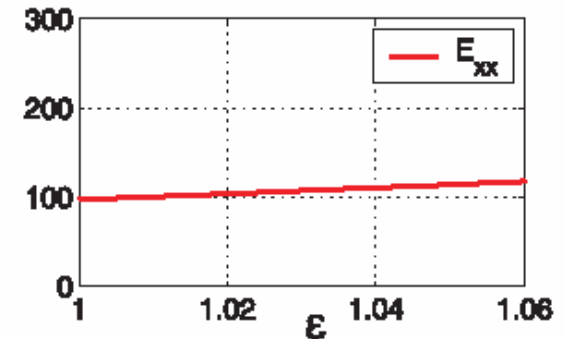
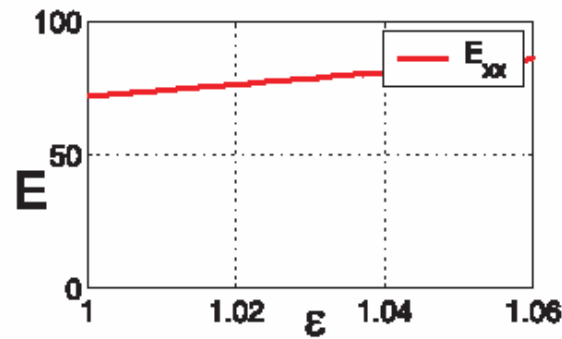
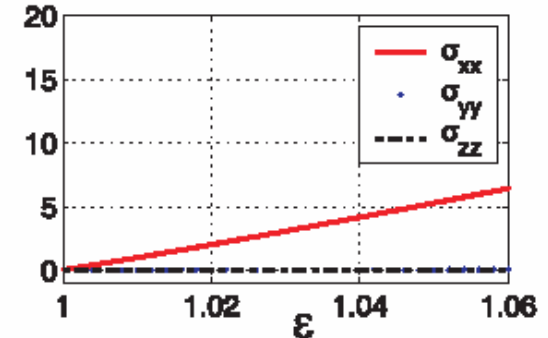
# Stress versus strain from atomistics...



uniaxial loading in [110] direction with Poisson relaxation



uniaxial loading in [111] direction with Poisson relaxation



Harmonic potential



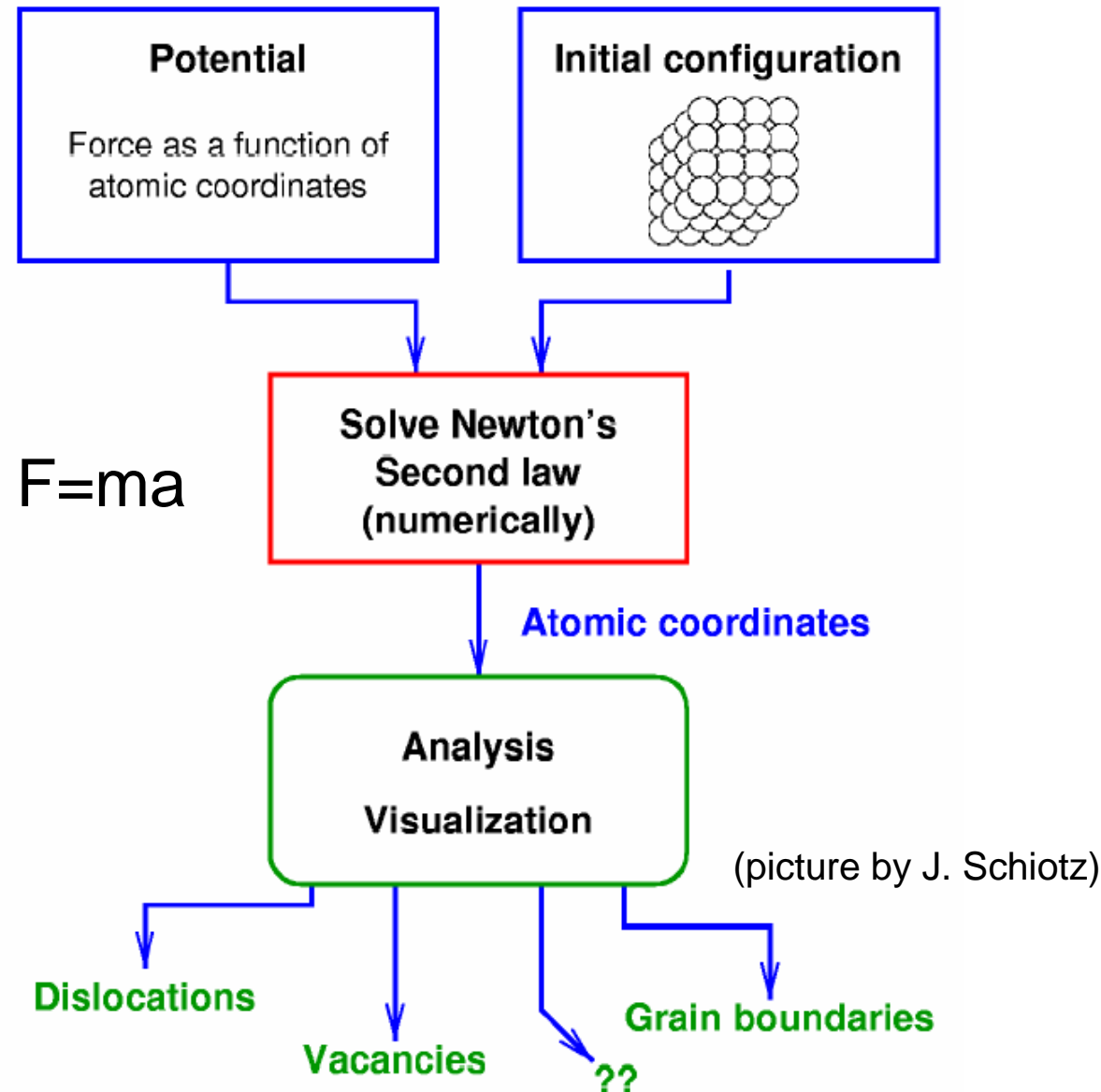
# Computation and numerical issues



# Typical simulation procedure



1. Pre-processing  
(define geometry, build crystal etc.)
2. Energy relaxation  
(minimization)
3. Annealing (equilibration  
at specific temperature)
4. “Actual” calculation; e.g.  
apply loading to crack
5. Analysis

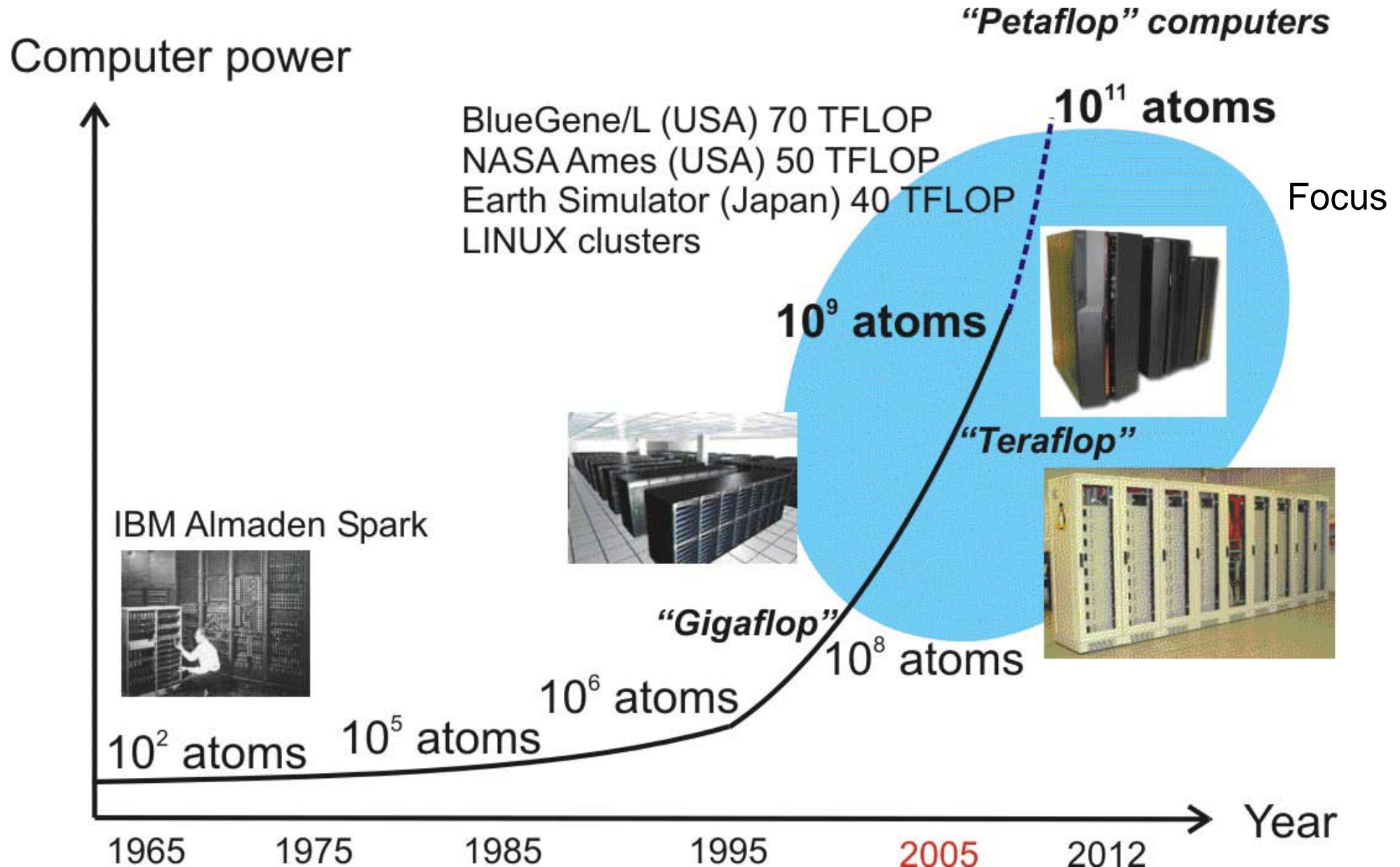


**Real challenge:**  
**Questions to ask and what to learn**



# Increase in computing power

## Classical molecular dynamics





# TOP500 List for November 2004



## TOP 5

### SUPERCOMPUTER SITES (November 2004)



1

#### BlueGene/L

DOE/IBM  
Rochester, USA  
BlueGene/L DD2  
Rmax: 70.72 TFlops



2

#### Columbia

NASA/Ames  
Mountain View, USA  
SGI Altix/Voltaire  
Rmax: 51.87 TFlops



3

#### Earth Simulator

Earth Simulator Center  
Yokohama  
NEC  
Rmax: 35.86 TFlops



4

#### MareNostrum

Barcelona Supercomputer Center  
Barcelona, Spain  
eServer BladeCenter JS20/Myrinet  
Rmax: 20.53 TFlops



5

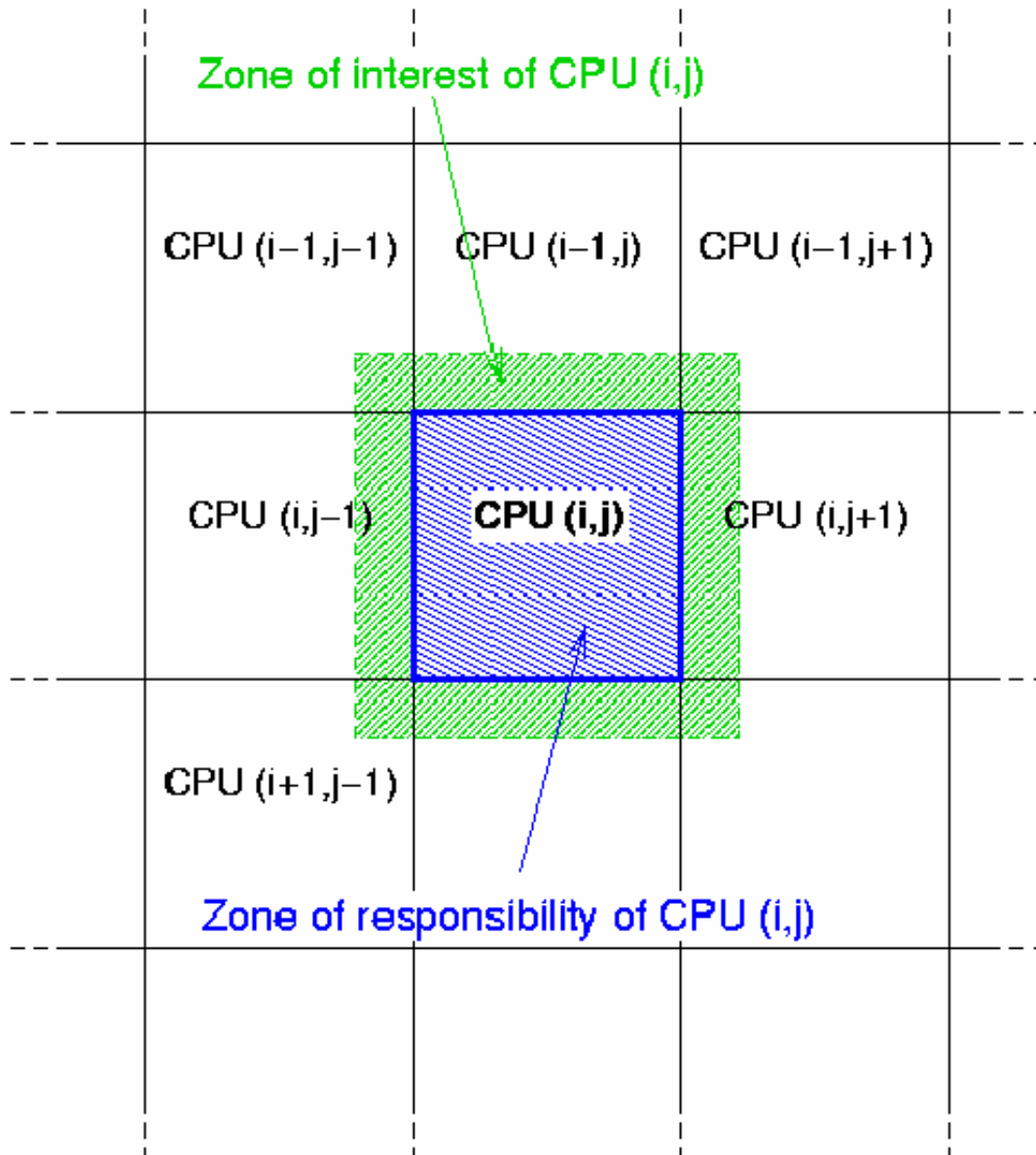
#### Thunder

Lawrence Livermore National Lab  
Livermore, USA  
Intel Itanium2 Tiger4/Quadrics  
Rmax: 19.94 TFlops

<http://www.top500.org>



# Parallel Molecular Dynamics



## Concept:

Divide the workload

No immediate long range interaction (only via dynamics)

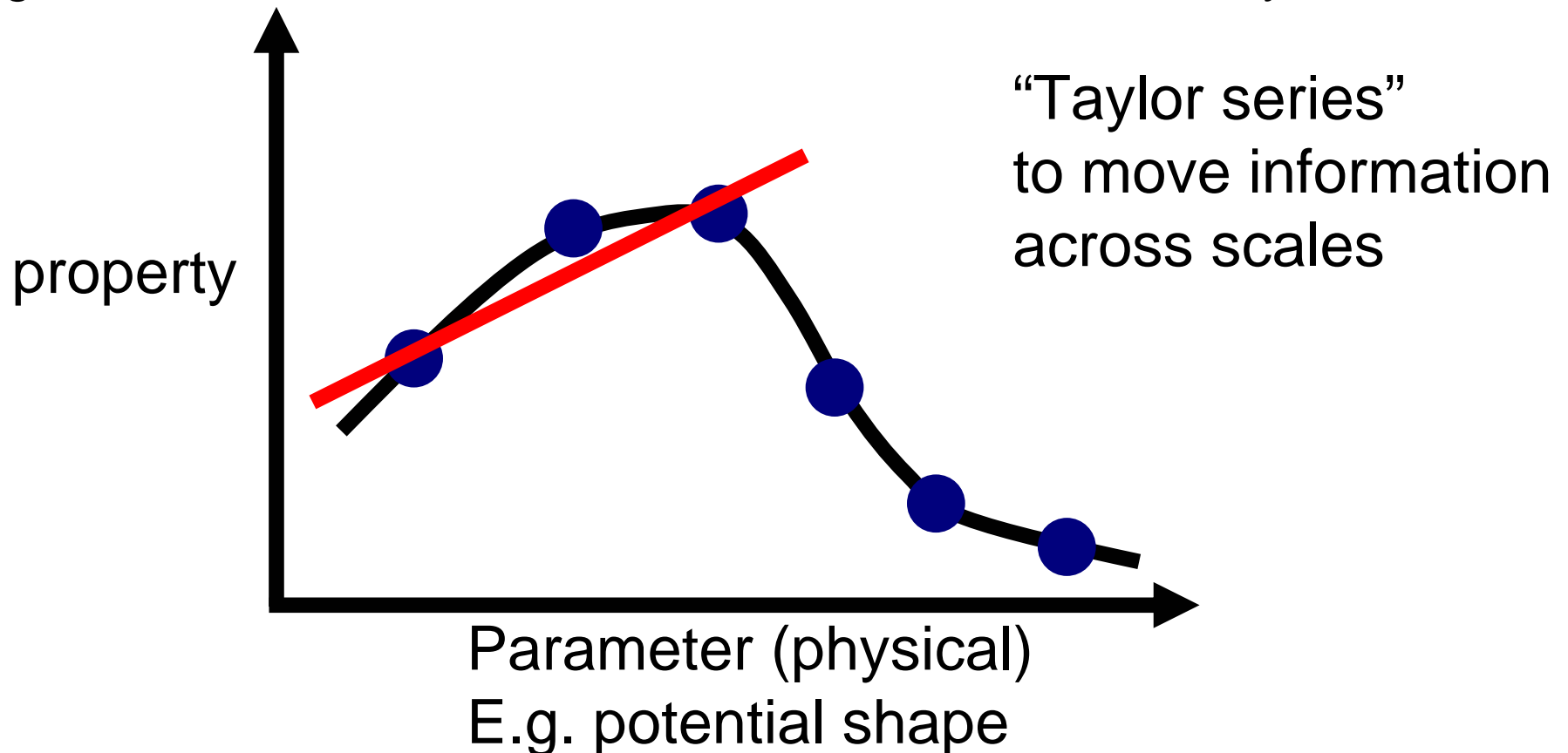
- Each CPU is responsible for part of the problem
- Atoms can move into other CPUs (migration)
- Need to know topology or the geometric environment on other CPUs (green region)



# Differential multi-scale modeling



- The strength of MD is not its predictive power (time scale limitations...)
- Rather use it in a differential way
- Hypothesis: MD only gives relative differential information
- Consequence: No quantitative number but only slope and thus additional integration needed to make information useful, use model systems







# Atomistic methods in mechanics



- Use MD methods to perform virtual experiments
- Computational microscope
- As long as valid, ideal method to gain fundamental understanding about behavior of materials
- Have intrinsic length scale given by the atomic scale (distance)
- Handles stress singularities intrinsically
- Ideal for deformation under high strain rate etc., not accessible by other methods (FE, DDD..)

# Experimental verification of intersonic cracking

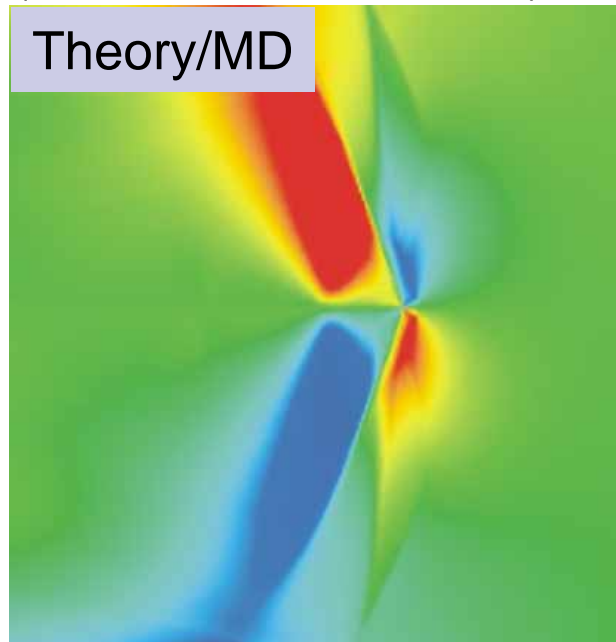
- Mike Marder's group at Univ. of Texas verified the phenomenon of intersonic cracking in a hyperelastic stiffening material (PRL, 2004)
- Agreement and confirmation of our theoretical predictions

## Cracks in Rubber Propagate Faster than the Speed of Sound

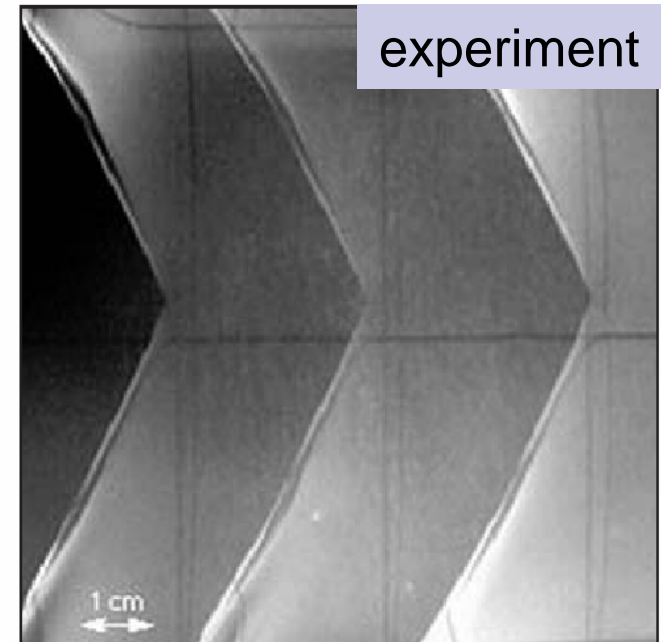
Since the classical work by Griffith, Inglis, and Irwin on the physics of cracking, one of the most fundamental questions associated with crack dynamics is the maximum speed that cracks can propagate. Depending on the type of loading (e.g., tensile, shear, or antiplane shear), there is a unique maximum speed cracks can achieve. For tensile-loaded cracks, theory predicts that this limiting speed is the Rayleigh wave speed, the speed of elastic waves on a surface. Recent theoretical work, including atomistic simulations, has challenged this classical view. Now, P.J. Petersan and co-workers from the University of Texas at Austin have shown experimentally that tensile-loaded cracks in rubber can actually propagate faster than the Rayleigh wave speed and even break the sound barrier.

As reported in the July issue of *Physical Review Letters* (105504), Petersan and colleagues identified the intersonic crack speed by the observation of shock fronts near the crack tip by high-speed photogra-

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



(Petersan *et al.*, PRL, 2004)



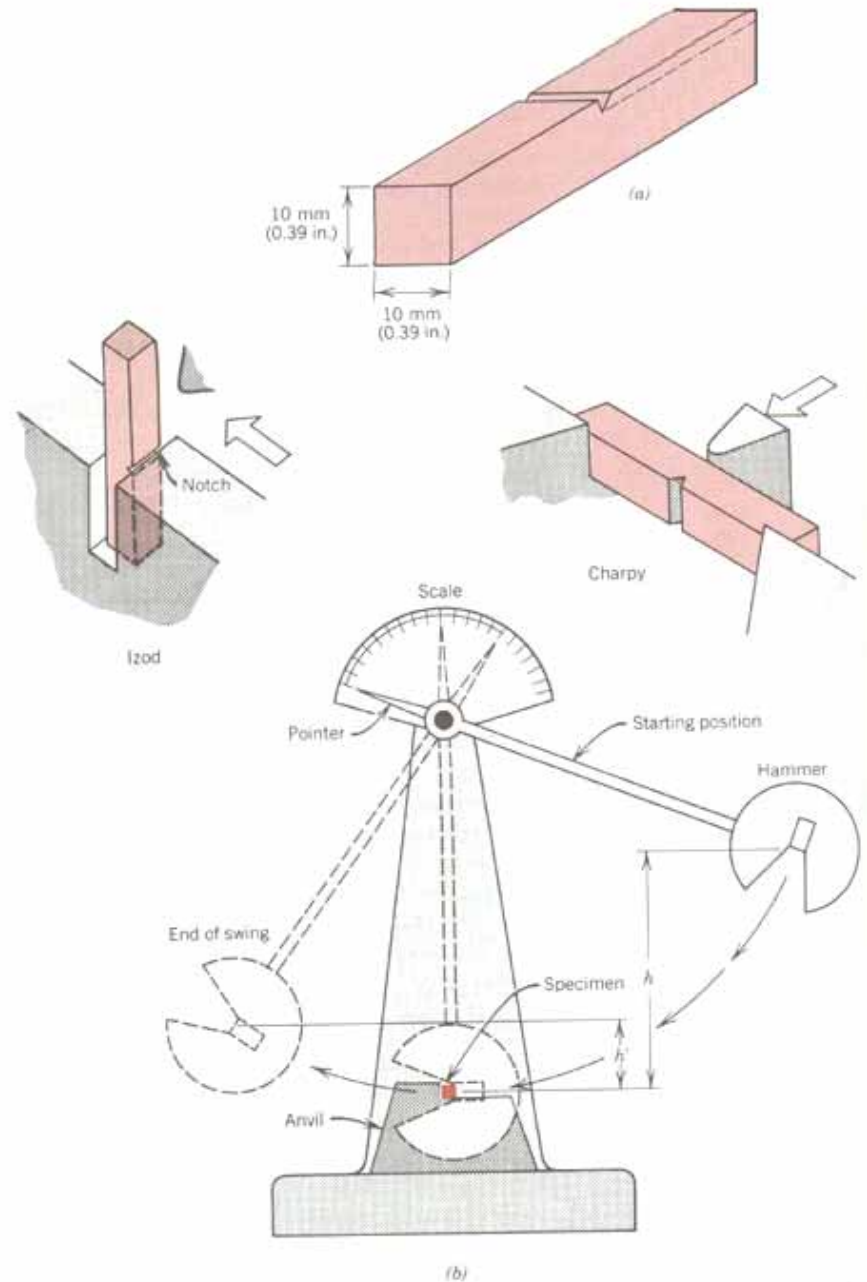
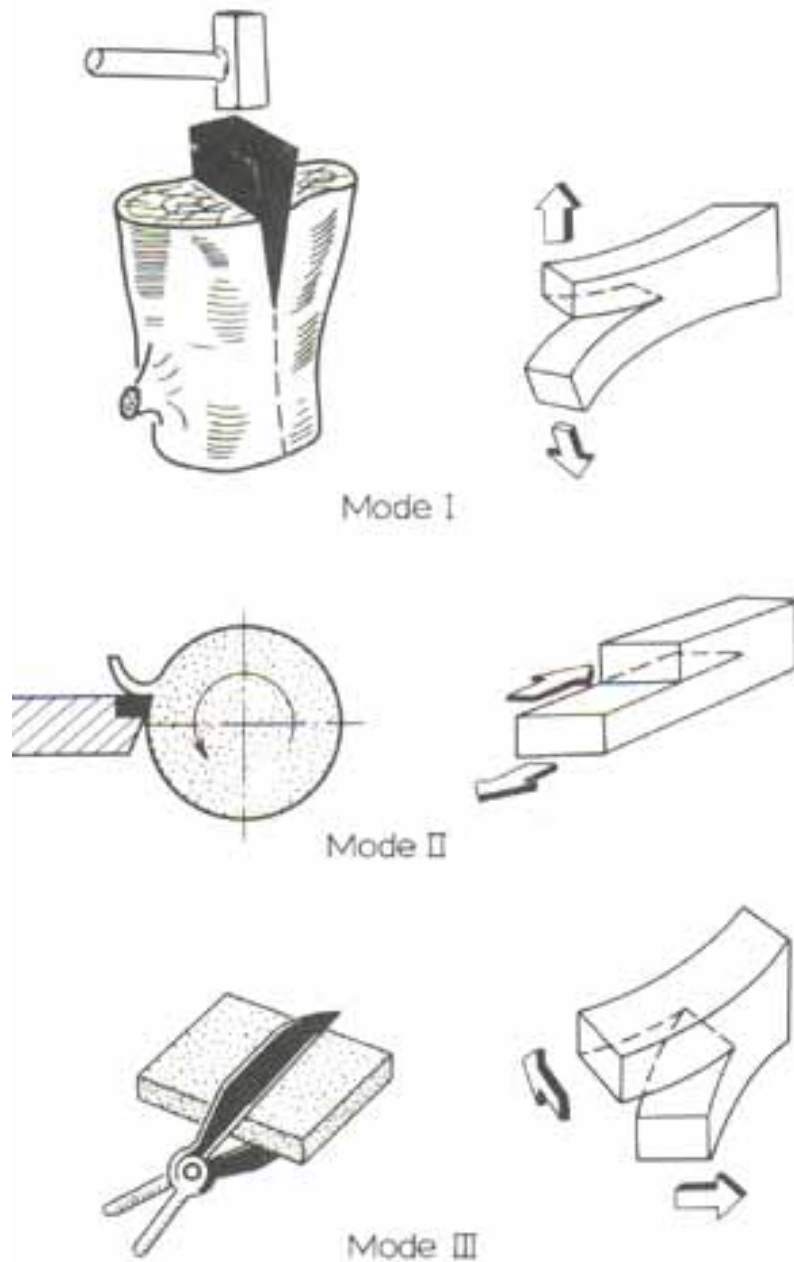
Multiple-exposure photograph of a crack propagating in a rubber sample ( $\lambda_x = 1.2$ ,  $\lambda_y = 2.4$ ); speed of the crack,  $\sim 56$  m/s (Petersan *et al.*).



# Some example applications



# How "stuff" deforms?

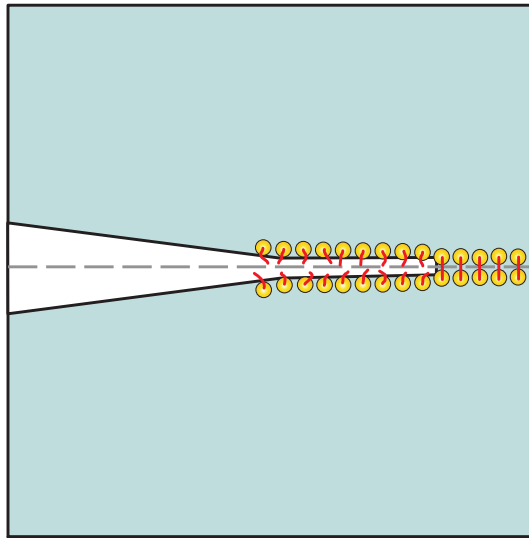




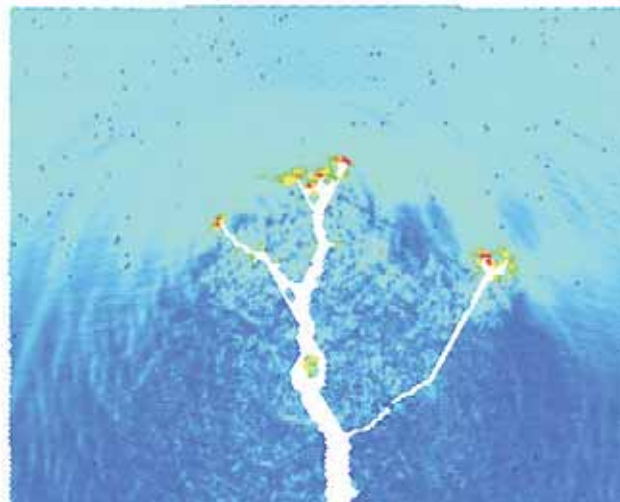
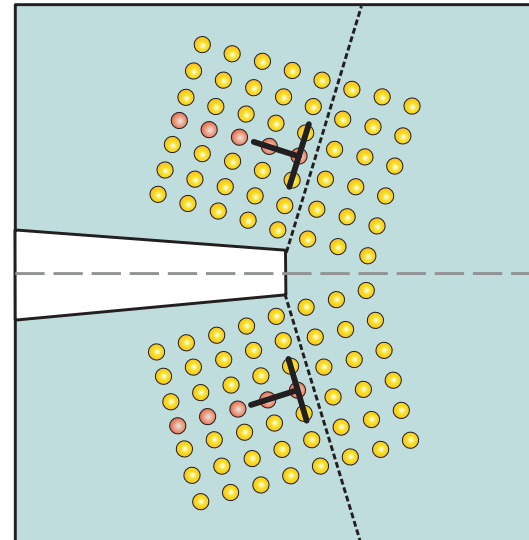
# Ductile versus brittle materials



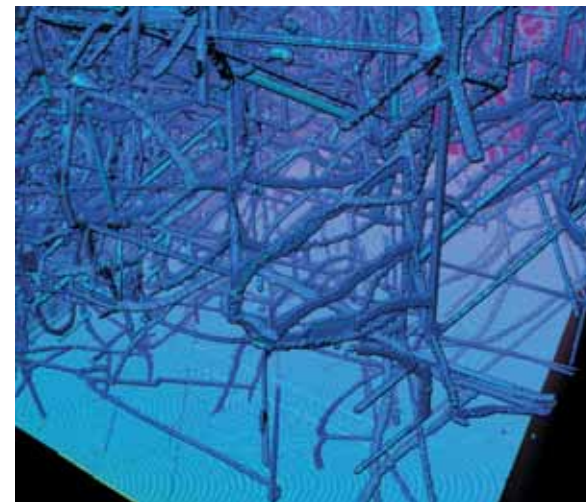
brittle



ductile



(a)



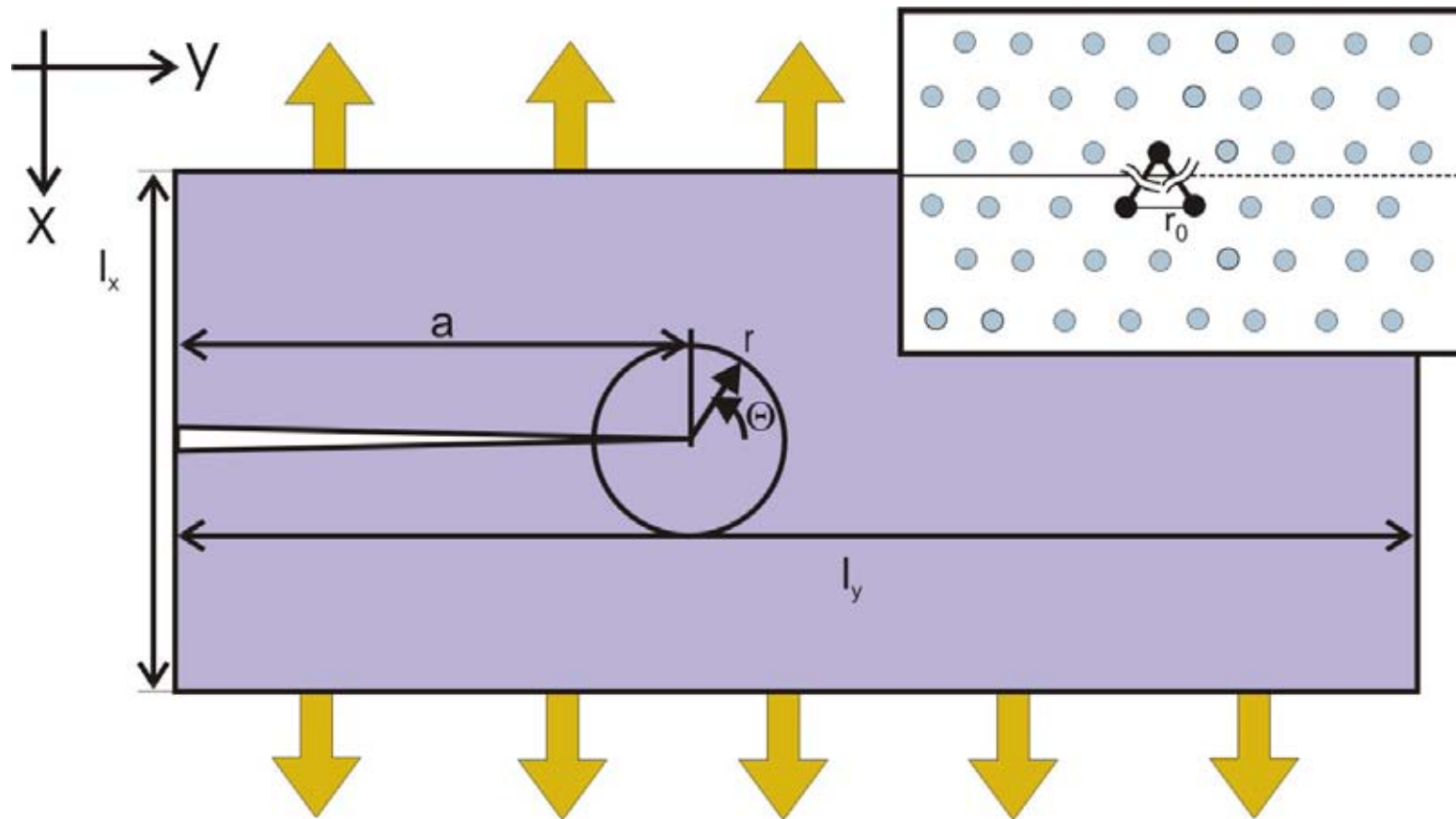
(b)

(Buehler, 2004)





# Geometry of fracture simulations



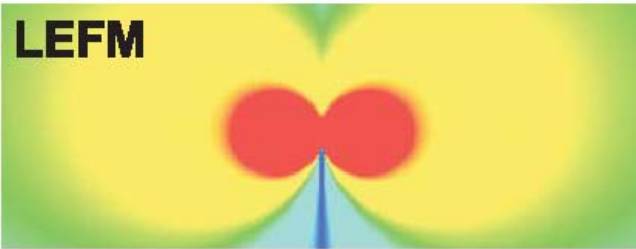
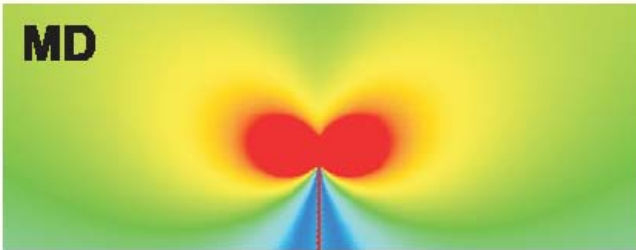
- Large-scale atomistic models with up to 70,000,000 atoms
- Simple model potential (next slide)



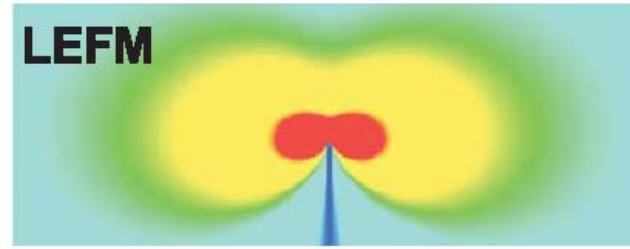
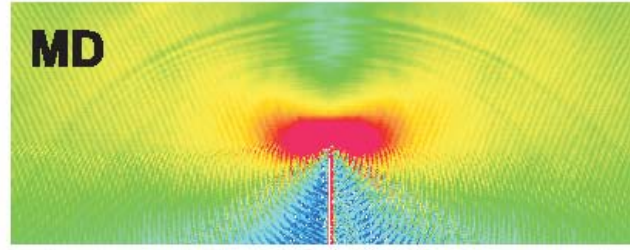
# Strain field close to cracks



$v/c_r=0$

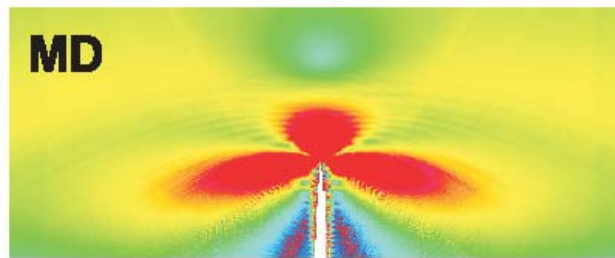


$v/c_r=0.5$



Atomic virial strain

$v/c_r=1$



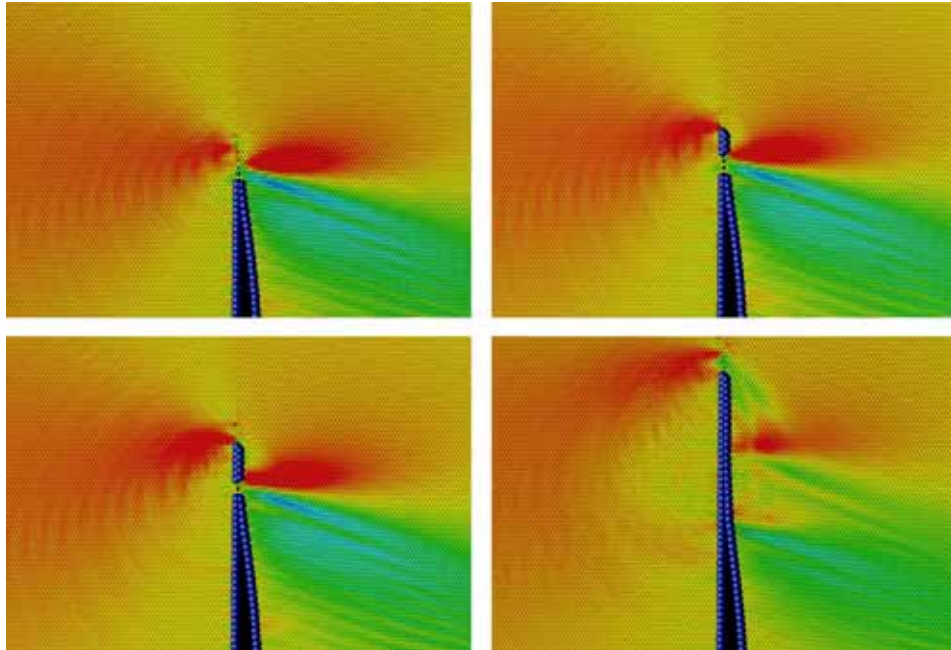
$$\sigma_{ij}(\Theta, v) = \frac{K_I(t, v)}{\sqrt{2\pi r}} \Sigma_{ij}(\Theta, v) + \sigma_{ij}^{(1)} + O(1)$$

(e.g. Freund, 1990)

Result: Reasonable agreement

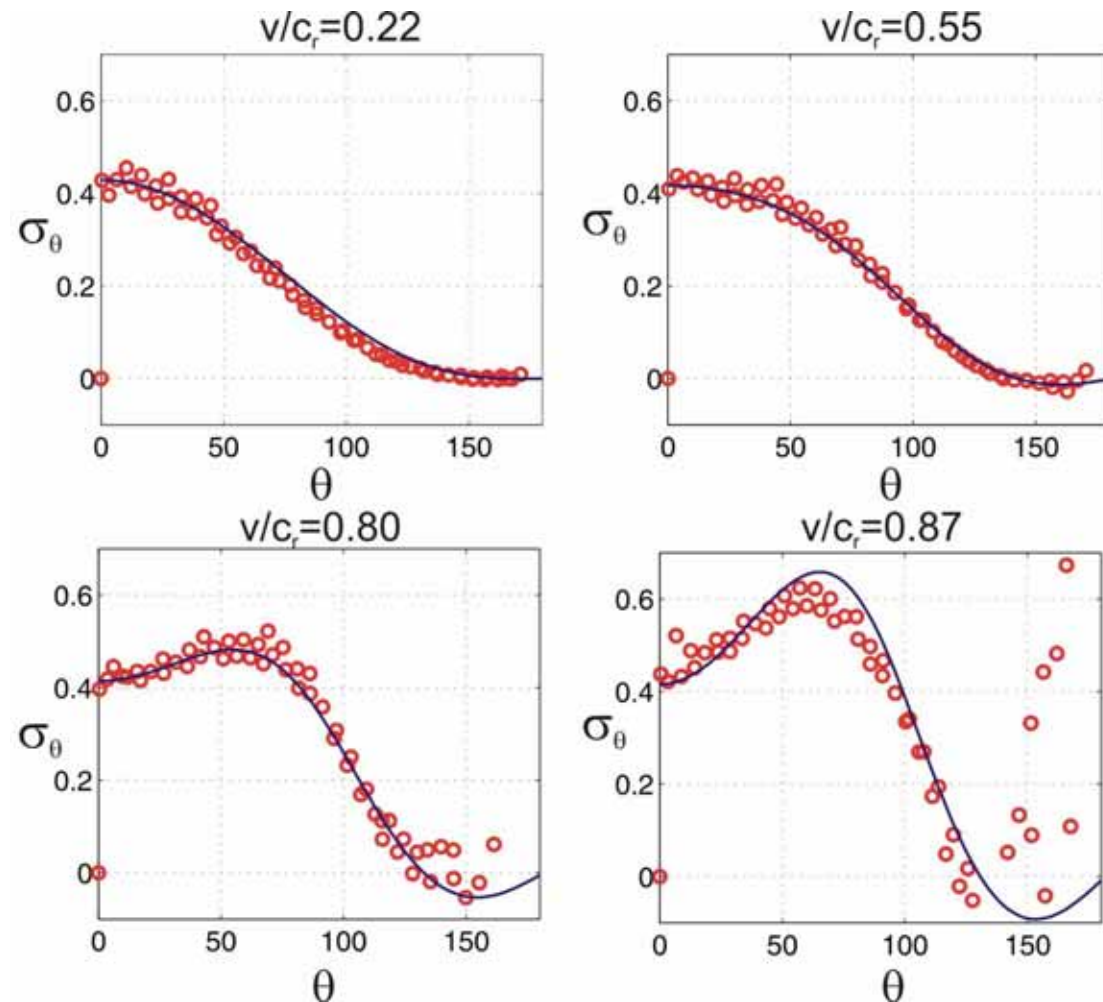


# Stress field close to cracks



## Shear stress near a crack at a bimaterial interface

(Buehler *et al.*, 2006)



## Hoop stress near a moving crack

(Buehler and Gao, Nature, to appear)



# Increase in computing power: Parallelization



**2000**

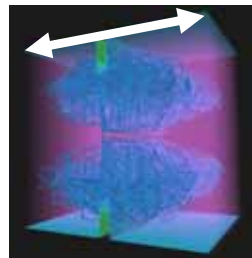
1,000,000,000  
particles  
10 TFLOP  
computers

**2005**

70,000,000,000  
particles  
70 TFLOP  
computers



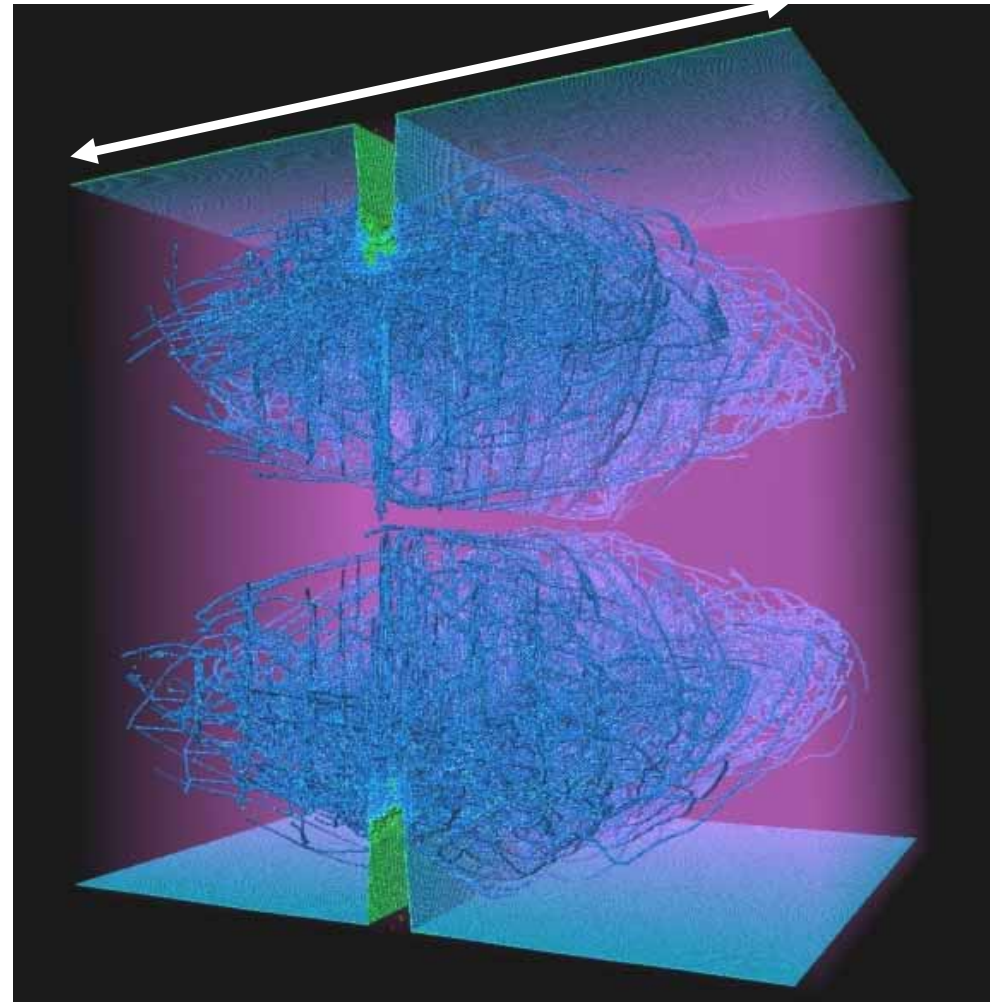
0.3  $\mu\text{m}$



1.2  $\mu\text{m}$



5  $\mu\text{m}$

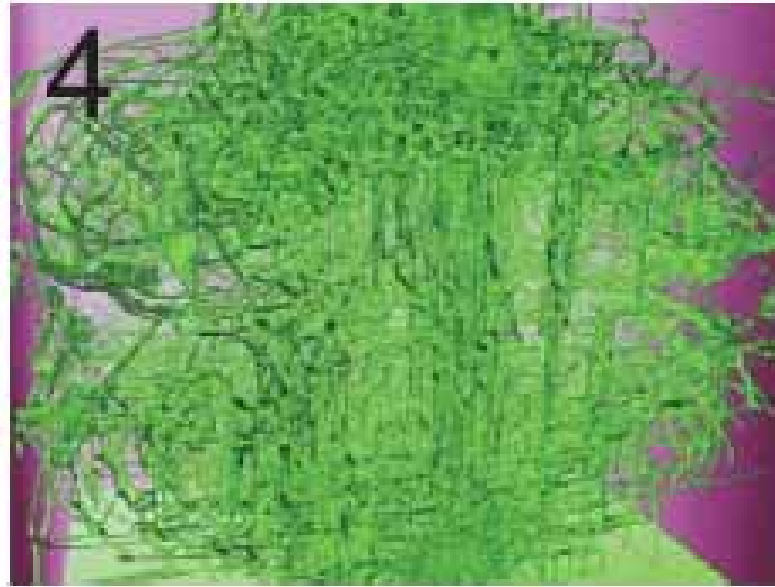
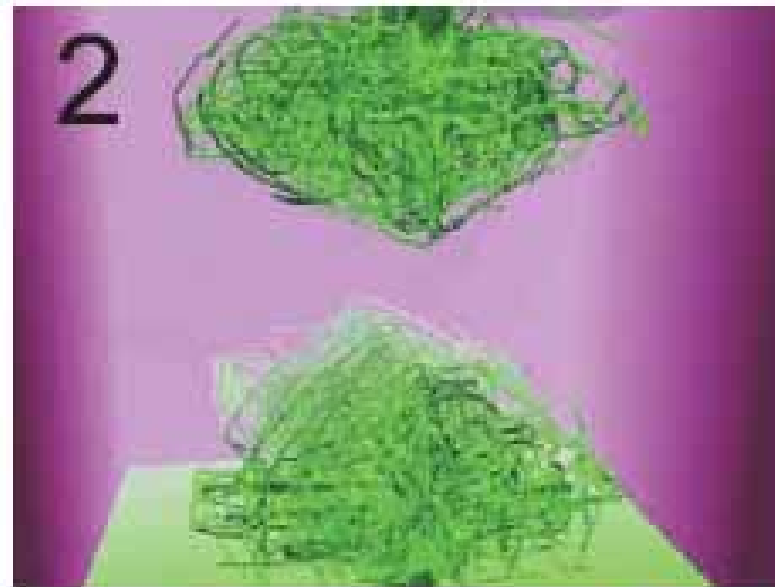


**2010**

7,000,000,000,000 particles  
1,000 TFLOP computers



# A simulation with 1,000,000,000 particles

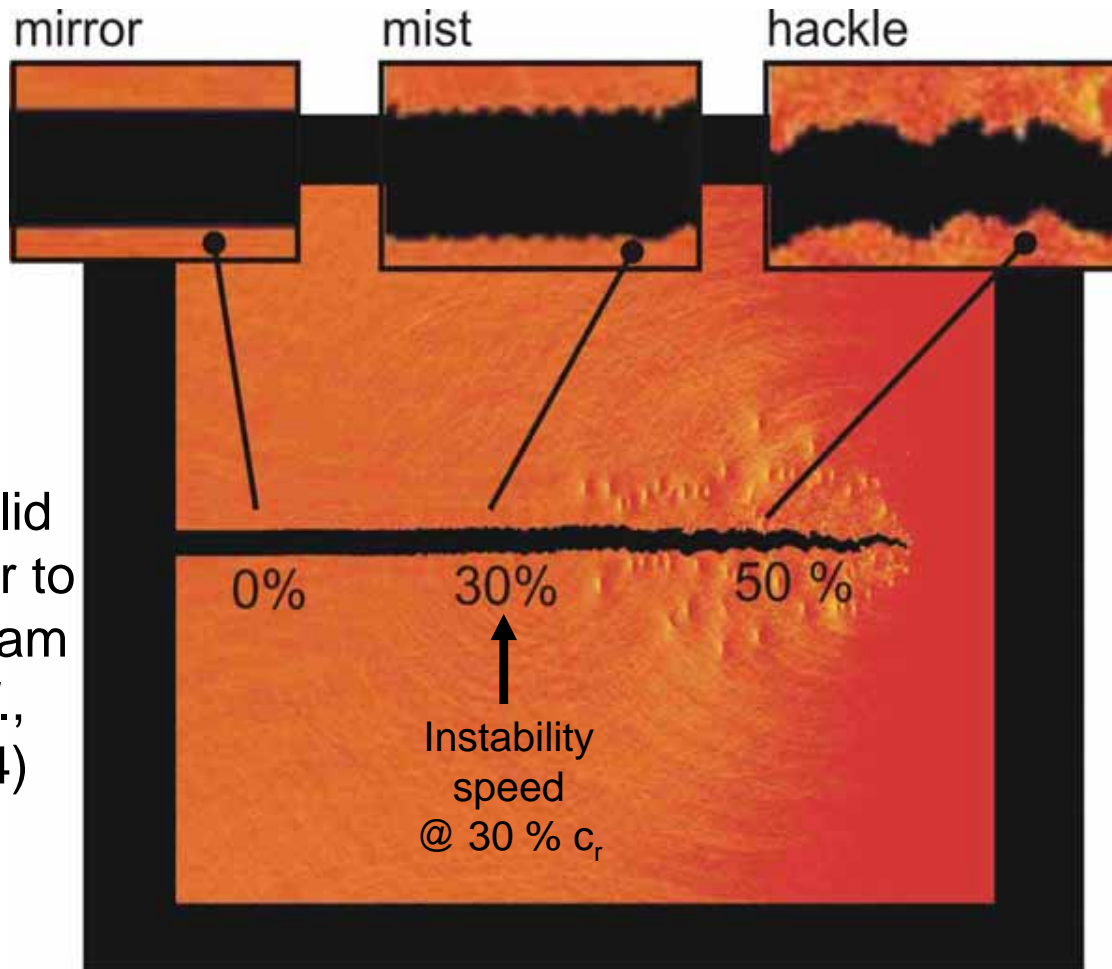


LJ  
potential...  
(simple  
interaction  
but VERY  
complex  
behavior!!)





# LJ in 2D... model system for brittle material



**Why 30% versus 73%?**

Does hyperelasticity play the governing role?

**Attempts of explanation:**

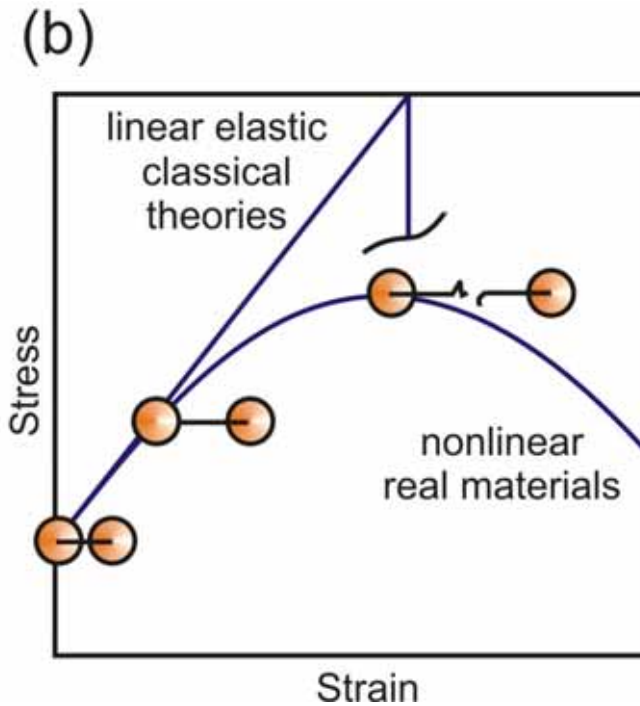
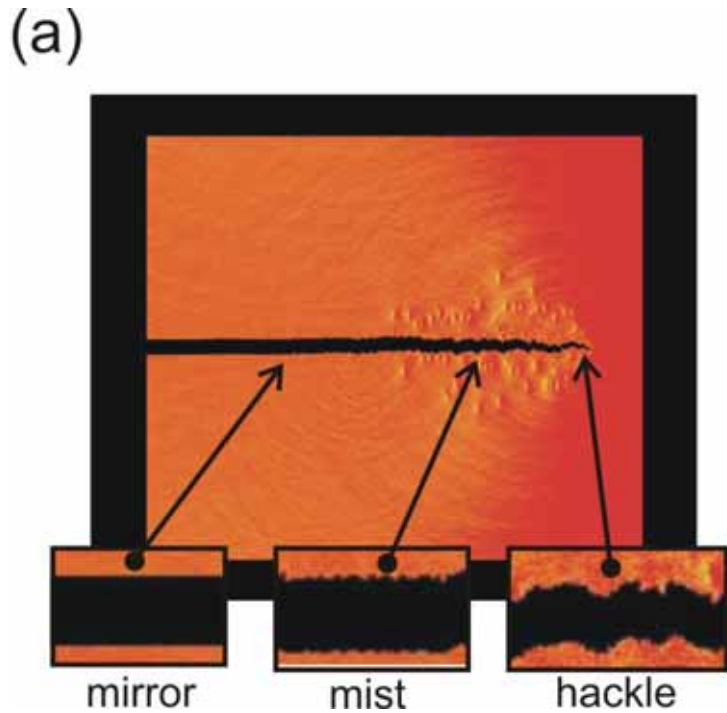
- Yoffe (linear elasticity, 1951)
- Gao (purely hyperelastic, 1996)
- Marder (lattice models, 1992-2000)
- Abraham (lattice vibration, 1994)

LJ-solid  
(similar to  
Abraham  
*et al.*,  
1994)

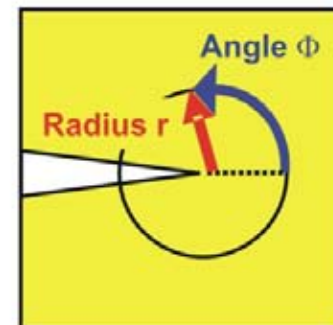
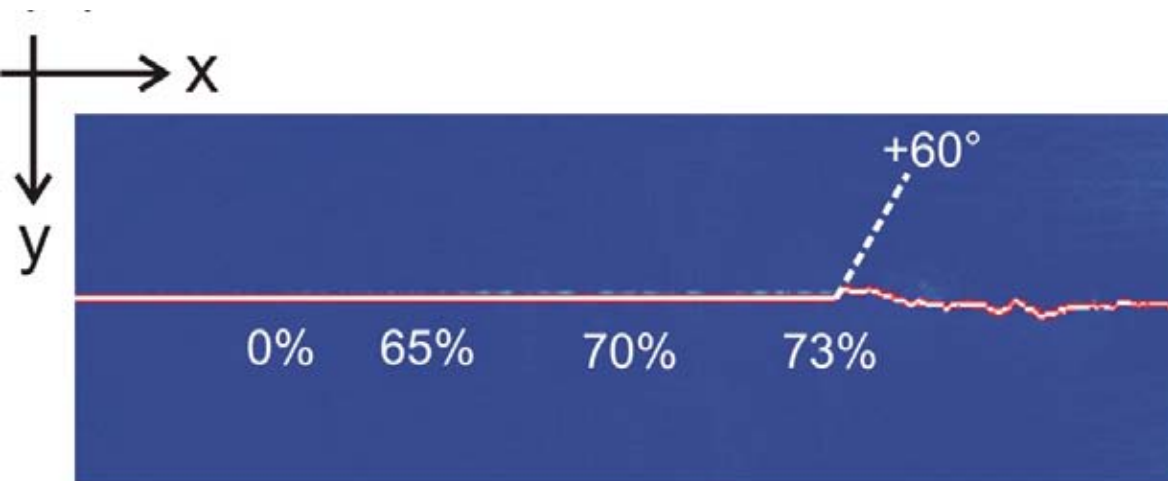
Critical speed for onset of surface roughening=instability speed



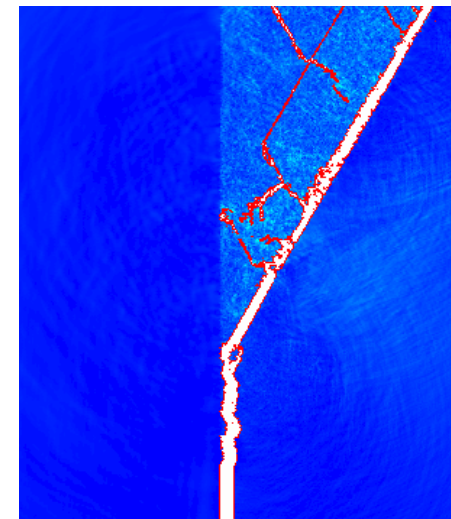
# Dynamical crack tip instabilities



- Developed new model to include material nonlinearities into instability theory



Interface fracture

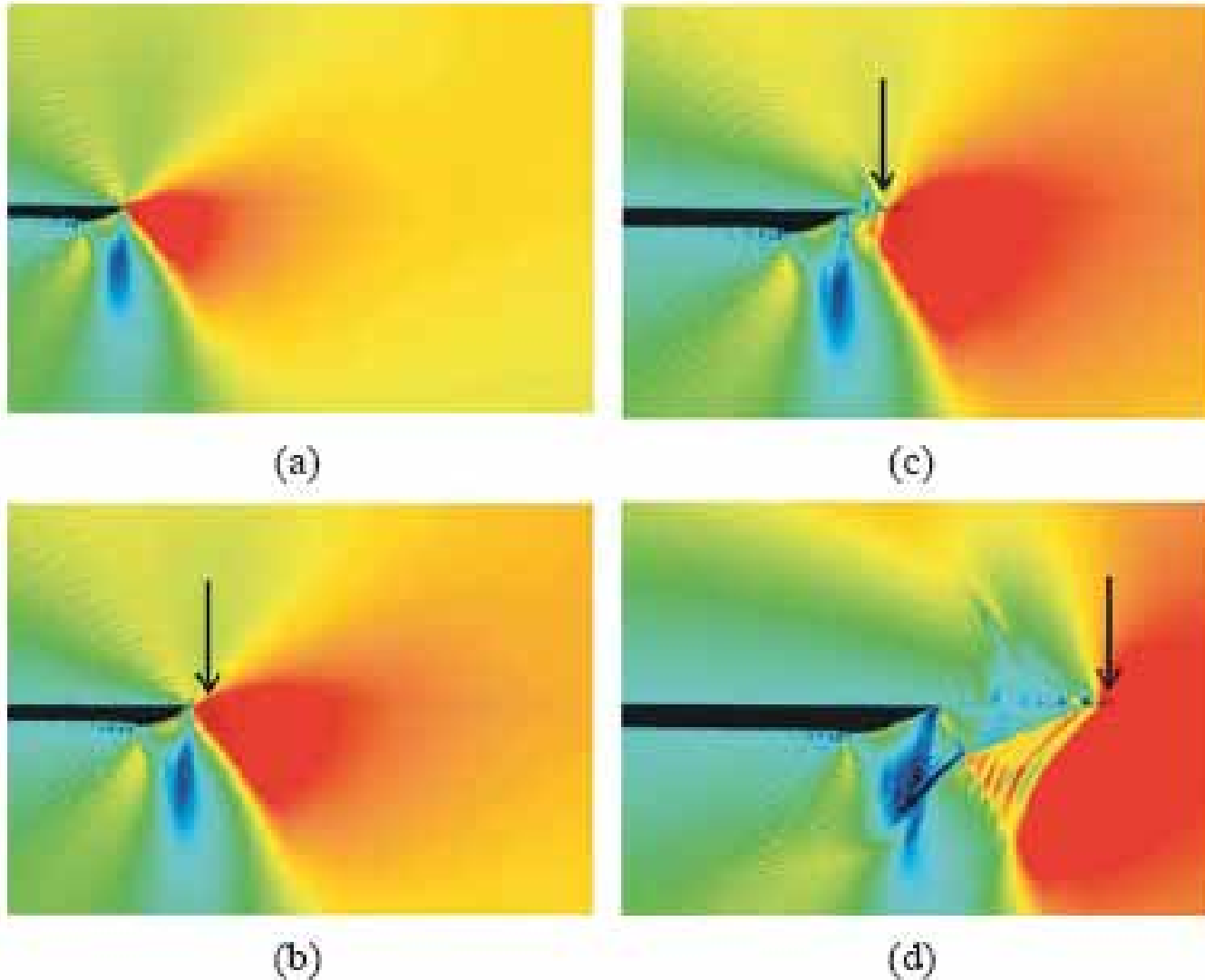


(Buehler and Gao, Nature, 2005 (to appear))

2005 Markus J. Buehler, CEE/MIT



# Supersonic interface cracking



- Shear dominated loading
- Bimaterial interface (upper part: stiff, lower part: soft)

(Buehler *et al.*, JCIE, 2005)

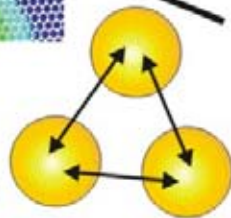
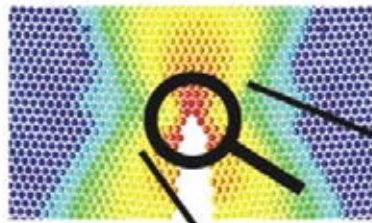
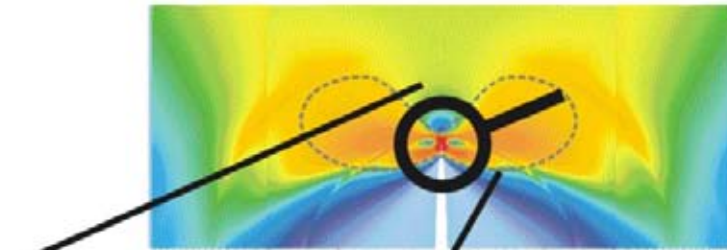


# Cross-scale interactions: Brittle fracture

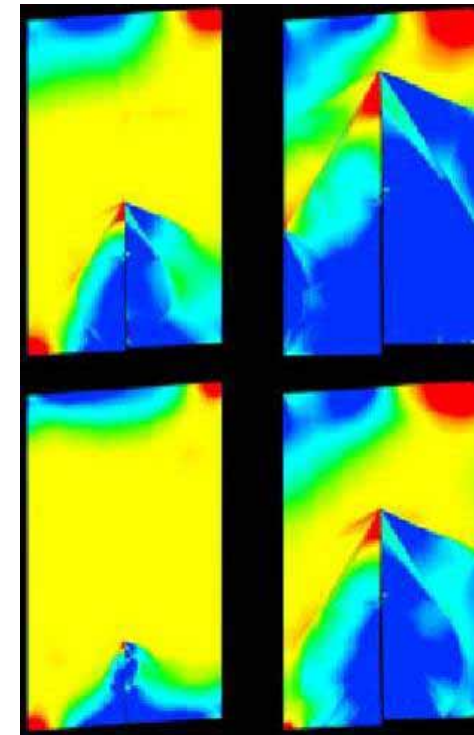
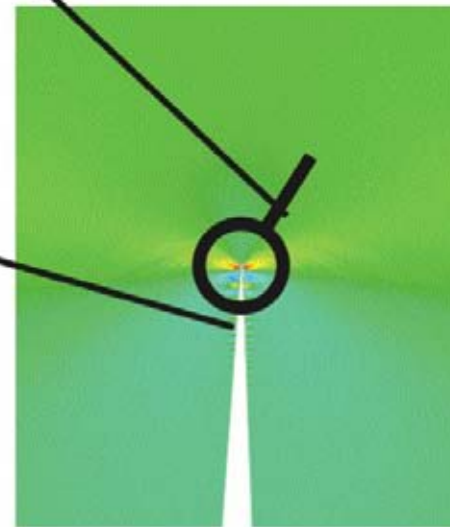
$10^{-8}$ m *energy flow*  
material nonlinearities

**engineering  
scale**

$10^{-6}$ m  
macroscale



$10^{-10}$ m  
atomic scale



Supersonic fracture  
(Buehler et al.)

$10^{-9}$ m  
breaking of  
atomic bonds  
nanoscale

*cohesive laws*

**quantum  
mechanics**

In brittle fracture, the macroscopic behavior of the materials depends on its underlying atomic interaction across several hierarchies of scales

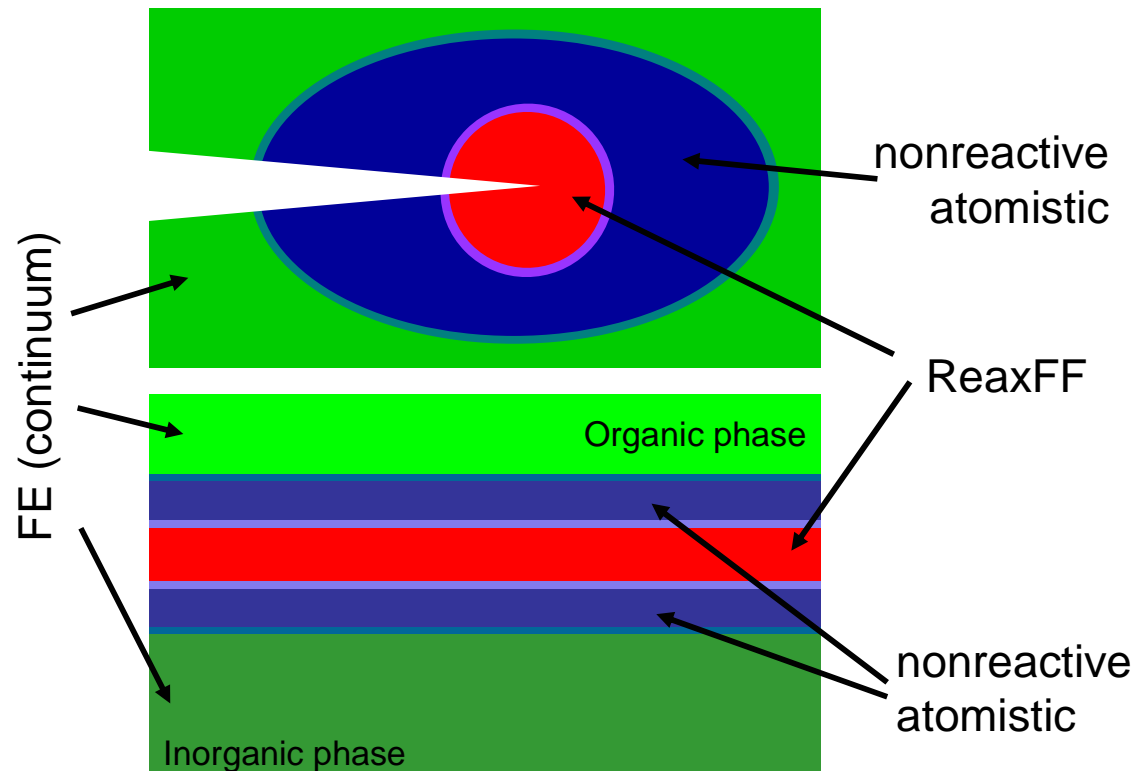
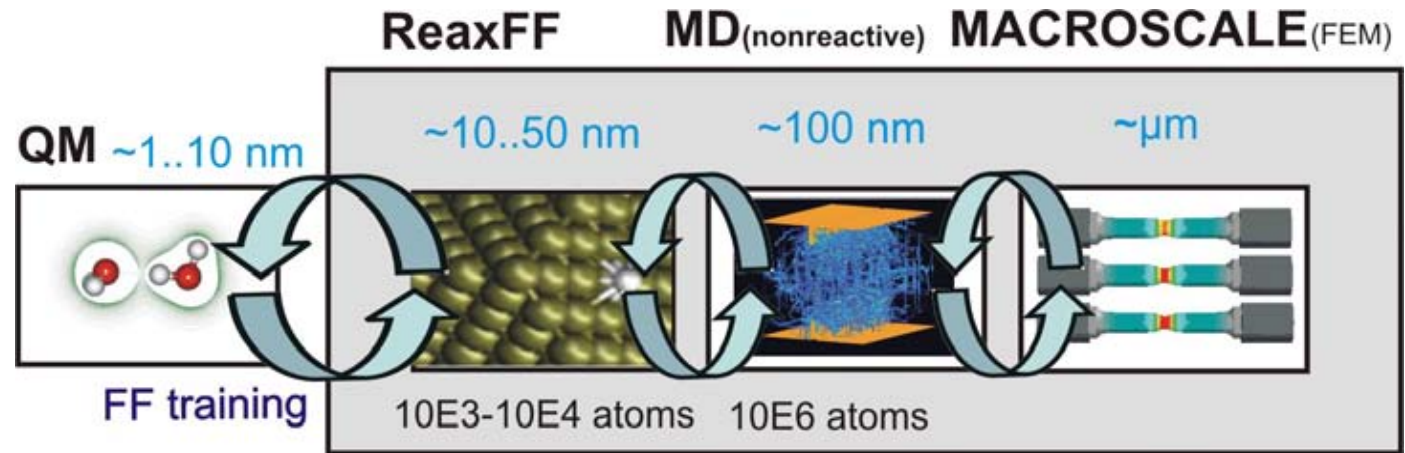




# Concurrent multi-scale simulations



Concurrent integration of various scales and paradigms

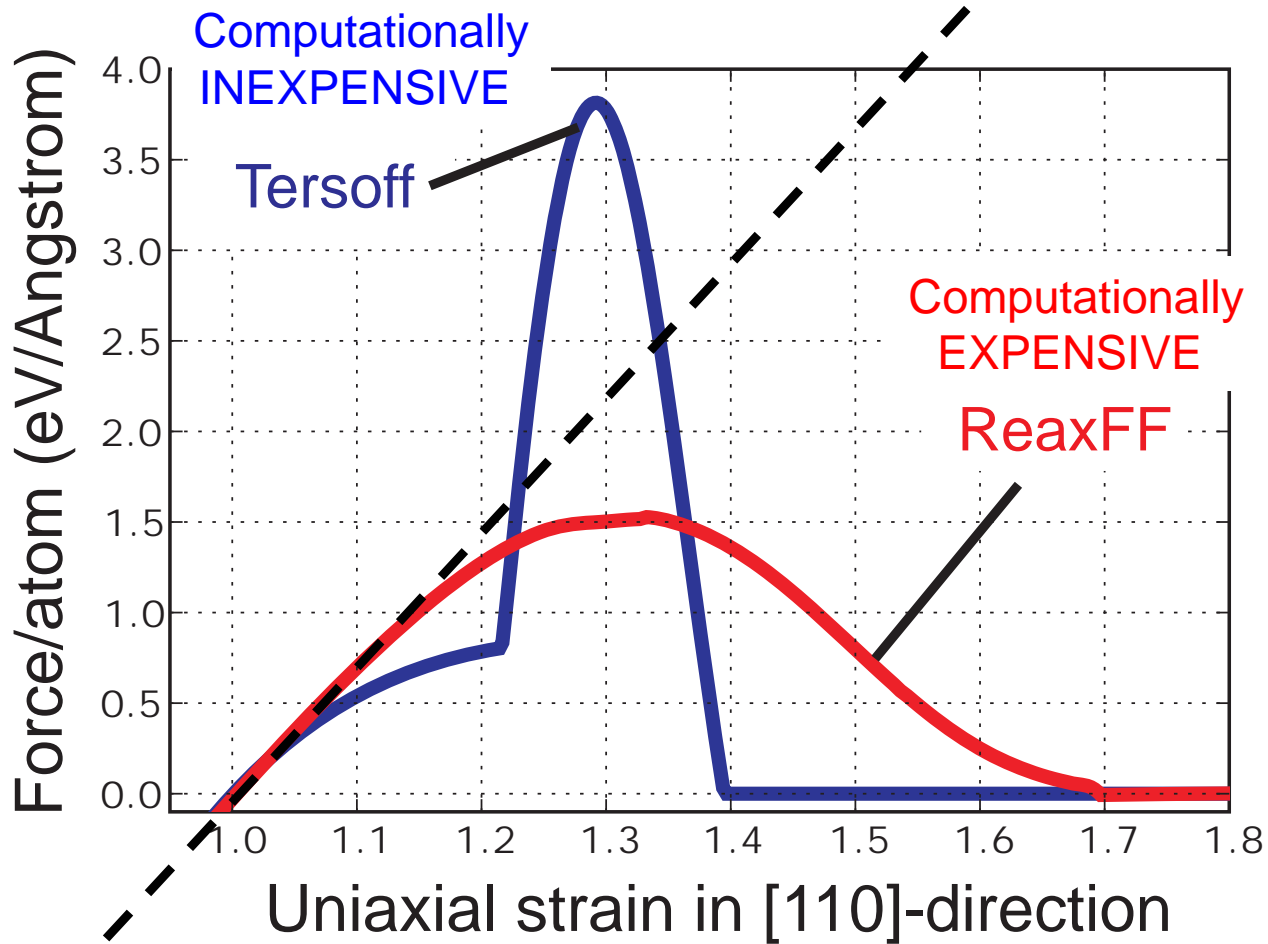


- Concurrent FE-atomistic-ReaxFF scheme in a crack problem (crack tip treated by ReaxFF) and an interface problem (interface treated by ReaxFF).
- Highlighted transition regions as handshake domains between different scale and methods.





# Example for code coupling: Concept of mixed Hamiltonian

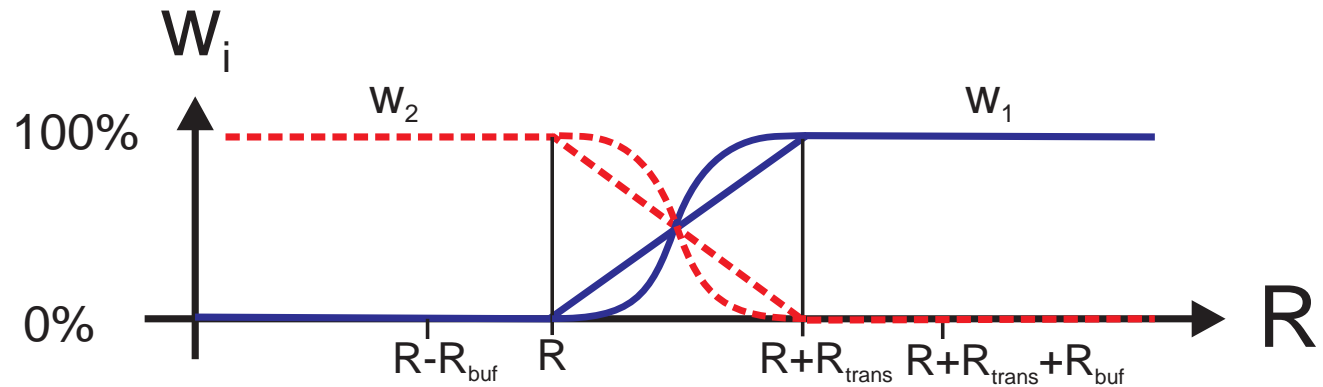
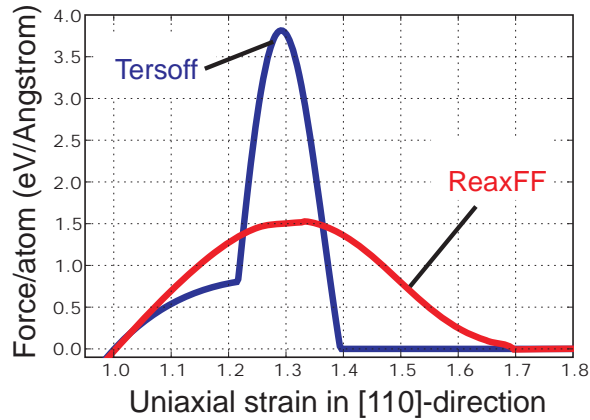


- Schematic showing the coupling of reactive and nonreactive potentials
- The simpler nonreactive potential is trained to resemble the reactive potential for small deviations from the equilibrium configuration.

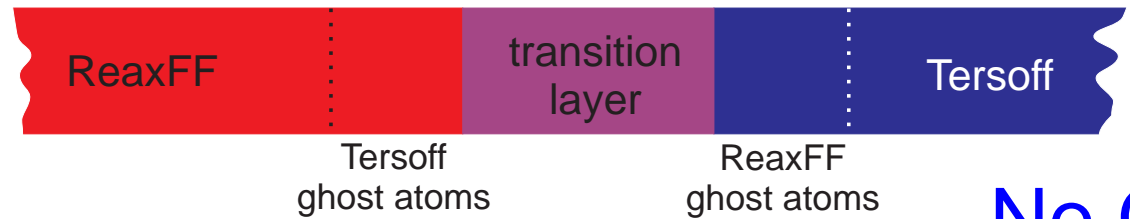
Agreement at small deformation: LINK



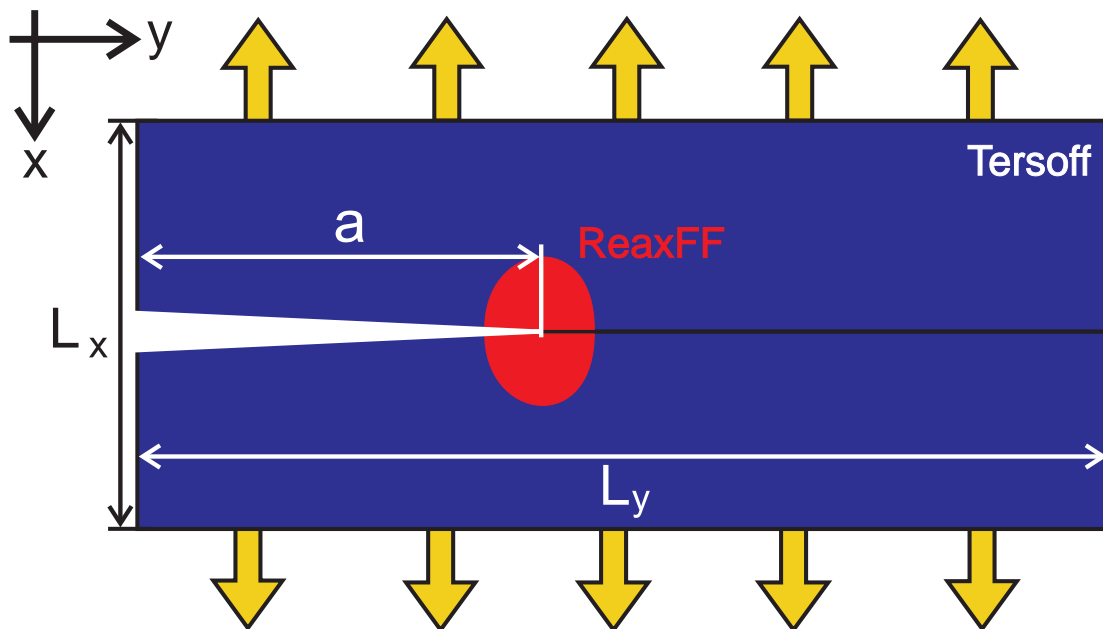
# Mixed Hamiltonians



Capture  
QM



No QM  
captured



- Bond breaking with QM accuracy
- Elasticity with inexpensive potentials



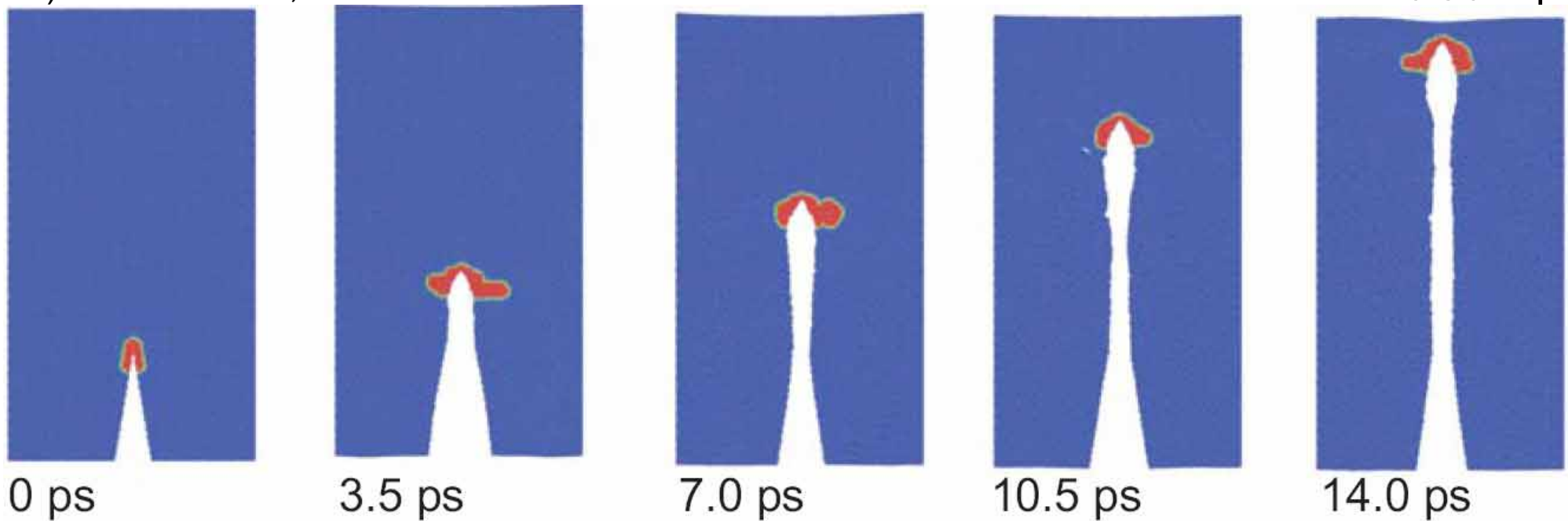
# Cracking in Silicon: Model within CMDF

- To model cracking in Silicon 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

(110) crack surface, 10 % strain

Reactive region is moving with crack tip



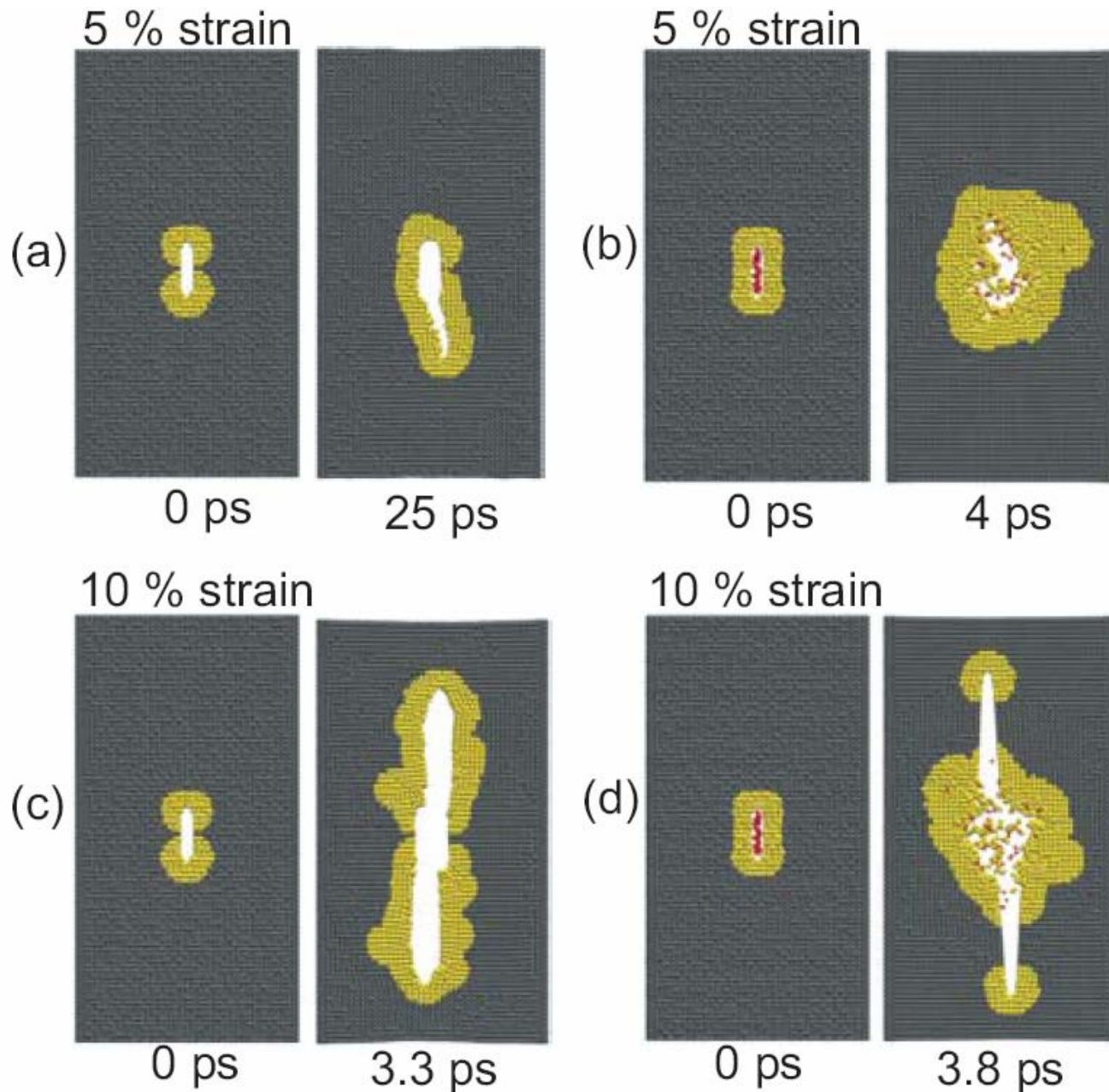
ReaxFF   
Tersoff 

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



# 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  $L_x \approx 160\text{\AA}$  and  $L_y \approx 310\text{\AA}$ .

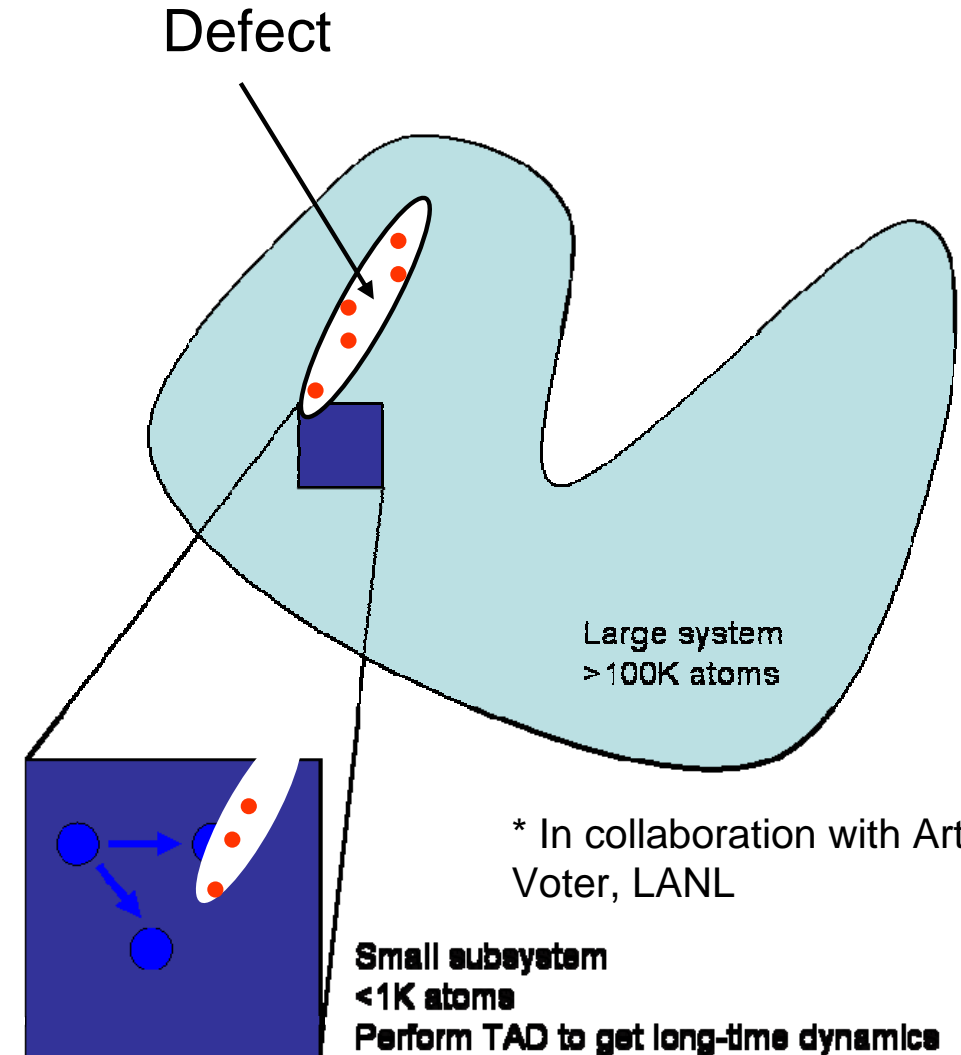
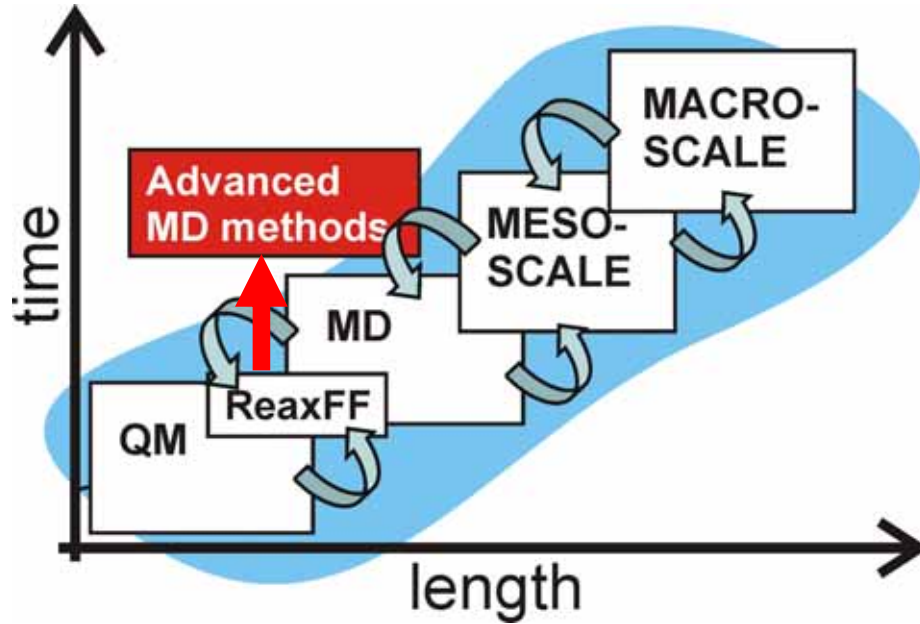


# Extension to large time scales: TAD\*



Concept: Find state transitions at high temperature, estimate times at low temperature

$$t_{\text{high, stop}} \equiv \frac{\ln(1/\delta)}{v_{\text{min}}} \left( \frac{v_{\text{min}} t_{\text{low, short}}}{\ln(1/\delta)} \right)^{\beta_{\text{high}}/\beta_{\text{low}}} \quad t_{i, \text{low}} = t_{i, \text{high}} e^{E_i(\beta_{\text{low}} - \beta_{\text{high}})}$$



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

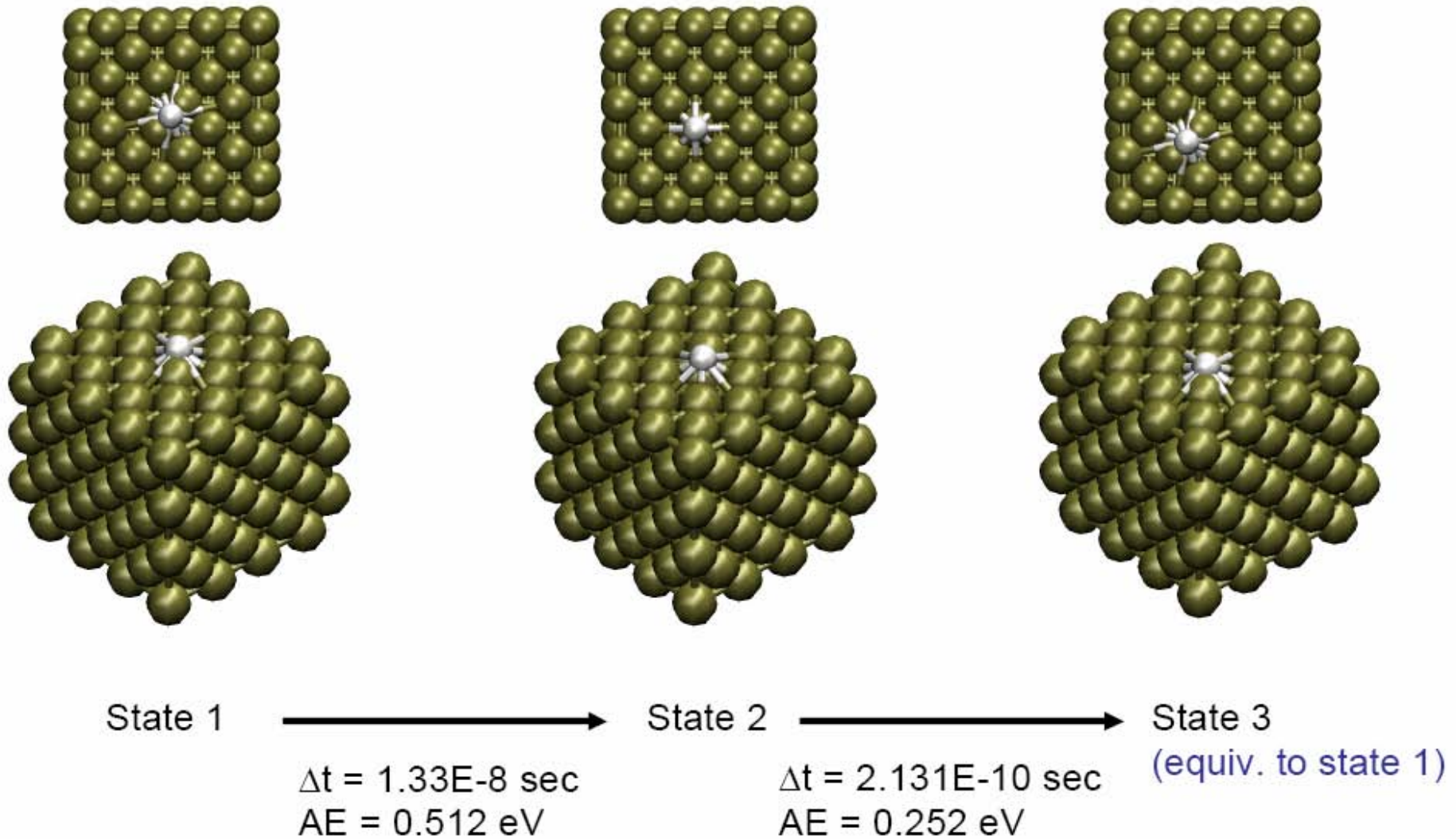




# Diffusion of H on Pt



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



(Collaboration with Art Voter, LANL)

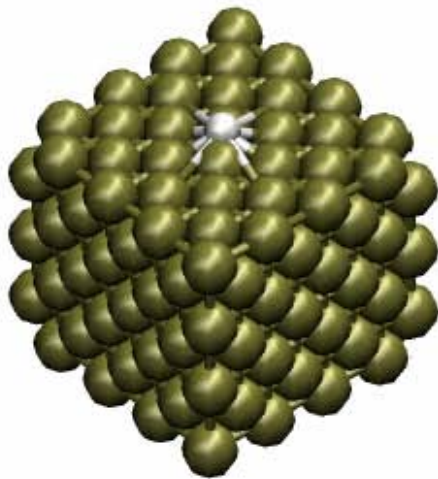


# Diffusion of H on Pt



	#Atoms	Simulated Time	CPU Time
ReaxFF Standalone	200	50 nanoseconds	7 days
Pt-H System	257	220 nanoseconds	4.4 days

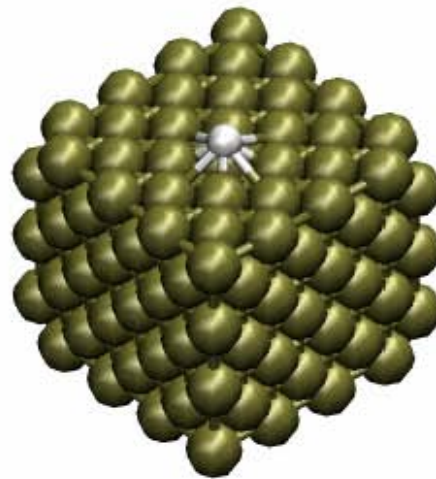
→ **8.8 boost factor**



State 1



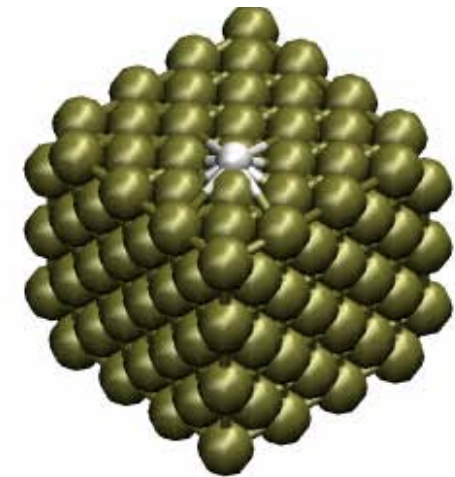
$\Delta t = 1.33\text{E-}8$  sec  
AE = 0.512 eV



State 2



$\Delta t = 2.131\text{E-}10$  sec  
AE = 0.252 eV



State 3

(equiv. to state 1)

(Collaboration with Art Voter, LANL)

ReaxFF interfaced with TAD through CMDf

© 2005 Markus J. Buehler, CEE/MIT



# Summary and wrap-up



# Do we need atoms to describe how materials behave?

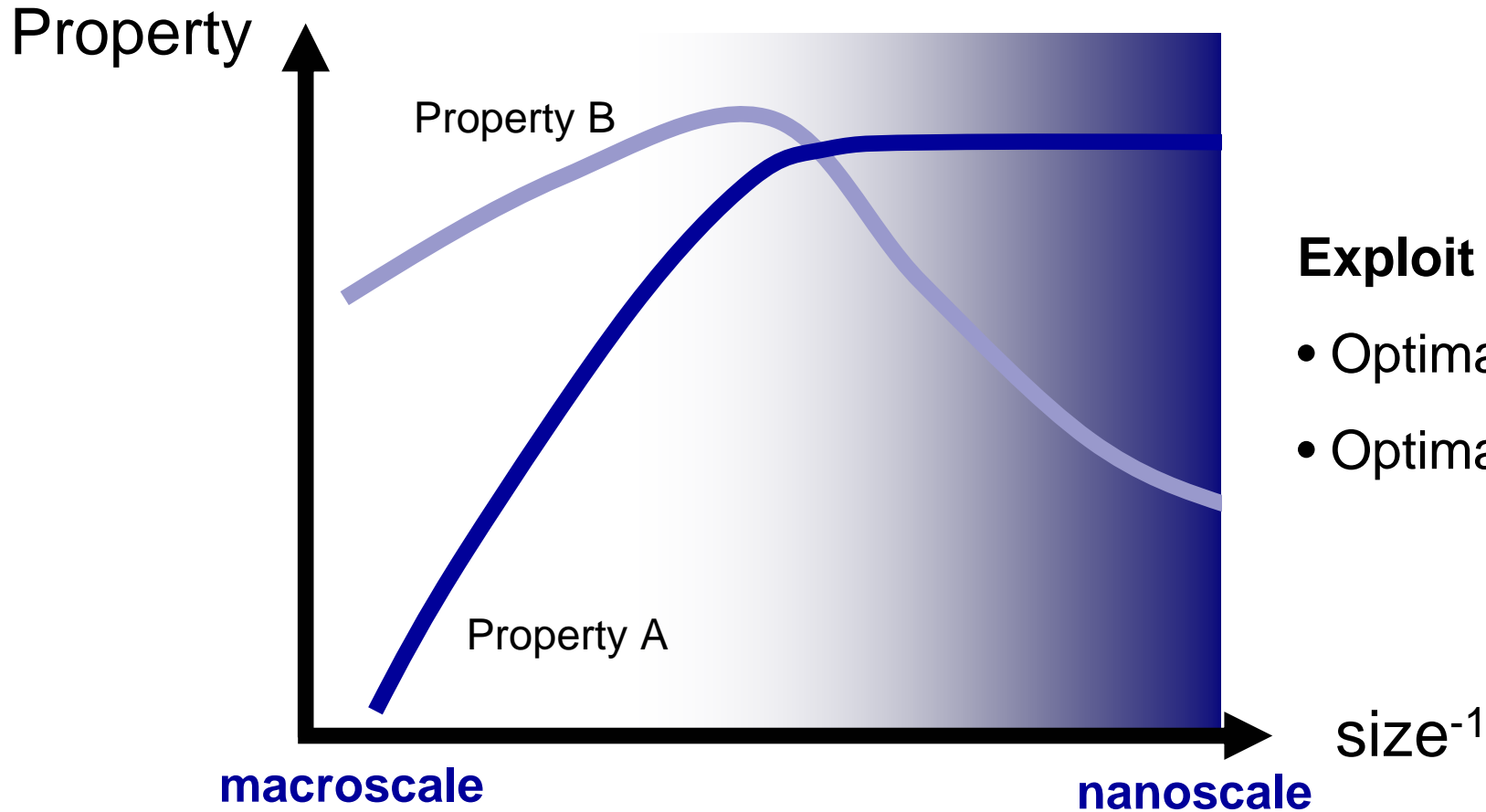


Atomic details needed for some applications and situations, including:

- Small-scale materials: Miniaturization as a new engineering frontier and potential (nanomaterials and small-scale structures)
  - Thin films, IC technology
  - Basis for modern technologies: Coatings
  - New metals, alloys, composites, including structural applications
  
- Interfaces between dissimilar materials (living systems and technologies, bio-chips or N/MEMS)  
  
“Interfacial materials” (incl. nanomaterials)
  
- Quantum effects, confinement, size effects: Now important for engineers and exploited for technologies
  
- Thus: MD may play a critical role as engineering tool ( “new” engineers trained in physics, chemistry, biology etc. and the intersections of various scientific disciplines)



# Size effects in materials



## Exploit scale effects

- Optimal size?
- Optimal structure?

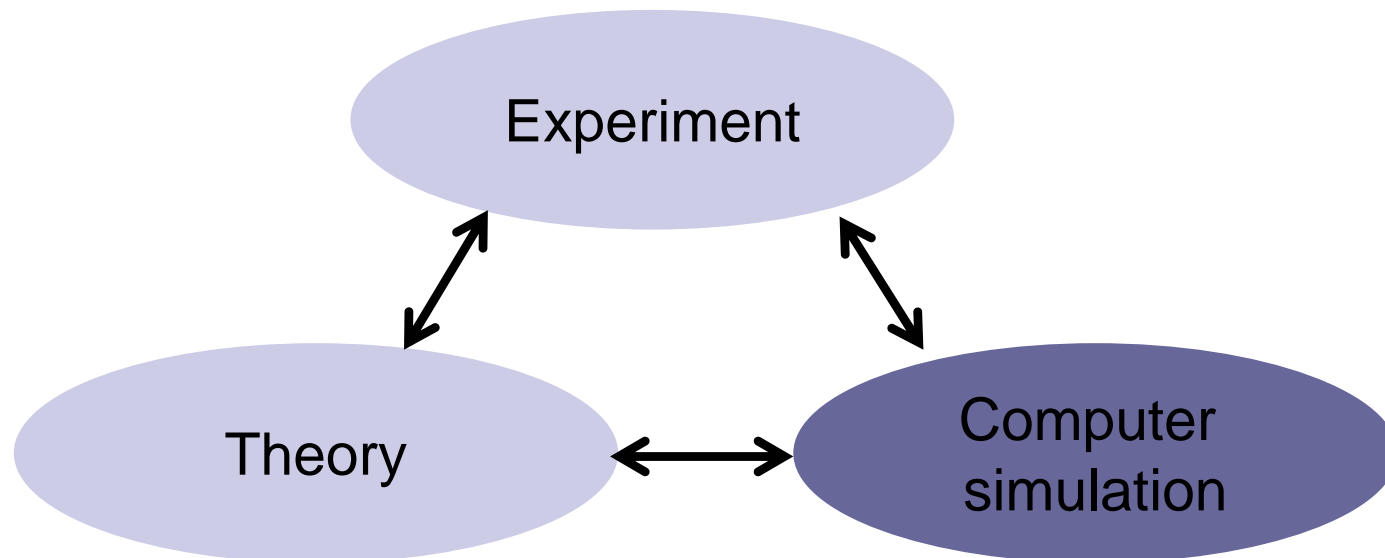
This helps to define novel machine and materials design principles





# Linkage of experiment-theory-simulation

- ✓ Atomistic simulations is an increasingly important tool in materials science; it can be used to...
  - Advance theory and discover new physical phenomena
  - Augment and explain experiment
- ✓ With its **limitations** understood, MD simulation is an ideal tool to study small-scale dynamics materials phenomena; gain insight into mechanisms

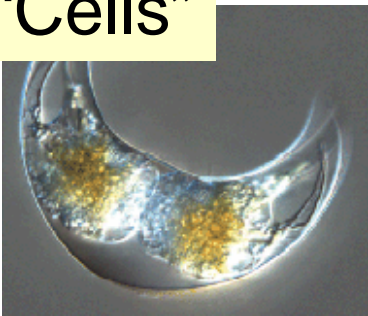




# Scales covered at CEE: From nano to macro to help understand the “world”



“Cells”



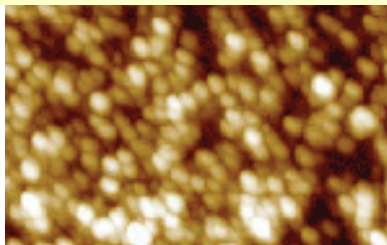
Penny Chisholm  
Bacteria, viruses, microbes

“City/region”

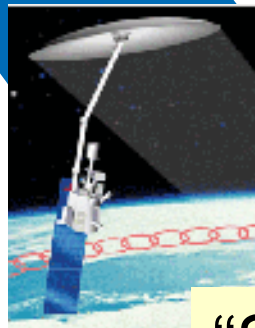


Moshe Ben-Akiva  
Traffic  
DynaMIT

“Nano/Micro-materials”



Franz Ulm  
Materials (cement, bone), Genoming



“Space”

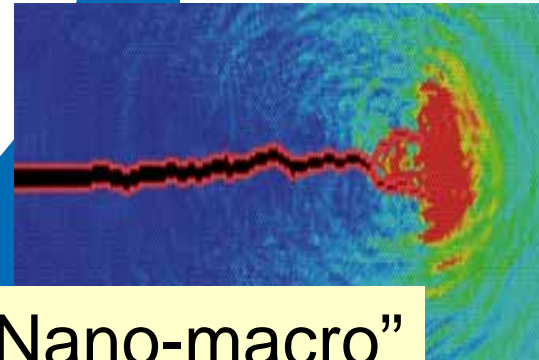
Dara Entekhabi  
Space instruments

“Coastal areas”



Heidi Nepf  
Environmental fluid mechanics

“Nano-macro”



Markus Buehler  
Fracture, natural & biological materials



# Nanoscale at CEE



- At CEE, we use a holistic approach to understand the scientific concepts “how” the world works
- A key focus is the “system perspective” and integration of dissimilar hierarchies of materials, methods, and interactions of technology-human/society
- Genuine interest in multi-scale phenomena and their modeling, experimental investigation and understanding
- To develop deep understanding of scale problems we need different perspectives and views, including nano-view (atomistic), systems perspective, macroscale properties and many others
- This involves a variety of numerical, theoretical and experimental approaches across scales and disciplines, including atomistic and mesoscale simulations
- Helps to understand the similarities in behavior across disciplines and across the scales for development of new engineering concepts



# 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: 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/>



# Additional references



- [http://www.ch.embnet.org/MD\\_tutorial/pages/MD.Part1.html](http://www.ch.embnet.org/MD_tutorial/pages/MD.Part1.html)
- Alder, B. J. and Wainwright, T. E. J. Chem. Phys. 27, 1208 (1957)
- Alder, B. J. and Wainwright, T. E. J. Chem. Phys. 31, 459 (1959)
- Rahman, A. Phys. Rev. A136, 405 (1964)
- Stillinger, F. H. and Rahman, A. J. Chem. Phys. 60, 1545 (1974)
- McCammon, J. A., Gelin, B. R., and Karplus, M. Nature (Lond.) 267, 585 (1977)
- D. Frenkel and B. Smit Understanding Molecular Simulations: from Algorithms to Applications, Academic Press, San Diego, 2nd edition (2002).
- M.J. Buehler, A. Hartmaier, M. Duchaineau, F.F. Abraham and H. Gao, “The dynamical complexity of work-hardening: A large-scale molecular dynamics simulation”, under submission to Nature.
- M.J. Buehler, A. Hartmaier, M. Duchaineau, F.F. Abraham and H. Gao, “The dynamical complexity of work-hardening: A large-scale molecular dynamics simulation”, MRS Proceedings, Spring meeting 2004, San Francisco.
- M.J. Buehler, A. Hartmaier, H. Gao, M. Duchaineau, and F.F. Abraham, “Atomic Plasticity: Description and Analysis of a One-Billion Atom Simulation of Ductile Materials Failure.” In the press: Computer Methods in Applied Mechanics and Engineering (to appear 2004).
- B. deCelis, A.S. Argon, and S. Yip. Molecular-dynamics simulation of crack tip processes in alpha-iron and copper. J. Appl. Phys., 54(9):4864–4878, 1983.
- See additional references & material on the website:  
<http://web.mit.edu/mbuehler/www/Teaching/LS/lecture-1-supp.htm>