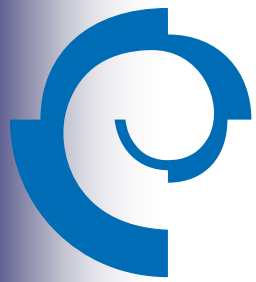
From nano to macro: Introduction to atomistic modeling techniques

IAP 2006

Introduction to classical molecular dynamics: Brittle versus ductile materials behavior

Lecture 1



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Introduction – IAP Course

- 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
  - Ductile materials
  - Brittle materials
  - Small-scale (“nano”-) materials
- Focus on brittle versus ductile materials behavior and introduction to hands-on procedure of atomistic modeling of fracture
- **Target group:** Undergraduate and graduate students, postdocs

Format

- 4+1 lectures ~60 minutes each, with time for discussion and questions
- Last lecture: Introduction to problem set
- Hands-on problem set (last part, project), introducing the typical tasks in molecular modeling of fracture and deformation of copper
  - Nanocrystal with crack under tension
  - Tensile test of a copper nanowire
- Course material posted on the website (introductiory papers, books, etc.)

  http://web.mit.edu/mbuehler/www/Teaching/IAP2006/intro.htm

  Check for updates and supplementary material

- UROP opportunities available (please contact mbuehler@MIT.EDU)

Outline

- Jan. 9 (Monday): **Introduction to classical molecular dynamics: Brittle versus ductile materials behavior** (basic concepts of MC/MD, interatomic potentials, failure dynamics of materials and brittle versus ductile behavior)
- Jan. 11 (Wednesday): **Deformation of ductile materials like metals using billion-atom simulations with massively parallelized computing techniques** (geometry of dislocations, plasticity, dislocation nucleation and propagation, stacking fault, dislocation reactions, work hardening mechanisms, ultra-large scale computing)
- Jan. 13 (Friday): **Dynamic fracture of brittle materials: How nonlinear elasticity and geometric confinement governs crack dynamics** (dynamic fracture in brittle materials and the role of hyperelasticity, crack limiting speed, instability dynamics, cracks at interfaces)
- Jan. 16 (Monday): **Size effects in deformation of materials: Smaller is stronger** (size effects in materials, Griffith criterion of fracture initiation, adhesion and size effects, shape optimization, fracture of protein crystals)
- Jan. 18 (Wednesday): **Introduction to the problem set: Atomistic modeling of fracture of copper** (code compilation and usage, commands, pre- and post-processing)

Course reference material

Research articles and additional lecture notes

- http://web.mit.edu/mbuehler/www/Teaching/IAP2006/intro.htm

Modeling and Simulation

- *Allen, M. P. and Tildesley, D. J., Computer Simulation of Liquids* (Oxford University Press, 1989)
- *Frenkel, D., Smit, B.* Understanding Molecular Simulation: From Algorithms to Applications

Mechanics of materials - Introductory

- *Courtney, T.H.* Mechanical Behavior of Materials, 2nd edition, McGraw Hill, 2000
- *Hull, D.* and Bacon D.J., Introduction to Dislocations, Butterworth Heinemann, 4th edition, 2001
- *Anderson, T. L.,* Fracture mechanics: Fundamentals and applications (CRC Press, 1991)

Advanced

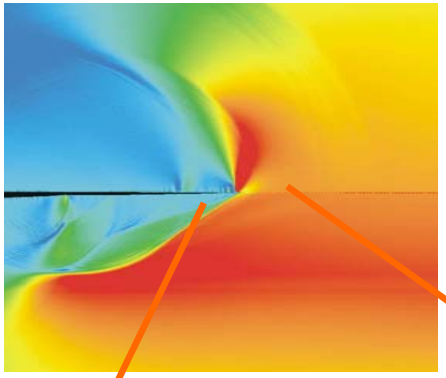
- *Hirth J.P. and Lothe J.* Theory of dislocations, New York: McGraw-Hill.
- *Broberg, K.B.* Cracks and Fracture (Academic Press, 1990)
- *Ashby, M. F. and D. R. H. Jones.* Engineering Materials, An Introduction to their Properties and Applications. 2nd ed. Butterworth Heinemann, 1996

Outline and content (Lecture 1)

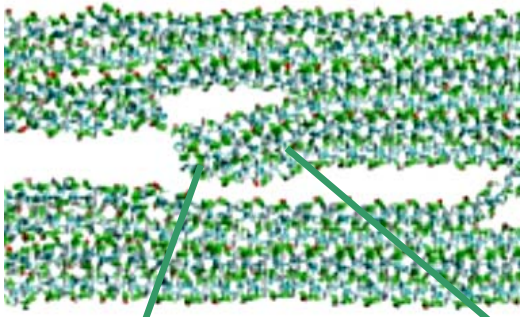
- The BIG challenge to couple atomistic, molecular or nano-scale with macro, as well as understanding the scales between “mesoscale”
- Historical perspective: The behavior of materials – modeling and experiment
- How atomistic simulations are carried out, including:
  - Definitions of terminology and numerical issues
  - Time scale dilemma
  - Pre-processing and input parameters
  - Atomic interactions (potential energy surface)
  - Computing strategies
  - Analysis and visualization, data extraction
- Research examples using atomistic methods: Modeling of fracture
- Discussion and conclusion:
  Are all atoms necessary to describe how materials behave?
- Outlook

Introduction

From nano to macro



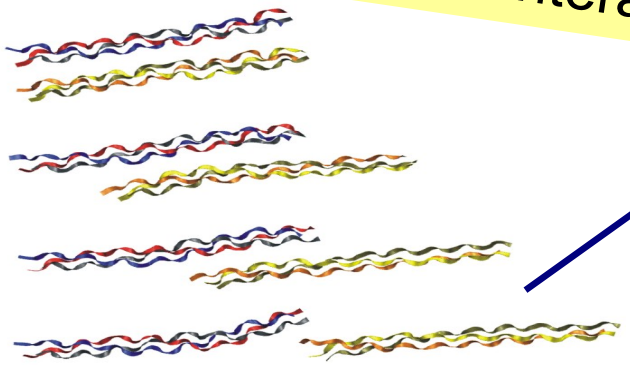
Crack dynamics at micrometers (**macroscale**)



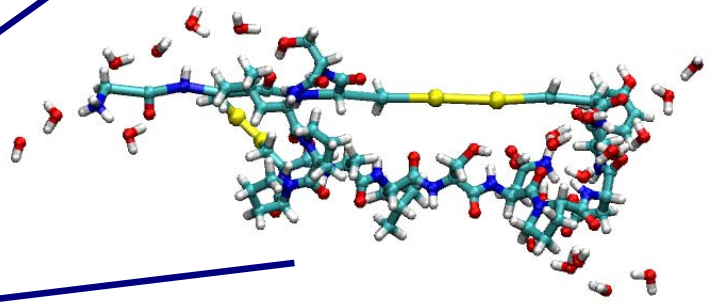
Dynamics of fracture in protein crystals (**mesoscale**)

- 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)

scale-interactions **versus** scale-specific properties



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



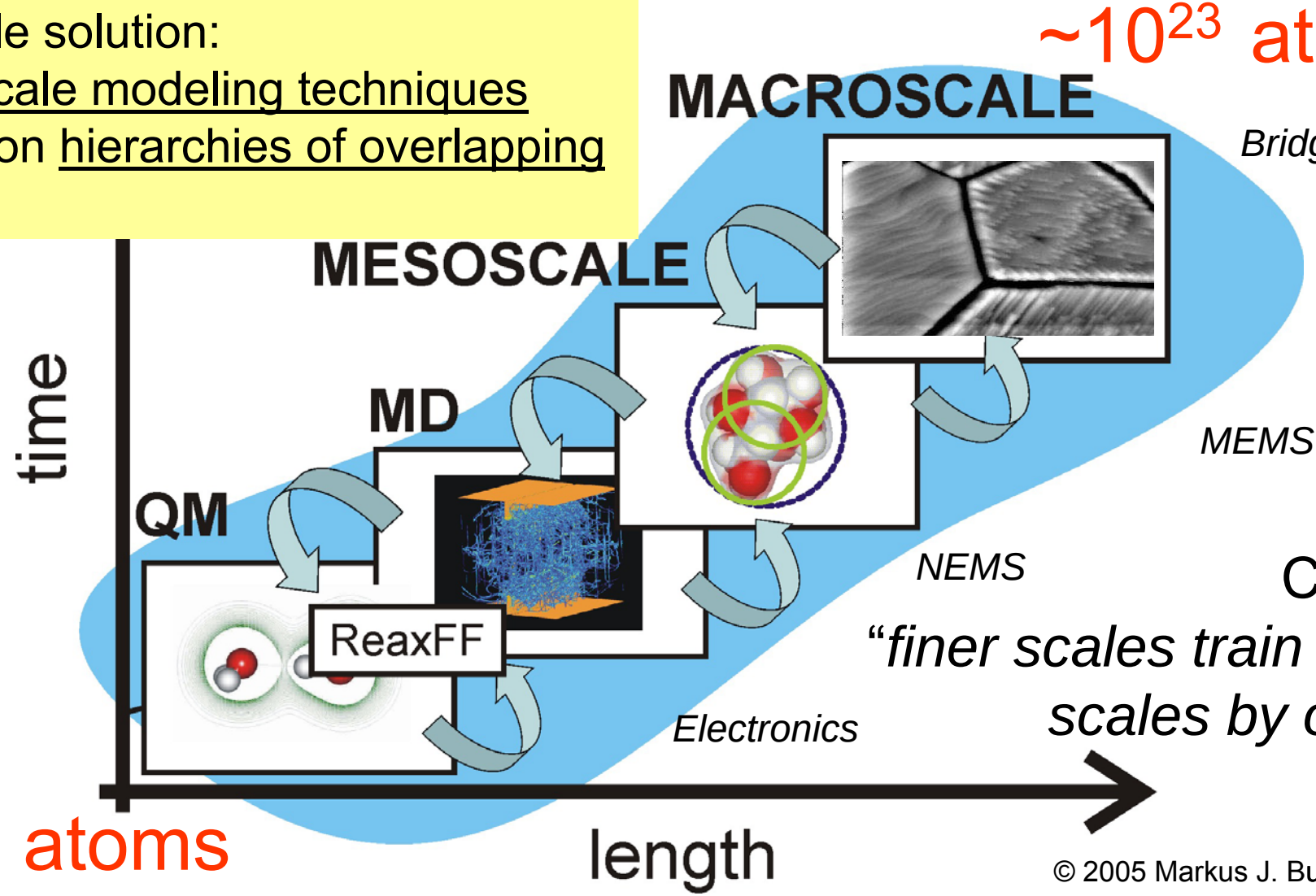
Chemistry (**atomic scale**)

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



Concept:
"*finer scales train coarser scales by overlap*"

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) and others

Continuum

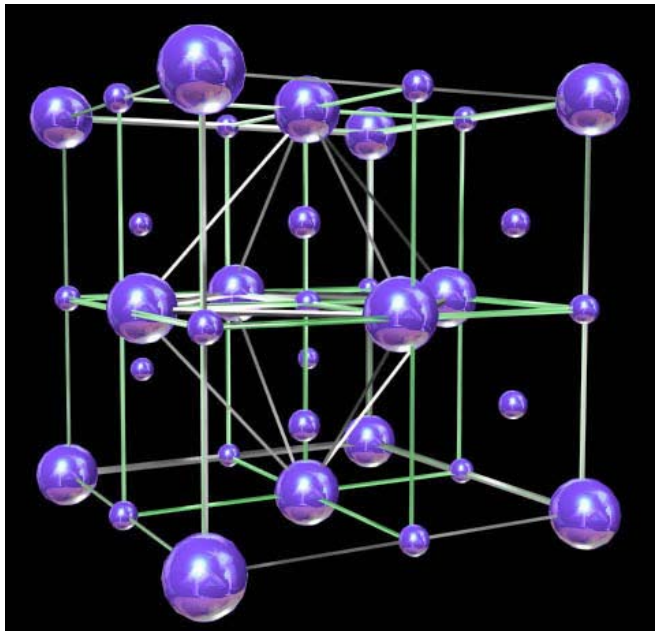
Atomistic

- 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).

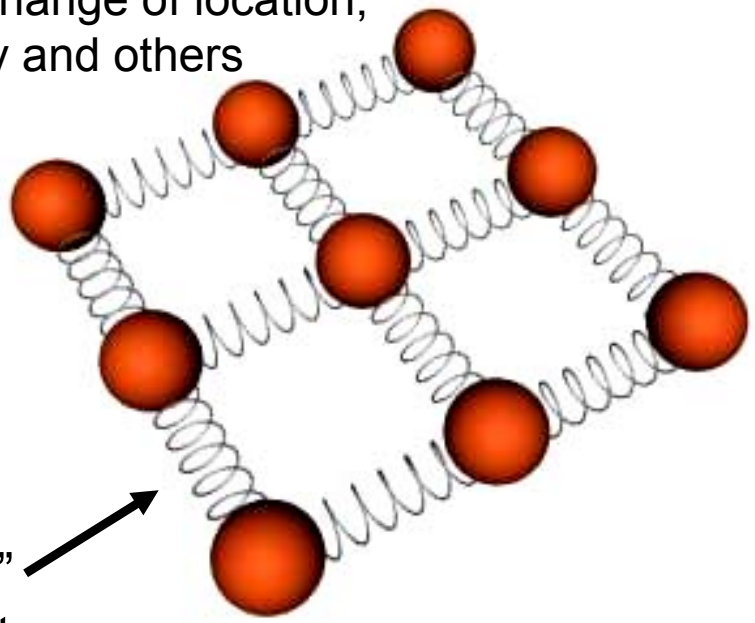
The problem to solve

- In atomistic simulations, the goal is to model, analyze and understand 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 or macro-scale phenomena
- Extraction of information from atomistic dynamics is often challenging



http://www.freespiritproductions.com/pdatom.jpg

Vibration, change of location, connectivity and others



"Spring" connects atoms…

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, and
  - forces

  of all atoms, as a function of time

Hamiltonian=sum of kinetic and potential energy

$$H = K(\{p_i\}) + V(\{q_i\}) = \sum_i \frac{p_i^2}{2m} + V(q_i)$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \qquad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}$$

EOM derived from Hamiltonian
p=momentum, q=position

Classical molecular dynamics (MD)

- 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, by providing averaging procedure or links between microscopic system states of the many-particle system and macroscopic thermodynamical properties, such as temperature, pressure, heat capacity etc.

Temperature $$T = \frac{2}{3}\frac{E_{kin}}{Nk_b} = \frac{1}{3Nk_b}\sum_{i=1}^{N}\frac{p_i^2}{m}$$

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

- Velocity Verlet (popular)

Update of positions

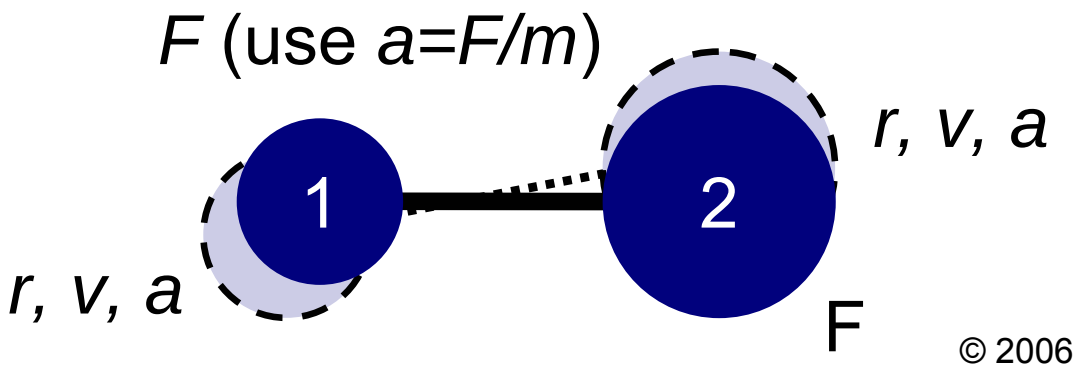
$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2$$

Update of velocities

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

- NVE, NVT, NPT calculations

- Most calculations in mechanics field are NVE (nonequilibrium phenomena such as fracture)



NVE, NVT and other ensembles

- NVE ensemble: Constant number of particles, constant volume and constant energy
- NVT ensemble (canonical): Constant temperature but no energy conservation
- NpT ensemble: Constant pressure and temperature, no energy conservation
- Various algorithms exist to obtain dynamics for different ensembles, as for example Nosé-Hoover, Langevin dynamics, Parinello-Rahman and others
- **Energy minimization:** Obtain ground state energy with no kinetic energy (zero temperature); various computational methods exist, such as Conjugate Gradient, GLOK etc.

Example: Nosé-Hoover NVT thermostat

- The integral thermostat method, also referred to as the *extended system method* introduces additional degrees of freedom into the system's Hamiltonian
- Equation of motion are derived for new Hamiltonian.
- These equations for the additional degrees of freedom are integrated together with "usual" equations for spatial coordinates and momenta.
- Nosé-Hoover: Reduce effect of big heat bath attached to system to one degree of freedom

$$H^* = \sum_{i=1}^{N} \frac{\pi_i^2}{2ms} + U(\rho_1, \rho_2, ..., \rho_N) + \frac{\pi_s^2}{2M_s} + gk_bTln(s)$$

$g = 3N + 1$ number of degrees of freedom

heat beath

$$\frac{d\vec{q}_i}{dt} = \frac{\vec{p}_i}{m_i}$$

$$\frac{d\vec{p}_i}{d\tau} = -\frac{\partial U}{\partial \vec{q}_i} - \zeta \vec{p}_i$$

M_s

Coupling inertia transfer coefficient

$$\frac{\partial ln(s)}{\partial t} = \zeta$$

$$\frac{d\zeta}{dt} = \frac{1}{M_s}\left(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} - gk_bT\right), \quad p_i \equiv |\vec{p}_i|$$

http://phycomp.technion.ac.il/~phsorkin/thesis/node42.html

NVT with Berendsen thermostat

- Even simpler method is the Berendson thermostat, where the velocities of all atoms are rescaled to move towards the desired temperature

Rescaling step

$$\underline{v}(t+\frac{1}{2}\Delta t) \leftarrow \eta\left(\underline{v}(t-\frac{1}{2}\Delta t)+\Delta t\frac{\underline{f}(t)}{m}\right)$$

Integration step

$$\underline{r}(t+\Delta t) \leftarrow \underline{r}(t)+\Delta t\underline{v}(t-\frac{1}{2}\Delta t)$$

- The parameter τ is a time constant that determines how fast the desired temperature is reached

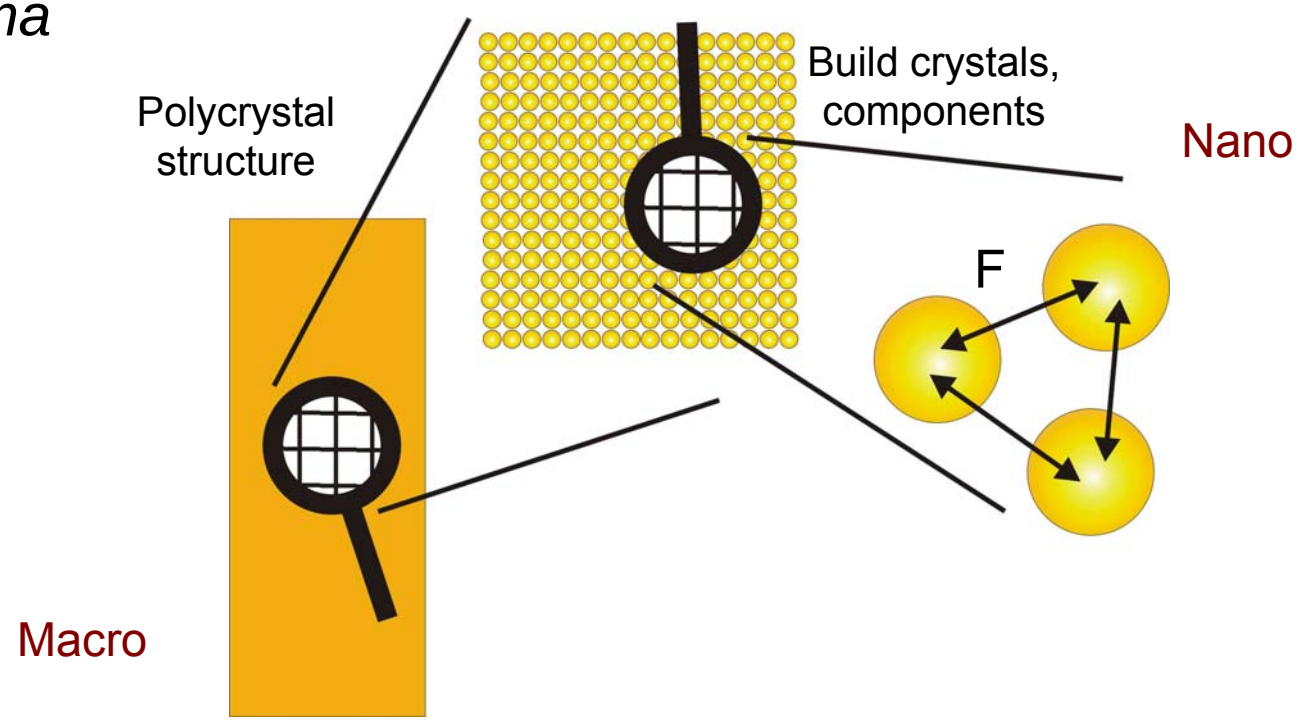
$$\eta \leftarrow \sqrt{\left[1+\frac{\Delta t}{\tau}\left(\frac{T_{ext}}{T}-1\right)\right]}$$

http://www.cmmp.ucl.ac.uk/~lev/codes/SciFi/manual_3_51/node22.html

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: **<u>can not parallelize time</u>**

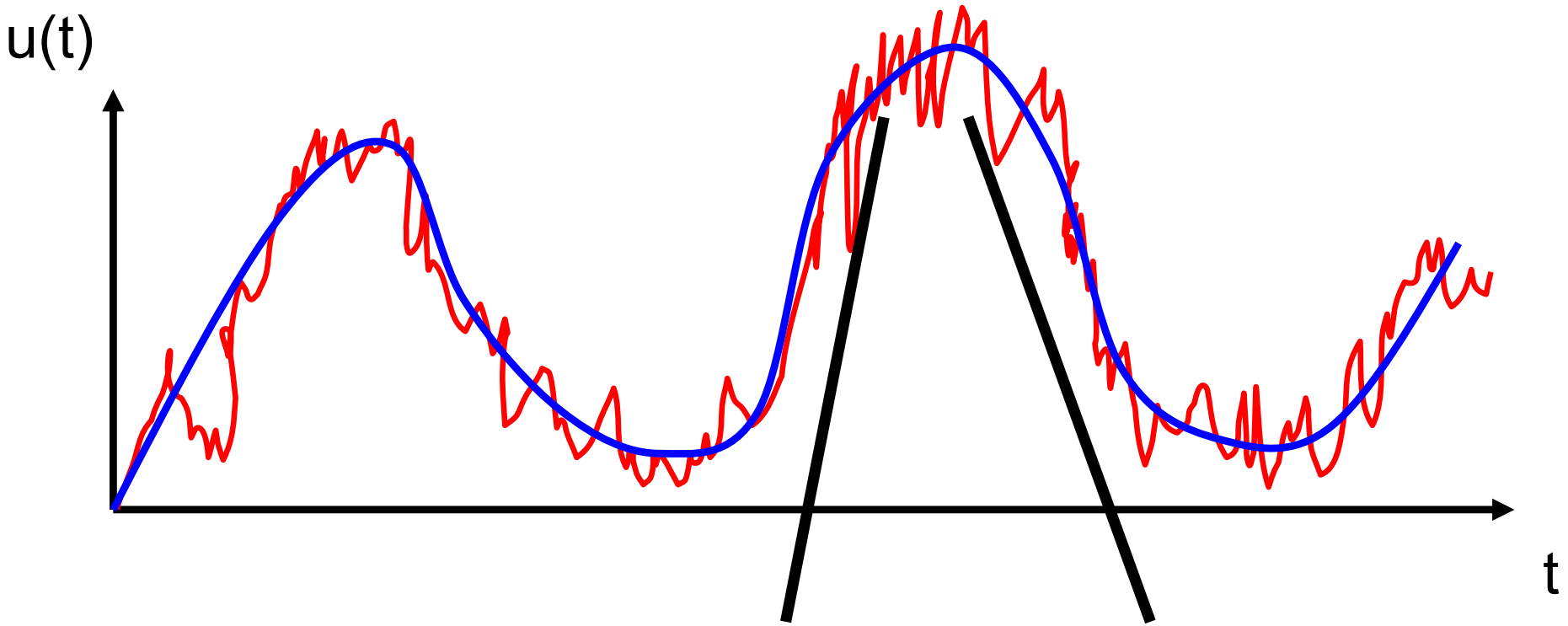
Time scale dilemma…

$$u(t) = \bar{u}(t) + u'(t)$$

coarse **fine**

The atomic displacement field consists of a low-frequency (“coarse”) and high frequency part (“fine”)

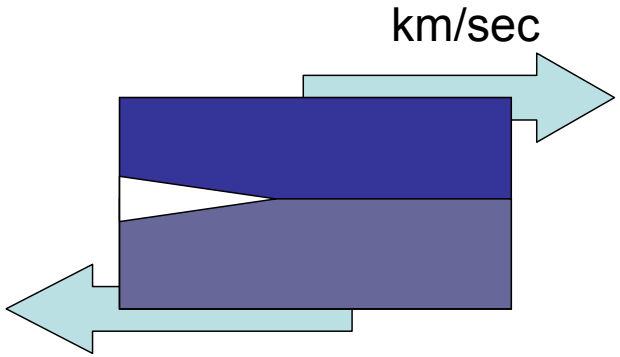
Requires $\Delta t \approx$ fs or less



Need to resolve!

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)

http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf
See also article by Art Voter *et al.* on the time scale dilemma

Monte Carlo (MC) techniques

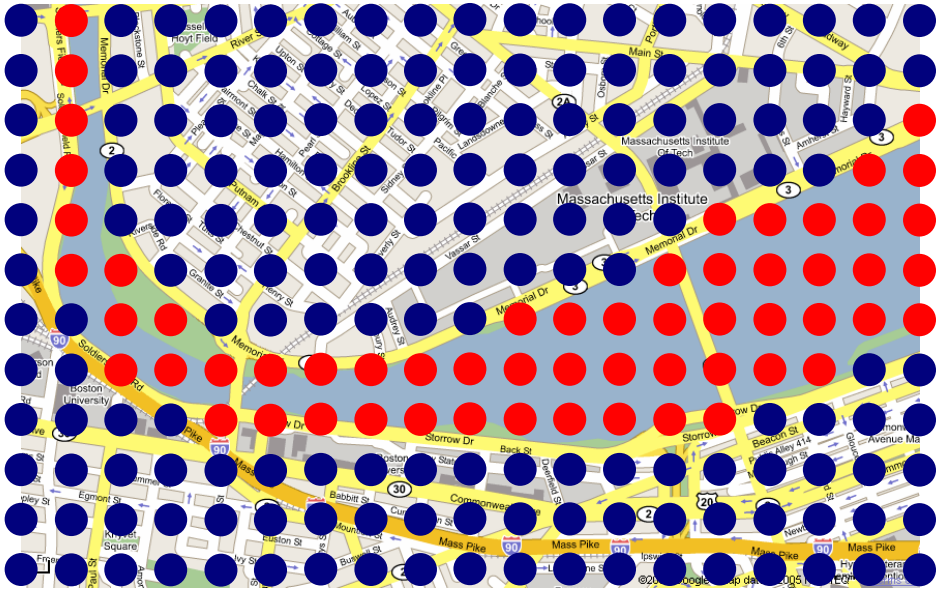
- Monte Carlo (MC) techniques and alike have been developed to overcome some of the limitations of dynamical (MD) atomistic calculations
- Instead of integrating the EOM, MC performs a random walk to measure properties: Randomly probing the geometry of the molecular system (configuration space, acceptance 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).

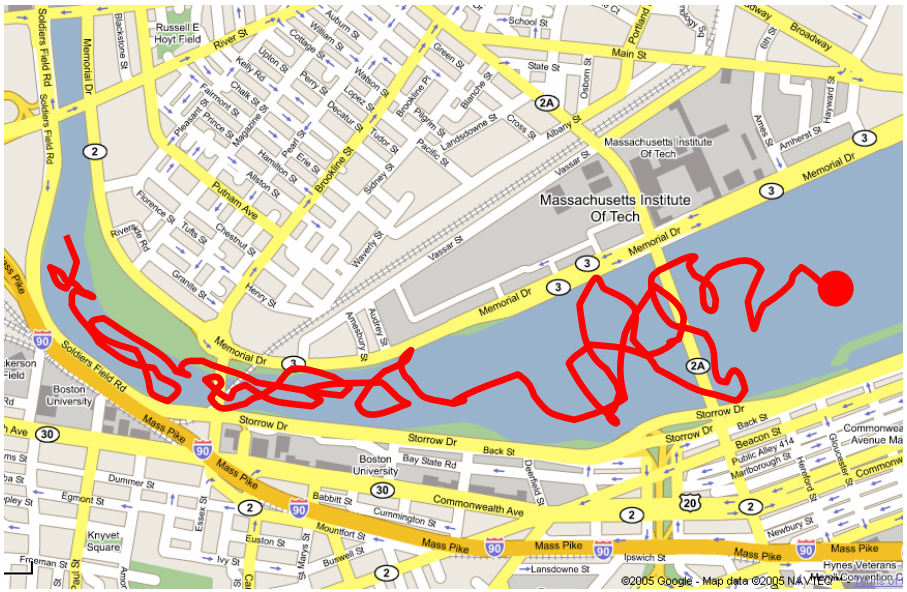
http://www.ccl.net/cca/documents/molecular-modeling/node9.html

Example: Measuring the average depth of the Charles River



Classical grid-based quadrature scheme:

Discretize problem and perform measurements at grid points



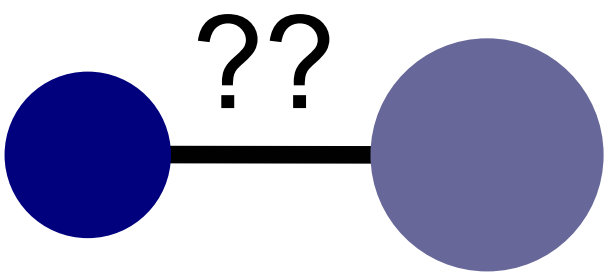
Monte Carlo:

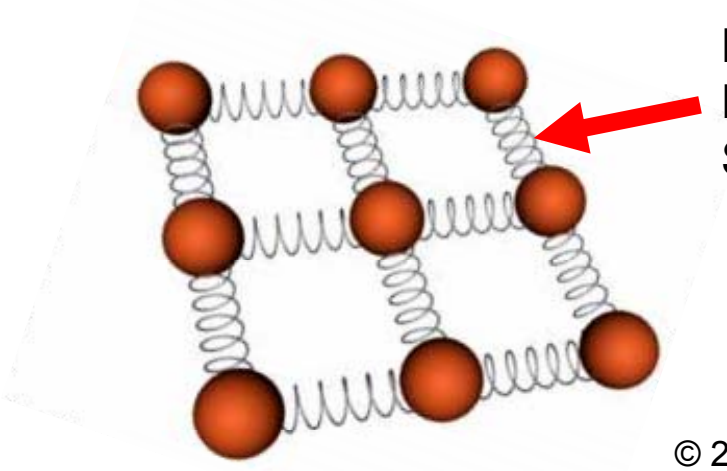
Perform random walk through the river; measurements are performed only at accepted locations

http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf, http://maps.google.com/

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…)





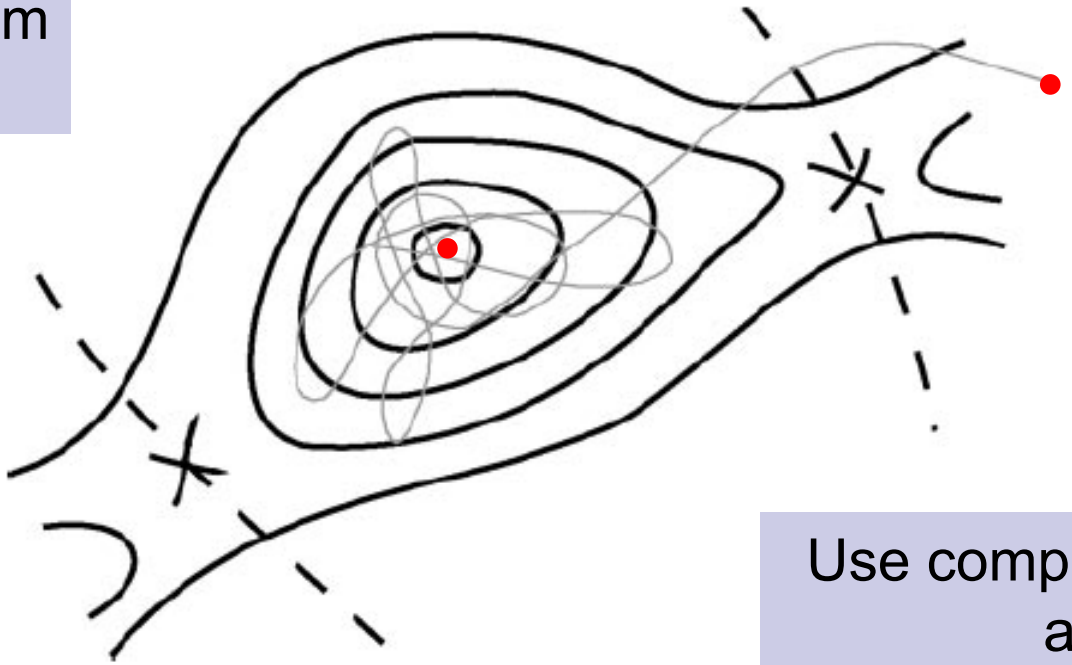
DFT or
Empirical or
Semi-empirical…

http://www.sr.bham.ac.uk/xmm/images/structures/springespring_300_248.jpg

Bridging time scales: Advanced MD methods

- Similar to bridging length scales, the bridging of time scales is a similarly difficult (maybe more difficult…) matter
- In past years, many methods have been proposed; among the most prominent ones are bias potential methods, temperature accelerated dynamics, or parallel replica methods (many more)…

How to escape from local basin?

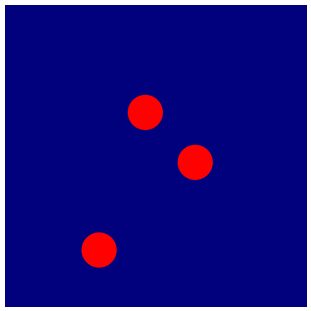


Use computational methods to achieve rapid escape

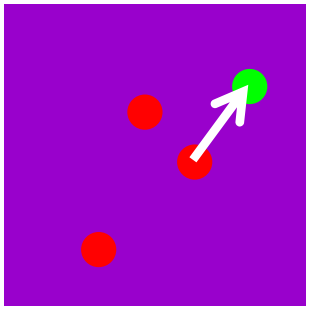
http://www.t12.lanl.gov/home/afv/publications.html;
http://www.t12.lanl.gov/home/afv/acceleratedynamics.html

Bridging time scales

- **Example**:
  Temperature accelerated dynamics (TAD); developed by Art Voter
  Can reach up to microseconds and longer, while retaining atomistic length scale resolution



System of interest
(low temperature T_0)



Sample for state transitions at high temperature T_1)

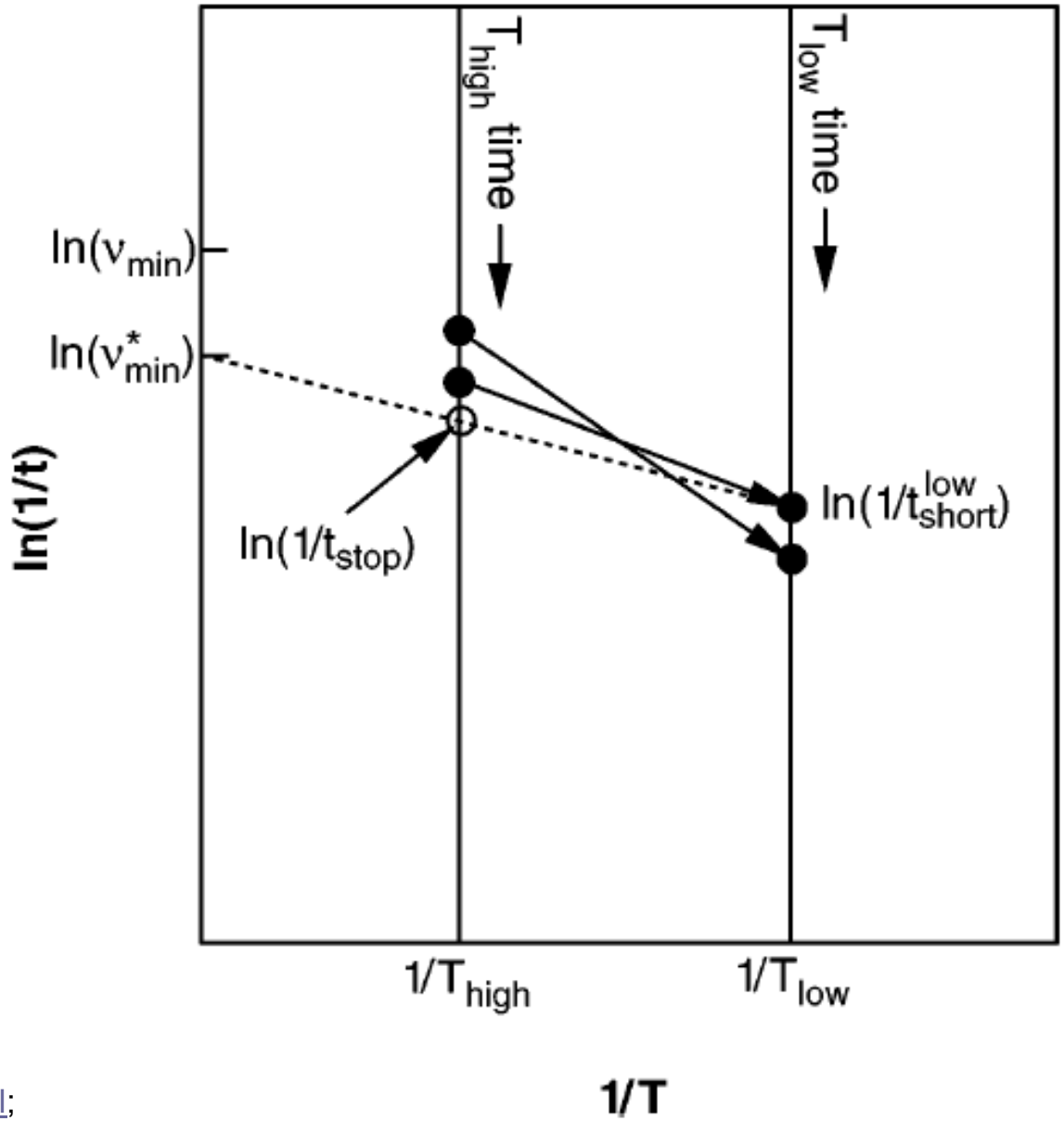
Using transition state theory, calculate when this event would have happened at low temperature

$$t_{high,stop} \equiv \frac{\ln(1/\delta)}{\nu_{min}} \left(\frac{\nu_{min} t_{low,short}}{\ln(1/\delta)} \right)^{T_{low}/T_{high}}$$

http://www.t12.lanl.gov/home/afv/publications.html;
http://www.t12.lanl.gov/home/afv/acceleratedynamics.html

Bridging time scales

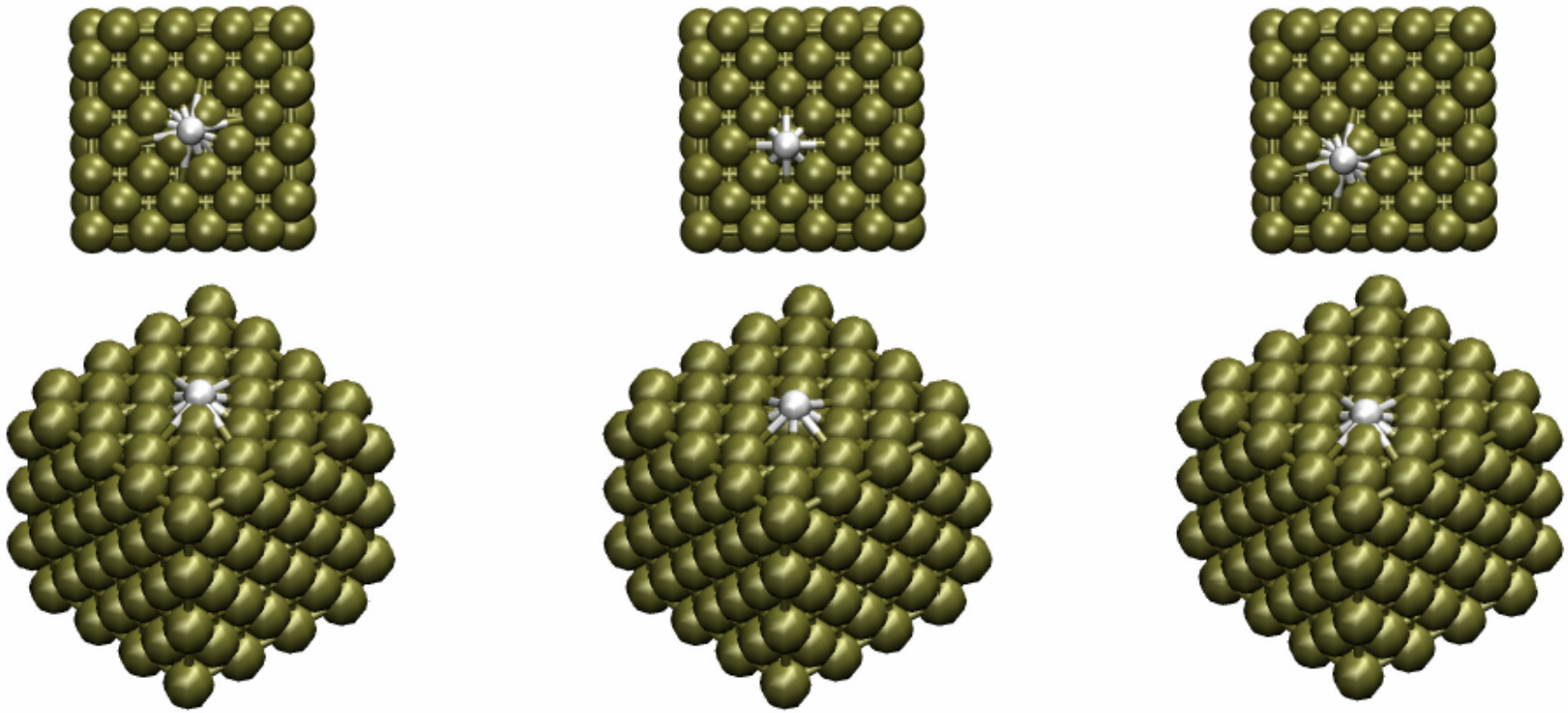
- Knowing time at high temperature allows to estimate dynamics at lower temperature



http://www.t12.lanl.gov/home/afv/publications.html;
http://www.t12.lanl.gov/home/afv/acceleratedddynamics.html

Diffusion of H on Pt: Reactive description with ReaxFF

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



State 1 → State 2 → State 3 (equiv. to state 1)

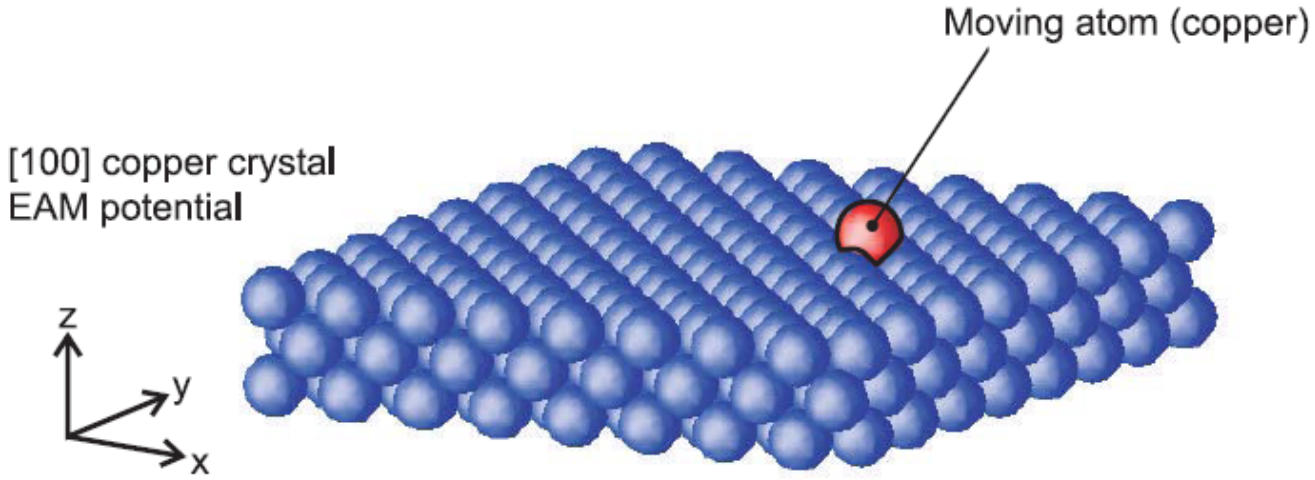
Δt = 1.33E-8 sec
AE = 0.512 eV

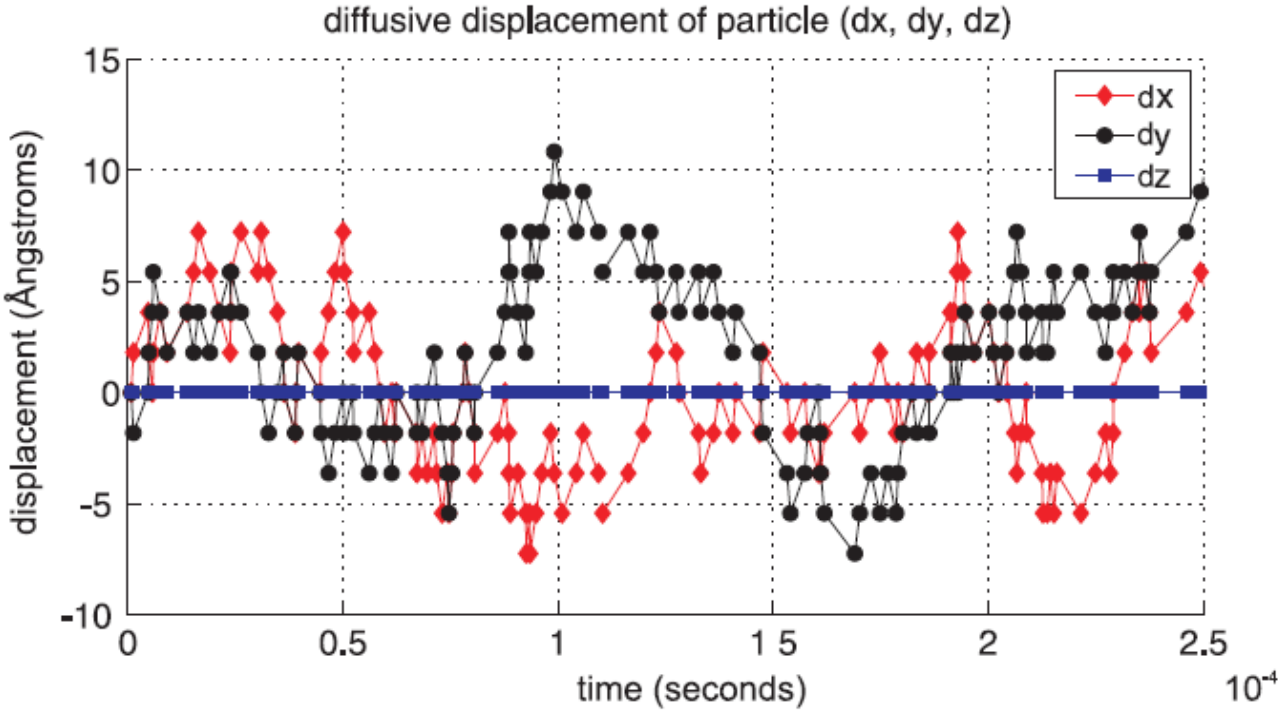
Δt = 2.131E-10 sec
AE = 0.252 eV

(Buehler, Goddard *et al.*, in collaboration with Art Voter, LANL)

ReaxFF interfaced with TAD through CMDF

Surface diffusion





The TAD method enables to model the atomic motion over time scales approaching fractions of seconds

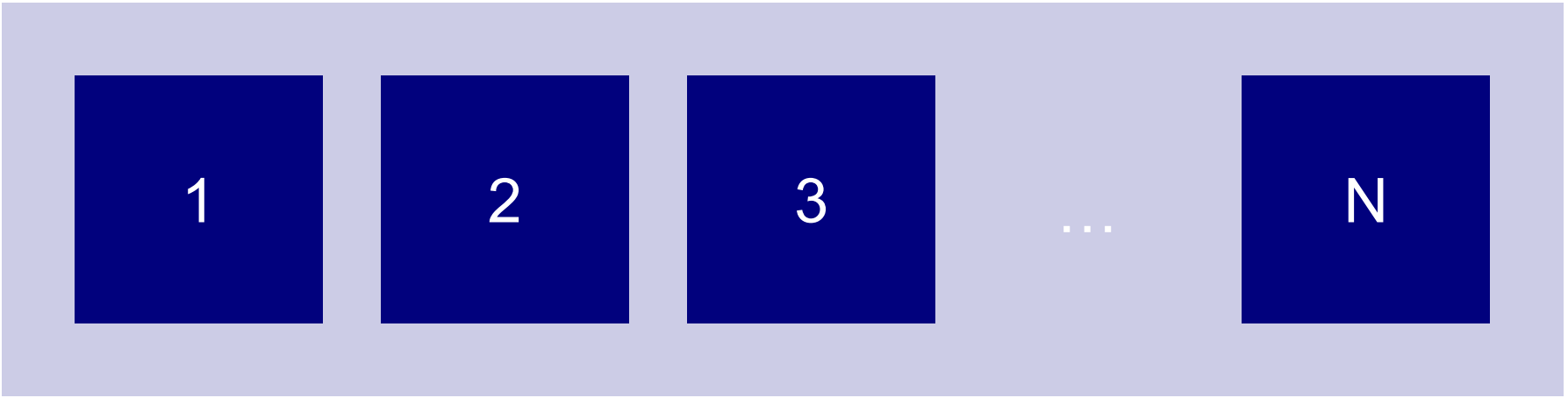
Diffusivities:

$$D_s^{\mathrm{MD}} = 7.53 \times 10^{-14}\ \mathrm{m}^3/\mathrm{s}$$

$$D_s^{\mathrm{exp}} \approx 11 \times 10^{-14}\ \mathrm{m}^3/\mathrm{s}$$

Parallel replica method

- Generate N copies of the (small) system on N CPUs
- Evolve dynamics in each system, with random, uncorrelated initial conditions, stop when event it detected on any of the systems
- Speedup up to N times, thus can reach microsecond time scale on ~1,000 CPUs
- Easy to parallelize
- Use combination of parallel replica and TAD

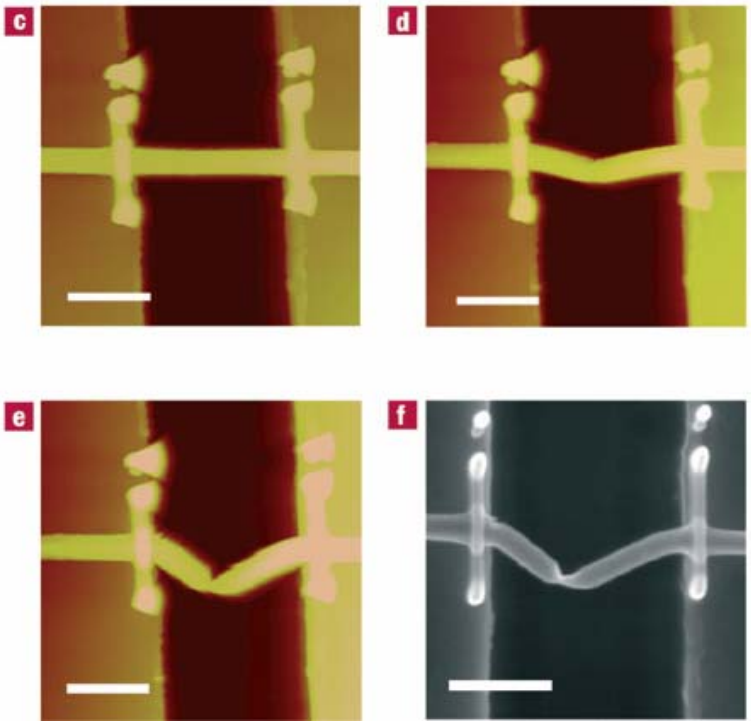


Interatomic potentials

Deformation of materials

http://www.gsi.gov.in/images/ex1.gif

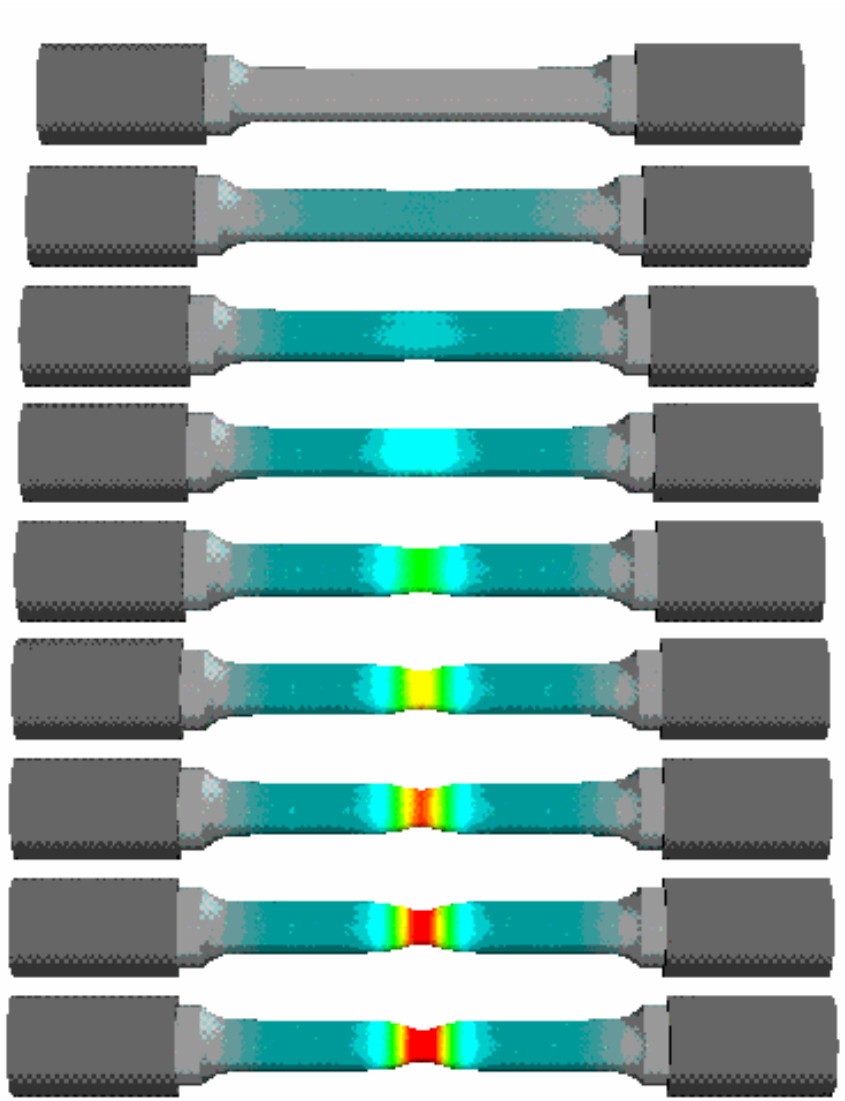
Big scale
"earth"



Small scale
"nano"

Bin Wu *et al.*,
Nature Materials,
2005

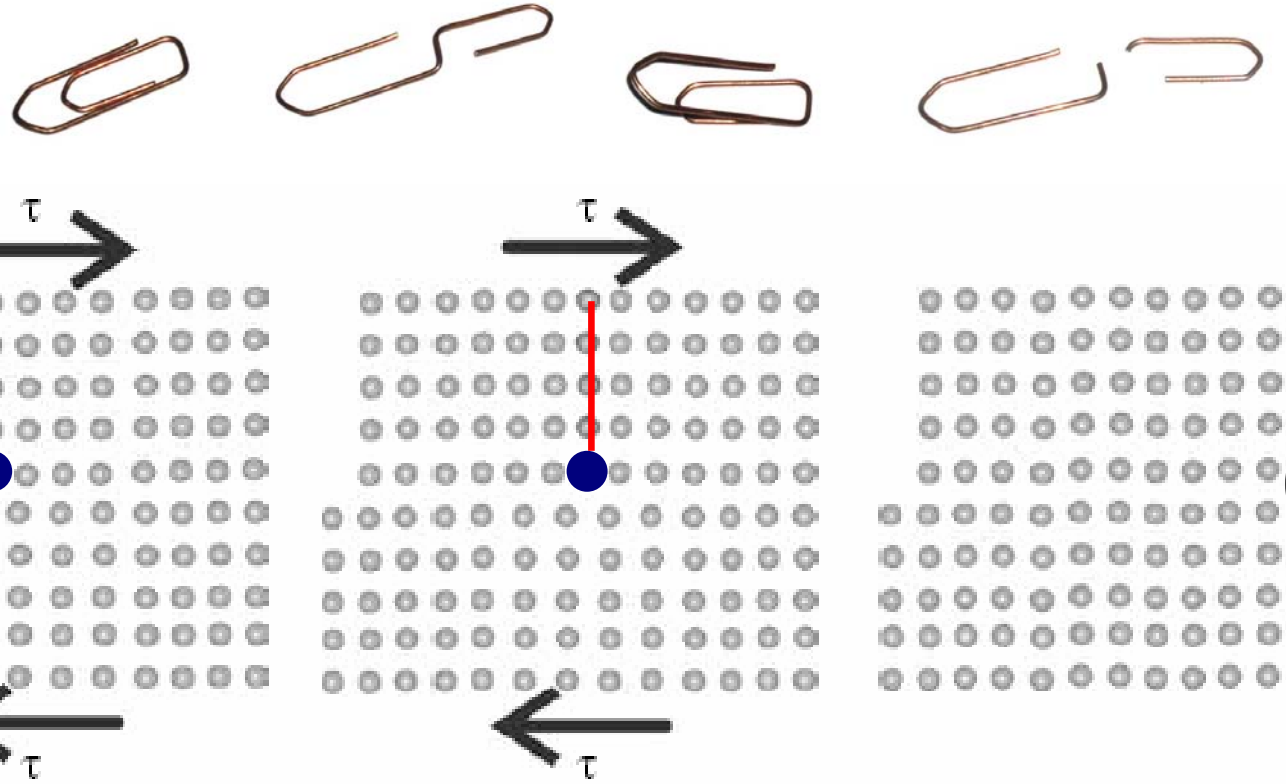
http://www.nature.com/nmat/journal/v4/n7/images/nmat1403-f2.jpg

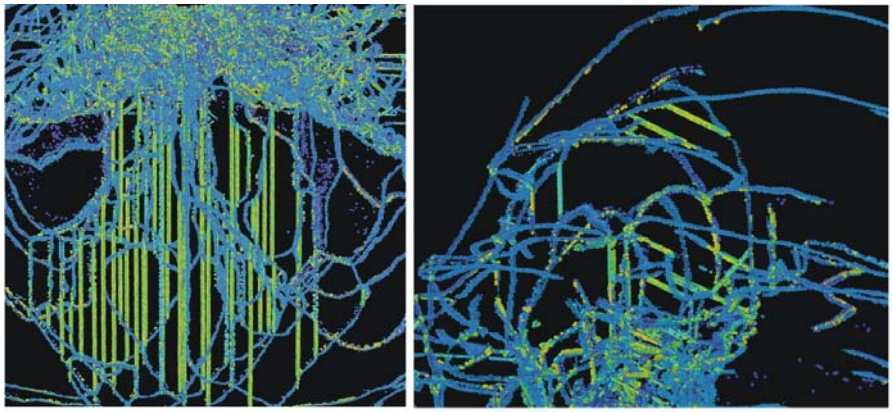


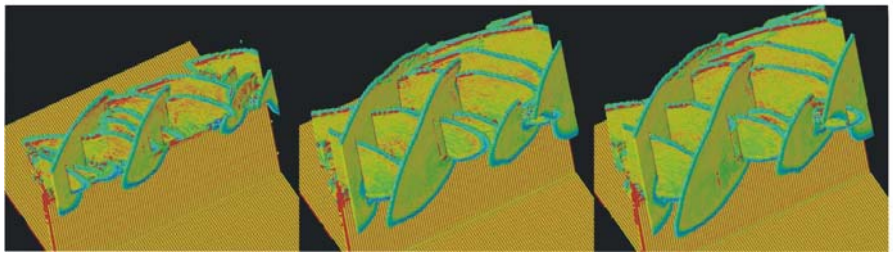
http://www.arasvo.com/comp_figures/fig_wf3.htm

First principles description of mechanics: Dislocations carry plasticity in metals

Dislocations are made out of atoms

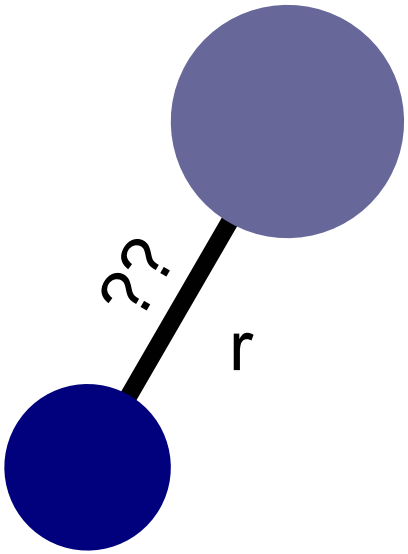


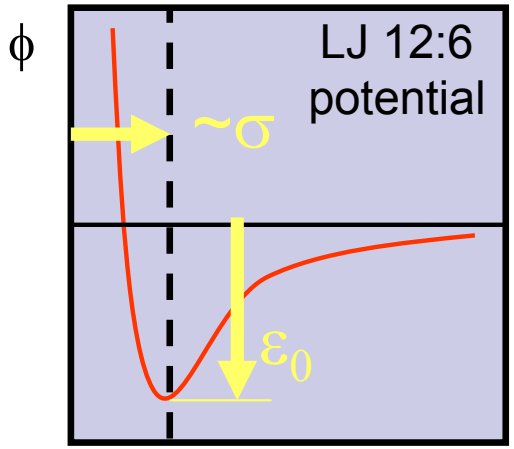




The interatomic potential

- 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 dϕ/dr

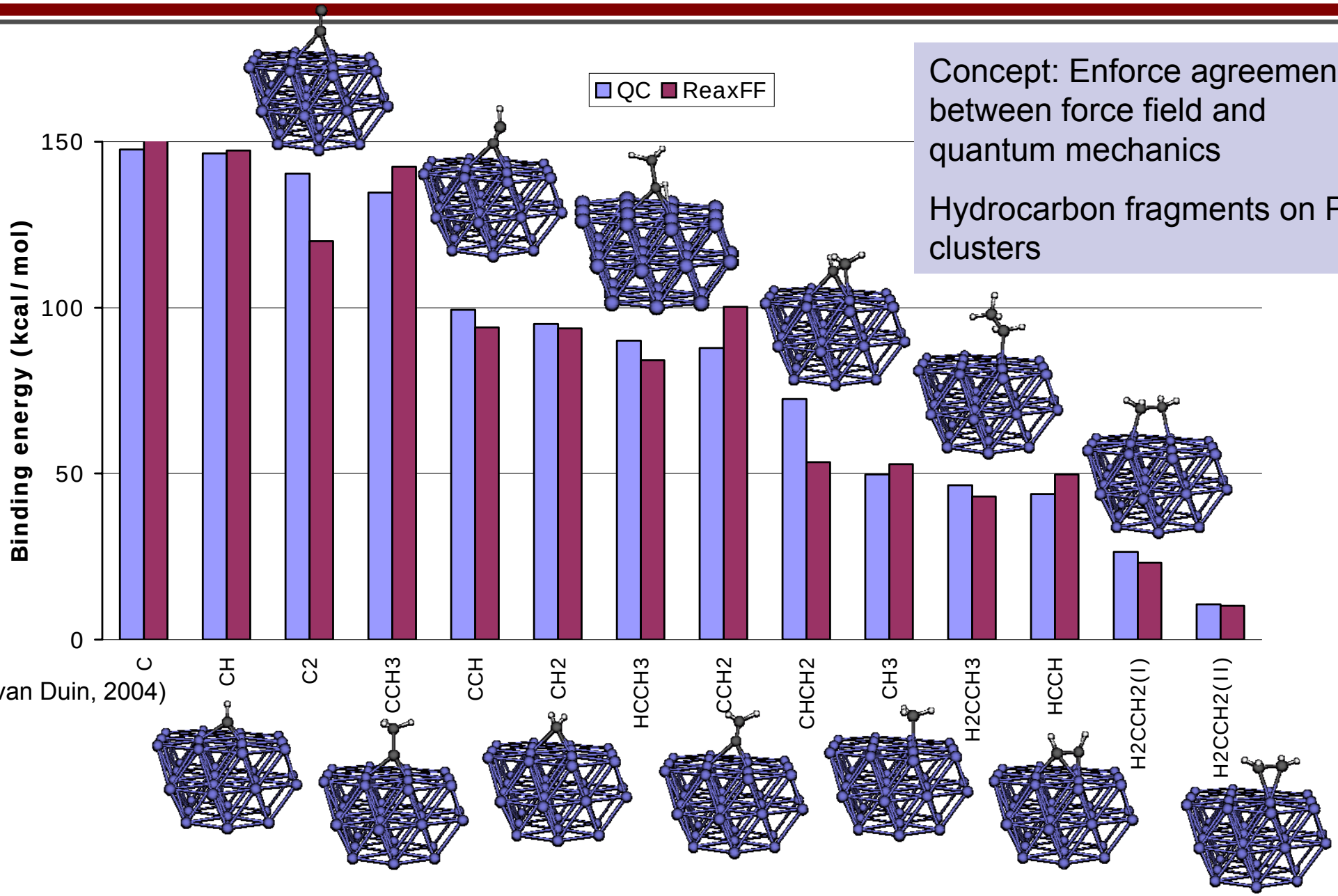
Parameters

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 ReaxFF Force Field: Hydrocarbon-Pt interactions



(van Duin, 2004)

Concept: Enforce agreement between force field and quantum mechanics

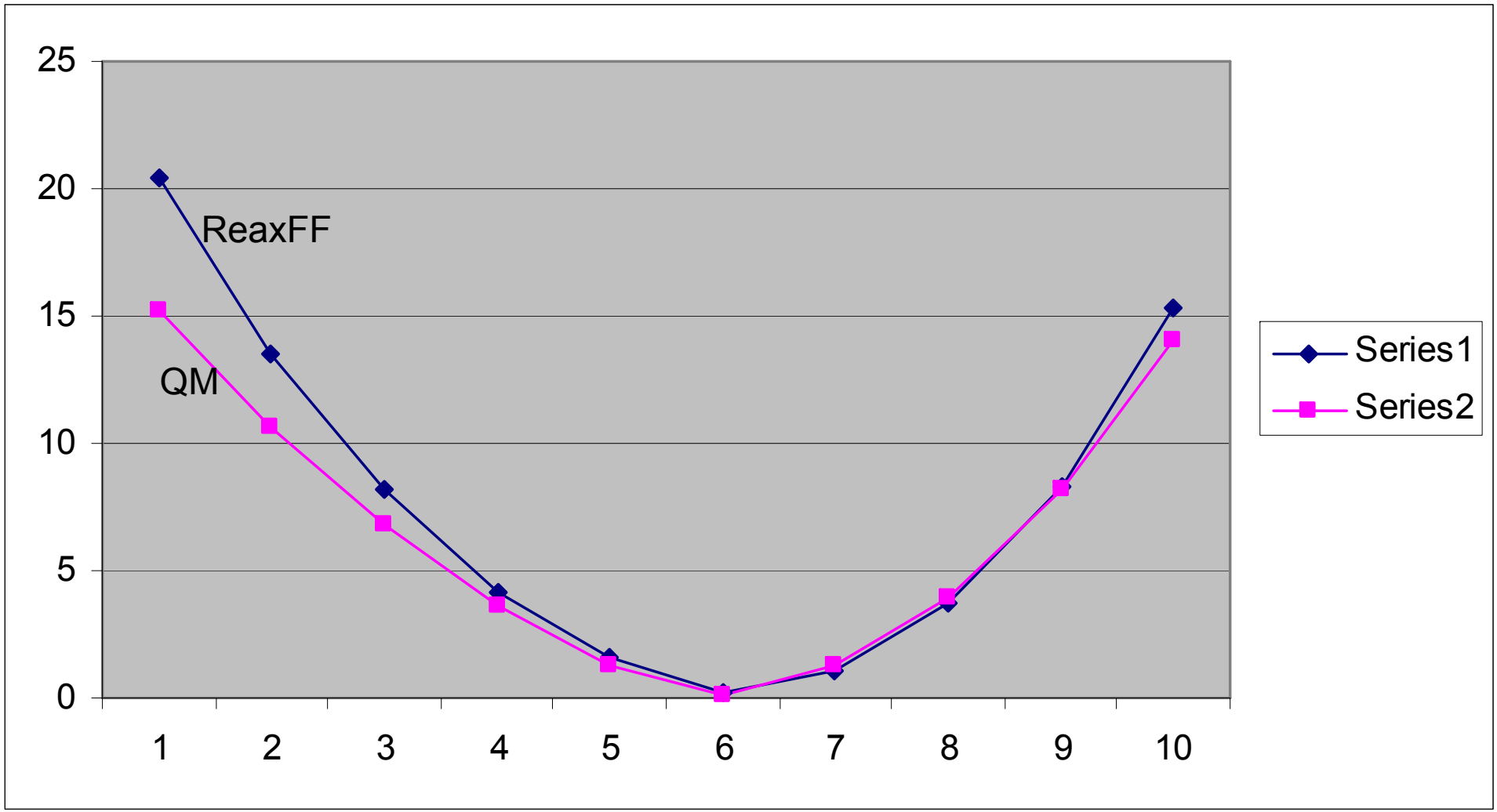
Hydrocarbon fragments on Pt_{35}-clusters

ReaxFF can describe different C-Pt bonding modes

Training of ReaxFF Force Field: Equation of state FCC calcium

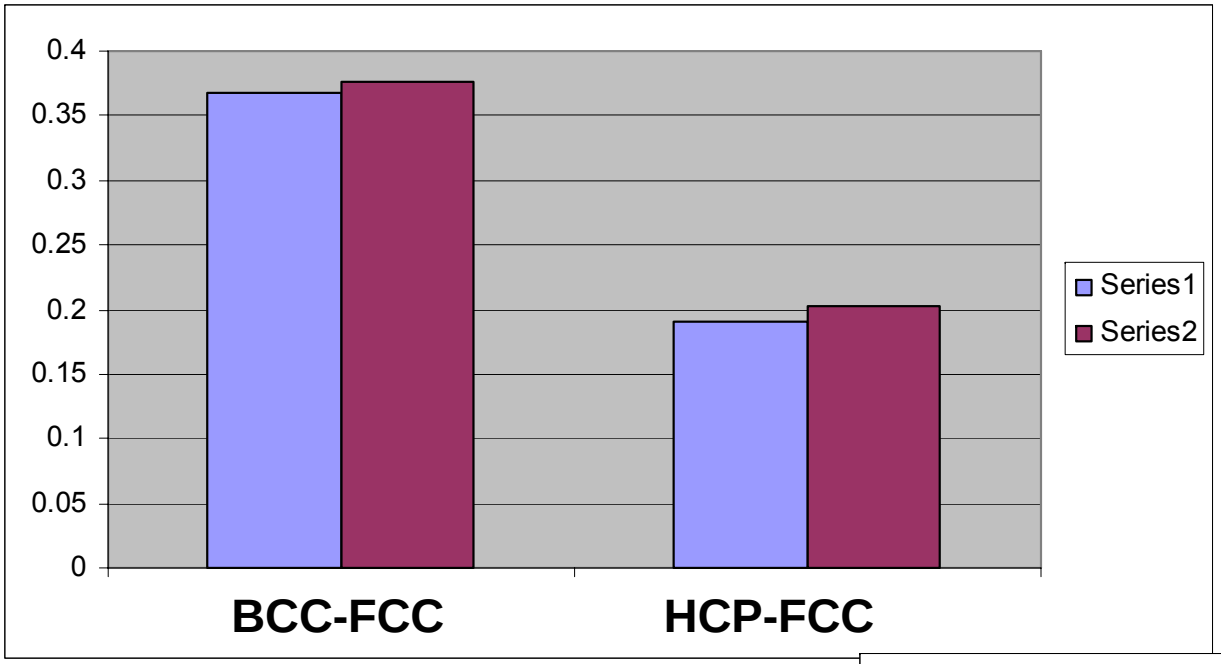
All energies in kcal/mol

Calcium ReaxFF



* QM data by Först & Yip

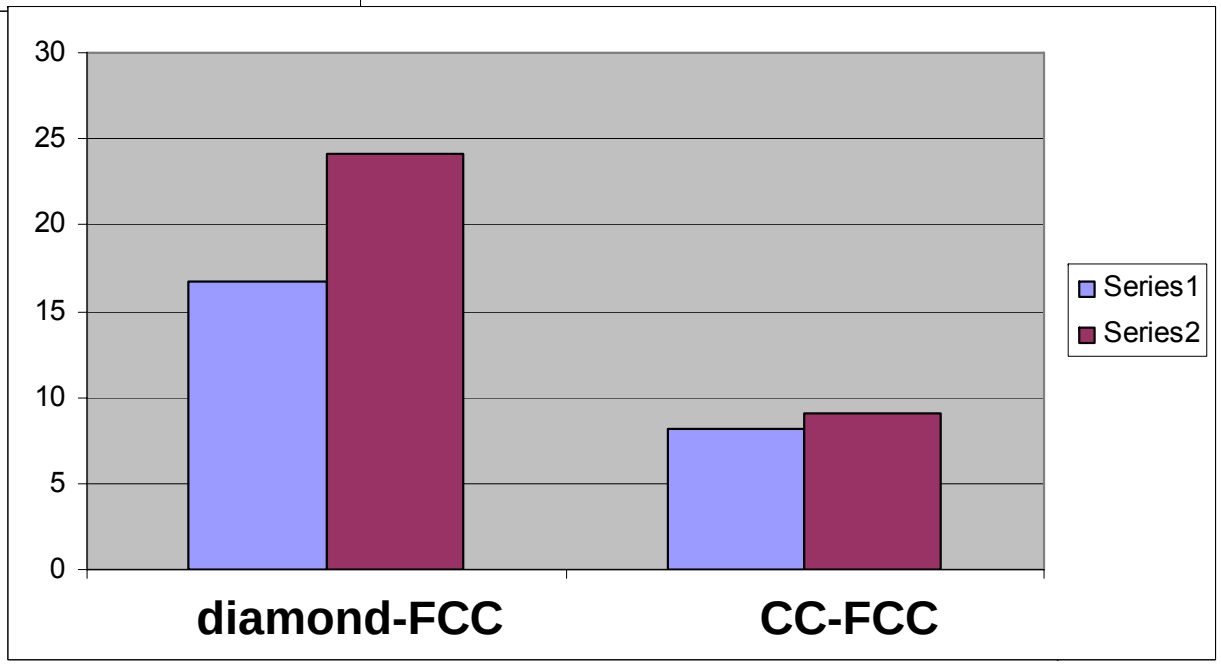
Training of ReaxFF Force Field: Phase stability FCC-HCP-diamond-CC



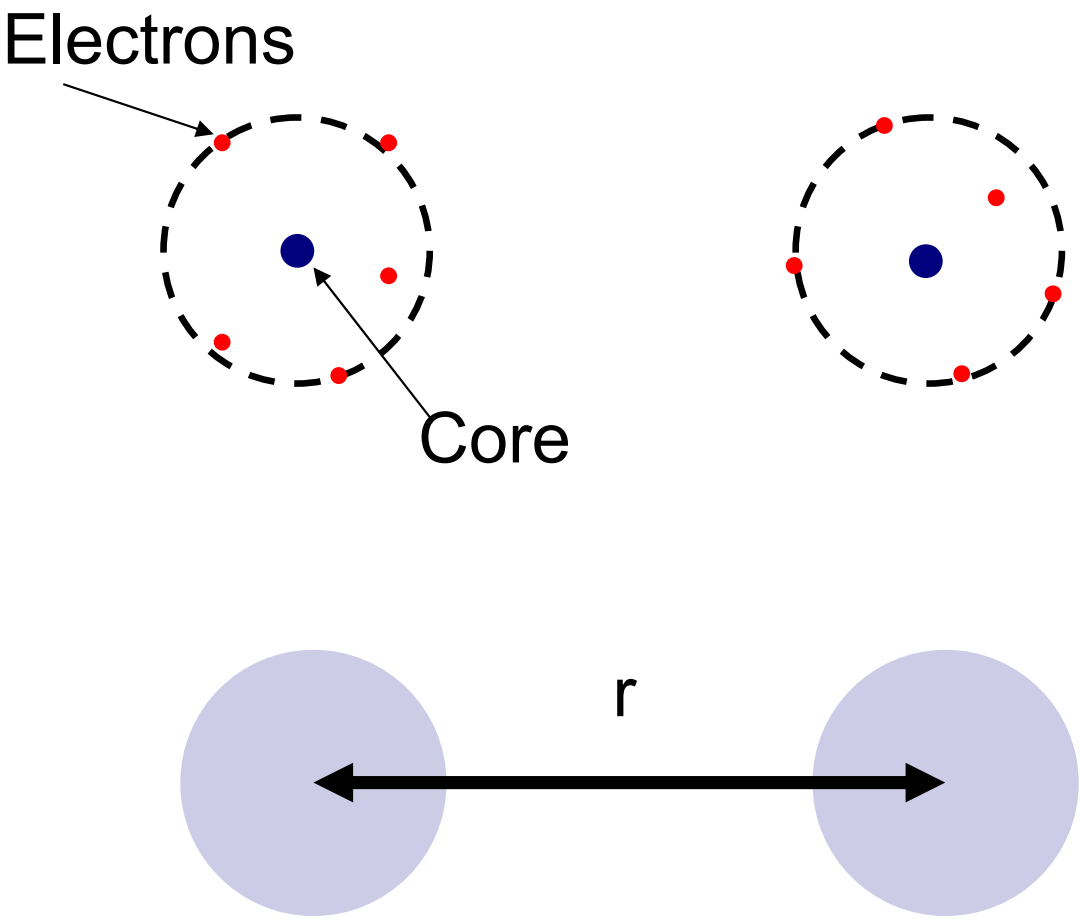
Calcium ReaxFF

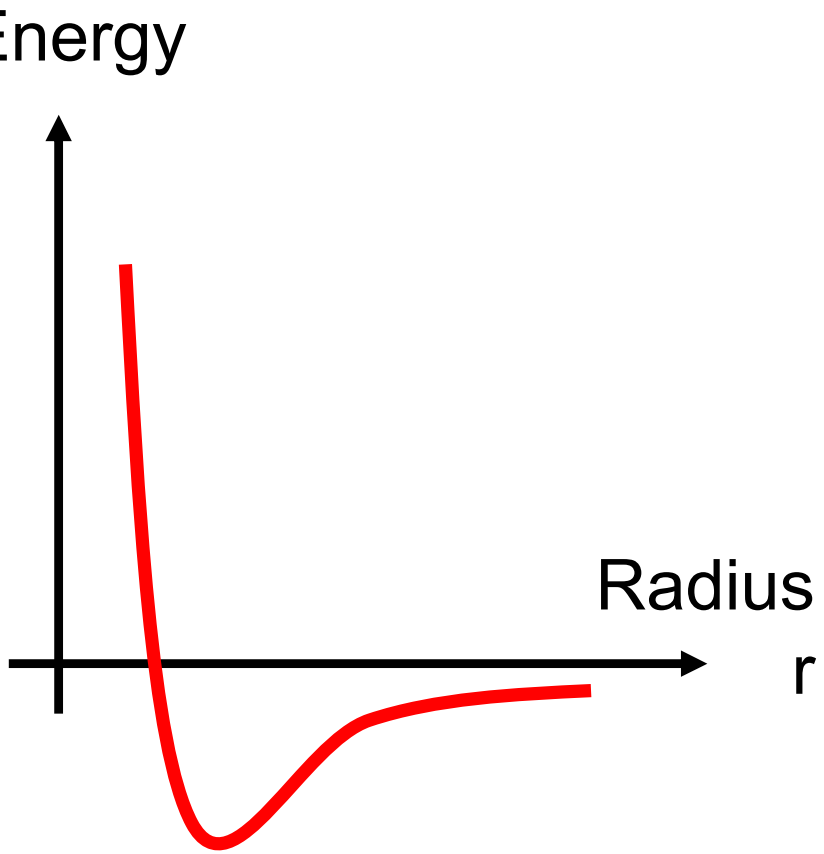
QM

ReaxFF

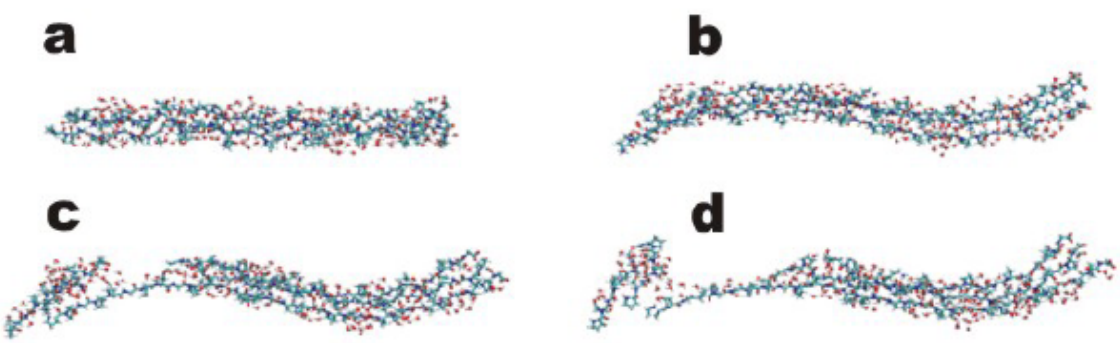


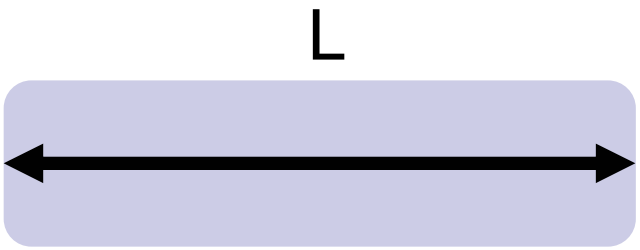
From electrons to atoms

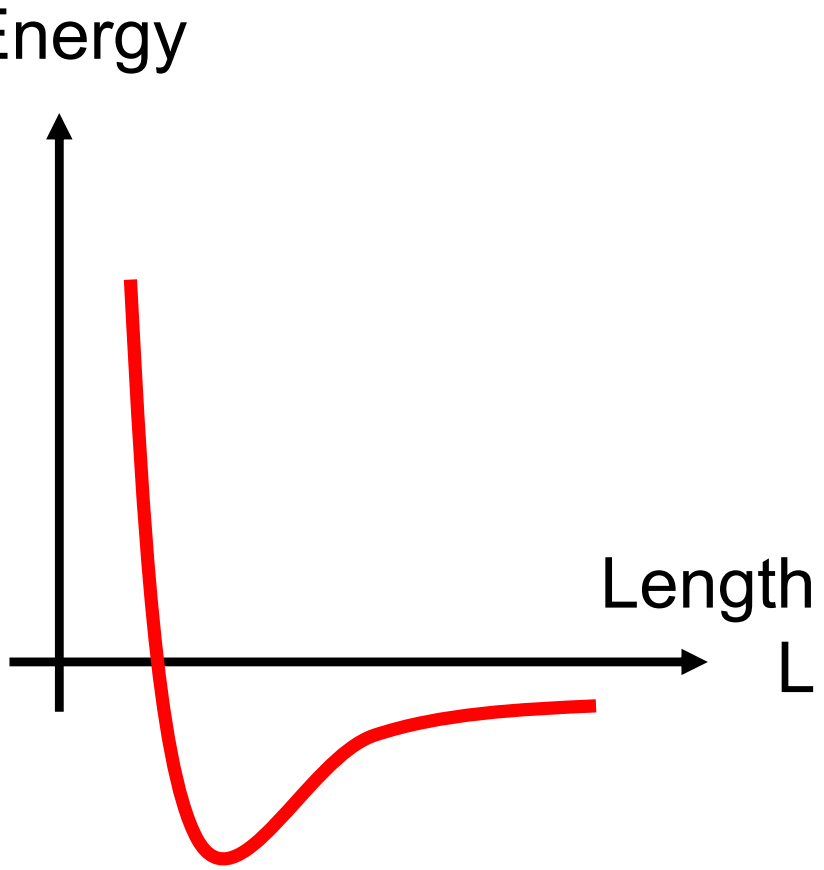




From atoms to molecules



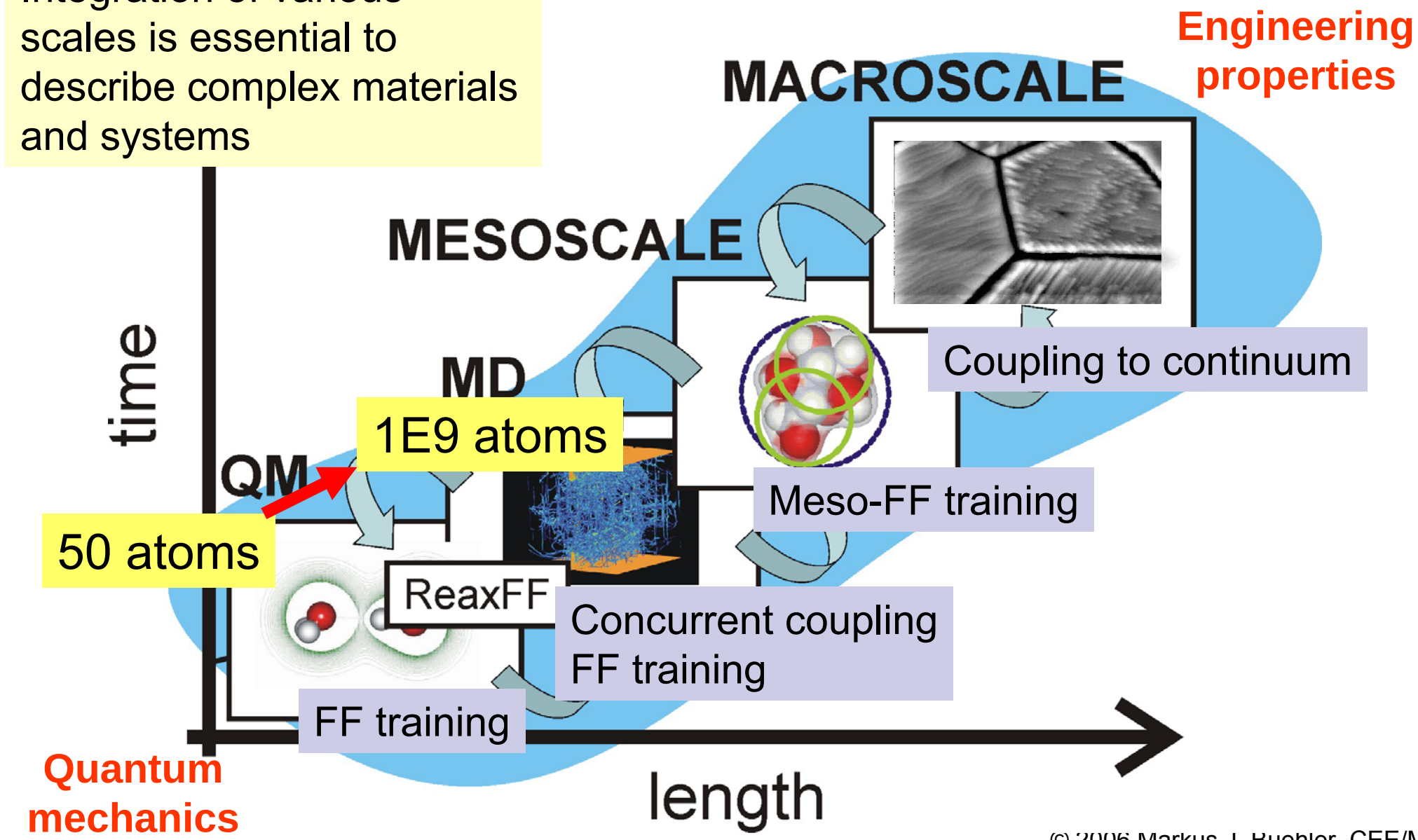




- Effective interaction laws can be derived at various levels of detail
- Here: Focus on atomistic interactions

Challenge: Coupling of various scales From QM to Macroscale

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



Example: Potentials for metals

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

http://phycomp.technion.ac.il/~phsorkin/thesis/node18.html

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

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

Lennard-Jones 12-6
Good for noble gases

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

Morse

$$C_{12} = C_{44}$$

Electron density

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

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

Quality varies: Good for copper, nickel, to some extend 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).

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

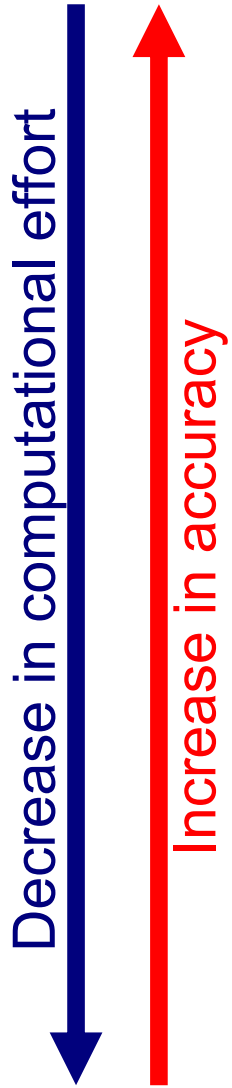
ReaxFF: Bridge between QM and empirical FFs (charge flow)

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, CMDF)

Tersoff: Bond order potentials (covalent systems), simple

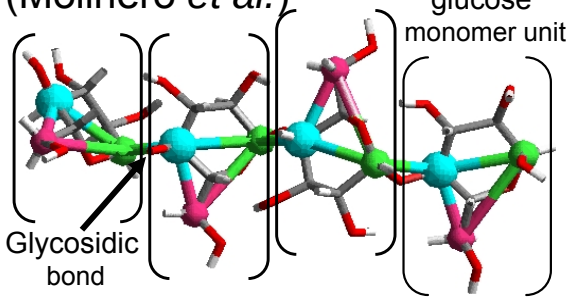
Organic force fields (harmonic): Proteins, organics etc., CHARMM, DREIDING, AMBER (codes: NAMD, GROMACS, CHARMM…)
Pair potentials: Noble gases (Ar) or model materials



Less accuracy does not mean less science can be done

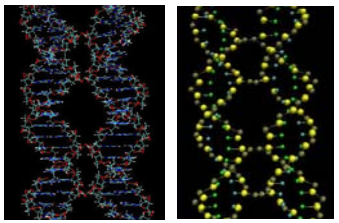
Concurrent versus hierarchical multi-scale simulations

(Molinero *et al.*)

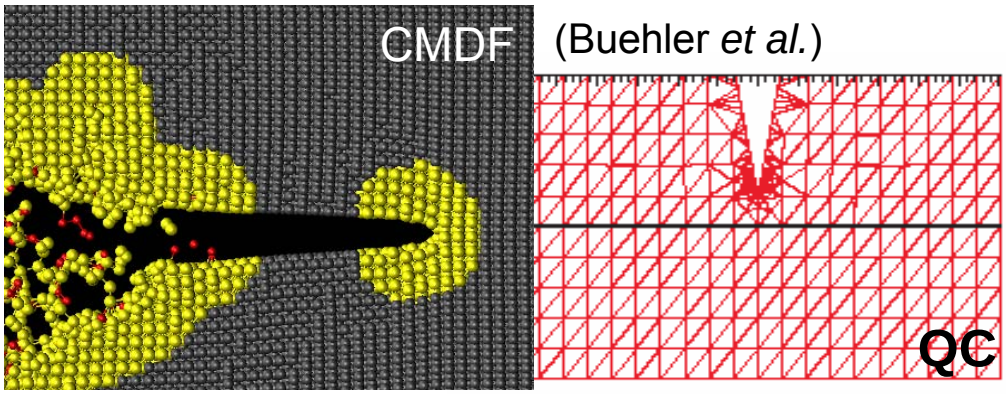


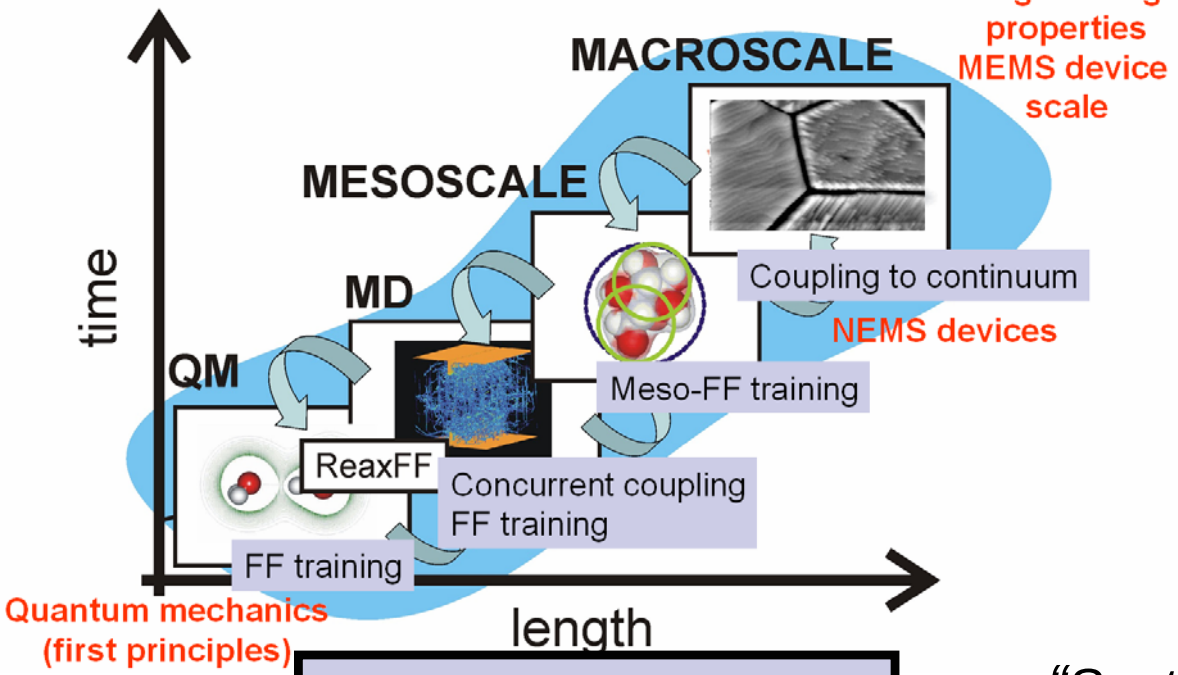
atomistic and M3B meso model of oligomer

DNA



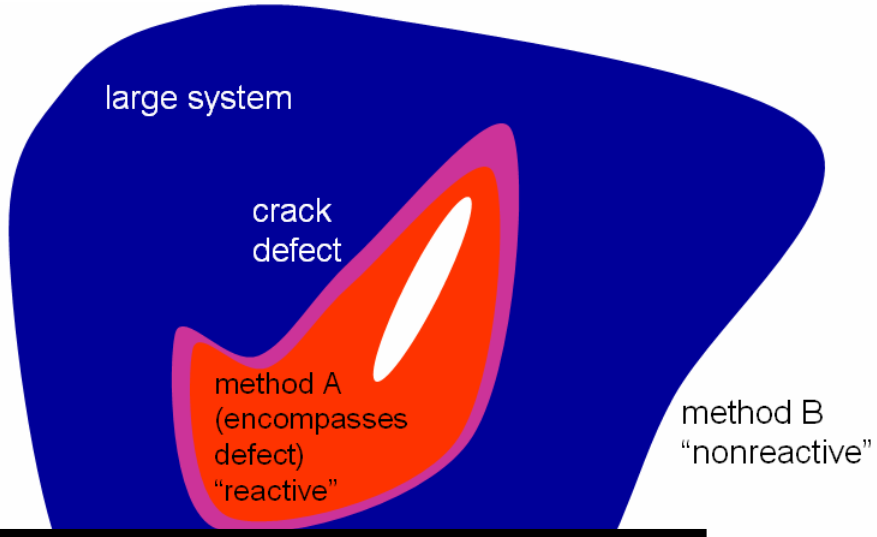
(Pascal *et al.*)





Hierarchical coupling

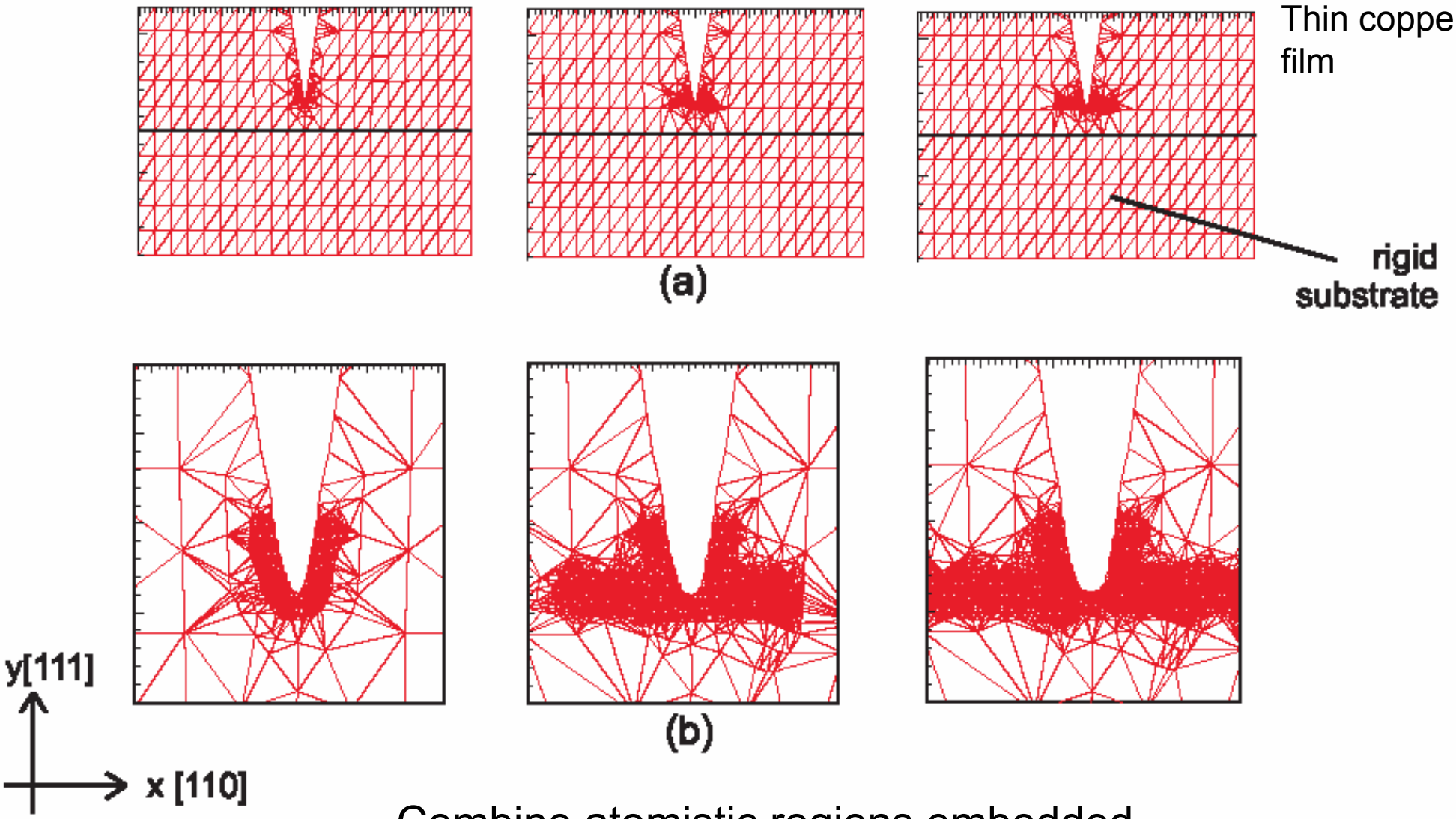
"finer scales train coarser scales"



Concurrent coupling
(QC-Tadmor, Ortiz, Phillips,…
MAAD-Abraham *et al.*, Wagner *et al.*)

"Spatial variation of resolution and accuracy"

The Quasi-Continuum (QC) Method



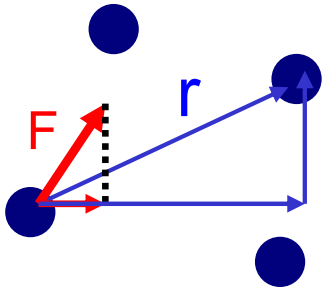
Combine atomistic regions embedded in continuum region

(Buehler *et al*., 2006)

Atomic stress tensor: Cauchy stress

Virial stress:

$$\sigma_{ij} = \frac{1}{2\Omega} \sum_{\alpha,\beta} \left(\overbrace{-\frac{1}{r}\frac{\partial \phi}{\partial r}}^{\text{Force } F_i} r_i r_j \; |_{r=r_{\alpha\beta}} \right)$$



where r_i is the projection of the interatomic distance vector **r** along coordinate *i*, Ω is the atomic volume

- 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.

http://ej.iop.org/links/q12/tWFV6mZig3VMoH,nK2DO8w/nano3_11_009.pdf
http://ej.iop.org/links/q67/dpRsM7WvMemOvng7LbbU7A/msmse4_4_S03.pdf

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 *et al.*

Atomic strain tensor

Atomic virial strain

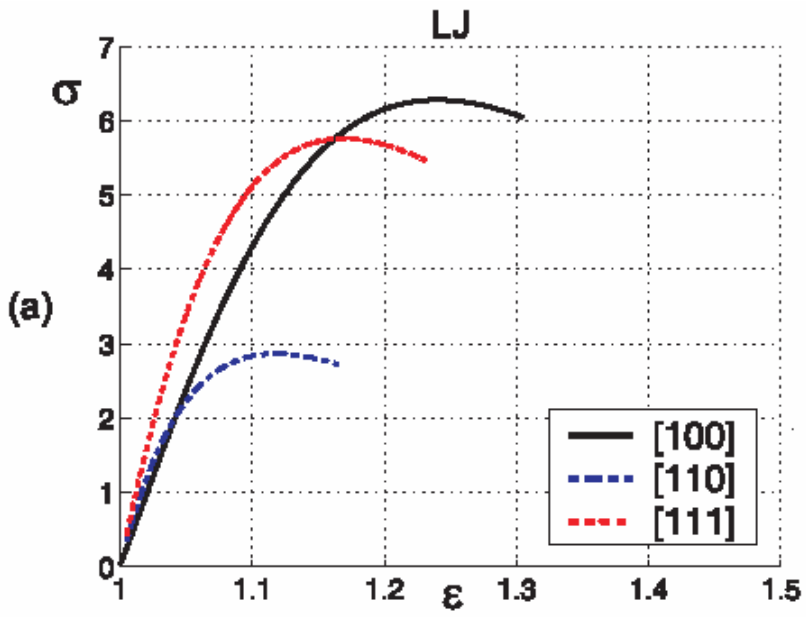
$$q_{ij}^{l} = \frac{1}{N}\sum_{k=1}^{N}\left(\frac{\Delta x_i^{kl}\Delta x_j^{kl}}{r_0^2}\right) \qquad b_{ij}^{l} = \frac{N}{\lambda}q_{ij}^{l} = \frac{1}{\lambda}\sum_{k=1}^{N}\left(\frac{\Delta x_i^{kl}\Delta x_j^{kl}}{r_0^2}\right)$$

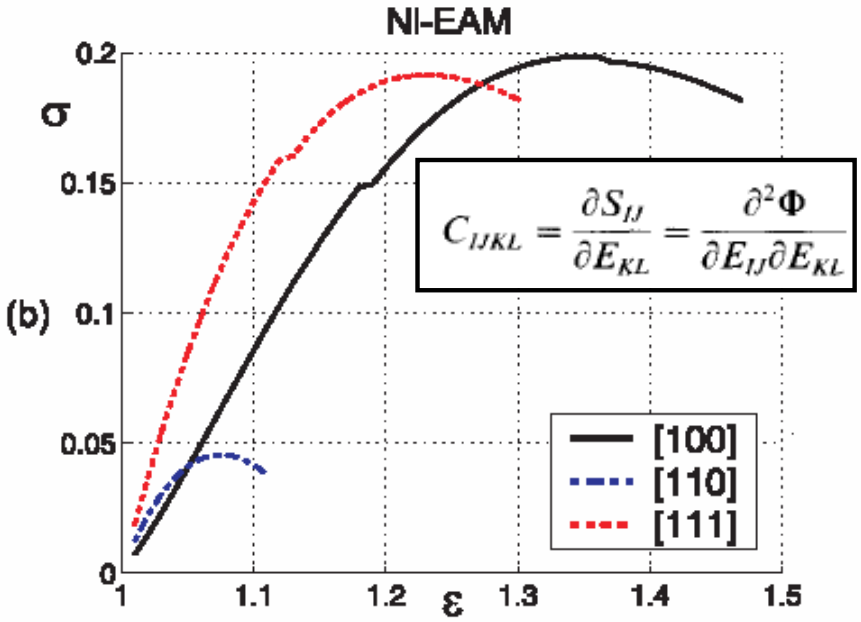
- The strain field is a measure of geometric deformation of the atomic lattice
- The local atomic strain is calculated by comparing the local deviation of the lattice from a reference configuration.
- Usually, the reference configuration is taken to be the undeformed lattice.
- In the atomistic simulations, 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.

Jonathan Zimmerman, Continuum and atomistic modeling of dislocation nucleation at crystal surface ledges. PhD Thesis, Stanford University, 1999.

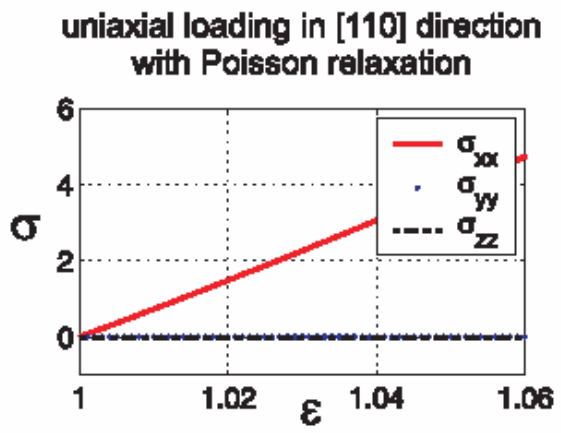
Stress versus strain from atomistics…

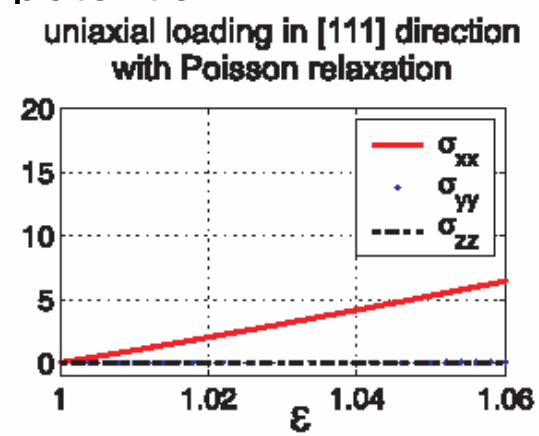


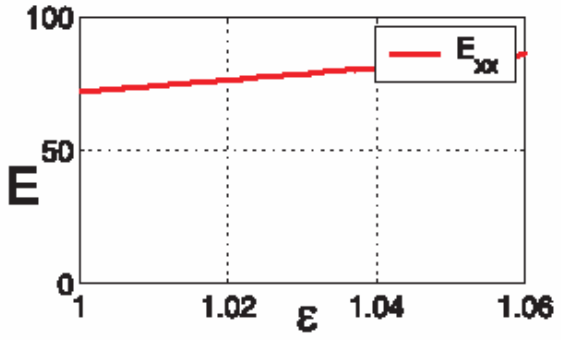


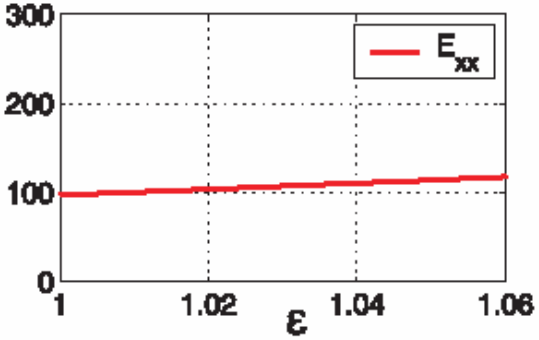
$$C_{IJKL} = \frac{\partial S_{IJ}}{\partial E_{KL}} = \frac{\partial^2 \Phi}{\partial E_{IJ} \partial E_{KL}}$$

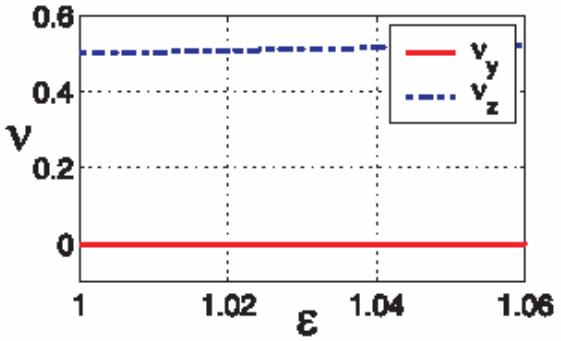
Harmonic potential

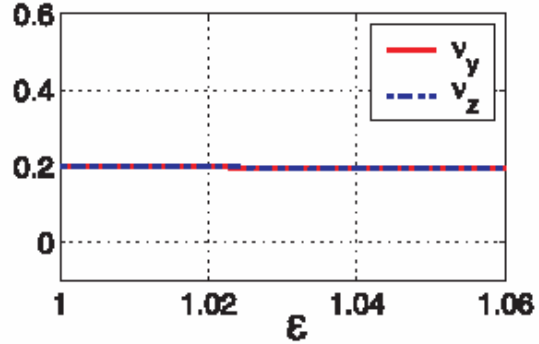




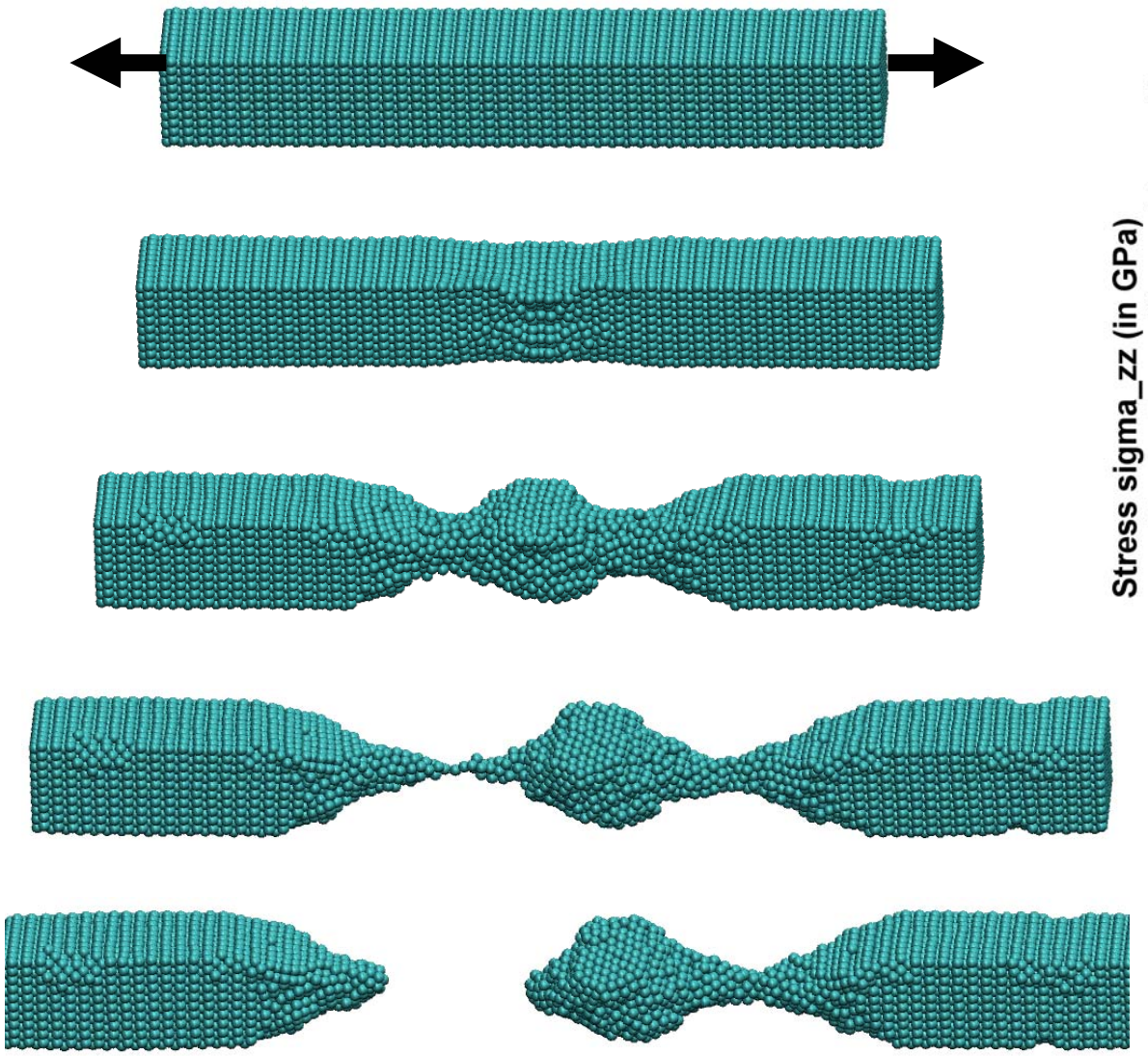


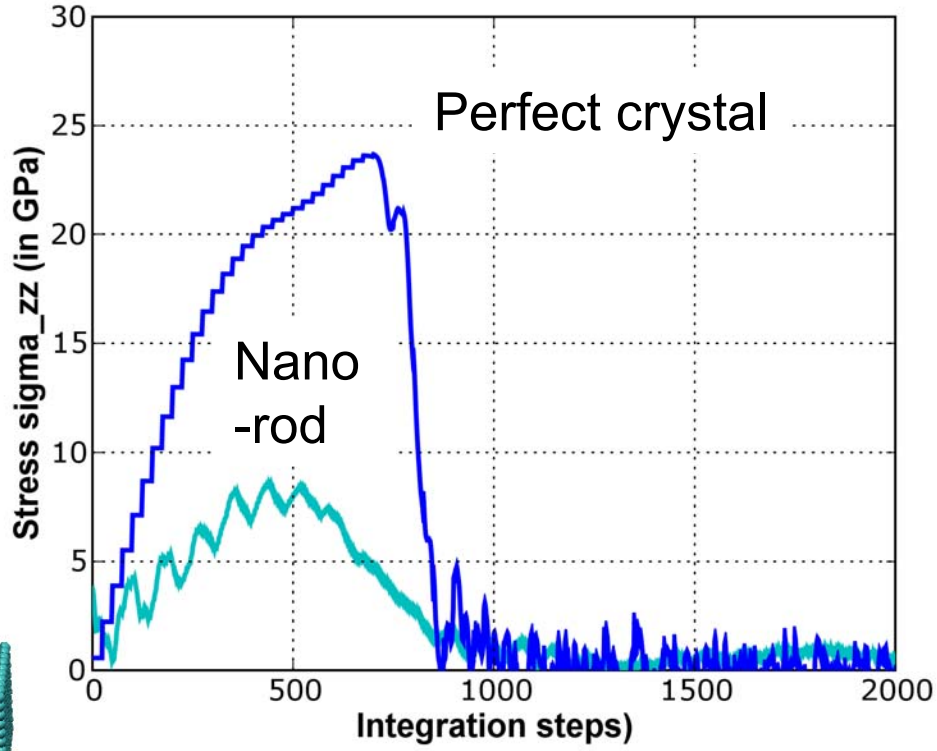






Example: Tensile test of Cu nano-rod





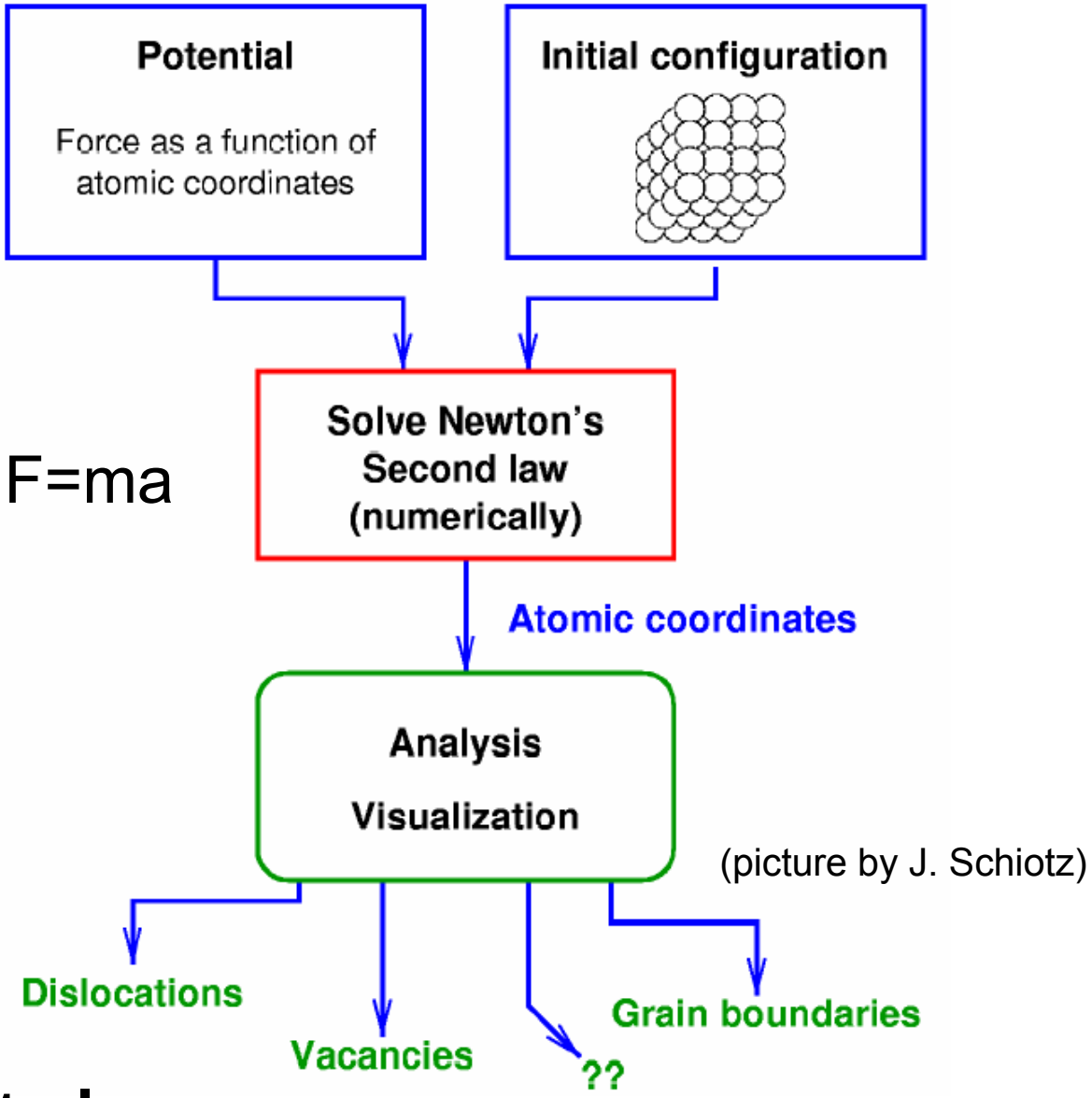
→ Assignment

z ⟶

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



(picture by J. Schiotz)

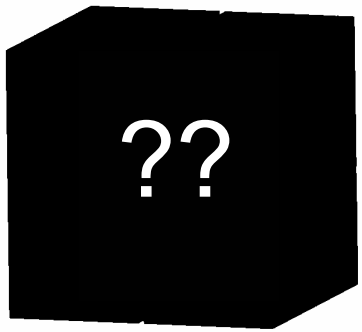
Real challenge:
Questions to ask and what to learn

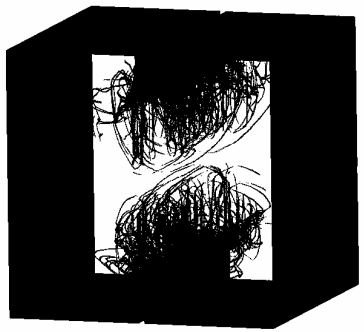
Visualization

- Visualization and “clever” data analysis plays an integral role in atomistic modeling, as all information obtained is atomic-scale
- Visualization provides the “window” into the data and brings the data to life, and enables us to “understand”

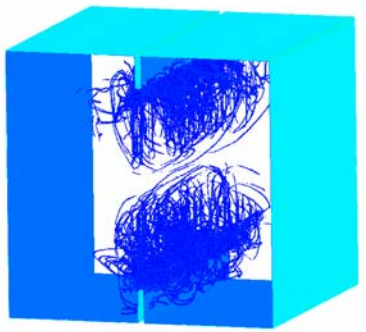
No visualization

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

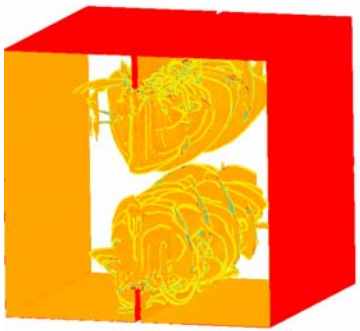




Energy analysis



Color scheme

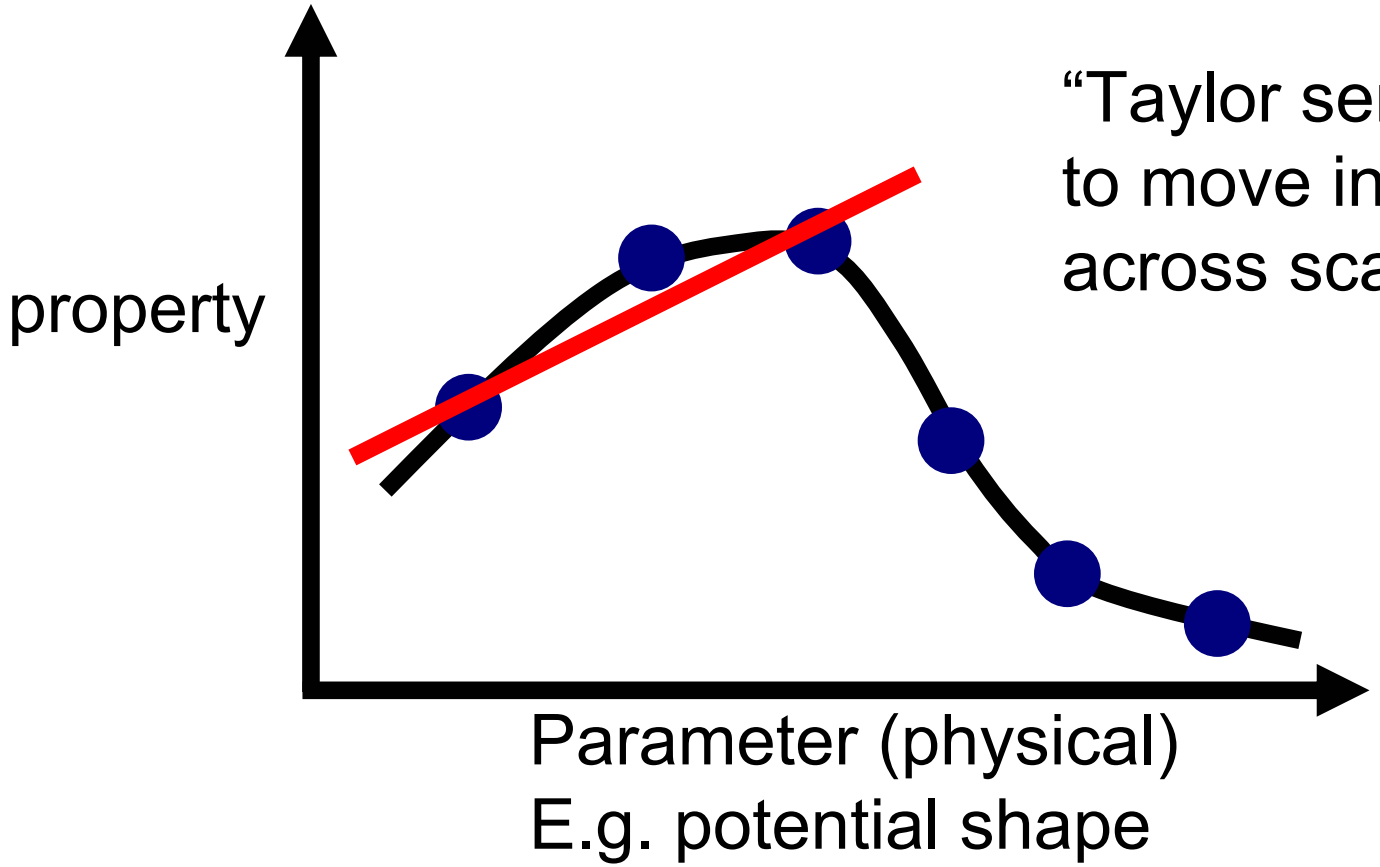


Centrosymmetry

Many schemes exist for crystal defects, including slip vector, cetrosymmetry, energy method…

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



"Taylor series expansion" to move information across scales

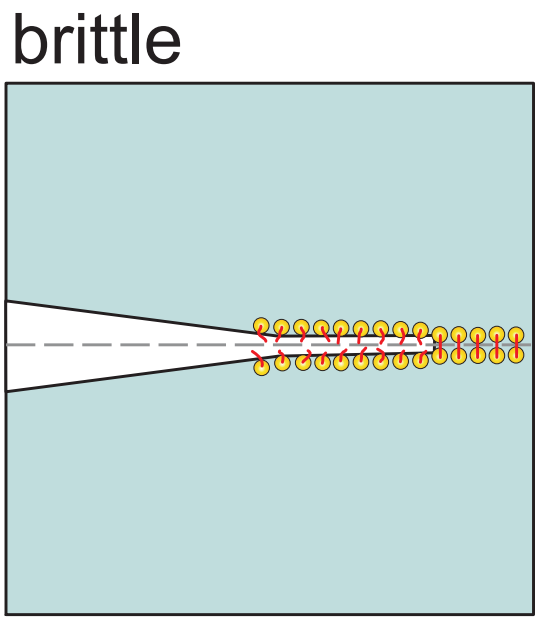
Atomistic methods in mechanics

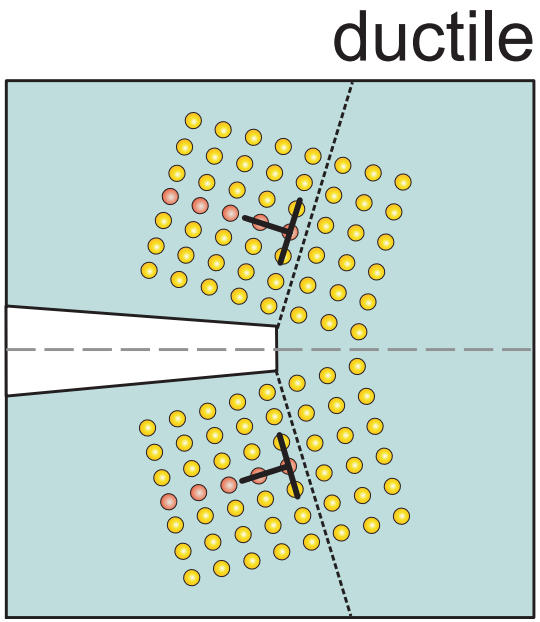
Ductile versus brittle behavior

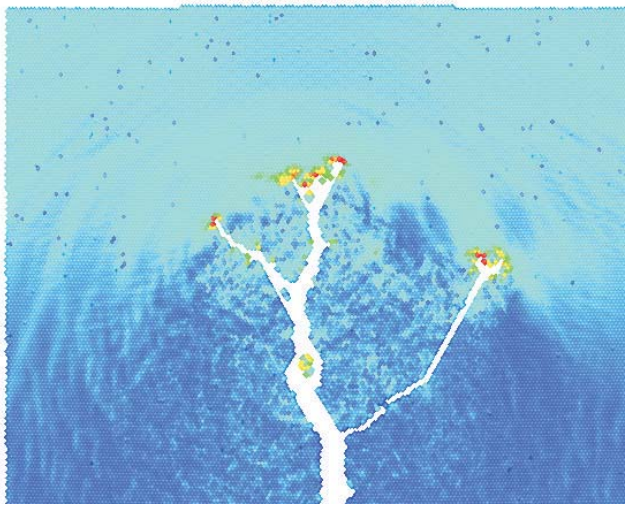
Atomistic methods in mechanics

- 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..)

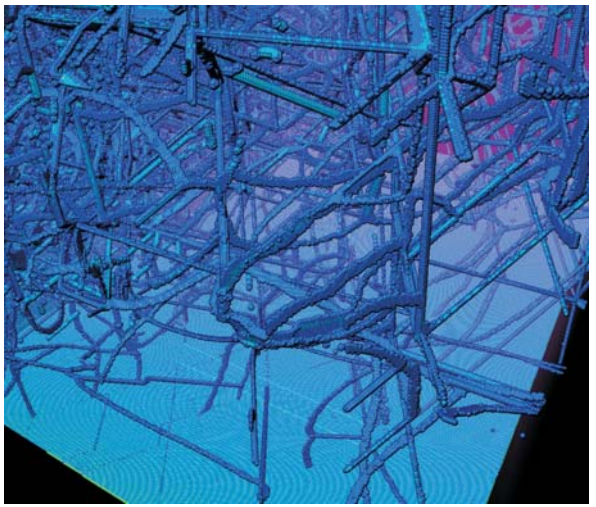
Ductile versus brittle materials







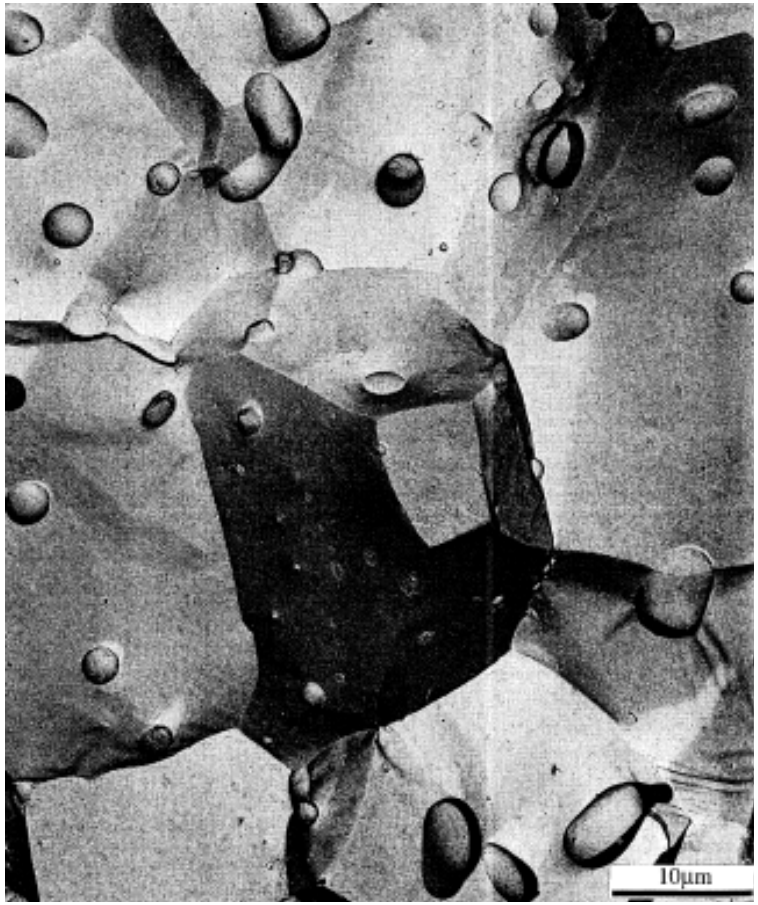
(a)

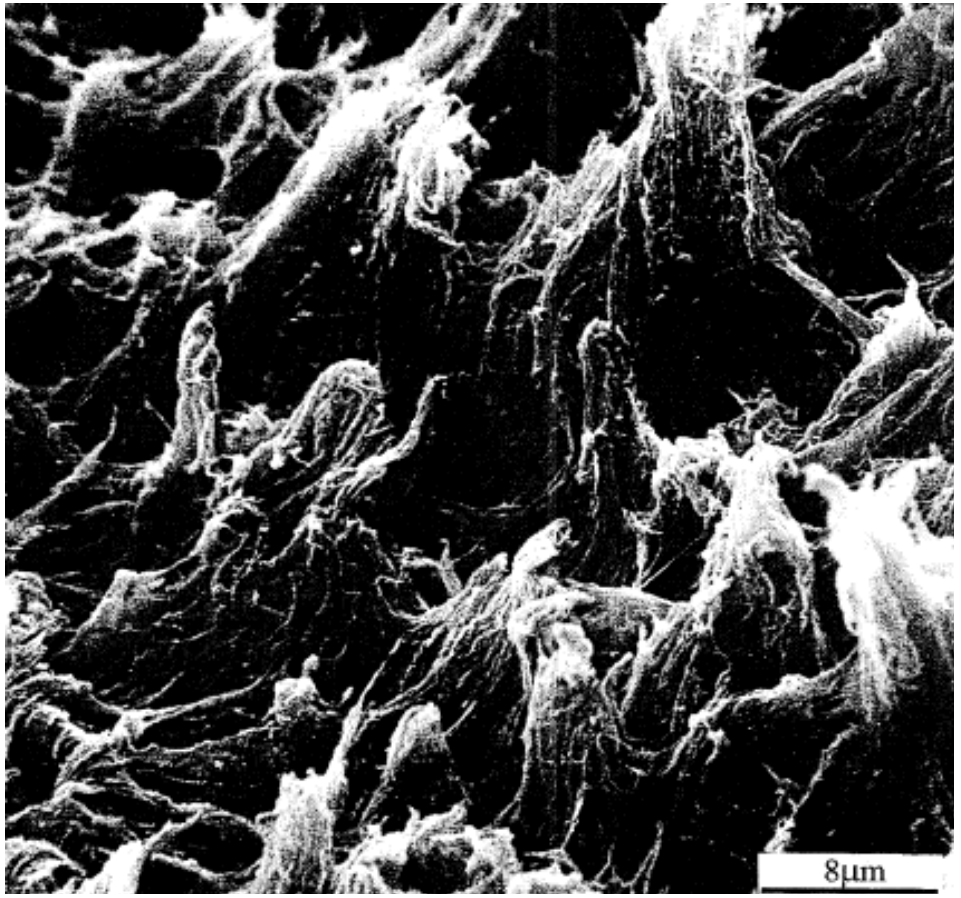


(b)

(Buehler, 2004)

Ductile versus brittle materials: Experiment



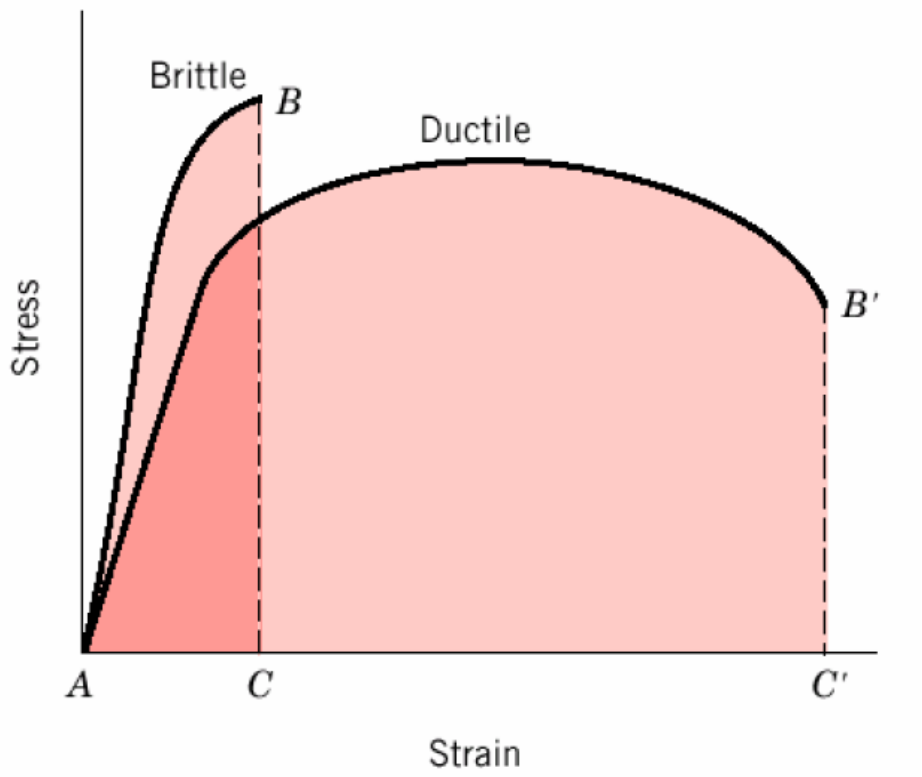


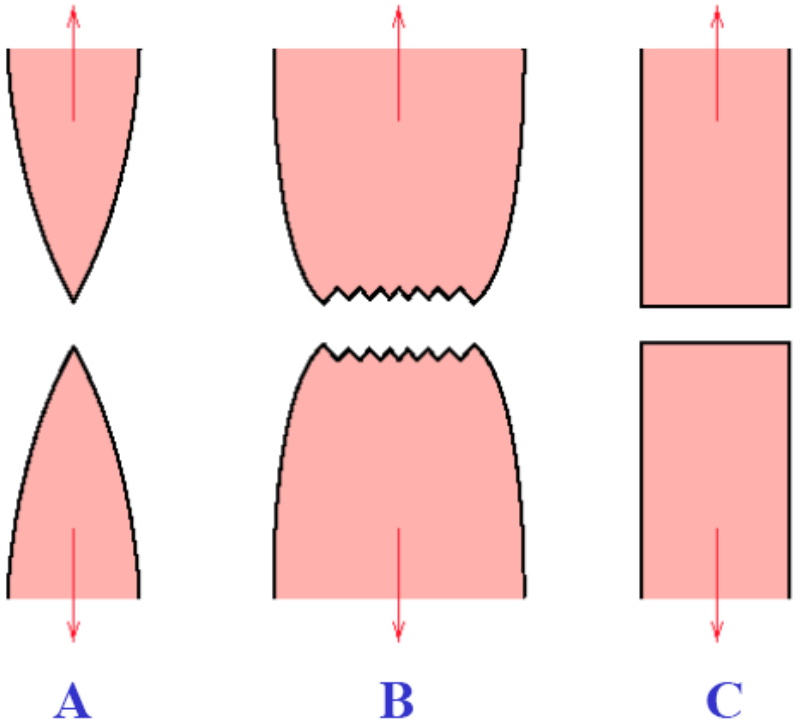
"brittle"
Separation long grain boundaries, Cleavage

"ductile"
Dislocations, material deformation (microscopic)

Pictures courtesy: Fractography: Observing, Measuring and Interpreting Fracture Surface Topography, Derek Hull, Cambridge University Press, 1999.

Ductile versus brittle materials: Experiment





A. Very ductile, soft metals (e.g. Pb, Au) at room temperature, other metals, polymers, glasses at high temperature.

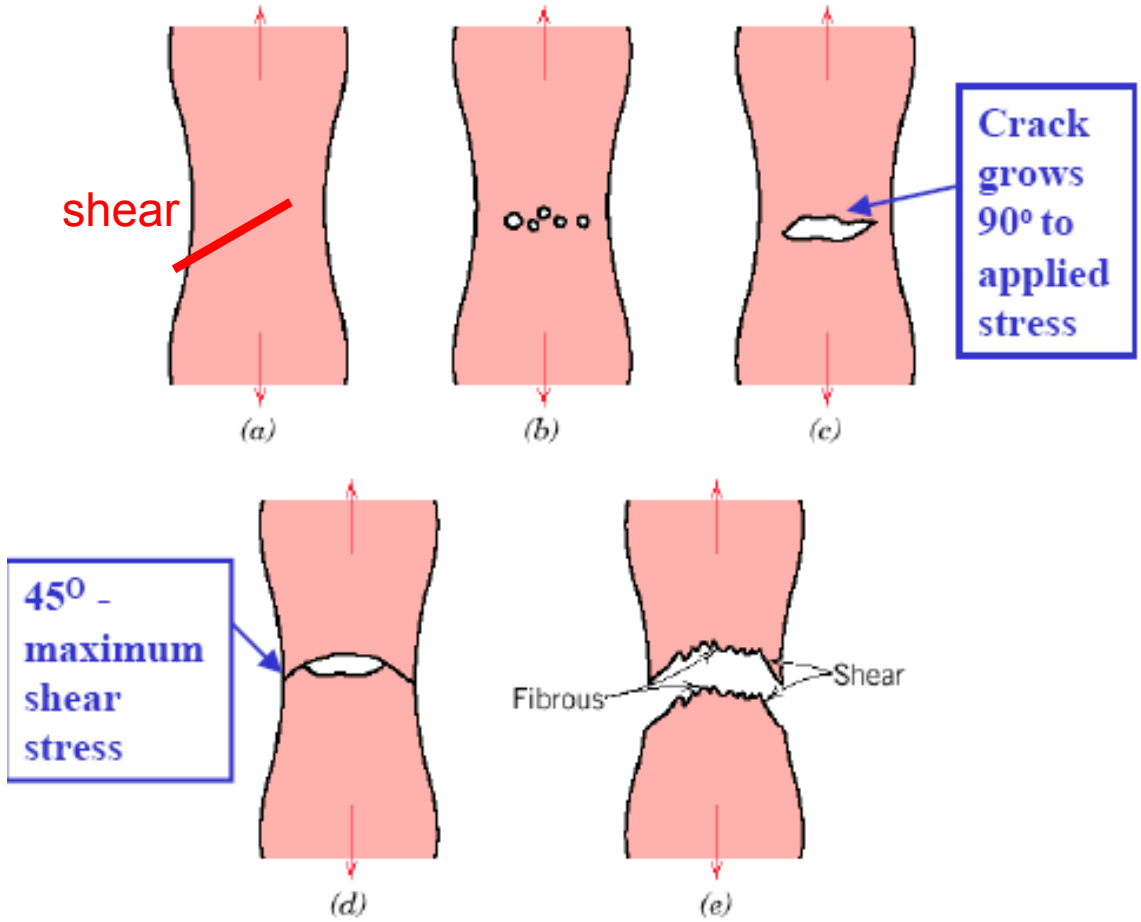
B. Moderately ductile fracture, typical for ductile metals

C. Brittle fracture, cold metals, ceramics.

http://www.people.virginia.edu/~lz2n/mse209/Chapter8.pdf

Ductile fracture

(a) Necking,
(b) Cavity Formation,
(c) Cavity coalescence to form a crack,
(d) Crack propagation,
(e) Fracture



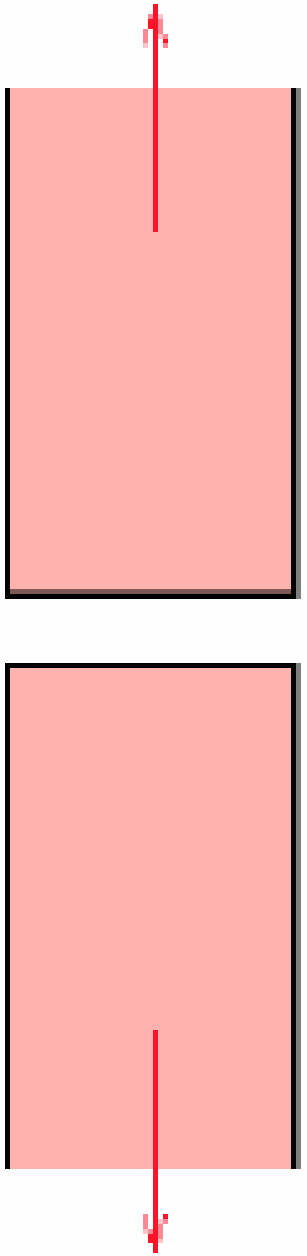
http://www.people.virginia.edu/~lz2n/mse209/Chapter8.pdf

Brittle fracture

- No appreciable plastic deformation

- Crack propagation is very fast
- Crack propagates nearly perpendicular to the direction of the applied stress

- Crack often propagates by cleavage – breaking of atomic bonds along specific crystallographic planes (cleavage planes).



http://www.people.virginia.edu/~lz2n/mse209/Chapter8.pdf

Ductile versus brittle materials

- Ductile failure: Nucleation of dislocations at crack tip (γ_{us})
- Brittle fracture: Creation of two new surfaces ($\gamma_{surface}$)
- Rice and others (1990s) have quantified this transition from brittle to ductile for various materials, by investigating the relative ease of either crack propagation or shear and dislocation nucleation:

  Use energy argument

$$G = 8\frac{1+(1-\nu)\tan^2\phi}{(1+\cos\theta)\sin^2\theta}\gamma_{us}$$ "ductile"

$$G = 2\gamma_s$$ "brittle"

$$\frac{\gamma_s}{\gamma_{us}} > 4\frac{1+(1-\nu)\tan^2\phi}{(1+\cos\theta)\sin^2\theta}$$

- These early results already suggested the great importance of the atomic interaction in determining the materials behavior.
- This was later verified in many studies, including for cases of brittle fracture

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

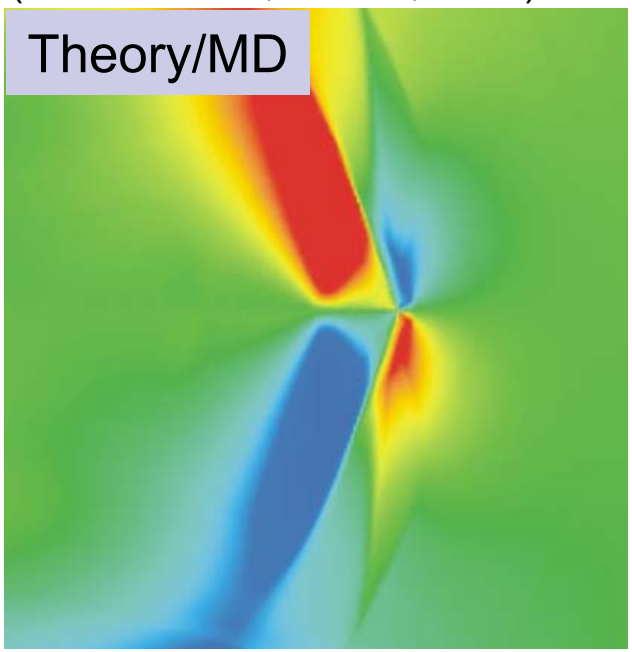
Cracks in Rubber Propagate Faster than the Speed of Sound

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.

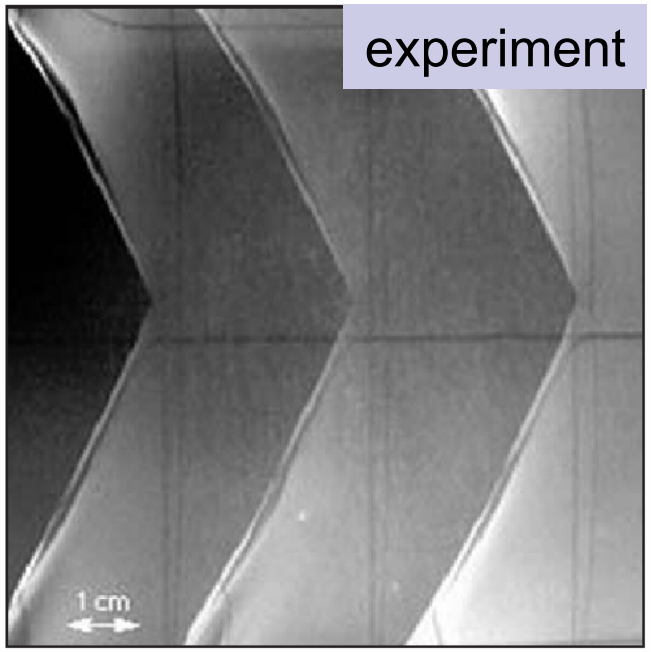
As reported in the July issue of *Physical Review Letters* (105504), Petersan and colleagues identified the intersonic crack speed by the observation of shock fronts near the crack tip by high-speed photogra-

MRS BULLETIN/OCTOBER 2004

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



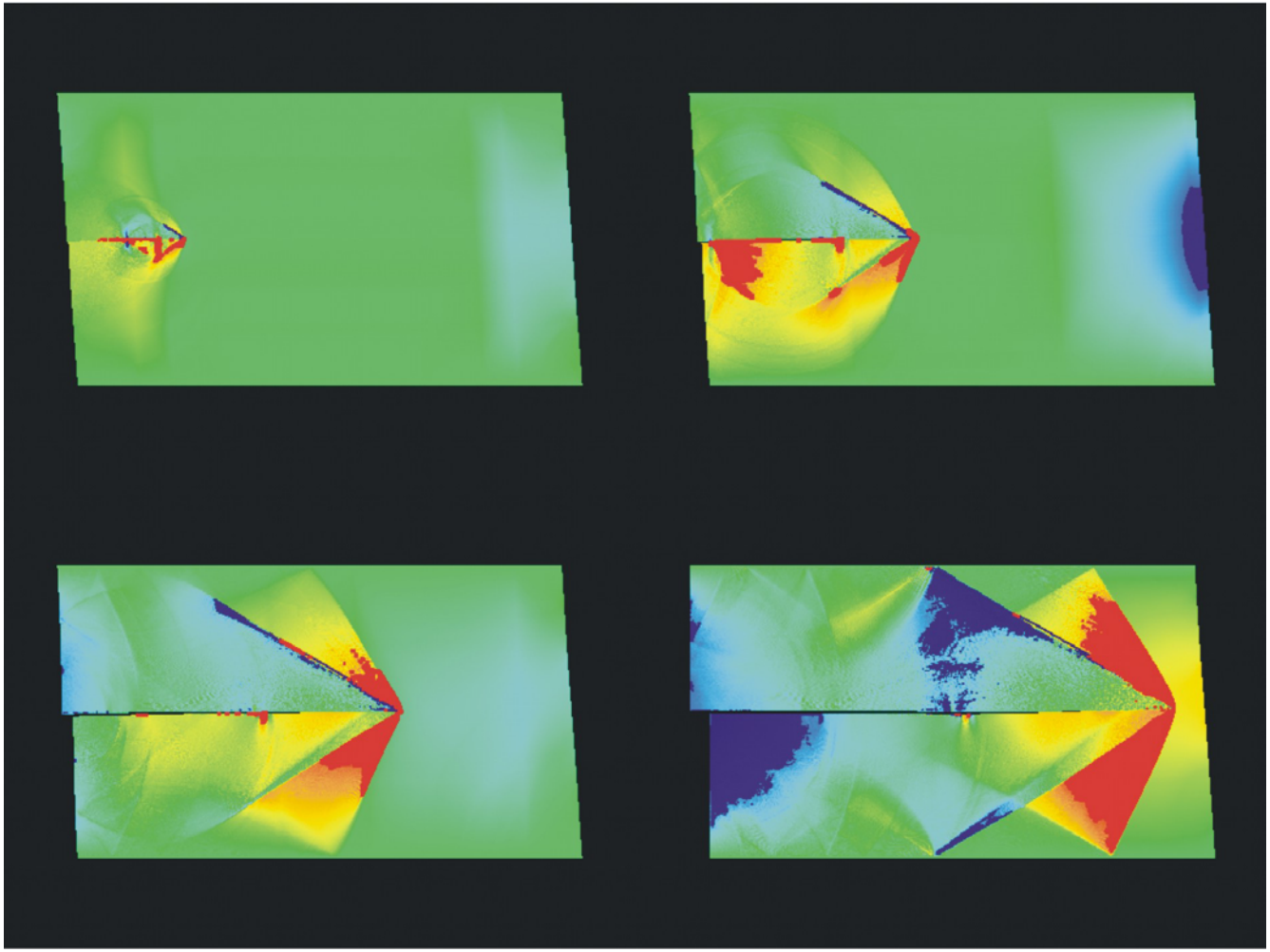
(Petersan *et al*., PRL, 2004)



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

See lecture 2

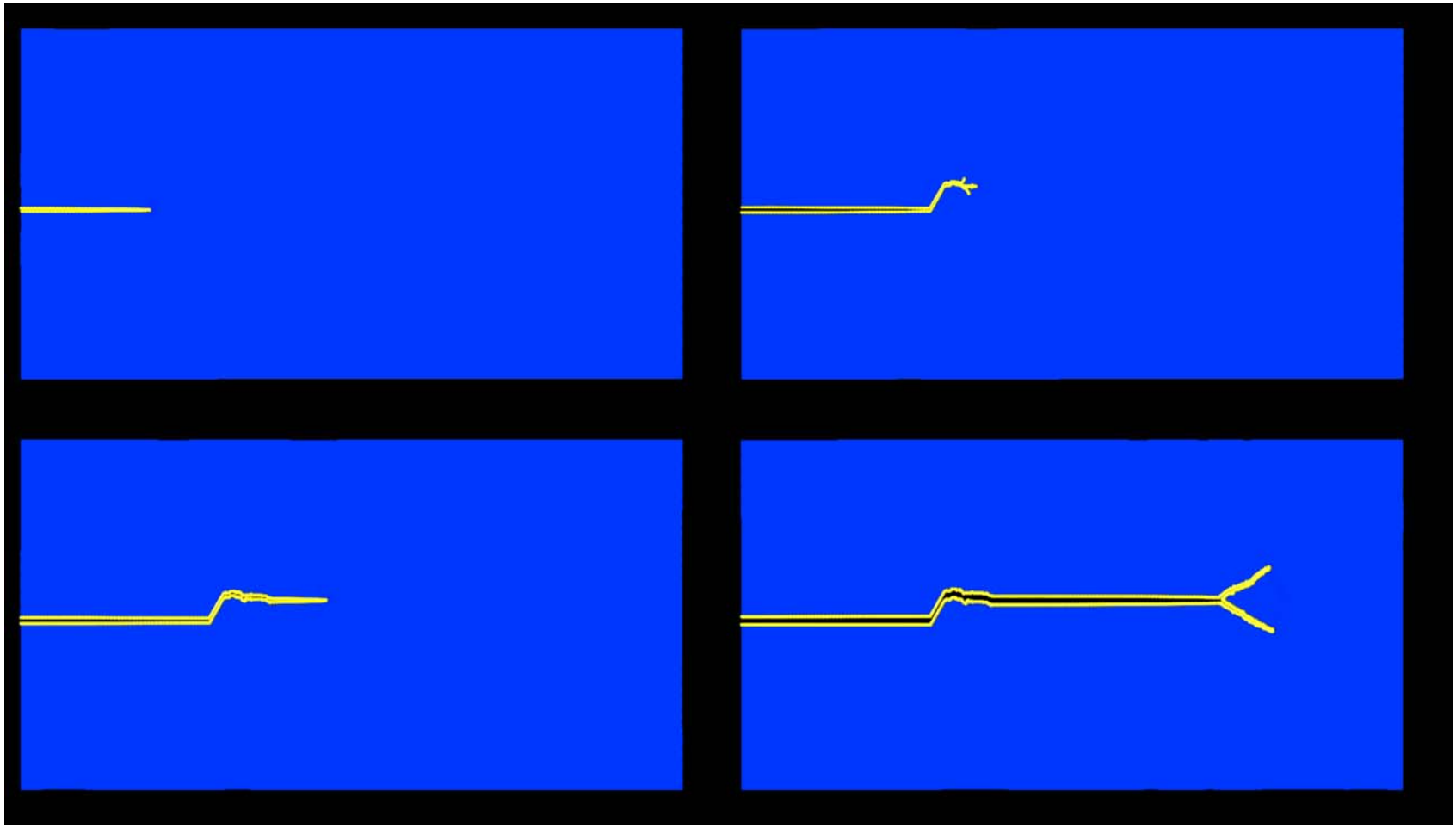
Supersonic fracture: Brittle fracture mechanism breaks the sound barrier



See lecture 2

Buehler *et al*., Nature, 2003

Dynamical fracture instabilities

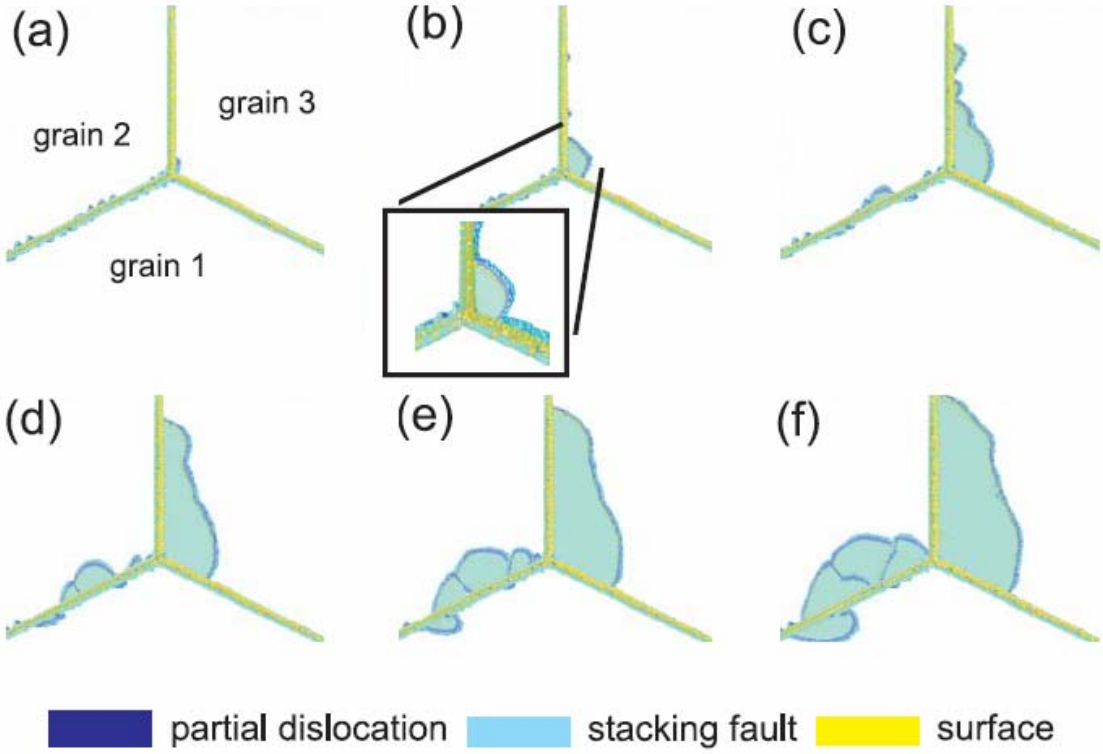


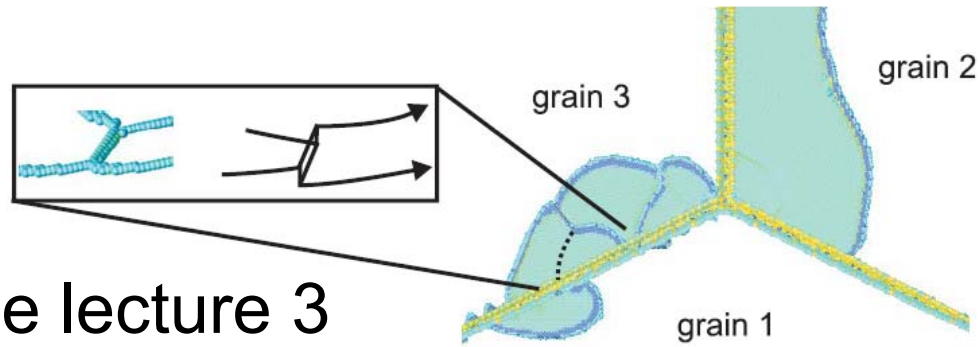
New theory explains dynamical crack instabilities as observed in many experiments and computer simulations

See lecture 2

Buehler and Gao, Nature, 2006 (to appear in Jan. 19 issue)

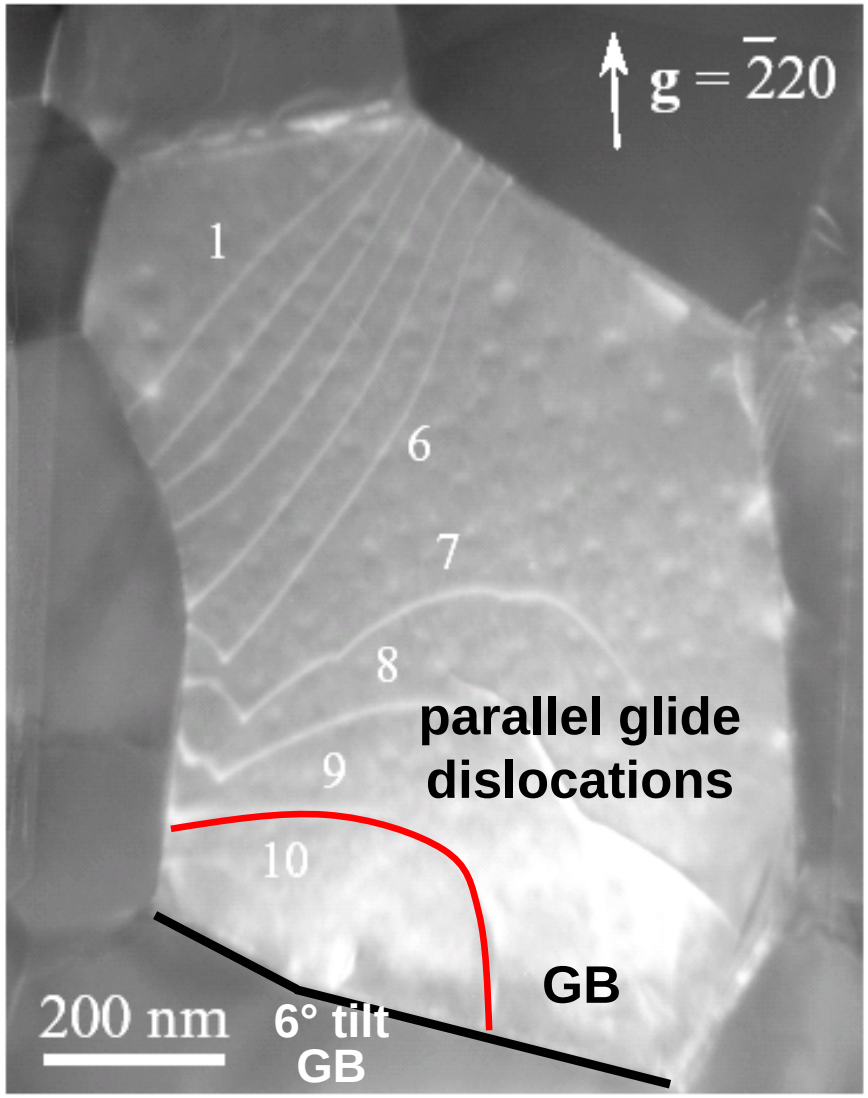
Dislocation nucleation in thin metal films





See lecture 3

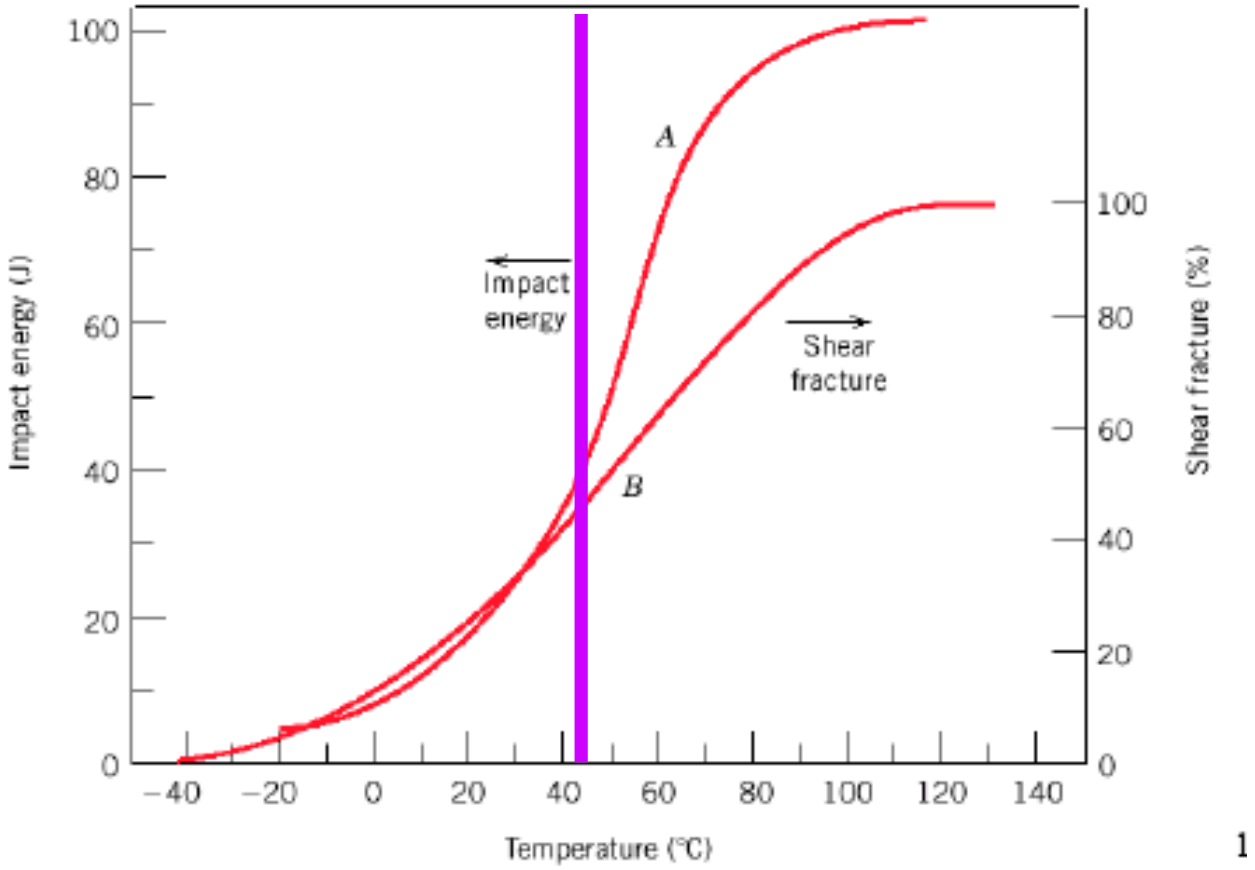
Buehler *et al*., 2003-2006



(Balk, Dehm *et al.* 2001, 2002)

Brittle-to-ductile transition: Temperature effect

“ductile”



1

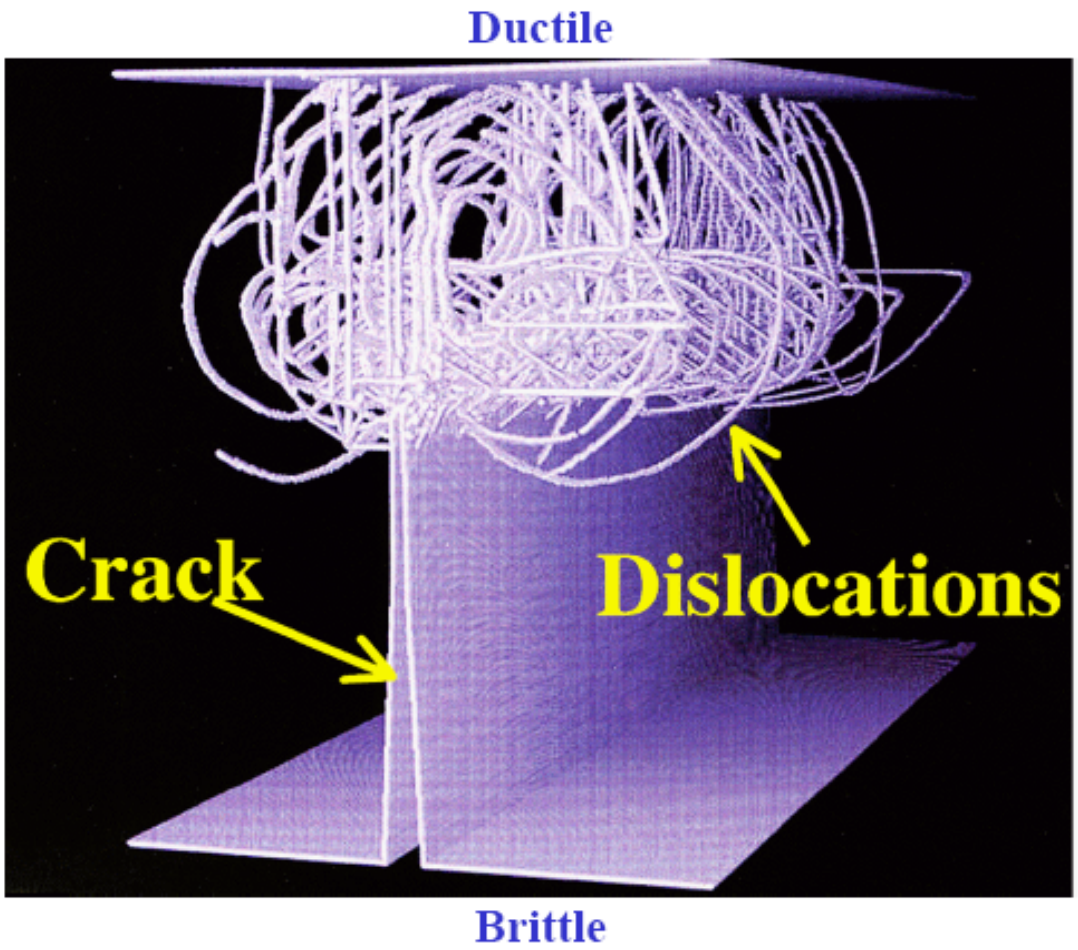
“brittle”

As temperature decreases a ductile material can become Brittle:

Ductile-to-brittle transition

http://www.people.virginia.edu/~lz2n/mse209/Chapter8.pdf

Brittle-to-ductile transition: Crack speed effect



As the crack speed increases, fracture becomes ductile

V. Bulatov *et al*., Nature Vol. 391, No. 6668, 669 (1998)

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

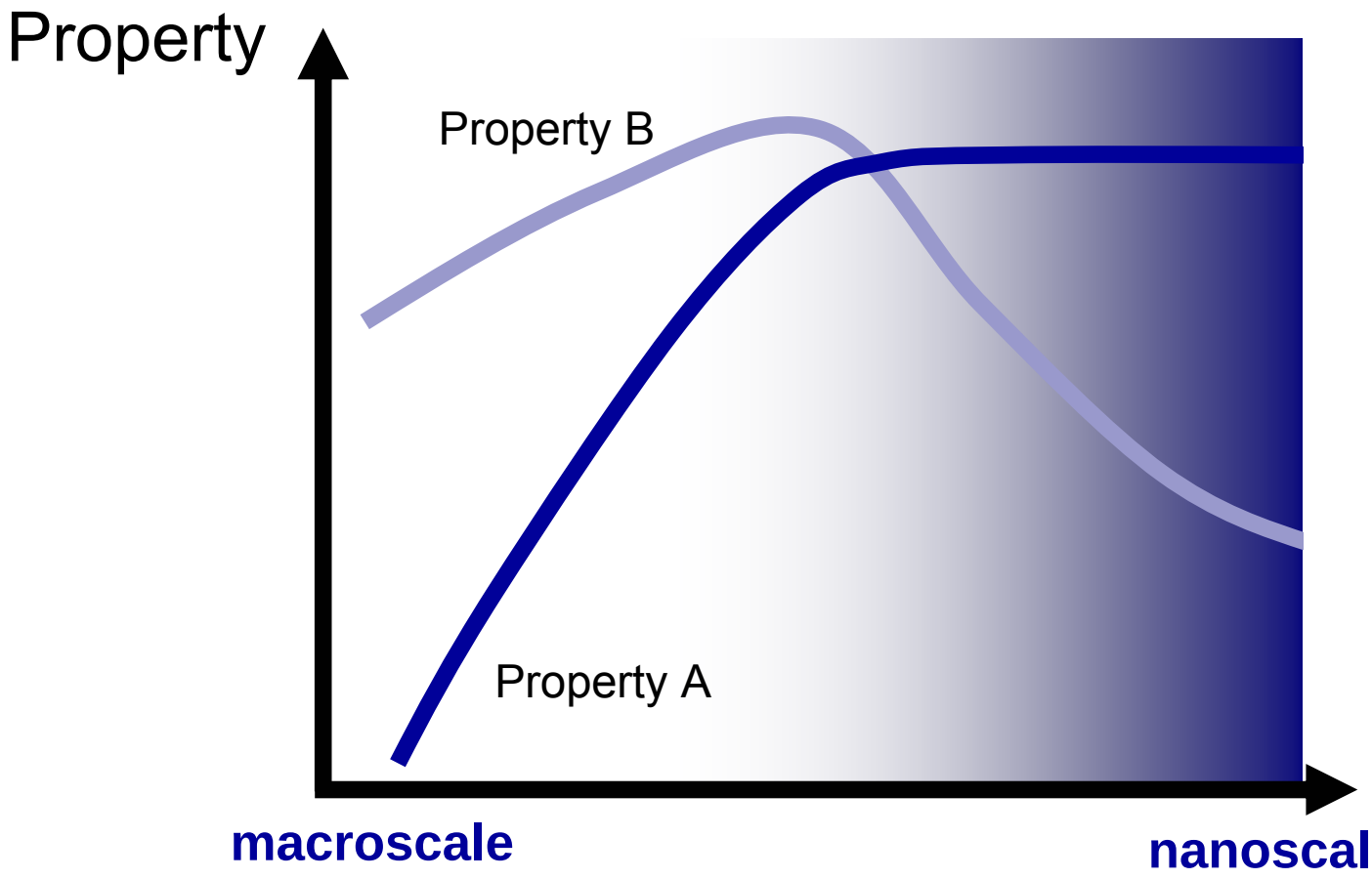
- Interfaces between dissimilar materials (living systems and technologies, bio-chips or N/MEMS)

  "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

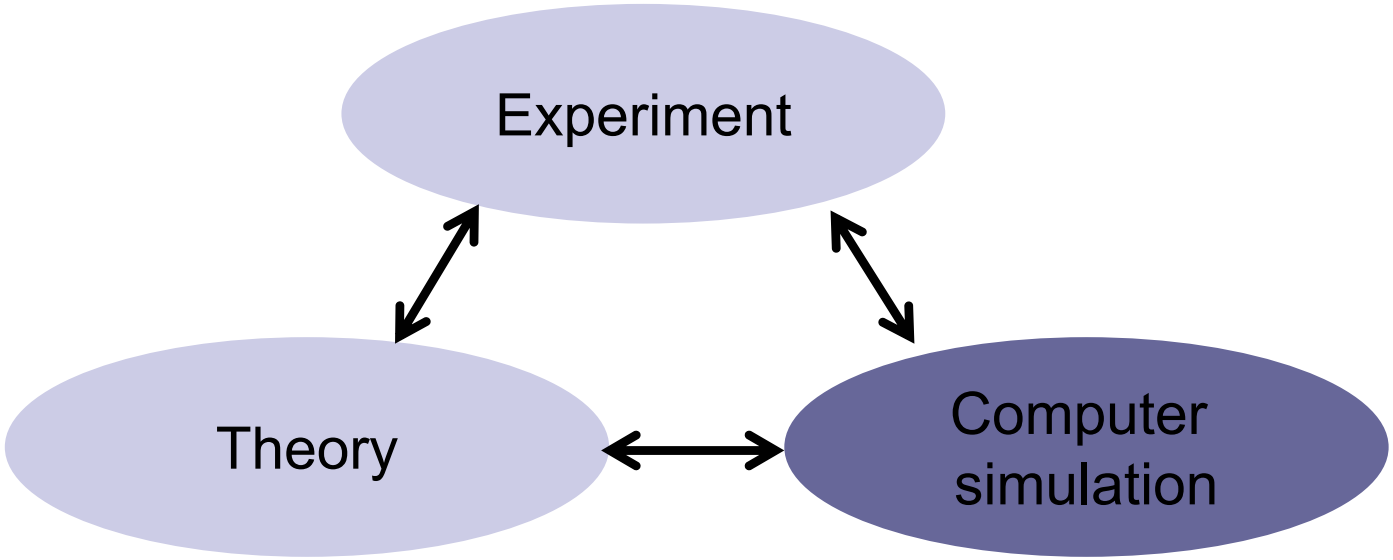
See lecture 4

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



The atomic viewpoint…

"If in some cataclysm all scientific knowledge were to be destroyed and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see there is an enormous amount of information about the world, if just a little imagination and thinking are applied."

--Richard Feynman

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- See additional references & material on the website: http://web.mit.edu/mbuehler/www/Teaching/LS/lecture-1-supp.htm
- http://www.people.virginia.edu/~lz2n/mse209/