**PASI 06**

**Pan-American Advanced Study Institute Nano and Biotechnology**

**San Carlos de Bariloche, Argentina**

**November 13 – 22, 2006**

---

# Nanomechanics:
# Atomistic Measures of Strength, Deformation and Toughness

**Sidney Yip**

Department of Nuclear Science and Engineering
and Materials Science and Engineering
Massachusetts Institute of Technology, Cambridge, MA 02139

syip@mit.edu

Collaborators

Clemens Foerst, McKinley Associates
Jinpeng ang, Deutches Bank
Ju Li, Ohio State University
Xi Lin, MIT
Shigenobu Ogata, Osaka University
Xiao-Feng Qian, MIT
Subra Suresh, MIT
Krystyn Van Vliet, MIT
Ting Zhu, Georgia Tech

**A set of concepts, some results and videos to think about mechanical behavior at the nanoscale, in the broad context of multiscale modeling and simulation**

I. **Overview**
Emergence of computational science

II. **Ideal Strength of Materials**
Elastic/vibrational Instability, A Lesson from Melting

III. **Shear Localization – Homogeneous Nucleation of Defects**
Nano-indentation, Slip-twinning competition in affine shear

IV. **Crack-tip Plasticity – Reaction Pathway Sampling**
Dislocation nucleation in Cu, Kink mechanism in Si

V. **An Outlook – Problems in Reactive Transport**
Conductance across molecular junctions
Charge localization in conducting polymers
Oxidation of ultra-high temperature ceramics
Viscosity of glass-forming liquids
Molecular modeling of cement paste

# I. Overview

# The Jiggling and Wiggling of Atoms

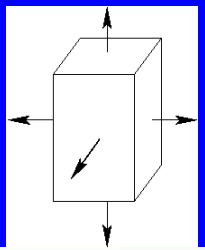
"Certainly no subject is making more progress on so many fronts than biology, and if we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that *all things are made of atoms*, and that everything that living things do can be understood in terms of the jiggling and wiggling of atoms."

-- Richard Feynman, Lectures on Physics, vol. 1, p.3-6 (1963)

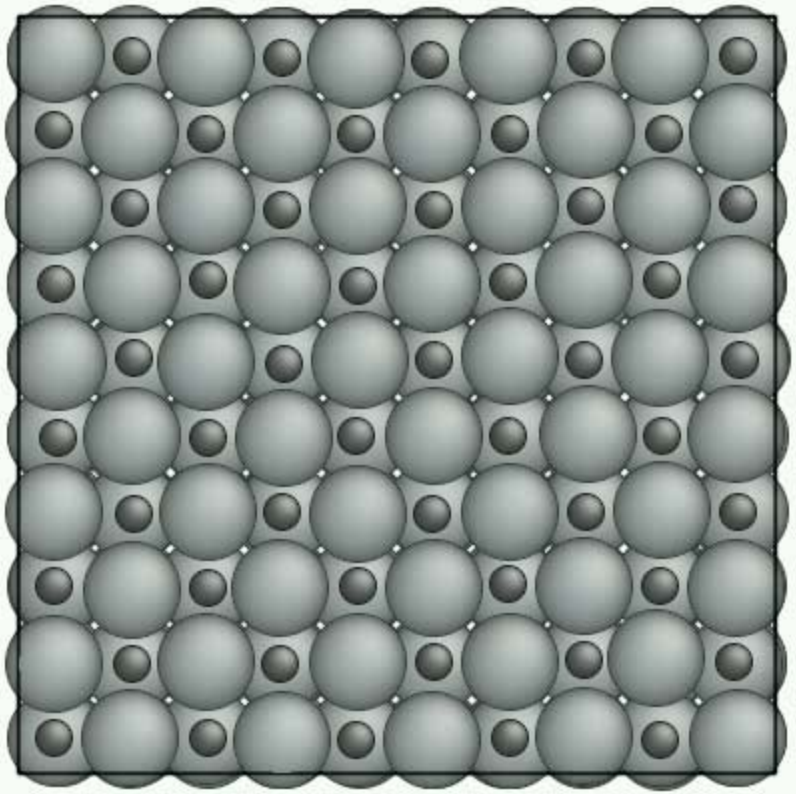
[1]

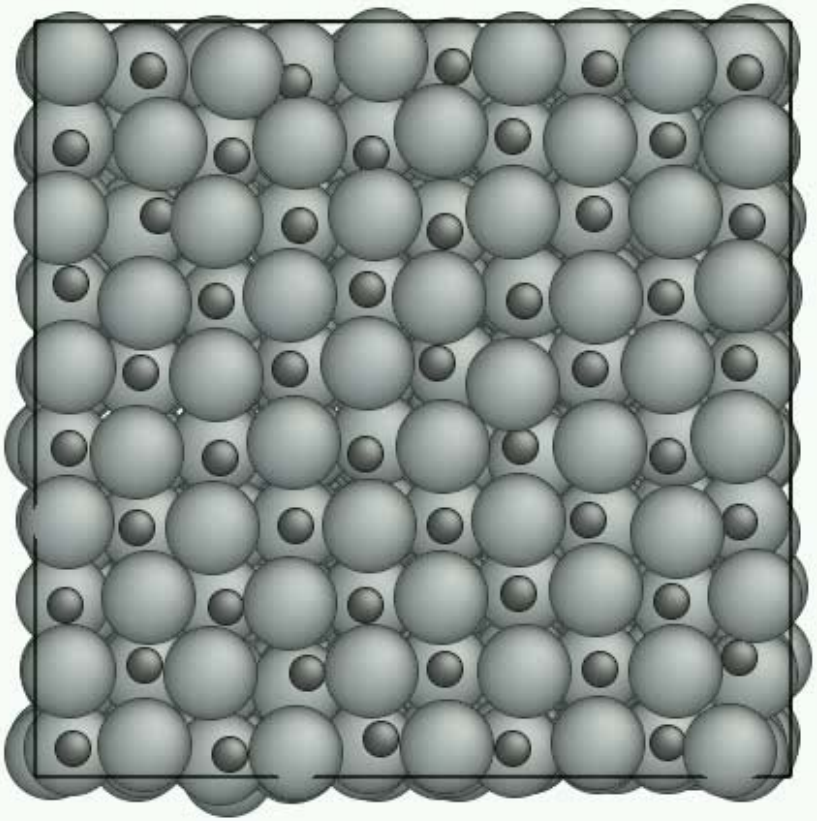
# Failure of ZrC under Hydrostatic Tension – Temperature Effects

Low T (300°K) Cleavage

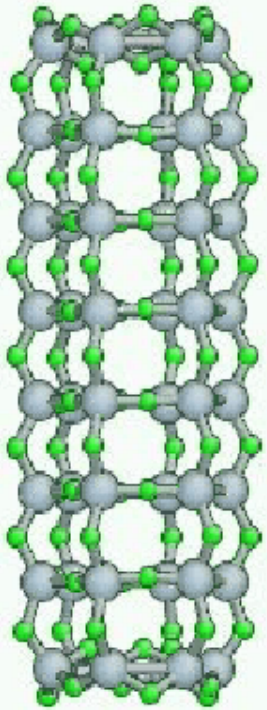


High T (3500°K) Cavitation



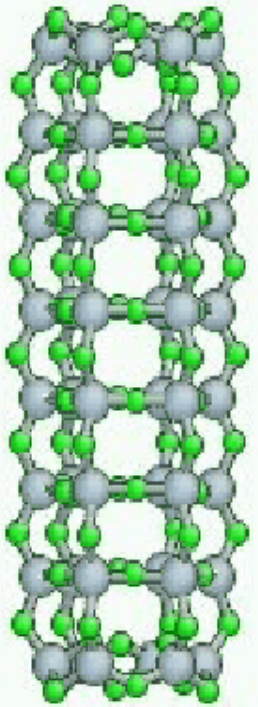


1nm

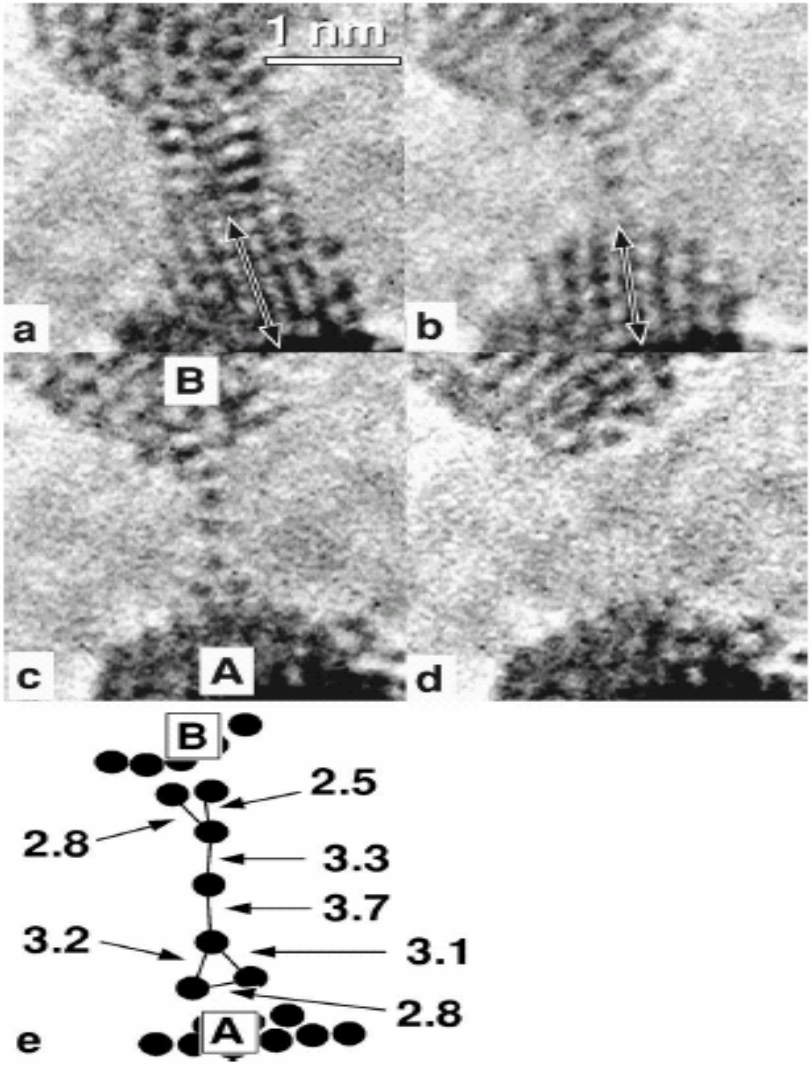


Tensile failure at 1$^{o}$K

nanorod_1K.avi

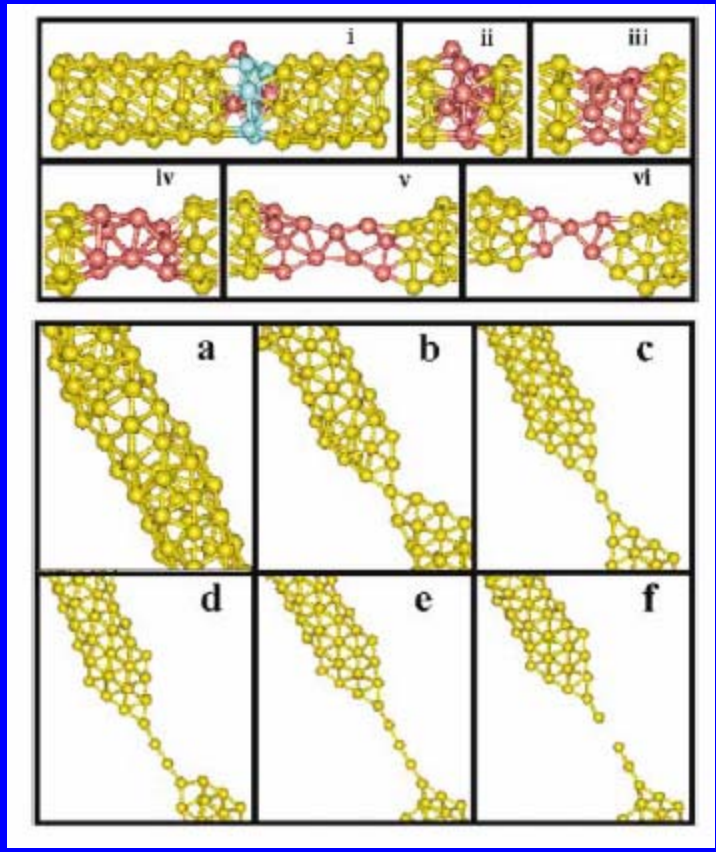


Tensile failure at 100$^{o}$K




Real-time imaging gold nanojunctions

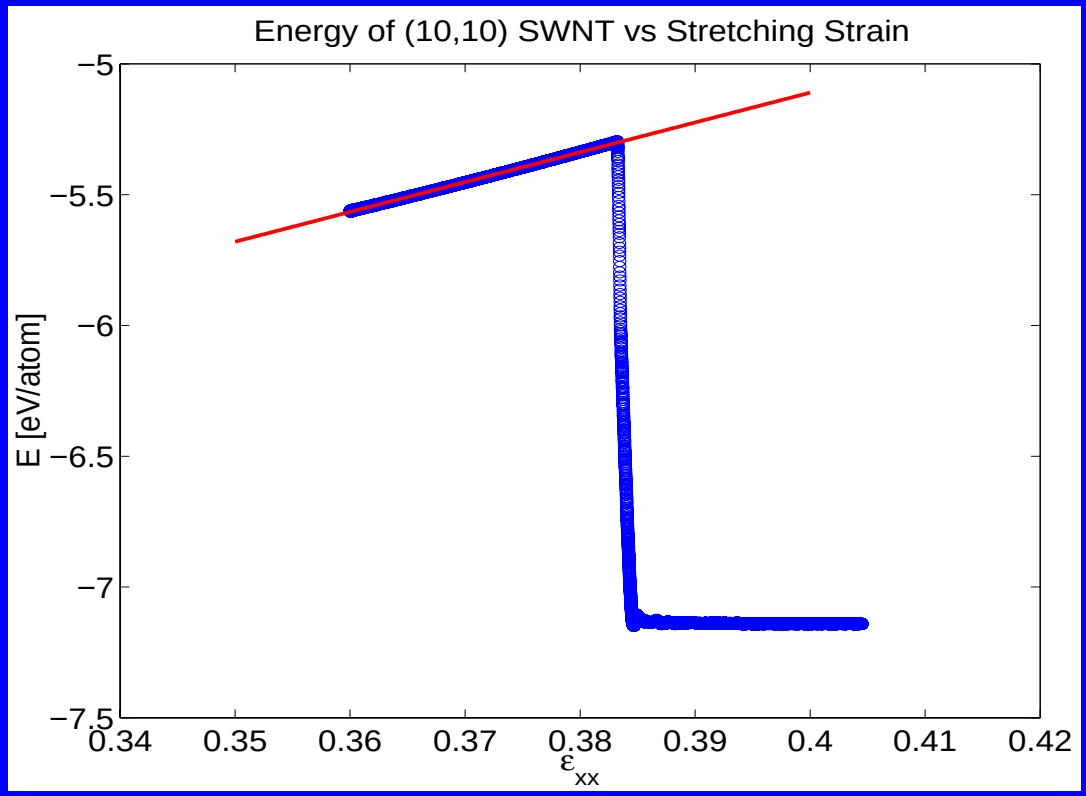
*Rodrigues and Ugarte*, PRB (2001)



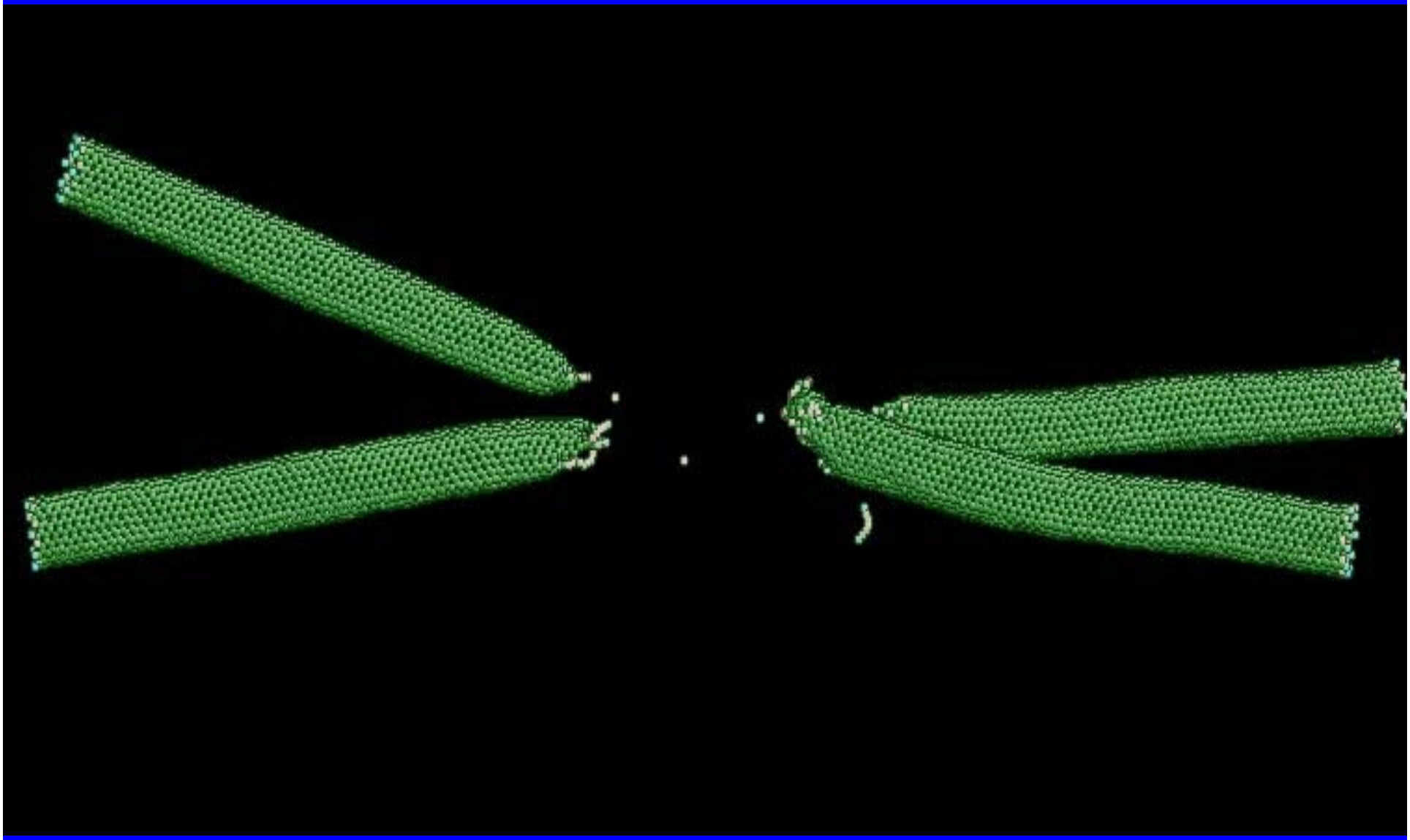

TB-MD simulations

*Da Silva et al.*, PRL (2001)

# Tensile Strength of Carbon Nanotube (molecular dynamics simulation)



# (10,10) SWNT Junction Strength

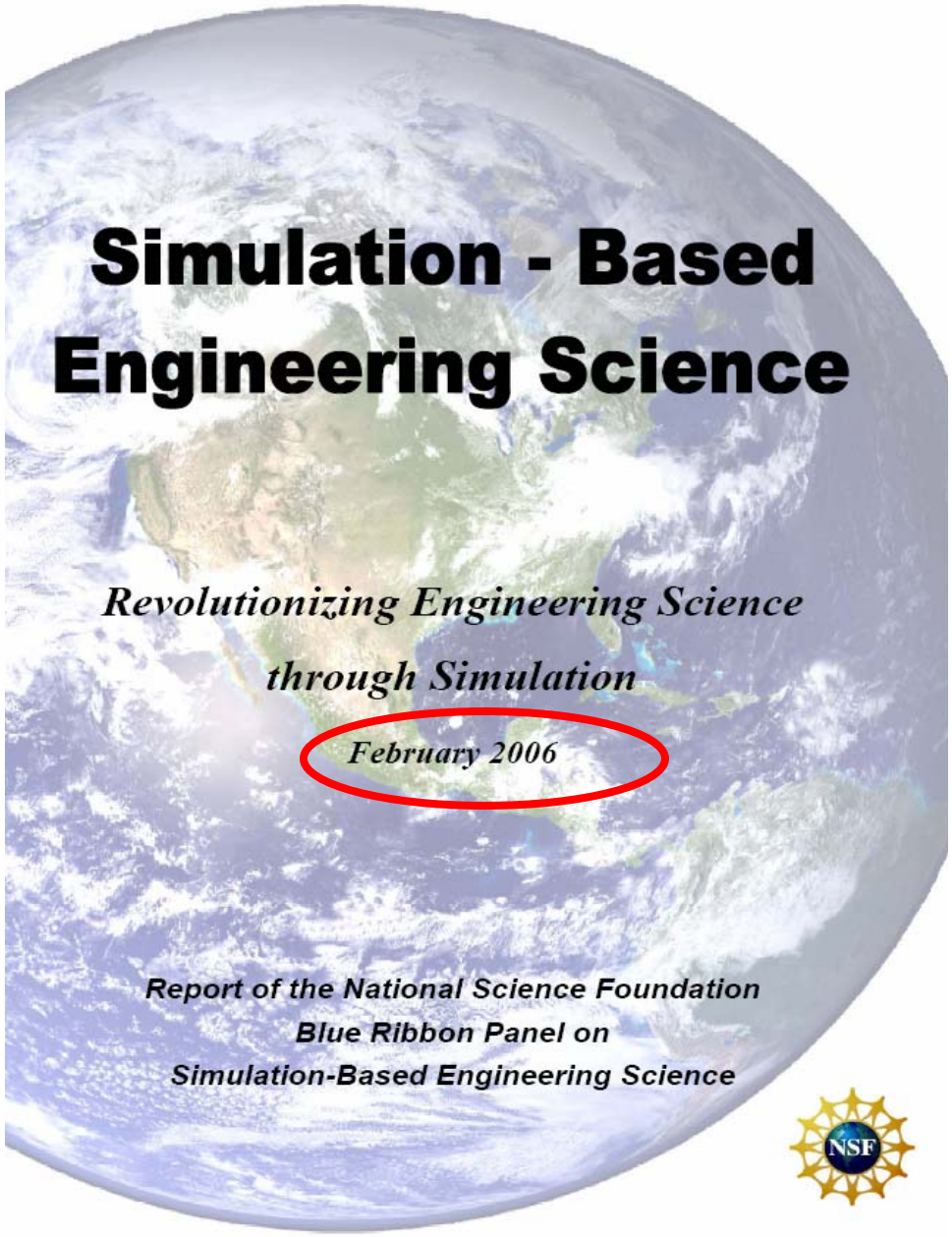


REPORT TO THE PRESIDENT

# Computational Science: Ensuring America's Competitiveness

President's Information Technology Advisory Committee

June 2005



# Simulation - Based Engineering Science

*Revolutionizing Engineering Science through Simulation*

*February 2006*

*Report of the National Science Foundation Blue Ribbon Panel on Simulation-Based Engineering Science*

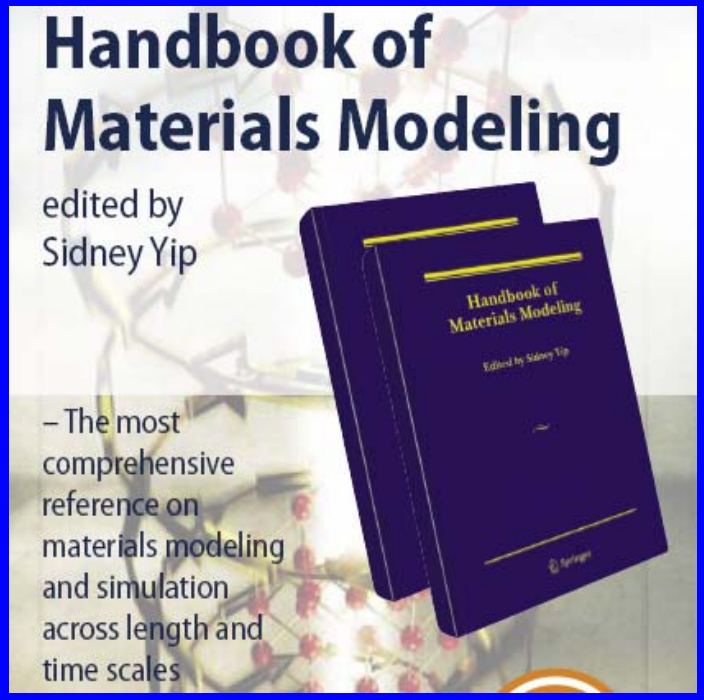
"Computational Science – the use of advanced computing capabilities
to understand and solve complex problems -- has become critical
to scientific leadership, economic competitiveness, and national security."

"Computational science is now indispensable to the solution of complex problems
in every sector … using computational models to capture and analyze
unprecedented amounts of experimental and observational data, and
to address problems previously deemed intractable" ---- (PITAC Report 2005)

Challenges and opportunities in Materials Modeling (theory and simulation) across length/time scales – electrons and atoms to the continuum

Computational Science + MMM = Computational Materials

S. Yip, "Synergistic Science", Nature Materials **2**, 3 (2003)



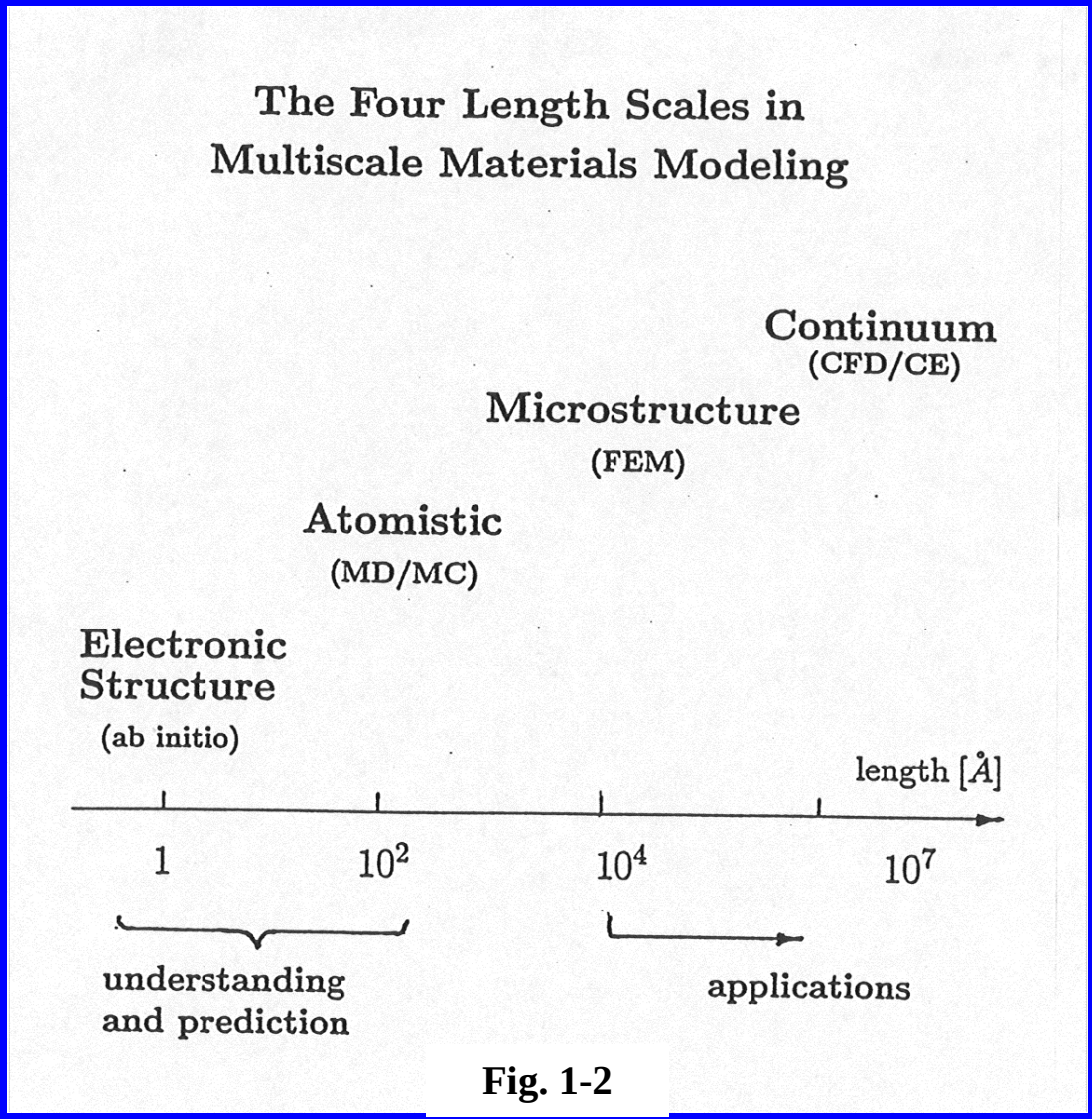

The Four Length Scales in
Multiscale Materials Modeling
Continuum
(CFD/CE)
Microstructure
(FEM)
Atomistic
(MD/MC)
Electronic
Structure
(ab initio)
length [Å]
1
$10^2$
$10^4$
$10^7$
understanding
and prediction
applications

**Fig. 1-2**

# MMM in Crystal Plasticity – ASCI (LLNL)

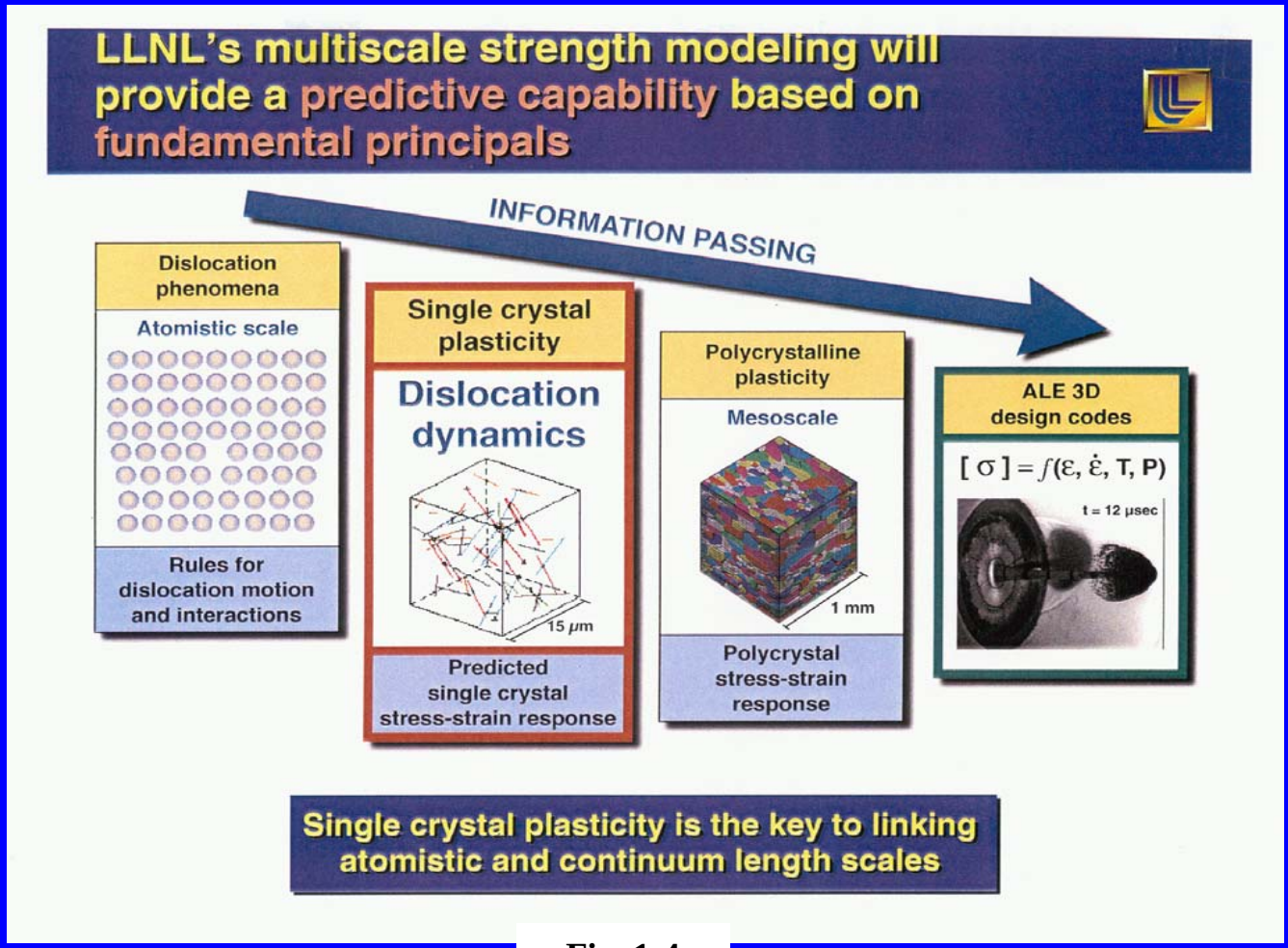
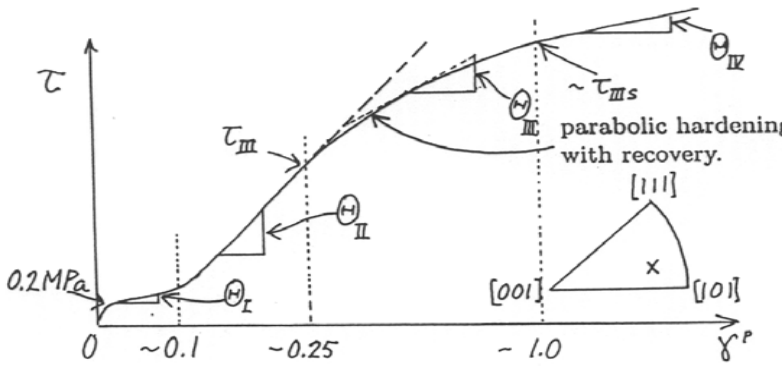



**Fig. 1-4**

## Tensile Strength – Cu 300K

TENSILE STRESS/STRAIN CURVES OF COPPER
AT ROOM TEMPERATURE
(Seeger, 1957)




**Underlying Microstructures?**

**Dislocations:**

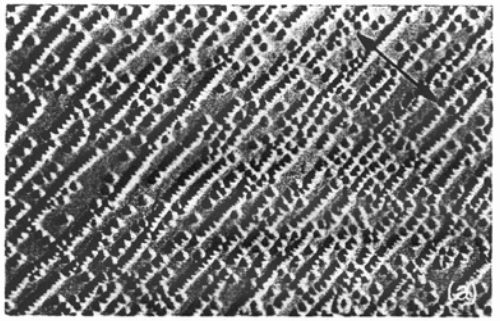
**density, mobility, patterning**

**atomic-level processes governing dislocation microstructures?**

**Fig. 1-5**

## Dislocation Microstructure

DISLOCATION AGGREGATION IN STAGE I in
Cu, SURFACE ETCH PITS and TEM
(LATE STAGE I, EARLY STAGE II)
AT 295K



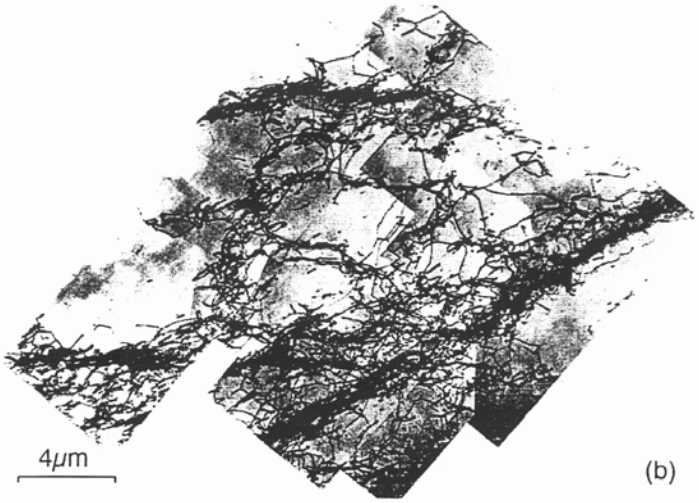



**Fig. 1-6**

# Simulation of Crystal Melting

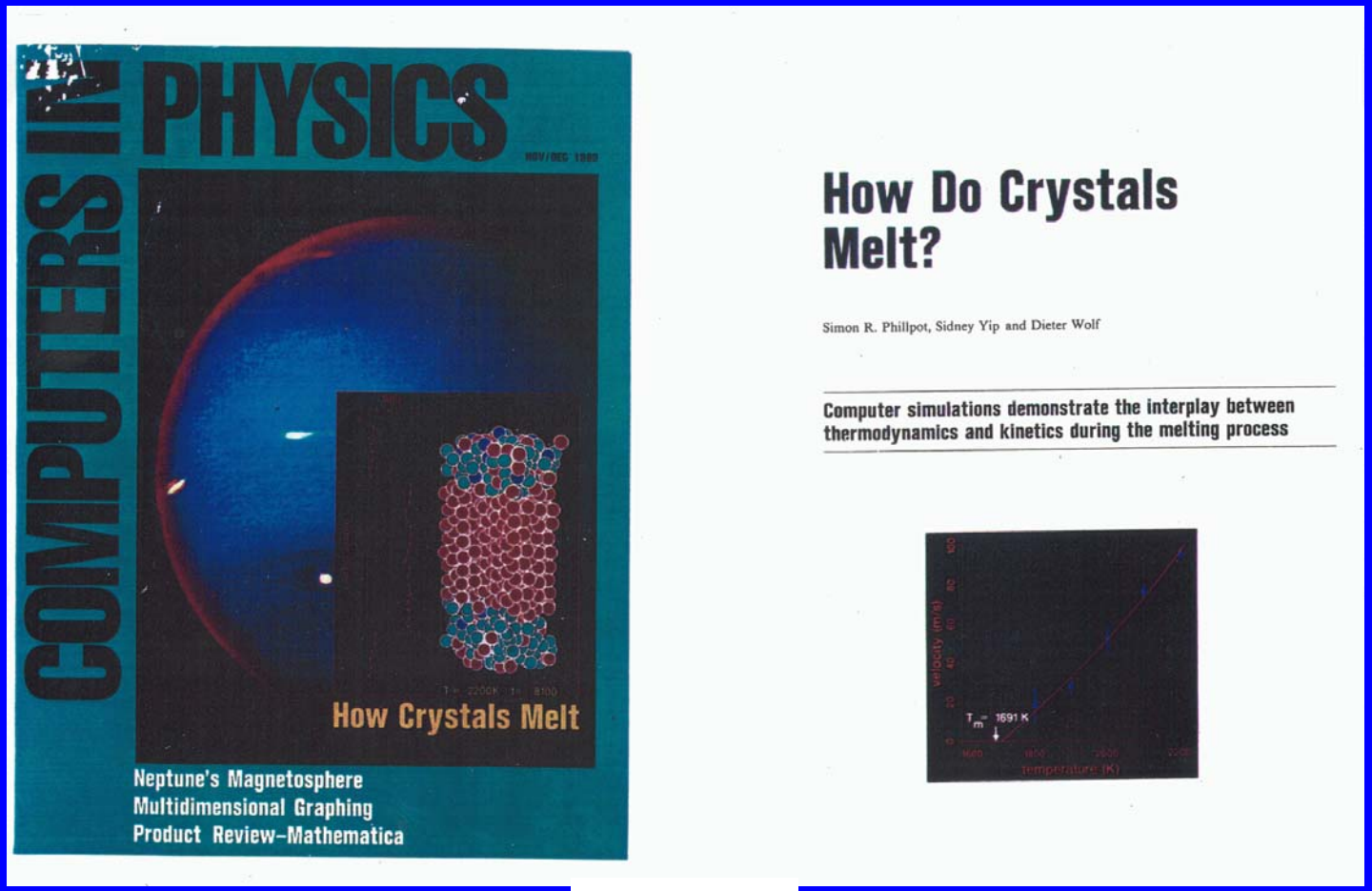



**Fig. 1-7**

S. R. Phillpot, S. Yip and D. Wolf, "How do crystals melt?“, Computers In Physics **3**, 20 (1989).

# Dislocation Loop Emission at Crack Tip -- 100 Million Particle Simulation (F. Abraham)

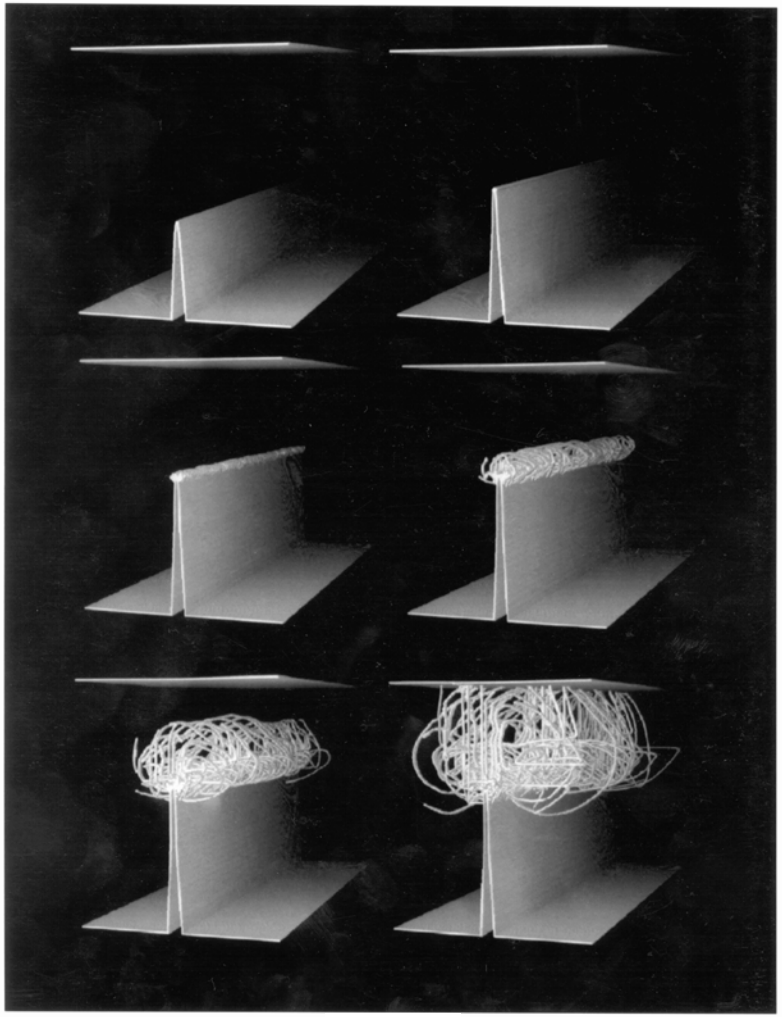


**Fig. 1-9**

# Dislocation Junction Formation and Unzipping

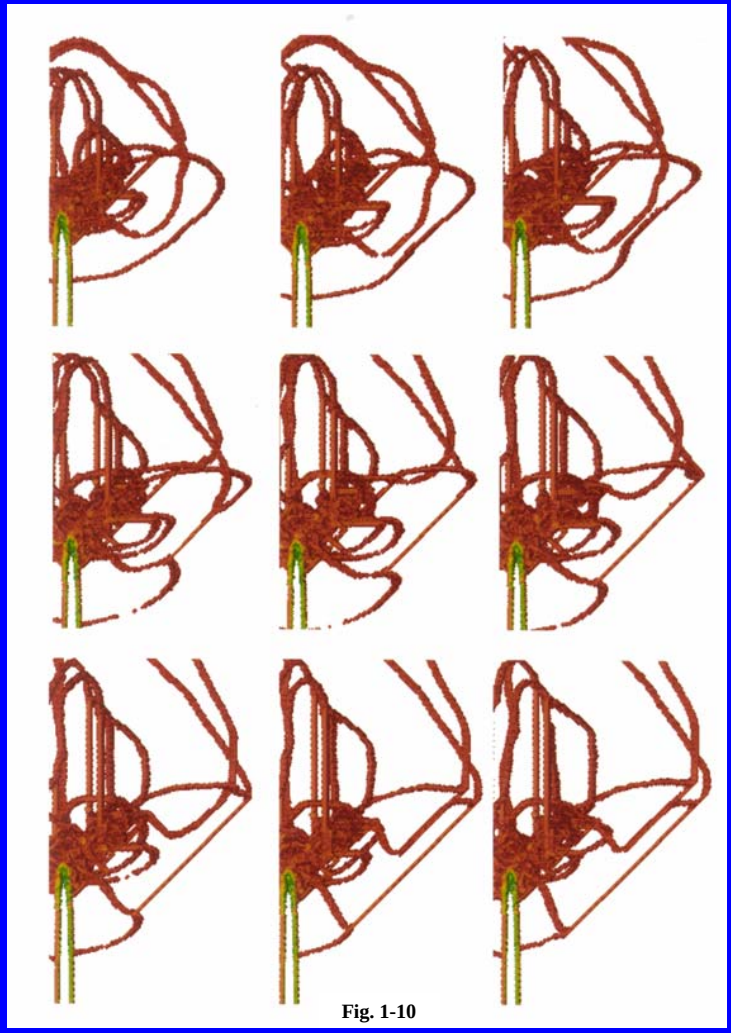
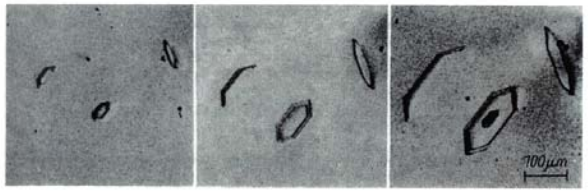


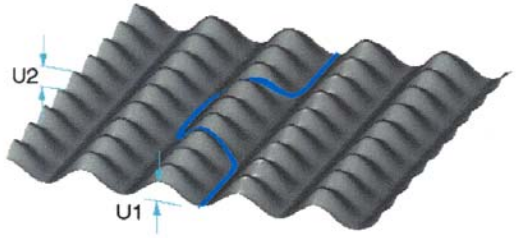
Fig. 1-10

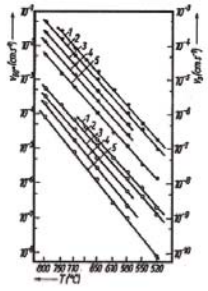
V. Bulatov, et al., "Dislocation Junctions and Crystal Plasticity: Linking Atomistic and Mesoscale Simulations", Nature **391**, 669 (1998).

# Dislocation Mobility via Kink Mechanism

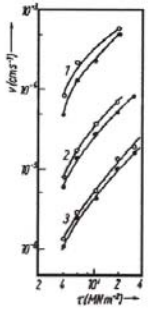
## Si Experiments and Theory

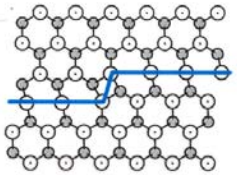


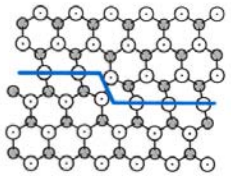


$$v \sim \tau^n \exp\left(\frac{Q}{k_B T}\right)$$







George and Champier (1979)

Left Kink

Right Kink

**Fig. 1-8**

W. Cai, et al., "Dislocation Mobility in Si", Physical Review Letters **84**, 3346 (2000).

# Brittle-to-Ductile Transition in α–Fe

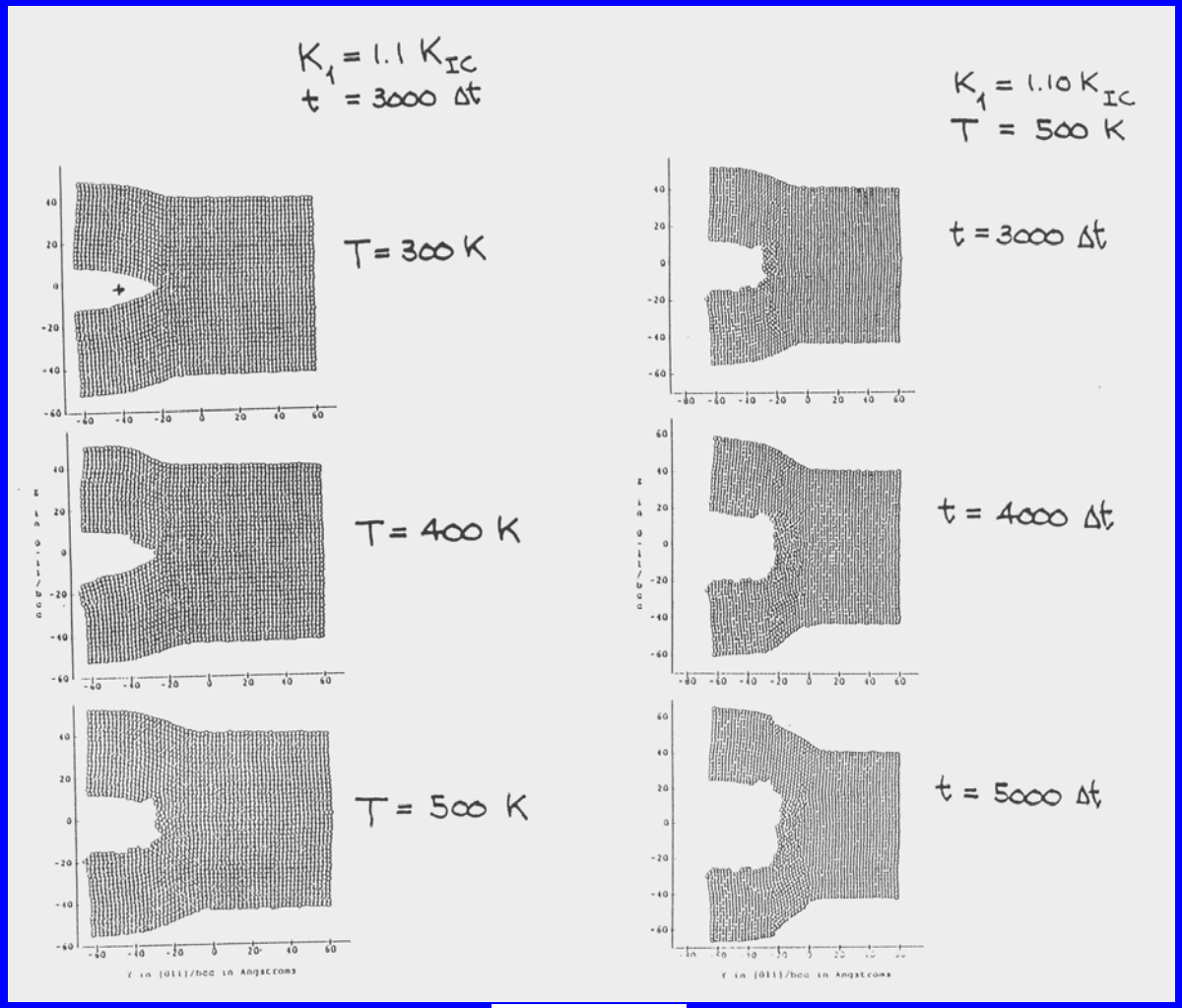
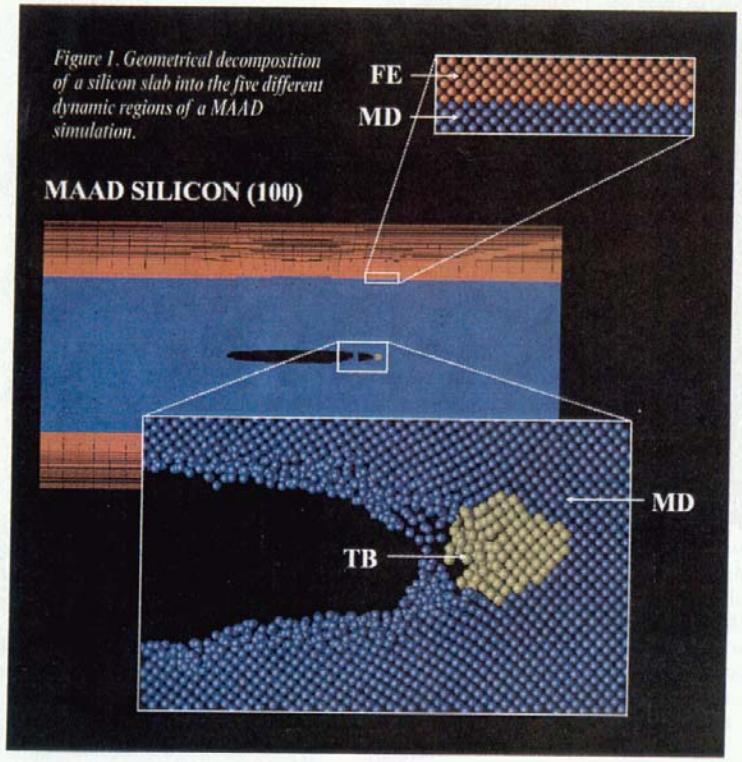



**Fig. 1-11**

K. S. Cheung and S. Yip, "Brittle-ductile transition in intrinsic fracture behavior of crystals", Physical Review Letters **65**, 2804 (1990).

# Multiscale Simulation of Si Crack Tip




## Spanning the Length Scales in Dynamic Simulation

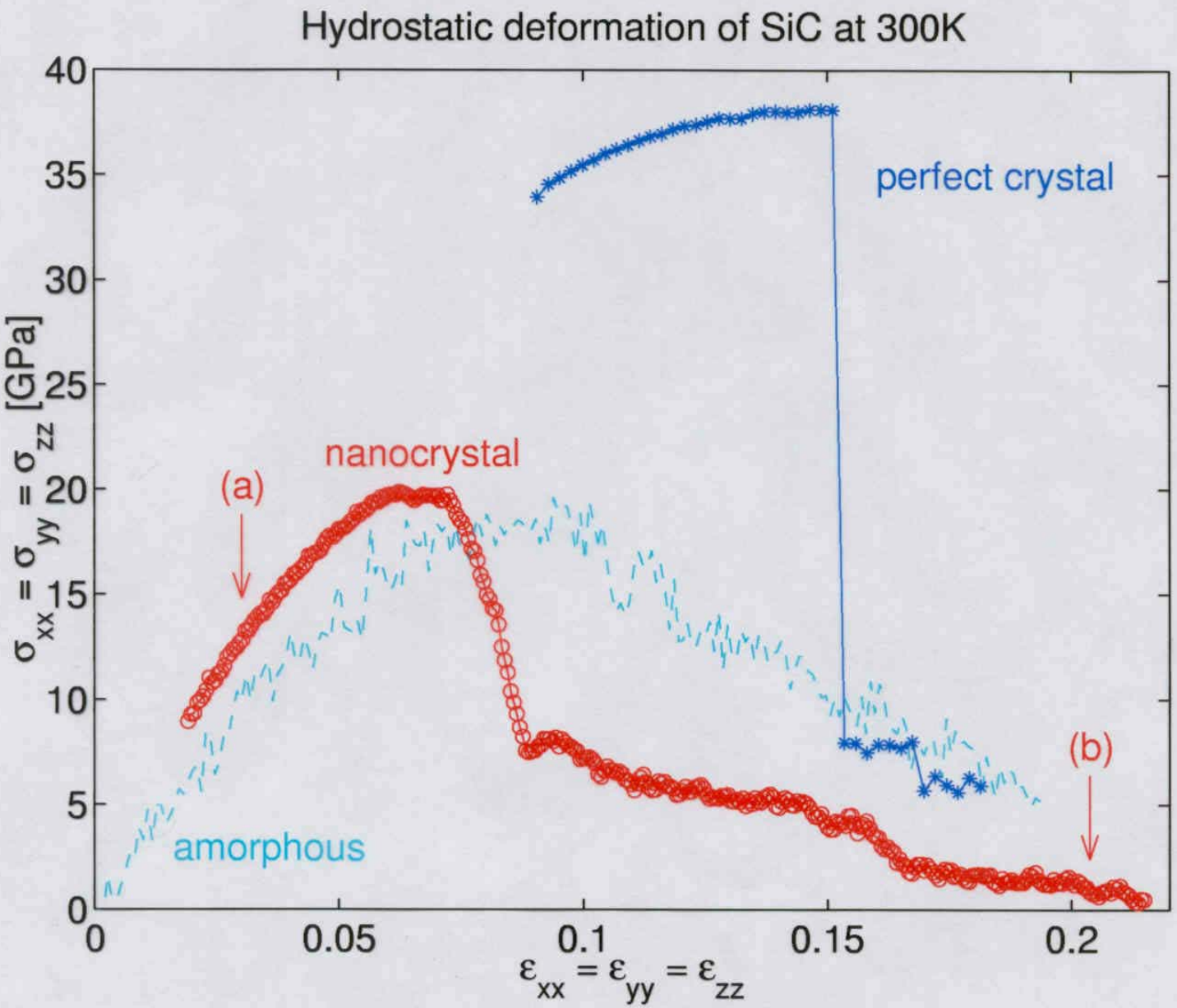
Farid F. Abraham, Jeremy Q. Broughton, Noam Bernstein, and Efthimios Kaxiras

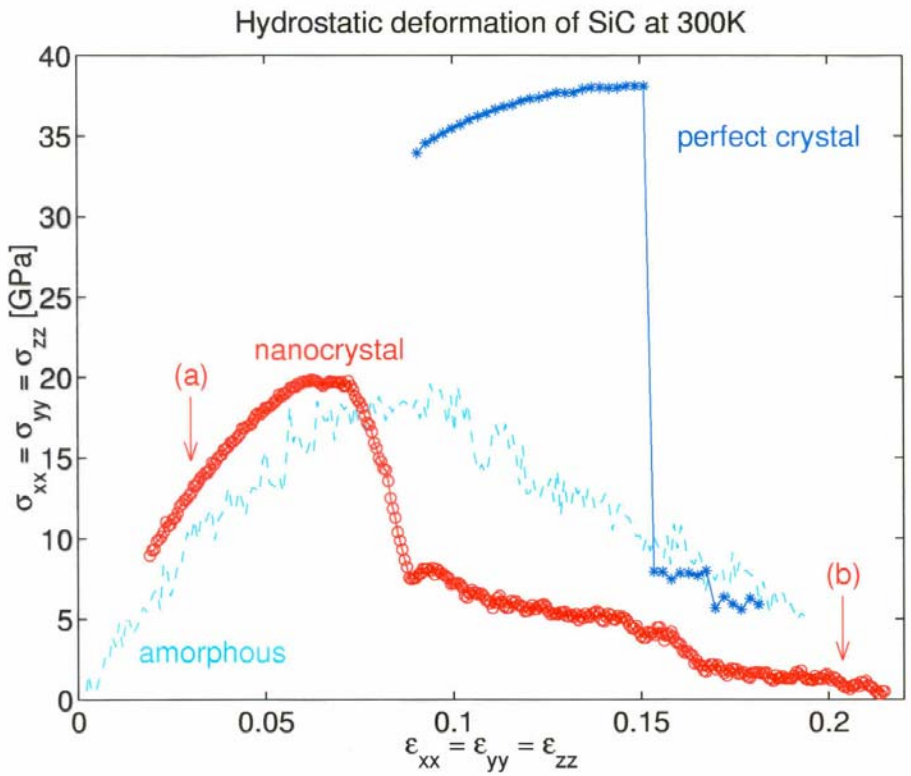
*A computational approach to the simulation of crack propagation in silicon seamlessly unites quantum, atomistic, and continuum descriptions of matter*

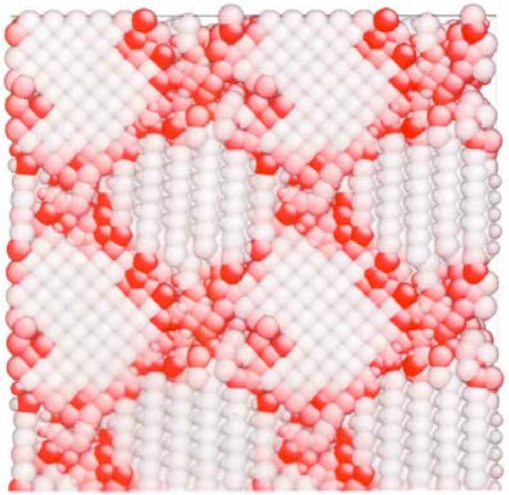
COMPUTERS IN PHYSICS, VOL. 12, NO. 6, NOV/DEC 1998 539

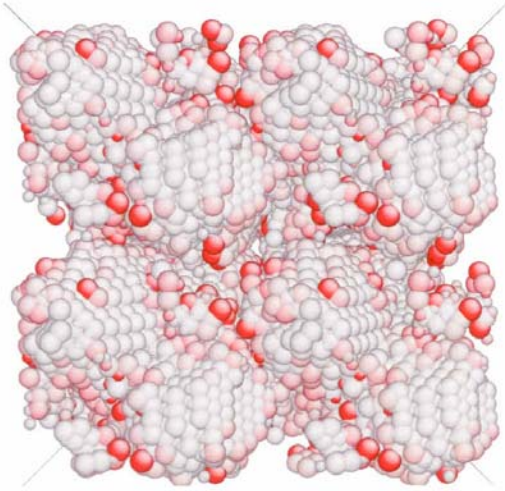
**Fig. 1-12**

# II. Ideal Strength of Materials

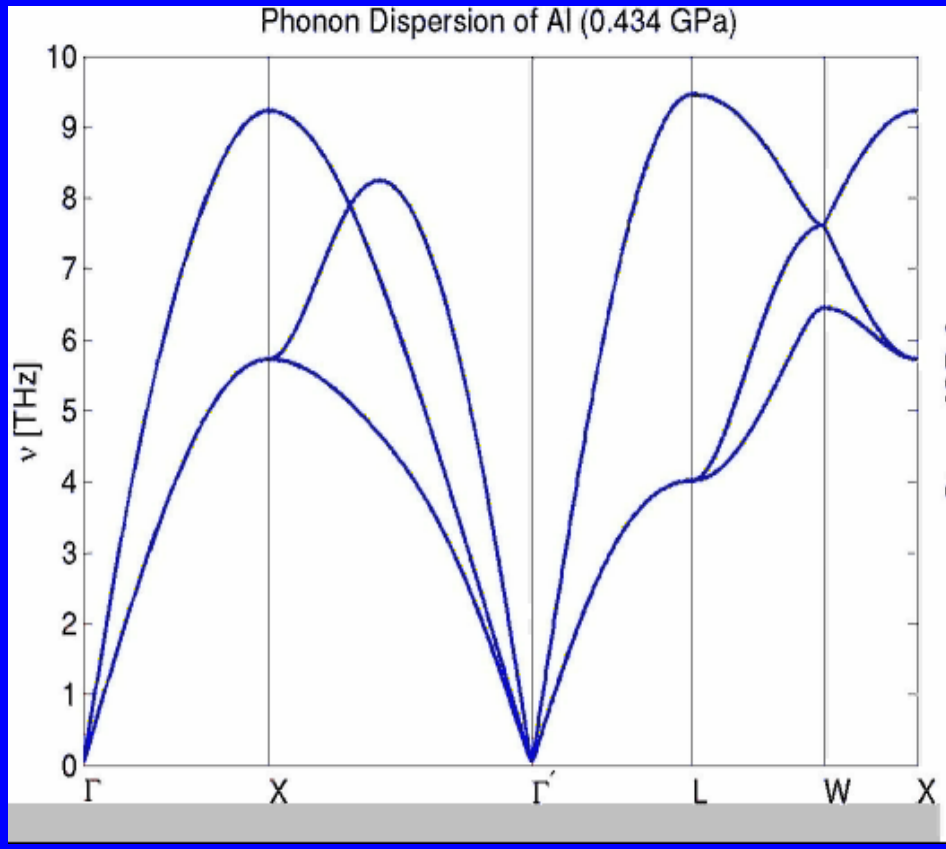

Hydrostatic deformation of SiC at 300K
perfect crystal
nanocrystal
(a)
(b)
amorphous
$\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ [GPa]
$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$
0
5
10
15
20
25
30
35
40
0
0.05
0.1
0.15
0.2

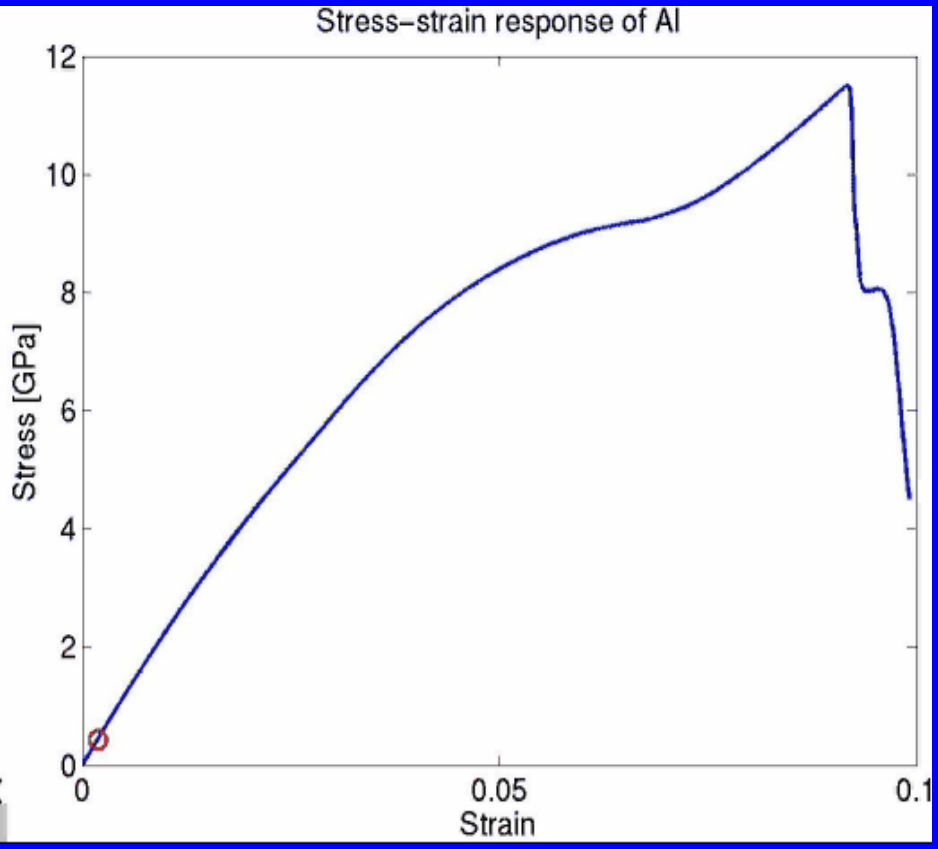

Hydrostatic deformation of SiC at 300K
perfect crystal
nanocrystal
(a)
(b)
amorphous
$\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ [GPa]
$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$
0
5
10
15
20
25
30
35
40
0
0.05
0.1
0.15
0.2





# Phonon softening in a highly-strained lattice -- correspondence between soft modes and critical deformation behavior




phonon dispersion calculations (finite stress)

Direct MD Simulation at 10K

J. Li and S. Yip, “Atomistic Measures of Materials Strength”, Computer Modelling in Engineering and Sciences **3**, 219 (2002).

**Two Criteria due to M. Born:**

**I. Elastic Stability (1940)** **cubic lattice**

$$C_{11} + 2C_{12} > 0$$

$$C_{11} - C_{12} > 0$$

$$C_{44} > 0$$

**II. Thermoelastic Theory of Melting (1939)**

$$C_{44} = 0 \quad @\ T = T_m$$

$$C_{ijkl} = \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}}$$

# Thermodynamics of Crystals and Melting

MAX BORN
*Tait Professor of Natural Philosophy, University of Edinburgh, Edinburgh, Scotland*

(Received May 25, 1939)

The Helmholtz free energy, $A$, of a rigid body is a function of temperature, and of the six homogeneous strain components. If the crystal is to be rigid, three inequalities must be satisfied for the derivatives of $A$ with respect to the six strain components, for a regular (cubic) lattice. This enables one to limit the pressure-temperature range for which the crystal is stable. The violation of the condition $c_{44}>0$, that the crystal resist shearing, is interpreted as leading to melting. From a knowledge of the forces between the molecules the phase integral, and therefore the free energy, may be calculated as a function of $T$, $V$, and the six strain components. The numerical calculations are carried out for a body-centered cubic lattice. The product of all the frequencies is calculated directly, so that the assumption that the Debye equation for the frequency distribution holds, is not necessary. The melting curve, pressure against temperature, is then determined.

THERE exist many attempts to derive theoretically the laws of melting. I mention Lindemann's[1] formula, Grüneisen's[2] general thermodynamics of isotropic solids, the theories of Braunbeck,[3] Raschevsky[4] and of Herzfeld and Goeppert-Mayer.[5] The newest contribution to this problem is an ingenious paper of Lennard-Jones and Devonshire[6] who apply the "method of order and disorder" invented by Bragg and Williams.[7]

All these papers use different "criteria" of melting: e.g. Lindemann, the collision of a vibrating molecule with its neighbor; Raschevsky, the instability of a particle under the action of its neighbors; Braunbeck, the instability of the vibration of two rigid simple lattices against one another; Herzfeld and Goeppert-Mayer, the minimum of pressure with respect to changes of volume; Lennard-Jones, the transition of the structure from order into disorder.

In actual fact there can be no ambiguity in the definition of, or the criterion for, melting. The difference between a solid and a liquid is that the solid has elastic resistance against shearing stress while the liquid has not. Therefore, *a theory of melting should consist of an investigation of the stability of a lattice under shearing stress*. As far as I know, the only author who has made an attempt to apply this natural definition of melting is Brillouin.[8] The short published account of his considerations indicates that he uses Debye's approximation for calculating the frequencies of the crystal; this method is objectionable, not only because it neglects the short waves, but because it does not lead to a reduction of the observable quantities to atomic forces.

Independently of this work of Brillouin, I have developed a method for treating thermodynamics of a crystal lattice in such a way that the formulae are valid over a wide range of temperature, in the hope that this range might include the melting point.

This theory is in some way the counterpart of Mayer's rigorous treatment[9] of condensing gases where the liquid state was reached from the other side, at least in so far as the existence of a condensation point could be proved with the methods of kinetic theory of gases.

The chief point in our method is the clear distinction between *molecular variables* and *molar parameters* as defined in statistical mechanics. The molecular variables are the generalized coordinates and conjugate momenta $q_1, p_1; q_2, p_2; \cdots$ which are distributed at random according to statistical laws. The molar parameters $a_1, a_2, \cdots$ describe the (macroscopic) external influences on the system (e.g. the volume of a gas). The energy of the system depends on both

[1] F. A. Lindemann, Physik. Zeits. **11**, 609 (1910).
[2] E. Grüneisen, Ann. d. Physik (4) **39**, 257 (1912).
[3] W. Braunbeck, Zeits. f. Physik **38**, 549 (1926).
[4] N. v. Raschevsky, Zeits. f. Physik **40**, 214 (1927).
[5] K. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934).
[6] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A169**, 317 (1939).
[7] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934); **151**, 540 (1935); **152**, 230 (1935).
[8] L. Brillouin, Phys. Rev. **54**, 916 (1938).
[9] J. Mayer, in collaboration with Ph. G. Ackermann and S. F. Harrison, J. Chem. Phys. I, 5, 67; II, 5, 74 (1937); III, 6, 87; IV, 6, 101 (1938).
See also M. Born and K. Fuchs, Proc. Roy. Soc. **A166**, 391 (1938); B. Kahn and G. E. Uhlenbeck, Physica V **4**, 399 (1938).



Proc. Camb. Philos. Soc. 36, 160 (1940)



# ON THE STABILITY OF CRYSTAL LATTICES. I

BY MAX BORN

*Received* 15 September 1939

## 1. STABILITY CRITERIA

The usual method of investigating the stability of a crystal lattice consists in comparing its lattice energy with that of other possible lattices built from the same particles. The results obtained are rather meagre (Born and Goeppert-Meyer (6)), since the calculations are tedious and hardly reliable, owing to the fact that the differences of the lattice energies are small. On the other hand, Goldschmidt(5) has very successfully predicted the lattice type of ionic and other lattices from no other knowledge than that of the radii of the atoms or ions concerned; generalizing the idea of densest packing which holds for equal particles he assumes that the most stable configuration of two different kinds of particles is that lattice in which each particle has a maximum number of neighbours (coordination number) of the other kind in the shortest distance possible. Though this geometrical principle is very plausible there is no satisfactory dynamical justification*.

In common dynamical problems of stability we have, apart from the method of comparing the absolute values of energy, the well-known method of small vibrations. The application of this method to the case of crystals seems to be difficult since the number of normal vibrations is practically infinite. The complete vibrational spectrum must be worked out, and this has only been tried for a few special cases (Blackman(7), Herzfeld and Lyddane(8), Kellermann (10)).

I have considered this question in connexion with a new theory of melting which has just appeared (Born (9)). A crystal at a given temperature $T$ is not a dynamical, but a thermodynamical, system, to which the principles of statistical mechanics must be applied. In each thermodynamical system we have to distinguish between the atomic coordinates $q_1, q_2, \ldots$, which are subject to statistical distribution, and the molar parameters $a_1, a_2, \ldots$, describing the outer "macroscopic" conditions.

If we restrict ourselves to sufficiently high temperatures (Boltzmann statistics) the energy $\epsilon$ must be given as a function of $q_1, p_1, q_2, p_2, \ldots$, and $a_1, a_2, \ldots$, where

* Qualitative dynamical considerations on the stability of diatomic crystals have been published by Niggli(4) who took into account not only the forces between first neighbours (attraction between unequal particles) but also those between second neighbours (repulsions between equal particles).

## Stability Criteria of Homogeneous Crystals

Wang, Yip, Phillpot, Wolf, Phys. Rev. Letters 71, 4182 (1993)
Wang, Li, Yip, Phillpot, Wolf, Phys. Rev. B, November 1 (1995)

Under arbitrary load $\underline{\underline{\sigma}}$, stability condition is

$$\det\left|\underline{\underline{B}}\right| = 0$$

ext. stress

$$\underline{\underline{B}} = \underline{\underline{C}} + \underline{\underline{\Lambda}}$$

elastic stiffness coefficients — elastic constant tensor

$$\Lambda_{ijkl} = \frac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il}) - \sigma_{ij}\delta_{kl}$$

cubic lattice, $\sigma_{ij} = -P\delta_{ij}$, hydrostatic

K(P) $(C_{11} + 2C_{12})/3 + P/3 > 0$

G'(P) $\frac{1}{2}(C_{11} - C_{12}) - P > 0$

G(P) $C_{44} - P > 0$


J. Wang, et al., "Crystal instabilities at finite strain" Physical Review Letters **71**, 4182 (1993).

J. Wang, et al., "Mechanical Instabilities of Homogeneous Crystals", Physical Review B **52**, 12627 (1995).

# Test of Born's Thermo-elastic Theory of Melting (1939)

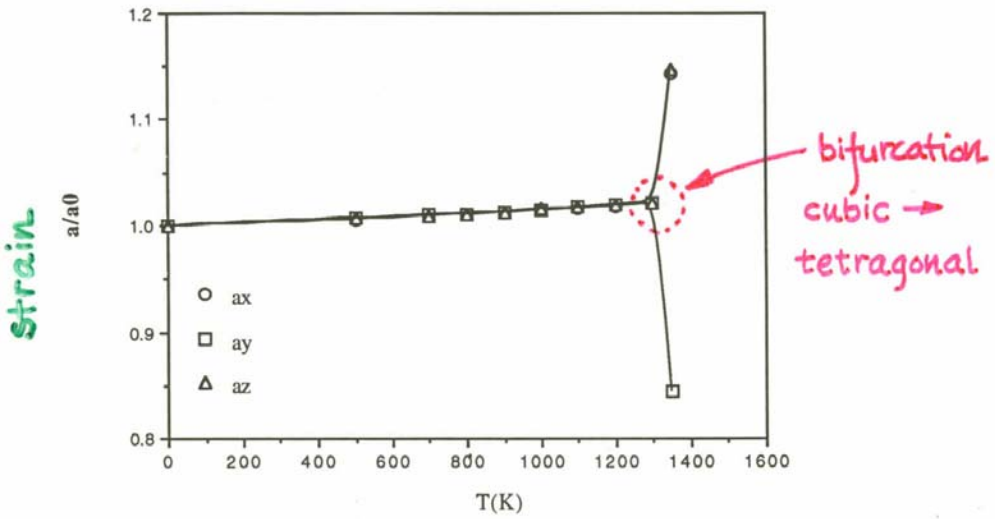
Single crystal with pbc (no surfaces)

Isobaric heating at $P = 0$

Does lattice melt when $C_{44}$ vanishes?

J. Wang, et al., "Unifying two criteria of Born: Elastic stability and melting of homogeneous crystals", Physica A 240, 396 (1997).

# Heating a Crystal at P = 0 (pbc)



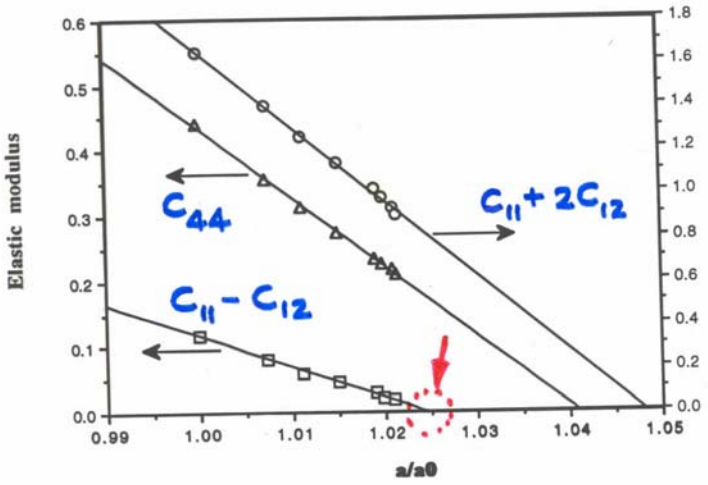

f.c.c. crystal under heating-to-melting at P=0

N = 1372
EAM (Al)

a : lattice constant

$a_0$ : equilibrium

# Stability Criteria during Heating Simulation



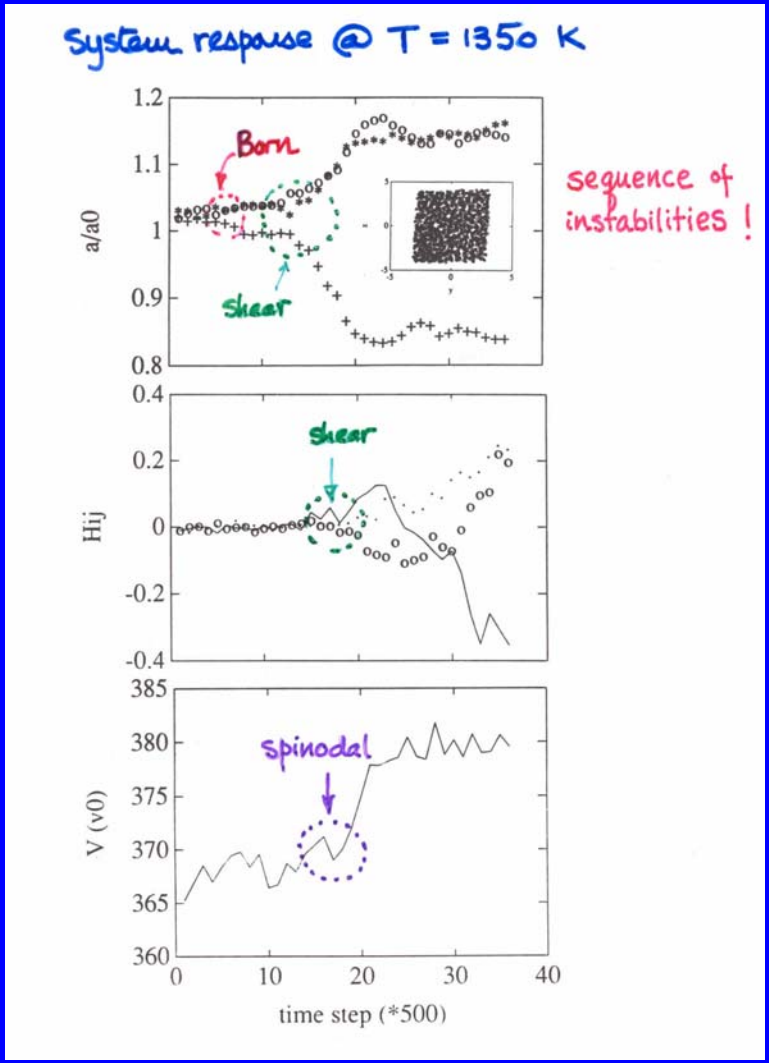

instability during heating-to-melting @ P=0

(predicted) 1.02449

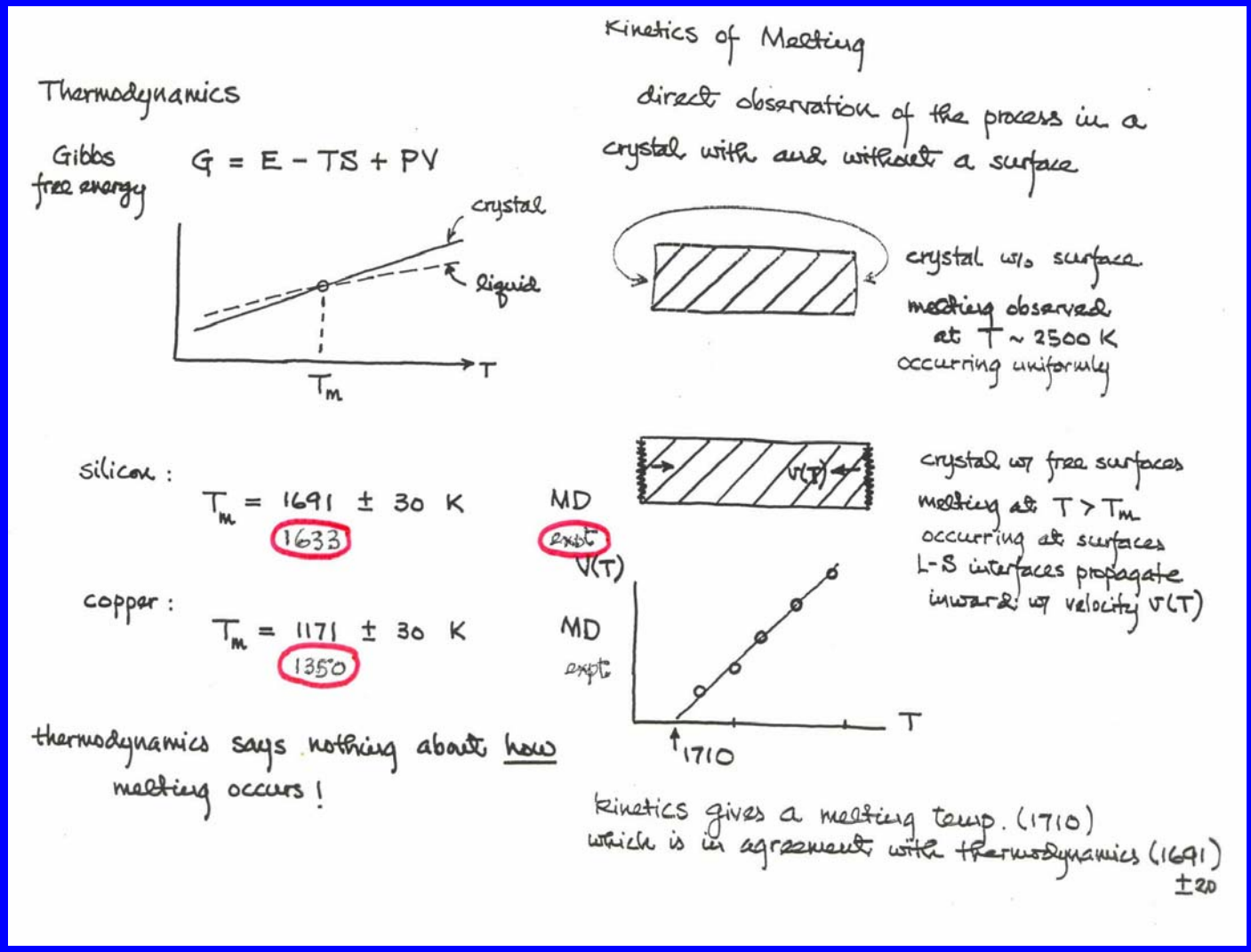
(observed MD) 1.02376

sequence of instabilities: Born, shear, spinodal

# Dynamic System Response at T = 1350 K

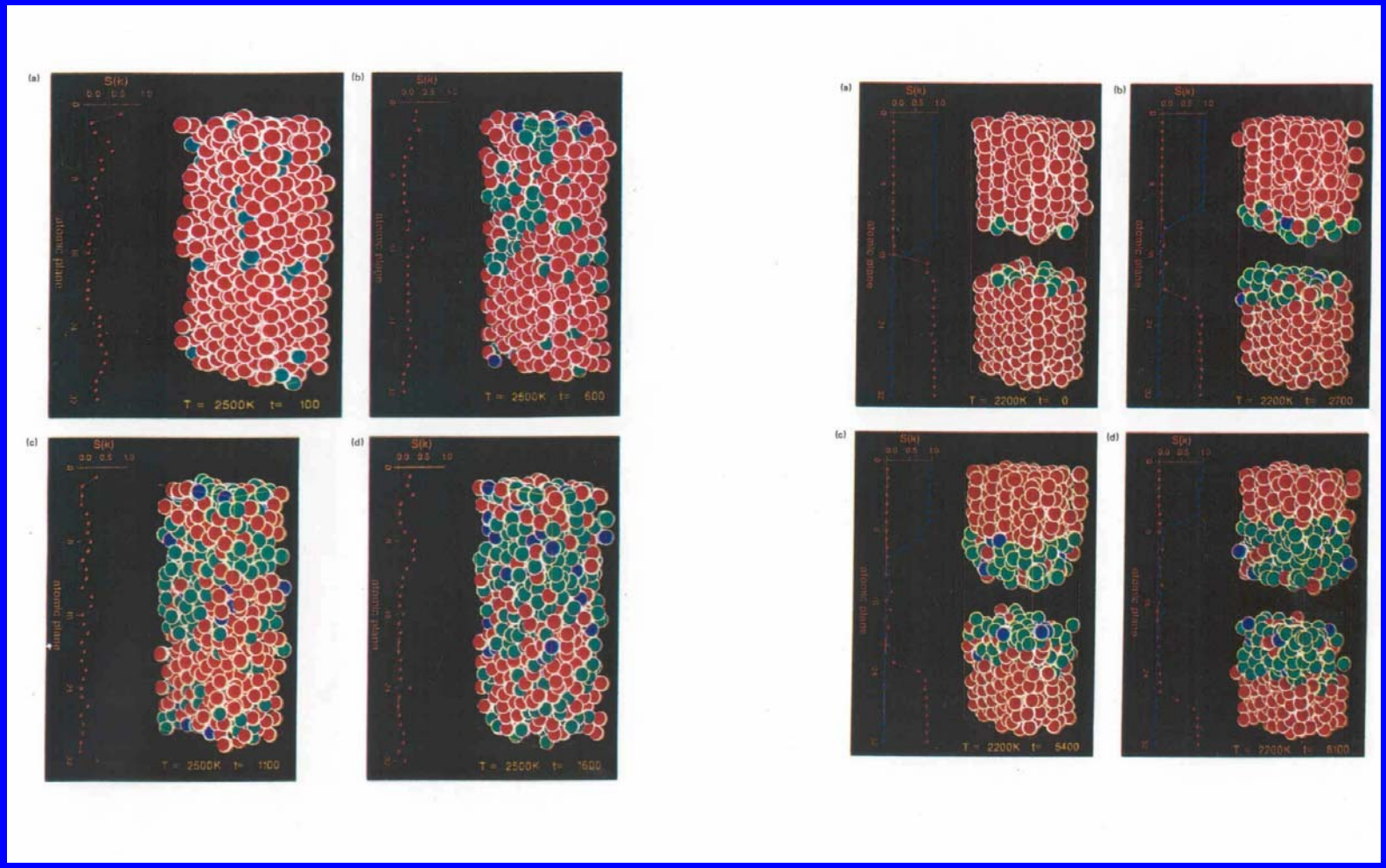


# Thermodynamic Melting at $T_m$

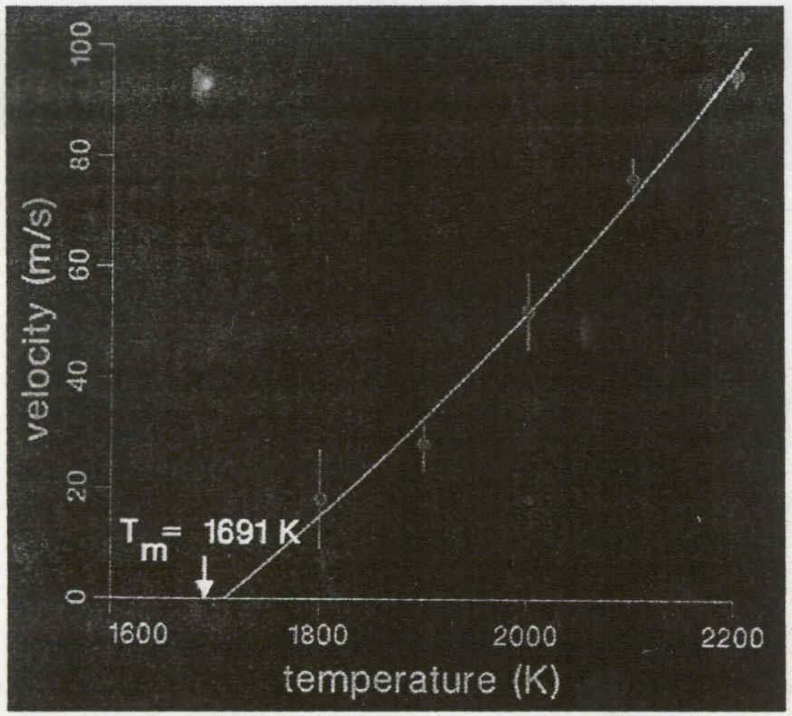



S. R. Phillpot, S. Yip and D. Wolf, "How do crystals melt?“ Computers In Physics **3**, 20 (1989).

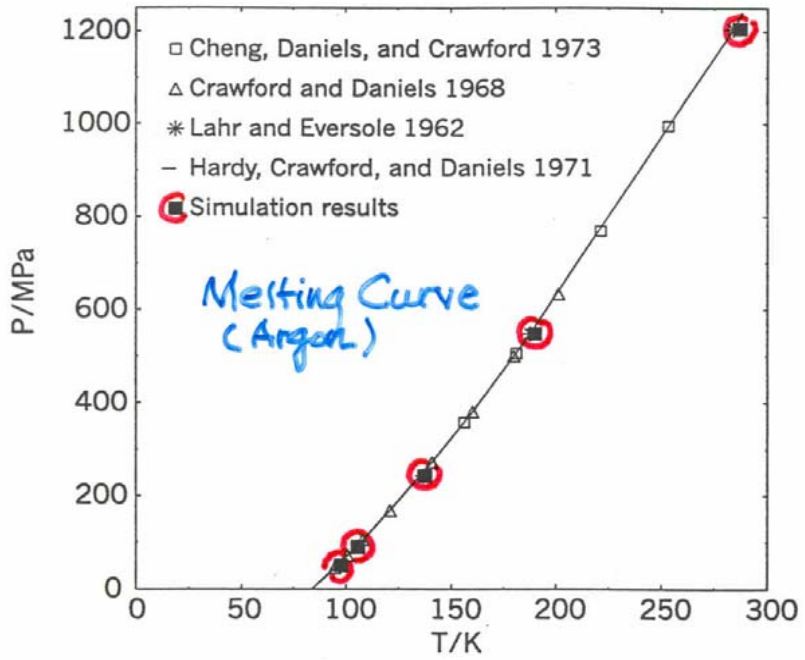
# Mechanical and Thermodynamic Melting of Si



# $T_m$ Determination by Extrapolation



# MD Prediction of Argon Melting Curve




Solca et al
Chem. Phys. 224, 253 ('97)

# What we have learned from MD simulations on Melting ?

Simulation demonstrates two melting transitions

Thermodynamic Melting is heterogeneous –
free-energy coexistence, defect-induced nucleation and growth

Mechanical Melting is homogeneous –
upper limit of metastability occurs when Thermodynamic Melting is kinetically suppressed

Born’s 1939 criterion (G’ or G) applies only to Mechanical Melting

# III. Shear Localization – Homogeneous Nucleation of Defects

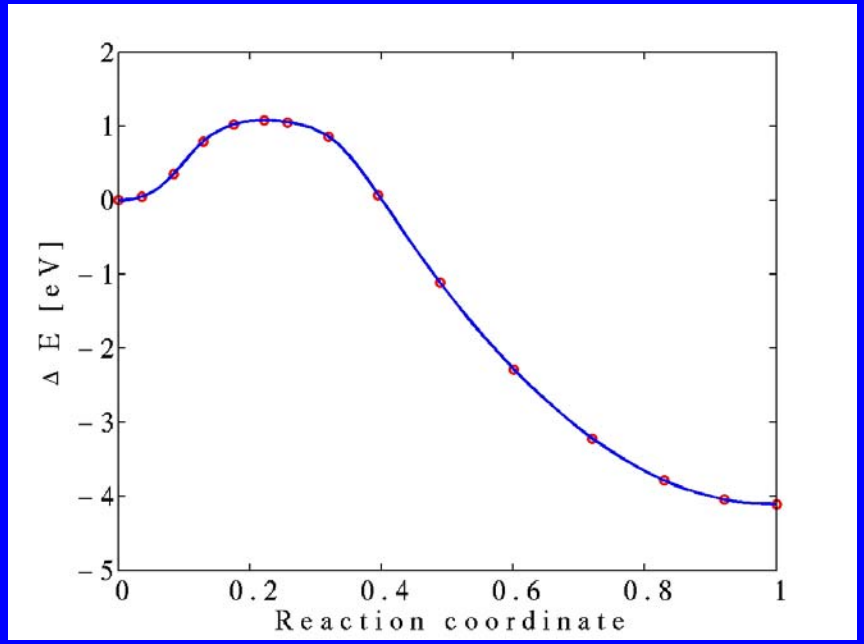
*probing large-strain deformation through atomistic simulation --*

*nano-indentation, charge density redistribution at saddle points,*

*reaction pathway sampling (MEP - activation barrier, atomic configurations),*

*dislocation and twin nucleation, crack extension, water-silica reaction*

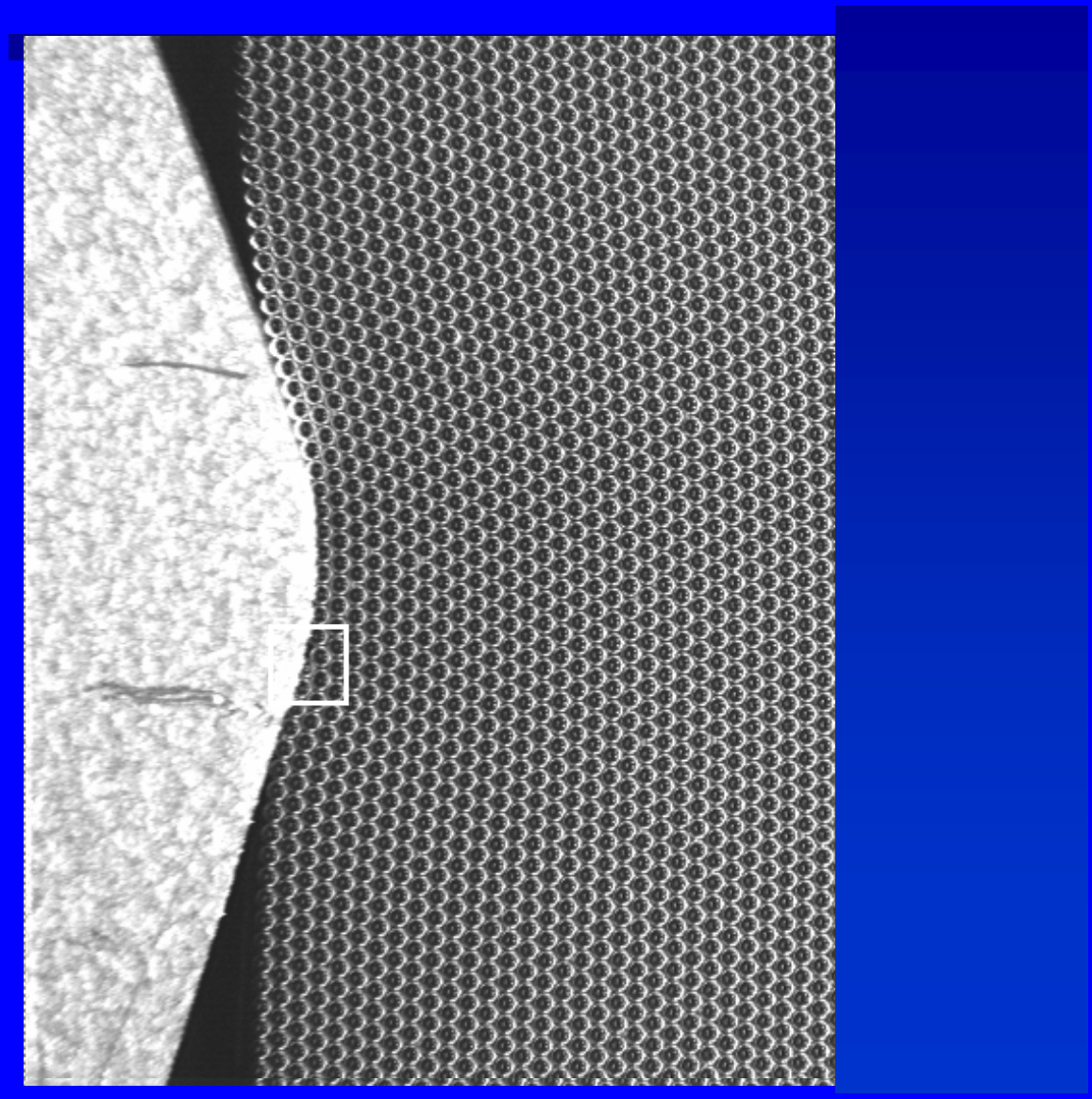

*MEP*




activation barrier
atomic configurations

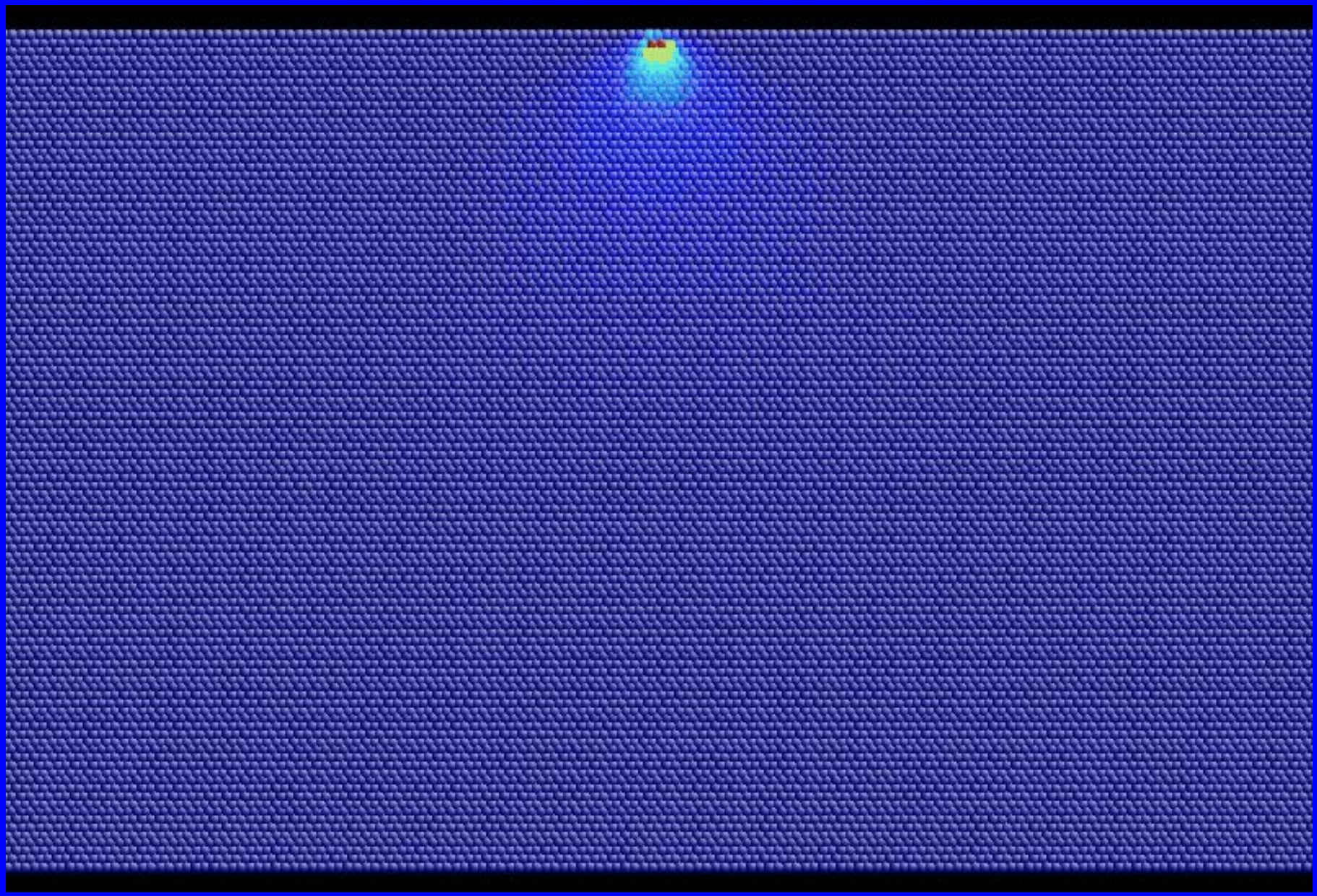
# *Experimental Observations of yield onset*

- formation of
- slip step



A. Gouldstone, K. Van Vliet and S. Suresh, Nature, 2001.

# Nanoindentation in 2D (MD): von Mises Stress Invariant Distribution



Stability criteria for defect nucleation in a perfect lattice
under inhomogeneous deformation

A general continuum formulation by R. Hill (1962) invoking ‘acceleration discontinuity’

A similarly general derivation of condition for shear localization by J. R. Rice (1976)

We can show -- $\Delta F = \frac{1}{2}\int_{V(x)} D_{ijkl} u_{ij}(x) u_{kl}(x) dV$

$D_{ijkl} = C_{ijkl} + \tau_{jl}\delta_{ik}$ $\qquad$ $u_{ij} = \partial u_i(x)/\partial x_j$

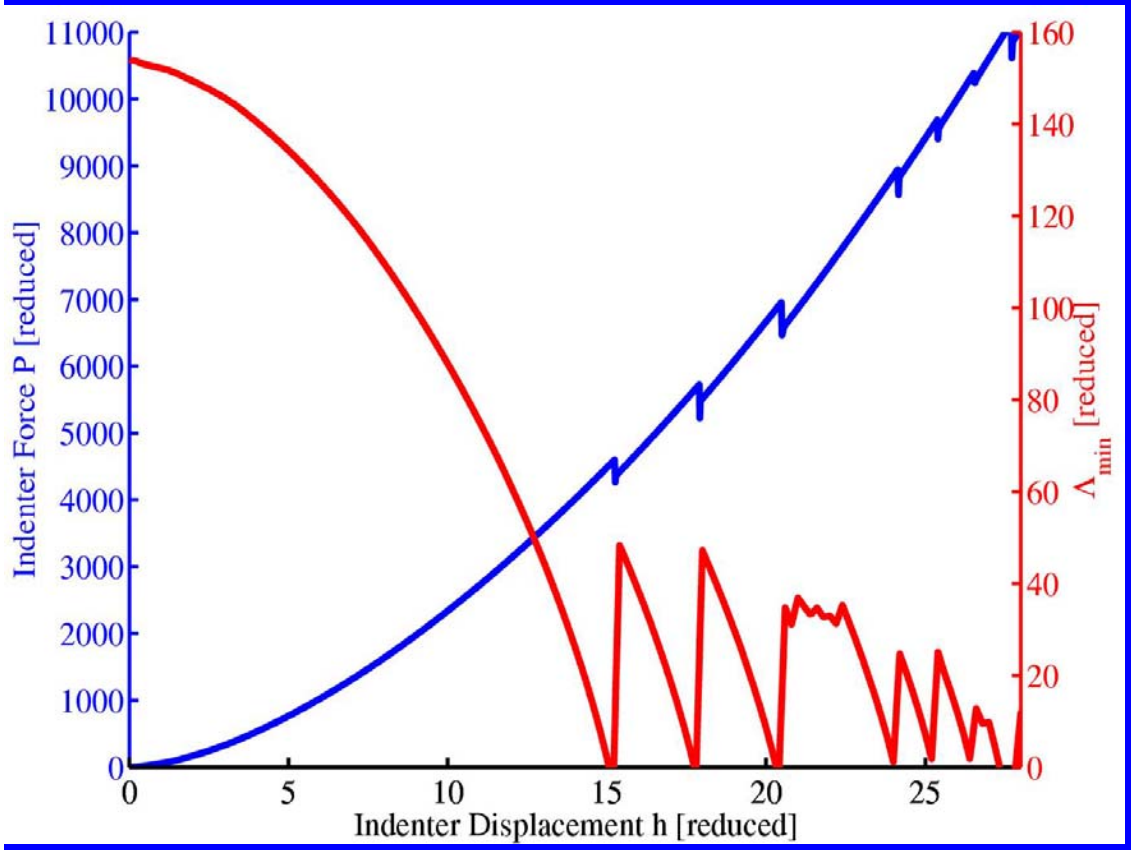
$u_i(x) = w_i e^{ikx}$

$\Lambda(w,k) = (C_{ijkl} w_i w_k + \tau_{jl}) k_j k_l = 0$ is the condition for defect nucleation

This criterion is *local* because we determine C and τ using atomistic expressions

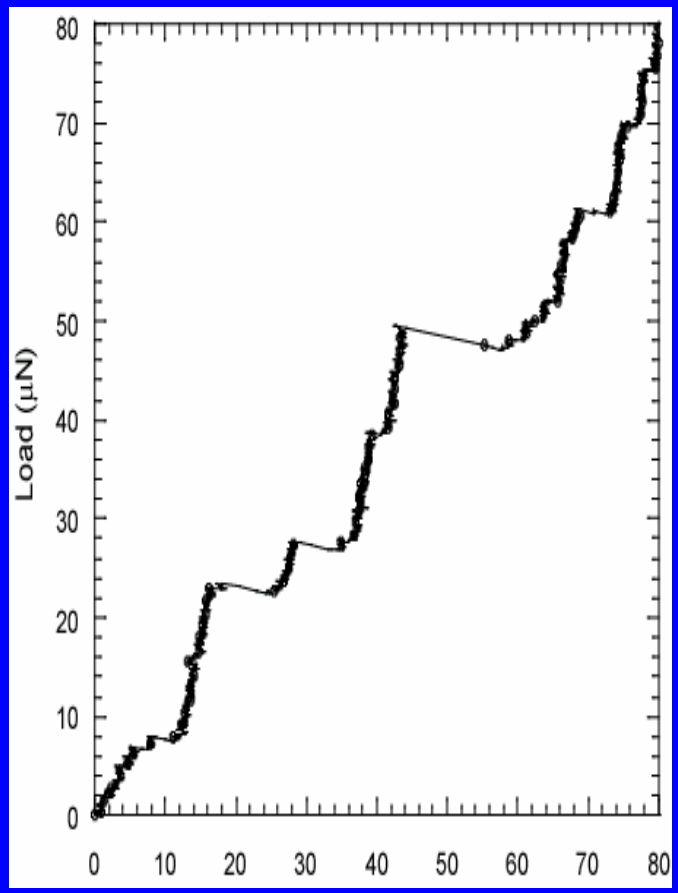
---

J. Li, K. J. Van Vliet, T. Zhu, S. Suresh, S. Yip, "Atomistic Mechanisms Governing Elastic Limit and Incipient Plasticity in Crystals", Nature **418**, 307 (2002).

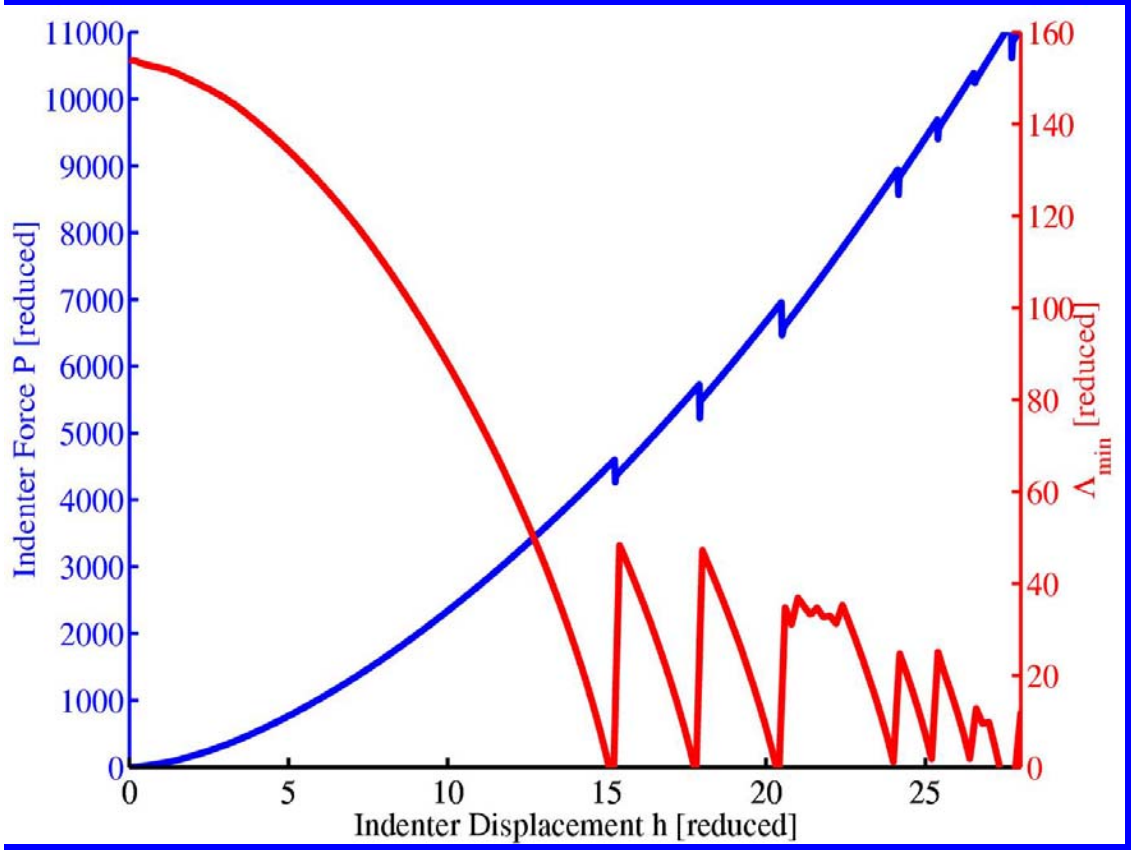



predicted instabilities vs. observed in MD

load-displacement measurement in nano-indentation

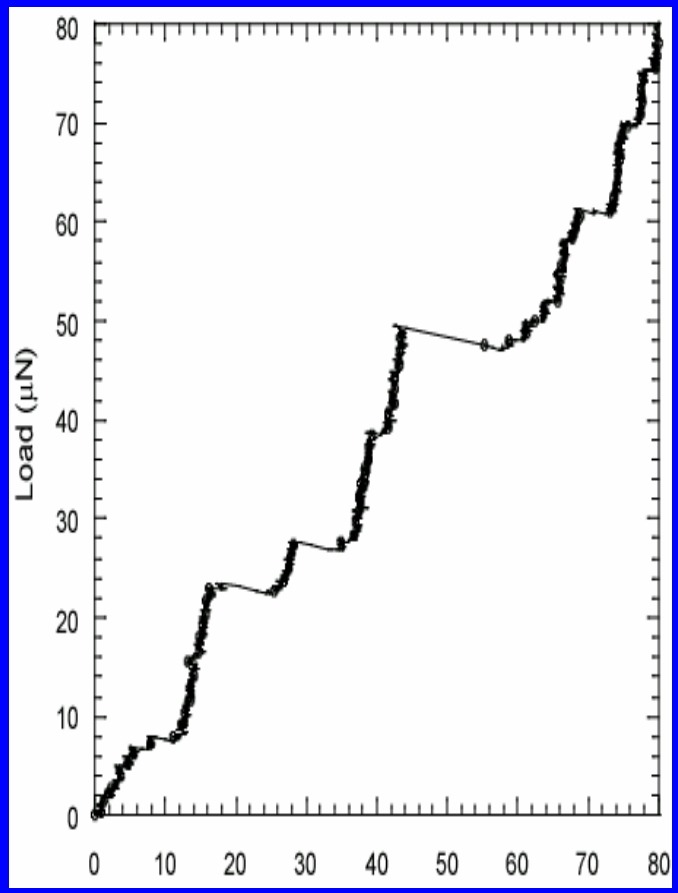



depth [nm]

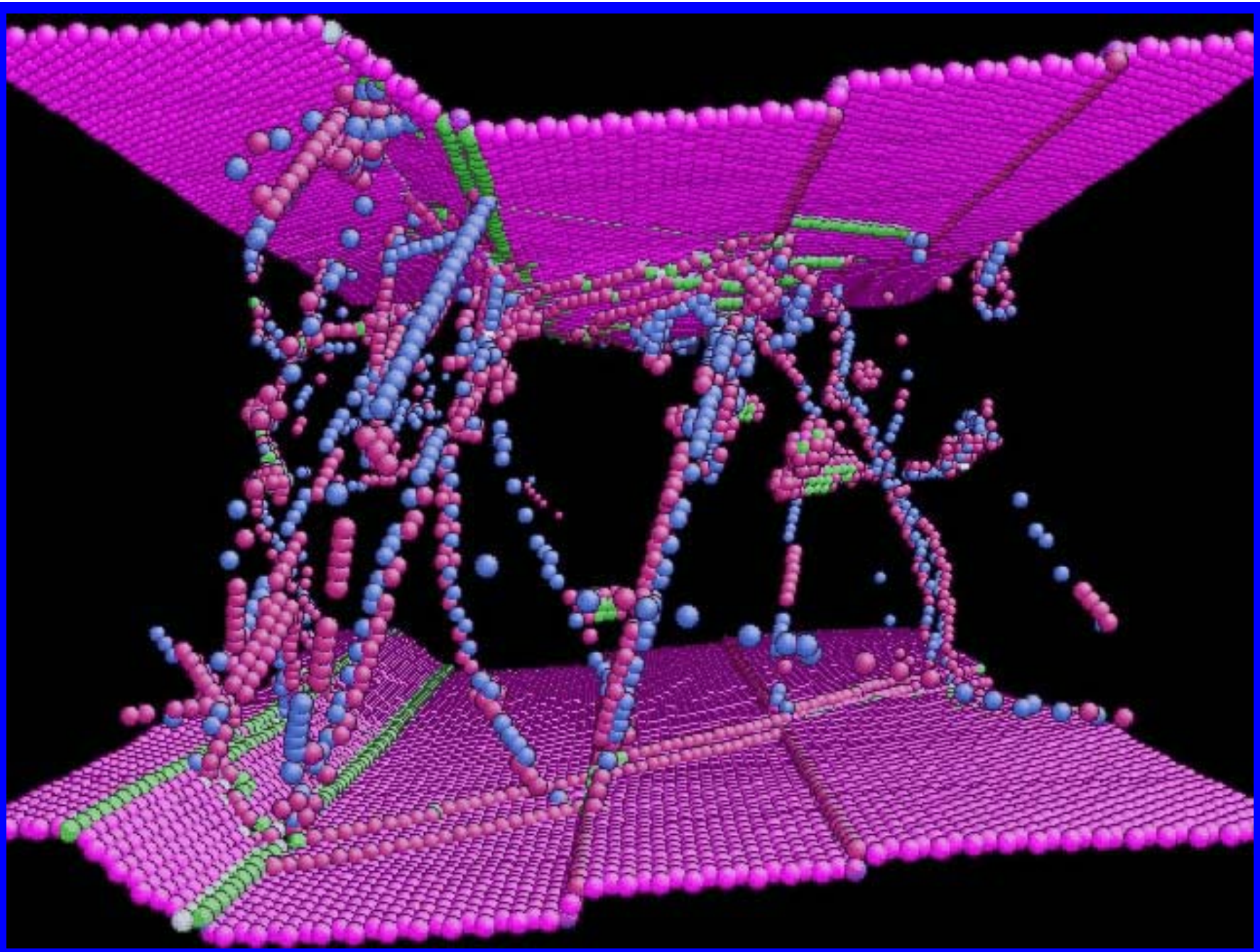



predicted instabilities vs. observed in MD

load-displacement measurement in nano-indentation



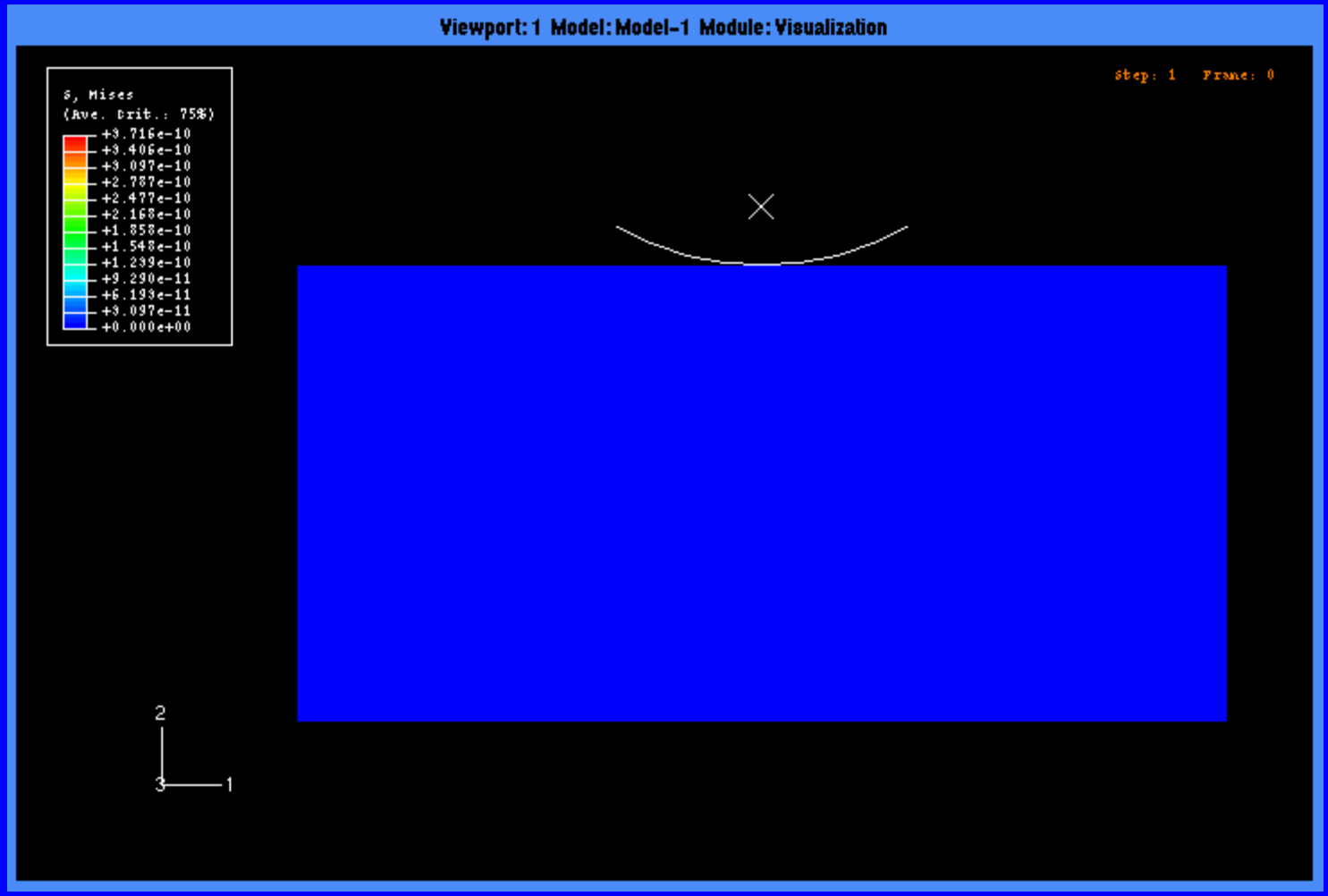

depth [nm]



MD simulation of incipient plasticity

J. Li et al., Nature 2002

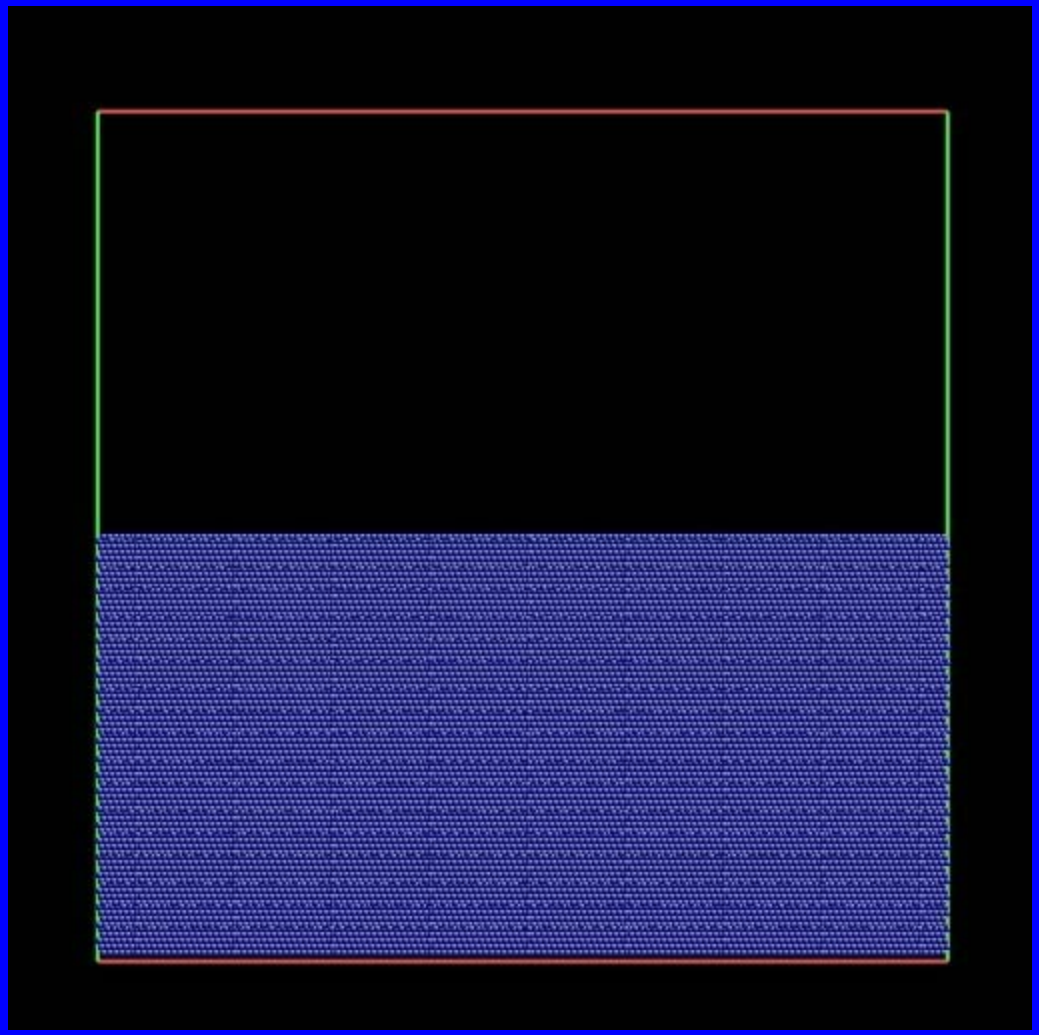
# IPFEM – Cu (2D)



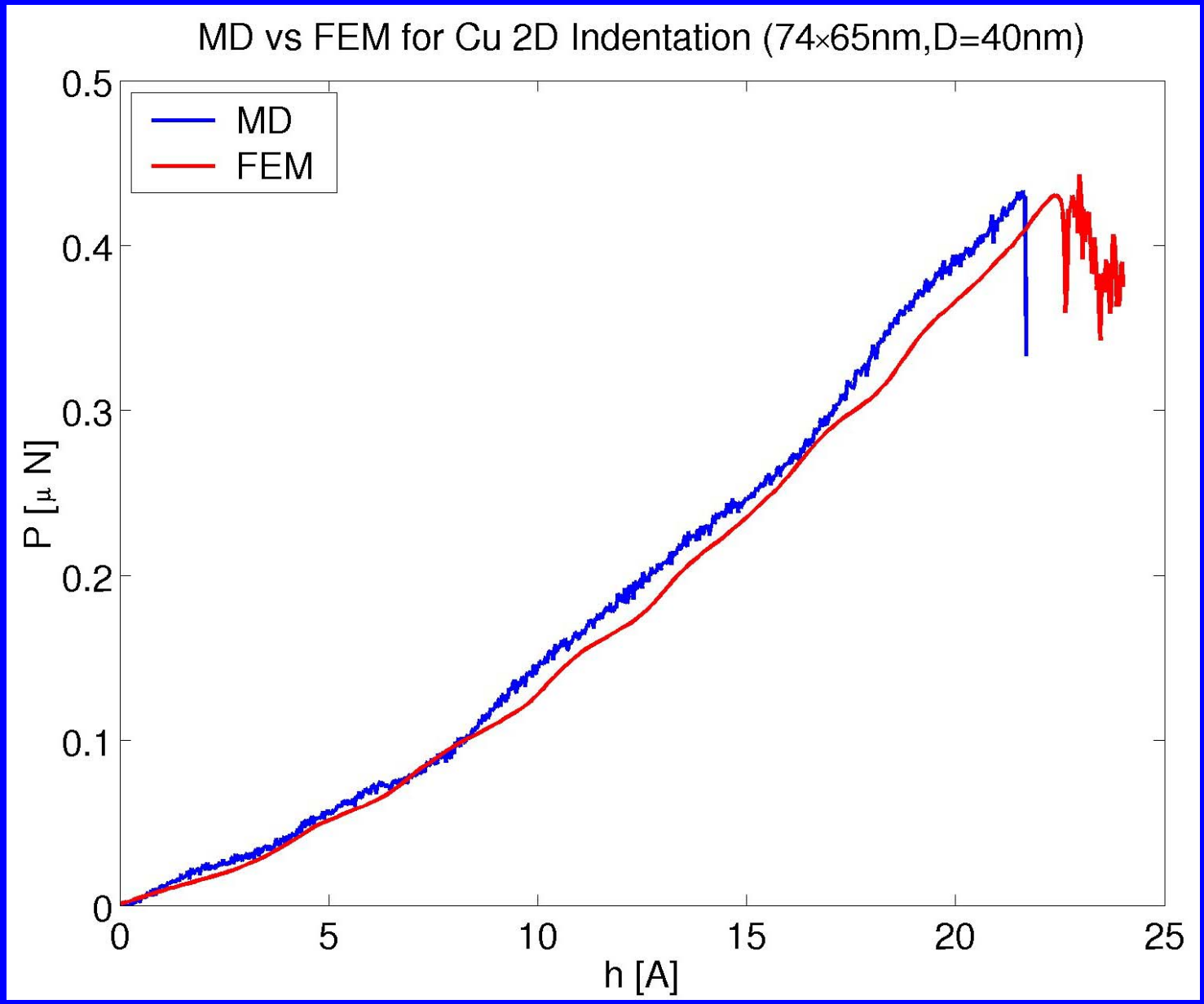

FEM Simulation (abacus + Cauchy-Born)

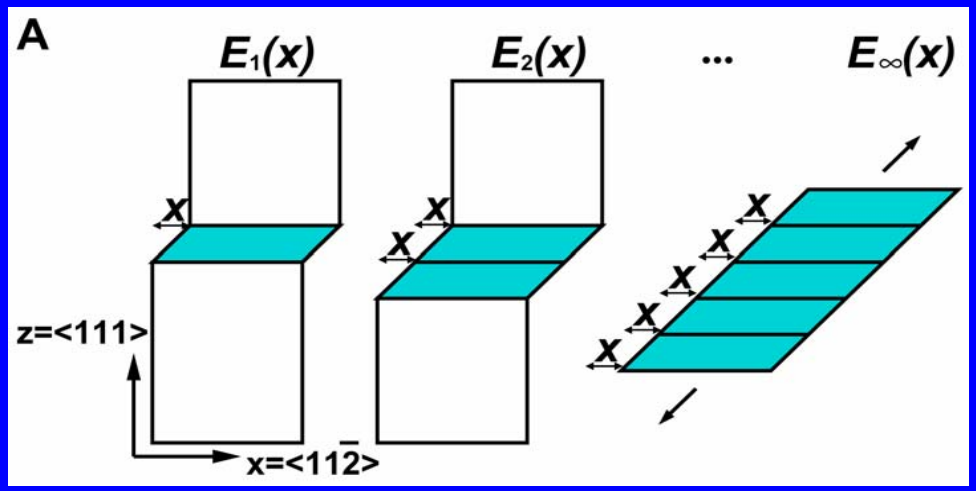
T. Zhu et al., "Predictive Modeling of Nanoidentation-Induced Homogeneous Nucleation of Dislocation in Copper", J. Mech. Phys Solids **52**, 691 (2004).

# MD Cu (2D) – Mises stress



MD Simulation


MD vs FEM for Cu 2D Indentation (74×65nm,D=40nm)
MD
FEM
P [μ N]
h [A]
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25




Multiplane Generalized Stacking Fault Energy

$$\gamma_n(x) \equiv \frac{E_n(x)}{nS_0}, \qquad n = 1,2,3,\ldots,\infty$$

$\gamma_1(x)$: GSF surface

$\gamma_1(b_p) = \gamma_{SF}$: intrinsic stacking fault

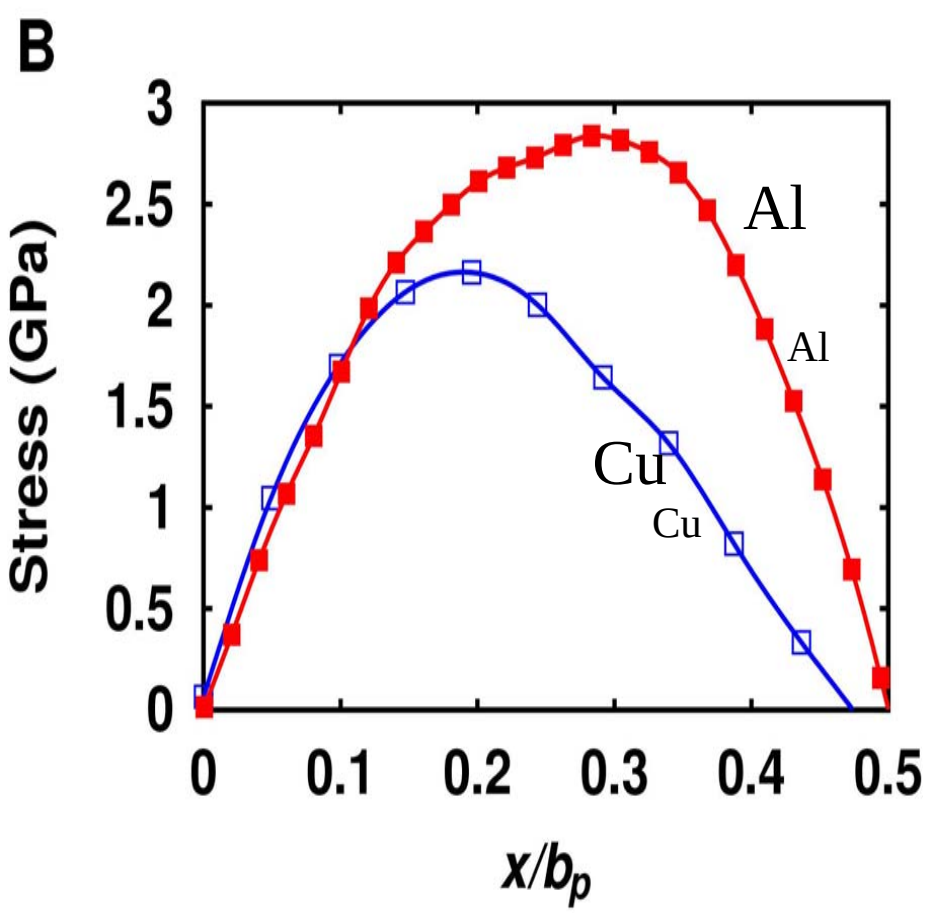
$\frac{d\gamma_1(x < b_p)}{dx} = 0 \rightarrow \gamma_{US}$: unstable stacking energy

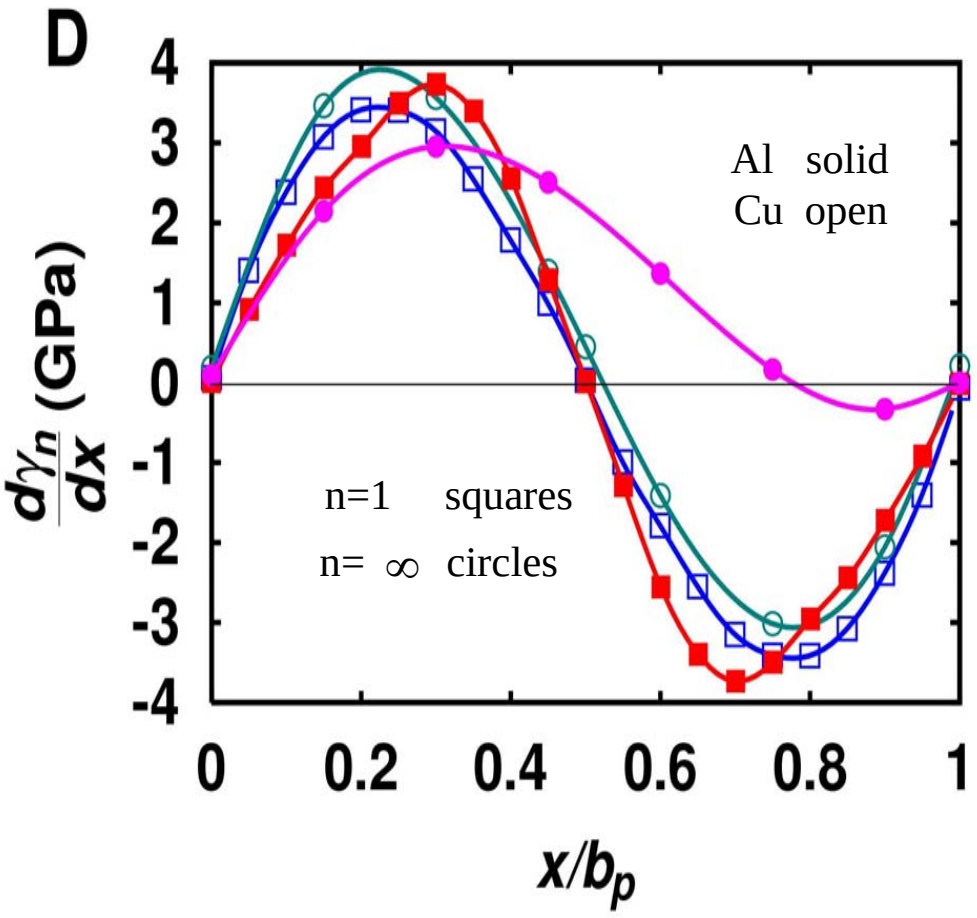
**Table 1.** Benchmark results, comparison of present calculations (Calc), experiments (Expt), and previous calculations (Oth calc). Dashes indicate that results are not available.

| Variable | Al | | | Cu | | |
|---|---|---|---|---|---|---|
| | Calc* | Expt | Oth calc | Calc* | Expt | Oth calc |
| $a_0$ (Å) | 4.04 | 4.03† | 4.04‡ | 3.64 | 3.62† | 3.64§ |
| $G_r'$ (GPa) | 25.4 | 27.4‖ | 19–25¶ | 31.0 | 33.3‖ | 26–34¶ |
| $G_u'$ (GPa) | 25.4 | 27.6‖ | 24–30¶ | 40.9 | 44.4‖ | 36–44¶ |
| $\gamma_{sf}$ (mJ/m$^2$) | 158 | 166# | 143**, 164†† | 39 | 45# | (49)‡‡ |
| $\gamma_{us}$ (mJ/m$^2$) | 175 | — | 183**, 224†† | 158 | — | (210)‡‡ |

*VASP, US-GGA, 18 × 25 × 11 Monkhorst-Pack $\vec{k}$ points. †(25) Al at temperature $T$ = 0 K, Cu at $T$ = 298 K. ‡(26) GGA. §(27) Full-potential linearized augmented plane wave method (WIEN97 program), GGA. ‖(28) calculated from elastic constants at $T$ = 0 K. ¶(4) LDA. #(29). **(30) LDA. ††(31) LDA. ‡‡(5) LDA, unrelaxed.

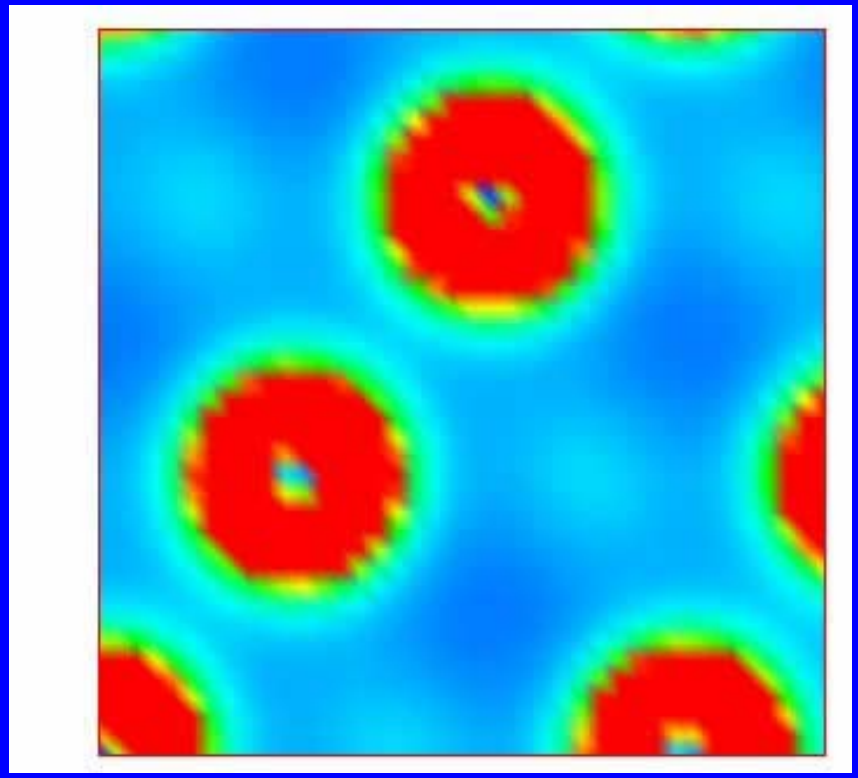
# Pure Shear Stress-Displacement Curve



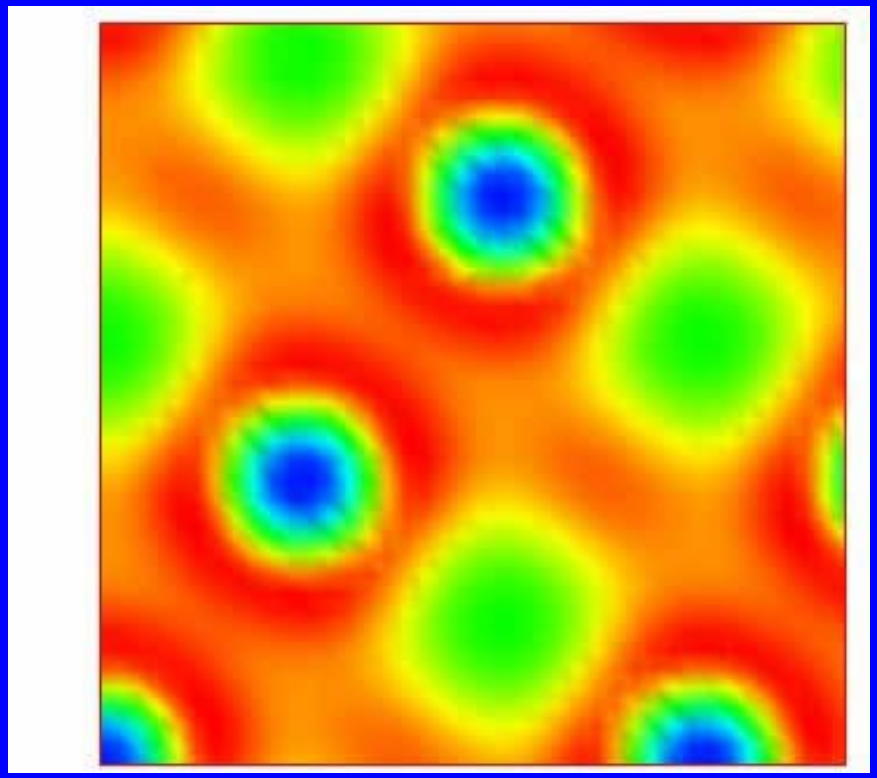




S. Ogata, J. Li, S. Yip, "Ideal Pure Shear Strength of Aluminum and Copper", Science **298**, 807 (2002).

Charge density redistributions during affine shear in two fcc metals
(DFT calculations)

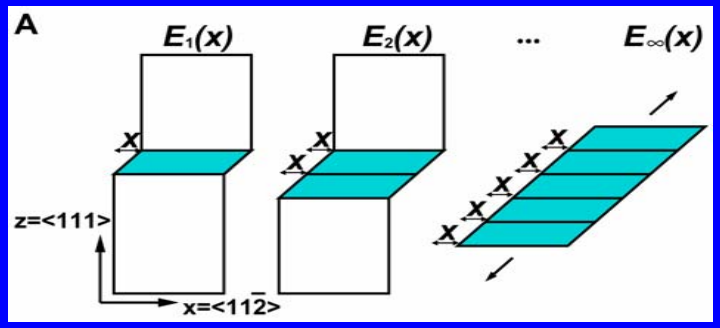


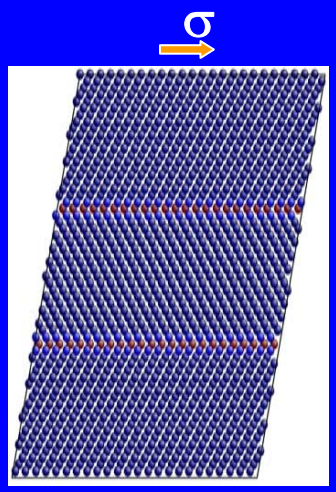
Cu



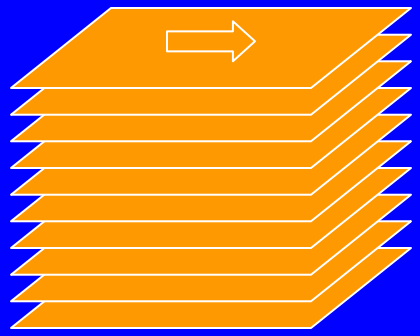
Al

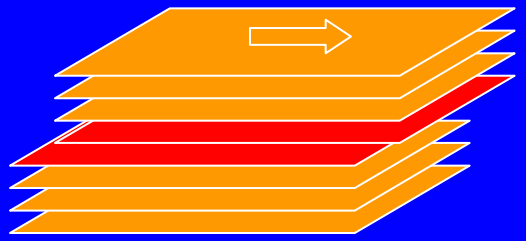
# Twinning vs. Slip



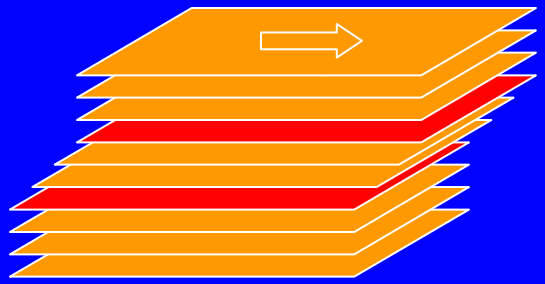




- alternative plastic deformation mechanism in metals
- common in hcp metals, favored in bcc at low T
- operates at low T, high σ, high $\dot{\gamma}$, limited slip systems





**slip**

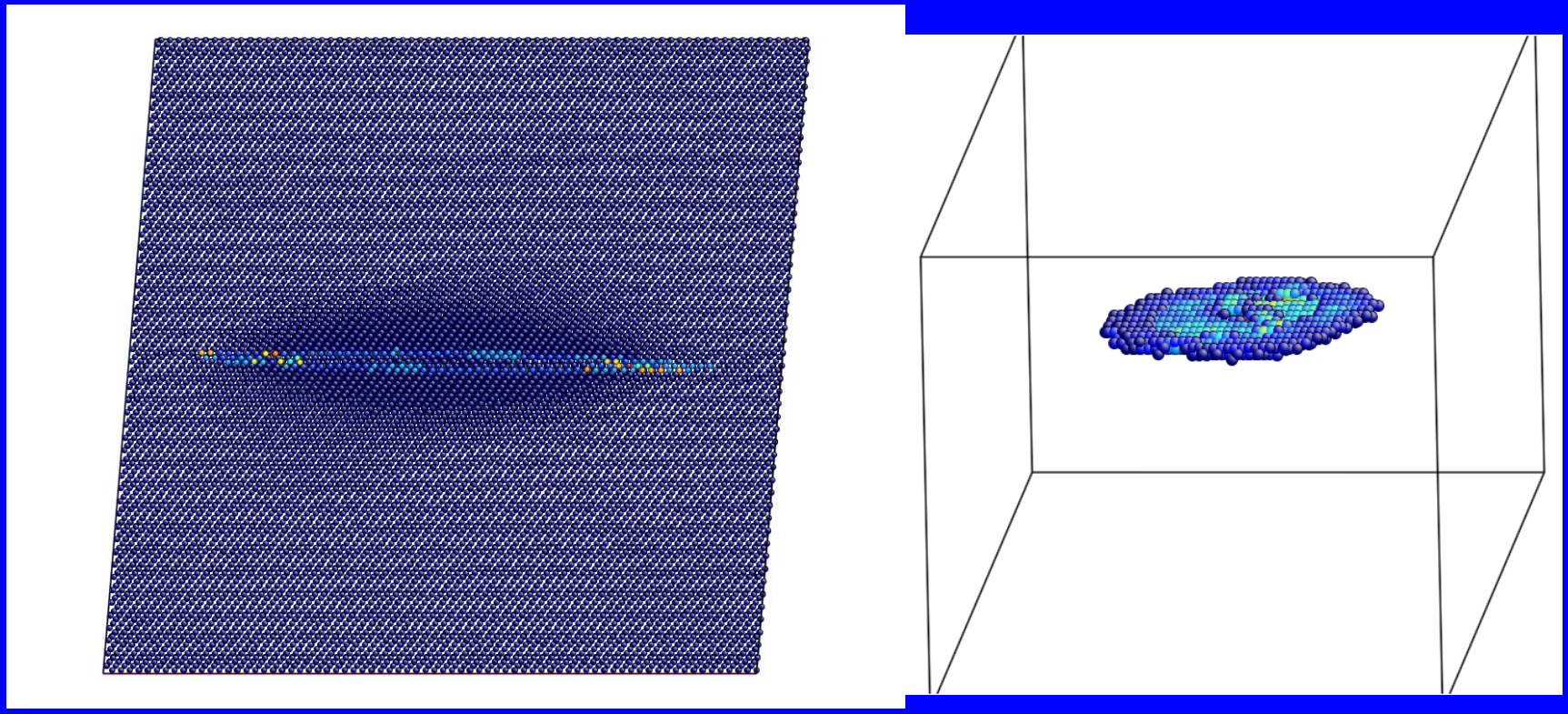


***twinning***

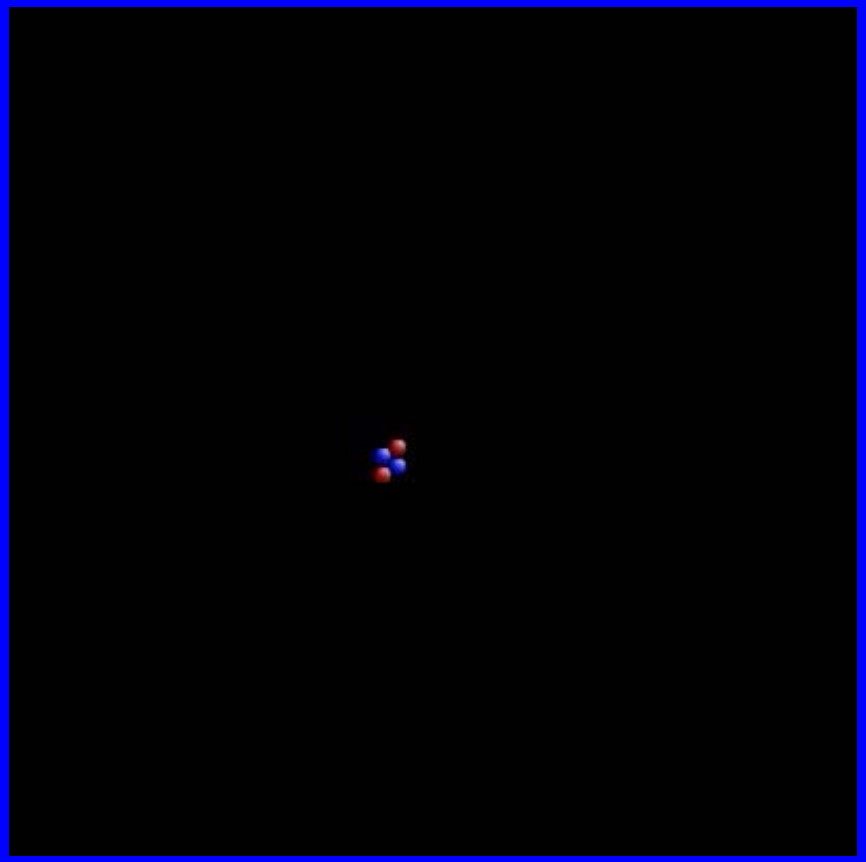
**Atomistics of Defect Nucleation and Mobility: Dislocation and Twinning in BCC Metals**

direct observation of nucleation of 3D deformation twin

# twinning in affine shear



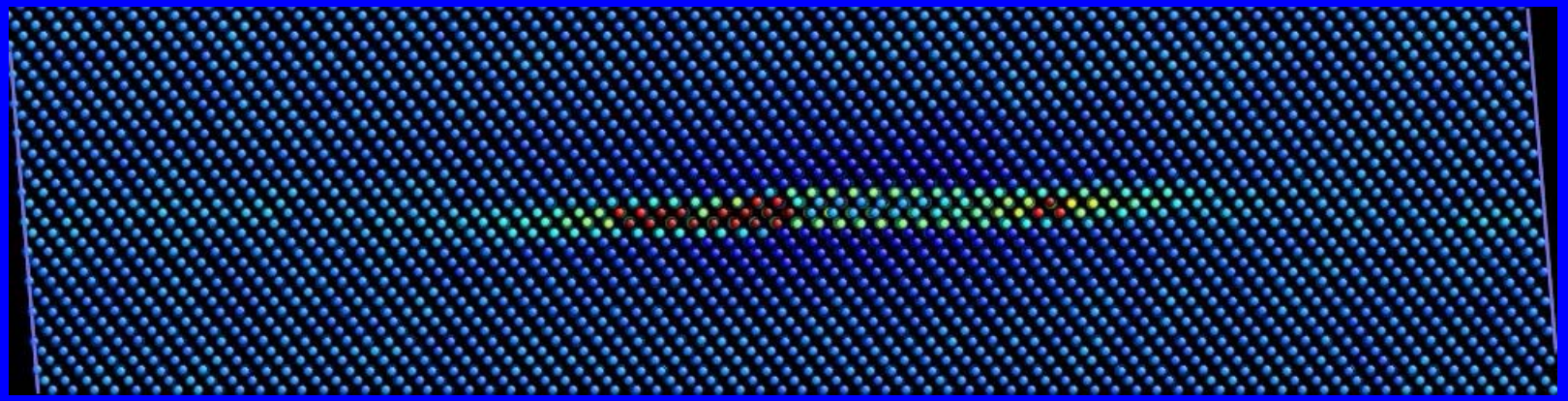
3D homogeneous shear of perfect Mo crystal on $(1\bar{1}2)[111]$. (T=10K, 0.5M atoms)
Twin nucleation at shear stress of 12.2GPa and 7.84% strain

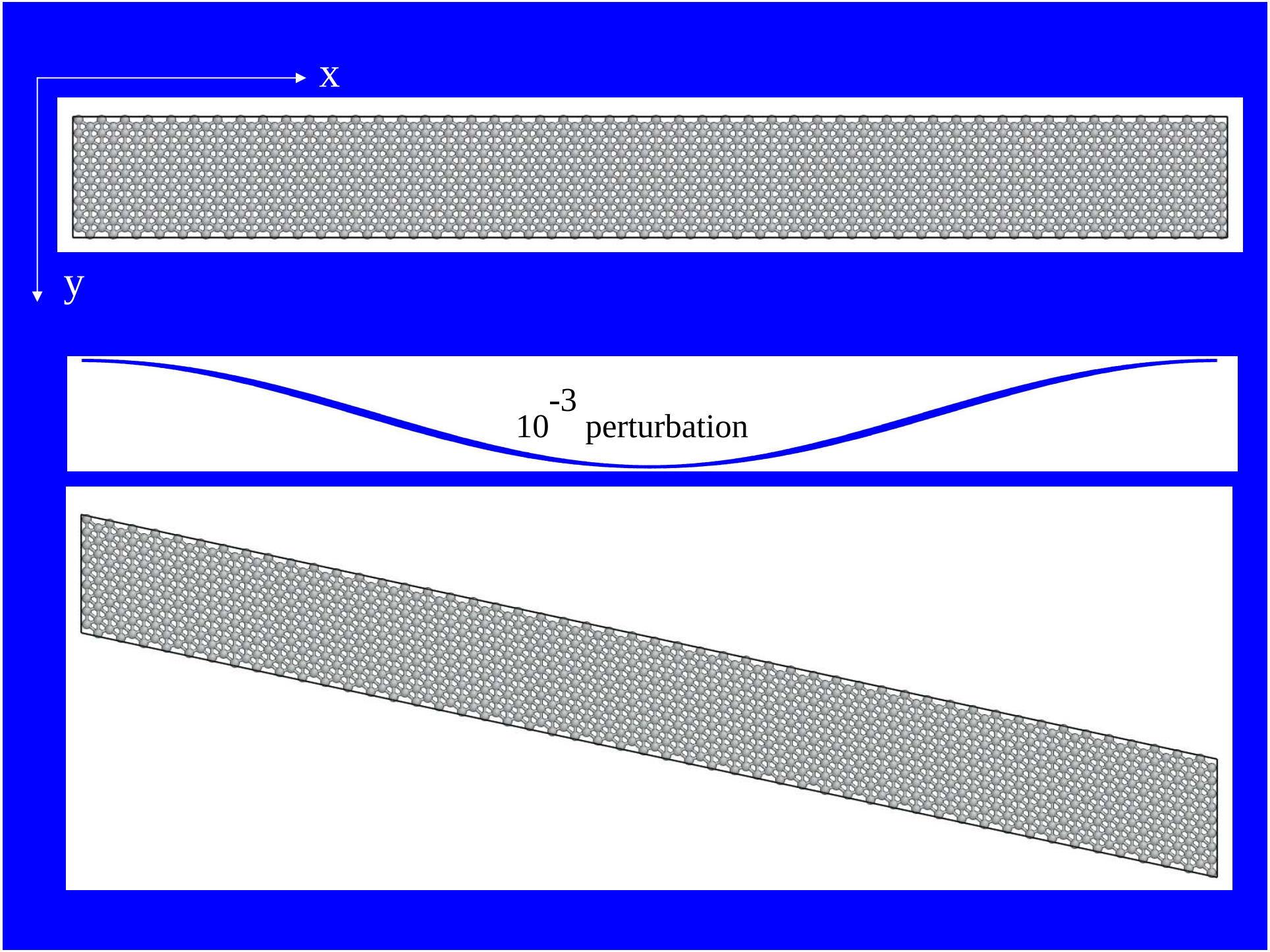


–

- twin nucleation at shear stress of 12.2GPa and 7.84% strain
- 3D homogeneous shear of perfect Mo crystal on (112)[111], T=10K, 0.5M atoms
- propagation speed of twin head:

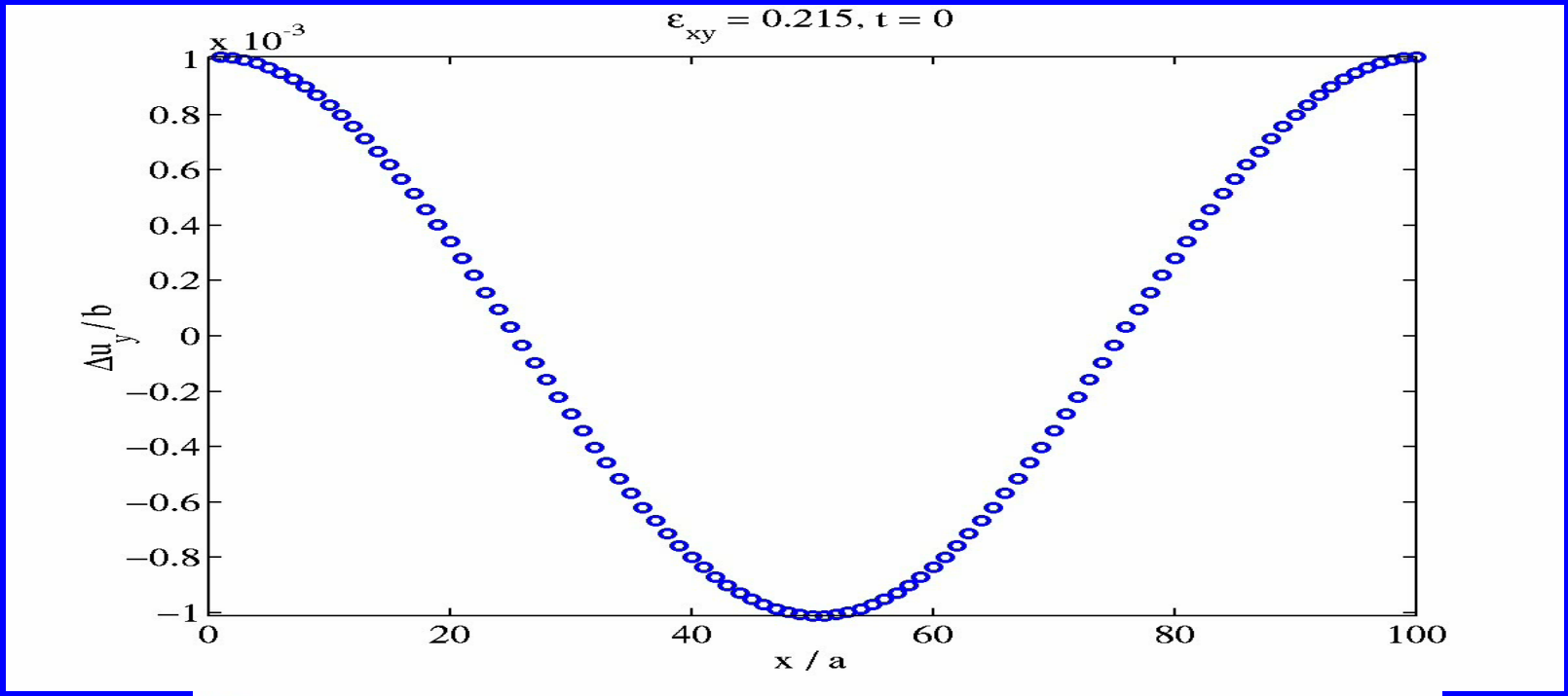
  edge type dislocation→
  ~6000 m/s (longitudinal wave speed)
  screw type dislocation→
  ~3000 m/s (Rayleigh velocity)

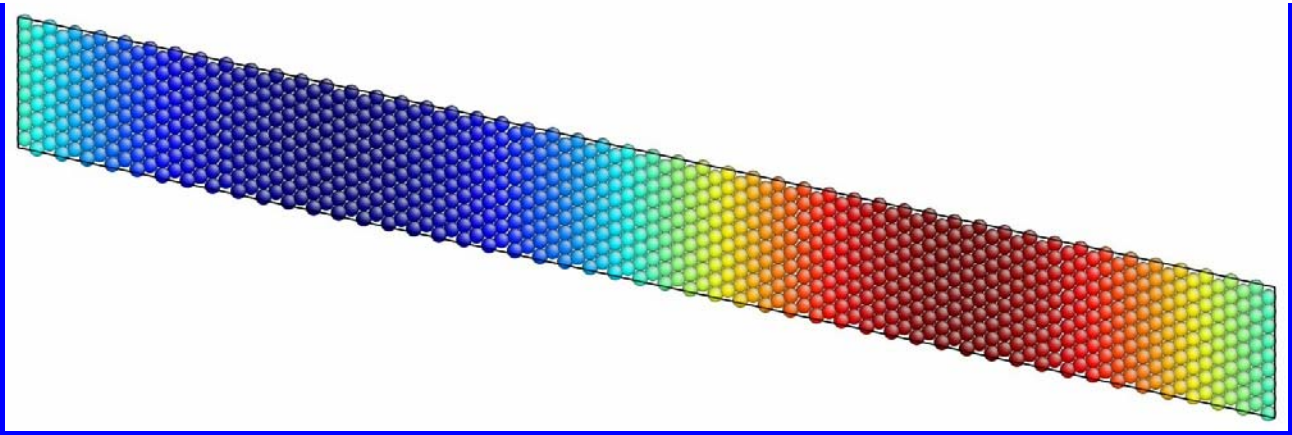



x
y
$10^{-3}$ perturbation

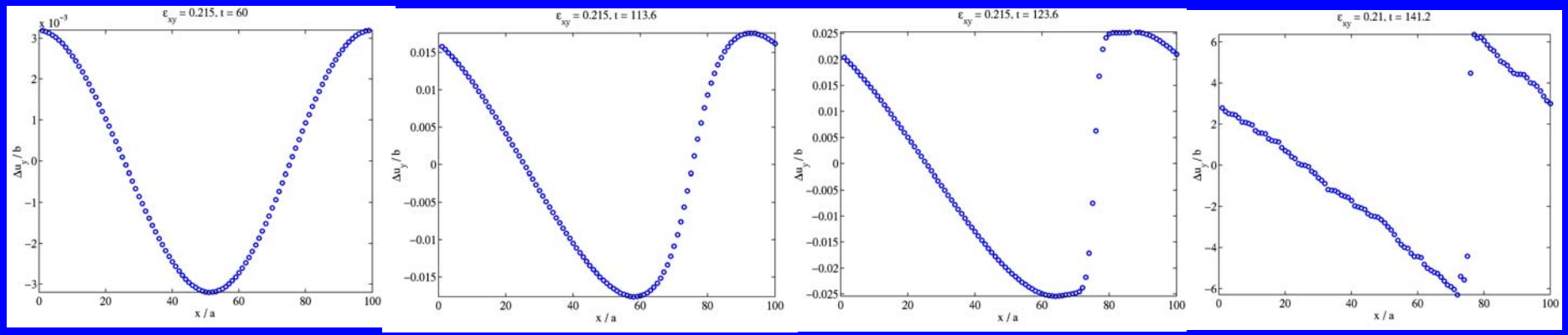
*(visualizing strain localization)*

breakup of a modulating wave as a deformation twin is nucleated



# 4-stage wave distortion scenario




1. Linear Growth
shape preserved, amplitude increases
continuum description

2. Non-Linear Growth
wave-front steepens due to increasing non-linearity
continuum description

3. Shock Formation
wave-front steepens atomic-scale shock
→ atomistic description

4. Atomic Defect Stabilized
atomic-level decision governed by atomistic energy landscape

self-similar (scale-invariant) behavior –
turning an instability into a steady state (I. Kevrekidis)

Jinpeng Chang, PhD Thesis, MIT (2003).

# IV. Crack-tip Plasticity and Water-Silica Interaction Reaction Pathway Sampling

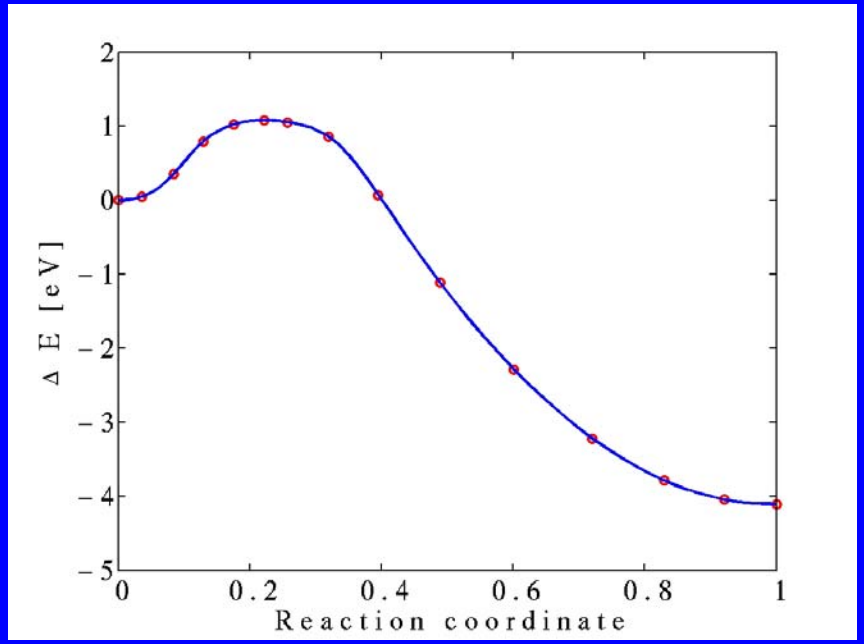
*probing large-strain deformation through atomistic simulation --*

*nano-indentation, charge density redistribution at saddle points,*

*reaction pathway sampling (MEP - activation barrier, atomic configurations),*

*dislocation and twin nucleation, crack extension, water-silica reaction*


*MEP*



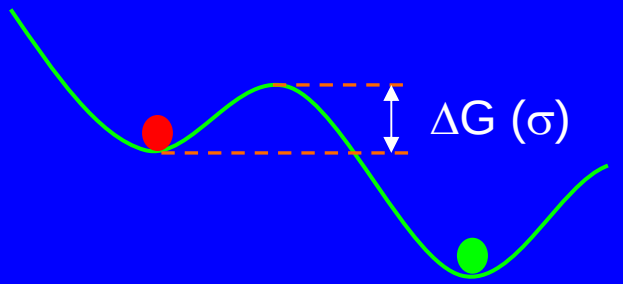

activation barrier
atomic configurations

# Chemical effect on bond breaking = Stress effect on chemical reactivity

## Extending time scale based on transition state theory (TST)

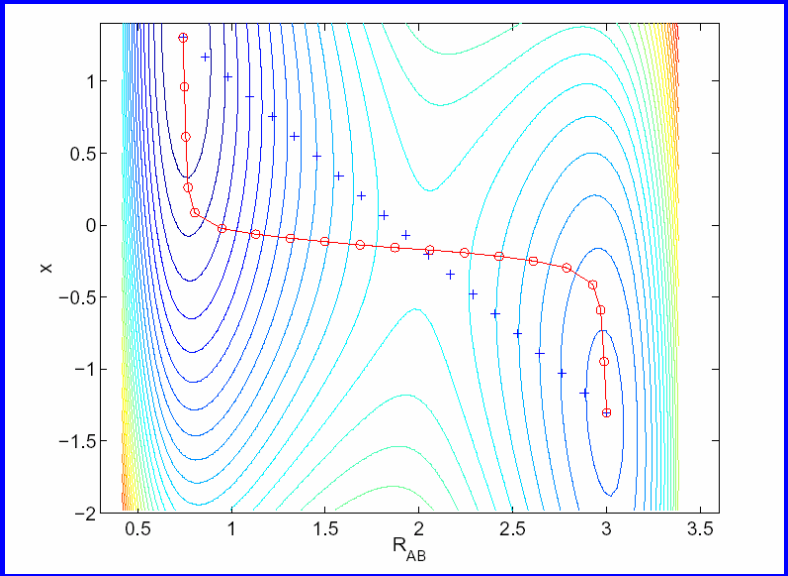
Voter et al., Ann Rev Mater Res (2002)

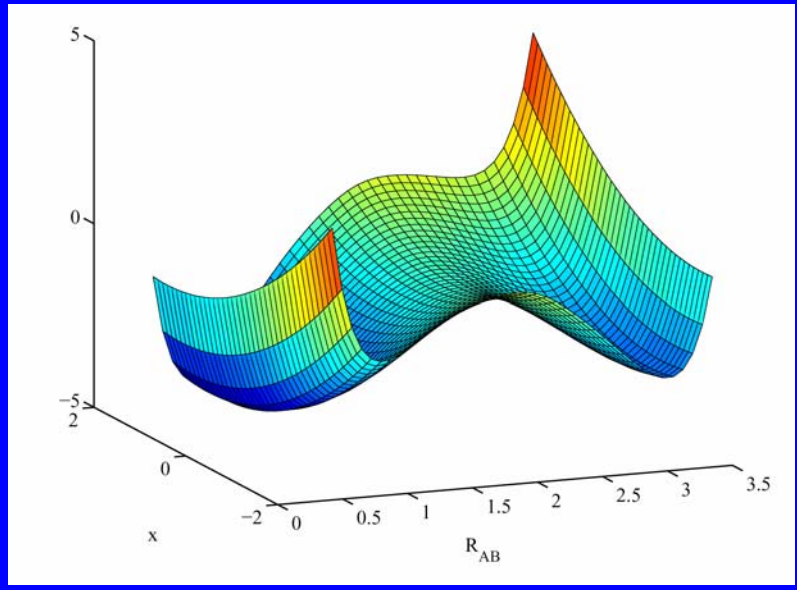
$$\text{transition rate} \propto \nu \exp\left(-\frac{\Delta G(\sigma)}{kT}\right)$$




## Nudged elastic band (NEB) method

Mills & Jonsson PRL (1994) - Hessian free, enable study of larger system using QM force field



Reaction pathway sampling can map out Minimum Energy Path for crack front extension in metal (Cu) and semiconductor (Si)

T. Zhu, J. Li, S. Yip, "Atomistic Study of Dislocation Loop Emission from a Crack Tip", Phys. Rev. Lett. **93**, 025503 (2004).

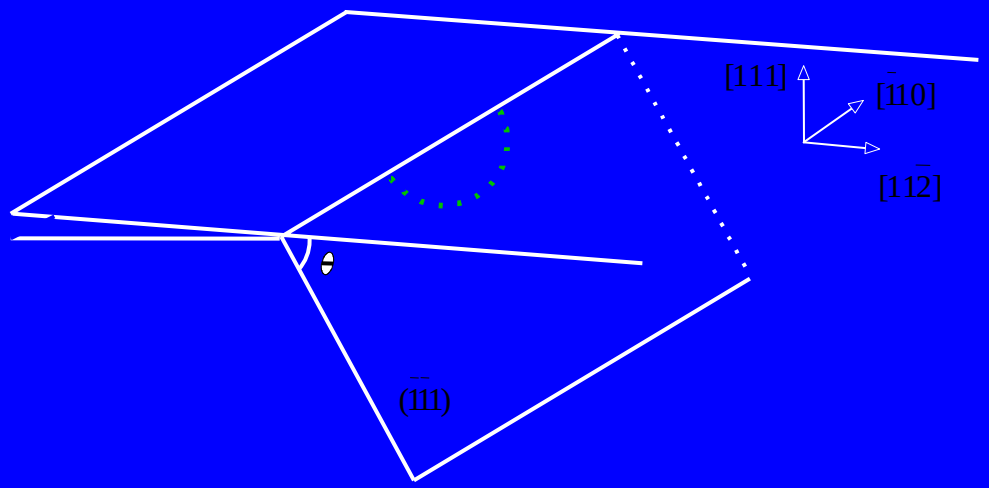
T. Zhu, J. Li, S. Yip, "Atomistic Configurations and Energetics of Crack Extension in Silicon", Phys. Rev. Lett. **93**, 205504 (2004).

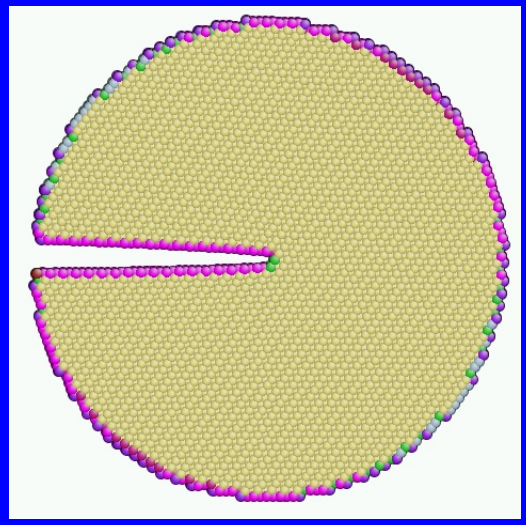
## Nucleation of a dislocation loop from a straight crack front is intrinsically a 3D problem for atomistic simulation

- Direct MD simulation can easily overdrive the system, obtaining sufficient details is a challenge

- We have obtained shear and opening displacement distributions at the saddle point, without loading the system to critical stress

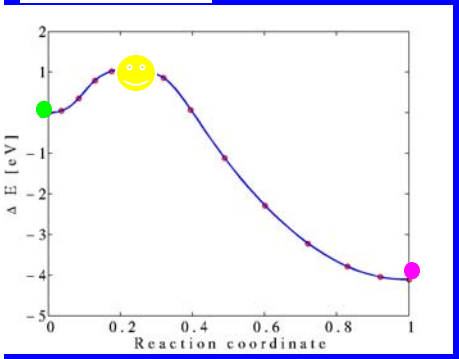
Results for Cu (Mishin potential)

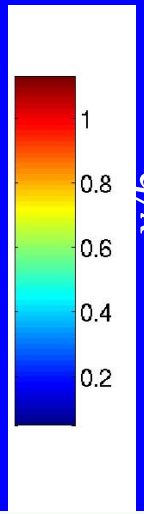


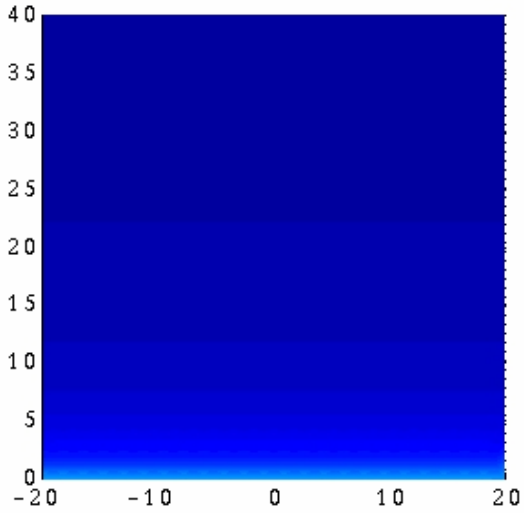



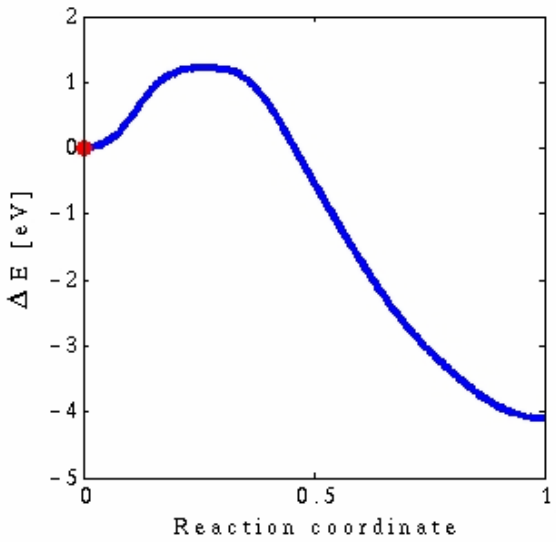
# Minimum Energy Pathway of Dislocation Loop Emission

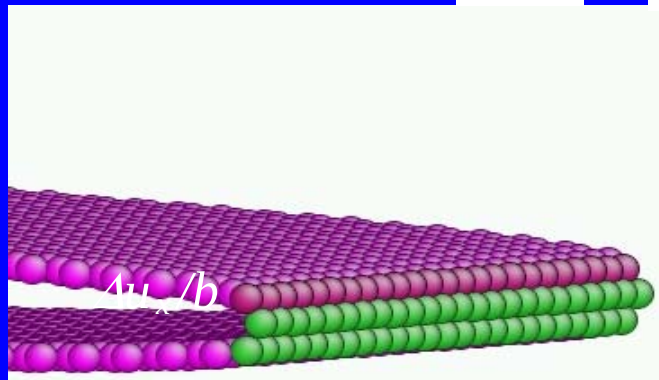
$$\frac{G_I}{G_I^{emit}} = 0.75$$



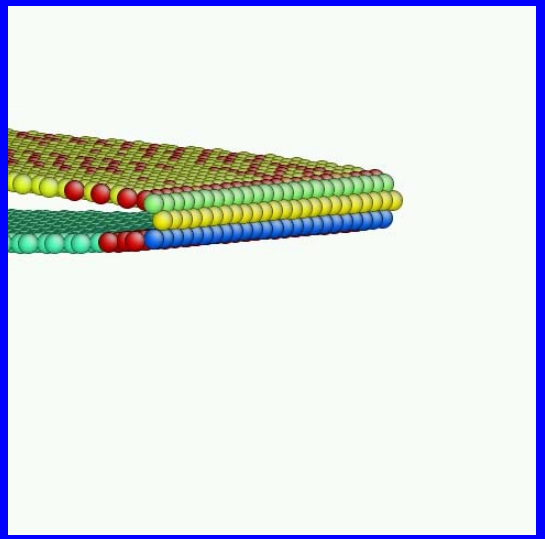



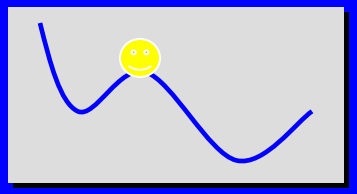


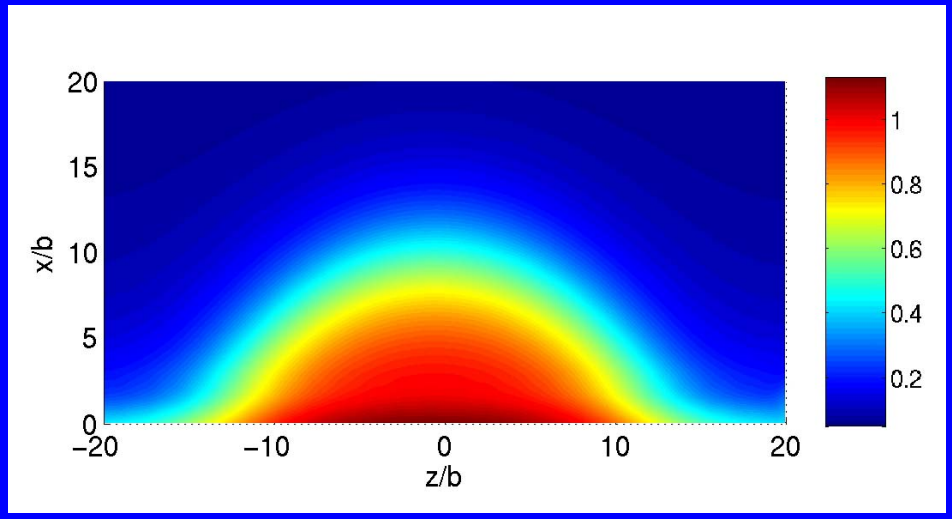

*z/b*

normalized shear displacement distribution

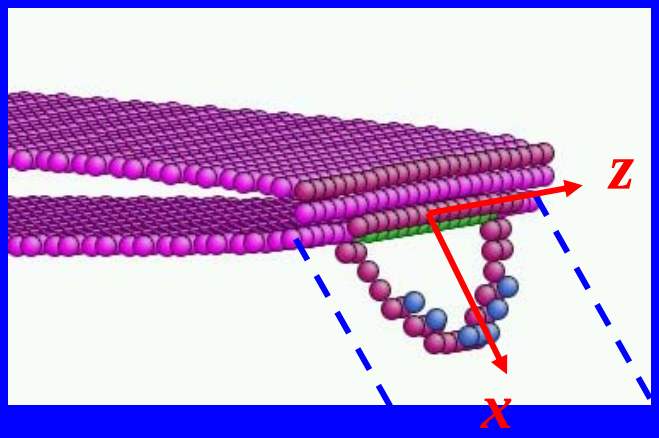




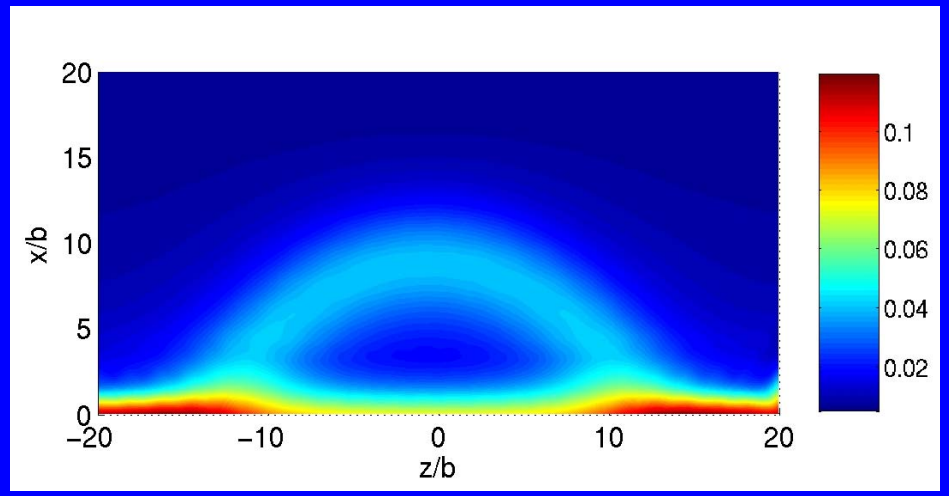
# Saddle-Point Configuration




Shear displacement

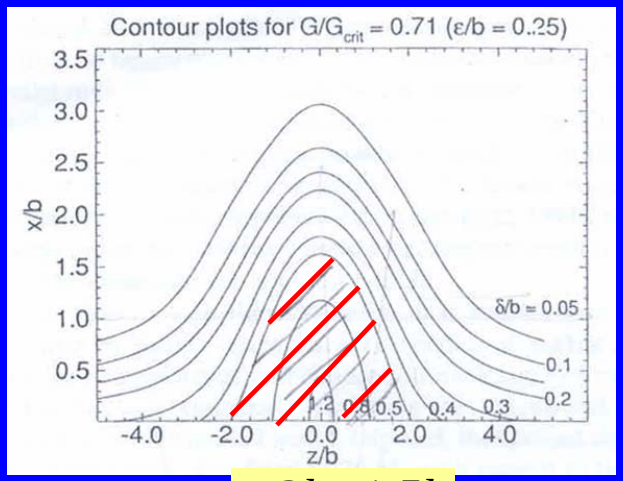



Atomic configuration



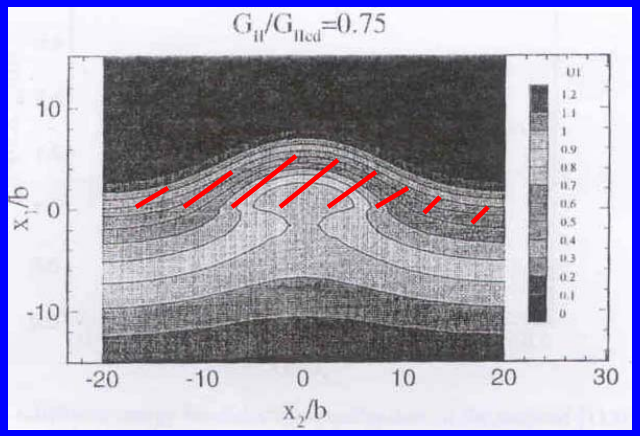

Opening displacement

# comparing atomistic simulation with continuum calculations




$\sim 2b \times 1.5b$

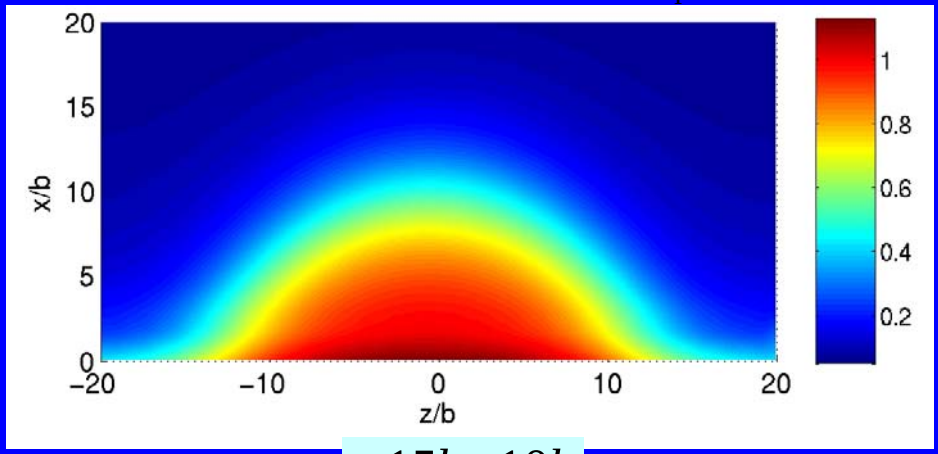
Rice and Beltz, JMPS, 1994




$\sim 10b \times 5b$

Xu, Argon, Ortiz, Phil. Mag. A, 1995

Atomistic calculation for $G_I / G_I^{\text{emit}} = 0.75$




$\sim 15b \times 10b$

$E_{\text{act}}^{\text{3D}} = 0.18\text{eV}$

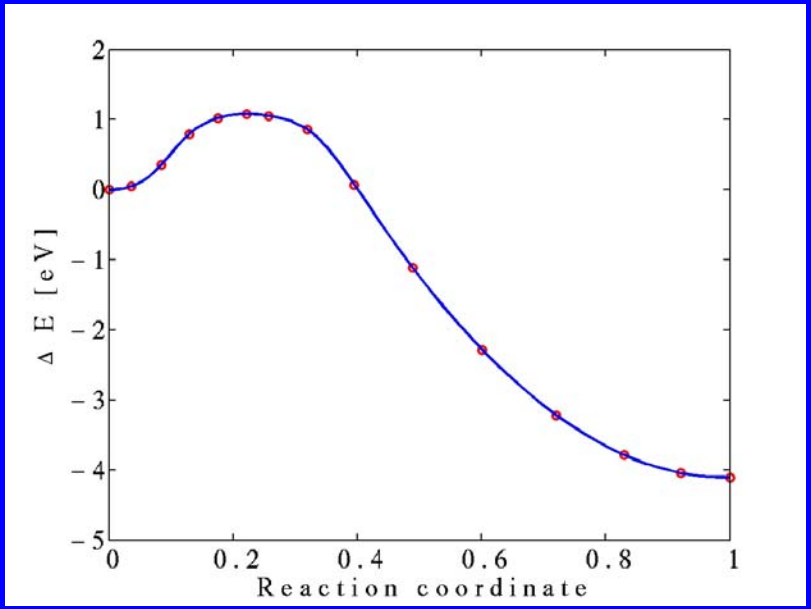
$E_{\text{act}}^{\text{3D}} = 0.41\text{eV}$

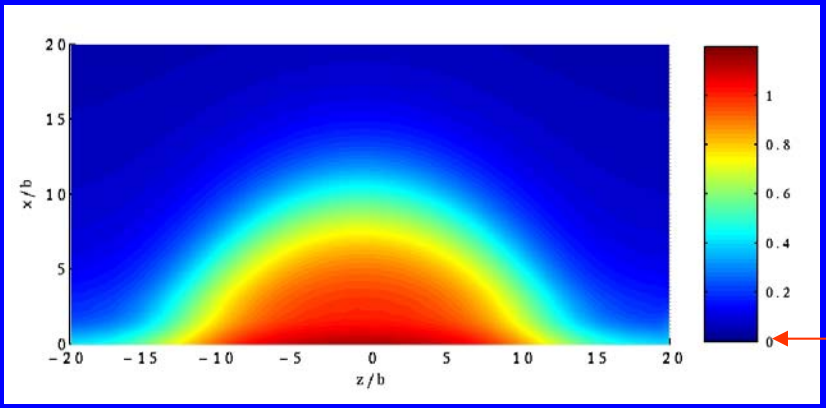
$E_{\text{act}}^{\text{3D}} = 1.1\text{eV}$

ledge production effects in atomistic result

Significantly larger activation volume (= activation area x h)

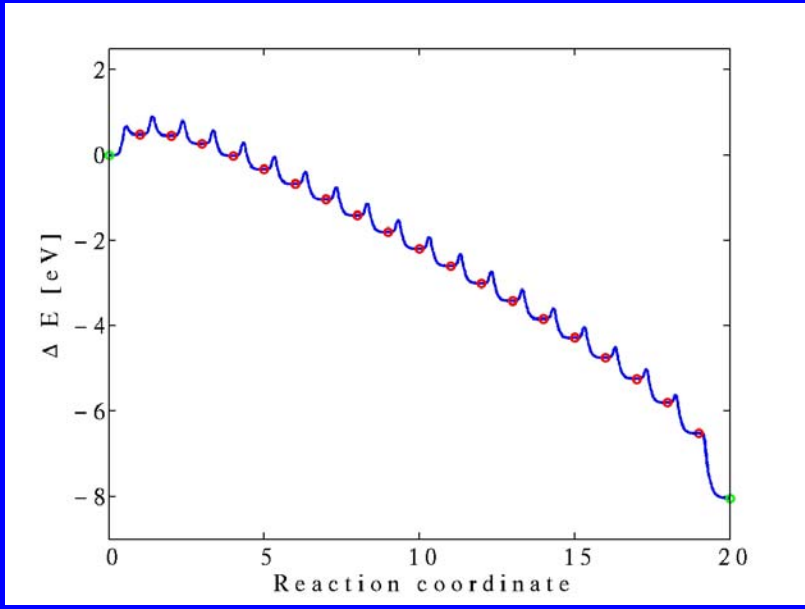
# Dislocation Emission in Cu



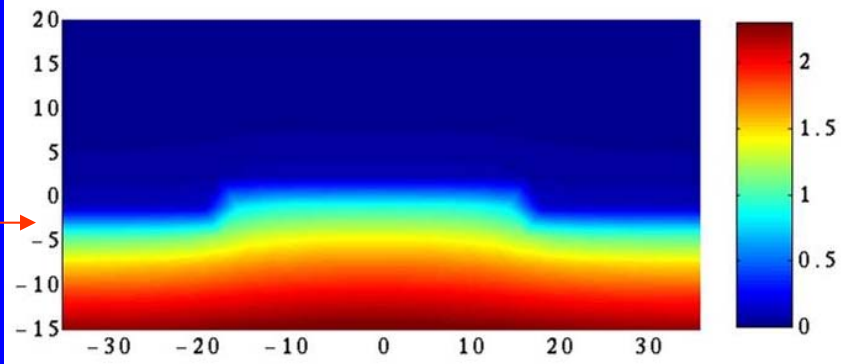




Shear Displacement

# Cleavage Fracture in Si

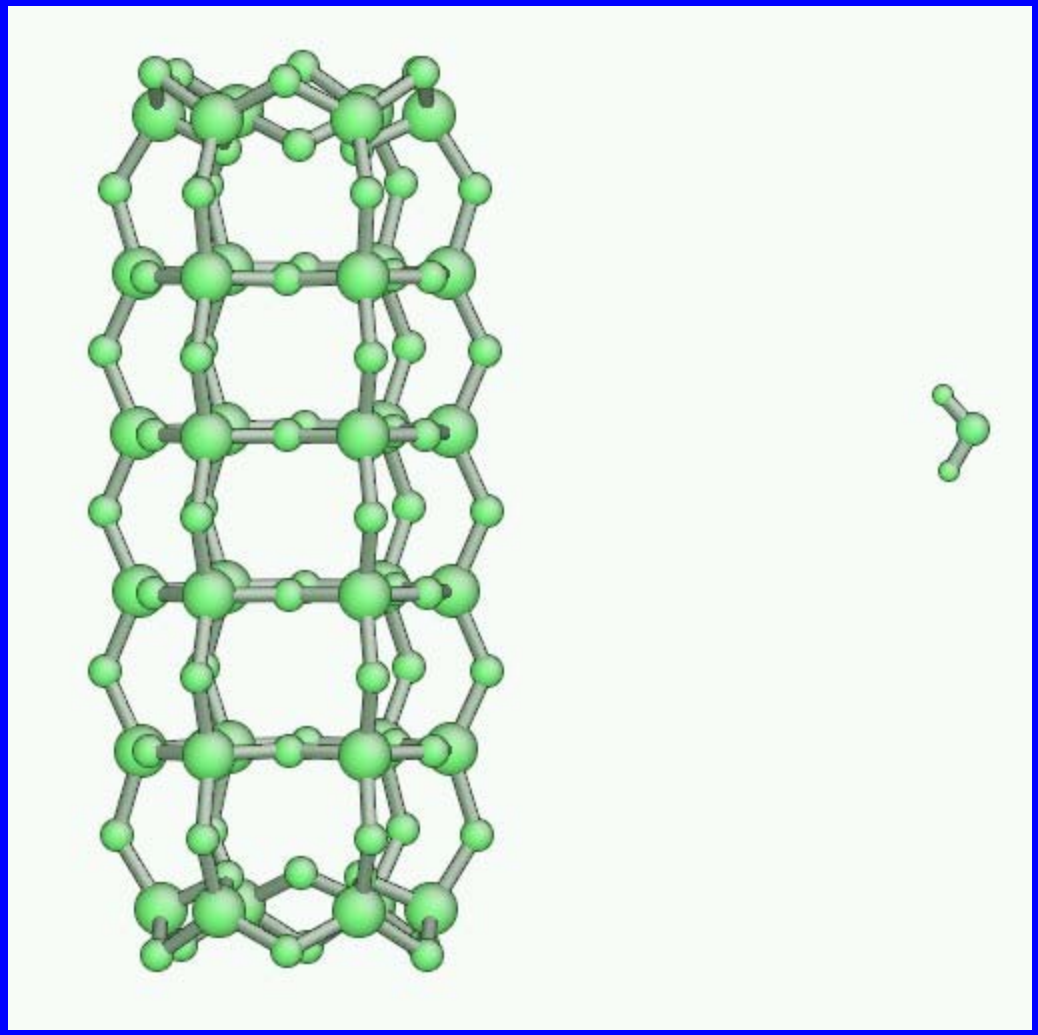



front



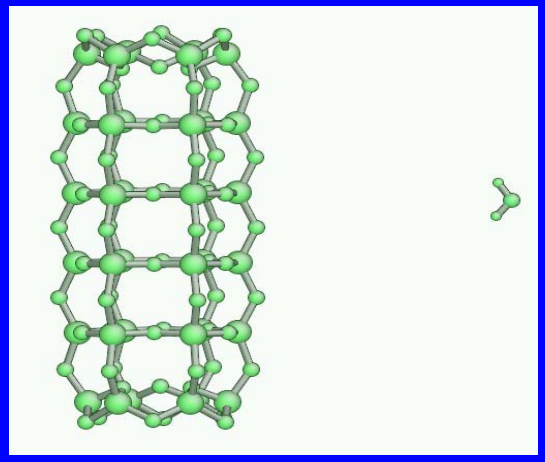
Open Displacement

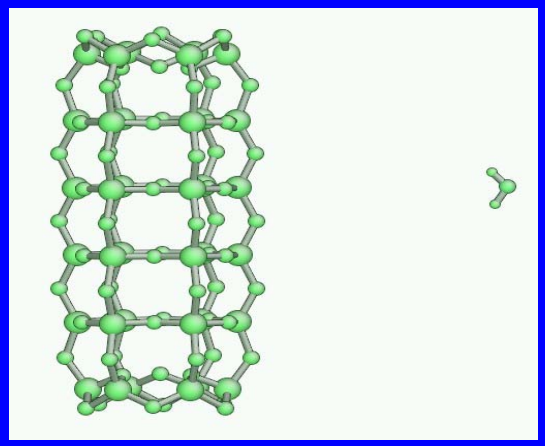
## Attack of water molecule on quartz ($SiO_2$)

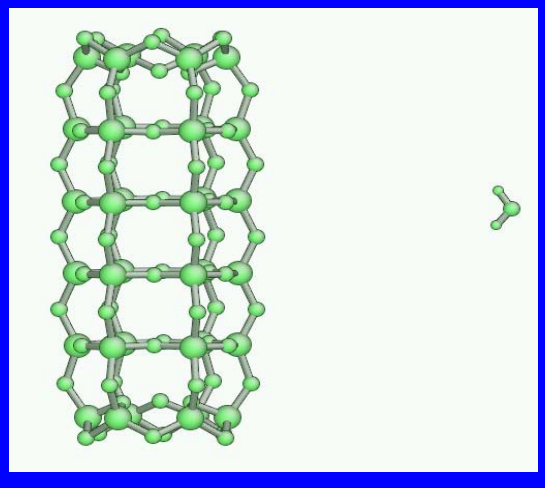


$$H_2O + Si\text{-}O\text{-}Si \longrightarrow 2SiOH$$

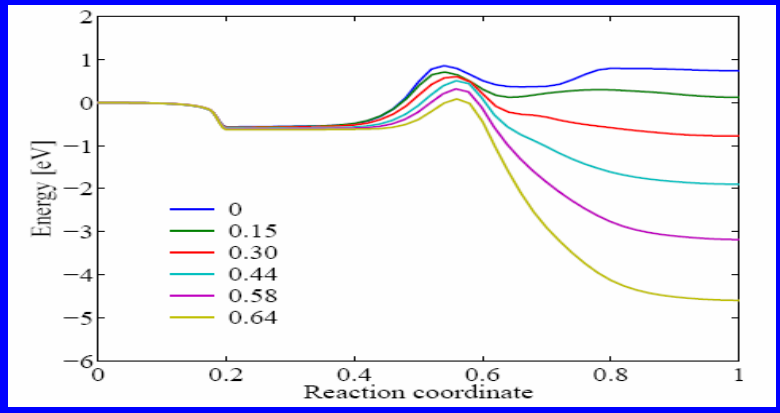
T. Zhu, J. Li, S. Yip, “Stress-dependent molecular pathways of silica-water reaction”, Journal of Mechanics and Physics of Solids **53**, 1597 (2005).



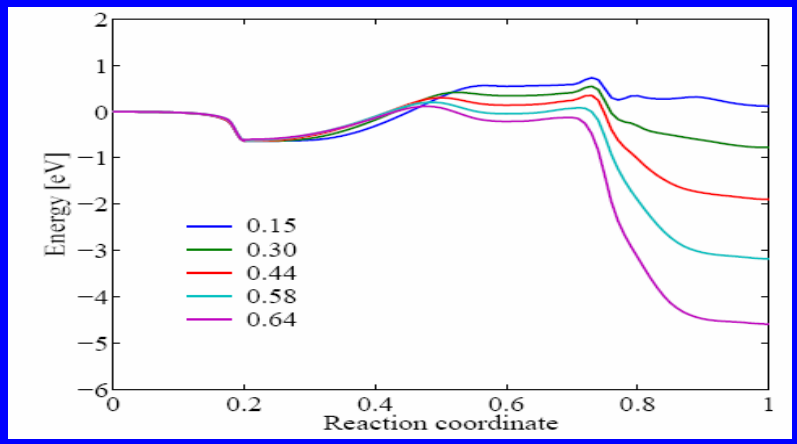




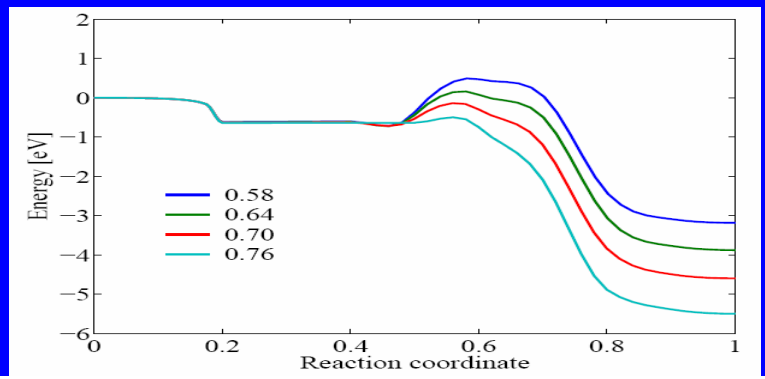
## Mechanism I: Water Dissociation




## Reaction Mechanism II: Pentavalent Chemisorption




## Mechanism III: Direct Siloxane Bond Breaking



## V. An Outlook

Reactive transport: Toward a new class of problems for multiscale materials modeling?

Modeling is the physicalization of a concept,

Simulation is the computational implementation of that concept

*t*

# Applications-inspired Challenges in Modeling Reactive Transport*

*Electron dynamics in molecular-junction conductance*

*Charge localization in conducting polymers -- electron-phonon coupling, electron-electron correlations*

*Oxygen transport in ultra-high temperature ceramics*

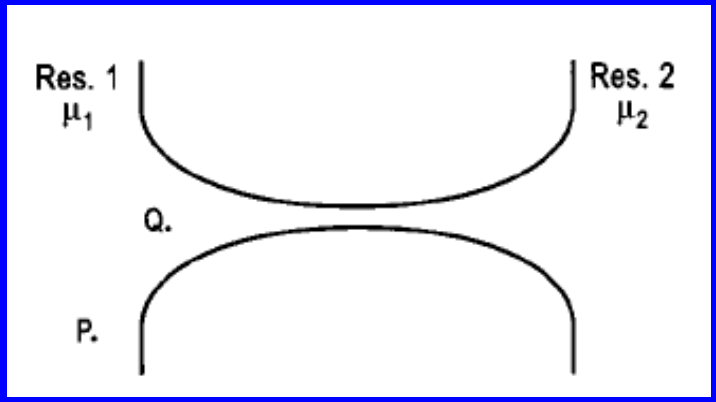
* Distribution of mobile, reacting atomic or molecular species, role of electronic dofs, extreme deformation, rates, environment

## Electric conductance viewed as transmission (Landauer)

Calculating electrical conductance by Non-equilibrium Green's function method --

Present estimate (TranSIESTA) 10-100 times larger than experiments (Au-m-Au)

Possible causes: inadequate treatment of electron dynamics (inelastic scattering and electron correlation), electrode interface and atomic basis-set




See Lu, Bernholc, PRL (2005) for I-V behavior of Si-molecule-Si junction

Alternative approach: time-dependent density function theory with USPP and PAW

dynamical electron correlation (improved band gap)

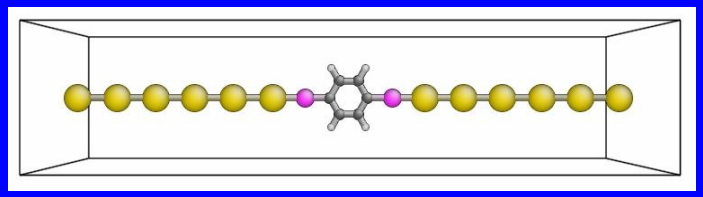
static ion approximation

real-time evolution of Kohn-Sham wavefunction with norm-conserved Crank-Nicolson expansion ( nonlinear transport behavior)

plane-wave basis-set, ground state DFT (DACAPO)

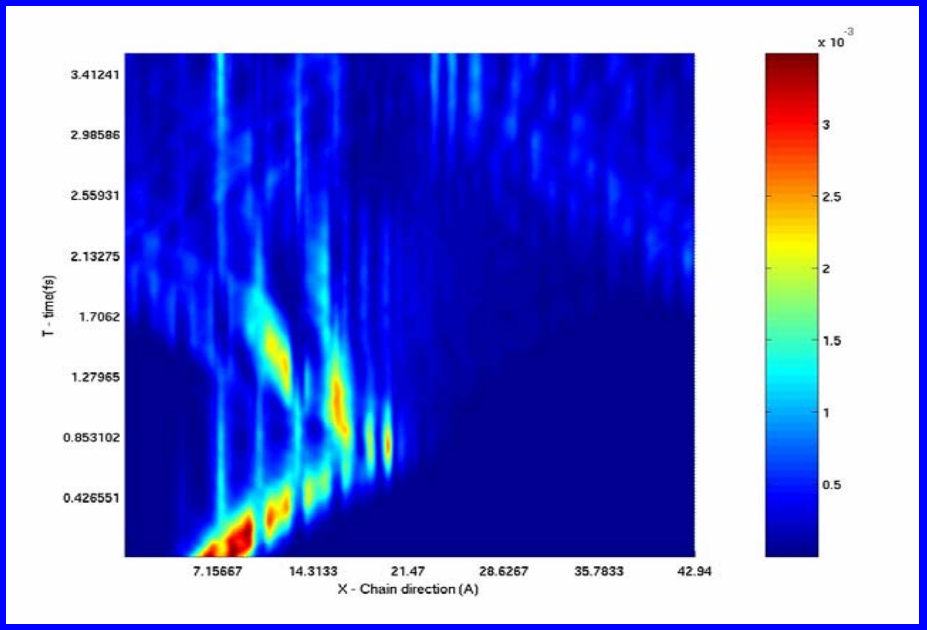
X. Qian, J. Li, X. Lin, S. Yip, "*Time-dependent density functional theory with ultrasoft pseudopotentials*", Phys. Rev. B 73 (2006).

# Zero-bias conductance of 1D chain Au-S-(C6H4)-S-Au by Fermi electron transmission



Position along chain direction (Å)

Time (fs)




Transmission (this work) = 0.05-0.07

NEGF at V=0 ~ 0.05 Xue et al., PRB (2003)

complex band structure ~ 0.10 Tomfohr et al., PRB (2002)

# Soliton theory of charge localization in conducting polymers: Beyond Su-Schrieffer-Heeger

W. P. Su, J. R. Schrieffer, A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

Conventional solition theory does not describe mechanical actuation --
In domain walls, longer bond become shorter; shorter bonds become longer, while overall chain length unchanged, without strain there will be no actuation.

Inclusion of 2nd and 3rd neighbor e-p interactions leads to bending and twisting distortions of *trans*- and *cis-polyacetylene* as a result of a generic coupling between the self-localized solitons and the polymer chain conformations.

X. Lin, J. Li, S. Yip, "Controlling Bending and Twisting of Conjugated Polymers via Solitons", Phys. Rev. Lett. **95,** 198303 (2005).

Oxygen Transport in Refractory Ceramics, T > 2000°C –

Microstructural evolution in the presence of multi-phase reactions and mass transport

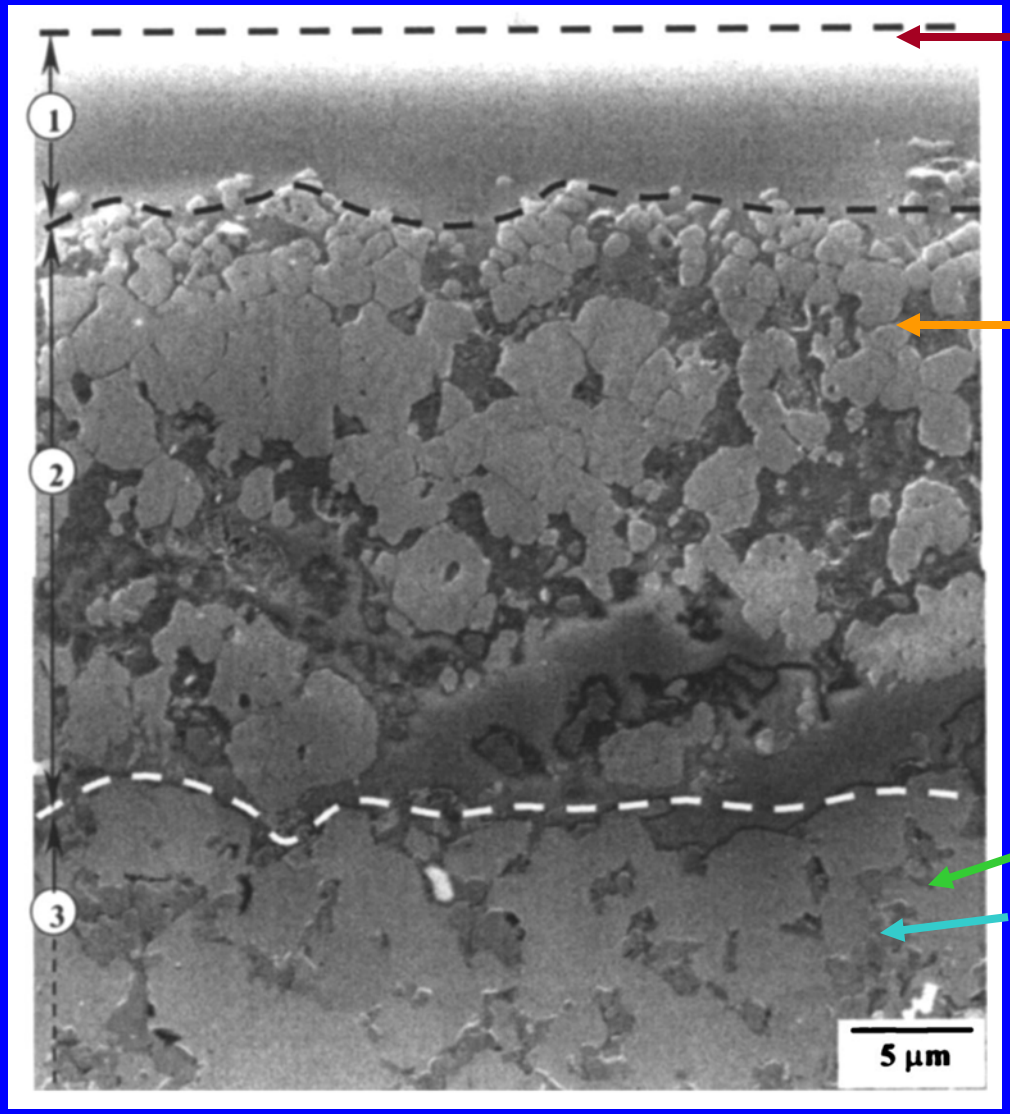
complex morphology and kinetics in protective oxide layer

*diffusion pathway (NEB) in glassy media*

*molecular vs. atomic oxygen*

A. Bongiorno et al. "*A Perspective on Modeling Materials in Extreme Environments: Oxidation of Ultrahigh-Temperature Ceramics*", MRS Bulletin **31**, 410 (2006).

$ZrB_2$ ($HfB_2$) – SiC composite UHTC exhibit relatively good oxidation resistance above 1600°C




Borosilicate glass layer

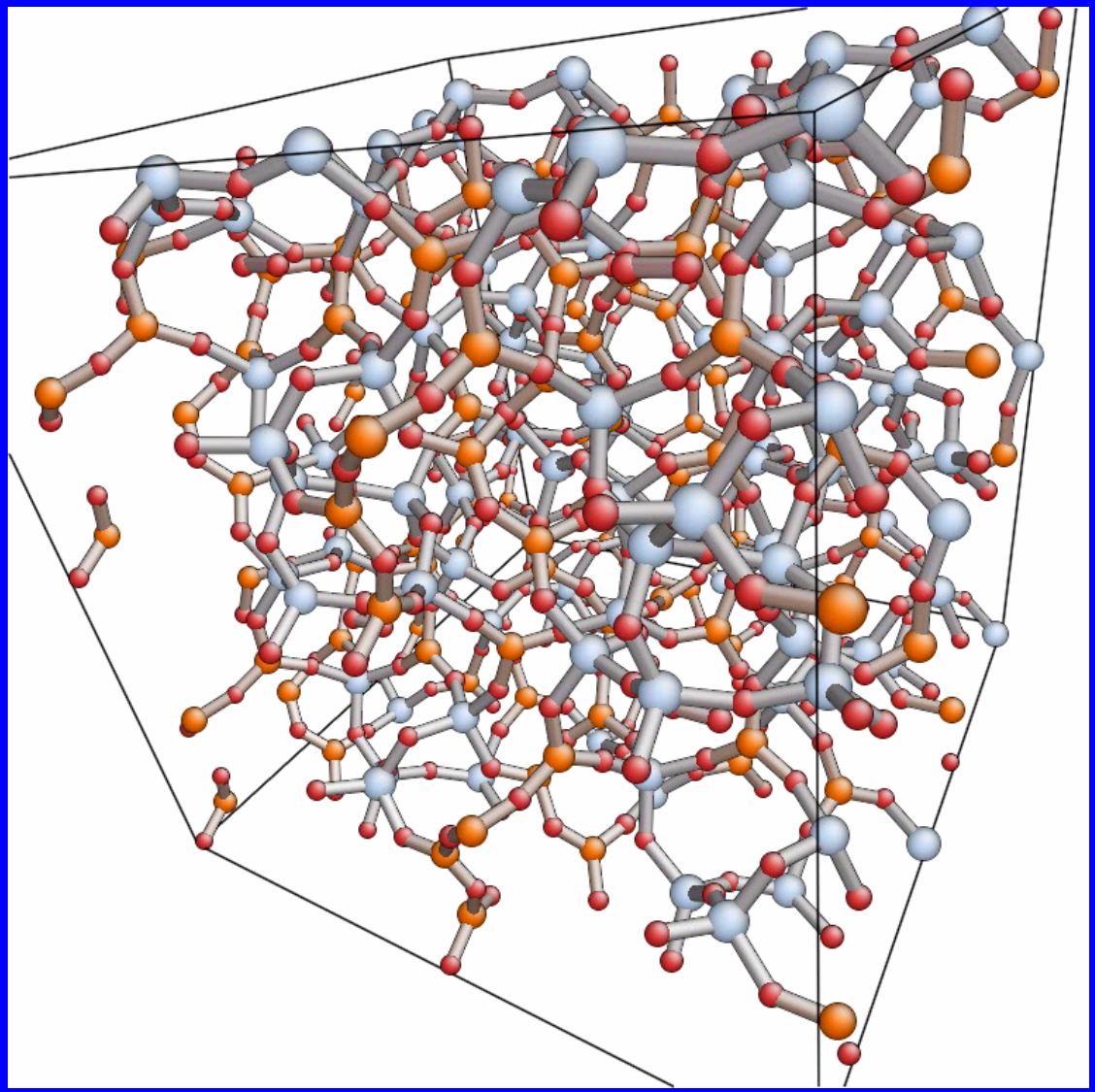
$ZrO_2$

unreacted $ZrB_2$

SiC

Monteverde and Bellosi,
J. Electrochem. Soc. **150** (2003) B552.

# ab initio MD simulation at 2500°C for 11 picoseconds



DFT
supercell
2×2×2
replicated

oxygen: red
boron: orange
silicon: silver

# O or $O_2$ ?

Incorporation energy $O_2$(gas) -> $O_2$(dissolved): 0.73eV  (no entropy effects)

Incorporation energy ½ $O_2$(g) -> O (dissolved): 1.78eV

However:

- O has an entropic advantage over $O_2$
- mobility of O is expected to be higher than that of $O_2$

We expect a competition between O and $O_2$ at high temperatures

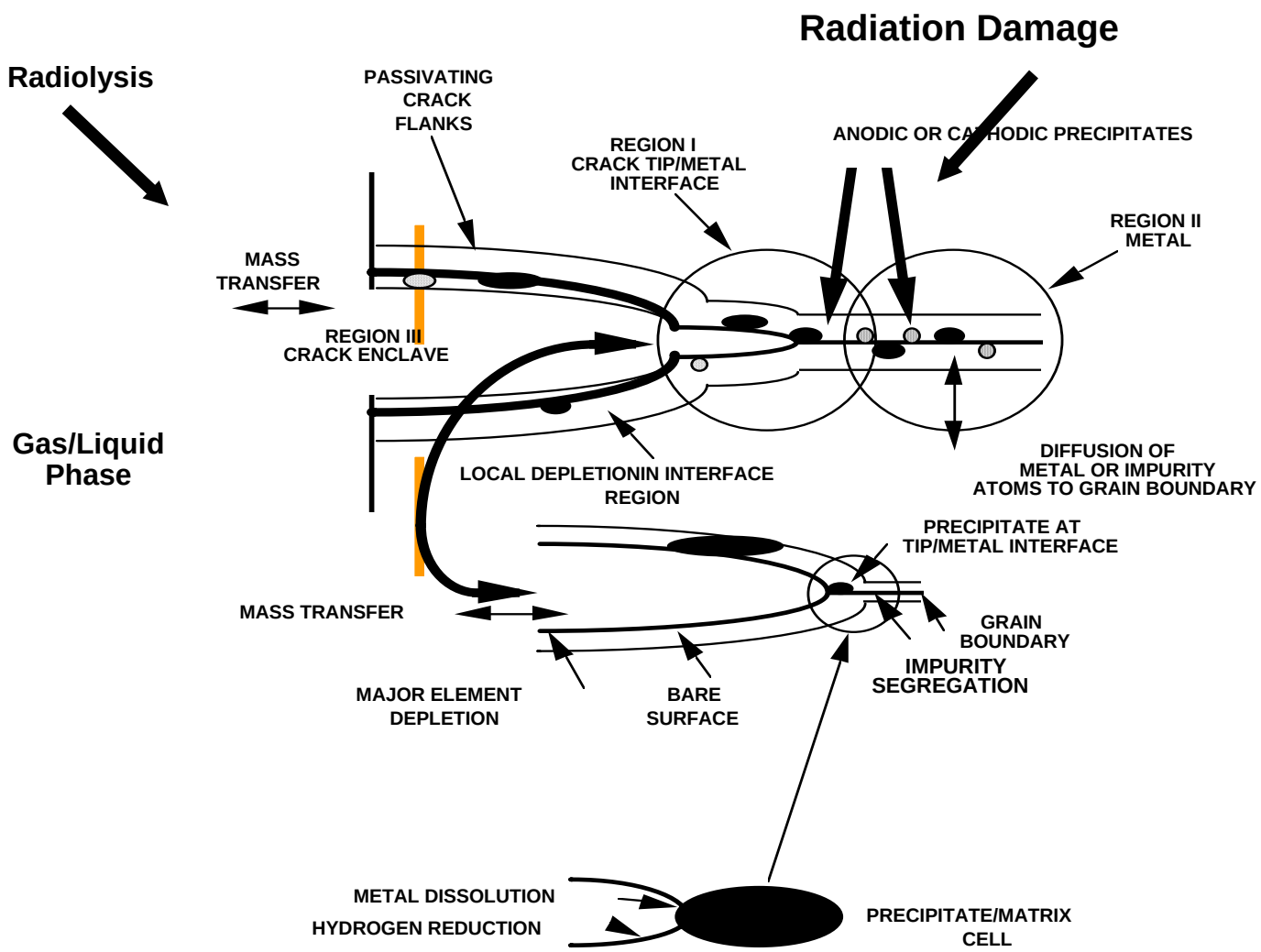
Future Prospects …

problems with increasingly complex microstructure

*Hydrolytic Weakening of Quartz*

*Molecular Model of Cement (CSH)*

*Stress Corrosion Cracking*




## Nano-Scale

- Radiation Damage
- Dislocation Mechanics
- Charge Transfer
- Double Layer Interactions
- Surface Effects

## Micro-Scale

- Microstructural Evolution
- Radiation Effects
  - RIS, Hardening, Swelling
  - He/H Embrittlement
- Electrochemistry
- Radiolysis
- Film Formation

## Macro-Scale

- Macro-stresses
- Crack Initiation
- Crack Propagation
- Fluid Mechanics
- Heat Transfer

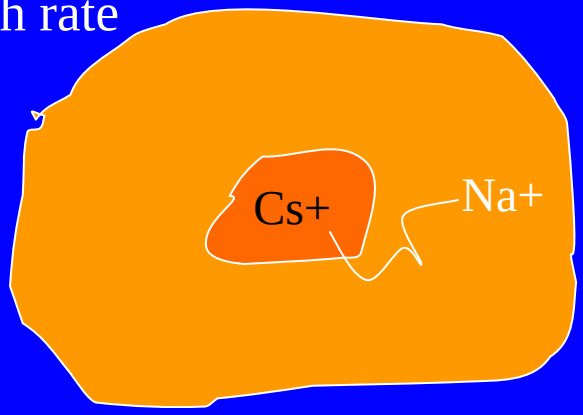
A Grand Challenge problem in nuclear waste migration –

Atomistic simulation of radionuclide transport in nuclear wasteform

Mapping out the migration pathway of radioactive ions, such as $Cs^{+}$ in zeolite, in cation exchange with Na+ in the surrounding ground water

State-of-the-art reaction pathway sampling using first principles (quantum mechanical) and classical molecular dynamics and kinetic Monte Carlo techniques to determine the saddle-point configuration and corresponding activation barrier

Develop a robust transition-state theory to predict leech rate from chemo-mechanical structures



Collaborators

Clemens Foerst, McKinley Associates
Jinpeng Chang, Deutches Bank
Ju Li, Ohio State University
Xi Lin, MIT
Shigenobu Ogata, Osaka University
Xiao-Feng Qian, MIT
Subra Suresh, MIT
Krystyn Van Vliet, MIT
Ting Zhu, Georgia Tech