The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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2145-36

Spring College on Computational Nanoscience

17 - 28 May 2010

**Mechanical Properties at the Nanoscale
(Making and Breaking of Atomic Bonds: Fracture and Tribocontacts)**

Peter GUMBSCH

*Fraunhofer-Inst. fuer Werkstoffmechanik
Freiburg
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Making and Breaking of Atomic Bonds:

Fracture and Tribocontacts

Peter Gumbsch

Michael Moseler, Lars Pastewka

Application-oriented research with industry

-- research in direct interaction with partners in industry
-- often has direct relevance to products,
which may already be on the market
-- gives direct value to your work
this is very rewarding!

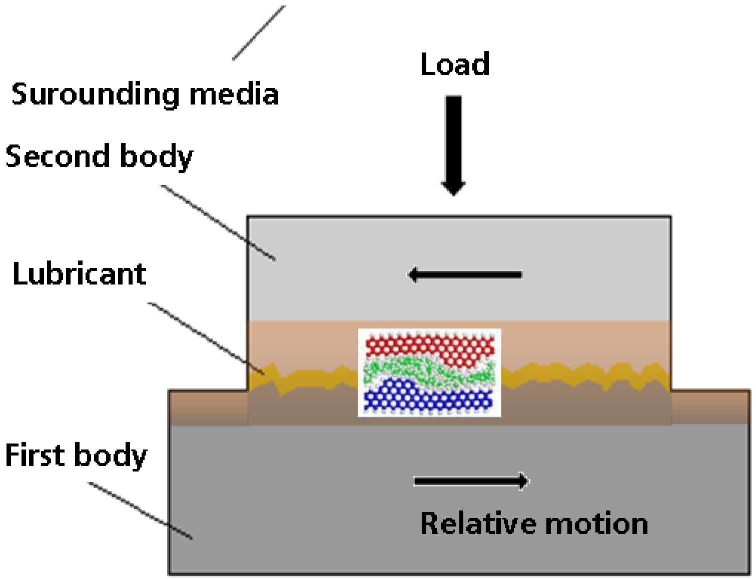
-- industry never pays for all the basic research needed to solve the problem
-- unfortunately, teir problems are not well posed for scientific investigation

-- industry oriented research is a very valuable source of scientific questions
-- Fraunhofer funding
industry : public grants : base funding – 40:30:30

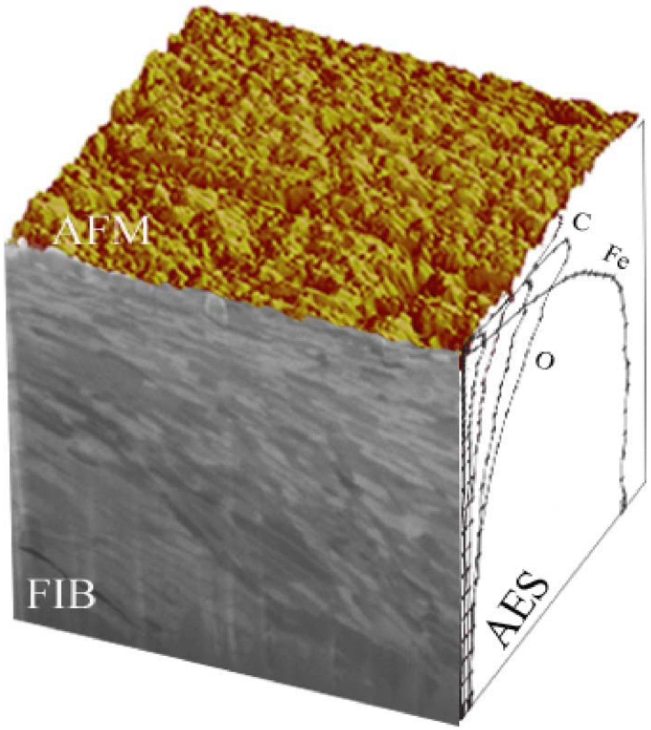
Making and Breaking of Chemical Bonds, Tribology

greek τριβω: I rub

-- the science and technology of interacting surfaces in relative motion
-- the science and technology of friction, lubrication, and wear



wear rates ~nm/h
M. Scherge, et al., Wear 260(2006)458

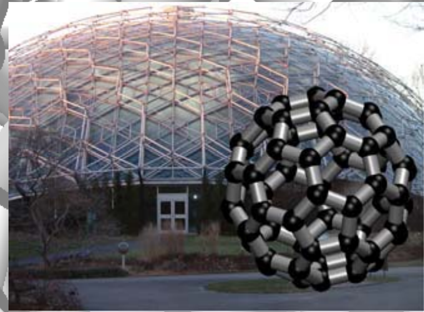


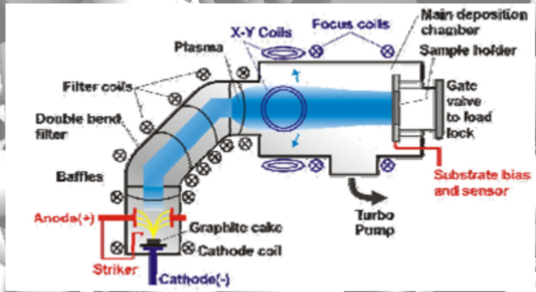
How can physics based modelling and simulation possibly contribute to the understanding of such complicated processes?

Carbon: building block for nanostructures

Diamond-like carbon (DLC)

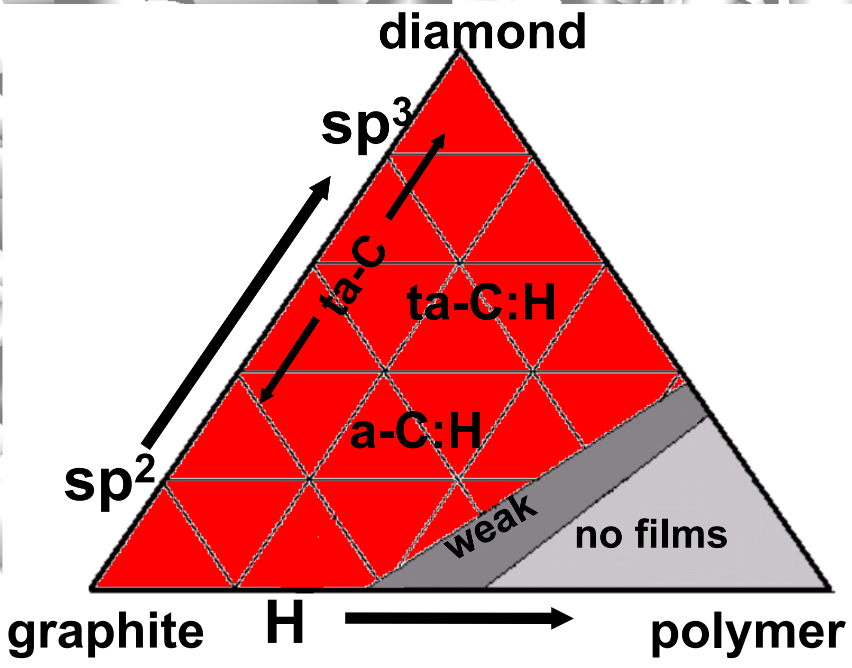
A dense, partially sp^3 bound, metastable phase of non-crystalline carbon (with or without H contents)





Superior properties of DLC coatings

- very low friction
- very smooth
- very hard
- chemically inert

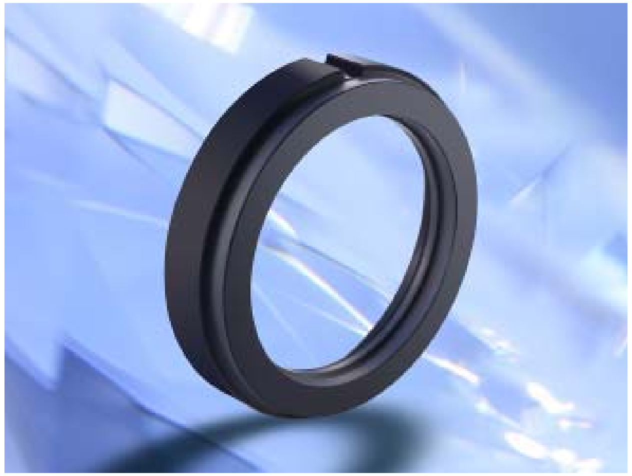


Diamond coated ceramic sliding ring seal

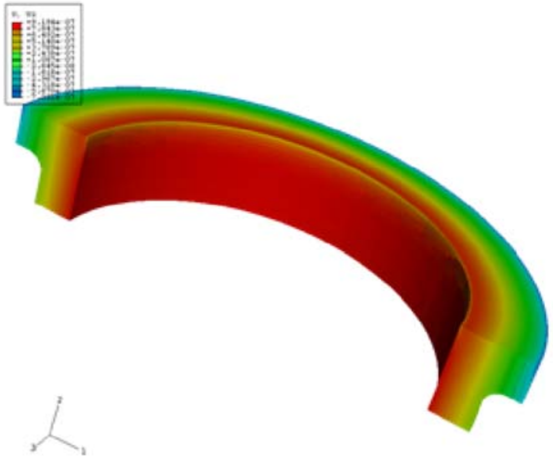
After a Fraunhofer-Project and the BMBF-Projekt DiaCer, EagleBurgmann developed their DiamondFaces® technology to protect mechanical seals for pumps from wear.

2007 EagleBurgmann introduced DiamondFaces® (www.diamondfaces.com)

2008 DiamondFaces® wins the Product Innovation Award 2008 (Frost & Sullivan) and the InnovationAward 2008 (FlowControl)



DiamondFaces® mechanical seal from EagleBurgmann



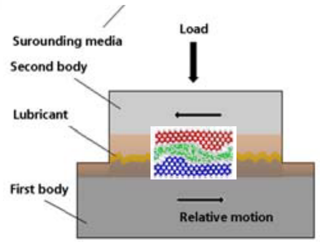
EagleBurgmann.

The New Dimension in Mechanical Seal Technology

DiamondFaces®

Making and Breaking of Atomic Bonds in Carbon Tribocontacts

- **Fracture**: brittle cleavage fracture, anisotropy, embedding
- **Fracture**: dynamic fracture, LOTF
- **Fracture**: bond breaking in simple models
- **Tribology**: topography of DLC
- **Tribology**: running-in of DLC (in progress)
- **Tribology**: polishing of diamond, wear



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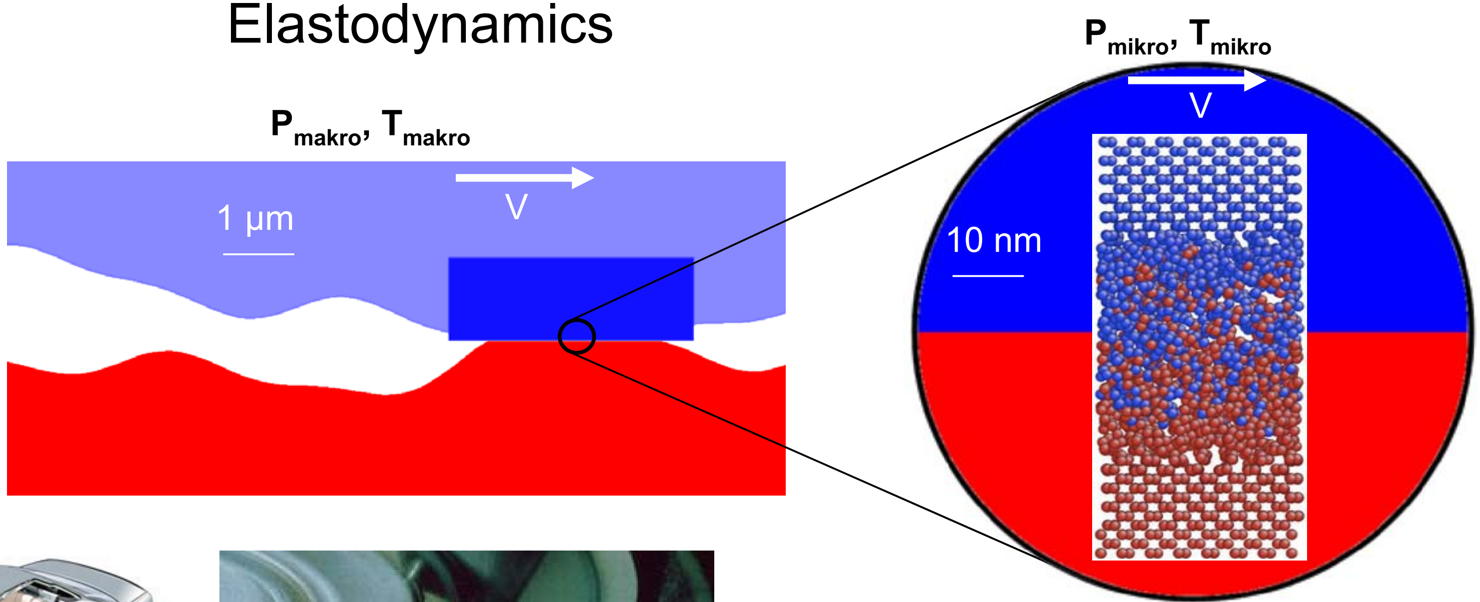
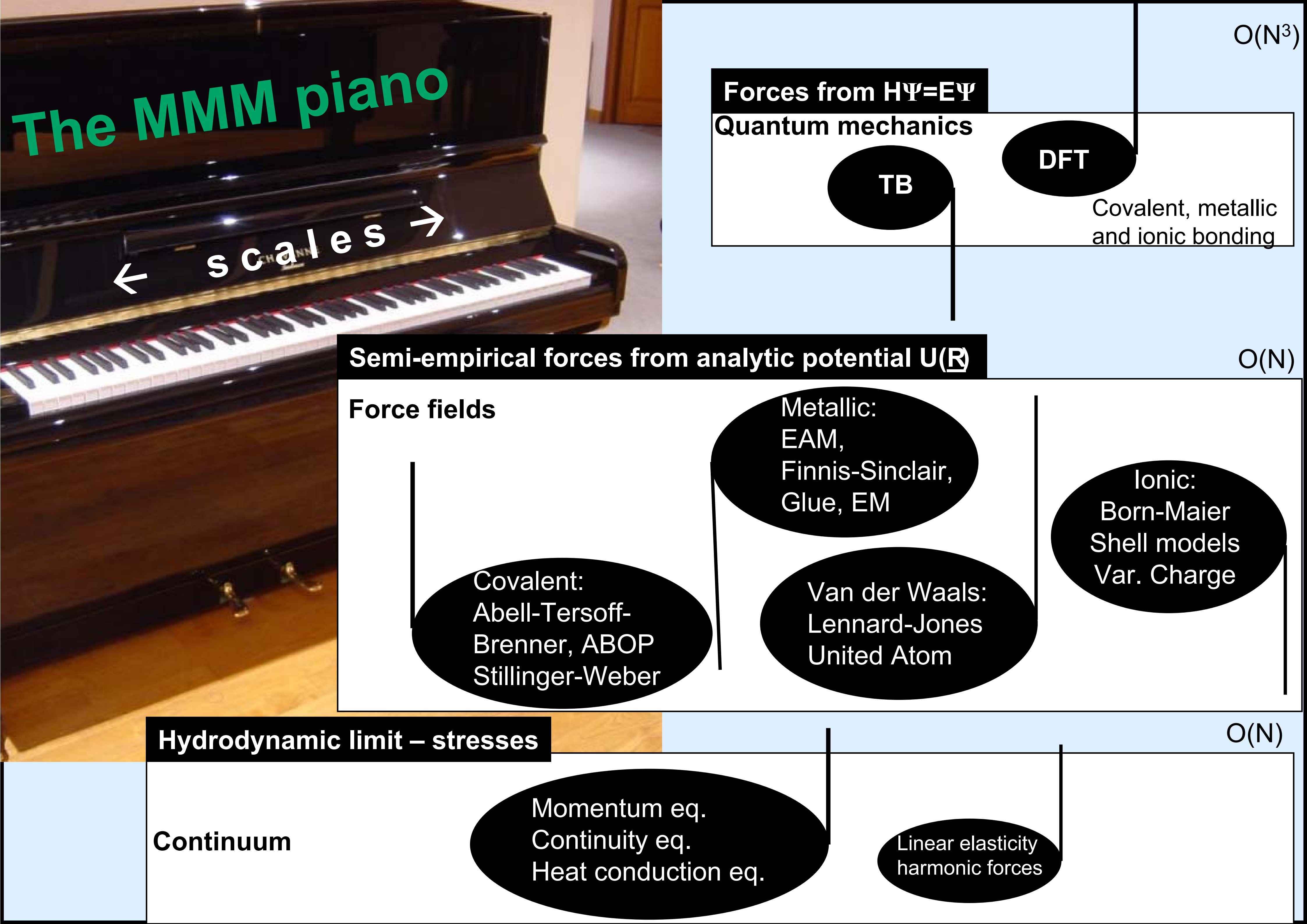
Taking into account the multiple length scales

Molecular Dynamics

Elastodynamics



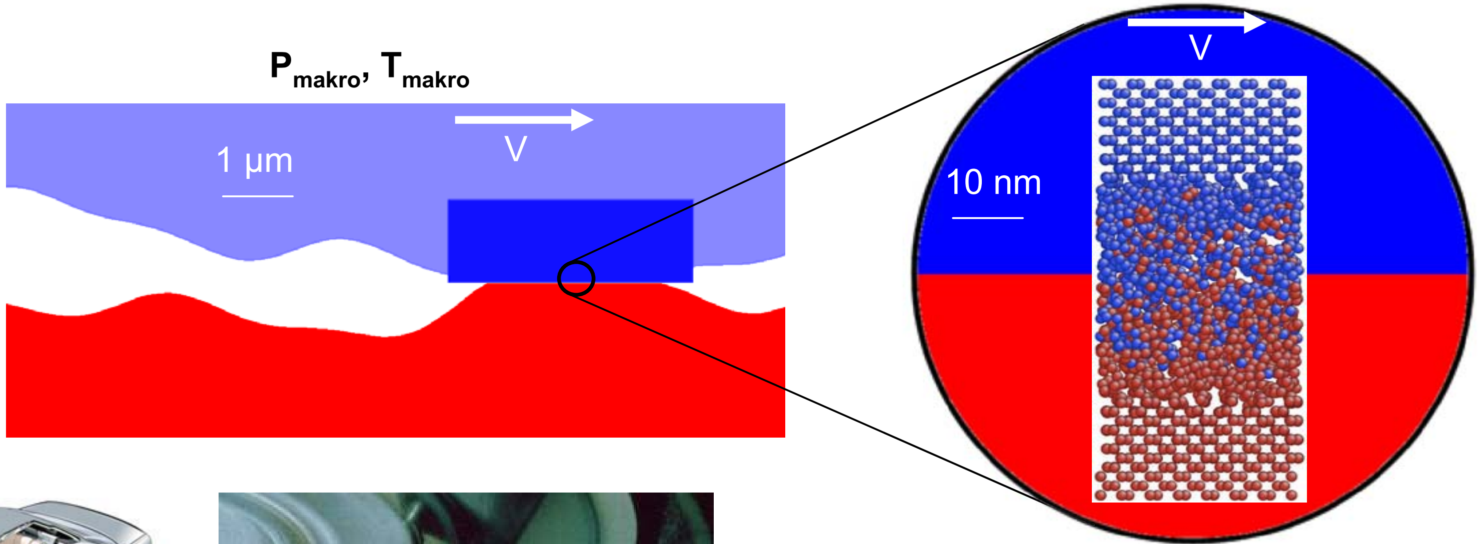
representative volume


The MMM piano
← scales →
O(N^3)
Forces from HΨ=EΨ
Quantum mechanics
TB
DFT
Covalent, metallic and ionic bonding
Semi-empirical forces from analytic potential U(R)
O(N)
Force fields
Metallic: EAM, Finnis-Sinclair, Glue, EM
Covalent: Abell-Tersoff-Brenner, ABOP Stillinger-Weber
Van der Waals: Lennard-Jones United Atom
Ionic: Born-Maier Shell models Var. Charge
Hydrodynamic limit – stresses
O(N)
Continuum
Momentum eq.
Continuity eq.
Heat conduction eq.
Linear elasticity harmonic forces

Taking into account the multiple length scales

Molecular Dynamics

Elastodynamics



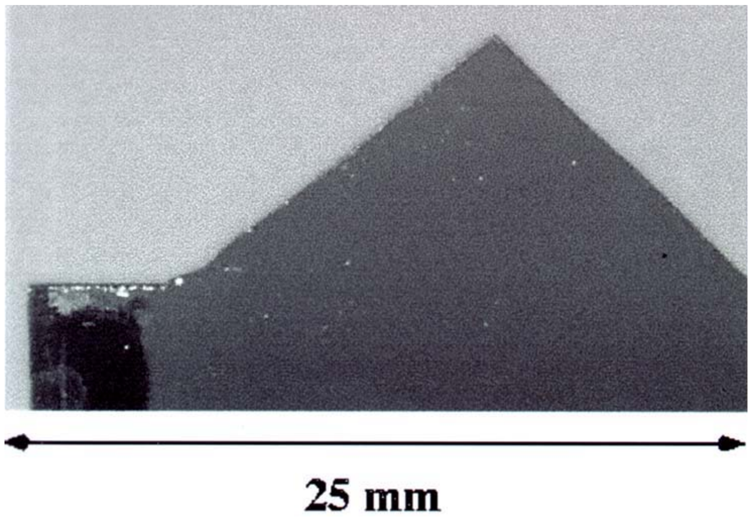
representative volume

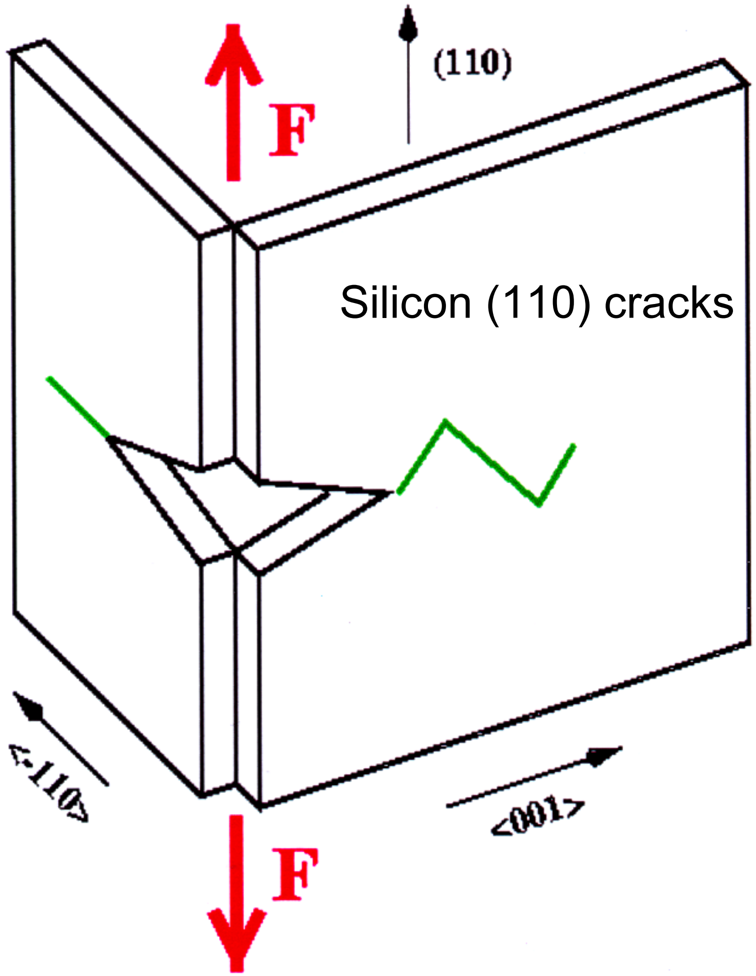
requires reliable model
for the atomic interaction

Cleavage of Silicon and Diamond

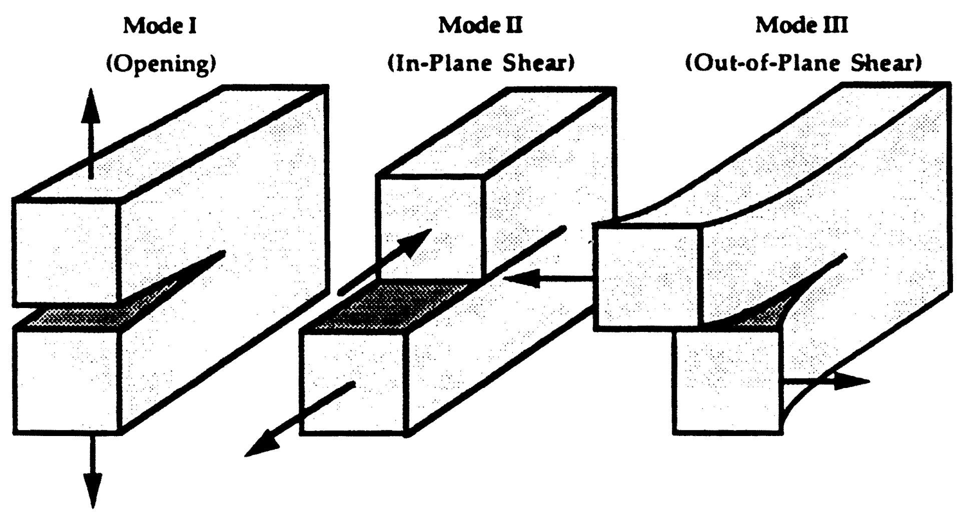
What are the cleavage planes of a crystal?
smallest barrier vs lowest surface energy

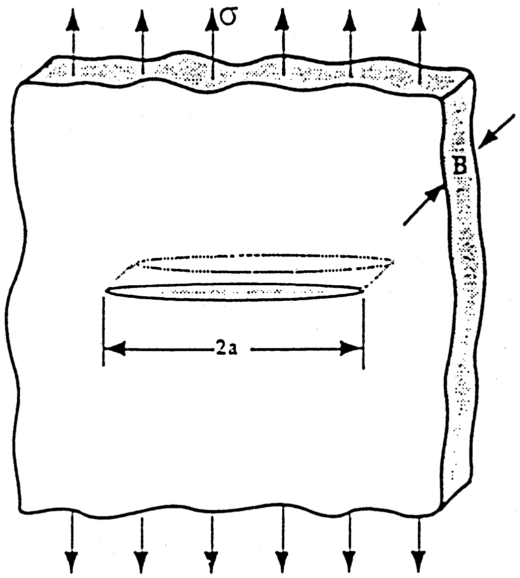
Why are there preferred propagation directions?
what are they…

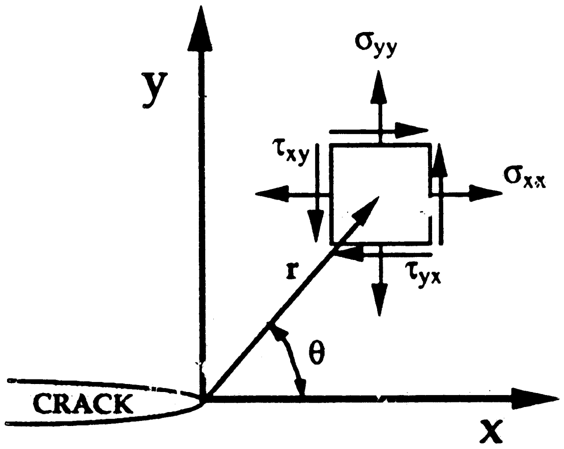




linear elastic fracture mechanics







$$\lim_{r \to 0} \sigma_{ij}^{(I)} = \frac{K_I}{\sqrt{2\pi r}} f_{ij}^{(I)}(\theta)$$

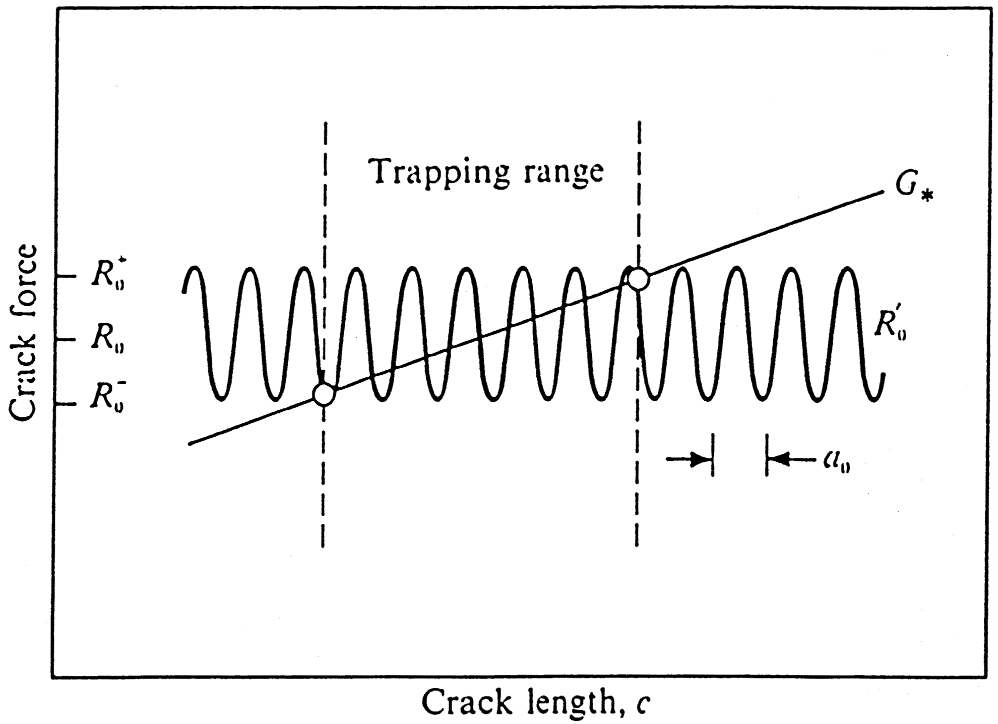
$$U_S = 4a\gamma$$

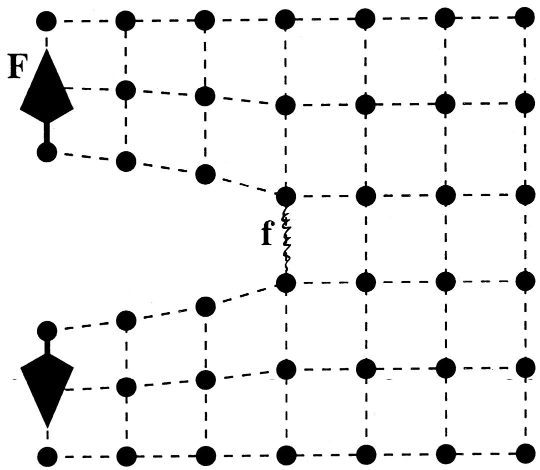
$$U_M = \frac{\pi a^2 \sigma^2}{E}$$

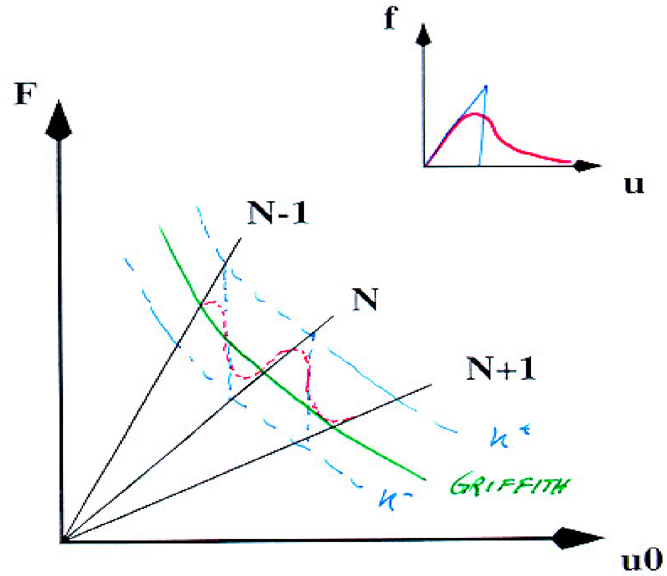
lattice trapping - bond trapping

Driving force on a crack $$G = \frac{dU_M}{da}\left(\propto K^2\right)\propto a$$

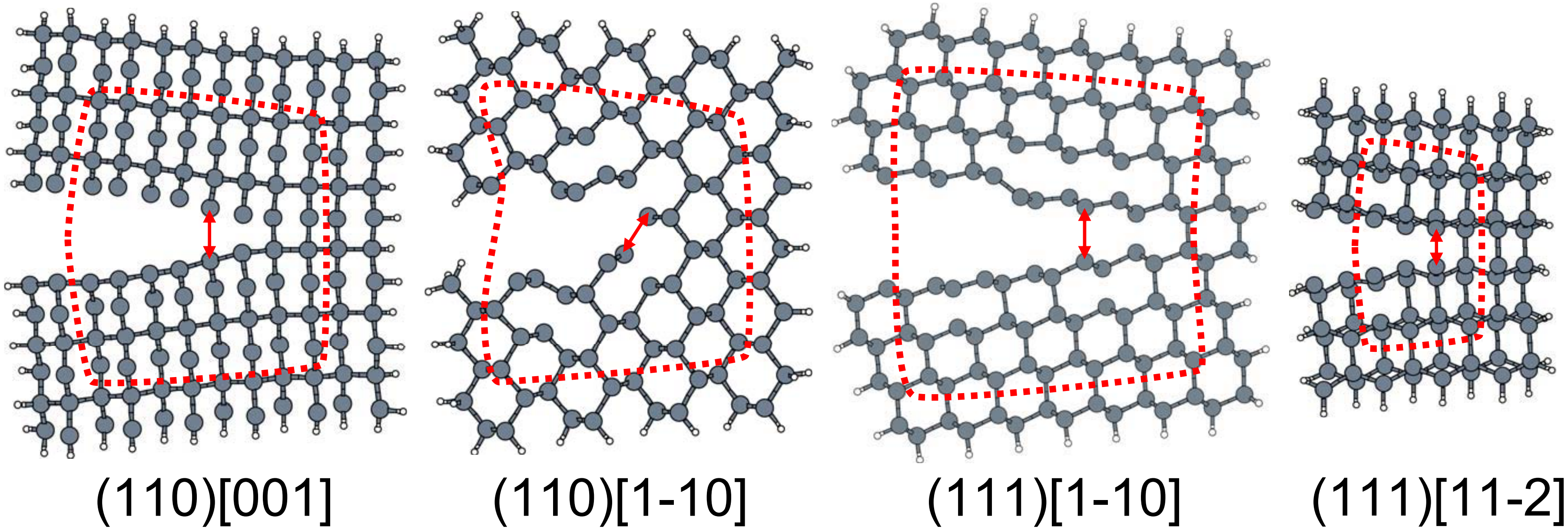
Crack growth resistance of a material (Griffith, 1920) $$R = \frac{dU_S}{da} = 2\gamma$$





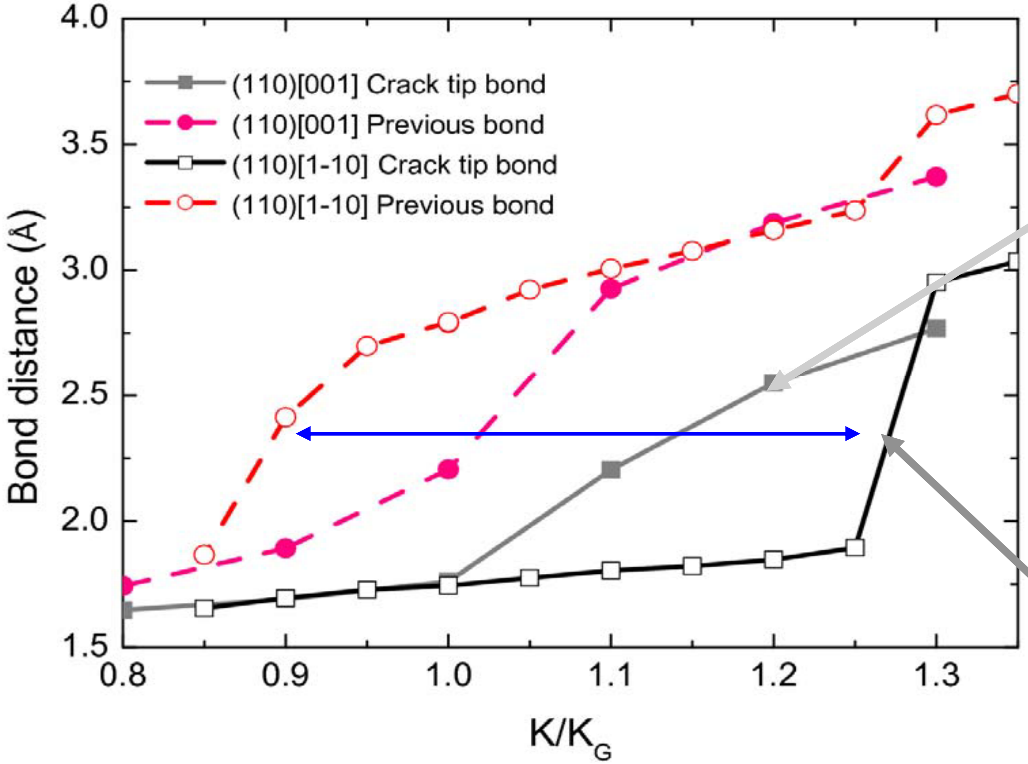


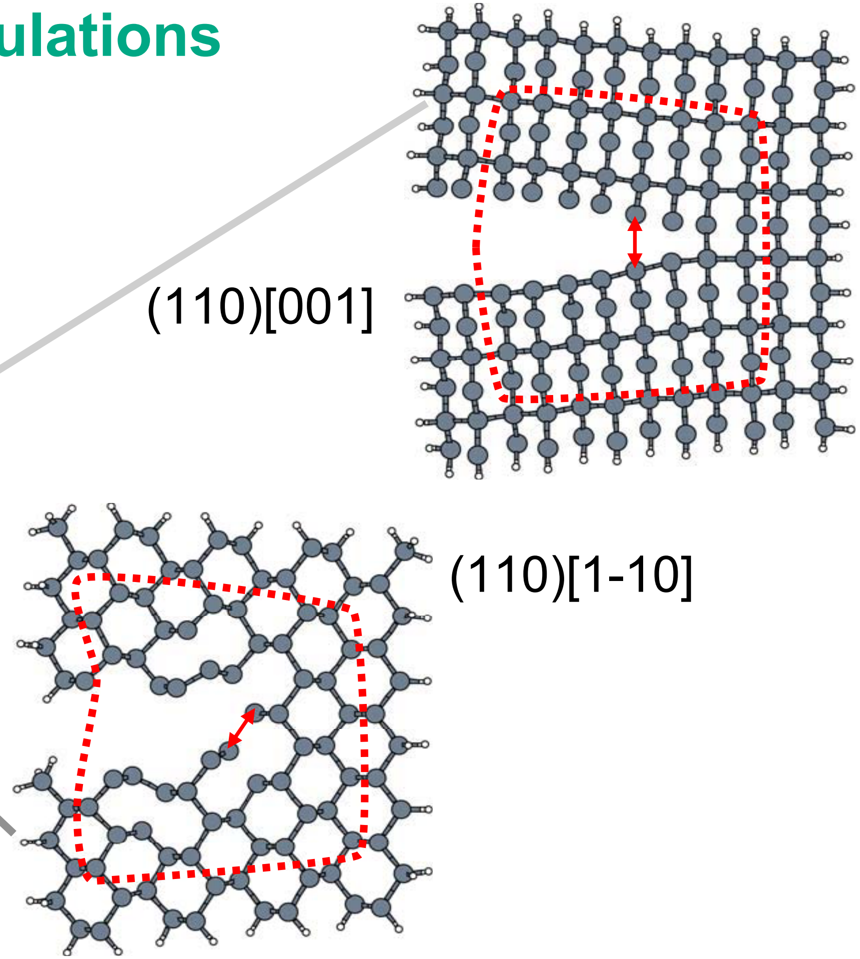
Bond breaking barriers – crack tip simulations in diamond



- Outer atoms fixed at positions given by anisotropic linear elasticity
- Inner atoms relaxed with DFT

Bond breaking barriers – crack tip simulations





Silicon: R. Pérez, P. Gumbsch, PRL 84 (2000) 5347,
R. Pérez, P. Gumbsch, Acta mater. 48 (2000) 4517

Diamond: L. Pastewka, P. Pou, R. Pérez, P. Gumbsch, M. Moseler, PRB 78 (2008) 161402, 1-4

(111) plane shows "easy" propagation for both directions

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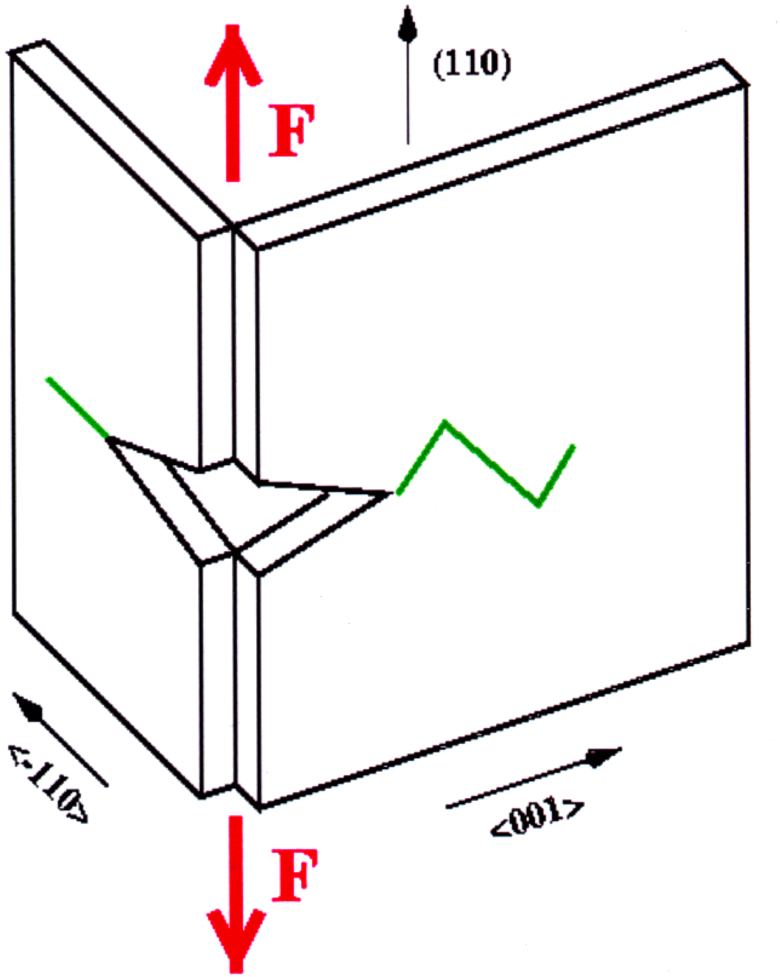
Cleavage of Diamond



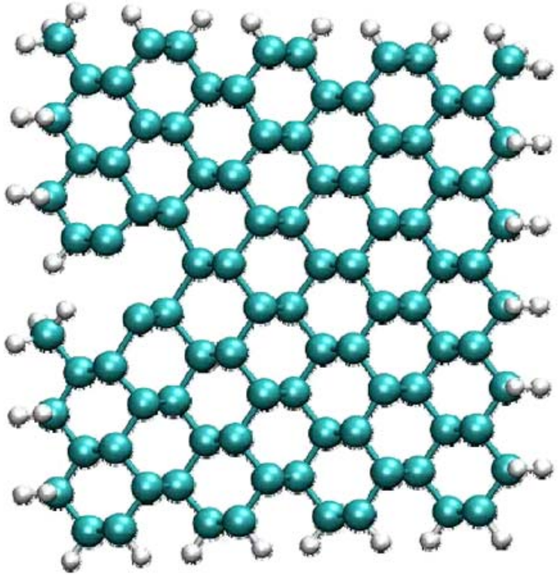
	(110)[001]	(110)[1-10]
Bond breaking	Continuous (mimics continuum mechanics)	Discontinuous (rearrangements of few atoms at crack tip)
Lattice trapping	Small	Large (0.9-1.3)
Variation with system size	Decreased	No change
Propagation	Easy	Difficult

Bond Breaking with a Simple Potential

$$E_b = \sum_i \sum_{j\,(>i)} [V^R(r_{ij}) - b_{ij} V^A(r_{ij})]$$

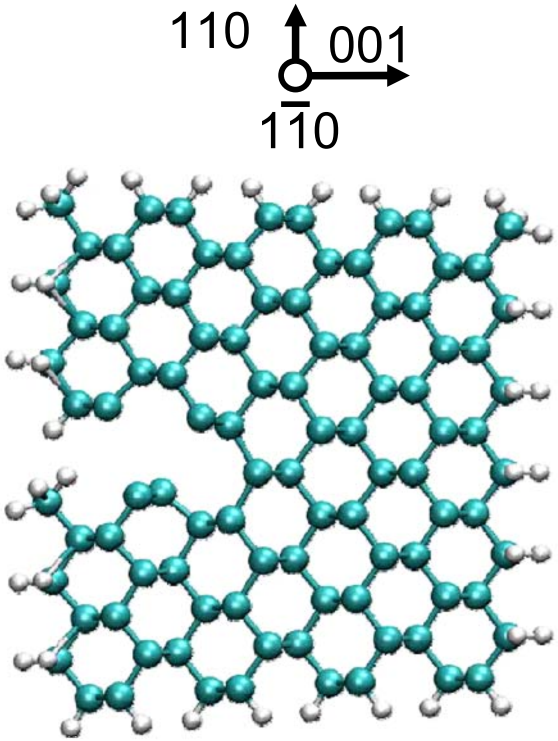
$$V^R(r) = f^c(r)(1 + Q/r) A e^{-\alpha r}$$

$$V^A(r) = f^c(r) \sum_{n=1,3} B_n e^{-\beta_n r}$$



DFT

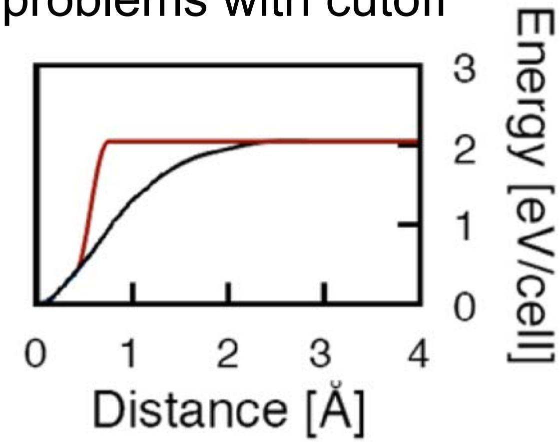
L. Pastewka, P. Pou, R. Pérez, PG, M. Moseler, PRB 78 (2008) 161402



Brenner

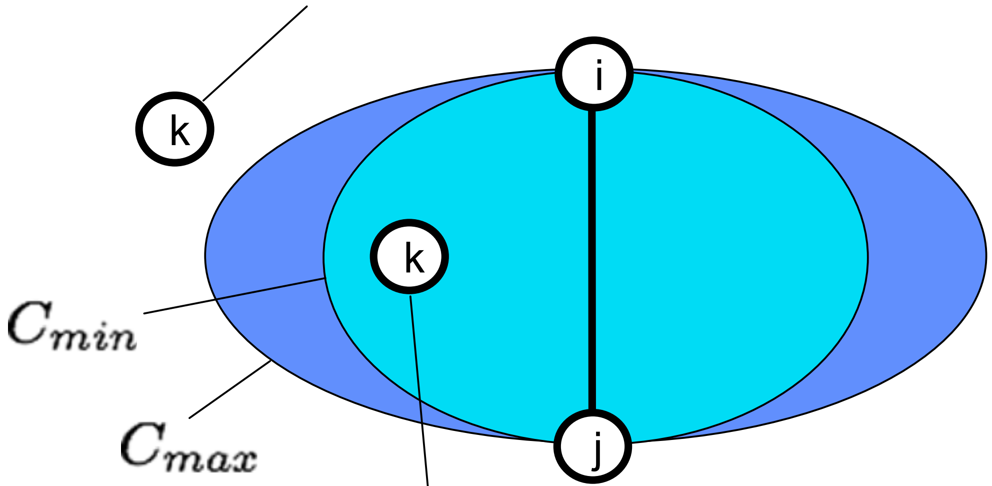
excellent potential, used in hundreds of simulations
J. Phys.: Condens. Matter **14** 783 (2002)

problems with cutoff



Screening: Geometrical formulation

i-j interaction is not screened by k



i-j interaction is completely screened by k

ratio of the two axis of the ellipse

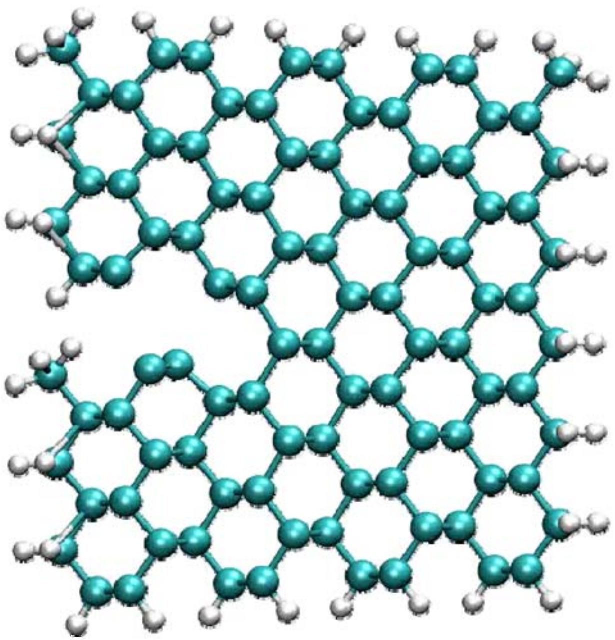
$$C = \frac{2(X_{ik} + X_{jk}) - (X_{ik} - X_{jk})^2 - 1}{1 - (X_{ik} - X_{jk})^2}$$

$$X_{ik} = \left(\frac{r_{ik}}{r_{ij}}\right)^2$$

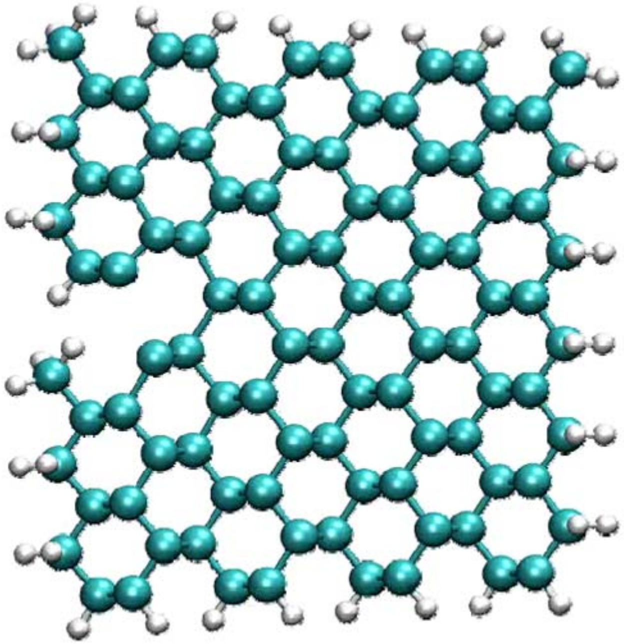
$$f_C^{(ij)} \rightarrow S^{(ij)} f_C^{(ij)}$$

M. I. Baskes, J. E. Angelo and C. L. Bisson, Modelling Simul. Mater. Sci. Eng. 2, 505 (1994)

Back to the crack



Brenner + Screening



DFT

L. Pastewka, P. Pou, R. Pérez, P. Gumbsch, M. Moseler, Phys. Rev. B 78 (2008) 161402

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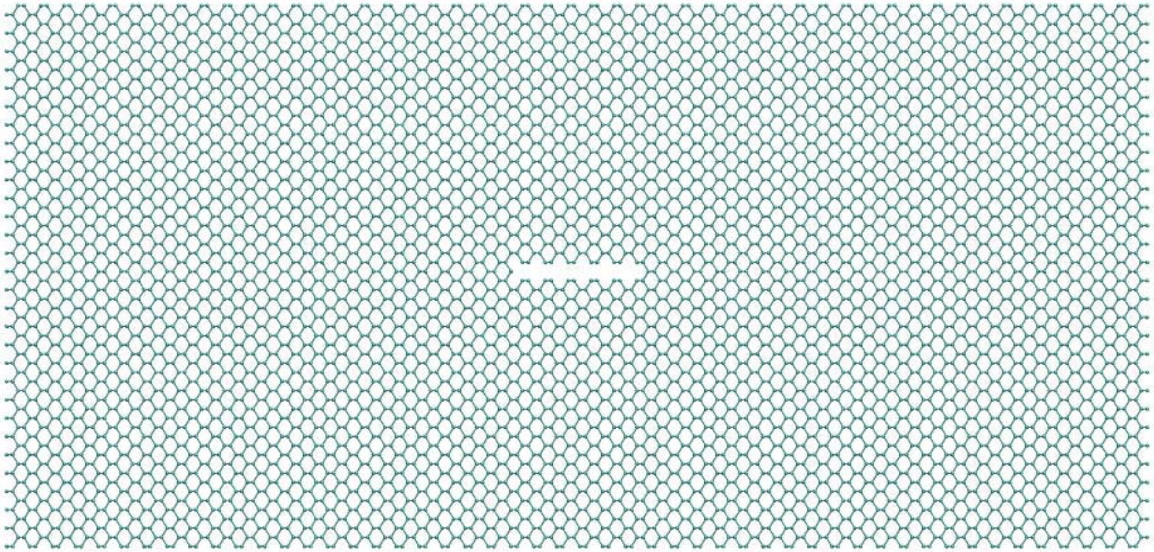
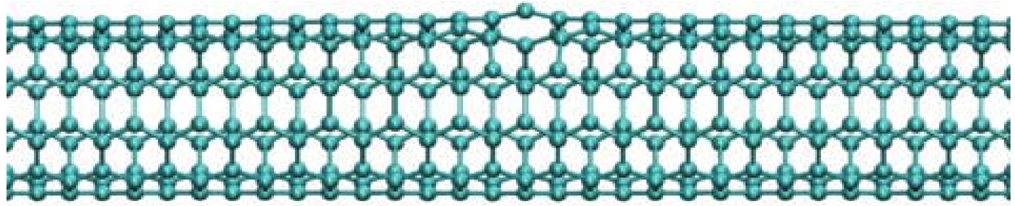
Crack growth: original Brenner

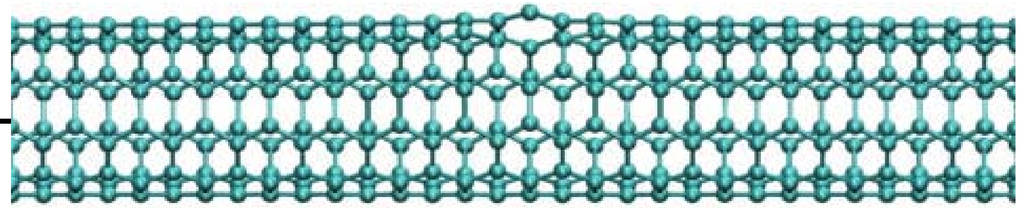


CNT (5,5)

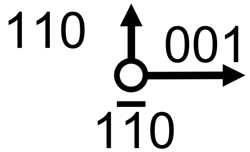
Brenner

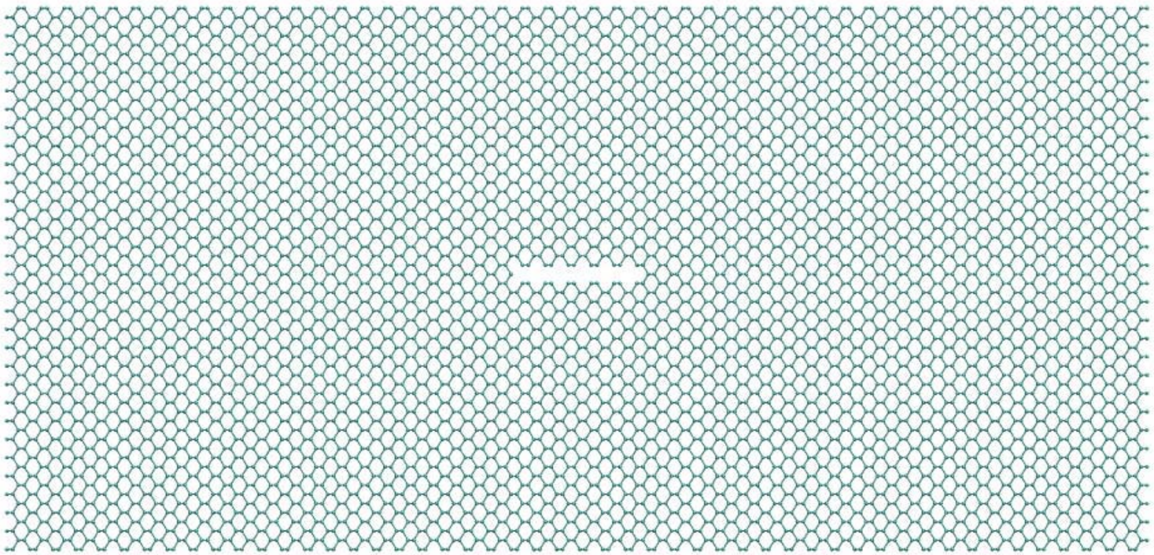


screened Brenner

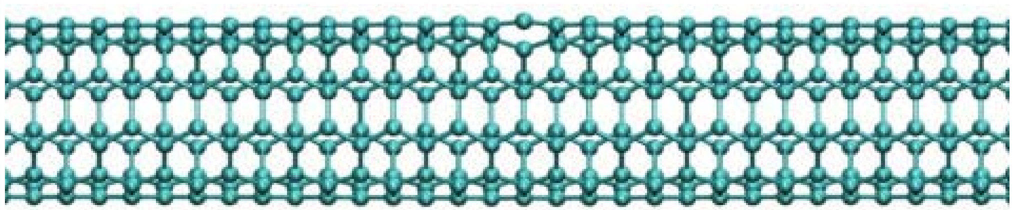


With screening



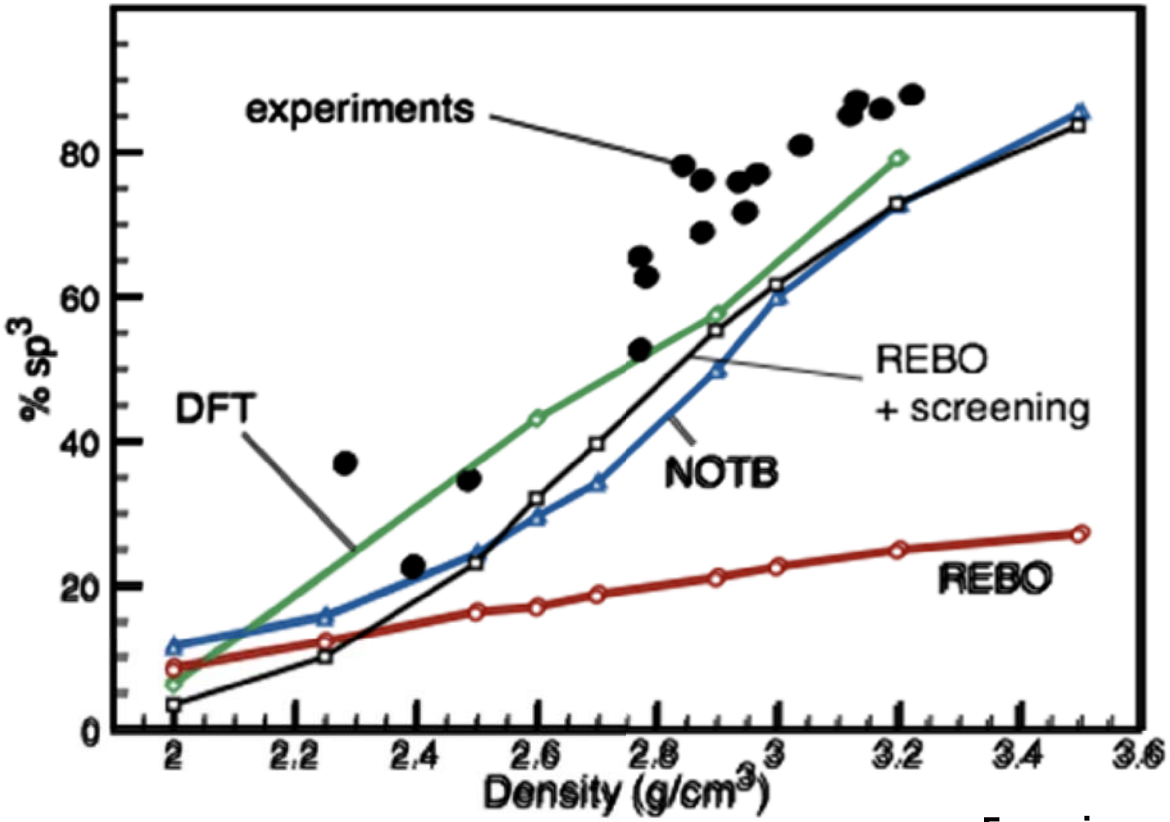


DFTB

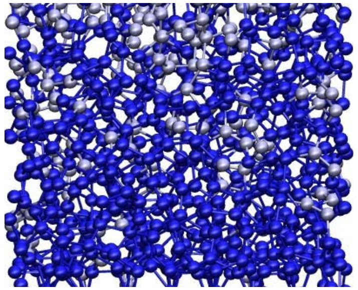


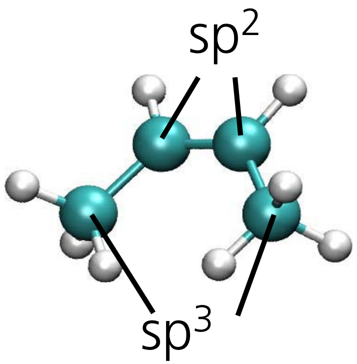
L. Pastewka, P. Pou, R. Pérez, P. Gumbsch, M. Moseler, Phys. Rev. B 78 (2008) 161402

Getting the amorphous phase right
Deficiencies of REBO



Quenching liquid carbon
from 5000K to 300K





Experiments: C. Casiraghi et al., *Phys. Rev. B* **72**, 085401 (2005)
DFT: D. G. McCulloch et al. *Phys. Rev. B* **61**, 2349 (2000)

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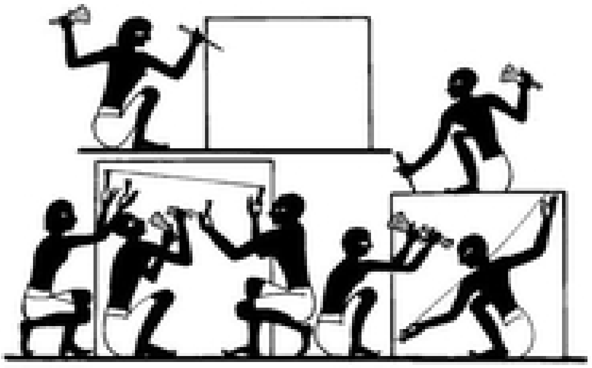
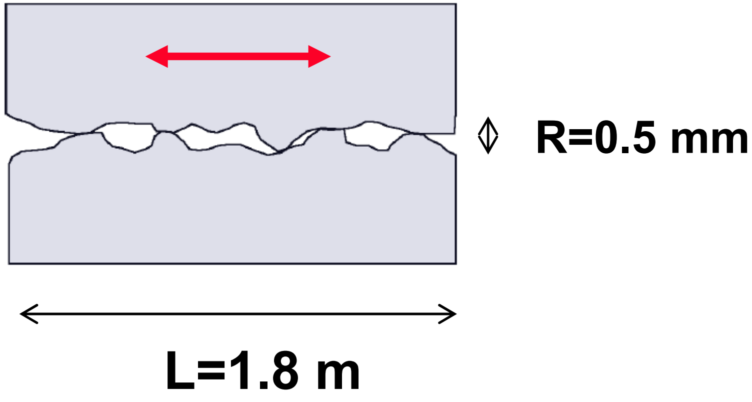
The importance of topography



(B.N.J. Persson, Sliding Friction, Springer 1998)

Design of surface:



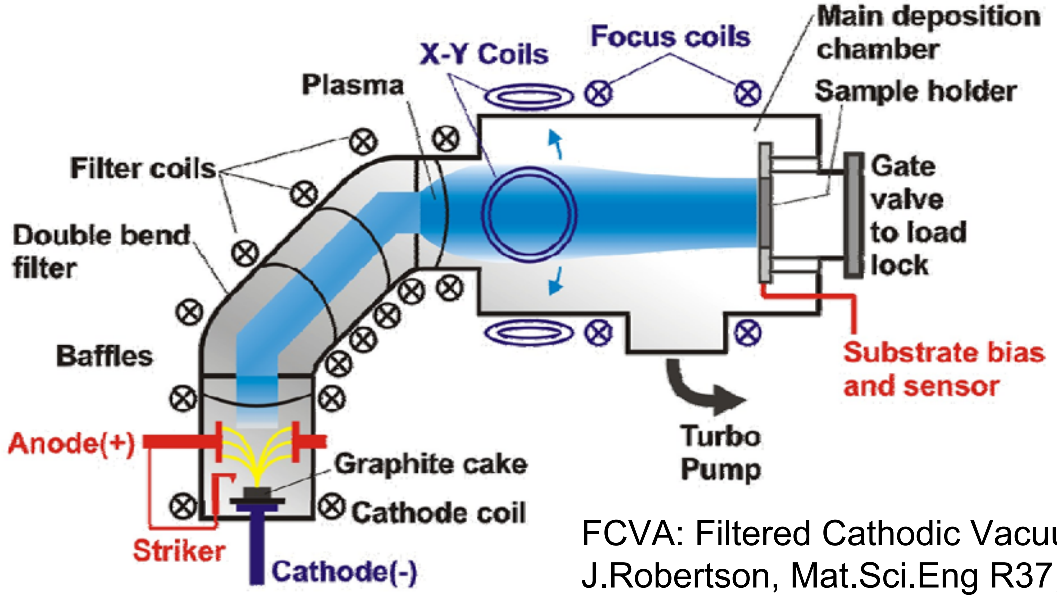
Very smooth: R/L=0.2 ‰

Lubricant : Gypsum mortar

Ultrasmooth: R/L=10^{-5}

Ultrasmooth amourphous carbon coatings

CAMBRIDGE UNIVERSITY
DEPARTMENT OF ENGINEERING

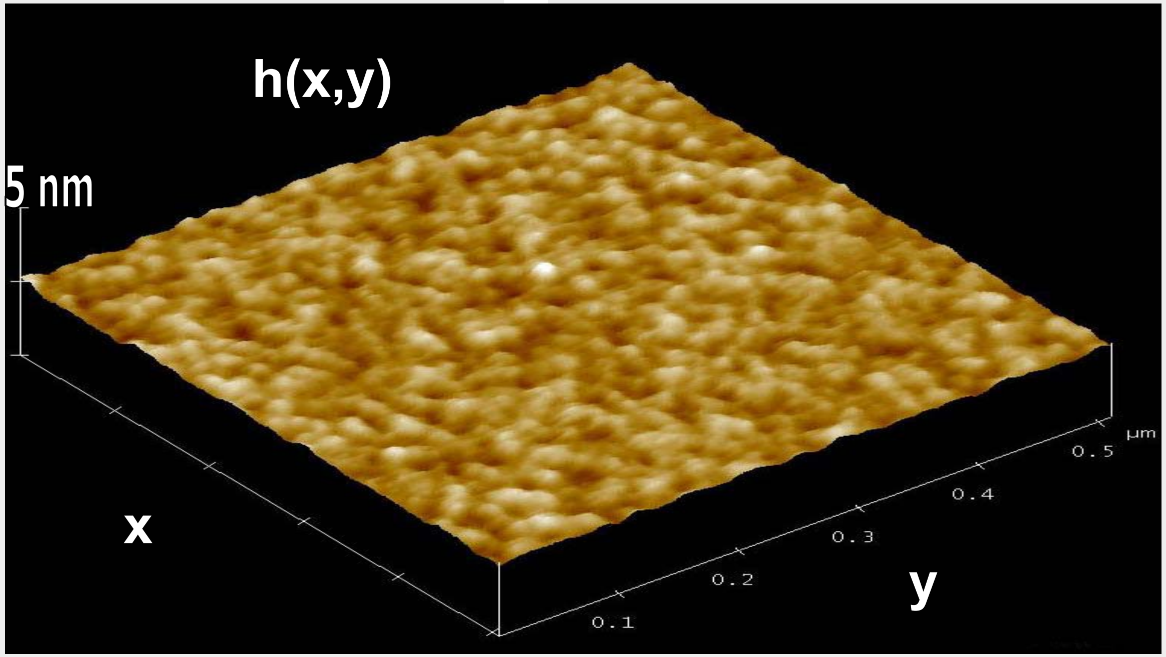


FCVA: Filtered Cathodic Vacuum Arc
J.Robertson, Mat.Sci.Eng R37, 129 (2002)

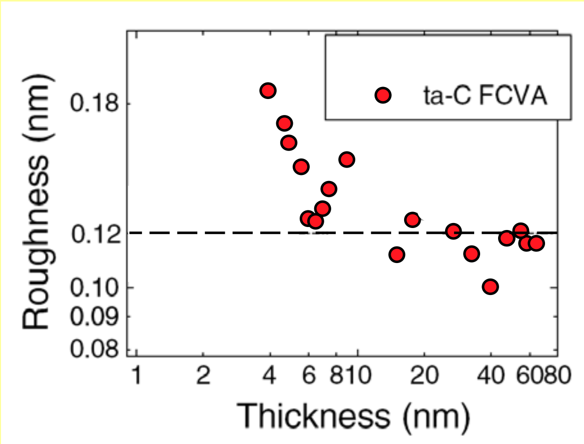
Atomic force microscope

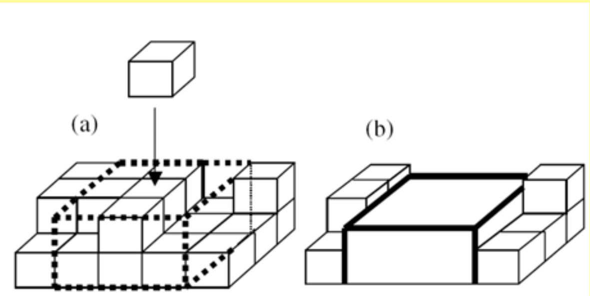
R=0.1nm L=10μm

Ultrasmoothness: R/L=10^{-5}



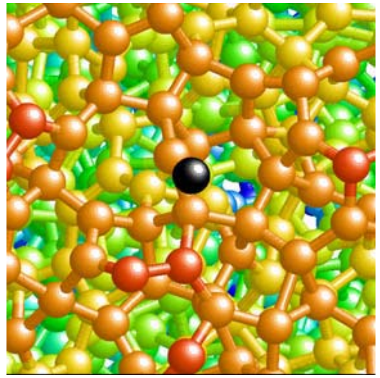
Evolution of the topography

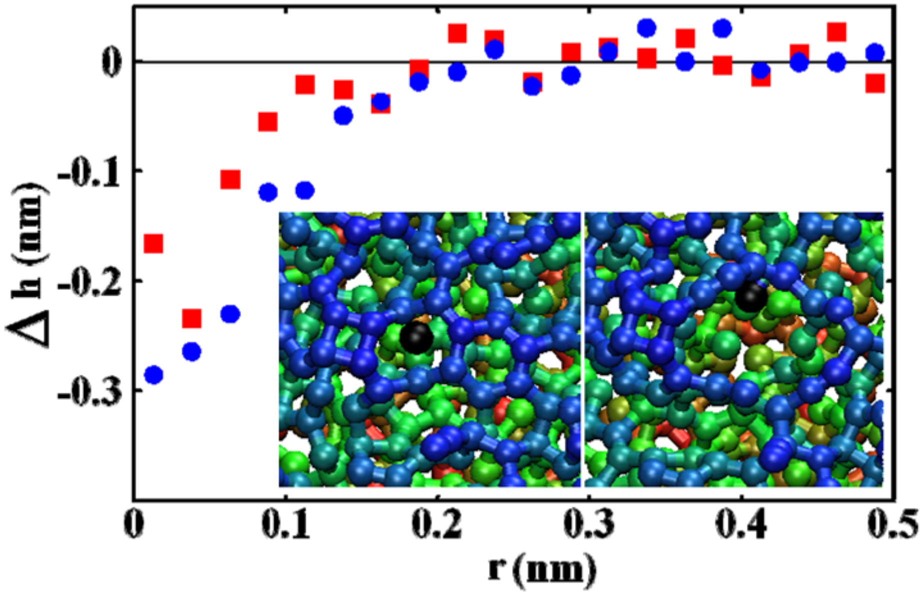




Casiraghi, Ferrari, Ohr, Flewitt, Chu, Robertson, PRL **91**, 226104 (2003)

C impinges on ta-C with 100 eV





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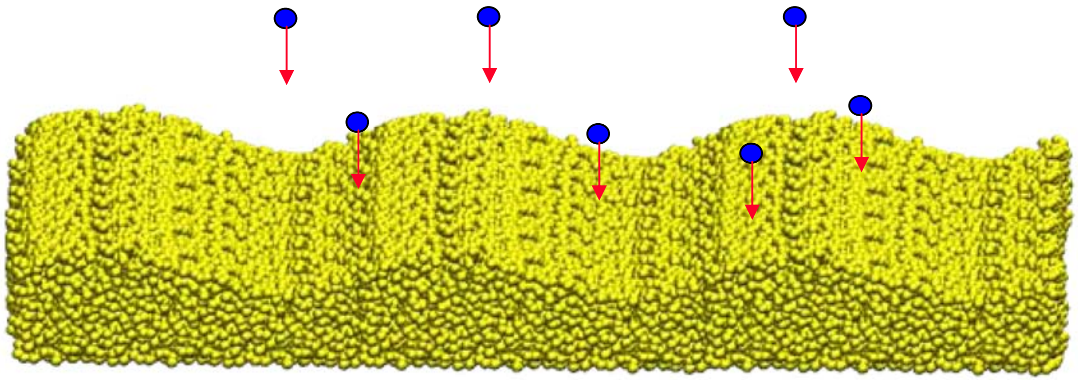
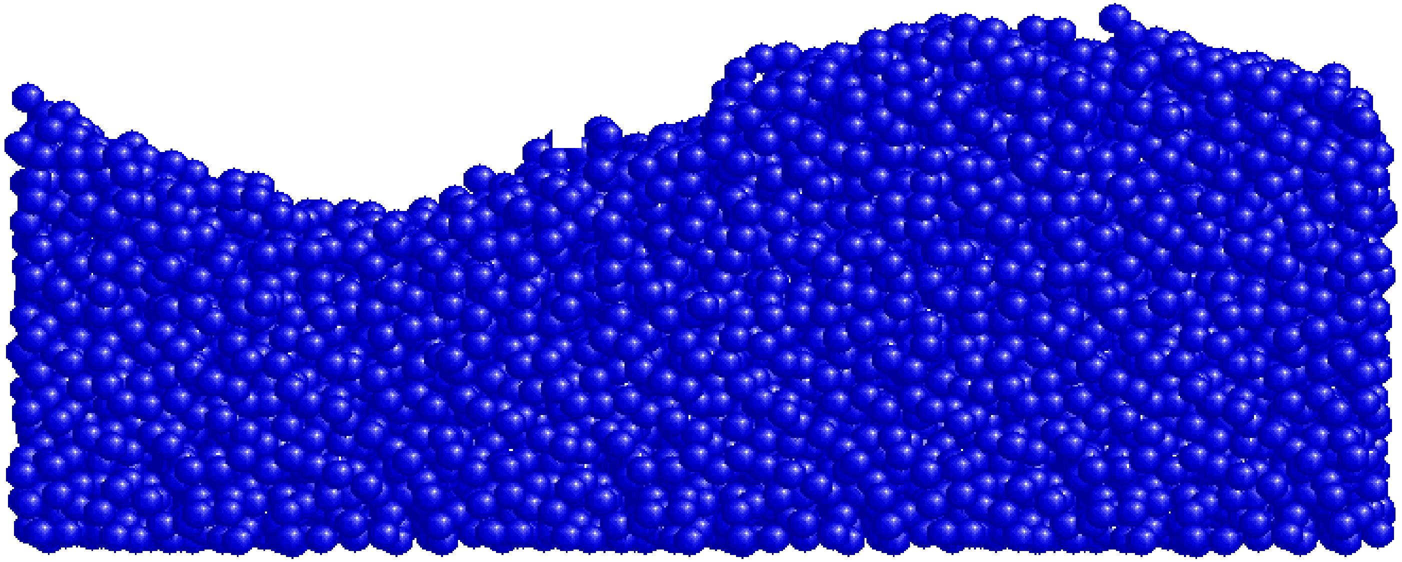
Atomistic simulation of film growth

The smoothing of a rough DLC film
4000 C-atoms
with 100 eV
hit a film
with an area
7.05nm x 2.35nm





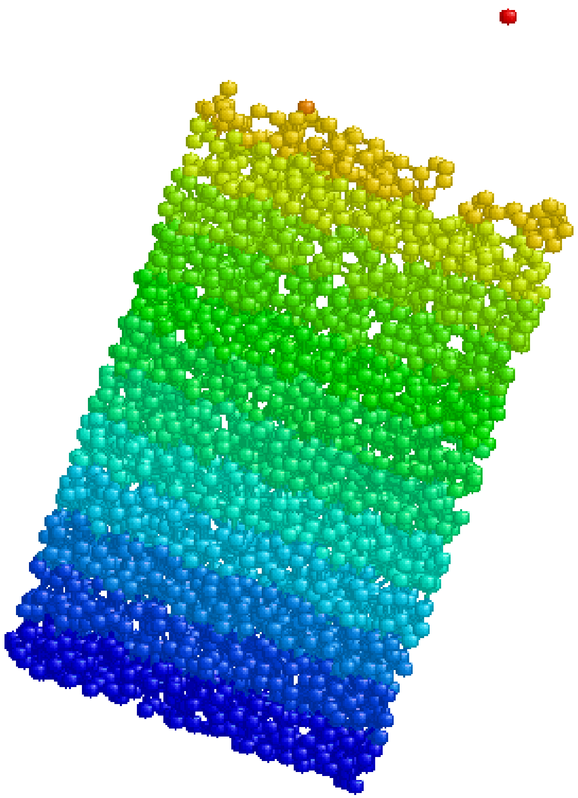
The constitutive law

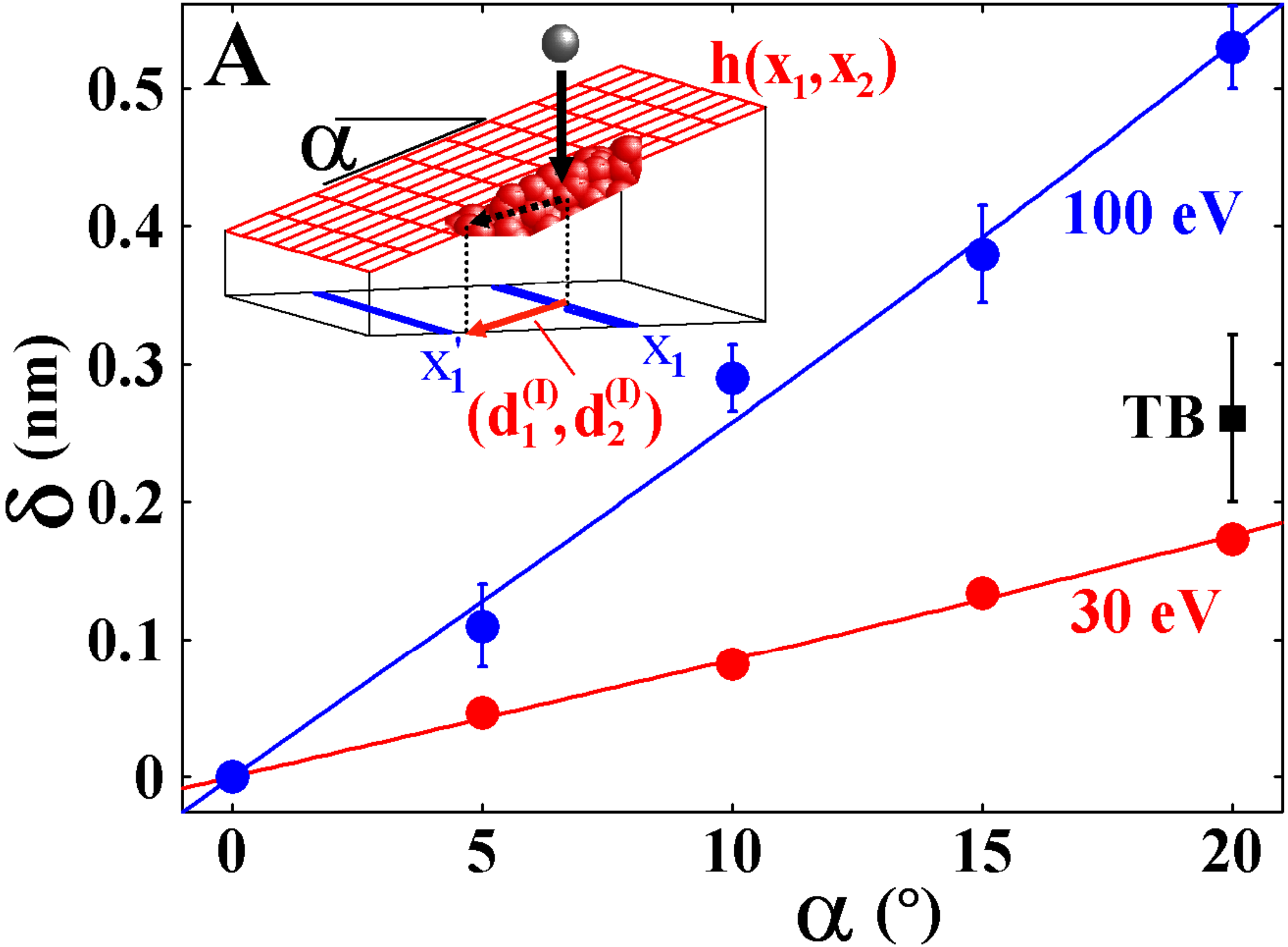
Sum of the displacements:

$$\delta(\alpha,E)=\sum_I d_1^{(I)}$$

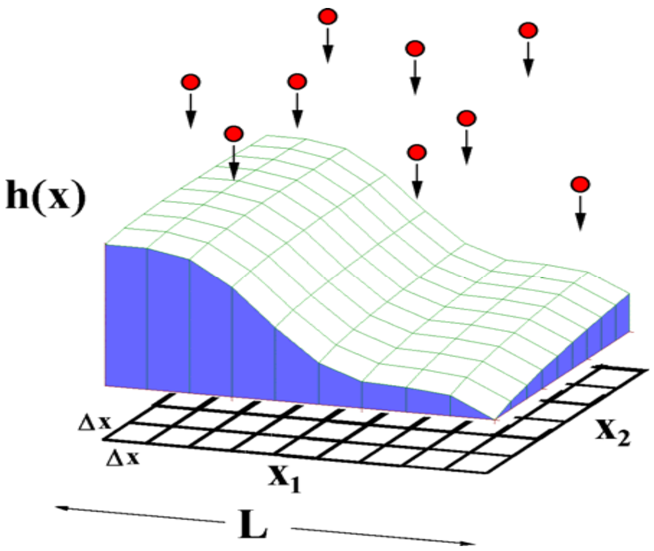
Particle current:

$$\mathbf{j}(\mathbf{x})=-\nu\nabla h(\mathbf{x})$$





Mesoscale description with stochastic differential equations



Stanley&Barabasi,
Fractal concepts in Surface Growth

Continuity eq.

$$\partial h(\mathbf{x},t)/\partial t = -\Omega\nabla\cdot\mathbf{j}(\mathbf{x},t) + \eta(\mathbf{x},t)$$

$$\langle\eta(\mathbf{x},t),\eta(\mathbf{x}',t')\rangle = r\Omega^2\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')$$

$$\boxed{\mathbf{j}(\mathbf{x},t) = -\nu\nabla h(\mathbf{x},t)}$$

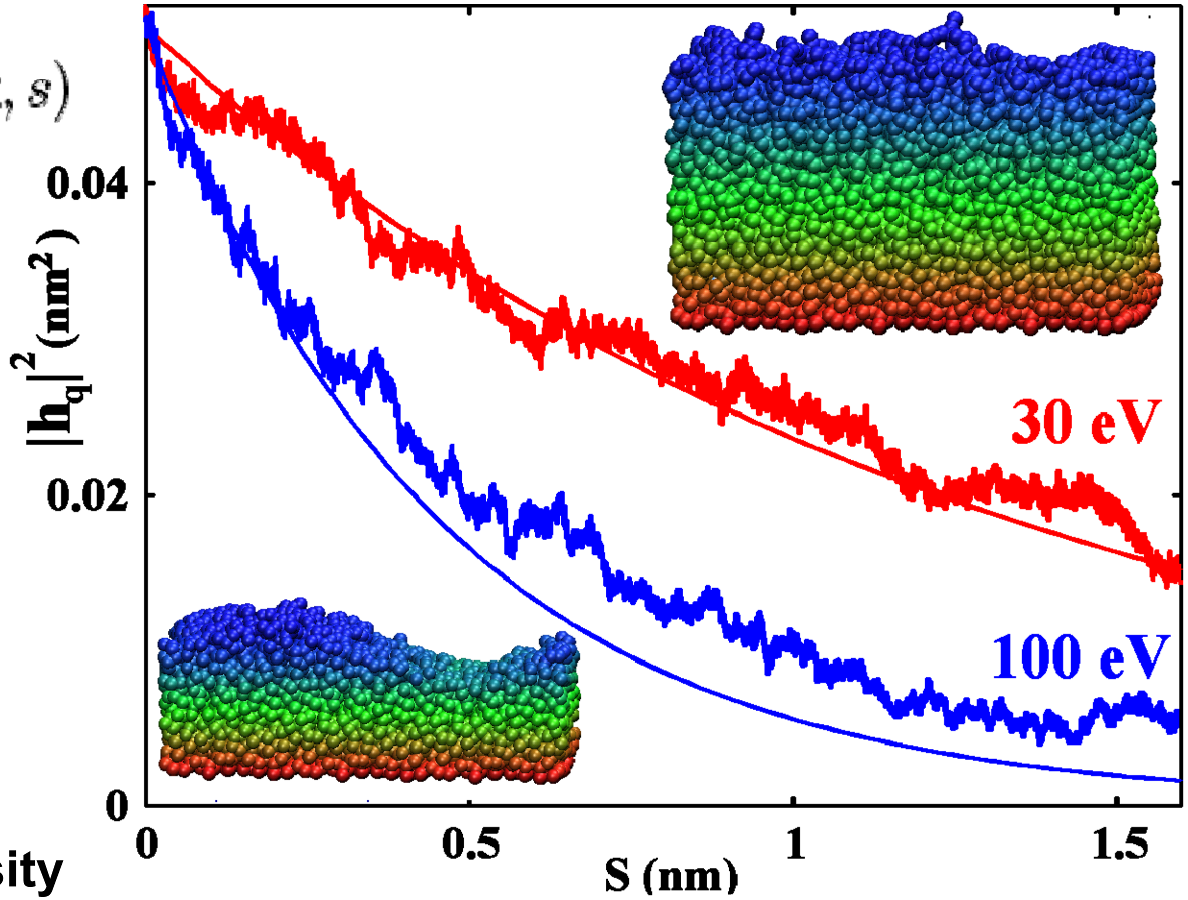
r: deposition rate, Ω: average atomic volume

The Edwards-Wilkinson equation

$$\partial h(\mathbf{x},s)/\partial s = \nu\nabla^2 h(\mathbf{x},s) + \eta(\mathbf{x},s)$$

s ~ t

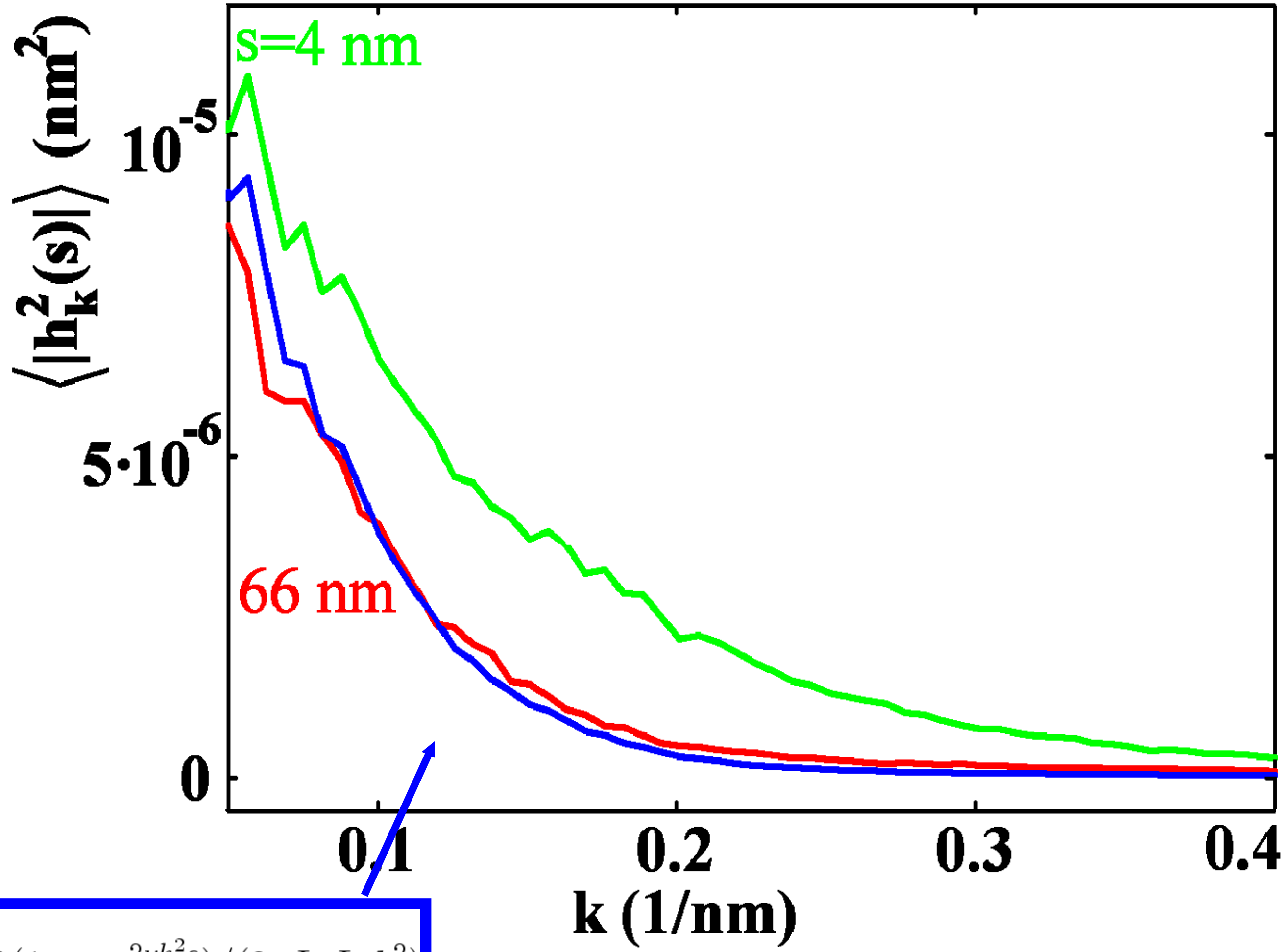
$$h(\mathbf{x},s) \xleftrightarrow{FT} h_k(s)$$



Solution: Power spectral density

$$\langle |h_{\mathbf{k}}(s)|^2\rangle = e^{-2\nu k^2 s}\langle |h_{\mathbf{k}}(0)|^2\rangle + \Omega(1-e^{-2\nu k^2 s})/(2\nu L_1 L_2 k^2)$$

Evolution of the power spectral density

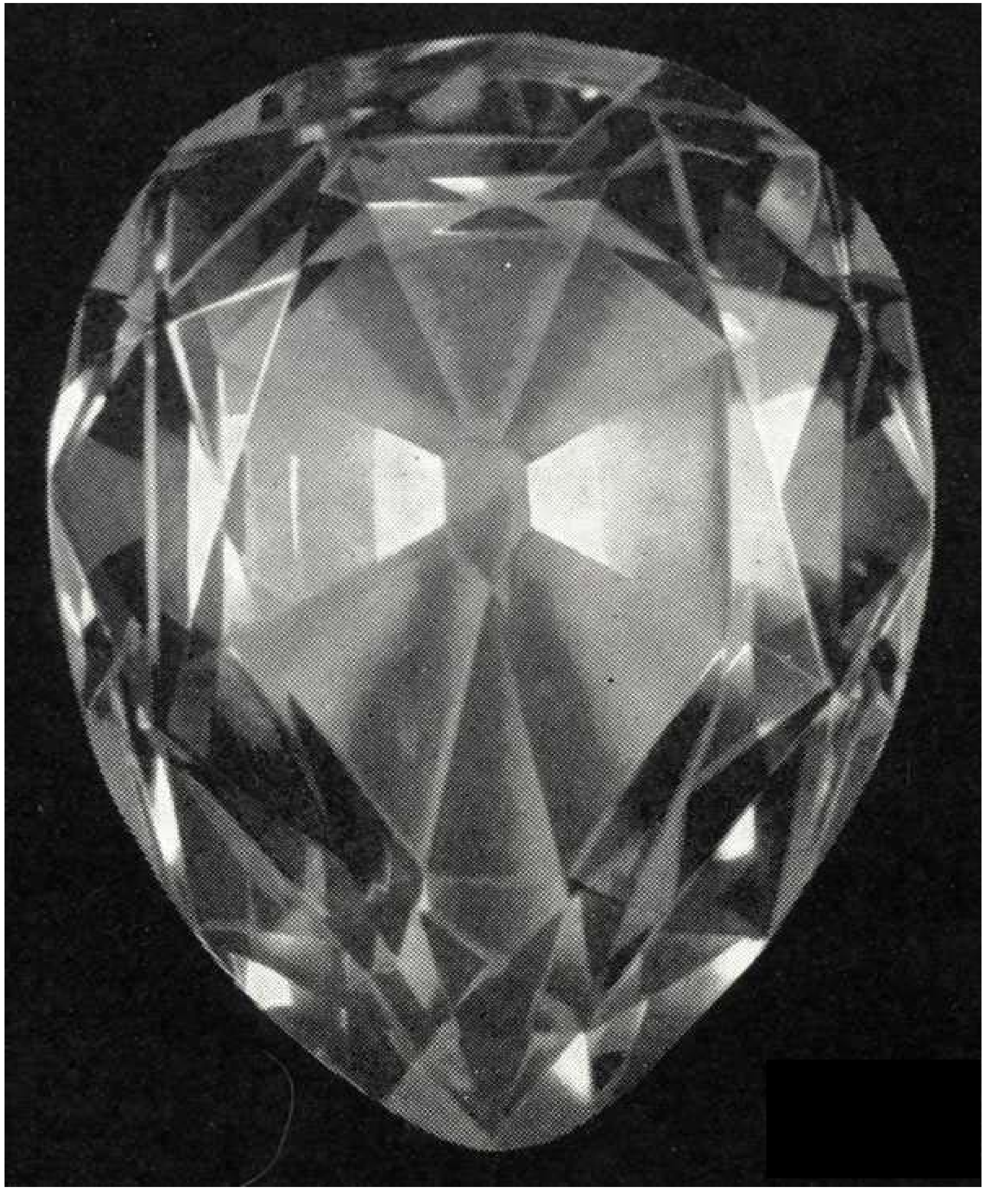


$$\langle|h_{\mathbf{k}}(s)|^2\rangle = e^{-2\nu k^2 s}\langle|h_{\mathbf{k}}(0)|^2\rangle + \Omega(1 - e^{-2\nu k^2 s})/(2\nu L_1 L_2 k^2)$$

M. Moseler, PG, et al., Science 309 (2005) 1545-1548

Polishing diamond is hard

Biggest diamond ever found:
the 3106 carat Cullinan.
Polished by three diamond cutters,
each working 14 hours a day
for eight months straight!



The tricks of the trade

- Diamond: the hardest material
- Exact mechanisms are not understood
- Scaife: cast iron wheel with embedded diamond grits
- {111} is hard to polish (small wear rates, bad surface quality)
- {001} has 4 soft directions (high wear) in <100>
- {011} has 2 soft directions (high wear) in <100>
- Grits in the iron matrix are oriented in soft direction
- AFM studies for hard directions: abrasion
- soft directions: plastic flow

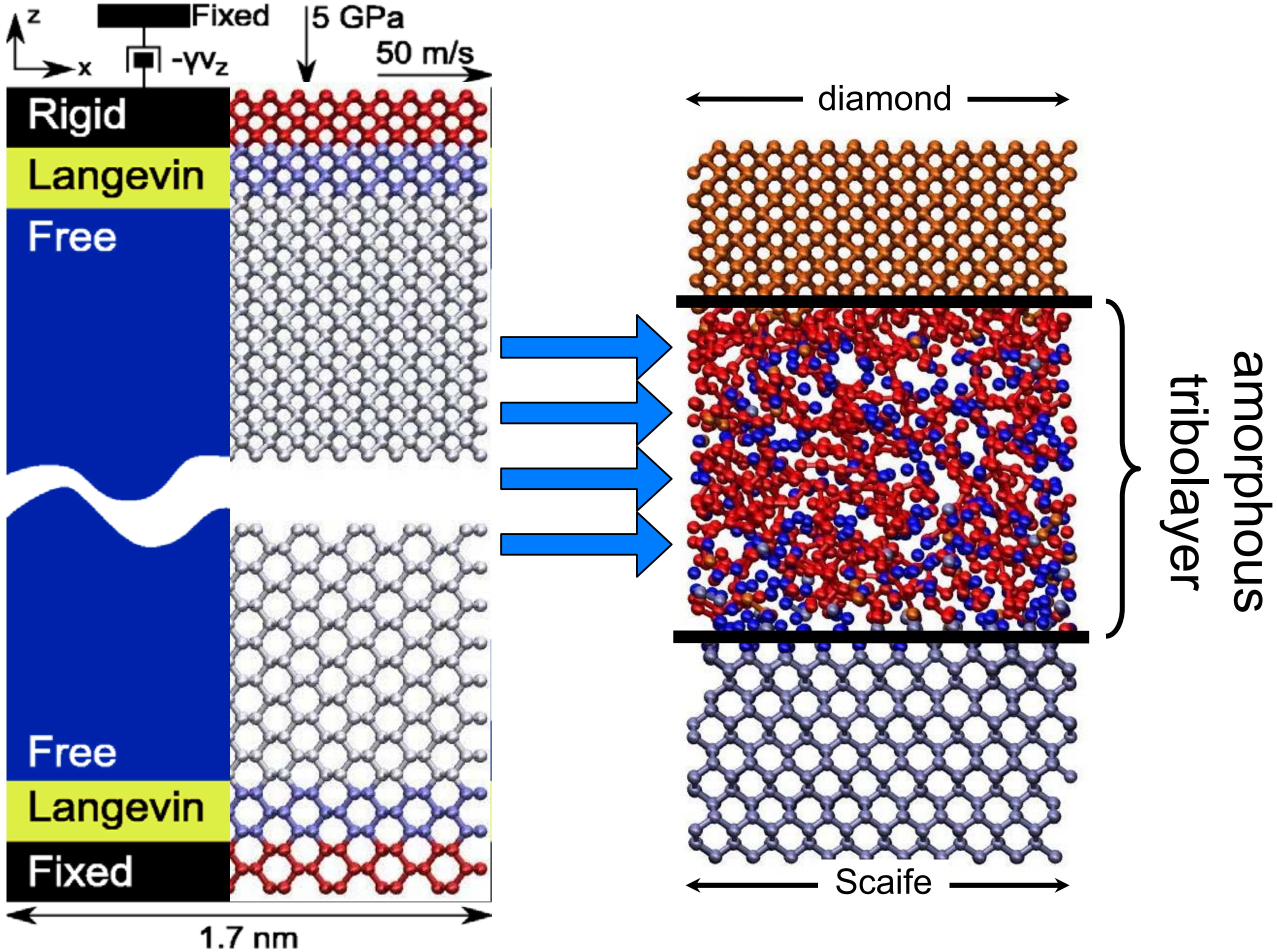
What are the dominant wear processes?

What explains the anisotropy?

J.Hird, J.Field, Proc. R. Soc. Lond. A (2004) 460, 3547

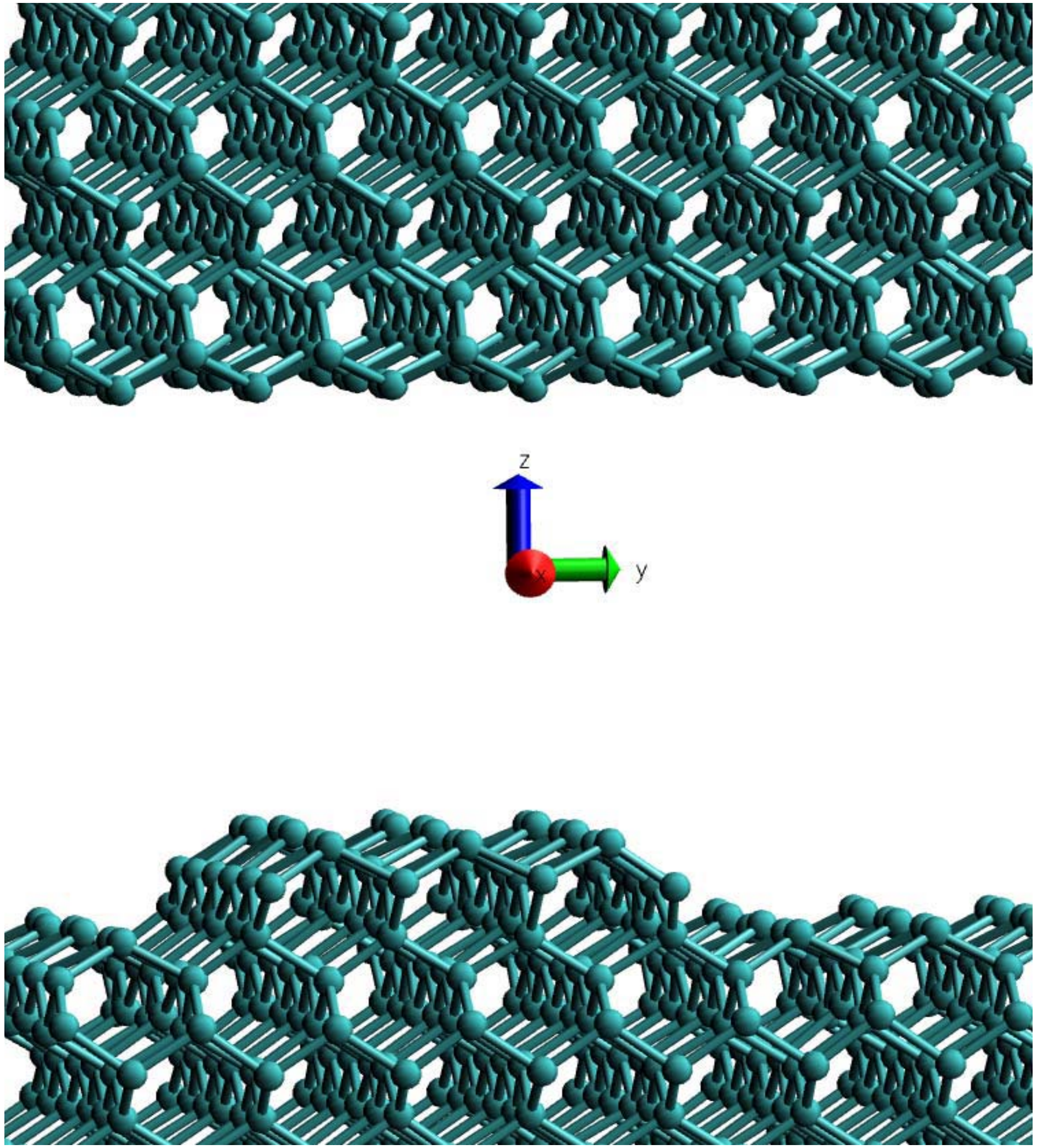
Mechanochemical reactions, diamond polishing

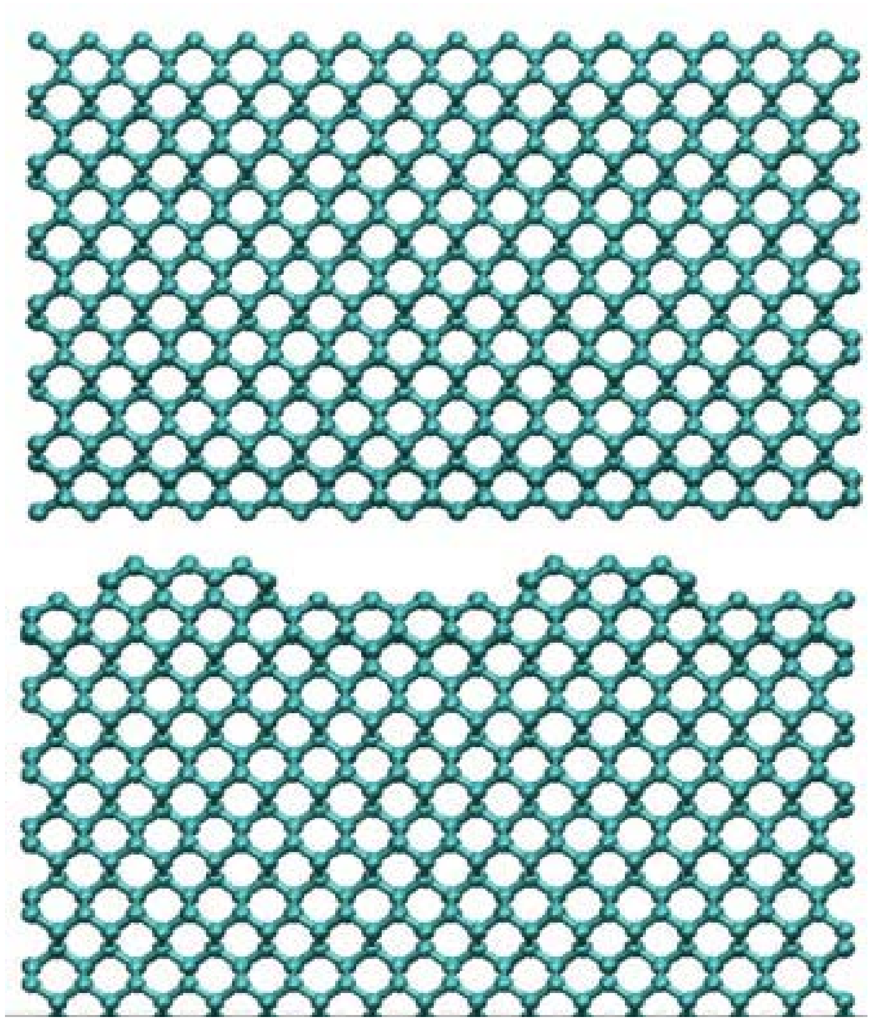
Bildquelle: http://www.costerdiamonds.com



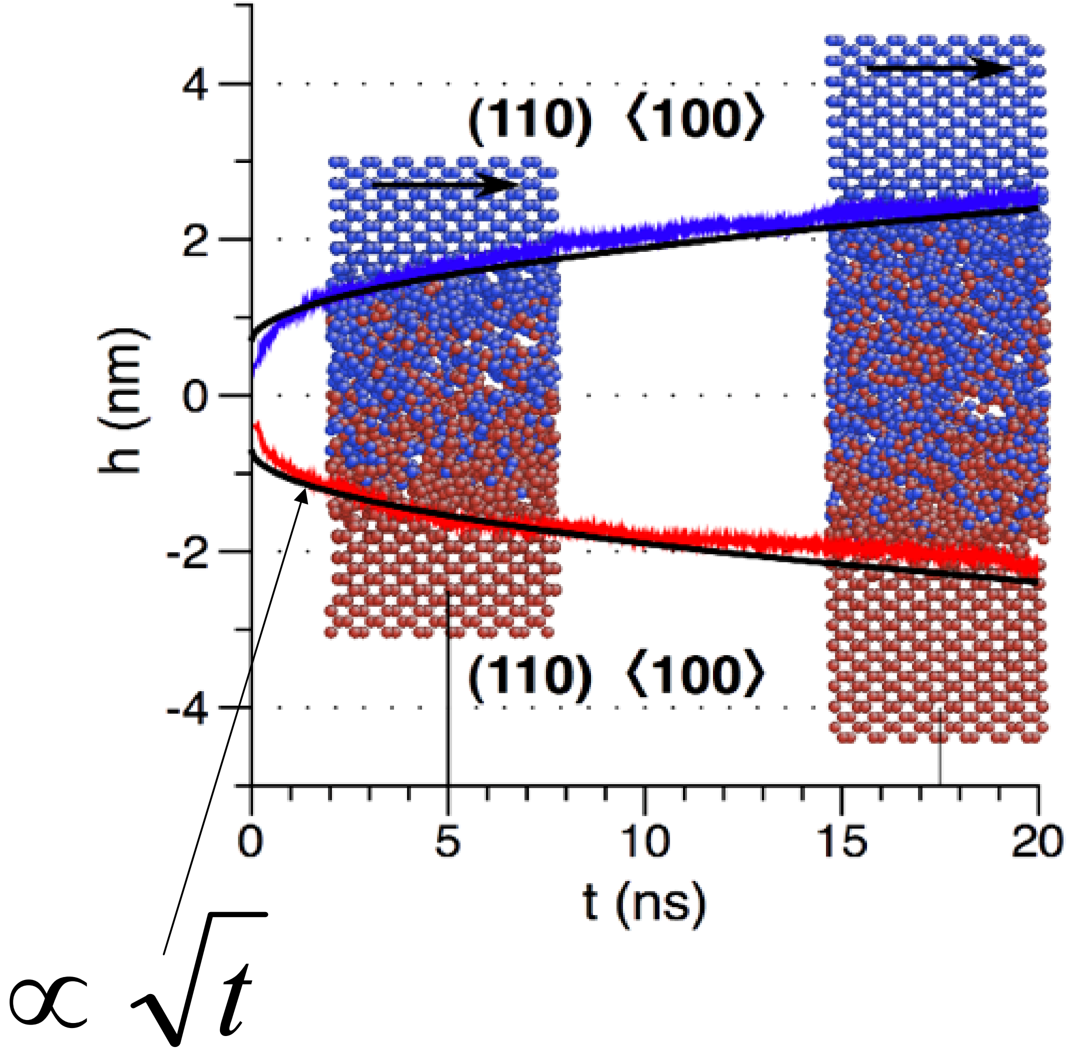
Polishing of diamond

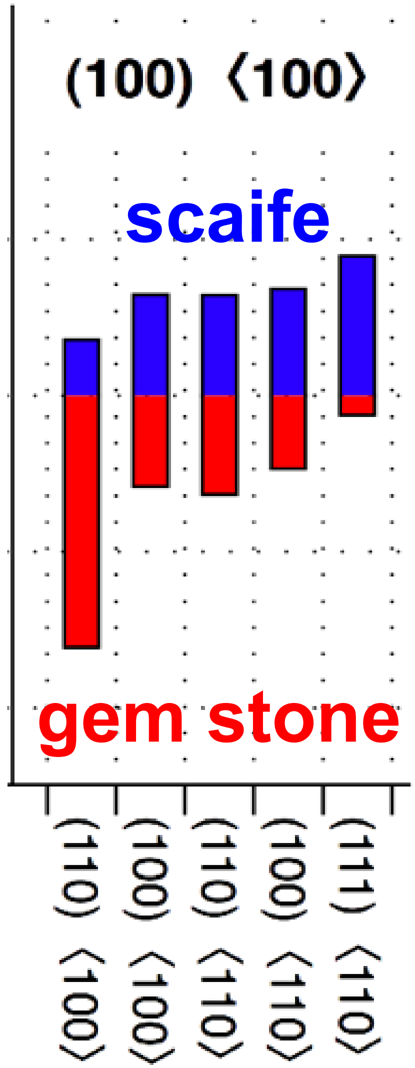
diamond (110) surface, motion in <001>
velocity 50 m/s, normal load 5 GPa
screened Brenner potential





The anisoptropy





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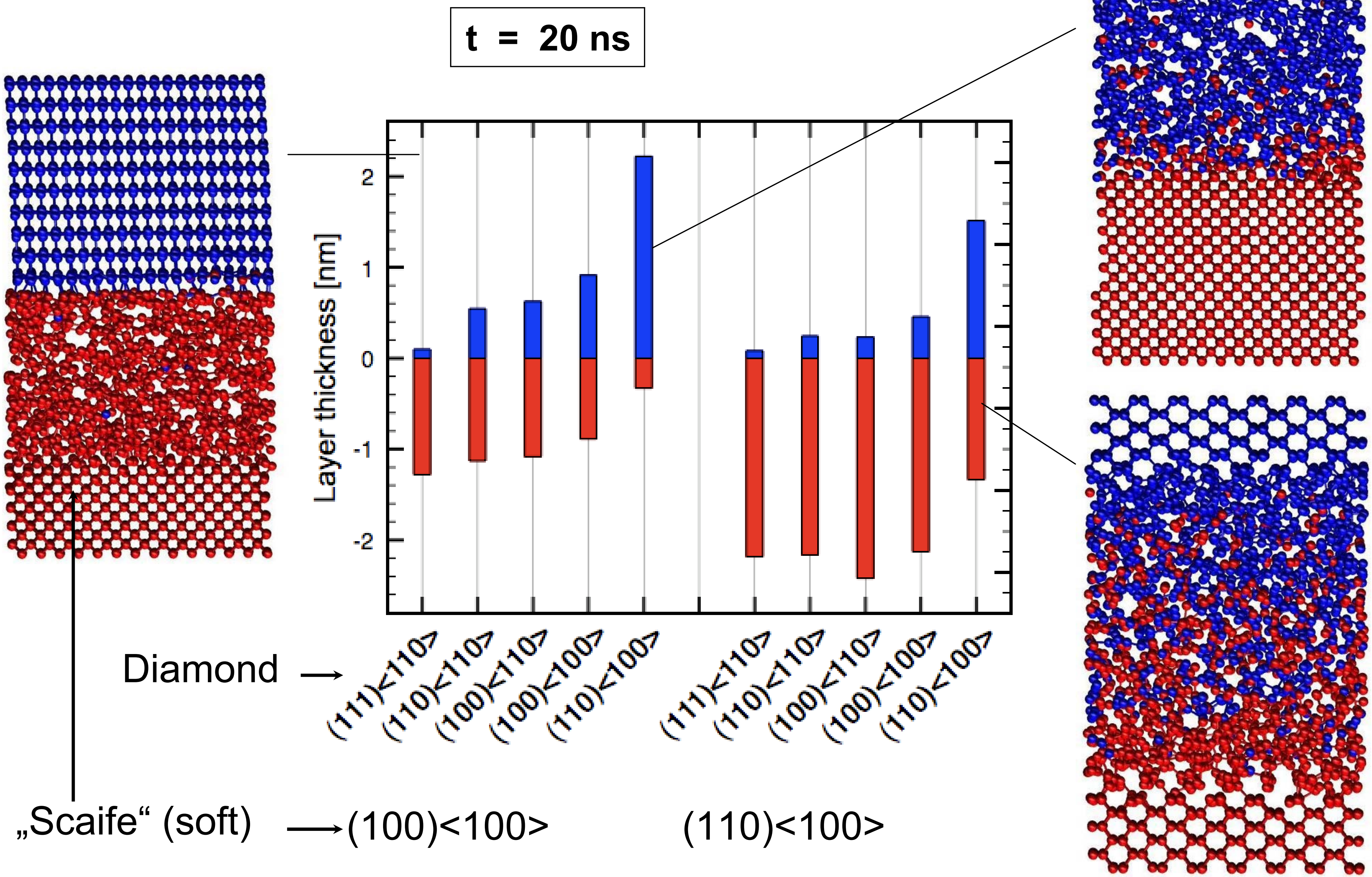
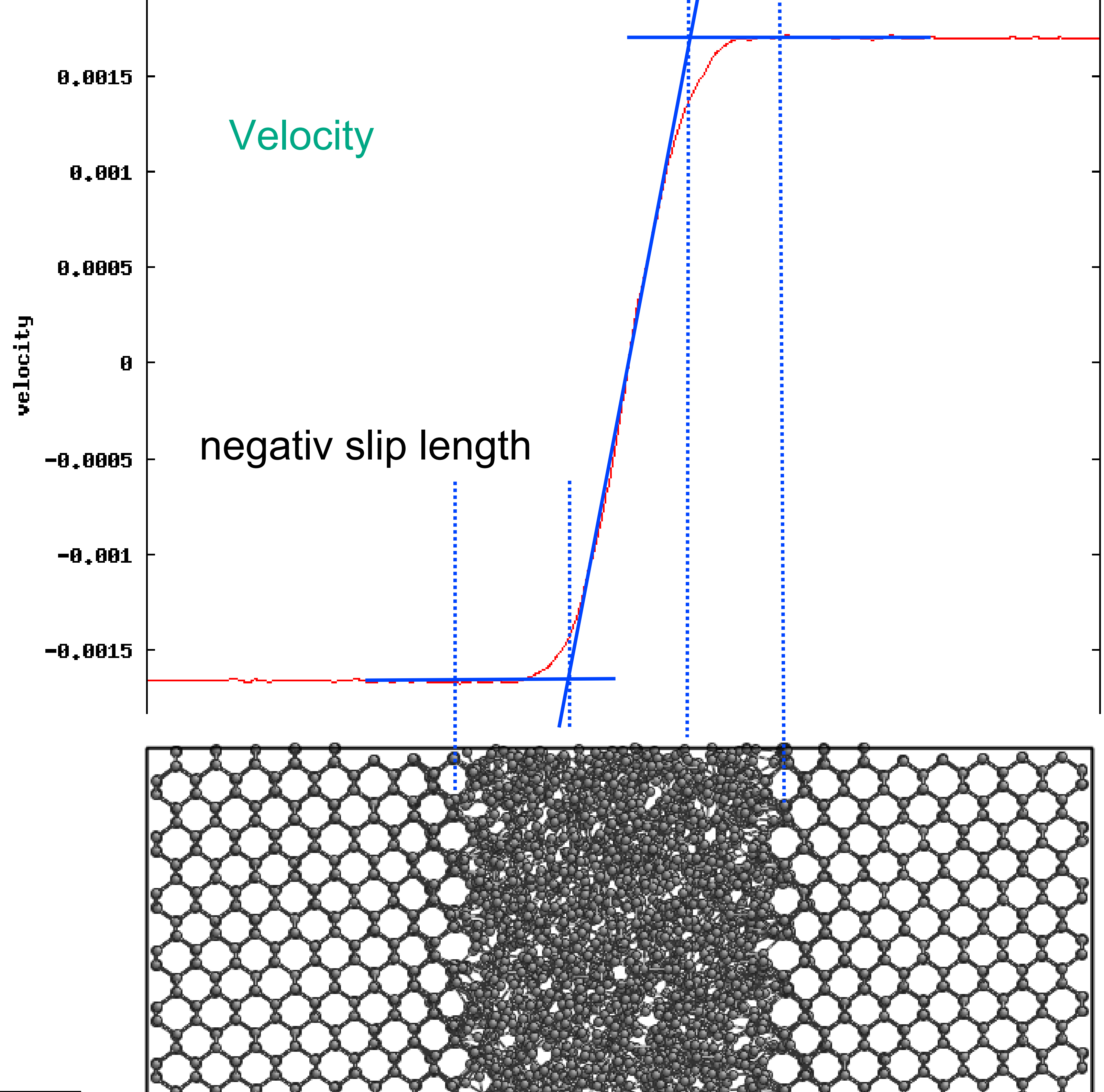
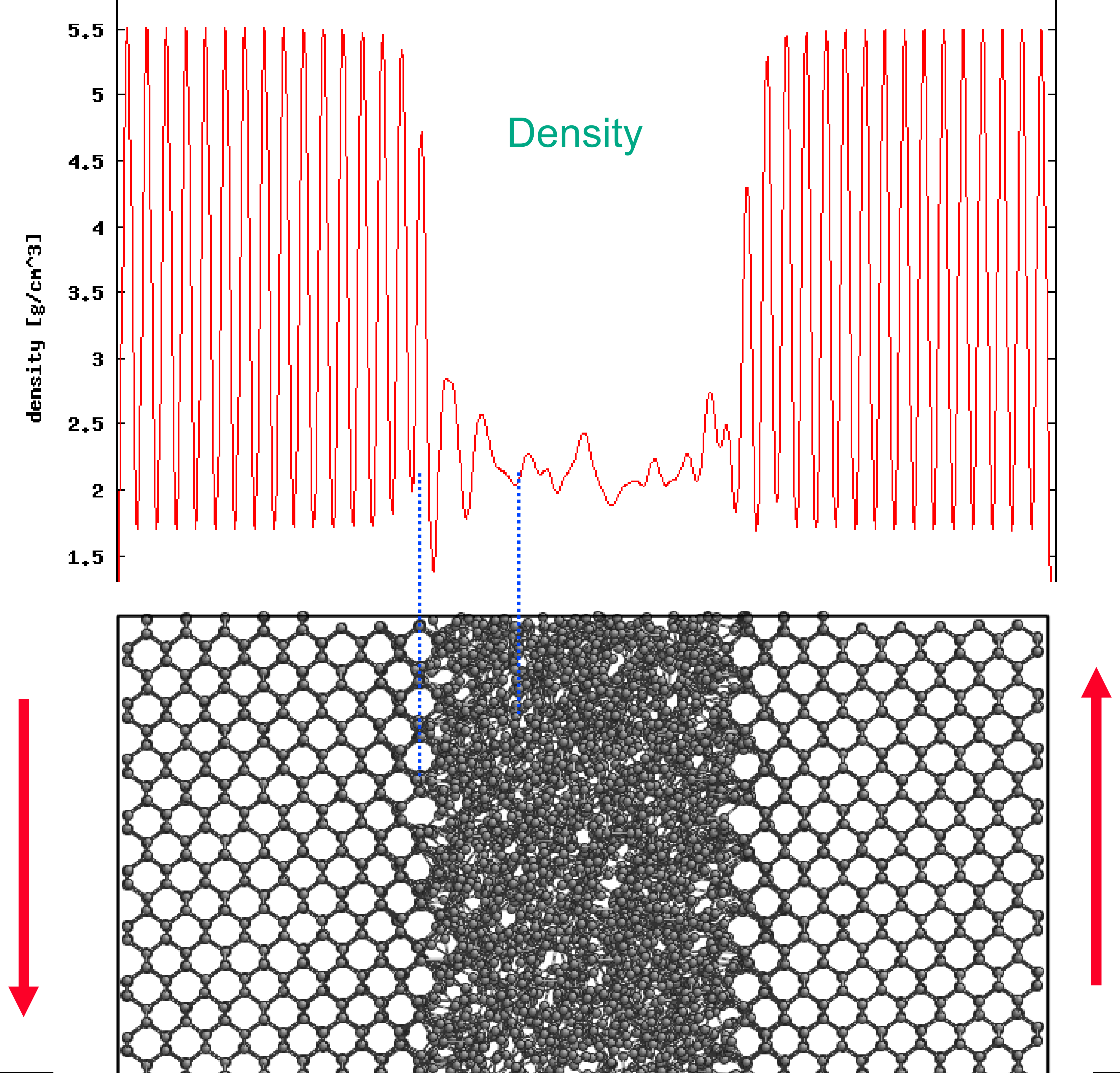
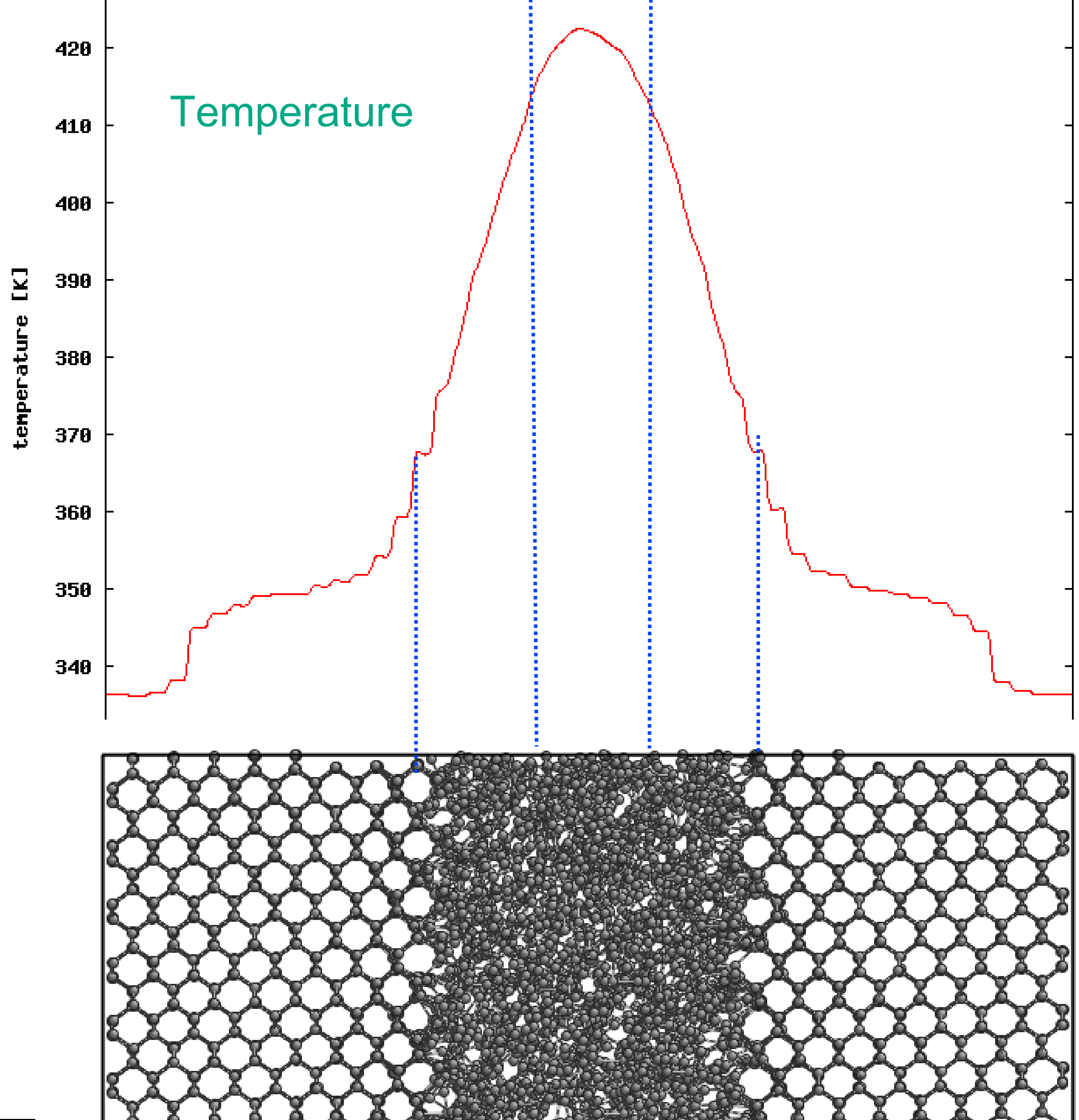
Anisoptropy: amorphous Nanolayer



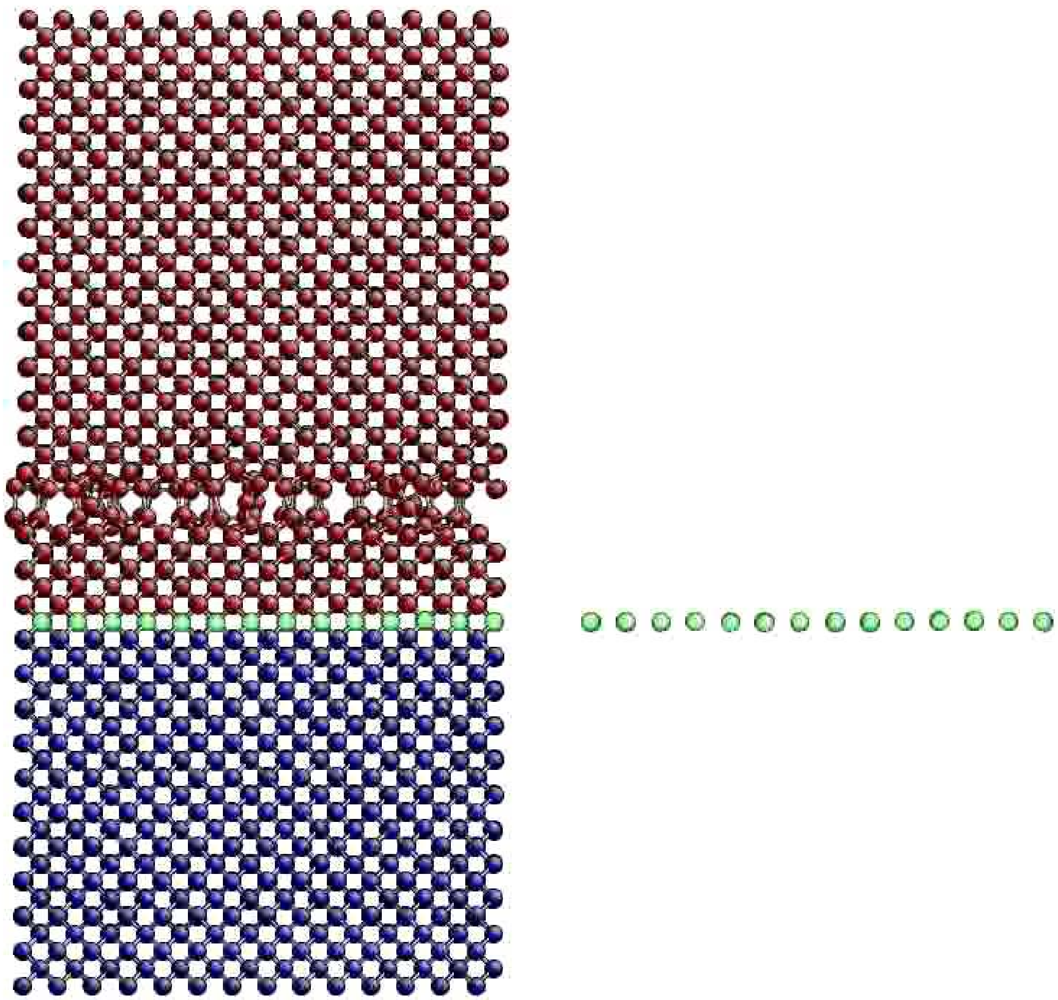

0.0015
0.001
0.0005
0
-0.0005
-0.001
-0.0015
velocity
Velocity
negativ slip length

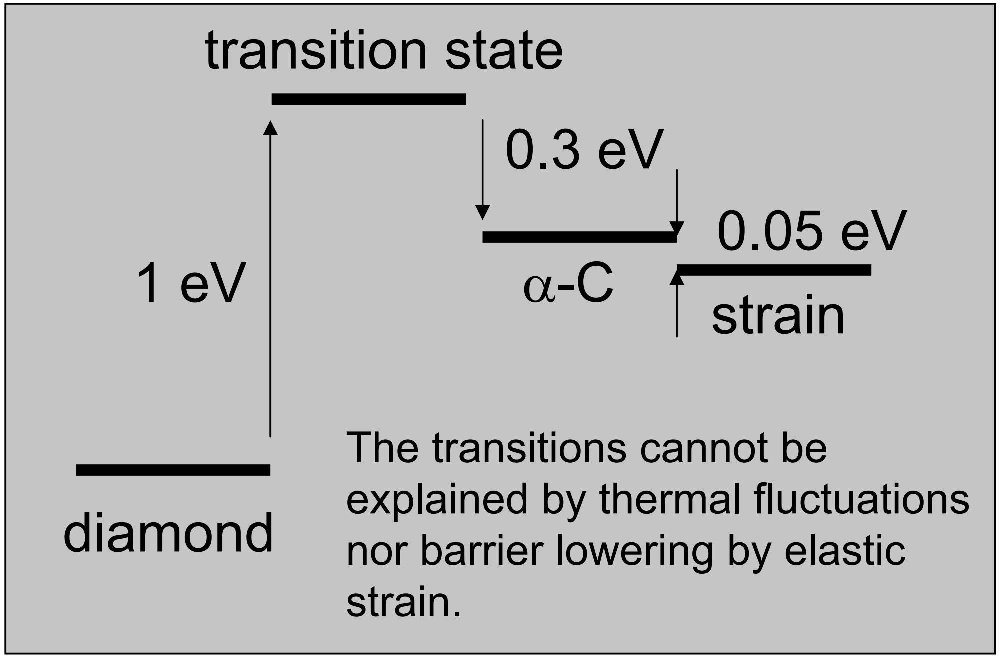


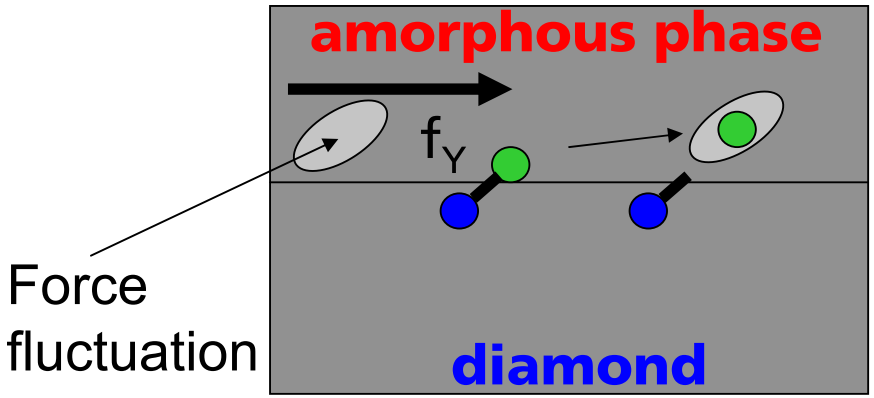
Density
density [g/cm^3]
5.5
5
4.5
4
3.5
3
2.5
2
1.5


Temperature
temperature [K]
420
410
400
390
380
370
360
350
340

Amorphisation process





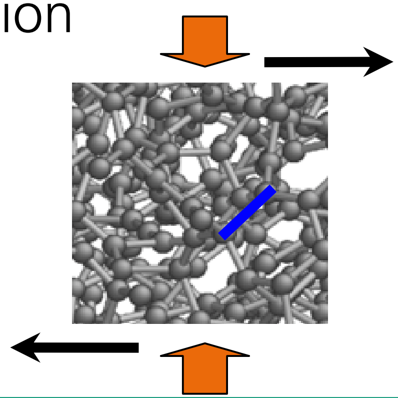


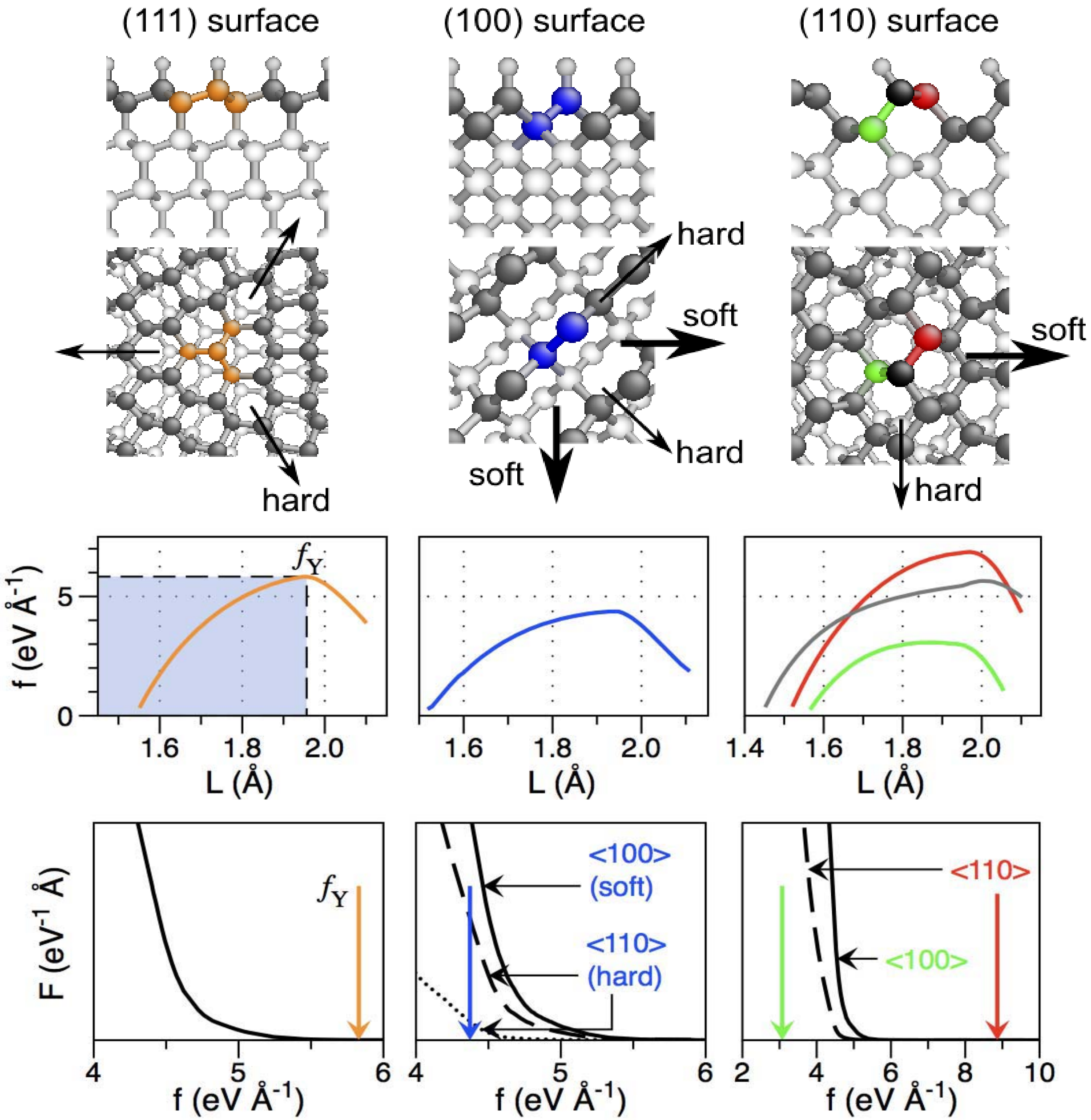
Polishing diamond
Stress-fluctuations

- Crystallographic structure
- Yield force
- Force distribution in bond-direction

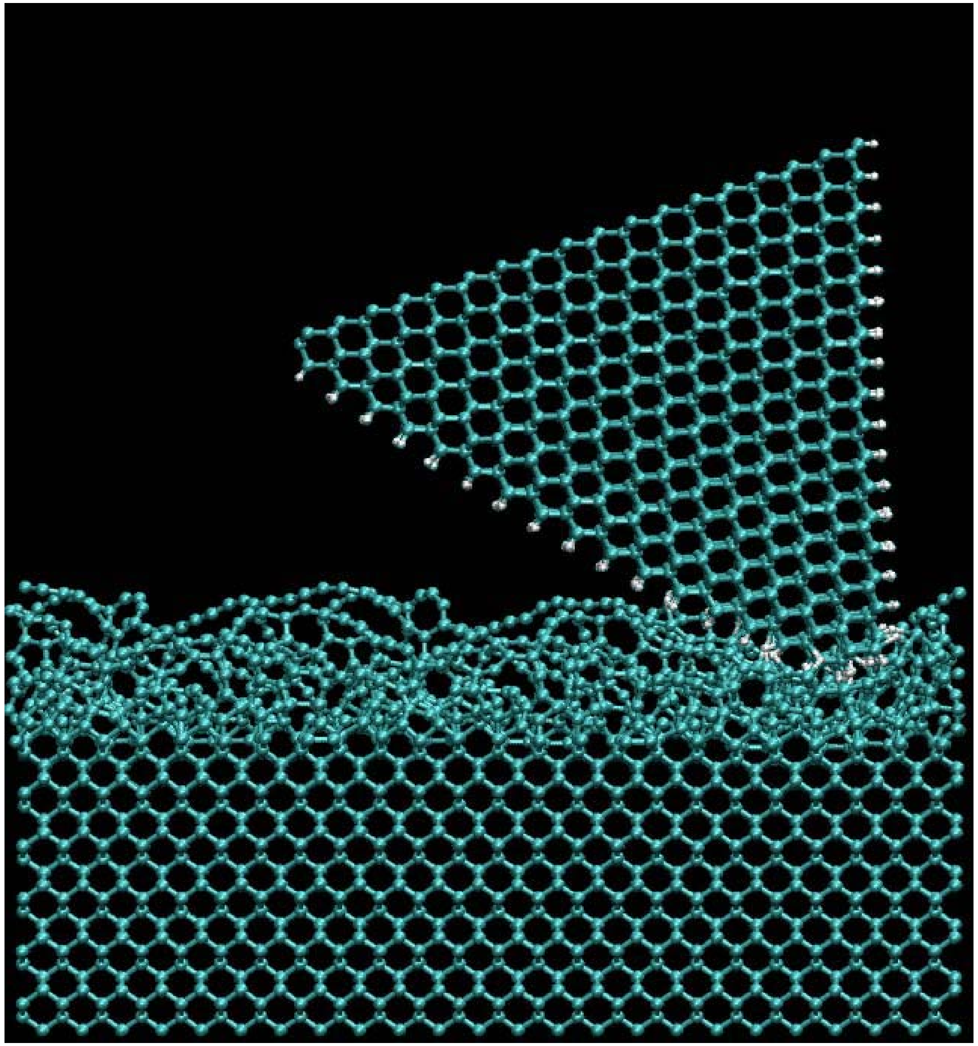
  from sheared a-C

10 GPa



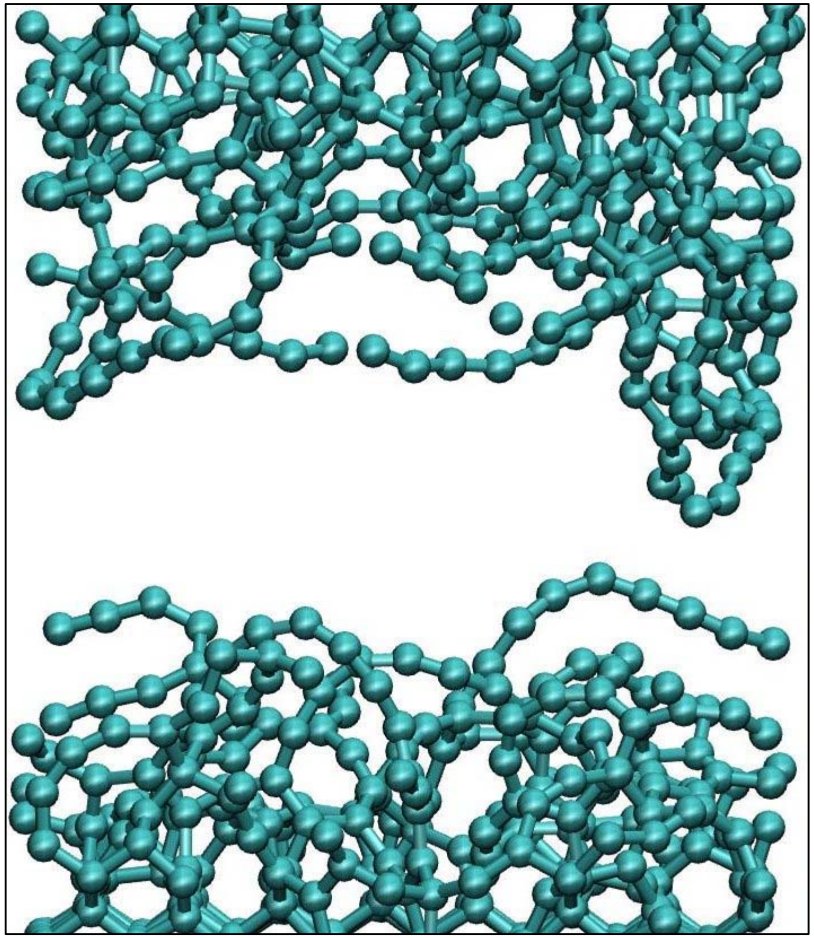


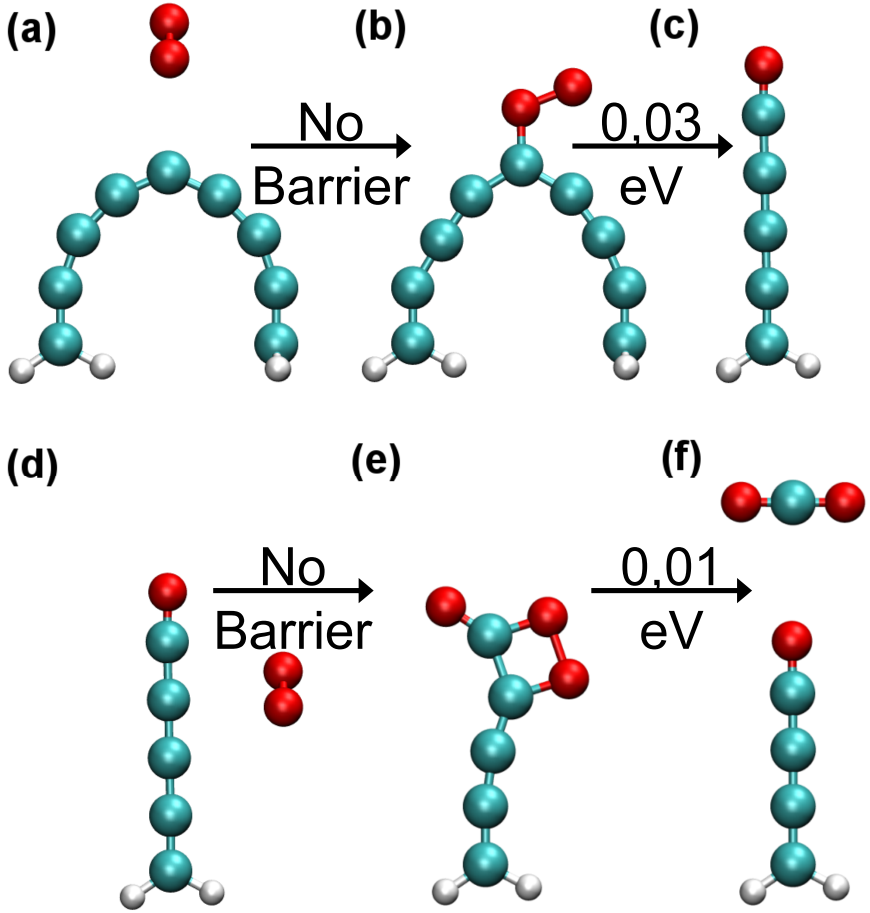
Mechanical wear



Experiments find amorphous carbon dust after diamond polishing

Chemical wear



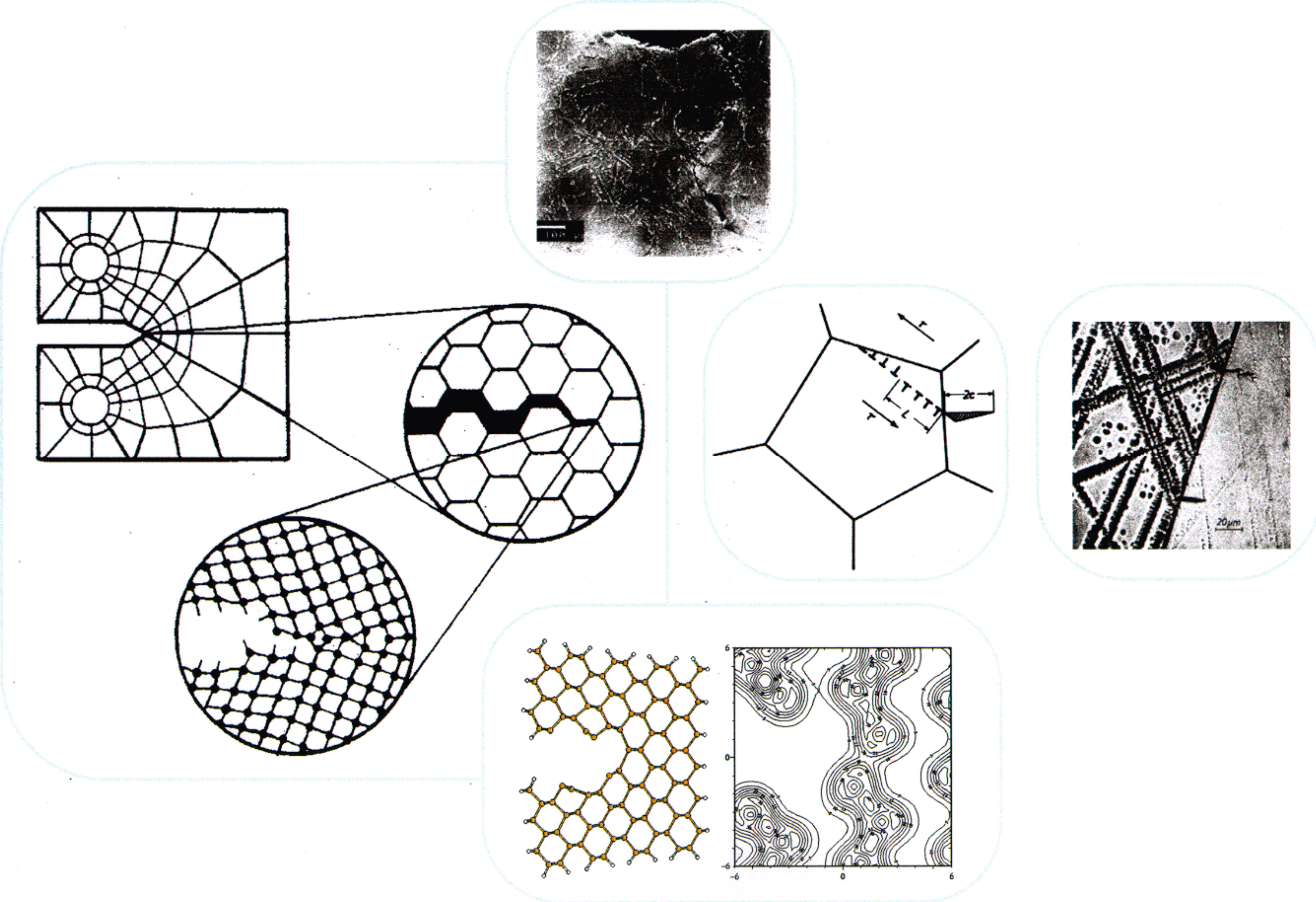


Conclusions (1)

Bond breaking processes are somewhat difficult to built into empirical potentials – screening seems to do a good job for bond order potentials

Tribology, friction and wear are becoming accessible to modelling and simulation

- understand cleavage anositropy of silicon and diamond
- understand ultra-flatness of amorphous carbon (ta-C) films
- wear of diamond (dia-C) is a consequence of a (athermal) mechanically driven amorphization



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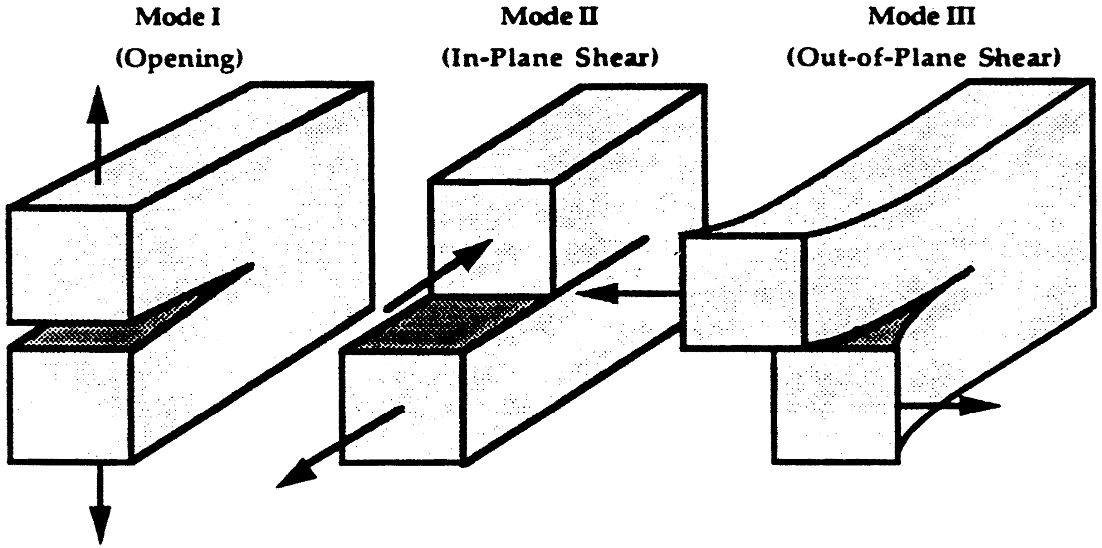
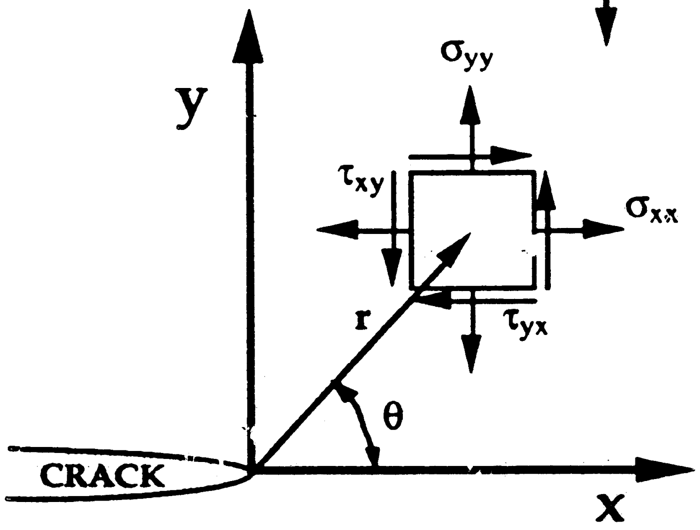
continuum mechanics
of cracks

linear elastic fracture
mechanics





$$\lim_{r\to 0}\sigma_{ij}^{(I)} = \frac{K_I}{\sqrt{2\pi r}} f_{ij}^{(I)}(\theta)$$

$$G = \frac{K_I^2}{E} + \frac{K_{II}^2}{E} + \frac{K_{III}^2}{2\mu}$$

brittle to ductile transition

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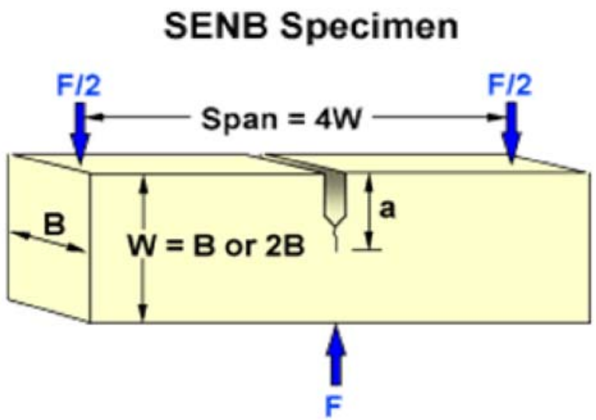
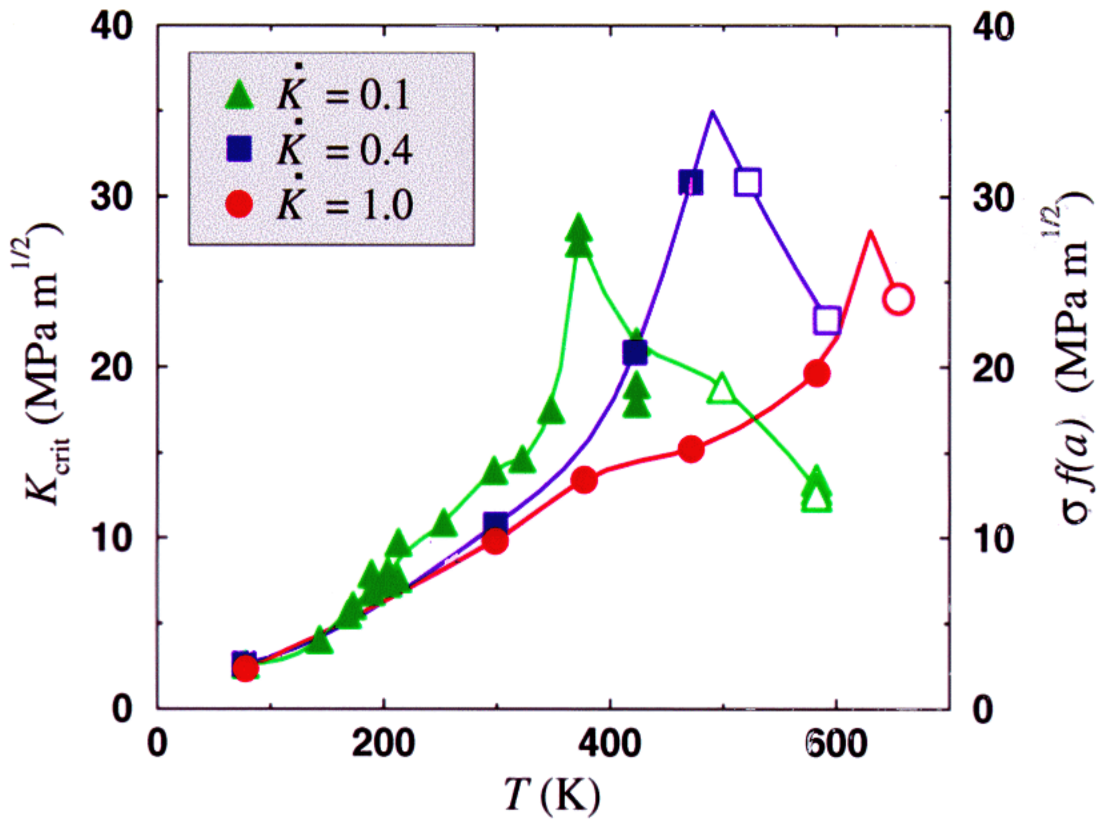
fracture toughness (loading rate, temperature, …)

Fracture experiments on tungsten single crystals

(110)<-110> orientation

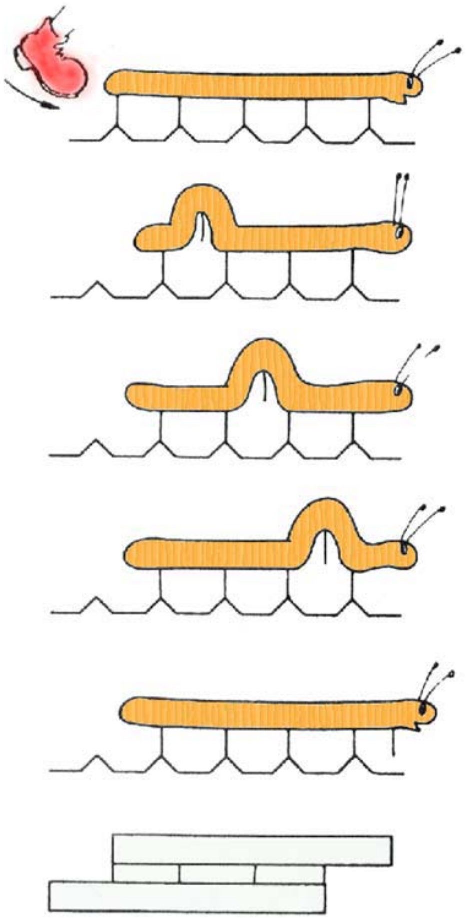


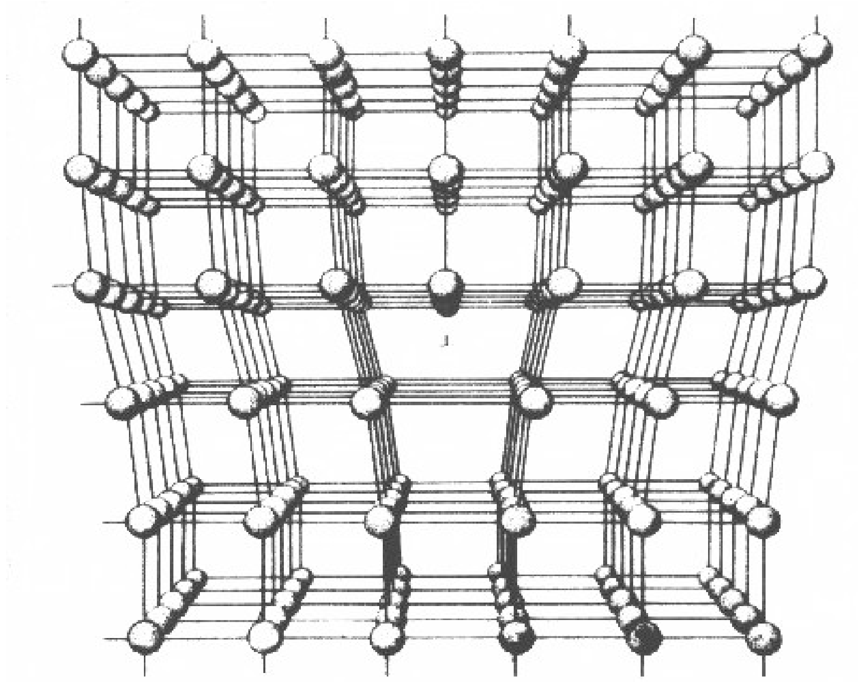


$[\dot{K}] = 1\text{MPa m}^{1/2} / \text{s}$

[PG et al., Science 282 (1998) 1293]

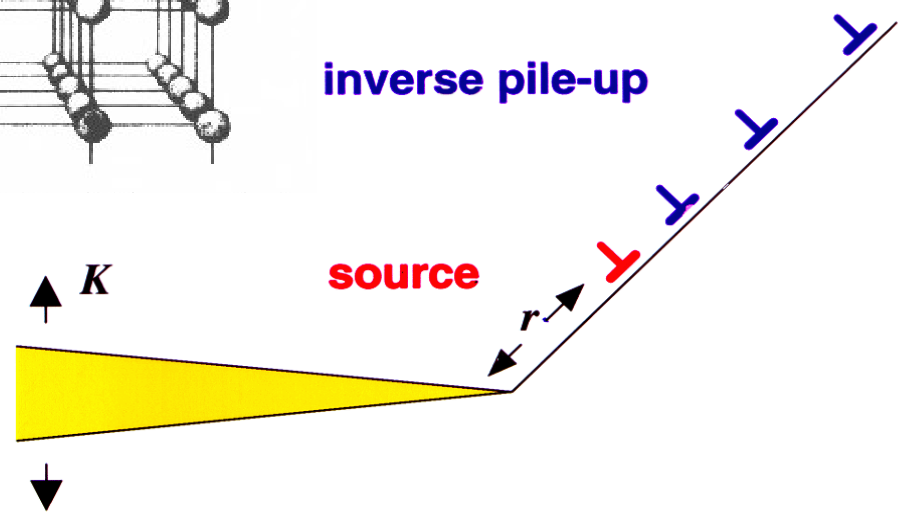
dislocation, the carrier of plastic deformation



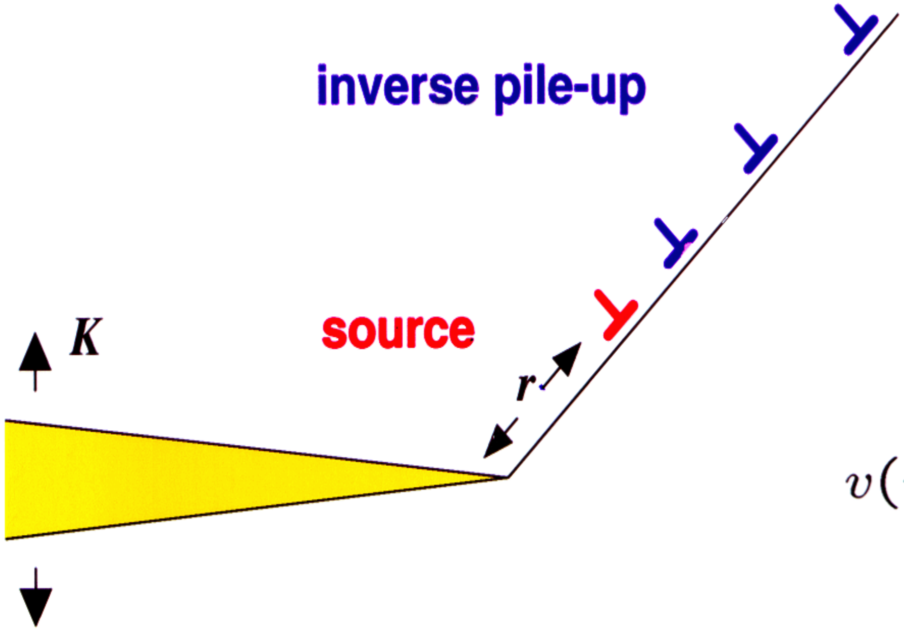


$$\sigma_{disloc} \propto 1/R$$

$$\sigma_{crack} \propto 1/\sqrt{R}$$



2D Model -> Scaling



$$\tau = \tau^{\text{crack}} + \tau^{\text{image}} + \tau^{ij} + \tau^{\text{fric}}$$

$$v(\tau, T) = A \left(\frac{\tau}{\tau_0}\right)^{m(T)} \exp\left(-\frac{U}{kT}\right)$$

(Schadler, 1964: $A = 3\,\frac{\text{nm}}{\text{s}}$, $m = \frac{590\text{K}}{T} + 2.8$, $U = 0.3\text{eV}$)

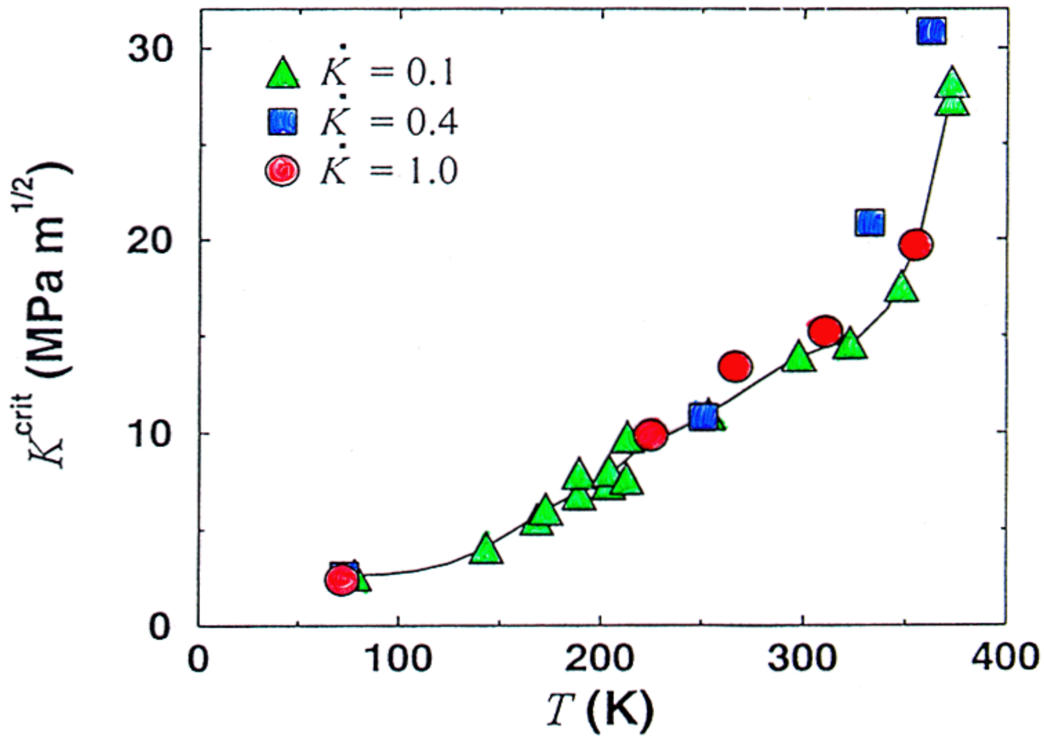
*Roberts, 1996; Lin and Thomson, 1986

scaling behaviour

$$\dot{K}_1 = A \exp\left(-\frac{U_{\mathrm{BDT}}}{k_B T_1}\right)$$

$$\dot{K}_2 = A \exp\left(-\frac{U_{\mathrm{BDT}}}{k_B T_2}\right)$$

$$T_2 = \left[\frac{k_B}{U_{\mathrm{BDT}}} \ln \frac{\dot{K}_1}{\dot{K}_2} + \frac{1}{T_1}\right]^{-1}$$



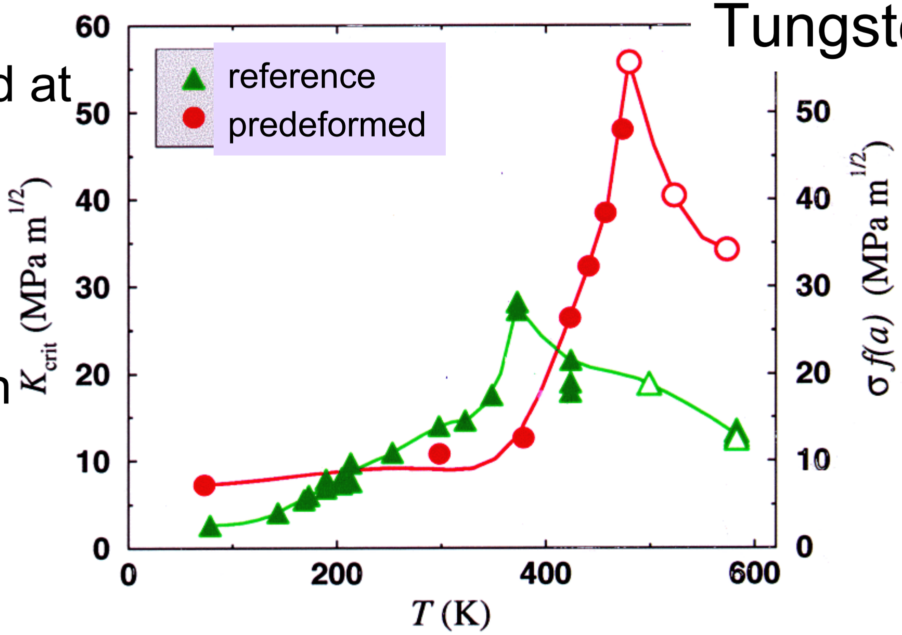
The scaling behavior of the experimental T-K^{crit}-curves is described by an Arrhenius-type law [Equation (6.4)] with an apparent activation energy of U_{BDT} = 0.19 eV.

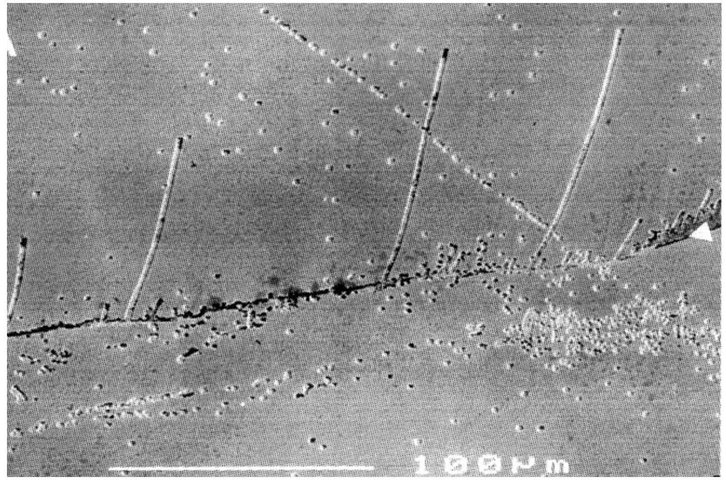
[A. Hartmaier and PG, Phys. Rev. B 71 (2005) 024108]

BDT and Dislocation Nucleation in Experiments

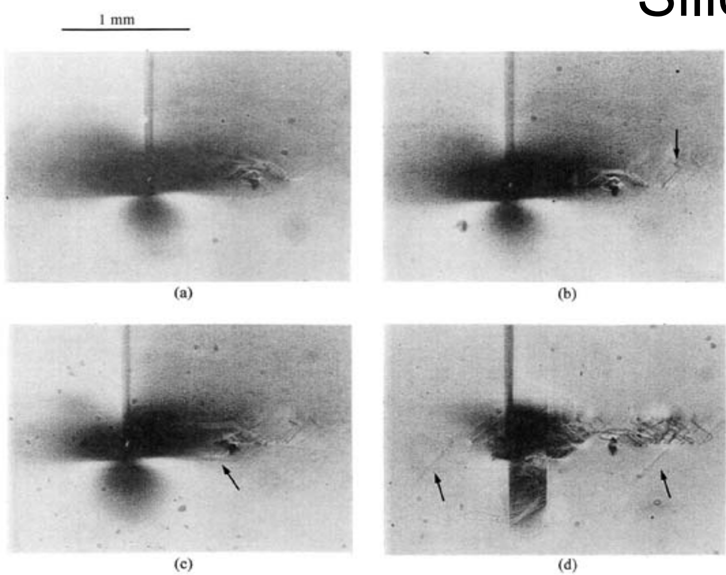
- BDT nucleation limited at low T (and low ρ)
- Crack arrest requires dislocation nucleation
- Sources rarely contain just one b
- Dislocation nucleation can be stimulated by incoming (pre-existing) dislocation
- Si: Michot et al.
- Si Arrest: Argon et al.
- W: Gumbsch et al.

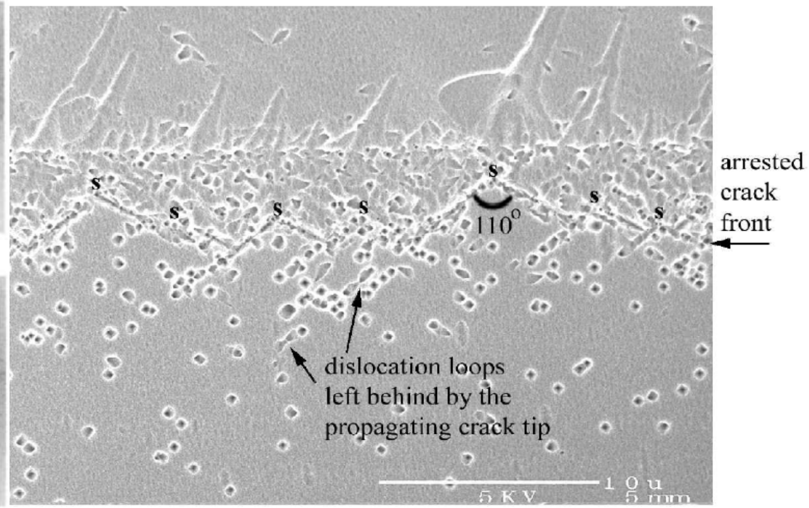
Tungsten





Silicon





Dislocation-Crack Interaction

Questions:

Mechanisms of dislocation nucleation at crack front

Mechanisms of dislocation interaction with crack front

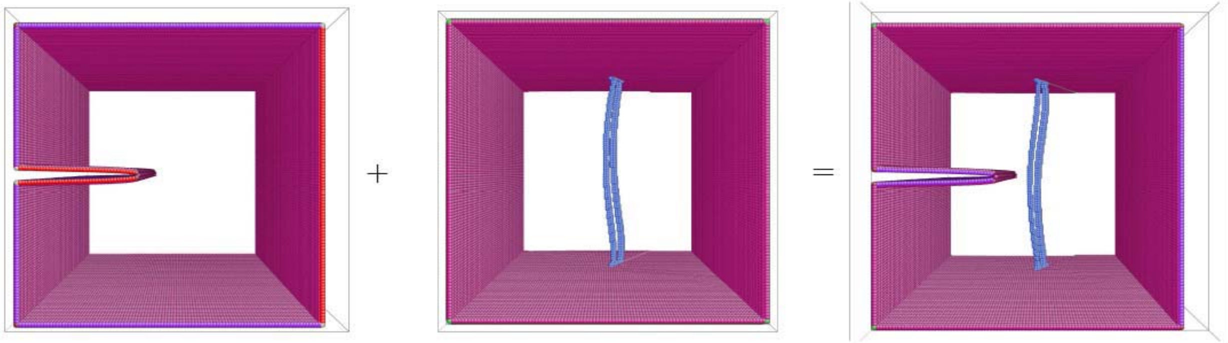
Methods:

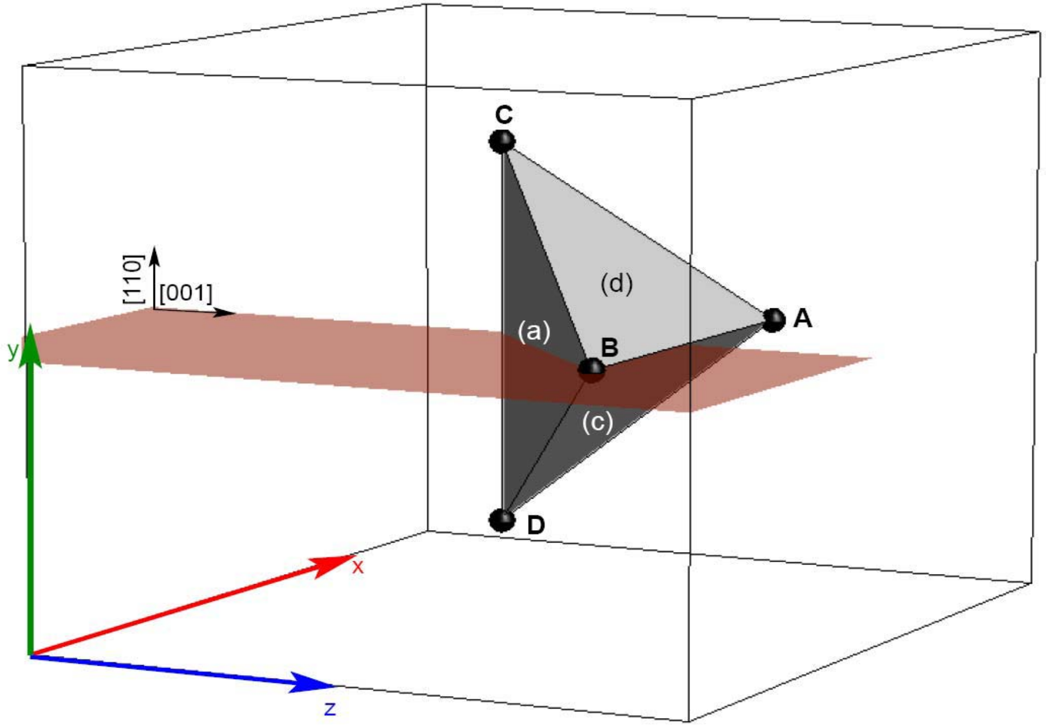
Dislocation impinging into stationary crack

Propagating crack hitting obstacle (e.g. dislocation)

fcc Ni-EAM, MD (starting at 0K)

γ orientation





I	$AC(b) \equiv BD(a)$	$BC(a) \equiv AD(b)$
II	$AC(d) \equiv BD(c)$	$BC(d) \equiv AD(c)$
III	$AB(d) \equiv DC(a)$	$AB(c) \equiv DC(b)$

Parameter Space

Burgers vector

glide plane

crack front sharp, blunted

plane strain, plane stress

static or dynamic crack

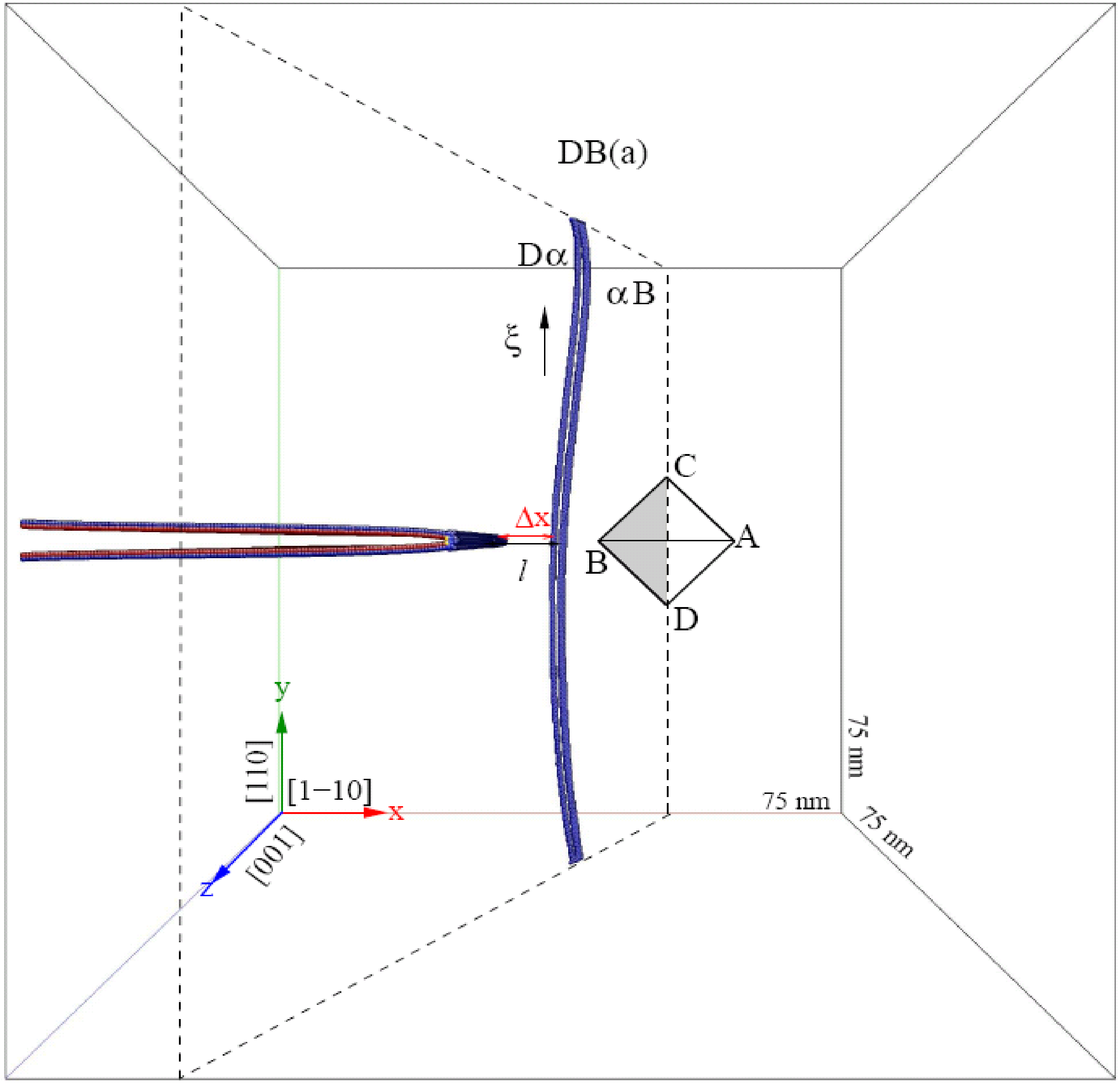
orientation of dislocation

dislocation velocity

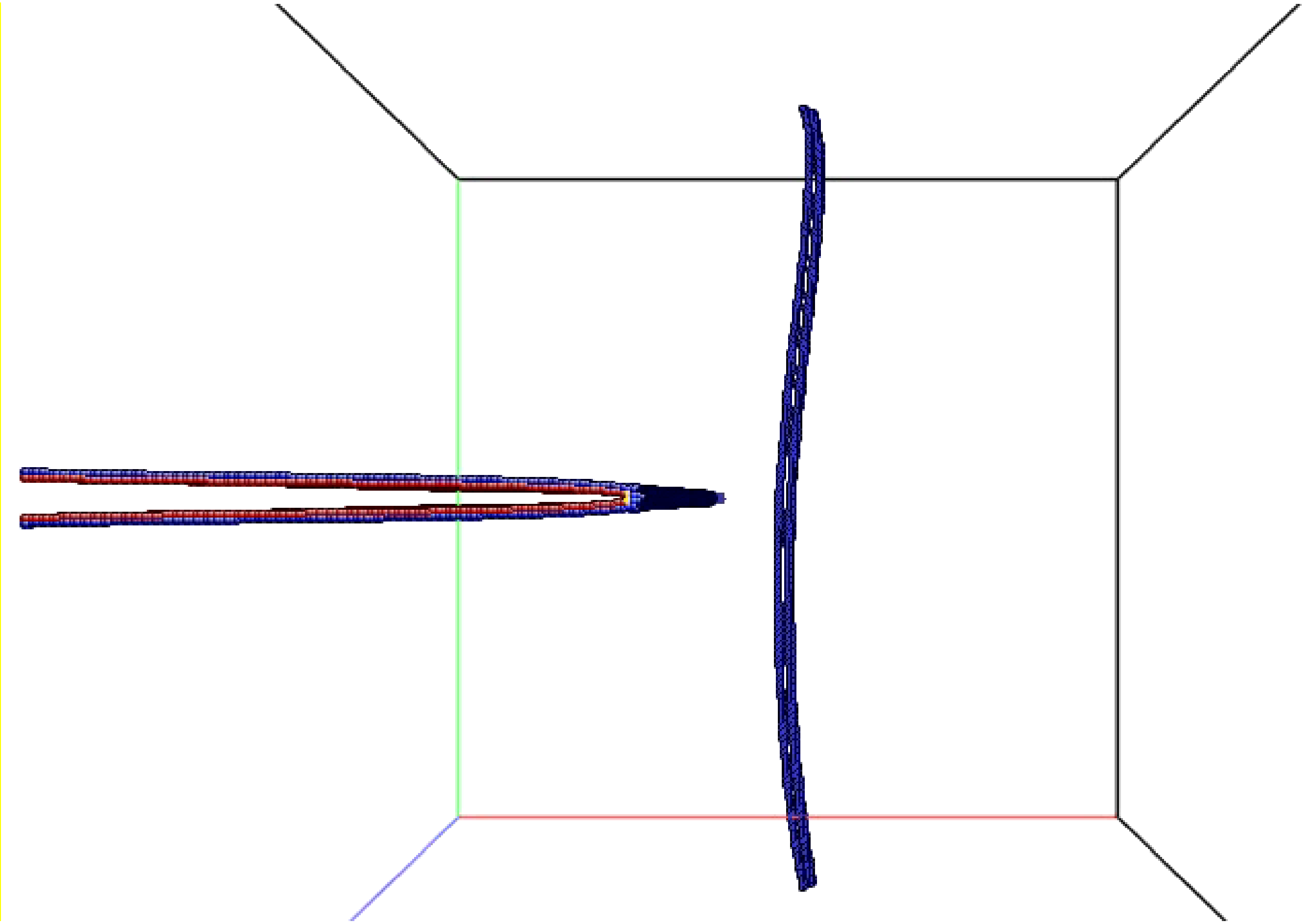
temperature

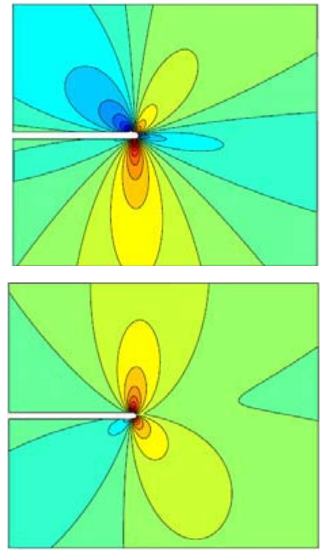
boundary conditions

…



Example: 60˚ dislocation DB(a)





stationary, blunted crack, 0.92ε_G

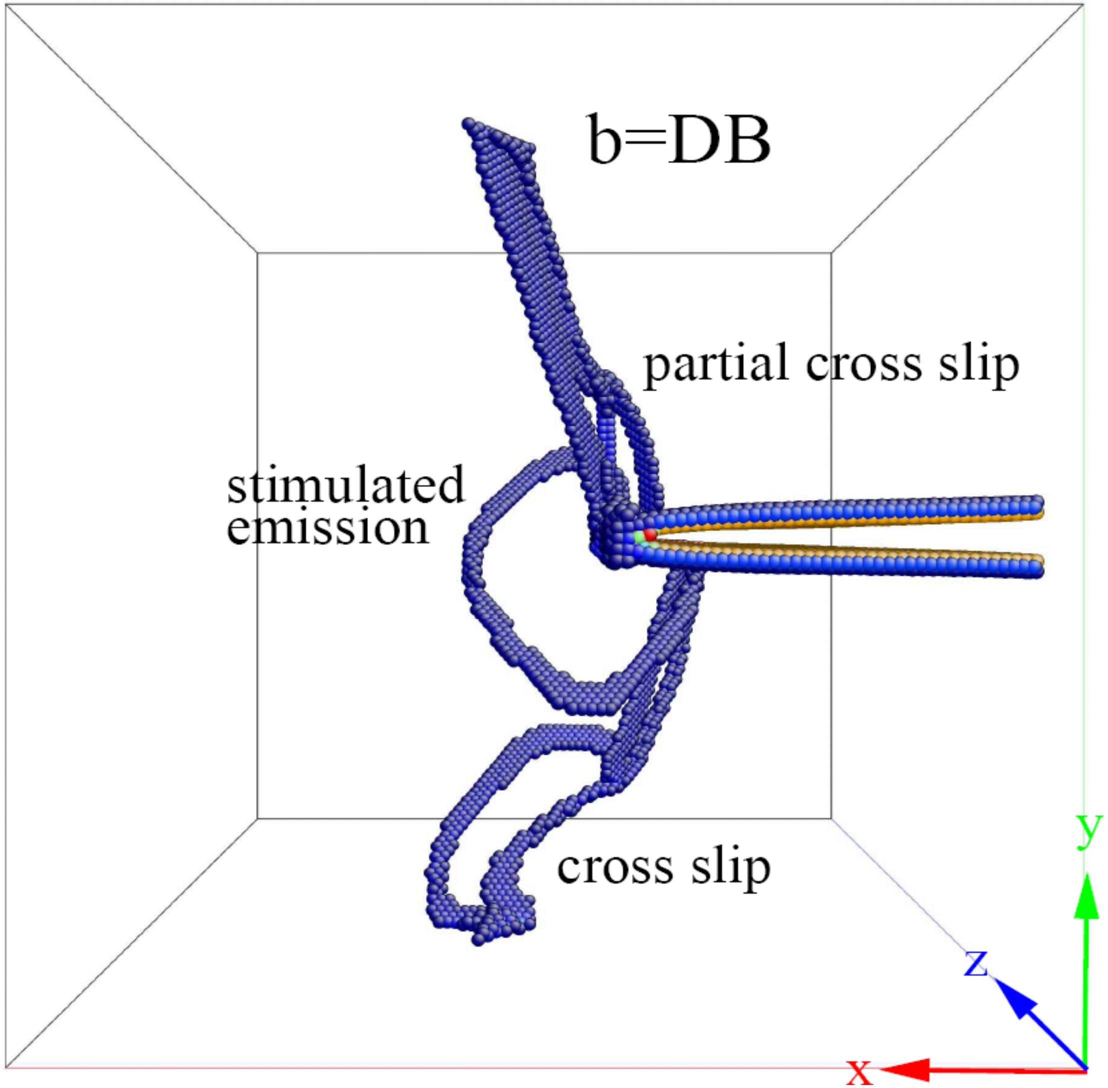
Typical processes for stationary crack

Stimulated dislocation emission

partial cross slip above crack front

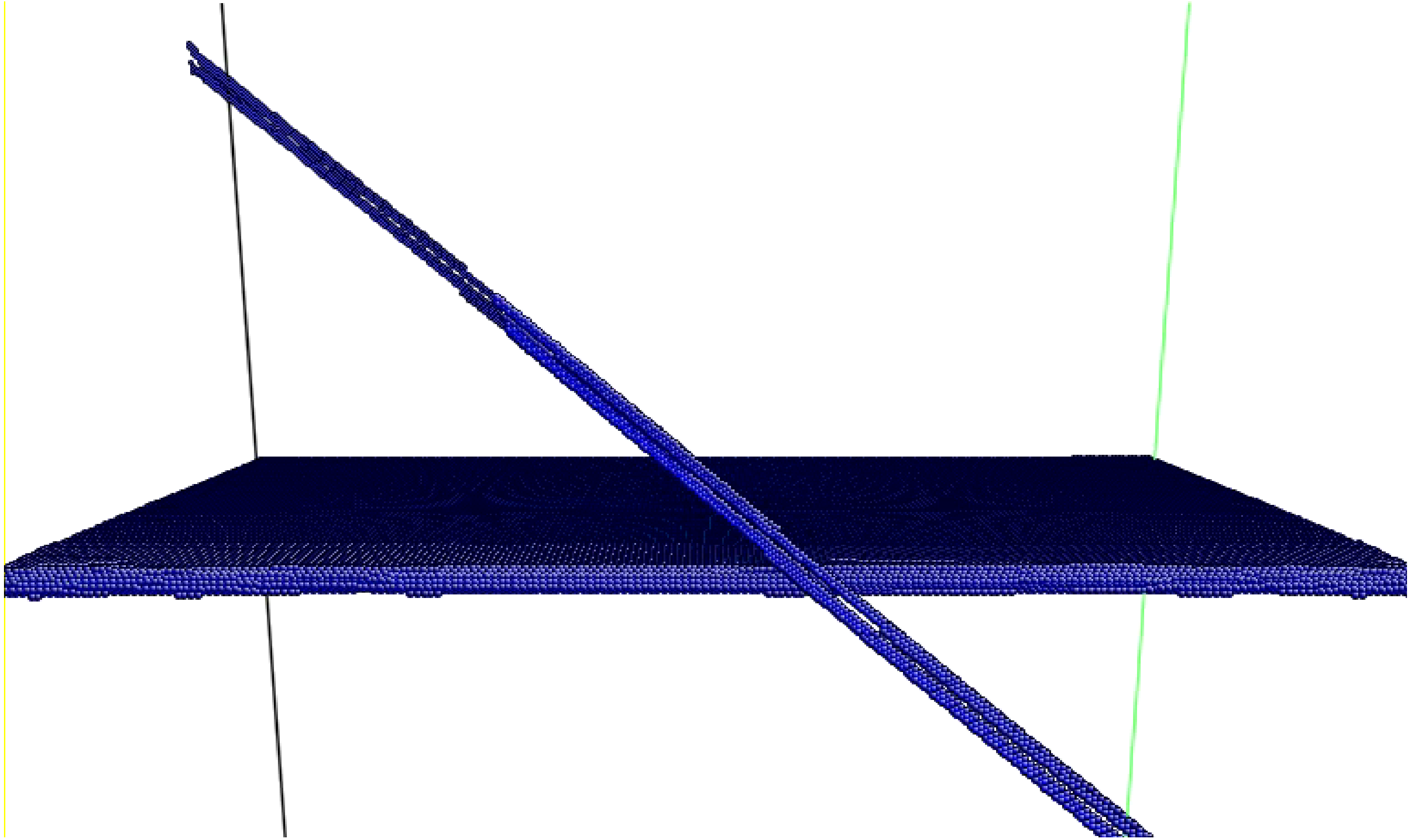
Cross slip of screw segments of incoming dislocations (Fleischer-mechanism)

(partial) crack opening or closing, local crack reorientation

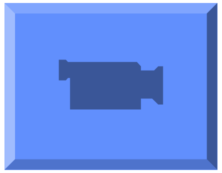


E. Bitzek and PG unpublished

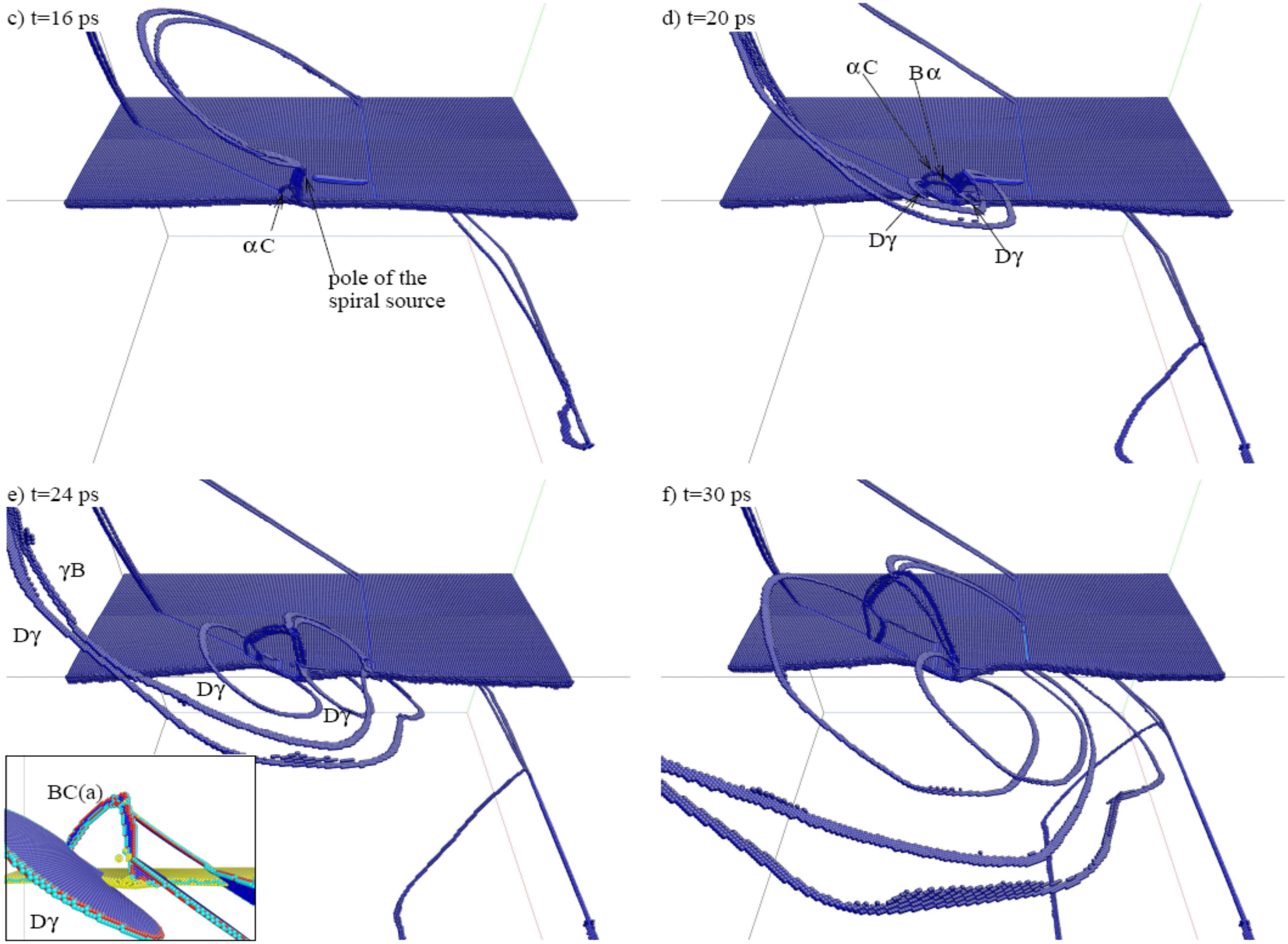
Example: screw dislocation DB(a)

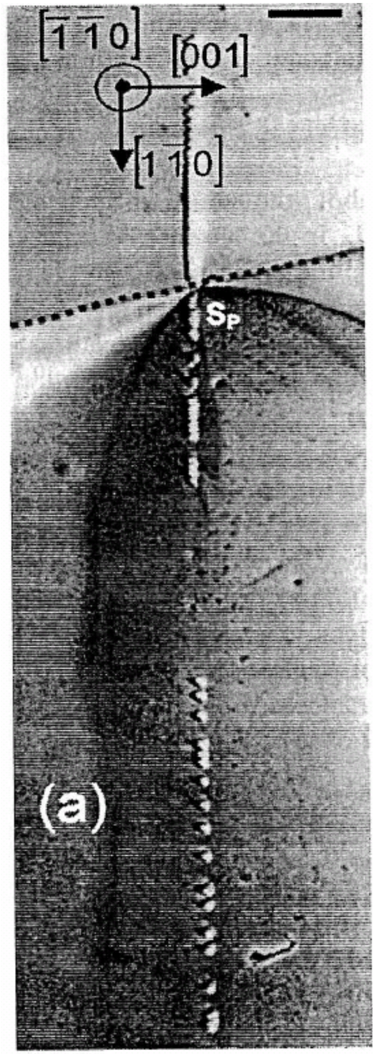


Stationary, sharp crack tip, ε_G

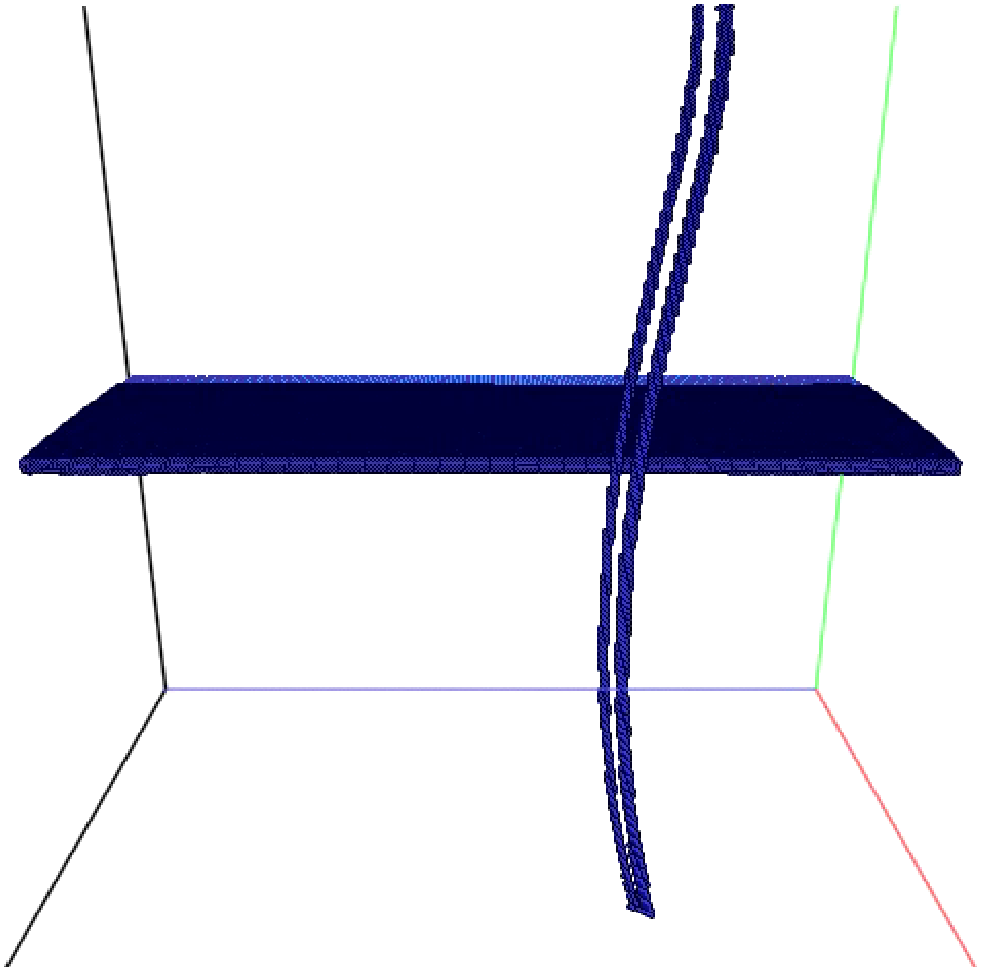


Spiral source at crack front:
(rare) one-Burgers vector source (Michot)





Propagating crack hits 60° DB(a)



dynamically propagating sharp crack, 1.04 ε_G

void

Interaction of propagating crack with dislocation

Blunting from dislocation emission leads to local reorientation/stoppage of the crack front

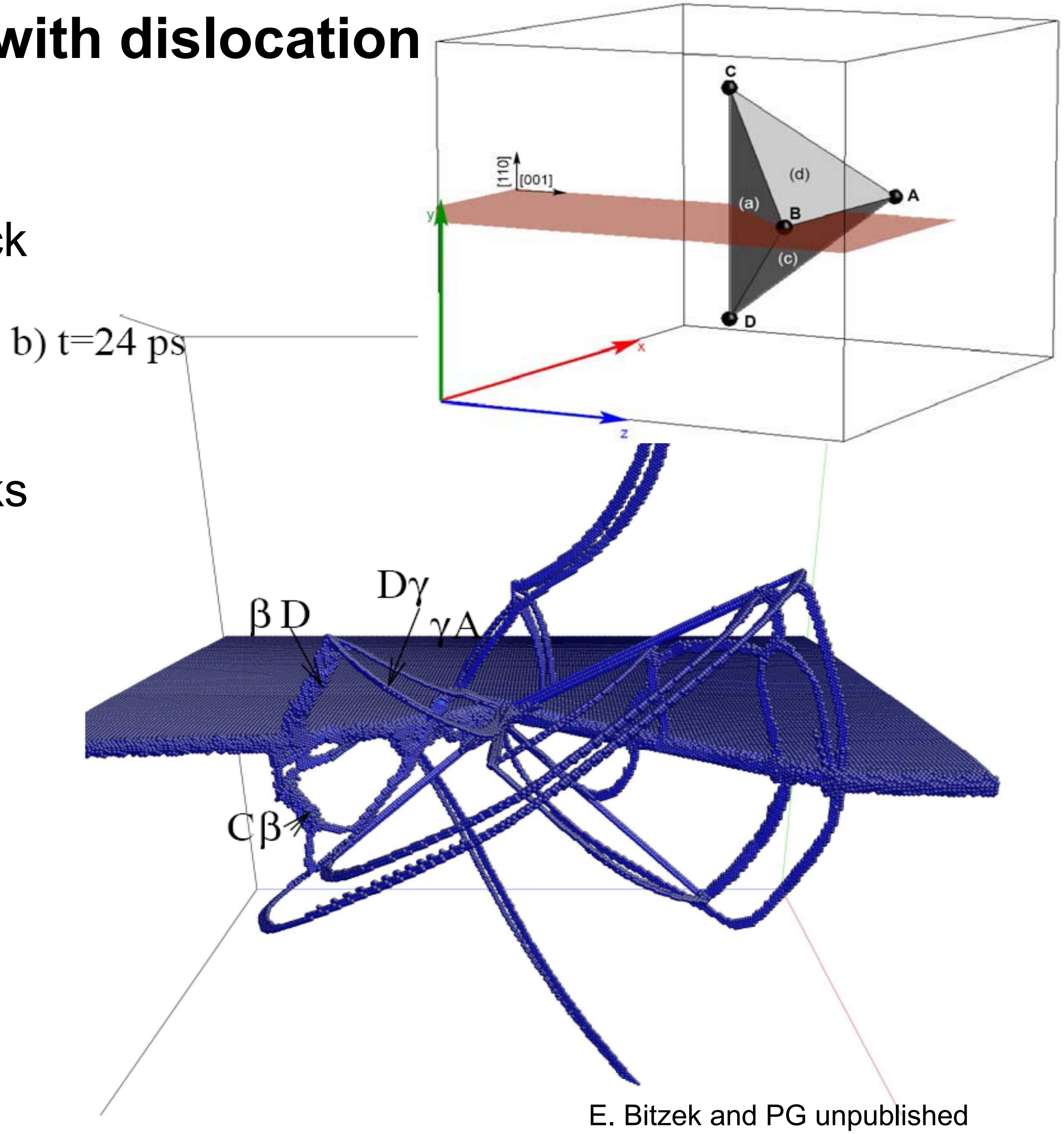
Specific to dynamically propagating cracks

Multiple active glide systems

- stationary crack experiments (George & Michot '93)

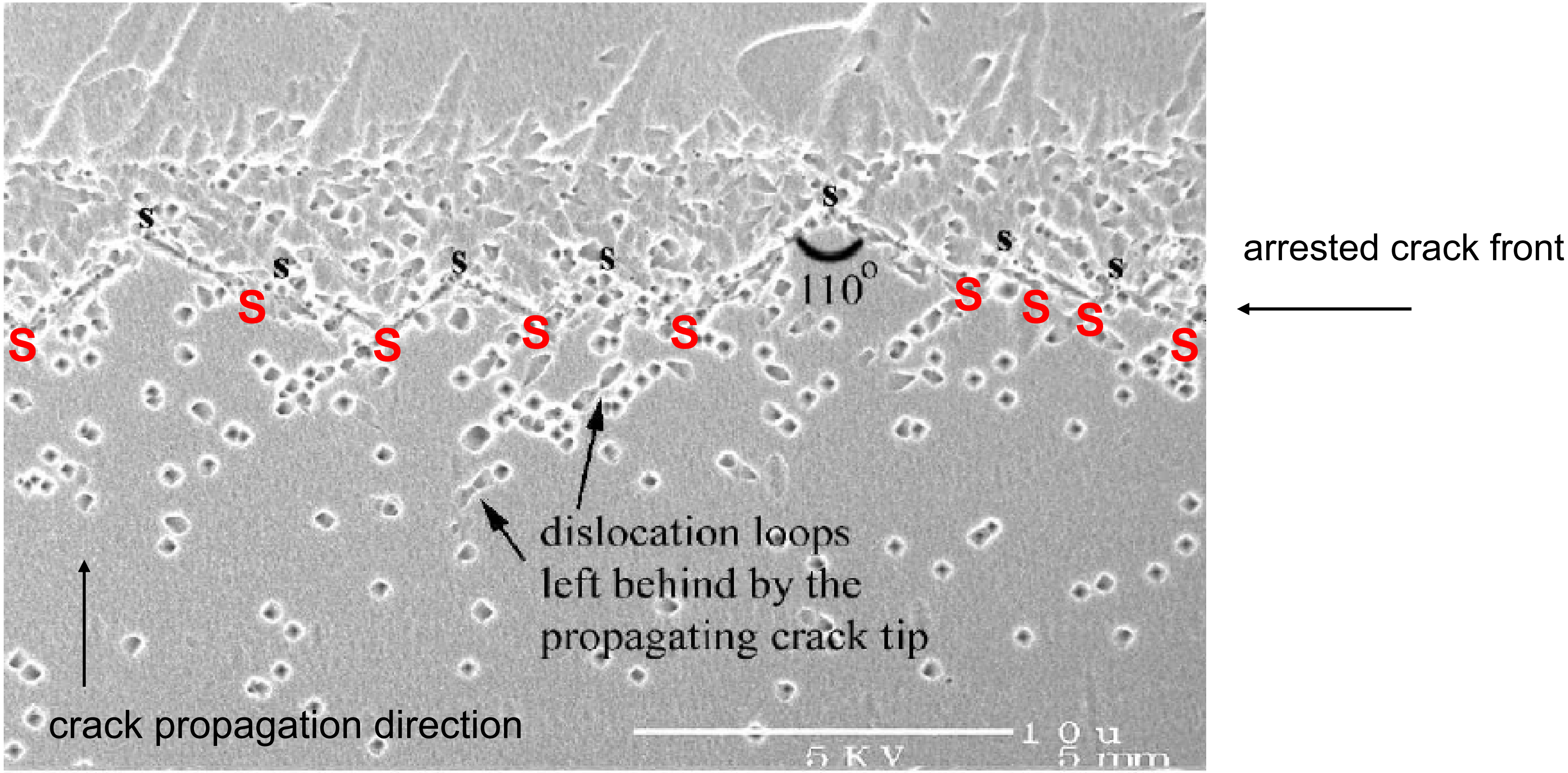
- crack arrest in T-gradient (Gally & Argon '00)

new model for V-sources



E. Bitzek and PG unpublished

Alternative explanation for V-sources



Gally & Argon '00: backward oriented emission of screw dislocations

Local reorientation of crack front due to emission of blunting dislocations

Conclusions (2)

Fracture is a true multi-scale problem

Brittle fracture but also dislocation nucleation from crack tips are atomistic in nature -> stimulated emission

Dependence of fracture toughness on temperature and strain rate correlates with mobility of dislocations in the field of the crack scaling relation, master curve

5th International Conference Multiscale Materials Modeling
MMM2010, Oct. 4-8 2010, Freiburg, Germany
also featuring symposia on
Tribology and Micromechanics

many projects on friction and fracture

phD students, PostDocs welcome

peter.gumbsch@kit.edu

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