1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2018

How to model chemical interactions

Lecture 6

Markus J. Buehler

Laboratory for Atomistic and Molecular Mechanics
Department of Civil and Environmental Engineering
Massachusetts Institute of Technology

E-mail: mbuehler@MIT.EDU

URL: http://web.mit.edu/mbuehler/www/

Massachusetts Institute of Technology

Content overview

I. Fundamentals of particle methods

Lectures 1-12
February/March

1. Atoms, molecules, chemistry
2. Statistical mechanics
3. Molecular dynamics, Monte Carlo
4. Visualization and data analysis
5. Mechanical properties – application: how things fail (and how to prevent it)
6. Multi-scale modeling paradigm
7. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Advanced topics in particle methods

Lectures 13-24
March/April/May

1. Quantum Weirdness: The Theory of Quantum Mechanics
2. The Many-Body Problem: From Many-Body to Single-Particle
3. Quantum modeling of materials
4. From Atoms to Solids
5. Basic properties of materials
6. Advanced properties of materials
7. Materials Informatics

Lecture 6: How to model chemical interactions

Outline:

1. Review
2. Example: Model of fracture of brittle materials

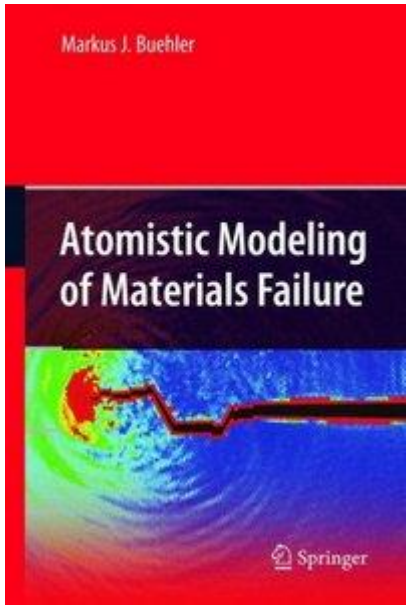
Goal of today's lecture:

- Get to know basic methods to model chemical bonds (starting with simple "pair potentials")
- Practice problem
- Learn how to identify parameters for models of chemical bonds (for pair potentials)
- Case study of brittle fracture
  - Movies, etc.

Optional reading assignments

"Atomistic Modeling of Materials Failure"

- Chapter 2, pp. 31-54 and pp. 90-94
- Chapter 4, pp. 132-142
- Chapter 6, pp. 185-201 (brittle fracture)



http://www.springer.com/us/book/9780387764252#otherversion=9781441945518

Further reading…

Chapters of particular relevance

The Materiome
Pages 27-60

Computational Approaches and Simulation
Pages 213-263

Mechanical Characterization in Molecular Simulation
Pages 265-296

http://www.springer.com/us/book/9789400716100

Other books, reading

- M. P. Allen, D. J. Tildesley (1989) Computer simulation of liquids. Oxford University Press. ISBN 0-19-855645-4.
- D. C. Rapaport (1996) The Art of Molecular Dynamics Simulation. ISBN 0-521-44561-2.
- Frenkel, Daan; Smit, Berend (2002) [2001]. Understanding Molecular Simulation : from algorithms to applications. San Diego: Academic Press. ISBN 0-12-267351-4.
- J. M. Haile (2001) Molecular Dynamics Simulation: Elementary Methods. ISBN 0-471-18439-X
- Andrew Leach (2001) Molecular Modelling: Principles and Applications. (2nd Edition) Prentice Hall. ISBN 978-0-582-38210-7.

1. Review

Atomic interactions – different types of chemical bonds

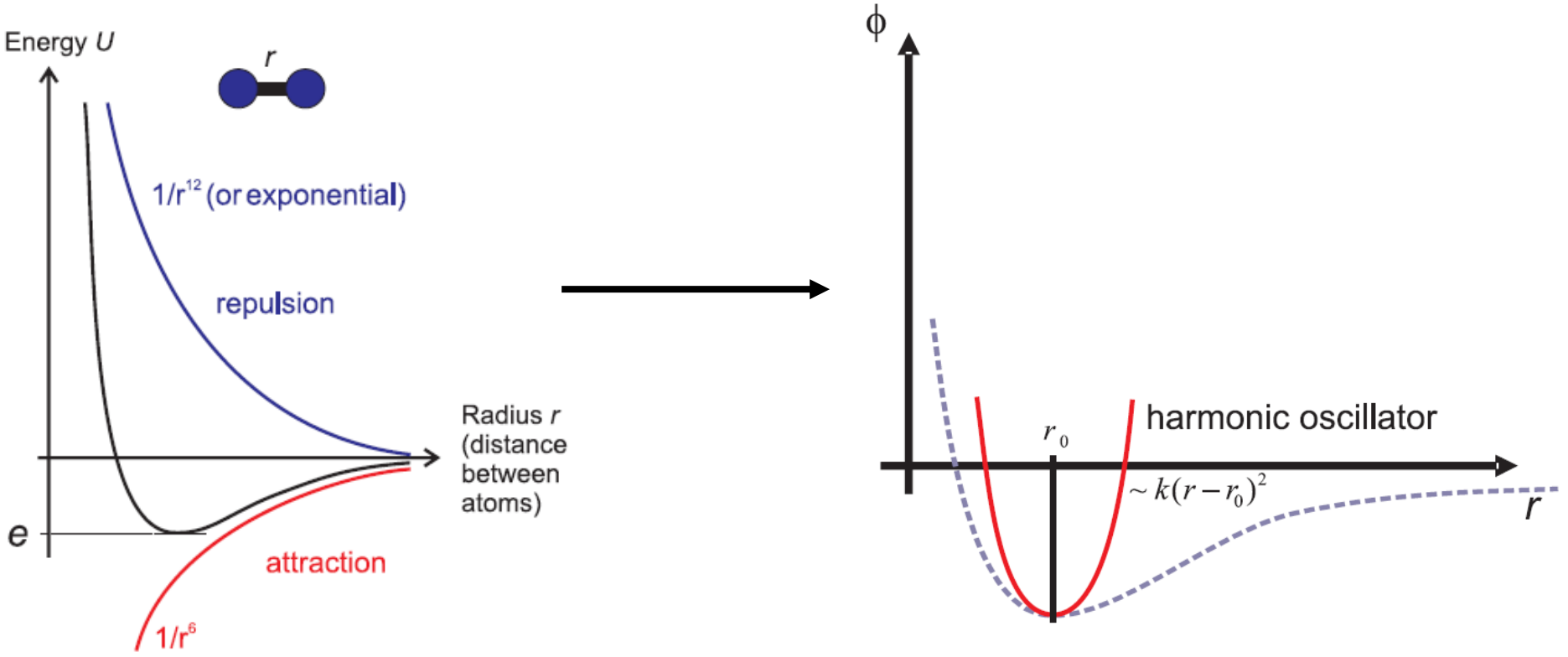
- **Primary bonds (“strong”)**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver)
    (high melting point, 1000-5,000K)

- **Secondary bonds (“weak”)**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)
    (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

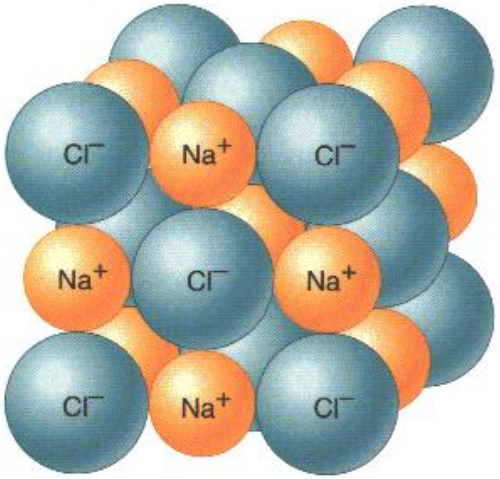
Difference of material properties originates from different atomic interactions

Interatomic bond - model



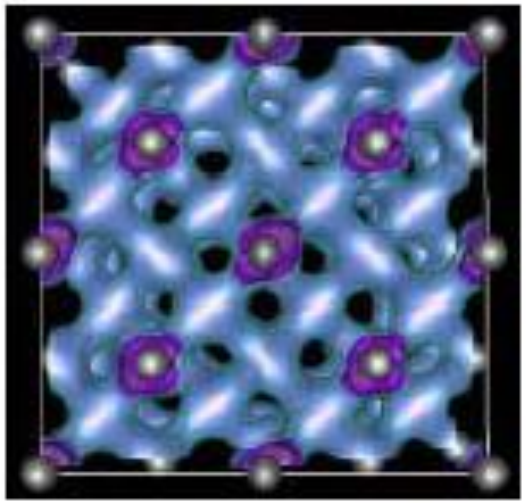
Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)

Types of bonding (illustrations)



charge
+/-

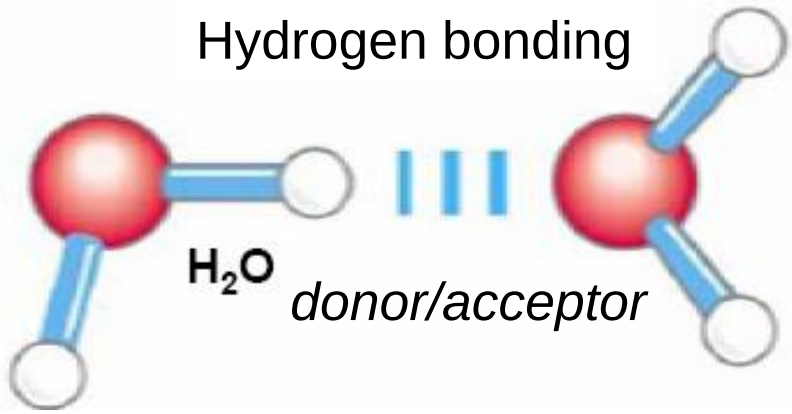
Ionic bonding



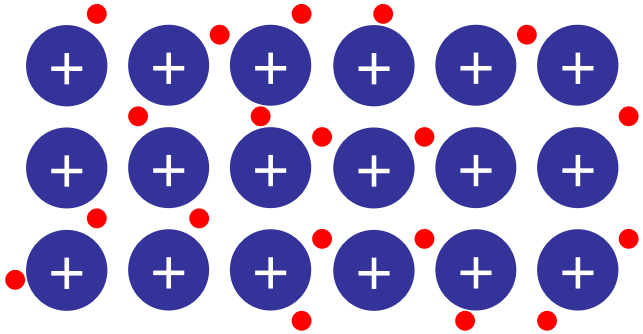
electron density (localized!)

Covalent bonding

Hydrogen bonding



donor/acceptor



Metallic bonding

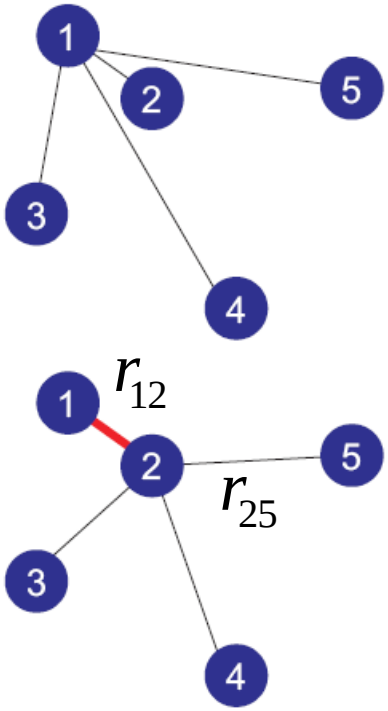
After: Pavel Korzhavyi, *Royal Institute of Technology (KTH)*

Overview - pair potentials: total energy calculation

Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system

Pair wise interaction potential

$$\phi(r_{ij})$$



Pair wise summation of bond energies

Energy of atom i $$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$

avoid double counting

$$U_{total} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij})$$

$r_{ij} =$ distance between particles i and j

Interatomic pair potentials: examples

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Morse potential

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Lennard-Jones 12:6 potential
(excellent model for noble Gases, Ar, Ne, Xe..)

$$\phi(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\sigma}\right) - C\left(\frac{\sigma}{r_{ij}}\right)^{6}$$

Buckingham potential

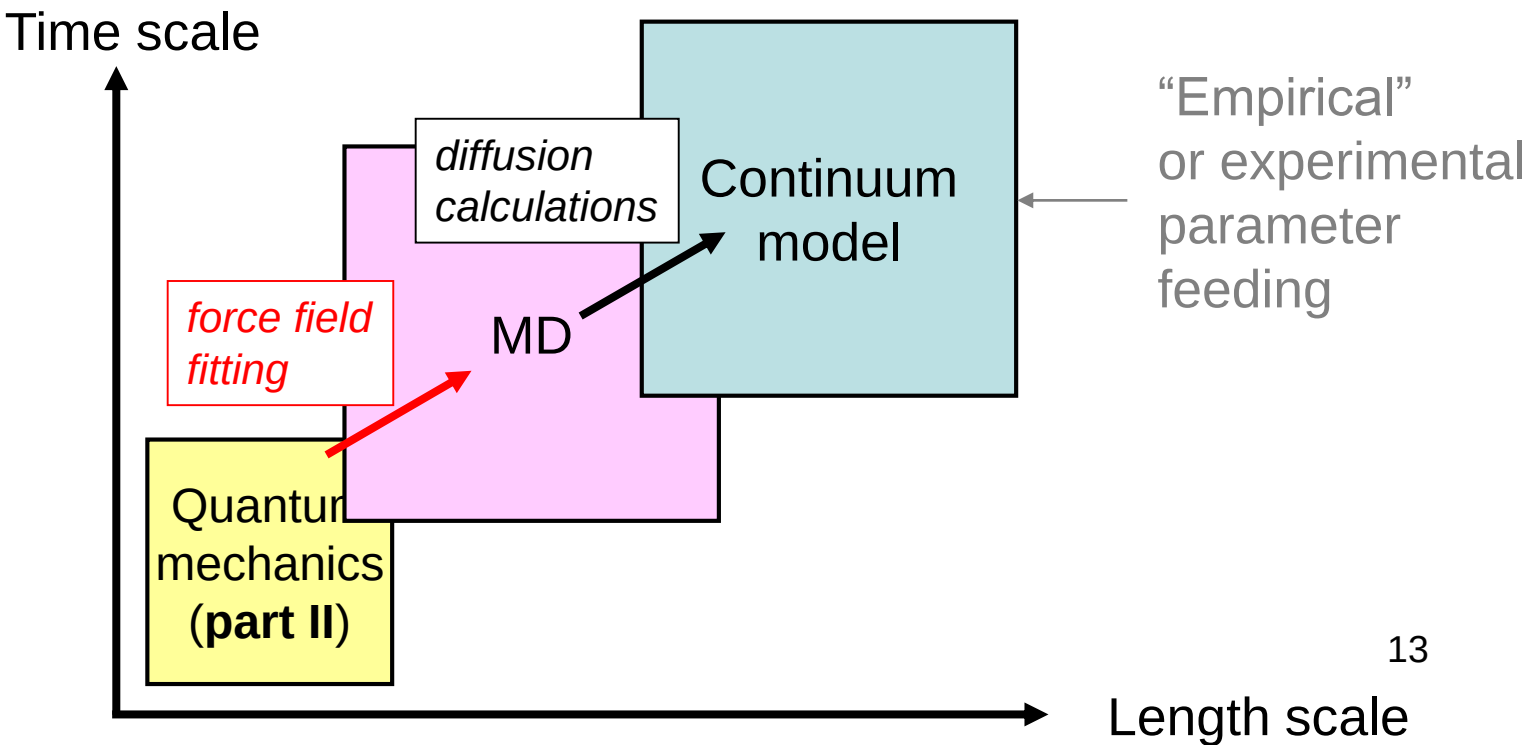
$$\phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij}-r_0)^2$$

Harmonic approximation
(no bond breaking)

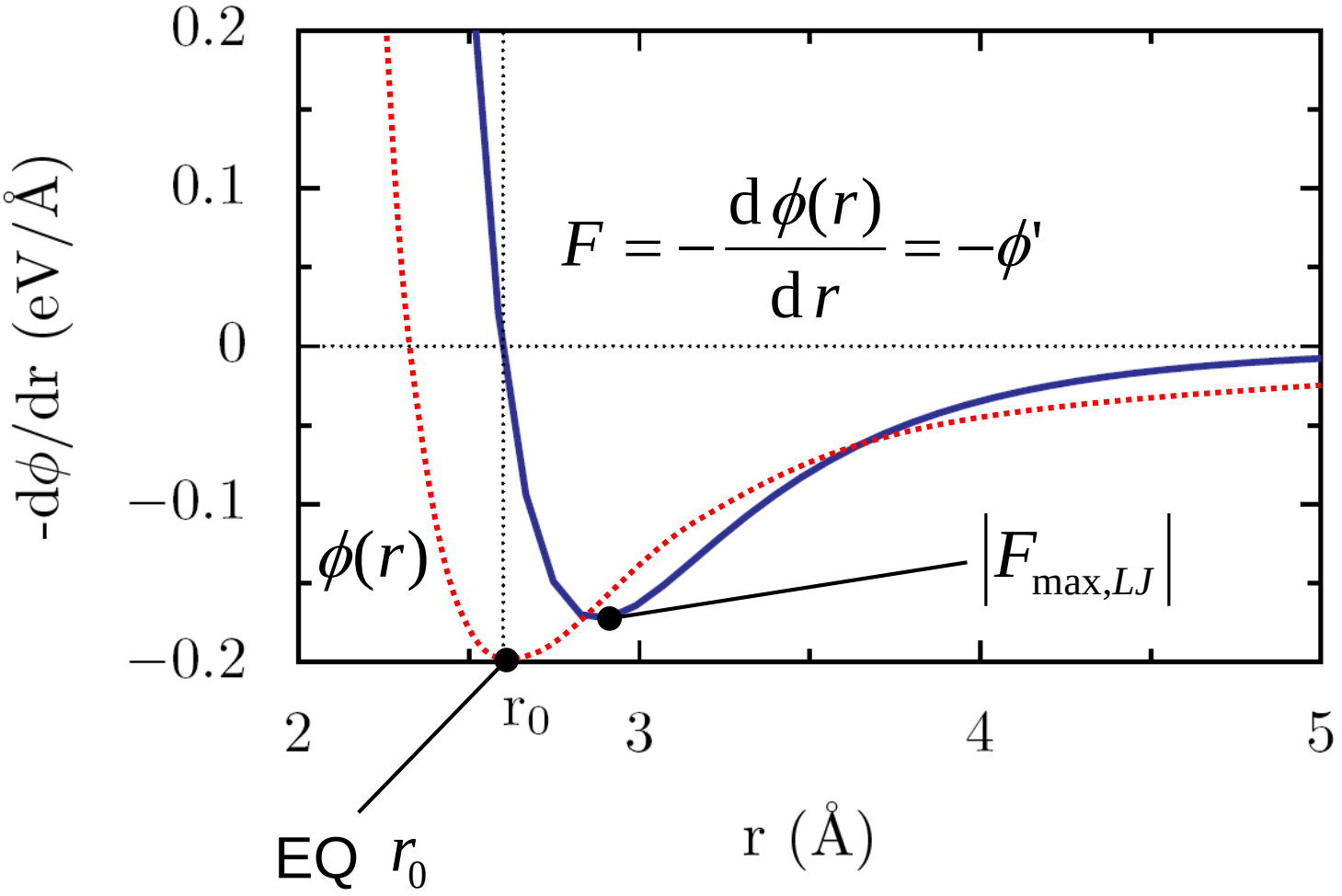
Multi-scale paradigm

- Show earlier: molecular dynamics provides a powerful approach to relate the diffusion constant that appears in continuum models to atomistic trajectories

- Force field fitting to identify parameters for potentials (based on quantum mechanical results) is yet another “step” in this multi-scale paradigm



Derivative of LJ potential ~ force



relates to equilibrium spacing crystal

Properties of LJ potential as function of parameters ε, σ

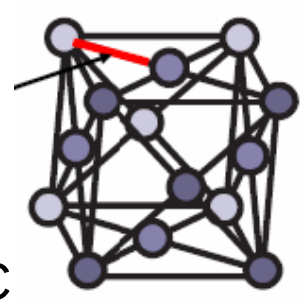
Equilibrium distance between atoms r_0 and maximum force

$$\sigma\sqrt[6]{2} = r_0 \qquad F_{\max,LJ} = \frac{2.394\varepsilon}{\sigma}$$

first derivative zero (force)

second derivative zero (=loss of convexity, spring constant=0)

Copper, NN: 2.556 Å (a_0=3.615 Å))



FCC

$r_0 =$ distance of nearest neighbors in a lattice

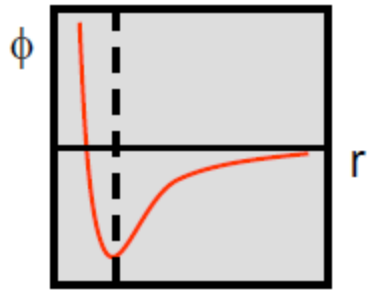
Case study: plasticity in a micrometer crystal of copper

Simulation details

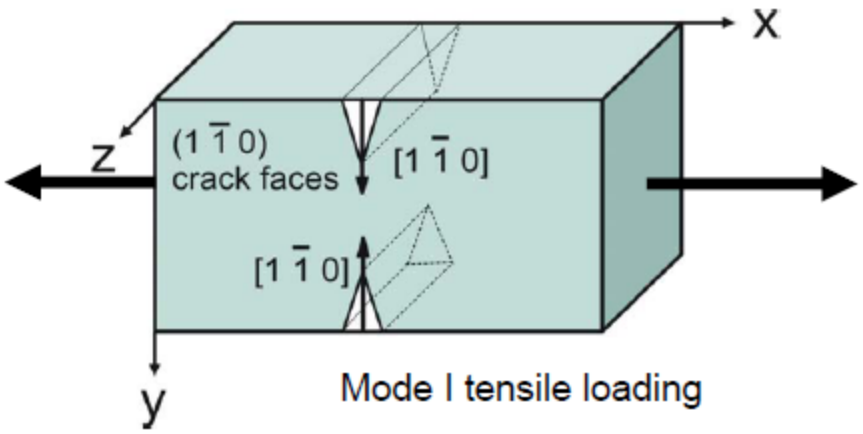
- 1,000,000,000 atoms (0.3 micrometer side length)

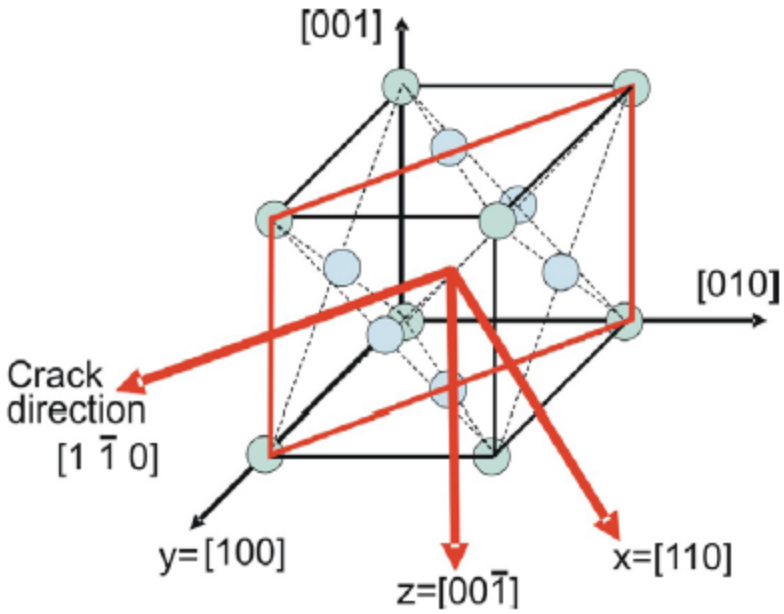
- 12:6 Lennard-Jones ductile material, for copper

- Visualization using energy filtering method (only show high energy atoms)

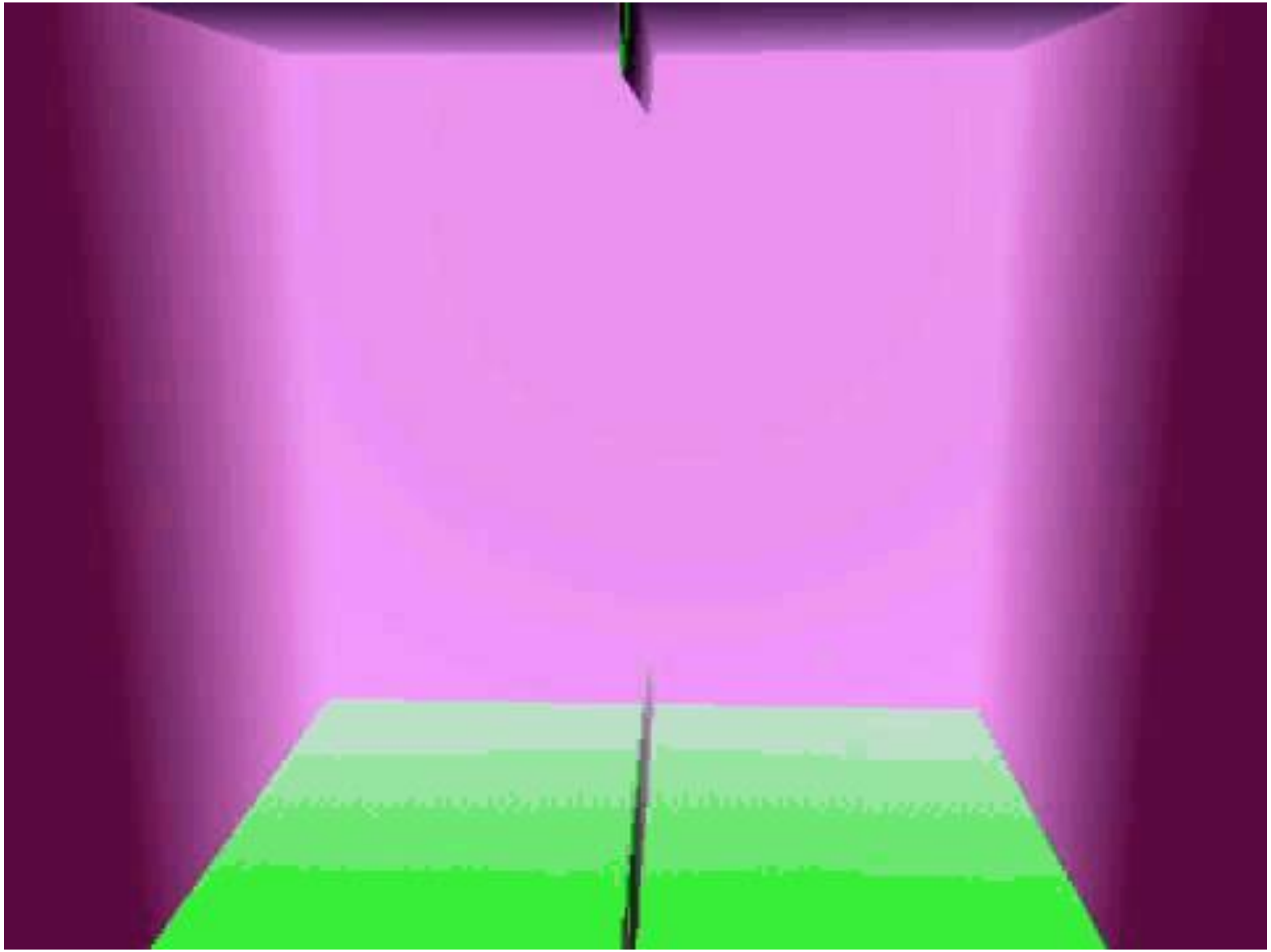


Generic features of atomic bonding: „repulsion vs. attraction“

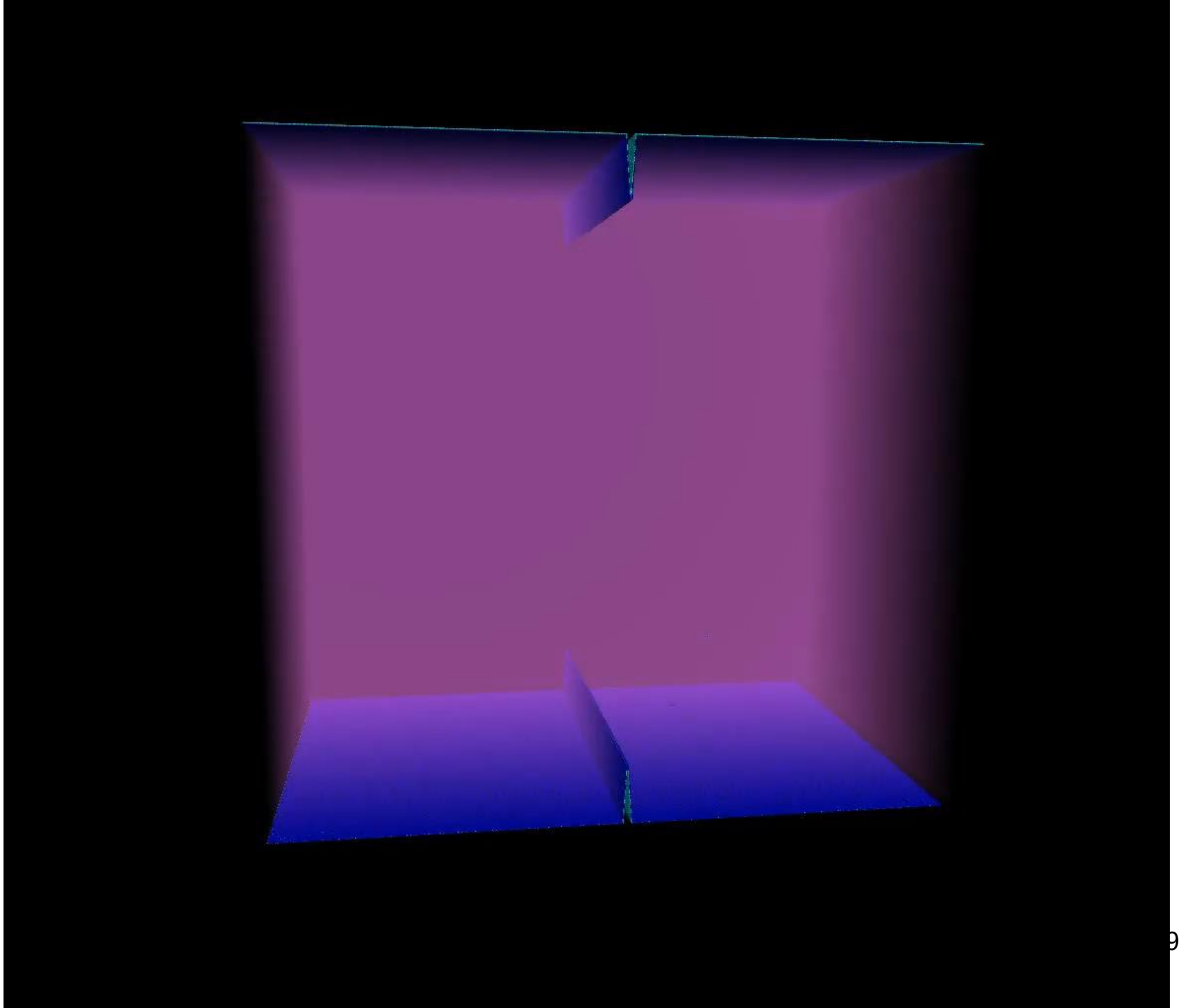




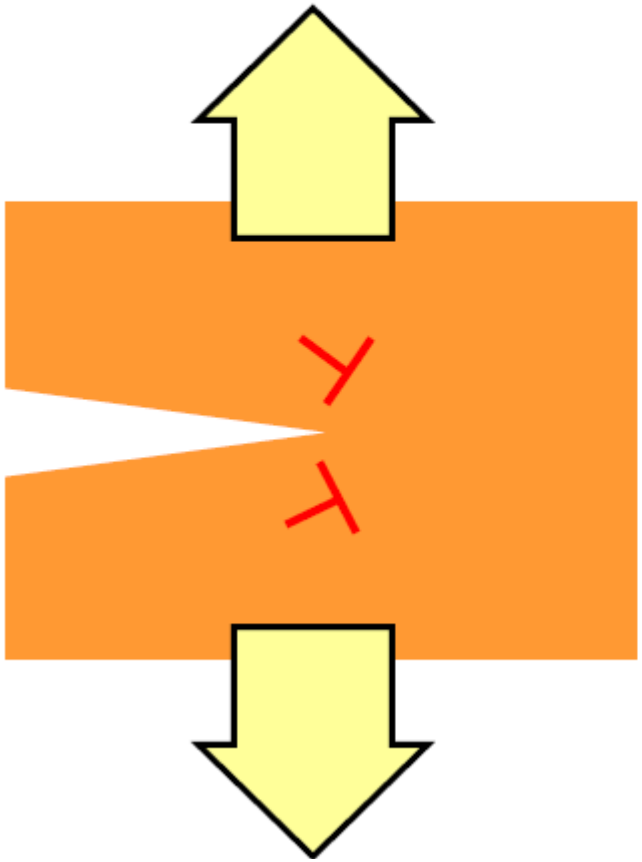
A simulation with 1,000,000,000 particles
Lennard-Jones - copper

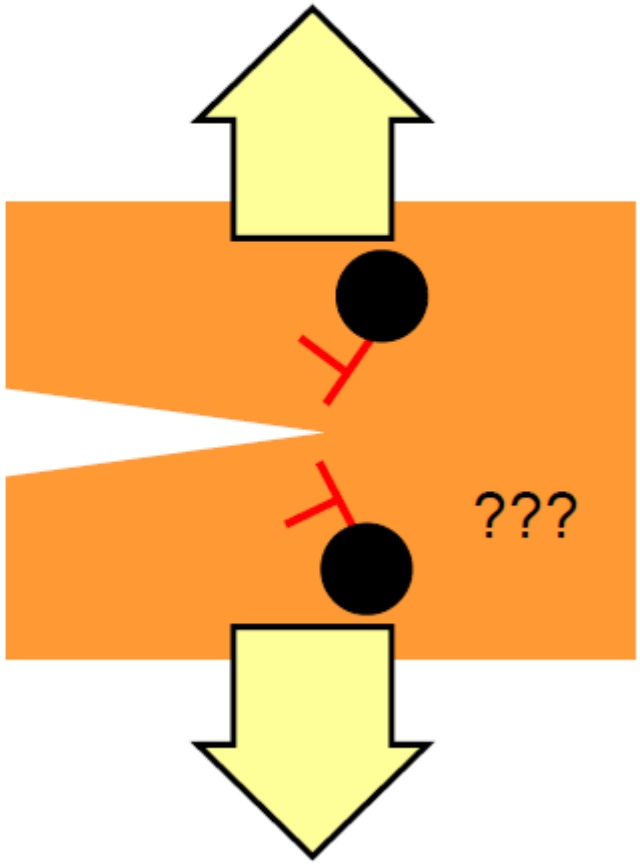


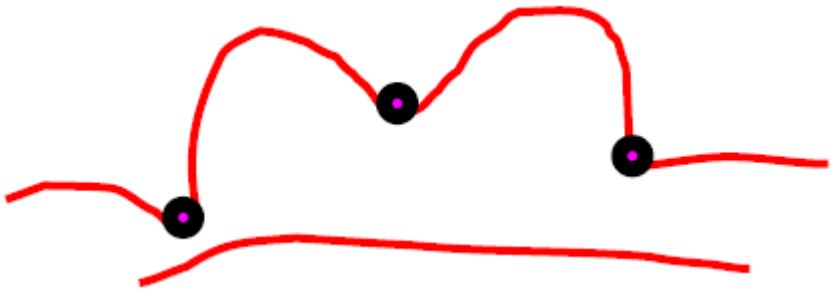
F.F. Abraham, *et al*., 2000



Strengthening mechanisms

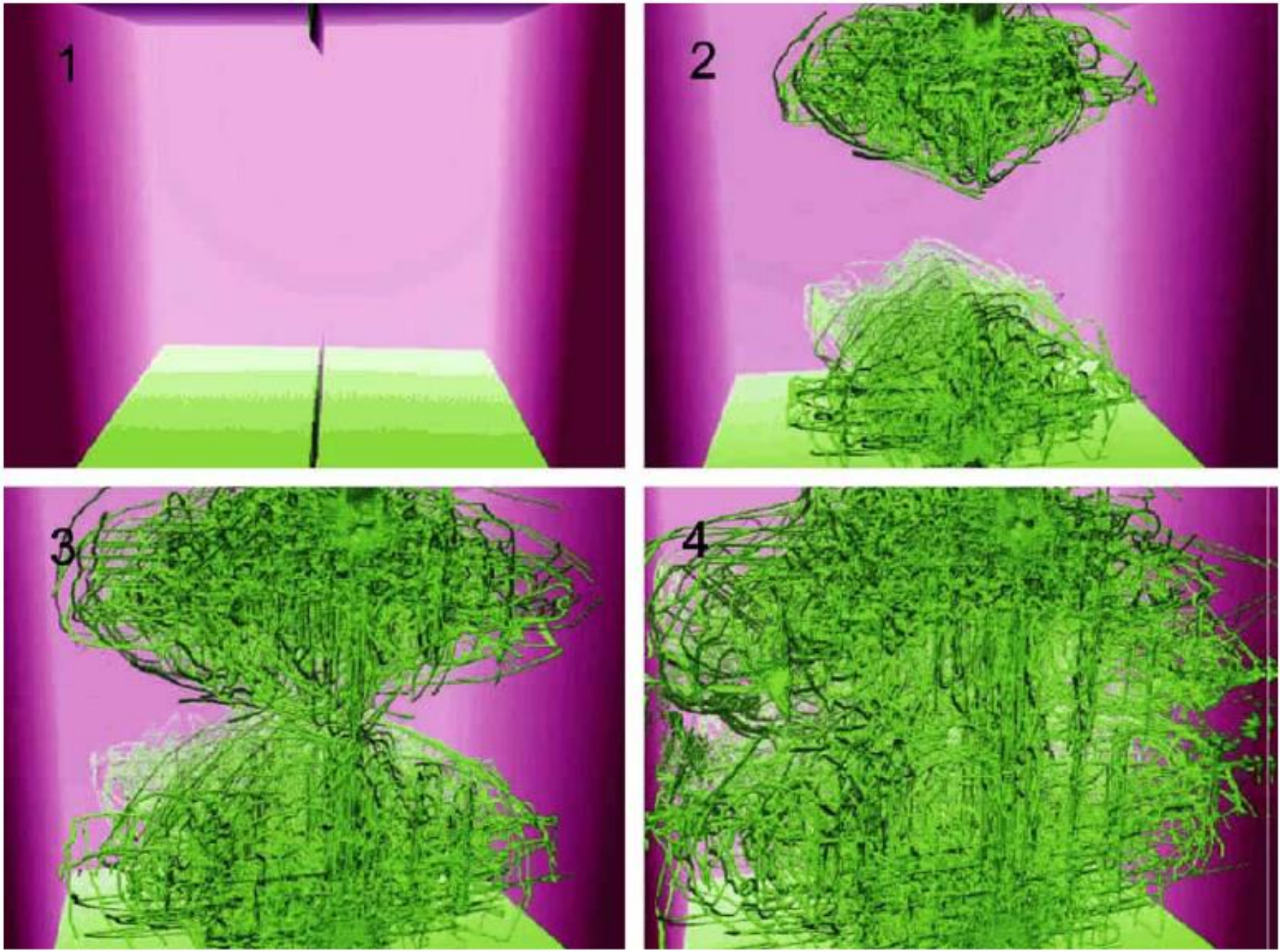


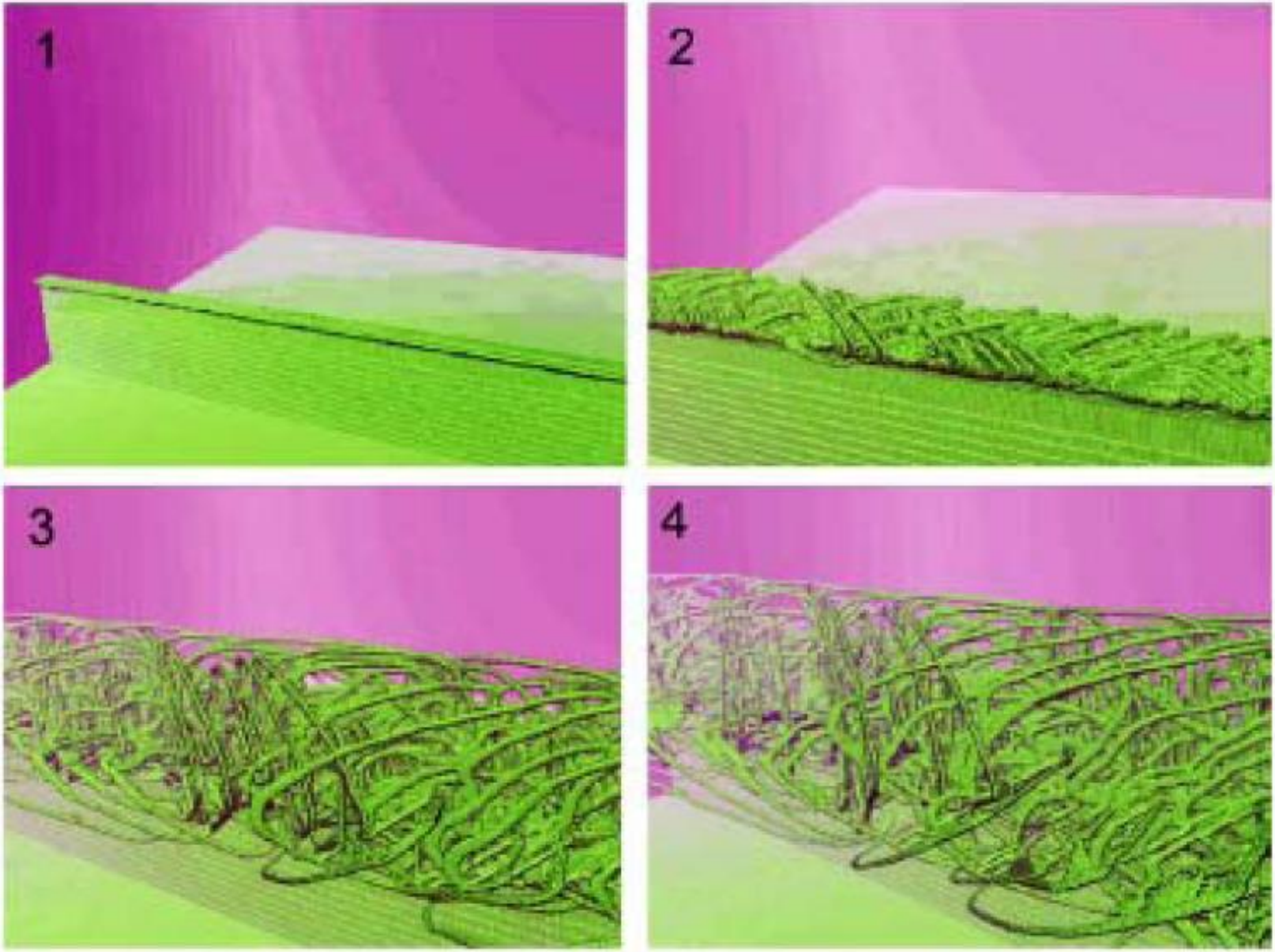




Strengthening caused by hindering dislocation motion

If too difficult, ductile modes break down and material becomes brittle


1
2
3
4


1
2
3
4

MD updating scheme: Complete

(1) Updating method (integration scheme)

$$r_i(t_0+\Delta t) = -r_i(t_0-\Delta t) + 2r_i(t_0)\Delta t + a_i(t_0)(\Delta t)^2 + \ldots$$

Positions at t_0-Δt | Positions at t_0 | Accelerations at t_0

(2) Obtain accelerations from forces

$$f_i = ma_i \qquad a_i = f_i / m$$

(3) Obtain forces from potential

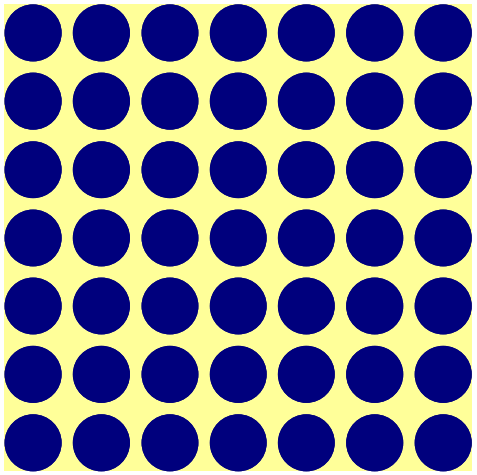
$$F = -\frac{\mathrm{d}\,\phi(r)}{\mathrm{d}\,r} \qquad f_i = F\,\frac{x_i}{r}$$

Potential

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

(4) Crystal (initial conditions)

Positions at t_0



Practice problem

Pair potential formulation

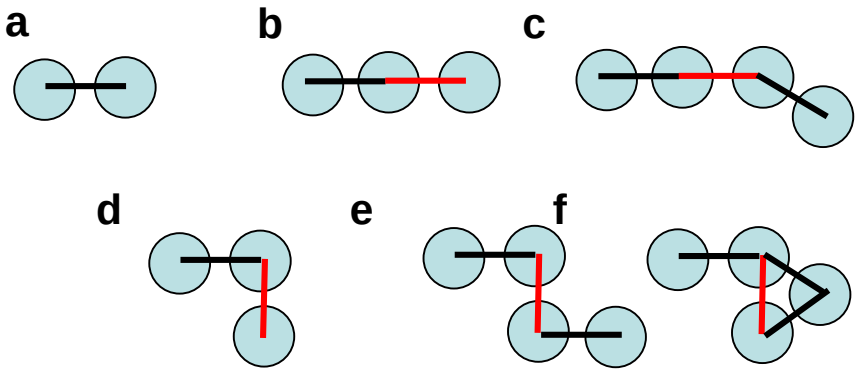
1. List **all parameters** and their respective dimension for the following pair potentials:

   Lennard-Jones
   Morse
   Harmonic

2. Explain the **physical meaning** of each parameter in the **harmonic potential.**

3. Explain the **physical meaning** of each parameter in the **Morse potential.** To solve this problem sketch the Morse potential for different parameter choices and observe changes in the potential shape.

4. Calculate the **potential energy** for the structures shown below (lines between atoms indicate equal distance at r_0), for a Morse pair potential, with cutoff $r_{cut} = 1.1\ r_0$



Morse potential

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Lennard-Jones (LJ) potential

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Harmonic potential

$$\phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij}-r_0)^2$$

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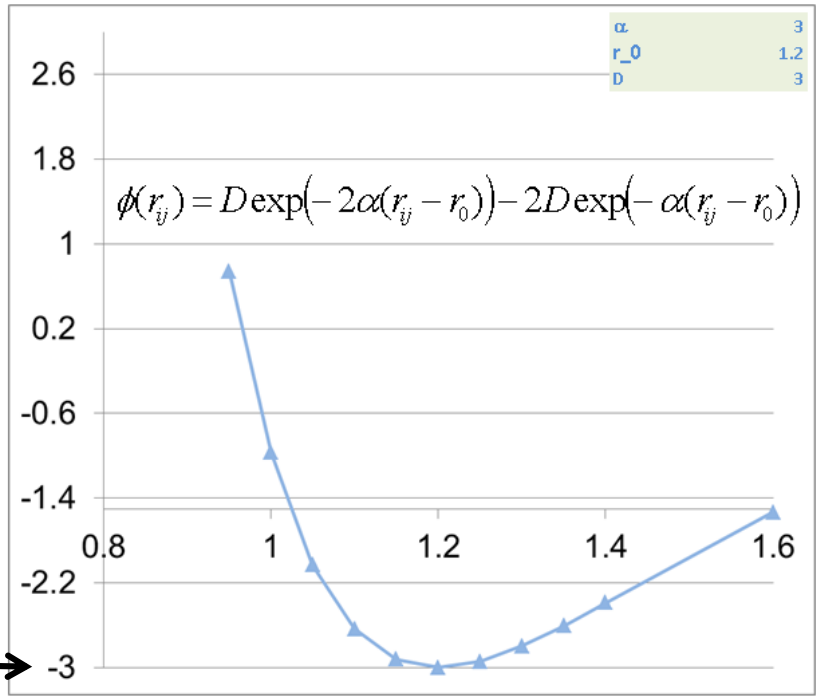
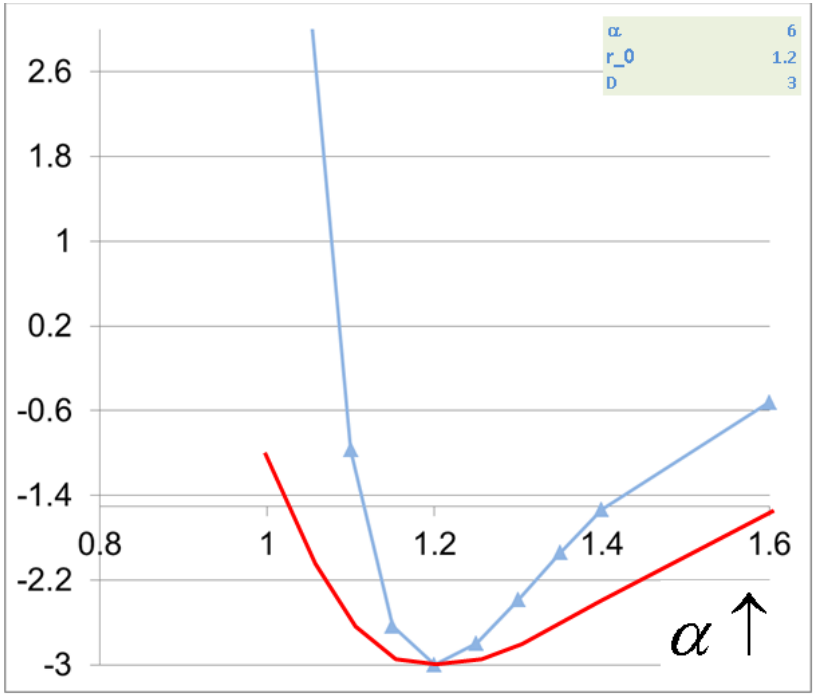
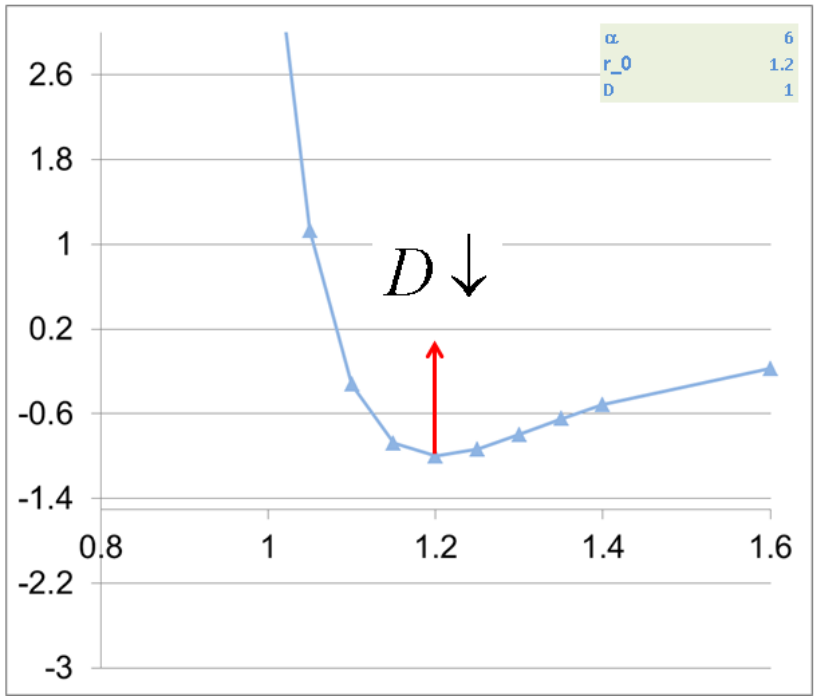
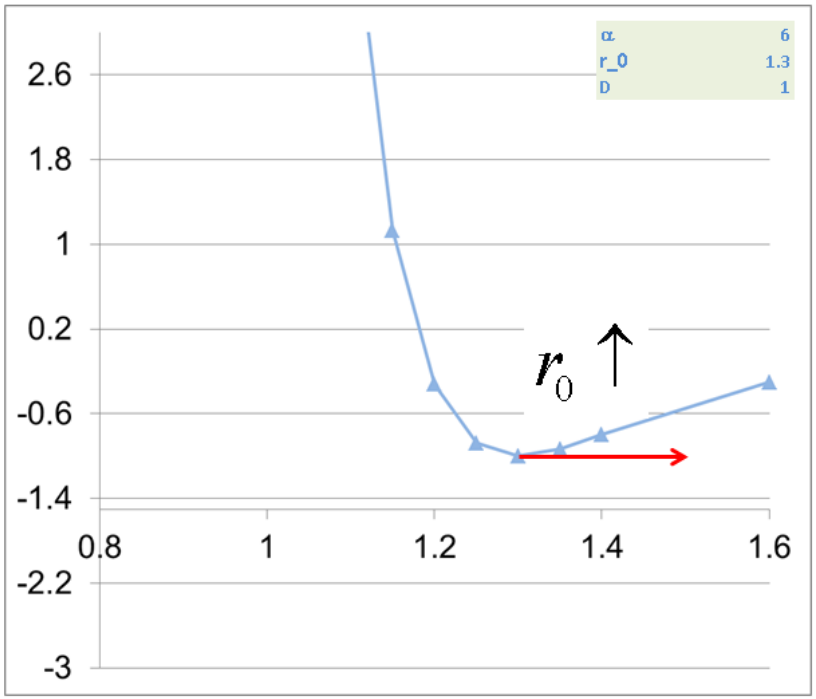

α 3
r_0 1.2
D 3
$\phi(r_{ij}) = D\exp(-2\alpha(r_{ij}-r_0)) - 2D\exp(-\alpha(r_{ij}-r_0))$
2.6
1.8
1
0.2
-0.6
-1.4
-2.2
-3
0.8
1
1.2
1.4
1.6

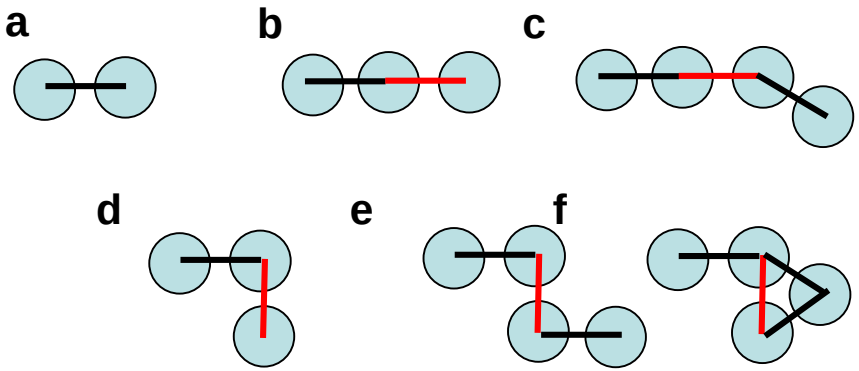
-D →


α 6
r_0 1.2
D 3
2.6
1.8
1
0.2
-0.6
-1.4
-2.2
-3
0.8
1
1.2
1.4
1.6
α ↑


α 6
r_0 1.2
D 1
2.6
1.8
1
0.2
-0.6
-1.4
-2.2
-3
0.8
1
1.2
1.4
1.6
D ↓


α 6
r_0 1.3
D 1
2.6
1.8
1
0.2
-0.6
-1.4
-2.2
-3
0.8
1
1.2
1.4
1.6
r_0 ↑

4. Calculate the **potential energy** for the structures shown below (lines between atoms indicate equal distance at r_0), for a Morse pair potential, with cutoff $r_{cut} = 1.1\ r_0$

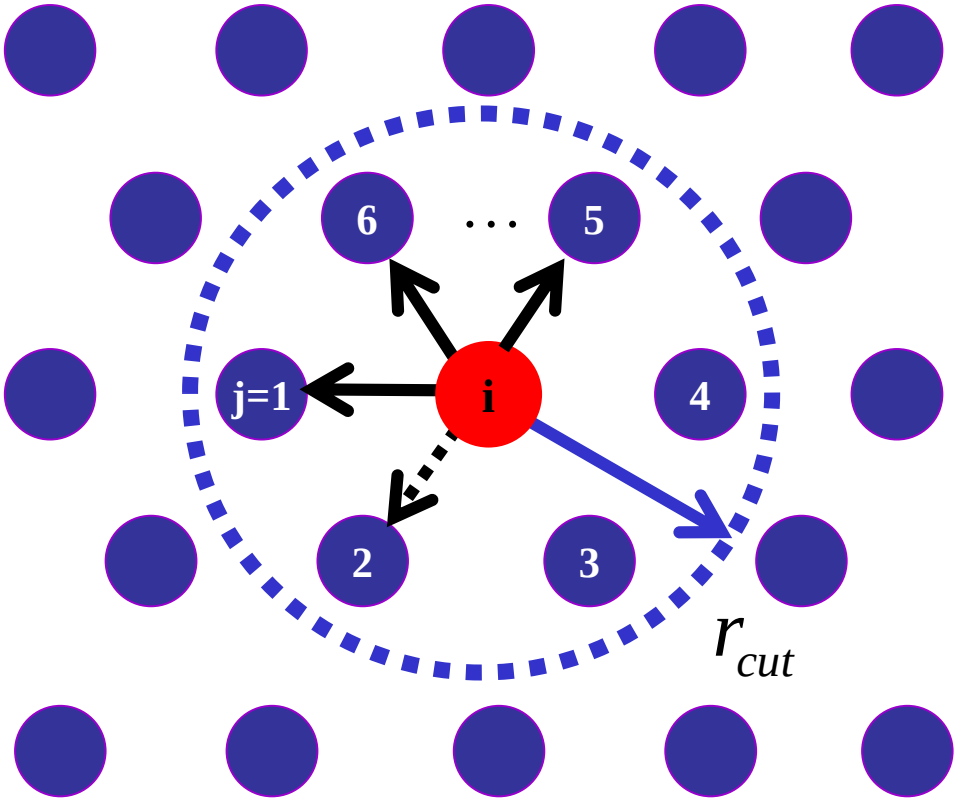


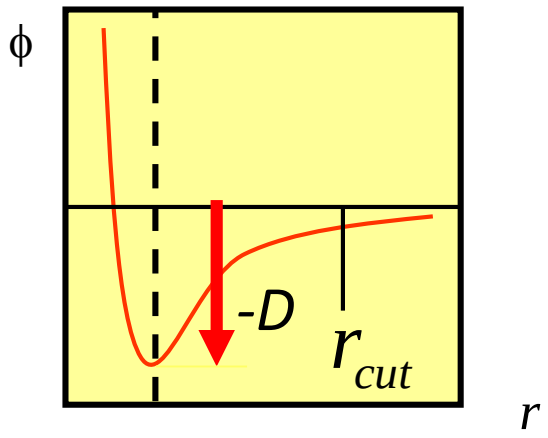
Cutoff radius

$$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$

$$\downarrow$$

$$U_i = \sum_{j=1..N_{neigh}} \phi(r_{ij})$$

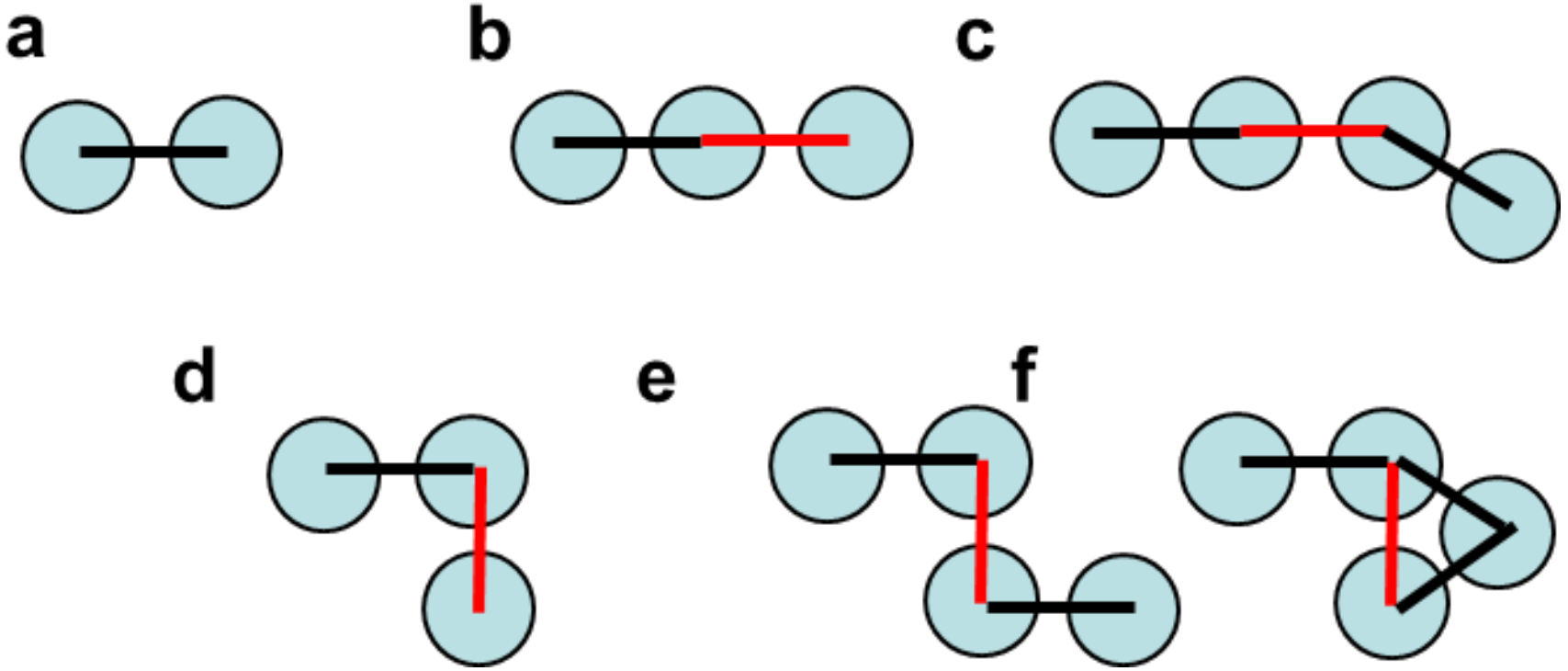




Cutoff radius = considering interactions only to a certain distance
Basis: Force contribution negligible (slope)

Practice problem

4. Calculate the **potential energy** for the structures shown below (lines between atoms indicate equal distance at r_0), for a Morse pair potential, with cutoff $r_{cut} = 1.1\ r_0$



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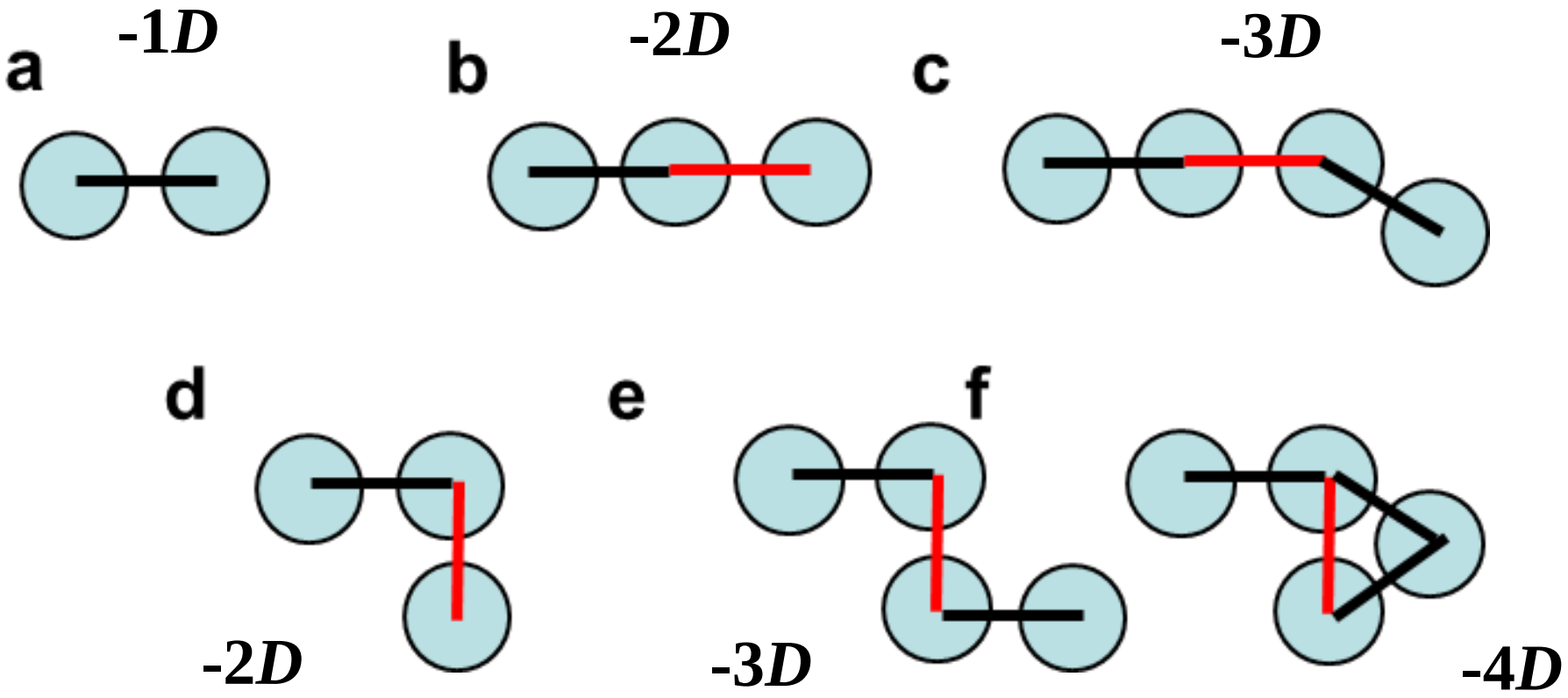
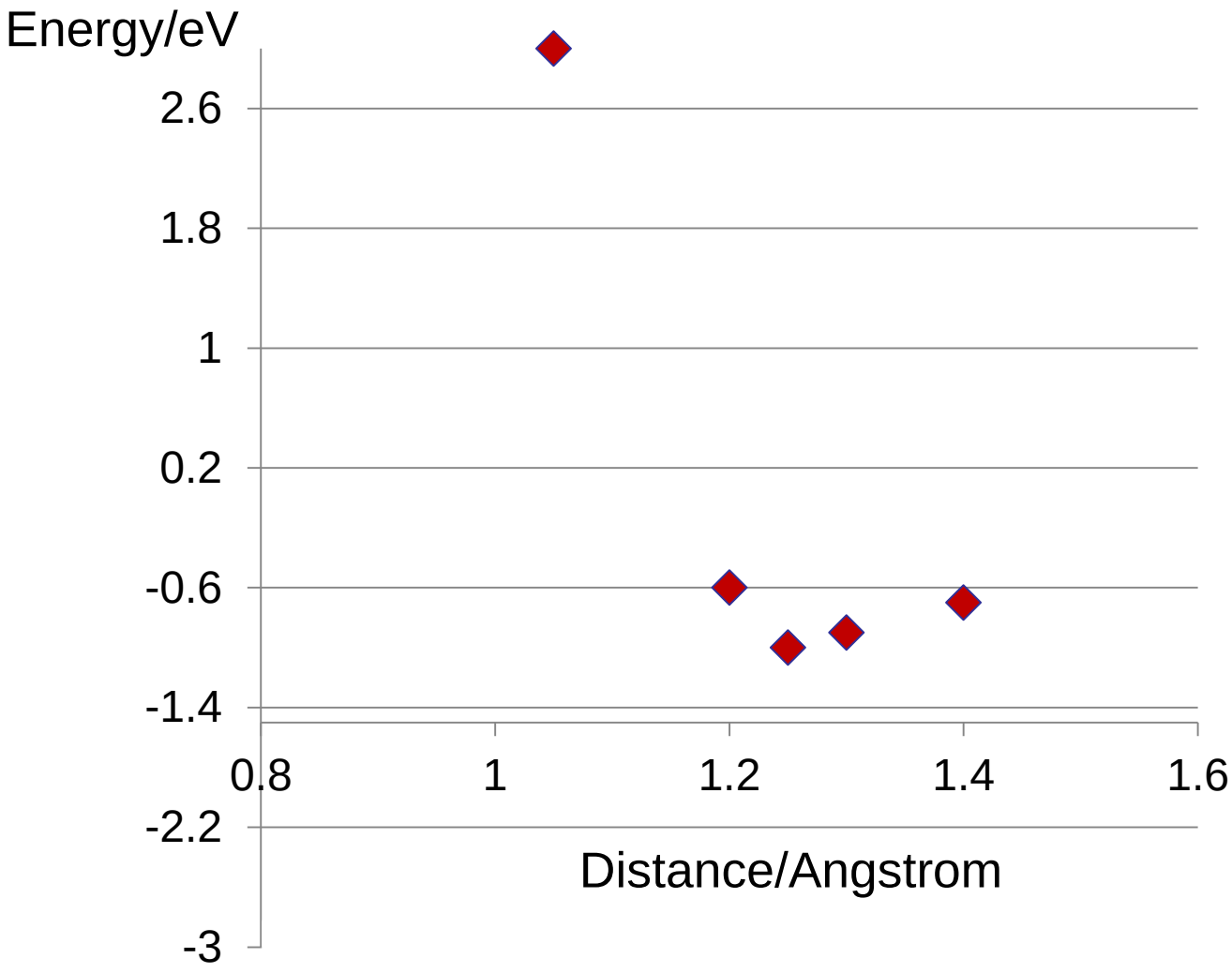


Example: How to fit a potential

Problem statement

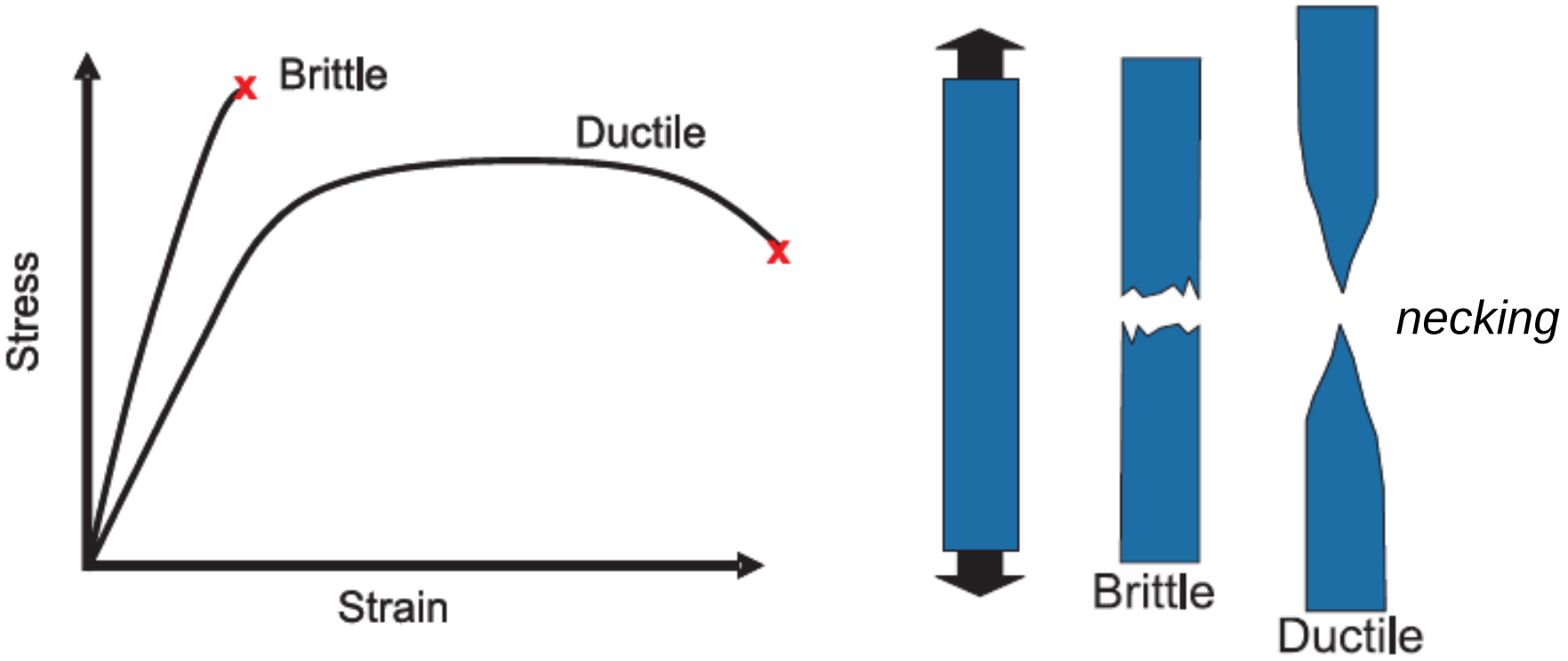


Given: QM data: energy vs. distance between Ne-Ne
Determine suitable **Morse potential**

2. Example: Model of fracture of brittle materials

Tensile test of a wire

copper nanowire? (pset #1)

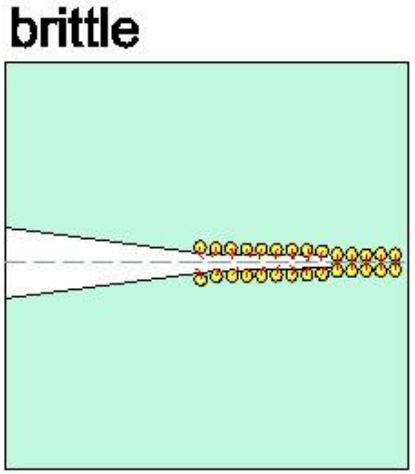


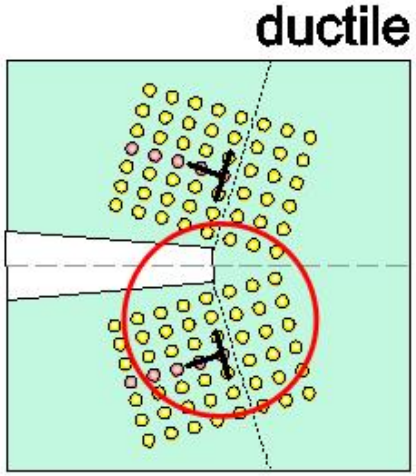
stress == applied force / cross-sectional area of specimen

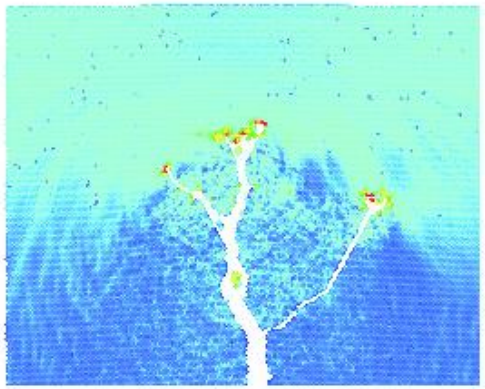
Ductile versus brittle materials

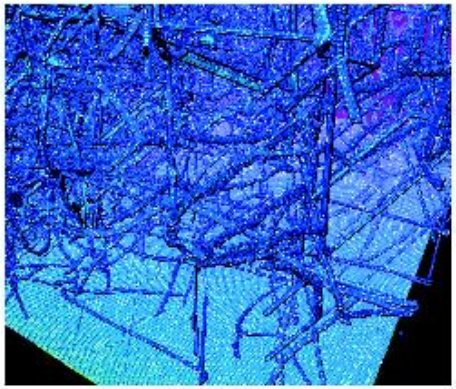
Glass
Polymers
Ice
Silicon

Difficult to deform, breaks easily









Copper,
Gold,
Nickel
Platinum

Easy to deform hard to break

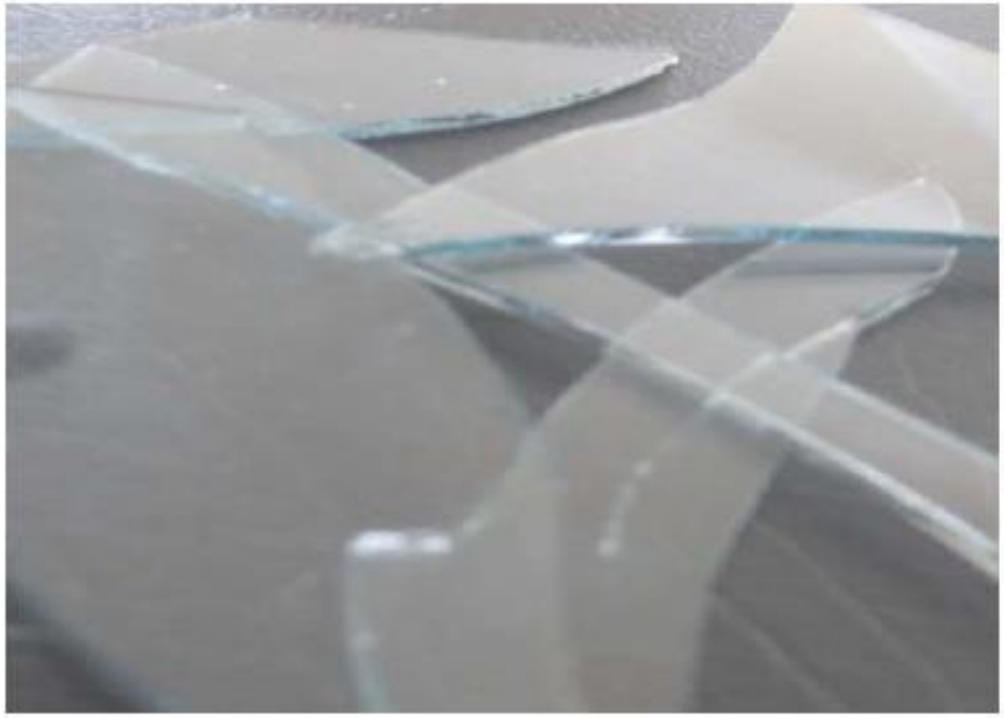
Deformation of materials:
Nothing is perfect, and flaws or cracks matter

Failure of materials initiates at cracks

Griffith, Irwine and others: Failure initiates at defects, such as cracks, or grain boundaries with reduced traction, nano-voids, other imperfections

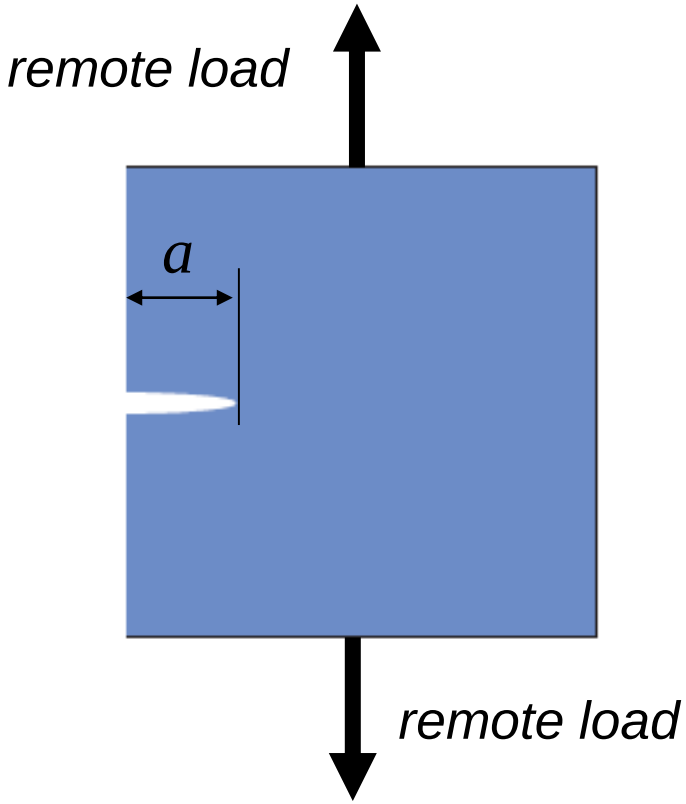
Introduction: brittle fracture

- Materials: **glass, silicon, many ceramics, rocks**
- At large loads, rather than accommodating a shape change, materials break



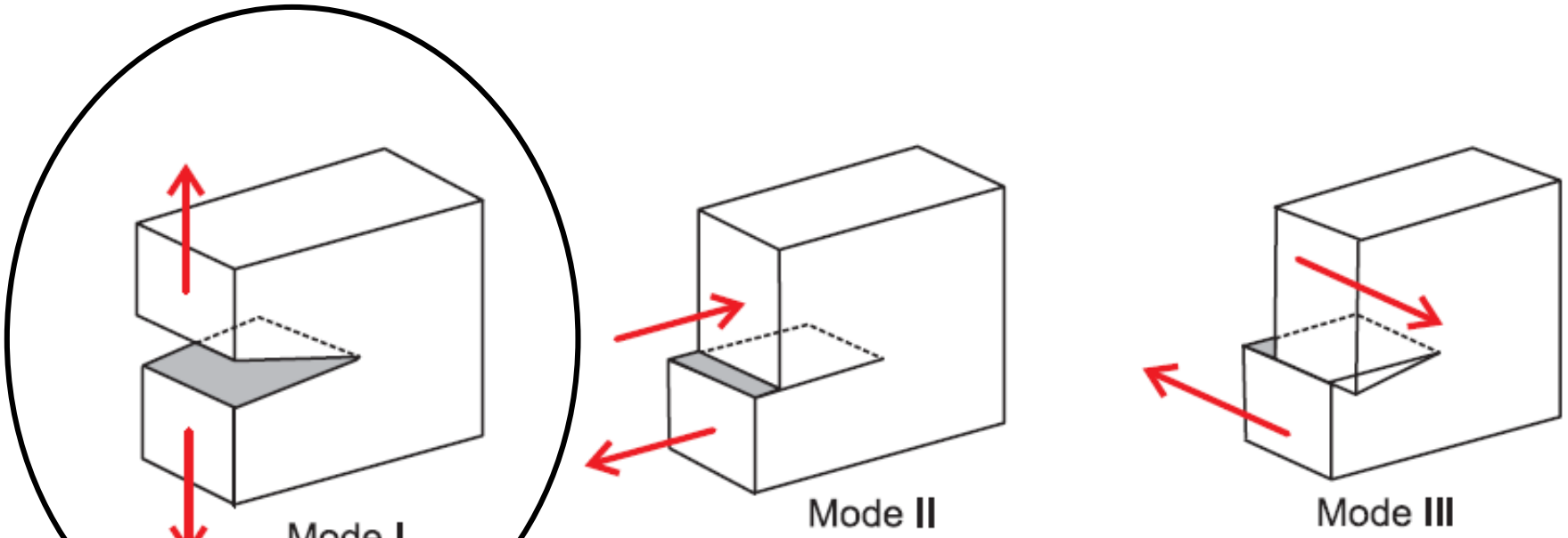
Science of fracture: model geometry

- Typically consider a single crack in a crystal
- Remotely applied mechanical load
- Following discussion focused on single cracks and their behavior



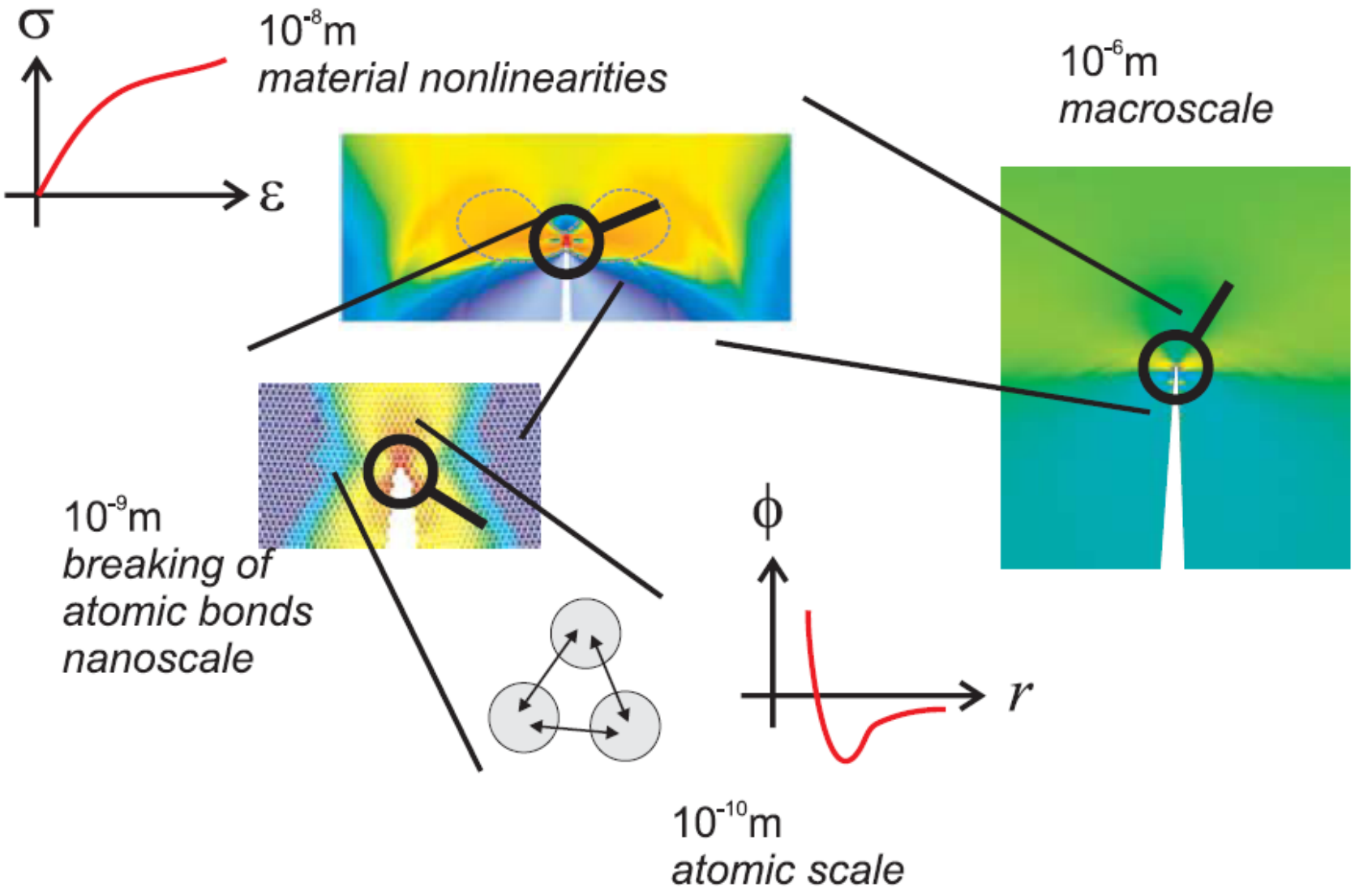
Brittle fracture loading conditions

- Commonly consider a single crack in a material geometry, under three types of loading: mode I, mode II and mode III



Tensile load, focus of this lecture

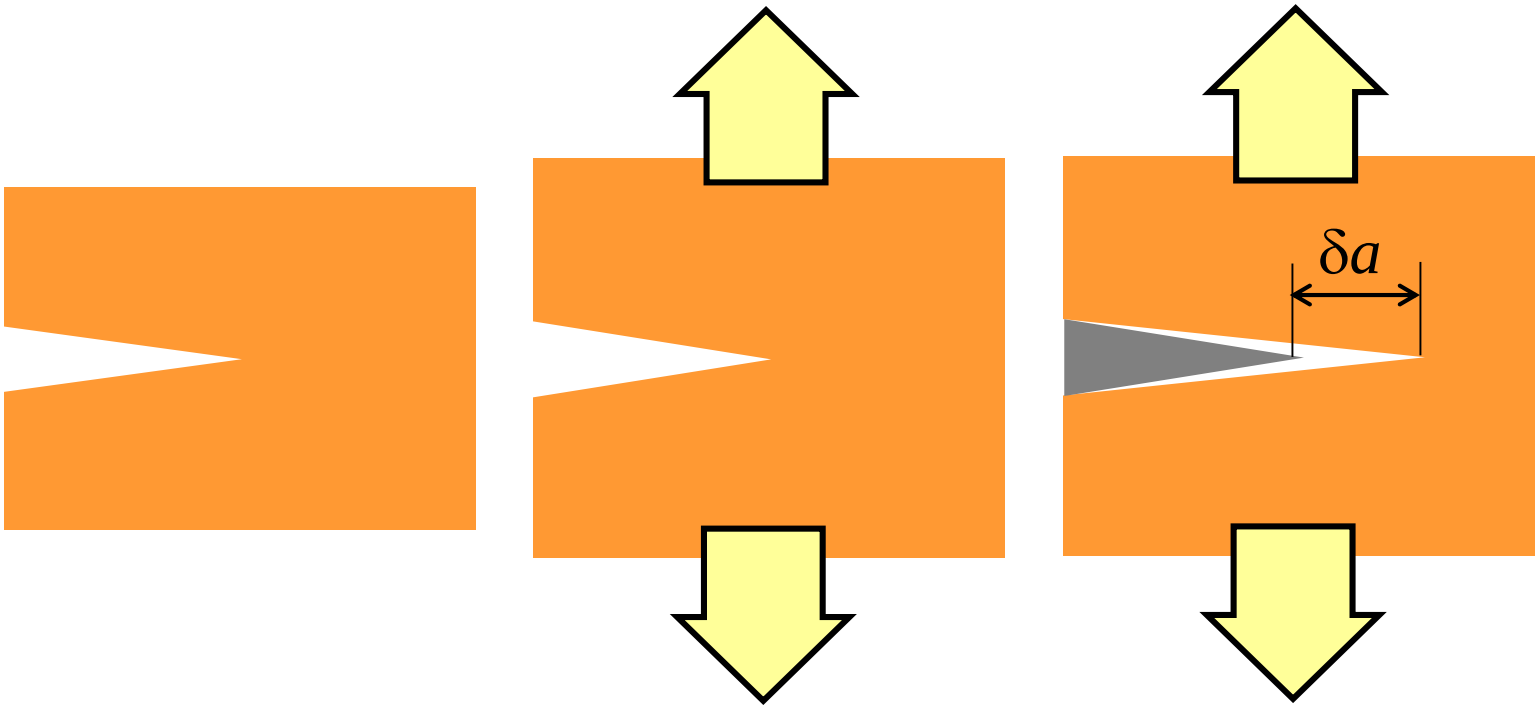
Brittle fracture mechanisms: fracture is a multi-scale phenomenon



Questions to be answered

- **Basic fracture process**: dissipation of elastic energy
- **Fracture initiation**, that is, at what applied load to fractures initiate
- **Fracture dynamics**, that is, how fast can fracture propagate in material
- Relevance to **earthquakes** (speed and nature of spreading!)

Basic fracture process: dissipation of elastic energy



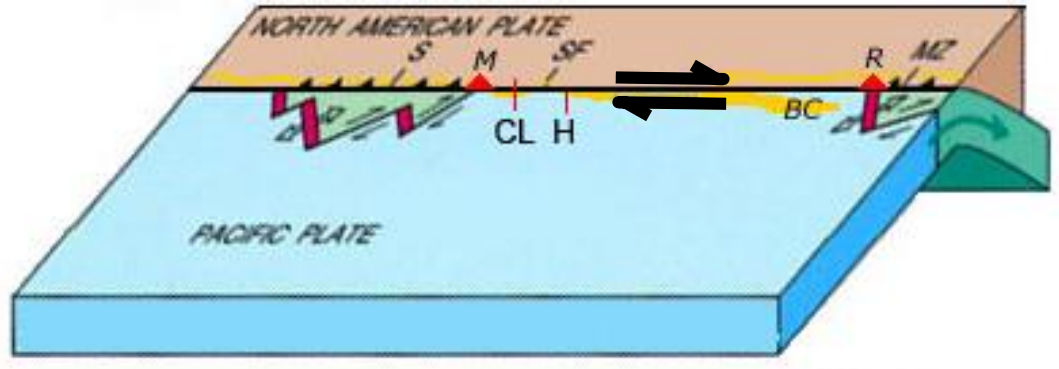
Undeformed

Stretching=store elastic energy

Release elastic energy dissipated into breaking chemical bonds

---SURFACE ENERGY!

Earthquakes: “brittle” failure of the Earth



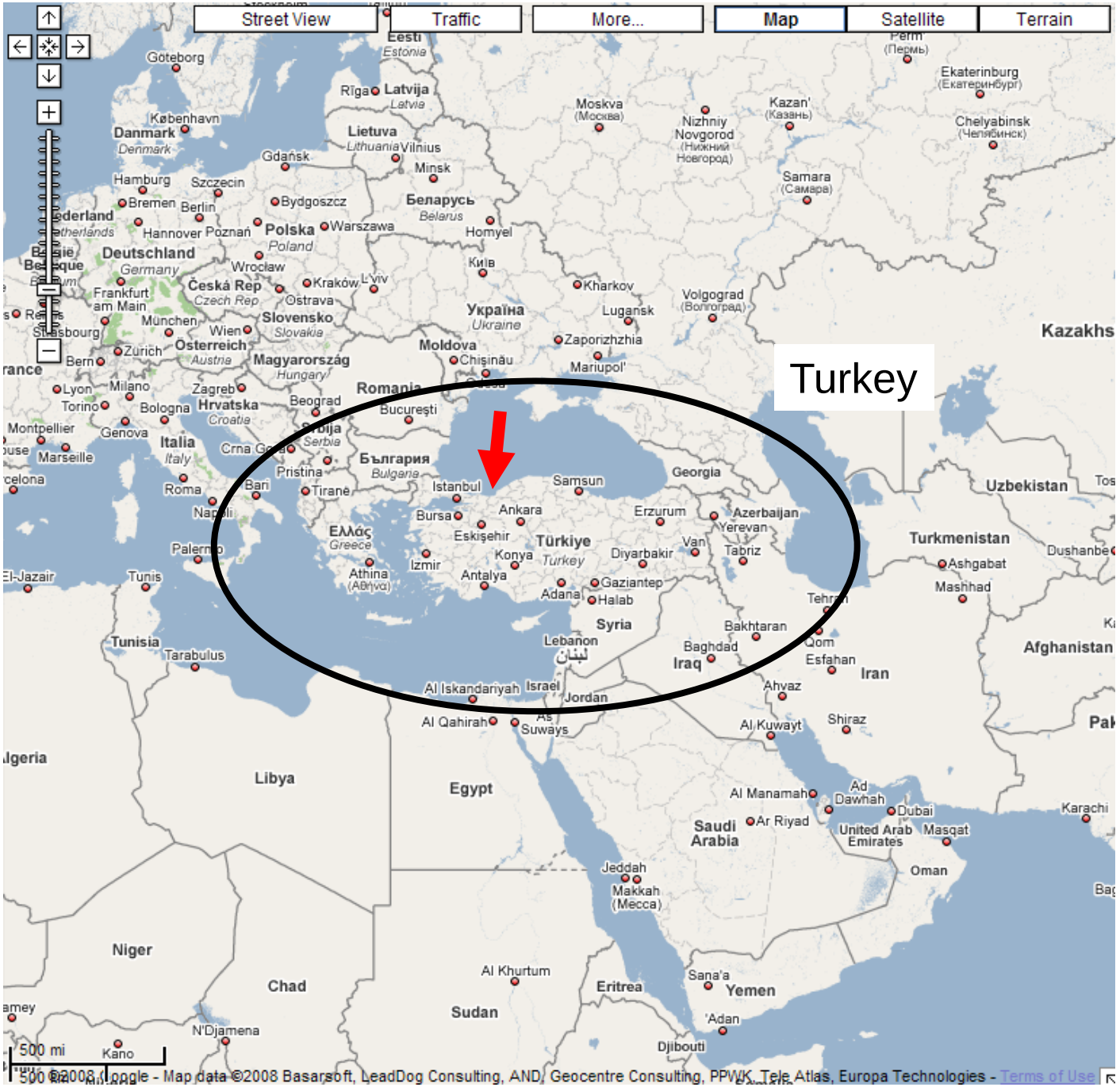
Once critical load exceeds, failure initiates

Critical condition given by “critical energy release rate”: Dissipation of recoverable (elastic) energy equals surface energy

Undeformed

Stretching=store elastic energy

Release elastic energy dissipated into breaking chemical bonds


Street View
Traffic
More...
Map
Satellite
Terrain
Turkey
Göteborg
København
Danmark
Denmark
Eesti
Estonia
Rīga
Latvija
Latvia
Lietuva
Lithuania
Vilnius
Minsk
Беларусь
Belarus
Gdańsk
Bydgoszcz
Warszawa
Polska
Poland
Homyel
Київ
Kharkov
Hamburg
Szczecin
Bremen
Berlin
Hannover
Poznań
Deutschland
Germany
Wrocław
Česká Rep
Czech Rep
Kraków
L'viv
Ostrava
Slovensko
Slovakia
Frankfurt am Main
München
Wien
Österreich
Austria
Zürich
Bern
Magyarország
Hungary
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Αθήνα
Palermo
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Gaziantep
Adana
Halab
Syria
Lebanon
لبنان
Tunisia
Tarabulus
Bakhtaran
Baghdad
Iraq
Qom
Esfahan
Iran
Al Iskandariyah
Israel
Jordan
Ahvaz
Al Qahirah
As Suways
Al Kuwayt
Shiraz
Libya
Egypt
Al Manamah
Ad Dawhah
Dubai
Ar Riyad
Saudi Arabia
United Arab Emirates
Masqat
Oman
Jeddah
Makkah (Mecca)
Niger
Chad
Sudan
Al Khurtum
Eritrea
Sana'a
Yemen
'Adan
Djibouti
N'Djamena
Kano
Kazakhs
Uzbekistan
Turkmenistan
Ashgabat
Mashhad
Tehran
Afghanistan
Pak
Karachi
Dushanbe
Moskva (Москва)
Nizhniy Novgorod (Нижний Новгород)
Kazan' (Казань)
Samara (Самара)
Perm' (Пермь)
Ekaterinburg (Екатеринбург)
Chelyabinsk (Челябинск)
500 mi
500 km
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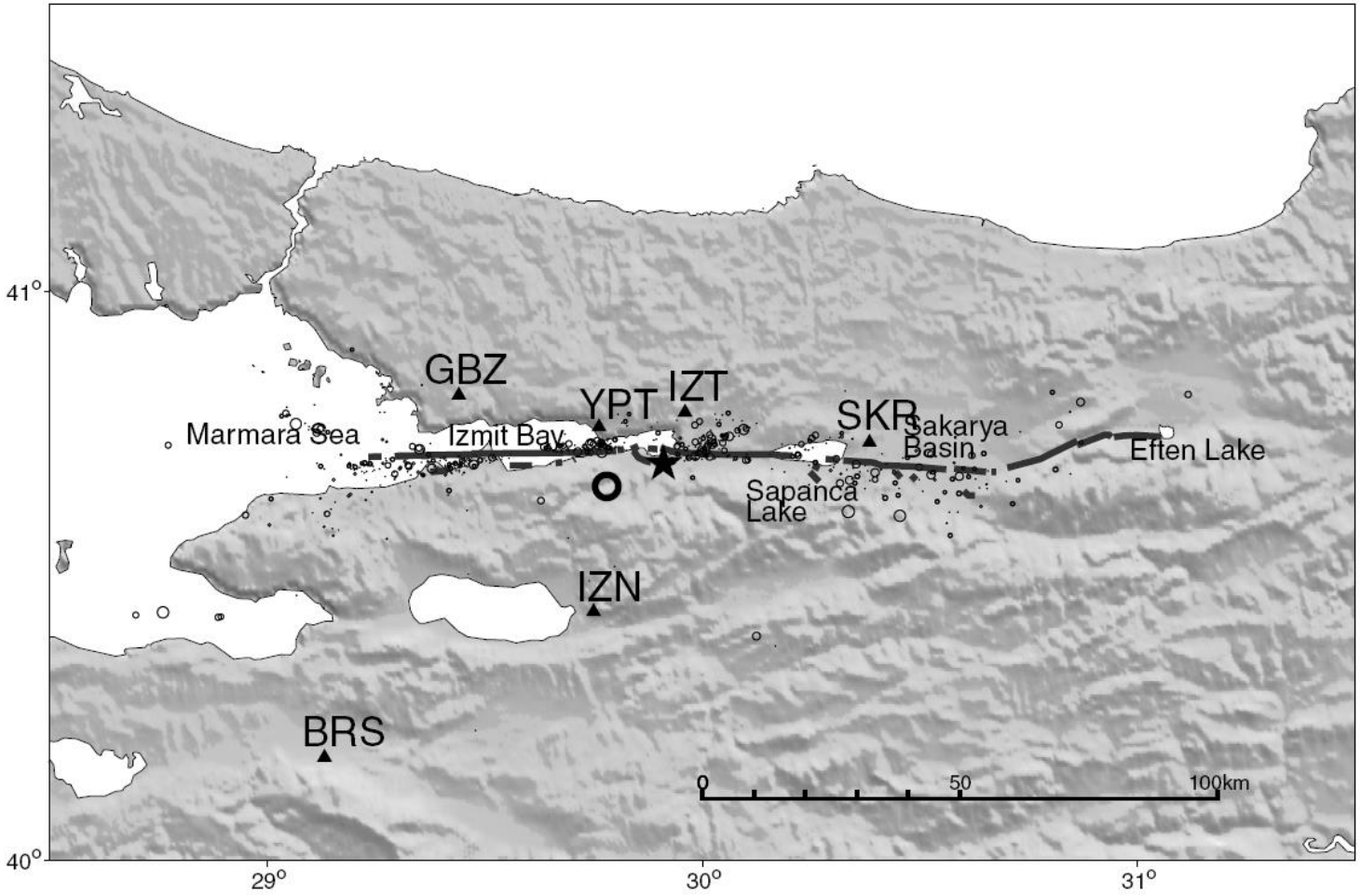
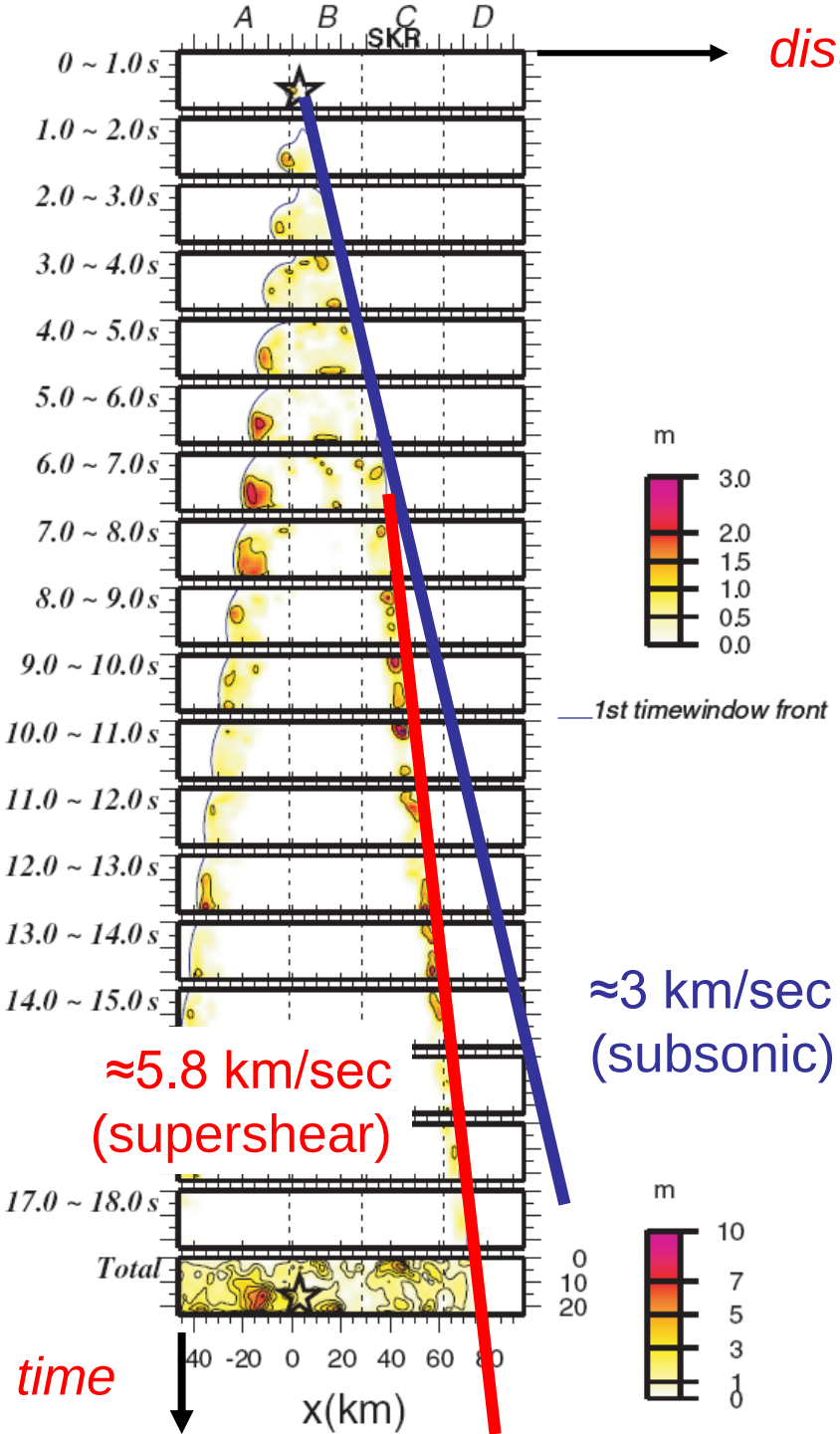
Earthquake dynamics (1999 Kocaeli, Turkey)



Sekiguchi *et al., Bulletin of the Seismological Society of America, 92, 1, pp. 300–311, February 2002*

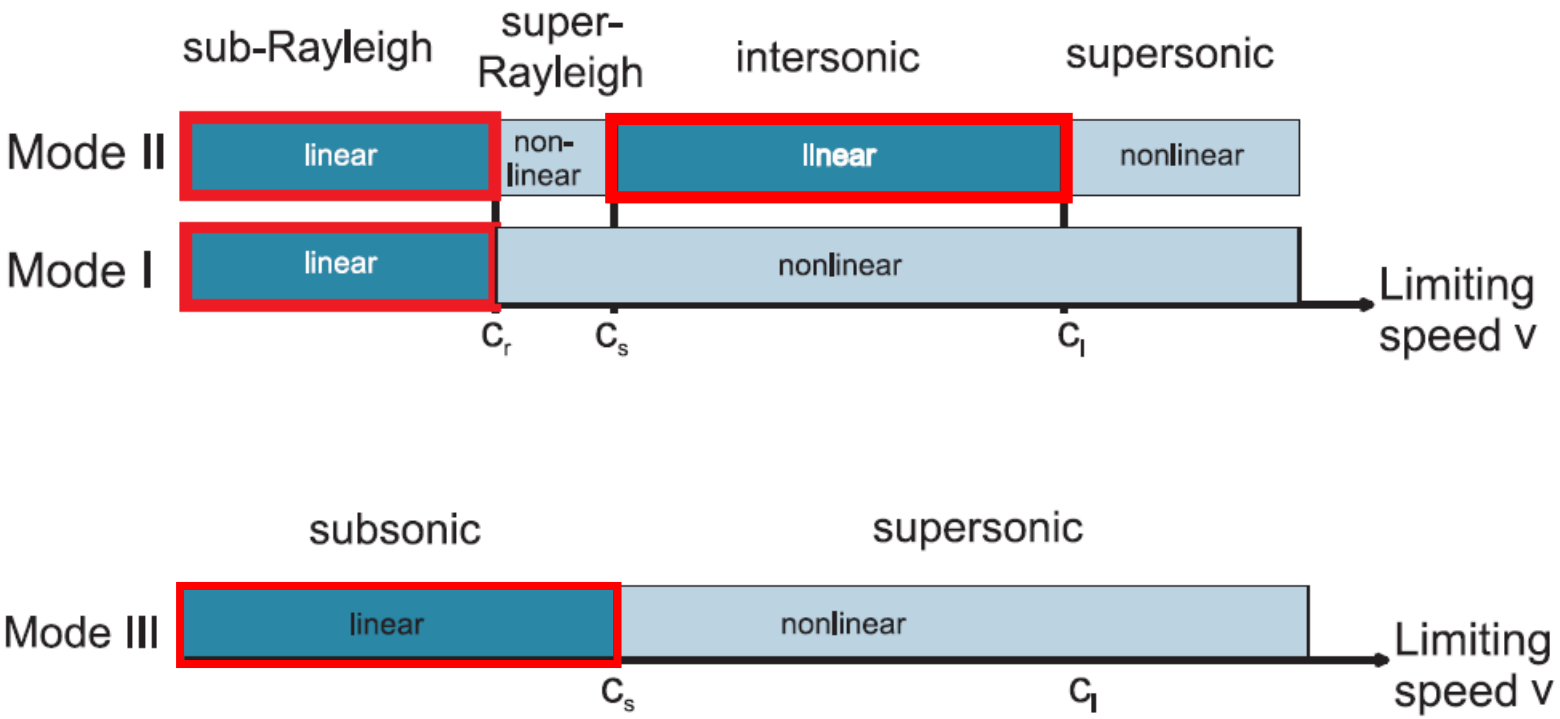


"Then about 7.0 sec after the origin time, a strong moment release is triggered just behind the first time-window front moving at 5.8 km/sec […]"

Significance: *hints at intersonic fracture!*

Sekiguchi *et al., Bulletin of the Seismological Society of America, 92, 1, pp. 300–311, February 2002*

Limiting speeds of cracks: linear elastic continuum theory



- Cracks **can not exceed** the limiting speed given by the corresponding wave speeds **unless material behavior is nonlinear**
- Cracks that exceed limiting speed would produce energy (physically impossible - ***linear elastic continuum theory***)

Sound speeds in materials: overview

Material	c_R (in m/s)	c_s (in m/s)	c_l (in m/s)
Steel	2,940	3,200	6,000
Al	2,850	3,100	6,300
Glass	3,030	3,300	5,800
PMMA	920	1,000	2,400

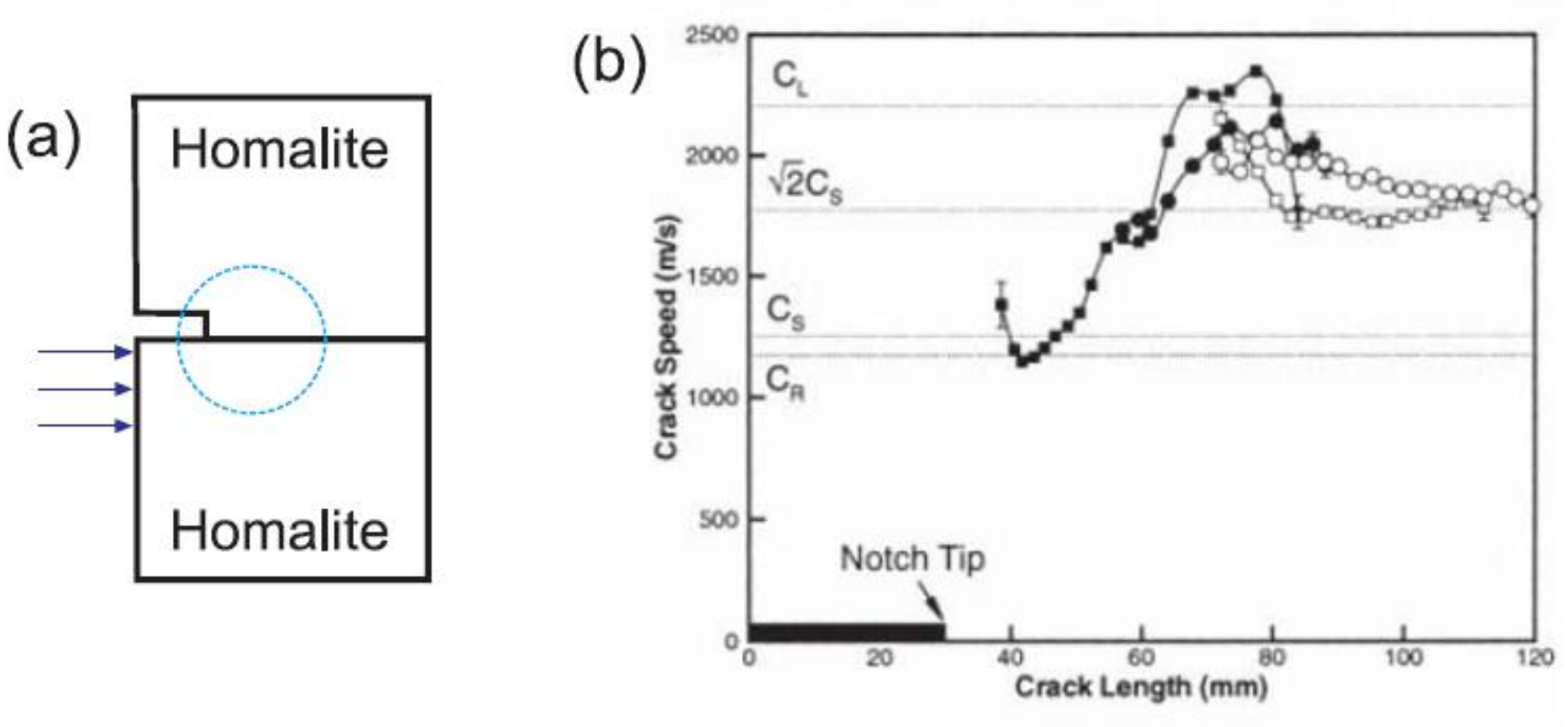
Wave speeds are calculated based on elastic properties of material

$$c_l = \sqrt{\frac{3\mu}{\rho}} \qquad c_s = \sqrt{\frac{\mu}{\rho}} \qquad c_R \approx \beta c_s \qquad \beta \approx 0.923$$

μ = shear modulus $\qquad E = 8/3\mu \qquad \mu = 3/8E$

Experiment evidence (“laboratory earthquakes” at Caltech)

Experiment: intersonic cracks

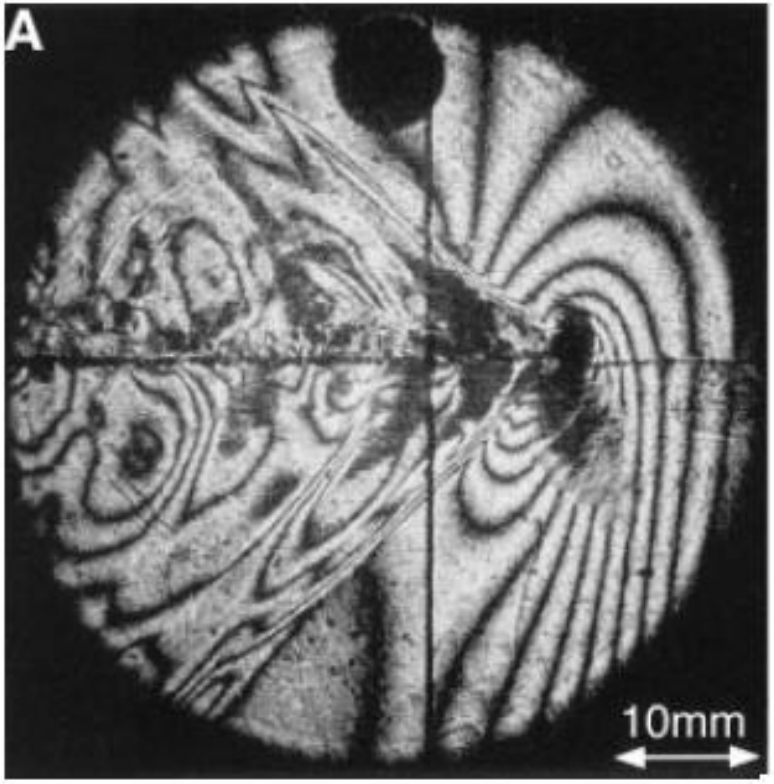


Rosakis et al., *Science*, 1999

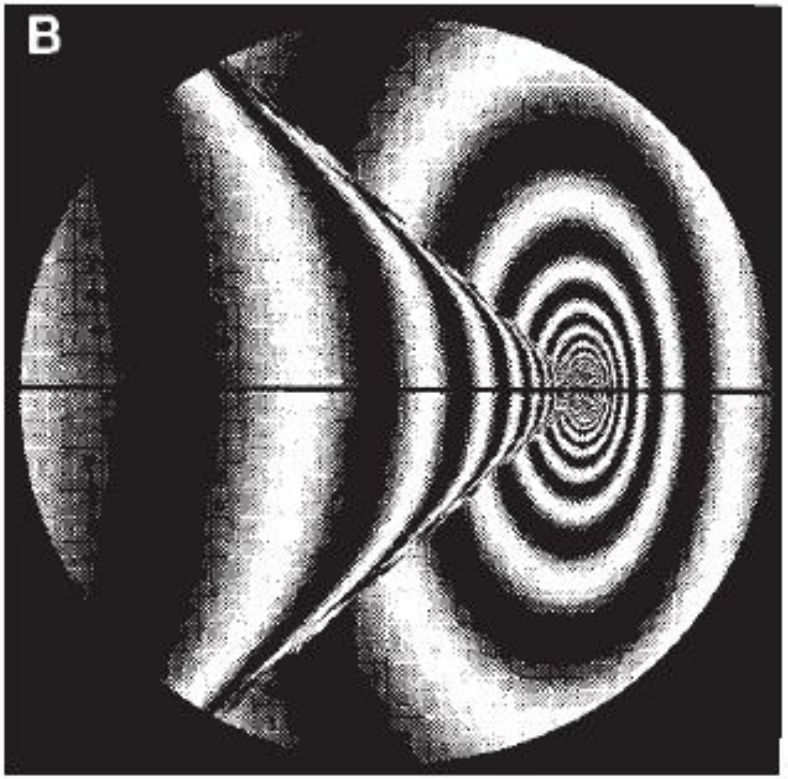
Paper posted on Stellar

Experiment: intersonic cracks (47% faster than shear wave speed)

Isochromatic fringe pattern around a steady-state mode II intersonic crack along a weak plane in Homalite-100

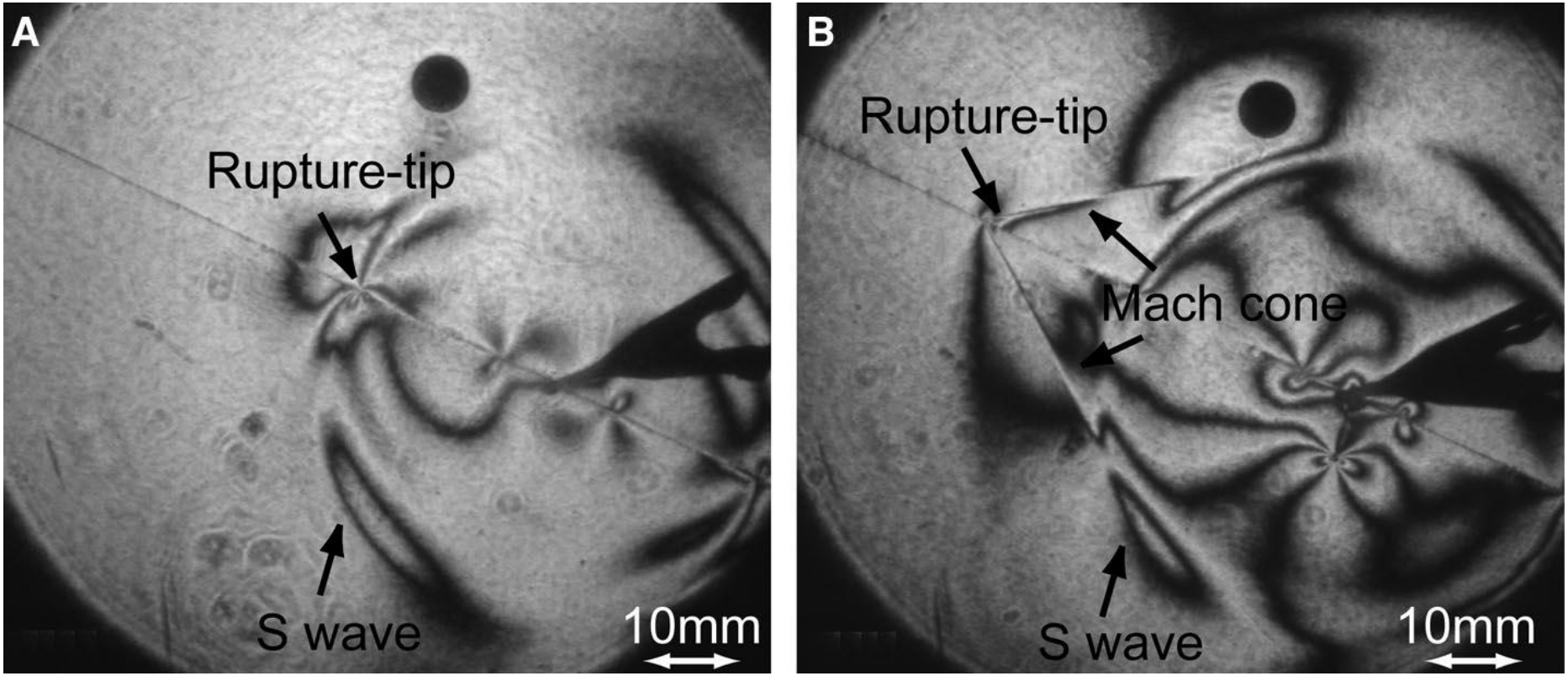


Experiment



Theory (L.B. Freund)

Experiment: intersonic cracks



K. Xia, A. Rosakis et al., *Science*, 2004

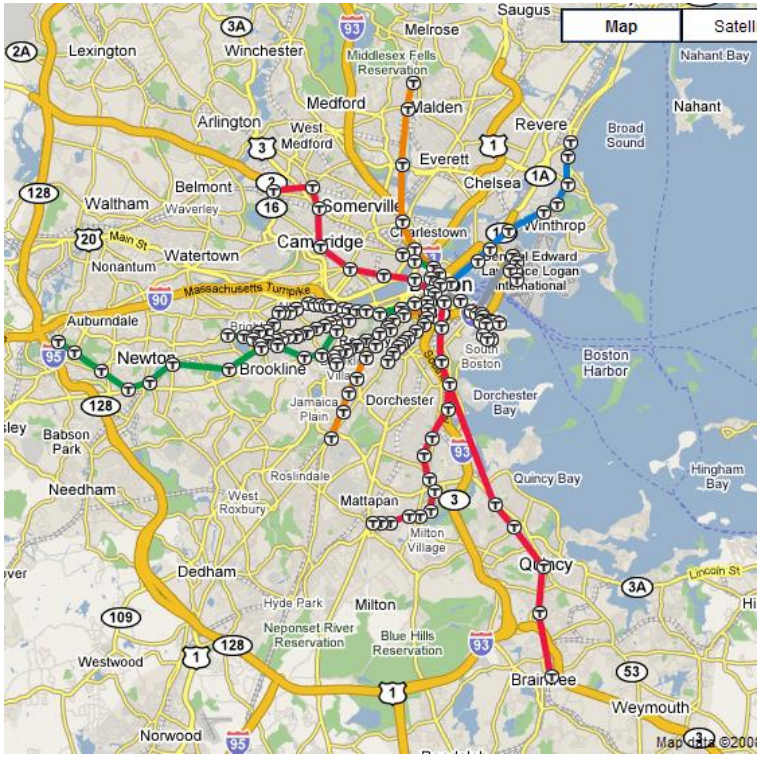
Paper posted on Stellar

Building an atomistic model

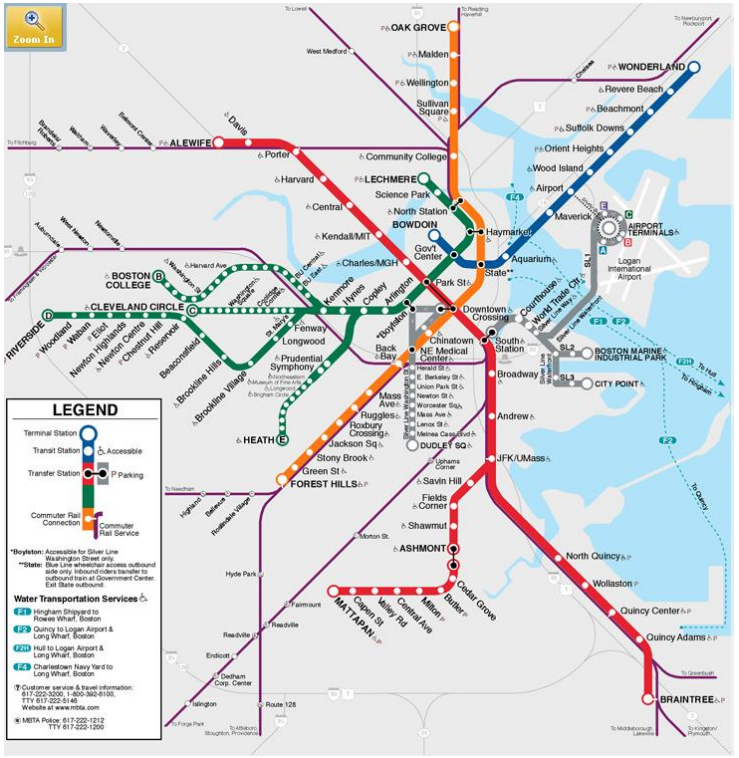
Model building - review

Mike Ashby (Cambridge University):

- *A model is an idealization. Its relationship to the real problem is like that of the map of the London tube trains to the real tube systems: a gross simplification, but one that captures certain essentials.*



"Physical situation"



"Model"

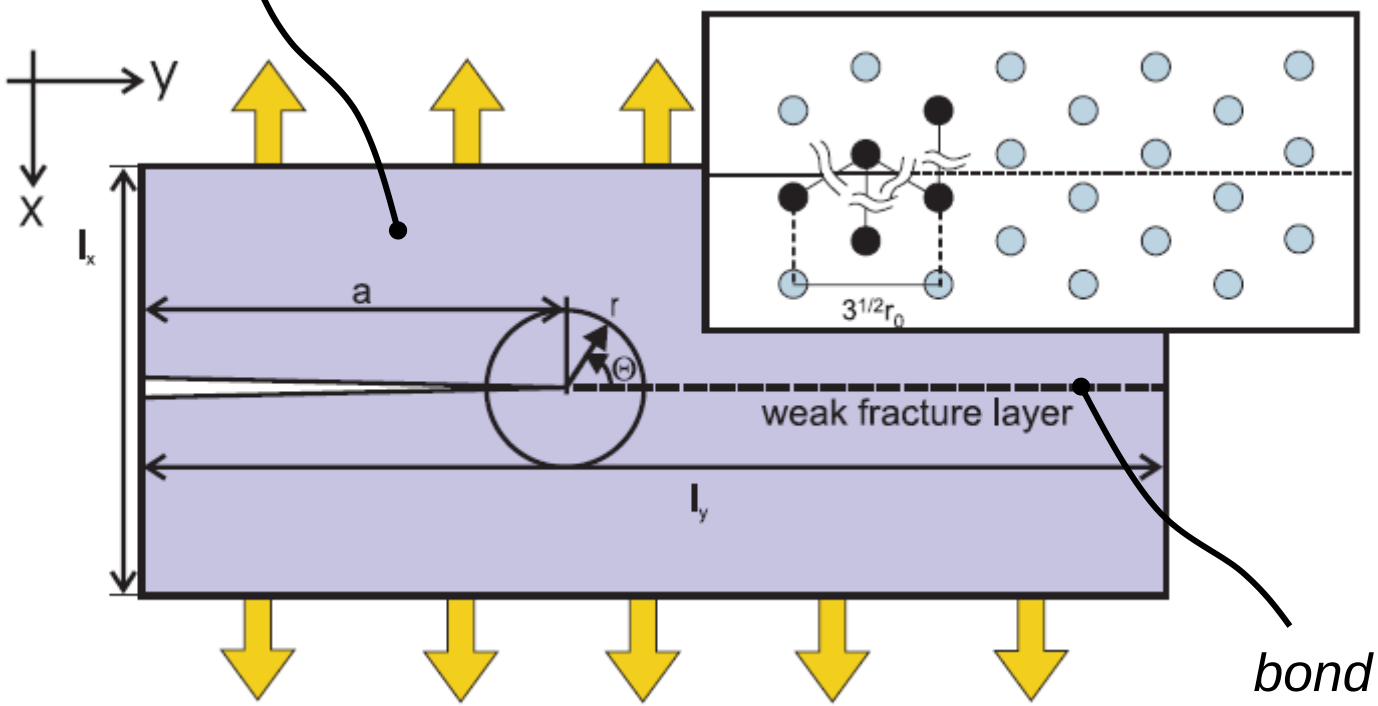
A “simple” atomistic model: geometry

$$\phi = \frac{1}{2} k_0 (r - r_0)^2$$

elasticity (store energy)

stable configuration of pair potential

2D triangular (hexagonal) lattice

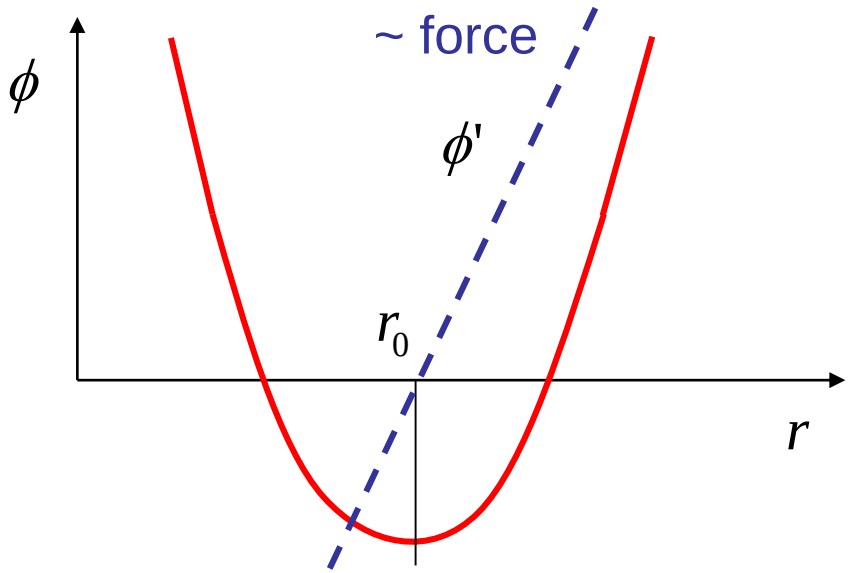


bond can break

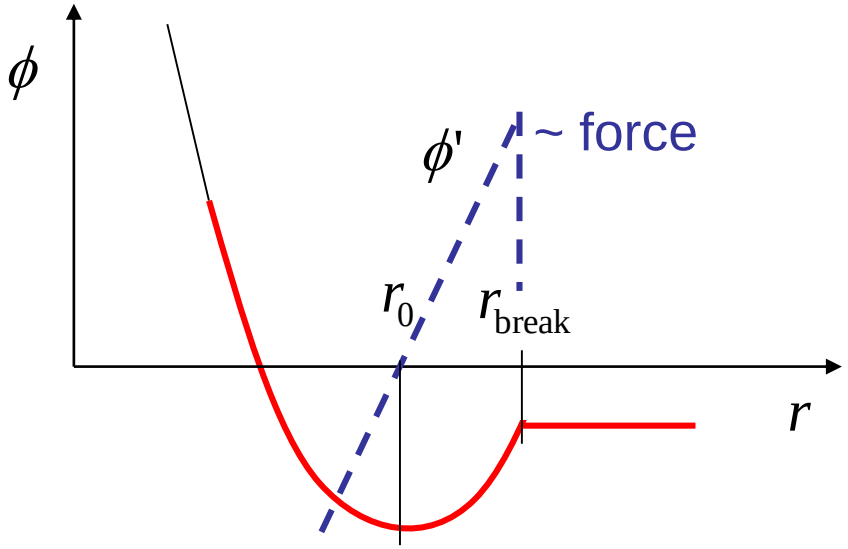
Pair potential to describe atomic interactions
Confine crack to a 1D path (weak fracture layer):
Define a pair potential
whose bonds never break (bulk) and a potential
whose bonds break

$$\phi = \begin{cases} \frac{1}{2} k_0 (r - r_0)^2 & r < r_{\text{break}} \\ \frac{1}{2} k_0 (r_{\text{break}} - r_0)^2 & r \geq r_{\text{break}} \end{cases}$$

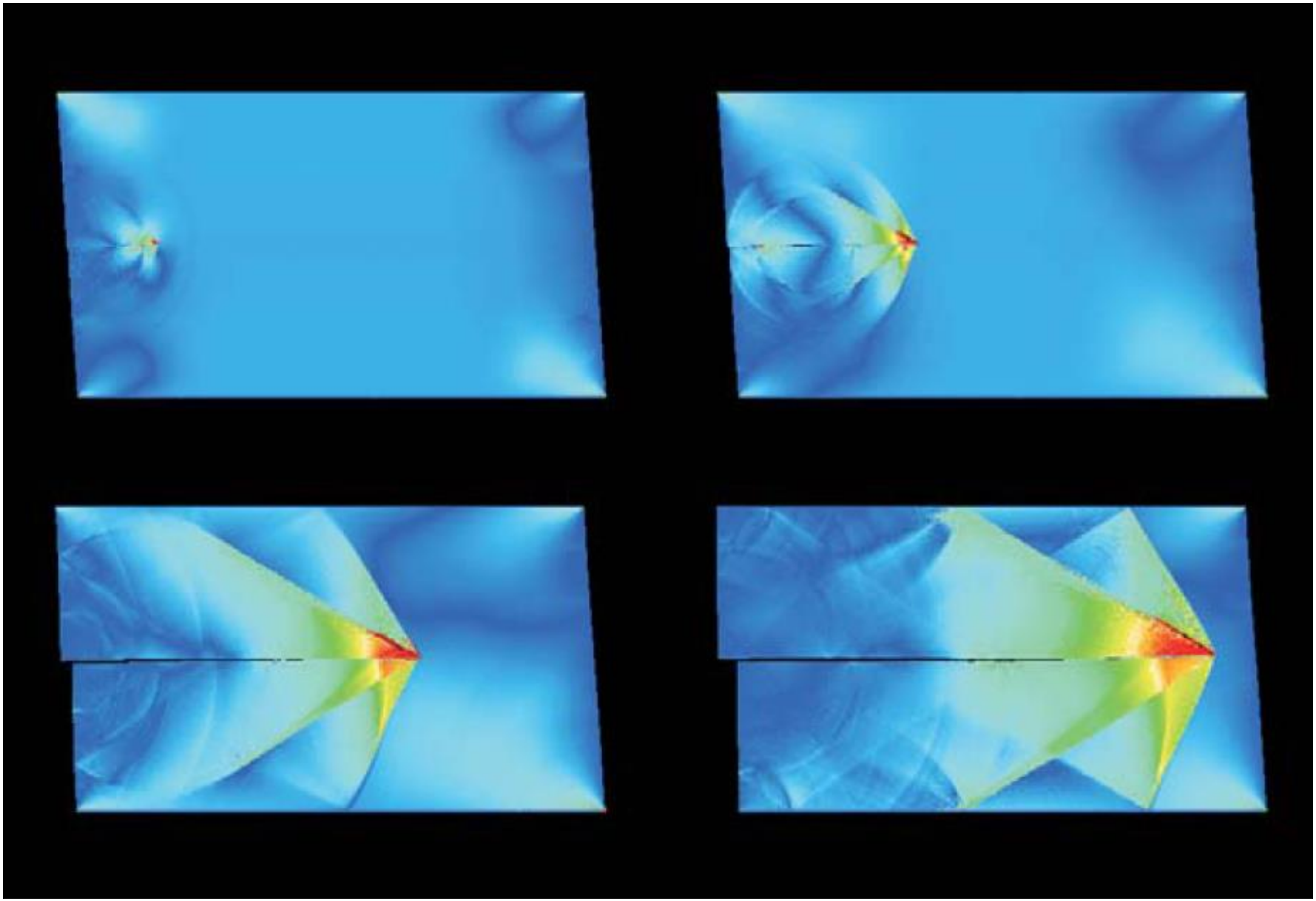
Harmonic and harmonic bond snapping potential



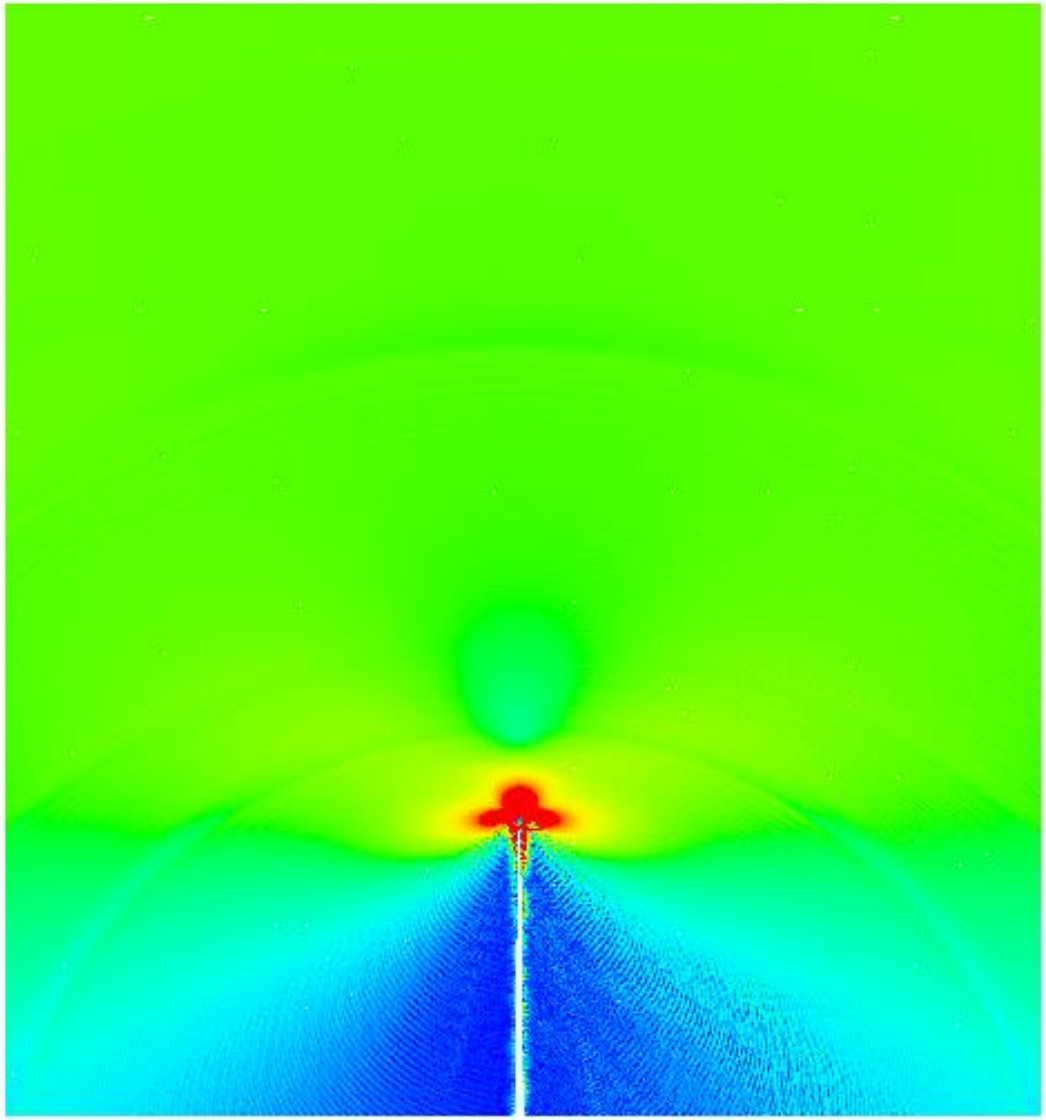
$$\phi = \frac{1}{2} k_0 (r - r_0)^2$$

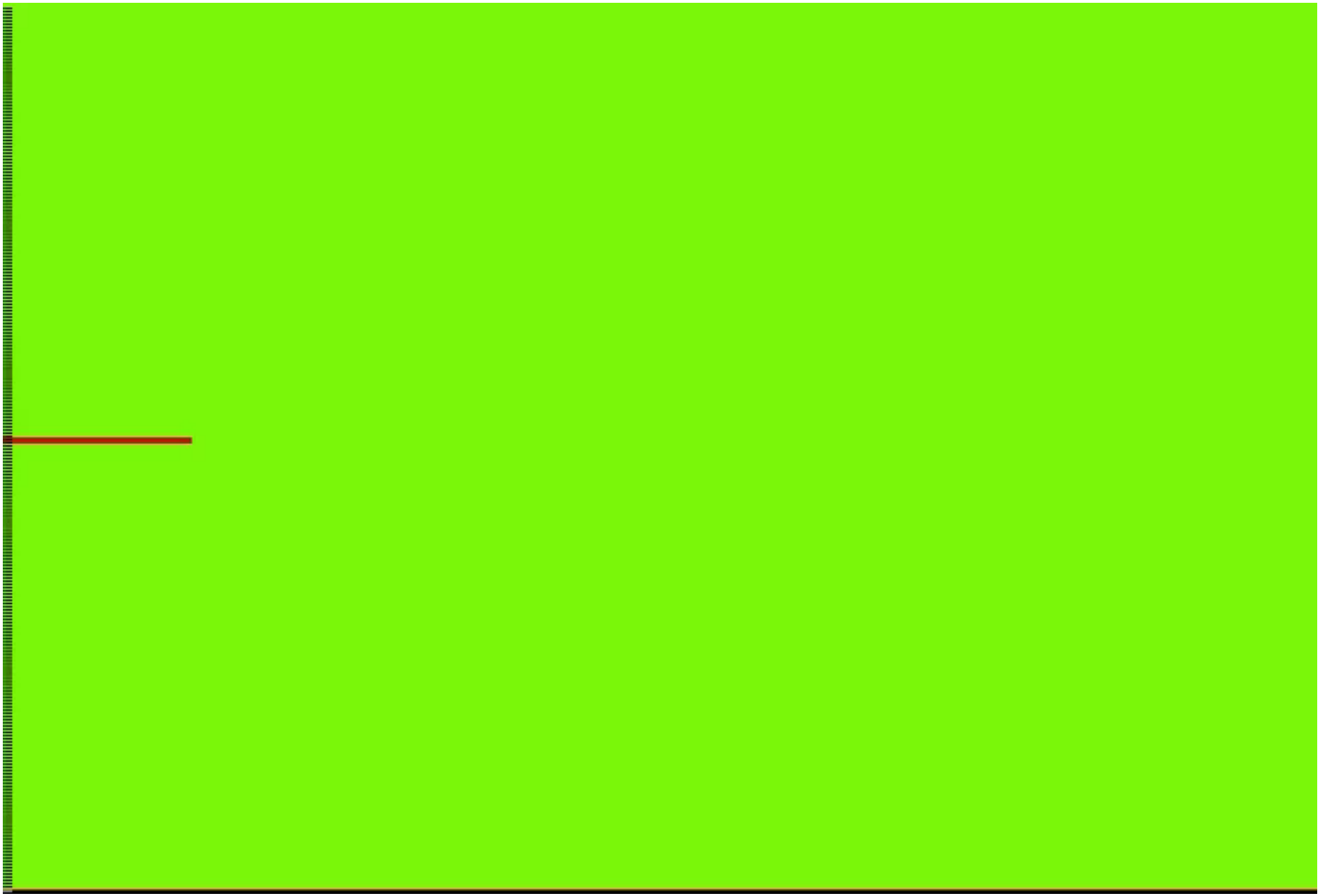


$$\phi = \begin{cases} \frac{1}{2} k_0 (r - r_0)^2 & r < r_{\text{break}} \\ \frac{1}{2} k_0 (r_{\text{break}} - r_0)^2 & r \geq r_{\text{break}} \end{cases}$$



Supersonic fracture





APPENDIX: Parameters for Morse potential

(for reference)

Morse potential parameters for various metals

Metal	αa_0	β	L(ev) $\times 10^{-22}$	$\alpha = \mathrm{A}^{-1}$	$r_0 = \mathrm{A}$	D(ev)
Pb	2.921	83.02	7.073	1.1836	3.733	0.2348
Ag	2.788	71.17	10.012	1.3690	3.115	0.3323
Ni	2.500	51.78	12.667	1.4199	2.780	0.4205
Cu	2.450	49.11	10.330	1.3588	2.866	0.3429
Al	2.347	44.17	8.144	1.1646	3.253	0.2703
Ca	2.238	39.63	4.888	0.80535	4.569	0.1623
Sr	2.238	39.63	4.557	0.73776	4.988	0.1513
Mo	2.368	88.91	24.197	1.5079	2.976	0.8032
W	2.225	72.19	29.843	1.4116	3.032	0.9906
Cr	2.260	75.92	13.297	1.5721	2.754	0.4414
Fe	1.988	51.97	12.573	1.3885	2.845	0.4174
Ba	1.650	34.12	4.266	0.65698	5.373	0.1416
K	1.293	23.80	1.634	0.49767	6.369	0.05424
Na	1.267	23.28	1.908	0.58993	5.336	0.06334
Cs	1.260	23.14	1.351	0.41569	7.557	0.04485
Rb	1.206	22.15	1.399	0.42981	7.207	0.04644

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Girifalco *et al*., *Phys. Rev.* 1958

Further Morse potential parameters

Table 3
Morse potential parameters used in MD simulation of uniaxial tensile loading [24]

Material	Crystal structure	Dissociation energy, D (eV)	Equilibrium radius, r_o (Å)	α-parameter (Å^{-1})	Lattice constant (Å)
Aluminium	FCC	0.2703	3.253	1.1650	4.05
Copper	FCC	0.3429	2.866	1.3590	3.62
Nickel	FCC	0.4205	2.780	1.4199	3.52
Iron	BCC	0.4172	2.845	1.3890	2.87
Chromium	BCC	0.4414	2.754	1.5721	2.89
Tungsten	BCC	0.9906	3.032	1.4116	3.17

Komanduri *et al.*