

Outline of Lectures 2-3

- Assumptions and limitations of classical MD
 - Classical description of interatomic interaction
 - Classical description of atomic motion
 - Small length scales (up to 100s of nm), short times (up to 100s of ns)
 - Difficulty in providing quantitative description of real materials
- Examples of applications of molecular dynamics
- Discussion of projects suggested by students

Limitations of molecular dynamics (I)

1. Classical description of interatomic interaction

- Electrons are not present explicitly, they are introduced through the potential energy surface that is a function of atomic positions only (Born-Oppenheimer approximation).
- The potential energy surface, in turn, is approximated by an analytic function that gives the potential energy U as a function of coordinates. Forces are obtained as the gradient of a potential energy function,
$$\vec{F}_i = -\vec{\nabla}_{r_i} U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Potential energy surfaces (solutions of electronic Schrödinger equation within the Born-Oppenheimer approximation) are not available for practically interesting systems. The choice of a potential function that *approximates* the actual (unknown) solution of the Schrödinger equation is a difficult task. Design of the potential function and choice of the parameters is often based on fitting to available experimental data (e.g. equilibrium geometry of stable phases, cohesive energy, elastic moduli, vibrational frequencies, temperatures of the phase transitions, etc.).

Availability of good potential functions is one of the main conditions for expansion of the area of applicability of the MD simulations to the realistic quantitative analysis of the behavior and properties of real materials.

Limitations of molecular dynamics (II)

2. Classical description of atomic motions

- In classical MD we replace Schrödinger equation for nuclei with classical Newton equation.

One indicator of the validity of the replacement is the de Broglie wavelength Λ . Quantum effects are expected to become significant when Λ is much larger than inter-particle distance.

For the thermal motion we can use the thermal de Broglie wavelength: $\Lambda_{th} = \frac{h}{\sqrt{2 \pi m k_B T}}$

where $h = 6.626 \times 10^{-34}$ J s is the Plank's constant and m is the mass of the particle

For $T = 300$ K we have $\Lambda_{th} = 1$ Å for a H atom ($m_H = 1$ amu)

$\Lambda_{th} = 0.19$ Å for a Si atom ($m_{Si} = 28$ amu)

$\Lambda_{th} = 0.07$ Å for a Au atom ($m_{Au} = 197$ amu)

Typical interatomic spacing in solid-state materials is $d \sim 1-3$ Å. Therefore:

- All atoms, except for the lightest ones such as H, He, Ne, can be considered as “point” particles at sufficiently high temperature ($d \gg \Lambda$) and classical mechanics can be used to describe their motion.

Limitations of molecular dynamics (IV)

3. Time- and length-scale limitations

- The limitations on the size of the MD computational cell (number of atoms) and time of the simulation constrain the range of problems that can be addressed by the MD method.

Time-scale:

The maximum timestep of integration in MD simulation is defined by the fastest motion in the system. Vibrational frequencies in a molecular system are up to 3000 cm^{-1} which corresponds to a period of $\sim 10\text{ fs}$. Optical phonon frequencies are $\sim 10\text{ THz}$ - period of $\sim 100\text{ fs}$. Therefore, a typical timestep in MD simulation is on the order of a **femtosecond**.

Using modern computers it is possible to calculate $10^6 - 10^8$ timesteps. Therefore we can only simulate processes that occur within **1 – 100 ns**. This is a serious limitation for many problems that involve thermally-activated processes, cluster/vapor film deposition, annealing of irradiation damage, etc.

Several methods for acceleration of infrequent thermally activated events within the framework of molecular dynamics have been proposed by Voter (Los Alamos), Fichthorn (Penn State) and others. The methods have been applied to study processes of surface diffusion and film growth.

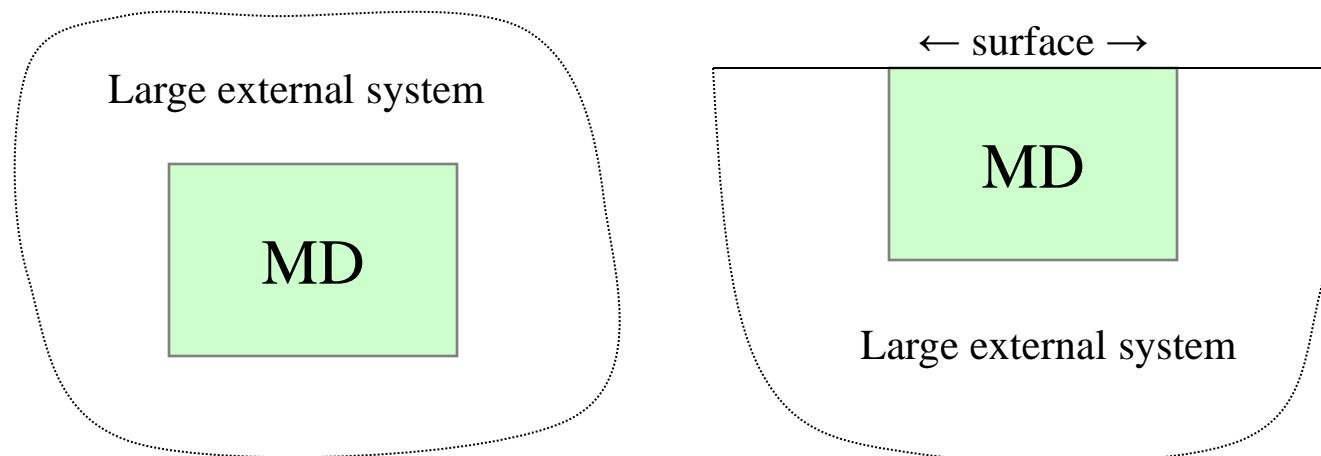
Limitations of molecular dynamics (V)

Length-scale:

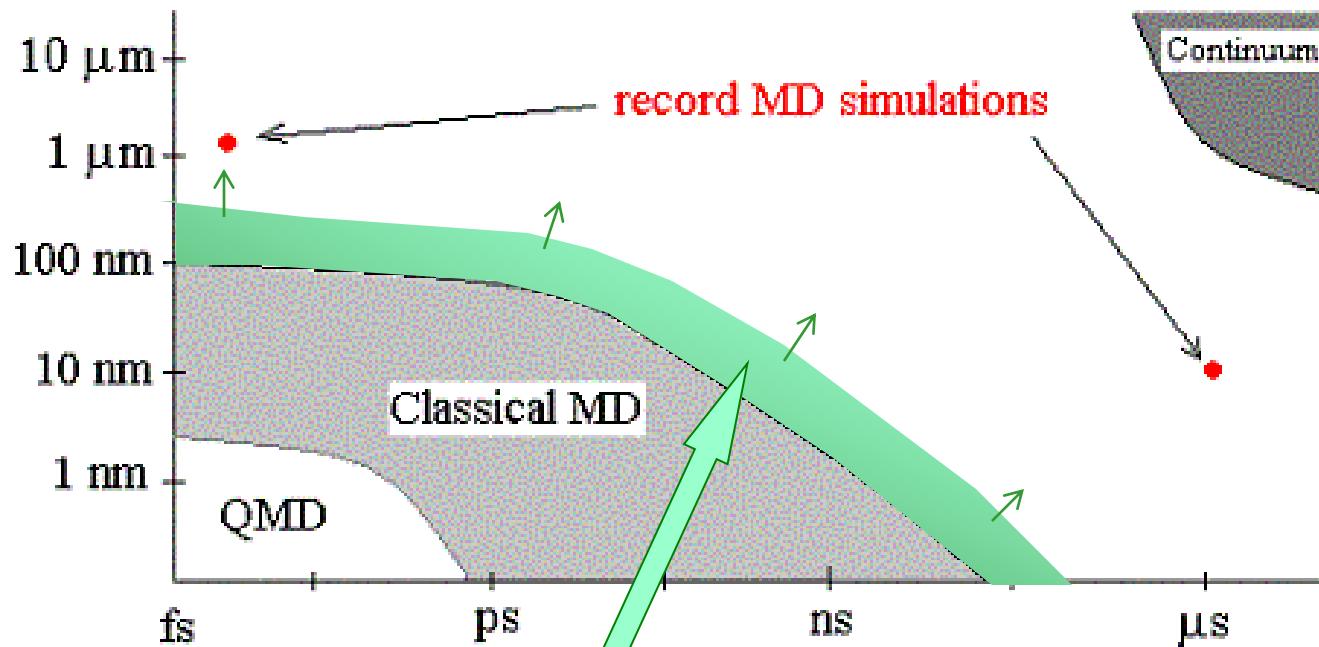
The size of the computational cell is limited by the number of atoms that can be included in the simulation, typically $10^4 - 10^7$. This corresponds to the size of the computational cell on the order of **tens of nm**. Any structural features of interest and spatial correlation lengths in the simulation should be smaller than the size of the computational cell.

To make sure that the finite size of the computational cell does not introduce any artifacts into the simulation results, one can perform simulations for systems of different size and compare the measured properties.

Due to the limitations on the size of the MD computational cell, an important aspect of any MD simulation is an adequate description of the “interaction” of atoms in the MD computational cell with surrounding “infinite” material. We have to define **boundary conditions** and apply special **methods for temperature and pressure control** in the MD cell (heat and work exchange between the MD computational cell and the surroundings).



Limitations of MD: Small time- and length-scales



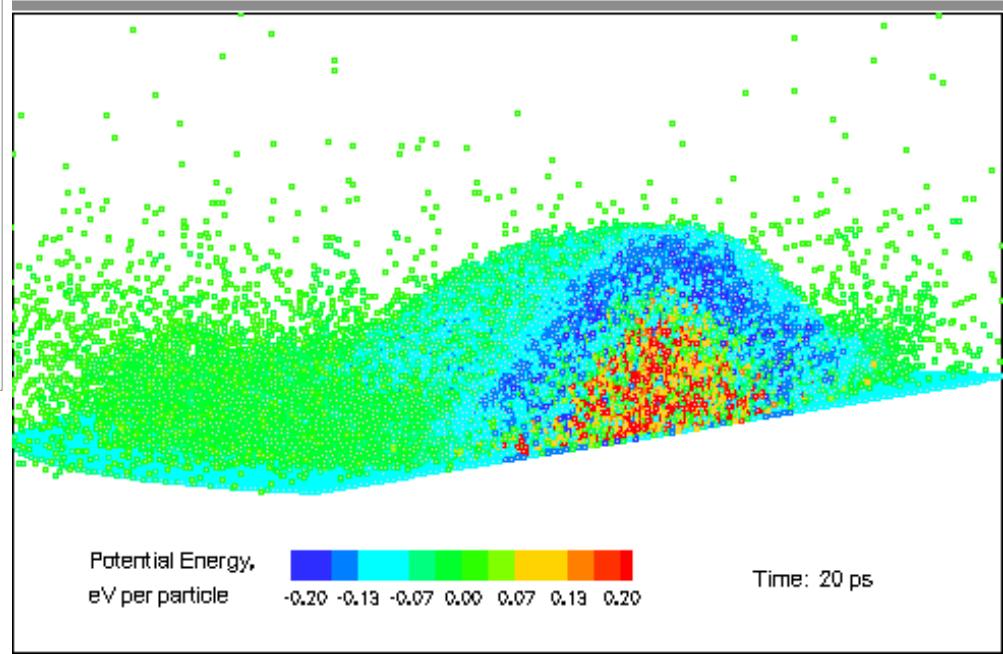
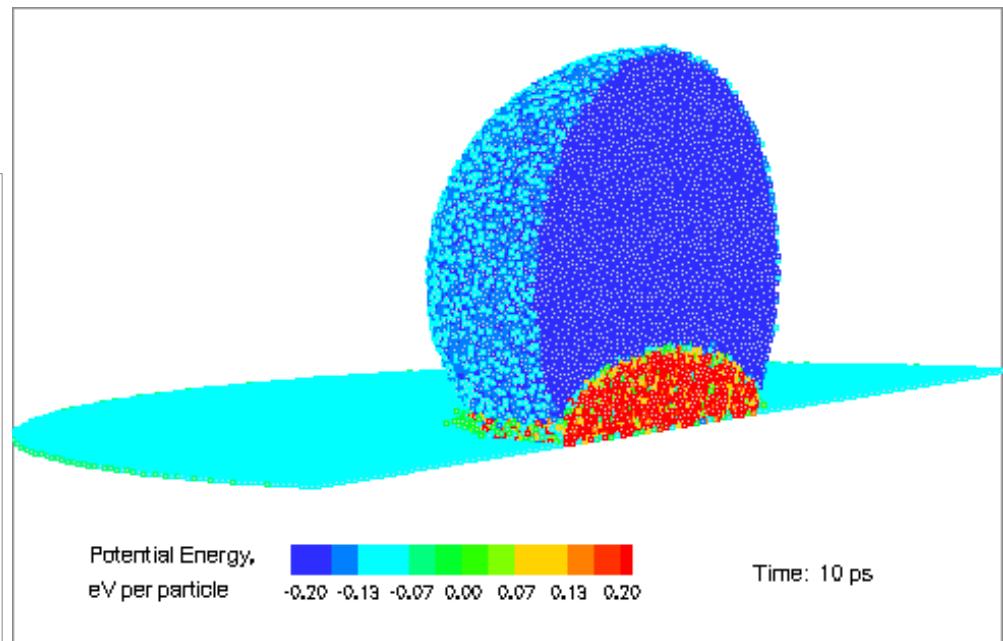
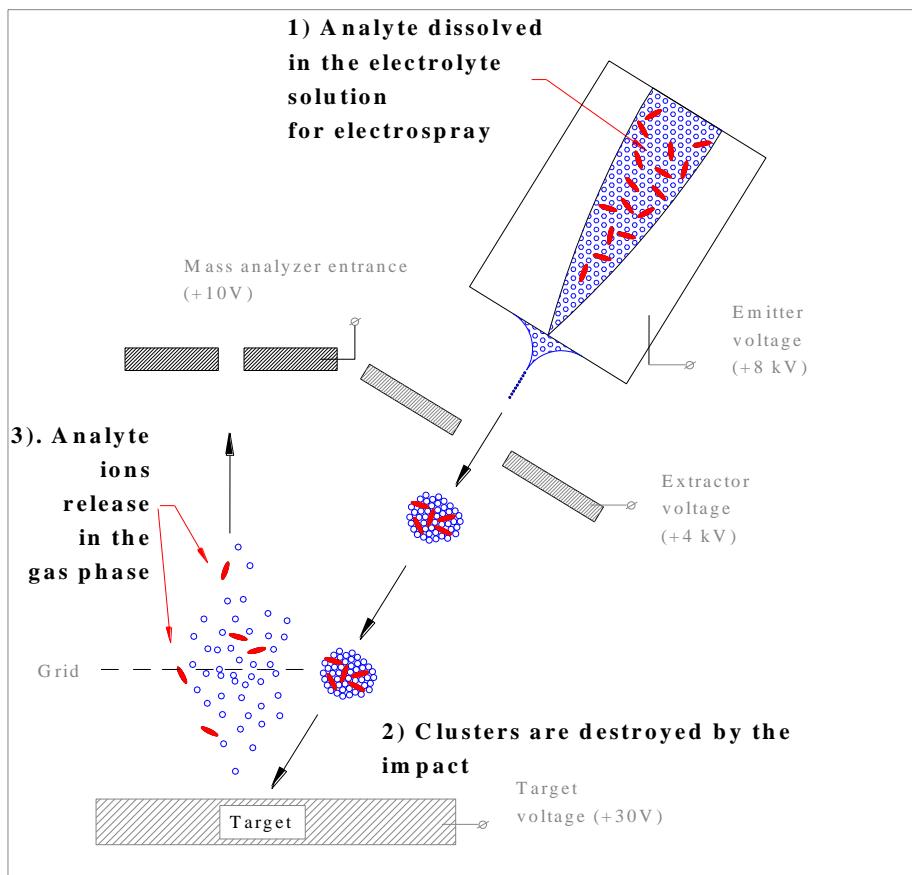
Number of atoms \sim (size of the system)³

Computational cost \sim (number of atoms)ⁿ
 $n > 1$

ASCI White (LLNL), the RS/6000 SP supercomputer developed by IBM, 2001

Examples of MD simulations: Collision of a droplet with a substrate

MD simulation by Yasushi Katsumi
(term project for MSE 627)

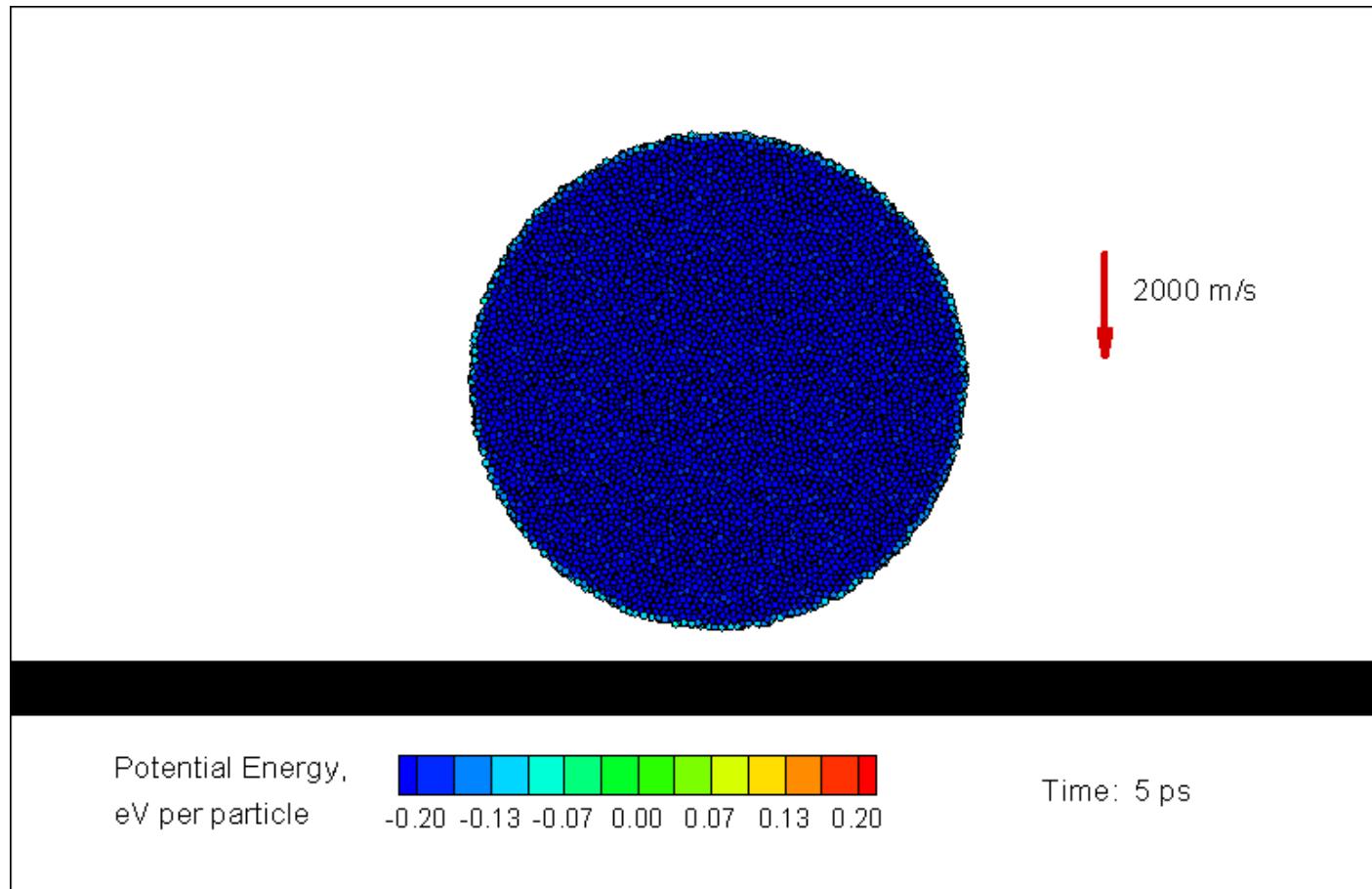


Experiment: Sergei Aksyonov and Peter Williams (Impact Desolvation of Electrosprayed Clusters (IDEC))

Examples of MD simulations: Collision of a droplet with a substrate

MD simulation by Yasushi Katsumi (term project for MSE 627)

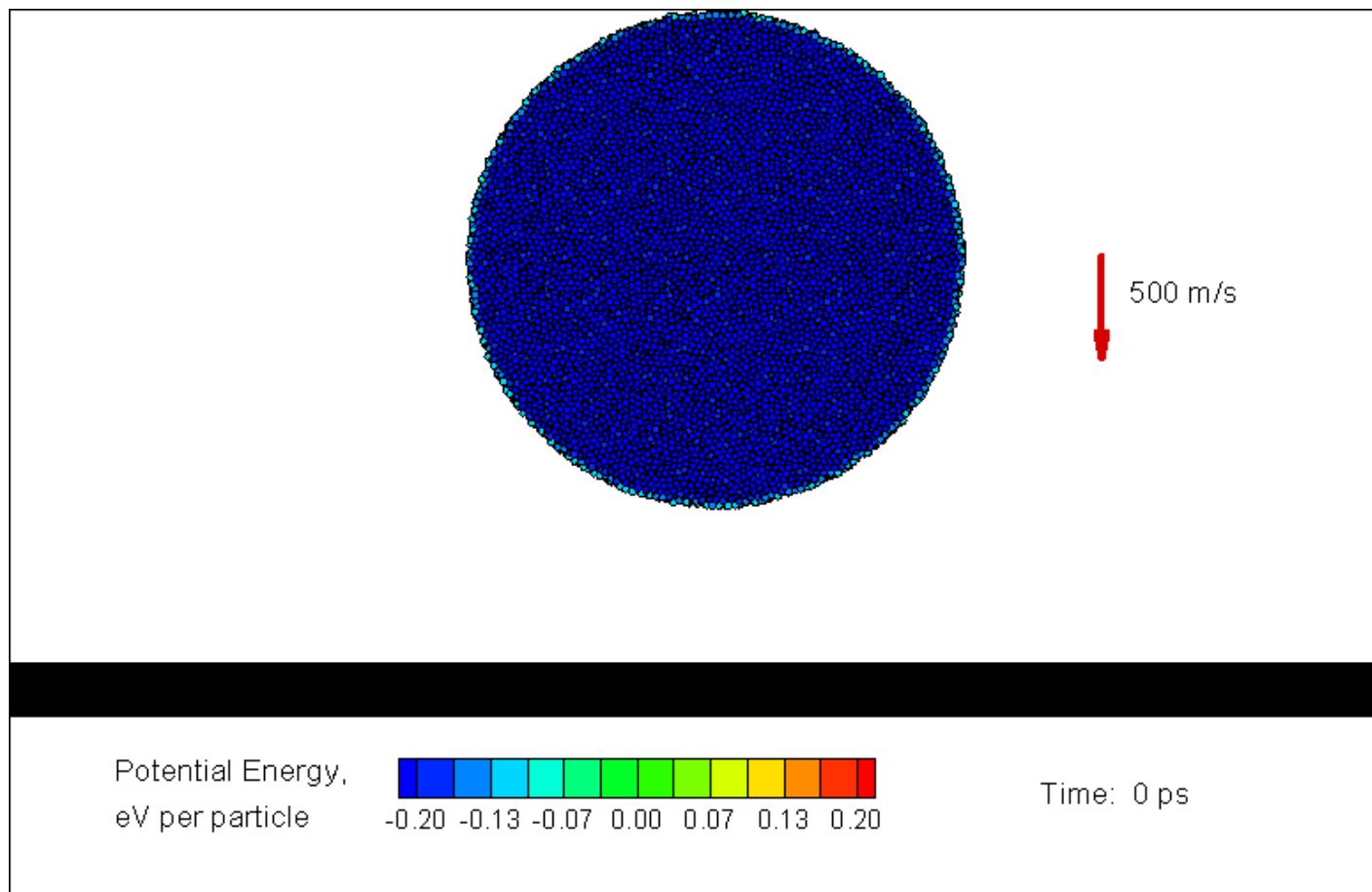
Impact velocity is 2000 m/s



Examples of MD simulations: Collision of a droplet with a substrate

MD simulation by Yasushi Katsumi (term project for MSE 627)

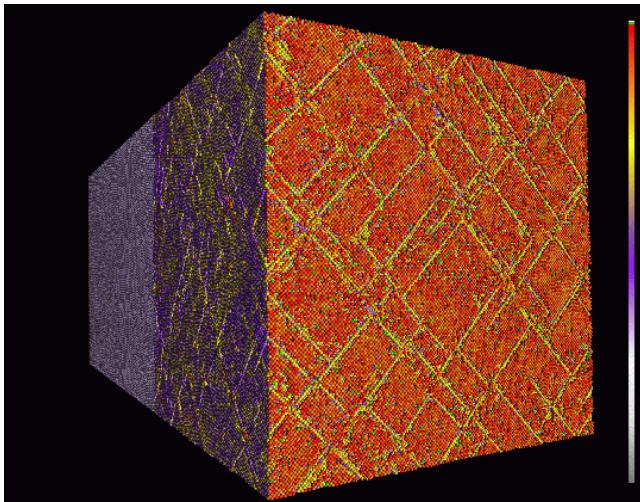
Impact velocity is 500 m/s



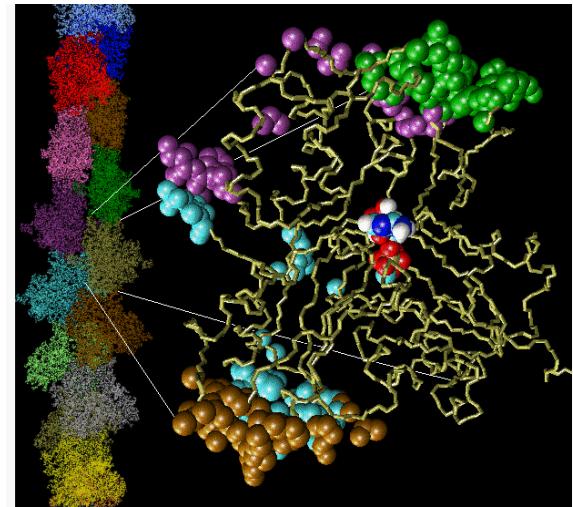
Examples of MD simulations

Since the time the MD method was introduced, it has been used to investigate a wide range of problems in different research fields, e.g.

- **Chemistry and Biochemistry:** molecular structures, reactions, drug design, vibrational relaxation and energy transfer, structure of membranes, dynamics of large biomolecules, protein folding, ...
- **Statistical Mechanics and Physics:** theory of liquids, correlated many-body motion, properties of statistical ensembles, structure and properties of small clusters, phase transitions..
- **Materials Science:** point, linear, and planar defects in crystals and their interactions, microscopic mechanisms of fracture, surface reconstruction, melting and faceting, film growth, friction, ...



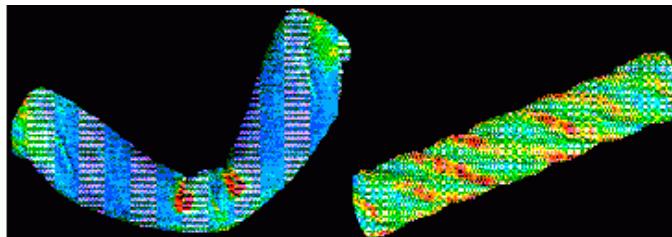
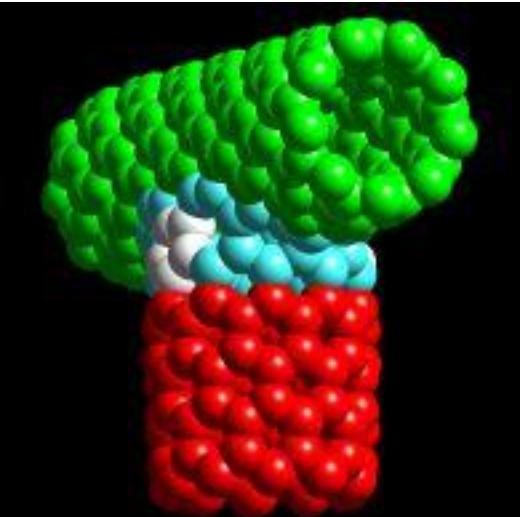
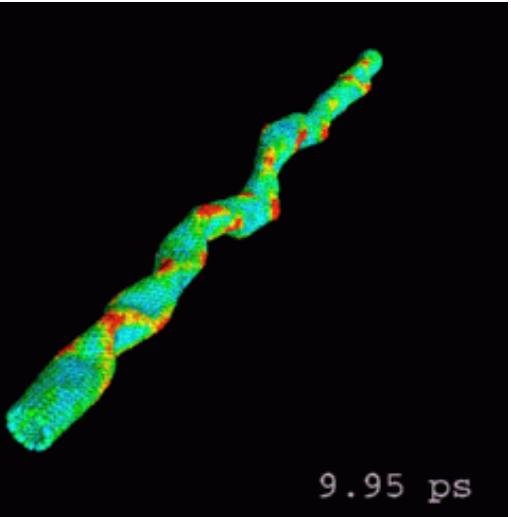
Shockwave-induced plasticity [B.L. Holian and P.S. Lomdahl, *Science* **280**, 2085 (1998)]



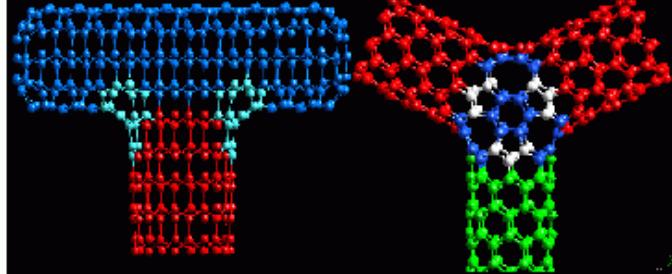
Actin filaments, simulation by W. Wriggers, University of Illinois

Examples of MD simulations: Computational nanotechnology at NASA

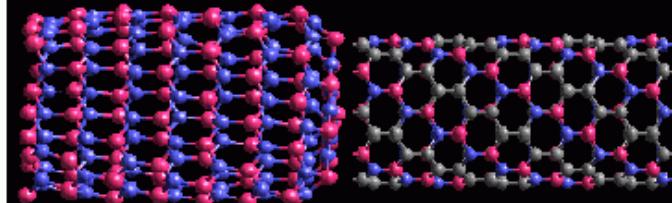
Carbon nanotubes are expected to be an important building block in future nanoscale materials, sensors, machines, and computers.



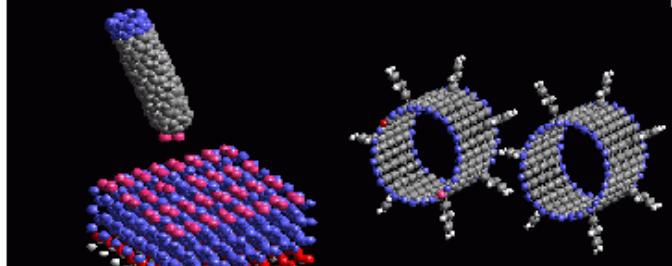
Nanotube – Nanomechanics



Carbon based Nanoelectronics



C_xB_yN_z – Heteroatomic Nanotubes



Nano-electromechanical Systems

by Deepak Srivastava, NASA Ames

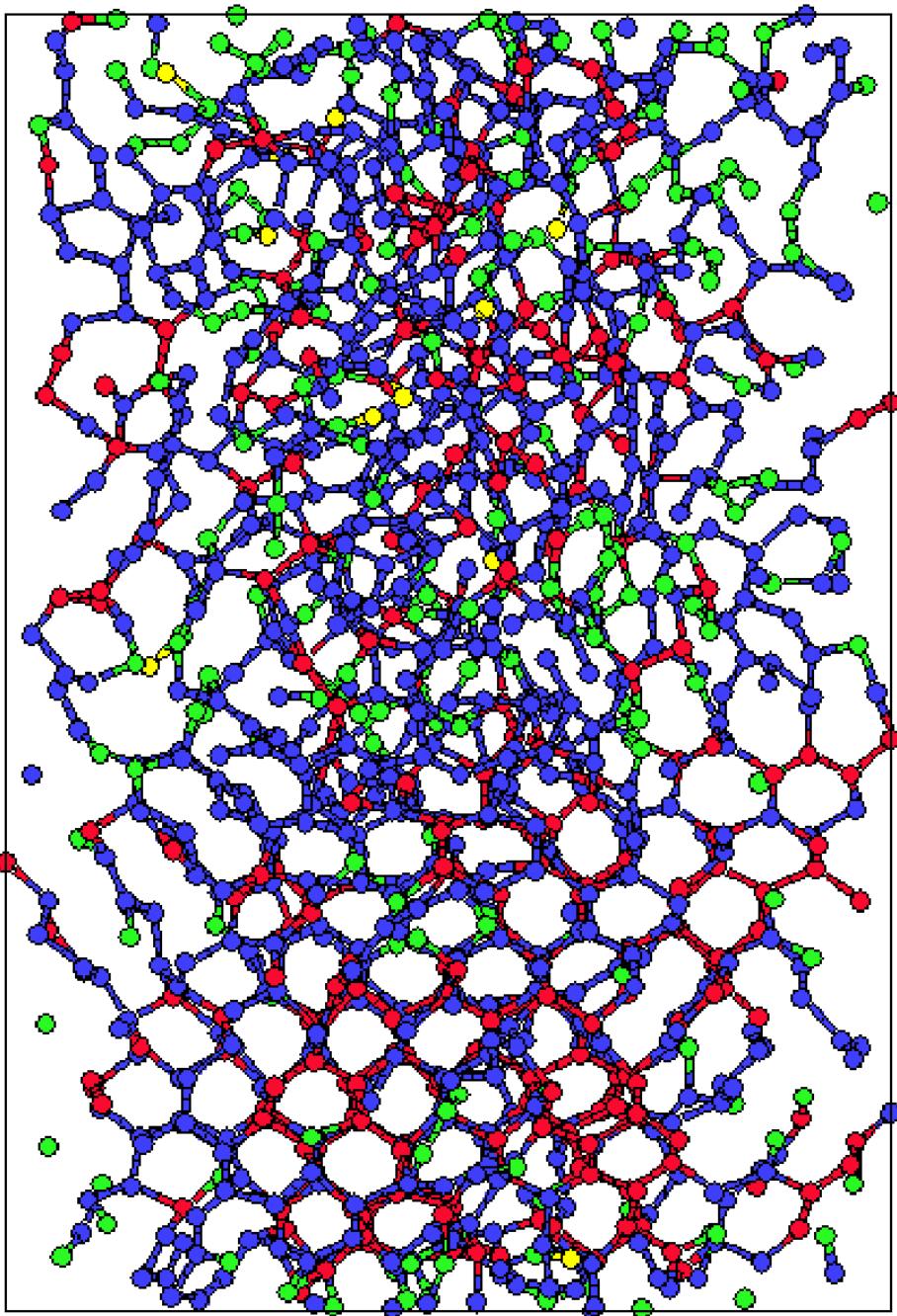
<http://www.ipt.arc.nasa.gov/carbonnano.html>

Examples of MD simulations: Melting of diamond crystal

Tight Binding Molecular Dynamics with up to 10,000 atoms.

1024 node Paragon XP/S 150 supercomputer is used in calculations.

The figure shows a snapshot of 2000 carbon atoms at $T > 6000$ K with the lower half in a diamond lattice and the upper half in a liquid phase. **Four-fold bonded (diamond-like) atoms are colored red, three-fold bonded (graphitic) atoms are colored blue.**



Picture from

<http://cmp-o1.ameslab.gov/cmsn/otherlinks/ssi/diamond.html>

Examples of MD simulations: Laser melting of nanocrystalline Au films

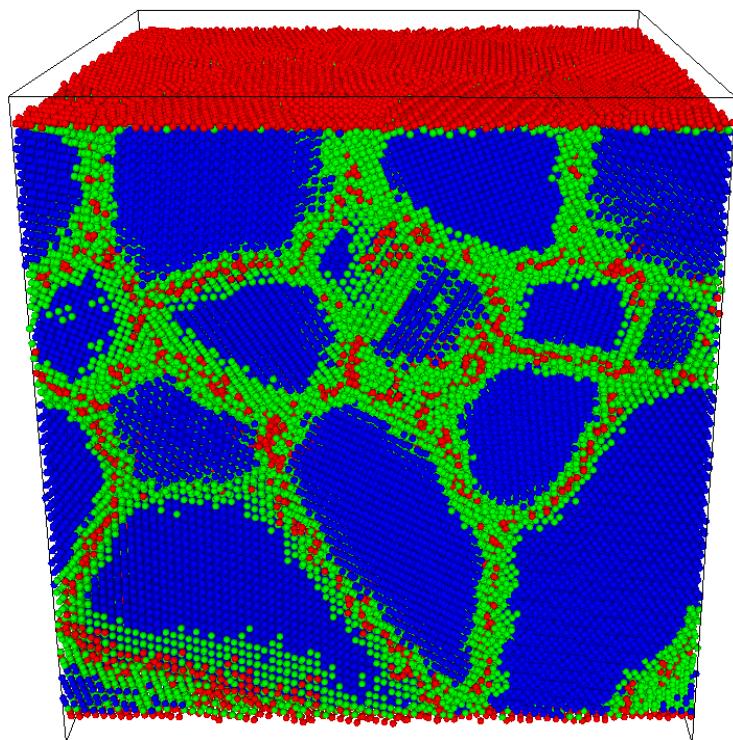
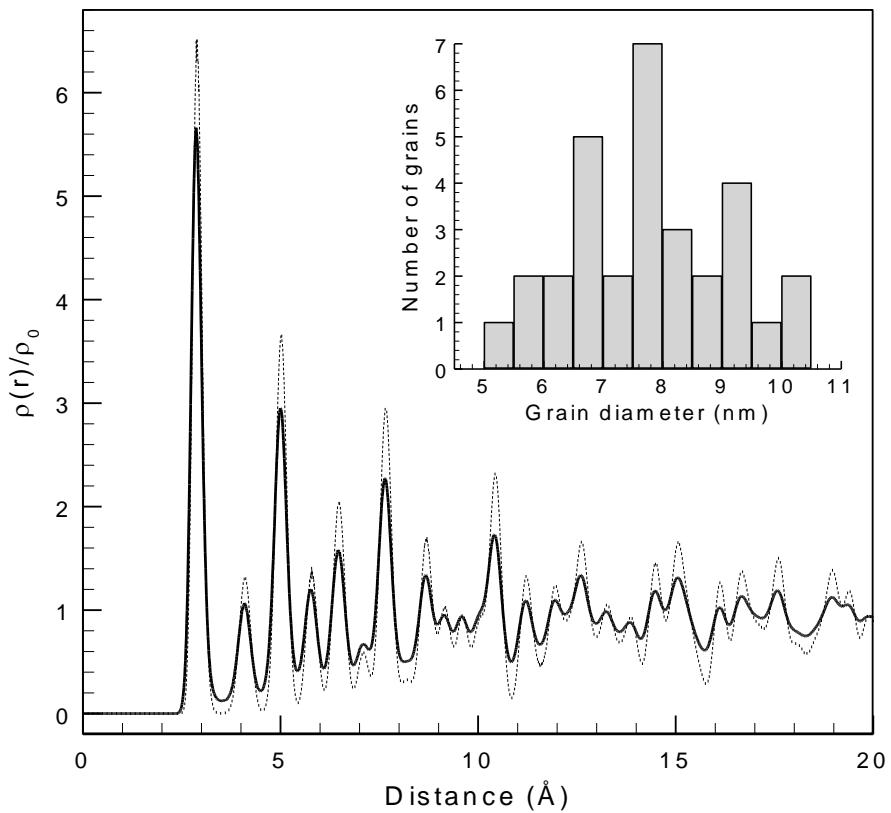
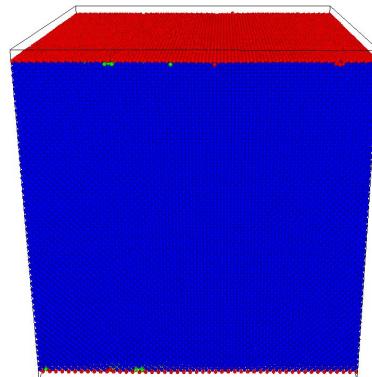
20 nm Au films – similar to electron diffraction experiments

[Dwyer et al., *Philos. Trans. R. Soc. London, Ser. A* **364**, 741, 2006]

Periodic boundary conditions in lateral directions

Films are equilibrated at 300 K before irradiation

Atoms are colored by centrosymmetry parameter (blue – fcc)

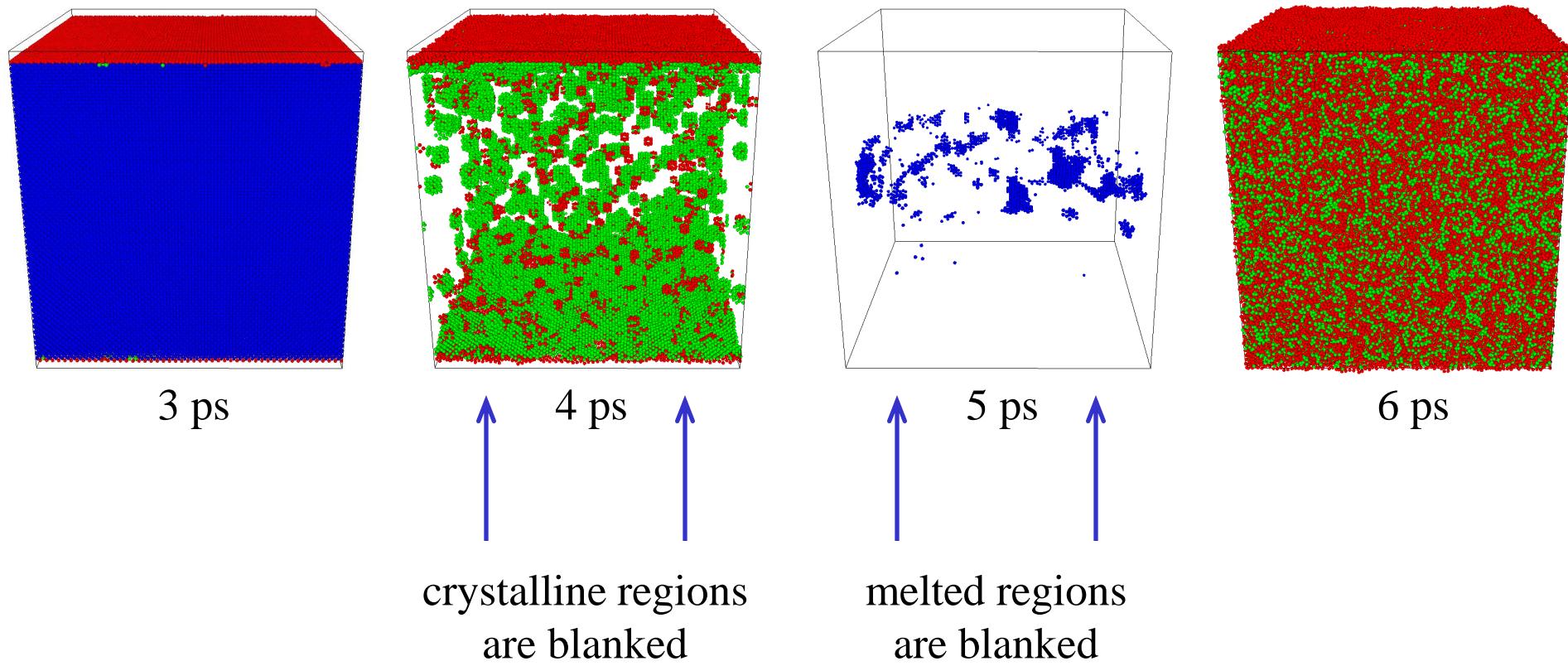


~500,000 atoms

31 grains, average grain diameter: 8 nm

Melting of single crystal and nanocrystalline films, high fluence (180 J/m^2)

single crystal film:

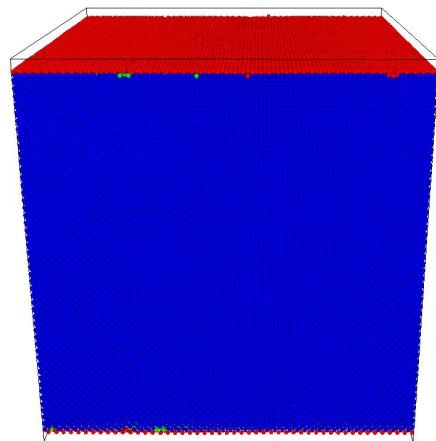


Melting mechanism: rapid collapse of the lattice overheated above the limit of its stability. No time to create well-defined liquid nuclei.

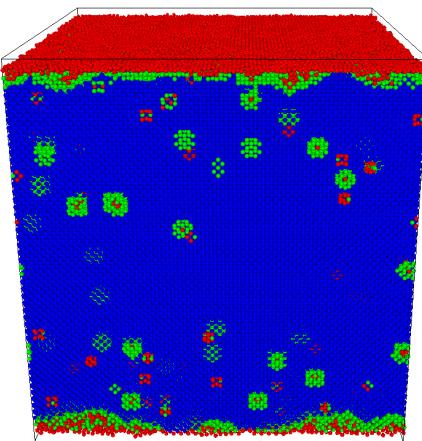
Generation of a large number of point defects (vacancy – interstitial pair) creates a “background” of the elevated potential energy and contributes to the collapse of the crystalline structure. No time to form clusters of point defects [Forsblom, Grimvall, *Nat. Mater.* **4**, 388, 2005].

Melting of single crystal and nanocrystalline films, high fluence (180 J/m²)

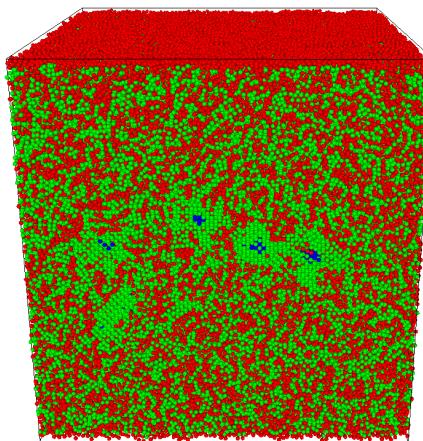
single crystal film:



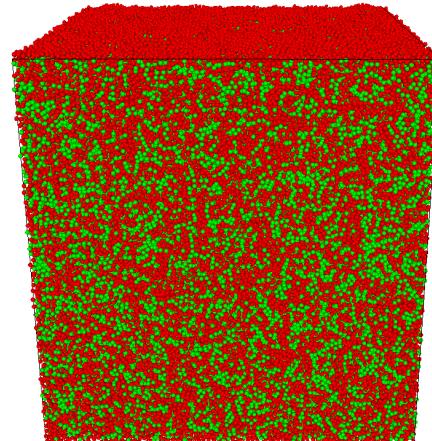
3 ps



4 ps

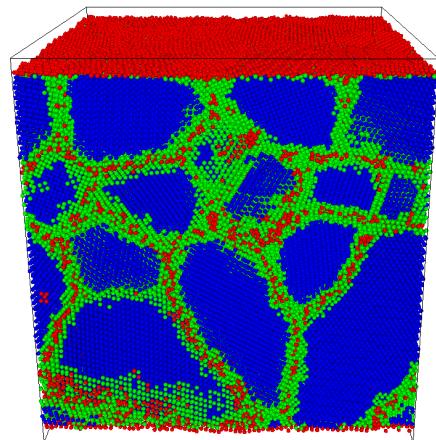


5 ps

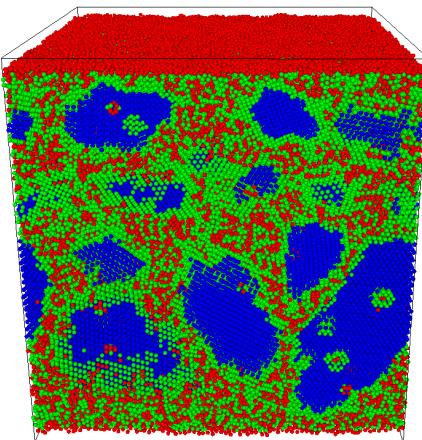


6 ps

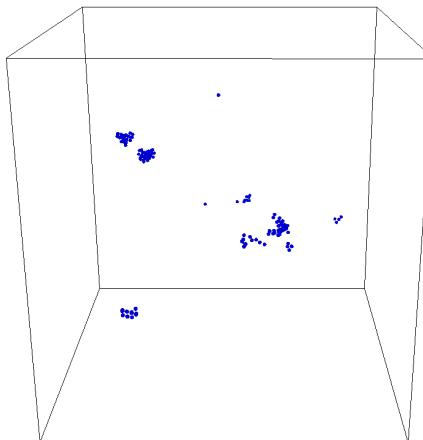
nanocrystalline film:



3 ps



4 ps

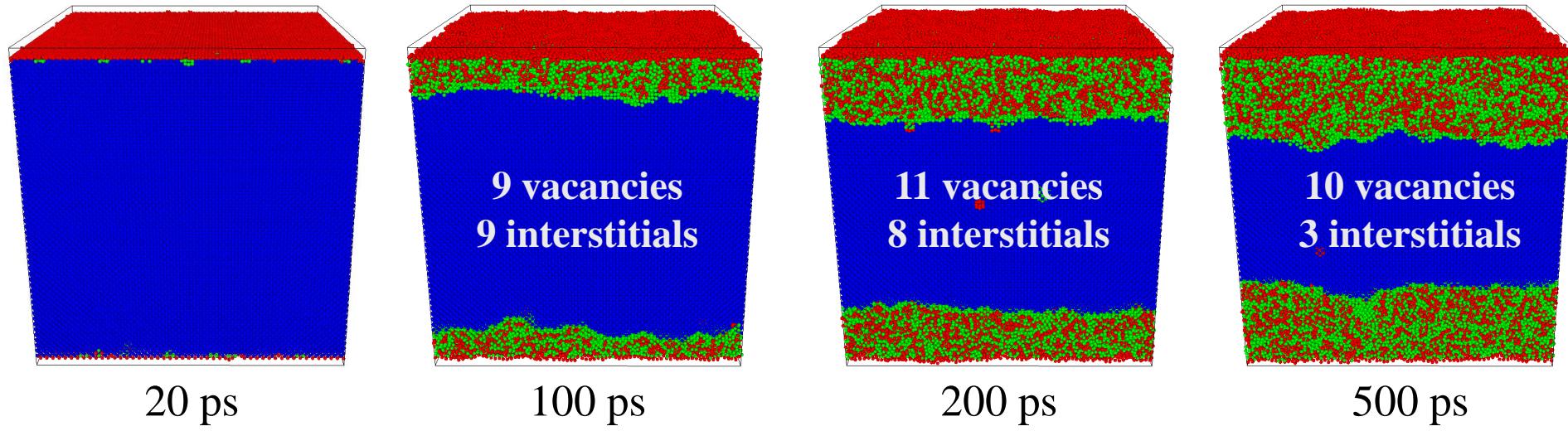


5 ps

melted regions
are blanked

Melting of single crystal and nanocrystalline films, low fluence (45 J/m^2)

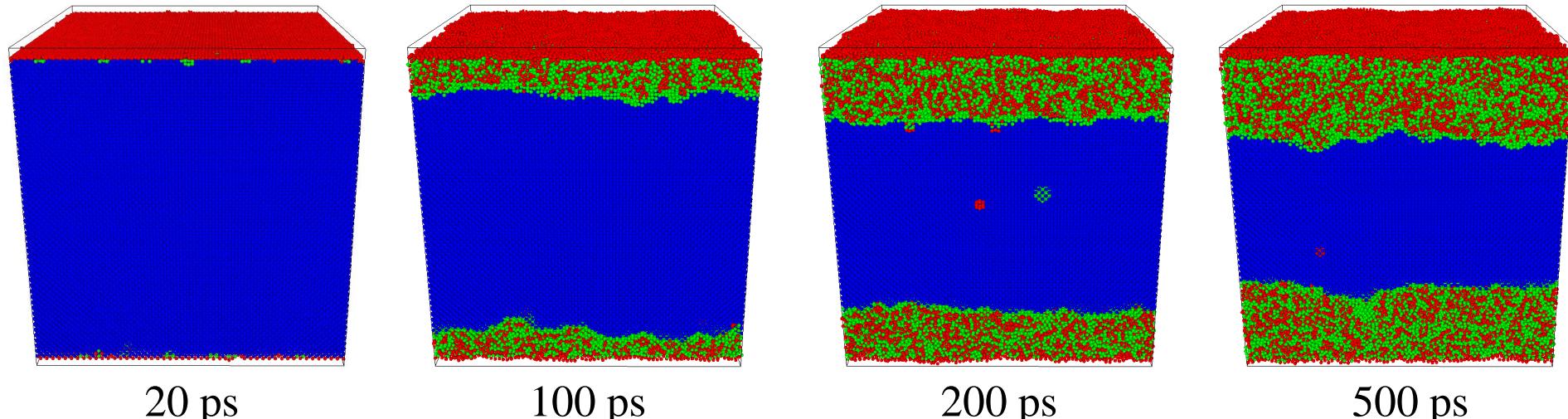
single crystal film:



Melting mechanism: propagation of two melting fronts from two free surfaces of the film.

Melting of single crystal and nanocrystalline films, low fluence (45 J/m^2)

single crystal film:



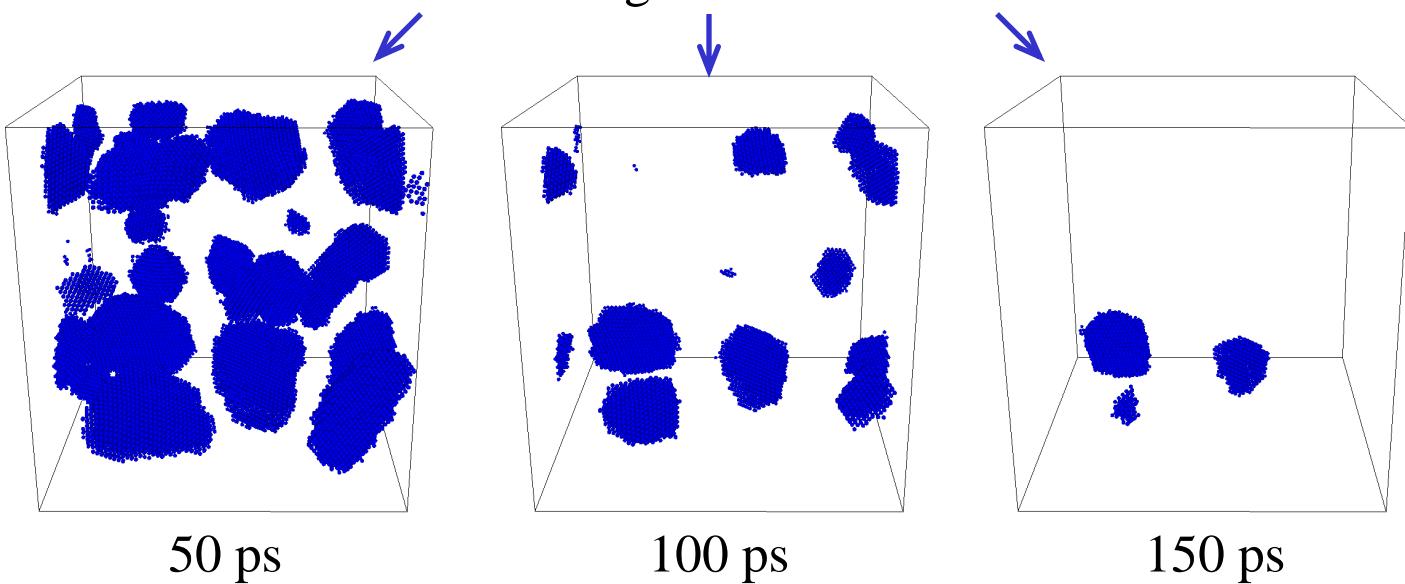
20 ps

100 ps

200 ps

500 ps

nanocrystalline film:



20 ps

50 ps

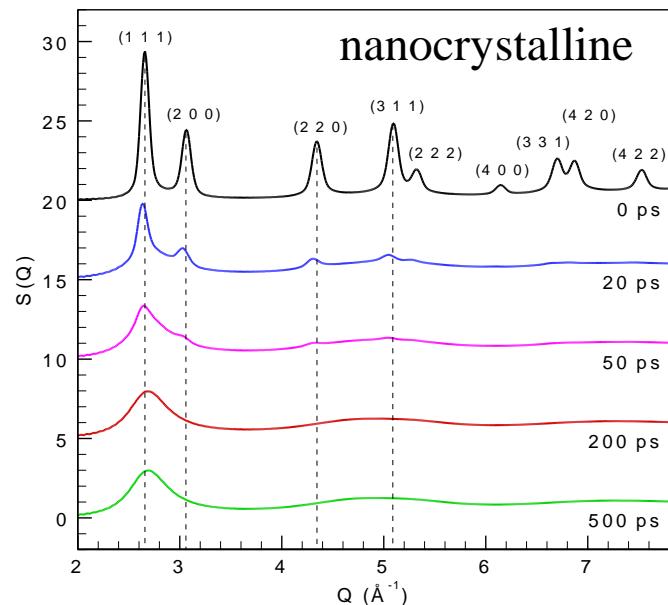
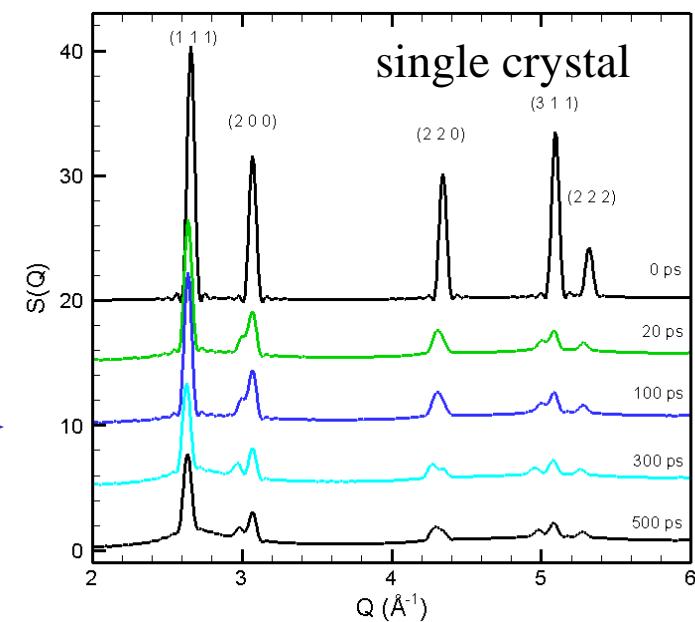
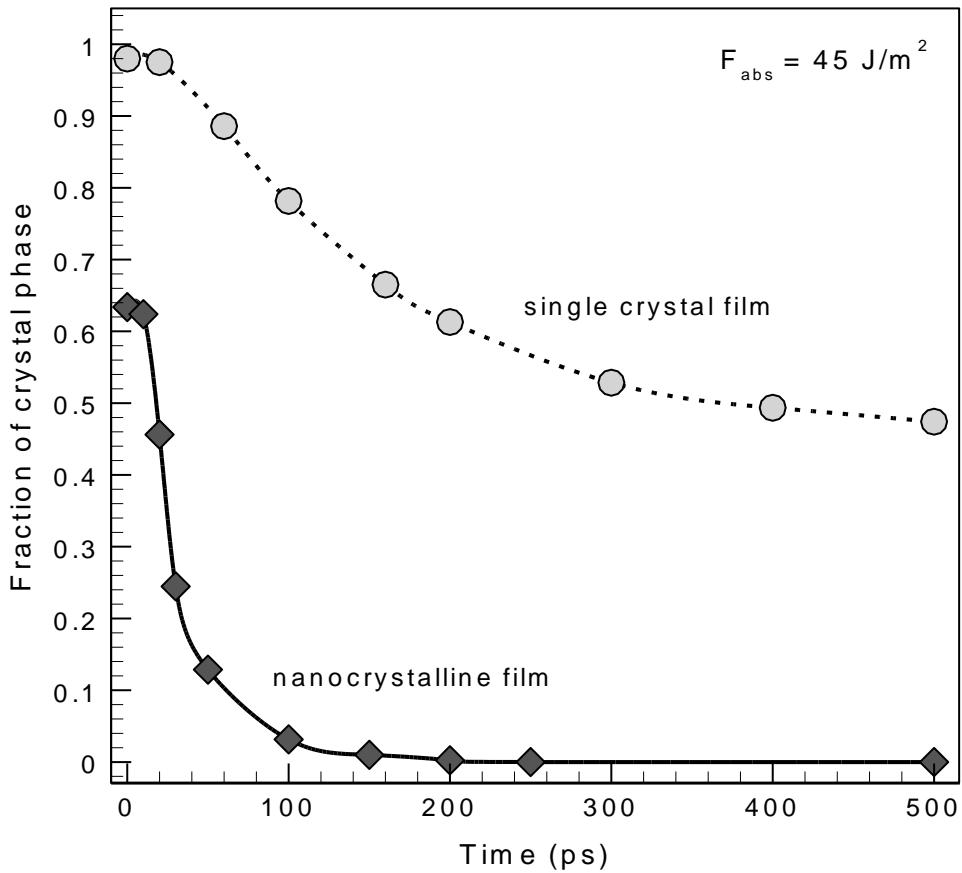
100 ps

150 ps

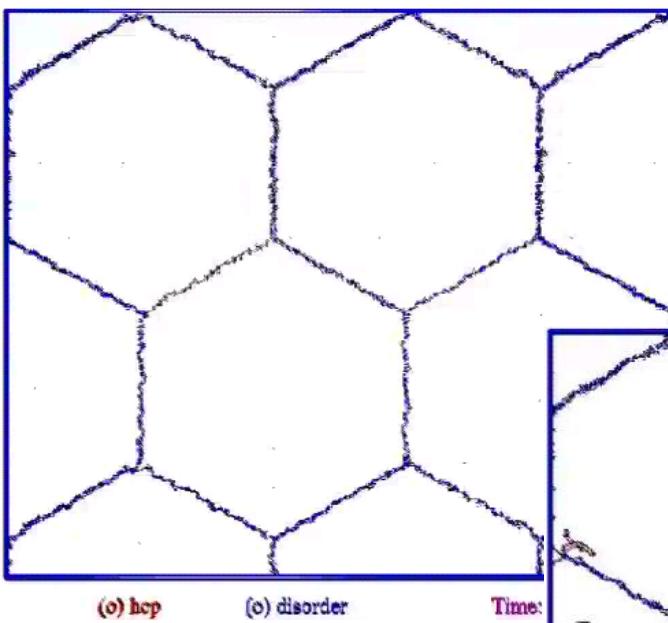
melted regions are blanked

Fraction of atoms in the crystalline parts of the films

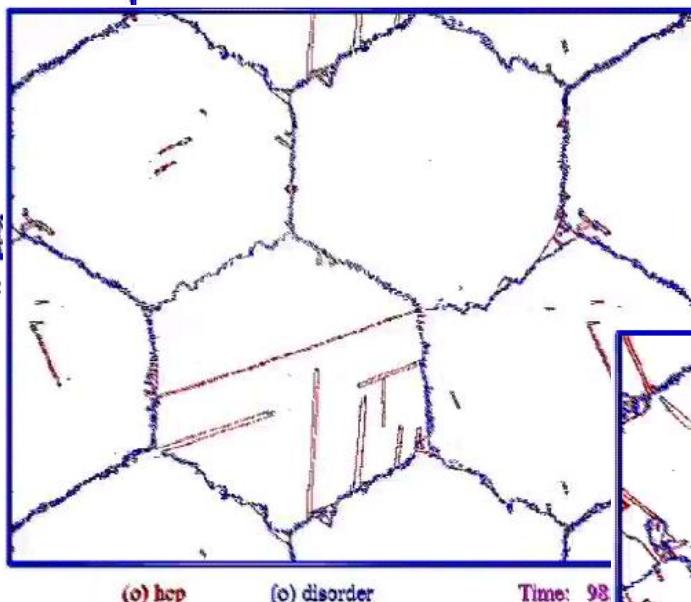
single crystal (dashed lines) and nanocrystalline (solid lines)



Examples of MD simulations: Deformation of nanocrystalline aluminum

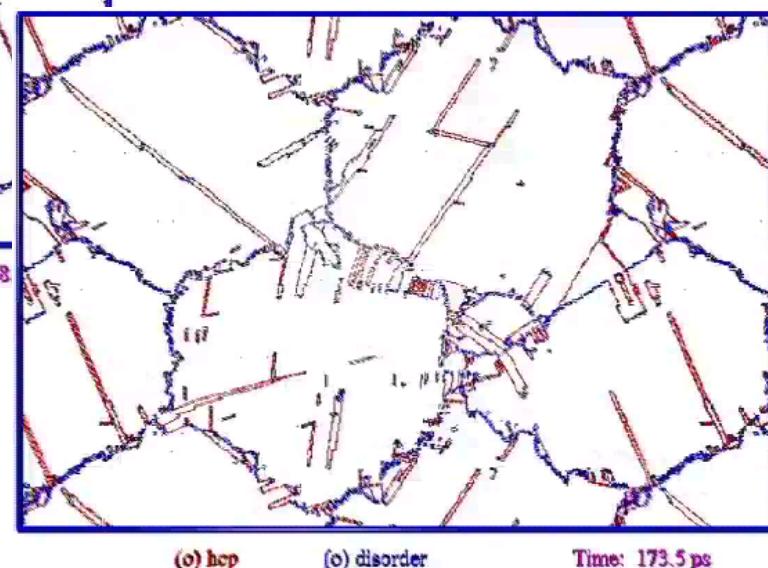


MD simulations of plastic deformation of nanocrystalline Al performed under constant tensile loads of 2.3–2.5 Pa, high deformation rate of 10^7 s $^{-1}$ and temperature of T = 300 K.



Four grains 20 and 70 nm in size (97,000 and 1,021,000 atoms) are simulated.

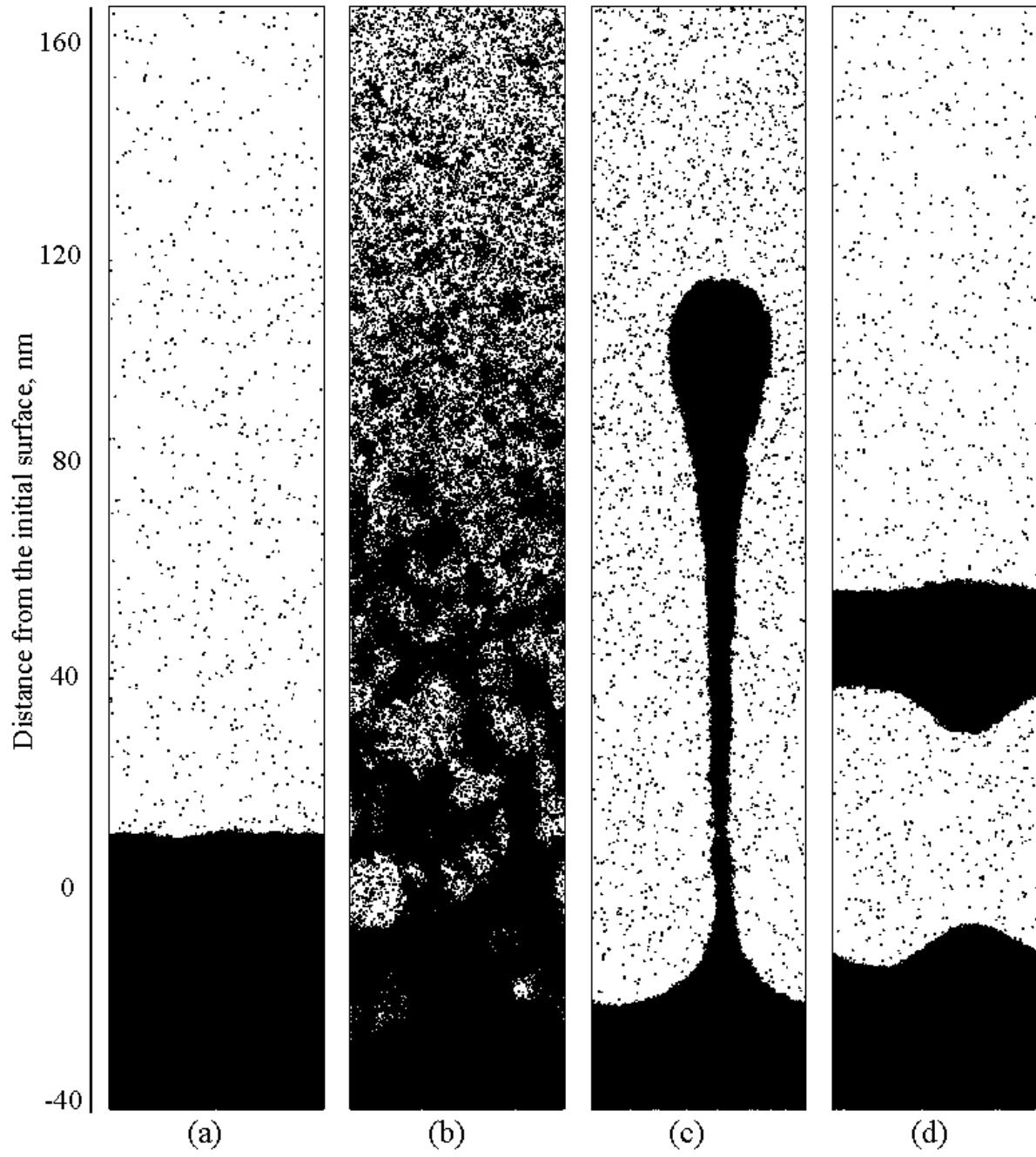
Mechanical twinning plays an important role in plastic deformation of nanocrystalline Al.



V. Yamakov, D. Wolf, S.R. Phillpot, A. K. Mukherjee, and H. Gleiter, *Nature Materials* **1**, 45–49 (2002).

A movie from the simulation can be found at
<http://www.nature.com/nmat/journal/v1/n1/extref/nmat700-s1.mov>

Examples of MD simulations: generation of clusters in laser ablation

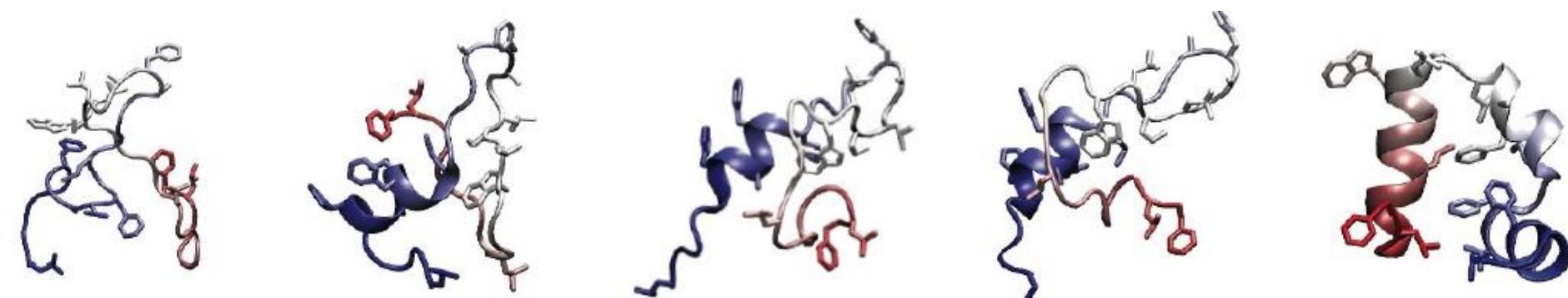


Animations from these simulations can be found at
<http://www.faculty.virginia.edu/CompMat/ablation/animations/>

Record simulations (time-scale): quest for milliseconds

Protein folding

The protein-folding problem is one of the major challenges of molecular biology. Functionality of proteins is directly related to their conformation - the complex folds allow proteins to latch onto other molecules and carry out its biological role. To investigate the protein folding problem in MD simulation one has to follow the evolution of a large molecule in a solution for at least microseconds.

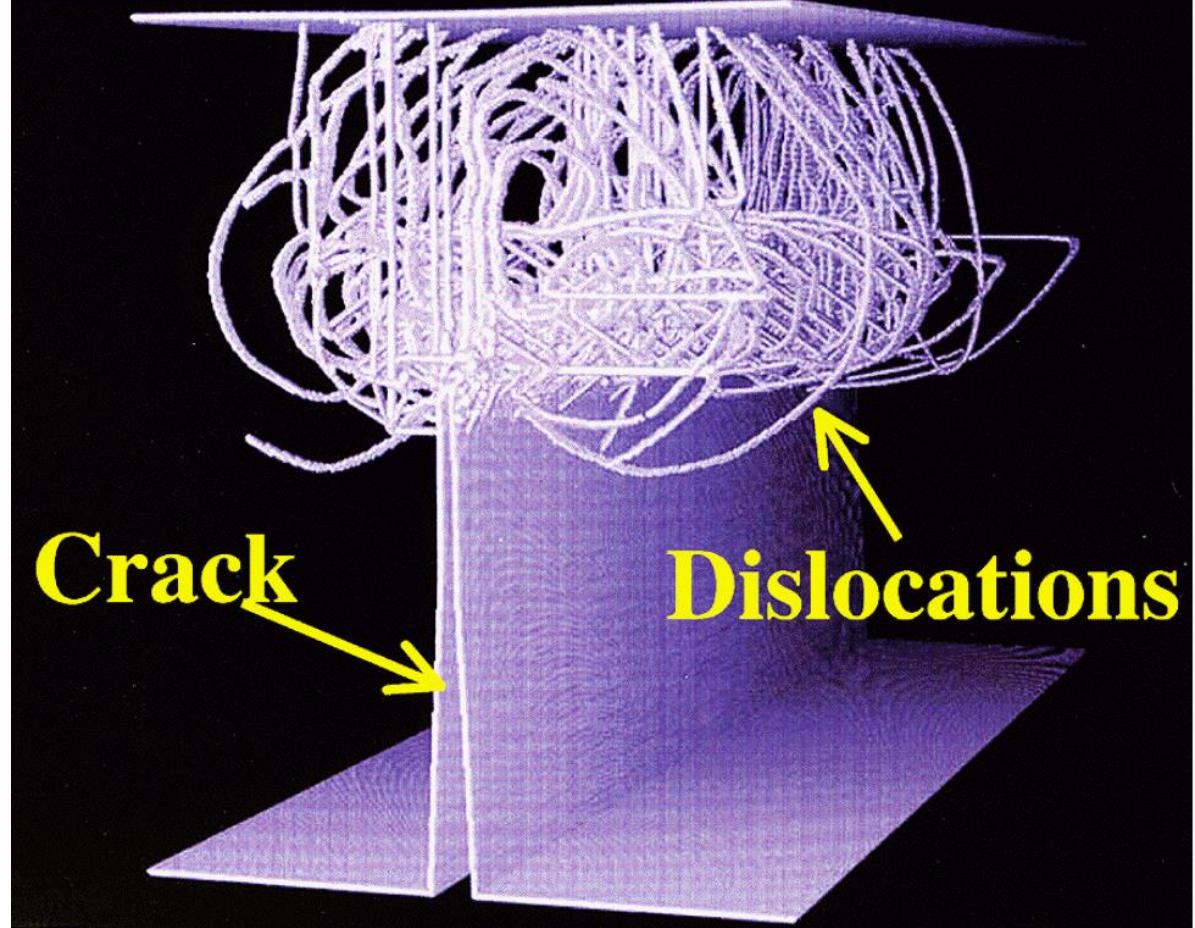


MD simulation of the folding of the villin headpiece, one of the fastest-folding proteins
Nature 451, 240, 2008

Folding@home: a distributed computing project - people from around the world download and run software to make a virtual “supercomputer,” allowing for simulations of milliseconds of folding time. <http://folding.stanford.edu/>

Examples of MD simulations: Large-scale simulation of crack propagation

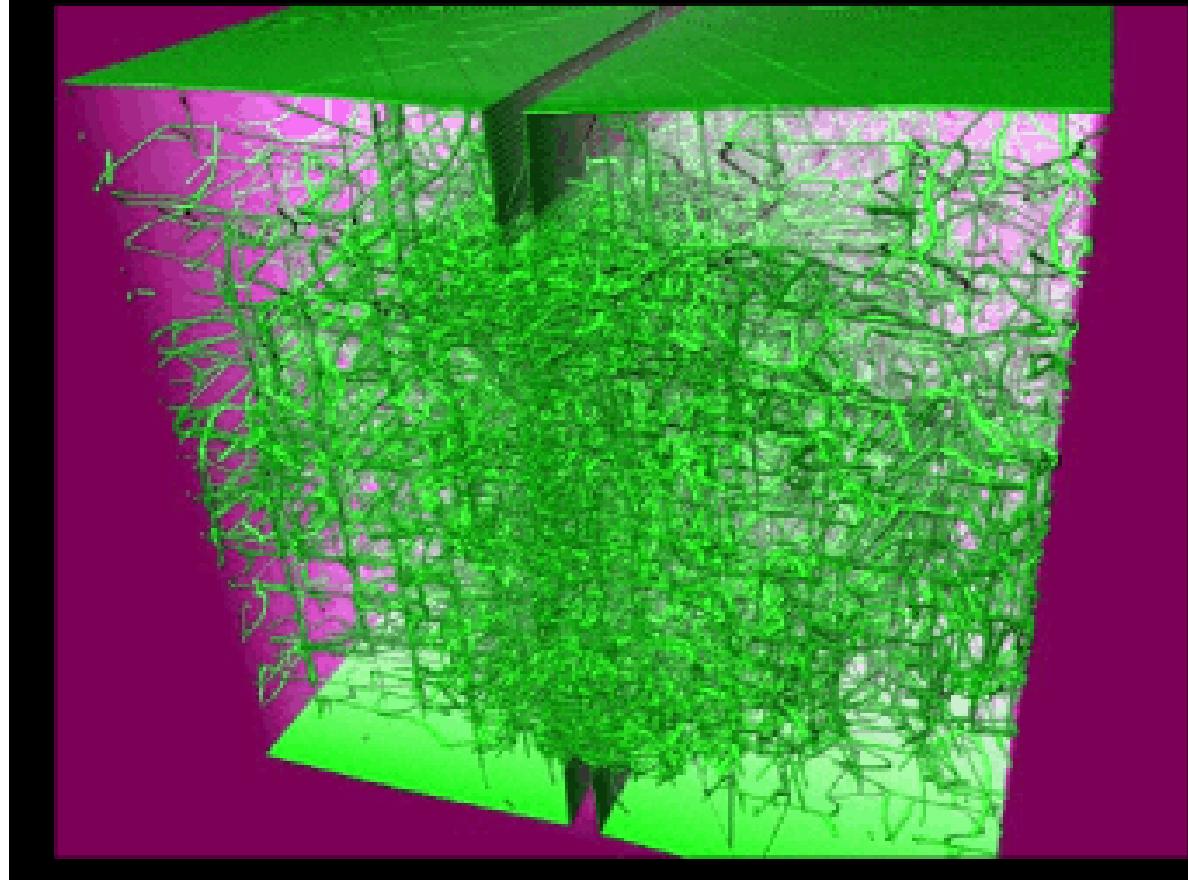
by F. F. Abraham *et al.*



Molecular dynamics simulation with ~1 billion atoms illustrates crack propagation in a ductile metal. At first, the crack moves very rapidly and local bonds break in a "brittle" manner, but at some point the crack-tip begins to emit dislocations (the tangles in the picture) and stops propagating. Such a crack is said to become blunted and begins to cause **intense local deformation** but not failure.

Examples: Large-scale simulation of crystal fracture

IBM-LLNL collaboration
2002

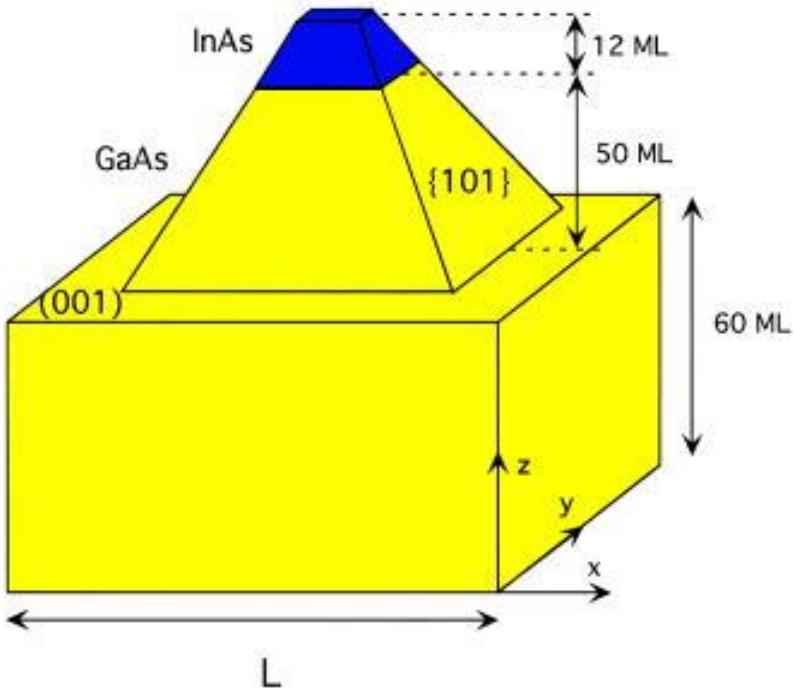


Simulation of work-hardening and ductile failure of a FCC solid under tension. The system is a FCC crystallite with a total number of atoms of 1,023,103,872. The simulation time is 200,000 timesteps. It takes 1.7 seconds per timestep for a 4096-node simulation on ASCI White computer (~four clock-days of total simulation time).

A movie from the simulation can be found at

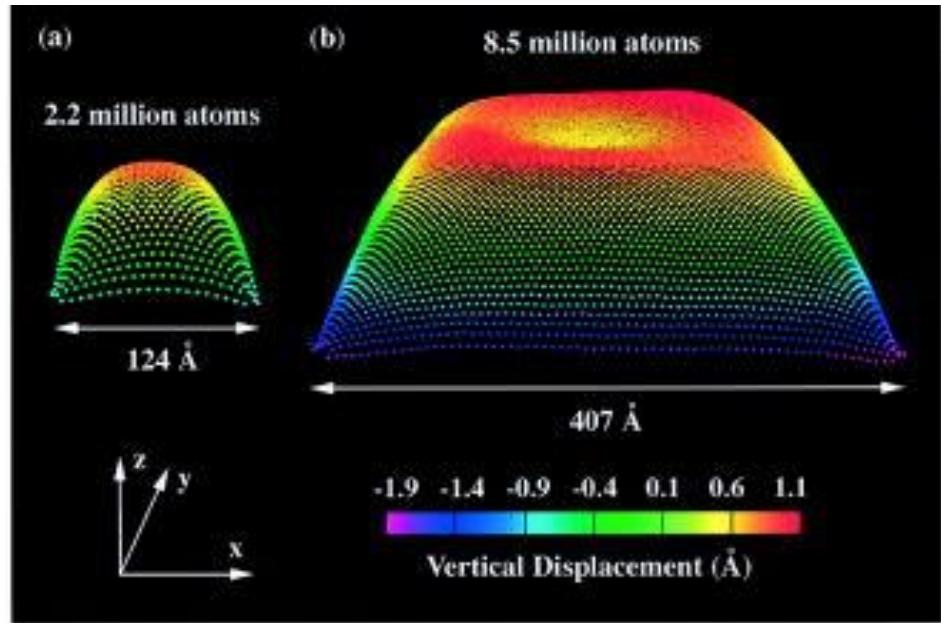
http://domino.research.ibm.com/comm/pr.nsf/pages/news.20020429_fracture_simulation.html

Examples of MD simulations: Relaxation of heteroepitaxial islands



InAs/GaAs mesa with $\langle 100 \rangle$ oriented square base and $\{101\}$ sidewalls on a GaAs(001) substrate

Su et al., Appl. Phys. Lett. **79**, 4577, 2001
multimillion-atom MD study



Vertical displacement of As atoms in the first As layer above the first In layer in the (a) 2.2 million atom, and (b) 8.5 million atom nanomesas.

Conclusion: existence of a critical lateral size for stress domain formation (a single stress domain on a small, <40 nm mesa, several stress domain on larger mesas) – can be related to experimentally observed chains of InAs islands on GaAs stripe mesa top.