Molecular dynamics modeling of thermal and mechanical properties

Alejandro Strachan
School of Materials Engineering
Purdue University
strachan@purdue.edu

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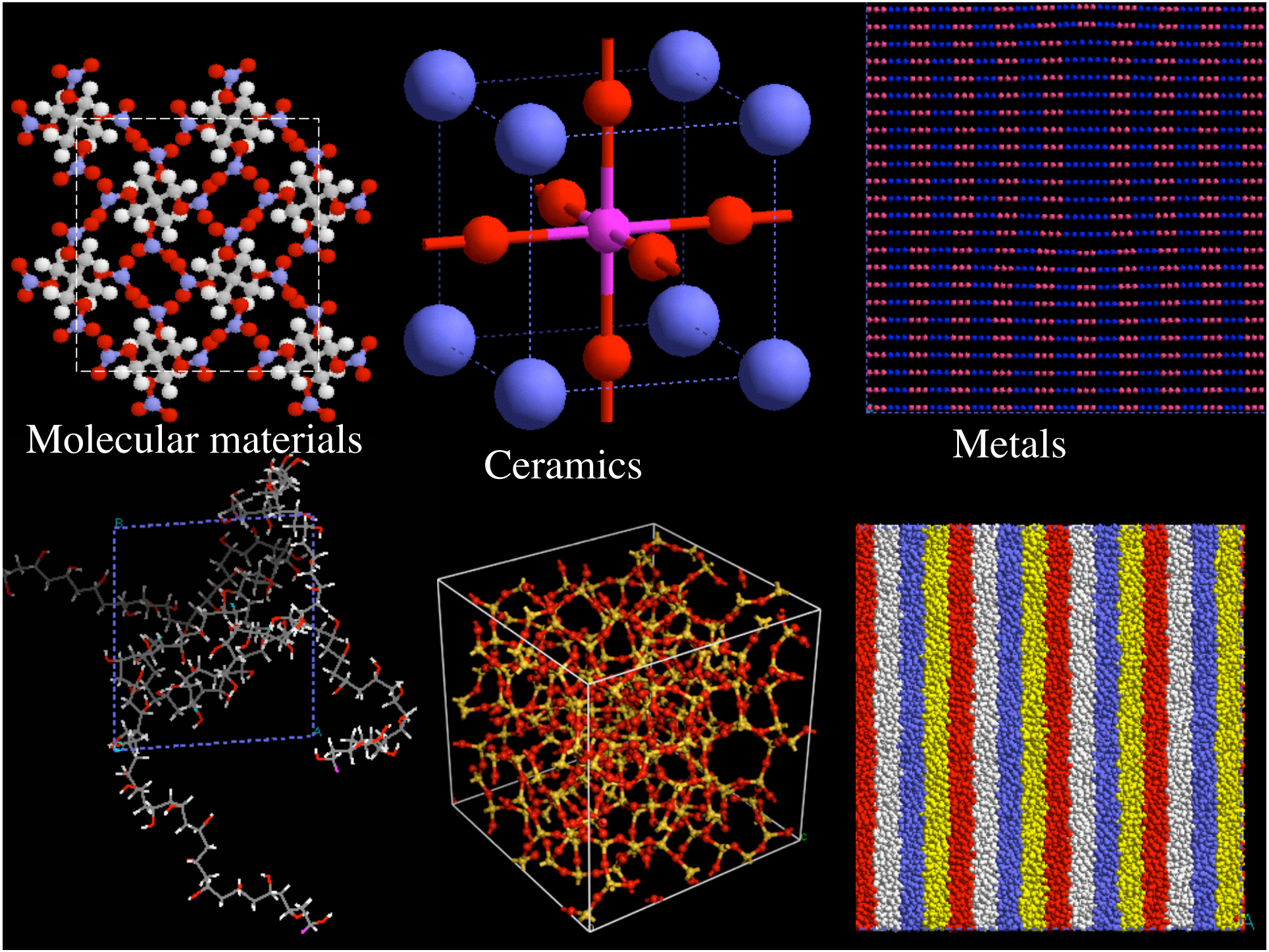

Molecular materials
Ceramics
Metals

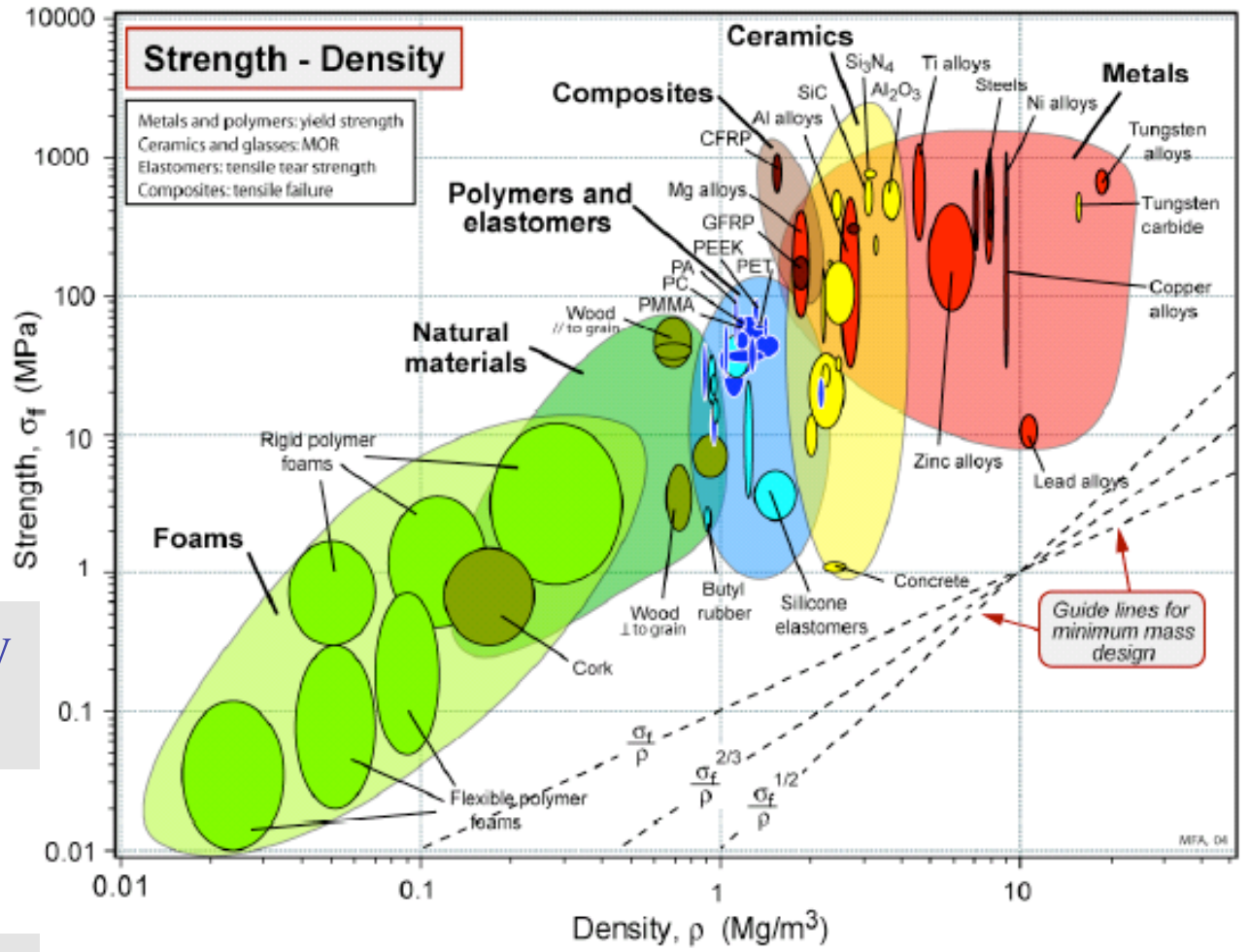
Materials properties charts

Materials look very different

Materials properties vary by many orders of magnitude

Composition/chemistry **Microstructure**

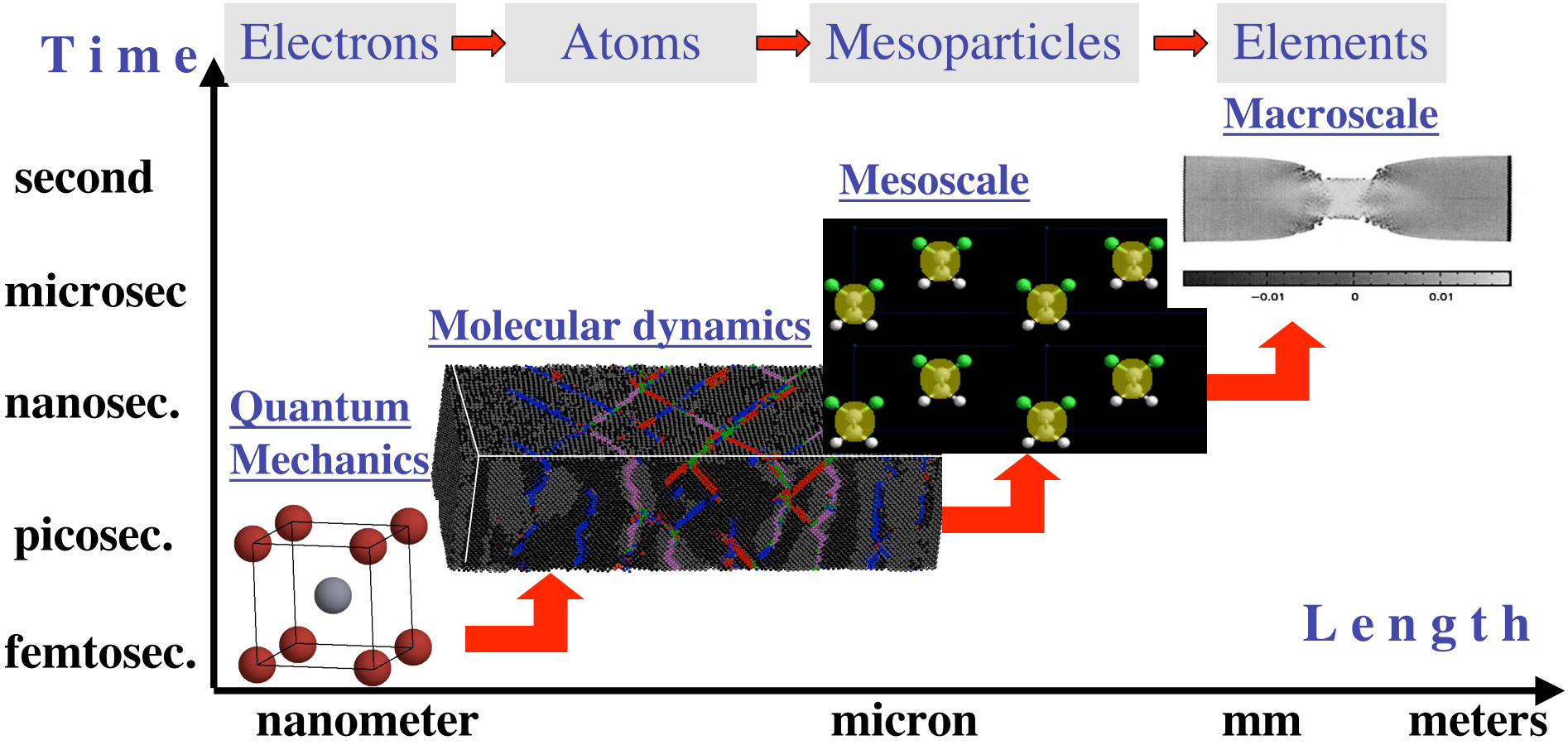
A variety of mechanisms govern materials behavior



Materials Selection in Mechanical Design (3rd edition) by MF Ashby, Butterworth Heinemann, 2005

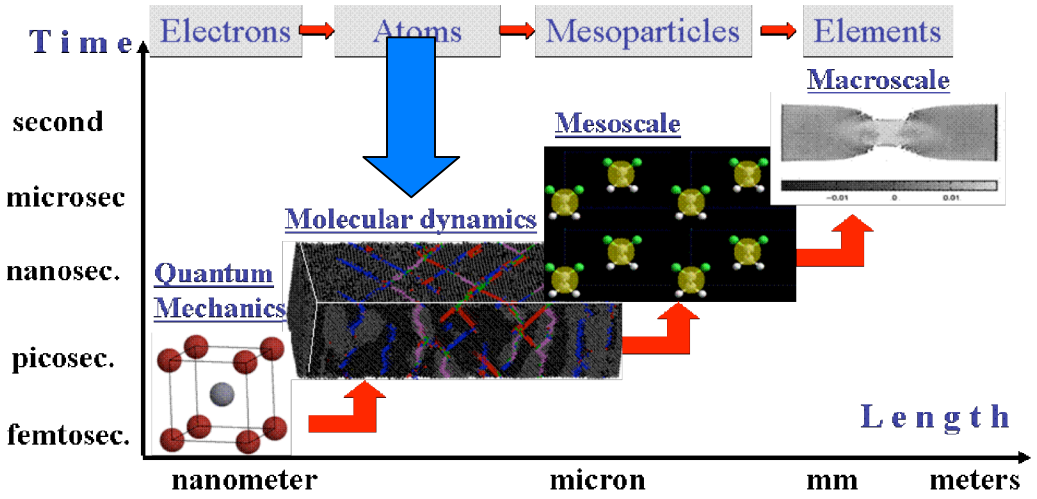
Multiscale modeling of materials

- Understand the molecular level origins of materials behavior
- *Predict* the behavior of materials from first principles



- Help design new materials or devices with improved performance

Molecular dynamics

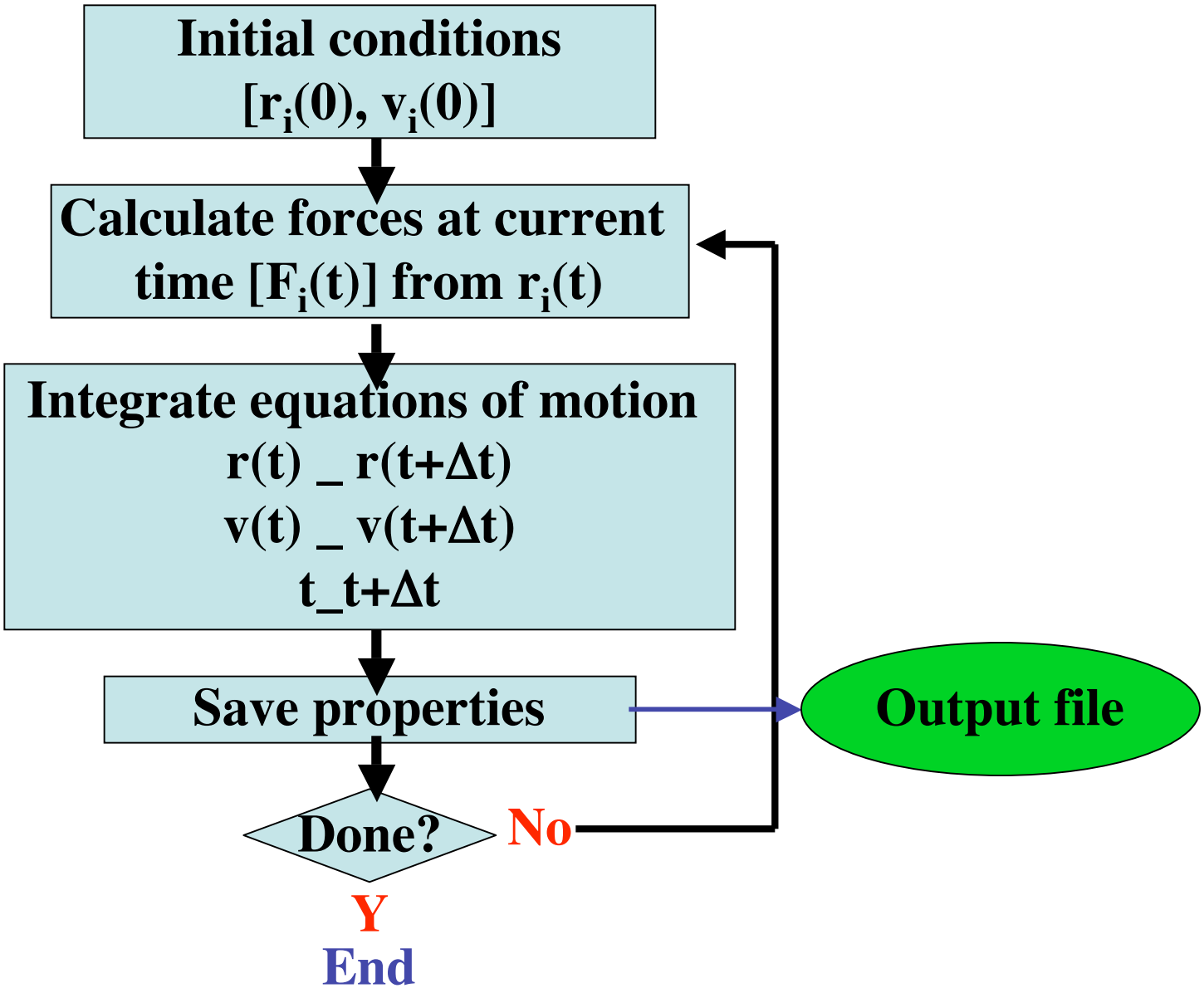


Explicitly solve the dynamics of all atoms of the material of interest

Newton's equations of motion

with forces obtained from the inter-atomic potential

MD: structure of an MD code



MD: integrating the equations of motion

Taylor expansion of positions with time

$$r_i(t+\Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 + \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathrm{O}(\Delta t^4)$$

$$r_i(t-\Delta t) = r_i(t) - \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 - \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathrm{O}(\Delta t^4)$$

The Verlet algorithm

MD: thermodynamic ensembles

$$\dot{r}_i = u_i$$

$$\dot{u}_i = \frac{F_i}{m_i} \quad \text{with} \quad F_i = -\nabla_{R_i} E$$

Temperature:

$$\frac{3}{2} NkT = \langle K(t) \rangle_{time} = \left\langle \frac{1}{2} \sum_{i=1}^{N} m u_i^2(t) \right\rangle_{time}$$

Instantaneous temperature (T^*):

$$\frac{3}{2} NkT^*(t) = K(t) = \frac{1}{2} \sum_{i=1}^{N} m u_i^2(t)$$

MD: isothermal molecular dynamics

How can we modify the EoM so that they lead to constant temperature?

Berendsen's thermostat

$$\dot{r}_i = u_i$$

$$\dot{u}_i = \frac{F_i}{m_i}$$

Nose-Hoover thermostat

$$\dot{r}_i = u_i$$

$$\dot{u}_i = \frac{F_i}{m_i}$$

MD applications: melting

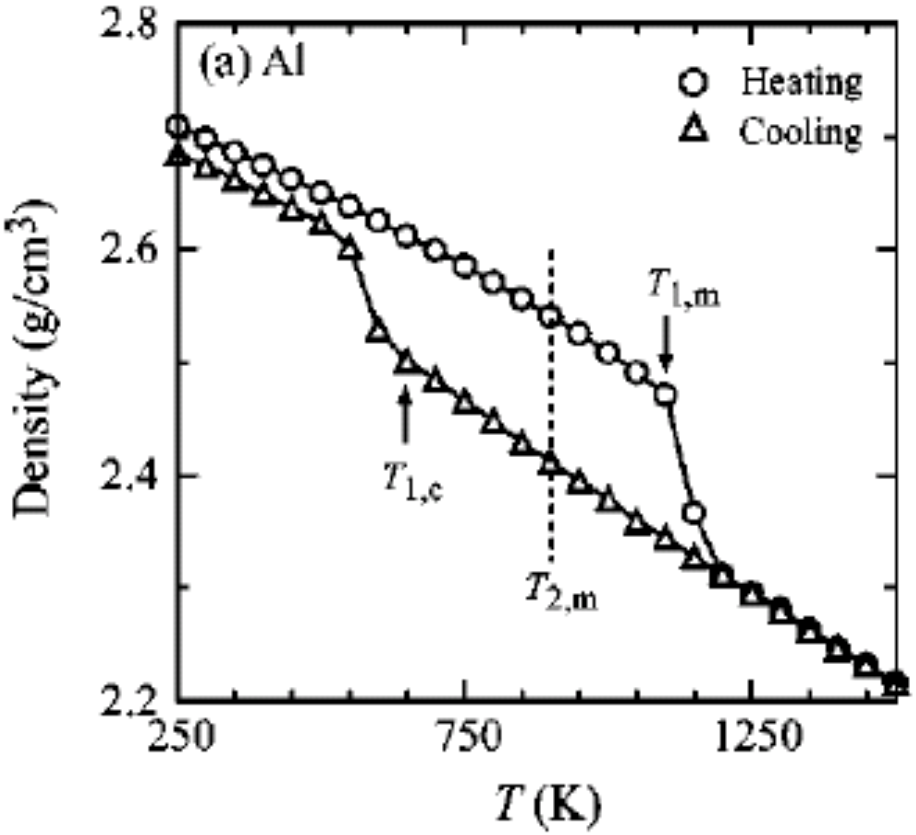
Simples and most direct approach:

- Take a solid and heat it up at constant pressure until it melts
- Then cool the melt until it re-crystalizes

Problems

Superheating of the solid & undercooling of the liquid

Why?

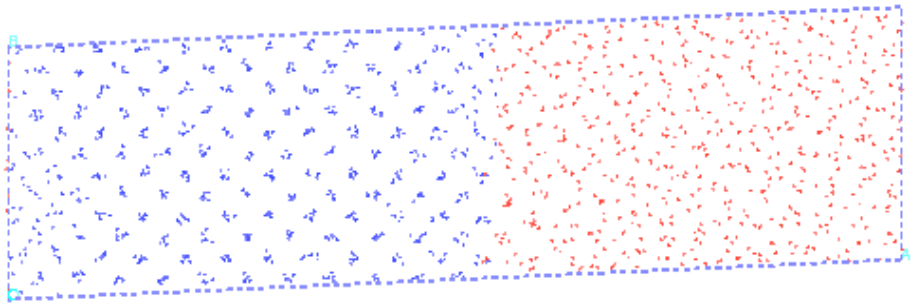


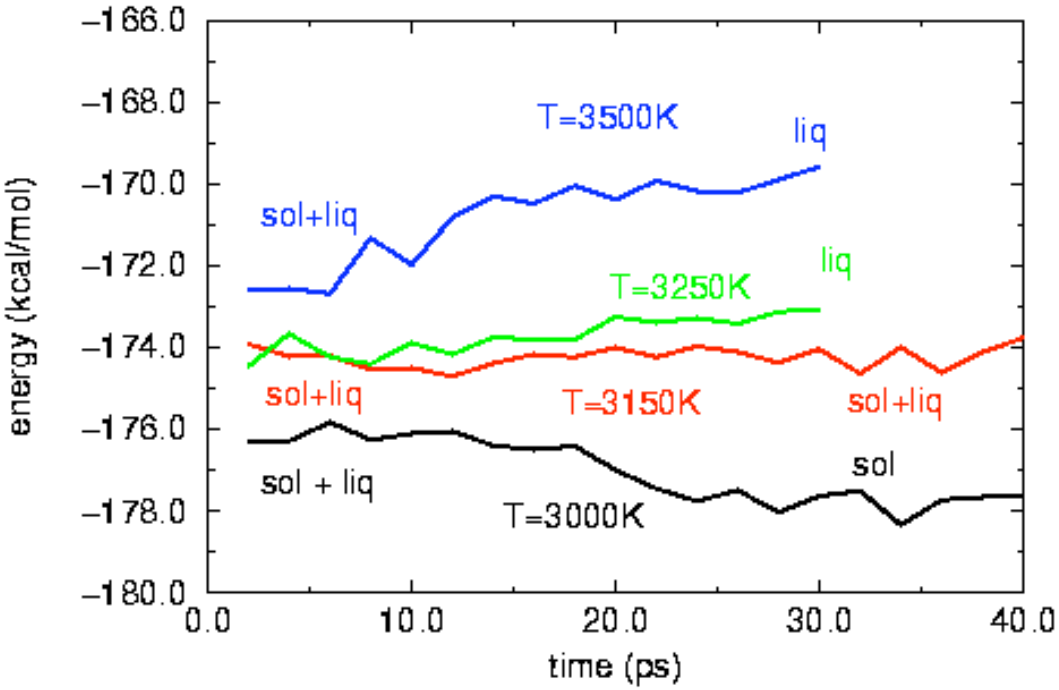
Luo et al. PRB 68, 134206 (2003)

MD applications: melting

2-phase MD simulations

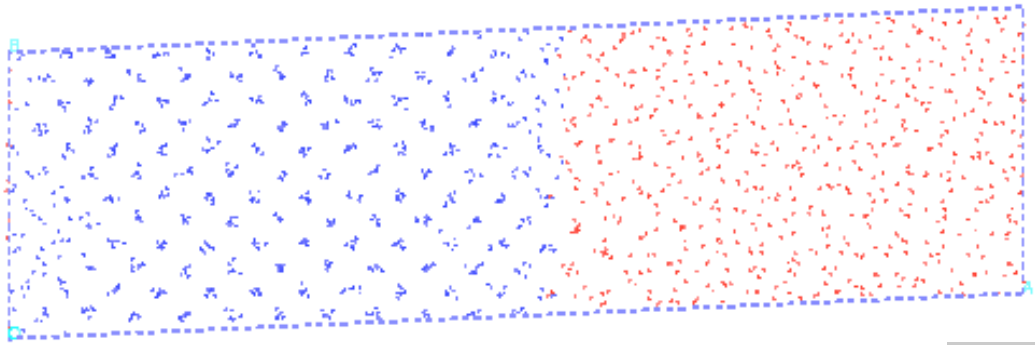
- Place liquid and solid in one cell
- Run NPT simulations at various T





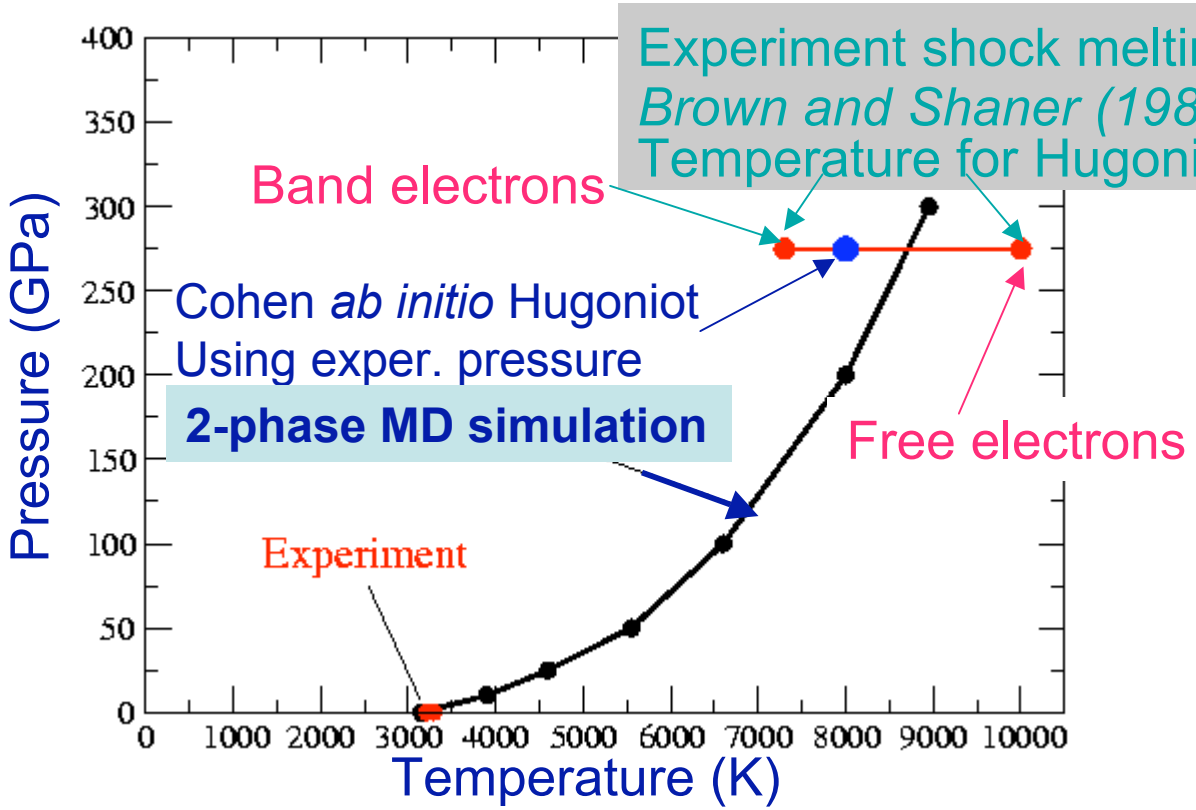
MD applications: melting

2-phase MD simulation



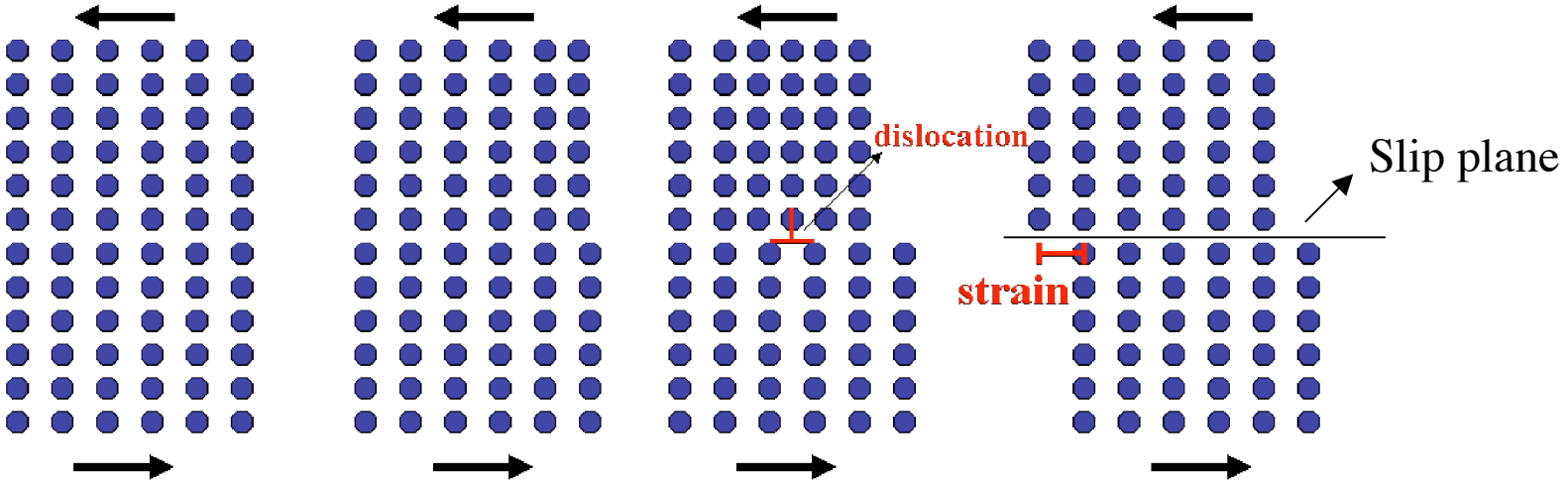
Melting at ambient pressure

- Simulation: 3150±50 K (4%)
- Experiment: 3290±50 K

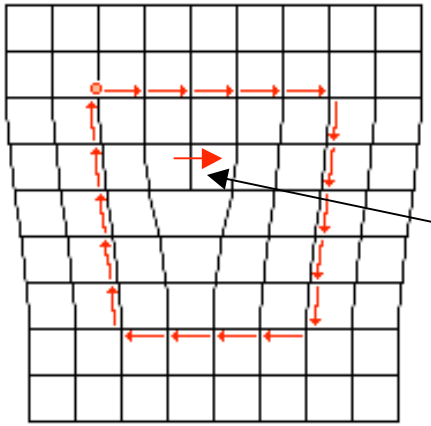


MD applications: nano-mechanics of deformation

Mechanisms of plastic deformation – Materials strength

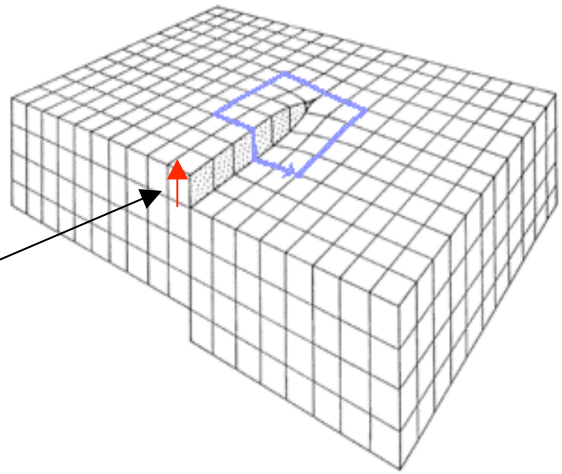


Edge dislocation

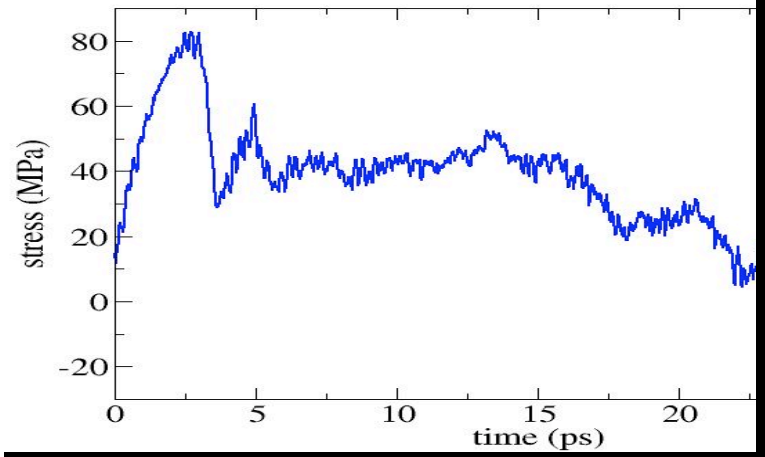


Burgers vector

Screw dislocation



MD applications: nano-mechanics of deformation



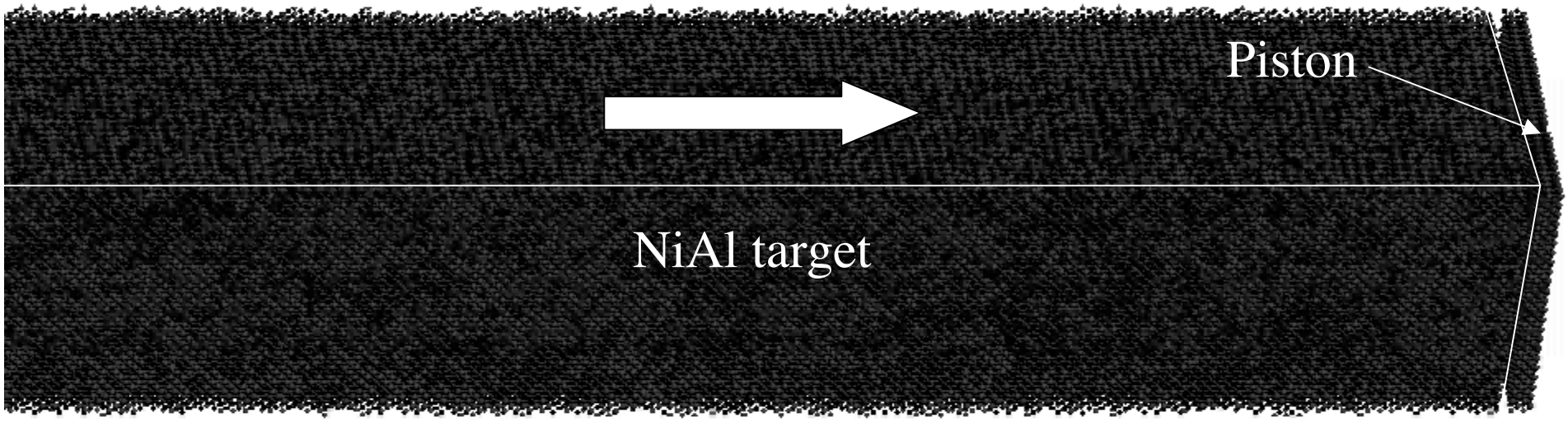
initial

elastic deformation

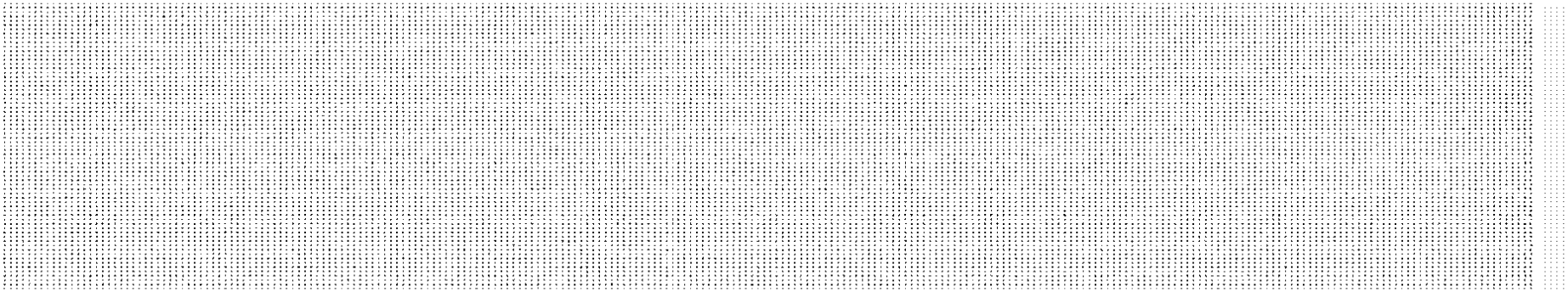
plastic deformation

ε=0.0 ε=0.07 ε=0.09 ε=0.59 ε=0.74

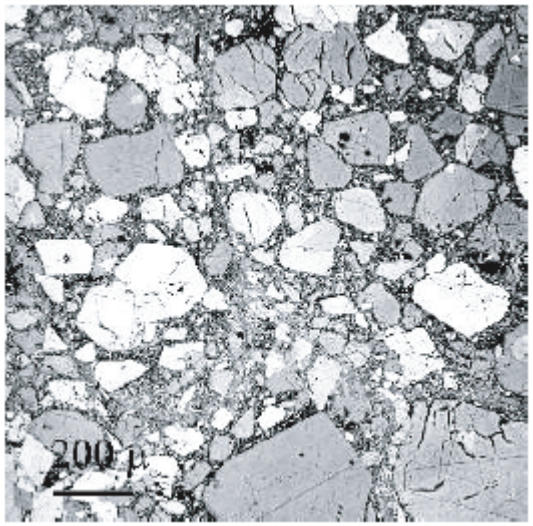
MD applications: nano-mechanics of deformation



- NiAl alloy: plastic deformation induced by shock compression
- MD enables a detailed characterization of the mechanisms of plastic deformation



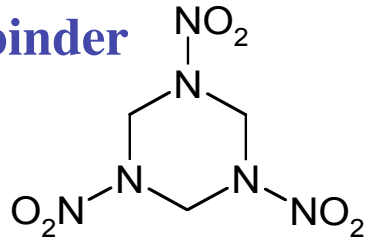
MD applications: condensed-matter chemistry



Plastic bonded explosives

- Energetic material particles in a rubbery binder
- C-NO_2 (TATB, TNT)
- N-NO_2 (HMX, RDX)
- O-NO_2 (PETN)
- Secondary explosives (initial reactions are endothermic)
- Sensitivity to undesired detonation

RDX



Propellants

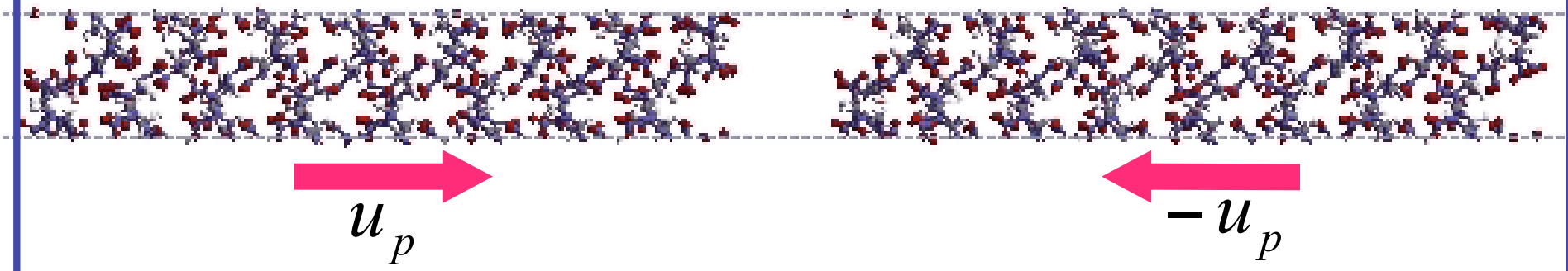
- Nitramine used in propellant composites
- Secondary HE _ exothermic reactions far from the surface _ lower temperature at burn surface
- Large specific impulse (Isp)

Thermal and shock induced decomposition and reaction of high energy materials

MD applications: decomposition of RDX

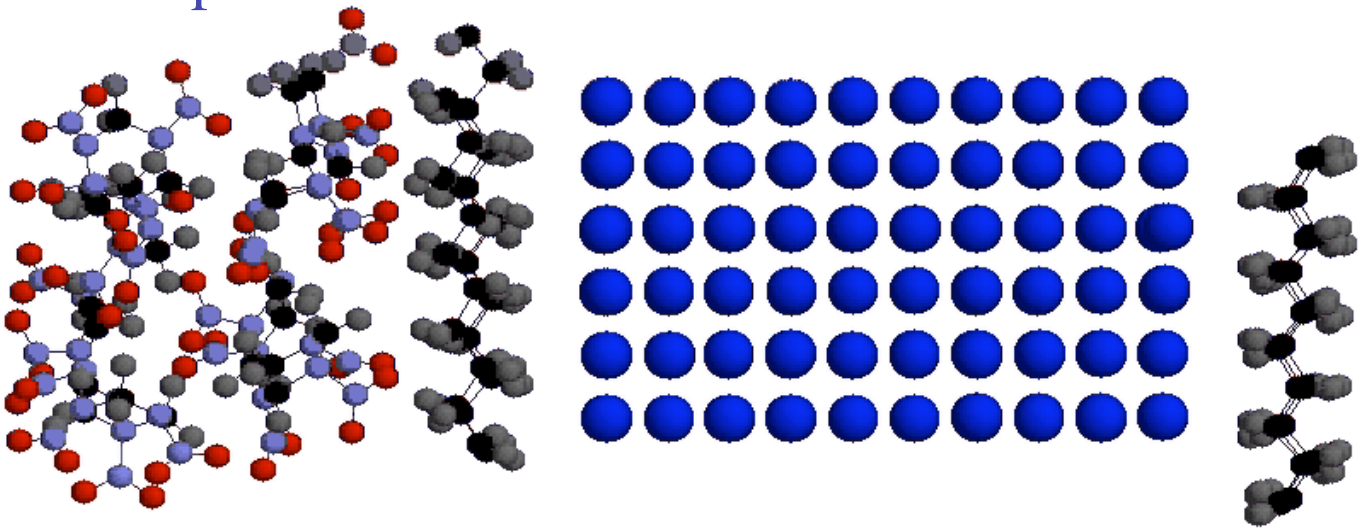
Shock decomposition

32 RDX molecules on 32 RDX molecules



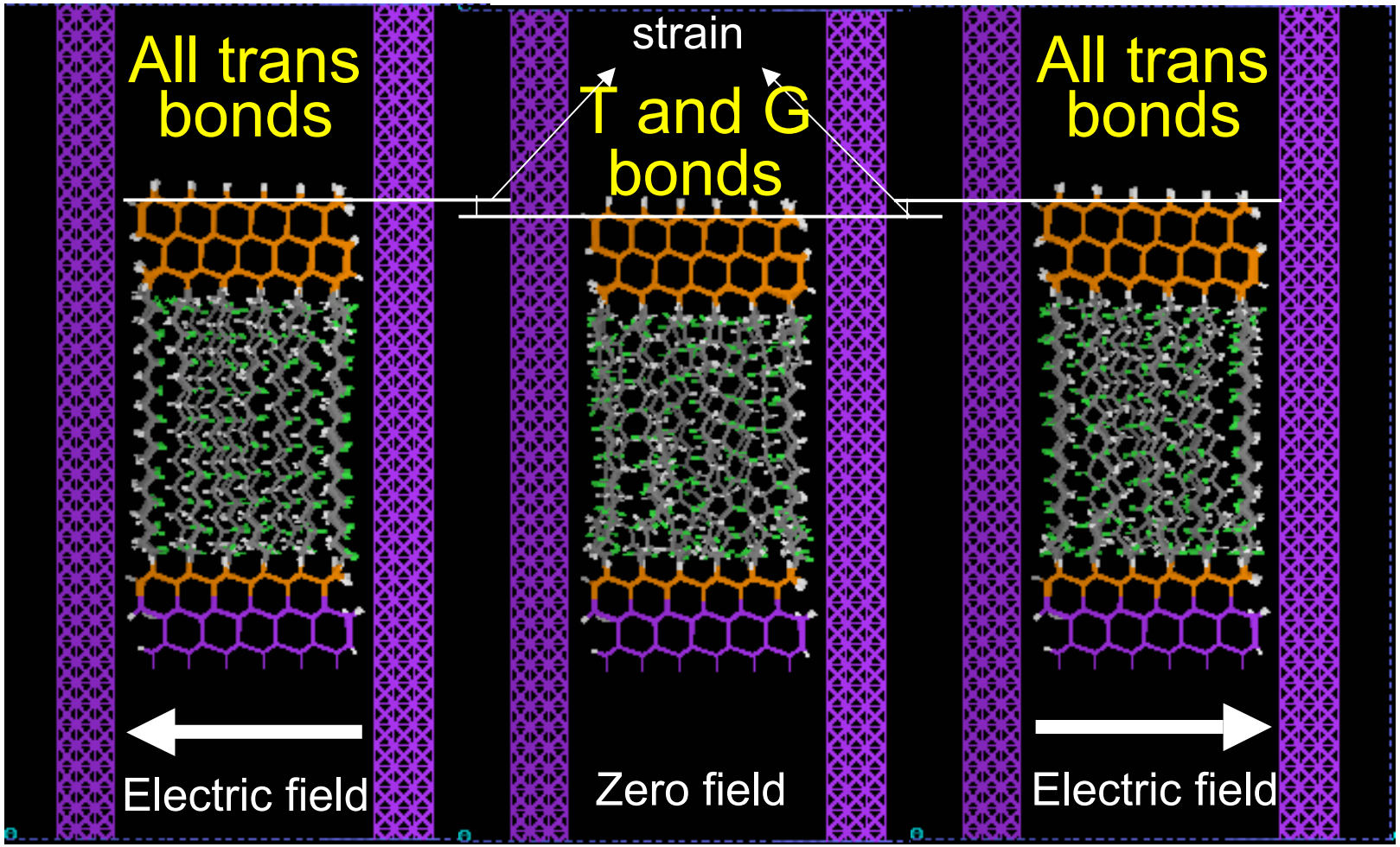
Strachan et al. Phys. Rev. Lett. (2003)

Thermal decomposition



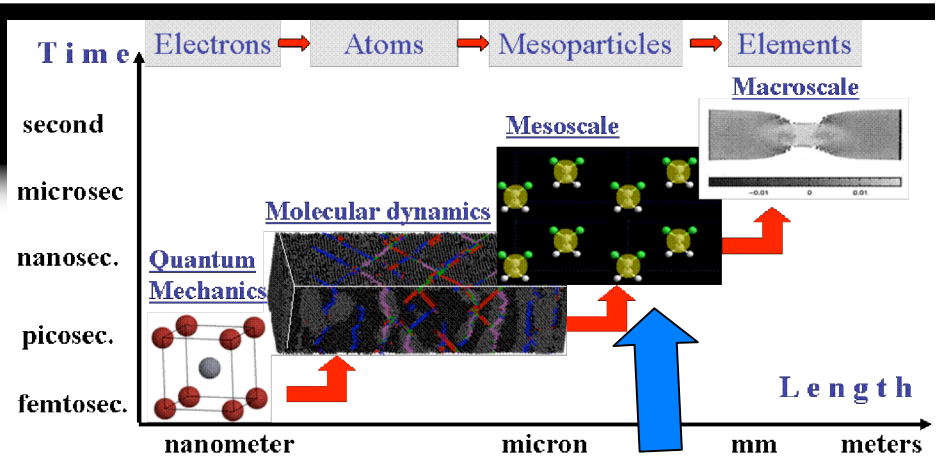
MD applications: computational materials design

- Polymer-based nano-actuator
- Make use of structural transition to achieve large strains



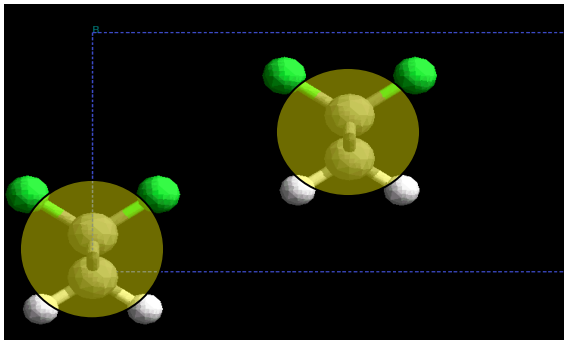
Strachan and Goddard, Appl. Phys. Lett (2005)

Mesoscale: beyond MD



All atom MD is very expensive

- Particles with long range interactions (electrostatics)
- Short time step necessary
  - C-H bond vibrational period ~10 fs = 10^{-14}s
  - MD time-step: <1 fs
- MD is always classical (C_V~3Nk)

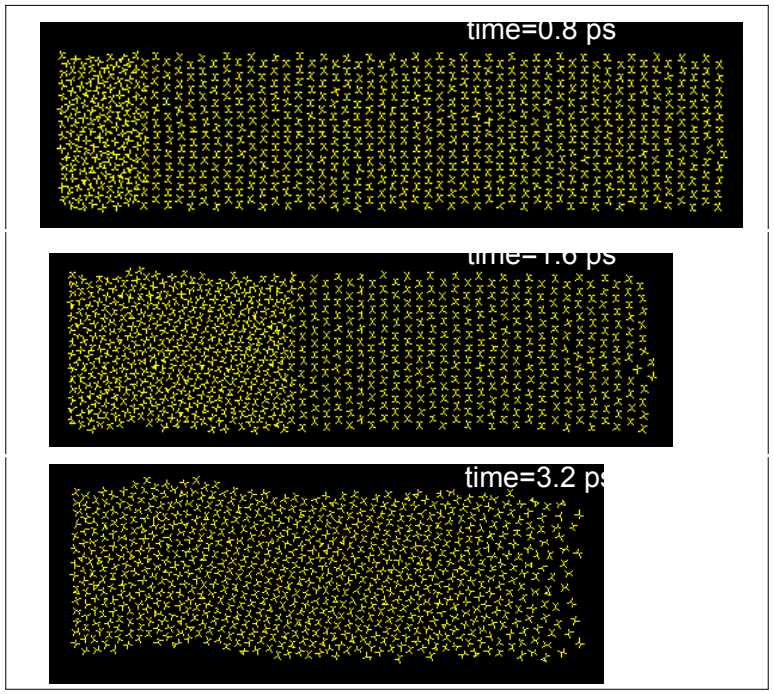


Mesodynamics

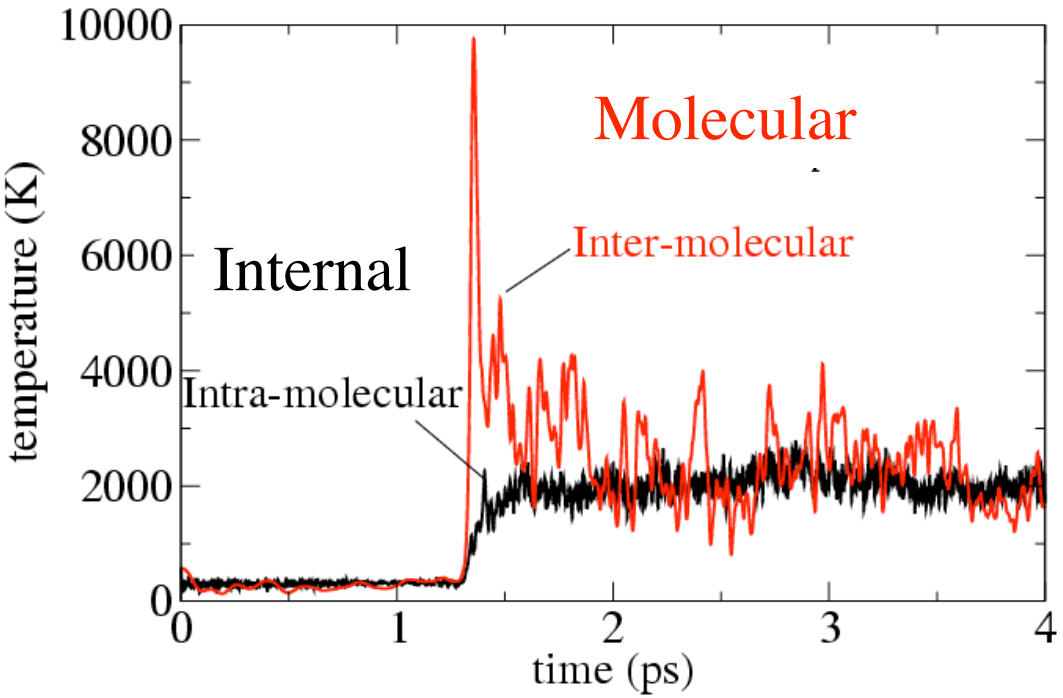
- Mesoparticles represent groups of atoms
- Molecules or grains in a polycrystalline solid (B.L. Holian)
- Mesopotential (effective interactions between mesoparticles)
- Thermal role of implicit degrees of freedom

Mesoscale: temperature rise during shock loading

Test case: shock on a crystalline polymer



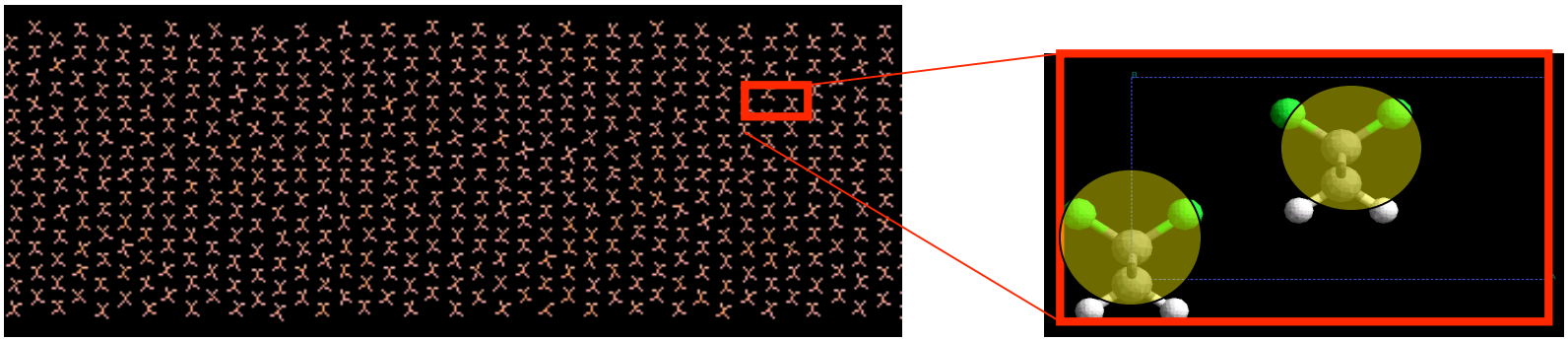
All atom MD simulation

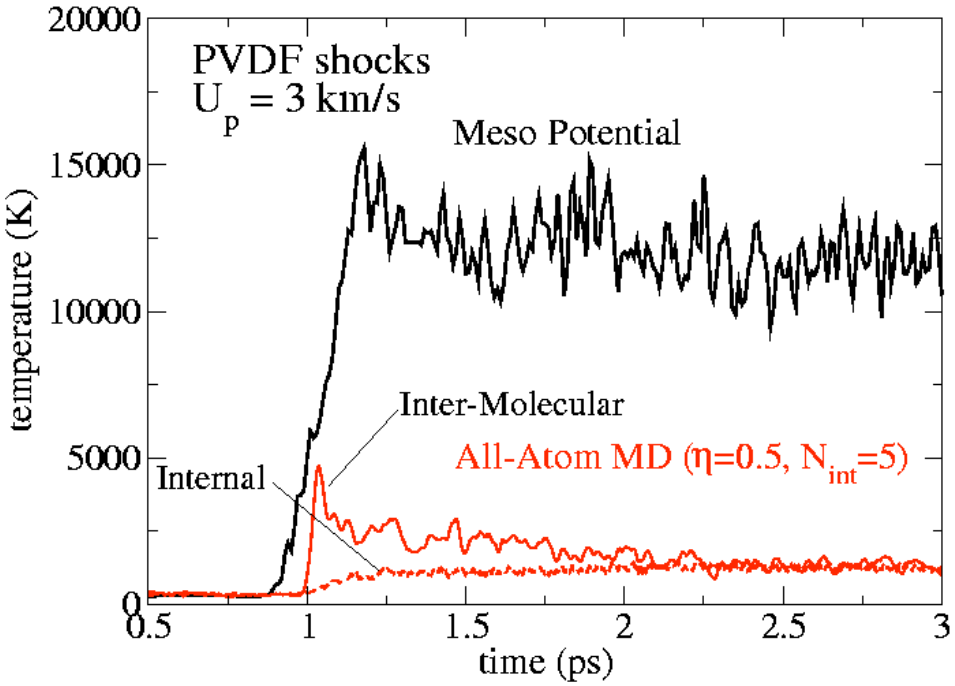


Molecular: c.m. velocity of molecules around translation

Internal: atomic velocities around c.m. vel. of molecules

Mesoscale: limitation of traditional approach



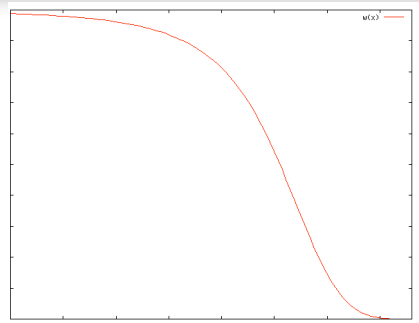


- Energy increase due to shockwave described accurately
- Reduced number of modes to share the energy

Large overestimation of temperature

Mesoscale: new approach

Local mesoparticle velocity: $< u >_i = \frac{\sum_j m_j u_j w(r_{ij})}{\sum_j m_j w(r_{ij})}$



Local mesoparticle temperature: $3kT_i^{meso} = \frac{\sum_j m_j \left| u_j - < u >_i \right|^2 w(r_{ij})}{\sum_j w(r_{ij})}$

Equations of motion:

$$\dot{r}_i = u_i + \chi_i F_i$$

$$\dot{u}_i = \frac{F_i}{m_i} - \eta_i (u_i - < u >_i)$$

Change in mesoparticle energy:

Change in internal energy so that total energy is conserved:

Mesoscale: New equations of motion

- **Allow energy exchange between mesoparticles and internal DoFs**
- **Couple local meso temperature with internal temperature**

$$\dot{r}_i = u_i + \chi_i F_i$$

$$\dot{u}_i = \frac{F_i}{m_i}$$

$$\dot{E}_i^{\text{int}} = \frac{\dot{T}_i^{\text{int}}}{C_i^{\text{int}}} = \chi_i F_i \cdot F_i$$

$$\chi_i \propto \gamma \left(\frac{T_i^{meso} - T_i^{\text{int}}}{T_0} \right)$$

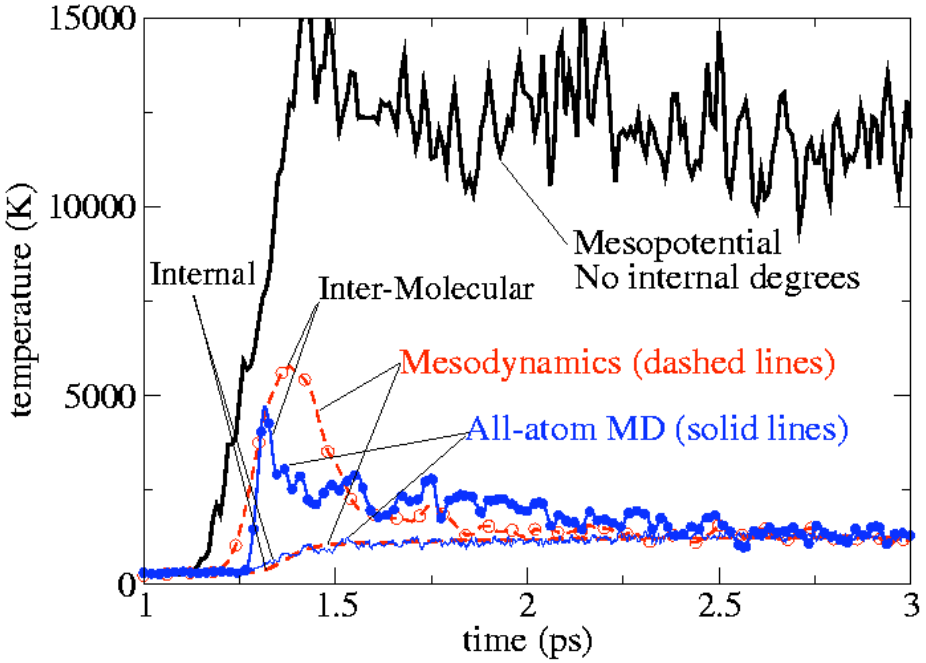
- **Couple through the position update equation**
- **Finite thermostats**

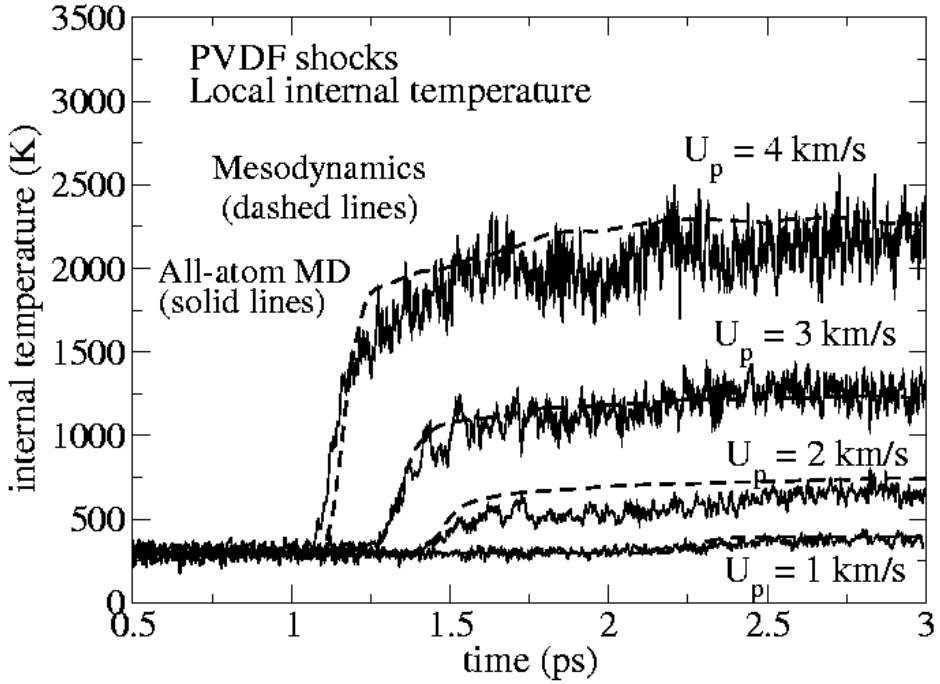
Key features

- Total energy (meso + internal) is conserved
- c.m. velocity is conserved
- Galilean invariant
- Correct description of the ballistic regime

Strachan and Holian (PRL, Jan 2005)

Mesodynamics: thermodynamically accurate





- **Thermodynamically accurate mesoscale description**
- **Thermal role of implicit degrees of freedom described by their specific heat**
  - **Can incorporate C_V based on quantum statistical mechanics**

Running MD @ nanoHUB

The Network for Computational Nanotechnology at Purdue developed the nanoHUB (www.nanohub.org)

- nanoHUB provides online services for **research**, **education** and **collaboration**
- The materials simulation toolkit at nanoHUB
- Developed by the Strachan group
- Enables running real MD simulations using simply a web-browser
- All you have to do is register to the nanoHUB (preferably before lab session)