Purdue MSE597G Lectures on Molecular Dynamics simulations of materials

Lecture 7

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Molecular Dynamics simulations

Introduction
- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

Part 1: the theory behind molecular dynamics
- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

Part 2: total energy and force calculations
- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: "averaging electrons out"

Part 3: advanced techniques, mesodynamics, verification and validation
- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
- Before you perform production runs
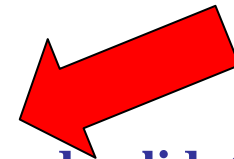
- **Tutorial to perform MD simulations using the nanoMATERIALS simulation tool at the nanoHUB**
- **Homework exercises**

MD at constant temperature

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = \vec{F}_i$$

Sys

Bath
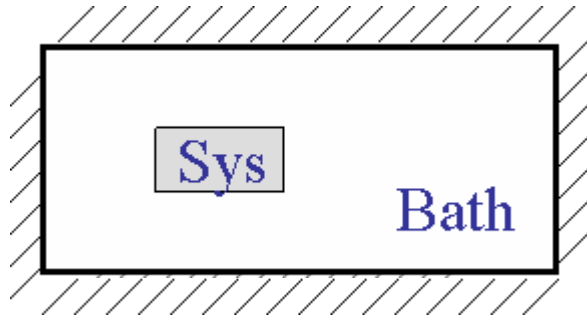
Canonical (NVT) ensemble averages ⟷ Time averages

What do we expect from an NVT MD simulation?

• Average kinetic energy should correspond to desired temperature

• Dynamics of system to be consistent with the canonical distribution

Isothermal MD: Andersen approach

Coupling of system with heat bath:

Stochastic collisions between randomly selected particles with the bath that result in a new velocity consistent with the desired temperature

1. Integrate equations of motion for time Δt

2. Number of atoms that underwent collisions during Δt is: $\nu\Delta t$ – select them randomly

3. Assign new velocities to selected atoms from a Maxwell-Boltzmann distribution at temperature T

PROS:
Leads to canonical distribution

CONS:
Collisions affect atomic dynamics (e.g. diffusion coefficient)

Andersen, J. Chem. Phys. 72, 2384 (1980)

Isothermal MD: Berendsen approach

Can we modify the equations of motion to obtain desired temperature?

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t)$$

Berendsen thermostat
- Direct feedback to control temperature
- γ is a heat flow variable (can be negative or positive)
- γ defined in terms of instantaneous temperature (T) and thermostat temperature (T_0)
- MD temperature converges to desired thermostat temperature

PROS:
Thermalizes system to desired temperature efficiently

CONS:
Does not lead to the canonical distribution

Berendsen, Postma, van Gunsteren, DiNola and Haak, J. Chem. Phys. 81, 3684 (1984).

Isothermal MD: Nosé-Hoover approach

Berendsen thermostat

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t) - \gamma(t)\,\vec{p}_i(t)$$

$$\gamma(t) = \nu\,\frac{T(t) - T_0}{T(t)}$$

Nosé-Hoover thermostat

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t)$$

- Heat flow variable has its own equation of motion: integral feedback
- Enables kinetic energy fluctuations

PROS:
- Leads to canonical distribution
- Time reversible

Andersen, J. Chem. Phys. 72, 2384 (1980)
Nosé, Mol. Phys. 52, 255 (1984)
Hoover, Phys. Rev A, 31 1695 (1985)
Holian, Voter, and Ravelo, Phys. Rev. E. 52, 2338 (1995).

CONS:
- Approach to equilibrium: can lead to oscillations
- Persistent, non-canonical oscillations can occur if care is not taken

Isothermal-isobaric molecular dynamics

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} + \frac{p_\varepsilon}{W}$$

$$\dot{\vec{p}}_i = \vec{F}_i - \left(1 + \frac{1}{N}\right)\frac{p_\varepsilon}{W}\,\vec{p}_i - \frac{p_{\xi_1}}{Q_1}\,\vec{p}_i$$

Thermostat with variables:

$$\xi_1 \qquad p_{\xi_1} \qquad Q_1$$

Barostat with variables:

$$\varepsilon = \log\left(\frac{V}{V(t=0)}\right)$$

W Mass associated with ε

p_ε Momentum conjugate to ε

Equations for the evolution of volume:

Applied external pressure

Instantaneous internal pressure

$$\dot{V} = \frac{3Vp_\varepsilon}{W}$$

$$\dot{p}_\varepsilon = 3V\left(P_{\text{int}} - P_{ext}\right) + \frac{1}{N}\sum_{i=1}^{N}\frac{p_i^2}{m_i} - \frac{p_{\xi_1}}{Q_1}\,p_\varepsilon$$

Melchionna, Ciccoti and Holian, Mol Phys. 78, 533 (1993)

Martyna, Tobias, and Klein, J. Chem. Phys. 101 4177 (1994)

Further reading

- Andersen, J. Chem. Phys. 72, 2384 (1980)

- Parrinello and Rahman, Phys. Rev. Lett., 45, 1196 (1980)

- Parrinello and Rahman, J. Appl. Phys. 52, 7182 (1981)

- Nosé, Mol. Phys. 52, 255 (1984)

- Hoover, Phys. Rev A, 31 1695 (1985)

- Melchionna, Ciccoti and Holian, Mol Phys. 78, 533 (1993)

- Martyna, Tobias, and Klein, J. Chem. Phys. 101 4177 (1994)

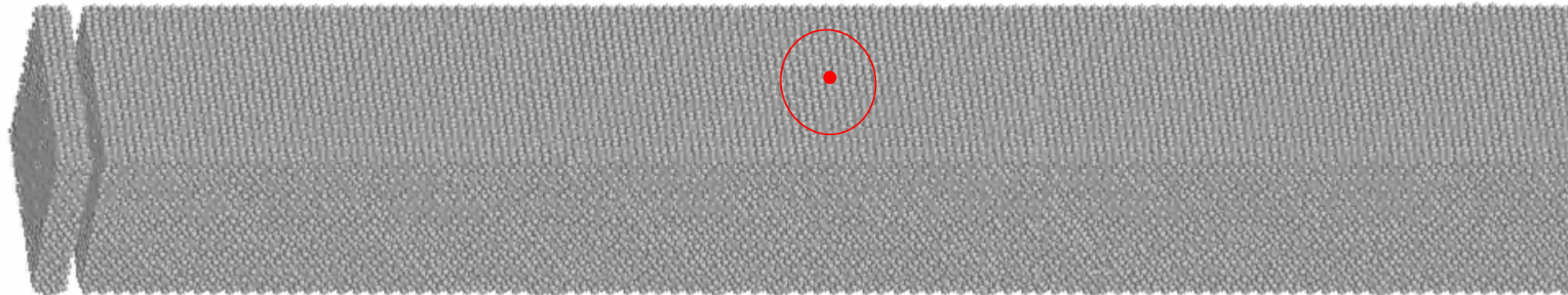- Holian, Voter, and Ravelo, Phys. Rev. E. 52, 2338 (1995).

Computing forces: linear methods
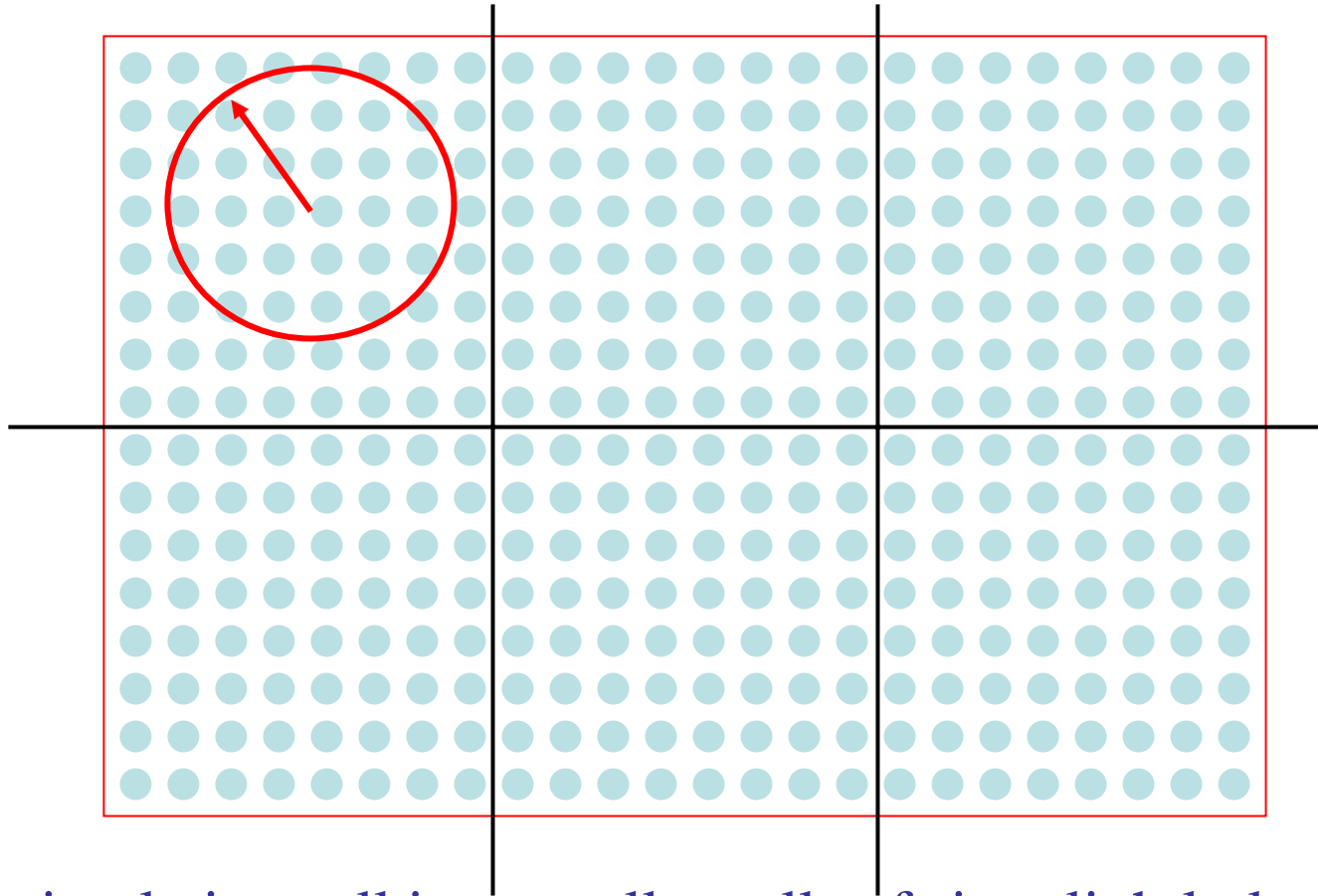
Suppose we have a two body potential:

$$V(\{r_i\}) = \sum_{i<j} \phi(r_{ij})$$

energy

distance

Cut-off radius
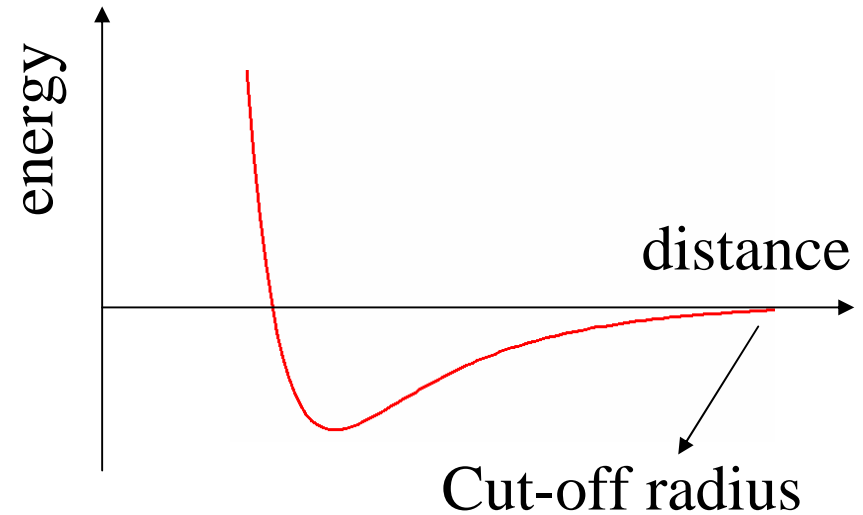
- Brute force approach: go over all 1/2N(N-1) neighbors
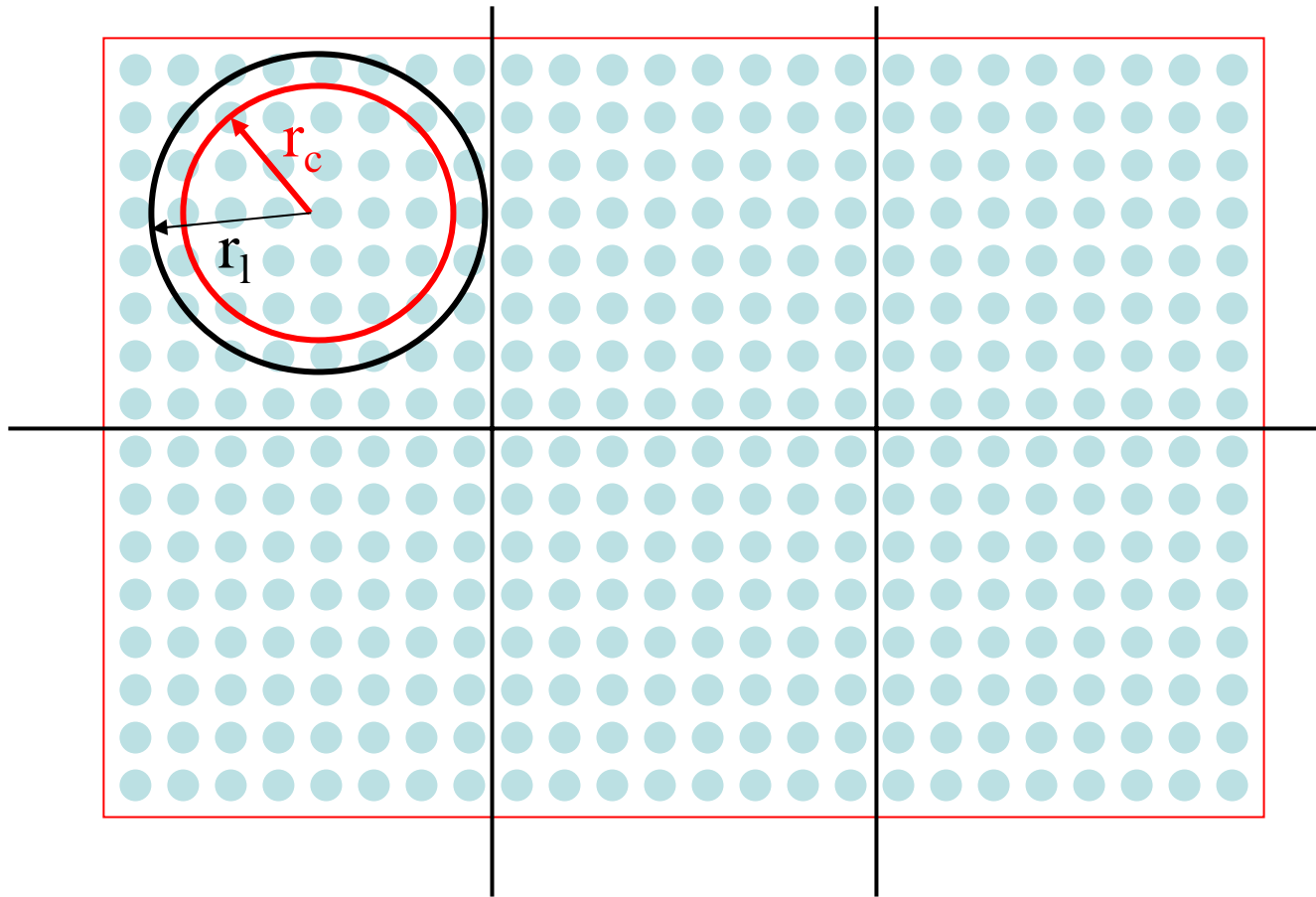 - Double the size of simulation and force calculations takes ~4 times longer

# *Spatial decomposition & cell lists*

- Divide simulation cell into smaller cells of size slightly larger than r_c
- Atoms only interact with other atoms in the same of nearest neighbor cell
  - Allocating atoms to cells can be done in order *N*
 - Calculating interactions is also order *N*

Verlet lists

- Make a list of neighbors within $r_l = r_c + \Delta$

- If atoms move less that Δ with Δt the same list can be used for more than one MD step

Beyond MD
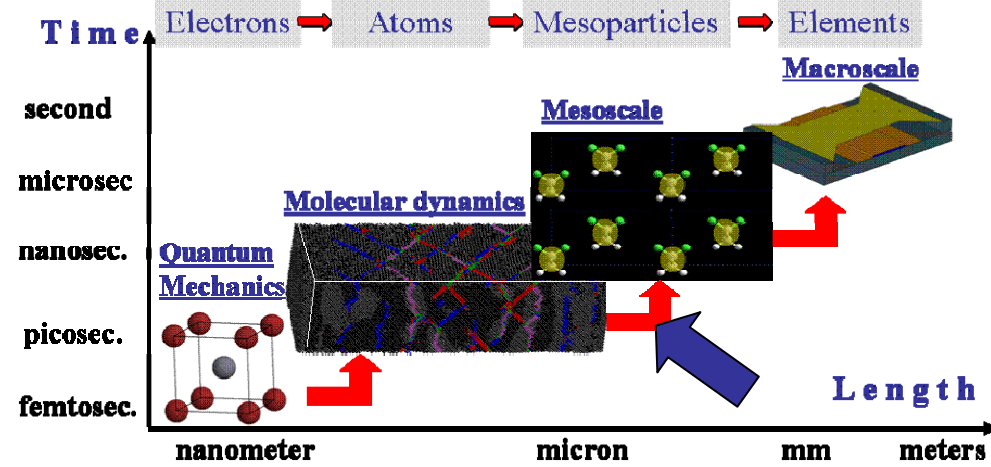
All atom MD is very expensive

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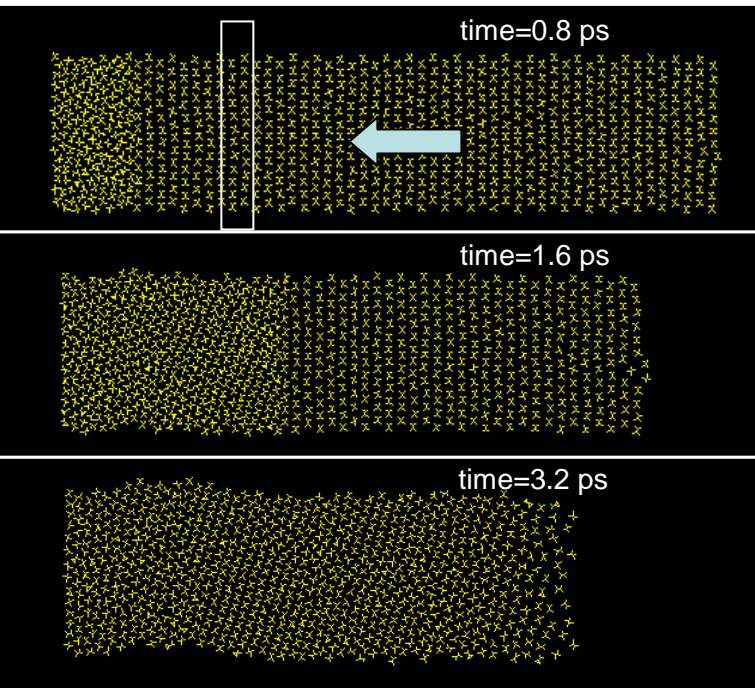   - MD time-step: <1 fs
- MD is always classical (C_V~3Nk)
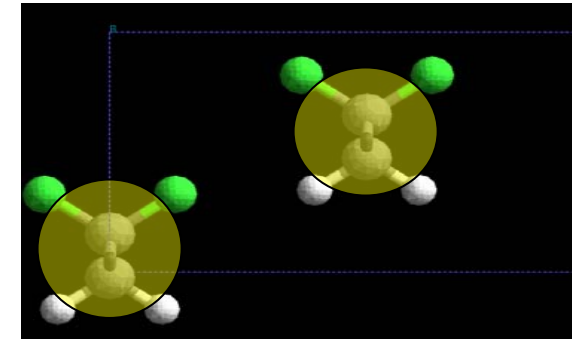
Mesodynamics

- 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

Test case: dynamical loading of a polymer

All atom MD simulation

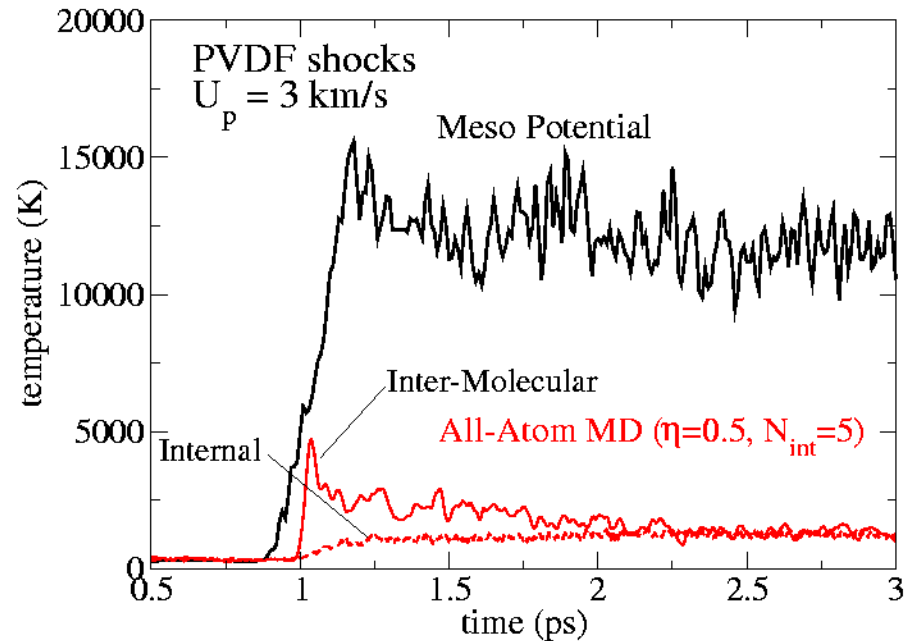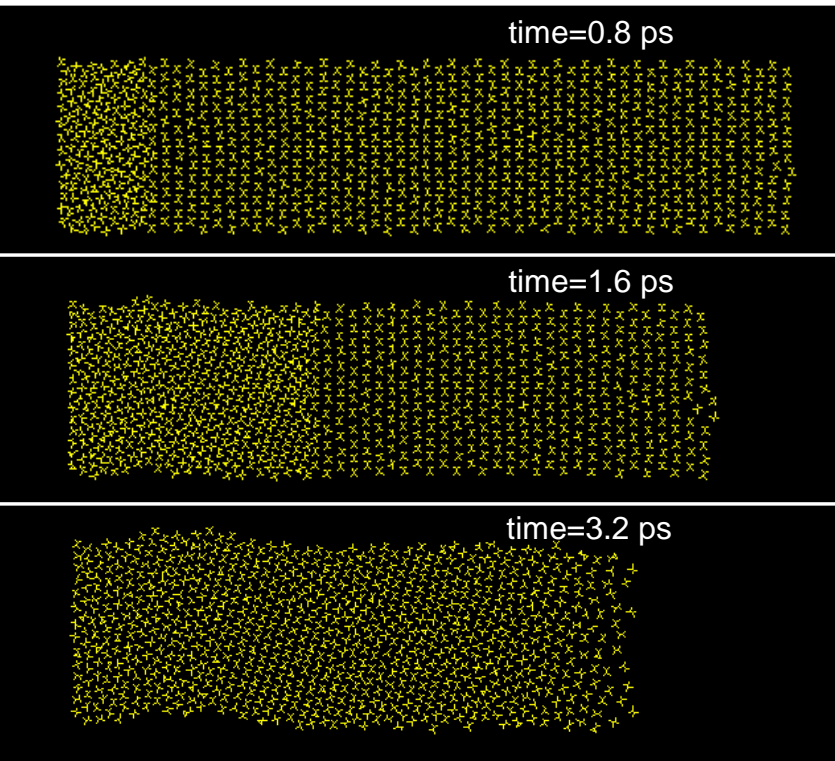time=0.8 ps

time=1.6 ps

time=3.2 ps

Temperature rise caused by shock
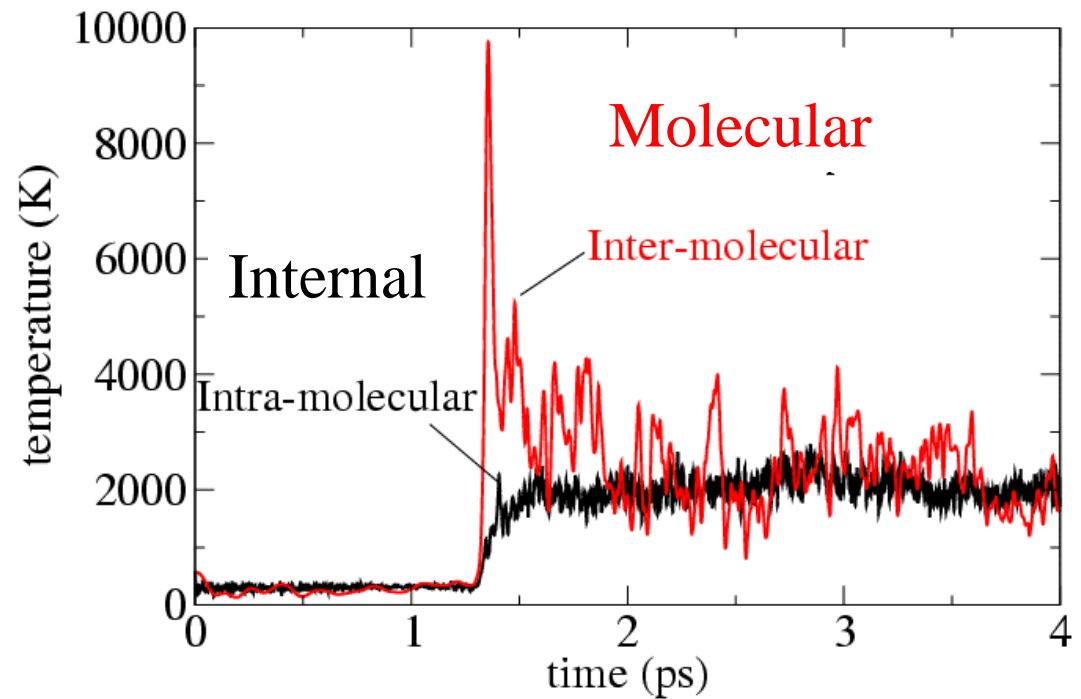
Molecular: c.m. velocity of molecules around translation

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

The problem with mesodynamics

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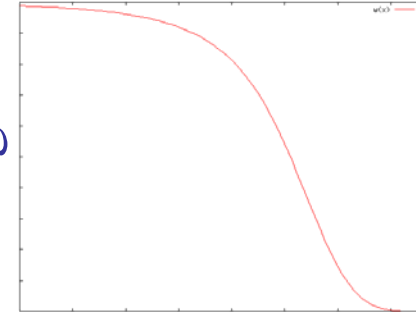**Reduced number of modes to share the energy**

Large overestimation of temperature

Energy exchange: mesoparticles ↔ implicit modes

Local mesoparticle velocity:

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

weight

distance

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:

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

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

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

Not Galilean invariant

Change in mesoparticle energy:

$$\dot{E}^{meso} = \sum_i \left[-m_i \eta_i \left(u_i - <u>_i \right) \cdot u_i - \chi_i F_i \cdot F_i \right] = \sum_i \dot{E}_i^{meso}$$

Change in internal energy so that total energy is conserved:

$$\dot{E}_i^{int} = -\dot{E}_i^{meso} = \frac{\dot{T}_i^{int}}{C_i^{int}} = m_i \eta_i \left(u_i - <u>_i \right) \cdot u_i + \chi_i F_i \cdot F_i$$

Mesodynamics equations of motion

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

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

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

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

$$\chi_i \propto \gamma \left(\frac{T_i^{meso} - T_i^{\text{int}}}{T_0} \right)$$
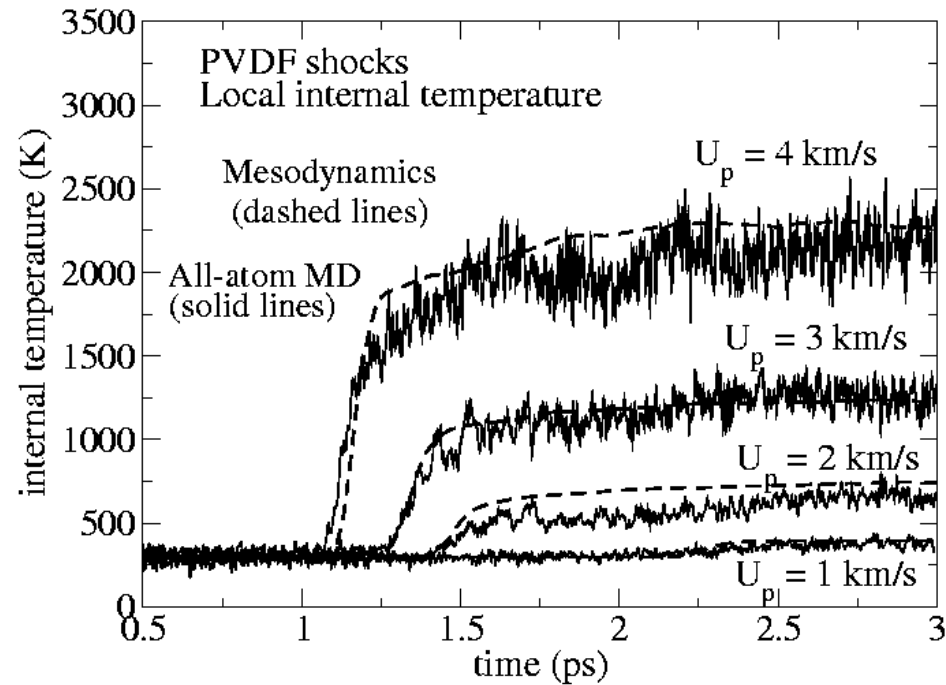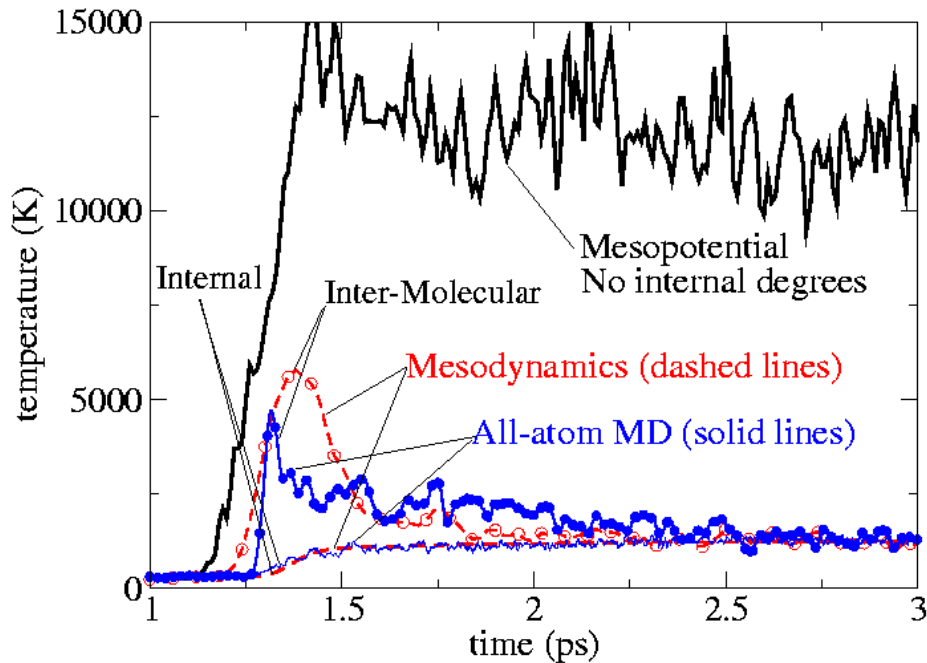
- **Couple through the position update equation**

- **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, Phys. Rev. Lett. **94**, *014301-1-4 (2005).*

New mesodynamics solves the problem

- **Accurate shock temperature due to correct treatment of implicit modes (accurate thermodynamics)**
- **Specific heat of internal degrees of freedom is classical**
- **Quantum effects can be incorporated via a temperature dependent specific heat**

Before you run production simulations

Verification and Validation (V&V)

Verification:
Am I solving the equations correctly?

Validation:
Am I solving the right equations?

Before you run production simulations

Verification in MD simulations

Integrators:

Conserved quantities

- NVE: energy, linear momentum, angular momentum
- NVT: depends on the method (conserved "Hamiltonian", linear momentum)

- Relaxation time-scales as a function of coupling constants with barostats and thermostats
- Fluctuations (energy, volume) are related to response functions (specific heat, elastic constants) that can be measured independently

Interatomic potentials:

Analytical solutions for energy, stress and force usually exist for simple geometries:

- Perfect crystals or di-atomic molecules
- Unrelaxed vacancy and surface energies

Before you run production simulations

Validation of MD simulations

Comparison with appropriate experiments (comparison against more accurate theories e.g. DFT can provide partial validation)

- Validation of classical equations of motion:
    - Remember quantum effects when
    - Are my barostat and thermostat appropriate for my problem
- Validation of interatomic potential
    - Lattice parameter or density
    - Cohesive energies
    - Elastic constants
    - Thermal expansion and melting temperature
    - Defect energies (vacancies, surfaces)
    - Phonon dispersion curves
    - Thermal and mass transport

Further reading

Books on molecular modeling

- Frenkel and Smit, "*Understanding molecular simulation*"
- Allen and Tildesley, "*Computer simulations of liquids*"
- Rapaport, "*The art of molecular dynamics simulations*"
- Many other books and papers

Additional online resources at nanoHUB

- Materials strength: does size matter? nanoMATERIALS simulation toolkit tutorial
    - https://www.nanohub.org/resources/2322
- First Principles-based Atomistic and Mesoscale Modeling of Materials
    - https://www.nanohub.org/resources/434

Summary & outlook

- Lots of progress in last 25 years
  - Thermostats & barostats
  - Accurate first principles-based force fields
  - Coarse graining

- Still lots to do and learn …

Remember homework assignments and hands-on activities

nanoHUB.org
online simulations and more