

# ***Lectures on Molecular Dynamics simulations of materials***

## **Lecture 3: advanced techniques and coarse graining**

**Alejandro Strachan**

School of Materials Engineering

Purdue University

*[strachan@purdue.edu](mailto:strachan@purdue.edu)*

# Lectures on Molecular Dynamics simulations

## Introduction

- What is molecular dynamics (MD)? Examples of current research
- What will I learn in these lectures?

## Lecture 1: the theory behind molecular dynamics

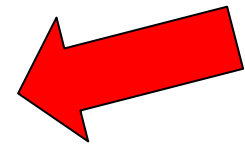
- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

## Lecture 2: total energy and force calculations

- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

## Lecture 3: advanced techniques and mesodynamics

- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom



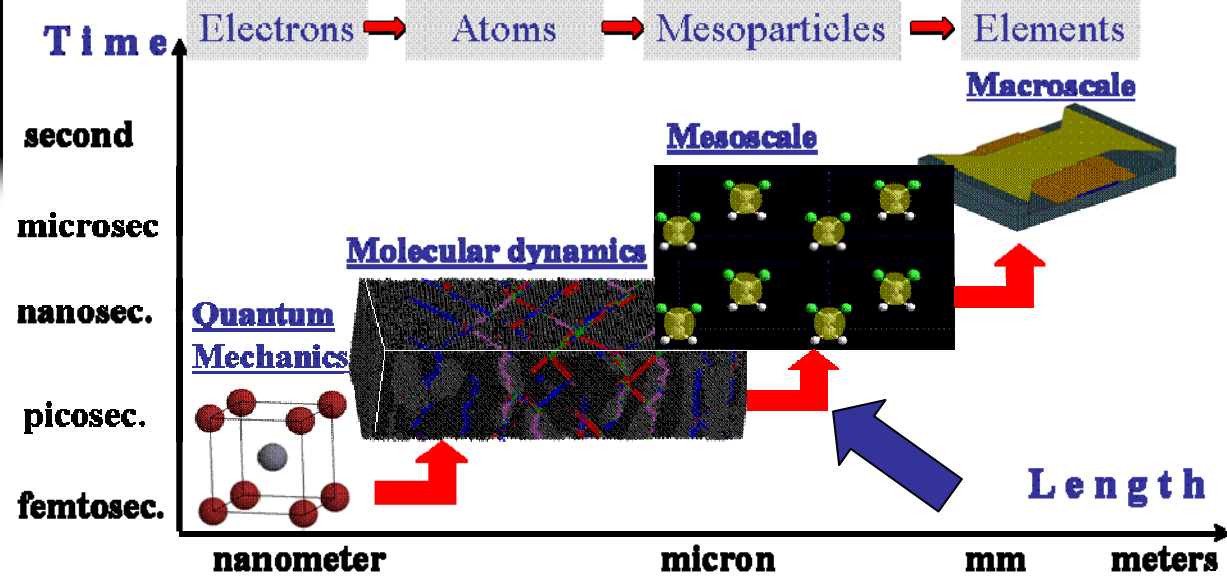
# Lecture 3

MD= solve:

$$\vec{F}_i = m_i \vec{a}_i$$

Forces from:

$$\vec{F}_i = -\vec{\nabla}_{r_i} V(\{r_j\})$$

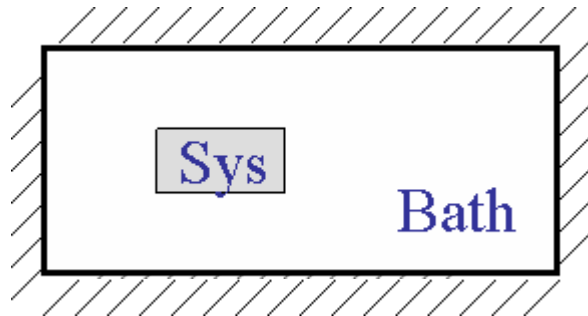


Constant energy simulation: describes the microcanonical ensemble (NVE)

## Lecture 3 topics:

- MD under isothermal and isobaric conditions:
  - Stochastic and deterministic approaches
- Force calculation efficiently
- Beyond MD
  - Coarse graining or mesodynamics
  - Role of implicit degrees of freedom (DID)

# MD at constant temperature



Canonical (NVT)  
ensemble averages



Time averages

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \quad +?$$
$$\dot{\vec{p}}_i = \vec{F}_i$$

What do we expect from an NVT MD simulation?

- Average kinetic energy should correspond to desired temperature

$$\frac{3}{2} NkT = \langle K \rangle$$

Instantaneous  
temperature

$$\frac{3}{2} NkT(t) = K(t)$$

- Dynamics of system to be consistent with the canonical distribution

$$P(\{\{r_i\}\}\{\{p_i\}\}) = e^{-\beta H(\{\{r_i\}\}\{\{p_i\}\})} / Z(NVT)$$

# 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  $\Delta t$
  2. Number of atoms that underwent collisions during  $\Delta t$  is:  $\nu \Delta t$  – select them randomly
  3. Assign new velocities to selected atoms from a Maxwell-Boltzmann distribution at temperature  $T$
- Coupling constant  
↓

## PROS:

Leads to canonical distribution

## CONS:

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

# ***Isothermal MD: Berendsen approach***

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

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

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

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

## **Berendsen thermostat**

- Direct feedback to control temperature
- $\gamma$  is a heat flow variable (can be negative or positive)
- $\gamma$  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

# Isothermal MD: Nosé-Hoover approach

Berendsen thermostat

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

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

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

Nosé-Hoover thermostat

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

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

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

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

## PROS:

- Leads to canonical distribution
- Time reversible

## CONS:

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

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

Nosé, Mol. Phys. 52, 255 (1984)

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

# Nosé-Hoover and the canonical distribution

Regardless of initial conditions the Nosé-Hoover equations of motion should lead to the canonical distribution:

$$P(x) = \frac{e^{-\beta H(x)}}{\sum_{\text{microstates}} e^{-\beta H(x)}}$$

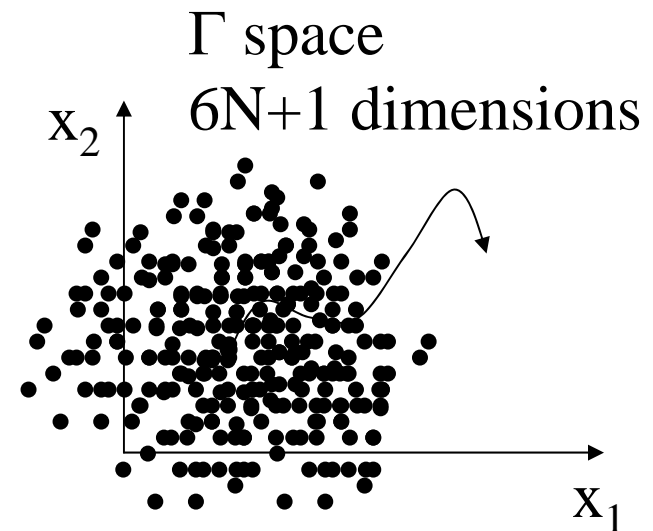
Where:

$$x = \{r_i\}, \{p_i\}, \gamma$$

and:

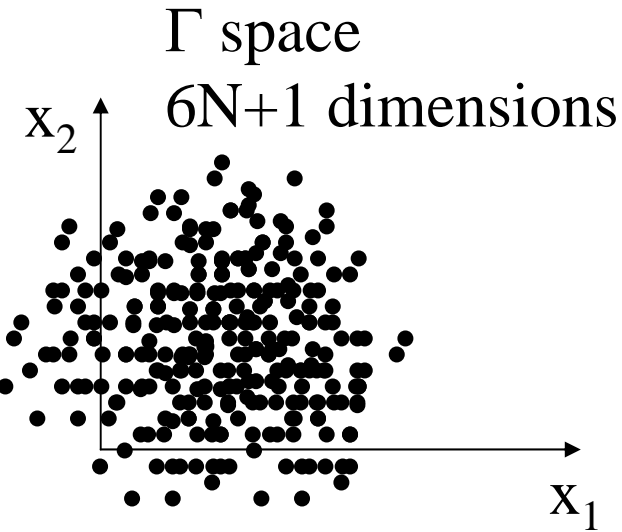
$$H(x) = V(\{r_i\}) + K(\{p_i\}) + \frac{3}{2} NkT_o \gamma^2$$

- Our system at time zero in phase space ( $x$ )
- Temporal evolution is given by N-H equations
- Now consider an ensemble of points with some distribution  $\rho(x, t=0)$
- How does  $\rho$  change with time? What is the stationary (time independent) solution?





# Nosé-Hoover and the canonical distribution



- Temporal evolution of  $\rho$  is described by Liouville equation (continuity):

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho \dot{x}) = 0$$

$\dot{x}$  given by N-H equations

- Maxwell Boltzmann distribution is the stationary solution for the Liouville equation with Nose-Hoover equations

$$\rho_0(x) = \frac{e^{-\beta H(x)}}{\sum_{\text{microstates}} e^{-\beta H(x)}}$$

$$x = \{r_i\}, \{p_i\}, \gamma$$

$$H(x) = V(\{r_i\}) + K(\{p_i\}) + \frac{3}{2} NkT_o \gamma^2$$

# 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:

$$\xi_1 \quad p_{\xi_1} \quad Q_1$$

Barostat with variables:

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

$W$  Mass associated with  $\varepsilon$   
 $p_\varepsilon$  Momentum conjugate to  $\varepsilon$

Equations for the evolution of volume:

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

Applied external pressure

Instantaneous internal pressure

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

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

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

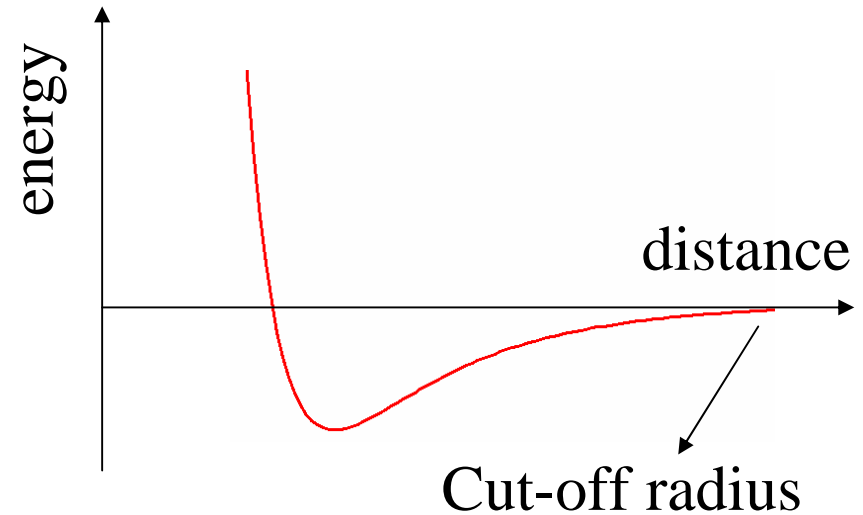
# ***Further reading***

- 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).

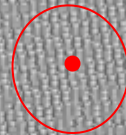
# Computing forces: linear methods

Suppose we have a two body potential:

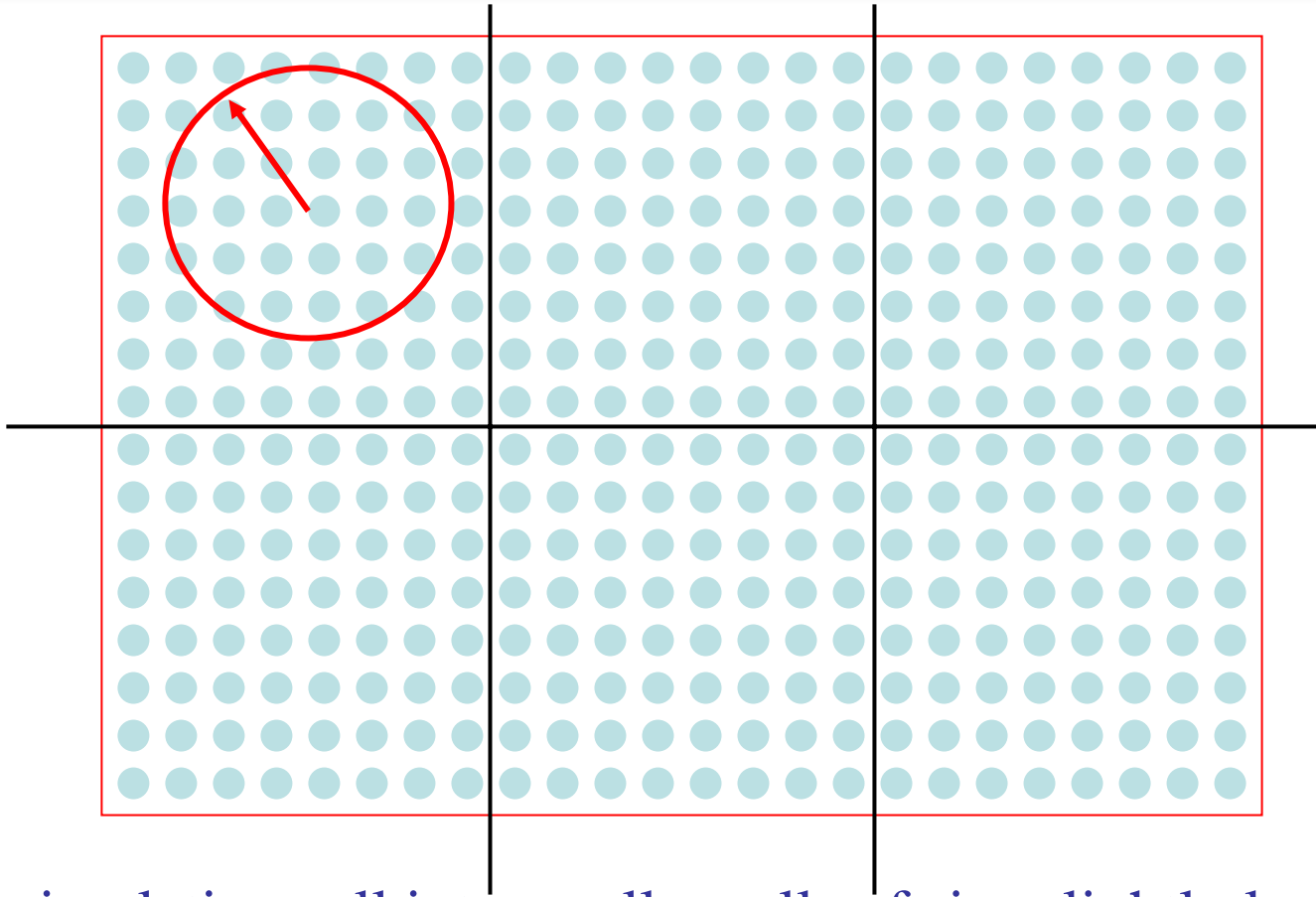
$$V(\{r_i\}) = \sum_{i < j} \phi(r_{ij})$$



- Brute force approach: go over all  $1/2N(N-1)$  neighbors
  - Double the size of simulation and force calculations takes  $\sim 4$  times longer

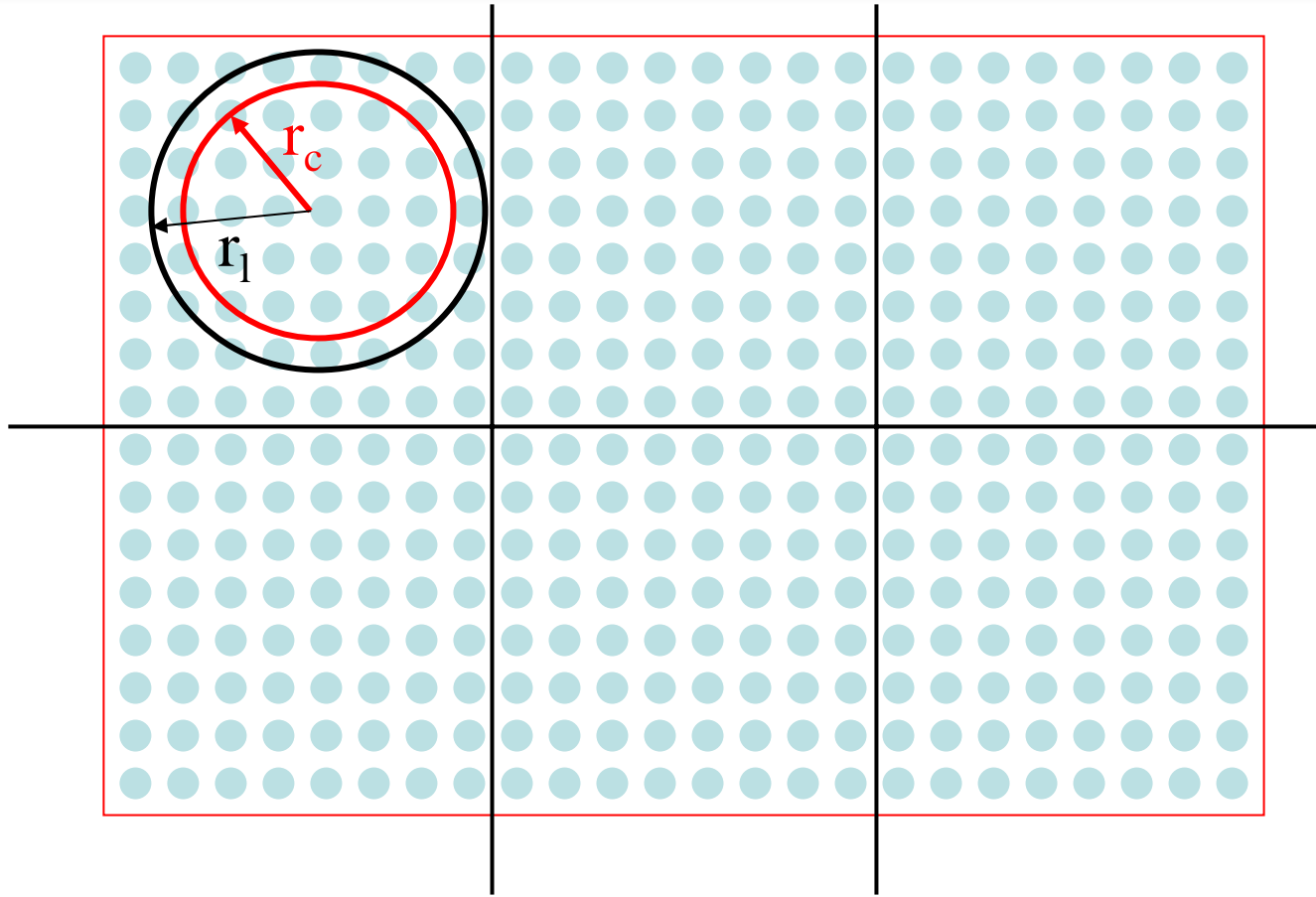


# Spatial decomposition & cell lists



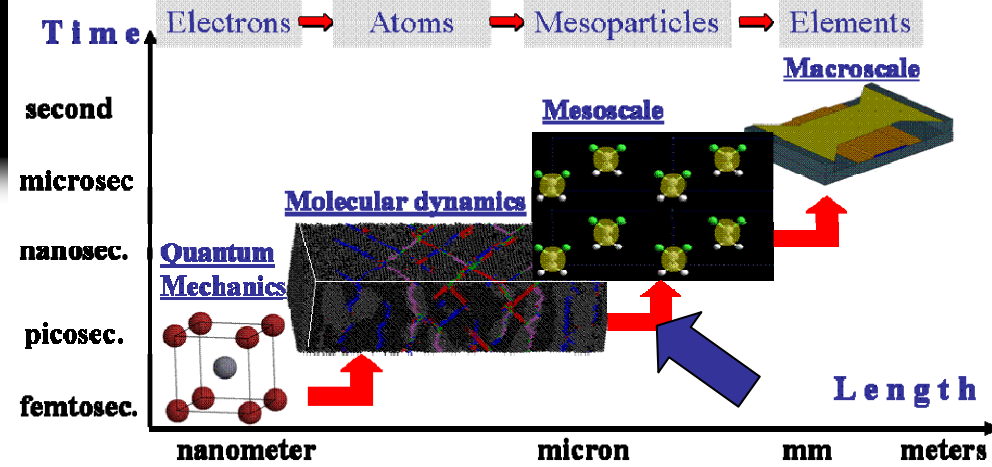
- Divide simulation cell into smaller cells of size slightly larger than  $r_c$
  - Atoms only interact with other atoms in the same or nearest neighbor cell
- Allocating atoms to cells can be done in order  $N$
  - Calculating interactions is also order  $N$

# Verlet lists



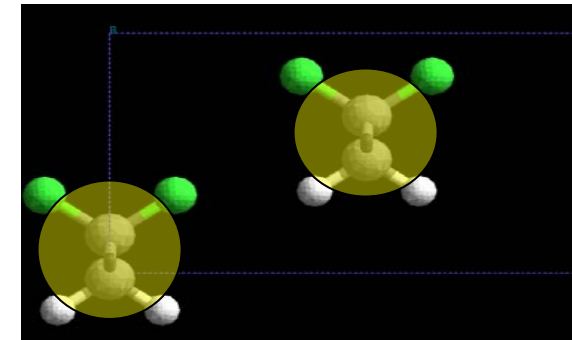
- Make a list of neighbors within  $r_1 = r_c + \Delta$
- If atoms move less than  $\Delta$  with  $\Delta t$  the same list can be used for more than one MD step

# Beyond MD



## All atom MD is very expensive

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

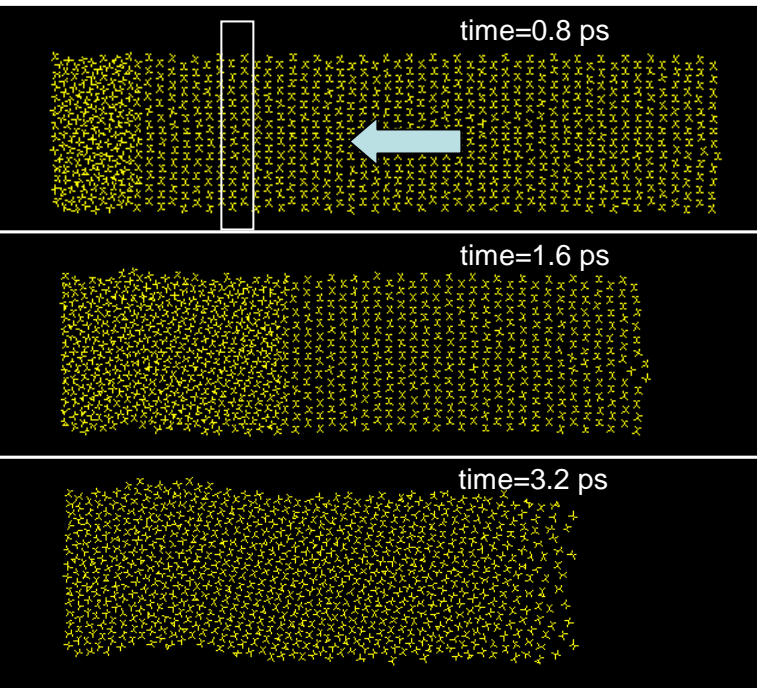


## Mesodynamics

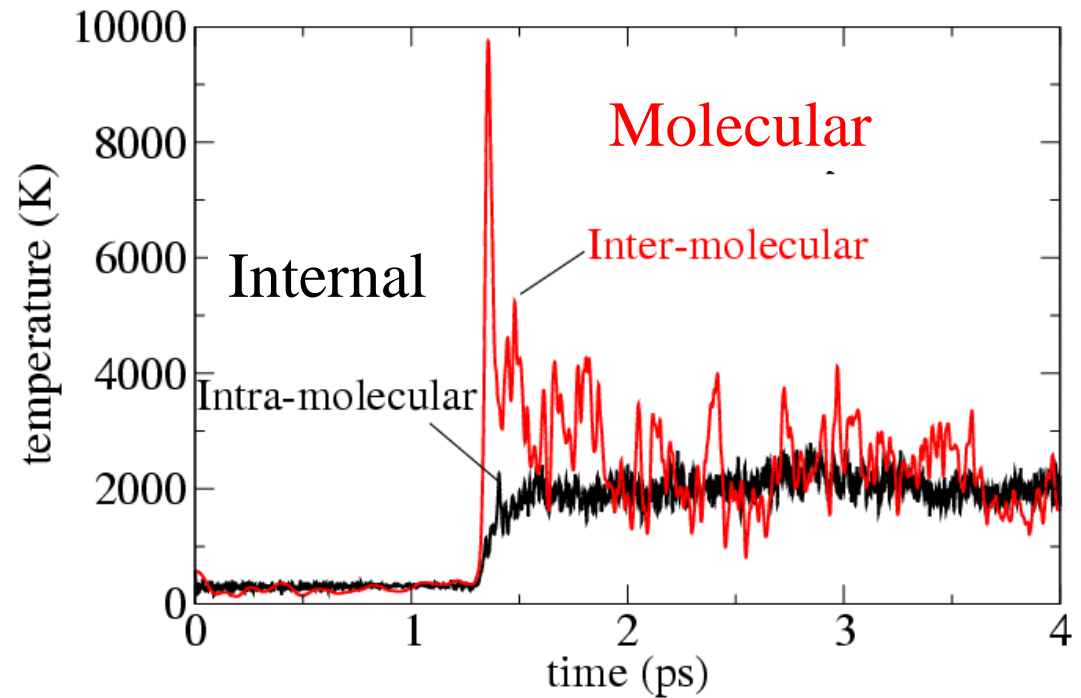
- Mesoparticles represent groups of atoms
- Molecules or grains in a polycrystalline solid (B.L. Holian)
- Mesopotential (effective interactions between mesoparticles)
- Thermal role of implicit degrees of freedom

# Test case: dynamical loading of a polymer

All atom MD simulation



Temperature rise caused by shock



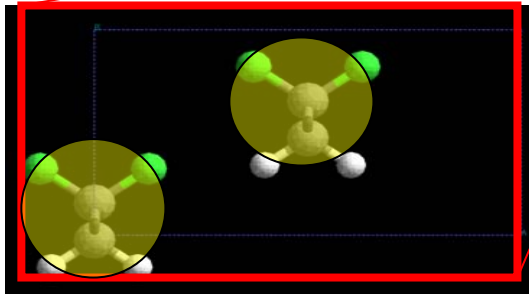
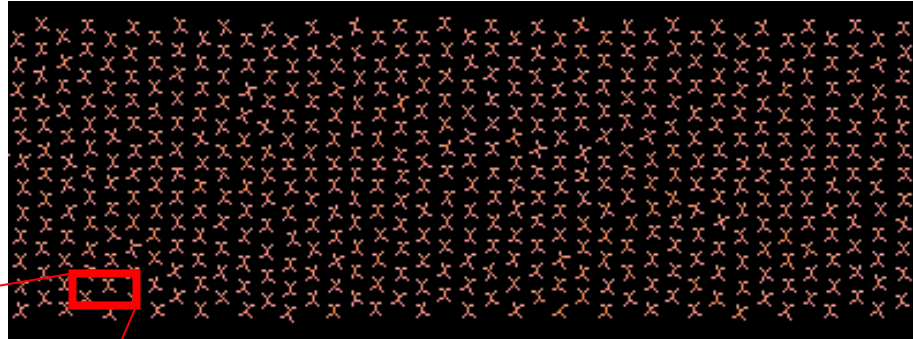
**Molecular: c.m. velocity of molecules around translation**

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



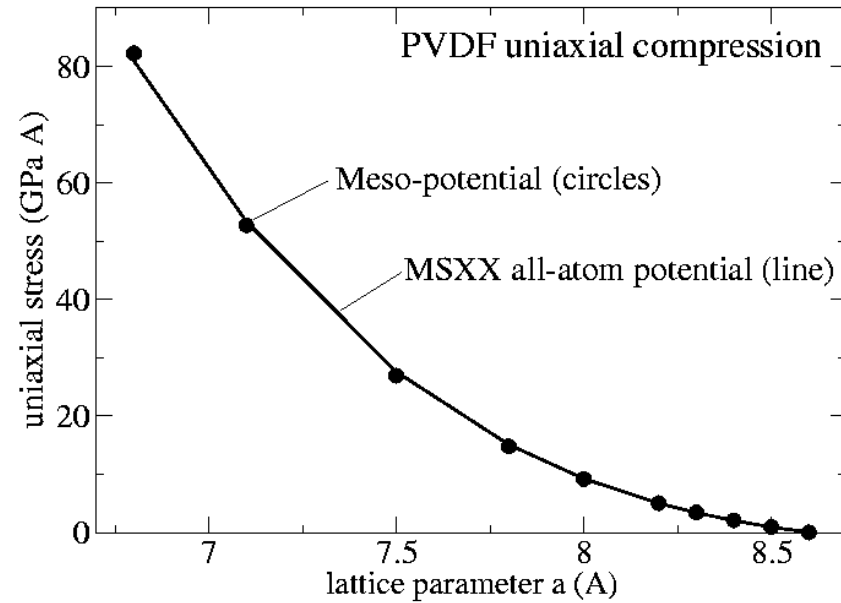
# MesoDynamical description: mesopotential

PVDF  $\beta$  crystal structure

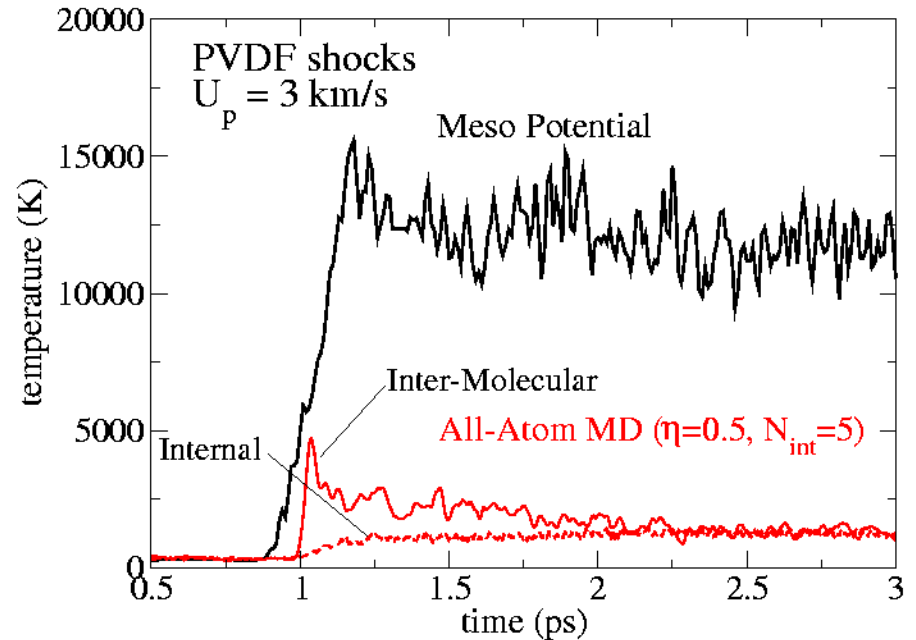
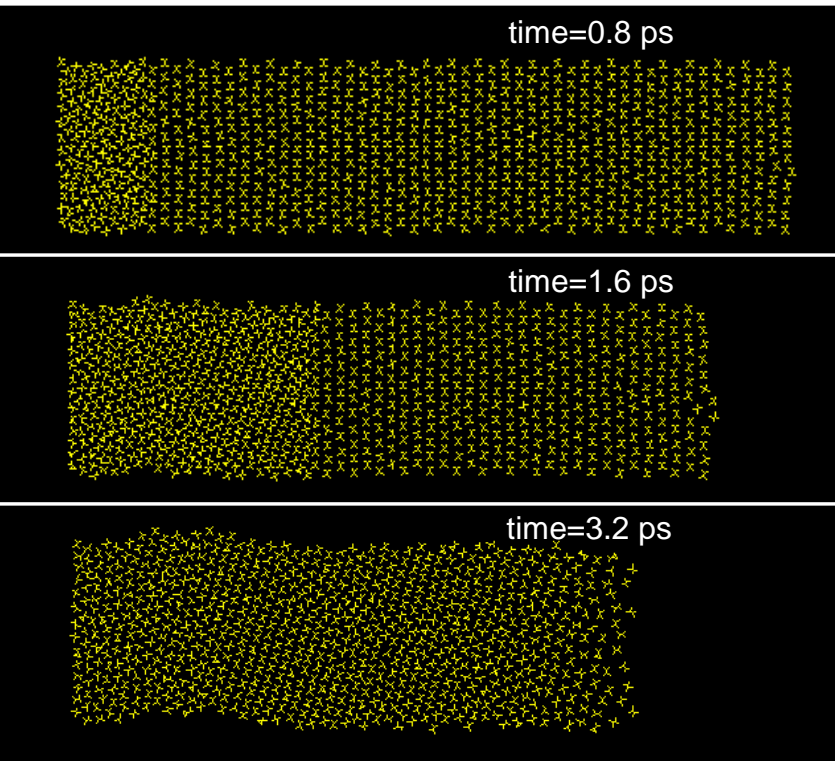


Quasi-hexagonal 2-D lattice

- Represent each chain with single particle
- Obtain meso-potential to reproduce uniaxial compression



# The problem with mesodynamics



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

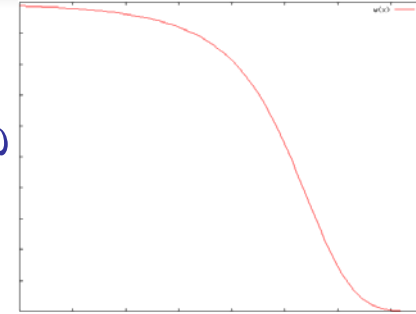


**Large overestimation of temperature**

# Energy exchange: mesoparticles $\leftrightarrow$ implicit modes

Local mesoparticle velocity:  $\langle u \rangle_i = \frac{\sum_j m_j u_j w(r_{ij})}{\sum_j m_j w(r_{ij})}$

weight



distance

Local mesoparticle temperature:  $3kT_i^{meso} = \frac{\sum_j m_j |u_j - \langle u \rangle_i|^2 w(r_{ij})}{\sum_j w(r_{ij})}$

Equations of motion:

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

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

Change in mesoparticle energy:

$$\dot{E}^{meso} = \sum_i [-m_i \eta_i (u_i - \langle u \rangle_i) \cdot u_i - \chi_i F_i \cdot F_i] = \sum_i \dot{E}_i^{meso}$$

Not Galilean invariant

Change in internal energy so that total energy is conserved:

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

# New equations of motion for mesodynamics

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

$$\dot{r}_i = u_i + \chi_i F_i$$
$$\dot{u}_i = \frac{F_i}{m_i}$$
$$\dot{E}_i^{\text{int}} = \frac{\dot{T}_i^{\text{int}}}{C_i^{\text{int}}} = \chi_i F_i \cdot F_i$$

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

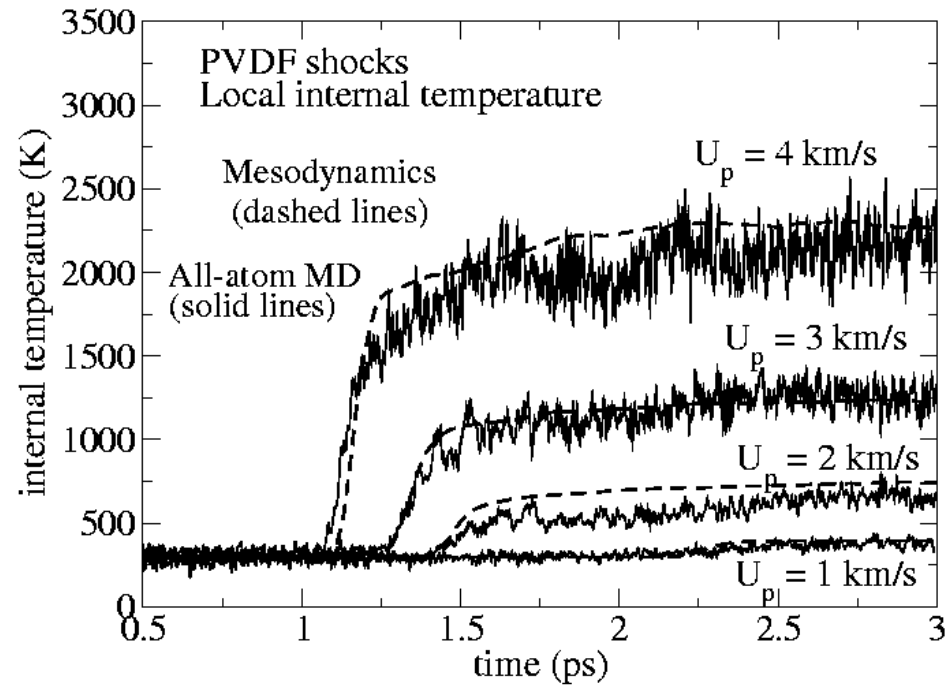
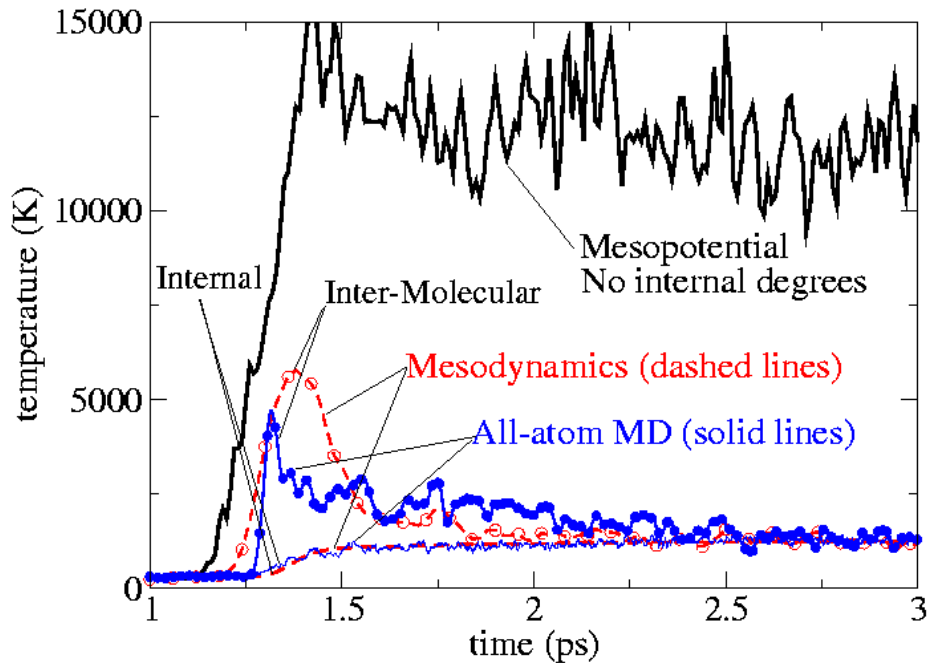
• Couple through the position update equation

• Finite thermostats

## Key features

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

# 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

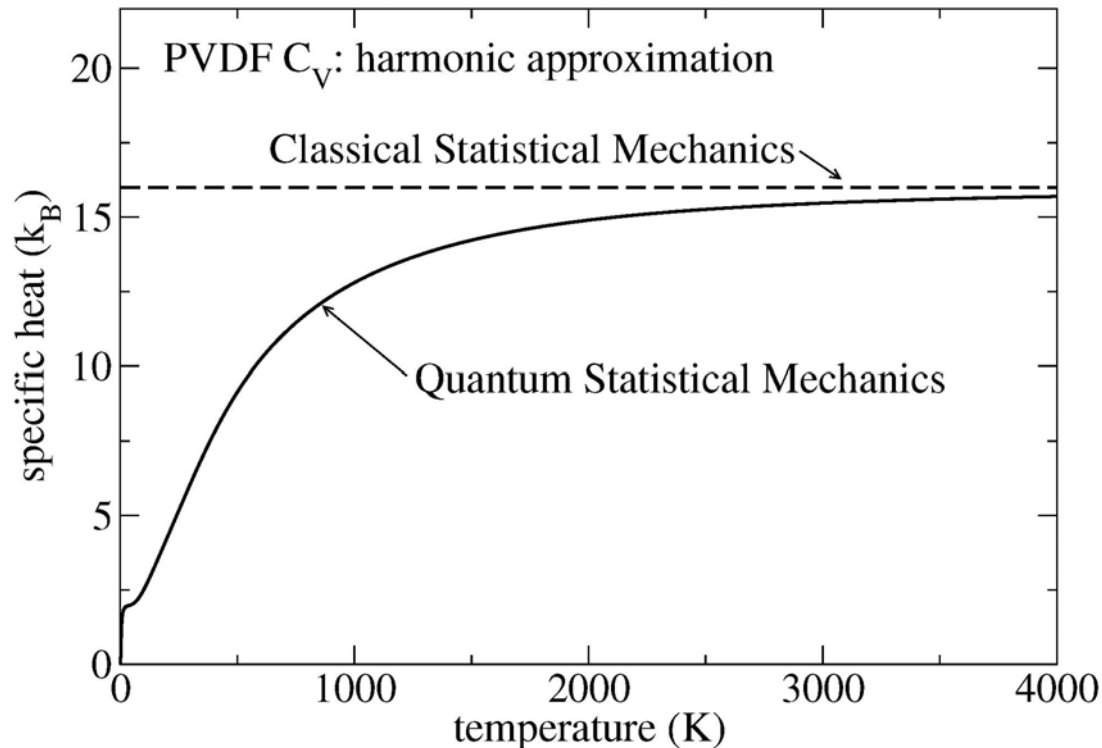
# Quantum description of internal degrees

Classical description of the internal degrees of freedom (harmonic)

Equipartition of energy:  $E_{CM}^{int} \cong N_{int} kT$

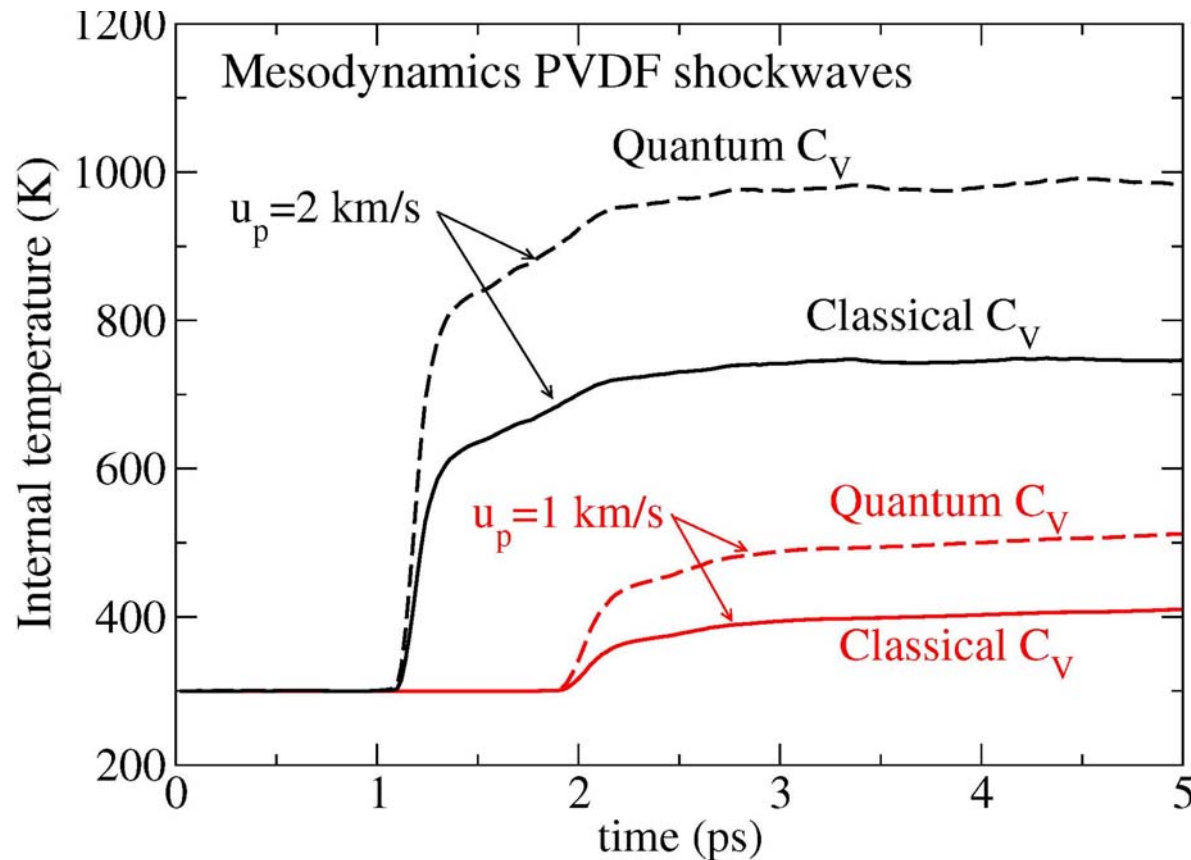
Quantum description of the internal degrees of freedom (harmonic)

$$e_{\omega_i}(n_i) = h\omega_i \left( \frac{1}{2} + n_i \right) \quad E_{QM}^{int} = \sum_i^{N_{int}} \left( \frac{1}{2} + h\omega_i \frac{1}{\exp(h\omega_i / kT) - 1} \right)$$



# Quantum description of thermal behavior

Quantum vs. classical specific heat



Classical description (including MD) underestimates the temperature of the shocked material

# ***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



# Lectures on Molecular Dynamics simulations

- Lots of progress in last 25 years
  - Thermostats & barostats
  - Accurate force fields
  - Coarse graining
- Still lots to do and learn ...

Remember homework assignments and hands-on activities

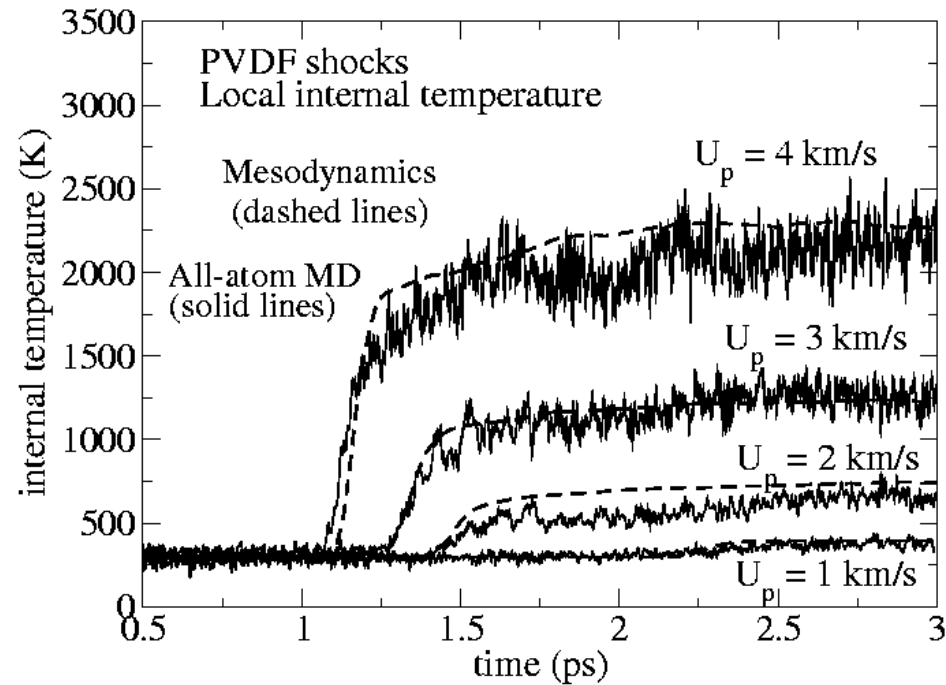
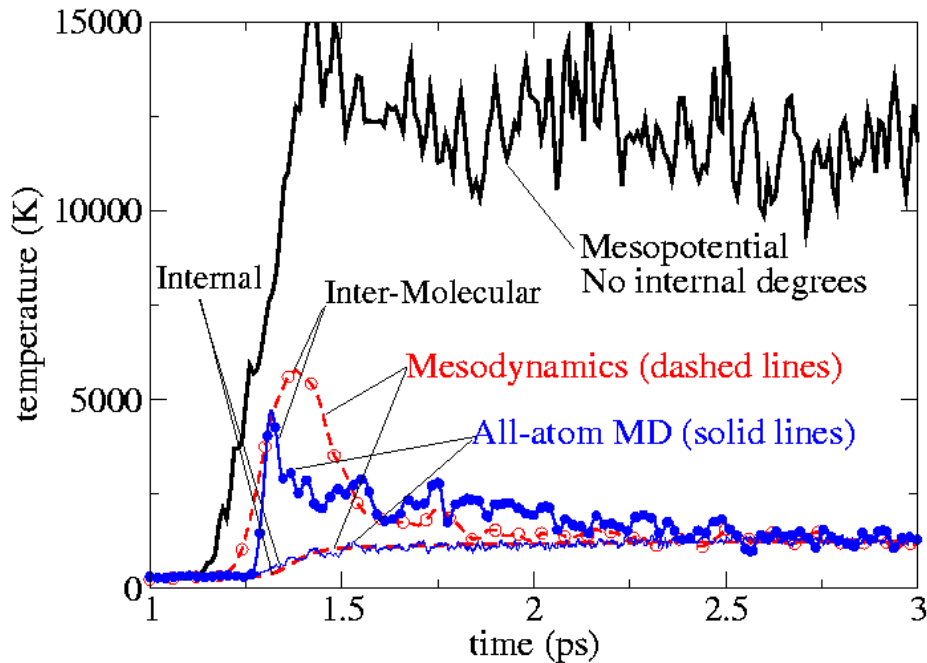


[nanoHUB.org](http://nanoHUB.org)

online simulations and more

# Questions & Answers

# 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

# Questions & Answers