Atomistic Simulation Methods and Multiscale Modeling

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DOE Summer Institute, Corvallis, June, 2007

Overview of Presentation

Part 1: Introduction to Atomistic Simulation Methods.

Part 2: Introduction to Multi-scale Modeling.

Overview of Part 1.

Part 1: Introduction to Atomistic Simulation Methods.

1) Main idea of atomistic methods.

2) Empirical inter-atomic potentials.

3) In more detail:
   - Monte Carlo methods (MC)
   - Molecular Mechanics (MM)
   - Molecular Dynamics (MD)

4) Examples of atomistic simulations.

Why Need Atomistic?

Problem: continuum methods (such as FEM) use *averaged* description for modeling the material properties. As a result, they are not capable of modeling phenomena at the atomic scale.

Localized non-linear deformation, defects (crack tips, dislocations, etc.), micro/nano-scale materials and structures (e.g. CNTs) as well as various nano-scale phenomena (e.g. atomic-scale friction) need to be modeled with the atomic scale accuracy.

Solution: use atomistic methods that explicitly consider every individual atom. However, there are different ways to do it.

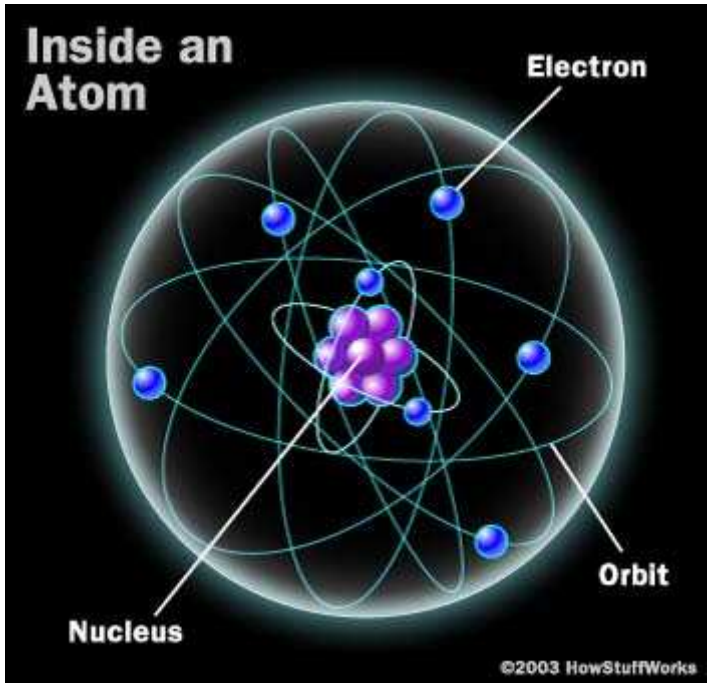
Atomistic Methods Overview: QM

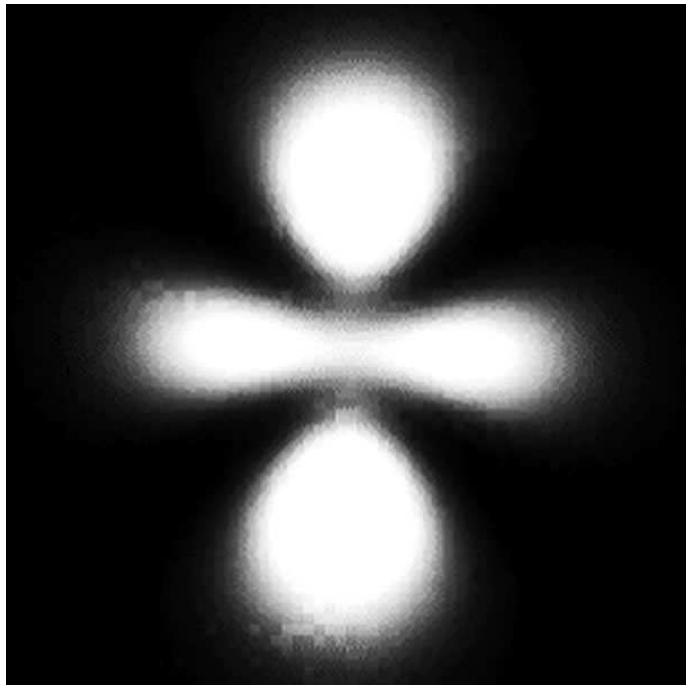
1) Quantum-mechanical (QM), or *ab initio* methods:

Main Idea: solution of electronic Schrodinger equation for atoms and molecules, as well as various approximations of that solution. Electronic structure of each atom is accounted for.

Major Methods: Density Functional Theory (DFT), Hartree-Fock (HF), Tight Binding (TB)

QM methods are very accurate, but extremely expensive.



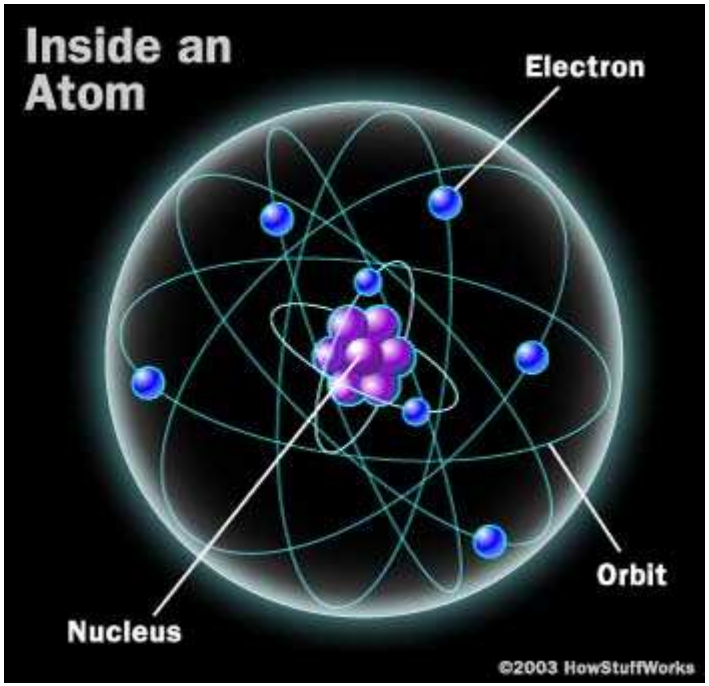


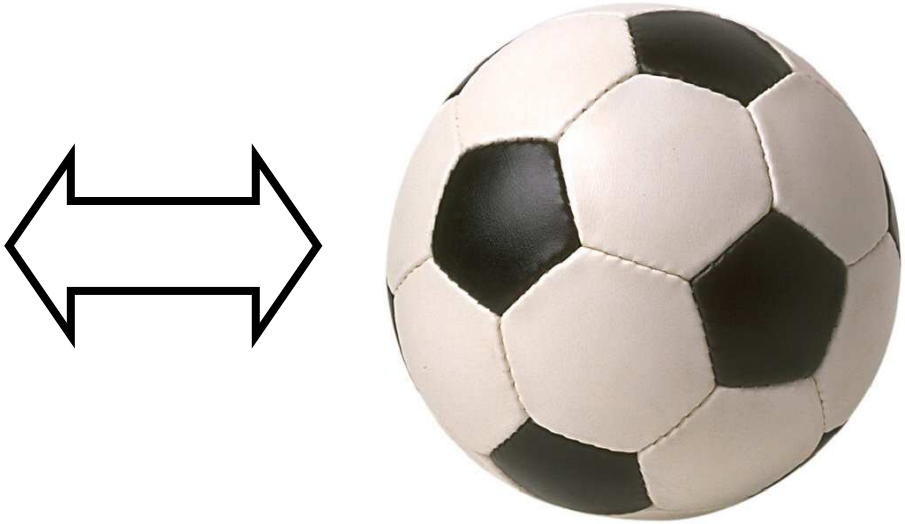
Atomistic Methods Overview

2) Atomistic methods using empirical inter-atomic potentials.

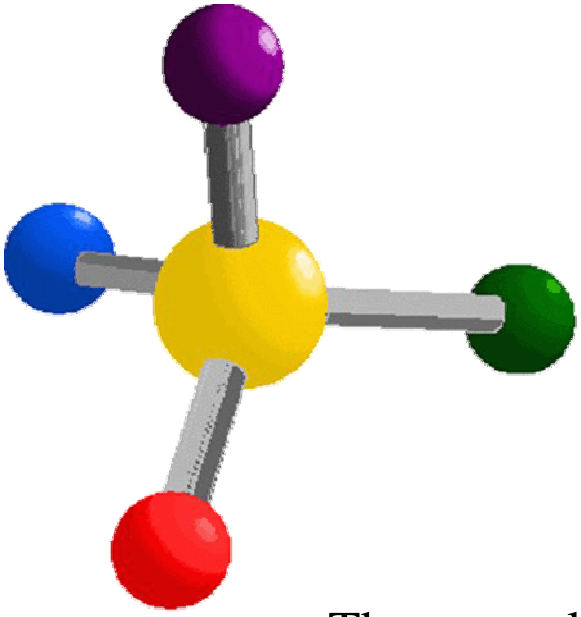
Main Idea: the whole atom is modeled just as a ball (soft sphere).
No account of the complex electronic structure of each atom.

Major Methods: Molecular Mechanics (MM), Molecular Dynamics (MD), Monte Carlo (MC)
These methods are less accurate, but relatively inexpensive.





Modeling inter-atomic interactions



Need to model interactions between atoms!

Forces between atoms are derived from empirical inter-atomic potentials that are obtained from fitting material properties (e.g., lattice constant, elastic constants, vacancy-formation energy, etc.) from experimental data or QM calculations.

They may depend on the distance between the atoms, angles between bonds, angles between planes, etc.

The general form of the total potential of the N-atom system:

$$V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_i V_1(\mathbf{r}_i) + \sum_{i,j>i} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j>i,k>j} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots$$

one-body part two-body part three-body part

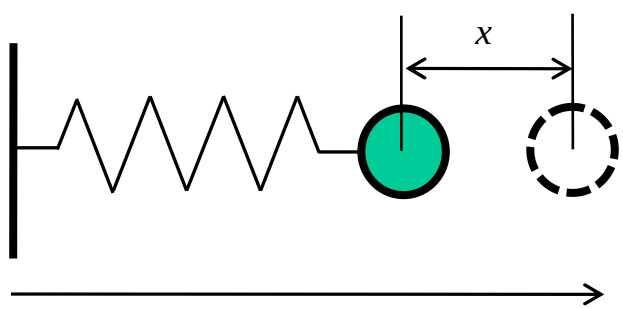
Force acting on atom *i*: $\mathbf{F}_i = -\dfrac{\partial V}{\partial \mathbf{r}_i}$

Inter-atomic Potentials: One-body

The **one-body** potential V_1 describes external force fields (e.g. gravitational filed), and external constraining fields (e.g. the "wall function" for particles in a chamber). Depends on the distance between the atom and the external source.

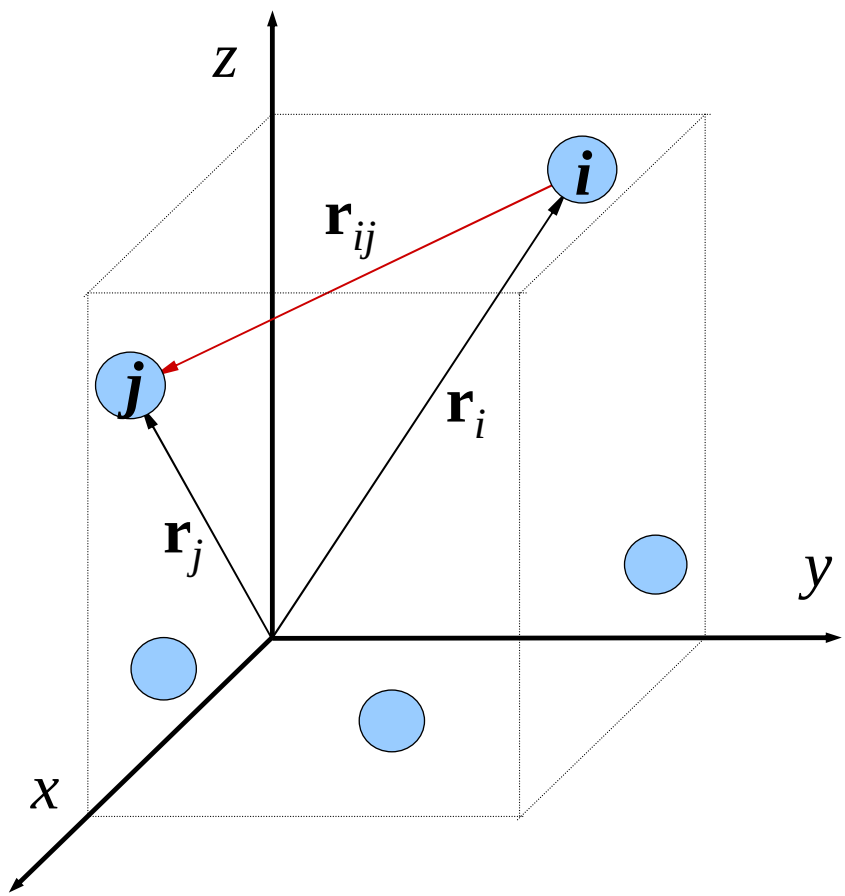
<u>Example</u>: harmonic oscillator (mass on a spring)

$$V_1(x) = \frac{1}{2}kx^2, \qquad F(x) = -\frac{\partial V}{\partial x}$$



Inter-atomic Potentials: Two-body

The **two-body (pair-wise)** potential V_2 describes dependence of the potential energy on the distances between pairs of atoms in the system:

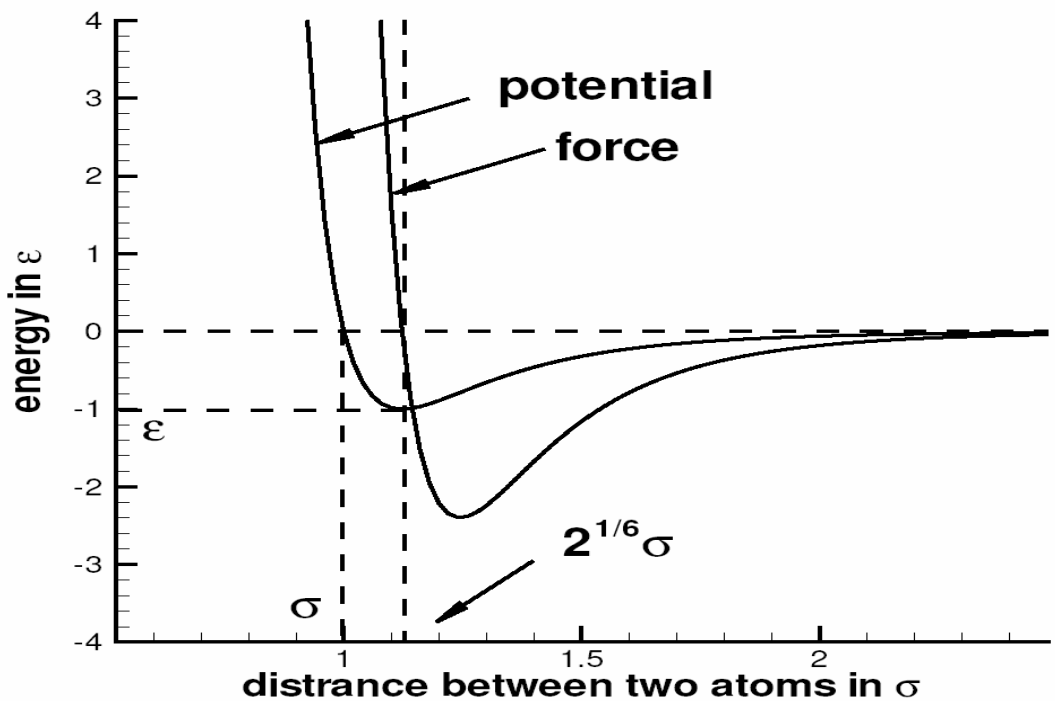


$$V_2(\mathbf{r}_i, \mathbf{r}_j) = V_2(r),$$

$$r = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$$

Pair-wise Potentials: Lennard-Jones

$$W_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \quad F_{LJ}(r) = -\frac{\partial W_{LJ}(r)}{\partial r} = 24\frac{\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right]$$



ε is the depth of the potential energy well

σ is the value of r where potential energy becomes zero;

ρ is the equilibrium distance:

$$F_{LJ}(\rho) = 0 \quad \rightarrow \quad \rho = \sqrt[6]{2}\sigma$$

The *first term* represents repulsive interaction (at small distances atoms repel).
The *second term* represents attractive interaction at large distances

Pair-wise Potentials: Morse

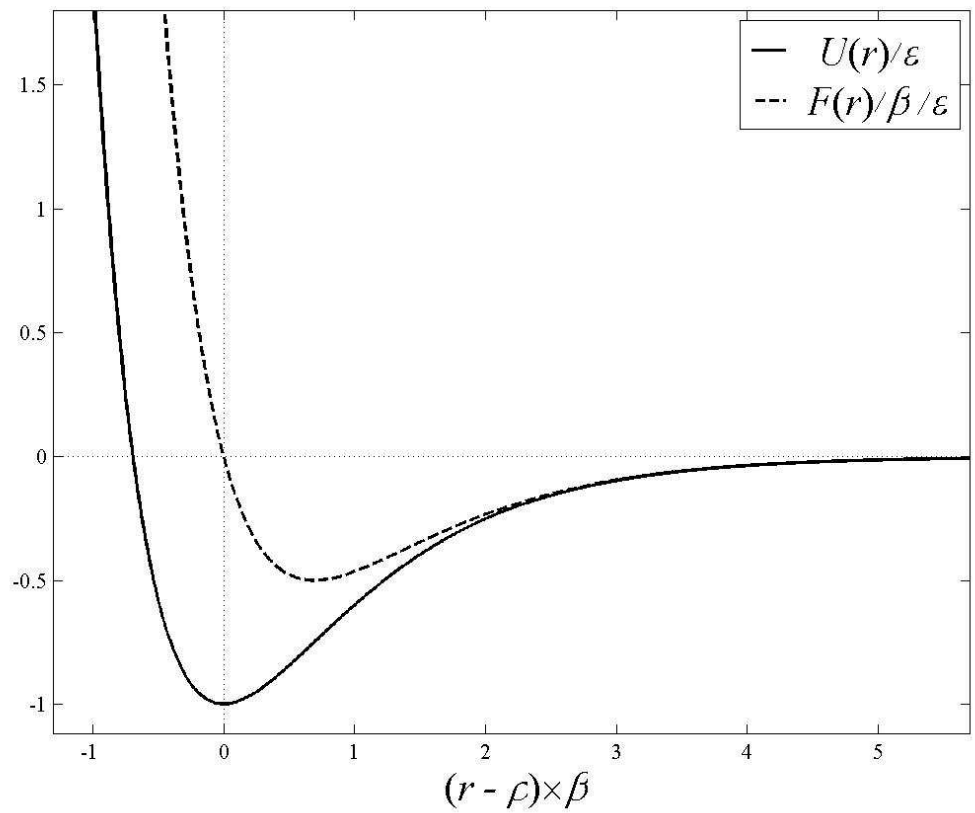
Another pair-wise potential model is *Morse potential*:

$$V_M(r) = \varepsilon\left[e^{2\beta(\rho-r)} - 2e^{\beta(\rho-r)}\right],\ F_M(r) = 2\varepsilon\beta\left[e^{2\beta(\rho-r)} - e^{\beta(\rho-r)}\right]$$

ε is the depth of the potential energy well,
β is a scaling factor (potential width);
ρ is the equilibrium distance:

$$F_M(\rho) = 0$$

Similarly to the L-J potential, the *first term* represents repulsive interaction, the *second term* represents attractive interaction



Pair-wise Potentials: Truncation

Technically, the pair-wise interaction is non-zero even at very large distances.

- Consider a system of N atoms:
  - there are $\frac{1}{2}N(N-1)$ unique pair interactions
  - if all pair interactions are sampled, the number increases as square of the number of atoms

- Potential truncation allows for reduction of computational cost:
  - Neglect pair interactions beyond some distance r_c
  - Example: Lennard-Jones potential

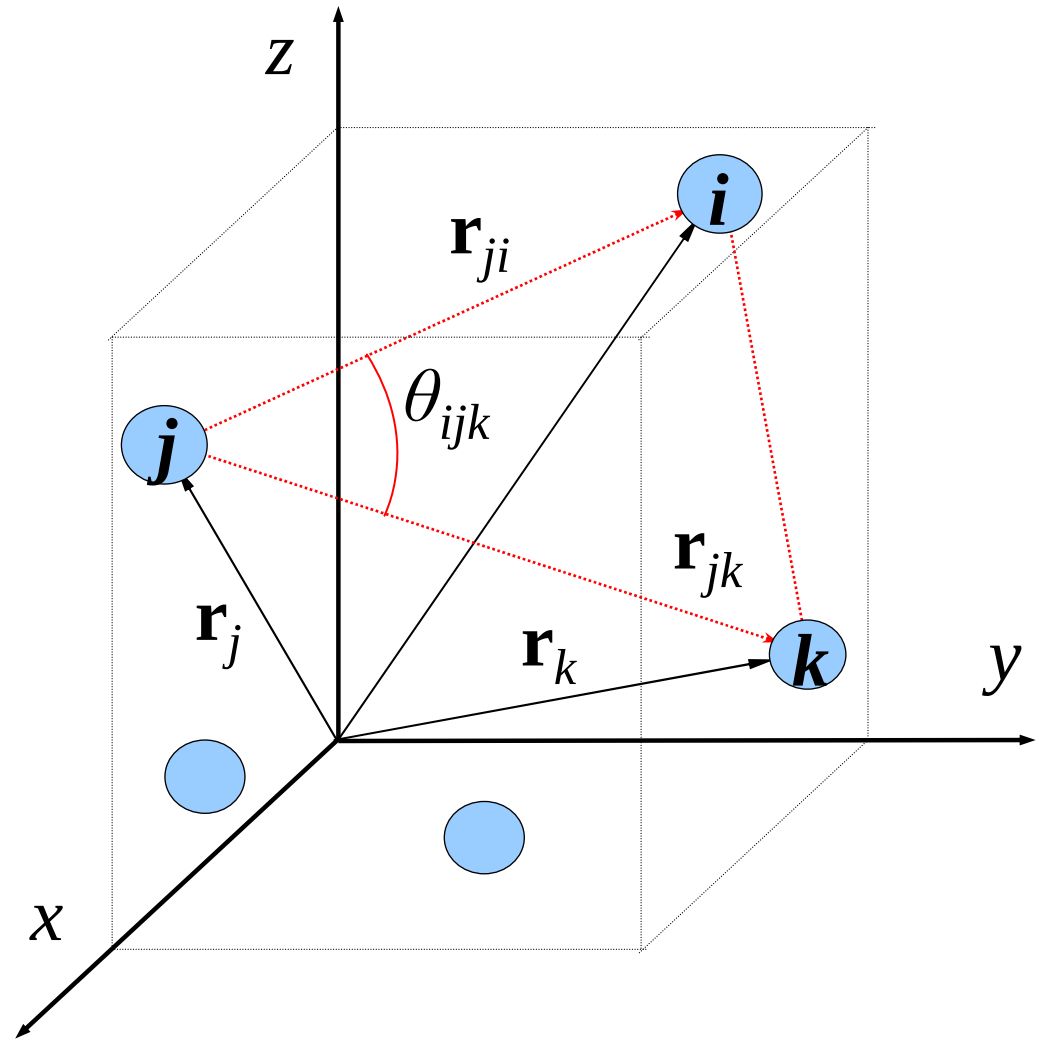
$$W_{LJ}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & r \le r_c \\ 0 & r > r_c \end{cases}$$

Inter-atomic Potentials: Three-body

The **three-body** part provides dependence on the geometry of the atomic arrangement/bonding. For instance, a dependence on the angle between three mass points is given by

$$V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = V_3(\cos\theta_{ijk}),$$

$$\cos\theta_{ijk} = \frac{\mathbf{r}_{ji} \cdot \mathbf{r}_{jk}}{|\mathbf{r}_{ji}|\,|\mathbf{r}_{jk}|}$$



Bonded and Non-bonded interactions

Two types of interactions: bonded and non-bonded.

Bonded –

- usually corresponds to strong covalent bonds,
- the number of neighbors is preset and is dictated by the lattice structure (e.g. carbon atoms – 3-4 neighbors),
- preset list of neighbors for each atom may be used throughout the calculations,
- used for crystalline solids with well defined bonds,
- example: graphite, diamond.

Non-bonded –

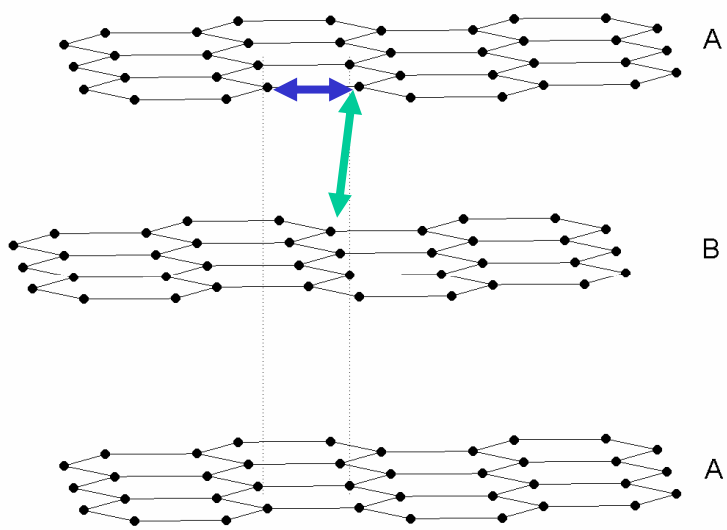
- relatively weak forces,
- the number of neighbors may be changing and is found based on the cut-off radius every *n* steps,
- usually used for amorphous materials,
- example: amorphous solids, liquids.

Example: Multi-layered graphite

Two inter-atomic potentials are used:

one is for in-layer *bonded* interactions - multi-body (Tersoff-Brenner)

the other for inter-layer *non-bonded* interactions - pair-wise (Lennard-Jones)



References:

The Art and Science of an Analytic Potential.
D.W. Brenner, Phys. stat. sol. (b) 217, 23 (2000)

A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. Donald W Brenner *et al*
J. Phys.: Condens. Matter **14** 783-802 (2002)

EAM Potential

Embedded Atom Method (EAM) potential: $$E = \sum_{i,j} V(r_{ij}) + \sum_{i} F_i(\rho_i)$$

Consists of pair-wise interaction part and the multi-body term.

A pair-wise part of the potential (primarily repulsive) describes the interaction of the positively charged metal core ions with one another.

A multi-body term (attractive interaction) models "embedding" a positively charged pseudo-atom core into the "sea" of free electrons created by the surrounding atoms.

Is commonly used for metals.

References:
M.S. Daw, M.I. Baskes. Phys. Rev. Lett. **50**, 1285 (1983);
M.S. Daw, M.I. Baskes. *Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals*. Phys. Rev. B 29, 6443 - 6453 (1984)

Atomistic Methods

There is a number of ways to update atomic positions based on the calculated inter-atomic forces. Hence, different methods.

Major methods:

- Atomistic Monte-Carlo method (MC)
- Molecular Mechanics (MM)
- Molecular Dynamics (MD)

All use inter-atomic potentials for calculation of forces, but use different approaches to find atomic positions.

MC – stochastic (i.e. based on guessing or randomness)
MM and MD – deterministic

Atomistic Monte Carlo

As follows from its name, MC is based on guessing and usually uses random number generation

General procedure of the original Monte Carlo:

1)Compute the total potential energy, V, from the atomic positions.

2)Randomly choose one atom and move it from its original position for a random distance in a random direction. Compute the total potential energy V*.

3)Accept or decline the move:

if $V^* < V$, accept;

if $V^* > V$, accept with a probability proportional to $exp[-\beta(V^*-V)]$,

where $\beta=1/kT$ (probability depends on temperature).

4) Repeat the procedure.

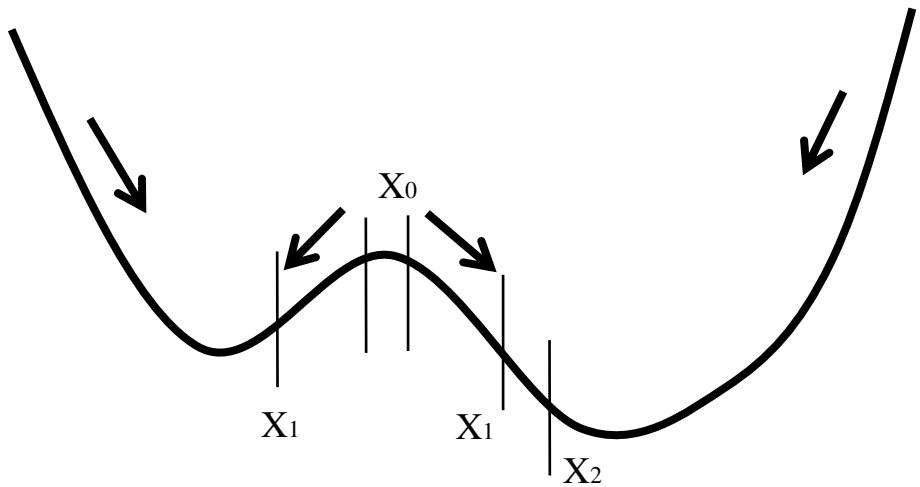
References:

N. Metropolis and S. Ulam, "The Monte Carlo Method", Journal of the American Statistical Association, volume 44, number 247, pp. 335–341 (1949).

Many modifications exist (e.g., force-biased MC, kinetic MC)

Molecular Mechanics (Statics)

MM is based on finding potential energy minimum of a system



- Iteration methods are applied for the energy minimization procedure:
  Gradient Methods (Steepest Descent, Conjugate Gradient) are the most popular.

- Each next iteration the energy is supposed to be smaller than on the previous iterations.

- The results depend on the starting point.

Molecular Dynamics

MD is based on the Newtonian classical dynamics

• Atoms are represented as mass points that interact with each other according to assigned inter-atomic potentials

• The time evolution of interacting atoms is pursued by integrating the corresponding equations of motion (total 3N equations)

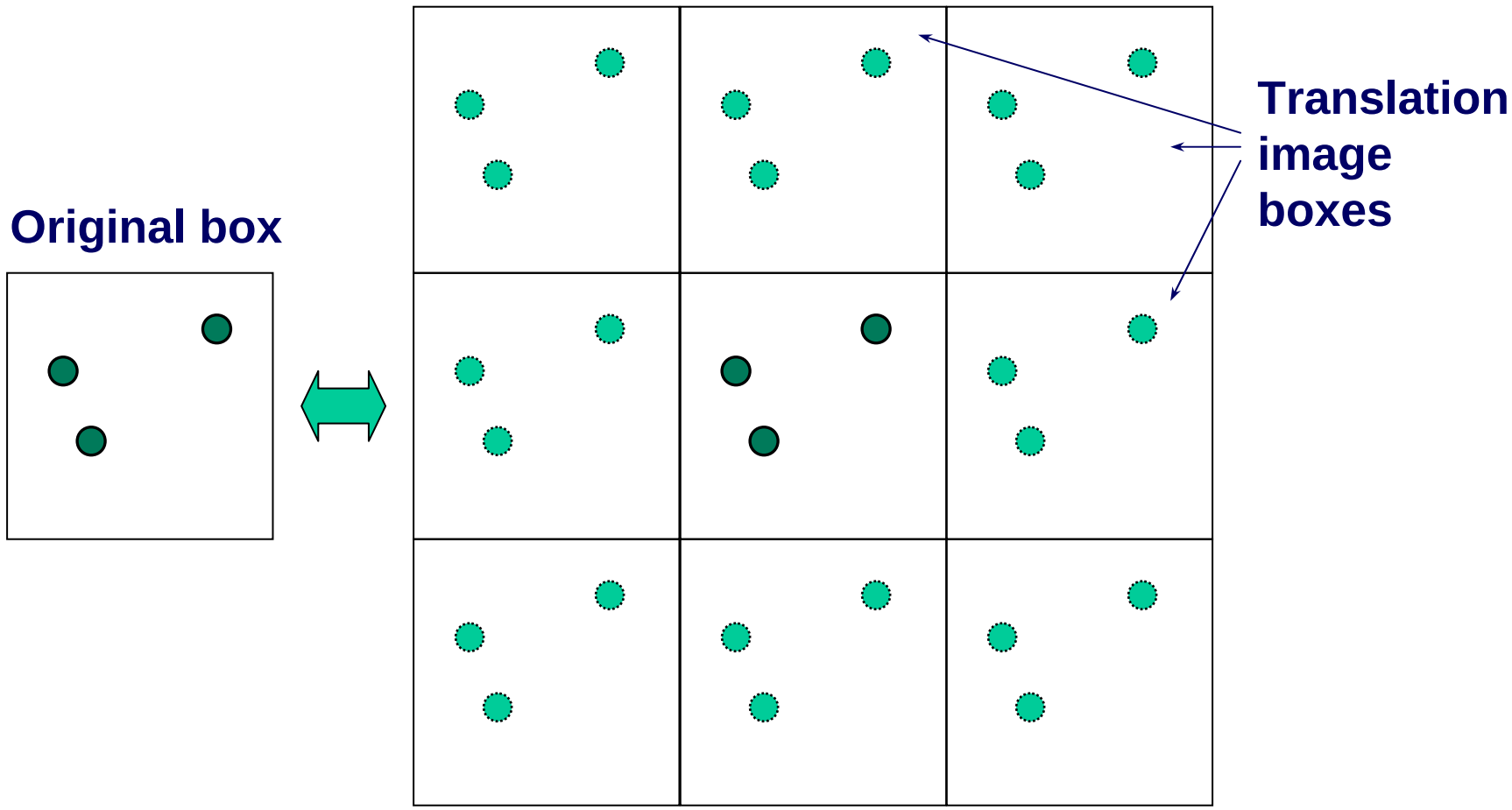
• Time scale is explicitly present in the simulation (unlike MC or MM)

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i, \qquad \mathbf{F}_i = \left(F_{x,i}, F_{y,i}, F_{z,i}\right) = -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}_i}$$

References:

• J.M. Haile, *Molecular Dynamics Simulation*, Wiley, 2002, pages 46-59, 188-204, 224-234, 277-282.

Periodic Boundary Conditions

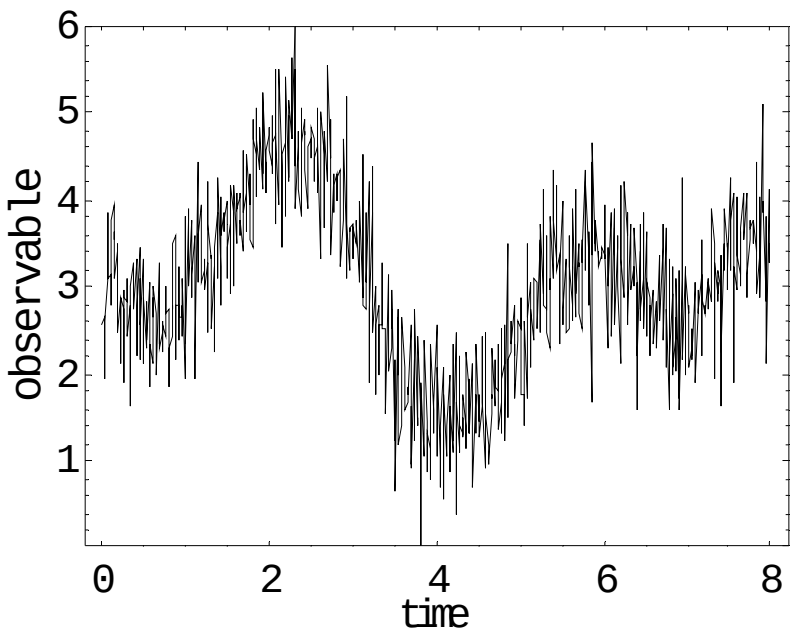


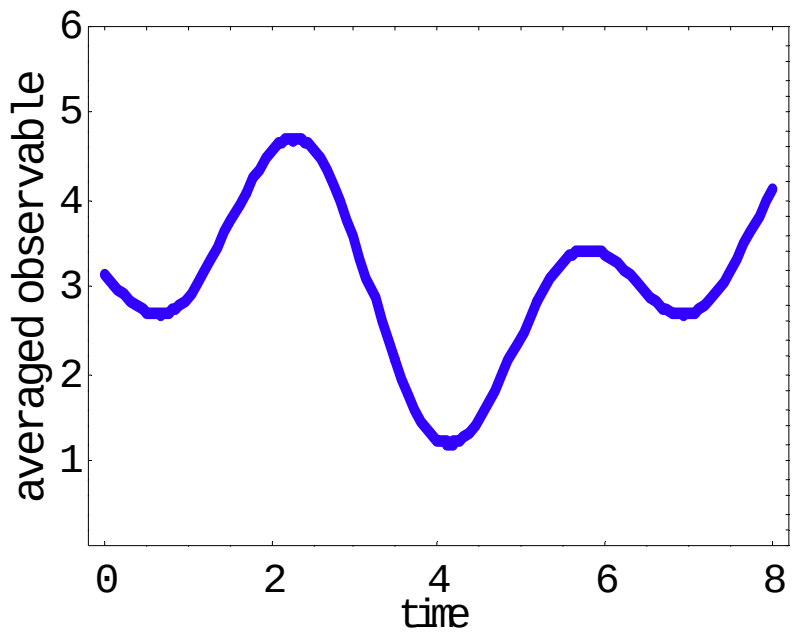
Motivation: domain reduction, to perform analysis of a representative substructure only. Only one box is modeled explicitly. Each particle interacts with other particles in the box and with their images in nearby boxes.

Computing macroscopic properties

During the MD simulations, most quantities are not constant, but fluctuating (e.g. kinetic energy, temperature, etc.)

Macroscopic properties of interest can be determined from the behavior of individual atoms by time-averaging.





Averaging of a fluctuating value $F(t)$ over period of time t_1 to t_2: $$\bar{F}(t) = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} F(t)\,dt$$

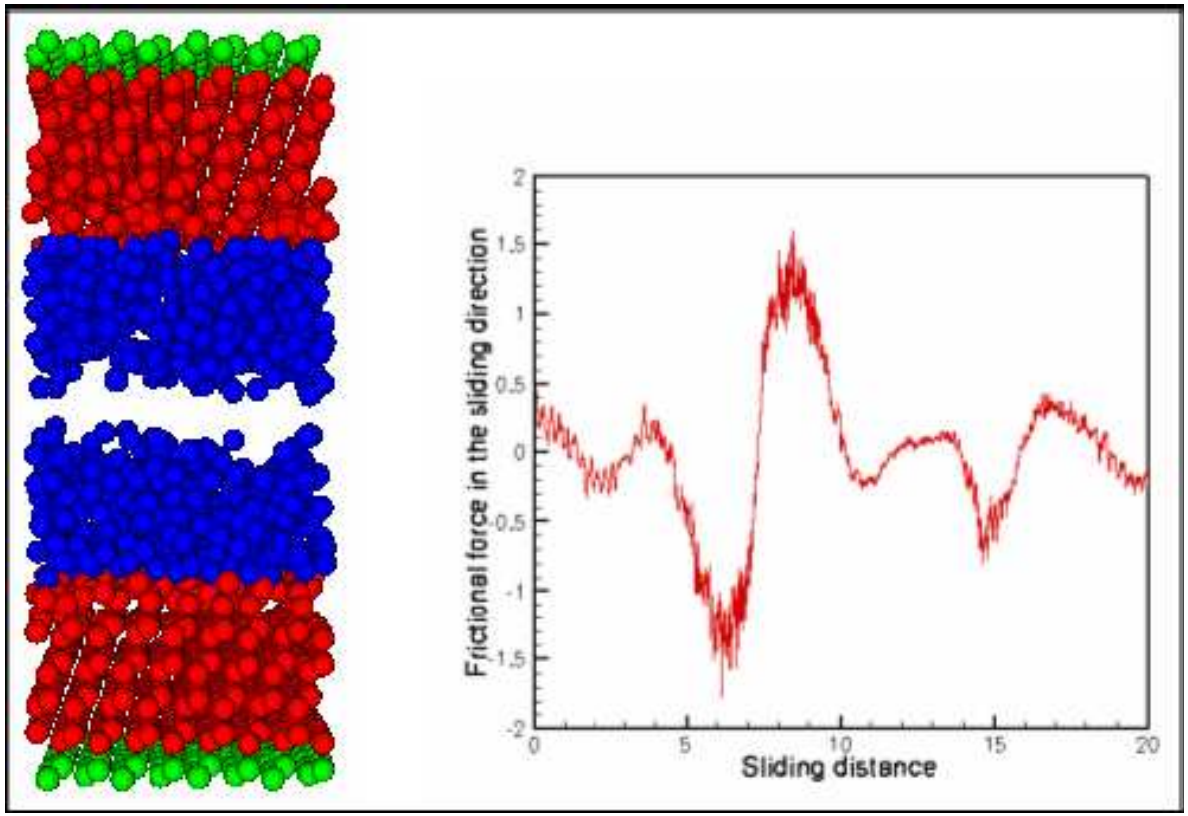
MD: Procedure

General procedure of Molecular Dynamics:

- Assign initial atomic positions (build lattice structure, introduce defects, etc.)
- Relax the structure (may use energy minimization)
- Calculate neighbor lists, pair-tables for inter-atomic interactions
- Compute the forces acting on the atoms.
- Solve equations of motion. Update positions of atoms.

  Use one of the numerical algorithm for time integration (Euler, Predictor-Corrector, Runge-Kutta, Verlet, etc.). Ensure the time step *dt* needed for algorithmic stability if method is conditionally stable.
- Advance with a time step *dt* and repeat the previous 2 steps until reach the end of simulation.
- Analyze the simulation data to investigate the collective behavior and various phenomena of interest (evolution of defects, crack propagation speed, etc.)

Example: Hydrogenated carbon films

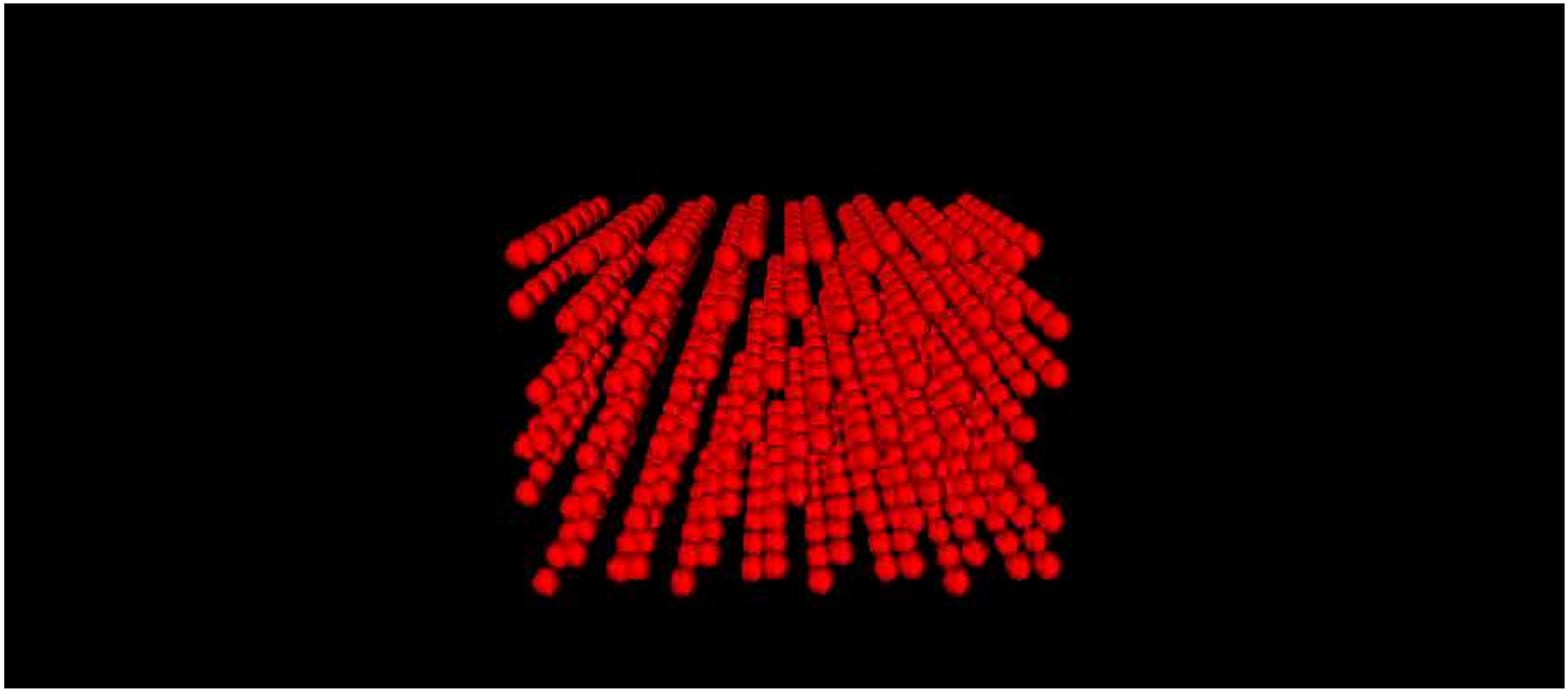


Hydrogen deposition was performed to make hydrogenated amorphous carbon film and study the friction dependency on the hydrogen presence.

S. Zhang, G. Wagner, S. N. Medyanik, W. K. Liu, Y. H. Yu and Y. W. Chung. "Experimental and molecular dynamics simulation studies of friction behavior of hydrogenated carbon films." *Surface and Coatings Technology*, 177/178, 818-823, 2004.

MD Movie:

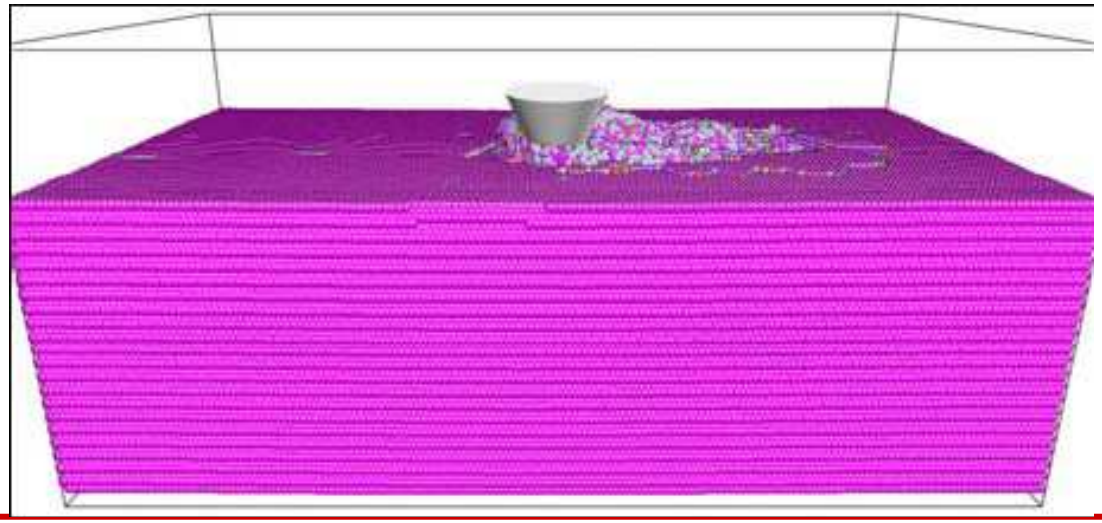
hydrogen deposition on a diamond film



Example: Nano-scratching

Scratching single crystal aluminum thin film on (111) surface with AFM:

- Molecular dynamics simulation using EAM potential
- Periodic boundary condition (side) & free boundary conditions (top & bottom)
- AFM tip is modeled by a repulsive potential (radius & hardness of the tip)
- Focused on defect mechanism (rather than the Interaction between tip and surface)
- 1K target temperature with Berendsen thermostat
- Visualization using the atomic coordination number
- Domain : 105 (nm) x 53 (nm) x 18 (nm)
- Number of Atoms : 6,060,600
- 32 CPUs with shared memory
- Time Step: 5 (fs)
- Scratching Velocity: 100 (m/s)
- Scratching Depth : 4 (nm)
- Tip Radius: 5.0 (nm)



by Sukky Jun and coworkers
(KAIST)

Overview of Part 2.

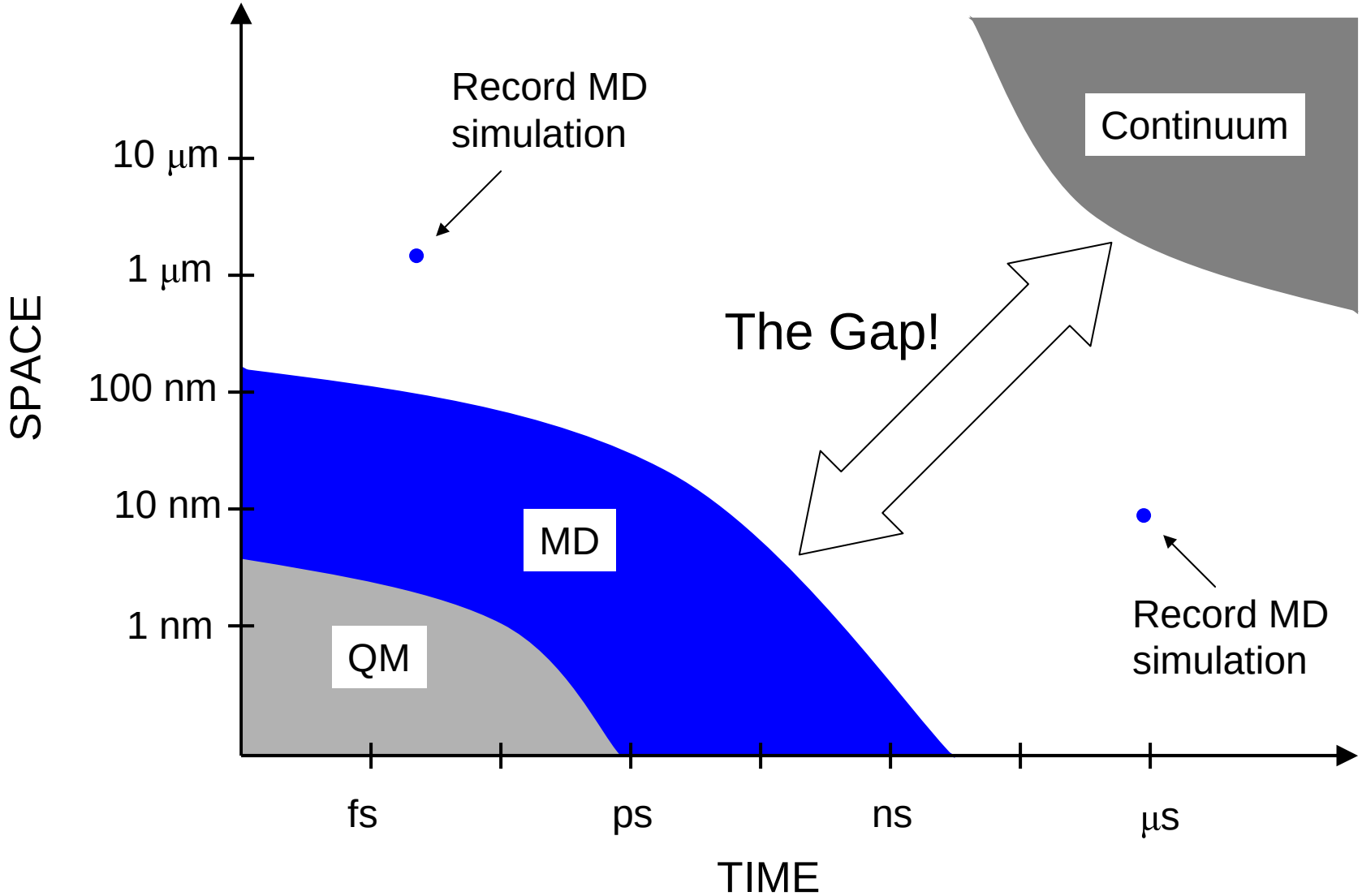
Part 2: Introduction to Multi-scale Modeling.

1) Limitations of atomistic methods.

2) Common multi-scale approaches.
   - multiple length scale methods
   - multiple time scale methods (MD)

3) Examples of multi-scale simulations.

Limitations of Atomistic Methods



Motivation for Multi-Scale Modeling

Filling The Gap!

Problem: Accurate methods (such as atomistic simulations) can handle only small time and length scales (much smaller than those in real-life nano-experiments)

Solution: *Multi-scale methods* are used to fill the gap between Atomistic and Continuum length and time scales.

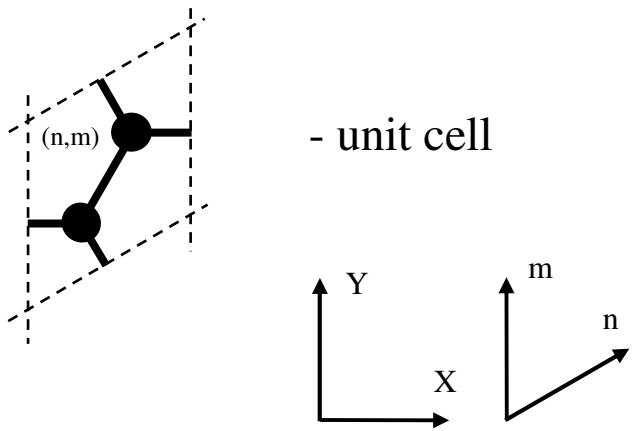
Two major directions in multi-scale modeling:

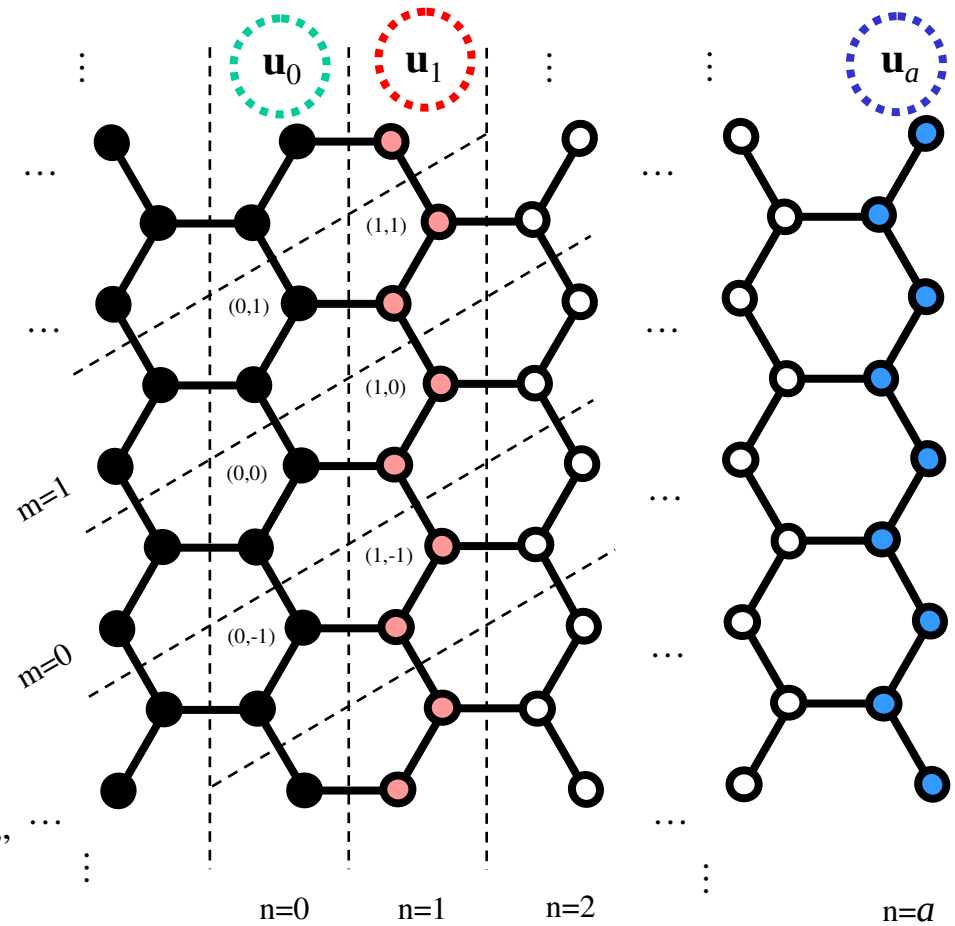
- extending the atomistic ***length*** scales (*spatial* multi-scale methods)
- extending the atomistic ***time*** scales (*temporal* multi-scale methods).

For instance, for the length scale extension, atomistic-continuum coupling may be applied: atomistic method can be used in the region of localized deformation where resolution down to atomic scale is desired (fine scale domain), and continuum method (e.g. FEM) everywhere else (coarse scale domain).

Method of Multi-Scale BCs (MSBC)

The method is designed for crystalline solids with regular periodic lattice structure. It is based on the lattice Green's function approach. The domain is discretized into unit cells. The choice of a representative unit cell depends on the *geometry* of crystal structure and the type of inter-atomic *forces.*



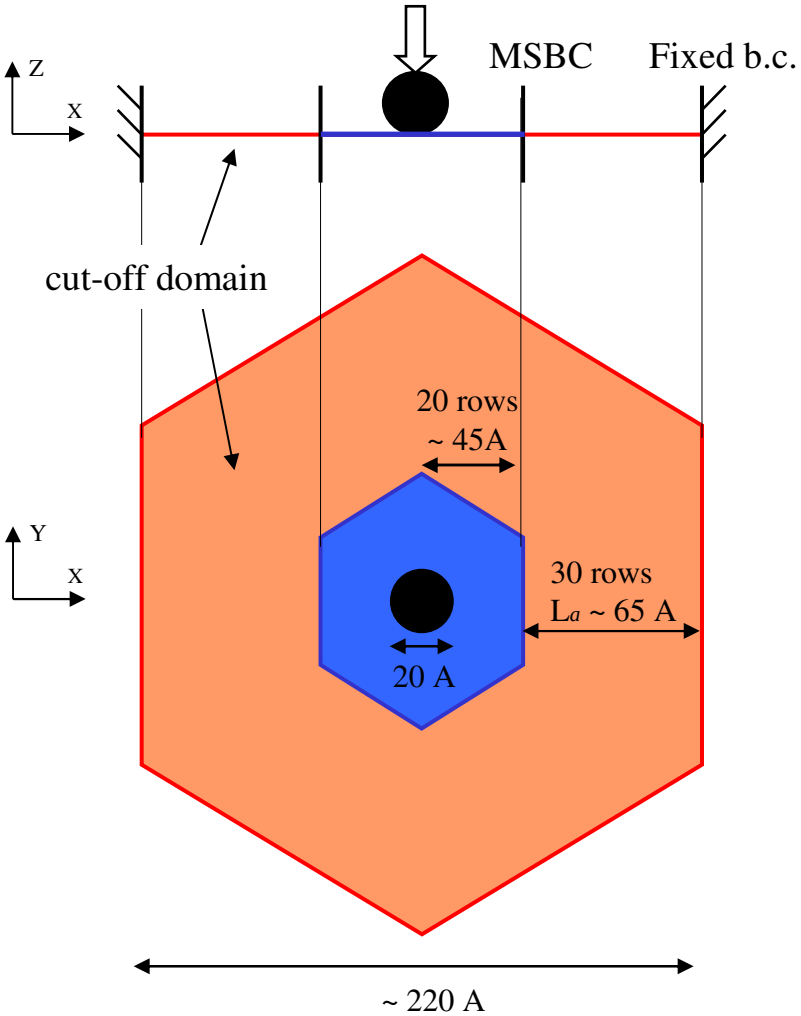


Multi-Scale Boundary Conditions:

$$\mathbf{u}_{1,m} = \sum_{m'=m-m_c}^{m+m_c} \left(\mathbf{\Theta}_{m-m'} \mathbf{u}_{0,m'} + \mathbf{\Xi}_{m-m'} \mathbf{u}_{a,m'} \right)$$

Reference: S. N. Medyanik, E.G. Karpov, W. K. Liu. "Domain reduction method for atomistic simulations." *Journal of Computational Physics*, 218, p. 836–859 (2006).

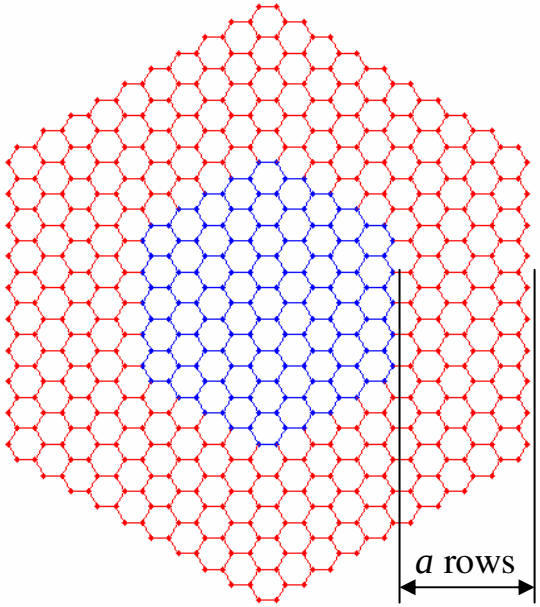
Nanoindentation of a Single Graphene Layer



Multi-Scale Boundary Conditions (MSBC) are applied at the six sides of the hexagonal *reduced domain* (blue, small hexagon). The rest of the full domain (red, larger hexagon) is cut-off and calculations are performed only for the reduced domain.

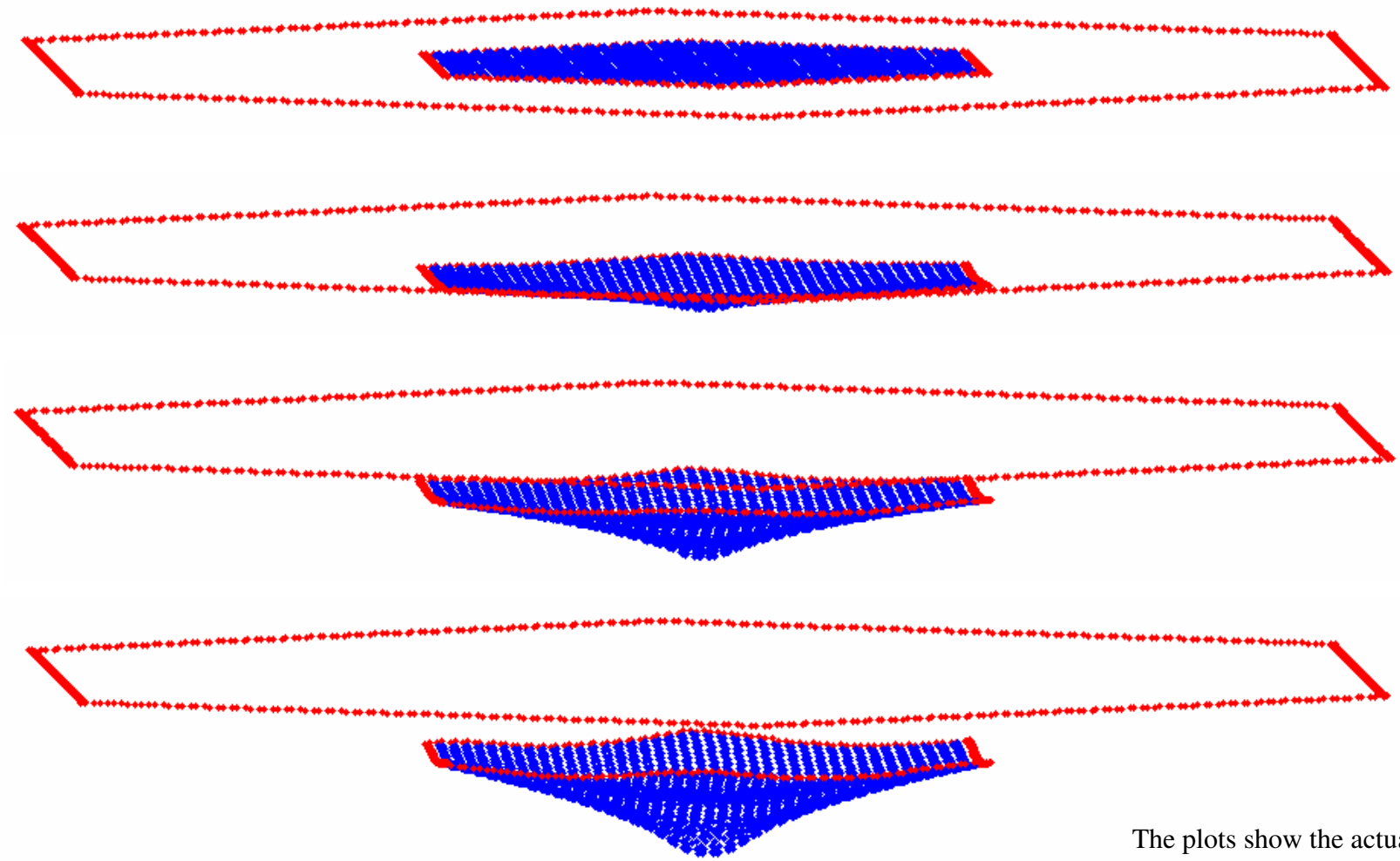
'a' is a *Domain Reduction Parameter*, it defines the size of the cut-off domain and is equal to the number of unit cells between the boundary of the reduced domain and the boundary of the full domain, here a=30.

Special treatment of the Multi-Scale boundaries intersections is needed. Extrapolation for the "non-existing" atoms outside the reduced domain.



MSBCs single layer results

Full domain size is 15,000 atoms. Reduced domain – 2,400 atoms.



Step 0.

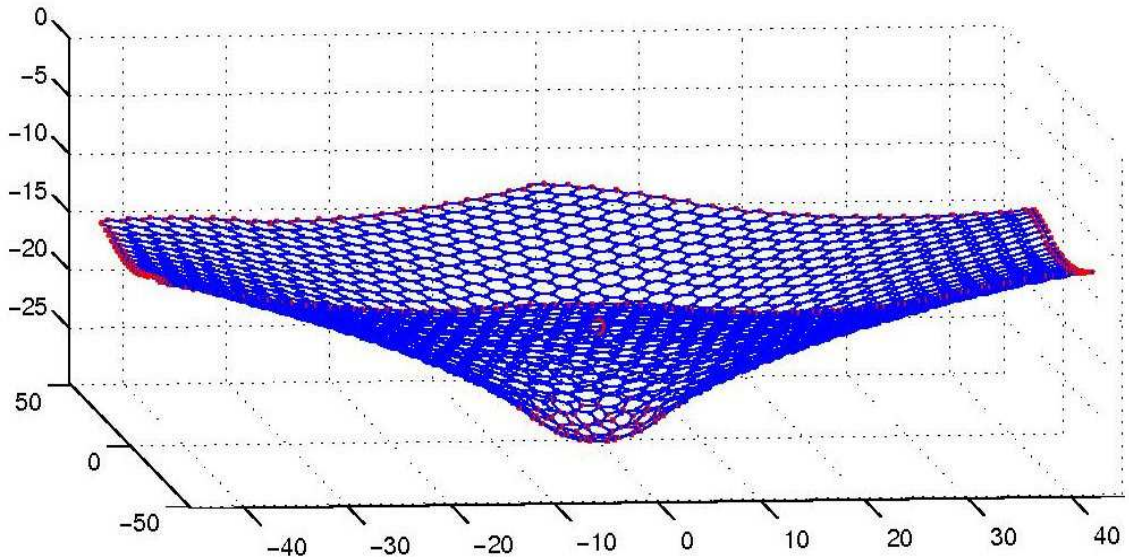
Step 20, depth=10A

Step 40, depth=20A

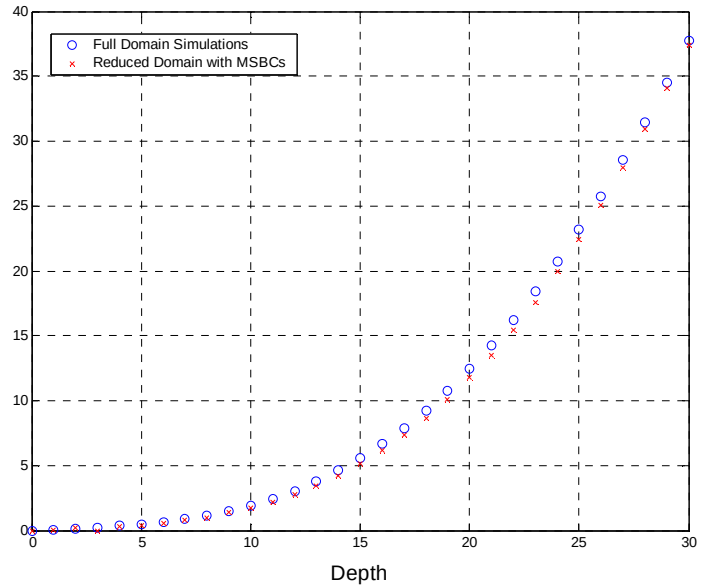
Step 60, depth=30A

The plots show the actual scale deformation.

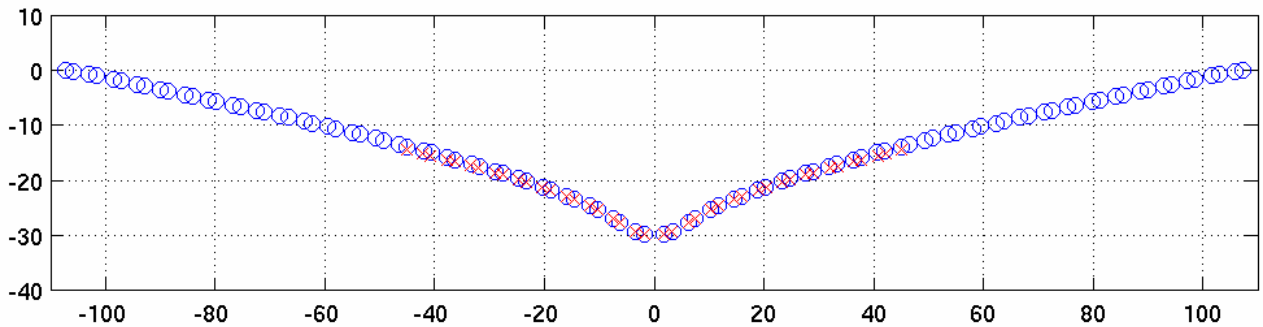
Multi-scale vs. full domain solution



Deformed configuration of Reduced Domain with MSBCs.

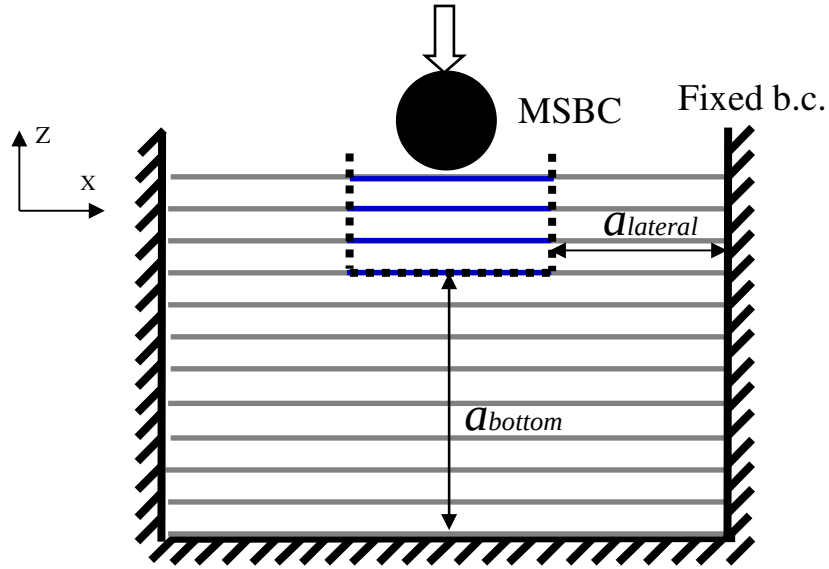


Force-Depth curve



Middle line cross-section. Full Domain (blue) vs. Reduced with MSBCs (red) vertical displacements.

Nanoindentation of Multi-layered Graphite



Application of the method to multi-layered graphite:

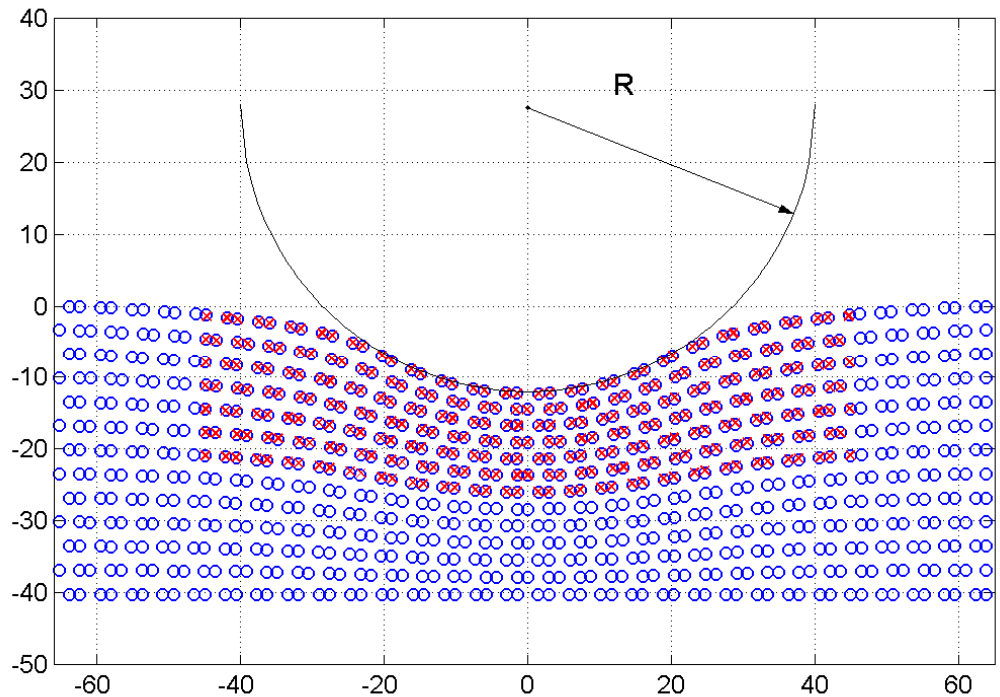
- new type of MSBCs needed to model bottom Multi-Scale boundary:

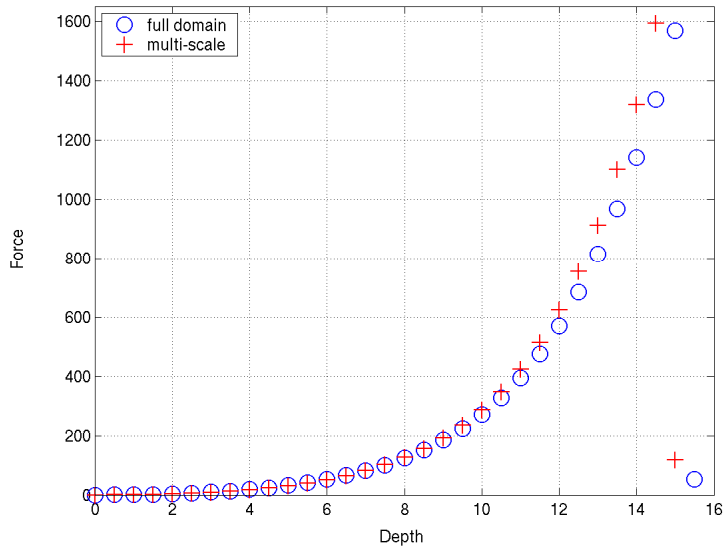
$$\mathbf{u}_{n,m,1} = \sum_{n'=n-n_c}^{n+n_c} \sum_{m'=m-m_c}^{m+m_c} \mathbf{\Theta}_{n-n',m-m'} \, \mathbf{u}_{n',m',0}$$

- matrices $\mathbf{\Theta}_{n,m}$ are derived based on the inter-layer interactions (LJ potential is used)
- two Domain Reduction Parameters: $a_{lateral}$ and a_{bottom}

Graphite: lateral and bottom MSBCs

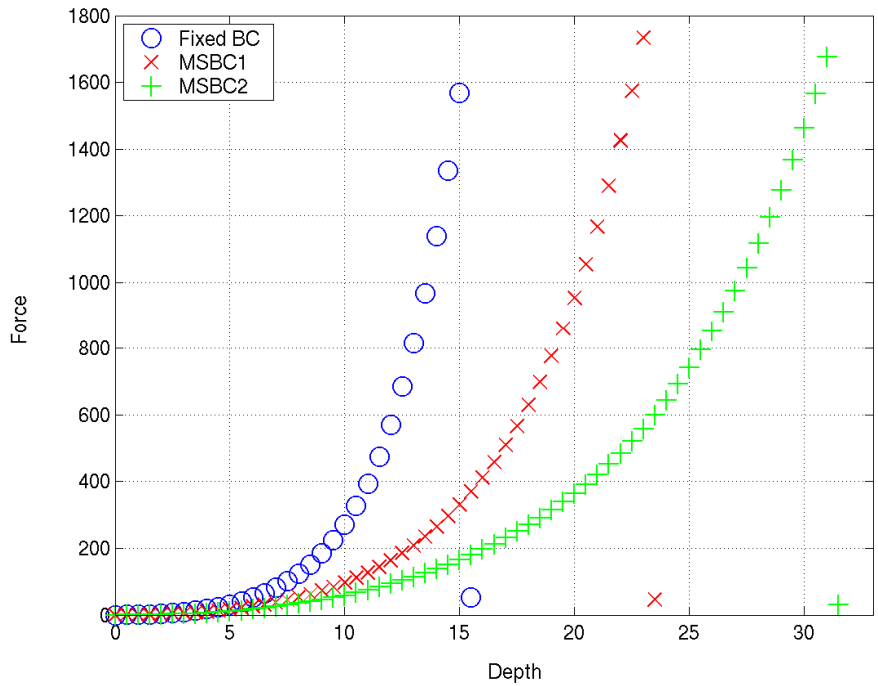
Domain is reduced in the all directions,
MSBCs applied to the lateral sides and to the bottom layer.





R=40A, DRPs: $a_{lateral}$ = 10; a_{bottom} = 4 (corresponds to 6 graphene layers);
Reduced domain size (7 layers) - 18,522 atoms, Full domain size (13 layers) – 70,200 atoms.
Size of the reduced domain is almost 4 times smaller.

Graphite: Large Domains.



R=40A, Domain size (13 layers) – 70,200 atoms.

MSBC1- DRPs: $a_{lateral} = 30$, $a_{bottom} = 6$ (corresponds to 10 graphene layers);
Full domain size (23 layers) – 480,378 atoms.

MSBC2- DRPs: $a_{lateral} = 50$, $a_{bottom} = 20$ (corresponds to 38 graphene layers);
Full domain size (51 layer) – 1,909,746 atoms.
The domain reduction is almost 30 times.

Time Scale Issues

- MD simulations have to follow high frequency vibrations of individual atoms (atomic mass is too small, the frequency is too high)

- Time scales accessible through direct MD simulations stay well below 1 microsecond (typically on the order of nanoseconds)

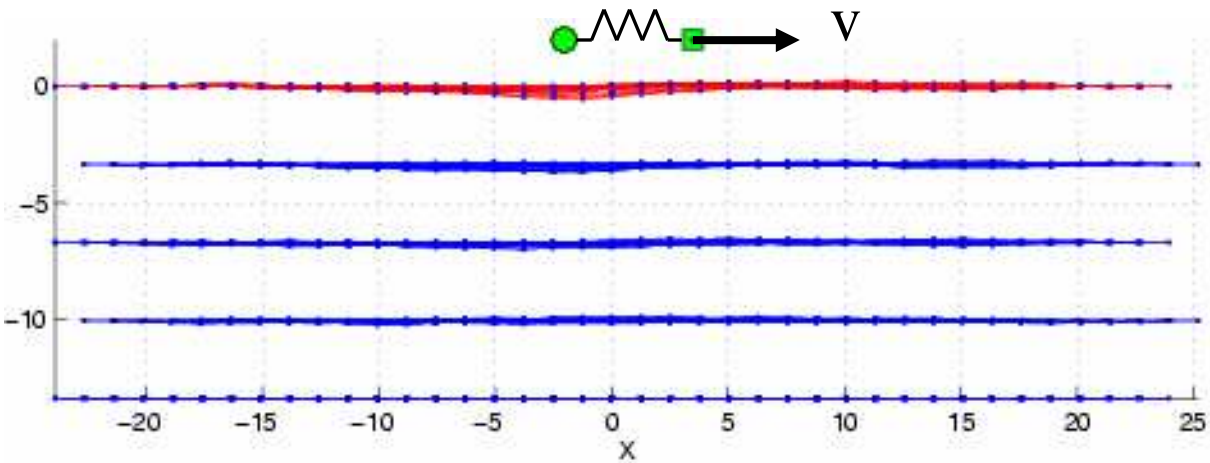
- Short time scales result in unrealistically high loading velocities and strain rates (on the order of 1 m/s), which may affect the modeled mechanical behavior of nano-mechanical systems

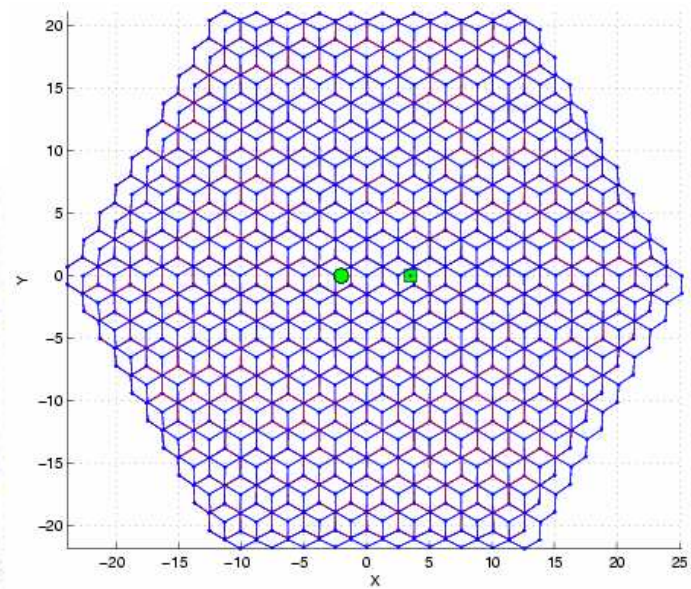
- Massively parallel computers helped to extend the computational domain *size* (using spatial domain decomposition), but had little impact on extending the *time* scales (temporal evolution is sequential)

Different techniques have been used, such as multiple time steps, accelerated dynamics (AD), coarse-graining (imposing constraints), etc.

However, the problem is not resolved in general.

MD simulations of atomic-scale friction





Model: 5 layers of graphite, TB potential for in-layer interactions, LJ for inter-layer and tip-substrate interactions.

Total 3,000 atoms. Scanning velocity V = 10 m/s. Scan for 4 lattice spacings. Takes 1 hour to compute.

Typical time step of MD is around 1 femtosecond (10^{-15} second).

Scanning velocity in actual AFM experiments is on the order of **microns** per second.

To model the same experiment with V=1 micron/s will take **10^7 hours -**

1,140 years!

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