Limitations of MD: Small time- and length-scales

Number of atoms $\sim (\text{size of the system})^3$

Computational cost $\sim (\text{number of atoms})^n$

$n > 1$
Direct MD simulations is nanostructured materials

(1) MD simulations of individual structural elements (nanofibers, nanoparticles, interfacial regions, grain boundaries, etc.) → difficult to predict macroscopic properties of nanomaterials

(2) Direct large-scale MD simulations of nanomaterials. Nanocrystalline materials - system with tens of nanograins (~$10^6$-$10^8$ atoms) can be simulated and the effective properties can be investigated, particularly in the regime of ultrafast mechanical loading (e.g. shock wave) or heating (e.g. by short laser pulse).
Direct MD simulations is nanostructured materials

Nucleation, growth, and coalescence of voids in dynamic failure in nanocrystalline Cu subjected to shock pulse loading.

Bridging the gap: The need for mesoscopic models

D. Qian et al., APL 76, 2868 (2000)

Hennrich et al., PCCP 4, 2273 (2002)

Phani et al., Acta Mater. 59, 2172 (2011)

Dislocation structures

CNT materials and CNT-polymer matrix nanocomposites
Bridging the gap: The need for mesoscopic models

Examples of mesoscopic models:

- **Dislocation Dynamics** for early stages of plastic deformation
- **Mesoscopic methods for evolution of grain structure** in polycrystalline materials (e.g. phase field models, cellular automata, kinetic Monte Carlo Potts models)
- **Coarse-grained models** for molecular and biomolecular systems
- **Mesoscopic models for carbon nanotubes and nanofibrous materials**
General Strategy for Mesoscopic Modeling

1. identifying the collective degrees of freedom relevant for the phenomenon under study,

2. designing a mesoscopic force field that governs the dynamics of the collective degrees of freedom (from experiments and/or atomic-level simulations),

3. adding a set of rules describing changes in the properties of the dynamic elements in response to the external conditions.

Ellipsoids in a sheared suspension
http://math.nist.gov/mcsd/savg/parallel/dpd/

Polymer matrix carbon nanotube composite
Phys. Rev. B 71, 165417, 2005
Structure and properties of carbon nanotube materials ("buckypaper")

Structure of carbon nanotube (CNT) films and mats:
Continuous network of interconnected CNT bundles

AFM image of buckypaper [Wang et al., *Composites A* 35, 1225, 2004]

array of “all-tube” flexible transparent thin-film transistors on a plastic substrate

SEM micrograph
A. Thess et al., Science 273, 483, 1996

flexible, stretchable, transparent CNT thin film loudspeakers [Xiao et al., *Nano Lett.* 8, 4539, 2008]

enhancement of mechanical properties of polymer matrix composites prepared by infiltration into buckypaper [Tai et al., *Carbon* 42, 2774, 2004]
Shape-based mesoscopic dynamic model for carbon nanotubes

Nanotubes are represented as chains of stretchable cylindrical segments


Independent dynamic variables (degrees of freedom): \( \mathbf{X} = \left( \vec{r}_i^t, \vec{r}_k^m, R_i^t, R_k^m, \theta_i^t \right) \)

Equations of motion:

\[
\mathbf{M} \frac{d^2 \mathbf{X}}{dt^2} = - \frac{\partial U}{\partial \mathbf{X}} + \mathbf{F}_d
\]

Translational motion

\[
C \frac{dT}{dt} = Q_{T_i} + Q_{T_c} + Q_{T_d}
\]

Internal state of CNTs

\[
\mathbf{U} = \mathbf{U}_{T \text{ (int)}} + \mathbf{U}_{T - T} + \mathbf{U}_{M \text{ (int)}} + \mathbf{U}_{M - M \text{ (non-bonded)}} + \mathbf{U}_{M - T}
\]

- Internal CNT modes
- CNT-CNT interactions
- Internal matrix modes
- Inter-molecular interactions
- CNT-matrix interactions
Mesoscopic model: Basic features

The mesoscopic model is parameterized based on the results of atomistic simulations and experimental data. It accounts for:

- Internal stretching and bending of CNTs [Phys. Rev. B 71, 165417, 2005]
- Axial and bending buckling of CNTs [ACS Nano 4, 6187, 2010]
- Van der Waals inter-tube interactions [J. Phys. Chem. C 114, 5513, 2010]
- Intrinsic thermal conductivity of CNTs [Int. J. Heat Mass Transfer 70, 954, 2014]
Spontaneous formation of bundles in a thin CNT film

Color of nanotubes corresponds to their local inter-tube interaction energy

500 × 500 × 20 nm³ sample, density 0.2 g/cm³, ~1500 (10,10) CNTs of 200 nm length

Periodic boundary conditions in the plane of the film
Structure of CNT network materials: Comparison to experimental data

**Simulation**
(color corresponds to the bundle thickness)

**Experiment**
[S. Wang et al., Nanotechnology 12, 095708, 2007]

- Diameter of bundles: 3 nm - 15 nm
- Buckypaper produced in a simulation
  - $500 \times 500 \times 100 \text{ nm}^3$
- SEM micrograph of the surface of buckypaper
  - 500 nm

- Diameter of bundles: 2 nm - 20 nm
Structure of CNT network materials: Comparison to experimental data

Simulated network structure (color corresponds to the bundle thickness)

Experiment [S. Wang et al., Nanotechnology 12, 095708 2007]
Hexagonal arrangement of CNTs in a bundle

Cross-section of a bundle

Simulation

SEM micrograph

[A. Thess et al., Science 273, 483, 1996]
Structure of CNT “forests” (vertically-aligned CNT arrays)

Futaba et al., Nat. Mater. 5, 987, 2006

density 0.02 g/cm³; SWCNT diameter 1.36 nm

density 0.029 g/cm³; SWCNT diameter 2.8 nm
Thermal conductivity of CNT network materials

\[ k = \frac{L \times Q}{T_1 - T_2} \]

\[ k_{\text{network}} \propto L_T^{2.2} \]
\[ k_{xx} \text{ network} \propto L_T^{2} \]
\[ k_{xx} \text{ film} \propto L_T^{2} \]
\[ k_{zz} \propto L_T^{0.59} \]

\[ k_{3D} \propto L_T^{2} \]

**References:**

High-velocity impact of a spherical projectile on a free-standing CNT film

Diameter of the sphere: 100 nm
Initial velocity: 1000 m/s
Film thickness: 20 nm
Film density 0.2 g/cm$^3$
Nanotubes are colored by their local kinetic energy
Ejection and transport of CNTs in MAPLE

MAPLE target is loaded with 150 nm long CNTs at concentration of 17 wt.%

CNTs form a continuous network of bundles

~20 millions of matrix molecules + more than 1000 of CNTs

large tangles of CNT bundles are torn out from the continuous network of bundles and are ejected with the matrix plume

no significant splitting and thinning of bundles

mass of the ejected CNT agglomerates (network fragments) exceeds 50 MDa

nanotubes are shown as red cylinders, matrix molecules are shown as small gray dots

Summary on mesoscopic modeling of CNT materials

Realistic representation of structural self-organization in CNT network materials

Broad range of potential future applications of the model:
  fracture, impact resistance, gas/fluid permeability, nanocomposites ....

PCCP 6, 3540, 2004
Dislocation Dynamics: Basic ideas

Dislocations: Long-range (1/r) elastic strain field (90% of the energy) + inelastic core (~10% of the energy).

Long-range (1/r) interactions + large number of local reactions = complex non-linear behavior.

Basic idea of Dislocation Dynamics: Solve the dynamics of dislocation lines in elastic continuum and include information about reactions. It was first developed for 2D simulations of infinite parallel dislocations [Lépinoux and Kubin, Scripta Met. 21, 833 (1987)] and then expanded to 3D systems [Kubin et al., Solid State Phenomena 23-24, 455 (1992)].

Dislocation Dynamics: Space discretization

Space discretization. An elastic continuum is grided with grid parameter that is larger than the distance of spontaneous annihilation of two edge dislocations (e.g. ~1.6 nm for Cu).

Discretization of the dislocation line curvature. One of the methods proposed by Brown, Phil. Mag. 10, 441 (1964), is to approximate dislocation line by a chain of connected dislocation segments. In a simple formulation the dislocation line can be represented by “edge-screw” model where only two types of dislocation segments are allowed.

New segments are introduced if two adjacent segments becomes too long (the curvature is too crudely described).

**Dislocation Dynamics: Calculation of forces**

**External Force.** Constant Peach - Koehler force due to the applied external stress.

**Dislocation – dislocation interaction.** Calculated as sum of all Peach–Koehler forces between the segments of all other dislocations in the system.

**Self force.** Interaction between segments of the same dislocation, “line tension” force.

**Peierls force.** Constant force in the glide plane that is always directed against the dislocation motion. It is small for FCC metals but can be significant for BCC metals, semiconductors, ionic materials.

**Image force** due to the finite size of the simulated system. This contribution result from the stress relaxation in the vicinity of free surface or internal surface.

**Obstacle force** due to the interaction with lattice defects other than dislocations.
Dislocation Dynamics: Equations of motion (I)

Different methods has been proposed for description of dislocation motion.

If the thermally activated nature of dislocations glide is important (e.g. screw dislocations in BCC metals) a temperature dependent velocity law is used. Dislocations move in a discontinuous manner with a succession of waiting and flying times. If the waiting time is dominant, the effective dislocation velocity follows Arrhenius law:

\[ v = A \left( \frac{\tau^*}{\tau_0} \right)^m \exp \left( - \frac{\Delta U}{kT} \right) \]

where \( \Delta U \) is the activation energy for dislocation motion, \( \tau^* \) is effective shear stress on a dislocation, \( \tau_0 \) is a stress normalization constant, \( m \) is the stress exponent parameter.
Dislocation Dynamics: Equations of motion (II)

If the flying time is dominant, the velocity of the segments is taken to be proportional to the force (viscous drag).

\[ v = \tau^* \frac{b}{B} \]

where B is a constant drag coefficient.

Starting from an initial set of segments coordinates at time t, the segment positions at time \( t + \Delta t \) can be calculated as

\[ r(t + \Delta t) = r(t) + \Delta v(t) \]

The solution of this equation cannot be exactly reproduced in the case of discrete displacements on the grid. The equation is solved in real space but the effective displacement of a segment takes place only when the true displacement of the segment is larger than the elementary translation vector on the grid in the glide direction.

Choice of the time step is defined by the dislocation velocity and by the mean gliding distance between two dislocation reactions.
Dislocation Dynamics: short range interactions and cross-slip

Dislocation – dislocation short-range interactions

Short-range dislocation reactions are very important, they control yield stress and work hardening. Two types of reactions can be distinguished, coplanar reactions of dislocations that belong to the same glide plane and non-coplanar reactions of dislocations in non parallel glide planes. Detailed analysis of dislocation reactions is important but is beyond this short review.

Dislocation cross-slip

Cross-slip gives the possibility for a screw dislocation to leave its glide plane in order to avoid obstacle and to relax internal stresses. It also allows a screw dislocation to change its glide plane and to annihilate with another “attractive” dislocation (dislocation density recovery at room $T$). Cross-slip is thermally activated process and is sometimes reproduced using Monte Carlo approach.
Dislocation Dynamics: Example - Frank-Read source

One of the main mechanisms for dislocation multiplication under stress is the Frank-Read mill or Frank-Read source. The operation of a Frank-Read source can be observed on a dislocation segment pinned at its ends.

A nice collection of animations from dislocation dynamics simulations can be found at http://zig.onera.fr/DisGallery/
Dislocation Dynamics: Example – plastic deformation

Dislocation dynamics during deformation of an FCC single crystal (Cu) of linear dimension 15 micrometers.

http://zig.onera.fr/DisGallery/
Dislocation Dynamics: Example - dislocation networks in relaxed quantum-dot structures

The cone or pyramid-like island structures grow epitaxially on semiconductor surface and, because of their high strain fields, become dislocated above a certain size. The picture at right shows dislocation patterns observed in a CoSi$_2$ island growing on a (111) silicon surface, compared to the numerical simulations.

http://www.research.ibm.com/dislocationdynamics/
Dislocation dynamics simulations of plastic deformation of bcc molybdenum demonstrated that interactions among three dislocations result in the formation of multi-junctions. Multi-junctions present nearly indestructible obstacles to dislocation motion and can act as Frank-Read sources of dislocation multiplication. As a result, they play an important role in the strength evolution (strain hardening).

Near the yield strain (0.2%), dislocations multiply and their collisions produce the first few multi-junctions (shown by white color) (b). Continued dislocation multiplication results in increasingly frequent dislocation collisions leading to strain hardening and growth of the sub-network of multi-junctions (c, d).
Dislocation Dynamics: Example - dislocation multi-junctions and strain hardening

Intersection of two dislocations leads to the formation of dislocation junction (a, b), which can unzip under stress (c). \[ \frac{1}{2} [\overline{1} 1 1] + \frac{1}{2} [1 \overline{1} 1] = [001] \quad \vec{b}_1^2 + \vec{b}_2^2 / (\vec{b}_1 + \vec{b}_2)^2 = 1.5 \]

The interaction among three dislocations can form a long multi-junction (d, e), which can act as a Frank–Read source.

\[ \vec{b}_1^2 + \vec{b}_2^2 + \vec{b}_3^2 / (\vec{b}_1 + \vec{b}_2 + \vec{b}_3)^2 = 3 \quad \frac{1}{2} [\overline{1} 1 1] + \frac{1}{2} [1 \overline{1} 1] + \frac{1}{2} [1 1 \overline{1}] = \frac{1}{2} [1 1 1] \]
The role of multi-junction in plastic deformation of bcc metals is “confirmed” in atomistic simulations and experiments.

A multi-junction formed in an atomistic simulation.

TEM micrograph of molybdenum single crystal containing a symmetric 4-node. The length of the scale bar is 0.2 μm.
General strategy for design of dynamic mesoscopic models

- identifying the collective degrees of freedom that are relevant for the phenomenon under study,

- designing a mesoscopic force field that governs the dynamics of the collective degrees of freedom (from experiments and/or atomic-level simulations),

- adding a set of rules describing changes in the properties of the dynamic elements in response to the external conditions (e.g. thermal degradation of mechanical properties) and energy exchange with the degrees of freedom that are not explicitly represented.

predictive power of a mesoscopic model relies on incorporation of all the relevant “physics” and “chemistry” into the model
Summary

The role of computer modeling – to provide a bridge between the basic physics, chemistry, thermodynamics laws and complex behavior/properties of real materials.

There are no universal computational model that would cover all the materials science phenomena at all time- and length-scales - different models should be used/combined.

Atomistic – Mesoscopic – Continuum models

Practical steps in any computer simulation

Choose an appropriate mathematical model
Choose a mathematical algorithm that can solve the equations
Implementing the algorithm in a computer code
Perform simulations, analyze the results

Basic ideas of MD, Metropolis and kinetic MC