Introduction to Modeling and Simulation

Part II - lecture 4

Atomistic and molecular methods
Content overview

I. Continuum methods
1. Discrete modeling of simple physical systems:
   Equilibrium, Dynamic, Eigenvalue problems
2. Continuum modeling approaches, Weighted residual (Galerkin) methods,
   Variational formulations
3. Linear elasticity: Review of basic equations,
   Weak formulation: the principle of virtual work,
   Numerical discretization: the finite element method

II. Atomistic and molecular methods
1. Introduction to molecular dynamics
2. Basic statistical mechanics, molecular dynamics, Monte Carlo
3. Interatomic potentials
4. Visualization, examples
5. Thermodynamics as bridge between the scales
6. Mechanical properties – how things fail
7. Multi-scale modeling
8. Biological systems (simulation in biophysics) – how proteins work and
   how to model them

III. Quantum mechanical methods
1. It’s A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?
Overview: Material covered

- **Lecture 1: Introduction to atomistic modeling** (multi-scale modeling paradigm, difference between continuum and atomistic approach, case study: diffusion)

- **Lecture 2: Basic statistical mechanics** (property calculation: microscopic states vs. macroscopic properties, ensembles, probability density and partition function, solution techniques: Monte Carlo and molecular dynamics)

- **Lecture 3: Basic molecular dynamics** (advanced property calculation, chemical interactions)

- **Lecture 4: Interatomic potential and force field** (pair potentials, fitting procedure, force calculation, multi-body potentials-metals/EAM & applications, neighbor lists, periodic BCs, how to apply BCs)

- **Lecture 5: Interatomic potential and force field (cont’d)** (organic force fields, bond order force fields-chemical reactions, additional algorithms (NVT, NpT), application: mechanical properties – basic introduction, Cauchy-Born rule as link between chemistry and mechanics – impose deformation field)

- **Lecture 6: Application to mechanics of materials-ductile materials** (significance of fractures/flaws, brittle versus ductile behavior [motivating example], basic deformation mechanisms (cracking, dislocations), modeling approaches: metals-EAM, brittle-pair potential/ReaxFF (silicon))

- **Lecture 7: Application to mechanics of materials-brittle materials**; case study: supersonic fracture (example for model building); case study: fracture of silicon (hybrid model)

- **Lecture 8: Review session**

- **Lecture 9: QUIZ**
Important dates

- **Problem set 1:**
  handout: March 31, due Monday April 7

- **Problem set 2:**
  handout: Monday April 7, due Monday April 14

- **Review lecture:** Tuesday April 15

- **Quiz:** Thursday April 17
II. Atomistic and molecular methods

Lecture 4: Interatomic potential and force field

Outline:
1. MD algorithm - overview
2. How to model chemical interactions
   2.1 Pair potentials & how to define a pair potential
   2.2 Multi-body potentials-metals/EAM & applications
   2.3 Bookkeeping matters: neighbor lists, periodic BCs, how to apply BCs

Goal of today’s lecture:
- How to model chemical interactions in MD and how to develop the models (parameter determination)
- How to model crystalline materials, in particular metals
- How to implement force calculation in a MD code (algorithm, bookkeeping, efficient approaches)
1. MD algorithm - overview
Molecular dynamics: A “bold” idea

Generate new positions

\[ \vec{r}_i(t_0 + \Delta t) = -\vec{r}_i(t_0 - \Delta t) + 2\vec{r}_i(t_0)\Delta t + \vec{a}_i(t_0)(\Delta t)^2 + \ldots \]

Positions at \( t_0-\Delta t \)

Positions at \( t_0 \)

Accelerations at \( t_0 \)

Based on atomic accelerations, which can be obtained from interatomic forces

\[ \vec{a}_i = \frac{\vec{f}_i}{m_i} \]

Forces between atoms… how to obtain?
Recall: what we need for MD

- **Initial positions** of atoms (e.g. crystal structure)
- **Initial velocities** (assign random velocities according to a distribution of velocities, e.g. Maxwell-Boltzmann distribution, so that it corresponds to a certain temperature)
- **Time stepping method** (e.g. Verlet central difference method)

- **Model for chemical bonds**
  (potentials or force fields, to be covered today)
2. How to model chemical interactions

**Concept:** Define energy landscape of chemical interactions, then take spatial derivatives to obtain forces, to be used in MD algorithm
**Atomic scale – how atoms interact**

- Atoms are composed of electrons, protons, and neutrons. Electron and protons are negative and positive charges of the same magnitude, with $1.6 \times 10^{-19}$ Coulombs.
- Chemical bonds between atoms by interactions of the electrons of different atoms.
- Distribution of electrons is described by “orbitals”.

Figure by MIT OpenCourseWare.
Atomic interactions – quantum perspective

Density distribution of electrons around a H-H molecule

How electrons from different atoms interact defines nature of chemical bond

Images remove due to copyright restrictions. Please see http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma/index.html

Much more about it in part III

http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma/index.html
Concept: Repulsion and attraction

Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)
Generic shape of interatomic potential

Many chemical bonds show this generic behavior

**Attraction:** Formation of chemical bond by sharing of electrons

**Repulsion:** Pauli exclusion (too many electrons in small volume)
Atomic interactions – different types of chemical bonds

- **Primary bonds (“strong”)**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver)  
    (high melting point, 1000-5,000K)

- **Secondary bonds (“weak”)**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)  
    (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

*Difference of material properties originates from different atomic interactions*
Wax

Soft, deformable, does not break under deformation

Rocks

Image courtesy of Wikimedia Commons.
Rocks and sand on Mars

Image courtesy of NASA.
Gold

Image courtesy of Wikimedia Commons.
Silicon

Image courtesy of NASA.
Spider web

Image courtesy of U.S. Fish and Wildlife Service.
Tree’s leaf

Image courtesy of Wikimedia Commons.
2.1 Pair potentials & how to define a pair potential
Models for atomic interactions: pair potential

- Atom-atom interactions are necessary to compute the forces and accelerations at each MD time integration step: Update to new positions!

- Usually define interatomic potentials, that describe the energy of a set of atoms as a function of their coordinates:

\[
U_{total} = U_{total}(r)
\]

\[
F_i = -\nabla_{\vec{r}_i} U_{total}(r) \quad i = 1..N
\]

\[
\nabla_{\vec{r}_i} = \left( \frac{\partial}{\partial r_{1,i}}, \frac{\partial}{\partial r_{2,i}}, \frac{\partial}{\partial r_{3,i}} \right)
\]

Change of potential energy due to change of position of particle \(i\) (“gradient”)
Pair potentials: energy calculation

Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system

\[ U_{total} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij}) \]

Pair wise interaction potential

Energy of atom \( i \)

\[ U_i = \sum_{j=1}^{N} \phi(r_{ij}) \]

Pair wise summation of bond energies

Avoid double counting

\( r_{ij} \) = distance between particles \( i \) and \( j \)
Interatomic pair potentials: examples

\[ \phi(r_{ij}) = D \exp\left(-2\alpha(r_{ij} - r_0)\right) - 2D \exp\left(-\alpha(r_{ij} - r_0)\right) \]  
Morse potential

\[ \phi(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \]  
Lennard-Jones 12:6 potential  
(excellent model for noble Gases, Ar, Ne, Xe..)

\[ \phi(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\sigma}\right) - C \left( \frac{\sigma}{r_{ij}} \right)^6 \]  
Buckingham potential

\[ \phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij} - r_0)^2 \]  
Harmonic approximation
Lennard-Jones potential: schematic

\[ \phi (r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]

\( \varepsilon \): well depth (energy per bond)

\( \sigma \): force vanishes (EQ distance between atoms)

Sir J. E. Lennard-Jones (Cambridge UK)
Lennard-Jones potential – example for copper

LJ potential – parameters for copper (Cleri et al., 1997)
Atomic-Scale Mechanism of Crack-Tip Plasticity: Dislocation Nucleation and Crack-Tip Shielding

Fabrizio Cleri,1,2 Sidney Yip,3 Dieter Wolf,1 and Simon R. Phillpot1
1Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
2Divisone Materiali Avanzati, ENEA, Centro Ricerche Casaccia, 00100 Roma A.D., Italy
3Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 14 April 1997)

By isolating the process of dislocation emission from a crack tip under an applied tensile stress, we extract from a molecular dynamics simulation the atomic-level displacement and stress fields on the activated slip plane before and after the nucleation event. The stress-displacement relations so obtained provide a direct link with recent continuum descriptions of brittle versus ductile behavior in crack propagation. Crack-tip shielding by the emitted dislocations is demonstrated, as is the role of surface steps in dislocation nucleation and crack-tip blunting. [S0031-9007(97)03869-6]

PACS numbers: 61.72.Lk, 61.72.Na, 62.20.Fe, 62.20.Mk

Paper posted on MIT Server
Force calculation – pair potential

Forces can be calculated by taking derivatives from the potential function

**Force magnitude:** Negative derivative of potential energy with respect to atomic distance

\[ F = -\frac{d\phi(r_{ij})}{dr_{ij}} \]

To obtain force vector \( F_i \), take projections into the three axial directions

\[ f_i = F \frac{x_i}{r_{ij}} \]

\[ r_{ij} = |\vec{r}_{ij}| \]
Derivative of LJ potential ~ force

Image removed due to copyright restrictions.
Please see Fig. 2.14 in Buehler, Markus J. Atomistic Modeling of Materials Failure. New York, NY: Springer, 2008.
Properties of LJ potential

Equilibrium distance between atoms $r_0$ and maximum force

$$\sigma^6\sqrt{2} = r_0$$

$$F_{\text{max,LJ}} = \frac{2.394\varepsilon}{\sigma}$$

- First derivative zero (force)
- Second derivative zero (=loss of convexity, spring constant=0)

$r_0 = \text{distance of nearest neighbors in a lattice}$
Determination of parameters for atomistic interactions

- Often, parameters are determined so that the interatomic potential reproduces experimental results / quantum mechanical results (part III)

- **Example** (based on elastic properties):

$$
\phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
$$

Calculate $K$ as a function of $\varepsilon$ and $\sigma$ (for LJ potential):

$$
K = 64\varepsilon / \sigma^3
$$

Then find two (or more) properties (experimental, for example), that can be used to fit the LJ parameters (e.g. Young's modulus $E = 120$ GPa)

**This concept is called potential or force field fitting (training)**
Provides quantitative link from quantum mechanics / experiment to MD model
Bending a copper wire until it breaks
A closer look

http://www2.ijs.si/~goran/sd96/e6sem1y.gif

Courtesy of Goran Drazic. Used with permission.
A simulation with 1,000,000,000 particles
Lennard-Jones - copper

Image removed due to copyright restrictions.
### Morse Potential Parameters for 16 Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\alpha a_0$</th>
<th>$\beta$</th>
<th>$L \times 10^{-22}$ (eV)</th>
<th>$\alpha$ (A$^{-1}$)</th>
<th>$r_0$ (A)</th>
<th>$D$ (eV)</th>
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<td>Pb</td>
<td>2.921</td>
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<td>1.399</td>
<td>0.42981</td>
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</table>


The Morse potential is given by:

$$\phi(r_{ij}) = D \exp\left(-2\alpha(r_{ij} - r_0)\right) - 2D \exp\left(-\alpha(r_{ij} - r_0)\right)$$
Cutoff radius

\[ U_i = \sum_{j=1}^{N} \phi(r_{ij}) \]

Cutoff radius = considering interactions only to a certain distance

Basis: Force contribution negligible (slope)
Derivative of LJ potential $\sim$ force

Beyond cutoff: Changes in energy (and thus forces) small
Crystal structure and potential

- The regular packing (ordering) of atoms into crystals is closely related to the potential details.
- Many **local minima** for crystal structures exist, but materials tend to go to the structure that minimizes the energy; often this can be understood in terms of the energy per atomic bond and the equilibrium distance (at which a bond features the most potential energy).

### 2D example

- **N=4 bonds**
- **N=6 bonds per atom**

**Square lattice**

**Hexagonal lattice**
Example

Initial: cubic lattice  
Transforms into triangular lattice

http://polymer.bu.edu/java/java/LJ/index.html
Face centered cubic (FCC), body centered cubic (BCC)

- **Aluminum**, NN: 2.863 Å ($a_0=4.04$ Å)
- **Copper**, NN: 2.556 Å ($a_0=3.615$ Å)
- **Chromium**, NN: 2.498 Å ($a_0=2.91$ Å)
- **Iron**, NN: 2.482 Å ($a_0=2.86$ Å)

Image from Wikimedia Commons, [http://commons.wikimedia.org](http://commons.wikimedia.org)

Hexagonal closed packed (HCP)

**Cobalt**
- $a$: 250.71 pm
- $b$: 250.71 pm
- $c$: 406.95 pm
- $\alpha$: 90.000°
- $\beta$: 90.000°
- $\gamma$: 120.000°
- NN: 2.506 Å

**Zinc**
- $a$: 266.49 pm
- $b$: 266.49 pm
- $c$: 494.68 pm
- $\alpha$: 90.000°
- $\beta$: 90.000°
- $\gamma$: 120.000°
- NN: 2.665 Å

Figures by MIT OpenCourseWare.

Image courtesy of the U.S. Navy.
RDF and crystal structure

Peaks in RDF characterize NN distance, can infer from RDF about crystal structure

http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html
Graphene/carbon nanotubes

NN: 1.42 Å, second NN 2.46 Å …
MD updating scheme: Complete

(1) Updating method (integration scheme)

\[ r_i(t_0 + \Delta t) = -r_i(t_0 - \Delta t) + 2r_i(t_0)\Delta t + a_i(t_0)(\Delta t)^2 + \ldots \]

(2) Obtain accelerations from forces

\[ f_i = ma_i \quad a_i = f_i / m \]

(3) Obtain forces from potential

\[ F = -\frac{d\phi(r)}{dr} \quad f_i = F \frac{x_i}{r} \]

Potential

\[ \phi(r) = 4\varepsilon \left( \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^6 \right) \]

(5) Crystal (initial conditions)

“Verlet central difference method”
2.2 Multi-body potentials—metals/EAM & applications

**Pair potential**: Total energy sum of all pairs of bonds
Individual bond contribution does not depend on other atoms
“all bonds are the same”

\[ U_{\text{total}} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij}) \]

*Is this a good assumption?*
Are all bonds the same? - valency in hydrocarbons

All bonds are not the same!
Adding another $H$ is not favored

$\text{C}_2\text{H}_6$
Are all bonds the same? – metallic systems

Pair potentials: All bonds are equal!

Reality: Have environment effects; it matter that there is a free surface!

Bonds in a molecular structure depend on the environment!
Are all bonds the same?

Bonding energy of red atom in \[ \begin{array}{c}
\includegraphics[width=1cm]{atom1}
\end{array} \] is six times bonding energy in \[ \begin{array}{c}
\includegraphics[width=1cm]{atom2}
\end{array} \]

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials.

For pair potentials \[ \sim Z \]

For metals \[ \sim \sqrt{Z} \]

Coordination = how many immediate neighbors an atom has.

Bonds get “weaker” as more atoms are added to central atom.
Bond strength depends on coordination

energy per bond

Nickel

\[ Z \sim \sqrt{Z} \]

Transferability of pair potentials

- Pair potentials have limited **transferability**:
  
  Parameters determined for molecules can not be used for crystals, parameters for specific types of crystals can not be used to describe range of crystal structures

- E.g. difference between FCC and BCC can not be captured using a pair potential

- Pair potentials can not capture certain elasticity coefficients, e.g. (Cauchy relation, violated in most real metals)

\[ C_{12} = C_{44} \]
Example: Metallic bonding

- Need to consider more details of chemical bonding to understand environmental effects

Delocalized valence electrons moving between nuclei generate a binding force to hold the atoms together: Electron gas model (*positive ions in a sea of electrons*)

Mostly non-directional bonding, but the bond strength indeed depends on the environment of an atom, precisely the electron density imposed by other atoms
Modeling attempt: Multi-body potential

- Multi-body potential depend on more than pairs of atoms, but instead also on the environment of each atom
- Important for metals due to existence of “electron gas”

\[ \phi_i = \sum_{j=1}^{N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \]

\[ \rho_i = \sum_{j=1}^{N_{\text{neigh}}} \pi(r_{ij}) \]

First proposed by Finnis, Sinclair, Daw, Baskes et al. (1980s)
Embedded-atom method (EAM)

\[ \phi_i = \sum_{j=1 \ldots N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \]

Pair potential energy

Embedding energy as a function of electron density

\( \rho_i \)  Electron density at atom \( i \) based on a pair potential:

\[ \rho_i = \sum_{j=1 \ldots N_{\text{neigh}}} \pi(r_{ij}) \]

Models other than EAM (alternatives):
- Glue model (Ercolessi, Tosatti, Parrinello)
- Finnis Sinclair
- Equivalent crystal models (Smith and Banerjee)
Embedding term: example

Embedding energy

$$\phi_i = \sum_{j=1\ldots N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i)$$

Pair potential energy

Embedding energy as a function of electron density

Figure by MIT OpenCourseWare.

Electron density

G (eV)

$\rho (\text{Å}^{-3})$
Pair potential term: example

\[ \phi_i = \sum_{j=1 \ldots N_{\text{neigh}}} \left( \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \right) \]

*Pair contribution*

![Graph showing the relationship between \( R (\text{Å}) \) and \( U (\text{eV}) \)](Figure by MIT OpenCourseWare.)

- Pair potential energy
- Embedding energy as a function of electron density
Effective pair interactions

Can describe differences between bulk and surface

Figure by MIT OpenCourseWare.
Fitting parameter/performance

Text removed due to copyright restrictions.
## Diffusion: Activation energies

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<thead>
<tr>
<th>System</th>
<th>EAM</th>
<th>Exp.</th>
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<tbody>
<tr>
<td>Ag in Cu</td>
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<td>2.02</td>
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<td>Au in Cu</td>
<td>1.88</td>
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<tr>
<td>Ni in Cu</td>
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<td>Pd in Cu</td>
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<td>Au in Pt</td>
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<td>Ag in Pt</td>
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Comparison EAM model vs. experiment

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<td>Ni</td>
<td>1740</td>
<td>1726</td>
</tr>
<tr>
<td>Pd</td>
<td>1390</td>
<td>1825</td>
</tr>
<tr>
<td>Pt</td>
<td>1480</td>
<td>2045</td>
</tr>
</tbody>
</table>

Melting point (in K)

Summary: EAM method

- State of the art approach to model metals
- Very good potentials available for Ni, Cu, Al since late 1990s, 2000s
- Numerically efficient, can treat billions of particles
- Not much more expensive than pair potential, but describes physics much better

- Recommended for use!
2.3 Bookkeeping matters: neighbor lists, periodic BCs, how to apply BCs
Algorithm of force calculation

for $i = 1 \ldots N$

for $j = 1 \ldots N (i \neq j)$
Force calculation for $N$ particles

- Requires two nested loops, first over all atoms, and then over all other atoms to determine the distance

for $i=1..N$:

  for $j=1..N$ ($i \neq j$):

    determine distance between $i$ and $j$

    calculate force and energy (if $r_{ij} < r_{\text{cut}}$, cutoff radius)

    add to total force vector / energy

**time** $\sim N^2$: *computational disaster*
Strategies for more efficient computation

Two approaches

1. **Neighbor lists:** Store information about atoms in vicinity, calculated in an $N^2$ effort, and keep information for 10..20 steps

2. **Domain decomposition into bins:** Decompose system into small bins; force calculation only between atoms in local neighboring bins
Neighbor lists

- Bookkeeping device often used in MD simulation is a **neighbor list**: keeps track of who are the nearest, second nearest, ... neighbors of each particle (arrays).

- Saves time from checking every particle in the system every time a force calculation is made.

- The list can be used for several time steps before updating (atoms move slowly).

- Each update is expensive since it involves $N \times N$ operations for an $N$-particle system.

In low-temperature solids where the particles do not move very much, it is possible to do an entire simulation without or with only a few updating, whereas in simulation of liquids, updating every 5 or 10 steps is quite common.
Domain decomposition into bins

- Divide into computational cells ("bins", "containers", etc.)
- Cell radius $R > R_{\text{cut}}$ (cutoff)
- Search for neighbors within cell atom belongs to and neighboring cells (8+1 in 2D)
- Most classical MD potentials/force fields have finite range interactions
- Bin re-distribution only necessary every 20..30 integration steps (parameter)
Numerical implementation of multi-body EAM potential

- Requires two loops over atoms within each cell

**Loop 1:**

(i) Pair contributions (derivatives and potential)

(ii) Calculate electron density

**Loop 2:**

(iii) Calculate embedding function and derivatives

\[ F_i = - \sum_{j \neq i} \left( \phi'(r_{ij}) + [U'(n_i) + U'(n_j)]\rho'(r_{ij}) \right) \frac{r_{ij}}{r_{ij}} \]

---

Due to additional (i) calculation of electron density and (ii) embedding contribution EAM potentials are 2-3 times slower than pure pair potentials.
Periodic boundary conditions

- **Periodic boundary conditions** allows studying bulk properties (no free surfaces) with small number of particles (*here: \(N=3\)), all particles are “connected”
  - Original cell surrounded by 26 image cells; image particles move in exactly the same way as original particles (8 in 2D)

Particle leaving box enters on other side with same velocity vector.

Figure by MIT OpenCourseWare. After Buehler.
Periodic boundary conditions

JAVA script - example

http://polymer.bu.edu/java/java/LJ/index.html
How to apply BCs: displacement
Domain decomposition

**Example:** Stretching of a metal nanowire

Modify Verlet integration method, boundary atoms do not move to dynamical equations but are displaced according to prescribed boundary condition (e.g. fixed displacement rate)

simulate tensile test

group of atoms that does **NOT** follow \( F=ma \)
Instron testing - macroscale

Image removed due to copyright restrictions.

Photograph of instron testing apparatus.