2011 NCN Summer School

Part II: Molecular Dynamics simulations of materials

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What is molecular dynamics?

Follow the dynamics (motion) of all the atoms in your material.

Numerically solve classical equations of motion (Newton’s):

Approximation

\[ \vec{F}_i = m_i \ddot{\vec{r}}_i \quad \text{or} \quad \begin{cases} \dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \\ \dot{\vec{p}}_i = \vec{F}_i \end{cases} \]

Forces on atoms come from the interaction with other atoms:

\[ \vec{F}_i = -\nabla_{\vec{r}_i} E(\{\vec{r}_j\}) \]

Total potential energy (from QM or interatomic potential) Approximated (in almost all cases)
Classical mechanics: Hamilton’s picture

William Hamilton reformulation of classical mechanics (1800’s)

Hamiltonian:

\[ H(\{r_i\}, \{p_i\}) = V(\{r_i(t)\}) + \sum_{i=1}^{3N} \frac{p_i(t)^2}{2m_i} \]

\( i \) denotes atom and Cartesian component (x, y, or z)

Equations of motion can be derived from the Hamiltonian:

\[ \dot{r}_i = \frac{\partial H}{\partial p_i} \]
\[ \dot{p}_i = -\frac{\partial H}{\partial r_i} \]

• These equations can only be solved analytically for very few cases
• MD solves the dynamics of many atoms (billions in supercomputers)
Let's calculate the time derivative of the Hamiltonian:

\[
\frac{dH}{dt} = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial r_i} \dot{r}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right)
\]

Using the equations of motion we get:

Other constants of motion are:

• Linear momentum:

• Angular momentum:
**Structure of a minimalist MD code**

1. **Initial conditions** 
   \[ [r_i(0), v_i(0)] \]

2. **Calculate forces at current time** 
   \[ [F_i(t)] \] from \( r_i(t) \)

3. **Integrate equations of motion**
   \[ r(t) \rightarrow r(t+\Delta t) \]
   \[ v(t) \rightarrow v(t+\Delta t) \]
   \[ t \rightarrow t+\Delta t \]

4. **Save properties**

5. **Done?**
   - **Y**: Output files
   - **No**: End
Analysis/interpretation of MD: statistical mechanics

Relate microscopic phenomena and macroscopic properties
• Given a thermodynamic state of a material, what are the probabilities of finding the system in the various possible microscopic states?
• Given a series of microscopic states, what is the corresponding macroscopic state?

Goal: describe concepts that enable relating molecular dynamics with macroscopic (thermo) properties
### Various important ensembles

<table>
<thead>
<tr>
<th>Microcanonical (NVE)</th>
<th>Canonical (NVT)</th>
<th>Isobaric/isothermal (NPT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P({r_i}, {p_i}) = \frac{1}{\Omega(E, V, N)}$</td>
<td>$P({r_i}, {p_i}) = e^{-\frac{H({r_i}, {p_i})}{kT}} Z(T, V, N)$</td>
<td>$P({r_i}, {p_i}, V) = e^{-\frac{1}{kT}[H({r_i}, {p_i}) - PV]} Z_p(T, P, N)$</td>
</tr>
<tr>
<td>$\Omega(E, V, N) = \sum V \delta(E - H({r_i}, {p_i}))$</td>
<td>$Z(T, V, N) = \sum \delta(E - H({r_i}, {p_i}))$</td>
<td>$Z_p(T, P, N) = \sum V \sum \delta(E - PV)$</td>
</tr>
<tr>
<td>$F(T, V, N) = -kT \log Z$</td>
<td>$G(T, P, N) = -kT \log Z_p$</td>
<td>(atomistic ↔ macroscopic thermodynamics)</td>
</tr>
</tbody>
</table>

- Free energies (atomistic ↔ macroscopic thermodynamics)
Consider a variable that appears squared in the Hamiltonian:

\[ H(\{r_i\}, \{p_i\}) = \lambda p_1^2 + V(\{r_i(t)\}) + \sum_{i=2}^{3N} \frac{p_i(t)^2}{2m_i} = \lambda p_1^2 + H' \]

\[ \langle \lambda p_1^2 \rangle = \frac{\int d^3N p \int d^3N p \lambda p_1^2 e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{\int d^3N p \int d^3N p e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}} = \frac{\int d^3N p \int d^{3N-1} p e^{-\frac{H'}{kT}}}{\int d^3N p \int d^{3N-1} p e^{-\frac{H'}{kT}}} \int dp_1 \lambda p_1^2 e^{-\frac{\lambda p_1^2}{kT}} \]

Change of variable:

\[ \frac{\lambda p_1^2}{kT} = x^2 \quad \text{and} \quad dp_1 = \frac{kT}{\lambda} dx \]

\[ \langle \lambda p_1^2 \rangle = \frac{(kT)^2}{\lambda} \int dx \ x^2 e^{-x^2} = \frac{1}{2} kT \]

**Equipartition of energy**: Any degree of freedom that appears squared in the Hamiltonian contributes \(1/2kT\) of energy
Equipartition of energy: MD temperature

\[ \langle K \rangle = \frac{3N}{2} kT \]

In most cases c.m. motion is set to zero at time zero (constant of motion → it remains zero)

\[ \langle K \rangle = \frac{3N - 3}{2} kT \]

Often angular momentun is zeroed (and remains zero)

\[ \langle K \rangle = \frac{3N - 6}{2} kT \]

Temperature is related to average kinetic energy. Instantaneous temperature:

\[ K(t) = \frac{N_{\text{eff}}}{2} kT(t) \]
Fluctuations from equilibrium are also related to materials properties

\[ \langle \delta A^2 \rangle = \frac{1}{\tau} \int_0^\tau [A(t) - \langle A \rangle]^2 dt = \langle A^2 \rangle - \langle A \rangle^2 \]

Specific heat:

\[ C_V = \left. \frac{\partial E}{\partial T} \right|_{NVT} \]

\[ \langle \delta H^2 \rangle_{NVT} = kT^2 C_V \]

Compressibility:

\[ \beta_V = \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_{NVT} \]

\[ \langle \delta V^2 \rangle_{NPT} = k\langle V \rangle T \beta_T \]
Quantum effects

When does classical mechanics for atoms stop working?

High temperature: atoms move around
Decrease temperature – atoms slow down
Zero temperature: atom at the bottom of the well

Temperature at which quantum effects kick in depends on frequency

\[ kT >> \hbar \omega \] Classical regime
\[ kT \sim< \hbar \omega \] Quantum regime
Integrating the equations of motion

\[
\ddot{r}_i = \frac{\dot{p}_i}{m_i}
\]

\[
\dot{p}_i = F_i
\]

**Verlet algorithm:** Taylor expansion of positions with time

\[
r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2} \ddot{r}_i(t)\Delta t^2 + \frac{1}{6} \dddot{r}_i(t)\Delta t^3 + O(\Delta t^4)
\]

\[
r_i(t - \Delta t) = r_i(t) - \dot{r}_i(t)\Delta t + \frac{1}{2} \ddot{r}_i(t)\Delta t^2 - \frac{1}{6} \dddot{r}_i(t)\Delta t^3 + O(\Delta t^4)
\]

Sum two equations:
**Verlet algorithm: various equivalent formulations**

**Velocity Verlet:**
\[
\begin{align*}
  p_i\left(t + \frac{1}{2}\Delta t\right) &= p_i(t) + \frac{1}{2} F_i(t) \Delta t \\
  r_i(t + \Delta t) &= r_i(t) + \frac{p_i\left(t + \frac{1}{2}\Delta t\right)}{m_i} \Delta t \\
  p_i(t + \Delta t) &= p_i\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2} F_i(t + \Delta t) \Delta t
\end{align*}
\]

Advance \( p \) half step

Advance \( r \) full step (with \( p \) half step ahead)

Advance \( p \) half step (with \( F \) at \( t + \Delta t \))

**Leap-Frog Verlet:**
\[
\begin{align*}
  r_i\left(t + \frac{1}{2}\Delta t\right) &= r_i\left(t - \frac{1}{2}\Delta t\right) + v_i(t) \Delta t \\
  v_i(t + \Delta t) &= v_i(t) + \frac{1}{m_i} F_i\left(t + \frac{1}{2}\Delta t\right)
\end{align*}
\]

Calculate force

Position:  \hspace{2cm} Velocity:  \hspace{2cm} time
Verlet algorithm: features and advantages

• Exactly time reversible
  • If velocities are reversed at a given time the algorithm traces back its steps
• Symplectic
  • Conserves volume in phase space (as Hamiltonian dynamics does)

• No long-term energy drifts
• The trajectory stays very close to the constant energy hypersurface in phase space

Remember:  \[ S = k \log \Omega(E, V, N) \]
How do we calculate atomic forces?

1. **Initial conditions**
   
   \[
   [r_i(0), v_i(0)]
   \]

2. **Calculate forces at current time**
   
   \[F_i(t)\] from \(r_i(t)\)

3. **Integrate equations of motion**
   
   \[
   \begin{align*}
   r(t) & \rightarrow r(t+\Delta t) \\
   v(t) & \rightarrow v(t+\Delta t) \\
   t & \rightarrow t+\Delta t
   \end{align*}
   \]

4. **Save properties**

5. **Done?**

   - **No**
     - 
   - **Y**
     - Output files
     - End
Pair-wise potentials

Simplest, non-trivial, function

\[ V(\{r_i\}) = \sum_{i < j} \phi(\|r_i - r_j\|) \]

Sum of pair-wise terms

Lennard-Jones (6-12)

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

Distance & energy

Exponential-6

\[ \phi_{\text{exp-6}}(r) = \varepsilon \left[ e^{-r} - Ar^{-6} \right] \]

Morse

\[ \phi_{\text{Morse}}(r) = \varepsilon \left[ \exp \left( \gamma \left( 1 - \frac{r}{r_0} \right) \right) - 2 \exp \left( \frac{\gamma}{2} \left( 1 - \frac{r}{r_0} \right) \right) \right] \]

Distance, energy, & curvature
Two-body potentials: limitations

- Only closed-packed structures (fcc, hcp)
- Vacancy formation ~ cohesive energy
- Metals: $\varepsilon_{\text{vac}} \sim \frac{1}{3} E_{\text{coh}}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Ecoh (eV)</th>
<th>Evac (eV)</th>
<th>Evac/Ecoh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.39</td>
<td>0.75</td>
<td>0.22</td>
</tr>
<tr>
<td>Ni</td>
<td>3.516</td>
<td>1.6</td>
<td>0.46</td>
</tr>
<tr>
<td>Cu</td>
<td>3.615</td>
<td>1.2</td>
<td>0.33</td>
</tr>
<tr>
<td>Ag</td>
<td>4.086</td>
<td>1.15</td>
<td>0.28</td>
</tr>
<tr>
<td>Pt</td>
<td>3.924</td>
<td>1.4</td>
<td>0.36</td>
</tr>
<tr>
<td>Au</td>
<td>4.079</td>
<td>0.95</td>
<td>0.23</td>
</tr>
</tbody>
</table>

- Two-body potentials and elastic constants: $c_{12} = c_{44}$
- Metals: $c_{12} > c_{44}$

- Pair potentials can only describe simple non-bond interactions
  - Closed-shell atoms (Ne, Ar, Kr, etc.)
  - Atoms that are fully coordinated (e.g. inter-molecular)

- Pauli repulsion at short distances
- London dispersion at longer distances  
  \{ van der Waals
Capturing many-body effects in metals

Embedded atom model (EAM)
Mike Baskes and collaborators 1980’s + other groups

\[ V = \sum_{i<j} \phi(r_{ij}) + \sum_i^N F(p_i) \]

Embedding energy

Local electronic density at the location of atom \( i \)

Accurate description of:
• Environment dependence of bonding in metals (vacancy and surfaces)
• Elastic constants and plastic deformation
• Phase transformations (melting & solid-solid)
• Alloys

Not very accurate for:
• Cases where bonding is highly directional
Directional bonding in semiconductors

Diamond, zincblende and wurtzite structures

Computer simulation of local order in condensed phases of silicon

Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)

\[ V(\{r_i\}) = \sum_{i<j} f_2(r_{ij}) + \sum_{i<j<k} f_3(r_i, r_j, r_k) \]

\[ f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases} \]

\[ f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \]

\[ h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \times (\cos \theta_{jik} + \frac{1}{3})^2 \]
Interatomic potentials for molecular materials

\[ V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) \]

\[ + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\}) \]

vdW interactions between bonded atoms:

Most molecular potentials use exclusions
No vdW for:
- Bonded atoms
- 1-3 (atoms separated by two covalent bonds)
- 1-4 (atoms separated by three covalent bonds)
Electrostatics & periodic boundary conditions

Coulomb interaction decays very slowly

\[ V_{elec} = C_{unit} \sum_{i<j} \frac{q_i q_j}{r_{ij}} \]

With periodic boundary conditions (infinite system):

• The Coulomb sum is conditionally convergent:
  • Result depends on the order of the summands
  • Result depends on charge arrangement on the surface

• Need to use special sum techniques and boundary conditions
  • Ewald method [part of the sum in real space and part in reciprocal Fourier space]
  • Particle-mesh Ewald and other techniques

Molecular materials

\[ V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\}) \]

Interaction between atoms separated by chemical bonds

Bond stretch:

\[ \phi_{\text{bond}}(r) = \begin{cases} \frac{1}{2} k_{ij} (r - r_{ij}^0)^2 & \text{Morse, } L - J \end{cases} \]

Angle bending:

\[ \phi_{\text{angle}}(\theta) = \begin{cases} \frac{1}{2} k_{ijk} (\theta - \theta_{ijk}^0)^2 \\ \frac{1}{2} \sin^2 \theta_{ijk}^0 \left[ \cos \theta - \cos \theta_{ijk}^0 \right]^2 \end{cases} \]
Covalent interactions

Torsion bending (dihedral angles)

\[ \phi_{torsions}(\varphi) = k_{ijkl} \left[ 1 - \cos(n_{jk} (\varphi - \varphi_{0}^j)) \right] \]

Ethylene (planar)

\[ \text{sp}^2 \text{ hybridization} \]
- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
  - Rotating around C-C bond breaks the PI bond

Ethane (staggered)

\[ \text{sp}^3 \text{ hybridization} \]
- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
  - Dominated by vdW between H
Atom types in molecular force fields

• Element alone is not enough to determine the interactions
  • E.g.: sp3 carbon and sp2 carbon behave differently

• In traditional molecular force fields the user specifies force field types to establish the character of the atom
  • Force field types & connectivities need to be determined prior to MD simulation
  • FF types and connectivities are kept fixed during run

Widely used force fields for molecular simulations:


**COMPASS**: 
Reactive force fields

No predetermined connectivities
Bond distance $\rightarrow$ bond order $\rightarrow$ bond energy

- Bond stretch, angle, & torsion terms depend on bond orders involved
  - E.g. distinguish between sp$^2$ and sp$^3$ carbon
- As a bond order goes to zero all terms involving also tend to zero
  - Bond orders are pre-factors for all covalent terms
- Over-coordination penalty
  - Limit the number of bonds an atom can make
Reactive force fields: key developments

- **Reactive Empirical Bond Order (REBO):**

- **AI-REBO:**

- **ReaxFF:**
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 $\Delta t$

2. Number of atoms that underwent collisions during $\Delta t$ is: $v\Delta t$ – 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)

Isothermal MD: Berendsen approach

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

\[
\begin{align*}
\dot{r}_i(t) &= \frac{p_i(t)}{m_i} \\
\dot{p}_i(t) &= F_i(t) - \gamma \rho(t)
\end{align*}
\]

**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

\[
\begin{align*}
\dot{r}_i(t) &= \frac{\vec{p}_i(t)}{m_i} \\
\dot{\vec{p}}_i(t) &= \vec{F}_i(t) - \gamma(t) \vec{p}_i(t) \\
\gamma(t) &= \nu \frac{T(t) - T_0}{T(t)}
\end{align*}
\]

Nosé-Hoover thermostat

\[
\begin{align*}
\dot{r}_i(t) &= \frac{\vec{p}_i(t)}{m_i} \\
\dot{\vec{p}}_i(t) &= \vec{F}_i(t) - \nu \frac{T(t)}{T} \vec{p}_i(t) \\
\dot{\gamma}(t) &= \nu \frac{T(t) - T}{T}
\end{align*}
\]

- 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

Further reading

- Melchionna, Cicotti and Holian, Mol Phys. 78, 533 (1993)
Demos and examples
Non-equilibrium MD

- **Heat flux** \( J = -\kappa \nabla T \)
  - \( \nabla T \): temperature gradient
  - \( \kappa \): thermal conductivity

- **To calculate** \( \kappa \):
  1. **Step 1.** Impose a heat flux
  2. **Step 2.** Measure the corresponding temperature gradient
  3. **Step 3.** Obtain thermal conductivity, \( \kappa \)


Picture from: Ya Zhou, Final Defense at Purdue University (2010)
Thermal Conductivities of Bulk Si and Ge

- **Kinetic theory:**
  \[
  \kappa = \frac{1}{3} C_v l \quad \text{and} \quad l = \sum_i \frac{1}{\tau_i}
  \]
  \[
  \frac{1}{\kappa} = \frac{l_{\infty}}{\kappa_{\text{bulk}}} \left(\frac{1}{l_{\infty}} + \frac{2}{L_z}\right)
  \]

  - **Sample size:** distance between cold/hot slabs
  - **Sample thermal conductivity**
  - **Phonon mean-free-path in the bulk**

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Intercept</th>
<th>Bulk $\kappa$ (W/m*K)</th>
<th>Phonon mfp (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge (NVT)</td>
<td>15.32171</td>
<td>0.0109</td>
<td>76</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>0.65891</td>
<td>0.00219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge (Experiment)</td>
<td>58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (NVT)</td>
<td>10.93991</td>
<td>0.09789</td>
<td>132</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>-145</td>
<td>3.39084E-4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (Experiment)</td>
<td>130</td>
<td></td>
<td></td>
<td>200-300</td>
</tr>
</tbody>
</table>
Structure of Nanolaminates and Nanowires

- Sample Size: 10x10x158 unit cells (126400 atoms)
- Lattice Parameter: $a_{Si} = a_{Ge} = b_{Si} = b_{Ge} = 0.554 \text{ nm}$, $c_{Si} = c_{Ge} = 0.55055 \text{ nm}$

**longitudinal view**

- Periodicity: 0.275275 nm
- Periodicity: 0.5055 nm
- Periodicity: 1.1011 nm
- Periodicity: 2.2022 nm

**Heat Baths**

- Periodicity: 4.4044 nm
- Periodicity: 8.8088 nm
- Periodicity: 17.6176 nm
- Periodicity: 35.252 nm
Keng-Hua Lin and A. Strachan (in preparation)
Ultimate properties of polymers

Nanoscale contact mechanics

Coherency limit in nanostructures
Additional online resources

**Molecular dynamics simulations of materials**

by Alejandro Strachan

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**What is MD?**

Molecular dynamics involves the numerical solution of the classical equations of motion (F=ma) for every single atom in material. The result is a very detailed description of the temporal evolution of the material: we obtain the position, velocity and force of every atom as a function of time. The total force acting on an atom comes from its interaction with other atoms and external fields and an accurate model to describe atomic interactions is critical in any MD simulation. If you are interested in MD read on; you will find more information, additional resources, simulation codes, and online tool that enables running live MD simulations using simply your web-browser.