Molecular Dynamics Primer

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Simulation vs. Experiment

Experiment
- Setup - experimental conditions
- Measure - quantity of interest
- Analyze - apply theory

Simulation
- Setup - Model and approximations
- Calculate - subject setup to conditions
- Analyze - measure, match, possibly predict.
What is Molecular Dynamics?

Molecular Dynamics (MD) is **classical**!

\[
\vec{F} = m \cdot \vec{a}
\]

**Force on an atom** \( \vec{F} \) \( \quad \) **Mass of an atom** \( m \) \( \quad \) **Acceleration of an atom** \( \vec{a} \)

Think Of Pool!

Adapted from http://www.worldofstock.com
What is Molecular Dynamics?

Molecular Dynamics (MD) is classical!

\[ \vec{F} = m \cdot \vec{a} \]

- Force on an atom
- Mass of an atom
- Acceleration of an atom

MD As Hard-Spheres
Continued...

MD is the application of classical mechanics to treat the evolution of atoms interacting via a determined potential at nanometer length and picosecond time scales.

Adapted from www.wag.caltech.edu
What Do Atoms Look Like in MD

QM vs. MD Atom

The Approach

- Nuclei and Electrons are not explicitly treated
- Describe atoms with an interatomic potential (i.e. Model)
- Given Newton's laws of motion evolve a system
- Modify equations to include temperature, pressure, etc.
Limitations of MD

- Time and length scale: nanoseconds and nanometers
- Interatomic potentials dictate potential energy surface
- Chemistry should be carefully interpreted
- Know the limitations of the MD model

Should You Use Other Methods

- Does your phenomena fall outside the range of time and length scale of MD:
  - Spatial - Dislocation Dynamics
  - Time - Diffusion
- Do you need the effects of electrons - QM calculations
Classifying Materials

Since we have eliminated the direct interaction of electrons which are responsible for chemistry (i.e. bonding) are models need to same something about the bonding.

- Dispersion forces
- Ionic bonding
- Covalent bonding
- Metallic bonding

Adapted from http://www.abc.net.au
Cohesive Energy

- Potential energy is the sum of all interacting atoms
- Cohesive energy is the energy need to move all the atoms infinitely apart

\[ E_{coh} = E_{atoms} - \sum_{i=1}^{N} E_i \]

Cohesive Energy \( E_{coh} \)
Energy of \( N \) interacting atoms \( E_{atoms} \)
Energy of isolated atom \( \sum_{i=1}^{N} E_i \)
Pair Potentials

- Energy and force are sum of atom pair interactions
- Only dependent on separation distance
- Some examples are: Lennard-Jones, Buckingham, and Morse

Adapted from Callister, William D., Jr. Materials Science And Engineering: An Introduction, 7th ed.
Dispersion forces

- No directionality to bond
- Pairwise interaction between atoms
- Repulsive nature due need for electron orthogonality (i.e. Pauli exclusion principle)
- Attractive nature from instantaneous electron fluctuations around nuclei

Adapted from LeSar, Richard. Introduction to Computational Materials Science: Fundamentals to Applications, 1st ed.
Lennard-Jones

Very common simple interatomic potential good for noble gases and molecular interactions.

\[
E(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]
\]

\[\epsilon\]: potential well depth

\[\sigma\]: distance where energy is zero
Continued…

Adapted from http://chemwiki.ucdavis.edu
How Well Does LJ Do!

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<th>Ne</th>
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<td>$u_o$ (eV/atom)</td>
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<tr>
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<td>3.2</td>
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</table>

Other Simple Potentials

- Mie Potential - adds two more variables for fitting
- Morse Potential - approach from diatomic bond potentials
Ionic Bonding

Coulombic In Nature

- Atoms in ionic materials behave like point charges
- Simple to describe by Coulomb potential
- Very long-range interactions

\[ E_{\text{coul}} = \frac{1}{4\pi\varepsilon_o} \frac{q_i q_j}{r_{ij}} \]

Terms Added For Correction

- Usually a repulsive ”Wall” is needed
- Also Dipole-Dipole or Multipole expansion added: \( \frac{C}{r_{ij}^6} \)
- Referred to as Born or Born-Huggins-Meyer potential
Pair Potential Limitations

- Pair Potentials only function of distance
- For pure solids will always produce simple structures (e.g. FCC)
- Pair potentials obey Cauchy relations: $c_{12} = c_{44}$
- Predominately make use of empirical data
Many-body Potentials

Types of Systems

Primarily used to describe metallic and covalent materials. Fit using empirical and *ab-initio* data.

Metals

- Embedded atom method/Modified embedded atom method:

\[ E_i = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}) + F_i \left( \sum_{i \neq j} \rho(r_{ij}) \right) \]

- Environment dependent interatomic potentials
- Glue Model/Effective medium theory

Types of Systems

- Metals
  - Embedded atom method/Modified embedded atom method:
    \[ E_i = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}) + F_i \left( \sum_{i \neq j} \rho(r_{ij}) \right) \]
    - pairwise term
    - embedding term
    - electron density
Covalent Materials

- Stillinger-Weber: 2-body plus 3-body
- Tersoff (Bond-Order)
- REBO/AIREBO - adds hydrocarbon descriptions

Example: Tersoff

\[
E_i = f_R(r_{ij}) + b_{ij} f_A(r_{ij}); b_{ij}(r_{ij}, r_{ik}, \theta_{ijk})
\]

Other Approaches

Force Fields

- Used predominately is chemistry and biology
- Force Field descriptions:

\[ E = E_{bond} + E_{angle} + E_{dihedral} + E_{coul} + E_{vdw} \]

- Force Fields use fixed description of bonds i.e. single, double, triple
- Allows for simulation of mixed interactions

Adapted from http://mmb.irbbarcelona.org
Advanced Potentials

- Reactive Force Fields
- Multi-component systems
- On-The-fly determination of bond-order
- Also includes charge transfer (IMPORTANT to define chemistry)
- Parametrized from large ab-initio data sets
- 10-100x more computationally expensive

Adapted from http://www.rxffconsulting.com: battery electrolyte with graphite electrodes
Integration of Newton's Equations

Verlet Algorithm

- Taylor expansion of position in time:

\[
\begin{align*}
  r(t + \Delta t) &= r(t) + v(t)\Delta t + \frac{1}{2!} a(t)\Delta t^2 + \cdots \\
  r(t + \Delta t) &= r(t) - v(t)\Delta t + \frac{1}{2!} a(t)\Delta t^2 - \cdots \\
  r(t + \Delta t) &= r(t) + v(t)\Delta t + \frac{a(t)}{2} \Delta t^2
\end{align*}
\]

- Accurate \((O(\Delta t^4))\) and simple
- No need to calculate velocity
- Unfortunately need to calculate velocity indirectly:

\[
v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}
\]
Continued…

Velocity Verlet Algorithm

- Most widely used
- Makes use of half time steps:

\[ v\left(t + \frac{\Delta t}{2}\right) \]

- Calculates positions from velocity, then updates velocity:

\[ r(t + \Delta t) = r(t) + v\left(t + \frac{\Delta t}{2}\right) \Delta t \]

\[ v(t + \Delta t) = v\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2} a(t + \Delta t) \Delta t \]

- Simple to implement and stable
- Time reversible as well
Continued...

High-Order Algorithm

- Predictor-corrector algorithm
- Measures error in acceleration and correct
- Gear Predictor-corrector even more accurate
- typical timestep for all algorithms is 1-5 fs
Potential Cutoffs & Neighbor Lists

Techniques

- Most computationally expensive part of MD is calculating energy and forces.
- Use cutoffs to reduce computing time, $r_c$
  - EAM: 5 Å
  - Tersoff: 3-5 Å
  - Coulombic: long-range summation needed
  - Pair potentials: 10-15 Å
- Populate a list of neighbors every $\Delta t$

Adapted from http://catalyst.blogs.rice.edu/
Boundary Conditions

- Periodic Boundary Conditions - make use of images
- Free Surface Boundary Conditions - vacuum above surface

Adapted from http://catalyst.blogs.rice.edu/
Position and Velocities

- MD requires some knowledge of initial structure
- We can prescribe velocities using a distribution corresponding to a desired temperature

Defining Temperature & Pressure

- Use equipartition theorem:

\[
\langle E_{ke} \rangle = \frac{3}{2} N k_b T = \langle \sum_i \frac{1}{2} m v_i^2 \rangle
\]

\[
T(t) = \frac{1}{3N k_b} \sum_i m v_i^2
\]

- Virial pressure:

\[
P = \frac{N k_b T}{V} + \sum_i \frac{r_i \cdot f_i}{dV}
\]

\[\text{ensemble pressure} \quad \text{atomic pressure}\]
Ensembles

- Atoms in a simulation box during MD run sample many microstates
- Thermodynamic limit - at equilibrium all possible configurations sampled
- We can impose external conditions on ensembles (i.e. Temperature, pressure, volume)

List of Ensembles

<table>
<thead>
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<tbody>
<tr>
<td>Microcanonical</td>
<td>N, V, E</td>
<td>Adiabatic $S = k \ln \Omega_{NVE}$</td>
</tr>
<tr>
<td>Canonical</td>
<td>N, V, T</td>
<td>Isothermal $F = kT \ln \Omega_{NVT}$</td>
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<tr>
<td>Isobaric-Isothermal</td>
<td>N, P, T</td>
<td>$G = -kT \ln \Omega_{NPT}$</td>
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<tr>
<td>Grand Canonical</td>
<td>$\mu$, V, T</td>
<td>$\mu = -kT \ln \frac{\Omega_{\muVT}}{N}$</td>
</tr>
</tbody>
</table>

E-energy, N-atoms/moles, V-volume, P-Pressure, T-Temperature, and $\mu$ - Chemical potential.
Implementation Example: Thermostats

- Berendsen - rescale velocities
- Nose-Hoover - modify the Hamiltonian of the system
- Langevin - force damping
- Barostats are carried out in a similar fashion
Analysis

Some Key Aspects

- When running NVE, system must conserve energy!
- The net linear momentum of the simulation cell should be zero
- Try to identify if in a local minimum
- Check for numerical errors: bad dynamics, too large $\Delta t$, etc.

Time-Averaging

Since the thermodynamic quantities we calculate are instantaneous we take the time average at equilibrium.
Visualization

Inspect For Issues

- Visualize trajectories of atoms
- Color code according to properties (e.g. energy per atom)
- Check for any mistakes in initial structure

Simply Look!
Equilibrium
Properties

- Bulk modulus: $B = -V \left( \frac{\partial P}{\partial V} \right)_{NVT}$
- Lattice parameter, $a$
- Thermal expansion coefficient: $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{NPH}$
- Heat Capacity
- Elastic Constants

Structural Information

[Structural diagram and graphs showing coordination numbers and radius in Angstroms for different materials like NaCl, Na-Zn, Na-CI, Zn-CI, Zn-Zn, and Zn-Zn with coordination numbers and radius changes.]
Other Properties

Viscosity: Green-Kubo Method

Thermal Conductivity: Green-Kubo Method
Go To Texts

- Frenkel & Smit, Understanding Molecular Simulation: From Algorithms to Applications. Probably most through text on MD.

- Allen & Tildesley, Computer Simulation of Liquids. Great MD intro and algorithms.

- Rapaport, The Art of Molecular Dynamics Simulation. MD cookbook text, ideal for developing your own code.
User Texts


- J.G. Lee, Computational Materials Science: An Introduction. Ideal for quickly using LAMMPS and VASP.

- R. Lesar, Introduction to Computational Materials Science: Fundamentals to Applications. Great multiscale introductory with strong emphasis on understanding and using.
Questions?

If you would like to obtain a copy of this presentation you can email me at stefanb@email.arizona.edu