Molecular Dynamics Primer

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April 2, 2014

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?

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Overview

Potentials
Pair Potentials
Many-body Potentials

Solving Equations
of Motion

Cutoffs, Boundary
Conditions, and
Neighbour-list

Initialization &
Ensembles

Analysis

Reference Texts

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

$$\underbrace{\vec{F}}_{\text{Force on an atom}} = \underbrace{m}_{\text{Mass of an atom}} \cdot \underbrace{\vec{a}}_{\text{Acceleration of an atom}}$$
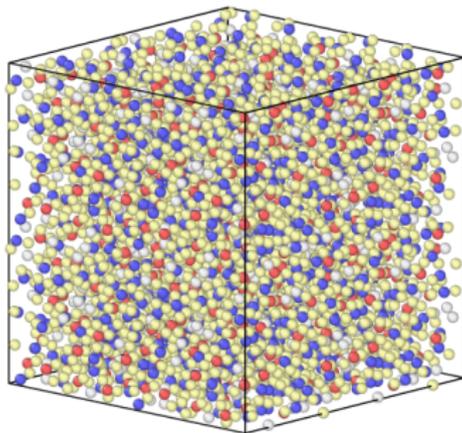
Think Of Pool!

Adapted from http://www.worldofstock.com

What is Molecular Dynamics?

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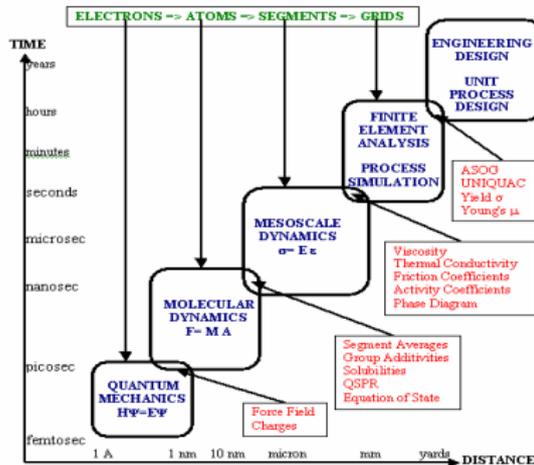
MD As Hard-Spheres

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Solving Equations
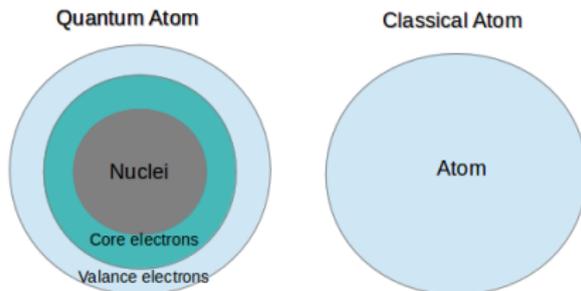of Motion

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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 Newtons 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

$$\underbrace{E_{coh}}_{\text{Cohesive Energy}} = \underbrace{E_{atoms}}_{\text{Energy of N interacting atoms}} - \underbrace{\sum_{i=1}^{N} E_i}_{\text{Energy of isolated atom}}$$

Pair Potentials

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- Energy and force are sum of atom pair interactions
- Only dependent on separation distance
- Some examples are: Lennard-Jones, Buckingham, and Morse
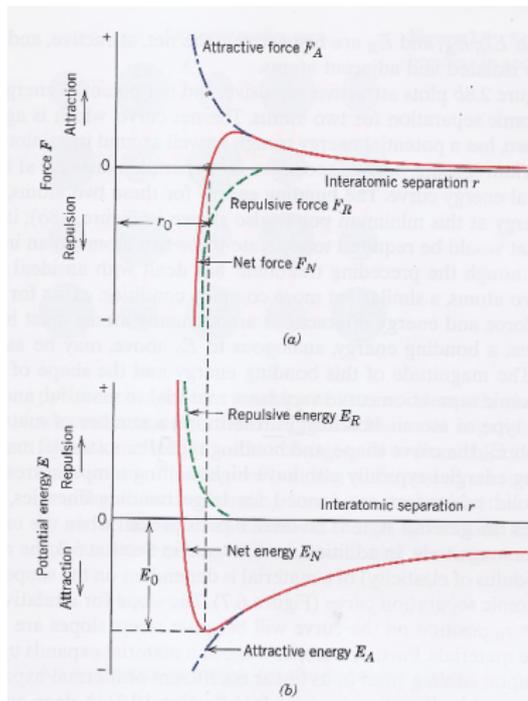
Adapted from Callister, William D. ,Jr. Materials Science And Engineering An Introduction, 7th ed.

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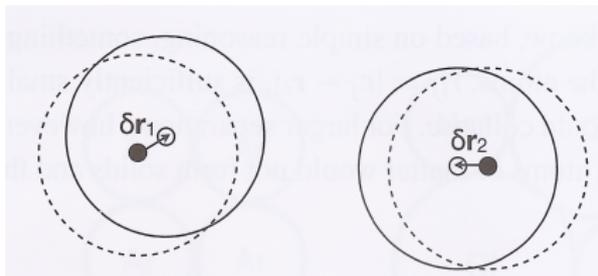
Adapted from LeSar, Richard. Introduction to Computational Materials Science: Fundamentals to Applications, 1st ed.

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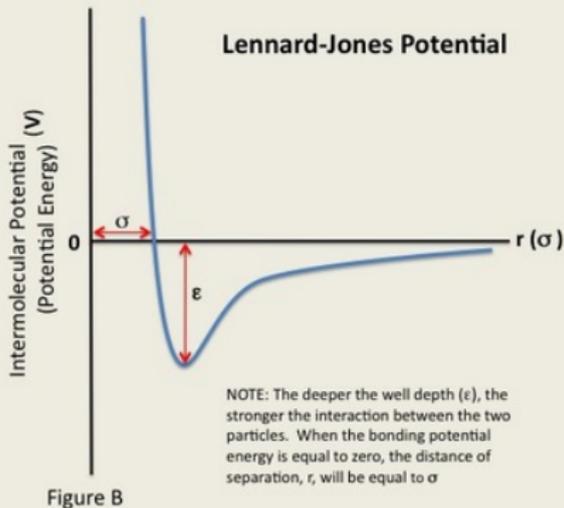Ensembles

Analysis

Reference Texts

Lennard-Jones

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

$$E(r_{ij}) = 4\epsilon \left[\underbrace{\left(\frac{\sigma}{r_{ij}}\right)^{12}}_{\text{Repulsive part}} - \underbrace{\left(\frac{\sigma}{r_{ij}}\right)^{6}}_{\text{Attractive part}} \right]$$

ϵ: potential well depth
σ: distance were energy is zero

Continued...

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Adapted from http://chemwiki.ucdavis.edu

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How Well Does LJ Do!

		Ne	Ar	Kr	Xe
r_o $(\mathring{A})$	Experiment	3.13	3.75	3.99	4.33
	Theory	2.99	3.71	3.98	4.34
u_o $\left(\frac{eV}{atom}\right)$	Experiment	-0.02	-0.08	-0.11	-0.17
	Theory	-0.027	-0.089	-0.120	-0.172
B_o (GPa)	Experiment	1.1	2.7	3.5	3.6
	Theory	1.8	3.2	3.5	3.8

Other Simple Potentials

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

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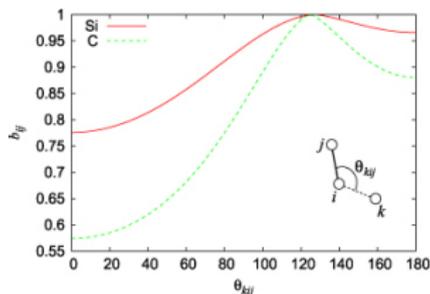Initialization &
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Ionic Bonding

Coulombic In Nature

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

$$E_{coul} = \frac{1}{4\pi\epsilon_o} \frac{\overbrace{q_i q_j}^{\text{Charge on atom i and j}}}{\underbrace{r_{ij}}_{\text{Distance between atom i and j}}}$$

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

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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:

$$E_i = \frac{1}{2} \overbrace{\sum_{i \neq j} \phi\left(r_{ij}\right)}^{\text{pairwise term}} + F_i \overbrace{\underbrace{\left(\sum_{i \neq j} \rho\left(r_{ij}\right) \right)}_{\text{electron density}}}^{\text{embedding term}}$$

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

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Covalent Materials

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

Example: Tersoff

$$E_i = f_R(r_{ij}) + \overbrace{b_{ij}}^{\text{bond-order term}} f_A(r_{ij}); \; b_{ij}(r_{ij}, r_{ik}, \theta_{ijk})$$

Umeno, Y., et al. Ideal Shear Strength under Compression and Tension in C, Si, Ge, and Cubic SiC: An
Ab Initio Density Functional Theory Study. J. Phys.: Condens. Matter 2011, 23

Other Approaches

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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

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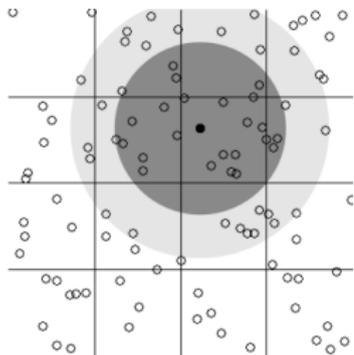
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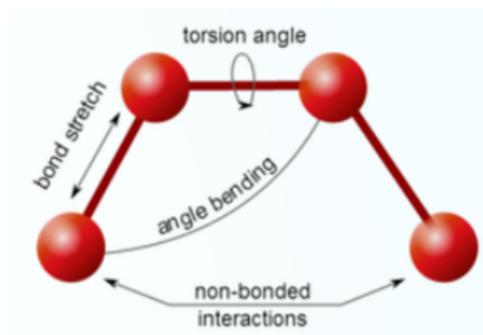
Advanced Potentials

- 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
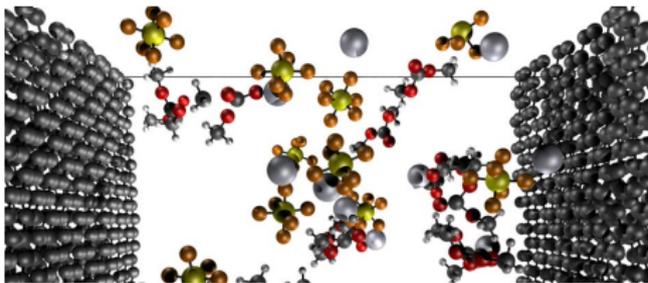
Adapted from http://www.rxffconsulting.com : battery electrolyte with graphite electrodes

Integration of Newtons Equations

Verlet Algorithm

- Taylor expansion of position in time:

$$r\left(t + \Delta t\right) = r(t) + v(t)\Delta t + \frac{1}{2!}a(t)\Delta t^2 + \cdots$$

$$r\left(t + \Delta t\right) = r(t) - v(t)\Delta t + \frac{1}{2!}a(t)\Delta t^2 - \cdots$$

$$r\left(t + \Delta t\right) = r(t) + v(t)\Delta t + \frac{a(t)}{2}\Delta t^2$$

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

$$v(t) = \frac{r\left(t + \Delta t\right) - r\left(t - \Delta t\right)}{2\Delta t}$$

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:

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

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

- 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

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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 Δt

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

- Verlet list
- Link-cell list

Boundary Conditions

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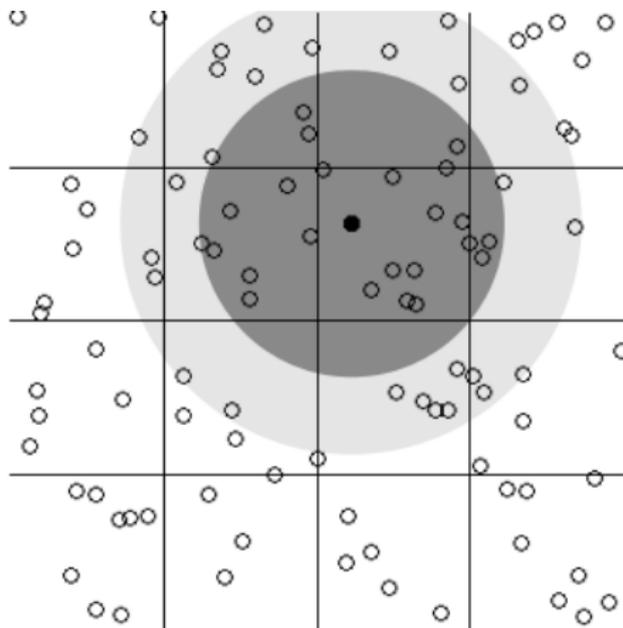
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Position and Velocities

- 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:

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

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

- Virial pressure:

$$P = \underbrace{\frac{N k_b T}{V}}_{\text{ensemble pressure}} + \underbrace{\frac{\sum_i r_i \cdot f_i}{dV}}_{\text{atomic pressure}}$$

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

Ensemble Type	Variables	Stat. Mech.
Microcanonical	N,V,E	Adiabatic $S = k \ln \Omega_{NVE}$
Canonical	N,V,T	Isothermal $F = kT \ln \Omega_{NVT}$
Isobaric-Isothermal	N,P,T	$G = -kT \ln \Omega_{NPT}$
Grand Canonical	μ ,V,T	$\mu = -kT \ln \frac{\Omega_{\mu VT}}{N}$

E-energy, N-atoms/moles, V-volume, P-Pressure, T-Temperature, and μ - Chemical potential.

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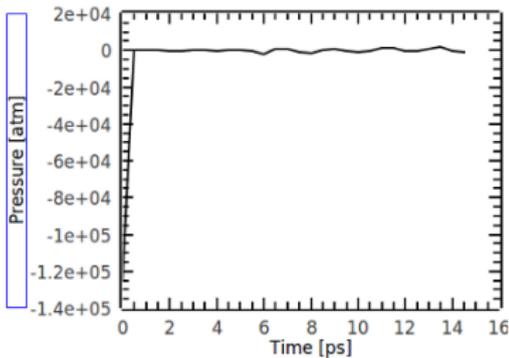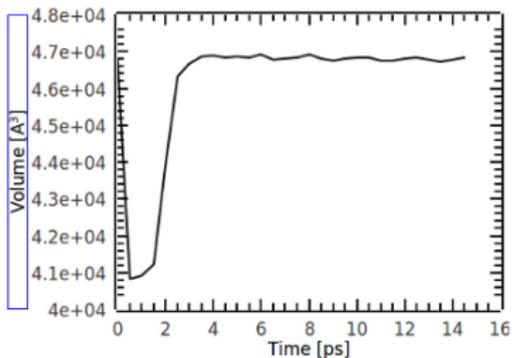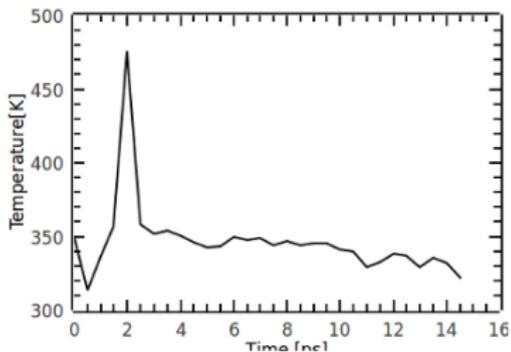Many-body Potentials

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Visual Aid
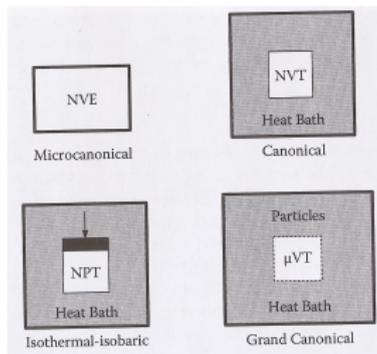
Adapted from Lee, June Gunn. Computational Materials Science: An Introduction; CRC Press, 2012.

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

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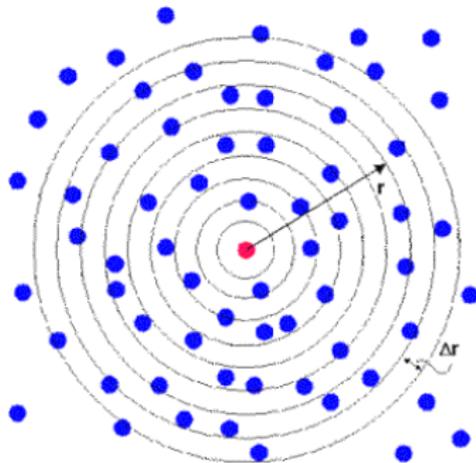Neighbour-list

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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 Δt, 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)
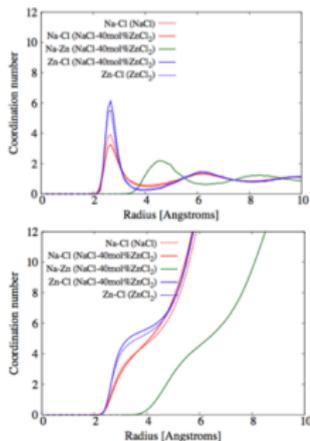- Check for any mistakes in initial structure

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

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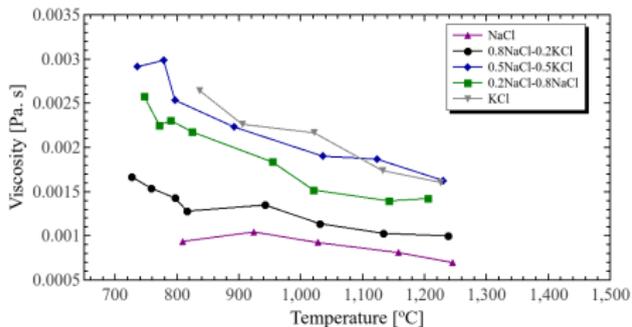Cutoffs, Boundary
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Other Properties

Viscosity: Green-Kubo Method
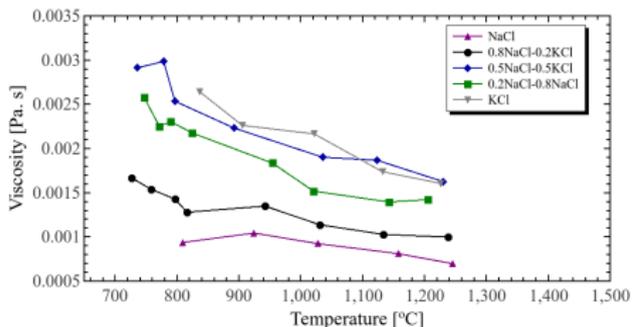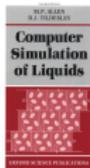

Thermal Conductivity: Green-Kubo Method

Go To Texts

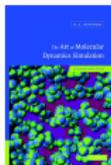- Frenkel & Smit, Understanding Molecular Simulation: From Algorithms to Applications.Probably most through text on MD.

- 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. Fan, Multiscale Analysis of Deformation and Failure of Materials. Nice section on using various codes.

- 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?

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