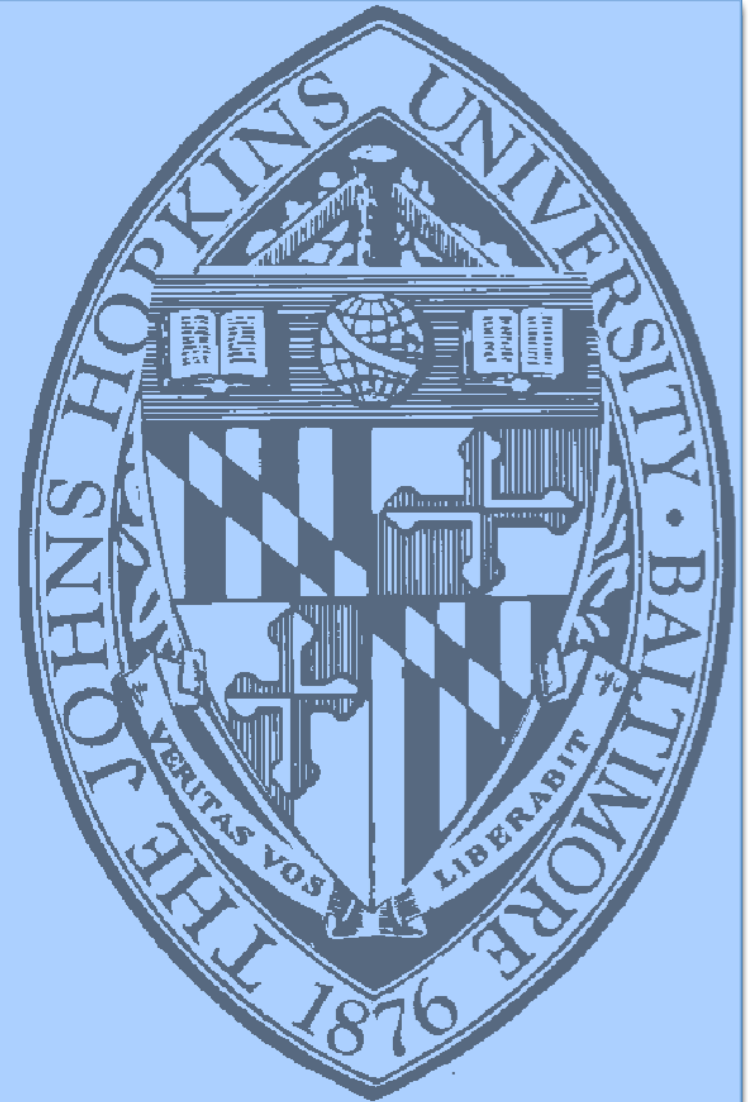


A Brief Introduction to **Molecular Dynamics Simulation**

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My Thread This Week

Mon
Intro to
Mechanics
of Materials

Tues
Intro to
Molecular
Dynamics

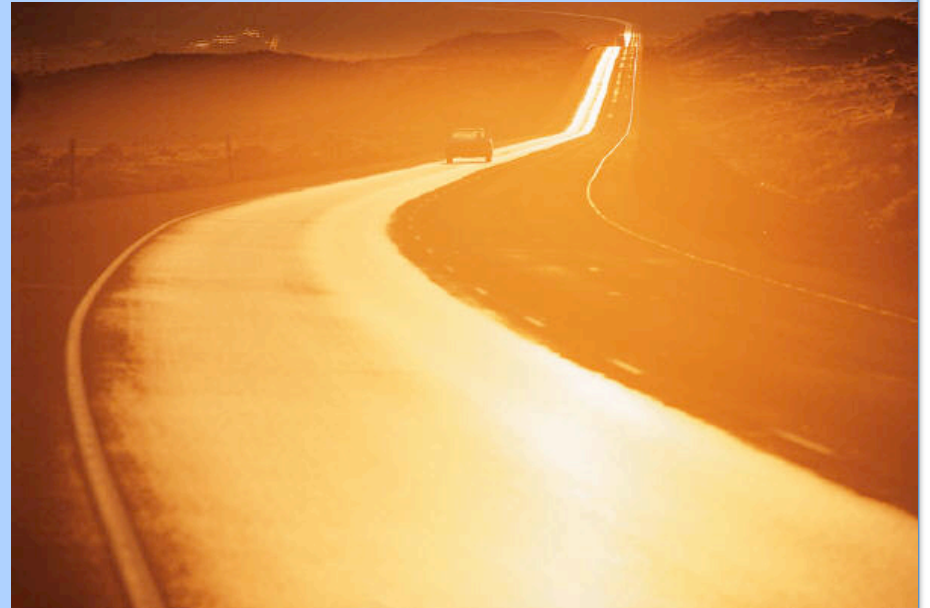
Wed
Plasticity in
Amorphous
Materials

Thurs
STZ
Constitutive
Theory

A Cautionary Thought

..In that Empire, the craft of Cartography attained such Perfection that the Map of a Single province covered the space of an entire City, and the Map of the Empire itself an entire Province. In the course of Time, these Extensive maps were found somehow wanting, and so the College of Cartographers evolved a Map of the Empire that was of the same Scale as the Empire and that coincided with it point for point. Less attentive to the Study of Cartography, succeeding Generations came to judge a map of such Magnitude cumbersome, and, not without Irreverence, they abandoned it to the Rigours of sun and Rain. In the western Deserts, tattered Fragments of the Map are still to be found, Sheltering an occasional Beast or beggar; in the whole Nation, no other relic is left of the Discipline of Geography.

Jorge Luis Borges,
Labyrinths



Born Oppenheimer Approximation

- We wish to examine the dynamics of a collection of atoms.
- The energy of the system has three contributions
 - Kinetic Energy from the momenta of nuclei
 - Potential Energy from electrostatic interactions of nuclei
 - Energy associated with the electrons: both kinetic and from their interactions

$$H = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + E_{el}$$

$$\sum_{k=1}^n \left\{ \frac{\hbar^2}{2m_e} \nabla_k^2 - \sum_{i=1}^N \frac{Z_i e^2}{4\pi\epsilon_0 r_{ik}} + \sum_{l=k+1}^n \frac{e^2}{4\pi\epsilon_0 r_{lk}} \right\} \psi(\vec{r}_1, \dots, \vec{r}_n) = E_{el} \psi(\vec{r}_1, \dots, \vec{r}_n)$$

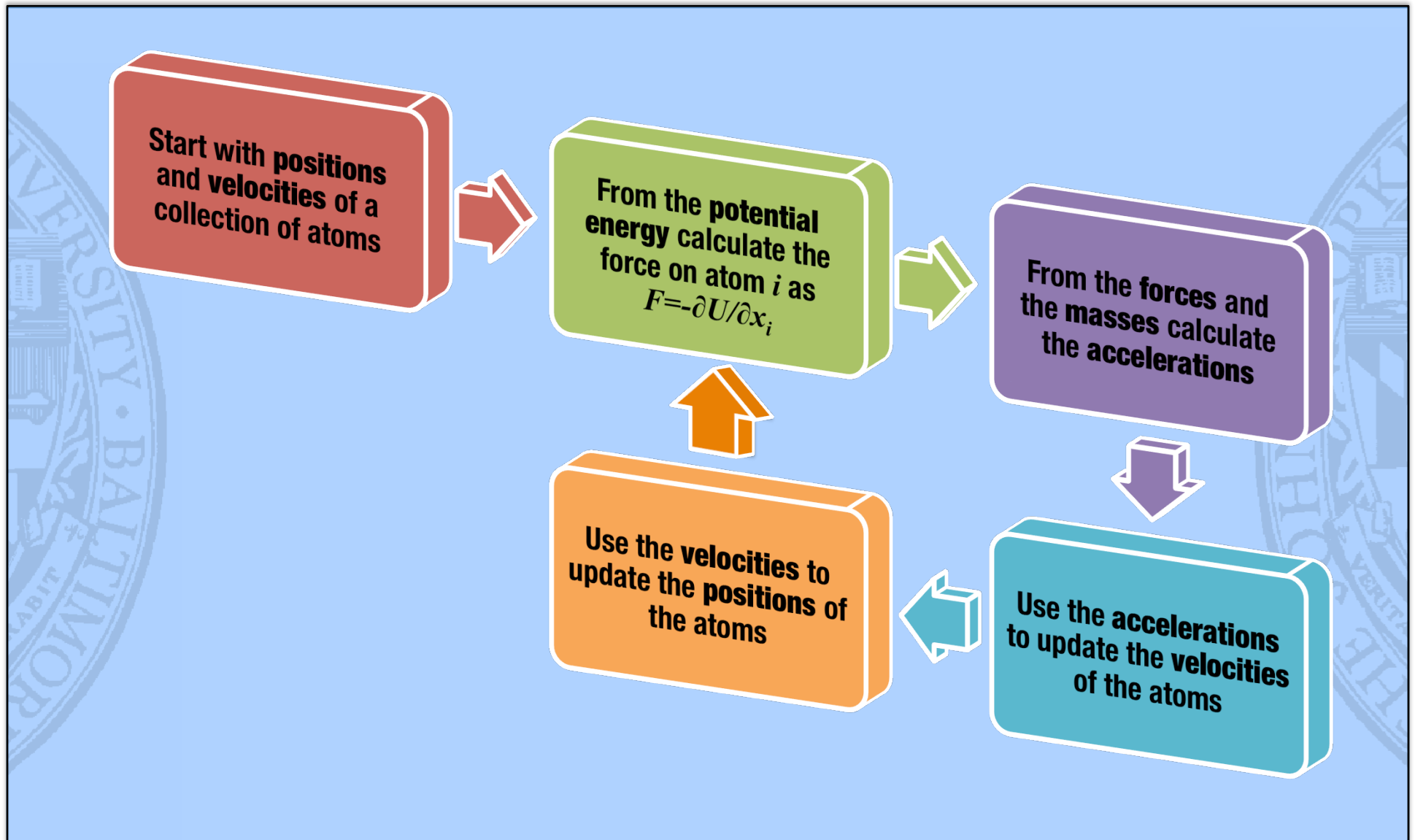
Born Oppenheimer Approximation

- The electronic degrees of freedom typically equilibrate much faster than the nuclear positions
- The Schrödinger equation can, **in principle**, be solved for each instantaneous nuclear configuration, and we can **assume the system occupies the ground state**
- Under these assumptions the electronic contribution to the energy is simply a **function of the nuclear positions**

$$H = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + E_{el}(\vec{r}_1, \dots, \vec{r}_N)$$

$$H = K(\vec{p}_1, \dots, \vec{p}_N) + U(\vec{r}_1, \dots, \vec{r}_N)$$

Overview of Molecular Dynamics



Overview of Molecular Dynamics

- Consider a system with a phase space consisting of a 3N dimensional position vector and a 3N dimensional momentum vector

$$\vec{x} = \{x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N\}$$

$$\vec{p} = \{p_{x1}, p_{y1}, p_{z1}, p_{x2}, p_{y2}, p_{z2}, \dots, p_{xN}, p_{yN}, p_{zN}\}$$

$$\mathbf{m} = \{m_1, m_1, m_1, \dots, m_N, m_N, m_N\}$$

- The potential energy is expressed as a function of 3N DOFs

$$U = U(\vec{x}) = U(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N)$$

- Integrate the equations below forward in time

$$\frac{d\vec{x}}{dt} = \vec{v} \quad \frac{d(\mathbf{m} \cdot \vec{v})}{dt} = -\frac{\partial U}{\partial \vec{x}}$$

Numerical Implementation

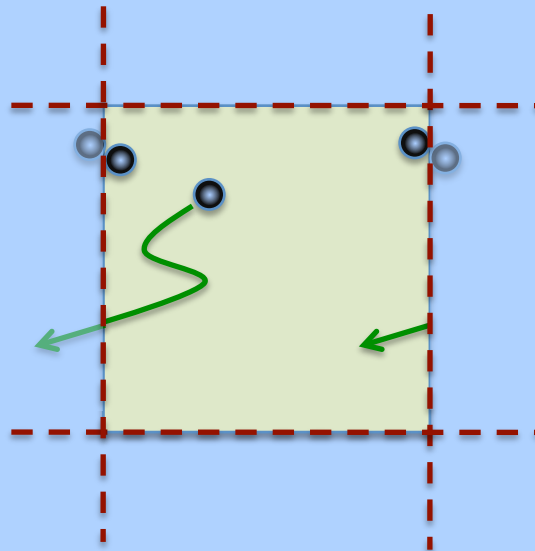
- In order to integrate these equations forward from an initial condition a finite differencing scheme is used
- There the choice of the interval between calculated times is crucial for determining numerical stability
- Too large a time interval results in errors growing out of bound
- The time step must be significantly smaller than the shortest physically relevant process
 - Gas: time for the fastest atom to cross an atomic radius (a/v^*)
 - Solid: period of vibration for an atom in the presence of its neighbors (inverse of the Einstein frequency)

Boundary Conditions

- Another critical issue is that the number of atoms is typically limited to 10^6 (10^9 on very large supercomputers)
- For a cube of one million simulated atoms the sample material is 100 atoms on a side.
- This means at least $6 \cdot 100^2 \sim 10^5$ atoms are surface atoms, **not behaving like bulk material**
- This is $\sim 10\%$ of all atoms!

Periodic Boundary Conditions

- To avoid this effect it is typical to impose periodic boundary conditions.
- This ensures that all atoms are in a bulk environment, although it does not eliminate system size effects



Limitations of an Isolated System

- The system we have described so far is entirely isolated and at constant volume (for the periodic case).
- Energy is conserved to within numerical error.
- We are confined to the constant energy manifold in phase space.
- The system explores the micro-canonical (NVE) ensemble.
- This is quite different than most experimental systems.

MD in the Canonical Ensemble

- To simulate the canonical ensemble (NVT) the system must be able to exchange energy with a heat bath.
- Typically one measures T by using the fact that in equilibrium $\langle KE \rangle = \frac{3}{2} Nk_B T$
- One typical practice is to rescale the velocities to impose this condition, but this **does not** reproduce a constant T ensemble.

Andersen Thermostat

- Randomly assume a particle has undergone a collision with a particle from the heat bath.
- Replace its velocity by a velocity chosen from the Boltzmann distribution.
- Maintaining a true thermal distribution of kinetic energies.
- Introduces odd discontinuities in the dynamics that can alter the rates of thermally activated events.

Langevin Thermostat

- Similar to Andersen except the effect of interaction with the heat bath is implemented by a random white noise in the force field.
- This is accompanied by a Stokesian drag term.
- Approximates the dynamics of a colloidal particle in a fluid.

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \quad \dot{\vec{p}}_i = -\frac{\partial U}{\partial \vec{r}_i} - \eta \vec{p}_i + \vec{f}_i(t)$$

$$\langle \vec{f}_i(0) \cdot \vec{f}_i(t) \rangle = \frac{6kT\eta}{m_i} \delta(t)$$

Nosé-Hoover Thermostat

- Introduce a Stokesian drag term, but allow its value to vary with time, even being negative!
- The dynamics of the drag term maintain constant temperature.
- If $\eta > 0$ heat is drawn out of the system, if $\eta < 0$ heat enters the system.

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \quad \dot{\vec{p}}_i = \vec{F}_i - \eta \vec{p}_i$$

- Can show formally that this reproduces the canonical ensemble.

$$\dot{\eta} = \frac{1}{\tau} \left[\frac{\sum_{i=1}^N \frac{p_i^2}{2m_i}}{\frac{3}{2} N k_B T_{bath}} - 1 \right]$$

Nosé-Hoover Thermostat

- **This method disproportionately effects fast moving particles.**
- **It is important to realize that this method breaks translational symmetry (as does the Langevin method).**
- **This means that rigid body motion and sound waves are also directly affected.**

Heat in MD

- **It is important to note that since MD only simulates the kinetics of the nuclei it does not include electronic effects.**
- **Therefore heat capacity and thermal conductivity due to electrons must be neglected or put in by hand.**
- **Phonon effects enter naturally.**

Simulating Other Ensembles

- Methods have been developed to handle other ensembles.
- Parinello-Rahman scheme allows for NPT simulations.
- Note that controlling P only requires rescaling the box size, while controlling σ (the full pressure-stress tensor) requires the box lengths to vary independently and the box shape to adjust, *ie* to a parallelepiped.
- Grand Canonical methods also exist that insert or remove particles using a chemical potential.

Approximating Potential Energy

At the heart of MD is the calculation of the potential energy and its derivatives.

Empirical Potentials

(Lennard Jones, Embedded Atom, Stillinger-Weber, Tersoff)

Up to 10^9 atoms

Semi-empirical Methods

(Tight Binding, LCAO)

Up to 10^4 atoms

Ab initio Methods

(Density Functional Theory w/LDA, GGA)

Up to 10^3 atoms

Pair Potentials

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N U_2(|\mathbf{r}_i - \mathbf{r}_j|)$$

- **Harmonic Potential**

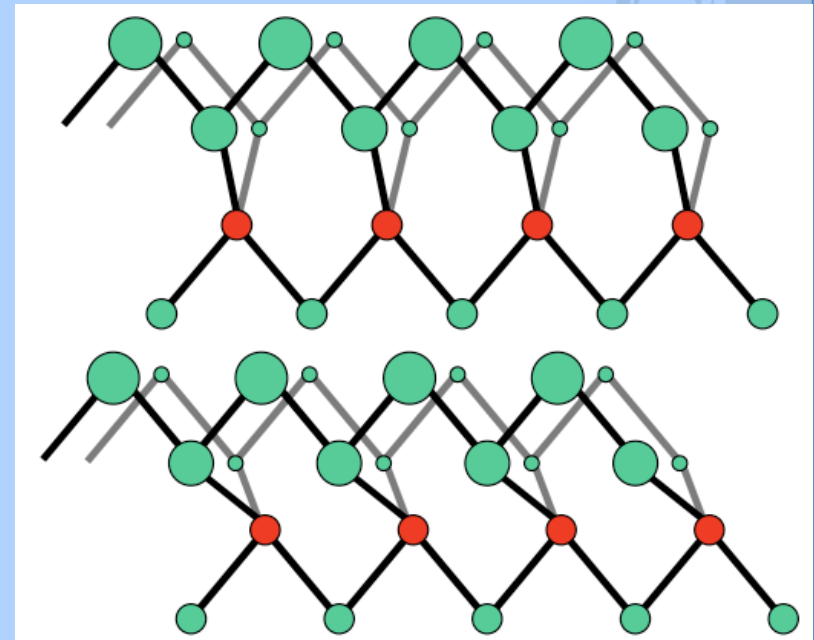
$$U_2(r) = \frac{k}{2}(r - r_0)^2$$

- **Lennard Jones Potential**

$$U_2(r) = 4a \left[\left(\frac{b}{r} \right)^{12} - \left(\frac{b}{r} \right)^6 \right]$$

When Pair Potentials Fail

- Many materials exhibit a Cauchy discrepancy, ie $C_{1122} \neq C_{1212}$
- The more bonds the more stable the material is, so only the most densely packed systems (FCC) are stable.
- Other structures, such as diamond cubic lattice, are unstable to shear.



Cluster Potentials

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N U_2(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} \sum_{k=j+1}^N U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

- **Harmonic**

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{k_{123}}{2} \left(\frac{\mathbf{r}_{12} \cdot \mathbf{r}_{13}}{r_{12} r_{13}} + \frac{1}{3} \right)^2 + \frac{k_{231}}{2} \left(\frac{\mathbf{r}_{21} \cdot \mathbf{r}_{23}}{r_{21} r_{23}} + \frac{1}{3} \right)^2 + \frac{k_{312}}{2} \left(\frac{\mathbf{r}_{31} \cdot \mathbf{r}_{32}}{r_{31} r_{32}} + \frac{1}{3} \right)^2$$

- **Stillinger Weber**

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = h(r_{12}, r_{13}, \mathbf{r}_{12} \cdot \mathbf{r}_{13}) + h(r_{21}, r_{23}, \mathbf{r}_{21} \cdot \mathbf{r}_{23}) + h(r_{31}, r_{32}, \mathbf{r}_{31} \cdot \mathbf{r}_{32})$$

$$h(a, b, c) = \begin{cases} a < r_c \wedge b < r_c : \frac{k}{2} \left(\frac{c}{ab} + \frac{1}{3} \right)^2 e^{\gamma/(a-r_c)} e^{\gamma/(b-r_c)} \\ a \geq r_c \vee b \geq r_c : 0 \end{cases}$$

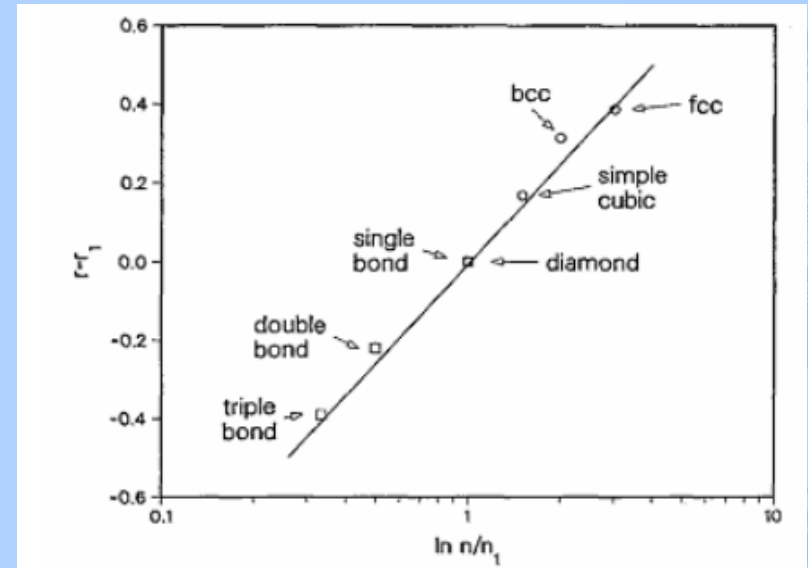
Issues with Cluster Potentials

- The limitation of cluster potentials is that they hard-wire one bonding morphology, ie sp^3 bonding, to the exclusion of all else.
- So in Stillinger-Weber silicon, even undercoordinated Si maintain a 109.5° bond angle.

Embedded Atom Method

- Consider the following observation by Linus Pauling
- As coordination number increases bond length also increases

$$r \propto \ln(n/n_1)$$



Embedded Atom Method

- In order to create a potential that reflects this relationship Daw and Baskes considered adding an “Embedding Energy” related to the density

$$U = \frac{1}{2} \sum_{i=1}^N \left[F(\rho_i) + \sum_{j \neq i} U_2(r_{ij}) \right]$$

- Here F is the cohesive embedding energy and U_2 is the repulsion between neighboring atoms.

$$F(\rho) = \frac{AZ_0}{2} \rho [\ln(\rho) - 1] \quad \rho_i = \frac{1}{Z_0} \sum_{j \neq i} \exp[-\beta(r_{ij} - r_0)]$$

Embedded Atom Method

- **This method can reproduce a number of different phases depending on the parameters, but does a better job at FCC, BCC, ie cubic densely packed phases.**
- **Approximating the behavior of materials with other equilibrium phases require adding terms that better model covalent bonding**
- **See MEAM (Modified Embedded Atom Model)**

Cluster Functional Potentials

- One last class of potential attempts a similar feat for covalent solids.
- These include “Bond Order Potentials” such as the Tersoff and Brenner potentials for Si and C

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} f_C(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

- Here f_C is a cutoff function that is **0** beyond some radius r_c and **1** below a radius $r_c - \delta$
- The functions f_R and f_A are the repulsive and attractive potentials respectively and have simple forms

$$f_R(r) = A \exp(-\lambda r) \quad f_A(r) = -B \exp(-\mu r)$$

Cluster Functional Potentials

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} f_C(r_{ij}) \left[f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right]$$

- All the important physics is in the b_{ij} term which relates the bond angles to the bond strength.
- An early potential by Abell showed that if this term is equal to $Z^{-1/2}$ the Pauling relation is maintained
- A typical form would be

$$b_{ij} = \left[1 + \sum_{k \neq i, j} f_C(r_{ij}) g \left(\frac{\mathbf{r}_{ki} \cdot \mathbf{r}_{kj}}{r_{ki} r_{kj}} \right) \right]^{-1/2}$$

$$g(\cos\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}$$

Empirical Potentials: Shortcomings

- Typically functional form is fit to ground state of one, perhaps multiple phases
- Furthermore parameters are fit to measurements typically related to expansions around ground state
 - Elastic constants (curvature of potential)
 - Thermal expansion (anharmonicity)
- Some potentials fit to relative energies of phases
- No potential is fit to the transition states that often control kinetic and non-equilibrium processes
- Few potentials are compared to amorphous phases, which are typically much harder to characterize.

Empirical Potentials: Shortcomings

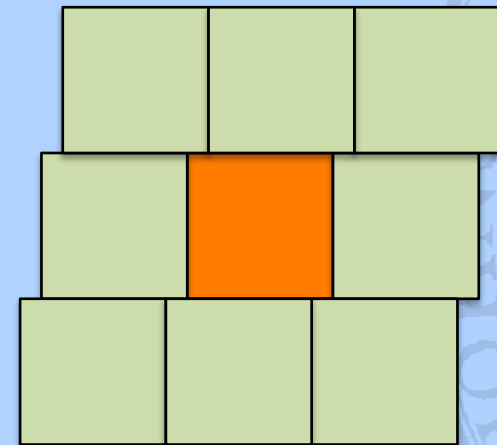
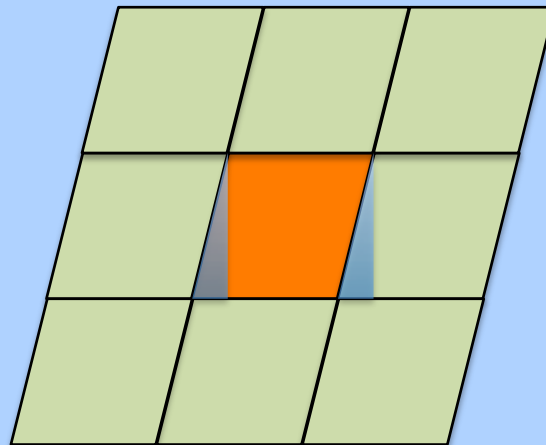
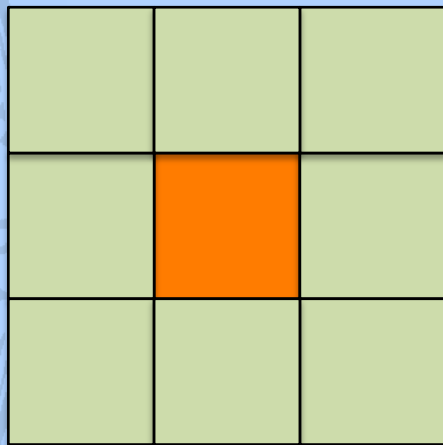
- However, empirical potentials provide a **simple model** that can be investigated in detail with relatively **large numbers of atoms** (10^4 - 10^9).
- Other more precise methods like tight-binding and DFT **have their own pseudo-potentials and fitting parameters**, so there is no method that obviates the need for approximation.
- These less approximate methods **severely limit the system size** that can be simulated.
- So which is appropriate depends on the nature of the question being asked.

Non-equilibrium MD Simulations

- A number of methodologies have been developed to investigate **non-equilibrium systems** for problems in fracture, shear flow, etc.
- Choices arise between fidelity to **local dynamics** and mitigation of **system-size/boundary effects**
- Often this arises as a choice between setting up boundary **reservoirs** for thermostating vs. maintaining **periodicity** during simulation

Non-equilibrium with Periodicity

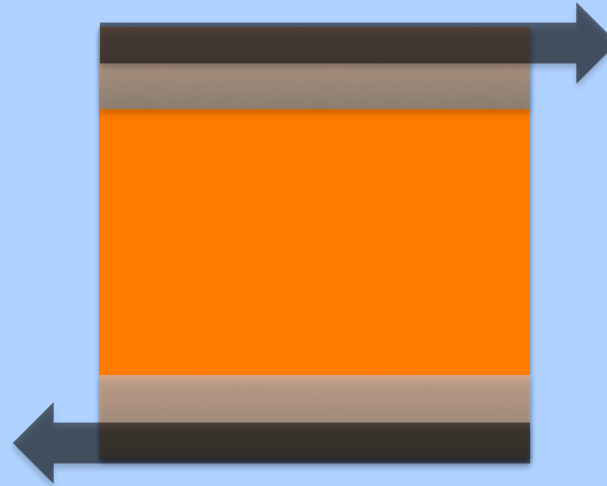
- Example: Shear
- Lees-Edwards boundary conditions



- **Thermostating throughout**
 - Can be done perpendicular in 3D
 - Can be done relative to a uniform shear profile

Non-equilibrium w/o Periodicity

- **Example: Shear**
- **Periodic in 2 of 3 directions, Boundaries used as grips**



- **Thermostating performed in reservoir near edge**
- **Issues can arise near boundaries of these grip/reservoir regions**

System Size Issues

- We must also consider that after a time related to the size of the system divided by the sound speed system size effects set in, as the dynamics of the crack or shearing region communicates with the boundary or periodic image.

Challenge of Data Analysis

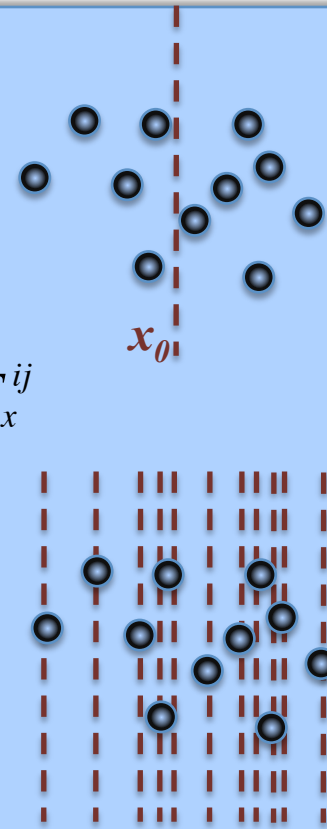
- **The problem in analyzing simulation data is often the opposite of experiment**
- **Instead of needing to interpret relatively little hard-won data as in experiment we know all atomic positions and velocities for all time.**
- **The challenge lies in determining what data is interesting and relevant to the question at hand.**

Extracting Stress from MD

$$\sigma_{xx} = \frac{1}{A} \sum_{x_i < x_0} \sum_{x_j > x_0} F_x^{ij}$$

$$\overline{\sigma_{xx}} = \frac{1}{AL} \int_0^L dx_0 \sum_{x_i < x_0} \sum_{x_j > x_0} F_x^{ij} = \frac{1}{V} \sum_{k=1}^{N-1} (x_{k+1} - x_k) \sum_{i=1}^k \sum_{j=k+1}^N F_x^{ij}$$

$$\overline{\sigma_{xx}} = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^N F_x^{ij} \sum_{k=i}^j (x_{k+1} - x_k) = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^N F_x^{ij} x^{ij}$$



This plus a kinetic term generalizes to an expression to the stress tensor

$$\overline{\sigma_{\alpha\beta}} = \frac{1}{V} \left[\sum_{i=1}^{N-1} \sum_{j=i+1}^N F_{\alpha}^{ij} r_{\beta}^{ij} + \sum_{i=1}^N \frac{p_{\alpha}^i p_{\beta}^i}{m_i} \right]$$

Extracting Strain from MD

- We need a reference configuration.
- Use the locations of atoms at a previous time.
- Our object is to choose a strain that allows us to determine the new position of an atom relative to a particular neighbor if we know its original relative position to that neighbor.
- For each atom we choose a local region, and designate the atoms in this region to be neighbors.

$$D_{min}^2 = \sum_{j \in n_i} \sum_{\alpha} \left[r_{\alpha}^{ij}(t) - \sum_{\beta} (\delta_{\alpha\beta} + \epsilon_{\alpha\beta}^i) r_{\beta}^{ij}(0) \right]^2$$

$$X_{\alpha\beta}^i = \sum_{j \in n_i} r_{\alpha}^{ij}(t) r_{\beta}^{ij}(0)$$

$$Y_{\alpha\beta}^i = \sum_{j \in n_i} r_{\alpha}^{ij}(0) r_{\beta}^{ij}(0)$$

$$\epsilon_{\alpha\beta}^i = \sum_{\gamma} X_{\alpha\gamma}^i (Y^i)_{\beta\gamma}^{-1} - \delta_{\alpha\beta}$$

Summary

- MD methods involve explicit integration of Newton's equation of motion on a collection of particles.
- Additional dynamics need to be included to include coupling to a heat bath or to the external medium through pressure/stress.
- The simulation requires the selection of a suitable approximation of the bonding energy for which there are many models at various levels of sophistication and computational expense.
- Atomistic data must be processed properly to obtain continuum quantities that can be compared to theory.

References

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- **D.C. Rapaport, “The Art of Molecular Dynamics Simulation,” Cambridge © 1995.**
- **J.M. Haile, “Molecular Dynamics Simulation,” Wiley © 1992.**
- **A. Leach, “Molecular Modeling: Principles and Applications,” Longman ©1996**