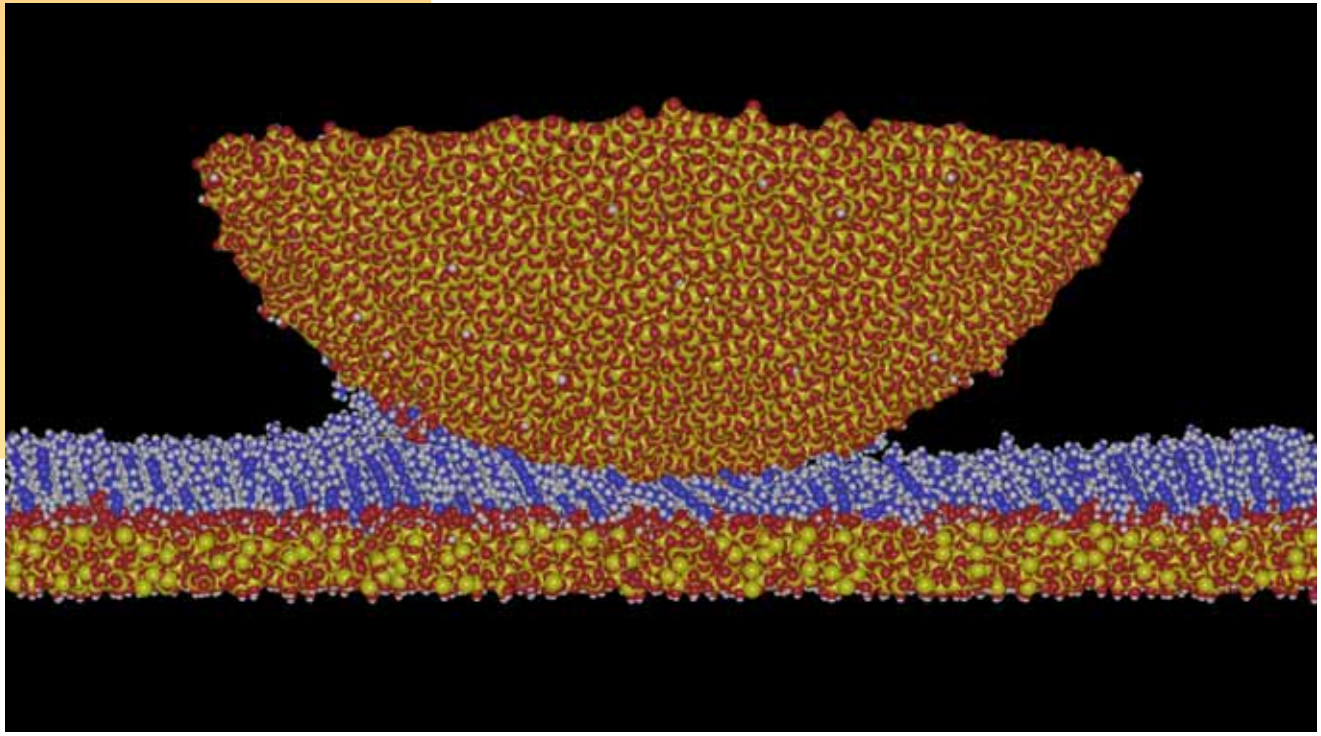
An Introduction to Molecular Dynamics



Michael Chandross

Sandia National Laboratories, Albuquerque, NM

Presented at the Nanotribology Tutorial/Panel Session,
STLE/ASME International Joint Tribology Conference,
October 20-22, 2008, Miami, Florida, USA

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
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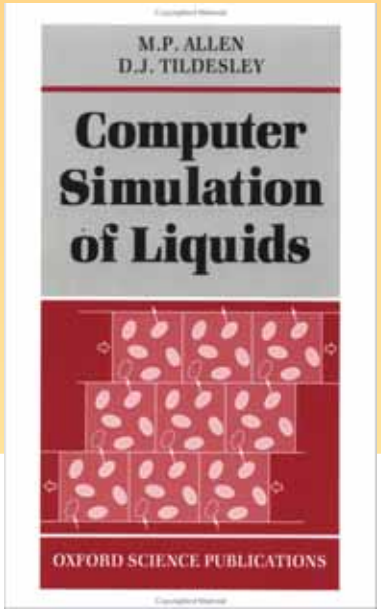
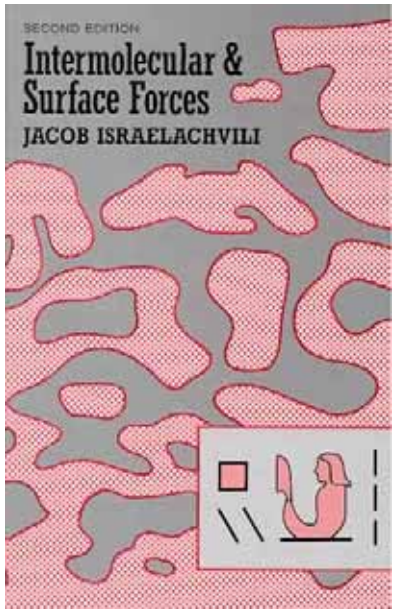
under contract DE-AC04-94AL85000.

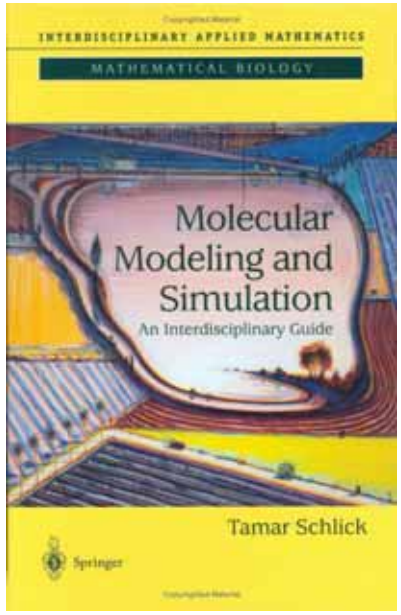
NNSA National Nuclear Security Administration

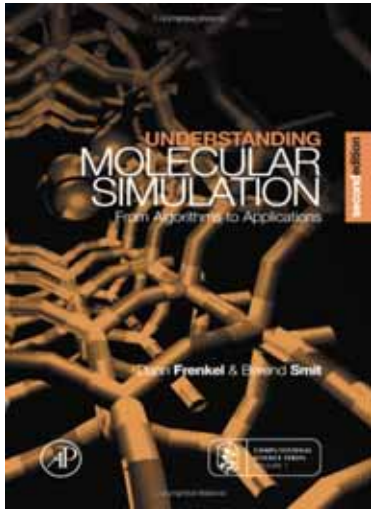
Sandia National Laboratories

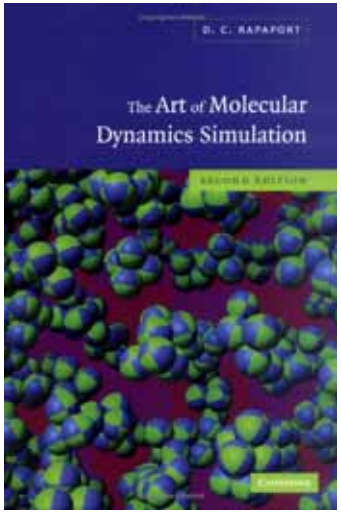
References


M.P. ALLEN
D.J. TILDESLEY
Computer Simulation of Liquids
OXFORD SCIENCE PUBLICATIONS


SECOND EDITION
Intermolecular & Surface Forces
JACOB ISRAELACHVILI

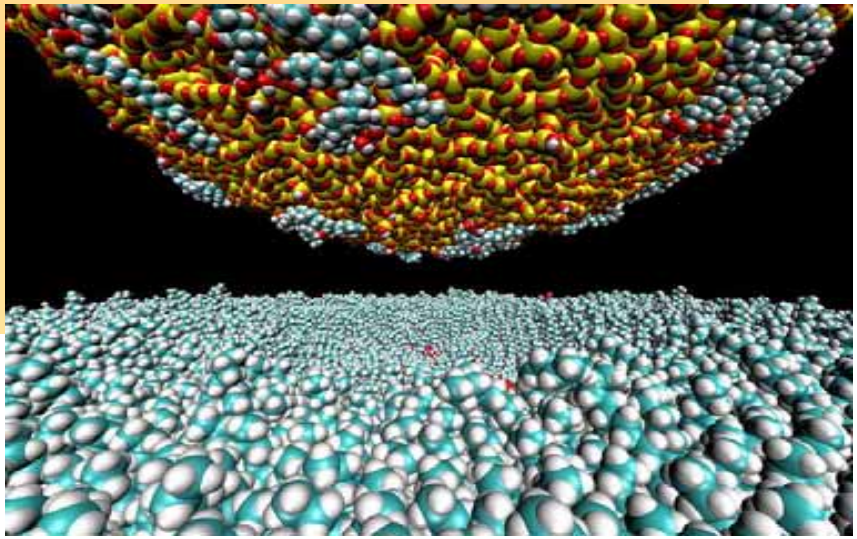

INTERDISCIPLINARY APPLIED MATHEMATICS
MATHEMATICAL BIOLOGY
Molecular Modeling and Simulation
An Interdisciplinary Guide
Tamar Schlick
Springer


UNDERSTANDING
MOLECULAR SIMULATION
From Algorithms to Applications
second edition
Daan Frenkel & Berend Smit


D. C. RAPAPORT
The Art of Molecular Dynamics Simulation

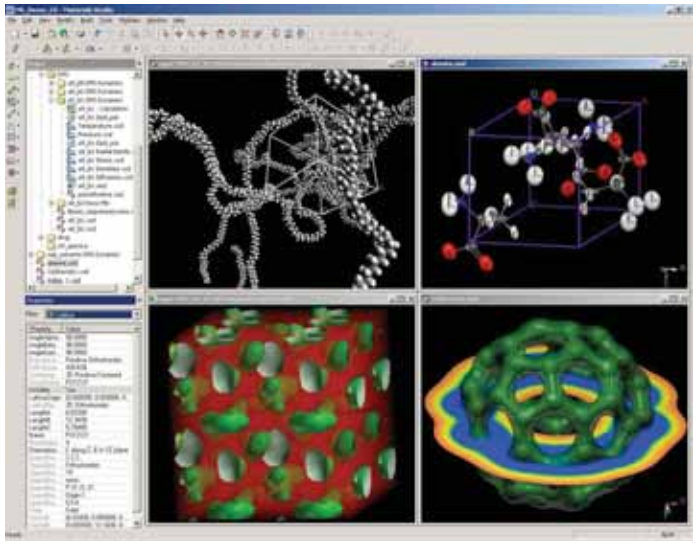
Codes

LAMMPS



lammps.sandia.gov

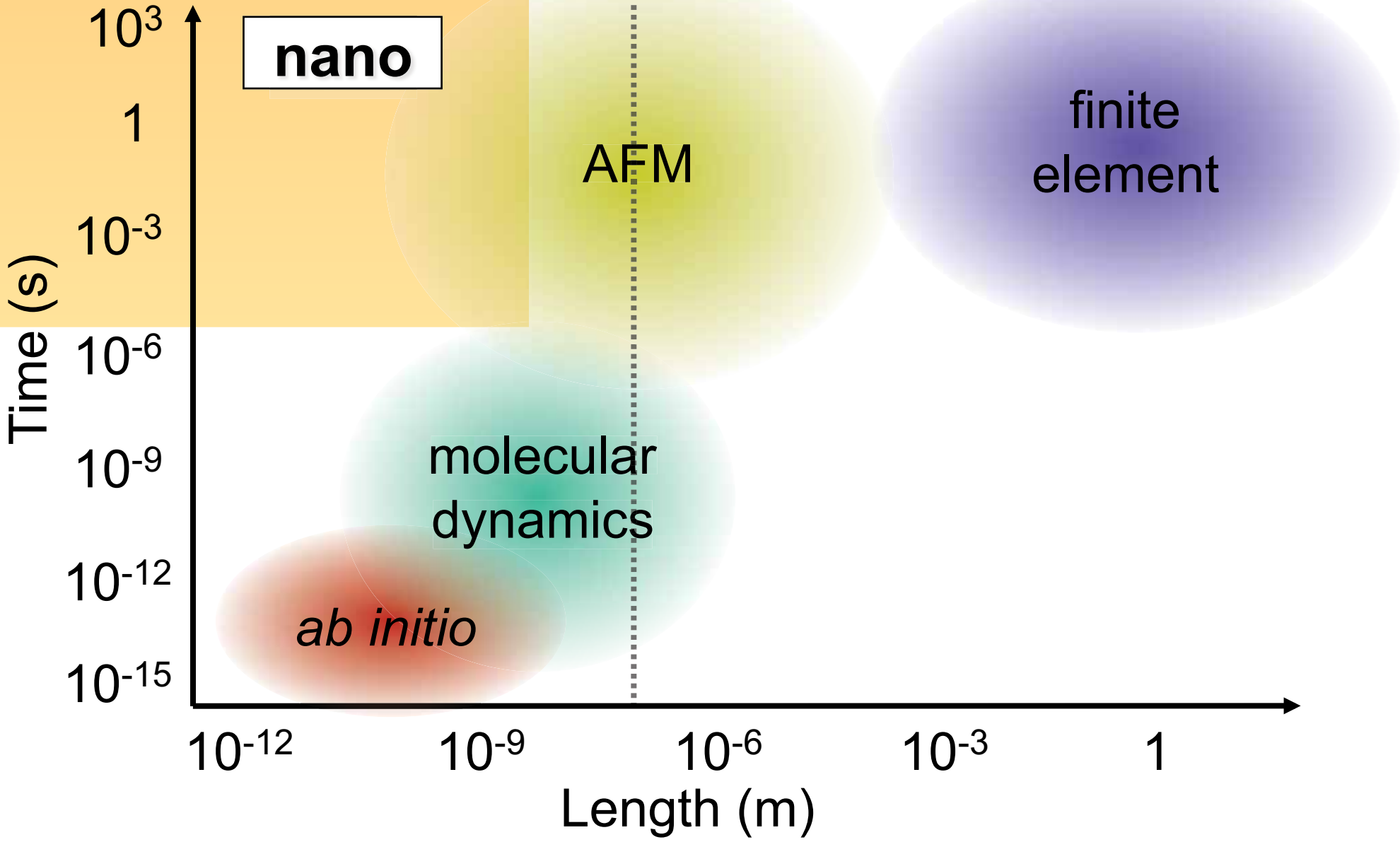
Materials Studio



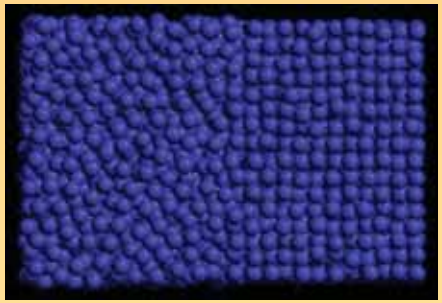
accelrys.com/products/materials-studio/

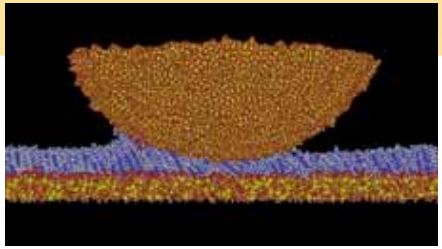
- LAMMPS: powerful, free, need some background
- Materials Studio: powerful, expensive, easy to use
- Many others out there!

Why Molecular Dynamics?



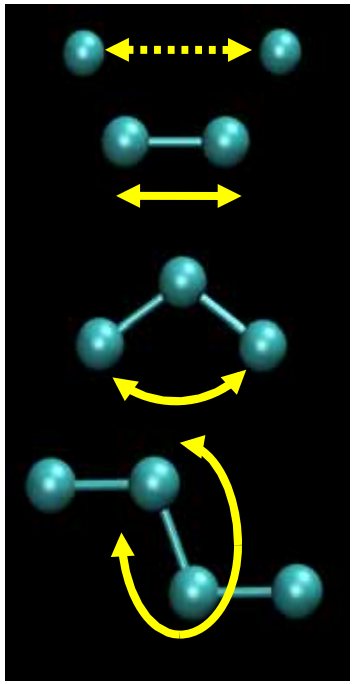
What is Molecular Dynamics?





Phitias Positions and Posotitios

Phobtiadbmiti Podbntias



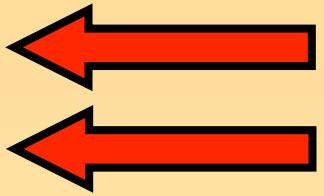
⇨

Positions and Posotitios ad sadbtitimos

Thanks to Aidan Thompson

Steps of a Simulation

1) Choose a force field
2) Create a model system
    1) Place all the atoms
    2) Define atom types & interactions
    3) Define bonds/angles/dihedrals, etc.
    4) Decide on # of processors
3) Integrate (time step ~ 1 fs)
    1) Equilibrate (~ 1 week)
    2) Compress (~ 2 weeks)
    3) Shear (~ 4 weeks per load)
4) Analyze, make movies, etc.



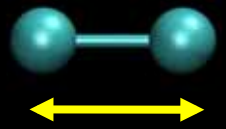
Interatomic Potentials -- General

non-bonded

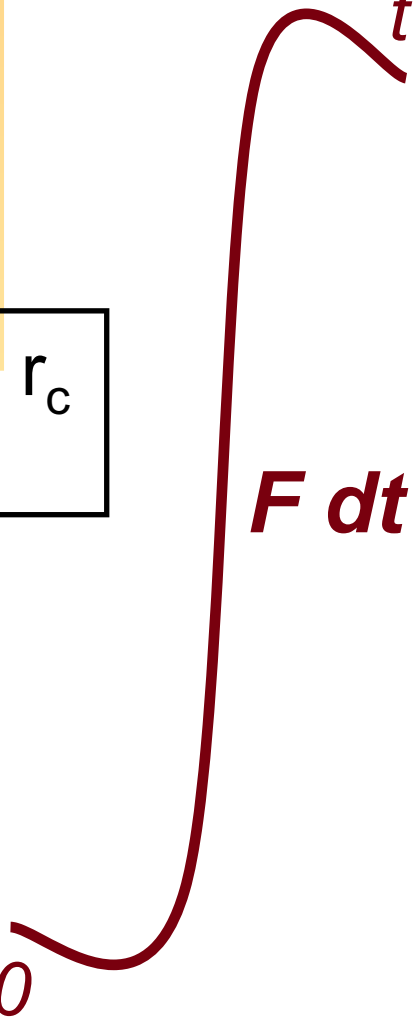
$4\varepsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}\,] \quad r < r_c$

$C\,q_i q_j/\varepsilon r$

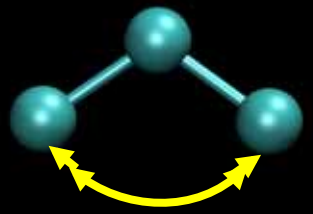
bonded



$\frac{1}{2}\,k_1\,(r - r_0)^2$

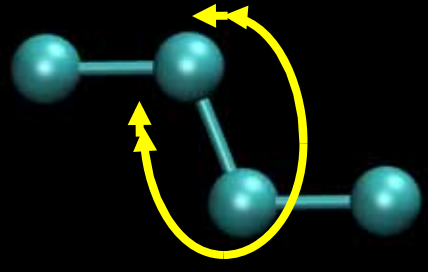


angular



$\frac{1}{2}\,k_2\,(\theta - \theta_0)^2$

torsional



$\Sigma_n\,A_n\cos^{n-1}(\phi)$

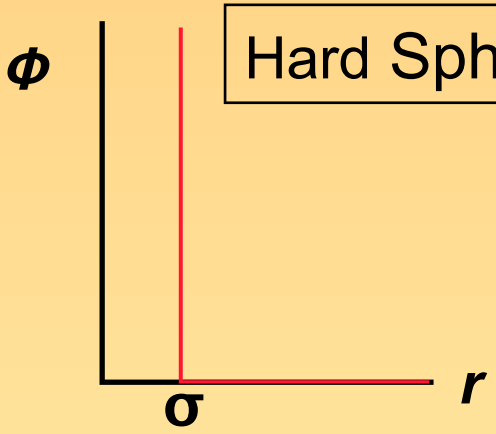
Cost of Interatomic Potentials

Force Field Style	Creators	Year	Cost
Pair Potentials			
Hard Sphere	Boltzmann	1898	1
Lennard-Jones	Lennard-Jones	1924	1
Coulomb	Coulomb	1785	1
Cluster Potentials			
Bonds, Angles, Torsions	Morse,....	1929	1
Stillinger-Weber	Stillinger & Weber	1985	2
Pair Functionals			
EAM	Daw & Baskes	1983	2
Finnis-Sinclair	Finnis & Sinclair	1984	2
Cluster Functional			
Tersoff	Tersoff	1988	4
REBO	Brenner	1990	10
MEAM	Baskes	1987	10
Most Complicated			
ReaxFF	van Duin et al.	2001	1000
BOP	Pettifor	1989	1000
GPT	Moriarty	1988	1000

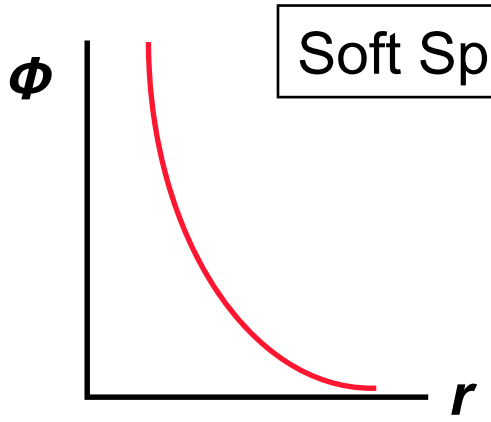
Thanks to Aidan Thompson

Pair Potentials

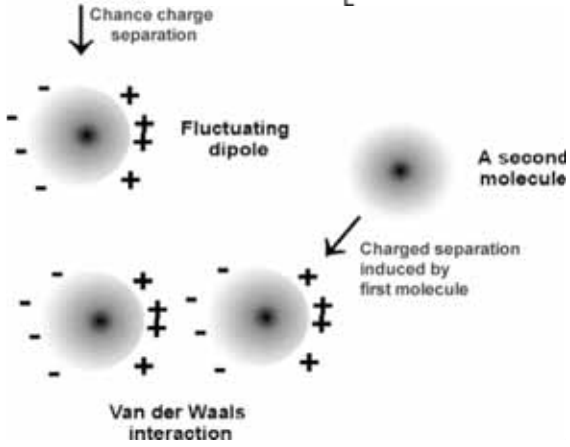
Hard Sphere

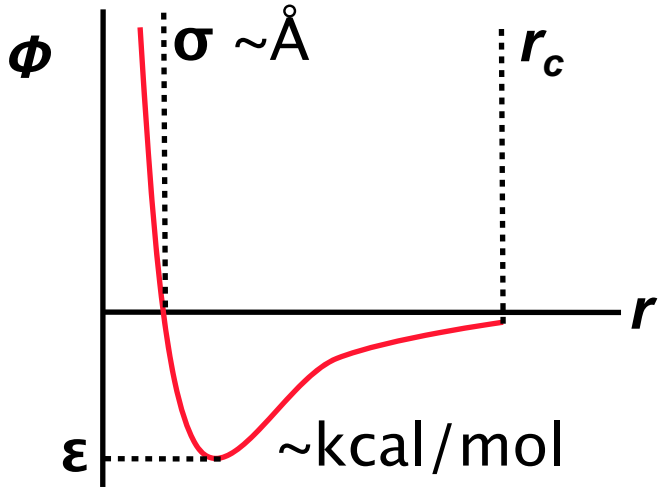


Soft Sphere

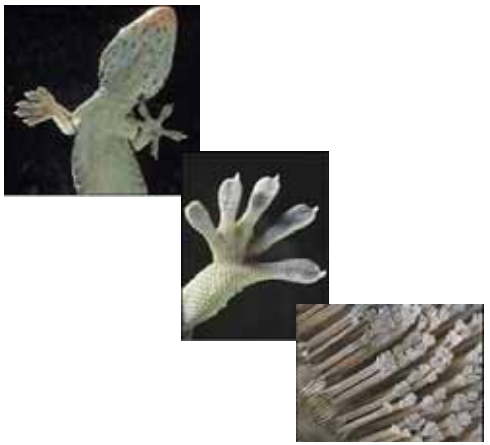


$$\phi = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$





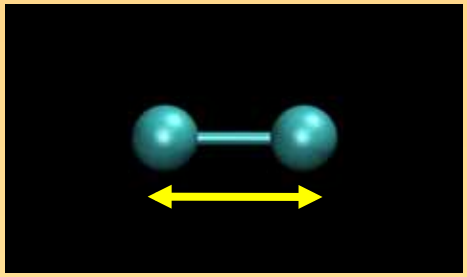
Lennard-Jones

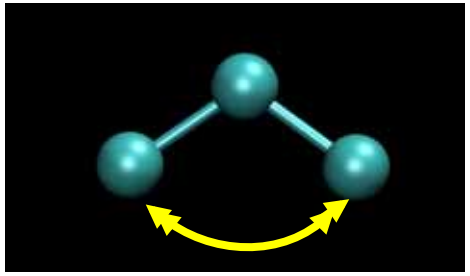


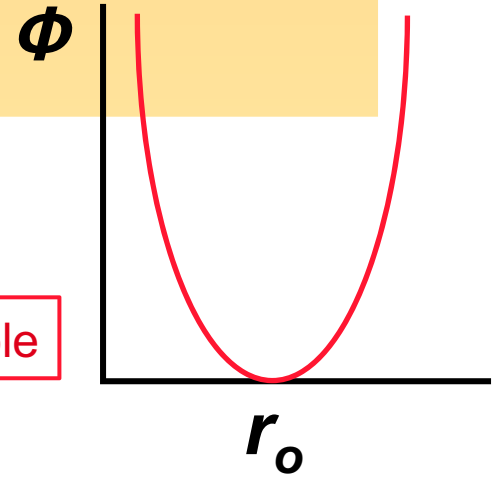
www.columbia.edu/cu/biology/courses/c200507/lectures/lec2_07.html

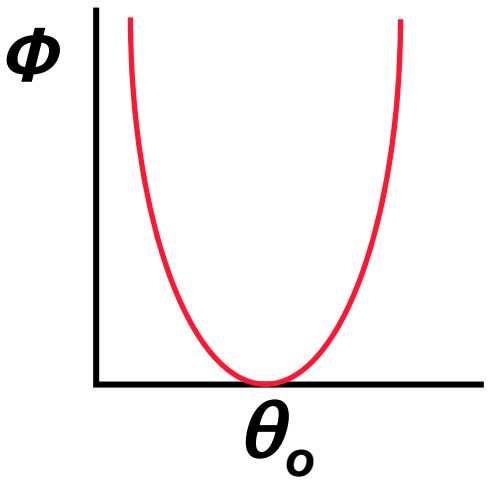
http://www.nytimes.com/2005/08/30/science/30geck.html

Bonds and Angles









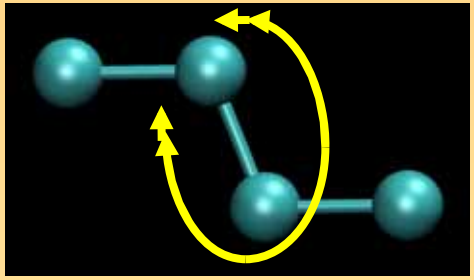
bonds

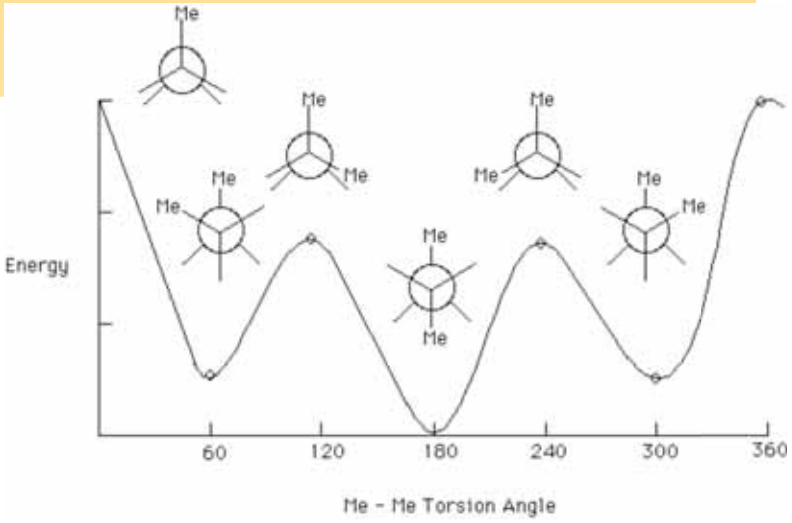
$\phi \neq 0$ ➔ unbreakable

angles

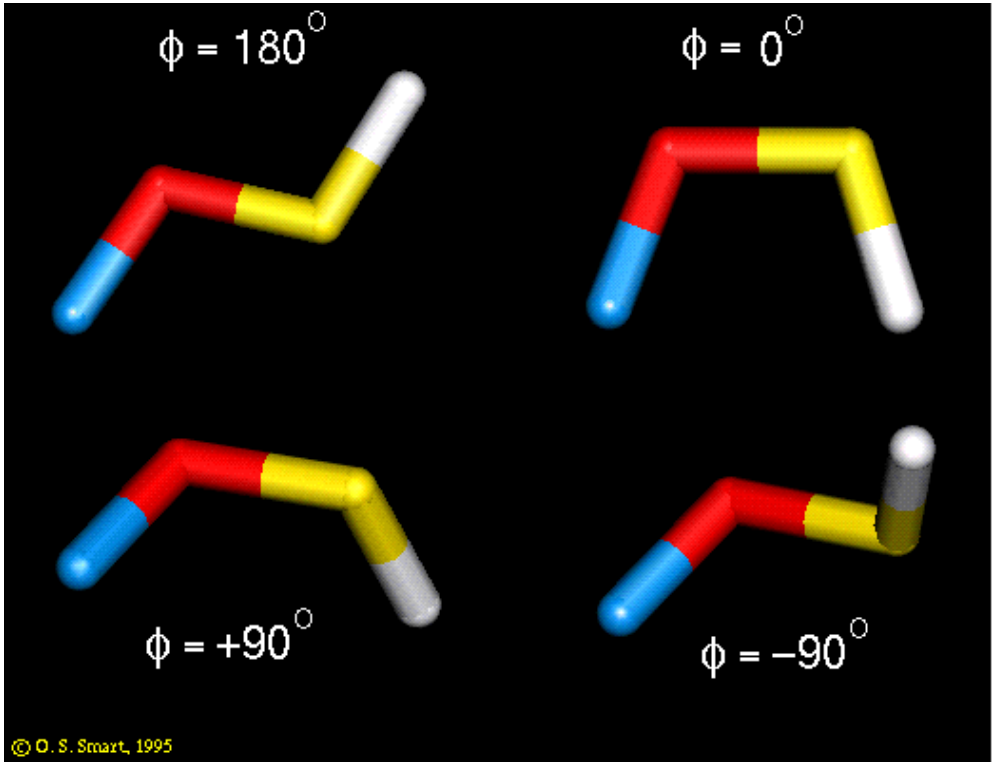
QM shows bonds and angles are reasonably harmonic for small perturbations

Dihedrals / Torsions





http://www.netsci.org/Science/Compchem/feature01.html



http://www.bip.bham.ac.uk/osmart/course/os_cov.html

Models rotational energy barriers, sometimes with steric effects

More Fun With Potentials

- Pick one:

12-6 plus 12-10 H-bond
- o Weiner et al. 1984
- o Weiner et al. 1986
- o Dick and Ritchie 1994

12-6 plus solvation
- o Charmm19 EEF1
- o Charmm19 SASA

12-9-6
- o Frischknecht and Curro 2003

9-6
- o COMPASS Version 1
- o QMFF-VIII

Buffered 14-7
- o MMFF94

Double Exponential
- o MCY 1976 water

Embedded Atom Method
- o Ackland et al. 2004 Fe and P
- o Hoyt et al. 2003 Cu and Pb
- o Mendelev et al 2003 Fe

Exponential-12-6
- o Catlow and Faux

Exponential-6
- o Kramer Farragher van Beest van Santen (also known as BKS)
- o MM2

Gordon n-6
- o Gordon

Hard 2580 Multistep or Repulsive 2580 Multistep
- o Cui and Elliott 2002

Hard Sphere or Repulsive Sphere
- o Hard Sphere

Lennard-Jones
- o Alavi et al. H2
- o Amber param96
- o Aqvist 1990 cations
- o Charmm22
- o Charmm22fe
- o supplementary parameters for fluoroethanes in CHARMM22 Charmm27
- o Charmm27x some supplementary parameters for CHARMM27
- o Charmm27 rigid water
- o ClayFF
- o Coon et al. 1987 O2 and N2
- o Cui et al. 1998 perfluorinated alkane models
- o DACNIS United Atom
- o DREIDING
- o Dubbeldam et al. alkanes and zeolites
- o Galassi and Tildesly 1994 diatomic gasses
- o Gromos 43A1
- o Jaramillo et al. 2001 Hydrofluorocarbons
- o Lastoskie et al. 1993 N2
- o Lennard-Jones beads
- o Lybrand Ghosh McCammon 1985 anions
- o Morrow and Maginn 2002 ionic liquids
- o NERD United Atom (Version 1)
- o NERD United Atom (Version 2)
- o NERD United Atom (Version 3)
- o OPLS-aa
- o OPLS-ua
- o OPLS-1996
- o OPLS-2001
- o Panagiotopoulos 1989 noble gasses
- o Potter et al. 1997 fluoromethanes
- o Richards et al. 1995 N2 and O2 in zeolite Li-X
- o Shah and Maginn 2004 ionic liquids
- o Shukla 1987 gasses
- o SKS n-alkanes
- o Smith and Dang 1994 NaCl
- o SMMK (main text) alkanes
- o SMMK (note added in proof) alkanes
- o SPC-E water
- o Sum et al. 2003
- o Teleman et al. 1987 water
- o TIP3P water
- o TIP4P water
- o TIP5P water
- o TraPPE Explicit Hydrogen
- o TraPPE United Atom
- o TraPPE United Atom flexible bonds
- o Walther et al. 2001 carbon nanotubes and water

Multiwell
- o Elliott 2002 n-alkanes and benzene

Stillinger-Weber
- o Ding and Anderson 1986 Ge
- o Stillinger and Weber 1985 Si
- o Vink et al. 2001 Si

Square Well or Repulsive Well
- o SquareWell
- o Vega et al. 1992

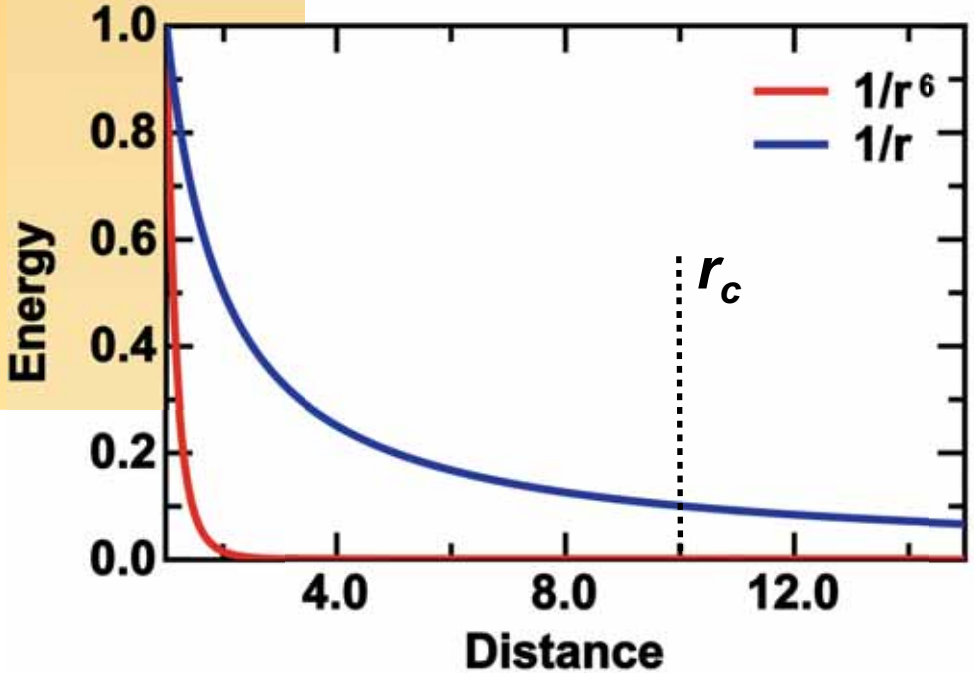
Tabulated Pair
- o No forcefield files currently available for this potential.

UFF 12-6
- o Universal Force Field (UFF)

Common Potentials

- OPLS – liquid densities, heats of vaporization
- CHARMM – Quantum chemical interactions with water
- AMBER – bio-molecules, proteins
- DREIDING – based on general hybridization
- TIP*n*P, SPC/E – water
- EAM – metals
- ReaxFF, REBO, AIREBO, TERSOFF – chemistry

Coulomb Interactions

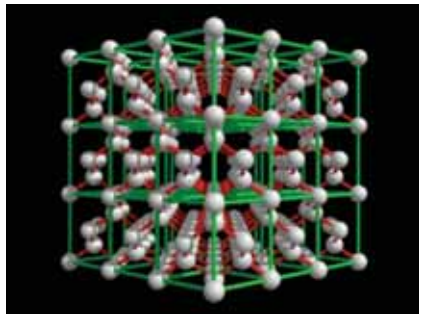


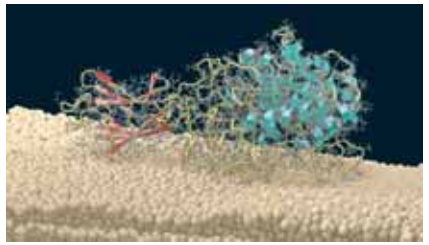
- Partial charges
- Much longer range than van der Waals
- Use Ewald summation instead of cutoff
- Calculates force between ion and potential images

Create Your System

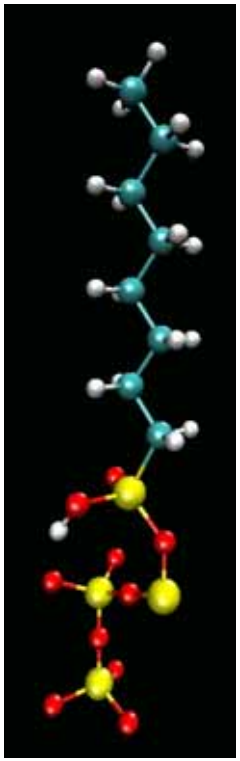
- Write or steal a creation code
  - Crystals – lattice types, orientations
  - Polymers – bonds, angles, dihedrals
  - Liquids – pressures/densities
- Periodic Boundary Conditions
  - Represent a larger system
  - Eliminate surface effects
  - Save time and effort

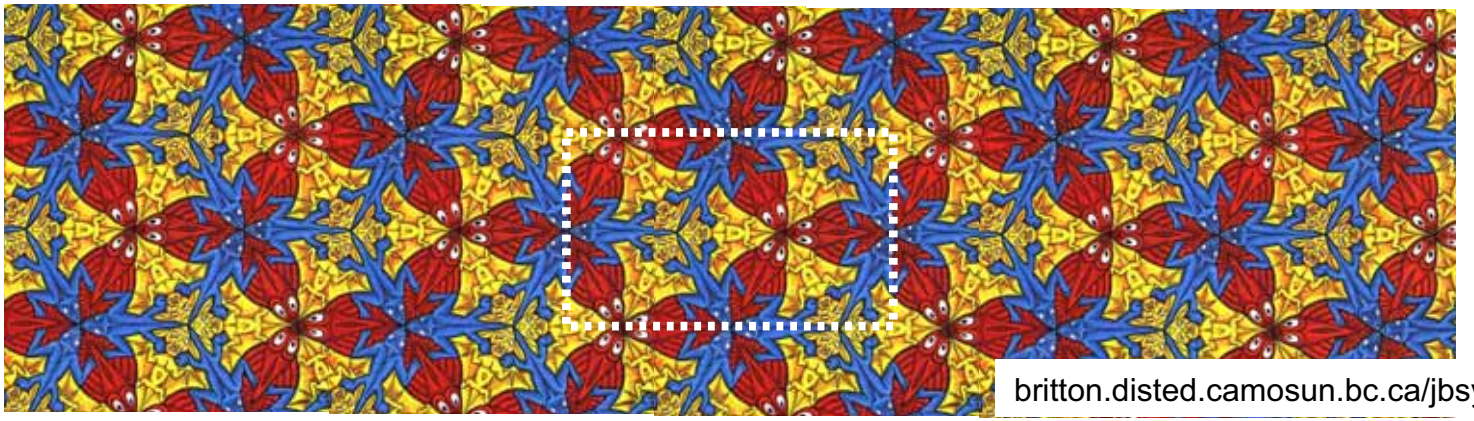
www.uncp.edu/home/mcclurem/lattice/hcp.htm





www.scidacreview.org/0704/html/hardware.html

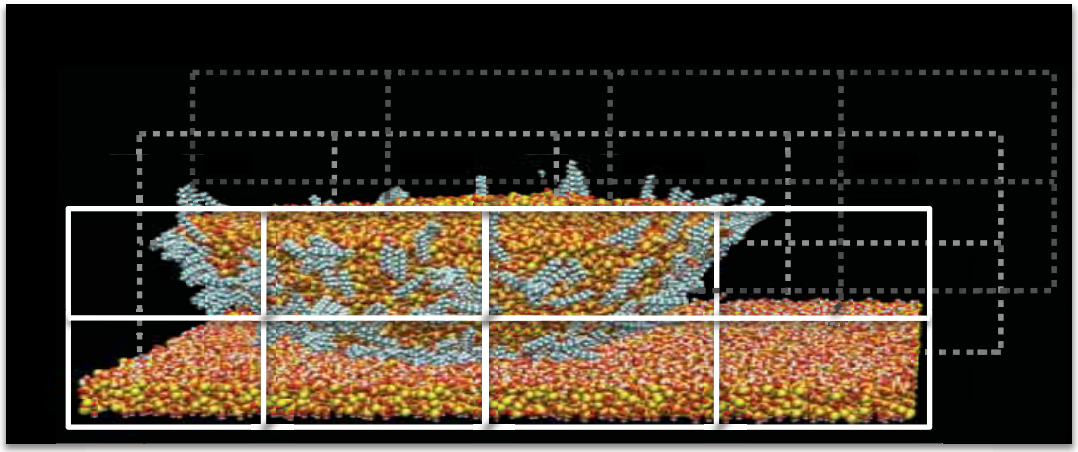


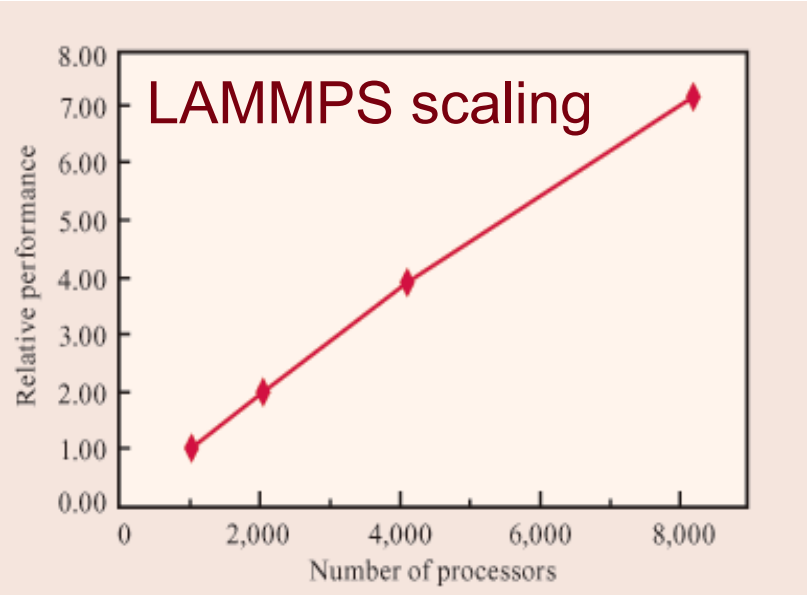


britton.disted.camosun.bc.ca/jbsymteslk.htm

Processors and Runtime

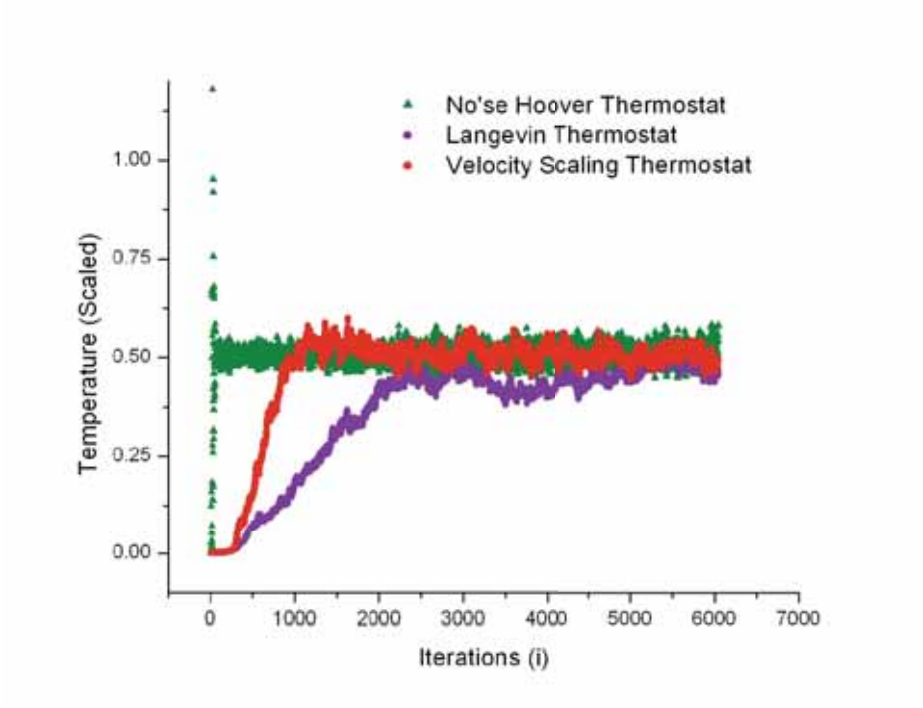
- CPU time scales with *N* and *T*
  - *N* = number of particles
  - *T* = total number of timesteps
- On *P* processors
  - Cost scales as *NT/P*
  - Load-balanced (*N/P* > 1000)
- Expected runtimes
  - Cheap potentials: 1-10 ns/day
  - Expensive potentials: 10^{-2} - 10^{-1} ns/day





www.research.ibm.com/journal/rd/521/team.html

Other Things: Thermostat

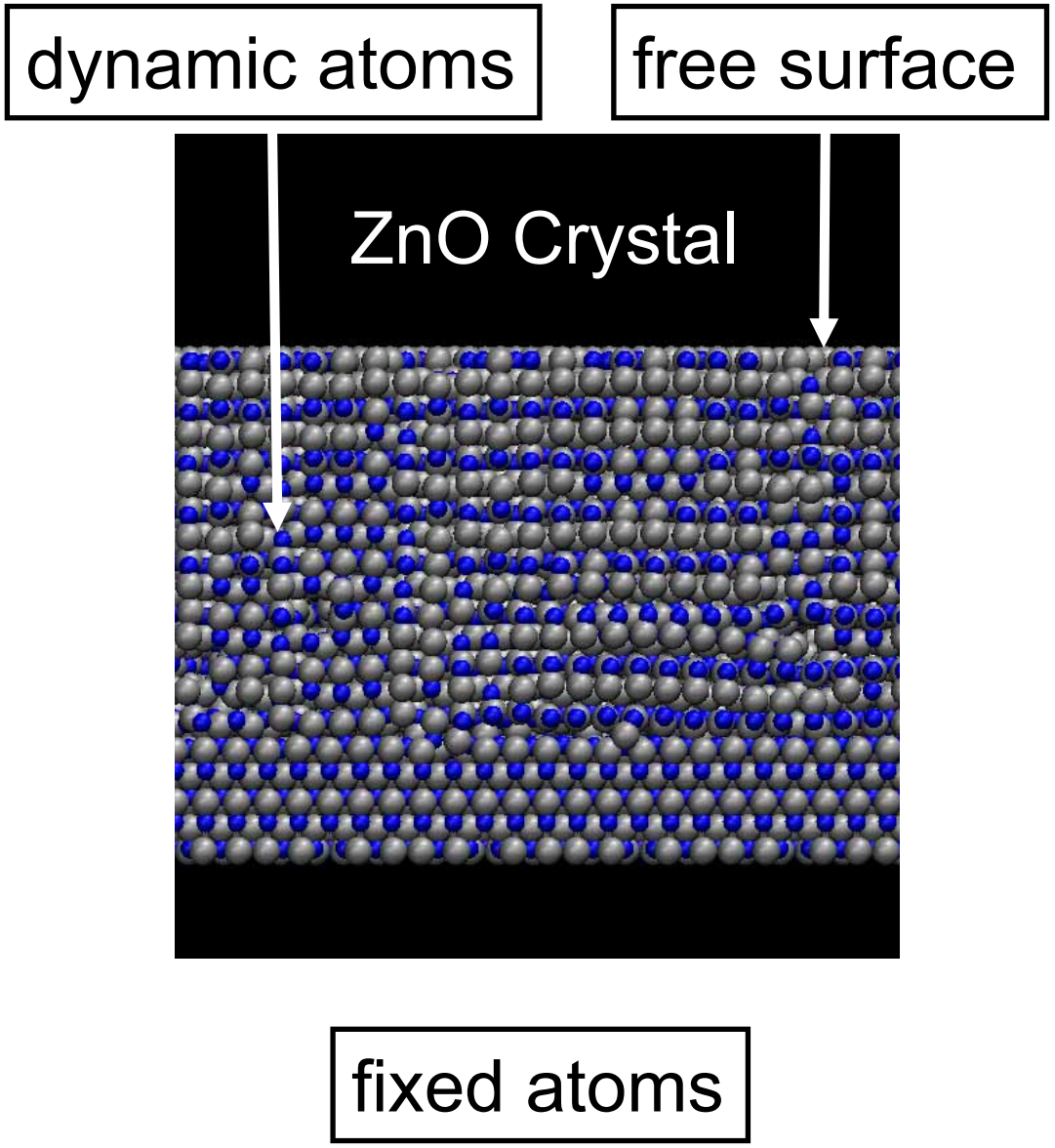


www.personal.psu.edu/auk183/MolDynamics/ThermostatComp.JPG

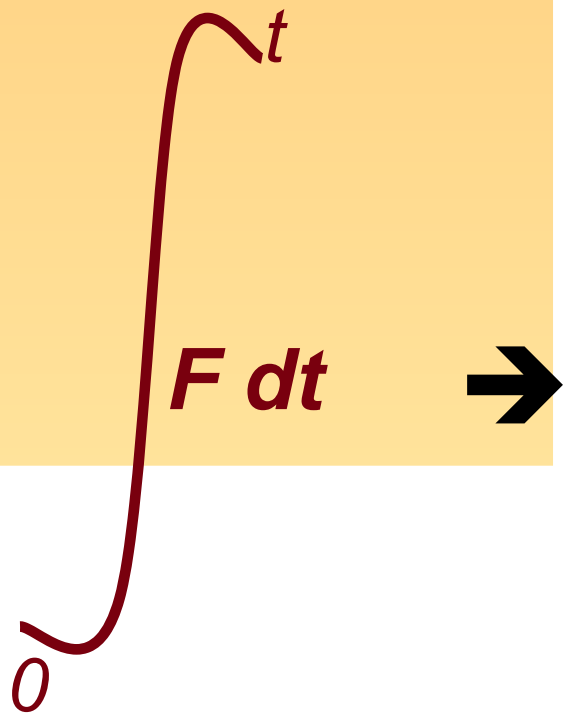
- Choice of Ensemble: NVE, NVT, NPT, etc.
- Thermostats: Velocity rescaling, Nosé-Hoover, Langevin, others.
- Choice depends on application

Other Things: Fixes

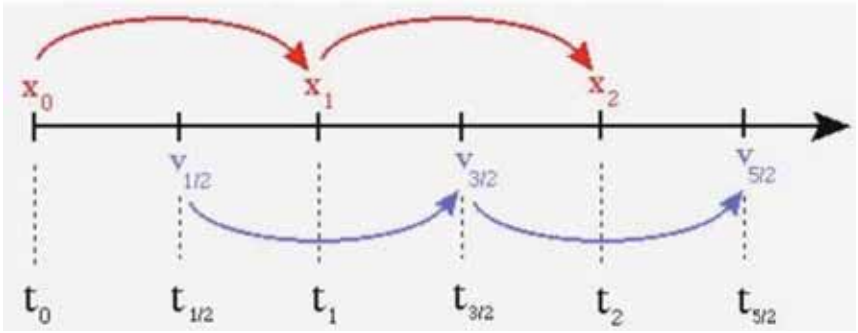
- Apply external constraints
  - Forces
  - Velocities
  - Positions
  - SHAKE/RATTLE
    - Bonds
    - Angles
- Know the effects on results
  - Dynamics
  - Temperature



Other Things: Integrators



$$v_{x,n+\frac{1}{2}} = v_{x,n-\frac{1}{2}} + \Delta t\, a_x(x_n, y_n, t)$$
$$x_{n+1} = x_n + \Delta t\, v_{n+\frac{1}{2}}$$
$$v_{x,\frac{1}{2}} = v_0 + \frac{\Delta t}{2} a_x(x_0, y_0, 0) + \left(\frac{\Delta t}{2}\right)^2 \frac{\partial a_x}{\partial x}|_{(x_0,y_0,0)}$$

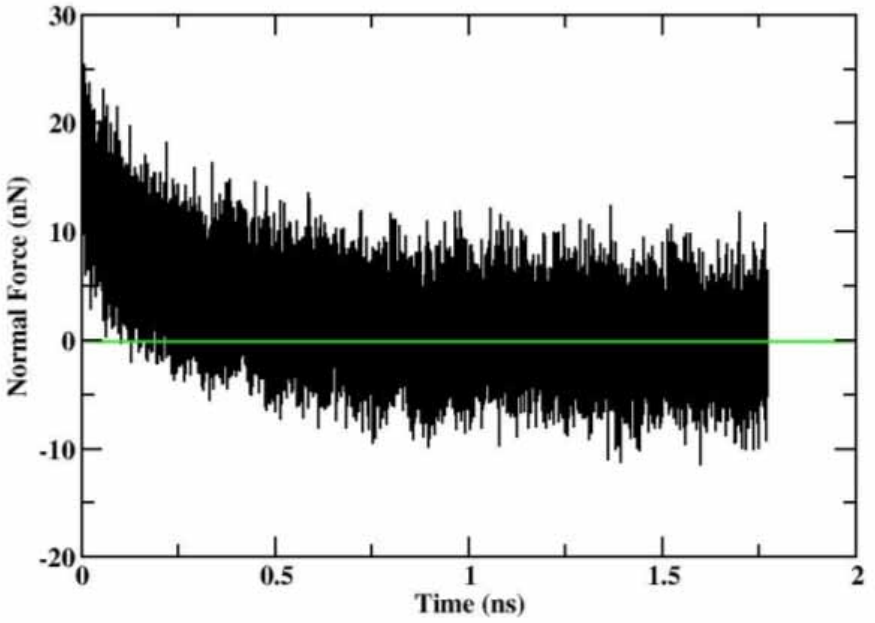


rainman.astro.uiuc.edu/ddr/ddr-galaxy/parameters.html

- *6N* coupled ODEs in *x, v*
- Velocity Verlet, leapfrog, Fifth Order Gear Predictor
- *Δt* is tied to the fastest motion in the system
  - bond vibrations ~ 10^2 fs
  - *Δt ~ 1 fs*

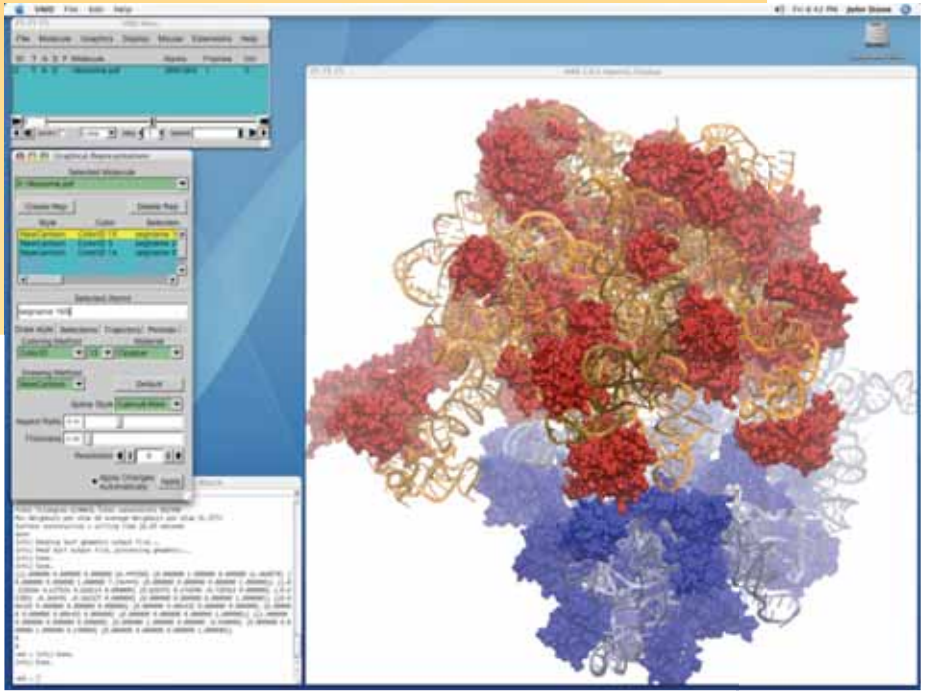
Now What?

- Run!
  - Equilibrate / Steady State
  - Take Data
- Dump Data
  - F, V, x
  - How often?
- Analyze
  - What do you want to know?
  - Error bars?
    - Actual errors?
    - Statistical Inefficiency
- Visualize



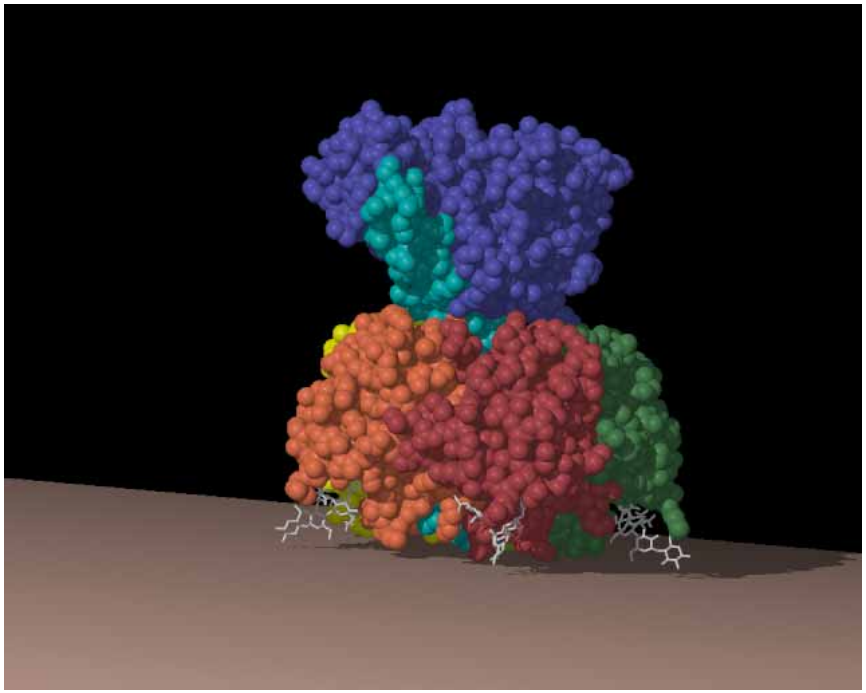
A Picture is Worth a Thousand Words

VMD



www.ks.uiuc.edu/Research/vmd/

Raster3D



skuld.bmsc.washington.edu/raster3d/

But it doesn't mean they are right!

Summary

A trained monkey can run an MD simulation.
-me

- (At least) Three phases
  - Initial planning
  - Simulation itself
  - Post analysis
  - Repeat?
- Lots of potential pitfalls
  - Be careful
  - Be critical