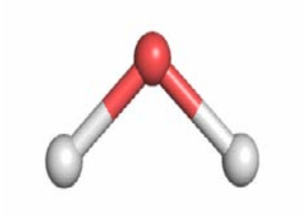
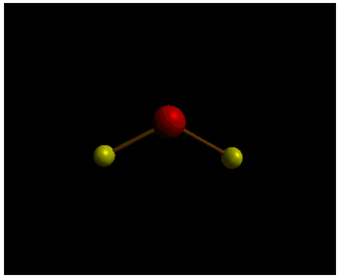
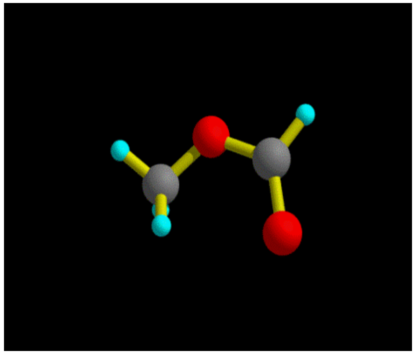
Stretch



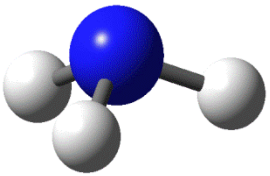
Bend



Torsion

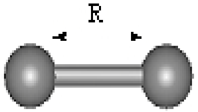
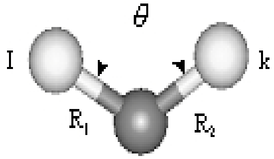
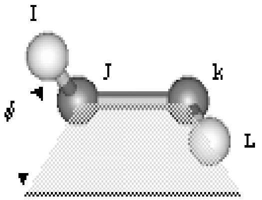
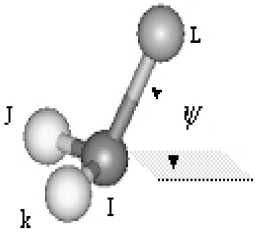


Inversion



- Energy and Forces

$$E_{total} = E_{valence} + E_{non\text{-}bond}$$

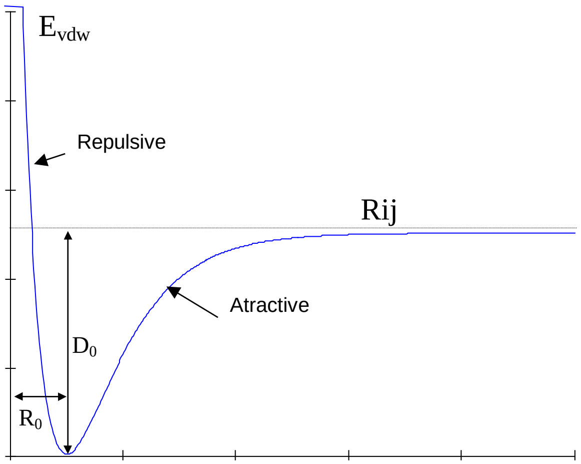
Description	Illustration	Potential
Bond Stretch		$U(r) = \frac{1}{2}k_b(R - R_0)^2$
Bond Angle bend		$U(\theta) = \frac{1}{2}k_\theta(cos\theta - cos\theta_0)^2$
Torsion		$U(\phi) = \sum_{n=1}^{p}\frac{1}{2}k_\phi(1 - cos(n\phi))$
Inversion		$U(\psi) = \frac{1}{2}k_\psi(cos\psi - cos\psi_0)^2$

Non-Bond Force Field
Coulomb and van der Waals

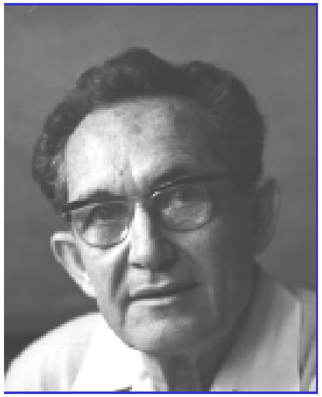
$$E_q(R_{ij}) = \Sigma_{ij}\frac{q_iq_j}{\epsilon R_{ij}}$$

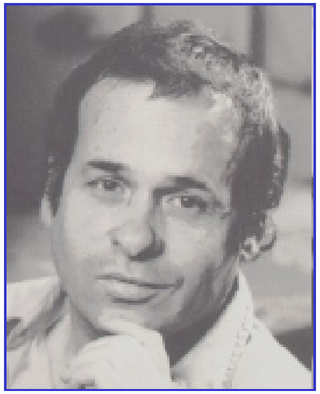
$$E_{disp}(R_{ij}) = D_0[(R/R_0)^{-12} - 2(R/R_0)^{-6}]$$

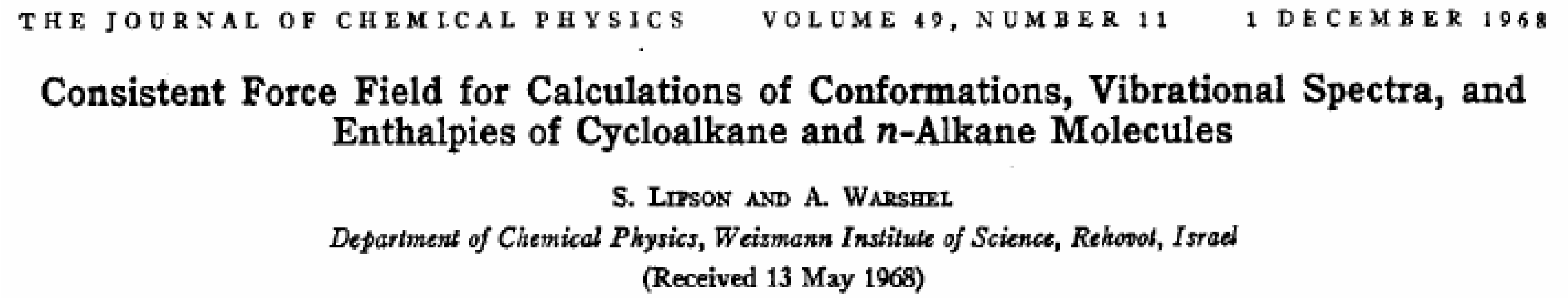
$$E_{hbond}(R_{ij}) = D_{hb}[5(R/R_0)^{-12} - 6(R/R_0)^{-6}]cos^4\theta$$



CONSISTENT FORCE-FIELD 1968







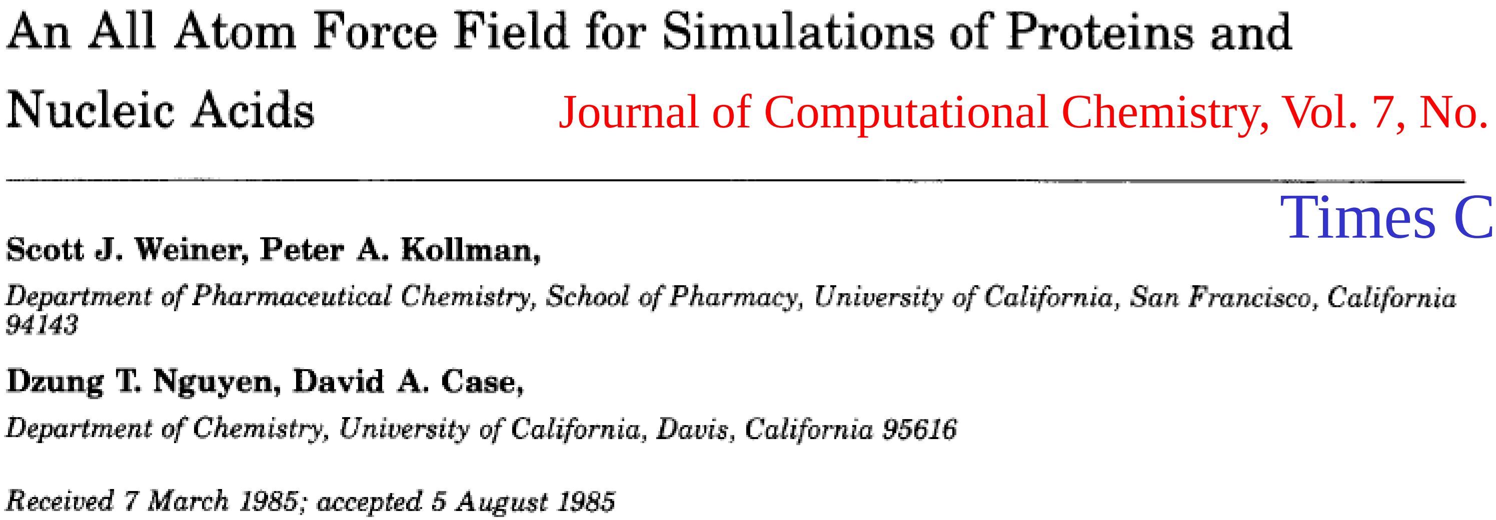
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 11 1 DECEMBER 1968

Consistent Force Field for Calculations of Conformations, Vibrational Spectra, and Enthalpies of Cycloalkane and *n*-Alkane Molecules

S. Lifson and A. Warshel

Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

(Received 13 May 1968)



An All Atom Force Field for Simulations of Proteins and Nucleic Acids

Journal of Computational Chemistry, Vol. 7, No. ***2, 230-252 (1986)***

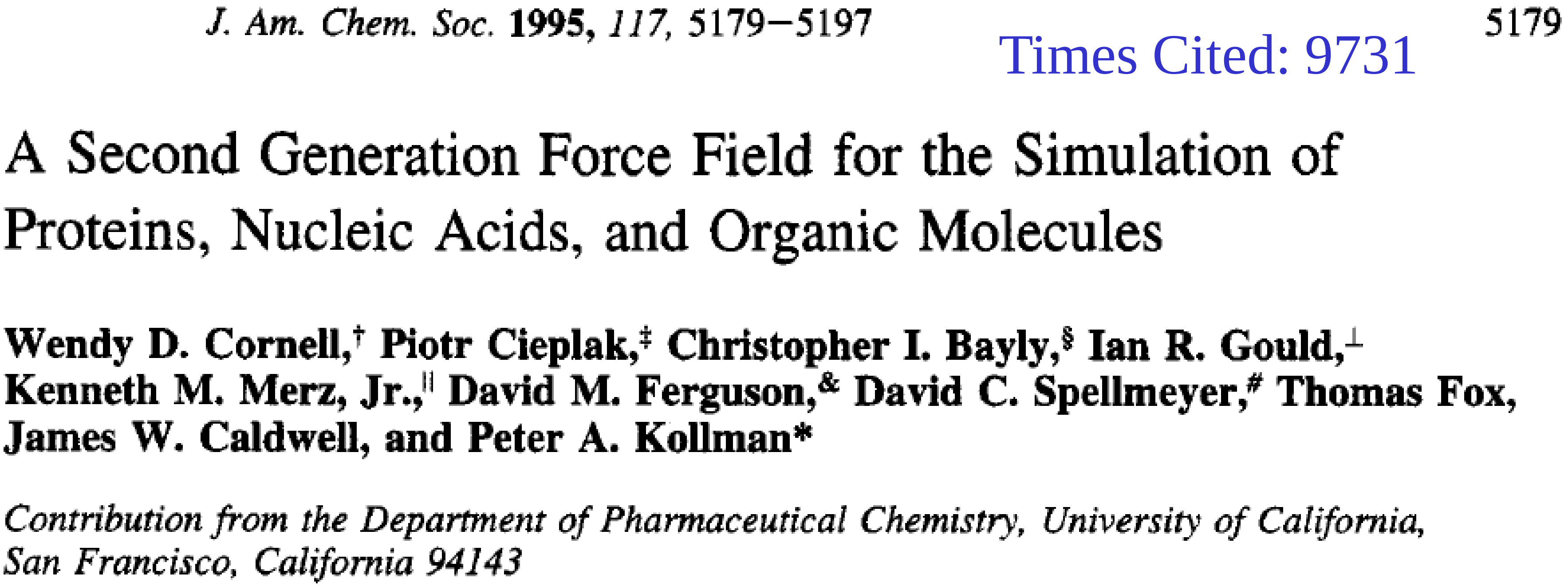
Times Cited: 4739

Scott J. Weiner, Peter A. Kollman,
Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143

Dzung T. Nguyen, David A. Case,
Department of Chemistry, University of California, Davis, California 95616

Received 7 March 1985; accepted 5 August 1985

AMBER



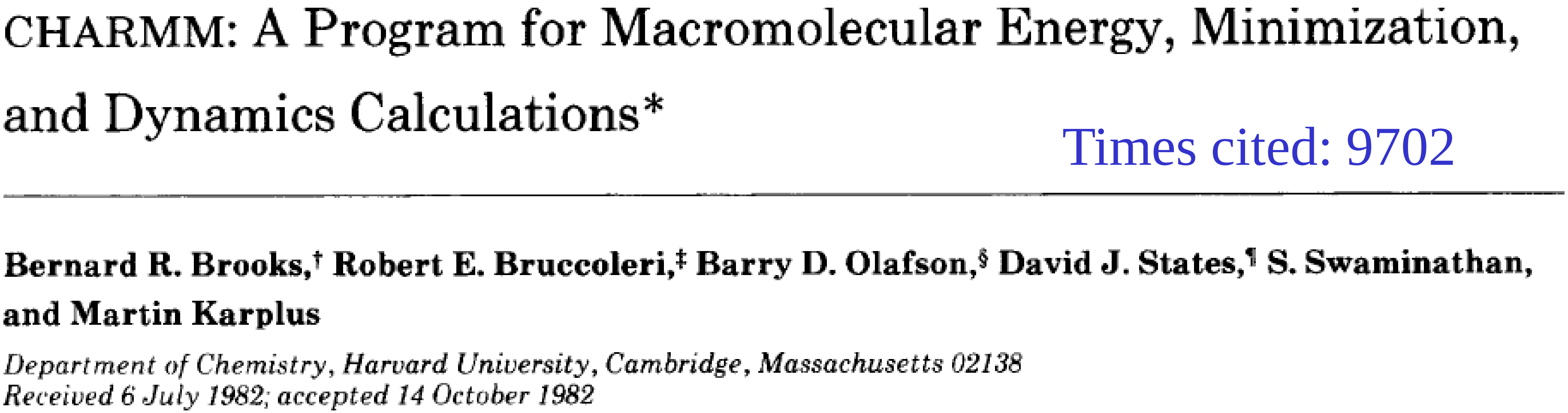
J. Am. Chem. Soc. **1995,** *117,* 5179−5197

Times Cited: 9731

A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules

Wendy D. Cornell,[†] Piotr Cieplak,[‡] Christopher I. Bayly,[§] Ian R. Gould,[⊥] Kenneth M. Merz, Jr.,[||] David M. Ferguson,[&] David C. Spellmeyer,[#] Thomas Fox, James W. Caldwell, and Peter A. Kollman*

Contribution from the Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143



CHARMM: A Program for Macromolecular Energy, Minimization, and Dynamics Calculations*

Bernard R. Brooks,[†] Robert E. Bruccoleri,[‡] Barry D. Olafson,[§] David J. States,[¶] S. Swaminathan, and Martin Karplus

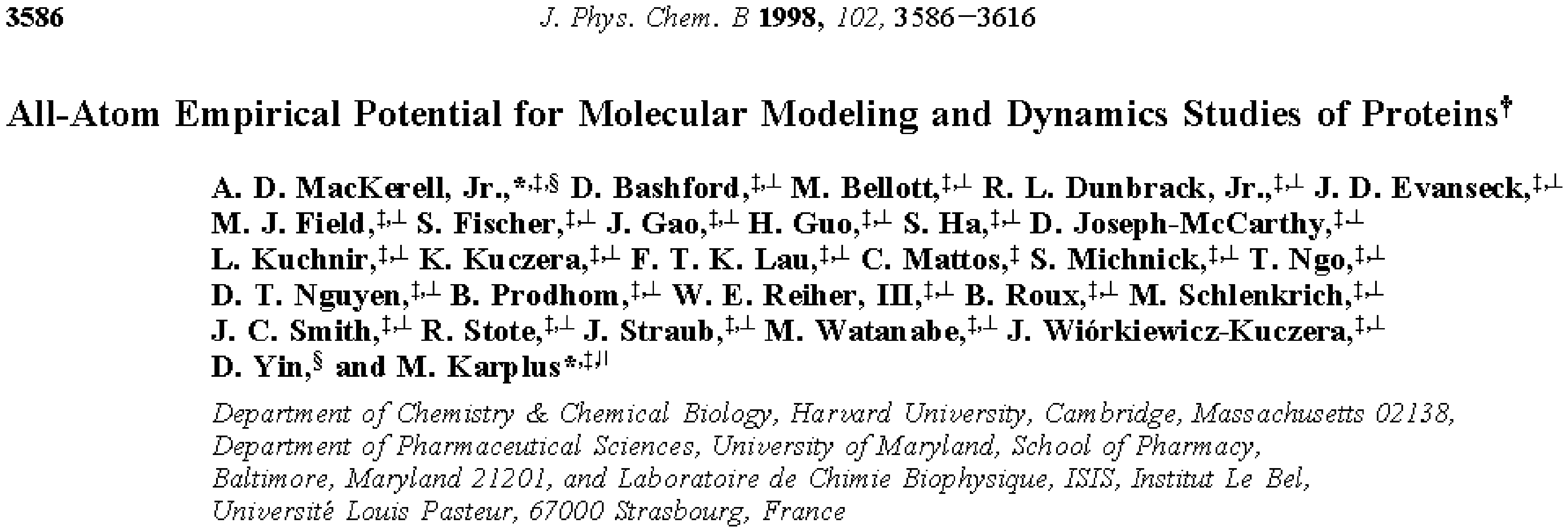
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received 6 July 1982; accepted 14 October 1982

Times cited: 9702

CHARMM

Times cited: 7736



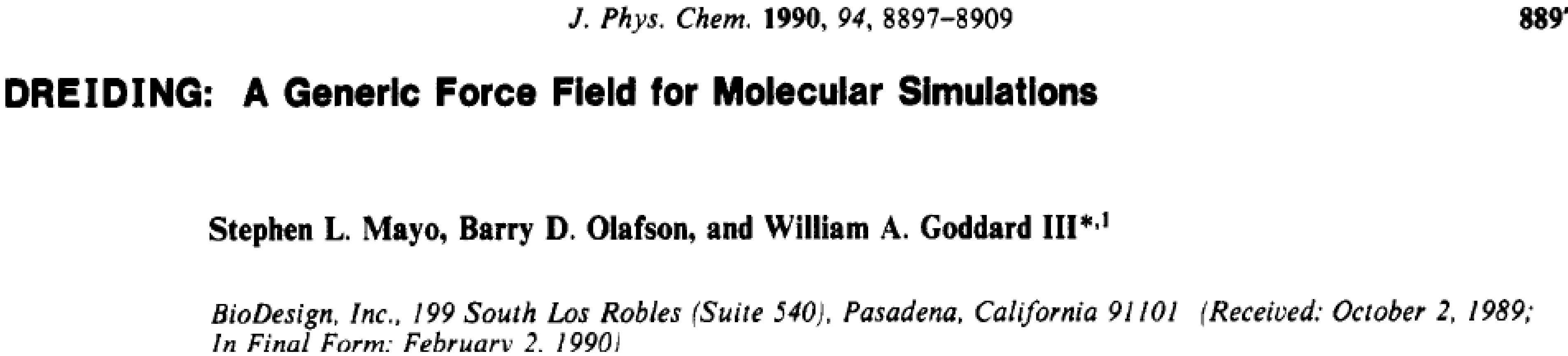
3586 *J. Phys. Chem. B* **1998,** *102,* 3586–3616

All-Atom Empirical Potential for Molecular Modeling and Dynamics Studies of Proteins[†]

A. D. MacKerell, Jr.,[*,‡,§] D. Bashford,[‡,⊥] M. Bellott,[‡,⊥] R. L. Dunbrack, Jr.,[‡,⊥] J. D. Evanseck,[‡,⊥] M. J. Field,[‡,⊥] S. Fischer,[‡,⊥] J. Gao,[‡,⊥] H. Guo,[‡,⊥] S. Ha,[‡,⊥] D. Joseph-McCarthy,[‡,⊥] L. Kuchnir,[‡,⊥] K. Kuczera,[‡,⊥] F. T. K. Lau,[‡,⊥] C. Mattos,[‡] S. Michnick,[‡,⊥] T. Ngo,[‡,⊥] D. T. Nguyen,[‡,⊥] B. Prodhom,[‡,⊥] W. E. Reiher, III,[‡,⊥] B. Roux,[‡,⊥] M. Schlenkrich,[‡,⊥] J. C. Smith,[‡,⊥] R. Stote,[‡,⊥] J. Straub,[‡,⊥] M. Watanabe,[‡,⊥] J. Wiórkiewicz-Kuczera,[‡,⊥] D. Yin,[§] and M. Karplus[*,‡,∥]

Department of Chemistry & Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, Department of Pharmaceutical Sciences, University of Maryland, School of Pharmacy, Baltimore, Maryland 21201, and Laboratoire de Chimie Biophysique, ISIS, Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France

Times cited: 3208

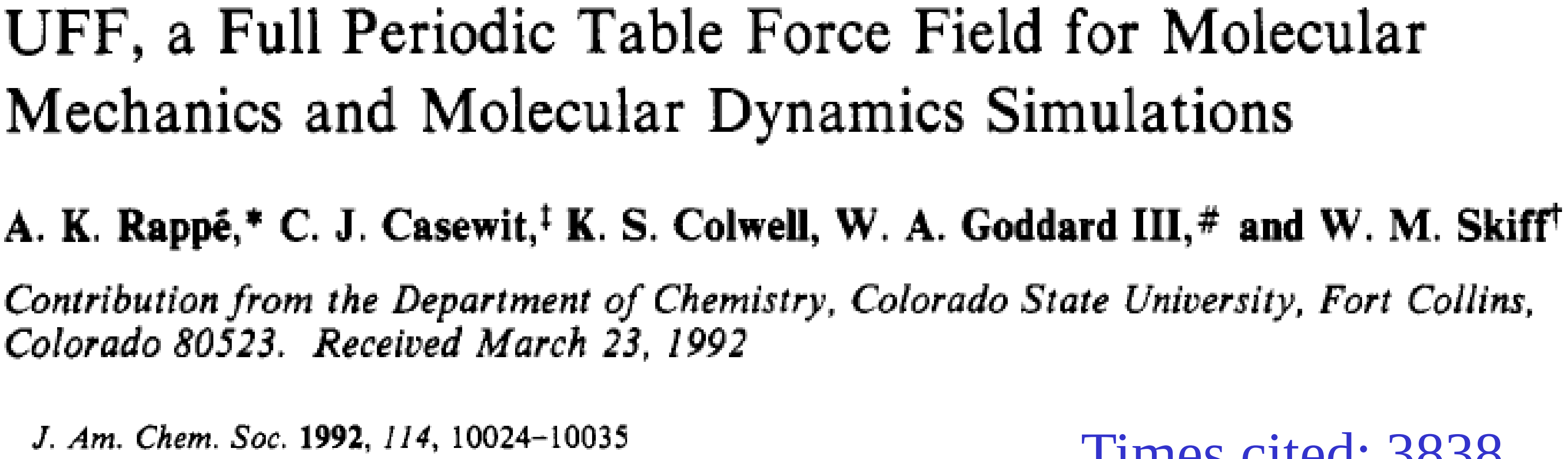


J. Phys. Chem. 1990, 94, 8897–8909 889

DREIDING: A Generic Force Field for Molecular Simulations

Stephen L. Mayo, Barry D. Olafson, and William A. Goddard III*[1]

BioDesign, Inc., 199 South Los Robles (Suite 540), Pasadena, California 91101 (Received: October 2, 1989; In Final Form: February 2, 1990)



UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations

A. K. Rappé,* C. J. Casewit,‡ K. S. Colwell, W. A. Goddard III,# and W. M. Skiff†

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received March 23, 1992

J. Am. Chem. Soc. 1992, 114, 10024–10035

Times cited: 3838

Potential Energy Function

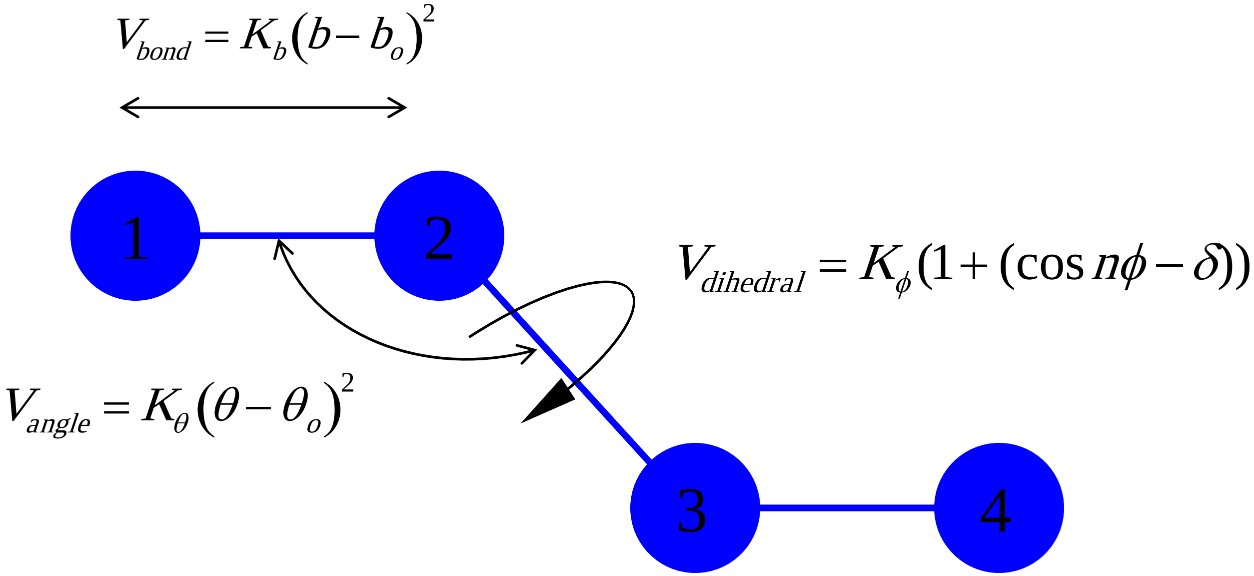
Intramolecular (internal, bonded terms)

$$\sum_{bonds} K_b (b - b_o)^2 + \sum_{angles} K_\theta (\theta - \theta_o)^2 + \sum_{torsions} K\phi \left(1 + \cos(n\phi - \delta)\right)$$

$$+ \sum_{impropers} K_\varphi (\varphi - \varphi_o)^2 + \sum_{Urey-Bradley} K_{UB} (r_{1,3} - r_{1,3,o})^2$$

Intermolecular (external, nonbonded terms)

$$\sum_{nonbonded} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right]$$



$$V_{bond} = K_b(b - b_o)^2$$

$$V_{dihedral} = K_\phi(1 + (\cos n\phi - \delta))$$

$$V_{angle} = K_\theta(\theta - \theta_o)^2$$

Intermolecular interactions between bonded atoms

1,2 interactions: 0

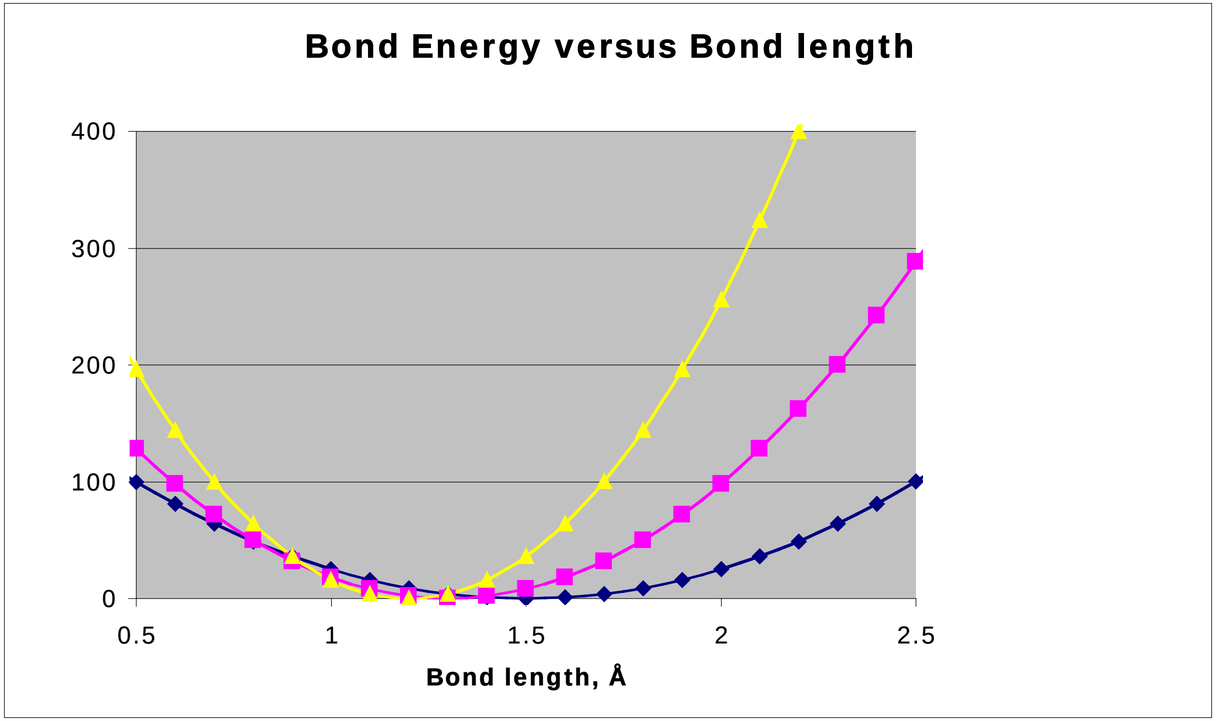
1,3 interactions: 0

1,4 interactions: 1 or scaled

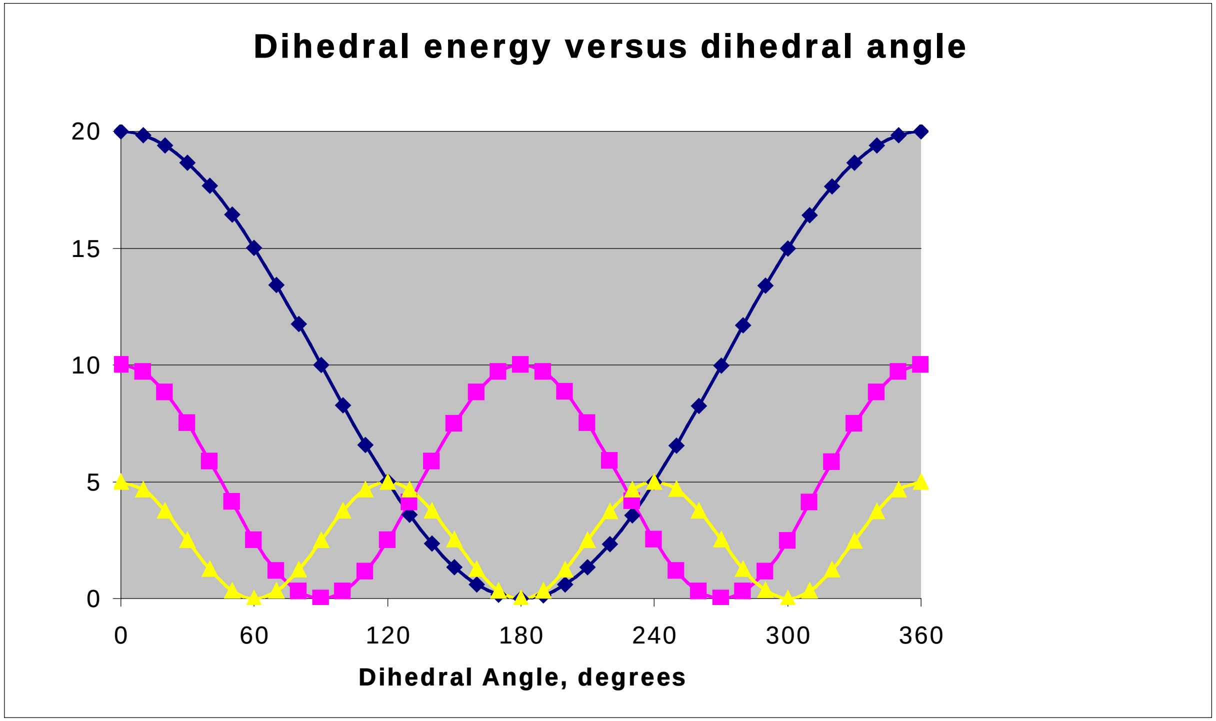
> 1,4 interactions: 1

$$V_{bond} = K_b (b - b_o)^2$$

Chemical type	K_{bond}	b_o
C-C	100 kcal/mole/Å^2	1.5 Å
C=C	200 kcal/mole/Å^2	1.3 Å
C=-C	400 kcal/mole/Å^2	1.2 Å



$$V_{dihedral} = K_{\phi}(1 + (\cos n\phi - \delta))$$

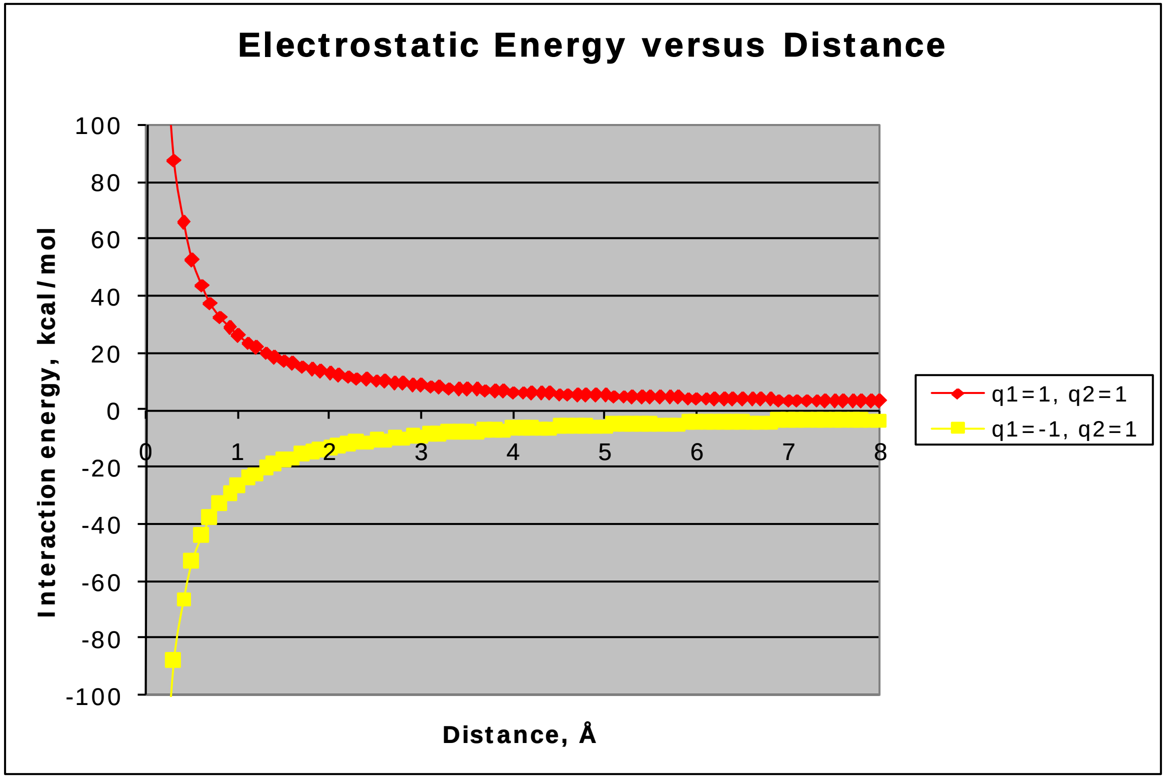


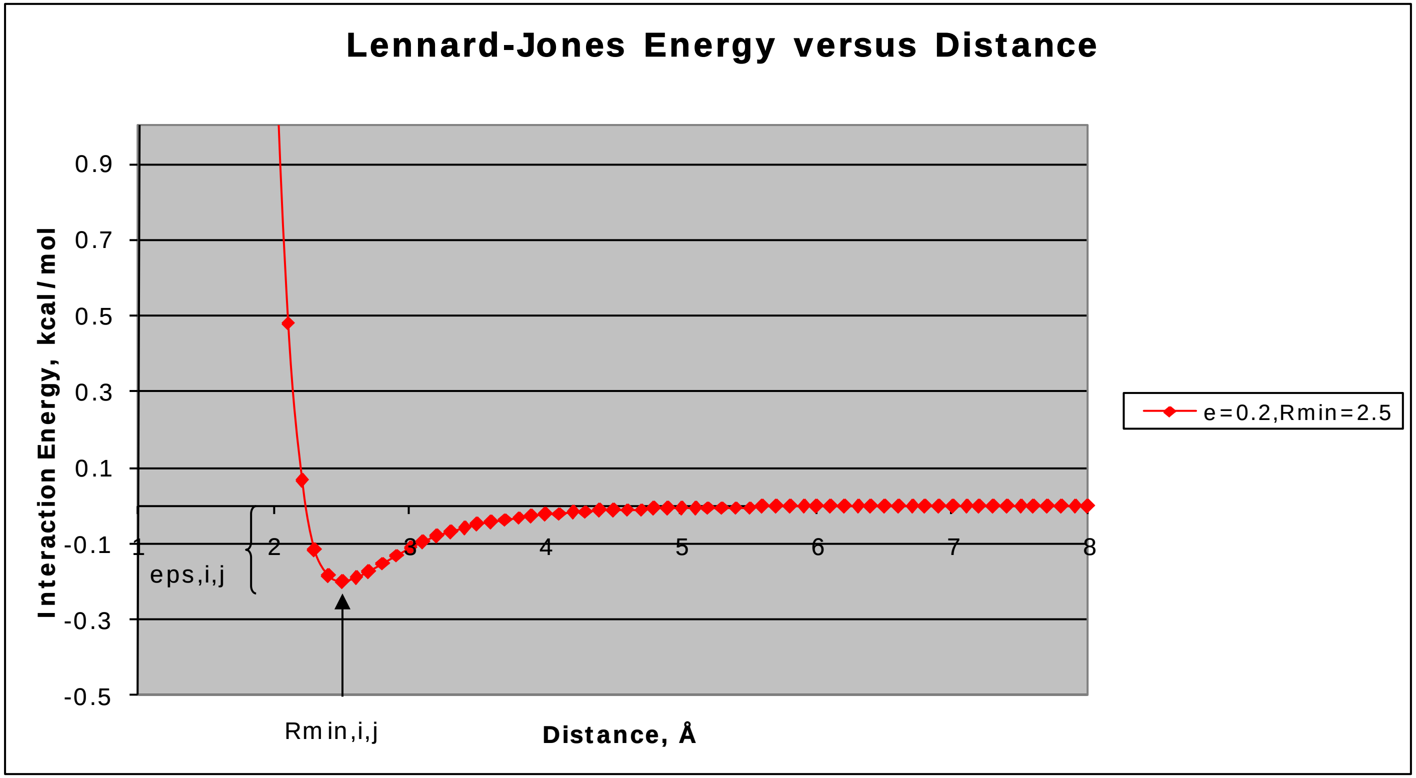
$\delta = 0^\circ$

Intermolecular parameters

$$\sum_{nonbonded} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right]$$

q_i: partial atomic charge
D: dielectric constant
ε: Lennard-Jones (LJ, vdW) well-depth
R_{min}: LJ radius (R_{min}/2 in CHARMM)
Combining rules (CHARMM, Amber)
$R_{min\ i,j} = R_{min\ i} + R_{min\ j}$
$\varepsilon_{i,j} = \mathrm{SQRT}(\varepsilon_i * \varepsilon_j)$


Electrostatic Energy versus Distance
Interaction energy, kcal/mol
100
80
60
40
20
0
-20
-40
-60
-80
-100
0
1
2
3
4
5
6
7
8
Distance, Å
q1=1, q2=1
q1=-1, q2=1



$$\varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12}-2\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right]$$

Alternate intermolecular terms

$$V_{Hbond} = \sum_{Hbonds} \varepsilon_{HB} \left[\left(\frac{R_{HB,A-H}}{r_{A-H}} \right)^{12} - \left(\frac{R_{HB,A-H}}{r_{A-H}} \right)^{10} \right] * \cos(\theta_{A-H-D})$$

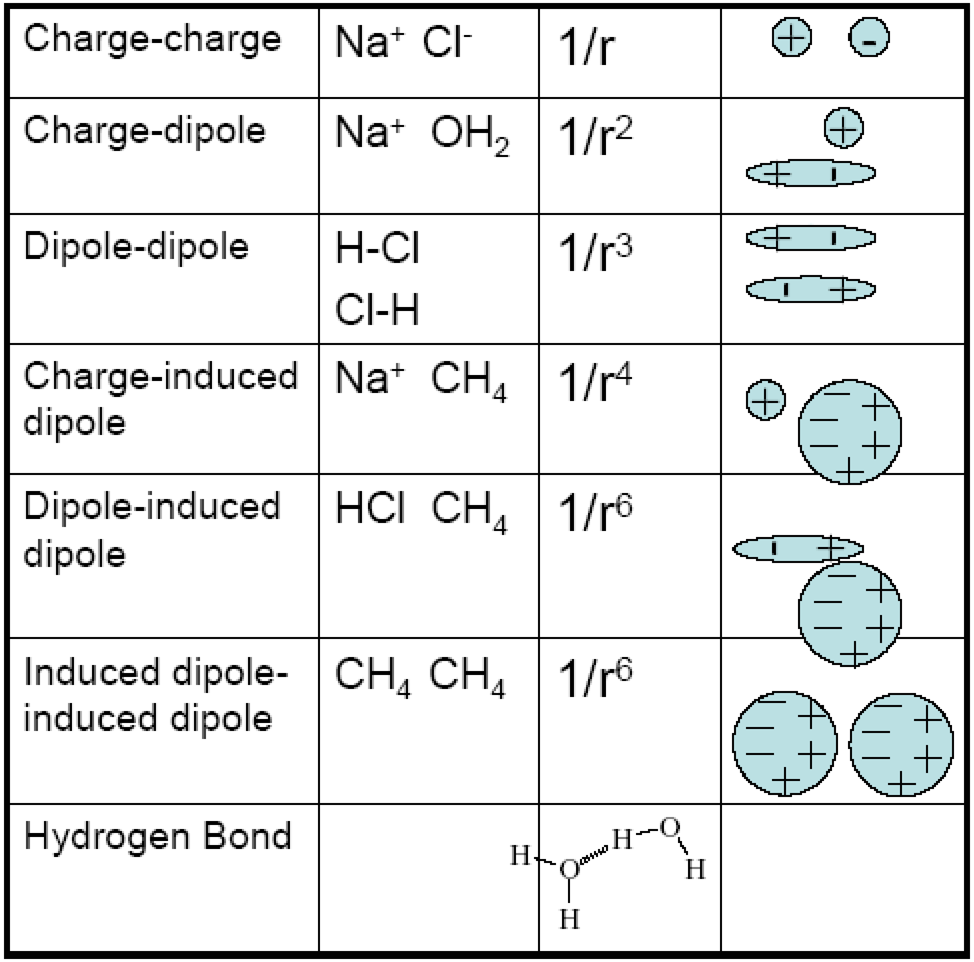
$$V_{vdw} = \sum_{vdw} \varepsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{9} - \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right]$$

$$V_{vdw} = \sum_{vdw} \varepsilon_{ij} \left(e^{\frac{-ar_{ij}}{R_{\min,ij}}} - \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right)$$

Buckingham potential

$$V_{Morse} = D_e \left(1 - e^{\alpha(R_e - r)} \right)^2$$

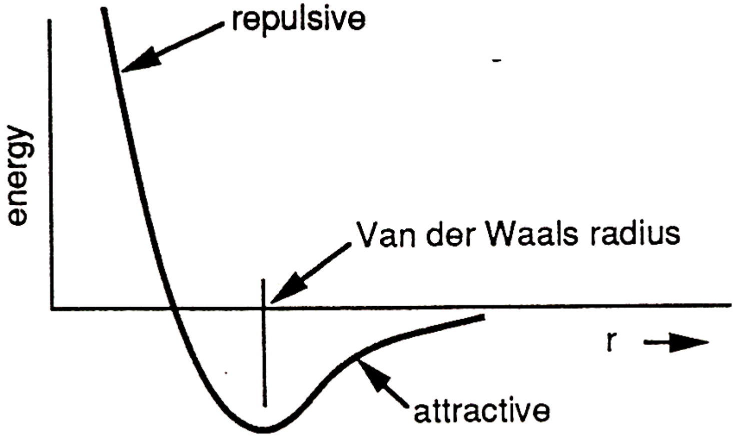
Various kind of non-bond interactions



Charge-charge	Na^+ Cl^-	$1/r$	
Charge-dipole	Na^+ OH_2	$1/r^2$	
Dipole-dipole	H-Cl Cl-H	$1/r^3$	
Charge-induced dipole	Na^+ CH_4	$1/r^4$	
Dipole-induced dipole	HCl CH_4	$1/r^6$	
Induced dipole-induced dipole	CH_4 CH_4	$1/r^6$	
Hydrogen Bond			

van der Walls
Dispersion forces

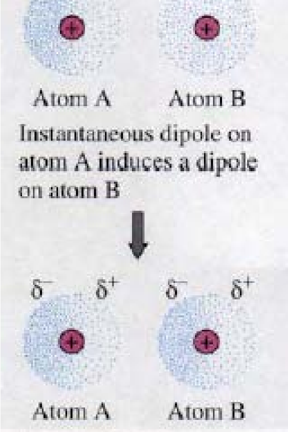
A simple model to explain dispersive interaction was proposed by London using quantum mechanics. The dispersive force is due to the instantaneous dipoles which arise during fluctuations of electron clouds. An instantaneous dipole in a molecule can in turn induce a dipole in the neighboring atoms, giving rise to an attractive interactions.

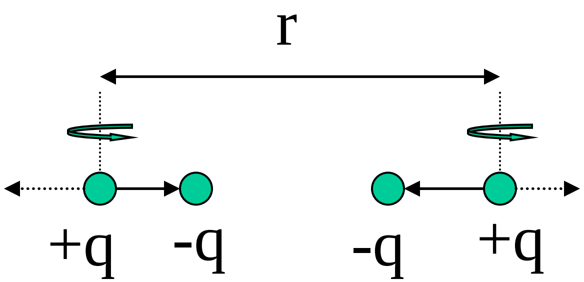


Dispersive Forces (London dispersive forces, van der Waals)

$V_{VDW} = -a/r^6$ (Attractive force)

Lennard-Jones Potential: $V(r)_{LJ} = -(a/r^6 - b/r^m)$





The negative charge performs simple harmonic motion with angular frequency ω along the z-axis about the stationary positive charge.

Think about Hydrogen atom (electron moving around proton). See Chaikin and Lubensky for an alternative derivation.

If the force constant of the oscillation is k and if the mass of the oscillating charge is m, then the potential energy of an isolated Drude molecule is $1/2kz^2$, where z is the separation of the charges and ω is related to the force const. $\omega=\sqrt{k/m}$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial z^2}+\frac{1}{2}kz^2=E\psi$$

Energy of the system is given by $E_n = (n+1/2)\,\hbar\omega$. The ZPE is $1/2\,\hbar\omega$

We now introduce a second Drude molecule, identical to the first, with positive charge also located on the z-axis and an oscillating negative charge. When the two molecules are infinitely seperated they do not interact and the total ground state energy of the system is just twice the ZPE ~ħω. The instantaneous dipole of each molecule is *qz*. As they are close interaction arises due to the dipolar interaction given by (*r* is the separation of the molecules)

$$v(\mu_1,\mu_2)=-2\frac{\mu_1\mu_2}{4\pi\varepsilon_0 r^3}=-2\frac{z_1 z_2 q^2}{4\pi\varepsilon_0 r^3}$$

The Schrodinger equation for this system is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial z_1^2}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial z_2^2}+[\frac{1}{2}kz_1^2+\frac{1}{2}kz_2^2-2\frac{z_1 z_2 q^2}{4\pi\varepsilon_0 r^3}]=E\psi$$

The equation can be solved by making following transformation

$$a_1=\frac{z_1+z_2}{\sqrt{2}};\, a_2=\frac{z_1-z_2}{\sqrt{2}};\, k_1=k-\frac{2q^2}{4\pi\varepsilon_0 r^3};\; k_2=k+\frac{2q^2}{4\pi\varepsilon_0 r^3}$$

With the above transformation the above equation becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial a_1^2}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial a_2^2}+[\frac{1}{2}ka_1^2+\frac{1}{2}ka_2^2]=E\psi$$

This is the Schrodinger equation for two independent oscillators with frequencies given as follows

$$\omega_1=\omega\sqrt{1-\frac{2q^2}{4\pi\varepsilon_0 r^3 k}};\ \omega_2=\omega\sqrt{1+\frac{2q^2}{4\pi\varepsilon_0 r^3 k}}$$

The ground state energy of the system is just the sum of the ZPE of two oscillators

$$E_0=\frac{1}{2}\hbar(\omega_1+\omega_2)$$

If we now substitute for ω_1 and ω_2 and expand the square roots

$$E_0(r)=\hbar\omega-\frac{q^4\hbar\omega}{2(4\pi\varepsilon_0)^2 r^6 k^2}$$

The interaction energy of the two oscillators is the difference between this ZPE and the energy of the system when the oscillators are infinitely separated

$$v(r) = -\frac{q^4 \hbar\omega}{2(4\pi\varepsilon_0)^2 r^6 k^2}$$

The force constant k is related to the polarisability of the molecule as follows: suppose a single Drude molecule is exposed to an external electric field E. In the electric field, a force *qE* acts on each charge (in opposite directions as the charges are of opposite sign). This force causes the charges to separate and equilibrium is reached when the restoring force due to the stretching of the bond (*kz*) is equal to the electrostatics force: *qE =kz*

This separation of the charges is equivalent to a static dipole given by

$$\mu_{ind} = qz = q^2 E / k = \alpha \boldsymbol{E}$$

Thus the polarisability is given by

$$\alpha = q^2 / k$$

So the interaction energy is given by

$$v(r) = -\frac{\alpha^4 \hbar\omega}{2(4\pi\varepsilon_0)^2 r^6}$$

The Drude model only considers dipole-dipole interactions, if higher order terms such as dipole-quadrupole etc are included the interaction energy can be written as a series expansion

$$V(r) = a/r^6 + b/r^8 + c/r^{10}$$

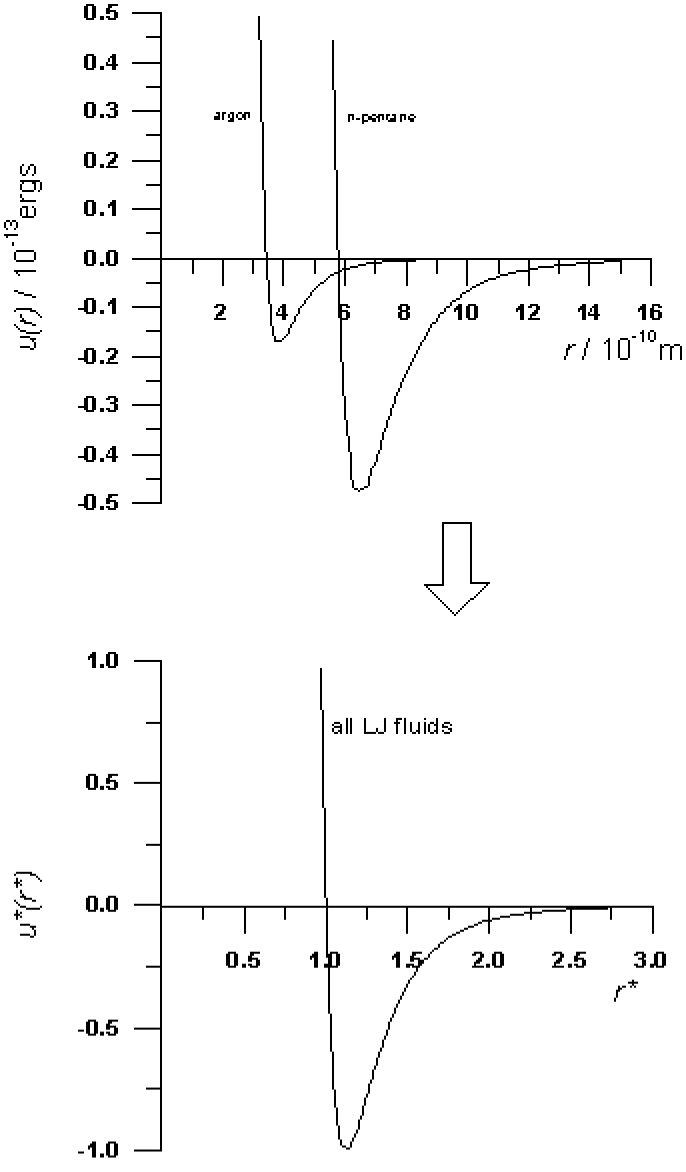
All coefficients are negative

Dimensions and Units 3. Conformal Solutions

- Lennard-Jones potential in dimensionless form

$$u^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$

- Parameter independent!
- Dimensionless properties must also be parameter independent
  - convenient to report properties in this form, e.g. P*(ρ*)
  - select model values to get actual values of properties
  - Basis of corresponding states
- Equivalent to selecting unit value for parameters



Energy conservation in Molecular dynamics

$$E(t) = \mathrm{K}(T) + V(t)$$

We want to derive an expression for the rate of change of energy with time dE/dt. First we consider the kinetic energy term

$$\frac{dk}{dt} = \sum_{i=1}^{N} \frac{d}{dt}\left(\frac{1}{2} m_i v_i^2\right) = \sum_{i=1}^{N} m_i v_i \frac{dv_i}{dt} = \sum_{i=1}^{N} v_i f_i$$

The potential energy is written as a series of pairwise interaction

$$V(t) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} v(r_{ij}(t))$$

The derivative of the potential energy wrt to time is given by

$$\frac{dV}{dt} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{\partial V}{\partial v(r_{ij})} \frac{dv(r_{ij})}{dt}$$

$\frac{\partial V}{\partial v(r_{ij})}$ equals 1 for each pairwise combination i and j. Each term $v(r_{ij})$ is a function of the positions of atom i and j (r_i and r_j) and we can write

$$\frac{dv(r_{ij})}{dt} = \frac{dv(r_{ij})}{dr_i}\frac{dr_i}{dt} + \frac{dv(r_{ij})}{dr_j}\frac{dr_{ij}}{dt}$$

For a given atom i, there will be a total of N-1 terms of the form $v(r_{ij})$ in the expression for the potential energy due to the interactions between I and all other atoms j. Hence we can write dV/dt as follows

$$\frac{dV}{dt} = \sum_{i=1}^{N}\sum_{i\neq j}\frac{\partial v(r_{ij})}{\partial r_i}\frac{dr_i}{dt} = \sum_{i=1}^{N}\frac{dr_i}{dt}\sum_{i\neq j}^{N}\frac{\partial v(r_{ij})}{\partial r_i}$$

The force on atom I due to its interaction with atom j equals minus the gradient with respect to r_i or $-\frac{\partial v(r_{ij})}{\partial r_i}$

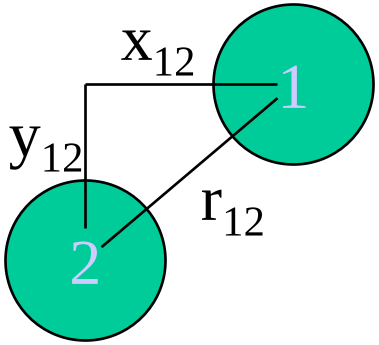
Thus the total force on the atom is equal to $-\sum_{i\neq j}^{N}\frac{\partial v(r_{ij})}{\partial r_i}$

So we have $$\frac{dV}{dt} = -\sum_{i=1}^{N}\frac{dr_i}{dt} f_i = -\sum_{i=1}^{N} v_i f_i$$

Thus dV/dt + dK/dt = dE/dt =0, which imply that energy is constant

Forces 1. Formalism

- Force is the gradient of the potential



$$r_{12} = \left[(x_2 - x_1)^2 + (y_2 - y_1)^2\right]^{1/2}$$

Force on 1, due to 2

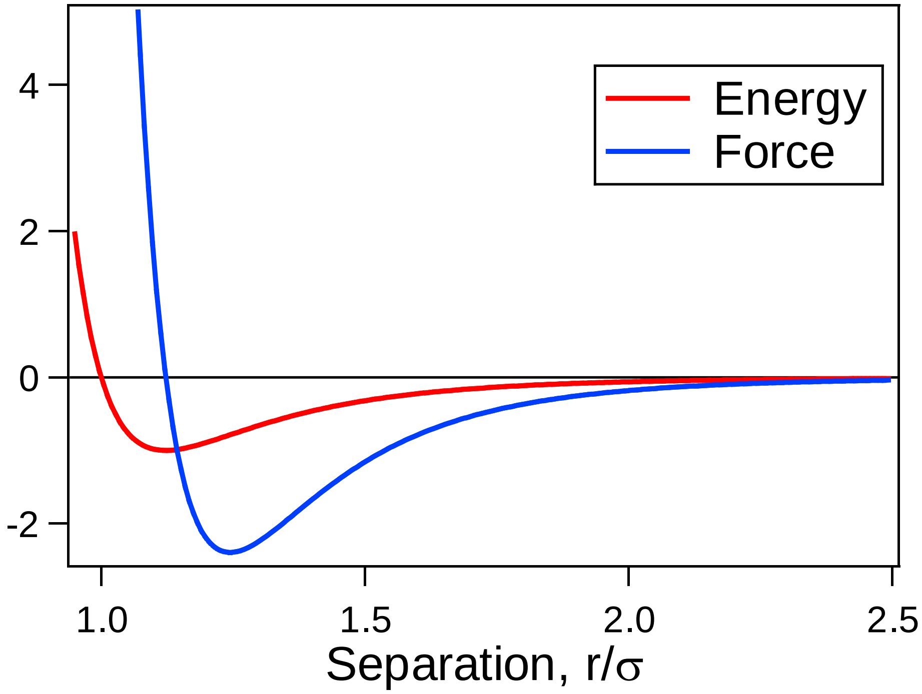
$$\mathbf{F}_{2\to1} = -\nabla u(r_{12})$$

$$= -\frac{\partial u(r_{12})}{\partial x_1}\mathbf{e}_x - \frac{\partial u(r_{12})}{\partial y_1}\mathbf{e}_y$$

$$= -\frac{du(r_{12})}{dr_{12}}\left[\frac{\partial r_{12}}{\partial x_1}\mathbf{e}_x + \frac{\partial r_{12}}{\partial y_1}\mathbf{e}_y\right]$$

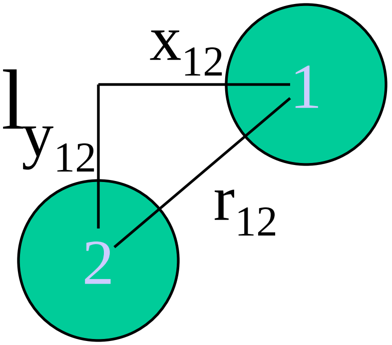
$$= -\frac{f(r_{12})}{r_{12}}\left[x_{12}\mathbf{e}_x + y_{12}\mathbf{e}_y\right]$$

$$\mathbf{F}_{2\to1} = -\mathbf{F}_{1\to2}$$



Forces 2. LJ Model

- Force is the gradient of the potential



$$\mathbf{F}_{2\to 1} = -\frac{f(r_{12})}{r_{12}}\left[x_{12}\mathbf{e}_x + y_{12}\mathbf{e}_y\right]$$

e.g., Lennard-Jones model

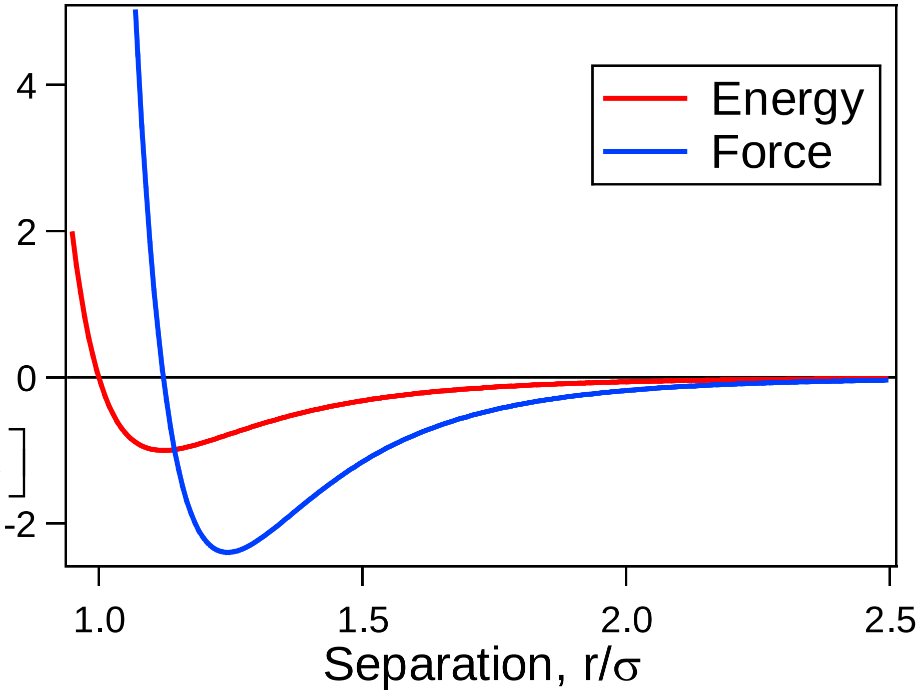
$$r_{12} = \left[(x_2 - x_1)^2 + (y_2 - y_1)^2\right]^{1/2}$$

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

$$f(r) = -\frac{du}{dr}$$

$$= +\frac{48\varepsilon}{\sigma}\left[\left(\frac{\sigma}{r}\right)^{13} - \frac{1}{2}\left(\frac{\sigma}{r}\right)^{7}\right]$$

$$\mathbf{F}_{2\to 1} = -\frac{48\varepsilon}{\sigma^2}\left[\left(\frac{\sigma}{r_{12}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{12}}\right)^{8}\right]\left[x_{12}\mathbf{e}_x + y_{12}\mathbf{e}_y\right]$$



Boundary Conditions

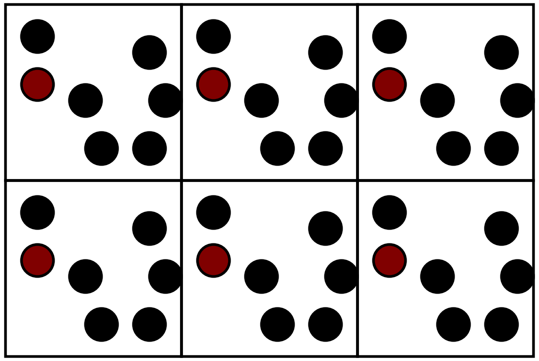
- Small system is simulated to study/mimic the bulk properties
- Surface effect: a large fraction of the small sample lie on the surface. For example for 1000 molecules arranged in 10x10x10 cube, almost 400 molecules appear on the cube faces. Surface molecules/atoms experience different force than in the bulk.
- Impractical to contain system with a real boundary
  - Enhances finite-size effects
  - Artificial influence of boundary on system properties

Solution: Periodic boundary condition

•The problem of surface effect can be overcome by using. “Periodic Boundary Conditions” (PBC). The bounding box is replicated throughout space to form an infinite lattice. In the course of simulation as a molecule moves in the original box, its periodic images in the each of the neighboring boxes

•As the molecule leaves the central box, one of its image will enter through the opposite face.

•No physical wall at the boundary and so no surface molecules.

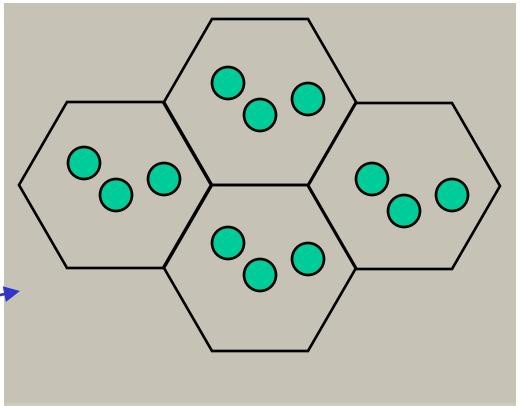


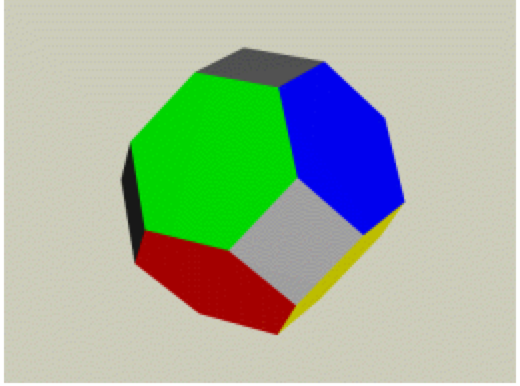
Issues with Periodic Boundary Conditions

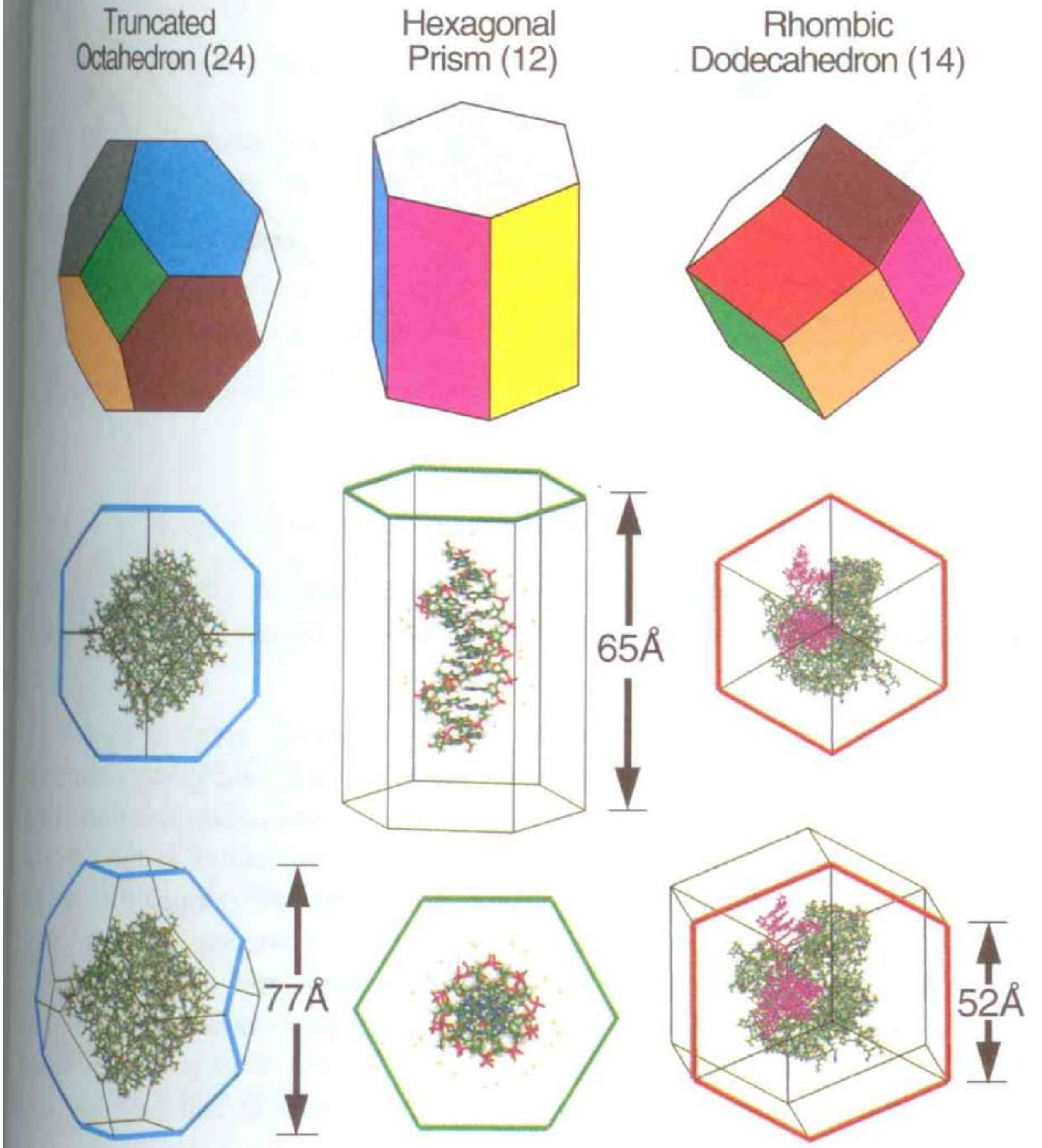
- Suppress fluctuation that have wavelength greater than the length of the simulation cell. This could be problem near critical point where fluctuation plays dominant role.
- new artificial correlations
- It can also affect the rate at which a simulated liquid nucleates and forms a solid or glass when rapidly cooled (Honeycutt and Andersen 1984)
- Artifact of PBC can be determined by performing simulations using a variety of cell sizes and shape

Issues with Periodic Boundary Conditions

- Other issues arise when dealing with longer-range potentials
  - accounting for long-range interactions
  - nearest image not always most energetic
  - splitting of molecules (charges)
  - discuss details later
- Other geometries possible
  - any space-filling unit cell
    - hexagonal in 2D
    - truncated octahedron in 3D
    - rhombic dodecahedron in 3D
  - surface of a (hyper)sphere
  - variable aspect ratio useful for solids
    - relieves artificial stresses





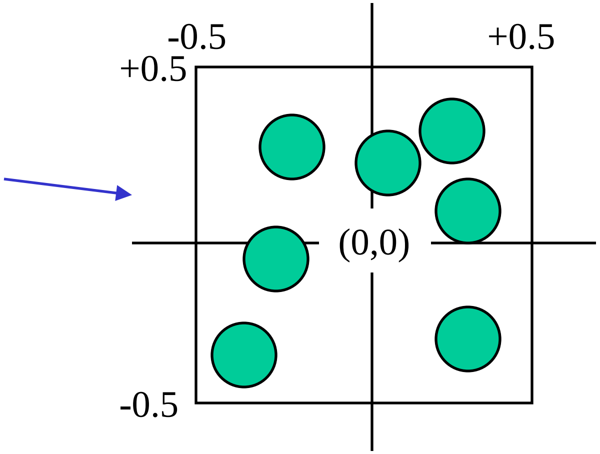

Truncated Octahedron (24)
Hexagonal Prism (12)
Rhombic Dodecahedron (14)
65Å
77Å
52Å

Implementing Cubic Periodic Boundaries

- How do we handle PBC and the minimum image convention
  - Box origin
    - center of box, coordinates range from *-L/2* to *+L/2*. When a molecule leaves a box crossing one of the boundary, its image enters the box and is accomplished either by adding or subtracting *L* to the particle coordinate.

If (drx[I] > L/2) rx[I]   = rx[I] – L

If (drx[I] > -L/2) rx[I] = rx[I] +L



A more convenient way to handle PBC as well as minimum image convention is to use reduce (scaled coordinates) in the range (-1/2,1/2)

- Box size
  - unit box, coordinates scaled by box length
  - `sep[0] = sep[0] – NINT(sep[0])`
  - `define NINT(x)   ((x) < 0.0 ? (int) ((x) - 0.5) : (int) ((x) + 0.5))`

Implementing Cubic Periodic Boundaries 3

```
void periodic_boundary_conditions(int n_atoms, double **h,
   double **scaled_atom_coords, double **atom_coords)
{
int i, j;
for (i = 0; i < n_atoms; ++i) {
      for (j = 0; j < NDIM; ++j)
     scaled_atom_coords[i][j] -= NINT(scaled_atom_coords[i][j]);
      atom_coords[i][0] = h[0][0] * scaled_atom_coords[i][0]
         + h[0][1] * scaled_atom_coords[i][1]
         + h[0][2] * scaled_atom_coords[i][2];
      atom_coords[i][1] = h[1][1] * scaled_atom_coords[i][1]
         + h[1][2] * scaled_atom_coords[i][2];
      atom_coords[i][2] = h[2][2] * scaled_atom_coords[i][2];
   }}
```

Implementing Cubic Periodic Boundaries

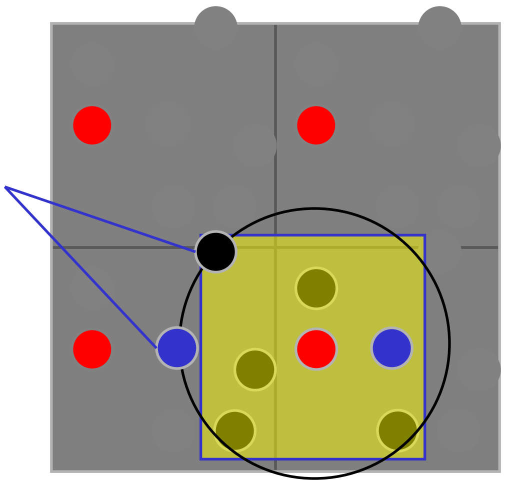
```
void scaled_atomic_coords(int n_atoms, double **h_inv, double **atom_coords,
  double **scaled_atom_coords)
{
  int i;
for (i = 0; i < n_atoms; ++i) {
scaled_atom_coords[i][0] = h_inv[0][0] * atom_coords[i][0]
      + h_inv[0][1] * atom_coords[i][1]
      + h_inv[0][2] * atom_coords[i][2];
    scaled_atom_coords[i][1] = h_inv[1][1] * atom_coords[i][1]
      + h_inv[1][2] * atom_coords[i][2];
    scaled_atom_coords[i][2] = h_inv[2][2] * atom_coords[i][2];
  }
}
```

Truncating the Potential

- For system with pair wise additive interactions force on a particle I is computed by all its neighbors. This means for a system of N particles we have to evaluate N(N-1)/2 pair interactions. So the time needed for evaluation of energy/force scales as N^2. This is one of the main bottleneck in the simulation field.
- Bulk system modeled via periodic boundary condition
  - not feasible to include interactions with all images
  - must truncate potential at half the box length (at most) to have all separations treated consistently
- Contributions from distant separations may be important

Minimum image convention and Truncating the Potential

How do we evaluate force on the red atom in the simulation box. Assuming pair wise interaction we should include interaction of the red atom with all other atoms in the simulation box. There are N-1 such term. However, we must also include interaction coming from images lying in the surrounding boxes. That is an infinite number of terms.



These two are same distance from central atom, yet:

Black atom interacts Blue atom does not

Minimum image convention

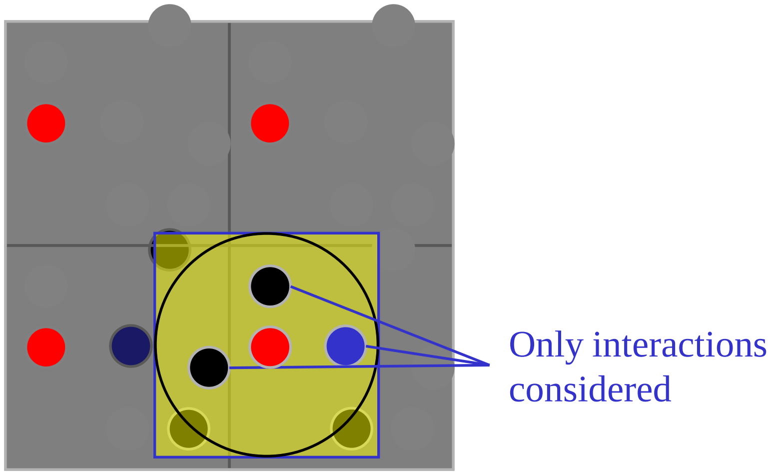
Construct a simulation box of same size as the the original box with the red atom at its center. Now minimum image convention says that the red atom interact with those atoms which lie in this region, that is with the closest periodic images of the other N-1 atoms.

Truncating the Potential

With the minimum image convention energy/force computation involves 1/2N(N-1) terms.This is significant for large system size.

For short range interaction major contribution comes from the neighbors close to the atom of interest. So use a spherical cutoff to truncate the interaction.

So the red atom interact only with the atoms lying inside the cutoff region (2 black and one blue)



Points to remember

- ❑The cutoff distance should be smaller than L/2 to be consistent with the minimum image convention
- ❑Thermodynamic properties are different for a truncated potential compared to a non-truncated case. However, we can apply long range correction to get back approximately the non-truncated properties.
- ❑Cutoff introduces discontinuity in the force and energy computation. This has serious consequences on the energy conservation and stability of the simulation

Truncating the Potential contd

Potential truncation introduces discontinuity

- Corresponds to an infinite force
- Problematic for MD simulations
    - ruins energy conservation

- Shifted potentials: a constant term is subtracted from the potential at all values

$$u_s(r) = \begin{cases} u(r) - u(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

- Removes infinite force
- Still discontinuity in force: at the cutoff distance, the force will have a finite value which drops to zero just beyond the cutoff

Truncating the Potential

Shifted-force potentials : a linear term can be added to the potential, making the derivative to be zero at the cutoff

$$u_{sf}(r) = \begin{cases} u(r) - u(r_c) - \left(\dfrac{du}{dr}\right)_{r=r_c}(r - r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

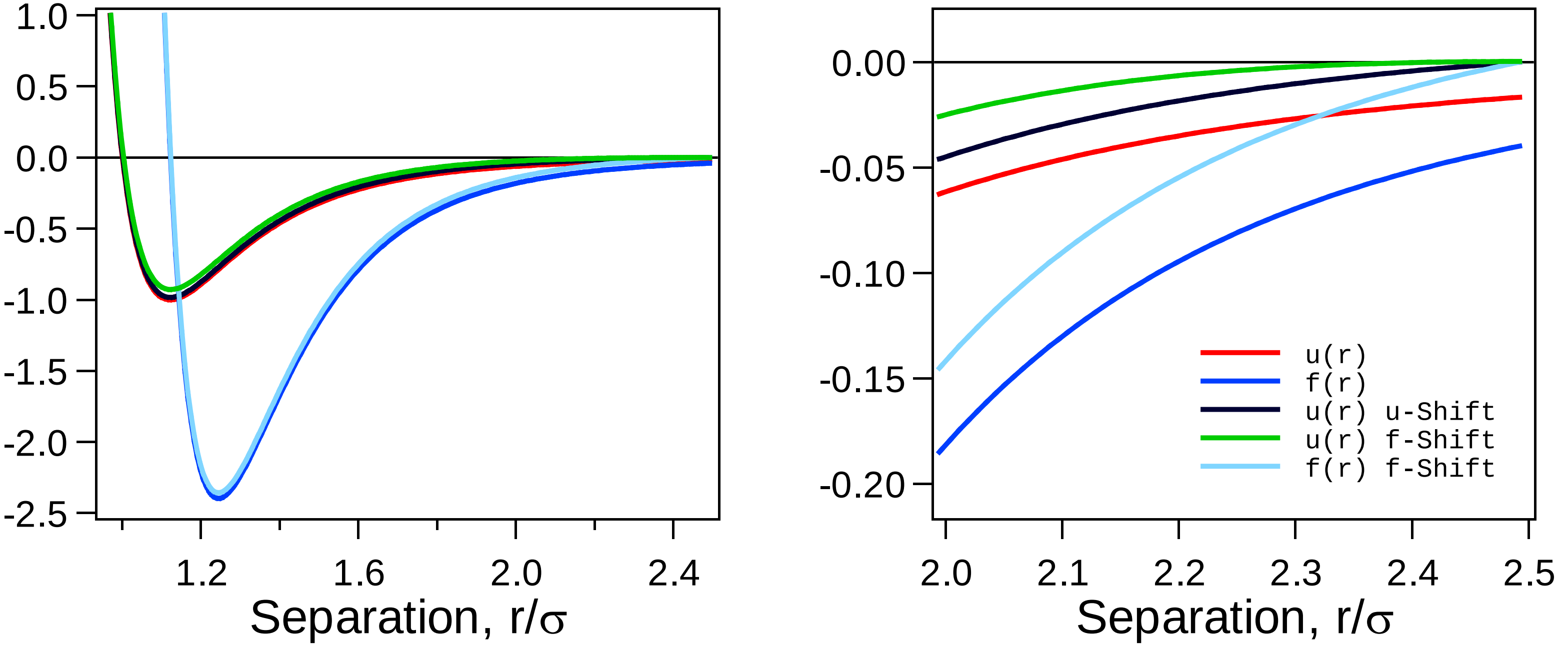
- The discontinuity now appears in the gradient, not in the force itself. The force goes smoothly to zero at cutoff.
- The shift makes the potential deviate from the true potential, so the calculated thermodynamic properties will be changed
- True values can be retrieved but is difficult to do so, so rarely used in simulation

Eliminate discontinuities in the energy and force by a switching function

Truncating the Potential

- Lennard-Jones example
  - $r_c = 2.5\sigma$

$$u_s(r) = \begin{cases} u(r) - u(r_c) & r \le r_c \\ 0 & r > r_c \end{cases} \qquad u_{sf}(r) = \begin{cases} u(r) - u(r_c) - \dfrac{du}{dr}(r - r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$



Switching function

Potential function is multiplied by a polynomial which is a function of distance

$$u_S(r) = u(r)S(r)$$

S(r) gradually taper the potential between two cutoff values : it smoothly changes its value of 1 to a value of 0 between two cutoff : r_l (lower cutoff) and r_u (upper cutoff) and satisfies the following criteria

$$S_{r=r_l} = 1.0 \qquad \left(\frac{dS}{dr}\right)_{r=r_l} = 0 \qquad \left(\frac{d^2S}{dr^2}\right)_{r=r_l} = 0$$

$$S_{r=r_u} = 0 \qquad \left(\frac{dS}{dr}\right)_{r=r_u} = 0 \qquad \left(\frac{d^2S}{dr^2}\right)_{r=r_u} = 0$$

Switching function contd.

Zero first derivative ensures that the force approaches to zero smoothly at the cutoffs. A continuous second derivative ensures the stability of the integration algorithm.

$$S(r) = (r_u^2 - r^2)^2 \frac{2}{\gamma^3}\left[\frac{3\gamma}{2} - (r_u^2 - r^2)\right] \qquad \text{where } \gamma = r_u^2 - r_l^2$$

$$= c_0 (r_u^2 - r^2) + c_1 (r_u^2 - r^2)^2 + c_2 (r_u^2 - r^2)^3$$

$$S(r_l) = 1$$

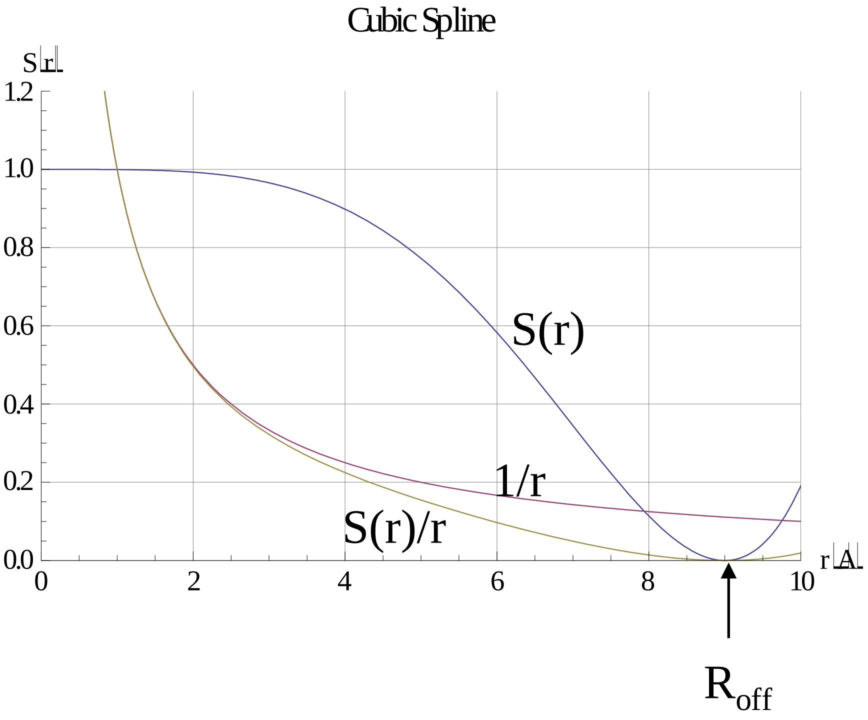
$$S(r_u) = 0$$

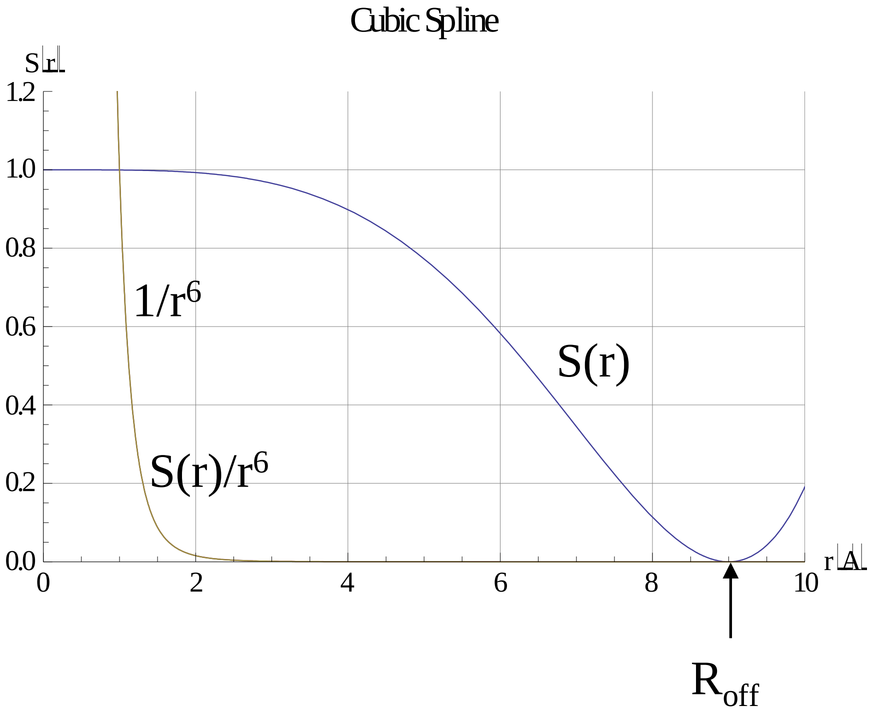
Generally r_u is taken to be ~ 1 to 2 Å smaller than r_c so that atom pairs that are initially greater than r_u apart do not move closer than r_u during the time that the NB List is not updated. Common choice is r_c= 12 Å, r_u= 10 Å, r_l= 8 Å.

```
/* Calculate pair interaction. The LJ pair potential is switched off smoothly between r_on and
r_off. */

      one_over_r2_sep = 1.0 / r2_sep;
     rho_2 = comb_par[id_0][id_1][2] * one_over_r2_sep;
     rho_6 = CUBE(rho_2);
     rho_12 = SQR(rho_6);
     *u_vdw = rho_12 - rho_6;
    *f_vdw = rho_12 + *u_vdw;
     four_epsilon = comb_par[id_0][id_1][3];
     (*u_vdw) *= four_epsilon;
     (*f_vdw) *= 6.0 * one_over_r2_sep * four_epsilon;
     if (r2_sep > r2_on) {
        sw1 = r2_off - r2_sep;
        sw2 = two_over_gamma_cubed * sw1;
        sw3 = sw1 * sw2 * (three_gamma_over_two - sw1);
        sw4 = 6.0 * sw2 * (gamma - sw1);
        *f_vdw = sw4 * (*u_vdw) + sw3 * (*f_vdw);
        (*u_vdw) *= sw3;
```

Cubic Spline





R_{on} = 0 A, R_{off} = 9 A

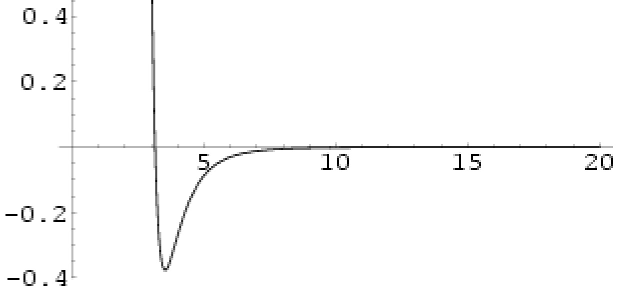
Switching function contd.

We can use higher order polynomial also

$$S(r) = c_0 + c_1\left[\frac{r - r_l}{r_u - r_l}\right] + c_2\left[\frac{r - r_l}{r_u - r_l}\right]^2 + c_3\left[\frac{r - r_l}{r_u - r_l}\right]^3 + c_4\left[\frac{r - r_l}{r_u - r_l}\right]^4 + c_5\left[\frac{r - r_l}{r_u - r_l}\right]^5$$

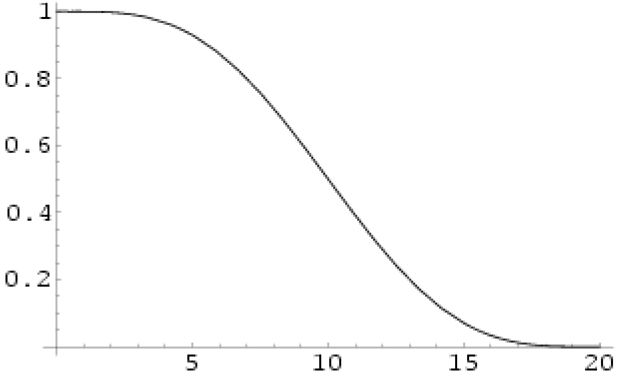
With the coefficients satisfying the previous criteria and that gives

C0=1, c1=0, c2=0, c3=-10, c4=15, c5=-6



```
Graphics
```

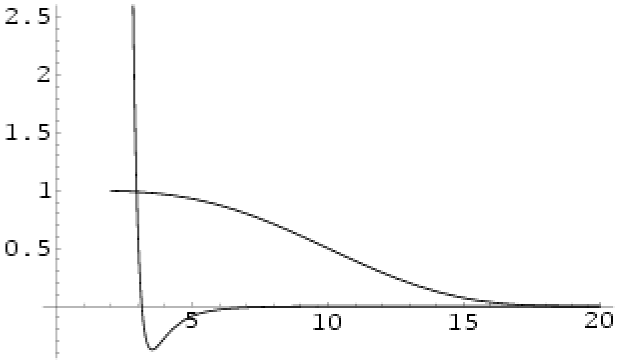
```
Plot@1 - 0.00021875 * x^4 + 2.625 * 10^-5* x^5 - 1.09375 * 10^-6* x^6
  + 1.5625 * 10^-8* x^7,  8x, 0, 20<D
```

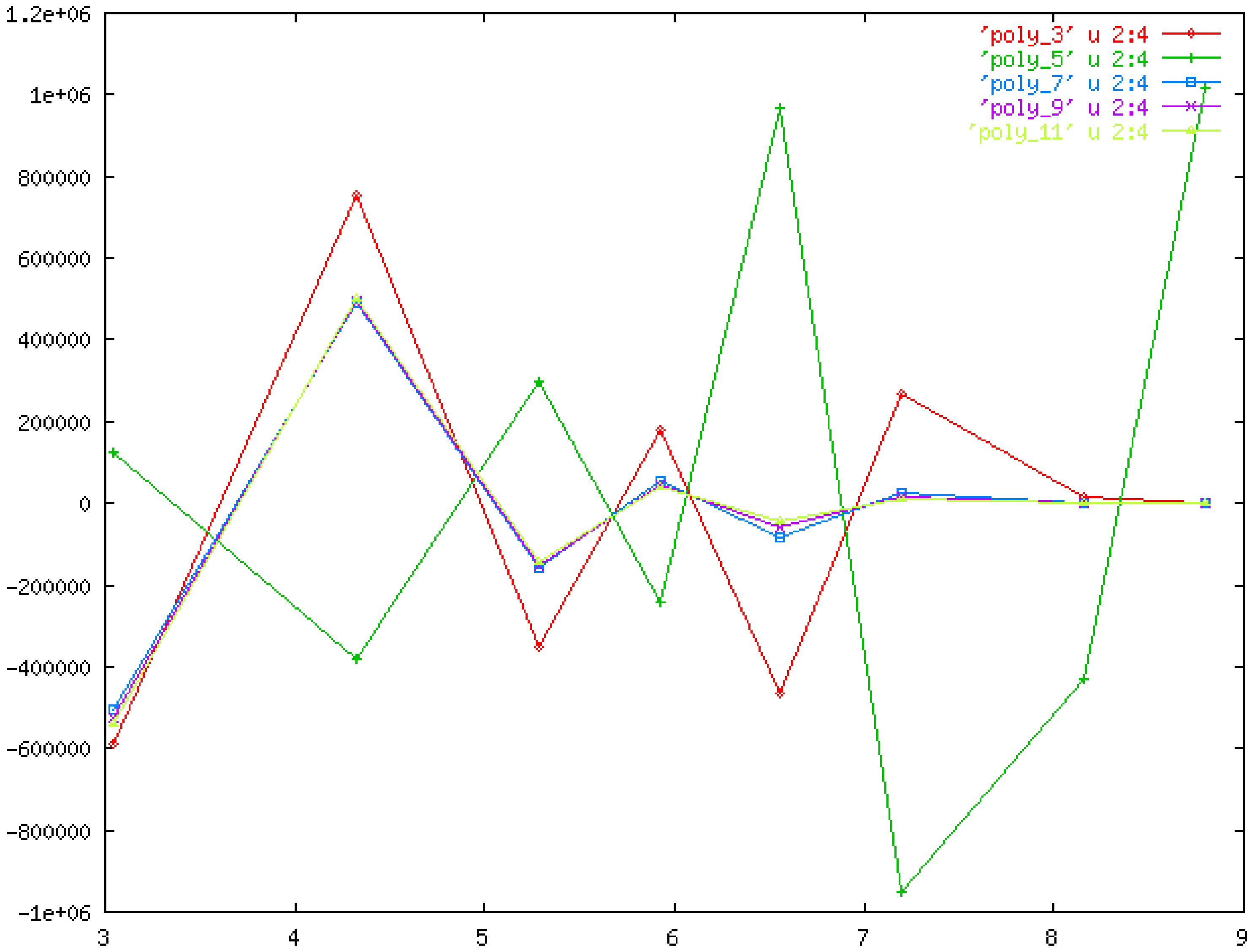


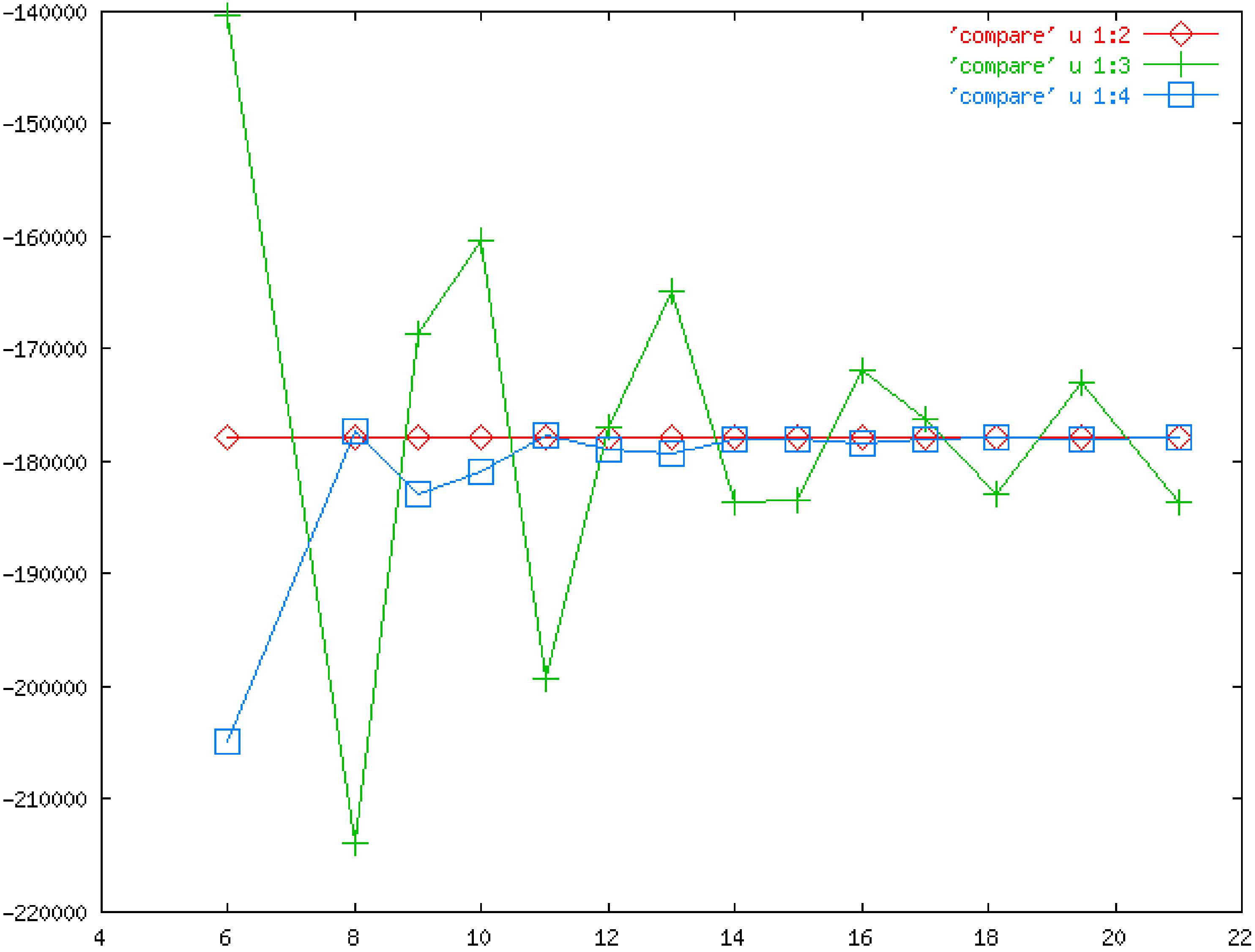
```
Graphics

Graphics
```

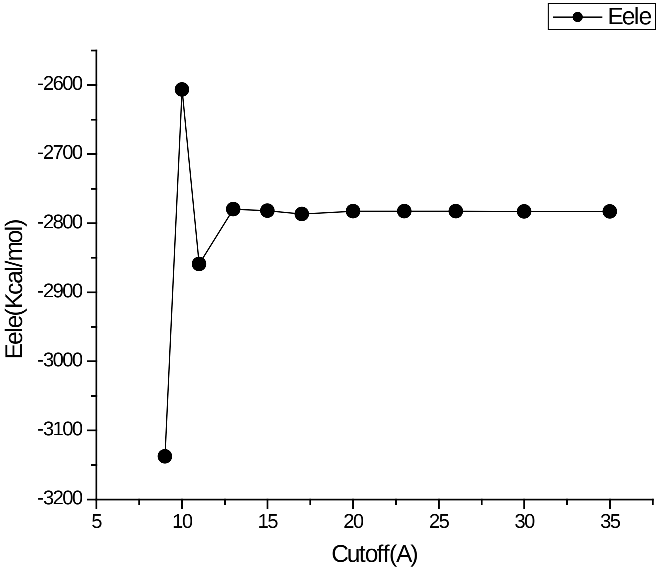
```
Plot@81381290* x^-12 - 1442.04 * x^-6, 1 - 0.00021875 * x^4 +
   2.625 * 10^-5* x^5 - 1.09375 * 10^-6* x^6 + 1.5625* 10^-8 * x^7<,  8x, 2, 20<D
```

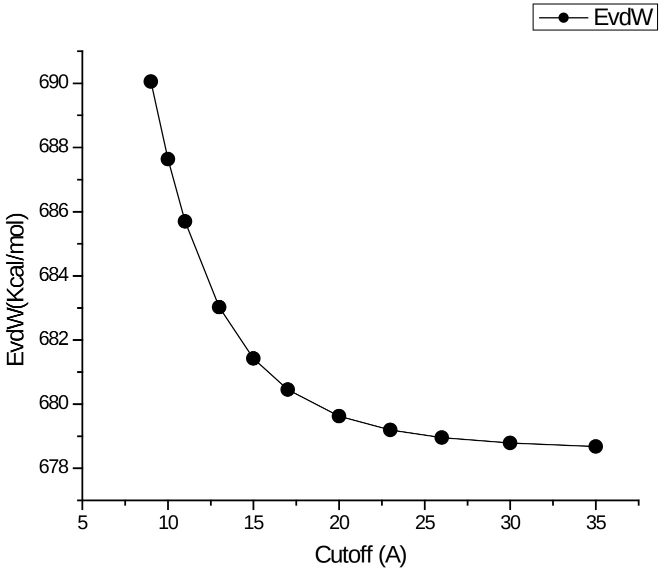


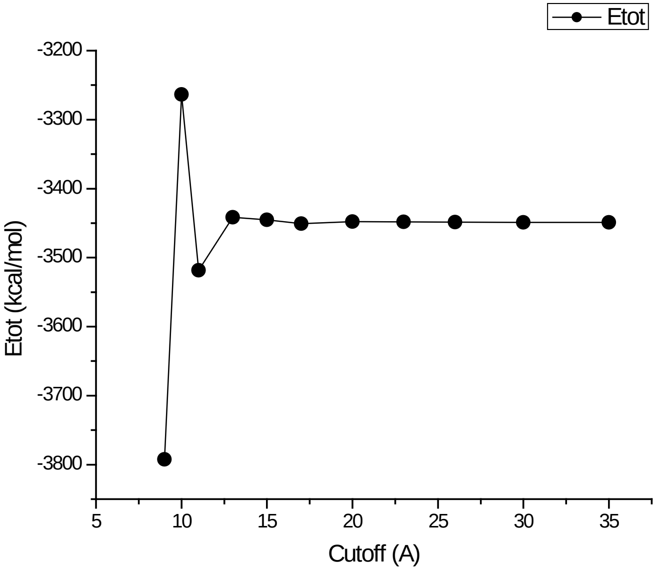

1.2e+06
1e+06
800000
600000
400000
200000
0
-200000
-400000
-600000
-800000
-1e+06
3
4
5
6
7
8
9
'poly_3' u 2:4
'poly_5' u 2:4
'poly_7' u 2:4
'poly_9' u 2:4
'poly_11' u 2:4

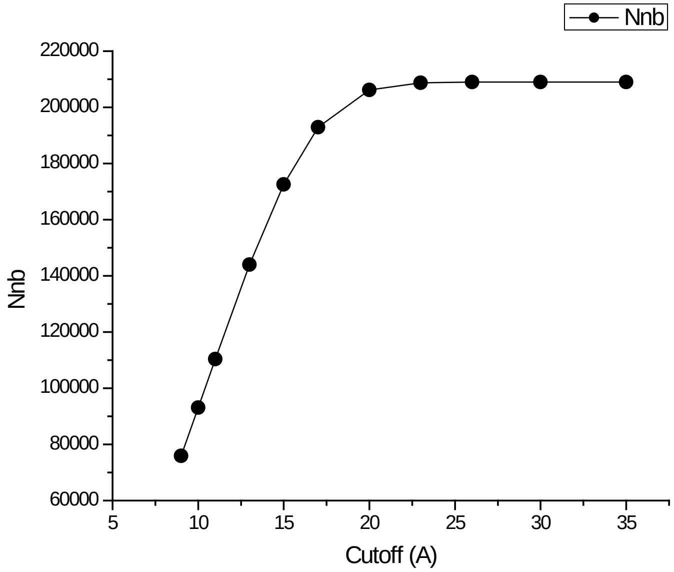

'compare' u 1:2
'compare' u 1:3
'compare' u 1:4
-140000
-150000
-160000
-170000
-180000
-190000
-200000
-210000
-220000
4
6
8
10
12
14
16
18
20
22

Effect of NB cutoff (216 water molecules)









Electrostatic interaction is most sensitive to NB cutoff (R_{off}) since it falls off more slowly than vdW. Energy converges at R_{off} = ~15 A (R_{on} = 0 A, R_{cut}=R_{off}+1A).

Radial Distribution Function

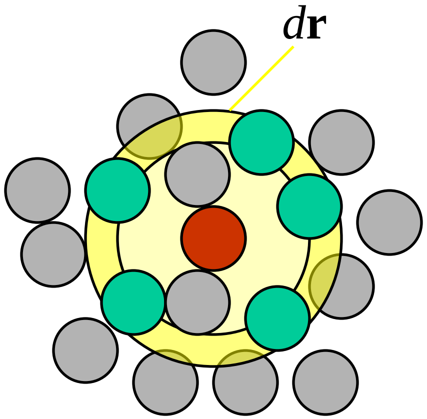
- Radial distribution function, g(r)
  - key quantity in statistical mechanics
  - quantifies correlation between atom pairs
- Definition

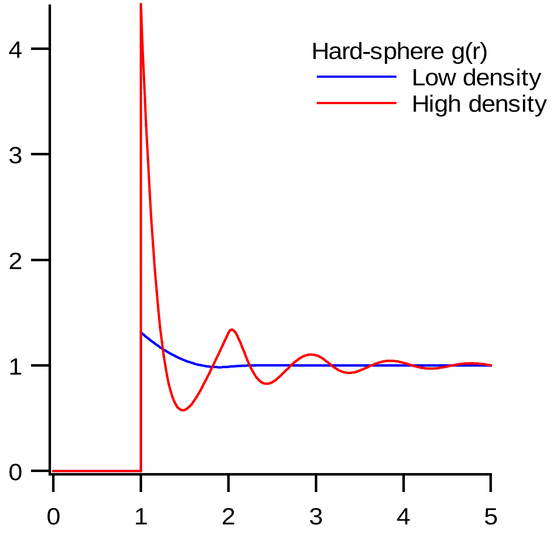
$$g(r) = \frac{\rho(r)d\mathbf{r}}{\rho^{id}(r)d\mathbf{r}}$$

Number of atoms at r in actual system

Number of atoms at r for ideal gas

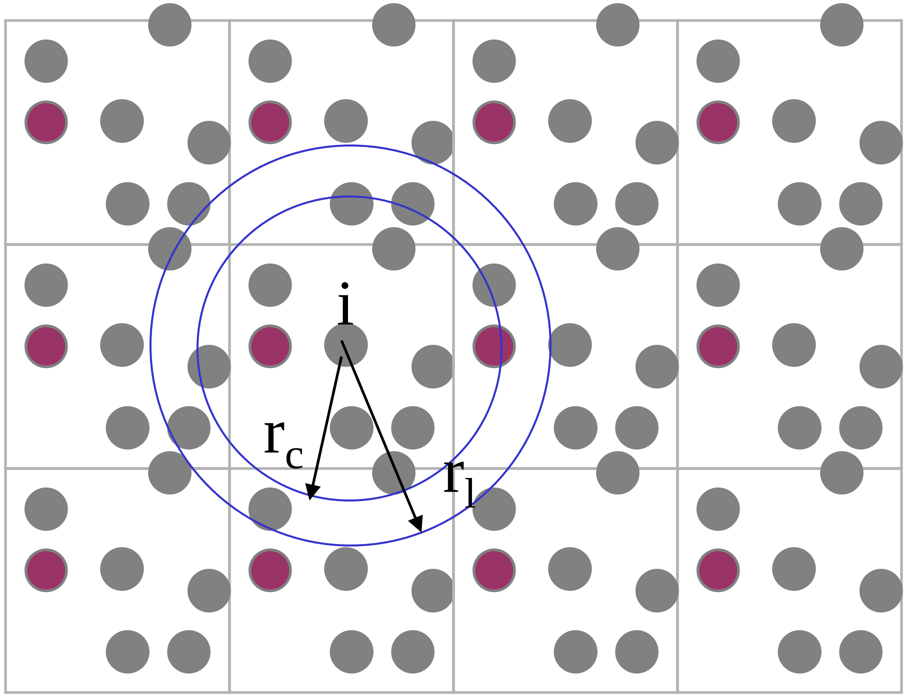
$$\rho^{id}(r)d\mathbf{r} = \frac{N}{V}d\mathbf{r}$$





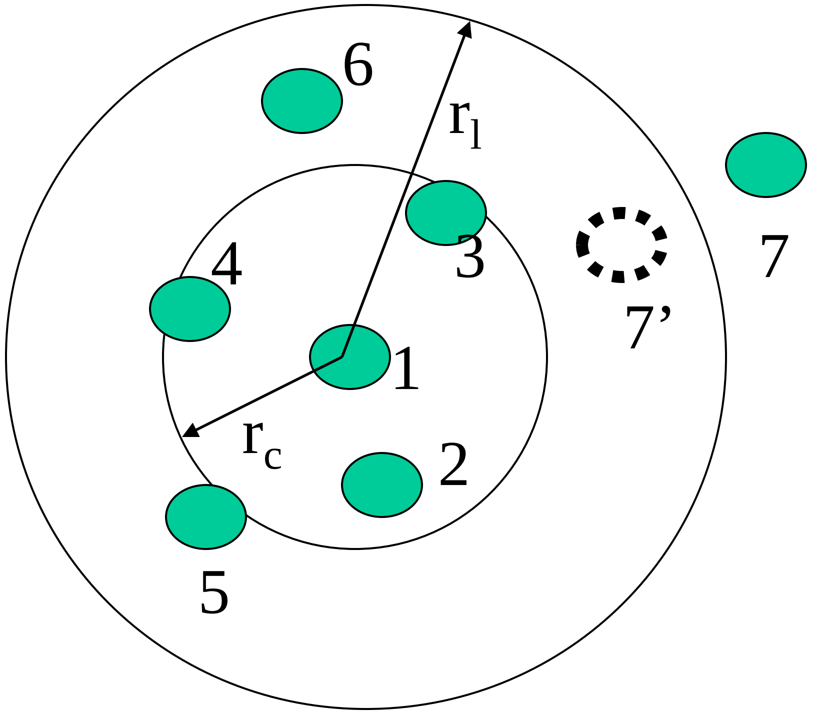
Verlet List

- Particles outside cutoff do not contribute to the energy of the particle I.
- Exclude those particles from the energy computation
- Verlet List: Introduce a second cutoff radius $r_l > r_c$
- Make a list of all the particles within a radius of r_l of particle *i*
- If the maximum displacement of the particles is less than $(r_l - r_c)$ we have to consider only the particles in this list for the energy/force computation



Update the Verlet list as soon as one of the particle is displaced more than $(r_l - r_c)$

For MD it is sufficient to have a Verlet list with half the number of particles for each particle as long as interaction *i-j* is accounted for in either the list of particle *i* or that of *j*



The skin is thick enough such that when reconstructing an atom 7, which was not in the original list of atom 1can not penetrate the r_c sphere. Atom 3, 4 can move in and out but their interaction get counted as they are in the original list until the list get updated.

The cutoff sphere and its skin around an atom 1. Atoms 2,3,4,5 and 6 are on the list of atom 1, but 7 is not. Among these only 2,3,4 are within the r_c when the list is made

From Allen and Tildesley

For a periodic system Verlet list has an elegant implementation due to Bekker et. al. (Mol. Sim. 14, 137-151, 1995)

In a periodic system total force on particle *i* can be written as

$$F_i = \sum_{j=1}^{N} \sum_{k=-13}^{13}{}' F_{i(jk)}$$

Where the prime denotes that summation is performed over the nearest image of the particle j in the central box (k=0) or in one of its 26 periodic images (or 8 in 2-d). (j.k) denotes the periodic image of particle j in box k. Box k is defined by the integer numbers n_x, n_y, n_z

$$k = 9n_x + 3\,n_y + n_z$$

Problem with Verlet List

As the size of the system increases neighbor list becomes too large to store easily

Also the testing of every pair separation is also very inefficient

Make the neighbor list using Cell list

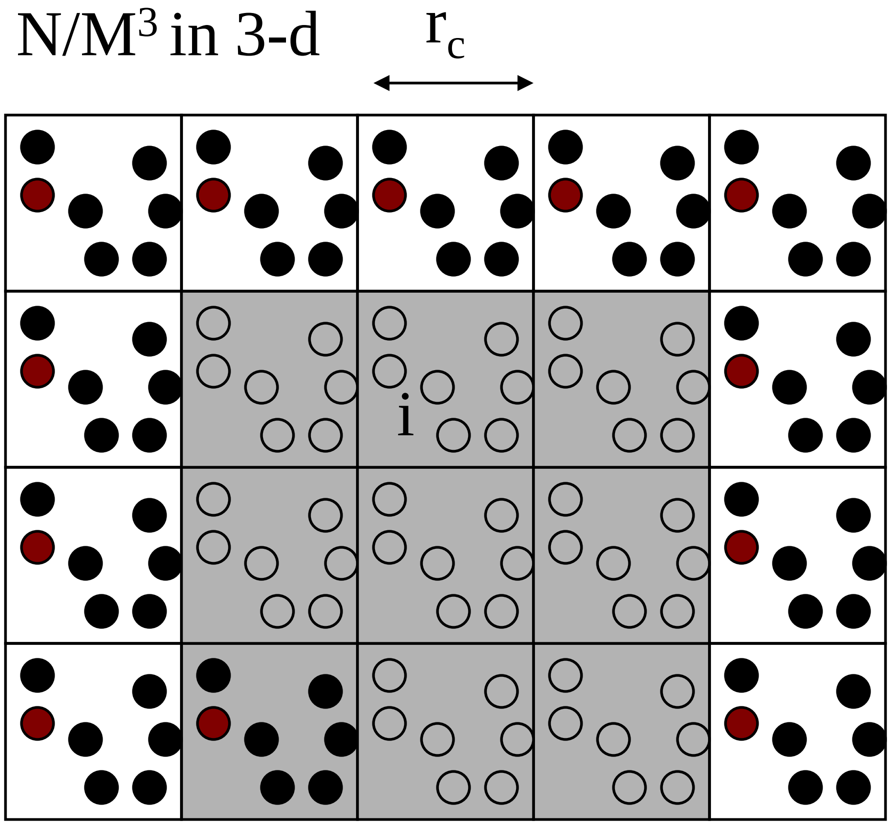
Cell Lists or Linked-list

- The simulation box is divided into cells with size equal to or slightly larger than the cutoff r_c
- Distribute the particle to the cell according to their position
- Each particle in a given cell interacts with only those particles in the same or neighboring cells
- This scales as N

$N_c = N/M^2$ in 2-d

$N_c = N/M^3$ in 3-d

The simulation cell is divided into cells of size r_c x r_c, a particle *i* interacts with those particles in the same cell or neighboring cell (in 2D 9 cells; in 3D 27 cells)



# of pair = $9NN_c$ in 2-d

# of pair = $27NN_c$ in 3-d

The Cell list is created using the linked list methods:

- Sorting of atoms to their respective cells
- Two arrays are created (HEAD AND LIST)
- HEAD (head of the chain) array has one element for each cell. This contains the identification number of one of the molecules sorted into that cell
- LIST (linked list array) contains the number of next molecules in that cell.
- HEAD (head of the chain) array element is used to address the LIST array element.
- If we follow the trail of linked-list we will eventually reach an element of LIST which is zero. This indicates that there are no more molecules in that cell and we move on to the head of chain of the next cell.

See Allen and Tildesley for details

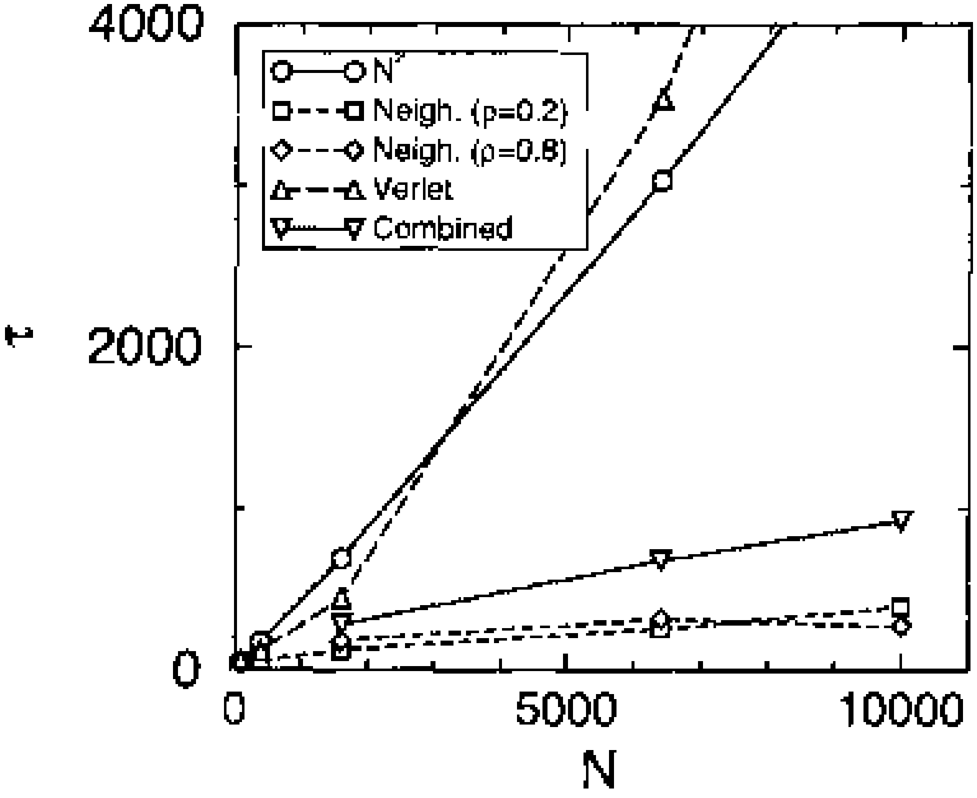
```
void neighbor_lists_period()
/* Purge neighbor lists. */
   for (i = 0; i < n_atoms; ++i)
      nl_tail[i] = NULL;

    /* Update cell lists. */
   update_cells(period_switch, n_atoms, h, scaled_atom_coords, atom_coords,
     atom_cells, first, last, phantoms, kc, phantom_skip, nc, nc_p);
 /* Update positions of phantom atoms. */
   update_phantoms(n_atoms, atom_cells, phantom_skip, phantoms, atom_coords);


   /* Loop over central atoms. */
   for (i = 0; i < n_atoms; ++i) {


      /* Get attributes of atom i. */
      for (k = 0; k < NDIM; ++k)
```

Comparison of efficiency of various cut-off scheme



See Frenkel and Smit for details