CE 530 Molecular Simulation

Lecture 14
Molecular Models

David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu

Review

○ Monte Carlo

- *ensemble averaging, no dynamics*
- *easy to select independent variables*
- *lots of flexibility to improve performance*

○ Molecular dynamics

- *time averaging, yields dynamical properties*
- *extended Lagrangians permit extension to other ensembles*

○ Models

- *atomic systems only*

  hard sphere, square well

  Lennard-Jones

Modeling Molecules

○ Quantitative calculations require more realistic treatment of molecular interactions

○ Quantum mechanical origins

○ Intermolecular forces

○ Intramolecular forces

○ Effects of long-range interactions on properties

○ Multibody interactions

Quantum Mechanical Origins

○ Fundamental to everything is the Schrödinger equation

- $H\Psi = i\mathrm{h}\dfrac{\partial \Psi}{\partial t}$ *Nuclear coordinates*

- *wave function* $\Psi(R,r,t)$

- *H = Hamiltonian operator*   *Electronic coordinates*

$$H = K + U = -\frac{\mathrm{h}}{2m}\sum_i \nabla_i^2 + U$$

- *time independent form*

$$H\Psi = E\Psi$$

○ Born-Oppenheimer approximation

- *electrons relax very quickly compared to nuclear motions*

- *nuclei move in presence of potential energy obtained by solving electron distribution for fixed nuclear configuration*

  it is still very difficult to solve for this energy routinely

- *usually nuclei are heavy enough to treat classically*

Force Field Methods

○ Too expensive to solve QM electronic energy for every nuclear configuration

○ Instead define energy using simple empirical formulas

- *"force fields" or "molecular mechanics"*

○ Decomposition of the total energy

Neglect 3- and higher-order terms

$$U(\mathbf{r}^N) = \sum_i u^{(1)}(\mathbf{r}_i) + \sum_i \sum_{j<i} u^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j<i} \sum_{k<j} u^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + K$$

Single-atom energy (external field)   *Atom-pair contribution*   *3-atom contribution*

○ Force fields usually written in terms of pairwise additive interatomic potentials

- *with some exceptions*
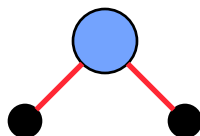
Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = \underbrace{U_{str} + U_{bend} + U_{tors} + U_{cross}} + U_{vdW} + U_{el} + U_{pol}$$

Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy
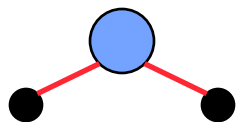
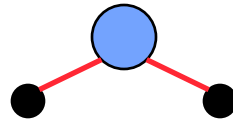○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$

Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
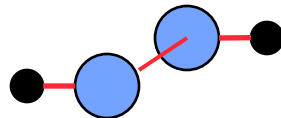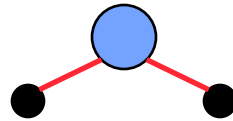
Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = \underbrace{U_{str} + U_{bend} + U_{tors} + U_{cross}}_{} + U_{vdW} + U_{el} + U_{pol}$$

Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
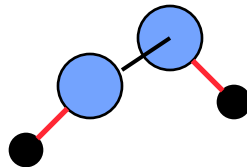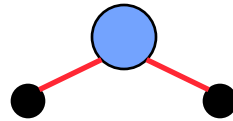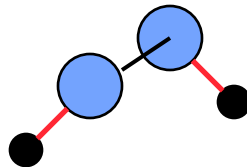
Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$

Intramolecular only
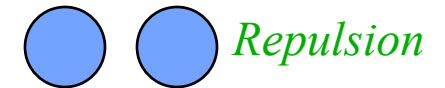
○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

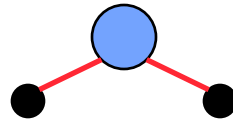○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
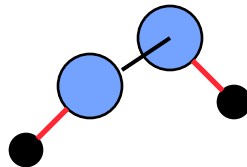
Intramolecular only

Repulsion

○ U_{str} stretch

○ U_{bend} bend
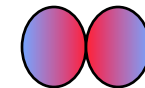
○ U_{tors} torsion

○ U_{cross} cross   *Mixed terms*

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$

Intramolecular only

Repulsion

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross   *Mixed terms*

○ U_{vdW} van der Waals

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

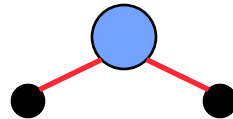○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
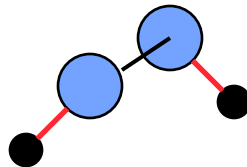
Intramolecular only
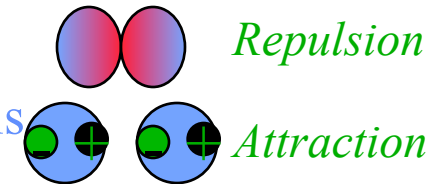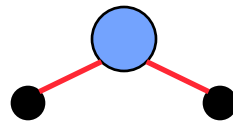
○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross *Mixed terms*

○ U_{vdW} van der Waals *Repulsion*

Attraction

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
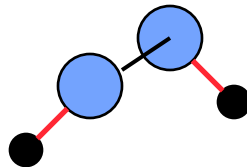
Intramolecular only
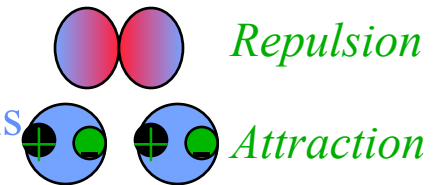
○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross   *Mixed terms*

○ U_{vdW} van der Waals   *Repulsion*

Attraction

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy
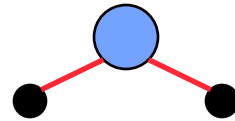
○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
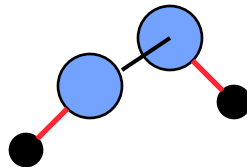
Intramolecular only

○ U_{str} stretch

○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross   *Mixed terms*

○ U_{vdW} van der Waals

Repulsion

Attraction

○ U_{el} electrostatic

○ U_{pol} polarization

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$

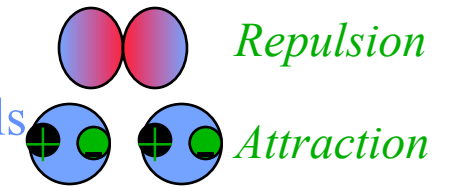*Intramolecular only*

○ U_{str} stretch
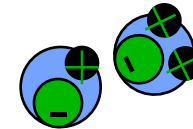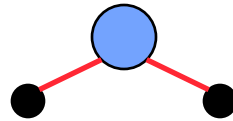
○ U_{bend} bend

○ U_{tors} torsion

○ U_{cross} cross   *Mixed terms*

Repulsion

○ U_{vdW} van der Waals   *Attraction*
$u^{(2)}$

○ U_{el} electrostatic
$u^{(2)}$

○ U_{pol} polarization
$u^{(N)}$

Contributions to Potential Energy

○ Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{cross} + U_{vdW} + U_{el} + U_{pol}$$
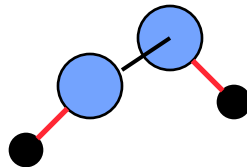
Intramolecular only
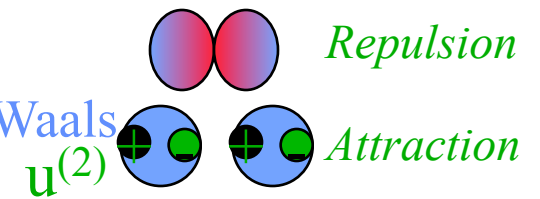
○ U_{str} stretch

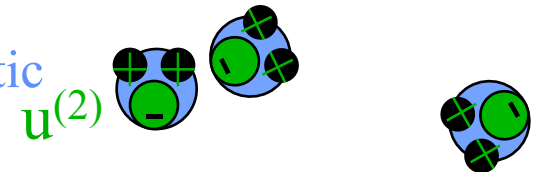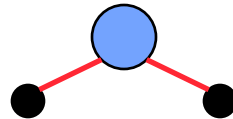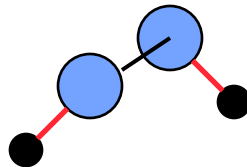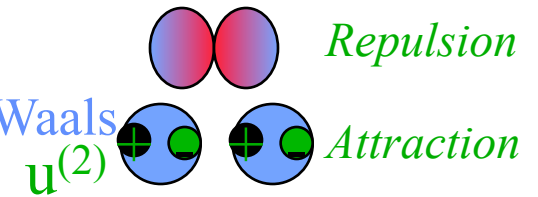○ U_{bend} bend

○ U_{tors} torsion
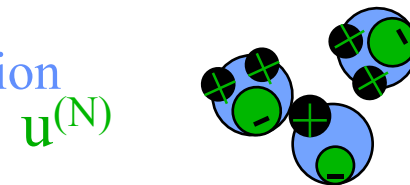
○ U_{cross} cross   *Mixed terms*

○ U_{vdW} van der Waals   *Repulsion*

Attraction

$u^{(2)}$

○ U_{el} electrostatic

$u^{(2)}$

○ U_{pol} polarization

$u^{(N)}$

Stretch Energy

○ Expand energy about equilibrium position

$$U(r_{12}) = U(r_{12}^o) + \frac{dU}{dr}\bigg|_{r=r^o}(r_{12} - r_{12}^o) + \frac{d^2U}{dr^2}\bigg|_{r=r^o}(r_{12} - r_{12}^o)^2 + K \quad \textit{(neglect)}$$

define   *minimum*

$$U(r_{12}) = k(r_{12} - r_{12}^o)^2 \quad \textit{harmonic}$$
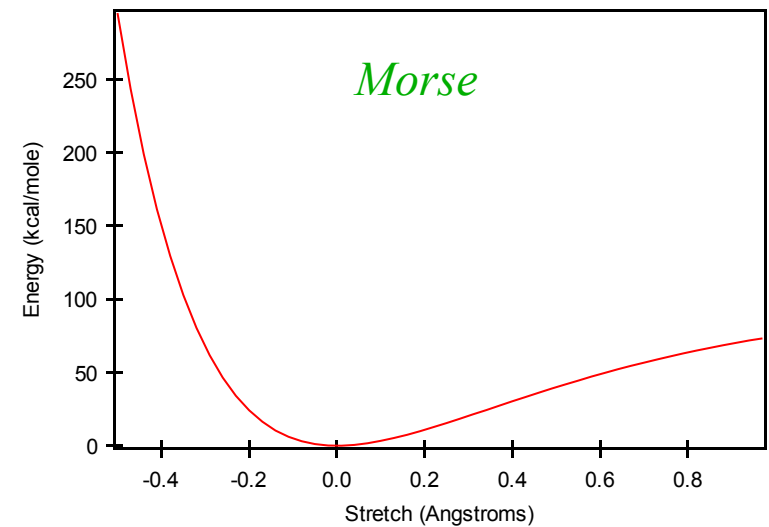
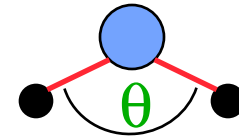○ Model fails in strained geometries

• *better model is the Morse potential*

$$U(r_{12}) = D\left(1 - e^{\alpha r_{12}}\right)^2$$

dissociation
energy   *force constant*

Morse

Energy (kcal/mole) vs Stretch (Angstroms)

Bending Energy

○ Expand energy about equilibrium position

$$U(\theta) = U(\theta^o) + \left.\frac{dU}{d\theta}\right|_{\theta=\theta^o} (\theta - \theta^o) + \left.\frac{d^2U}{d\theta^2}\right|_{\theta=\theta^o} (\theta - \theta^o)^2 + K \qquad \textit{(neglect)}$$
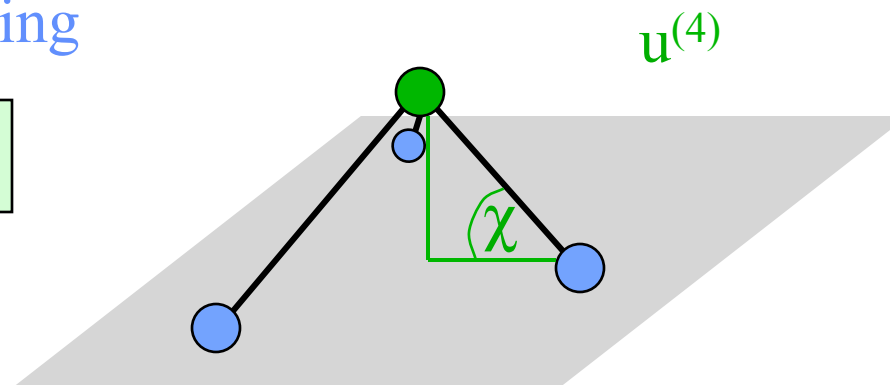
define   *minimum*

$$U(\theta) = k(\theta - \theta^o)^2$$ *harmonic*

• *improvements based on including higher-order terms*

○ Out-of-plane bending

$$U(\chi) = k(\chi - \chi^o)^2$$

$u^{(4)}$

Torsional Energy
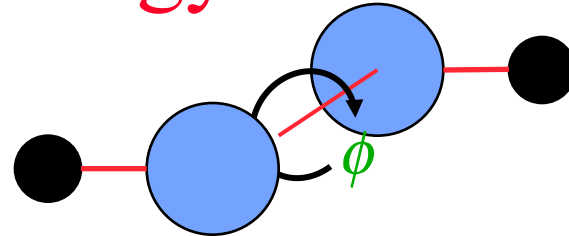
○ Two new features

- *periodic*
- *weak (Taylor expansion in f not appropriate)*

○ Fourier series

$$U(\phi) = \sum_{n=1} U_n \cos(n\phi)$$

- *terms are included to capture appropriate minima/maxima*

  depends on substituent atoms

  – e.g., ethane has three mimum-energy conformations

  - $n = 3, 6, 9$, etc.

  depends on type of bond

  – e.g. ethane vs. ethylene

- *usually at most n = 1, 2, and/or 3 terms are included*

Van der Waals Attraction

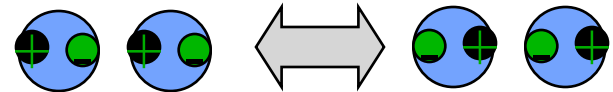○ Correlation of electron fluctuations

○ Stronger for larger, more polarizable molecules

  • $CCl_4 > CH_4$; $Kr > Ar > He$

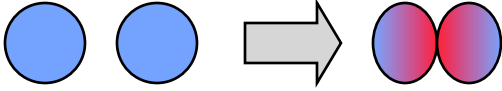○ Theoretical formula for long-range behavior

$$U_{vdW}^{att} : \frac{C}{r^6} + O(r^{-8})$$

○ Only attraction present between nonpolar molecules

  • *reason that Ar, He, CH_4*, etc. form liquid phases

○ a.k.a. "London" or "dispersion" forces

Van der Waals Repulsion

○ Overlap of electron clouds

○ Theory provides little guidance on form of model

○ Two popular treatments

inverse power

$$U_{vdW}^{rep} : \frac{A}{r^n}$$
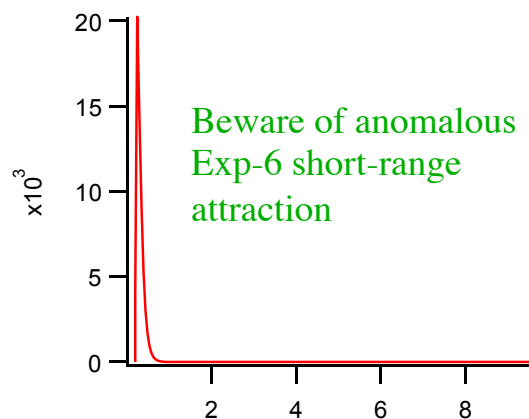
typically $n \sim 9 - 12$

exponential

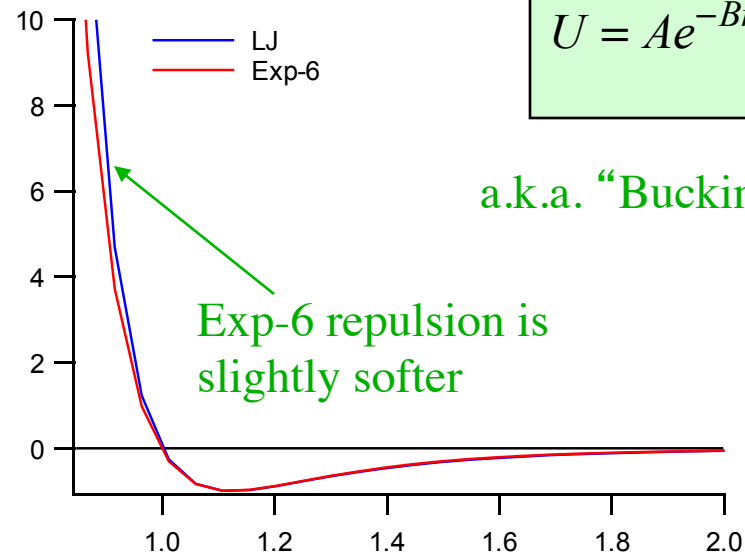$$U_{vdW}^{rep} : Ae^{-Br}$$

two parameters

○ Combine with attraction term

• *Lennard-Jones model*

$$U = \frac{A}{r^{12}} - \frac{C}{r^6}$$

Exp-6

$$U = Ae^{-Br} - \frac{C}{r^6}$$

a.k.a. "Buckingham" or "Hill"

Beware of anomalous Exp-6 short-range attraction

Exp-6 repulsion is slightly softer
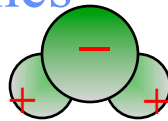
x10³

Electrostatics 1.
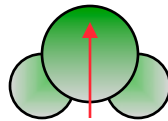
○ Interaction between charge inhomogeneities
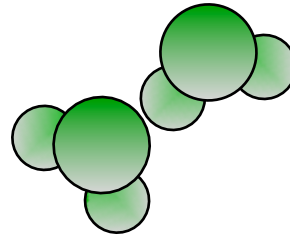
○ Modeling approaches
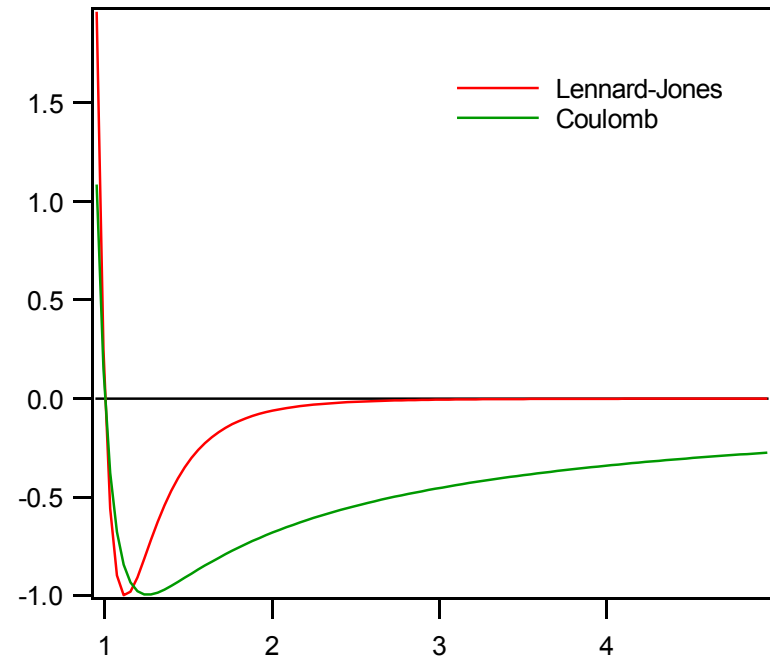
- *point charges*
- *point multipoles*

○ Point charges

- *assign Coulombic charges to several points in the molecule*
- *total charge sums to charge on molecule (usually zero)*
- *Coulomb potential*

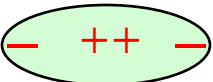$$U(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r}$$

very long ranged

Electrostatics 2.

○ At larger separations, details of charge distribution are less important

○ Multipole statistics capture basic features

- *Dipole* $\vec{\mu} = \sum_i q_i \mathbf{r}_i$ Vector $\mu \neq 0, Q = 0$

- *Quadrupole* $\mathbf{Q} = \sum_i q_i \mathbf{r}_i \mathbf{r}_i$ Tensor $\mu = 0, Q \neq 0$

- *Octopole, etc.*

○ Point multipole models based on long-range behavior

- *dipole-dipole*
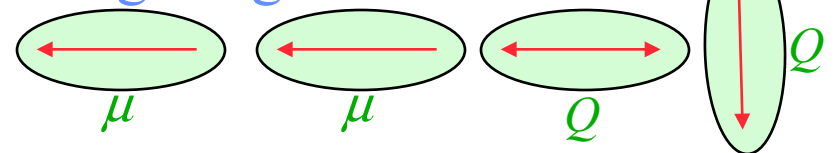
$$u_{dd} = -\frac{\mu_1 \mu_2}{r^3}\left[3(\hat{\mu}_1 \cdot \hat{\mathbf{r}})(\hat{\mu}_2 \cdot \hat{\mathbf{r}}) - (\hat{\mu}_1 \cdot \hat{\mu}_2)\right]$$

- *dipole-quadrupole*

$$u_{dQ} = \frac{3}{2}\frac{\mu_1 Q_2}{r^4}\left[(\hat{\mu}_1 \cdot \hat{\mathbf{r}})\left(5(\hat{Q}_2 \cdot \hat{\mathbf{r}})^2 - 1\right) - 2(\hat{\mu}_1 \cdot \hat{\mu}_2)(\hat{Q}_2 \cdot \hat{\mathbf{r}})\right]$$

Axially symmetric quadrupole

- *quadrupole-quadrupole*

$$u_{QQ} = \frac{3}{4}\frac{Q_1 Q_2}{r^5}\left[1 - 5c_1^2 - 5c_2^2 + 2c_{12}^2 + 35c_1^2 c_2^2 - 20c_1 c_2 c_{12}\right]$$

Electrostatics 3.
Some Experimental/Theoretical Values

Molecule	μ, Debye	Q, B	α, A^3
He	0	0	0.206
Ar	0	0	1.642
O_2	0	-0.4	1.48
N_2	0	→ -1.4	1.7
Cl_2	0	4.2	4.6
HF	→ 1.8	2.6	→ 0.8
CO_2	0	→ -4.3	2.9
H_2O	→1.85	+1.97 (xx) -1.89 (yy) -0.08 (zz)	1.5 (xx) 1.43 (yy) 1.45 (zz)
CH_4	0	0	2.6
CCl_4	0	0	→11.2
C_6H_6	0	→ -9.5	→10.6
NH_3	1.5	-2.3	2.22
C_2H_6	0	-1.2	4.4

Polarization

○ Charge redistribution due to influence of surrounding molecules

- *dipole moment in bulk different from that in vacuum*
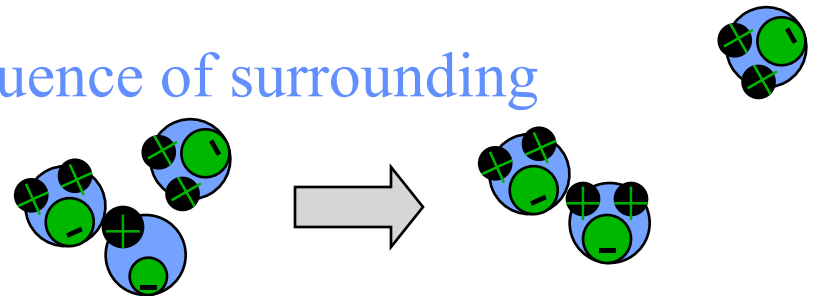
○ Modeled with polarizable charges or multipoles

○ Involves an iterative calculation

- *evaluate electric field acting on each charge due to other charges*
- *adjust charges according to polarizability and electric field*
- *re-compute electric field and repeat to convergence*

○ Re-iteration over all molecules required if even one is moved
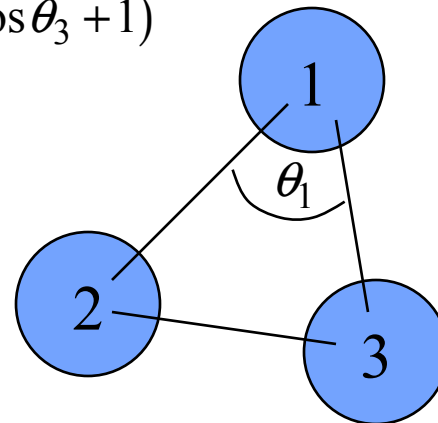
Explicit Multibody Interactions

○ Axilrod-Teller $\quad u^{(3)}$

- *consider response of atoms 2 and 3 to fluctuation in dipole moment of atom 1*

- *average over all fluctuations in 1*

$$u(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \frac{3}{2}\frac{E\alpha_1\alpha_2\alpha_3}{r_{12}^3 r_{23}^3 r_{13}^3}\left(3\cos\theta_1\cos\theta_2\cos\theta_3 + 1\right)$$

Unlike-Atom Interactions

○ "Mixing rules" give the potential parameters for interactions of atoms that are not the same type
- *no ambiguity for Coulomb interaction* $\quad U(r) = \dfrac{q_i q_j}{4\pi\varepsilon_0 r}$
- *for effective potentials (e.g., LJ) it is not clear what to do*

○ Lorentz-Berthelot is a widely used choice

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2)$$

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$$

○ Treatment is a very weak link in quantitative applications of molecular simulation

Common Approximations in Molecular Models

- Rigid intramolecular degrees of freedom
  - *fast intramolecular motions slow down MD calculations*
- Ignore hydrogen atoms
  - *united atom representation*
- Ignore polarization
  - *expensive n-body effect*
- Ignore electrostatics
- Treat whole molecule as one big atom
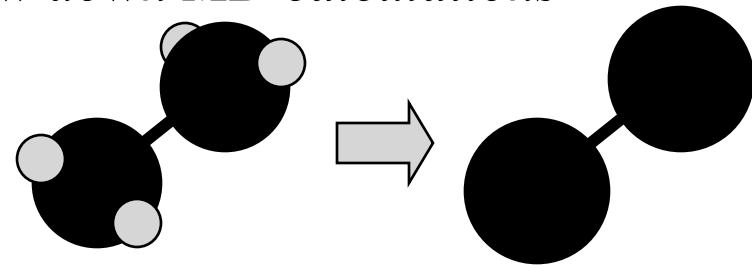 - *maybe anisotropic*
- Model vdW forces via discontinuous potentials
- Ignore all attraction
- Model space as a lattice
  - *especially useful for polymer molecules*

Qualitative models

Summary

○ Intermolecular forces arise from quantum mechanics

  - *too complex to include in lengthy simulations of bulk phases*

○ Empirical forms give simple formulas to approximate behavior

  - *intramolecular forms: bend, stretch, torsion*
  - *intermolecular: van der Waals, electrostatics, polarization*

○ Unlike-atom interactions weak link in quantitative work