Force fields in computer simulation of soft nanomaterials

Recommended reading:
Leach Chapter 4
Force Field Methods

• Force field methods are simulation methods that use classical *force fields* to describe the interactions between atoms or molecules or particles. (E.g. molecular mechanics and molecular dynamics)

• Force field methods rely on Born-Oppenheimer, ignore electronic motions and calculate the energy of a system as a function of nuclear positions only.

• Thus simulations of much larger systems can be performed.
  - Up to billions of atoms possible on the largest supercomputers (nearly a cubic micrometer - beyond that should not need to resolve everything at the atomic or molecular level)!
Enter Force Field Methods

- In many cases, just as accurate as QM calculations, but much faster.

- Also allows statistical phenomena to be explored, and classical and statistical mechanical theories to be explicitly tested.

- Thus force field methods are not just to save time or if system too large for QM; also to probe qualitatively different processes from what is probed with QM methods.

- *If some phenomena not understood on a fundamental level can be mimicked accurately or even just qualitatively by more “coarse-grained” methods, no reason to bring out “the big guns”.*
Force Fields

• What is a force field?
  An expression for the interactions between atoms (or molecules, or particles).

• Force fields rely on:
  - Validity of Born-Oppenheimer approximation.
  - Relatively “simple” expressions that capture the stretching of bonds, the opening and closing of angles, rotations about bonds...
  - Transferability: the ability to apply a given form for a force field to many materials by tweaking parameters (e.g. polystyrene vs. polyethylene)
Force Field Methods

Simulation methods that use force fields/interaction potentials

Particle-based mesoscale simulation

Field-based mesoscale and continuum mechanics

Time Scale (log_{10} seconds)

-12
-9
-6
-3

Length Scale (log_{10} meters)

-10
-8
-6
-3

Ab Initio/Electronic Structure

Explicit atomistic models

Coarse-grained models

MD and MC

Time and length scales overlap with neutron scattering, NMR, etc.

BD

DPD

ChE/MSE 557 Lecture 2b Fall 2006
Force Fields

• The force can be written in terms of the gradient of the interaction energy (interaction potential):

\[
\mathbf{F} = -\nabla U(\{\mathbf{r}_i\})
\]

• The term “force field” refers to the interaction potential \( U \) (i.e. the potential field from which forces are derived)!

• Recall when a force is derivable from the gradient of a scalar potential, the force is conservative.
Force Fields

- Many molecular modeling force fields in use today (especially for soft materials) can be written in terms of five simple types of interactions:

  - Bond stretching
  - Angle bending
  - Bond rotation (torsion)
  - Non-bonded (van der Waals)
  - Non-bonded (electrostatic)
A typical force field

\[ U(\{r_i\}) = \sum_j \frac{k_j^l}{2} (l_j - l_j^0)^2 + \sum_j \frac{k_j^\theta}{2} (\theta_j - \theta_j^0)^2 \]

\[ + \sum_{\text{torsions}} \frac{V_n}{2} (1 + \cos(n\varphi - \gamma)) \]

\[ + \sum_{i,j=1}^N \frac{q_i q_j}{r_{ij}} + \sum_{i,j=1}^N 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \]

**Bond stretch**  **Valence angle bend**

**Electrostatic (Coulomb)**  **van der Waals (Lennard-Jones)**

**Intra-**  **Inter-**

**Molecular**  **molecular**

**Intra-**  **Inter-**

**Molecular**
Example: Propane

- $\text{C}_3\text{H}_8$ has ten bonds: 2 C-C bonds and 8 C-H bonds.

  The C-H bonds fall into two classes
  - The H’s bonded to the central (methylene) carbon
  - The H’s bonded to the end (methyl) carbons
  - Some fancier force fields treat these two differently.

- 18 valence angles & 18 torsional terms

- 27 non-bonded interactions (if 1,4’s neglected)

- 73 total terms to calculate for a single molecule: still many fewer than the number of integrals that would be involved in an equivalent ab initio calculation.
General Features of Force Fields

• Defining a force field means defining both the functional form and the parameters.

• Two or more FF’s with the same form but different parameters, or with different forms, may give results of comparable accuracy for the same material and property.

• Typically, FF’s are developed to reproduce structures or spectra or thermodynamic quantities.
  – Just because it does one or two things well, doesn’t mean it gets everything right! This is not a failure of the FF.
  – A single FF can’t do everything, even just for one material.
General Features of Force Fields

• Force fields are empirical; there is no one ‘correct’ form.

• Although most of the FF’s in use today have similar overall forms, that doesn’t mean better forms can’t be found.

• FF’s are a compromise between accuracy and computational efficiency.
  – We’ll see this when we look at the van der Waals’ term.
  – Forms should be “nice” since first and second derivatives of the energy wrt atomic coordinates are required in molecular mechanics/molecular dynamics.
Force Fields

• Let’s delve more deeply into the individual terms that make up a force field (read Ch. 4 in Leach).

• In the many force fields in use today (MM2, MM3, Amber, Compass, Dreiding, UFF, ...), some of these terms are written slightly differently, and treated with different emphasis, and some force fields contain additional terms.

• *When using a force field, it is important to know what is being included and how, and what isn’t.*
Bond Stretching

The potential energy curve measured for a typical bond looks like the red curve at the right.
Bond Stretching

- This can be modeled by a Morse potential:

\[ u(l) = D_e \left( 1 - \exp \left[ -a(l - l_0) \right] \right)^2 \]

- \( D_e \) = depth of potential energy minimum
- \( a = \omega \sqrt{\mu / 2D_e} \)
- \( \mu \) = reduced mass
- \( \omega \) = frequency of bond vibration, related to stretching constant by \( \omega \sqrt{k/\mu} \)
- \( l_0 \) = reference bond length

Rarely used except for when bond-breaking needed*, since exponential is computationally slow.
Bond Stretching: Approximating Morse

**Harmonic:**

\[ u(l) = \frac{k}{2} (l - l_0)^2 \]

**Harmonic + higher orders:**

\[ u(l) = \frac{k}{2} (l - l_0)^2 \times \left[ 1 - k'(l - l_0) + \ldots \right] \]

- cubic - used in MM2

- **MM3 uses quartic to fix large l catastrophe**
## Bond Stretching

<table>
<thead>
<tr>
<th>Bond</th>
<th>$l_0$ (Å)</th>
<th>$k$ (kcal mol$^{-1}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Csp$^3$ - Csp$^3$</td>
<td>1.523</td>
<td>317</td>
</tr>
<tr>
<td>Csp$^3$ - Csp$^2$</td>
<td>1.497</td>
<td>317</td>
</tr>
<tr>
<td>Csp$^2$ - Csp$^2$</td>
<td>1.337</td>
<td>690</td>
</tr>
<tr>
<td>Csp$^3$ = 0</td>
<td>1.208</td>
<td>777</td>
</tr>
<tr>
<td>Csp$^3$ - Nsp$^3$</td>
<td>1.438</td>
<td>367</td>
</tr>
<tr>
<td>C - N</td>
<td>1.345</td>
<td>719</td>
</tr>
</tbody>
</table>

Allinger 1977 (from Leach)
Bond Angle Bending Interactions

- The deviation of the angle between two bonds is also often modeled with a harmonic (Hooke’s law) potential:

\[ u(\theta) = \frac{k}{2} (\theta - \theta_0)^2 \]

- Angles between different types of bonds have different force constants \( k \) and different reference angles \( \theta_0 \).

- As with bond stretching terms, higher accuracy is achieved by including higher order terms.
# Bond Angle Bending Interactions

<table>
<thead>
<tr>
<th>Angle</th>
<th>$\theta_0$ (deg)</th>
<th>$k$ (kcal mol$^{-1}$ deg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Csp$^3$ - Csp$^3$ - Csp$^3$</td>
<td>109.47</td>
<td>0.0099</td>
</tr>
<tr>
<td>Csp$^3$ - Csp$^3$ - H</td>
<td>109.47</td>
<td>0.0079</td>
</tr>
<tr>
<td>H - Csp$^3$ - H</td>
<td>109.47</td>
<td>0.0070</td>
</tr>
<tr>
<td>Csp$^3$ - Csp$^2$ - Csp$^3$</td>
<td>117.2</td>
<td>0.0099</td>
</tr>
<tr>
<td>Csp$^3$ - Csp$^2$ = Csp$^2$</td>
<td>121.4</td>
<td>0.0121</td>
</tr>
<tr>
<td>Csp$^3$ - Csp$^2$ = 0</td>
<td>122.5</td>
<td>0.0101</td>
</tr>
</tbody>
</table>

*Allinger 1977 (from Leach)*

*Smaller force constants compared to bonds = much less energy req'd to bend than to stretch or compress*
Bond Rotation (Torsional) Interactions

• Barriers to rotation about chemical bonds arise from antibonding interactions between the H atoms on the (1,4) atoms.
  – Antibonding interactions are minimized when conformation is staggered and maximized when it is eclipsed.

• In organic macromolecules, torsional potentials are nearly always used for each A-B-C-D since major conformational changes are due to rotations about bonds.

• In inorganic materials, torsional potentials are often neglected and non-bonded interactions between every pair of (1,4) atoms are tweaked to achieve the desired energy profile.
Bond Rotation (Torsional) Interactions

Torsional energy profile along dihedral angle Si-C-C-C in propyl-POSS

From Cummings, et al.
Bond Rotation (Torsional) Interactions

- Torsional potentials modeled by a cosine series expansion:

\[ u(\varphi) = \sum_{n=0}^{\infty} \frac{V}{2} (1 + \cos(n\varphi - \gamma)) \]

or

\[ u(\varphi) = \sum_{n=0}^{\infty} C_n \cos(\varphi)^n \]

- \( n \) is “multiplicity” = number of minima as bond rotated through 360°
- \( \gamma \) is phase factor: determines where \( \varphi \) passes through minimum
- \( V_n \) is called “barrier height”, but not exactly, since non-bonded contributions from (1,4) atoms affect rotation.
  - \( V_n \) for double bond > \( V_n \) for single bond
Bond Rotation (Torsional) Interactions

• Again, different force fields may use different numbers of terms in cosine series (e.g. Amber contains just one, MM2 uses more).

• More accurate potentials will use more terms, since the more parameters you have in your FF, the better you can generally fit experimental data.

• Drawback of using more terms: Many more parameters to fit is more complicated and time consuming. Necessary for some systems.
Cross Terms b/t Stretch, Bend, Torsion

- Many force fields also include cross terms, such as:
  - Stretch - stretch
  - Stretch - torsion
  - Stretch - bend
  - Bend - torsion
  - Bend - bend

*Again, in general, the more terms you include, the more accurate the FF, but the harder it is to parameterize and use.*
Coulomb Interactions

- The distribution of charge in a molecule may be represented by an arrangement of fractional point charges (partial charges).

- The electrostatic interaction between two molecules or between different parts of the same molecule is calculated as a sum of interactions between pairs of point charges using \textit{Coulomb’s law}:

\[
V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}
\]
Coulomb Interactions: multipole expansion

• Electrostatic interactions can be calculated via a multipole expansion, in which one sums over the individual electric moments or multipoles in an efficient way.

• Charged molecules have the charge (a monopole) as their lowest non-zero term; uncharged molecules may have the dipole or quadrupole or octupole or ... as their lowest non-zero term, depending on the asymmetry of the charge distribution within the molecule.

\[ V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \]
Coulomb Interactions: multipole expansion

- But, the multipole expansion approach to summing the electrostatic interactions is typically used only for small molecules whose conformations are kept fixed during the calculation, and where the interactions between molecules act at their centers of mass.

- Leach describes several other approaches to dealing with charges; it is a complicated business, and can be important when studying, e.g., charged macromolecules in aqueous solutions.

- For many studies, especially of uncharged species, the electrostatic interaction is ignored.
van der Waals Interactions

• Electrostatic forces don’t account for all the non-bonded interactions in a system.

• Van der Waals’ forces describe deviations from ideal gas behavior not accounted for by electrostatics.

Johannes Diderik
Van der Waals
1837-1923
van der Waals Interactions

• The interaction energy between two isolated Argon atoms has the following dependence on the distance between the atoms:

\[ U = 0 \text{ at infinite distance, negligible at long distances. As separation is reduced, } U \text{ decreases, passing thru a minimum at } r = 0.38 \text{ nm for Argon. } U \text{ then rapidly increases as separation decreases further.} \]
van der Waals Interactions

• The VdW curve arises from a balance between long-range attractive forces and short-range repulsive forces.

• The attractive contribution is due to dispersive forces (London forces), which arise from instantaneous dipoles that arise from fluctuations in the electron density distribution (electron cloud), and which induce dipoles in neighboring atoms.

• The Drude model predicts that the dispersion interaction varies as $1/r^6$, and is negative (attractive). Additional negative, higher order even powers result if higher order induced multipoles are considered.
van der Waals Interactions

• The repulsive contribution has a quantum mechanical origin and arises due to the Pauli exchange principle, which prohibits any two electrons in a system from having the same set of quantum numbers.
• The exchange force prohibits the electrons in the two atoms from occupying the same region of space.
• This results in a reduced electron density between the two nuclei, which leads to repulsion between the incompletely shielded nuclei.
• At very small separations, the interaction energy due to nuclear repulsion varies as $1/r$.
• At larger (but still small) separations, the energy decays exponentially as $\exp(-2r/a_0)$, where $a_0$ is the Bohr radius.
van der Waals Interactions

- The dispersive (attractive) and exchange (repulsive) interactions can be calculated using QM (not trivial, however).

- There are several empirical models for the van der Waals potential.

- Required for molecular simulations: a simple expression, because there are MANY non-bonded interactions to include (at least $N*(N-1)/2$, not counting Coulomb).
The Lennard-Jones Interaction Potential

• The most popular model of the van der Waals non-bonded interactions between atoms is the Lennard-Jones model.

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

- Collision diameter
- Typical cutoff at 2.5\( \sigma \)
- Minimum at \( r = 1.122\sigma \)
- Sir John Edward Lennard-Jones 1894-1954

\[ r = r_{ij} \]
The $1/r^6$ term in the LJ potential has the same form as that found from theoretical calculations of the Drude model for the dispersive interactions.

There are no strong theoretical arguments in support of the $1/r^{12}$ term, which is not a particularly good approximation to $1/r$ times an exponential.

- While the $1/r^{12}$ term works well for rare gases, it is usually too steep for hydrocarbons.
Nevertheless, the 6-12 LJ potential is widely used, especially for large simulations, since the $1/r^{12}$ is rapidly calculated by squaring the $1/r^6$ term, which in turn is found from $r^2$ without any costly square roots.

These are the types of considerations that go into developing force fields!
Lennard-Jones Model

- LJ original potential was written in the general form:

\[ U(r) = k\varepsilon \left( \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^m \right) \]

where:

\[ k = \frac{n}{n-m} \left( \frac{n}{m} \right)^{m/(n-m)} \]

- Several force fields use \( n \neq 12 \).
- Several formulations in which \( 1/r^{12} \) term is replaced by a more realistic potential have been proposed, such as the Buckingham potential:

\[ U(r) = \varepsilon \left( \frac{6}{\alpha - 6} e^{-\alpha \left( \frac{r}{r_m} \right)} - \frac{\alpha}{\alpha - 6} \left( \frac{r}{r_m} \right)^6 \right) \]

Careful, when separation very small \( U \) is steeply attractive.
Lennard-Jones Model

- Between different types of atoms, the LJ interaction takes the form:

\[ U_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left( \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right) \]

- A system with N different types of atoms has \( N(N-1)/2 \) different sets of parameters for interactions between unlike atoms.
- Since vdW parameters are difficult to obtain, we assume parameters for cross interactions between unlike atoms can be obtained from those for like atoms through mixing rules.
Lorenz-Berthelot Mixing Rules

- A common mixing rule used to calculate LJ parameters between unlike atoms is the Lorenz-Berthelot mixing rule.

- Collision diameter $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ - (arithmetic mean)

- Well depth $\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2}$ - (geometric mean)

- These mixing rules are most successful between similar types of atoms.
  - Major drawback: well depth can be overestimated by geometric mean. Some force fields also use geometric mean for collision diameter.

- VdW parameters are typically optimized to reproduce thermodynamic properties such as densities and enthalpies of vaporization, and structure.
Many Body Effects b/t Non-bonded Atoms

• In real materials, there are many body effects between non-bonded atoms that cannot be simply described by pairwise forces.

• The interaction between two atoms can be affected by the presence of other atoms.
Many Body Effects b/t Non-bonded Atoms

• Some force fields include three-body terms at the expense of greatly increased computational effort.
  
  – # of intramolecular terms increases linearly with N
  
  – # of non-bonded forces increases as \( N^2 \)
    • \( N(N-1)/2 \) interactions to evaluate in a pair-wise potential.
  
  – \( N(N-1)(N-2)/6 \) unique three-body interactions.
  
  – For 1000 atom system:
    • 499,500 pairwise terms
    • 166,167,000 three-body terms
    • In gen’l, \( N/3 \) times more three-body than two-body terms.
Comparison of Force Fields and QM

- **UFF** (Universal Force Field)
  - Used for many nanoscale carbon structures (Buckyballs, nanotubes)

- **COMPASS** (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies)
Comparison of Force Fields and QM

Structure of POSS(H)$_8$ cube determined from various QM and MM energy minimizations.

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>Plane Wave (VASP)</th>
<th>Atomic Orbital (DMOL)</th>
<th>RHF (cc-pVdz) (GAUSSIAN 98)</th>
<th>Molecular Mechanics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cerius$^2$ UFF</td>
</tr>
<tr>
<td>Si-O</td>
<td>1.619</td>
<td>1.630</td>
<td>1.654</td>
<td>1.650</td>
<td>1.592</td>
</tr>
<tr>
<td>Si-H</td>
<td>1.48</td>
<td>1.463</td>
<td>1.481</td>
<td>1.462</td>
<td>1.470</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>147.5°</td>
<td>146.7°</td>
<td>145.9°</td>
<td>148.7°</td>
<td>146.8°</td>
</tr>
<tr>
<td>O-Si-O</td>
<td>109.6°</td>
<td>109.6°</td>
<td>109.6°</td>
<td>109.1°</td>
<td>110.0°</td>
</tr>
</tbody>
</table>
Biological and Biochemical Force Fields

- CHARMM, GROMOS, AMBER, OPLS, ...
  - Optimized to work in the temperature and density range relevant to living systems
  - Little concern for accuracy beyond this regime
United Atom Force Fields

- There are essentially three “classes” of force field models, each of which corresponds to a different level of detail:
  
  - Explicit atom (all atoms represented explicitly)
    - Used to model a specific system
  - United atom (coarse-grained)
    - Used to model a specific system
  - Mesoscopic (coarse-grained)
    - Used to model phenomena characteristic of a class of systems
United Atom Force Fields

• Since the number of non-bonded interactions scales as \( N^2 \), for large systems explicitly including every atom is prohibitive.
• In united atom force fields, some atoms (usually just the hydrogens) are subsumed into the atoms to which they are bonded.
  – E.g. \( \text{CH}_3 \) is treated as a single “united atom”.
• The interaction parameters for each term in the force field are modified to account for the “subsumed” atoms.
• Many hydrocarbons are modeled with united atom force fields. In some UA models of proteins, only some of the hydrogens are eliminated.
• Good alkane UA models: Toxvaerd, Siepmann, Smith & Paul
Explicit Atom & United Atom Force Fields

- Force field development is something of an art.
- Experimental data and QM calculations are used to help parameterize force fields.
- Incredibly important to have good force fields, since your simulation is only as good as the model you use.
- Few simulators develop force fields; many use them.
- Force fields developed for metals, ceramics, polymers, liquids, solids, gases have different requirements and there is a different culture.
- Challenge for nanoscience: Force fields for dissimilar materials are not easy to obtain. *Future studies rely on new force fields.* Major area of research for nanoscience researchers.
Explicit Atom & United Atom Force Fields

• How well can these force fields do?
  - Structure: within a few percent considered good.
  - Thermodynamics: within a few percent considered good.
  - Dynamics: within 20% considered good.

• Limitations
  - With MD, $10^{16}$ atom-steps on large supercomputer possible, ($10^{12}$ atom-steps usual) depending on terms in force fields, approximations, tricks used, etc.
  - For many problems, less computationally intensive models are needed in order to study larger systems.
Mesoscopic Molecular Models

• **Explicit atom** and **united atom** force fields are used to model *particular* systems, and to predict properties with *quantitative accuracy*.

• Sometimes we do not seek to model specific systems, but rather we seek to model phenomena *characteristic of* a class of systems.

• For such studies, further coarse-graining is done and **mesoscopic “molecular” models** are used. These models contain some of the same terms used in force fields and thus look like force fields; they’re used like force field models, but not generally called force fields.
A Mesoscopic Polymer Model

• “Bead-spring” polymer

\[ V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] - \frac{k}{2}R_o^2\ln\left[1 - \left(\frac{r}{R_o}\right)^2\right] \]

- all monomer pairs
- bonded pairs only

Coarse-grained “mesoscopic” molecular model of a polymer melt.

Eg. \(k=30, R_o=1.5, \varepsilon=1, \sigma=1\)
A mesoscopic model for colloids

• The Yukawa potential is commonly used to model the interaction between charged colloids in solvent where the interactions are screened due to the solvent:

\[ U_{Yukawa}(r; \kappa) = \varepsilon \frac{\exp[-\kappa(r/\sigma)]}{r/\sigma} \]

Here \( \sigma \) = particle diameter, \( \kappa \) = inverse screening length, and \( \varepsilon \) = surface potential, \( r \) = distance between two colloid centers.
• Important area of current research:
  – Coarse-graining detailed EA or UA models to mesoscopic models
  – Mapping mesoscopic models to EA or UA models

• We’ll learn more about this later in the class.