

Computational Nanoscience
NSE C242 & Phys C203
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Lecture 6:
Pair Distribution Function &
More on Potentials
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Radial Distribution Function Refresher

The probability $p(r)$ of finding any two particles at a given distance, say between r and $r+dr$ clearly depends on r , since the shell of thickness dr is $4\pi r^2 dr$.

Thus, all other things being equal, more particles will occupy a larger volume.

That is why we do not use $p(r)$ but rather $g(r)$, the pair (or radial) distribution function, which has a **normalization**.

From Lecture 3:

The pair distribution function provides a measure of the probability $p(r)$ of finding any two particles at a given physical distance, r .

Typically, this is defined (in 3 dimensions) as: $g(r) = (N - 1) \frac{p(r)}{r^2}$

The prefactor is defined in such a way so that: $\frac{\int r^2 g(r) dr}{\int r^2 dr} = 1 - \frac{1}{N}$

Radial Distribution Function Refresher

A little more detail here: that normalization is based on the fact that if the atoms are uncorrelated, then the expected number of atoms at r is simply the average number of atoms per unit volume times the volume of the shell.

$$N_{ideal}(r) = \frac{N}{V} \times V_{shell}(r)$$

When we normalize the observed number of atoms in our simulation by this uncorrelated value, we obtain:

$$\frac{N}{V} \int d^3r g(r) = (N - 1)$$

We can think of $g(r)$ as the ratio of the average number density $\rho(r)$ at a distance r from any given atom and the density at a distance r from from an atom in an **ideal gas** at the same overall density.

By construction, any deviation in $g(r)$ from 1 reflects correlations between particles due to the intermolecular interactions.

Radial Distribution Function

Once the radial distribution function is known, a whole bunch of thermodynamic functions can be readily computed. For example:

$$\langle U \rangle = \frac{N^2}{V} \int d\mathbf{r} v(\mathbf{r}) g(\mathbf{r})$$

Potential energy

$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT} \int r \frac{dv}{dr} g(r) 4\pi r^2 dr$$

Pressure

$$-\frac{\mu}{kT} = \log \rho \Lambda^3 + \frac{\rho}{kT} \int_0^1 dk \int v(r) g(r, k) 4\pi r^2 dr$$

Chemical potential

$$kT\rho\alpha = 1 + \rho \int (g(\mathbf{r}) - 1) d\mathbf{r}$$

Compressibility

More on Interatomic Potentials

In cases where the electronic motions can be ignored, interatomic potentials, or **force field methods** can be used.

This is a general way of describing what we've been doing in this class thus far - namely, using a simple method for describing the energy between particles that only depends on their nuclear coordinates.

One important assumption of any simulation that uses force field models is that the system is well-described within the **Born-Oppenheimer** approximation.

Another, is that the potentials are **transferable**.

Typically, an empirical potential is based on a rather simple model of the interactions within a system.

In fact, there are really mostly only 4 types of interactions that go into a model...

More on Interatomic Potentials

In a typical force field model, energies are computed based on 4 components:

1. Deviation of bonds from their equilibrium values (stretching)
2. Deviation of angles from their equilibrium values (bending)
3. Rotation of bonds
4. Electrostatic (“non-bonded”) interactions

Many functional forms exist to describe these energy contributions.

For example,

$$V(r) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_{i,0})^2 + \sum_{\text{torsions}} \frac{V_n}{2} (1 + \cos(n\omega - \gamma)) + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$$

Note that even for a simple molecule the number of parameters can be ~100.

Force Field Models

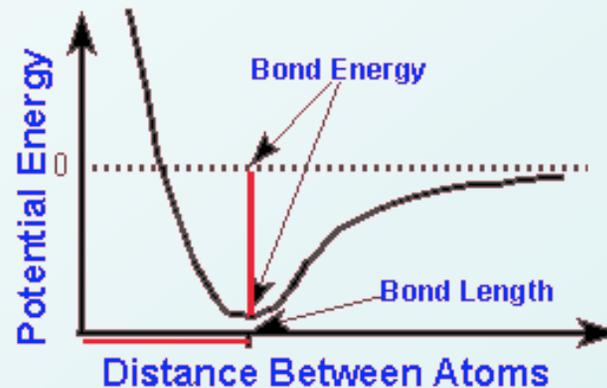
A couple of things to note about force fields:

- They are usually designed to predict certain properties and are parameterized accordingly.
- Other properties, not included in the parameterizations, may still be modeled accurately. However, there are no guarantees.
- Transferability of both the functional form and the parameters themselves is an important feature.
- Force fields are **empirical**. There is no “correct” functional form.
- As we’ve discussed it’s useful to be able to calculate the derivatives of the energy, for MD and energy minimization.
- Typically an “atom type” is defined. This is not just the atomic number, but contains much more information.

Let’s take a quick look at the four typical contributions to a force field.

Bond Stretching

A typical potential energy curve for a bond might look like this picture I found on Google:



One decent form that could model such a curve was suggested by Morse:

$$v(l) = D_e \left\{ 1 - \exp[-a(l - l_o)] \right\}^2$$

And yet, the Morse potential is not usually used in empirical potentials since it's inefficient and also it has 3 parameters per bond.

Bond Stretching

Since it's rare for bonds to deviate far from their equilibrium values, we can use a much simpler expression.

The easiest (and most common) approach is to use Hooke's Law, in which the energy varies as the square of the displacement.

$$V(r) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2$$

Note the “reference” bond length, l_0 in this equation. Is this the same as the equilibrium bond length?

Can this be modified to be more accurate at bond stretches that are somewhat far from equilibrium?

Angle Bending

The same simple Hooke's law is usually what one uses to describe the deviation of angles from their reference value:

$$\sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_{i,0})^2$$

Much less energy is usually required to bend an angle as opposed to stretch a bond, so the force constants are typically much smaller.

For example, the C(sp³)-C(sp³) force constant is 317 kcal/mol per Å²

Whereas the C(sp³)-C(sp³)-C(sp³) angle bending force constant is 0.0099 kcal/mol per degree.

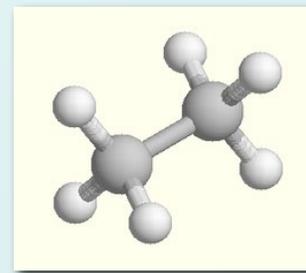
Torsional Terms

Even though the bond stretching and angle bending terms are the strongest of the four typical empirical parameters, the other two are usually at the heart of interesting variations in structure and energy.

Energy barriers to bond rotation is fundamental to understanding the structure of molecules.

A classic example, the ethane molecule, has a maximum and minimum conformation with respect to CH_3 group rotations.

While the bond stretch involves 2 atoms, the angle bend 3 atoms, the torsional term involves 4 atoms.



How many individual torsion terms are there in ethane?

Torsional Potentials

Torsional potentials are nearly always expressed as a cosine series expansion, for example:

$$V(r) = \sum_{\text{torsions}} \frac{V_n}{2} (1 + \cos(n\omega - \gamma))$$

Where ω is the torsion angle and V_n gives a qualitative barrier height to bond rotation.

n is the multiplicity - i.e., it gives the number of minimum points in the function as the bond is rotated through 360 degrees.

γ is a phase factor that determines where the torsion angle passes through its minimum value.

One can begin to think of torsional potential parameters in terms of the types of bonding. For example, two sp^3 carbon atoms may have $n=3$ and $\gamma=0$, while two sp^2 carbon atoms could have $n=2$ and $\gamma=180$.

What would be the differences in the V_n for these cases?

Electrostatic (“non-bonded”) Interactions

Last, but certainly not least, let’s take a look at the electrostatic terms.

Different elements in a molecule have different electronegativities.

This leads to a non-uniform charge redistribution, which is what a good electrostatic potential attempts to capture.

One common approach is to represent the charges as an arrangement of fractional point charges throughout the molecule.

If the charges are restricted to the nuclear centers (called partial atomic charges), then for the energy between two molecules one simply writes down Coulomb’s law:

$$V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Where the sums run over the number of atoms in each molecule, N_A and N_B .

Central Multipole Expansion

Often times alternative approaches are used to compute electrostatic interactions.

For example, in the *central multipole expansion*, one treats the molecule as a single entity.

This method is based on representing the molecule by its electric moments, e.g., the charge, dipole, quadrupole, octopole, etc.

Each multipole moment can be represented by an appropriate distribution of charges. A dipole is represented with 2 charges the right distance apart, a quadrupole with 4 charges, etc.

If all non-zero electric moments are specified, then one obtains a complete description of the charge distribution around a molecule.

Note that the lowest non-zero moment is different for different molecules: for example, compare Na^+ with CO with CO_2 and N_2 .

Central Multipole Expansion

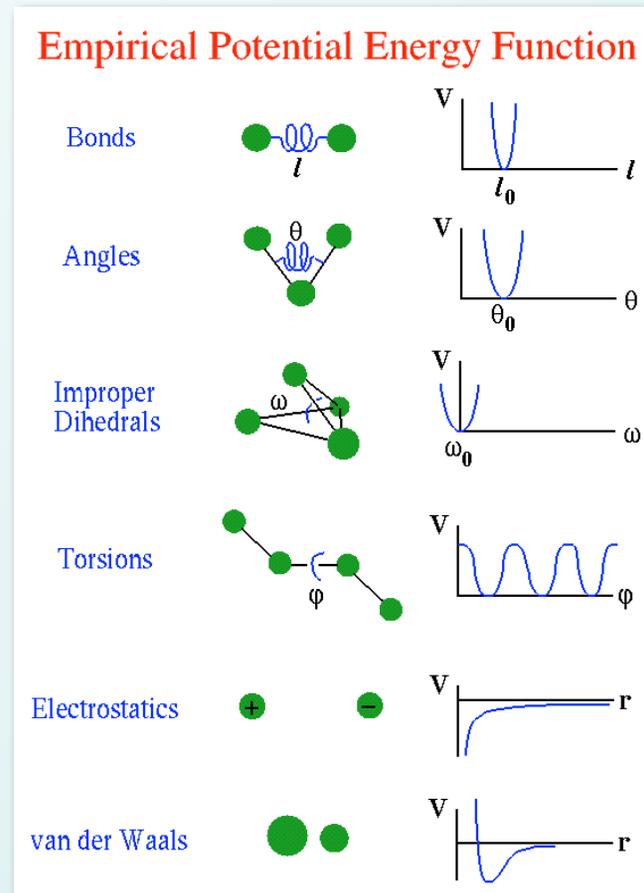
There are a number of difficulties that arise with the multipole expansion method.

A few of note are:

- The method is not applicable when the molecules are separated by distances comparable with the molecular dimensions.
- The moments are properties of the entire molecule, so this method cannot be used to determine intramolecular interactions.
- This makes it an approach mostly limited to small molecules with fixed structural conformations.
- Force calculations can be quite tricky for higher moments.

Point-Charge Electrostatic Models

So, to summarize, let's grab another image from a random Google search:



http://cmm.info.nih.gov/intro_simulation/node15.html