# Activity 1: Building a force field file

## Overview

In this exercise we will examine a simple fixed-charge force field (GAFF2) for a simple molecule (ethane) and see how it is "coded" into an XML file for OpenMM. You will then create an analogous XML file for simulating butane with OpenMM.

## A brief recap of force fields

As we discussed, a great many fixed-charge force fields have used the following functional form to describe intra- and intermolecular interactions:

$$U = U_{bond} + U_{angle} + U_{torsion} + U_{elec} + U_{vdw}$$

where for individual bonds (between two atoms), angles (between atoms separated by two bonds), torsions (between atoms separated by three bonds), or atom pairs separated by three bonds/nonbonded atom pairs:

$$U_{bond} = \tfrac{1}{2}k_l(l - l_{eq})^2, \quad U_{angle} = \tfrac{1}{2}k_\theta(\theta - \theta_{eq})^2, \quad U_{torsion} = \sum_{n=1}^{n_{max}} U_n[1 + cos(n\phi - \gamma_n)]$$

$$U_{elec} = k_e q_i q_j / r_{ij}, \quad U_{vdw} = 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]$$

## Worked application: ethane

To help make sense of these equations let's examine ethane ($C_2H_6$), which is perhaps the simplest molecule that requires all of these terms for accurate modeling.
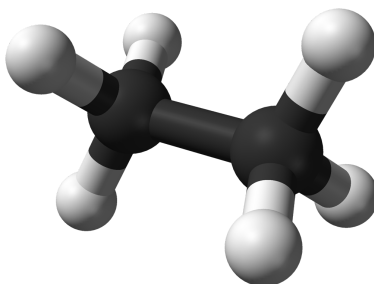


From the 3D structure above (see also *ethane.pdb*) we can reason that in ethane there are two types of bonds (C-C and C-H), two types of angles (H-C-H and H-C-C), and one torsion (H-C-C-H). By examining the symmetry of this molecule, it is reasonable to assume that the

partial atomic charges ($q_i$) and van der Waals parameters ($\varepsilon_i$ and $\sigma_i$) will be the same for both carbon atoms and likewise for all six hydrogen atoms.  The GAFF2 force field assigns the following SI parameters for all of these interactions:

| Interaction | Parameters |
|---|---|
| C-C bond | $l_{eq}$ = 0.1538 nm, $k_l$ = 1.946 x 10$^6$ kJ/mol·nm$^2$ |
| C-H bond | $l_{eq}$ = 0.1097 nm, $k_l$ = 3.146 x 10$^6$ kJ/mol·nm$^2$ |
| H-C-H angle | $\theta_{eq}$ = 1.878 rad, $k_\theta$ = 326.0 kJ/mol·rad$^2$ |
| H-C-C angle | $\theta_{eq}$ = 1.916 rad, $k_\theta$ = 391.8 kJ/mol·rad$^2$ |
| H-C-C-H torsion | $\gamma_3$ = 0 rad, $U_3$ = 0.5021 kJ/mol |
| C atom (nonbonded) | $q_C$ = –0.0951$e$, <br> $\sigma_C$ = 0.3398 nm, $\varepsilon_C$ = 0.4510 kJ/mol |
| H atom (nonbonded) | $q_H$ = 0.0317$e$, <br> $\sigma_H$ = 0.2600 nm, $\varepsilon_H$ = 0.0870 kJ/mol |

If you examine the file *ethane.gaff2.xml*, you will first see that we define two types of atoms (0 for the C atoms and 1 for the H atoms).  The next section describes which types apply to the atoms in ethane.  In addition, much like a PDB file, this XML file conveys connectivity/topology information by describing which atoms are bonded to each other.  Finally, you should see multiple sections that convey the force field information given above.

**Your turn: butane**

Now consider the slightly more complex molecule butane ($C_4H_{10}$; see also *butane.pdb*):
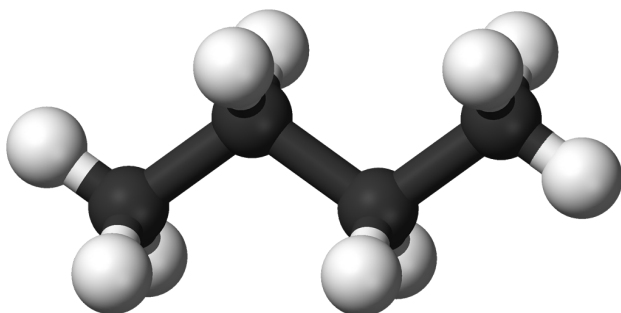


From the 3D structure we can immediately see that the same types of bonds that are present in ethane (i.e., C-C and C-H) are also present in butane. Likewise, the same types of angles are also present, but in butane there is also a C-C-C angle. For torsions there are two new possibilities: H-C-C-C and C-C-C-C. Finally, we will assume (using chemical intuition) that the van der Waals parameters for the C and H atoms are the same as in ethane. However, the partial atomic charges of the two "outer" carbon atoms probably can't be the same as the two "inner" C atoms. The same is also true for the partial atomic charges of the six "outer" H atoms vs. those of the four "inner" H atoms. (Why?)

With all this in mind, use the parameters from *ethane.gaff2.xml*, the connectivity and atom names in *butane.pdb*, and the following information to complete the OpenMM force field file *butane.gaff2.xml*:

| Interaction | Parameters |
|---|---|
| C-C-C angle | $\theta_{eq}$ = 1.946 rad, $k_\theta$ = 543.0 kJ/mol·rad$^2$ |
| H-C-C-C torsion | $\gamma_3$ = 0 rad, $U_3$ = 0.3347 kJ/mol |
| C-C-C-C torsion | $\gamma_1$ = 0 rad, $U_1$ = 0.4602 kJ/mol <br> $\gamma_2$ = 3.1416 rad, $U_2$ = 1.2134 kJ/mol <br> $\gamma_3$ = 0 rad, $U_3$ = 0.5439 kJ/mol |
| "Outer" C atom (nonbonded) | $q_C$ = –0.0932e, $\sigma_C$ and $\varepsilon_C$ same as ethane |
| "Inner" C atom (nonbonded) | $q_C$ = –0.0814e, $\sigma_C$ and $\varepsilon_C$ same as ethane |
| "Outer" H atom (nonbonded) | $q_H$ = 0.0324e, $\sigma_H$ and $\varepsilon_H$ same as ethane |
| "Inner" H atom (nonbonded) | $q_H$ = 0.0387e, $\sigma_H$ and $\varepsilon_H$ same as ethane |